

Unprecedented Sulfone-Functionalized Metal–Organic Frameworks and Gas-Sorption Properties

Eleftheria Neofotistou,^[a] Christos D. Malliakas,^[b] and Pantelis N. Trikalitis*^[a]

Porous, metal–organic frameworks (MOFs) or coordination polymers (PCPs) represent a unique class of crystalline open framework solids with unprecedented structures, diverse chemical composition, adjustable pores sizes, large surface areas and pore volumes.^[1] These hybrid porous materials result from molecular self-assembly reactions between metal ions or clusters and bridging multidentate organic ligands, usually performed under hydro(solvo)thermal conditions. The combination of accessible porosity and framework functionalities in these solids, arising from both the inorganic and organic component, results in unique properties that could lead to applications in technologically important fields including gas storage,^[2] separation^[3] and catalysis.^[4]

The availability of a large number of different organic linkers as building blocks not only offers the potential for the construction of structurally and topologically diverse MOFs but also the opportunity to create functionalized porous frameworks with the functional species (atoms or groups) being exposed inside the pore space. This could lead to tailor-made materials for specific applications. For example, porous MOFs with metal-free organic groups such as amines are currently explored for applications in base-catalyzed reactions^[5] and as sorbents for selective CO₂ capture and storage.^[6] However, post-synthetic functionalization of MOFs is not straightforward because of the limited stability of the framework during the post-modification reaction.^[7] Alternatively, the direct synthesis of MOFs using functionalized organic ligands is limited either by the relative stability of the functional groups under the specific reaction conditions or by the competition of these groups with the donor

atoms of the ligands towards metal atoms. In some cases, these problems could be avoided by using tagged frameworks with non-reactive groups which then can be converted to the desired active functional groups.^[8]

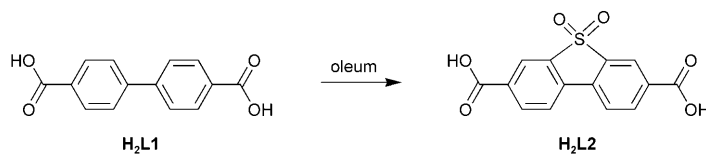
We are interested in the development of MOFs with free Lewis base sites and in particular with sulfonate (-SO₃⁻) groups. In contrast to a number of MOFs with Lewis acid sites originating from unsaturated metal sites upon solvent removal, free Lewis base functionalized MOFs are rarely observed because of the coordination affinity of these groups towards metal atoms. It is expected that basic porous surfaces will reveal significant gas sorption and catalytic properties based on acid–base interactions. Recently, Kitagawa and co-workers reported a robust porous coordination polymer, with free -SO₃⁻ Lewis base groups, which shows interesting sorption properties for CO₂ and MeOH.^[9]

We chose to functionalize the ligand (1,1'-biphenyl)-4,4'-dicarboxylic acid (**H₂L1**) (see Scheme 1) with -SO₃H groups and use it as a linker to construct coordination polymers. However, using the powerful sulfonating agent fuming sulfuric acid, (oleum: H₂SO₄, 20% SO₃) we isolated not the sulfonated product of **H₂L1** but its sulfone (-SO₂) derivative, namely the ligand 4,4'-bibenzoic acid-2,2'-sulfone (**H₂L2**) (see Scheme 1).^[10] This ligand has never been used before in the entire family of MOFs or PCPs and represents a new, rigid carboxylate-based linker, in contrast to its flexible parent **H₂L1**. The sulfone group has locked the two phenyl rings and it was expected that **H₂L2** would lead to the formation of new functionalized isorecticular MOFs when reacted, for example, with Zn²⁺ under solvothermal conditions in dimethylformamide (DMF) or diethylformamide (DEF).

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Scheme 1. Preparation of the sulfone functionalized ligand **H₂L2** from **H₂L1** using H₂SO₄ 20%SO₃ (oleum).

