

Modulation of Physical Properties of Ter(9,9-ditolyfluorene) by Backbone-Embedded Heteroarenes

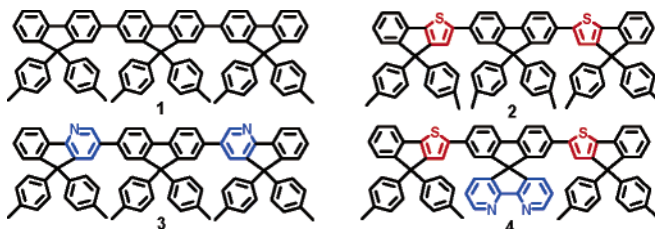
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Received January 23, 2006

ABSTRACT



Novel ter(9,9-ditolyfluorene) analogues containing thiophene and pyridine rings embedded as functional constituents within the parent hydrocarbon backbone have been synthesized. These new molecules exhibit highly efficient photoluminescence and high thermal and morphological stability. The electronic structure of the terfluorene backbone is significantly perturbed, which allows modulation of the backbone energy levels.

π -Conjugated materials are of great interest for organic electronics including light-emitting diodes (OLEDs), thin film transistors, and photovoltaic cells. Although π -conjugated materials possessing pure hydrocarbon main chains usually do not exhibit properties that are desirable for their use in efficient devices, their physical behavior can be modulated dramatically by incorporating electron-rich or electron-deficient arenes directly into their conjugated backbones.¹ Materials prepared by using such a molecular design strategy offer many alternatives for device engineering. In this paper, we demonstrate that implanting π -electron-rich thiophene and π -electron-deficient pyridine moieties into the backbone of terfluorene facilitates the ready manipulation of its electronic

structure (HOMO/LUMO levels) and consequent physical properties.

Among the organic π -conjugated materials, terfluorene **1** (Figure 1) is one of the most promising blue light emitters for highly efficient OLEDs because of its superior physical properties.² Direct modification of the π -conjugated backbone of terfluorene through functional substitution remains a

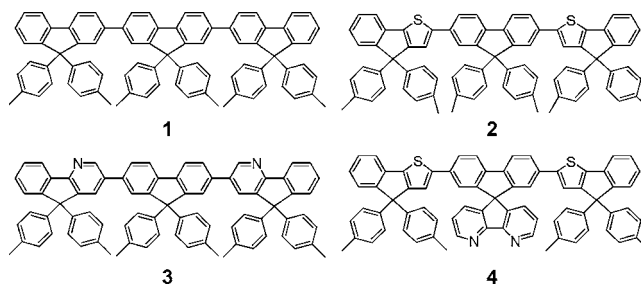


Figure 1. Molecular structures of terfluorene (**1**) and its heteroarene-substituted (**2** and **3**) and bipolar (**4**) analogues.

(1) (a) Li, W.; Katz, H. E.; Lovinger, A. J.; Laquindanum, J. G. *Chem. Mater.* **1999**, *11*, 458. (b) Alam, M. M.; Jenekhe, S. A. *Chem. Mater.* **2002**, *14*, 4775. (c) Jenekhe, S. A.; Lu, L.; Alam, M. M. *Macromolecules* **2001**, *34*, 7315. (d) Barbarella, G.; Favaretto, L.; Sotgiu, G.; Zambianchi, M.; Bongini, A.; Arbizzani, C.; Mastragostino, M.; Anni, M.; Gigli, G.; Cingolani, R. *J. Am. Chem. Soc.* **2000**, *122*, 11971. (e) Facchetti, A.; Yoon, M.-H.; Stern, C. L.; Katz, H. E.; Marks, T. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3900. (f) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662.

challenge; therefore, it is difficult to manipulate the electronic properties of its backbone. We anticipated that the new terfluorene analogues **2** and **3** (Figure 1) would drastically reconstitute the properties of the main chain of **1** for a couple of reasons: (1) The π -electron-rich thiophene substitutions should raise the HOMO level and, thus, offer the resulting new molecule with better capability for hole injection. In contrast, the π -electron-deficient pyridine substitutions should lower the LUMO energy, and thus enhance electron injection capability. (2) Flattening of the functional arene substitutions through intramolecular cyclization should reduce their conformational disorder, maintain effective coplanarity of the molecular geometry, and preserve the highly efficient photoluminescence of the parent terfluorene chromophore.

