Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Luminescent MOF as a fluorescent sensor for the sequential detection of Al^{3+} and phenylpyruvic acid

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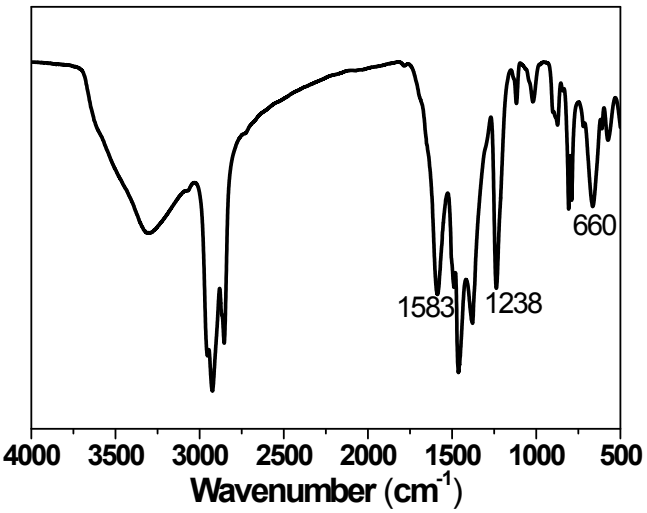

Fig. S1 FT-IR spectrum of as-prepared UiO-66-$(OH)_2$ sample. The intensive peak at 1238 cm^{-1} could be assigned to the C−O stretching vibration of the hydroxyl groups on $dhtp^{2-}$ ligand. The carboxyl groups gave absorption peak at 1586 cm^{-1}, instead of the range of 1650−1730 cm^{-1}, showing that it is completely deprotonated upon the formation of MOF structure.

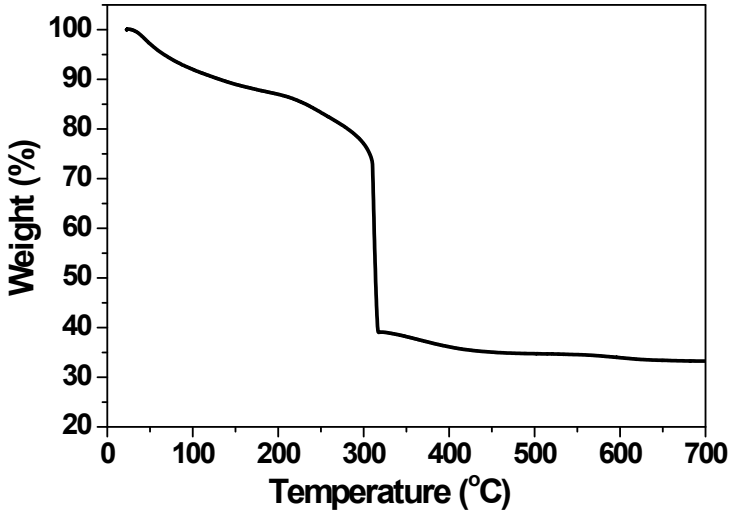

Fig. S2 Thermogravimetry curve of UiO-66-$(OH)_2$. The overall weight loss from room temperature to 700 °C is 66.8%, which is consistent with the loss of all H_2O molecules and organic components with ZrO_2 as residue (calcd 67.2%) based on the formula of $[Zr_6O_4(OH)_4(dhtp)_6](DMF)_3(H_2O)_{10}$.

