

An efficient synthesis of novel spiro[[8*H*]indeno[2,1-*b*]-thiophene-8,9'-fluorene] building block for blue light-emitting materials

Ling-Hai Xie,^a Ting Fu,^a Xiao-Ya Hou,^a Chao Tang,^a Yu-Ran Hua,^a Rui-Jie Wang,^a Qu-Li Fan,^a Bo Peng,^a Wei Wei^a and Wei Huang^{a,b,*}

^a*Institute of Advanced Materials (IAM), Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China*

^b*Faculty of Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Republic of Singapore*

Received 17 March 2006; revised 23 June 2006; accepted 26 June 2006

Abstract—We have developed efficient synthetic routes to obtain a novel building block spiro[[8*H*]indeno[2,1-*b*]thiophene-8,9'-fluorene] (SITF), a monothiophene-containing spirobifluorene analogue, and constructed blue light-emitting materials, including 2',7'-bis([1,1'-biphenyl]-4-yl)-spiro[indeno[2,1-*b*]thiophene-8,9'-fluorene] (BBP-SITF) and 2',7'-bis(9,9'-spirobifluorene-2-yl)spiro[[8*H*]indeno[2,1-*b*]thiophene-8,9'-fluorene] (BSBF-SITF). BSBF-SITF has shown to be a stable blue light-emitting material with high PL quantum efficiency (89%) and unique regioselective feature at the C2 of thiophene, which indicate that BSBF-SITF will be useful for constructing complicated optoelectronic systems.

© 2006 Elsevier Ltd. All rights reserved.

Organic π -conjugated materials continue to attract considerable interest because of their potential applications in various optoelectronic devices, especially in organic light-emitting diodes (OLEDs).¹ Since Tour and co-workers early introduced spirobifluorene unit into organic electronics in 1996,² spirobifluorene-containing oligomers and polymers are becoming promising candidates for electroluminescent materials due to their high luminescence efficiency, carrier mobility, as well as excellent thermal stability. Salbeck et al. exploited spirobifluorene building blocks to construct various oligomers.³ Fully spiro-configured terfluorenes, monodisperse spirobifluorene trimmers and spirobifluorene-linked anthracene have also been synthesized and used as blue light-emitting materials with high thermal stability.⁴ Carrier-transporting materials of spirobifluorene with high T_g temperature show excellent nondispersive hole transporting and ambipolar carrier transporting properties.⁵ Our group firstly introduced the spirobifluorene unit into π -conjugated polymers to enhance the

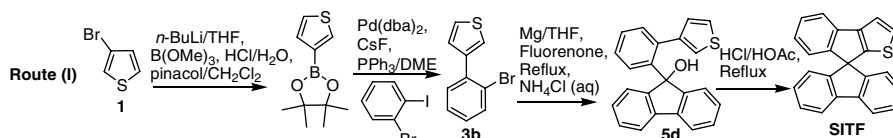
morphological stability in film states and to demonstrate the increase of thermally spectral stability.⁶ In addition, spirobifluorene derivatives have also been applied to solar cells, organic phototransistors, NLO and laser materials.⁷ However, the disadvantage of this kind of oligomers is the difficulty to tune the electronic structure and incorporate other functional groups, which greatly limits their applications in the field of organic electronics and construction of complicated optoelectronic systems.

Incorporating heteroaryl groups, for example, thiophene, pyridine, carbazole, into spiro compounds will be a useful strategy to expand the application of spiro compounds. However, so far, spiro compounds with heteroaryl groups have seldom been reported.⁸ To explore the complicated light-emitting system and gain better insight into the effect of spiro-substituted moieties on the electronic structures, in this contribution, we present the design and synthesis of a novel thiophene-containing ter(9,9'-spirobifluorene)s analogue with regioselective features, and the investigation of absorption and emission spectra as well as electrochemical properties as blue light-emitting materials.

