Synthesis and Characterization of 2,3,7,8,12,13-Hexabromotruxene and Its Hexaaryl Derivatives

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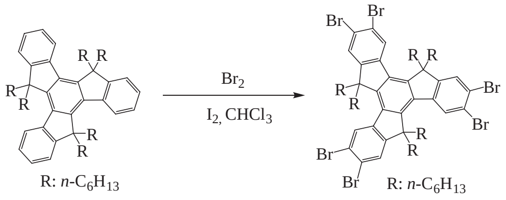
The first synthesis of 2,3,7,8,12,13-hexabromotruxene is reported. Its potential for further functionalization toward highly substituted conjugated materials is examined.

Starburst molecules, in which radial π-conjugated subtituents are joined together by a central core, have been attracting a great deal of interest with regard to their novel structures and their potential optoelectronic applications.[1–3] Generally, the core structure is of particular importance in determining the molecular shape and the architectural topology as well as governing the optoelectronic properties. Various core structures with either three- or four-substituted scaffolds have been explored.[1] Among them, truxene has received much attention as a promising building block for the construction of dendritic conjugated materials because of its interesting three-fluorene-fragment structure, facile chemical functionalization, and intriguing optoelectronic properties.[3–5] A substantial number of truxene derivatives mainly based on three-substituted truxene scaffold have been reported to date.[3,4] Highly substituted 2,3,7,8,12,13-hexaaryltruxenes remain largely unexplored,[2d] although increasing the molecular complexity and dimensionality would bring about unique physical properties.[2] As we know, only some C_3-symmetric truxene derivatives with six-substituted nonconjugated ester or ether functional groups have been studied so far.[5]

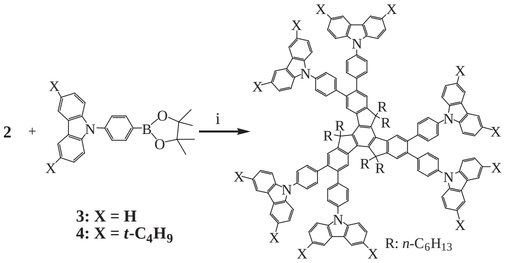
Our recent interest in starburst conjugated materials for optoelectronic applications encouraged us to explore highly substituted robust structures having exotic core functionalities.[2] With this ultimate goal, we report herein our preliminary efforts on the first synthesis of 2,3,7,8,12,13-hexabromotruxene and its hexaaryl derivatives.

The synthesis of 2,3,7,8,12,13-hexabromotruxene **2** is depicted in Scheme 1. It was obtained by excess bromination of **1**[3a,3b] in the presence of iodine. The reaction proceeded efficiently and the target was isolated in good yield (94%) by column chromatography. It should be noted that, unlike traditional three-fold bromination of truxene units,[3a,3b] the presence of catalytic amount of iodine was found to be necessary for the full six-fold bromination of the truxene core. In the ^{1}H NMR spectrum (c.f. Supporting Information, SI)[6] only two singlet signals arising from aromatic regions were observed for compound **2**. Such a simple resonance pattern suggested the symmetry of the molecular structure in **2**. Further characterization by ^{13}C NMR, mass spectra, and elemental analysis also confirmed the proposed molecular structure.



1 **2**

Scheme 1. Synthesis of 2,3,7,8,12,13-hexabromotruxene **2**.



3: **X = H**
4: **X = t-C_4H_9**

5: **X = H**
6: **X = t-C_4H_9**

Scheme 2. Synthesis of 9-phenylcarbazole-functionalized 2,3,7,8,12,13-hexaaryltruxenes **5** and **6**: (i) microwave heating, pressurized-vessel, $Pd(PPh_3)_4$, THF, 150 °C, 15 min.

With hexabromotruxene **2** in hand, to examine the reactivity of this robust skeleton and its feasibility for further functionalization towards highly substituted materials, conversion into the six-fold 2,3,7,8,12,13-hexaaryltruxene derivatives was explored. 9-phenylcarbazoles **3** and **4** as functional groups were selected. As shown in Scheme 2, following a microwave-enhanced six-fold Suzuki coupling procedure,[2b] we successfully realized the full arylization of the 2,3,7,8,12,13-hexabromotruxene core. The expected 2,3,7,8,12,13-hexaaryltruxene derivatives **5** and **6** were obtained in good purity and reasonable chemical yields (75–78%). It is interesting to note that, compared to its triazatruxene analogue,[2e] good solubility for compound **5** in common organic solvents, i.e. $CHCl_3$ and THF, was observed, even though six rigid 9-phenylcarbazole units were incorporated and no solubilizing groups (i.e. t-butyl) were attached. The structure and purity of the synthesized compounds were confirmed by ^{1}H NMR, ^{13}C NMR, MALDI-TOF-MS, and elemental analysis (c.f. SI).[6]

The thermal properties of **5** and **6** were investigated by TGA and DSC analysis. A 5% weight loss temperature (T_d) of **5** and **6** were observed at 423 and 433 °C by TGA. No distinct endothermic or exothermic processes due to the melting or crystallization transitions were observed during the DSC scanning cycles (20–250 °C). The results indicate that the six-substituted starburst truxene derivatives are amorphous materials with good thermal stability. These might probably originate from the bulky highly substituted nonplanar structure arrangements that allow six 9-phenylcarbazole moieties to be surrounded at the periphery.

