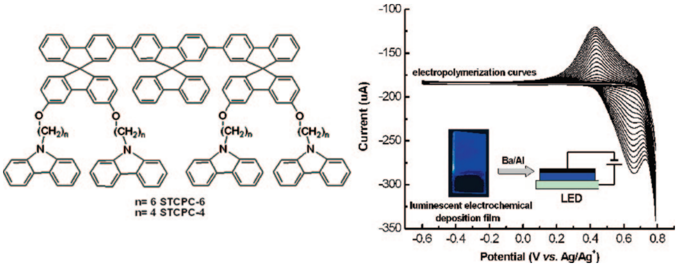
# Synthesis and Electrochemical Properties of Peripheral Carbazole Functional Ter(9,9-spirobifluorene)s

Shi Tang, Meirong Liu, Cheng Gu, Yang Zhao, Ping Lu, Dan Lu, Linlin Liu,
Fangzhong Shen, Bing Yang, and Yuguang Ma*

*State Key Laboratory for Supramolecular Structure and Materials, Jilin University, Changchun, China*

*ygma@jlu.edu.cn*

*Received March 21, 2008*



A facile approach for synthesis of spirobifluorene trimers with peripheral carbazole functional groups by utilizing Suzuki coupling as the key reaction has been developed. These novel compounds exhibit blue emission with high quantum yields in solution and thin films, and excellent spectral stability upon photoirradiation and annealing in air. By the introduction of carbazole groups, the oxidation potentials of spirobifluorene trimers **STCPC-6** and **STCPC-4** were significantly lower than that of model compound **STHPH** without peripheral carbazole groups, which reflect that the title compounds process higher HOMO energy level and better hole-injection ability. Highly luminescent films were obtained by electrochemical coupling between carbazole units. Pure blue-emission single-layer LEDs based on electrochemical deposition films as light emitting layers were achieved.

## 1. Introduction

Fluorene-based polymers and oligomers have been recognized as very promising classes of organic semiconductors in electronic devices,[1] especially in light-emitting diodes (LEDs),[2] because of their high photoluminescence (PL) and electroluminescence (EL) efficiencies. However, the traditional 9,9-dialkylated fluorene derivatives have shown poor stabilities, with a drastic loss in quantum yield and the emerging of an undesired green emission after a short-term operation.[3] In the literature, it is attributed to both the excimer/interchain aggregates[4] and the keto defects.[5] Recently, more powerful evidence confirmed that the formation of fluorenone that originated from thermal-oxidative, photooxidative, or electrooxidative degradation of 9,9-dialkylated fluorene is mainly responsible for this green emission.[6] To overcome this problem, many previous reports have concluded that the introduction of bulky phenyl side groups

---

(1) (a) Yasuda, T.; Fujita, K.; Tsutsui, T.; Geng, Y.; Culligan, S. W.; Chen, S. H. *Chem. Mater.* **2005**, *17*, 264. (b) Rothe, C.; Galbreche, F.; Scherf, U.; Monkman, A. *Adv. Mater.* **2006**, *18*, 2137. (c) Geng, Y.; Culligan, S. W.; Trajkovska, A.; Wallace, J. U.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 542. (d) Geng, Y.; Trajkovska, A.; Katsis, D.; Ou, J. J.; Culligan, S. W.; Chen, S. H. *J. Am. Chem. Soc.* **2002**, *124*, 8337.

(2) (a) Culligan, S. W.; Geng, Y.; Chen, S. H.; Klubek, K.; Vaeth, K. M.; Tang, C. W. *Adv. Mater.* **2003**, *15*, 1176. (b) Sudhakar, M.; Djurovich, P. I.; Hogen-Esch, T. E.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7796. (c) Yang, Y.; Pei, Q.; Heeger, A.L. J. *Appl. Phys.* **1996**, *79*, 934. (d) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477. (e) Shu, C.-F.; Dodda, R.; Wu, F.-I.; Liu, M. S.; Jen, A. K.-Y. *Macromolecules.* **2003**, *36*, 6698. (f) Chuang, C.-Y.; Shih, P.-I.; Chien, C.-H.; Wu, F.-I.; Shu, C.-F. *Macromolecules.* **2007**, *40*, 247. (g) Chen, X.; Liao, J.-L.; Liang, Y.; Ahmed, M. O.; Tseng, H.-E.; Chen, S.-A. *J. Am. Chem. Soc.* **2002**, *125*, 636. (h) Liu, J.; Zhou, Q.; Cheng, Y.; Geng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Adv. Mater.* **2005**, *17*, 2974.

(3) (a) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477. (b) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965. (c) Gaal, M.; List, E. J. W.; Scherf, U. *Macromolecules* **2003**, *36*, 4236. (d) Lupton, J. M.; Craig, M. R.; Meijer, E. W. *Appl. Phys. Lett.* **2002**, *24*, 4489.

(4) (a) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099. (b) Lee, J. I.; Klärner, G.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1083. (c) Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Göbel, E. O.; Müllen, K.; Bässler, H. *Chem. Phys. Lett.* **1995**, *240*, 373. (d) Cimrová, V.; Scherf, U.; Neher, D. *Appl. Phys. Lett.* **1996**, *69*, 608. (e) Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Klärner, G.; Miller, R. D.; Miller, D. C. *Macromolecules* **1999**, *32*, 361.

(5) (a) Gong, X.; Iyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Xiao, S. S. *Adv. Funct. Mater.* **2003**, *13*, 325. (b) Zhao, W.; Cao, T.; White, J. M. *Adv. Funct. Mater.* **2004**, *14*, 783. (c) Chi, C. Y.; Im, C.; Enkelmann, V.; Ziegler, A.; Lieser, G.; Wegner, G. *Chem.−Eur. J.* **2005**, *11*, 6833. (d) Zhou, X.-H.; Zhang, Y.; Xie, Y.-Q.; Cao, Y.; Pei, J. *Macromolecules* **2006**, *39*, 3830.

