A novel Co(II)-based MOF with selective fluorescence as a turn-on sensor for biomarker methylmalonic acid

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1 Experimental section

1.1 Materials and methods

All chemicals used in this work are available commercially and were used without further purification. 2,6-di(4-carboxylphenyl)-4-(4-(triazol-1-ylphenyl))pyridine (H_2L) and 4,4′-bis(imidazolyl)biphenyl (bibp) were acquired from Jinan Henghua Sci. & Tech. Co., Ltd. The Fourier-transform infrared (FT-IR) spectrum (4000–400 cm^{-1}) was recorded with KBr pellets on the Nicolet 170SX spectrometer. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA-7 thermal analyzer in flowing N_2 with a heating rate of 10 °C min^{-1}, ranging from 30 to 800 °C. The powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 ADVANCE-ray diffractometer in the 5–50° range of 2θ. Photoluminescence spectra were carried out using a Hitachi F-4600 FL spectrofluorophotometer at the room temperature. The fluorescence lifetimes of samples were measured using an Edinburgh FLS 1000 transient/stable fluorescence spectrometer. The UV-vis absorption spectra were recorded in application of a Shimadzu UV-2550 spectrophotometer.

1.2 Synthesis of $\{[Co(L)(bibp)]\cdot bibp\cdot 2H_2O\}_n$ (1)

$Co(NO_3)_2\cdot 6H_2O$ (29.1 mg, 0.1 mmol), H_2L (23.2 mg, 0.05 mmol) and bibp (14.5 mg, 0.05 mmol) were dissolved in a 6 mL mixture of DMF/H_2O (v/v = 3:3) and ultrasound for 20 min at room temperature. Then, the obtained reaction mixture was transferred to a 25 mL Teflon-lined stainless-steel vessel and heated at 130 °C for 3 days. Subsequently, the vessel was cooled to room temperature at the rate of 2.5 °C h^{-1}

and its contents were washed with methanol. Purplish red rod crystals of **1** were obtained in 15.4 % yield (based on Co). FT-IR (KBr pellet, cm^{-1}): 3422 (m), 3132 (s), 1654 (w), 1593 (s), 1559 (s), 1511 (s), 1440 (w), 1410 (w), 1379 (s), 1308 (s), 1295 (m), 1217 (w), 1213 (w), 1190 (w), 1148 (w), 1130 (m), 1109 (w), 1053 (s), 1003 (w), 978 (w), 961 (s), 941 (w), 854 (m), 821 (s), 794 (s), 734 (m), 703 (w), 655 (s), 556 (w), 522 (m), 499 (m), 485 (w).

1.3 X-ray structure determination

X-ray crystallographic data of **1** were collected on a Bruker APEX-II CCD diffractometer. The reflections were collected using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). The structure was solved directly and then refined with the software SHELXTL. [1] The details of the crystal data are summarized in Table 1. The selected bond lengths (Å) and angles for **1** are listed in Table S1 (for details, see CCDC 2249073).

1.4 Fluorescence sensing experiments

The fluorescence sensing experiments were carried out using **1** suspension. In a typical selectivity tests experimental setup, the dried sample powder (2.0 mg) of **1** was added to 3.5 mL deionized water to form a suspension. Then, the major serum chemicals (NaCl, KCl, $CaCl_2$, $MgCl_2$, urea, glucose, $NaHCO_3$ and L-proline (L-pro)) or urine chemicals (NaCl, KCl, NH_4Cl, Na_2SO_4, urea, glucose, creatine and creatinine) (0.5 mL, 1mg/mL) was added into the above suspension, respectively, and the fluorescence spectra of suspensions were measured after sonication for 20 min. The titration experiments were carried out by adding different amounts of MMA solutions to the suspensions, and the corresponding luminescence spectra were collected. For the cycle experiment, the suspension of **1** and MMA solution are added to the cuvette, and the fluorescence spectra are recorded. The above system is centrifuged, washed with deionized water and dried, and the fluorescence intensity is re-recorded.

