Chemistry–A European Journal
Research Article
doi.org/10.1002/chem.202300268
Chemistry Europe
European Chemical Societies Publishing
www.chemeurj.org

Balancing Attraction and Repulsion: The Influence of London Dispersion in [10]Cycloparaphenylene-Fullerene Complexes

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Abstract: Herein we present a systematic study of the influence of different alkyl chains in malonyl ester fullerene adducts with [10]cycloparaphenylene ([10]CPP]) and a *tert*-butyl (*t*Bu) ester-substituted [10]CPP analogue. The association constants between the nanoring hosts and the fullerene guests were determined by fluorescence quenching experiments. The trends in association were rationalized by an interplay of repulsion arising from an extended volume and London dispersion as an attractive counterpart.

Introduction

On a basic level, every noncovalent interaction between two molecular species can be regarded as supramolecular chemistry. One prominent example of molecular structures exploited in supramolecular assemblies, especially in the field of carbon nanomaterials, are fullerenes. Their spheric structure makes them ideal candidates especially for curved host molecules. Cycloparaphenylenes ([*n*]CPP), strained carbon nanohoops,[1] are a prime example of such a molecular motif in this regard. The complex between C_{60} and [10]CPP represents the perfect fit regarding the size of guest and host.[2] Here, mainly π–π interactions between the concave side of the CPP and the convex fullerene surface are the driving force within this process. The high association is rationalized by ideal distance between the aromatic entities, making this peapod a curved analogue of two graphene layers. Generally, the association can be tuned by the complementarity in size, shape and interactions. For instance, changing the size of the CPP from [10] to [8], [9] or [11] decreases the association by more than one order of magnitude (K_{SV}).[2] In methylene bridged macrocycles, such as cyclotriveratrylenes and calixarenes, the increased flexibility increases the complementarity in size, while it decreases in shape.[3,4] Additionally, the extension of such systems, such as the substitution on cyclotriveratrylenes with additional phenyl groups, drastically increases the association.[3] A similar behavior was observed for the π-extension in hexa-*peri*-hexabenzocoronene embedded [12]CPP. While the diameter is too large for an efficient complexation of C_{70}, the extended π-interactions lead to a remarkable high association constant.[5] The conceptual binding motif between fullerene and CPP was used to study a Russian doll-type complex between [15]CPP, [10]CPP and C_{60},[6] as well as the differences to the fullerene derivative C_{70}.[7] The strong interaction between the entities was further used in a π–π templating strategy to build a rotaxane based on fullerenes and one [10]CPP unit.[8] In addition to these all-carbon buckyballs, endohedral fullerenes were studied in this manner as well. Here, the interaction is additionally based on charge transfer.[9] This driving force has also been assigned in the complex between [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), an electron acceptor material in organic solar cells, and a porphyrin unit connect to a [10]CPP unit.[10] Our group exploited this binding motif in order to study the stabilizing effect of the nanoring on a fullerenyl radical,[11] as well as the electronic communication between two CPP units through a dumbbell shaped fullerene dimer.[12] We found that the binding is influenced by London dispersion forces which stabilize the 2:1 complex and thus contribute to a positive cooperativity.

Even though this is an illustrative example of weak forces controlling supramolecular complexes no in-depth study has been done to elucidate the different forces operating. Molecular balances offer an experimental tool to quantify these often neglected weak forces.[13] Crucial for these balances is a high sensitivity for energy changes, as these forces are weak for small molecules, but can reach large values for extended systems, though. Cockroft and co-workers adapted a system originally designed by the group of Wilcox to study alkyl-alkyl interactions.[14] In this system two main conformers, the dispersion promoting folded and the dispersion prohibiting unfolded conformer, could be distinguished and quantified by ^{1}H NMR spectroscopy.[15] An additional example of a balance system relying on the interconversion of two different con-

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202300268 formers is realized in a thiobarbiturate system, in which the *anti* and *syn* relationship between two *tert*-butyl (*t*Bu) groups is analyzed.[16] Furthermore, the bond isomerism in cyclooctatetraene was used for the purpose of investigating London dispersion, as the substituents are only in close proximity in one diastereomer.[17] A balance system consisting of an intermolecular system was presented by Chen and co-workers and is based on N-heterocycles which form a proton-bound dimer.[18] The change of dissociation energy was investigated in solution and in the gas phase as well as computationally.

