

## Supporting Information

### **Floral and lamellar europium (III)-based metal-organic framework as the high sensitivity luminescence sensor for acetone**

Xiaoying Zhang<sup>1,2</sup>, Xiaoli Kang<sup>1</sup>, Wen Cui<sup>1</sup>, Qing Zhang<sup>1</sup>, Zhou Zheng<sup>1</sup>,  
Xudong Cui<sup>1\*</sup>

*(1 Sichuan Research Center of New Material of Institute of Chemical  
Materials, China Academy of Engineering Physics, Chengdu 610200;  
2 School of Materials Science and Engineering, Chongqing Jiaotong  
University, Chongqing 400074 )*

*E-mail: [xudcui@163.com](mailto:xudcui@163.com)*

## 1. Experimental section

### 1.1 Materials and general methods

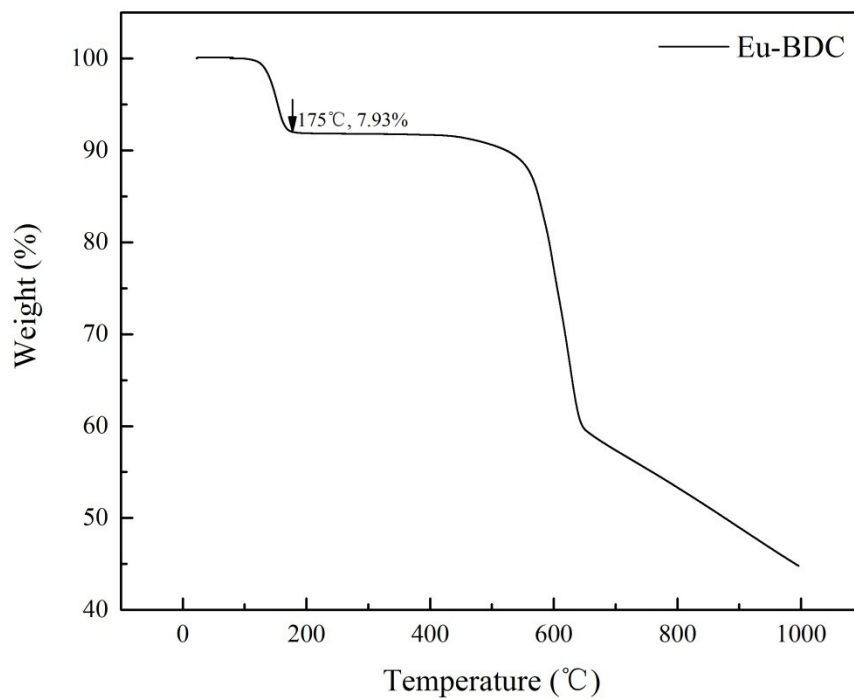
All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. H<sub>2</sub>BDC was purchased from Shanghai Aladdin industrial co., H<sub>3</sub>BTC was purchased from J&K Scientific Ltd., Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was purchased from Adamas Reagent Co., Ltd. X-ray powder diffraction (XRD) patterns of Eu-BDC, Eu-BTC and the relative immersed compounds were recorded on a Haoyuan DX-2700 X-ray Diffractometer (Japan) using Cu-Kα ( $\lambda = 1.5405 \text{ \AA}$ , 40 KV, 30 mA) radiation from 5 to 50°. Thermogravimetric analysis (TGA) was carried out at a ramp rate of 10 °C min<sup>-1</sup> in a nitrogen flow using a Mettler-Toledo TGA/Q500 instrument. The solution fluorescence spectra were measured on a Hitachi F-4600. Both excitation and emission slit widths were 1 nm. The emulsion was prepared by introducing 1 mg of Eu-MOFs powder into 3.00 mL of methanol, aged 24 h after ultrasound, then for follow-up detection. The intensity of Eu-BDC was recorded at 615 nm, and excitation was performed at 323 nm. The intensity of Eu-BTC was recorded at 619 nm, and excited by 301 nm. The UV-vis diffuse reflection was performed on a Lambda 750 spectrophotometer. The cyclic voltammetry measurement was performed on a CHI660 by giving an applied voltage to the platinum working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode in a three-electrode system at room temperature, using 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> solution as the supporting electrolyte. N<sub>2</sub> adsorption isotherms after desorption with 473 K for 24 h were taken with a Micrometrics ASAP 2020 HD88 instrument at 77 K.

