

## Supporting Information

for

# Two nanocage anionic metal-organic frameworks with *rht* topology and $\{[M(H_2O)_6]_6\}^{12+}$ charge aggregation for rapid and selective adsorption of cationic dyes

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### Experimental Section

All starting materials and solvents were purchased commercially and used without purification except for H<sub>6</sub>TATAT, which was synthesized according to the literature<sup>[1]</sup> with minor modifications. IR spectra were recorded in the range of 400-4000 cm<sup>-1</sup> on a Nicolet Avatar-370 spectrometer. The elemental analyses (CHN) were performed with German elemental analyzer Vario ELIII. The thermogravimetric analysis was performed with a STA409PC instrument. The X-ray powder diffraction patterns were collected by a Rigaku D/max-2200. The absorption spectra were performed with a PUXI TU-1900. Crystallographic data were collected with Oxford diffractometer (Mo<sub>kα</sub>, λ = 0.71073 Å and Cu<sub>kα</sub>, λ = 1.54178 Å). CCDC: 1014848-1014849.

Synthesis of H<sub>6</sub>TATAT: 0.084 mol 5-aminoisophthalic acid, 0.134 mol NaOH and 0.104 mol NaHCO<sub>3</sub> were added into 140 mL H<sub>2</sub>O in a round-bottomed flask, the mixture was stirred at 0 °C for 30 min, then 70 mL 1,4-dioxane containing 0.02 mol cyanuric chloride was slowly added with constant stirring. The final mixture was refluxed at 110°C for 24h. After cooling to room temperature, the solution was adjusted to pH = 1 with concentrated HCl. 11.55g white solid was collected by centrifugation, washed with distilled water and EtOH, and dried in air (yield: 94 %). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 500 MHz): δ=8.12 (3H), 8.47 (6H), 9.68 (3H), 13.0 (6H) ppm.

### Single-crystal studies:

Crystallographic data of **1** and **2** were collected on an Oxford diffractometer (Mo<sub>kα</sub>, λ = 0.71073 Å and Cu<sub>kα</sub>, λ = 1.54178 Å). The structures were solved by direct methods and refined by full-matrix least-squares calculations (*F*<sup>2</sup>) by using the SHELXTL-97 software.<sup>[2]</sup> All non-H atoms were refined in the anisotropic approximation against *F*<sup>2</sup> for all reflections. Some H atoms of the coordinated H<sub>2</sub>O molecules could not be located, but they were included in the formula. Because guest molecules (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>+</sup> in the channels were highly disordered and could not be modeled properly, the SQUEEZE routine of PLATON was applied to remove their contributions to the scattering. The reported refinements are of the guest-free structures obtained by the SQUEEZE routine, and the results were attached to the CIF file. PLATON/SQUEEZE<sup>[3]</sup> were employed to calculate their contributions to the distorted molecules and given a set of guest-free diffraction intensities. The structures were then refined again using the generated data. Crystallographic data of **1** and **2** are summarized in **Table S1**.

**Table S1.** Crystallographic data for **1** and **2**.

Compound	1	2
Molecular formula	C <sub>216</sub> H <sub>96</sub> Co <sub>18</sub> N <sub>48</sub> O <sub>156</sub> (CH <sub>3</sub> -NH-CH <sub>3</sub> ) <sub>12</sub> (H <sub>2</sub> O) <sub>12</sub> *	C <sub>216</sub> H <sub>96</sub> N <sub>48</sub> Ni <sub>18</sub> O <sub>156</sub> (CH <sub>3</sub> -NH-CH <sub>3</sub> ) <sub>12</sub> (H <sub>2</sub> O) <sub>22</sub> *
Fw	7810.32	7986.16
Temperature, <i>T</i> / K	150(2)	140(2)
crystal system	cubic	cubic
space group	<i>Fm-3m</i>	<i>Fm-3m</i>
<i>a</i> , Å	39.7703(2)	39.7164(8)
<i>b</i> , Å	39.7703(2)	39.7164(8)
<i>c</i> , Å	39.7703(2)	39.7164(8)
<i>V</i> , Å <sup>3</sup>	62903.8(5)	62648(2)
<i>Z</i>	4	4
<i>D</i> , g/cm <sup>3</sup>	0.731	0.733
<i>F</i> (000)	13848	13920
<i>R</i> <sub>int</sub>	0.0222	0.0215
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0565, <i>wR</i> <sub>2</sub> = 0.1875	<i>R</i> <sub>1</sub> = 0.0826, <i>wR</i> <sub>2</sub> = 0.2577
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> (all data)	<i>R</i> <sub>1</sub> = 0.0703, <i>wR</i> <sub>2</sub> = 0.1920	<i>R</i> <sub>1</sub> = 0.0988, <i>wR</i> <sub>2</sub> = 0.2650
Goodness-of-fit, GOF	0.971	1.071
CCDC number	1014849	1014848

<sup>a</sup>*R*<sub>1</sub> = ||*F*<sub>o</sub>| - |*F*<sub>c</sub>||/|*F*<sub>o</sub>|; *wR*<sub>2</sub> = [w(|*F*<sub>o</sub><sup>2</sup> - |*F*<sub>c</sub><sup>2</sup>||<sup>2</sup>)/w|*F*<sub>o</sub><sup>2</sup>|<sup>2</sup>]<sup>1/2</sup>.

\*Distorted CH<sub>3</sub>-NH-CH<sub>3</sub> and crystalline H<sub>2</sub>O were calculated by PLATON/SQUEEZE program, which is not shown in final formulae in CIF files.

**Dye adsorption and separation:**

Compounds **1** and **2** (20 mg) were soaked in aqueous solutions (10 mL) containing **MB & MR**, **CV & Fluorescein**, **MG & Orange II**, **BR2 & MO** (1/1, 8 ppm) in 25 mL sealed glass bottles. UV-Vis spectra were used to record the rapid and selective dyes adsorption ability of **1** and **2**.

**Methylene Blue (MB)**

**Crystal Violet (CV)**

**Malachite Green (MG)**

**Basic Red 2 (BR2)**

**Methyl Red (MR)**

**Fluorescein**

**Orange II**

**Methyl Orange (MO)**

**Figure S1.** The structures of dye molecules that were used in the dye adsorption and separation experiment.

### ICP metal analysis:

Compounds **1** and **2** (10 mg) were soaked in aqueous solutions (10 mL) containing **MB**, **CV**, **MG**, **BR2** (4 mg) in a 25 mL sealed glass vial for 3 days at room temperature and filtered. The resulting filtrate was analyzed on a Thermo Elemental *ICAP6300* to detect the concentration of  $\text{Co}^{2+}$  /  $\text{Ni}^{2+}$ . The ICP data of  $\text{Co}^{2+}$  /  $\text{Ni}^{2+}$  concentration in the filtrate are summarized in **Table S2**.