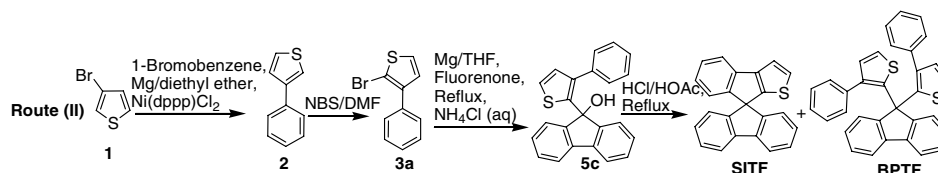
To successfully synthesize spiroindeno[thiophene]fluorene (SITF), it is necessary to concurrently consider three

Keywords: Spiro compounds; Spiroindeno[thiophene]fluorene; Blue light-emitting materials; $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

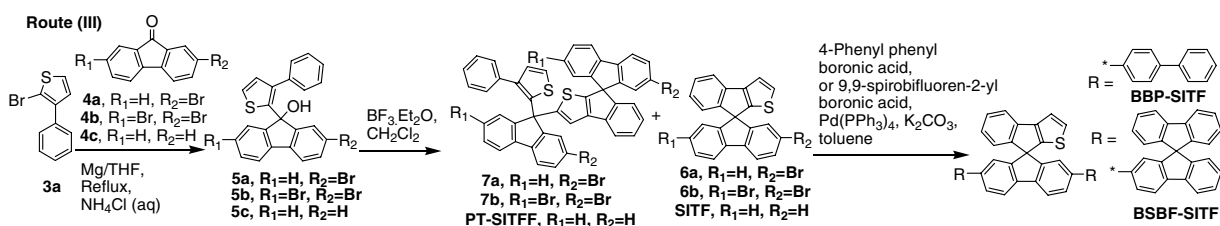
* Corresponding author. Tel.: +86 21 5566 4188/4198; fax: +86 21 6565 5123; e-mail addresses: wei-huang@fudan.edu.cn; chew@nus.edu.sg



Scheme 1.



Scheme 2.



Scheme 3.

important factors, that is, synthesis of *o*-halobiaryls, their reactivity in the preparation of Grignard reagent, and the Friedel–Crafts reactivity in the dehydration cyclization. We have attempted three routes to prepare and obtain the SITF, as summarized in Schemes 1–3. We examined the effect of *o*-halobiaryls, for example, 2-bromo-3-phenylthiophene (**3a**) and 3-(2-bromophenyl)thiophene (**3b**), and conditions of dehydration cyclization, for example, HCl/AcOH and $\text{BF}_3\text{Et}_2\text{O/CH}_2\text{Cl}_2$ on the dehydration cyclization.

First of all, **3b** was selected as *o*-halobiaryls and prepared by Suzuki coupling reaction between thienyl boronate ester and *o*-iodobromobenzene.⁹ Grignard reagent from **3b** was treated with **4c** to obtain tertiary alcohol **5d**, followed by dehydration cyclization with a total yield of nearly 80%. However, Suzuki reaction for **3b** is very expensive. Compound **3a** was selected as *o*-halobiaryls, which was easily prepared by the bromination of 3-phenylthiophene. However, the dehydration cyclization of **5c** was not efficient under the condition of HCl/AcOH and gave SITF in a low yield (35.7%). SITF and byproduct BPTF were separated and confirmed by single crystal X-ray diffraction (Fig. 1).¹⁰ BPTF was probably formed in the electrophilic substitution reaction between 3-phenylthiophene, a decomposition product of **5c** at 110 °C, and **5c**. Fortunately, we found that yield of SITF was effectively improved to 50.2% under $\text{BF}_3\text{Et}_2\text{O}$ condition in dilute CH_2Cl_2 (**5c** in CH_2Cl_2 , 4.8×10^{-3} M) at room temperature.¹¹

The desirable blue light-emitting materials 2',7'-bis([1,1'-biphenyl]-4-yl)-spiro[indeno[2,1-*b*]thiophene-8,9'-fluorene] (BBP-SITF) and 2',7'-bis(9,9'-spiro[fluorene-2-yl]spiro-[[8*H*]indeno[2,1-*b*]thiophene-8,9'-fluorene] (BSBF-SITF) have been prepared by Suzuki coupling reactions.¹² The structures of SITF and its derivatives were confirmed by ^1H NMR, ^{13}C NMR, GC-MS, MALDI-TOF-MS, and elemental analysis.