For an unknown urine sample, after being diluted 50 times with deionized water, 2 mg of **1** powder was simply immersed into deionized water and the unknown solutions, respectively, and their emission spectra were recorded after sonication for 20 min.

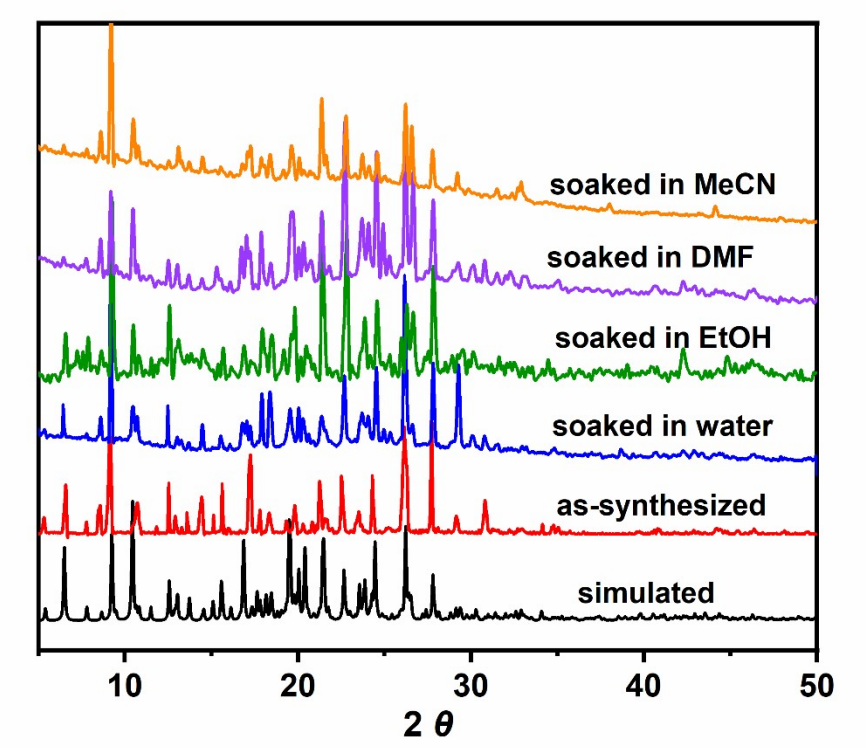

Figure S1 The Powder X-ray diffraction patterns of **1** immersing in common solvents (H_2O, N,N'-dimethylformamide (DMF), ethanol(EtOH) and acetonitrile (MeCN)) for 6 h.

