Electronic Supplementary Information (ESI)

Anthracene-based bipolar deep-blue emitters for efficient white OLEDs with ultra-high stabilities of emission color and efficiency

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1. General Information

All the chemicals and reagents were purchased from commercial sources and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 500 spectrometer in deuterated dichloromethane. High resolution mass spectra (HRMS) were recorded on a Agilent1290/Bruker maxis mass spectrometer operating in HRMS positive mode. TGA analysis was carried out on a TG209F1 under dry nitrogen at a heating rate of 20 °C min^{-1}. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. Cyclic voltammetry was measured on a CHI 610E A14297.

2. Experimental Section

2.1 Synthesis and characterization

10-(4-(10-Bromo-2,6-di-*tert*-butylanthracen-9-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (compound 3): 1 (0.90 g, 2.0 mmol), **2** (0.82 g, 2 mmol), $Pd(PPh_3)_4$ (240 mg, 0.2 mmol), Na_2CO_3 (0.85 g, 8 mmol), and a mixed solvent system of tetrahydrofuran (THF) and H_2O (v/v = 4:1) were added into a 250 mL two-necked round bottom flask and heated to reflux for 8 h under nitrogen. After cooled down to room temperature, the mixture was poured into water and extracted with dichloromethane for several times. The combined organic layers were washed successively with brine and water, and then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by a rotary evaporation. The crude product was purified by column chromatography on silica-gel using petroleum/dichloromethane as eluent. White solid of **3** was obtained in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 8.58−8.54 (m, 2H), 7.85 (d, J = 10.0 Hz, 1H), 7.72−7.67 (m, 3H), 7.63−7.52 (m, 6H), 7.10−6.98 (m, 4H), 6.51 (d, J = 10.0 Hz, 2H), 1.75 (s, 6H), 1.52 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 149.32, 147.72, 141.01, 140.62, 138.99, 135.95, 133.73, 131.44, 130.86, 130.16, 129.79, 129.47, 129.10, 127.66, 126.85, 126.45, 125.39, 122.62, 122.34, 121.18, 120.72, 113.99, 36.10, 35.39, 35.03, 31.32, 30.95, 30.62. HRMS ($C_{43}H_{43}BrN$): *m/z* 652.2570 ($[M + H]^+$, calcd 652.2579).

10-(4-(10-(4-(Carbazol-9-yl)phenyl)-2,6-di-*tert*-butylanthracen-9-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (Cz-TAn-DMAC): The synthetic procedure of Cz-TAn-DMAC is identical with that of compound **3**. The dosage of the used materials are listed below: **3** (1.30 g, 2.0 mmol), **4** (0.69 g, 2.4 mmol), $Pd(PPh_3)_4$ (240 mg, 0.2 mmol) and Na_2CO_3 (0.85 g, 8 mmol). White solid of Cz-TAn-DMAC was obtained in 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 8.23 (d, J = 10.0 Hz, 2H), 7.95–7.90 (m, 1H), 7.90–7.82 (m, 3H), 7.79–7.75(m, 5H), 7.69–7.49 (m, 11H), 7.41–7.34 (m, 2H), 7.14–7.07 (m, 2H), 7.04–6.98 (m, 2H), 6.59–6.54 (m, 2H), 1.77 (s, 6H), 1.37 (s, 9H), 1.36 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.34, 147.18, 141.06, 141.00, 140.42, 139.56, 138.60, 136.89, 135.82, 135.63, 133.85, 132.87, 131.40, 130.14, 129.77, 129.69, 128.64, 128.52, 128.40, 127.50, 127.01, 126.51, 126.45, 126.06, 126.02, 125.35, 124.90, 124.88, 123.53, 120.96, 120.67, 120.45, 120.06, 114.04, 109.83, 36.09, 35.07, 31.30, 30.78, 30.65. HRMS ($C_{61}H_{54}N_2$): *m/z* 815.4392 (M^+, calcd

815.4365).

