Electronic Supplementary Information

Pyrene-based Blue AIEgens: tunable intramolecular conjugation, good hole mobility and reversible mechanochromism

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Experimental section

Characterization

¹H and ¹³C NMR spectra were measured on a Mecuryvx300 spectrometer. Elemental analyses of carbon and hydrogen were measured on a Perkin-Elmer microanalyzer. Mass spectra were measured on a ZAB 3F-HF mass spectrophotometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C/min from room temperature to 250 °C under argon. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C

instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C/min from room temperature to 650 °C. Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer in a three-electrode cell with a Pt counter electrode, a Ag/AgCl reference electrode, and a glassy carbon working electrode at a scan rate of 100 mV s⁻¹ with 0.1 M tetrabutylammonium perchlorate (purchased from Alfa Aesar) as the supporting electrolyte, in anhydrous dichloromethane solution or THF solution purged with nitrogen. The potential values obtained in reference to the Ag/Ag⁺ electrode were converted to values versus the saturated calomel electrode (SCE) by means of an internal ferrocenium/ferrocene (Fc⁺/Fc) standard. Single-crystal X-ray diffraction (SXRD) data of TPE-2*p*Br were collected on a Bruker diffractometer using Cu Ka radiation ($\lambda = 1.54178$ Å). The powder X-ray diffraction patterns were recorded by Rigaku MiniFlex 600 with an X-ray source of Cu Ka ($\lambda = 1.5418$ Å) at 25 °C at 40 KV and 15 mA at a scan rate of 10° (20)/min (scan range: 2 - 50°). IR spectra (500–4000 cm⁻¹) were recorded using a Nicolet 380 FT-IR using pure KBr as the background. Melting points were recorder on SGW X-4B microscopic melting point meter.

Computational details

The geometrical and electronic properties were optimized at B3LYP/6-31g* level using Gaussian 09 program. The molecular orbitals were obtained at the same level of theory.

OLED device fabrication and measurement

The EL devices were fabricated by vacuum deposition of the materials at a base pressure of 5×10^{-6} torr onto glass pre-coated with a layer of indium tin oxide (ITO) with a sheet resistance of 25 Ω /square. Before the deposition of an organic layer, the clear ITO substrates were treated with oxygen plasma for 3 min. The deposition rate of organic compounds was 0.9-1.1 Å s⁻¹. After the

hole-injection layer MoO₃, hole-transporting layer 1,4-bis(1-naphthylphenyl-amino)biphenyl (NPB), emission layer, electron-transporting layer 1,3,5-tris(N-phenyl-benzimidazol-2-yl)benzene (TPBi), and lithium fluoride (LiF) were deposited by the thermal evaporation under a base vacuum of $\sim 10^{-6}$ torr, aluminium (Al) metal was evaporated in another vacuum chamber without breaking the vacuum. The *J*–*V*–*L* of the devices was measured with a Keithley 2400 Source meter and Keithley 2000 Current meter. The EL spectra were measured by JY SPEX CD3000 fluorescence spectrophotometer and PR650 Spectra Scan Photometer. All measurements were carried out at room temperature under ambient conditions.

Preparation of compounds

Solvents for chemical synthesis were purified according to the standard procedures. Py-1BO, Py-2BO, Py-4BO, compound 4 and compound 5 were synthesized according to the literatures.¹ All other chemicals and reagents were obtained from commercial sources and used as received.

TPE-2*p*Br

A solution of *n*-butyl lithium in hexane (2.1 M, 5.7 mL, 12 mmol) was added dropwise to a solution of 4, 4'-di-*tert*-butyldiphenylmethane (1) (4.2 g, 15 mmol) in anhydrous tetrahydrofuran (40 mL) at 0 $^{\circ}$ C under an atmosphere of argon. After stirring for 1 h at this temperature, 4, 4'-dibromobenzophenone (2) (3.4 g, 10 mmol) in THF (50 mL) was added. After 2 h, the mixture was slowly warmed to room temperature. Then, the reaction was quenched with an aqueous solution of ammonium chloride and the mixture was extracted with dichloromethane. The organic layer was evaporated after drying with anhydrous sodium sulfate, and the resultant crude product was dissolved in toluene (100 mL). The *p*-toluenesulfonic acid (0.38 g, 2 mmol) was added, and the mixture was refluxed overnight and cooled to room temperature. The mixture was evaporated and

the crude product was purified by silica gel column chromatography using petroleum ether as eluent to obtain a white powder in the yield of 50% (3.0 g). ¹H NMR (300 MHz, CDCl₃, δ): 7.19-7.22 (d, 4H), 7.10-7.13 (d, 4H), 6.84-6.91 (m, 8H), 1.26 (s, 18H). ¹³C NMR (75Hz, CDCl₃, δ): 149.7, 142.7, 142.6, 142.1, 139.9, 137.2, 133.0, 130.8, 124.6, 120.3, 34.4, 31.2. MS (EI), m/z: 602.43 ([M+], calcd for C₃₄H₃₄Br₂, 602.10). Anal. Calcd for C₃₄H₃₄Br₂: C, 67.79; H, 5.69; Br, 26.53. Found: C, 68.23; H, 5.57.