10.1021/jo8006094 CCC: $40.75

instead of long alkyl chains can effectively suppress the degradation phenomenon.[7] In this context, the spirobifluorene with unusual rigid three-dimensional structure is an ideal building block in construction of stable blue-light emitting[8] and plastic laser materials.[9] Recently, Bo and co-workers[10] reported a full spirobifluorene polymer and spiro-bridged ladder-type oligo-*p*-phenylenes, which exhibited extraordinary thermal and PL spectral stability. Furthermore, Wong and Wu et al.[11] reported the novel optoelectronic material constructed by spirobifluorene trimer **Mod I** (the chemical structure is shown in Scheme 1). This monodisperse trimer exhibited excellent thermal-stability and high fluorescence quantum yields both in solution (~100%) and in solid state (90%). However, the EL efficiency (1.1 cd A$^{-1}$) using **Mod I** is unsatisfactory compared with its very high solid PL efficiency.[11c] One of the possibilities is the unbalanced injection of electrons and holes and their transport abilities in the film of **Mod I**. Previous investigations have demonstrated that the injection of electrons predominates for fluorene-based polymers and oligomers.[12] Thus, the introduction of chromophores with low oxidation potentials, for example, carbazole,[13] into the **Mod I** is significantly interesting. Furthermore, in our earlier research, an electrochemically deposition (ED) operation has been found to prepare the luminescent film applied for OLEDs.[14] In the ED process, the luminescent precursor can be directly deposited on the Indium−Tin Oxida (ITO) electrodes through an oxidation coupling reaction of the electroactive carbazole units.[15] Thus, our goal here is to improve stability of fluorene derivatives and introduce carbazole units for facile hole injection and transport while retaining the excellent optoelectronic and thermal properties of **Mod I**. For this purpose, a novel series of fluorene trimers with spirobifluoren backbone and peripheral carbazole functional groups are synthesized. Additionally, we have also synthesized their homologous compound without carbazole groups for comparison in the same condition.

## 2. Results and Discussion

**2.1. Synthesis.** The synthetic route of **STCPC-6** and **STCPC-4**, which contain a spirobifluorene backbone and peripheral carbazole groups, is depicted in Scheme 1. The synthesis starts with commercially available 3-bromoanisole (**1**) to achieve the key monomers **7** and **8**, which can undergo Suzuki coupling reaction with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirofluorene (preparation and purification according to previous report)[11a] to afford the title compounds. First, treatment of **1** with excess amounts of *n*-butyllithium at −78 °C in THF and subsequent reaction with trimethyl borate could afford 3-methoxyphenyl boronic acid (**2**) in 70% yield. 3,3′-Bis-(methoxy)-biphenyl (**3**) was obtained with 82% yield by Pd-catalyzed Suzuki coupling reaction between **1** and **2** in a biphasic system (toluene/aqueous $Na_2CO_3$). Bromination of **2** with equimolar NBS in DMF at 0 °C gave 2-bromo-5,3′-bis-(methoxy)-biphenyl (**4**) in 69% yield. The treated **4** with *n*-butyllithium at −78 °C was trapped with 2-bromo-9-fluorenone to afford the hydroxy intermediate 9-(5,3′-bis(methoxy)-biphenyl-2-yl)-2-bromofluorene-9-ol. Then, a successionally acid-promoted dehydration cyclization reaction in a mixture of acetic acid and hydrochloric acid to afford 2-bromo-3′,6′-bis(methoxy)-9,9′-spirofluorene (**5**) with total yield of 60%. The geometrical isomer of **5**, that is, 2-bromo-1′,6′-bis(methoxy)-9,9′-spirofluorene, was not obtained by controlling volume ratio between acetic acid and hydrochloric acid and concentration of **5** in mixed acid.[16] Demethylation of **5** with boron tribromide in $CH_2Cl_2$ at 0 °C gave 2-bromo-9,9′-spirofluorene-3′,6′-diol (**6**) in 88% yield. 2-bromo-3′,6′-bis(*N*-carbazolyl-hexyloxy)-9,9′-spirofluorene (**7**) and 2-bromo-3′,6′-bis(N-carbazolyl-butoxy)-9,9′-spirofluorene (**8**) have been obtained by reaction of *N*-(6-bromohexane)-carbazole or *N*-(4-bromobutane)-carbazole and **6** in the presence of potassium carbonate in DMF with 70% and 61% yield, respectively. Finally, Suzuki coupling reactions between monomers **7** or **8** and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene were performed in a biphasic system (toluene/aqueous $Na_2CO_3$) using $Pd(PPh_3)_4$ as a catalyst precursor, which give the compounds **STCPC-6** and **STCPC-4** with different alkoxy length in 80% and 61% yields, respectively. The model compound **STHPH** with only alkoxy substitutions was also afforded from **6** in nearly the same manner

---

(6) (a) List, E. J. W.; Guentner, R.; Scandiucci de Freitas, P.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374. (b) Romaner, L.; Pogantsch, A.; Scandiucci de Freitas, P.; Scherf, U.; Gaal, M.; Zojer, E.; List, E. J. W. *Adv. Funct. Mater.* **2003**, *13*, 597. (c) Romaner, L.; Heimel, G.; Wiesenhofer, H.; Scandiucci de Freitas, P.; Scherf, U.; Brédas, J.-L.; Zojer, E.; List, E. J. W. *Chem. Mater.* **2004**, *16*, 4667. (d) Yang, X. H.; Jaiser, F. J.; Neher, D.; Lawson, P. V.; Brédas, J.-L.; Zojer, E.; Güntner, R.; Scandiucci de Freitas, P.; Forster, M.; Scherf, U. *Adv. Funct. Mater.* **2004**, *14*, 1097.

(7) (a) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946. (b) Surin, M.; Hennebicq, E.; Ego, C.; Marsitzky, D.; Grimsdale, A. C.; Müllen, K.; Brédas, J.-L.; Lzzaroni, R.; Leclére, P. *Chem. Mater.* **2004**, *16*, 994. (c) Li, J.; Bo, Z. S. *Macromolecules* **2004**, *37*, 2013. (d) Vak, S.; Chun, C.; Lee, C. L.; Kim, J.-J.; Kim, D.-Y. *J. Mater. Chem.* **2004**, *14*, 1342. (e) Vak, D.; Lim, B.; Lee, S.-H.; Kim, D.-Y. *Org. Lett.* **2005**, *7*, 4229. (f) Li, Z. H.; Wong, M. S. *Org. Lett.* **2006**, *8*, 1499. (g) Fu, Y.; Li, J.; Yan, S.; Bo, A. S. *Macromolecules* **2004**, *37*, 6395. (h) Cho, H.-J.; Jung, B.-J.; Cho, N. S.; Lee, J.; Shim, H.-K. *Macromolecules* **2003**, *36*, 6704.

