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Dendritic Host Materials with Non-Conjugated Adamantane Core for Efficient Solution-Processed Blue Thermally Activated Delayed Fluorescence OLEDs

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Measurements and characterization

The ^{1}H and ^{13}C NMR spectra were tested on Bruker Avance 500 NMR spectrometer in $CDCl_3$ using tetramethylsilane as a reference. Matrix-assisted laser desorption ionization/time-of-flight (MALDI-TOF) mass spectra were measured on AXIMA CFR MS apparatus. Elemental analysis (EA) was tested via a Bio-Rad elemental analysis system. The decomposition temperature (T_d) and glass transition temperature (T_g) of the hosts were performed on the PerkinElmer-TGA 7 instrument under N_2 with a heating rate of 10 °C min^{-1}. Abs and PL spectra were recorded on PerkinElmer Lambda 35 UV/vis spectrometer and PerkinElmer LS50B spectrofluorometer, respectively. The phosphorescent spectra were measured in toluene at 77K with a gate time of 0.5 ms. CV experiments were performed with EG&G 283 (Princeton Applied Research) using three-electrode system (reference electrode: $Hg/HgCl_2$; counter electrode: platinum; working electrode: platinum). The measurements were carried out in dichloromethane, ferrocene was used as a standard and *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte. The HOMO energy levels were calculated according to the equation $E_{HOMO} = -e\,[E_{onset,\,ox} + 4.8V]$ where $E_{onset,\,ox}$ was the onset of the oxidation potential.

Device fabrication and characterization

Patterned glass substrates coated with indium tin oxide (ITO) were cleaned in an ultrasonic bath sequentially with detergent, isopropanol and distilled water. The substrates were treated with ultraviolet-ozone for 40 min after drying at 120 °C for 4 h. Then poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, (Clevious P AI4083), 30 nm) was spin-coated on the top of ITO and baked at 120 °C for 40 min, after which the substrutes were transferred to a glove box. The dendritic hosts and the blue TADF emitter (SpiroAC-TRZ, 10 and 20 wt%) were dissolved in chlorobenzene and filtered through a 0.22 mm filter, which was spin-coated on PEDOT:PSS as the emissive layer (EML, 40 nm). Afterwards, the substrate was loaded into a vacuum thermal evaporator and TSPO1 (8 nm) and TmPyPB (42 nm) were evaporated on top of the EML in sequence under the pressure of 10^{-6} torr. Finally, LiF (1 nm)/Al (100) nm were deposited subsequently as cathode. The current density-voltage and brightness-voltage curves were measured using Keithley 2400/2000 source meter coupled with a calibrated silicon photodiode at room temperature under ambient atmosphere. The EL spectra and CIE coordinates were obtained via a PR650 spectra colorimeter. EQEs of the devices were calculated on the basis of the current density, luminance and EL spectrum assuming a Lambertian emission distribution. According to the similar procedure, hole-only devices were fabricated for Ad-4D1 and Ad-4D2 with structure of ITO (130 nm)/PEDOT:PSS (30 nm)/ Ad-4D1 or Ad-4D2 (90 nm)/Au (60 nm).

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Experimental Section

General

The carbazole-based dendrons 3,6-di-*tert*-butyl-9*H*-carbazole (D1) and 3,6-bis(3,6-di-*tert*-butylcarbazol-*N*-yl)carbazole (D2) were synthesized according to the literature.[1]

Synthesis of 1,3,5,7-tetrakis(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)adamantane (Ad-4D1)