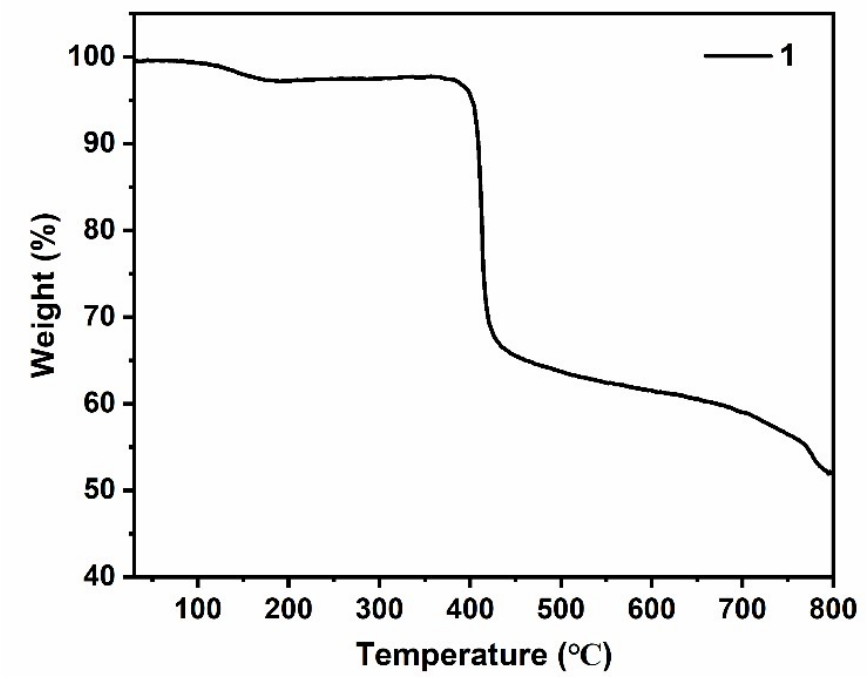

Figure S2 The TGA plot of **1**.

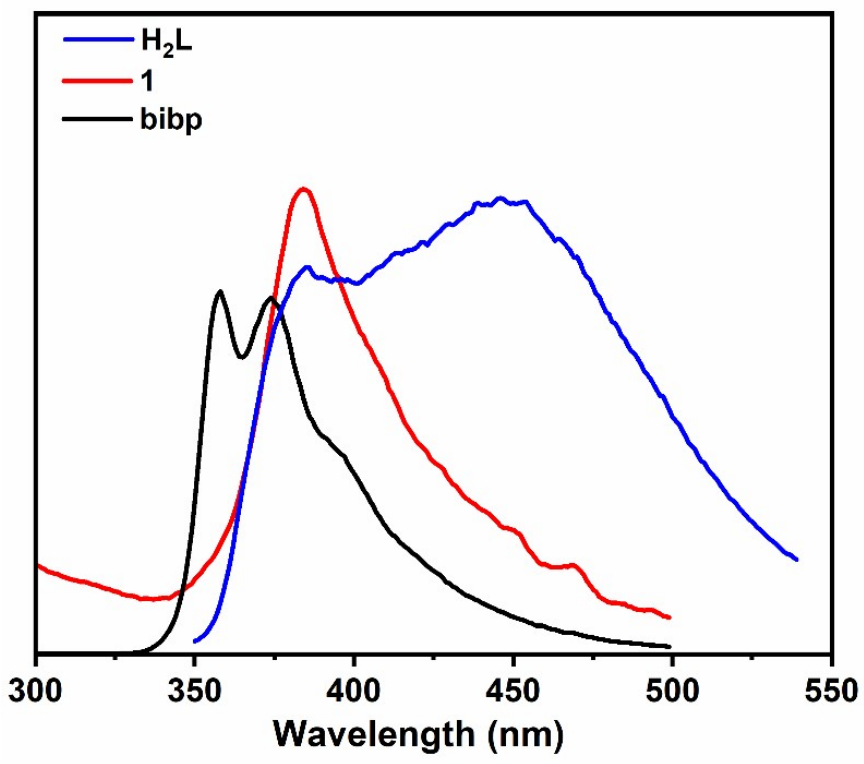

Figure S3 Emission spectra of **1** and raw organic linkers.