The synthesis of the π -electron-rich terfluorene analogue **2** is depicted in Figure 2.

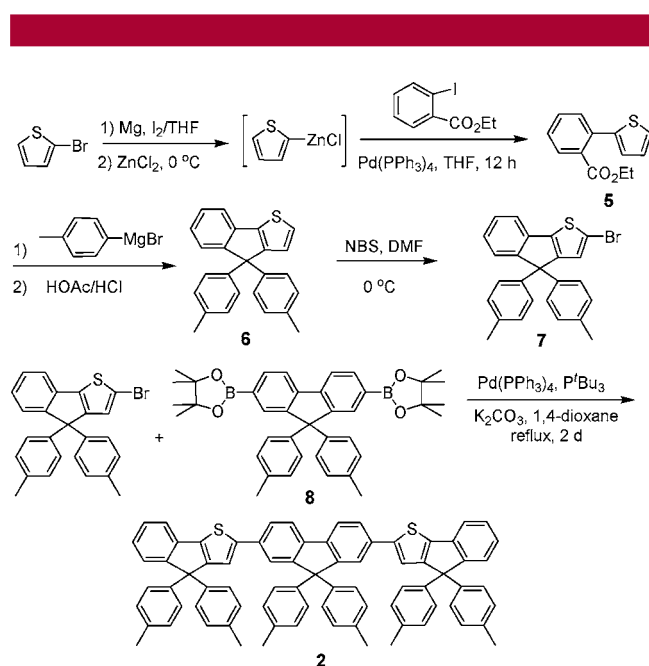


Figure 2. Synthesis of the π -electron-rich terfluorene analogue **2**.

The Pd-catalyzed Negishi coupling reaction of ethyl 2-iodobenzoate with thienyl zinc chloride gave ester **5** in 82% yield. Double alkylation of the ester group of **5** with p -tolylmagnesium bromide and subsequent acid-catalyzed intramolecular Friedel–Crafts arylation afforded the ditolyl-substituted indenothiophene **6** in 73% yield. Bromination of **6** with NBS at 0°C gave the aryl bromide **7** in high yield (87%). Subsequently, reaction of **7** with the diboronic ester (**8**) provided the desired product **2** in an isolated yield of 75%.

Figure 3 presents the synthesis of the π -electron-deficient terfluorene analogue **3**.

(2) (a) Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Wang, C.-F.; Lin, Y.-T.; Chiang, H.-H.; Hsieh, P.-Y.; Wu, C.-C.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *J. Am. Chem. Soc.* **2002**, *124*, 11576. (b) Wu, C.-C.; Liu, T.-L.; Hung, W.-Y.; Lin, Y.-T.; Wong, K.-T.; Chen, R.-T.; Chen, Y.-M.; Chien, Y.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 3710.

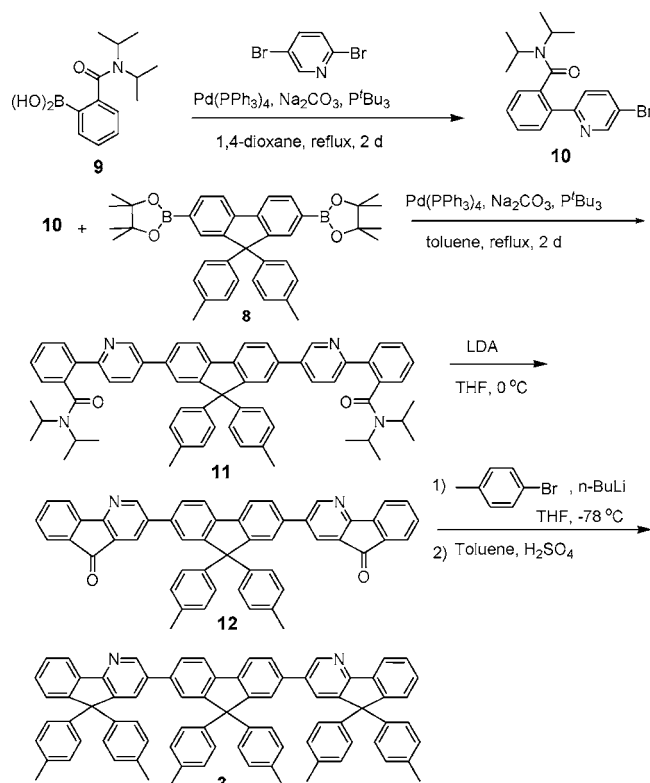


Figure 3. Synthesis of the π -electron-deficient terfluorene analogue **3**.