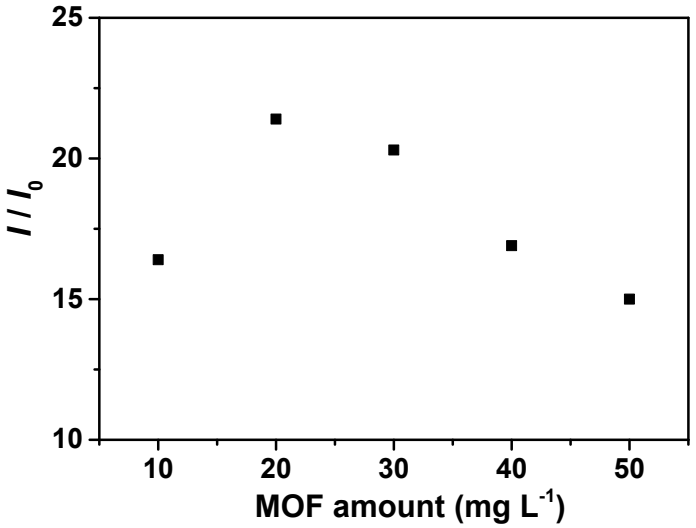

Fig. S3 Relative fluorescence enhancement induced by 50 μM Al^{3+} at different addition amounts of UiO-66-$(OH)_2$.

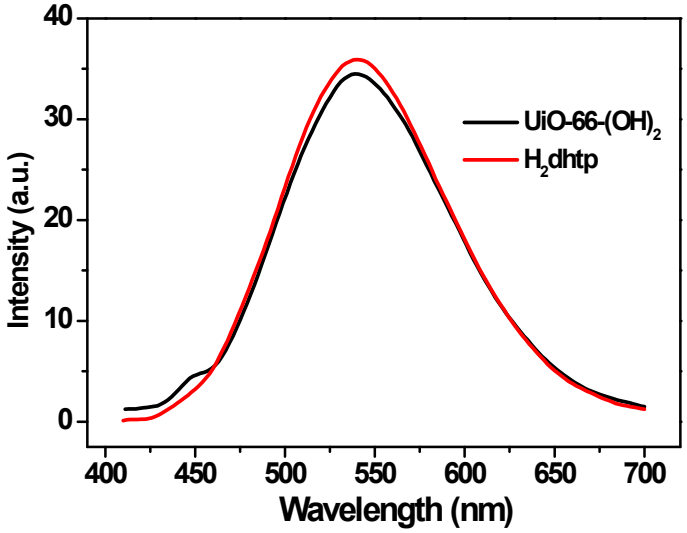

Fig. S4 Comparison between the fluorescence spectra of UiO-66-$(OH)_2$ (20 mg L^{-1}) and free H_2dhtp ligand (16 μM, dissolving H_2dhtp by 2 equiv. of NaOH) in aqueous media, λ_{ex} = 385 nm.

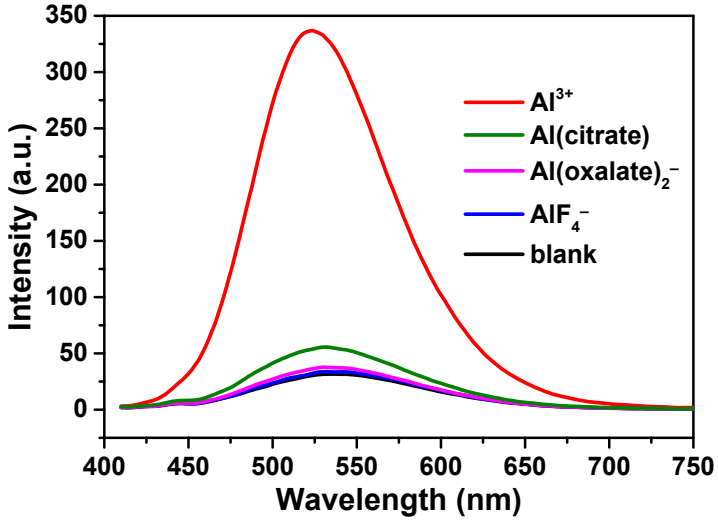

Fig. S5 Comparison among the fluorescent responses of UiO-66-$(OH)_2$ to Al^{3+}, AlF_4^-, Al(citrate) and $Al(oxalate)^{2-}$.

