Electronic supplementary information (ESI)

Cucurbit[6]uil-based multifunctional supramolecular assemblies: synthesis, removal of Ba(II) and fluorescence sensing of Fe(III)

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Table S1. Selected bond lengths (Å) and angles (°) for assembly **2**[a]

Ba(1)-O(1)#2	2.882(7)	Ba(1)-O(4)	2.707(6)
Ba(1)-O(1W)	2.632(8)		
O(4)#1-Ba(1)-O(4)	160.50(7)	O(1W)-Ba(1)-O(1)#2	85.36(15)
O(1W)#1-Ba(1)-O(1W)	159.94(8)	O(4)-Ba(1)-O(1)#2	127.92(13)
O(1W)-Ba(1)-O(4)#1	101.6(2)	O(1W)-Ba(1)-O(1)#3	111.10(15)
O(1W)-Ba(1)-O(4)	74.9(2)	O(4)-Ba(1)-O(1)#3	69.93(11)
O(1)#2-Ba(1)-O(1)#3	73.5(2)		

Symmetry codes: #1 -x+1,-y,-z+1; #2 x,y,z+1; #3 -x+1,y,-z.

Table S2. Hydrogen bonding data of **1** and **2**.

		1		
D–H ··A	d(*D*–H) (Å)	d(H ··A) (Å)	d(*D* ··A)(Å)	*D*–H ··A (°)
O(6)-H(6) ··O(6)	0.8500	1.6100	2.454(6)	171
N(8)-H(8A) ··O(2)	0.8800	2.2600	2.931(11)	133
N(8)-H(8C) ··O(1)	0.9100	2.5000	3.127(12)	126
N(8)-H(8D) ··O(4)	0.8900	1.9300	2.813(10)	178
C(3)-H(3A) ··O(7)	0.9900	2.5000	3.178(7)	125
C(3)-H(3B) ··O(7)	0.9900	2.4400	3.428(7)	178
C(8)-H(8) ··O(6)	1.0000	2.5900	3.447(7)	144
C(9)-H(9A) ··O(6)	0.9900	2.5400	3.448(7)	152
C(11)-H(11) ··O(5)	0.9500	2.5000	3.417(7)	161
C(15)-H(15) ··O(1)	0.9500	2.8300	3.512(7)	129
		2		
O(1W)-H(1W1) ··O(2)	0.9300	2.1000	3.022(6)	173
O(7)-H(7) ··O(7)	1.229(12)	1.229(12)	2.457(5)	175(11)
C(4)-H(4) ··O(7)	1.0000	2.6000	3.512(7)	152
C(6)-H(6B) ··O(6)	0.9900	2.4200	3.406(7)	174
C(13)-H(13) ··O(8)	0.9500	2.3400	3.268(6)	165

Table S3. Adsorption capacity of some adsorbent material reported in literature for removal of Ba^{2+}.

adsorbent	Maximum reported adsorption capacity (mg/g)	Reference
Hydrous cerium oxide	0.115	1
Hydrous bismuth oxide	0.131	2
Expanded perlite	2.486	3
Dolomite powder	3.958	4
Mxene	9.3	5
Mag-tit PVA-alginate beads	19.45	6
Solvent-extracted peat	~ 40	7
Fe_3O_4@titanate nanocomposites	118.4	8
Fungus-titanate nanotube	120	9
Q[6]-based supramolecular assembly	72.4	This study

