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Supporting Information

For

Acridin-9(10*H*)-one based thermally activated delayed fluorescence material: Simultaneous optimization of RISC and radiation processes to boost luminescence efficiencies

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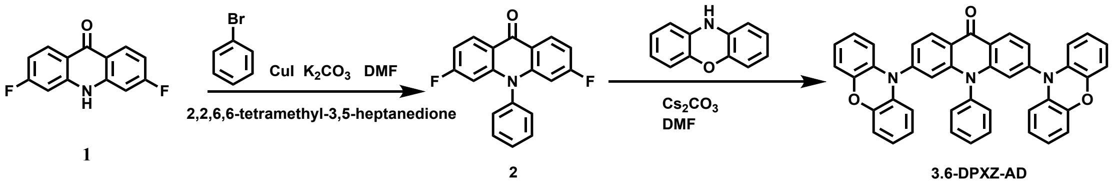
Contents

1. Experimental Section

Compound Synthesis and Characterization.

Important intermediates 3,6-difluoroacridin-9(10H)-one (1) and 3,6-difluoro-10-phenylacridin-9(10H)-one (2) were synthesized according to literature methods.[1]



Scheme S1. Chemical structures and synthetic routes for 3,6-DPXZ-AD

Synthesis of 2: 1-bromobenzene (192 mg, 1.22 mmol), 1 (255 mg, 1.10 mmol), K_2CO_3 (170 mg, 1.21 mmol.), CuI (21 mg, 0.11 mmol.), 2,2,6,6-tetramethyl-3,5-heptanedione (38 mg, 0.21 mmol) were dissolved in dry N,N-Dimethylformamide (DMF) (10 mL) in a three-necked round flask. The mixture was degassed and refluxed under nitrogen atmosphere for 24 h. After cooling to room temperature, the reaction mixture was quenched with H_2O and extracted with dichloromethane (DCM, 3×10 mL). The combined organic phase was dried and treated by rotary evaporator to remove the solvent. The generated residue was then isolated by column chromatography (eluent: DCM/petroleum ether =1:1) to provide compound 2 (198 mg,). Yield: 60%. TOF-EI-MS (*m/z*): cal. for $C_{19}H_{11}F_2NO$ 307.0809; Found 307. 0814 $[M]^+$.

Synthesis of 3,6-DPXZ-AD: A mixture of 2 (400 mg, 1.30 mmol), phenoxazine (PXZ) (523 mg, 2.86 mmol), cesium carbonate (1694 mg, 5.2 mmol) and 20 mL of dry DMF was stirred and refluxed at 165 °C for 24 h. After cooling down to room temperature, the reaction mixture was poured into water and the precipitated solid was filtered under reduced pressure. The residue was purified by column chromatography on silica gel using DCM as the eluent to give a light orange red solid. Repeated recrystallization from $CHCl_3/CH_3OH$ gave pure product.

3,6-DPXZ-AD: a light orange red solid, 452 mg, yield 50%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84 (d, J = 8.4 Hz, 2H), 7.66 (t, J = 7.3 Hz, 2H), 7.62 – 7.57 (m, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 6.80 (s, 2H), 6.70 (q, J = 7.6 Hz, 8H), 6.62 (t, J = 7.4 Hz, 4H), 5.97 (d, J = 7.9 Hz, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ: 176.87, 145.14, 144.07, 143.97, 137.94, 133.53, 131.74, 130.85, 130.30, 129.28, 123.68, 123.27, 121.93, 121.49, 118.85, 115.74, 113.37. TOF-MALDI-MS (m/z): cal. for $C_{43}H_{27}N_3O_3$ 633.2052; Found: 633.2033 $[M]^+$. Anal. Calcad for $C_{43}H_{27}N_3O_3$: C, 81.50; H, 4.29; N, 6.63; Found: C, 81.48; H, 4.30; N, 6.61.

