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A flexible Cd^{2+} metal organic framework with a unique (3,3,6)-connected topology, unprecedented secondary building units and single crystal to single crystal solvent exchange properties†

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A new flexible Cd^{2+} metal organic framework (MOF), denoted as **UCY-3**, which is the second example of a MOF with the ligand H$_3$CIP [H$_3$CIP = 5-(4-carboxybenzylideneamino)isophthalic acid], is reported. It shows a unique (3,3,6)-connected topology and is based on a neutral non-oxo triangular [Cd$_3$(COO)$_6$] secondary building unit that appears for the first time in MOFs chemistry. **UCY-3** displays significant structural flexibility, capability for exchange of the guest solvents by various organic molecules in a single-crystal-to-single-crystal fashion as well as breathing capacity allowing the incorporation of relatively large amount of benzene into its pores. Overall this work indicates that MOFs based on semi-rigid polytopic ligands may adopt unprecedented structural types and exhibit unexpectedly high absorption capacities for relatively bulky organic molecules, as a result of their flexibility and breathing capability.

Introduction

The interest in metal-organic frameworks (MOFs) continues to grow, since these compounds revealed a wide variety of topologies[1,2] and attractive physical properties and structural characteristics that led to several applications in diverse areas including gas storage and separation,[2–6] catalytic activity,[7] magnetism,[8] sensing[9] and capability for drug delivery.[10] Flexible MOFs constitute an intriguing subcategory of these materials, showing not only novel structural features, but also unique reactivity deriving from the nature (*i.e.* flexibility) of their frameworks.[11–13] Thus, such materials often exhibit high potential for Single-Crystal-to-Single-Crystal (SCSC) transformations, which have been proven to be a powerful method to modify or tune the properties of MOFs *via* the post-synthetic introduction of suitable guest molecules or organic functional groups into their structures.[11,14–23] In addition, flexible MOFs may display additional attributes, not shown by the conventional porous materials, such as gate-type gas sorption properties, enhanced drug storage/delivery capacity, alteration of guest properties, *etc.*[11] For all the above reasons, it would be attractive to develop synthetic approaches towards new flexible MOF

materials. One strategy that has been employed for this purpose involves the use of semi-rigid polytopic ligands.[12] We have thus designed, synthesized and reported the H$_3$CIP [H$_3$CIP = 5-(4-carboxybenzylideneamino)isophthalic acid] tricarboxylic ligand, which features a semi-rigid imine (CH=N) linkage between its phenyl-carboxylate moieties inducing some (but not unlimited) rotational freedom to the phenyl rings of this organic molecule (Fig. 1).[24] A Nd^{3+}-CIP^{3-} MOF (**UCY-2**), also synthesized and reported by our group, showed an extraordinary capability for SCSC solvent exchange transformations and breathing capacity arising from the flexible nature of the CIP^{3-} ligand.[24]

In addition, we have been exploring reactions of the H$_3$CIP ligand with other metal ions besides lanthanides. We herein present the initial result of these investigations, a new Cd^{2+} MOF [Cd$_3$(CIP)$_2$(DMF)$_3$]·DMF·10H$_2$O denoted as **UCY-3** (UCY = University of Cyprus), which exhibits a 3D-structure with a unique structural type and novel non-oxo triangular
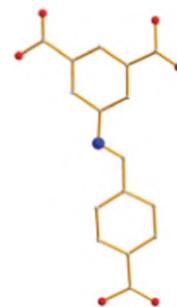
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Fig. 1 Representation of the H$_3$CIP ligand. Colour code: O, red; N, blue; C, grey. The H atoms have been omitted for clarity.

$[Cd_3(COO)_6]$ secondary building units (SBUs). Furthermore, **UCY-3** shows a significant degree of structural flexibility and capability for SCSC transformations comprising the exchange of its guest solvents by a variety of organic molecules. Noticeably, **UCY-3** displays a high exchange capacity for benzene, a quite harmful organic contaminant, reaching up 23 wt% per formula unit.

