

## Supporting Information

### **Simple/Efficient Phosphor-Only Emitting Systems: From Sky-Blue to Warm-White Organic Electroluminescence Based on a Novel Bipolar Phosphorescent Emitter as Host**

Xuming Zhuang,<sup>a</sup> Xinze Liu,<sup>b</sup> Shuonan Chen,<sup>a</sup> Hao Zhang,<sup>a</sup>

Yu Liu<sup>\*a</sup> and Yue Wang<sup>a</sup>

#### **General information**

Materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran was distilled with sodium benzophenone ketyl under nitrogen atmosphere and degassed by the freeze-pump-thaw method. All glassware, syringes, magnetic stirring bars and needles were dried in a convection oven for 2 hours. Reactions were monitored with thin layer chromatography (TLC). Commercial TLC plates (Silica gel 60 F254, Merck Co.) were developed and the spots were seen under UV light at 254nm and 365nm. Silica column chromatography was done with silica gel 60G (particle size 5-40  $\mu$  m, Merck Co.). <sup>1</sup>H NMR spectrum was recorded on a Bruker AVANVE 500MHz spectrometer with tetramethylsilane as an internal standard. Mass spectra were measured on a GC/MS mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. Absorption spectra were obtained using a Shimadzu UV-2550 UV-vis spectrometer. PL spectra were recorded on a Perkin-Elmer LS-55 fluorescence spectrometer with a Xe arc lamp excitation source. Emission lifetime experiments were performed by the time-correlated single-photon counting (TCSPC) system under right-angle sample geometry. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station. The sample for TOF measurement was prepared on the glass substrate covered with indium tin oxide (ITO) layer with the structure of [ITO/FMPYPCA (1  $\mu$ m)/Al]. An intense short duration (5-6 ns) light pulse from a frequency-tripled (355 nm) Nd:YAG laser was incident at one side of the sample to generate photocarriers. The sample was mounted in a vacuum and the measurement was made at the electric field of  $5.0 \times 10^{-5}$  V cm<sup>-1</sup> at 293 K.

#### **Fabrication of the OLEDs and EL measurements**

The ITO (indium-tin oxide) coated glass substrates (20  $\Omega$ /square) were first cleaned in ethanol, acetone, and soap ultrasonic baths. All organics were purified by gradient sublimation and thermally evaporated at a rate of 1.0  $\text{\AA}$  s<sup>-1</sup> at a pressure of ca.  $3.5 \times 10^{-4}$  Pa. A LiF layer was deposited at a rate of 0.2  $\text{\AA}$  s<sup>-1</sup>. The Al cathode was deposited at a rate of 5  $\text{\AA}$  s<sup>-1</sup>. EL spectra and luminance-current density-voltage characteristics were measured by combining a Spectrascan PR-655 spectrophotometer with a computer-controlled direct-current power supply Keithley model 2400 voltage-current source under ambient conditions at room temperature.

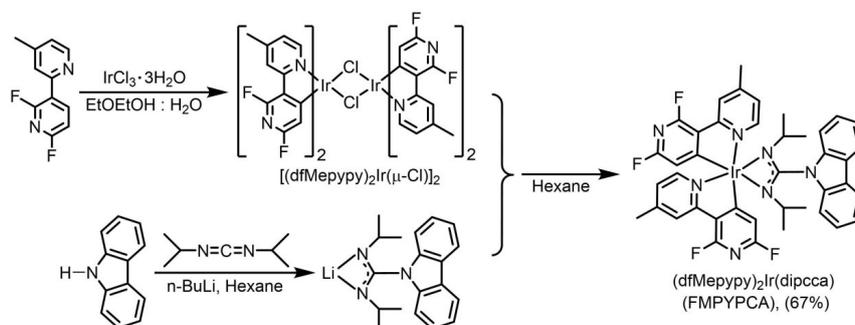
#### **Materials**

[(dfMepypy)<sub>2</sub>Ir( $\mu$ -Cl)]<sub>2</sub> were synthesized according to a modified Nonoyama procedure by refluxing IrCl<sub>3</sub>·3H<sub>2</sub>O (2.5 g, 7mmol) with 2.5 equiv of the ligands (3.4 g of 2',6'-difluoro-4-methyl-2,3'-bipyridine) in a 3:1 (v/v) mixture of 2-methoxyethanol and water for 8 hours. The reaction