For the synthesis of **3**, using a similar synthetic pathway as for **2** was unsuccessful. Therefore, we applied a neighboring group-assisted lithiation/cyclization³ strategy to construct the coplanar azafluorenone skeleton and subsequently introduced the peripheral aryl substituents. Thus, the Suzuki reaction of 2,5-dibromopyridine with 2-(diisopropylcarbamoyl)phenylboronic acid (**9**)⁴ occurred regioselectively at the 2-position of the pyridine ring to afford the coupled product **10** in 80% yield. The reaction of **10** with the diboronic ester (**8**) gave the diamide **11** (58%), which upon treatment with LDA at 0°C furnished the diketone **12** in 80% isolated yield. The tolyl substituents of the 4-azafluorene units of **3** were then introduced through the addition of 4-methylphenyllithium to **12** and subsequent acid-catalyzed Friedel–Crafts arylation to afford **3** in 20% yield.

Previously, we described a feasible molecular doping strategy for terfluorene **1** through the introduction of a 4,5-diazafluorene unit as a peripheral substituent.⁵ This strategy provides a terfluorene derivative that possesses improved electron injection ability while retaining the photophysical properties of the terfluorene chromophore. Combining the backbone modification and spiro-linked substitution strate-

(3) Fu, J.-M.; Zhao, B.-P.; Sharp, M. J.; Snieckus, V. *J. Org. Chem.* **1991**, *56*, 1683.

(4) (a) Fischer, M.; Shi, Y.; Zhao, B.-p.; Snieckus, V.; Wan, P. *Can. J. Chem.* **1999**, *77*, 868. (b) Laufer, R. S.; Dmitrienko, G. I. *J. Am. Chem. Soc.* **2002**, *124*, 1854.

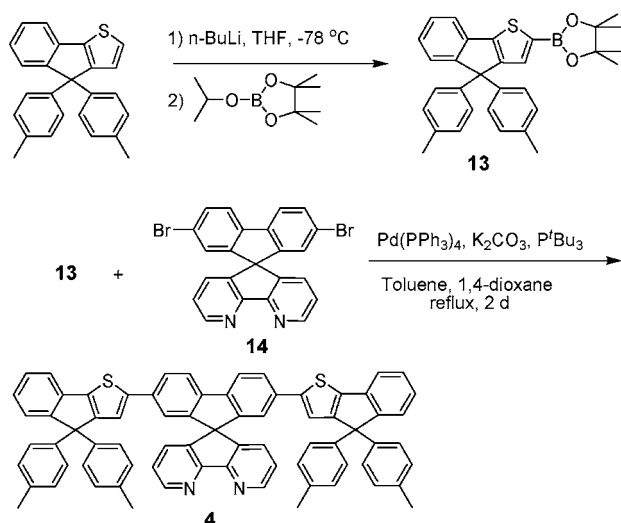
(5) Wong, K.-T.; Chen, R.-T.; Fang, F.-C.; Wu, C.-C.; Lin, Y.-T. *Org. Lett.* **2005**, *7*, 1979.

