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A fluorescence probe based on Tb^{3+}/Cu^{2+} co-functionalized MOFs to urinary sarcosine detection

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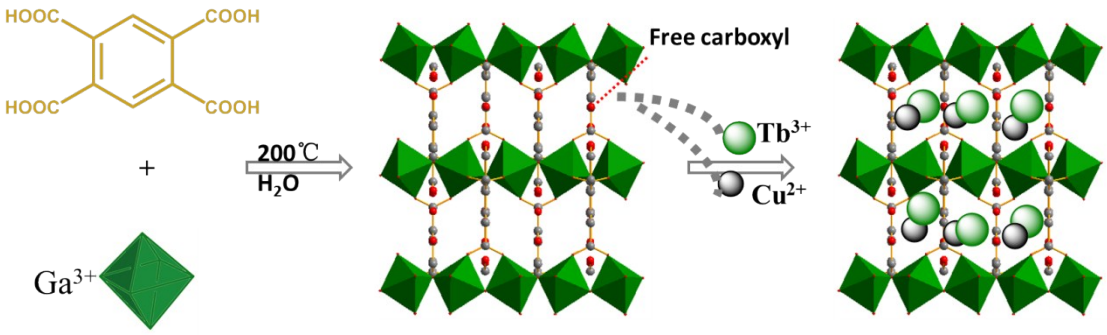

Figure S1 The procedures to synthesize MOF-1 with hydrothermal method and Tb^{3+}@MOF-1 based on PSM method.

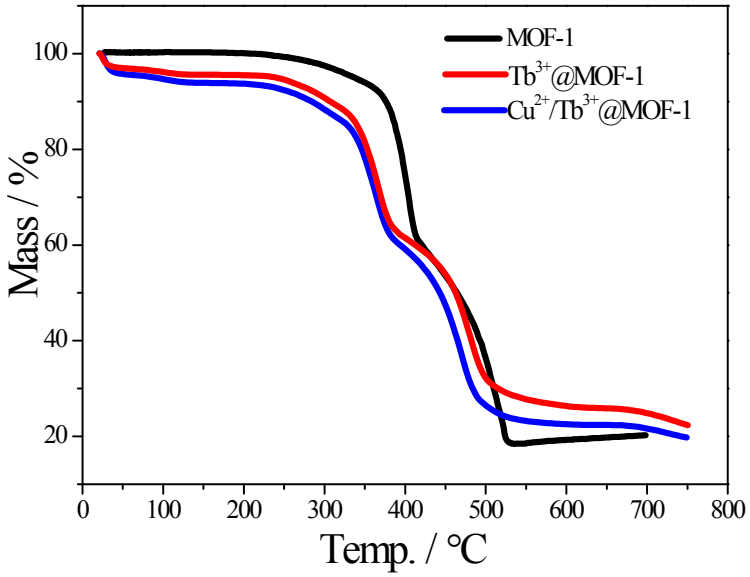

Figure S2 Thermal gravimetric analysis of MOF-1 (black line), Tb^{3+}@MOF-1 (red line) and Cu^{2+}/Tb^{3+}@MOF-1 (dark blue line).

