

Supporting Information

Regulating optoelectronic properties of red TADF emitters based on an acenaphthylene-1,2-dione through electron-donating engineering

Shujing Jin, Bin Ma, Zhongxin Zhou, Jie Pan,
Yongtao Zhao, Weiguo Zhu,^{a*} and Yu Liu^{a*}

^aSchool of Materials Science and Engineering, Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, National Experimental Demonstration Center for Materials Science and Engineering, Changzhou University, Changzhou 213164, China

*Authortowhom any correspondence should be addressed.

zhuwg18@126.com (W. Zhu)

liuyu03b@126.com (Y. Liu)

Experimental Section

Table of Contents

1. Experimental Section	2
1.1. General experimental methods	2
1.2. Device fabrication and measurement	3
2. Synthetic	3
2.1. Synthetic details	4
2.2. Supportive figures for NMR characterization	7
3. Thermogravimetric analysis and electrochemical properties	10
4. Photophysical properties	10
5. Electroluminescent properties	10

1. Experimental Section

1.1. General experimental methods

Materials Unless otherwise specified, most of the solvents and reagents are commercially available (TCI, energy chemical) and used without further purification. Suzuki reaction were conducted under an N₂ atmosphere using the aard Schlenk line techniques to avoid the oxidation of the reactants by oxygen. Flash column chromatography and preparative TLC were carried out using silica gel. All the ¹H and ¹³C NMR spectra were recorded on Bruker Avance III 400 and 500 MHz NMR spectrometer using CDCl₃ as the solvent and TMS as the internal standard. High-resolution mass spectra were performed using auto flex MALDI-TOF mass spectrometer. Thermogravimetric analysis (TG-DTA) was performed by Bruker TG-DTA 2400SA with a heating rate of 10 °C min⁻¹ from 25 °C to 600 °C under nitrogen atmosphere. the temperature at 5% weight loss was used as the decomposition temperature (*T_d*). At room temperature, cyclic voltammograms (CV) were performed by the electrochemical workstation CHI630E, the oxidation potential (*E_{ox}*) was tested using the purified dry dichloromethane as the solvent and 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as the electrolyte. Using platinum wire as the counter electrode, Ag/AgCl as the reference electrode, a platinum spar (0.8 mm) working electrode, and ferrocene (Fc/Fc⁺) as the internal standard, the cyclic voltammetry curves were measured by a scanning speed at 100 mV/s. UV-Vis absorption spectra of the two NIR-TADF materials were obtained at room temperature using a Shimadzu UV-2600, The photoluminescence (PL) spectra were recorded on Edinburgh FLS1000, while time-resolved measurements were carried out using time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh FLS1000), and EPL 450 laser were used as excitation source, and delayed life VPL450 laser in the Edinburgh Transient Fluorescence Spectrometer. Fluorescence and phosphorescence spectra at 77 K were measured in degassed toluene using an Edinburgh FLS1000 transient fluorescence spectrophotometer. The photoluminescence quantum yields (PLQYs) were recorded with an integrating sphere coupled with Edinburgh FLS1000 under ambient condition.

Quantum chemical calculations were performed with Gaussian 09 program, in which density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed at the B3LYP/def2SVP level. The optimal geometries, as well as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for both emitters were obtained by DFT calculations. The excited states (S_n and T_n states) and NTOs (natural transition orbitals) were obtained by TD-DFT calculations.^[1,2]

