

Supporting Information

Enhancing the Electroluminescent Efficiency of Acridine-Based Donor-Acceptor (D-A) Materials: Quasi-Equivalent Hybridized Local and Charge-Transfer (qHLCT) State

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S-I Characterization and Measurements

General information: The ^1H NMR and ^{13}C NMR spectra were recorded on AVANCE 500 spectrometers at 298 K by utilizing deuterated dimethyl sulfoxide (DMSO) as solvents and tetramethylsilane (TMS) as a standard. The compounds were characterized by a Flash EA 1112, CHNS-O elemental analysis instrument. The MALDI-TOF-MS mass spectra were recorded using an AXIMA-CFRTM plus instrument.

Electrochemical characterization: Cyclic voltammetry (CV) was performed with a BAS 100W Bioanalytical Systems, using a glass carbon disk ($\Phi = 3$ mm) as the working electrode, a platinum wire as the auxiliary electrode with a porous ceramic wick, Ag/Ag^+ as the reference electrode, standardized for the redox couple ferricinium/ferrocene. All solutions were purged with a nitrogen stream for 10 min before measurement. The procedure was performed at room temperature and a nitrogen atmosphere was maintained over the solution during measurements.

Thermal stability measurements: Thermal gravimetric analysis (TGA) was undertaken on a PerkinElmer thermal analysis system at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ and a nitrogen flow rate of 80 mL min^{-1} .

S-II Synthesis

All the reagents and solvents used for the synthesis were purchased from Aldrich or Acros and used as received. All reactions were performed under nitrogen atmosphere.

1-bromoacridine, 9-(4-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)phenyl)-9H-carbazole and **N-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan -2-yl)-phenothiazine** was synthesized as our previous work¹⁻⁴.

1-(4-(9H-carbazol-9-yl)phenyl)acridine

A mixture of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (2.4 mmol), 1Br-bromoacridine (2.0 mmol), sodium carbonate (20 mmol), toluene (15 mL), absolute alcohol (10 mL) and deionized water (10 mL), with Pd(PPh₃)₄ (60 mg) acting as catalyst was refluxed at 90 °C for 48 h under nitrogen. After the mixture was cooled down, 40 mL water was added to the resulting solution and the mixture was extracted with CH₂Cl₂ for several times. The organic phase was dried over Na₂SO₄. After filtration and solvent evaporation, the liquid was purified by chromatography using the mixture of CH₂Cl₂/petroleum ether as the eluent to afford a white solid (0.60 g, yield 71%). MS (ESI): m/z 422.2 (M(H)⁺). ¹H NMR (500 MHz, DMSO) δ 9.16 (s, 1H), 8.36 – 8.25 (m, 4H), 8.22 (d, J = 8.9 Hz, 1H), 7.99 (t, J = 7.4 Hz, 1H), 7.97 – 7.86 (m, 5H), 7.73 (d, J = 6.5 Hz, 1H), 7.64 (t, J = 9.0 Hz, 3H), 7.52 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 140.81 (s), 139.76 (s), 138.60 (s), 137.51 (s), 131.56 (s), 130.79 (s), 129.88 (s), 129.19 (s), 128.65 (s), 127.09 (s), 126.57 (d, J = 16.6 Hz), 126.08 (s), 125.89 (s), 125.37 (s), 123.60 (s), 120.46 (s), 120.21 (s), 109.87 (s). Elemental analysis. Found: C, 88.80; H, 4.67; N, 6.57%. Calc. for C₃₂H₂₁N: C, 88.54; H, 4.79; N, 6.66%.

