Communication

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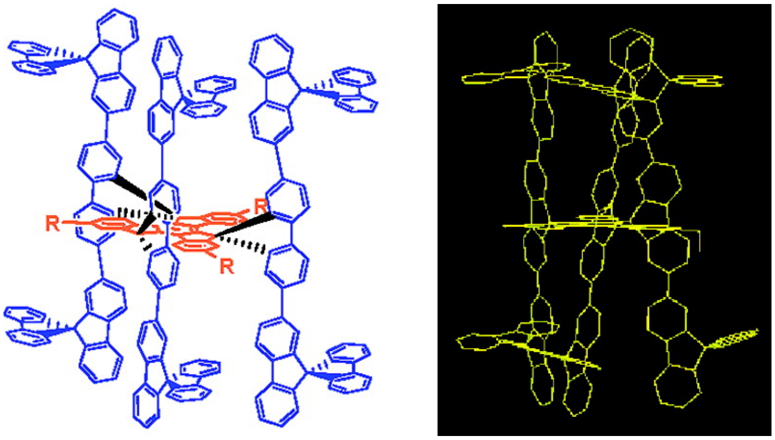

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Three-Dimensional Architectures for Highly Stable Pure Blue Emission

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Blue emission materials have attracted considerable interest due to their particular importance in the development of large-area flat-panel displays such as organic light-emitting diodes (OLEDs).[1] Although a number of small molecules, conjugated oligomers, and polymers have been developed to achieve efficient blue electroluminescence (EL),[2] their color purity and electric stability are main obstacles in fabrication of OLEDs with good performance.[3] In view of the special importance of blue emission materials, we wish to explore new small molecular blue emitters in which threefold 9,9′-spirobifluorene units are bound together to form three-dimensional architecture to achieve pure blue color.

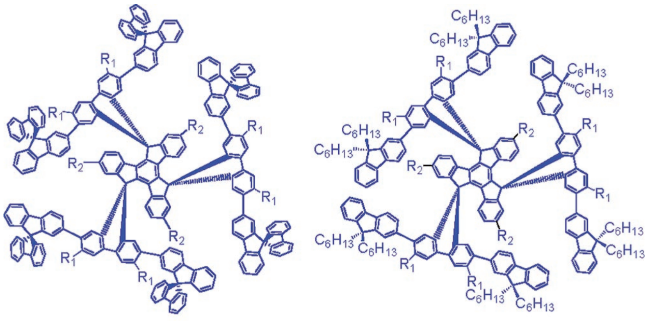
In this contribution, we report the development of a new family of highly stable small molecular blue emitters with spiro-annulated structural features. Spiro compounds as organic molecular materials have become promising candidates for optoelectronic devices.[4] For example, 9,9′-spirobifluorene derivatives exhibited high T_g, good thermal stability, and no long-wavelength emission in comparison with oligo- and polyfluorene derivatives (PFs).[4b−h] Trispirocyclic compounds with the spirotruxene skeleton exhibit good hole-transporting ability and desired thermal stability.[5] Also, these rigid three-dimensional (3D) spirotruxene-type materials can form excellent amorphous states to prevent the formation of the long-wavelength emission induced by excimers (aggregates) or ketone defects. Their photophysical, electrochemical, and electroluminescent properties are comparable with those of 9,9′-spirobifluorenes as well as PFs.

Scheme 1 illustrates the structures of four 3D molecules **1a**−**d**. Their synthetic route is shown in the Supporting Information. The trispirocyclic skeletons were constructed through the intramolecular Friedel−Crafts reaction of tertiary alcohols catalyzed by BF_3 or CH_3SO_3H. Finally, we obtained the desired molecules **1a**−**d** through the Suzuki coupling between the bromides and 9,9′-spirobifluorenyl-2-boronic ester or 9,9-dihexylfluorenyl-2-boronic acid in good yields. The structural difference between **1a** and **1b** or **1c** and **1d** is that the methoxy substituents of **1b** or **1d** were at the truxene unit, while they were at the 9,9′-spirobifluorene unit for **1a** or **1c**.