To a mixture of 1,3,5,7-tetrakis(4-iodophenyl)adamantane (0.47 g, 0.5 mmol), 3,6-di-*tert*-butyl-9*H*-carbazole (D1) (0.84 g, 2.4 mmol), $Pd_2(dba)_3$ (55 mg, 0.06 mmol), (t-Bu)$_3$PH-BF_4 (70 mg, 0.24 mmol) and *t*-BuONa (0.58 g, 6 mmol), 30 mL dry toluene was added under argon. The reaction was kept reflux for 48 h. After cooling to room temperature, the mixture was poured into water, extracted with dichloromethane. The combined organic phases were dried with anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified via silica gel column chromatography with petroleum/dichloromethane = 6 / 1 (v/v) as the eluent to get a white solid (0.62 g, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ[ppm] 8.15 (s, 8H), 7.83 (d, J = 10 Hz, 8H), 7.62 (d, J = 5 Hz, 8H), 7.46 (d, J = 10 Hz, 8H), 7.39 (d, J = 10 Hz, 8H), 2.49 (s, 12H), 1.47 (s, 72H). ^{13}C NMR (125 MHz, $CDCl_3$): δ[ppm] 147.8, 142.8, 139.3, 136.3, 126.7, 126.5, 123.5,123.3, 116.3, 109.2, 47.5, 39.5, 34.7, 32.0. MALDI-TOF (m/z): $[M+H]^+$ 1549.0. Found: C, 88.15; H, 8.24; N, 3.40. Calc. for $C_{114}H_{124}N_4$: C, 88.32; H, 8.06; N, 3.61.

Synthesis of Ad-4D2

Ad-4D2 was synthesized according to the procedure similar to that of Ad-4D1. Under argon, 30 mL was added to a mixture of 1,3,5,7-tetrakis(4-iodophenyl)adamantane (0.47 g, 0.5 mmol), 3,6-bis(3,6-di-*tert*-butylcarbazol-*N*-yl)carbazole (D2) (1.73 g, 2.4 mmol), $Pd_2(dba)_3$ (55 mg, 0.06 mmol), (t-Bu)$_3$PH-BF_4 (70 mg, 0.24 mmol) and *t*-BuONa (0.58 g, 6 mmol). The reaction was kept refluxing for 48h. Then the reaction mixture was cooled to room temperature, poured into water, and extracted with dichloromethane. The crude product was purified by silica gel column chromatography using petroleum/dichloromethane = 4 / 1 (v/v) as the eluent. The obtained product was white powder (1.20 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ[ppm] 8.26 (s, 8H), 8.16 (s, 16H), 8.01 (d, J = 10 Hz, 8H), 7.84 (d, J = 5 Hz, 8H), 7.69 (d, J = 5 Hz, 8H), 7.62 (d, J = 10 Hz, 8H), 7.45 (d, J = 10 Hz, 16H), 7.33 (d, J = 10 Hz, 16H), 2.64 (s, 12H), 1.45 (s, 144H). ^{13}C NMR (125 MHz, $CDCl_3$): δ[ppm] 148.8, 142.6, 140.5, 140.2, 135.7, 131.0, 127.3, 127.0, 126.0, 124.0, 123.6, 123.2, 119.4, 116.3, 111.1, 109.1, 47.5, 39.8, 34.7, 32.1. MALDI-TOF (m/z): $[M+H]^+$ 3317.9. Found: C, 87.39; H,7.59; N, 4.96. Calc. for $C_{242}H_{244}N_{12}$: C, 87.53; H, 7.41; N, 5.06.

