

Insertion of Functional Groups into a Nd^{3+} Metal–Organic Framework via Single-Crystal-to-Single-Crystal Coordinating Solvent Exchange

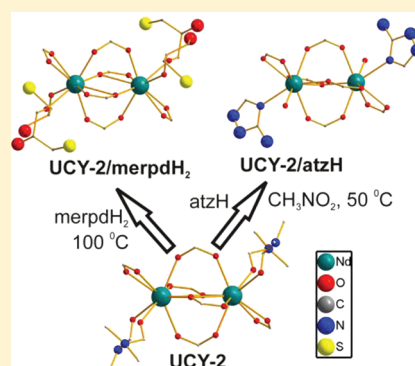
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S Supporting Information

ABSTRACT: Single-crystal-to-single-crystal (SCSC) transformations represent some of the most fascinating phenomena in chemistry. They are not only intriguing from a basic science point of view but also provide a means to modify or tune the properties of the materials via the postsynthetic introduction of suitable guest molecules or organic functional groups into their structures. Here, we describe UCY-2, a new flexible Nd^{3+} metal–organic framework (MOF), which exhibits a unique capability to undergo a plethora of SCSC transformations with some of them being very uncommon. These structural alterations involve the replacement of coordinating solvent molecules of UCY-2 by terminally ligating solvents and organic ligands with multiple functional groups including $-\text{OH}$, $-\text{SH}$, $-\text{NH}-$, and $-\text{NH}_2$ or their combinations, chelating ligands, anions, and two different organic compounds. The SCSC coordinating solvent exchange is thus demonstrated as a powerful method for the functionalization of MOFs.



INTRODUCTION

The current intense interest in metal–organic frameworks (MOFs) stems not only from their unique structural features^{1,2} but also from their potential applications in fields as diverse as gas storage and separation,^{3–6} magnetism,⁷ sensing,⁸ drug delivery,⁹ and catalysis.¹⁰ One of the most recent and important advances in the chemistry of MOFs is related to the development of efficient methods for their postsynthetic modification.^{11,12} It is preferable for such modifications to proceed in a single-crystal-to-single-crystal (SCSC) fashion, in order to gain direct structural information for the modified compounds via their complete characterization with single crystal X-ray crystallography. SCSC transformations are usually observed in MOFs with highly ordered porous structures and framework flexibility (also called soft porous crystals).¹² They involve mainly three different types of structural alterations: (a) insertion/removal of guest molecules,^{13–15} (b) modifications of the organic ligands,^{11,16–18} and (c) changes in the coordination environment of metal ions.^{11,13a,19,20} Such postsynthetic modifications are particularly important, since they can afford MOFs with guest-induced properties and multiple functions [from the introduction of suitable guests, SCSC of type (a)] or MOFs with fine-tuned properties [from the introduction of proper functional groups, SCSC of types (b) and (c)].^{12,19,21} However, SCSC transformations of types (b) and (c) are scarce because they involve the break of covalent or coordination bonds and formation of new ones that usually deteriorate the crystallinity and long-range structural order of the pristine

compounds. Although it is very difficult to rationally synthesize MOFs susceptible to SCSC transformations, a strategy that may assist in the isolation of MOFs with such properties consists of the use of semirigid or flexible polytopic ligands.¹² On the other side, Ln^{3+} MOFs with polycarboxylate ligands can be excellent materials for studying SCSC transformations, because of their high stability in air and various solvents as well as their weakly bound solvent ligands that could be easily released.²²

We herein present a new MOF $[\text{Nd}_2(\text{CIP})_2(\text{DMF})_{2.8}(\text{H}_2\text{O})_{1.2}]$ denoted as UCY-2 (UCY = University of Cyprus) that was prepared from the initial use of a semirigid tricarboxylic ligand H_3CIP [H_3CIP = 5-(4-carboxybenzylideneamino)isophthalic acid] (Figure 1a). It exhibits a flexible 3D-porous structure and an extraordinary capability to undergo a series of SCSC transformations. The latter comprise the exchange of the coordinating and/or guest solvent molecules of UCY-2 by (i) terminally ligating solvent molecules and organic ligands with multiple functional groups, (ii) chelating organic ligands, (iii) anions, (iv) two different organic molecules, and (v) guest solvent molecules. Although SCSC transformations are known for many years,^{13a} to the best of our knowledge, there is no other material reported that is susceptible to such a large variety of SCSC structural alterations. The facile solvent exchange properties of UCY-2