4-(acridin-1-yl)-N,N-diphenylaniline

A mixture of N,N-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (2.6 mmol), 1Br-bromoacridine (2.0 mmol), sodium carbonate (20 mmol), toluene (15 mL), absolute alcohol (10 mL) and deionized water (10 mL), with Pd(PPh₃)₄ (60 mg) acting as catalyst was refluxed at 90 °C for 48 h under nitrogen. After the mixture was cooled down, 40 mL water was added to the resulting solution and the mixture was extracted with CH₂Cl₂ for several times. The organic phase was dried over Na₂SO₄. After filtration and solvent evaporation, the liquid was purified by chromatography using the mixture of CH₂Cl₂/petroleum ether as the eluent to afford a green solid (0.55 g, yield 65%). MS (ESI): m/z 423.4(M(H)⁺). ¹H NMR (500 MHz, DMSO): δ 9.04 (s, 1H), 8.26 – 8.13 (m, 3H), 7.99 – 7.82 (m, 2H), 7.67 – 7.58 (m, 1H), 7.55 (dd, J = 11.6, 7.7 Hz, 3H), 7.40 (t, J = 7.8 Hz, 4H), 7.24 – 7.08 (m, 8H). ¹³C NMR (126 MHz, CDCl₃) δ 147.65, 130.87, 129.44, 128.67, 126.48, 126.11, 125.69, 125.51, 124.86, 123.35, 122.96. Elemental analysis. Found: C, 88.12; H, 5.25; N, 6.63%. Calc. for C₃₂H₂₃N: C, 88.62; H, 5.19; N, 6.60%.

3-(acridin-1-yl)-10-phenyl-10H-phenothiazine

A mixture of 10-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazine (2.6 mmol), 1Br-bromoacridine (2.0 mmol), sodium carbonate (20 mmol), toluene (15 mL), absolute alcohol (10 mL) and deionized water (10 mL), with $\text{Pd}(\text{PPh}_3)_4$ (60 mg) acting as catalyst was refluxed at 90 °C for 48 h under nitrogen. After the mixture was cooled down, 40 mL water was added to the resulting solution and the mixture was extracted with CH_2Cl_2 for several times. The organic phase was dried over Na_2SO_4 . After filtration and solvent evaporation, the liquid was purified by chromatography using the mixture of CH_2Cl_2 /petroleum ether as the eluent to afford a green solid (0.59 g, yield 65%). MS (ESI): m/z 454.2 ($\text{M}(\text{H})^+$). ^1H NMR (500 MHz, DMSO) δ 8.96 (s, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 8.16 (dd, $J = 8.7, 3.5$ Hz, 2H), 7.87 (dt, $J = 9.0, 6.0$ Hz, 2H), 7.75 (t, $J = 7.8$ Hz, 2H), 7.66 – 7.53 (m, 4H), 7.50 (d, $J = 6.8$ Hz, 1H), 7.33 (d, $J = 1.9$ Hz, 1H), 7.19 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.14 (d, $J = 7.5$ Hz, 1H), 6.99 (t, $J = 7.1$ Hz, 1H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.35 (d, $J = 8.4$ Hz, 1H), 6.21 (d, $J = 8.2$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.07 (s), 140.78 (s), 139.52 (s), 131.02 (d, $J = 13.3$ Hz), 128.80 – 128.42 (m), 128.04 (s), 127.08 (s), 126.84 (s), 126.49 (s), 125.73 (d, $J = 11.5$ Hz), 125.44 (s), 122.74 (s), 119.62 (s), 116.08 (s), 115.77 (s). Elemental analysis. Found: C, 82.80; H, 4.40; N, 6.13; S, 7.30%. Calc. for $\text{C}_{31}\text{H}_{20}\text{N}_2\text{S}$: C, 82.27; H, 4.45; N, 6.19; S, 7.08%.