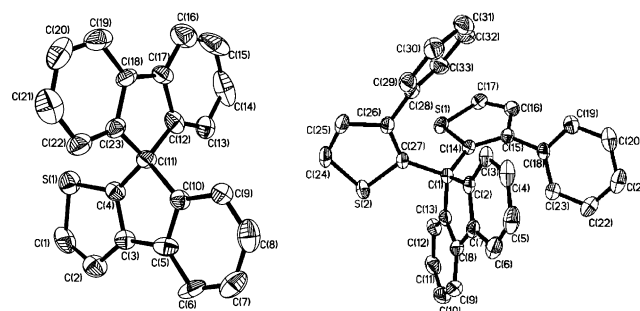


Figure 1. The single-crystal X-ray structures of SITF and BPTF.

The absorption spectra of BBP-SITF and BSBF-SITF (Fig. 2) exhibit maximum peaks at ca. 345 and 353 nm, respectively, which indicates that the conjugated chain length of biphenyl moieties is shorter than that of fluorene moieties. Their emission spectra show typical feature of terfluorene derivatives. The quantum yields of BSBF-SITF in dichloromethane were measured to be 89% by using 9,10-diphenylanthracene as standards (Table 1). These results indicate that the introduction of heteroaryl substituents via the spiro center slightly affects the light emitting character by comparison with other manners, such as copolymerization. In addition, the electroluminescent spectrum has a similar profile compared with the solid film and no shift was

The absorption spectra of BBP-SITF and BSBF-SITF (Fig. 2) exhibit maximum peaks at ca. 345 and 353 nm, respectively, which indicates that the conjugated chain length of biphenyl moieties is shorter than that of fluorene moieties. Their emission spectra show typical feature of terfluorene derivatives. The quantum yields of BSBF-SITF in dichloromethane were measured to be 89% by using 9,10-diphenylanthracene as standards (Table 1). These results indicate that the introduction of heteroaryl substituents via the spiro center slightly affects the light emitting character by comparison with other manners, such as copolymerization. In addition, the electroluminescent spectrum has a similar profile compared with the solid film and no shift was

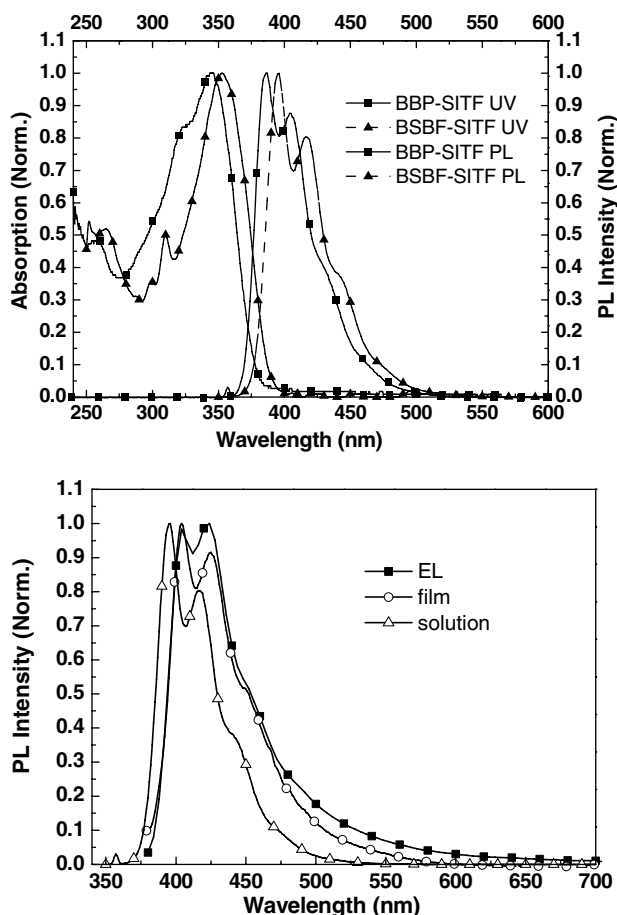


Figure 2. (Top) UV and PL of BBP-SITF and BSBF-SITF in CH_2Cl_2 solution; (bottom) EL and PL of BSBF-SITF in the solid state.

observed, which illustrates that BSBF-SITF is a stable blue light-emitting material. Cyclic voltammetry (CV) was performed to investigate the electrochemical behaviors as well as the HOMO and LUMO energy levels of BBP-SITF and BSBF-SITF (Fig. 3). The oxidation onset potential and reduction onset potential of BBP-SITF were measured to be $E_{\text{onset}}^{\text{ox}} = 0.97$ and $E_{\text{onset}}^{\text{red}} = -2.28$ V. Thus, the HOMO and LUMO energy levels were estimated to be -5.72 and -2.47 eV, respectively. These results indicate that incorporation of heteroaryl groups via the spiro structure slightly affects the electronic structures of main chains.

