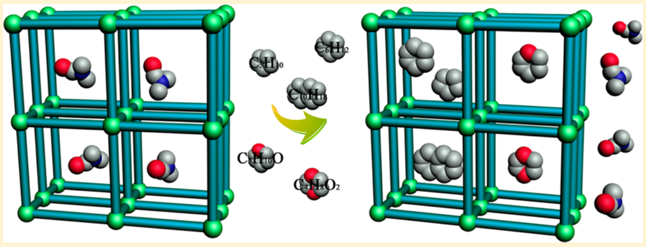
Inorganic Chemistry
Article
pubs.acs.org/IC

Series of Solvent-Induced Single-Crystal to Single-Crystal Transformations with Different Sizes of Solvent Molecules

Yuan-Chun He, Jin Yang,* Ying-Ying Liu, and Jian-Fang Ma*

Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, No. 5268, Renmin Street, Changchun 130024, People's Republic of China

Supporting Information



ABSTRACT: A highly stable soft porous coordination polymer (PCP), namely $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot 2H_2O\cdot 2DMF$ (**1**), has been synthesized via an *in situ* synthesis of 4-tetrazole pyridine (TP) under solvothermal conditions (DMF = *N,N*′-dimethylformamide). Remarkably, the solvent molecules in **1** can be respectively exchanged with cyclohexane (C_6H_{12}), cyclopentane (C_5H_{10}), decahydronaphthalene ($C_{10}H_{18}$), 1,4-dioxane ($C_4H_8O_2$), and tetrahydropyrane ($C_5H_{10}O$) in single-crystal to single-crystal (SCSC) manners to yield $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot 3C_6H_{12}$ (**1a**), $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot 2C_5H_{10}$ (**1b**), $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot H_2O\cdot C_{10}H_{18}$ (**1c**), $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot C_4H_8O_2$ (**1d**), $[Cu_3(TP)_4(N_3)_2]\cdot 3C_4H_8O_2$ (**1e**), and $[Cu_3(TP)_4(N_3)_2]\cdot 2H_2O\cdot C_5H_{10}O$ (**1f**). