A novel self-assembly Na{$Cu_{12}Zn_4$} as a multifunctional material: First report of a discrete coordination compound for detection of Ca^{2+} ion and selective adsorption of cationic dye in water

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Formula for calculating the percentage of Nitrobenzene fluorescence intensity quenching:

$(I_o\text{-}I)/I_o$ **x 100%**

Where, I_o = initial fluorescence intensity,

I = intensity of **1** containing Ca^{2+} solution.

Stern-Volmer equation:

$I_0/I = K_{SV}[A] + 1$

Where, I_0 = fluorescent intensity of **1** before the addition of the analyte

I = fluorescent intensity after the addition of the respective analyte

K_{SV} = Stern-Volmer constant

[A] = molar concentration of the analyte (M^{-1}).

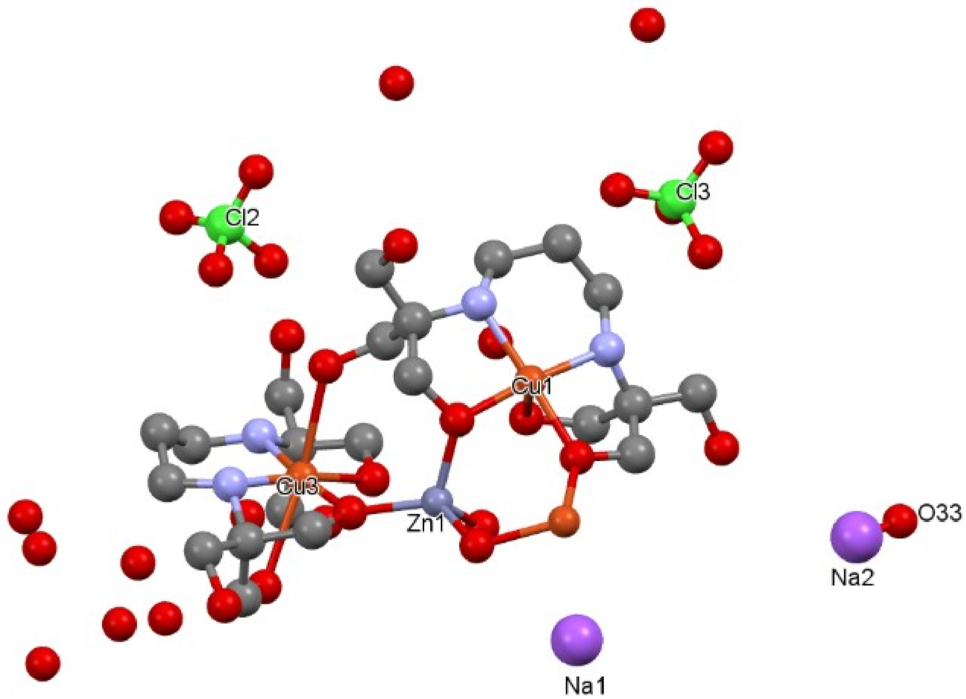

Fig. S1: Asymmetric unit of **1.**

Table S1: Selected bond lengths (Å) for **1**

Atom	Atom	Bond length(Å)
Zn1	O3	1.938(3)
Zn1	O9	1.930(3)
Zn1	O13	1.964(3)
Zn1	O14	1.971(3)
Cu1	O3	1.919(3)
Cu1	O6	1.956(3)
Cu1	N1	2.018(4)
Cu1	N2	2.005(4)
Cu2	O6	1.927(3)
Cu2	O12	1.945(3)
Cu2	O13	1.972(3)
Cu2	O14	1.959(3)
Cu3	O9	1.955(3)
Cu3	O12	1.916(3)
Cu3	N3	2.011(4)
Cu3	N4	2.016(4)

Table S2: Selected bond angles for **1**

Atom	Atom	Atom	Bond angle (degree)
O9	Zn1	O3	
O13	Zn1	O3	112.81(12)
O13	Zn1	O9	95.22(12)
O14	Zn1	O3	119.02(12)
O14	Zn1	O9	115.08(12)
O14	Zn1	O13	109.02(12)
O6	Cu1	O3	105.23(12)
N1	Cu1	O3	91.28(12)

