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Quinolyl functionalized spiro[fluorene-9,9′-xanthene] host materials with bipolar characteristics for green and red phosphorescent organic light-emitting diodes

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ABSTRACT

Spiro[fluorene-9,9′-xanthene] (SFX) bipolar hosts bearing one, two and three quinolyl substituents, namely SFX-bPy, SFX-DbPy and SFX-TbPy, were designed and synthesized for phosphorescent organic light emitting diodes (PhOLEDs). The successive substitution of quinoline at 2′, 2 and 7′ positions of SFX results in reduced LUMO energy levels while leaving the HOMO energy levels nearly intact. The impact of quinoline substitution in these SFX-based hosts on PhOLED performance was investigated in detail through green and red model devices. For the green emitting devices, the device based on SFX-bPy host showed better performance (23.6 cd A^{-1}, 23.4 lm W^{-1}, 6.3%) due to high triplet energy level (T_1) and balanced carriers-transporting ability. In contrast, for the red PhOLED devices, the device hosted by SFX-DbPy displayed higher performance (15.8 cd A^{-1}, 16.0 lm W^{-1}, 9.1%), attributable to the well matched T_1 and separated frontier molecular orbitals. This work thus sheds light on the rational design of SFX-based bipolar hosts for more efficient PhOLEDs.

1. Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) have attracted immense interests since they can, in theory, approach a 100% internal quantum efficiency by harvesting both singlet and triplet excitons simultaneously and show great potential in flat-panel display and solid-state lighting [1–3]. To avoid the self-aggregation quenching and triplet-triplet annihilation (TTA) in solid state, phosphorescent emitters are usually doped into an appropriate host as the emitting layer (EML) [4,5]. An ideal host material for PhOLEDs is expected to meet the following intrinsic requirements: i) a triplet energy level (T_1) higher than that of the phosphorescent dopant to maintain effective exothermic energy transfer from host to guest; ii) good carriers injecting/transporting properties to balance the charge flux and reduce the driving voltage; iii) thermal and morphological stability to obtain the long lifetime and stable CIE (Commission Internationale de I'Eclairage) chromaticity coordinates of corresponding devices. Large conjugated length is generally undesirable for host material to achieve high T_1, therefore small footprint molecules with considerable carriers injecting/transporting ability and high T_1, such as carbazole [6], triphenylamine [7], fluorene [8–10], are utilized as the chromophores to construct hosts. Furthermore, a host with bipolar feature is highly desired to achieve high and balanced charge transporting ability, which is helpful to simplify the device structure and reduce the cost of PhOLEDs, such as single-layer device [11]. One straightforward strategy to achieve bipolar transport in organic molecules is to incorporate both electron-donating and electron-withdrawing groups, the so-called donor-acceptor (D-A) structure, into a single molecule [12,13]. Another way to construct

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bipolar hosts is to use a building block that possesses the characteristics of dual channel for transporting both electron and hole, such as spiro aromatics. Chart 1 lists some representative spiro molecules that are employed as host materials for PhOLEDs [14–20]. Among these, spirobifluorene (SBF) is a classical spiro building unit for organic electronics with three-dimensional orthogonal configuration and two independent π-systems interrupted by intramolecular sp^3 carbon atom at the 9-position of fluorene, which can confer good thermal and morphological stability, as well as binary channels injecting/transporting ability for carriers. Hence, SBF is a versatile structural unit to build high performance host materials for PhOLEDs [21–26]. Nevertheless, the synthetic procedure of SBF is complicated, and the electronic properties of SBF is relative monotonous because of the same fluorene unit at the flanks of sp^3 carbon atom.

Compared with SBF, spiro[fluorene-9,9′-xanthene] (SFX) has the following features: i) it can be synthesized by a facile “one-pot” route, thus is very cost-effective; ii) it contains orthogonally arranged fluorene and xanthene moieties, which incurs independent electronic properties with separated frontier molecular orbitals (FMOs) and bipolar characteristics; iii) there are multiple positions on the aromatic units for functionalization [27,28]. Therefore, SFX has emerged as versatile molecular backbone for use in the field of organic electronics [29–32]. In the area of OLEDs, SFX-based materials have been employed as deep-blue and green fluorescent emitter [33–36], as universal hosts for phosphorescent and thermally activated delayed fluorescence (TADF) OLEDs [37–43], as ligands for Pt^{II} and Eu^{III}-based emitter [44,45], and as the hole-transporting materials [46]. In our previous works, a series of SFX-based host materials had been synthesized and investigated for PhOLEDs. Electron-withdrawing groups (e.g. phosphine oxide (PO)) [37–39], electron-donating groups (e.g. methyl/methoxy-arylfluoene) [40] and electroneutral unit (e.g. phenylfluorene) [41] had been introduced into SFX by insulating linkage, and the PhOLEDs devices based on these hosts display low driving voltages and high efficiencies. For instance, the dimeric SFX is an efficient host materials, and the corresponding red, green and blue PhOLEDs devices all possess low turn-on voltages between 2.4 and 3.1 V [42]. Besides, it was found that a compromise is also required between the T_1 and HOMO/LUMO levels of the hosts for enhancing the carriers injecting/transporting ability and the device performance [37]. We have discovered that fine tuning frontier molecular orbital energy levels without affecting the high T_1 could be realized by introducing insulating linker-bridged arylfluorene on SFX [40]. All of the research results indicate that the SFX is a promising building block to construct bipolar hosts for PhOLEDs.

