

## Supplementary Information

# Over 800 nm Emission via Harvesting Triplet Excitons in Exciplex Organic Light-Emitting Diodes

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## General information

### Characterization

Mass spectra were measured on a Thermo ISQ mass spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were measured on a Bruker 400 or Agilent DD2 600 MHz spectrometer at 298 K with chemical shifts ( $\delta$ , ppm) relative to tetramethyl silane ( $\text{Me}_4\text{Si}$ ) for the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra. Thermogravimetric analysis (TGA) was performed on TA SDT 2960 instrument at a heating rate of 10  $^\circ\text{C}/\text{min}$  under nitrogen, the temperature at 5% weight loss was used as the decomposition temperature ( $T_d$ ), while the glass transition temperature ( $T_g$ ) was measured with a TA DSC 2010 unit. phorescent spectra were performed on Hitachi F-4600 fluorescence spectrophotometer or Horiba JY FL-3 fluorescence spectrophotometer. The absolute PLQY values were measured using Hamamatsu C9920-02G in integrating sphere at nitrogen atmosphere. The PL quantum yields (PLQYs) measurement range can cover from 300 to 950 nm. Transient spectra were obtained by using Quantaurs-Tau fluorescence lifetime measurement system (C11367-03, Hamamatsu Photonics Co.) in vacuum. Ultraviolet photoelectron spectroscopy (UPS) measurement was carried out in a Kratos AXIS UltraDLD surface

analysis system. The UPS (He I, 21.22 eV) spectra were plotted with respect to the determined Fermi level. The base vacuum of the system was about  $1 \times 10^{-10}$  Torr.

## Synthesis

Starting material 5-bromoacenaphthylene-1,2-dione were synthesized according to the literature procedure. (10.1021/ja4085308) All other chemicals and solvents used are purchased from commercial supplier without purification.

### **5-([1,1':3',1''-terphenyl]-5'-yl)acenaphthylene-1,2-dione (APDO-tPh)**

To a mixture of 5-bromoacenaphthylene-1,2-dione (3.0 g, 11.5 mmol), [1,1':3',1''-terphenyl]-5'-ylboronic acid (3.78 g, 13.8 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.66 g, 0.58 mmol) in 120 mL THF, 30 mL of degassed 2 M  $\text{Na}_2\text{CO}_3$  aqueous was added and the mixture was refluxed overnight under nitrogen condition. After the reaction was complete, the reaction mixture was cooled to room temperature. THF was removed under reduced pressure. The solid residue was dissolved in DCM and washed with water three times. The organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Then DCM was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent:  $\text{PE}/\text{DCM} = 2:3$ , v/v). 3.0 g green-yellow powder was obtained. Yield 63.6%

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (d,  $J$  = 8.0 Hz, 1H), 8.22 (d,  $J$  = 7.2 Hz, 1H), 8.16 (d,  $J$  = 6.5 Hz, 1H), 7.98 (s, 1H), 7.95 (d,  $J$  = 7.3 Hz, 1H), 7.85 (t,  $J$  = 7.0 Hz, 1H), 7.80 (s, 2H), 7.73 (d,  $J$  = 7.0 Hz, 4H), 7.51 (t,  $J$  = 7.5 Hz, 4H), 7.43 (t,  $J$  = 7.3 Hz, 2H).

$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  188.51, 187.81, 146.60, 146.16, 142.67, 140.42, 139.19, 131.60, 129.57, 129.12, 129.05, 128.94, 128.74, 128.03, 127.99, 127.35, 127.10, 126.61, 122.18, 122.16.

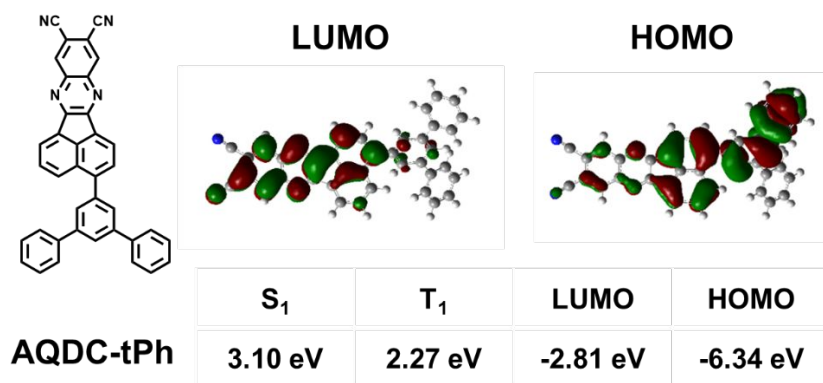
**3-([1,1':3',1''-terphenyl]-5'-yl)acenaphtho[1,2-b]quinoxaline-9,10-dicarbonitrile  
(AQDC-tPh)**