N1	Cu1	O6	85.13(14)
N2	Cu1	O3	175.08(14)
N2	Cu1	O6	172.12(14)
N2	Cu1	N1	84.50(13)
O12	Cu2	O6	99.46(15)
O13	Cu2	O6	111.54(12)
O13	Cu2	O12	109.64(12)
O14	Cu2	O6	114.45(12)
O14	Cu2	O12	118.37(12)
O14	Cu2	O13	96.19(12)
O12	Cu3	O9	106.22(13)
N3	Cu3	O9	90.78(12)
N3	Cu3	O12	84.92(14)
N4	Cu3	O9	173.08(14)
N4	Cu3	O12	175.21(13)
N4	Cu3	N3	85.22(13)
Cu1	O3	Zn1	99.31(15)
C4	O3	Zn1	118.56(14)
C4	O3	Cu1	124.0(3)
Cu2	O6	Cu1	111.3(2)
C11	O6	Cu1	126.88(15)
C11	O6	Cu2	111.9(2)
Cu3	O9	Zn1	118.8(2)
C12	O9	Zn1	125.92(15)
C12	O9	Cu3	119.0(3)
Cu3	O12	Cu2	111.9(3)
C20	O12	Cu2	117.53(14)
C20	O12	Cu3	122.9(2)
Cu2	O13	Zn1	111.4(2)
Cu2	O14	Zn1	107.09(13)
			107.29(14)

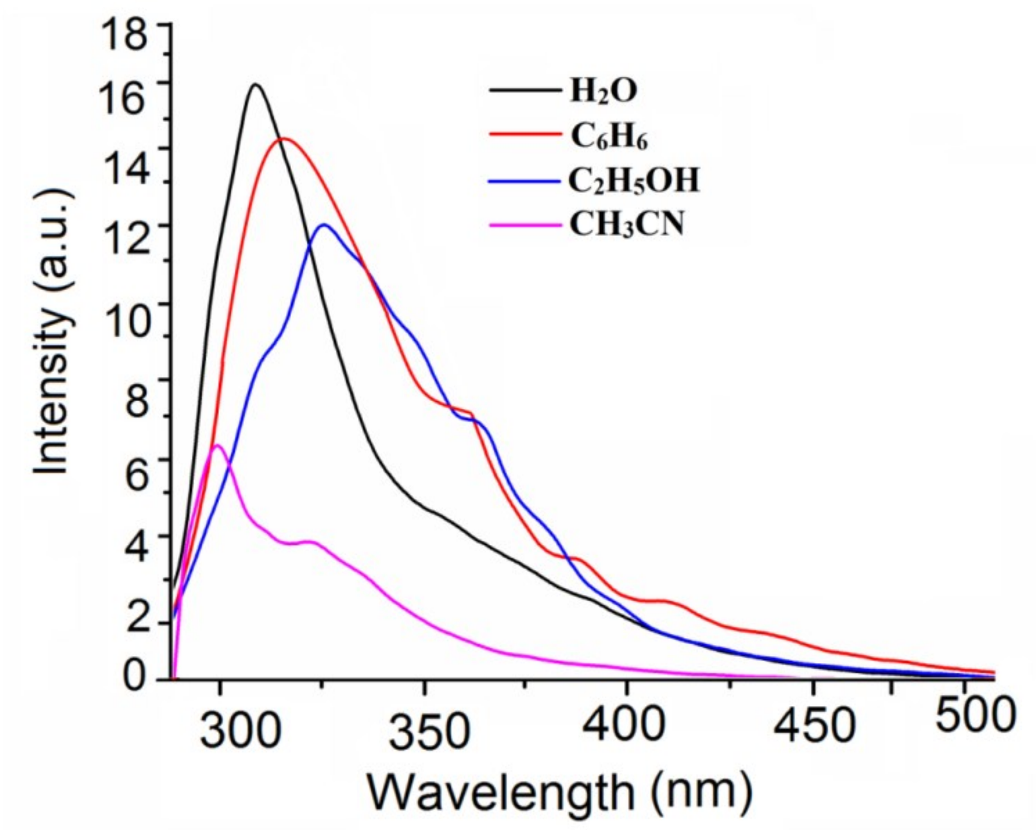

Fig. S2: Emission spectra of **1** dispersed in different solvents upon excitation at 260 nm.

