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Synthesis, Polymerization, and Unusual Properties of New Star-Shaped Thiophene Oligomers

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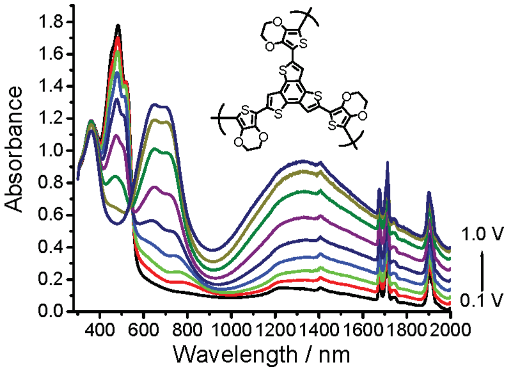
ABSTRACT



Terthienobenzene (TTB, 6) was prepared through a new, high yield route along with π-extended derivatives 10 and 11. Electropolymerization of tris-EDOT derivative 11 results in a highly stable cross-linked conjugated polymer that shows polaron confinement between the TTB units as confirmed by UV−vis−NIR spectroelectrochemistry and EPR.

Thiophene-based π-conjugated oligomers with complex molecular architectures such as star-shaped,[1] X-shaped[2] and dendritic[3] oligothiophenes have been the focus of recent research[4] as promising organic semiconductors. Their increased dimensionality (2D or 3D), different from the linear structure of most conjugated oligomers and polymers, offers new opportunities to control the morphology of the material in thin film devices[5,6] and to build new nanostructured materials.[7]

Star-shaped oligothiophenes have been constructed with benzene,[1a] triarylamine,[8] truxene[9] and several other cores, and in every instance, the steric constraints of the core resulted in rotation of the linked (oligo)thiophene arms out of the plane. Roncali's group has previously reported synthesis[1d] and remarkable performance in photovoltaic devices[10] of star-shaped oligothiophenes based on terthienobenzene (TTB, **6**) core. The improved semiconducting

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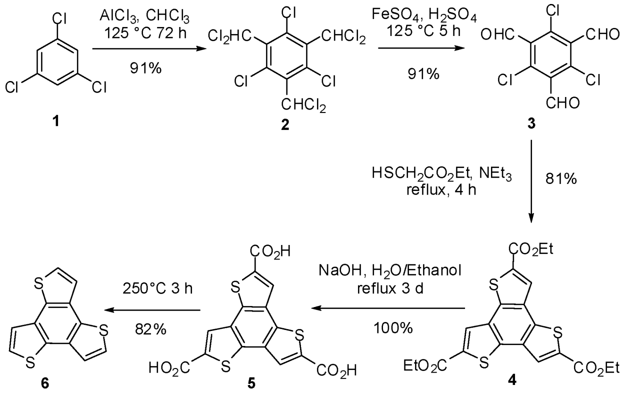
properties were believed to result from increased planarity of such derivatives (compared to benzene-core derived oligomers). In our search for high-dimensional organic semiconductors, we turned our attention to TTB derivatives as tridentate monomers for creating two-dimensional conjugated polymers.[11]

Here, we report the synthesis of new star-shaped oligothiophenes composed of the TTB core and three symmetrically positioned thiophene or 3,4-ethylenedioxythiophene (EDOT) end groups, their electroxidative polymerization and spectroelectrochemical studies. In addition, we describe an improved route for synthesis of TTB **6** in five simple steps from 1,3,5-trichlorobenzene. An alternative procedure[12,1d] relied on a more expensive 2,3-dibromothiophene and involved two metallorganic couplings, oxidative aromatization and photooxidative cyclization affording **6** with overall 34% yield. The scale up of this procedure is hampered by the final photooxidative coupling which proceeds in low and variable yield (20−50% in our hands) and requires high dilution conditions (to prevent polymerization).

In this work, the known trialdehyde precursor **3** was prepared from 1,3,5-trichlorobenzene **1** through Friedel−Crafts alkylation[13] with chloroform and subsequent hydrolysis in H_2SO_4,[14] with an improved yield (overall 83%, Scheme 1).