4-(2,6-Di-*tert*-butyl-10-(4-(9,9-dimethylacridin-10-yl)phenyl)anthracen-9-yl)-*N*,*N*-diphenylaniline (TPA-TAn-DMAC): The synthetic procedure of TPA-TAn-DMAC is analogous to that of compound **3**. The dosage of the used materials are listed below: **3** (1.30 g, 2.0 mmol), **5** (0.69 g, 2.4 mmol), $Pd(PPh_3)_4$ (240 mg, 0.2 mmol) and Na_2CO_3 (0.85 g, 8 mmol). White solid of TPA-TAn-DMAC was obtained in 84% yield. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (TMS, ppm): 7.90–7.84 (m, 2H), 7.76–7.70 (m, 3H), 7.64–7.49 (m, 7H), 7.41–7.29 (m, 8H), 7.25 (d, J = 8.3 Hz, 4H), 7.09–7.05 (m, 4H), 6.99–6.96 (m, 2H), 6.54 (d, J = 8.0 Hz, 2H), 1.73 (s, 6H), 1.35 (s, 9H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 148.51, 147.71, 147.57, 141.64, 140.95, 140.18, 137.07, 135.83, 134.46, 133.93, 132.75, 131.88, 130.69, 130.37, 130.29, 129.86, 129.19, 128.95, 127.21, 126.95, 126.89, 125.86, 125.29, 125.06, 124.76, 124.56, 123.39, 121.82, 121.42, 121.13, 114.61, 36.56, 35.49, 35.47, 31.67, 31.03, 30.94. HRMS ($C_{61}H_{56}N_2$): *m/z* 817.4528 (M^+, calcd 817.4522).

2.2 Device fabrication and measurement

Glass substrates precoated with a 90 nm layer of indium tin oxide (ITO) with a sheet resistance of 15 ~ 20 Ω per square were successively cleaned in ultrasonic bath of acetone, isopropanol, detergent, and deionized water, respectively, taking 10 minutes for each procedure. Then, the substrates were totally dried in a 70 ℃ oven. Before the fabrication processes, the substrates were treated by O_2 plasma for 10 minutes to improve the hole injection ability of ITO. The vacuum-deposited OLEDs were fabricated under a pressure of $< 5 \times 10^{-4}$ Pa in the Fangsheng OMV-FS380 vacuum deposition system. Deposition rate of organic materials, LiF and Al are 1~2 A s^{-1}, 0.1 A $s^{-1}$and 5 A s^{-1}, respectively. For monochromatic OLEDs, the luminance–voltage–current density characteristics and electroluminescent spectra were obtained via a Konica Minolta CS-200 Color and Luminance Meter and an Ocean Optics USB 2000^+ spectrometer, along with a Keithley 2400 Source Meter. For white OLEDs, the luminance–voltage–current density characteristics and electroluminescent spectra were obtained via a PhotoResearch PR670 spectroradiometer, with a Keithley 2400 Source Meter. The external quantum efficiencies were estimated utilizing the normalized EL spectra and the current efficiencies of the devices, assuming that the devices are Lambertian emitters. The effective emitting area of the devices was 9 mm^2, determined by the overlap between anode and cathode. All the characterizations were conducted at room temperature in ambient conditions without any encapsulation, as soon as the devices were fabricated.

3. Additional data

Table S1. Device performance of some conventional fluorescent blue non-doped OLEDs.

Compound	PLQY (%) (Solid)	External quantum efficiency (%)		Color coordinates (CIE)		Ref.
		Maximum	At 1000 cd m^{-2}	x	y	
TPA-TAn-DMAC	54	4.9	4.3	0.14	0.18	This work
OMeNPI-PITPA	97	4.9	-	0.15	0.07	[1]
TPAPyPI	-	4.7	4.4	0.14	0.13	[2]
DmCzTrz	-	6.8	-	0.15	0.08	[3]
TPB-AA-TPA	-	6.4	-	0.14	0.19	[4]
4PF	52	5.9	5.0	0.15	0.08	[5]
TPA-BIPI	87	4.5	4.34	0.15	0.10	[6]
CzB-FMPPI	92	4.1	-	0.15	0.12	[7]
CN-TPB-TPA	93	7.3	6.6	0.15	0.08	[8]
p-PO15NCzDPA	61	6.4	5.6	0.15	0.06	[9]
FL-BPI	63	5.4	4.4	0.15	0.05	[10]
2FPPIPCz	79	5.6	5.4	0.15	0.08	[11]
PTPBTPA	99	7.1	6.2	0.15	0.09	[12]
TPA-DFCP	67	7.7	-	0.15	0.08	[13]
TPBPPI-PBI	92	5.9	5.7	0.16	0.06	[14]
TFPBI	-	5.7	4.8	0.15	0.05	[15]
CzB-MOPPI	91	6.0	-	0.16	0.08	[16]
IDC-Py	-	6.1	6.0	0.15	0.08	[17]