This approach allows an estimation of dispersive interactions between the substrates by comparing the obtained data in the different states. A further example consisting of two entities is the dimerization of a titanium triscatecholate helicate, in which different ester moieties were investigated on their ability to stabilize the dimers by noncovalent interactions.[19] The symmetry of this system increases its accuracy as the signals obtained are threefold amplified. Our group contributed with the use of azobenzene photoswitches with which we could investigate London dispersion as well as solvent effects.[20,21]

In this study we aim to apply the ability of the [10]CPP-C_{60} host-guest system to enforce close proximity of two molecular entities in order to study the influence of substitution of the buckyball on the binding behavior with [10]CPP and a substituted CPP derivative. For this purpose we employed a bis-*tert*-butyl ester-substituted CPP (s[10]CPP) which we reported earlier.[22] As guest molecules we synthesized and employed malonyl ester-substituted fullerene derivatives. To evaluate the interactions between substituents, the effects of the different substitution on the fullerene or the CPP have to be outlined (Figure 1). The backbone motif consists of [10]CPP and C_{60} whose association is mainly driven by π-π interactions (ΔG_1). The introduction of substituents on the fullerene adds an entropic penalty of reduced rotation in the complex, as well as interactions between the substituents on the fullerene and the unsubstituted [10]CPP (ΔG_2). Attachment of *t*Bu ester on the CPP provides the substituted analogue s[10]CPP, which adds strain energy to the equation which is built by dihedral interactions between the substituted phenyl ring and the neighboring ones as well as interaction energies between the substituents and C_{60} (ΔG_3). The association between substituted fullerenes and s[10]CPP can thus be divided into the measurable energies ΔG_1, ΔG_2, ΔG_3, including the unknown interaction energies as well as the substituent-substituent interaction energy [$\Delta G_{\text{Interactions}}(S_F{-}S_C)$], which is then the only unknown variable in this equation.

Results and Discussion

Synthesis of materials

Employing the Bingel-Hirsch reaction to a mixture of C_{60} and symmetric malonyl esters gave access to a library of substituted fullerene derivatives.[23] The employed malonyl esters for this cyclopropanation reaction were formed applying nucleophilic catalysis under Steglich conditions. In this manner, the targeted fullerene derivatives carrying linear as well as branched alkyl chains could be effectively synthesized in two steps from commercially available starting materials (Scheme 1). Besides the linear C_1–C_4 substituents [methyl (Me), ethyl (Et), *n*-propyl (*n*Pr), *n*-butyl (*n*Bu)] different branched substituents [*i*-propyl (*i*Pr), *tert*-butyl (*t*Bu) and 1-adamantyl (Ad)] were incorporated. The unsubstituted nanoring [10]CPP was synthesized following a procedure published by Jasti and co-workers,[24] and *t*Bu ester-substituted [10]CPP was prepared as recently described by us,[22] which follows a "class III" strategy for substituted CPPs,