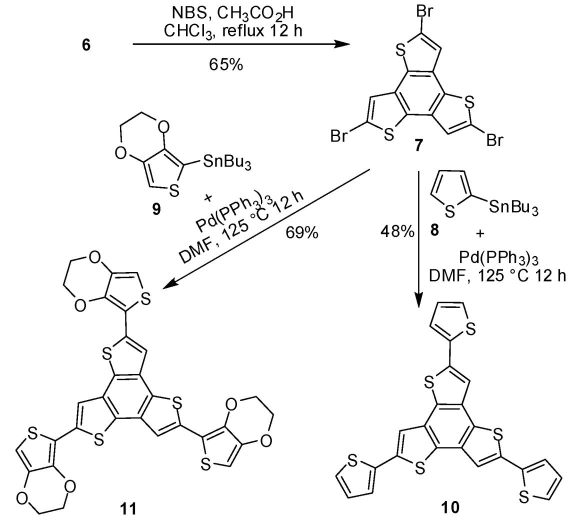
Scheme 1. Synthesis of Terthienobenzene



A ring closing reaction with ethyl mercaptoacetate gave TTB-triester **4**, which was previously reported only in a patent.[15] Saponification of **4** quantitatively afforded TTB-triacid **5**, which was efficiently decarboxylated by simple heating in inert atmosphere, to yield parent TTB **6** in 82% yield. The described approach involved simple isolation procedures (no chromatography/ recrystallization), was cost-effective, and afforded TTB **6** in 60−68% overall yield from **1**.[16]

Bromination of **6** with NBS yielded tribromo-TTB **7** (65%) (Scheme 2). Subsequent Stille couplings with tributyltin-thiophene **8** or tributyltin-EDOT **9** provided access to monomers **10** and **11**, with 48 and 69% yields, respectively. Moderate yields of these reactions are likely due to low solubility of planar TTB derivatives.

Scheme 2. Synthesis of Oligothiophenes **10** and **11**



UV−vis absorption of TTB **6** at λ_{max} 260 nm (4.77 eV) with a weaker vibronic peak at 288 nm can be attributed mostly to HOMO−LUMO transition (DFT calculated gap E_g^{calcd} = 4.89 eV) (Figure 1, Table 1). Extending the conjugation results in a predictable bathochromic shift to 343 nm (3.62 eV) for thiophene-capped **10** and even a larger shift (355 nm, 3.49 eV) for EDOT-capped **11**. These can still be ascribed to their HOMO−LUMO transitions (calculated gaps of 3.69 and 3.62 eV for **10** and **11**, respectively). While TTB **6** shows only weak fluorescence in the UV part of the spectrum, the oligomers **10** and **11** emit blue light at λ_{max} 427 and 434 nm respectively, with photoluminescence quantum yields of $\Phi_{PL} \approx 3.5\%$. This is somewhat unexpected since introducing EDOT moieties most often results in fluorescence quenching.[17] The observed Stokes shifts were quite large (0.71 eV for **10** and 0.63 eV **11**), which is typical for oligothiophenes (0.61 eV for quarterthiophene[18]).

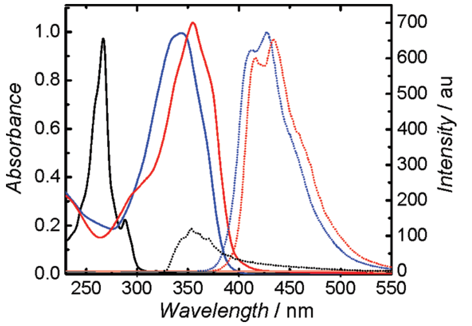


Figure 1. UV−vis spectra (solid line) and fluorescence spectra (dotted line) of compounds **6** (black), **10** (blue), and **11** (red).

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Table 1. Electronic Properties of TTB Monomers **6**, **10** and **11**

	6	**10**	**11**
$E_{\mathrm{HOMO}}^{\mathrm{calcd}}$ (eV)[a]	−5.92	−5.50	−5.05
$E_{\mathrm{g}}^{\mathrm{calcd}}$ (eV)[a]	4.89	3.69	3.63
$E_{\mathrm{pa}}^{\mathrm{ox}}$ (V)[b]	1.39	1.12	0.78
$E_{\mathrm{HOMO}}^{\mathrm{exp}}$ (eV)[c]	−6.19	−5.92	−5.58
$\lambda_{\max}^{\mathrm{abs}}$(nm)[d]	260	343	355
$E_{\mathrm{g}}^{\mathrm{opt}}$ (eV)[e]	4.79	3.62	3.49
$\lambda_{\max}^{\mathrm{PL}}$(nm)[f]	353	427	434
Φ_{fl} (%)	<1[g]	3.6[h]	3.5[h]
Stokes shift (eV)	1.15	0.71	0.63