In conclusion, we have successfully designed and synthesized ter(9,9'-spirobifluorene)s analogue BSBF-SITF

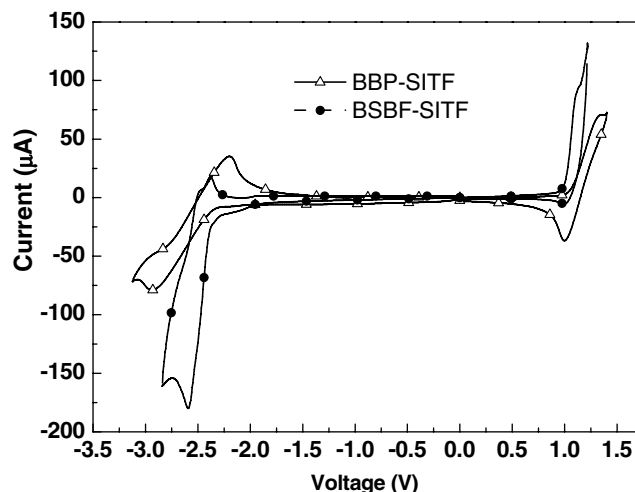


Figure 3. The redox cyclic voltammograms of BBP-SITF and BSBF-SITF on Pt electrodes in $\text{CH}_2\text{Cl}_2/\text{THF}$ supported by $n\text{Bu}_4\text{N}^+\text{PF}_6^-$ (0.1 M) at a scan rate of 0.1 V/s.

with regioselective feature as a blue light-emitting material. BSBF-SITF has shown excellent thermal stability and luminescent properties in the spirobifluorene system, which indicate that BSBF-SITF will be promising for constructing complicated optoelectrical systems.

Acknowledgments

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

References and notes

- (a) Tang, C. W.; Van Slyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913; (b) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
- Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906.
- (a) Salbeck, J.; Yu, N.; Bauer, J.; Weissortel, F.; Bestgen, H. *Synth. Met.* **1997**, *91*, 209; (b) Pudzich, R.; Salbeck, J. *Synth. Met.* **2003**, *138*, 21.
- (a) Katsis, D.; Geng, Y. H.; Ou, J. J.; Culligan, S. W.; Trajkovska, A.; Chen, S. H.; Rothberg, L. J. *Chem. Mater.* **2002**, *14*, 1332; (b) Wong, K.-T.; Chien, Y.-Y.;

Table 1. Physical data of spirans SITF, BBP-SITF, and BSBF-SITF

Compound	$\lambda_{\text{max}}^{\text{a}}$ (nm/abs)	$\lambda_{\text{max}}^{\text{a}}$ (nm/PL)	$Q_{\text{sol}}^{\text{b}}$ (%)	T_{d}^{c} ($^{\circ}\text{C}$)	T_{g} (or T_{m})	$E_{\text{onset}}^{\text{ox}}$	(HOMO/eV) ^d	$E_{\text{onset}}^{\text{red}}$	(LUMO/eV) ^d	Bandgap
SITF	311, 298	333	—	247	188	1.09	-5.84	—	—	—
BBP-SITF	322, 345	387, 404	73%	406	321	0.97	-5.72	-2.28	-2.47	3.25
BSBF-SITF	309, 353	395, 416	89%	429	>350	0.80	-5.66	-2.23	-2.52	3.14

^a— Represents no characteristics.

^a Measured in CH_2Cl_2 solvent.

^b 9,10-Diphenylanthracene in cyclohexane solvent as a standard.

^c The temperature was recorded corresponding to a 5% weight loss.

^d HOMO/LUMO = $-(E_{\text{onset}} - 0.0468 \text{ V}) - 4.8 \text{ eV}$, where the value 0.0468 V is for FOC versus Ag/Ag^+ .

