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A novel bipolar phenanthroimidazole derivative host material for highly efficient green and orange-red phosphorescent OLEDs with low efficiency roll-off at high brightness

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CONTENTS

SI-1. General Procedures

^{1}HNMR and ^{13}CNMR measurements were recorded with a Varian Gemin-400 spectrometer. Mass spectra were performed with a PE SCIEX APIMS spectrometer. Thermal gravity analysis (TGA) and differential scanning calorimetry (DSC) measurements were recorded with a TA Instrument TGAQ50 and a TA Instrument DSC2910 respectively. Absorption and photoluminescence spectra were determined with a Shimadzu UV-Vis-2600 spectrophotometer and a Perkin-Elmer LS50B Luminescence spectrophotometer. The phosphorescence spectrum was measured in 2-MeTHF glass matrix at 77 K using a Hitachi F-4600 fluorescence spectrometer. Cyclic voltammetry was performed on a BAS 100 B/W electrochemical analyser. The electrolytic cell was a conventional three-electrode cell in which a glassy carbon working electrode, a platinum wire auxiliary electrode, and an aqueous saturated calomel electrode (SCE) as the reference electrode were employed. The ferrocene/ferrocenium couple was used as the internal standard. 0.10 M TBAPF$_6$ was used as the supporting electrolyte and DCM as the solvent, respectively. Theoretical calculation of the compound was carried out using the Gaussian-03 program. Density functional theory (DFT) B3LYP/6-31G (d) was used to determine and optimize the structure. Elemental analysis (C, H, N) was performed using a Vario EL III CHNS elemental analyzer.

SI-2. Synthesis

A three-steps synthetic route was showed in **Scheme S1,** All the compounds have a good yield, their chemical structure was fully confirmed by mass spectrometry and ^{1}HNMR spectrometry. The final product was futher confirmed by ^{13}CNMR spectrometry and elemental analysis, the starting material **1** was prepared as reported previously.[1]

4'-(9-(4-bromophenyl)-9H-fluoren-9-yl)-[1,1'-biphenyl]-4-carbaldehyde (2)

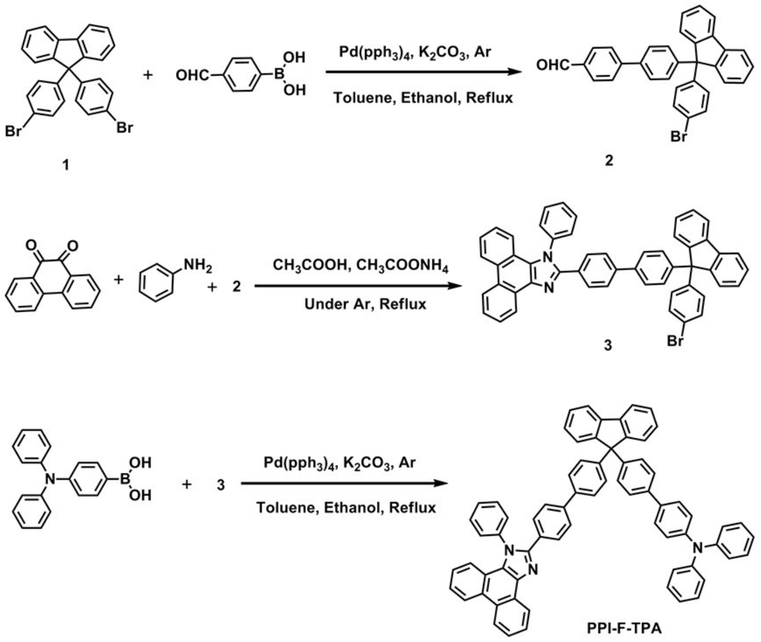
The staring material 1 (3.2 g, 6.8 mmol), (4-formylphenyl)boronic acid (0.68 g, 4.5 mmol), Pd(PPh$_3$)$_4$ (0.26 g, 0.23 mmol), and K$_2$CO$_3$ aqueous (2 M, 5 mL) in toluene (20 mL) and ethanol (4 mL) was heated to reflux in an argon atmosphere for 12 h. The solution was cooled to room temperature and extracted with dichloromethane. The extracts were dried with anhydrous Na$_2$SO$_4$ and concentrated by rotary evaporation. The residue was further purified by column chromatography (petroleum ether: CH$_2$Cl$_2$, 2:1) to get pure white powder (1.5 g, 68%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 10.02 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.56 (dd, *J* = 19.9, 8.1 Hz, 4H), 7.44 – 7.37 (m, 4H), 7.31 (dd, *J* = 15.9, 7.8 Hz, 4H), 6.99 (d, *J* = 8.0 Hz, 2H). MS (ESI) (m/z): Calculated for $C_{32}H_{21}BrO$: 501.41 Found [M$^+$]: 501.19.

