

Supporting Information

Highly Efficient Deep Blue Organic Light-emitting Diodes (OLEDs) Based on Hot-exciton Materials with Multiple Triplet Excitons Conversion Channels

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S1 Materials and Measurements

S1.1 Materials

All raw materials involved in the synthesis process were purchased from Aldrich Chemical Co. or Energy Chemical Co., China. The organic and metallic materials for transporting layers in OLEDs fabrication were purchased from P-OLED (Shanghai) Technology CO., LTO. The other organic solvents and reagents were all commercially available analytical-grade products and used as received without further purification.

S1.2 Measurements

NMR spectra were recorded on a Mercury 500 spectrometer. MALDI-TOF-MS mass spectra were measured using an AXIMA-CFRTM plus instrument. The dates of thermal gravimetric analysis (TGA) are from Perkin-Elmer thermal analysis system with the temperature of 50-800 °C under a heating rate of 10 °C /min and the nitrogen atmosphere. The dates of Differential scanning calorimetry (DSC) are from NETZSCH (DSC-204) instrument with the temperature of 50-500 °C at a heating rate of 10 °C /min and a nitrogen flow rate of 80 mL/min. UV-vis absorption spectra were measured on a Hitachi U-4100 spectrophotometer. Fluorescence measurements were measured on a Hitachi F-4600 spectrophotometer. Cyclic voltammetry (CV) analysis of the materials was recorded on a three-electrode cell with tetra-n-butyl-ammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Two platinum wires were used as counter electrode and reference electrode. The scan rate is 100 mV/s, and all the potentials were corrected to the ferrocene/ferrocene⁺ (Fe/Fe⁺) standard under room temperature. The oxidation curve is obtained by dissolving the product and

electrolyte in dichloromethane (DCM), and the reduction curve is obtained in *N, N*-Dimethylformamide (DMF).

S1.3 Theoretical calculation.

The DFT calculations were carried out with the Gaussian 09 B.01 Package at the level of M062X/6-31+G(d,p). And Natural transition orbital (NTO) calculations were obtained on Multiwfn program. The influence of solvent environment on the optical property of DCAT, DCAO and CNAT can be understood using the Lippert-Mataga equation, which can describe the interactions between the solvent and the dipole moment of solute.

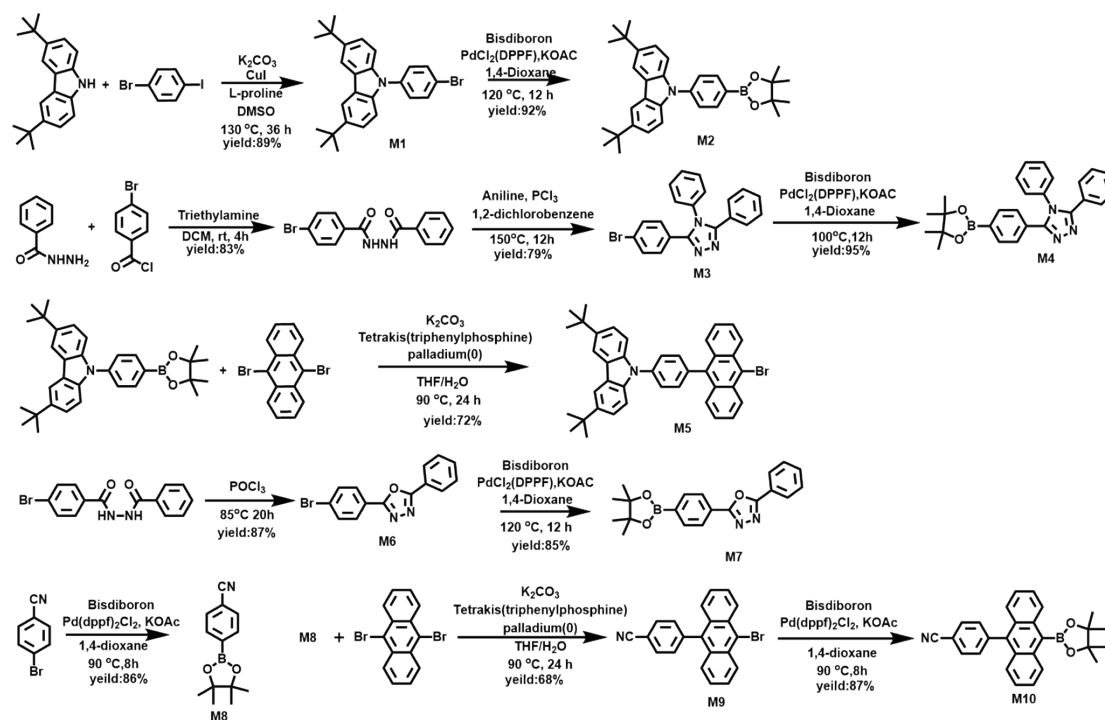
S1.4 Device fabrication.

ITO-coated glass with a sheet resistance of 15-20 Ω square⁻¹ was used as the substrate. Before device fabrication, the ITO glass substrates were cleaned with acetone, HellmanexTM III and deionized water, dried 12 h in an oven at 120 °C, the substrates were treated by O₂ plasma for 7 minutes to improve the hole injection ability of ITO. Finally transferred to a vacuum deposition system with a pressure of $< 1.6 \times 10^{-4}$ Pa. The current-voltage-brightness characteristics were measured by using a Keithley source measurement unit (Keithley 2450 and LS-160), EL spectra were measured with Flame-S (Serial Number: FLMS16791, Range: > 350 nm). EQEs were calculated from the luminance, current density, and EL spectrum, all the results were measured in the forward-viewing direction without using any light out-coupling technique. According to equation following (Formula S1).

$$EQE = \frac{\pi \cdot L \cdot e}{683 \cdot I \cdot h \cdot c} \cdot \frac{\int_{380}^{780} I(\lambda) \cdot \lambda \cdot d\lambda}{\int_{380}^{780} I(\lambda) \cdot K(\lambda) \cdot d\lambda} \quad (1)$$

where L (cd m^{-2}) is the total luminance of device, I (A) is the current flowing into the EL device, λ (nm) is EL wavelength, $I(\lambda)$ is the relative EL intensity at each wavelength and obtained by measuring the EL spectrum, $K(\lambda)$ is the Commission International de L'Eclairage chromaticity (CIE) standard photopic efficiency function, e is the charge of an electron, h is the Planck's constant, c is the velocity of light.

S2 Synthesis and routines



Scheme. S1 Molecular synthesis route.