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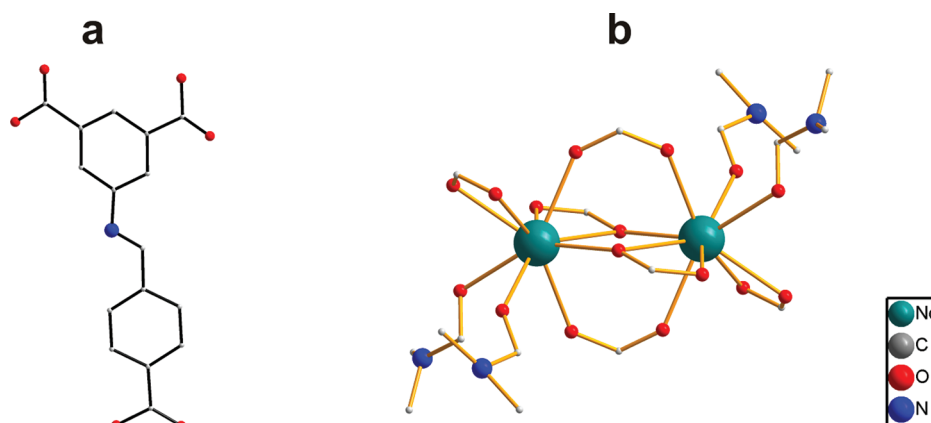


Figure 1. Representations of the (a) H_3CIP ligand and (b) dinuclear SBU of UCY-2. The H atoms and water molecules disordered with DMF ligands have been omitted for clarity.

resulted not only in very uncommon SCSC transformations [e.g., cases (ii)–(iv)] but also in the insertion of a variety of unbound functional groups into the framework structure, including functionalities such as $-\text{SH}$ that have not been previously introduced into the structure of any MOF. Overall, this work demonstrates the SCSC solvent exchange as a powerful method for the functionalization of MOFs.

EXPERIMENTAL METHODS

Materials. Reagent grade chemicals were obtained from Aldrich and used without further purification.

Syntheses. All synthetic procedures were carried out in air.

$\text{H}_3\text{CIP} \cdot 2\text{EtOH}$. A suspension of 5-amino-isophthalic acid (1.2 g, 6.6 mmol) and 4-formylbenzoic acid (1.0 g, 6.7 mmol) in EtOH (30 mL) was heated under reflux conditions for ~ 3 h. During this period, the solids were dissolved and a light yellow solution was formed. Upon cooling of the solution at 5°C for ~ 12 h, white needle-like crystals of $\text{H}_3\text{CIP} \cdot 2\text{EtOH}$ were precipitated which were isolated by filtration, washed several times with EtOH and diethylether, and dried under vacuum. Yield: $\sim 70\%$. The dried crystalline product was analyzed as $\text{H}_3\text{CIP} \cdot 2\text{EtOH} \cdot \text{H}_2\text{O}$ (see Supporting Information).

UCY-2. $\text{H}_3\text{CIP} \cdot 2\text{EtOH} \cdot \text{H}_2\text{O}$ (0.150 g, 0.35 mmol) was dissolved in DMF (5 mL) in a 20 mL glass vial. Then, solid $[\text{Nd}(\text{NO}_3)_3] \cdot x\text{H}_2\text{O}$ (0.120 g, 0.36 mmol) was added to the solution of the H_3CIP ligand. The mixture was sonicated for 3 min and, then, heated without stirring at 100°C for 20 h. During this period, colorless plate-like crystals of UCY-2 were formed. They were isolated by filtration, washed several times with DMF and diethylether, and dried under vacuum. Yield: $\sim 40\%$. The dried crystalline product was analyzed as UCY-2 $\cdot 2\text{H}_2\text{O}$ (see Supporting Information).

UCY-2/ X ($X = \text{MeOH}$, EtOH, THF, Acetone, py, BME, merpd₂). Single crystals of UCY-2 $\cdot 2\text{H}_2\text{O}$ (0.025 g, 0.04 mmol) and the solvent or liquid organic compound (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 or 100°C (the reactions took place at 100°C in the syntheses of UCY-2/py, UCY-2/BME, and UCY-2/merpd₂), remained undisturbed at this temperature for 2 days, and then was allowed to cool at room temperature. The crystals of the exchanged compound were isolated by filtration and dried in the air.