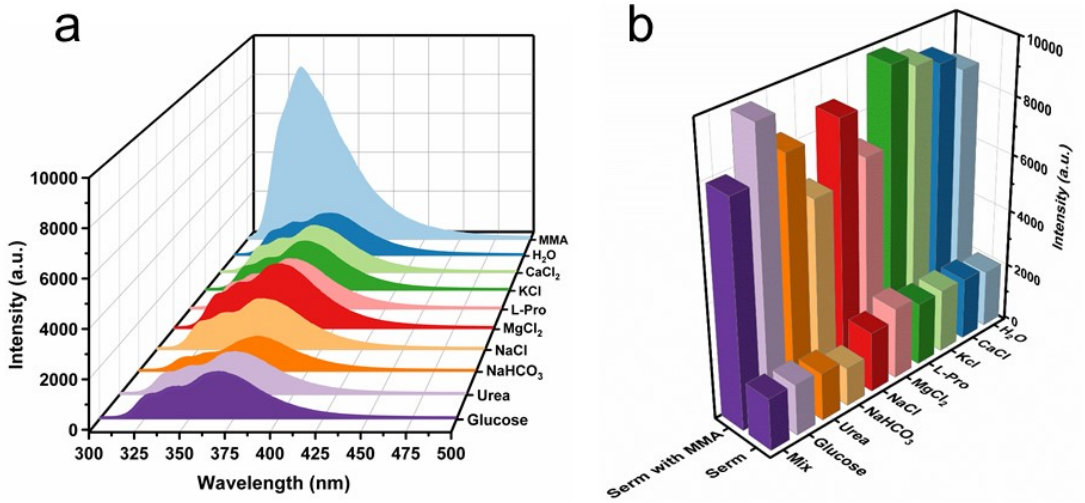

Figure S4 Fluorescence spectrum of **1** dispersed in H_2O with various serum components. (b) Comparison of fluorescence intensity of **1** with various serum interference substances in the absence and presence of MMA.

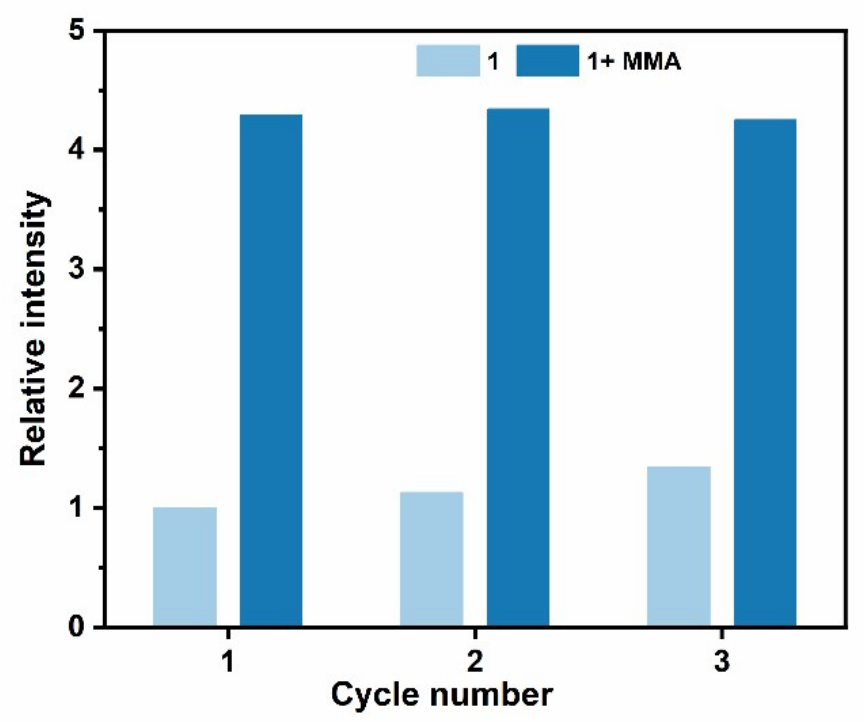

Figure S5 Three cycles test of **1** suspension for MMA.

