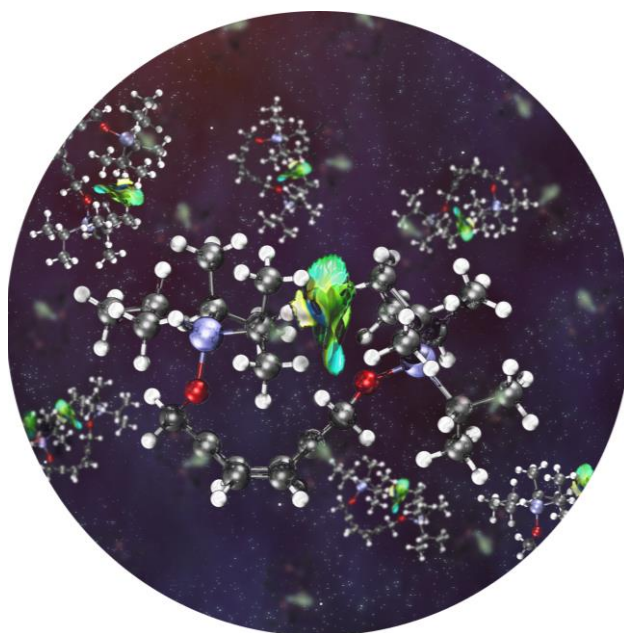


Silyl Groups as Dispersion Energy Donors

Inaugural dissertation for the award of a doctorate in the natural sciences (*Dr. rer. nat.*) in the Department of Organic Chemistry (Faculty 08) at the Justus Liebig University Giessen, and for the degree of *Doctor of Philosophy* from Macquarie University, Sydney (School of Natural Sciences)



by

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*I love a sunburnt country,
A land of sweeping plains,
Of ragged mountain ranges,
Of droughts and flooding rains.
I love her far horizons,
I love her jewel-sea,
Her beauty and her terror -
The wide brown land for me!*

~2nd stanza of *My Country* (1908) by Dorothea Mackellar.

*But in me a newer yearning wakes,
I hasten on, drinking his endless light:
The dark behind me: and ahead the day.
Heaven above me: and the waves below,
A lovely dream, although it vanishes.
Ah! Wings of the mind, so weightless
No bodily wings could ever be so.*

~From the play *Faust: A Tragedy* (1790) by Johann Wolfgang von Goethe.

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Declaration & Statement of Originality

I, Henrik Ferdinand König, thus affirm that the research presented in this thesis is my original work. Every attempt is taken to clearly express the contributions of others, with citations to the relevant literature and recognition of collaborative research and conversations. The projects presented herein were performed under the supervision of Associate Professor Dr. Koushik Venkatesan and Professor Dr. Alison Rodger at Macquarie University in Sydney, Australia, and under supervision of Prof. Dr. Peter R. Schreiner, PhD at Justus Liebig University Gießen.

This work has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the thesis itself. This thesis is being submitted to Macquarie University and Justus Liebig University Gießen in accordance with the Cotutelle agreement dated 01.07.2022.

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Abstract

The introduction of silyl groups as protecting groups for alcohols has substantially changed synthetic organic chemistry. Although heavily utilized, some aspects of silyl groups, especially their potential to function as so called ‘dispersion energy donors’ in catalyst and functional material design remains mostly untapped, despite their generally greater polarizability and bulkiness in comparison to known carbon-based dispersion energy donors.

In the first publication (section 2.1/2.2) of this work, we report an experimental and computational study on a rigid cyclooctatetraene molecular balance, a molecular system exhibiting a conformational equilibrium by means of which non-covalent interactions can be quantified, substituted with common silyl protecting groups. We were able to quantify the relative steric demand of silyl groups and found conformational strain and Pauli exchange repulsion contributions to counteract significant stabilization from intramolecular London dispersion forces in the conformational equilibrium.

The second publication (section 2.3/2.4) addresses the London dispersion dominated attractive potential of bulky silyl groups by employing a similar cyclooctatetraene molecular balance. Strain build-up was avoided by introducing rotatable spacers between the silyl groups and the balance scaffold. We found our experimental findings to be in line with our theoretical predictions on the potential of silyl groups to function as dispersion energy donors, despite entropy mitigating the net effect in this particular case.

In a third publication (section 2.5/2.6), we studied a cyclooctatetraene molecular balance featuring a spacer moiety and two hydroxy groups. We found the folded state of the balance to closely resemble the geometric arrangement of a cyclic water dimer transition state. By taking strain and solvation contributions into account, we were able to provide an estimate for the hydrogen bonding energy of the cyclic water dimer transition state, which proved to be in good agreement with high-level computational results. Furthermore, we were able to identify a significant contribution from London dispersion to the hydrogen bonding energy through computational energy decomposition analyses.

In the final chapter (section 2.7), we report the preparation of a set of phosphorescent platinum(II) phenylacetylide complexes substituted with bulky silyl groups, and their respective carbon-counterparts. We studied their photophysical properties in solution and thin film, and thus were able to identify the ideal silyl group substitution pattern for application in a pure-blue hyperfluorescent device. Our experimental findings agreed well with the

computational conclusions. So we are able to interrogate the details of the calculations to understand the interplay of London dispersion-controlled aggregation and the electronic effects of the silyl groups resulting in improvements in photophysical properties over the parent unsubstituted compound.

Zusammenfassung

Die Einführung von Silylgruppen als Schutzgruppen für Alkohole hat die synthetische organische Chemie wesentlich verändert. Obwohl Silylschutzgruppen breite Anwendung finden, bleibt insbesondere ihr Potenzial als so genannte "Dispersionsenergiedonoren" bei der Entwicklung von Katalysatoren und funktionellen Materialien weitestgehend ungenutzt, obwohl sie im Vergleich zu bekannten kohlenstoffbasierten Analoga von Natur aus polarisierbarer und voluminöser sind.

In unserer ersten Veröffentlichung (Abschnitt 2.1/2.2) haben wir eine experimentelle und computerchemische Studie über rigide Cyclooctatetraen-Molekularwaagen durchgeführt, welche mit häufig verwendeten Silylschutzgruppen substituiert waren. Es gelang, den relativen sterischen Anspruch der untersuchten Silylgruppen zu quantifizieren und wir stellten fest, dass Beiträge aus Konformerenspannung und Pauli-Repulsion die signifikante Stabilisierung durch intramolekulare London'sche Dispersionsinteraktionen im Konformerengleichgewicht überlagerten.

Die Folgeveröffentlichung (Abschnitt 2.3/2.4) befasst sich mit dem attraktiven Potential voluminöser Silylgruppen, welches im Wesentlichen von London'scher Dispersion dominiert wird. Hierzu wurden Konformerengleichgewichte ähnlicher Cyclooctatetraen-Molekularwaagen untersucht. Der Aufbau von Konformerenspannung wurde jedoch durch die Einführung frei drehbarer Gruppen zwischen den Silylsubstituenten und der eigentlichen Cyclooctatetraen-Molekularwaage vermieden. Unsere experimentellen Ergebnisse stimmten mit den theoretischen Vorhersagen über das Potenzial von Silylgruppen als Dispersionsenergiedonoren überein, obwohl entropische Effekte in diesem speziellen Fall die Gesamtauswirkungen auf das Konformerengleichgewicht abschwächten.

In einer dritten Veröffentlichung (Abschnitt 2.5/2.6) untersuchten wir eine Cyclooctatetraen-Molekularwaage, welche ebenfalls über frei drehbare Substituenten verfügte, jedoch lagen in diesem Falle zwei ungeschützte Hydroxygruppen vor. Es stellte sich heraus, dass im gefalteten Zustand der Molekularwaage die Geometrie des Übergangszustandes des zyklischen Wasserdimers sehr gut widergespiegelt wird. Durch die Berücksichtigung von Spannungs- und Solvatationsbeiträgen konnten wir die Wasserstoffbrückenbindungsenergie des zyklischen Wasserdimer-Übergangszustands erstmals experimentell abschätzen. Es wurde eine gute Übereinstimmung der experimentellen Werte mit hochwertigen theoretischen Daten festgestellt. Darüber hinaus konnten wir durch computerchemische Analysen einen

erheblichen Beitrag von London'scher Dispersion zur Wasserstoffbrückenbindungsenergie identifizieren.

Im letzten Abschnitt (Abschnitt 2.7) dieser Arbeit wurden eine Reihe von phosphoreszierenden Platin(II)-phenylacetylen-Komplexen, welche mit sperrigen Silylgruppen substituiert waren, sowie ihre entsprechenden Kohlenstoffanaloga hergestellt. Die photophysikalischen Eigenschaften der Komplexe wurden in Lösung- und Dünnschicht-Proben untersucht und es konnte so das ideale Silylgruppen-Substitutionsmuster für die potenzielle Anwendung in blauen hyperfluoreszenten Leuchtdioden identifiziert werden. Unsere experimentellen Ergebnisse stimmen gut mit computerchemischen Untersuchungen überein, welche ein Zusammenspiel aus Aggregation und elektronischen Effekten der Silylgruppen als Ursache für die verbesserten photophysikalischen Eigenschaften vorhersagen.

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1. General Introduction and Motivation

1.1 London Dispersion Interactions and their relation to other Non-covalent Interactions

Van der Waals forces

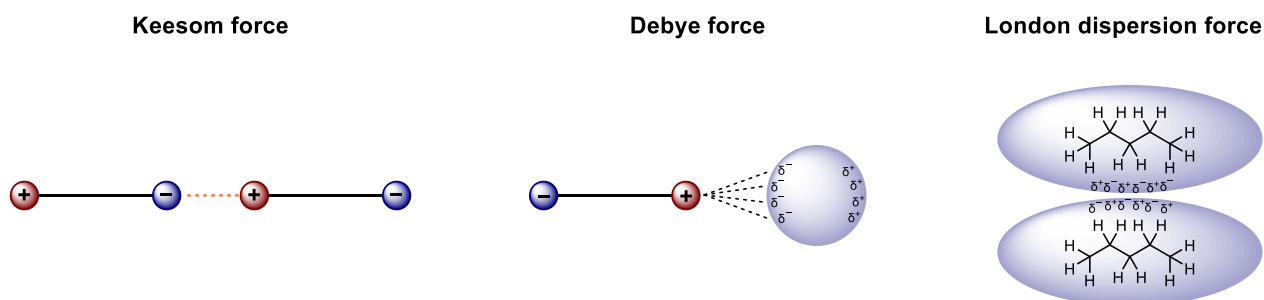


Figure 1: Classical schematic representation of attractive van der Waals forces.¹ From left to right: Permanent dipole-dipole/multipole-multipole interaction (Keesom force²), permanent dipole/multipole-induced dipole/multipole interaction (Debye force³), and induced dipole-induced dipole interaction (London dispersion force⁴⁻⁸).

Nearly a century ago, London and Heitler for the first time described the long-range, R^{-6} dependent (where R is the distance between the two species) attractive interactions of electrons of closed-shell atoms, molecules, or molecular fragments.⁴ These interactions have been termed in London's honor as "London dispersion interactions/forces" (LD interactions/forces), often described as transient induced dipole-induced dipole interactions. LD interactions are the weakest (per interaction) attractive component of the van der Waals (vdW) forces¹ (Figure 1), and hence are often seen as irrelevant in the light of undoubtedly stronger electrostatic (Keesom forces²) and inductive interactions (Debye forces³). One could even be tempted to interpret LD interactions as being a type of dipole interaction, based on the classical textbook description of instantaneous dipole-induced dipole interactions (Figure 1). However, in the framework of this classical view of non-covalent interactions (NCIs), it would be counterintuitive to assume two "clouds" of electrons, as charged particles of the same sign, would attract each other. Furthermore, the existence of fluctuating dipoles seems almost unearthly in this context. Why would a spontaneously occurring fluke of nature lead to a net effect large enough to promote even partial charge separation? Notably, London never resorted to a classical treatment at all in his original publications,⁴⁻⁸ but rigorously derived the necessary equations, that are still mostly

valid today, from quantum mechanical perturbation theory. He arrived at the following approximate equation⁸ for two interacting atoms ρ and κ :

$$U_{\rho\kappa} = E_{\rho\kappa}^{\text{disp}} = -\frac{3}{2} \frac{\alpha_{\rho} \alpha_{\kappa}}{R^6} \frac{I_{\rho} I_{\kappa}}{I_{\rho} + I_{\kappa}} \quad (1)$$

Although dipole moments are not immediately involved in equation (1), the dependence of $E_{\rho\kappa}^{\text{disp}}$ on ionization potentials I alongside polarizabilities α draws a picture of an electrostatic interaction at first sight. However, the proportionality between $E_{\rho\kappa}^{\text{disp}}$ and ionization potentials I could also simply be viewed from the perspective of an involvement of electronic excitations, that do not necessarily involve charge separation. In fact, the now widely agreed upon quantum physical description of LD interactions, although still invoking seemingly mysterious fluctuations as a result of zero-point energy, explain the former by means of ‘virtual’ excited electronic states in interacting atoms, molecules or molecular fragments.^{9,10} The immediate response of the ensemble of nearby electrons to the excitation leads to a lowering in energy of the entire system, and hence attraction. Put in other terms, the motion of one electron of a system is influenced by the motion of all surrounding electrons and the other way around. This effect is also known as (dynamic) electron correlation,^{11–15} and properly accounting for the former in a computationally sound fashion has been a long-standing challenge in quantum chemistry, owing to its nature as a many-body problem. However, capturing as much correlation energy as possible is a fundamental requirement for theoretical methods to achieve chemical accuracy,¹⁶ as in quantum chemistry realms, the correlation energy is defined as the energy difference between the Hartree-Fock method with an infinite basis set, and the exact electronic energy eigenvalue obtained from solving the Schrödinger equation.¹⁷ In recent years, theoretical chemists have made tremendous progress in solving this problem by introducing empirical dispersion correction terms for density functional theory models,^{18–23} and developing local selection schemes for coupled cluster theory,^{24,25} which have improved the accuracy of computational models, and sped up computations by orders of magnitude.

Technological developments and advances in computational chemistry have also made energy decomposition analyses based on various *ab initio* methods accessible to the broader chemistry community.^{26–29} As a consequence, we can now look back on a pool of studies in which most NCIs relevant in chemical and biological systems have been decomposed into their fundamental components at a reliable level of theory.^{30–41} The greater picture is, that many non-covalently bound systems cannot be reduced to being entirely dominated by just electrostatic, inductive, or

LD contributions. In this regard, hydrogen bonding is probably one of the most prominent examples.³⁸ Typically understood as an electrostatic Keesom interaction of permanent dipoles or multipoles, it was shown in a recent study that, although electrostatics account for most of the attraction in an average neutral hydrogen bond, London dispersion contributes 30% to the overall bonding energy.³⁸

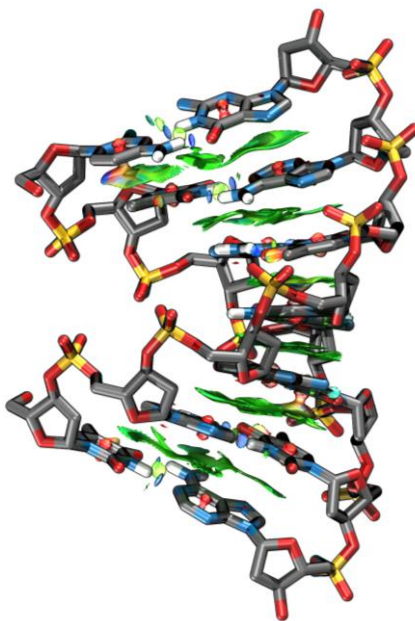


Figure 2: Intramolecular NCI-plot of a TAGCTAG DNA fragment generated using conformational parameters from experimental fiber-diffraction data.^{42,43} Hydrogen atoms not involved in hydrogen bonding omitted for clarity. Isosurfaces colored red represent repulsive interactions, green isosurfaces represent weak NCIs (LD interactions), and blue isosurfaces represent strong attractive interactions (hydrogen bonds). Isovalues of 0.3, in the range of $\text{sign}(\lambda_2)\rho = -0.05$ to $+0.05$ [a.u.].

In context of the relevance of hydrogen bonding for the molecular structure of DNA^{44–46} or proteins,^{47–50} contributions from London dispersion to intramolecular hydrogen bonding easily sum up to hundreds of kcal mol^{-1} and more in such biopolymers.^{31,41,51} Further LD interaction contributions are present in the form of π - π -stacking,^{31,41,52} an interaction commonly mislabeled as a Keesom quadrupole-quadrupole interaction, which in most relevant cases is actually dominated by London dispersion.⁵³ An NCI-plot (Figure 2) illustrates the importance of LD interactions for the structural integrity of DNA. Briefly, NCI-plots are a computational method for visualizing intra- and intermolecular NCIs, through the use of electron densities and reduced density gradients.^{54,55} The resulting visualizations indicate strong attraction (e.g., electrostatic attraction from hydrogen bonds) in the form of blue colored isosurfaces, weak non-covalent interactions (LD interactions) as green isosurfaces, and repulsive interactions as red isosurfaces (Figure 2).

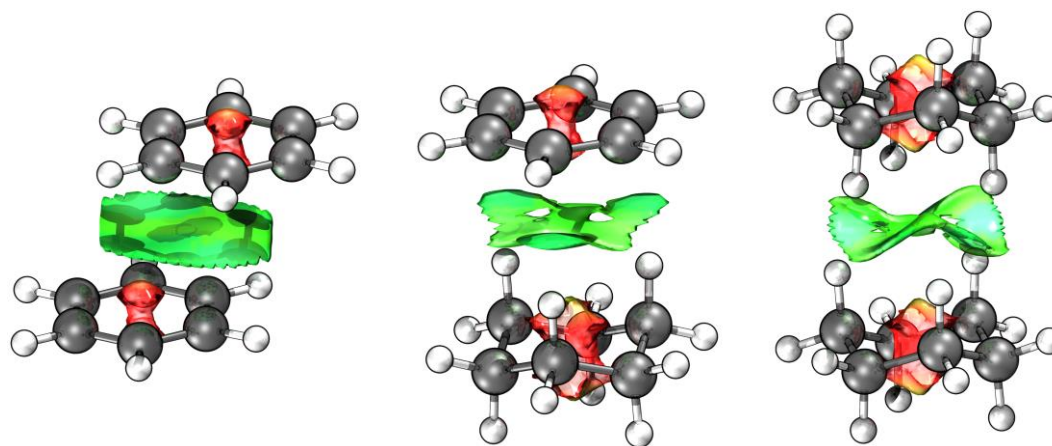


Figure 3: Intermolecular NCI-plots of (from left to right) a benzene dimer, benzene-cyclohexane dimer, and a cyclohexane-cyclohexane dimer computed at the PBEh-3c⁵⁶ level of theory. Isosurfaces colored red represent repulsive interactions, green isosurfaces represent weak NCIs (LD interactions), and blue isosurfaces represent strong attractive interactions. Isovalues of 0.3, in the range of $\text{sign}(\lambda_2)\rho = -0.05$ to $+0.05$ [a.u.].

Third in the league of attractive vdW forces are dipole/multipole-induced dipole/multipole interactions (Debye force, Figure 1).³ If we consider benzene as a prototypical permanent quadrupole, one would expect an energy decomposition analysis of a cyclohexane-benzene dimer to yield an induction dominated interaction. However, recent studies have shown, that irrespective of the dimer geometry, the interaction is mostly dominated by London dispersion.⁵⁷ The latter can also be seen from a comparison of NCI-plots of dimeric structures of benzene and cyclohexane (Figure 3), which do not reveal any strong electrostatic interactions through the presence of blue isosurfaces. Furthermore, literature studies suggest all of the dimers shown in Figure 3 to have a comparable interaction energy on the order of -3 kcal mol^{-1} .⁵⁸ Similar to the π - π -stacking of small aromatic systems,⁵³ the interaction of cyclohexane and benzene is an example of a clearly dispersion dominated interaction prone to being misunderstood as an electrostatic, or in this particular case, inductive interaction.

Having discussed only a few illustrative examples, it is apparent that, characterizing non-covalent interactions is not necessarily trivial, as there exists a continuum between the classical categories of vdW forces. It also seems, LD interactions are not only underestimated, but are often mistaken for a completely different type of interaction. However, as LD interactions are better viewed as an embodiment of dynamic electron correlation, it is certainly true, that a quantum chemical description of any molecular or atomic system is never actually complete without considering London dispersion.

1.2 Dispersion Energy Donors in Catalyst Design, Functional Materials, and Molecular Chemistry

Bulky and highly polarizable functional groups, in particular the 'butyl group, are referred to as 'dispersion energy donors' (DEDs) by those explicitly utilizing such functional groups in the design of molecular systems to control certain properties through LD interactions.^{59–61}

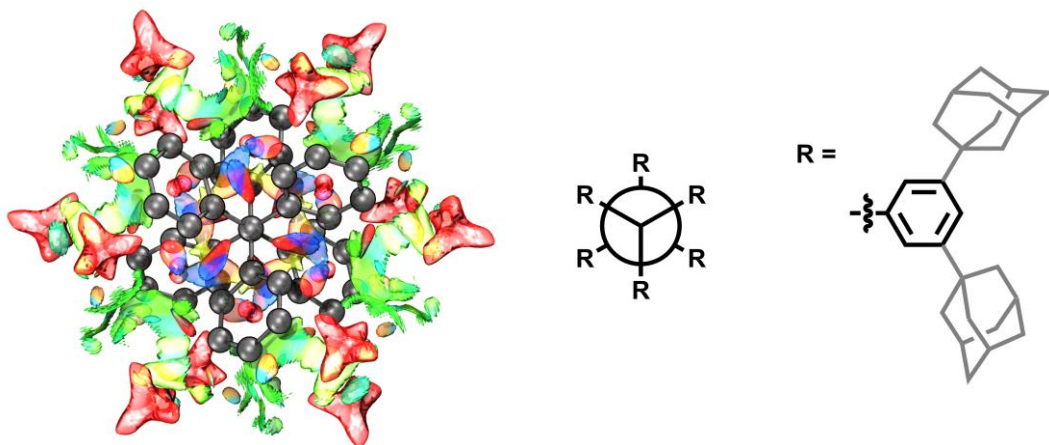


Figure 4: Intramolecular NCI-plot of *all-meta* adamantyl hexaphenylethane, generated from data published by Schreiner *et al.*⁶² Hydrogen atoms and adamantyl moieties omitted for clarity reasons. Isosurfaces colored red represent repulsive interactions, green isosurfaces represent weak NCIs (LD interactions), and blue isosurfaces represent strong attractive interactions. Isovalues of 0.3, in the range of $\text{sign}(\lambda_2)\rho = -0.05$ to $+0.05$ [a.u.].

An exceptional application of DEDs, which has led to discoveries broadening our understanding of chemical bonds is the use of DEDs in stabilizing elusive molecular species.^{62–73} One of the molecular systems standing out are hexaphenylethanes (HPEs), due to their historic role in driving the development of models on (mesomeric) resonance and radicals.^{62,69,72–75} The reason for the instability of plain unsubstituted HPE is steric repulsion between the phenyl rings^{62,71,72}, resulting in formation of quinoid-like dimers, which are in equilibrium with long-lived triphenylmethane radicals in solution.^{74,75} Thus, the attachment of bulky DEDs, counterintuitively, leads to a stabilising countering of the steric repulsions through peripheral London dispersion interactions (Figure 4).^{62,71,72} Notably, non-dispersion corrected DFT methods predict unphysical dissociation energies for DED-substituted HPEs.⁷¹ The effect of peripheral LD attraction leading to stabilization of elusive bonding modes has been termed 'corset effect',⁶³ an effect also responsible for the ambient condition stability of 'butyl- and trimethylsilyl tetrahedrane.^{63,64} Beyond the stabilization of unusual molecular species, the introduction of DEDs has been shown to have a considerable effect on the behavior of azobenzene molecular switches in solution by Wegner and co-coworkers.^{76–81} Through peripheral installment of DEDs

on a diphenyl azobenzene scaffold, substantial stabilization of the crowded, and inherently thermodynamically disfavored Z-isomer could be achieved. This resulted in an isomerization/switching rate that is lowered by more than an order of magnitude in comparison to the parent diphenyl azobenzene.⁷⁶ Expanding the concept to a system for practical use, DED-substitution was recently shown to improve energy storage capabilities of azobenzene-based solar thermal energy storage materials by Wegner and co-workers.⁷⁷

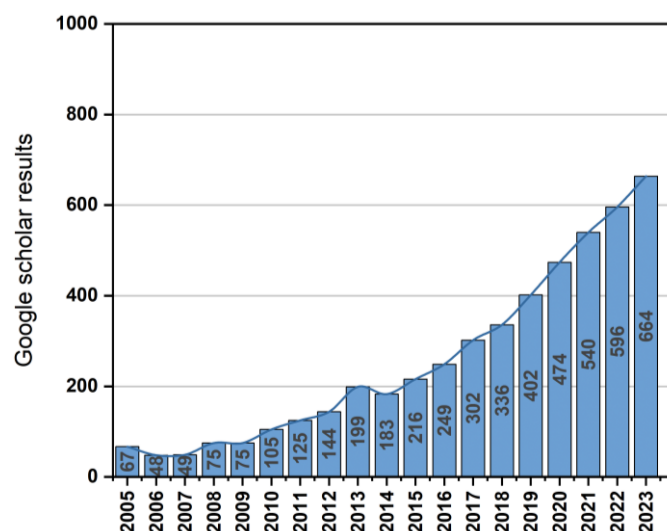


Figure 5: Google scholar results for the keyword combination of “London dispersion” and “catalysis” in the years from 2005 to 2023.⁸²

The substantial conceptual efforts on DEDs have been accompanied by an increasing acknowledgement of LD interactions in other fields of research, such as catalysis (Figure 5).^{61,82} Nonetheless, ground-up approaches for catalyst designs involving the use of DEDs are still far from common. While the incorporation of such moieties certainly increases the chance of a catalyst interacting with a substrate through LD interactions, unless the models invoked to predict the outcome are accurate and reliable, there is no guarantee of achieving an improvement of a system through DEDs. The situation is further complicated by LD interactions of non-polar groups/molecules being inherently non-directional, and hence making pen-and-paper models particularly prone for erroneous predictions. However, as computational methods for exploring chemical hypersurfaces have become very reliable, fast, and semi- to fully-automated, this problem can be solved much more efficiently nowadays.^{83,84}

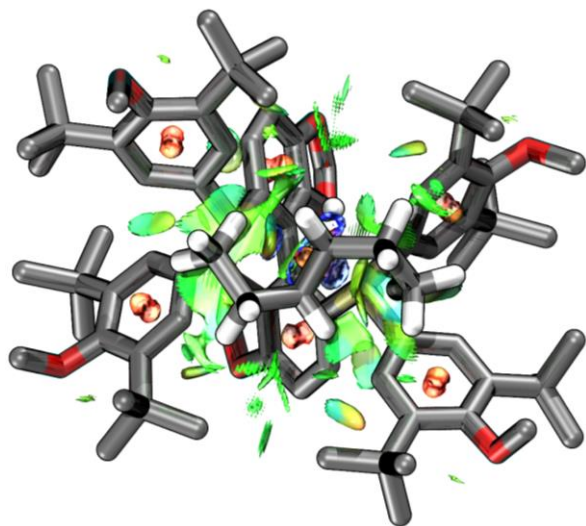


Figure 6: Intermolecular NCI-plot of the rate determining transition state of the copper/SEGPBOS catalyzed hydroamination of unactivated alkenes reported by Liu *et al.*⁸⁵ Generated from data published in the original work, hydrogen atoms on SEGPBOS ligand omitted for clarity.⁸⁵ Isosurfaces colored red represent repulsive interactions, green isosurfaces represent weak NCIs (LD interactions), and blue isosurfaces represent strong attractive interactions. Isovalues of 0.3, in the range of $\text{sign}(\lambda_2)\rho = -0.05$ to $+0.05$ [a.u.].

One example of successful DED incorporation can be found in the copper catalyzed hydroamination of unactivated alkenes employing DED-substituted phosphine ligands, which was recently reported by Liu and co-workers.⁸⁵ Briefly, the activation barrier of the rate determining transition state could be reduced by several kcal mol^{-1} for all investigated classes of phosphine ligands through *all-meta* substitution with bulky *t*-butyl groups. Computational models predicting improved catalyst-substrate binding through LD interactions (Figure 6) were in good agreement with yield improvements of 80% and more.⁸⁵ Another noteworthy example of an application of DEDs in catalysis was recently reported by Hartwig and co-workers in the form of an asymmetric copper-catalyzed hydroboration reaction.⁸⁶ Employing chiral biphosphine ligands carrying either peripheral *t*-butyl, trimethylsilyl (TMS), or trimethylgermanium moieties, increasing bulkiness and polarizability was found to improve selectivity and the overall reaction rate, due to enhanced LD interactions between catalyst and substrate.⁸⁶

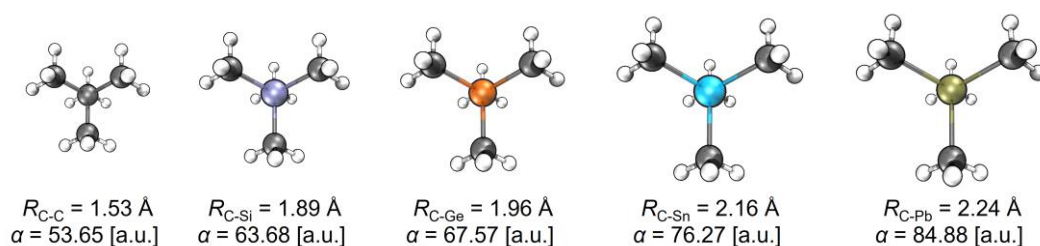


Figure 7: Geometries and polarizabilities of group 14 neopentyl derivatives computed at the PBEh-3c⁵⁶ level of theory.

The latter example highlights the potential of higher group 14 element-based moieties to function as DEDs featuring greater vdW surface areas and polarizabilities in comparison to carbon DEDs (Figure 7). However, when following this approach chemical inertness has to be kept in mind, as covalent bond lengths in DEDs generally increase going from carbon to tin- or even lead-centered moieties.⁸⁷ Silyl groups offer a reasonable tradeoff between polarizability, bulkiness, and chemical inertness. In organic synthesis, silyl groups are highly valued as protecting groups for alcohols, due their ease of installation under mild conditions, highly tunable stability, and selective cleavability.⁸⁸ Consequently, the chemical behavior of silyl groups is well understood following decades of heavy use in synthesis, and a library of various bulky silyl groups is commercially available.^{88–92}

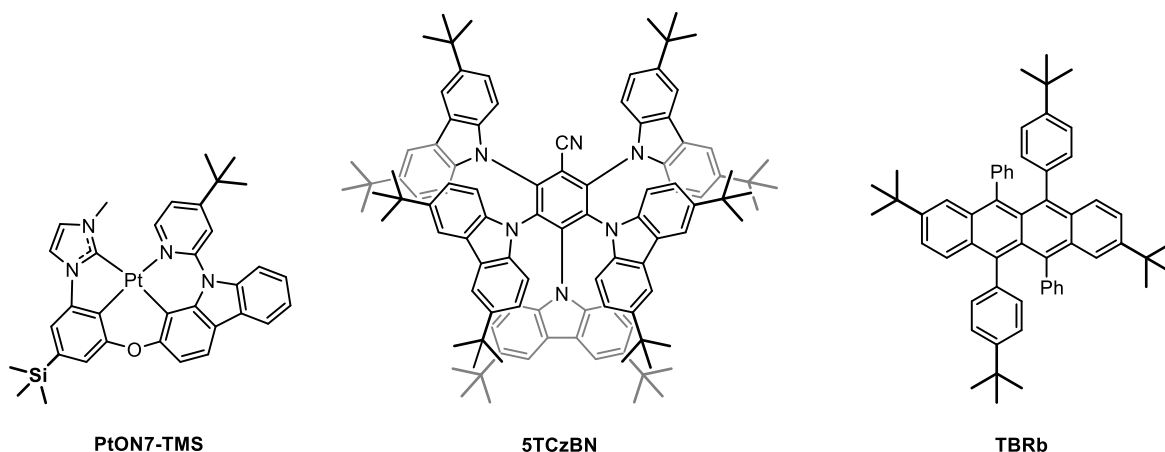


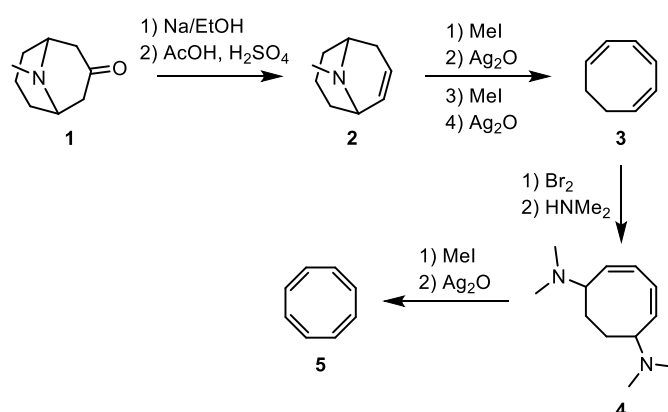
Figure 8: Examples of DED-substituted luminescent compounds utilized in organic light emitting diodes (OLEDs).^{93–95}

Both ^tbutyl, and TMS, have also found use in the field of organic/organometallic luminescent materials (Figure 8).^{93–97} In this field of application, DEDs are typically viewed as being steric bulk providers, and thus hindering oligomerization induced non-radiative decay of excitons, which reduces the efficiency and chemical stability of (organic) light emitting diodes (OLEDs).⁹⁶ However, multiple studies on DED-substituted molecular species indicate free aggregation to be

thermodynamically favored as a consequence of DED attachment.^{77,98} This of course only holds true for cases where aggregation is not enforced, possibly leading to an increasing influence of steric repulsion. Hence, DEDs are much more likely to affect geometrical parameters of aggregates, which can lead to photophysical improvements.⁹³ The implication of aggregate geometries being of great importance, leads to challenges because DED-incorporation at different points of a molecular backbone can lead to opposing effects. Consequently, even though computationally investigating large and heavy-atom containing systems can be tedious and computationally challenging, it is very likely worthwhile to study such oligomerization processes *in silico*.⁸⁴

As can be seen from the examples discussed in this section, strategically incorporating DEDs into catalysts and functional materials has several potential advantages, as DEDs are bulky, highly-polarizable hydrocarbon moieties, they combine aspects of lipophilicity, chemical inertness, and solubility. However, a key component for the successful exploitation of DEDs in such applications is supplementary computational analysis of the chemical space.

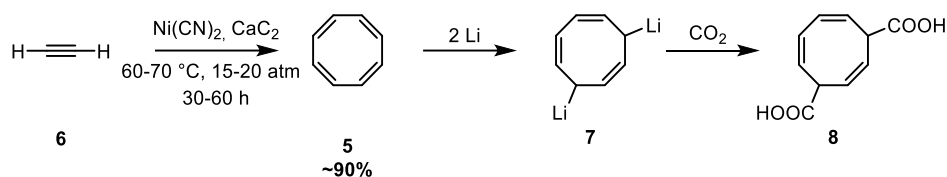
1.3 Cyclooctatetraenes – History, Synthetic pathways, and Utility as Molecular Balances



Scheme 1: The first reported synthesis route for cyclooctatetraene **5**.⁹⁹

Cyclooctatetraene (COT) **5** is an annulated olefin featuring four double bonds adopting a tub-shaped, *D*_{2d}-symmetric geometry. COT was first prepared in the beginning of the 20th century, when rising interest in the chemistry of eight-membered unsaturated hydrocarbons saw Willstätter publishing a synthesis route for the parent COT molecule starting from pseudopelletierine **1** (Scheme 1).⁹⁹ The latter, an eight-membered bridged cyclic ketone, was isolated from the bark of pomegranate trees on a 100 kg scale.^{99,100} This process yielded about

100 g of pseudopelletierine **1**, which gave 3-4 g of COT following Willstätter's synthesis route.^{99,100}



Scheme 2: Nickel-catalyzed annulation of acetylene **6**, and first reported 2-e⁻ reduction of cyclooctatetraene **5**, published by Reppe *et al.*¹⁰⁰

Therefore, it was not until Reppe's efforts on high pressure acetylene chemistry were published more than 30 years later, that the chemistry of COT could be widely explored at a reasonable cost (Scheme 2).¹⁰⁰ Reppe and co-workers found COT as the main product in yields of up to 90%, when pressurized reaction vessels charged with tetrahydrofuran and acetylene were heated for extended periods of time in the presence of either nickel(II) cyanide or thiocyanate.¹⁰⁰ It was envisioned, *in situ* formed nickel(II) acetylide complexes would not only catalyze radical polymerization steps, but in particular favor COT-annulation.¹⁰⁰ Achieving the preferred formation of COT in a catalytic system, over the thermodynamically strongly preferred benzene, stands out as a remarkable achievement even more than 80 years later. Besides characterizing COT and comparing analytical results to Willstätter's originally reported values, the reactivity of COT was explored under various conditions.¹⁰⁰ These included oxidative and reductive conditions, halogenations, and Diels-Alder reactions.¹⁰⁰ Although not formally recognized as aromatic, the formation of the COT-di-anion **7/17** via 2-e⁻ reduction with alkali metals was also described for the first time (Scheme 2).¹⁰⁰

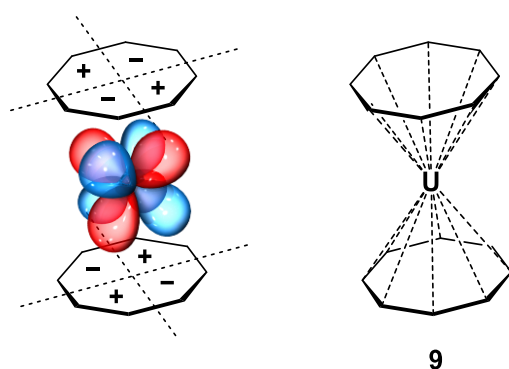
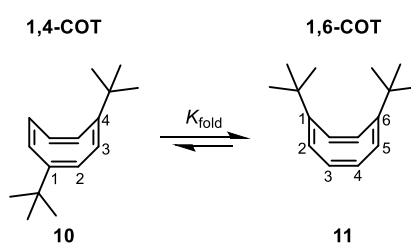


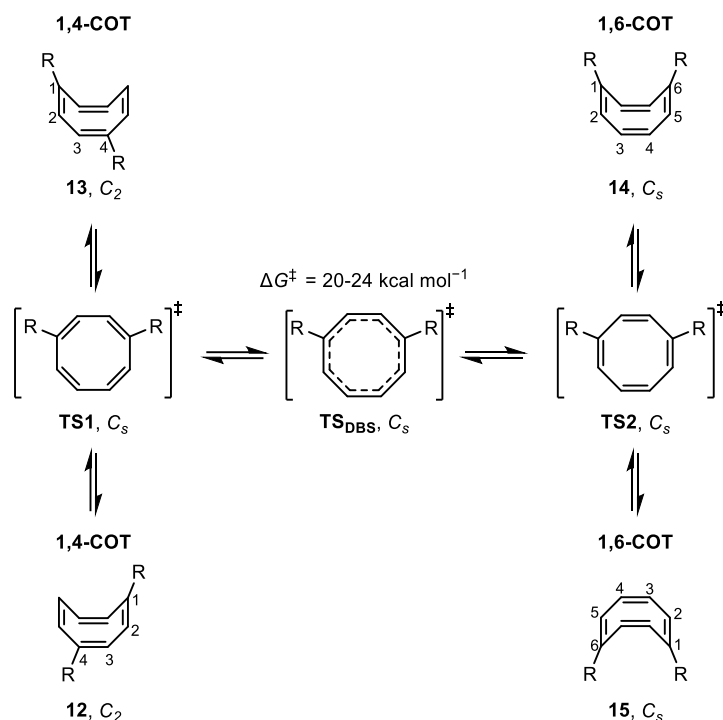
Figure 9: Orbital signs of the HOMOs of COT-di-anion ligands, and $f_{\pm 2}$ orbitals of U⁴⁺ cation (left). Chemical structure of uranocene **9** (right).¹⁰¹

The latter approach proved to be particularly useful for di-functionalization of COT,^{102–105} and for the preparation of lanthanide^{106–111} and actinide^{112–117} complexes. The use of COT (derivatives) as ligands in their di-anionic form brought a breakthrough for obtaining f-block sandwich metallocenes.¹⁰¹ Only a few years after the compounds had been suggested to exist theoretically,¹¹⁸ Streitwieser and Müller-Westerhoff were first to report on the successful synthesis of such a complex (uranocene **9**) in 1968 (Figure 9).¹¹² The extensive studies on COT lanthanocenes and actinocenes that followed, helped to expand the models on metal ring bonding known from d-block metallocenes.¹⁰¹ The bonding in f-block metallocenes can be understood from a simple orbital symmetry analysis of COT-di-anion HOMOs and the unoccupied *f*-orbitals of the metal cation (Figure 9).¹⁰¹



Scheme 3: Folding equilibrium of di-^tbutyl COT **10/11** described by Streitwieser *et al.*¹¹⁹

Notably, Streitwieser was also co-authoring the first reported synthesis of di-^tbutyl COT **10/11**, which showed an unusual equilibrium behavior.¹¹⁹ The sterically crowded 1,6-valence isomer **10** was found to be favored over the 1,4-isomer in ¹H-NMR studies, irrespective of the temperature in CDCl₃ solution.¹¹⁹ While Kluttz, Streitwieser, and Lyttle correctly identified “van der Waals attraction” as the source of stabilization of the 1,6-isomer **11**, they did not address the isomerization mechanism in this publication. One year after, Paquette *et al.* hypothesized a ring-inversion bond shift mechanism, to be responsible for the dynamical behavior observable via ¹H-NMR of such COT derivatives (Scheme 4).¹²⁰



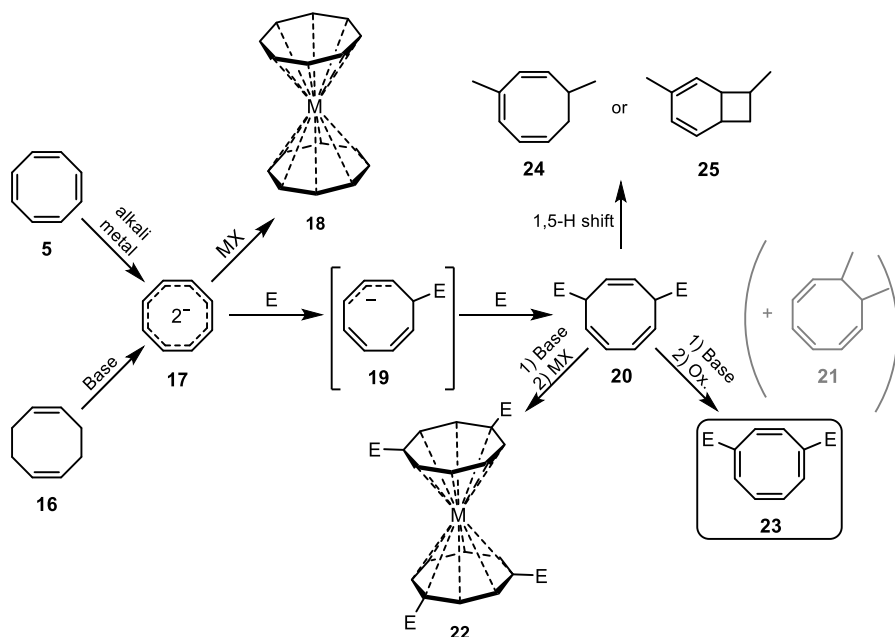
Scheme 4: Ring-inversion double-bond-shift isomerization mechanism of 1,4/1,6-cyclooctatetraenes.^{120–123}

The mechanism shown in Scheme 4 has been validated at high computational levels¹²³ and via spectroscopic techniques.¹²² Considering 1,4/1,6-di-substituted cyclooctatetraenes, if the 1,4-isomer **12** drawn in the bottom left corner of Scheme 4 is arbitrarily set as the starting point, it can be seen that, ring inversion proceeds through the planar C_s symmetric transition state structure **TS1**, in which the double bonds are localized. In this way the C_2 symmetric 1,4-isomers **12** and **13** are interconverted. The latter are mirror images of each other, and hence are indistinguishable in conventional NMR spectroscopy. The same relation holds true for the 1,6-isomers **14** and **15**, which interconvert through **TS2**, yet belong to the C_s point group, with an intramolecular plane of symmetry.

The difference in symmetry between the 1,4- **12/13** and 1,6-isomers **14/15** is reflected in their respective NMR spectra as well, with the 1,4-isomer exhibiting a singlet and two AB-quartet signals, while the 1,6-isomer shows three singlet signals.¹⁰⁵

Transition state structure **TS1** can undergo a double-bond-shift to **TS2** and vice versa, passing through the antiaromatic, C_s symmetric planar transition structure **TS_{DBS}**, in which the double bonds are delocalized. As **TS_{DBS}** is higher in energy than **TS1** or **TS2**, it resembles the rate determining transition state.¹²² The activation barrier for **TS_{DBS}** has been determined experimentally for various di-substituted derivatives, with $\Delta G^\ddagger$ typically in the range of

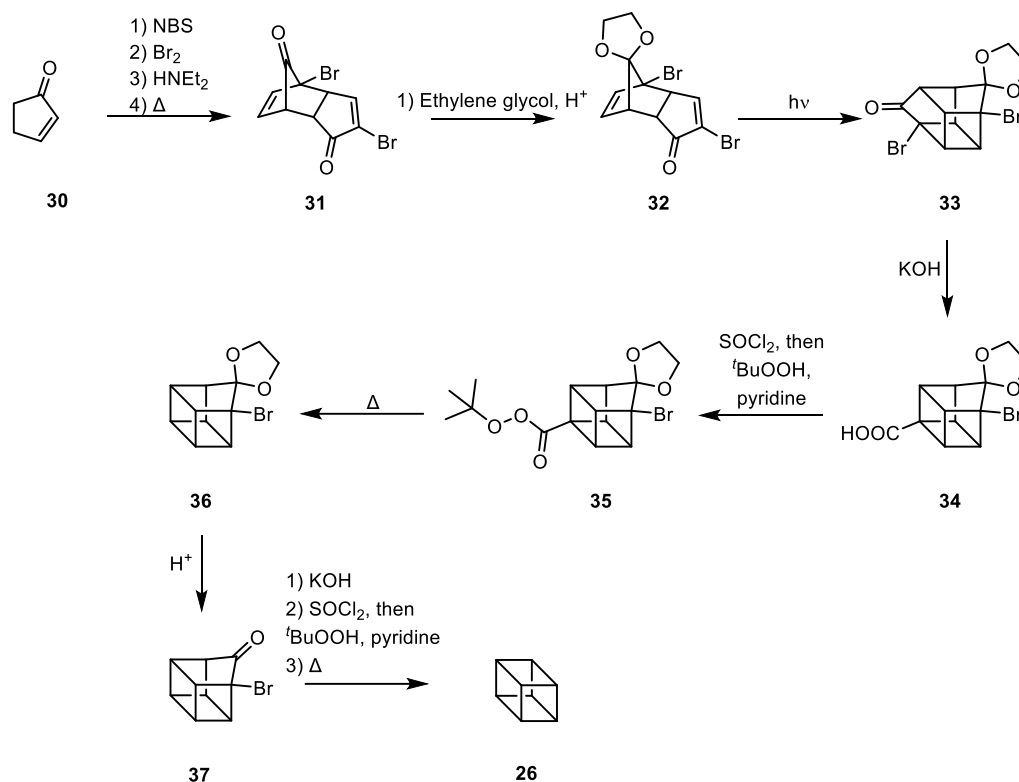
20-24 kcal mol⁻¹, which implies the system should reach equilibrium within a few hours at near ambient temperatures according to transition state theory.¹²⁰



Scheme 5: Overview of synthetic pathways, based on COT-di-anion **7/17**, for obtaining di-functionalized COTs **23** and metallocenes **18/22**.^{102–105,124}

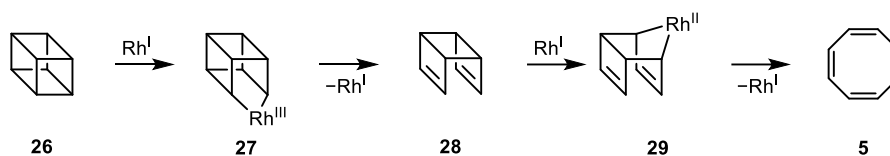
Over the years, various synthetic approaches based on either the COT-di-anion **7/17**,^{102–105,124} eight-membered precursors,¹²⁵ or bottom-up Diels Alder approaches¹²⁶ have emerged, mostly motivated by metallocene synthesis. The COT-di-anion approach in particular stands out, as 1,4/1,6-di-substitution can be achieved in a single synthesis step using either COT **5** or the much cheaper 1,5-cyclooctadiene **16** as starting material (Scheme 5).¹²⁴ The obtained alkali metal COT-di-anion complexes can be reacted with electrophiles **E**, such as trimethylsilyl chloride.¹⁰⁵ Depending on the final application, the intermediate di-substituted 1,3,6-cyclooctatrienes **20** can be deprotonated forming a functionalized COT-di-anion, which might be utilized directly for preparing metallocenes **22**.¹²⁷ Alternatively, the functionalized di-anion can be oxidized, to obtain the corresponding COT derivatives **23**.¹⁰⁵ The latter might be useful for long-term storage, as the abovementioned 1,3,6-cyclooctatrienes **20** have a tendency to undergo 1,5-hydride shifts forming either 1,3,5-cyclooctatrienes **24** or bicyclo[4.2.0]octadienes **25**.¹⁰⁴ The prime limitation of the di-anion approach for obtaining 1,4/1,6-di-substitution lies in the rivaling 1,2-addition of electrophiles (**21**), as can be seen from resonance structures of the intermediate anionic tri-ene **19** (Scheme 5).¹⁰²

One of the more unusual approaches for obtaining COT derivatives is based on the valence isomerization of cubanes.¹²⁸ Cubane chemistry has seen a renaissance in recent years due to potential applications of cubanes in the field of functional materials,¹²⁹ and as bioisosteres of benzene in medicinal chemistry.^{129–131}



Scheme 6: Original synthesis pathway for cubane **26** published by Eaton *et al.*^{128,132}

Cubane **26** was first prepared by Eaton *et al.* in 1964, utilizing 2-bromocyclopentadienone, which had to be prepared in a three-step process starting from cyclopentenone **30** (Scheme 6).^{128,132} 2-Bromocyclopentadienone dimerizes in analogy to cyclopentadiene in a Diels-Alder reaction. The bridgehead ketone of the resulting dimer **31** was acetal protected, before an intramolecular [2+2] photo-cycloaddition was carried out forming the caged precursor **33**. A sequence of Favorskii rearrangements, followed by decarboxylation steps was then utilized to obtain cubane **26** in a total of 10 synthesis steps and a respectable yield of 6% starting from **30**.^{128,132} A streamlined synthesis starting from cyclopentanone was published a few years later,¹³³ and has recently been further optimized, allowing for the synthesis of the 1,4-cubane dicarboxylic acid on a 0.5 kg scale in ~30% yield overall.¹³⁴

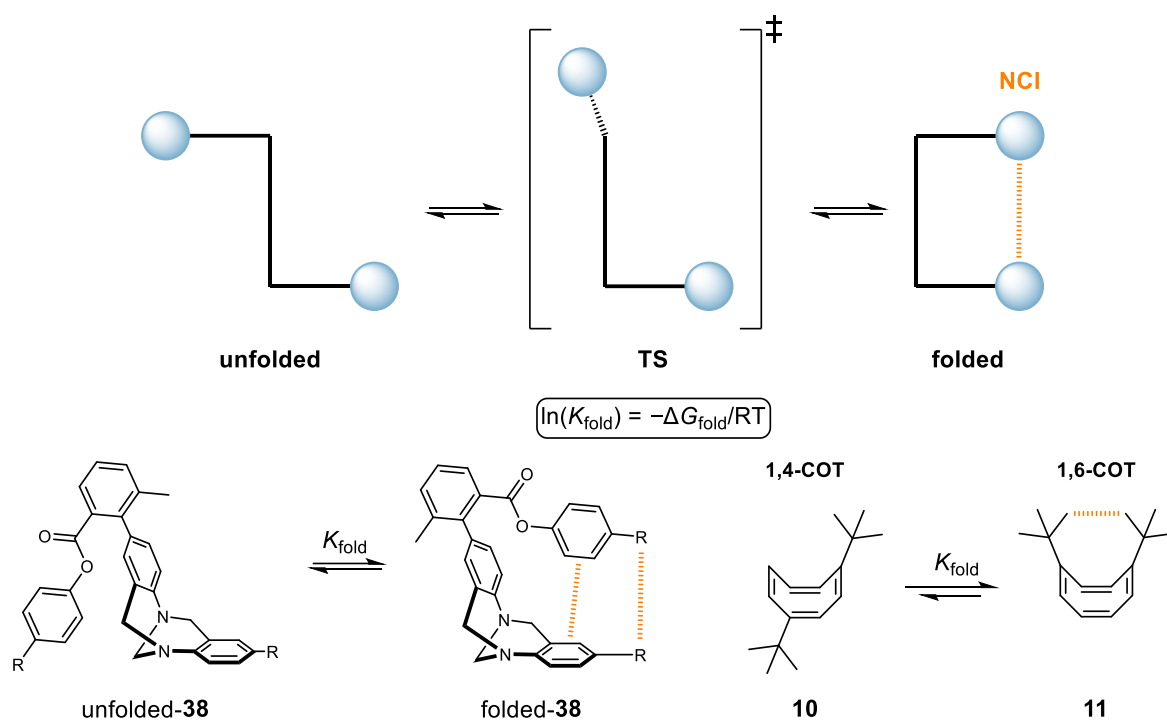


Scheme 7: Rhodium(I)-catalyzed valence isomerization of cubane **26**.¹³⁵

In 1970, Eaton and co-workers were also first to report on the Rh(I)-catalyzed valence isomerization of cubane, forming tricyclooctadienes **28** initially, which further isomerize forming the respective COTs (Scheme 7).¹³⁵ The reaction is believed to proceed *via* a sequence of oxidative additions, forming metal-organic Rh(III) species **27/29**, followed by reductive elimination, which yields two double bonds in each sequence.¹³⁵

The valence isomerization of cubanes offers various advantages for obtaining 1,4/1,6-di-substituted COTs in particular. Oppose to the abovementioned di-anion route (Scheme 5), the valence isomerization proceeds with good functional group tolerance,^{136–138} and does not involve the use of strong bases or oxidizing agents. Furthermore, the reaction will specifically yield 1,4/1,6-di-substituted COTs, given an accordingly functionalized 1,4-cubane derivative was utilized as starting material.^{136–138} Various derivatization procedures have been established for obtaining the latter cubanes, allowing for a wide range of COT derivatives to be prepared in this manner.^{129,139–142} Besides the practical limitations, that arise from the need of a well-established, but nonetheless elaborate preparation of cubanes, most other synthetic limitations stem from possible unwanted rearrangements of the cubane scaffold during derivatization steps prior to valence isomerization, in particular when transition-metal cross-coupling conditions are applied.¹⁴¹

Overall, both the valence isomerization (Scheme 7), and COT-dianion approach (Scheme 5) resemble attractive synthetic pathways for obtaining 1,4/1,6-di-substituted COT derivatives, with certain advantages and drawbacks depending on the type of target molecules that should be obtained. While the COT-dianion approach appears to be particularly useful for direct attachment of bulky substituents in 1,4/1,6-position of the COT scaffold,¹⁰² utilizing the valence isomerization approach allows for obtaining COT derivatives with a wider variety of less bulky substituents in 1,4/1,6-position.^{136–138}



Scheme 8: Schematic representation of a molecular balance system (top) and literature examples (bottom). *N*-arylimide type molecular balance system **38**¹⁴³ (bottom, left) and 1,4/1,6-di-*n*-butyl COT¹¹⁹ **10/11** (bottom, right).

Although COTs have been in the slipstream of recent publications on biologically active cubanes,^{136,137} and some COT lanthanide complexes have shown promising single-molecule magnet properties,¹⁴⁴ widespread applications of COTs are yet to be found. However, the abovementioned folding equilibrium of 1,4/1,6-di-substituted COTs, which can be observed by ¹H-NMR, make the system privileged for application as a molecular balance.^{143,145–153} The latter are molecular systems displaying a chemical equilibrium between a folded and an unfolded state (Scheme 8).^{146,149,150} While in the folded state of the balance, the moieties of interest are in close proximity, and exert an intramolecular NCI on one another, in the unfolded state of the balance the moieties are pointing away from each other.^{146,149,150} Readout of the molecular balance system is usually carried out *via* spectroscopic techniques, and the obtained folding equilibrium constants $K_{\text{fold}}/K_{\text{eq}}$ give direct access to the Gibbs free energy of folding ΔG_{fold} (Scheme 8).^{146,149,150} Thereby, NCIs can be quantified through the study of an appropriately functionalized molecular balance. One of the most well-known systems is the *N*-arylimide type molecular torsion balance **38**, which was first utilized by Wilcox *et al.* to study LD Aryl-aryl interactions (Scheme 8).^{143,145} *N*-arylimide balances were later extensively utilized to investigate various non-covalent interactions,^{146,149,150} as well as solvophobic effects.^{147,154} However, this type of molecular balance contains heteroatoms, which can function as hydrogen bond-acceptors, and can furthermore lead to significant differences in the molecular dipole-moment between the

folded and unfolded state.¹⁵² This can lead to complex solvation effects, making an interpretation of the solvent- and substituent-dependent folding behavior of the balance non-trivial.¹⁵²

In this regard, COT molecular balances have an advantage, as the plain balance scaffold is a pure hydrocarbon. Furthermore, the compactness of the balance system helps to minimize solvation effects resulting from geometric differences between the folding isomers. Therefore, the obtained equilibrium constants K_{fold} , and thereby the folding free enthalpies ΔG_{fold} , usually have a high meaningfulness with respect to capturing the magnitude of the intramolecular NCI at hand.¹⁵⁵

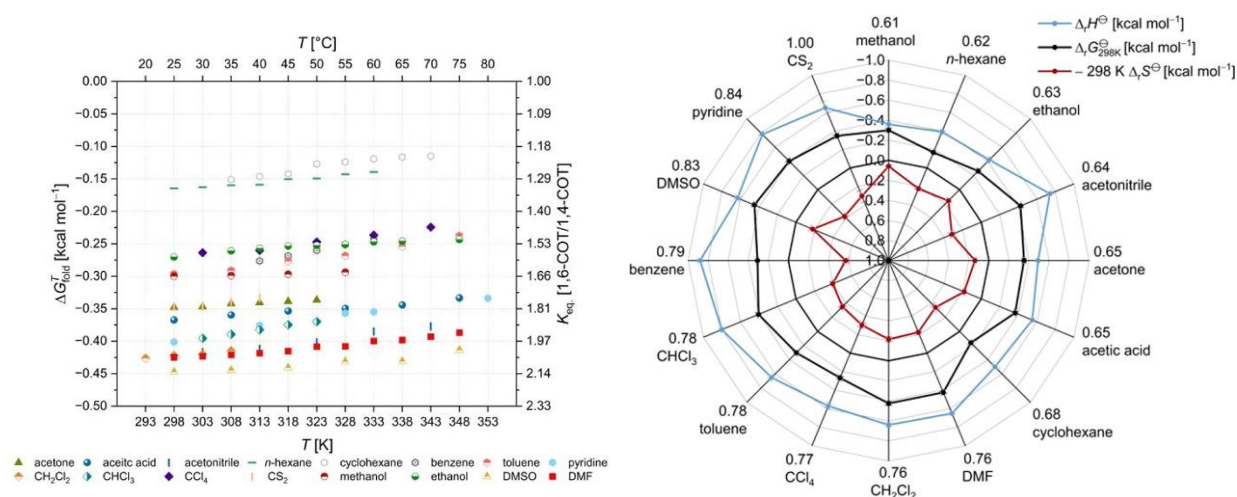


Figure 10: Solvent and temperature dependence of the folding equilibrium of 1,4/1,6-di-⁴butyl COT **10/11** (left) and van't Hoff analysis (right). Adapted with permission from Schreiner *et al.*¹⁵⁵ Copyright 2021 American Chemical Society.