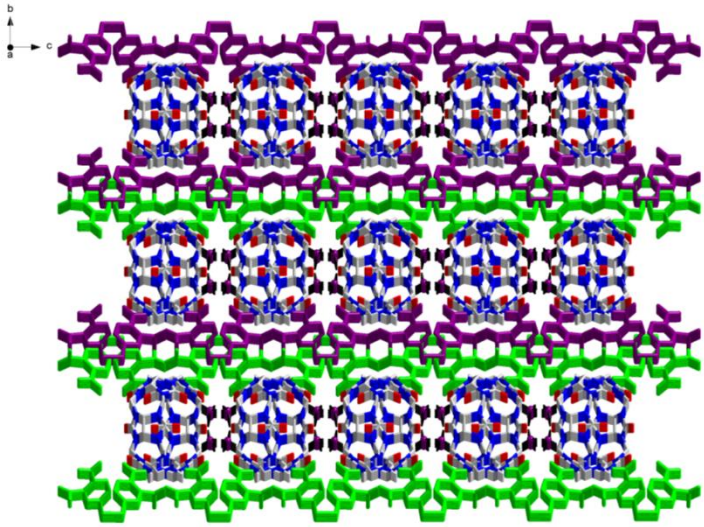
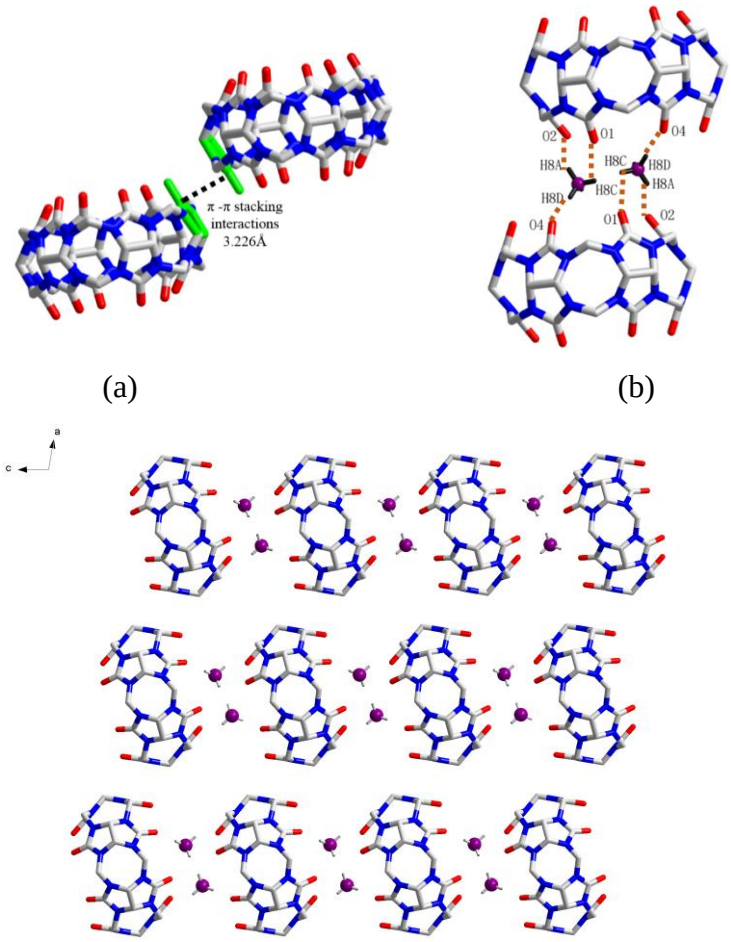


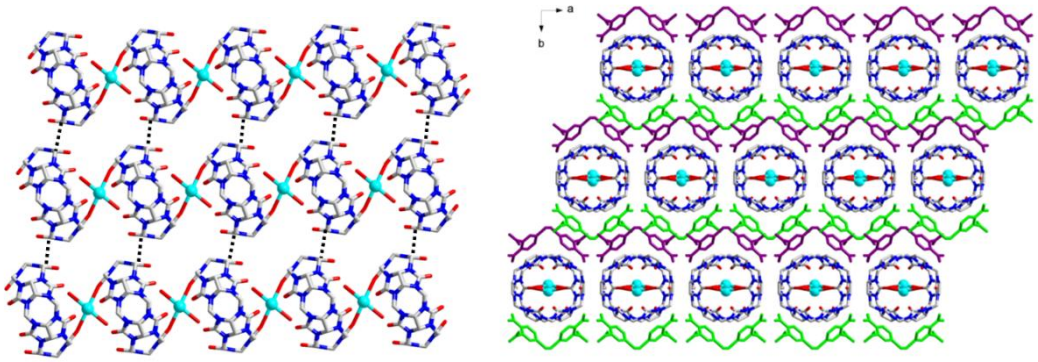
Fig. S1. Q[6] sandwiched by $HDTNB^-$ in the assembly **1**.



(a) (b)

(c)

Fig. S2. (a) Interactions between Q[6] molecules. (b) Hydrogen-bonding interactions between NH_4^+ and Q[6] molecules. (c) The 2D layer constructed by NH_4^+ and Q[6]s.



(a) (b)

Fig. S3. (a) 2D network constructed by the 1D Q[6]-Ba^{2+}-based chains through π -π stacking interactions. (b) Structure of assembly **2** with alternating Q[6]-Ba^{2+}-based layers and $HDTNB^{-}$ layers.

