# Supporting information

## An intensely luminescent metal-organic framework based on a highly light harvesting dyclo-metalated iridium(III) unit showing effective detection of explosives

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## 1. General information

All the solvents and reagents were purchased and used as received without further purification. Elemental analyses were determined on an Elemental vario EL III analyzer. The FT-IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT-IR spectrometer in the range of 4000-400 $cm^{-1}$. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ range of 5−40° with a scan step of 0.05° in a glass sheet on a Rigaku MiniFlex diffractometer. The fluorescence measurements were performed on an Edinbergh Analytical instrument FLS920. The thermal decomposition behavior was analyzed by thermogravimetric analysis-mass spectrometry (TGA-MS) using a NETSCH STA-449C thermoanalyzer coupled with a NETSCH QMS403C massspectrometer. UV/visible absorbance was collected in the solid state at room temperature on a Perkin-Elmer Lambda 650S UV/vis spectrometer equipped with Labsphere integrating over the spectral range 200-800 nm using BaSO4 as reflectance standards. The diffuse reflectance measured was converted to Kubelka-Munk Function (*Z. Tech. Phys.*, **1931**, 12, 593). The optical band gap was estimated to be 2.02 eV, as indicated in Figure S8.

## 2. Synthesis

**$Ir_2(ppy)_4Cl_2$.** $IrCl_3 \cdot 3H_2O$ (112 mg, 0.32 mmol) and 2.5 equivalents of ppy (99 mg, 0.8 mmol) were refluxed in 2-ethoxyethanolmixed with water (3:1) for 24 h. After cooling, the product was filtered and washed with ethanol and acetone to removed excess ppy (yield 88% based on $IrCl_3$).

**$Ir(ppy)_2(Hdcbpy)$.** A mixture of 2, 2'-bipyridine-4, 4'-dicarboxylic acid ($H_2$dcbpy, 0.4 mmol) and $Ir_2(ppy)_4Cl_2$ (0.2 mmol) was dissolved in $CH_3OH$ (60 mL). Excessive $Na_2CO_3$ (1 mmol) was added to the reaction mixture and then heated to reflux under stirring for 3 h. After having cooled to room temperature, the solvent was removed under reduced pressure. Deionized water (10 mL) was added to the precipitation to resolve by stirring, and the complex was achieved by the addition the 1 mol/L HCl solution, then filtered and dried (yield 72% based on Ir). Anal. Found for $C_{34}H_{23}IrN_4O_4$: C, 52.41; H, 3.48; N, 7.02. Calcd: C, 52.37; H, 3.49; N, 7.18. HRMS (ESI T $CH_3OH$) calcd for $C_{34}H_{24}IrN_4O_4$, 745.1427 ([MtH] T ); found, 745.1431.

Synthesis of **1**: A mixture of **L-H** ligand (0.02 mmol, 14.9 mg) and $Zn(NO_3)_2 \cdot 4H_2O$ (0.04 mmol, 18.5 mg) was dissolved in DMF / $H_2O$ in a 20 mL vial, and then was added an aqueous solution of hydrochloric acid. The resulting solution was heated for 3 days at 90 °C. The product was obtained as crystal (yield 52% based on **L**). Anal. Calcd for $C_{77}H_{75}ZnIr_2N_{11}O_{16}$: C, 49.70; H, 4.06; N, 8.28%. Found: C, 49.28; H, 4.18; N, 8.26%. IR (cm-1): 3480(m, br), 2926(w), 1650(m), 1605(m), 1555(vs), 1440(m), 1395(s), 1285(w), 1114(w), 1068(w), 1014(w), 940(w), 862(w), 775(w), 734(w), 668(w).

The microscale of **1** was synthesized by only changing the ratio of DMF/$H_2O$ to 10:1 and the reaction time to 3 hours.

