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Rapid mechanochemical synthesis of two new Cd(II) based metal-organic frameworks with high removal efficiency of congo red

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Two new three-dimensional porous Cd(II)-based metal−organic frameworks, $[Cd_2(oba)_2(4\text{-}bpdb)_2]_n\cdot(DMF)_x$ (**TMU-8**) and $[Cd(oba)(4,4'\text{-}bipy)]_n\cdot(DMF)_y$ (**TMU-9**) have been synthesized via mechanosynthesis, by using a nonlinear dicarboxylate and linear N-donor ligands then characterized by single-crystal X-ray crystallography. The effect of using different N-donor ligands 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) and 4,4′-bipyridine (4,4′-bipy) as pillars on the final structure has been studied. Also removal efficiency and order reaction kinetics of these MOFs in presence of congo red were investigated.

Introduction

Three-dimensional (3D) metal–organic frameworks (MOFs) are a new class of porous materials which are highly attractive because of their potential applications as functional materials in structure-dependent applications, such as gas storage and separation, ion exchange, sensing, catalysis, and drug delivery.[1-6] Recently, the removal of hazardous compounds using MOFs as adsorbent materials has been widely expanded due to the remarkable characteristics of well-defined channels and cavities of regular size and shape.[7-10]

The MOFs can be designed by choosing appropriate organic ligands and inorganic secondary building units (SBUs).[11-15] Of the many ligands that have been employed for preparation of MOF structures, using a combination of organic aromatic polycarboxylate ligands and N-donor ligands can generate multidimensional networks and interesting topologies.[16-20] V-shaped flexible dicarboxylate ligand 4,4′-oxybis(benzoic acid) (H_2oba), has already been proven to be efficient for generation of MOFs especially in combination with N-donor pillars.[21-23]

MOFs can be synthesized by different methods such as, conventional heating,[24-26] solvothermal reaction,[27, 28] sonochemistry,[29] microwave synthesis,[30, 31] mechanosynthesis[32-37] and other methods.[38, 39] Rapid development of MOFs necessitates rapid, economical and environmentally friendly approaches for their synthesis. Mechanosynthesis is a powerful alternative to conventional solution reactivity that has recently been shown to be effective for efficient and rapid synthesis of MOFs. Mechanochemical synthesis encompasses reactions conducted using mechanical force.[40-42] Mechanochemistry takes effect by milling or grinding solid reactants together through different efficient methodologies such as liquid-assisted grinding (LAG),[43, 44] ion- and liquid-assisted grinding (ILAG),[45] film grinding[46] or grinding–annealing.[47, 48]

Usage of synthetic dyes such as azo-dyes especially in the textile industries and the discharge of waste material containing these compounds with intensive color and toxicity into the aquatic systems, are considered as environmental threats.[49-51] Several methods including physical, chemical and biological methods have been investigated for removal of dye from waste water. Among them, removal of dye by adsorption technologies is regarded as one of the most competitive methods due to high efficiency, economic feasibility and simplicity of operation.[52-54] In this study we synthesized two new Cd(II) based MOFs by choosing oba oxygen donor ligand and investigating the effect of N-donor ligands 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) and 4,4′-bipyridine (4,4′-bipy) as pillars. Interestingly, both MOFs were synthesized easily and rapidly via mechanosynthesis. Also, we demonstrate the capability of two MOFs in removal of congo red dye.

Experimental section

Materials and Physical Techniques

All reagents for the synthesis and analysis were commercially available from Aldrich and Merck Company and used as received. The ligand 4-bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) was prepared by the reported method.[55] Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using Thermo Nicolet IR 100 FT-IR. The samples were characterized with a field emission scanning electron microscope (FE-SEM) ZEISS SIGMA VP (Germany) with gold coating.

The thermal behaviour was measured with a PL-STA 1500 apparatus with the rate of 10 ºC.min^{-1} in a static atmosphere of nitrogen. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with mono chromated Cu-K$_\alpha$ radiation. Elemental analyses were collected on a CHNS Thermo Scientific Flash 2000 elemental analyzer. A simultaneous inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Vista-PRO, Springvale, Australia) with a radial torch coupled to a concentric nebulizer and Scott spray chamber and equipped with a charge-coupled detector (CCD) was used for ICP measurements.

Data collection for **TMU-8** was performed at 100 K on a ADSC Quantum 210r Synchrotron, with Silicon Double Crystal monochromated MoK_α radiation, λ = 0.71073 Å. Data collection for **TMU-9** was performed at 100(2) K on a Bruker APEX II CCD area detector X-ray diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å).

