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Excellent blue fluorescent trispirobifluorenes: synthesis, optical properties and thermal behaviors

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Abstract—Tetraiodotrispirobifluorene (**1**) was synthesized through cyclization of 2,7-diiodofluorene with pentaerythrityl tetrabromide under base condition. Subsequent treatment of **1** with arylboronic acid or arylacetylene under Pd-catalyzed coupling condition led to corresponding tetraaryl trispirobifluorenes (**3**–**8**). These trispirobifluorene derivatives exhibited bright-violet to blue photoluminescence (PL) with excellent quantum efficiencies and showed high thermal stabilities. 'Green-emission tail' could not be detected for those tetraaryl substituted trispirobifluorenes (**3**–**8**) annealed both in N_2 and in air.

Spirobifluorene derivatives have attracted much attention due to their potential utilities in organic light emitting devices (OLEDs),[1] organic photovoltaic cells,[2] optically pumped solid-state lasers,[3] organic phototransistors,[4] nonlinear optics,[5] photochromic materials,[6] and as asymmetric catalysts.[7] Spiro-linked molecules compared with the corresponding nonspiro-linked parent compounds exhibit greater morphological stability and more intense fluorescence.[8] Furthermore, steric factors can lead to an enhanced rigidity in the spiro center, thereby preventing rotation of the adjacent aryl groups, which reduce close packing and intermolecular interaction between chromophores in the solid-state.[9] Thus, the resulted stacking mode of the spiro-linked molecules can efficiently suppress the appearance of 'green-emission tail' which is detrimental to OLEDs.[10] However, general synthesis of the spirobifluorene derivatives is onerous.[11] 9,9′-Spiro-bifluorene core could be prepared in two steps. Nucleophilic addition of 2-biphenylmagnesium bromide to 9-fluorenone generated a tertiary alcohol, which could be subsequently dehydrated in a mixture of hydrochloride and acetic acid and led to 9,9′-spirobifluorene. However, isolation of the brominated 9,9′-spirobifluorenes was challengeable.[12] Although Shu and Chen reported the improved synthetic method for pure 2,2′-dibromo-9,9′-spirobifluorene in four steps, the overall yield was 28%.[13] Therefore, it is necessary to design new types of spirofluorenes and to find facile and efficient synthetic methods.

Ephritikhine's group had ever reported the synthesis of trispirobifluorene **2** from fluorenyl potassium salt, but this family of compounds and their optical properties had rarely been investigated by far.[14] In this Letter, we present a facile route to trispirobifluorene derivatives and their electrochemical, optical properties and thermal behaviors are investigated.

Tetraiodotrispirobifluorene (**1**) was synthesized by cyclization of 2,7-diiodofluorene with pentaerythrityl tetrabromide in THF under base condition in 55% yield and the detailed procedure is described in Supplementary data. In similar way, **2** was synthesized in 56% yield. Arylboronic acids and arylacetylenes purchased from Acros were used without further purification except that 9,9′-diheptylfluoren-2-ylacetylene[15] and 4-(3,6-di-*tert*-butylcarbazol-9-yl)-phenyl boronic acid[16] were synthesized as reference methods. Subsequently, Pd-catalyzed coupling reactions, such as Suzuki reaction or Sonogashira reaction, were employed to prepare trispirobifluorenes in moderate yields (70–90%) (see Scheme 1).

Figures 1 and 2 show the UV–vis absorption and emission spectra of **2**–**8** in cyclohexane with a concentration of 1×10^{-6} M, respectively. A summary of their optical, electrochemical, and thermal properties is listed in Table 1. In cyclohexane solutions, all seven

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Keywords: Trispirobifluorenes; Blue photoluminescence; Optical stability; Thermal stability.