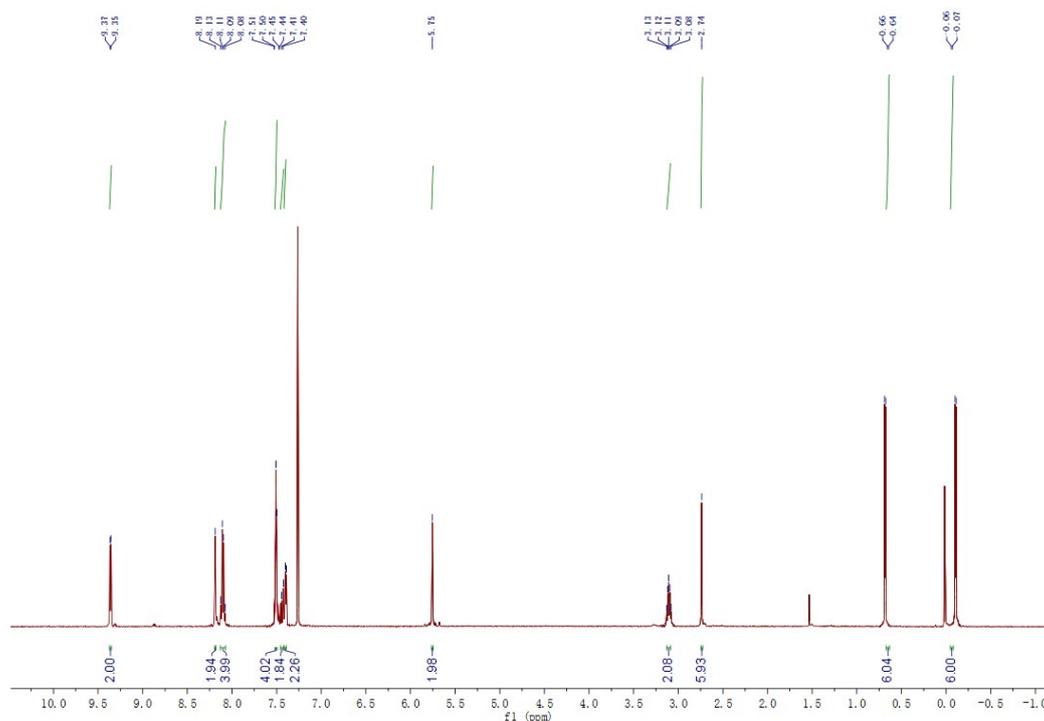
mixture was cooled to room temperature and water was added to precipitate the product. The resulting mixture was filtered and then washed with hexane and ethyl ether several times to provide  $[(dfMepypy)_2Ir(\mu-Cl)]_2$  in 80% yields.

**$(dfMepypy)_2Ir(dipcca)$  (FMPYPCA):** A hexane solution of *n*-BuLi (0.20ml  $\times$  25M) was added to carbazole (83 mg, 0.5 mmol) in hexane (10 ml) under argon. The reaction mixture was stirred at room temperature for 30 min, and then added dropwise to *N,N*-diisopropylcarbodiimide (63 mg, 0.5 mmol). The colorless solution was stirred for another 30 min, and then added to  $[(dfMepypy)_2Ir(\mu-Cl)]_2$  (304 mg, 0.25 mmol) in hexane solvent (20 ml). After stirring at room temperature for 8 hours, the solvent was evaporated under vacuum, and the product was washed with  $Et_2O$  (20 mL) three times to give a green powder  $(dfMepypy)_2Ir(dipcca)$  (FMPYPCA) in 67% yields.