Synthesis of 9-(4-(10-bromoanthracen-9-yl)phenyl)-3,6-di-*tert*-butyl-9H-carbazole (M5):

M2 (4.0 g, 8.3 mmol), 9,10-dibromoanthracene (3.3 g, 9.8 mmol), K_2CO_3 (1.2 g, 12.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.28 g, 0.24 mmol), THF (50 mL) and deionized water (10 mL), the mixture was reacted at 90°C for 24 hours under nitrogen atmosphere. Then remove the

solvent, wash the crude product with water and dichloromethane, dry it with MgSO₄ and filter, then separate by column chromatography (the eluent is petroleum ether: dichloromethane 3: 1). The product M5 was obtained. (3.6 g, 72%).

Synthesis of 2-phenyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,4-oxadiazole (M7):

M6 (3 g, 9.9 mmol), Bisdiboron (3.1 g, 12.2 mmol), PdCl₂(DPPF) (0.22 g, 0.3 mmol), CH₃COOK (2.9 g, 29.54 mmol) and 1,4-Dioxane (30 mL), the mixture was reacted at 100 °C for 12 hours under nitrogen atmosphere, then remove the solvent, wash the crude product with water and dichloromethane, dry it with MgSO₄ and filter, then separate by column chromatography (the eluent is ethyl acetate: dichloromethane 1: 12). M7 was obtained (2.94 g, 85%).

Synthesis of 4-(10-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracen-9-yl)benzotrile (M10):

4-bromobenzotrile (3 g, 16.5 mmol), Bisdiboron (5.02 g, 19.8 mmol), PdCl₂(DPPF) (0.36 g, 0.5 mmol), CH₃COOK (4.85 g, 49.4 mmol) and 1,4-Dioxane (30 mL), the mixture was reacted at 100 °C for 12 hours under nitrogen atmosphere, then remove the solvent, wash the crude product with water and dichloromethane, dry it with MgSO₄ and filter, then separate by column chromatography (pure dichloromethane). M8 was obtained (3.24 g, 86%).

M8 (8.5 g, 37.1 mmol), 9,10-dibromoanthracene (9.78 g, 29.1 mmol), K₂CO₃ (6.0 g, 43.4 mmol), Pd(PPh₃)₄ (1.0 g, 0.86 mmol), THF (50 mL) and deionized water (10 mL), the mixture was reacted at 90 °C for 24 hours under nitrogen atmosphere. Then remove the solvent, wash the crude product with water and dichloromethane, dry it with MgSO₄ and filter, then separate by column chromatography (the eluent is petroleum ether: dichloromethane 2: 1). The product M9 was obtained. (9.0 g, 68%).

M9 (3 g, 8.3 mmol), Bisdiboron (2.55 g, 10.04 mmol), PdCl₂(DPPF) (0.18 g, 0.25 mmol), CH₃COOK (2.5 g, 25.47 mmol) and 1,4-Dioxane (30 mL), the mixture was reacted at 100 °C for 12 hours under nitrogen atmosphere, then remove the solvent, wash the crude product with water and dichloromethane, dry it with MgSO₄ and filter, then separate by column chromatography (the eluent is petroleum ether:

dichloromethane 3: 1). M10 was obtained (2.95 g, 87%).

Synthesis of 3,6-di-*tert*-butyl-9-(4-(10-(4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-yl)phenyl)anthracen-9-yl)phenyl)-9*H*-carbazole (DCAT):

M5 (3.0 g, 4.9 mmol), M4 (2.5 g, 5.8 mmol), K₂CO₃ (0.72 g, 7.3 mmol), Pd(PPh₃)₄ (0.17 g, 0.14 mmol), THF (50 mL) and deionized water (10 mL), the mixture was reacted at 90 °C for 24 hours under nitrogen atmosphere. Then remove the solvent, wash the crude product with water and dichloromethane, dry it with MgSO₄ and filter, then separate by column chromatography (the eluent is ethyl acetate: dichloromethane 3: 1). The product DCAT was obtained. (2.7 g, 66%). ¹NMR (500 MHz, Chloroform-d) δ 8.21 (d, J = 1.8 Hz, 2H), 7.86 – 7.79 (m, 4H), 7.72 – 7.69 (m, 2H), 7.68 – 7.64 (m, 4H), 7.61 (dd, J = 8.6, 1.4 Hz, 2H), 7.57 – 7.49 (m, 8H), 7.48 – 7.41 (m, 3H), 7.40 – 7.31 (m, 7H), 1.50 (d, J = 1.5 Hz, 18H). ¹³C NMR (126 MHz, Chloroform-d) δ 155.00, 154.73, 143.08, 140.60, 139.23, 132.65, 131.54, 130.11, 129.96, 129.84, 129.71, 128.85, 128.78, 128.48, 127.99, 127.01, 126.89, 126.74, 126.47, 125.37, 123.71, 123.57, 116.35, 109.39, 34.80, 32.06. MALDI-TOF MS (mass m/z): calcd for C₆₀H₅₀N₄, 827.4035; found, 851.4114 [M+H]⁺. Anal. calcd for C₆₀H₅₀N₄: C, 87.13; H, 6.09; N, 6.77. Found: C, 87.44; H, 6.20; N, 6.36.

Synthesis of 2-(4-(10-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)anthracen-9-yl)phenyl)-5-phenyl-1,3,4-oxadiazole (DCAO):

M5 (3.0 g, 4.9 mmol), M7 (2.05 g, 5.9 mmol), K₂CO₃ (0.72 g, 7.3 mmol), Pd(PPh₃)₄ (0.17 g, 0.14 mmol), THF (50 mL) and deionized water (10 mL), the mixture was reacted at 90 °C for 24 hours under nitrogen atmosphere. Then remove the solvent, wash the crude product with water and dichloromethane, dry it with MgSO₄ and filter, then separate by column chromatography (the eluent is ethyl acetate: dichloromethane 3: 1). The product DCAO was obtained. (2.5 g, 67%). ¹H NMR (500 MHz, Chloroform-d) δ 8.46 (d, J = 8.2 Hz, 2H), 8.28 – 8.23 (m, 4H), 8.20 – 8.18 (m, 1H), 7.93 – 7.86 (m, 4H), 7.76 (ddd, J = 9.9, 7.9, 5.6 Hz, 6H), 7.66 (d, J = 8.6 Hz, 2H), 7.63 (dd, J = 5.7, 1.8 Hz, 3H), 7.60 (dd, J = 8.6, 2.0 Hz, 3H), 7.52 – 7.44 (m, 4H), 1.55 (s, 18H). ¹³C NMR (101 MHz, Chloroform-d) δ 164.80, 164.64, 143.11, 139.24, 136.95, 132.66, 132.25, 131.86, 130.01, 129.71, 129.20, 127.16, 127.04, 127.01, 126.61, 126.53, 125.62,

125.49, 124.01, 123.73, 123.59, 116.37, 109.40, 77.23, 34.81, 32.07. MALDI-TOF MS (mass m/z): calcd for $C_{54}H_{45}N_3O$, 751.3563; found, 751.3567 $[M]^+$. Anal. calcd for $C_{54}H_{45}N_3O$: C, 86.25; H, 6.03; N, 5.59; O, 2.13. Found: C, 85.93; H, 6.26; N, 5.60; O, 2.21.

