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Regioselective Synthesis of *meta*-Tetraaryl-Substituted Adamantane Derivatives and Evaluation of Their White Light Emission

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In memory of Klaus Hafner

New *meta*-substituted tetraaryl adamantane derivatives were synthesized through one-step Friedel-Crafts adamantylation by using $AlCl_3$ in combination with *t*-butyl bromide. The products exhibit improved (over tetraphenyl adamantane) highly directional white-light emission upon irradiation with a continuous wave (CW) laser diode.

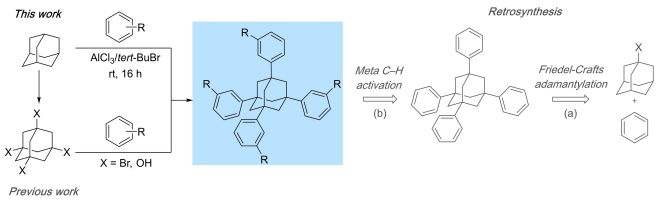
Introduction

The selective modifications of adamantane molecules and their physical properties have been studied[1] widely to make them applicable to medicinal[2] as well as material chemistry,[3] and catalysis.[4] Adamantane tectons have been used as highly thermally stable material building blocks[5] and polymer components.[6] A highly suitable approach for connecting adamantyl moieties to, e.g., aryl scaffolds is through Friedel-Crafts (FC) chemistry[7] of arenes with adamantyl halides or alcohols.[8] There are systematic studies of this reaction type in the presence of various catalysts such as $FeCl_3$,[9] $Hf(OTf)_4$,[10] Pd/C,[11] $InCl_3$,[12] CF_3CO_2H,[13] $H_3[P(M_3O_{10})_4]$ (M=Mo, W),[14] $Ga(OTf)_3$,[15] $B(OTf)_3$,[16] and super acids[17] for the monoadamantylation of substituted benzenes; the *para*-isomers hereby form preferentially. The first tetraarylation of adamantane was published by Newman using $AlCl_3$ as catalyst and 1-bromoadamantane (**2**) as the reactant.[8a] Later, tetraarylation with substituted benzenes was reported as a two-step approach, e.g., by synthesizing 1,3,5,7-tetrakis(*m*-bromophenyl)adamantane from **2** via 1,3,5,7-tetrabromoadamantane in the presence of $AlBr_3$ as the catalyst. Here, the *meta*-isomer forms (70%) in slight preference over the *para*-isomer in a total of 50%.[18] In general, the selective preparation of *meta*-substituted tetraaryl adamantane derivatives is challenging and typically requires FC adamantylation (*a*) followed by *meta* C–H activation (*b*) (Scheme 1). A selective one-step synthesis of *all-meta*-tetrasubstituted aryl adamantane derivatives from adamantane has not been reported.

The motivation for developing a procedure for this substitution pattern derives from the recent finding that tetraphenyl adamantane ($AdPh_4$)[19] and inorganic adamantane-like clusters $[(R\text{-}PhSn)_4S_6]$[20] entered the field of organic light emitters with remarkable nonlinear optical properties.[21] As these can be fine-tuned through the stereoelectronic effects of the phenyl substituents, convenient synthesis of such derivatives also has a practical dimension.

Results and Discussion

We first investigated the reaction of adamantane (**1**) with fluorobenzene in the presence of various Lewis acids to explore the reaction conditions (Table 1). There are only a few examples of fluoroaryl substituted adamantane derivatives; the bromo,[22] iodo,[18a,23] methoxy[24] and cyano[25] derivatives are well known. A catalytic amount of $AlCl_3$ (0.1 equiv.) proved ineffective for tetrasubstitution at room temperature. The major product was monoarylated *m*-fluorophenyladamantane and *o*/*p*-fluorophenyladamantane with complete conversion of **1**. Increasing the amount of $AlCl_3$ (0.3 equiv.) without additives led to 1,3-di(*m*-fluorophenyl)adamantane also with 100% conversion. As found



Scheme 1. Approaches to the arylation of adamantane with a *meta*-substitution pattern.

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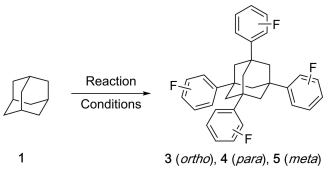
Table 1. Screening of catalysts/conditions for adamantylation of fluorobenzene.

