

Synthesis and Properties of a Fluorene-Capped Isotruxene: A New Unsymmetrical Star-Shaped π -System

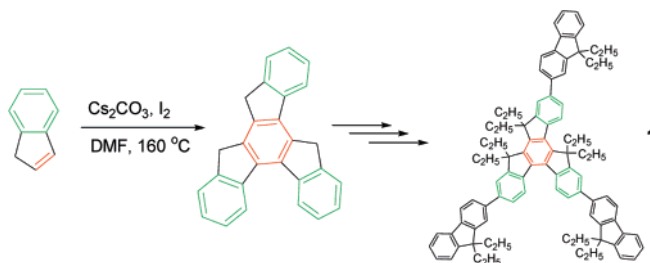
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ABSTRACT



An unsymmetrical star-shaped π -system (1) with an isotruxene core and three fluorene arms has been synthesized, and its photophysical, electrochemical, and thermochemical properties have been investigated and compared with the corresponding symmetrical truxene derivatives 2a–d (Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. J. *Am. Chem. Soc.* 2004, 126, 13695–13702). Stronger electronic couplings between the arms in 1 vs 2a–d lead to lower optical band gap, larger splitting in oxidation potentials, and superior thermostability.

The differences in electronic properties (e.g., photoluminescence, conductivity, and nonlinear optics) between *p*- and *m*-phenylene (*p*-Ph and *m*-Ph)-derived π -conjugated systems have recently attracted much attention.^{1–7} Both theoretical

and experimental studies have shown that electronic coupling between the *m*-Ph-linked segments is nonnegligible but the size strongly depends on the nature of segments.^{1–5} For pure hydrocarbon π -segments, the coupling mediated by *m*-Ph linkers is generally weak, which is particularly evident in polymeric systems such as poly(*p*-phenylenevinylene)s (PPVs), poly(*p*-phenylene)s (PPPs), and poly(*p*-phenyleneethynylene)s (PPEs), where the electronic spectra are substantially blue-shifted when *m*-Ph linkers are introduced into the conjugated backbones.^{2,3} In addition to the disubstituted

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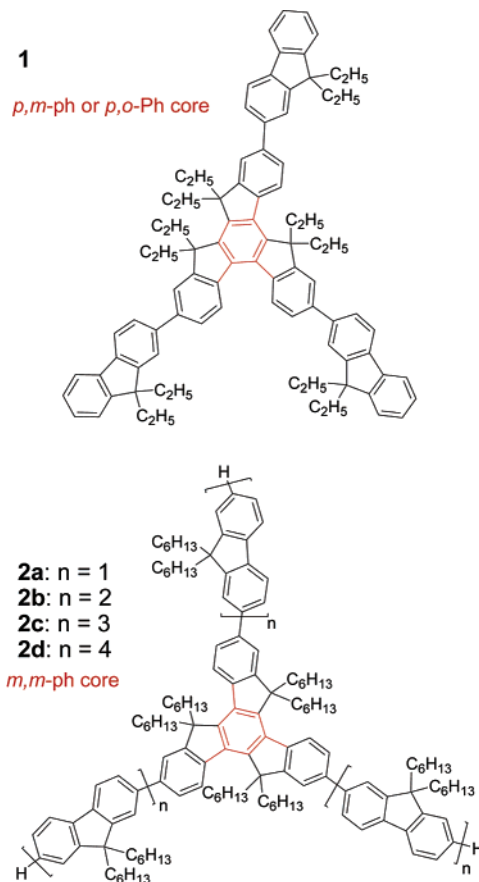
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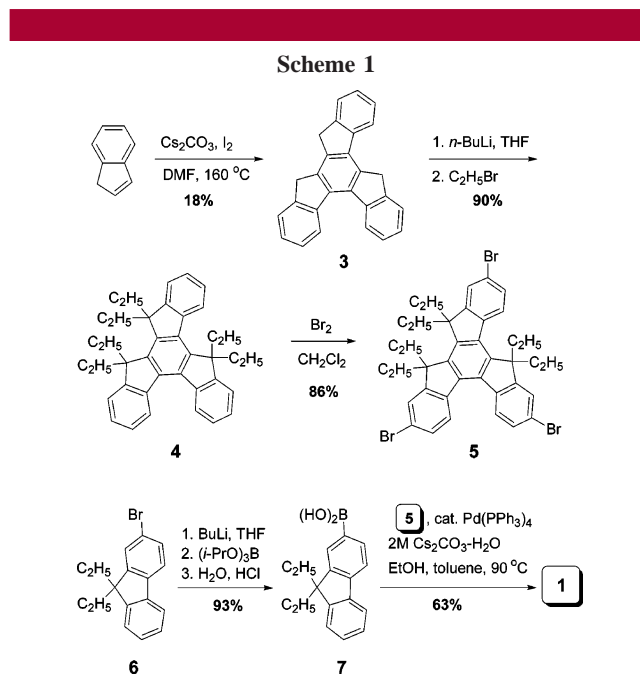
(5) Electron-rich segments such as arylamino and alkoxy substituted phenylacetylene groups could induce significant conjugation interactions in *m*-Ph linked systems. For examples, see: (a) Yang, J.-S.; Liao, K.-L.; Tu, C.-W.; Hwang, C.-Y. *J. Phys. Chem. A* 2005, 109, 6450–6456. (b) Yamaguchi, Y.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *Angew. Chem., Int. Ed.* 2005, 44, 7040–7044. (c) Yamaguchi, Y.; Ochi, T.; Miyamura, S.; Tanaka, T.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *J. Am. Chem. Soc.* 2006, 128, 4504–4505.