TPE-2*m*Br

Prepared by following the similar procedure to TPE-2*p*Br from 3, 3- dibromobenzophenone (3). White solid. Yield: 60%. ¹H NMR (300 MHz, CDCl₃, δ): 7.21-7.23 (d, 2H), 7.10-7.14 (m, 6H), 6.90-6.97 (m, 8H), 1.26 (s, 18H). ¹³C NMR (75Hz, CDCl₃, δ): 149.9, 145.4, 143.2, 139.5, 136.8, 134.0, 130.7, 129.9, 129.4, 129.1, 124.5, 121.6, 34.4, 31.2. MS (EI), m/z: 602.42 ([M+], calcd for C₃₄H₃₄Br₂, 602.10). Anal. Calcd for C₃₄H₃₄Br₂: C, 67.79; H, 5.69; Br, 26.53. Found: C, 68.13; H, 5.74.

General procedure for the synthesis of TPE-2Py(*p*,1), TPE-2Py(*m*,1), TPE-2Py(*p*,2), TPE-2Py(*m*,2), TPE-2Py(*p*,4), TPE-2Py(*m*,4)

TPE-2Py(*p*,**1**)

TPE-2*p*Br (301 mg, 0.5 mmol), Py-1BO (345 mg, 1.05 mmol), Pd(PPh₃)₄ (0.10 g, 0.08 mmol) and potassium carbonate (346 mg, 2.5 mmol) in toluene (20 mL) and distilled water (7 mL) were added into a 200 mL Schlenk tube. The resultant mixture was refluxed for 2 days under argon, then extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using chloroform/petroleum ether (v/v=1/4) as eluent, and further purified by recrystallization in petroleum ether. A yellow solid was finally produced in the yield of 33% (140 mg). ¹H NMR (300 MHz, CDCl₃, δ): 8.15-8.24 (m, 8H), 8.10 (s, 4H), 8.00-8.05 (m, 6H), 7.43-7.46 (d, 4H), 7.34-7.36 (d, 4H), 7.24-7.26 (d, 4H), 7.14-7.16 (d, 4H), 1.36 (s, 18H). MS (EI), m/z: 844.93 ([M+], calcd for C₆₆H₅₂, 844.41). Anal. Calcd for C₆₆H₅₂: C, 93.80; H, 6.20. Found: C, 93.41; H, 6.31. Melting point: 302 °C. IR (KBr) v (cm⁻¹): 2978, 2922, 2863.

TPE-2Py(*m*,1)

White solid (yield: 54%). ¹H NMR (300 MHz, CDCl₃, δ): 8.09-8.19 (m, 6H), 8.06 (s, 6H), 7.97-8.02 (m, 2H), 7.90 (s, 4H), 7.50-7.52 (d, 2H), 7.40-7.44 (m, 6H), 7.24-7.26 (m, 4H), 7.09-7.12 (d, 4H), 1.33 (s, 18H). ¹³C NMR (75Hz, CDCl₃, δ): 149.3, 144.2, 141.9, 140.9, 140.8, 140.2, 139.9, 137.6, 134.0, 131.3, 131.2, 130.8, 130.3, 130.1, 128.6, 128.2, 127.6, 127.5, 127.4, 127.3, 127.2, 125.8, 125.2, 124.9, 124.8, 124.6, 124.5, 124.4, 34.5, 31.4. MS (EI), m/z: 844.85 ([M+], calcd for C₆₆H₅₂, 844.41). Anal. Calcd for C₆₆H₅₂: C, 93.80; H, 6.20. Found: C, 93.33; H, 5.95. Melting point: 276 °C. IR (KBr) ν (cm⁻¹): 3048, 2956, 2926, 2857.

TPE-2Py(*p*,**2**)

Yellow solid (yield: 43%). ¹H NMR (300 MHz, CDCl₃, δ): 8.36 (s, 4H), 8.22 (s, 4H), 8.08 (s, 8H), 7.67-7.70 (d, 4H), 7.26 (S, 4H), 7.17-7.19 (d, 4H), 7.08-7.10 (d, 4H), 1.59 (s, 18H), 1.29 (s, 18H). ¹³C NMR (75Hz, CDCl₃, δ): 149.7, 143.7, 141.1, 139.3, 138.4, 132.5, 131.6, 131.4, 131.2, 128.1, 127.7, 127.3, 124.8, 123.5, 122.6, 35.5, 34.7, 32.2, 31.6. MS (EI), m/z: 956.91 ([M+], calcd for C₇₄H₆₈, 956.53). Anal. Calcd for C₇₄H₆₈: C, 92.84; H, 7.16. Found: C, 92.29; H, 7.23. Melting

point: 230 °C. IR (KBr) v (cm⁻¹): 3037, 2959, 2918, 2865.