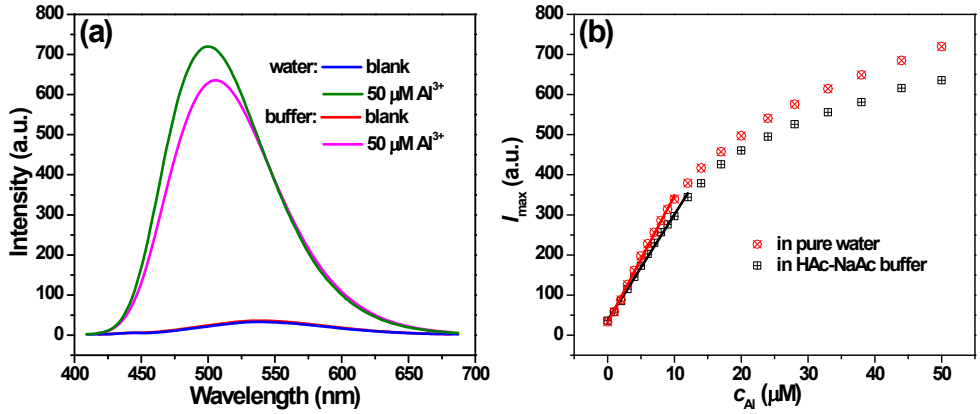

Fig. S6 Comparison between the changes of (a) fluorescent spectrum and (b) maximum emission intensity of UiO-66-$(OH)_2$ in pure water and HAc-NaAc buffer (10 mM, pH = 5.0) upon Al^{3+} addition.

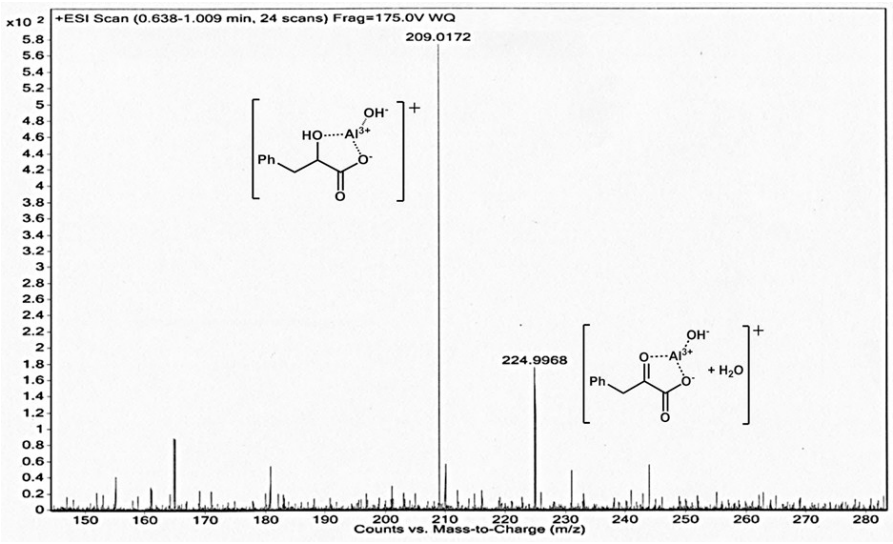

Fig. S7 ESI-MS spectrum of the solution after the sensing of PPA by UiO-66-$(OH)_2$-Al^{3+}, MOF sensor was separated by filtration.

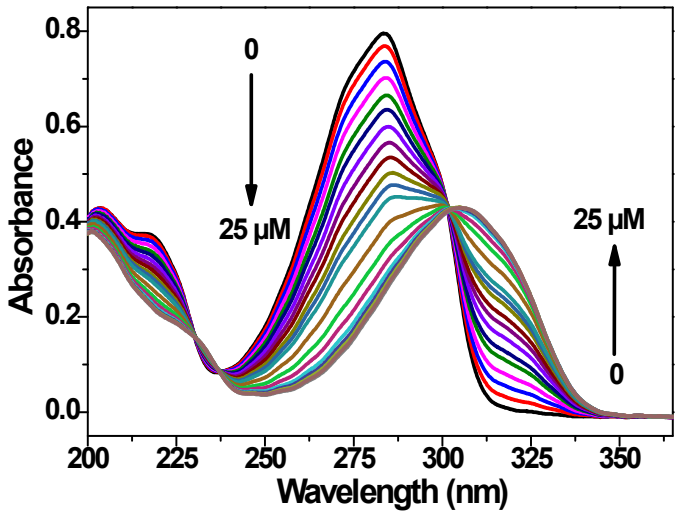

Fig. S8 UV-Vis spectra of PPA (50 μM) in the presence of Al^{3+}.

