Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Benzimidazole-triazine based exciplex films as emitters and hosts to construct highly efficient OLEDs with small efficiency roll-off

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General Information

All starting materials were purchased from commercial sources and used without further purification. Solvents for synthetic reactions were analytical grade and used as received. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Mercury 500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard. Mass spectra were recorded on a Thermo Fisher ITQ 1100 mass spectrometer. Element analyses were performed on a Flash EA 1112 elemental analyser. DSC measurements were performed on a Netzsch DSC 204 F1 instrument at a heating rate of 10 K min^{-1} under nitrogen. Thermogravimetric analyses (TGA) were performed on a TA Q500 thermogravimeter by measuring their weight loss while heating at a rate of 10 ℃ min^{-1} from 25 to 800 ℃ under nitrogen atmosphere. UV−vis absorption spectra were recorded by a Specord 210 Plus spectrophotometer (Analytik Jena AG, Germany). The fluorescence spectra of solutions and films were recorded using a Shimadzu RF-5301 PC spectrometer. The phosphorescence spectra at 77 K were captured by an optical fiber detector that connected to a Maya 2000 Pro CCD spectrometer. The fluorescence lifetime and quantum yield of the blend films were measured using a calibrated integrating sphere combined with an Edinburgh FLS920 spectrometer. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station calibrated against a ferrocene/ferrocenium redox couple, in which glassy carbon, Pt wire and Ag/AgCl were used as working, counter and reference electrodes, respectively. The oxidation and reduction potentials were measured in dichloromethane and *N*,*N*-dimethylformamide containing 0.1 mol/L of n-Bu_4NPF_6 as a supporting electrolyte at a scan rate of 50 mV s^{-1}, respectively.