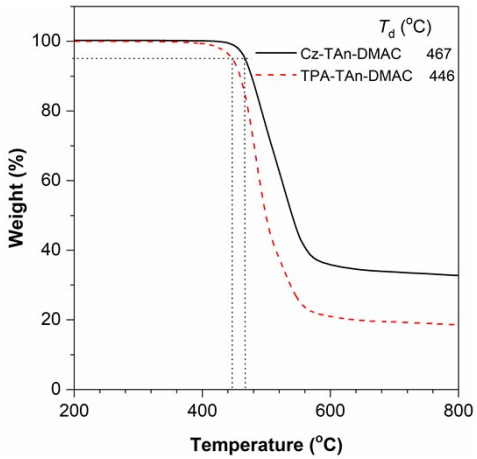

Fig. S1 TGA curves of Cz-TAn-DMAC and TPA-TAn-DMAC recorded under nitrogen atmosphere (heating rate: 20 °C min^{-1}).

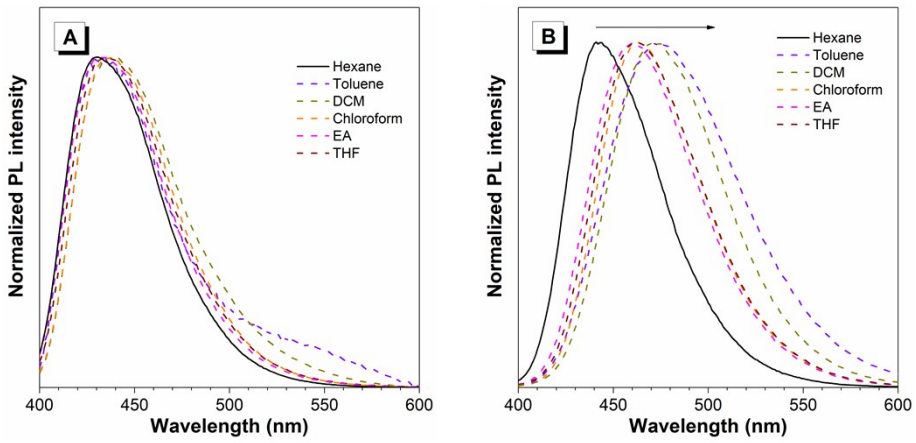

Fig. S2 Photoluminescence (PL) spectra of (A) Cz-TAn-TADMA and (B) TPA-TAn-TADMA in different solvents.