Remarkably, that was not the case and we report here two novel, three dimensional (3D), non-isoreticular porous MOFs with unprecedented structures, isolated from controlled solvothermal reactions between **H₂L2** and Zn(NO₃)₂·6H₂O. The unique structural features of these MOFs, denoted here as UoC-1 and UoC-2, include the formation of novel inorganic secondary building units (SBUs) with an unprecedented double organic bridging connectivity in all directions, which represents a rare example of an organic SBU. We also report preliminary sorption properties for selected gases including N₂, H₂, CO₂ and CH₄.

The reaction between Zn(NO₃)₂·6H₂O and **H₂L2** in DMF/H₂O (67:1 v/v) at 90 °C for 24 h afforded UoC-1 as cubic-like, colorless crystals in good yield, suitable for single crystal X-ray analysis. We found that the water content and the reaction temperature are very crucial parameters in obtaining UoC-1. When the same reaction is performed using only DMF as a solvent, a new MOF is obtained, UoC-2, as colorless rod-like crystals in good yield.

UoC-1 crystallizes in the trigonal system (space group *R* $\bar{3}$) with large unit cell parameters.^[11a] The inorganic SBU, shown in Figure 1, is a novel heptanuclear anionic cluster with formula [Zn₇(μ₃-OH)₃(CO₂)₆]⁻ composed of one octahedral and six tetrahedral Zn²⁺ cations (see Figure 1 a,b). In this cluster, the octahedral zinc atom is located on a three-fold axis and it is surrounded, through μ₃-OH bridges, with three pairs of tetrahedral, corner shared zinc atoms (see Figure 1 b). This connectivity results in an asymmetric SBU with a cage-like topology. Each SBU is linked to six other by twelve **L2**²⁻ ligands, following a pseudo-octahedral connectivity, as shown in Figure 1c. In each direction, two ligands stack in parallel, one on the top of the other and serve as linkers between two SBUs. The distance between these two ligands is approximately 3.6 Å which is typical of aromatic, face-to-face π-π stacking. (see Figure 1d). Each pair of ligands is in fact an organic SBU, stabilized by weak π-π interactions, which link together the six-connected inorganic SBUs, resulting in the non-interpenetrating 3D open structure of UoC-1 (see Figure 1e). The three (crystallographically equivalent), out of the twelve ligands that connect each SBU, bind from one side in a monodentate fashion (C1-O3 1.273(10), C1-O4 1.244(10) Å), while from the other adopt a bidentate coordination mode, bridging two tetrahedral zinc atoms. The other nine ligands (crystallographically equivalent) adopt a bis(bidentate) coordination mode.

The single crystal X-ray analysis of UoC-1 revealed the presence of an oxygen-type atom (O15) located on the threefold axis of the SBU and close to the cavity of its cage at a distance of 5.029(5) Å from the central octahedral Zn1 atom (see Figure 1 a). In addition, three, crystallographically equivalent DMF molecules were found below this oxygen atom. As shown in Figure 1 a, this isolated atom is located at an octahedral site formed by the three, non-coordinated oxygen atoms (O15-O4 2.417(10) Å) of the monodentate carboxylate groups and the three oxygen atoms from the DMF molecules (O15-O13 2.355(10) Å). These findings,