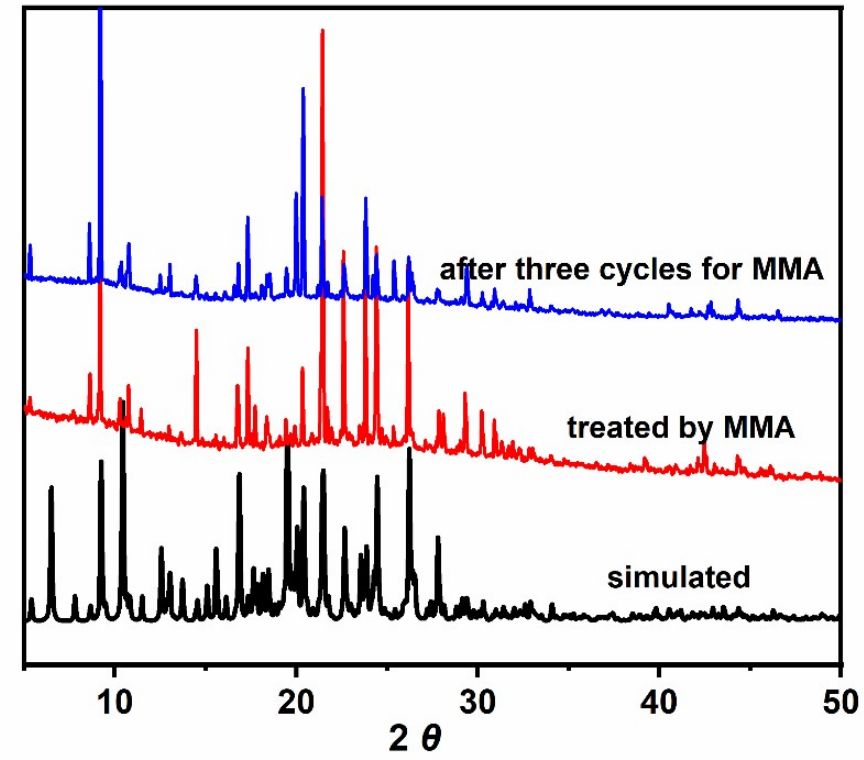

Figure S6 PXRD patterns of **1** after treated with MMA.

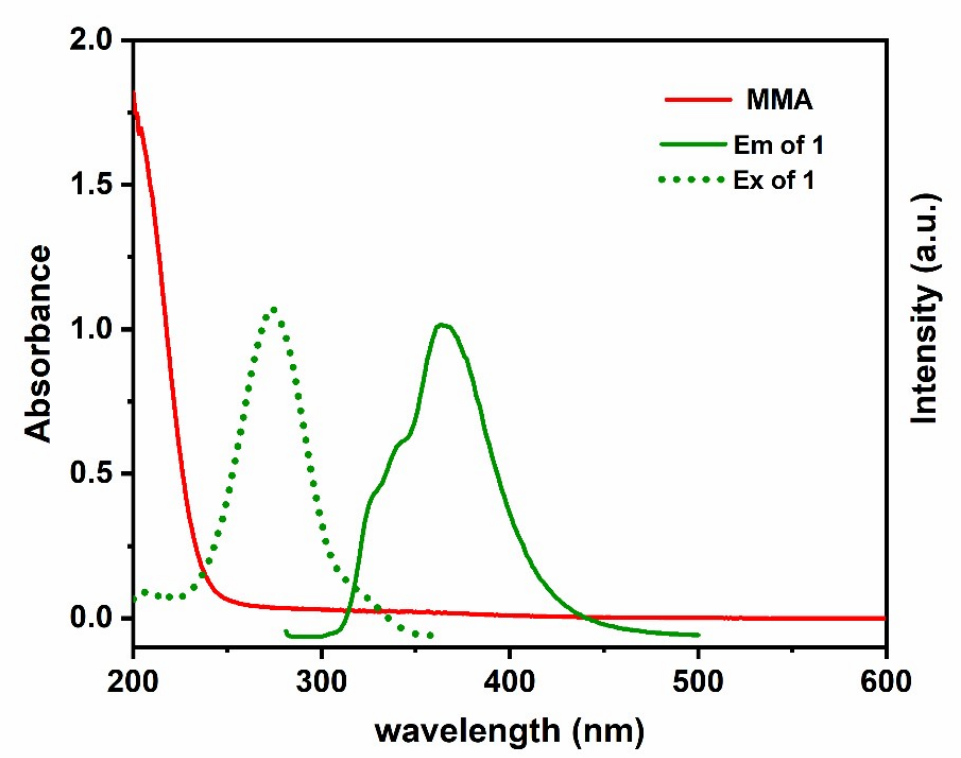

Figure S7 The comparison of liquid-state UV spectra of MMA (red) and the excitation spectrum and emission spectra of **1** in H_2O.