The unit cell contains 8 higly disordered DMF molecules, the contribution of the solvent was removed from overall scattering by using PLATON/SQUEEZE program. Density, molecular weight and composition are given taking solvate molecules into account.

The structures were solved by direct methods and refined by refinement of F^2 against all reflections. Structure solution and refinement were accomplished using SIR97, SHELXL97 and WinGX.[56]

Synthesis of [$Cd_2(oba)_2(4\text{-bpdb})_2]_n{\cdot}(DMF)_x$ (**TMU-8**; where x varies depending on the synthetic methodology used; for mechanosynthesis: x = 0; for conventional heating: x = 3.5)

Conventional heating: Single crystals of **TMU-8** suitable for X-ray diffraction were obtained by mixing $Cd(NO_3)_2.4H_2O$ (0.308 g, 1 mmol), H_2oba (0.254 g, 1 mmol) and 4-bpdb (0.213 g, 1mmol) in 30 ml of DMF. This mixture was sonicated until all solid was uniformly dispersed (~ 3 minutes) and heated at 80 ˚C. After 72 hours, yellow crystals (0.459 g, yield 65% based on oba) of **TMU-8** were collected. d.p. >300 °C. IR data (KBr pellet, ν/cm^{-1}): 516(m), 657(m), 687(m), 783(m), 825(w), 875(m), 1011(w), 1091(m), 1160(m), 1238(vs), 1305(w), 1396(vs-br), 1540(vs), 1599(vs), 1672(vs), 2927(w), 3060(w) and 3439(w-br). Elemental analysis (%) calculated for $[Cd_2(C_{14}O_5H_8)_2(C_{12}H_{10}N_4)_2]{\cdot}(C_3NOH_7)_{3.5}$: C: 53.1, H: 4.3, N: 11.4; Found: C: 53.8, H: 4.4, N: 11.3.

Mechanochemical synthesis: **TMU-8** was also isolated after grinding $Cd(OAc)_2{\cdot}2H_2O$ (1 mmol), H_2oba (1 mmol) and 4-bpdb (1 mmol) by hand for 25 minutes. The resulting powder was washed with small amounts of DMF (3 ml) in order to remove any unreacted starting material, and then dried at 100 °C for 24 h (yield: 80%). IR data (KBr pellet, ν/cm-1): 516(m), 654(m), 685(m), 779(m), 816(w), 873(m), 1009(w), 1097(m), 1157(s), 1237(vs), 1311(w), 1390(vs-br), 1540(vs), 1599(vs), 2927(w), 3056(w) and 3425(m-br). Elemental analysis (%) calculated for $[Cd_2(C_{14}O_5H_8)_2(C_{12}H_{10}N_4)_2]$: C: 53.9, H: 3.1, N: 9.7; Found: C: 53.2, H: 2.8, N: 9.8.

Synthesis of [$Cd(oba)(4,4'\text{-bipy})]_n{\cdot}(DMF)_y$ (**TMU-9;** where y varies depending on the synthetic methodology used; for mechanosynthesis: x = 0; for conventional heating: x = 1)

Conventional heating: Colorless crystals of **TMU-9** were obtained using the same reaction conditions and ratios as used for the isolation of **TMU-8**, but using 4,4'-bipy instead of 4-bpdb. Yield: 0.376 g (63% based on oba). IR data (KBr pellet, ν/cm^{-1}): 501(s), 627(s), 656(m), 700(w), 785(s-br), 873(s), 1009(w), 1088(s), 1161(s), 1240(vs), 1398(vs-br), 1545(vs), 1599(vs), 1677(vs), 2929(w), 3058(w) and 3439(m-br). Elemental analysis (%) calculated for $[Cd(C_{14}O_5H_8)(C_{10}H_8N_2)]{\cdot}(C_3NOH_7)_1$: C: 54.2, H: 3.9, N: 7.0; Found: C: 53.8, H: 3.3, N: 7.3.

