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Synthesis and Properties of Novel C_3-Symmetric Coplanar Chromophores

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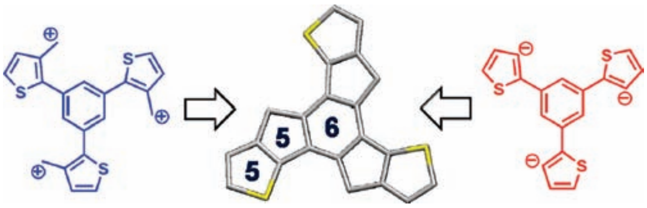
ABSTRACT



New synthetic pathways for novel C_3-symmetric molecules featured with a thiophene-fused *six-five-five* carbon-bridged coplanar core structure have been established. The incorporation of thiophene as the constituent of a C_3-symmetric core provides effective modulation of the physical properties and imparts extra flexibility for π-conjugated functionalization stemming from either the embedded thiophene or pendant aryl substitutions.

C_3-symmetric molecules intrigue organic chemistry scientists for their new synthetic pathways and optoelectronic applications.[1] A major goal for C_3-symmetric material chemistry is to design new families of π-conjugated star-shaped molecules with novel core structures, and to investigate their structure−property relationships. Among the reported C_3-symmetric polycyclic aromatics, truxene (Figure 1) is one of the most promising and versatile building blocks for the synthesis of fascinating molecules with various applications such as organic field-effect transistors (OFETs), solar cells, and electroluminescent devices.[2] In addition to truxene, C_3-symmetric coplanar analogues with bridging heteroatoms (N, O, S; Figure 1) have also been explored,[3] making possible direct manipulations on the electronic structure (HOMO/LUMO levels) and consequent physical properties of the truxene analogues. For example, triazatruxene-based materials have been exploited as the precursor of a triaza-analogue of crushed fullerenes[4] and have been utilized as liquid crystals,[5] as two-photon absorption materials,[6] and in OLED applications.[7] To the best of our knowledge, the reported C_3-symmetric coplanar structures are generally composed of *six-five-six* fused rings. To date, an analogous C_3-symmetric coplanar structure featuring *six-five-five* fused rings has not been reported. In this communication, we report for the first time the synthetic routes and physical properties of a novel class of thiophene-embedded C_3-symmetric star-shaped coplanar molecules. The incorporation of electron-rich thiophene rings as the π-conjugated constituent of this new C_3-symmetric coplanar structure drastically perturbs the electronic properties of

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the core, namely raising the HOMO level as compared to the pure hydrocarbon homologues.

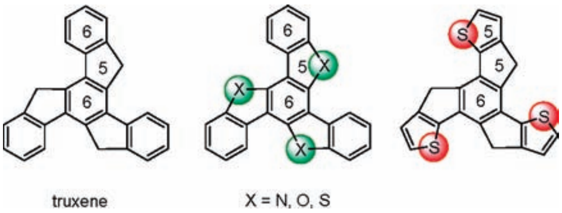
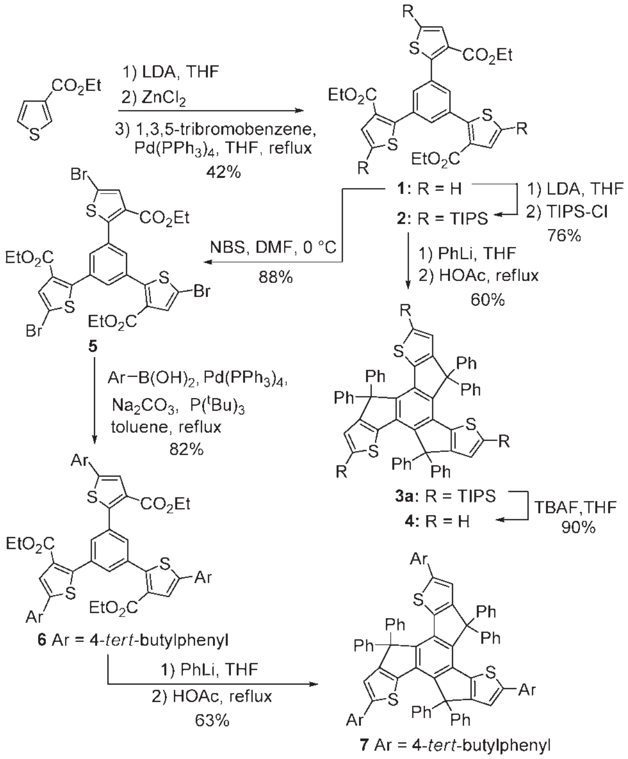


Figure 1. Chemical structures of truxene and its heterohomologues.

