Electronic Supplementary Information

A robust Zn(II)/Na(I)-MOF decorated with $[(OAc)_2(H_2O)_2]_n^{2n-}$ anions for luminescent sensing of copper ion based on the inner filter effect

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Materials and physical measurements

All the chemicals were commercially available reagents of analytical grade unless otherwise specified, and were used without further purification. Fourier transform infrared (FT-IR) spectrums were conducted on a Thermo Nicolet iS50 spectrometer. Powder X-ray diffraction (PXRD) data were collected on PANalytical X'Pert PRO MPD system (PW3040/60). X-ray photoelectron spectroscopy (XPS) were obtained with a Thermo Escalab 250 spectrometer with monochromated $Al_{K\alpha}$ excitation. Field emission scanning electron micrographs (SEM) were obtained with a JSM 6701F microscope. Thermogravimetric analysis (TGA) were carried out on a Netzsch STA-449F3 thermogravimetric analyzer in the nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The zeta potential were determined using dynamic light scattering (DLS) on Malvern Instruments Nanosizer-ZS. The luminescence excitation/emission spectra of the samples were measured at room temperature on a Hitachi F-4600 fluorescence spectrophotometer.

X-Ray data collection and structure determination

Single crystal of **1** was obtained directly from the above preparation. All measurement was made on a Bruker Smart Apex-II CCD area detector by using graphite monochromated Mo Kα (λ = 0.071073 nm). Its crystal was mounted on glass fibers at 296 K. Cell parameter was refined by using the program Bruker *SAINT*. The collected data was reduced by using the program Bruker *SAINT* A, and the absorption correction (multi-scan) was applied. The reflection data was also corrected for Lorentz and polarization effects. The crystal structure of **1** was solved by direct method refined on F^2 by full-matrix least-squares technique with the SHELXTL-97 program.[1] All H atoms in **1** were placed in geometrically idealized positions and constrained to ride on their parent atoms.

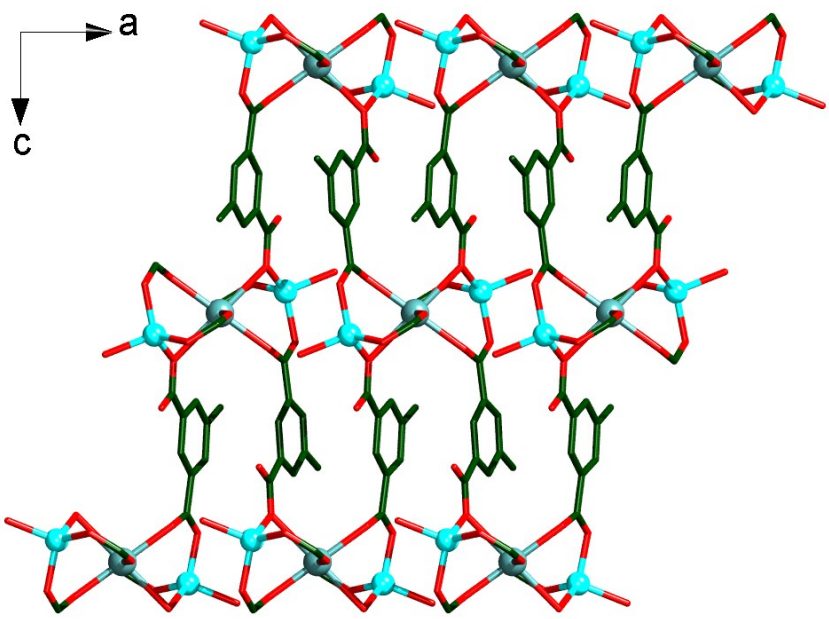

Figure S1. A view of the 2D network of MOF **1** extending in the *ac* plane.