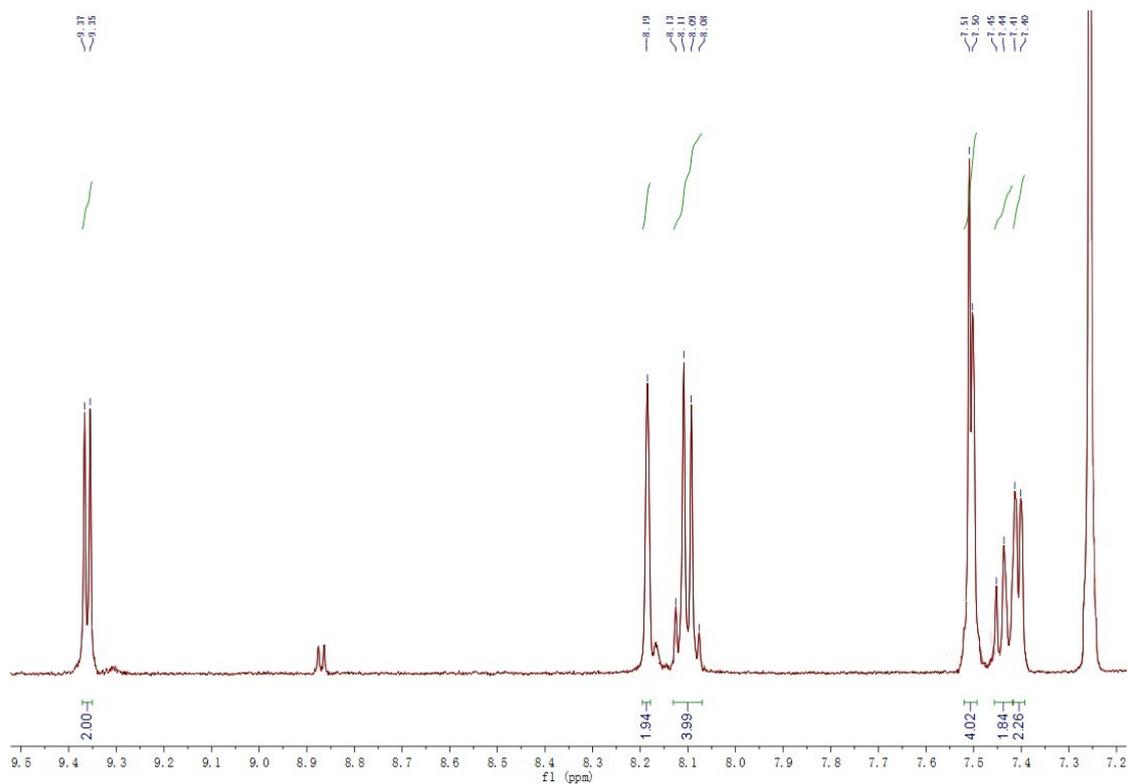
$(dfMepypy)_2Ir(dipcca)$  (FMPYPCA):  $^1H$  NMR (500MHz,  $CDCl_3$ )  $\delta$  9.39 (d,  $J = 5.9$  Hz, 2H), 8.21 (s, 2H), 8.13 (q,  $J = 8.3$  Hz, 4H), 7.53 (d,  $J = 3.4$  Hz, 4H), 7.50 – 7.42 (m, 4H), 5.78 (s, 2H), 3.12 (dd,  $J = 12.6, 6.3$  Hz, 2H), 2.76 (s, 6H), 0.68 (d,  $J = 6.3$  Hz, 6H), -0.04 (d,  $J = 6.3$  Hz, 6H). Elemental analysis: found C, 54.89%; H, 4.23%; N, 10.88%; calc. for  $C_{41}H_{38}F_4IrN_7$ : C, 54.96%; H, 4.16%; N, 10.94%. MS  $m/z$ : 896.52 [M $^+$ ] (calc. 896.01).