Experimental section

Materials

All procedures were performed under aerobic conditions. Solvents and reagents were obtained from commercial sources and used as received. $H_3CIP \cdot 2EtOH \cdot H_2O$ was prepared as described elsewhere.[24]

Syntheses

UCY-3: $[Cd(NO_3)_2] \cdot 4H_2O$ (0.075 g, 0.24 mmol) was added to a solution of $H_3CIP \cdot 2EtOH \cdot H_2O$ (0.150 g, 0.35 mmol) in DMF (5 mL) in a 20 mL glass vial. The mixture was heated without stirring at 100 °C for 20 hours. During this period, light brown polyhedral crystals of **UCY-3** were formed, isolated by filtration, washed several times with DMF and diethylether and dried under vacuum. Yield: ~70%. The dried crystalline product was analyzed as **UCY-3**·DMF·$14H_2O$. Anal. Calc. for $C_{44}H_{72}Cd_3N_6O_{30}$: C, 35.18; H, 4.83; N, 5.59. Found: C, 35.21; H, 4.75; N, 5.50%. Selected IR data (KBr pellet, cm^{-1}): 3075 (w), 2930 (w), 1655(s), 1549 (s), 1385 (s). The purity of the product was also confirmed by comparison of the experimental powder X-ray diffraction pattern to that calculated from the single crystal X-ray data (see Fig. S1 in ESI†).

UCY-3/X (X = chloroform, benzene, toluene): Single crystals of **UCY-3**·DMF·$14H_2O$ (0.025 g, 0.018 mmol) and the solvent X (5 mL) were mixed in a 23 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and placed in an oven operated at 50 °C. It remained undisturbed at this temperature for 3 days and then was allowed to cool at room temperature. For the collection of the single crystal X-ray diffraction data, suitable crystals were picked directly from the mother liquor in order to prevent loss of lattice solvents and crystallinity. **UCY-3/Dry** was prepared after drying single—crystals of **UCY-3/** chloroform in the atmosphere.

Single crystal X-ray crystallography

Single Crystal X-ray diffraction data were collected on an Oxford-Diffraction SuperNova diffractometer, equipped with a CCD area detector utilizing Mo-Kα (λ = 0.71073 Å) or Cu-Kα (λ = 1.54184 Å) radiation. Suitable crystals were attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software.[25] The structures were solved by direct methods using SIR2004[26] and refined on F^2 using full-matrix least squares with SHELXL97.[27] Software packages used: CrysAlis CCD for data collection,[25] CrysAlis RED for cell refinement and data reduction,[25] WINGX for geometric calculations,[28] and DIAMOND[29] for molecular graphics. The non–H atoms were treated anisotropically,

whereas the H atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. The aldehydic H atoms of the DMF molecules for all compounds as well as the imine H atoms of CIP^{3-} ligands for **UCY-3/** chloroform, **UCY-3/**dry and **UCY-3/**toluene could not be located. Electron density contributions from disordered lattice H_2O molecules were handled using the SQUEEZE procedure from the PLATON software suit.[30] Several restraints (DFIX, ISOR, DELU) have been applied in order to limit the disorder of the CIP^{3-} ligands, DMF (ligated and lattice solvent molecules), $CHCl_3$ (for **UCY-3/**chloroform), benzene (for **UCY-3/**benzene) and toluene (for **UCY-3/**toluene) guest molecules. For **UCY-3/** toluene, a relatively high residual peak (~ 4.7 e/$Å^3$) was found 0.96 Å close to Cd3. Although, we have measured several crystals in either Mo or Cu X-ray source and also tried twinning refinement, we were unable to resolve the above issue. For **UCY-3/Dry** the structure could not be refined to a satisfactory level because of poor diffraction due to partial loss of crystallinity of the material after the removal of guest solvent molecules. However, we were able to confirm that its structure is analogous to that of the pristine **UCY-3**. A relatively high residual peak (~ 4.6 e/$Å^3$) was found 1.12 Å close to Cd2 for this structure, which is obviously due to its poor refinement. Selected crystal data for all compounds are given in Table 1. Full details can be found in the CIF files provided in the ESI.†

Physical measurements

Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Cyprus, Chemistry Department. IR spectra were recorded on KBr pellets in the 4000–400 cm^{-1} range using a Shimadzu Prestige – 21 spectrometer. PXRD diffraction patterns were recorded on a Shimadzu 6000 Series X-ray diffractometer (CuKα radiation, λ = 1.5418 Å). UV/Vis/NIR diffuse reflectance spectra were obtained at room temperature on a Shimadzu, UV-3600 UV-VIS-NIR spectrophotometer in the wavelength range of 200–2500 nm. $BaSO_4$ powder was used as a reference (100% reflectance) and base material on which the powder sample was coated. The reflectance data were converted to absorption using the Kubelka–Munk function, and the band edge for each sample was estimated from the intercept of the line extrapolated from the high-energy end of the absorption to the baseline.[31] Photoluminescence (PL) spectra were obtained on an Edinburgh Xe900 spectrofluorometer. Thermal stability studies were performed with a Shimadzu TGA 50 thermogravimetric analyzer.