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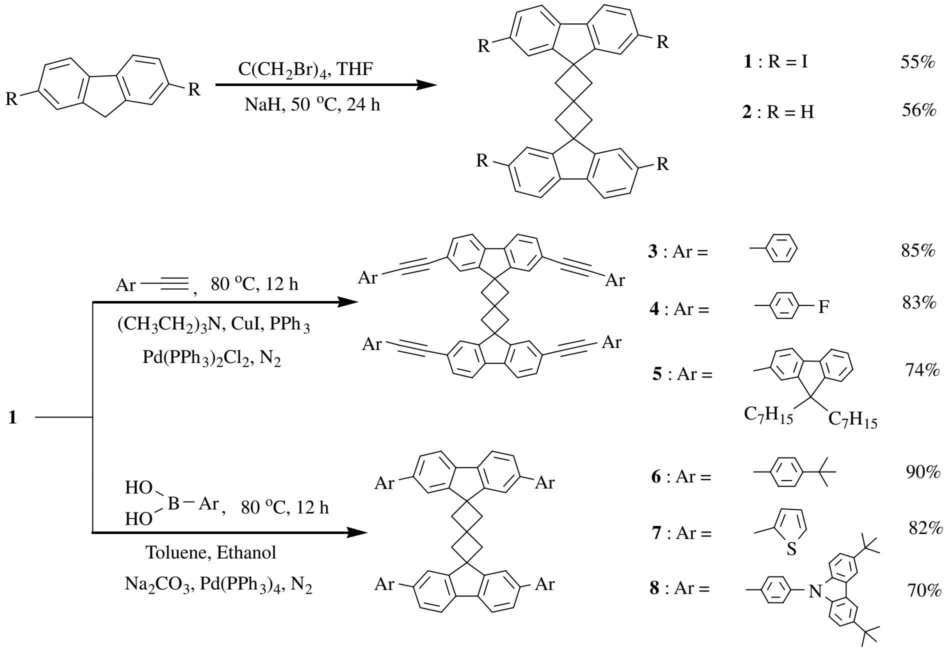

Scheme 1. Synthesis of compounds **1**–**8**.

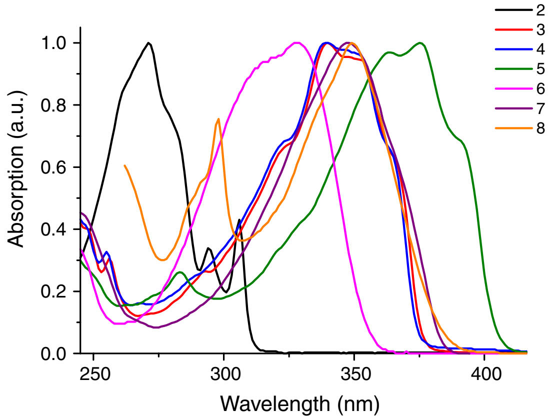

Figure 1. Normalized UV–vis spectra of **2**–**8** in cyclohexane (1×10^{-6} M).

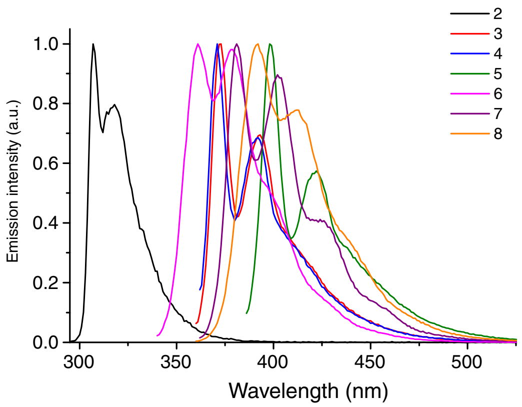

Figure 2. Normalized fluorescence spectra of **2**–**8** in cyclohexane (1×10^{-6} M).

compounds exhibited strong absorptions with their maximum absorption wavelengths in a range of 271–375 nm. The maximum absorption wavelength of bare compound **2** was found to be 271 nm. Compared with **2**, the maximum absorption wavelengths of substituted compounds **3**–**8** were all red-shifted (56–104 nm) as the effective conjugation length increased. Compound **6** exhibited shorter maximum absorption wavelength (327 nm) than that of **3** (340 nm) because of its twisted biphenyl unit, which reduced the efficiency of conjugation.[17] Compound **5** showed the longest absorption wavelength (375 nm) with the most efficient conjugation length and indicated the smallest HOMO–LUMO transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

The maximum emission wavelengths of **2**–**8** are in a range of 308–399 nm with high PL quantum efficiencies of 81–100% (**3**–**8**) in cyclohexane solutions referring to 9,10-diphenylanthracene standard. Emission spectra in powders were all red-shifted (16–66 nm) resembling those emissions in cyclohexane solutions as expected. But a surprising emission band (537 nm) was observed for **7** in the powder (Table 1 or Fig. S1). It could be explained by the stacking mode that thiophene-substituted spirofluorene could form an effective π-stacking in crystal alignment.[17] This was also the reason why there were significant bathochromic shifts of **7** in its absorption and emission compared with those of **6** although they had similar efficient conjugation length.