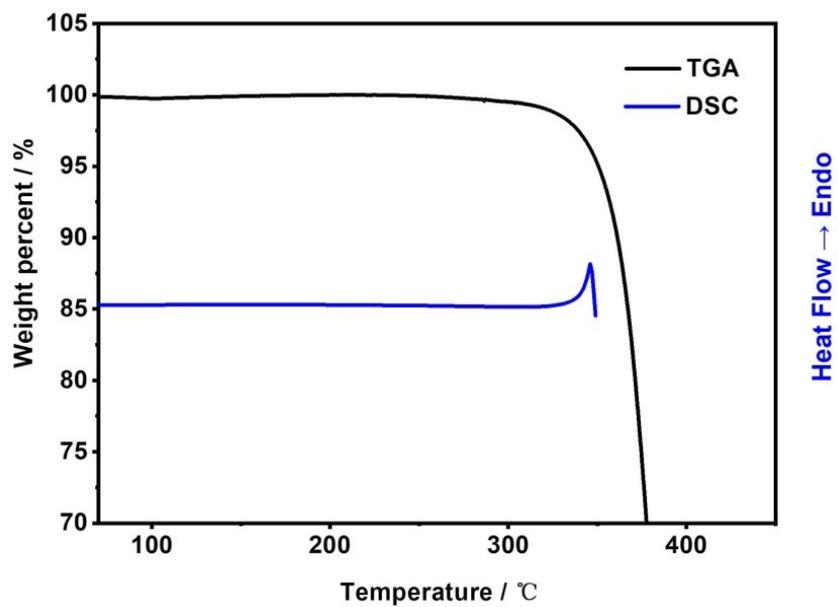
**S-Scheme 1.** Synthetic procedure and structure of FMPYPCA.



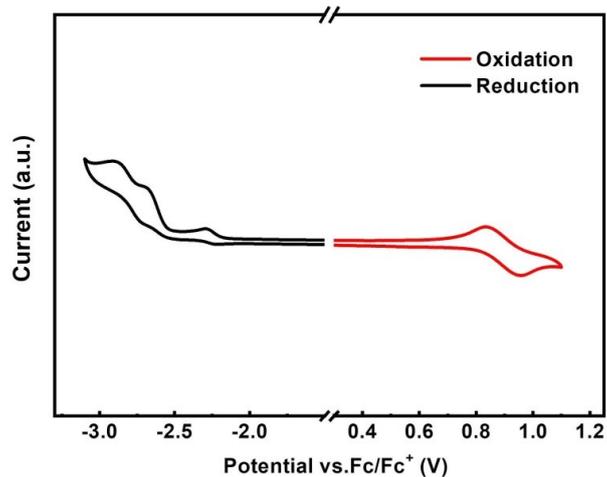
**S-Fig. 1** Full  $^1\text{H}$  NMR spectrum of FMPYPCA in  $\text{CDCl}_3$ .



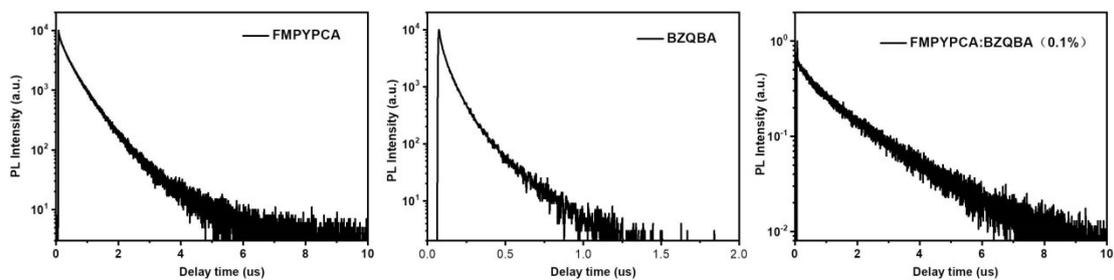
**S-Fig. 1-1** Magnified  $^1\text{H}$  NMR spectrum of FMPYPCA in  $\text{CDCl}_3$  with the  $\delta$  values from 9.5 to 7.0.