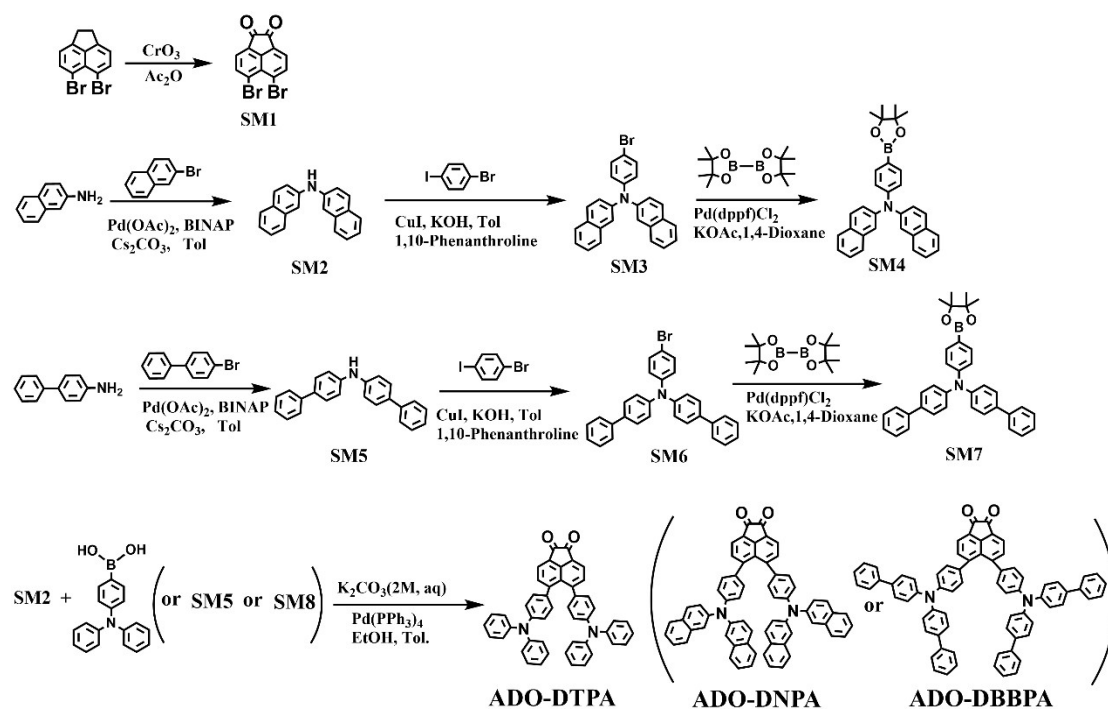
1.2. Device fabrication and measurement

The structure of the doped devices is ITO/PEDOT:PSS (40 nm)/PVK (10 nm)/CBP:emitter (x wt%,30 nm)/DPEPO (20 nm)/TmPyPB (45 nm)/LiF (1.2 nm)/Al (120 nm).³ All devices with the emitting layers (EMLs) based on CBP doped with emitter, with different doping concentrations of 10 wt%, 20 wt%, 30 wt% and 100 wt%, respectively. The PEDOT:PSS is used as a hole injection layer, the TmTyPB is used as an electron transport layer (ETL) and a hole blocking layer (HBL), and LiF is used as an electron injection layer. The films of PEDOT:PSS(40nm) were spin-coated on precleaned ITO glass substrates and annealed at 150 °C for 20 min. Then the light emitting layer and the layer of TmPyPb was evaporated onto the active layer. Finally, the LiF/Al layer was deposited on the top of the emitting layer. In order to prevent degradation and emission quenching caused by oxygen and water, all the above operations are performed in a nitrogen atmosphere or a vacuum state (1×10^{-4} Pa), and the OLED is encapsulated before characterization. The EL spectra and current density(J)–voltage(V)–radiance(R) curves were obtained using a PHOTORESEARCH Spectra Scan PR735 photometer and a KEITHLEY 2400 Source Meter constant current source at room temperature. The EQE values were calculated by assuming a Lambertian distribution.

2. Synthetic

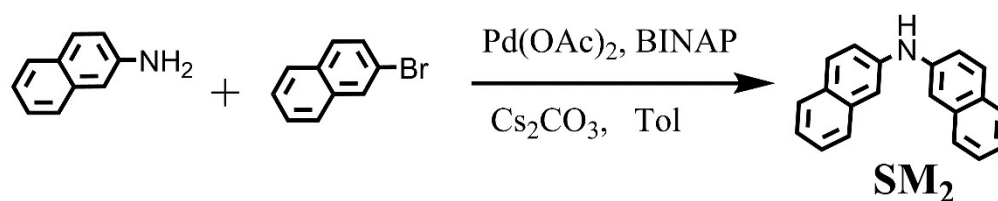
Herein, the synthetic routes of ADO-DTPA, ADO-DNPA and ADO-DBBPA is shown in Scheme S1. Some intermediates (SM1, SM5, SM6 and SM7) and their corresponding target compounds (ADO-DTPA and ADO-DBBPA) were reported by

our previous work.^[3] Meanwhile, the synthesized process of SM2, SM3, SM4 and ADO-DNPA are described below. All other chemicals and solvents used were purchased from commercial suppliers without further purification.



Scheme S1. Synthetic routes of ADO-DTPA, ADO-DNPA and ADO-DBBPA.

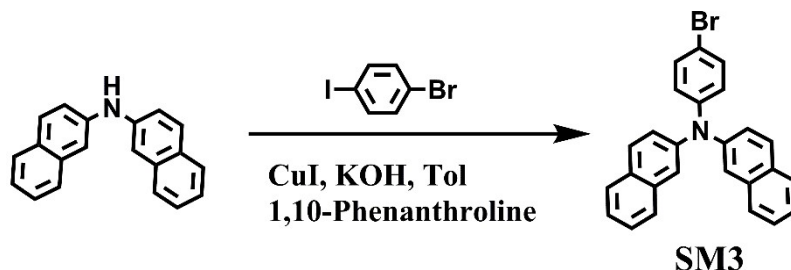
2.1. Synthesis of di(naphthalen-2-yl)amine (SM2)



In 500 mL three-mouth flask, a mixture of 2-naphthylamine (10.0 g, 48.5 mmol), 2-bromonaphthalene (8.5 g, 58.2 mmol), Pd(PPh₃)₄ (500.0 mg, 0.49 mmol), 1,1'-binaphthyl-2,2'-bis(diphenyl phosphine) (BINAP) (0.6 g, 0.95 mmol) and CsCO₃ (23.0 g, 97.0 mmol) were dissolved in toluene solution (200 mL) and stirred at 120 °C and refluxed for 24 h under nitrogen atmosphere. The reaction mixture was filtered, and the filtrate was concentrated by evaporation, and the residue was separated by column chromatography using petroleum ether/dichloromethane (1:2, V:V) as eluent to give a white solid of 12.5 g in 80% yield. ¹H NMR (400 Hz, CDCl₃, TMS, δppm): δ 7.78 (t, *J* = 7.9 Hz, 4H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 2.1 Hz, 2H), 7.45 – 7.39 (m, 2H),