phenylene linkers, trisubstituted phenylene branching groups have been largely employed in constructing star-shaped or dendritic π -systems.⁶ However, most examples adopt the 3-fold symmetrical *m,m*-Ph branching units, and much less attention was paid to systems with the unsymmetrical *p,m*-Ph (or *p,o*-Ph) ones. Recent reports by Peng et al. have shown that switching of the *m,m*-Ph to *p,m*-Ph branching units in phenylacetylene monodendrons can significantly enhance the light-harvesting properties.⁷ We report herein the synthesis of a new star-shaped conjugated system with the *p,m*-Ph linker in the core: namely, the fluorene-capped isotruxene **1**. When compared with the corresponding *m,m*-Ph-derived truxene analogs **2a–d** recently reported by Kanibolotsky et al.,⁸ the photoluminescent, electrochemical, and thermal properties of **1** are more like those of **2d** than those of **2a–c**, indicating the presence of strong electronic couplings among the fluorene arms in **1**.

Isotruxene (**3**) can be considered as three “overlapping” fluorene moieties, which arrange in a way different from the symmetrical truxene isomer. Although the synthesis of isotruxene has been known for more than 45 years⁹ and many truxene derivatives have recently been investigated as light-emitting and light-harvesting materials,^{10,11} the chemistry of isotruxene is essentially an unexplored area. One of the possible reasons is the lack of facile methods for the preparation of isotruxene. The currently known synthetic method for isotruxene is a one-step reaction from indene, but it requires high pressure (20 atm) and high temperature (350 °C).⁹ Thus, improvement of the reaction conditions will be an important step toward the development of isotruxene-based materials. In the following, we will show that in the



presence of appropriate catalysts (I_2 and carbonate salts) the reaction can be carried out at much lower temperatures and under ambient atmosphere (Scheme 1).



As shown in Table 1, the conversion of indene to isotruxene is very sensitive to the reaction conditions, including the amount of iodine, the nature of base and

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Table 1. Comparison of Yields of Different Reaction Conditions for Isotrxene Formation from Indene

entry	I ₂ (equiv)	base ^a	solvent	T (°C)	yield ^b (%)
1	0.4	K ₂ CO ₃	DMF	140	12
2	0	K ₂ CO ₃	DMF	140	0
3	0.6	K ₂ CO ₃	DMF	140	7
4	0.4	K ^t BuO	DMF	140	0
5	0.4	pyridine	DMF	140	0
6	0.4	Cs ₂ CO ₃	DMF	140	12
7	0.4	K ₂ CO ₃	DMF	160	7
8	0.4	Cs ₂ CO ₃	DMF	160	18
9	0.4	Cs ₂ CO ₃	mesitylene	160	0