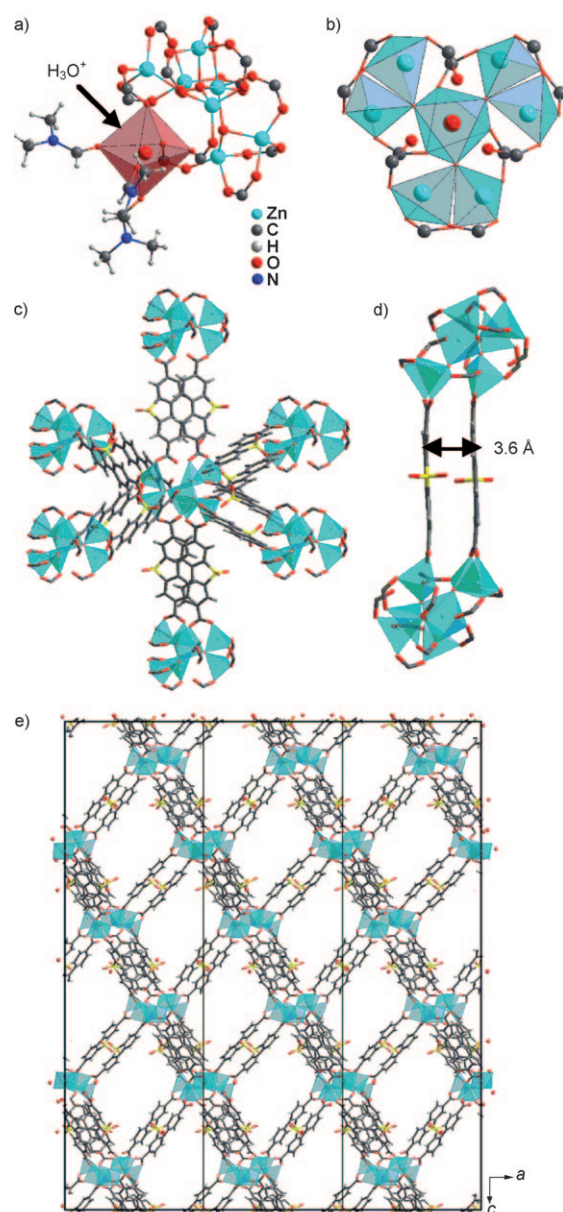


Figure 1. a) Novel heptanuclear [Zn₇(μ₃-OH)₃(CO₂)₆]⁻ SBU in UoC-1, charged balanced by an hydronium cation, b) SBU looking down its C₃ axis, c) pseudo-octahedral connectivity of six SBUs, d) pair of a π-π stabilized **L2**²⁻ ligands connecting two adjacent SBUs, and e) pore system in UoC-1 looking down the *b* axis.

along with charge balance considerations strongly indicate that this isolated oxygen-type atom is in fact a hydronium H₃O⁺ cation that compensates the anionic charge of the SBU. The observed O...O distances indicate the existence of strong hydrogen bonds, as expected. It is important to note here that the C₃ axis found on the atom O15 is in agreement with the expected C_{3v} symmetry of hydronium H₃O⁺ cations.^[12] These results explain why the synthesis of UoC-1 strictly requires the use of a DMF/H₂O mixture as solvent instead of DMF only.

The 3D open structure of UoC-1 shows parallelogram shaped 3D intersecting channels, with a window size of ap-

proximately $10 \times 10 \text{ \AA}$ (measured between oxygen atoms of opposite $-\text{SO}_2$ groups, excluding van der Waals radii) which are filled with guest DMF molecules and presumably with a very small amount of H_2O molecules (see Figure 1 e). The solvent accessible volume, as calculated using the program PLATON,^[13] is 69% of the total unit cell volume. Thermogravimetric analysis (TGA) data show that the as-made solid contains approximately 13 DMF molecules per formula unit, leading to an overall charged balanced formula $[\text{H}_3\text{O}][\text{Zn}_7(\mu_3\text{-OH})_3(\text{L}2)_6](\text{DMF})_{13}$. The crystals are found to be air sensitive and therefore more accurate elemental analysis was unable to be performed.

When only DMF was used instead of a DMF/ H_2O mixture, in otherwise similar solvothermal reaction conditions between $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{H}_2\text{L}2$, a novel MOF was obtained in good yield. UoC-2 crystallizes in the triclinic space group $P\bar{1}$.^[11b] The inorganic SBU, shown in Figure 2 a, is a new hexanuclear anionic cluster with formula $[\text{Zn}_6(\mu_3\text{-OH})$