Mechanochemical synthesis: **TMU-9** was synthesized by grinding $Cd(OAc)_2{\cdot}2H_2O$ (1 mmol), H_2oba (1 mmol) and 4,4'-bipy (1 mmol) by hand for 20 minutes. The resulting powder was washed with small amounts of DMF (3 ml) in order to remove any unreacted reactants, and then dried at 100 °C for 24 h (Yield: 79%). IR data (KBr pellet, ν/cm-1): 498(w), 624(m), 654(w), 696(w), 780(m-br), 872(m), 1008(w), 1099(w), 1157(s), 1241(vs), 1393(vs-br), 1544(s), 1598(vs), 3063(w) and 3408(w-br). Elemental analysis (%) calculated for $[Cd(C_{14}O_5H_8)(C_{10}H_8N_2)]$: C: 54.9, H: 3.1, N: 5.3; Found: C: 54.2, H: 3.4, N: 5.5.

Evaluation of removal efficiency

Congo red (CR) (C.I. Direct Red 28 $C_{32}H_{24}N_6O_6S_2{\cdot}2Na$) was chosen as a model pollutant to evaluate the adsorption capacity of the MOFs. An aqueous stock solution of CR was prepared by dissolving CR in deionized water. Aqueous solution with desired concentration of CR was obtained by dilution of the stock solution with water. Adsorption experiments of CR were carried out on stirred aqueous solutions in a cylindrical quartz UV-reactor containing about 50 mL of 50 ppm CR aqueous solution in presence of about 25 mg of MOFs. The suspension was sonicated for 5 min. Temperature of the solutions did not exceed 20˚C using tap water circulating in jacket of the reactor. Samples for analyses were taken from the reaction suspension at specified reaction times and immediately centrifuged at 6000 rpm for 10 min to remove the particles and were further analyzed by monitoring the absorbance at 497 nm using UV–Vis spectrophotometer (Shimadzu UV 2100). The concentration of dye in each sample was determined at λ_{max} = 497 nm, using a calibration curve. By this method, degree of removal (percent) of CR may be obtained in different intervals. The percent removal is calculated by the following equation:

$\% \text{ Removal} = (C_i - C_t)/C_i \times 100$

where, C_i is the initial concentration of dye and C_t is the concentration of dye at any specified time.

Results and discussion

Two new three-dimensional porous Cd(II) based metal-organic frameworks, $[Cd_2(oba)_2(4\text{-bpdb})_2]_n{\cdot}(DMF)_x$ (**TMU-8: TMU** stands for **T**arbiat **M**odares **U**niversity) and $[Cd(oba)(4,4'\text{-bipy})]_n{\cdot}(DMF)_y$ (**TMU-9**) have been readily and quickly synthesized by mechanosynthesis (grinding by hand) of a mixture of $Cd(OAc)_2{\cdot}2H_2O$, H_2oba, and 4-bpdb or 4,4'-bipy for ~ 25 min. The SEM images of these mechanosynthesized MOFs show plate like morphology (Fig. 1). Comparison between the simulated (derived from the single crystal structures of **TMU-8** and **TMU-9**) and experimental (resulting from the mechanosynthesized powder) powder X-ray diffraction (PXRD) patterns confirm that mechanosynthesized **TMU-8** and **TMU-9** were structurally identical to **TMU-8** and **TMU-9** prepared via conventional heating (Fig. 2) (as also evidenced by elemental analysis).

Single crystals of each MOF, suitable for X-ray diffraction, were prepared by heating a mixture of $Cd(NO_3)_2.4H_2O$, H_2oba, and either 4-bpdb or 4,4'-bipy, in DMF at 80 °C for 3-4 days. The IR spectra of these MOFs produced by conventional heating show the symmetric ν_{sym}(COO) and asymmetric ν_{as}(COO) vibrations of the carboxylate groups around 1400 cm^{-1} and 1600 cm^{-1}, respectively. Also the characteristic absorption peak ($\nu_{C=O}$ = 1673 cm^{-1}) of DMF molecules are present in the IR spectra for these MOFs (Fig. 3). The IR spectra of mechanosynthesized **TMU-8** and **TMU-9** are similar to those synthesized by conventional heating, except that the absorption peak of DMF around 1673 cm^{-1} is disappeared.