Figure 1 presents the absorption and photoluminescence (PL) spectra of compounds **5** and **6**. In dilute THF solution, we observed two strong absorption peaks which were due to

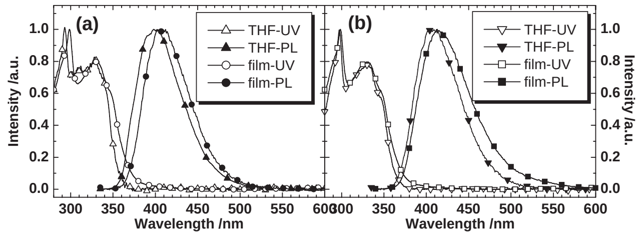


Figure 1. UV–vis absorption and photoluminescence (PL) spectra of **5** (a) and **6** (b) in THF solution and as films.

π–π^* transitions, for both **5** and **6** (293 and 328 nm for **5**; 297 and 330 nm for **6**). The characteristic absorption peak of carbazole units at around 290 nm was clearly identified. In the PL spectra, compounds **5** and **6** exhibited intense structureless deep-blue emission with peak positions centered at 398 and 406 nm, respectively. The lack of vibration structures in PL spectra is consistent with the disorder of the resulting bulky hexaaryl materials. When entering the solid state, both **5** and **6** exhibited almost identical absorption and emission patterns with respect to those in their solution state. Only slight red-shifts ($\approx$6–7 nm) in PL spectra were observed. The results suggest comparable ground-/excited-state electronic structures for these hexaaryl materials, with no substantial aggregation or excimer formation in the condensed state. The highly substituted bulky hexaaryl molecular structure with its strong steric hindrance that can effectively limit intermolecular close-packing is likely to play a key role.

Cyclic voltammetry of compounds **5** and **6** revealed interesting redox behavior (Figure 2). Lower onset oxidation potential (0.62 V for **5** vs. 0.70 V for **6**) was determined for compound **5**, while the onset reduction potentials for **5** and **6** were determined to be almost the same (2.57 V). Considering the structural features, the lower onset oxidation potential for compound **5** might arise from the oxidation of carbazole units at the reactive 3,6-positions, which were passivated by capping with *t*-butyl groups in **6**. The results revealed the potential reactivity of **5** to be further functionalized.

To explore this possibility, a twelve-fold bromination of compound **5** was carried out (Scheme 3). To our surprise, with *N*-bromosuccinimide (NBS) as the brominating agent, a soluble twelve-fold brominated compound **7** was obtained in quantitative yield (94.4%). The facile synthesis also reflected the advantage of incorporating this robust six-substituted truxene scaffold as core structure on inducing good solubility.

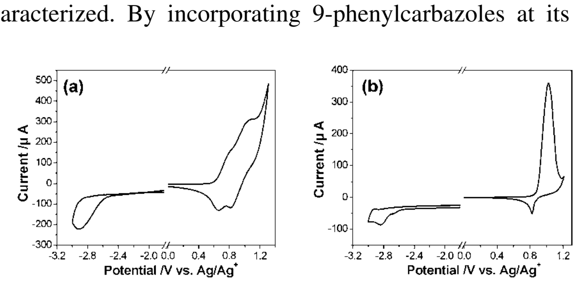
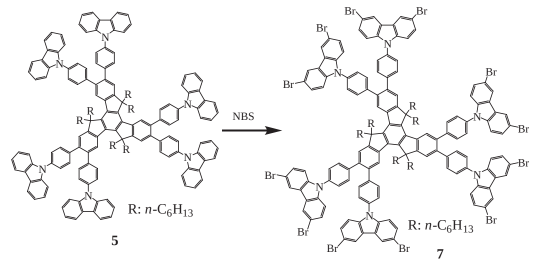


Figure 2. Cyclic voltammogram curves of **5** (a) and **6** (b) as drop-coated films measured in 0.1 M Bu_4NPF_6 acetonitrile solution at a scan rate of $50\,mV\,s^{-1}$ (versus Ag/Ag^+).



Scheme 3. Synthetic scheme of twelve-fold bromination.

In summary, a new multisubstituted building block, 2,3,7,8,12,13-hexabromotruxene, has been synthesized and characterized. By incorporating 9-phenylcarbazoles at its periphery, highly substituted hexaaryl derivatives **5** and **6** were successfully constructed. The investigation of their thermal and photophysical properties further confirmed the significance of constructing highly substituted hexaaryl structure on improving the amorphous properties and on the suppression of aggregation and excimer formation. In addition, due to the good solubility induced by the incorporation of the six-substituted truxene core scaffold, a soluble twelve-fold brominated robust core scaffold **7** was synthesized. It is expected that the facile synthesis and good solubility of these robust core structures are beneficial to exploring sophisticated highly substituted functional materials for optoelectronic applications. Further study on this line is currently in progress.

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References and Notes

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6 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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