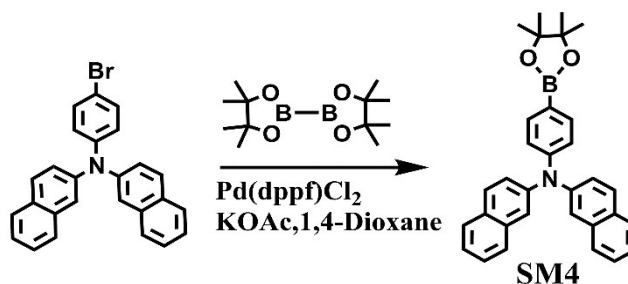
7.32 (td, $J = 9.1, 1.8$ Hz, 4H), 6.05 (s, 1H).

2.2. Synthesis of *N*-(4-bromophenyl)-*N*-(naphthalen-2-yl)naphthalen-2-amine (SM3)



In 250 mL three-mouth flask, a mixture of **SM2** (6.4 g, 23.6 mmol), 1-bromo-4-iodobenzene (5.6 g, 19.6 mmol), CuI (72 mg, 0.3 mmol), 1,10-phenanthroline (68 mg, 0.3 mmol) and KOH (5.48 g, 98 mmol) were dissolved in 150 mL toluene solution and stirred at 130 °C and refluxed for 24 h under nitrogen atmosphere. The reaction mixture was filtered, and the filtrate was concentrated by evaporation, and the residue was separated by column chromatography using petroleum ether/dichloromethane (1:3, V:V) as eluent to give a white solid of 6.54 g in 78% yield. ^1H NMR(400 Hz, CDCl_3 , TMS, δ ppm): δ 7.75 (td, $J = 15.2, 14.2, 7.9$ Hz, 6H), 7.59 (d, $J = 7.9$ Hz, 2H), 7.51 (s, 2H), 7.40 (p, $J = 6.5$ Hz, 4H), 7.33 (dd, $J = 8.8, 2.1$ Hz, 2H), 7.14 (d, $J = 8.2$ Hz, 2H), 1.35 (s, 12H).

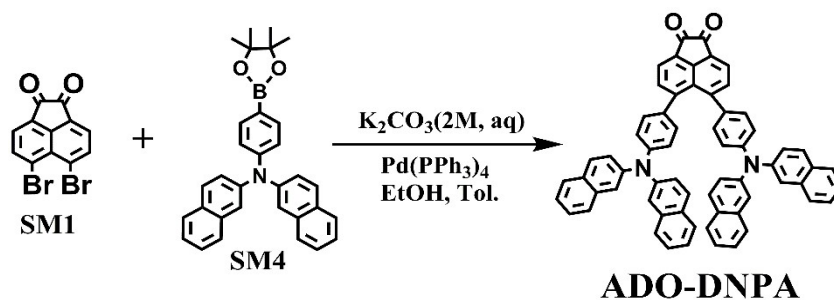
2.3. Synthesis of *N*-(naphthalen-2-yl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) naphthalen-2-amine (SM4)



In 250 mL three-mouth flask, a mixture of **SM3** (6.0 g, 13.6 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (4.13 g, 16.3 mmol), Pd(dppf) Cl_2 (90 mg, 0.13 mmol) and K_2CO_3 (6.7 g, 68.0 mmol) were dissolved in 150 mL 1, 4-dioxane solution, then stirred at 110 °C and refluxed for 24 h under nitrogen atmosphere. The reaction mixture was filtered, and the filtrate was concentrated by evaporation, and the residue was separated by column chromatography using petroleum

ether/dichloromethane (1:2, V:V) as eluent to give a white solid of 3.54 g in 57% yield. ¹H NMR (400 Hz, CDCl₃, TMS, δppm): δ = 7.81 - 7.69 (td, *J* = 15.2, 14.2, 7.9, 6H), 7.62 - 7.57 (d, *J* = 7.9, 2H), 7.53 - 7.49 (s, 2H), 7.44 - 7.36 (p, *J* = 6.5, 4H), 7.35 - 7.30 (d, *J* = 8.8, 2H), 7.17 - 7.11 (d, *J* = 8.2, 2H), 1.38 - 1.31 (s, 12H).

2.4. *Synthesis of 5,6-bis(4-(di(naphthalen-2-yl)amino)phenyl)acenaphthylene-1,2-dione (ADO-DNPA)*