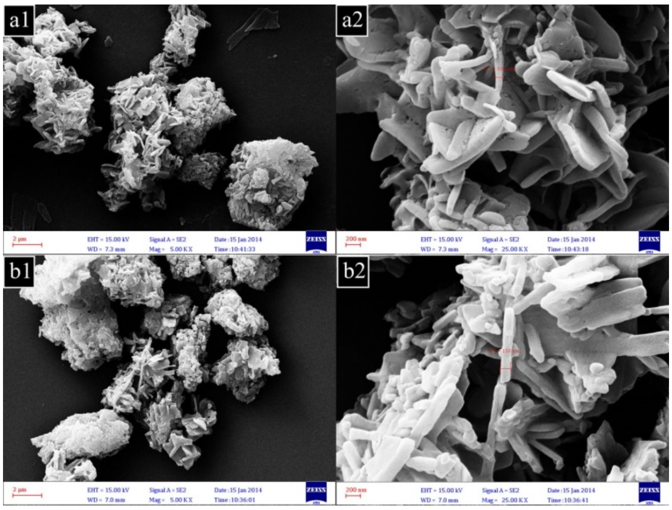

Fig. 1 FE-SEM images of (a) **TMU-8** and (b) **TMU-9** synthesized by mechanochemical reaction (#2 is magnified image of #1).

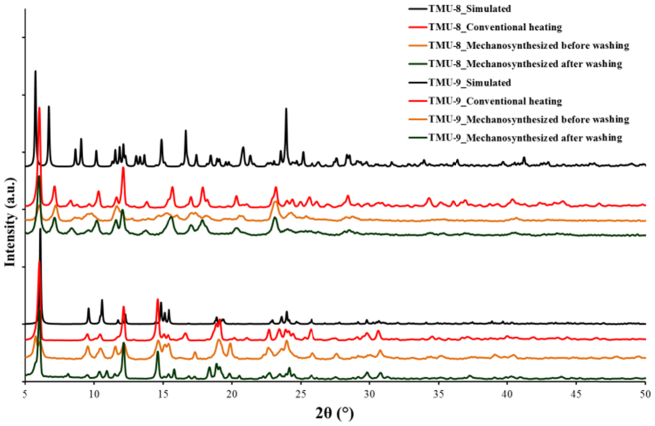

Fig. 2 Comparison of XRD patterns for **TMU-8** and **TMU-9**: simulated, conventional heating and mechanosynthesized before and after washing with DMF.

TMU-8 is based on two crystallographically independent binuclear Cd_2 units (Cd#1 and Cd#2), in which both Cd(II) centres are seven coordinated (Cd#1O_5N_2 and Cd#2O_5N_2). Cd#1 and Cd#2 centers are coordinated to five carboxylate O atoms (O1, O2, O2#1, O6 and O7 for Cd#1, O4, O5, O9, O10 and O10#4 for Cd#2) from four fully deprotonated oba ligands and two N atoms (N1 and N4 for Cd#1 and N5 and N8 for Cd#2) from two 4-bpdb ligands (Fig. 4a and Table 2). The distances between Cd#1-Cd#1 and Cd#2-Cd#2 are 3.992 Å and 3.982 Å, respectively. Each non-linear (C8-O3-C5 = 119.6(7)° and C22-O8-C19 = 119.7(7)°) dicarboxylate oba ligand binds three consecutive Cd(II) centers from two different units (Cd#1 and two Cd#2 or Cd#2 and two Cd#1). The oba ligands exhibit two types of coordination modes, one carboxylate group of an oba ligand adopts a chelating bidentate mode while the other adopts a chelating-bridging coordination mode. The oba ligands bind Cd_2 units and form 2D sheets (Fig 4b) that are connected through the linear 4-bpdb, extending the structure in three-dimensions. **TMU-8** possesses two channels running along the *a*-axis (aperture size: 9.3 × 3.9 Å and 6.7 × 3.0 Å, taking into account the van der Waals radii; 44.3% void space per unit cell)[57] occupied by DMF guest molecules (Fig. 4e). As observed in Fig. 4f, these pores are decorated with azine groups of 4-bpdb linear pillar ligands (shown in blue).

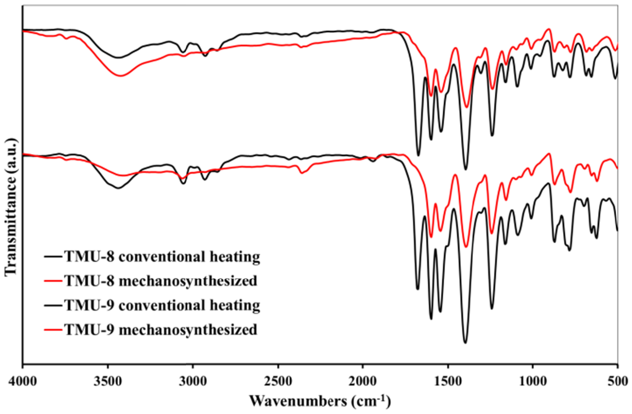

Fig. 3 IR spectra of **TMU-8** and **TMU-9** produced by either conventional heating or mechanosynthesis.