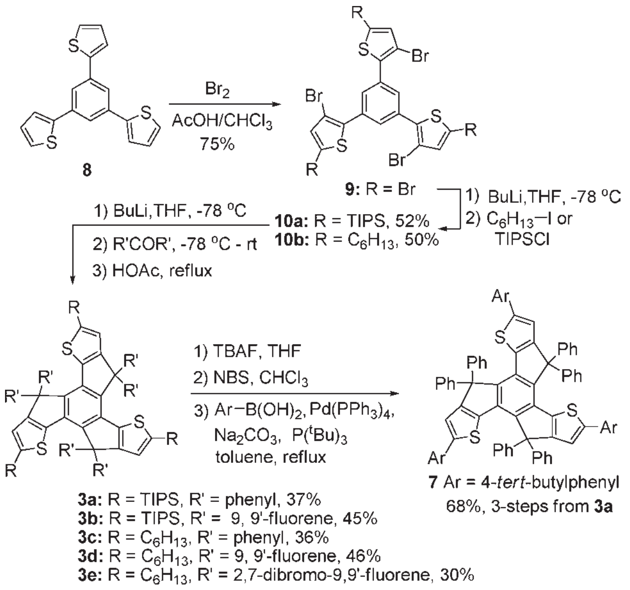
Scheme 1 depicts our synthetic approaches of the target C_3-symmetric chromophores. Based on our previously established synthesis of sp^3-carbon bridge coplanar ring systems,[8] a double addition of aryl organometallics onto an ortho ester group of biaryls followed by intramolecular Friedel–Crafts cyclization is generally involved.

Scheme 1. Synthesis of the Thiophene-Fused C_3-Symmetric Coplanar Molecules



The crucial triester intermediate **1** was furnished in 42% yield by the Negishi cross-coupling reaction of 1,3,5-tribromobenzene with 3-(ethoxycarbonyl)-2-thienyl zinc cholride. Before carrying out the nucleophilic addition on the ester groups of **1** with aryl lithium, a triisopropylsilyl (TIPS) group was introduced to block the reactive sites of the α-thienyl groups. Thus, deprotonation of **1** with LDA followed by quenching with TIPS-Cl afforded compound **2** in good yield (76%). Subsequent addition of phenyllithium, followed by intramolecular Friedel–Crafts cyclization, gave the desired product **3a** in 60% yield. Finally, the hexaphenyl substituted coplanar molecule **4** was isolated with an excellent yield of 90% after protodesilylation with tetrabutylammonium fluoride (TBAF). Instead of using TIPS as the reactive site blocking group, bromination of triester **1** with NBS gave the versatile tribromide **5** in high yield. The regioselective bromination indicates that π-conjugated derivatives stemming from the new thiophene-fused coplanar core structure could be feasibly achieved. Along this line, a Pd-catalyzed Suzuki coupling reaction of intermediate **5** with 4-*tert*-butylphenyl boronic acid gave triester **6** with an isolated yield of 82%. The addition of an excess amount of phenyllithium onto the ester groups of **6** gave the corresponding triaryl alcohol. Without further purification, the crude triaryl alcohol was subjected to acid-mediated triple cyclization to afford the coplanar C_3-symmetric product **7** with an isolated yield of 63%. Scheme 2 depicts an alternative pathway for the synthesis of thiophene-fused C_3-symmetric coplanar molecules.

Scheme 2. Alternative Synthetic Route of the Thiophene-Fused C_3-Symmetric Coplanar Molecules



For this approach, the lithiated core was utilized to add onto the diarylketones for generating the tertiary alcohols used for the proton-promoted intramolecular cyclization. The synthesis started from the bromination of 1,3,5-trithienylbenzene **8** to yield hexabromo intermediate **9** with a yield of 78%. Treatment of compound **9** with *n*-BuLi at −78 °C regioselectively gave the trilithiated intermediate,

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which was quenched with TIPS-Cl and 1-iodohexane, giving TIPS and hexyl-substituted tribromo compounds **10a** and **10b**, respectively. A subsequent Li/Br exchange reaction of tribromo compound **10** with *n*-BuLi gave the reactive lithiated intermediate, which was then quenched with various diarylketones to afford the corresponding tertiary alcohols. Without further purifications, these alcohols underwent acid-mediated intramolecular cyclization to give the coplanar cores **3a**–**e** in moderate yields. After protodesilylation of **3a** with TBAF followed by regioselective NBS bromination, the resulting tribromine intermediate can be directly exploited for a Suzuki coupling reaction with 4-*tert*-butylphenyl boronic acid to give molecule **7** in 68% yield (three steps). This synthetic strategy provides extra flexibility for the functionalization of the aryl substitutions, as we can envision that further decoration on the peripheral bromo-substituted fluorene moieties of **3e** would give rise to new structural features arranging perpendicularly relative to the coplanar C_3-symmetric core.