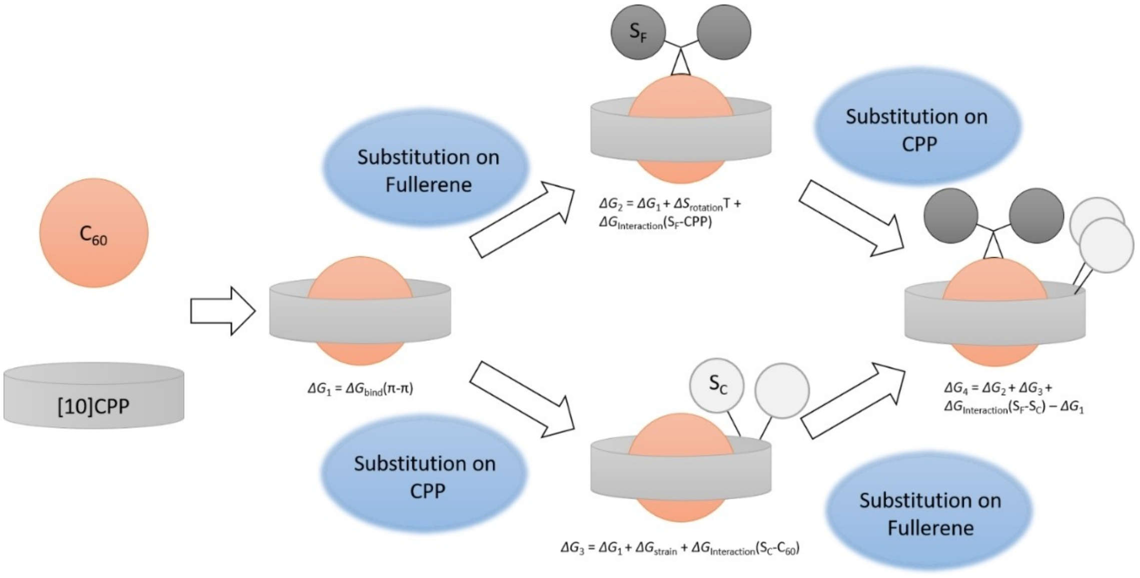
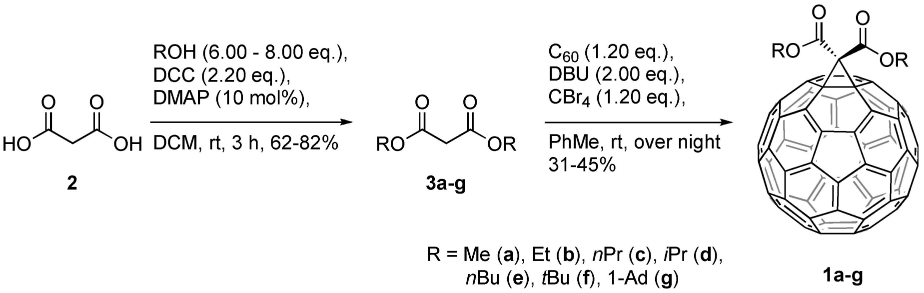


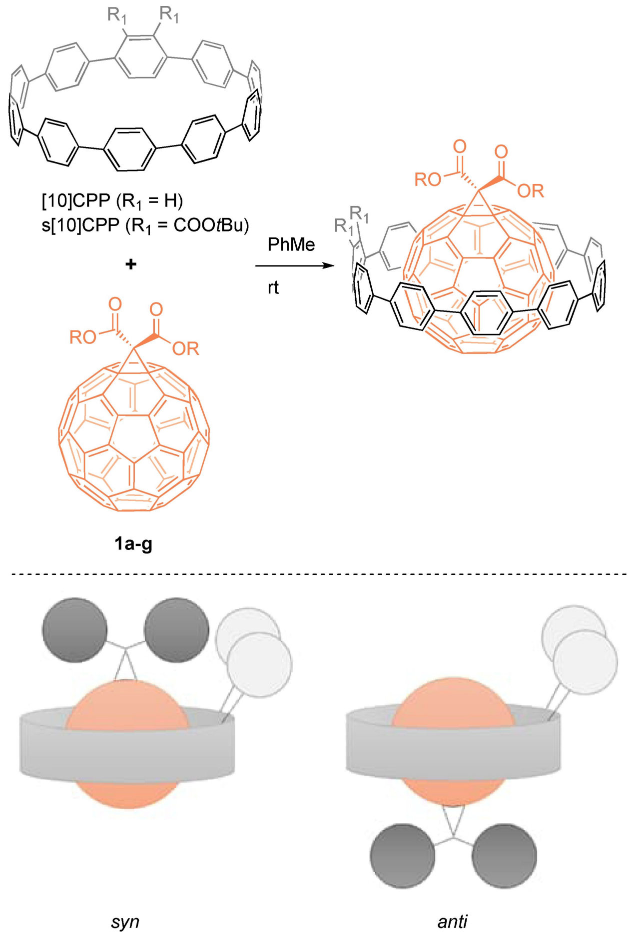
Figure 1. Schematic visualization of the methodological approach for evaluating the noncovalent interactions (S_F = substituents on fullerene, S_C = substituents on s[10]CPP).