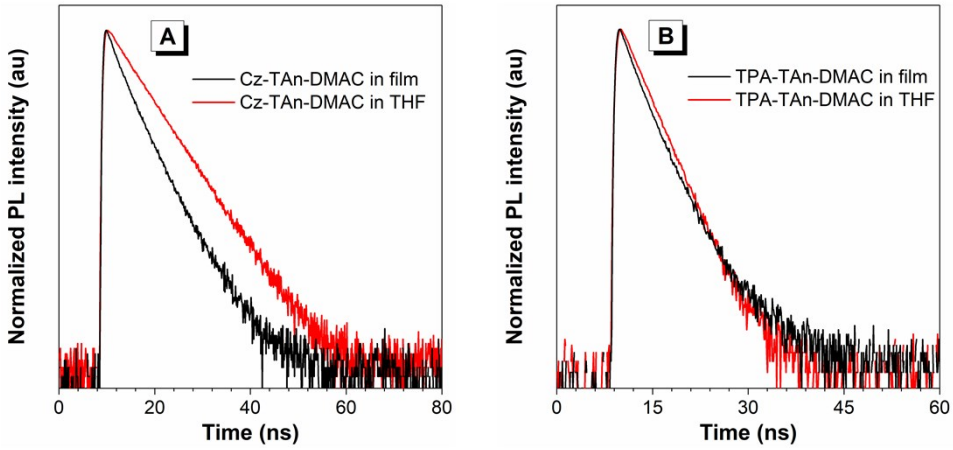

Fig. S3 Fluorescence decay profiles of (A) Cz-TAn-DMAC and (B) TPA-TAn-DMAC in film and THF.

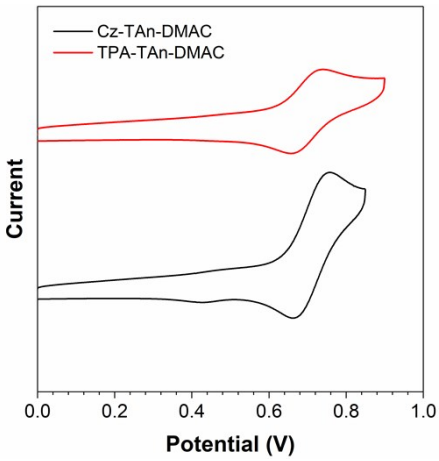

Fig. S4 Cyclic voltammetry of Cz-TAn-DMAC and TPA-TAn-DMAC, measured in dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (0.1 M) at a scan rate of 50 mV s^{-1}.

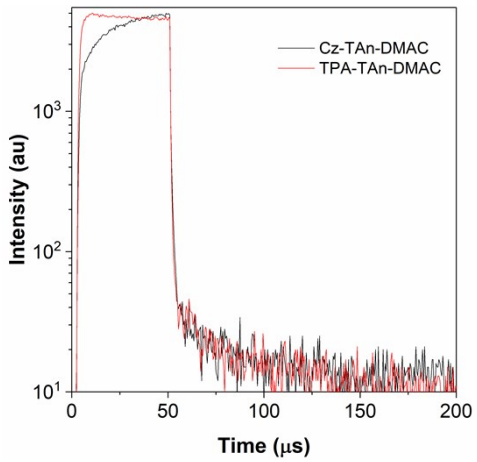

Fig. S5 Transient electroluminescence decay curves of the non-doped devices under an excitation pulse voltage of 5 V.

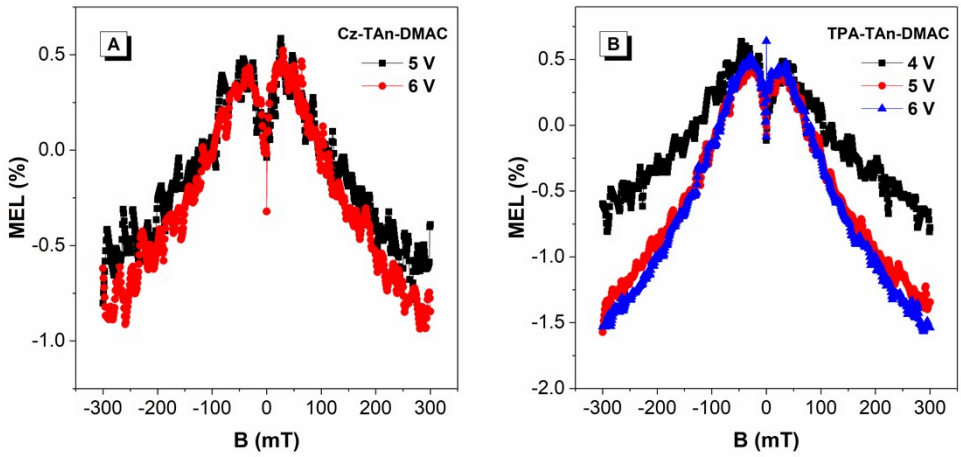

Fig. S6 Magneto-electroluminescence (MEL) responses of non-doped OLEDs of (A) Cz-TAn-DMAC and (B) TPA-TAn-DMAC under different applied voltages.

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