Synthesis of 4-(10-(4-(4,5-diphenyl-4*H*-1,2,4-triazol-3-yl)phenyl)anthracen-9-yl)benzotrile (CNAT):

M10 (3.0 g, 8.3 mmol), M3 (2.6 g, 6.9 mmol), K_2CO_3 (1.45 g, 10.46 mmol), $Pd(PPh_3)_4$ (0.24 g, 0.2 mmol), THF (50 mL) and deionized water (10 mL), the mixture was reacted at 90 °C for 24 hours under nitrogen atmosphere. Then remove the solvent, wash the crude product with water and dichloromethane, dry it with $MgSO_4$ and filter, then separate by column chromatography (the eluent is ethyl acetate: dichloromethane 3: 1). The product CNAT was obtained. (3.8 g, 78%). 1H NMR (500 MHz, Chloroform- d) δ 7.91 – 7.89 (m, 2H), 7.68 (d, $J = 7.9$ Hz, 2H), 7.63 – 7.57 (m, 4H), 7.54 – 7.47 (m, 8H), 7.39 (dd, $J = 7.5, 5.7$ Hz, 3H), 7.37 – 7.33 (m, 5H), 7.32 – 7.30 (m, 3H). ^{13}C NMR (126 MHz, Chloroform- d) δ 155.01, 144.35, 140.26, 135.35, 134.92, 132.32, 132.24, 131.41, 130.11, 129.86, 129.75, 129.56, 129.34, 128.83, 128.78, 128.48, 127.97, 126.86, 126.12, 125.78, 125.45, 118.86, 111.72, 77.23. MALDI-TOF MS (mass m/z): calcd for $C_{41}H_{26}N_4$, 574.2157; found, 575.2236 $[M+H]^+$. Anal. calcd for $C_{41}H_{26}N_4$: C, 85.69; H, 4.56; N, 9.75. Found: C, 85.80; H, 4.83; N, 9.37.

S3 Supplementary figures

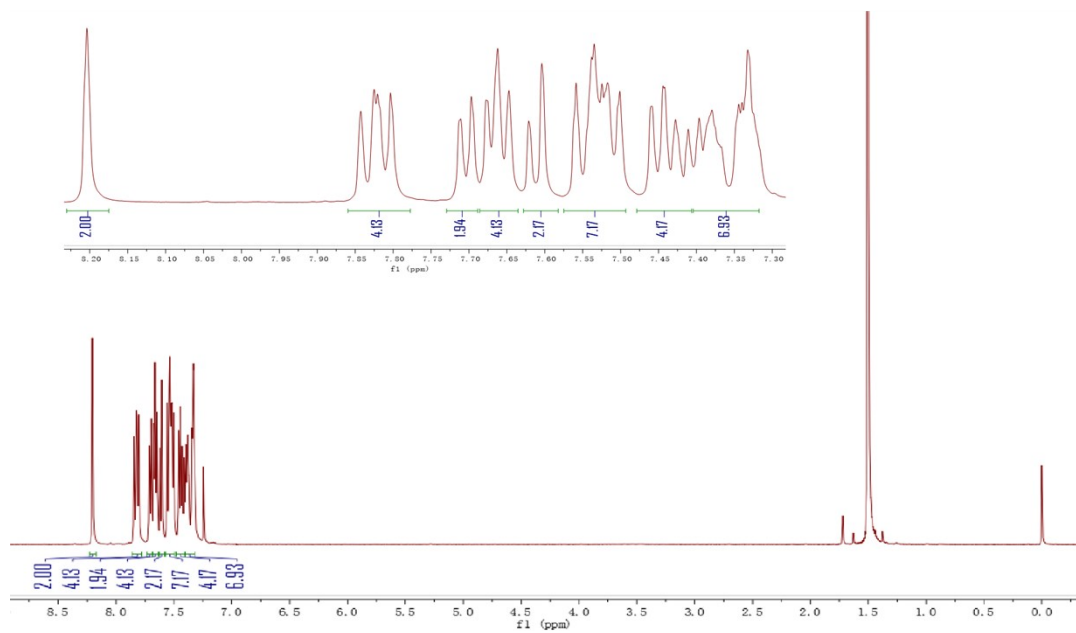


Figure. S1 ^1H -spectrum of DCAT.

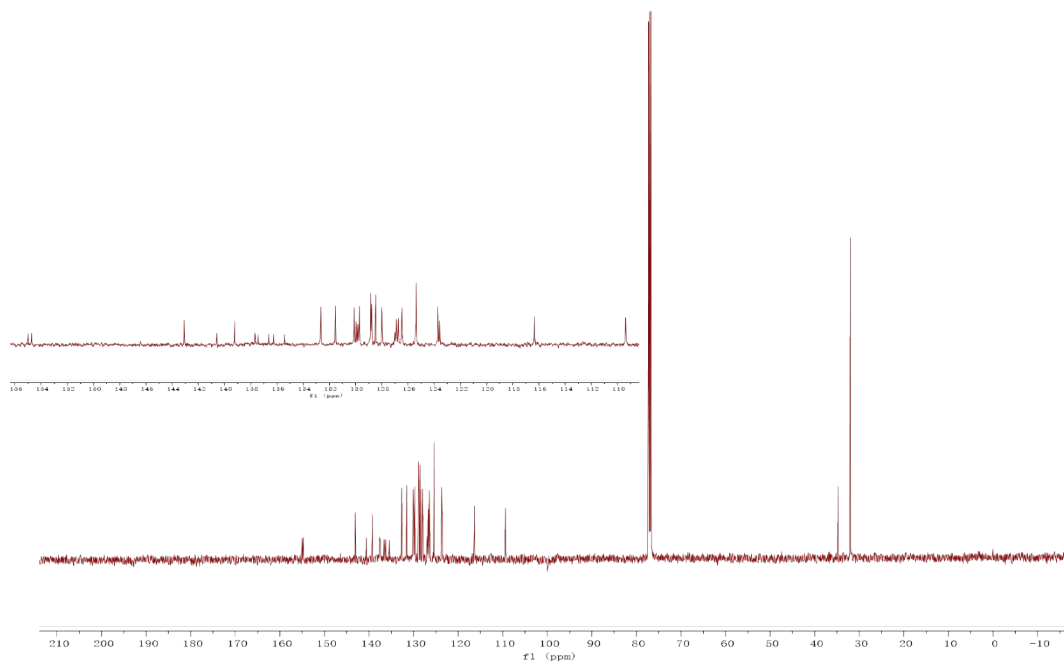


Figure. S2 ^{13}C -spectrum of DCAT.

