



Dumbbell effects of solution-processed pyrene-based organic semiconductors on electronic structure, morphology and electroluminescence

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ABSTRACT

The number of bulky groups in hindrance-capped π -systems is closely relative to thin film morphology, stability and luminescent features in printing electronics. Herein, we demonstrated advantages of dumbbell-shape over mono-substituted organic semiconductors by designing two highly bulky 3',6'-bis(octyloxy) spiro[fluorene-9,9'-xanthene] (OSFX)-functionalized pyrene derivatives, OSFXPy and DOSFXPy. Their differences in terms of thermal, photophysical and electrochemical properties, and film morphologies were characterized via thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-vis absorption and photoluminescence (PL), cyclic voltammetry and atomic force microscopy (AFM). DOSFXPy has higher thermal and electrochemical stability, more suitable energy levels and smaller bandgap than that of OSFXPy. Thin film of DOSFXPy is smooth and pin-hole free, while OSFXPy is easy to crystallize and form large crystal domains. Solution-processed non-doped electroluminescent devices based on DOSFXPy exhibit stable deep-blue emission with excellent $CIE_{x,y}$ color coordinates ($x=0.15, y=0.13$) at the luminance of 1000 cd/m^2 , and the maximum luminance of up to 3200 cd/m^2 and maximum current efficiency of 2.07 cd/A , respectively. Moreover, solution-processed doped OLEDs with DPAVBi show greenish-blue emission with optimum current efficiency of 4.52 cd/A at doping concentration of 3 wt%.

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1. Introduction

Organic light-emitting devices (OLEDs), since first reported in 1987 [1], have been developed rapidly and achieved by mass production, and some products can be commercially available, such as mobile phones, TVs [2]. For OLEDs, full-color displays need three-color emission (red, green, blue) with high efficiency, color purity and long operation lifetime. Comparison with the other two

color emissions, blue light emission is still not satisfying with color purity and device efficiency because blue emitters require a wide bandgap, which results in insufficient and imbalanced carrier injection and transport. Therefore, many efforts have been taken to develop high-performance blue emitters throughout the world. Meanwhile, solution processing is more promising and intriguing technology than vacuum deposition for time saving, low energy-consumption, flexibility, and large-area fabrication. Recently, Yang et al. reported high performance solution-processed deep-blue OLEDs based on starburst oligofluorenes with impressive maximum current efficiency of 6.99 cd/A [3]. However, the efficiency of solution-processed deep-blue OLEDs is still inferior to that of vacuum-deposited OLEDs and high performance solution-processed deep-blue OLEDs are rarely reported until now [3–8].

During the exploitation of efficient blue emitters, many highly efficient chromophore cores are being developed, such as fluorene

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[9–11], anthracene [12–14], di(styryl) arylene [15,16], pyrene [17,18]. Among them, pyrene fluorophore is widely used in OLED active layers due to its easy chemical modification, thermal stability, and high quantum efficiency and carrier mobility [18]. However, due to largely π -conjugated planarity, pyrene tends to aggregate in dense solution and solid state easily, and lead to light-emission quenching and long-wave emission. Using bulky groups to functionalize organic semiconductors is one effective solution to solve this issue by changing π - π stacking and molecular packing behaviors. Up to date, various bulky hindrances were linked to pyrene with different substitution numbers [18–32]. Our group reported tetra-substituted pyrene derivatives served as blue emitter of solution-processed OLEDs with a medium device performance [4,22,27]. Sonar group reported solution-processed OLED based on tetra-butylxyl substituted pyrene (Py-PhOC4) shows high luminance of 5015 cd/m² and impressive current efficiency (CE) of 2.56 cd/A [23]. An excited result reported by Chan et al. with a record CE of 10.5 cd/A based on solution-processable 3D calixarene-functionalized mono-substituted pyrene derivative [25]. However, the device exhibited the greenish blue electroluminescent (EL) spectra with Commission Internationale de L'Eclairage (CIE) coordinates of $x=0.15$ and $y=0.24$. Although considerable efforts have achieved, it is necessary to carefully examine the effects of the types, sizes, and number of bulky hindrance groups on various photophysics, electrochemical and morphological properties as well as various device parameters toward the commercialization requirement of organic printable materials and devices.

