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Facile Synthesis of 5,10,15-Hexaaryl Truxenes: Structure and Properties

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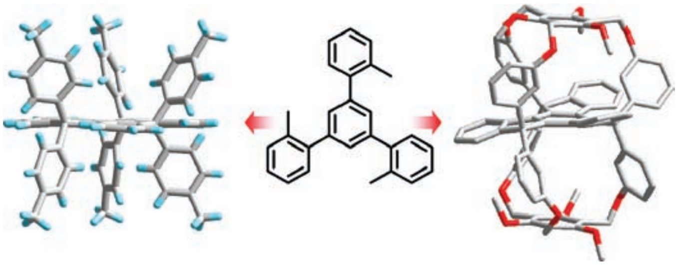
ABSTRACT



A new synthesis of 5,10,15-hexaaryltruxene derivatives has been developed. Experimental observations and theoretical calculations confirmed that the presence of aryl substituents on the sp^3-hybridized bridge carbon atoms had an effect on the photophysical properties of the truxene core. Interestingly, the cage compound 11 possessing a distorted truxene core was verified by X-ray diffraction analysis; the influence of the peripheral aryl substituents on the photophysical properties of the truxene core was diminished because of its molecular rigidity.

Truxene, an interesting C_3-symmetric coplanar structure, has emerged as an important core block for the preparation of novel starburst oligomers[1] and dendrimers[2] that have potential applications in various systems, including liquid crystals,[3] two-photon absorption systems,[4] organic light-emitting diodes,[5] photovoltaics,[6] light-harvesting systems,[7] and field effect transistors.[8] The physical properties of truxene-based materials can be manipulated by extending the π-conjugation emanating from the truxene core and also by introducing rigid peripheral units on the sp^3-hybridized carbon bridges.[9] Truxene-centered materials are generally derived through modification of the truxene core, which is typically synthesized through the condensation of indanones.[10] The peripheral substituents attached to the saturated C5, C10, and C15 carbon bridges are typically introduced by the alkylation of truxene or nucleophilic addition of truxene-5,10,15-trione.[11] To the best of our knowledge, no facile syntheses of 5,10,15-hexaaryl-substituted truxene derivatives have been reported previously. Herein, we describe an efficient synthetic pathway toward such compounds and report

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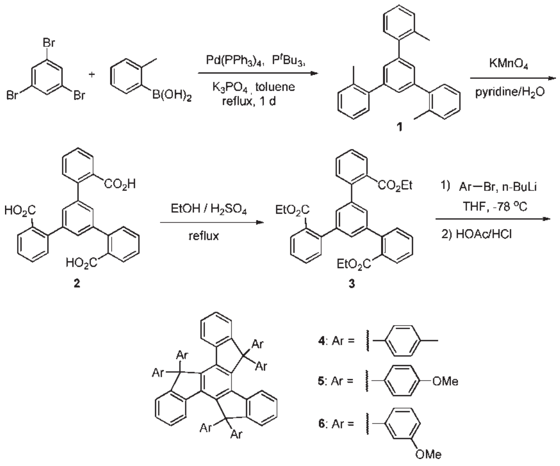
several novel truxene-based molecules possessing intriguing structures and interesting physical properties.

Scheme 1 presents our synthetic pathway toward 5,10,15-hexaaryltruxenes. Palladium-catalyzed Suzuki coupling of 1,3,5-tribromobenzene with 2-methylphenyl boronic acid gave 1,3,5-tri(*o*-tolyl)benzene (**1**), which was previously adopted to synthesize truxene-5,10,15-trione.[12] Oxidation of **1** with $KMnO_4$ in the presence of pyridine afforded the triacid **2** in an isolated yield of 87%. Esterification of **2** with ethanol in the presence of concentrated H_2SO_4 gave the triester **3** in a moderate yield (55%). Double arylations of the triester **3** with various aryl lithium reagents and subsequent acid-catalyzed intramolecular Friedel–Crafts cyclizations provided the 5,10,15-hexaaryltruxene derivatives **4**–**6** in high yields (76–85%).