HOMO energy levels were determined using cyclic voltammetry, while LUMO energy levels were calculated based on the HOMO energy levels and the lowest-energy absorption edges of the UV–vis absorption spectra,[18] respectively. The oxidative onset potentials

Table 1. Optical, electrochemical and thermal properties of compounds (**2**–**8**)

	E_g[a] (eV)	E_{onset}^{ox}[b] (V)	HOMO/LUMO[c] (eV)	ΔE[d] (eV)	HOMO/LUMO[d] (eV)	T_d[e] (°C)	Solution[f]			Powder
							λ_{max}(A) (nm)	λ_{max} (FL) (nm)	Φ_{PL}[g]	λ_{max}(FL) (nm)
2	3.99	1.69	−6.09/−2.10	8.48	−8.86/−0.39	277	271, 294, 306	308, 318	0.23	324, 343, 360
3	3.28	1.36	−5.76/−2.48	7.39	−8.32/−0.94	459	340, 353	373, 393	0.99	439
4	3.30	1.41	−5.81/−2.51	7.33	−8.46/−1.13	310	339, 352	371, 391	0.85	403
5	3.05	1.27	−5.67/−2.62	7.18	−8.17/−1.00	394	362, 375	399, 423	1.00	451
6	3.45	1.34	−5.74/−2.29	7.72	−8.29/−0.57	353	316, 327	361, 378	0.81	392
7	3.22	1.19	−5.59/−2.37	7.42	−8.25/−0.83	322	348	382, 403	0.90	417, 437, 537
8	3.20	1.03	−5.43/−2.23	7.17	−7.99/−0.82	429	297, 349	390, 410	1.00	413, 424

[a] Determined from UV–vis absorption spectra.

[b] E_{onset}^{ox}: onset oxidation potential; potentials versus Ag/AgCl, working electrode Pt, 0.1 M Bu_4NPF_6–CH_2Cl_2, scan rate 100 mV/s.

[c] HOMO = E_{onset}^{ox} + 4.4;[18] LUMO = HOMO − E_g.

[d] ΔE and HOMO/LUMO were calculated by semiempirical AM1 method.

[e] T_d was defined as the temperature at which a 5% weight loss is recorded by the TGA analysis.

[f] Determined in cyclohexanes.

[g] Quantum yields (Φ_{PL}) in cyclohexane were determined using 9,10-diphenylanthracene as the standard (Φ_{PL} = 0.95 in cyclohexane); **2** was determined using p-terphenyl as the standard (Φ_{PL} = 0.93 in cyclohexane).

of these compounds were determined in a range of 1.03–1.69 V; correspondingly, their HOMO and LUMO levels were at ca. 5.43–6.09 and 2.10–2.62 eV, respectively. Among **3**, **4**, and **5**, the highest oxidative onset potential (1.41 V) and lowest HOMO energy (5.81 eV) of **4** could be explained by fluorine atom with electron-withdrawing nature.[19] On the other hand, among **6**, **7**, and **8**, the lowest oxidative onset potential (1.03 V) and highest HOMO energy (5.43 eV) of **8** could be ascribed to carbazole group with electron-donating nature. It could be concluded that inductive effect of substituents would efficiently adjust their electron-donating abilities and thereafter influence the oxidative potentials. Theoretical calculation was in good accordance with the experimental observation, which is listed in Table 1. Relative wide energy gaps ($E_g \geqslant 3.05$ eV) indicated that **2**–**8** could be used as efficient bright-violet to blue fluorescence emitters. Compared with **2**, tetraaryl substituted trispirofluorenes **3**–**8** had smaller optical energy gaps.

Optical stabilities of **3**–**8** were explored by annealing powder samples both in N_2 and in air at 150 °C for 10 h, respectively. After annealing, samples were dissolved in cyclohexane and fluorescence spectra were re-measured. No new emission bands were detected for the annealed compounds (**3**–**8**) both in N_2 and in air. 'Green-emission tail', which was assigned to the fluorenone defect and was the key issue in material application, was not detected even for **5**, which consisted of six fluorene units. Figure 3 shows the emission spectra of **5** annealed both in N_2 and in air, respectively. In a word, tetrasubstituted trispirobifluorene could efficiently suppress the appearance of 'green-emission tail' and might be used as optical materials.

