Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Materials and Methods

All the reagents to perform synthesis obtained from commercial sources were of analytical grade and used without further purification. Powder X-ray diffraction (PXRD) data were collected using Bruker ADVANCE X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) at 50 kV, 20 mA with a scanning rate of 6°/min and a step size of 0.02°. Fourier transforms infrared (FT-IR) spectrum for **1** in KBr disc was recorded on Nicolet Impact 750 FTIR in the range of 400-4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. The photocatalytic investigations were carried out using Shimadzu UV-Vis 2501PC recording spectrophotometer.

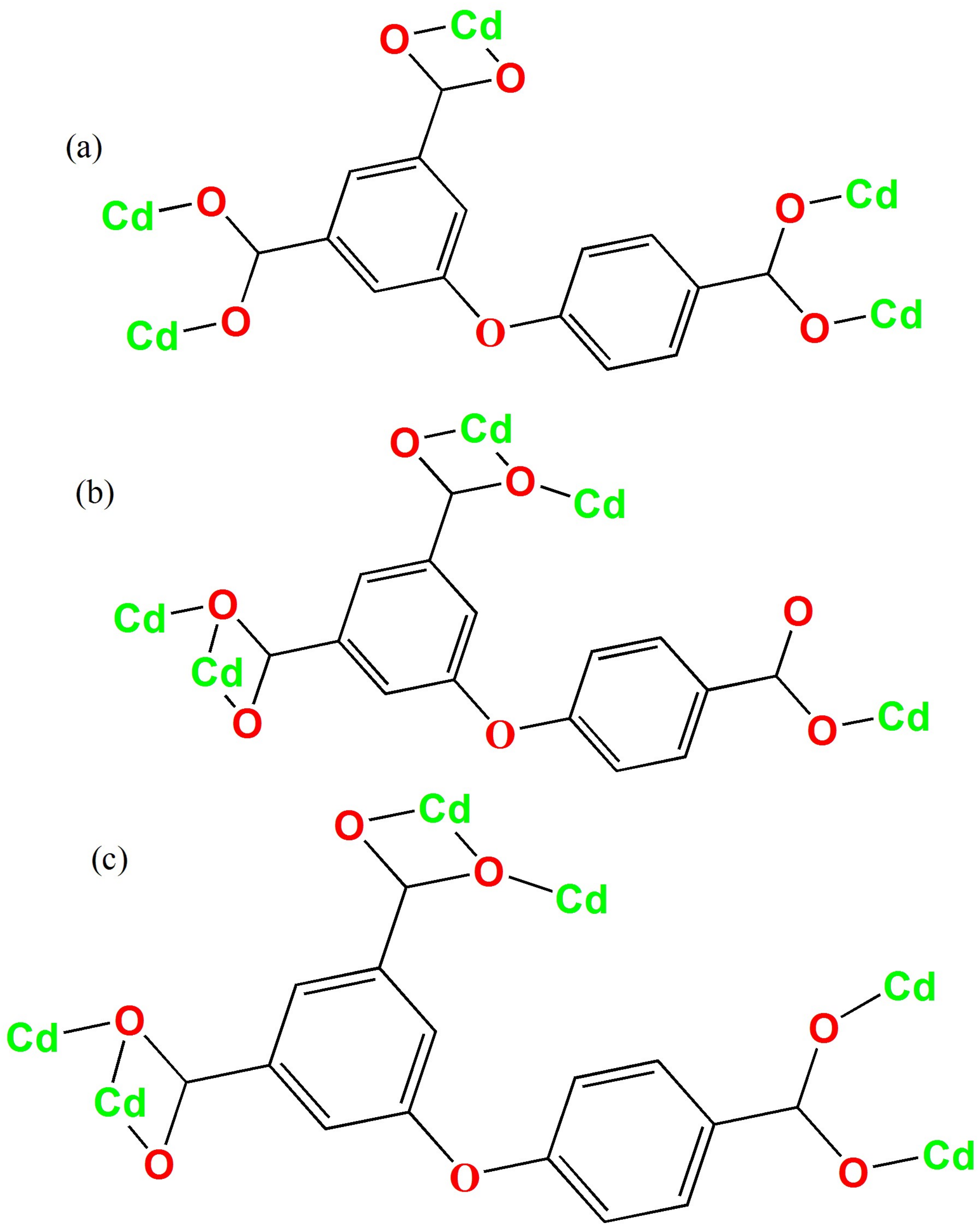
X-ray Crystallography

The single crystal X-ray diffraction data for **1-2** was collected using Bruker SMART APEX diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å) employing ω-scan technique. The structure was solved by direct method (SHLEXS-2014) and refined using the full-matrix least-square procedure based on F^2 (Shelxl-2014). All the hydrogen atoms were generated geometrically and refined isotropically employing riding model while non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details and selected bond dimensions for **1-2** are listed in Tables S1-S3, respectively. CCDC number: 2183494-2183495.

Photocatalytic Method

The finely divided powder of **1** or **2** (40 mg) was dispersed in 50 mL aqueous solutions of MB, MO and Rh B (10 mg/L) and the mixtures were stirred in dark for 30 min to ensure the establishment of adsorption-desorption equilibrium. The photocatalytic degradations of dyes were conducted on UV-400 type photochemical reactor having 100 W mercury lamp (mean wavelength 365 nm). Aliquots of 5.0 mL were isolated at specified time intervals and separated through centrifugation and then subsequently the intensity of UV-Vis bands of dyes were recorded using UV–visible spectrophotometer. These control experiments were also conducted where the photodecompositions of dyes were performed under the identical conditions without adding **1** and **2**.

The electrochemical measurements were performed in an electrochemical workstation (CHI660C Apparatuses) with a three electrode system, including a saturated calomel reference electrode, a platinum auxiliary electrode and a glassy carbon disk electrode (GCE, 3 mm). Samples and 0.5 mL DMF were well mixed into a 5 mL centrifuge tube to form a uniform suspension under sonificatio. 5.0 μL Samples **1**/**2** suspension was coated on the GCE surface to prepare a working electrode. 0.2 M Na_2SO_4 solution was used as the electrolyte in the all electrochemical measurements. EIS plots were recorded under dark circumstance at open circuit potential in the frequency range between 10^{-2} and 10^5 Hz. The ozone gas (30 mg/L, 25 mL/min) was inlet into the Na_2SO_4 solution for 30 min if needed. The Mott-Schottky measurement was conducted to measure the band positions of the samples using impedance-potential model.