2-(4'-(9-(4-bromophenyl)-9H-fluoren-9-yl)-[1,1'-biphenyl]-4-yl)-1-phenyl-1H-phenanthro[9,10-d]imidazole (3)

The compound 2 (1.5 g, 3 mmol), 9,10-phenanthrenequinone (0.63 g, 3 mmol), aniline (0.3 ml, 3 mmol), and ammonium acetate (2.89 g, 22.5 mmol) were added into glacial acetic acid (40 mL) and the mixture refluxed for 12 h under an argon atmosphere. After cooling to room temperature, an orange-yellow mixture was obtained and poured into methanol under stirring. The raw product was separated by filtration and washed with methanol, and then dried under vacuum. The product was purified by column chromatography (petroleum ether: CH$_2$Cl$_2$, 1:2) on silica gel to give a white powder. (1.72 g, 70.3%). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.76 (dd, *J* = 21.2, 8.2 Hz, 2H), 7.85 – 7.79 (m, 2H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.66 (p, *J* = 6.2 Hz, 6H), 7.61 – 7.53 (m, 4H), 7.53 – 7.44 (m, 5H), 7.44 – 7.35 (m, 4H), 7.35 – 7.12 (m, 7H), 6.98 (d, *J* = 8.5 Hz, 2H). MS (ESI) (m/z): Calculated for $C_{52}H_{33}BrN_2$: 765.73 Found [M$^+$]: 764.62

N,N-diphenyl-4'-(9-(4'-(1-phenyl-1H-phenanthro[9,10-d]imidazol-2-yl)-[1,1'-biphenyl]-4-yl)-9H-fluoren-9-yl)-[1,1'-biphenyl]-4-amine (PPI-F-TPA)

The synthetic procedures were similar to the intermediated 1. Yield:74.2 % (1.2 g white powder) ^{1}H NMR (400 MHz, CD2Cl2) δ 8.79 (d, J = 8.3 Hz, 1H), 8.73 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 7.5 Hz, 2H), 7.80 – 7.61 (m, 8H), 7.61 – 7.37 (m, 16H), 7.35 – 7.23 (m, 11H), 7.22 – 7.00 (m, 8H). ^{13}C NMR (100 MHz, CD2Cl2) δ[ppm] 151.08, 147.73, 147.29, 145.47, 144.29, 140.21, 139.12, 138.86, 138.54, 134.55, 130.19, 129.86, 129.64, 129.17, 128.53, 128.30, 128.23, 127.70, 127.50, 127.25, 126.75, 126.43, 126.27, 126.10, 125.56, 124.88, 124.44, 124.02, 123.75, 123.04, 122.62, 120.90, 120.27, 65.09. MS (ESI) (m/z): Calculated for $C_{70}H_{47}N_3$: 930.14 Found [M+]: 929.12. Anal. Calcd (%) for $C_{70}H_{47}N_3$: C 90.39, H 5.09 N 4.52 Found: C 90.35, H 5.15, N 4.50.



Scheme S1. The molecular structure and synthetic route of PPI-F-TPA

SI-3. Device fabrication and measurement

Pre-patterned indium tin oxide (ITO) glass substrates with a sheet resistance of 15 Ω per square were cleaned with isopropyl alcohol and Decon 90 solution, then rinsed in deionized water and dried in an oven. After a 15 min UV-ozone treatment, the ITO substrates were immediately transferred into a deposition chamber with a base pressure of 5×10^{-7} torr for organic and cathode depositions. Organic materials were deposited via thermal deposition at a rate of 1 Å s^{-1}, while the cathodes were completed via deposition of LiF (0.1–0.2 Å s^{-1}) and Al (5–6 Å s^{-1}) successively. Electroluminescent spectra and the corresponding Commission Internationale de l'Eclairage (CIE) coordinates were measured with a Spectra scan PR650 photometer. Current–voltage–luminance (J–V–L) characteristics were recorded with a Keithley 2400 Source meter under ambient atmosphere without device encapsulation.