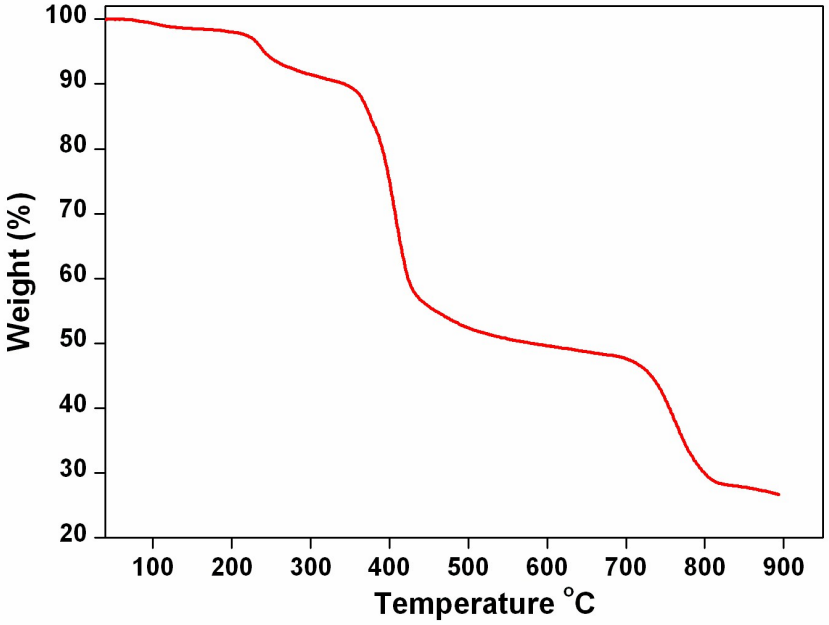

Figure S2. TGA curve of MOF **1**.

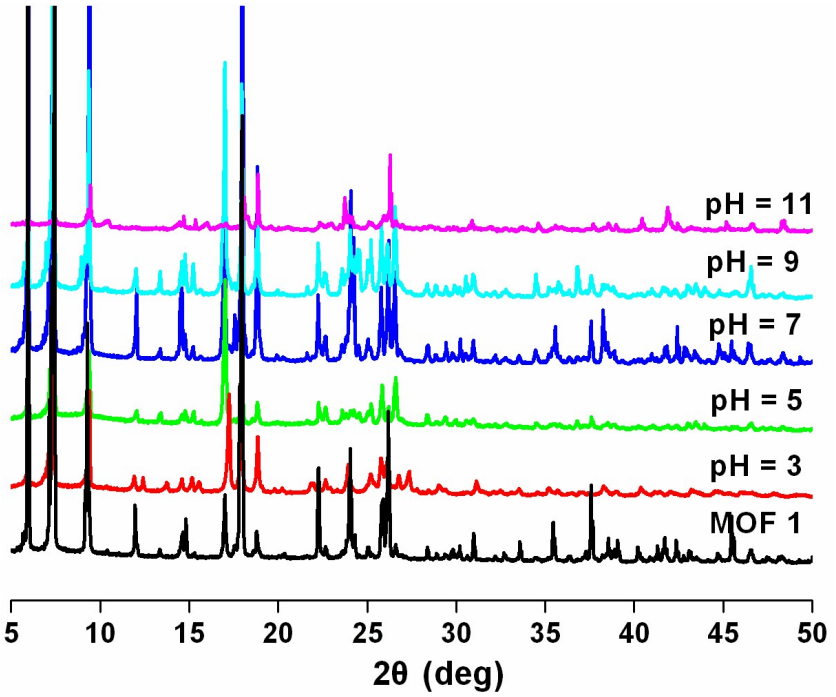

Figure S3. PXRD patterns of MOF **1** after immeresing in aqueous solution at pH = 3, 5, 7, 9, 11 (24 h).

