ORGANIC LETTERS

2006
Vol. 8, No. 17
3701−3704

# Facile Synthesis of Complicated 9,9-Diarylfluorenes Based on $BF_3 \cdot Et_2O$-Mediated Friedel–Crafts Reaction

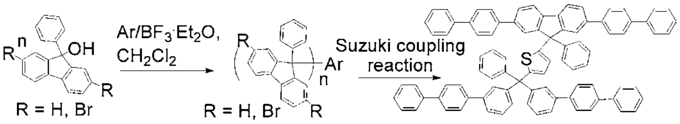
**Ling-Hai Xie,[†,‡] Xiao-Ya Hou,[†] Yu-Ran Hua,[†] Chao Tang,[†,‡] Feng Liu,[†]
Qu-Li Fan,[†,‡] and Wei Huang*,[†,‡,§]**

*Institute of Advanced Materials (IAM), Fudan University, 220 Handan Road,
Shanghai 200433, People's Republic of China, Institute of Advanced Materials (IAM),
Nanjing University of Posts and Telecommunications, 66 New Mofan Road,
Nanjing 210003, People's Republic of China, and Faculty of Engineering,
National University of Singapore, 9 Engineering Drive 1,
Singapore 117576, Republic of Singapore*

*wei-huang@fudan.edu.cn; chehw@nus.edu.sg*

Received May 25, 2006

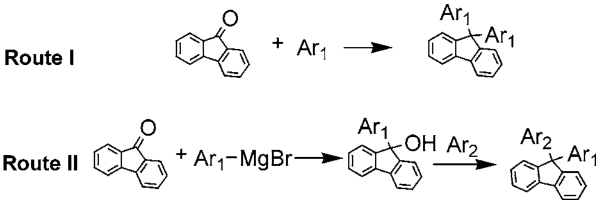
## ABSTRACT



**$BF_3 \cdot OEt_2$-mediated Friedel–Crafts reaction of 9-phenyl-fluoren-9-ol with electron-rich aromatic substrates to prepare a new family of complicated 9,9-diarylfluorenes is described. The 9,9-diarylfluorenes tethered with various functional substituents, e.g., bulky spiro units, hole-transporting moieties, and fluorescent dyes, will be promising building blocks for the construction of optoelectronic materials.**

Recently, oligofluorenes and polyfluorenes have been recognized as very promising classes of organic semiconductors in the field of organic electronics, especially in OLEDs and PLEDs.[1] 9,9-Diarylfluorenes are of great importance because aryl moieties at the C9 position of fluorene can afford various functionalities, e.g., improvement of solubility,[2] increase of charge carrier mobility,[3] tunable electronic structures,[4] and aggregate suppression to improve morphological stability.[5]

**Scheme 1.** Two Synthetic Routes for the Preparation of 9,9-Diarylfluorene



Two synthetic routes have been utilized to introduce aryl substituents into the C9 position of fluorene starting from fluorenone in the literature, as shown in Scheme 1 (route I and route II). Route I provides an effective method to introduce the two same substituents into the C9 position of fluorene. Müllen has employed synthetic route I to introduce two bulky triphenylamine groups into the C9 position of

---

[†] Fudan University.
[‡] Nanjing University of Posts and Telecommunications.
[§] National University of Singapore.

(1) (a) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737−1750. (b) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477−487. (c) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 403−428. (d) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416−7417.

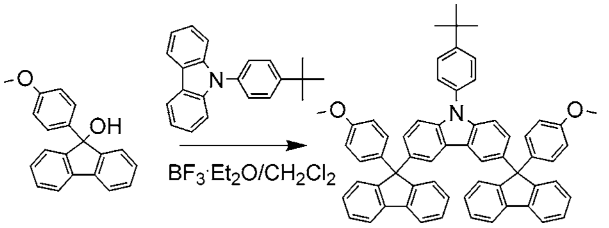
(2) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Mullen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946−953.

(3) 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*, 3710−3711.

10.1021/ol061268j CCC: $33.50

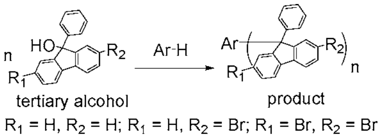
fluorene.[6] Chou has also exploited synthetic route I to achieve coupling of “Fréchet-type” dendrons and POSS to fluorene.[7] Route II mainly involves an addition reaction of the Grignard reagent to fluorenone and a Friedel−Crafts reaction of tertiary alcohol. Wong has achieved a series of efficient large-gap blue-light emitters and hole-transporting materials with highly morphological stability via route II.[8] However, Friedel−Crafts reaction has not been fully exploited for the preparation of 9,9-diarylfluorenes. For example, an alternative pathway could be utilized for the carbazole derivative in the literature,[9] as shown in Scheme 2.