UCY-2/ Y ($Y = 2\text{hpH}_2$, im, atzH, mlma). Single crystals of UCY-2 $\cdot 2\text{H}_2\text{O}$ (0.025 g, 0.04 mmol) and a solution of Y (0.60 mmol) in CHCl_3 or CH_3NO_2 (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 , remained undisturbed at this temperature for 2 days, and then was allowed to cool at room temperature. The crystals of UCY-2/ Y were isolated by filtration and dried in the air.

UCY-2/ Cl . The synthetic procedure that resulted in UCY-2/Im was repeated with the use ImHCl instead of Im. The crystals of the exchanged compound were isolated by filtration and dried in the air.

UCY-2/Im-atzH. Single crystals of UCY-2 $\cdot 2\text{H}_2\text{O}$ (0.025 g, 0.04 mmol) and a solution of atzH (0.050 g, 0.59 mmol) and Im (0.040 g, 0.59 mmol) in CH_3NO_2 (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 , remained undisturbed at this temperature for 2 days, and then was allowed to cool at room temperature. The crystals of UCY-2/Im-atzH were isolated by filtration and dried in the air.

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 $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) or Cu $K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) 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 (multiscan based on symmetry-related measurements) were applied using CrysAlis RED software.²³ The structures were solved by direct methods using SIR2004²⁴ and refined on F^2 using full-matrix least-squares using SHELXL97.²⁵ Software packages used were as follows: CrysAlis CCD for data collection,²³ CrysAlis RED for cell refinement and data reduction,²³ WINGX for geometric calculations,²⁶ and DIAMOND²⁷ for molecular graphics. The non-H atoms were treated anisotropically, whereas the aromatic and hydroxy- and alkyl-hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. The H atoms of water and the formyl-group of DMF terminal ligands could not be located. Electron density contributions from disordered guest molecules were handled using the SQUEEZE procedure from the PLATON software suit.²⁸ Selected crystal data for H_3CIP , UCY-2, and the exchanged compounds are summarized in Tables S1 and S2 in the Supporting Information. CCDC 848176–848190 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Physical Measurements. Elemental analyses (C, H, N) were performed by the in-house facilities of the University of Cyprus, Chemistry Department, and are reported in the Supporting Information. IR spectra were recorded on KBr pellets in the $4000\text{--}400 \text{ cm}^{-1}$ range using a Shimadzu Prestige 21 spectrometer. PXRD diffraction patterns were recorded on a Shimadzu 6000 Series X-ray diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$).

RESULTS AND DISCUSSION

Synthesis and Structures of H_3CIP Ligand and UCY-2. The H_3CIP ligand was synthesized via a Schiff base condensation of 5-amino-isophthalic acid with 4-formylbenzoic acid in ethanol. Its crystal structure was determined by single-crystal X-ray crystallography (Figure 1a). H_3CIP is significantly extended compared to many commonly used tricarboxylic acids (e.g., trimesic acid)^{1,2} and also contains a semirigid imine ($\text{CH}=\text{N}$) linkage between its phenyl-carboxylate moieties,

which induce some (but not unlimited) rotational freedom to the phenyl rings of this organic molecule. Compound **UCY-2** was prepared by a reaction of $\text{Nd}(\text{NO}_3)_3$ and H_3CIP in DMF at 100 °C. It crystallizes in the monoclinic space group $C2/c$ and contains the dinuclear building block $[\text{Nd}_2(\text{COO})_6(\text{DMF})_{2.8}(\text{H}_2\text{O})_{1.2}]$ as the secondary building unit (SBU), Figure 1b. Each SBU consists of two nine-coordinated Nd^{3+} ions and six COO^- from six different CIP^{3-} ligands. Four of the COO^- groups bridge the two Nd^{3+} centers in either *syn,syn*- η^1 : η^1 : μ_2 or η^1 : η^2 : μ_2 fashion. The remaining two COO^- groups act as chelating ligands, with each of them coordinating to a single Nd^{3+} ion. The coordination sphere of each Nd^{3+} is completed by two oxygen atoms from highly disordered DMF and mixed DMF/ H_2O (40%/60%) terminal ligands.