Scheme 1. Synthesis of malonyl ester-substituted fullerenes **1 a–g**.

using a [2+2+2] cycloaddition before macrocyclization through cross coupling allowing an efficient build-up.[25]

In principle the association between the two entities can have two different binding states (*syn* andor *anti*) (Scheme 2) which both contribute to the overall association as they quench the fluorescence of the CPP. The contribution of the substituent-substituent interactions within the assembly can still be estimated as this is the only additional force in the case of both substituted entities. To prove the existence of this alignment we conducted a HH NOESY experiment for the complex of s[10]CPP and **1 g** which revealed an noncovalent interaction between the *t*Bu groups and the adamantly groups which can only exist in the *syn* alignment (Figure S3 in the Supporting Information).



Scheme 2. Top: Representative procedure for the complex formation. Bottom: Schematic visualization of the two binding modes in the case of the s[10]CPP.

The association constants between the substituted fullerenes **1 a–g** and [10]CPP as well as s[10]CPP were determined by fluorescence quenching. Following the decreasing fluorescence intensity of the nanoring upon addition of the fullerene guest allowed operation at low concentrations; this is beneficial for complexes for which large association constants are expected.[26] A triple determination was executed to prove the reliability and test the accuracy of the results. Two emission wavelengths of the s[10]CPP were analyzed which further improved the accuracy of the measurements.

Discussion of association constants

For an easier insight into the interactions between the substituents we considered the associations found in relation to the corresponding complex with bare C_{60}. Thus, we could cancel out additional effects like an increased strain in the nanohoop upon substitution which is built by enforcing a small dihedral angle in the complex or simple substituent-buckyball (S_F-CPP) or substituent-nanohoop (S_C-C_{60}) interactions (Figure 1).

Now we could directly evaluate the impact of a substituent on the binding behavior in the final complex. For a consistent and reliable data set, the association constant of [10]CPP and C_{60} was determined in the first step to gain the necessary ΔG_1, being in good agreement with the values determined by the group of Hirsch,[27] which differ from the original values reported by the group of Yamago.[2] By substitution of the fullerene the association to the nanohoops is decreased which can be rationalized by the locked rotation and, hence, entropic penalty as well as substituent-fullerene interactions (Scheme 1, ΔG_2). Starting with the association of parent [10]CPP with substituted fullerenes we found a maximum for the Me/Et derivatives. The binding constant is in comparison to the value of C_{60} ~80% lower. For longer and more branched alkyl groups it is further decreased (by 80–82%; Figure 2, Table 1). The adamantyl fullerene derivative **1 g** deviates in this context,

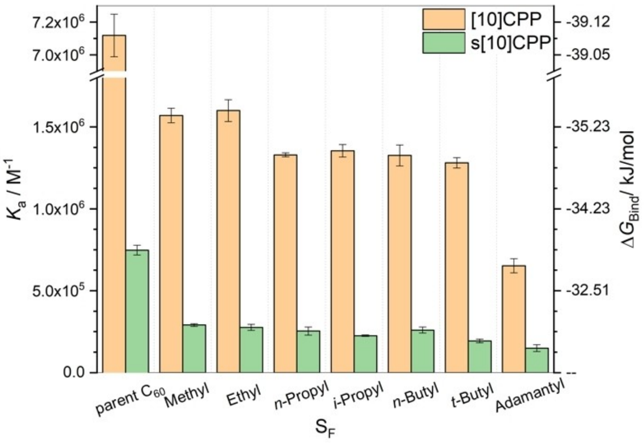


Figure 2. Summary of association constants K_a and binding energies ΔG_{bind} for the fullerene complexes of the parent and *t*Bu ester-substituted [10]CPP.

Table 1. Summary of the determined association energies ΔG_{bind} of the fullerenes C_{60}, and **1 a**–**g** with s[10]CPP and [10]CPP, respectively.

Guest	Energy [kJ mol^{-1}] $\Delta G_{bind,s[10]CPP}$	 $\Delta G_{bind,[10]CPP}$
$\mathbf{C_{60}}$	-33.5 ± 0.1	-39.09 ± 0.05
1 a	-31.17 ± 0.07	-35.35 ± 0.07
1 b	-31.0 ± 0.2	-35.4 ± 0.1
1 c	-30.8 ± 0.2	-35.1 ± 0.3
1 d	-30.54 ± 0.05	-34.98 ± 0.07
1 e	-30.9 ± 0.2	-34.9 ± 0.1
1 f	-30.2 ± 0.2	-34.84 ± 0.06
1 g	-29.5 ± 0.4	-33.2 ± 0.2

having an association of roughly one order of magnitude lower relative to C_{60}. This finding can be explained by the increased steric demand of this bulky substituent.