To a mixture of 5-([1,1':3',1''-terphenyl]-5'-yl)acenaphthylene-1,2-dione (0.6 g, 1.46 mmol) and 4,5-diaminophthalonitrile in 70 mL THF/EtOH (1:1), 1 mL of HCl was added and the mixture was reflux overnight under nitrogen condition. After the reaction was complete, the reaction mixture was cooled to room temperature. Solvent were removed under reduced pressure. The solid residue was dissolved in DCM and washed with water three times. The organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Then DCM was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: DCM). 0.65 g green powder was obtained. Yield 83%. MS (EI)  $m/z$  calculated for  $\text{C}_{38}\text{H}_{20}\text{N}_4$ : 532.17; found: 532.16 $[\text{M}^+]$ .

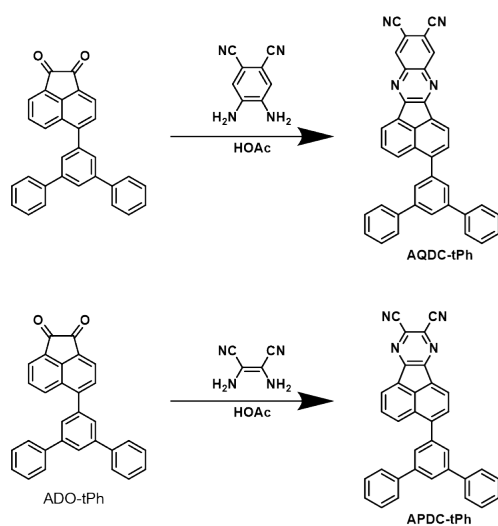
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.67 (s, 2H), 8.62 (d,  $J$  = 7.3 Hz, 1H), 8.57 (d,  $J$  = 7.0 Hz, 1H), 8.46 (dd,  $J$  = 8.5, 0.6 Hz, 1H), 8.05 (d,  $J$  = 7.2 Hz, 1H), 8.00 - 7.93 (m, 2H), 7.86 (s, 2H), 7.77 - 7.73 (m, 4H), 7.54 - 7.50 (m, 4H), 7.46 - 7.41 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.32, 156.87, 145.12, 142.51, 142.44, 142.30, 140.54, 139.47, 136.88, 136.85, 130.53, 130.24, 129.92, 129.45, 129.04, 128.69, 127.94, 127.78, 127.39, 126.31, 123.93, 123.89, 115.29, 113.39, 113.28.

### **Device fabrication and measurements**

Devices were fabricated on patterned indium tin oxide (ITO, 15  $\Omega/\text{square}$ ) glass substrates. Before device fabrication, ITO glasses were treated with UV-ozone for 15 min, and then transferred into high vacuum chamber. The deposition rate was controlled below 1  $\text{\AA}/\text{s}$  for organic materials, and 8  $\text{\AA}/\text{s}$  for Al anode. The OLED devices were tested with a power source meter (Keithley 2400) by voltage scan mode, and PMA-12 (Hamamatsu C10028-01) with photonic multichannel analyzer was utilized to measure EL spectra. The external quantum efficiency (360-950 nm) of the devices was calculated by measuring the light intensity in the forward direction with an integrating sphere in air.



**Figure S1.** Molecular structure of AQDC-tPh (left), LUMO and HOMO distributions and calculated values of  $S_1$ ,  $T_1$ , LUMO and HOMO of AQDC-tPh (right).