[a] B3LYP/6-311G(d,p) calculations. [b] In DCM, 0.1 M $n\mathrm{Bu_4NPF_6}$ as supporting electrolyte, V vs. Ag/AgCl. [c] Calculated as $-4.8-E_{\mathrm{ox}}$ (vs. $\mathrm{Fc/Fc^+}$). [d] In DCM. [e] Calculated as $1240/\lambda_{\max}$. [f] In DCM, upon excitation at 373 nm. [g] Benzene ($\Phi_{\mathrm{PL}} = 5\%$) as the standard. [h] 9,10-diphenylanthracene ($\Phi_{\mathrm{PL}} = 90\%$) as the standard.

Cyclic voltammetry (CV) experiments with **6**, **10**, and **11** revealed their irreversible oxidation at +1.39, +1.12 and +0.78 V vs Ag/AgCl, respectively (Table 1). For all three monomers, multiple potential scans lead to progressive growth of a visible polymer film on platinum electrode (Figure 2). The onset *p*-doping potential of the polymers (1.14 V for poly-**6**, 0.6 V for poly-**10**, 0.0 V for poly-**11**) follows the trend of the HOMO energies of corresponding monomers. Also, the electrochemical stability of the polymer depends drastically on the structures of the constituting monomers. Films of poly-**6** were found to be rather unstable, and completely and rapidly degraded during multiple CV scans (in either propylene carbonate or benzonitrile solvents). Poly-**10** film was electrochemically stable in propylene carbonate, but slowly degraded upon multiple CV scans in a stronger solvent (benzonitrile). In contrast, the EDOT-based poly-**11** exhibited remarkable stability upon oxidation in both propylene carbonate and benzonitrile. 1400 Complete CV cycles of poly-**11** on ITO at 100 mV s^{-1}, in *air-saturated* electrolyte ($\mathrm{Bu_4NPF_6}$ in propylene carbonate, in open air atmosphere) resulted in less than 5% loss of the redox activity. The improved electrochemical robustness of an EDOT derived polymer is not unusual,[19] albeit the very high stability of poly-**11** even in air atmosphere could also be due to the cross-linked architecture of this polymer. While expected planarity of **11** might potentially lead to planar 2D conjugated polymer sheets, no evidence of such a structure has yet been obtained. Further studies of electropolymerization on atomically flat substrates[20] are currently underway.

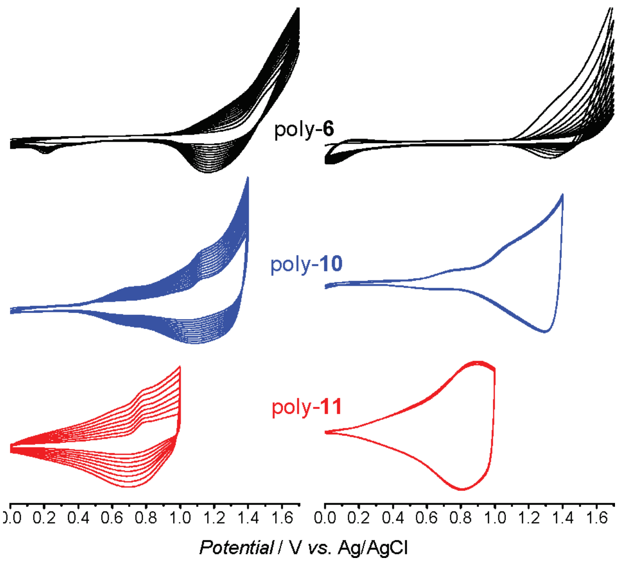

Figure 2. (left column) Electropolymerization of **6** (0.02 M in DCM), **10** (0.01 M in DCM), and **11** (7 mM in DCM); (right column) CVs of the corresponding polymer films in propylene carbonate.

For optical studies, monomers **10** and **11** were electropolymerized on an indium tin oxide (ITO) transparent electrode. UV−vis spectra of the prepared films reveal vibronically structured bands at $\lambda_{\max}$ of 444 nm (2.79 eV) and 480 nm (2.58 eV) for poly-**10** and poly-**11**, respectively. Interestingly, DFT calculations (see Supporting Information) predict the HOMO−LUMO gap to reduce significantly upon dimerization (from 3.64 to 2.72 eV for **11** vs di-**11**) but almost no effect from the continuing polymerization (2.68 eV for tri-**11**, 2.66 eV for tetra-**11**). The limited effective conjugation length in these polymers is clearly due to a "meta-type" connection through the TTB core. As a result, the HOMO and LUMO are localized between the benzene rings (see Supporting Information) and are not significantly affected by the increasing polymerization number.