^a 1 equiv of indene. ^b Reaction time is 24 h.

solvent, and the reaction temperature. Preliminary studies indicate that the condition of 2 M of indene in DMF along with 0.4 equiv of iodine and 1 equiv of cesium carbonate at 160 °C provided the best yield (18%, entry 8 in Table 1). Although the isolated yield for isotrxene is unsatisfactory, it appears to be comparable to that from the harsh reaction conditions.¹² A possible mechanism for this reaction, which is initiated by abstraction of the benzylic hydrogen of indene by elemental iodines, is proposed in the Supporting Information (Scheme S1). However, more concrete evidence is required to draw firmer conclusions on the reaction mechanism.

The synthesis of compound **1** was conducted by following the same methodology for compound **2a**⁸ by replacing truxene with isotrxene as the starting material (Scheme 1). It should be noted that the use of shorter alkyl chains, the ethyl groups, for **1** instead of the longer hexyl groups adopted by **2a** reflects the fact that isotrxene is more soluble than truxene in organic solvents,⁹ presumably due to its lower molecular symmetry.

The absorption and fluorescence spectra for **1** in toluene are shown in Figure 1. Unlike the single intense absorption bands ($\lambda_{\text{max}} = 343\text{--}372\text{ nm}$) observed for all four cases of **2a–d**,⁸ the absorption spectrum for **1** displays a maximum at 348 nm and a shoulder at 380 nm. The fluorescence spectrum for **1** shows vibronic bands, but the overall spectrum is less structured than those for **2a–d**.⁸ It is interesting to note that the maximum of the 0–0 fluorescence band (427 nm) for **1** is red-shifted relative to those of **2a–d** (375–411 nm). The fluorescence quantum yield for **1** is high but slightly lower than that for **2a–d**. All these spectroscopic data along with the corresponding data for **2a–d**⁸ are reported in Table 2.

The spectral features clearly indicate that the exciton is delocalized in all 10 phenyl rings of **1** but essentially localized in the individual arms of **2a–d**. More specifically, compound **2d** possesses 10 phenyl rings in each arm so that it is more comparable than **2a–c** to **1** in terms of the peak maxima. With the same 10 phenyl rings for exciton delocalization, the deviations in peak maxima between **1** and **2d**

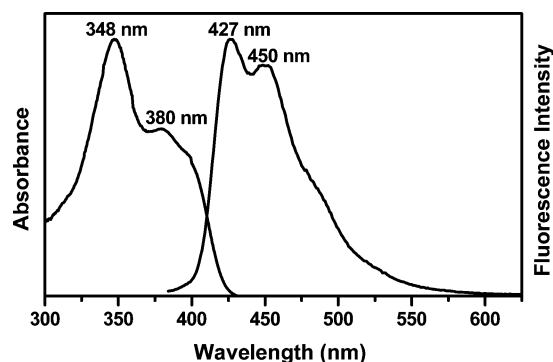


Figure 1. Normalized absorption and fluorescence spectra of **1** in toluene.

reflect the difference in the phenyl ring connections and thus the electronic couplings. In the case of **1**, the presence of two absorption bands is a characteristic of coupling-induced band splitting in *o*-Ph- or *m*-Ph-linked π -systems.^{7b,13} The absence of band splitting in the *m,m*-Ph-linked systems **2a–d** indicates weak exciton couplings between the arms. Accordingly, the band splitting observed for **1** should be attributed to the *ortho* conjugated effect, and the central phenyl ring in isotrxene is better described as a *p,o*-Ph rather than a *p,m*-Ph branching group. Since band splitting often reduces the oscillator strength for the $S_0 \rightarrow S_1$ transition, corresponding to the slightly lower log ϵ value for **1** (4.82) vs **2a–d** (4.97–5.67) (Table 2), this might account for the somewhat lower fluorescence quantum yields for **1** vs **2a–d**.