**Table S2.** The ICP data and the exchange percent of the filtrate

dye@1	<b>MB</b>	<b>CV</b>	<b>MG</b>	<b>BR2</b>
adsorption capacity (mg dye /10 mg <b>1</b> )	3.47	3.31	3.22	1.34
Released $\text{Co}^{2+}$ concentration ( $C_0$ , ppm in 10 mL aqueous solution )	14.04	12.42	17.08	9.31
Exchanged $\text{Co}^{2+}$ percentage ( $2n_{\text{Co}^{2+}}/n_{\text{dye}} \times 100$ )	51.3	52.0	83.5	82.7
Exchanged $(\text{CH}_3)_2\text{NH}_2^+$ percentage	48.7	48.0	16.5	17.3
dye@2	<b>MB</b>	<b>CV</b>	<b>MG</b>	<b>BR2</b>
adsorption capacity (mg dye/10mg <b>2</b> )	3.51	3.36	3.29	1.47
Released $\text{Ni}^{2+}$ concentration ( $C_0$ , ppm in 10 mL aqueous solution)	14.29	13.58	15.06	11.70
Exchanged $\text{Ni}^{2+}$ percentage ( $2n_{\text{Ni}^{2+}}/n_{\text{dye}}$ )	51.8	56.1	72.4	95.0
Exchanged $(\text{CH}_3)_2\text{NH}_2^+$ percentage	48.2	43.9	27.6	5.0

### Calculation: example MB@1

$$\text{Exchange percent (\%)} = \frac{2n(\text{Co}^{2+})}{n(\text{MB})} = \frac{\frac{2C_0(\text{Co}^{2+}) \cdot V}{M_r(\text{Co}^{2+})}}{\frac{m(\text{MB})}{M_r(\text{MB})}} = \frac{\frac{2 \times 14.04 \times 10^{-3} \times 10^{-2}}{58.9332} \text{ mol}}{\frac{3.47 \times 10^{-3} \text{ g}}{373.90 \text{ g} \cdot \text{mol}^{-1}}} = \frac{2 \times 2.38}{9.28} = 51.3 \%$$

Where:

$$m(\text{MB}) = 3.47 \text{ mg}$$

$$M_r(\text{MB}) = 373.90 \text{ g} \cdot \text{mol}^{-1}$$

$$M_r(\text{CV}) = 407.98 \text{ g} \cdot \text{mol}^{-1}$$

$$M_r(\text{MG}) = 463.50 \text{ g} \cdot \text{mol}^{-1}$$

$$M_r(\text{BR2}) = 350.85 \text{ g} \cdot \text{mol}^{-1}$$

$$M_r(\text{Co}^{2+}) = 58.9332 \text{ g} \cdot \text{mol}^{-1}$$

$$M_r(\text{Ni}^{2+}) = 58.6934 \text{ g} \cdot \text{mol}^{-1}$$

$$C_0(\text{Co}^{2+}) = 14.02 \text{ ppm} = 14.04 \times 10^{-3} \text{ g} \cdot \text{L}^{-1}$$

$$V = 1.0 \times 10^{-2} \text{ L}$$

**Table S3.** Maximum adsorption capacity of **Methylene Blue (MB)** on various adsorbents.

Adsorbent	Maximum Adsorption Capacity (mg g <sup>-1</sup> )	Reference
Chitosan-g-poly(acrylic acid)-vermiculite hydrogel composite	1685	<i>J. Environ. Sci.</i> <b>2010</b> , <i>22</i> , 486.
Amino-MIL-101-Al	762 ± 12	<i>J. Mater. Chem. A.</i> <b>2014</b> , <i>2</i> , 193.
Crystal <b>1</b> (crystal <b>2</b> )	<b>725 (708)</b>	<b>In this work</b>
Activated carbon produced from New Zealand coal	588	<i>Chem. Eng. J.</i> <b>2008</b> , <i>135</i> , 174.
Poly(vinylidene fluoride)-derived activated carbon fibers	486	<i>Carbon.</i> <b>2001</b> , <i>39</i> , 207.
Caulerpa lentillifera	417	<i>Bioresour. Technol.</i> <b>2007</b> , <i>98</i> , 1567.
Activated carbon	400	<i>J. Hazard. Mater.</i> <b>2006</b> , <i>134</i> , 237.
MOF-235	187	<i>J. Hazard. Mater.</i> <b>2011</b> , <i>185</i> , 507.
Zn-MOF	0.75	<i>Chem. Eur. J.</i> <b>2013</b> , <i>19</i> , 3639.

**Table S4.** Maximum adsorption capacity of **Crystal Violet (CV)** on various adsorbents.

Adsorbent	Maximum Adsorption Capacity (mg·g <sup>-1</sup> )	Reference
Zn-MOF	0.70	<i>Chem. Eur. J.</i> <b>2013</b> , <i>19</i> , 3639.
Jute fiber carbon	27.99	<i>J. Hazard. Mater.</i> <b>2007</b> , <i>143</i> , 311.
Coniferous pinus bark powder (CPBP)	32.78	<i>J. Hazard. Mater.</i> <b>2009</b> , <i>171</i> , 767.
Semi-IPN hydrogels	35.09	<i>Bioresour. Technol.</i> <b>2010</b> , <i>101</i> , 2197.
Kaolin	47.27	<i>Appl. Clay. Sci.</i> <b>2009</b> , <i>42</i> , 583.
Phosphoric acid activated carbon (PAAC)	60.42	<i>J. Hazard. Mater.</i> <b>2006</b> , <i>136</i> , 800.
Magnetic nanocomposite	81.70	<i>J. Hazard. Mater.</i> <b>2011</b> , <i>12</i> , 1462.
Sulphuric acid activated carbon (SAAC)	85.84	<i>J. Hazard. Mater.</i> <b>2006</b> , <i>136</i> , 800.
Crystal <b>1</b> (crystal <b>2</b> )	<b>607 (630)</b>	<b>In this work</b>

**Table S5.** Maximum adsorption capacity of **Malachite Green (MG)** on various adsorbents.

Adsorbent	Maximum Adsorption Capacity (mg·g <sup>-1</sup> )	Reference
Bentonite clay	7.72	<i>Chemosphere</i> . <b>2006</b> , 63, 1842.
Activated carbons commercial grade (ACC)	8.27	<i>Colloids Surf. A: Physicochem. Eng. Aspects</i> . <b>2005</b> , 264, 17.
Arundo donax root carbon (ADRC)	8.69	<i>J. Hazard. Mater.</i> <b>2008</b> , 150, 774.
Activated carbons laboratory grade (ACL)	42.18	<i>Colloids Surf. A: Physicochem. Eng. Aspects</i> . <b>2005</b> , 264, 17.
rattan sawdust (RSD)	62.71	<i>J. Hazard. Mater.</i> <b>2008</b> , 02, 54.
Cyclodextrin-based material	91.9	<i>Sep. Purif. Technol.</i> <b>2007</b> , 53, 97.
Chitosan bead	93.55	<i>J. Hazard. Mater.</i> <b>2008</b> , 154, 254.
Activated carbon prepared waste apricot	116.27	<i>J. Hazard. Mater.</i> <b>2006</b> , 135, 232.
Lignite activated carbon	149	<i>J. Hazard. Mater.</i> <b>2007</b> , 146, 194.
Oil palm trunk fibre	149.35	<i>J. Hazard. Mater.</i> <b>2008</b> , 154, 237.
Groundnut shell-based powdered activated carbon (GSPAC)	222.22	<i>Waste Manage.</i> <b>2007</b> , 27, 1129.
Commercial powder activated carbon (CPAC)	222.22	<i>Waste Manage.</i> <b>2007</b> , 27, 1129.
Bamboo-based activated carbon	263.58	<i>J. Hazard. Mater.</i> <b>2007</b> , 12, 105.
Crystal 1 (crystal 2)	<b>484 (502)</b>	<b>In this work</b>

