ORGANIC LETTERS

2006
Vol. 8, No. 13
2787−2790

Unexpected One-Pot Method to Synthesize Spiro[fluorene-9,9′-xanthene] Building Blocks for Blue-Light-Emitting Materials

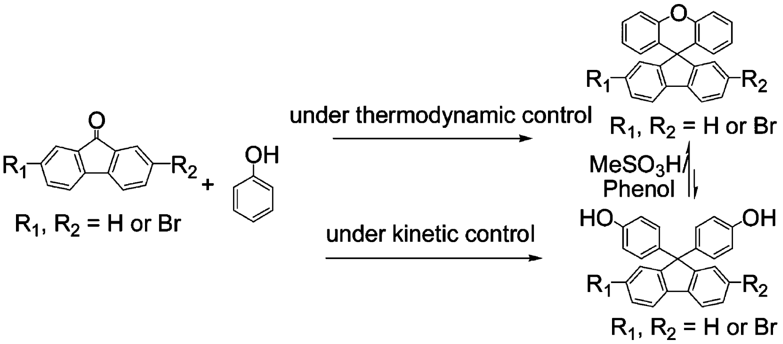
**Ling-Hai Xie,[†,‡] Feng Liu,[†] Chao Tang,[†,‡] Xiao-Ya Hou,[†] Yu-Ran Hua,[†]
Qu-Li Fan,[†,‡] and Wei Huang*,[†,‡,§]**

Institute of Advanced Materials (IAM), Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China, Institute of Advanced Materials (IAM), Nanjing University, 22 Hankou Road, Nanjing 210093, 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 April 10, 2006

ABSTRACT



An unexpected one-pot synthetic approach toward spiro[fluorene-9,9′-xanthene] (SFX) under excessive $MeSO_3H$ conditions has been developed. The key step involves a thermodynamically controlled cyclization reaction. Blue-light-emitting materials based on SFX building blocks that exhibit high thermal stability have also been synthesized.

In recent years, spiro compounds have attracted much attention because of their promising applications in the fields of molecular tectonics,[1] enantioselective molecular recognition,[2] molecular electronics,[3] and optoelectronic devices.[4] For example, supramolecular tectons and synthons based on spirobifluorene have been used to construct porous hydrogen-bonded networks and linear polymeric metal−organic frameworks with square cavities.[1] Spiro homopolymers exhibit excellent spectrum stability even in air-annealing experi-

---

[†] Fudan University.

[‡] Nanjing University.

[§] National University of Singapore.

(1) (a) Wong, K.-T.; Liao, Y.-L.; Peng, Y.-C.; Wang, C.-C.; Lin, S.-Y.; Yang, C.-H.; Tseng, S.-M.; Lee, G.-H.; Peng, S.-M. *Cryst. Growth Des.* **2005**, *5* (2), 667−671. (b) Fournier, J.-H.; Maris, T.; Wuest, J. D. *J. Org. Chem.* **2004**, *69*, 1762−1775. (c) Fournier, J.-H.; Maris, T.; Wuest, J. D. *J. Org. Chem.* **2003**, *68*, 240−246.

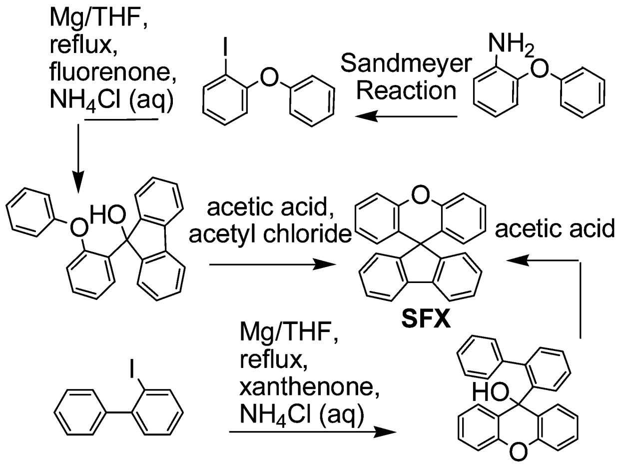
(2) (a) Smith, D. K.; Diederich, F. *J. Chem. Soc., Chem. Commun.* **1998**, 2501−2502. (b) Lustenberger, P.; Martinborough, E.; Denti, T. M.; Diederich, F. *J. Chem. Soc., Perkin Trans. 2* **1998**, 747−762. (c) Smith, D. K.; Zingg, A.; Diederich, F. *Helv. Chim. Acta* **1999**, *82*, 1225−1241. (d) Tejeda, A.; Oliva, A. I.; Simón, L.; Grande, M.; Caballero, M.-C.; Morán, J. R. *Tetrahedron Lett.* **2000**, *41*, 4563−4566.