Scheme S1 view of the different coordination mode of H_3L in this work.

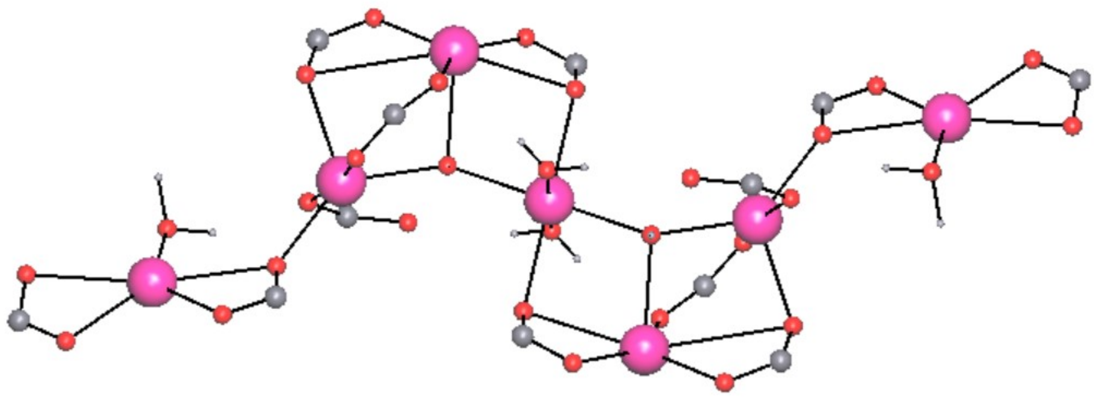


Fig. S1 view of the $[Cd_7(COO)_{12}]$ node.

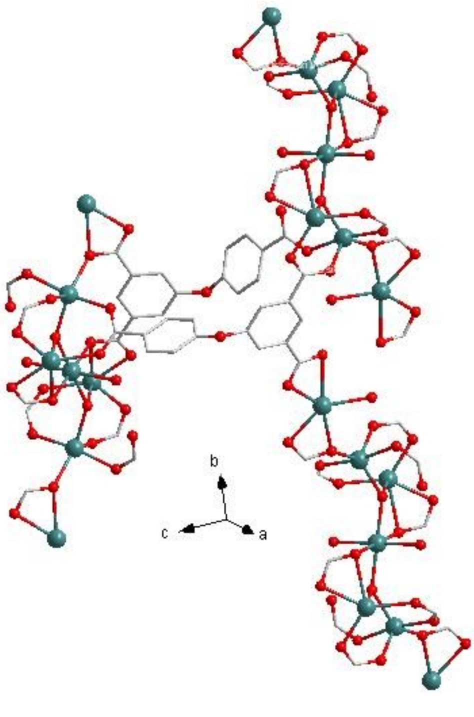


Fig. S2 view of the connections of the adjacent $[Cd_7(COO)_{12}]$ nodes.

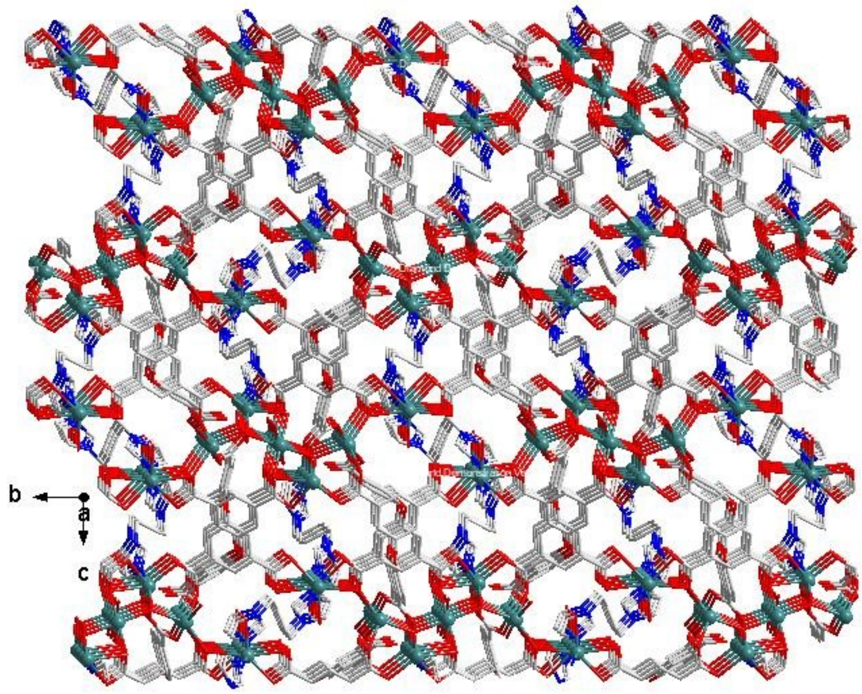


Fig.S3 the 3D supramolecular nework.

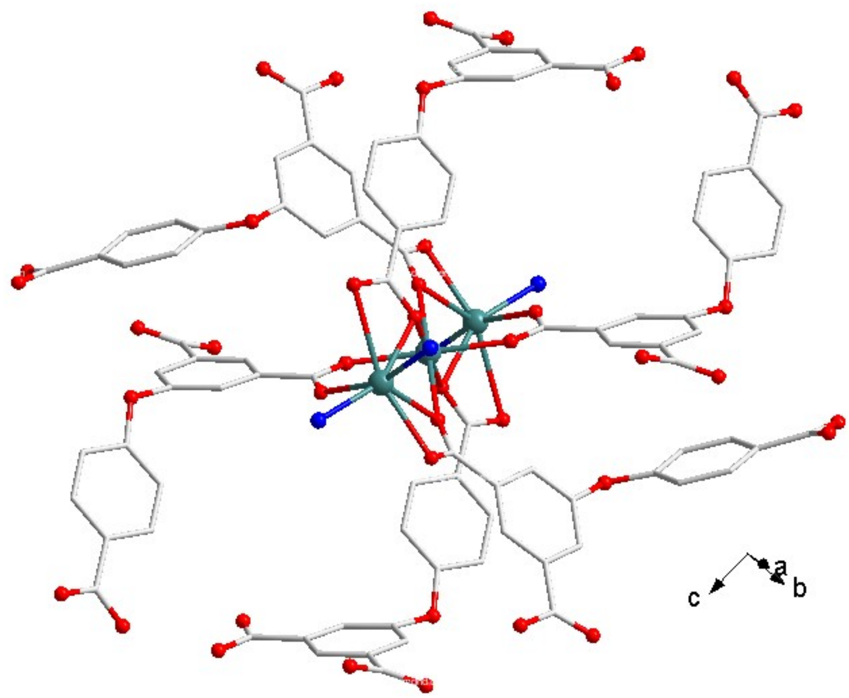


Fig. S4 view of the a trimeric [Cd_3(COO)6] SBU in **2**.