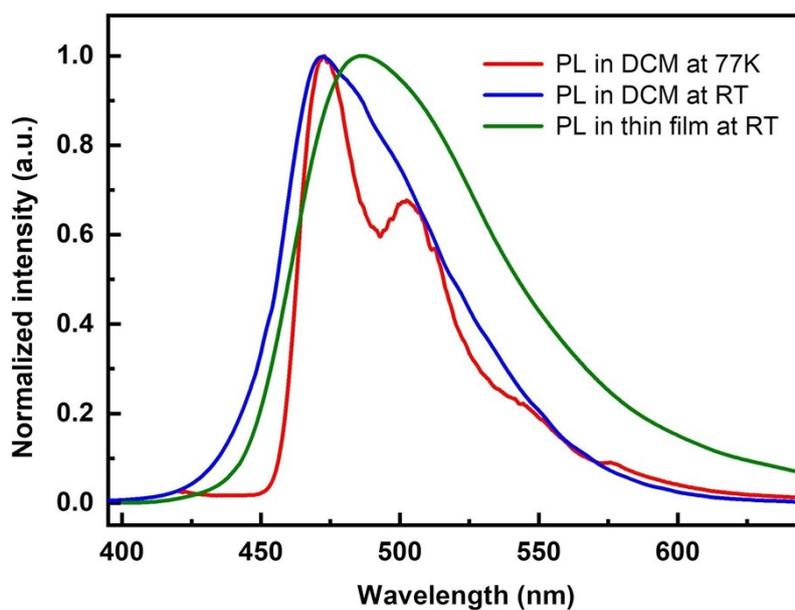
**S-Fig. 2** Thermal analyses of FMPYPCA: TGA thermograms and DSC thermograms.



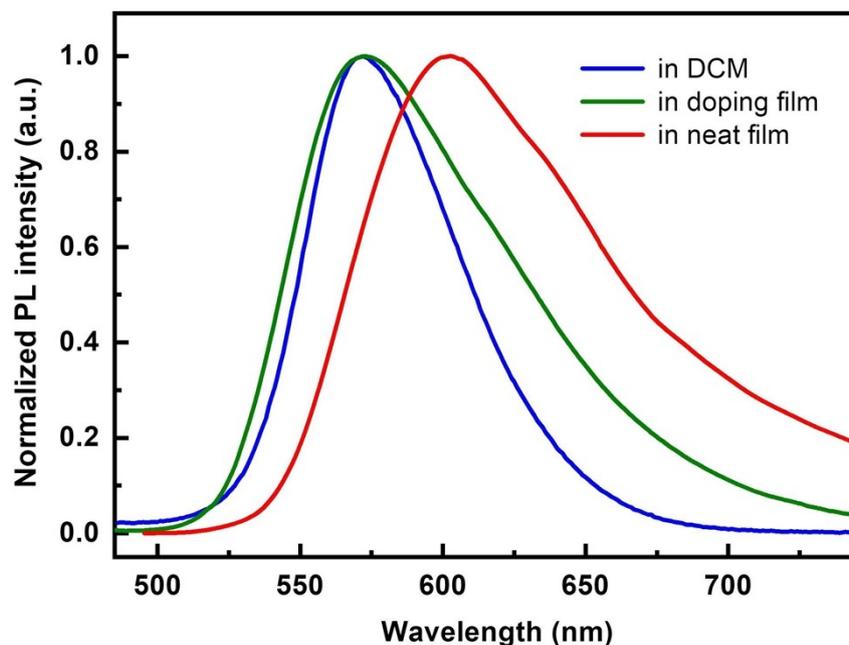
**S-Fig. 3** Cyclic voltammograms (CV) curves of FMPYPCA recorded in  $\text{CH}_2\text{Cl}_2$  for oxidation and in THF for reduction.



**S-Fig. 4** Transient PL spectra of FMPYPCA, BZQBA, and FMPYPCA:BZQBA(0.1%) under 375 nm excitation.



**S-Fig. 5** PL spectra of FMPYPCA in dilute solution of dichloromethane (DCM,  $10^{-5}$  M) at room temperature (RT) and at 77K, and in the neat thin film at RT.