(8) (a) Katsis, D.; Geng, Y.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332. (b) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828. (c) Wong, K.-T.; Wang, C.-F.; Chou, C. H.; Su, Y. O.; Lee, G.-H.; Peng, S.-M. *Org. Lett.* **2002**, *4*, 4439. (d) Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 4924. (e) Wu, F.-I.; Dodda, R.; Reddy, S.; Shu, C.-F. *J. Mater. Chem.* **2002**, *12*, 2893. (f) Bach, U.; Cloedt, K. D.; Spreitzer, H.; Gratzel, M. *Adv. Mater.* **2000**, *12*, 1060. (g) Bach, U.; Tachibana, Y.; Haque, S. A.; Moser, J.-E.; Durrant, J. R.; Gratzel, M.; Klug, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 7445. (h) Johansson, N.; Salbeck, J.; Bauer, J.; Weissörtel, F.; Bröms, P.; Andersson, A.; Salaneck, W. R. *Adv. Mater.* **1998**, *10*, 1136. (i) Wong, K.-T.; Liao, Y.-L.; Lin, Y.-T.; Su, H.-C.; Wu, C.-C. *Org. Lett.* **2005**, *7*, 5131. (j) Wong, K.-T.; Chen, R.-T.; Fang, F.-C.; Wu, C.-C.; Lin, Y.-T. *Org. Lett.* **2005**, *7*, 1979.

(9) (a) Salbeck, J.; Schörner, M.; Fuhrmann, T. *Thin Solid Films* **2002**, *417*, 20. (b) Salbeck, J.; Yu, N.; Bauer, J.; Weissortel, F.; Bestgen, H. *Synth. Met.* **1997**, 209. (c) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011.

(10) (a) Wu, Y.; Li, J.; Fu, Y.; Bo, Z. *Org. Lett.* **2004**, *6*, 3485. (b) Wu, Y.; Zhang, J.; Bo, Z. *Org. Lett.* **2007**, *9*, 4435.

(11) (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. (c) Wu, C.-C.; Lin, Y.-T.; Wong, K.-T.; Chen, R.-T.; Chien, Y.-Y. *Adv. Mater.* **2004**, *16*, 61. (d) Wu, C.-C.; Liu, T.-L.; Lin, Y.-T.; Hung, W.-Y.; Ke, T.-H.; Wong, K.-T.; Chao, T.-C. *Appl. Phys. Lett.* **2004**, *85*, 1172. (e) Wu, C.-C.; Liu, W.-G.; Hung, W.-Y.; Liu, T.-L.; Wong, K.-T.; Chien, Y.-Y.; Chen, R.-T.; Hung, T.-H.; Chao, T.-C.; Chen, Y-M. *Appl. Phys. Lett.* **2005**, *87*, 052103.

(12) Chang, S.-C.; He, G.; Chen, F.-C.; Guo, T.-F.; Yang, Y. *Appl. Phys. Lett.* **2001**, *79*, 2088.

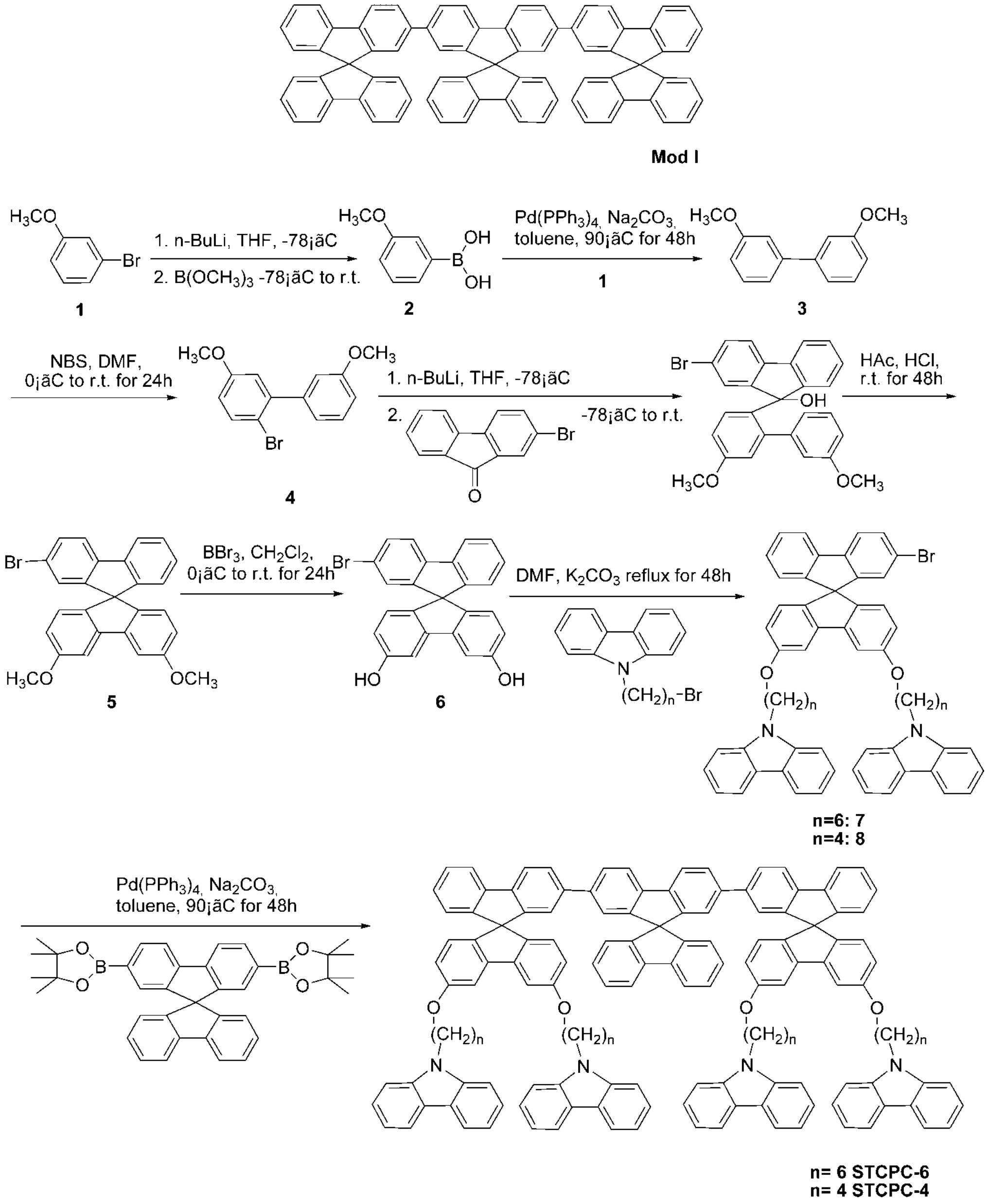
(13) (a) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854. (b) Liu, B.; Yu, W-L.; Lai, Y.-H.; Huang, W. *Chem. Mater.* **2001**, *13*, 1984. (c) Li, J.; Liu, D.; Li, Y.; Lee, C.-S.; Kwong, H.-L.; Lee, S. *Chem. Mater.* **2005**, *17*, 1208. (d) Li, J.; Ma, C.; Tang, J.; Lee, C.-S.; Lee, S. *Chem. Mater.* **2005**, *17*, 615.