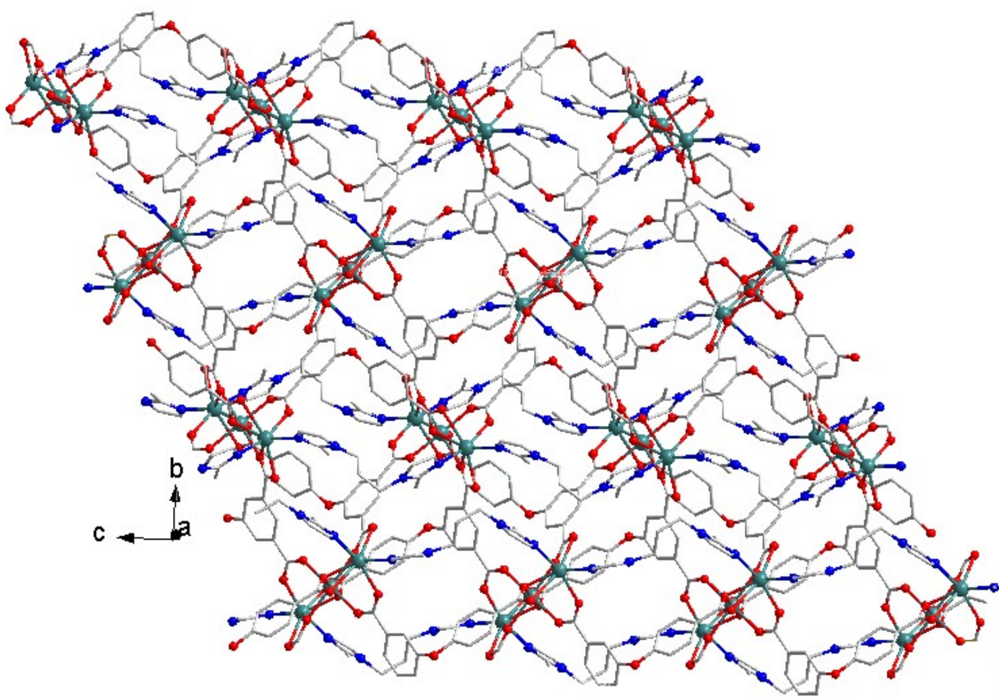


Fig. S5 view of the 2D layer in 2.

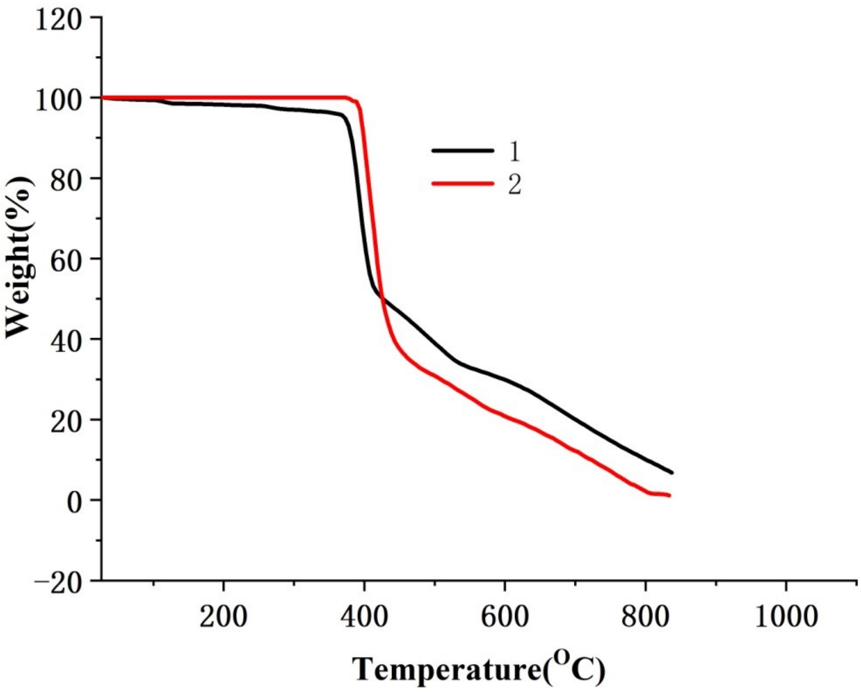


Fig. S6 view of the TGA.