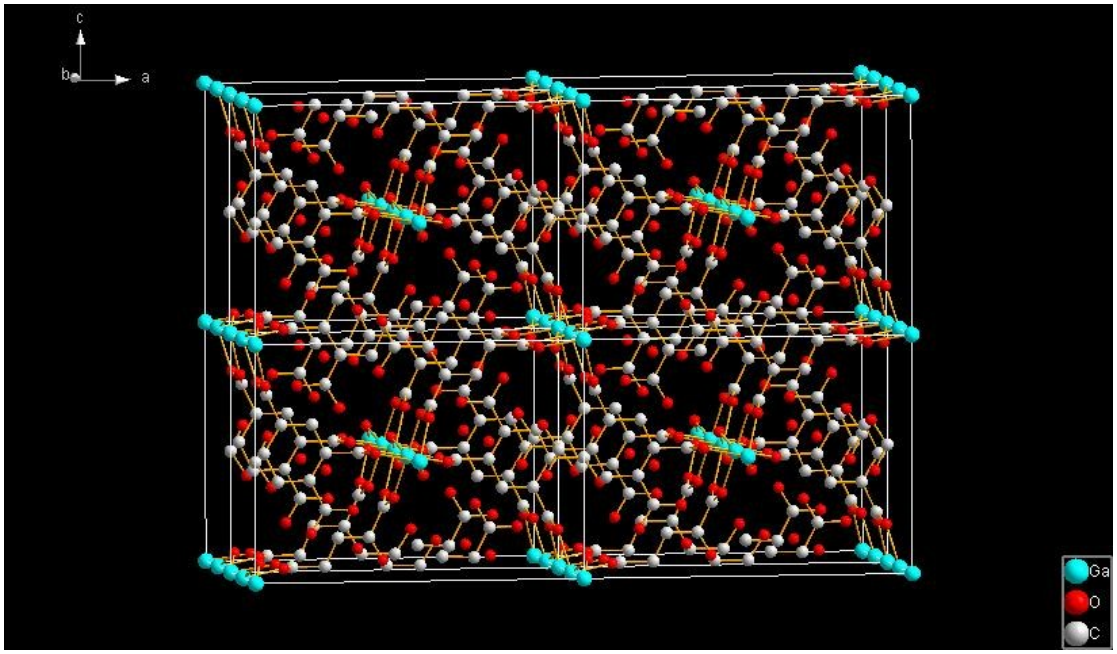

Figure S3 The 3D structure composition of MOF-1 with the free uncoordinated carboxyl group.[1]

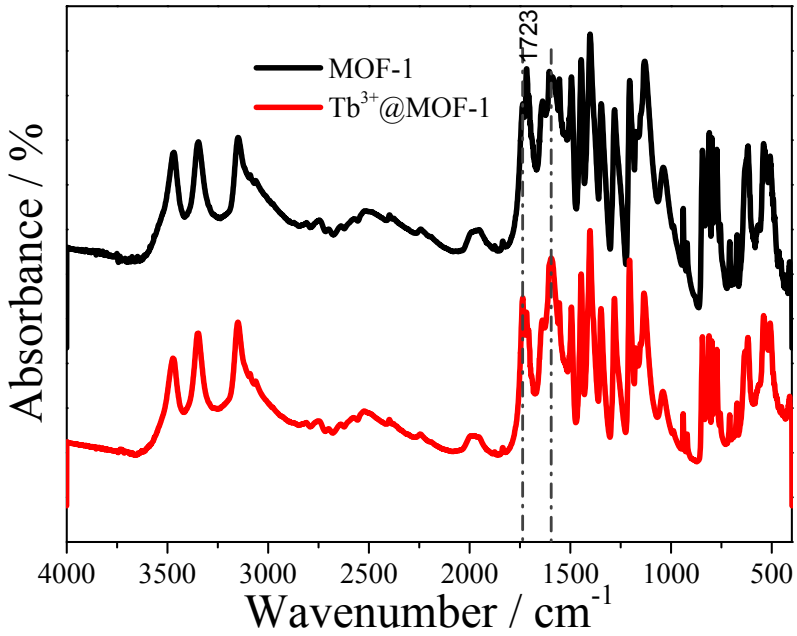

Figure S4 FT-IR spectra of MOF-1 and Tb^{3+}@MOF-1. The two absorption bands appearing at ~1723 cm^{-1} and 1595 cm^{-1} are assigned to the non-coordinated carboxyl group and asymmetric and symmetric stretching vibrations of C=O, respectively.

