**Electronic Supplementary Information (ESI)** 

## A superior fluorescent sensor for Al<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup> based on Co(II) metal–organic framework with exposed pyrimidyl Lewis base site

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Figure S1: IR of 1.



Figure S2: TGA curve of 1.



Figure S3: Comparison of powder XRD patterns of 1.



PXRD patterns of 1: a) simulated, b) experimental, c) after immersion in a  $Al^{3+}$  DMF solution for three days, d) after immersion in a  $UO_2^{2+}$  solution for three days, e) after immersion in DMF:water (v:v = 25:1) for one day, f) after immersion in water for one day.



Figure S4: Solid state excitation spectra of dmimpym and H2nda.

Compound	1		
Empirical formula	C <sub>72</sub> H <sub>48</sub> Co <sub>4</sub> N <sub>12</sub> O <sub>16</sub>		
Formula weight	1572.94		
Temperature/K	298.15		
Crystal system	monoclinic		
Space group	P21/c		
a/Å	15.673(4)		
b/Å	15.378(4)		
c/Å	15.991(4)		
a/°	90		
β/°	95.467(3)		
γ/°	90		
Volume/Å <sup>3</sup>	3836.7(18)		
Ζ	2		
$\rho_{calc}g/cm^3$	1.362		
µ/mm <sup>-1</sup>	0.920		
F(000)	1600.0		
$2\Theta$ range for data collection	5.6 to 127.6°		
Index ranges	$-30 \le h \le 31, -22 \le k \le 22, -33 \le l \le 32$		
Reflections collected	67744		
Independent reflections	12397 [R <sub>int</sub> = 0.0512, R <sub>sigma</sub> = 0.0419]		
Data/restraints/parameters	12397/0/715		
Goodness-of-fit on F <sup>2</sup>	1.047		
Final R indexes [I>=2σ (I)]	$R_1 = 0.0378, wR_2 = 0.0985$		
Final R indexes [all data]	$R_1 = 0.0432, wR_2 = 0.1017$		
Largest diff. peak/hole / e Å <sup>-3</sup>	2.11/-0.99		

 Table S1: Crystal Data and Structure Refinement Parameters of Compound 1.

Compound 1					
Co1—Co2	2.8459 (10)	Co2—O6	2.036 (3)		
Co1—O2	2.104 (3)	Co2—O7 <sup>ii</sup>	2.064 (3)		
Co1—O4 <sup>i</sup>	2.013 (3)	Co2—N6 <sup>iii</sup>	2.044 (4)		
Co1—O5	2.018 (3)	O3—Co2 <sup>iv</sup>	2.029 (3)		
Co1—O8 <sup>ii</sup>	2.009 (4)	O4—Co1 <sup>iv</sup>	2.013 (3)		
Co1—N1	2.047 (3)	07—Co2 <sup>v</sup>	2.064 (3)		
Co2—O1	2.005 (3)	O8—Co1 <sup>v</sup>	2.009 (4)		
Co2—O3 <sup>i</sup>	2.029 (3)	N6—Co2 <sup>vi</sup>	2.044 (4)		
O2—Co1—Co2	73.20 (10)	O1—Co2—Co1	88.81 (10)		
O4 <sup>i</sup> —Co1—Co2	79.37 (11)	01—Co2—O3 <sup>i</sup>	90.62 (16)		
O4 <sup>i</sup> —Co1—O2	86.94 (17)	O1—Co2—O6	92.20 (15)		
04 <sup>i</sup> —Co1—O5	161.20 (14)	01—Co2—O7 <sup>ii</sup>	160.40 (15)		
O4 <sup>i</sup> —Co1—N1	101.68 (15)	O1—Co2—N6 <sup>iii</sup>	104.26 (15)		
O5—Co1—Co2	81.88 (9)	O3 <sup>i</sup> —Co2—Co1	82.21 (10)		
O5—Co1—O2	86.43 (16)	O3 <sup>i</sup> —Co2—O6	162.44 (13)		
O5—Co1—N1	95.71 (14)	O3i—Co2—O7ii	86.68 (16)		
O8 <sup>ii</sup> —Co1—Co2	89.79 (12)	O3 <sup>i</sup> —Co2—N6 <sup>iii</sup>	100.12 (15)		
O8 <sup>ii</sup> —Co1—O2	162.97 (16)	O6—Co2—Co1	80.53 (9)		
O8 <sup>ii</sup> —Co1—O4 <sup>i</sup>	89.34 (18)	06—Co2—O7 <sup>ii</sup>	84.87 (15)		
O8 <sup>ii</sup> —Co1—O5	91.88 (17)	O6—Co2—N6 <sup>iii</sup>	95.97 (15)		
O8 <sup>ii</sup> —Co1—N1	108.57 (16)	O7 <sup>ii</sup> —Co2—Co1	71.59 (12)		
N1—Co1—Co2	161.59 (11)	N6 <sup>iii</sup> —Co2—Co1	166.64 (11)		
N1—Co1—O2	88.46 (14)	N6 <sup>iii</sup> —Co2—O7 <sup>ii</sup>	95.32 (16)		
Symmetry codes: (i) $-x$ , $y-1/2$ , $-z+1/2$ ; (ii) $-x+1$ , $y-1/2$ , $-z+1/2$ ; (iii) x, y, $z-1$ ; (iv) $-x$ , $y+1/2$ ,					
-z+1/2; (v) $-x+1$ , y+1/2, $-z+1/2$ ; (vi) x, y, z+1.					

### Table S2: Selected bond lengths and angles for compound 1.

Figure S5: Luminescence decay curve for 1.



Figure S6: (a) SEM image of a typical morphology of 1 after loading Al<sup>3+</sup>; (b) Overlapped element mapping; (c) O element mapping; (d) N element mapping; (e) Co element mapping; (g) Al element mapping.