Compound **SM1** (1.00 g, 2.90 mmol), **SM4** (2.83 g, 6.00 mmol) and Pd(PPh₃)₄ (0.25 g, 0.20 mmol) were dissolved in THF (60 mL) under an argon atmosphere. After stirring the resultant mixture at 50 °C for 10 min, 20 mL of degassed K₂CO₃ (2M) aqueous was added and then the mixture was heated to reflux overnight. The reaction mixture was cooled down to room temperature, and the solvent was removed under reduced pressure. The crude product was dissolved in 60 mL of dichloromethane and washed with water. The organic layer dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. The remaining solid was purified by column chromatography using petroleum ether/dichloromethane (1/3) as eluent to give 1.12 g of a red solid in 36% yield. ¹H NMR (400 Hz, CDCl₃, TMS, δppm): δ 8.22 (d, *J* = 7.3 Hz, 1H), 7.87 (d, *J* = 7.3 Hz, 1H), 7.73 (dd, *J* = 23.5, 8.4 Hz, 4H), 7.62 (s, 2H), 7.48 (dd, *J* = 12.9, 8.5 Hz, 4H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.10 – 6.96 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 187.56, 147.48, 145.94, 143.74, 133.51, 133.30, 130.96, 129.50, 129.42, 128.42, 126.99, 126.57, 126.22, 125.89, 125.43, 124.05, 124.03, 120.89, 120.85, 120.39. TOF-MS (ESI):*m/z* 869.3164. Calcd for C₅₁H₃₂N₄O: 869.04.

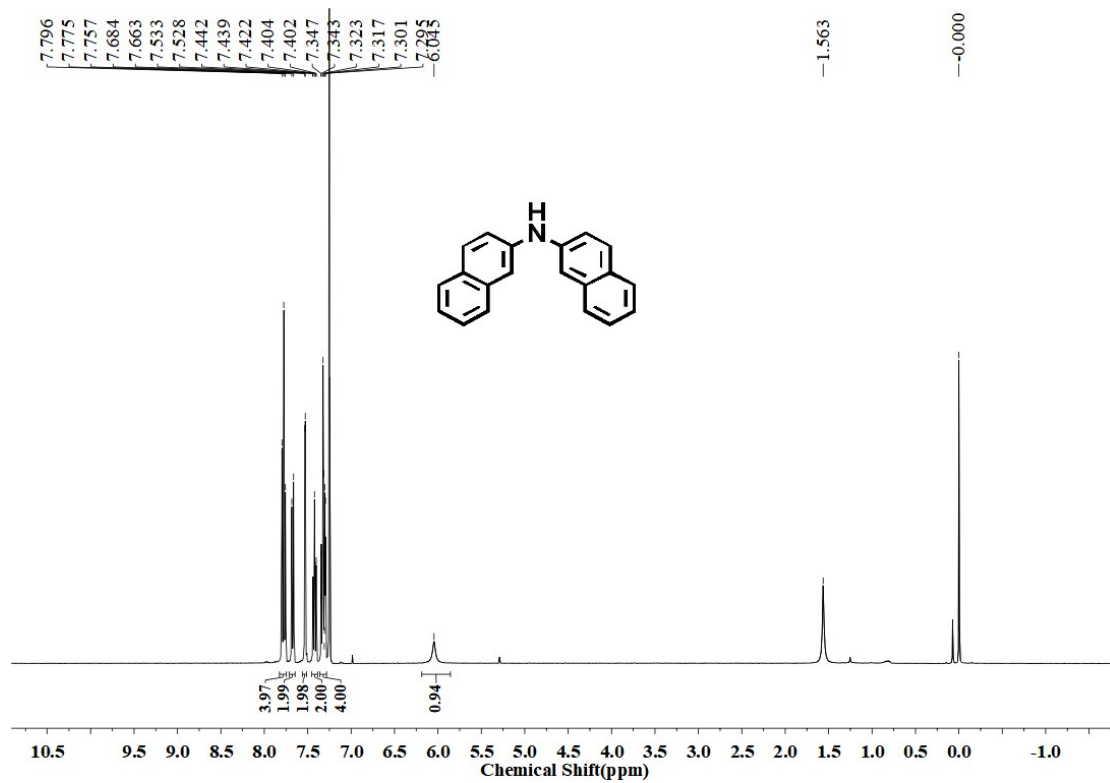


Fig.S1. ¹H NMR spectrum of SM2 in CDCl₃.