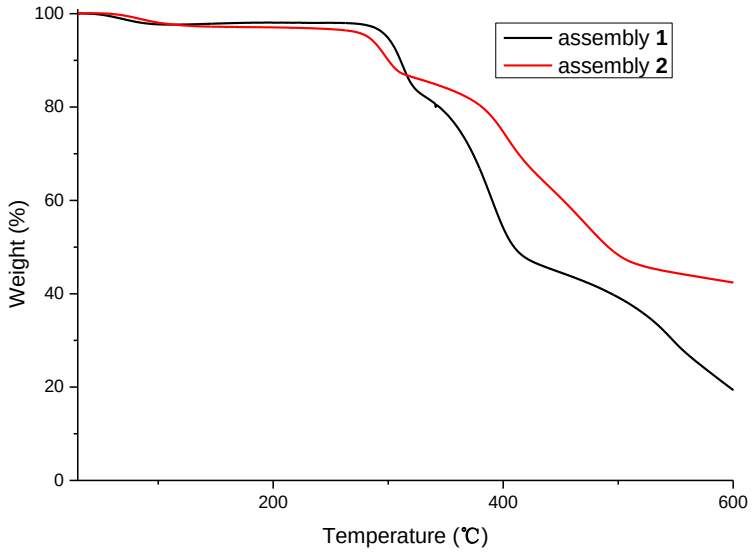
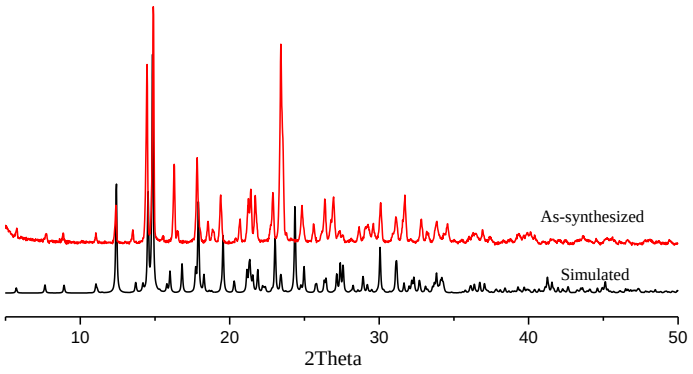
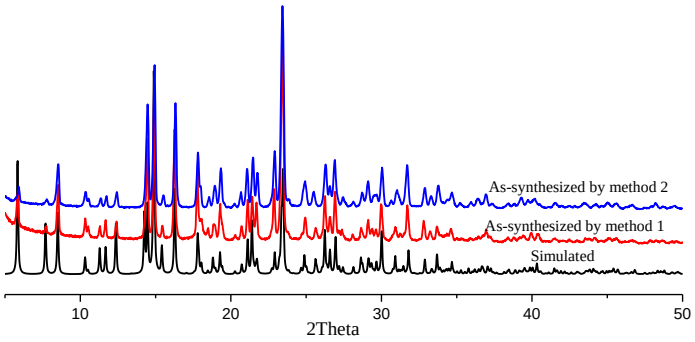


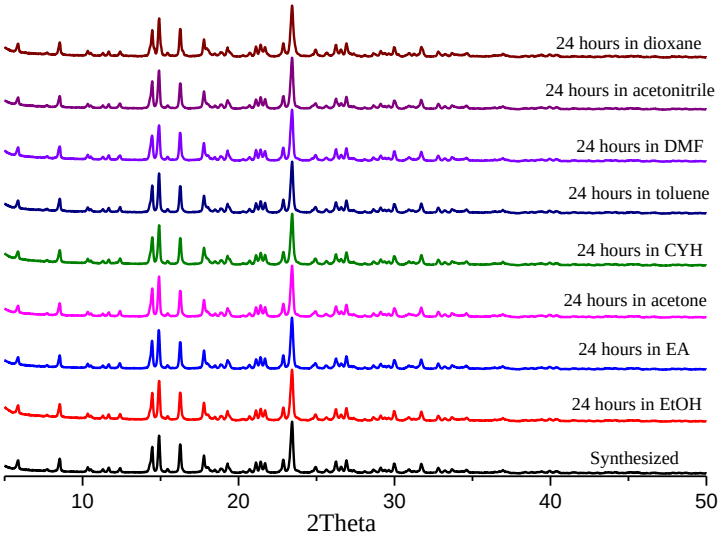
Fig. S4.TG curves of **1** and **2**.