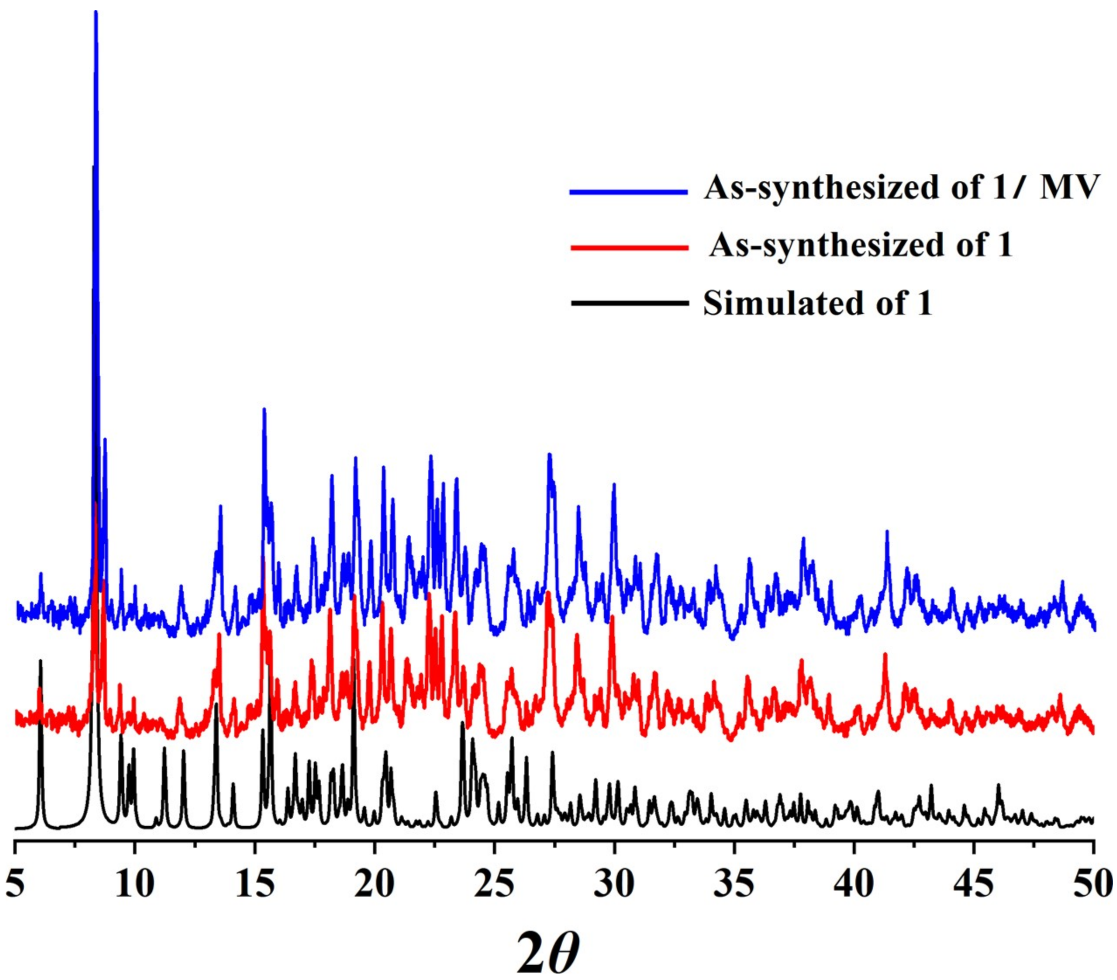


Fig. S7 view of the PXRD patterns of as-synthesized and after photocatalysis of MV in **1**.

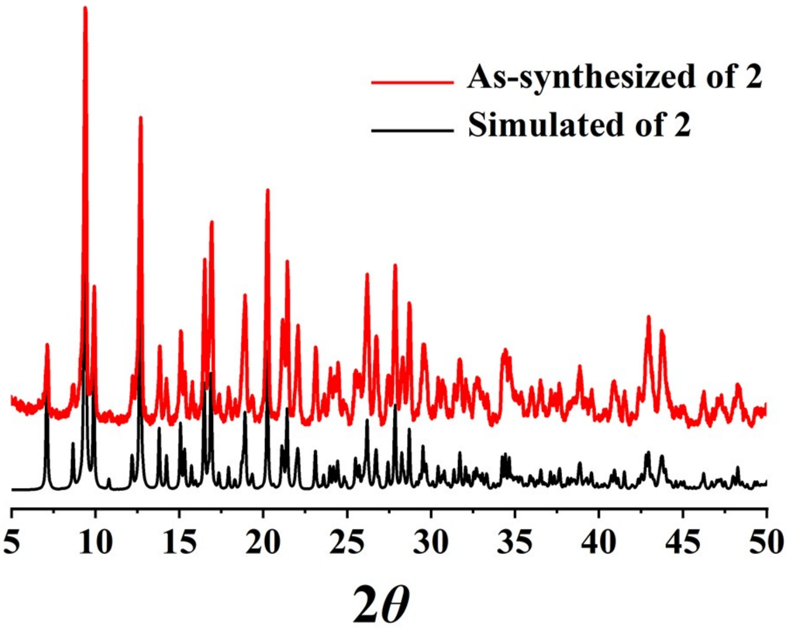


Fig. S8 the PXRD pattern of as-synthesized sample in **2.**

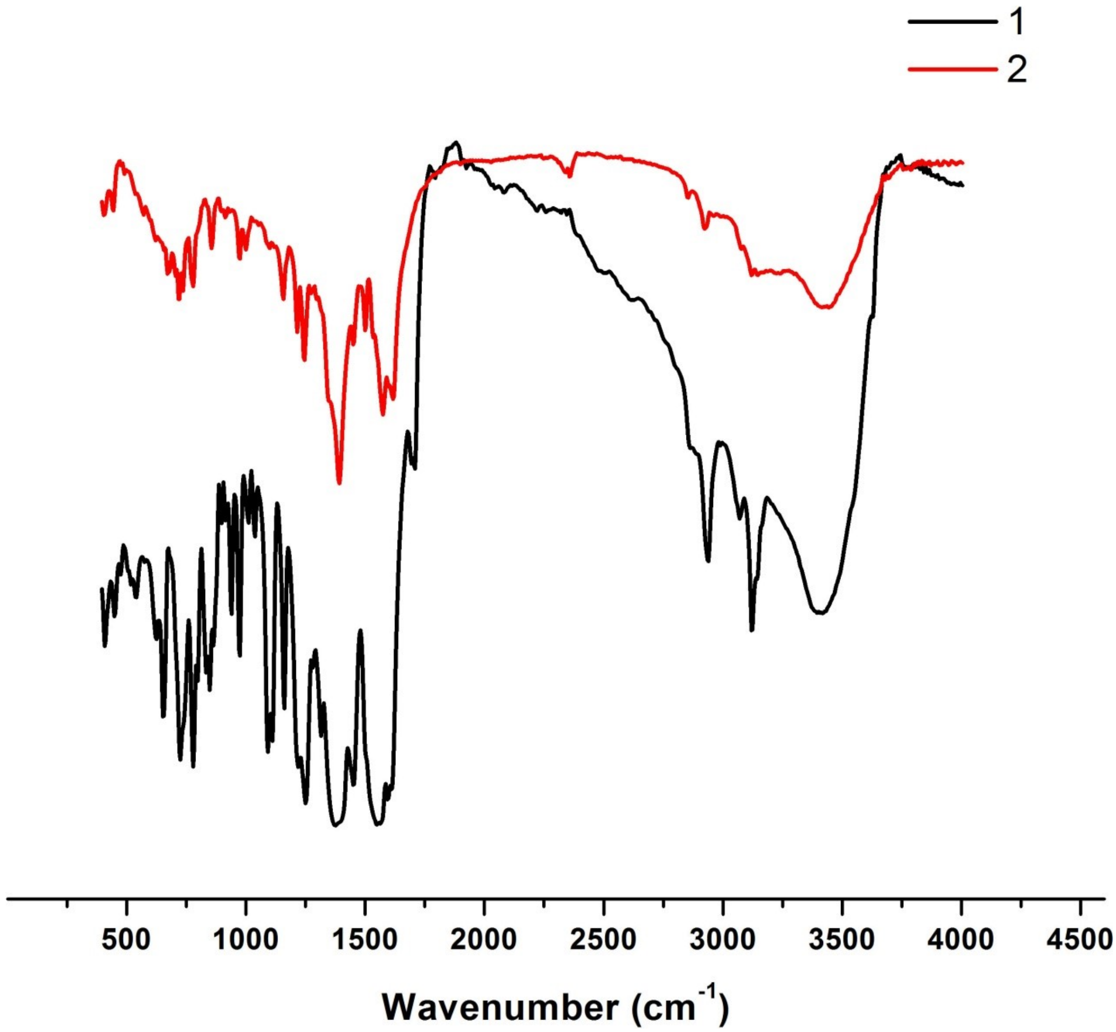


Fig. S9 view of the IR.