Results and discussion

Synthesis and structure of UCY-3

Compound **UCY-3** was prepared by a reaction of $Cd(NO_3)_2$ and H_3CIP in DMF at 100 °C. It crystallizes in the monoclinic space group $C2/c$ and contains the triangular building block $[Cd_3(COO)_6(DMF)_3]$ as the secondary building unit (SBU), Fig. 2. Each SBU consists of three crystallographically independent Cd^{2+} ions and six COO^- from six different CIP^{3-} ligands. Three of the COO^- groups bridge a pair of Cd^{2+} centers in either *syn,anti*-η^1: η^1:μ_2 (Cd1–Cd2, Cd2–Cd3) or η^1: η^2:μ_2 (Cd1–Cd3) fashions, two link all three Cd^{2+} exhibiting the η^1: η^2:μ_3 or η^1:

Table 1 Selected crystal data for the pristine **UCY-3** and exchanged compounds

| Compound	UCY-3	UCY-3/chloroform	UCY-3/Dry	UCY-3/benzene	UCY-3/toluene
Chemical formula	$C_{44}H_{60}Cd_3N_6O_{26}$	$C_{42}H_{48}Cd_3Cl_3N_5O_{21.50}$	$C_{41}H_{56}Cd_3N_5O_{26}$	$C_{68}H_{60}Cd_3N_5O_{15}$	$C_{48}H_{58}Cd_3N_5O_{23}$
Formula mass	1426.18	1410.40	1372.11	1524.41	1410.19
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
$a/Å$	34.034(2)	34.628(2)	33.943(2)	35.319(3)	34.799(2)
$b/Å$	18.7606(4)	18.2216(6)	18.522(2)	18.233(2)	18.467(2)
$c/Å$	22.3666(7)	23.136(2)	21.217(2)	23.452(2)	23.031(2)
$\alpha/°$	90.00	90.00	90.00	90.00	90.0
$\beta/°$	116.429(4)	118.404(9)	116.291(9)	120.17(2)	118.79(2)
$\gamma/°$	90.00	90.00	90.00	90.00	90.0
Unit cell volume/$Å^3$	12788.4(6)	12841(2)	11960(2)	13057(2)	12971(2)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$	$C2/c$
No. of formula units per unit cell, Z	8	8	8	8	8
Radiation type	MoKα	MoKα	MoKα	MoKα	CuKα
Absorption coefficient, μ/mm^{-1}	1.066	1.176	1.136	1.038	8.453
No. of reflections measured	28140	25299	25176	31147	24341
No. of independent reflections	11248	11087	10505	11471	11504
R_{int}	0.0631	0.0385	0.0672	0.0403	0.0287
Final R_1 values ($I > 2\sigma(I)$)[a]	0.0608	0.0920	0.1416	0.0694	0.0724
Final $wR(F^2)$ values ($I > 2\sigma(I)$)[b]	0.1555	0.2796	0.3656	0.1849	0.2118
Goodness of fit on F^2	0.963	1.188	1.305	1.094	1.069

[a] $R_1 = \Sigma ||Fo| - |Fc||/\Sigma|Fo|$. [b] $wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)2]/\Sigma[wF_o^2)2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (m \cdot p)^2 + n \cdot p]$, $p = [max(F_o^2,0) + 2F_c^2]/3$, and m and n are constants.
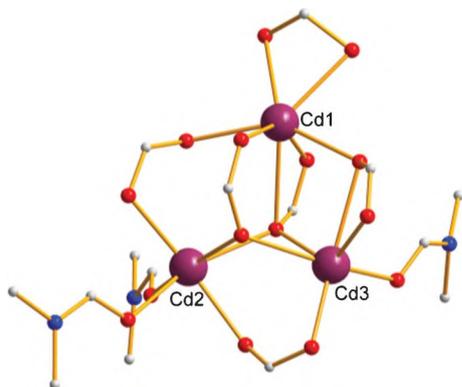
Fig. 2 Partially labelled representation of the trinuclear SBU of **UCY-3**. Colour code: Cd, purple; O, red; N, blue; C, grey. The H atoms have been omitted for clarity.