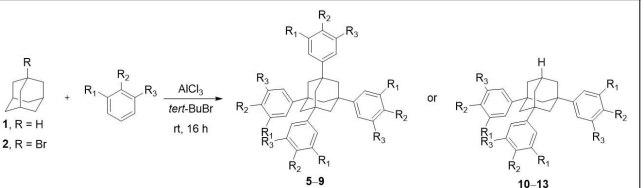


1 3 (*ortho*), 4 (*para*), 5 (*meta*)

Entry	Catalyst[a] [equiv.]	Additives [equiv.]	Time [h]	Conv [%]	Isomer dist.[b] [%] 3/4	5
1	$AlCl_3$ (0.5)	*t*-BuBr (4.0)	16	100	10	75
2	$AlBr_3$ (0.5)	*t*-BuBr (4.0)	3	100	20	55
3	CF_3CO_2H (0.5)	*t*-BuBr (4.0)	16	10	–	–
4	$MeSO_3H$ (0.5)	*t*-BuBr (4.0)	16	5	–	–
5	PCl_5 (0.5)	*t*-BuBr (4.0)	16	8	–	–
6	$TiCl_4$ (0.5)	*t*-BuBr (4.0)	16	10	–	–
7	$Pd(OAc)_2$ (0.1)	*t*-BuBr (4.0)	16	8	–	–
8	Pd/C (0.1)	*t*-BuBr (4.0)	16	5	–	–
9	$AlCl_3$ (0.5)	PrBr (4.0)	16	66	–	–
10	$AlCl_3$ (0.5)	*i*-PrBr (4.0)	16	41	–	–
11	$AlCl_3$ (0.5)	CCl_3Br (4.0)	16	10	–	–
12	$AlCl_3$ (0.5)	*n*-BuBr (4.0)	16	50	–	–
13	$AlCl_3$ (0.5)	*s*-BuBr (4.0)	16	80	–	–

[a] Reaction conditions: **1** (500 mg, 3.68 mmol), fluorobenzene as solvent (4 mL), rt. [b] The progress of the reaction was monitored by ^{19}F-NMR/GCMS.

Table 2. $AlCl_3$-catalyzed arylation of adamantane.



Entry	Starting material	R_1	R_2	R_3	Product	Yield [%][a]
1	**1**	F	H	H	**5**	65
2	**2**	F	H	H	**5**	60
3	**1**	F	F	H	**6**	95
4	**1**	F	CH_3	H	**7**	67[b]
5	**1**	F	H	CH_3	**8**	88
6	**1**	H	H	H	**9**	85
7	**1**	Br	H	H	**10**	82
8	**1**	CH_3	CH_3	H	**11**	91
9	**1**	CH_3	H	CH_3	**12**	88
10	**1**	F	CH_3	H	**13**	90

[a] Reaction conditions: Starting material (500 mg), $AlCl_3$ (0.5 equiv.), *t*-BuBr (4.0 equiv.), substituted benzene as solvent (4.0 mL), rt, 16 h. [b] 48 h with additional amounts of $AlCl_3$ (0.2 equiv.) and *o*-fluorotoluene (2.0 mL).

previously, addition of 4.0 equiv. *t*-BuBr facilitates tetraarylation in the presence of $AlCl_3$[8a] but, to our pleasant surprise, leads to 1,3,5,7-tetrakis(*m*-fluorophenyl)adamantane (**5**) at room temperature (Table 1, entry 1). The products originate from the fact that the tertiary adamantyl cation is more stable than the *t*-butyl cation. Equally, the adamantylated products are thermodynamically more stable than the *t*-butylated products. We detected only a trace amount of 2-(*t*-butyl)fluorobenzene in the GCMS data. With $AlBr_3$ the yield is significantly lower (Table 1, entry 2). Various other catalysts (Table 1, entries 3–8) did not provide the desired product but inseparable mixtures instead. Similarly, none of the other additives gave **5** (Table 1, entries 9–13). We also varied the substrate as indicated in Table 2, by utilizing 4.0 equiv. *t*-BuBr in the presence of 0.5 equiv. $AlCl_3$ at room temperature. With **1** or **2** as starting materials, we obtained **5** in 65% and 60% yield with only trace amounts of the *ortho/para*-isomers (Table 2, entries 1 and 2). 1,2-Difluorobenzene, *o*-fluorotoluene, *m*-fluorotoluene, and benzene afforded good to excellent yields (Table 2, entries 3–6). Bromobenzene, *o*-xylene, *m*-xylene, and *o*-fluorotoluene provided exclusively *meta*-substituted triaryl adamantane derivatives in good yields (Table 2, entries 7–10). If allowed to react significantly longer (48 h instead of 16 h), **7** (entry 4) forms via **13** (entry 10) upon adding 0.2 equiv. of $AlCl_3$ and 2.0 mL of *o*-fluorotoluene. An important factor that affects the formation of tetraaryl adamantane derivatives may be the insolubility of some of the triaryl adamantane intermediates that causes them to precipitate so that the fourth substitution does not take place. To increase their solubility, we explored the ionic liquids [BMIM][OTf] and [EMIM][ESO_4] as co-solvents[29] but without much success. Higher temperatures (70, 90, and 100 °C) only led to mixtures of complex products.[18b]