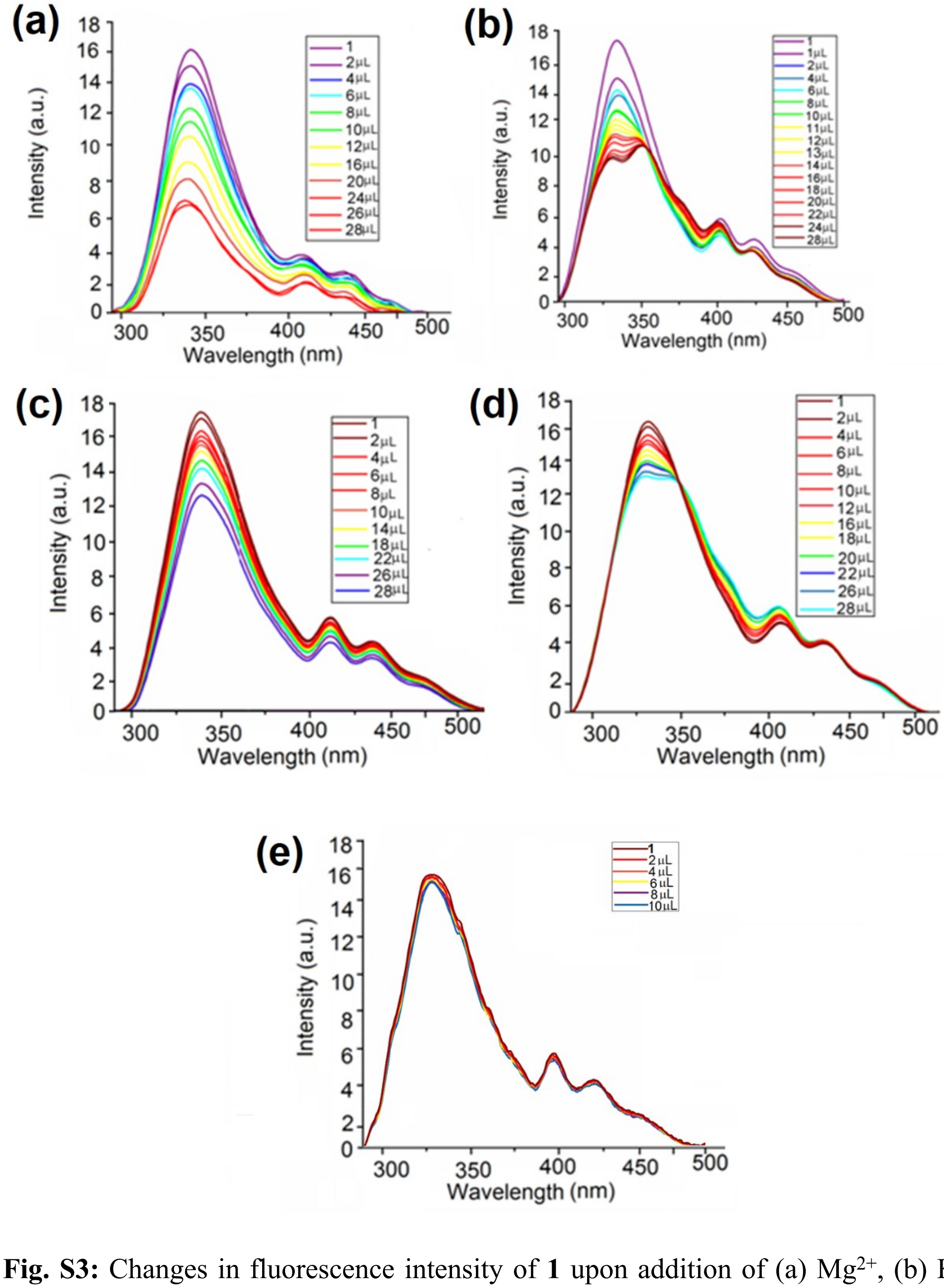

Fig. S3: Changes in fluorescence intensity of **1** upon addition of (a) Mg^{2+}, (b) K^{+}, (c) Sr^{2+}, (d) Ba^{2+} and (e) Cd^{2+} cationic solutions.