According to our previous reports, bulky spiro[fluorene-9,9'-xanthene] (SFX) is an eco-friendly building block to improve thermal and morphological stability, EL spectra and efficiency [32–40]. Dumbbell-shaped SFX-functionalized pyrene, 1,6-di(spiro[fluorene-9,9'-xanthene]-2-yl) pyrene (DSFXPy), can effectively suppress intermolecular π - π stacking. Deep-blue nondoped OLEDs based on DSFXPy gave high CE and external quantum efficiency (EQE) of 7.4 cd/A and 4.6%, respectively [32]. In this context, we examine the dumbbell effects on various parameters by comparison of mono- and di-substituted pyrene derivatives in the area of printable OLED display technology. Mono- and di-substituted pyrene derivatives, 1,6-bis(3',6'-bis(octyloxy)-spiro[fluorene-9,9'-xanthene]-2-yl) pyrene (DOSFXPy) and 3',6'-bis(octyloxy)-2-(pyren-1-yl) spiro[fluorene-9,9'-xanthene] (OSFXPy) were designed and synthesized. Four long octylxoyl chains are introduced to parent compound DSFXPy to improve solubility and morphology, so DOSFXPy is suitable for solution processing. The bulk and rigidity of OSFX moieties in DOSFXPy can ensure thermal and morphological stability and color purity. As a result, DOSFXPy shows higher solubility and glass transition temperature (T_g), and better film morphology than that of OSFXPy. Solution-processed nondoped OLEDs based on DOSFXPy show impressive EL performance with stable deep-blue emission and high CE of 2.07 cd/A, and excellent CIE coordinates of $x=0.15$ and $y=0.13$ at luminance of 1000 cd/m². EL performance can further improve through doping DPAVBi into DOSFXPy.

2. Experimental section

2.1. Chemicals

All of chemicals were purchased from J&K Scientific Co., Ltd., and were used without further purification unless otherwise state. THF was distilled from Na/benzophenone and dichloromethane was distilled from P₂O₅. The synthetic approaches of 2-bromospiro[fluorene-9,9'-xanthene]-3',6'-diol and 2-bromo-3',6'-bis(octyloxy) spiro[fluorene-9,9'-xanthene] were according to the reported literature with mild modification [33,41].

2.2. Synthesis

2.2.1. 2-(3',6'-Bis(octyloxy) spiro[fluorene-9,9'-xanthene]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Under N₂ atmosphere, a mixture of 2-bromo-3',6'-bis(octyloxy) spiro[fluorene-9,9'-xanthene] (2.0 g, 3.0 mmol), bis(pinacolato) diboron (1.52 g, 6 mmol), Pd(OAc)₂ (0.030 g, 0.15 mmol), dppf (0.166 g, 0.3 mmol), KOAc (0.71 g, 7.2 mmol) and DMSO (30 ml) was stirred and heated at 90 °C for 12 h. The mixture was poured into water and abstracted with dichloromethane, and then the combined abstracts was washed with water and dried by anhydrous MgSO₄. The solvent was evaporated under vacuum condition. The crude product was purified by silica gel column chromatography to afford white solid (2.03 g) with 95% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, $J=7.6$ Hz, 1H), 7.78 (d, $J=7.6$ Hz, 2H), 7.55 (s, 1H), 7.33(t, $J=7.6$ Hz, 1H), 7.19 (t, $J=7.4$ Hz, 1H), 7.10 (d, $J=7.6$ Hz, 1H), 6.70 (d, $J=2.4$ Hz, 2H), 6.34 (dd, $J=8.8, 2.4$ Hz, 2H), 6.24 (t, $J=8.8$ Hz, 2H), 3.92 (t, $J=6.6$ Hz, 4H), 1.79–1.72 (m, 4H), 1.46–1.39 (m, 4H), 1.32–1.26 (m, 16H), 0.88 (t, $J=6.8$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 158.86, 156.80, 154.77, 151.96, 142.87, 138.93, 134.53, 131.95, 129.02, 128.85, 127.50, 125.63, 120.19, 119.10, 116.22, 111.01, 101.57, 83.73, 68.11, 53.26, 31.82, 29.34, 29.24, 29.22, 26.06, 25.03, 22.66, 14.10.