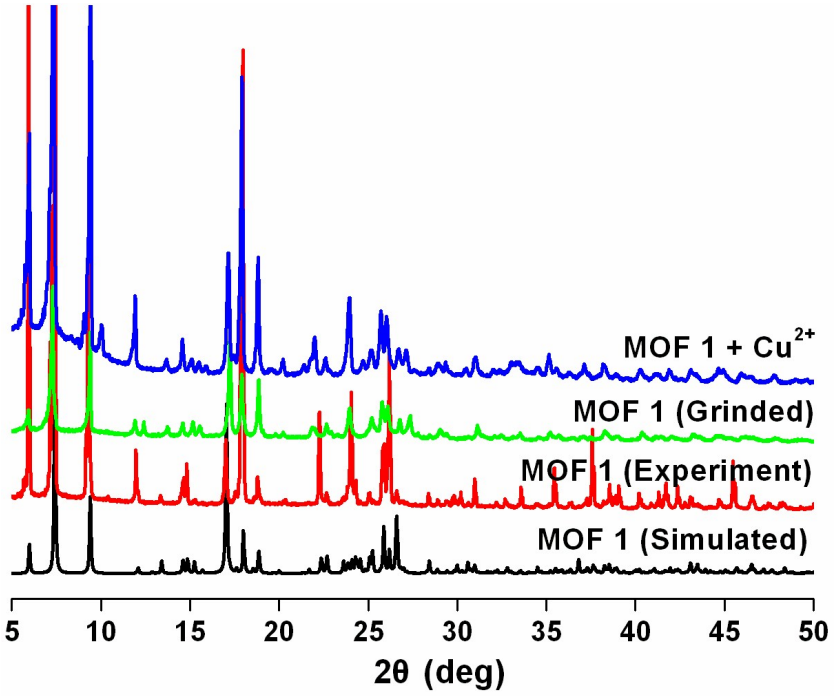

Figure S4. The PXRD patterns of simulated single crystal data MOF **1**, as-synthesized MOF **1**, the grined MOF **1** and the grined MOF **1** after adding Cu^{2+} ion.

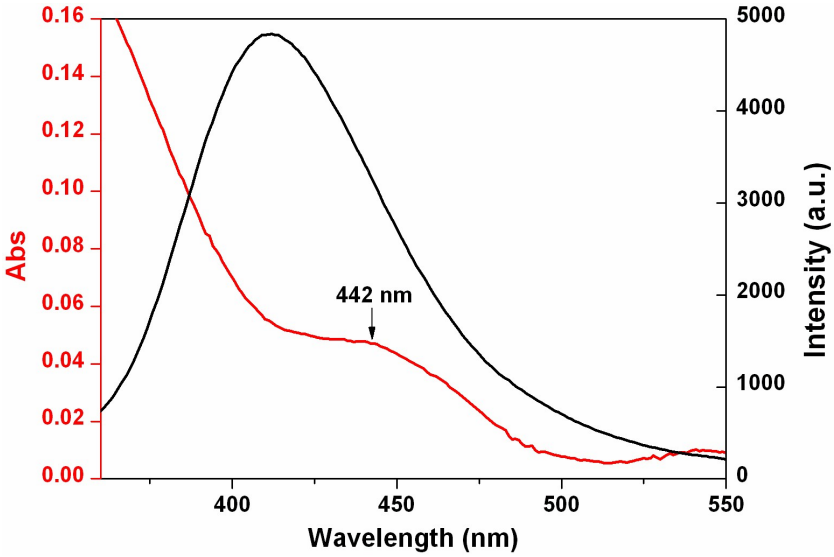

Figure S5. UV−Vis absorbance (red line) of Cu^{2+}, fluorescent emission spectrum (black line) of MOF **1** with a maximum at 412 nm.