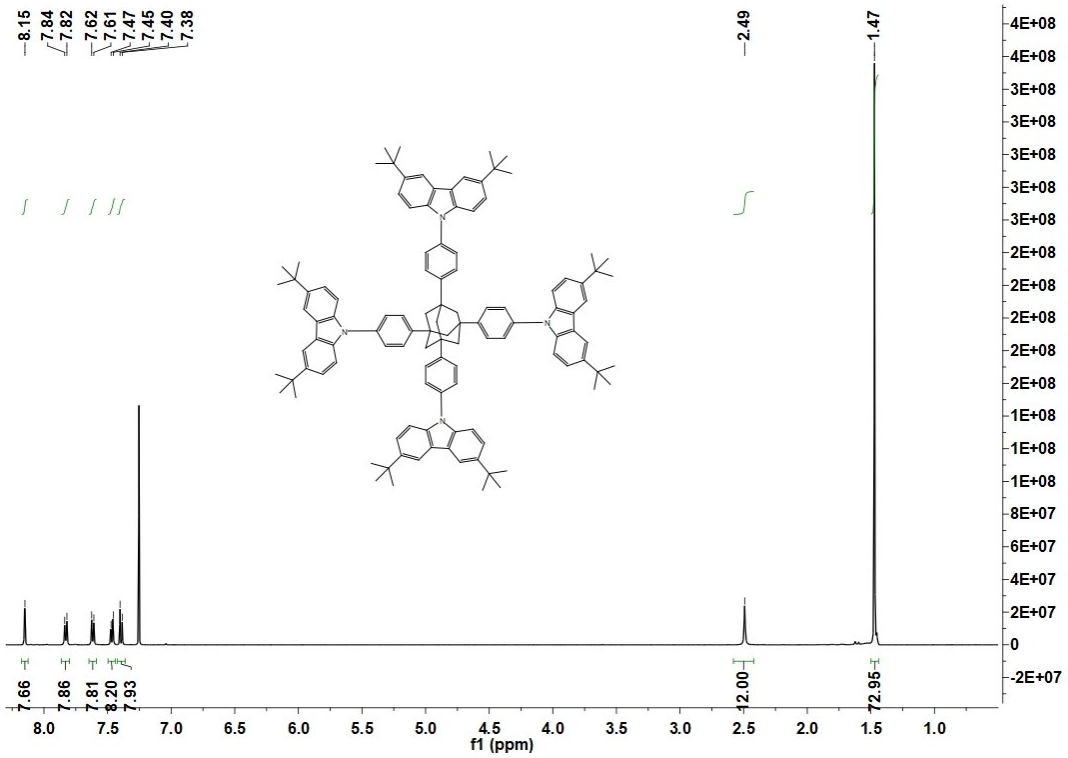

Fig. S1 ^{1}H NMR spectrum of Ad-4D1

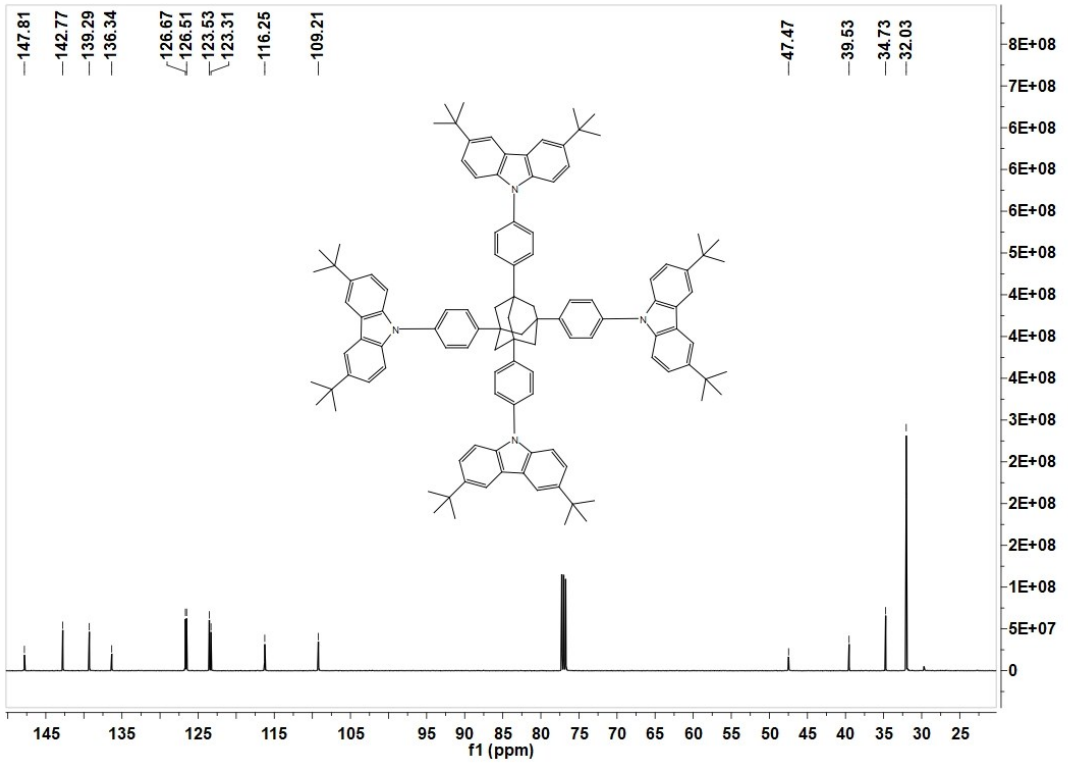

Fig. S2 ^{13}C NMR spectrum of Ad-4D1