### 1.2 Synthesis of the Eu-BDC Eu-BTC complex

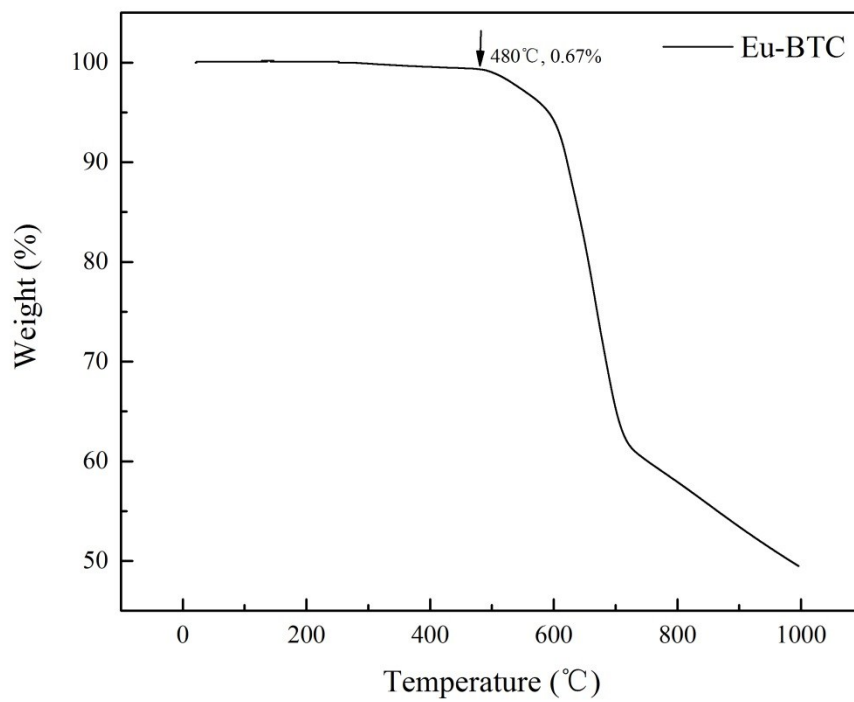
Eu-BDC was synthesized through the solvothermal reaction of NaOH (57.66 mg), H<sub>2</sub>BDC (120.96 mg) and Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (218.74 mg) solved in a mixture of H<sub>2</sub>O/methanol (17:3, 15 mL) in a screw capped vial. The resulting mixture was placed in an oven at 150 °C for 3 days. White powder were obtained after 3 times centrifugation washed with H<sub>2</sub>O and then under vacuum at 100 °C for 24 h.

Eu-BTC was synthesized through the solvothermal reaction of NaOH (49.92 mg), H<sub>3</sub>BTC (132.47 mg) and Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (189.38 mg) solved in a mixture of H<sub>2</sub>O/methanol (17:3, 15 mL) in a screw capped vial. The resulting mixture was placed in an oven at 150 °C for 3 days. White powder were obtained after 3 times centrifugation washed with H<sub>2</sub>O and then under vacuum at 100 °C for 24 h.

2. **Figure S1** (a) TGA traces of Eu-BDC ranging from room temperature to 1000 °C.