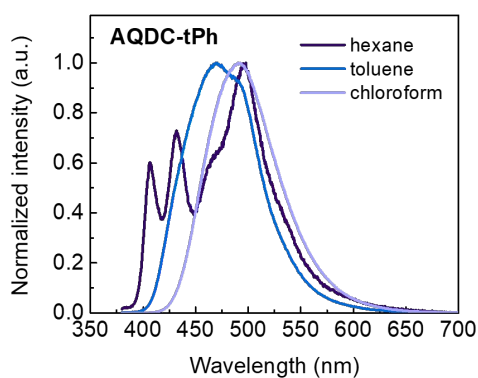


**Scheme S1.** Synthetic route and molecular structure of AQDC-tPh and APDC-tPh.

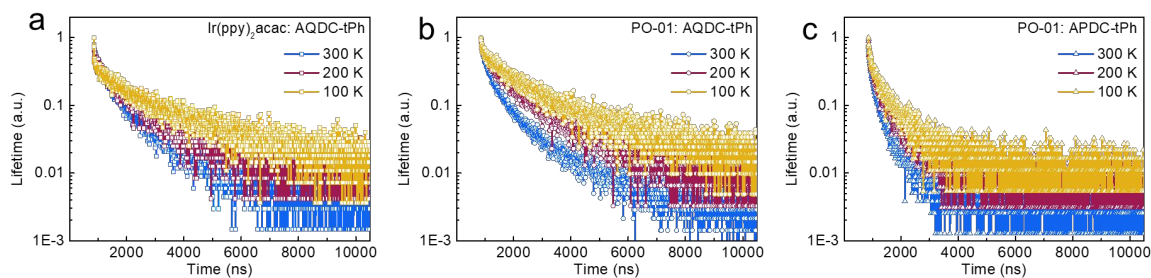
**Table S1.** The energy levels of AQDC-tPh, APDC-tPh, Ir(ppy)<sub>2</sub>acac and PO-01.

	HOMO <sup>a)</sup> (eV)	LUMO <sup>b)</sup> (eV)
AQDC-tPh	-6.62	-3.88
APDC-tPh	-6.70	-3.95
Ir(ppy) <sub>2</sub> acac	-5.60	-3.00
PO-01	-5.10	-2.70

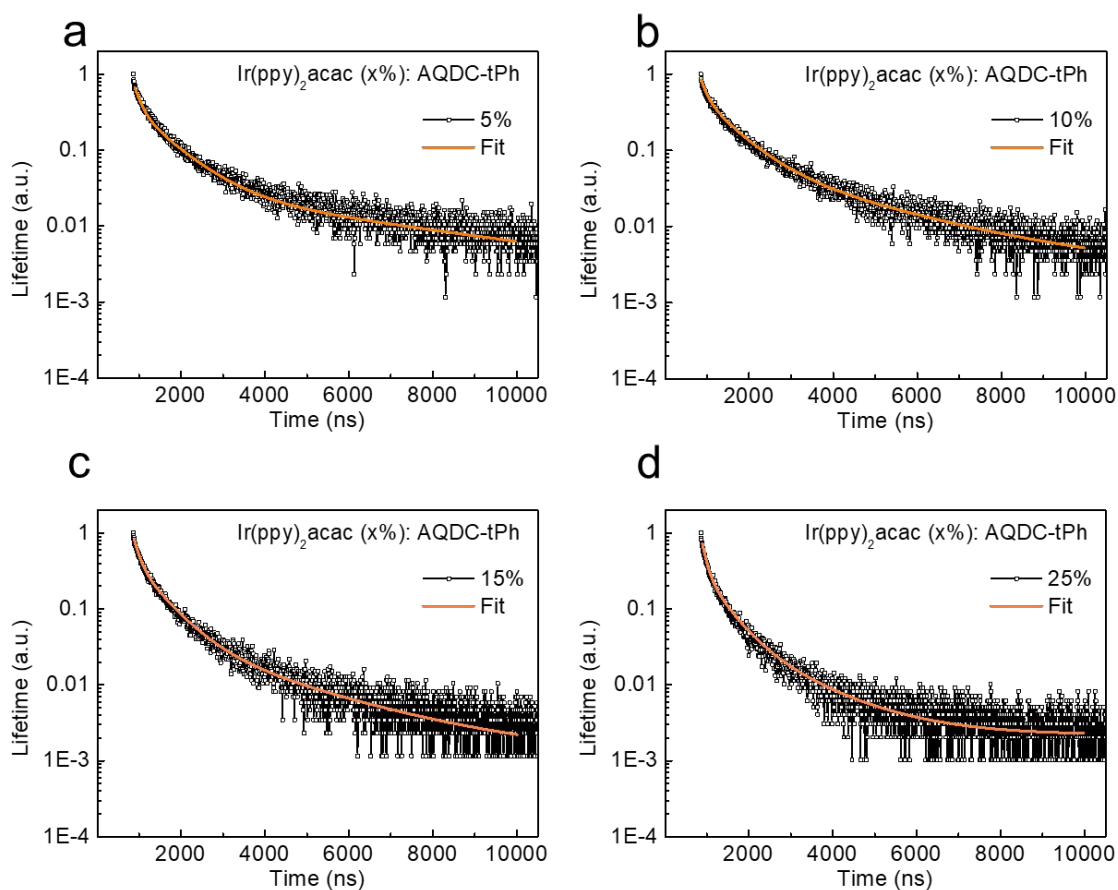
a) Determined by UPS. b) Determined by HOMO value and energy gap.