2.2.2. 3',6'-Bis(octyloxy)-2-(pyren-1-yl) spiro[fluorene-9,9'-xanthene] (OSFXPy)

Under N₂ atmosphere, a mixture of 2-(3',6'-bis(octyloxy) spiro[fluorene-9,9'-xanthene]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.81 g, 2.5 mmol), 1-bromopyrene (0.56 g, 2.0 mmol), Pd(OAc)₂ (0.023 g, 0.1 mmol), dppf (0.111 g, 0.2 mmol), 2 M K₂CO₃ solution (2.5 ml) and toluene/THF (40 ml, 1:1 v/v) was stirred and heated at 90 °C for 18 h. The mixture was abstracted with dichloromethane, and then the combined abstracts were dried by anhydrous MgSO₄. The solvent was evaporated under vacuum condition. The crude product was purified by silica gel column chromatography to afford white solid (1.27 g, yield: 81%). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, $J=7.6$ Hz, 1H), 8.13 (t, $J=7.6$ Hz, 2H), 8.07–8.05 (m, 3H), 7.99 (d, $J=7.6$ Hz, 1H), 7.95 (d, $J=7.6$ Hz, 1H), 7.92 (d, $J=9.2$ Hz, 1H), 7.90 (d, $J=7.6$ Hz, 1H), 7.87 (d, $J=7.6$ Hz, 1H), 7.65 (dd, $J=7.6, 1.2$ Hz, 1H), 7.43 (s, 1H), 7.42 (t, $J=7.6$ Hz, 1H), 7.28–7.25 (m, 2H), 6.70 (d, $J=2.4$ Hz, 2H), 8.16 (d, $J=8.8$ Hz, 2H), 6.44 (dd, $J=8.8, 2.4$ Hz, 2H), 3.92 (t, $J=6.4$ Hz, 4H), 1.79–1.72 (m, 4H), 1.46–1.39 (m, 4H), 1.32–1.26 (m, 16H), 0.88–0.85 (t, $J=6.8$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 159.02, 155.85, 155.82, 152.15, 141.17, 139.31, 128.74, 137.60, 131.46, 130.92, 130.53, 130.28, 128.71, 128.45, 128.37, 127.94, 127.76, 127.61, 127.41, 127.38, 127.35, 125.95, 125.73, 125.19, 125.06, 124.97, 124.87, 124.73, 124.56, 120.00, 119.68, 116.63, 111.13, 101.69, 68.16, 53.64, 31.82, 29.35, 29.24, 29.21, 26.06, 22.66, 14.11.

2.2.3. 1,6-Di(3',6'-bis(octyloxy) spiro[fluorene-9,9'-xanthene]-2-yl)-pyrene (DOSFXPy)

Under N₂ atmosphere, a mixture of 2-(3',6'-bis(octyloxy) spiro[fluorene-9,9'-xanthene]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.53 g, 3.5 mmol), 1,6-dibromopyrene (0.51 g, 1.4 mmol), Pd(OAc)₂ (0.016 g, 0.07 mmol), dppf (0.079 g, 0.14 mmol), 2 M K₂CO₃ solution (3.5 ml) and toluene/THF (40 ml, 1:1 v/v) was stirred and heated at 90 °C for 24 h. The mixture was abstracted with dichloromethane, and then the combined abstracts were dried by anhydrous MgSO₄. The solvent was evaporated under vacuum condition. The crude product was purified by silica gel column chromatography to afford light yellow solid (1.45 g) with 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, $J=8.0$ Hz, 2H), 8.04 (d, $J=9.2$ Hz, 2H), 7.94 (d, $J=8.0$ Hz, 2H), 7.88 (s, 2H), 7.86 (t, $J=4.0$ Hz, 4H), 7.64 (d, $J=8.0$ Hz, 2H), 7.40 (t, $J=7.2$ Hz, 4H), 7.25 (t, $J=7.2$ Hz, 2H), 7.20 (d, $J=7.6$ Hz, 2H), 6.69 (d, $J=2.0$ Hz, 4H), 6.46 (d,

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