Dye adsorption performance of an anionic Cd^{2+} MOF material based on semi-rigid hexacarboxylic acid

Yuxuan Xiong, Dandan Li, Jie-Hui Yu[a,*] and Qingfeng Yang[b,*]

a. College of Chemistry, and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, Jilin, 130012, P. R. China

b. State Key Laboratory Cultivation Base of Natural Gas Conversion, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, 750021, P. R. China

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Equation S2.

Materials and physical measurements

All chemicals were of reagent grade quality and obtained from commercial sources without further purification. Cadmium chloride ($CdCl_2 \cdot 1.5H_2O$), N,N-dimethylacetamide (C_4H_9NO, DMA, ⩾99%), nitric acid (HNO_3, ⩾98%) were obtained from Aladdin Chemistry Co., Ltd. Methylene blue, Rhodamine B, Azure A chloride, Bromocresol Purple and Methyl Orange were bought from Beijing Chemical Works. H_6L=5,5',5''-(benzene-1,3,5-triyltris(oxy)) triisophthalic acid was purchased from Jinan Heng Hua technology Co., Ltd. Powder X-ray diffraction (XRD) data were collected on a Rigaku/max-2550 diffractometer with Cu-Kα radiation (λ = 1.5418 Å) at 298 K. Elemental analysis for C, H and N was performed on a Perkin-Elmer 2400LS II elemental analyzer. Infrared (IR) spectrum was recorded on a Perkin Elmer Spectrum 1 spectrophotometer in 4000-450 cm-1 region using a powdered sample on a KBr plate at 298 K. Thermogravimetric analysis (TGA) was collected on a NETZSCH STA 459F3 analyzer with a ramp rate of 10 °C per minute from 40 °C to 800 °C under air flow. Ultraviolet-Visible (UV-Vis) spectra were measured on a Shimadzu UV-1601PC spectrophotometer at room temperature.

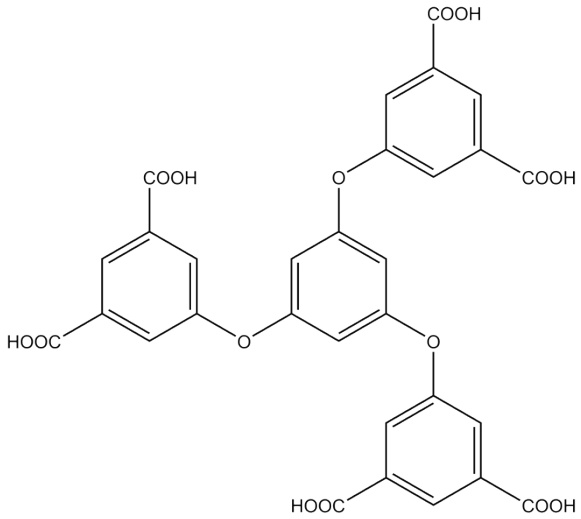

Chart S1. Molecular structure of H_6L.

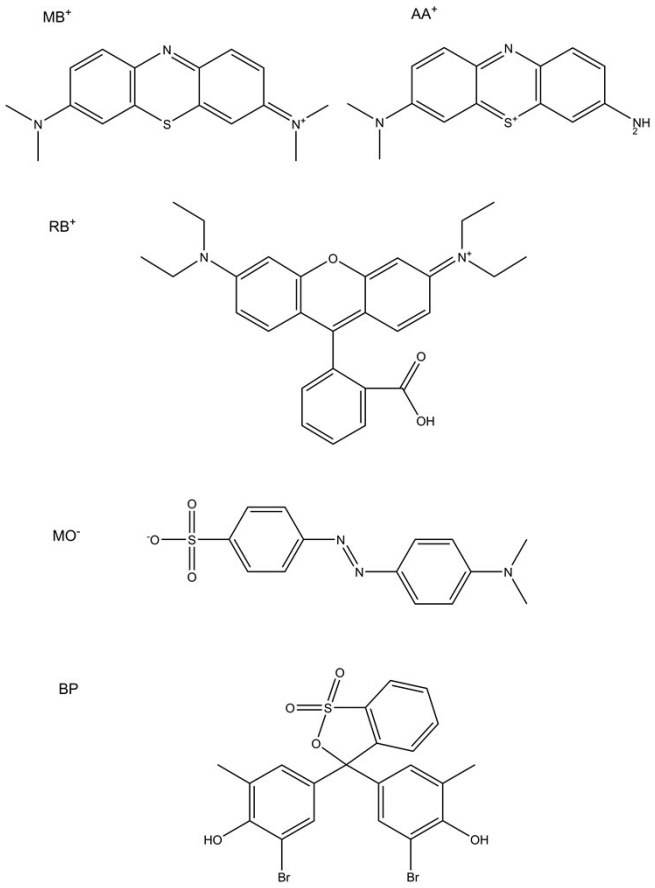

Chart S2. Molecular structure of five dyes.