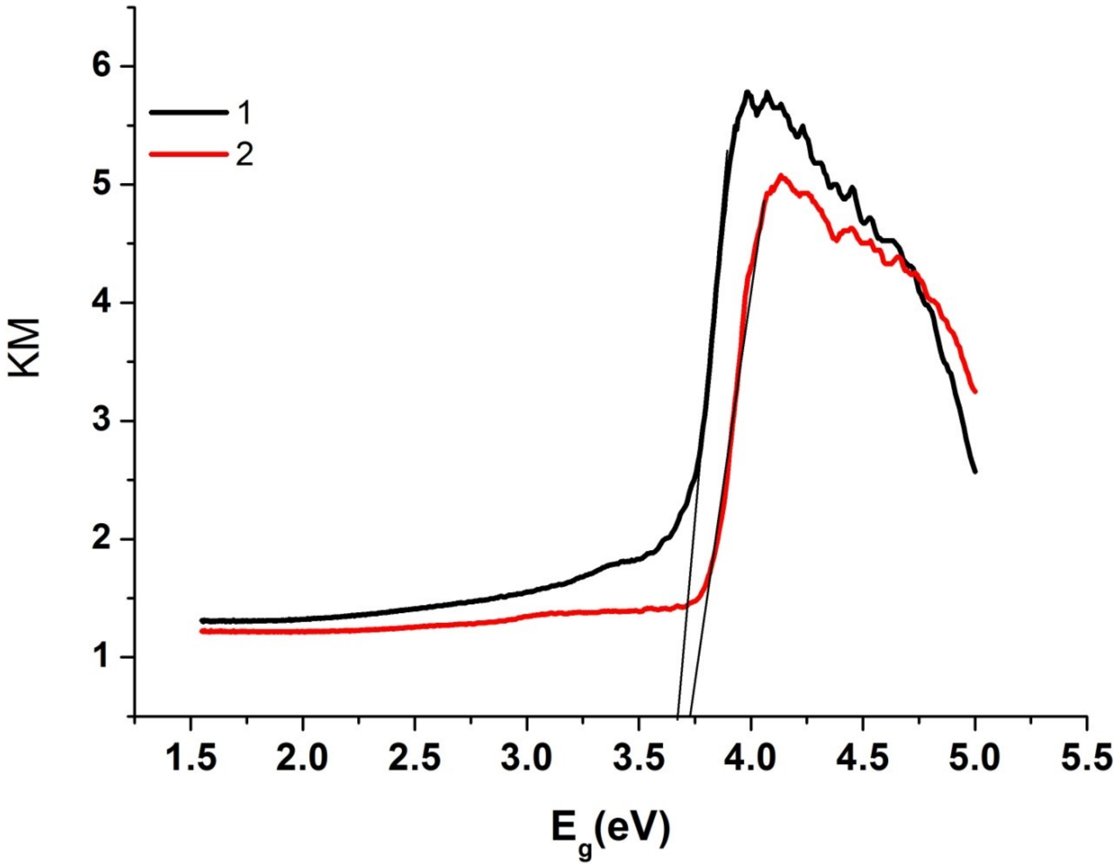


Fig. S10 UV-vis spectrum of **1** and **2.**

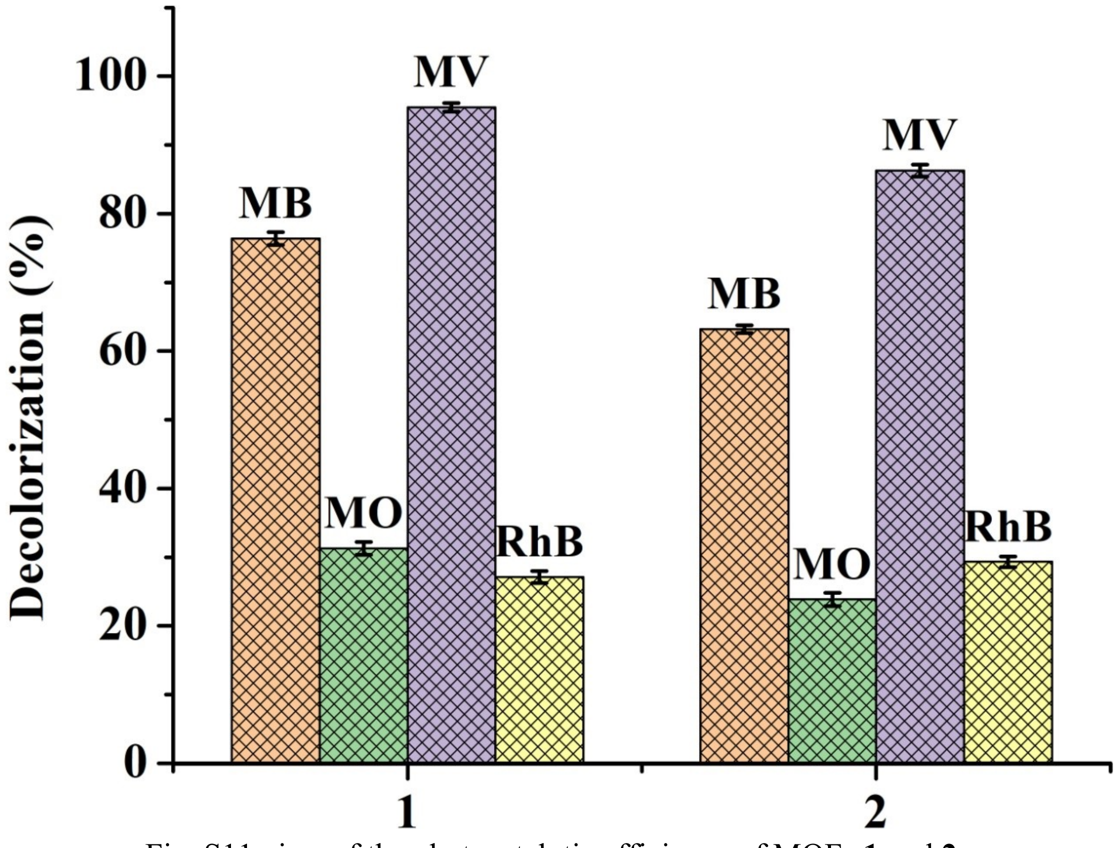


Fig. S11 view of the photocatalytic efficiency of MOFs **1** and **2.**

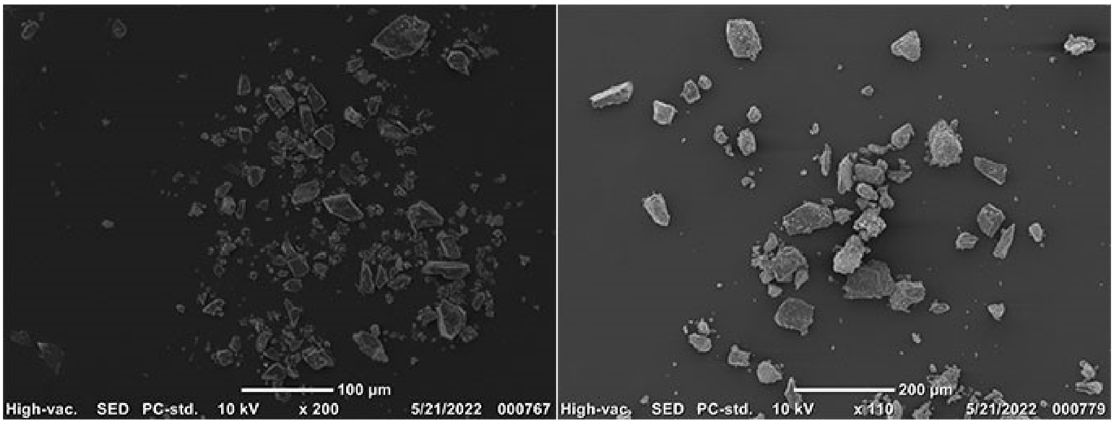