TPE-2Py(*m*,**2**)

White solid (yield: 45%). ¹H NMR (300 MHz, CDCl₃, δ): 8.20 (s, 4H), 7.99-8.06 (m, 12H), 7.63-7.69 (t, 4H), 7.26-7.38 (m, 6H), 7.16-7.19 (d, 6 H), 1.58 (s, 18H), 1.27 (s, 18H). ¹³C NMR (75Hz, CDCl₃, δ): 149.5, 148.9, 144.3, 142.1, 141.0, 140.5, 138.4, 132.0, 131.9, 131.2, 131.1, 130.8, 130.0, 128.3, 127.7, 127.4, 125.6, 124.6, 123.6, 123.4, 122.6, 122.2, 35.2, 34.5, 31.9, 31.3. MS (EI), m/z: 956.66 ([M+], calcd for C₇₄H₆₈, 956.53). Anal. Calcd for C₇₄H₆₈: C, 92.84; H, 7.16. Found: C, 93.11; H, 6.92. Melting point: 380 °C. IR (KBr) ν (cm⁻¹): 3040, 2959, 2919, 2864.

TPE-2Py(*p*,**4**)

White solid (yield: 60%). ¹H NMR (300 MHz, CDCl₃, δ): 8.19-8.22 (d, 8H), 8.01-8.05 (d, 6H), 7.49-7.52 (d, 4H), 7.35-7.38 (d, 4H), 7.22-7.26 (m,10H), 1.58 (s, 18H), 1.50 (s, 18H). ¹³C NMR (75Hz, CDCl₃, δ): 148.7, 148.1, 143.9, 142.8, 141.5, 139.2, 139.1, 133.2, 131.5, 130.9, 130.7, 130.4, 129.8, 129.4, 127.8, 127.7, 127.6, 127.2, 126.6, 123.1, 122.3, 122.0, 121.8, 121.1, 35.3, 35.1, 31.9. MS (EI), m/z: 956.84 ([M+], calcd for C₇₄H₆₈, 956.53). Anal. Calcd for C₇₄H₆₈: C, 92.84; H, 7.16. Found: C, 92.61; H, 7.25. Melting point: 391 °C. IR (KBr) υ (cm⁻¹): 3039, 2958, 2916, 2852.

TPE-2Py(*m*,**4**)

Yellow solid (yield: 45%). ¹H NMR (300 MHz, CDCl₃, δ): 8.24 (s, 2H), 8.15-8.16 (d, 4H), 8.11

(s, 2H), 8.02 (s, 4H), 7.54 (s, 2H), 7.44-7.48 (m, 4H), 7.23-7.38 (m, 14H), 1.58 (s, 18H), 1.43 (s, 18H). ¹³C NMR (75Hz, CDCl₃, δ): 148.6, 148.1, 144.0, 143.7, 141.0, 140.5, 139.1, 133.2, 131.5, 130.8, 130.6, 130.4, 130.2, 129.6, 128.3, 128.1, 127.9, 127.6, 127.2, 126.5, 123.0, 122.2, 122.0, 121.9, 121.7, 120.9, 35.2, 35.1, 31.9, 31.8. MS (EI), m/z: 956.75 ([M+], calcd for C₇₄H₆₈, 956.53). Anal. Calcd for C₇₄H₆₈: C, 92.84; H, 7.16. Found: C, 92.32; H, 7.11. Melting point: 182 °C. IR (KBr) ν (cm⁻¹): 3040, 2961, 2919, 2852.



Chart S1 Some good pyrene-based blue luminogens in which the pyrene core were decorated by bulky side groups.



Chart S2 Some good pyrene-based blue luminogens in which pyrene groups acted as side groups to decorate bulky cores.



Chart S3 Our previous works of pyrene-based blue luminogens in which pyrene cores were decorated by bulky side groups.



Scheme S1 Synthetic routes for TPE-2Py(p,1), TPE-2Py(m,1), TPE-2Py(p,2), TPE-2Py(m,2), TPE-2Py(p,4) and TPE-2Py(m,4).



Figure S1. TGA thermograms of TPE-2Py(p,1), TPE-2Py(p,2), TPE-2Py(p,4), TPE-2Py(m,1), TPE-2Py(m,2) and TPE-2Py(m,4), recorded under N₂ at a heating rate of 10 °C/min.