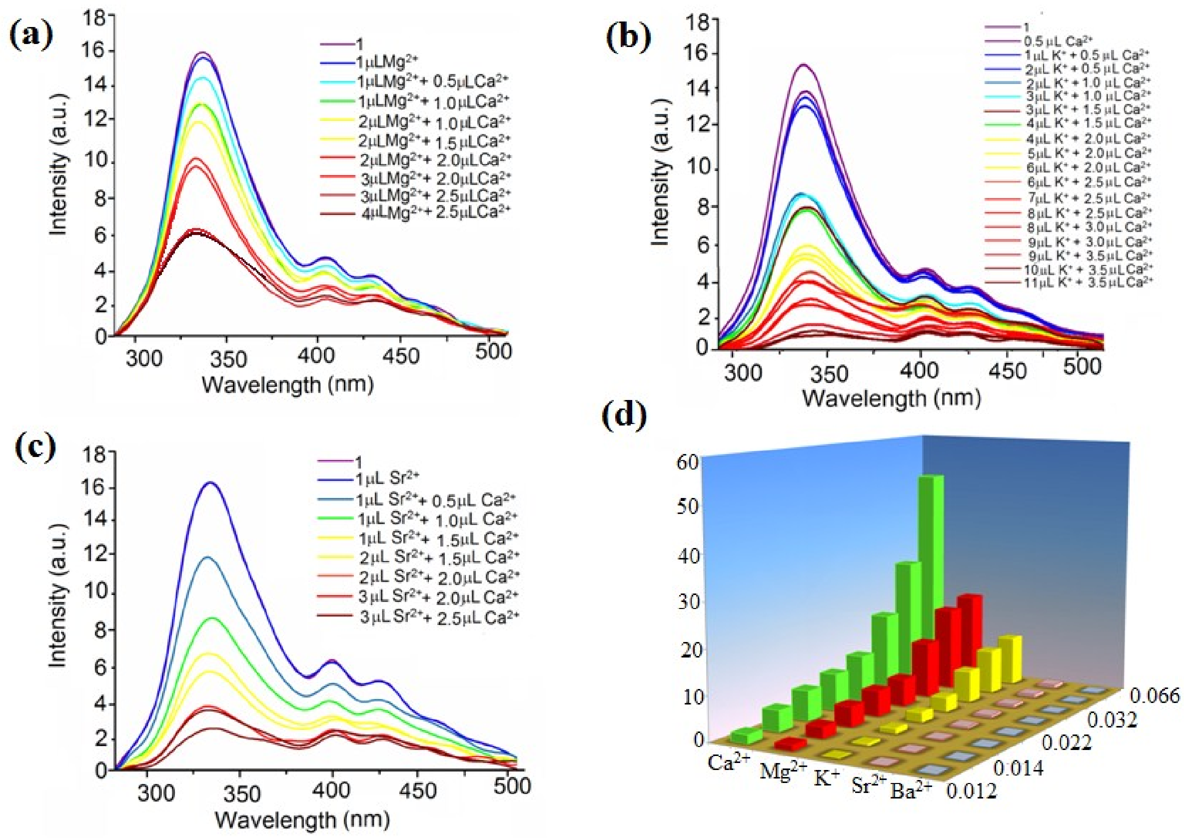

Fig. S4: (a), (b) and (c) Luminescent intensities for **1** immersed in the individual aqueous solutions of MCl_2 (1 mM) and mixed metal ions including Ca^{2+} ions (1 μM). (d) 3D representation of Stern-Volmer (SV) plots of **1** for various light metal ions.

Calculation of standard deviation:

Table S4: Standard deviation for **1.**

Blank Readings (only probe)	**FL Intensity of 1**
Reading 1	16.66
Reading 2	18.00
Reading 3	17.32
Reading 4	18.05
Reading 5	16.50
Standard Deviation (σ)	2.10

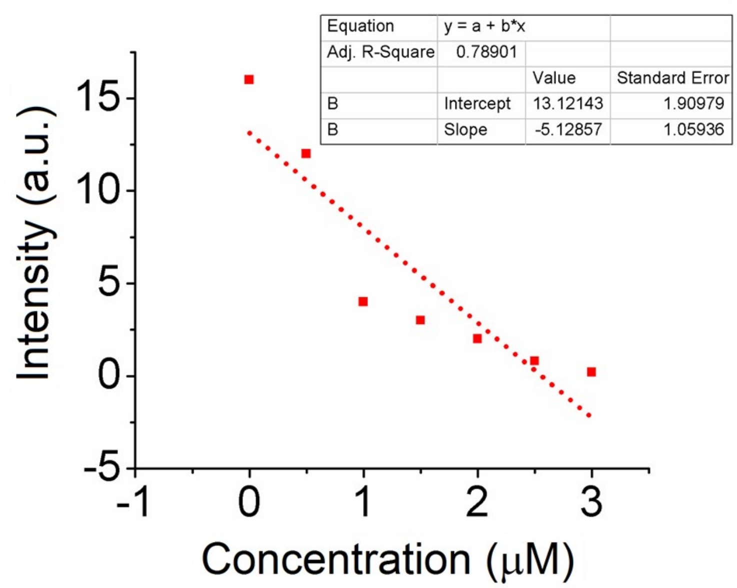

Fig. S5 (a): Plot to calculate LOD for **1** towards Ca^{2+}.