Kinetic parameters calculation of photo-physical processes

To quantificationally discuss and compare the RISC process of materials, rate constants of different kinetic processes were calculated following equations[2] as shown below:

$K_P=1/\tau_{PF}$

$K_D=1/\tau_{DF}$

$K_R=\Phi_{PF}/\tau_{PF}$

$\Phi_{PL}=K_R/(K_R+K_{NR})$

$\Phi_{PF}=K_R/(K_R+K_{ISC}+K_{NR})$

$K_{RISC}=K_PK_D\Phi_{DF}/K_{ISC}\Phi_{PF}$

K_P, K_D, K_R, K_{NR}, K_{ISC}, K_{RISC} represent the rate constants of prompt process, delay process, radiation, non-radiation, intersystem crossing, and reverse intersystem crossing, respectively. Φ_{PL}, Φ_{PF}, Φ_{DF}, τ_{PF}, and τ_{DF} represent total PLQY, quantum yield of the prompt component, quantum yield of the delayed component, average lifetimes of the prompt and delayed components, respectively.

2. Supplemental tables and figures

Table S1 Experimentally obtained physical parameters of 3,6-DPXZ-AD.

compound	λ_{abs}[a] (nm)	λ_{em}[a] (nm)	S_1[b] (eV)	T_1[b] (eV)	HOMO /LUMO [d] (eV)	T_d/ T_g[e] (°C)
3,6-DPXZ-AD	376/395/437	566	2.24 [c] 2.20/2.15	2.44 [c] 2.34/ (2.35, 2.47)	-5.10 /-2.79	441.3 /148.7
AD-Ph	374/392	400/421	3.02	2.60		
PXZ-Ph	324	292/389	3.39	2.72		

[a] Absorption and fluorescence peak wavelengths in dilute toluene solutions; [b] Estimated from the fluorescence and phosphorescence peaks of 3,6-DPXZ-AD, AD-Ph and PXZ-Ph at 77 K in 2-MeTHF; [c] Estimated from the fluorescence and phosphorescence peaks of 3,6-DPXZ-AD at 77 K in THF, and DCM; [d] Determined from electrochemical measurements; [e] Decomposition temperature (T_d) at 5 wt% weight loss obtained from TGA measurements, and glass transition temperature (T_g) obtained from DSC measurements.

Table S2. Crystal data and structure refinement of 3,6-DPXZ-AD.

Identification code	3,6-DPXZ-AD (CCDC: 2068551)
Empirical formula	$C4_3H_{27}N_3O_3$ ($CHCl_3$)
Formula weight	753.04
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	12.8076(7)
b/Å	12.8293(8)
c/Å	13.3517(7)
α/°	92.432(2)
β/°	115.385(2)
γ/°	114.570(2)
Volume/Å^3	1736.32(17)
Z	35
ρ_{calc}g/cm^3	1.440
μ/mm^{-1}	0.129
F(000)	770.0
Crystal size/mm^3	0.14 × 0.16 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.534 to 59.988
Index ranges	$-17 \leq h \leq 18$, $-18 \leq k \leq 18$, $-18 \leq l \leq 18$
Reflections collected	51766
Independent reflections	10102 [R_{int} = 0.0807, R_{sigma} = 0.0670]
Data/restraints/parameters	10102/0/478
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0653, wR_2 = 0.1826
Final R indexes [all data]	R_1 = 0.1098, wR_2 = 0.2094
Largest diff. peak/hole / e Å^{-3}	0.59/-0.92

Table S3. Summary of device performance data of the TADF-OLED. [a]

Device	V_{on} [V]	η_c [cd A^{-1}]	η_p [lm W^{-1}]	η_{ext} [b] [%]	CIE (x, y)
3,6-DPXZ-AD: CBP	2.2	98.0	109.9	30.6/28.9/22.4	(0.43,0.55)

[a] V_{on}, turn-on voltage at a brightness of 1 cd m^{-2}; η_c and η_p, maximum current efficiency and power efficiency, respectively; CIE (x, y), Commission International de I'Eclairage coordinates at 7.0 V; [b] η_{ext}, external quantum efficiency in the order of maximum, and at the brightness of 100 and 1000 cd m^{-2}, respectively.

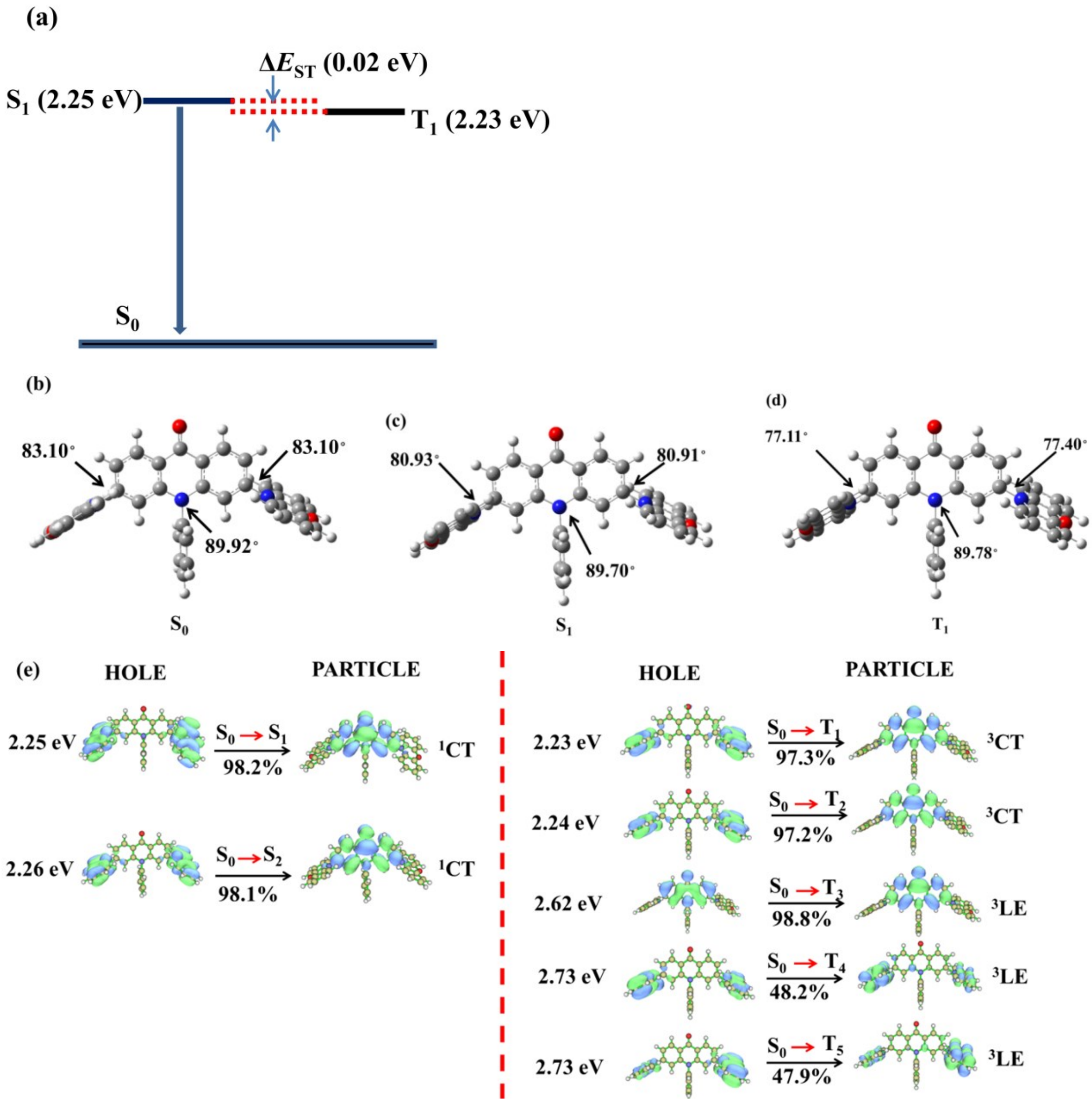


Fig. S1 Calculated energies for the S_1 and T_1 excited states (a), the optimized geometries for the S_0, S_1, and T_1 states (b-d) by TD-DFT method, and the NTOs calculated using Multiwfn 3.5 (e)[3] of 3,6-DPXZ-AD.

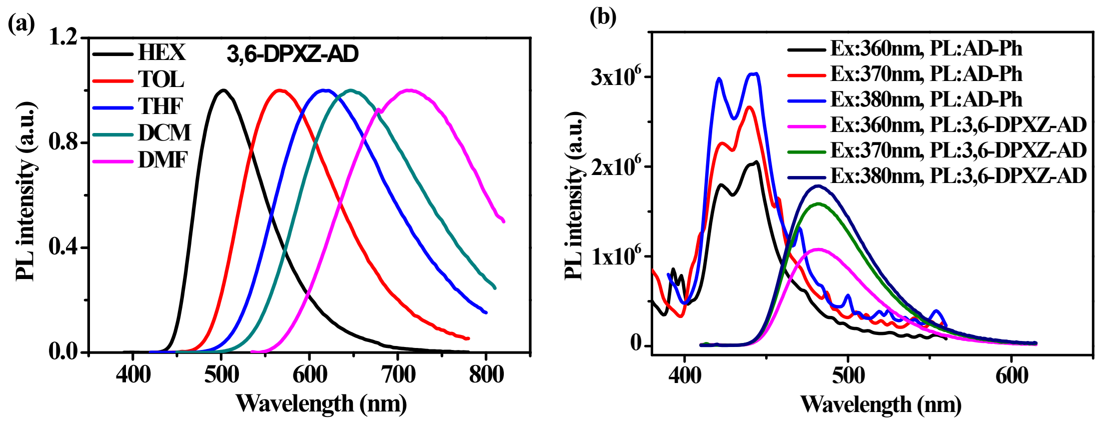
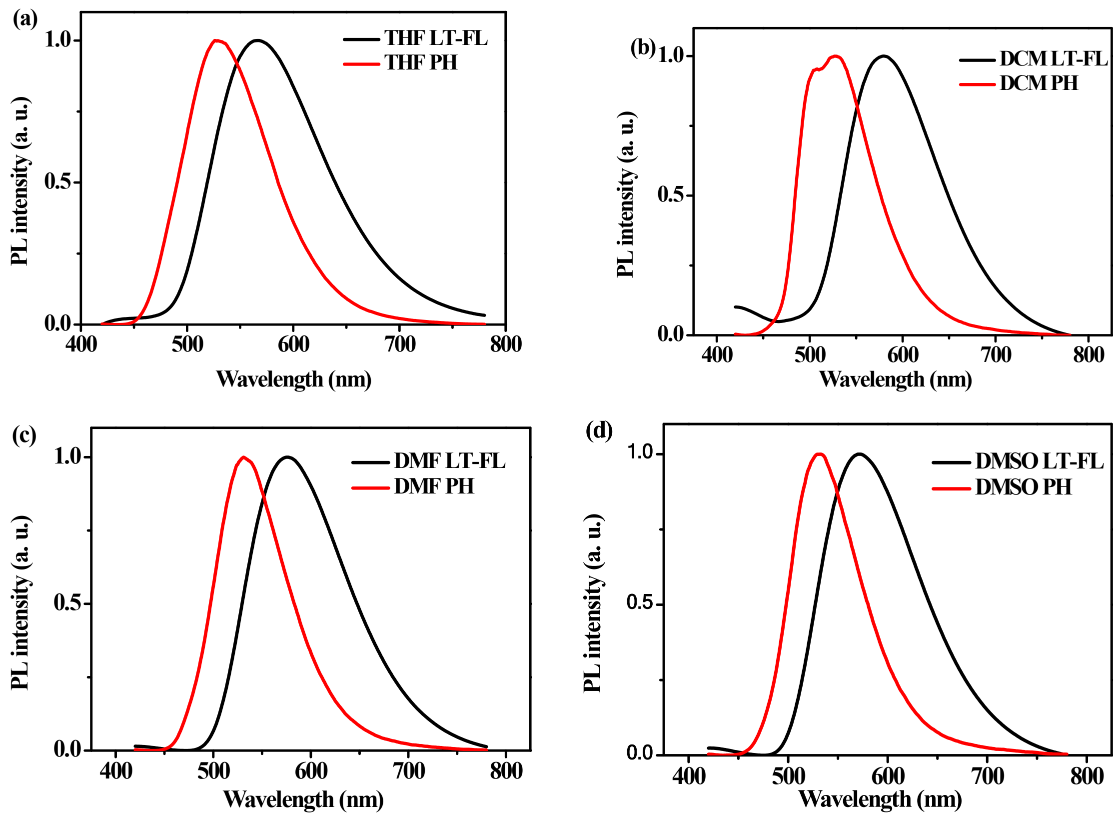


Fig. S2 The steady-state PL spectra of 3,6-DPXZ-AD in different solvents (a) and of AD-Ph and 3,6-DPXZ-AD at different excitation wavelengths (from 360 to 380 nm) in toluene (TOL) solution (b).



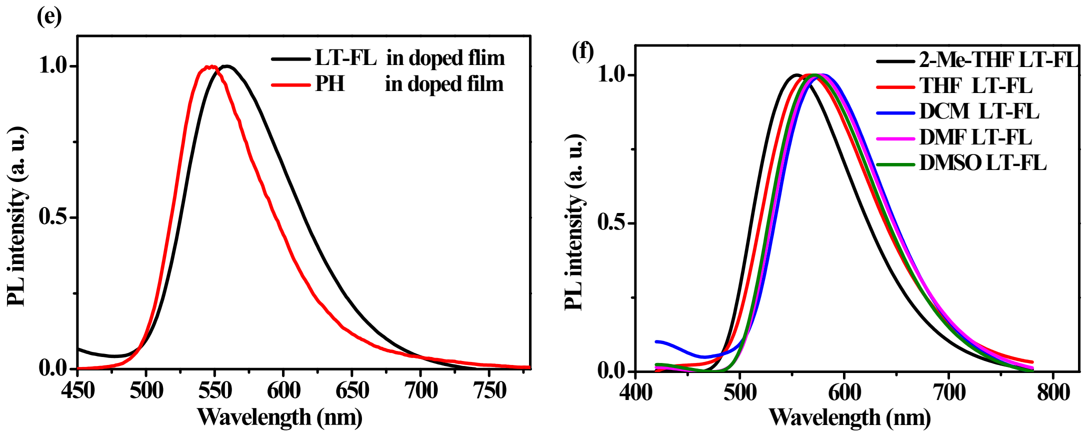


Fig. S3 LT-FL and PH spectra of 3,6-DPXZ-AD in frozen THF (a), DCM (b), DMF (c) and DMSO (d) solutions and doped film (e) at 77 K, fluorescence spectra in these solvents are compared in (f).

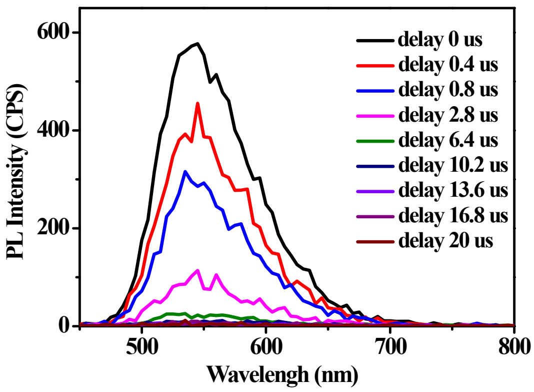


Fig. S4 Time-resolved spectra of 7 wt% 3,6-DPXZ-AD:CBP film at different delay time.

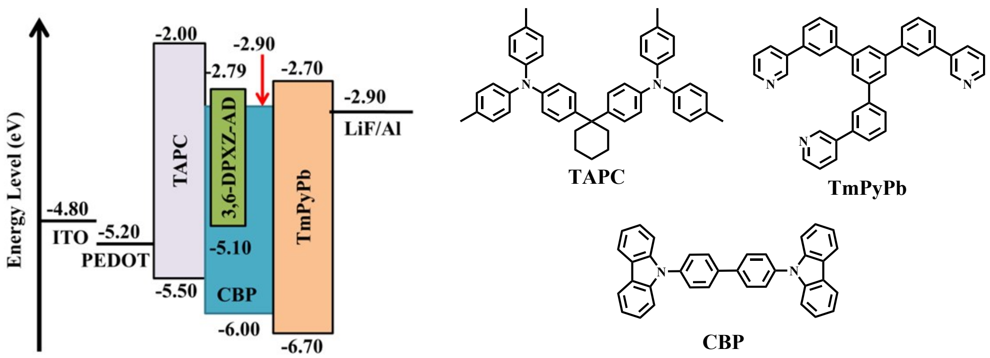


Fig. S5 Energy diagram of the 3,6-DPXZ-AD based OLED and the chemical structures of the materials.

3. References

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