S-III Tables and Figures

Table S1 The ground state and excited state geometries of CZP-1AC, TPA-1AC and PTZ-1AC

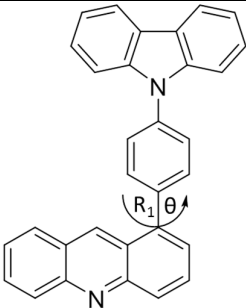
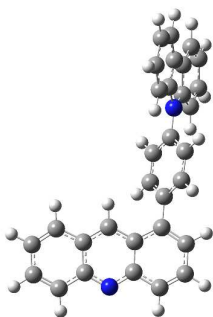
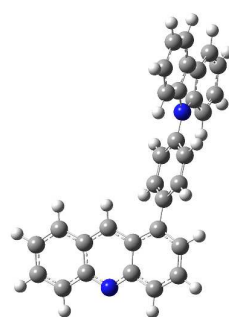
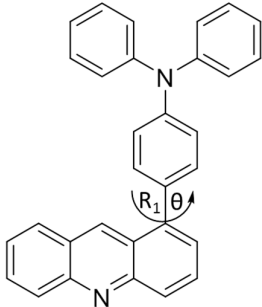
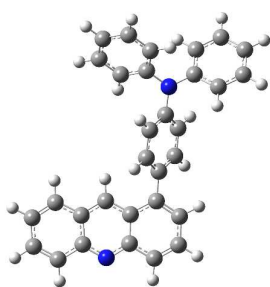
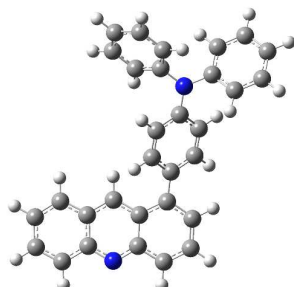
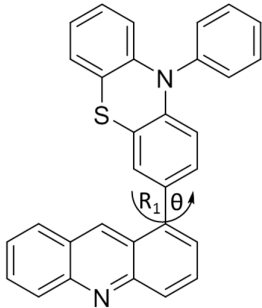
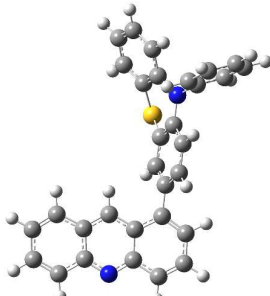
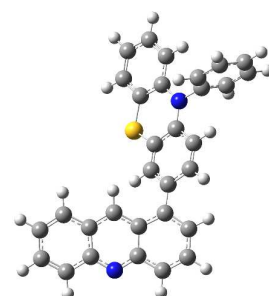
Molecules	Ground state	Excited state
 CZP-1AC		
Optimized geometry parameters	$R_1=1.4888\text{\AA};$ $\theta=52.19^\circ;$	$R_1=1.4603\text{\AA};$ $\theta=37.51^\circ;$
 TPA-1AC		
Optimized geometry parameters	$R_1=1.4868\text{\AA};$ $\theta=50.06^\circ;$	$R_1=1.4502\text{\AA};$ $\theta=34.82^\circ;$
 PTZ-1AC		
Optimized geometry parameters	$R_1=1.4872\text{\AA};$ $\theta=49.93.30^\circ;$	$R_1=1.4518\text{\AA};$ $\theta=33.87^\circ;$

Table S2 Detailed absorption and emission peak positions of three acridine derivatives in different solvents

solvents	$f(\varepsilon, n)$	CZP-1AC		
		λ_a (nm)	λ_f (nm)	$\nu_a-\nu_f(\text{cm}^{-1})$
Hexane	0.0012	359	434	4813
Butyl ether	0.096	359	442	5230
Isopropyl ether	0.145	359	444	5332
Ethyl ether	0.167	358	443	5359
Ethyl acetate	0.200	359	460	6116
Tetrahydrofuran	0.210	359	466	6396
Acetone	0.284	358	497	7812
Acetonitrile	0.305	358	527	8958

solvents	$f(\varepsilon, n)$	TPA-1AC		
		λ_a (nm)	λ_f (nm)	$\nu_a-\nu_f(\text{cm}^{-1})$
Hexane	0.0012	386	462	4261
Triethylamine	0.048	389	479	4830
Butyl ether	0.096	390	491	5274
Isopropyl ether	0.145	389	496	5545
Ethyl ether	0.167	386	507	6182
Ethyl acetate	0.200	390	532	6844
Tetrahydrofuran	0.210	391	535	6883
Dichloromethane	0.217	396	555	7234
Dimethyl formamide	0.276	390	566	7584
Acetonitrile	0.305	390	572	8158