Scheme 1. Synthetic Pathway of 5,10,15-Hexaaryltruxenes



To verify the molecular structures of these products, we used a two-layer (THF/hexane) crystallization technique to obtain single crystals of the hexa(*p*-tolyl)truxene **4** that were suitable for X-ray diffraction analysis (Figure 1). The presence of the six *p*-tolyl groups at the bridge centers C5, C10, and C15 did not alter the coplanar structural feature of the truxene core. Two groups of three peripheral *p*-tolyl substituents sit on the top and bottom faces, respectively, of the truxene core; this arrangement would appear to prevent intermolecular interactions between neighboring truxene core units.

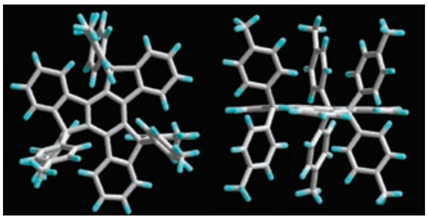


Figure 1. Solid state structure of 5,10,15-hexa(*p*-tolyl)truxene (**4**).

The electronic absorption spectrum of the truxene derivative **4** in $CHCl_3$ revealed an absorption maximum centered at 313 nm, while the corresponding photoluminescence (PL) spectrum features an emission maximum at 377 nm (Figure 2); π–π^* electronic transitions of the truxene core reasonably account for both features. The truxene derivatives **5** and **6** exhibited almost the same photophysical properties as those of **4** (data are summerized in Table S-1, Supporting Information (SI)). It is generally believed that the saturated bridge units impede the extension of π-conjugation from the central truxene core to the aryl peripheral groups. Therefore, the photophysical properties should be irrespective of the nature of the peripheral groups (aryl or alkyl). Notably, however, our new aryl-substituted truxene derivatives exhibit photophysical characteristics that differ from those of their alkyl-substituted counterparts. For example, the absorption maximum of the hexa(*p*-tolyl)truxene **4** was red-shifted by 6 nm relative to that of C5,C10,C15-hexahexyl truxene (**7**); in addition, the PL spectrum of **4** featured a broad band lacking vibronic features that was red-shifted by 7 nm relative to that of **7**. These results suggest the presence of subtle orbital interactions between the peripheral tolyl substituents and the truxene core.

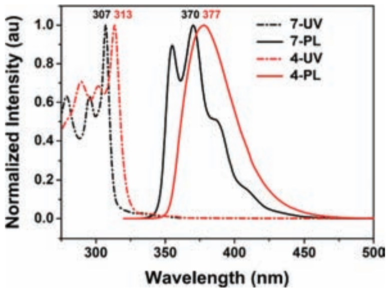


Figure 2. Absorption and emission spectra of C5,C10,C15-hexa(*p*-tolyl)truxene (**4**) and C5,C10,C15-hexahexyltruxene (**7**).

We performed theoretical calculations of the truxene derivative **4** to obtain more detailed insight into its peculiar photophysical behavior. Figure 3 reveals that the active moecular orbitals (MOs) of **4** include a non-negligible fraction from the π- or π^*-orbitals of the tolyl groups. Population analysis using the AOMix program[13] indicated that more than 10% of the population was delocalized to the tolyl groups in the active MOs listed. In comparison, a similar analysis of C5,C10,C15-hexaethyltruxene (**7a**)

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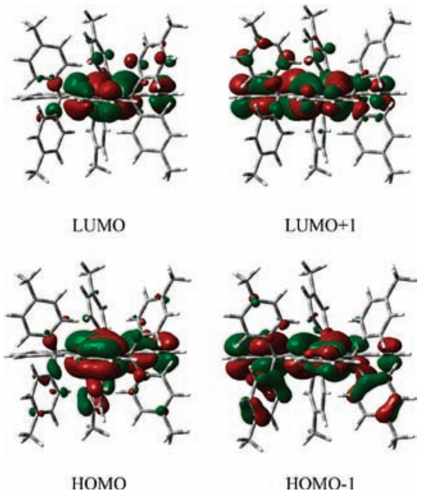
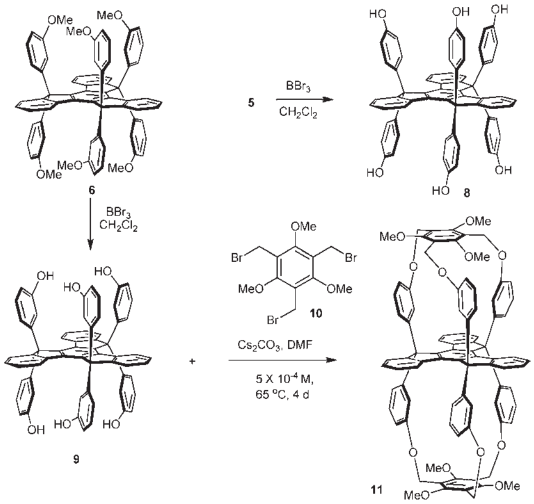