**Figure S2.** PL spectra of AQDC-tPh in different solvents. ( $10^{-5}$  M, excitation wavelength: 340 nm)

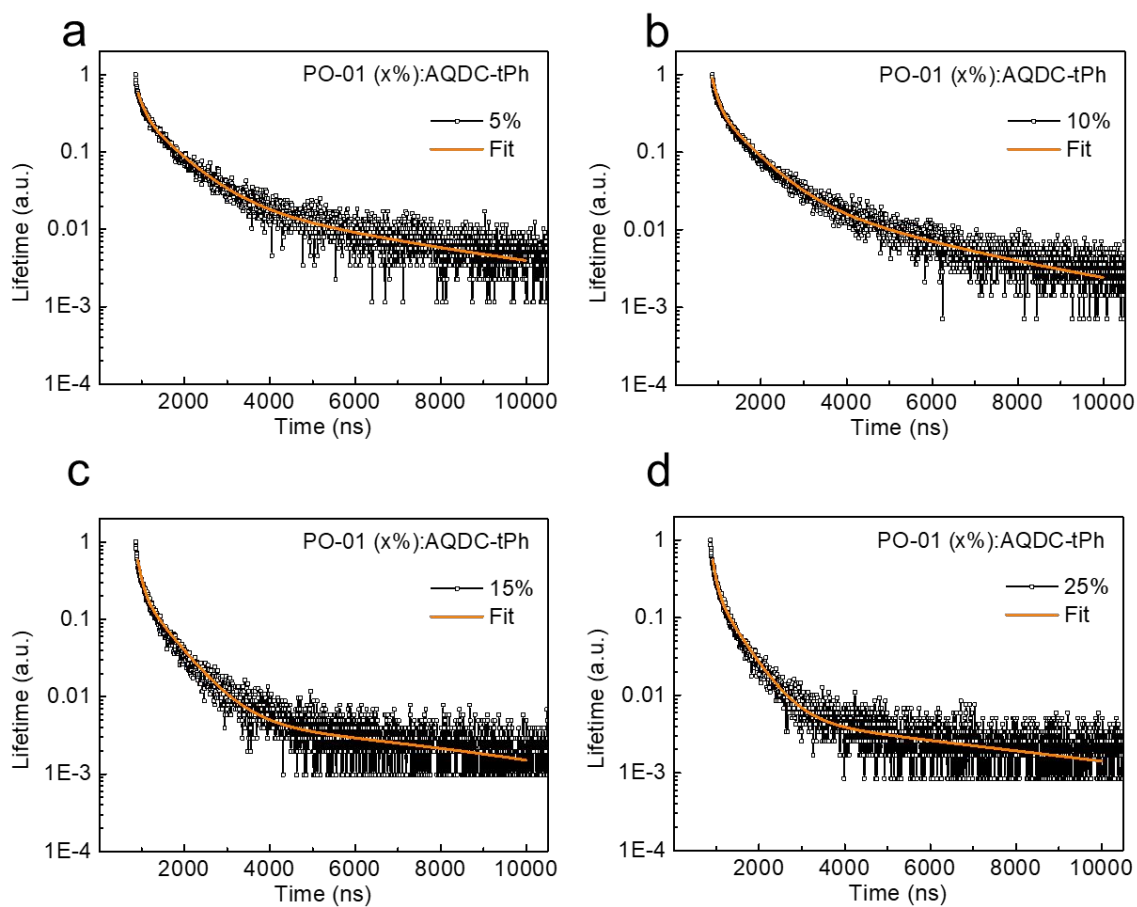


**Figure S3.** Temperature-dependent transient PL decay curves (100-300 K), a) Ir(ppy)<sub>2</sub>acac (15%): AQDC-tPh, b) PO-01 (15%): AQDC-tPh, c) PO-01 (15%): APDC-tPh (doped film, excitation wavelength: 373 nm)

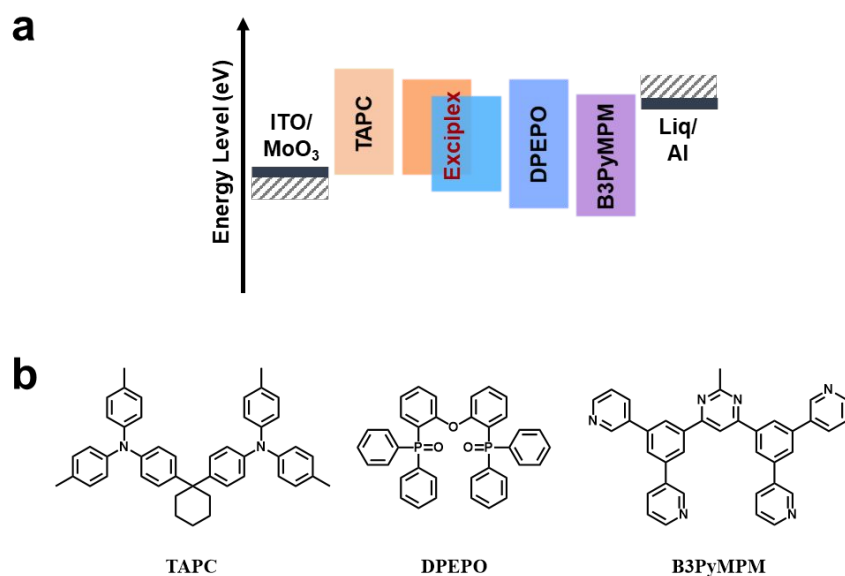


