Electronic Supplementary Material (ESI) for Analyst.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Highly Selective and Sensitive Fluorescent Sensor Based on Tb^{3+} Functionalized MOFs to Determinate Arginine in Urine: A Potential Application for Diagnosis of Cystinuria

*Ruixue Cui, Yongyan Wan, Guanfeng Ji and Zhiliang Liu**

Inner Mongolia Key Laboratory of Chemistry and Physics of Rare Earth Materials, School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, P.R. China. E-mail: cezlliu@imu.edu.cn. Fax/Tel: +86-471-4994375.

Contents

1.Tables

Table S1 The main crystal and refinement data for Cd-MOF

Compound	Cd-MOF
Formular	$C_{54}H_{25}Cd_4N_9O_{25}$
Fw	1649.43
Temperature (K)	293(2) K
Wavelength (Å)	1.54184
Crystal system	Orthorhombic
Space group	$Pna2_1$
a/ Å	20.1853(7)
b/ Å	12.0295(6)
c/ Å	28.4889(8)
α/(°)	90
β/(°)	90
γ/(°)	90
Volume / $Å^3$	6917.6(5)
Z	4
Dc/g cm^{-3}	1.584
F(000)	3216
Reflections collected / unique	38515/11273
GOF on F^2	0.975
R_1^a [I>2σ(I)]	0.0629
wR_2^b [all data]	0.1622

^{a} $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$ ^{b} $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[(wF_0^2)^2]]^{1/2}$

Table S2 Selected bond lengths (Å) and angles (°) for Cd-MOF

Bond length (Å)			
Cd(1)–O(1)	2.487(8)	Cd(1)–O(2)	2.270(8)
Cd(1)–O(4)#2	2.437(8)	Cd(1)–O(15)	2.646(8)
Cd(1)–O(16)	2.266(8)	Cd(1)–O(18)	2.207(9)
Cd(1)–O(10)#1	2.404(7)	Cd(2)–O(3)#3	2.199(8)
Cd(2)–O(20)	2.261(9)	Cd(2)–O(14)#4	2.281(8)
Cd(2)–O(1)#5	2.397(8)	Cd(2)–O(20)#6	2.526(9)
Cd(2)–O(13)#4	2.604(8)	Cd(3)–O(5)	2.231(9)
Cd(3)–O(19)#7	2.299(8)	Cd(3)–O(13)#8	2.300(8)
Cd(3)–O(19)#1	2.323(8)	Cd(3)–O(24)#9	2.381(9)
Cd(3)–O(23)#9	2.427(9)	Cd(4)–O(12)#10	2.257(8)
Cd(4)–O(15)	2.275(9)	Cd(4)–O(25)	2.285(10)
Cd(4)–O(9)#1	2.313(9)	Cd(4)–O(17)	2.315(8)
Cd(4)–O(10)#1	2.567(8)	Cd(4)–O(11)#10	2.583(8)

Bond Angle (°)			
O(18)–Cd(1)–O(16)	111.1(3)	O(18)–Cd(1)–O(2)	93.9(3)
O(16)–Cd(1)–O(2)	155.0(3)	O(18)–Cd(1)–O(10)#1	120.0(3)
O(16)–Cd(1)–O(10)#1	87.0(3)	O(2)–Cd(1)–O(10)#1	82.1(3)
O(18)–Cd(1)–O(4)#2	82.0(3)	O(16)–Cd(1)–O(4)#2	84.8(3)
O(2)–Cd(1)–O(4)#2	97.0(3)	O(10)#1–Cd(1)–O(4)#2	158.0(3)
O(18)–Cd(1)–O(1)	137.9(3)	O(16)–Cd(1)–O(1)	102.3(3)
O(2)–Cd(1)–O(1)	54.6(3)	O(10)#1–Cd(1)–O(1)	85.7(3)
O(4)#2–Cd(1)–O(1)	76.1(3)	O(18)–Cd(1)–O(15)	74.6(3)
O(16)–Cd(1)–O(15)	51.5(3)	O(2)–Cd(1)–O(15)	143.8(3)
O(10)#1–Cd(1)–O(15)	75.0(3)	O(4)#2–Cd(1)–O(15)	114.6(3)
O(1)–Cd(1)–O(15)	147.4(3)	O(3)#3–Cd(2)–O(20)	142.9(3)
O(3)#3–Cd(2)–O(14)#4	95.0(3)	O(20)–Cd(2)–O(14)#4	119.2(3)
O(3)#3–Cd(2)–O(1)#5	98.5(3)	O(20)–Cd(2)–O(1)#5	84.1(3)
O(14)#4–Cd(2)–O(1)#5	76.7(3)	O(3)#3–Cd(2)–O(20)#6	83.3(3)
O(20)–Cd(2)–O(20)#6	80.3(3)	O(14)#4–Cd(2)–O(20)#6	125.6(3)
O(1)#5–Cd(2)–O(20)#6	155.5(3)	O(3)#3–Cd(2)–O(13)#4	86.6(3)
O(20)–Cd(2)–O(13)#4	120.4(3)	O(14)#4–Cd(2)–O(13)#4	52.3(3)
O(1)#5–Cd(2)–O(13)#4	126.9(3)	O(20)#6–Cd(2)–O(13)#4	75.5(3)
O(5)–Cd(3)–O(19)#7	107.8(3)	O(5)–Cd(3)–O(13)#8	165.7(3)
O(19)#7–Cd(3)–O(13)#8	81.6(3)	O(5)–Cd(3)–O(19)#1	87.4(3)
O(19)#7–Cd(3)–O(19)#1	125.7(3)	O(13)#8–Cd(3)–O(19)#1	78.3(3)
O(5)–Cd(3)–O(24)#9	87.5(3)	O(19)#7–Cd(3)–O(24)#9	79.4(3)
O(13)#8–Cd(3)–O(24)#9	105.1(3)	O(19)#1–Cd(3)–O(24)#9	154.7(3)
O(5)–Cd(3)–O(23)#9	90.6(3)	O(19)#7–Cd(3)–O(23)#9	126.9(3)
O(13)#8–Cd(3)–O(23)#9	91.6(3)	O(19)#1–Cd(3)–O(23)#9	101.8(3)
O(24)#9–Cd(3)–O(23)#9	53.6(3)	O(12)#10–Cd(4)–O(15)	136.0(3)
O(12)#10–Cd(4)–O(25)	100.2(4)	O(15)–Cd(4)–O(25)	91.4(4)
O(12)#10–Cd(4)–O(9)#1	93.5(3)	O(15)–Cd(4)–O(9)#1	126.9(3)

O(25)–Cd(4)–O(9)#1	91.0(3)	O(12)#10–Cd(4)–O(17)	96.1(3)
O(15)–Cd(4)–O(17)	82.0(3)	O(25)–Cd(4)–O(17)	162.0(3)
O(9)#1–Cd(4)–O(17)	80.4(3)	O(12)#10–Cd(4)–O(10)#1	145.5(3)
O(15)–Cd(4)–O(10)#1	78.4(3)	O(25)–Cd(4)–O(10)#1	77.4(3)
O(9)#1–Cd(4)–O(10)#1	52.5(3)	O(17)–Cd(4)–O(10)#1	84.9(3)
O(12)#10–Cd(4)–O(11)#10	52.3(3)	O(15)–Cd(4)–O(11)#10	84.1(3)
O(25)–Cd(4)–O(11)#10	114.1(3)	O(9)#1–Cd(4)–O(11)#10	139.2(3)
O(17)–Cd(4)–O(11)#10	82.0(3)	O(10)#1–Cd(4)–O(11)#10	159.4(3)

Symmetry codes: #1 1/2– *x*, *y*–1/2, *z*+1/2; #2 1/2– *x*, *y*+1/2, *z*–1/2; #3 –*x*, –*y*, *z*–1/2; #4 *x*, *y*–1, *z*; #5 *x*–1/2, 1/2–*y*, z; #6 –*x*–1/2, *y*–1/2, *z*–1/2; #7 *x*+1, *y*–1, *z*; #8 1/2–*x*, *y*–3/2, *z*+1/2; #9 *x*+1/2, 1/2–*y*, *z*; #10 –*x*, 2–*y*, *z*+1/2; #11 –*x*, –*y*, *z*+1/2; #12 –*x*, 2–*y*, *z*–1/2; #13 1/2–*x*, *y*+3/2, *z*–1/2; #14 *x*, *y*+1, *z*; #15 *x*–1, *y*+1, *z*; #16 –1/2–*x*, *y*+1/2, *z*+1/2.

Table S3 Fluorescence sensing to amino acids by MOFs materials

MOF-based fluorescent materials	Analyte	*LOD*	Solven	Ref.
$[Zn_2(L)_{1.5}(H_2O)_2{\cdot}Me_2NH_2]$	His	–	water	[16]
Cd−PPCA	Hcy	40 nM	HEPES buffer	[18]
Ag^+ @ Eu-complex	Asp	0.8 ppm	water	[17]
$[Zn_2($ D-Cam$)_2$(4,4'-bpy)$]_n$	Tyr	0.1 µg/mL	water	[20]
MN-ZIF-90	Cys	3.02 ppm	water	[22]
SUMOF-7II	Trp	34 ppm	water	[19]
Tb@Cd–MOF	Arg	0.69 ppm	water	This work

2. Figures

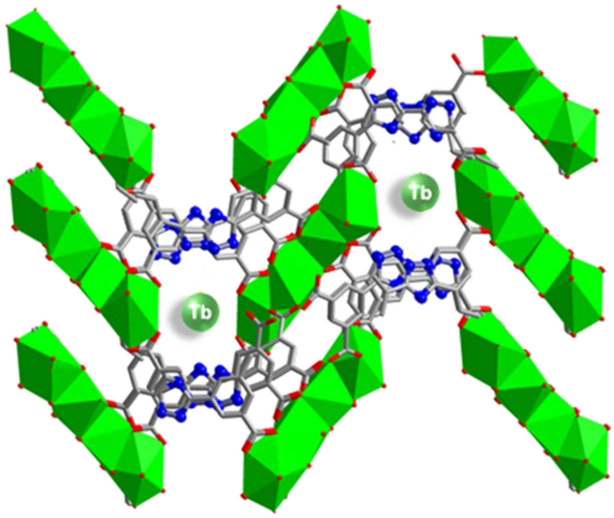

Fig. S1 The Lewis base sites (N) and Lewis acid sites (-COOH) in the pore of Cd-MOF

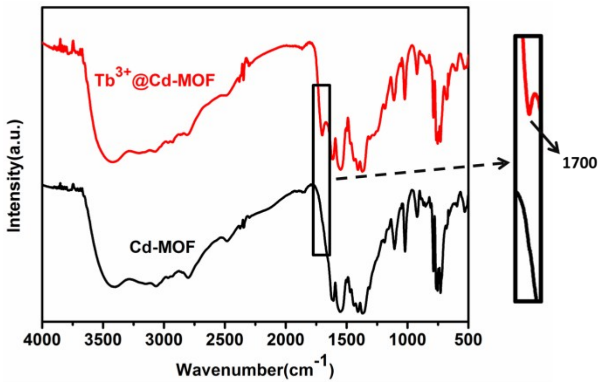

Fig. S2 The IR spectrum of Cd–MOF and Tb^{3+}@Cd–MOF

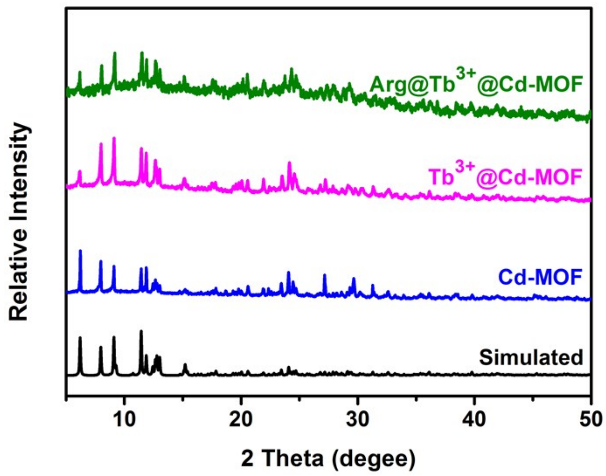

Fig. S3 Powder XRD patterns of simulated Cd–MOF, as-synthesis Cd–MOF, postsynthetic modification Tb^{3+}@Cd–MOF and Arg@Tb^{3+}@Cd–MOF

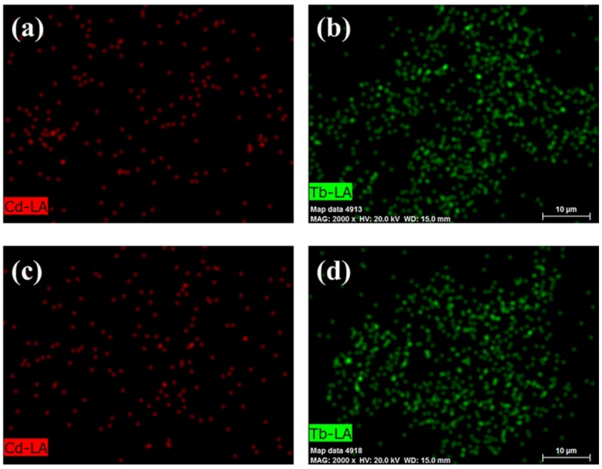

Fig. S4 Energy dispersive X-ray spectroscopy (EDS) mapping of Cd and Tb atom in the Tb^{3+}@Zn-MOF (a, b) and Arg/Tb^{3+}@Zn-MOF (c, d)

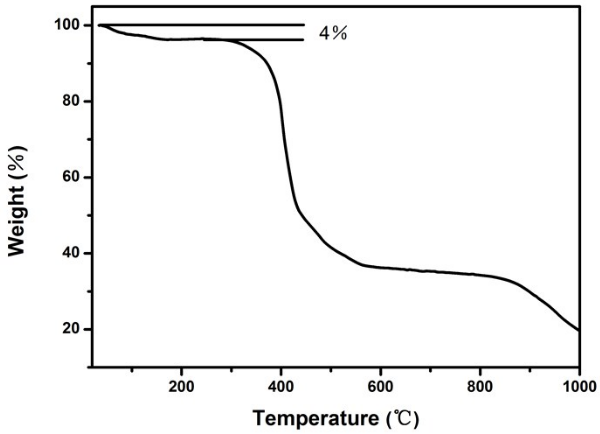

Fig. S5 The TGA curve of Cd–MOF

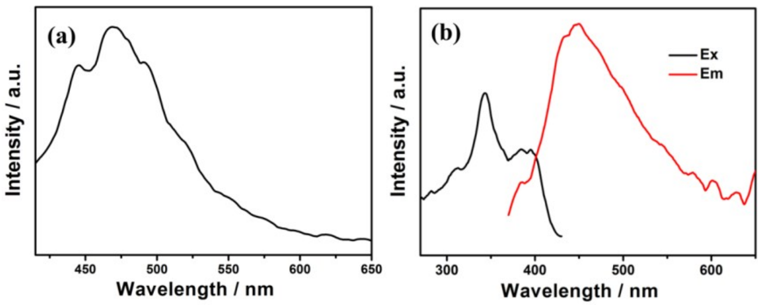

Fig. S6 (a) Emission spectra of H_4L (b) Excitation and emission spectra of Cd–MOF

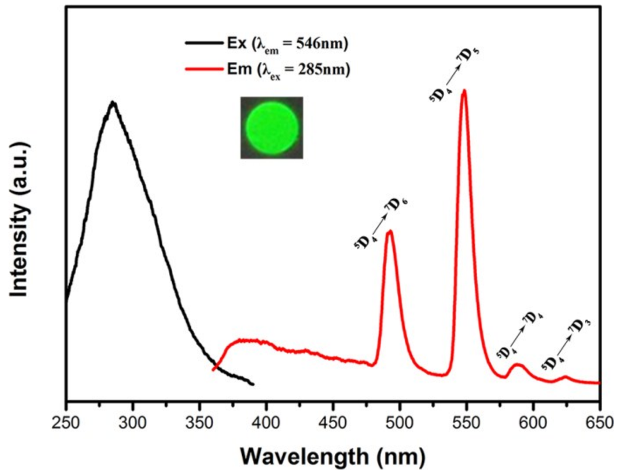

Fig. S7 Solid state fluorescence spectroscopy of Tb^{3+}@Cd-MOF

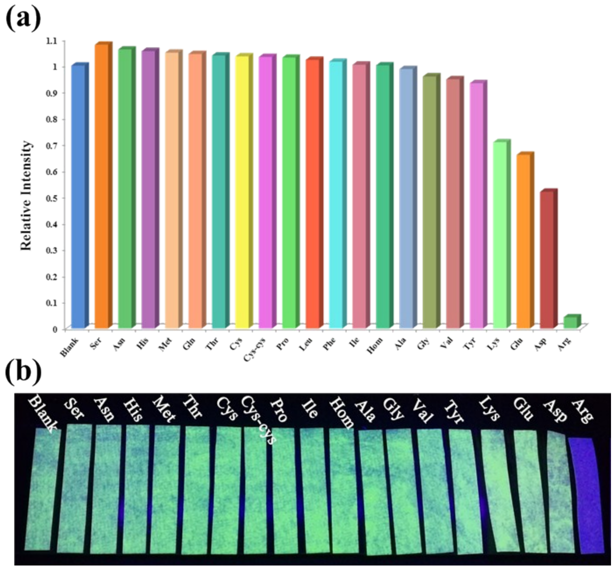

Fig. S8 (a) Fluorescence intensities of Tb^{3+}@Cd–MOF at 546 nm in different amino acids aqueous solution excited by 285 nm. (b) The fluorescent test paper of Tb^{3+}@Cd–MOF treated by different amino acids solutions under the UV irradiation

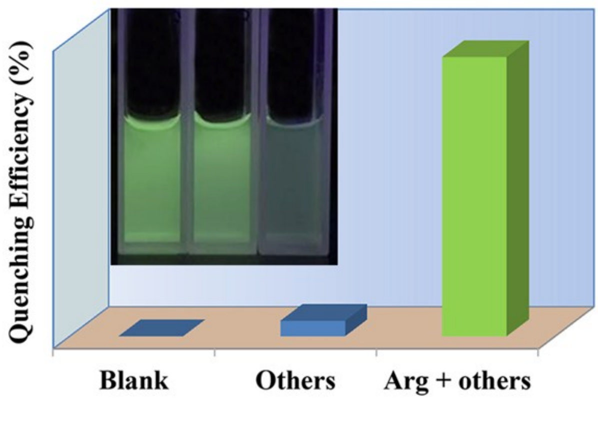

Fig. S9 The selectivity to Arg of Tb^{3+}@Cd–MOF while other amino acids exist

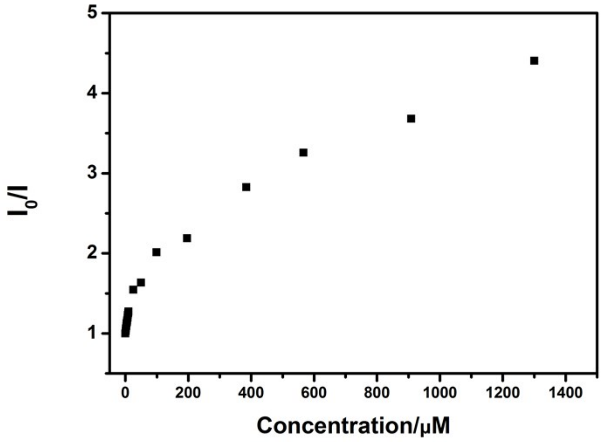

Fig. S10 Stern-Volmer plot for arginine in full concentration region

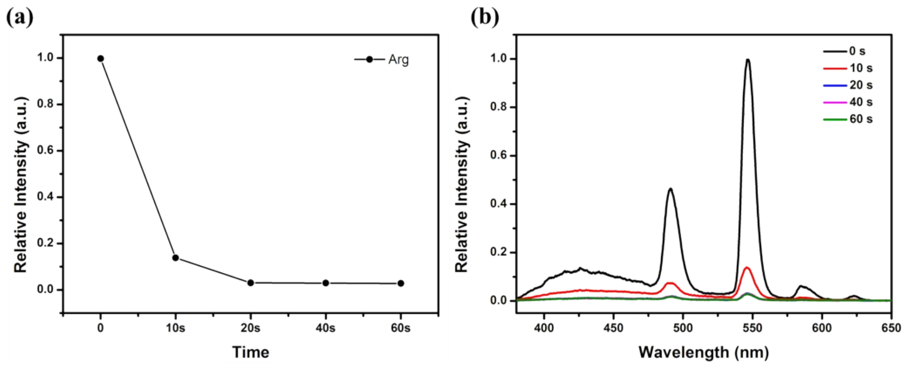

Fig. S11 Fluorescence Spectra of Tb^{3+}@Cd–MOF at different detection times

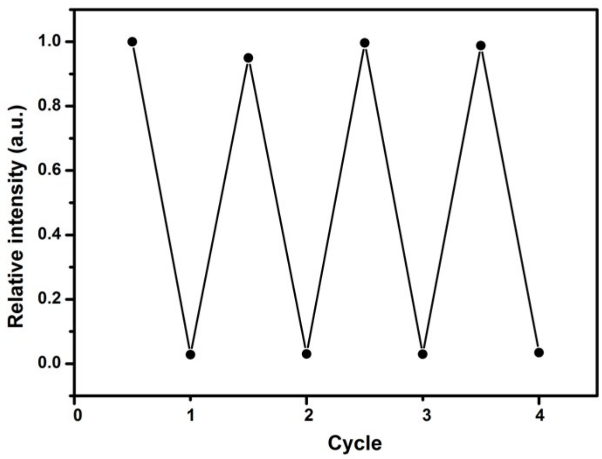

Fig. S12 Fluorescence intensity comparison after detecting arginine five cycles test

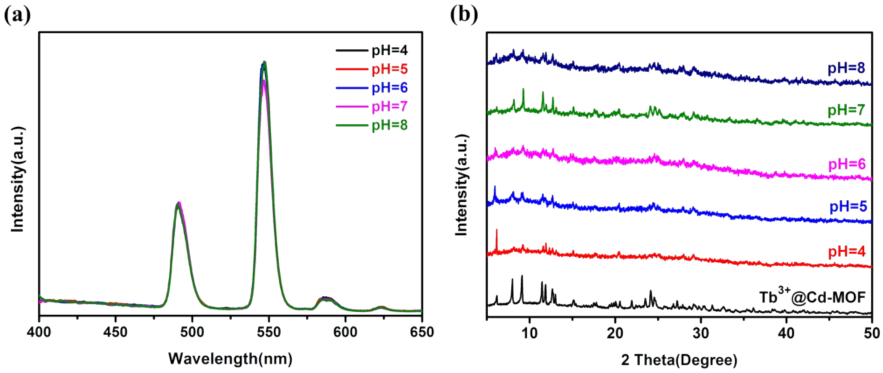

Fig. S13 (a)PL spectra and (b) PXRD pattern of Tb^{3+}@Cd–MOF immersing in aqueous solutions with different pH values (4.0, 5.0, 6.0, 7.0, 8.0) for 24 h

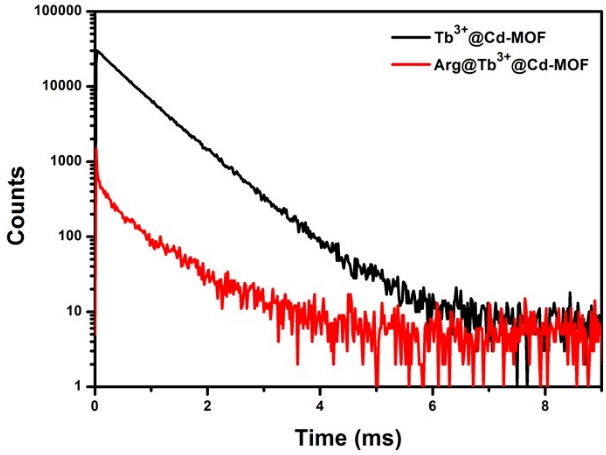

Fig. S14 Fluorescence life curve before and after treated with arginine of Tb^{3+}@Cd–MOF

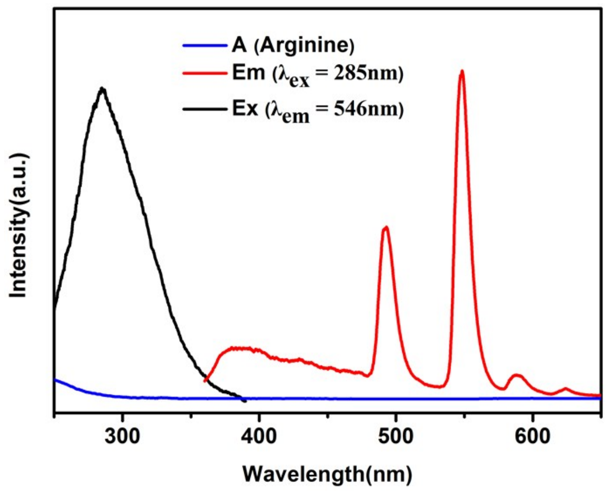

Fig. S15 Comparison between UV-vis absorption of arginine and the excited and the emitted wavelength of Tb^{3+}@Cd–MOF

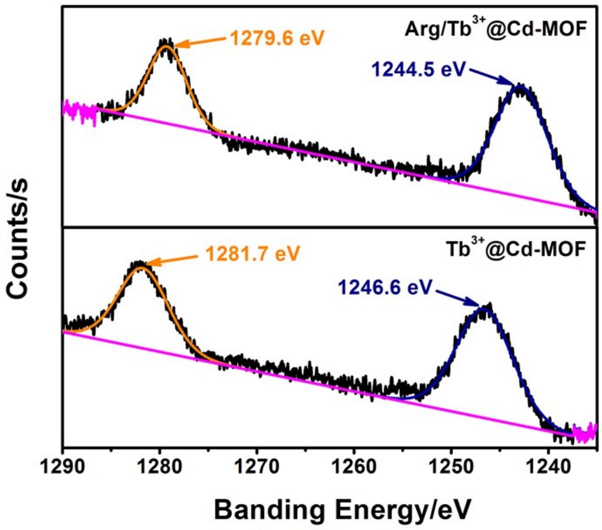

Fig. S16 Partial enlarged spectra of Tb 3d in Tb^{3+}@Cd-MOF and Arg/Tb^{3+}@Cd-MOF