Although COT derivatives have been utilized for studying NCIs in solution decades ago,^{119,126,156–158} it was not until recently, that the potential of a COT molecular balance was fully exploited.¹⁵⁵ Revisiting the folding equilibrium of 1,4/1,6-di-⁴butyl COT **10/11**, an extensive study was conducted by Schreiner *et al.*, involving temperature-dependent NMR measurements in a wide range of organic solvents.¹⁵⁵ This allowed the folding free enthalpy ΔG_{fold} to be further decomposed into enthalpic ΔH_{fold} (LD interactions) and entropic ΔS_{fold} (solvent reorganization) contributions by means of a van't Hoff analysis (Figure 10). It was found that LD contributions were decisive for the equilibrium in all solvents, with some attenuation as a consequence of solvent reorganization.¹⁵⁵ Nonetheless, the folded 1,6-isomer was found to be favored in all solvents and at all temperatures investigated.¹⁵⁵

1.4 Phosphorescent *trans*-Pt(II)-NHC phenylacetylides

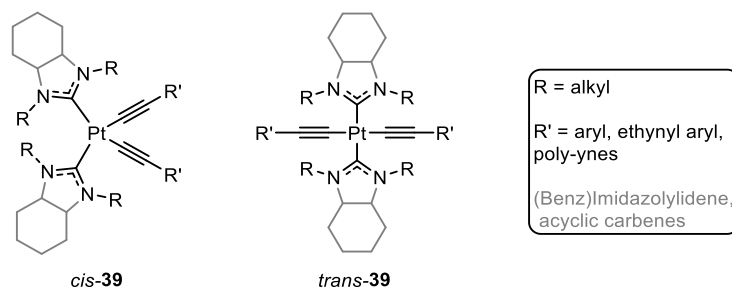
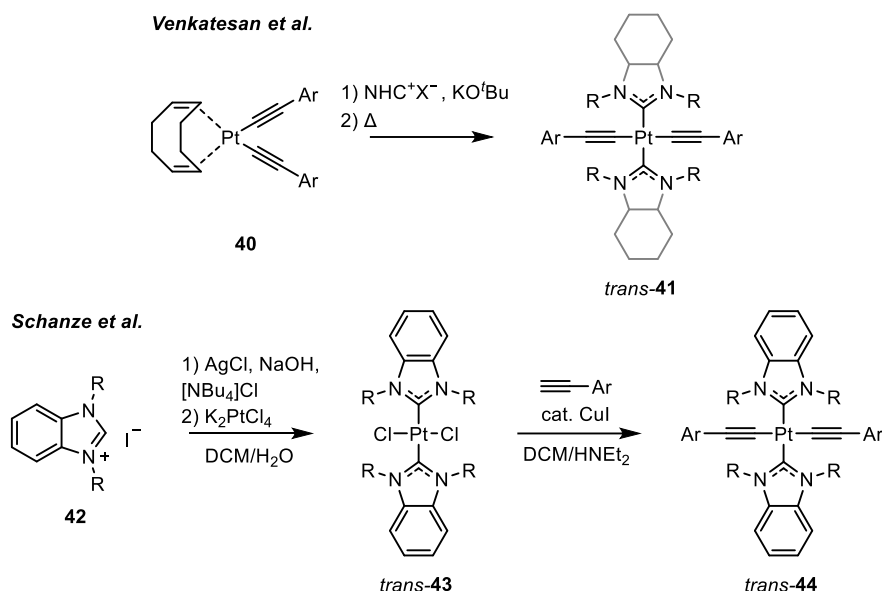


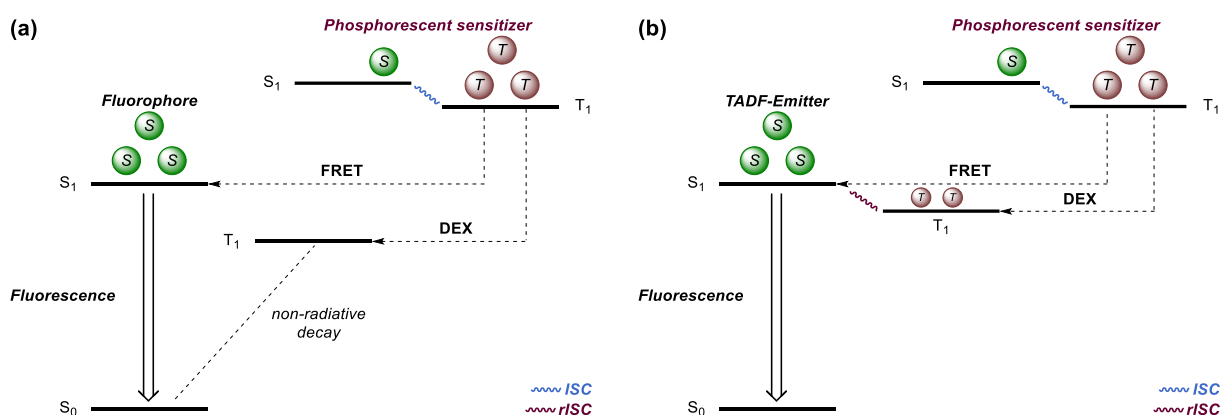
Figure 11: Chemical structures of phosphorescent *cis/trans*-Pt(II)-NHC acetylides.^{159–168}

Recent work has shown the potential of organometallic compounds, such as the *cis/trans*-Pt(II)-*N*-heterocyclic carbene acetylides (*cis/trans*-Pt(II)-NHC acetylides) shown in Figure 11,^{159–168} for light emitting applications.^{169–172} They are generally included in the category of organic light emitting diodes (OLEDs) despite the presence of the metal.^{169–172} The heavy metal generally facilitates intersystem crossing (ISC), due to strong spin-orbit coupling (SOC), between the first excited singlet state S_1 and the first excited triplet state T_1 .^{169–172} If relaxation of T_1 to the singlet ground state S_0 occurs radiatively, a spin-forbidden phosphorescent emission can be observed. In OLED devices excitation is promoted electrically, leading to the formation of singlet and triplet electron-hole pairs, so called ‘excitons’.^{169–172} The utilization of phosphorescent materials in OLED devices hence offers the advantage of achieving conversion of both singlet and triplet excitons into light, which results in a higher efficiency that can theoretically be achieved with phosphorescent OLEDs (phOLEDs).^{169–172} The photoluminescence quantum yield (PLQY) gives the ratio of the number of photons absorbed over the number of photons emitted by an emissive material. In the context of research on OLED emitter materials, PLQYs are an important, experimentally easily accessible, indicator for the efficiency that can potentially be obtained in an OLED device fabricated from the same material.^{169–172}



Scheme 9: Established synthetic pathways for the preparation of *trans*-Pt(II)-NHC phenylacetylides.^{160,173}

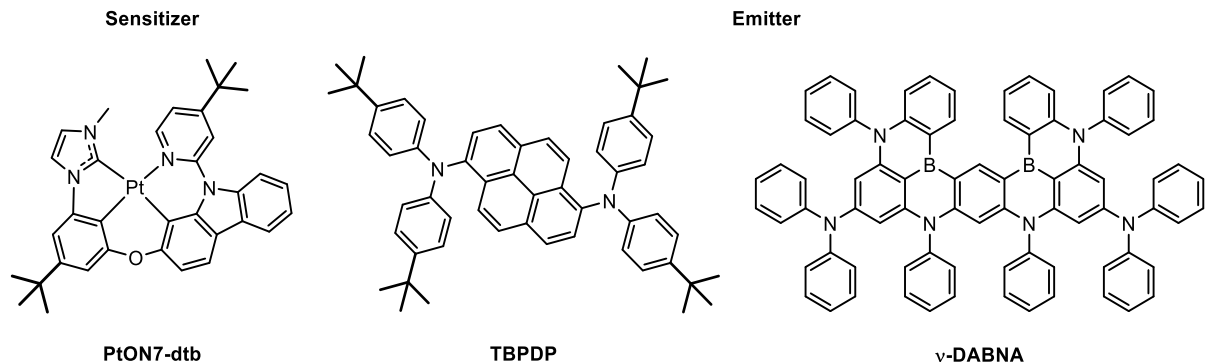
trans-Pt(II)-NHC phenylacetylides were first described by Venkatesan and co-workers in 2013,¹⁶⁰ and were amongst the first monodentate Pt(II)-NHC acetylides to be utilized in phOLED devices.¹⁶⁵ The complexes were initially prepared through isomerization of the respective *cis*-Pt(II) complexes at high temperatures.¹⁶⁰ Soon after, a synthesis procedure utilizing *trans*-Pt(II)-NHC dichlorides was published, which allowed a more convenient synthesis of *trans*-Pt(II)-NHC phenylacetylide derivatives.¹⁷³ Due to the high flexibility in the complex structure, *trans*-Pt(II)-NHC phenylacetylides display low PLQYs in solution, with much higher PLQYs (approaching 60%) typically found in thin film samples.^{159,165} However, at thin film doping concentrations of 10wt% and more, which are relevant for potential application in OLEDs, a significant drop-off of PLQYs is typically found, which is believed to be due to aggregation induced triplet-triplet annihilation.^{159,165} Nonetheless, the benzimidazolylidene derivatives have shown promising photoluminescence properties in the deep-blue region, while also showing good thermodynamic stability. Hence, they are attractive candidates for application in deep-blue or pure-blue OLEDs, given the issue of phosphorescence quenching at higher doping concentrations can be solved. In this regard, silyl-DEDs, could be useful for manipulating the aggregation behavior of *trans*-Pt(II)-NHC phenylacetylides. Especially, since silyl groups have recently shown to improve the photophysical properties of pyrene based fluorescent¹⁷⁴ and tetradentate Pt(II) phosphorescent⁹³ emitters in terms of quantum yield and color purity. Although believed to be mostly related to the steric bulk of TMS groups, detailed literature on the nature of this seemingly universal PLQY-boosting effect of silyl groups remains sparse.



Scheme 10: Emission mechanisms of hyperfluorescent OLED systems utilizing either fluorescent (a), or TADF (b) emitters.

One of the major challenges in the field of OLED research lies in obtaining highly efficient and deep-blue (450-484 nm) narrowband emission with good device stability, which is required for application e.g., in lighting or display technology.^{96,175,176} For phOLEDs the latter is particularly challenging due to the radical character of the long-lived high energy triplet states involved in the emission mechanism (Scheme 10).^{169–172} In phosphorescent Pt(II)-complexes, and other phosphorescent transition metal complexes, radiative decay of the first excited triplet state T₁ to the S₀ ground state is spin forbidden, which results in T₁ usually being long lived, and therefore prone to undergo non-radiative decay through triplet-triplet annihilation or polaron-induced exciton quenching.^{159,177,178} The latter processes can also lead to chemical degradation of emitter materials and thus severely limit device lifetime.^{169–172} A possible workaround to this inherent problem of organometallic phOLEDs, is the utilization of suitable singlet emissive co-dopants, which transforms phOLEDs into so called ‘hyperfluorescent’ OLEDs.^{96,175} In such a hyperfluorescent OLED device, triplet excitons harvested by the phosphorescent sensitizer are converted to singlet excitons *via* Förster resonance energy transfer (FRET) and are emitted through the S₁ state of the co-dopant (Scheme 10).^{96,175} Fluorescent materials (Scheme 10 (a)) as well as thermally activated delayed fluorescence (TADF, Scheme 10 (b)) emitters can be suitable co-dopants, given there exists a decent overlap between the emission spectrum of the phosphorescent sensitizer and the absorption spectra of the co-dopants.^{96,175} The utilization of TADF emitters has the added advantage of preventing triplet exciton build-up, as excitons that are transferred from the phosphorescent sensitizer to the co-dopants triplet state (Dexter energy transfer, DEX) can be up-converted to a singlet exciton through reverse intersystem crossing (RISC), due to the small S₁-T₁ gap of such emitters.^{179,180} Furthermore, multi-resonant TADF

(MR-TADF) emitters¹⁸⁰ usually exhibit narrowband emission (high color purity), which is one of the fundamental requirements for achieving high efficiency in electroluminescent devices.¹⁷⁶



Scheme 11: Chemical structures of sensitizer and emitter materials utilized in the study of Choi *et al.*^{181–186}

The concept of a organometallic hyperfluorescent OLED device was recently demonstrated by Choi and co-workers,¹⁸¹ utilizing a tetradentate Pt(II) phosphorescent sensitizer (PtON7-dtb¹⁸⁶), in conjunction with a MR-TADF (v-DABNA¹⁸²), or pyrene-based fluorescent emitter (TBPDP^{183–185}) (Scheme 11). Although the investigated hyperfluorescent devices emitted closer in the cyan region (490–520 nm) of the visible spectrum, the EQE could be more than doubled in comparison to the phosphorescent device.¹⁸¹ While achieving a peak EQE of more than 25%, device lifetime could also be improved by nearly an order of magnitude over the purely phosphorescent OLED device.¹⁸¹ The aforementioned, *trans*-Pt(II)-NHC phenylacetylides are interesting candidates for application in hyperfluorescent devices, as they generally show a more hypsochromic electroluminescence (439 nm¹⁶⁵) in comparison to PtON7-dtb (457 nm¹⁸⁶), paving the way for deep-blue hyperfluorescent OLED devices.

1.5 Motivation

As outlined in the preceding sections, the concept of strategically incorporating bulky moieties to function as dispersion energy donating sites in the design of various molecular systems has just recently flourished in the chemical community.⁶¹ With few exceptions, such efforts have been limited to the use of carbon-based moieties. However, silyl groups clearly hold great potential to function as DEDs owing to their basic physical properties (polarizability and bulkiness), with the added advantage of the availability of a structurally diverse library of synthetic precursors to choose from. At the same time, the 1,4/1,6-di-substituted COT system has recently proven to be a particularly robust molecular balance system for obtaining quantitative experimental insights into LD interactions of DEDs.¹⁵⁵

Therefore, the aim of this work was to study the utility of silyl groups as dispersion energy donors on a conceptual level utilizing appropriately substituted COT molecular balances. Furthermore, we were interested in testing the capabilities of COT as a molecular balance system against the background of the fundamental nature of LD interactions as a hidden source of stabilization in other NCIs. To investigate potential practical applications of silyl-DEDs, we aimed at exploiting the latter for guiding aggregation and fine-tuning electronic properties of luminescent functional materials for use in OLED devices.

We hence prepared silyl COT molecular balances featuring a modest (section 2.1/2.2)¹⁸⁷ and higher (sections 2.3/2.4)¹⁸⁸ degree of flexibility and investigated their folding behavior. In efforts related to the molecular balances prepared in section 2.3/2.4, we studied a COT molecular balance system modeling an elusive hydrogen bonded dimer (cyclic water dimer transition state¹⁸⁹) in the folded state of the balance (section 2.5/2.6).¹⁹⁰ Finally, we investigated the aggregation behavior and photophysical properties of *trans*-Pt(II)-NHC phenylacetylides substituted with silyl- and carbon-DEDs (section 2.7), with the goal of producing molecules with the potential for blue-emitting OLEDs.

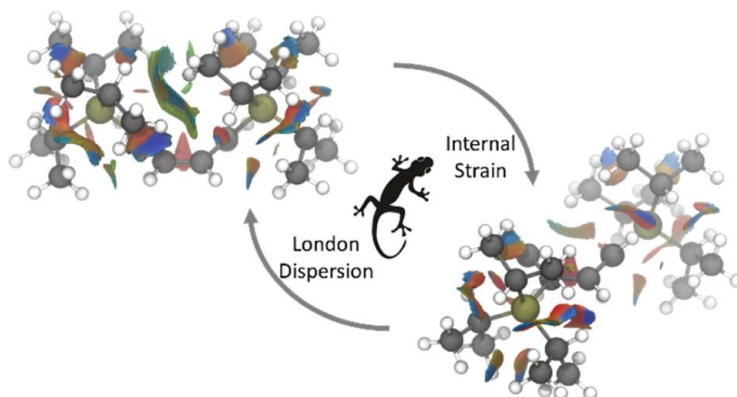
2. Publications & Manuscripts

2.1 Gauging the Steric Effects of Silyl Groups with a Molecular Balance – Introduction

In the framework of our first publication¹⁸⁷, we quantified the steric influence and LD induced stabilization effects exerted by commonly utilized silyl groups on the conformational equilibrium of a 1,4/1,6-di-substituted cyclooctatetraene molecular balance system. The molecular balances were prepared utilizing the di-anion route described in section 1.3, and the folding equilibrium of the balances was investigated *via* ¹H-NMR in deuterated toluene, in a temperature range of 40 °C to 100 °C (313 K to 373 K). This allowed us to dissect our experimentally obtained ΔG_{eq} values into enthalpic and entropic contributions. We conducted detailed computational analyses employing homodesmotic equations and energy decomposition analyses at various levels of theory, to quantify the magnitude of LD stabilization in the 1,6-isomer and other attractive or repulsive interactions. We also computed activation barriers utilizing multi-reference methods, in order to estimate equilibration kinetics.

We found the equilibrium of the molecular balance to shift, favoring the unfolded 1,4-isomer, the bulkier the investigated silyl group. Solely the di-trimethylsilyl (TMS) molecular balance favored the sterically congested 1,6-isomer. Our computational investigations revealed LD interactions to be the decisive contributor to the stability of folded 1,6-isomers. However, the LD governed alignment of silyl groups in the 1,6-isomers also induced substantial strain on the COT backbone in bulkier derivatives, resulting in an overall preference for the 1,4-isomer. However, as our experimentally determined ΔG_{eq} and ΔH_{eq} values correlated very well with steric parameters of the respective substituents, we were able to interpolate steric parameters for the recently introduced tri-*iso*-butylsilyl (TIBS) protecting group.¹⁹¹ We furthermore found TIBS to be a particularly good DED, contributing around -6 kcal mol^{-1} of LD interactions to the stability of the 1,6-isomer. The latter was found to be very likely related to the ‘distal’ substitution pattern. TIBS also displayed a considerably smaller apparent bulkiness than comparable DEDs such as tri-*iso*-propyl silyl (TIPS).

2.2 Paper 1: Gauging the Steric Effects of Silyl Groups with a Molecular Balance



Abstract:

We present an experimental and computational study of a cyclooctatetraene (COT)-based molecular balance di-substituted with commonly used silyl groups. Such groups often serve as protecting groups and are typically considered innocent bystanders. Our motivation here is to determine the actual steric effects of such groups by employing a molecular balance. While in the unfolded 1,4-valence isomer the silyl groups are far apart ($d_{\sigma-\sigma} \geq 5.15 \text{ \AA}$), the folded 1,6-isomer is affected greatly by noncovalent interactions due to close σ – σ contacts ($d_{\sigma-\sigma} \leq 2.58 \text{ \AA}$). In order to investigate the thermodynamic equilibrium between the 1,6- and 1,4-valence isomers, we employed temperature-dependent nuclear magnetic resonance measurements. Additionally, we assessed the nature of attractive and repulsive interactions in 1,6-disilyl-COT derivatives via a combination of local energy decomposition analysis (LED) and symmetry-adapted perturbation theory (SAPT) at the DLPNO-CCSD(T)/def2-TZVP and sSAPT0/aug-cc-pVDZ levels of theory. We identified London dispersion interactions as the main contributor to the molecular stability of the folded states, whereas Pauli exchange repulsion and a resulting internal strain favor the unfolded diastereomer.

Reference:

Henrik F. König, Lars Rummel, Heike Hausmann, Jonathan Becker, Jan M. Schümann, and Peter R. Schreiner, *J. Org. Chem.* **2022**, 87, 7, 4670–4679. DOI: 10.1021/acs.joc.1c03103

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Gauging the Steric Effects of Silyl Groups with a Molecular Balance

Henrik F. König,[§] Lars Rummel,[§] Heike Hausmann, Jonathan Becker, Jan M. Schümann, and Peter R. Schreiner*Cite This: *J. Org. Chem.* 2022, 87, 4670–4679

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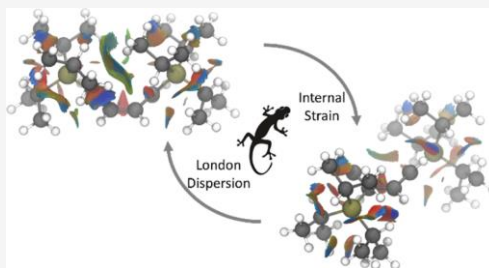
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ABSTRACT: We present an experimental and computational study of a cyclooctatetraene (COT)-based molecular balance disubstituted with commonly used silyl groups. Such groups often serve as protecting groups and are typically considered innocent bystanders. Our motivation here is to determine the actual steric effects of such groups by employing a molecular balance. While in the unfolded 1,4-valence isomer the silyl groups are far apart ($d_{\sigma-\sigma} \geq 5.15$ Å), the folded 1,6-isomer is affected greatly by noncovalent interactions due to close $\sigma-\sigma$ contacts ($d_{\sigma-\sigma} \leq 2.58$ Å). In order to investigate the thermodynamic equilibrium between the 1,6- and 1,4-valence isomers, we employed temperature-dependent nuclear magnetic resonance measurements. Additionally, we assessed the nature of attractive and repulsive interactions in 1,6-disilyl-COT derivatives via a combination of local energy decomposition analysis (LED) and symmetry-adapted perturbation theory (SAPT) at the DLPNO-CCSD(T)/def2-TZVP and sSAPT0/aug-cc-pVDZ levels of theory. We identified London dispersion interactions as the main contributor to the molecular stability of the folded states, whereas Pauli exchange repulsion and a resulting internal strain favor the unfolded diastereomer.



INTRODUCTION

Silyl groups often are conveniently employed to transform, for example, “reactive” hydroxyl groups to “unreactive” silyl ethers.^{1,2} These groups enjoy great popularity due to their commercial availability, simple attachment, as well as mild and selective detachment procedures. Such silyl-protecting groups are commonly chosen on the basis of their stability under typically neutral or basic reaction conditions. The bulkiness of silyl-protecting groups is mostly considered only with regards to selective cleavability.³ The use of abbreviations such as TPS (triphenylsilyl) further obfuscates the spatial demand of such groups. However, attaching bulky silyl-protecting groups to a flexible backbone can significantly alter conformational preferences and hence the stereoelectronic properties of a system. This is highlighted by so-called “super-armed” glycosyl donors, for which exclusive protection with bulky silyl ethers enforces an all-axial conformation.^{4,5} As a consequence, this results in a reactivity increase by more than an order of magnitude in comparison to the benzylated derivatives.^{4,5} Clearly, bulkiness is an important feature of the most frequently utilized silyl-protecting groups, but this fact is often not given much attention. Consequently, only a few efforts have been made to quantify the steric demand of such groups.^{6–8}

In recent years, the role of London dispersion (LD) interactions^{9–12} as a decisive structural factor for conformational preferences and transition structures emerged in a variety of molecular systems.^{13–19} Because LD interactions are

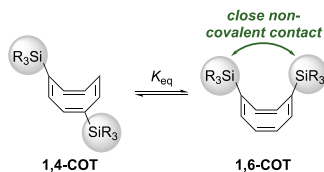
approximately additive pairwise interactions, it is clear that large alkyl and silyl groups must be more than just providers of steric bulk. While LD interactions between alkyl groups, allegedly, are capable of facilitating labile compounds such as hexaphenylethane^{20–23} or coupled diamondoids²⁴ by offering intramolecular stabilization, the effects of commonly utilized silyl groups have not been studied in detail. Apart from intramolecular noncovalent interactions, intermolecular stabilization via silyl groups, that is, in transition structures, can be of great importance. Hartwig et al.²⁵ already demonstrated the impact of trimethylsilyl (TMS) as a dispersion energy donor group²⁶ (DED^{11,27}) in hydroboration reactions. Here, the TMS groups increased reaction rates by binding the substrate more efficiently. With the aim to utilize silyl groups as variable steric directing groups, we chose a cyclooctatetraene (COT)-based molecular balance to gauge the size and potential of commonly used silyl groups to act as DEDs.

A systematic study of the di-*tert*-butyl-substituted COT molecular balance in various solvents highlighted the attractive nature of LD interactions.²⁸ The disubstituted COT system, initially presented by Streitwieser et al.²⁹ using di-*tert*-butyl

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Scheme 1. Equilibrium of 1,4- and 1,6-Disilyl Substituted Cyclooctatetraene

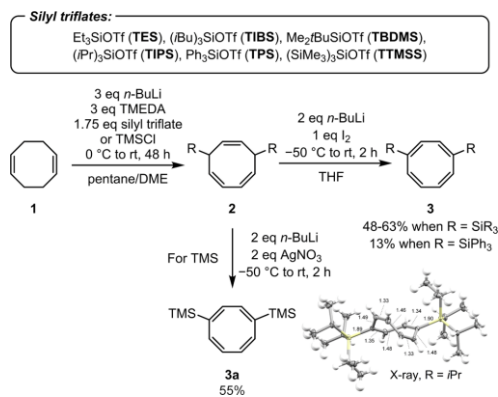
substituents and its folding mechanism (a double-bond valence shift and ring inversion^{30,31}), has been studied both experimentally^{32–34} and computationally.^{35,36} All studies confirmed the sterically more hindered 1,6-di-*tert*-butyl COT to be the preferred valence isomer in solution and in the gas phase.

We chose the COT system to enforce close σ – σ contacts in the 1,6-disilyl-COT (Scheme 1) valence isomer. On the other hand, the 1,4-disilyl-COT does not display close contacts between the silyl groups. An analysis of the equilibrium between 1,6- and 1,4-disilyl-COT should offer insights into the attractive and repulsive nature between the silyl groups. While di-*tert*-butyl substituted COT prefers the folded isomer independent of the solvent, bulky silyl groups are expected to disfavor this valence isomer due to an increasing number of repulsive contacts.²⁸ Therefore, our system is suitable to gauge the relative bulkiness of various silyl groups.

RESULTS AND DISCUSSION

We utilized the COT molecular balance substituted with trimethylsilyl³⁷ (TMS), triethylsilyl (TES), *tert*-butyldimethylsilyl³⁸ (TBDMS), tri-*iso*-propylsilyl³⁹ (TIPS), tri-*iso*-butylsilyl (TIBS), tris(trimethylsilyl)silyl (TTMSS), and triphenylsilyl^{40,41} (TPS).

We adopted modified literature procedures^{37–41} to synthesize the disilyl COT derivatives (Scheme 2). We gathered

Scheme 2. Synthetic Procedure for the Preparation of Disilyl COT Derivatives (Left) and Single Crystal X-ray Structure of di-TIPS COT (Bottom Right, Bond Distances in Å)^a

^aThermal ellipsoid plot of the molecular structure obtained by single-crystal X-ray diffraction was drawn at 50% probability level.

single-crystal X-ray structural data for di-TIPS-COT (Scheme 2) and di-TTMSS-COT (see Supporting Information). Both compounds crystallize in the unfolded valence isomer form, thereby maximizing intermolecular alkyl–alkyl interactions. In solution, di-TIPS-COT equilibrates between both diastereomers. The thermodynamic equilibria were subjected to van't Hoff analyses utilizing temperature-dependent nuclear magnetic resonance (NMR) measurements to dissect the isomerization enthalpies (ΔH_{eq}) and entropies (ΔS_{eq}).

NMR samples were equilibrated for 16 h at 40 °C prior to the experiment (Figure 1) and measured in the temperature range of 313–373 K (steps of 10 K; for details, see Supporting Information). All COT balances show linear regressions with $R^2 > 0.97$. As the folding equilibrium of di-*tert*-butyl substituted COT varies with the NMR solvent in a range from $K_{eq} = 1.18$ –2.13, toluene was chosen for temperature-dependent measurements, as it lies in the middle of the solvent bias range ($K_{eq} = 1.55$).²⁸

We also analyzed the noncovalent interactions between the silyl groups computationally utilizing the well-established B3LYP^{42,43} functional excluding and including LD interactions with the Becke–Johnson (BJ) damped dispersion D3 correction of Grimme et al.^{27,44} This provides an estimate of the LD correction. To validate this method, we compared our results with those computed using the M06-2X⁴⁵ and ω B97X-D⁴⁶ functional combinations. Ahlrich's def2-TZVPP basis set⁴⁷ was used for all computations. Because all methods show the same trend, the B3LYP-D3(BJ)/def2-TZVPP-optimized geometries were utilized as the basis for DLPNO-CCSD(T)/def2-TZVPP single-point energy computations^{48,49} (see Supporting Information). This approach has demonstrated good agreement with experimental data for COT molecular balances.²⁸ The rate-determining double-bond valence shift barrier was computationally estimated to be around 24 kcal mol^{−1} for alkyl-substituted silyl groups, which is similar to that of di-*tert*-butyl COT.²⁸ In contrast, the activation barrier for di-TIPS-COT was estimated to be around 35 kcal mol^{−1}, that is, thermally out of reach for our experimental parameters (see Supporting Information).

While the silyl groups are even more demanding in size than a *tert*-butyl substituent (with van der Waals Volume of around 101 Å³, Scheme 3 and Supporting Information), the equilibria between 1,6- and 1,4-disilyl-COT were assumed to shift markedly toward the unfolded balance. Figure 2 displays the experimental enthalpies ΔH_{eq} (black markings) and the computed values (red markings). While computations suggest that the di-TMS-COT is nearly thermoneutral ($\Delta H_{eq} \approx 0$ kcal mol^{−1}), larger silyl groups shift the equilibrium toward 1,4-disilyl-COT. The computed increase in energy for the equilibrium depicted in Figure 2 between di-TBDMS-, di-TES-, di-TIPS-, and di-TTMSS-COT ranges from 0.3 to 1.4 kcal mol^{−1}, favoring 1,4-disilyl-COT. The computational assessment and the experimental data agree within ± 0.6 kcal mol^{−1} with an experimental error smaller than 0.13 kcal mol^{−1}. The experimentally determined enthalpy value for di-TMS-COT is with $\Delta H_{eq} = -0.6$, only 0.1 kcal mol^{−1} higher in energy than the di-*tert*-butyl substituted COT.²⁸ While di-TTMSS-COT is completely in favor of 1,4-disilyl-COT and therefore cannot be measured, the di-TIPS-COT equilibrium shows the highest enthalpy ($\Delta H_{eq} = 1.7$ kcal mol^{−1}). Interestingly, di-TIBS-COT does not follow the expected pattern that a larger van der Waals surface or volume introduces more steric hindrance into the system. Both the computational and

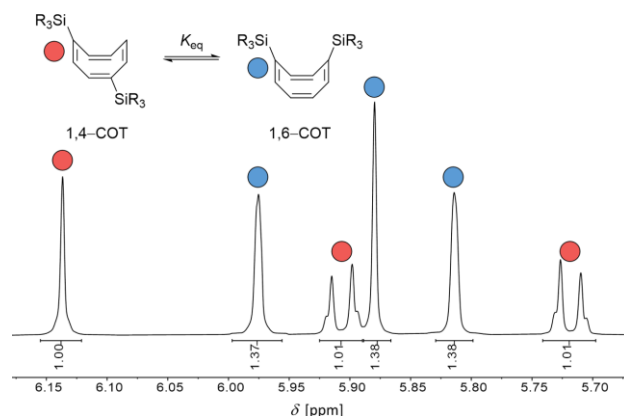


Figure 1. ^1H NMR spectra (600 MHz) and signal assignment of the equilibrium between 1,4- (red) and 1,6-di-TMS (blue) COT at 40 °C.

Scheme 3. Comparison of van der Waals Surfaces and Volumes of Tri-substituted Silyl Groups (Optimized with the Silane Geometry) at the B3LYP-D3/def2-TZVPP Level of Theory

Structure						
Abbreviation	TMS	TBDMs	TES	TIPS	TIBS	TTMSS
Van der Waals Surface [$\text{\AA}^2$]	127.8	171.1	173.3	219.2	295.7	340.2
Van der Waals Volume [$\text{\AA}^3$]	109.2	155.5	151.5	199.6	285.2	328.8

experimental values give a ΔH_{eq} as high as di-TBDMs- and di-TES-COT ($\Delta H_{\text{eq}} \approx 0.8 \text{ kcal mol}^{-1}$). Therefore, an additional source of stabilization must be present.

Three questions arise from the data collected:

1. What is the origin of the stabilization of the folded di-TMS-COT?
2. Why do larger silyl groups not show similar behavior?
3. Why does di-TIBS-COT not follow that trend?

To answer the first question, we focused on the noncovalent interactions between the interacting groups. By utilizing homodesmotic equations,^{50,51} we extracted the magnitude of the LD interactions due to close σ - σ contacts between the silyl groups in 1,6-disilyl-COT. Including and excluding LD interactions via Grimme's D3(BJ) correction results in an LD correction estimate, which we take, in a first approximation, as a measure of the dispersion energy. This seems reasonable, as we are comparing similar groups in the same molecular system where absolute magnitudes are less important than relative measures for comparison.

The analysis reveals large LD contributions between the silyl groups (Figure 3). Whereas the DFT computations excluding LD (red bars) demonstrate the general assumption that large substituents repel each other due to steric hindrance, including LD (blue bars) suggests the opposite trend. The magnitude of LD interactions (green bars) increases with the size of the silyl

groups. Therefore, the largest alkyl substituent (TTMSS) stabilizes 1,6-disilyl-COT by around $\Delta E_{\text{disp}} = -5.0 \text{ kcal mol}^{-1}$. Only di-TIBS-COT deviates from the general trend observed.

For better energy estimates of the intramolecular LD interactions, we performed local energy decomposition^{52–54} (LED) analyses as implemented in ORCA.⁵⁵ Thereby, we separated each balance into three molecular fragments (F1, F2, and F3) according to Figure 4 and dissected the interaction energy into its main parts. Because this process involves bond splitting, the resulting radical fragment interactions involve large electrostatic interactions. As a consequence, we can only isolate an energy term for LD interactions between F2 and F3.

Apart from di-TIBS substituted COT, the results of this analysis (Figure 4) fit qualitatively to the results of the homodesmotic equation (Figure 3). While in both cases the magnitude of intramolecular LD interactions increases from di-TMS- to di-TTMSS-COT, di-TIBS-COT is the strongest dispersion energy donor (DED) group within the LED analysis. On the other hand, di-TMS-COT benefits the least from stabilizing LD interactions. Nevertheless, it is the only case favoring 1,6-disilyl-COT. Counteracting repulsive interactions do not outweigh the LD stabilization in di-TMS-COT. The strong stabilizing contacts between two TIBS groups translate into a measurable shift in the equilibrium as well. In comparison to di-TMS-COT, the interaction is not prominent

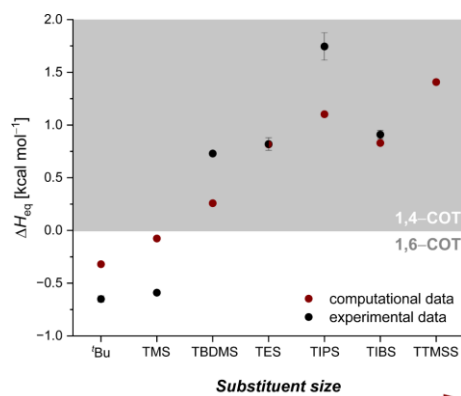


Figure 2. Enthalpies for the equilibrium of 1,4- and 1,6-disilyl substituted cyclooctatetraene. Experimental data (black markings) were derived from van't Hoff analyses. Computations (red markings) at the DLPNO-CCSD(T)/def2-TZVP//B3LYP-D3/def2-TZVP level of theory. The silyl groups were ordered according to increasing van der Waals surface. All datapoints within the shaded area favor 1,4-disilyl-COT. Data for ^tBu was extracted from the work of Schümmann et al.²⁸

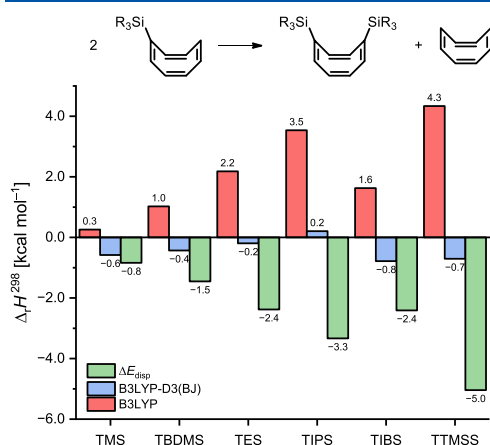


Figure 3. Homodesmotic equation and reaction enthalpies (ΔH^{298}) in kcal mol⁻¹ at B3LYP(D3(BJ))/def2-TZVP.

enough to favor 1,6-disilyl-COT. Because larger groups favor 1,4-disilyl-COT, destabilizing interactions must counteract LD.

To answer the second question, we aimed at isolating the contributions of Pauli repulsion for 1,4- and 1,6-disilyl-COT. We employed symmetry-adapted perturbation theory (SAPT) at the sSAPT0/aug-cc-pVDZ level of theory utilizing a scaled protocol according to Parker et al.⁵⁷ To isolate interactions between the silyl groups, we employed B3LYP-D3/def2-TZVP optimized structures, removed the COT backbone, and saturated the radical sites.⁵⁸ The total interaction energy E_{tot} can then be decomposed into its main components (Figure 5). Whereas the inductive energy E_{ind} (yellow markings) and the electrostatic energy E_{elst} (blue markings) terms marginally stabilize 1,6-disilyl-COT, the main

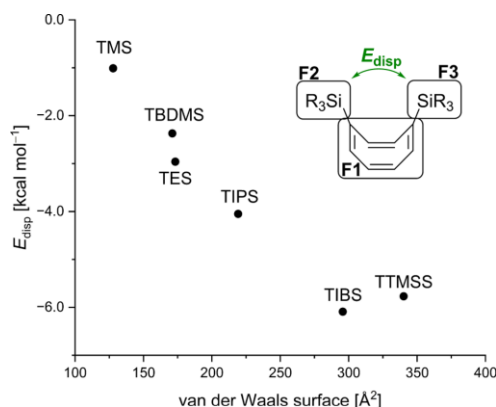


Figure 4. LED analysis of two silyl groups in their 1,6-disilyl-substituted cyclooctatetraene geometry at DLPNO-CCSD(T)/def2-TZVP//B3LYP-D3(BJ)/def2-TZVP.

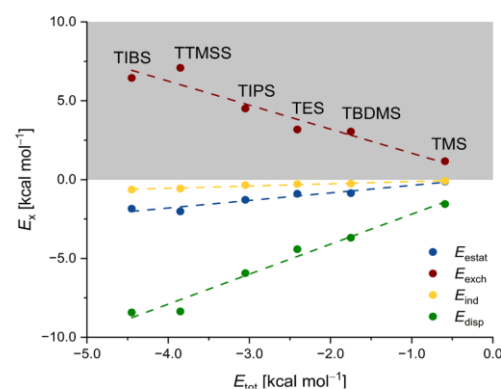


Figure 5. sSAPT analysis of two silyl groups in geometries of the respective 1,6-COT derivative at sSAPT0/aug-cc-pVDZ. The dashed lines are used as a guide to the eye.

contributors to the total interaction energy are LD interactions E_{disp} (green markings) and Pauli exchange repulsion E_{exch} (red markings). While 1,4-disilyl-COT is hardly influenced by repulsive interactions, the close σ - σ contacts in 1,6-disilyl-COT result in significant Pauli repulsion (Figure 5). The latter is, however, largely offset by LD interactions for all studied derivatives and hence cannot be the decisive factor for the shift in folding equilibria. In particular, di-TIBS-COT benefits from stabilizing LD interactions coupled with fewer steric constraints than di-TTMSS-COT. Therefore, flexible alkyl groups align more efficiently and optimize the balance between attractive and repulsive contacts.

The SAPT analysis does not directly yield an explanation for our findings, and the origin of increasing destabilization must lie elsewhere. When assessing optimized 1,6-disilyl-COT structures, we noticed significant deviations in the geometric parameters of the respective COT backbone with differing silyl groups, that is, the dihedral angle α (Figure 6). Consequently, we carried out a strain analysis, with the aim of capturing ring strain introduced in both the COT scaffold and the silyl

groups. To account for the ring strain, we utilized the B3LYP-D3/def2-TZVPP optimized structures, split off the substituents attached to Si, and saturated the compound with H to give a strained disilane COT. Next, the single-point energies of these compounds were compared to a disilane COT optimized at the same level of theory. Additionally, we utilized the optimized structures, removed the COT molecular backbone, and saturated the radical sites to give the corresponding strained silanes. Again, the difference in energy between strained silanes and geometry optimized compounds was taken into account (for details, see [Supporting Information](#)).

Figure 6 displays the sum of strain energy ΔE_{strain} exerted on the ring due to the substituents of the corresponding di-silyl substituted COT derivative and van der Waals strain introduced in the silyl groups due to repulsive contacts (see [Supporting Information](#) for details). While the incorporation of six methyl groups does not affect ΔE_{strain} (0.0 kcal mol⁻¹ for di-TMS-COT), the introduction of bulkier substituents leads to a rise in strain up to 1.9 kcal mol⁻¹ for di-TTMSS-COT. For smaller and flexible silyl substituents up to TIBS ΔE_{strain} is mostly comprised of strain from the silyl substituents (see [Supporting Information](#)). The influence of ring strain increases significantly for bulkier and rigid substituents (TIPS and TTMSS). The strain energy is a result of the attenuation of Pauli repulsion between both silyl groups. By increasing the distance between substituents the release in repulsive interaction energy is directly exerted on the COT molecular backbone. Because LD decreases slower with respect to the distance (r^{-6}) in comparison to Pauli repulsion (r^{-12}), the ratio of both energy components is optimized.^{9,10}

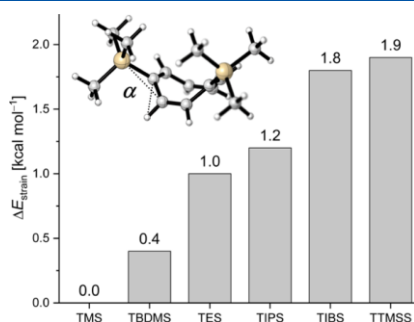


Figure 6. Strain energy ΔE_{strain} for disilyl-substituted cyclooctatetraene. The energy values correspond to the relative strain between 1,4- and 1,6-disilyl-substituted cyclooctatetraene.

By mapping the obtained experimental data to parameters capturing steric bulk, such as A-values,^{7,8,59} solvolysis rates,⁶ and Tolman's steric parameter θ ,^{60,61} the suitability of disilyl COTs to gauge the steric size of silyl groups can be further rationalized. While θ resembles an empirical measure, it is nevertheless often used to assess the steric demand of ligands. Figure 7 showcases the correlation between θ and ΔG_{eq} values of the disilyl COT balances. Because of the strong correlation observed, it is possible to predict θ from computed or experimental ΔG_{eq} values. For instance, TIBS has recently found use as a protecting group in organic synthesis but has not been characterized within the framework of steric parameters. According to the data collected (Figure 7), we

can determine $\theta = 144^\circ$ for the TIBS group (red marking), which is in accordance with Tolman's parameter for P(^tBu)₃ ($\theta = 143^\circ$).⁶⁰ Similar correlations of ΔG_{eq} to steric parameters such as A-values and solvolysis rates are observed (see [Supporting Information](#)).

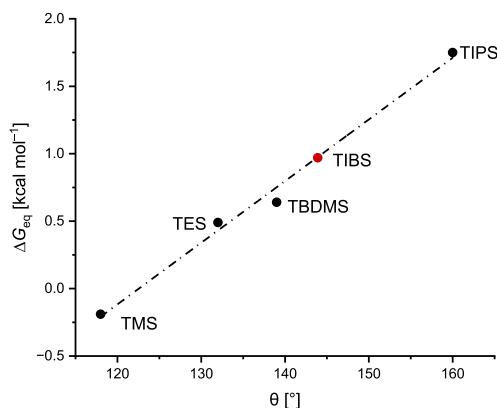


Figure 7. Correlation of experimental free energy values (ΔG_{eq}) of the COT molecular balances and Tolman's steric parameter. The dashed line is derived from linear regression of the black data points. The red marking was calculated according to a linear regression as a guide to the eye.

CONCLUSIONS

We prepared a variety of 1,4- and 1,6-disilyl-substituted cyclooctatetraene structures and conducted temperature-dependent NMR measurements to determine equilibrium parameters. By comparing the thus obtained ΔH_{eq} values to computed thermochemical data (ΔH_{298}° and ΔE_{strain}), we were able to pinpoint LD interactions as a key factor affecting the folding equilibria. The main interaction energy component that counteracts LD is Pauli exchange repulsion, while the induced strain is a mechanism to either attenuate repulsion or optimize LD. With the exception of di-TMS-COT, ring strain overcompensates the stabilizing contribution of LD interactions in the folded 1,6-isomer. Hence, the equilibrium shifts toward the unfolded 1,4-isomer as bulkier silyl groups are installed.

Our experimentally determined ΔG_{eq} values correlate well with steric parameters for silyl groups known from the literature. The ring strain observed in the 1,6-valence isomers can be interpreted as a “fingerprint” of the respective group. This renders the COT molecular balance system suitable for gauging the relative bulkiness of silyl and, in the future, other groups.

LD interactions turn out to play a key role in stabilizing the folded 1,6-isomers. This is particularly evident from LED and SAPT analyses (vide infra). Without the LD contributions, the equilibria are predicted to favor the unfolded 1,4-isomer much more strongly than what is observed experimentally.

While the incorporation of bulky substituents directly attached to Si (TMS, TBDMS, TIPS, and TTMSS) results in a linear correlation between the actual size (van der Waals surface, [Scheme 3](#)) and the apparent relative bulkiness (ΔG_{eq} and ΔH_{eq} , [Figure 2](#)) of silyl groups, a remote substitution

pattern as in di-TIBS-COT stabilizes the folded 1,6-valence isomer via LD interactions.

■ EXPERIMENTAL SECTION

General Information. Thin-layer chromatography was carried out using PolyGram SIL G/UV₂₅₄ plates with detection via UV λ = 254 nm and by staining with a 10 wt % ethanolic phosphomolybdic acid (PMA) stain solution. All chemicals were commercially obtained from Acros Organics, TCI, and Sigma-Aldrich and used without further purification. Anhydrous solvents were purchased from Acros Organics. Unless otherwise noted, all reactions were carried out under standard Schlenk conditions employing N₂ as the inert gas. Standard NMR spectra were obtained using Bruker Avance II 400 MHz and Bruker Avance III HD 400 MHz (¹³C spectra) spectrometers. Temperature-dependent NMR experiments were carried out with a Bruker Avance III HD 600 MHz spectrometer. High-resolution mass spectra were obtained with a Bruker micrOTOF mass spectrometer. For temperature-dependent measurements, NMR samples were equilibrated for 16 h at 40 °C prior to the experiment utilizing an IKA ICC basic eco 8 immersion circulator.

Temperature-Dependent NMR Experiments. After sample transfer from the thermostat to the NMR spectrometer, equilibration was continued for another hour in the spectrometer before the first spectrum (40 °C) was recorded. Spectra were recorded in 10 °C steps. From 60 °C onward, the equilibration period before measurement was reduced to 30 min.

Synthetic Procedures. Triphenylsilyl Triflate (4). Triphenylsilyl triflate was prepared according to a modified literature procedure.⁶² To a stirred suspension of 3.592 g (14 mmol) of AgOTf in 30 mL of DCM was added a solution of 4.428 g (15 mmol) triphenylsilyl chloride in 20 mL of DCM at room temperature. After complete addition, the reaction mixture was stirred under the exclusion of light at room temperature for another 12 h. The mixture was then filtered to remove AgCl, yielding a clear colorless filtrate. The filtrate was then concentrated under reduced pressure to yield 6.032 g of a colorless solid, which was used without further purification in the preparation of di(TPS)cyclooctatetraene 3g.

Tris(trimethylsilyl)silyl Triflate (5). Tris(trimethylsilyl)silyl silane (4.63 mL, 15 mmol) was diluted with 7 mL of *n*-pentane. Afterward, 1.25 mL (14 mmol, 0.95 equiv) of trifluoromethanesulfonic acid was added dropwise (gas formation) and the resulting mixture was stirred for 1 h at room temperature. The resulting solution was used without further purification in the preparation of di(TTMSS)-cyclooctatetraene 3f.

Tri(isobutyl)silyl Triflate (6). Triisobutylsilane 3.87 mL (15 mmol) was diluted in 5 mL of *n*-pentane. Afterward, 1.23 mL (14 mmol, 0.95 equiv) of trifluoromethanesulfonic acid was added dropwise (gas formation) and the resulting mixture was stirred for 1 h at room temperature. The resulting solution was used without further purification in the preparation of di(TIBS)cyclooctatetraene 3c.

5,8-Di(silyl)cycloocta-1,3,6-trienes (2).^{37–41} 5,8-Di(silyl)-cycloocta-1,3,6-trienes were prepared according to the following general procedure: to a stirred solution of 0.98 mL (8.0 mmol) of 1,5-cyclooctadiene in 10 mL of *n*-pentane was added 9.60 mL (24 mmol, 3.0 equiv) of a *n*-butyllithium solution (2.5 M in hexanes) at 0 °C. Afterward, 3.60 mL (24 mmol, 3.0 equiv) of TMEDA was added dropwise and the yellow solution was kept stirring at 0 °C for 15 min. The cooling bath was removed thereafter, and stirring was continued at room temperature for 48 h. To the then orange mixture was added 20 mL of DME, and stirring was continued for another 15 min at room temperature. The mixture was then filtered to yield a deep red filtrate that was cooled to –50 °C and treated with 1.75 equiv of the corresponding silyl triflate or silyl chloride. After 30 min at –50 °C, the reaction mixture was quenched with 20 mL of a saturated aqueous NaHCO₃ solution. Phases were separated, and the aqueous phase was extracted with *n*-hexane (3 × 50 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to yield the corresponding crude products as either off-white oils or solids. Purification was carried out by filtering

through a pad of silica eluting with *n*-hexane or a 10:1 mixture of *n*-hexane and ethyl acetate (5,8-di(TPS)cycloocta-1,3,6-triene 2g). Because of their instability, the 5,8-di(silyl)cycloocta-1,3,6-triene 2 precursors were used immediately in the next synthetic step.

Di(TMS)cyclooctatetraene (3a). 1.264 g (5.0 mmol) of 5,8-di(TMS)cycloocta-1,3,6-triene was dissolved in 20 mL of THF and cooled to –50 °C. While stirring, 4.45 mL (11 mmol, 2.2 equiv) of 2.5 M *n*-butyllithium in hexanes was added dropwise. After stirring for 15 min at –50 °C, the reaction mixture was allowed to reach 0 °C by replacing the liquid nitrogen–acetone cooling bath with an ice-water cooling bath. Stirring of the solution was continued for 2 h at 0 °C. The now deep red solution was brought to –30 °C, and 1.712 g (10 mmol, 2.0 equiv) of silver nitrate was added in small portions. The reaction mixture was stirred for a further 16 h at room temperature before quenching was carried out with 20 mL of water. Phases were separated, and the aqueous phase was extracted with *n*-hexane (3 × 50 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to yield the crude product as an off-white solid. The crude product was purified by crystallization using methanol at –25 °C, yielding 1.093 g (4.4 mmol, 55% over two steps) of 3a as a colorless solid.

¹H NMR (400 MHz, CDCl₃), 1,4-3a: δ 6.11 (s, 2H), 5.99–5.84 (m, 2H), 5.73 (q, *J* = 2.8 Hz, 2H), 0.07 (s, 18H).

¹H NMR (400 MHz, CDCl₃), 1,6-3a: δ 5.99–5.84 (m, 6H), 0.08 (s, 18H).

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.3, 148.8, 139.6, 138.4, 134.2, 132.9, 132.3, 129.3, –1.4, –1.6.

HRMS (APCI-TOF) *m/z*: [M + H]⁺ calcd for C₁₄H₂₄Si₂, 249.1494; found, 249.1487.

Di(silyl)cyclooctatetraenes (3).^{37–41} With the exception of di(trimethylsilyl)cyclooctatetraene 3a, all cyclooctatetraenes were prepared according to the following general procedure: a 0.25 M solution of the corresponding 5,8-di(silyl)cycloocta-1,3,6-triene 2 in THF was prepared and cooled to –50 °C. While stirring, 2.2 equiv of *n*-butyllithium (2.5 M in hexanes) was added dropwise. After stirring for 15 min at –50 °C, the reaction mixture was allowed to reach 0 °C by replacing the liquid nitrogen–acetone cooling bath with an ice-water cooling bath. Stirring of the deep red solution was continued for 2 h at 0 °C before cooling the solution to –30 °C. Upon complete addition of 1.1 equivalents of elemental iodine at –30 °C in small portions, the color of the solution faded completely. The reaction mixture was stirred for another 15 min before quenching was carried out with 20 mL of a saturated aqueous Na₂SO₃ solution. Phases were separated, and the aqueous phase was extracted with *n*-hexane (3 × 50 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to yield the corresponding crude products as either off-white oils or solids. The di(silyl)cyclooctatetraenes were purified either by trituration with cold methanol (–20 °C) or by silica flash column chromatography eluting with *n*-hexane or a 10:1 mixture of *n*-hexane and ethyl acetate (di(TPS)cyclooctatetraene 3g).

Di(TES)cyclooctatetraene (3b). 3.16 mL (14 mmol, 1.75 equiv) of triethylsilyl triflate was utilized according to the general procedure described above for the preparation of 5,8-di(silyl)cycloocta-1,3,6-trienes (2). 1.686 g (5.0 mmol) of 5,8-di(TES)cycloocta-1,3,6-triene 2b was obtained as a colorless oil. Compound 2b was dissolved in 20 mL of THF and subsequently treated as in the general procedure for the preparation of di(silyl)cyclooctatetraenes (3) described above. 4.43 mL (11 mmol) of 2.5 M *n*-butyllithium in hexanes and 1.404 g (5.5 mmol) of elemental iodine were utilized for the preparation of di(TES)cyclooctatetraene (3b). After purification by flash column chromatography, 1.408 g (4.2 mmol, 53%) of 3b was obtained as a colorless oil.

¹H NMR (400 MHz, CDCl₃), 1,4-3b: δ 6.09 (s, 2H), 5.96–5.79 (m, 2H), 5.69 (q, *J* = 2.8 Hz, 2H), 0.98–0.89 (m, 18H), 0.65–0.52 (m, 12H).

¹H NMR (400 MHz, CDCl₃), 1,6-3b: δ 5.96–5.79 (m, 6H), 0.98–0.89 (m, 18H), 0.65–0.52 (m, 12H).

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 146.0, 145.2, 141.2, 139.9, 135.0, 132.9, 132.6, 128.8, 7.6, 7.5, 3.1, 3.0.

HRMS (APCI-TOF) m/z : $[M + H]^+$ calcd for $C_{20}H_{36}Si_2$, 333.2434; found, 333.2427.

Di(TIBS)cyclooctatetraene (3c). Tri(isobutyl)silyl triflate (**6**) was utilized according to the general procedure described above for the preparation of 5,8-di(silyl)cycloocta-1,3,6-trienes (**2**). 2.495 g (5.0 mmol) of 5,8-di(TIBS)cycloocta-1,3,6-triene **2c** was obtained as a colorless oil. Compound **2c** was dissolved in 20 mL of THF and subsequently treated as in the general procedure for the preparation of di(silyl)cyclooctatetraenes (**3**) described above. 4.40 mL (11 mmol) of 2.5 M *n*-butyllithium in hexanes and 1.385 g (5.5 mmol) of elemental iodine were utilized for the preparation of di(TES)-cyclooctatetraene (**3b**). After purification by flash column chromatography, 2.085 g (4.2 mmol, 52%) of **3c** was obtained as a colorless oil.

1H NMR (400 MHz, $CDCl_3$), 1,4-**3c**: δ 6.05 (s, 2H), 5.93 (q, J = 2.7 Hz, 2H), 5.65 (q, J = 2.8 Hz, 2H), 1.86–1.74 (m, 6H), 0.96–0.90 (m, 36H), 0.69–0.54 (m, 12H).

1H NMR (400 MHz, $CDCl_3$), 1,6-**3c**: δ 5.99 (s, 2H), 5.85 (s, 2H), 5.84 (s, 2H), 1.86–1.74 (m, 6H), 0.96–0.90 (m, 36H), 0.69–0.54 (m, 12H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 147.5, 146.6, 141.4, 140.3, 135.3, 132.9, 132.9, 129.2, 26.9, 26.8, 26.8, 26.7, 24.9, 24.9, 24.1, 23.7.

HRMS (APCI-TOF) m/z : $[M + H]^+$ calcd for $C_{32}H_{60}Si_2$, 501.4312; found, 501.4308.

Di(TBDMs)cyclooctatetraene (3d). 3.22 mL (14 mmol) of *tert*-butyldimethylsilyl triflate was utilized according to the general procedure described above for the preparation of 5,8-di(silyl)-cycloocta-1,3,6-trienes (**2**). 2.821 g (5.6 mmol) of 5,8-di(TBDMs)-cycloocta-1,3,6-triene **2d** was obtained as a colorless solid. Compound **2d** was dissolved in 22 mL of THF and subsequently treated as in the general procedure for the preparation of di(silyl)cyclooctatetraenes (**3**) described above. 4.93 mL (12 mmol) of 2.5 M *n*-butyllithium in hexanes and 1.570 g (6.2 mmol) of elemental iodine were utilized for the preparation of di(TBDMs)cyclooctatetraene (**3d**). After purification by trituration with cold methanol, 2.523 g (5.0 mmol, 63%) of **3d** was obtained as a colorless solid.

1H NMR (400 MHz, $CDCl_3$), 1,4-**3d**: δ 6.10 (s, 2H), 6.01–5.84 (m, 2H), 5.68 (q, J = 2.8 Hz, 2H), 0.90 (s, 18H), 0.08–0.01 (m, 12H).

1H NMR (400 MHz, $CDCl_3$), 1,6-**3d**: δ 6.01–5.84 (m, 6H), 0.89 (s, 18H), 0.08–0.01 (m, 12H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 146.6, 145.9, 141.8, 140.9, 136.0, 133.2, 132.9, 128.8, 27.0, 27.0, 17.4, 17.2, –5.6, –5.7, –5.7, –6.2.

HRMS (APCI-TOF) m/z : $[M + H]^+$ calcd for $C_{20}H_{36}Si_2$, 333.2434; found, 333.2428.

Di(TIPS)cyclooctatetraene (3e). 3.76 mL (14 mmol) of triisopropylsilyl triflate was utilized according to the general procedure described above for the preparation of 5,8-di(silyl)-cycloocta-1,3,6-trienes (**2**). 2.113 g (5.0 mmol) of 5,8-di(TIPS)-cycloocta-1,3,6-triene **2e** was obtained as a colorless solid. Compound **2e** was dissolved in 20 mL of THF and subsequently treated as in the general procedure for the preparation of di(silyl)cyclooctatetraenes (**3**) described above. 4.43 mL (11 mmol) of 2.5 M *n*-butyllithium in hexanes and 1.412 g (5.5 mmol) of elemental iodine were utilized for the preparation of di(TIPS)cyclooctatetraene (**3e**). After purification by trituration with cold methanol, 1.650 g (4.0 mmol, 50%) of **3e** was obtained as a colorless solid.

1H NMR (400 MHz, $CDCl_3$), 1,4-**3e**: δ 6.11 (s, 2H), 6.03–5.83 (m, 2H), 5.67 (q, J = 2.8 Hz, 2H), 1.15–1.01 (m, 42H).

1H NMR (400 MHz, $CDCl_3$), 1,6-**3e**: δ 6.03–5.83 (m, 6H), 1.15–1.01 (m, 42H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 144.3, 142.6, 142.2, 141.9, 136.6, 133.5, 132.8, 128.5, 19.0, 19.0, 18.8, 18.7, 11.4, 11.2.

HRMS (APCI-TOF) m/z : $[M + H]^+$ calcd for $C_{26}H_{48}Si_2$, 417.3373; found, 417.3368.

Di(TTMS)cyclooctatetraene (3f). Tris(trimethylsilyl)silyl triflate (**5**) was utilized according to the general procedure described above for the preparation of 5,8-di(silyl)cycloocta-1,3,6-trienes (**2**). 2.872 g (4.8 mmol) of 5,8-di(TTMS)cycloocta-1,3,6-triene **2f** was obtained as a colorless solid. Compound **2f** was dissolved in 19 mL of THF and

subsequently treated as in the general procedure for the preparation of di(silyl)cyclooctatetraenes (**3**) described above. 4.22 mL (10 mmol) of 2.5 M *n*-butyllithium in hexanes and 1.328 g (5.3 mmol) of elemental iodine were utilized for the preparation of di(TTMS)-cyclooctatetraene (**3f**). After purification by trituration with cold methanol, 2.295 g (3.8 mmol, 48%) of **3f** was obtained as a colorless solid.

1H NMR (400 MHz, $CDCl_3$), 1,4-**3f**: δ 6.01 (s, 2H), 5.89 (q, J = 2.8 Hz, 2H), 5.59 (q, J = 2.8 Hz, 2H), 0.21–0.17 (m, 54H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 142.2, 141.4, 138.2, 126.9, 1.5.

HRMS (APCI-TOF) m/z : $[M + H]^+$ calcd for $C_{26}H_{60}Si_2$, 597.2927; found, 597.2924.

Di(TPS)cyclooctatetraene (3g). Triphenylsilyl triflate (**4**) was utilized according to the general procedure described above for the preparation of 5,8-di(silyl)cycloocta-1,3,6-trienes (**2**). 1.391 g (2.2 mmol) of 5,8-di(TPS)cycloocta-1,3,6-triene **2g** was obtained as a colorless solid. Compound **2g** was dissolved in 9 mL of THF and subsequently treated as in the general procedure for the preparation of di(silyl)cyclooctatetraenes (**3**) described above. 1.96 mL (4.9 mmol) of 2.5 M *n*-butyllithium in hexanes and 0.631 g (2.5 mmol) of elemental iodine were utilized for the preparation of di(TPS)-cyclooctatetraene (**3g**). After purification by flash column chromatography (10:1 *n*-hexane and ethyl acetate), 0.638 g (1.0 mmol, 13%) of **3g** was obtained as a colorless solid.

1H NMR (400 MHz, CD_2Cl_2), 1,4-**3g**: δ 7.61–7.25 (m, 30H), 6.24 (s, 2H), 6.10 (q, J = 2.8 Hz, 2H), 5.91–5.84 (m, 2H).

1H NMR (400 MHz, CD_2Cl_2), 1,6-**3g**: δ 7.61–7.25 (m, 30H), 6.24 (s, 2H), 5.96 (s, 2H), 5.91–5.84 (m, 2H).

$^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 147.2, 146.2, 143.6, 143.4, 136.7, 136.7, 135.9, 134.3, 134.1, 134.0, 133.6, 130.8, 130.0, 129.9, 128.3, 128.1.

HRMS (APCI-TOF) m/z : $[M + H]^+$ calcd for $C_{44}H_{37}Si_2$, 621.2434; found, 621.2427.

Computational Details. To compute the LD interactions, we utilized multiple tools recognized in the literature. We started our investigation with a conformer search in the gas-phase using the Conformer-Rotamer Ensemble Sampling Tool (crest) developed by Grimme et al.⁶³ The results for 1,6- and 1,4-disilyl-COT (the conformers lowest in energy) were further optimized with Gaussian16⁶⁴ in the gas phase using B3LYP,^{12,43} B3LYP-D3(BJ),^{27,44} M06-2X,⁴⁵ and ω B97X-D⁴⁶ in conjunction with the def2-SVPP and def2-TZVPP basis sets.⁴⁷ Hereby, the highest possible symmetry was employed (C_2 for 1,4-disilyl-COT and C_s/C_1 for 1,6-disilyl-COT). All structures were characterized as minima on the potential energy hypersurface. Additionally, single-point energy computations at the DLPNO-CCSD(T)/def2-TZVP level of theory^{48,49} were performed on the B3LYP-D3(BJ)/def2-TZVPP optimized geometries. Tables S23–S28 summarize the results of the thermochemical analyses.

Homodesmotic (error-balancing) equations^{50,51} were performed to estimate the strength of the intramolecular LD interactions. As described above, the crest program was utilized to identify all conformers lowest in energy, which were then optimized in the gas phase using B3LYP/def2-TZVPP including (GD3BJ) and excluding LD interactions. The dispersion energy was computed according to the following equation

$$E_{\text{disp}} = \sum E(\text{product}) - D3(\text{BJ}) - \sum E(\text{starting material}) - D3(\text{BJ}) - \sum E(\text{product}) - \sum E(\text{starting material})$$

Figures S13–S18 summarize the results of the homodesmotic equations.

A local energy decomposition^{52–54} (LED) analysis was performed by using the Orca program⁵⁵ version 4.2.1. The B3LYP-D3(BJ)/def2-TZVPP-optimized geometries were utilized, and the molecules were split into fragments (F1–F3), which are defined in detail in the Supporting Information. The LED analysis was performed at DLPNO-CCSD(T)/def2-TZVP utilizing tight pair natural orbital

(TightPNO) settings. Tables S29–S34 summarize the results of the LED analyses of all silyl COT derivatives.

Finally, a scaled Symmetry-Adapted Perturbation Theory⁵⁶ (sSAPT) analysis was performed using the PSI4 program.^{55,66} In order to isolate the interactions between the silyl groups, the molecular backbone of the COT balance was removed and the groups were saturated with hydrogens. A nonrelaxed dimer scan was performed at the sSAPT0/aug-cc-pVDZ level of theory. The empirical recipe for scaled SAPT0 was utilized in order to improve the performance according to Parker et al.⁵⁷ Tables S35–S40 and Figures S19–S24 summarize the results of the sSAPT analysis.