(3) (a) Tour, J. M.; Wu, R.-L.; Schumm, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 5662−5663. (b) Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 8104−8113.

(4) (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.

10.1021/ol060871z CCC: $33.50

Scheme 1. Typical Synthetic Route to **SFX**[9a]

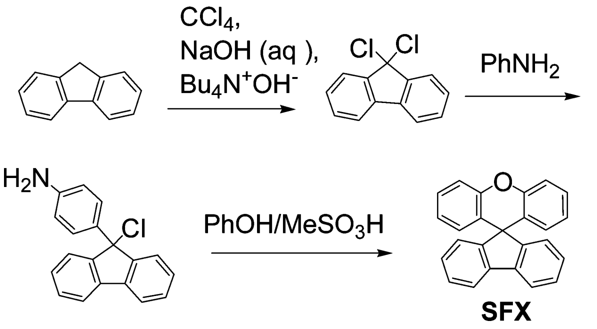


ments.[5] Spiro compounds also possess other interesting properties, including high solubility, high fluorescent quantum efficiency, nondispersive hole-transporting ability, and ambipolar carrier transporting properties.[6] Although spiro compounds are becoming an important class of building blocks in materials and supramolecular science, much effort has been devoted to exploring spirobifluorene derivatives instead of other spiro compounds, e.g. spiro[fluorene-9,9′-xanthene]. This is partially because of the lack of convenient and efficient synthetic routes. Therefore, developing efficient synthetic methodologies of spiro structures is critical to further expanding the scope of applications of spiro compounds.

To date, to the best of our knowledge, there have been few examples for the development of spiro compounds via a one-pot route.[7] A one-pot approach is appealing because of its inherent simplicity. Recently, Shu et al. repeatedly conducted a one-step condensation reaction of 2,7-dibromo-9-fluorenone with resorcinol to form spiro frameworks directly, using $ZnCl_2$/HCl as a condensing reagent.[8] To expand the scope of preparation and facilitate the development of spiro compounds, a one-pot synthetic route utilizing readily available reagents has been developed in our laboratory and is described in the present letter, to produce a series of spiro[fluorene-9,9′-xanthene]s (**SFXs**). To explain this process theoretically, a thermodynamically controlled mechanism has been hypothesized. In addition, an **SFX** building block has been exploited to construct blue-light-emitting materials with high thermal stability.

In the literature, **SFX** has been arduously synthesized by means of two multistep routes with complicated procedures.[9]

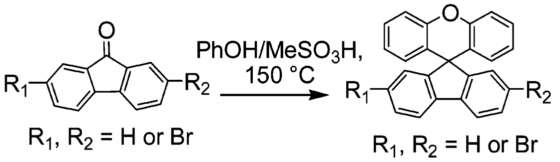
Scheme 2. Additional Synthetic Route to **SFX**[9b]



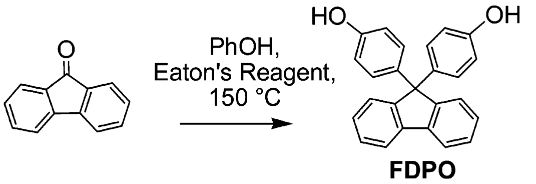
One method starts from two different kinds of *o*-halobiaryls, as shown in Scheme 1. The other involves dichlorofluorene and was patented in 1995, as shown in Scheme 2. However, **SFX** has not previously been prepared with a one-step route as of yet.