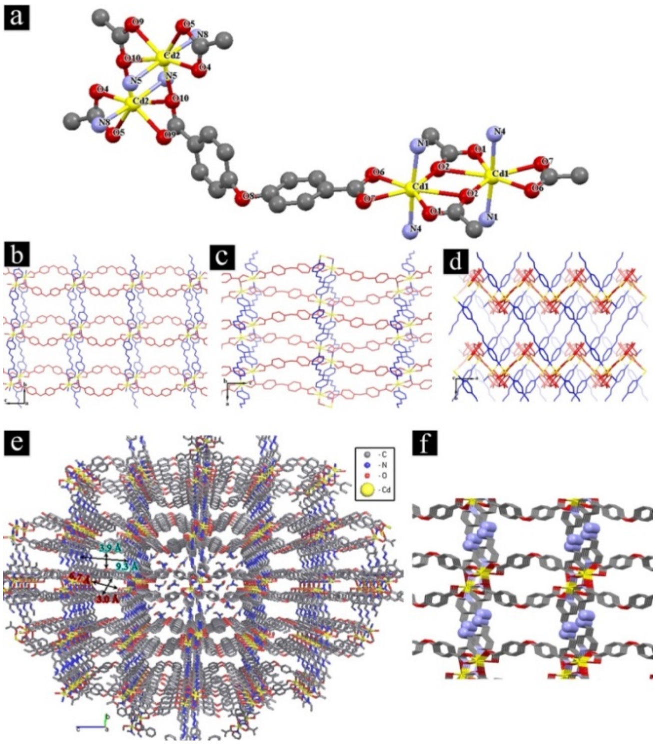

Fig. 4 Views of **TMU-8,** (a) Ball and stick representation of the binuclear Cd_2 unit. (b) Layers of Cd(II)-oba (in red) pillared by 4-bpdb (in blue) in **TMU-8**

along the *a* axis. (c) and (d) Representation of **TMU-8** along *b*- and *c*-axes. The N-donor ligand, 4-bpdb, connects the 2D layers to yield the 3D structure of **TMU-8**. (e) Perspective view of the **TMU-8** structural unit shows the pore sizes and DMF guest molecules accommodate in the pores. (f) Representation of the pores, highlighting the azine groups (in blue). Hydrogen atoms and DMF molecules are omitted for clarity. Color code: O: red; N: blue; C: gray and Cd: yellow.

Table 1. Crystal data and structural refinement for **TMU-8** and **TMU-9**.

Identification code	**TMU-8**	**TMU-9**
Empirical formula	$C_{70}H_{78}Cd_2N_{14}O_{16}$	$C_{24}H_{16}CdN_2O_5$
Formula weight	1596.26	524.79
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	C2/c
Unit cell dimensions	a = 9.0720(18) Å	a = 15.5064(10) Å
	b = 13.140(3) Å	b = 11.7116(8) Å
	c = 30.700(6) Å	c = 29.7359(19) Å
	α = 92.72(3)°	α = 90.00°
	β = 90.20(3)°	β = 103.6011(12)°
	γ = 90.01(3)°	γ = 90.00°
Cell volume, $Å^3$	3655.5(13)	5248.7(6)
Z value	2	8
Density (calc.) ($g.cm^{-3}$)	1.450	1.328
Absorption coefficient	0.657 mm^{-1}	0.864 mm^{-1}
F(000)	1640	2096
θ range for data collection	1.66 to 27.12°	2.20 to 29.00°
Reflections collected/unique	42584/14836 [R(int) = 0.0359]	6967/6967 [R(int) = 0.0000]
Max. and min. transmission	0.9679 and 0.8273	0.926 and 0.867
Data/restraints/parameters	14836/0/931	6967/0/290
Goodness-of-fit on F^2	1.158	0.914
Final R indices (I>2.00σ(I))	R1 = 0.0872, wR2 = 0.2533	R1 = 0.0333, wR2 = 0.0698
R indices (all data)	R1 = 0.0953, wR2 = 0.2594	R1 = 0.0567, wR2 = 0.0742
Largest diff. Peak, hole	2.426 and -2.272 e.$Å^{-3}$	0.627 and -0.791 e.$Å^{-3}$