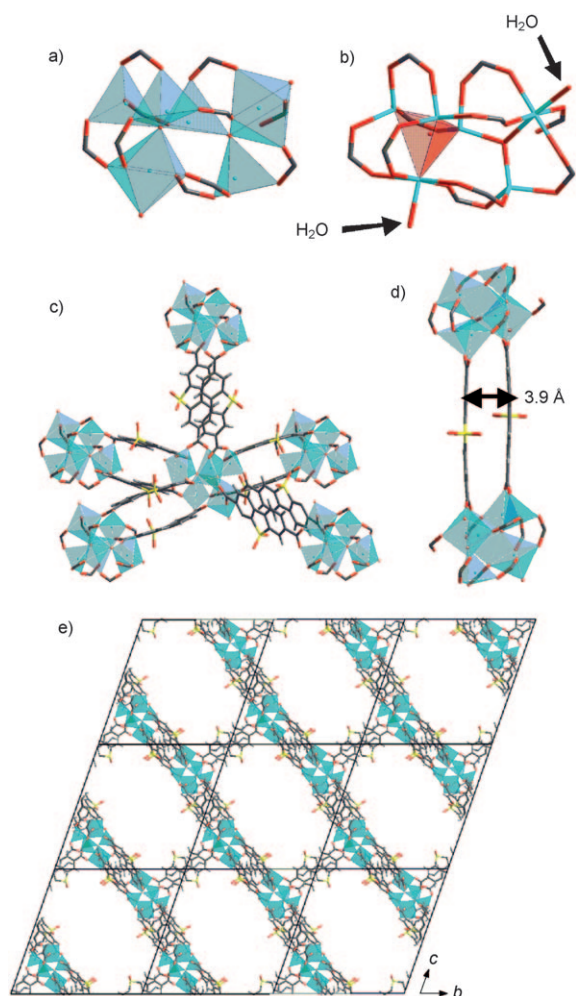


Figure 2. a) Novel hexanuclear $[\text{Zn}_6(\mu_3\text{-OH})(\mu_4\text{-O})(\text{H}_2\text{O})_2(\text{CO}_2)_5]^-$ SBU in UoC-2, b) stick representation of the SBU showing the two coordinated H_2O molecules and the Zn_4O tetrahedron, c) pseudo-square pyramidal connectivity of five SBUs, d) pair of a π - π stabilized $\text{L}2^{2-}$ ligands connecting two adjacent SBUs, and e) pore system in UoC-2 looking down the a axis.

$(\mu_4\text{-O})(\text{H}_2\text{O})_2(\text{CO}_2)_5]^-$ composed of two octahedral and four tetrahedral Zn^{2+} cations. In this cluster, one octahedral and three tetrahedral zinc atoms share a common corner forming a regular Zn_4O tetrahedron while one of these tetrahedral zinc atoms share a corner with the fourth tetrahedral and the second octahedral zinc atom, forming an $\mu_3\text{-OH}$ bridge (see Figure 2 a,b). In addition, a H_2O ligand was found in one of the apical positions of the two octahedral zinc atoms ($\text{Zn}3\text{-O}33$ 2.090(3), $\text{Zn}5\text{-O}34$ 2.039(5) \AA) (see Figure 2 b). Each SBU is linked to five other by ten $\text{L}2^{2-}$ ligands, following a pseudo-square pyramidal connectivity, as shown in Figure 2 c. Remarkably, as in UoC-1, a pair of $\text{L}2^{2-}$ ligands stabilized by weak π - π interactions ($\sim 3.9 \text{ \AA}$), serve as a linking organic SBU between each pair of adjacent inorganic SBUs (see Figure 2 d). One, out of the five crystallographically independent ligands, binds from one side in a monodentate fashion while from the other adopts a bidentate coordination mode, bridging one octahedral and one tetrahedral zinc atom. The other four ligands adopt a bis(bidentate) coordination mode.

The non-interpenetrating structure of UoC-2 shows large, 3D intersecting channels. The window size along the $[100]$ lattice vector is approximately $16 \times 10 \text{ \AA}$ (measured between oxygen atoms of opposite $-\text{SO}_2$ groups, excluding van der Waals radii), see Figure 2 e. The calculated solvent accessible volume^[13] is 73% of the total unit cell volume.