## Dye release:

The initial dye@1 and dye@2 samples were obtained by soaking 1 and 2 (20 mg) in 10 mL **MB**, **CV**, **MG** and **BR2** aqueous solution (8 ppm) for 10 h respectively. Then 20 mg samples were placed in a saturated NaCl aqueous solution and deionized water (10 mL, RT) respectively. The release experiment was monitored by UV-Vis spectra. The UV-Vis spectra data of adsorption and release for 1 and 2 are summarized in **Table S6**.

**Table S6.** Dye release experiments data for 20 mg dye@1 and dye@2 (8.0 ppm dye, 10 mL soaked for 10 hrs).

		<b>MB</b>	<b>CV</b>	<b>MG</b>	<b>BR2</b>
dye@1	Final concentration / ppm	0.689	1.00	0.581	2.68
	Concentration after release (40 min) / ppm	0.981	1.86	2.33	2.10
	Release percent (40 min) / %	13.4	26.6	31.4	39.5
	Concentration after release (120 min) / ppm	1.31	3.04	2.97	2.74
	Release percent (120 min) / %	17.9	43.4	40.0	51.5
dye@2	Final concentration / ppm	0.660	0.961	0.431	2.69
	Concentration after release (40 min) / ppm	1.07	1.37	2.36	2.10
	Release percent (40 min) / %	14.6	19.5	31.2	39.5
	Concentration after release (120 min) / ppm	1.36	3.09	3.02	2.78
	Release percent (120 min) / %	18.5	43.9	39.9	52.4

### Calculation: example MB@1

$$\text{Release percent (40 min)} = \frac{C_{(\text{release})}}{C_0 - C_1} = \frac{0.981}{8.00 - 0.689} = 13.4 \%$$

$$\text{Release percent (120 min)} = \frac{C'_{(\text{release})}}{C_0 - C'_1} = \frac{1.311}{8.00 - 0.689} = 17.9 \%$$

Where:

$$C_0 = 8.0 \text{ ppm}$$

$$C_1 = 0.689 \text{ ppm}$$

$$C'_1 = 0.689 \text{ ppm}$$

$$\text{if } t = 40 \text{ min, } C_{(\text{release})} = 0.981 \text{ ppm}$$

$$\text{if } t = 120 \text{ min, } C'_{(\text{release})} = 1.31 \text{ ppm}$$

### Column chromatography experiments:

The chromatographic columns were prepared by using the compounds **1** and **2** (40 mg) as the filter, the diameter of the column is 1.6 mm. 50 mL aqueous solutions containing four cationic dyes molecules with the concentration of **10** ppm were passed through with flow rate of 0.5 mL/min, respectively. The removal percent and rate were monitored by UV-Vis absorption spectroscopy. The UV-Vis spectra data of adsorption and release for **1** and **2** are summarized in **Table S7** and **Table S8**.

**Table S7.** Column chromatography experiments using compound **1** as filler

		<b>1 (40mg)</b>			
Effluent concentration of dye / ppm		<b>MB</b>	<b>CV</b>	<b>MG</b>	<b>BR2</b>
Time(min)					
2		0	0	0.037	0.114
5		0.005	0.017	0.074	0.199
10		0.023	0.094	0.516	1.03
30		0.28	0.22	1.07	1.68
60		0.54	0.41	2.06	2.87
120		1.33	0.69	2.25	5.70
Removal / %		<b>MB</b>	<b>CV</b>	<b>MG</b>	<b>BR2</b>
Time(min)					
2		100	100	99.63	98.86
5		99.95	99.83	99.26	98.01
10		99.77	99.06	94.84	89.75
30		97.20	97.80	89.30	83.20
60		94.60	95.90	79.40	71.30
120		86.70	93.10	77.50	43.00

#### Calculation: example MB@1, t=10 min

$$\text{Removal percent (\%)} = \frac{C_0 - C_1}{C_0} = \frac{10.0 - 0.023}{10.0} = 99.77 \%$$

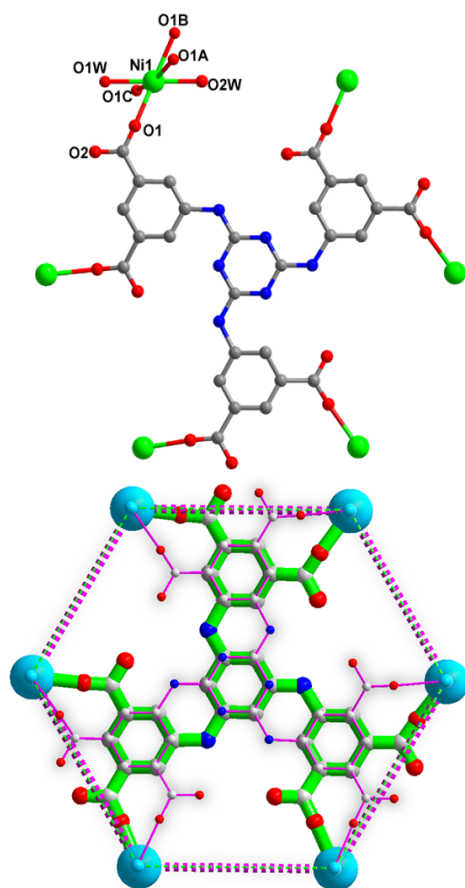
Where

$$\text{if } t = 10 \text{ min, } C_0 = 10.0 \text{ ppm, } C_1 = 0.023 \text{ ppm}$$