Fig. S12 the appearance of SEM before and after the catalytic experiment.

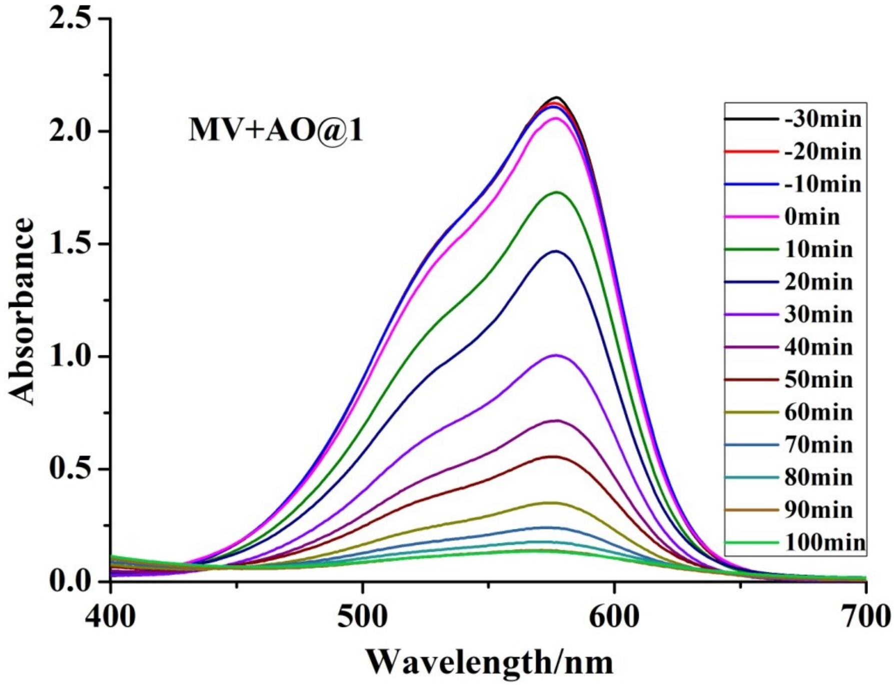


Fig. S13 Time-dependent UV-vis absorption spectra of **1+AO** in MV solution.

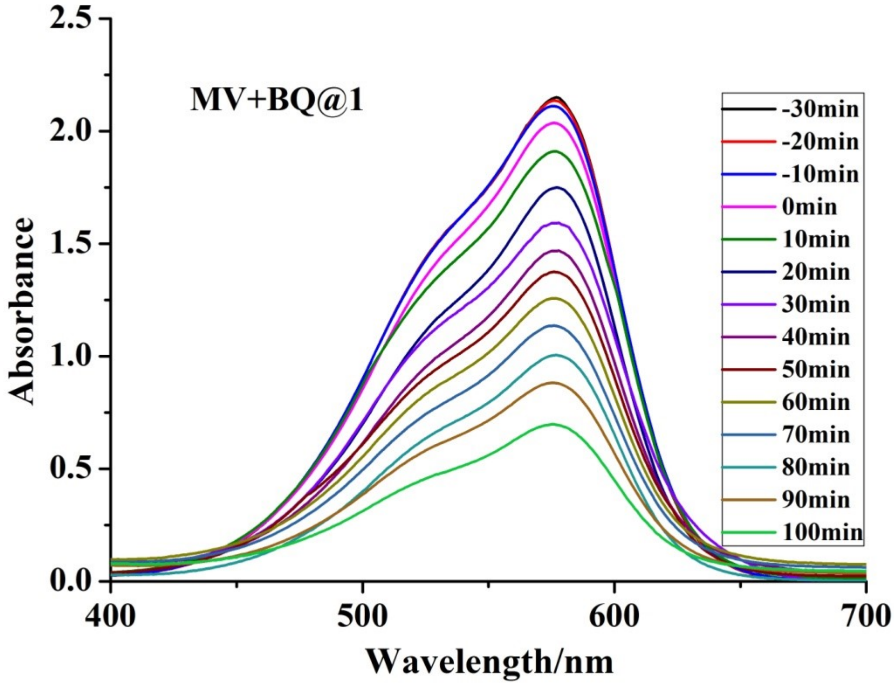


Fig. S14 Time-dependent UV-vis absorption spectra of **1+BQ** in MV solution.