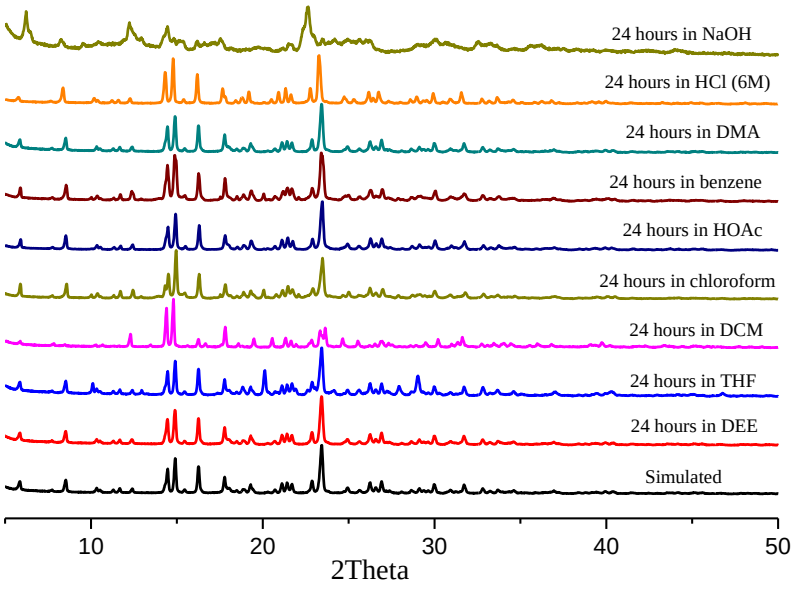

As-synthesized
Simulated
10
20
30
40
50
2Theta

(a)


As-synthesized by method 2
As-synthesized by method 1
Simulated
10
20
30
40
50
2Theta

(b)


24 hours in dioxane
24 hours in acetonitrile
24 hours in DMF
24 hours in toluene
24 hours in CYH
24 hours in acetone
24 hours in EA
24 hours in EtOH
Synthesized
10
20
30
40
50
2Theta



(c)

Fig. S5.PXRD patterns of **1** (a), **2** (b) and **1** dispersed in different solvent (c).

Fig. S6. Image of the solid samples of assembly **1** before (white) and after (red) dispersed in basic solution.

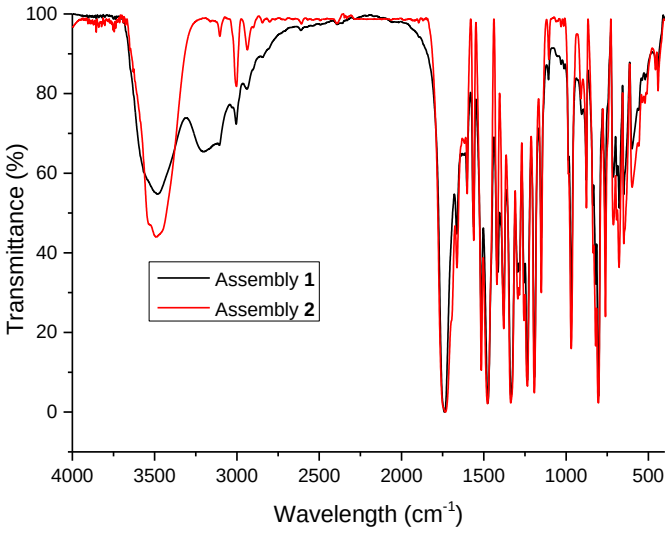


Fig. S7. IR spectra at room temperature of **1** and **2**.

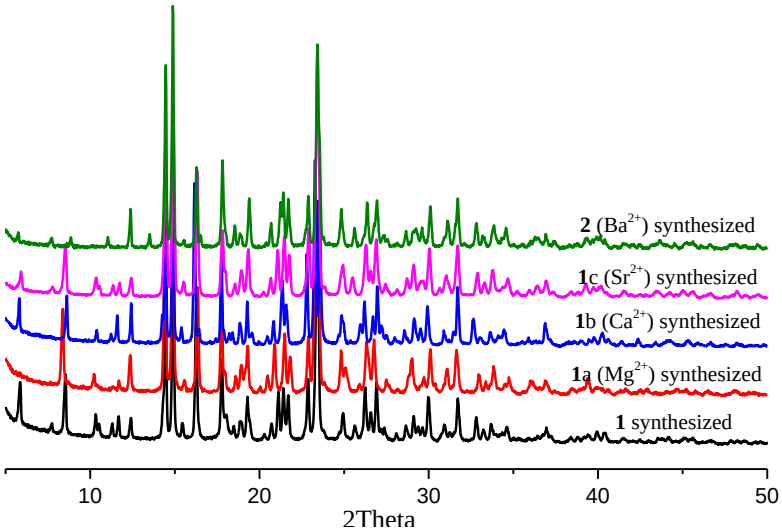


Fig. S8. PXRD patterns of **1**a, **1**b, **1**c and **2**.