The NMR analysis of the products was very difficult because they are extremely sparingly soluble in many organic solvents. Thus, the products were characterized by single crystal X-ray diffraction measurements to firmly identify their structures (Figure 1; for details see Supporting Information). By dissolving the products in *o*-xylene, refluxing them at 160 °C overnight and letting them cool very slowly, we obtained crystals suitable for X-ray diffraction analysis.[24]

For a complementary synthesis of 1,3,5,7-tetrakis(*p*-fluorophenyl)adamantane (**4**), we also explored using *t*-BuBr as an additive in combination with $InCl_3$, which is a common and well-explored FC alkylation catalyst.[12] Indeed, at 85 °C, $InCl_3$ efficiently catalyzes the formation of **4** in 59% yield (Figure 1). Analogous reaction conditions at room temperature gave *p*-fluorophenyladamantane in low yield. This result may be due to kinetic control as a likely explanation for the preferential formation of the *p*-isomer, which is, according to our B3LYP-D3(BJ)/6-311++G(3df,3pd)[26] computations 1.9 kcal mol^{-1} less stable than **5** at 298 and 358 K. However, a control experiment in which a 1:1 mixture of **4** and **5** was allowed to react with $InCl_3$ or $AlCl_3$ did not indicate changes in the equilibrium ratio after 24 h. This does not exclude kinetic control but the origin of this selectivity apparently lies in the key interactions in the transition structures with the catalysts.

With the target compounds in hand, we set out to evaluate the non-linear optical responses of all fluoro-compounds (**4**–**8**).[20] We previously established that continuous wave (cw) laser irradiated powdered $AdPh_4$ (**9**) emits a white light continuum. Gratifyingly, **4**–**7** emit white light with different intensities (Figure 2) upon 900 nm cw-laser irradiation (728 mW) shown as the photopic function[27] (the original spectra can be found in the Supporting Information). Compound **8** only displays very low intensity. In the context of unraveling the hitherto not fully

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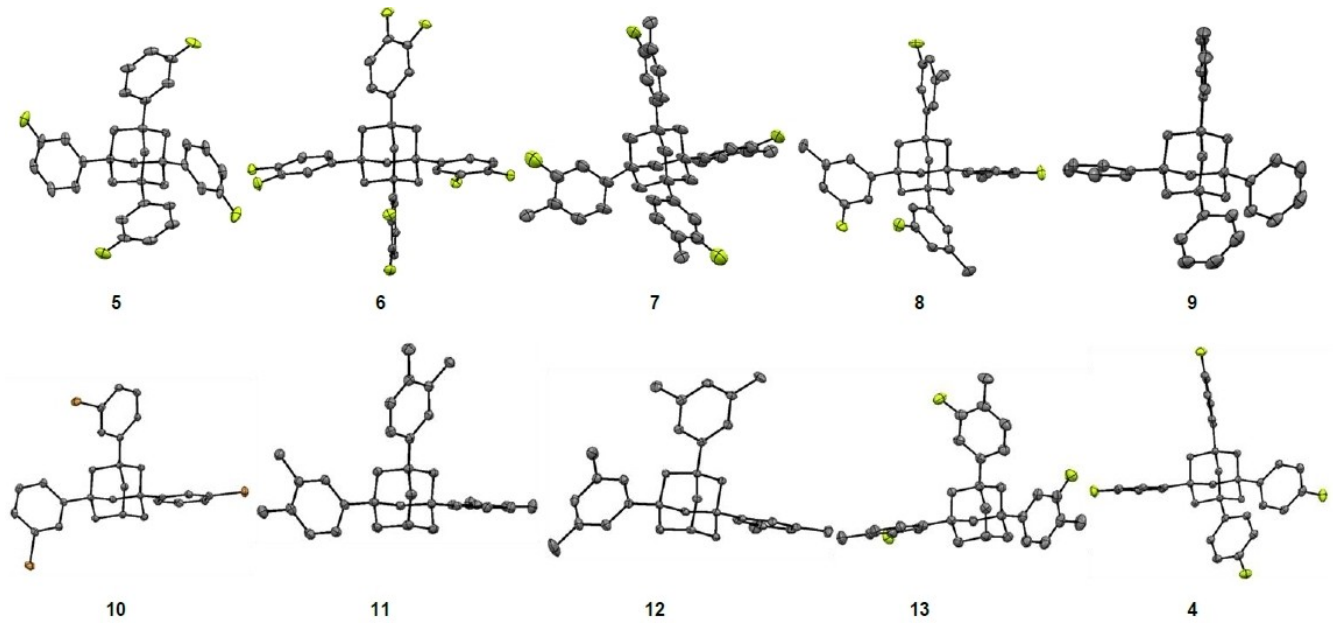

Figure 1. Molecular structures of **4**–**13** determined by X-ray single crystal structure analysis. H atoms omitted for clarity, anisotropic displacement ellipsoids set to 50% probability.