Figure 3. Active frontier MOs of C5,C10,C15-hexa(*p*-tolyl)-truxene (**4**).

revealed only 2−3% delocalization. The delocalization in **4** resulted in a smaller energy gap between its highest occupied MO (HOMO) and lowest unoccupied MO (LUMO), as well as lower excitation energies [Table S1, SI]. The truxene core has C_{3h} symmetry; the first two excitations are symmetry-forbidden (Table S1). This result is consistent with the large Stokes shift observed between the absorption and emission spectra; the main absorption peak is probably due to the optically active S_3 state, followed by internal conversion to the S_1 state where emission originates. For slightly symmetry-broken structures, the S_2 state is slightly more allowed than the S_1 state in all cases. Because an interaction exists between the orbitals of the tolyl groups and truxene core, we might expect that low frequency torsional modes would perturb this interaction and modulate the excitation energy; such a situation would lead to a broad emission spectrum with a much less vibronic structure.

The PL quantum yields of the truxene derivatives **4**, **5**, and **6**, measured using an integration sphere (Hamamatsu C10027), were 0.12, 0.02, and 0.02, respectively. We ascribe the low PL quantum yields of the truxene derivatives **5** and **6**, relative to that of **4**, to the presence of their electron-rich methoxyphenyl substituents, which may facilitate photoinduced electron transfer (PET) to quench the excited truxene core. PET is strongly dependent on the electron density of the donor site. In this regard, phenoxide ions, which are better electron donors than methoxyphenyl groups, should have a more-pronounced PET effect. To confirm that PET occurs in hexaphenoxyl-substituted truxene derivatives, we used BBr_3 to demethylate the truxene derivatives **5** and **6**, obtaining the C5,C10,C15-hexaphenoxyltruxenes **8** and **9**, respectively, in excellent yields (Scheme 2). In CH_3CN, the hexa(*p*-hydroxyphenyl)-truxene derivative **8** exhibits a PL emission maximum centered at 375 nm that is associated with a long wavelength weak emission centered at 550 nm (Figure S1, SI).

Scheme 2. Synthetic Pathway of New Truxenes **8**, **9**, and **10**



When the pH of the solution was increased to 10.5 (by adding standard 0.01 M NaOH and monitoring using a pH meter), the intensity of the short wavelength emission (375 nm) was strongly reduced along with the evident growth of the long wavelength emission. Thus, prominent PET occurs between the local excited state originating from the truxene core of **8** and the electron-donating peripheral phenoxide units, leading to efficient quenching of the UV emission. This efficient electron transfer gives rise to a low-band-gap, charge-separated excited state, which is intrinsically weakly fluorescent.

Inspired by the elegant syntheses of C_3-symmetric cage molecules by Ahn,[14] Gomez-Lor and Echavarren,[15] and Pei,[11a] we subjected the hexa(*m*-hydroxyphenyl)truxene derivative **9** to double-capping with the tribromomesitylene compound **10**.[16] We isolated the cage molecule **11** in 10% yield (Scheme 2). We used a two-layer (hexane/toluene) crystallization technique to obtain single crystals of **11** suitable for X-ray diffraction analysis. Figure 4 displays the triple-decker structure of the cage molecule **11** in the solid state.

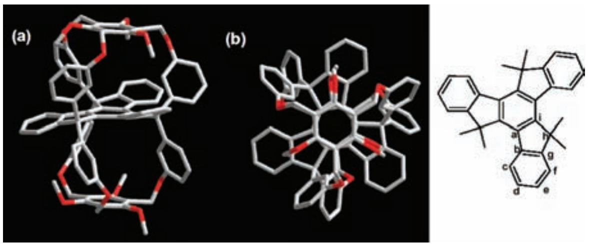


Figure 4. Solid state structure of the cage molecule **11** with hydrogen atoms omitted for clarity; chemical structure of the core of **11** with atom labeling.