Table 1. Properties of Terfluorene **1** and Analogues **2–4**

compd	abs ^a λ_{\max} (nm)	PL ^b λ_{\max} (nm)	Q.Y. ^c (%)	$E_{1/2 \text{ oxd}}^d$	$E_{1/2 \text{ red}}^e$	T_g (°C)	T_d (°C)	HOMO/LUMO (eV) ^f
1	354	393, 420	85	1.35, 1.60	-1.99, -2.18	201	411	-5.69/-2.18
2	407	448, 477	71	1.05, 1.22	-1.88, -2.06	197	444	-5.39/-2.29
3	359	401, 413	72	1.51	-1.88, -2.06	159	524	-5.85/-2.29
4	407	448, 474	70	1.11, 1.26	-1.83, -2.06, -2.27	nd	463	-5.45/-2.34

^a In CHCl₃. ^b In CHCl₃, upon excitation at the absorption maximum. ^c In CHCl₃, measured by calibrated integrating sphere. ^d In CH₂Cl₂ containing 0.1 M *n*Bu₄NPF₆ as a supporting electrolyte. ^e In THF containing 0.1 M *n*Bu₄NClO₄ as a supporting electrolyte. ^f HOMO and LUMO levels with respect to zero vacuum level were estimated directly from CVs.

gies, we synthesized a new bipolar terfluorene analogue **4** (Figure 4). Indenothiophene **6** was converted to boronic ester

**Figure 4.** Synthesis of terfluorene analogue **4**.

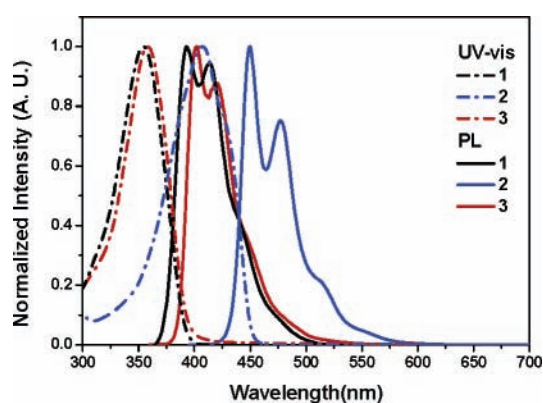
(**13**) in 70% yield, followed by coupling with 4',7'-dibromo-9,9'-spirobifluorene (**14**) to form the desired coupled product **4** in an isolated yield of 75%.

Incorporating the thiophene and pyridine moieties into the main conjugated chain and making them into coplanar configurations through intramolecular annulation with their neighboring phenylene rings renders the resulting molecules rather rigid and bulky. These properties are highly beneficial to the thermal stabilities, as indicated by their high decomposition (5% weight loss) temperatures (T_d) and rather high glass transition temperatures (T_g) (Table 1), determined by thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC), respectively. As a consequence, these novel analogues can form homogeneous and stable amorphous films—an essential property for any potential device applications—upon thermal evaporation.

The absorption and photoluminescence of the thiophene-containing analogue **2** exhibit substantial red shifting relative to those of the parent terfluorene **1** (Figure 5).

This result clearly indicates the improved π -conjugation that occurred upon replacing the six-membered phenylene

rings in **1** with five-membered thiophene rings.⁶ In contrast, the analogue **3**, which contains 4-azafluorene moieties,

**Figure 5.** Absorption and photoluminescence spectra of terfluorene **1** and its analogues **2** and **3**.

possesses only a slightly extended effective conjugation length of its backbone, as indicated by the relatively smaller red shifts in its absorption and emission with respect to those of terfluorene **1**. The bipolar analogue **4**, possessing a spiro-linked 4,5-diazafluorene on the central fluorene ring, exhibits spectroscopic properties very similar to those of the indenothiophene-containing analogue **2** (see Figure S-1, Supporting Information). This result indicates that the spiro-linked 4,5-diazafluorene moiety does not perturb the electronic transitions of the main conjugated unit. In addition, the terfluorene analogues **2–4** exhibit relatively high photoluminescence quantum yields (each $\geq 70\%$, but slightly lower than that of the parent terfluorene **1**) because of the coplanar molecular configurations of their embedded heteroarene units with respect to their adjacent phenylene rings, and consequent conformational inflexibility.

Cyclic voltammetry (CV) was used to probe the electrochemical behavior of **1** and its novel heterocyclic analogues **2–4** (Figure 6; Table 1). Indenothiophene-containing analogue **2** exhibits two reversible oxidation potentials at 1.05

(6) (a) Lee, S. A.; Hotta, S.; Nakanishi, F. *J. Phys. Chem. A* **2000**, *104*, 1827. (b) Apperloo, J. J.; Groenendaal, L. B.; Verheyen, H.; Jayakannan, M.; Janssen, R. A. J.; Dkhissi, A.; Beljonne, D.; Lazzaroni, R.; Brédas, J.-L. *Chem. Eur. J.* **2002**, *8*, 2384.