The molecular structure of thiophene-fused C_3-symmetric molecules **3a** and **3d** can be verified by X-ray crystallography (Figure 2). The averaged dihedral angles of the pivotal phenylene ring and peripheral thiophene rings of molecules **3a** and **3d** were calculated to be 6.67° and 6.15°, respectively, suggesting slight deviations from a perfect coplanar plane due to the manner of fused *six-five-five* rings. The aryl substitutions on the saturated carbon bridge position on the top and bottom faces of the molecular plane imparts a low tendency for interchromophore interactions. In addition, the rigid and coplanar spirofluorene substituents are orthogonal relative to the molecular plane of **3d**, giving an interesting tripod-like molecule.

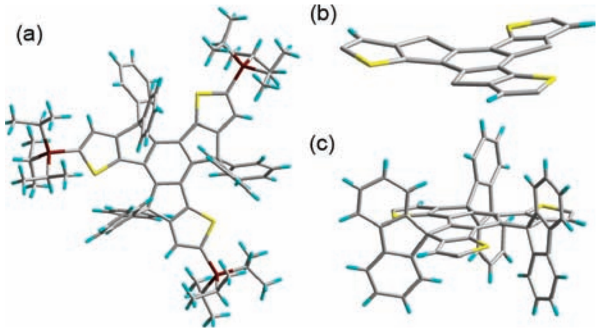

Figure 2. (a) Top view of molecular structure of **3a**. (b) C_3-symmetric core structure of **3a**. (c) The tripod-like **3d** with orthogonal spirofluorene substituents; the alkyl side chains are omitted for clarity.

The introduction of aryl substitutions on the top and bottom faces of the thiophene-fused C_3-symmetric coplanar core makes the resulting molecules rather bulky and rigid. Differential scanning calorimetry (DSC) analysis indicated that these new thiophene-fused C_3-symmetry materials exhibit no obvious glass transition temperatures (T_g) except for **3d** (120 °C). Thermogravimetric analysis (TGA) revealed the high heat tolerance of these new compounds with decomposition temperatures (T_d) (5% weight loss) ranging from 365 to 433 °C. The data are summarized in Table 1.

The absorption (UV–vis) and photoluminescent (PL) sepecta of molecules **4** and **7** are compared to those of pure hydrcarbon parent counterpart **T1** (Figure 3). The UV–vis and PL spectra of the thiophene-fused coplanar molecule **4** exhibited substantial red shifts relative to those of truxene derivative **T1**. This result clearly indicates the effect of reducing the optical gap when thiophene was introduced as the constitutent of the C_3-symmetric coplanar core. An evident Stokes shift (6832 cm^{-1}) of **4** was observed which may be a result of the first two excitations being symmetry-forbidden. If so, the main absorption peak could result from the electronic transition to higher states, followed by internal conversion to the S1 state where emission originates.[9] The PL quantum yields (QYs) of these C_3-symmetric molecules are comparable as compared to that of the parent truxene **T1** (Table 1). In addition, the extension of the π-conjugation from the thiophene-fused core can pronouncedly alter the photophysical behavior as evidenced by the significant red shifts in UV–vis and PL spectra and improved PL efficiency of compound **7**.

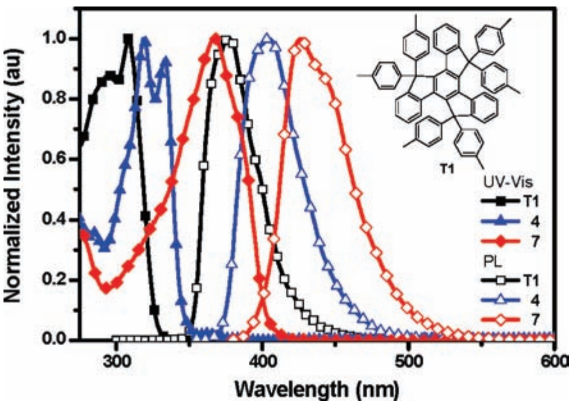

Figure 3. UV–vis absorption spectra (solid symbol) and photoluminescence spectra (open symbol) of **T1**, **4**, and **7**.