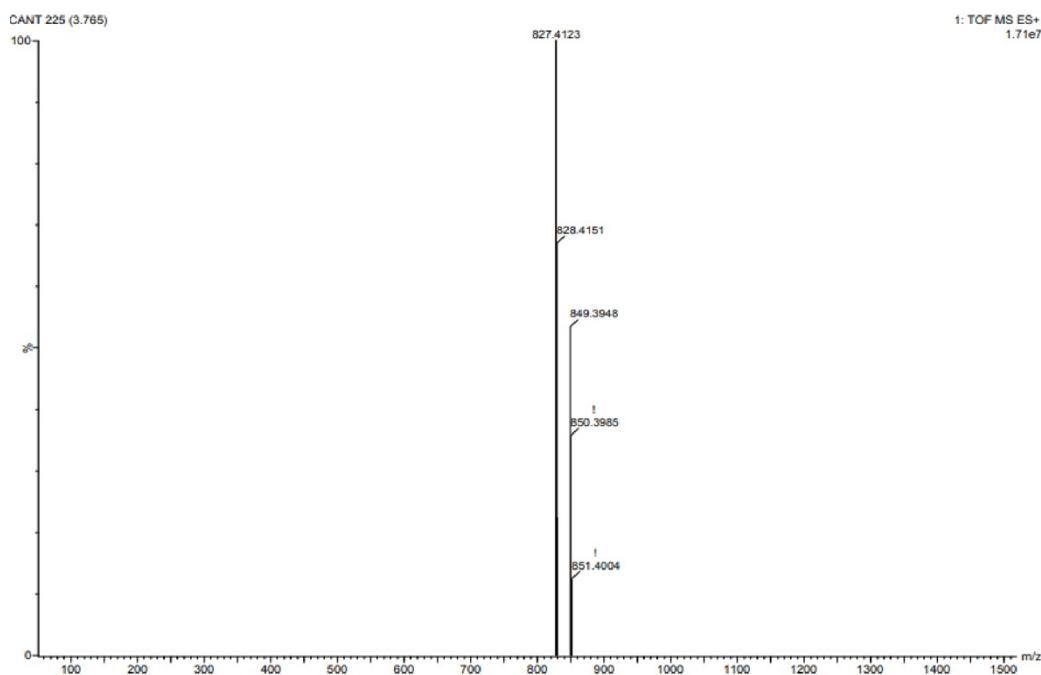


Figure. S3 Mass Spectrum $[M+H]^+$ of DCAT

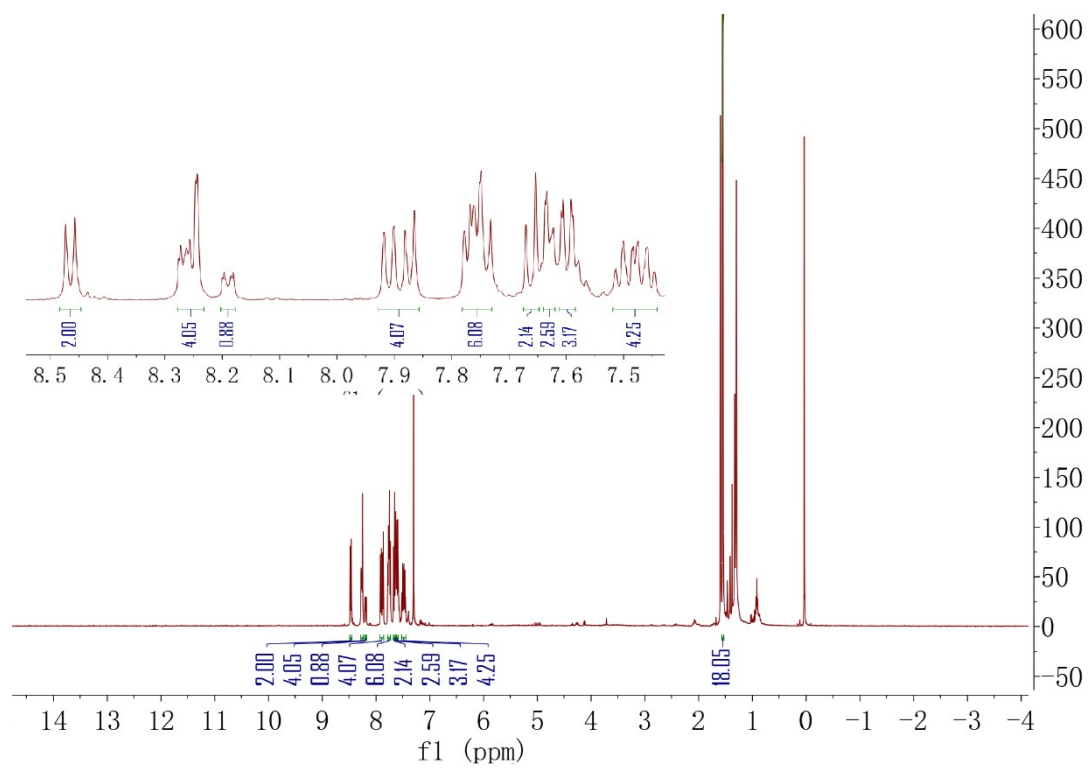


Figure. S4 1H -spectrum of DCAO.