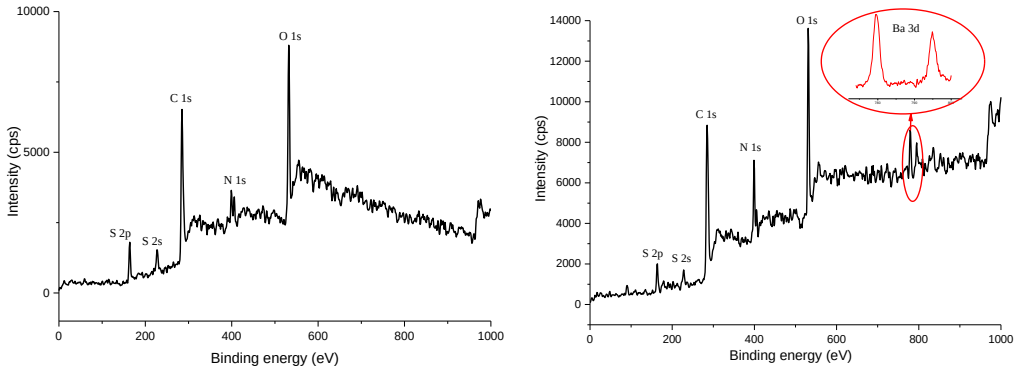


Fig. S9. XPS data of assembly **1** before (a) and after (b) immersed in mixed solution of alkaline-earth metal ions.

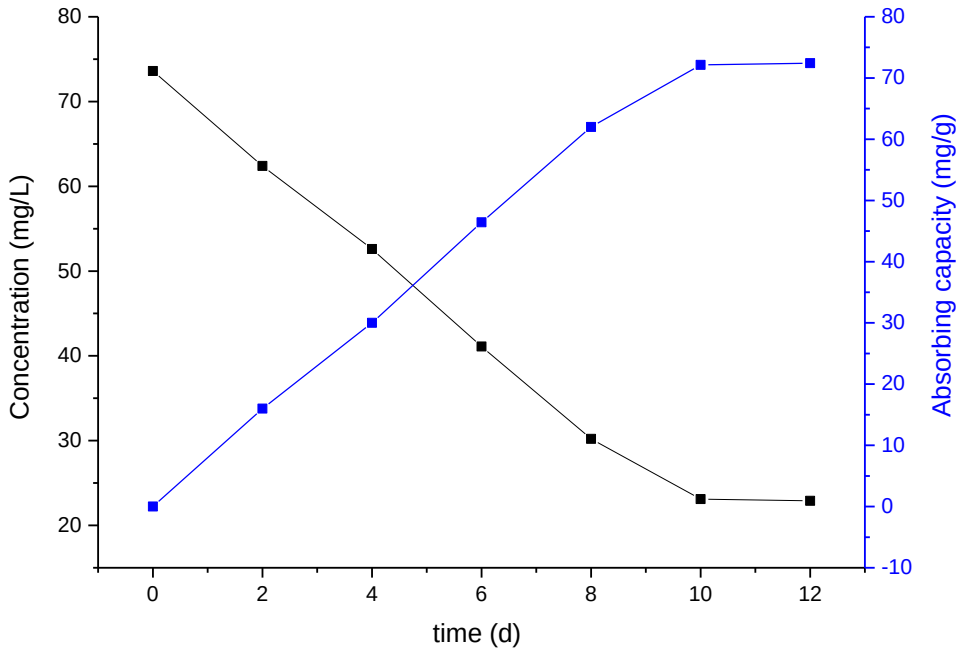


Fig. S10. ICP results of the concentration of Ba^{2+} and the absorbing capacity against time (70 mg of the assembly **1** immersed in $BaCl_2$ concentration).

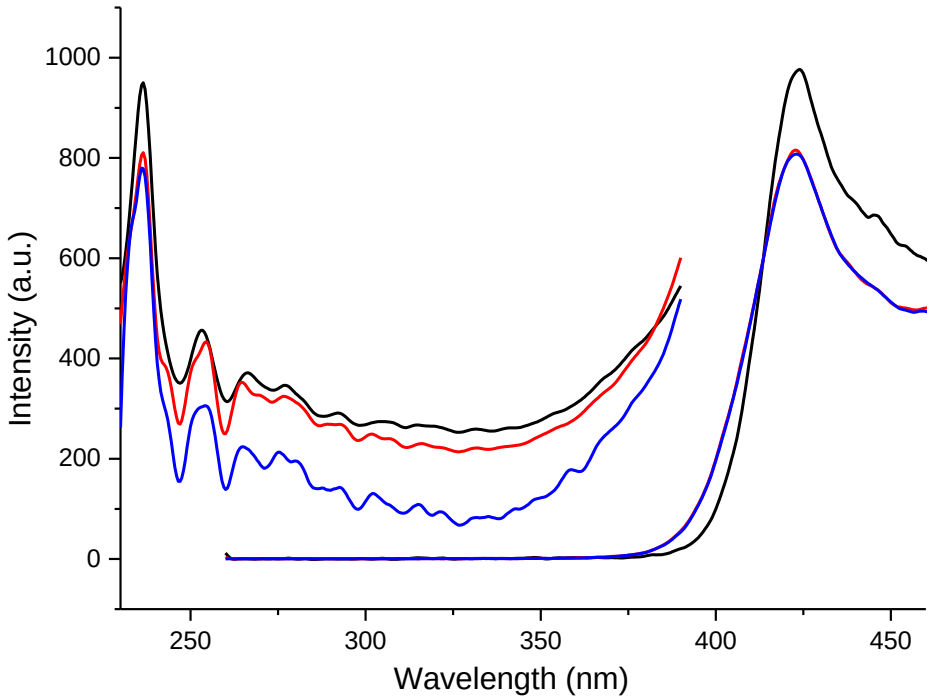
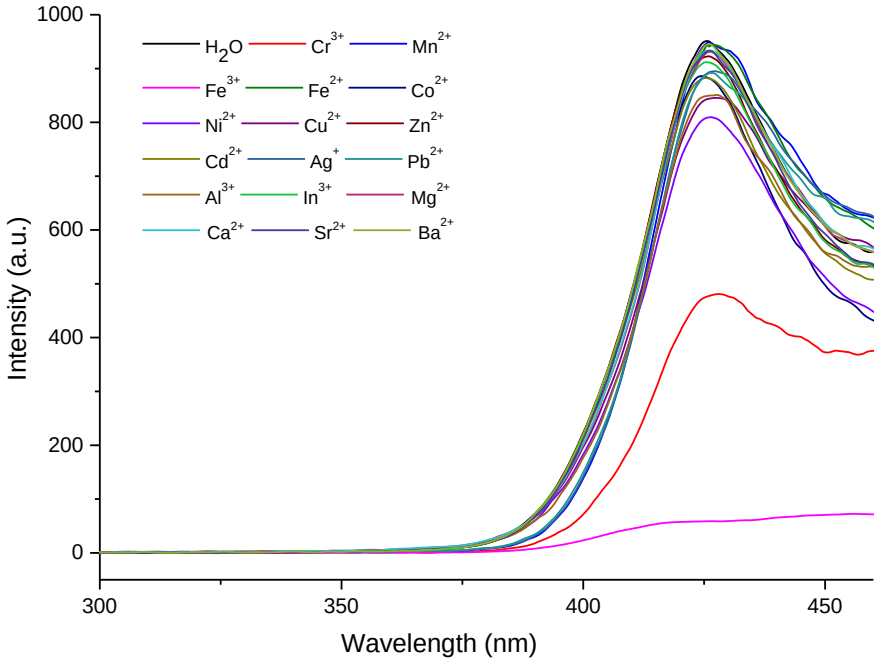
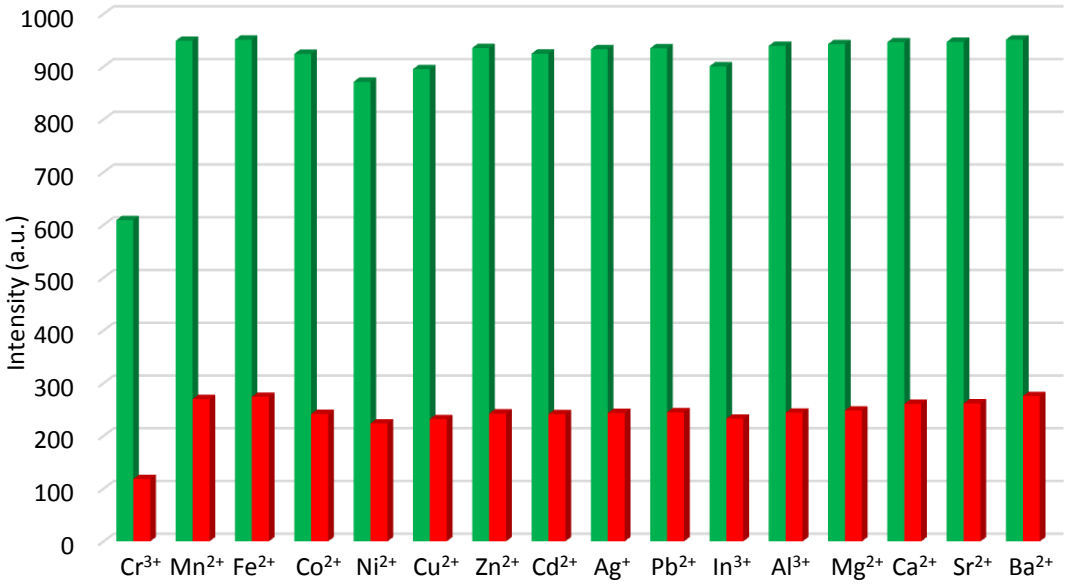


Fig. S11. The excitation and emission spectra of the aqueous suspension of H_2DTNB, assembly **1** and assembly **2** (black: H_2DTNB, Red: assembly **1**, blue: assembly **2**).

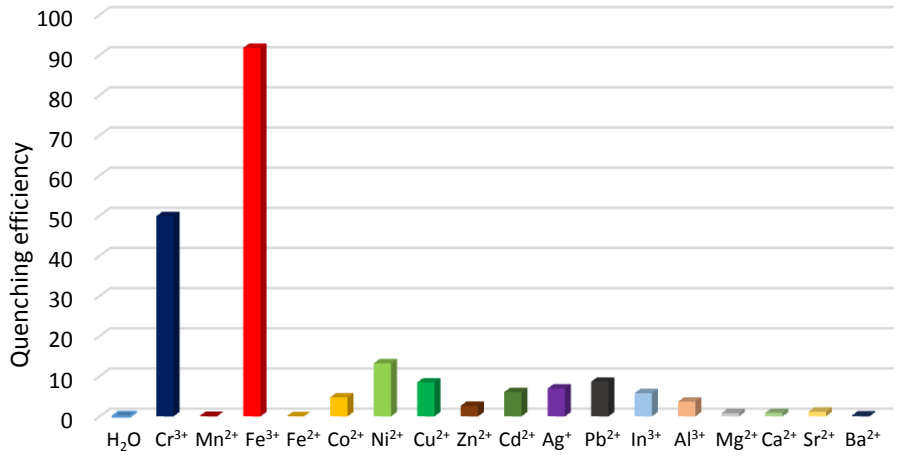


(a)

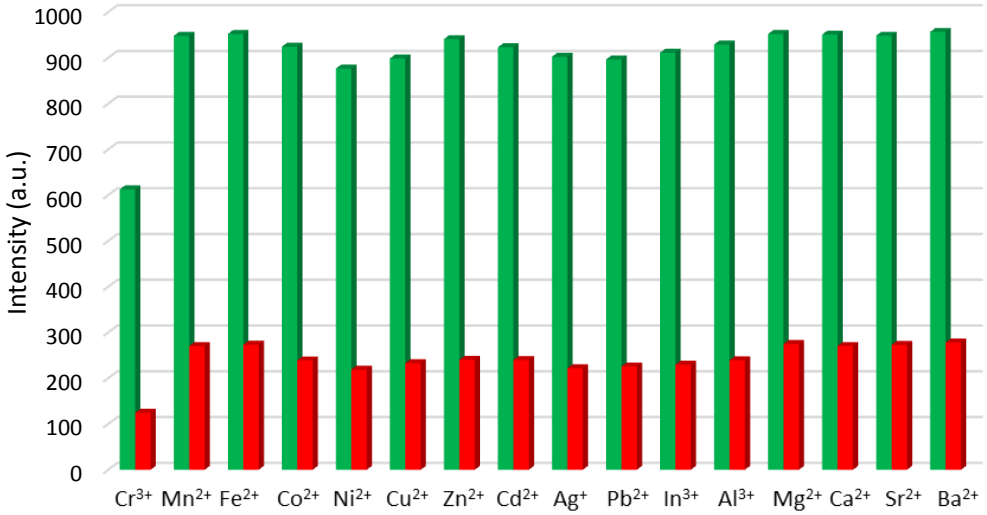


(b)