The SBUs extend infinitely creating a three-dimensional (3,6)-connected net with the dinuclear unit and the ligands representing the 6-c and 3-c nodes, respectively (Figure 2). The

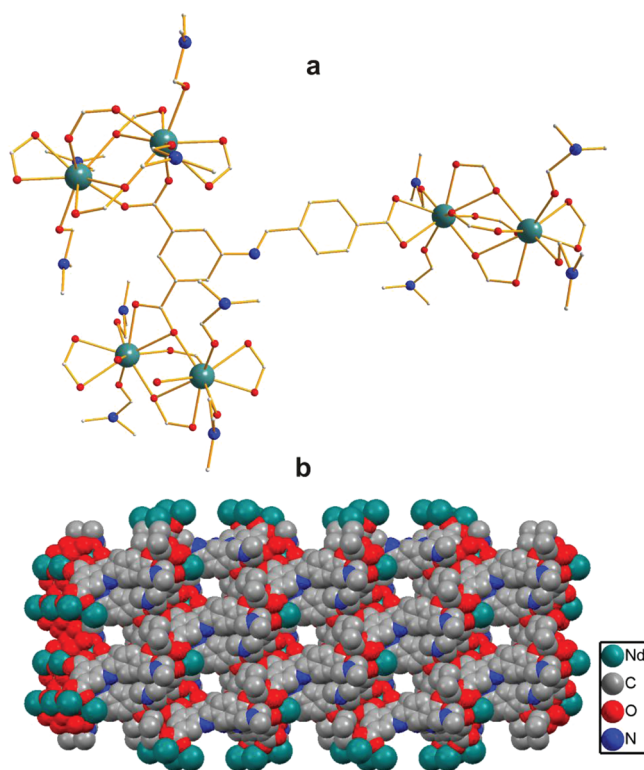


Figure 2. Representations of the (a) connectivity of three SBUs via one CIP^{3-} ligand and (b) 3-D porous structure of **UCY-2**. The H atoms and water molecules disordered with DMF ligands have been omitted for clarity.

point symbol for this net is $(4^2.6)_2\{4^4.6^2.8^7.10^2\}$. This is a subnet of the **flu**-net and can be called **flu-3,6-C2/c** (Figure S1, in Supporting Information). Such a topology has been observed in relatively few MOFs.^{29–33}

The solvent-accessible volume of **UCY-2** calculated by PLATON²⁸ is 1493.6 Å³ corresponding to 27% of the unit cell volume. The 3D-structure contains small cavities with diameters of 3–4 Å as found by PLATON (taking into account the van der Waals radii of the atoms). A representation of the pore network of **UCY-2** with the structure visualization program MERCURY³⁴ reveals that the pores communicate

through narrow passages that are only ~2 Å wide (Figure S2, Supporting Information).

SCSC Transformations Involving Insertion of Solvent Molecules. The presence of highly disordered coordinating solvent molecules in **UCY-2** in combination with its relatively open structure and excellent stability in air (for several months) and various solvents (including water) prompted us to investigate the solvent exchange properties of this compound. Thus, solvent exchange experiments of finely ground powder samples of **UCY-2** were performed in order to replace its coordinating solvent molecules by others such as MeOH, EtOH, acetone, etc. Infrared data indicated in all cases the complete removal of DMF molecules (by the disappearance of the characteristic C=O band of DMF at ~1660 cm⁻¹), while PXRD measurements showed that the structure and crystallinity of the materials were preserved after the exchange of the DMF molecules (Figures S3–S5, Supporting Information). These exchange processes were fully reversible as it was indicated by PXRD and IR data. Single crystal solvent exchange experiments were carried out to unambiguously confirm the replacement of coordinating DMF molecules, by the various solvents, by X-ray crystallography. Thus, heterogeneous solvent-exchange reactions of single crystals of **UCY-2** with the corresponding solvents at 50–100 °C resulted in single crystals that were macroscopically very similar in size and shape with those of the pristine **UCY-2** compound (Figure S6, Supporting Information). All these processes were proven to be SCSC transformations by the determination of the crystal structures of the exchanged compounds. Furthermore, the retention of the crystallinity of the exchanged compounds is reflected on the excellent refinement of their crystal structures (all reported R_1 values are <6%; see Table 1). Note, that in all

Table 1. Selected Crystal Data for the Pristine **UCY-2** and Exchanged Compounds

compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	space group	<i>V</i> (Å ³)	<i>R</i> ₁ (%) ^a
UCY-2	28.89	14.27	13.64	<i>C2/c</i>	5541	5.9
/MeOH	28.48	14.52	12.30	<i>C2/c</i>	4872	5.8
/EtOH	28.66	14.83	12.63	<i>C2/c</i>	5221	4.8
/THF ^b	28.83	14.38	13.25	<i>C2/c</i>	5397	4.5
/Acetone	28.62	14.46	12.83	<i>C2/c</i>	5160	4.8
/py ^c	13.68	15.00	15.65	<i>P1̄</i>	2934	5.0
/merpdH ₂ ^d	29.17	14.45	13.09	<i>C2/c</i>	5454	5.3
/BME ^e	28.54	15.00	13.28	<i>C2/c</i>	5593	4.4
/2hpH ₂ ^f	28.22	15.16	13.59	<i>C2/c</i>	5724	4.1
/Im ^g	28.62	14.07	13.28	<i>C2/c</i>	5215	4.8
/atzH ^h	28.93	13.83	13.16	<i>C2/c</i>	5145	4.0
/Cl	28.53	14.77	13.70	<i>C2/c</i>	5701	5.8
/mIma ⁱ	29.04	13.80	13.08	<i>C2/c</i>	5148	5.3
/Im-atzH	29.85	12.58	14.12	<i>C2/c</i>	5277	4.5