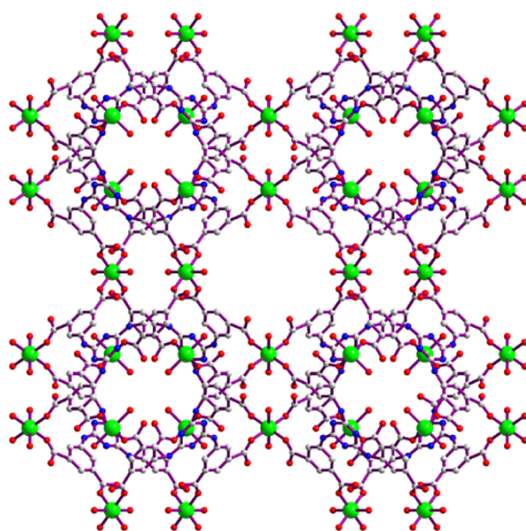


**Table S8.** Column chromatography experiments using compound **2** as filler

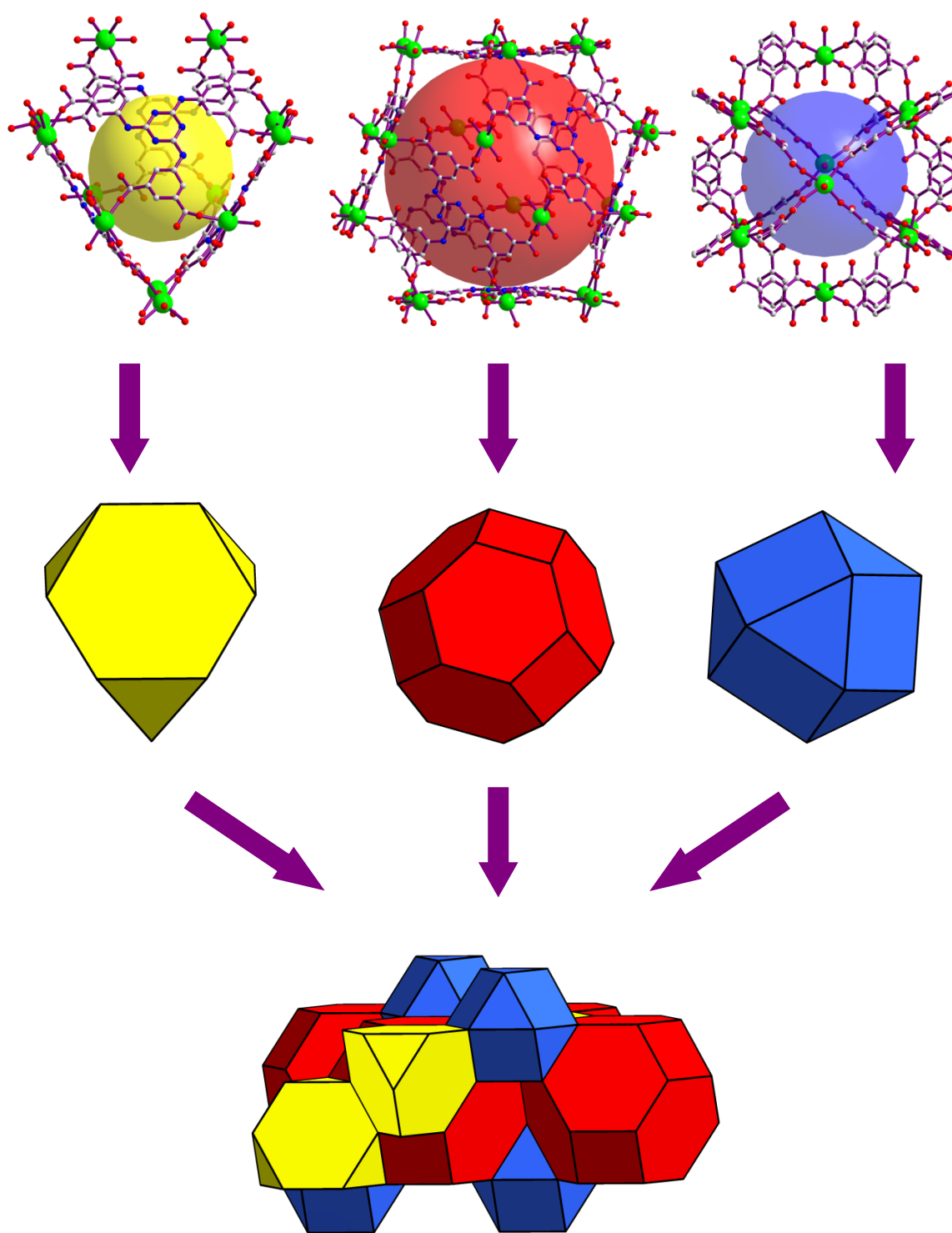
	<b>2 (40mg)</b>			
Effluent concentration of dye / ppm	<b>MB</b>	<b>CV</b>	<b>MG</b>	<b>BR2</b>
Time(min)				
0	10	10	10	10
2	0	0	0.037	0.070
5	0.005	0.011	0.074	0.114
10	0.019	0.083	0.492	0.883
30	0.28	0.22	1.02	1.68
60	0.52	0.40	2.03	2.75
120	1.32	0.67	2.21	5.66
Removal / %	<b>MB</b>	<b>CV</b>	<b>MG</b>	<b>BR2</b>
Time(min)				
2	100	100	99.63	99.30
5	99.95	99.89	99.26	98.86
10	99.81	99.17	95.08	91.17
30	97.20	97.80	89.80	83.20
60	94.80	96.00	79.70	72.50
120	86.80	93.30	77.90	43.40



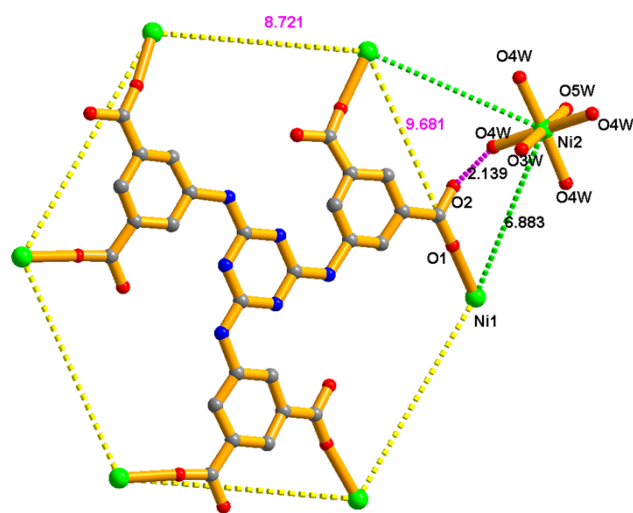
**Figure S2.** The coordination environment of  $\text{Ni}^{2+}$  ion and the coordination model of TATAT ligand in **2** (top). Colour code: Ni, green; O, red; N, blue; C gray. The ligand has two positions (thick green bonds with larger atoms and thinner purple bonds with smaller atoms) with equal occupancy (bottom). For clarity, only one position were shown in all other Figures.