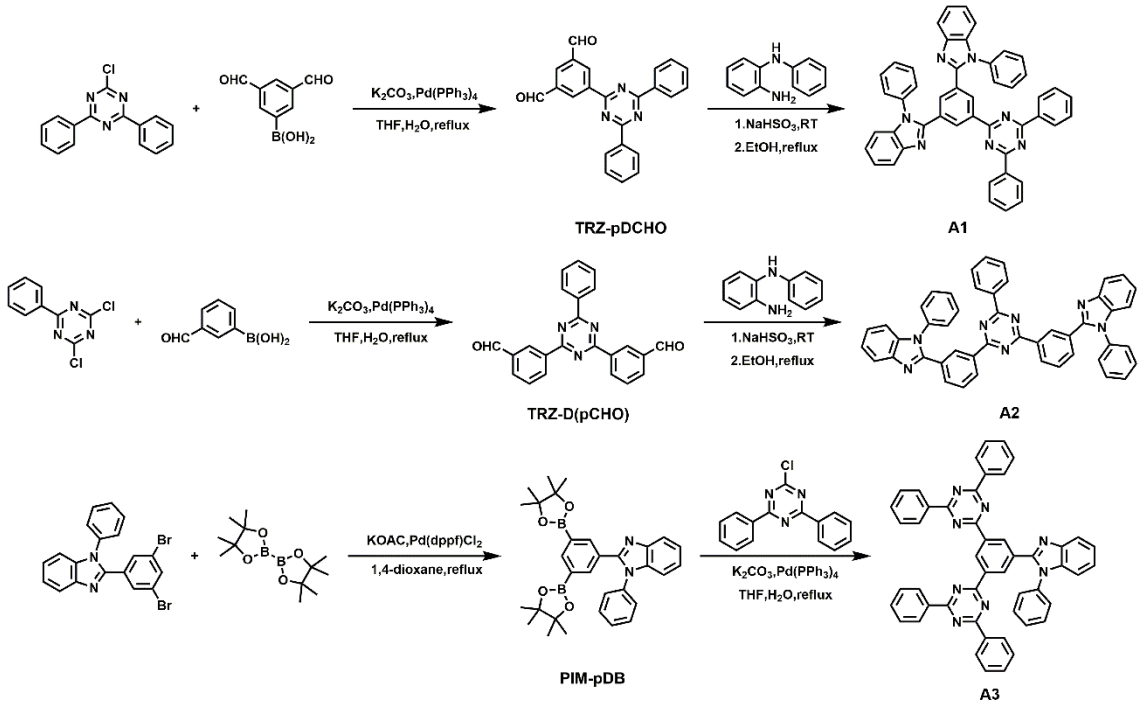
Theoretical calculations method

The ground state geometries of gas state were fully optimized by B3LYP method including Grimme's dispersion correction with 6-31G (d,p) basis set using Gaussian 09 software package.[1-5] HOMO and LUMO were visualized with Gaussview 5.0. The excited state properties were calculated by TD-DFT with the

same theory level as DFT. After which NTO of S0→S1 transitions were analyzed using Multiwfn 3.6.[6]

Device Fabrication and Measurement

The devices were fabricated through vacuum deposition of the materials at a base pressure around 5×10^{-4} Pa. The ITO coated glass substrates (20 Ω/square) were pre-cleaned carefully in deionized water, acetone, and isopropanol and then dried in an oven. After treated by plasma for 5 min, the ITO substrates were transferred into a deposition chamber. All organic materials were thermally evaporated at a rate of 1.0 Å s^{-1}. A thin LiF layer (1.0 nm) was deposited at a rate of 0.1 Å s^{-1} and the Al metal cathode was deposited at a rate of 5 Å S^{-1}. The thicknesses of the organic and the cathode layers were controlled by using a quartz crystal thickness monitor. The electrical characteristics of the devices were measured with a Keithley 2400 source meter. The EL spectra and luminance of the devices were recorded on a PR650 spectrometer. Current-Voltage characteristics of single-carrier devices were measured using the same semiconductor parameter analyzer. All device characterizations were carried out under ambient atmosphere.



Scheme S1. Synthetic routes of **A1**, **A2**, and **A3**.

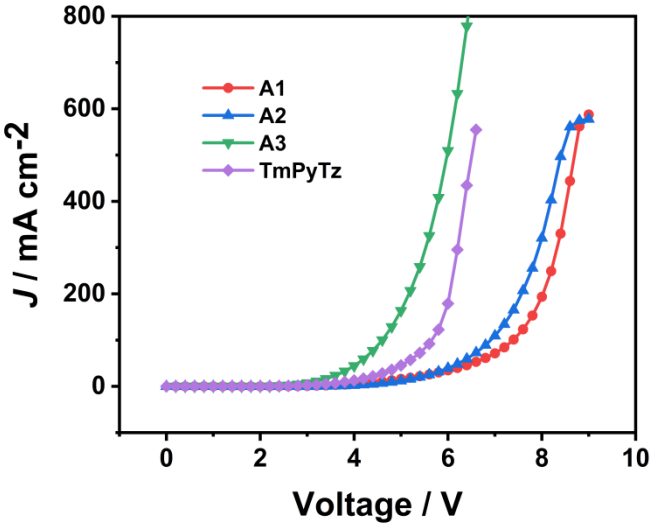


Fig. S1 Electron-only carrier devices of **A1, A2,** and **A3** and TmPyTz (2,4,6-tris(3-(pyridin-3-yl)phenyl)-1,3,5-triazine). ITO/Bphen (10 nm)/ **A1** or **A2** or **A3** or TmPyPz (60 nm)/Bphen(10 nm)/LiF (1 nm)/Al (100 nm). Here, Bathophenanthroline (Bphen) is used to prevent holes and help electrons injection from the anode and cathode, respectively.