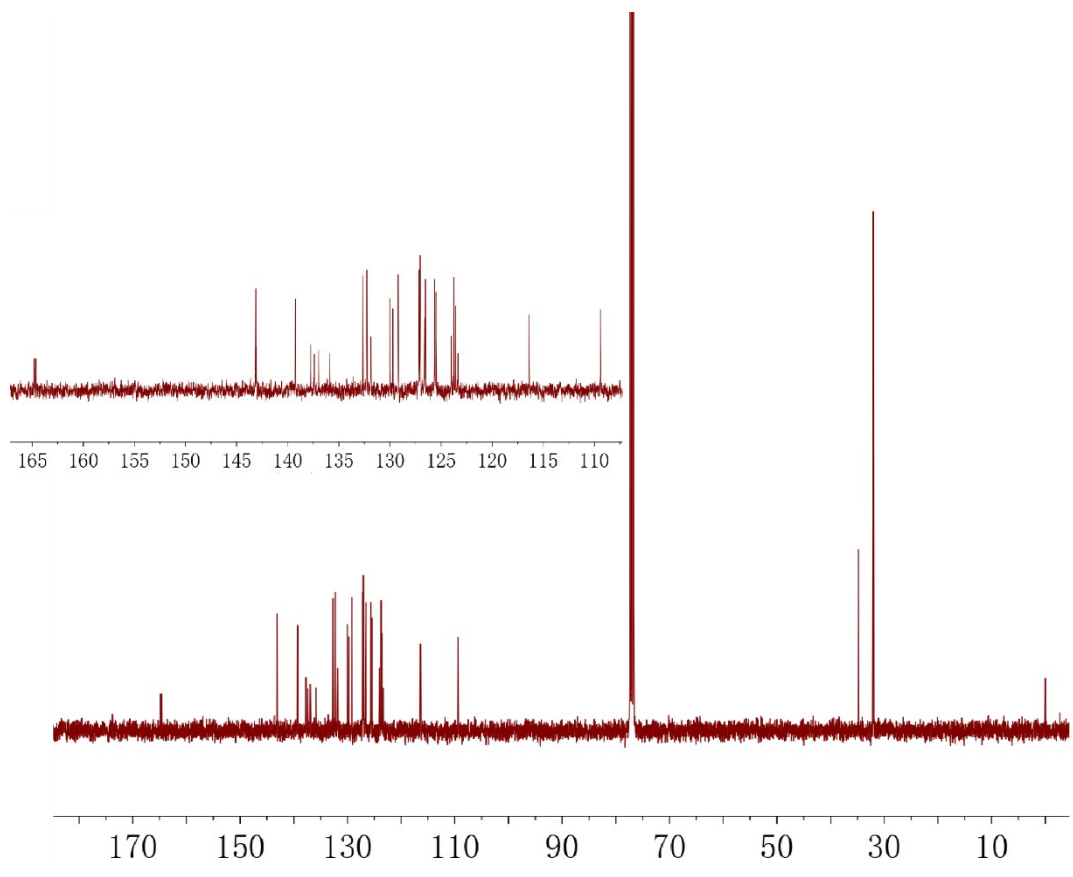


Figure. S5 ^{13}C -spectrum of DCAO.

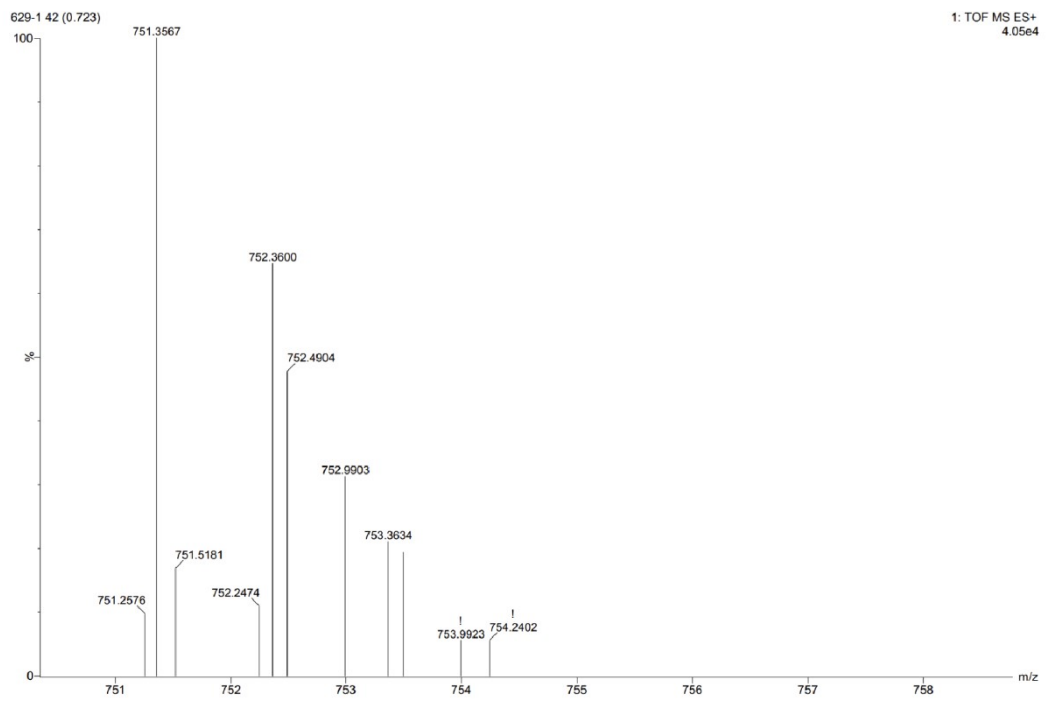


Figure. S6 Mass Spectrum $[\text{M}]^+$ of DCAO

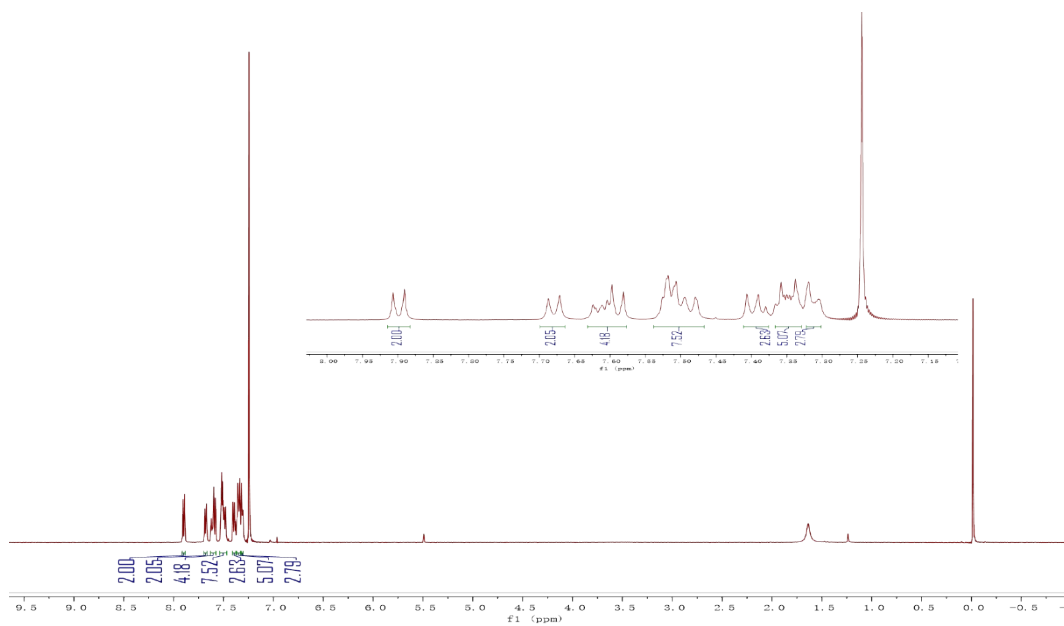


Figure. S7 ^1H -spectrum of CNAT.