Thermal stabilities of **2**–**8** were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) as these behaviors played a critical role on stability and lifetime of devices. TGA charts of **2**–**8** were shown in Figure 4. A heating rate of 10 °C/min was used to melt and decompose the compounds. DSC analysis of **2**–**8** gave no melting peaks except **6**. Compounds **2**–**8** exhibited high thermal stabilities with relative high decomposition temperatures (T_d) being recorded at 277–459 °C, and no weight losses were observed at lower temperature. Compound **3** presented the highest decomposition temperature (T_d = 459 °C)

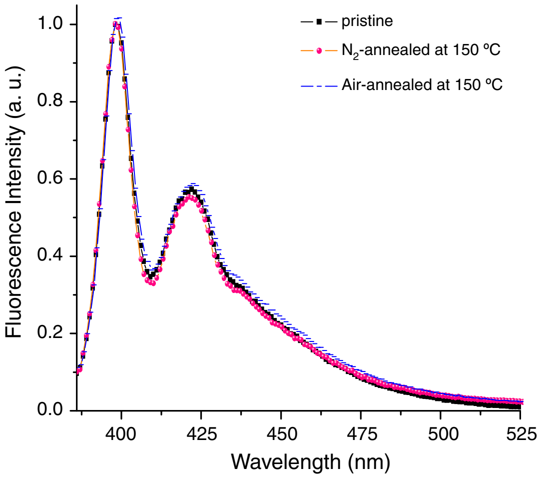

Figure 3. Photoluminescence spectra of **5** (in cyclohexane) (1×10^{-6} M), pristine (square line), annealed in N_2 (sphere line) and in air (bar line).

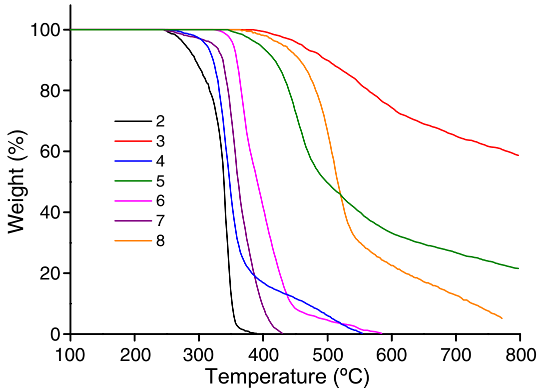

Figure 4. TGA thermograms of **2**–**8** under nitrogen at a heating rate of 10 °C/min.

and only 40% weight loss was detected when the sample was heated to 800 °C. The thermal stability of trispirofluorene is comparable to those linker-free fluorene derivatives. Taking **3** as an example, 2′,7′-diphenylethynyl-spiro(cyclopropane-1,9′-fluorene),[10] which had identical substituents with **3**, the decomposition temperature was detected to be 302 °C.

In conclusion, we have described a facile and efficient route to highly fluorescent trispirobifluorenes (**1**–**8**). Compounds **2**–**8** exhibited bright violet to blue emission with excellent quantum efficiencies in cyclohexane solutions. Compounds **3**–**8** showed relative optical stabilities and high thermal stabilities. These properties implied that these compounds might be used as optoelectronic materials in the future. Further studies on them as materials in OLEDs are in progress.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.10.137.