Table S1. Crystallographic parameters of MOF-1.

Formula	$C_{46}H_{59}N_5O_{20}Cd_2$
M	1226.82
T (K)	301(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	10.1258(10)
b (Å)	17.1023(18)
c (Å)	17.3953(18)
α (°)	98.8930(3)
β (°)	105.7720(3)
γ (°)	100.3190(3)
V (Å^3)	2785.6000(5)
Z	2
D_c (g·cm^{-3})	0.998
μ (mm^{-1})	0.804
Reflections collected	33660
Unique reflections	9792
R_{int}	0.1024
Gof	1.119
R_1, $I>2\sigma(I)$	0.0967
wR_2, all data	0.3165

Table S2. Selected bond lengths [Å] and angles [°] for MOF-1.

Cd(1)-O(1)	2.231(7)	O(1)-Cd(1)-O(7)#1	139.2(3)
Cd(1)-O(7)#1	2.244(8)	O(1)-Cd(1)-O(12)#2	95.6(3)

Cd(1)-O(12)#2	2.293(7)	O(7)#1-Cd(1)-O(12)#2	101.6(3)
Cd(1)-O(4)#3	2.356(8)	O(1)-Cd(1)-O(4)#3	84.2(3)
Cd(1)-O(8)#1	2.471(8)	O(7)#1-Cd(1)-O(4)#3	123.7(3)
Cd(1)-O(3)#3	2.531(7)	O(12)#2-Cd(1)-O(4)#3	108.1(3)
Cd(1)-O(2)	2.584(7)	O(1)-Cd(1)-O(8)#1	102.7(3)
Cd(1)-C(16)#1	2.697(10)	O(7)#1-Cd(1)-O(8)#1	54.7(3)
Cd(2)-O(11)#4	2.191(8)	O(12)#2-Cd(1)-O(8)#1	156.2(3)
Cd(2)-O(5)#5	2.280(8)	O(4)#3-Cd(1)-O(8)#1	89.0(3)
Cd(2)-O(3)	2.289(8)	O(1)-Cd(1)-O(3)#3	131.2(3)
Cd(2)-O(10)#2	2.320(8)	O(7)#1-Cd(1)-O(3)#3	88.4(3)
Cd(2)-O(9)#2	2.388(9)	O(12)#2-Cd(1)-O(3)#3	79.7(3)
Cd(2)-O(6)#5	2.436(9)	O(4)#3-Cd(1)-O(3)#3	52.9(2)
Cd(2)-C(23)#2	2.685(12)	O(8)#1-Cd(1)-O(3)#3	98.9(3)
Cd(2)-C(15)#5	2.695(11)	O(1)-Cd(1)-O(2)	53.3(3)
O(3)-Cd(1)#6	2.531(7)	O(7)#1-Cd(1)-O(2)	91.2(3)
O(4)-Cd(1)#6	2.356(8)	O(12)#2-Cd(1)-O(2)	85.8(3)
O(5)-Cd(2)#7	2.280(8)	O(4)#3-Cd(1)-O(2)	136.8(3)
O(6)-Cd(2)#7	2.436(9)	O(8)#1-Cd(1)-O(2)	93.0(3)
O(7)-Cd(1)#1	2.244(8)	O(3)#3-Cd(1)-O(2)	165.1(3)
O(8)-Cd(1)#1	2.471(8)	O(2)-Cd(1)-C(16)#1	92.9(3)
O(9)-Cd(2)#2	2.388(9)	O(3)-Cd(2)-O(10)#2	95.6(3)
O(10)-Cd(2)#2	2.320(7)	O(11)#4-Cd(2)-O(9)#2	84.8(3)
O(11)-Cd(2)#4	2.191(8)	O(3)-Cd(2)-O(9)#2	108.3(3)
O(12)-Cd(1)#2	2.293(7)	O(10)#2-Cd(2)-O(9)#2	55.0(3)

Symmetry transformations used to generate equivalent atoms: #1: -x+1, -y+1, -z+1; #2: -x+1, -y+2, -z+1; #3: x+1, y, z; #4: -x, -y+2, -z+1.