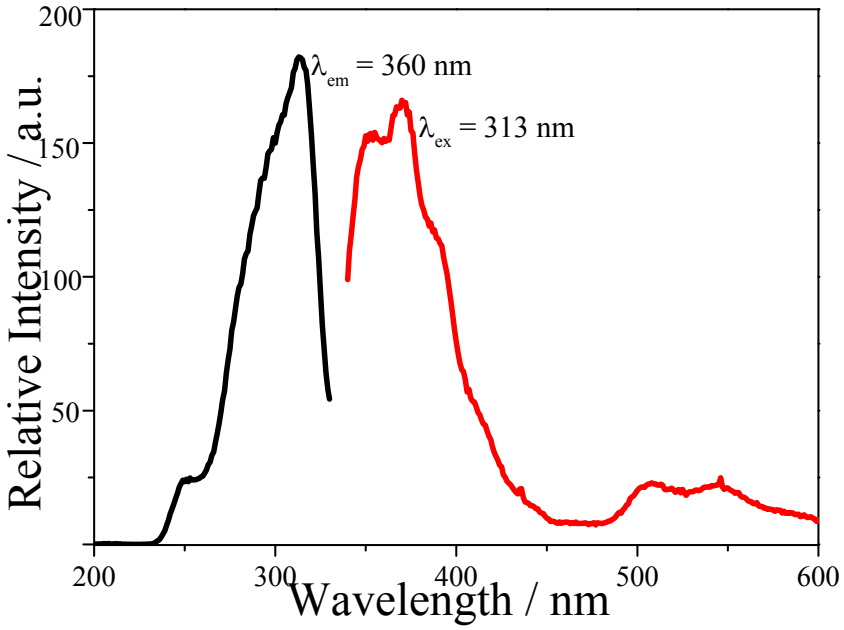

Figure S5 The excitation spectrum (black line) and emission spectrum (red line) of the ligand H_4btec.

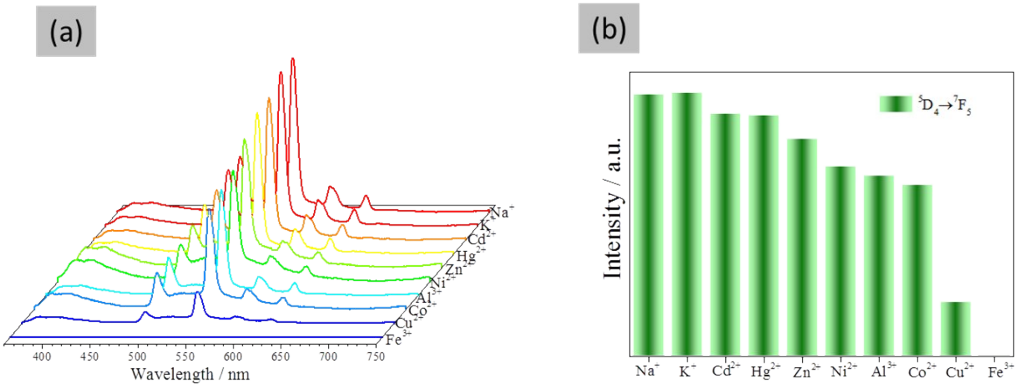

Figure S6 (a) The fluorescence responses of Cu^{2+}/Tb^{3+}@MOF-1 towards different metal aqueous solutions and (b) the corresponding intensity of $^5D_4 \rightarrow {}^7F_5$.

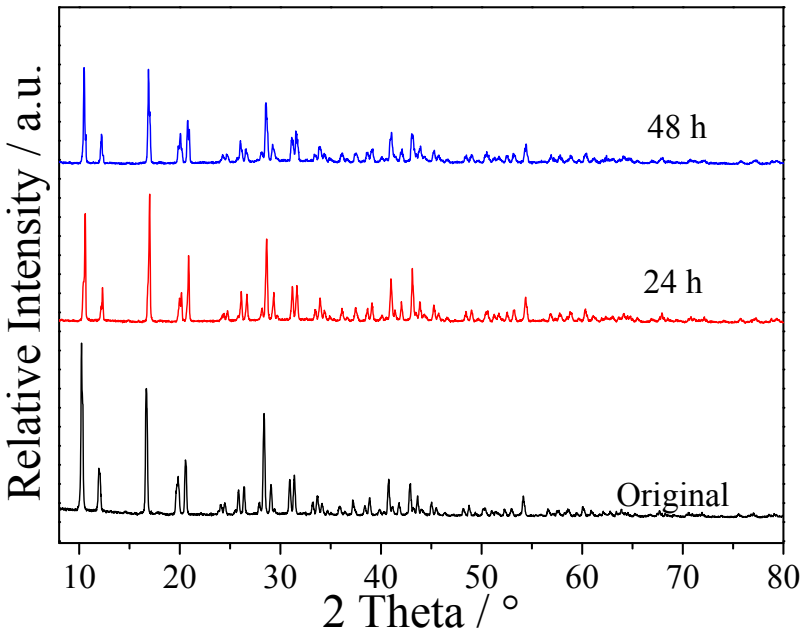

Figure S7 PXRD patterns of Cu^{2+}/Tb^{3+}@MOF-1 immersed in water at different times.