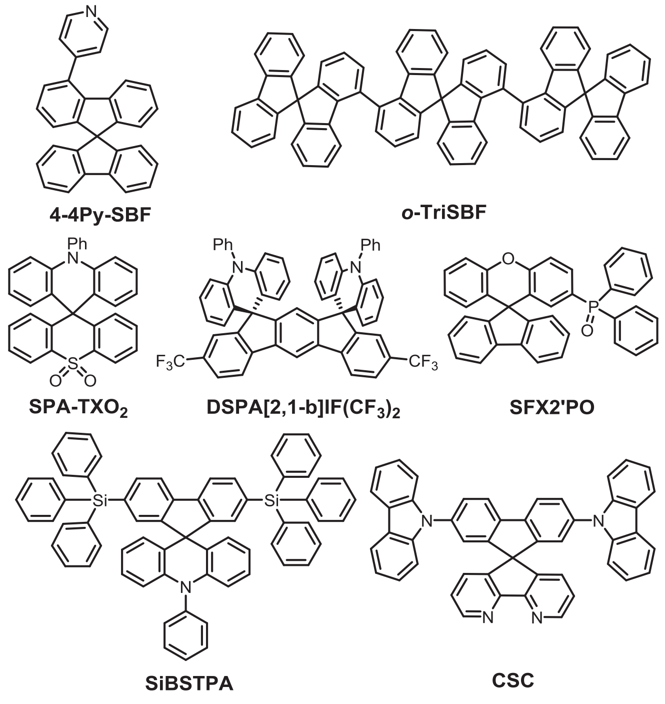

Chart 1. Some examples of spiro compounds as host materials for PhOLEDs.

In this contribution, a series of quinolyl-substituted SFX hosts (Scheme 1) were designed and synthesized. Quinoline unit was utilized considering the wide use of its analogues in organic optoelectronic devices because of the high electron transporting ability and thermal stability [47–49]. In order to improve/balance carrier injection/transport, quinoline was also introduced as electron transporting (ET) unit into SFX via conjugated linkage. The influence of substitution position and number of quinolyl groups on the electrochemical and optophysical properties of SFX was explored in detail. The relationship between the structure and performance of these hosts for PhOLEDs was evaluated by testing the green and red model devices.

2. Experimental section

2.1. Synthesis of 2-(spiro[fluorene-9,9′-xanthen]-2′-yl)quinoline (SFX-bPy)

SFX was synthesized according to our previously published method [27]. Under N_2 protection, $AlCl_3$ (3.0 g 22.5 mmol), and SFX (3.32 g, 10 mmol) were mixed in 50 mL anhydrous CH_2Cl_2. CH_3COCl (0.71 mL, 10 mmol) was dissolved in 30 mL anhydrous CH_2Cl_2 and added dropwise into the above mixture, stirred for 30 min, and then reacted over a period of 2 h at room temperature. The resulting mixture was washed with 12% HCl and extracted with CH_2Cl_2. The combined organic layers were then subjected to silica-gel column chromatography to afford 2.23 g white powder **1** in 61% yield. Following the similar procedure, compounds **2** and **3** can be obtained by changing the ratio of reactants.

Under N_2 protection, **1** (1.12 g, 3.0 mmol), *o*-aminobenzaldehyde (0.40 g, 3.3 mmol) and saturated aqueous solution of K_2CO_3 (5 mL) were mixed in 25 mL ethanol, and the mixture was reacted at 90 °C for 24 h. The resulting mixture was washed by water and extracted with CH_2Cl_2. The combined organic layers were subjected to silica-gel column chromatography to afford 0.61 g white solid in 44% yield. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.13 (dd, $J = 8.6$, 1H), 8.0 (m, 2H), 7.84 (d, $J = 7.63$, 2H), 7.71 (d, $J = 8.04$, 1H), 7.64 (t, $J = 6.98$, 1H), 7.41 (m, 5H), 7.28 (s, 1H), 7.22 (m, 5H), 7.08 (s, $J = 2.16$, 1H), 6.80 (s, $J = 8.12$, 1H), 6.44 (s, $J = 7.81$, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.48, 154.86, 152.58, 151.24, 148.06, 139.73, 136.43, 135.01, 129.54, 128.48, 128.16, 127.94, 127.29, 127.15, 126.83, 125.99, 125.78, 125.10, 123.53, 120.06, 118.68, 117.51, 116.82, 77.33, 77.01, 76.69, 54.41. IR (KBr): $v = 3064$, 2372, 2314, 1596, 1568, 1478, 1455, 1427, 1281, 1241, 1123, 1095 cm^{-1}. GC-MS (EI) m/z 459 $[M]^+$. Anal.calcd for $C_{34}H_{21}NO$: C, 88.86; H, 4.61; N, 3.05; found: C, 88.83; H, 4.65; N, 3.02.

2.2. Synthesis of 2,2′-(spiro[fluorene-9,9′-xanthene]-2,2′-diyl) diquinoline (SFX-DbPy)

The procedures were similar to SFX-DbPy. **2** (1.3 g, 3.1 mmol) and *o*-aminobenzaldehyde (0.79 g, 6.5 mmol) were used, and the product was obtained as a white solid (0.74 g, 40% yield). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.37 (d, $J = 7.99$, 1H), 8.16 (m, 1H), 8.11 (m, 2H), 7.99 (m, 4H), 7.90 (d, $J = 7.62$, 1H), 7.76 (d, $J = 8.64$, 2H), 7.68