The single crystal X-ray analysis of UoC-2 did not reveal an exact location of a charge balancing cation for the cluster $[\text{Zn}_6(\mu_3\text{-OH})(\mu_4\text{-O})(\text{H}_2\text{O})_2(\text{CO}_2)_5]^-$. Given the fact that it is generally difficult to completely formulate the exact composition of all guest molecules in highly porous MOFs and also that dimethylammonium cations, $(\text{CH}_3)_2\text{NH}_2^+$, are formed in situ upon heating of DMF,^[14] it is natural to consider these as charge balancing cations, leading to an overall charged balanced formula $[(\text{CH}_3)_2\text{NH}_2][\text{Zn}_6(\mu_3\text{-OH})(\mu_4\text{-O})(\text{H}_2\text{O})_2\text{L}2_5](\text{DMF})_x$. Accurate thermogravimetric and elemental analysis was not possible to be performed due to the limited stability of UoC-2 in air.

The large free volume in both UoC-1 and UoC-2 prompts us to investigate the possibility to remove the guest molecules and access the pore space. Because of their limited stability in air, we performed solvent exchange reactions inside a moisture-free, nitrogen filled glove-box.^[10] While UoC-2 was not stable upon solvent removal, for UoC-1 we found that CH_2Cl_2 is a suitable solvent to remove the guest molecules. TGA analysis of vacuum-dried, CH_2Cl_2 -exchanged crystals, revealed the formation of a solvent-free solid, denoted here as UoC-1', which is stable up to 350°C .^[10] However, optical observation of UoC-1' revealed a significant loss of the initial transparent, cubic-like morphology of the crystals. Powder X-ray diffraction measurement shows the formation of a different phase with poor crystallinity.^[10] Nevertheless, the nitrogen adsorption recorded at 77 K revealed a mixed type-I/II isotherm, see Figure 3. The sharp uptake at low relative pressures ($p/p_0 < 0.1$) indicate the presence of microporosity (type-I isotherm) while the almost linear uptake between $0.1 < p/p_0 < 1$ (type-II iso-

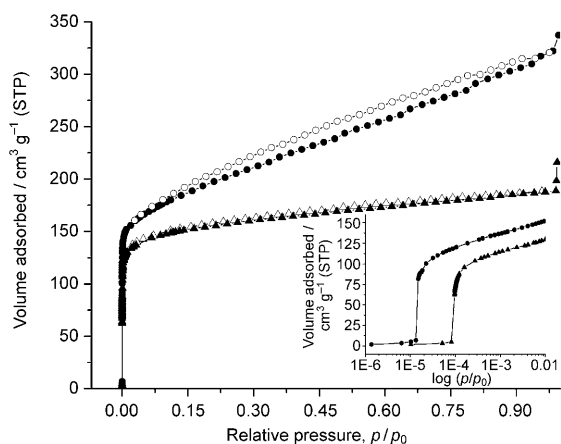


Figure 3. Nitrogen and argon adsorption (filled symbols)/desorption (open symbols) isotherms of UoC-1' recorded at 77 K. Inset shows the low relative pressure region in logarithmic scale.

therm) is characteristic of adsorption by a non-porous solid.^[15] Similar mixed type-I/II nitrogen adsorption isotherms have been observed in some evacuated MOFs.^[16] These results indicate a partial collapse of the framework in UoC-1 upon solvent removal, in agreement with the powder X-ray analysis data.^[10] The argon adsorption isotherm recorded at 77 K confirmed the presence of microporosity in UoC-1'. (see Figure 3). The apparent Langmuir surface area calculated from the N₂ adsorption isotherm, is 649 m² g⁻¹ and the micropore volume 0.24 cm³ g⁻¹ at 0.019 p/p_0 . Detailed micropore analysis using N₂ and Ar at 77 K shows a sharp uptake at very low relative pressures (onset at 1.0×10^{-5} and 1.0×10^{-4} , respectively), see inset of Figure 3. The much lower pore filling pressure for nitrogen clearly indicates that the attractive interactions of nitrogen molecules with the pore surface in UoC-1' are much stronger as compared to argon. The estimated pore size, obtained by applying the Sato and Foley (SF)^[15] calculation method on the N₂ data, is 7.7 Å.^[10] Interestingly, a very similar pore size was obtained from both N₂ and Ar data, when a non-local density functional theory (NLDFT), implementing a carbon equilibrium transition kernel based on a slit-pore model, was applied.^[10]