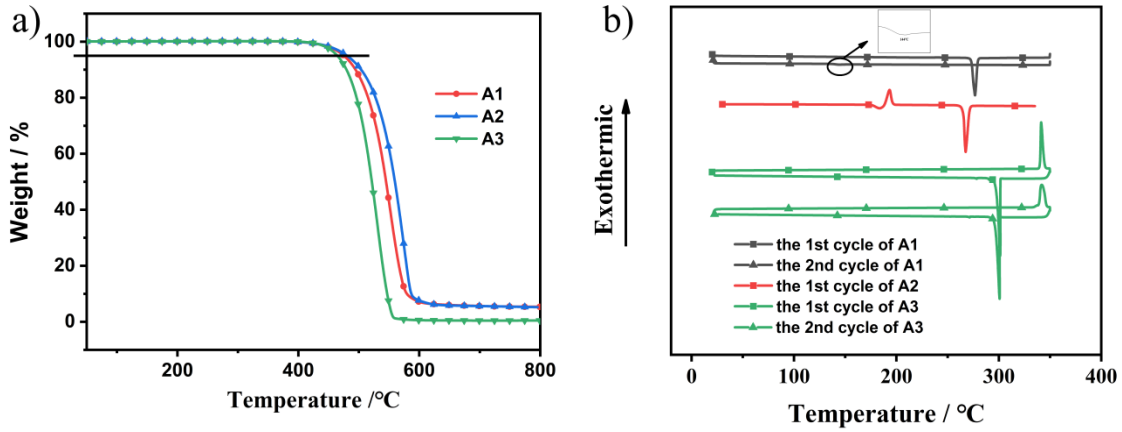


Fig. S2 TGA (a) and DSC (b) of **A1**, **A2**, and **A3**.

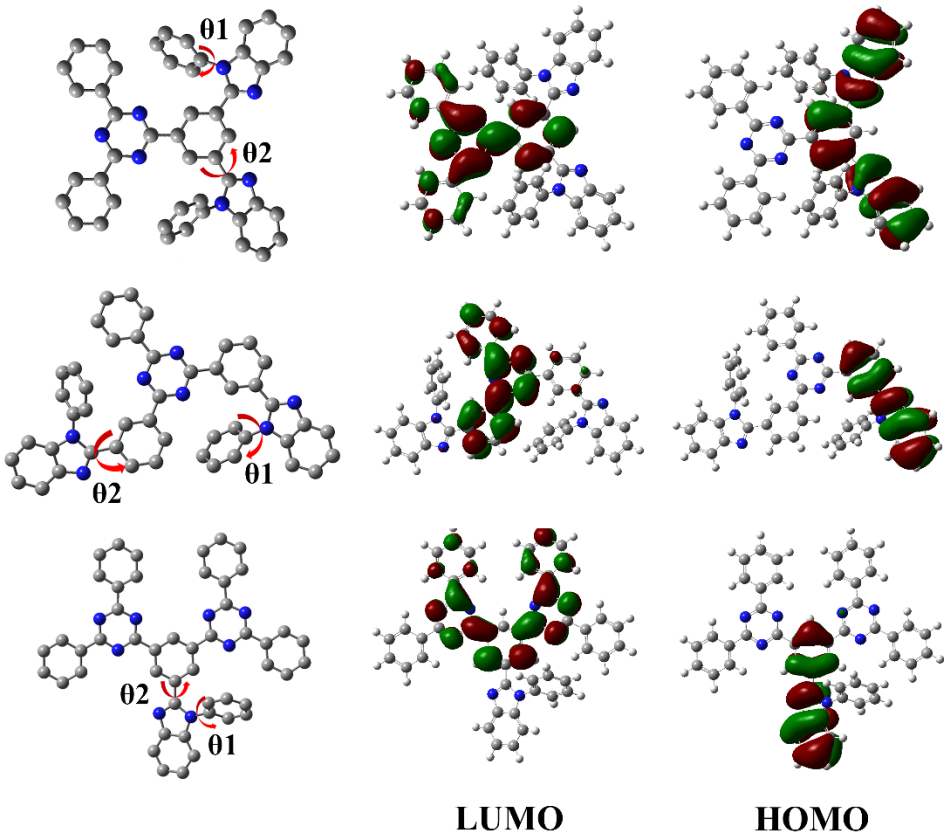


Fig. S3 Optimized configurations and distribution of HOMO and LUMO of **A1**, **A2**, and **A3**.