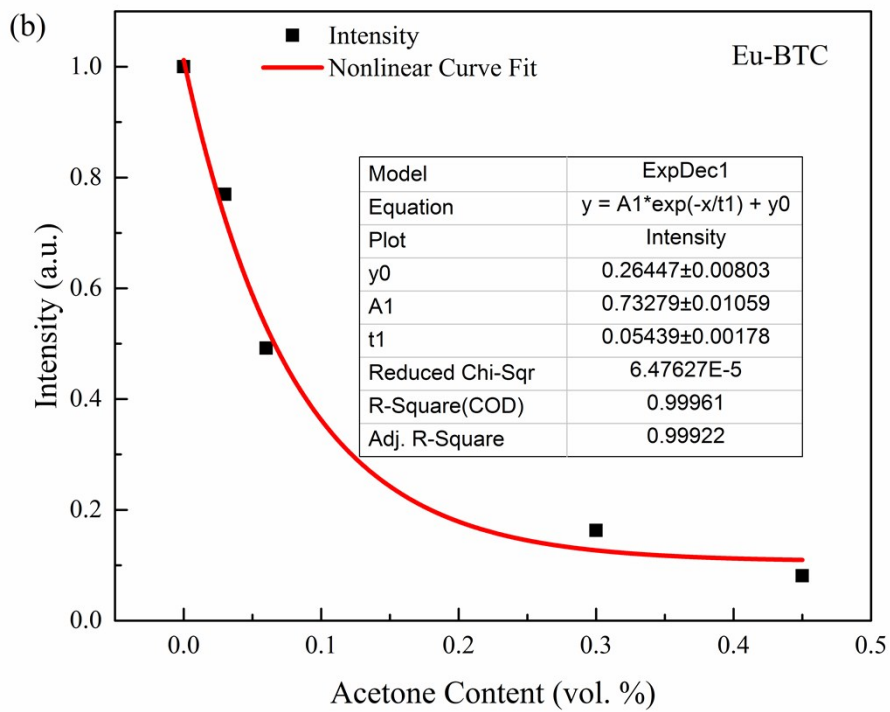
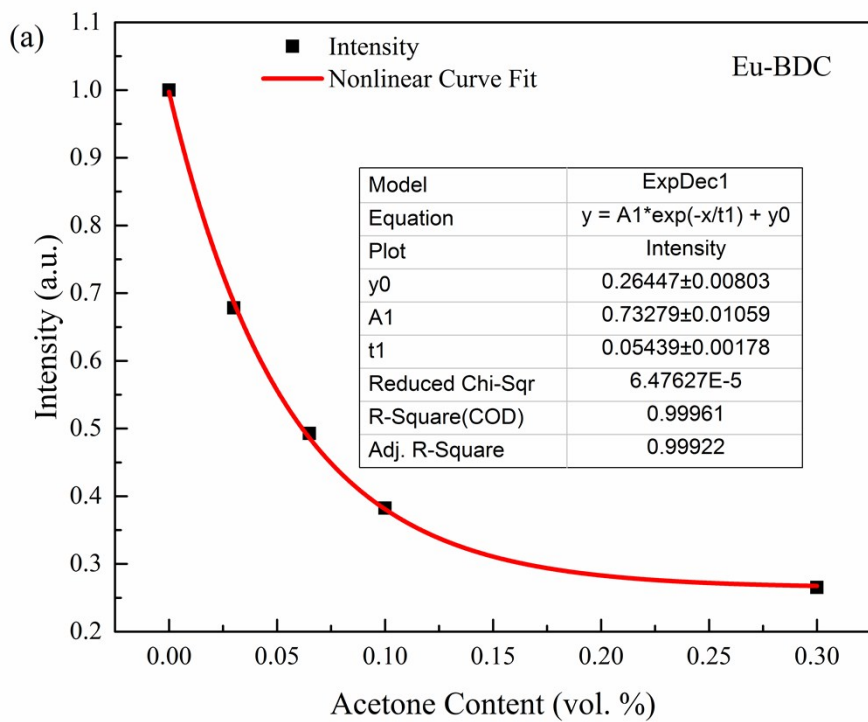
(b) TGA traces of Eu-BTC ranging from room temperature to 1000 °C.