**Figure S4.** Transient PL decay and fitting curves of Ir(ppy)<sub>2</sub>acac (x%): AQDC-tPh films at their peak wavelength, respectively. (excitation wavelength: 373 nm, x represents doping ratio of phosphors in exciplexes).





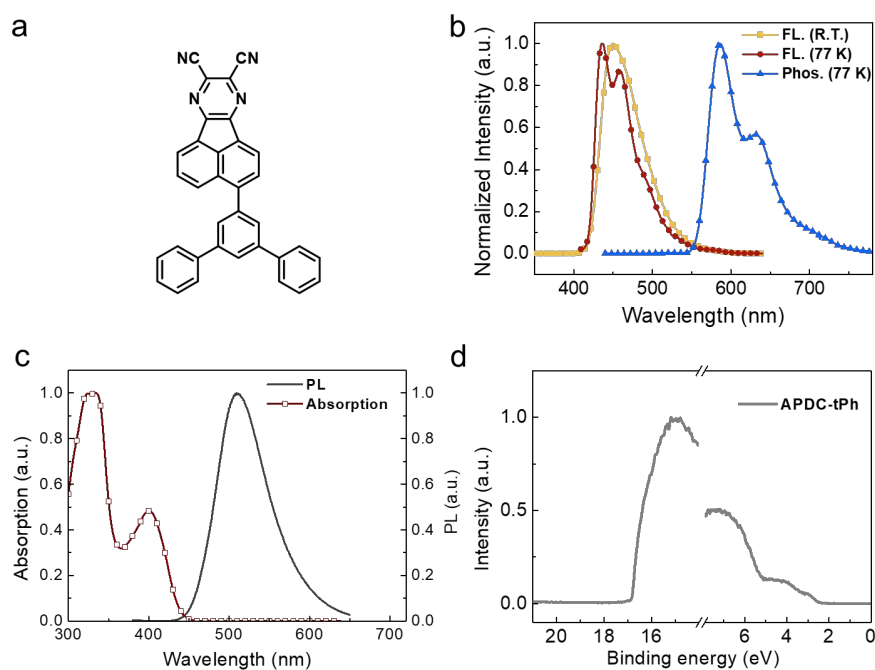
**Figure S5.** Transient PL decay and fitting curves of PO-01 (x%): AQDC-tPh films at their peak wavelength, respectively. (excitation wavelength: 373 nm, x represents doping ratio of phosphors in exciplexes).