solvents	$f(\varepsilon, n)$	PTZ-1AC		
		λ_a (nm)	λ_f (nm)	$\nu_a-\nu_f(\text{cm}^{-1})$
Hexane	0.0012	407	487	4036
Triethylamine	0.048	407	525	5522
Butyl ether	0.096	407	533	5808
Isopropyl ether	0.145	407	546	6255
Ethyl ether	0.167	407	549	6355
Ethyl acetate	0.200	407	474/572	3473/7087
Tetrahydrofuran	0.210	407	476/583	3561/7417
Dichloromethane	0.217	407	483/606	3866/8068

Dimethyl formamide	0.276	407	495	4368
Acetone	0.284	407	495	4368
Acetonitrile	0.305	407	504	4728

Details of the Lippert-Mataga solvatochromic model

First, the larger slope in the Lippert-Mataga solvatochromic model could indicate the generation of CT or CT-like (such as HLCT) excitons. According to the definition of dipole moment (μ) of an exciton:

$$\mu = q \cdot d$$

where q is the partial charge of hole and electron moieties, and d is the distance between the electronic centers of them. Generally, CT excitons are always of relatively larger dipole moments than the LE excitons due to that the q and d of CT excitons are obviously larger than the charge-unseparated LE excitons, especially for the two excited state components (LE and CT) in one compound. Therefore, the energy of CT excitons will be stabilized in the solvents with larger polarity, and results in larger Stokes shift than the LE excitons and larger slope in the Lippert-Mataga solvatochromic model. Usually, the dipole moment of LE exciton is near or smaller than 10 Debye, while that of the HLCT or CT excitons is always larger, especially for the pure CT excitons, it could be > 20 Debye.

Next, the shape of the Lippert-Mataga solvatochromic model can be the criteria for judging the hybridization status of different materials, instead of simply judging from the scale of the dipole moments. As we have mentioned in the maintext, in Figure 5b, the three materials demonstrate three typical hybridization statues. In CZP-1AC, a two-section line can be fitted, corresponding to two excited dipole moments of 7.5 Debye (in small polarity circumstance) and 16.7 Debye (in large polarity circumstance). Similarly, in PTZ-1AC, a three-section line corresponding to the dipole moments of 13.2 Debye, 13.9 Debye and 31.2 Debye can be fitted. In these two situations, the excited state components could be distinguished, which could be assigned to smaller coupling (J) between LE and CT components as we mentioned in the part of theoretical calculations, representing the LE-dominated state and the

CT-dominated state. However, TPA-1AC only demonstrate one straight line with a dipole moment of 14.8 Debye, meaning that its state coupling is relatively larger, corresponding to a well-hybridized state.

Table S3 The thermal properties and electrochemical of CZP-1AC, TPA-1AC and PTZ-1AC

	CZP-1AC	TPA-1AC	PTZ-1AC
T_d^a (°C)	384	360	384
HOMO ^b (eV)	-5.60	-5.24	-5.01
LUMO ^b (eV)	-2.89	-2.85	-2.86
E_g^c	2.71	2.39	2.15

^a T_d is thermal-decomposition temperature at a weight percentage of 95%. ^b HOMO and LUMO levels were measured based on ferrocene as reference (Fc) (4.8 eV). ^c E_g (eV) = LUMO (eV) - HOMO (eV).