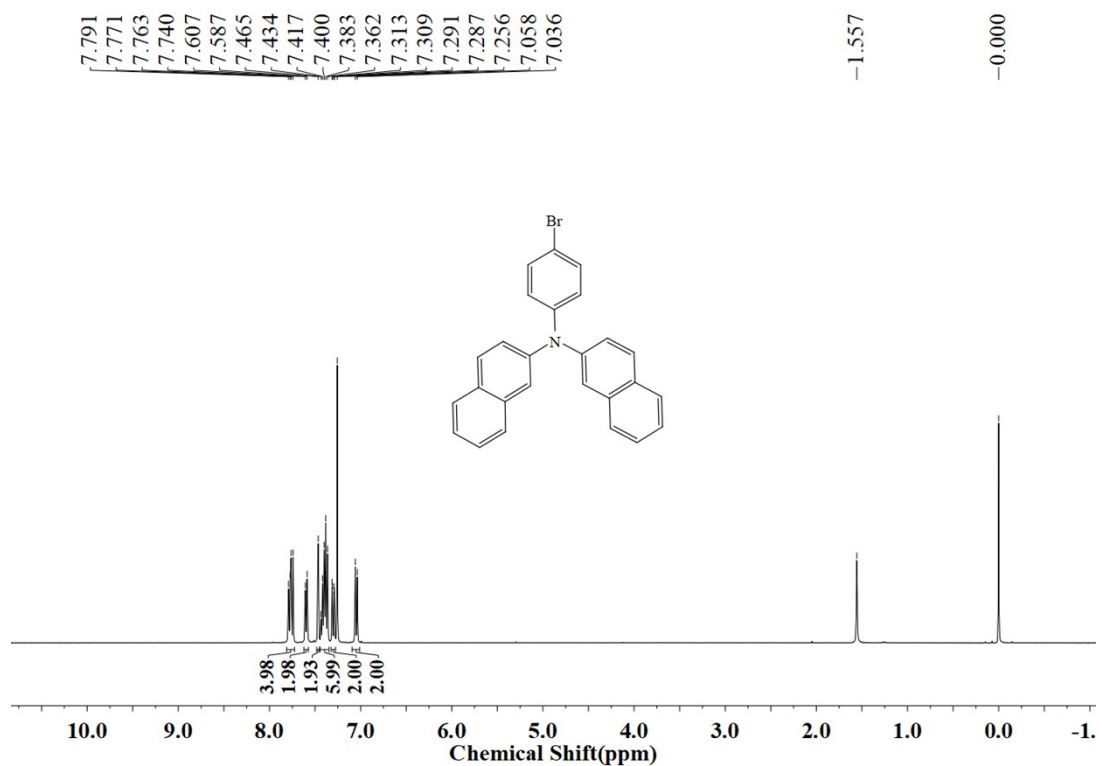


Fig.S2. ¹H NMR spectrum of SM3 in CDCl₃.

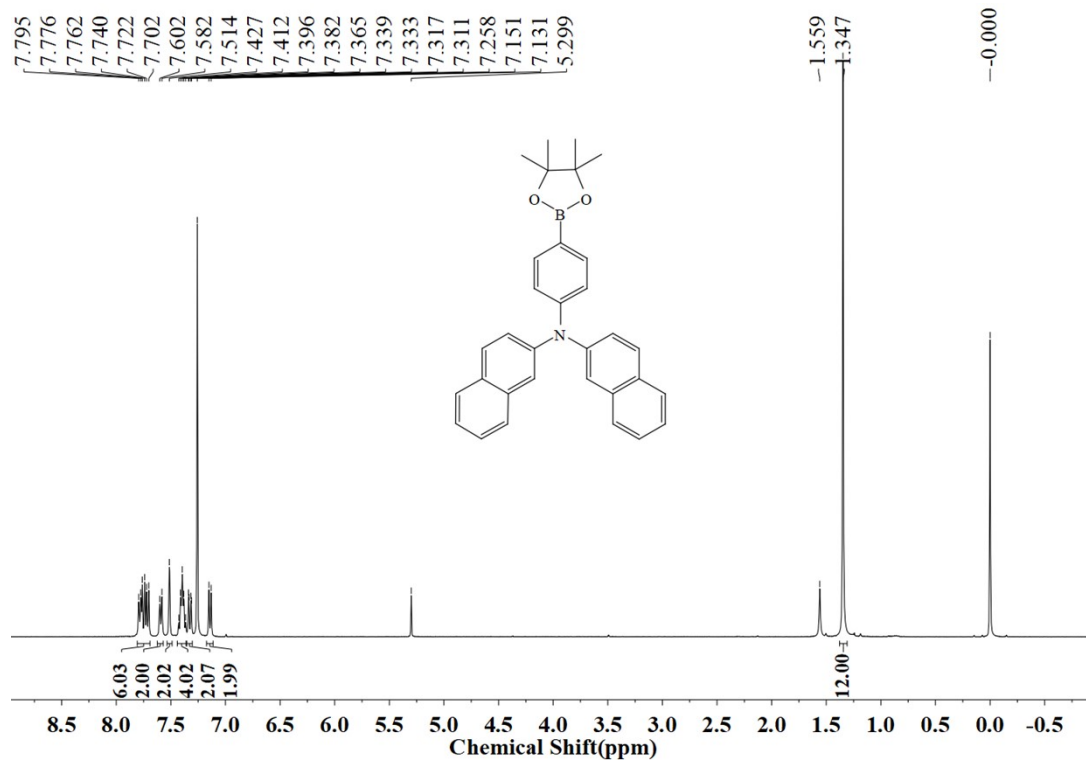


Fig.S3. ¹H NMR spectrum of SM4 in CDCl₃.

