Supporting Information

Organic π -Conjugated Trimers as Fluorescent Molecules for Colorful Electroluminescence

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1. Experimentals

Reagents and materials

All reagents were obtained from Sigma-Aldrich or TCI Europe, and the evaporated material came from Xi'an Yuri Solar Co., Ltd. and used without further purification.

Measurements

¹H and ¹³C NMR spectra were recorded at ambient temperature with a 400 MHz Bruker Avance Spectrometer with 5 mm BBFO probe in the appropriate deuterated solvent (in CDCl3 or d6-DMSO with an internal standard of tetramethylsilane). The photoluminescence spectrum of fluorescent small molecules was measured by Agilent Cary Eclise's fluorescence spectrophotometer. Ultraviolet-visible-near-infrared (UV-vis-NIR) absorption spectra were measured on a Shimadzu UV-3600 plus spectrometer. Ultraviolet Photoelectron Spectroscopy (UPS) was performed by PHI 5000 Versa Probe III with He I source (21.22 eV) under an applied negative bias of 9.0 V. Atomic force microscopy (AFM) using a Bruker Multimode 8 in tapping mode was used to observe the surface topography of the trimers. Films were prepared on quartz glass by spin-coating of Fluorescent ultrasmall molecule DMSO solution.

Device fabrication and Measurements

The patterned ITO substrates were washed with acetone three times under sonication, each time for 15 minutes, followed by 15 min of UV-ozone-treatment. After surface treatment, the PEDOT:PSS layer was spin-coated onto the ITO substrate as the hole-injecting layer, followed by annealing at 145°C for 15 min. The emissive layers were prepared by spin-coating onto the PEDOT:PSS followed by annealing at 120°C for 15 min. The electron-transporting layer and the cathode materials were thermally evaporated and deposited onto the emitter layer in a vacuum chamber. The thermally evaporated deposition rates were 0.6-1 Å s⁻¹for the organic layers, 0.1 Å s⁻¹ for Liq and 2.5 Å s⁻¹ for the Al electrode, respectively. The current-voltage-luminance (J-V-L) characteristics and the electroluminescence spectra of the devices were obtained simultaneously by using aintegrating sphere and a Keithley 2400 Source Meter unit under ambient atmosphere at room temperature. In the devices, the emitter layer is a blend of the host matrix Poly(N-vinyl carbazole) (PVK), 2,2'-(1,3-Phenylene)-bis[5-(4-tert-butylphenyl)-1,3,4-oxadiazole] (OXD-7) and the Fluorescent Molecules. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) serves as the hole injection layer, while 1,3,5-Tris(1-phenyl-1H-benzimidazol-2yl)benzene (TPBi) act as the electron-transport layers, respectively. LiF and Al serve as the cathode.

Synthesis of small molecules

Synthesis of B1



Scheme S1. Synthesis of B1.

B1 was synthesized using Suzuki coupling reactions. In brief, 500 mg of 4,7-dibromo-2, 1, 3-benzothiadiazole and 1 g of 9H-Carbazole-2-boronic acid pinacol ester (in a 1:2 ratio) were dissolved in 120 ml of toluene and 160 ml of methanol in a flame-dried round-bottom flask. The solution was degassed with argon for 15 minutes, and then 1.2 g of K_2CO_3 was added in one portion. The resulting mixture was stirred at 40°C for 10 minutes. Subsequently, 56 mg of PEPPSITM-IPr catalyst was added under argon flow, and the flask was sealed. The reaction was stirred at 70°C for 4 hours. The reaction mixture was filtered, washed with toluene and methanol, and the precipitate was dried under vacuum to obtain a light green powder with a yield of 61.7%. The 1H NMR (400 MHz, DMSO-d6) spectrum showed peaks at δ 11.46 (s, 2H), 8.30 (d, 2H), 8.26 (d, 2H), 8.20 (d, 2H), 8.11 (s, 2H), 7.83 (dd, 2H), 7.55 (d, 2H), 7.43 (dt, 2H), 7.22 (dt, 2H). 13C NMR (400 MHz, DMSO-d6) δ 154.25, 140.93, 140.34, 134.66, 133.27, 129.05, 126.38, 122.88, 122.62, 120.91, 120.72, 120.34, 119.24, 112.29, 111.54.



Fig. S1. ¹H NMR spectrum of B1 in DMSO.



id

Fig. S2. ¹³C NMR spectrum of B1 in DMSO.

Synthesis of Q1



Scheme S2. Synthesis of Q1

Q1 was synthesized through the Still cross-coupling reaction. Firstly, 863.8 mg of 5,8-Dibromoquinoxaline and 1.15 mL of 2-(Tributylstannyl) thiophene (two equivalents) were dissolved in 100 mL of tetrahydrofuran (THF) in a flame-dried round-bottom flask. To degas the solution, it was bubbled with argon for 15 minutes. Subsequently, 50 mg of PdCl2(PPh3)2 was added to the reaction mixture in one portion. The mixture was stirred for 3 h at 65°C. The reaction mixture was then poured into dichloromethane and washed with water three times. The organic phase was dried with sodium sulfate and concentrated. The crude was purified on silica gel by flash column chromatography using hexane/dichloromethane 1:1. After solvent removal, an orange powder was obtained with a yield of 62.5%. The 1H NMR (400 MHz, DMSO-d6) of the powder showed δ values of 9.10 (s, 2H), 8.33 (s, 2H), 7.97 (dd, 2H), 7.73 (dd, 2H), and 7.22

(dd, 2H). The ¹³C NMR (400 MHz, DMSO-d6) showed δ values of 144.83, 138.97, 137.87, 131.47, 130.13, 127.94, 127.67, and 127.33.