## 3. Additional Figures

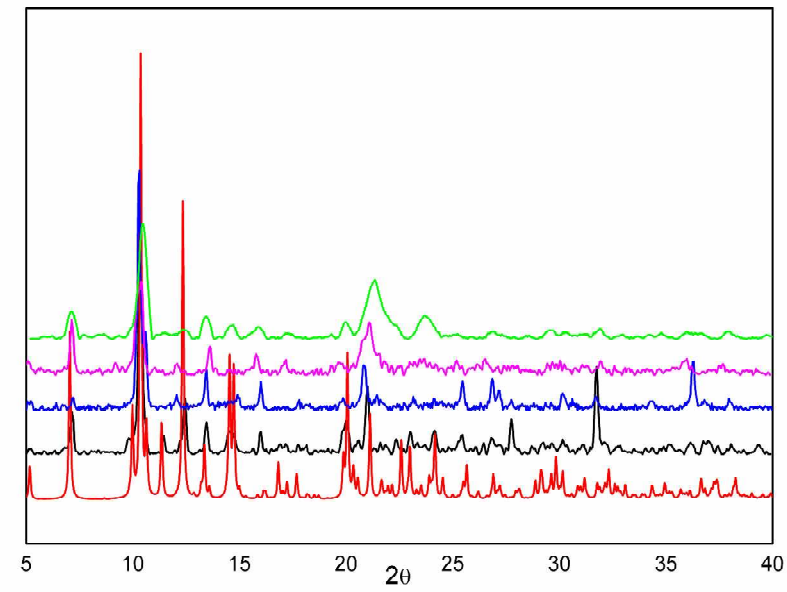


**Figure S1.** Powder X-ray diffraction (PXRD) patterns of simulated **1** (red), as-synthesized (black), microscale-synthesized (blue), **1** immersed in methanol (pink) and **1** after the sensing experiment (green).

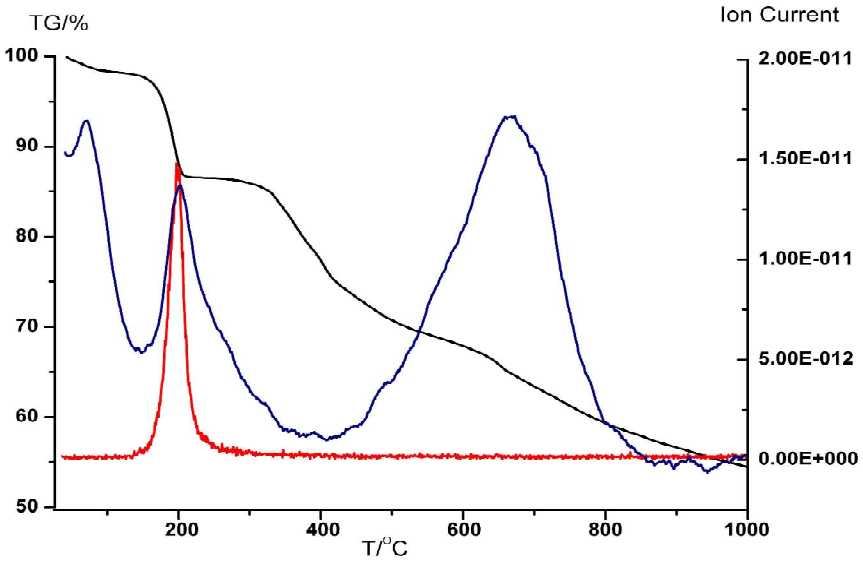


**Figure S2.** TGA coupled with QMS analyses of **1** with ion current signal for *m*/*z* =73 (red), *m*/*z* = 18 (blue).

