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Ter(9,9-diarylfluorene)s: Highly Efficient Blue Emitter with Promising Electrochemical and Thermal Stability

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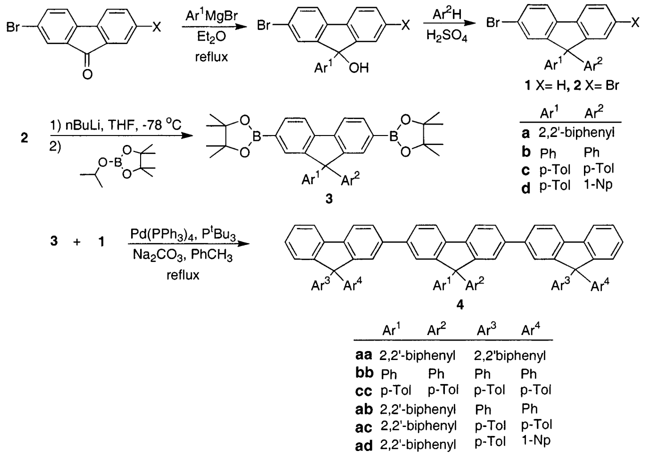
Advances made in the molecular design of modern optoelectronic materials have made significant contributions toward the development of organic electronics. The organic light-emitting devices (OLED) employing monodisperse[1] or polymeric conjugated materials[2] possess the most promising prospects. However, materials suitable for long-term use as blue light emitters are still far from optimization in terms of stability. Terfluorenes,[3] fully spiro-configured terfluorene,[4] oligomeric fluorenes,[3a,5] and polyfluorenes[6] are generally regarded as the most promising candidates for blue OLEDs. However, the long-wavelength emission due to the photo- or electrooxidized cleavage of C9-substituted alkyl pendant group(s),[7] results in poor color purity and has inhibited their prospective utilization. In this communication, we report a convergent synthesis, the single-crystal structure, and intriguing properties of novel ter(9,9-diarylfluorene)s. These ter(9,9-diarylfluorene)s which contain intrinsically stronger Csp^3-Csp^2 bonds between the pendant aryl groups and the C9 carbon of fluorene exhibit excellent morphological and thermal stability. Together with the high quantum yields in thin films, these terfluorenes are promising for applications in OLEDs as efficient blue emitters.

The desired 9,9-diaryl substituted 2-bromofluorene **1a**−**d** and 2,7-dibromofluorene **2a**−**d** were synthesized in good yields (75−92%) by aryl Grignard addition onto the corresponding 2-bromofluorenone and 2,7-dibromofluorenone respectively,[8] followed by a sulfuric acid-promoted Friedel−Crafts reaction (Scheme 1). The transformation of the dibromide **2** into the corresponding dipinacolato boronic esters **3** was achieved in modest yields (54−70%) by lithiating **2** with an excess amount of *n*-BuLi at −78 °C and by successively treating the dilithiated complex with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane. Finally, Pd-catalyzed Suzuki coupling reactions of diboronic esters **3** and **1** were accomplished by adding a catalytic amount of bulky tri-*tert*-butylposphine as a promoter to afford the target ter(9,9-diaryfluorene)s in good yields (Table 1).

Due to the rigidity of the peripheral aryl substituents, colorless single crystals of **4aa** suitable for X-ray analysis were obtained by carefully layering the THF solution of **4aa** with hexane. Inspection of the molecular structure (Figure 1a) indicates the two outside fluorene moieties of the conjugated chromophore backbone are highly twisted relative to the central one by 134.6° and −128.3° respectively, rendering the conjugated chromophore a helical conformation as viewed along the molecular axis (Figure 1b). This conformation effectively releases the steric interaction between the fluorene moieties and prevents inter-chromophore interactions.

Scheme 1. Synthetic Pathways of Ter(9,9-diaryfluorene)s



All ter(9,9-diarylfluorene)s in this study are highly fluorescent with an emission maximum centered at ca. 394 nm along with vibronic features at ca. 413 and ca. 441 nm (Table 1, also see Supporting Information). The photoluminescent (PL) features reveal typical characteristics of conjugated fluorene derivatives.[3,4] The quantum yields of terfluorenes **4** in ethyl acetate were measured to be close to 100% by using Coumarin 1 and 9,10-diphenylanthracene as standards. More importantly, the vacuum-deposited thin films of terfluorenes **4** exhibit excellent quantum yields (Table 1), which were determined by using a calibrated integrating sphere system. These results indicate that the C9 aryl substituents play a less relevant role in the absorption and emission maxima but have a pronounced effect on the solid-state PL efficiencies. The introduction of aryl substituents is significantly beneficial in improving the morphological stability and the resistance to thermal decomposition. Except for crystalline **4aa**, terfluorenes **4** exhibit distinct glass transition temperatures (T_g) ranging from 189 to 231 °C. The highly crystalline feature of ter(spirobifluorene) **4aa** can be attributed to the rigidity of its peripheral 2,2′-biphenyl substituents. Thus, combining the rigid-relaxed fluorene moieties **1b** and **1c** with **3a** generates terfluorene **4ab** and **4ac** with distinct T_g's, respectively. It is noteworthy that the C9 carbon of **1d** is a chiral center. Therefore, combining **1d** with **3a** affords **4ad** as a diastereomeric mixture**,** which exhibited a high T_g up to 231 °C. More importantly, no further phase transition was observed upon heating **4ad** over its T_g to 350 °C. *This result represents a new approach for the molecular design of amorphous materials by introducing chiral centers in close proximity of the conjugated chromophore backbone.* By TGA analysis, these terfluorenes were found to be thermally

