

Electronic Supplementary Information (ESI)

Strategic modification of ligands for remarkable piezochromic luminescence (PCL) based on a neutral Ir(III) phosphor

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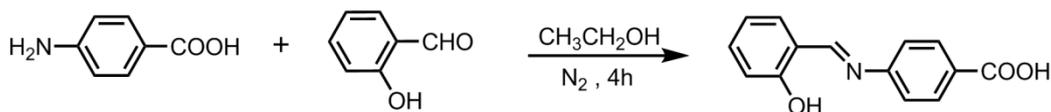
1. Experimental - general information

Materials obtained from commercial suppliers were used without further purification unless otherwise stated. All glassware, syringes, magnetic stirring bars, and needles were thoroughly dried in a convection oven. Reactions were monitored using thin layer chromatography (TLC). Commercial TLC plates were used and the spots were visualized under UV light at 254 and 365 nm. ^1H NMR spectra were recorded at 25 °C on a Varian 500 MHz spectrometer and were referenced internally to the residual proton resonance in $\text{DMSO-}d_6$ (δ 2.5 ppm). Mass spectra were obtained on matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry instrument. Elemental analyses were measured on a Flash EA1112 analyzer. Transmission electron microscopy (TEM) and electron diffraction analyses of the samples were obtained using a TECNAI F20 microscope. The samples were prepared by placing microdrops of the solution on a holey carbon copper grid. UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The emission spectra were recorded by an F-7000 FL spectrophotometer. The excited-state lifetime and photoluminescence quantum yields (PLQYs) were measured using a transient spectrofluorimeter (Edinburgh FLS920). X-ray photoelectron spectroscopy (XPS) analyses were performed on a Quantum 2000 spectrometer. Powder X-ray diffraction (PXRD) patterns were obtained with a Rigaku Dmax 2000 instrument. Differential scanning calorimetry (DSC) curves were collected on a NETZSCH thermal analysis DSC200 F3 instrument under argon with a heating rate 10 °C min⁻¹. FTIR spectra were recorded on a Magna 560 FTIR spectrometer with KBr disks. The X-ray crystal data was obtained on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Cu K α radiation ($\lambda = 1.54178$).

Synthesis of Schiff base ligand

4-Aminobenzoic acid (0.274 g, 2.0 mmol) and salicylaldehyde (0.200 g, 1.63 mmol) were refluxed in ethanol (20 mL) at 78 °C for 5 h under a nitrogen atmosphere. The suspension was filtered, dried and purified by silica gel column chromatography with

ethyl acetate/acetone (2:1 v/v) as eluent. The Schiff base was obtained as a yellow solid in 82% yield (0.320 g).



Scheme S1 Synthetic route for Schiff base ligand

2. ^1H NMR Spectrum of complex **1** at room temperature

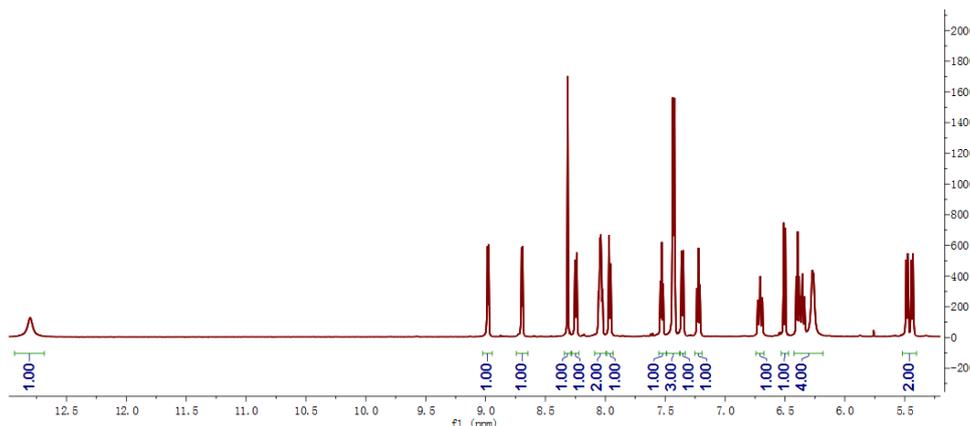


Fig. S1 ^1H NMR spectrum of complex **1** in $\text{DMSO-}d_6$ at room temperature.