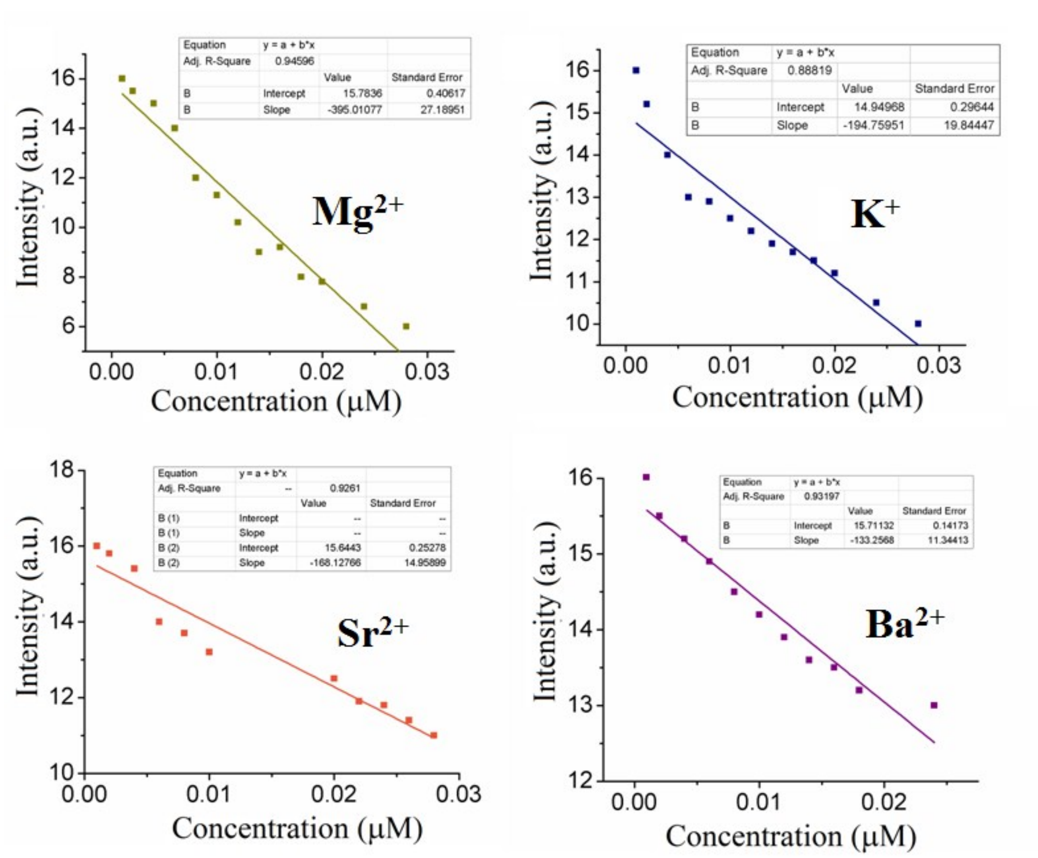

Fig. S5 (b): Plots to calculate LOD for **1** toward multiple S-block cations.

Calculation of Detection Limit:

Table S5: Detection limit calculation of **1** for Cations

Cations	**Slope from Graph (m)**	**Detection limit ($3\sigma/m$) (nM)**
Ca^{2+}	**1384.30034**	**4.5**
Mg^{2+}	**395.01077**	**15.9**
K^{+}	**195.75951**	**32.2**
Sr^{2+}	**166.12766**	**37.9**
Ba^{2+}	**135.25680**	**46.6**

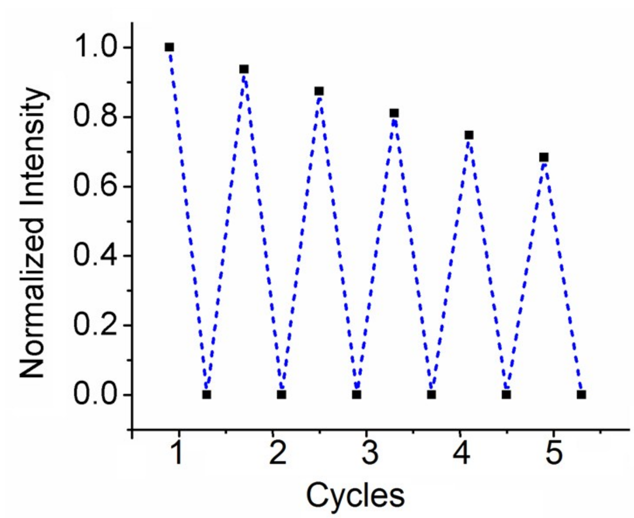

Fig. S6: The quenching and recyclability test of **1**, the upper dots represent the initial luminescence intensity and the lower dots represent the intensity upon addition of Ca^{2+} solution.

