Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Forcing Dimethylacridine Crooked to Improve the Efficiency of Orange-Red Thermally Activated Delayed Fluorescent Emitters

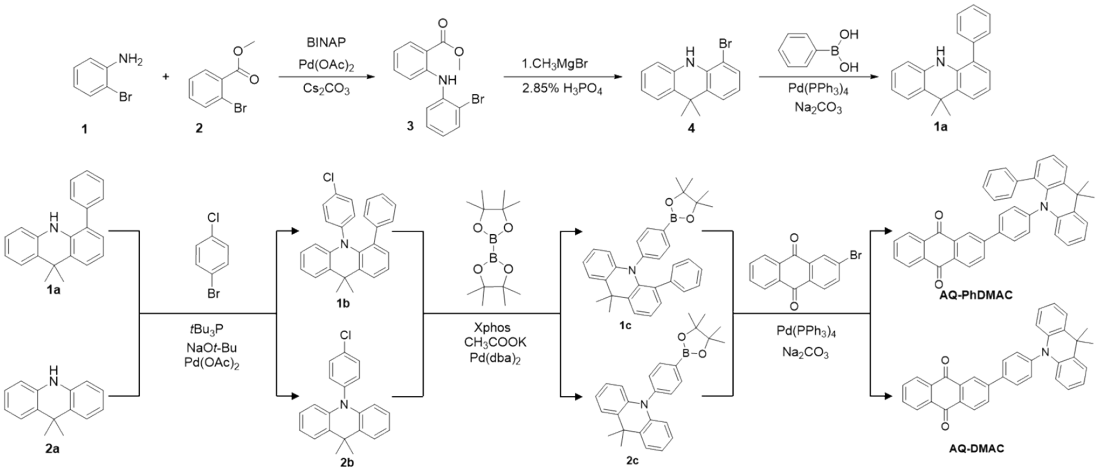
Feng-Yan Hao,‡ Yi-Zhong Shi,‡ Kai Wang,* Xiao-Chun Fan, Lin Wu, Jun Ye,* Cai-Jun Zheng, Yan-Qing Li, Xue-Mei Ou and Xiao-Hong Zhang*

Contents

1. General Information

All reagents and solvents were commercially available without further purification. Nuclear magnetic resonance (NMR) spectral data were obtained using a Bruker Advance-400 spectrometer with chemical shifts reported in ppm. The Absorption and photoluminescence (PL) spectra were obtained using a Hitachi ultraviolet-visible (UV-Vis) spectrophotometer U-3010 and a Hitachi fluorescence spectrometer F-4600, respectively. The transient photoluminance decay characteristics were measured using an Edinburgh Instruments F980 spectrometer. The photoluminescence quantum yield of the doped solid film was obtained using a QY-2000 Fluorescence Spectrometer and estimated via an F-3018 Integrating Sphere. Lastly, cyclic voltammetry (CV) was performed using a CHI660E electrochemical analyzer. The theoretical calculations were performed using the Gaussian-09 program. Density functional theory (DFT) B3LYP/6-31G (d) was used to determine and optimize the structures.

2. Experimental procedures



Scheme S1. Experimental procedure of AQ-PhDMAC and AQ-DMAC.

Synthesis of methyl 2-((2-bromophenyl)amino)benzoate **(3):** A mixture of 2-bromoaniline (5.2 g, 30.0 mmol), methyl 2-bromobenzoate (7.1 g, 33.0 mmol), $Pd(OAc)_2$ (336.8 mg, 1.5 mmol), BINAP (1.9 g, 3.0 mmol) and Cs_2CO_3 (19.0 g, 60.0 mmol) was stirred and refluxed in anhydrous toluene (80 mL) for overnight under the N_2. After cooled to room temperature and the solvent had been removed, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (8/1, v/v) as the eluent to afford **3** as a colorless oil, with a yield of 57 % (5.3 g).^{1}H NMR (600 MHz, DMSO-d_6) δ 9.47 (s, 1H), 7.91 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.68 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.43 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.37 – 7.32 (m, 1H), 7.16 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.01 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 6.87 (ddd, *J* = 8.1, 7.2, 1.1 Hz, 1H), 3.85 (s, 3H). MS (EI) m/z: $[M]^+$ calcd for $C_{14}H_{12}BrNO_2$, 305.01; found, 305.07.

Synthesis of 4-bromo-9,9-dimethyl-9,10-dihydroacridine **(4):** The methyl 2-((2-bromophenyl)amino)benzoate (3.4 g, 11.1 mmol) was dissolved in anhydrous tetrahydrofuran (60 mL) under argon and cooled to -10 °C. Then methyl magnesium bromide (CH_3MgBr, 3 M in THF, 8 mL, 24.0 mmol) was added dropwise under stirred. After 2 h reaction at 0 °C, the mixture was gradually warmed up to 35 °C and reacted overnight. After the completion of the reaction, it was been quenched by water (2 mL). Then the solvent was removed and the crude product was used without further purified. A mixture of the crude product in 85 % phosphoric acid (50 mL) was stirred at 35 °C for 5 h. The reaction mixture was then poured into ice and extracted with

ethyl acetate and water. The organic layer was dried over anhydrous $MgSO_4$, and concentrated to give the crude product which was purified by column chromatography on silica gel using petroleum ether/dichloromethane (4/1, v/v) as the eluent to afford **4** as a colorless oil, with a yield of 62 % (2.0 g). ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.95 (s, 1H), 7.43 – 7.31 (m, 3H), 7.23 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.12 – 7.01 (m, 1H), 6.90 – 6.82 (m, 1H), 6.75 (td, *J* = 7.8, 1.0 Hz, 1H), 1.51 – 1.41 (m, 6H). MS (EI) m/z: $[M]^+$ calcd for $C_{15}H_{14}BrN$, 287.03; found, 287.09.