The stable *p*-doped poly-**11** films were then characterized by EPR. The doped polymer shows an intense symmetric signal with a *g*-factor of 2.006, which can be ascribed to a polaron (Figure 3). Increasing the doping level at a higher oxidative potential creates more polarons in the polymers leading to higher intensity of the EPR signal, with little change of the fwhm. In contrast, the films of PEDOT prepared under identical conditions show a *decrease* of the EPR intensity at higher doping level. These changes in

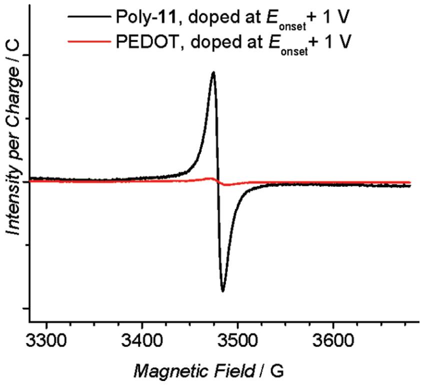

Figure 3. X-band EPR spectra of electrochemically doped poly-**11** (solid line) and PEDOT (dashed line) films on Pt wire. The intensities are normalized by the doping charge.

PEDOT can be rationalized by formation of low-spin bipolarons,[21] a well-known effect for linearly conjugated polymers at a high doping level.[22]

The sole polaron nature of the charge carriers in poly-**11** (throughout the tested potential window) was confirmed in a UV−vis-NIR spectroelectrochemical experiment. A distinct electrochromic switching between the neutral (red) and doped (blue) polymer was observed (Supporting Information). Gradual increase of the potential from 0 to $+1$ V extenuates the absorption band at 480 nm and two new bands at λ_{max} 680 and 1316 nm appear indicating formation of a polaron state. The doped polymer became the major species at 0.8 V and the only species at 1.0 V. A characteristic isosbestic point at 548 nm indicates that a clear transition between the two distinctive species (neutral and radical cation/polaron) takes places during the doping. At higher voltages, a gradual decrease of all absorption bands started to occur, but no new species with NIR absorbance (cf. bipolaron) were seen. This observation is also consistent with the EPR data.

The observed special behavior of poly-**11** is a result of the topology of the TTB core which precludes direct resonance conjugation between the arms. As a result, the polarons are isolated on the bis-EDOT arms and cannot recombine into a bipolaron. This is in sharp contrast to other polythiophenes (and most conjugated polymers) where no isosbestic point is observed in spectroelectrochemistry due to bipolaron formation at higher potentials.[23,24]

In summary, we demonstrated an efficient synthetic route to terthienobenzene **6** and its π-extended star-shaped derivatives **10** and **11**. All three compounds and particularly EDOT-functionalized **11** can be used as monomers to prepare high-dimensional conjugated polymers by electrooxidation. The spectroelectrochemical studies of poly-**11** showed switching between red- and blue-colored stable states and revealed a distinctive isosbestic point characteristic of a clear transition between a neutral and polaron state. Complete suppression of the bipolaron formation (also confirmed by EPR spectroscopy) is interesting for the design of high-spin materials.

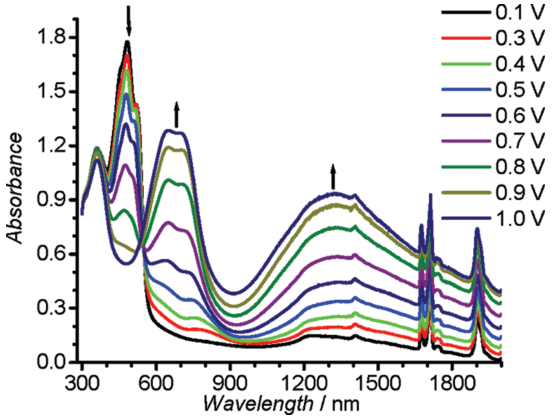

Figure 4. Spectroelectrochemistry of the poly-**11** film on ITO.

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Supporting Information Available: Experimental details; variable temperature ^{1}H NMR of **2**; movie file showing electrochromic switching of poly-**11**; EPR spectra; results of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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