**Scheme 2.** Alternative Synthetic Route to the Carbazole Derivative[9]

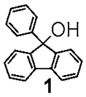
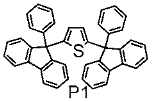
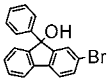
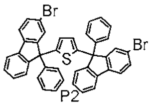
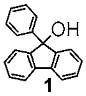
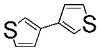
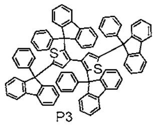
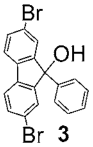
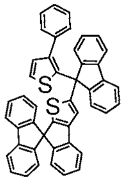
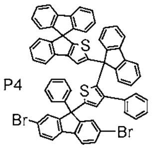
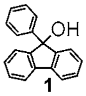
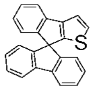
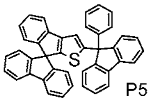
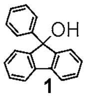
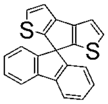
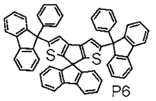
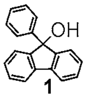
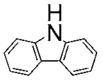
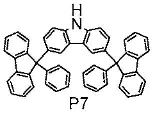
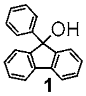
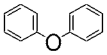
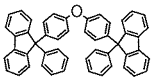
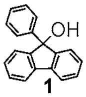
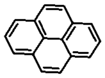
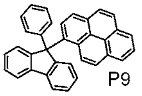
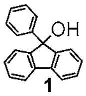
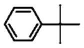
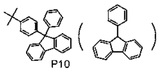


In this contribution, we focus on the $BF_3•OEt_2$-mediated Friedel−Crafts reaction for the preparation of various optoelectronic building blocks based on 9,9-diarylfluorenes via route II. Using our strategy, we have designed and synthesized a series of wonderful functional building blocks by incorporating bulky spiro structures, hole-transporting carbazole, and fluorescent dye pyrene into the C9 position of fluorene. In addition, multibrominated diarylfluorenes with nonplanar conformations will be useful monomers for the hyperbranched architectures and potential interrupting monomers for semiconjugated polymers.

**Table 1.** Reaction of Tertiary Alcohol with Different Substrates[a]



$R_1$ = H, $R_2$ = H; $R_1$ = H, $R_2$ = Br; $R_1$ = Br, $R_2$ = Br

| entry | alcohol | arene | product[b] | yield |
|---|---|---|---|---|
| 1 |  **1** |  |  P1 | 97% |
| 2 |  **2** |  |  P2 | 96% |
| 3 |  **1** |  |  P3 | 69% |
| 4 |  **3** |  |  | 70% |
| 5 |  **1** |  |  | 85% |
| 6 |  **1** |  |  | 73% |
| 7 |  **1** |  |  P7 | 74% |
| 8 |  **1** |  |  P8 | 70% |
| 9 |  **1** |  |  | 30% |
| 10 |  **1** |  |  | 0%<br>(70%) |

[a] Reaction conditions: 0.6, 1.2, or 4.8 mmol of tertiary alcohol, 0.5 mmol of aryl derivatives, and 0.6, 1.2, or 4.8 mmol of the $BF_3·Et_2O$ complex in 100 mL of $CH_2Cl_2$ at room temperature for 30 min to 10 h. [b] The main products for entries 1, 2, 6, 7, and 8 are 2:1 adducts, and the main products for entries 4, 5, 9, and 10 are 1:1 adducts.

Our expectation that the $BF_3•OEt_2$ complex[10] as a Lewis acid may be an effective catalyst for the Friedel−Crafts reaction of 9-phenyl-fluoren-9-ol (tertiary alcohol **1**) with aromatic substrates was experimentally confirmed. A 1:2 mixture of thiophene and tertiary alcohol **1** in $CH_2Cl_2$ did react smoothly at room temperature, as shown in Table 1 (entry 1). To our delight, the efficiency of $BF_3•OEt_2$ could

---

(4) (a) Wu, F.-I.; Reddy, D. S.; Shu, C.-F.; Liu, M. S.; Jen, A. K.-Y. *Chem. Mater.* **2003**, *15*, 269−274. (b) Shu, C.-F.; Dodda, R.; Wu, F.-I.; Liu, M. S.; Jen, A. K.-Y. *Macromolecules* **2003**, *36*, 6698−6703.