SI-4. The PL spectra of the thin films as EMLs

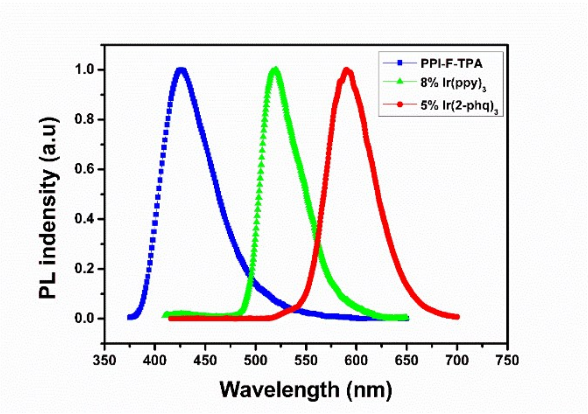


Figure S1. The PL spectra of the thin films as EMLs, PPI-F-TPA (blue), PPI-F-TPA: 8 wt% Ir(ppy)$_3$ (green), PPI-F-TPA: 5 wt% Ir(2-phq)$_3$ (orange-red).

SI-5. The energy levels diagrams of materials utilized in devices

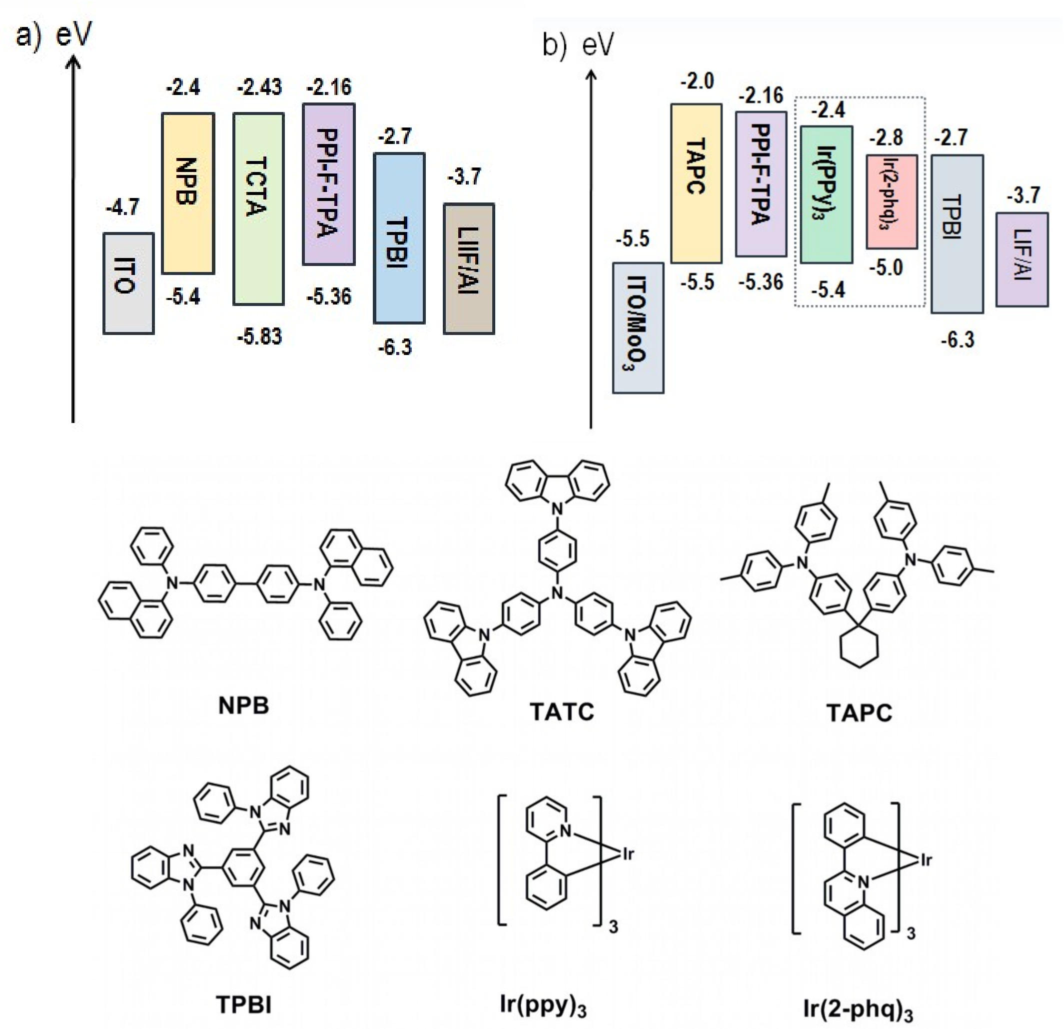


Figure S2. The energy levels diagrams and structures of materials used in all devices (a) Device 1: ITO/NPB (40 nm)/(TCTA) (5 nm)/PPI-F-TPA (30 nm)/TPB (30 nm)/LiF (1 nm)/Al (100 nm). (b) Device 2 and 3: ITO/MoO$_3$ (1 nm)/(TAPC) (40 nm)/PPI-F-TPA: 8 wt% Ir(ppy)$_3$ or 5 wt% Ir(2-phq)$_3$ (30 nm) /TPBI (30 nm)/LiF (1 nm)/Al (100 nm).

SI-6. The EL spectra of all devices at different voltages

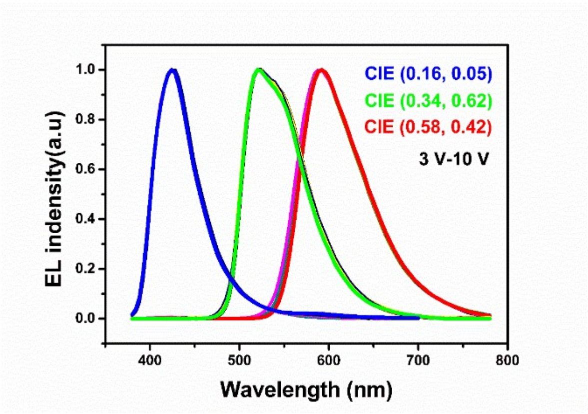


Figure S3. The EL spectra of device 1(blue), device 2 (green) and device 3 (orange-red) at different voltages

SI-7. Summary of recent reported orange or orange-red devices with low efficiency roll-off