Visualizations of noncovalent interactions (NCI-plots⁶⁷) were plotted as a reduced density gradient in regions of low electron density. The B3LYP-D3(BJ)/def2-TZVPP-optimized geometries were utilized for the visualization of noncovalent interactions. All plots were generated with NCIPLOT⁶⁸ and visualized with VMD.⁶⁹ The density cut-off of the reduced density gradient ($\rho(r) = -0.2$ to $+0.2$ a.u.) and the color scale data range (-2 to $+2$ a.u.) were kept consistent throughout all NCI plots. Thereby, red isosurfaces indicate strongly repulsive interactions, green isosurfaces correspond to weak noncovalent contacts, and blue isosurfaces indicate strongly attractive interactions. Figures S25–S30 show all visualizations of 1,6- and 1,4-disilyl-COT.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.1c03103>.

¹H NMR and ¹³C{¹H} NMR data for all molecular balances; error estimation for experimental data; single-crystal X-ray diffraction data; HRMS data; and computational details (PDF)

XYZ files for 1,6- and 1,4-cyclooctatetraene (ZIP)

Accession Codes

CCDC 2124606–2124607 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

This paper is dedicated to the memory of Andrew Streitwieser who taught us so much about organic chemistry.

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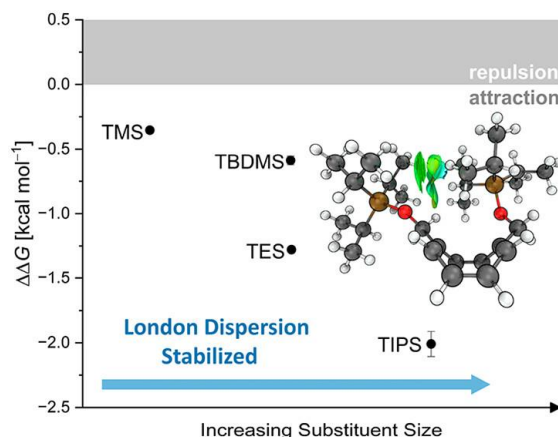
2.3 Silyl Groups Are Strong Dispersion Energy Donors – Introduction

In our previous publication on the steric effects exerted by commonly utilized silyl groups,¹⁸⁷ we found TIBS to be a remarkably good DED, which we saw as indicative of a peripheral substitution and molecular flexibility being beneficial for enhancing LD interactions. Furthermore, our computations suggested conformational strain induced in the COT backbone to be the cause of an increasing preference for the unfolded 1,4-isomer in COTs functionalized with bulkier silyl groups.

In an effort to validate these findings, and to study the DED capabilities of silyl groups experimentally in a system showing attractive behavior, we investigated COT molecular balances featuring a higher degree of structural flexibility.¹⁸⁸ The molecular balances were substituted with $-\text{CH}_2\text{O}-$ spacer groups between the COT backbone and the silyl groups. In this way, the chemical environment in which silyl protecting groups are utilized in synthesis could be modeled more closely as well. We prepared a set of six molecular balances employing a valence isomerization synthesis route, as described in section 1.3. Experimental readout of ΔG_{eq} values was carried out by measuring high-resolution ^1H -NMR spectra at 40 °C. In analogy to our previous publication (see section 2.1 and 2.2), we studied the molecular balance system computationally utilizing perturbation theory-based energy decomposition analyses to unravel the nature of the non-covalent interactions at play, and to quantify their individual contributions. We also computed ΔG_{eq} for each molecular balance by applying a Boltzmann treatment to large conformer ensembles of the respective 1,4- and 1,6-isomers, which is required to obtain robust ΔG_{eq} values for such highly flexible systems.¹⁹²

Our experimental results followed the expected ‘counterintuitive’ trend of bulkier substituents leading to an increased favoring of the folded 1,6-isomer, with the exception of ‘butyldiphenylsilyl- (TBDPS-) and tris(trimethylsilyl)silyl- (TTMSS-) substituted balances. We were able to computationally trace back the behavior of the latter to contributions of pseudo-folded structures to the 1,4-conformer ensemble, with significant LD interactions between silyl groups. Overall, we found the computationally obtained trend of ΔG_{eq} values to qualitatively reproduce our experimental results and agree well quantitatively within the expected error margin. Although we computationally determined LD contributions of up to -5 kcal mol^{-1} for TIPS substitution,¹⁸⁸ LD stabilization was found to be counteracted by a strong entropic disfavoring of the 1,6-isomer, due to substantial constraints on rotational degrees of freedom. However, in comparison to the ‘rigid’ molecular balances in our previous study,¹⁸⁷ we found the respective 1,6-isomers to be stabilized by up to -2 kcal mol^{-1} (TIPS).¹⁸⁸

2.4 Paper 2: Silyl Groups Are Strong Dispersion Energy Donors



Abstract:

We present an experimental and computational study to investigate noncovalent interactions between silyl groups that are often employed as “innocent” protecting groups. We chose an extended cyclooctatetraene (COT)-based molecular balance comprising unfolded (1,4-disubstituted) and folded (1,6-di-substituted) valence bond isomers that typically display remote and close silyl group contacts, respectively. The thermodynamic equilibria were determined using nuclear magnetic resonance measurements. Additionally, we utilized Boltzmann weighted symmetry-adapted perturbation theory (SAPT) at the sSAPT0/aug-cc-pVDZ level of theory to dissect and quantify noncovalent interactions. Apart from the extremely bulky tris(trimethylsilyl)silyl “supersilyl” group, there is a preference for the folded 1,6-COT valence isomer, with London dispersion interactions being the main stabilizing factor. This makes silyl groups excellent dispersion energy donors, a finding that needs to be taken into account in synthesis planning.

Reference:

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Silyl Groups Are Strong Dispersion Energy Donors

Lars Rummel,[#] Henrik F. König,[#] Heike Hausmann, and Peter R. Schreiner*Cite This: *J. Org. Chem.* 2022, 87, 13168–13177

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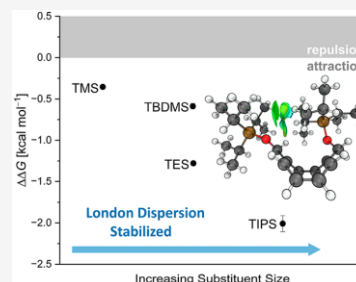
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INTRODUCTION

Bulky substituents, such as *tert*-butyldimethylsilyl (TBDMS) or tri-*iso*-propylsilyl (TIPS), are usually considered to be repulsive, thereby affecting chemical reactions on the basis of their steric bulk.^{1–3} The attractive components of noncovalent interactions (NCIs) of such large and highly polarizable groups are usually not considered. Although similar sterically demanding substituents, for example, *tert*-butyl groups, have amply been demonstrated to interact strongly *via* stabilizing London dispersion (LD) interactions;^{4–7} similar behavior is generally not attributed to silyl groups.

This is surprising because bulky substituents are nowadays incorporated as design elements to increase intramolecular stability or facilitate intermolecular aggregation.^{13–19} Examples include organic compounds such as hexaphenylethane,^{20–24} coupled diamondoids,²⁵ or tetrahedranes,^{8,9} which are substantially stabilized by forming a strongly interacting LD shell around a labile core.^{6,23,26} In this context, tetrakis-(trimethylsilyl)tetrahedrane (Figure 1, left) as the most stable tetrahedrane derivative reported thus far is particularly remarkable. Its even greater stability than *tert*-butyl analogue may be attributed to a combination of the “corset effect”, electronic stabilization of the tetrahedrane core, and LD interactions.^{8,9,25} While the “corset effect” is presumed to provide kinetic stabilization through steric inhibition of cage opening, the thermodynamic stability of tetrakis-(trimethylsilyl)tetrahedrane is boosted by an increased σ -donor ability of trimethylsilyl (TMS) groups and LD interactions between them. Furthermore, LD interactions have also proven to be relevant in stabilizing exotic organometallic compounds⁷ such as disilanes,^{27,28} carbene analogues^{29,30} (Figure 1, middle), and *meta*-terphenyl

dimers^{10,11} of heavy group 14 elements. Because LD interactions are not only pairwise additive⁴ but also highly distance dependent (with R^{-6}), LD interactions are suited to stabilizing transition structures as well because of their increased polarizability as compared to the ground states.^{16,18} While the silylation of secondary alcohols is greatly assisted by LD^{31,32} (especially for large silyl substituents), their use as dispersion energy donors^{6,33} (DEDs) is currently limited to TMS. Hartwig *et al.*¹² utilized higher tetrel congeners (Si and Ge) of the *tert*-butyl DED to increase catalyst–substrate binding affinities to accelerate reactions (Figure 1, right).

We chose the evaluation of a disubstituted cyclooctatetraene^{34,35} (COT) molecular balance as an appropriate system to determine the strengths of NCIs between several commonly employed silyl groups.³⁶ This molecular balance consists of two distinct valence isomers (Scheme 1) that can equilibrate *via* a double-bond valence bond isomerization.^{37,38} For bulky *tert*-butyl substituents, experimental^{35,36,39,40} and computational^{41,42} studies suggest the “folded” 1,6-isomer to be preferred in solution and in the gas phase. Considering the steric size of commonly utilized silyl groups, it is reasonable to hypothesize about the potential of these groups to serve as DEDs because they are far more polarizable.⁴³ In a recent study, we have addressed the effective size of commonly used silyl groups by utilizing a disubstituted COT molecular balance

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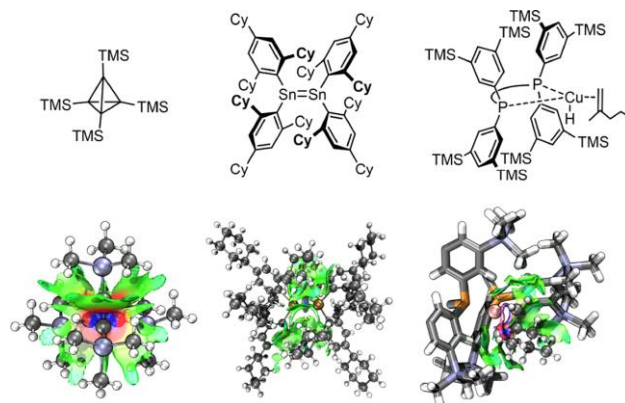
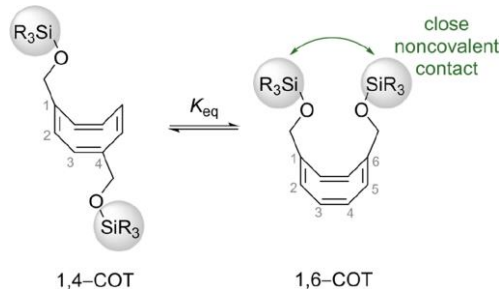


Figure 1. Intramolecular NCI plots of tetrakis(trimethylsilyl)tetrahedrane^{8,9} (left), $\{\text{Sn}(\text{C}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2\}_2$ (Cy = cyclohexyl, middle),^{10,11} and the favored si face hydrocupration transition structure according to Hartwig *et al.*¹² (selected functional groups omitted for clarity). Isosurfaces (isovalue s of 0.5, ranging from $\text{sign}(\lambda_2)\rho = -0.05$ to $+0.05$ a.u.) are color-coded red (indicating strong repulsion), blue (strong attractive interactions), and green (corresponding to weak NCIs).

Scheme 1. Equilibrium of 1,4- and 1,6-Di-*O*-silyl Substituted COT



with silyl groups directly attached in the 1,4-/1,6-position, and we demonstrated that an increase in size from TMS to extremely bulky tris(trimethylsilyl)silyl (TTMSS) leads to destabilizing internal strain on the COT backbone dominating the equilibrium between 1,4- and 1,6-COT.⁴⁴ The extended COT system under consideration here circumvents this problem. Computations suggested a balance between Pauli repulsion (“steric hindrance”) and attractive LD interactions, with the latter being the larger component. We hypothesized that the introduction of a $-\text{CH}_2\text{O}-$ spacer to the system would considerably reduce the internal strain in the 1,6-isomer (Scheme 1), and we demonstrate in the following that this is indeed the case. On the other hand, an increase in flexibility might come at the cost of an entropic penalty for the 1,6-isomer in which rotational degrees of freedom are significantly restrained.^{45,46} Because the investigated silyl groups are often employed as protecting groups for alcohols, another advantage of such a molecular balance lies in the close structural relationship to the common use case.

RESULTS AND DISCUSSION

We chose somewhat of an unusual route to generate the diol precursor (3) starting from dimethyl 1,4-cubanedecarboxylate

(1) that can be rearranged catalytically with rhodium.^{47,48} This choice was made on the basis that other synthetic routes *via* cyclooctatriene or COT toward 2 turned out to be very low-yielding; 1 is commercially available but can also readily be prepared.⁴⁹ Reduction of the COT dimethyl ester (2), 3, and preparation of the targeted silyl ethers (4) was accomplished *via* a standard alcohol protecting procedure⁵⁰ (Figure 2, top) utilizing TMS, triethylsilyl (TES), TBDMS, TIPS, *tert*-butyldiphenylsilyl (TBDPS), and TTMSS groups.

We utilized nuclear magnetic resonance (NMR) measurements to determine the valence isomer equilibrium constants. The allylic CH_2 groups of the spacer in conjunction with characteristic signals in the olefinic region enabled us to quantify the 1,4- and 1,6-isomers (Figure 2, bottom). Due to signal broadening at higher temperatures and resulting signal overlap, the thermodynamic equilibria could not be subjected to van't Hoff analyses to determine the individual ΔH and ΔS contributions. Each NMR sample was equilibrated for 16 h at 40 °C, and the equilibration was monitored *via* NMR. Chloroform was chosen as the solvent to ensure signal separation between the isomers. Figure 3 shows the results of the experiments (black markings) correlated to polarizability values of each silyl group (computed at revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c).

In general, the overall influence of silyl groups on the equilibria is small. Still, $\Delta_r G^{313}$ could be measured very accurately with error bars an order of magnitude below the measured values (see Supporting Information for details). While the di-OTMS-COT equilibrium is essentially thermoneutral ($\Delta_r G^{313} \approx 0 \text{ kcal mol}^{-1}$), larger silyl groups shift the equilibrium toward more crowded 1,6-COT. Despite their similar size and surface area of around $170 \text{ \AA}^2$ (see Supporting Information), the OTBDMS and OTES substituted systems differ in their behavior as DED groups. With $\Delta_r G^{313} = -0.08 \pm 0.00(4) \text{ kcal mol}^{-1}$ for di-OTBDMS-COT, its energy in favor of 1,6-COT is twice as large as that of di-OTES-COT. This can be rationalized by an increasing entropic penalty for the more flexible TES group in 1,6-COT.⁵¹ The most stabilizing effect stems from the interaction of two TIPS groups. The di-OTIPS-COT equilibrium most clearly favors the folded 1,6-COT

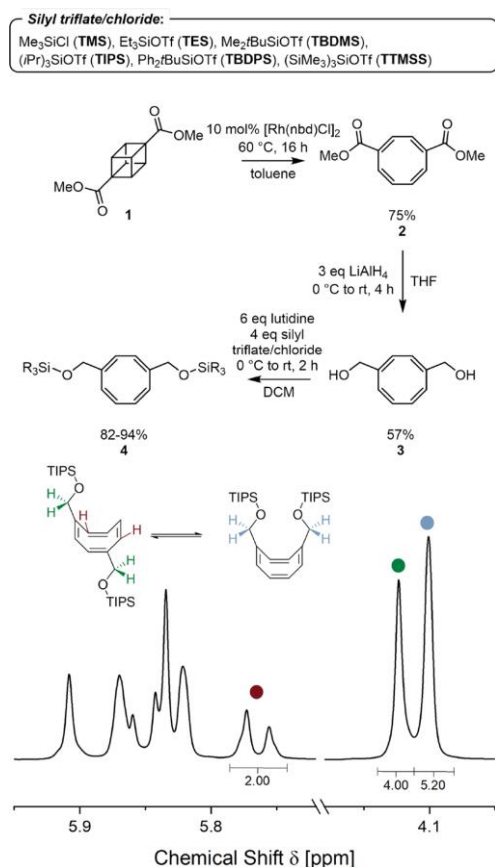


Figure 2. Top: Synthesis of 1,4- and 1,6-di-O-silyl substituted COTs (4); bottom: ^1H NMR spectra (600 MHz) and signal assignment of the equilibrium between 1,4- (green) and 1,6-di-OTIPS (blue) COT at 40°C in chloroform.

($\Delta_r G^{313} = -0.14 \pm 0.01 \text{ kcal mol}^{-1}$) isomer. More polarizable groups such as TBDPS and TTMSS appear to be less effective DEDs (vide infra). While TBDPS favors the more crowded 1,6-COT, the di-OTTMSS substitution pattern prefers the “unfolded” 1,4-COT by $\Delta_r G^{313} = +0.13 \pm 0.01 \text{ kcal mol}^{-1}$. While the $-\text{CH}_2\text{O}-$ spacer reduces internal strain, entropic contributions significantly dampen the effects of attractive NCIs; the conformational entropy penalty due to the spacer group amounts to $\Delta S_{\text{conf}} \approx +1.1 \text{ kcal mol}^{-1}$ at 40°C computed according to Grimme and co-workers.^{52,53} Still, such small $\Delta_r G^{313}$ values are quite relevant for transition structures, where even small effects lead to large changes in rates and/or selectivities.

Apart from experimental investigations, we also examined the equilibria computationally, notwithstanding the challenges associated with recovering such small ΔG values. While the inclusion of a spacer group and the utility of flexible silyls (such as TES) increases the number of possible conformers per valence isomer significantly, the identification of a single

most prominent structure can prove to be ineffective.⁵⁴ The computational error due to conformational complexity was shown by Lledós *et al.*⁵⁵ to surmount up to 10 kcal mol^{-1} for bulky and flexible ligands. To account for a larger conformational space,^{52,56} multiple conformers must be included in thermochemical investigations⁵⁷ as well as spectral predictions.^{58,59} Recently, the necessity of a conformational analysis has been demonstrated by Chen *et al.*⁶⁰ to rationalize the interplay of bulky DEDs with cation- π interactions. We utilized the conformer-rotamer ensemble sampling tool (CREST)⁶¹ to identify the conformers lowest in energy. The resulting structures were further optimized using the PBEh-3c^{62–66} method due to its efficient performance to give accurate geometries for large molecular systems.⁶⁶ With the aim to qualitatively sort and weigh conformers, all PBEh-3c optimized structures were utilized in a Boltzmann distribution and their probability was calculated at 313.15 K . To reduce the number of conformers, only molecules with a Boltzmann probability $> 1\%$ were used for single point computations at the revDSD-PBEP86-D4/def2-QZVPP^{67–72} level of theory, including solvation effects (chloroform) via the PCM^{73,74} model. Accordingly, all conformers that do not play a dominant role at 315.15 K were omitted from the analysis. The Boltzmann weighted Gibbs free energies are also depicted in Figure 3 (green makings), and we are pleased that the qualitative agreement is very good: the relative energies are significantly shifted toward the more crowded 1,6-COT structures. However, the computed absolute values are significantly overestimated. This may be due to errors in the computations (for the chosen functional and basis set, errors are estimated around $\pm 2 \text{ kcal mol}^{-1}$ of absolute weighted mean average deviation according to Martin *et al.*⁷¹) and possibly incomplete inclusion of solvation effects with the simple continuum model.^{47,36,75} Furthermore, incorporation of the $-\text{CH}_2\text{O}-$ spacer promotes free rotation of the silyl groups, hence leading to very flat conformational hypersurfaces. To include the most relevant conformers of a conformer ensemble in the thermodynamic analysis, a Boltzmann distribution analysis was performed. As a result, the entropy error could be minimized and the relative difference in energies be reproduced.⁵² The strongest effect is observed for di-OTIPS-COT, which favors the folded over the unfolded isomer by around $-2.7 \text{ kcal mol}^{-1}$. The bulkiest but most polarizable substituent (TTMSS) is the only group favoring 1,4-COT by around $0.3 \text{ kcal mol}^{-1}$.

To quantify intramolecular LD stabilization, we utilized symmetry-adapted perturbation theory⁷⁶ (SAPT) at the sSAPT0/aug-cc-pVDZ level of theory in conjunction with the PBEh-3c optimized structures. The scaled protocol was employed according to Parker *et al.*⁷⁷ to increase performance. Because we did not identify a single conformer for each isomer but rather studied an ensemble to address structural flexibility, we applied a Boltzmann distribution analysis for the energy decomposition method as well. Consequently, all conformers utilized for single point energy computations were taken into account in the scaled SAPT (sSAPT) analysis. To assess the interaction energy between two silyl groups, the molecular backbone and the spacer groups were removed, and the resulting radicals were saturated (*cf.* Scheme S1 in the Supporting Information).⁷⁸ The resulting energies were applied against the probability that each conformer is occupied at 298 K according to the revDSD-PBEP86-D4/def2-QZVPP single point energy computations. Figure 4 depicts the relative

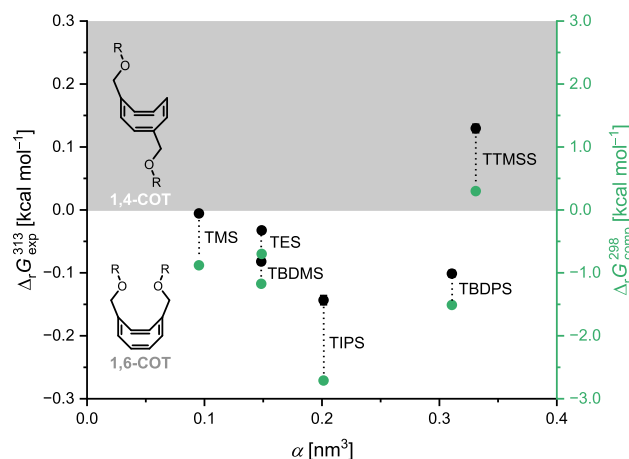


Figure 3. Correlation of the Gibbs free energies for the equilibrium of 1,4- and 1,6-di-O-silyl substituted COT in chloroform. The experimental data (black markings) were derived from NMR measurements at 40 °C. The computational data (green markings) were derived from Boltzmann distribution analysis at PCM(chloroform)-revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c. All data points in the white area favor 1,6-disilyl-COT.

energy differences (ΔE_X) between the folded and unfolded isomers.

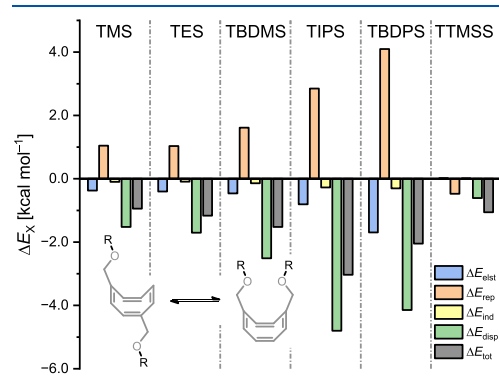


Figure 4. Relative energies between the folded and unfolded isomers of a Boltzmann weighted sSAPT analysis of silyl groups of all relevant conformers according to the conformer ensemble of each isomer. Computations were performed at the sSAPT0/aug-cc-pVDZ level of theory.

The sSAPT analysis dissects the relative total interaction energy ΔE_{tot} (gray bars) into its main components (for absolute energy values, see the [Supporting Information](#)). While inductive effects ΔE_{ind} (yellow bars) play only a minor role throughout all conformers, relative electrostatic interactions ΔE_{elst} (blue bars) can contribute to the stability of the folded isomer by up to $-1.7 \text{ kcal mol}^{-1}$ (TBDPS dimer). Nevertheless, electrostatic contributions are not important for the dimerization of alkylsilanes. Here, ΔE_{elst} does not exceed $-0.8 \text{ kcal mol}^{-1}$ (TIPS dimer). For TTMSS dimers, electrostatic and inductive effects cancel and do not contribute to the relative total interaction energy. The most prominent effects governing the dimerization of silanes are attractive LD

interactions ΔE_{disp} (green bars) and Pauli (exchange) repulsion ΔE_{rep} (orange bars). While the latter increases with the size of silyl groups from TMS to TBDPS, the largest substituent slightly favors the folded over the unfolded isomer with respect to repulsive interactions. This hints to similar distances of the TTMSS groups in the folded ($d_{\sigma-\sigma} \approx 2.53 \text{ \AA}$) and unfolded ($d_{\sigma-\sigma} \approx 2.64 \text{ \AA}$) isomers, implying a rotation of the spacer group to minimize repulsive interactions in the folded isomer. The largest ΔE_{rep} is observed for the TBDPS dimer, with $\Delta E_{\text{rep}} = 4.1 \text{ kcal mol}^{-1}$ destabilizing the folded isomer. Nevertheless, the steric repulsion due to close silyl contacts is insufficient to rationalize the observed experimental and computational data ([Figure 3](#)). The largest interaction counteracting Pauli (exchange) repulsion is LD. As a matter of fact, ΔE_{disp} is the largest contributor to ΔE_{tot} for all dimers. The TIPS system benefits the most from LD interactions of around $-4.8 \text{ kcal mol}^{-1}$. Both TBDPS and TTMSS show lower ΔE_{disp} and, therefore, appear to be weaker DEDs than TIPS. Nevertheless, the relative total interaction energy ΔE_{tot} and ΔE_{disp} can be directly correlated to the overall observed and computed Gibbs free energies ([Figure 3](#)). The similar trend of both energies and experimental Gibbs free energies confirms that the observed effects stem from NCIs of the silyl groups, with LD as the main contributor for all systems studied.

While the results of TMS, TES, TBDMS, and TIPS fit qualitatively to the logical series of size and polarizability, those of TBDPS and TTMSS do not. To shed more light on this, we analyzed the conformer ensemble of each isomer. Contrary to expectations, the unfolded 1,4-disubstituted COT displays stabilizing intramolecular interactions similar to those of the folded isomer. Accordingly, the spacer group allows the silyl groups to bend around the 1,4-COT moiety to enable close intramolecular interactions. We depicted the most prominent conformer of the folded and unfolded TIPS and TBDPS system for comparison *via* an intramolecular NCI plot,^{79,80} highlighting only NCIs between the silyl groups ([Figure 5](#)). Therefore, we plotted the reduced density gradient in regions of low electron density between the silyl groups. The resulting

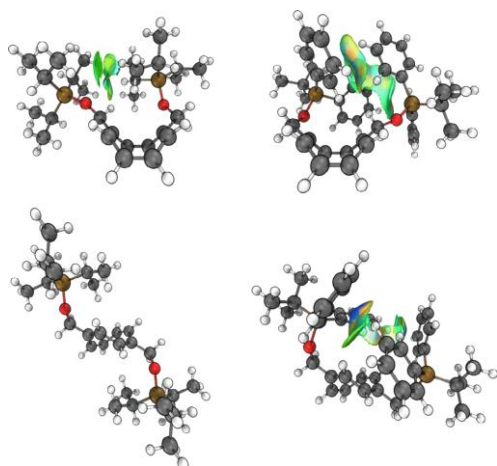


Figure 5. Intramolecular NCI plot of the folded 1,6-COT with TIPS (top, left) and TBDPS (top, right) and the unfolded 1,4-COT with TIPS (bottom, left) and TBDPS (bottom, right) at PBEh-3c. The most stable conformers were chosen according to the Boltzmann analysis. Isosurfaces (isovalue s of 0.5, ranging from $\text{sign}(\lambda_2)\rho = -0.05$ to $+0.05$ a.u.) are color coded red (indicating strong repulsion), blue (strong attractive interactions), and green (corresponding to weak NCIs).

isosurfaces are color coded in red, blue, and green. Whereas the first two correspond to strongly repulsive and attractive interactions, respectively, the latter can be described as weakly noncovalent, that is, LD, interactions.

Both experimental and computational data suggest the TIPS group to be the strongest DED group in the system studied. In accordance with the concept of molecular balances, the folded isomer (Figure 5, top, left) consists of close σ - σ contacts ($d_{\sigma-\sigma} \approx 2.33$ Å as shortest contact) between both silyl groups. Therefore, the NCI plot shows a green isosurface, indicating LD interactions. According to the SAPT analysis, these interactions correspond to $E_{\text{disp}} = -5.1$ kcal mol $^{-1}$ for the entire ensemble of LD interactions. On the other hand, the unfolded isomer (Figure 5, bottom, left) shows no interaction in the NCI plot due to the LD distance dependence. Nevertheless, SAPT suggests a small contribution of $E_{\text{disp}} = -0.3$ kcal mol $^{-1}$ for 1,4-COT. As a result, the relative energy $\Delta E_{\text{disp}} = -4.8$ kcal mol $^{-1}$ (Figure 4) strongly favors the folded isomer. While experimental data suggest fewer stabilizing interactions for TBDPS in the folded 1,6-COT (Figure 3), the NCI plot does not agree. The folded 1,6-disubstituted system shows larger isosurfaces between the phenyl moieties than for the σ -contacts in the TIPS system. The absolute value for the LD interactions for the folded TBDPS-COT rises up to $E_{\text{disp}} = -15.7$ kcal mol $^{-1}$ for the entire Boltzmann-weighted ensemble. The origin of stabilization lies in two offset T-shaped phenyl contacts ($d_{\text{CH}-\pi} \approx 2.33$ Å). While this classifies TBDPS as a strong DED, the overall effect is smaller than for TIPS. The observed ratio can be rationalized with an analysis of the unfolded isomer. Due to the flexibility of the spacer group, TBDPS twists around to form two T-shaped phenyl contacts ($d_{\text{CH}-\pi} \approx 2.56$ Å) in the unfolded 1,4-COT as well. According to SAPT, the interaction stabilizes the unfolded isomer by

around $E_{\text{disp}} = -11.5$ kcal mol $^{-1}$. A similar but weaker effect can be observed for TTMSS ($E_{\text{disp}} = -4.0$ kcal mol $^{-1}$ for the entire Boltzmann-weighted ensemble of the folded isomer).

While the measured absolute values with the di-O-silyl substituted COT are small (Figure 3), the impact of the spacer group becomes apparent by comparing the computed data with experimental measurements.⁴⁴ Note that the di-silyl substituted COTs were investigated in toluene, while the di-O-silyl substituted COTs were investigated in chloroform due to an incomplete signal separation of the latter in toluene. The ΔG difference due to solvation can be estimated to be around -0.1 kcal mol $^{-1}$ for the COT system going from toluene to chloroform.³⁶ While direct attachment of silyl groups at COT suffers from strain (ΔE_{strain}), the incorporation of a spacer group increases the flexibility, resulting in an entropic penalty in favor of the unfolded balance (ΔS). As already mentioned, di-O-TMS-COT does not benefit from the incorporation of $-\text{CH}_2\text{O}-$ groups but suffers from an entropic penalty⁵¹ due to increasing flexibility without additional stabilization due to LD. Figure 6 shows the total energy differences $\Delta\Delta E$ of the relative

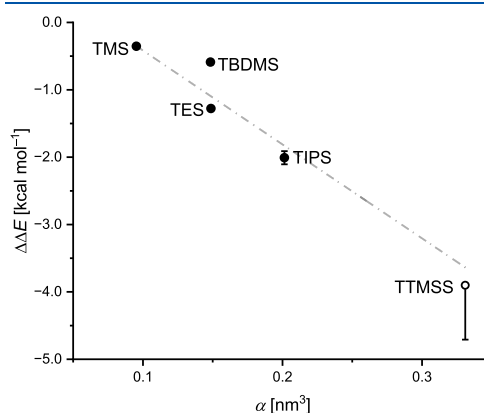


Figure 6. Correlating the total energy difference $\Delta\Delta E$ between di-O-silyl COT and di-silyl-COT with polarizabilities excluding strain energy (ΔE_{strain}) and entropic penalties (ΔS). Negative energy values correspond to attractive interactions. For TTMSS, the smallest energy difference was approximated.

Gibbs free energy values $\Delta\Delta G$ with $\Delta\Delta G = \Delta G_{\text{di-O-Si-COT}} - \Delta G_{\text{di-Si-COT}}$. Additionally, ΔE_{strain} and ΔS were considered computationally to exclude them from the analysis. Consequently, $\Delta\Delta E$ was calculated according to the following equation:

$$\Delta\Delta E = \Delta\Delta G - \Delta E_{\text{strain}} - \Delta S$$

$\Delta\Delta E$ corresponds to the total energy gain (negative energy values in Figure 6) arising from close silyl group contacts, excluding entropic penalties and energy gain due to strain release. In combination with the SAPT results (Figure 4) and NCI plots (Figure 5), most of the interactions can be assigned to LD. The largest energy change was observed for the TTMSS group ($\Delta\Delta E = -3.9$ kcal mol $^{-1}$). Because only the 1,4-di-TTMSS-COT could be reported in the earlier study, the $\Delta\Delta G$ for TTMSS (unfilled circle) represents the minimal shift in energy toward the folded isomer. The exact energy gap is larger but could not be determined. Accordingly, the TIPS group

shows the highest stabilizing interaction energy detected for both molecular balances ($\Delta\Delta E = -2.0 \text{ kcal mol}^{-1}$).

CONCLUSIONS

We report on our approach to quantifying NCIs between silyl groups in a molecular balance based on a COT motif. By including a $-\text{CH}_2\text{O}-$ spacer group between the COT molecular balance and the silyl groups, we measured the equilibria between 1,4- and 1,6-di-*O*-silyl substituted COT, identifying attractive interactions due to $\sigma-\sigma$ or $\text{CH}-\pi$ contacts. Counterintuitively, NMR measurements reveal that the bulky TIPS group shifts the equilibrium between 1,4- and 1,6-di-*O*-silyl substituted COT furthest toward the folded and more crowded valence isomer. Computational thermochemical data underscore this trend.

An SAPT analysis identifies LD interactions as the key NCIs between the silyl groups. The incorporation of a flexible $-\text{CH}_2\text{O}-$ spacer group allowed the silyl groups to maximize these stabilizing interactions. However, flexibility comes at the cost of an unfavorable folding entropy, and the SAPT analysis furthermore revealed 1,4-isomers of balances substituted with very bulky silyl groups to be significantly stabilized by LD interactions as well. These two effects work in opposite ways but still favor the 1,6-isomer. On the other hand, comparison of the current more flexible molecular balance with previously studied di-silyl substituted COTs (lacking a $-\text{CH}_2\text{O}-$ spacer) highlights how a system governed by repulsion may be modified to profit from bulky DED substituents.

Our results demonstrate that silyl groups are more than just providers of steric bulk and can counterintuitively affect conformational preferences *via* their actions as good DEDs.

EXPERIMENTAL SECTION

Thin layer chromatography was carried out using Polygram SIL G/UV₂₅₄ plates with detection *via* UV $\lambda = 254 \text{ nm}$ and by staining with a 10 wt % ethanolic phosphomolybdic acid stain solution. All chemicals were commercially obtained from Acros Organics, TCI, Boron Molecular, and Sigma-Aldrich and were used without further purification. Anhydrous solvents were purchased from Acros Organics. Unless otherwise noted, all reactions were carried out under standard Schlenk conditions employing N_2 as inert gas. Standard NMR spectra were obtained using Bruker AVANCE II 400 MHz and Bruker AVANCE III HD 400 MHz (^{13}C spectra) spectrometers. Elevated temperature NMR experiments were carried out with a Bruker AVANCE III HD 600 MHz spectrometer. High resolution mass spectra were obtained with a Bruker micrOTOF mass spectrometer. For elevated temperature measurements, NMR samples were equilibrated for 16 h at 40°C prior to the experiment, utilizing an IKA ICC basic eco 8 immersion circulator.

Elevated Temperature NMR Experiments. After sample transfer from the thermostat to the NMR spectrometer, equilibration was continued for another hour in the spectrometer before the spectra were recorded at 40°C .

Solutions of tri(*isobutyl*)silyl triflate and TTMSS triflate were prepared according to a modified literature procedure and were used without further purification.⁸¹

Dimethyl-cyclooctatetraene-1,4/1,6-dicarboxylate (2). Compound 2 was prepared according to a literature procedure⁴⁸ from commercially obtained 1 (Boron Molecular). 1.160 g (5.27 mmol) of 1 and 242.8 mg (0.53 mmol, 0.10 equiv) of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ were dissolved in 80 mL of anhydrous toluene. The reaction mixture was subsequently heated to 60°C for 16 h utilizing an oil bath. Afterward, the solvent was removed under reduced pressure and purification of the crude product *via* silica flash column chromatography (2:1 mixture of *n*-hexane and ethyl acetate) yielded 870.5 mg (3.95 mmol, 75%) of 2 as a yellow solid.

^1H NMR (400 MHz, CDCl_3), 1,4-2: δ 7.09 (s, 2H), 6.07 (q, $J = 2.8 \text{ Hz}$, 2H), 5.99 (q, $J = 2.8 \text{ Hz}$, 2H), and 3.77 (s, 6H); ^1H NMR (400 MHz, CDCl_3), 1,6-2: δ 7.03 (s, 2H), 6.16 (s, 2H), 6.03 (s, 2H), and 3.75 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 166.0, 165.9, 141.8, 140.0, 135.1, 133.8, 133.2, 132.3, 130.7, 129.4, 52.4, and 52.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4\text{Na}$, 243.0633; found, 243.0628.

This is in agreement with previously published data.⁴⁸

Cyclooctatetraene-1,4/1,6-dimethanol (3). To a solution of 821.2 mg (3.73 mmol) of 2 in 90 mL of anhydrous tetrahydrofuran was added 426.3 mg (11.2 mmol, 3 equiv) of LiAlH_4 in small portions at 0°C . After complete addition (approx. 30 min), the reaction mixture was allowed to reach room temperature and was left stirring for another 3 h and 30 min. The reaction mixture was then carefully quenched with 20 mL of saturated aqueous Na_2SO_4 solution. The obtained mixture was then transferred to a separatory funnel and extracted with ethyl acetate ($3 \times 100 \text{ mL}$). The combined organic phases were dried over anhydrous MgSO_4 , and the solvent was evaporated under reduced pressure, yielding the crude product as an orange oil. After purification *via* silica flash column chromatography (ethyl acetate), 350.1 mg (2.13 mmol, 57%) of 3 was obtained as a slightly yellow oil.

^1H NMR (400 MHz, $\text{DCM}-d_2$), 1,4-3: δ 5.96–5.76 (m, 6H) and 4.00 (s, 4H); 1.97 (s, 2H); ^1H NMR (400 MHz, $\text{DCM}-d_2$), 1,6-3: δ 5.96–5.76 (m, 6H) and 3.99 (s, 4H); 1.97 (s, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DCM}-d_2$): δ 144.0, 143.8, 133.4, 133.3, 131.9, 131.7, 127.7, 127.0, and 66.5; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{Na}$, 187.0733; found, 187.0735.

1,4-/1,6-Di-*O*-silyl Cyclooctatetraenes (4a–g). Di-*O*-silyl cyclooctatetraenes 4a–g were prepared according to the following general procedure: compound 3 (~30 mg) was dissolved in 8 mL of anhydrous dichloromethane (DCM) while stirring. 6 equiv of 2,6-lutidine was added at room temperature, and the reaction mixture was cooled to 0°C . 4 equiv of the corresponding silyl triflate or silyl chloride was then added, and the reaction mixture was allowed to reach room temperature. After 2 h at room temperature, the reaction was quenched by addition of 3 mL of deionized water. After extraction with DCM ($3 \times 10 \text{ mL}$), the combined organic phases were dried over MgSO_4 and concentrated under reduced pressure. The crude products were purified *via* silica column chromatography (2:1 mixture of *n*-hexane and DCM), yielding compounds 4a–g as colorless oils.

1,4-/1,6-Di-*O*-TMS-COT (4a). 31.4 mg (0.19 mmol) of 3, 0.13 mL (1.12 mmol, 6 equiv) of 2,6-lutidine, and 0.10 mL (0.79 mmol, 4 equiv) of TMSCl were mixed. After purification *via* silica column chromatography (2:1 mixture of *n*-hexane and DCM), 53.8 mg (0.17 mmol, 90%) of 4a was obtained as a colorless oil.

^1H NMR (400 MHz, CDCl_3), 1,4-4a: δ 5.89–5.72 (m, 6H) and 4.01 (s, 4H); 0.12 (s, 18H); ^1H NMR (400 MHz, CDCl_3), 1,6-4a: δ 5.89–5.72 (m, 6H) and 3.99 (s, 4H); 0.12 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 142.8, 142.4, 132.6, 132.3, 131.3, 131.3, 126.3, 126.1, 65.9, 65.8, –0.2, and 0.3; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{28}\text{O}_2\text{Si}_2\text{Na}$, 331.1526; found, 331.1521.

1,4-/1,6-Di-*O*-TES-COT (4b). 28.7 mg (0.17 mmol) of 3, 0.12 mL (1.04 mmol, 6 equiv) of 2,6-lutidine, and 0.16 mL (0.71 mmol, 4 equiv) of TESOTf were mixed. After purification *via* silica column chromatography (2:1 mixture of *n*-hexane and DCM), 60.1 mg (0.15 mmol, 87%) of 4b was obtained as a colorless oil.

^1H NMR (400 MHz, CDCl_3), 1,4-4b: δ 5.89–5.70 (m, 6H), 4.04 (s, 4H); 0.96 (t, $J = 7.9 \text{ Hz}$, 18H) and 0.65–0.57 (m, 12H); ^1H NMR (400 MHz, CDCl_3), 1,6-4b: δ 5.87–5.70 (m, 6H) and 4.03 (s, 4H); 0.96 (t, $J = 7.9 \text{ Hz}$, 18H) and 0.65–0.57 (m, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 143.0, 142.4, 132.5, 132.2, 131.7, 131.3, 126.0, 125.7, 66.0, 65.8, 6.9, 4.6 and 4.6; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{40}\text{O}_2\text{Si}_2\text{Na}$, 415.2464; found, 415.2458.

1,4-/1,6-Di-*O*-TBDMS-COT (4c). 30.1 mg (0.18 mmol) of 3, 0.13 mL (1.12 mmol, 6 equiv) of 2,6-lutidine, and 0.17 mL (0.74 mmol, 4 equiv) of TBDMSOTf were mixed. After purification *via* silica column chromatography (2:1 mixture of *n*-hexane and DCM), 67.7 mg (0.17 mmol, 94%) of 4c was obtained as a colorless oil. Preparation of 4c

was also carried out on a larger scale, applying the reaction conditions outlined above. 40 mL of anhydrous DCM as the solvent, 145.8 mg (0.89 mmol) of **3**, 0.62 mL (5.34 mmol, 6 equiv) of 2,6-lutidine, and 0.82 mL (3.57 mmol, 4 equiv) of TBDMSOTf were utilized. The reaction mixture was quenched with 15 mL of deionized water and extracted with DCM (3 × 40 mL). Purification via silica column chromatography (2:1 mixture of *n*-hexane and DCM) yielded 319.3 mg (0.81 mmol, 91%) of **4c** as a colorless oil.

¹H NMR (400 MHz, CDCl₃), 1,4-**4c**: δ 5.89–5.71 (m, 6H) and 4.04 (s, 4H); 0.91 (s, 18H) and 0.07 (s, 12H); ¹H NMR (400 MHz, CDCl₃), 1,6-**4c**: δ 5.89–5.71 (m, 6H) and 4.01 (s, 4H); 0.91 (s, 18H) and 0.07 (s, 12H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.0, 142.5, 132.5, 132.2, 131.7, 131.3, 125.8, 125.6, 66.3, 66.1, 26.1, 18.6, –5.1, and –5.2; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₂H₄₀O₂Si₂Na, 415.2464; found, 415.2460.

1,4-/1,6-Di-*O*-TIBS-COT (**4d**). 32.5 mg (0.18 mmol) of **3**, 0.14 mL (1.21 mmol, 6 equiv) of 2,6-lutidine, and an *n*-pentane solution (0.79 mmol, 4 equiv) of TIBSOTf (0.22 mL [0.84 mmol] of triisobutyl silane and 0.07 mL [0.79 mmol] of trifluoromethanesulfonic acid in 2 mL of *n*-pentane) were mixed. After purification via silica column chromatography (2:1 mixture of *n*-hexane and DCM), 66.3 mg (0.17 mmol, 85%) of **4d** was obtained as a colorless oil.

¹H NMR (400 MHz, CDCl₃), 1,4-**4d**: δ 5.87–5.70 (m, 6H) and 4.01 (s, 4H); 1.90–1.76 (m, 6H), 0.96 (s, 36H) and 0.66–0.58 (m, 12H); ¹H NMR (400 MHz, CDCl₃), 1,6-**4d**: δ 5.87–5.70 (m, 6H), 3.98 (s, 4H); 1.90–1.76 (m, 6H), 0.94 (s, 36H) and 0.66–0.58 (m, 12H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.8, 142.2, 132.4, 132.2, 131.7, 131.3, 125.9, 125.4, 65.7, 65.5, 26.6, 25.5, 25.4 and 24.4; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₃₄H₆₄O₂Si₂Na, 583.4342; found, 583.4341.

1,4-/1,6-Di-*O*-TIPS-COT (**4e**). 29.6 mg (0.18 mmol) of **3**, 0.13 mL (1.12 mmol, 6 equiv) of 2,6-lutidine, and 0.19 mL (0.71 mmol, 4 equiv) of TIPSOTf were mixed. After purification via silica column chromatography (2:1 mixture of *n*-hexane and DCM), 77.5 mg (0.16 mmol, 90%) of **4e** was obtained as a colorless oil.

¹H NMR (400 MHz, CDCl₃), 1,4-**4e**: δ 5.95–5.71 (m, 6H) and 4.12 (s, 4H); 1.01–1.16 (m, 42H); ¹H NMR (400 MHz, CDCl₃), 1,6-**4e**: δ 5.95–5.71 (m, 6H) and 4.09 (s, 4H); 1.01–1.16 (m, 42H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.1, 142.3, 132.4, 132.2, 131.7, 131.3, 125.5, 125.2, 66.3, 66.2, 18.2 and 12.2; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₈H₅₂O₂Si₂Na, 499.3404; found, 499.3397.

1,4-/1,6-Di-*O*-TBDPS-COT (**4f**). 30.3 mg (0.18 mmol) of **3**, 0.13 mL (1.12 mmol, 6 equiv) of 2,6-lutidine, and 0.22 mL (0.74 mmol, 4 equiv) of TBDPSOTf were mixed. After purification via silica column chromatography (2:1 mixture of *n*-hexane and DCM), 109.4 mg (0.17 mmol, 92%) of **4f** was obtained as a colorless oil.

¹H NMR (400 MHz, CDCl₃), 1,4-**4f**: δ 7.75–7.64 (m, 8H), 7.45–7.34 (m, 12H), 6.01–5.70 (m, 6H) and 4.10 (s, 4H); 1.08 (s, 18H); ¹H NMR (400 MHz, CDCl₃), 1,6-**4f**: δ 7.75–7.64 (m, 8H), 7.45–7.34 (m, 12H), 6.01–5.70 (m, 6H) and 4.05 (s, 4H); 1.06 (s, 18H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 142.7, 142.0, 135.7, 135.6, 133.8, 133.7, 132.6, 132.2, 131.5, 131.3, 129.8, 129.8, 127.8, 127.8, 125.9, 125.4, 66.8, 66.5, 27.0, 26.9 and 19.4; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₄₂H₄₈O₂Si₂Na, 663.3091; found, 663.3080.

1,4-/1,6-Di-*O*-TTMSS-COT (**4g**). 34.0 mg (0.21 mmol) of **3**, 0.14 mL (1.21 mmol, 6 equiv) of 2,6-lutidine, and an *n*-pentane solution (0.79 mmol, 4 equiv) of TTMSSOTf (0.26 mL [0.84 mmol] of trimethylsilyl silane and 0.07 mL [0.79 mmol] of trifluoromethanesulfonic acid in 2 mL of *n*-pentane) were mixed. After purification via silica column chromatography (2:1 mixture of *n*-hexane and DCM), 111.5 mg (0.17 mmol, 82%) of **4g** was obtained as a colorless oil.

¹H NMR (400 MHz, CDCl₃), 1,4-**4g**: δ 5.85–5.61 (m, 6H) and 3.88 (s, 4H); 0.19 (s, 54H); ¹H NMR (400 MHz, CDCl₃), 1,6-**4g**: δ 5.85–5.61 (m, 6H) and 3.86 (s, 4H); 0.19 (s, 54H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.0, 142.2, 132.6, 132.0, 131.3, 131.2, 125.2, 125.0, 70.5, 70.4 and 0.49; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₈H₆₄O₂Si₈Na, 679.2958; found, 679.2950.

Computational Details. We utilized the CREST developed by Grimme *et al.*⁶¹ to identify conformers lowest in energy. Due to the flexibility of the system, CREST located hundreds of conformers for each isomer within 6 kcal mol^{−1} energy margin. We reduced the number of conformers by focusing only on molecules in a 1 kcal mol^{−1} energy margin. The identified structures were optimized using the PBEh-3c functional.^{62–69} All structures located on energy minima of the hypersurface were utilized in a Boltzmann distribution, and their probability was calculated at 298 K. Conformers with a probability > 1% were used for single point computations at the revDSD-PBEP86-D4/def2-QZVPP^{67–72} level of theory including solvation effects (chloroform) via the PCM^{73,74} model. All optimizations and energy computations were performed using the ORCA program version 5.0.^{82,83}

For the energy decomposition analysis, we used an sSAPT⁷⁶ analysis as implemented in the PSI4 program.^{84,85} As a starting point, we utilized all conformers identified previously to be relevant for the conformer ensemble with a probability > 1%. The geometries are based on PBEh-3c. In the analysis, we focused on the interaction between silyl groups. Therefore, the molecular backbone (COT) and space group were removed, and the resulting silyl radicals were saturated with hydrogens. The sSAPT analysis was performed at the sSAPT0/aug-cc-pVDZ level of theory. The scaled protocol was utilized according to Parker *et al.*⁷⁷

The NCI plots⁷⁹ were plotted as a reduced density gradient in regions of low electron density. The resulting isosurfaces are color-coded in red, blue, and green. Whereas the first two correspond to strongly repulsive and attractive interactions, respectively, the latter can be described as weak noncovalent, that is, LD, interactions. The density cut-off of the reduced density gradient (isovalue *s* of 0.5, ranging from sign(λ_2)*p* = −0.05 to +0.05 a.u.) and the color scale data range were kept consistent throughout all NCI plots. We utilized the most probable conformer according to the Boltzmann analysis based on PCM(chloroform)-revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c for depiction. All plots were generated with NCIPLOT⁸⁰ and visualized with VMD.⁸⁶

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.2c01633>.

All experimental (NMR spectra) and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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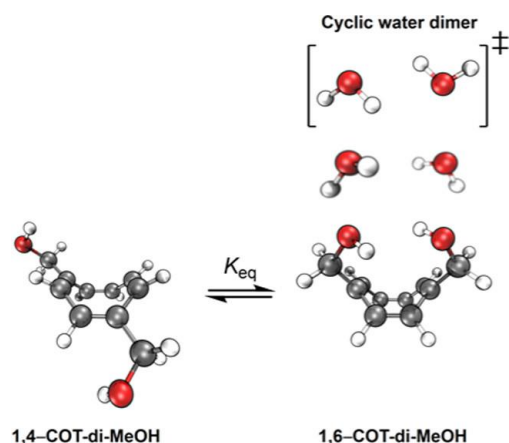
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2.5 Assessing the Experimental Hydrogen Bonding Energy of the Cyclic Water Dimer Transition State with a Cyclooctatetraene-Based Molecular Balance – Introduction

In our investigation of the flexible $-\text{CH}_2\text{O}-$ spacer COT molecular balances,¹⁸⁸ we had prepared cyclooctatetraene-1,4/1,6-dimethanol as a precursor to the silyl ethers. In conducting NMR experiments for characterization purposes, we noticed a remarkably weak favoring of the 1,6-isomer of COT-dimethanol, potentially indicating the prevalence of an unusual hydrogen bonding mode. A detailed conformational analysis of 1,6-COT-dimethanol yielded a conformer in which the OH-moieties adopt a trapezoid arrangement, in close resemblance of the C_i symmetric cyclic water dimer transition state (TS),¹⁸⁹ to be strongly favored over all other conformers. As we were interested in studying potential contributions of LD interactions to other NCIs, this finding prompted us to conduct a detailed computational and experimental study of the folding equilibrium of 1,4/1,6-COT-dimethanol. In order to verify the applicability of 1,6-COT-dimethanol as a model system for the cyclic water dimer TS, we compared our DFT computed geometries with the corresponding water dimer geometries obtained from high-level computations.¹⁸⁹ We studied the hydrogen bond character of 1,6-COT-dimethanol and structures derived from the latter and compared them to the cyclic water dimer TS utilizing high-level energy decomposition methods and quantum chemical descriptors. We also investigated the folding mechanism of 1,4/1,6-COT-dimethanol by means of DFT methods supplemented by high-level correlated methods, as well as multireference methods. Experimentally, we determined K_{fold} , and thereby ΔG_{eq} , via $^1\text{H-NMR}$ in a range of polar and non-polar solvents at room temperature.

Our computational findings suggest the OH arrangement in 1,6-COT-dimethanol to model the hydrogen bonding of the cyclic water dimer TS very well, both in character and strength. As deduced from our energy decomposition analyses, we found LD interactions to contribute nearly a third of the total hydrogen bonding energy (HBE). The experimentally observed attenuation of H-bonding, which manifested itself in the obtained ΔG_{eq} values can be explained by a combination of folding strain on the COT backbone, and solvation effects. If the latter effects were accounted for, the estimated HBEs derived from experimental ΔG_{eq} values agreed well with the best computational estimate from literature studies.¹⁸⁹

2.6 Paper 3: Assessing the Experimental Hydrogen Bonding Energy of the Cyclic Water Dimer Transition State with a Cyclooctatetraene-Based Molecular Balance



Abstract:

We have conducted an experimental and computational study of cyclooctatetraene-1,4/1,6-dimethanol (**1,4** and **1,6**) as a molecular balance with the goal in mind to determine the otherwise inaccessible hydrogen bonding energy (HBE) of the cyclic water dimer, which constitutes a transition state. The **1,4/1,6** folding equilibrium is governed by an intramolecular hydrogen bond in the folded **1,6**-isomer, in which the OH groups adopt a cyclic planar geometry, akin to the structure of the cyclic water dimer transition state. We characterized hydrogen bonding in **1,6** and reference complexes utilizing SAPT2 + (3) δ MP2/aug-cc-pVTZ and selected quantum theory of atoms in molecule descriptors at M06-2XD3(0)/ma-def2-TZVPP. Additionally, we computed HBEs at the DLPNO-CCSD(T)/aug-cc-pVQZ level of theory. We find that hydrogen bonding in **1,6** is very similar to the interaction in the C_i symmetric cyclic water dimer TS, both in magnitude and character. We experimentally determined the Gibbs free energy of the folding process (ΔG_{eq}) in a variety of organic solvents via nuclear magnetic resonance spectroscopy measurements at room temperature. By combining experimentally obtained ΔG_{eq} values with corrections derived from accurate computational methods, we provide estimates for the HBE of cyclic water dimers and the cyclic water dimer TS, as the most stable cyclic water dimer.

Reference:

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Assessing the Experimental Hydrogen Bonding Energy of the Cyclic Water Dimer Transition State with a Cyclooctatetraene-Based Molecular Balance

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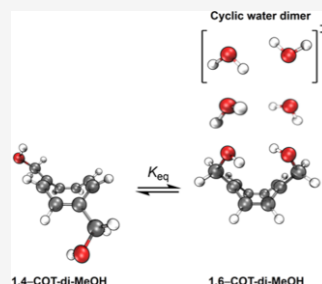
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ABSTRACT: We have conducted an experimental and computational study of cyclooctatetraene-1,4/1,6-dimethanol (**1,4** and **1,6**) as a molecular balance with the goal in mind to determine the otherwise inaccessible hydrogen bonding energy (HBE) of the cyclic water dimer, which constitutes a transition state. The **1,4/1,6** folding equilibrium is governed by an intramolecular hydrogen bond in the folded **1,6**-isomer, in which the OH groups adopt a cyclic planar geometry, akin to the structure of the cyclic water dimer transition state. We characterized hydrogen bonding in **1,6** and reference complexes utilizing SAPT2 + (3) δ MP2/aug-cc-pVTZ and selected quantum theory of atoms in molecule descriptors at M06-2XD3(0)/ma-def2-TZVPP. Additionally, we computed HBEs at the DLPNO-CCSD(T)/aug-cc-pVQZ level of theory. We find that hydrogen bonding in **1,6** is very similar to the interaction in the C_2 symmetric cyclic water dimer TS, both in magnitude and character. We experimentally determined the Gibbs free energy of the folding process (ΔG_{eq}) in a variety of organic solvents via nuclear magnetic resonance spectroscopy measurements at room temperature. By combining experimentally obtained ΔG_{eq} values with corrections derived from accurate computational methods, we provide estimates for the HBE of cyclic water dimers and the cyclic water dimer TS, as the most stable cyclic water dimer.



INTRODUCTION

Hydrogen bonding is commonly seen as a decisive noncovalent interaction (NCI) mostly responsible for the three-dimensional structure of nature's most essential macromolecules. Proteins owe various secondary structure elements such as alpha-helices,^{1–10} beta-sheets,^{3,5–9,11,12} and beta-loops^{3,5–9,13} to intramolecular hydrogen bonds and nucleobase “stair steps” in helical DNA^{14–18} molecules are similarly connected by hydrogen bonds. With nature as a role model, chemists have successfully exploited hydrogen bonding in a myriad of applications. In organocatalysis, for example, substrates may be bound and activated through hydrogen bonding to a catalyst.^{19–23} Furthermore, hydrogen bond donor and acceptor sites have proven to be useful design elements for controlling supramolecular aggregation.^{24–29}

In classic terms, hydrogen bonding can be understood as electrostatic attraction between partially positively charged hydrogen atoms and partially negatively charged acceptor atoms. In molecular orbital (MO) theory language, hydrogen bonding is described as a through-space donation of electron density from a nonbonding orbital or a lone pair of a donor atom into an antibonding H–X acceptor orbital (hyperconjugation).³⁰ Such models provide chemically intuitive descriptions of hydrogen bonding and are well supported by quantum chemical computations, which provide powerful tools for the quantitative characterization of hydrogen bonds. As

demonstrated in a recent study by Emamian et al.,³¹ symmetry-adapted perturbation theory^{32–34} (SAPT) may be utilized to reveal the nature of hydrogen bonds by decomposing hydrogen bonding energies (HBEs) into their fundamental energy components. The latter HBEs, as pure interaction energies, equal the lowering in electronic energy of the system (ΔE) due to the hydrogen bonding interaction. With the framework provided by Emamian et al.,³¹ hydrogen bonds in water dimers, as prototypical neutral hydrogen bonded complexes, can be categorized as being mostly dominated by electrostatics and LD interactions.^{35,36} The combination of stereoelectronics and energy decomposition techniques hence provides a well-rounded description, offering both qualitative and quantitative insights into hydrogen bonding.

The water dimers have been subjected to a vast amount of experimental and computational studies, since they offer an adequate basis for understanding bulk properties of water and are a model for OH...O hydrogen bonding in general.^{37–65} In the early days of water dimer research, cyclic^{66,67} or

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bifurcated^{66,68} arrangements have been considered besides the trans-linear isomer^{69,70} (Figure 1). However, through the

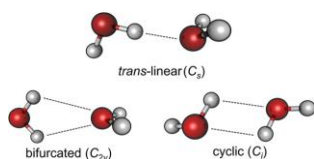


Figure 1. Three commonly considered water dimer isomers. The C_s symmetric trans-linear isomer marks the global minimum, and bifurcated (C_{2v}) and cyclic arrangements (C_i) are transition states (TS) on the water dimer potential energy surface (PES).

advent of high-resolution spectroscopy and computational chemistry, it is by now clear that the latter isomer marks the global minimum on the water dimer potential energy surface (PES). Although cyclic arrangements of molecules interacting via hydrogen bonding are a common sight,^{71,72} side-on OH hydrogen bonding interactions, where the oxygen and hydrogen atoms resemble vertices of a trapezoid (Figure 1, bottom), are far less common. Although such interactions have been observed in organic crystals,^{73–75} few examples are known, where said interactions alone provide stabilization of a molecular aggregate. This is due to the lower HBE^{35,51,76,77} of the interaction in comparison to a trans-linear hydrogen bond; hence, an ensemble of water molecules interacting via hydrogen bonding will preferably arrange in a way so that the amount of trans-linear interactions is maximized. Cyclic water dimers, as transition states (TS) or higher order saddle points,^{35,77,78} probably resemble the most prominent examples of such structures. Nevertheless, bifurcated or cyclic arrangements of water molecules might play a crucial role in the formation of larger water clusters.^{79–82}

Molecular balances offer a way to spatially confine (functional) groups that potentially exert a type of NCI on each other as part of a single molecule.^{83–91} Such systems exhibit an equilibrium between an unfolded and a folded state, in which the moieties of interest are in close spatial proximity and can therefore interact with each other. Readout of molecular balances is typically carried out by obtaining folding equilibrium data (K_{eq}) via spectroscopic techniques, such as nuclear magnetic resonance (NMR) spectroscopy.^{27,28} As a result, the nature and the magnitude of an interaction can readily be studied experimentally. The 1,4/1,6-substituted cyclooctatetraene^{90–96} (COT) molecular balance, in particular, has been utilized in an NMR study of LD interactions between bulky *tert*-butyl groups,⁹⁰ which found the folded 1,6-isomer to be favored irrespective of solvent or temperature. Computational and experimental studies suggest COT isomerization between the 1,6-isomer and the 1,4-isomer to progress via a valence bond shift mechanism.^{90,97–99} For di-*tert*-butyl-substituted COT isomerization, barriers have been experimentally and computationally estimated to be around 24.0–27.0 kcal mol^{−1},⁹⁰ while for less bulky substituents, such as methyl groups, an experimental value of about 17.5 kcal mol^{−1}¹⁰⁰ has been derived. Hence, COT molecular balances typically reach an equilibrium state ($\Delta K_{eq} = 0$) on a timescale of hours at room temperature. These properties in conjunction with the simplicity and the relatively broad solubility range in common organic solvents make substituted COT an attractive molecular balance for solution-phase NMR studies.