- 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; (c) Kim, Y. H.; Shin, D. C.; Kim, S. H.; Ko, C. H.; Yu, H. S.; Chae, Y. S.; Kwon, S. K. *Adv. Mater.* **2001**, *13*, 1690.
- (a) Bach, U.; De Cloedt, K.; Spreitzer, H.; Grätzel, M. *Adv. Mater.* **2000**, *12*, 1060; (b) Poplavskyy, D.; Nelson, J. *J. Appl. Phys.* **2003**, *93*, 341; (c) 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.
 - (a) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828; (b) Zeng, G.; Yu, W.-L.; Chua, S.-J.; Huang, W. *Macromolecules* **2002**, *35*, 6907.
 - Bach, U.; Lupo, D.; Compte, P.; Moser, J. E.; Weissörtel, F.; Salbeck, J.; Speitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583.
 - (a) Mitschke, U.; Bäuerle, P. *J. Chem. Soc., Perkin Trans. I* **2001**, 740; (b) Wong, K.-T.; Chen, R.-T.; Fang, F.-C.; Wu, C.-C.; Lin, Y.-T. *Org. Lett.* **2005**, *7*, 1979–1982.
 - Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 5616.
 - Data for X-ray structure analysis were collected at room temperature on a Bruker SMART 1K CCD area detector with Mo K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$). Structures were solved by direct methods and refined against F^2 with the full-matrix, least-squares methods using SHELXS-97 and SHELXL-97, respectively. Crystal data for SITF. $C_{23}H_{14}S$, $M = 322.40$, colorless diamond $0.15 \times 0.10 \times 0.04 \text{ mm}$, hexagonal, $P6_5$, $Z = 6$, $a = 19.158(4)$, $b = 19.158(4)$, $c = 8.518(4)$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 2707.6(13) \text{ \AA}^3$, $F(000) = 1008$, $D_c = 1.186 \text{ Mg m}^{-3}$, μ (Mo K_{α}) = 0.178 mm^{-1} . Crystal data for BPTF. $C_{33}H_{22}S_2$, $M = 482.63$, colorless cuboid $0.35 \times 0.30 \times 0.25 \text{ mm}$, monoclinic, $P2_1/c$, $Z = 4$, $a = 13.492(3)$, $b = 12.732(3)$, $c = 15.427(3)$, $\alpha = 90^\circ$, $\beta = 112.29(3)^\circ$, $\gamma = 90^\circ$, $V = 2452.0(8) \text{ \AA}^3$, $F(000) = 1008$, $D_c = 1.307 \text{ Mg m}^{-3}$, μ (Mo K_{α}) = 0.238 mm^{-1} . Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication numbers CCDC 298219 and 298220. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
 - Compound **6a**: 1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, $J = 7.6 \text{ Hz}$, 1H), 7.69 (d, $J = 8 \text{ Hz}$, 1H), 7.60 (d, $J = 7.6 \text{ Hz}$, 1H), 7.51 (d, $J = 8 \text{ Hz}$, 1H), 7.39 (d, $J = 7.6 \text{ Hz}$, 1H), 7.33–7.29 (m, 3H), 7.17 (t, $J = 7.6 \text{ Hz}$, 1H), 7.00 (t, $J = 7.6 \text{ Hz}$, 1H), 6.97 (d, $J = 2 \text{ Hz}$, 1H), 6.83 (d, $J = 8 \text{ Hz}$, 1H), 6.63 (d, $J = 7.6 \text{ Hz}$, 1H). ^{13}C NMR ($CDCl_3$, ppm): δ 152.40, 149.90, 148.70, 148.12, 