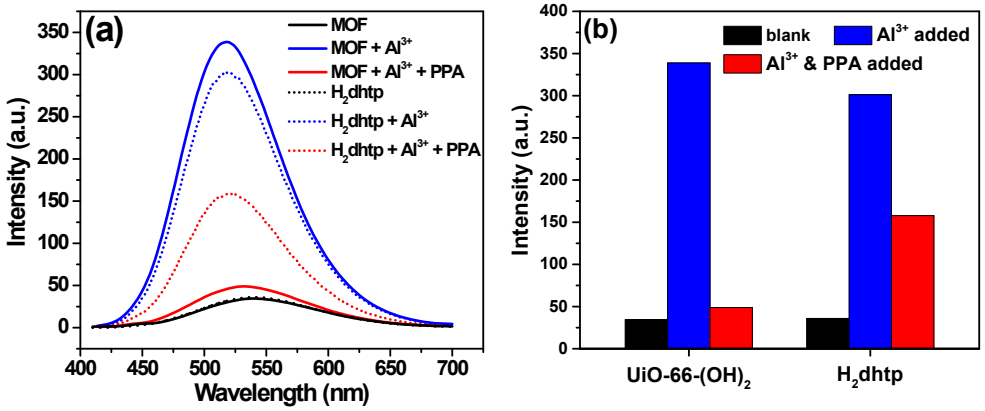

Fig. S9 (a) Fluorescent spectra of the suspension of UiO-66-$(OH)_2$ (20 mg L^{-1}) and the solution of H_2dhtp (16 μM) after the sequential addition of Al^{3+} (12 μM) and PPA (50 μM). (b) Comparison between the fluorescent responses of UiO-66-$(OH)_2$ and H_2dhtp.

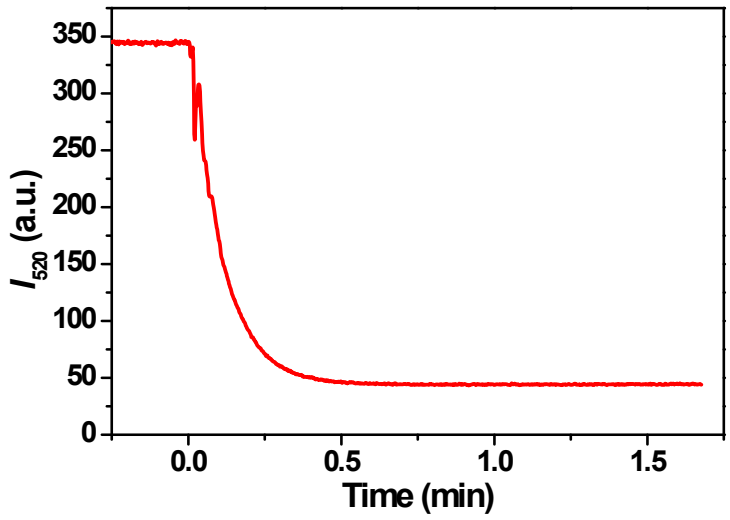

Fig. S10 Emission intensity change of UiO-66-$(OH)_2$-Al^{3+}after the addition of PPA (50 μM).