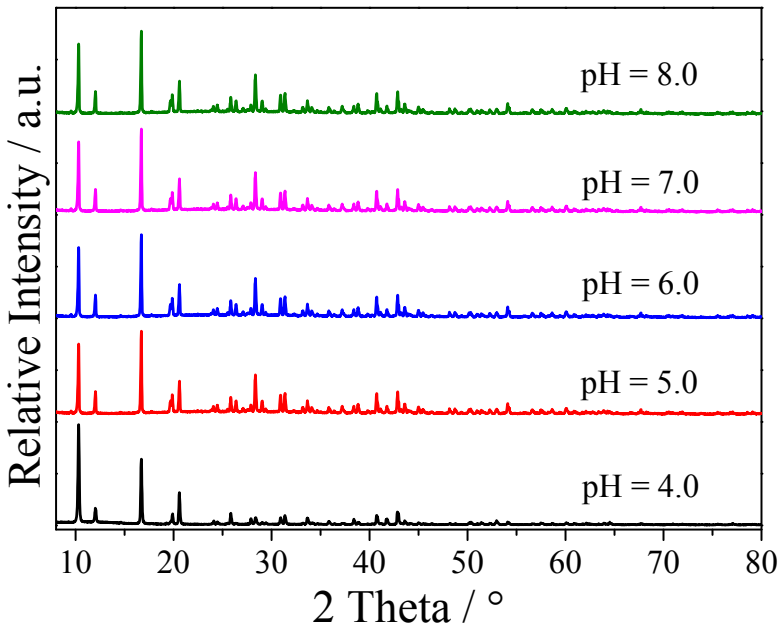

Figure S8 PXRD patterns of Cu^{2+}/Tb^{3+}@MOF-1 after immersed in aqueous solutions with a series of different pH values (4.0-8.0).

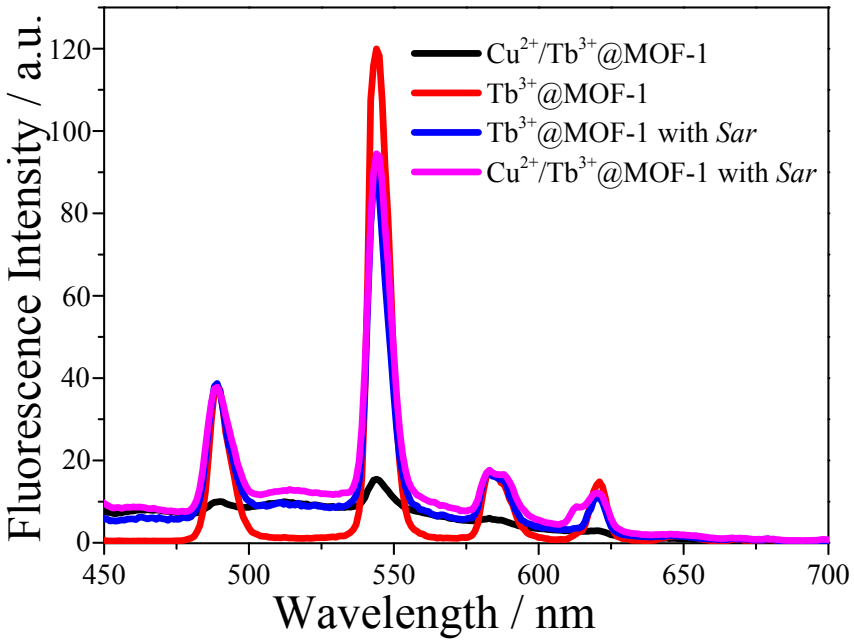

Figure S9 the fluorescence responses of Tb^{3+}@MOF-1 in the presence of sarcosine (blue line) and in the absence of sarcosine (red line) as well as the responses of Cu^{2+}/Tb^{3+}@MOF-1 in the aqueous solution (black line) and upon addition of sarcosine (pink line).