References and notes

1. (a) Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature* **2003**, *421*, 829; (b) 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; (c) He, G.; Pfeiffer, M.; Leo, K.; Hofmann, M.; Birnstock, J.; Pudzich, R.; Salbeck, J. *Appl. Phys. Lett.* **2004**, *85*, 3911; (d) Chuen, C. H.; Tao, Y. T.; Wu, F. I.; Shu, C. F. *Appl. Phys. Lett.* **2004**, *85*, 4609; (e) Suh, M. C.; Chin, B. D.; Kim, M.-H.; Kang, T. M.; Lee, S. T. *Adv. Mater.* **2003**, *15*, 1254; (f) 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; (g) Steuber, F.; Staudigel, J.; Stössel, M.; Simmerer, J.; Winnacker, A.; Spreitzer, H.; Weissörtel, F.; Salbeck, J. *Adv. Mater.* **2000**, *12*, 130.
2. (a) Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissörtel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583; (b) Schmidt-Mende, L.; Bach, U.; Humphry-Baker, R.; Horiuchi, T.; Miura, H.; Ito, S.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2005**, *17*, 813; (c) Schmidt-Mende, L.; Zakeeruddin, S. M.; Grätzel, M. *Appl. Phys. Lett.* **2005**, *86*, 013504.
3. (a) Johansson, N.; Salbeck, J.; Bauer, J.; Weissörtel, F.; Bröms, P.; Andersson, A.; Salaneck, W. R. *Adv. Mater.* **1998**, *10*, 1136; (b) Schneider, D.; Rabe, T.; Riedl, T.; Dobbertin, T.; Kröger, M.; Becker, E.; Johannes, H.-H.; Kowalsky, W.; Weimann, T.; Wang, J.; Hinze, P.; Gerhard, A.; Stossel, P.; Vestweber, H. *Adv. Mater.* **2005**, *17*, 31.
4. Saragi, T. P. I.; Pudzich, R.; Fuhrmann, T.; Salbeck, J. *Appl. Phys. Lett.* **2004**, *84*, 2334.
5. (a) Kim, S. Y.; Lee, M.; Boo, B. H. *J. Chem. Phys.* **1998**, *109*, 2593; (b) Fu, W.; Feng, J.-K.; Pan, G.-B. *J. Mol. Struct. (Theochem)* **2001**, *545*, 157.
6. (a) Tian, H.; Chen, B.; Liu, P.-H. *Chem. Lett.* **2001**, 990; (b) Chun, C.; Kim, M.-J.; Vak, D.; Kim, D. Y. *J. Mater. Chem.* **2003**, *13*, 2904.
7. (a) Cheng, X.; Zhang, Q.; Xie, J.-H.; Wang, L.-X.; Zhou, Q.-L. *Angew. Chem., Int. Ed.* **2005**, *44*, 1118; (b) Ferrand, Y.; Poriel, C.; Maux, P. L.; Rault-Berthelot, J.; Simonneaux, G. *Tetrahedron: Asymmetry* **2005**, *16*, 1463.
8. Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828.
9. Salbeck, J.; Weissortel, F.; Bauer, J. *Macromol. Symp.* **1997**, *125*, 121.
10. Wang, Z.-X.; Shao, H.-X.; Ye, J.-C.; Zhang, L.; Lu, P. *Adv. Funct. Mater.* **2007**, *17*, 253.
11. Wu, R.; Schumn, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906.
12. (a) Pei, J.; Ni, J.; Zhou, X.-H.; Cao, X.-Y.; Lai, Y.-H. *J. Org. Chem.* **2002**, *67*, 4924; (b) Wu, F.-I.; Dodda, R.; Reddy, D. S.; Shu, C.-F. *J. Mater. Chem.* **2002**, *12*, 2893.
13. Chiang, C.-L.; Shu, C.-F.; Chin, C.-T. *Org. Lett.* **2005**, *7*, 3717.
14. (a) Moll, O. P. Y.; Borgne, T. L.; Thuéry, P.; Ephritikhine, M. *Tetrahedron Lett.* **2001**, *42*, 3855; (b) Fukuda, M.; Genda, K. *Jpn. Kokai Tokkyo Koho* **2004**, 577 pp; (c) Yamada, T.; Kita, H. *Jpn. Kokai Tokkyo Koho* **2004**, 37 pp.
15. (a) Kelley, C. J.; Ghiorghis, A.; Kauffman, J. M. *J. Chem. Res. (S)* **1997**, *12*, 446; (b) Chow, H.-F.; Wan, C.-W.; Low, K.-H.; Yeung, Y.-Y. *J. Org. Chem.* **2001**, *66*, 1910.
16. (a) Gibson, V. C.; Spitzmesser, S. K.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2003**, 2718; (b) Hameurlaine, A.; Dehaen, W. *Tetrahedron Lett.* **2003**, *44*, 957; (c) Park, J. H.; Kim, K.; Hong, Y.-R.; Jin, J.-I.; Sohn, B.-H. *Macromol. Symp.* **2004**, *212*, 51.
17. (a) Tirapattur, S.; Belletête, M.; Drolet, N.; Bouchard, J.; Ranger, M.; Leclere, M.; Durocher, G. *J. Phys. Chem. B* **2002**, *106*, 8959; (b) Destri, S.; Pasini, M.; Botta, C.; Porzio, W.; Bertini, F.; Marchiò, L. *J. Mater. Chem.* **2002**, *12*, 924; (c) Tirapattur, S.; Belletête, M.; Leclere, M.; Durocher, G. *J. Mol. Struct. (Theochem)* **2003**, *625*, 141.
18. Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.
19. Zhang, X.-W.; Gao, J.; Yang, C.-L.; Zhu, L.-N.; Li, Z.-G.; Zhang, K.; Qin, J.-G.; You, H.; Ma, D.-G. *J. Organomet. Chem.* **2006**, *691*, 4312.