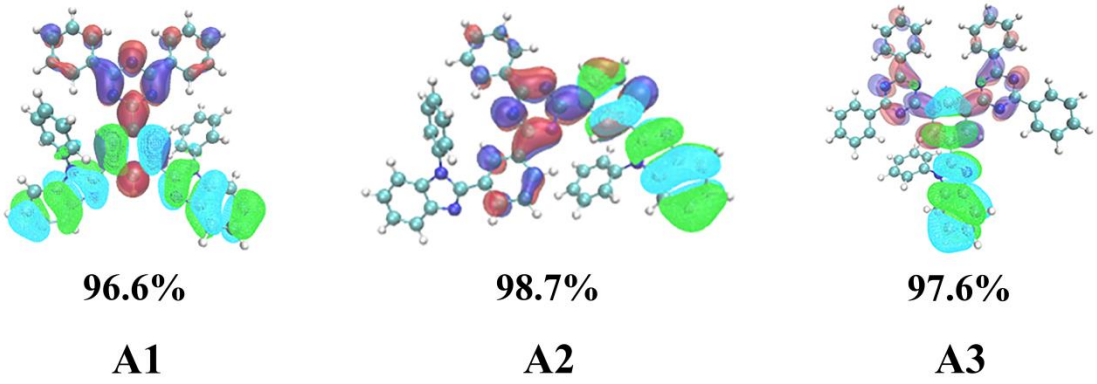


Fig. S4 NTOs of S0→S1 (mesh, hole; transparent, particle).

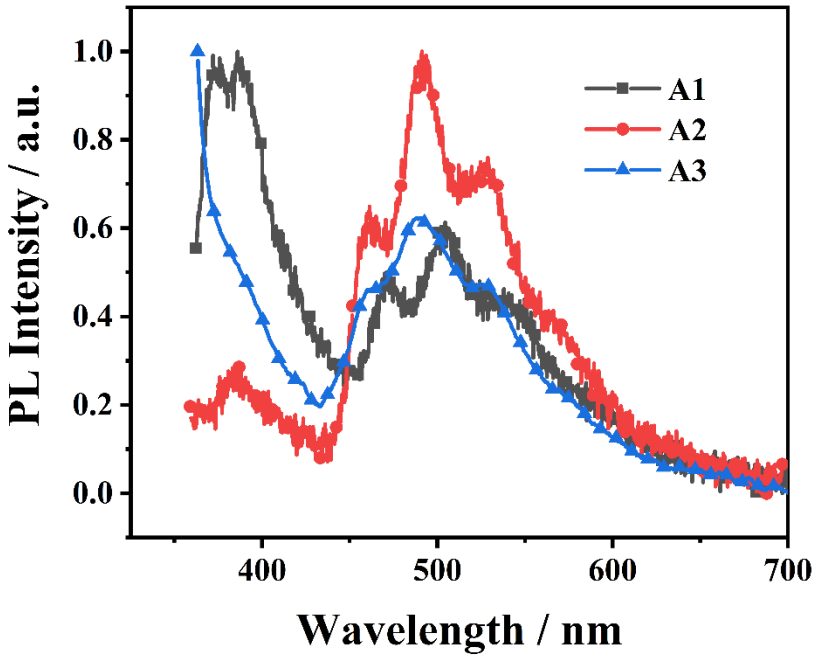


Fig.S5 PL spectra of **A1**, **A2**, and **A3** in toluene (10^{-5} M) at 77K (excited at 335 nm).