^a $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^bTetrahydrofuran. ^cPyridine. ^d3-Mercapto-1,2-propanediol. ^e2-Mercapto-ethanol. ^f2-Hydroxymethyl-phenol. ^g1-midazole. ^h3-Amino-1H-1,2,4-triazole. ⁱ5-Methyl-1H-imidazole-4-carbaldehyde.

cases several single crystals were examined and found to have identical unit cell parameters. The quantitative transformation of **UCY-2** to the solvent exchanged analogues was also confirmed by FT-IR spectroscopy, which revealed the disappearance of the characteristic band at ~1660 cm⁻¹ assigned to the DMF molecules. The X-ray structural

determination of the exchanged compounds (Figure 3) unambiguously proved the complete replacement of DMF by the various solvents.

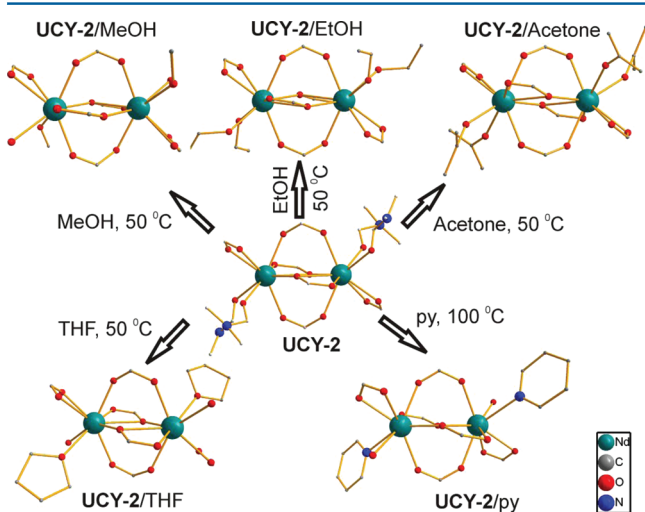


Figure 3. SCSC transformations that resulted in the exchange of terminal solvent ligands of UCY-2 by MeOH, EtOH, acetone, THF, and py; only the SBUs of the pristine and the exchanged products (excluding H atoms) are shown for clarity.

The MeOH-exchanged material (UCY-2/MeOH) contains one MeOH and one H₂O terminal ligands connected to each Nd³⁺ center (Figure 3), with the water molecule presumably originating from residual H₂O in the MeOH solvent. Interestingly, the replacement of the terminal solvents of UCY-2 by MeOH/H₂O resulted in 12% reduction of its unit cell volume, a fact that indicates the framework flexibility of this MOF. The X-ray structural analysis of single crystals obtained from reactions with the less hydrophilic (longer chain) alcohol EtOH revealed the substitution of all terminal ligands by EtOH (compound UCY-2/EtOH) (Figure 3).

Complete exchange of the terminal solvent molecules of UCY-2 was also achieved by treating the single crystals with other common solvents, such as acetone. Thus, the determination of the crystal structure of the acetone-exchanged material (UCY-2/acetone) indicated the existence of two terminal acetone ligands per Nd³⁺ (Figure 3). It is noticeable that the structure of the material retains its crystallinity after heating the acetone-exchanged material at 70 °C under vacuum as revealed by PXRD data (Figure 4). The retention of the integrity of the pore structure of the material after the removal of the coordinating acetone molecules was also confirmed by the fact that the acetone-containing material can be fully restored, as indicated by PXRD (Figure 4), by treating the solvent-free compound with acetone.