Unexpectedly, we discovered a novel one-pot route to synthesize **SFX**, as shown in Scheme 3. Originally, we intended to prepare 4,4′-(9-fluorenylidene)diphenol (**FDPO**) starting from commercially available fluorenone according to the procedure reported in the literature[10] (Scheme 4).

Scheme 3. One-Pot Approach for the Synthesis of **SFX** and Its Derivatives



Scheme 4. Synthesis of 4,4′-(9-Fluorenylidene)diphenol



However, the Eaton's reagent was replaced by the excessive mixture of $MeSO_3H$ and P_2O_5 (3:1), and the reaction time was lengthened to 24 h. An unknown compound was obtained with the molecular mass (M^+) of 322 amu, as determined by GC-MS. TLC demonstrated that its polarity was lower than that of fluorenone. Thus, it was confirmed

---

(5) (a) Vak, D.; Chun, C.; Lee, C. L.; Kim, J.-J.; Kim, D-Y. *J. Mater. Chem.* **2004**, *14*, 1342−1346. (b) Wu, Y.; Li, J.; Fu, Y.; Bo, Z. *Org. Lett.* **2004**, *6*, 3485−3487. (c) Vak, D.; Lim, B.; Lee, S.-H.; Kim, D.-Y. *Org. Lett.* **2005**, *7*, 4229−4232. (d) Tseng, Y.-H.; Shih, P.-I.; Chien, C.-H.; Dixit, A. K.; Shu, C.-F.; Liu, Y.-H.; Lee, G.-H. *Macromolecules* **2005**, *38*, 10055−10060.

(6) 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.

(7) Bischoff, F.; Adkins, H. *J. Am. Chem. Soc.* **1923**, *45*, 1030−1033.

(8) Tseng, Y.-H.; Shih, P.-I.; Chien, C.-H.; Dixit, A. K.; Shu, C.-F.; Liu, Y.-H.; Lee, G.-H. *Macromolecules* **2005**, *38*, 10055−10060.

(9) (a) Clarkson, R. G.; Gomberg, M. *J. Am. Chem. Soc.* **1930**, *52*, 2881−2891. (b) Walters, M. E.; Richey, W. F.; Clement, K. S.; Brewster, S. L.; Tasset, E. L.; Puckett, P. M.; Durvasula, V. R.; Nguyen, H. A. U.S. Patent 789 232, 1995.

(10) (a) Morgan, P. W. *Macromolecules* **1970**, *3*, 536−544. (b) Chou, C.-H.; Shu, C.-F. *Macromolecules* **2002**, *35*, 9673−9677.

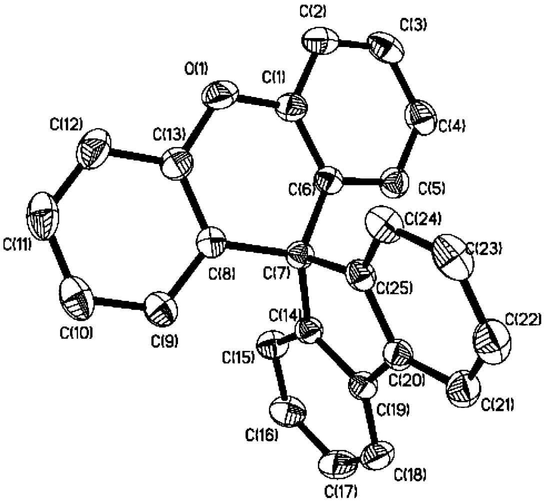


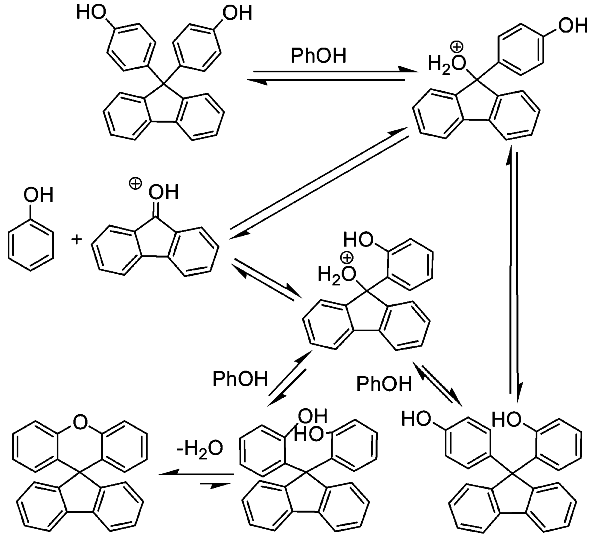
Figure 1. ORTEP drawing of **SFX**. The ellipsoid probability is 30%.