The structure of **TMU-9** is built up from a binuclear cadmium(II) unit, $Cd_2(CO_2)_4N_4$, in which both metal centres are seven coordinated to five O atoms (O1, O2, 2 × O3, and O5) from four adjacent oba ligands and two N atoms (N1 and N2) from two 4,4'-bipy ligands (Fig. 5a). Similar to **TMU-8**, oba ligands adopt chelating and chelating-bridging coordination modes. As in **TMU-8**, the orientation of the non-linear (C–O–C = 120.2°) dicarboxylate oba ligands around the Cd_2 units leads to the formation of 2D layers pillared by 4,4'-bipy ligands to yield a 3D framework (Fig. 5b). **TMU-9** contains narrow channels running along *a*- and *b*-axes (aperture size 8.2 × 1.6 Å and 10.9 × 2.9 Å, respectively, taking into account the van der Waals radii; 27.8% void space per unit cell)[57] (Fig. 5c and d).

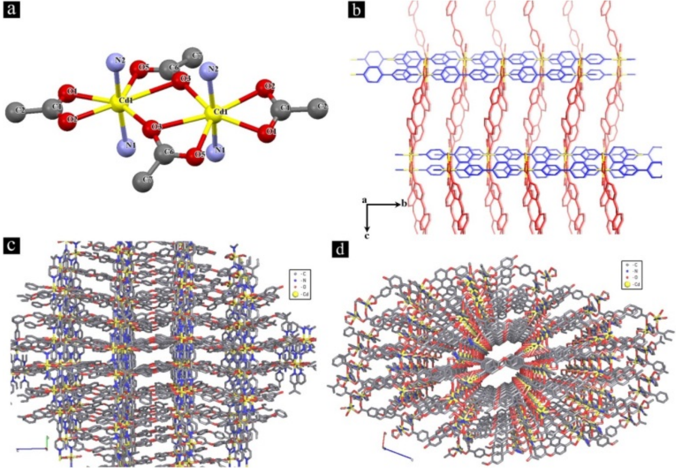

Fig. 5 Views of **TMU-9,** (a) Ball and stick representation of the binuclear Cd_2 unit. (b) Layers of Cd(II)-oba (in red) pillared by 4,4′-bipy (in blue) in **TMU-9** along the *a* axis. (c) and (d) Representation of pores along *a* and *b* directions. Hydrogen atoms and DMF molecules are omitted for clarity.

To examine the thermal stability of these MOFs thermogravimetric analyses (TGA) were carried out between 25 and 600 °C. Thermogravimetric analysis (TGA) of **TMU-8** and **TMU-9** revealed a weight loss in the temperature range of 50-260 °C (18.5%, expected: 18.1%) and 100−290 °C (11.2%, expected: 12.2%), respectively, attributed to the loss of guest DMF molecules (Fig. 6). **TMU-8** and **TMU-9** are thermally stable up to 260°C and 290 °C, above which they begin to decompose. The TGA curves of mechanosynthesized **TMU-8** and **TMU-9** show a plateau in the range of 30 to 260 ºC and 30 to 290 ºC respectively, revealing that their pore channels were devoid of any guest molecules (Fig. 6). Above these temperatures the MOFs begin to decompose.

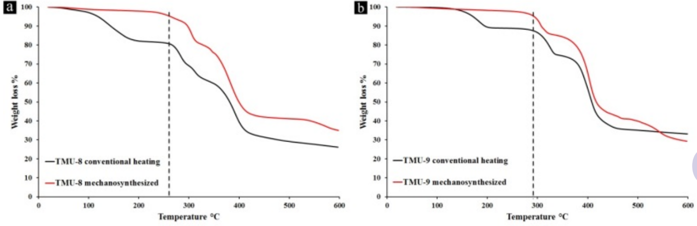

Fig. 6 Thermogravimetric profiles of **TMU-8** (a) and of **TMU-9** (b) isolated by either conventional heating or mechanosynthesis.

Removal efficiency of these MOFs in presence of 50 ppm CR aqueous solution was investigated (Fig. 7). The absorption spectra show that the maximum percent removal of CR is roughly 97.3% (97.3 mg/g, 112.7 g/mol) and 92% (92 mg/g, 48.3 g/mol) for 25 and 60 min in TMU-8 and TMU-9, respectively. On the other hand, there is a large change in the CR concentration in a shorter time with the **TMU-8** MOF. This observation can be attributed to larger pore size and void space of **TMU-8**.