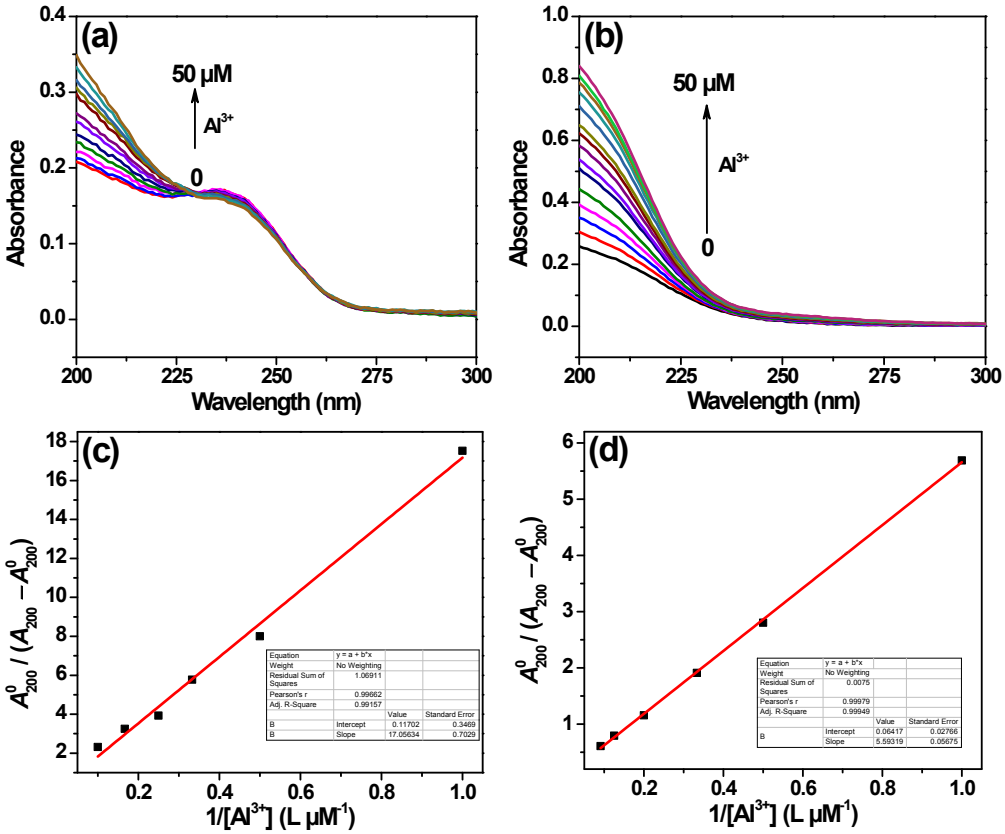

Fig. S11 Absorption spectra of (a) 100 μM pyruvic acid and (b) 100 μM α-ketoglutaric acid in the presence of different concentrations of Al^{3+}. Linear fitting of the absorbance change of (c) pyruvic acid at 200 nm and (d) α-ketoglutaric acid at 200 nm with Al^{3+} addition based on Benesi-Hildebrand equation.

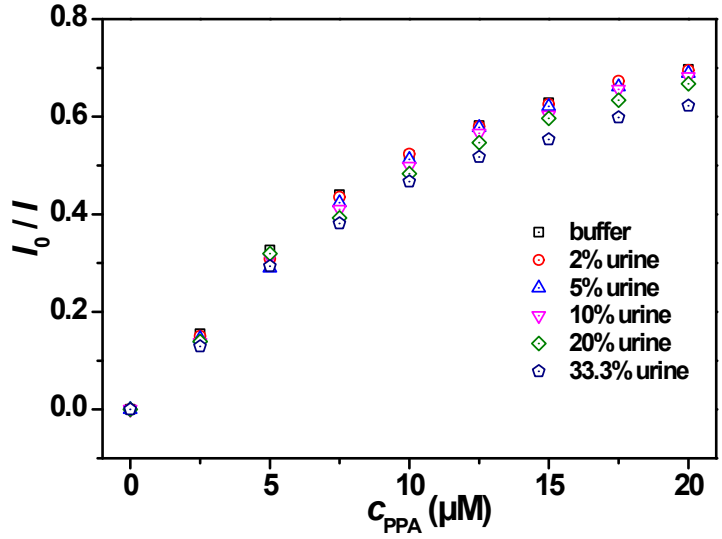

Fig. S12 Fluorescent response of UiO-66-$(OH)_2$-Al^{3+} to PPA in dilutions of artificial urine.