The accessible porosity found in UoC-1' prompts us to investigate further its gas sorption properties. Hydrogen, carbon dioxide and methane adsorption isotherms were recorded at different temperatures. The hydrogen uptake at 1 bar and 77 K is 0.87 wt% (see Figure 4a). The isosteric heat of adsorption (Q_{st}) calculated from the respective adsorption isotherms at 77 and 87 K employing the Clausius–Clapeyron equation, is approximately 6.8 kJ mol⁻¹ at zero coverage.^[10] This value is close to the corresponding values found for the most promising MOFs for hydrogen storage.^[17] More interestingly, UoC-1' shows a completely reversible, high CO₂ adsorption at near ambient temperature (see Figure 4b). The CO₂ uptake at 1 bar and 273 K is 2 mmol g⁻¹, which is higher compared to the corresponding values of some representative MOFs and ZIFs including MOF-5

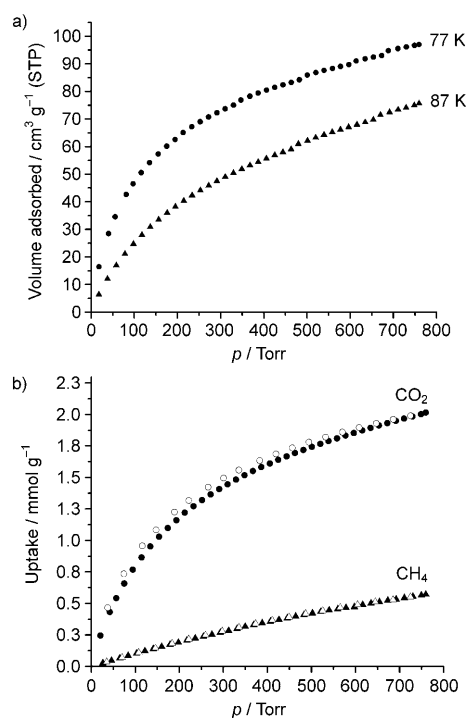


Figure 4. a) Hydrogen adsorption isotherms at 77 K and 87 K and b) carbon dioxide and methane adsorption (filled symbols)/desorption (open symbols) isotherms at 273 K, of UoC-1'.

(1.5 mmol g⁻¹) and ZIF-100 (1.7 mmol g⁻¹).^[18] The CH₄ uptake under the same conditions is 0.57 mmol g⁻¹. To calculate the CO₂/CH₄ selectivity from the corresponding Henry's law constants, we performed a nonlinear fitting of the adsorption isotherms using the Toth model.^[10] Accordingly, the selectivity found at 273 K is 15.7 while at 263 K is 21.5. For comparison, the CO₂/CH₄ selectivity of ZIF-100 and the prototypical adsorbent BPL carbon at 298 K, is 5.9 and 2.5, respectively.^[18] Given the fact that UoC-1' shows negligible N₂ and H₂ adsorption at near ambient temperature (data not shown), its large and highly selective CO₂ adsorption is an important property and indicates that this material may serve as an efficient adsorbent to capture and store CO₂.^[19] Preliminary theoretical calculations show that the observed selectivity results from a significant stronger interaction of CO₂ molecules with the polar sulfone (-SO₂) groups as compared to the other gases. These results will be published in detail elsewhere.