The electronic conjugation interactions among the three arms of **1** are also revealed by its electrochemical behavior. As shown in Figure 2, compound **1** displays two reversible

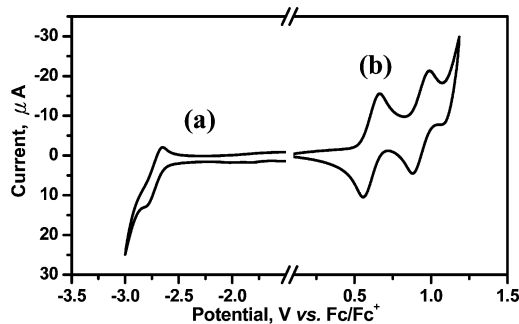


Figure 2. Cyclic voltammogram of **1** in (a) THF (for reduction) and (b) dichloromethane (for oxidation); electrode Pt for reduction and glassy carbon for oxidation; electrolyte 0.1 M Bu₄NPF₆, scan rate 100 mV s⁻¹.

oxidation processes with similar current values. Although the values of $\Delta E_{\text{pa-pc}}$ (85–100 mV) are somewhat larger

(12) The reaction in ref 9 generated a mixture of isotrxene and truxene with a yield of 40%, but no isolated yield was reported for isotrxene.

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Table 2. Spectral, Electrochemical, and Thermal Data for **1** and **2a–d**^a

compd	log ϵ^b	$\lambda_{\text{abs}},^b$ nm	$\lambda_{\text{fl}},^b$ nm	Φ_{fl}^b	$E_{1/2}^{\text{oxd}},^c$ V	$E_{1/2}^{\text{red}},^d$ V	$T_{\text{g}},^{\circ}\text{C}$	$T_{\text{d}},^{\circ}\text{C}$
1	5.01, 4.82	348, 380	427, 450	0.65	0.61, 0.94	−2.74	160	415
2a ^a	4.97	343	375sh, 396, 416sh	0.70	0.80, 1.05	−2.80	63	401
2b ^a	5.50	360	399, 422, 443sh	0.83	0.76, 0.84, 1.03	−2.74	86	408
2c ^a	5.61	370	408, 431, 460sh	0.83	0.76, 0.94	−2.70	101	410
2d ^a	5.67	374	411, 436, 460sh	0.86	0.74, 0.87	−2.66	116	413

^a Data for **2a–d** are from ref 8. ^b In toluene solutions. ^c In dichloromethane solution. ^d In THF solution.

than the theoretical value of 59 mV, both oxidation processes are essentially one-electron steps, corresponding to the formation of radical cation and dication species.^{8,14} The separation between the two oxidation peaks (ΔE_{ox}) is ca. 0.33 eV. More than one cyclic voltammetric oxidation peaks are also observed for **2a–d**, but the separations between the peaks are all less than 0.3 eV (0.08–0.25).⁸ A larger ΔE_{ox} value for **1** vs **2a–d** suggests a stronger electronic coupling among the arms, which is consistent with the observations in electronic spectra.

The thermal and morphological stabilities of **1** have also been investigated and compared with **2a–d**. As shown in Table 2, both the glass transition temperature (T_{g}) and the TGA 5% decomposition temperature for **1** are larger than those for **2a–d**, indicating that isotruxene-based star-shaped π -systems are promising candidates for optoelectronic applications.

In summary, we have synthesized the first isotruxene-based star-shaped π -system **1**, which displays promising light-

emitting properties and thermostabilities. In addition, comparison of **1** and the corresponding truxene derivatives **2a–d** provide a new example toward a better understanding of the *p,o*-Ph vs *m,m*-Ph effect on the properties of π -conjugated systems. Further studies on the synthesis and properties of new isotruxene derivatives are in progress.

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Supporting Information Available: Experimental methods, synthetic procedures, characterization data, a proposed mechanism for isotruxene formation, and ¹H and ¹³C NMR spectra for all new compounds and DSC and TGA scans for compound **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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