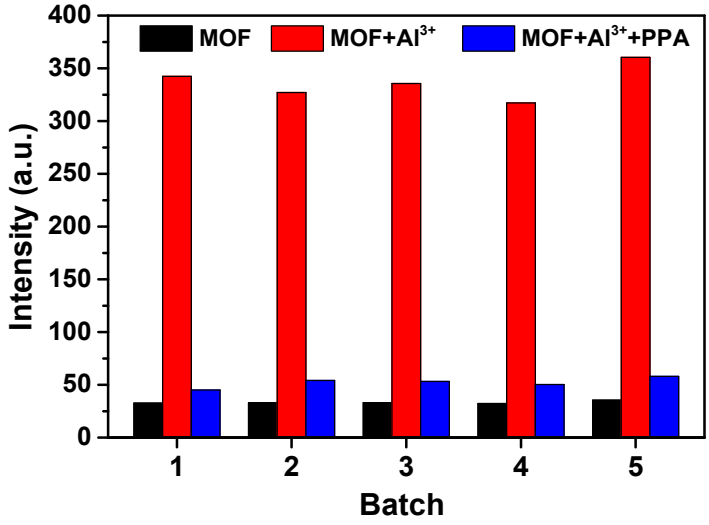

Fig. S13 Fluorescent responses of UiO-66-$(OH)_2$ samples from five different batches to Al^{3+} and PPA.

Table S1 Detection limits of recently reported Al^{3+} detection based MOF system.

Material	Mode	Detection limit	Ref.
TMU-60	colorimetric	3.7 μM	1
$[Co_2(dmimpym)(nda)_2]_n$	fluorometric	0.7 μM	2
UiO-66-NH_2-SA	fluorometric	6.89 μM	3
$[Tb(ppda)(ox)_{0.5}(H_2O)_2]_n$	fluorometric	5.66 μM	4
Mg−TPP−DHBDC	fluorometric	28 nM	5
[Eu(BTB)(phen)]	fluorometric	50 nM	6
UiO-66-$(OH)_2$	fluorometric	47 nM	This work

Table S2 The quenching efficiencies of tested interfering substances on the emission of UiO-66-$(OH)_2$-Al^{3+}.

Interfering substance	Concentration	$1 - I/I_0$ (%)
cysteine	1 mM	−1.0
ascorbic acid	1 mM	9.2
phenylalanine	1 mM	0.1
sarcosine	1 mM	2.2
creatinine	1 mM	−0.5
hippuric acid	1 mM	3.7
urea	1 mM	0.2
uric acid	1 mM	7.1
pyruvic acid	50 μM	7.0
α-ketoglutaric acid	50 μM	12.3

References

1. F. Rouhani, F. Rafizadeh-Masuleh and A. Morsali, *J. Mater. Chem. A*, 2019, **7**, 18634−18641.
2. W. M. Chen, X. L. Meng, G.L. Zhuang, Z. Wang, M. Kurmoo, Q. Q. Zhao, X. P. Wang, B. Shan, C. H. Tung and D. Sun, *J. Mater. Chem. A*, 2017, **5**, 13079−13085.
3. S. Y. Zhu and B. Yan, *Dalton Trans.*, 2018, **47**, 1674−1681.
4. Z. Zhan, Y. Jia, D. Li, X. Zhang and M. Hu, *Dalton Trans.*, 2019, **48**, 15255−15262.
5. Y. P. Li, X. H. Zhu, S. N. Li, Y. C. Jiang, M. C. Hu and Q. G. Zhai, *ACS Appl. Mater. Interfaces*, 2019, **11**, 11338−11348.
6. H. Xu, B. Zhai, C. S. Cao and B. Zhao, *Inorg. Chem.*, 2016, **55**, 9671−9676.