Table 2. Selected Bond Lengths (Å) and Angles (°) of **TMU-8**.

TMU-8					
Cd1—O1	2.277(6)	O1—Cd1—N1	93.8(2)	O9—Cd2—N5	93.4(2)
Cd1—O2	2.711	O6—Cd1—N1	92.9(2)	O4#3—Cd2—N5	93.1(2)
Cd1—O6	2.301(6)	O1—Cd1—O2#	126.7(2)	O9—Cd2—O10#4	127.4(2)
Cd1—N1	2.313(7)	O6—Cd1—O2#1	87.1(2)	O4#3—Cd2—O10#4	86.4(2)
Cd1—O2#1	2.338(7)	N1—Cd1—O2#1	85.5(3)	N5—Cd2—O10#4	85.4(3)
Cd1—N4#2	2.355(7)	O1—Cd1—N4#2	88.5(2)	O9—Cd2—N8#5	88.9(2)
Cd1—O7	2.493(6)	O6—Cd1—N4#2	87.9(2)	O4#3—Cd2—N8#5	87.9(2)
Cd2—O9	2.279(6)	N1—Cd1—N4#2	174.6(3)	N5—Cd2—N8#5	174.3(3)
Cd2—O4#3	2.299(6)	O2#1—Cd1—N4#2	89.2(3)	O10#4—Cd2—N8#5	89.1(3)
Cd2—N5	2.315(7)	O1—Cd1—O7	90.9(2)	O9—Cd2—O5#3	90.8(2)
Cd2—O10#4	2.327(7)	O6—Cd1—O7	55.1(2)	O4#3—Cd2—O5#3	55.1(2)
Cd2—N8#5	2.348(8)	N1—Cd1—O7	101.1(2)	N5—Cd2—O5#3	101.1(2)
Cd2—O5#3	2.494(6)	O2#1—Cd1—O7	141.6(2)	O10#4—Cd2—O5#3	141.1(2)
Cd2—O10	2.718	N4#2—Cd1—O7	83.7(2)	C8—O3—C5	119.6(7)
O1—Cd1—O6	146.0(2)	O9—Cd2—O4#3	145.9(2)	C22—O8—C19	119.7(7)

Symmetry transformations used to generate equivalent atoms for **TMU-8**: #1 1-x, 1-y, 1-z; #2 -1+x, 1+y, z; #3 x, y, -1+z; # 4 2-x, 1-y, -z; #5 1+x, 1+y, z; #6 x, y, 1+z; #7 1+x, -1+y, z; #8 -1+x, -1+y, z.

Table 3. Selected Bond Lengths (Å) and Angles (°) of **TMU-9**

TMU-9					
Cd(1)-O(3)	2.2980(18)	O(3)-Cd(1)-N(2)	83.47(7)	O(5)-Cd(1)-O(1)	83.34(6)
Cd(1)-N(2)	2.310(2)	O(3)-Cd(1)-O(5)	125.13(6)	N(1)-Cd(1)-O(1)	87.57(7)
Cd(1)-O(5)	2.3275(18)	N(2)-Cd(1)-O(5)	97.91(7)	O(3)-Cd(1)-O(2)	96.42(6)
Cd(1)-N(1)	2.337(2)	O(3)-Cd(1)-N(1)	89.14(7)	N(2)-Cd(1)-O(2)	85.49(8)
Cd(1)-O(1)	2.3784(18)	N(2)-Cd(1)-N(1)	172.56(7)	O(5)-Cd(1)-O(2)	138.45(6)
Cd(1)-O(2)	2.3881(17)	O(5)-Cd(1)-N(1)	87.08(7)	N(1)-Cd(1)-O(2)	94.45(7)
Cd(1)-O(3)	2.670	O(3)-Cd(1)-O(1)	151.13(6)	O(1)-Cd(1)-O(2)	55.32(6)
		N(2)-Cd(1)-O(1)	98.45(7)	C(10)-O(4)-C(13)	120.2(2)

Symmetry transformations used to generate equivalent atoms for **TMU-9**: #1 -x+1,y,-z-1/2, #2 -x+3/2,-y+1/2,-z, #3 x,y+1,z, #4 x,y-1,z.