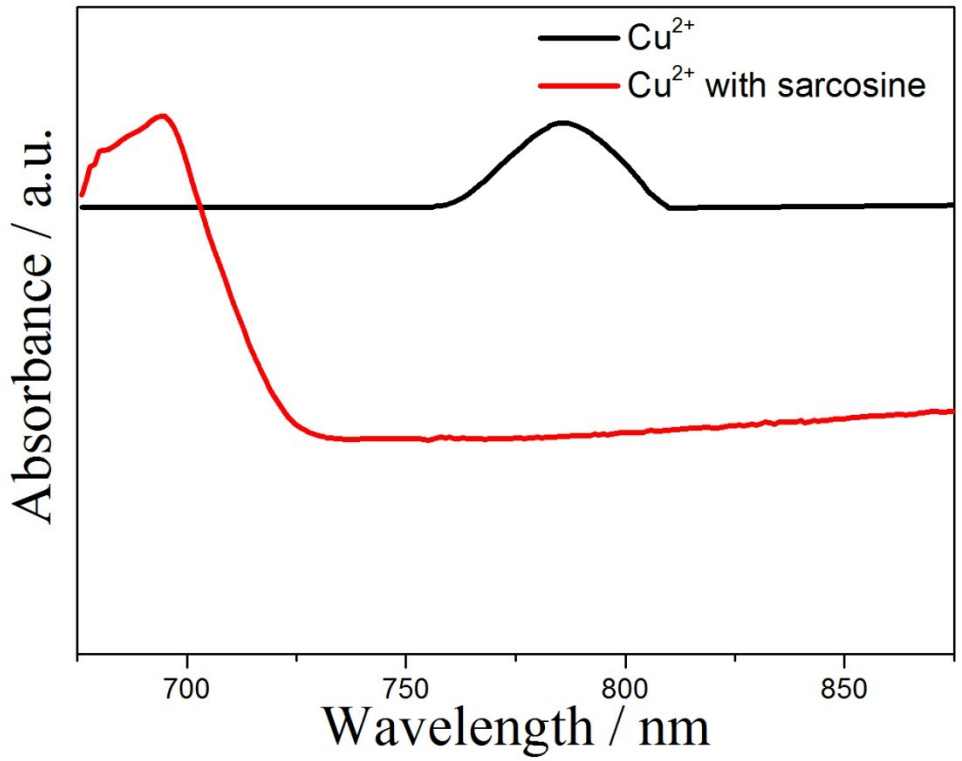

Figure S10 The UV-Vis spectrum of Cu^{2+} aqueous solution (0.01 M) and mixed solution of Cu^{2+} and sarcosine.

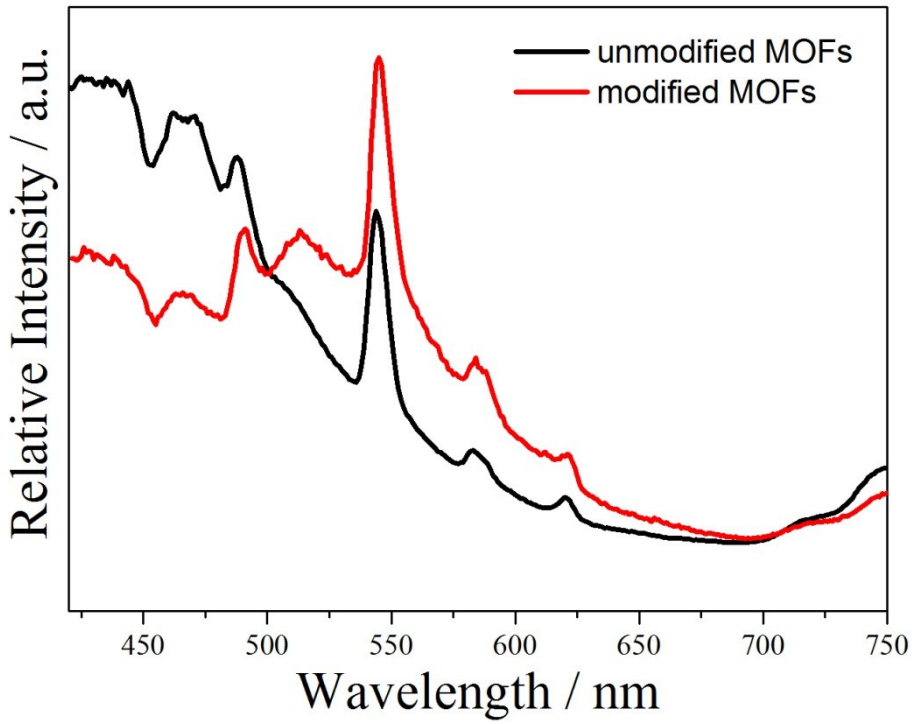

Fig. S11 the solid-state spectra of unmodified and modified MOFs before and after sarcosine absorption.

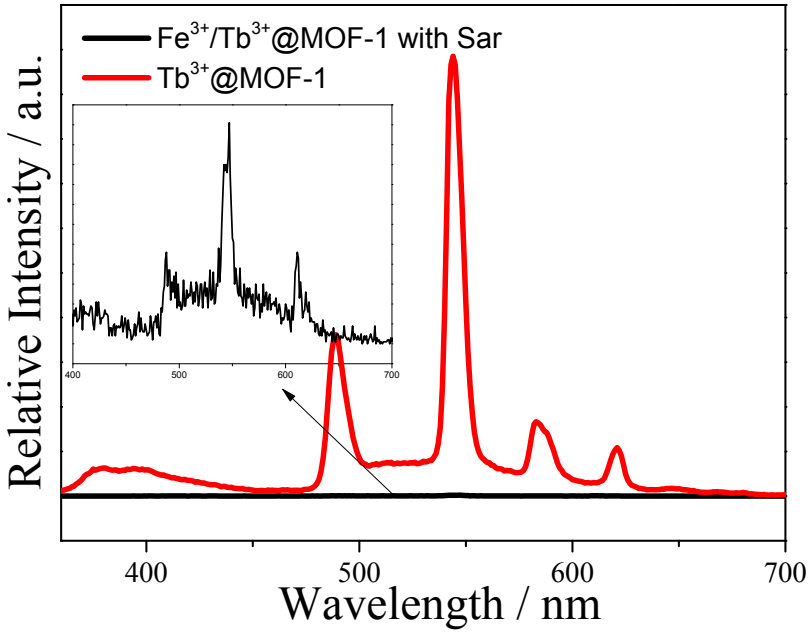

Figure S12 the comparison of emission spectrum of Fe^{3+}/Tb^{3+}@MOF-1 in the presence of sarcosine and emission spectrum of Tb^{3+}@MOF-1.

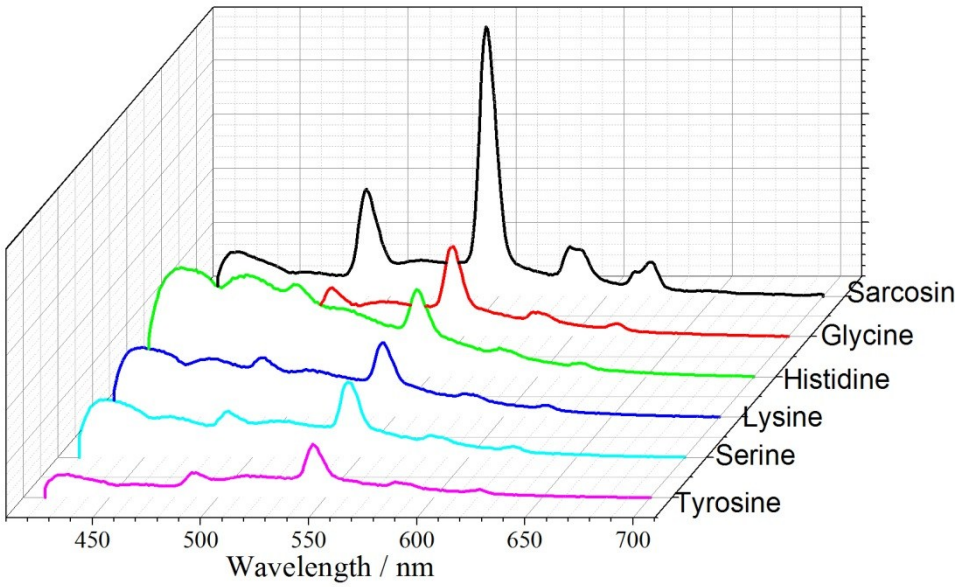

Fig S13 the fluorescence responses of Cu^{2+}/Tb^{3+}@MOF-1 towards different kinds of amino acid aqueous solutions.