**3. Table S1** A comparison between the acetone sensing performance of Ln-MOFs materials and our work

Sample	Selectivity	Sensitivity (EC <sub>50</sub> Vol%)	Reference
Eu-BTC	Methanol, DCM, ethanol, ACN, DMF, DMA, Water, acetone	0.06%	This work
Eu-BDC	Methanol, DMF, Water, DCM, ACN, DMA, ethanol, acetone	0.065%	This work
Eu-BPDA	Methanol, ethanol, ACN, THF, DMF, DCM, Water, acetone	0.028%/0.35%	[3]
SiO <sub>2</sub> @Eu-DPA	Ethanol, CHCl <sub>3</sub> , C <sub>2</sub> H <sub>4</sub> Cl, DMF, CH <sub>3</sub> CN, CH <sub>2</sub> Cl <sub>2</sub> , THF, ether, butyl alcohol, amyl alcohol, ethylene glycol, methanol, acetone	0.25%	[42]
Eu-L	DMF, methanol, ethanol, chloroform, CH <sub>3</sub> CN, 2-propanol, THF, acetone	<<0.5%	[41]
Eu-BPDC-OX	Ethanol, methanol, 1,4-dioxane, DMF, diethylene glycol, ethylene glycol, ether, trichloromethane, ACN, DMA, n-hexane, DEF, acetone	0.467%	[44]
Tb-PA	H <sub>2</sub> O, DMF, DMSO, benzene, o-xylene, propanol, THF, CHCl <sub>3</sub> , acetone	7%	[35]
Tb-L	Ethanol, 1,4-dioxane, CHCl <sub>3</sub> , THF, 1-pentanol, DMF, 1-hexanol, isopropanol, methanol, ethylene glycol, ethyl acetate, ACN, CH <sub>2</sub> Cl <sub>2</sub> , acetone	10%	[43]

**4. Figure S2** The Stern-Völmer plot of I/I<sub>0</sub> versus the concentration of acetone



5. LUMO and HOMO of acetone calculated by DFT and Eu-BDC, Eu-BTC gained by solid UV-vis diffuse reflection and cyclic voltammetry

### 5.1 LUMO and HOMO of acetone

Gaussian 09:

```
# opt freq b3lyp/6-311++g(3df,3pd) scrf=(solvent=methanol) geom=connectivity
```

LUMO = -0.03001 Hartree = -0.82 eV

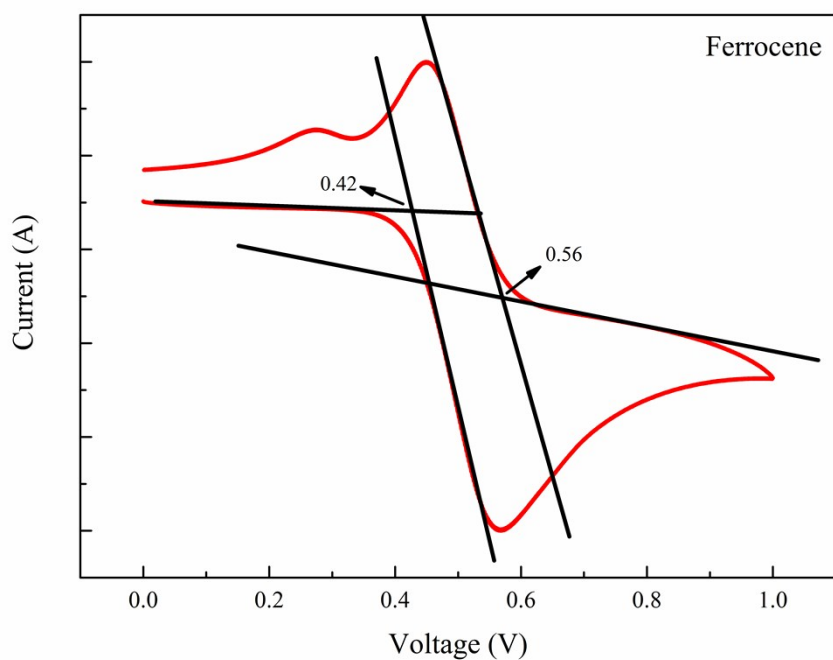
HOMO = -0.26535 Hartree = -7.22 eV

$E_g = \text{LUMO} - \text{HOMO} = -0.82 - (-7.22) = 6.40 \text{ eV}$

### 5.1 LUMO, HOMO of Eu-BDC and Eu-BTC

A conventional three-electrode configuration consisting of a platinum working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode were used. The solvent in all measurements was  $\text{CH}_2\text{Cl}_2$ , and the supporting electrolyte was 0.1 M  $[\text{Bu}_4\text{N}]\text{PF}_6$ . Ferrocene was added as a calibrant after each set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium couple at a scan rate of 100 mV/s.