that the unknown compound was not **FDPO**. Finally, its structure was determined to be **SFX** by single-crystal X-ray diffraction,[11] as shown in Figure 1.

To confirm the process, the reaction was replicated several times following the same conditions. To expand the scope of this preparation, we attempted to synthesize dibromo-substituted **SFX** which is a useful building block for the construction of optoelectronic materials, under the same conditions as **SFX**. However, a complicated mixture was obtained that could not be well characterized. Thus, the excess P_2O_5/$MeSO_3H$ mixture was not efficient for the development of dibromo-substituted **SFX**. However, we occasionally attempted to synthesize the monobromo-**SFX** using only $MeSO_3H$ as the catalyst. Surprisingly, the monobromo-**SFX** was obtained with a high yield of 72% and determined by GC-MS, ^1H, and ^{13}C NMR. Thus, excess P_2O_5 was not essential in this one-pot ring-closure reaction. The repeated experiments also confirmed the course, and the dibromo-substituted **SFX** was also successfully prepared with a high yield of 78%.

Scheme 5 describes a plausible reaction pathway of the ring-closure process in the one-pot method. First, an electrophilic attack of protonized fluorenone to the o- or p-position of phenol and the loss of equivalent water give a carbon cation, which then attacks the o- or p-position of another phenol to afford diphenol. Subsequently, intramolecular cyclization through the loss of H_2O produces the **SFX** product in the presence of an acid catalyst if diphenol is the o,o-substituted intermediate. Meanwhile, the equilibrium should be hypothesized between the o,o-substituted intermediates and the o,p-substituted or p,p-substituted intermediates. Because the last ring-closure step is not reversible, the equilibrium moves forward when the ether bond is formed with the loss of H_2O. As the reaction time lengthens, the yield of **SFX** increases. Compared with the reaction time of 6 h with a yield of 40%, a reaction time of 24 h results in higher yields of up to 80% for **SFX**. In the meantime, **FDPO** in a reaction mixture can be separated by silicon gel chromatography if the reaction time is shorter than 6 h. Therefore, **SFX** is a thermodynamic-controlled product and **FDPO** is a kinetic-controlled product. Following the mechanism, we deduce that **FDPO** can be transformed into **SFX** under $MeSO_3H$ conditions, which is similar to the transformation of 3,4-dimethylphenol into 9,9-dimethylxanthenes in the literature.[12] The conclusion is confirmed by the efficient transformation experiment of **FDPO** into **SFX** under $MeSO_3H$/phenol conditions in a high yield of 55%. It should be noted that an important factor for this reaction is the amount of $MeSO_3H$ acid used because the formation of the ether bond needs an excessive acid catalyst, which leads to the movement of the equilibrium. Nevertheless, theoretical elucidation is needed to confirm this hypothesis; however, this is beyond the scope of the present work.

Scheme 5. Plausible Mechanism of the One-Pot Method



Finally, we made use of **SFX** to construct a blue-light-emitting model compound with high morphological stability by means of the Suzuki coupling reaction, as shown in Scheme 6. The reactions of monobromo-**SFX** with 2,7-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolane-2-yl)-9,9-dioctylfluorene under $Pd(PPh_3)_4$/K_2CO_3 catalytic conditions gave 2,7-bis[spiro[fluorene-9,9′-xanthene]-2-yl]-9,9-dioctylfluorene (**BSFXF**) with a yield of 90%.