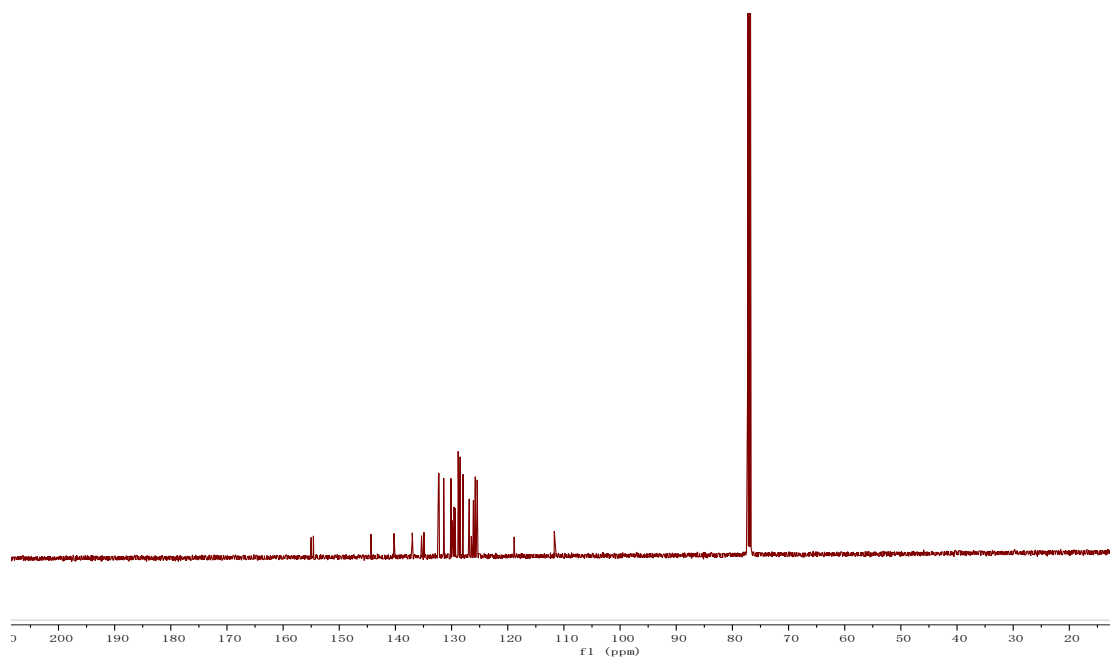


Figure. S8 ^{13}C -spectrum of CNAT.

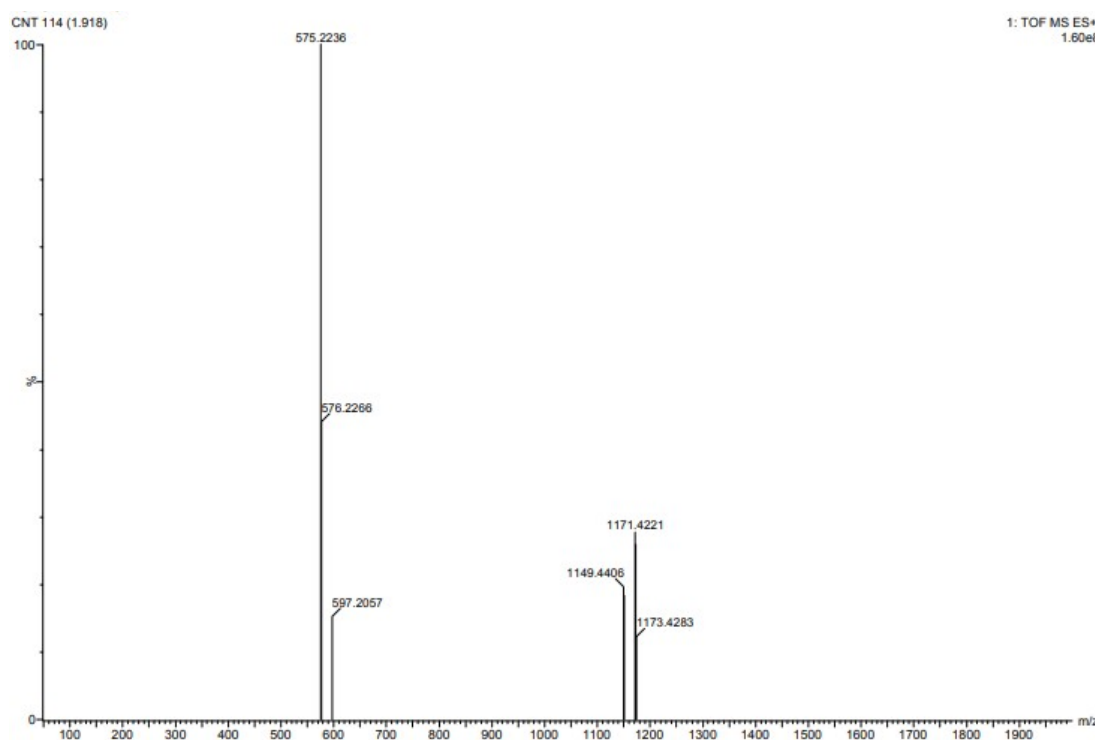


Figure. S9 Mass Spectrum $[M+H]^+$ of CNAT

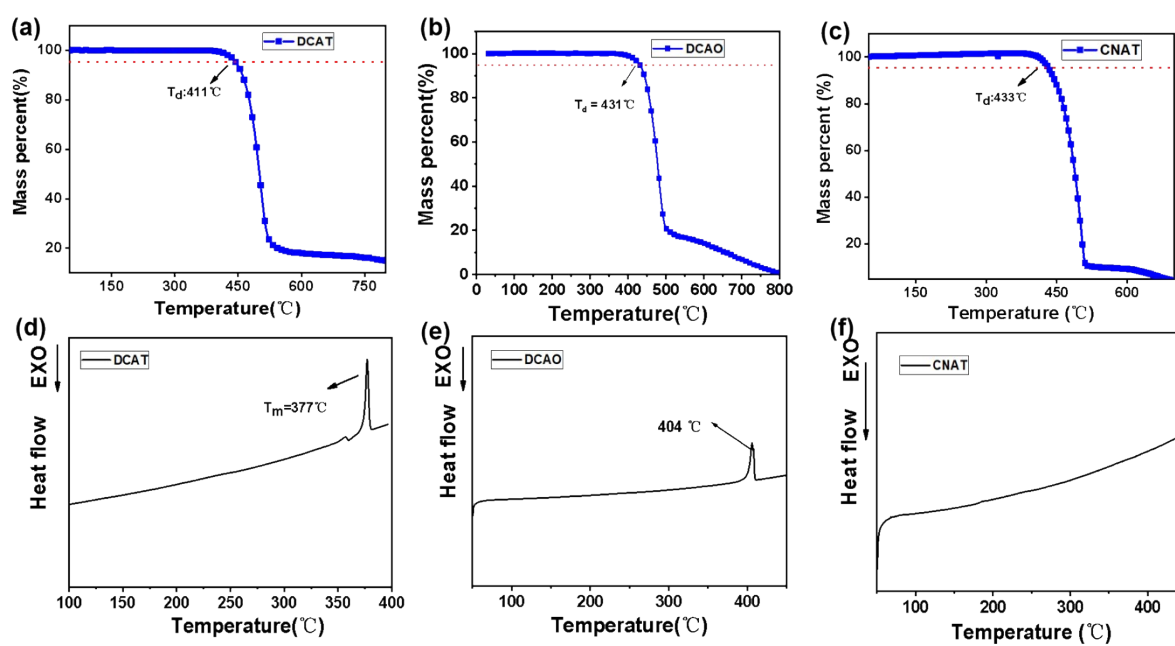


Figure. S10 Thermal properties of three molecules, TGA including (a), (b) (c), and DSC including (d), (e) (f).