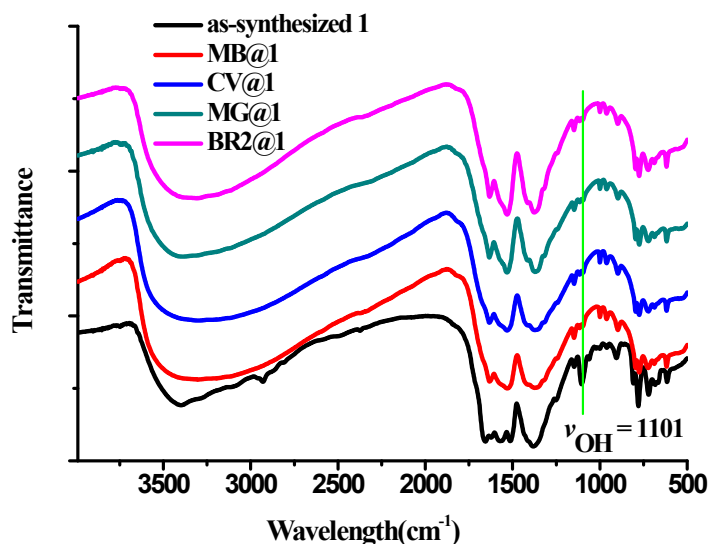
**Figure S3.** The 3D network of **2** viewed along  $a/b/c$  axis. Green balls are metal ions



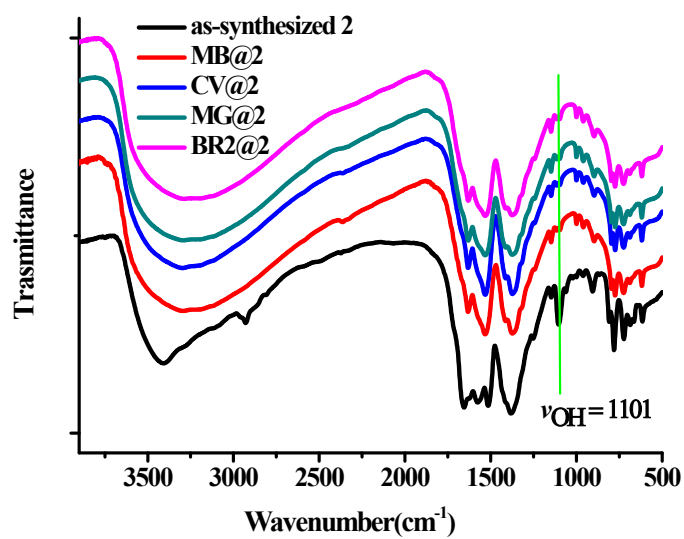
**Figure S4.** Three kinds of cages of Truncated tetrahedron (T-T<sub>d</sub>, yellow), Cuboctahedron (cub-O<sub>h</sub>, blue) and Truncated octahedron (T-O<sub>h</sub>, red), and *rht* network structure of **2**.



**Figure.S5** The hydrogen bond between the coordinated water on  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and carboxyl oxygen atom.



**Figure S6.** Infrared spectra of as-synthesized 1; MB@1; CV@1; MG@1 and BR2@1.



**Figure S7.** Infrared spectra of as-synthesized 2; MB@2; CV@2; MG@2 and BR2@2.

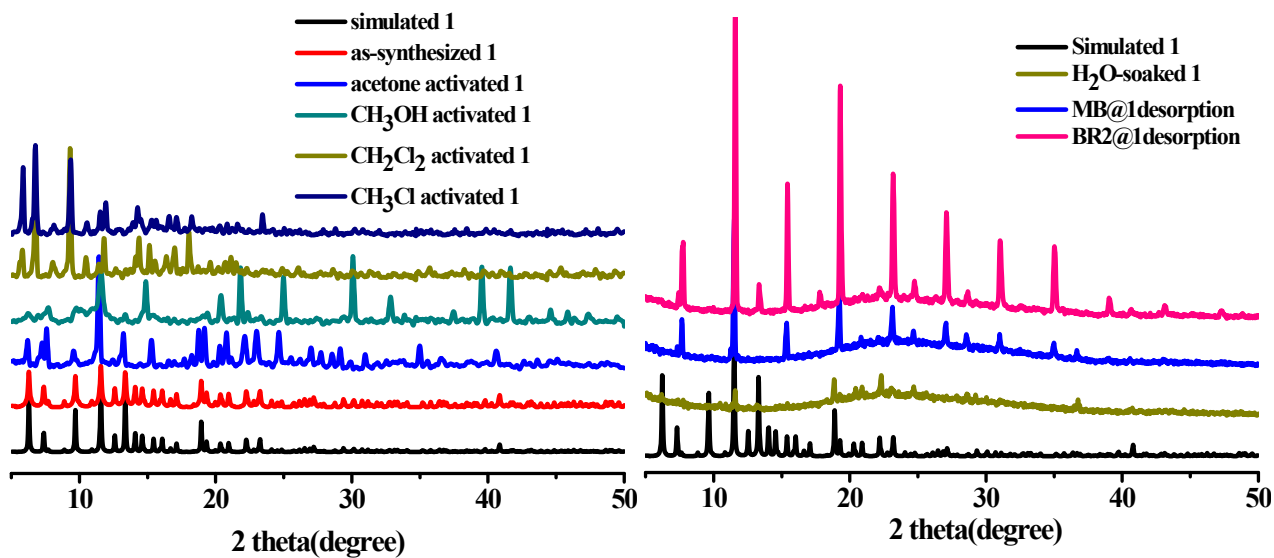


Figure S8. PXRD patterns for 1: simulated1; as-synthesized 1; 1  $\supset$  acetone; 1  $\supset$  CH<sub>3</sub>OH; 1  $\supset$  CH<sub>2</sub>Cl<sub>2</sub>, 1  $\supset$  CH<sub>3</sub>Cl (left) and H<sub>2</sub>O-soaked 1, desorption samples of MB@1 and BR2@1 (right).

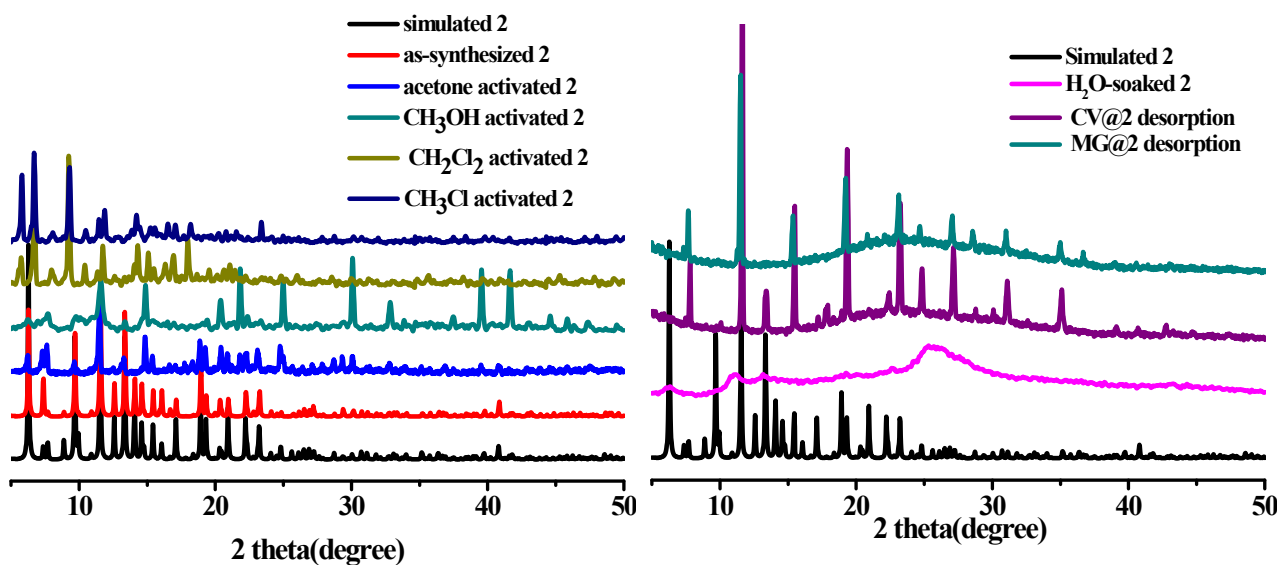


Figure S9. PXRD patterns for 2: simulated1; as-synthesized 2; 2  $\supset$  acetone; 2  $\supset$  CH<sub>3</sub>OH; 2  $\supset$  CH<sub>2</sub>Cl<sub>2</sub> and 2  $\supset$  CH<sub>3</sub>Cl (left) and H<sub>2</sub>O-soaked 2, desorption samples of CV@2 and MG@2 (right).