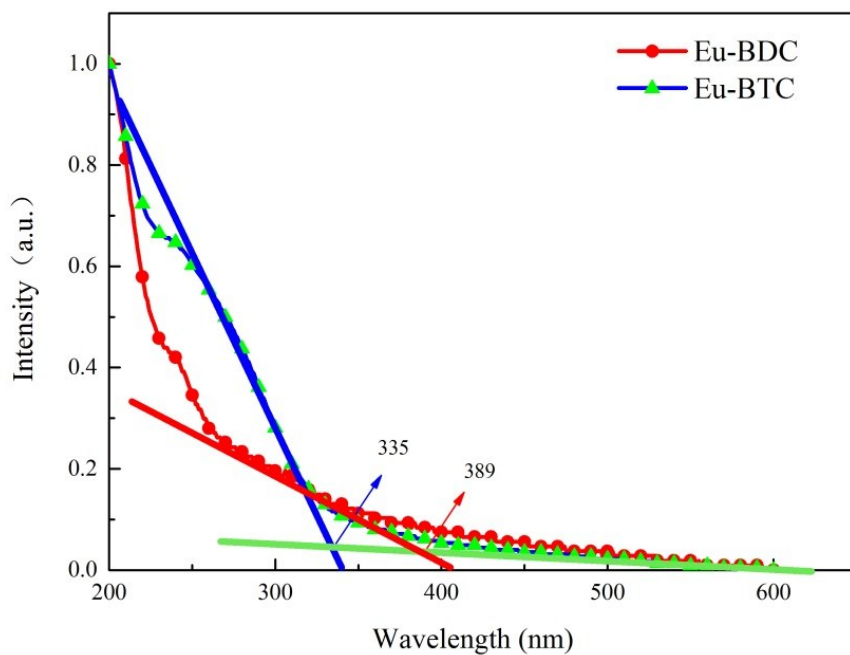
**Figure S3 (a)** Cyclic voltammetry of ferrocene



The LUMO levels of Eu-BPDA, Eu-BDC, Eu-BTC were measured from cyclic voltammetry using ferrocene substance.  $E_{re}$  and  $E_{ox}$  are redox potential of materials and oxidation potential of ferrocene, respectively. according to the following equations.

$$\begin{aligned} \text{LUMO} &= -(E_{re} + 4.8 - E_{ox}) \\ \text{HOMO} &= \text{LUMO} - E_g \\ E_{ox} &= (0.42 + 0.56) / 2 = 0.49 \text{ eV} \end{aligned}$$