(14) (a) Li, M.; Tang, S.; Shen, F.; Liu, M.; Xie, W.; Xia, H.; Liu, L.; Tian, L.; Xie, Z.; Lu, P.; Hanif, M.; Lu, D.; Cheng, G.; Ma, Y. *J. Phys. Chem. B* **2006**, *110*, 17784. (b) Li, M.; Tang, S.; Shen, F.; Liu, M.; Xie, W.; Xia, H.; Liu, L.; Tian, L.; Xie, Z.; Lu, P.; Hanif, M.; Lu, D.; Cheng, G.; Ma, Y. *Chem. Commun.* **2006**, 3393. (c) Li, M.; Tang, S.; Lu, D.; Shen, F.; Liu, M.; Wang, H.; Lu, P.; Hanif, M.; Ma, Y. *Semicond. Sci. Technol.* **2007**, *22*, 855.

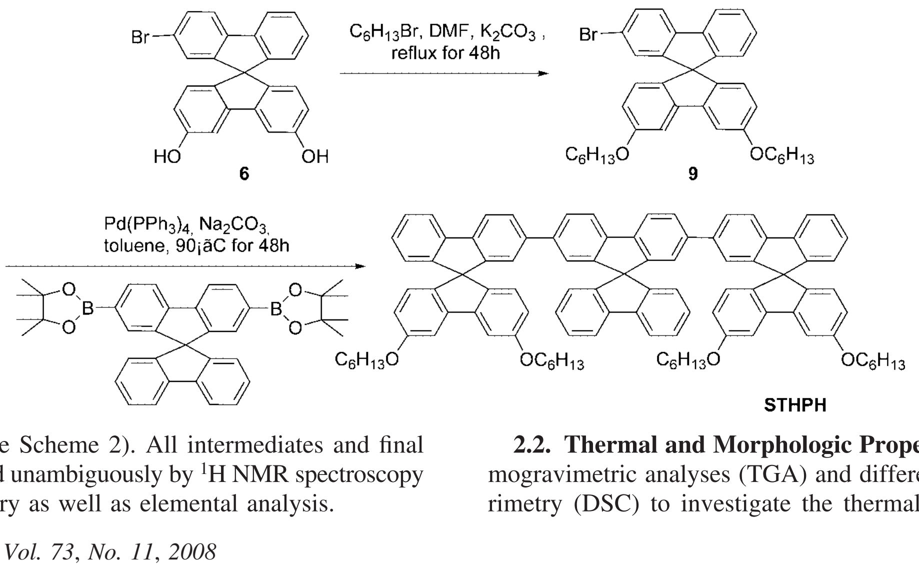
(15) Xia, C.; Advincula, R. C.; Baba, A.; Knoll, W. *Chem. Mater.* **2004**, *16*, 2852.

(16) Lee, H.; Oh, J.; Chu, H. Y.; Lee, J.-I.; Kim, S. H.; Yang, Y. S.; Kim, G. H.; Do, L.-M.; Zyung, T.; Lee, J.; Park, Y. *Tetrahedron* **2003**, *59*, 2773.

**SCHEME 1. Synthesis Route Used to Prepare STCPC-6 and STCPC-4, and Chemical Structure of Mod I**



**SCHEME 2. Synthesis Route Used to Prepare STHPH**



as synthesis of **9** (see Scheme 2). All intermediates and final products were verified unambiguously by $^1$H NMR spectroscopy and mass spectrometry as well as elemental analysis.

**2.2. Thermal and Morphologic Properties.** We used thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) to investigate the thermal properties of these

**TABLE 1. Summary of Physical Measurements of STCPC-6, STCPC-4, and STHPH**

| trimer | $\lambda_{max}^{abs\,a}$/nm | $\lambda_{max}^{emi\,a,b}$/nm in solution | $\lambda_{max}^{emi\,b,c}$/nm in films | $Q_{PL}{}^{a,d}$/% in solution | $Q_{PL}{}^{c,e}$/% in films | $T_g{}^f$/°C | $T_d{}^g$/°C | $E_{onset}^{ox}{}^h$/V | HOMO$^i$/eV |
|---|---|---|---|---|---|---|---|---|---|
| **STCPC-6** | 346 | 394 | 429 | 99 | 82 | 138 | 440 | 0.78 | 5.47 |
| **STCPC-4** | 346 | 394 | 430 | 99 | 78 | 165 | 453 | 0.80 | 5.49 |
| **STHPH** | 350 | 394 | 423 | 99 | 65 | 108 | 401 | 0.98 | 5.67 |

[a] Measured in dilute THF. [b] Excited at 350 nm. [c] Measured in films (~100 nm) by spin-coated method. [d] Measured using quinine sulfate in 1 M sulfuric acid as standard. [e] Measured by calibrate integrating sphere system. [f] Determined by DSC from remelt after cooling with a heating rate of 10 °C/min under $N_2$. [g] Determined by TGA with a heating rate of 10 °C/min under $N_2$. [h] Estimated by CV using a glass carbon disk as working electrode, platinum wire as auxiliary electrode, Ag/Ag$^+$ as reference electrode, [$n$-NBu$_4$][PF$_6$] as supporting electrolyte in $CH_2Cl_2$. [i] Estimated using the energy level of the ferrocene (Fc) reference (4.8 eV) and calibrated with $E_{1/2}$(Fc/Fc$^+$) = 0.11 V.