RESULTS AND DISCUSSION

Here, we chose cyclooctatetraene-1,4/1,6-dimethanol (1,4 and 1,6) as the target system for our study. The 1,4/1,6 equilibrium mixture has been prepared previously,¹⁰¹ but the utility of 1,4/1,6 as a molecular balance system has not been explored so far. The unfolded 1,4- and the folded 1,6-valence isomer can readily be distinguished, and their ratio is quantified by ¹H NMR spectroscopy (Figure 2).^{90–96} Due to

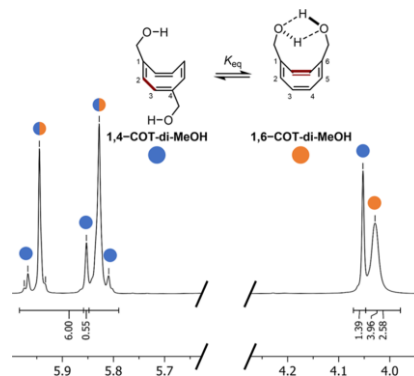


Figure 2. Ambient temperature ¹H-NMR spectrum (600 MHz, olefinic region and methylene protons) of 1,4/1,6-COT-Di-MeOH in CDCl₃. Overlapping signals are marked with bicolored (blue/orange) dots.

the tub-shaped COT moiety, the OH groups in 1,6 are forced to arrange in a similar fashion as found for the cyclic water dimer. Therefore, the 1,4/1,6 equilibrium is a suitable system for emulating the latter, allowing for an experimental solution-phase study of the cyclic water dimer, which otherwise would be experimentally inaccessible because of its nature as a saddle point on the water dimer PES.⁷⁷

We began our studies on the 1,4/1,6 system by establishing a synthesis route starting from dimethyl cubane-1,4-dicarboxylate (**1**) based on modified literature procedures (Scheme 1).^{102,103} The Rh(II)-catalyzed rearrangement yielded diester **2**, which was subsequently reduced utilizing lithium aluminum hydride to yield 1,4/1,6.

With a feasible synthesis route in hand, we first aimed at thoroughly investigating the system in silico. To validate our theoretical methods and to probe our working hypothesis, we first compared the computed geometries (M06-2XD3(0)/ma-def2-TZVPP) and HBEs (DLPNO-CCSD(T)/aug-cc-pVQZ) of the most stable C_i symmetric cyclic water dimer TS⁷⁷ with reference values computed at the DLPNO-CCSD(T)/CBS level of theory.³⁵ For simplicity reasons, we will refer to the C_i symmetric cyclic water dimer as “the cyclic water dimer” from here on. We found a total geometric root-mean-square deviation of 0.09 Å and a deviation of +0.05 kcal mol^{−1} in HBEs, hence rendering our chosen methods reasonable, given the size of the systems studied herein.

The M06-2XD3(0)/ma-def2-TZVPP optimized geometries of 1,6 and the cyclic water dimer reveal the following structural differences (Figure 3, top right):

1. An increased O–O distance of 3.05 Å in 1,6 versus the cyclic water dimer (2.73 Å).

Scheme 1. Synthesis Route for 1,4/1,6

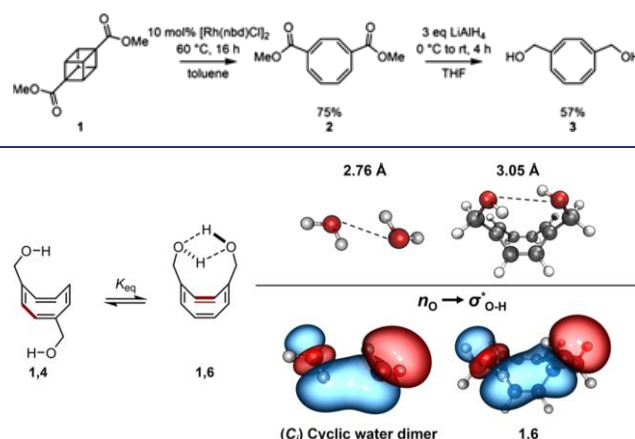
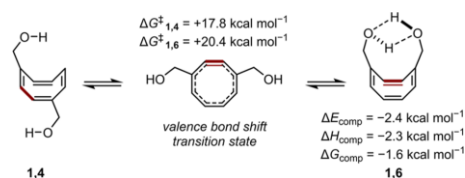


Figure 3. Folding equilibrium (left) of cyclooctatetraene-1,4/1,6-dimethanol (**1,4** and **1,6**) and comparison of geometries (right top) of the cyclic water dimer and **1,6**. NBO plots (bottom right, orbital isovalues = 0.03) of selected orbitals. Computations carried out at the M06-2XD3(0)/ma-def2-TZVPP level of theory.

2. A “flipped” arrangement of O—C bonds with respect to peripheral O—H bonds in the cyclic water dimer.

The first observation should result in a slightly weakened hydrogen bond in **1,6** in comparison to the cyclic water dimer. The flipped arrangement is not expected to have a significant effect, due to symmetry of the orbitals involved in hydrogen bonding. This is supported by a comparison of natural bond orbital (NBO) plots of **1,6** and the cyclic water dimer (Figure 3, right bottom).

We then focused our computations on the **1,4/1,6** folding equilibrium. By utilizing *n*-electron valence state perturbation theory (NEVPT2) computations, we were able to estimate activation barriers for the **1,4/1,6** valence isomerization (Scheme 2). The computed values suggest that the system

Scheme 2. Folding Mechanism of 1,4/1,6^a

^aActivation barriers computed at the DLPNO-NEVPT2(8,8)/cc-pVTZ//CAS-SCF(8,8)/cc-pVDZ level of theory. Equilibrium thermochemical quantities computed at the DLPNO-CCSD(T)/aug-cc-pVQZ//M06-2XD3(0)/ma-def2-TZVPP level of theory.

may reach equilibrium after about 16 min at 295 K, which we took as a guideline for sample equilibration in our experiments. Our computed ΔE ($-2.4 \text{ kcal mol}^{-1}$) value for the **1,4/1,6** folding equilibrium deviates from the computed HBE estimate for the cyclic water dimer ($-4.3 \text{ kcal mol}^{-1}$).⁷⁷ Having previously observed strain in related COT molecular balances,⁹¹ we suspected additional destabilizing effects to be present in **1,6**. Therefore, we carried out an analysis of **1,6**

aimed at extracting strain energy contributions (see the Supporting Information) to be able to correct for these. We identified $1.1 \text{ kcal mol}^{-1}$ of strain energy in the hydrocarbon moiety of **1,6** as a result of intramolecular hydrogen bonding, thereby bringing our computational results significantly closer to the expected HBE range.

Having explored the thermochemical parameters of **1,4/1,6**, we characterized the hydrogen bonding in order to put the suitability of **1,6** to model cyclic water dimers to the test. By comparing HBEs (computed at the DLPNO-CCSD(T)/aug-cc-pVQZ level of theory) of a methanol dimer and a water dimer in the geometry of the **1,6**-isomer with the cyclic water dimer, we found weaker hydrogen bonding in **1,6** (Figure 4). As mentioned above, this is very likely associated with an increase in O—O distance with respect to the cyclic water dimer. We further analyzed hydrogen bonding employing SAPT2 + (3) δ MP2/aug-cc-pVTZ computations, which allowed us to decompose the total HBE into physically interpretable components.³¹ Minor deviations are found in the energetic compositions of all investigated hydrogen bonding interactions (Figure 4). Moreover, hydrogen bonding is predicted to be dominated by electrostatics with significant contributions from LD interactions and diminishing inductive contributions. Neglecting LD interactions would in all cases lead to a strong attenuation of the HBE, as Pauli exchange repulsion rivals stabilizing electrostatic interactions (see the Supporting Information).

We furthermore analyzed the dimeric species mentioned above and **1,6** utilizing Bader's quantum theory of atoms in molecules (QTAIM).¹⁰⁴ QTAIM descriptors (Table 1) were obtained with Multiwfn version 3.8^{31,105} on the basis of M06-2XD3(0)/ma-def2-TZVPP computations. We found that QTAIM descriptors associated with absolute hydrogen bond strength such as total electron density $\rho(r)$ at the respective bond critical points (BCPs) and electronic energy density $H(r)$ indicate stronger interactions in the cyclic water dimer in comparison to all other species, while relative descriptors are

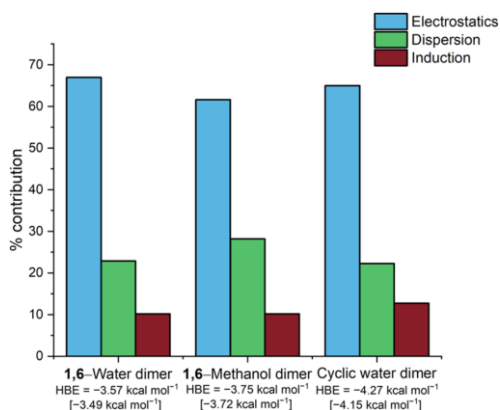


Figure 4. Percentage contribution of electrostatics, dispersion, and induction to the total attractive potential of dimeric species (SAPT2 + (3)δMP2/aug-cc-pVTZ level of theory). The structures labeled 1,6-water dimer and 1,6-methanol dimer were constructed from the structure of the 1,6-isomer in which the COT moiety was replaced by H or CH₃, respectively, keeping the hydrogen bonding substructure constant while optimizing the added fragments. Geometries optimized at the M06-2XD3(0)/ma-def2-TZVPP level of theory. DLPNO-CCSD(T)-derived HBEs below the x-axis with SAPT2 + (3)δMP2 in brackets.

Table 1. Selected QTAIM Descriptors of Dimeric Species and 1,6 (M06-2XD3(0)/ma-def2-TZVPP Wave Functions)^a

	$\rho(r)$ [a.u.]	$H(r)$ [a.u.]	$\frac{H(r)}{\rho(r)}$	$\frac{ V(r) }{G(r)}$
1,6-MeOH dimer	0.0102	0.0018	0.1786	-0.791
1,6-water dimer	0.0100	0.0019	0.1881	-0.782
1,6-COT-Di-MeOH	0.0102	0.0019	0.1851	-0.784
cyclic water dimer	0.0159	0.0031	0.1959	-0.813

^aWe use the same nomenclature as described in the caption of Figure 4.

found to deviate to a significantly smaller extent. Both $-\frac{H(r)}{\rho(r)}$ and the modulus of absolute potential energy density over the Lagrangian kinetic energy density $\frac{|V(r)|}{G(r)}$, representing descriptors of covalency for neutral hydrogen bonds,³¹ deviate by less than 10% in all cases. Negligible deviations are found between QTAIM descriptors of methanol and water dimers derived from the geometry of the 1,6-isomer and actual descriptors of 1,6-COT-di-MeOH. This indicates an insignificant effect of COT on hydrogen bond strength and nature.

We thus studied via NMR the 1,4/1,6 equilibrium at room temperature in a variety of common organic solvents to determine K_{eq} and thereby ΔG_{eq} (Table 2). For two solvents (D₂O and DMSO), ΔG_{eq} was found to be near 0 kcal mol⁻¹, which is likely due to strong solute–solvent hydrogen bonding, allowing for free rotation of –CH₂–OH groups in both valence isomers. As a result, intramolecular hydrogen bonding cannot be observed in these solvents. The experimentally obtained ΔG_{eq} values in non-chlorinated solvents were found to be in good agreement with computed ΔG values, when solvation was considered implicitly with the SMD model¹⁰⁶

Table 2. Experimental Gibbs Free Energy of Folding (ΔG_{eq}) for 1,4/1,6-COT-di-MeOH in Different Solvents at Room Temperature^a and Comparison with Computations ($\Delta G_{comp,SMD}$)

solvent	ΔG_{eq}	$\Delta G_{comp,SMD}$	HBE _{1,6}	HBE _{CWD}
cyclohexane	−0.90	−0.81	−3.56	−4.08
toluene	−0.43	−0.66	−3.24	−3.76
benzene	−0.33	−0.68	−3.12	−3.64
pyridine	−0.12	−0.06	−3.53	−4.05
nitrobenzene	−0.07	+0.02	−3.56	−4.08
CCl ₄	−1.03	−0.70	−3.80	−4.32
CHCl ₃	−0.39	+0.11	−3.97	−4.49
CH ₂ Cl ₂	−0.28	+0.25	−4.00	−4.52
1,1,2,2-TCE	−0.12			
DMSO	−0.03	−0.01		
D ₂ O	−0.02	+0.54		

^aAll experimental errors ($\Delta\Delta G_{eq}$) were in the range of ± 0.03 kcal mol⁻¹. HBE_{1,6} denotes the estimated HBE of 1,6, and HBE_{CWD} denotes the estimated HBE of the cyclic water dimer derived from our experiments. Theoretical values were computed at the DLPNO-CCSD(T)/aug-cc-pVQZ//M06-2XD3(0)/ma-def2-TZVPP level of theory. Bulk solvation was treated implicitly with the SMD model¹⁰⁶ for the respective solvent. All values in kcal mol⁻¹.

($\Delta G_{comp,SMD}$). The largest deviation of around 0.5 kcal mol⁻¹ between experiment and theory was found for water, which is, however, still within the mean unsigned error range of the SMD model.¹⁰⁶ It has to be kept in mind that besides parametrization in the cavitation dispersion solvent-structure (CDS) formalism of the SMD model,¹⁰⁶ hydrogen bonding is nonetheless treated implicitly in the latter. However, as mentioned above, explicit solute–solvent interactions are very likely decisive for the experimental folding behavior of 1,4/1,6 in DMSO and water. The good agreement between measured and computed ΔG values in the case of the remaining non-chlorinated solvents is a further indication of this. For chlorinated solvents, the overall experimental trend is reflected in the $\Delta G_{comp,SMD}$ values, but the deviation from experimentally obtained ΔG values is slightly larger.

Experimental and computational solution-phase ΔG values were found to be systematically higher than the computed gas-phase Gibbs free energy (ΔG_{comp}). The experimentally and computationally reduced preference of the folded 1,6 isomer with increasing polarizability and polarity of the solvent can likely be attributed to both solvation effects and an attenuation of hydrogen bonding in 1,6, through solute–solvent interactions. Due to the exposed OH groups of 1,4, it features an increased solvent accessible surface area and stronger solute–solvent interactions via electrostatic (dipole–dipole and dipole–induced dipole), hyperconjugation, and LD interactions. At the molecular level, such interactions may include OH– π interactions when, for instance, cyclohexane is replaced with benzene as the solvent. Since the OH groups are not fully exposed in the 1,6-isomer, solvation favors the 1,4-isomer. Furthermore, the hydrogen bonding interactions in the 1,6-isomer are attenuated through similar solute–solvent interactions, which stabilize the 1,4-isomer. Hence, increasing solvent polarity and polarizability reduces the preference for the 1,6-isomer.

Utilizing our experimental ΔG_{eq} values and computationally derived corrections accounting for solvation (SMD model), thermochemistry (0.8 kcal mol⁻¹; Scheme 2), and folding

strain (1.1 kcal mol⁻¹), the HBE of 1,6 (HBE_{1,6}, Table 2) can be estimated for each datapoint. In non-chlorinated solvents, the estimated HBE of 1,6 spans a range of -3.12 to -3.56 kcal mol⁻¹, in good agreement with the computed HBE of -3.75 kcal mol⁻¹ (Figure 4). Chlorinated solvents provide similarly good agreement, giving a range of -3.80 to -4.00 kcal mol⁻¹ for the HBE of 1,6. Note that the best estimate for the HBE is likely to be obtained in cyclohexane or carbon tetrachloride, as these solvents are expected to affect the folding equilibrium the least. Including the effect of the increased O–O distance in 1,6 in comparison to the cyclic water dimer (Figures 3 and 4), by introducing a correction of -0.5 kcal mol⁻¹ to HBE_{1,6}, the HBE of the cyclic water dimer can be assessed (HBE_{CWD}, Table 2). The thus-obtained HBE_{CWD} values (-4.08 to -4.32 kcal mol⁻¹) are in good agreement with the best computational estimate from the literature⁷⁷ of -4.32 kcal mol⁻¹.

Consequently, a comparison of our experimentally derived association energies (-D₀) with literature values⁷⁷ for the cyclic water dimer also yields good agreement (Table 3). We

Table 3. Experimental Estimates of the HBEs and the ZPVE-Corrected Association Energy (-D₀) of the Cyclic Water Dimer Derived from the 1,4/1,6 System^a

	cyclohexane (1,6)	CCl ₄ (1,6)	1,6-MeOH dimer	cyclic water dimer
$\Delta E = -D_e$ (HBE)	-4.08	-4.32	-3.75	-4.32 ^b
$\Delta H_0 = -D_0$ ($\Delta E + \text{ZPVE}$)	-2.15	-2.39	-1.82	-2.39

^aComputed (1,6-methanol dimer) and literature values for the cyclic water dimer in adjacent columns. $\Delta \text{ZPVE} = +1.93$ kcal mol⁻¹ (DLPNO-CCSD(T)/CBS).³⁵ All values in kcal mol⁻¹. ^bAccording to the best estimate (average of correlated methods up to the CBS limit) from the literature.⁷⁷

applied a ΔZPVE of +1.93 kcal mol⁻¹ according to Altun et al.,³⁵ as comparing an intramolecular to an intermolecular process would otherwise lead to an erroneous overestimation of -D₀ derived from our experiments. According to our estimates, association of the cyclic water dimer should be disfavored in comparison to the trans-linear water dimer⁷⁶ by 0.76–1.00 kcal mol⁻¹.

Finally, we hypothesized that incorporation of a water molecule in the structure of 1,6-COT-di-MeOH might lead to the formation of a water trimer-like structure.¹⁰⁷ We hence also studied the influence of a small amount of D₂O on the folding equilibrium in benzene. We could, however, not detect a significant influence of D₂O even at saturation-level concentrations (see the Supporting Information).

CONCLUSIONS AND OUTLOOK

We investigated the utility of 1,4/1,6 as a molecular balance system mimicking hydrogen bonding in the cyclic water dimer and performed a detailed computational analysis followed by determining ΔG_{eq} via ¹H NMR spectroscopy in ten organic solvents at room temperature. All ΔG_{eq} values favor the folded 1,6 form.

The computations suggest hydrogen bonding in 1,6 to be smaller by ~0.5 kcal mol⁻¹ in comparison to the cyclic water dimer as a result of geometric constraints. However, deviations in hydrogen bond character, as deduced from SAPT energy decomposition analyses and QTAIM descriptors, are found to be minor. We identified electrostatics and London dispersion

interactions as important terms for hydrogen bond stability, in line with previous analyses of the cyclic water dimers.¹⁰⁸

Experimental solution-phase ΔG_{eq} values are smaller by comparison and may be utilized to gauge the HBE of 1,6 and the cyclic water dimer as outlined previously. The thus-obtained experimental estimates for the HBE of the cyclic water dimer (-4.08 and -4.32 kcal mol⁻¹) are in line with the computed literature value of 4.32 kcal mol⁻¹.⁷⁷

We hence find the 1,4/1,6 equilibrium to be a suitable model system for cyclic water dimers, species which, owing to their properties as transition states or higher order saddle points, can otherwise not be directly experimentally investigated. This offers the unique opportunity to study a hydrogen bonding system closely resembling the cyclic water dimer via readily available analytical techniques at room temperature, thereby illuminating an otherwise blind spot on the PES of dimeric water.

EXPERIMENTAL SECTION

General Information. NMR spectra were obtained using either Bruker Avance II 400 MHz, Bruker Avance III HD 400 MHz, Bruker Avance III HD 600 MHz, or Bruker Avance Neo 700 MHz spectrometers. High-resolution mass spectra were obtained utilizing a Bruker micrOTOF mass spectrometer.

Synthesis of 1,4/1,6-COT-di-MeOH. Dimethyl-cyclooctatetraene-1,4/1,6-dicarboxylate (2). Compound 2 was prepared according to a literature procedure^{102,103} from commercially obtained 1 (boron molecular). We used 1.160 g (5.27 mmol) of 1, 242.8 mg (0.53 mmol, 0.10 equiv) of [Rh(nbd)Cl]₂, and 80 mL of anhydrous toluene. After purification via silica flash column chromatography (2:1 mixture of *n*-hexane and ethyl acetate), 870.5 mg (3.95 mmol, 75%) of 2 was obtained as a yellow solid.

¹H NMR (400 MHz, CDCl₃), 1,4-2: δ 7.09 (s, 2H), 6.07 (q, *J* = 2.8 Hz, 2H), 5.99 (q, *J* = 2.8 Hz, 2H), 3.77 (s, 6H); ¹H NMR (400 MHz, CDCl₃), 1,6-2: δ 7.03 (s, 2H), 6.16 (s, 2H), 6.03 (s, 2H), 3.75 (s, 6H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 166.0, 165.9, 141.8, 140.0, 135.1, 133.8, 133.2, 132.3, 130.7, 129.4, 52.4, 52.2; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₁₂H₁₂O₄, 243.0633; found, 243.0628.

In agreement with previously published data.¹⁰³

Cyclooctatetraene-1,4/1,6-dimethanol (3). To a solution of 821.2 mg (3.73 mmol) of compound 2 in 90 mL of anhydrous THF was added 426.3 mg (11.2 mmol, 3 equiv) of LiAlH₄ in small portions at 0 °C. After complete addition (approx. 30 min), the reaction mixture was allowed to reach room temperature and was left stirring for another 3 h and 30 min. The reaction mixture was then carefully quenched with 20 mL of saturated aqueous Na₂SO₄ solution. The obtained mixture was then transferred to a separatory funnel and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were dried over anhydrous MgSO₄, and the solvent was evaporated under reduced pressure, yielding the crude product as orange oil. After purification via silica flash column chromatography (ethyl acetate), 350.1 mg (2.13 mmol, 57%) of 3 was obtained as slightly yellow oil.

¹H NMR (400 MHz, DCM-*d*₂), 1,4-3: δ 5.96–5.76 (m, 6H), 4.00 (s, 4H); 1.97 (s, 2H); ¹H NMR (400 MHz, DCM-*d*₂), 1,6-3: δ 5.96–5.76 (m, 6H), 3.99 (s, 4H); 1.97 (s, 2H); ¹³C{¹H} NMR (100 MHz, DCM-*d*₂): δ 144.0, 143.8, 133.4, 133.3, 131.9, 131.7, 127.7, 127.0, 66.5; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₁₀H₁₂O₂, 187.0733; found, 187.0735.

Computational Details. We investigated the conformational space of 1,4/1,6-COT-di-MeOH with Grimme's Conformer-Rotamer Ensemble Sampling Tool (crest version 2.11.2) at the GFN2¹⁰⁹ level of theory.¹¹⁰ The resulting lowest energy 1,4/1,6-COT-di-MeOH conformers were subsequently optimized with Gaussian16¹¹¹ employing the M06-2XD3(0)^{85,86} functional in conjunction with the minimally augmented ma-def2-TZVPP^{112,113} basis set. Bulk solvation was considered implicitly with the SMD model¹⁰⁶ for the respective

solvent and used with default settings as implemented in Gaussian16. NBO^{114,115} plots were generated with Gaussian16 and VMD¹¹⁶ from M06-2XD3(0)/ma-def2-TZVPP wave functions.

For analyzing the folding mechanism of 1,4/1,6-COT-di-MeOH, geometries were optimized at the CASSCF(8,8)¹¹⁷ level of theory utilizing Dunning's correlation-consistent cc-pVDZ basis set.^{118–121} To obtain accurate electronic energies, computations at the DLPNO-NEVPT2(8,8)¹²²/cc-pVTZ level of theory were conducted utilizing previously obtained CASSCF(8,8) geometries. Equilibrium thermochemical quantities of the 1,4/1,6-COT-di-MeOH system were computed at the DLPNO-CCSD(T)^{123,124}/aug-cc-pVQZ//M06-2XD3(0)/ma-def2-TZVPP level of theory. All DLPNO-CCSD(T), DLPNO-NEVPT2, and CASSCF computations were carried out with the ORCA^{125,126} 5.0.1 ab initio, DFT, and semiempirical SCF-MO package.

SAPT analyses at the SAPT2 + (3)δMP2³⁴/aug-cc-pVTZ level of theory were carried out utilizing M06-2XD3(0)/ma-def2-TZVPP optimized geometries with the PSI4^{127,128} program package.

QTAIM descriptors were obtained with Multiwfn^{31,105} version 3.8 utilizing M06-2XD3(0)/ma-def2-TZVPP wave functions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c06141>.

NMR spectra and computational data (PDF)

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Notes

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2.7 Paper 4: Dispersion Energy Donor guided aggregation of phosphorescent Pt(II) phenylacetylides for application in hyperfluorescent OLED devices

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(Manuscript in preparation)

2.7.1 Introduction

Since the initial report on phosphorescent *trans*-Pt(II)-NHC phenylacetylides in 2013,¹⁶⁰ substantial efforts have been undertaken in order to tune and control their photophysical properties through the electronic nature of the *N*-heterocyclic carbene (NHC) or phenylacetylide ligands.^{164,165,167,168} Notably, *trans*-Pt(II)-NHC phenylacetylide carrying a benzimidazolylidene NHC ligand have shown deep-blue electroluminescence (439 nm) with a peak external quantum efficiency (EQE) of 14%.¹⁶⁵ However, the investigated devices suffered from substantial efficiency roll-off at higher luminance (>100 cd/m²). The latter observation is probably related to the comparatively long triplet lifetimes of ~ 20 μ s of *trans*-Pt(II)-NHC phenylacetylides, in conjunction with the tendency of square planar Pt(II) complexes for aggregating in closely packed structures, leading to triplet quenching at high charge-carrier densities.^{159,165} In a recent study on phosphorescent tetradentate Pt(II) complexes, the introduction of a trimethylsilyl (TMS) group led to significantly improved EQEs in organic light emitting diode (OLED) devices fabricated from the TMS-substituted complex.⁹³ Even at doping concentrations of more than 15% a respectable EQE of around 14% could be achieved at a luminance of 1000 cd/m². The improvements were attributed to the bulky nature of the TMS group preventing aggregation.⁹³ However, as bulky silyl groups are known dispersion energy donors (DEDs),^{61,187,188} and are hence more likely to promote aggregation, these findings raise the question of the importance of aggregate structures on the observed improved photoluminescence and electroluminescence behavior. Furthermore, as silyl groups have considerable polarizability, which can result in a net electron-donating effect,¹⁹³ this raises the question of a possible electronic influence on the emissive behavior of phosphorescent Pt(II) complexes.

In so called ‘hyperfluorescent’ OLED devices, phosphorescent sensitizer materials are used in conjunction with singlet emitters, in order to achieve higher EQEs and an improved device lifetime.^{96,175} The introduction of bulky substituents is also expected to be beneficial for

materials utilized in hyperfluorescent OLED devices, as the resulting aggregates are less likely to promote unproductive Dexter energy transfer (DEX), e.g., from the first triplet excited state T_1 of a phosphorescent sensitizer to the non-emissive T_1 of a fluorescent emitter material.^{96,175} Derivatization with bulky silyl-DEDs could hence also render *trans*-Pt(II)-NHC phenylacetylides attractive candidates for application as phosphorescent sensitizers in pure/deep-blue hyperfluorescent OLEDs. In this way, problems related to the long triplet lifetime of this group of complexes could also be circumvented. Furthermore, depending on the attachment of silyl-DEDs, the electronic effect of the latter could be utilized for fine-tuning properties to improve compatibility with common host-materials.¹⁶⁵

With this work we aim at systematically studying the effects silyl-DED attachment in the peripheral region (phenylacetylene ligands) has on the electronic properties and the aggregation behavior of *trans*-Pt(II)-NHC phenylacetylides. We prepared mono- and di-TMS-substituted *trans*-Pt(II)-NHC phenylacetylides complexes (Pt-1 and Pt-2), their respective *t*-butyl counterparts (Pt-3 and Pt-4), and the unsubstituted parent compound Pt-5. As *t*-butyl and TMS moieties are nearly on-par in terms of their steric demand, comparison of experimental and computational data of both respective analogues should allow us to gain insight into additional electronic and London dispersion (LD) related effects exerted by TMS groups. We studied the photophysical properties of aforementioned complexes in solution, and polymethyl methacrylate (PMMA) thin films of different doping concentrations. We furthermore conducted detailed computational analyses on their electronic structures and respective aggregation behavior. We also investigated the applicability of the best performing complex in a hyperfluorescent system, employing both a blue fluorescent emitter (TBPDP^{183–185}) and a pure-blue MR-TADF emitter (DABNA-NP-*tb*¹⁹⁴).

2.7.2 Results and Discussion

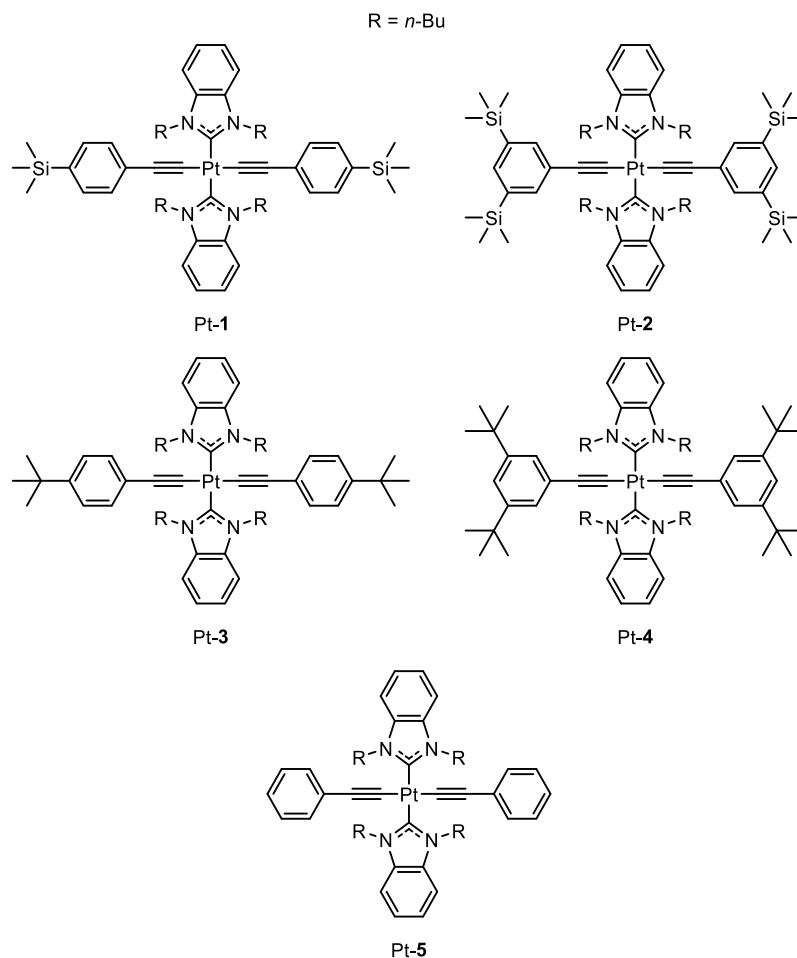


Figure 12: Chemical structures of Pt(II) complexes Pt-1-5 subject of this investigation.

2.7.2.1 Synthesis and characterization

Phenylacetylene ligands and TMS-protected ligand precursors were prepared according to modified literature procedures, utilizing a Sonogashira coupling protocol followed by deprotection in methanolic basic medium.^{195,196} The target *trans*-Pt(II)-NHC phenylacetylides Pt-1-5 were also obtained under modified literature conditions¹⁷³ *via* transmetalation of *in situ* formed phenylethynyl cuprates on bis(*N,N*-dibutylbenzimidazol-2-ylidene)platinum(II) dichloride, which was prepared following literature conditions.¹⁷³ Characterization of Pt-1-5 was carried out *via* ¹H- and ¹³C-NMR (section 2.7.4.X), as well as elemental analysis (EA, section 2.7.4.X). The presence of a single multiplet (triplet) in the 4.70-5.00 ppm region of the ¹H-NMR spectra of Pt-1-5 confirmed the *trans* stereochemistry of the target complexes. Finally, both TBPDP¹⁸³⁻¹⁸⁵ and DABNA-NP-tb¹⁹⁴ were prepared following literature procedures.

2.7.2.2 Photophysical properties – Platinum complexes

The focus of the work was to study the photoluminescence behavior of complexes Pt-1-5 in PMMA thin films, as a model system for potential OLED device applications. However, we also studied the photophysical properties of Pt-1-5 in solution. UV-Visible absorption (UV-Vis) spectra of compounds Pt-1-5 were measured at room temperature in DCM and are shown in Figure 13 (a). In agreement with similar literature known compounds,¹⁶⁴ Pt-1-5 show an intense absorption band in the 290 nm region, with a peak shoulder extending into the 320 nm region. Notably, the mono-substituted compounds Pt-1 and Pt-3 displayed significantly higher extinction coefficients in the main absorption region than the di-substituted (Pt-2 and Pt-4), and unsubstituted parent compound Pt-5. As deduced from our time-dependent density-functional theory (TD-DFT) computations (see section 2.7.2.4 (TD-)DFT analyses of Platinum complexes) and in agreement with previous literature¹⁶⁰ the 320 nm shoulder in the absorption spectra can be attributed to a singlet intraligand charge-transfer (¹ILCT) ($\pi_{\text{alkyne}} \rightarrow \pi^*_{\text{alkyne}}$) transition, while the main absorption band at 290 nm can be traced back to a singlet ligand-to-ligand charge-transfer (¹LLCT) ($\pi_{\text{alkyne}} \rightarrow \pi^*_{\text{NHC}}$) transition with singlet metal-to-ligand charge-transfer (¹MLCT) ($5d(\text{Pt}) \rightarrow \pi^*_{\text{NHC}}$) contributions. All investigated compounds were found to be strongly luminescent at room temperature in degassed dichloromethane (DCM) solution when excited with light $\lambda_{\text{exc}} > 315$ nm. A strong narrow emission band in the 438-448 nm deep-blue region accompanied by a broad less intense shoulder at 460-470 nm was observed (Figure 13 (b)). The emission red shift in the series of Pt-5-1 can be attributed to the modest electron donating ability/polarizability of the ^tbutyl and TMS groups, with the greater polarizability of TMS groups leading to a greater bathochromic shift. Our computations (see section 2.7.2.4) suggest ^tbutyl, and more so TMS groups, to stabilize the first excited triplet state (T_1) relative to the ground state (S_0). This is in agreement with the phosphorescent emission being attributed mostly to a triplet intraligand charge-transfer ³ILCT ($\pi_{\text{alkyne}} \rightarrow \pi^*_{\text{alkyne}}$) transition.¹⁶⁰

The relative intensity of the broad shoulder correlates with the substitution pattern of the complexes. As they are most pronounced for the di-substituted complexes Pt-2 and Pt-4 (with Pt-2 > Pt-4), this could be indicative of DED induced aggregation processes promoting excimeric emission.^{162,163} Although mono- and di-substitution appear to affect the emission shoulder, only a miniscule red-shift can be observed for the main emission band when comparing Pt-1 vs. Pt-2, and Pt-3 vs. Pt-4 respectively. The latter is indicative of similar electronic structures of the mono- and di-substituted complexes.

Overall, we found minor differences in the absorption and PL spectra of solution *versus* thin film samples for each investigated platinum complex (see section 2.7.4.7 for spectra). Differences in spectra shapes and relative intensities of emission/absorption bands between thin film and solution measurements could be related to matrix effects, due to the different electronic characteristics (solvent/matrix polarizability and polarity) of PMMA in comparison to DCM. As outlined above the increasing relative intensity of red-shifted emission side-bands with doping concentration, could be an aggregation related effect. However, as said emission bands typically had an even higher relative intensity under extremely dilute conditions in DCM solution, it could also be solvent/matrix related effect.

The "occurrence", or rather greater visibility of lower energy absorption bands is also very likely related to the different electronic characteristics of PMMA as a host-matrix in comparison to DCM as a solvent.

Compounds Pt-1 to Pt-5 display commission internationale de l'éclairage 1931 (CIE 1931)¹⁹⁷ [x, y]-coordinates close to 0.16 for x, and span a range of 0.12-0.18 for y, with Pt-3 to Pt-5 residing in the deep-blue/blue region, while Pt-1 and Pt-2 are close to the blue/sky-blue region (Figure 13 (c)).

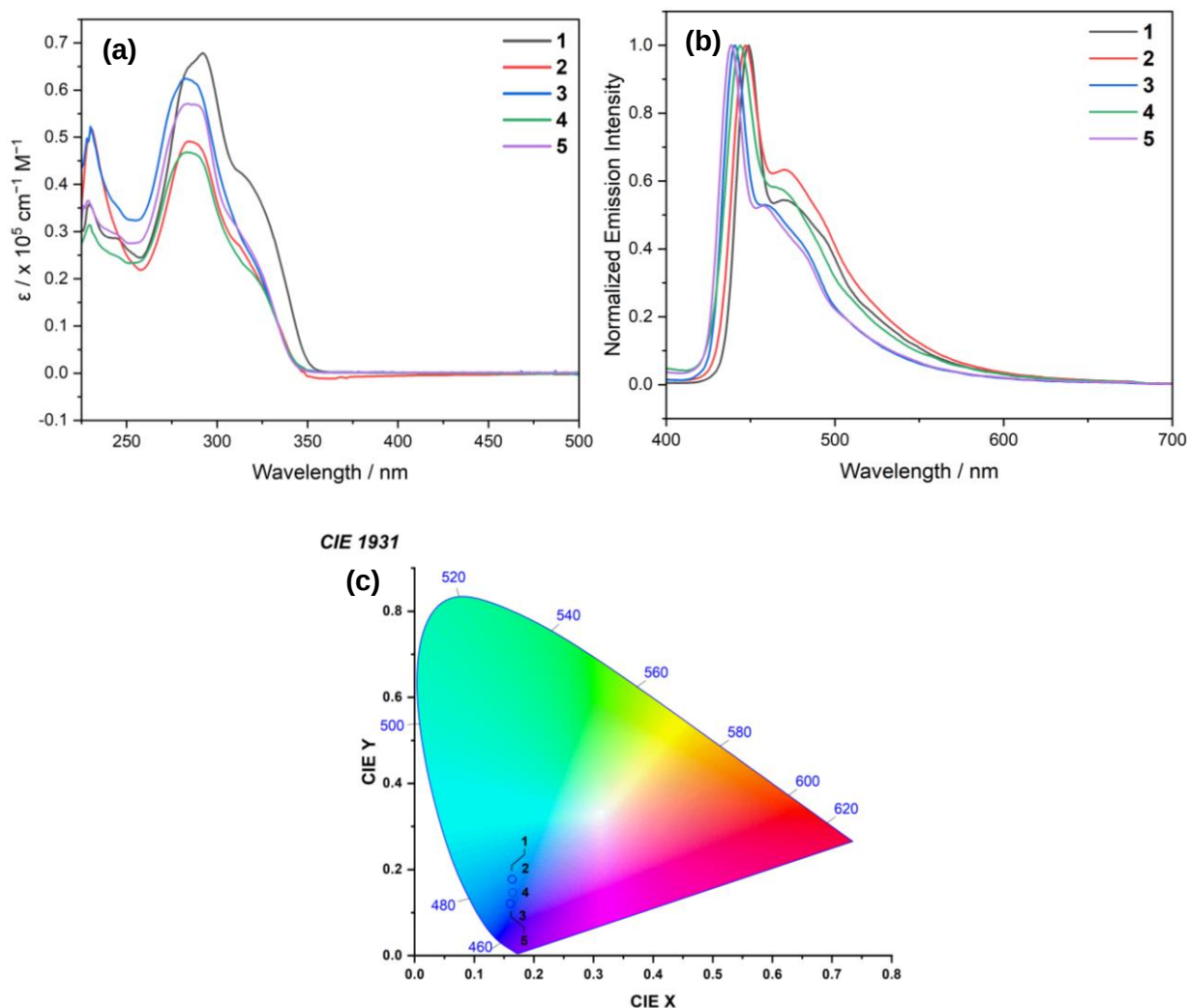


Figure 13: Absorption spectra (a), normalised emission (b), and CIE¹⁹⁷ coordinates of compounds Pt-1-5 (c), measured at room temperature in degassed DCM.

The complexes were found to display a similar photoluminescence behavior in PMMA thin films as in solution, except for longer excited state lifetimes (photophysical data of all complexes are summarized in Table 1). This is due to the greatly reduced possibilities for thermal deactivation of the triplet state in the solid PMMA matrix.^{159,165} The latter effect is dominant in solution, as a result of the low rigidity of this family of complexes.^{159,165} The mono-substituted compounds exhibit greater PLQYs at high doping concentrations than the di-substituted compounds, indicating an altered aggregation behavior and hence lower non-radiative decay through

triplet-triplet annihilation. As expected from the greater DED-ability of silyl groups,^{61,187,188} compound Pt-2 exhibits the lowest PLQY at 10 wt% doping concentration.

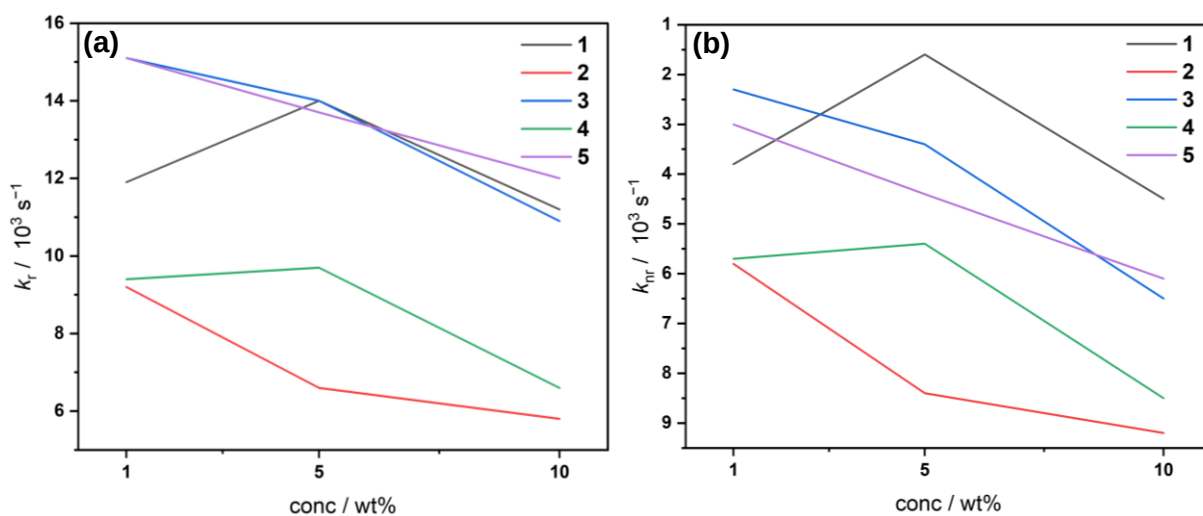


Figure 14: Correlation of doping concentrations (wt%) of complexes Pt-1-5 in PMMA with radiative k_r (a), and non-radiative decay rates k_{nr} (b). Solid lines drawn as a guide to the eye.

The silyl-substituted compounds Pt-1/Pt-2 also display a somewhat longer excited state lifetime in comparison to their carbon counterparts. This could be associated with both aggregation effects leading to an increasing contribution from long-lived excimeric species and/or electronic effects (aforementioned T_1 stabilization, or greater polarizability of silyl groups leading to greater destabilization of non-emissive d-d triplet metal-centered (^3MC) states^{159,165}). As a consequence, the radiative decay rates k_r (Figure 14, (a)) of higher concentration thin film samples of Pt-1 are on-par with the parent compound Pt-5 and the carbon analogue Pt-3, despite the superior PLQY of Pt-1. On the other hand, thin films of Pt-1 display the lowest non-radiative decay rates at relevant doping concentrations (Figure 14, (b)). Due to the low PLQYs of Pt-2 and Pt-4 with comparable excited state lifetimes, the latter overall show the lowest radiative decay rates and highest non-radiative decay rates. These findings are in support of the previously outlined substitution pattern related change in aggregation behavior, and a possible electronic influence of silyl groups.

Overall, complex Pt-1 was found to be best performing in terms of PLQY, even when compared to the deep-blue emissive parent compound Pt-5. Hence, Pt-1 was investigated with respect to applicability as a phosphorescent sensitizer in a hyperfluorescent system, offering the best compromise between photophysical properties and desirable structural characteristics.

Table 1: Room temperature photophysical data for compounds Pt-1-5.

	$\lambda_{\text{abs}}^{(a)} / \text{nm}$ ($\epsilon / \text{cm}^{-1} \text{mol}^{-1}$)	wt% in PMMA	$\lambda_{\text{PL}}^{(b)} / \text{nm}$	$\tau_0^{(c)} / \mu\text{s}$	$\phi_{\text{PL}}^{(d)}$	$k_r^{(e)} / 10^3 \text{s}^{-1}$	$k_{\text{nr}}^{(e)} / 10^3 \text{s}^{-1}$
Pt-1	315 ^{sh} (41000) 291 (68000)	1	448, 473 ^{sh} (448, 472 ^{sh})	63.8 (2.6)	76	12	3.8
		5			90	14	1.6
		10			71	11	4.5
Pt-2	312 ^{sh} (27000) 285 (49000)	1	448, 473 ^{sh} (447, 471 ^{sh})	66.7 (1.1)	61	9.2	5.8
		5			44	6.6	8.4
		10			39	5.8	9.2
Pt-3	313 ^{sh} (29000) 283 (62000)	1	441, 460 ^{sh} (441, 460 ^{sh})	57.5 (-)	87	15	2.3
		5			80	14	3.4
		10			63	11	6.5
Pt-4	317 ^{sh} (22000) 283 (47000)	1	445, 473 ^{sh} (444, 469 ^{sh})	66.2 (-)	62	9.4	5.7
		5			64	9.7	5.4
		10			44	6.6	8.5
Pt-5	314 ^{sh} (29000) 285 (57000),	1	439, 459 ^{sh} (439, 459 ^{sh})	55.4 (-)	84	15	3.0
		5			76	14	4.4
		10			66	12	6.1

^(a) Measured in degassed DCM. ^(b) Values in parentheses were measured in degassed DCM. ^(c) Lifetime values for 1-10 wt% thin films were identical, values in were measured in degassed DCM. ^(d) Absolute quantum yields (ϕ_{PL}) measured with integrating sphere. ^(e) Radiative (k_r) and non-radiative (k_{nr}) decay rates were calculated according to the following equations: $k_r = \phi_{\text{PL}}/\tau_0$, $k_{\text{nr}} = (1-\phi_{\text{PL}})/\tau_0$.

2.7.2.3 Photophysical properties – hyperfluorescent thin films

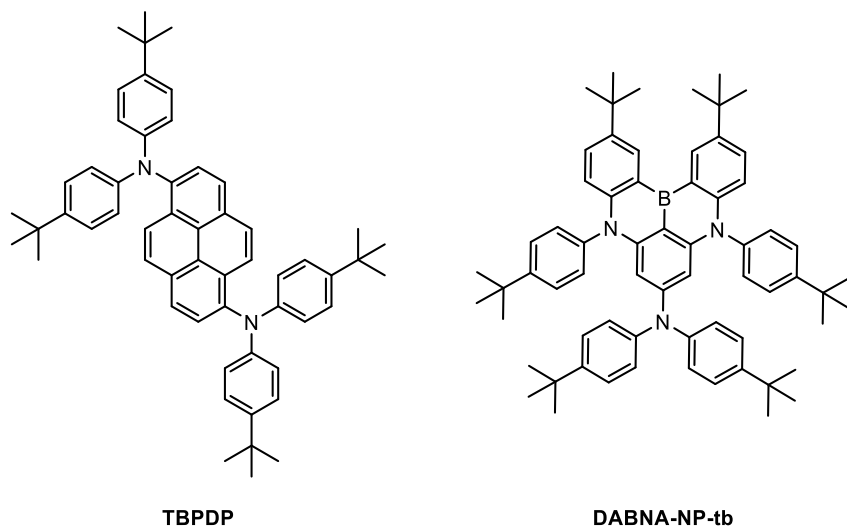


Figure 15: Chemical structures of the fluorescent emitter TBPDP^{183–185} and the MR-TADF emitter DABNA-NP-tb¹⁹⁴ utilized in the hyperfluorescence investigations on Pt-1.

One important requirements for efficient energy transfer between phosphorescent sensitizer materials (Pt-1) and co-doped emitter materials (TBPDP^{183–185} or DABNA-NP-tb¹⁹⁴) is spectral overlap of the emission spectrum of Pt-1 and the absorption spectrum of the respective emitter. Thus, the photophysical properties of PMMA thin films doped either solely with Pt-1 (10 wt%), TBPDP (3 wt%) or DABNA-NP-tb (3 wt%), and thin films consisting of 10 wt% of Pt-1 and 3 wt% of either TBPDP or DABNA-NP-tb were studied. For both material combinations, overlaying emission and absorption spectra yields a decent degree of spectral overlap (Figure 16 (a) and (b)).

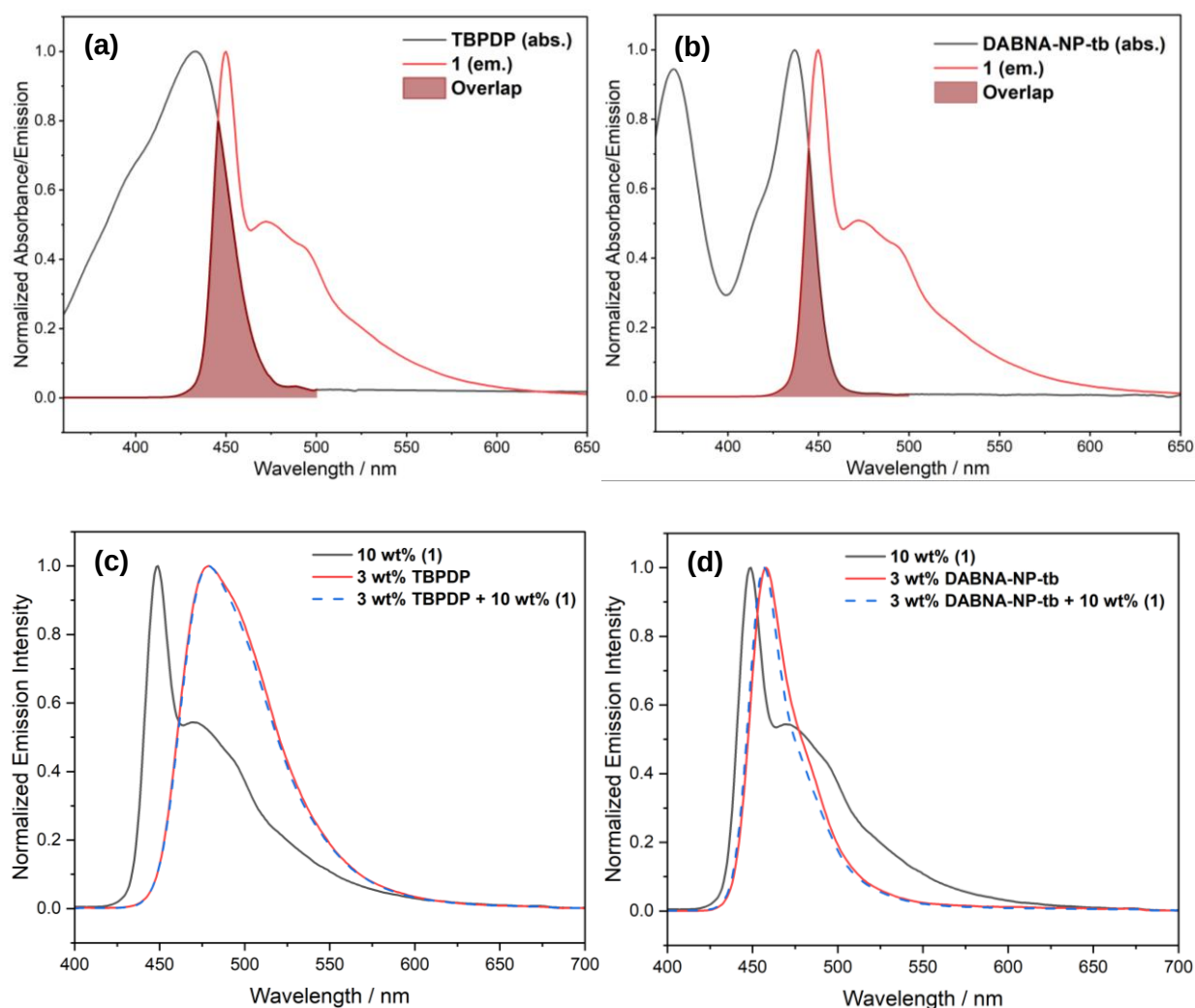


Figure 16: Spectral overlap of emission of Pt-1 (10 wt% in PMMA) with absorption of TBPDP (3 wt% in PMMA) (a), and DABNA-NP-tb (3 wt% in PMMA) (b), normalized emission spectra of Pt-1, TBPDP and hyperfluorescent system of Pt-1 and TBPDP in PMMA matrix, normalized emission spectra of Pt-1 (c), DABNA-NP-tb and hyperfluorescent system of Pt-1 and DABNA-NP-tb in PMMA matrix (d).

The emissive properties of the thin films were studied under ambient condition (results summarized in Table 2). A comparison of the emission spectra of a pure TBPDP thin film and a hyperfluorescent thin film of Pt-1 co-doped with TBPDP revealed miniscule differences and practically identical emission lifetimes (Figure 16 (c), Table 2). The absolute photoluminescence quantum yield of the hyperfluorescent thin film was found to be approximately 20% greater in comparison to the plain TBPDP thin film. Very similar results are found for DABNA-NP-tb thin films, with the emission of the samples being in the deep-blue region, whereas the TBPDP thin films displayed the expected sky-blue emission (see CIE coordinates in Table 2). Overall, the results indicate efficient energy transfer between Pt-1 and TBPDP or DABNA-NP-tb, and hence

Pt-1 is found to be a suitable candidate for application as a phosphorescent sensitizer in hyperfluorescent OLED devices.

Table 2: Room temperature photophysical data of hyperfluorescent PMMA thin films.

Thin film (PMMA)	$\lambda_{\text{PL}}^{(a)}$ / nm	τ_0 / μs	$\phi_{\text{PL}}^{(b)}$	$k_r^{(c)} / 10^3 \text{ s}^{-1}$	$k_{\text{nr}}^{(c)} / 10^3 \text{ s}^{-1}$	CIE (x, y)
10 wt% Pt-1	448, 473 ^{sh}	63.8	71	11	4.5	(0.16, 0.18)
3 wt% TBPDP	479	$6.1 \cdot 10^{-3}$	68	$1.1 \cdot 10^5$	$5.2 \cdot 10^4$	(0.15, 0.34)
10 wt% Pt-1 + 3 wt% TBPDP	479	$6.1 \cdot 10^{-3}$	83	$1.4 \cdot 10^5$	$2.8 \cdot 10^4$	(0.15, 0.33)
3 wt% DABNA-NP-tb	458	$7.0 \cdot 10^{-3}$	31	$4.4 \cdot 10^4$	$9.9 \cdot 10^4$	(0.14, 0.10)
10 wt% Pt-1 + 3 wt% DABNA-NP-tb	457	$7.8 \cdot 10^{-3}$	36	$4.6 \cdot 10^4$	$8.2 \cdot 10^4$	(0.14, 0.10)

^(a) λ_{exc} was 350 nm in all cases. ^(b) Absolute quantum yields (ϕ_{PL}) measured with integrating sphere. ^(c) Radiative (k_r) and non-radiative (k_{nr}) decay rates were calculated according to the following equations: $k_r = \phi_{\text{PL}}/\tau_0$, $k_{\text{nr}} = (1-\phi_{\text{PL}})/\tau_0$.

2.7.2.4 (TD)-DFT analyses of Platinum complexes

The photophysical properties of compounds Pt-1-5 were also studied *in silico* employing hybrid-DFT and TD-DFT methods implemented in the ORCA 5.0.1 ab initio, DFT, and semiempirical SCF-MO program package.^{198,199} To reduce computational cost, the *n*-butyl moieties of the benzimidazolylidene ligand of Pt-1-5 were replaced with methyl groups for all computations (full computational details outlined in supporting information). Qualitative photophysical characteristics were similar for all investigated complexes, and hence the computational findings are discussed exemplary for complex Pt-1. TD-DFT treatment of the optimized ground state geometry of Pt-1 implied states S_1 ($\lambda = 348 \text{ nm}$, $f = 1.49$), S_4 ($\lambda = 297 \text{ nm}$, $f = 0.36$), and S_8 ($\lambda = 273 \text{ nm}$, $f = 0.23$) to be the lowest energy excited states with relevant oscillator strengths f , which is in good agreement with our experimentally obtained absorption spectra (Figure 13 (a), Table 3).

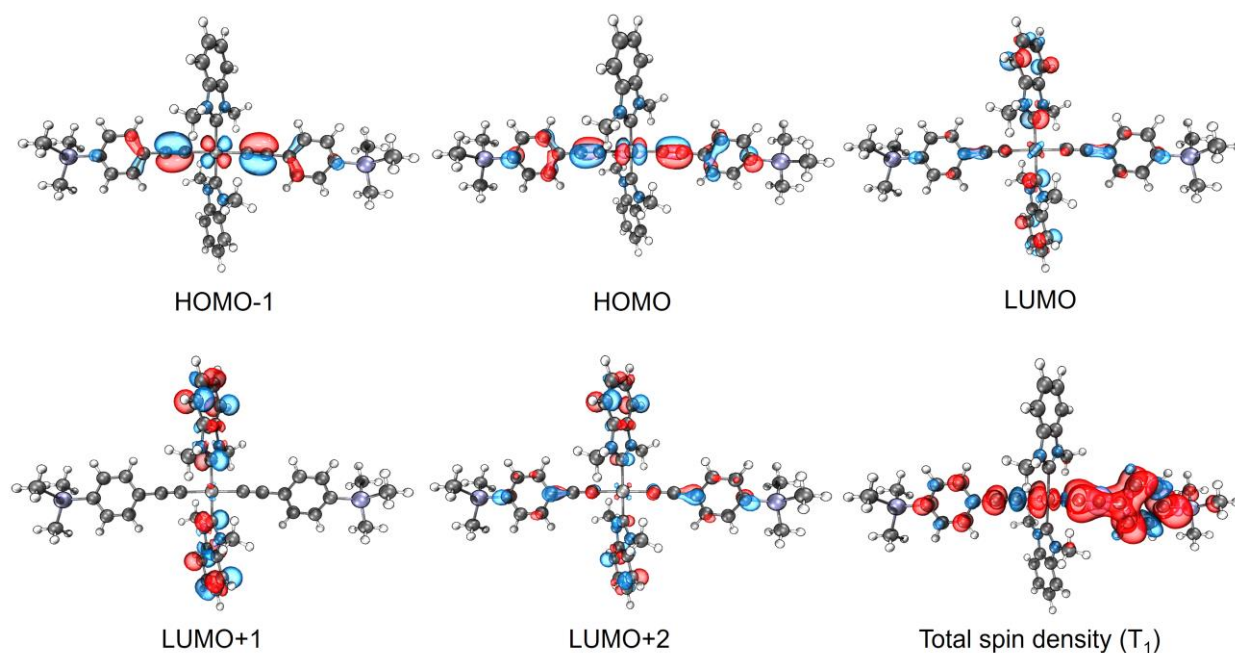


Figure 17: Orbital plots of molecular orbitals (Mos) involved in relevant lowest energy transitions of Pt-1.

While S_1 is computationally assigned to the highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (HOMO $\rightarrow$ LUMO) transition, S_4 is predicted to be dominated by the HOMO $\rightarrow$ LUMO+2 transition, and S_8 is dominated by the HOMO-1 $\rightarrow$ LUMO+1 transition. According to the obtained orbital plots, the HOMO is mostly localized at the alkyne ligands, with some Pt 5d contributions, while the π^* LUMO is mostly localized on the benzimidazolylidene ligands (Figure 17). Hence, the lowest energy transition can be described as being of ${}^1\text{LLCT}$ ($\pi_{\text{alkyne}} \rightarrow \pi^*_{\text{NHC}}$) and partially of ${}^1\text{MLCT}$ ($5d(\text{Pt}) \rightarrow \pi^*_{\text{NHC}}$) character. The LUMO+2, which is of π^* character, resides primarily on the carbene and alkyne ligands, which leads to a transition that is mostly comprised of ${}^1\text{LLCT}$ ($\pi_{\text{alkyne}} \rightarrow \pi^*_{\text{NHC}}$) and ${}^1\text{ILCT}$ ($\pi_{\text{alkyne}} \rightarrow \pi^*_{\text{alkyne}}$) character with somewhat weaker ${}^1\text{MLCT}$ ($5d(\text{Pt}) \rightarrow \pi^*_{\text{NHC/alkyne}}$) contributions. Lastly, for the S_8 excited state, the HOMO-1 appears to have a similar character to the HOMO, and the π^* LUMO+1 resides nearly exclusively on the benzimidazolylidene ligands, making the transition dominated by ${}^1\text{LLCT}$ ($\pi_{\text{alkyne}} \rightarrow \pi^*_{\text{NHC}}$) with ${}^1\text{MLCT}$ ($5d(\text{Pt}) \rightarrow \pi^*_{\text{NHC}}$) contributions. An assessment of the total spin-density of the T_1 geometry of compound Pt-1 characterizes the phosphorescence to be a ${}^3\text{ILCT}$ ($\pi^*_{\text{alkyne}} \rightarrow \pi_{\text{alkyne}}$) transition. Notably the spin-density plot extends to the TMS group of one of the alkyne ligands, which could be indicative of a possible electronic influence of the TMS group on the T_1 excited state.

Quantitative results of TD-DFT computations for complexes Pt-1-5 reveal subtle differences between *t*-butyl-substituted compounds Pt-3/4 and TMS-substituted compounds 1/2 (Table 3).

While the silyl-substituted compounds appear to leave the energy level of the HOMO unaffected, while slightly stabilizing the LUMO, the ^tbutyl-substituted compounds show the expected destabilizing effect on the HOMO, with simultaneous stabilization of the LUMO. The electronic differences arising from mono- *versus* di-substitution with either ^tbutyl or TMS appear to be minor. In comparison to the parent unsubstituted compound Pt-5 both ^tbutyl- and TMS-substitution result in a reduced singlet-triplet gap $\Delta E(S_1-T_1)$, and a bathochromic shift of the emission indicating stabilization of T_1 in relation to the S_0 ground state. However, spin-orbit corrected TD-DFT computations revealed an apparent greater interaction of T_1 with low energy singlet states S_n in the series of Pt-5 < Pt-3 < Pt-1. The computationally obtained data for absorption and emission of compounds Pt-1-5 are overall in good agreement with the experimentally obtained data.

Table 3: Quantitative TD-DFT data for compounds Pt-1-5 computed at the PBE0(D4)/SARC-ZORA-TZVP(ZORA-def2-TZVP)//PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP) level of theory. Bulk solvation was considered implicitly with the CPCM model for DCM.

	$(\lambda_{\text{abs}}, f)^{(a)}$	$\lambda_{\text{em}} / \text{nm}$	$\Delta E(S_1-T_1) / \text{eV}$	$E_{\text{HOMO}} / \text{eV}$	$E_{\text{LUMO}} / \text{eV}$	$\sum_{\text{absol., soc}}^{(b)} / \text{cm}^{-1}$
Pt-1	(348, 1.49) (297, 0.36) (273, 0.23)	457	0.70	-5.19	-1.09	3984.9
Pt-2	(348, 1.19) (299, 0.34) (274, 0.23)	456	0.68	-5.16	-1.06	-
Pt-3	(345, 1.17) (298, 0.55) (276, 0.19)	447	0.82	-5.06	-0.98	3231.8
Pt-4	(346, 1.02) (302, 0.47) (276, 0.16)	456	0.65	-5.05	-0.98	-
Pt-5	(340, 1.10) (294, 0.38) (273, 0.22)	444	0.86	-5.18	-1.03	2774.7

Absorption wavelength and oscillator strengths f for three lowest energy singlet excited states ($f > 0.05$).