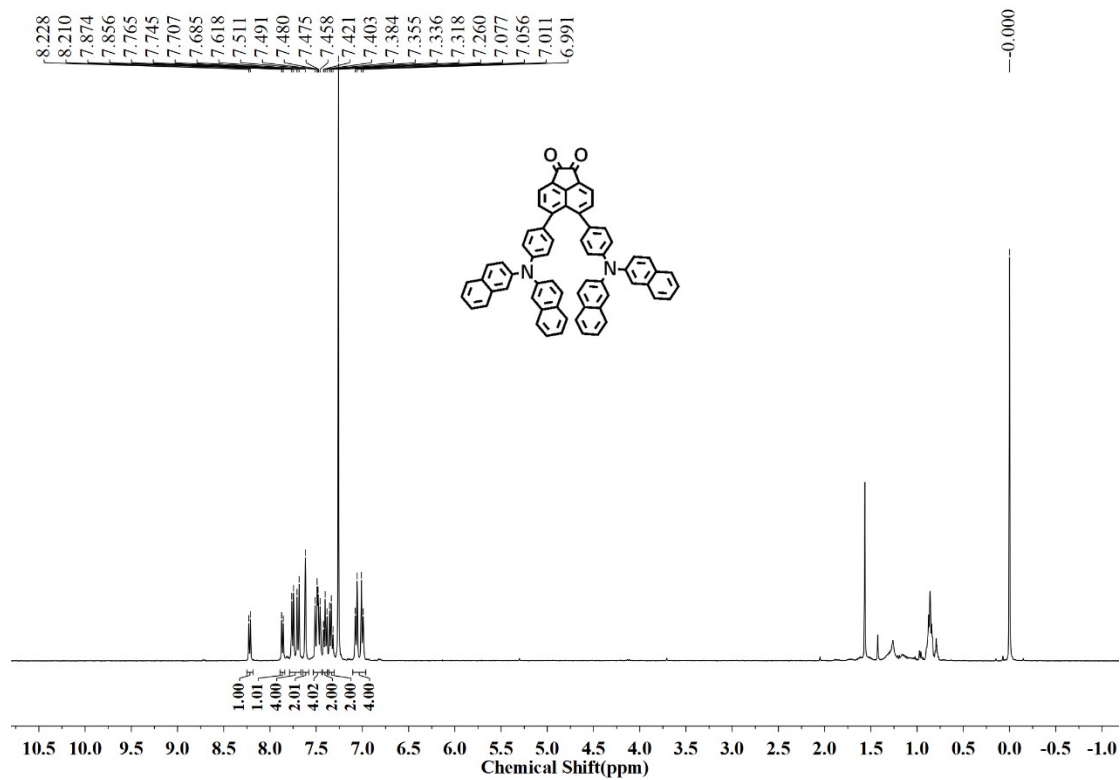


Fig.S4. ¹H NMR spectrum of ADO-DNPA in CDCl₃.

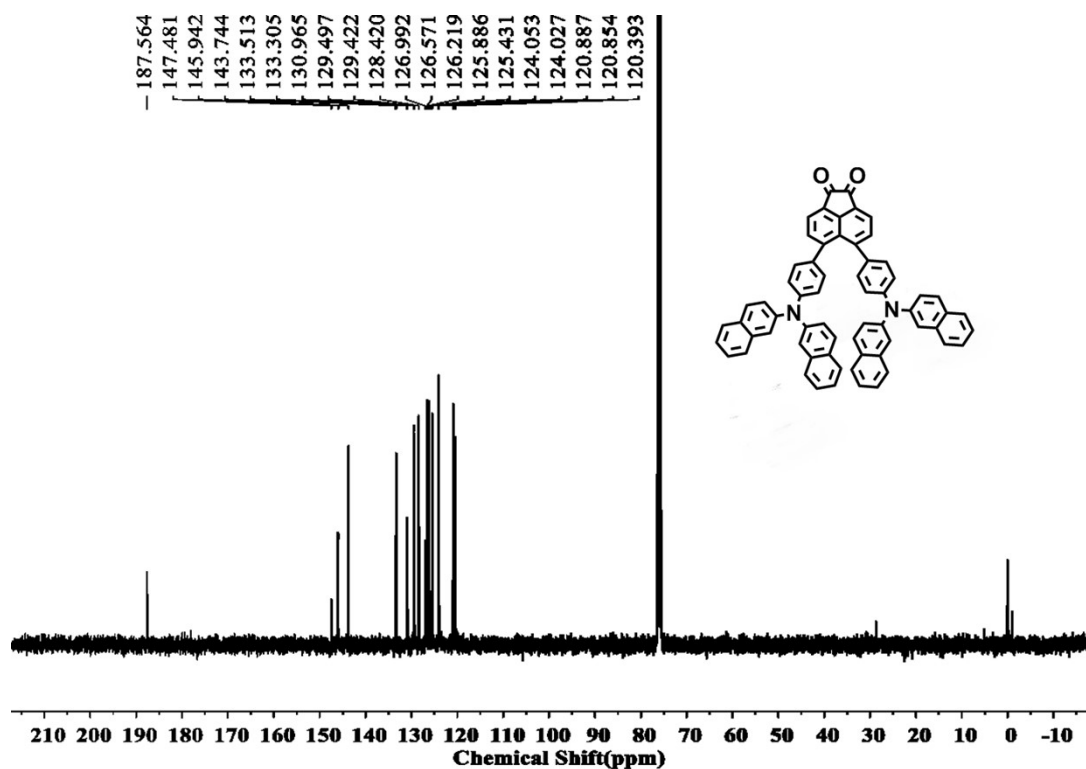


Fig.S5. ^{13}C NMR spectrum of ADO-DNPA in CDCl_3 .