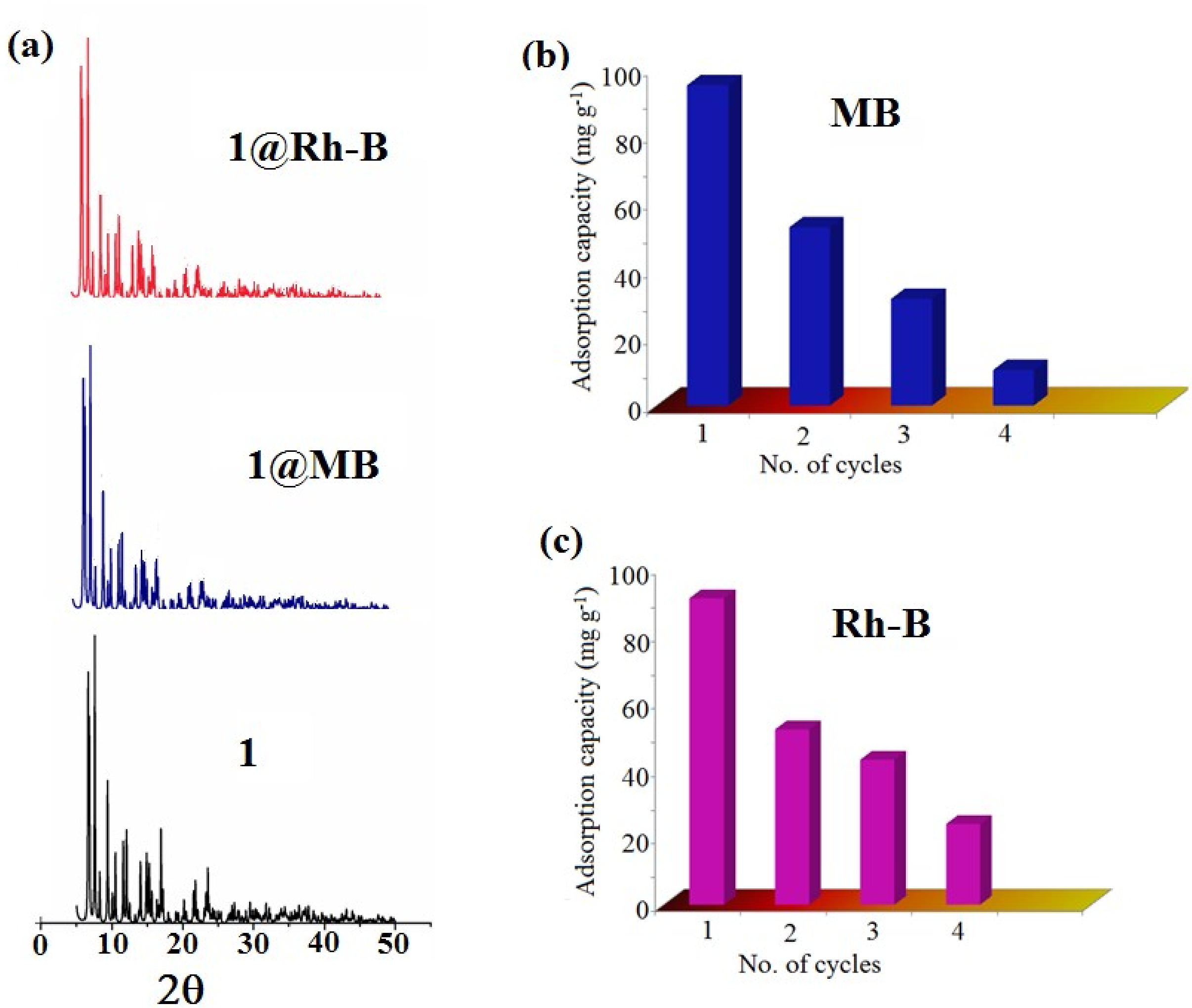

Fig. S7: (a) PXRD patterns of 1 before and after the adsorption of Rh-B and MB. (b) and (c) desorption plot of MB from **1** for four cycles.