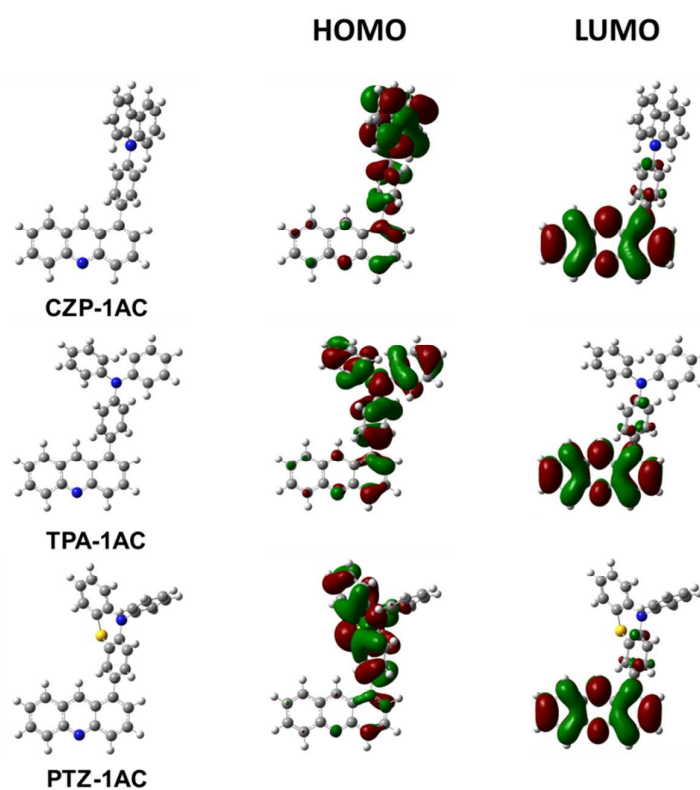


Figure S1 The frontier molecular orbitals (HOMO and LUMO) in the ground state of CZP-1AC, TPA-1AC and PTZ-1AC.

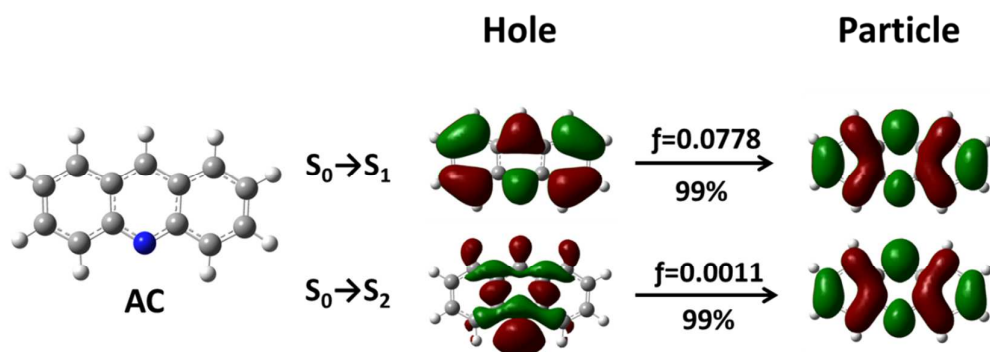


Figure S2 NTO of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transition for AC at S_1 -geometry.