(5) (a) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828−831. (b) Zeng, G.; Yu, W.-L.; Chua, S.-J.; Huang, W. *Macromolecules* **2002**, *35*, 6907−6914. (c) Chao, T.-C.; Lin, Y.-T.; Yang, C.-Y.; Hung, T. S.; Chou, H.-C.; Wu, C.-c.; Wong, K.-T. *Adv. Mater.* **2005**, *17*, 992−996.

(6) Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Müllen, K. *Adv. Mater.* **2002**, *14*, 809−811.

(7) (a) Chou, C.-H.; Shu, C.-F. *Macromolecules* **2002**, *35*, 9673−9677. (b) Chou, C.-H.; Hsu, S.-L.; Dinakaran, K.; Chiu, M.-Y.; Wei, K.-H. *Macromolecules* **2005**, *38*(3), 745−751.

(8) (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*, 11576−11577. (b) Wong, K.-T.; Wang, Z.-J.; Chien, Y.-Y.; Wang, C.-L. *Org. Lett.* **2001**, *3*, 2285−2288. (c) Wong, K.-T.; Liao, Y.-L.; Lin, Y.-T.; Su, H.-C.; Wu, C.-c. *Org. Lett.* **2005**, *7*, 5131−5134. (d) Wong, K.-T.; Chen, R.-T.; Fang, F.-C.; Wu, C.-c.; Lin, Y.-T. *Org. Lett.* **2005**, *7*, 1979−1982.

(9) Wong, K.-T.; Chen, Y.-M.; Lin, Y.-T.; Su, H.-C.; Wu, C.-c. *Org. Lett.* **2005**, *7*, 5361−5364.

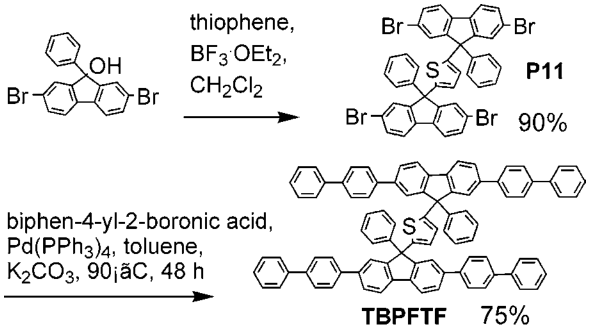
(10) Mitschke, U.; Bäuerle, P. *J. Chem. Soc., Perkin Trans. 1* **2001**, 740−753.

be further confirmed by the following reaction of thiophene derivatives with tertiary alcohol **1**. The reaction of 3,3-bithiophene with 4 equiv of **1** gave the congested tetrasubstituted products **P3** with a high yield of 69% (entry 3). The electrophilic substitution reaction illustrated that steric hindrance showed little impact on the reactivity of tertiary alcohol **1**, which was useful information for the complicated optoelectronic system, e.g., dendrimers. The fact was also demonstrated by entry 4, a reaction of a highly sterically hindered substrate with tertiary alcohol **3** in a good yield of 70%. In addition, this reaction reveals that the dibromo substituents hardly have an impact on the reactivity of tertiary alcohol **3**. We also prepared the spiro-containing 9,9-diarylfluorenes **P5** and **P6** in good yields (entries 5 and 6), which are potential building blocks for the construction of stable amorphous molecular glasses.

We then examined Friedel−Crafts reaction of tertiary alcohol **1** with other electron-rich substrates, e.g., carbazole and phenyl ether, which indeed exhibits the excellent reactivity with yields of 74% and 70% (entries 7 and 8), respectively. We have also attempted the reaction with weakly electron-rich substrates, such as pyrene and *tert*-butylbenzene (entries 9 and 10). As a result, a low yield of 30% was observed for the monosubstituted product **P9**, and no **P10** was obtained. The main byproduct, 9-phenylfluorene, in entry 10 was obtained in a yield of 70%, in which the mechanism is still unknown. Therefore, the $BF_3 \cdot OEt_2$-mediated Friedel−Crafts reactions are more favorable for strongly electron-rich substrates.

Finally, a stable blue-light emitter 2,5-bis(2,7,-bis([1,1′-biphenyl]-4-yl)-9- phenyl-fluoren-9-yl) thiophene (TBPFTF) with nonplanar conformation was constructed by a Suzuki coupling reaction of 4 equiv of biphenyl boronic acid with the tetrabrominated **P11**, which was obtained from the reaction of thiophene with tertiary alcohol **3** (Scheme 3).