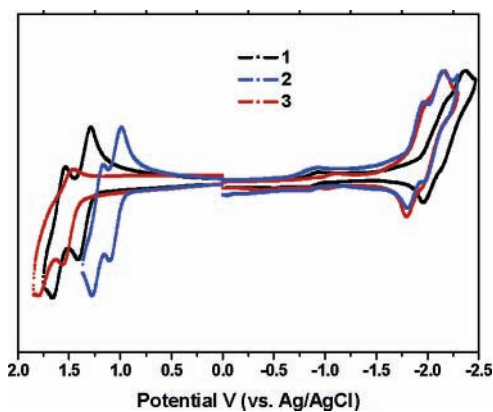


Figure 6. Cyclic voltammograms of terfluorene **1** and its analogues **2** and **3**.

and 1.22 V (vs Ag/AgCl); these values are significantly lower than those of parent terfluorene **1** (1.35 and 1.60 V). This result clearly indicates the significant HOMO-raising effect of using π -electron-rich thiophene units as constitutional moieties. The analogue **3**, possessing 4-azafluorene moieties in its main π -conjugated chain, undergoes only one oxidation, at a higher potential than those of the first oxidations of **1** and **2**, presumably because of the π -electron-deficient pyridine rings rendering oxidation more difficult.⁷ Surprisingly, both of the indenothiophene- and 4-azafluorene-containing analogues **2** and **3**, respectively, exhibited two reversible reductions at the same potentials. The lower reduction potentials of **2** (−1.88 and −2.06 V), relative to those of **1** (−1.99 and −2.18 V), are consistent with its higher degree of π -conjugation resulting from incorporation of the thiophene moieties into the main backbone. The better π -conjugation of **2** is also partially attributed to the increased planarity by the reduced steric interactions between the embedded thiophene rings and the central fluorene moiety. For **3**, however, the lower reduction potentials arise mainly from the π -electron deficiency of its pyridine rings. The electrochemical behavior of **2** was further modified upon introducing the peripheral 4,7-diazafluorene. The dipolar molecule **4** displays slightly higher oxidation and lower

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reduction potentials relative to those of **2** (Table 1, also see Figure S-2, Supporting Information), possibly because of the electronic induction effect of the electronegative diazafluorene substituent. Analogue **4** also exhibits a third reduction potential at −2.27 V, which is ascribed to the reduction occurring at the peripheral diazafluorene moiety.⁵

Table 1 lists the HOMO and LUMO energy levels of **1–4** taken directly from the cyclic voltammograms (see the Supporting Information for detail). The electronic structure of the parent terfluorene **1** is perturbed significantly after its main chain modifications. Implanting the parent backbone with thiophene rings extends the π -conjugation effectively, raising the HOMO level in particular. The improved π -conjugation also lowers the LUMO level of **2**, which leads to a smaller energy gap. Upon embedding pyridine rings as constituent moieties of the parent hydrocarbon backbone, this modification leads to shifts of both the HOMO and LUMO levels of **3** in the same direction, i.e., to lower levels, with respect to those of parent terfluorene **1**. The results presented for the bipolar compound **4** indicate that the modulation of energy levels can be realized independently through either main chain electronic perturbation or peripheral substitution through a spiro-linkage.

In summary, we have established efficient syntheses of novel heteroarene-embedded (**2** and **3**) and bipolar (**4**) terfluorene analogues. The physical properties of the parent terfluorene are significantly altered upon introducing heteroarene units as constituents. The presence of the heteroarenes and their coplanarity with adjacent phenylene rings provides these novel terfluorene analogues with promising properties. We are presently fabricating light-emitting devices that incorporate these molecules as active materials and will reported our results in due course.

Acknowledgment. This study was supported financially by the National Science Council and Ministry of Economic Affairs of Taiwan.

Supporting Information Available: Detailed experimental procedures; spectroscopic characterization and NMR spectra of new compounds; absorption and emission spectra and cyclic voltammogram of **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL060183F