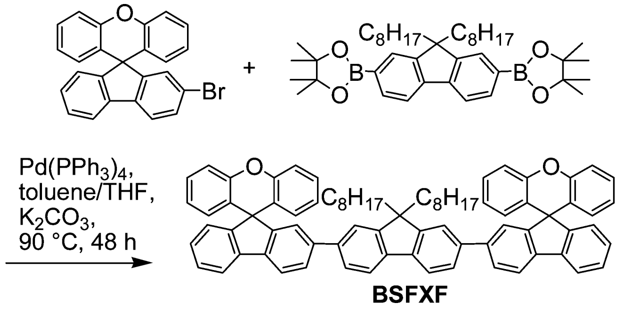
BSFXF is soluble in common organic solvents such as dichloromethane, toluene, and tetrahydrofuran. The absorption spectrum of **BSFXF** in dilute chloroform with an absorption peak at 361 nm is shown in Figure 2. The

---

[11] Crystal data for **SFX**: Crystals were grown from CH_2Cl_2/alcohol. The structure was solved on a Bruker SMART CCD diffractometer using Mo Kα radiation. $C_{25}H_{16}O$ (M_r = 332.38); orthorhombic, space group $P2_12_12_1$, D_c = 1.293 g cm^{-3}, a = 10.699(2), b = 16.752(3), c = 9.5269-(18) Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, V = 1707.5(6) Å^3, $Z = 4$, λ = 0.71073 Å, μ = 0.077 mm^{-1}, T = 293(2) K, R = 0.0338 for 8370 observed reflections [$I > 2\sigma I$] and R_w = 0.0882 for all 3344 unique reflections.

[12] Caruso, A. J.; Lee, J. L. *J. Org. Chem.* **1997**, *62*, 1058−1063.

Scheme 6. Synthesis of a Blue-Light-Emitting Model Compound



emission spectrum exhibits a typical feature of terfluorene with the maximum emission peaks at 398 and 417 nm and a high quantum yield of 87%. PL in the solid state shows a red shift of about 20 nm by comparison with that in solution, which could be attributed to different dielectric environments. The annealing experiments exhibited no red shift and low-energy green emission bands in PL spectra, which reveals that no excimer or keto defect is formed. The thermal properties of **BSFXF** were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under a nitrogen atmosphere at the scan rate of 10 °C/min. **BSFXF** exhibits a high decomposition temperature up to 380 °C (5% weight loss temperature) and a T_g up to 154 °C, which is higher than that of polyfluorene ($T_g = 75$ °C).[13] The above results indicate that **BSFXF** based on the **SFX** building block has high thermal stability and spectral stability similar to that for the materials based on the spirobifluorene building block.[5b]

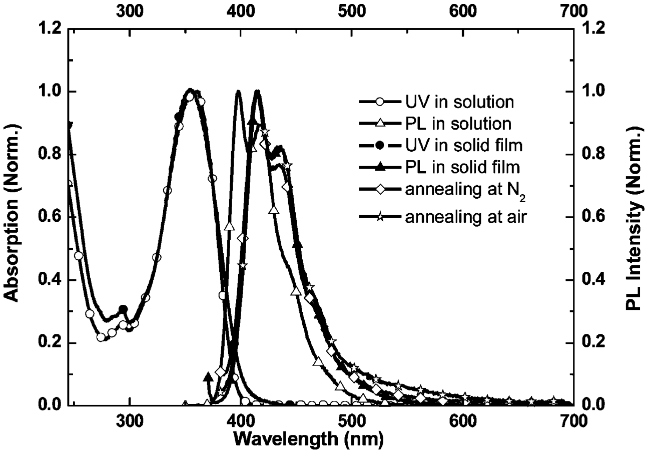


Figure 2. UV−vis and photoluminescence (PL) spectra of **BSFXF** in chloroform (1 μM) and as solid films and annealing PL at 150 °C for 12 h under a nitrogen and air atmosphere.

In conclusion, an efficient and convenient one-pot approach for the preparation of **SFX** has been developed, which is a thermodynamic-controlled process under excessive acid catalyst. Blue-light-emitting materials based on the **SFX** building blocks have been created. The development of a one-pot procedure for the preparation of other xanthene derivatives 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. L.H.X. appreciates technical support from Ms. Zhi-Pei Qin with the University of Waterloo, Canada.

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

OL060871Z

---

[13] Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798.