Synthesis and Properties of Novel Thiophene-Based Conjugated Homologues: 9,9-Diphenylfluorene-Capped Oligothiophenes

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Received September 30, 2002

ABSTRACT

A series of novel 9,9-diarylfluorene-capped oligothiophenes were synthesized by Suzuki coupling reactions in good yields. The color of the emissions can be controlled by varying the conjugation length of the oligothiophene core. The bulky and rigid terminal groups of the resulting oligomers are significantly beneficial for their high morphological and thermal stability. These new oligothiophenes exhibit intriguing reversible oxidation and reduction redox behavior.

Oligothiophenes with well-defined structures are of great interest due to their unique electronic properties. Oligothiophenes have been used in many applications as active materials, including, for example, field-effect transistors and light-emitting diodes. The primary properties of crystalline oligothiophenes can be modified or improved upon by introducing pendant groups into the conjugated backbone. The strategy of introducing different terminal groups to cap oligothiophenes has been used to diversify the structure of a conjugated backbone, giving a new possibility of efficiently tuning the electronic and optical properties. For example, oligothiophenes terminated with phenyl or biphenyl groups exhibit interesting electroluminescent behavior. Oligothiophenes with terminal groups bearing diarylamino functional groups recently have been used as efficient emitters and have been reported to be potential hole-transporting materials. The introduction of planar fluorene moieties as the end groups of bithiophene facilitates the π–π stacking of the crystals, resulting in the formation of new materials that exhibit extremely high field-effect mobility. Other oligothiophene end-capping groups, including diarylboryl,
pyridyl, diphenylphosphine, and groups capable of charge transfer, have also been documented. We report in this communication a novel series of color-tunable amorphous emitters based on oligothiophene moieties with varying conjugation lengths as core chromophores. Bulky and rigid 9,9-diphenylfluorene was introduced as the terminal group to prevent intermolecular interactions and improve the morphological and thermal stability of the resulting oligomers.

The synthesis of 9,9-diphenylfluorene-capped oligothiophenes is illustrated in Scheme 1.

### Scheme 1

The single-crystal X-ray structure analysis of FT2 is shown in Figure 1. The bithiophene core of FT2 adopts a nearly planar conformation with an interplanar twist angle of 1.0°, while the two sulfur atoms are in an unusual cis configuration. In contrast, the bulky fluorene moieties are in an anti configuration and are highly twisted from the planar bithiophene core with interplanar twist angles of −21.5 and 151.4°, respectively. The antiparallel arrangement between the two neighboring molecules is beneficial for better crystal packing. However, the bulkiness of the terminal 9,9-diphenylfluorene moieties plays an important role in preventing intermolecular interactions. The closest plane-to-plane distance between the two neighboring planar bithiophene cores is calculated to be ca. 3.9 Å; thus, the intermolecular π–π interactions in the crystal are negligible.

The electronic absorption behavior of the 9,9-diphenylfluorene-capped oligothiophenes FTn exhibits a perfect correlation to the conjugation length, i.e., the absorption maximum is significantly red-shifted as the conjugation length of the respective oligothiophene core increases (See Supporting Information for the spectra). The structureless broad absorption indicates that the central oligothiophenes are relatively flexible for the formation of different conformers in the ground state. All 9,9-diphenylfluorene-capped oligothiophenes FTn in this study are highly fluorescent. The quantum yields of the fluorescence in a dilute solution of

### Table 1. Chemical Yields and Physical Properties of 9,9-Diphenylfluorene-Capped Oligothiophenes FTn

<table>
<thead>
<tr>
<th>FTn</th>
<th>yield (%)</th>
<th>λmax (nm)a</th>
<th>λmax (nm)b</th>
<th>Q (%)b</th>
<th>E1/2red (V)c</th>
<th>E1/2ox (V)d</th>
<th>Tg (°C)e</th>
<th>Td (°C)f</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT1</td>
<td>75</td>
<td>374, 493</td>
<td>424, 447</td>
<td>52</td>
<td>1.19, 1.60</td>
<td>−1.87, −2.11</td>
<td>153</td>
<td>393</td>
</tr>
<tr>
<td>FT2</td>
<td>71</td>
<td>404, 480</td>
<td>465, 493</td>
<td>26</td>
<td>1.01, 1.36</td>
<td>−1.80, −2.02</td>
<td>153</td>
<td>483</td>
</tr>
<tr>
<td>FT3</td>
<td>82</td>
<td>425, 485</td>
<td>494, 528</td>
<td>35</td>
<td>0.86, 1.19</td>
<td>−1.76, −1.94</td>
<td>154</td>
<td>448</td>
</tr>
<tr>
<td>FT4</td>
<td>85</td>
<td>440, 466</td>
<td>515, 545</td>
<td>32</td>
<td>0.81, 1.09</td>
<td>−1.65, −1.79</td>
<td>153</td>
<td>449</td>
</tr>
</tbody>
</table>