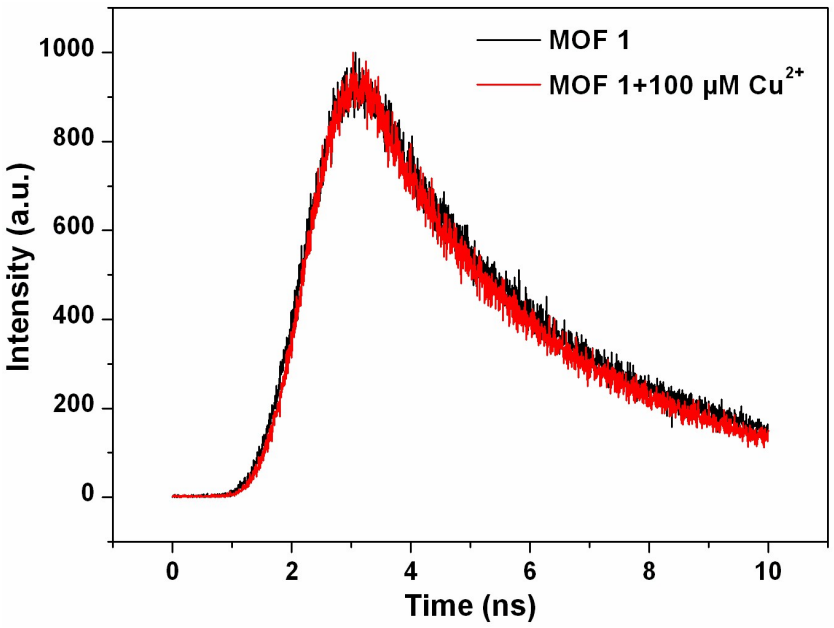

Figure S6. The fluorescence lifetime of MOF **1** in the absence (black) and presence (red) of 100 μM Cu^{2+}.

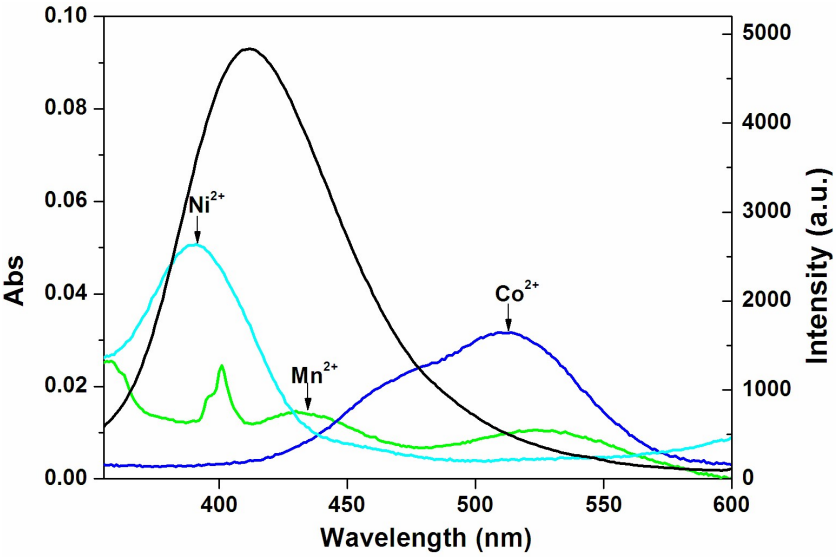

Figure S7. UV−Vis absorbance of Ni^{2+}, Mn^{2+} and Co^{2+}, fluorescent emission spectrum (black line) of MOF **1** with a maximum at 412 nm.