Besides small-sized solvent molecules, UCY-2 was also capable of exchanging its terminal solvent ligands with larger heterocyclic aliphatic and aromatic molecules. Thus, the tetrahydrofuran (THF)-exchanged compound was isolated (UCY-2/THF), and its crystal structure revealed the presence of one THF and one water terminal ligand per Nd³⁺ (Figure 3) as well as guest THF molecules that form relatively strong hydrogen bonds (~ 2.7 Å) with the coordinating water molecules (Figure S7, Supporting Information). Furthermore, the crystal structure determination of the pyridine (py)-exchanged material (UCY-2/py) indicated the existence of

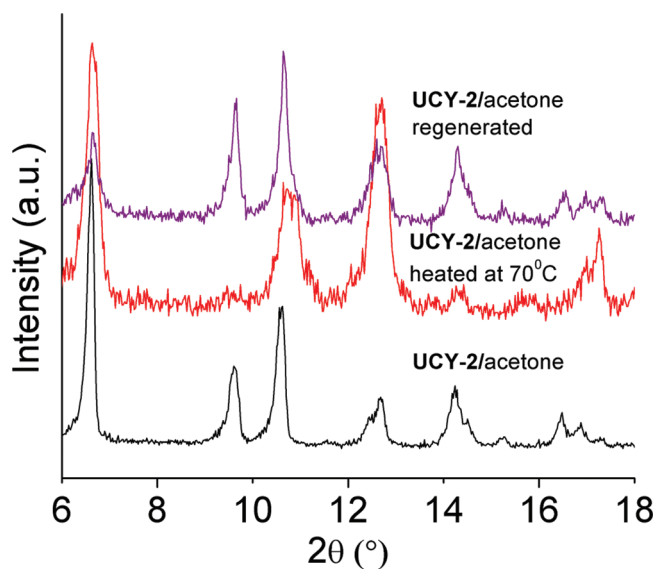


Figure 4. PXRD patterns of UCY-2/acetone, the thermally treated UCY-2/acetone, and the regenerated acetone-exchanged compound.

one coordinating py and one H₂O per Nd³⁺ ion (Figure 3) and also guest py molecules forming relatively strong hydrogen bonds (~ 2.7 – 2.8 Å) with the terminal H₂O ligands (Figure S8, Supporting Information). Although all other exchanged compounds and the pristine UCY-2 crystallize in the monoclinic space group *C2/c*, UCY-2/py displays lower symmetry (triclinic *P1*). This structural differentiation of the py-exchanged compound can be explained by the very different distortions of the CIP³⁻ ligands in this compound compared to those of UCY-2 and other analogues. Specifically, the dihedral angles between the planes of the phenyl rings of CIP³⁻ ligands in UCY-2/py are ~ 28.7 and 52.2° (Figure S9, Supporting Information), whereas the corresponding angles in the pristine UCY-2 and the other exchanged compounds are in the range of 35 – 40° . Remarkably, despite the substantial structural differentiation between UCY-2 and UCY-2/py, the pristine UCY-2 can be fully regenerated (as indicated by the determination of the unit cell parameters of the regenerated material) by treating the py-exchanged compound with DMF at 100 °C.

The absorption of py by UCY-2 is unexpected because py has much larger size (>2.7 Å) than that of the passages between the pores of the framework (~ 2 Å; see Figure S2, Supporting Information). A close examination of the pore network of UCY-2/py (Figure S10, Supporting Information) revealed that the passages between the pores of the py-containing material are ~ 3.4 Å wide (excluding all solvents from the pores) and the maximum pore size and the solvent-accessible volume of this material are 5.7 Å and $\sim 41\%$, respectively. Thus, in all cases, the observed values are much higher than those found for the pristine UCY-2 (see above). Therefore, the pores and channels of UCY-2 significantly expand upon treatment with py to allow the diffusion of this organic molecule into the framework. The insertion of py into UCY-2 is thus due to the “breathing” of the framework,^{2,12} which is favored by the flexibility of the structure of this MOF.

SCSC Functionalization Reactions. Encouraged by the above results, we extended our investigations to solvent exchange reactions of UCY-2 with organic molecules containing multiple functional groups. The solvent exchange reactions involving liquid organic molecules were performed by

immersing single crystals of **UCY-2** into these liquids followed by the thermal treatment of the mixtures at 50–100 °C. When, however, these organic compounds were solids, their incorporation into the framework of **UCY-2** was achieved via a solvent-exchange reaction of single crystals of **UCY-2** with a solution of the corresponding organic molecule in a non-coordinating solvent (e.g., CHCl_3 , CH_3NO_2) at 50–100 °C. Again, the structures of the exchanged materials were accurately identified (all reported R_1 values are <6%, Table 1). Thus, these solvent exchange reactions resulted in the (partial or complete) replacement of the terminal solvent molecules of **UCY-2** by 2-hydroxymethyl-phenol (2hpH₂), mercapto-alcohols [2-mercapto-ethanol (BME), 3-mercapto-1,2-propanediol (merpdH₂)], imidazole (Im), and 3-amino-1H-1,2,4-triazole (atzH), Figure 5. The inserted organic molecules were terminally ligated to the