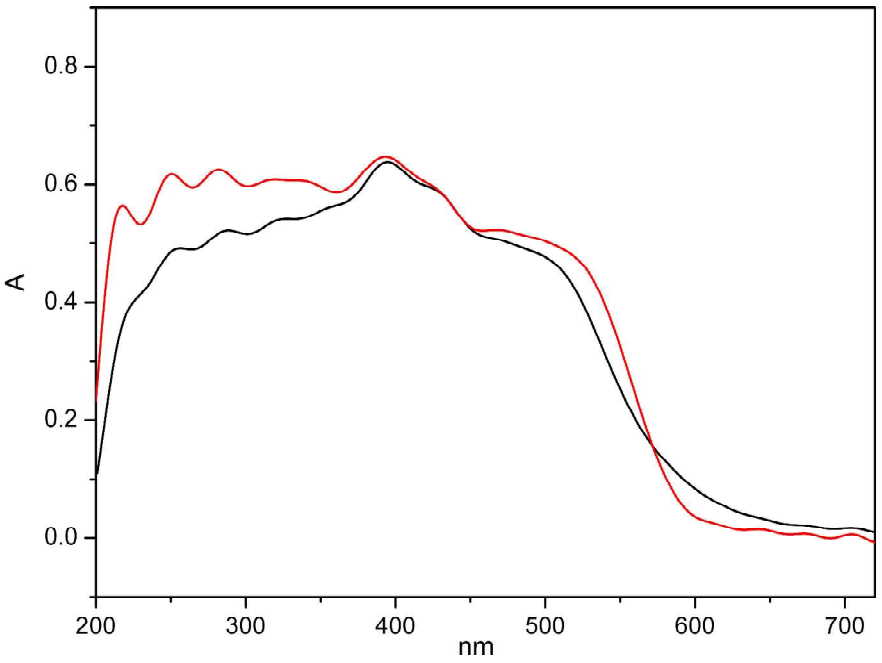


**Figure S3.** The optical absorption spectra of **1** (red) and L-H ligand (black).

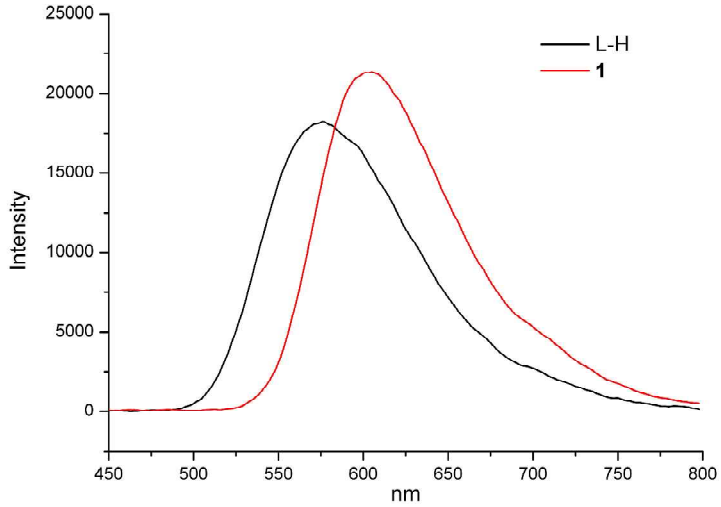


**Figure S4.** The PL spectra of **1** (red) and L-H ligand (black).

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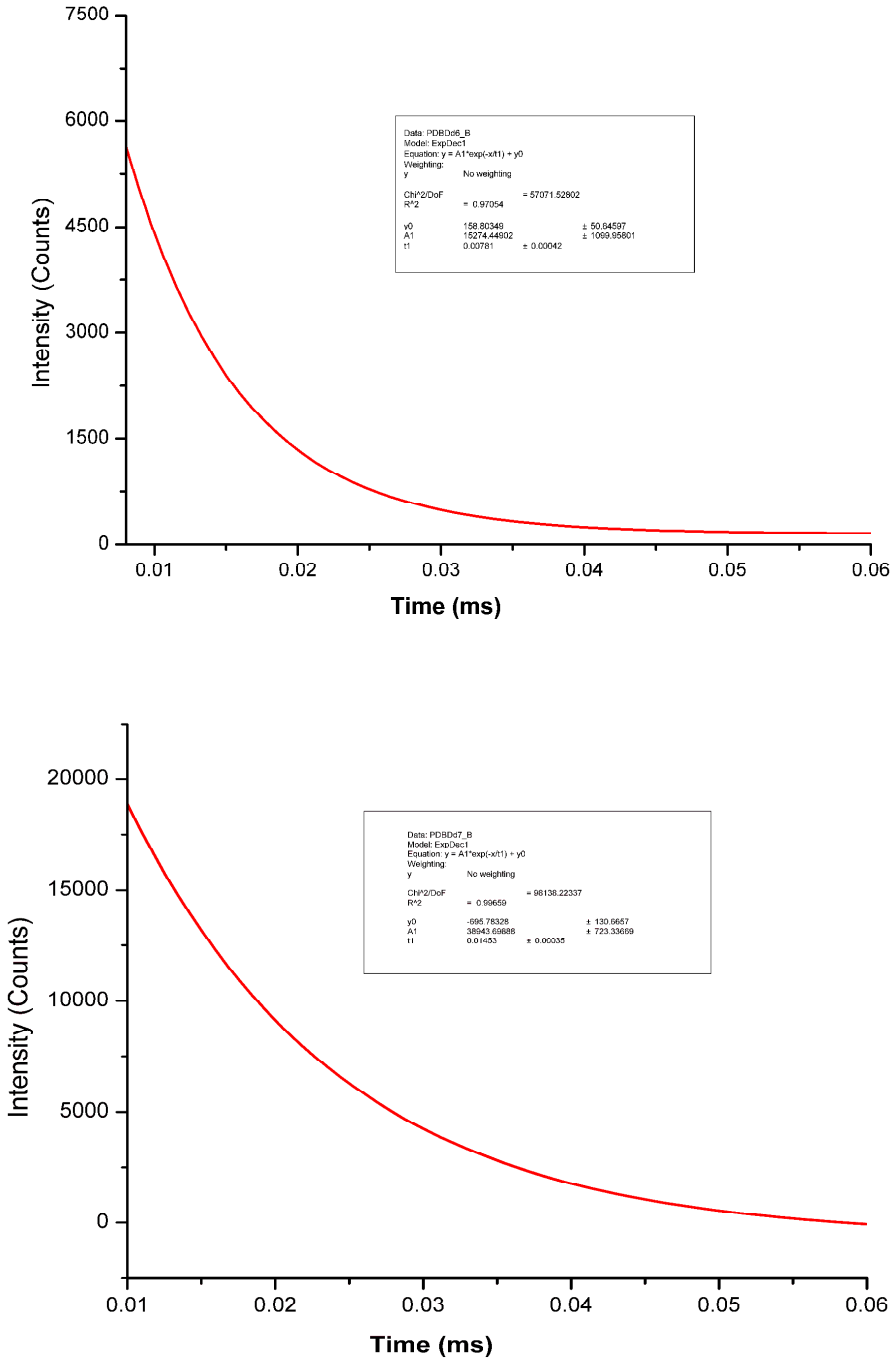