Synthesis of 9,9-dimethyl-4-phenyl-9,10-dihydroacridine **(1a):** A mixture of 4-bromo-9,9-dimethyl-9,10-dihydroacridine (2.0 g, 6.9 mmol), phenylboronic acid (0.9 g, 7.3 mmol), $Pd(PPh_3)_4$ (0.4 g, 0.35 mmol) and Na_2CO_3 (10 mL, 2 M) in degassed toluene (75 mL) and degassed ethanol (15 mL) was refluxed overnight under an N_2 atmosphere. After cooled to room temperature and the solvent had been removed, the crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (8/1, v/v) as the eluent to afford **1a** as a white solid, with a yield of 81 % (1.6 g).^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 – 7.53 (m, 2H), 7.50 – 7.39 (m, 6H), 7.07 – 6.92 (m, 4H), 6.90 – 6.85 (m, 1H), 1.58 (s, 6H). MS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{19}N$, 285.15; found, 285.18.

Synthesis of 10-(4-chlorophenyl)-9,9-dimethyl-4-phenyl-9,10-dihydroacridine **(1b):** A mixture of 9,9-dimethyl-4-phenyl-9,10-dihydroacridine (1.6 g, 5.6 mmol), 1-bromo-4-chlorobenzene (1.1 g, 5.7 mmol), $Pd(dba)_2$ (161.2 mg, 0.3 mmol), tri-butyl phosphine (0.5 mL, 0.8 mmol, 10 % in toluene) and sodium tert-butoxide (1.4 g, 14.0 mmol) was stirred and refluxed in toluene (60 mL) for overnight under the N_2. After cooled to room temperature and the solvent had been removed, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (8/1, v/v) as the eluent to afford **1b** as a white solid with a yield of 63 % (1.4 g).^{1}H NMR (600 MHz, DMSO-d_6) δ 7.65 – 7.56 (m, 3H), 7.45 (d, *J* = 7.8 Hz, 3H), 7.38 (td, *J* = 7.7, 1.6 Hz, 1H), 7.31 (dt, *J* = 14.5, 7.5 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.96 – 6.91 (m, 2H), 6.74 (dd, *J* = 9.0, 1.7 Hz, 2H), 1.46 (s, 6H). MS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{22}ClN$, 395.14; found, 395.12.

Synthesis of 10-(4-chlorophenyl)-9,9-dimethyl-9,10-dihydroacridine **(2b): 2b** was prepared with a similar procedure of **1b** with **2a** instead of **1a. 2b** was obtained as a white solid with a yield of 83 % (1.9 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 – 7.69 (m, 2H), 7.49 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.45 – 7.34 (m, 2H), 6.94 (dtd, *J* = 28.6, 7.3, 1.5 Hz,

4H), 6.14 (dd, *J* = 8.2, 1.3 Hz, 2H), 1.61 (s, 6H). MS (EI) m/z: $[M]^+$ calcd for $C_{21}H_{18}ClN$, 319.83; found, 319.87.

Synthesis of 9,9-dimethyl-4-phenyl-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9,10-dihydroacridine **(1c):** A mixture of 10-(4-chlorophenyl)-1-phenyl-10H-phenoxazine (1.4 g, 3.8 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (1.9 g, 7.6 mmol), $Pd(dba)_2$ (108.8 mg, 0.2 mmol) , Xphos (270.7 mg, 0.6 mmol) and potassium acetate (0.9 g, 9.5 mmol) was stirred and refluxed in 1,4-dioxane (60 mL) for overnight under the N_2. After cooled to room temperature and the solvent had been removed, the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (4/1, v/v) as the eluent to afford **1c** as a white solid, with a yield of 74% (1.3 g).^{1}H NMR (600 MHz, DMSO-d_6) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 4H), 7.21 (t, *J* = 7.7 Hz, 3H), 6.73 (d, *J* = 8.3 Hz, 2H), 1.42 (s, 6H), 1.19 (s, 12H). MS (EI) m/z: $[M]^+$ calcd for $C_{33}H_{18}BNO_2$, 487.25; found, 487.21.

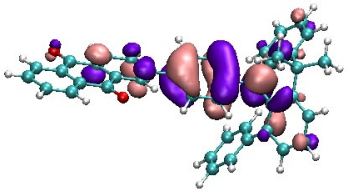
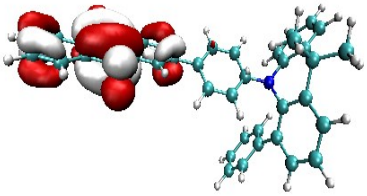
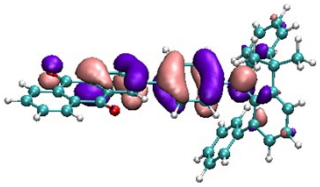
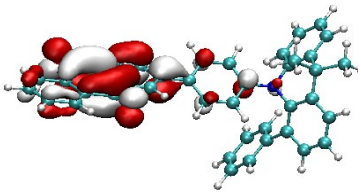
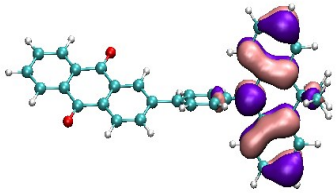
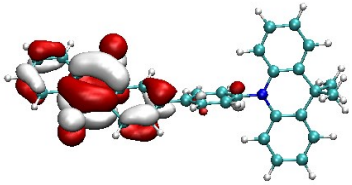
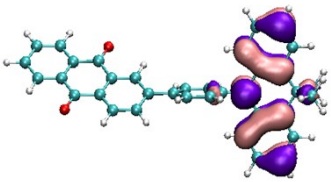
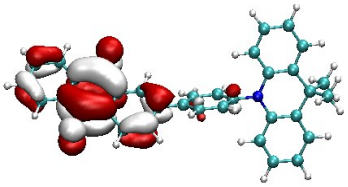
Synthesis of 9,9-dimethyl-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9,10-dihydroacridine **(2c): 2c** was prepared with a similar procedure of **1c** with **2b** instead of **1b. 2c** was obtained as a white solid with a yield of 78 % (1.9 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.44 (dd, *J* = 7.0, 2.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 6.92 (pd, *J* = 7.2, 1.7 Hz, 4H), 6.27 – 6.20 (m, 2H), 1.40 (s, 12H). MS (EI) m/z: $[M]^+$ calcd for $C_{27}H_{30}BNO_2$, 411.24; found, 411.26.

Synthesis of 2-(4-(9,9-dimethyl-4-phenylacridin-10(9H)-yl)phenyl)anthracene-9,10-dione **(AQ-PhDMAC):** A mixture of 9,9-dimethyl-4-phenyl-10-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9,10-dihydroacridine (1.0 g, 2.1 mmol) , 2-bromoanthracene-9,10-dione (0.6 g, 2.1 mmol), $Pd(PPh_3)_4$ (118.5 mg, 0.1 mmol) and Na_2CO_3 (3 mL, 2 M) in degassed toluene (45 mL) and degassed ethanol (15 mL) were refluxed overnight under an N_2 atmosphere. After cooling to room temperature and the solvent had been removed, the crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (4/1, v/v) as the eluent to afford **AQ-PhDMAC** as orange solid, with a yield of 86 % (1.0 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 – 8.13 (m, 4H), 8.02 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.96 – 7.88 (m, 2H), 7.73 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.63 (ddd, *J* = 9.6, 7.8, 1.5 Hz, 2H), 7.57 – 7.46 (m, 5H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.36 (tdd, *J* = 7.1, 3.9, 1.8 Hz, 4H), 7.24 – 7.18 (m, 1H), 6.92

(d, *J* = 9.0 Hz, 2H), 1.49 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 183.43, 182.76, 146.28, 145.77, 145.53, 144.68, 142.26, 140.07, 139.09, 138.02, 134.02, 133.80, 133.72, 133.60, 131.01, 130.94, 129.20, 128.75, 128.56, 128.22, 127.87, 127.21, 127.14, 127.08, 126.21, 126.03, 125.49, 125.33, 124.62, 124.11, 123.57, 114.50, 38.58, 27.70. MS (EI) m/z: $[M]^+$ calcd for $C_{41}H_{29}NO_2$, 567.22; found, 567.31.

***Synthesis of 2-(4-(9,9-dimethylacridin-10(9H)-yl)phenyl)anthracene-9,10-dione* (AQ-DMAC): AQ-DMAC** was prepared with a similar procedure of **AQ-PhDMAC** with **2c** instead of **1c. AQ-DMAC** was obtained as an orange solid with a yield of 84 % (1.0 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.9 Hz, 1H), 8.51 – 8.32 (m, 3H), 8.14 (dd, *J* = 8.1, 1.9 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.89 – 7.79 (m, 2H), 7.57 – 7.41 (m, 4H), 7.08 – 6.87 (m, 4H), 6.35 (dd, *J* = 8.0, 1.3 Hz, 2H), 1.72 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 182.90, 182.60, 145.66, 141.78, 140.49, 138.58, 134.04, 133.91, 133.78, 133.41, 133.37, 132.17, 131.88, 129.91, 129.58, 127.98, 127.11, 127.05, 126.19, 125.48, 125.09, 120.54, 113.80, 35.78, 31.05. MS (EI) m/z: $[M]^+$ calcd for $C_{35}H_{25}NO_2$, 491.19; found, 491.23.

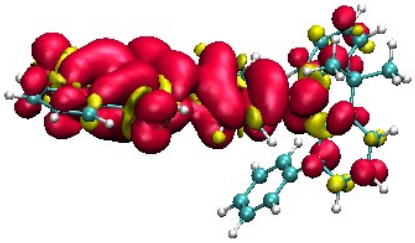
3. Theoretical Simulation Results

		Hole	Particle
AQ-PhDMAC	**Singlet**		
	Triplet		
AQ-DMAC	**Singlet**		
	Triplet		

	S_1/ eV	f	T_1/ eV	ΔE_{ST}/ eV
AQ-PhDMAC	2.4957	0.1851	2.1309	0.3648
AQ-DMAC	2.0042	0.0000	2.0030	0.0012

Fig. S1 Natural transition orbitals (NTO) analysis of the lowest excited states based on the optimal ground state geometry for AQ-PhDMAC and AQ-DMAC.

a



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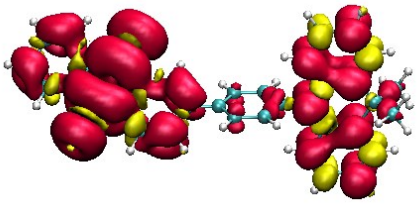


Fig. S2 Calculated spin density distributions of the lowest excited triplet states of a) AQ-PhDMAC and b) AQ-DMAC. The isovalue is 0.0004.

4. Electrochemical Properties

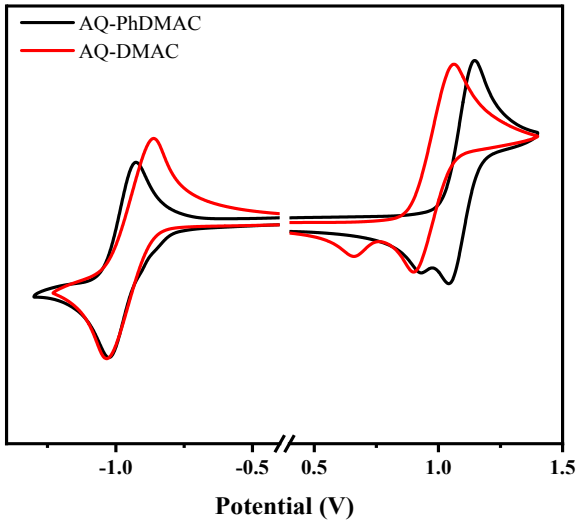


Fig. S3 Cyclic voltammograms of AQ-PhDMAC and AQ-DMAC in DCM.

5. TGA and DSC Measurements

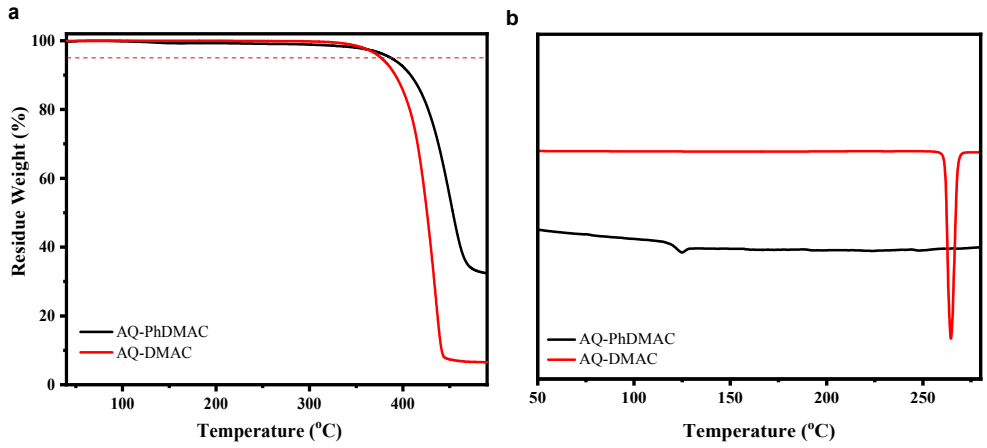


Fig. S4 a) TGA and b) DSC results of AQ-PhDMAC and AQ-DMAC.

6. Photophysical Properties

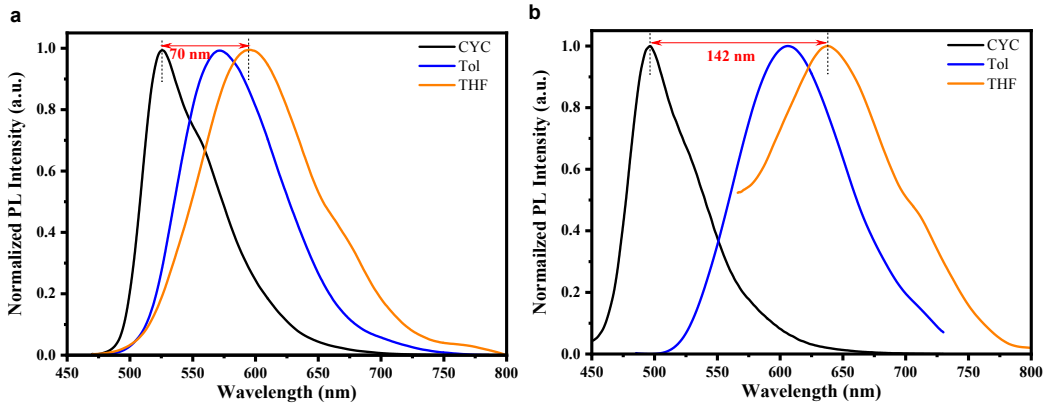


Fig. S5 Emission spectra of a) AQ-PhDMAC and b) AQ-DMAC in cyclohexane (CYC), toluene (Tol), and tetrahydrofuran (THF) at room temperature.

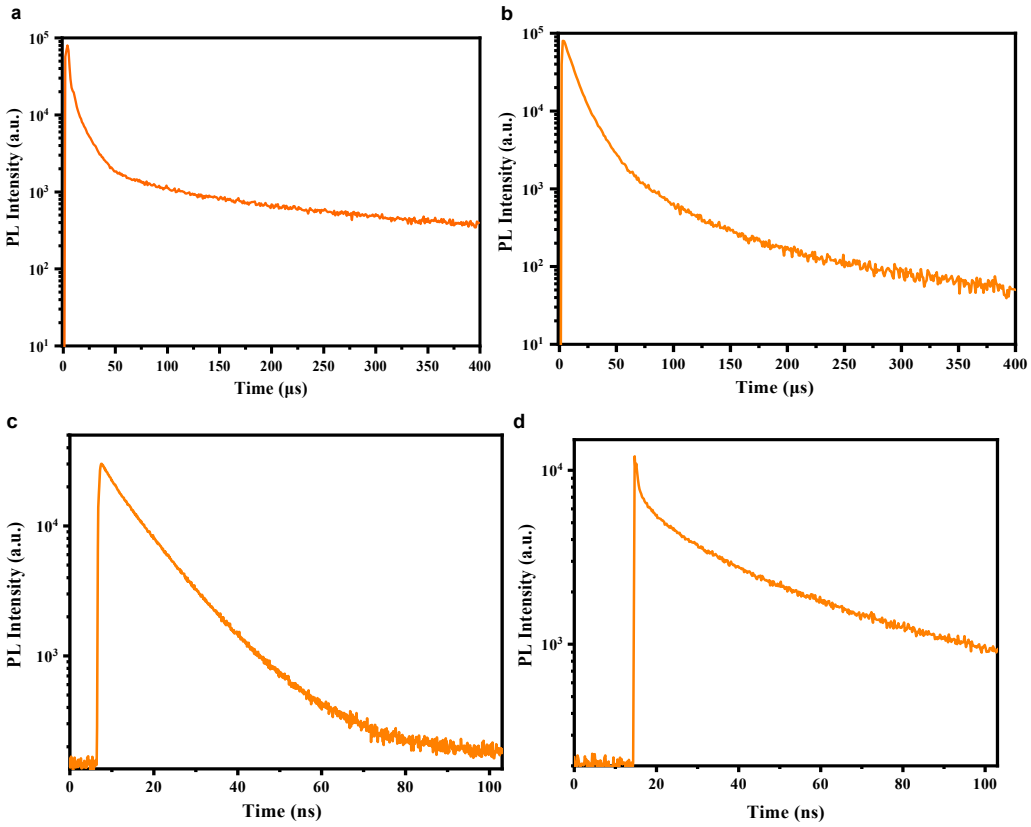


Fig. S6 Transient PL decay curves of 5 wt% AQ-PhDMAC doped CBP films in a range of a) 400 μs and c) 100 ns at room temperature. Transient PL decay curves of 5 wt% AQ-DMAC doped CBP films in a range of b) 400 μs and c) 103 ns at room temperature. (Excited at 300 nm)

7. Device Fabrication and Characterization

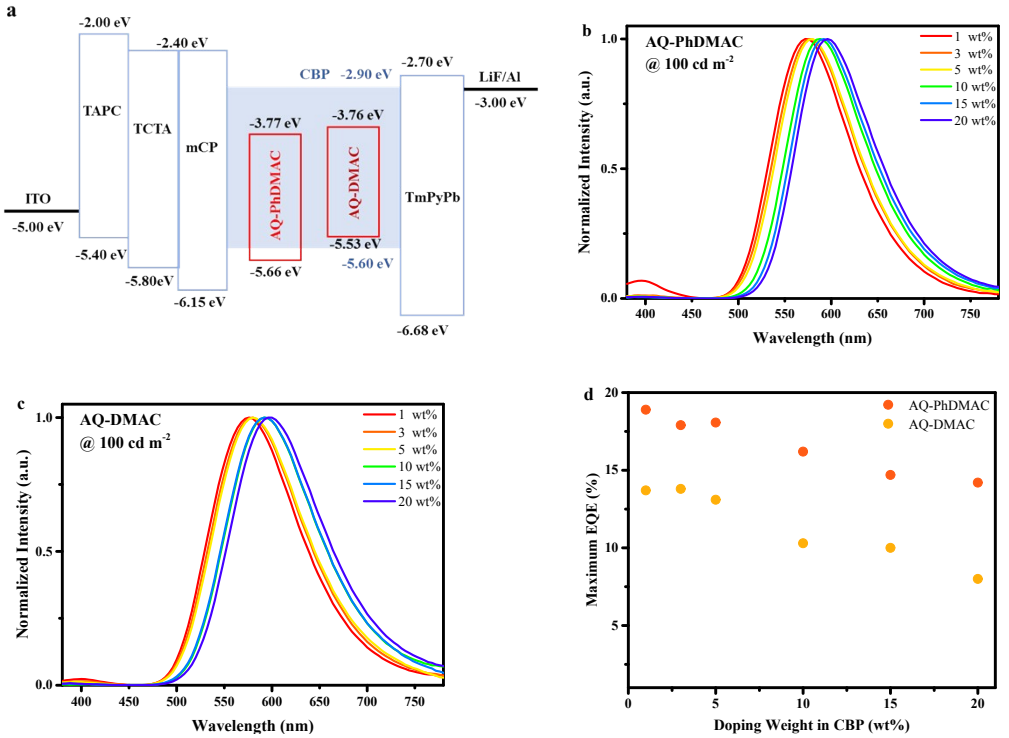


Fig. S7 a) Energy diagram of the device; Normalized EL spectra of b) AQ-PhDMAC and c) AQ-DMAC 1 wt%, 3 wt%, 5 wt%, 10 wt%, 15 wt% and 20 wt% doped in CBP at 100 cd m^{-2}; d) Maximum EQEs-Doping Weight in CBP characteristics of AQ-PhDMAC and AQ-DMAC.

Tab. S1 Key dynamic parameter of the studied compounds 5 wt% doped CBP films.

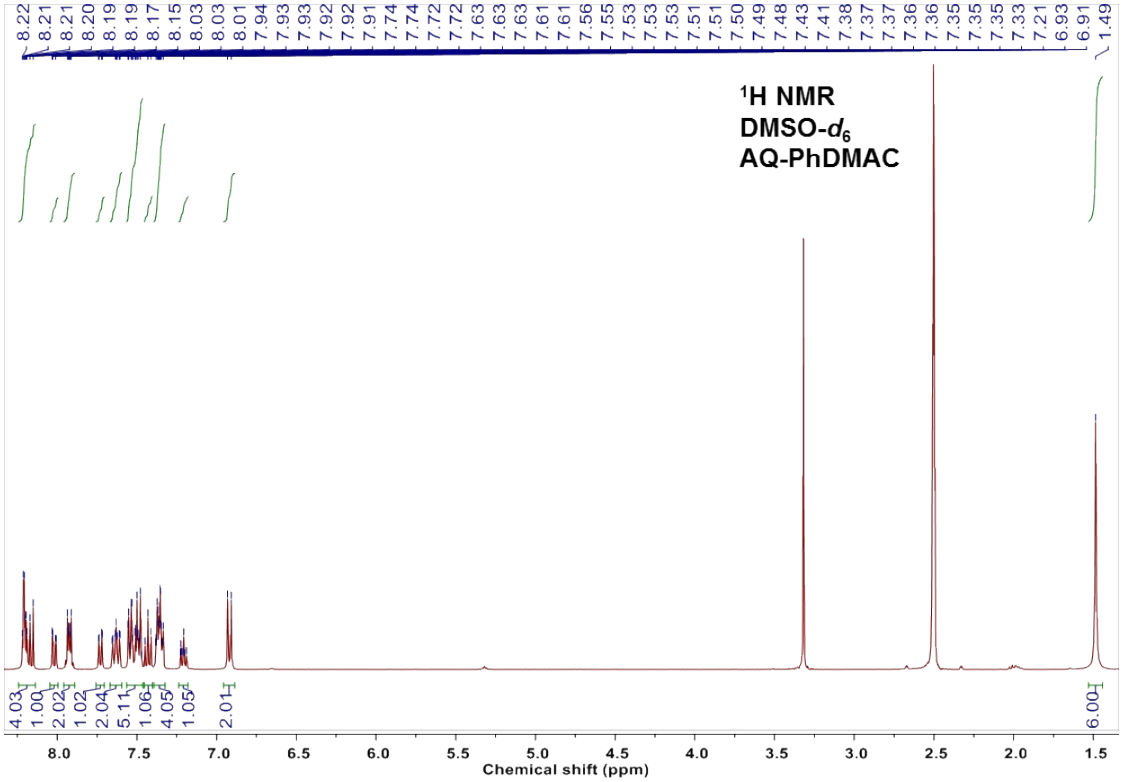
	τ_p (ns)	τ_d (μs)	φ_p (%)	φ_d (%)	k_F (10^7 s^{-1})	k_d (10^4 s^{-1})	k_{ISC} (10^7 s^{-1})	k_{RISC} (10^4 s^{-1})	k_{IC} (10^7 s^{-1})
AQ-PhDMAC	8.7	63.6	79.0	10.0	9.08	1.57	1.30	1.77	1.12
AQ-DMAC	12.7	21.2	27.4	35.6	2.16	4.71	4.45	10.80	1.27

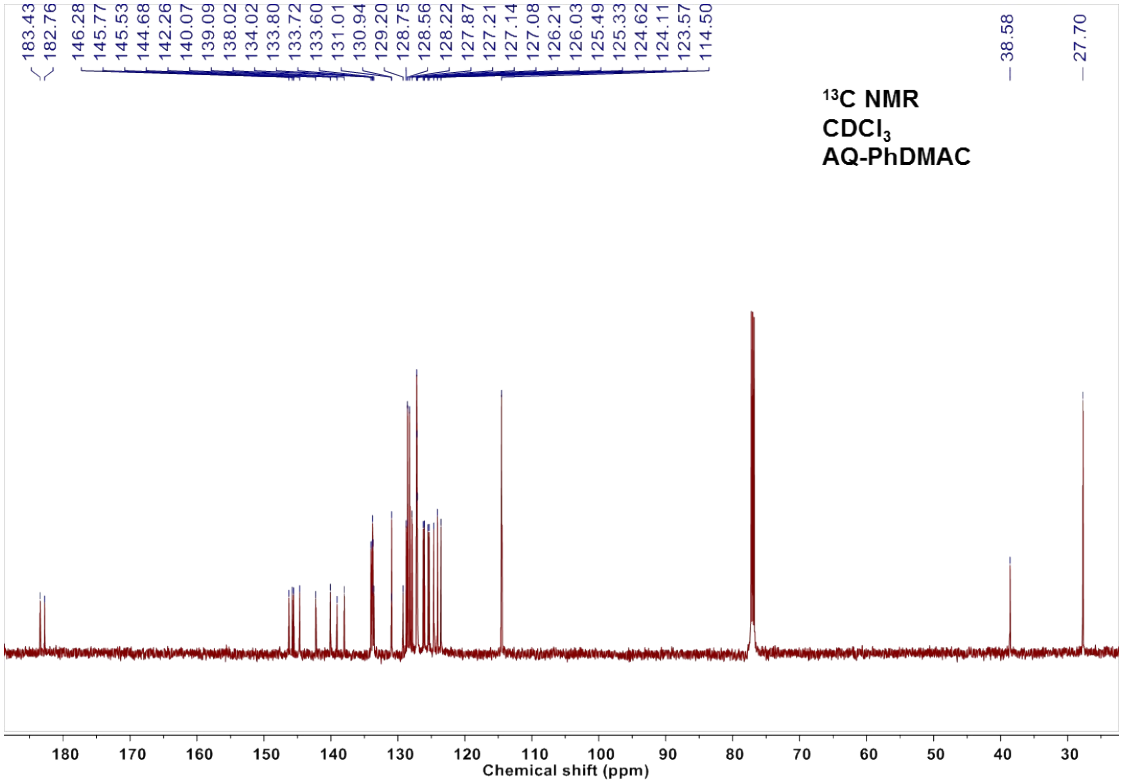
Tab. S2 Summary of the device performance.

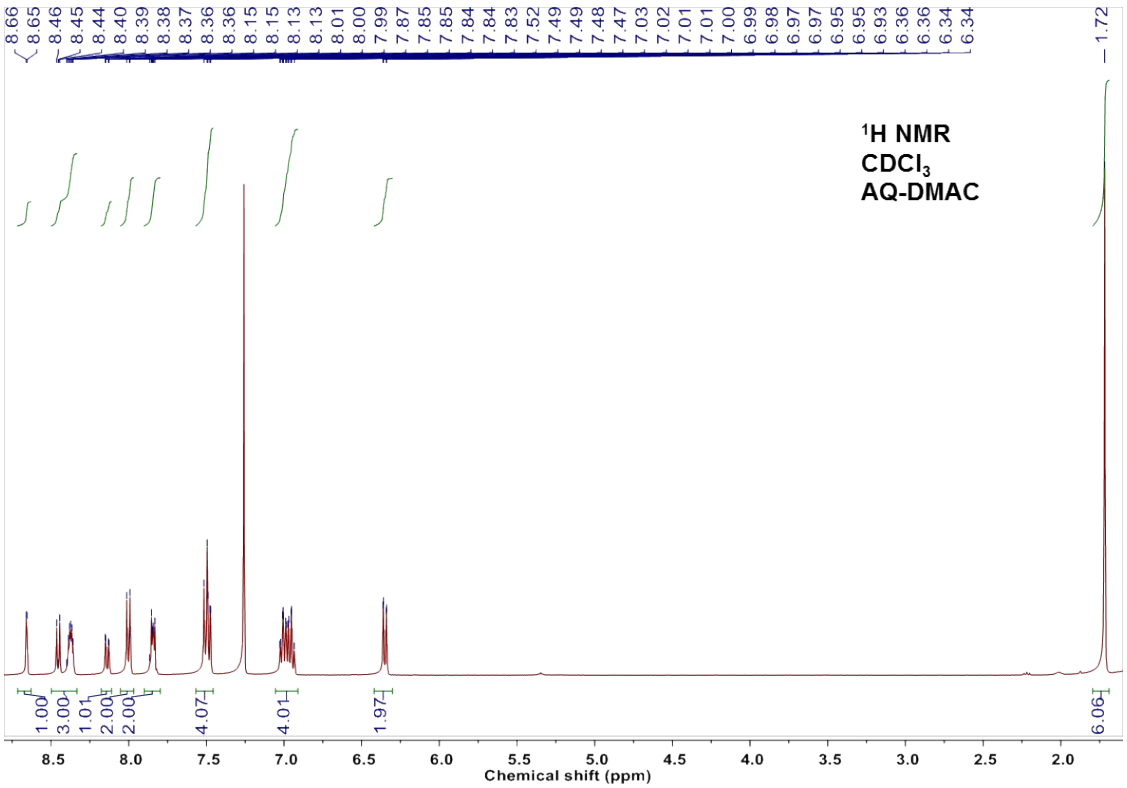
	Doping Weight (wt%)	V_{on}[a] (V)	Peak (nm)	Maximum CE/PE/EQE[b] (cd A^{-1}/lm W^{-1}/%)	CIE[c] (x, y)	FWHM[d] (nm)
AQ-PhDMAC	1	3.6	576	53.5/46.7/18.9	(0.47, 0.49)	100
	3	3.6	576	48.9/42.7/17.9	(0.48, 0.49)	100
	5	3.6	580	49.4/43.1/18.1	(0.49, 0.49)	100
	10	3.4	588	38.1/35.2/16.2	(0.52, 0.47)	100
	15	3.3	592	31.9/30.4/14.7	(0.54, 0.46)	100
	20	3.4	596	29.4/27.1/14.3	(0.55, 0.44)	100
AQ-DMAC	1	3.6	576	36.8/32.1/13.7	(0.48, 0.50)	110
	3	3.6	580	36.0/31.4/13.9	(0.49, 0.49)	111
	5	3.6	580	32.7/28.6/12.8	(0.50, 0.49)	111
	10	3.6	588	22.8/17.1/10.4	(0.53, 0.47)	114
	15	3.6	592	20.9/18.2/9.3	(0.53, 0.47)	115
	20	3.6	596	17.0/11.9/8.0	(0.54, 0.46)	117

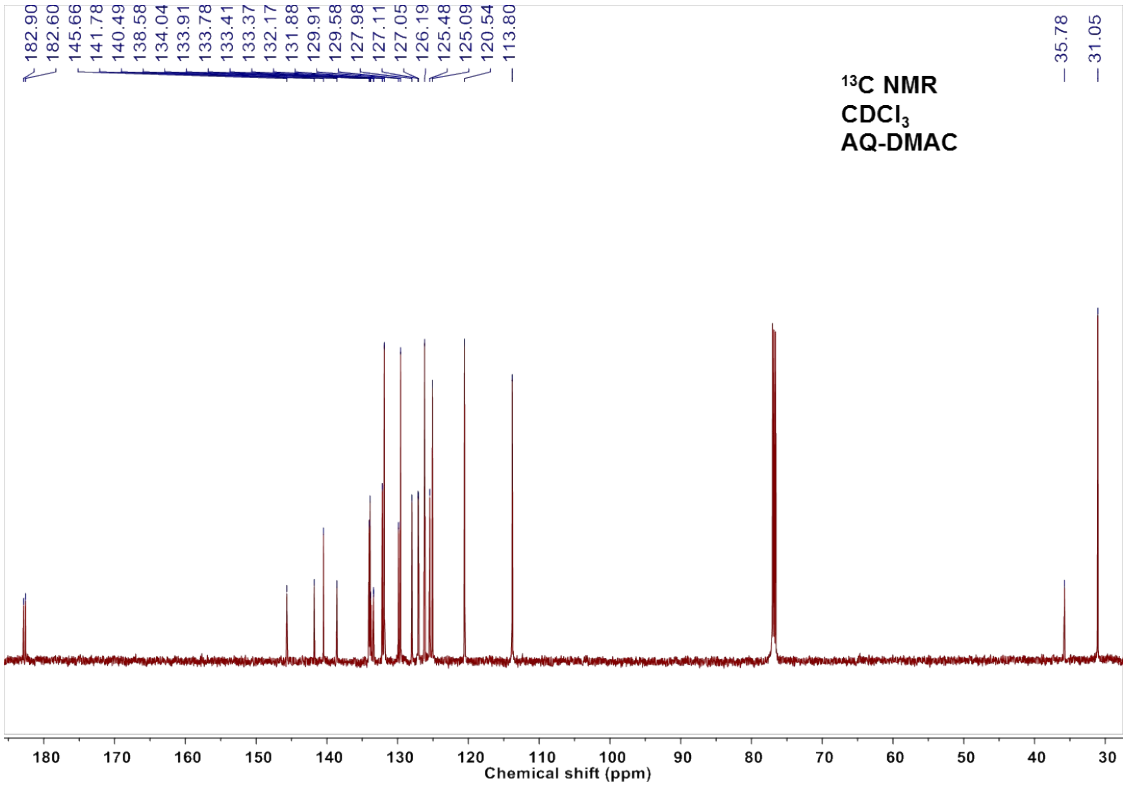
[a]Turn on voltage defined at 1 cd m^{-2}; [b]CE: current efficiency, PE: power efficiency and EQE: external quantum efficiency; [c]defined at 100 cd m^{-2}; [d]FWHM: full width at half maximum.

8. Nuclear Magnetic Resonance Spectra






8.66
8.65
8.46
8.45
8.44
8.40
8.39
8.38
8.37
8.36
8.36
8.15
8.15
8.13
8.13
8.01
8.00
7.99
7.87
7.85
7.85
7.84
7.84
7.83
7.52
7.49
7.49
7.48
7.47
7.03
7.02
7.01
7.01
7.00
6.99
6.98
6.97
6.97
6.95
6.95
6.93
6.36
6.36
6.34
6.34
1.72
^{1}H NMR
$CDCl_3$
AQ-DMAC
1.00
3.00
1.01
2.00
2.00
4.07
4.01
1.97
6.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical shift (ppm)


182.90
182.60
145.66
141.78
140.49
138.58
134.04
133.91
133.78
133.41
133.37
132.17
131.88
129.91
129.58
127.98
127.11
127.05
126.19
125.48
125.09
120.54
113.80
35.78
31.05
^{13}C NMR
$CDCl_3$
AQ-DMAC
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
Chemical shift (ppm)