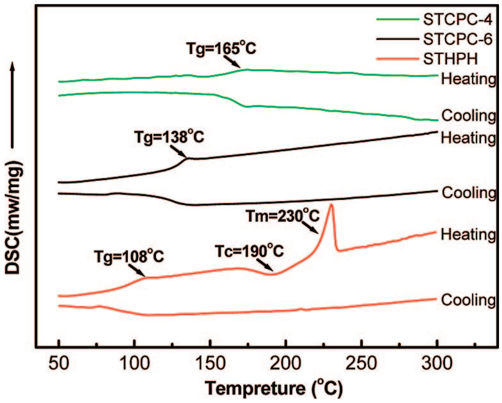


**FIGURE 1.** DSC scans of **STCPC-6**, **STCPC-4**, and **STHPH**.

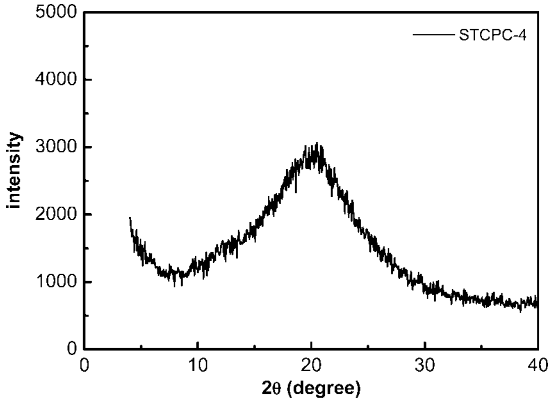


**FIGURE 2.** Powder XRD patterns of **STCPC-4**.

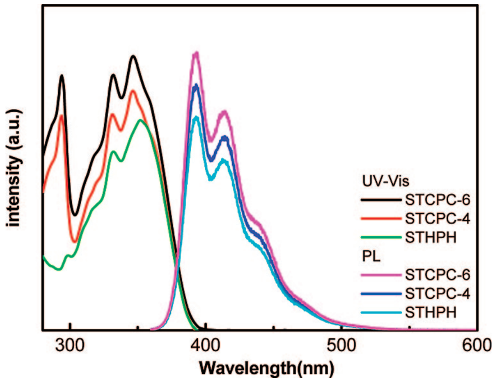


**FIGURE 3.** Absorption and PL spectra of **STCPC-6**, **STCPC-4**, and **STHPH** in dilute THF solution.

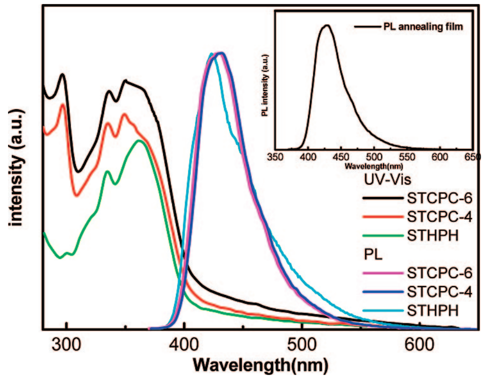


**FIGURE 4.** Absorption and PL spectra of **STCPC-6**, **STCPC-4**, and **STHPH** in films. (Inset) PL spectra of **STCPC-6** film after annealing at 200 °C in air for 8 h.

spirobifluorene trimers. In nitrogen atmosphere, they exhibit decomposition onset temperatures in the range of 401−453 °C (see Table 1). As shown in Figure 1, DSC studies indicated that **STCPC-4** and **STCPC-6** exhibit only a glass transition at 165 and 138 °C, respectively, whereas **STHPH** exhibit a glass transition at 108 °C, followed by crystallization at 190 °C and melting at 230 °C. Upon cooling from the melts, all of spirobifluorene trimers have transformed to glass states. The results reveal that the bulky carbazole units can efficiently hinder the crystallization process and increase molecular weight. To further validate morphologic properties in details, the powder X-ray diffraction analysis of **STCPC-4** was determined (see Figure 2). As can be seen, **STCPC-4** shows comparatively broad and random scattered peaks, demonstrating the noncrystalline amorphous nature in solid state.

**2.3. Optical Properties.** Figure 3 and Figure 4 illustrated the absorption and emission spectra of these spirobifluorene trimers in dilute THF solution and in films on quartz substrate by spin-coating, respectively, and the more detailed data was summarized in Table 1. The absorption bands of **STCPC-6** and **STCPC-4** appear at 346, 330, and 295 nm in dilute THF solution and in films. Furthermore, they exhibit very strong deep blue fluorescence with $\lambda_{max}$ at 394 nm and shoulder peaks at 414 and 435 nm as excitation under 350 nm light in solution, which feature the typical characteristics of the fluorene trimers.[17] Their emission spectra in films show a slight red shift ($\lambda_{max}$ at ~430 nm) compared to that in solution, however the spectra is still located at deep blue light region. These compounds exhibit high PL quantum yields both in the solution (~100%) and in films (65−82%), which attributes to reduce the probability of interchain interactions and prevent close packing of the backbone chains in tetrahedral steric demand of spirobifluorene structure.

**2.4. Annealing and Photodegradation.** The spectral stability of these spirobifluorene trimers were investigated by heat treatment and photodegradation of films. The inset of Figure 4 showed the PL spectra of **STCPC-6** film after annealing at 200 °C in air for 8 h. Although the trimer was annealed at a high

---

(17) Tang, S.; Liu, M.; Lu, P.; Xia, H.; Li, M.; Xie, Z.; Shen, F.; Gu, C.; Wang, H.; Yang, B.; Ma, Y. *Adv. Funct. Mater.* **2007**, *17*, 2869.

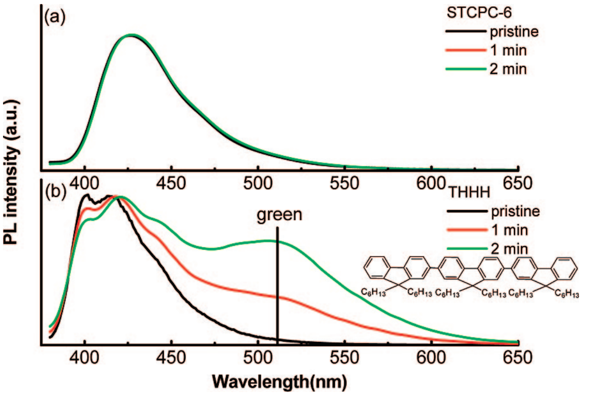


**FIGURE 5.** Normalized emission spectra of a pristine film and the subsequent photodegradation by a 125 W high-press mercury-arc light in air for (a) **STCPC-6** and (b) **THHH**.

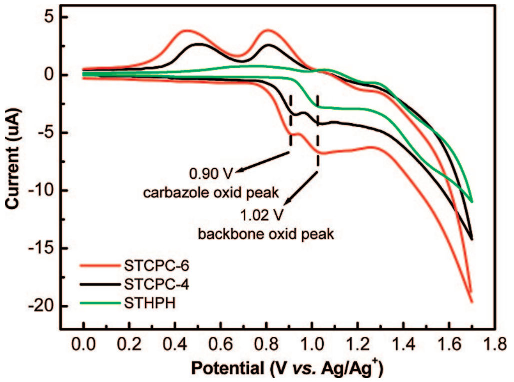


**FIGURE 6.** Oxidation part of the CV curves of **STCPC-6**, **STCPC-4**, and **STHPH**.

temperature, no emission spectral change was found. Figure 5 illustrated the emission spectra of the pristine films and the subsequent photodegradation under air. The emission spectra of traditional 9,9-dialkylated fluorene trimer (**THHH**) was also showed in the control experiment as compared. For the **STCPC-6**, no evident emission spectral change was found in the given degradation period. In contrast, the low-energy emission bands around 510 nm of **THHH** were emerged after degradation and the intensity was increased with the increase of the degradation time. Above, the result clearly reveals that the spirobifluorene structure can effectively restrain the photodegradation resulting from alkyl oxidation, hence improving the material stability.[18]