Fig. 3 Space-filling representation of the 3D-structure of **UCY-3** viewed down the c-axis. Colour code: Cd, purple; O, red; N, blue; C, grey. The H atoms and guest DMF molecules have been omitted for clarity.

η^3:μ_3 coordination modes and the remaining one acts as a chelating ligand, coordinating to a single Cd^{2+} ion (Cd1). Cd1 is coordinated by seven carboxylic oxygen atoms in a distorted pentagonal bipyramidal prismatic geometry. The coordination spheres of Cd3 and Cd2 include not only carboxylic O but also DMF oxygen atoms (one and two DMF O atoms for Cd3 and Cd2 respectively), with both Cd^{2+} ions being six-coordinated and adopting a distorted octahedral geometry. The structure of **UCY-3** contains two crystallographically independent CIP^{3-} ligands (A and B), which deviate significantly from the planarity (Fig. S2†). Specifically, the dihedral angle between the planes of the two phenyl rings of ligand A is 47°, while the corresponding dihedral angle for the ligand B is ~36°. These values are in good proximity with those found for the CIP^{3-} ligands in **UCY-2** and its analogues (35–52°).[24] Furthermore, the ligand B displays a significant distortion, since two of its carboxylic oxygen atoms and one of its phenyl rings are positionally disordered.

The SBUs extend infinitely creating a microporous three-dimensional framework (Fig. 3) with the $[Cd_3(COO)_6]$ units

Fig. 4 View of the unique (3,3,6)-connected net of **UCY-3**. Colour code: 6-c nodes, black; 3-c nodes, blue; 3-c nodes, red.
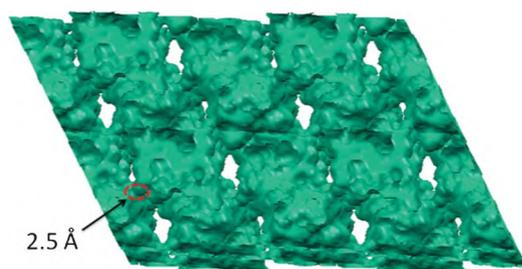
Fig. 5 View of the pore network (shown in green) of **UCY-3** with the indication of the sizes of the passages between the pores.
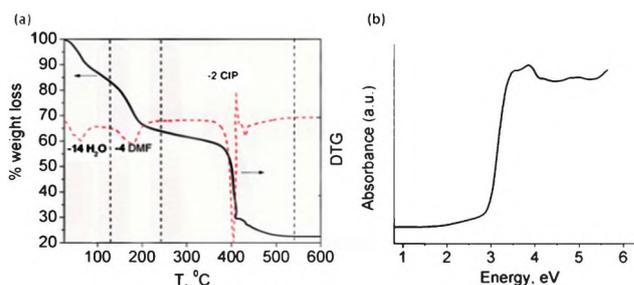

Fig. 6 (a) TGA and DTG (first derivative) curves with the assignment of the weight losses and (b) solid state NIR-UV-Vis spectrum for **UCY-3**.

serving as 6-connected nodes and the CIP^{3-} ligands as 3-connected nodes. At first glance this arrangement conforms to a binodal (3,6)-connected net but a more careful inspection of the underline net reveals that the two crystallographically independent CIP^{3-} ligands have different point symbols resulting in a (3,3,6)-connected net with point symbol $(4^2.6)(4^3)(4^5.6^4.8^6)$, Fig. 4. A careful inspection of the RCSR (Reticular Chemistry Structure Resource) database[32] reveals the presence of seven 3,6-heterocoordinated nets having three different vertices. These nets are **brk**, **muo**, **pdp**, **tsa**, **tsy**, **xbq** and **zxc**. Six of these nets (all except **pdp**) are (3,3,6)-connected but none of them has the same point symbol with the one found above for **UCY-3** and that makes the underline network of **UCY-3** unique.