The presence of the two mesitylene caps greatly increased the molecular rigidity, as evidenced by the distorted truxene core of **11** (Figure 4a) relative to that of the parent counterpart **4** (Figure 1), primarily because of distortion of the sp^3-hybridized carbon bridges from coplanarity. The average dihedral angle of the $C_b-C_g-C_h-C_i$ units of **11** was 14.66°. Interestingly, five of the six methyl groups on the caps are pointed toward the truxene core, closing the cage walls tightly and allowing more-compact crystal packing. The distances between the $-OCH_2-$**H** hydrogen atoms and the sp^2-hybridized carbon atoms of the outside phenylene rings of the truxene core were in the range from 2.7 to 3.6 Å, implying the possibility of weak $C-H\cdots\pi$ interactions. Our calculations suggest that this conformation is 17 kcal/mol more stable than the one in which all of the methyl groups point away from the truxene core. The existence of such hydrogen bonding interactions may also account for the outside phenylene rings of the truxene core having twisted away from coplanarity, since the distance of the outside phenylene rings to the CH bonds are shortened in many cases. The central benzene ring of the truxene core and the mesitylene rings of the caps are separated with centroid-to-centroid distances of 5.54 (top to center) and 5.25 Å (bottom to center), indicating no evident $\pi-\pi$ interactions, in agreement with our calculation of a negligible population of the caps of **11** in the active MOs (Table S1).

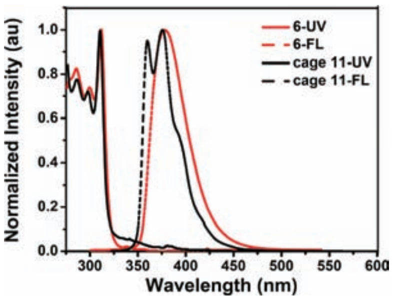


Figure 5. Absorption and emission spectra of the C5,C10,C15-hexaaryltruxene **6** and the cage molecule **11**.

The molecular rigidity of **11** has significant effects on its photophysical properties (Figure 5). This cage molecule exhibits an emission signal with fine vibronic structures that is slightly blue-shifted relative to that of its parent compound **4**; the blue shift is consistent with a lack of coplanarity for the truxene core of **11** and results in a slightly increased band gap. Moreover, the presence of the two capping units inhibits the free rotation of the aryl substituents, thereby decreasing the possibility of interaction between peripheral aryl groups and the truxene core. Indeed we observe a smaller population in the peripheral aryl substituents of **11** in the active MOs, relative to that for **4** (Table S2). The calculated excitation energy of the cage molecule **11** is slightly blue-shifted from those of **4** and **6**, probably due to similar conformational constraints. The lack of peripheral interference means that the truxene unit in the cage molecule **11** exhibits photophysical behavior similar to that of the hexaalkyltruxene derivative **7**. Interestingly, for the "open" hexa(*p*-tolyl)truxene derivative **4** we observed (both experimentally and computationally) significant interactions between the aryl groups attached to the sp^3-hybridized bridge centers and the truxene core, mediated through σ-bonds. When we extended the substituent framework further to give the "closed" truxene derivative **11**, however, the walling and capping aryl groups did not interact significantly with the core unit's π-orbitals. Thus, it is possible to fine-tune the electronic properties of a molecule through σ-bond connection to aryl substituents, but there is a limit to such mediation effects. In our case, layers of capping aryl groups inhibited any further photophysical communication.

In summary, we have established a new synthetic route toward truxene derivatives, providing the flexibility to introduce aryl groups at the saturated bridge carbon atoms. Through experimental observations and theoretical calculations, we also confirmed that σ-bond-separated aryl units could influence the physical properties of the truxene core. Capping of the peripheral aryl groups led to the intriguing triple-decker cage compound **11**, which possessed a distorted truxene core. The ability of the peripheral aryl units to perturb the photophysical properties of the truxene core was mitigated in the cage compound because of its molecular rigidity.

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Supporting Information Available. Detailed experimental procedures; spectroscopic characterization; photophysical data of new compounds; PL spectra of truxene derivative **8** at various values of pH; computational details; population analysis for the frontier MOs of **4**, **7a**, and **11**; ^{1}H, ^{13}C NMR spectra of new compounds; and cif files of compounds **4** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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