Figure S2. DSC thermograms of TPE-2Py(p,1) (A), TPE-2Py(p,2) (B), TPE-2Py(p,4) (C), TPE-2Py(m,1) (D), TPE-2Py(m,2) (E) and TPE-2Py(m,4) (F), recorded under N₂ at a heating rate of 10 °C/min.



Figure S3 UV spectra in THF solution. Concentration (μ M): 12.5, 14.0, 11.0, 13.0, 14.5 and 13.7 for TPE-2Py(*p*,1), TPE-2Py(*p*,2), TPE-2Py(*p*,4), TPE-2Py(*m*,1), TPE-2Py(*m*,2) and TPE-2Py(*m*,4), respectively.



Figure S4 PL spectra in THF/H₂O mixtures with different water fractions: (A)TPE-2Py(*p*,1), concentration (μ M): 12.5; excitation wavelength 350 nm; (B) TPE-2Py(*p*,2), concentration (μ M): 14.0; excitation wavelength 340 nm; (C) TPE-2Py(*m*,1), concentration (μ M): 13.0; excitation wavelength 350 nm; (D) TPE-2Py(*m*,2), concentration (μ M): 14.5; excitation wavelength 340 nm; (E) TPE-2Py(*m*,4), concentration (μ M): 13.7; excitation wavelength 340 nm. Inset: photos of TPE-2Py(*p*,1), TPE-2Py(*p*,2), TPE-2Py(*m*,1), TPE-2Py(*m*,2) and TPE-2Py(*m*,4) in THF/H₂O mixtures ($f_W = 0$ and 99%) taken under the illumination of a 365 nm UV lamp.



Figure S5 Calculated molecular orbital amplitude plots of LUMO, HOMO levels for pyrene by b3lyp/6-31g*.



Figure S6. The XRD patterns of the as-prepared, ground and fumed TPE-2*p*Br solids.



Figure S7. Perspective view of the packing arrangements in crystal of TPE-2*p*Br. The aromatic C–H $--\pi$ bonds are denoted by pink dotted lines.



Figure S8. (A) The XRD patterns of the as-prepared and ground TPE-2mBr solids; (B) their emission spectra (Inset: their photographs taken under UV illumination (365 nm)).



Figure S9. The emission spectra of the as-prepared, ground and fumed TPE-2Py(p,1) solids (Inset: their photographs taken under UV illumination (365 nm)).



Figure S10. The emission spectra of the as-prepared, ground and fumed TPE-2Py(p,2) solids (Inset: Their photographs taken under UV illumination (365 nm)).



Figure S11. The emission spectra of the as-prepared, ground and fumed TPE-2Py(m,1) solids (Inset: their photographs taken under UV illumination (365 nm)).



Figure S12. The emission spectra of the as-prepared, ground and fumed TPE-2Py(m,2) solids (Inset: their photographs taken under UV illumination (365 nm)).



Figure S13. The emission spectra of the as-prepared, ground and fumed TPE-2Py(m,4) solids (Inset: their photographs taken under UV illumination (365 nm)).



Figure S14 External quantum efficiency changed with the current density. Device configuration: ITO/MoO₃ (10 nm)/NPB (60 nm)/TPE-2Py(p,1), TPE-2Py(m,1), TPE-2Py(p,2), TPE-2Py(m,2), TPE-2Py(p,4), TPE-2Py(m,4) (15nm)/TPBi (35 nm)/LiF (1 nm)/Al.



Figure S15 The photoluminescence (PL) and electroluminescence (EL) spectra with hole-transporting layer (HTL) and without hole-transporting layer for (A) TPE-2Py(p,1); (B) TPE-2Py(p,2); (C) TPE-2Py(p,4); (D) TPE-2Py(m,1); (E) TPE-2Py(m,2); (F) TPE-2Py(m,4).



Figure S16 External quantum efficiency changed with the current density. Device configuration: ITO/MoO₃ (10 nm)/ TPE-2Py(p,1), TPE-2Py(m,1), TPE-2Py(p,2), TPE-2Py(m,2), TPE-2Py(p,4), TPE-2Py(m,4) (75 nm)/TPBi (35 nm)/LiF (1 nm)/Al.



Figure S17 FT-IR spectrum of TPE-2Py(*p*,1).



Figure S18 FT-IR spectrum of TPE-2Py(*m*,1).



Figure S19 FT-IR spectrum of TPE-2Py(*p*,2).



Figure S20 FT-IR spectrum of TPE-2Py(*m*,2).



Figure S21 FT-IR spectrum of TPE-2Py(*p*,4).



Figure S22 FT-IR spectrum of TPE-2Py(*m*,4).

References

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