The solvent-accessible volume of **UCY-3** calculated by PLATON[30] is 4633.7 $Å^3$ corresponding to 36.2% of the unit cell volume. The 3D-structure contains cavities with diameters 5–7 Å as found by PLATON (taking into account the van der Waals radii of the atoms and excluding all solvents of the pores). A representation of the pore network of **UCY-3** with the structure visualization program MERCURY[33] reveals that relatively large channels running along [100] communicate through narrow passages that are only ~ 2.5 Å wide (Fig. 5).

A Cambridge Crystallographic Database search revealed that the vast majority of M_3 SBUs in MOFs chemistry are oxide- or hydroxide-bridged triangular clusters.[1] Triangular non-oxo(hydroxo) M_3 carboxylate SBUs are unusual and are mainly limited to positively charged (containing five COO^-) trinuclear clusters.[34] To the best of our knowledge, compound **UCY-3** is the only known MOF consisting of triangular neutral $[M_3(COO)_6]$ SBUs.

Thermal stability studies

The thermal stability of **UCY-3** was investigated by means of the thermogravimetric analysis (TGA) technique in the temperature range 20–600 °C. The TG and DTG (first derivative) curves indicate a series of weight losses (Fig. 6a). The losses occurring from 20–128 °C are assigned to the removal of 14 water molecules (calculated loss = 16.7%; found = 16.7 %). This water content is in agreement with the elemental analysis data (see above) and close to that found from X-ray crystallography (~ 10 H_2O). The following weight loss (19.5%), which ends at ~ 243 °C, is attributed to the release of the 1 lattice and 3 coordinating DMF solvents (calc. weight loss ~ 19.5%) and this is consistent with the content of DMF found from elemental analysis and crystallography. The losses due to removal of the solvent molecules are followed by an abrupt weight change (41.3%), which corresponds to the decomposition of the CIP^{3-} ligands (calculated value 41.3%).

Optical properties

The optical properties of **UCY-3** were also explored. Specifically, the optical energy gap of the material was determined ~ 2.9 eV by solid state UV-VIS-NIR spectroscopy (Fig. 6b), indicating that **UCY-3** is a wide-band gap semiconductor.[35] The investigation of the photoluminescence (PL) properties of the ligand H_3CIP and **UCY-3** revealed that H_3CIP displays relatively strong emission at ~ 405 nm when excited at ~ 350 nm (Fig. S3), while compound **UCY-3** shows no detectable PL probably because of quenching effects.

SCSC solvent exchange properties

Prompted by the relatively open structure of **UCY-3** and the presence of flexible CIP^{3-} ligands and disordered guest DMF molecules, we decided to investigate its SCSC solvent exchange properties. Initially, exchange reactions were performed with $CHCl_3$, a solvent commonly employed in such reactions with DMF in MOFs.[1,2] Thus, a heterogeneous solvent-exchange reaction of single crystals of **UCY-3** with $CHCl_3$ at 50 °C resulted in single crystals that were macroscopically very similar in size and shape with those of the pristine **UCY-3** compound. This process was proven to be SCSC transformation by the determination of the crystal structure of the exchanged compound (Table 1). Specifically, the structural elucidation of the $CHCl_3$-containing compound (**UCY-3**/chloroform) revealed that it is isostructural to the pristine **UCY-3** with the difference that the guest DMF solvents were replaced by $CHCl_3$ molecules (Fig. 7). This solvent exchange is fully reversible, as the pristine **UCY-3** can be fully regenerated (as indicated by the determination of the unit cell parameters of the regenerated material) by treating the chloroform-exchanged compound with DMF.