(b) Solid UV-vis of Eu-BDC, Eu-BTC



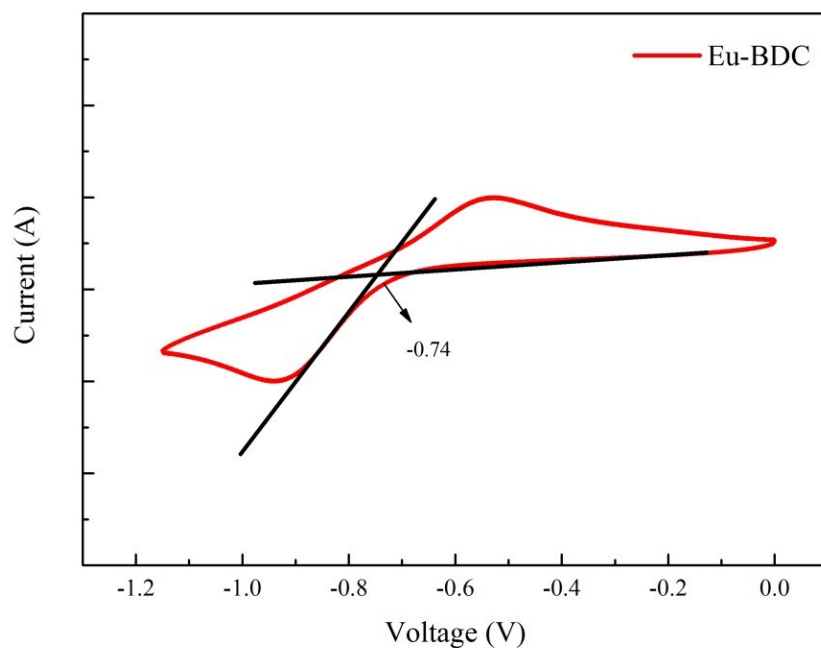
$$E_g = hv = hc/\lambda_{\text{onset}}$$

其中,  $h$  为普朗克常量,  $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s} = 4.136 \times 10^{-15} \text{ eV}\cdot\text{s}$ ;  $c$  为光速,  $c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1} = 2.998 \times 10^{17} \text{ nm}\cdot\text{s}^{-1}$ , 代入式中得,  $E_g = 1240/\lambda_{\text{onset}}$

$$E_{g_{\text{Eu-BDC}}} = 1240/389 = 3.19 \text{ eV}$$

$$E_{g_{\text{Eu-BTC}}} = 1240/335 = 3.70 \text{ eV}$$

(c) Cyclic voltammetry of Eu-BDC

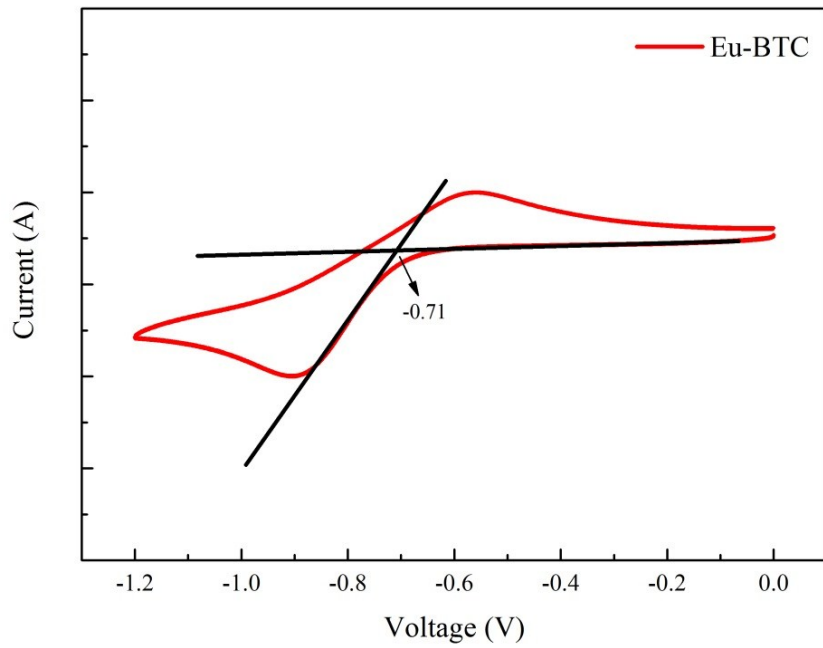


$$\text{LUMO} = -(-0.74 + 4.8 - 0.49) = -3.57 \text{ eV}$$



$$\text{HOMO} = \text{LUMO} - E_g = -3.57 - 3.19 = -6.76 \text{ eV}$$

(d) Cyclic voltammetry of Eu-BTC



$$\text{LUMO} = -(-0.71 + 4.8 - 0.49) = -3.60 \text{ eV}$$
$$\text{HOMO} = \text{LUMO} - E_g = -3.60 - 3.70 = -7.3 \text{ eV}$$