**Figure S5.** Transient emission decay profiles of $Ir(ppy)_2(Hdcbpy)$ (up) and **1** (down) in solid powder.

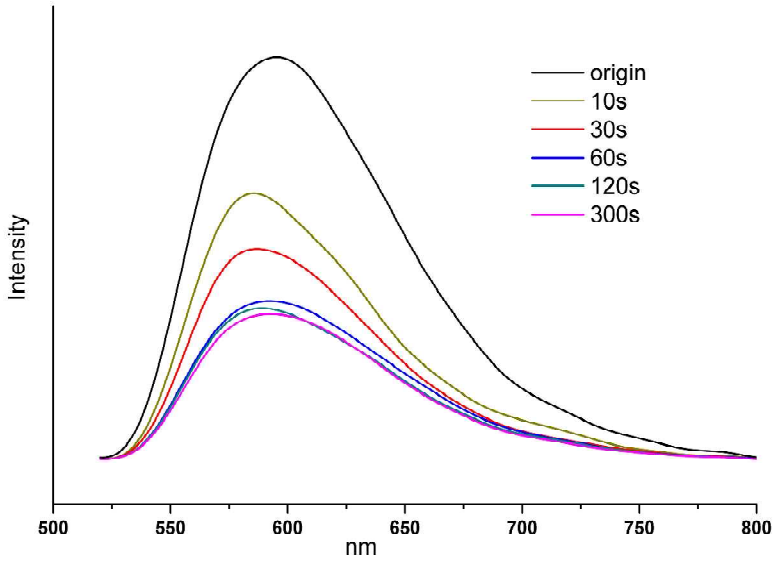


**Figure S6.** Time-dependent fluorescence quenching of 1 by TNT.

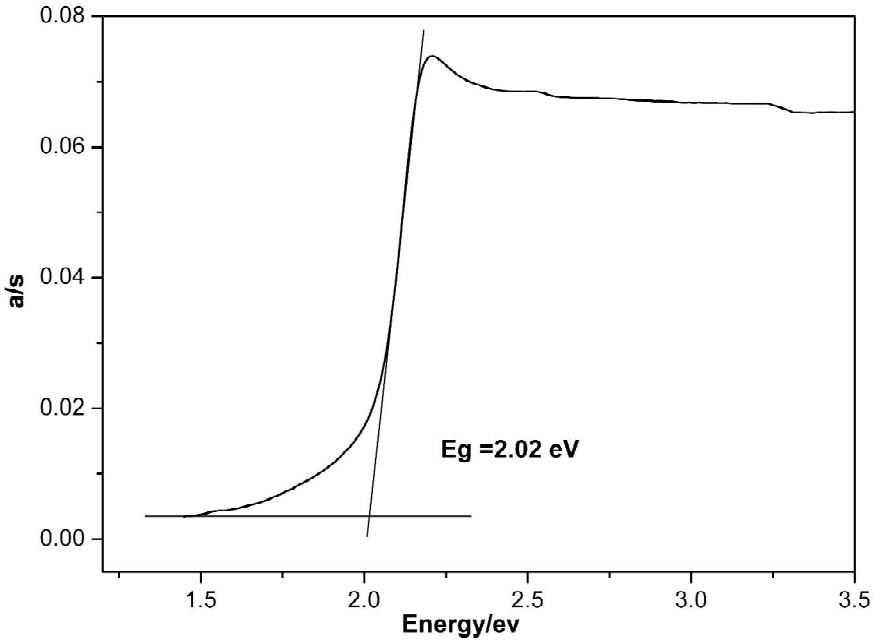


**Figure S7.** The optical diffuse reflectance spectrum of **1.**