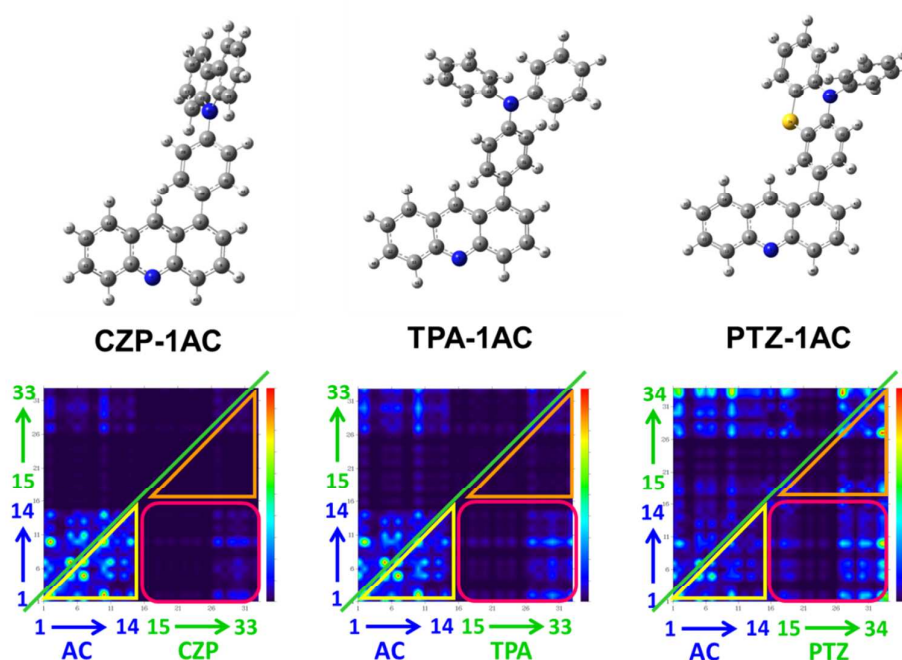


Figure S3 Atom labels for three compounds. We order the atoms from acridine (1-14) to donor. Since hydrogen atoms usually have little contribution to the transitions we are interested in, they are labeled at the latest and usually ignored by default in TDM calculations. The colored maps illustrate the matrix elements of the transitions from atoms on abscissa to atoms on ordinate for the three structures. Since we arrange their atoms sequentially along the positive direction of each axes, the left-lower region denotes the LE transition of acridine, the right-lower region denotes the CT transition from donor to acridine and the right-high region denotes the LE transition of donor. In this way, the LE:CT proportion of each structures could be directly calculated according to the calculus of matrix elements.

	CZP-1AC	TPA-1AC	PTZ-1AC
LE (AC)	0.48871	0.36623	0.15841
CT (from donor AC)	0.12086	0.22410	0.36211

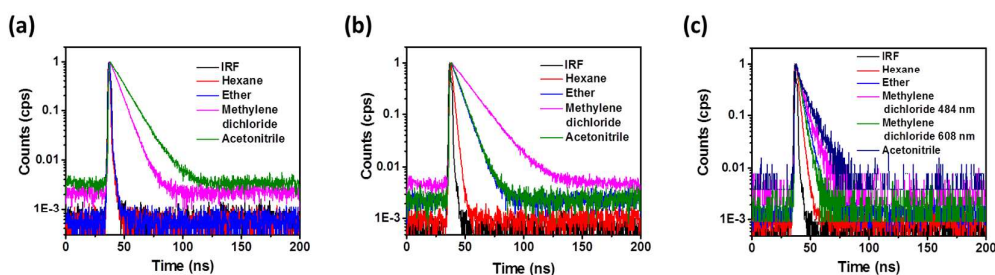


Figure S4 Lifetime measurements of CZP-1AC (a) ,TPA-1AC (b) and PTZ-1AC (c) in different solvents

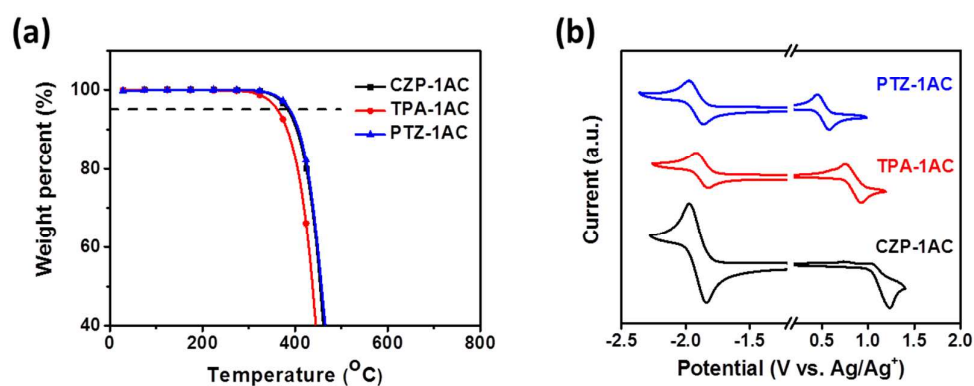


Figure S5 The thermal gravimetric analysis (TGA) (a) and cyclic voltammetry (CV) curves (b) of CZP-1AC, TPA-1AC and PTZ-1AC.