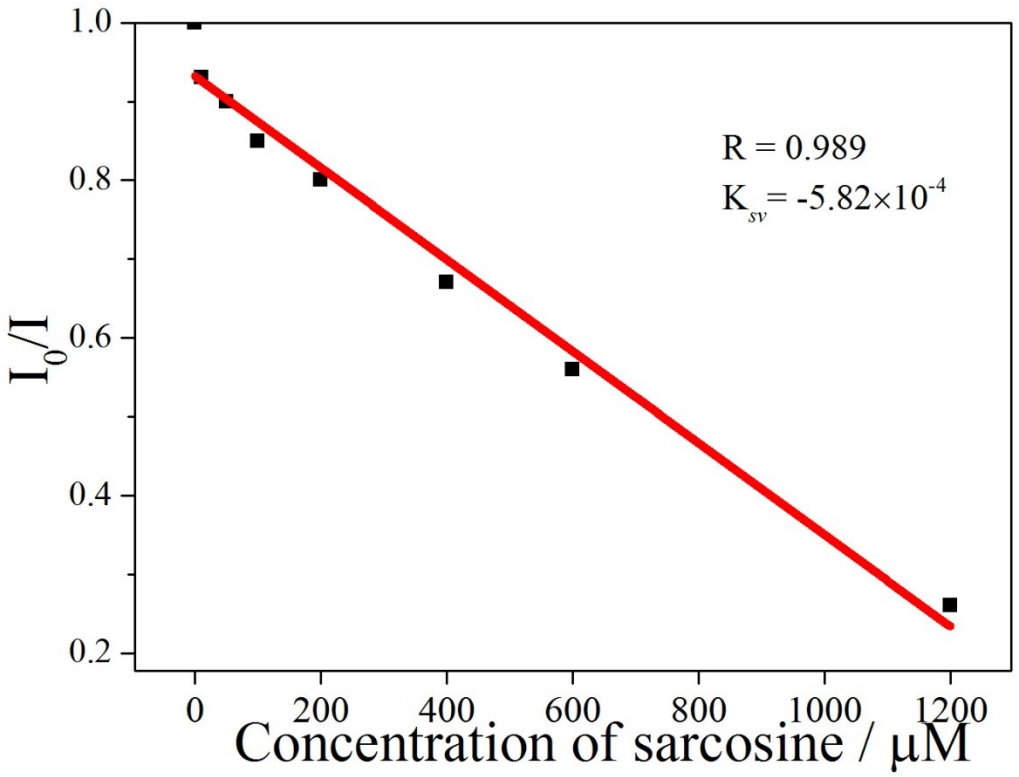

Fig S14 The fitting curve of the value of I_0/I of Cu^{2+}/Tb^{3+}@MOF-1 and the concentration of sarcosine.

Linear Equation: $Y = -5.82\times10^{-4}X + 0.93$ $R = 0.989$

$$S = 5.82\times10^{-4}M^{-1}$$

$$S_b = \sqrt{\frac{\sum (F_0 - F_1)^2}{N - 1}} = 4.46\times10^{-8} \quad (N=20)$$

