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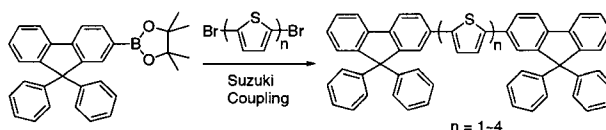
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ABSTRACT

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.[1] The primary properties of crystalline oligothiophenes can be modified or improved upon by introducing pendant groups into the conjugated backbone.[2] 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[3]

exhibit interesting electroluminescent behavior.[4] Oligothiophenes with terminal groups bearing diarylamino functional groups recently have been used as efficient emitters[5] and have been reported to be potential hole-transporting materials.[6] 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.[7] Other oligothiophene end-capping groups, including diarylboryl,[8]

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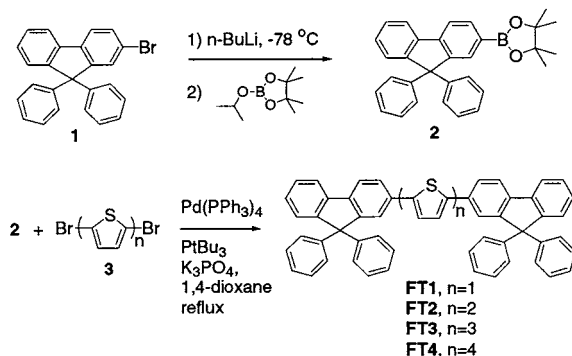(8) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714.

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

FTn	yield (%)	λ_{max} (nm)[a]; log ϵ	PL λ_{max} (nm)[a]	Q (%)[b]	$E_{1/2}^{ox}$ (V)[c]	$E_{1/2}^{red}$ (V)[d]	T_g (°C)[e]	T_d (°C)[f]
FT1	75	374; 4.93	424, 447	52	1.19, 1.60	−1.87, −2.11	153	393
FT2	71	404; 4.80	465, 493	26	1.01, 1.36	−1.80, −2.02	153	483
FT3	82	425; 4.85	494, 528	35	0.86, 1.19	−1.76, −1.94	154	448
FT4	85	440; 4.66	515, 545	32	0.81, 1.09	−1.65, −1.79	153	449

[a] Measured in $CHCl_3$; fluorescence was recorded by irradiating at the absorption maximum. [b] Measured in ethyl acetate with Coumarin I as a standard. [c] In CH_2Cl_2 (0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte). [d] In THF (glassy carbon electrode, 0.1 M nBu$_4$NClO$_4$ 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.

pyridyl,[9] diphenylphosphine,[10] and groups capable of charge transfer,[11] 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.
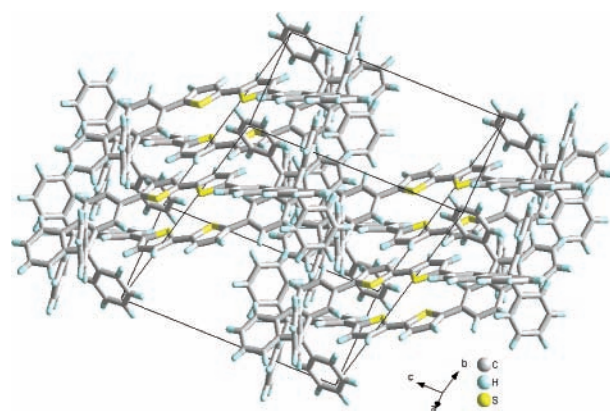
Scheme 1

Treatment of 2-bromo-9,9-diphenylfluorene (**1**) with *n*-BuLi at −78 °C, followed by quenching the lithiated complex with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane, afforded the boronic ester **2** in 82% yield. Pd-catalyzed Suzuki coupling reaction between **2** and dibromooligothiophen **3** (*n* = 1−4) was carried out in the presence of a catalytic amount of P^{t}Bu$_3$ as a cocatalyst.[12] The resulting 9,9-diphenylfluorene-capped oligothiophenes **FTn** (*n* = 1−4) were isolated in good yields (Table 1) with satisfactory spectroscopic characterizations.

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The single-crystal X-ray structure analysis of **FT2** is shown in Figure 1. The bithiophene core of **FT2** adopts a nearly

Figure 1. Crystal packing diagram of **FT2**.