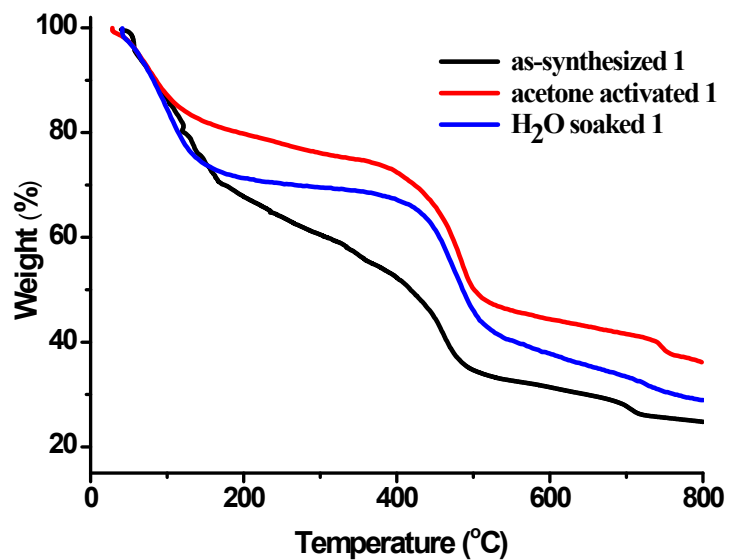


Figure S10. TG curves of as-synthesized 1, acetone activated 1 and H<sub>2</sub>O soaked 1.

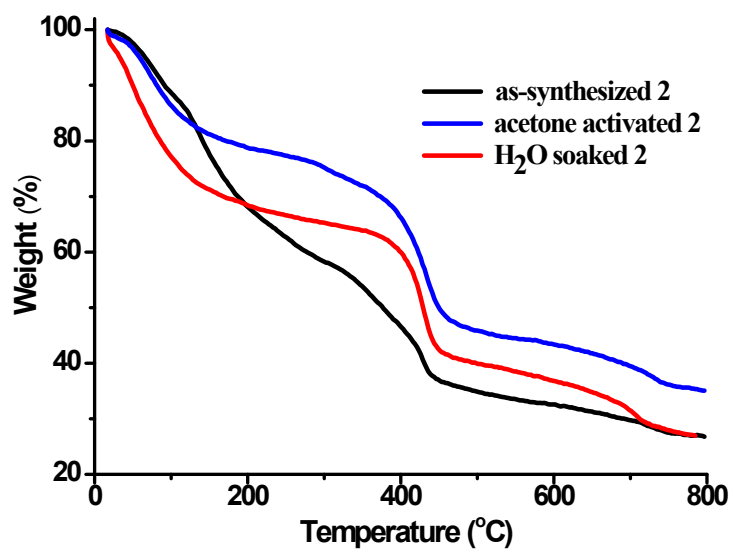
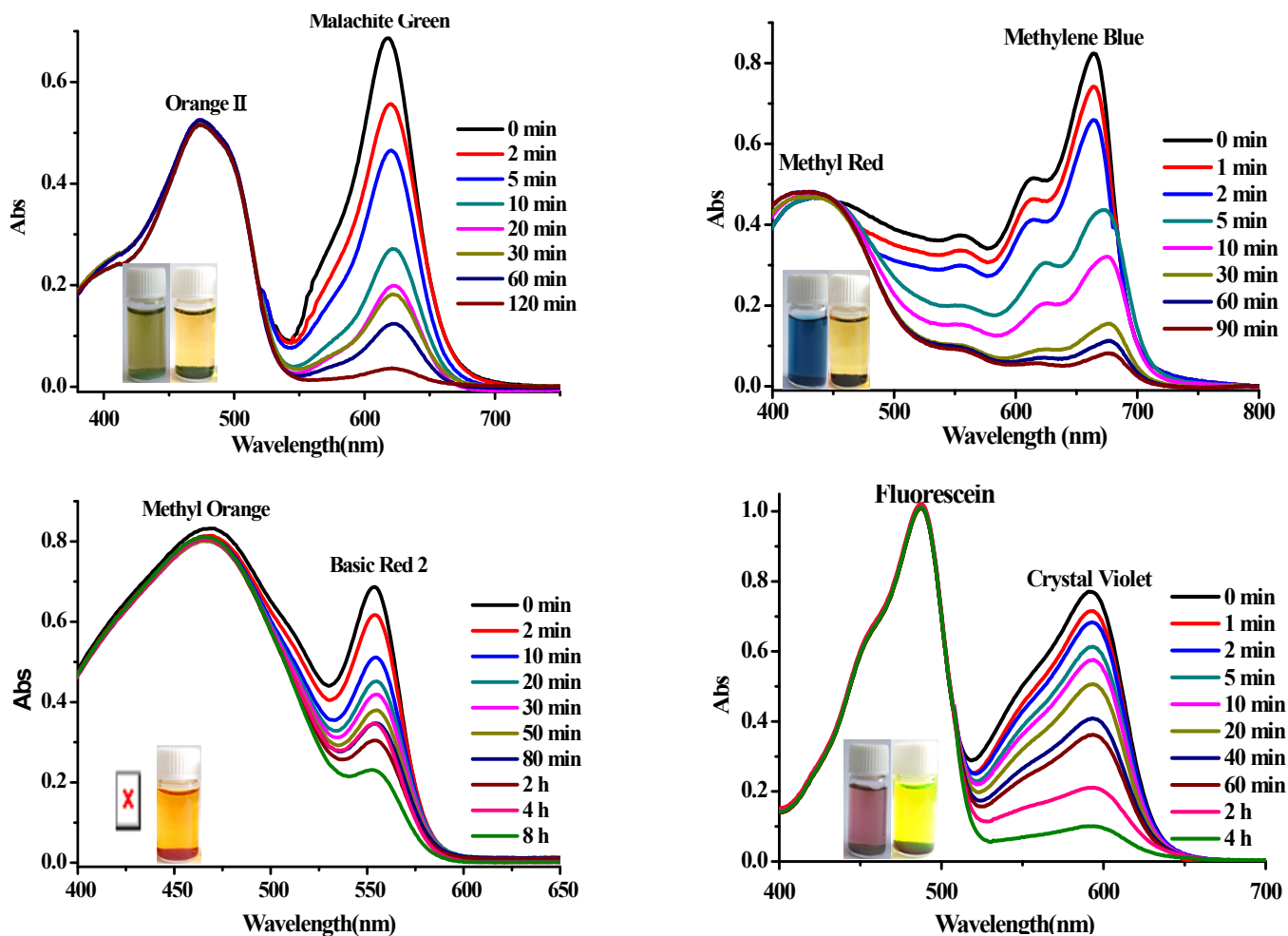
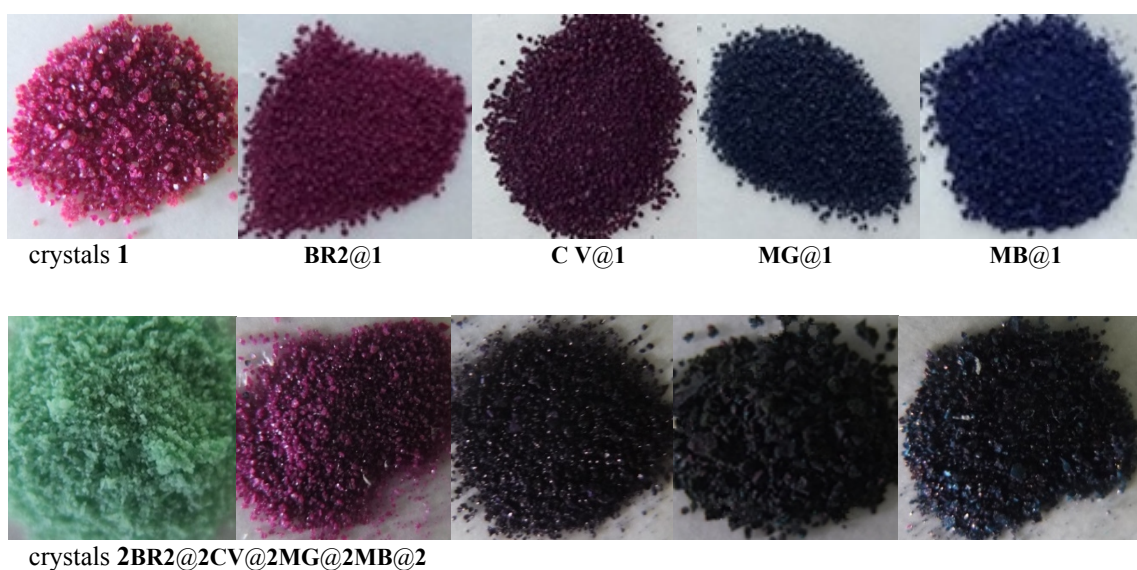