1a−**d** exhibited good solubility in common organic solvents such as chloroform, toluene, and THF. Their structures and purity were confirmed by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF MS, and elemental analysis (see the Supporting Information). The differential scanning calorimetry (DSC) measurement revealed no T_g and melting points of **1a**−**d** below their decomposition temperature (T_D) at 400 °C. The pattern of powder X-ray diffraction suggested that **1a** and **1b** formed uniform and amorphous films at room temperature via spin-coating by virtue of their relatively high molecular weights.

Figure 1 shows the absorption and photoluminescent (PL) spectra of **1a**−**d** in thin films. The absorption spectra of **1a**−**c** were structureless with the onset of absorption at about 410 nm (3.02 eV); however, the onset of absorption was about 400 nm for **1d**. The absorption peaked at 362 nm for **1a**, 347 nm for **1b**, 361 nm for **1c**, and 325 nm with a shoulder at 340 nm for **1d**. Similarly, the emission λ_{max} of **1a** (439 nm), **1b** (429 nm), and **1c** (419 nm) showed slight red-shift relative to those in dilute solution. However, the emission λ_{max} of **1d** (416 nm) showed slight blue-shift relative to that in dilute solution. These results revealed that such bulky 3D architectures effectively prevented the intermolecular aggregation both in the ground and in the excited states. Although the photophysical properties were similar, the molar extinction coefficients (ϵ) of **1a** and **1b** were almost 10 times that of ter(9,9′-spirobifluorene).[2b] The emission λ_{max} of **1a** red-shifted about 10 nm in comparison with that of **1b**, while the emission λ_{max} of **1c** red-shifted about 3 nm in comparison with that of **1d**, which was due to the different substituted positions of methoxy groups. Moreover, they did not exhibit long-wavelength emission, with very narrow full widths at half-maximum (fwhm) (about 50 nm).

Scheme 1. The Structures of **1a**-**d**



1a: R_1 = OCH_3, R_2 = H;
1b: R_1 = H, R_2 = OCH_3.

1c: R_1 = OCH_3, R_2 = H;
1d: R_1 = H, R_2 = OCH_3.

To investigate the thermal stability of these materials, the emission spectra of **1a**−**d** in thin films were recorded after heating treatment in air and under ambient light. Their thin films obtained by spin-coating on quartz plates were heated to 200 °C for a certain number of hours while exposed to air. After the films were cooled to room temperature, the emission spectra were measured. The same films were repeatedly used for varied heating times. As shown in Figure 2, such recorded PL exhibited no long-wavelength emission, and their color integrity remained even after annealing for 12 h at 200 °C. The PL quantum yields of these four compounds in thin film were measured to be about 35% for **1a**, 39% for **1b**, 54% for **1c**, and 67% for **1d** upon annealing. It was observed that their PL quantum efficiencies after thermal annealing were even slightly improved in comparison with those in their pristine films. Apparently, the emission spectra of these blue emitters were more thermally stable than those of alkyl-substituted polyfluorenes due to their rigid spiro architectures.[2g]

The HOMO and LUMO energy levels in thin films were estimated by cyclic voltammetry (CV) to be −5.50/−2.48 eV for

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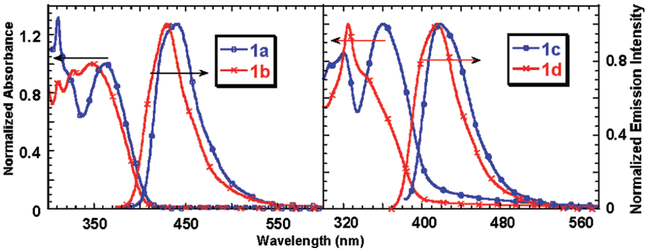

Figure 1. The absorption and PL spectra of **1a**−**d** in thin films.