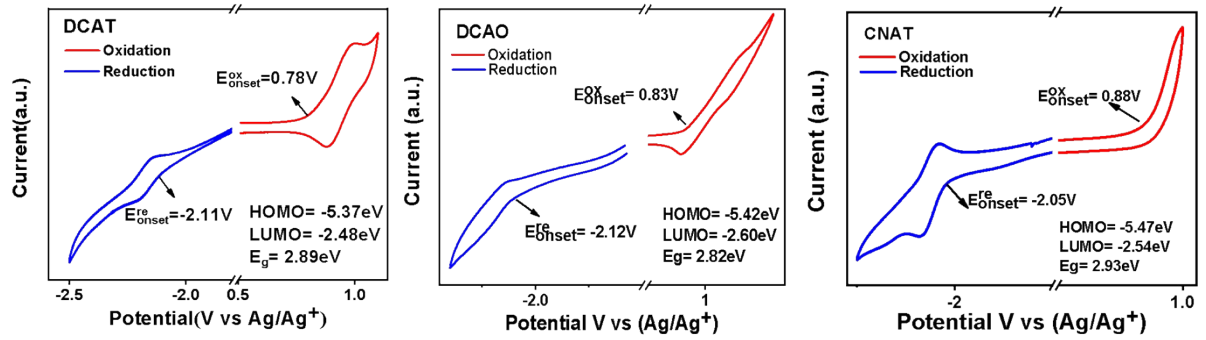


Figure. S11 The electrochemical properties of DCAT, DCAO and CNAT.

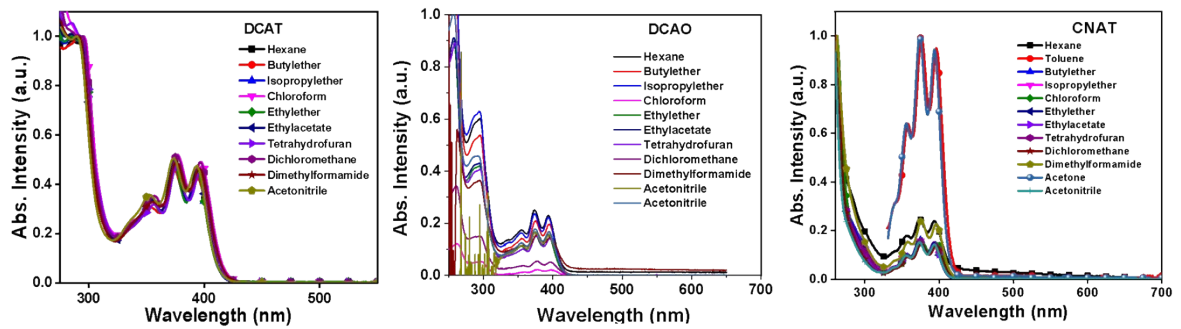


Figure. S12 The absorption spectra of DCAT, DCAO and CNAT under different solvents with different polarities.

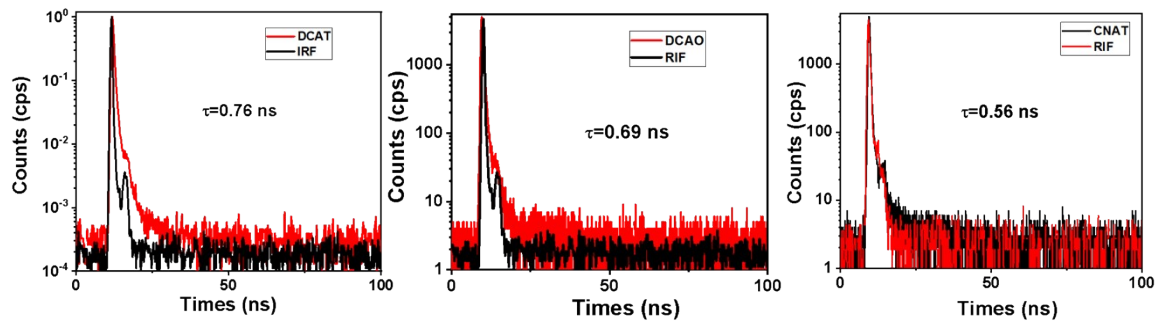


Figure. S13 Transient absorption spectrum of DCAT, DCAO and CNAT.

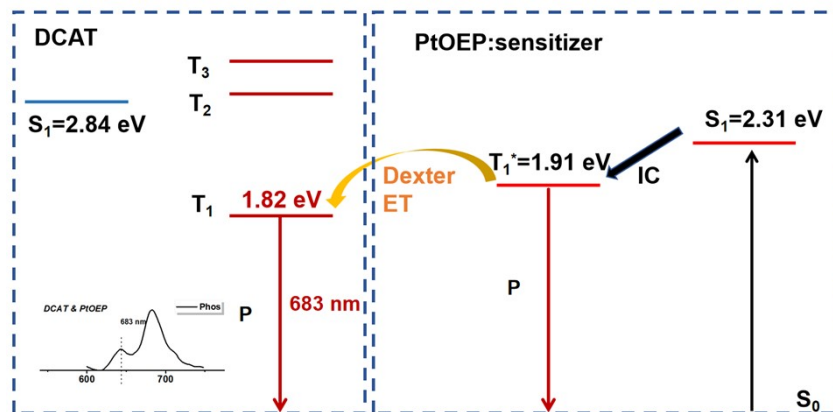


Figure. S14 Schematic of the photophysical dynamics in the PtOEP & DCAT solution. “ET” stands for energy transfer and “P” stands for phosphorescence.