Fig. S3. ¹H NMR spectrum of Q1 in DMSO-d6.

Fig. S4. ¹³C NMR spectrum of Q1 in DMSO-d6.

Synthesis of B2

Scheme S3. Synthesis of B2.

B2 was synthesized via a Suzuki coupling reaction. Briefly, 4,7-Dibromo-2,1,3benzothiadiazole (600)mg) and 4,4,5,5-tetramethyl-2-(4-methylthiophen-2-yl)-1,3,2dioxaborolane (890 mg) were dissolved in toluene/methanol (120:160 mL) in a flame-dried round-bottom flask. Argon was bubbled for 15 minutes in the solution to deaerate it. Then, K_2CO_3 (1.2 g) was added to the reaction in one portion and the mixture was heated to 40°C and stirred for 10 min. Then PEPPSITM-IPr catalyst (56 mg) were added under argon flow and the flask was sealed. The temperature was increased to 75°C and the mixture was stirred for 4h. The reaction mixture was poured in dichloromethane; thus, it was washed 3 times with water. The organic phase was dried over sodium sulfate and concentrated. The crude product was purified on silica gel by flash column chromatography (hexane/dichloromethane 1:1, v/v). After the removal of the solvent, a fluorescent orange powder was obtained (yield: 82%). 1H NMR (400 MHz, Chloroform-d) & 7.95 (d, 2H), 7.82 (s, 2H) 7.03 (t, 2H), 2.37 (d, 6H). 13C NMR (400 MHz, Chloroform-d) δ 152.64, 139.09, 138.73, 129.91, 126.00, 125.60, 122.22, 15.93.

Fig. S5. ¹H NMR spectrum of B2 in CDCl₃.

Fig. S6. ¹³C NMR spectrum of B2 in CDCl₃.

Synthesis of Q2

Scheme S4. Synthesis of Q2

The synthesis of **Q2** was carried out through Suzuki coupling reactions. Initially, 575.88 mg of 5,8-Dibromoquinoxaline and 1.07 g of EDOT boronic acid pinacol ester (two equivalents) were dissolved in toluene/methanol (120:160 mL) in a round-bottom flask that had been dried by flame. The solution was degassed with argon for 15 minutes. Then, 1.2 g of K_2CO_3 was added to the reaction in one portion. The mixture was heated to 40°C and stirred for 10 minutes. Subsequently, 46 mg of PEPPSITM-IPr catalyst was added under argon flow, and the flask was sealed. The reaction was stirred at 70°C for 4 hours. The reaction mixture was filtered and washed with toluene and methanol, and the resulting precipitate was dried under vacuum. This process yielded a red powder with a 73.3% yield. The 1H NMR spectrum (400 MHz, Chloroform-d) showed signals at δ 8.93 (s, 2H), 8.57 (s, 2H), 6.59 (s, 2H), and 4.39-4.30 (m, 8H), while the 13C NMR spectrum (400 MHz, Chloroform-d) showed signals at δ 142.0, 141.39, 140.33, 139.80, 129.49, 128.75, 112.89, 102.95, 64.96, and 64.36.

Fig. S7. ¹H NMR spectrum of Q2 in CDCl₃.

Fig. S8. ¹³C NMR spectrum of Q2 in CDCl₃.

Fig. S9. Schematic diagram of fluorescent molecule design.

Fig. S10. Thermogravimetric analysis (TGA) of four fluorescent molecules.

Fig. S11. PL spectra in DMSO at room temperature ($\lambda ex = 365$ nm).

Fig. S12. UV-Vis spectra in DMSO at room temperature.

Fig. S13. Transient fluorescence lifetime of four fluorescent molecules.

Fig. S14. UPS spectra of B1 film.

Fig. S15. UPS spectra of Q1 film.

Fig. S16. UPS spectra of B2 film.

Fig. S17. UPS spectra of Q2 film.

Fig. S18. AFM surface and cross-sectional height of B1 films.

Fig. S19. AFM surface and cross-sectional height of Q1 films.

Fig. S20. AFM surface and cross-sectional height of B2 films.

Fig. S21. AFM surface and cross-sectional height of Q2 films.

2. Electroluminescent property

Fig. S22. Electroluminescence spectra at different voltages. (a) B1. (b) Q1. (c) B2. (d) Q2.

Fig. S23. CIE coordinates of the devices.

3. Theoretical calculations

All the theoretical calculations were performed with a Gaussian 09 program.¹ Diradicaloid character

Natural orbital occupation number (NOON) calculations were done by spin unrestricted UCAM-B3LYP/6-31G(d,p) method and the diradical character (y_0) was calculated according to Yamaguchi's scheme: $y_0=1-(2T/(1+T2))$, and $T = (n_{HOMO}-n_{LUMO})/2$ (n_{HOMO} is the occupation number of the HOMO, n_{LUMO} is the occupation number of the LUMO).²⁻⁵ A molecule with $y_0 = 0$ indicates a closed-shell structure, whereas a molecule with $y_0 = 1$ implies a pure diradical structure.

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