147.62, 140.67, 140.57, 139.09, 131.48, 130.69, 128.61, 128.50, 128.00, 127.32, 125.96, 124.15, 123.80, 121.78, 121.69, 120.43, 119.68, 118.89, 63.88. Anal. Calcd for $C_{23}H_{13}BrS$: C, 68.83; H, 3.27; Br, 19.91; S, 7.99. Found: C, 68.80; H, 3.22; S, 7.94. GC–MS (EI- m/z): 400/402 (M^+ , 100). Compound **6b**: 1H NMR (400 MHz, $CDCl_3$): δ 6.60 (d, $J = 7.6 \text{ Hz}$, 1H), 6.92 (s, 2H), 7.01 (t, $J = 7.6 \text{ Hz}$, 1H), 7.32 (t, $J = 7.6 \text{ Hz}$, 1H), 7.35 (d, $J = 4.4 \text{ Hz}$, 1H), 7.43 (d, $J = 5.2 \text{ Hz}$, 1H), 7.52 (d, $J = 8 \text{ Hz}$, 2H), 7.59 (d, $J = 7.6 \text{ Hz}$, 1H), 7.64 (d, $J = 8.0 \text{ Hz}$, 2H); ^{13}C NMR ($CDCl_3$, ppm): δ 63.59, 118.98, 119.85, 121.76, 122.24, 123.83, 126.11, 127.38, 128.29, 131.04, 131.71, 139.00, 139.57, 147.71, 148.34, 149.62, 151.61. Anal. Calcd for $C_{23}H_{12}Br_2S$: C, 57.53; H, 2.52; Br, 33.28; S, 6.68. Found: C, 57.49; H, 2.51; S, 6.64. GC–MS (EI- m/z): 478 (M^+), 480, 482. Compound **7a**: 1H NMR (400 MHz, $CDCl_3$): δ 7.73 (m, 1H), 7.62 (d, $J = 8.0 \text{ Hz}$, 1H), 7.58–7.52 (m, 3H), 7.47–7.41 (m, 3H), 7.37–7.21 (m, 6H), 7.21–7.12 (m, 2H), 6.95–6.88 (m, 3H), 6.81–6.77 (m, 4H), 6.55 (d, $J = 7.6 \text{ Hz}$, 1H), 6.29 (d, $J = 8.0 \text{ Hz}$, 2H). Anal. Calcd for $C_{46}H_{26}Br_2S_2$: C, 68.83; H, 3.27; Br, 19.91; S, 7.99. Found: C, 68.75; H, 3.26; S, 7.95. Compound **7b**: 1H NMR (400 MHz, $CDCl_3$): δ 6.32 (d, $J = 8.0 \text{ Hz}$, 2H), 6.55 (d, $J = 5.8 \text{ Hz}$, 1H), 6.84–6.86 (m, 3H), 6.91–6.92 (m, 3H), 6.99 (t, $J = 7.6 \text{ Hz}$, 1H), 7.22–7.26 (m, 3H), 7.30 (t, $J = 7.6 \text{ Hz}$, 1H), 7.36 (d, $J = 7.6 \text{ Hz}$, 2H), 7.46–7.48 (m, 3H), 7.56 (d, $J = 7.2 \text{ Hz}$, 1H), 7.60 (d, $J = 8.0 \text{ Hz}$, 1H), 7.62 (d, $J = 1.6 \text{ Hz}$, 2H). Anal. Calcd for $C_{46}H_{24}Br_4S_2$: C, 57.53; H, 2.52; Br, 33.28; S, 6.68. Found: C, 57.49; H, 2.53; S, 6.64. SITF: 1H NMR (400 MHz, $CDCl_3$): δ 6.61 (d, $J = 7.6 \text{ Hz}$, 1H), 6.82 (d, $J = 7.2 \text{ Hz}$, 2H), 6.96 (t, $J = 8 \text{ Hz}$, 1H), 7.14 (t, $J = 7.6 \text{ Hz}$, 2H), 7.28 (t, $J = 7.6 \text{ Hz}$, 1H), 7.34–7.40 (m, 4H), 7.58 (d, $J = 7.6 \text{ Hz}$, 1H), 7.82 (d, $J = 7.6 \text{ Hz}$, 2H). ^{13}C NMR (400 MHz, ppm): δ 64.10, 118.82, 119.51, 120.37, 123.79, 124.09, 125.82, 127.72, 128.19, 128.30, 130.37, 139.17, 141.68, 147.86, 147.92, 149.70, 153.21. Anal. Calcd for $C_{23}H_{14}S$: C, 85.68; H, 4.38; S, 9.95. Found: C, 85.71; H, 4.32; S, 9.99. GC–MS (EI- m/z): 322 (M^+). BPTF: 1H NMR (400 MHz, $CDCl_3$): δ 6.53 (d, $J = 8.0 \text{ Hz}$, 4H), 6.76 (t, $J = 7.6 \text{ Hz}$, 2H), 6.80 (d, $J = 4.8 \text{ Hz}$, 2H), 6.87–6.94 (m, 6H), 7.02 (t, $J = 8.0 \text{ Hz}$, 2H), 7.11 (t, $J = 8.0 \text{ Hz}$, 2H), 7.13 (d, $J = 5.2 \text{ Hz}$, 2H), 7.47 (d, $J = 7.6 \text{ Hz}$, 2H). ^{13}C NMR ($CDCl_3$, ppm): δ 148.99, 144.12, 139.79, 139.73, 137.93, 132.27, 129.16, 127.87, 127.71, 127.40, 126.61, 126.48, 122.13, 119.65, 59.45. Anal. Calcd for $C_{33}H_{22}S_2$: C, 82.12; H, 4.59; S, 13.29. Found: C, 82.11; H, 4.57; S, 13.26. GC–MS (EI- m/z): 482 (M^+). PT-SITFF: 1H NMR (400 MHz, $CDCl_3$): δ 6.24 (d, $J = 7.6 \text{ Hz}$, 2H), 6.54 (d, $J = 8.0 \text{ Hz}$, 1H), 6.73 (t, $J = 7.6 \text{ Hz}$, 2H), 6.77 (d, $J = 5.6 \text{ Hz}$, 1H), 6.80 (d, $J = 7.6 \text{ Hz}$, 2H), 6.86 (t, $J = 7.6 \text{ Hz}$, 1H), 6.92 (t, $J = 7.2 \text{ Hz}$, 1H), 7.09–7.17 (m, 5H), 7.20–7.25 (m, 3H), 7.32 (t, $J = 6.0 \text{ Hz}$, 2H), 7.40 (d, $J = 7.6 \text{ Hz}$, 2H), 7.46 (d, $J = 1.6 \text{ Hz}$, 1H), 7.48 (d, $J = 7.6 \text{ Hz}$, 1H), 7.52 (d, $J = 7.6 \text{ Hz}$, 2H), 7.76 (d, $J = 7.6 \text{ Hz}$, 2H). Anal. Calcd for $C_{46}H_{28}S_2$: C, 85.68; H, 4.38; S, 9.95. Found: C, 85.66; H, 4.36; S, 9.94. MS (MALDI-TOF): 644.3 (calcd for $C_{46}H_{28}S_2$: 644.2).
 - BBP-SITF: 1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, $J = 8.0 \text{ Hz}$, 2H), 7.70 (d, $J = 8.0 \text{ Hz}$, 2H), 7.63 (d, $J = 7.2 \text{ Hz}$, 1H), 7.59–7.54 (m, 12H), 7.45–7.39 (m, 6H), 7.36 (d, $J = 4.8 \text{ Hz}$, 1H), 7.34–7.29 (m, 2H), 7.09 (s, 2H), 7.00 (t, $J = 7.6 \text{ Hz}$, 1H), 6.74 (d, $J = 7.6 \text{ Hz}$, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.10, 149.51, 148.99, 148.08, 140.86, 140.75, 140.61, 140.31, 139.98, 139.17, 130.53, 129.01, 127.80, 127.65, 127.58, 127.22, 127.54, 127.37, 125.92, 123.99, 122.61, 120.76, 119.58, 118.86, 64.21. Anal. Calcd for $C_{47}H_{30}S$: C, 90.06; H, 4.82; S, 5.12. Found: C, 90.04; H, 4.81; S, 5.10. MS (MALDI-TOF): 626.3. BSBF-SITF: 1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, $J = 7.6 \text{ Hz}$, 4H), 7.80 (d, $J = 7.6 \text{ Hz}$, 2H), 7.76 (d, $J = 8.0 \text{ Hz}$, 2H), 7.66 (d, $J = 8.0 \text{ Hz}$, 2H), 7.58 (d, $J = 7.6 \text{ Hz}$, 1H), 7.39–7.31 (m, 12H), 7.26 (t, 1H), 7.12–7.06 (m, 6H), 6.94–6.88 (m, 5H), 6.74 (t, $J = 6.8 \text{ Hz}$, 4H), 6.68 (d, $J = 7.6 \text{ Hz}$, 2H), 6.59 (d, $J = 7.6 \text{ Hz}$, 1H). ^{13}C NMR ($CDCl_3$, ppm): δ 153.07, 149.51, 149.48, 149.33, 148.89, 148.65, 147.99, 141.41, 141.29, 141.14, 140.99, 140.32, 139.14, 141.99, 130.42, 128.08, 128.01, 127.95, 127.91, 127.68, 127.38, 125.84, 124.39, 124.12, 123.96, 122.81, 122.44, 120.39, 120.28, 120.24, 119.56, 118.87, 66.23, 64.13. Anal. Calcd for $C_{73}H_{42}S$: C, 92.18; H, 4.45; S, 3.37. Found: C, 92.16; H, 4.46; S, 3.35. MS (MALDI-TOF): 950.3.