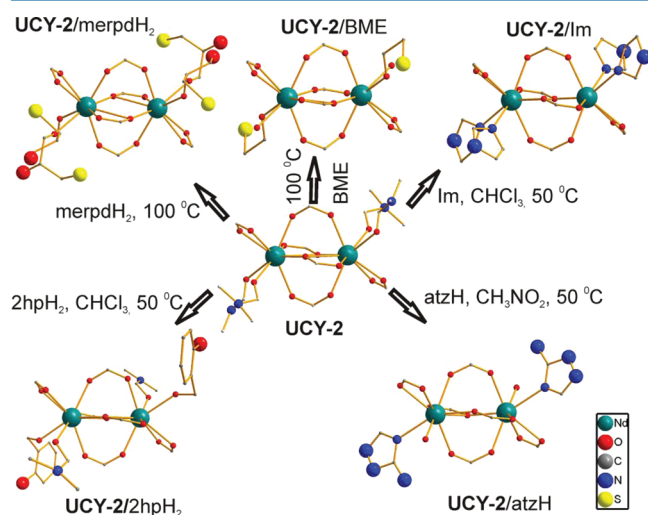


Figure 5. SCS transformations involving the exchange of terminal solvent ligands of **UCY-2** by merpdH₂, BME, Im, 2hpH₂, and atzH. For emphasis, the free functional groups are depicted as large balls. Only the SBUs of the exchanged products are shown for clarity. The H atoms and water molecules (35% occupancy) disordered with BME (65% occupancy) have been omitted.

Nd^{3+} ions through the OH groups and imidazole or triazole nitrogen atoms. Therefore, it was possible to obtain MOFs containing unbound –OH, –SH, –NH–, and –NH₂ functional groups or combinations of them. This functionalization method, which can be regarded as single crystal coordinating solvent exchange (SCCSE), has not been systematically employed so far for the postsynthetic modification of MOFs.¹⁹

The SCCSE method seems to be an efficient and facile method for the insertion of thiol-groups into the structure of MOFs, as indicated by the isolation of **UCY-2/BME** and **UCY-2/merpdH₂**. The complete removal of DMF and the insertion of ligands containing the –SH group has been confirmed not only by X-ray crystallography but also by IR spectroscopy (Figure S11, Supporting Information). **UCY-2/BME** and **UCY-2/merpdH₂** represent extremely rare examples of MOFs containing free –SH functionalities. To the best of our knowledge, there is only one other MOF containing such group; however, it was serendipitously isolated.³⁵ Note, that the direct synthesis of MOFs with unbound –SH groups is usually inhibited by the hydrolytic instability of thiols, and thus, the only rational method to introduce such groups into MOFs is via a postsynthetic modification. The isolation of thiol-functionalized materials is of significant importance because of their unique properties such as high binding affinity and sorption capacity for heavy metal ions³⁶ and excellent separation performance for CO₂ and CH₄ over H₂.³⁷ In addition, the SCCSE method appears to be useful for the synthesis of porous MOFs with uncoordinated polar groups (e.g. OH, NH₂, etc.), as demonstrated by the isolation of **UCY-2/2hpH₂**, **UCY-2/Im**, and **UCY-2/atzH**. Such materials often display interesting gas sorption properties such as high selectivity for CO₂.³⁸

In all SCS transformations described above, the terminal solvent molecules of **UCY-2** were substituted by other terminal ligands. However, the terminal ligands of **UCY-2** can also be exchanged by chelating ligands. Thus, the reaction of single crystals of **UCY-2** with 5-methyl-1H-imidazole-4-carbaldehyde (mIma) in CH_3NO_2 at 50 °C, resulted in the **UCY-2/mIma** analogue, in which the two terminal solvent molecules (per