Fig. S12. (a) Fluorescence spectra of **1** in different metal ions, revealing selective detection of Fe^{3+} over other metal ions; (b) fluorescence intensity ratio histogram of the stock dispersion of **1** (3 mL, 2 mg/mL) in the case of addition the aqueous solution of other metal ions (100 μL, 0.05 M) and then Fe^{3+} (100 μL, 0.05 M) subsequently.

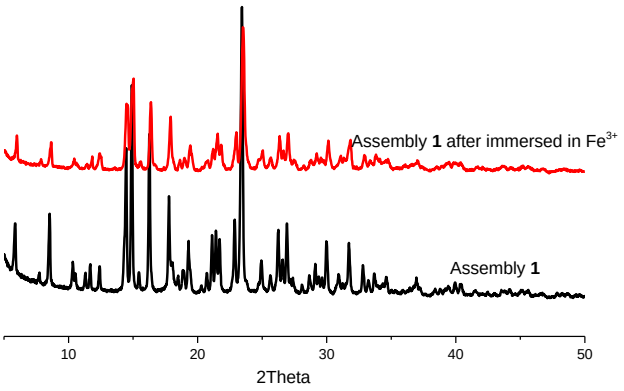


(a)

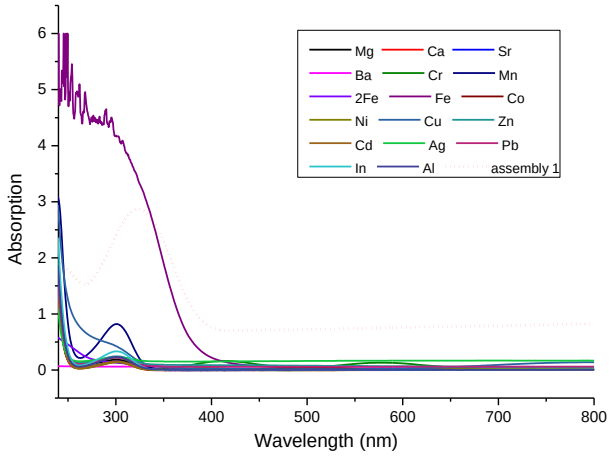


(b)

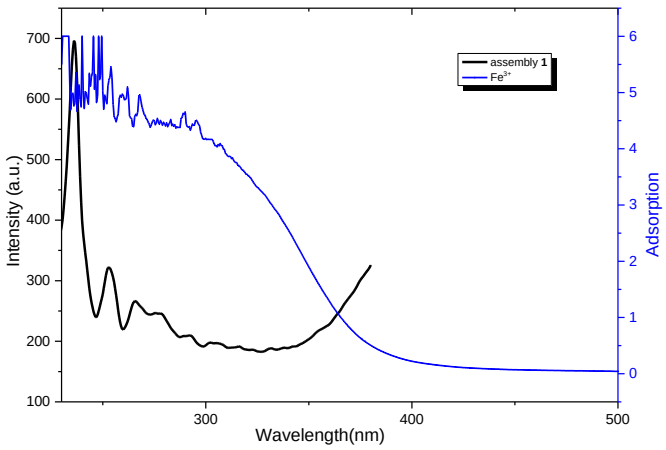
Fig. S13. (a) Quenching efficiency of **2** in different metal ions, revealing selective detection of Fe^{3+} over other metal ions. (b) fluorescence intensity ratio histogram of the stock dispersion of **2** (3 mL, 2 mg/mL) in the case of addition the aqueous solution of other metal ions (100 μL, 0.05 M) and then Fe^{3+} (100 μL, 0.05 M) subsequently.



(a)



(b)



(c)

Fig. S14. (a) The PXRD patterns of the assembly **1** before and after immersed in Fe^{3+}solution; (b) absorption spectra of aqueous suspension containing different metal ions and assembly **1**(10 mM); (c) the absorption spectrum of Fe^{3+} and excitation spectra of assembly 1 suspended stock solution in water.

Reference

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