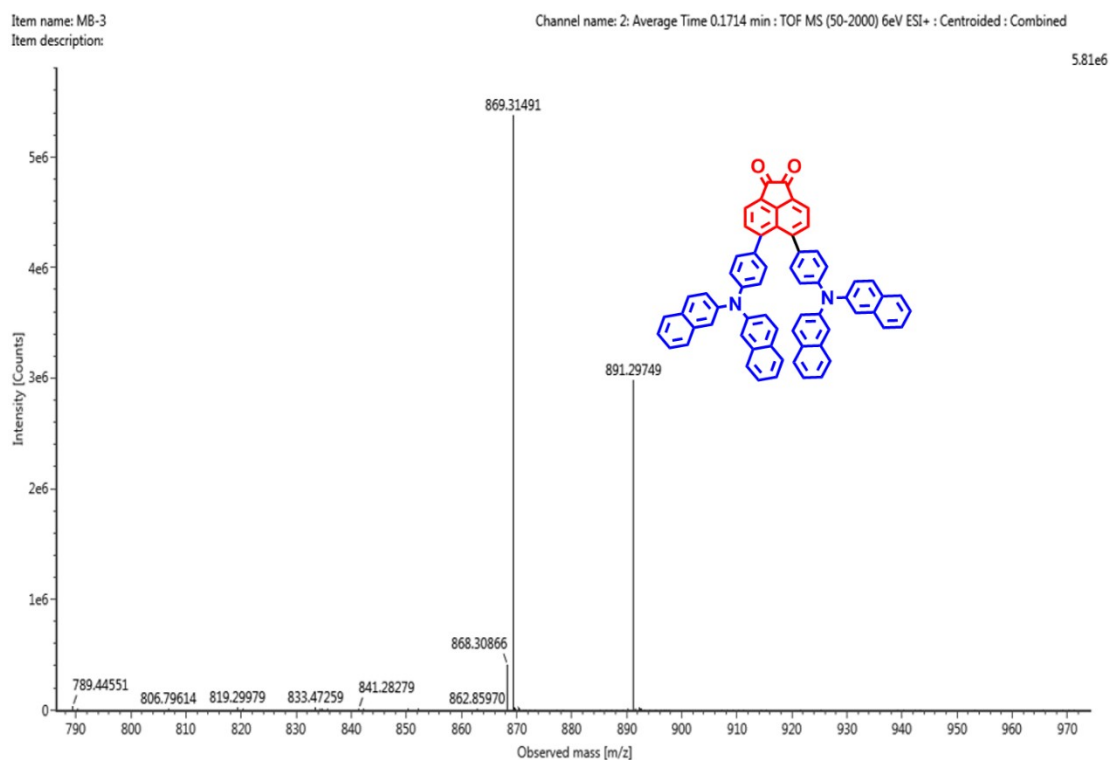


Fig.S6. MALDI-TOF-MS spectrum $[\text{M}+\text{Na}^+]$ of ADO-DNPA.

3. Thermogravimetric analysis and electrochemical properties.

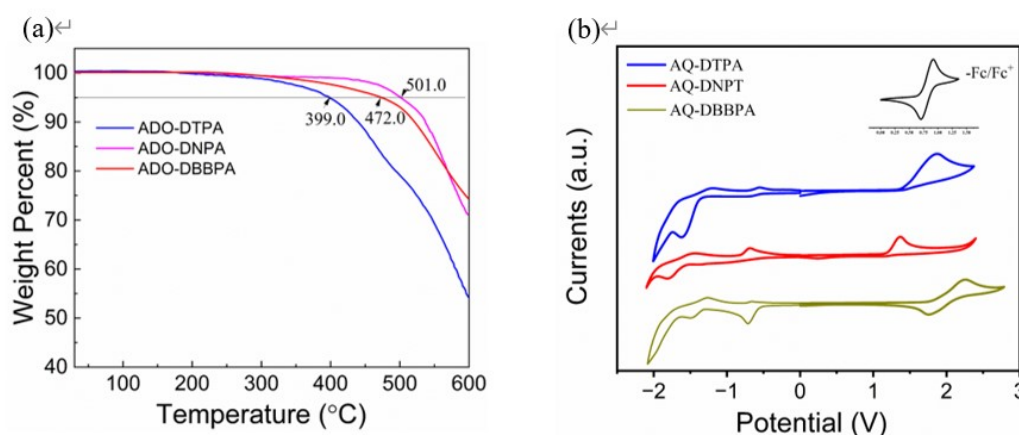


Fig.S7. TGA analysis and CV curves of the three emitters.

4. Photophysical properties

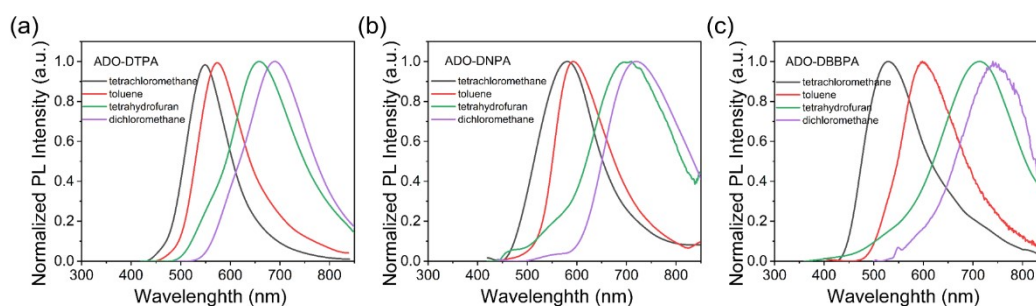


Fig.S8. PL spectra of (a) ADO-DTPA, (b) ADO-DNPA and (c) ADO-DBBPA in solvents with different polarity ($\lambda_{ex} = 580$ nm).