^(b)Absolute vector sum of T_1-S_n matrix as obtained from SOC-TD-DFT computations at the level of theory indicated above.

The aggregation behavior of complexes **Pt-1-5** was modeled by computationally investigating homo-dimerization. Due to the substantial computational resources required for large, heavy-atom containing structures, a robust and accurate semiempirical method (GFN2^{83,200}) was utilized for obtaining thermochemical data. Conformational sampling of the monomeric and dimeric structures was conducted prior to computing thermochemical data, in order to obtain the dimerization free enthalpies ΔG_{dim} for the lowest energy conformers of all investigated species. $\Delta\Delta E_{\text{disp}}$, which indicates additional stabilization of dimeric structures due to LD interactions, was determined from LD contributions to the electronic energies as part of the output of GFN2^{83,200} computations. $\Delta\Delta E_{\text{disp}}$ is determined in reference to the parent complex **Pt-5**. Table 4 provides a summary of the thermochemical data. To gain further qualitative insight into possible non-covalent interactions (NCIs) in the dimer structures, NCI-plots^{54,55} were computed, which allow to visualize the regions in a geometry, where non-covalent interactions are at play (Figure 18).

Table 4: Dimerization free enthalpies ΔG_{dim} of compounds **Pt-1-5** computed at the GFN2^{83,200} level of theory. LD contributions to ΔG_{dim} relative to unsubstituted compound **Pt-5**.

	$\Delta G_{\text{dim}} / \text{kcal mol}^{-1}$	$\Delta\Delta E_{\text{disp}} / \text{kcal mol}^{-1}$
Pt-1	−1.29	−2.73
Pt-2	−9.30	−13.02
Pt-3	−0.96	+0.91
Pt-4	−4.24	−6.64
Pt-5	+1.27	-

The thermochemical computations reveal good qualitative agreement with experimental findings in PMMA thin films, regarding mono-substituted compounds **Pt-1** and **Pt-3** having a lower aggregation tendency in comparison to di-substituted compounds **Pt-2** and **Pt-4**, which results in reduced aggregation induced triplet quenching, and thereby higher experimental quantum yields of the former at high doping concentrations (Table 2, Table 4). Remarkably, $\Delta\Delta E_{\text{disp}}$ of **Pt-3** is found to be positive in sign, which implies a significantly altered aggregation pattern for mono-substituted complexes **Pt-1** and **Pt-3**. Although complexes **Pt-5** and **Pt-3** are predicted to

favor aggregation the least, they were outperformed experimentally by Pt-1 with respect to quantum yields, which could be indicative of additional electronic effects of silyl groups (Table 3, Table 4).

Structurally, the most significant differences can be seen between the unsubstituted parent compound Pt-5, mono-substituted complexes Pt-1/3, and di-substituted complexes Pt-2/4. For Pt-1 and Pt-3 a significantly increased interplanar distance of the phenylacetylide ligands is found in comparison to the unsubstituted complex (on average 5.1 Å for Pt-5 and 6.2 Å for Pt-1). As the phosphorescence of the complexes is predicted to proceed *via* a $^3\text{ILCT}$ transition on the alkyne ligands, the latter finding could be relevant with respect to reduced bimolecular triplet quenching. Although di-substituted compounds displayed a similarly increased interplanar distance (e.g., 6.2 Å for Pt-2), the di-substitution also led to a more parallel-stacking of the phenyl rings.

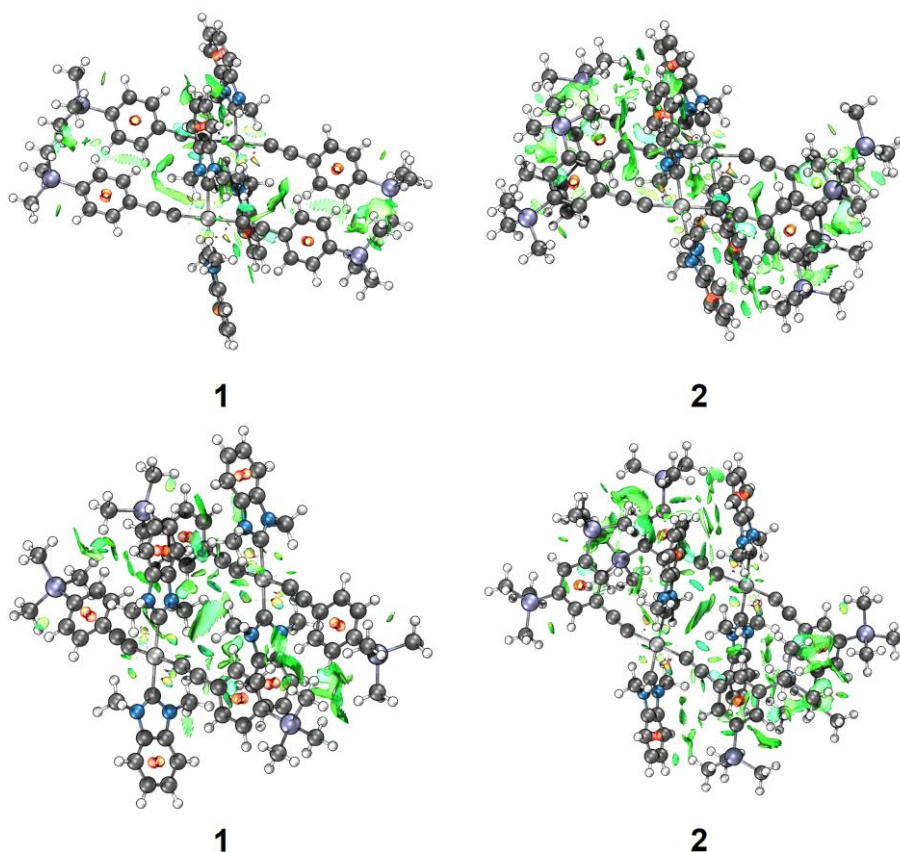


Figure 18: Intermolecular NCI-plots^{54,55} of compounds Pt-1 and Pt-2. Isosurfaces colored red represent repulsive interactions, green isosurfaces represent weak NCIs (LD interactions), and blue isosurfaces represent strong attractive interactions. Isovalue s of 0.3, in the range of $\text{sign}(\lambda_2)\rho = -0.05$ to $+0.05$ [a.u.]. Geometries computed at the GFN2^{83,200} level of theory.

Furthermore, as can be seen in the NCI-plot^{54,55} of the homo-dimers of Pt-1 and Pt-2 (Figure 18), di-substituted complexes display greater non-covalent contact areas than the mono-substituted complexes, which can overcompensate beneficial structural effects due to an increased aggregation tendency of the former.

2.7.2.5 Electrochemistry of Platinum complexes

Cyclic voltammetry (CV) was carried out to investigate the electrochemical properties of compounds Pt-1-5. DCM was chosen as the solvent with NBu₄PF₆ in 0.1 M concentration as the supporting electrolyte. The half wave potential of oxidation ($E_{\text{ox}}/2$) and reduction potential (E_{red}) were referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple, which functioned as an internal standard to estimate the HOMO levels. LUMO levels were not estimated, as the observed irreversible reduction likely corresponded to a decomposition process, and the expected reduction potentials were outside of the solvent/electrolyte window for cyclic voltammetry (Table 3; Figure 19, left).

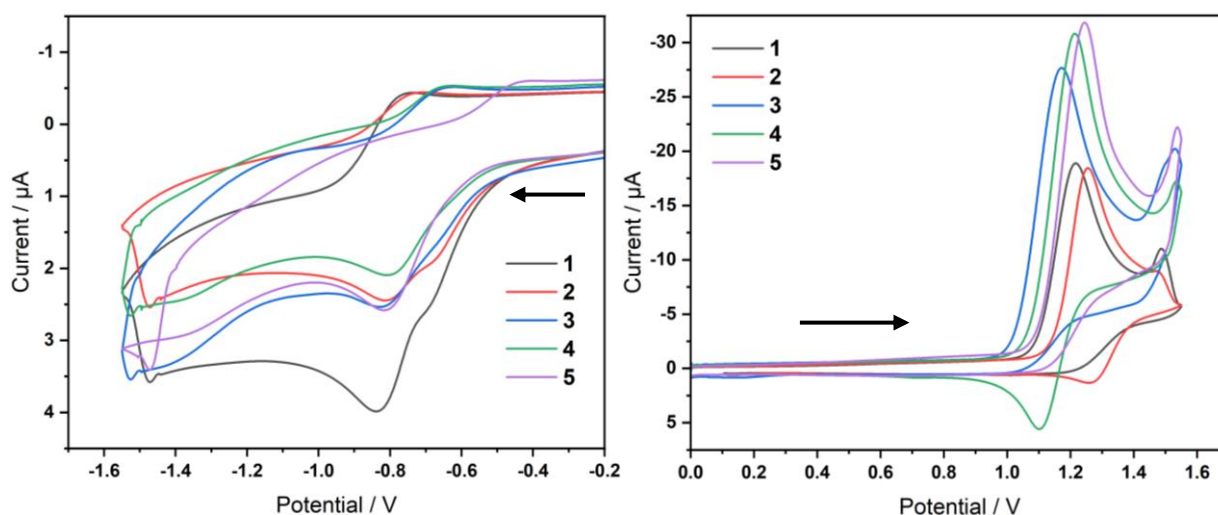


Figure 19: Cyclic voltammograms of reduction (left) and oxidation (right) of compounds Pt-1-5 in DCM with 0.1 M NBu₄PF₆ as supporting electrolyte. Measurements conducted at 298 K.

All complexes displayed irreversible oxidation in the 1.2 V potential region, likely corresponding to oxidation of the phenylacetylide ligands (Figure 19, right). For the di-substituted Pt-2 and Pt-4 complexes, some reversibility of the oxidation process could be observed, which might be related to the increased electron density of the ligands in comparison to the mono- or unsubstituted complexes. Overall, the estimates of the HOMO levels agree well with the computationally determined values (Table 3, Table 5).

Table 5: Half peak potential of oxidation ($E_{ox/2}$) and reduction potential (E_{red}) measured in DCM with 0.1 M Nbu₄PF₆ at room temperature (298K) and referenced against the ferrocene/ferrocenium (F_c/F_c^+) couple, as well as estimated HOMO energies (E_{HOMO}) of complexes Pt-1-5.

	E_{red} / V	E_{ox} / V	$E_{ox/2} / V$	E_{HOMO} / eV
1	−0.84	1.22	1.15	−5.34
2	−0.81	1.26	1.20	−5.37
3	−0.83	1.17	1.09	−5.28
4	−0.80	1.21	1.14	−5.33
5	−0.81	1.24	1.17	−5.36

^(a) $E_{HOMO} = -4.78 + (E_{ox/2}(F_c) - E_{ox/2})$.

2.7.3 Conclusion & Outlook

A set of five *trans*-Pt(II)-NHC phenylacetylides Pt-1-5 carrying either no additional moiety, or bulky ^tbutyl/TMS groups in two different substitution patterns were prepared. In this way, the effect TMS groups (in particular) have on aggregation and the photophysical properties of *trans*-Pt(II)-NHC phenylacetylides should be investigated. Our aim was to optimize *trans*-Pt(II)-NHC phenylacetylides with future applications in phosphorescent and hyperfluorescent OLED devices in mind.

Our experimentally obtained data suggests silyl groups to exhibit both a significant electronic effect, as well as affect the aggregation behavior of the *trans*-Pt(II)-NHC phenylacetylide system. In solution, compounds Pt-1-5 show a similar absorption and photoluminescence behavior, with a significant red-shift of the emission, for the silyl-substituted derivatives Pt-1/2. This indicates a stabilizing effect of the TMS groups on the T₁ state in relation to the electronic ground state. In PMMA thin films, we found the mono-silyl-substituted complex Pt-1 to give the highest PLQYs of ~71% at a high doping concentration of 10 wt%, with a low drop-off in comparison to the 1 wt% thin film of ~5%. Counterintuitively, much bulkier di-substituted complexes Pt-2 and Pt-4 gave the lowest PLQYs, which indicates a significant influence of LD interactions on the aggregation processes of the investigated *trans*-Pt(II)-NHC phenylacetylides.

The introduction of TMS groups came at the cost of somewhat higher triplet excited state lifetimes, in comparison to the ^tbutyl compounds Pt-3/4, and the parent compound Pt-5, which should however be negligible for hyperfluorescent applications.

We found complex Pt-1 to function as a phosphorescent sensitizer in hyperfluorescent thin films with a fluorescent (TBPDP) and MR-TADF (DABNA-NP-tb) emitter. The experimentally obtained photophysical data implies good exciton transfer in both cases, making Pt-1 an attractive candidate for future application in either a sky-blue hyperfluorescent OLED device (TBPDP), or deep-blue hyperfluorescent device (DABNA-NP-tb).

Computational analyses on the photophysical and aggregational behavior of complexes Pt-1-5, obtained *via* (TD-)DFT and semi-empirical methods, agree well with our experimental observations. Although standard TD-DFT treatment of the complexes did not reveal striking differences between the complexes, aside from a reduced singlet-triplet energy gap for Pt-1-4 in comparison to Pt-5, spin-orbit corrected computations suggest a greater interaction of T₁ with singlet states for compound Pt-1.²⁰¹ Computations on homo-dimerization of complexes Pt-1-5 showed a similar trend to the experimental PLQY data in thin films, with the bulkiest complexes Pt-2 and Pt-4 displaying the most exergonic dimerization process, and hence favoring aggregation the most. Structurally, mono-TMS- or mono-^tbutyl-substitution is predicted to lead to a greater interplanar distance between phenyl rings and should induce a slipped stacking motif. The latter possibly leads to reduced triplet-triplet annihilation in the solid state. Overall, we find computational assessment of aggregation processes utilizing a robust low-cost semiempirical treatment to be highly useful for predicting possible changes in aggregation patterns/behavior.

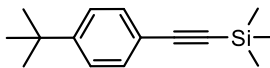
Our results indicate that in particular silyl-DEDs may hold significant potential, for not only inducing a beneficial change in the aggregation behavior of luminescent molecules, but also exerting an additional electronic effect, possibly enhancing T₁-S_n interactions. In this regard, MR-TADF emitters substituted with silyl-DEDs could be particularly attractive target systems. On one hand, due to their usually flat geometry, the photophysical properties of MR-TADF emitters are often strongly affected by aggregation. Furthermore, the unique ISC/rISC emission mechanism of MR-TADF emitters offers an opportunity to gain further insights into the electronic effect exerted by silyl-DEDs.^{179,180}

2.7.4. Supporting Information

2.7.4.1 Synthesis and characterization

Reactions were performed under an atmosphere of either nitrogen or argon using standard Schlenk techniques, unless stated otherwise. Anhydrous solvents were either obtained commercially from Sigma Aldrich or obtained by drying over microwave activated molecular sieves. Reaction progress was monitored by silica thin-layer chromatography (TLC) analysis (Merck Silica Gel 60G F₂₅₄ slides). TLC plates were visualized either *via* UV light, or by developing the plates with KMnO₄ stain (1% aqueous solution basified with K₂CO₃). Purification of crude products was carried out by flash column chromatography using P60 silica gel (40-63 μ m irregular particles). Compounds were characterized *via* ¹H- and ¹³C-NMR (Bruker Avance III HD 400 MHz), high resolution mass spectrometry (Bruker micrOTOF), and/or elemental analysis (Vario MICRO cube elemental analyzer). NMR Chemical shifts are reported in ppm relative to tetramethylsilane with solvent residual peaks used as internal standards for ¹H- and ¹³C-NMR experiments. Coupling constants *J* are reported in Hertz (Hz), with the following abbreviations for multiplicities: s (singlet), m (multiplet), d (doublet), t (triplet), q (quartet), qu (quintet), sx (sextet), dt (doublet of triplets). 1-Bromo-3,5-di-^tbutylbenzene, 1-bromo-4-^tbutylbenzene, 1-bromo-4-(trimethylsilyl)benzene, and phenylacetylene **a** were obtained commercially (Sigma Aldrich, TCI Europe). 1-Bromo-3,5-di-(trimethylsilyl)-benzene, TBPDP, and DABNA-NP-tb were prepared according to literature procedures.^{183–185,194,195} TMS-protected phenylacetylenes were prepared according to a modified literature procedure (see below).¹⁹⁶ Deprotection was carried out according to a literature procedure and the obtained crude products were used in subsequent synthesis steps without further purification.¹⁹⁶ 1,3-dibutylbenzimidazolium iodide and bis(*N,N*-dibutylbenzimidazol-2-ylidene)platinum(II) dichloride were prepared according to literature procedures.¹⁷³ Preparation of the final Pt(II) complexes was carried out utilizing a modified literature procedure described below.¹⁷³

Preparation of 1-(^tbutyl)-4-[2-(trimethylsilyl)ethynyl]benzene/General procedure for TMS-protected phenylacetylenes¹⁹⁶

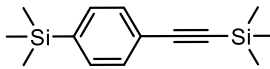

 Pd(PPh₃)₂Cl₂ (0.60 g, 0.85 mmol), CuI (0.32 g, 1.69 mmol), and PPh₃ (0.45 g, 1.72 mmol) were added to a Schlenk tube. Subsequently, TMS-acetylene (12 mL, 84.30 mmol), 1-bromo-4-^tbutylbenzene (3.60 g, 16.89 mmol), anhydrous THF (17 mL), and triethylamine (17 mL) were added, and the resulting mixture was heated to 70 °C for 16 h. Afterwards, the reaction mixture was allowed to reach room temperature and filtered through a pad of celite (eluent: *n*-hexane). The solvent was removed under reduced pressure and the crude residue was purified by silica gel flash column chromatography (eluent: *n*-hexane). The product was obtained as a yellow oil (2.85 g, 12.37 mmol, 73%).

¹H-NMR (400 MHz, CDCl₃): δ 7.40 (dt, *J* = 8.8 Hz, 2.2 Hz, 2H, Ar-H), 7.31 (dt, *J* = 8.8 Hz, 2.3 Hz, 2H, Ar-H), 1.30 (s, 9H, -^tBu), 0.24 (s, 9H, -SiMe₃);

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.9, 131.8, 125.3, 120.3, 105.5, 93.4, 34.9, 31.3, 0.2;

HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd. For C₁₅H₂₂Si 231.1569; found 231.1568.

Preparation of 1-(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]benzene

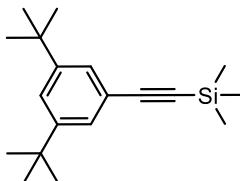

 1-(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]benzene was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 2.73 g (11.92 mmol) of 1-bromo-4-(trimethylsilyl)benzene. The product was obtained as a yellow oil (2.68 g, 10.89 mmol, 91%).

¹H-NMR (400 MHz, CDCl₃): δ 7.46-7.40 (m, 4H, Ar-H), 0.26 (s, 9H, -SiMe₃), 0.25 (s, 9H, -SiMe₃);

¹³C{¹H} NMR (100 MHz, CDCl₃): δ 141.5, 133.2, 131.1, 123.5, 105.4, 94.6, 0.14, -1.11;

HRMS (ESI-TOF) *m/z*: [M+H]⁺ calcd. For C₁₄H₂₂Si₂ 247.1338; found 247.1341.

Preparation of 1,3-Bis(1,1-dimethylethyl)-5-[2-(trimethylsilyl)ethynyl]benzene


 1,3-Bis(1,1-dimethylethyl)-5-[2-(trimethylsilyl)ethynyl]benzene was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 4.12 g (15.31 mmol) of 1-bromo-3,5-di-^tbutylbenzene. The product was obtained as an off-white solid (3.35 g,

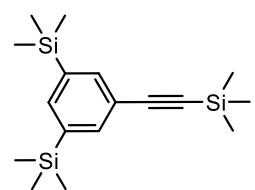
11.70 mmol, 76%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.38 (t, $J = 2.0$ Hz, 1H, Ar-H), 7.31 (d, $J = 2.4$ Hz, 2H, Ar-H), 1.31 (s, 18H, ^tBu), 0.26 (s, 9H, $-\text{SiMe}_3$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 150.8, 126.4, 123.1, 122.2, 106.6, 92.6, 34.9, 31.5, 0.24;

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{19}\text{H}_{30}\text{Si}$ 287.2195; found 287.2192.

Preparation of 1,3-Bis(trimethylsilyl)-5-[2-(trimethylsilyl)ethynyl]benzene

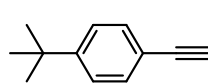
 1,3-Bis(trimethylsilyl)-5-[2-(trimethylsilyl)ethynyl]benzene was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 1.35 g (4.49 mmol) of 1-bromo-3,5-di(trimethylsilyl)-benzene. The product was obtained as an off-white solid (1.18 g, 3.70 mmol, 82%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 7.60 (d, $J = 1.2$ Hz, 2H, Ar-H), 7.57 (t, $J = 1.2$ Hz, 1H, Ar-H), 0.27 (s, 27H, $-\text{SiMe}_3$);

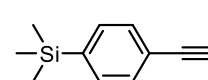
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 139.6, 137.9, 137.4, 122.0, 106.1, 94.0, 0.2, -1.0;

HRMS (ESI-TOF) m/z : $[\text{M}+\text{H}]^+$ calcd. For $\text{C}_{17}\text{H}_{30}\text{Si}_3$ 319.1733; found 319.1730.

Preparation of 1-(t butyl)-4-ethynyl-benzene/General procedure for phenylacetylenes¹⁹⁶

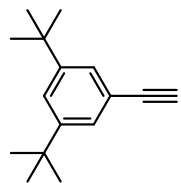
 1-(t butyl)-4-[2-(trimethylsilyl)ethynyl]benzene (0.82 g, 3.54 mmol) was dissolved in MeOH (32 mL) and potassium carbonate (2.00 g, 14.49 mmol) was subsequently added. The reaction mixture was stirred at room temperature for 7 h. After 7 h the reaction mixture was added to a separatory funnel containing 50 mL of water and 50 mL *n*-hexane. The aqueous phase was extracted another two times with 50 mL of *n*-hexane. The combined organic phases were dried over MgSO_4 and concentrated under reduced pressure, to yield a yellow oil (0.48 g, 3.01 mmol, 85%) which solidified upon cooling to -20°C . The crude product was used without further purification in subsequent synthesis steps.

Preparation of 1-(trimethylsilyl)-4-ethynyl-benzene

 1-(trimethylsilyl)-4-ethynyl-benzene was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 0.82 g

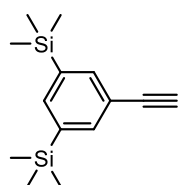
(3.34 mmol) of 1-(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]benzene. The product was obtained as a faintly yellow oil which solidified upon cooling to $-20\text{ }^{\circ}\text{C}$ (0.45 g, 2.60 mmol, 78%). The crude product was used without further purification in subsequent synthesis steps.

Preparation of 1,3-Bis(1,1-dimethylethyl)-5-ethynyl-benzene



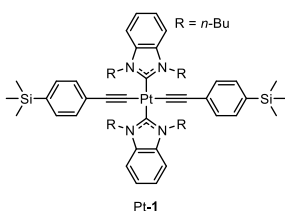
1,3-Bis(1,1-dimethylethyl)-5-ethynyl-benzene was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 0.81 g (2.82 mmol) of 1,3-Bis(1,1-dimethylethyl)-5-[2-(trimethylsilyl)ethynyl]benzene. The product was obtained as a yellow oil which solidified upon cooling to $-20\text{ }^{\circ}\text{C}$ (0.47 g, 2.22 mmol, 77%). The crude product was used without further purification in subsequent synthesis steps.

Preparation of 1,3-Bis(trimethylsilyl)-5-ethynyl-benzene



1,3-Bis(trimethylsilyl)-5-[2-(trimethylsilyl)ethynyl]benzene was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 0.82 g (2.56 mmol) of 1,3-Bis(trimethylsilyl)-5-[2-(trimethylsilyl)ethynyl]benzene. The product was obtained as a yellow oil which solidified upon cooling to $-20\text{ }^{\circ}\text{C}$ (0.52 g, 2.09 mmol, 81%). The crude product was used without further purification in subsequent synthesis steps.

Preparation of Pt-1/General procedure for *trans*-Pt(II)-NHC phenylacetylides¹⁷³



Bis(*N,N*-dibutylbenzimidazol-2-ylidene)platinum(II) dichloride (0.15 g, 0.21 mmol) was dissolved in a mixture of DCM (20 mL) and HNEt_2 (10 mL) and the solution was purged with Argon for 20 min. 0.17 g (0.95 mmol) 1-(trimethylsilyl)-4-ethynylbenzene (de-protected phenylacetylene), followed by 4.1 mg (0.02 mmol) of CuI were subsequently added and the

solution was heated to $45\text{ }^{\circ}\text{C}$ for 24 h under the exclusion of light. Afterwards another 10 mol% of CuI were added, and the reaction mixture was stirred for 24 h at $45\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to reach room temperature. A solid had formed and the mixture was transferred to a separatory funnel containing 50 mL of DCM and 30 mL of water. The organic phase was washed three times with 30 mL of water and afterwards dried over anhydrous Na_2SO_4 . After filtration the organic phase was concentrated under reduced pressure to yield an orange solid, which was washed with cold methanol (3 x 5 mL) and *n*-hexane (3 x 5 mL). The thus obtained colorless

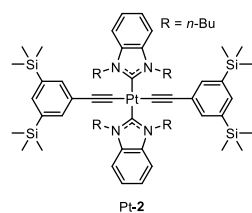
solid was further purified *via* silica flash column chromatography utilizing a 2/1 mixture of *n*-hexane/DCM as the eluent. Pt-1 was obtained as a colorless solid 0.12 g (0.12 mmol, 56%).

^1H -NMR (400 MHz, CD_2Cl_2): δ 7.50-7.44 (m, 4H, Ar-H), 7.32-7.26 (m, 4H, Ar-H), 7.18 (d, J = 8.0 Hz, 4H, Ar-H), 6.97 (d, J = 8.4 Hz 4H, Ar-H), 4.84 (t, J = 8.0 Hz 8H, $-\text{CH}_2-$), 2.24 (qu, J = 7.8 Hz 8H, $-\text{CH}_2-$), 1.58 (sx, J = 7.6 Hz 8H, $-\text{CH}_2-$), 1.02 (t, J = 7.4 Hz 12H, $-\text{CH}_3$), 0.15 (s, 18H, $-\text{SiMe}_3$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 181.8, 136.1, 135.0, 133.0, 130.0, 122.6, 110.8, 107.3, 106.4, 48.5, 31.9, 21.0, 14.3, -1.1;

Elemental analysis calcd (%) for $\text{C}_{52}\text{H}_{70}\text{N}_4\text{PtSi}_2$: C, 62.31; H, 7.04; N, 5.59; found: C, 61.85; H, 7.09; N, 5.41.

Preparation of Pt-2



Pt-2 was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 0.24 g (0.96 mmol) of 1,3-bis(trimethylsilyl)-5-ethynylbenzene. Purification *via* silica flash column chromatography utilizing a 3/1 mixture of *n*-hexane/DCM as the eluent.

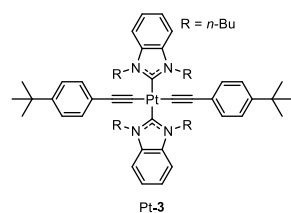
Pt-2 was obtained as a colorless solid 0.11 g (0.10 mmol, 44%).

^1H -NMR (400 MHz, CD_2Cl_2): δ 7.50-7.44 (m, 4H, Ar-H), 7.32-7.26 (m, 4H, Ar-H), 7.24 (t, J = 1.2 Hz, 2H, Ar-H), 7.16 (d, J = 1.2 Hz 4H, Ar-H), 4.85 (t, J = 7.6 Hz 8H, $-\text{CH}_2-$), 2.34-2.21 (m, 8H, $-\text{CH}_2-$), 1.60 (sx, J = 8 Hz 8H, $-\text{CH}_2-$), 1.04 (t, J = 8.0 Hz 12H, $-\text{CH}_3$), 0.14 (s, 36H, $-\text{SiMe}_3$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 181.9, 138.7, 136.5, 135.0, 134.1, 128.2, 122.6, 110.8, 106.7, 106.1, 48.6, 31.9, 21.1, 14.4, -1.1;

Elemental analysis calcd (%) for $\text{C}_{58}\text{H}_{86}\text{N}_4\text{PtSi}_4$: C, 60.75; H, 7.56; N, 4.89; found: C, 60.54; H, 7.68; N, 4.80.

Preparation of Pt-3



Pt-3 was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 0.15 g (0.93 mmol) of 1-(4-tert-butyl)-4-ethynylbenzene. Purification *via* silica flash column chromatography utilizing a 2.5/1 mixture of *n*-hexane/DCM as the

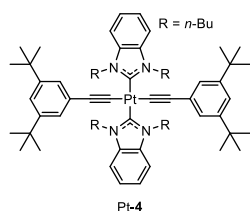
eluent. Pt-3 was obtained as a colorless solid 0.10 g (0.10 mmol, 48%).

$^1\text{H-NMR}$ (400 MHz, CD_2Cl_2): δ 7.41-7.35 (m, 4H, Ar-H), 7.23-7.17 (m, 4H, Ar-H), 6.96 (dt, $J = 8.4$ Hz, 2.4 Hz, 4H, Ar-H), 6.83 (dt, $J = 8.4$ Hz, 2.4 Hz, 4H, Ar-H), 4.75 (t, $J = 8$ Hz 8H, $-\text{CH}_2-$), 2.20-2.11 (m, 8H, $-\text{CH}_2-$), 1.50 (sx, $J = 7.6$ Hz 8H, $-\text{CH}_2-$), 1.10 (s, 18H, $-\text{tBu}$), 0.93 (t, $J = 7.2$ Hz 12H, $-\text{CH}_3$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 182.1, 147.6, 135.0, 130.7, 126.6, 122.8, 122.6, 110.8, 105.8, 104.9, 48.5, 34.6, 31.9, 31.3, 21.0, 14.3;

Elemental analysis calcd (%) for $\text{C}_{54}\text{H}_{70}\text{N}_4\text{Pt}$: C, 66.85; H, 7.27; N, 5.77; found: C, 66.14; H, 7.22; N, 5.62.

Preparation of Pt-4



Pt-4 was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 0.20 g (0.92 mmol) of 1,3-bis(1,1-dimethylethyl)-5-ethynylbenzene. Purification *via* silica flash column chromatography utilizing a 2.5/1 mixture of *n*-hexane/DCM as the eluent.

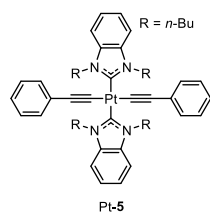
Pt-4 was obtained as a colorless solid 0.09 g (0.09 mmol, 41%).

$^1\text{H-NMR}$ (400 MHz, CD_2Cl_2): δ 7.50-7.43 (m, 4H, Ar-H), 7.32-7.25 (m, 4H, Ar-H), 7.03 (t, $J = 1.6$ Hz, 2H, Ar-H), 6.85 (d, $J = 2.0$ Hz, 4H, Ar-H), 4.86 (t, $J = 8.0$ Hz, 8H, $-\text{CH}_2-$), 2.33-2.22 (m, 8H, $-\text{CH}_2-$), 1.61 (sx, $J = 8.4$ Hz, 8H, $-\text{CH}_2-$), 1.17 (s, 36H, $-\text{tBu}$), 1.05 (t, $J = 7.2$ Hz, 12H, $-\text{CH}_3$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 182.1, 150.2, 135.0, 128.6, 125.3, 122.6, 119.2, 110.8, 107.1, 104.2, 48.6, 34.8, 31.9, 31.4, 21.1, 14.4;

Elemental analysis calcd (%) for $\text{C}_{62}\text{H}_{86}\text{N}_4\text{Pt}$: C, 68.79; H, 8.01; N, 5.18; found: C, 68.89; H, 8.20; N, 5.04.

Preparation of Pt-5



Pt-5 was prepared according to the general procedure outlined above with reagent and solvent amounts adjusted for 0.09 g (0.91 mmol) of phenylacetylene. Purification *via* silica flash column chromatography utilizing a 1.5/1 mixture of *n*-hexane/DCM as the eluent. Pt-5 was obtained as a

colorless solid 0.09 g (0.11 mmol, 53%).

^1H -NMR (400 MHz, CD_2Cl_2): δ 7.50-7.44 (m, 4H, Ar-H), 7.32-7.26 (m, 4H, Ar-H), 7.06-6.92 (m, 10H, Ar-H), 4.85 (t, J = 8 Hz, 8H, $-\text{CH}_2-$), 2.31-2.19 (m, 8H, $-\text{CH}_2-$), 1.59 (sx, J = 7.6 Hz, 8H, $-\text{CH}_2-$), 1.01 (t, J = 7.6 Hz, 12H, $-\text{CH}_3$);

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2): δ 181.9, 135.0, 131.2, 129.6, 128.0, 124.6, 122.7, 110.8, 106.2, 106.1, 48.5, 31.9, 21.0, 14.3;

Elemental analysis calcd (%) for $\text{C}_{46}\text{H}_{54}\text{N}_4\text{Pt}$: C, 64.39; H, 6.34; N, 6.53; found: C, 64.25; H, 6.22; N, 6.46.

2.7.4.2 UV/Visible and photoluminescence studies

UV/Visible absorbance spectra were measured with a PerkinElmer Lambda 19 UV-Vis spectrophotometer, while emission and excitation measurements were performed with an Edinburgh Instruments FLS980 spectrophotometer. The FLS980 used had a MCP-PMT temperature-controlled detector, single and double grating monochromators, and was used either in conjunction with a 450W Xenon arc lamp, or for lifetime measurements with a microsecond flashlamp ($\mu\text{F}2$, 100 Hz), an Edinburgh Instruments EPL series picosecond pulsed diode laser (λ = 371.8 nm, typical pulse width = 58.8 ps), or an Edinburgh Instruments picosecond pulsed LED (λ = 301 nm, typical pulse width = 790 ps). Absolute quantum yields were measured using an integrating sphere by Edinburgh Instruments. Quartz glass cuvettes with a rubber septum and screw cap were used for all solution measurements. Samples measured in solution were typically adjusted to have an optical density (OD) of 0.1 and were deoxygenated with nitrogen before measurement. CIE-1931 chromaticity diagrams were from normalized emission spectra in OriginLab. Thin film samples were prepared using quartz glass slides (10×10×1 mm). A Zehntner ZUA 2000 blade coater set to 200 μm was used to prepare the thin films from a solution of PMMA (average M_w ~15,000 by GPC, powder; Sigma Aldrich), the respective Pt(II) complexes Pt-1-5, and/or TBPDP and DABNA-NP-tb as co-dopants in spectroscopic grade DCM (Sigma Aldrich), which was also utilized for all solution measurements. Details on the amount of each compound, PMMA and volume of DCM for preparation of each of the thin films studied herein is summarized in the table below.

Substances	m / mg	V / mL	c
Pt complex	0.50	2.20	1 wt%
PMMA	49.50		
DCM			
Pt complex	1.25	1.10	5 wt%
PMMA	23.75		
DCM			
Pt complex	1.13	0.50	10 wt%
PMMA	10.23		
DCM			
Pt complex	1.54	0.76	10 wt%
Co-dopant (e.g., TBPDP)	0.46		3 wt%
PMMA	15.40		
DCM			

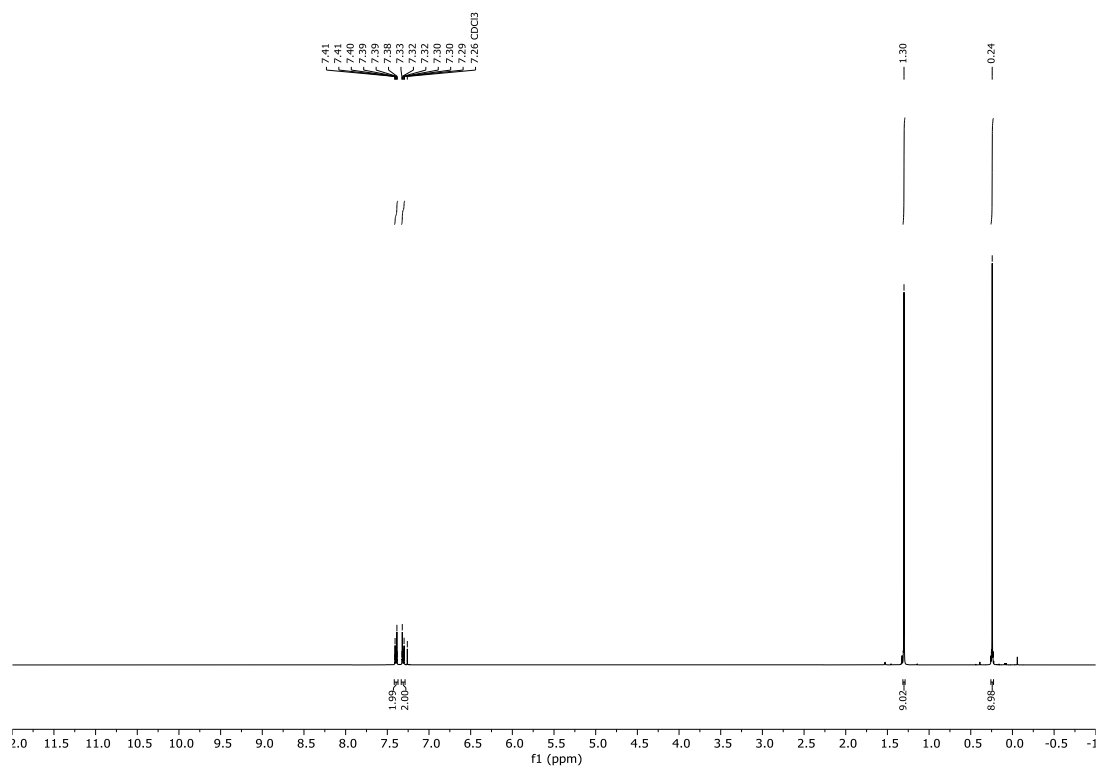
2.7.4.3 Computational details

For all DFT and TD-DFT computations, the ORCA 5.0.1 ab initio, DFT, and semiempirical SCF-MO program package was used.^{198,199} For geometry optimizations of monomeric structures, the PBE0²⁰² hybrid functional was utilized in conjunction with Grimme's D4 atom-pairwise dispersion correction,^{22,23,203} the relativistic SARC-ZORA-SVP basis set for Pt,^{204–210} with the ZORA-def2-SVP^{210,211} applied to remaining atoms. The absence of imaginary frequencies in vibrational frequency computations at the same level of theory confirmed the obtained geometries as minima on the respective potential energy surface. For each complex Pt-1-5 geometry optimizations of the S_0 ground state and the lowest energy triplet state T_1 were carried out. Additionally, TD-DFT data, electronic energies, molecular orbitals, and spin-densities were obtained from singlepoint PBE0(D4)/SARC-ZORA-TZVP(ZORA-def2-TZVP) computations at the double- ζ geometries. In order to account for solvation effects the CPCM²¹² model for DCM was applied.

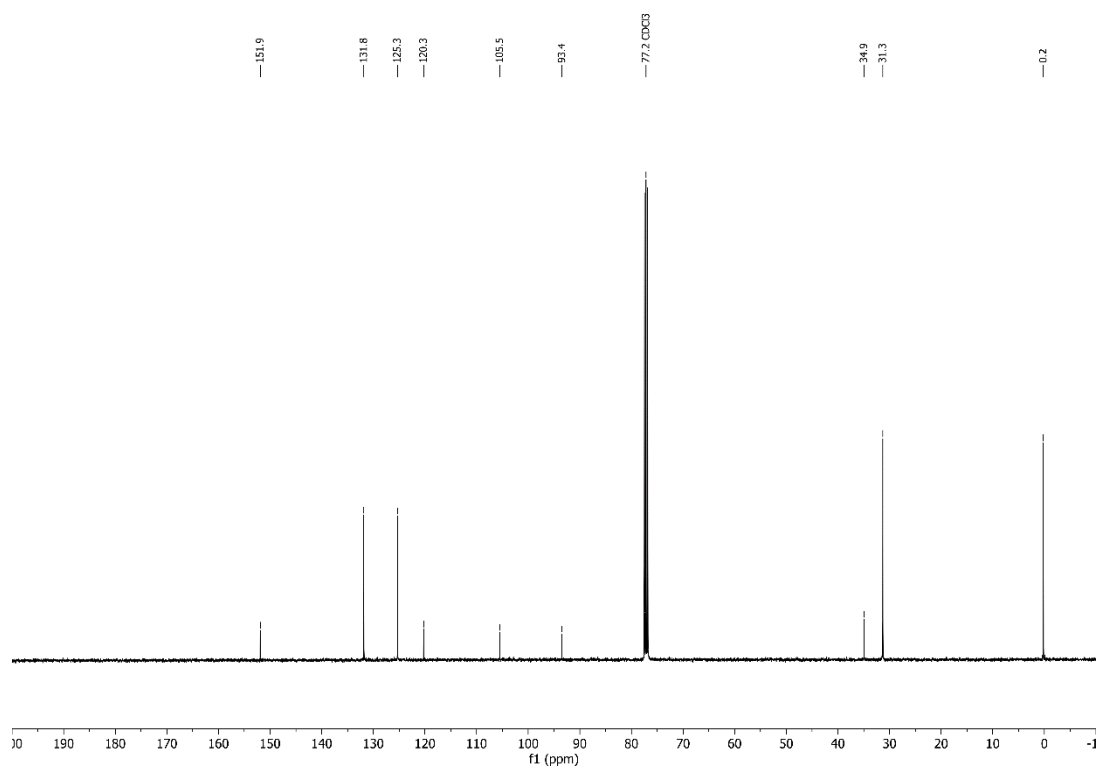
In order to study the aggregation behavior of Pt-1-5, the monomer dimer conformational space of each complex was sampled at the GFN2²⁰⁰ level of theory utilizing the Conformer-Rotamer Ensemble Sampling Tool (CREST, ver. 2.11.2) developed by Grimme and co-workers.⁸³ The resulting lowest energy conformers were re-optimized at the GFN2 level of theory to obtain thermochemical corrections, and thereby ΔG_{dim} , as well as estimates for London dispersion contributions. Non-covalent interactions in dimeric structures (GFN2 level of theory) were visualized as reduced density gradients in low electron density regions (NCI-plot^{54,55}). NCI-Plots were generated with the NCIPLOT program package and VMD.^{54,55,213} The reduced density

gradient cut-off was set at $\rho(r) = -0.2$ a.u. to $+0.2$ a.u., with a (-2 a.u. to $+2$ a.u.) color scale range, which results in red isosurfaces indicating strong repulsion, green isosurfaces corresponding to weak non-covalent interactions (LD interactions, and blue isosurfaces representing strongly attractive interactions (hydrogen bonds, etc.).

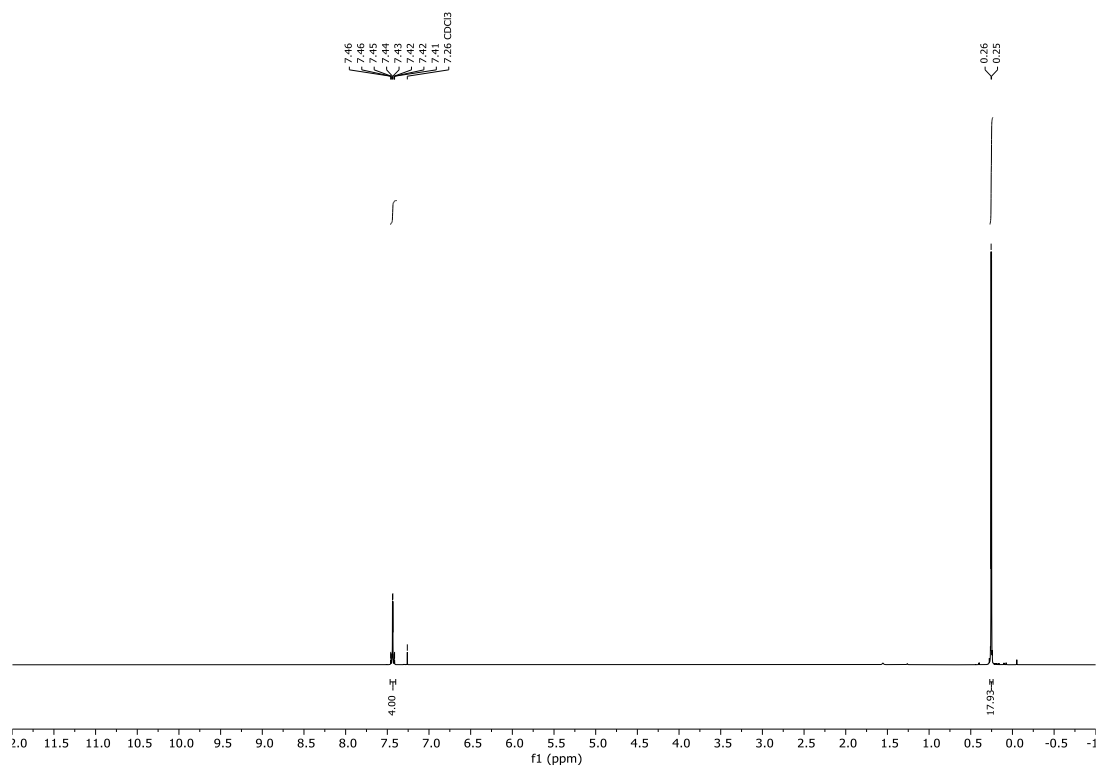
2.7.4.4 NMR data



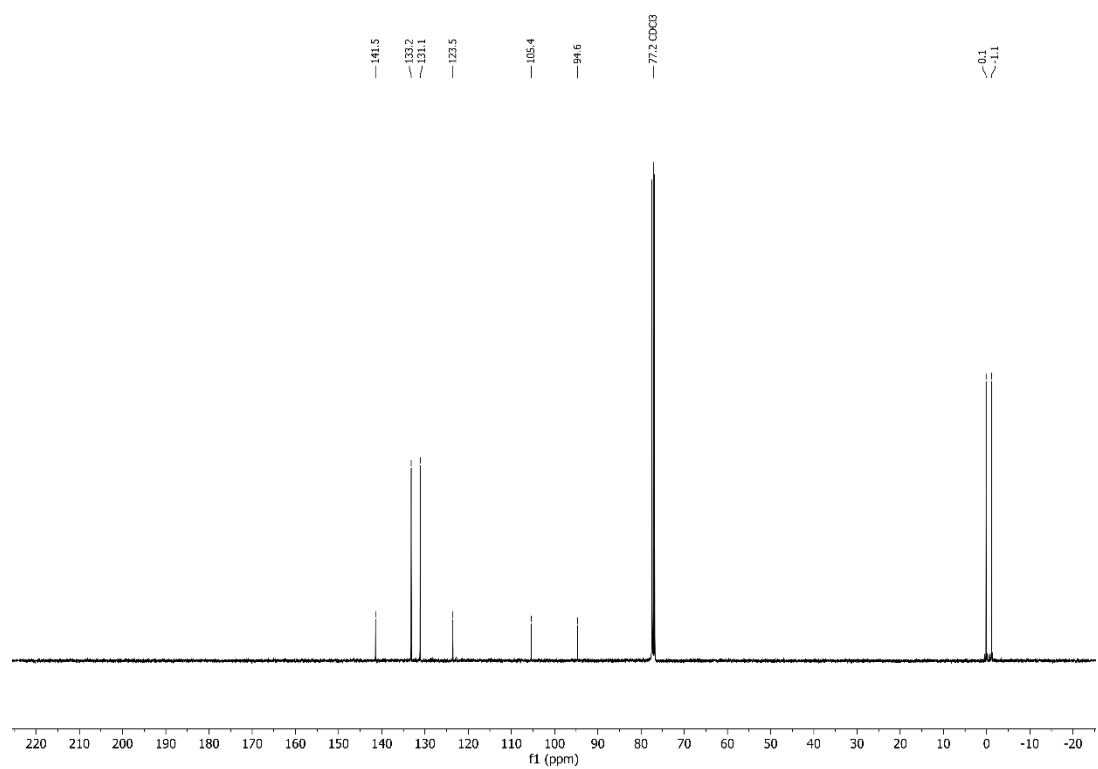
¹H-NMR (400 MHz, CDCl₃): 1-(^tbutyl)-4-[2-(trimethylsilyl)ethynyl]benzene.



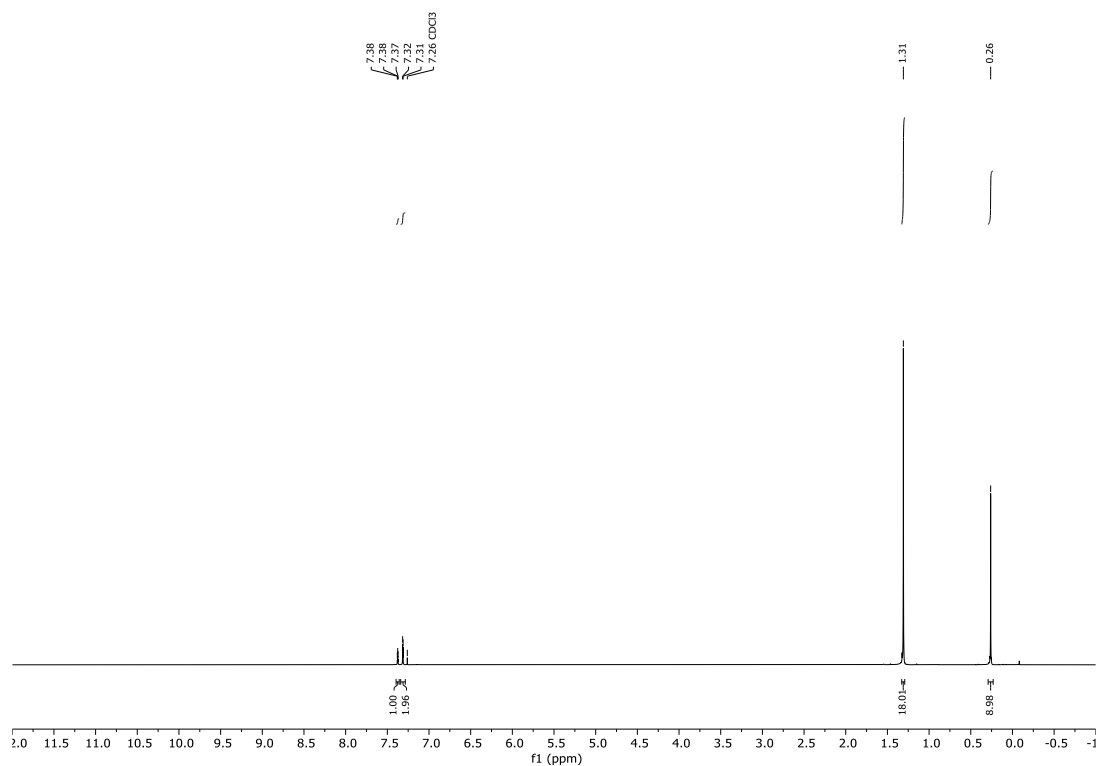
¹³C{¹H} NMR (100 MHz, CDCl₃): 1-(^tbutyl)-4-[2-(trimethylsilyl)ethynyl]benzene.



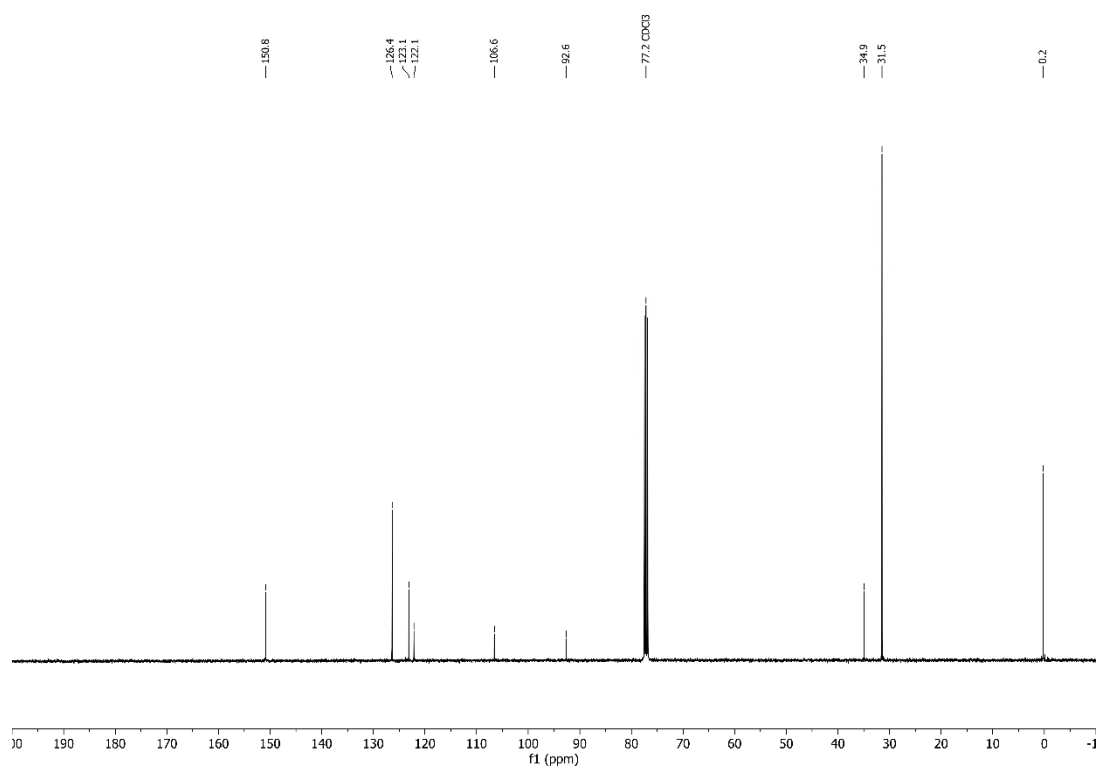
^1H -NMR (400 MHz, CDCl_3): 1-(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]benzene.



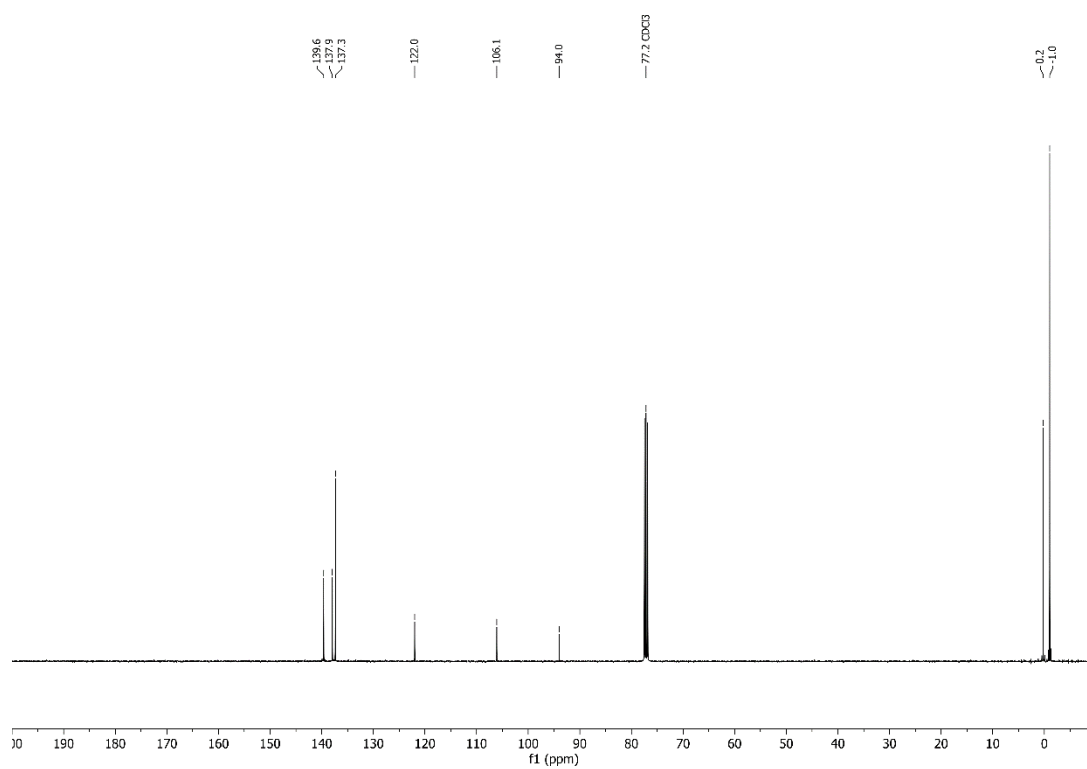
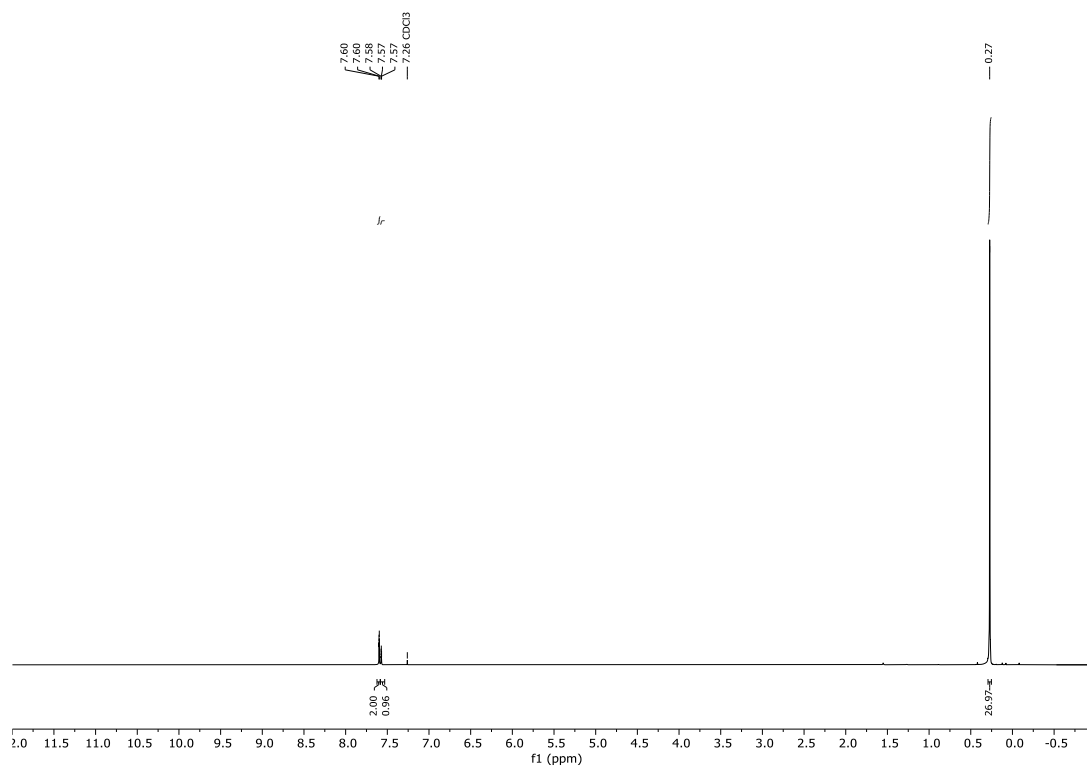
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): 1-(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]benzene.

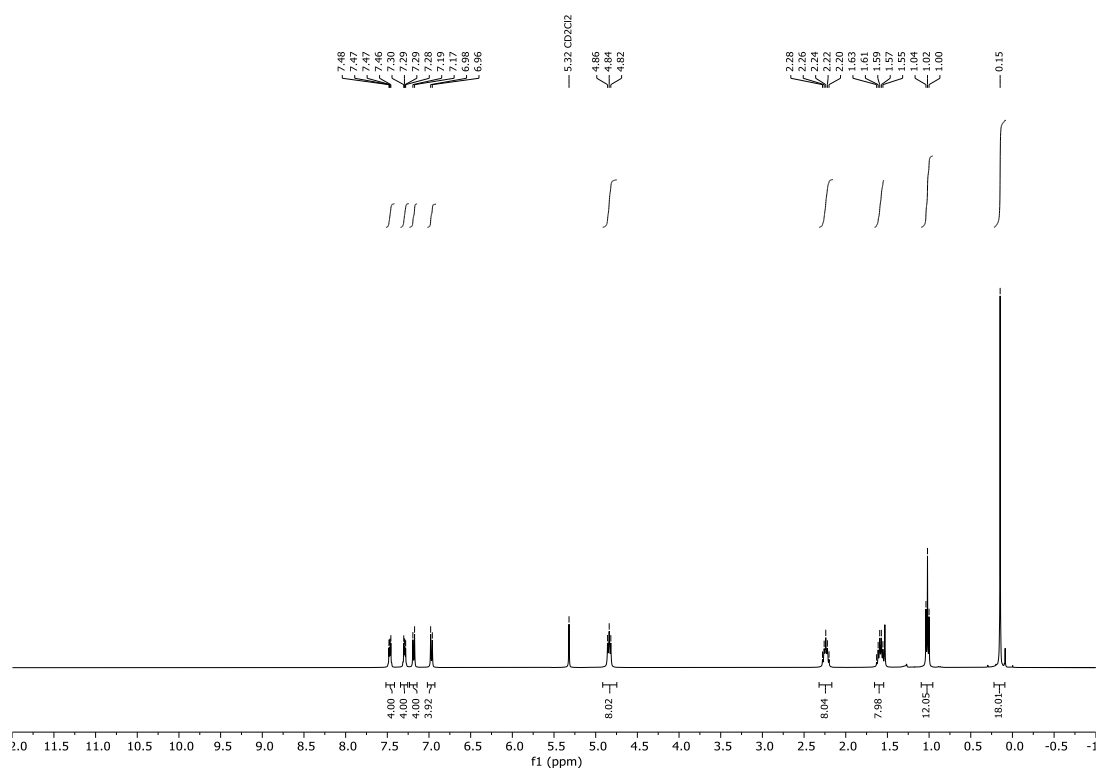


¹H-NMR (400 MHz, CDCl₃): 1,3-Bis(1,1-dimethylethyl)-5-[2-(trimethylsilyl)ethynyl]benzene.