Cyclic voltammetry (CV) was used to probe the electrochemical behavior of thiophene-fused C_3-symmetry coplanar molecules and parent molecule **T1** (Figure 4). The electrochemical data are summarized in Table 1. The oxidation potentials of the thiophene-embedded molecules are significantly lower than that of truxene **T1**. For example, the oxidation onset of **4** is 1.28 V, which is evidently lower than that of **T1** (1.44 V). This result clearly indicates the considerable HOMO-raising

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Table 1. Properties of Truxene **T1** and the Thiophene-Embedded Truxene Analogues

compd	abs$^a\lambda_{max}$ (log ε) [nm]	PL$^b\lambda_{max}$ [nm]	Q.Y.^{c} [%]	$T_g{}^d$ [°C]	$T_d{}^f$ [°C]	$E_{1/2\ oxd}{}^g$ [V]	HOMO^i [eV]	LUMO^i [eV]
T1	292, 308 (4.85)	377	12	n.d.^{e}	409	1.52	−5.85	−2.10
3a	326 (4.79), 342 (4.80)	410	12	n.d.	339	1.25	−5.58	−2.11
3b	324 (5.00), 341 (4.99)	408	9	n.d.	365	1.22	−5.55	−2.06
3c	324 (4.86), 339 (4.86)	411	11	n.d.	365	1.16	−5.49	−2.00
3d	321 (4.92), 337 (4.85)	409	6	120	380	1.14	−5.47	−1.93
4	316 (4.48), 330 (4.44)	403	10	n.d.	373	1.36^h	−5.69	−2.07
7	367 (4.95)	423	30	n.d.	433	1.15	−5.48	−2.39

[a] In $CHCl_3$. [b] In $CHCl_3$, upon excitation at the absorption maximum. [c] In CH_2Cl_2, measured by calibrated integrating sphere system (Hamamatsu C9920) [d] Analyzed using DSC. [e] n.d. = not detected. [f] Analyzed using TGA (5% weight loss). [g] In CH_2Cl_2 containing 0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte; potentials were recorded vs Ag/AgCl. [h] $E_p{}^a$, due to irreversible CV. [i] HOMO and LUMO were estimated from $E_{1/2\ oxd}$ and absorption onset.

effect upon the implantation of electron-rich thiophenes as the constitutional moieties of the C_3-symmetric coplanar core. It should be noted that the reduction peak observed at 0.89 V of **4** is due to the electrochemically dimerized species as the electroactive sites are unprotected (Figure S-2, Supporting Information). The extended π-conjugation is beneficial for giving a higher HOMO level and quasi-reversible oxidation and reduction potentials (Figure S-3).

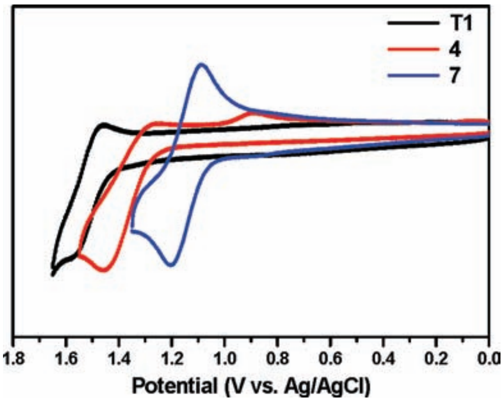

Figure 4. Cyclic voltammograms of compounds **T1**, **4**, and **7**.

In summary, for the first time, inventive synthetic pathways for novel C_3-symmetric molecules featuring a thiophene-fused *six-five-five* carbon-bridged coplanar structure have been successfully established. The versatile synthetic pathways provide the flexibility for further π-conjugated functionalization stemming from either the constituted thiophene ring or the pendant aryl substitutions. The molecular core structures were confirmed to be nearly coplanar by X-ray crystallography. The incorporation of thiophene as the constituent of a C_3-symmetric core provides effective modulation of the physical properties, particularly the HOMO-raisng effect, which was evidenced by the lower oxidation potential in CV and red-shifted absorption and emission in photophysics. With great thermal stability as a property, we could anticipate the great opportunity of these novel C_3-symmetric chromophores to serve as potential materials for optoelectronic devices.

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Supporting Information Available. Detailed experimental procedures; spectroscopic characterization; the crystal data and cif files of compounds **1**, **3a**, and **3d**; the X-ray crystal structure of compound **1**; cyclic voltammograms of compounds **T1**, **4**, and **7**; UV−visible absorption and photoluminescence spectra of **3a**−**d**; ^{1}H, ^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.