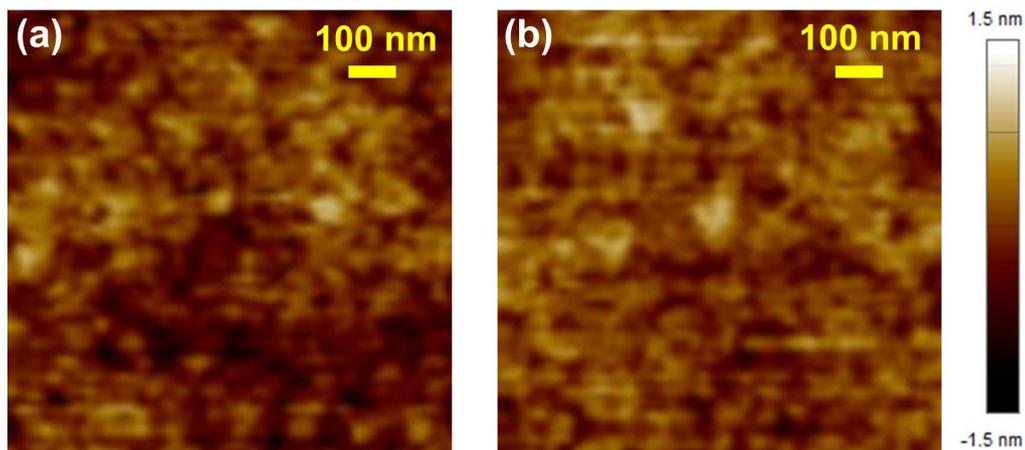


**S-Fig. 6** PL spectra of BZQBA in dilute solution of dichloromethane (DCM,  $10^{-5}$  M), and in doping film with FMPYPCA (5 wt%) and in the neat thin film.

**S-Table 1.** Summary of some photophysical properties of two phosphors.

	$\lambda_{\text{abs}}^a$ (nm)	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{PL}}^{a,d}$	$\tau_d^a$ ( $\mu\text{s}$ )	HOMO/LUMO (eV)
FMPYPCA	300/370/430	484 <sup>a</sup> 472 <sup>b</sup> 472/502 <sup>c</sup>	0.35 $\pm$ 0.03	0.96	-5.49/-1.57 <sup>e</sup> -5.40/-2.57 <sup>f</sup>
BZQBA	290/330/ 440/530	600 <sup>a</sup> 572 <sup>b</sup>	0.41 $\pm$ 0.03	0.10	-4.89/-2.75 <sup>f</sup>
FMPYPCA:BZQBA (0.1 wt%)	--	484/556 <sup>a</sup>	0.53 $\pm$ 0.03	0.62	--
FMPYPCA:BZQBA (5 wt%)	--	572 <sup>a</sup>	--	--	--

<sup>a</sup> Measured in thin films at room temperature (RT). <sup>b</sup> Measured in dilute solution of dichloromethane (DCM,  $10^{-5}$  M) at RT. <sup>c</sup> Measured in dilute DCM ( $10^{-5}$  M) At 77K. <sup>d</sup> Absolute PL quantum yield evaluated using an integrating sphere. <sup>e</sup> From density functional theory (DFT) calculations. <sup>f</sup> Determined by cyclic voltammetry (CV) method.



The AFM height images display the formation of the continuous film morphology with highly interconnected nanosized (~50–100 nm) granular domains and the smooth organic surface with small root mean square (RMS) roughness values of 0.626 nm for the neat film of FMPYPCA (a) and 0.478 nm for the thin film based on BZQBA doped into FMPYPCA with 5 wt% concentration (b). It is free of particle aggregation or phase separation, suggesting the good film-forming ability.

**S-Fig. 7** AFM height images of the neat film of FMPYPCA (a) and the film based on BZQBA doped into FMPYPCA with 5 wt% concentration (b).