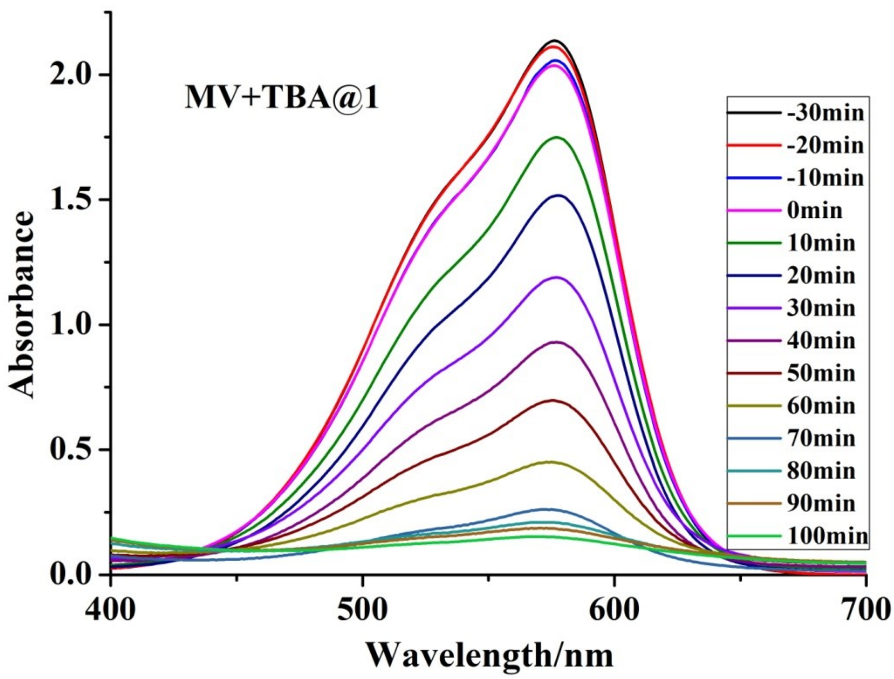


Fig. S15 Time-dependent UV-vis absorption spectra of **1+TBA** in MV solution.

Table S1 view of the photocatalytic efficiencies of **1**and **2**.

	Blank	**1**	**2**
MB	**11.58%**	**76.4 %**	**63.2 %**
MO	**18.98%**	**31.28 %**	**23.86%**
MV	**28.92%**	**95.5 %**	**86.28 %**
RhB	**18.91%**	**27.13 %**	**29.32 %**

Table S2 The fitting parameters of photocatalytic process

Material	***k*** **(min^{-1})**	***R^2***
1+MB	**0.01174**	**0.99288**
1+MO	**0.00326**	**0.98976**
1+MV	**0.02288**	**0.98436**
1+RhB	**0.00230**	**0.97677**
AO+MV@1	**0.03210**	**0.98691**
BQ+MV@1	**0.00866**	**0.99522**
TBA+MV@1	**0.03016**	**0.97020**
2+MB	**0.00860**	**0.98797**
2+MO	**0.00221**	**0.98008**
2+MV	**0.02215**	**0.98863**

2+RhB	**0.00257**	**0.97937**

Table S3. Crystallographic data and structure refinement details for 1-2

Parameter	**1**	**2**
Formula	$C_{90}H_{80}Cd_7N_{12}O_{34}$	$C_{52}H_{46}Cd_3N_8O_{14}$
Formula weight	2660. 46	1344. 17
Crystal system	Monoclinic	Monoclinic
Space group	*P21/n*	*P21/c*
Crystal Color	Colorless	Colorless
a, Å	11.0799(7)	12.6780(12)
b, Å	20.0518(14)	17.8838(17)
c, Å	21.6998(14)	11.3101(11)
α, °	90	90
β, °	102.557(1)	101.053(2)
γ, °	90	90
V, Å^3	4705.8(5)	2516.8(4)
Z	2	2
ρ_{calcd}, g/cm^3	1.878	1.774
μ, mm^{-1}	1.644	1.333
F(000)	2624	1340
θ Range, deg	1.4-27.7	1.6-27.7
Reflection Collected	28422	14986
Independent reflections (R_{int})	0.051	0.029
Reflections with $I > 2\sigma(I)$	7719	4724
Number of parameters	661	351
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0547，0.1364	0.0295, 0.0768
R_1, wR_2 (all data)**	0.0865，0.1586	0.0411, 0.0905

* $R = \sum(F_o - F_c)/\sum(F_o)$, ** $wR_2 = \{\sum[w(F_{O(2)} - F_c^2)^2]/\sum(F_{O(2)})^2\}^{1/2}$.

Table S4. Selected bond distances (Å) and angles (deg) for **1-2**

		1	
Cd(1)-O(1)	2.198(5)	Cd(1)-O(14)	2.224(4)
Cd(1)-O(15)	2.216(4)	Cd(1)-O(5)#5	2.255(5)
Cd(1)-O(9)#5	2.245(6)	Cd(2)-O(12)	2.300(4)
Cd(2)-O(15)	2.220(4)	Cd(2)-O(16)	2.382(7)
Cd(2)-O(12)#4	2.300(4)	Cd(2)-O(15)#4	2.220(4)
Cd(2)-O(16)#4	2.382(7)	Cd(3)-O(4)	2.251(5)
Cd(3)-N(1)	2.257(7)	Cd(3)-O(11)#2	2.347(5)
Cd(3)-O(12)#2	2.538(4)	Cd(3)-O(2)#6	2.308(5)
Cd(3)-O(15)#6	2.315(5)	Cd(4)-O(17)	2.365(4)
Cd(4)-N(4)	2.276(7)	Cd(4)-N(5)	2.272(7)
Cd(4)-O(13)#1	2.412(4)	Cd(4)-O(14)#1	2.511(4)
Cd(4)-O(6)#3	2.317(4)	Cd(4)-O(7)#3	2.577(4)
		2	
Cd(1)-O(4)	2.274(3)	Cd(1)-N(1)	2.293(2)
Cd(1)-O(1)#1	2.680(3)	Cd(1)-O(2)#1	2.326(2)
Cd(1)-N(4)#1	2.336(3)	Cd(1)-O(6)#2	2.582(3)
Cd(1)-O(7)#2	2.395(3)	Cd(2)-O(5)	2.214(2)
Cd(2)-O(2)#1	2.287(2)	Cd(2)-O(6)#2	2.329(2)
Cd(2)-O(5)#3	2.214(2)	Cd(2)-O(2)#4	2.287(2)
Cd(2)-O(6)#5	2.329(2)		