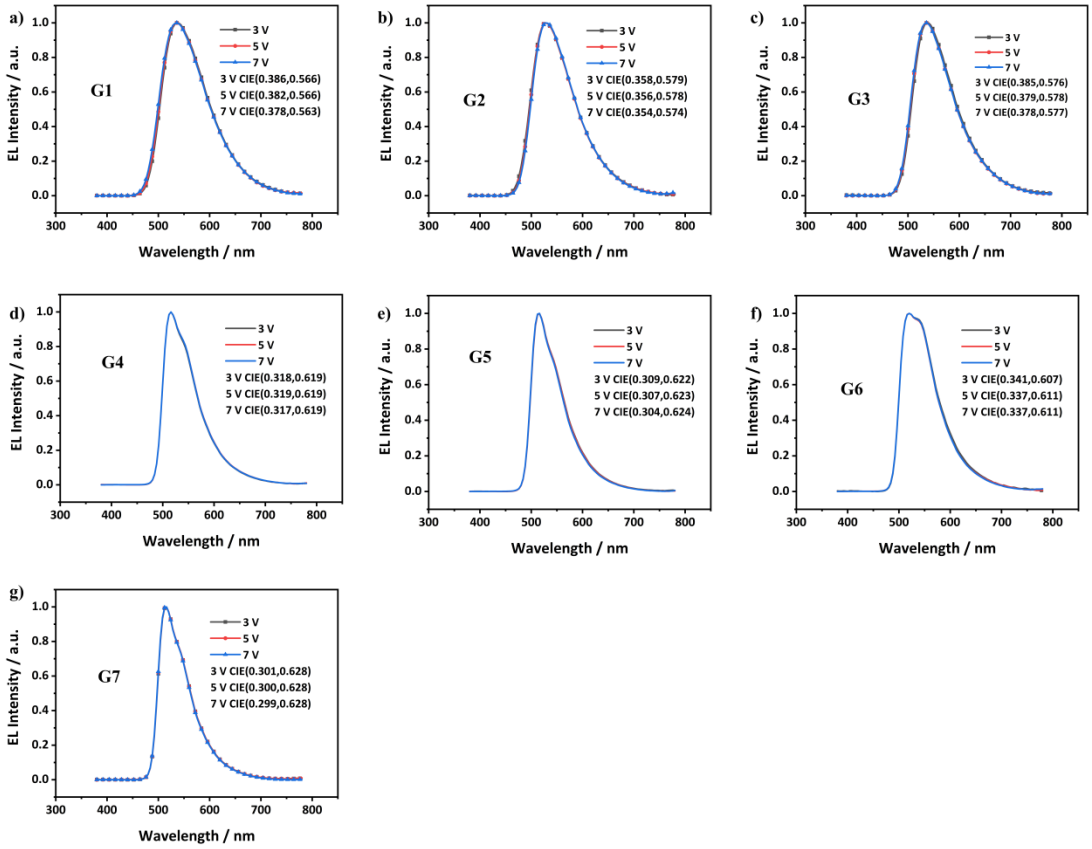


Fig. S6 EL spectra and CIE of devices **G1~G7** at 3V, 5V and 7V.

Table S1. Summary of high efficiency OLEDs based on $Ir(ppy)_3$.

References	Host	V_{on} [V]	EQE [%] max; at 1000 cd m^{-2}; at 10000 cd m^{-2}
This work	TAPC: **A2**	2.4	28.3, 28.1, 24.3
	TAPC: **A4**	2.4	29.6, 29.4, 25.8
Ref [7]	TCTA: B4PYMPM	2.3	27.0, 26.7, 23.9
Ref [8]	TCTA: B3PYMPM	2.7	24.7, -, -
Ref [9]	DPhPCz: DBFTrz	2.7	~17, ~16, ~13
Ref [10]	BP-DPPI	3.0	26.6, 23.6, -
	BP-DTPI	4.0	19.7, 13.9, -

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