$$LOD = 3S_b / S = 0.23\ mM$$

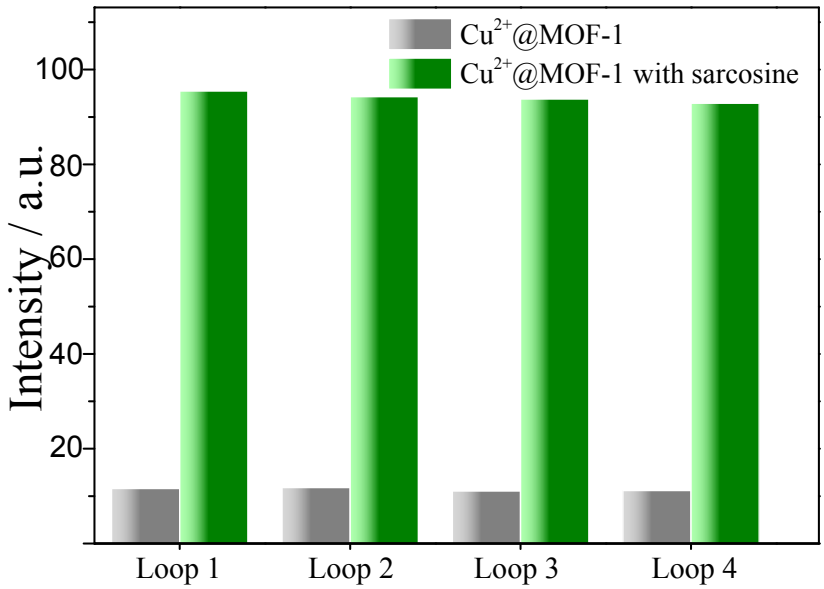

Figure S15 the luminescence intensity of Cu^{2+}/Tb^{3+}@MOF-1 at 543 nm after four loops.

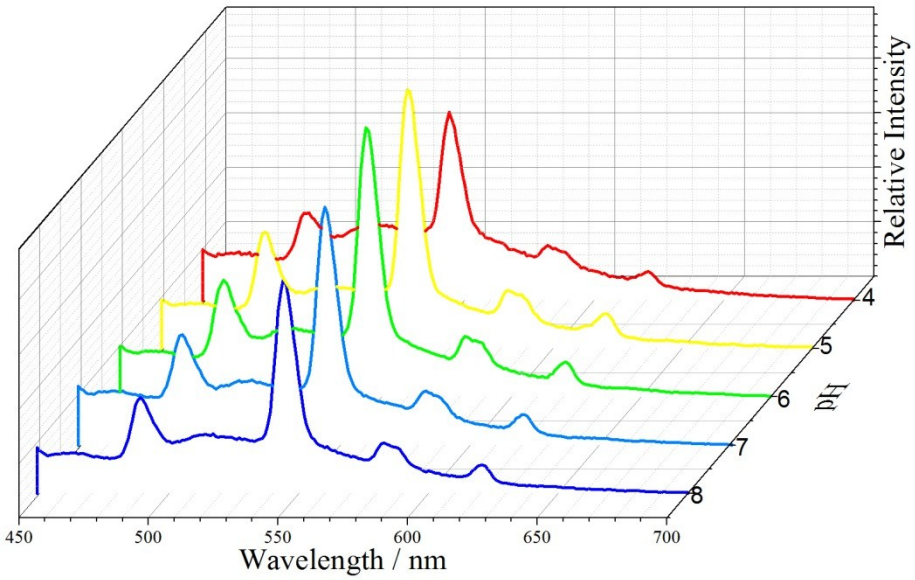

Figure S16 The fluorescence responses of Cu^{2+}/Tb^{3+}@MOF-1 towards the aqueous solutions of sarcosine with different pH.

Table S1 EDS element analysis of Cu^{2+}/Tb^{3+}@MOF-1.

Materials	Elements	Weight / %	Atomic / %
Cu^{2+}/Tb^{3+}@MOF-1	C	37.43	50.81
	O	44.59	45.45
	Ga	13.48	3.15
	Tb	2.18	0.24
	Cu	2.32	0.35

Table S2 The ICP data for Ga^{3+}, Tb^{3+} and Cu^{2+} in Cu^{2+}/Tb^{3+}@MOF-1.

Samples	Ga/Eu/Cu mass ratio	Ga/Eu/Cu molar ratio
Cu^{2+}/Tb^{3+}@MOF-1	14.7:4.9:3.4	6.64:1:0.68

Table S3 Luminescence lifetimes (τ) of Cu^{2+}/Tb^{3+}@MOF-1 upon addition of different urinary components.

Sample(Cu^{2+}/Tb^{3+}@MOF-1)	Lifetime (τ) / μs

Tb^{3+}@MOF-1	585
H_2O	209
Sarcosine	577
Cre	272
Urea	207
UA	206
NaCl	189
KCl	191
NH_4Cl	186
Na_3PO_4	145
Cretine	215

Reference

1. L. Thierry, M. Herve, H. Mohamed, T. Francis, F. Gerard, *Solid State Sci.*, 2005, **7**, 603.