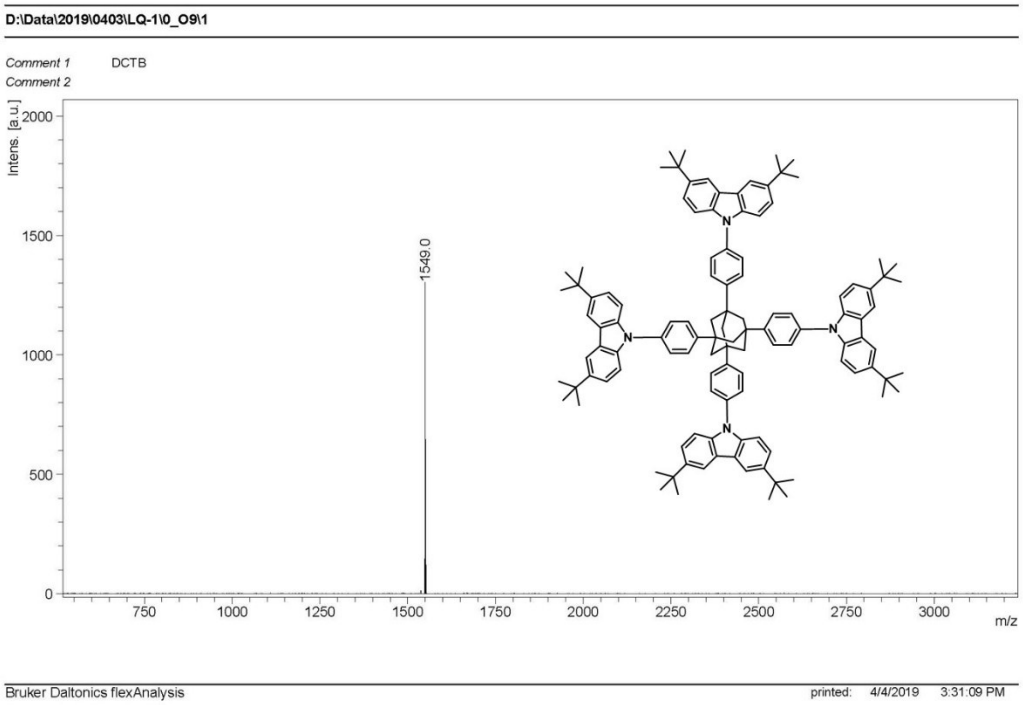

Fig. S3 Mass (MALDI-TOF) spectrum of Ad-4D1

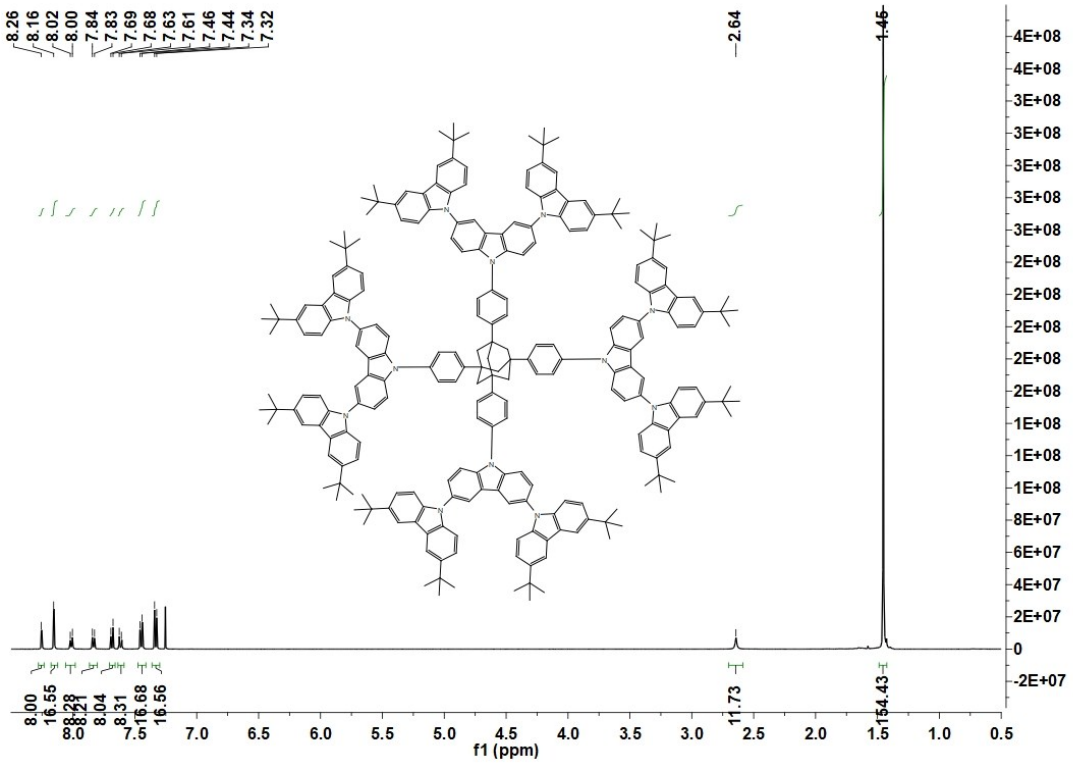

Fig. S4 ^{1}H NMR spectrum of Ad-4D2