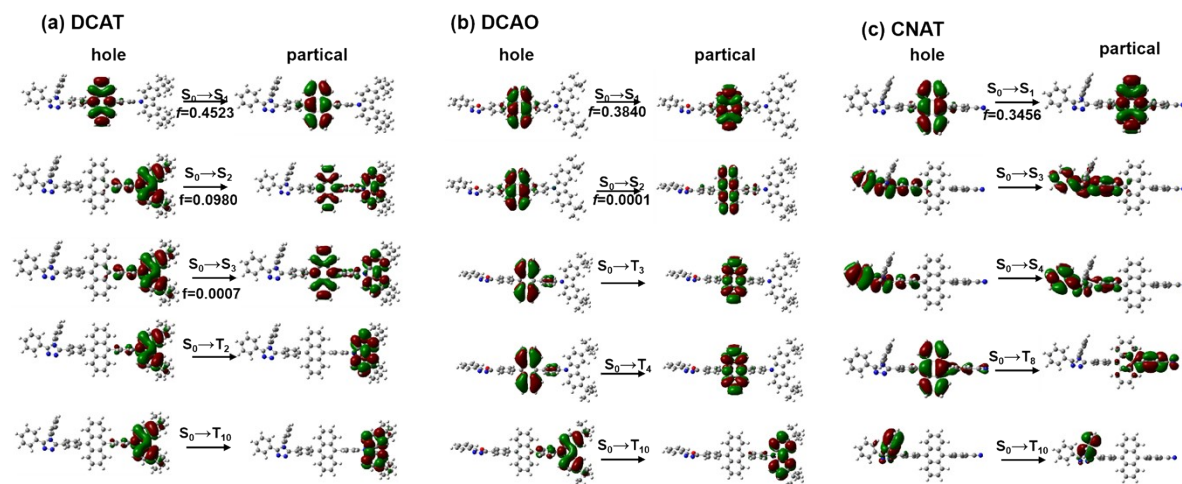


Figure. S15 Distribution of electron clouds in the natural transition orbitals of some energy levels of the three compounds that may undergo hRISC processes.

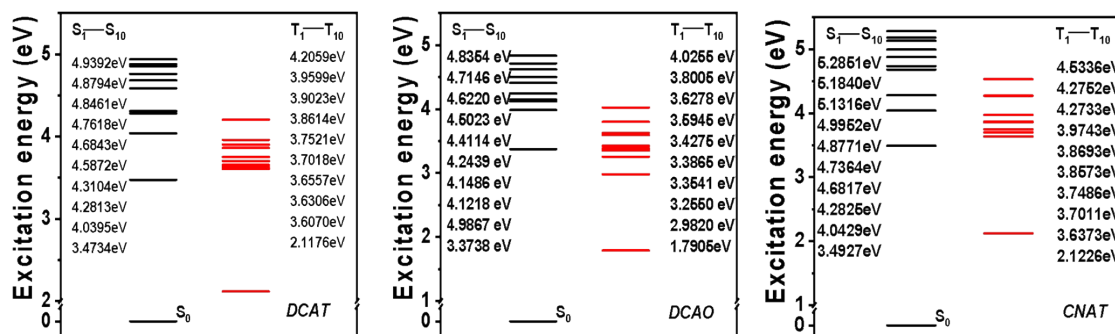


Figure. S16 Theoretical calculation of energy level distribution.

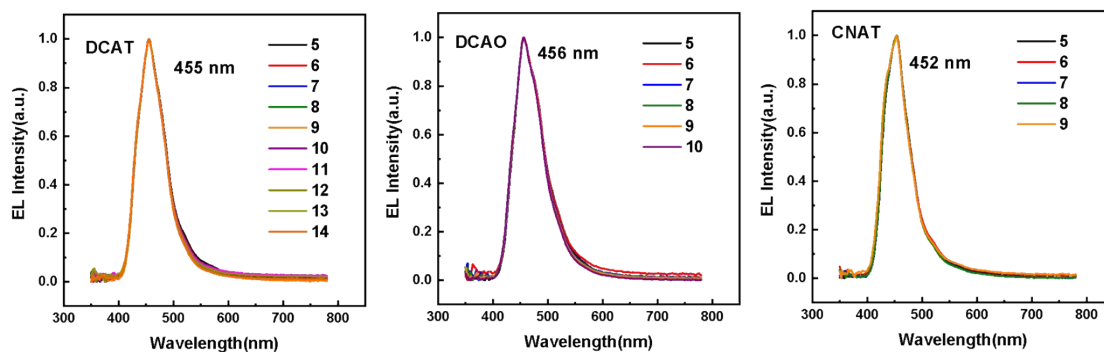


Figure. S17 Electroluminescence spectra of the three non-doped devices at different voltages.

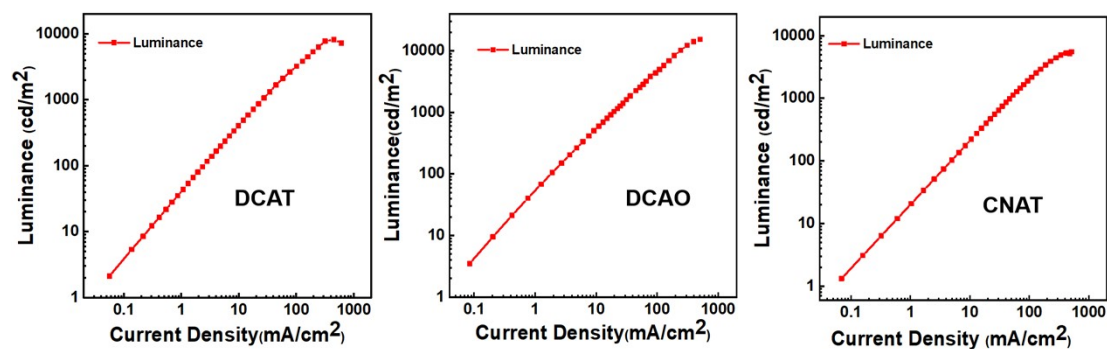


Figure S18. Luminance-current density of DCAT, DCAO and CNAT, this linear relationship can exclude TTA.

S4 Supplementary tables

Table S1. The absorption and emission peaks (Abs/PL) of three molecules in solvents with different polarities.

	DCAT (Abs/PL) [nm]	DCAO (Abs/PL) [nm]	CNAT (Abs/PL) [nm]
n-hexane	393/424	393/430	393/424
butyl ether	393/427	394/434	393/425
Isopropyl ether	393/430	393/433	392/426
Trichloromethane	397/435	397/444	393/434
Ether	393/434	393/434	395/434
ethyl acetate	394/430	393/435	393/429
Tetrahydrofuran	395/437	395/440	393/432
dichloromethane	395/439	395/445	393/430
DMF	396/442	395/447	390/434

acetone	393/438	394/444	393/431
acetonitrile	394/447	393/446	390/432

Table S2. Φ_{PL} under different solvents and thin films

Φ_{PL} [%]	DCAT	DCAO	CNAT
n-hexane	65.1	69.2	61.0
Ether	73.7	62.3	73.5
Tetrahydrofuran	70.9	55.4	69.1
acetonitrile	47.5	43.1	65.5
Film	47.7	45.5	62.2