**Scheme 3.** Divergent Synthetic Route to TBPFTF



The structures of all the above products were confirmed by $^1$H and $^{13}$C NMR, MALDI-TOF-MS, and elemental analysis. The monosubstituted pyrene (**P9**) was characterized by X-ray crystallographic analysis (Figure 1).[11] The sterically congested **P3** shows special splitting signals in the $^1$H NMR spectrum, as shown in Figure 2. It was found that, unexpectedly, two double peaks with an integrated ratio of 2:2 instead of a double peak with four protons are assigned to one of the two pairs of protons in the fluorene ring. The splitting phenomenon is probably attributed to nonequivalent magnetic environments due to steric hindrance among the 9-phenylfluorene groups.

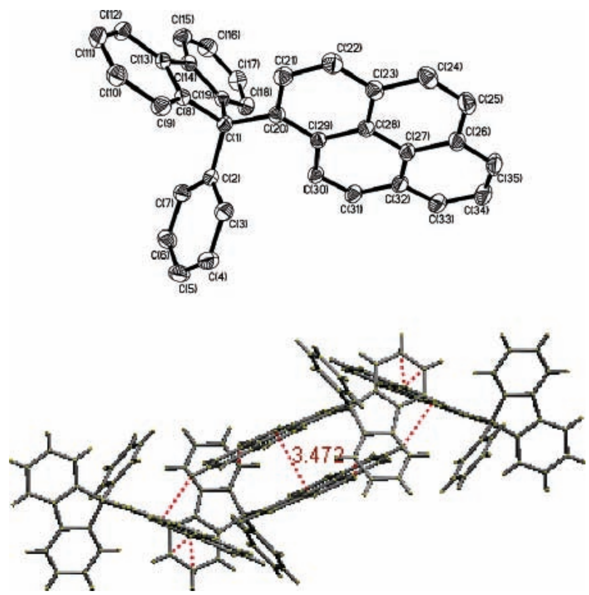


**Figure 1.** ORTEP drawing (30% probability) showing the X-ray structure of **P9** and the crystal packing.

TBPFTF has poor solubility in common organic solvents except for $CHCl_3$ and THF but has much higher solubility than the dispiro analogue.[12] The optical spectra of TBPFTF in chloroform are shown in Figure 3. TBPFTF exhibits a strong $\pi-\pi^*$ absorption with $\lambda_{max}$ at 341 nm and two well-resolved emission peaks at 386 and 405 nm with an optical band gap (3.19 eV). The thermal properties of TBPFTF were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). TBPFTF showed a high