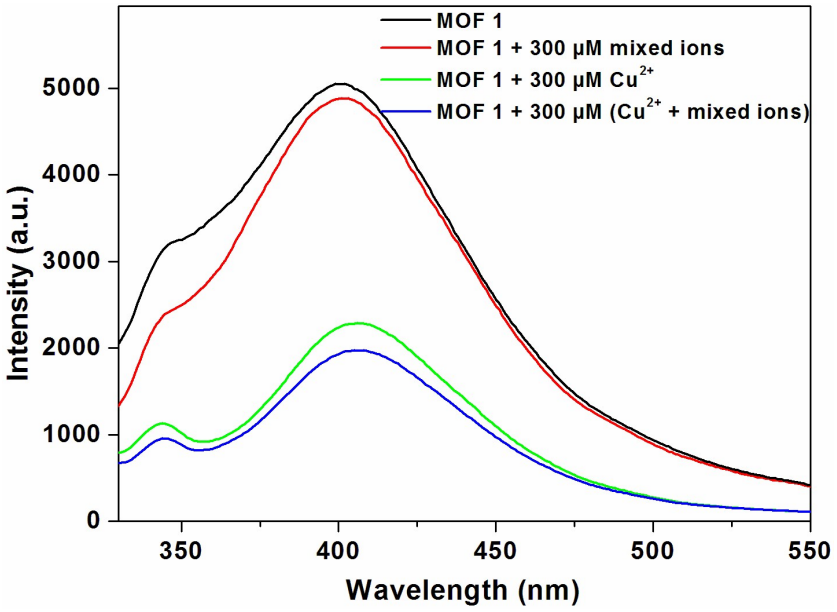

Figure S8. Emission spectra of MOF **1** after adding mixed ions (Cd^{2+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Ni^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Mg^{2+}, Co^{2+}, Li^{+}, Ba^{2+} and Sr^{2+}; red curve), Cu^{2+} ion (green curve) and the mixture ions of Cu^{2+}, Cd^{2+}, Mn^{2+}, Al^{3+}, Zn^{2+}, Ni^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Co^{2+}, Li^{+}, Ba^{2+} and Sr^{2+} (blue curve).

Table S1. Geometry parameters for hydrogen-bonding interactions in MOF **1**.

Interactions	D−H [Å]	H···A [Å]	D···A [Å]	Angle (D−H···A) [°]
O2W−H2WB···O7	0.85	1.99	2.841(4)	174.3
O1W−H1WA···O5[a]	0.85	2.31	3.100(3)	155.0
O1W−H1WB···O7[b]	0.85	2.37	3.212(4)	171.6
O2W−H2WA···O7[c]	0.85	1.93	2.750(3)	162.4
O4−H4···O1W[d]	0.85	2.51	3.006(3)	118.1
O4−H4···O6[d]	0.85	2.58	3.271(3)	139.6

Symmetry codes: a, $x + 1$, y, z, b, $- x + 1$, $- y + 1$, $- z - 1$; c, $x + 1$, $- y - 1/2$, $z + 1$; d, $- x + 1$, $- y + 1$, $- z$.

Table S2. Comparison of the Cu^{2+} quenching effect coefficients (*K*sv) in reported MOF sensors.

Compounds	*K*sv (M^{-1})	References
$Eu_2(FMA)_2(OX)(H_2O)_4 \cdot 4H_2O$	528.7	2
$[Mg_3(ndc)_{2.5}(HCOO)_2(H_2O)][NH_2Me_2] \cdot 2H_2O \cdot DMF$	1.986×10^3	3
ZnMGO	3.07×10^4	4
$\{[Eu_2(abtc)_{1.5}(H_2O)_3(DMA)] \cdot H_2O \cdot DMA\}_n$	529	5
$\{Mg(DHT)(DMF)_2\}_n$	170.2	6
$Zr_6O_4(OH)_4(TCPP\text{-}H_2)_3$	4.5×10^5	7
$[Tb_3(L)_2(HCOO)(H_2O)_5] \cdot DMF \cdot 4H_2O$	2021.8	8
$[Eu(pdc)_{1.5}(DMF)] \cdot (DMF)_{0.5}(H_2O)_{0.5}$	89.4	9
Eu^{3+}@UiO-66-COOH	5.35×10^4	10
$[H_2N(CH_3)_2][Eu_3(L_1)_2(HCOO)_2(DMF)_2(H_2O)]$	2350	11
MOF **1**	7.75×10^4	this work

References

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