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

ethyl acetate range from 0.26 to 0.52 (Table 1). The photoluminescence (PL) features reveal typical characteristics of conjugated fluorene derivatives.[13] More importantly, the emission maxima (Figure 2) of **FTn** can be controlled by
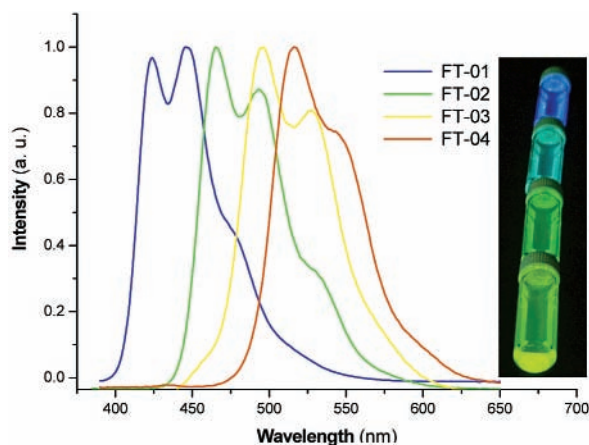

Figure 2. Photoluminescent spectra of **FTn** ($n = 1-4$). Inset shows the color of emission in CHCl$_3$, from top to bottom, **FT1**, **FT2**, **FT3**, **FT4**.

varying the number n ($n = 1-4$) of the oligothiophene moieties of the conjugated backbone. The color of the fluorescence can be achieved from light blue to bright yellow (Figure 2, inset).

Cyclic voltammetry (CV) experiments were conducted on fluorene-capped oligothiophenes **FTn** at room temperature to probe their electrochemical properties. For **FTn**, two discrete reversible oxidation potentials were observed in CH$_2$Cl$_2$ (0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte). Unexpectedly, two reversible reduction potentials were also detected in THF (glassy carbon electrode, 0.1 M nBu$_4$NClO$_4$ as a supporting electrolyte) (Table 1). This finding indicates the possibility that an n-doping property is induced in the oligomers when 9,9-diphenylfluorenes are incorporated into the oligothiophenes as the terminal groups. Figure 3 shows a comparison of the cyclic voltammogram of **FT2** and **FT4**. The oxidation potentials tend to decrease as the chain of the oliogothiophene core is lengthened, while **FTn** with shorter oligothiophene cores exhibit more negative reduction potentials. The oligomer with the longer conjugation length
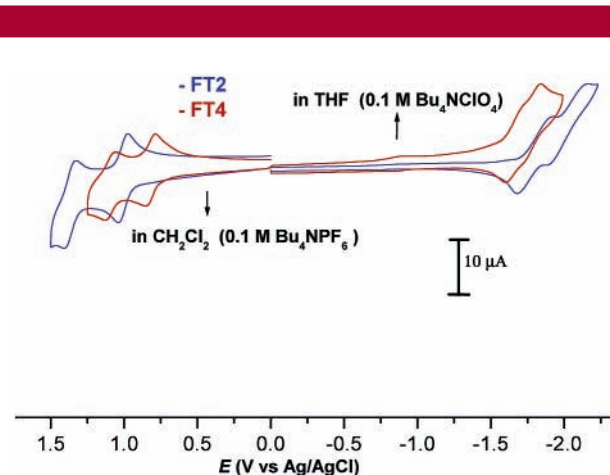
(12) **Representative Procedure for Synthesis of FT2.** 9,9-Diphenylfluorene-2-pinacol boronate (**2**) (930 mg, 2.1 mmol), 5,5′-dibromo-2,2′-bithiophene (**3**, $n = 2$) (324 mg, 1.0 mmol), Pd(PPh$_3$)$_4$ (23 mg, 0.02 mmol), 2 M K$_3$PO$_4$ (2 mL), 1,4-dioxane (20 mL), and tri-*tert*-butylphosphine (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 MgSO$_4$ and concentrated by rotary evaporation. The crude product after washing with hot hexane was recrystallized from CHCl$_3$/hexanes to afford **FT2** (567 mg, 71%) as a yellow solid (see the Supporting Information for spectroscopic characterization).