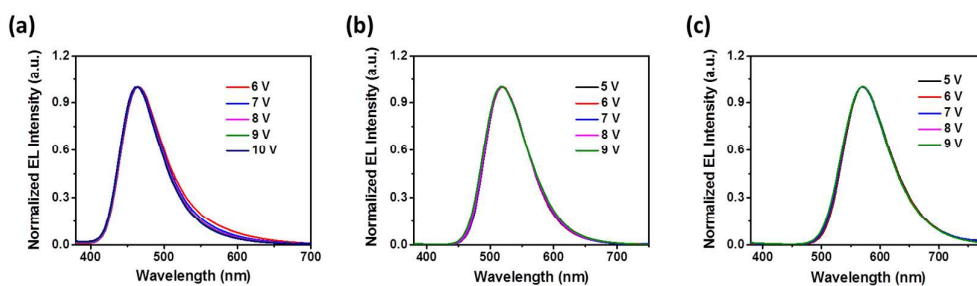


Figure S6 The EL spectra of CZP-1AC (a) TPA-1AC (b) and PTZ-1AC (c) based OLED at different driving voltages.

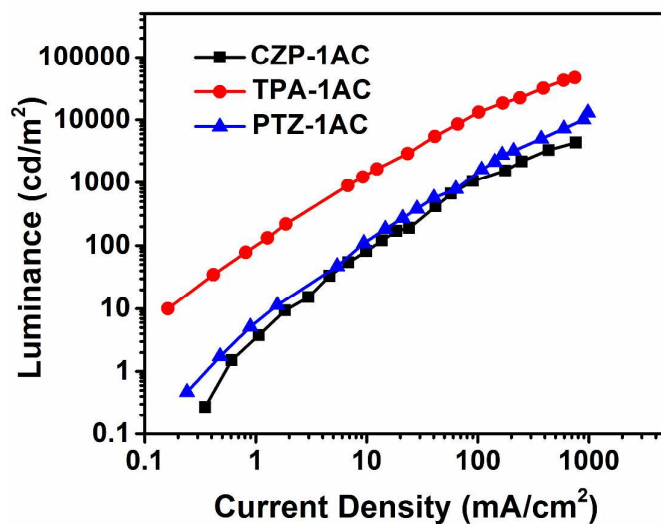


Figure S7 Luminance versus current density curves of CZP-1AC, TPA-1AC and PTZ-1AC devices.

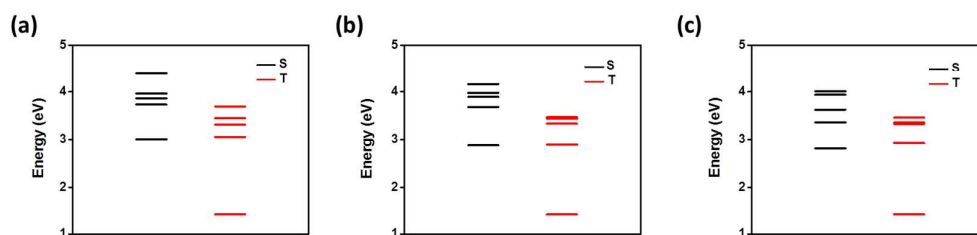


Figure S8 The energy landscape for singlet and triplet excited states of CZP-1AC (a), TPA-1AC (b) and PTZ-1AC (c).

S-IV References

- (1) Su, Q.; Li, P.; He, M.; Wu, Q.; Ye, L.; Mu, Y., Facile Synthesis of Acridine Derivatives by ZnCl₂-Promoted Intramolecular Cyclization of O-Arylamino-phenyl Schiff Bases. *Org. Lett.* **2014**, *16*, 18-21.
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