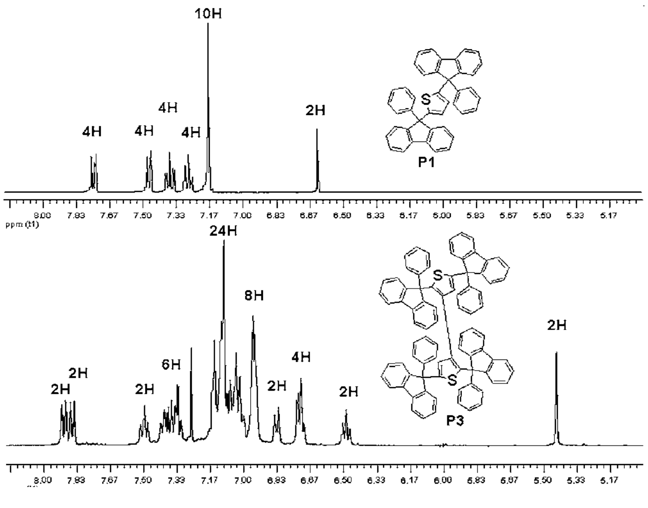


**Figure 2.** $^1$H NMR spectra of **P1** and **P3** in $CDCl_3$.

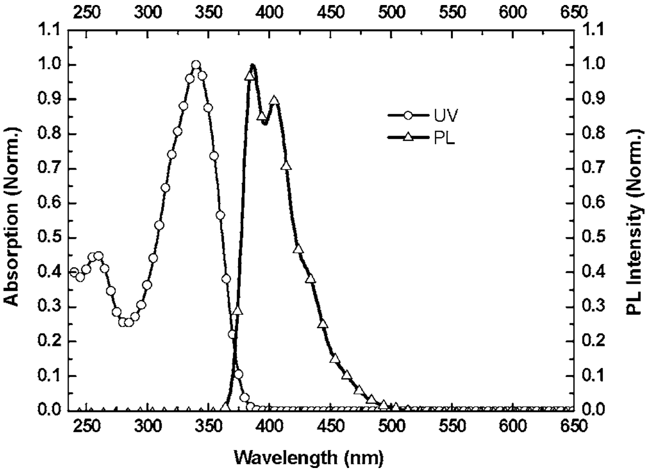


**Figure 3.** UV and PL spectra of TBPFTF in $CHCl_3$ solution.

decomposition temperature up to 470 °C (5% loss weight temperature) and a high $T_g$ up to 247 °C. Cyclic voltammetry was performed on the film of TBPFTF deposited on a glassy carbon electrode measured in $Bu_4^+PF_6^-$ (0.1 M)/acetonitrile with a platinum counter electrode and a $Ag^+/Ag$ reference electrode (Figure 4). On the basis of the onset potentials of the oxidation and reduction, the HOMO and LUMO energy levels of TBPFTF were estimated to be −5.82 and −2.28 eV, respectively, with regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level). Therefore, the electrochemical band gap (3.54 eV) does not closely match the optical band gap (3.19 eV). In addition, the HOMO energy level of the TBPFTF is lower than that reported for POF (−5.8 eV). The results indicate that the conjugation length of TBPFTF is shorter than that of POF.

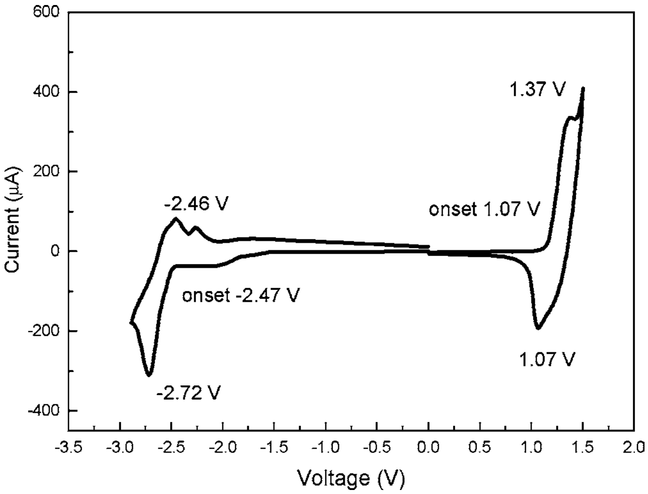


**Figure 4.** CV curve of TBPFTF.

In conclusion, we have utilized the $BF_3{\cdot}OEt_2$ complex as a Lewis acid catalyst to examine the reactivity of 9-phenyl-fluoren-9-ol and its derivatives with several aromatic substrates. The results show that the $BF_3{\cdot}OEt_2$ complex is an effective catalyst for the Friedel−Crafts reaction of strong electron-rich substrates. We also prepared a series of complicated 9,9-diarylfluorenes with nonplanar conformations bearing various functional substituents, and they are promising candidates for construction of organic semiconductors. Further attempts to synthesize special dendrimers on the basis of Friedel−Crafts reaction could be achieved via a rational design, which is currently being pursued.

**Acknowledgment.** This work was financially supported by the NNSFC under Grants 60325412, 90406021, and 50428303, the Shanghai Commission of Science and Technology under Grants 03DZ11016 and 04XD14002, and the Shanghai Commission of Education under Grant 03SG03.

**Supporting Information Available:** The experimental procedures for the new compounds and $^1H$ and $^{13}C$ NMR, MS spectra, TGA, DSC thermograms, and an X-ray crystallographic file (CIF) for **P9**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL061268J

---

(11) Crystal data for **P9**: Crystals were grown from $CDCl_3$. The structure was solved on a Bruker SMART CCD diffractometer using Mo Kα radiation. $C_{35}H_{22}$, ($M_r = 442.5$): monoclinic, space group $P2_1/c$, $D_c = 1.296$ g cm$^{-3}$, $a = 14.922(4)$, $b = 8.735(2)$, $c = 17.450(5)$ Å, $\alpha = 90°$, $\beta = 94.143(4)°$, $\gamma = 90°$, $V = 2268.5(11)$ Å$^3$, $Z = 4$, $\lambda = 0.71073$ Å, $\mu = 0.073$ mm$^{-1}$, $T = 297(2)$ K, $R = 0.0402$ for 12 903 observed reflections [$I > 2\sigma I$] and $R_w = 0.1017$ for all 4460 unique reflections.

(12) Xie, L.-H.; Hou, X.-Y.; Tang, C.; Hua, Y.-R.; Wang, R.-J.; Chen, R.-F.; Fan, Q.-L.; Wang, L.-H.; Wei, W.; Peng, B.; Huang, W. *Org. Lett.* **2006**, *8*(7), 1363−1366.