Table S3. A comparison of adsorption capacity of MB^+ for various materials.

Adsorbents	Adsorption capacity ($mg \cdot g^{-1}$)	Reference
MFC@NH_2-UiO-66	49.16	45
NH_2-UiO-66	63.70	45
T-CMP	128.32	46
Mn@RS	128.5	47
MoS_2 nanosheets	146.43	48
P-(EA-β-CD/KHA/AC) hydrogel	262.31	49
MC-Mn@RS	325.8	47
Fe_3O_4@MIL-100(Fe)	487.8	50
$H_3PW_{12}O_{40}$@ZIF-8	810	51
$([(CH_3)_2NH_2][Cd(L)DMA] \cdot 0.5DMA \cdot 1.5H_2O$	900	38
MOF-1	1220	This work

H_3L= 4,4',4"-s-triazine-2,4,6-tribenzoic acid

Table S4. Kinetic Parameters for MB^+ adsorption for various materials

Adsorbents	Adsorption capacity ($mg \cdot g^{-1}$)			Temperature/K	Reference
	$C_0/mg \cdot L^{-1}$	$k_2/g \cdot mg^{-1} \cdot min^{-1}$	R^2		
MIL-100(Fe)	400	0.936×10^{-5}	0.995	303	52
MIL-100(Cr)	400	1.713×10^{-4}	0.997	303	52
Fe_3O_4@MIL-100(Fe)	10	4×10^{-4}	0.9995	310	50
P-(EA-β-CD/KHA/AC) hydrogel	200	1.2437×10^{-3}	0.99992	298	49

MOF-1	10	1.77×10^{-3}	0.992	298	This work

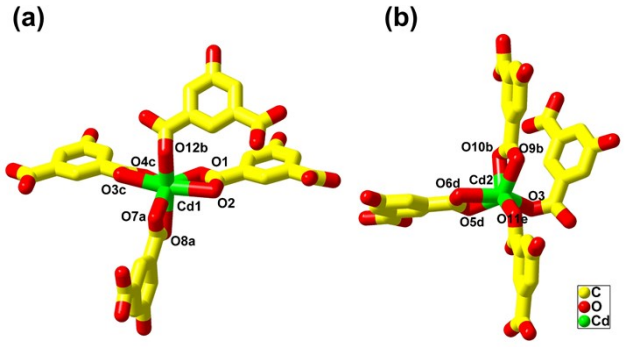

Figure S1. Coordination environment around Cd1 (a) and Cd2 (b) (a: 1 – x, 1–y, 1–z; b: 1 – x, 2 – y, 1 – z; c: x + 1, y, z; d: x – 1, y, z; e: -x, 2 – y, 1 – z).

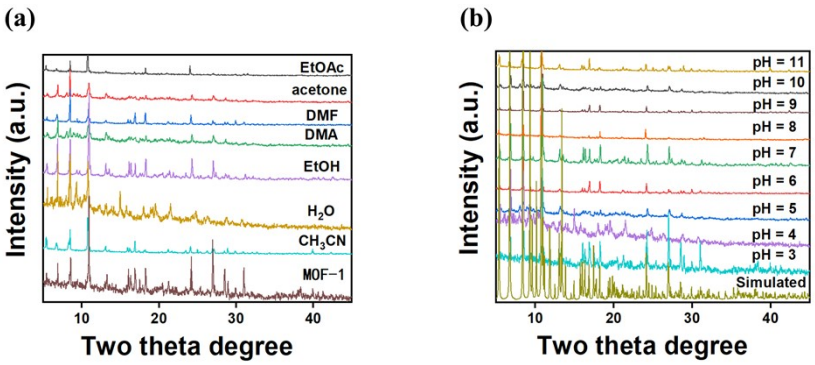

Figure S2. Powder XRD patterns of MOF-1' in different solvents (a) and in deionised water at pH = 3-11 (b).