**2.5. Electrochemical Properties.** The electrochemical properties of new spirobifluorene trimers are characterized using CV in a standard three-electrode electrochemical cell in $CH_2Cl_2$ at room temperature. Figure 6 showed CV curves for the first scan. During anodic scans, **STCPC-6** exhibits two oxidation peaks at 0.90 and 1.02 V. The oxidation peak at the relatively low potentials of 0.90 V is ascribed to the oxidation of carbazole units.[19] The oxidation species of carbazyl radical cation can react with each other to form dimeric carbazole, which is the electropolymeric process on the surface of electrode. The oxidation of the relatively high potential of 1.02 V is attributed to oxidation of the backbone of the fluorene trimer.[20] In subsequent scans in the potential range, the reduction peak at 0.81 V is observed, which combines with oxidation peak at 1.02 V as reversible p-doping processes of the trimer backbone. Another reduction peak at 0.45 V is attributed to the formation of neutral dimeric carbazole from dimeric carbazyl cations.[19] The first CV scan of **STCPC-4** shows very slight difference compared with **STCPC-6**. In contrast, **STHPH** without carbazole groups shows the only oxidation peak of the trimer backbone at 1.02 V, which is consistent with oxidation peak of the backbone of **STCPC-6**. The reduction peak of the trimer backbone is not observed obviously for **STHPH**. In view of our system, the introduction of carbazole groups can enhance electrochemical stability of materials. The HOMO energy levels of three compounds estimated from the onset potentials are 5.47 eV for **STCPC-6**, 5.49 eV for **STCPC-4** and 5.67 eV for **STHPH**, respectively. These results reveal that the introduction of carbazole groups can clearly raise HOMO energy level, thereby improving the hole injection ability in device.

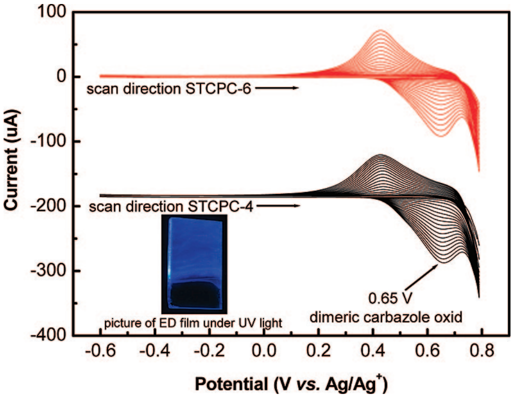


**FIGURE 7.** Electropolymerization of **STCPC-6** and **STCPC-4** during multiple CV scans. (Inset) Picture of electrochemically deposition film under UV light (350 nm).

**2.6. Electropolymeric and Electroluminescent Properties.** From the second CV scan between −0.6 and 0.8 V as shown in Figure 7, a new peak appears at oxidation potential (0.65 V), which can be assigned to the oxidation of newly formed dimeric carbazole in first cycle on the working electrode. As the electropolymerization proceeds, the oxidation and reduction currents are increased in successive cycles, indicating the occurrence of coupling reaction between the carbazole units and the growth of the film on the working electrode. As shown in the inset of Figure 7, the electrochemically deposited (ED) films exhibit strongly blue fluorescence. It is because that the coupling reaction of pendant carbazole groups occur in relatively low potentials, which do not effect on luminescent units of ter(spirobifluorene)s backbone. The ED film from **STCPC-6** also exhibits very smooth surface morphology with a root-mean-square (rms) roughness of 2.8 nm (see Figure 8). The EL device is fabricated by ED method using the most simple device structure ITO/**STCPC-6** (ED film)/Ba (5 nm)/Al (200 nm). The device exhibits pure blue emission with $\lambda_{max}$ at 423 nm and CIE coordinates (0.15, 0.09). The luminance-voltage and external quantum efficiency-voltage characteristics of the single layer device were shown in Figure 9. The device using **TCPC-6** exhibited a maximum luminance of 401 cd $m^{-2}$ and a maximum external quantum efficiency of 0.44% (corresponding to luminance efficiency of 0.16 cd $A^{-1}$). Although such EL performance

---

(18) Liu, L.; Tang, S.; Liu, M.; Xie, Z.; Zhang, W.; Lu, P.; Hanif, M.; Ma, Y. *J. Phys. Chem. B* **2006**, *110*, 13734.

(19) (a) Marrec, P.; Dano, C.; Guentner-Simonet, N.; Simonet, J. *Synth. Met.* **1997**, *89*, 171. (b) Inzelt, G. *J. Solid State Electrochem.* **2003**, *7*, 503.

(20) (a) Sonntag, M.; Strohriegl, P. *Chem. Mater.* **2004**, *16*, 4736. (b) Kanibolotsky, A. L.; Berridge, R.; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695.