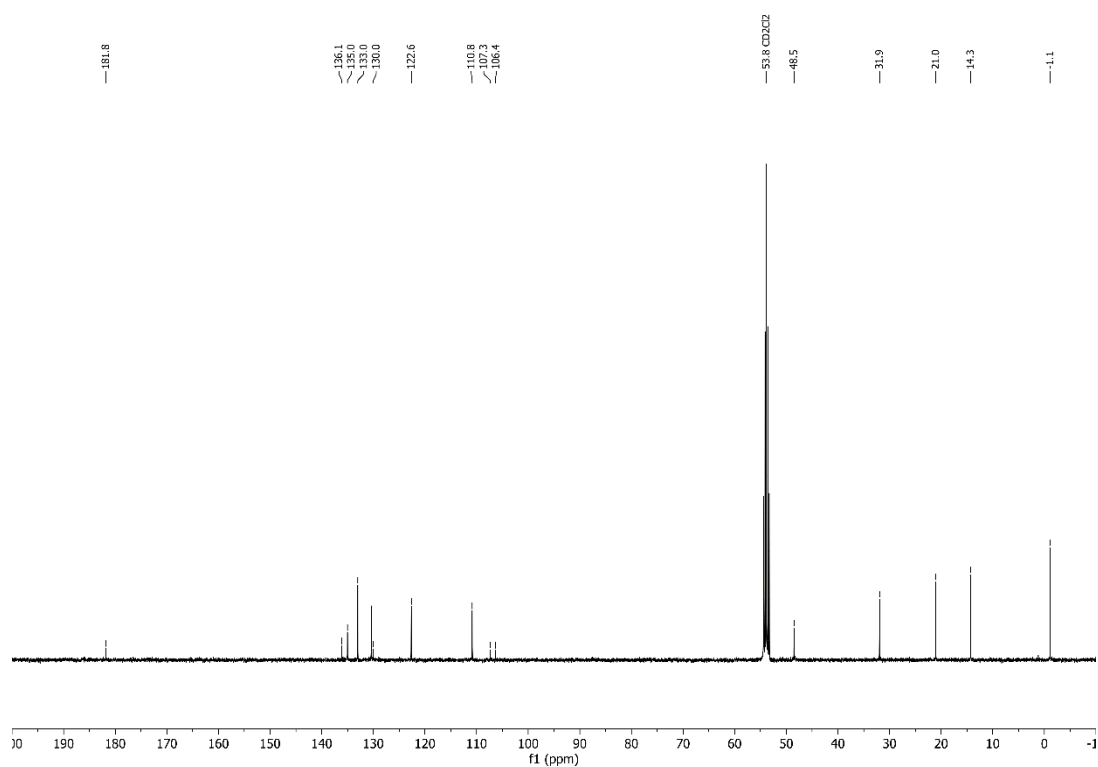


¹³C{¹H} NMR (100 MHz, CDCl₃): 1,3-Bis(1,1-dimethylethyl)-5-[2-(trimethylsilyl)ethynyl]benzene.

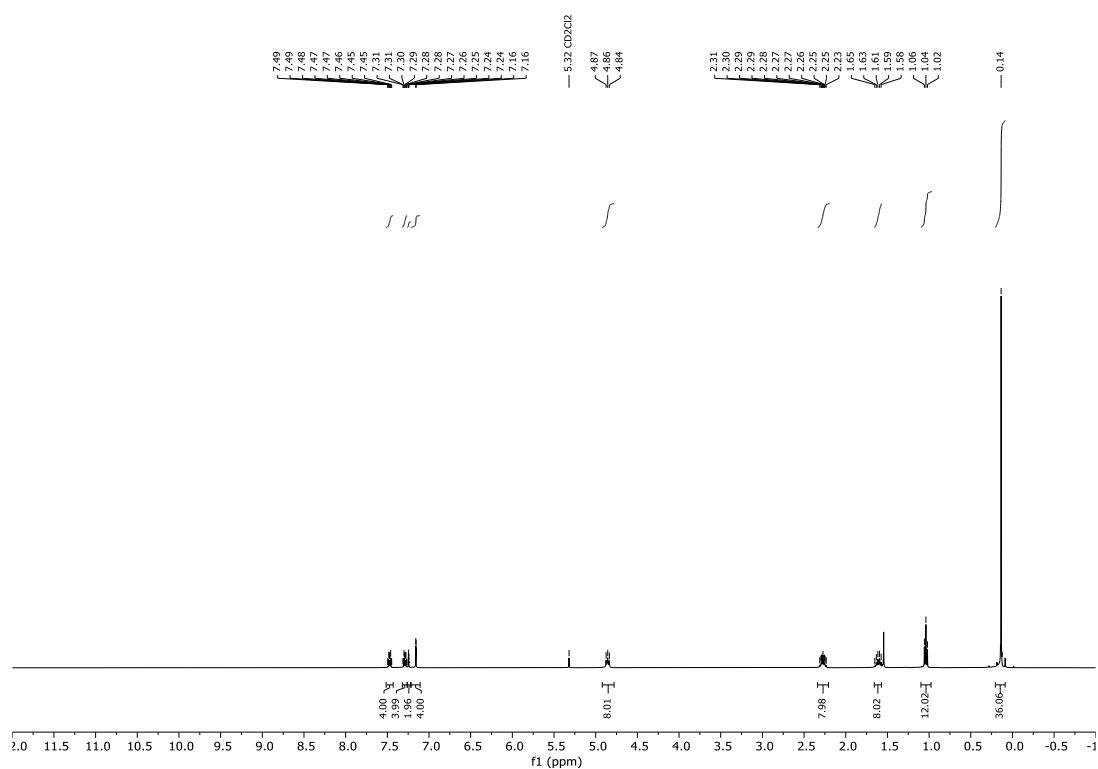




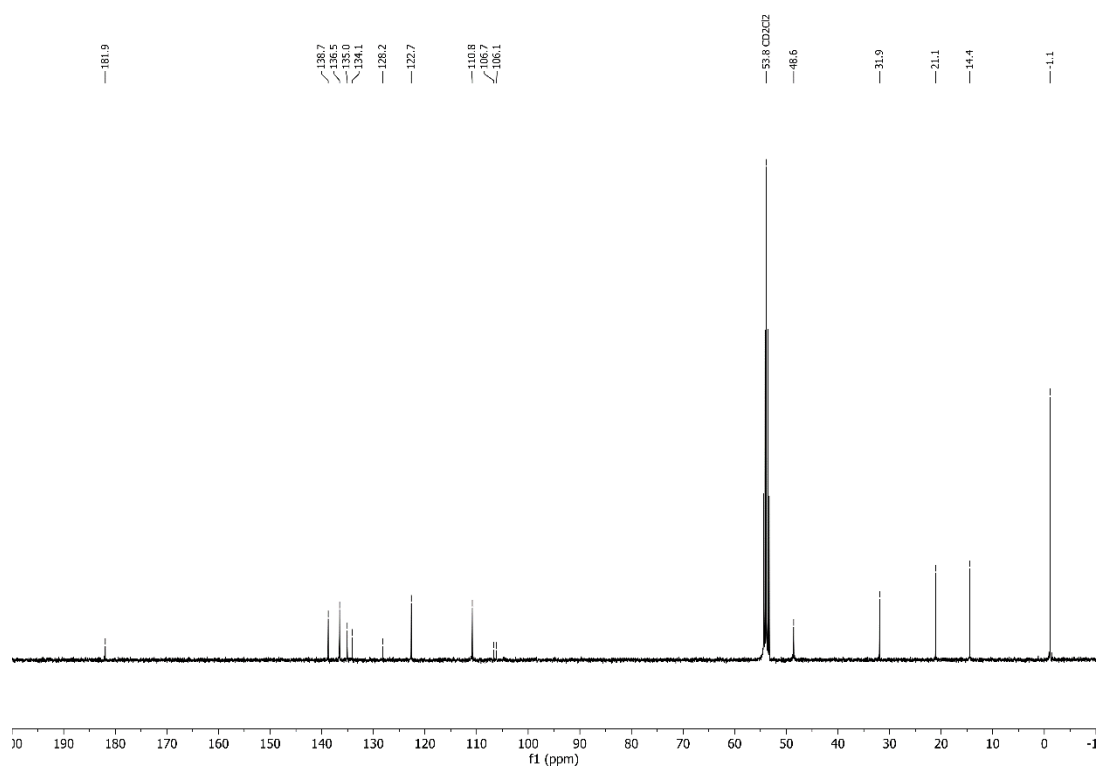
¹H-NMR (400 MHz, CD₂Cl₂): Compound Pt-1.



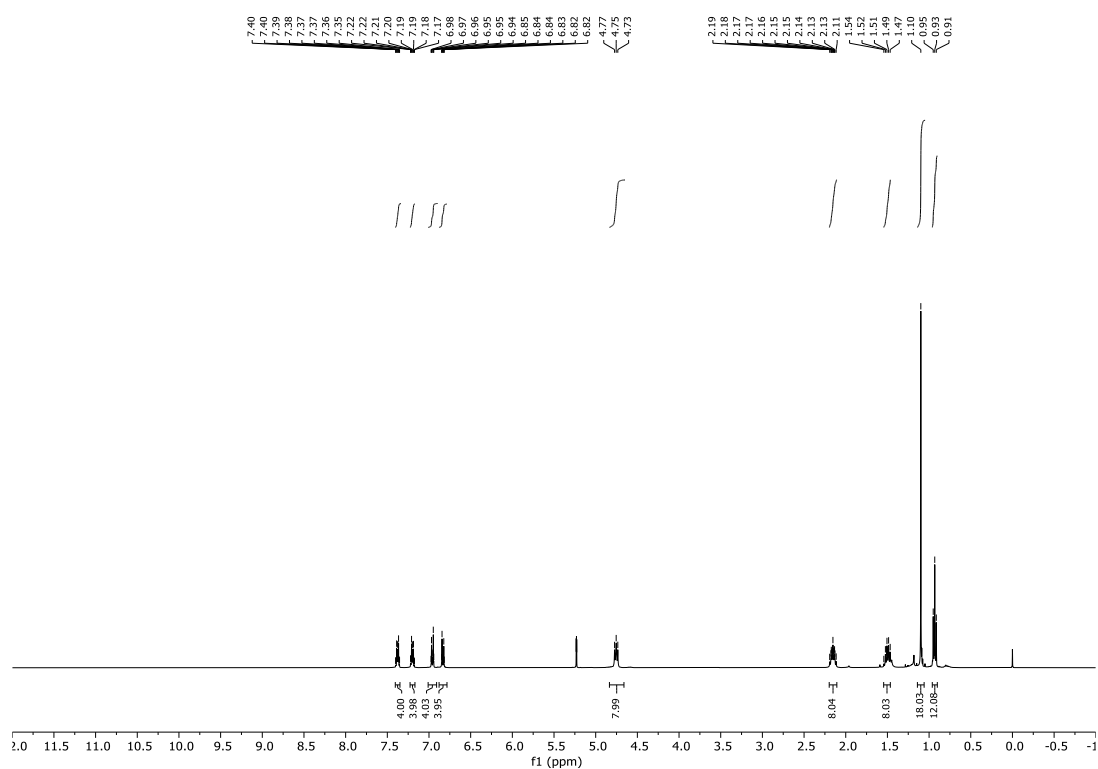
¹³C{¹H} NMR (101 MHz, CD₂Cl₂): Compound Pt-1.



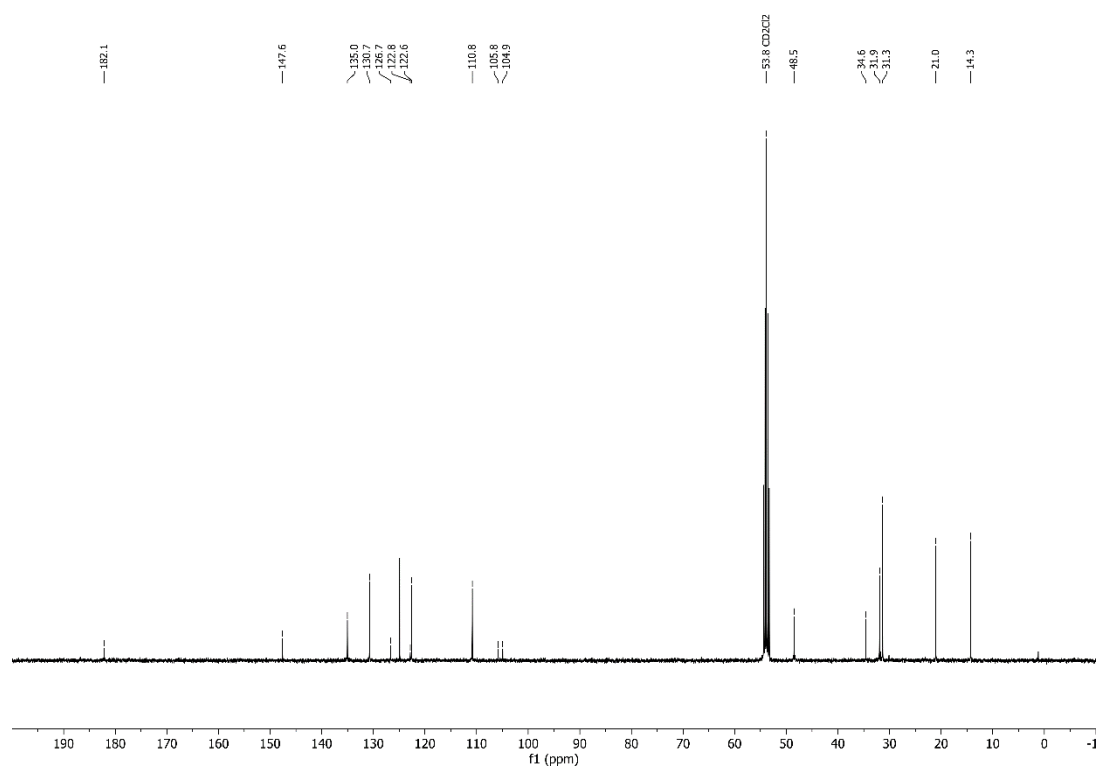
¹H-NMR (400 MHz, CD₂Cl₂): Compound Pt-2.



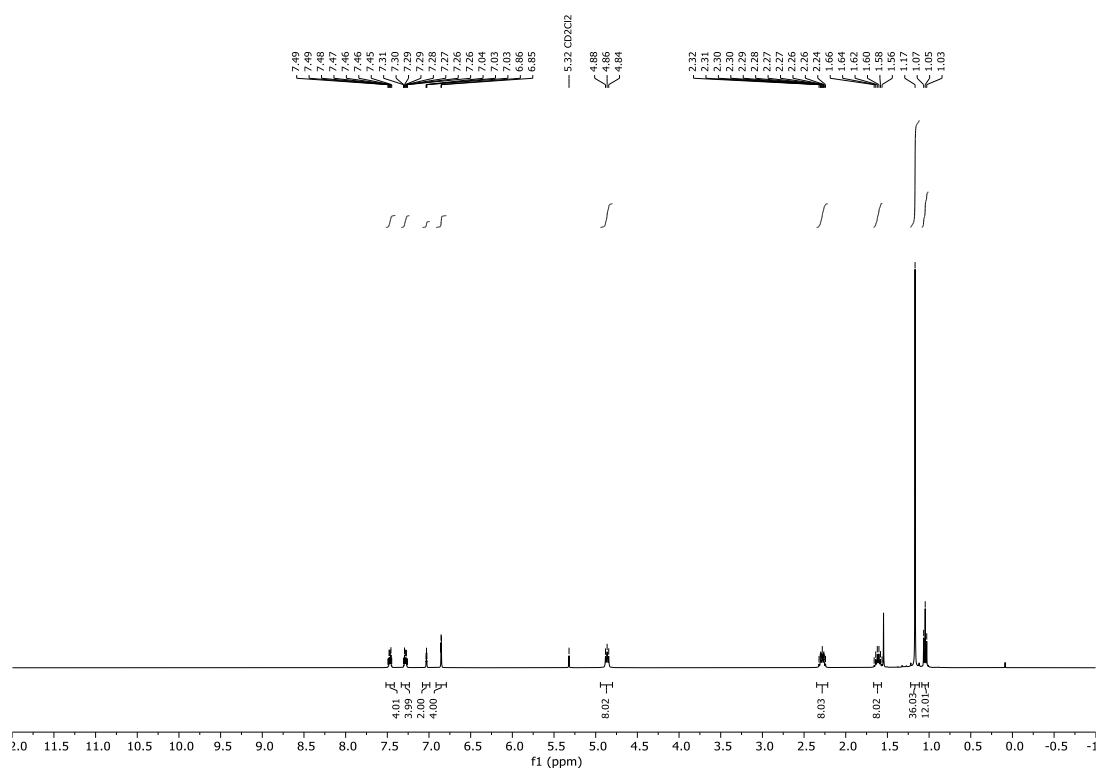
¹³C{¹H} NMR (101 MHz, CD₂Cl₂): Compound Pt-2.



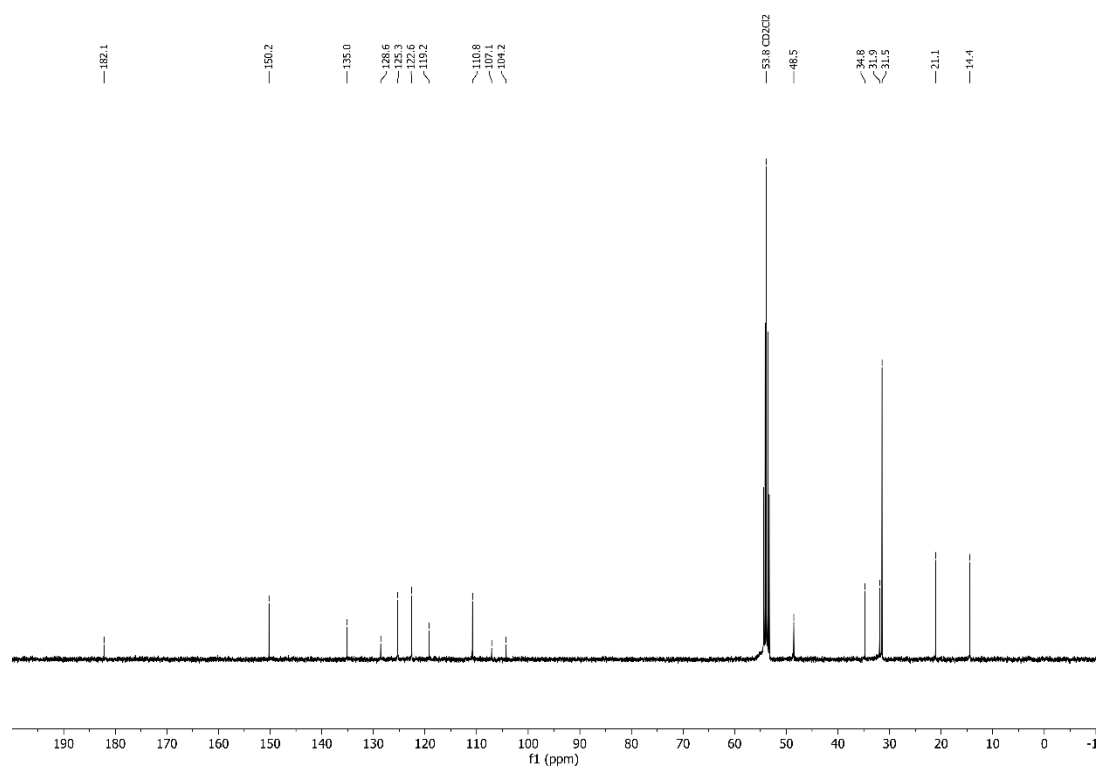
¹H-NMR (400 MHz, CD₂Cl₂): Compound Pt-3.



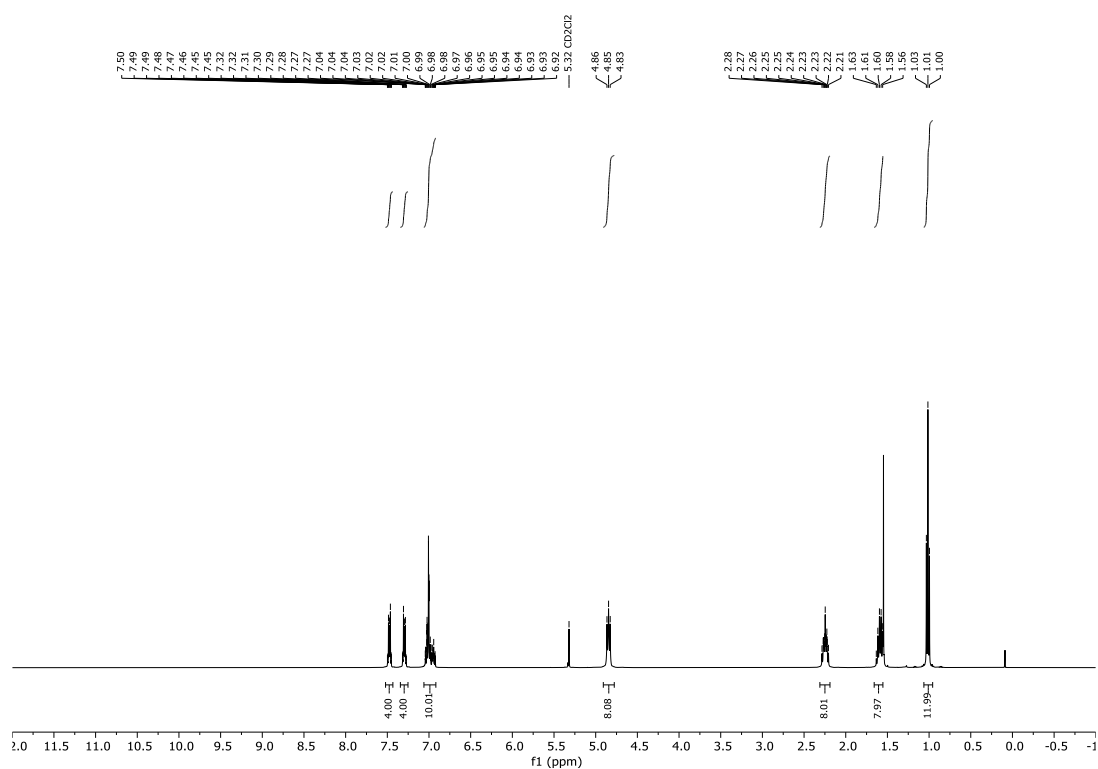
¹³C{¹H} NMR (101 MHz, CD₂Cl₂): Compound Pt-3.



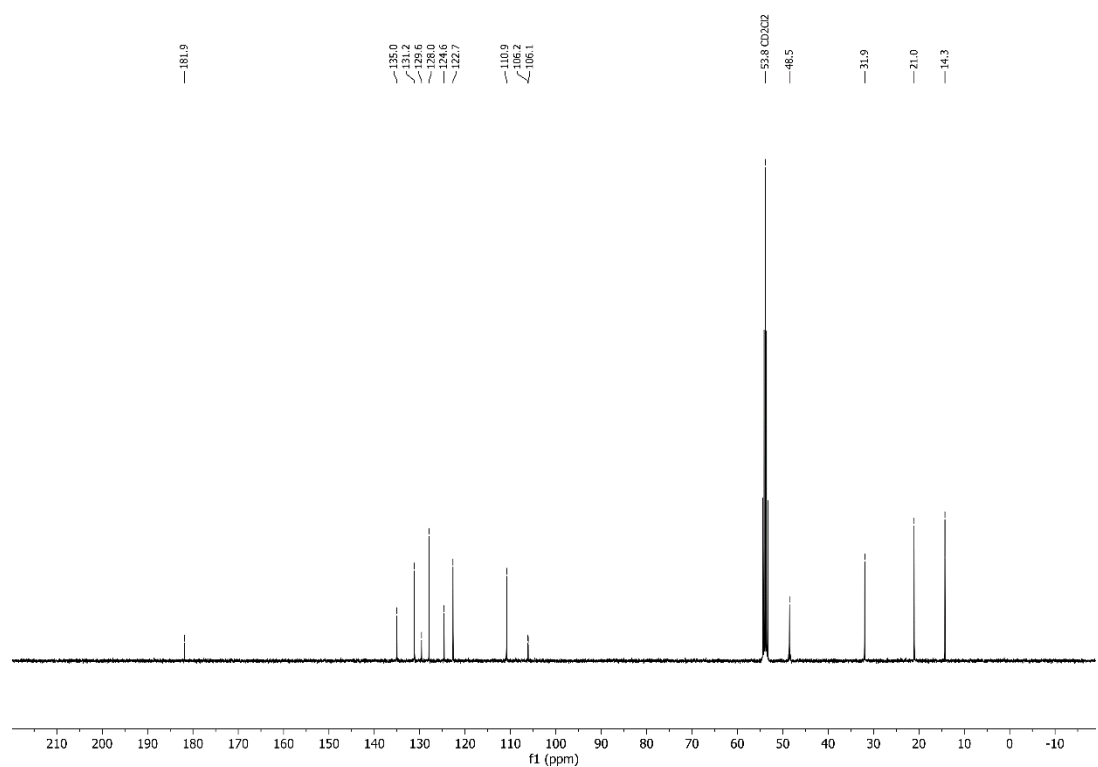
¹H-NMR (400 MHz, CD₂Cl₂): Compound Pt-4.



¹³C{¹H} NMR (101 MHz, CD₂Cl₂): Compound Pt-4.



¹H-NMR (400 MHz, CD₂Cl₂): Compound Pt-5.



¹³C{¹H} NMR (101 MHz, CD₂Cl₂): Compound Pt-5.

2.7.4.5 Elemental analysis data

Compound Pt-1

Sample ID	Weight, mg	C, %	H, %	N, %	S, %
HK475	1.202	62.09	6.98	5.45	0.00
HK475	1.305	61.61	7.21	5.37	0.00
Avg		61.85	7.09	5.41	0.00
Theoretical values	-	62.31	7.04	5.59	0.00

Elemental Microanalysis Report No. 20230828-3 performed by Dr. Aleksei Marianov (Macquarie Analytical and Fabrication Facility).

Compound Pt-2

Sample ID	Weight, mg	C, %	H, %	N, %	S, %
HK_All_meta_TMS_Pt_NHC	1.437	60.59	7.67	4.78	0.0
HK_All_meta_TMS_Pt_NHC	1.247	60.5	7.68	4.83	0.0
Avg		60.54	7.68	4.80	
Theoretical values	-	60.75	7.56	4.89	0.00

Elemental Microanalysis Report No. 20231018-3 performed by Dr. Aleksei Marianov (Macquarie Analytical and Fabrication Facility).

Compound Pt-3

Sample ID	Weight, mg	C, %	H, %	N, %	S, %
HK_p_tBu_Pt_NHC	1.206	66.18	7.2	5.59	0.0
HK_p_tBu_Pt_NHC	1.315	66.09	7.25	5.66	0.0
Avg		66.14	7.22	5.62	
Theoretical values	-	66.85	7.27	5.77	0.00

Elemental Microanalysis Report No. 20231018-3 performed by Dr. Aleksei Marianov (Macquarie Analytical and Fabrication Facility).

Compound Pt-4

Sample ID	Weight, mg	C, %	H, %	N, %	S, %
HK_All_meta_tBu_Pt_NHC	1.339	68.95	8.16	5.07	0.0
HK_All_meta_tBu_Pt_NHC	1.251	68.82	8.23	5.01	0.0
Avg		68.89	8.20	5.04	
Theoretical values	-	68.79	8.01	5.18	0.00

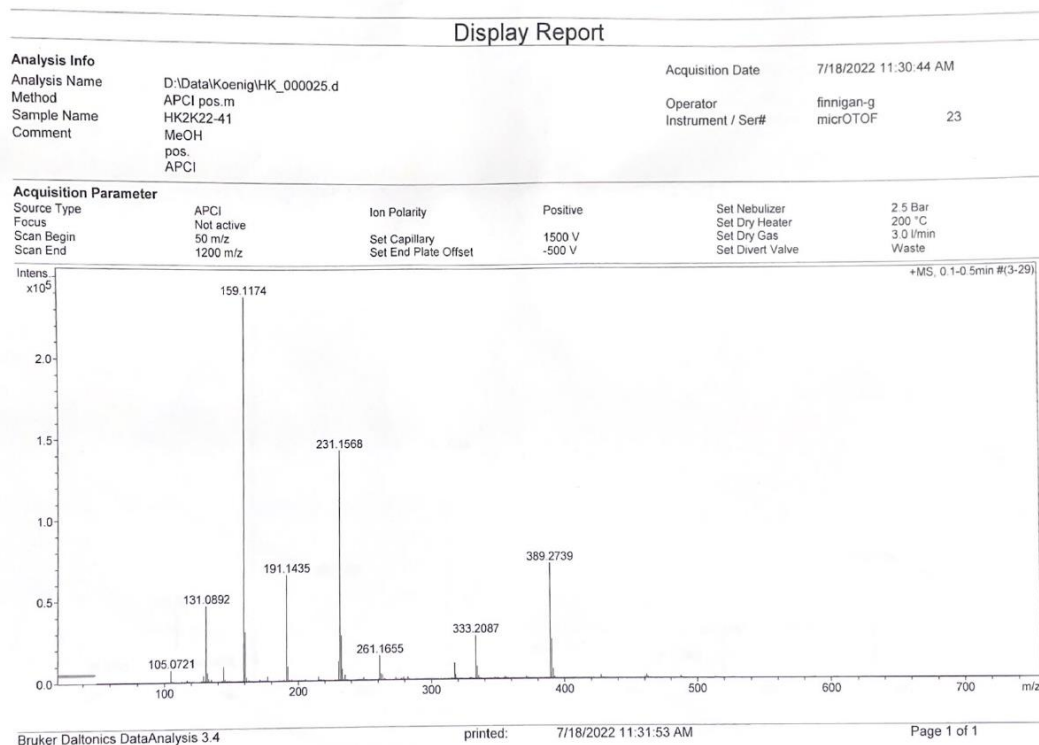
Elemental Microanalysis Report No. 20231018-3 performed by Dr. Aleksei Marianov (Macquarie Analytical and Fabrication Facility).

Compound Pt-5

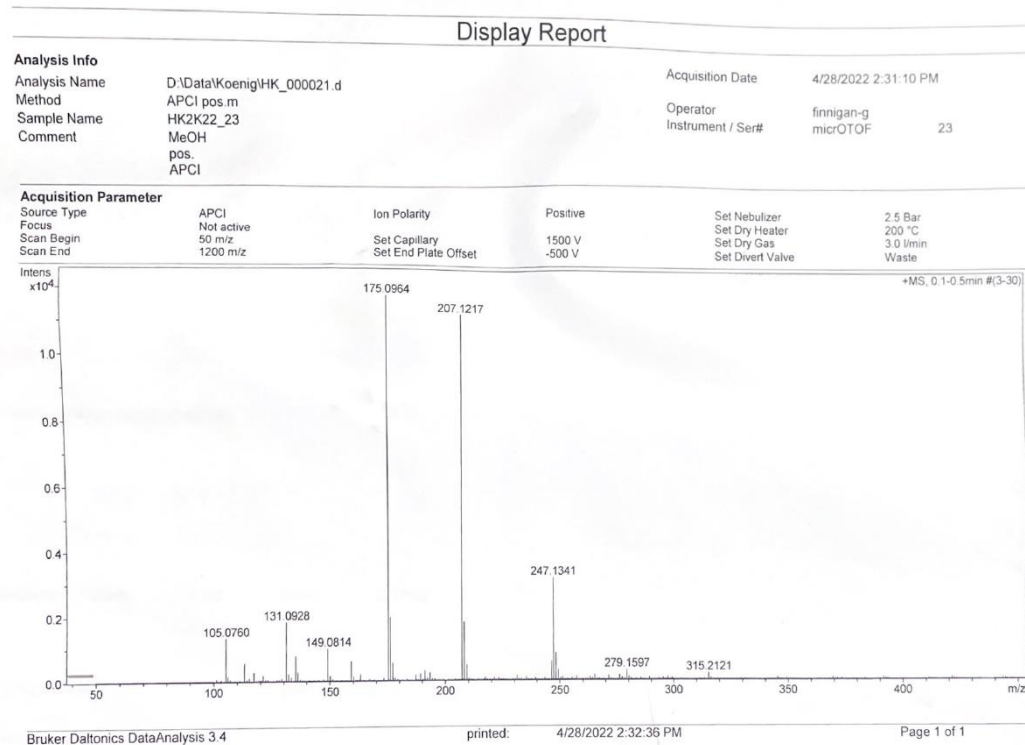
Sample ID	Weight, mg	C, %	H, %	N, %	S, %
HK_Pt01	1.222	64.25	6.15	6.43	0.0
HK_Pt01	1.232	64.25	6.3	6.48	0.0
Avg		64.25	6.22	6.46	
Theoretical values	-	64.39	6.34	6.53	0.00

Elemental Microanalysis Report No. 20231018-3 performed by Dr. Aleksei Marianov (Macquarie Analytical and Fabrication Facility).

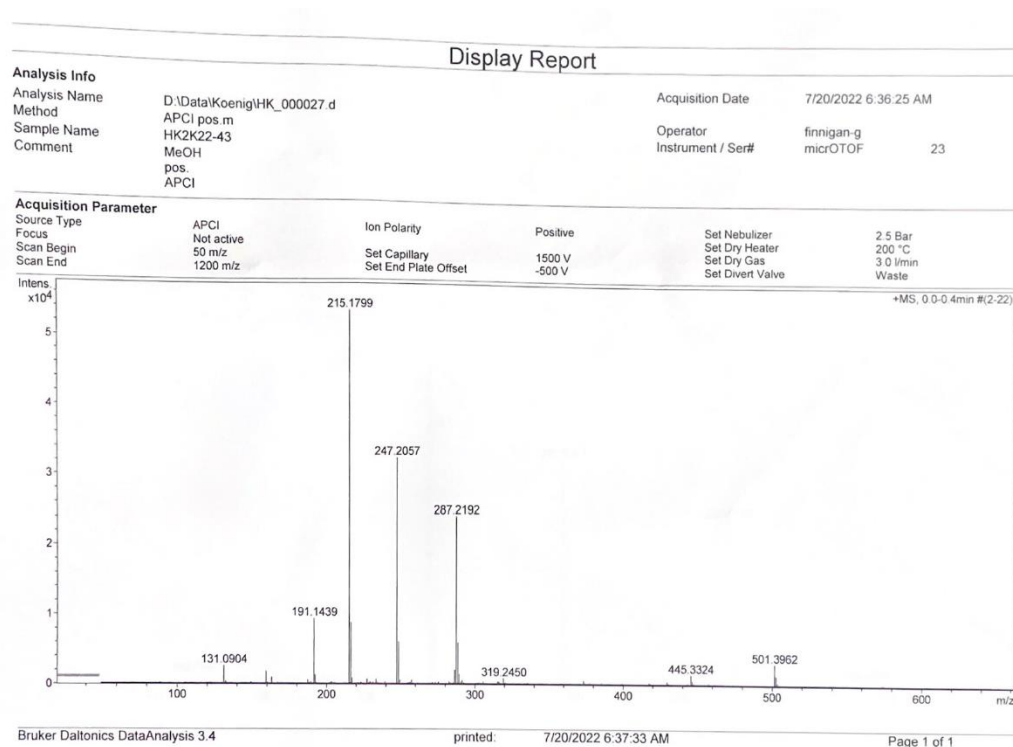
2.7.4.6 HRMS reports



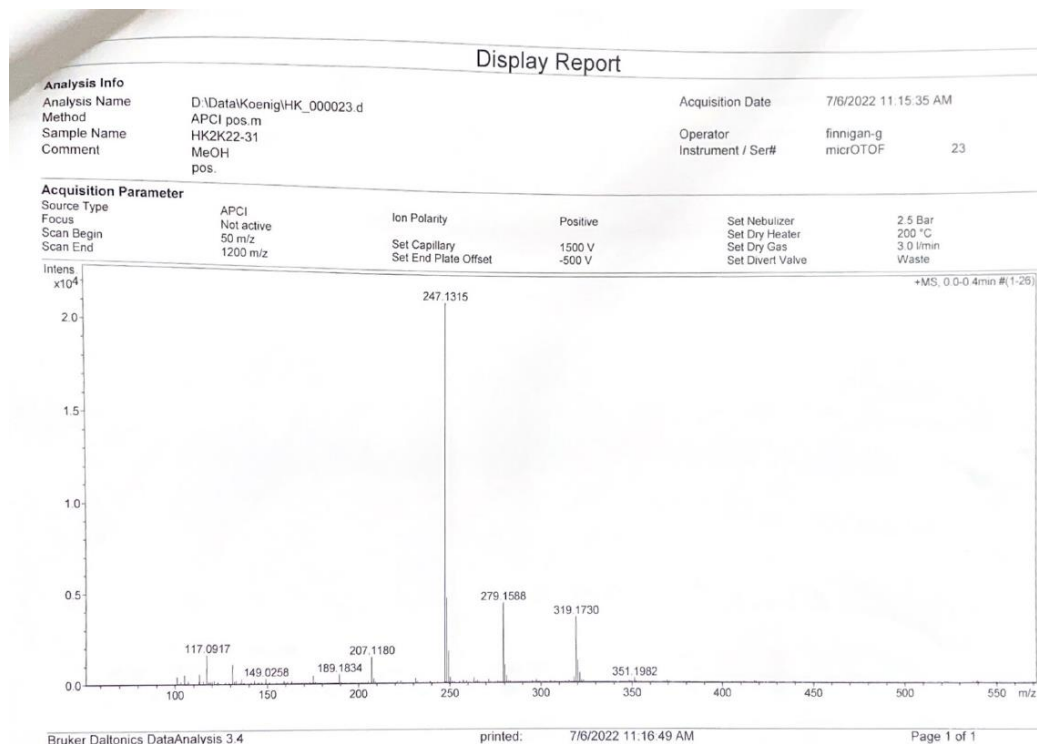
HRMS (ESI-TOF) report for 1-(⁴butyl)-4-[2-(trimethylsilyl)ethynyl]benzene, performed at the analytical facility of JLU Gießen.



HRMS (ESI-TOF) report for 1-(trimethylsilyl)-4-[2-(trimethylsilyl)ethynyl]benzene, performed at the analytical facility of JLU Gießen.



HRMS (ESI-TOF) report for 1,3-Bis(1,1-dimethylethyl)-5-[2-(trimethylsilyl)ethynyl]benzene, performed at the analytical facility of JLU Gießen.



HRMS (ESI-TOF) report for 1,3-Bis(trimethylsilyl)-5-[2-(trimethylsilyl)ethynyl]benzene, performed at the analytical facility of JLU Gießen.

2.7.4.7 Additional photophysical data for Pt-1-5

Compound 1

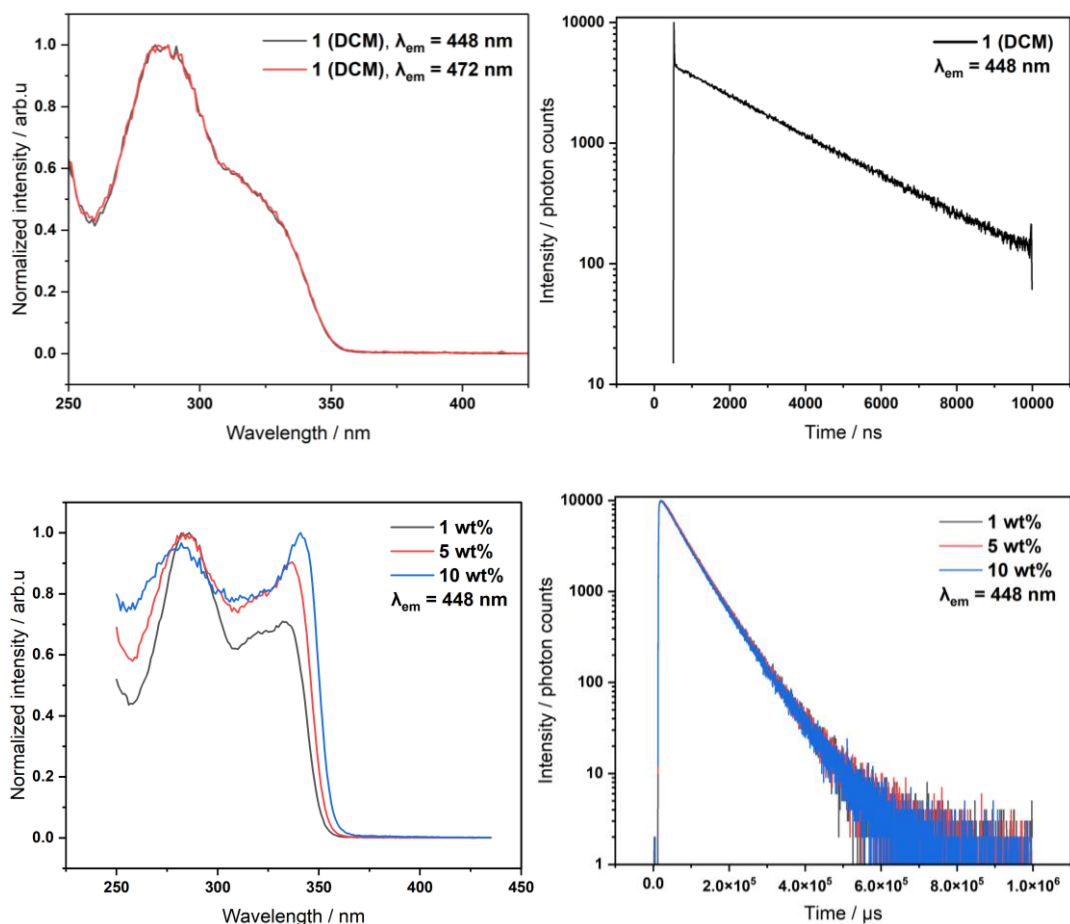


Figure S1: Normalised excitation spectra (left, top) and lifetime measurements in DCM (right, top) at room temperature for compound Pt-1. Normalised excitation spectra (left, bottom) and lifetime measurements (right, bottom) of different wt% PMMA thin films of Pt-1 (room temperature measurements).

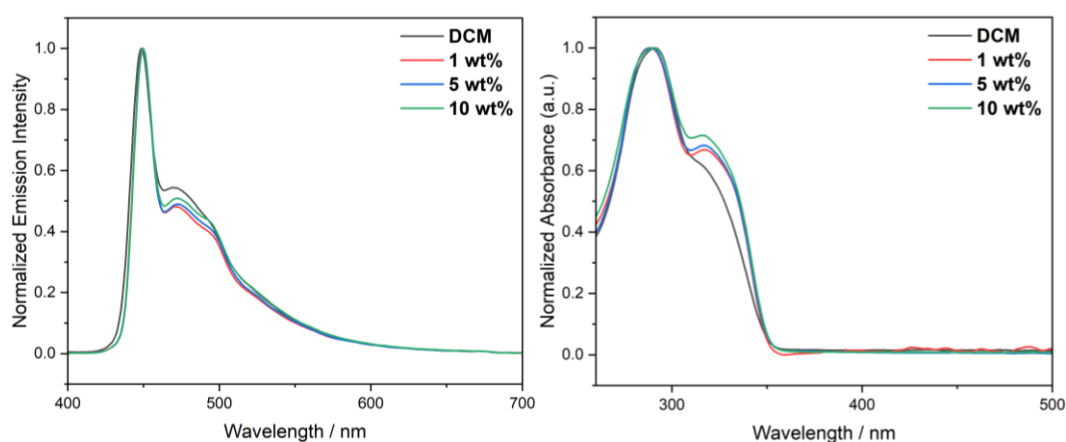


Figure S2: Normalised emission (left) and absorption (right) spectra of different wt% PMMA thin films of Pt-1 in comparison to DCM solution measurements (room temperature measurements).

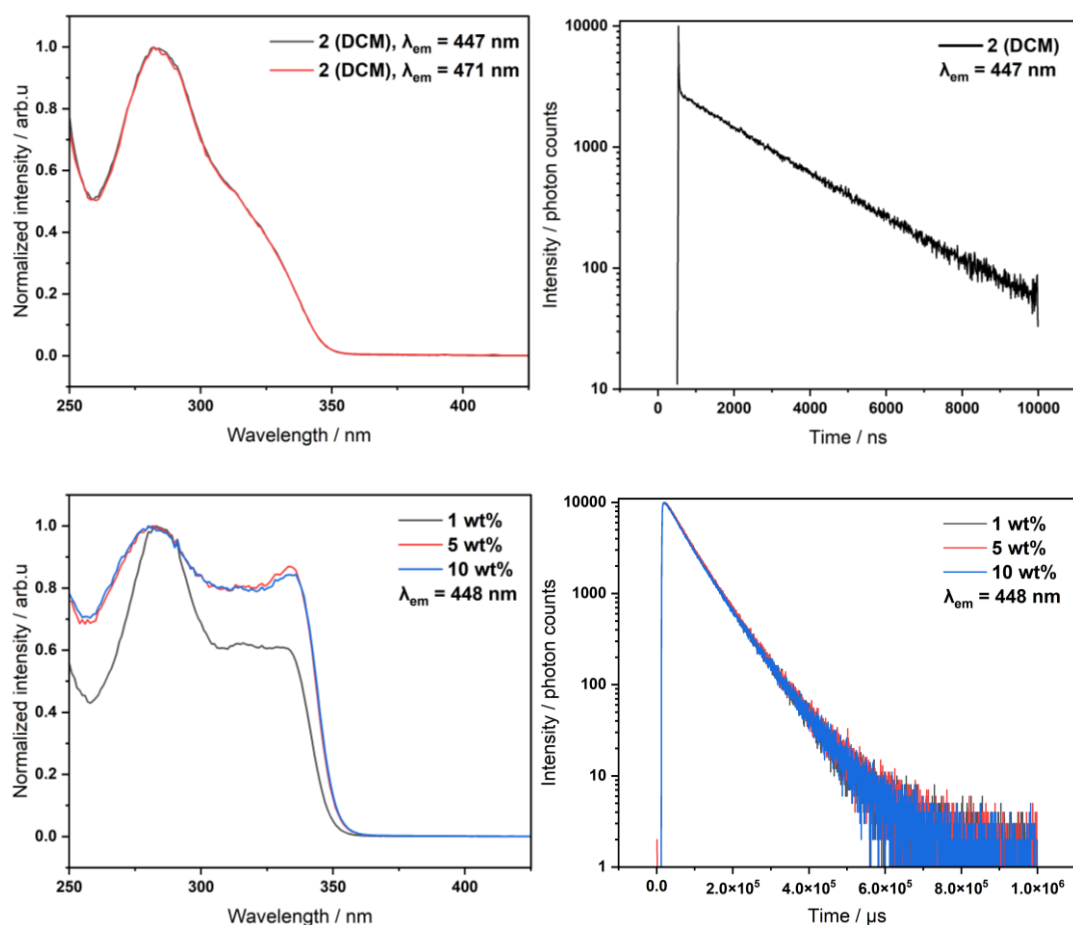
Compound Pt-2

Figure S3: Normalised excitation spectra (left, top) and lifetime measurements in DCM (right, top) at room temperature for compound Pt-2. Normalised excitation spectra (left, bottom) and lifetime measurements (right, bottom) of different wt% PMMA thin films of Pt-2 (room temperature measurements).

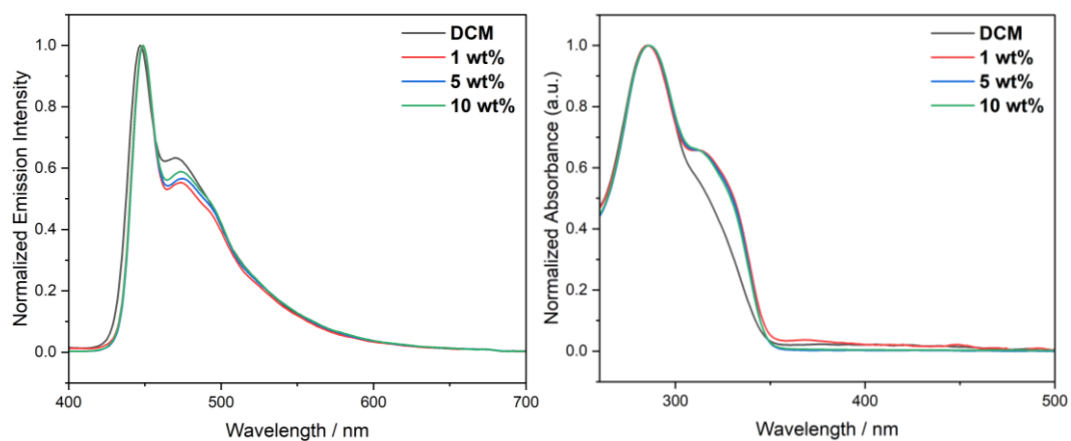


Figure S4: Normalised emission (left) and absorption (right) spectra of different wt% PMMA thin films of Pt-2 in comparison to DCM solution measurements (room temperature measurements).

Compound 3

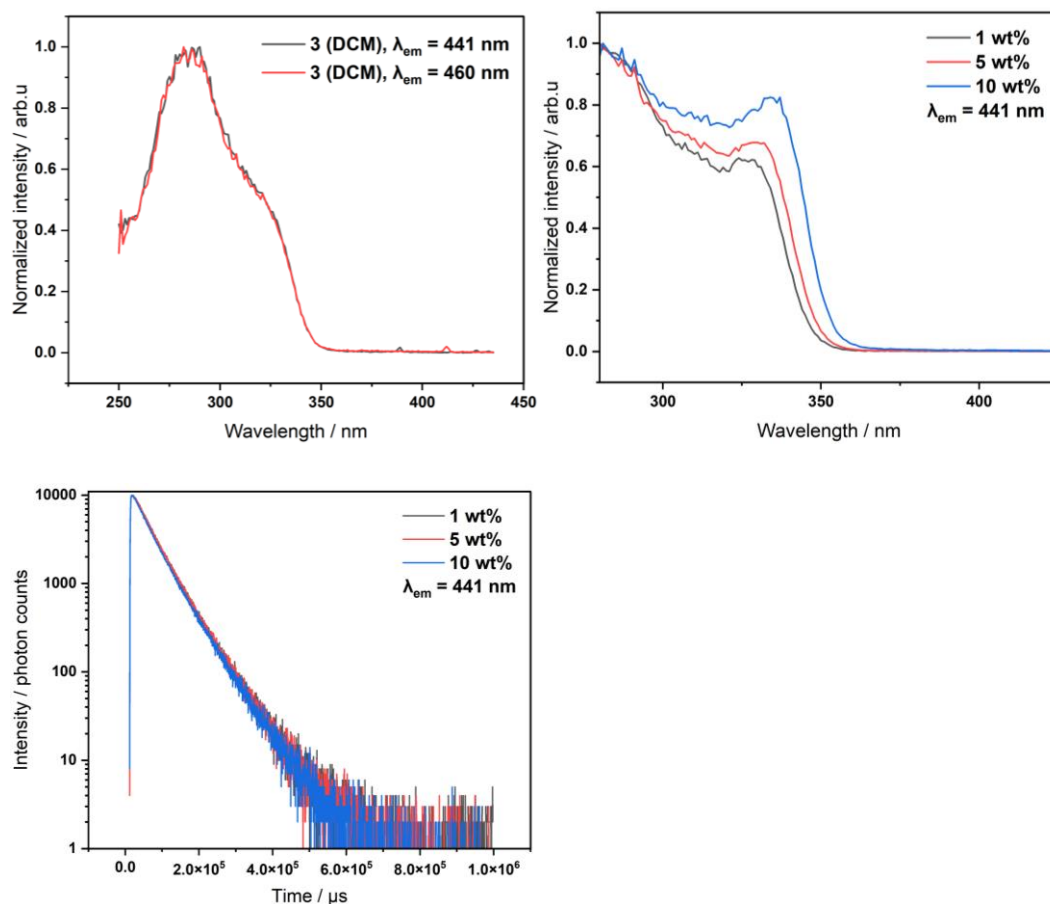


Figure S5: Normalised excitation spectra (left, top) in DCM measured at room temperature for compound Pt-3. Normalised excitation spectra (right, top) and lifetime measurements (left, bottom) of different wt% PMMA thin films of Pt-3 (room temperature measurements).

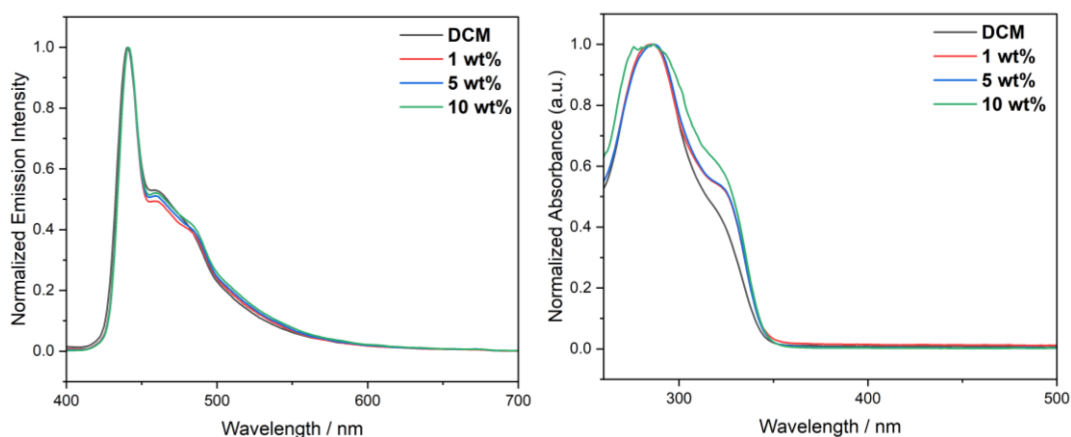


Figure S6: Normalised emission (left) and absorption (right) spectra of different wt% PMMA thin films of Pt-3 in comparison to DCM solution measurements (room temperature measurements).

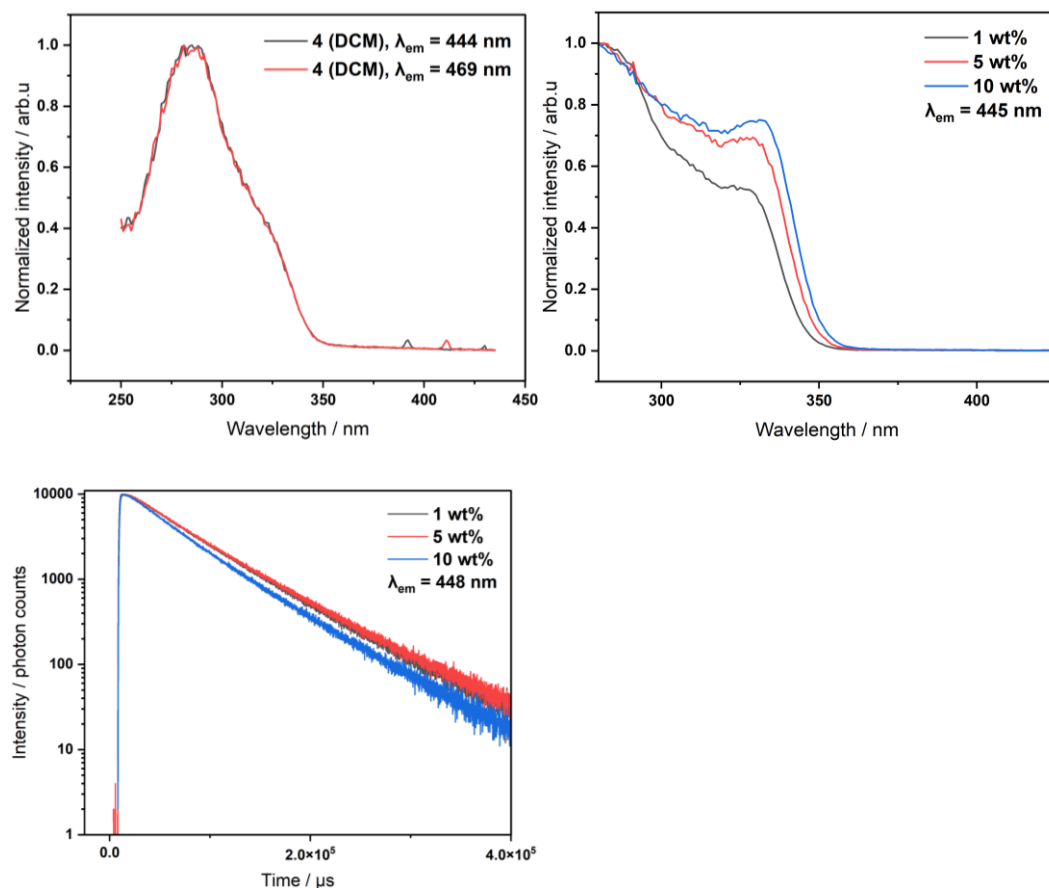
Compound Pt-4

Figure S7: Normalised excitation spectra (left, top) in DCM measured at room temperature for compound Pt-4. Normalised excitation spectra (right, top) and lifetime measurements (left, bottom) of different wt% PMMA thin films of Pt-4 (room temperature measurements).

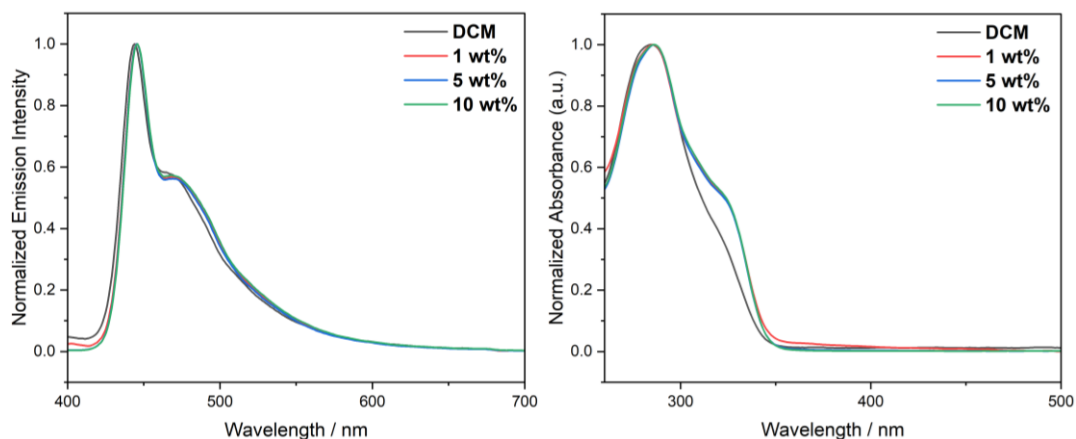


Figure S8: Normalised emission (left) and absorption (right) spectra of different wt% PMMA thin films of Pt-4 in comparison to DCM solution measurements (room temperature measurements).

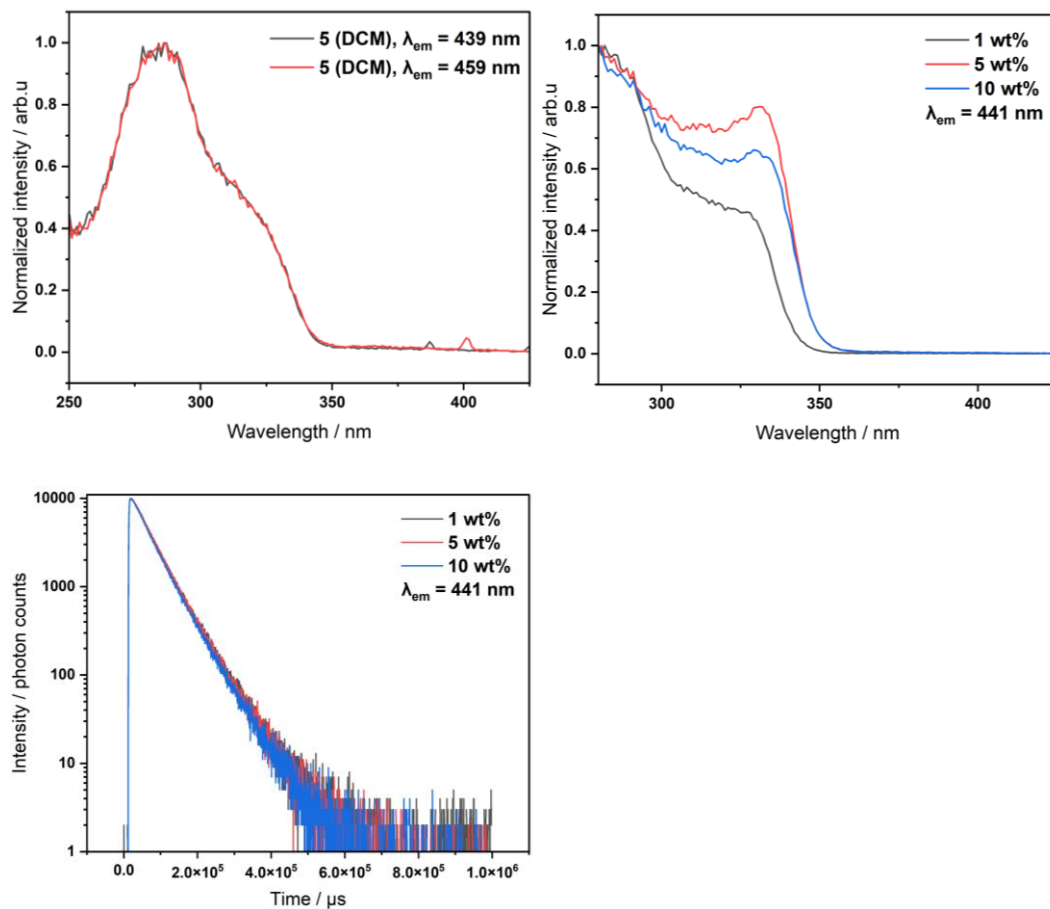
Compound Pt-5

Figure S9: Normalised excitation spectra (left, top) in DCM measured at room temperature for compound Pt-5. Normalised excitation spectra (right, top) and lifetime measurements (left, bottom) of different wt% PMMA thin films of Pt-5 (room temperature measurements).

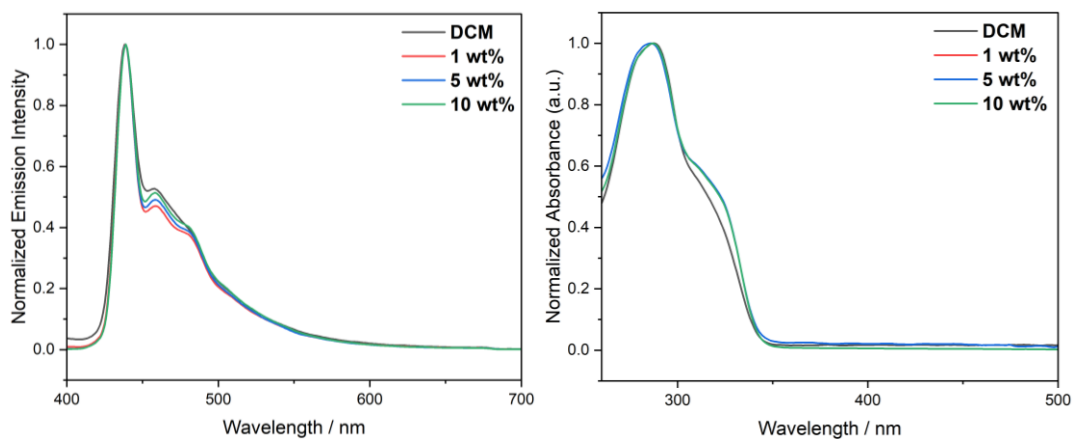


Figure S10: Normalised emission (left) and absorption (right) spectra of different wt% PMMA thin films of Pt-5 in comparison to DCM solution measurements (room temperature measurements).