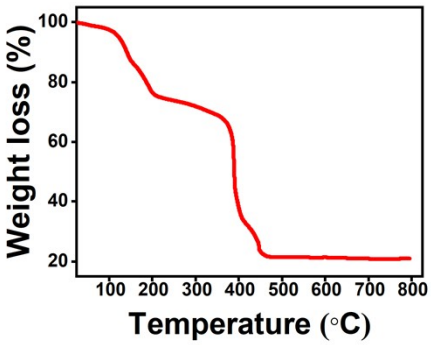

Figure S3. TG curve of MOF-1.

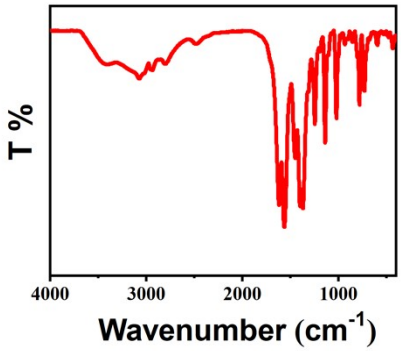

Figure S4. IR spectra of MOF-1.

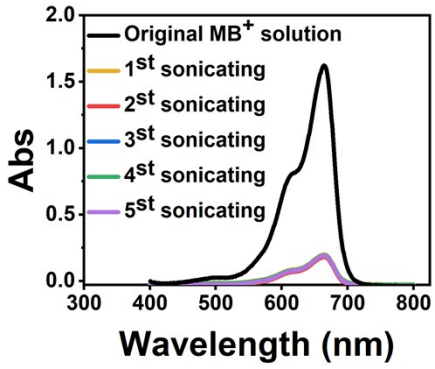

Figure S5. Desorption amount of MB^+ *vs.* sonicating number plots for MOF-1'-1.

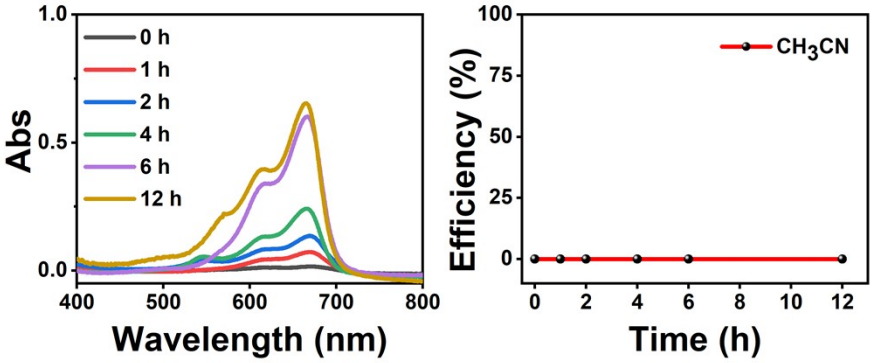

Figure S6. Temporal evolution of UV-vis spectra absorption of MOF-1'-1 loaded with 1 mg MB^+ in 40 ml saturated NaCl acetonitrile (a); Temporal evolution of UV-vis spectra absorption of MOF-1'-1 loaded with 1 mg MB^+ in 40 ml pure acetonitrile solution (b).

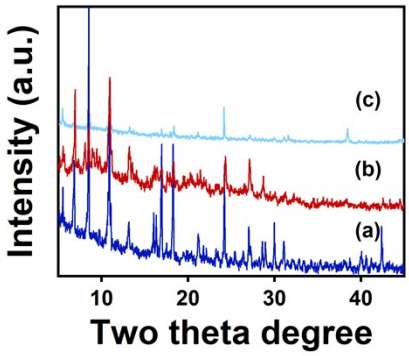

Figure S7. Powder XRD patterns of MOF-1' (a), MOF-1' after one cycles of MB^+ desorption (b) and MOF-1' after five cycles of MB^+ desorption (c).

Equation S1.

$$qe = \frac{V\left(c_0 - c_e\right)}{m} \qquad \text{* MERGEFORMAT (S1)}$$

In which q_e: equilibrium removal capacity (mg·g^{-1}), C_0: initial concentration of dye solution (mg·L^{-1}), C_e: equilibrium concentration of dye solution (mg·L^{-1}), V: solution volume (L), and m: adsorbate mass (g).

Equation S2.

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \text{* MERGEFORMAT (S2)}$$

where q_t represents adsorbed amount at moment t (mg·g^{-1}), q_e is adsorbed amount at equilibrium moment (mg·g^{-1}), t is adsorption time (min), and k_2 is adsorption rate constant (g·mg^{-1}·min^{-1}).