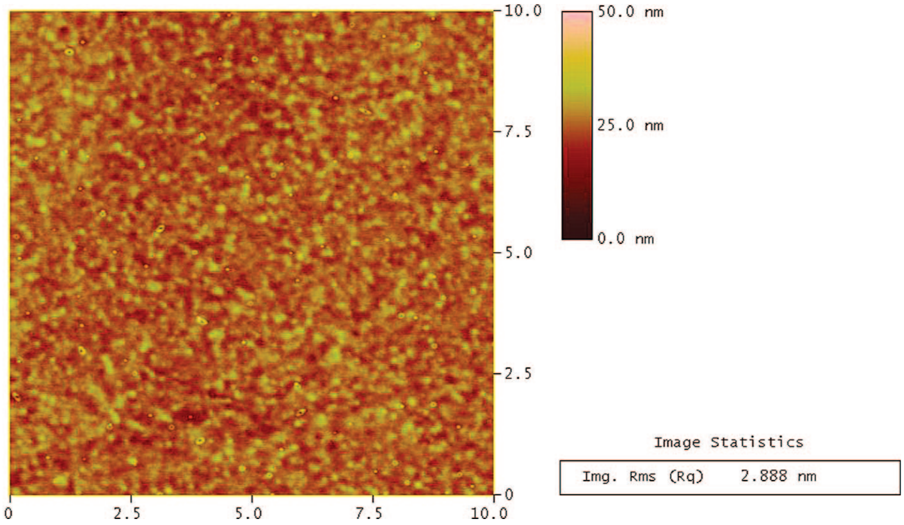


**FIGURE 8.** AFM image showing 10 μ × 10 μ areas of electrochemically deposition film of **STCPC-6**.

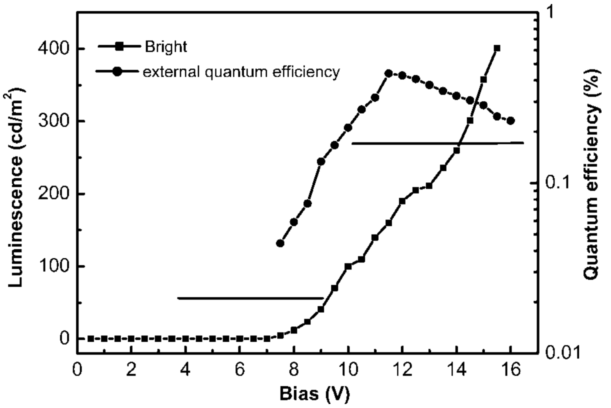


**FIGURE 9.** Luminance-voltage and external quantum efficiency-voltage characteristics in ITO/**STCPC-6** (ED film)/Ba/Al device.

is not high, it should be noted that such device based on ED technique is relatively simple in device fabrication compared with currently technology such as ink-jet printing for polymer materials[21] and shadow masks for small molecule materials.[22]

## 3. Conclusions

In summary, a series of fluorene trimers with spirobifluorene backbone and peripheral carbazole functional alkoxy-substitution have been synthesized. These compounds exhibit blue emission with high quantum yields in the solution and in films, amorphous morphology with high $T_g$ and excellent color stability. Through incorporating electroactive carbazole groups as the side chain, the first oxidation potential is reduced significantly and the HOMO energy level is heightened, indicating an increased hole inject ability of the title compounds. Furthermore, **STCPC-6** and **STCPC-4** are found to have an ability to form highly luminescent films through electrochemical polymerization, and then to prepare the LED devices using these ED films. The single-layer LEDs using ED films as a light emission layer achieve pure blue emission with CIE coordinates (0.15, 0.09) and maximum external quantum efficiency of 0.44%. Our findings provide an alternative approach to design luminescent materials with electropolymerization behaviors for facile LEDs fabrication.

## 4. Experimental Section

Compounds **2**, **3**, and **4** were prepared following a method similar to that of ref 16, and detailed experimental procedure and characterization of duplicated compounds **8**, **9**, **STCPC-4**, and **STHPH** are shown in the Supporting Information.

**2-Bromo-3′,6′-bis(methoxy)-9,9′-spirofluorene (5).** A solution of **4** (1.43 g, 4.875 mmol) dissolved in dried THF was cooled to −78 °C. Then, 3 mL of *n*-butyllithium (2.5 M/L, 7.5 mmol) was added slowly. The reaction mixture was stirred for 1 h at −78 °C. After 1 h, 2-bromo-9-fluorenone (2.14 g, 6.34 mmol) dissolved in dried THF was added slowly, and the resulting mixture was warmed to room temperature and stirred for 24 h. Some water poured into solution and extracted with ether several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and the solvent were removed by rotary evaporation, the crude product of 9-(5,3′-bis(methoxy)-biphenyl-2-yl)-2-bromofluorene-9-ol was afforded. This crude product was mixed with acetic acid (150 mL) and hydrochloric acid (3 mL) and stirred for 36 h at room temperature. Some water added to the resulting solution and white solid appeared at once. The precipitate was collected and purified by column chromatography on silica gel (silica gel, hexane/$CH_2Cl_2$) to afford a white solid (yield 60%). Mp 203−206 °C. $^1$H NMR (500 MHz, $CDCl_3$): δ7.79−7.77 (d, 1H, Ar−H), δ7.68−7.66 (d, 1H, Ar−H), δ7.47−7.45 (d, 1H, Ar−H), δ7.36−7.32 (m, 3H, Ar−H), δ7.14−7.11 (t, 1H, Ar−H), δ6.85 (s, 1H, Ar−H), δ6.73−6.72 (d, 1H, Ar−H), δ6.69 (s, 1H, Ar−H), δ6.67 (s, 1H, Ar−H), δ6.62−6.60 (d, 2H, Ar−H), δ3.89 (s, 6H, $OCH_3$), δ3.83 (s, 3H, $CH_3$). $^{13}$C NMR (500 MHz, $CDCl_3$): δ160.4, 151.7, 149.3, 141.1, 140.9, 131.1, 128.6, 128.1, 127.6, 125.1, 124.4, 121.6, 120.4, 114.5, 105.7, 56.0, MS (*m*/*z*) 454.2. Anal. Calcd for $C_{27}H_{19}BrO_2$: C, 71.22; H, 4.21 Found: C, 71.47; H, 4.10.

**2-Bromo-9,9′-spirofluorene-3′,6′-diol (6).** A solution of boron tribromide (1 mL) in $CH_2Cl_2$ (10 mL) was slowly added to a solution of **5** in $CH_2Cl_2$ (30 mL) at ice−water bath. After the addition was completed, the ice−water bath was removed and the reaction mixture was stirred for 24 h at room temperature. The resulting solution was poured into water (100 mL) and stirred for 1 h, and then extracted with $CH_2Cl_2$ several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration

---

(21) (a) de Gans, B. J.; Duineveld, P. C.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 203. (b) Burrows, P. E.; Bulovic, V.; Forrest, S. R.; Sapochak, L. S.; McCarty, D. M.; Thompson, M. E. *Appl. Phys. Lett.* **1994**, *65*, 2922. (c) Burrows, P. E.; Shen, Z.; Bulovic, V.; McCarty, E. M.; Forrest, S. R.; Cronin, J. A.; Thompson, M. E. *J. Appl. Phys.* **1996**, *10*, 79.