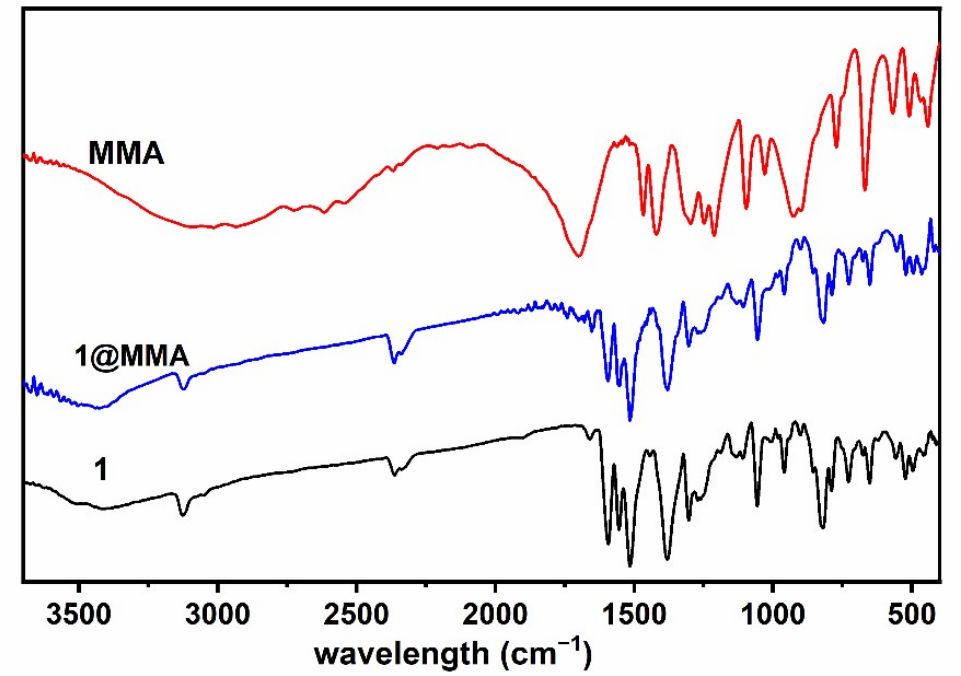

Figure S8 FTIR of **1** before and after soaking in aqueous solutions of MMA for 6 h.

Table S1 Selected bond lengths (Å) and angles (°) for **1**

Selected bond lengths		Selected bond lengths angle	
Co1—O4^{i}	1.976(2)	O4^{i}—Co1—N4^{ii}	109.95(10)
Co1—O1	1.973(2)	O4^{i}—Co1—N1	125.64(10)
Co1—N4^{ii}	2.040(3)	O1—Co1—O4^{i}	106.72(9)
Co1—N1	2.023(2)	O1—Co1—N4^{ii}	94.21(9)
		O1—Co1—N1	111.08(10)
		N1—Co1—N4^{ii}	104.71(10)

Symmetry code: (i) *x*+1/2, -*y*+3/2, *z*-1/2; (ii) -*x*+9/2, *y*+1/2, -*z*+1/2.

Table S2 Non-bonding interactions geometry (Å, °)

Complex	D—H…A	d(D—H)	d(H…A)	d(D…A)	∠DHA
1	O_5—H_{5B}…N_9	0.860	2.343	2.966	129.63
	C_{20}—H_{20}…O_5	0.940	2.349	3.106	137.24
	C_{63}—H_{63}…O_3	0.940	2.610	3.225	123.49
	O_{18}—H_{18}…O_5	0.940	2.693	3.612	165.77

Table S3 **1** was used to detect the concentration of MMA in human urine.

Complex	Add (μM)	Found (μM)	Recovery (%)	RSD (%)
1	25.0	24.7	98.8	3.25
	50.0	51.9	103.8	3.47
	75.0	76.8	102.5	3.36

References

1. G. M. Sheldrick, *Acta Crystallogr C Struct Chem*, 2015, **71**, 3-8.