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## **Electronic supplementary information**

## High-performance white organic light-emitting diodes with doping-

## free device architecture based on exciton adjusting interfacial

## exciplex

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**Fig. S1** (a) Current density–luminance–voltage characteristics of the device with the structure of ITO/ HAT-CN (15 nm)/ TAPC (45 nm)/ TCTA (5 nm)/ 26DCzPPy (10 nm)/ PO-T2T (45 nm)/ LiF (1 nm)/ Al (150 nm). The inset shows EQE versus luminance characteristics. (b) Current efficiency and power efficiency versus luminance characteristics of the device. (c) Fluorescent and phosphorescent spectra of 26DCzPPy:PO-T2T mixed film measured at 298 and 77 K, and EL spectra of the device at the voltage of 6 V. (d) Transient PL decay characteristic of 26DCzPPy film with 340 nm excitation (Observed at 393 nm).



Fig. S2 Chemical structures (a) and energy levels (b) of the organic materials used in this study.

Device	PE <sub>max/1000</sub> <sup>a</sup>	CE <sub>max/1000</sub> <sup>a</sup>	EQE <sub>max/1000</sub> <sup>a</sup>	CIE(x, y) <sup>b</sup>	
	[lm W <sup>-1</sup> ]	[cd A <sup>-1</sup> ]	[%]		
BD1	59.5/36.0	49.5/45.7	24.7/23.0	(0.15, 0.33)	
GD1	69.5/34.5	53.8/48.2	15.7/13.9	(0.35, 0.61)	
YD1	72.4/38.0	59.9/52.9	19.5/17.0	(0.48, 0.51)	
RD1	35.2/17.9	29.3/26.2	20.0/17.1	(0.61, 0.39)	

Table S1. Summary of key EL parameters for the monochromatic OLEDs

 $^{\rm a}$  The maximum efficiencies and values taken at 1000 cd m-2 ;  $^{\rm b}$  Measured at the voltage of 6 V.



Fig. S3 Normalized EL spectra of two-color WOLEDs at the voltage from 3 to 8 V. (a) WD1-0. (b) WD1-1. (c) WD1-2. (d) WD1-3. (e) WD1-4. (f) WD1-5.



**Fig. S4** Normalized EL spectra of WOLEDs with the thickness of 26DCzPPy varying from 0 to 5 nm (**WD1-0**, **WD1-1**, **WD1-2**, **WD1-3**, **WD1-4**, and **WD1-5**) at the voltage of 4 V. (b) CIE chromaticity coordinates variation of **WD1-0**, **WD1-1**, **WD1-2**, **WD1-3**, **WD1-4**, and **WD1-5** at the voltage of 4 V.



**Fig. S5** Normalized UV-vis absorption spectra of FIrpic and Ir(tptpy)<sub>2</sub>acac in dichloromethane and EL spectra of 26DCzPPy/PO-T2T interface exciplex.



**Fig. S6** (a) Schematic structure diagram of the four white devices (**D1**, **D2**, **D3**, and **D4**) fabricated by inserting blue ultrathin layer at 0, 1, 2, 3 nm away from the interface between 26DCzPPy and PO-T2T. (b) EQE versus luminance characteristics of the white devices. The inset shows normalized EQE versus luminance characteristics. (c) EL spectra of the white devices **D1**, **D2**, **D3**, and **D4** at the voltage of 5 V.



Fig. S7 (a) Current density–luminance–voltage characteristics of the devices WD2-1 and WD2-2.(b) EQE versus luminance characteristics of the devices WD2-1 and WD2-2.

Device	PE <sub>max/100/1000</sub> <sup>a</sup> [lm W <sup>-1</sup> ]	CE <sub>max/100/1000</sub> <sup>a</sup> [cd A <sup>-1</sup> ]	EQE <sub>max/100/1000</sub> <sup>a</sup> [%]	ССТ <sup>ь</sup> [K]	CIE(x, y) <sup>b</sup>	CRI <sup>b</sup>
WD2-1	50.1/32.0/21.1	44.7/35.5/30.0	16.3/16.0/14.2	2679	(0.49, 0.46)	86
WD2-2	43.4/26.7/18.0	38.6/30.6/25.8	15.3/15.1/13.4	2405	(0.49, 0.43)	84

Table S2. Summary of key EL parameters for three-color WOLEDs

 $^{\rm a}$  The maximum efficiencies and values taken at 100 and 1000 cd  ${\rm m}^{-2}$  ;  $^{\rm b}$  Measured at the voltage of 5 V.