Hyperfluorescent thin films

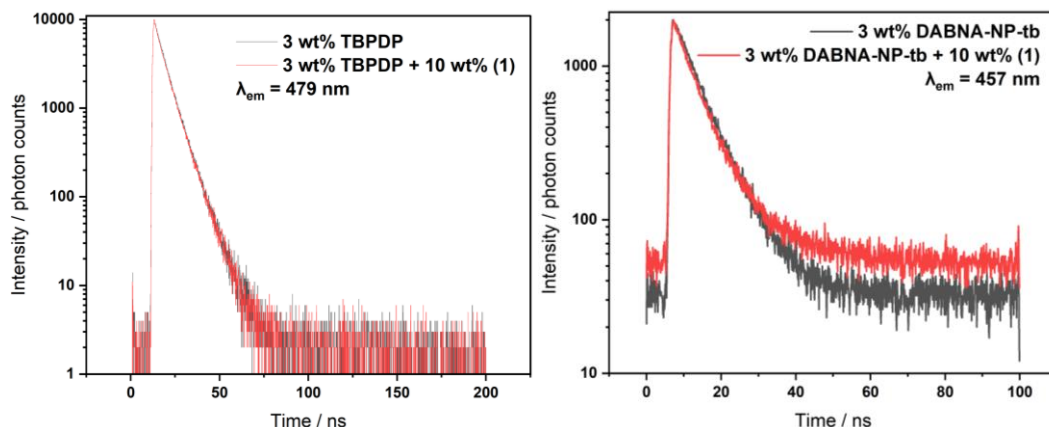


Figure S11: Lifetime measurements of PMMA thin films consisting of indicated concentration of TBPDP (left), DABNA-NP-tb (right) and 10 wt% of compound Pt-1 (room temperature measurements).

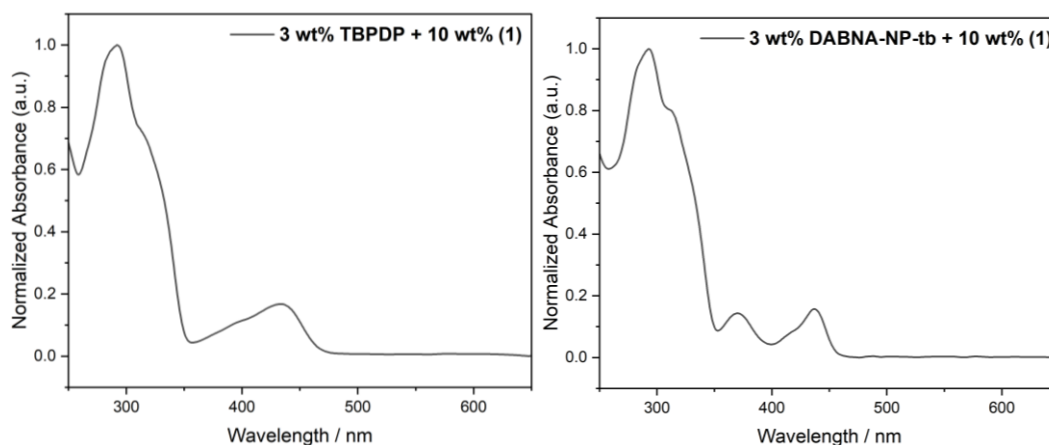


Figure S12: Normalised absorption spectra of PMMA thin films consisting of indicated concentration of TBPDP (left), DABNA-NP-tb (right) and 10 wt% of compound Pt-1 (room temperature measurements).

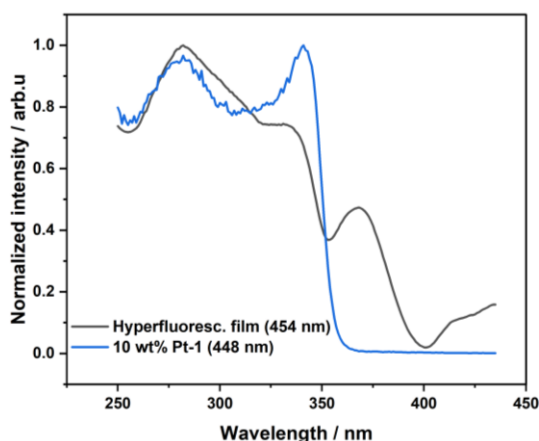


Figure S13: Normalised excitation spectra of hyperfluorescent film (Hyperfluoresc. film) consisting of 3 wt% of DABNA-NP-tb and 10 wt% of compound Pt-1 doped into PMMA in comparison to a film sample consisting of 10 wt% Pt-1 doped into PMMA.

2.7.4.8 Electrochemical analyses

Cyclic voltammetry of complexes Pt-1-5 was performed on a 600 series electrochemical workstation by CH instruments. Compounds Pt-1-5 were dissolved in a degassed, anhydrous DCM electrolyte solution (electrolyte: NBu_4PF_6 , 0.1 M) under a N_2 inert gas atmosphere. A glassy carbon electrode was utilized as the working electrode and was polished with sub-micrometer alumina powder prior to each run. Platinum wire was used as a counter electrode, with a Ag/AgCl pseudo-reference electrode. Commercially obtained ferrocene functioned as internal standard for the measurements.

2.7.4.9 Computed monomer geometries of complexes 1-5

Compound Pt-1 (So)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	0.163090000	-2.311878000	-0.287397000
6	0.183632000	-0.319234000	-0.223672000
6	0.245301000	0.907573000	-0.159832000
6	0.192953000	-4.305190000	-0.319190000
6	0.243771000	-5.533992000	-0.318671000
6	-1.846951000	-2.337788000	-0.151470000
7	-2.728217000	-1.797801000	-1.028376000
7	-2.585116000	-2.922614000	0.823115000
6	2.172846000	-2.313374000	-0.433822000
7	2.905292000	-2.826153000	-1.451637000
7	3.057129000	-1.822904000	0.467715000
6	0.354271000	2.324469000	-0.069596000
6	-0.765553000	3.131115000	0.215174000
6	1.594149000	2.966174000	-0.252133000
6	-0.641043000	4.511168000	0.313860000
6	1.705020000	4.348570000	-0.149374000
6	0.594258000	5.157420000	0.136252000
1	-1.731805000	2.651342000	0.362975000
1	2.468905000	2.357780000	-0.477279000
1	-1.533606000	5.098296000	0.539099000
1	2.684772000	4.804671000	-0.295532000
6	0.325611000	-6.955366000	-0.300031000
6	1.566600000	-7.606396000	-0.165167000
6	-0.827779000	-7.758298000	-0.405747000
6	1.644736000	-8.994393000	-0.129260000
6	-0.735463000	-9.143856000	-0.368075000
6	0.499327000	-9.799583000	-0.225633000
1	2.467835000	-7.000837000	-0.081300000
1	-1.795498000	-7.271594000	-0.517829000
1	2.625816000	-9.457951000	-0.019930000
1	-1.654197000	-9.727999000	-0.451281000
6	-2.057075000	-3.614601000	1.973935000
1	-2.413512000	-4.650522000	1.988951000
1	-0.968130000	-3.625695000	1.897360000
1	-2.363334000	-3.104995000	2.895185000
6	-2.379269000	-1.079179000	-2.230305000
1	-2.677978000	-1.650016000	-3.117636000
1	-2.874810000	-0.102177000	-2.239193000
1	-1.298615000	-0.921150000	-2.234200000
6	2.714448000	-1.186208000	1.716800000
1	1.629059000	-1.075456000	1.758892000
1	3.062881000	-1.792543000	2.561287000
1	3.167240000	-0.189871000	1.767585000
6	2.369374000	-3.451634000	-2.636267000
1	2.693100000	-2.905539000	-3.530111000
1	2.700801000	-4.494101000	-2.698610000
1	1.279920000	-3.439221000	-2.566432000
14	0.723696000	7.032366000	0.275301000
14	0.579054000	-11.680338000	-0.144400000
6	-0.278868000	7.832725000	-1.108034000
1	0.111384000	7.538309000	-2.090144000
1	-1.330371000	7.522502000	-1.060272000
1	-0.245668000	8.927768000	-1.039477000
6	2.527498000	7.560259000	0.133392000
1	3.140477000	7.104826000	0.921339000
1	2.952767000	7.276741000	-0.837535000
1	2.613286000	8.650085000	0.229594000
6	0.029281000	7.579518000	1.941824000
1	-1.017052000	7.268646000	2.054524000
1	0.600157000	7.134015000	2.765964000
1	0.069023000	8.671312000	2.047341000
6	-0.368184000	-12.274762000	1.375375000
1	-1.415746000	-11.950377000	1.336786000
1	-0.356373000	-13.370189000	1.445386000
1	0.073751000	-11.867348000	2.293042000

6	2.375132000	-12.239472000	-0.028678000
1	2.858664000	-11.849974000	0.876020000
1	2.430733000	-13.334855000	0.008739000
1	2.955429000	-11.904482000	-0.897693000
6	-0.217030000	-12.409786000	-1.691208000
1	0.326365000	-12.099932000	-2.592446000
1	-0.220458000	-13.506756000	-1.653283000
1	-1.256204000	-12.073270000	-1.796096000
6	-5.259544000	-1.706895000	-1.178377000
6	-6.397535000	-2.120221000	-0.487809000
6	-4.027165000	-2.040960000	-0.624459000
1	-7.380313000	-1.878670000	-0.888473000
6	-6.304270000	-2.841717000	0.711761000
6	-3.934284000	-2.764500000	0.572505000
1	-7.216172000	-3.147517000	1.221330000
6	-5.069435000	-3.176813000	1.264233000
1	-4.997119000	-3.738033000	2.193389000
1	-5.333606000	-1.148893000	-2.109363000
6	5.387403000	-3.025603000	-1.933060000
6	4.255522000	-2.670934000	-1.204979000
6	6.624400000	-2.712774000	-1.372398000
1	7.533922000	-2.975084000	-1.909706000
6	4.353898000	-2.024864000	0.035157000
6	6.723072000	-2.068548000	-0.129970000
1	7.707538000	-1.841960000	0.275241000
6	5.588376000	-1.712996000	0.597114000
1	5.665873000	-1.213953000	1.560688000
1	5.311379000	-3.526994000	-2.895544000

E = -21388.23841605 Eh
ZPVE = 0.76400345 Eh

Compound Pt-1 (So)

GFN2

78	-2.866613927	4.866037117	-6.855626729
6	-3.250257179	6.628654071	-5.986211448
6	-3.184031190	7.651282750	-5.335739975
6	-2.467972239	3.107071502	-7.724890708
6	-2.491904513	2.084637620	-8.378353164
6	-4.678282679	4.480306091	-7.586666711
7	-5.060770132	4.624676234	-8.874440301
7	-5.656117590	3.791794350	-6.957130324
6	-1.069450029	5.265285523	-6.093073716
7	-0.122906283	6.055298325	-6.646092062
7	-0.705738984	5.050088919	-4.809386672
6	-3.142588991	8.849815776	-4.586138026
6	-4.260842093	9.679052000	-4.474270819
6	-1.964113665	9.224264426	-3.935074934
6	-4.192615151	10.840188684	-3.735583001
6	-1.913852035	10.389729422	-3.199551725
6	-3.022622215	11.225915468	-3.080513128
1	-5.177606362	9.397667557	-4.975134101
1	-1.089137921	8.589881612	-4.014527069
6	-2.483064092	0.889411614	-9.134436233
6	-1.367690823	0.049163401	-9.156480310
6	-3.605883058	0.528998775	-9.884245610
6	-1.384026718	-1.108024171	-9.904709391
6	-3.604259158	-0.631356203	-10.629256666
6	-2.496950938	-1.477764080	-10.660506586
1	-0.493488571	0.318923016	-8.579087845
1	-4.479300698	1.170127515	-9.872394711
6	-5.608424397	3.431973345	-5.568020529
1	-5.482426403	2.352860240	-5.453582599
1	-4.751658818	3.948618795	-5.121069296
1	-6.523485653	3.744388848	-5.061702745
6	-4.264196339	5.284107338	-9.870116574
1	-3.864887714	4.559772196	-10.583793976
1	-4.857732856	6.029620568	-10.401889450
1	-3.432958097	5.777922751	-9.354673786
6	-1.485728057	4.279933644	-3.882311480
1	-2.251128320	3.745191273	-4.456128581
1	-0.854653149	3.559812154	-3.359162204
1	-1.970717090	4.934206430	-3.153657931
6	-0.173088111	6.526837122	-8.001009812

1	-0.356555963	7.603461383	-8.025774775
1	0.762705343	6.306916500	-8.517909261
1	-0.996941595	6.007023183	-8.502158339
6	-7.060919313	3.852265184	-10.211257798
6	-8.244338969	3.151395179	-10.061135474
6	-6.270056776	4.006308514	-9.084555633
1	-8.885166935	3.008131886	-10.917709642
6	-8.628547591	2.622190858	-8.831666256
6	-6.657133258	3.469032267	-7.842472101
1	-9.559567625	2.080804597	-8.760991324
6	-7.844405940	2.679821917	-7.701373556
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6	2.716059249	7.283999271	-4.609198548
1	3.607469523	7.892477431	-4.614116411
6	0.454864615	5.728142314	-4.522711558
6	2.340876710	6.641928409	-3.431833105
1	2.949043064	6.766537335	-2.548931958
6	1.206100370	5.853191297	-3.365790600
1	0.915390149	5.363307541	-2.449846230
1	2.263003133	7.669420966	-6.677275226
1	-4.483551474	-0.889059874	-11.202964378
1	-0.510509241	-1.745769965	-9.907358081
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1	-0.991572148	10.659039853	-2.704044641
14	-2.486601807	-3.089040356	-11.655576051
14	-2.983681308	12.835382733	-2.083604197
6	-3.359235203	14.303812065	-3.247147855
1	-2.598739550	14.405560359	-4.015689143
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1	-3.402625612	15.240839488	-2.700093305
6	-1.277397083	13.100272083	-1.274288683
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1	-0.488751217	13.160787072	-2.017906584
1	-1.260022248	14.024305127	-0.704567113
6	-4.317527180	12.765554118	-0.717194864
1	-5.302094038	12.586135183	-1.137989470
1	-4.117072660	11.968833748	-0.006951960
1	-4.363306372	13.697998623	-0.162503560
6	-2.652091193	-4.568376723	-10.456243940
1	-3.606182951	-4.551151236	-9.937581877
1	-2.579740854	-5.515628083	-10.982413718
1	-1.871283361	-4.550337512	-9.701723175
6	-0.843530731	-3.243590560	-12.617042091
1	0.005331825	-3.302445145	-11.943069488
1	-0.832290879	-4.137628263	-13.233310611
1	-0.683509793	-2.390926207	-13.270206726
6	-3.932018973	-3.127769090	-12.899999635
1	-3.909127006	-2.268980002	-13.563919036
1	-3.887208620	-4.020146140	-13.516841774
1	-4.892776882	-3.130462424	-12.394637282

E = -128.747616240412 Eh

ZPVE = 0.736703911903 Eh

Compound Pt-1 (T1)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	0.134159000	-2.322253000	-0.121803000
6	0.178530000	-0.371916000	-0.067908000
6	0.247402000	0.897128000	-0.036293000
6	0.142315000	-4.307733000	-0.180038000
6	0.200509000	-5.538030000	-0.221826000
6	-1.880119000	-2.310875000	0.031851000
7	-2.759798000	-1.713399000	-0.809667000
7	-2.619378000	-2.901735000	1.002590000
6	2.148856000	-2.356890000	-0.273621000
7	2.872059000	-2.897285000	-1.284087000
7	3.042423000	-1.861633000	0.617106000
6	0.352854000	2.250499000	-0.006760000
6	-0.815635000	3.122014000	0.101564000
6	1.654134000	2.917566000	-0.088424000
6	-0.681746000	4.477961000	0.114027000

6	1.750093000	4.279415000	-0.074072000
6	0.599544000	5.128069000	0.022965000
1	-1.796446000	2.654516000	0.176920000
1	2.542999000	2.293626000	-0.171214000
1	-1.581788000	5.090360000	0.197556000
1	2.739156000	4.734113000	-0.141587000
6	0.307582000	-6.954012000	-0.267885000
6	1.565898000	-7.583913000	-0.189000000
6	-0.831489000	-7.776260000	-0.393932000
6	1.674054000	-8.969030000	-0.231042000
6	-0.707859000	-9.158724000	-0.435529000
6	0.544184000	-9.793282000	-0.354091000
1	2.455220000	-6.963530000	-0.087109000
1	-1.811438000	-7.306264000	-0.461823000
1	2.666447000	-9.416114000	-0.164214000
1	-1.614800000	-9.758487000	-0.534737000
6	-2.098138000	-3.645159000	2.124183000
1	-2.442052000	-4.684706000	2.084700000
1	-1.008187000	-3.639230000	2.063987000
1	-2.423944000	-3.183409000	3.063689000
6	-2.419785000	-0.971637000	-1.999960000
1	-2.915514000	-1.414943000	-2.871580000
1	-2.723076000	0.076394000	-1.897505000
1	-1.336130000	-1.009440000	-2.130038000
6	2.717876000	-1.201948000	1.858985000
1	1.632530000	-1.215582000	1.979950000
1	3.192668000	-1.726443000	2.696473000
1	3.054378000	-0.159268000	1.838186000
6	2.330637000	-3.531907000	-2.461672000
1	2.721247000	-3.042313000	-3.361370000
1	2.589271000	-4.596547000	-2.475716000
1	1.243187000	-3.441761000	-2.431226000
14	0.713246000	6.995527000	0.017309000
14	0.669663000	-11.673226000	-0.403069000
6	-0.215220000	7.688134000	-1.476432000
1	0.231197000	7.331343000	-2.412751000
1	-1.266335000	7.373006000	-1.466216000
1	-0.192181000	8.785848000	-1.480273000
6	2.519607000	7.531212000	-0.064067000
1	3.087765000	7.152526000	0.794999000
1	3.003146000	7.168435000	-0.979857000
1	2.593574000	8.626138000	-0.058173000
6	-0.082558000	7.690447000	1.583995000
1	-1.126781000	7.364923000	1.672920000
1	0.451337000	7.346531000	2.478468000
1	-0.071370000	8.788250000	1.577676000
6	-0.295471000	-12.398754000	1.046651000
1	-1.348980000	-12.093868000	1.010570000
1	-0.261509000	-13.495835000	1.033743000
1	0.119370000	-12.053893000	2.001821000
6	2.476888000	-12.194229000	-0.284070000
1	2.930654000	-11.852392000	0.654663000
1	2.560088000	-13.287989000	-0.316568000
1	3.066423000	-11.789400000	-1.116319000
6	-0.071238000	-12.305540000	-2.018497000
1	0.479733000	-11.909712000	-2.880631000
1	-0.040034000	-13.401726000	-2.065380000
1	-1.118374000	-11.993541000	-2.119985000
6	-5.287152000	-1.512036000	-0.891964000
6	-6.424955000	-1.904180000	-0.188841000
6	-4.057451000	-1.917404000	-0.381087000
1	-7.405809000	-1.606777000	-0.555137000
6	-6.333848000	-2.672710000	0.981323000
6	-3.966585000	-2.685536000	0.787398000
1	-7.245626000	-2.959092000	1.502216000
6	-5.101667000	-3.077791000	1.491194000
1	-5.031500000	-3.675386000	2.397497000
1	-5.358964000	-0.913505000	-1.797542000
6	5.350108000	-3.139958000	-1.766389000
6	4.224764000	-2.755075000	-1.043069000
6	6.592370000	-2.828773000	-1.216708000
1	7.497015000	-3.113442000	-1.750827000
6	4.335053000	-2.084278000	0.182399000
6	6.702802000	-2.157340000	0.010224000
1	7.691185000	-1.931845000	0.406360000
6	5.574901000	-1.772345000	0.732787000

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1 5.661504000 -1.249524000 1.682836000
1 5.265199000 -3.663157000 -2.716363000
E = -21388.13890848 Eh
ZPVE = 0.76066906 Eh

Compound Pt-2 (So)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	-0.235952000	0.327366000	-0.313130000
6	-0.540306000	2.038845000	0.662587000
6	-0.528547000	3.098409000	1.287368000
6	0.095601000	-1.374426000	-1.292842000
6	0.144476000	-2.451304000	-1.884369000
6	-2.190411000	-0.043223000	-0.640251000
7	-3.036223000	0.692610000	-1.401435000
7	-2.876713000	-1.150354000	-0.265495000
6	1.725261000	0.700937000	-0.046240000
7	2.640437000	0.937883000	-1.016963000
7	2.365392000	0.872764000	1.135549000
6	-0.339589000	4.290075000	2.044858000
6	-1.412650000	5.032891000	2.573086000
6	0.967953000	4.744515000	2.301581000
6	-1.201289000	6.182835000	3.338731000
6	1.220816000	5.887868000	3.067028000
6	0.121421000	6.590899000	3.578268000
1	-2.423587000	4.680539000	2.369681000
1	1.792250000	4.169431000	1.876468000
6	0.057910000	-3.718310000	-2.527883000
6	1.197386000	-4.463969000	-2.879847000
6	-1.207186000	-4.270302000	-2.807761000
6	1.094261000	-5.720083000	-3.485476000
6	-1.352503000	-5.525183000	-3.405494000
6	-0.187697000	-6.233729000	-3.737001000
1	2.173891000	-4.033779000	-2.659456000
1	-2.084467000	-3.680908000	-2.540550000
6	-2.369519000	-2.209743000	0.572829000
1	-2.306262000	-3.147670000	0.009827000
1	-1.364370000	-1.937566000	0.899556000
1	-3.022801000	-2.340890000	1.443399000
6	-2.714047000	1.957807000	-2.015449000
1	-2.627365000	1.848084000	-3.103064000
1	-3.493086000	2.692536000	-1.784021000
1	-1.764912000	2.307434000	-1.601434000
6	1.774187000	0.714573000	2.442508000
1	0.746131000	0.371365000	2.314800000
1	2.343965000	-0.020225000	3.023181000
1	1.754287000	1.673999000	2.971806000
6	2.382715000	0.873251000	-2.435444000
1	2.342687000	1.880385000	-2.867372000
1	3.171863000	0.295647000	-2.928823000
1	1.427259000	0.365073000	-2.587524000
14	-2.629848000	7.176382000	4.066934000
14	2.998718000	6.452481000	3.352889000
14	-3.064232000	-6.233810000	-3.763489000
14	2.620845000	-6.727847000	-3.947713000
1	0.298597000	7.483941000	4.181680000
1	-0.280400000	-7.218096000	-4.203128000
6	-4.352353000	-5.313169000	-2.737530000
1	-4.392991000	-4.245436000	-2.986638000
1	-5.350969000	-5.733019000	-2.914306000
1	-4.133788000	-5.403718000	-1.665729000
6	-3.087114000	-8.062486000	-3.302053000
1	-4.078121000	-8.498201000	-3.483231000
1	-2.359872000	-8.635324000	-3.890920000
1	-2.841863000	-8.199501000	-2.241547000
6	-3.456634000	-6.043806000	-5.598231000
1	-2.701975000	-6.552633000	-6.211070000
1	-4.438098000	-6.470499000	-5.842140000
1	-3.461866000	-4.985135000	-5.885820000
6	4.180021000	-5.760516000	-3.518812000
1	4.228962000	-5.536595000	-2.445780000
1	5.073441000	-6.341296000	-3.781038000
1	4.223808000	-4.811100000	-4.067095000
6	2.594046000	-8.355702000	-2.994911000

1	1.677971000	-8.920347000	-3.209787000
1	3.451003000	-8.987116000	-3.262479000
1	2.626904000	-8.172917000	-1.913680000
6	2.578904000	-7.091639000	-5.798349000
1	3.440790000	-7.699427000	-6.102426000
1	1.667838000	-7.639284000	-6.070686000
1	2.593844000	-6.160218000	-6.377699000
6	4.049645000	4.963046000	3.842023000
1	3.652555000	4.483488000	4.745482000
1	4.069792000	4.216298000	3.038159000
1	5.085988000	5.265172000	4.041057000
6	3.045049000	7.748437000	4.720666000
1	2.477064000	8.645598000	4.443843000
1	2.626659000	7.355381000	5.655792000
1	4.079186000	8.058874000	4.917206000
6	3.679740000	7.187294000	1.755345000
1	4.725583000	7.499127000	1.872942000
1	3.633054000	6.451657000	0.942460000
1	3.093238000	8.062161000	1.448388000
6	-2.576578000	7.042461000	5.948116000
1	-3.371358000	7.640736000	6.412110000
1	-2.702582000	5.999952000	6.265822000
1	-1.614239000	7.396324000	6.338944000
6	-2.437010000	8.985255000	3.566505000
1	-1.479663000	9.392631000	3.915018000
1	-2.468517000	9.092379000	2.475123000
1	-3.239188000	9.600117000	3.994512000
6	-4.270065000	6.507801000	3.425374000
1	-4.320669000	6.563097000	2.330697000
1	-4.419977000	5.461801000	3.720877000
1	-5.105564000	7.092398000	3.830995000
6	-5.409121000	0.369804000	-2.242959000
6	-6.460801000	-0.543036000	-2.182674000
6	-4.249331000	0.045828000	-1.545181000
1	-7.383645000	-0.327465000	-2.718039000
6	-6.354502000	-1.735603000	-1.451547000
6	-4.144864000	-1.144489000	-0.811892000
1	-7.195124000	-2.426751000	-1.433903000
6	-5.193919000	-2.057027000	-0.749870000
1	-5.109738000	-2.985395000	-0.189412000
1	-5.491313000	1.290871000	-2.816042000
6	5.077717000	1.647330000	-1.027382000
6	3.856376000	1.291085000	-0.463046000
6	6.115006000	1.958670000	-0.149878000
1	7.084632000	2.245131000	-0.552912000
6	3.678088000	1.247184000	0.926939000
6	5.936127000	1.914468000	1.240876000
1	6.768951000	2.168635000	1.893871000
6	4.713111000	1.555303000	1.805207000
1	4.573831000	1.523754000	2.883707000
1	5.217568000	1.687041000	-2.105551000

E = -22206.85295790 Eh
ZPVE = 0.96786673 Eh

Compound Pt-2 (So)

GFN2

78	-0.050399463	1.223026734	-2.626424323
6	-0.480618731	2.964063018	-1.733568227
6	-0.395694226	4.004055853	-1.114248120
6	0.391341285	-0.506790551	-3.534076350
6	0.354875219	-1.519615506	-4.201191910
6	-1.793835574	0.880714216	-3.523646224
7	-2.101752856	1.197198067	-4.800973551
7	-2.783037016	0.083336839	-3.063378706
6	1.682244374	1.601099464	-1.717588884
7	2.642119059	2.437863420	-2.171951726
7	1.968211864	1.338366108	-0.422594758
6	-0.298308450	5.221759007	-0.397379144
6	-1.387271534	6.080953733	-0.256816979
6	0.920906272	5.573577285	0.181806018
6	-1.275688226	7.273372780	0.445961234
6	1.068047182	6.759024844	0.890401039
6	-0.041851279	7.589770575	1.010334340

1	-2.329391389	5.804540034	-0.709125387
1	1.766279349	4.905043406	0.072912028
6	0.323136435	-2.708978160	-4.970197959
6	1.416241542	-3.572392003	-5.027674747
6	-0.831232694	-3.024533016	-5.688586134
6	1.372998689	-4.735203160	-5.785552789
6	-0.907955467	-4.178176129	-6.456690614
6	0.204304703	-5.015219290	-6.488693173
1	2.306745065	-3.322117452	-4.468609633
1	-1.677199170	-2.350996138	-5.640134736
6	-2.798797462	-0.481732502	-1.743900223
1	-2.634607371	-1.561045530	-1.786429158
1	-1.987556906	-0.013971036	-1.174812983
1	-3.751813627	-0.278661246	-1.252050200
6	-1.270292479	-2.014417944	-5.638509805
1	-0.788867415	1.408712531	-6.410137565
1	-1.860648781	2.801368477	-6.110920179
1	-0.502201422	2.467320534	-5.001521577
6	1.157676295	0.501888020	0.416313783
1	0.421270199	0.004690943	-0.224553412
1	1.772480883	-0.250151896	0.913955626
1	0.638196544	1.100868795	1.167972449
6	2.663908150	2.973012923	-3.503751126
1	2.395491304	4.032313287	-3.495391601
1	3.654112839	2.853087806	-3.946441031
1	1.929339750	2.417241499	-4.096781834
14	-2.765143595	8.427671214	0.662382572
14	2.751012615	7.190564570	1.647760869
14	-2.468489155	-4.633667962	-7.431169902
14	2.844716195	-5.926142665	-5.892541732
1	0.057194657	8.515068332	1.558195420
1	0.158333984	-5.917612822	-7.082821456
6	-3.764550974	-3.238336290	-7.326887446
1	-3.372725679	-2.299968824	-7.707266316
1	-4.648308505	-3.482746000	-7.908148009
1	-4.084965272	-3.066611064	-6.303921681
6	-3.216805515	-6.236337560	-6.707899982
1	-4.094674567	-6.549760577	-7.265172538
1	-2.500206381	-7.051490859	-6.737693903
1	-3.514280013	-6.101892648	-5.672082713
6	-2.015942402	-4.926177447	-9.263862388
1	-1.278362321	-5.716042260	-9.365971134
1	-2.887635971	-5.215632536	-9.843243917
1	-1.600339689	-4.031582798	-9.717933247
6	4.262886266	-5.372004379	-4.744108246
1	3.936985765	-5.312018792	-3.710233954
1	5.091524447	-6.072450116	-4.785813364
1	4.645641119	-4.396433885	-5.027623658
6	2.276343132	-7.677292243	-5.381911087
1	1.479568740	-8.035389253	-6.026496576
1	3.092816329	-8.390649058	-5.443416266
1	1.902013467	-7.691365143	-4.362645729
6	3.479337893	-5.976640167	-7.694338812
1	4.296314809	-6.683329099	-7.806364278
1	2.691131607	-6.274163432	-8.379250558
1	3.838792976	-5.003239891	-8.014739774
6	3.238456181	5.837140198	2.904788840
1	2.526459250	5.778933275	3.722675784
1	3.273446060	4.861854013	2.428450579
1	4.217912919	6.028633620	3.332847153
6	2.696326491	8.883240229	2.523810238
1	2.432577181	9.678899815	1.833925796
1	1.970593022	8.890019668	3.331125501
1	3.663323511	9.128962551	2.952049978
6	4.064734085	7.241324981	0.261211883
1	5.049622699	7.470038891	0.657345289
1	4.128758645	6.282993331	-0.244955523
1	3.826401822	7.993408012	-0.485057354
6	-3.625432687	8.039719665	2.324855633
1	-4.493731031	8.673482968	2.479213669
1	-3.959720009	7.007104290	2.362832510
1	-2.950838774	8.195010400	3.161635212
6	-2.187982927	10.247410473	0.664869659
1	-1.576812986	10.468448909	1.534175320
1	-1.599528225	10.479111145	-0.217745415
1	-3.035716243	10.925700522	0.683177484

6	-4.012075174	8.178664697	-0.761134496
1	-3.529716271	8.259018649	-1.730594110
1	-4.484642645	7.202806846	-0.708689565
1	-4.800962841	8.923844323	-0.723518332
6	-3.998874066	0.586124943	-6.354920210
6	-5.170157823	-0.149790178	-6.378626703
6	-3.275827678	0.587144825	-5.173445593
1	-5.758584929	-0.177153602	-7.282733100
6	-5.605693872	-0.864813910	-5.265735331
6	-3.716855242	-0.134455168	-4.048227297
1	-6.522805335	-1.430093439	-5.331118730
6	-4.888748278	-0.872221418	-4.082336285
1	-5.226546126	-1.432472914	-3.224543948
1	-3.661851469	1.132376490	-7.221974380
6	4.642873803	3.559899713	-1.111559445
6	3.524822749	2.743892623	-1.163978117
6	5.309096347	3.643163983	0.098578302
1	6.181324522	4.273309234	0.179163107
6	3.088549920	2.031484383	-0.030986736
6	4.877438432	2.938332182	1.219016002
1	5.425770458	3.035592415	2.143410712
6	3.761495749	2.120875495	1.176236719
1	3.426603883	1.582485361	2.048900612
1	4.977672243	4.112414403	-1.975580173
E = -153.188585021420 Eh			
ZPVE = 0.939659432626 Eh			

Compound Pt-2 (T1)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	0.082746000	0.138548000	-0.088262000
6	-0.220715000	1.851358000	0.869084000
6	-0.281023000	2.937757000	1.447050000
6	0.345825000	-1.514065000	-1.093837000
6	0.318336000	-2.600673000	-1.751342000
6	-1.896045000	-0.219173000	-0.299847000
7	-2.793992000	0.552049000	-0.959905000
7	-2.563998000	-1.329666000	0.099482000
6	2.056282000	0.531741000	0.097178000
7	2.947150000	0.717296000	-0.908399000
7	2.726164000	0.774702000	1.251123000
6	-0.234070000	4.189835000	2.118314000
6	-1.402976000	4.879006000	2.498043000
6	1.009168000	4.776489000	2.424544000
6	-1.347619000	6.107137000	3.160818000
6	1.105885000	6.001534000	3.091757000
6	-0.084371000	6.649774000	3.451768000
1	-2.362069000	4.419789000	2.259977000
1	1.908552000	4.240574000	2.117913000
6	0.133626000	-3.749610000	-2.451269000
6	1.232102000	-4.591049000	-2.924822000
6	-1.227897000	-4.190612000	-2.773519000
6	1.003296000	-5.734777000	-3.643456000
6	-1.470238000	-5.331193000	-3.492517000
6	-0.352532000	-6.114352000	-3.935876000
1	2.244505000	-4.270787000	-2.679217000
1	-2.044816000	-3.557264000	-2.426438000
6	-2.008533000	-2.427795000	0.853986000
1	-1.978035000	-3.337337000	0.243255000
1	-0.986943000	-2.167945000	1.139031000
1	-2.612113000	-2.602665000	1.752269000
6	-2.515217000	1.827168000	-1.575113000
1	-2.595357000	1.750009000	-2.665977000
1	-3.221354000	2.580662000	-1.209156000
1	-1.503650000	2.130773000	-1.296714000
6	2.179957000	0.679653000	2.583783000
1	1.170534000	0.270706000	2.515457000
1	2.808981000	0.021334000	3.194145000
1	2.119546000	1.671229000	3.046238000
6	2.667526000	0.581434000	-2.317489000
1	2.790665000	1.546468000	-2.823399000
1	3.341723000	-0.156254000	-2.766755000
1	1.638148000	0.233473000	-2.430620000
14	-2.909638000	7.041217000	3.659608000

14	2.800320000	6.753520000	3.445332000
14	-3.222253000	-5.872510000	-3.910719000
14	2.411991000	-6.817706000	-4.259492000
1	-0.027506000	7.605365000	3.977845000
1	-0.535642000	-7.024760000	-4.509452000
6	-4.472791000	-4.719504000	-3.097312000
1	-4.351093000	-3.682051000	-3.432865000
1	-5.495474000	-5.032285000	-3.344070000
1	-4.373196000	-4.732175000	-2.004889000
6	-3.486269000	-7.634354000	-3.285309000
1	-4.491138000	-7.997765000	-3.536236000
1	-2.758052000	-8.323194000	-3.731749000
1	-3.365647000	-7.682990000	-2.195873000
6	-3.449339000	-5.846069000	-5.783948000
1	-2.708912000	-6.489135000	-6.276181000
1	-4.448285000	-6.200151000	-6.069562000
1	-3.319847000	-4.829204000	-6.174747000
6	4.066285000	-6.142971000	-3.659981000
1	4.112070000	-6.118310000	-2.564075000
1	4.888747000	-6.775581000	-4.017207000
1	4.240191000	-5.125557000	-4.032171000
6	2.161338000	-8.572699000	-3.611156000
1	1.188710000	-8.971524000	-3.925591000
1	2.940266000	-9.249881000	-3.984569000
1	2.189015000	-8.588767000	-2.514516000
6	2.381151000	-6.849280000	-6.146824000
1	3.154591000	-7.517282000	-6.547336000
1	1.408562000	-7.197631000	-6.516650000
1	2.551149000	-5.844442000	-6.553060000
6	3.984405000	5.392258000	3.999908000
1	3.603652000	4.884261000	4.894801000
1	4.127011000	4.638284000	3.214889000
1	4.969866000	5.812263000	4.239270000
6	2.645995000	8.054032000	4.800791000
1	2.009397000	8.890594000	4.486422000
1	2.218277000	7.625294000	5.715699000
1	3.632801000	8.465584000	5.048539000
6	3.466543000	7.552262000	1.872471000
1	4.460639000	7.987739000	2.036833000
1	3.547188000	6.812014000	1.066552000
1	2.796316000	8.349488000	1.527668000
6	-2.868238000	7.361200000	5.517914000
1	-3.751824000	7.926217000	5.841532000
1	-2.842514000	6.416366000	6.074699000
1	-1.978436000	7.938811000	5.798468000
6	-2.953397000	8.691857000	2.747376000
1	-2.061259000	9.288352000	2.976306000
1	-2.980671000	8.535688000	1.661850000
1	-3.835420000	9.280077000	3.031579000
6	-4.431729000	6.022738000	3.215801000
1	-4.485378000	5.832999000	2.136394000
1	-4.428379000	5.054536000	3.731998000
1	-5.345669000	6.555620000	3.507344000
6	-5.242353000	0.299229000	-1.576646000
6	-6.303406000	-0.593858000	-1.438414000
6	-4.027345000	-0.069720000	-1.006375000
1	-7.269570000	-0.343417000	-1.872502000
6	-6.153398000	-1.809600000	-0.754694000
6	-3.878086000	-1.284008000	-0.323280000
1	-7.004190000	-2.483263000	-0.672814000
6	-4.936746000	-2.176544000	-0.183025000
1	-4.818962000	-3.121938000	0.341906000
1	-5.359793000	1.240370000	-2.109462000
6	5.382216000	1.420383000	-1.021207000
6	4.175551000	1.101215000	-0.405195000
6	6.439588000	1.786787000	-0.190246000
1	7.399390000	2.045851000	-0.633328000
6	4.030868000	1.142324000	0.988119000
6	6.293454000	1.832158000	1.204303000
1	7.141576000	2.127557000	1.819156000
6	5.085157000	1.509564000	1.820084000
1	4.971562000	1.549704000	2.901363000
1	5.496276000	1.388203000	-2.102610000

E = -22206.75325052 Eh

ZPVE = 0.96381567 Eh

Compound Pt-3 (So)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	0.387952000	-2.327431000	-0.204991000
6	0.380437000	-0.333516000	-0.172155000
6	0.383336000	0.895854000	-0.140619000
6	0.399859000	-4.321662000	-0.227614000
6	0.408937000	-5.551266000	-0.237162000
6	-1.621842000	-2.352467000	-0.084982000
7	-2.497418000	-1.829068000	-0.977392000
7	-2.365856000	-2.917307000	0.896910000
6	2.398033000	-2.326652000	-0.327804000
7	3.146142000	-2.859862000	-1.324201000
7	3.269611000	-1.812082000	0.573549000
6	0.391936000	2.319446000	-0.092640000
6	-0.768653000	3.049040000	0.231768000
6	1.558537000	3.054809000	-0.361139000
6	-0.750621000	4.435245000	0.285711000
6	1.564599000	4.445724000	-0.304684000
6	0.414278000	5.172854000	0.021365000
1	-1.686751000	2.504542000	0.446495000
1	2.469214000	2.516465000	-0.618900000
1	-1.672661000	4.955948000	0.544046000
1	2.494702000	4.965802000	-0.522542000
6	0.418531000	-6.975610000	-0.248552000
6	1.610137000	-7.702602000	-0.089085000
6	-0.768573000	-7.714756000	-0.418937000
6	1.613757000	-9.094700000	-0.098767000
6	-0.752789000	-9.102043000	-0.427044000
6	0.436050000	-9.831406000	-0.267339000
1	2.542332000	-7.156810000	0.048114000
1	-1.706455000	-7.176935000	-0.548561000
1	2.564002000	-9.607825000	0.031040000
1	-1.696331000	-9.630761000	-0.562207000
6	-1.843428000	-3.587986000	2.062736000
1	-2.192876000	-4.626066000	2.090847000
1	-0.753737000	-3.592597000	1.994836000
1	-2.160625000	-3.065724000	2.973206000
6	-2.140657000	-1.134266000	-2.191036000
1	-2.440753000	-1.719360000	-3.068611000
1	-2.629137000	-0.154015000	-2.218511000
1	-1.058994000	-0.983274000	-2.194122000
6	2.908874000	-1.148198000	1.803268000
1	1.824074000	-1.023920000	1.820302000
1	3.233018000	-1.741715000	2.666477000
1	3.372666000	-0.156438000	1.843814000
6	2.628956000	-3.512702000	-2.502431000
1	2.947941000	-2.974561000	-3.402931000
1	2.980542000	-4.549521000	-2.546602000
1	1.539078000	-3.520642000	-2.438345000
6	-5.027610000	-1.737368000	-1.142493000
6	-6.170130000	-2.134662000	-0.449811000
6	-3.798743000	-2.062251000	-0.575490000
1	-7.150315000	-1.899358000	-0.860455000
6	-6.084472000	-2.831935000	0.764535000
6	-3.713399000	-2.762092000	0.636199000
1	-6.999563000	-3.125637000	1.275537000
6	-4.853049000	-3.158249000	1.330014000
1	-4.786644000	-3.700822000	2.270636000
1	-5.095464000	-1.197833000	-2.084776000
6	5.634948000	-3.058281000	-1.769962000
6	4.492403000	-2.692832000	-1.064142000
6	6.863727000	-2.727756000	-1.201165000
1	7.780971000	-2.997766000	-1.721293000
6	4.572473000	-2.018841000	0.162435000
6	6.944098000	-2.056186000	0.027966000
1	7.922411000	-1.816493000	0.440535000
6	5.798686000	-1.689701000	0.732707000
1	5.862221000	-1.169616000	1.686154000
1	5.572900000	-3.580931000	-2.722095000
6	0.384809000	6.699659000	0.096594000
6	1.751120000	7.319107000	-0.204111000
6	-0.039157000	7.130068000	1.509291000
1	-1.034179000	6.749809000	1.767691000

1	0.666623000	6.753780000	2.260088000
1	-0.068876000	8.225228000	1.585364000
1	2.514735000	6.985878000	0.509824000
1	1.686405000	8.412050000	-0.133408000
1	2.095943000	7.072418000	-1.216041000
6	0.400315000	-11.359911000	-0.275438000
6	-0.196706000	-12.849515000	-1.603811000
6	-0.472164000	-11.849289000	0.891159000
1	-0.063720000	-11.510637000	1.851380000
1	-1.498904000	-11.472695000	0.815185000
1	-0.517265000	-12.946555000	0.905602000
1	-1.216932000	-11.477614000	-1.753949000
1	0.409441000	-11.509602000	-2.452564000
6	-0.626455000	7.237040000	-0.928109000
1	-0.347996000	6.936397000	-1.945749000
1	-1.637861000	6.860804000	-0.734928000
1	-0.664989000	8.334077000	-0.893084000
6	1.794921000	-11.970661000	-0.122837000
1	2.262617000	-11.684185000	0.827271000
1	1.724572000	-13.065379000	-0.139940000
1	2.462382000	-11.668530000	-0.939557000
1	-0.234208000	-12.946793000	-1.627407000

E = -20883.77940109 Eh

ZPVE = 0.78616912 Eh

Compound Pt-3 (So)

GFN2

78	-2.918854577	4.929502462	-6.914709748
6	-3.293541536	6.727998619	-6.116167334
6	-3.260408105	7.763862169	-5.485596383
6	-2.538603866	3.132709192	-7.714154008
6	-2.565869597	2.103899944	-8.356636995
6	-4.726186076	4.529459631	-7.651105267
7	-5.080426712	4.567179723	-8.954956422
7	-5.722988613	3.900858321	-6.988458464
6	-1.118659439	5.303929339	-6.152863187
7	-0.140788065	6.037074054	-6.728716536
7	-0.752167494	5.092087743	-4.869290172
6	-3.251932877	8.975656732	-4.754695210
6	-4.308919883	9.883834002	-4.825732328
6	-2.170683732	9.288292105	-3.931021564
6	-4.278406200	11.051063910	-4.093191894
6	-2.152863661	10.460524938	-3.200100314
6	-3.205456888	11.367011452	-3.260824745
1	-5.154770184	9.662382392	-5.462296536
1	-1.336023821	8.600956868	-3.866241681
6	-2.566786898	0.904883621	-9.108096996
6	-1.481655898	0.030823521	-9.100496233
6	-3.671386806	0.576343393	-9.897193170
6	-1.499039491	-1.124588687	-9.858046122
6	-3.675557392	-0.577618198	-10.650542668
6	-2.591726533	-1.454527035	-10.652199494
1	-0.617903558	0.266309067	-8.493623847
1	-4.529684353	1.236881531	-9.913124186
6	-5.709247280	3.657504853	-5.573542733
1	-5.593888637	2.590911401	-5.367341030
1	-4.859909479	4.205663532	-5.150701416
1	-6.633480121	4.015253552	-5.116366760
6	-4.256457967	5.129113030	-9.987354960
1	-3.842260723	4.339776965	-10.619104999
1	-4.833522722	5.822368520	-10.601586620
1	-3.435717591	5.666780936	-9.500551599
6	-1.553903196	4.365413387	-3.925694942
1	-2.368284718	3.887551884	-4.482635840
1	-0.957058078	3.599760754	-3.427144928
1	-1.974850181	5.041577096	-3.177768272
6	-0.180749913	6.483762204	-8.092257191
1	-0.267775730	7.571489456	-8.137002824
1	0.718240544	6.169518396	-8.625743991
1	-1.060684968	6.030143096	-8.561927938
6	-7.049685289	3.683402066	-10.268199728
6	-8.237500955	2.997321173	-10.087206374
6	-6.286502571	3.935012996	-9.139930400

1	-8.856648697	2.778958350	-10.943932288
6	-8.653216780	2.577194582	-8.826376634
6	-6.704841432	3.506742816	-7.866116387
1	-9.586508857	2.043308926	-8.732085396
6	-7.896884753	2.822832793	-7.694171960
1	-8.219870264	2.489941978	-6.720351319
1	-6.728870955	4.001772692	-11.247643378
6	2.024263440	7.040360855	-5.898816557
6	0.843874339	6.321071449	-5.812734685
6	2.792747863	7.132496703	-4.752034612
1	3.718058334	7.687400817	-4.779828690
6	0.447376732	5.710172688	-4.608164862
6	2.400039485	6.529469576	-3.559909547
1	3.029070613	6.630004633	-2.688605476
6	1.223020629	5.808411878	-3.464797562
1	0.920690915	5.347495697	-2.537581378
1	2.329324999	7.513056086	-6.819059371
1	-4.547928641	-0.794073414	-11.251123392
1	-0.634496638	-1.768611024	-9.819019796
1	-5.116012547	11.729346977	-4.174836370
1	-1.294539827	10.654843601	-2.576010330
6	-3.229007849	12.666665962	-2.471115092
6	-1.989172238	12.847294404	-1.590750998
6	-4.464476748	12.680895266	-1.559398498
1	-5.383490399	12.624621271	-2.136320267
1	-4.438234896	11.832769305	-0.877804339
1	-4.487837827	13.596431640	-0.971191082
1	-1.905175466	12.042212783	-0.864018564
1	-2.064519096	13.786299871	-1.045208188
1	-1.083170393	12.880282997	-2.191797094
6	-2.644807461	-2.707501666	-11.512656936
6	-3.850013976	-3.560807113	-11.092373496
6	-1.385683433	-3.569002495	-11.382130939
1	-0.501444723	-3.021567941	-11.700821238
1	-1.246424137	-3.904833036	-10.356916544
1	-1.481025040	-4.449874845	-12.014591844
1	-3.764696177	-3.840353870	-10.044023736
1	-3.894585828	-4.469534931	-11.689906946
1	-4.783700202	-3.020988935	-11.224949388
6	-2.789965270	-2.295250480	-12.984751862
1	-1.947073368	-1.675921591	-13.285740955
1	-2.816478922	-3.176731855	-13.622739398
1	-3.702944396	-1.728787139	-13.147872481
6	-3.294867193	13.847009379	-3.450861824
1	-2.427618777	13.837834687	-4.108423939
1	-4.188582336	13.799073162	-4.067178557
1	-3.306013574	14.789314994	-2.906188843

E = -129.641884651249 Eh

ZPVE = 0.756961311062 Eh

Compound Pt-3 (T1)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	0.150706000	-2.317835000	0.054016000
6	0.177457000	-0.368131000	0.073187000
6	0.231963000	0.902750000	0.052263000
6	0.171367000	-4.303102000	-0.002656000
6	0.233902000	-5.531504000	-0.080888000
6	-1.861912000	-2.327872000	0.218077000
7	-2.755472000	-1.751617000	-0.624506000
7	-2.588372000	-2.923540000	1.196280000
6	2.163945000	-2.338944000	-0.109481000
7	2.887136000	-2.895254000	-1.112312000
7	3.059411000	-1.818491000	0.766088000
6	0.315949000	2.256736000	0.019395000
6	-0.866511000	3.118846000	0.070409000
6	1.600933000	2.942898000	-0.082275000
6	-0.754461000	4.481366000	0.008573000
6	1.673607000	4.300725000	-0.139958000
6	0.504622000	5.137793000	-0.104444000
1	-1.842385000	2.645364000	0.162640000
1	2.503416000	2.334585000	-0.120527000
1	-1.664728000	5.076333000	0.048953000
1	2.655315000	4.767492000	-0.219817000

Publications & Manuscripts

6	0.347265000	-6.942505000	-0.202062000
6	1.606476000	-7.565009000	-0.282011000
6	-0.788451000	-7.775827000	-0.263523000
6	1.722374000	-8.943773000	-0.426962000
6	-0.659535000	-9.149403000	-0.404821000
6	0.596050000	-9.772469000	-0.495441000
1	2.500789000	-6.946020000	-0.226199000
1	-1.776161000	-7.321359000	-0.205622000
1	2.719565000	-9.373705000	-0.487851000
1	-1.565679000	-9.753326000	-0.450538000
6	-2.050085000	-3.648394000	2.321676000
1	-2.368245000	-4.696317000	2.287585000
1	-0.960457000	-3.615763000	2.261197000
1	-2.387449000	-3.189510000	3.258590000
6	-2.432251000	-1.017344000	-1.823946000
1	-2.925935000	-1.477088000	-2.688291000
1	-2.749848000	0.027349000	-1.731124000
1	-1.348636000	-1.041491000	-1.958609000
6	2.736945000	-1.136774000	1.996264000
1	1.652445000	-1.158950000	2.124829000
1	3.223084000	-1.639279000	2.840811000
1	3.062656000	-0.091358000	1.952070000
6	2.345261000	-3.552882000	-2.276986000
1	2.747989000	-3.089720000	-3.185329000
1	2.589677000	-4.620930000	-2.263909000
1	1.258829000	-3.448716000	-2.255696000
6	-5.286209000	-1.596275000	-0.699894000
6	-6.414865000	-2.004088000	0.009475000
6	-4.047693000	-1.974998000	-0.189893000
1	-7.402051000	-1.727894000	-0.356487000
6	-6.306360000	-2.761800000	1.184988000
6	-3.939494000	-2.732829000	0.984062000
1	-7.211202000	-3.061129000	1.710732000
6	-5.065252000	-3.140430000	1.694072000
1	-4.981428000	-3.730311000	2.604277000
1	-5.371593000	-1.006349000	-1.609931000
6	5.364303000	-3.131763000	-1.600695000
6	4.239588000	-2.739169000	-0.880551000
6	6.607296000	-2.799859000	-1.064333000
1	7.511277000	-3.089896000	-1.596731000
6	4.351129000	-2.041266000	0.329784000
6	6.718921000	-2.101263000	0.146974000
1	7.707558000	-1.860319000	0.533338000
6	5.591495000	-1.708632000	0.866682000
1	5.679020000	-1.164796000	1.804795000
1	5.278408000	-3.676655000	-2.538304000
6	0.662272000	6.647353000	-0.191347000
6	1.363648000	7.010615000	-1.512245000
6	1.518655000	7.140970000	0.988488000
1	1.035796000	6.905723000	1.944902000
1	2.510644000	6.674602000	0.992583000
1	1.660996000	8.228868000	0.933967000
1	2.350883000	6.540812000	-1.590277000
1	1.502978000	8.097554000	-1.589055000
1	0.768208000	6.679449000	-2.371888000
6	0.685462000	-11.289070000	-0.665669000
6	-0.043467000	-11.696075000	-1.955838000
6	0.020702000	-11.976627000	0.536854000
1	0.525740000	-11.702438000	1.471246000
1	-1.034339000	-11.695293000	0.633922000
1	0.067292000	-13.068638000	0.430059000
1	-1.101873000	-11.412120000	-1.930340000
1	0.007988000	-12.783520000	-2.100585000
1	0.410459000	-11.212620000	-2.829712000
6	2.133114000	-11.775594000	-0.758463000
1	2.702433000	-11.537524000	0.148736000
1	2.151239000	-12.865487000	-0.882545000
1	2.655257000	-11.335654000	-1.617333000
6	-0.682636000	7.375061000	-0.146972000
1	-1.330604000	7.081921000	-0.982414000
1	-1.220565000	7.179667000	0.789158000
1	-0.522531000	8.458409000	-0.216274000

E = -20883.67804177 Eh

ZPVE = 0.78264060 Eh

Compound Pt-4 (So)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	-0.003002000	0.094119000	0.005379000
6	-0.394726000	1.786636000	0.979606000
6	-0.435367000	2.879213000	1.542186000
6	0.369464000	-1.554729000	-1.050605000
6	0.359785000	-2.577278000	-1.733673000
6	-1.937470000	-0.393090000	-0.274227000
7	-2.841525000	0.293879000	-1.013695000
7	-2.547629000	-1.540499000	0.109554000
6	1.924615000	0.638223000	0.221753000
7	2.768373000	1.017322000	-0.768190000
7	2.574658000	0.866926000	1.388410000
6	-0.298869000	4.143773000	2.183321000
6	-1.407002000	4.907002000	2.584184000
6	0.994120000	4.648628000	2.414390000
6	-1.243061000	6.149686000	3.197417000
6	1.193168000	5.883591000	3.026952000
6	0.060942000	6.614875000	3.407154000
1	-2.396774000	4.499127000	2.399506000
1	1.836169000	4.045140000	2.085930000
6	0.132847000	-3.748555000	-2.512654000
6	1.154910000	-4.637110000	-2.862352000
6	-1.183150000	-4.027113000	-2.940121000
6	0.893865000	-5.785461000	-3.619902000
6	-1.477169000	-5.156822000	-3.693404000
6	-0.421222000	-6.025039000	-4.020798000
1	2.165677000	-4.411668000	-2.526666000
1	-1.960568000	-3.319270000	-2.664865000
6	-1.945186000	-2.585295000	0.902058000
1	-1.804737000	-3.488778000	0.297871000
1	-0.965267000	-2.240041000	1.236679000
1	-2.578462000	-2.807476000	1.768823000
6	-2.609420000	1.578376000	-1.628690000
1	-2.519376000	1.474766000	-2.716654000
1	-3.437444000	2.256318000	-1.394322000
1	-1.685901000	1.994590000	-1.217998000
6	2.040915000	0.616190000	2.704971000
1	1.084167000	0.102627000	2.593655000
1	2.736038000	-0.010060000	3.276043000
1	1.865062000	1.560190000	3.233388000
6	2.472050000	0.951483000	-2.179113000
1	2.279548000	1.953567000	-2.580688000
1	3.314721000	0.499930000	-2.713881000
1	1.588249000	0.322547000	-2.314700000
1	0.200753000	7.584887000	3.883125000
1	-0.641080000	-6.912612000	-4.608937000
6	-5.206508000	-0.169949000	-1.809441000
6	-6.202400000	-1.141838000	-1.726679000
6	-4.015446000	-0.425204000	-1.136619000
1	-7.147594000	-0.980188000	-2.241548000
6	-6.012504000	-2.324380000	-0.996541000
6	-3.825295000	-1.608381000	-0.408913000
1	-6.812994000	-3.060871000	-0.958091000
6	-4.819498000	-2.578497000	-0.322350000
1	-4.669908000	-3.497506000	0.240219000
1	-5.354285000	0.744901000	-2.379329000
6	5.074342000	2.076441000	-0.829651000
6	3.938726000	1.529093000	-0.240180000
6	6.080206000	2.522835000	0.026090000
1	6.982099000	2.961934000	-0.396379000
6	3.813081000	1.429895000	1.152976000
6	5.954085000	2.423075000	1.419596000
1	6.759244000	2.787527000	2.054824000
6	4.817797000	1.871485000	2.008742000
1	4.717843000	1.799881000	3.089650000
1	5.171426000	2.160819000	-1.909941000
6	-2.895341000	-5.475632000	-4.172680000
6	-3.335359000	-6.825482000	-3.585906000
6	-2.904239000	-5.553787000	-5.706778000
1	-2.582103000	-4.601569000	-6.146074000
1	-2.232406000	-6.336075000	-6.078712000
1	-3.914478000	-5.777084000	-6.075122000

1	-2.668922000	-7.639627000	-3.893635000	6	1.308530424	-4.595106185	-6.165114802
1	-4.350591000	-7.078344000	-3.919750000	6	-1.070059745	-4.137684462	-6.409255851
1	-3.334621000	-6.791097000	-2.489285000	6	0.051241021	-4.920726066	-6.663355200
6	2.049333000	-6.722538000	-3.980242000	1	2.393433719	-3.156583668	-4.984665901
6	1.588200000	-7.926680000	-4.803253000	1	-1.759470449	-2.363421754	-5.409517748
6	2.700321000	-7.241900000	-2.689388000	6	-2.433735151	-0.798762308	-1.616076930
1	3.082726000	-6.422936000	-2.069439000	1	-2.127692036	-1.845600933	-1.680144055
1	1.976294000	-7.804456000	-2.086960000	1	-1.656038189	-0.224887230	-1.099521438
1	3.541691000	-7.907772000	-2.923505000	1	-3.369526315	-0.727407161	-1.058959628
1	0.855998000	-8.535743000	-4.258413000	6	-1.509709813	1.857721898	-5.593963090
1	2.447287000	-8.569254000	-5.033063000	1	-1.019327891	1.312200476	-6.403718565
1	1.139680000	-7.621437000	-5.756962000	1	-2.223075650	2.568232817	-6.015086698
6	-2.429056000	7.011723000	3.638544000	1	-0.755047210	2.398960950	-5.012335681
6	-2.342002000	7.255316000	5.152649000	6	1.519456519	0.617008104	0.246599224
6	-3.772409000	6.345092000	3.335444000	1	0.821084191	0.024584215	-0.354943111
1	-3.904662000	6.167542000	2.261028000	1	2.261063363	-0.044155647	0.698596589
1	-3.876846000	5.385383000	3.856248000	1	0.968787004	1.136171674	1.034677204
1	-4.591943000	6.994575000	3.667724000	6	2.423680427	3.291280929	-3.725119658
1	-2.376916000	6.306017000	5.701187000	1	2.019288546	4.305644199	-3.682765493
1	-3.180237000	7.878292000	5.492150000	1	3.388873192	3.306494270	-4.234281371
1	-1.412348000	7.765648000	5.430046000	1	1.729715768	2.647263878	-4.276562386
6	2.589551000	6.457786000	3.278989000	1	-0.409666302	8.462492313	1.538020012
6	3.696945000	5.505419000	2.823174000	1	-0.057775194	-5.805091473	-7.263879893
6	2.767230000	6.719553000	4.781854000	6	-4.056880046	0.068052087	-6.139090125
1	2.028438000	7.435212000	5.160744000	6	-5.108787772	-0.830574944	-6.095324626
1	2.654633000	5.790877000	5.354909000	6	-3.274257071	0.181879327	-5.002040914
1	3.765267000	7.129663000	4.986306000	1	-5.735962234	-0.950890275	-6.965211945
1	3.655559000	4.547742000	3.356500000	6	-5.372279155	-1.590786965	-4.959146272
1	4.678075000	5.953990000	3.023898000	6	-3.541261622	-0.586248662	-3.852524166
1	3.644221000	5.293972000	1.748267000	1	-6.198078498	-2.285349712	-4.971504746
6	-3.905421000	-4.410551000	-3.739804000	6	-4.595510422	-1.483992860	-3.818475236
1	-3.657288000	-3.422606000	-4.146831000	1	-4.798313213	-2.081632216	-2.943598362
1	-4.905465000	-4.677129000	-4.104408000	1	-3.850692422	0.647960845	-7.024975322
1	-3.966732000	-4.317858000	-2.648906000	6	4.423784961	4.160037970	-1.439792739
6	3.087309000	-5.943672000	-4.802995000	6	3.443566040	3.181417525	-1.441568849
1	3.486996000	-5.089422000	-4.244855000	6	5.129140874	4.346731615	-0.263455518
1	3.930648000	-6.592464000	-5.074893000	1	5.894002906	5.106935844	-0.221965814
1	2.640620000	-5.557246000	-5.727570000	6	3.180377974	2.410766322	-0.293040818
6	-2.380588000	8.355458000	2.896014000	6	4.868468013	3.584866051	0.872318399
1	-1.456758000	8.06067000	3.108570000	1	5.437478807	3.769371637	1.770619720
1	-2.434003000	8.202723000	1.810964000	6	3.892054738	2.603731432	0.879340098
1	-3.225237000	8.990956000	3.194028000	1	3.687678816	2.022357171	1.764692528
6	2.736018000	7.776898000	2.505514000	1	4.622202831	4.760318051	-2.313947485
1	2.611742000	7.611934000	1.428171000	6	2.073005356	7.272639608	1.432845724
1	1.987295000	8.514480000	2.817523000	6	3.076866798	7.464860960	0.287479415
1	3.729099000	8.215164000	2.672558000	6	2.596941715	6.203860349	2.402371795
E = -21197.93450958 Eh				1	1.878443338	6.038611133	3.203031360
ZPVE = 1.01248076 Eh				1	2.767247238	5.258626403	1.893802364

Compound Pt-4 (So)