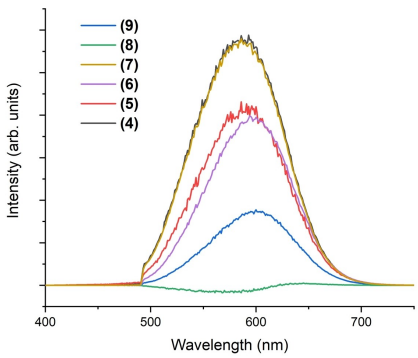

Figure 2. Nonlinear optical response of the powders of **4**–**9**. Upon irradiation with 900 nm cw-laser light, the powders emit white light (photopic presentation).

understood WLG mechanism, these findings will help us develop a better working hypothesis for this remarkable effect that is described in detail elsewhere.[28] In brief, we currently assume that WLG depends on the compounds' habitus and on the nature of the substituents. Obtaining amorphous materials thereby is key for supercontinuum generation and thus the emission of a broad light spectrum. Importantly, the emission retains the driving laser's directionality, a feature that is highly desirable for future applications. Crystalline samples, on the other hand lead to second harmonic generation, indicating a strong connection of the optical properties with the intermolecular order in the solid state.

Significant for the present study is that the intensity and maximum emission wave length is sensitive to the substitution pattern so that it can, in turn, be tuned by chemical modification. This allows the design of WLG emitters on the basis of chemical synthesis utilizing empirical rules to fine-tune the electronic properties.

Conclusion

We report a new *meta*-selective adamantane tetraarylation with substituted benzenes. This Friedel-Crafts type reaction produces high yields of all-*meta*-tetrafluorophenyl adamantane in the presence of *t*-BuBr as the additive and $AlCl_3$ as the catalyst. $InCl_3$ as catalyst produces only the *para*-isomer. Upon laser irradiation powders of **4**–**9** emit white light, also with increased intensity over parent **9**, and a small blue shift in the maximum emission, indicating that the photophysical response of these new materials can be understood on the basis of simple modifications of the core structure.

Experimental Section

All reagents were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on a Bruker Avance II 400 MHz (AV 400) spectrometer. Chemical shifts (δ) are given in ppm relative to residual solvent peaks.

General procedure: A mixture of adamantane (500 mg, 1.0 equiv., 3.68 mmol), *t*-BuBr (1.65 mL, 4.0 equiv., 14.72 mmol) in 4 mL of substituted benzene was added in an oven-dried round bottomed flask. $AlCl_3$ (244 mg, 0.5 equiv., 1.84 mmol) was added in small portions. The reaction was left stirring at room temperature for 16 h. During the reaction, evolving HCl gas (white smoke, caution!) was passed through a second flask containing concentrated aqueous sodium bisulfite. After 16 h, methanol was added to the heterogeneous reaction mixture. The crude solid precipitate was washed with 20 mL of DCM/methanol (1:3) four times. The desired

product was insoluble in chloroform, DCM, and methanol and partially soluble in toluene and o-xylene at elevated temperatures. The product was dissolved in o-xylene at 160 °C overnight and recrystallized by slow cooling to room temperature.

Measurement of the nonlinear optical response: For excitation a CW solid-state laser diode (Roithner RTLMDL-980-1W) with a wavelength of 980 nm was used. Measurements were performed with a maximum power of 728 mW at the sample position. The samples were placed in a small vacuum cell equipped with glass windows and kept at a pressure below 10^{-1} mbar. The vacuum cell was placed under a custom build confocal microscope with a 4× objective (Olympus RMS4X). The light from the sample was separated from the laser with a dichroic mirror (Thorlabs DMLP900R) and focussed onto the face of an optical fiber leading to the spectrometer using a silver-coated off-axis parabolic mirror. A dielectric short pass filter (Thorlabs FESH900) was placed in front of the fiber to further attenuate the fundamental laser line. The light was then detected using a miniature spectrometer with integrated grating (OceanOptics USB650, 350–1000 nm).

Crystallographic data: Details of the X-ray analyses and crystallographic data can be found in the Supporting Information.

Deposition numbers 2105902 (for **4**), 2105904 (for **5**), 2105901 (for **6**), 2105907 (for **7**), 2105900 (for **8**), 2105908 (for **10**), 2105906 (for **11**), 2105905 (for **12**), and 2105903 (for **13**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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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: Alkylation · Amorphous materials · Electrophilic substitution · Fluorine · Hydrocarbons

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[29] [BMIM][OTf] = 1-Butyl-3-methylimidazolium trifluoromethanesulfonate, [EMIM][ESO_4] = 1-Ethyl-3-methylimidazolium ethyl sulfate.

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