In conclusion, we have shown that the rigid, sulfone functionalized dicarboxylate ligand **H₂L2** is capable in directing the formation of novel, non-interpenetrating 3D MOFs, assembled from unprecedented inorganic SBUs. Another unique feature in both UoC-1 and UoC-2 is that adjacent SBUs are connected via a double rather than a single organic ligand. In addition, UoC-1 is a rare anionic MOF charged balanced by hydronium H₃O⁺ cations. Accessible porosity was found in the solid obtained after solvent removal from UoC-1. This material shows a remarkable selectivity for CO₂ over CH₄, N₂ and H₂ at near ambient temperature.

Finally, the synthesis of UoC-1 and UoC-2 demonstrates that the isorecticular principle, although valid up to date for strictly rigid ligands, does not apply in the case of **H₂L2** under the specific reaction conditions and a novel family of sulfone functionalized MOFs with important properties could be envisioned. The origin of this exception is currently under investigation and it could be related to the non-linear bridging mode of the ligand; the sulfone group bends the two phenyl rings causing the two carboxylate end-groups to form an angle of 163°. [10] Another factor that could act simultaneously is the increased acidity of the ligand caused by the electronegative sulfone group attached to the phenyl rings.

Experimental Section

Synthesis of UoC-1: In a 20 mL vial, Zn(NO₃)₂·6H₂O (0.147 g, 0.49 mmol) and **H₂L2** (0.05 g, 0.16 mmol) were dissolved in a mixture of DMF (10 mL) and H₂O (0.15 mL) at room temperature. The vial was placed in a temperature controlled oven at 95°C. Transparent cubic-like crystals were formed within 24 h. Yield: 0.136 g, based on Zn(NO₃)₂·6H₂O.

Synthesis of UoC-2: In a 20 mL vial, Zn(NO₃)₂·6H₂O (0.147 g, 0.49 mmol) and **H₂L2** (0.05 g, 0.16 mmol) were dissolved in DMF (10 mL) at room temperature. The vial was placed in a temperature controlled oven at 95°C. Transparent, rod-like crystals were formed within 24 h. Yield: 0.145 g, based on Zn(NO₃)₂·6H₂O.

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Keywords: adsorption • carbon dioxide • coordination polymers • metal–organic frameworks • sulfone

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- [10] See Supporting Information for details.
- [11] a) Single crystal X-ray diffraction data for UoC-1: trigonal, space group $R\bar{3}$, $a=b=23.0793(6)$, $c=71.787(2)$ Å, $\alpha=90$, $\beta=90$, $\gamma=120^\circ$, $V=33114.8(2)$ Å³, $Z=6$, $\rho_{\text{calcd}}=0.769$ g cm⁻³, $T=100.0(3)$ K, $2\theta_{\text{max}}=40^\circ$. Refinement of 457 parameters on 6848 independent reflections out of 63157 measured reflections ($R_{\text{int}}=0.0992$) led to $R_1=0.0783$ ($I>2\sigma(I)$), $wR_2=0.2304$ (all data), and $S=1.207$ with the largest difference peak and hole of 1.738 and -0.48 e Å⁻³; b) single crystal X-ray diffraction data for UoC-2: triclinic, space group $P\bar{1}$, $a=21.4410(2)$, $b=23.212(2)$, $c=24.646(3)$ Å, $\alpha=68.103(7)$, $\beta=67.490(7)$, $\gamma=79.993(7)^\circ$, $V=10507.0(2)$ Å³, $Z=2$, $\rho_{\text{calcd}}=0.622$ g cm⁻³, $\mu=0.757$ mm⁻¹, $T=100.0(3)$ K, $2\theta_{\text{max}}=40^\circ$. Refinement of 1011 parameters on 19544 independent reflections out of 69048 measured reflections ($R_{\text{int}}=0.1218$) led to $R_1=0.0492$ ($I>2\sigma(I)$), $wR_2=0.1371$ (all data), and $S=0.788$ with the largest difference peak and hole of 0.296 and -0.459 e Å⁻³. Electron density contributions from disordered guest molecules were handled using the SQUEEZE procedure from the PLATON software suit. See also Supplementary Information for details. CCDC 714151 (UoC-1) and 714152 (UoC-2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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