		1	
O(1)-Cd(1)-O(14)	87.93(17)	O(1)-Cd(1)-O(1)5	95.3(2)
O(1)-Cd(1)-O(5)#5	88.71(19)	O(1)-Cd(1)-O(9)#5	170.2(2)
O(14)-Cd(1)-O(1)5	137.33(16)	O(5)#5-Cd(1)-O(14)	124.71(18)
O(9)#5-Cd(1)-O(14)	86.9(2)	O(5)#5-Cd(1)-O(1)5	97.93(19)
O(9)#5-Cd(1)-O(15)	94.2(2)	O(5)#5-Cd(1)-O(9)#5	87.5(2)
O(12)-Cd(2)-O(15)	97.67(16)	O(12)-Cd(2)-O(16)	85.39(19)
O(12)-Cd(2)-O(12)#4	180.00	O(12)-Cd(2)-O(15)#4	82.33(16)
O(12)-Cd(2)-O(16)#4	94.61(19)	O(15)-Cd(2)-O(16)	81.6(2)
O(12)#4-Cd(2)-O(15)	82.33(16)	O(15)-Cd(2)-O(15)#4	180.00
O(15)-Cd(2)-O(16)#4	98.4(2)	O(12)#4-Cd(2)-O(16)	94.61(19)
O(15)#4-Cd(2)-O(16)	98.4(2)	O(16)-Cd(2)-O(16)#4	180.00
O(12)#4-Cd(2)-O(15)#4	97.67(16)	O(12)#4-Cd(2)-O(16)#4	85.39(19)
O(15)#4-Cd(2)-O(16)#4	81.6(2)	O(4) -Cd(3)-N(1)	95.2(2)
O(4) -Cd(3)-O(11)#2	84.11(18)	O(4) -Cd(3)-O(12)#2	136.31(18)
O(2)#6-Cd(3)-O(4)	126.3(2)	O(4) -Cd(3)-O(15)#6	98.6(2)
O(11)#2-Cd(3)-N(1)	96.9(2)	O(12)#2-Cd(3)-N(1)	99.32(18)
O(2)#6-Cd(3)-N(1)	83.4(2)	O(15)#6-Cd(3)-N(1)	164.4(2)
O(11)#2-Cd(3)-O(12)#2	53.46(14)	O(2)#6-Cd(3)-O(11)#2	149.58(18)
O(11)#2-Cd(3)-O(15)#6	91.71(17)	O(2)#6-Cd(3)-O(12)#2	96.33(18)

O(12)#2-Cd(3)-O(15)#6	75.48(14)	O(2)#6-Cd(3)-O(15)#6	82.57(18)
O(17)-Cd(4)-N(4)	86.3(2)	O(17)-Cd(4)-N(5)	88.6(2)
O(13)#1-Cd(4)-O(17)	136.49	O(14)#1-Cd(4)-O(17)	83.63(18)
O(6)#3-Cd(4) -O(17)	135.21(18)	O(7)#3-Cd(4) -O(17)	84.71(18)
N(4)-Cd(4)-N(5)	171.3(2)	O(13)#1-Cd(4) -N(4)	90.6(2)
O(14)#1-Cd(4) -N(4)	86.06(18)	O(6)#3-Cd(4) -N(4)	86.6(2)
O(7)#3-Cd(4) -N(4)	99.3(2)	O(13)#1-Cd(4) -N(5)	88.3(2)
O(14)#1-Cd(4) -N(5)	86.41(18)	O(6)#3-Cd(4)-N(5)	102.0(2)
O(7)#3-Cd(4)-N(5)	87.1(2)	O(13)#1-Cd(4)-O(14)#1	52.86(14)
O(6)#3-Cd(4)-O(13)#1	87.73(15)	O(7)#3-Cd(4)-O(13)#1	138.40(14)
O(6)#3-Cd(4)-O(14)#1	139.74(14)	O(7)#3-Cd(4)-O(14)#1	166.80(14)
O(6)#3-Cd(4)-O(7)#3	53.12(14)		
		2	
O(4)-Cd(1)-N(1)	80.73(9)	O(2)#1-Cd(2)-O(2)#4	180.00
O(1)#1-Cd(1)-O(4)	85.33(8)	O(2)#1-Cd(2)-O(6)#5	104.29(8)
O(2)#1-Cd(1)-O(4)	88.08(8)	O(5)#3-Cd(2)-O(6)#2	84.92(8)
O(4)-Cd(1)-N(4)#1	162.22(9)	O(2)#4-Cd(2)-O(6)#2	104.29(8)
O(4)-Cd(1)-O(6)#2	81.54(8)	O(6)#2-Cd(2)-O(6)#5	180.00
O(4)-Cd(1)-O(7)#2	108.40(9)	O(2)#4-Cd(2)-O(5)#3	90.91(9)
O(1)#1-Cd(1)-N(1)	103.72(9)	O(5)#3-Cd(2)-O(6)#5	95.08(8)
O(2)#1-Cd(1)-N(1)	154.00(9)	O(2)#4-Cd(2)-O(6)#5	75.71(8)
N(1)-Cd(1)-N(4)#1	99.84(9)	O(6)#2-Cd(1)-N(1)	130.13(8)
O(7)#2-Cd(1)-N(1)	91.26(9)	O(1)#1-Cd(1)-O(2)#1	51.68(8)
O(1)#1-Cd(1)-N(4)#1	77.24(9)	O(1)#1-Cd(1)-O(6)#2	120.75(7)

Symmetry Codes: **For 1**: #1= 2+x, y, z; #2= -1/2-x,1/2+y,1/2-z; #3= 3/2-x,1/2+y,1/2-z; #4= -1-x,1-y,1-z; #5= -1/2+x,3/2-y,1/2+z; #6= 1/2+x,3/2-y,-1/2+z. **For 2**: #1 = x, y, -1+z; #2 = 1-x, 1/2+y, 1/2-z; #3 = 1-x, 1-y, -z; #4 = 1-x, 1-y, 1-z; #5 = x, 1/2-y, -1/2+z.