Next, we investigated the association behavior between the s[10]CPP and the substituted fullerene derivatives to achieve ΔG_3 and ΔG_4. On a first glance, the association with bare C_{60} is one order of magnitude smaller than for unsubstituted [10]CPP. This corresponds to ~5.5 kJ mol^{-1} and can be attributed to dihedral strain which increases due to planarization in order to achieve efficient complexation. The association constants of s[10]CPP with the linear alkyl substituted fullerene derivatives **1 a**–**c**, **e** are around $^2/_3$ lower relative to the value for C_{60}. The decrease in binding strength is thus lower compared to the case of unsubstituted [10]CPP. In contrast to the complexation of unsubstituted [10]CPP with fullerene derivatives **1 a**–**g**, branching reduced the association in a linear trend with the Ad derivative **1 g** bearing the smallest association constant for the complexation with s[10]CPP. Even though the steric interactions between nanoring and fullerene should be more pronounced in the case of the s[10]CPP, the relative change in association for longer alkyl chains is less distinct than in the unsubstituted case with [10]CPP.

To get a better insight into the effect of substitution on the association (energies), the energies were subtracted from the values for C_{60}, thus directly providing the energetic penalties of substitution ($\Delta G_2-\Delta G_1$ for [10]CPP and $\Delta G_4-\Delta G_3$ for s[10]CPP). Figure 3 shows that all substituted derivatives are more endergonic than the complex with C_{60} whereby the complexes with substituted [10]CPP (green bars) pay a smaller penalty than for [10]CPP (orange bars). To envision the differences between the substituted fullerenes, the differences in energy penalties were subtracted and depicted in purple bars. The obtained values are equal to the interaction energies $\Delta G_{Interaction}(S_F-S_C)$. All these values are negative, meaning stabilization occurs for s[10]CPP in contrast to parent [10]CPP (Table 2). Within the fullerene derivatives two strategies were followed: On the one hand increasing the alkyl chain length (Me, Et, *n*Pr, *n*Bu) and on the other increasing branched alkyl substituents (Me, Et, *i*Pr, *t*Bu, Ad) to follow the trend of increasing bulk. Within the set of linear alkyl groups it is surprising that the Me fullerene derivative **1 a** is already with 1.4 kJ mol^{-1} stabilized. A further increase in alkyl chain length at the fullerene adduct towards Et fullerene derivative **1 b** (1.2 kJ mol^{-1}) and *n*Pr derivative **1 c** (1.3 kJ mol^{-1}) does not continue this effect. Only the *n*Bu fullerene derivative **1 e** has a higher value in this regard (1.6 kJ mol^{-1}). This is in agreement with an earlier study of our group in which *n*Bu groups had the strongest stabilizing effect on the *Z* isomer of azobenzene.[21] For branched substituents this trend is more obvious: exchanging one H with a methyl group in Et fullerene derivative **1 b** does not influence the stabilization (1.2 kJ mol^{-1} for *i*Pr fullerene derivative **1 d**) while it is reduced to 0.9 kJ mol^{-1} for the *t*Bu fullerene derivative **1 f**. This trend is inverted in the case of the Ad fullerene derivative **1 g**. Here the substituents have the strongest stabilizing effect in the set of investigated substituents with 1.9 kJ mol^{-1}. This relation between *t*Bu and the larger Ad group can also be found, for example, in a recent study on the equilibrium in alkyl substituted bifluorenylidenes.[28]