GFN2

78	0.018232802	1.211365866	-2.688755553	6	-3.965425617	7.014005724	1.338810728
6	-0.519229187	2.893584826	-1.744448243	6	-3.464070130	8.252765521	-0.787152735
6	-0.498671199	3.935580694	-1.122999860	1	-2.733671749	8.860804129	-1.317677500
6	0.525225042	-0.466942821	-3.660386639	1	-3.660880519	7.364172411	-1.380579986
6	0.437640742	-1.473514484	-4.333561474	1	-4.389793742	8.819209281	-0.703404247
6	-1.741047541	0.679269483	-3.451273502	1	-4.176550928	6.103784779	0.784341667
7	-2.172914248	0.947945787	-4.703385114	1	-4.898659048	7.559093010	1.468291468
7	-2.585488714	-0.237489443	-2.928531988	1	-3.589464436	6.734087652	2.321110155
6	1.757274182	1.783884041	-1.903013025	6	2.541151038	-5.445950062	-6.440140663
7	2.561522053	2.749735515	-2.402903105	6	2.240529068	-6.679513444	-7.296398750
7	2.154441545	1.560371914	-0.629462572	6	3.125191694	-5.927245563	-5.104413708
6	-0.495135689	5.156136340	-0.404225788	1	3.418568313	-5.090372362	-4.476757887
6	-1.657479715	5.904738302	-0.243973933	1	2.387358057	-6.516301021	-4.562825101
6	0.699528288	5.616259607	0.146897446	1	4.002602245	-6.547557347	-5.278145542
6	-1.640256065	7.101271214	0.456176412	1	1.524927600	-7.334209211	-6.803751706
6	0.744335405	6.808724976	0.851559910	1	3.158302321	-7.243789508	-7.452977171
6	-0.433241464	7.535736265	0.994506878	1	1.852094473	-6.395449720	-8.271985376
1	-2.570102963	5.525910344	-0.680965165	6	-2.452238768	-4.481972141	-6.947365603
1	1.591016414	5.018960843	0.010665318	6	-3.410571217	-4.685238584	-5.765588091
6	0.333292272	-2.647571989	-5.120098108	6	-2.465249175	-5.756934484	-7.795331396
6	1.437017216	-3.450725350	-5.392190223	1	-1.818041832	-5.656646637	-8.663832947
6	-0.914455654	-3.000714817	-5.632851118	1	-2.149602207	-6.619381808	-7.212498498
				1	-3.476934626	-5.944921703	-8.150915699

Publications & Manuscripts

1	-3.054945999	-5.493042154	-5.128660461
1	-4.405023120	-4.941330847	-6.126493412
1	-3.490307627	-3.783571801	-5.164281362
6	-2.951180841	-3.323755802	-7.822531592
1	-2.265507973	-3.157034336	-8.651206889
1	-3.934481436	-3.554773691	-8.228166334
1	-3.029251205	-2.402809609	-7.251129446
6	3.579001465	-4.593174204	-7.183484116
1	3.875128193	-3.729632740	-6.594315592
1	4.468753736	-5.182667960	-7.397143116
1	3.166248698	-4.236670012	-8.125430715
6	-2.762890488	9.183531300	1.403182299
1	-2.415066274	8.980059931	2.413574641
1	-2.061601518	9.854800684	0.912322134
1	-3.721411698	9.694705710	1.475305353
6	1.963452045	8.594863800	2.197327158
1	1.629396183	9.398773218	1.545135709
1	1.276469219	8.506815255	3.036091014
1	2.940932705	8.867680663	2.591488777

E = -154.978802621414 Eh

ZPVE = 0.980205837519 Eh

Compound Pt-4 (T₁)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	-0.073933000	0.219829000	-0.182697000
6	-0.454571000	1.906744000	0.793980000
6	-0.482927000	2.980127000	1.398223000
6	0.301112000	-1.405819000	-1.196771000
6	0.323217000	-2.502774000	-1.836013000
6	-2.021285000	-0.226274000	-0.483039000
7	-2.917341000	0.502629000	-1.192407000
7	-2.656659000	-1.368829000	-0.121667000
6	1.865262000	0.712118000	0.091905000
7	2.765107000	1.041004000	-0.867089000
7	2.479833000	0.921150000	1.281937000
6	-0.321402000	4.205650000	2.100544000
6	-1.412496000	4.953075000	2.575848000
6	0.983318000	4.685407000	2.328512000
6	-1.219756000	6.152204000	3.261970000
6	1.209853000	5.876997000	3.012278000
6	0.094340000	6.591205000	3.468249000
1	-2.410779000	4.566166000	2.391910000
1	1.810666000	4.096648000	1.940985000
6	0.160649000	-3.678166000	-2.495561000
6	1.273081000	-4.505375000	-2.951473000
6	-1.197066000	-4.159457000	-2.760327000
6	1.058197000	-5.693554000	-3.590145000
6	-1.424895000	-5.349043000	-3.391134000
6	-0.294723000	-6.124744000	-3.808276000
1	2.276251000	-4.136041000	-2.757335000
1	-2.014619000	-3.518109000	-2.440983000
6	-2.092746000	-2.437130000	0.668757000
1	-2.016861000	-3.355027000	0.074775000
1	-1.088097000	-2.140824000	0.977940000
1	-2.717455000	-2.615646000	1.551953000
6	-2.663434000	1.791835000	-1.788451000
1	-2.650437000	1.712286000	-2.882085000
1	-3.439249000	2.502618000	-1.483247000
1	-1.695809000	2.151960000	-1.430966000
6	1.891694000	0.700186000	2.581141000
1	0.940434000	0.182837000	2.442777000
1	2.564244000	0.086408000	3.191187000
1	1.695059000	1.655083000	3.081824000
6	2.531122000	0.979222000	-2.289236000
1	2.561806000	1.985158000	-2.724816000
1	3.288488000	0.349476000	-2.769239000
1	1.545499000	0.536181000	-2.453004000
1	0.255229000	7.527519000	4.001452000
1	-0.467561000	-7.072781000	-4.312444000
6	-5.307315000	0.127253000	-1.957896000
6	-6.328364000	-0.818704000	-1.884189000
6	-4.112885000	-0.179905000	-1.312589000
1	-7.276863000	-0.617222000	-2.378591000

6	-6.160270000	-2.025299000	-1.188750000
6	-3.944470000	-1.386620000	-0.620136000
1	-6.980316000	-2.740194000	-1.156158000
6	-4.964551000	-2.330284000	-0.541151000
1	-4.832920000	-3.267446000	-0.004981000
1	-5.438864000	1.061527000	-2.499448000
6	5.128785000	1.963769000	-0.846327000
6	3.940379000	1.491762000	-0.296742000
6	6.123825000	2.363401000	0.044466000
1	7.066339000	2.742743000	-0.345971000
6	3.754218000	1.416711000	1.090682000
6	5.936474000	2.290157000	1.432747000
1	6.735733000	2.615563000	2.095998000
6	4.747531000	1.812708000	1.981580000
1	4.601034000	1.760842000	3.058281000
1	5.274793000	2.023313000	-1.922762000
6	-2.384224000	6.998268000	3.784007000
6	-2.253510000	7.158908000	5.305957000
6	-3.741916000	6.360278000	3.483167000
1	-3.906267000	6.244005000	2.404839000
1	-3.840982000	5.373807000	3.952634000
1	-4.545615000	6.996648000	3.874245000
1	-2.278319000	6.181631000	5.803687000
1	-3.078860000	7.765824000	5.701366000
1	-1.314281000	7.650516000	5.584803000
6	2.617120000	6.424507000	3.262930000
6	3.703746000	5.497130000	2.714466000
6	2.838939000	6.584020000	4.774346000
1	2.113167000	7.271771000	5.223688000
1	2.742971000	5.618221000	5.285892000
1	3.843311000	6.979652000	4.976110000
1	3.672021000	4.507757000	3.186763000
1	4.693606000	5.926797000	2.913298000
1	3.617221000	5.355041000	1.630325000
6	-2.828356000	-5.883609000	-3.670923000
6	-2.991916000	-7.250928000	-2.989263000
6	-3.018185000	-6.037695000	-5.187604000
1	-2.918246000	-5.067872000	-5.690392000
1	-2.276787000	-6.717002000	-5.624366000
1	-4.015212000	-6.439608000	-5.412524000
1	-2.255658000	-7.978845000	-3.349270000
1	-3.991647000	-7.661148000	-3.184881000
1	-2.864916000	-7.159831000	-1.903311000
6	2.192464000	-6.591285000	-4.081198000
6	2.063075000	-6.783485000	-5.600233000
6	2.098490000	-7.954538000	-3.378818000
1	2.194064000	-7.837299000	-2.292274000
1	1.142093000	-8.452745000	-3.576232000
1	2.900481000	-8.621050000	-3.723296000
1	1.105875000	-7.241797000	-5.874687000
1	2.864893000	-7.432937000	-5.976109000
1	2.130736000	-5.819316000	-6.119146000
6	-3.916996000	-4.950133000	-3.139715000
1	-3.872762000	-3.959285000	-3.607946000
1	-4.907383000	-5.373271000	-3.350015000
1	-3.837338000	-4.813288000	-2.054279000
6	3.569435000	-5.994643000	-3.787284000
1	3.727909000	-5.855791000	-2.710723000
1	4.353674000	-6.667961000	-4.155469000
1	3.703673000	-5.024173000	-4.280981000
6	-2.341888000	8.380005000	3.113958000
1	-1.405454000	8.908419000	3.327765000
1	-2.429110000	8.286679000	2.024448000
1	-3.169667000	9.007018000	3.471237000
6	2.753019000	7.790995000	2.574515000
1	2.597455000	7.698057000	1.492685000
1	2.019909000	8.511809000	2.955191000
1	3.754200000	8.210001000	2.742056000

E = -21197.83508243 Eh

ZPVE = 1.00858585 Eh

Compound Pt-5 (S₀)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78 -0.571214000 -0.347694000 -0.374337000
6 -0.578865000 1.645958000 -0.334142000
6 -0.581379000 2.875370000 -0.307017000
6 -0.558937000 -2.341420000 -0.415462000
6 -0.543558000 -3.570649000 -0.445693000
6 -2.585751000 -0.359657000 -0.345124000
7 -3.415163000 0.182471000 -1.269547000
7 -3.378471000 -0.915292000 0.603157000
6 1.443398000 -0.341084000 -0.402548000
7 2.242399000 -0.850143000 -1.371411000
7 2.266597000 0.168739000 0.545520000
6 -0.582829000 4.299870000 -0.274538000
6 -1.766781000 5.018898000 -0.016679000
6 0.600097000 5.031570000 -0.499229000
6 -1.764912000 6.409503000 0.014640000
6 0.596288000 6.422141000 -0.467416000
6 -0.584850000 7.119563000 -0.210543000
1 -2.686185000 4.463730000 0.161683000
1 1.520264000 4.486269000 -0.702372000
1 -2.692036000 6.944838000 0.217224000
1 1.522674000 6.967427000 -0.645340000
1 -0.585633000 8.208341000 -0.185935000
6 -0.524855000 -4.995070000 -0.476898000
6 0.670522000 -5.709236000 -0.261799000
6 -1.700184000 -5.731502000 -0.724976000
6 0.686839000 -7.099733000 -0.293087000
6 -1.678108000 -7.121947000 -0.756032000
6 -0.485967000 -7.814523000 -0.540274000
1 1.584290000 -5.150418000 -0.066598000
1 -2.629018000 -5.189915000 -0.896112000
1 1.622541000 -7.631316000 -0.122582000
1 -2.598864000 -7.670907000 -0.951063000
1 -0.470923000 -8.903205000 -0.564714000
6 -2.915673000 -1.602815000 1.784361000
1 -3.306311000 -2.626264000 1.802935000
1 -1.825438000 -1.649580000 1.747882000
1 -3.238427000 -1.067985000 2.685481000
6 -2.998349000 0.875219000 -2.464921000
1 -3.308315000 0.316849000 -3.356222000
1 -3.435131000 1.879669000 -2.489170000
1 -1.910857000 0.971209000 -2.443195000
6 1.841686000 0.808285000 1.767340000
1 0.754048000 0.902255000 1.743890000
1 2.148398000 0.213277000 2.635762000
1 2.275593000 1.811868000 1.836820000
6 1.786941000 -1.488389000 -2.582808000
1 2.078074000 -0.895712000 -3.458145000
1 2.212869000 -2.494763000 -2.660804000
1 0.699588000 -1.575741000 -2.535375000
6 4.751423000 -1.003754000 -1.710278000
6 3.573458000 -0.667918000 -1.049528000
6 5.948481000 -0.666532000 -1.081090000
1 6.891903000 -0.913102000 -1.564717000
6 3.589149000 -0.014204000 0.190448000
6 5.964264000 -0.017253000 0.162532000
1 6.919666000 0.228355000 0.622552000
6 4.783544000 0.320854000 0.821452000
1 4.796873000 0.824677000 1.785593000
1 4.740265000 -1.507827000 -2.674314000
6 -5.934102000 0.326096000 -1.533351000
6 -7.110560000 -0.049852000 -0.887395000
6 -4.735451000 -0.026042000 -0.919957000
1 -8.068956000 0.207515000 -1.334583000
6 -7.086685000 -0.752295000 0.326853000
6 -4.711697000 -0.731689000 0.291087000
1 -8.026944000 -1.027788000 0.800937000
6 -5.885383000 -1.106189000 0.938556000
1 -5.867499000 -1.652179000 1.879379000
1 -5.953874000 0.870936000 -2.474814000
E = -20569.62598887 Eh
ZPVE = 0.56027708 Eh

Compound Pt-5 (S₀)

GFN2

78 -2.851207986 4.712333124 -6.923848276
6 -3.250710917 6.462715449 -6.033166941
6 -3.198609269 7.472904742 -5.362926864
6 -2.391879849 2.959084915 -7.774808736
6 -2.257043033 1.903749182 -8.356463758
6 -4.690543658 4.355155151 -7.593376371
7 -5.149398063 4.560902273 -8.847555882
7 -5.669604744 3.718656241 -6.912540324
6 -1.041374862 5.124377093 -6.195107867
7 -0.117745044 5.939008371 -6.750275650
7 -0.640196377 4.874642034 -4.929240868
6 -3.164601585 8.654593249 -4.584354863
6 -4.308801223 9.430736168 -4.389590053
6 -1.965053320 9.054195232 -3.988529264
6 -4.251442773 10.574324467 -3.617991061
6 -1.916804251 10.199104807 -3.218668709
6 -3.058016426 10.962721841 -3.029736054
1 -5.238190280 9.124786389 -4.850149678
1 -1.073823669 8.456683513 -4.135940495
6 -2.082785091 0.672170856 -9.032971024
6 -0.846909218 0.021817677 -9.036281618
6 -3.154272731 0.091798093 -9.716264531
6 -0.690583133 -1.174447743 -9.707734626
6 -2.989487793 -1.104638648 -10.385330911
6 -1.758676653 -1.741730299 -10.384941423
1 -0.015422181 0.467288001 -8.507378011
1 -4.114855562 0.590706361 -9.715054960
6 -5.549751774 3.317297923 -5.539105069
1 -5.445863749 2.232387631 -5.461299875
1 -4.654323267 3.798972600 -5.129906670
1 -6.424783993 3.638061067 -4.971791289
6 -4.385217818 5.201259503 -9.880309978
1 -4.158556272 4.496805553 -10.683410951
1 -4.931073663 6.053792811 -10.288761323
1 -3.448511810 5.548280584 -9.430030126
6 -1.385532339 4.066612696 -4.005679285
1 -2.139863476 3.515581464 -4.578705901
1 -0.725673953 3.359594985 -3.500879596
1 -1.882324269 4.693987477 -3.261265680
6 -0.208501161 6.450141957 -8.088513615
1 -0.364791205 7.531090974 -8.075928742
1 0.699740802 6.221728198 -8.649215679
1 -1.065252030 5.965954942 -8.569662655
6 -7.301105784 3.999361995 -10.047082996
6 -8.525402638 3.394336428 -9.825345042
6 -6.417387120 4.047377216 -8.981492511
1 -9.239799654 3.337283114 -10.632337922
6 -8.859068078 2.854661676 -8.585764072
6 -6.754381466 3.501698825 -7.728527765
1 -9.825198225 2.390828117 -8.458018432
6 -7.982307958 2.896701444 -7.516347099
1 -8.244096532 2.473306154 -6.559472539
1 -7.045408019 4.413236458 -11.009729315
6 1.998214123 7.031343296 -5.904430695
6 0.864510316 6.238523742 -5.836281403
6 2.777429695 7.118406799 -4.764485348
1 3.666885642 7.729594149 -4.778739257
6 0.524852335 5.550994093 -4.655955618
6 2.440204188 6.440041761 -3.595978345
1 3.074887245 6.540207916 -2.728769321
6 1.310413824 5.645229391 -3.519004930
1 1.049891486 5.127093583 -2.609562548
1 2.260189759 7.563481326 -6.805334141
1 -3.824887796 -1.545512898 -10.912269906
1 0.270308839 -1.670851843 -9.705563028
1 -5.142597709 11.169399077 -3.471853858
1 -0.984068873 10.499275967 -2.760802466
1 -1.632351837 -2.677393290 -10.910748493
1 -3.017350398 11.857660853 -2.425410235
E = -104.311745411685 Eh
ZPVE = 0.534073632990 Eh

Compound Pt-5 (T₁)

PBE0(D4)/SARC-ZORA-SVP(ZORA-def2-SVP)

78	-0.600216000	-0.332870000	-0.374806000
6	-0.602074000	1.615762000	-0.339596000
6	-0.584894000	2.889019000	-0.309980000
6	-0.578609000	-2.318501000	-0.412860000
6	-0.550498000	-3.550313000	-0.440884000
6	-2.619843000	-0.356470000	-0.342463000
7	-3.456683000	0.198775000	-1.253792000
7	-3.406809000	-0.938083000	0.595960000
6	1.419441000	-0.328750000	-0.405779000
7	2.214917000	-0.855649000	-1.368548000
7	2.247058000	0.196206000	0.531151000
6	-0.553321000	4.244896000	-0.276468000
6	-1.779044000	5.045830000	-0.231283000
6	0.712871000	4.982030000	-0.284128000
6	-1.725037000	6.410913000	-0.198263000
6	0.730652000	6.348089000	-0.251674000
6	-0.478341000	7.097652000	-0.207859000
1	-2.732384000	4.520235000	-0.217592000
1	1.637267000	4.408221000	-0.325118000
1	-2.650178000	6.985947000	-0.161916000
1	1.684629000	6.875083000	-0.261398000
1	-0.449931000	8.184784000	-0.182100000
6	-0.508699000	-4.970746000	-0.472311000
6	0.711001000	-5.663045000	-0.321932000
6	-1.683048000	-5.729894000	-0.656278000
6	0.750906000	-7.052343000	-0.354120000
6	-1.636065000	-7.119046000	-0.688551000
6	-0.420641000	-7.789098000	-0.537747000
1	1.623208000	-5.087211000	-0.174564000
1	-2.629647000	-5.205995000	-0.778037000
1	1.703820000	-7.566765000	-0.233932000
1	-2.555264000	-7.685670000	-0.833863000
1	-0.386617000	-8.877269000	-0.563085000
6	-2.941035000	-1.637461000	1.769004000
1	-3.261130000	-2.684934000	1.739965000
1	-1.849681000	-1.609062000	1.774065000
1	-3.332473000	-1.155697000	2.672801000
6	-3.055253000	0.912680000	-2.441796000
1	-3.475566000	0.427694000	-3.330811000
1	-3.394113000	1.953750000	-2.395164000
1	-1.964261000	0.902688000	-2.493926000
6	1.833600000	0.851792000	1.748349000
1	0.744130000	0.802856000	1.809589000
1	2.278538000	0.347765000	2.614389000
1	2.136329000	1.904945000	1.738454000
6	1.759266000	-1.509590000	-2.571458000
1	2.160508000	-0.994501000	-3.452199000
1	2.076250000	-2.558389000	-2.579081000
1	0.668096000	-1.477959000	-2.586349000
6	4.722373000	-1.024969000	-1.709553000
6	3.546980000	-0.671687000	-1.052846000
6	5.921972000	-0.674462000	-1.092517000
1	6.863418000	-0.933169000	-1.573622000
6	3.567937000	0.007918000	0.172727000
6	5.942935000	0.003474000	0.135571000
1	6.900230000	0.259613000	0.585762000
6	4.764929000	0.357858000	0.790913000
1	4.782258000	0.886746000	1.741419000
1	4.707170000	-1.553062000	-2.660523000
6	-5.977026000	0.335542000	-1.503945000
6	-7.148977000	-0.065332000	-0.864646000
6	-4.774189000	-0.024798000	-0.903335000
1	-8.110478000	0.197131000	-1.302056000
6	-7.116547000	-0.798438000	0.331037000
6	-4.741775000	-0.759046000	0.289974000
1	-8.053461000	-1.092688000	0.800427000
6	-5.911055000	-1.159175000	0.930518000
1	-5.886602000	-1.730078000	1.856218000
1	-6.003229000	0.906497000	-2.429591000

E = -20569.52385845 Eh

ZPVE = 0.55642051 Eh

Dimer of compound Pt-1 (S₀)

GFN2

78	-0.025169400	0.939649089	-2.341620722
6	-0.368354322	2.680003808	-1.406320830
6	-0.330281432	3.750563756	-0.834873171
6	0.350850551	-0.766491606	-3.316788380
6	0.412892841	-1.690205293	-4.101066348
6	-1.823051386	0.787090363	-3.200090948
7	-2.069042449	0.974735740	-4.513003185
7	-2.976447846	0.365935482	-2.633282766
6	1.753082690	1.152634189	-1.468592039
7	2.764838995	1.932146997	-1.910506437
7	2.057398848	0.784741846	-0.204881594
6	-0.303965685	5.046972175	-0.267594172
6	-1.397775886	5.907157185	-0.386105246
6	0.851061403	5.513913539	0.366089341
6	-1.327402561	7.194546524	0.101661384
6	0.902228497	6.802721160	0.851314778
6	-0.179001002	7.675177311	0.728395509
1	-2.299343444	5.552292174	-0.868288417
1	1.705255097	4.854492281	0.463672939
6	0.511630109	-2.773750608	-5.004922401
6	1.343180128	-3.864567169	-4.744100030
6	-0.229737655	-2.769864435	-6.190053035
6	1.424198140	-4.910662145	-5.639033381
6	-0.132978494	-3.821212509	-7.075061734
6	0.692202523	-4.917595459	-6.825673068
1	1.921868021	-3.878870776	-3.829950865
1	-0.886027134	-1.936746542	-6.408218997
6	-3.111776292	0.041094589	-1.241386155
1	-3.305647986	-1.025901867	-1.111852091
1	-2.170620419	0.302715243	-0.745980400
1	-3.926767721	0.612035972	-0.792616238
6	-1.067860419	1.362750530	-5.467709187
1	-0.753048791	0.498858414	-6.056137591
1	-1.458198796	2.128010642	-6.143023159
1	-0.203317265	1.747511347	-4.918237323
6	1.206055091	-0.038856834	0.606823299
1	0.388792362	-0.398231773	-0.029658737
1	1.761003959	-0.892347404	1.000070718
1	0.792790592	0.537256747	1.437957291
6	2.809408298	2.520987247	-3.219356044
1	2.758682466	3.610549081	-3.158000533
1	3.725066394	2.230675021	-3.737857783
1	1.944309919	2.150653593	-3.779379877
6	-4.100809675	0.670535284	-5.983400776
6	-5.429176973	0.290929105	-5.909399442
6	-3.374147498	0.659208014	-4.802972892
1	-6.026097622	0.288993507	-6.809179870
6	-6.015606131	-0.088254293	-4.702929997
6	-3.964381286	0.270903666	-3.585246555
1	-7.055295428	-0.378901888	-4.691995885
6	-5.296285486	-0.106579611	-3.520982731
1	-5.752811191	-0.407181727	-2.590977141
1	-3.652887222	0.970473126	-6.915941684
6	4.898014668	2.797902822	-0.871143772
6	3.709929938	2.087958481	-0.924809009
6	5.613494465	2.742128151	0.311675468
1	6.542874007	3.284891588	0.392674813
6	3.252751762	1.344551027	0.179592061
6	5.162647548	2.004663417	1.403699199
1	5.752379346	1.991181914	2.307480870
6	3.976643822	1.293487822	1.359347966
1	3.628985265	0.728284391	2.209701266
1	5.247305385	3.373529013	-1.713875680
78	-2.895692608	4.983075051	-6.976869242
6	-3.270621556	6.720350862	-6.055138772
6	-3.218259229	7.696350909	-5.335163816
6	-2.466324576	3.264601707	-7.917535887
6	-2.436252386	2.253584123	-8.590239450
6	-4.733195766	4.555843996	-7.626291020
7	-5.138204973	4.498016998	-8.914494052
7	-5.689210179	3.952583155	-6.882855535

6	-1.083636254	5.341705026	-6.224558861	1	-5.286524255	12.620836929	-0.944176183
7	-0.055356487	6.023975903	-6.773461264	1	-4.071118138	11.956899009	0.127186542
7	-0.774596693	5.123347761	-4.929822589	1	-4.274054386	13.693087360	0.003769249
6	-3.192050614	8.863609588	-4.535889466	6	1.140477387	10.427224950	0.244720494
6	-4.094785226	9.906459764	-4.755635967	1	2.134617686	9.990064603	0.266719464
6	-2.240766153	9.006768909	-3.521874094	1	0.809601452	10.423587447	-0.789818325
6	-4.031801162	11.053652769	-3.994880202	1	1.231482130	11.462685616	0.559457615
6	-2.190876525	10.163202883	-2.771377534	6	-1.781247240	10.265722618	1.390420545
6	-3.076813240	11.217439449	-2.990889125	1	-2.219118458	10.300088545	0.397610601
1	-4.837860516	9.803931758	-5.535320743	1	-2.464940440	9.720025632	2.034264485
1	-1.534996041	8.206648810	-3.334401418	1	-1.728523514	11.285355711	1.760401600
6	-2.409710314	1.036794942	-9.313703738	6	0.636711236	9.448742231	3.150710577
6	-1.325466518	0.160296580	-9.229765728	1	0.009001437	8.868420368	3.820318923
6	-3.502711149	0.674406754	-10.105118348	1	1.634297607	9.022335217	3.186991251
6	-1.341630923	-1.033222411	-9.919366151	1	0.698795859	10.457006026	3.548895115
6	-3.498401400	-0.519405019	-10.794561873	6	-2.793818481	-4.479127489	-10.458354728
6	-2.421424920	-1.401653833	-10.722028766	1	-3.822004381	-4.438855363	-10.110171997
1	-0.472535865	0.429557951	-8.620638320	1	-2.642490774	-5.445363686	-10.930743279
1	-4.355938969	1.339338922	-10.167676907	1	-2.154947825	-4.440086559	-9.581373908
6	-5.664671358	3.865383429	-5.448954779	6	-0.706833531	-3.304416197	-12.479116152
1	-5.547805602	2.828868353	-5.125809974	1	0.099129587	-3.236141425	-11.755580459
1	-4.820973545	4.462676239	-5.090529621	1	-0.641016042	-4.281137340	-12.949314306
1	-6.589911492	4.268875359	-5.033244678	1	-0.519585874	-2.557185236	-13.244850457
6	-4.382900015	5.031388027	-10.013013132	6	-3.740162381	-3.034481497	-13.035924735
1	-3.993276712	4.225448387	-10.638845892	1	-3.624058799	-2.179382754	-13.694858412
1	-5.005346932	5.693228878	-10.617610913	1	-3.671359892	-3.929604062	-13.646334627
1	-3.543232635	5.597076977	-9.596224455	1	-4.743356961	-3.000519535	-12.622381417
6	-1.669181471	4.500617355	-3.994501622	6	-0.877529041	-7.316874739	-8.020760815
1	-2.453439146	3.988316705	-4.563387618	1	-1.715004843	-6.668118911	-8.258020595
1	-1.134753943	3.784571592	-3.365249209	1	-0.876466411	-8.128973897	-8.741830956
1	-2.127594726	5.256842138	-3.353465572	1	-1.065785128	-7.746297880	-7.041021493
6	-0.033473865	6.467151319	-8.138639216	6	1.075986071	-5.689176436	-9.816737254
1	-0.005601221	7.557569564	-8.186424831	1	1.953383892	-5.050015683	-9.855828251
1	0.833580936	6.060208370	-8.662874522	1	1.228650964	-6.500246972	-10.522597872
1	-0.950625991	6.107806213	-8.617597774	1	0.229270423	-5.108618776	-10.167624317
6	-7.129449309	3.475716612	-10.086969048	6	2.192905377	-7.549706624	-7.597567821
6	-8.286111766	2.767622384	-9.813570583	1	2.024928921	-8.018712633	-6.633025588
6	-6.332461477	3.824953991	-9.008933629	1	2.281608471	-8.343108513	-8.333396388
1	-8.929568430	2.473247386	-10.628533168	1	3.148013579	-7.035239816	-7.554563113
6	-8.639851584	2.420548225	-8.511815559	E = -257.533455140669 Eh			
6	-6.690244059	3.474144653	-7.693799933	ZPVE = 1.475880732391 Eh			
1	-9.550300765	1.864935180	-8.346280347				
6	-7.851367960	2.766778856	-7.429059172				
1	-8.123721705	2.491336714	-6.422397177				
1	-6.856993852	3.737347690	-11.097380416				
6	2.122795732	6.935728766	-5.866750298				
6	0.908781401	6.269777415	-5.823236153				
6	2.843672610	7.012134060	-4.688279393				
1	3.790608599	7.530270703	-4.682592498				
6	0.438732082	5.691192725	-4.629310488				
6	2.373626492	6.444683550	-3.505660454				
1	2.962050697	6.539454505	-2.605238241				
6	1.165980548	5.772224420	-3.453081482				
1	0.799293704	5.339500892	-2.537116011				
1	2.487677640	7.383749952	-6.777638229				
1	2.073737345	-5.744987303	-5.414702732				
1	-4.352372673	-0.776182743	-11.405229945				
1	-0.492955386	-1.697786482	-9.834690237				
1	-0.714073300	-3.791378279	-7.986795075				
1	1.805617248	7.146856910	1.336292556				
1	-2.182445555	7.845299338	-0.010953226				
1	-4.736944761	11.850587807	-4.186121233				
1	-1.439406176	10.252900360	-1.998897803				
14	-2.413742342	-3.046317631	-11.664478188				
14	0.775281161	-6.357368572	-8.053326137				
14	-3.007464316	12.825469883	-1.990241232				
14	-0.057448175	9.452685261	1.371368905				
6	-3.442411670	14.297163100	-3.128140204				
1	-2.836621869	14.295397155	-4.029312771				
1	-4.483886648	14.271408260	-3.432998066				
1	-3.276750487	15.243538713	-2.622137953				
6	-1.258831219	13.111208570	-1.284578135				
1	-1.013736904	12.386863786	-0.515971913				
1	-0.502026599	13.038933897	-2.060028449				
1	-1.179234587	14.098894157	-0.840086156				
6	-4.279597292	12.767337220	-0.564152828				

Dimer of compound Pt-2 (So)

GFN2

78	0.088154568	1.083239488	-2.504703868
6	-0.340878552	2.819160859	-1.594656272
6	-0.304344963	3.852267079	-0.958031889
6	0.503095794	-0.655031233	-3.405897875
6	0.451118873	-1.633322949	-4.121516899
6	-1.680666400	0.788153331	-3.384014254
7	-1.929914280	0.934748535	-4.701510834
7	-2.795170375	0.267653004	-2.821604215
6	1.824902162	1.482646181	-1.609109639
7	2.768609315	2.327283552	-2.085124174
7	2.093564765	1.288876943	-0.298386530
6	-0.265350660	5.096353073	-0.279958528
6	-1.392172716	5.912611462	-0.192045268
6	0.937599705	5.536951032	0.271156025
6	-1.341655823	7.141865431	0.450875729
6	1.025346555	6.762914911	0.916440197
6	-0.127368389	7.537680968	1.006393307
1	-2.317295229	5.573261799	-0.637208613
1	1.815963373	4.908257484	0.186393557
6	0.387543410	-2.776506275	-4.956106402
6	1.450342865	-3.672760686	-5.057293743
6	-0.769729890	-3.007242585	-5.701692597
6	1.369226270	-4.791037816	-5.876134174
6	-0.886082023	-4.117322155	-6.526849280
6	0.192397390	-4.995568461	-6.591558422
1	2.347419746	-3.484568040	-4.484551422
1	-1.588150328	-2.302906233	-5.629486534
6	-2.910622399	-0.054087883	-1.427323132
1	-3.000887558	-1.133507148	-1.287599976

Publications & Manuscripts

1	-2.002967249	0.301963725	-0.928359685	1	-5.483931085	-0.776095034	-2.798303604
1	-3.780840508	0.439890600	-0.990961176	1	-3.485728251	0.769512508	-7.113245855
6	-0.959912644	1.384044721	-5.661199546	6	4.700081668	3.574117566	-1.039423616
1	-0.630337808	0.547484639	-6.281192712	6	3.617917390	2.710364611	-1.075110742
1	-1.386792825	2.155668302	-6.307081455	6	5.331830198	3.745301571	0.179915675
1	-0.100729431	1.782335585	-5.113144945	1	6.175180223	4.414935452	0.249194350
6	1.288467705	0.469725005	0.562958078	6	3.181028632	2.038461639	0.082131355
1	0.570110741	-0.067579316	-0.066120093	6	4.901770247	3.078380538	1.324164329
1	1.910875518	-0.249246739	1.098466583	1	5.423756326	3.242849200	2.254309923
1	0.747861921	1.087966715	1.283573411	6	3.820870912	2.214361568	1.297816372
6	2.829723900	2.775225555	-3.448100094	1	3.486861408	1.706619568	2.188952366
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14	-2.888782271	8.239136529	0.562199284	6	-3.374361805	7.709894233	-5.434813772
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1	3.536069436	9.433570329	2.693091098	6	-0.294427004	6.805644946	-8.169562109
6	3.974888372	7.342277391	0.176086614	1	-0.366170683	7.895200274	-8.156144977
1	4.956504242	7.645547268	0.527890542	1	0.601916772	6.508584788	-8.717629451
1	4.074380692	6.351251250	-0.257021624	1	-1.179541809	6.392377727	-8.664861243
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1	-3.221759798	7.995246486	3.049041996	1	-2.713236999	11.938136888	-2.371169943
6	-2.410643844	10.082836064	0.607164731	1	-2.213912932	-2.201044014	-11.347801341
1	-1.661853416	10.291857924	1.364956611	6	-6.459848503	-1.244920442	-9.964612864
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1	-3.276814845	10.697727981	0.829543847	1	-7.391954303	-1.665754167	-10.330082793
6	-4.014609817	7.919833982	-0.942286165	1	-6.189701394	-1.781158049	-9.060200950
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6	-3.912370765	0.435639565	-6.183162031	1	-4.463073562	-3.772626501	-10.993361348
6	-5.199525292	-0.067616691	-6.118514809	6	-5.640164835	-0.318531849	-12.798668029
6	-3.197581341	0.496571083	-4.997531942	1	-4.888843438	-0.326703861	-13.582724069
1	-5.783166310	-0.131794372	-7.023880996	1	-6.564625245	-0.697234824	-13.224301645
6	-5.756172978	-0.496900974	-4.914926943	1	-5.808010555	0.716505911	-12.515774927
6	-3.759878320	0.066018830	-3.780956461	1	1.898463579	-0.278425771	-11.117686947
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6	-7.274540659	10.925303844	-3.235323110	6	-5.450607894	0.306727530	-5.899863334
1	-7.401246203	10.846525814	-4.310589036	6	-3.888262697	0.673991324	-4.806782896
1	-7.337858870	9.923736852	-2.820868304	1	-6.049948619	0.292838251	-6.798019232
1	-8.115532129	11.493287414	-2.849180101	6	-6.037998891	-0.040683262	-4.684334164
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6	-6.219875617	3.545317597	-9.258611650	6	-5.315448005	-0.043010602	-3.504165067
1	-8.544323821	1.882758869	-10.999628549	1	-5.772726583	-0.319283426	-2.566965472
6	-8.324327214	1.822677019	-8.874520951	1	-3.669492176	0.944547237	-6.924977023
6	-6.566992129	3.113497389	-7.964704039	6	4.913179008	2.735234911	-0.861276212
1	-9.152521652	1.141239130	-8.753563332	6	3.715714880	2.041976843	-0.923263708
6	-7.626958233	2.246356291	-7.756889345	6	5.625171205	2.660589695	0.322658452
1	-7.890338584	1.908710904	-6.766970641	1	6.561715775	3.189985486	0.409887925
1	-6.655495625	3.436784214	-11.366012705	6	3.246219457	1.295862218	0.174236611
6	1.860435145	7.293006256	-5.900038453	6	5.161949199	1.920783306	1.407854052
6	0.691689245	6.549061890	-5.878996060	1	5.749438913	1.892124907	2.312807680
6	2.601353883	7.339106045	-4.731899495	6	3.966581160	1.225933842	1.355191348
1	3.514618271	7.913741426	-4.710078809	1	3.609458577	0.658646503	2.200287404
6	0.279031435	5.875930476	-4.713456950	1	5.272301398	3.312399662	-1.698819617
6	2.193897008	6.668423829	-3.580700785	78	-2.912716064	4.990550638	-7.001700311
1	2.798115735	6.734500527	-2.688817649	6	-3.298920669	6.747477569	-6.123983231
6	1.025919402	5.926776830	-3.547853475	6	-3.273755726	7.757949694	-5.453061737
1	0.703993772	5.417488789	-2.654472775	6	-2.488101580	3.259705777	-7.922317258
1	2.178545946	7.817839443	-6.787390409	6	-2.478215380	2.255368461	-8.605318529
E = -306.429337734447 Eh				6	-4.741707822	4.567203944	-7.675043751
ZPVE = 1.881504205097 Eh				7	-5.132977892	4.508484194	-8.967507728
				7	-5.707304276	3.967630169	-6.941106170
				6	-1.108820095	5.342481545	-6.229303071
				7	-0.076920583	6.023970466	-6.773372524
				7	-0.801530548	5.116455141	-4.935136098
				6	-3.273631103	8.956043321	-4.699180336
				6	-4.303789093	9.890084679	-4.815263758
				6	-2.224638989	9.238847248	-3.824545874
				6	-4.272352936	11.060663227	-4.088355682
				6	-2.203227132	10.417728376	-3.103860195
				6	-3.222322331	11.356586986	-3.220137983
				1	-5.127802963	9.687941428	-5.486104232
				1	-1.415470900	8.527453424	-3.714593050
				6	-2.475859576	1.041849551	-9.335798678
				6	-1.417429197	0.138648553	-9.257407429
				6	-3.571726992	0.705860665	-10.133788175
				6	-1.456910082	-1.057224833	-9.948273506
				6	-3.595531649	-0.486630574	-10.823670924
				6	-2.543882569	-1.398591735	-10.745516378
				1	-0.556436618	0.380915531	-8.648842843
				1	-4.409874640	1.388468870	-10.202507959
				6	-5.695214346	3.881048358	-5.507049184

Dimer of compound Pt-3 (So)

GFN2

78	-0.030019026	0.949696181	-2.357004010
6	-0.339608985	2.694064924	-1.414825023
6	-0.254427549	3.741574948	-0.806982239
6	0.339742031	-0.765920694	-3.318394672
6	0.439904756	-1.699493684	-4.085992595
6	-1.829747193	0.812885408	-3.211607198
7	-2.078385727	0.978553477	-4.527215218
7	-2.987363878	0.418261943	-2.632977044
6	1.748161591	1.136839449	-1.478798602
7	2.770929335	1.906472924	-1.912121776
7	2.044647635	0.754747257	-0.217383700
6	-0.171028061	5.007394125	-0.177614702
6	-1.195455476	5.947745861	-0.299497028
6	0.970690836	5.364702776	0.538805447
6	-1.067820865	7.197167442	0.266694121

Publications & Manuscripts

1 -5.595503877 2.843164469 -5.182546633
1 -4.844846700 4.466211286 -5.143394105
1 -6.617306264 4.298508857 -5.097954746
6 -4.362999430 5.036092565 -10.058463473
1 -3.970850223 4.227031767 -10.678740584
1 -4.974889305 5.700672867 -10.670871891
1 -3.524777423 5.597526697 -9.633090697
6 -1.697778018 4.491000288 -4.003217790
1 -2.479942695 3.979089341 -4.575463740
1 -1.163262231 3.774234387 -3.374345239
1 -2.158695180 5.245323015 -3.361534540
6 -0.053601230 6.476756816 -8.135336483
1 -0.025614135 7.567554279 -8.175443087
1 0.813649531 6.073146010 -8.661839214
1 -0.971026030 6.121286625 -8.617200712
6 -7.114375229 3.489831919 -10.159547798
6 -8.276322963 2.785954013 -9.897452953
6 -6.327764516 3.838177034 -9.073688214
1 -8.912234059 2.492754959 -10.718823644
6 -8.645052935 2.442036181 -8.599096750
6 -6.700699033 3.490391855 -7.761835487
1 -9.559231780 1.889923073 -8.442385906
6 -7.866879110 2.787280278 -7.508514564
1 -8.150971661 2.514505216 -6.504333143
1 -6.830359925 3.749267392 -11.167423735
6 2.106647742 6.917160573 -5.861835242
6 0.888325401 6.258856646 -5.821800327
6 2.830138027 6.978519896 -4.684031557
1 3.781085669 7.489459758 -4.675903162
6 0.415623300 5.674748338 -4.631493350
6 2.358341487 6.403715608 -3.505637693
1 2.950239216 6.484942015 -2.605945383
6 1.145485265 5.740253275 -3.455902119
1 0.778773778 5.299914075 -2.543440594
1 2.473340432 7.369870223 -6.769719472
1 2.207179867 -5.728608572 -5.303988635
1 -4.459329185 -0.707565595 -11.434431612
1 -0.613293797 -1.722149475 -9.850998353
1 -0.507648673 -3.817226642 -8.003078620
1 1.987110216 6.849024959 1.649753842
1 -1.880011862 7.899020927 0.142700175
1 -5.088112806 11.759794214 -4.207164463
1 -1.364839071 10.594057424 -2.448339113
6 -3.234314083 12.671399914 -2.455331413
6 -2.005697141 12.847824970 -1.558885246
6 -4.484417346 12.724835477 -1.565306965
1 -5.394097576 12.662472424 -2.156453365
1 -4.479591171 11.895490660 -0.860458880
1 -4.506819338 13.656237529 -1.002557458
1 -1.959400157 12.069822982 -0.800906367
1 -2.062166957 13.808720758 -1.050364360
1 -1.088115202 12.829775421 -2.142678512
6 0.163953892 8.962794530 1.570133335
6 1.483689668 9.212039357 2.305209085
6 -0.984296282 9.162060188 2.569745915
1 -1.951822031 9.041365148 2.089852005
1 -0.911472530 8.434573900 3.376073255
1 -0.939397310 10.160632939 3.000405191
1 1.602916581 8.525139040 3.140319501
1 1.492911015 10.226106554 2.700741404
1 2.332331989 9.106116782 1.632850919
6 -2.625827036 -2.699662642 -11.528607120
6 -3.889730259 -3.465402624 -11.110640589
6 -1.421145417 -3.612155657 -11.286046618
1 -0.494621672 -3.135298843 -11.598479716
1 -1.348219315 -3.880947430 -10.234698734
1 -1.536079584 -4.530476274 -11.859031746
1 -3.872788024 -3.664071317 -10.040537976
1 -3.944443521 -4.416070540 -11.637718149
1 -4.790288354 -2.901029152 -11.336752504
6 1.013176176 -6.054787097 -7.807208649
6 -0.370787608 -6.656577497 -8.090364316
6 1.928195272 -7.182196364 -7.321070252
1 2.937429347 -6.818104818 -7.142056093
1 1.544150763 -7.630500990 -6.407324465
1 1.982308893 -7.959856719 -8.080953603

1 -0.813812301 -7.029598062 -7.168841852
1 -0.284922035 -7.483817346 -8.792475059
1 -1.045720259 -5.919864198 -8.517146732
6 -2.687657758 -2.374321076 -13.027808496
1 -1.797451253 -1.825859558 -13.330146469
1 -2.743050440 -3.291654449 -13.610814996
1 -3.257516623 -1.766826824 -13.263704602
6 1.606006350 -5.484726945 -9.103895010
1 2.588525729 -5.057861406 -8.911323020
1 1.710502893 -6.271230164 -9.848938313
1 0.972905636 -4.705643672 -9.518885601
6 -3.262271911 13.834427778 -3.457536421
1 -2.390455487 13.790565069 -4.107589028
1 -4.152192139 13.799948586 -4.080100521
1 -3.252705517 14.786547192 -2.930178792
6 0.046161305 9.990079193 0.435605957
1 0.847337620 9.846478619 -0.287394500
1 -0.902467053 9.888893167 -0.084558265
1 0.115210907 11.001526793 0.832066132

E = -259.317178241236 Eh

ZPVE = 1.515226559888 Eh

Dimer of compound Pt-4 (So)

GFN2

78 0.229433274 1.044844341 -2.522353635
6 -0.309772681 2.743474773 -1.604417077
6 -0.360909215 3.772266953 -0.961822767
6 0.684442412 -0.663234617 -3.463418452
6 0.559300610 -1.622781976 -4.196817227
6 -1.533443446 0.616110243 -3.348199664
7 -1.857972402 0.893953708 -4.627231286
7 -2.523142046 -0.151173922 -2.840039403
6 1.969032058 1.615768027 -1.729851045
7 2.833122409 2.456780641 -2.345907986
7 2.275537250 1.632993436 -0.412124157
6 -0.448390834 5.017072072 -0.289092463
6 -1.661904008 5.691924458 -0.191207500
6 0.703813091 5.590608424 0.245379950
6 -1.739181160 6.927324374 0.432959292
6 0.654537369 6.824480287 0.874780778
6 -0.573128286 7.474471230 0.960081051
1 -2.539578745 5.224295921 -0.614024499
1 1.636746168 5.050283698 0.152866616
6 0.388388573 -2.739598493 -5.051695147
6 1.453699523 -3.543175607 -5.446359137
6 -0.894951446 -3.025883076 -5.517312670
6 1.252598760 -4.621323188 -6.295672274
6 -1.124674627 -4.099647021 -6.362505345
6 -0.038831081 -4.882626102 -6.742078401
1 2.438551353 -3.302820890 -5.072765731
1 -1.708586954 -2.386302143 -5.202958704
6 -2.513555733 -0.679972221 -1.505623179
1 -2.453402128 -1.770214069 -1.526051452
1 -1.628340586 -0.279573940 -0.999066388
1 -3.411882034 -0.377004123 -0.964013091
6 -0.996961222 1.604047426 -5.530777510
1 -0.543733512 0.906990788 -6.239018514
1 -1.557804757 2.356577052 -6.090966961
1 -0.208997835 2.083789913 -4.939727661
6 1.553119839 0.889650753 0.580877872
1 0.862877582 0.219898618 0.057302227
1 2.238895719 0.301043613 1.192903361
1 0.981270112 1.564561491 1.222072191
6 2.857094177 2.685155084 -3.763945202
1 2.542447106 3.705393333 -3.997184877
1 3.862978882 2.522222843 -4.155765857
1 2.169376493 1.971152462 -4.228681217
1 -0.623448943 8.428520240 1.452492901
1 -0.203628601 -5.716448631 -7.399547939
6 -3.790559254 0.268242279 -6.126485451
6 -4.972110028 -0.452856782 -6.106972140
6 -3.047513030 0.292016378 -4.956852813
1 -5.573095040 -0.497909874 -7.002323337

6	-5.396426480	-1.130408787	-4.966000194	6	2.391724532	6.417321211	-3.578910955
6	-3.479711773	-0.385393842	-3.800418226	1	3.007883421	6.468999685	-2.694372090
1	-6.318922188	-1.689866418	-4.998910894	6	1.142103351	5.828199702	-3.495639707
6	-4.660634110	-1.110245733	-3.793793633	1	0.772308024	5.417473890	-2.570718890
1	-4.990938419	-1.641437543	-2.914777417	1	2.491618465	7.342559567	-6.855283087
1	-3.456672567	0.70890496	-7.013566682	6	-5.004118618	11.737828474	-2.800245479
6	4.643123065	4.020382765	-1.535220610	6	-5.067920304	11.737750827	-1.266637081
6	3.653154166	3.058442619	-1.422111364	6	-6.378482994	11.319066393	-3.329848552
6	5.256124544	4.436332081	-0.366020762	1	-6.403488321	11.345311851	-4.416864682
1	6.024930077	5.192530409	-0.412523411	1	-6.637929543	10.317711540	-2.993350504
6	3.291224409	2.526165192	-0.169998231	1	-7.136728839	12.006811521	-2.959205286
6	4.900573840	3.908079910	0.872466893	1	-5.271379702	10.733636998	-0.901000404
1	5.400962638	4.265888485	1.759247371	1	-5.861824383	12.398408868	-0.922834779
6	3.915300853	2.943422057	0.994132118	1	-4.132817660	12.074485902	-0.827797157
1	3.636629982	2.544357306	1.956900579	6	-0.115031956	10.601933867	-2.719618765
1	4.915715705	4.435352394	-2.492963187	6	0.947558707	9.618255674	-3.216737269
78	-2.958846224	5.132789430	-7.039735206	6	-0.093657552	10.571814681	-1.185870468
6	-3.385079607	6.843622061	-6.090153194	1	-0.805782918	11.276181726	-0.763026573
6	-3.249002969	7.798074607	-5.352168018	1	-0.339652552	9.571787077	-0.832330205
6	-2.450205702	3.438895405	-7.983837581	1	0.898469005	10.834389373	-0.821182394
6	-2.411149273	2.421020107	-8.643971072	1	0.740326791	8.609656472	-2.865606594
6	-4.697644961	4.602966697	-7.862321224	1	1.924429968	9.912697894	-2.836397951
7	-4.994094604	4.671016898	-9.180769713	1	1.002458412	9.608253398	-4.303130457
7	-5.557669007	3.712353496	-7.311306186	6	1.941055146	7.415041287	1.434577521
6	-1.175663292	5.501227473	-6.226293314	6	2.948039665	7.582325761	0.287266074
7	-0.121621239	6.126589407	-6.796163851	6	2.516331260	6.458229692	2.488267093
7	-0.863977041	5.289663768	-4.931500702	1	1.806378437	6.325184010	3.302509994
6	-3.057967146	8.912123643	-4.497826751	1	2.733184436	5.483371362	2.059356575
6	-4.114746776	9.728009083	-4.100177555	1	3.440165269	6.862308471	2.898193553
6	-1.763273861	9.177784804	-4.047248926	1	3.217312548	6.619561885	-0.140617824
6	-3.890791858	10.807341973	-3.261036615	1	3.858076838	8.056442370	0.650426882
6	-1.511970850	10.254730849	-3.215384806	1	2.521946971	8.203765342	-0.498192243
6	-2.588186535	11.052019300	-2.836489488	6	-3.089219520	7.625881410	0.515738923
1	-5.100387375	9.490649737	-4.467228058	6	-4.057268667	6.737774260	1.311332826
1	-0.970357800	8.520659037	-4.370836738	6	-3.628296380	7.842451185	-0.904993069
6	-2.335889353	1.179674248	-9.323914566	1	-2.944336754	8.461907309	-1.480709415
6	-1.141388661	0.466297149	-9.366265335	1	-3.760752165	6.901166375	-1.431845027
6	-3.479993981	0.644495766	-9.911623444	1	-4.593261679	8.343821240	-0.869625114
6	-1.079169304	-0.779446215	-9.969953760	1	-4.190506215	5.770801725	0.833685678
6	-3.442365659	-0.592814217	-10.534766717	1	-5.031250573	7.217458472	1.387614037
6	-2.236719849	-1.287579656	-10.552370650	1	-3.674984777	6.571270618	2.316884291
1	-0.267238205	0.912028451	-8.914263381	6	2.444759584	-5.479303715	-6.698342119
1	-4.396618645	1.217487638	-9.866549873	6	2.065463857	-6.638186486	-7.624788520
6	-5.580011599	3.379943210	-5.914638004	6	3.080616850	-6.071725810	-5.432592701
1	-5.259141063	2.346814959	-5.757983703	1	3.436536533	-5.290590659	-4.766592868
1	-4.894313175	4.059858506	-5.398736417	1	2.351466849	-6.672804798	-4.892518935
1	-6.585930133	3.508413955	-5.510225969	1	3.924749494	-6.706652626	-5.695702213
6	-4.271001500	5.487768340	-10.113900892	1	1.361627417	-7.312513122	-7.141902683
1	-3.677751246	4.864760040	-10.787626877	1	2.958348585	-7.208724262	-7.874970442
1	-4.958618308	6.101154841	-10.698871020	1	1.630599277	-6.272948506	-8.552676899
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6	-1.775838738	4.734886009	-3.970315579	6	-3.435190708	-4.621996255	-5.601751394
1	-2.612278297	4.287380614	-4.517214082	6	-2.646945210	-5.605628106	-7.741135818
1	-1.280049549	3.978768304	-3.356714208	1	-2.054391946	-5.474977182	-8.644211613
1	-2.155793584	5.524983286	-3.318887986	1	-2.316741722	-6.505093615	-7.226135904
6	-0.090139814	6.544655547	-8.169067740	1	-3.683740696	-5.751287933	-8.040084468
1	-0.054826669	7.634011019	-8.238255950	1	-3.047949982	-5.452606286	-5.014549141
1	0.777248144	6.122100654	-8.679952233	1	-4.450408341	-4.861572716	-5.913028648
1	-1.006867143	6.181315841	-8.646309186	1	-3.476443568	-3.741001239	-4.966324389
1	-2.404110299	11.895944880	-2.189478315	6	-4.715254604	-1.134008549	-11.170404823
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Dimer of compound Pt-5 (S₀)

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E = -208.655158548469 Eh

ZPVE = 1.070714658359 Eh

3. Summary and Outlook

Our studies on silyl-substituted COT molecular balances allowed us to gain insights into the distinct physical features of various silyl-DED moieties.^{187,188} Although stabilization from LD interactions in the folded 1,6-isomers were counteracted by molecular strain for bulkier (> TMS) silyl groups in our first publication¹⁸⁷ (section 2.1/2.2), and unfavorable entropic contributions in our second publication¹⁸⁸ (section 2.3/2.4), we were able to computationally quantify stabilizing LD interaction contributions of more than -2 kcal mol^{-1} in most cases.^{187,188} Hence, if LD interactions were to be neglected, one would expect the folding equilibria to be shifted towards the unfolded 1,4-isomers to a much greater extent than what is observed experimentally. This would result in folded 1,6-isomers of most investigated silyl COTs to be nearly unobservable *via* $^1\text{H-NMR}$.

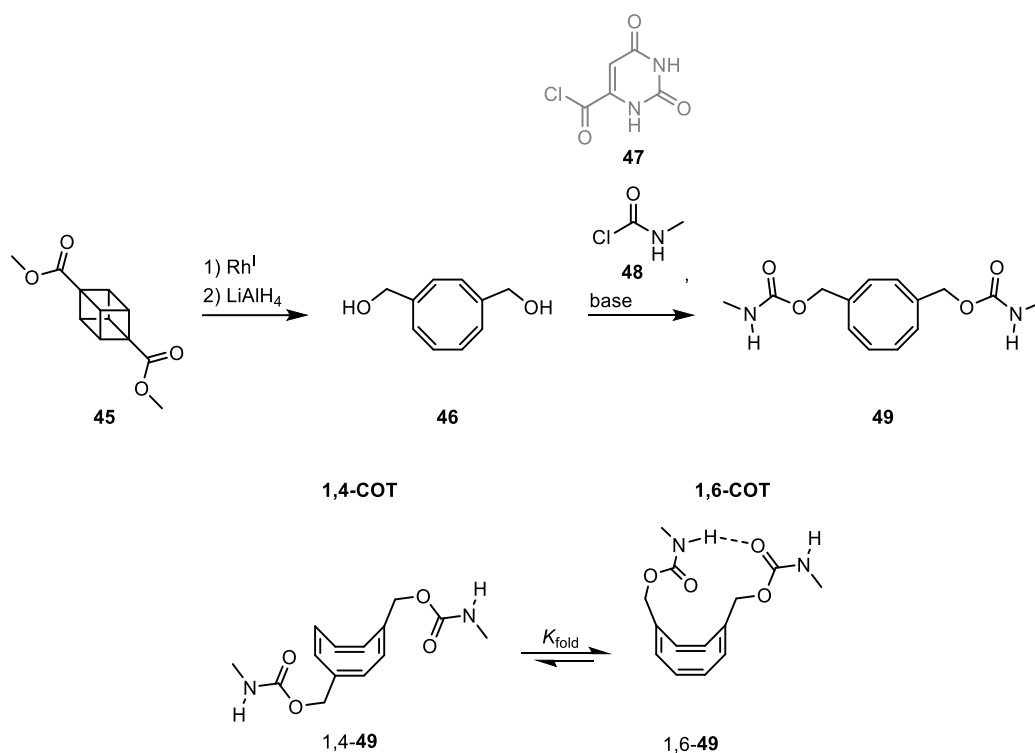
The rigid COT molecular balances addressed in our first publication allowed us to gauge the apparent bulkiness of common silyl groups, with our experimental and computational results correlating very well with established steric parameters.¹⁸⁷ On the other hand, the investigation of a more flexible balance system in our second publication yielded the expected qualitative result of greater bulkiness leading to a greater preference for the folded 1,6-isomers.¹⁸⁸ However, the increased flexibility resulted in unexpected conformational effects for some silyl groups (pseudo-folded 1,4-isomers), and the aforementioned entropic disfavoring of the 1,6-isomer.¹⁸⁸

Nonetheless, comparing the rigid and flexible molecular balances highlights, how subtle structural changes may transform molecular recognition systems (e.g., a catalyst) from exerting selectivity control through steric effects, to being governed by LD interactions.¹⁸⁸ The latter design strategy could be particularly useful for catalytic reactions carried out at low temperature (under kinetic control), where entropic contributions are expected to be miniscule.

Efforts on exploring the capabilities of the COT molecular balance with the broader aim of studying the significance of London dispersion for other non-covalent interactions lead to our investigations on 1,4/1,6-COT-dimethanol (section 2.5/2.6).¹⁹⁰ The hydrogen bonding mode found in the folded 1,6-COT-dimethanol isomer happened to closely resemble that of an unusual water dimer species, the cyclic water dimer transition state.^{189,190} By accounting for effects related to molecular strain and solvation computationally, we were able to refine our experimental thermochemical data, so an estimate for the hydrogen bonding energy (HBE) of the cyclic water dimer could be obtained. Our estimate agreed well with ‘gold-standard’ computational results of a HBE of $-4.32 \text{ kcal mol}^{-1}$.^{189,190} Furthermore, computational treatment

of the folded molecular balance revealed significant London dispersion contributions to the intramolecular hydrogen bond of approximately -1 kcal mol^{-1} .¹⁹⁰

Our findings underline the importance of London dispersion as a hidden component of hydrogen bonding and demonstrate the utility of the COT molecular balance systems for studying the properties of elusive molecular species experimentally, under ambient conditions, and with standard analytical techniques.



Scheme 12: Proposed synthetic pathway for a di-(N -methylcarbamate) COT **49** molecular balance.

As we have established a reliable synthetic procedure for obtaining 1,4/1,6-COT-dimethanol **46** in the framework of our studies,^{188,190} various novel molecular balances derived from the latter can be accessed. A particularly interesting molecular balance system, which could potentially be obtained in a single step from 1,4/1,6-COT-dimethanol **46**, can be found in 1,4/1,6-di-(N -methylcarbamate) COT **49** (Scheme 12).

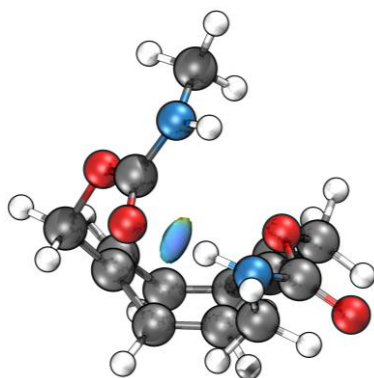


Figure 20: Intramolecular NCI-plot of 1,4/1,6-di-(*N*-methylcarbamate) COT **49**. Geometry optimized at the PBEh-3c⁵⁶ level of theory. Isosurfaces colored red represent repulsive interactions, green isosurfaces represent weak NCIs (LD interactions), and blue isosurfaces represent strong attractive interactions (hydrogen bonds). Isovalue s of 0.3, in the range of $\text{sign}(\lambda_2)\rho = -0.05$ to $+0.05$ [a.u.].

Such a system would allow to study an isolated intramolecular OHN hydrogen bond similar to the hydrogen bonds encountered in α -helices and β -sheet structures of proteins utilizing a COT molecular balance. Preliminary computations predict the conformational space of the folded 1,6-isomer of **49** to be dominated by one, singly hydrogen bonded conformer. 1,4/1,6-COT-dimethanol **46** could also be esterified utilizing orotic acid chloride **47** (Scheme 12). This would allow modeling of the hydrogen bonding motif found between base pairs in the double stranded helix of DNA. In this way, two of the most biochemically important hydrogen bonds/hydrogen bonded systems could be modeled and quantified with simple COT molecular balances.

We found the introduction of silyl-DEDs to be beneficial for the photophysical properties of *trans*-Pt(II)-NHC phenylacetylides with respect to future applications of the latter in electroluminescent devices (section 2.7). In agreement with our conceptual works on the DED capabilities of bulky silyl groups, we found an increased aggregation tendency and thereby substantial phosphorescence quenching for the bulkiest investigated di-TMS- and di-*t*-butyl-substituted complexes. However, mono-silyl-substitution led to improved quantum yields in highly concentrated thin films over the parent complex. Thus, our work highlights the requirement of balancing desired effects on aggregation patterns and a greater aggregation tendency due to enhanced intermolecular London dispersion interactions, when DEDs are introduced to luminescent compounds.

While the fabrication of corresponding phosphorescent/hyperfluorescent OLED devices is currently in progress, our results obtained so far certainly justify further investigations on the potential of silyl-DEDs for controlling the aggregation behavior of luminescent molecules.

Especially, given our findings on computational conformer sampling^{83,84} being able to correctly predict aggregation patterns can be expanded to other phosphorescent organometallic systems. In this regard, square planar phosphorescent d^8 metal complexes (e.g., Au(III) complexes) could be interesting target systems for further investigations, as their flat geometry makes them similarly prone to aggregation induced luminescence quenching.²¹⁴

Overall, we not only found bulky silyl groups to be good dispersion energy donors but were also able to exploit their properties as such in a practical application in the field of luminescent functional materials. Although the research conducted in the framework of this thesis spans across various topics, the underlying common ground is, that one could not make intuitive sense of many of our experimental findings if bulky functional groups were solely viewed from the perspective of exerting steric repulsion. Furthermore, none of our computational predictions would have held up to the physical reality of our experimental results if London dispersion was not properly accounted for *ab initio*.

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