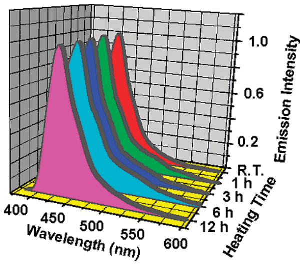

Figure 2. Thermal aging on PL spectra of **1b** in air and under ambient light.

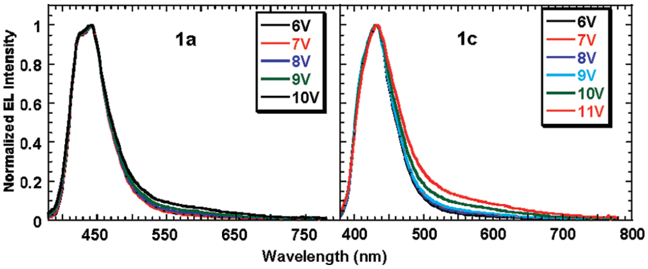

Figure 3. The EL spectra of **1a** and **1c** under different biases.

1a, −5.56/−2.50 eV for **1b**, −5.51/−2.39 eV for **1c**, and −5.63/−2.47 eV for **1d** (vs Ag/AgCl). Correspondingly, the band gaps were 3.02 eV for **1a**, 3.06 eV for **1b**, 3.12 eV for **1c**, and 3.16 eV for **1d**, which are similar to the value measured from their absorption spectra in the film. Among four molecules, **1d** showed the largest band gap, which was in agreement with the measurement of its photophysical properties. To investigate the EL properties of these new molecules, OLEDs using **1a**−**d** as the blue light emission layer were first fabricated in an ITO/PEDOT/PVK/**1**/TPBI/Ba/Al configuration. The thickness of the emission layer was about 70 nm. All devices exhibited good performance with the emission maximum at about 430 nm. Figure 3 shows the EL spectra of **1a** and **1c** under different biases. The EL λ_{max} of four molecules slightly red-shifted in comparison with their corresponding PL λ_{max}. The maximum external quantum efficiency of these devices was determined to be above 2.9% for **1a**, 2.4% for **1b**, 2.0% for **1c**, and 1.4% for **1d**. The data of device performance were summarized in Table 1. All devices emitted pure blue light with standard CIE coordinates for **1a** (0.16, 0.09), **1b** (0.17, 0.10), **1c** (0.17, 0.08), and **1d** (0.17, 0.08). The fwhm of their EL spectra was relatively narrow (about 60 nm). Moreover, different applied biases hardly affected their EL spectra in a range from 6 to 11 V.

In summary, four three-dimensionally architectured molecules **1a**−**d** with spiro-annulated structural features were designed and facilely developed. The PL spectra of spirotruxene molecules **1a**−**d** exhibit excellent thermal stability upon air annealing. Preliminary OLED fabrication reveals that **1a**−**d** exhibit both pure blue EL performance and good color integrity at different operating voltages. All results demonstrate that such spirotruxene molecules can be used as a novel class of pure blue emitters. It also provides us a platform to develop large energy band gap emitting molecules based on such spiro-annulated skeleton.

Table 1. The Device Performance of **1a**−**d**

compound	EL λ_{max} fwhm (nm)	V_{on}[a] (V)	EQE $_{max}$[b] (%)	brightness[c] (cd m^{-2}/V)	CIE 1931 x, y[d]
1a	442, 58	5.8	2.9	480/7.8	0.16, 0.09
1b	432, 67	5.0	2.4	997/6.7	0.17, 0.10
1c	432, 59	5.3	2.0	774/8.4	0.17, 0.08
1d	424, 63	3.9	1.4	1717/7.4	0.17, 0.08

[a] Turn-on voltage (at which EL is visible to the eyes). [b] EQE_{max} = the maximum external quantum efficiency. [c] The output luminescence at this voltage. [d] Color coordinates according to the 1931 CIE convention.

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Supporting Information Available: Detailed experimental procedures and characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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