Figure S11. TG curves of as-synthesized 2, acetone activated 2 and H<sub>2</sub>O soaked 2.



**Figure S12.** UV-Vis spectra of selective adsorption and separation dye molecules in aqueous solution for 2: (a) CV&Fluorescein; (b) MB&MR; (c) MG&Orange II and (d) BR2&MO.



**Figure S13.** Photographs of crystals 1; BR2@1; CV@1; MG@1 and MB @1 (top) and crystals 2; BR2@2; CV@2; MG@2 and MB@2 (bottom).



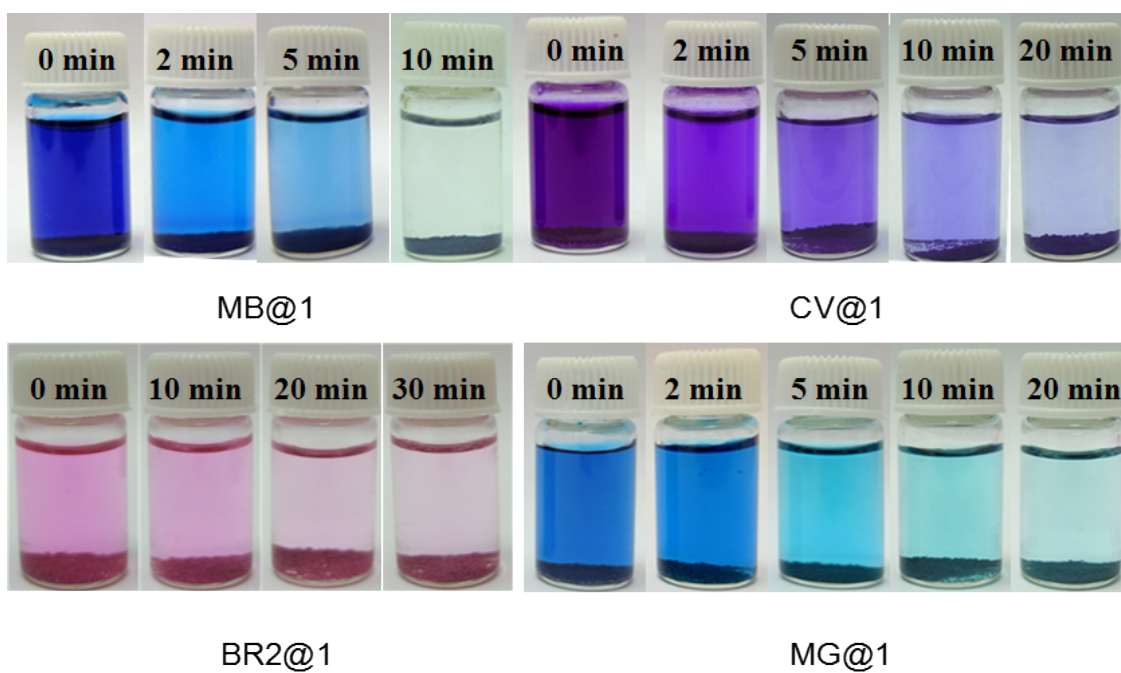


Figure S14. Photographs of 20 mg crystals 1 soaked in 2 mL dyes solution (40 ppm), MB@1; CV@1; BR2@1 and MG@1.