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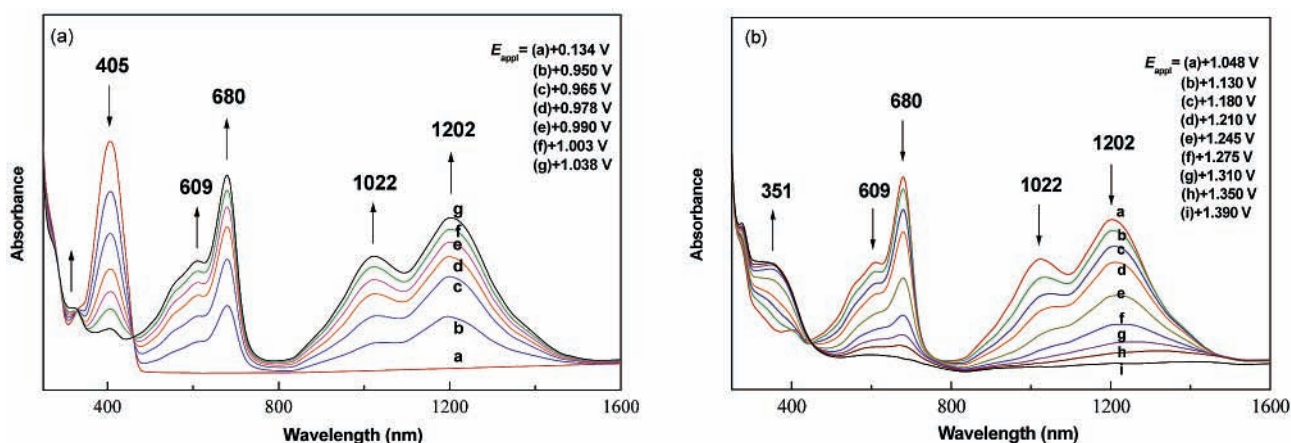
Figure 3. Comparison of the cyclic voltammogram of **FT2** and **FT4**.

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 4 shows the spectral response of **FT2** at various applied voltages. Between 0 and 1.00 V, the intensity of absorption at 405 nm of the neutral **FT2** decreased, while new peaks grew at 609, 680, 1022, and 1202 nm. Upon increasing the applied voltage, the intensity of these new peaks was continuously enhanced with an isosbestic point at 460 nm (Figure 4a). These new forming visible bands (609 and 680 nm) and strong near-IR absorption bands (1022 and 1202 nm) were ascribed to the absorption of the first oxidation state. When the applied voltages were above 1.00 mV, the intensity of the long wavelength peaks started to diminish in intensity, while a new peak appeared at 351 nm with increasing intensity until the applied voltage reached 1.40 V. These spectral changes could be fully restored when the voltage was cycled between 0.0 and 1.40 V. The spectral changes at various applied voltages were in agreement with the CV experiments, in which the first and second oxidation potentials of **FT2** were observed at 1.01 and 1.36 V, respectively. The spectroelectrochemistry indicated that the oxidation only involves a one-step one-electron redox process. In contrast, the spectral response of **FT2** in the reduction region by using platinum gauze or reticulated vitreous carbon as a working electrode did not exhibit any isosbestic point(s) (Supporting Information). For the latter case, the intensity of a new broad absorption (580 nm) increased upon increasing the negative voltage from −0.55 to −2.12 V. This result suggests that the radical anion is relatively more reactive during the electrolysis as compared to its radical cation.

Figure 4. Spectral response of **FT2** at various applied voltages in CH$_2$Cl$_2$ (0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte) at (a) the first oxidation state and (b) the second oxidation state.

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 **FTn** were investigated by DSC and TGA analysis, respectively.

It is noteworthy that all fluorene-capped oligothiophenes exhibited a distinct glass transition temperature (T_g) of ca. 153 °C (Table 1), irrespective of the conjugation length of the oligothiophene cores. The independence of T_g 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. **FT1**–**FT4** 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). **FT2** 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.

Supporting Information Available: Detailed experimental procedure, spectroscopic characterization of new compounds, comparison of the absorption spectra of **FTn** ($n = 1$−4), and an X-ray structure of **FT2** (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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