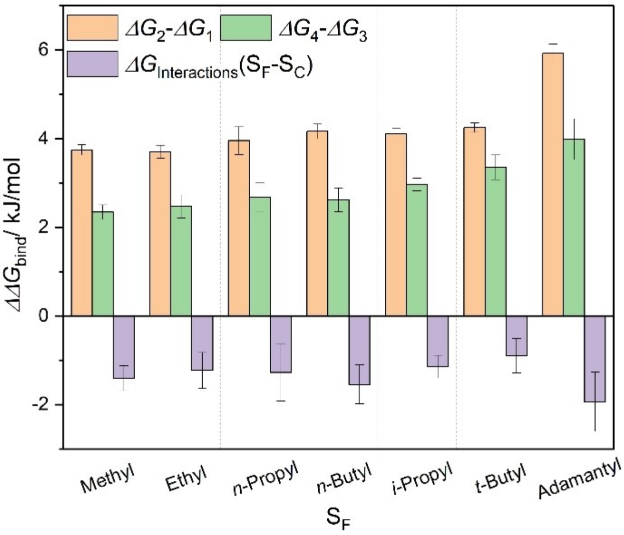


Figure 3. Energy differences relative to the complex with C_{60} for [10]CPP ($\Delta G_2-\Delta G_1$, orange bars), s[10]CPP ($\Delta G_4-\Delta G_3$, green bars) and the differences between them ($\Delta G_{Interactions}(S_F-S_C)$, purple bars).

Table 2. Energy differences $\Delta G_2-\Delta G_1$, $\Delta G_4-\Delta G_3$ and $\Delta G_{\text{Interaction}}(S_F-S_C)$ calculated with equations EQS2 and EQS3 (Supporting Information).

Guest	Energy difference [kJ mol^{-1}] $\Delta G_2-\Delta G_1$	 $\Delta G_4-\Delta G_3$	 $\Delta G_{\text{Interaction}}(S_F-S_C)$
1 a	3.75 ± 0.12	2.34 ± 0.16	−1.40 ± 0.28
1 b	3.70 ± 0.15	2.47 ± 0.26	−1.23 ± 0.40
1 c	3.95 ± 0.32	2.68 ± 0.33	−1.28 ± 0.65
1 d	4.11 ± 0.11	2.97 ± 0.14	−1.15 ± 0.26
1 e	4.16 ± 0.17	2.62 ± 0.27	−1.55 ± 0.44
1 f	4.25 ± 0.11	3.35 ± 0.28	−0.90 ± 0.39
1 g	5.92 ± 0.21	3.98 ± 0.46	−1.94 ± 0.67

Conclusion

In conclusion, we have presented a systematic supramolecular study of fullerene Bingel adducts bearing alkyl groups with different chain lengths with [10]CPP and the substituted [10]CPP derivative. We investigated the steric-repulsion versus London dispersion effects between *t*Bu ester and branched, and elongated alkyl chains. Interestingly, we found different trends for the investigated CPP derivatives. In absolute numbers, all cases led to an increased repulsion while adding the substituents to the buckyball. In order to evaluate the influence of substituents, the total interactions were dissected in individual contributions with reference systems that should cancel out additional, undesired interactions, allowing the substituent–substituent interactions to be quantified. These interactions were expected to be small in energy. Hence, the fluorescence quenching method was applied for these supramolecular complexes, as small energy changes can be reliably determined.

Increasing the chain length of the linear alkyl substituents did not have a large effect on the overall binding, whereby the *n*Bu fullerene derivative **1 e** showed the strongest stabilization (1.6 kJ mol^{-1}) of the complex with s[10]CPP. Overall, branched alkyl groups (*i*Pr **1 d**, *t*Bu **1 f**, 1-Ad **1 g**) showed a stronger effect, and both s[10]CPP and unsubstituted [10]CPP were more endothermic for larger substituents. However, the effect was more pronounced for [10]CPP, leading to a net stabilization for the Ad-substituted fullerene derivative **1 g**.

The presented system allowed low-energy interactions to be quantified efficiently and with high accuracy. Due to the complexity of interactions, only a qualitative rational of the operating effects can be formulated, though. Nevertheless, this proof-of-principle study shows potential for addressing multiple interactions in complex systems. Additionally, it provides guidelines for the design of carbon-based supramolecular functional systems in the future.

Experimental Section

Experimental details are described in the Supporting Information.

Acknowledgements

The authors are grateful for the financial support provided by the Justus Liebig university and the DFG (SPP 1807). The authors are grateful to Dr. Heike Hausmann for NMR measurements. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: cyclophanes · fullerenes · host-guest systems · pi interactions · supramolecular chemistry

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Manuscript received: January 26, 2023
Accepted manuscript online: February 14, 2023
Version of record online: March 3, 2023