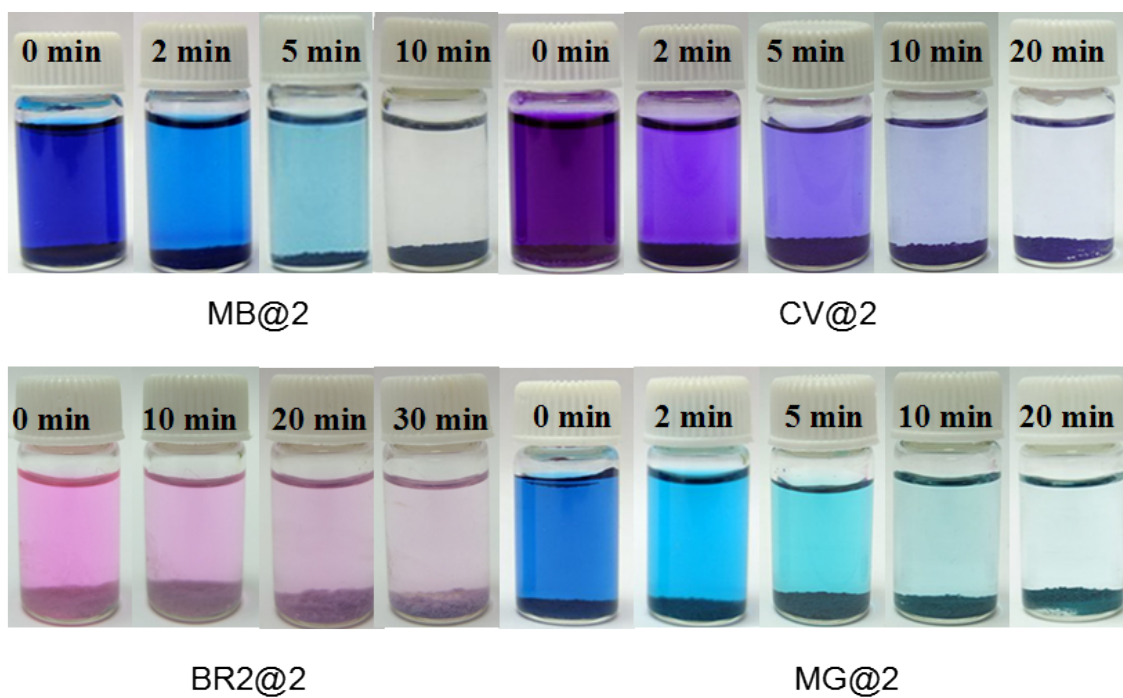
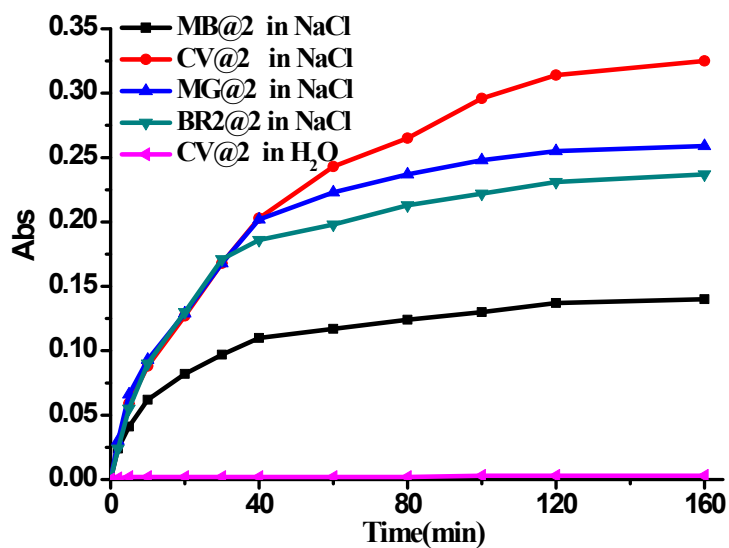
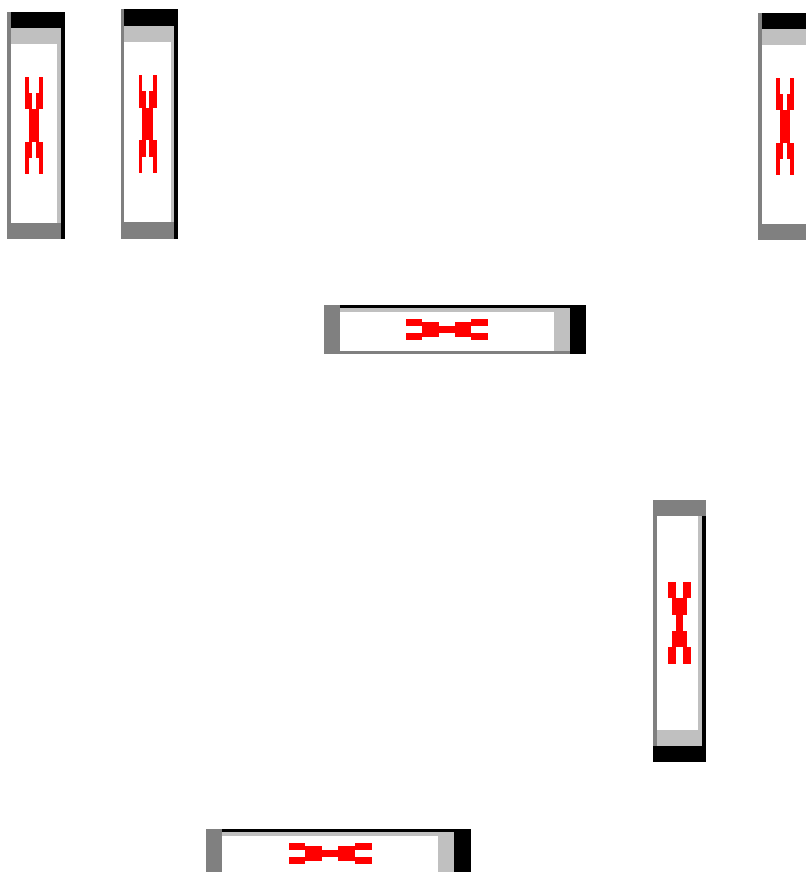


Figure S15. Photographs of 20 mg crystals 2 soaked in 2 mL dyes solution (40 ppm), MB@2; CV@2; BR2@2 and MG@2.



**Figure S16.** The four kinds of cationic dyes release from the dye@2 in a saturated NaCl aqueous solution and deionized water recorded by UV-Vis spectra, respectively.



0 min    2 min    5 min    10 min    20 min    40 min

Figure S17. Photographs of column chromatography experiment (CV@compound 2)

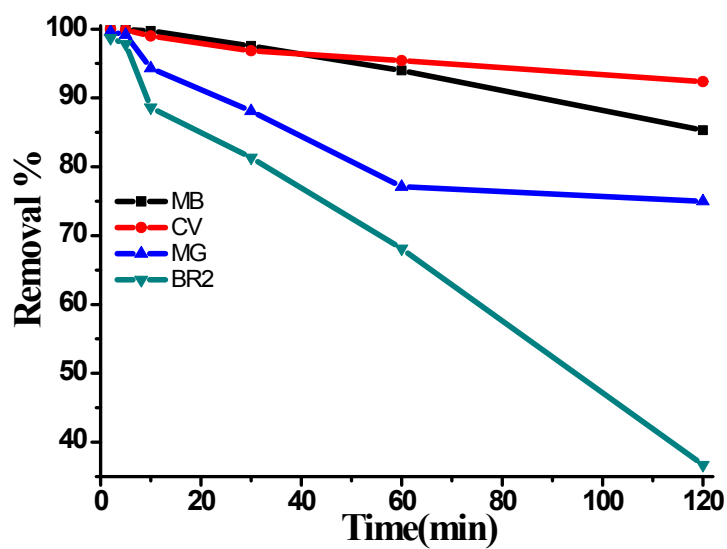


Figure S18. The UV-Vis spectra of removal percent during the four kinds of dyes passed through the MOF chromatographic column in which the crystals of 2 as the filler, respectively.

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