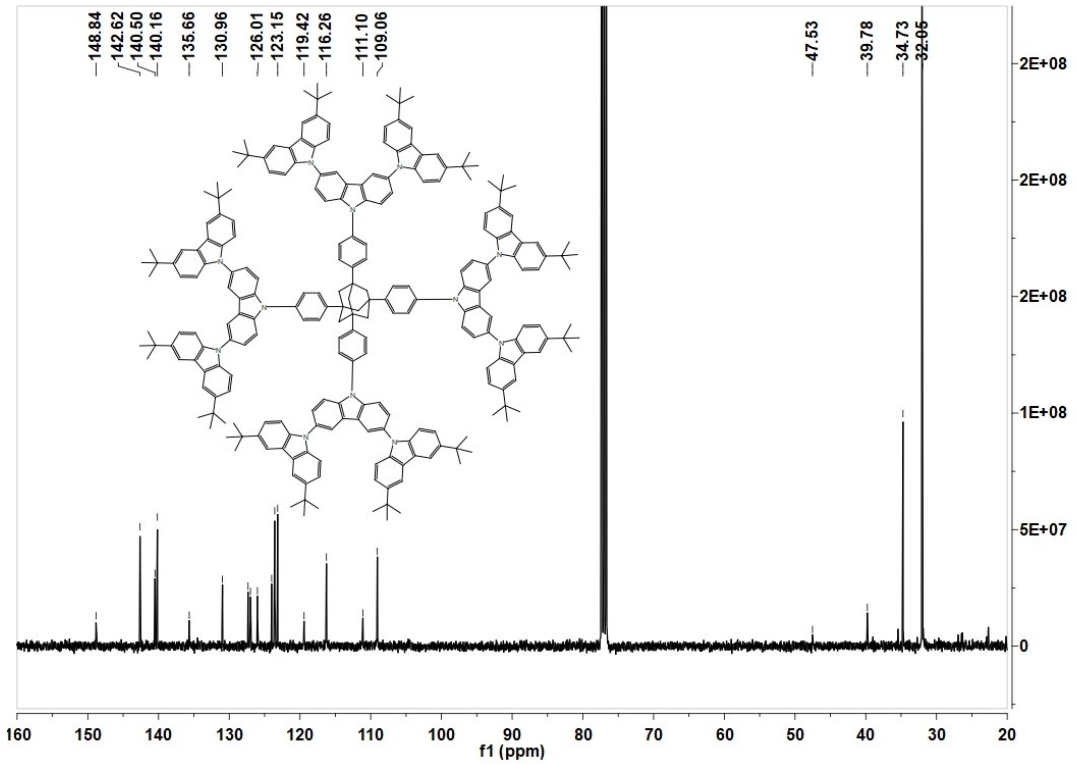

Fig. S5 ^{13}C NMR spectrum of Ad-4D2

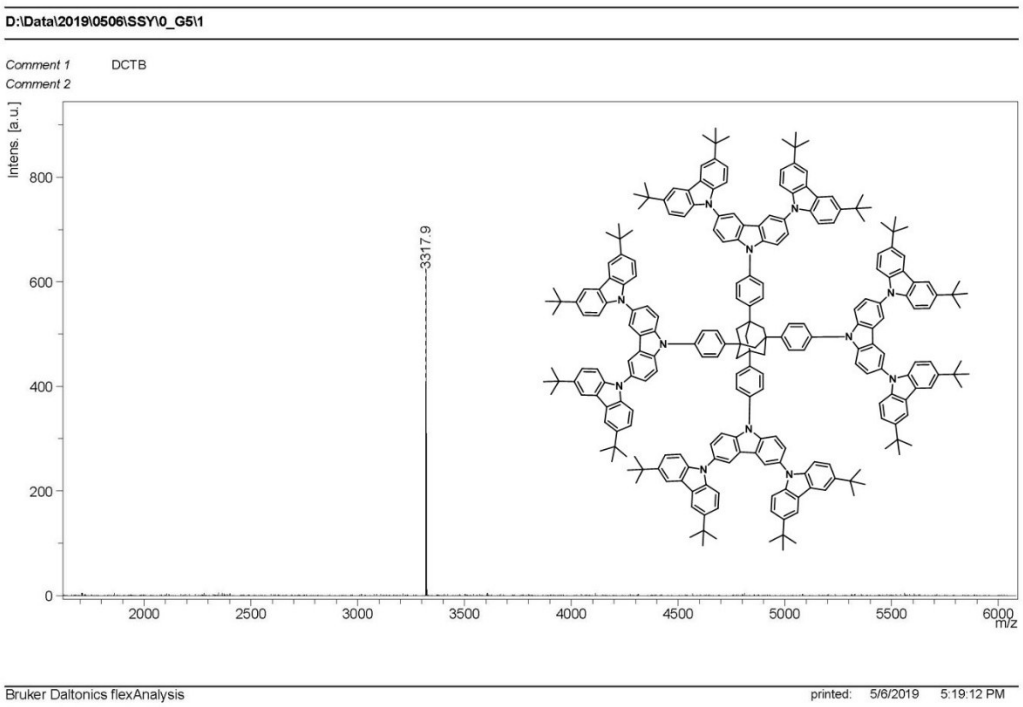

Fig. S6 Mass (MALDI-TOF) spectrum of Ad-4D2

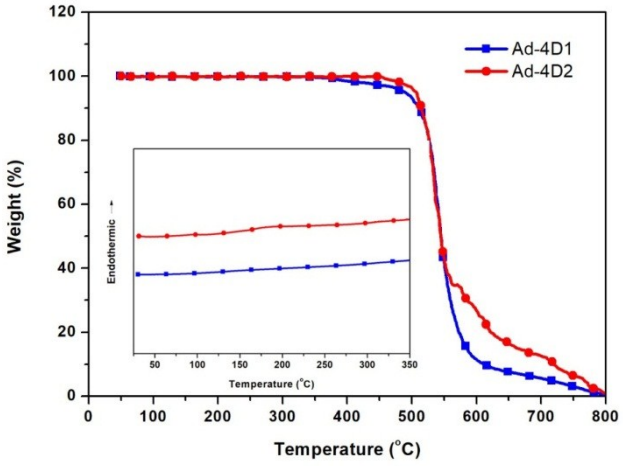

Fig. S7 TGA and DSC (inset) curves for Ad-4D1 and Ad-4D2 recorded at a heating rate of 10 °C min^{-1} under N_2.