5. Electroluminescent properties

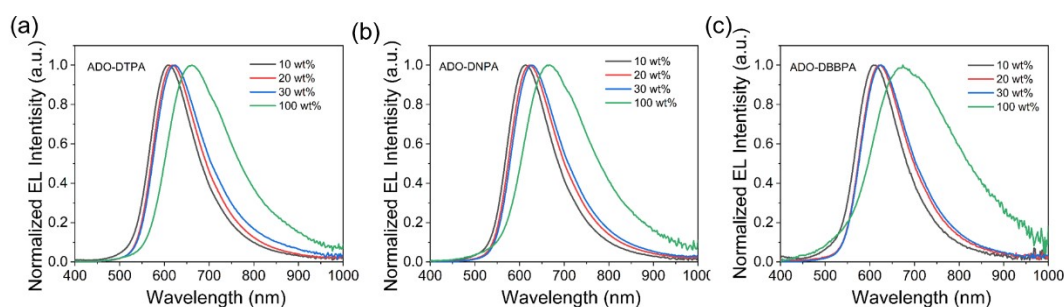


Fig.S9. EL spectra curves of (a) ADO-DTPA, (b) ADO-DNPA and (c) ADO-DBBPA doped devices at various concentrations from 10 to 100 wt % into CBP, respectively.

Table S1. Photophysical parameters for the CBP films doped with 20 wt% of different emitters.

^a Doping Ratios	^b τ_p/Φ_p (ns/%)	^c τ_d/Φ_d (μ spk /%)	^d k_p (10^8 s ⁻¹)	^e k_d (10^4 s ⁻¹)	^f k_{ISC} (10^8 s ⁻¹)	^g k_{RISC} (10^3 s ⁻¹)	^h k_r (10^6 s ⁻¹)	ⁱ k_{nr} (10^7 s ⁻¹)
20%TPA	2.2/1.03	25.86/6.77	4.59	3.87	3.99	3.02	4.71	5.57
20%NPA	1.2/0.28	23.94/7.95	8.03	8.03	7.76	3.44	2.23	2.48
20%BBPA	1.7/0.73	17.22/9.42	5.77	5.77	5.36	5.89	4.20	3.72

^aTPA, NPA and BBPA replaced with ADO-DTPA, ADO-DNPA, and ADO-DBBPA, respectively.

^bPrompted lifetime (τ_p) and Quantum efficiency (Φ_p). ^cDelayed fluorescence (τ_d) lifetime and Quantum efficiency (Φ_d). ^d k_p is the rate constant of prompt fluorescence. ^e k_d is the rate constant of delayed fluorescence. ^f k_{ISC} is the rate constants of ISC. ^g k_{RISC} is the rate constant of RISC; ^h k_r is the rate constants of radiative. ⁱ k_{nr} is the rate constants of non-radiative.

Table S2. EL performance of the three emitters-doped devices

Guest	Doping ratio (wt%)	$\lambda_{EL\ max}$ (nm)	V_{on} (V)	EQE_{max} (%)	L_{max} (cd/m ²)	CIE (x, y)
ADO-DTPA	10	608	7.6	1.214	158.2	(0.56, 0.42)
	20	618	6.8	1.324	282.8	(0.58, 0.39)
	30	626	6.4	0.839	309.5	(0.59, 0.38)
	100	662	5.6	0.131	46.94	(0.61, 0.36)
ADO-DNPA	10	614	7.6	1.268	165.5	(0.57, 0.41)
	20	624	6.8	1.462	328.6	(0.59, 0.40)
	30	626	6.4	0.995	348.7	(0.60, 0.40)
	100	668	5.6	0.0556	42.22	(0.59, 0.39)
ADO-DBBPA	10	610	7.2	1.467	222.3	(0.55, 0.41)
	20	626	6.4	1.479	300.1	(0.59, 0.39)
	30	627	6.0	1.178	369.9	(0.59, 0.39)
	100	674	6.0	0.0687	33.45	(0.55, 0.39)

References:

- [1] Q. Zhang, H. Kuwabara, W. Potscavage, J. Huang, Y. Hatae, T. Shibata and C. Adachi, *J. Am. Chem. Soc.*, 2014, **136**, 18070-18081.
- [2] Y. Yuan, Y. Hu, Y. Zhang, J. Lin, Y. Wang, Z. Jiang, L. Liao and S. Lee, *Adv.*

- Fun. Mater.*, 2017, **27**, 1700986.
- [3] B. Ma, Z. Ding, D. Liu, Z. Zhou, K. Zhang, D. Dang, S. Zhang, S. Su, W. Zhu and Y. Liu, *Chem. Eur. J.* 2023, **29**, e202301197.
- [4] J. Bergner, C. Walla, F. Rominger, A. Dreuw and M. Kivala, *Chem. Eur. J.* 2022, **28**, e202201554.