In order to know the kinetics of removal of CR in the solutions suspended on **TMU-8** and **TMU-9**, different kinds of kinetics orders are attempted expressing the reaction kinetics (Fig. 7c and Table 4). Each correlation coefficient was calculated from the kinetics equation, where R_0, R_1 and R_2 represent the correlation coefficients of zero, first and second order rate equations, respectively (Table 4). Comparison between these correlation coefficients shows that R_1 has the best correlation for two MOFs. Therefore, it is suggested that the removal of CR in the solutions suspended on MOFs belongs to first order reaction kinetics. Also, K_1 value for **TMU-8** is higher than that for **TMU-9** so this MOF has higher activity for removing CR.

Toxicity of Cd released by these MOFs, which were immersed in water for 10 days was measured by ICP study. The concentrations of Cd^{2+} in water were 100 and 30 ppb for **TMU-8** and **TMU-9**, respectively. This may be attributed to release of unreacted metal ions that may be trapped in MOFs frameworks.

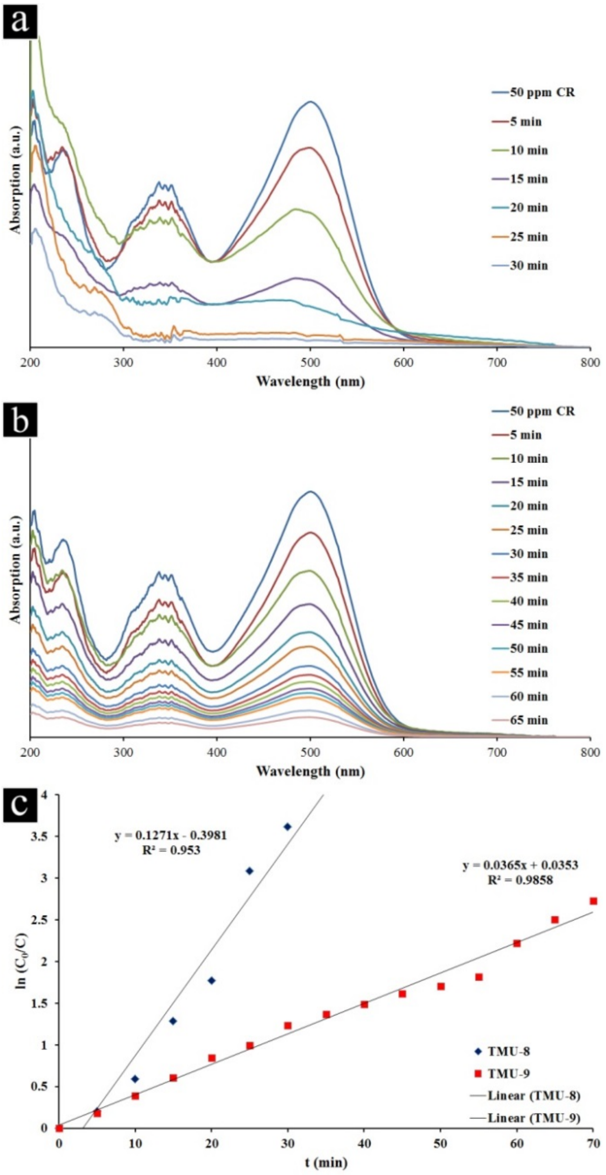

Fig. 7 Absorption spectra of a 50 ppm CR in presence of (a) **TMU-8** and (b) **TMU-9.** (c) Reaction kinetics of CR removal.

Table 4. Kinetics equation of CR removal.

MOFs	Order(s)	$K_1(min^{-1})$	R_0	R_1	R_2
TMU-8	$\ln (C_0/C)=0.1271t-0.3981$	0.1271	0.7281	0.953	0.7287
TMU-9	$\ln (C_0/C)= 0.0365t+0.0353$	0.0365	0.8142	0.9858	0.842

Conclusions

Two new MOFs, $[Cd_2(oba)_2(4\text{-}bpdb)_2]_n\cdot(DMF)_x$ (**TMU-8**) and $[Cd(oba)(4,4'\text{-}bipy)]_n\cdot(DMF)_y$ (**TMU-9**) were successfully synthesized via mechanochemical grinding of N-donor ligands with Cd(II) and H_2oba then analysed by X-ray crystallography. Single-crystal X-ray data show that **TMU-8** and **TMU-9** possess different structural topologies and different pore sizes. These two new MOFs can be synthesized easily, rapidly and in an environmentally friendly manner within 25 min via mechanosynthesis. These MOFs show high removal efficiency and first order reaction kinetics in presence of 50 ppm congo red solution.

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Notes and references

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