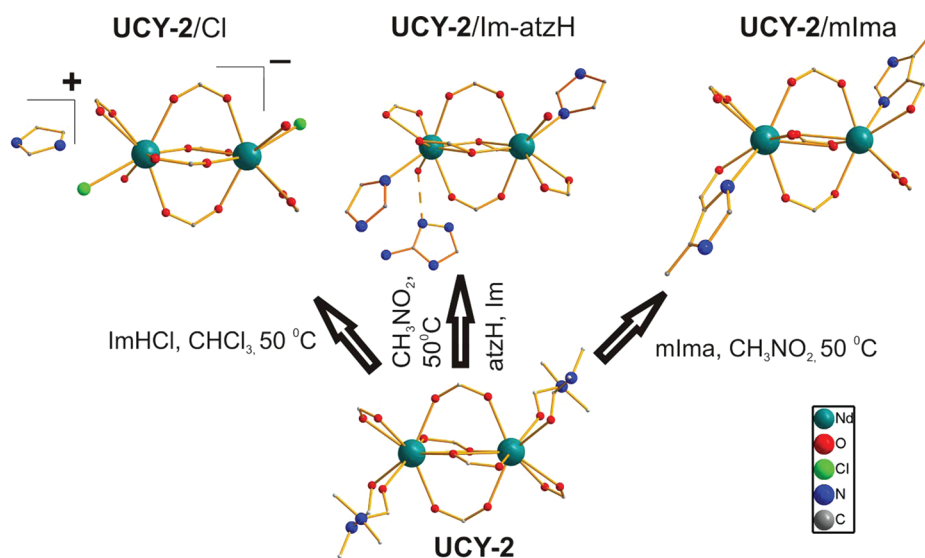


Figure 6. SCS transformations that led to the exchange of DMF ligands of **UCY-2** by ImHCl, mIma, and a combination of Im and atzH. The hydrogen bond between a water oxygen and a nitrogen atom of atzH is indicated as a dotted line. Only the SBUs of the exchanged products are shown. The H atoms for all structures and water O atoms disordered with Cl in **UCY-2/Cl** have been omitted.

Nd³⁺) were completely replaced by one mIma molecule chelating the Nd³⁺ through the nitrogen and aldehydic oxygen atoms (Figure 6).

A surprising result was obtained in our effort to exchange the terminal ligands of UCY-2 by the hydrochloride salt of imidazole (ImHCl). The structure elucidation of the exchanged material revealed the existence of 0.5 Cl[−] (mixed with 0.5 H₂O) and one water terminal ligand per Nd³⁺ (Figure 6). Thus, this exchange process resulted in the incorporation of negative charge into UCY-2, which is compensated by the positive charge of one protonated guest imidazole molecule. Such exchange of neutral molecules by anions is quite rare^{13a} and could be a potential method for obtaining MOFs with ion-exchange properties.

Finally, exchange reactions of UCY-2 with a combination of two different organic molecules were performed. Thus, the reaction of single crystals of UCY-2 with an equimolar mixture of Im and atzH in CH₃NO₂ afforded UCY-2/Im-atzH, which contains an imidazole and water terminal ligands per Nd³⁺ as well as a guest atzH molecule forming relatively strong hydrogen bonds (~2.8 Å) with the terminal water ligand (Figure 6). Therefore, the solvent exchange properties of UCY-2 can also be useful for producing materials with potentially unusual properties arising from the simultaneous presence of various organic molecules with different functionalities.

CONCLUSIONS

In conclusion, we have synthesized a Nd³⁺ MOF (UCY-2) that is based on a new semirigid tricarboxylic ligand. The new MOF displays a 3-D structure that incorporates both flexibility and rigidity. UCY-2 exhibits facile topotactic solvent exchange with a variety of organic molecules, as a result of the high mobility of its coordinating (and lattice) solvents and its flexible porous framework allowing breathing phenomena. It is remarkable that all these exchange processes proceed in a single-crystal-to-single-crystal fashion, thus providing the opportunity to obtain direct structural information for the exchanged compounds. Some highlights of these SCSC exchange reactions comprise the substitution of neutral terminal ligands by a chelating ligand or an anion leading to an anionic MOF as well as the simultaneous insertion of two different organic molecules into UCY-2 through an one step SCSC exchange process with a mixture of these organic molecules. UCY-2 represents a unique case of MOF being so susceptible to SCSC transformations and may be considered as a textbook example for these fascinating phenomena in chemistry and materials science. Finally, this solvent exchange capability of UCY-2 allowed us to demonstrate the potency of the SCCSE method as a means to introduce a plethora of functional groups into the framework of a MOF, including functionalities (such as −SH) that were incorporated into such materials for the first time. Given the number of porous MOFs with disordered and mobile coordinating solvents, the SCCSE method could be a general and efficient strategy for the functionalization of MOFs.

ASSOCIATED CONTENT

Supporting Information

PXRD, elemental analyses data, structural figures, selected FT-IR spectra, and single crystal X-ray crystallographic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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