Table S1. Key performance data for PPI-F-TPA-based orange-red device and other highly efficient orange or orange-red devices with low efficiency roll-off.

Device	CE (cd/A) [a]	PE (lm/W) [b]	EQE (%) [c]	Ref
	Max/1000 (cd/m^2)	Max/1000 (cd/m^2)	Max/1000/5000/10000 (cd/m^2)	
	27/26.8	28.3/17.9	12.5/12.42/11.5/10.9	This work
Ir(2-phq)$_3$-based	28.8/22.6	28.4/10.1	16.9/13.2/7.3/-	22d
	23.8/19.1	18.8/10.0	10.4/8.3/-/-	22c
	26.8/-	18.0/-	11.8/11.2/7.6/-	21b
	19.6/-	15.4/-	8.6/7.9//5.8/-	
PO-01-based	-/-	64.5/57.3	24.5/24.2/-/23.8	22a
	-/-	19.7/19.0	13.7/13.6/-/13.1	
[(fbi)$_2$Ir(acac)]-based	57.8/53.2	51.9/ 29.3	20.5/18.9/-/-	22b
BZQPG-based	-/-	77.1/63.2	27.3/27.2/26.3/-	22e

a) Current efficiency. b) Power efficiency. c) External quantum efficiency corresponding to the value at the maximum, 1000, 5000 and 10000 cd/m^2 respectively.

Reference

(1) D. H. Yu, F. C. Zhao, C. M. Han, H. Xu, J. Li, Z. Zhang, Z. P. Deng, D. G. Ma and P. F. Yan, *Adv. Mater.*, 2012, **24**, 509.