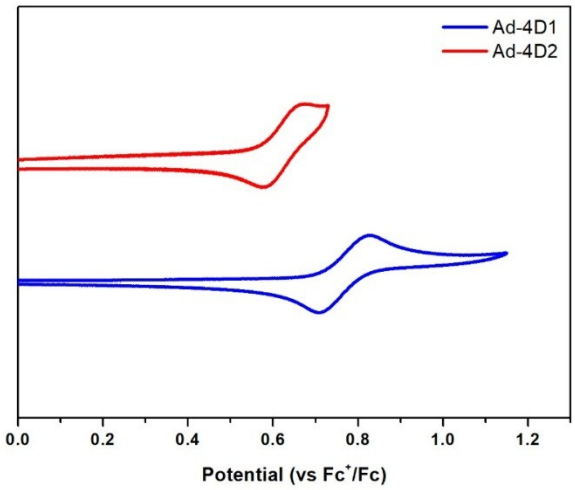

Fig. S8 CV curves of Ad-4D1 and Ad-4D2 in dichloromethane

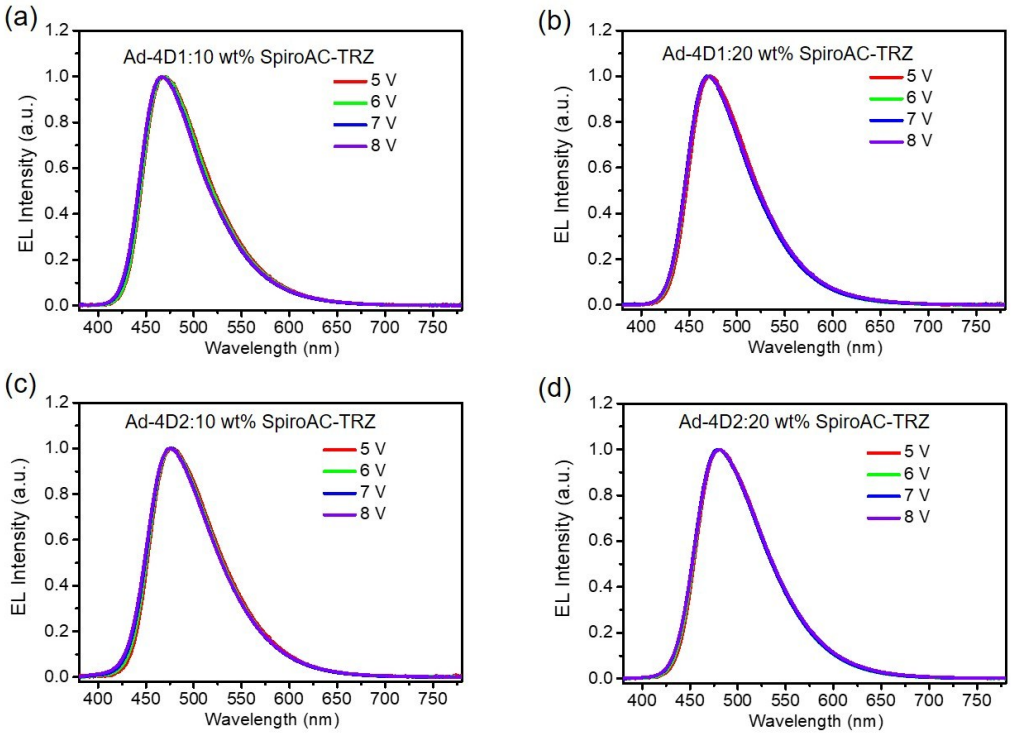

Fig. S9 EL spectra under different driving voltages for the solution-processed blue TADF OLEDs