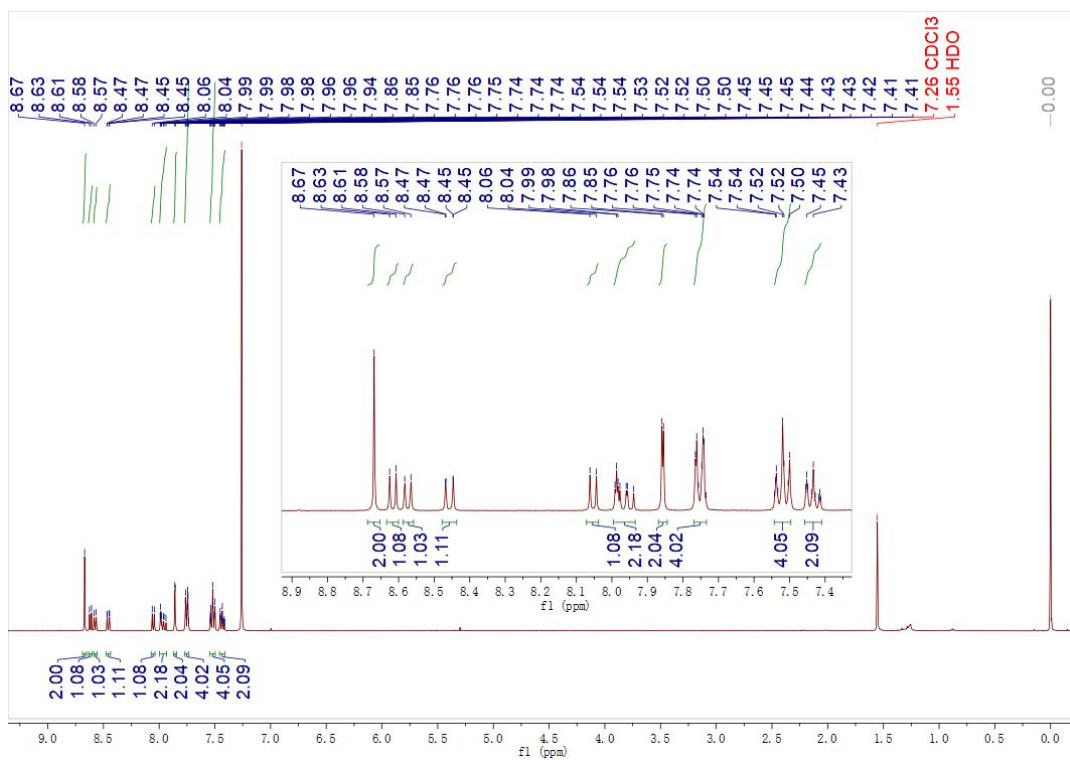
**Figure S6.** (a) Energy level diagram for the EL devices; (b) molecular structure of the materials used in OLEDs.

**Table S2.** Summary of emission peaks and EQEs of NIR devices based on Ir(ppy)<sub>2</sub>acac: AQDC-tPh, PO-01: AQDC-tPh and PO-01: APDC-tPh, respectively.