Molecular formula	Sensitivity	Responsive	Reference
[Co(OBA)(DATZ) <sub>0.5</sub> (H <sub>2</sub> O)]·(DATZ) <sub>0.5</sub> (H <sub>2</sub> O)]	57.5 ppb	Seconds	1
MOF-LIC-1(Eu)	10 <sup>-4</sup> M	Seconds	2
${[Eu(BTB)(phen)]} \cdot_{4.5}DMF \cdot 2H_2O_n$	5×10 <sup>-8</sup> M (1.35 ppb)	Seconds	3
${[H_{3}O]_{2}[Eu_{2.5}(BTB)_{3}(OAc)_{0.5}(H_{2}O)_{3}] \cdot 2DMA \cdot 2.5H_{2}O}_{n}$	10 <sup>-4</sup> M	Seconds	4
$C_{55}H_{41}IrN_7O_2PF_6$	10 <sup>-6</sup> M	Seconds	5
TriPP-COONa	10 <sup>-6</sup> M	Seconds	6
[H <sub>2</sub> N(CH <sub>3</sub> ) <sub>2</sub> ][Eu(H <sub>2</sub> O) <sub>2</sub> (BTMIPA)]·2H <sub>2</sub> O	10 <sup>-3</sup> M	72 h	7
[Co <sub>2</sub> (dmipm)(nda) <sub>2</sub> ] <sub>n</sub>	7×10 <sup>-7</sup> M (17.7 ppb)	Seconds	This work

# Table S3: Comparison of the detection sensitivity and responsive time of various Al<sup>3+</sup> sensors.

#### **Computational method**

All density functional theory calculations were carried out using the DMol3 module<sup>8</sup> in Material Studio software. Exchange-correlation (XC) effects were treated by the PBE generalized gradient approximation (GGA)<sup>9</sup>. For Al and U atom, the inner core was treated by the approach of effective core potential,<sup>9</sup> and the electrons in  $3s^23p^1$  for Al and  $5f^36d^{17}s^2$  for U were explicitly seen as valence electrons. The double numerical basis set plus polarization functional (DNP)<sup>10</sup>, which has a computational precision being comparable to the split-valence basis set 6-31g\*\*, was applied in the expanded electronic wave function. For all the calculations, the optimization convergence in energy and force were set to be  $1.0 \times 10^{-5}$  Ha and  $2.0 \times 10^{-3}$  Ha.Å<sup>-1</sup>, and the SCF convergence was set to be  $1.0 \times 10^{-6}$ . The binding energy was typically calculated as following formula:  $E_a = E(X/MOF) - E(X) - E(MOF)$  (X= Al, UO2), where E(X/MOF), E(X) and E(MOF) represents the energy of X-adsorbed MOF, X and pristine MOF.

#### **Density functional theory calculation results**

In order to identify the difference of binding energy between them, density functional theory calculations were carried out. Owing to the larger number of atoms (more than 300) in one unit cell, it is difficult to simulate the whole single cell with high accuracy. Inspection the microstructure of compound **1** can reveal that dmimpym ligand plays an important role in the adsorption of  $Al^{3+}$  and/or  $UO_2^{2+}$ . Thus, the theoretical model of compound **1** was simplified as one dmimpym ligand. Via the analysis of DFT results, we can conclude two respects, as follows:

(1) The obtained binding energy of -24.09 eV for Al<sup>3+</sup> and -8.33 eV for UO<sub>2</sub><sup>2+</sup> demonstrates that dmimpym ligand can more effectively coordinate with Al than UO<sub>2</sub><sup>2+</sup>. Such energy differences between them is dominated by geometrical structure. As shown in Fig. S7, electron-deficient Al<sup>3+</sup> ion coordinates with electron-rich pyrimidyl nitrogen (d(N-Al) = 2.109 Å) and imidazole carbon (d(C-Al) = 2.194 Å), featuring stable pentagon-chelating coordination geometry, while UO<sub>2</sub><sup>2+</sup> ion only coordinates with pyrimidyl nitrogen (d(N-U) = 2.596 Å). The torsion angles between pyrimidine plane and imidazole plane are 30.68° for Al-MOF and 64.78° for **UO<sub>2</sub>@1**. Such geometrical difference between them is result from the volume difference of Al<sup>3+</sup> and UO<sub>2</sub><sup>2+</sup> ions.

(2) Al@1 and UO<sub>2</sub>@1 exhibit different electronic structures. As shown in Fig. S8, the frontier molecular orbitals of Al@1 feature similar characteristic with pristine 1. But the UO<sub>2</sub>@1 shows very different orbital features, where adsorbed  $UO_2^{2+}$  completely destroy the conjugate property of dmimpym ligand (see Fig. S8c). Therefore, the HOMO-LUMO gap of Al@1 ( 0.34 eV ) approximates to pristine 1 ( 0.12 eV ), and is far less than that of UO<sub>2</sub>@1 ( 1.29 eV ). The increase of HOMO-LUMO gap in UO<sub>2</sub>@1, together with the destroyed conjugate character of dmimpym ligand, can effectively quench fluorescence of pristine 1. Essentially, the transformation of electronic structure is derived from the changes of geometrical structures.

Generally, the  $Al^{3+}$  and  $UO_2^{2+}$  ions in the channel of MOF feature adsorption structure and thereby induce the different changes of electronic structure of MOFs. Therefore,  $Al^{3+}$  ions can enhance the fluorescence of pristine **1**, while  $UO_2^{2+}$  ions show an opposite effect.



Figure S8 Frontier molecular orbitals of 1 (a), Al@1 (b) and UO<sub>2</sub>@1 (c): (1) HOMO; (2) LUMO;

(3)LUMO+1;(4) HOMO-2.

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