a Measured in CHCl3; fluorescence was recorded by irradiating at the absorption maximum. b Measured in ethyl acetate with Coumarin I as a standard. c In CHCl3 (0.1 M nBu4NPF6 as a supporting electrolyte). d In THF (glassy carbon electrode, 0.1 M nBuNCIO4 as a supporting electrolyte). e By DSC analysis of the liquid nitrogen-quenched melt sample. f By TGA analysis; the temperature was recorded corresponding to a 10% weight loss.
ethylenediamine (1.0 M) in toluene, 1.2 mL, 0.06 mmol) were stirred and refluxed under argon for 2–3 days. The cooled reaction mixture was quenched with saturated sodium bicarbonate and extracted with chloroform. The combined organic extracts were dried over MgSO4 and concentrated by rotary evaporation. The crude product after washing with hot hexane was recrystallized from CHCl3/hexanes to afford FT1 (567 mg, 71%) as a yellow solid (see the Supporting Information for spectroscopic characterization).

(11) Representative Procedure for Synthesis of FT2. 9,9-Diphenylfluorene-2-pinacol boronate (2) (930 mg, 2.1 mmol), 5,5′-dibromo-2,2′-bithiophene (3, n = 2) (324 mg, 1.0 mmol), Pd(PPh3)4 (23 mg, 0.02 mmol), 2 M K2PO4 (2 mL), 1.4-dioxane (20 mL), and tri-tert-butylphosphine (0.05 M in toluene, 1.2 mL, 0.06 mmol) were stirred and refluxed under argon for 2–3 days. The cooled reaction mixture was quenched with saturated sodium bicarbonate and extracted with chloroform. The combined organic extracts were dried over MgSO4 and concentrated by rotary evaporation. The crude product after washing with hot hexane was recrystallized from CHCl3/hexanes to afford FT2 (567 mg, 71%) as a yellow solid (see the Supporting Information for spectroscopic characterization).

(12) The oxidation potentials of FTn exhibit more negative values as the conjugation length is increased, while the reduction potentials are more positive. This indicates the greater stability of the radical cation relative to its neutral form. In contrast, the spectral response of FT2 shows a smaller potential difference between two redox processes. However, the pronounced potential differences between the two oxidations (410–280 mV) and two reductions (240–140 mV) indicate that the monocationic and monoanionic species could efficiently delocalize the charge over the entire conjugated backbone. These results are consistent with the significant red shifts in the absorption bands. The increasing conjugation length is due to an increasing delocalization of the π-electron system along the backbone.

Figure 2. Photoluminescent spectra of FTn (n = 1–4). Inset shows the color of emission in CHCl3, from top to bottom, FT1, FT2, FT3, FT4.

Figure 3. Comparison of the cyclic voltammogram of FT2 and FT4.
The introduction of bulky 9,9-diphenylfluorene into the oligothiophene cores as the end-capping group was significantly beneficial in improving the morphological stability and the resistance to thermal decomposition. The morphological stability and the thermal property of 9,9-diphenylfluorene-capped oligothiophenes FT<sub>n</sub> were investigated by DSC and TGA analysis, respectively.

It is noteworthy that all fluorene-capped oligothiophenes exhibited a distinct glass transition temperature (T<sub>g</sub>) of ca. 153 °C (Table 1), irrespective of the conjugation length of the oligothiophene cores. The independence of T<sub>g</sub> of the molecular weight of the homologues is different from other results reported in the literature.\(^7,14\) However, the result indicates that the bulkiness of the terminal groups could effectively preserve molecular morphological stability. FT<sub>1</sub>–FT<sub>4</sub> exhibited high thermal stability: no weight loss was detected below 380 °C. The temperature corresponding to a 10% weight loss upon heating under nitrogen ranged from 393–483 °C (Table 1). FT<sub>2</sub> displayed the highest decomposition temperature (up to 483 °C) compared with that of the other homologues.

In summary, we have synthesized a new series of 9,9-diphenylfluorene-capped oligothiophenes by using a Suzuki coupling reaction. The introduction of bulky and rigid 9,9-diphenylfluorene as the terminal group of oligothiophenes had significant effects on improving morphological and thermal stability. The fluorescent color of the resulting new materials could be readily controlled by varying the conjugation length of the oligothiophene core. These findings together with the bipolar property make these fluorene-capped homologues attractive for future application in OLEDs.

**Acknowledgment.** This work was financially supported by the National Science Council and Ministry of Education Taiwan. The authors thank Mr. S. C. Kao for DSC and TGA analyses.

**Supporting Information Available:** Detailed experimental procedure, spectroscopic characterization of new compounds, comparison of the absorption spectra of FT<sub>n</sub> (n = 1–4), and an X-ray structure of FT<sub>2</sub> (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.