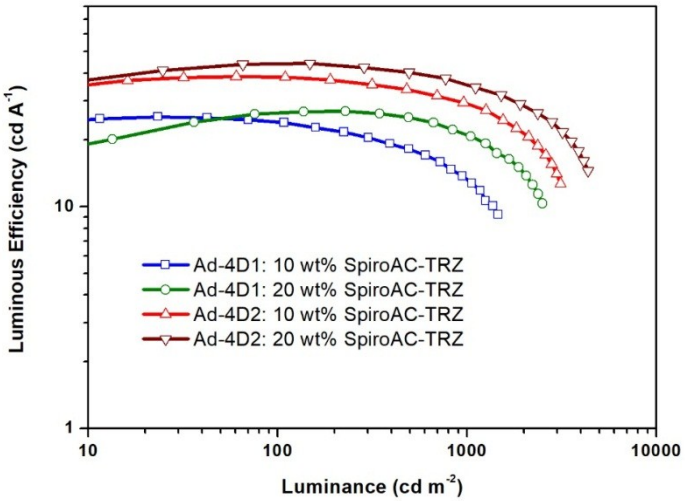

Fig. S10 *LE-L* characteristics for the solution-processed blue TADF OLEDs

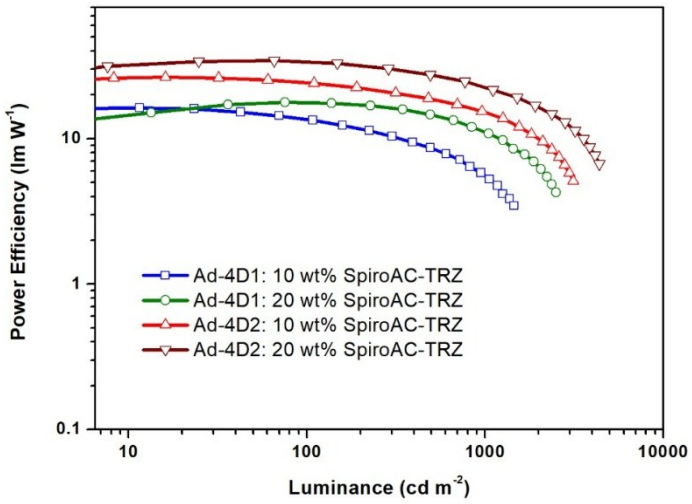

Fig. S11 *PE-L* characteristics for the solution-processed blue TADF OLEDs

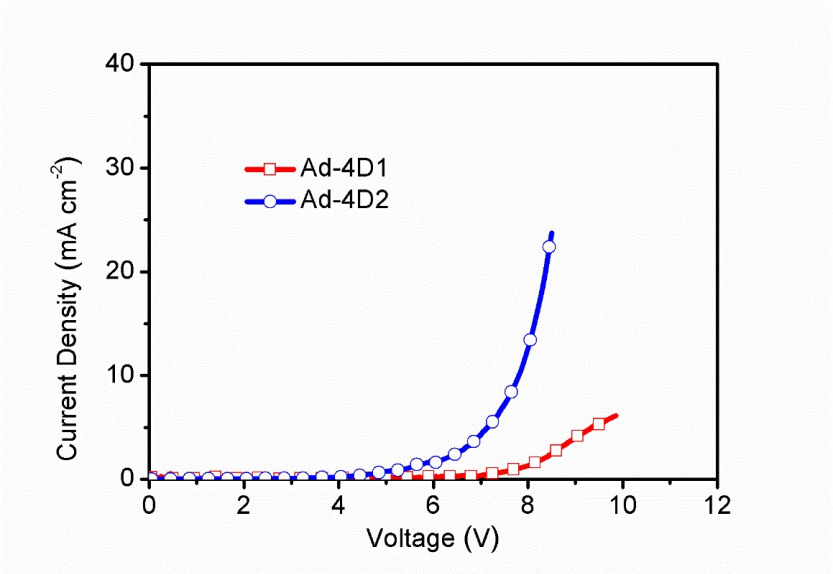

Fig. S12 *J-V* characteristics of the hole-only devices for Ad-4D1 and Ad-4D2 with configuration of ITO (130 nm)/PEDOT:PSS (30 nm)/ Ad-4D1 or Ad-4D2 (90 nm)/Au (60 nm).

1 J. Ding; J. Lu; Y. Cheng; Z. Xie; L. Wang; X. Jing and F. Wang, *Adv. Funct. Mater.*, 2008, **18**, 2754-2762.