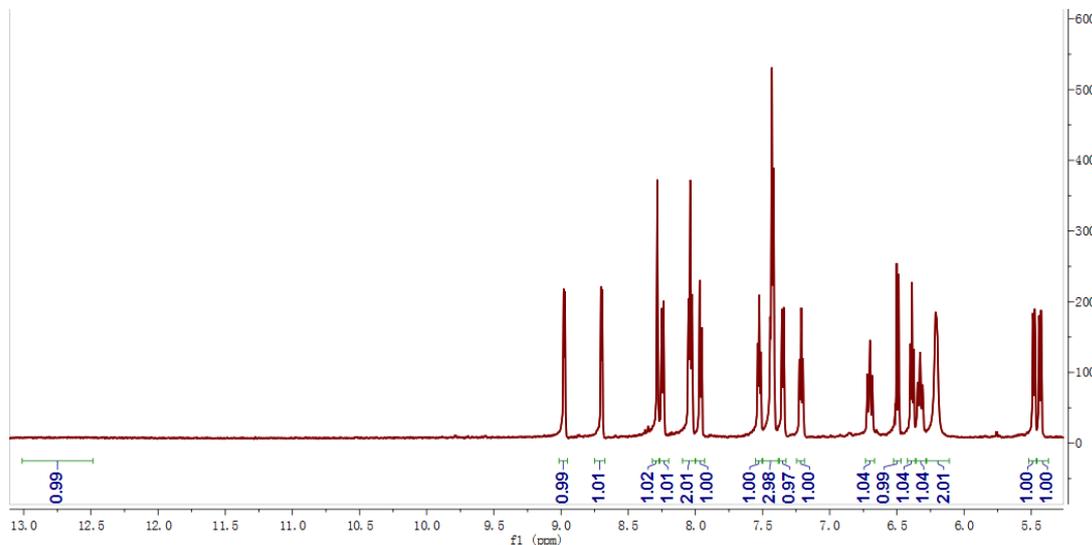


Fig. S2 ^1H NMR spectrum of complex **1** after grinding in $\text{DMSO-}d_6$ at room temperature.

3. X-ray crystallographic data

Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.54178$). Cell refinement and data reduction were made by the SAINT program. The structures were determined using the SHELXTL/PC program. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with CCDC deposition number 1922460. These data can be obtained free of

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal data and structure refinement for complex **1**.

1	
Empirical formula	C ₃₆ H ₂₂ F ₄ IrN ₃ O ₃
Formula weight	813.12
Temperature (K)	298
Crystal system	monoclinic
space group	P2 ₁ /n
a /Å	17.686(3)
b /Å	10.9614(16)
c /Å	19.865(3)
α /°	90
β /°	106.682(8)
γ /°	90
V/Å ³	3688.9(10)
Z	4
ρ _{calc} (g/cm ³)	1.622
μ/mm ⁻¹	7.595
R _{int}	0.0535
Goodness-of-fit on F ²	1.095
R ₁ ^a , wR ₂ ^b [I>2σ(I)]	0.0268,0.0602
R ₁ , wR ₂ (all data)	0.0352,0.0641

$$^a R_1 = \frac{\sum ||F_o| - |Fc||}{\sum |F_o|}, \quad ^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

4. Photophysical, TEM and XPS properties

Table S2 Photophysical characteristics of complex **1**

Absorption and emission at room temperature				$k_r \times 10^6 \text{ s}^{-1}$	$k_{nr} \times 10^6 \text{ s}^{-1}$
λ_{abs}^a (nm)	λ_{em}^b (nm)	Φ_{em}^b	τ^b [μs]		
285, 390	566	0.17	2.31	0.07	0.36

^a Measured in CH₃CN (1.0×10⁻⁵ M) solution. ^b Measured in solid state (λ_{ex} = 400 nm;

error for Φ_{em} ± 5 %).