In order to investigate whether the material retains its structure after removal of the guest solvents from the pores, single crystals of the **UCY-3**/chloroform were left to dry in the air for 24 h and then, X-ray diffraction data were collected on a single crystal of the dried product. The refinement of the crystal structure showed that the dry compound retains the overall structure of the pristine material, but it shows a significantly lower unit cell volume (11960 $Å^3$) compared to as-prepared **UCY-3** (12788 $Å^3$). This appreciable reduction of the unit cell volume (~ 6.5%) upon removal of the guest solvents with the parallel retention of the framework structure indicates that the
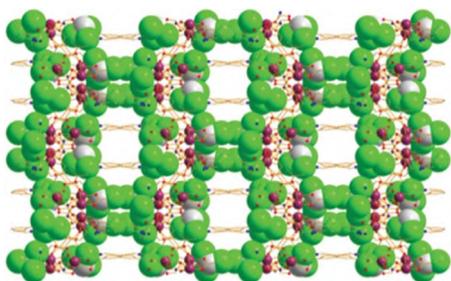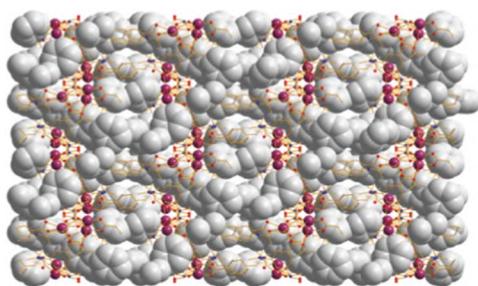
Fig. 7 View of the structure of **UCY-3**/chloroform with the CHCl₃ molecules represented with a space-filling model. Colour code: Cd, purple; O, red; N, blue; C, grey; Cl, green.

Fig. 9 View of the structure of **UCY-3**/toluene with the toluene molecules represented with a space-filling model. Colour code: Cd, purple; O, red; N, blue; C, grey.

structure incorporates not only flexibility but also rigidity. This interesting feature of the structure of **UCY-3** is presumably due to the presence of the CIP^{3-} ligand that contains the semi-rigid –CH=N– linkage with a significant but not unlimited rotational freedom.

Besides small-sized molecules, **UCY-3** was also capable to exchange its guest solvents by relatively large aromatic molecules such as benzene and toluene. The development of sorbents for such molecules is of interest for the remediation of organic waste as well as for separation of them from crude oil or gasoline.[36] Thus, reaction of single crystals of **UCY-3** with benzene or toluene at 50 °C resulted in the (complete or partial) replacement of the guest solvents by the corresponding organic molecules. These processes were also found to be fully reversible, as in the case of the CHCl₃ exchange. Again, the determination of the crystal structures of the compounds indicated that these exchange processes are SCSC transformations and the exchanged products are isostructural to the pristine **UCY-3** (Table 1). Specifically, the crystal structure of the benzene-exchanged product (**UCY-3**/benzene) revealed that all guest molecules (DMF and H₂O) of **UCY-3** were replaced by 4.5 benzene molecules per formula unit (Fig. 8), while the toluene-exchanged product (**UCY-3**/toluene) contains in its pores only one toluene molecule (and some disordered water molecules) per formula unit (Fig. 9). As expected the benzene- and toluene-exchanged products exhibit significantly larger unit cell volumes compared to the pristine material (Table 1).

It is remarkable that **UCY-3** displays such high exchange capacity for benzene (~23 wt%), considering the sizes of benzene and the pore/channels of **UCY-3**. As mentioned above, the channels of **UCY-3** communicate through very narrow passages
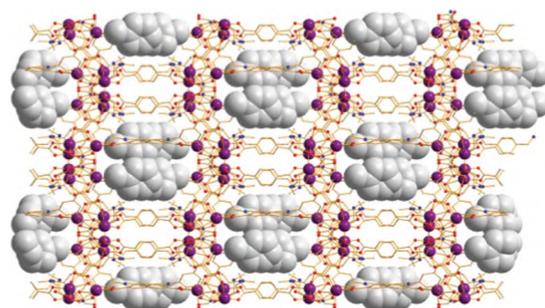
(~2.5 Å) and therefore, such a small pore system would not favour the absorption of relatively bulky molecules like benzene (diameter, from H across to H, ~5.0 Å). However, a close examination of the pore network of **UCY-3**/benzene (Fig. 10a) reveals that the passages between the channels of the benzene-containing material are ⩾4 Å wide (excluding all solvents from the pores) and the solvent-accessible volume of this material is ~41%. These values are much higher than those found for the pristine **UCY-3** (see above). Therefore, the channels of **UCY-3** significantly expand upon treatment with benzene to allow the diffusion of this organic molecule into the framework. The insertion of benzene into **UCY-3** is thus due to the 'breathing' of the framework,[2,11,13] which is favoured by the flexibility of the structure of this MOF arising from the presence of the CIP^{3-} ligands. Besides the changes in the solvent-accessible volume and the size of the channels, the two crystallographically independent CIP^{3-} ligands of **UCY-3**/benzene display substantially different distortions (dihedral angle ~56° and 3° for ligands A and B respectively, Fig. S4†) compared to those (47° and 36°) of the corresponding ligands in **UCY-3**. This is another indication that the structure of **UCY-3** exhibits high flexibility that allows the diffusion of the bulky benzene into the small pores of the MOF.