(22) (a) Shen, Z.; Burrows, P. E.; Bulovic, V.; Forrest, S. R.; Thompson, M. E. *Science* **1997**, *276*, 2009. (b) Lidzey, D. G.; Pate, M. A.; Weaver, M. S.; Fisher, T. A.; Bradley, D. D. C. *Synth. Met.* **1996**, *82*, 141. (c) Renak, M. L.; Bazam, G. C.; Roitman, D. *Adv. Mater.* **1997**, *9*, 392.

and solvent evaporation, the gray solid was recrystallized with $CH_2Cl_2$ to afford white solid (yield 88%). Mp 271−273 °C. $^1H$ NMR (500 MHz, DMSO-$d_6$): $\delta$9.55 (s, 2H, OH-H), $\delta$7.99−7.97 (d, 1H, Ar−H), $\delta$7.95−7.93 (d, 1H, Ar−H), $\delta$7.56−7.54 (d, 1H, Ar−H), $\delta$7.39−7.36 (t, 1H, Ar−H), $\delta$7.23 (s, 2H, Ar−H), $\delta$7.17−7.15 (d, 1H, Ar−H), $\delta$7.67 (s, 1H, Ar−H), $\delta$6.63−6.62 (d, 1H, Ar−H), $\delta$6.55−6.53 (d, 2H, Ar−H), $\delta$6.39−6.37 (d, 2H, Ar−H). $^{13}C$ NMR (500 MHz, $CDCl_3$): $\delta$158.5, 152.7, 149.8, 143.6, 141.2, 140.7, 139.1, 131.4, 129.2, 128.7, 126.9, 124.9, 124.4, 123.3, 121.5, 121.3, 116.1, 107.8. MS (*m*/*z*) 426.1. Anal. Calcd for $C_{25}H_{15}BrO_2$: C, 70.27; H, 3.54 Found: C, 70.59; H, 3.76.

**2-Bromo-3′,6′-bis(*N*-carbazolyl-hexyloxy)-9,9′-spirofluorene (7).** **6** (400 mg, 0.94 mmol), *N*-(6-bromohexane)-carbazole (927 mg, 2.82 mmol) and potassium carbonate (649 mg, 4.7 mmol) were dissolved in DMF. After the reaction mixture was stirred at 150 °C for 48 h, some water was added to the resulting solution, and then the mixture was extracted with chloroform several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the liquid was purified by column chromatography on silica gel (silica gel, petroleum ether/$CH_2Cl_2$) to afford white solid (yield 70%). Mp 115−117 °C. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$8.11−8.10 (d, 4H, Ar−H-car), $\delta$7.78−7.77 (d, 1H, Ar−H-flu), $\delta$7.67−7.66 (d, 1H, Ar−H-flu), $\delta$7.45−7.56 (m, 9H, Ar−H-flu-car), $\delta$7.34−7.34 (t, 1H, Ar−H-flu), $\delta$7.22−7.13 (m, 6H, Ar−H-flu-car), $\delta$7.11−7.10 (t, 1H, Ar−H-flu), $\delta$6.84 (s, 1H, Ar−H-flu), $\delta$6.72−6.73 (d, 1H, Ar−H-flu), $\delta$6.62−6.59 (d, 2H, Ar−H-flu), $\delta$6.57−6.56 (d, 2H, Ar−H-flu), $\delta$4.33−4.35 (t, 4H, O-$CH_2$), $\delta$3.99−3.97 (t, 4H, N-$CH_2$), $\delta$1.95−1.93 (m, 4H, $CH_2$), $\delta$1.79−1.77 (m, 4H, $CH_2$), $\delta$1.54−1.48 (m, 4H, $CH_2$), $\delta$0.87−0.84 (m, 4H, $CH_2$). $^{13}C$ NMR (500 MHz, $CDCl_3$): $\delta$159.7, 151.6, 149.9, 143.0, 141.1, 140.3, 131.1, 128.8, 128.2, 127.9, 126.3, 125.1, 124.1, 123.8, 121.8, 120.8, 120.4, 119.3, 115.2, 109.8, 106.0, 68.4, 42.2, 30.8, 29.4, 29.0, 27.9, 26.1. MS (*m*/*z*) 924.4. Anal. Calcd for $C_{61}H_{53}N_2BrO_2$: C, 79.12; H, 5.77; N, 3.03 Found: C, 79.13; H, 5.32; N, 3.18.

**STCPC-6.** 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-spirobifluorene (99.4 mg, 0.175 mmol) and **7** (324.1 mg, 0.35 mmol) were added to the $Na_2CO_3$ (2.0 M/L) and toluene (toluene/water was at a 3:2 ratio), and $Pd(PPh_3)_4$ (12 mg) acted as catalyst. After the reaction mixture was stirred at 90 °C for 48 h under a nitrogen atmosphere, some water was added to the resulting solution and then the mixture was extracted with chloroform for several times. The organic phase was dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the liquid was purified with column chromatography using petroleum ether/$CH_2Cl_2$ as the eluent to afford a white solid (yield 80%). $^1H$ NMR (500 MHz, DMSO-$d_6$): $\delta$8.11−8.09 (d, 4H, Ar−H-car), $\delta$7.90−7.83 (m, 4H, Ar−H-flu), $\delta$7.56−7.54 (m, 6H, Ar−H-flu-car), $\delta$7.39−7.38 (t, 4H, Ar−H-car), $\delta$7.32−7.30 (m, 4H, Ar−H-flu), $\delta$7.13−7.08 (t, 4H, Ar−H-car), $\delta$7.07−7.04 (t, 1H, Ar−H-flu), $\delta$6.98−6.96 (t, 1H, Ar−H-flu), $\delta$6.59−6.50 (m, 6H, Ar−H-flu), $\delta$6.38−6.37 (d, 2H, Ar−H-flu), $\delta$4.38−4.35 (t, 4H, O-$CH_2$), $\delta$3.93−3.91 (t, 4H, N-$CH_2$), $\delta$1.78−1.76 (m, 4H, $CH_2$), $\delta$1.65−1.63 (m, 4H, $CH_2$), $\delta$1.42−1.36 (m, 4H, $CH_2$), $\delta$0.85−0.83 (m, 4H, $CH_2$). $^{13}C$ NMR (500 MHz, $CDCl_3$): $\delta$159.6, 150.1, 149.9, 149.0, 143.4, 142.2, 141.8, 141.4, 141.3, 141.2, 140.8, 128.2, 128.1, 127.9, 127.5, 127.4, 126.0, 125.1, 124.7, 124.2, 123.3, 122.9, 122.8, 120.8, 120.4, 120.3, 120.2, 119.1, 114.8, 109.0, 106.1, 68.3, 43.3, 30.1, 29.6, 29.3, 27.4, 26.3. MALDI-TOF-MS ($M^+$) 2004.9 (100%). Anal. Calcd for $C_{147}H_{120}N_4O_4$: C, 87.99; H, 6.03; N, 2.79 Found: C, 87.73; H, 5.92; N, 2.76.

**Acknowledgment.** We are grateful for financial support from National Science foundation of China. (grant number 20474024, 90101026, 20573040, 50473001, 50473006, 90501001), and by Ministry of Science and Technology of China (grant number 2002CB6134003).

**Supporting Information Available:** General information, LED fabrication and measurement, $^1H$ NMR, $^{13}C$ NMR and MALDI-TOF-MS of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO8006094