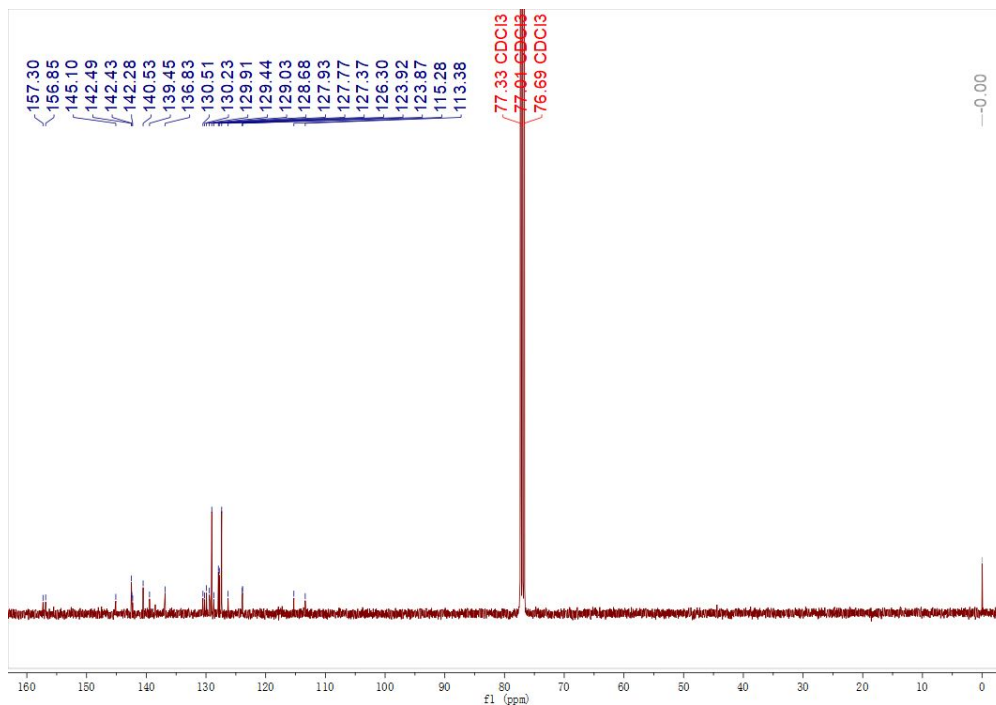
EML	$\lambda_{\text{EL}}$ (nm)	EQE (%)
Ir(ppy) <sub>2</sub> acac (5%): AQDC-tPh	733	0.14
Ir(ppy) <sub>2</sub> acac (10%): AQDC-tPh	737	0.15
Ir(ppy) <sub>2</sub> acac (15%): AQDC-tPh	742	0.17
Ir(ppy) <sub>2</sub> acac (25%): AQDC-tPh	748	0.19
PO-01 (5%): AQDC-tPh	732	0.16
PO-01 (10%): AQDC-tPh	744	0.17
PO-01 (15%): AQDC-tPh	750	0.23
PO-01 (25%): AQDC-tPh	756	0.20
PO-01 (10%): APDC-tPh	800	0.14
PO-01 (15%): APDC-tPh	824	0.16
PO-01 (20%): APDC-tPh	844	0.12



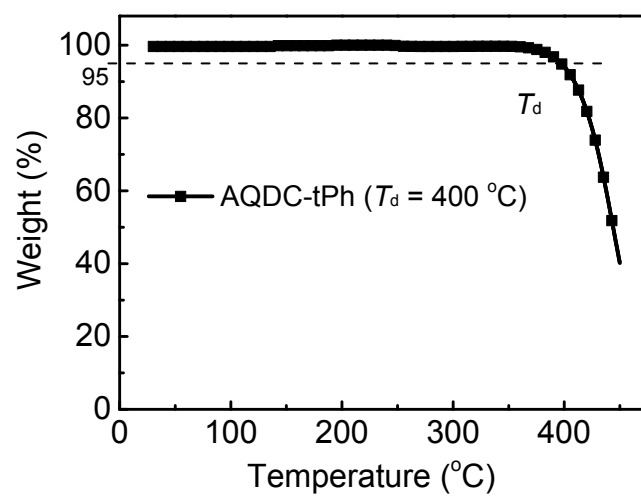
**Figure S7.** (a) Chemical structure of APDC-tPh. (b) The fluorescence and phosphorescence spectra of APDC-tPh in toluene at room temperature (R.T.) and 77 K, respectively. (c) The ultraviolet-visible absorption and PL spectra in thin film of APDC-tPh. (d) He I UPS of APDC-tPh in thin film deposited on a Si substrate thermally.



**Figure S8.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of AQDC-tPh.



**Figure S9.** <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) of AQDC-tPh.



**Figure S10.** TGA curves for AQDC-tPh.