On the other hand, the examination of the pore network of **UCY-3**/toluene indicates that the passages between the channels are ~3.6 Å wide (Fig. 10b) and the solvent accessible-volume is ~40 %, i.e. values which are greater than those for **UCY-3**. However, the dihedral angles for the two crystallographically independent CIP^{3-} ligands (48°, 36°) in the structure of **UCY-3**/toluene are very similar to those found in pristine **UCY-3** (47°, 36°). These data also reveal breathing of the framework to facilitate the diffusion of toluene into the structure of the MOF, although it happens in smaller degree compared to that observed in the benzene exchange process. The breathing phenomenon has
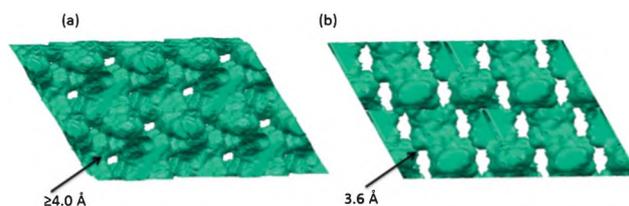

Fig. 8 View of the structure of **UCY-3**/benzene with the benzene molecules represented with a space-filling model. Colour code: Cd, purple; O, red; N, blue; C, grey.

Fig. 10 View of the pore networks (shown in green) of (a) **UCY-3**/benzene and (b) **UCY-3**/toluene with the indication of the sizes of the passages between the pores.

been also observed in the exchange of DMF of **UCY-2** by pyridine molecules, which is again a result of the flexible structure.[24] As a consequence of this phenomenon, **UCY-2** and **UCY-3** containing small pores and narrow channels showed unexpectedly high absorption capacities for relatively large organic molecules.

Finally, SCSC exchange reactions of **UCY-3** with an equimolar mixture of toluene and benzene were performed in order to determine whether **UCY-3** shows selectivity for any of these organic molecules. Several crystals of the exchanged product were measured and found to have identical cell parameters. The determination of the crystal structure of the product indicated that it contained only toluene in its pores (and a number of disordered water molecules), *i.e.* the product was **UCY-3**/toluene. Note that such exchange reactions with mixtures of benzene and toluene were performed under various reaction conditions [various temperatures (50 or 100 °C) and reaction times (2–8 days)] and in all cases, the isolated product was **UCY-3**/toluene. Such a selectivity for toluene against benzene is rather unexpected since **UCY-3** showed much higher exchange capacity for benzene (23 wt%) than for toluene (6.5 wt%). A possible explanation for this preference of **UCY-3** for toluene over benzene observed in mixtures of these molecules is that the diffusion of toluene into the framework is not accompanied by substantial structural changes and may be more favoured compared to that of benzene which resulted in dramatic changes in the configuration of the CIP^{3-} ligands.

Conclusions

In conclusion, we have synthesized a Cd^{2+} MOF (**UCY-3**), the second example of a MOF with the semi-rigid ligand H_3CIP. **UCY-3** displays a 3D microporous structure with a unique structural topology and is based on unprecedented trinuclear $[Cd_3(COO)_6]$ SBUs with a triangular geometry. It exhibits facile topotactic exchange of its guest solvents with a variety of organic molecules in a single crystal to single crystal fashion, thus providing the opportunity to obtain direct structural information for the exchanged compounds. Despite the fact that **UCY-3** displays small pores and channels, it shows high absorption capacity (23 wt%) for the relatively bulky benzene molecule. This property of **UCY-3** arises from its flexible structure allowing substantial geometrical changes in the CIP^{3-} ligands during the insertion of benzene and breathing phenomena. Another interesting finding of this work was the selectivity of **UCY-3** for toluene over benzene, observed for exchange reactions with mixtures of these organic solvents. These results overall indicate that flexible MOFs may display not only interesting structural features, but they can also be attractive as high capacity sorbents for bulky organic molecules even when their pores and channels are of relatively small size. Ongoing efforts are underway to isolate new MOFs with the H_3CIP ligand and these results will be presented in the near future.

Acknowledgements

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