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Table 1. Isolated Yields and Physical Properties of Ter(9,9-diarylfluorene)s **4**

cmpd	yield (%)	λ_{max} (nm), log ϵ	PL λ_{max} (nm)	$Q_{solution}$ (%)	Q_{film} (%)	T_g (°C)	TGA (°C)	oxid. E^1, E^2 (V)	red. E^1, E^2 (V)
4aa	83	353, 4.54	393, 412, 441	99	90	no	450	1.32, 1.56	−2.01, −2.21
4bb	81	355, 4.70	395, 413, 441	99	78	189	400	1.36, 1.60	−1.97, −2.15
4cc	75	354, 4.98	393, 414, 441	99	90	204	410	1.32, 1.57	−2.02, −2.18
4ab	68	353, 4.73	393, 412, 438	99	82	201	425	1.31, 1.56	−2.11, −2.23
4ac	63	353, 4.77	394, 414, 440	99	87	210	435	1.31, 1.56	−2.10, −2.22
4ad	86	356, 4.83	395, 415, 441	99	66	231	430	1.30, 1.55	−2.03, −2.17

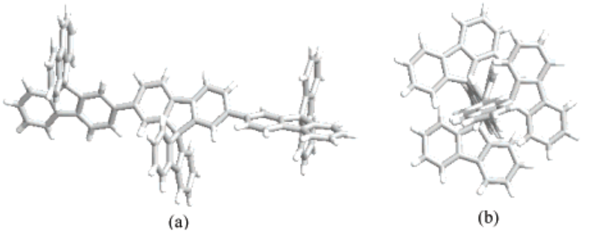

Figure 1. (a) Molecular view of X-ray structure of **4aa**. (b) Top view from the molecular axis.

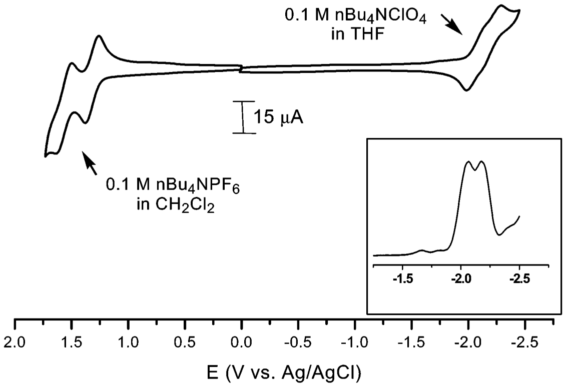

Figure 2. Cyclic voltammogram of terfluorene **4aa**. (Inset) Differential pulse voltammetry (DPV) of reduction region.

stable with temperatures corresponding to a 5% weight loss upon heating (20 °C/min) under nitrogen ranging from 400 to 450 °C.

Cyclic voltammetry experiments were conducted on terfluorenes **4** at room temperature to probe their electrochemical properties. Two discrete reversible oxidation potentials were observed in CH_2Cl_2 (0.1 M nBu$_4$NPF$_6$ as a supporting electrolyte), and two reversible reduction potentials were detected in THF (0.1 M nBu$_4$NClO$_4$ as a supporting electrolyte). A representative example of the cyclic voltammogram of **4aa** is depicted in Figure 2. Those of the two reductions are relatively poorly resolved compared to that of the oxidations. However, differential pulse voltammetry (DPV) clearly showed the appearance of two distinguishable reductions. Terfluorenes **4aa**, **4ab**, and **4ac**, which have the same structural features of the central subunit, that is, spirobifluorene, exhibited very similar redox behaviors. The pronounced potential differences in their oxidation regions (240−250 mV) and reduction regions (120−200 mV) indicate that the monocationic and anionic species can efficiently delocalize the charge over the entire conjugated chromophore.

The terfluorene derivatives with highest thin-film PL quantum yields have been subject to electroluminescent (EL) studies. The device structure used is ITO/PEDT:PSS (300 Å)/terfluorene **4aa** or **4cc** (500 Å)/TPBI (370 Å)/LiF (5 Å)/Al, where the conducting polymer polyethylene dioxythiophene:polystyrene sulfonate (PEDT:PSS) was used as the hole-injection layer, 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI) as the electron-transport layer, and 5 Å LiF as the electron-injection layer. These devices exhibit pure blue EL similar to PL spectra of terfluorenes (see Supporting Information), indicating emission purely from terfluorenes. The rather low turn-on voltage of ~3 V, defined as the voltage where EL emission becomes detectable, and low operation voltage (100 cd/m^2 at ~6 V, 1000 cd/m^2 at ~8 V) of these devices suggest these terfluorenes also function well as hole transporters. High EL external quantum efficiency of 2.5−3% photon/electron and high brightness over 5000 cd/m^2, were observed for these devices, consistent with the high thin-film PL quantum yields. High PL/EL quantum efficiencies in conjunction with carrier transport properties render these terfluorenes a very interesting and promising class of optoelectronic materials.

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Supporting Information Available: Complete experimental details, X-ray data of **4aa** (CIF), a comparison of UV−vis and PL spectra of **4aa** and **4cc**, and OLED devices characteristics (*I*−*V*, brightness-V, EL/PL) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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