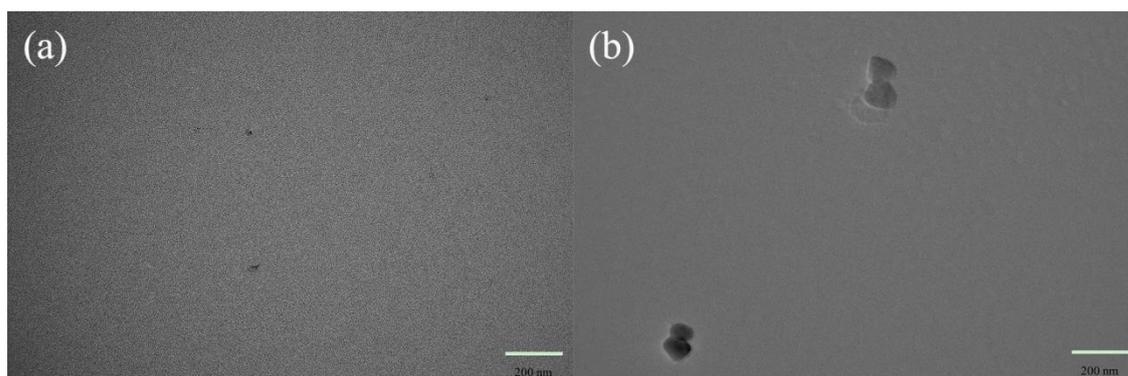


Fig. S3 TEM image of nanoaggregates of complex **1** formed in water-CH₃CN mixtures with 0% (a) and 90% (b) water fraction.

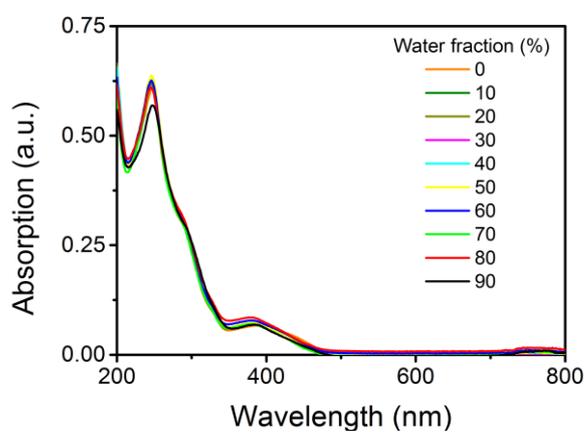


Fig. S4 The absorption spectra of complex **1** in water-CH₃CN mixtures with different water fractions (0–90% v/v) at room temperature.

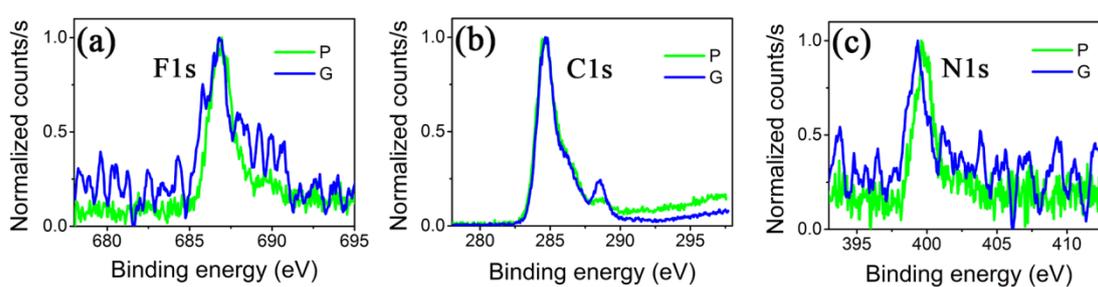


Fig. S5 XPS spectra of F 1s, C 1s and N 1s for complex **1**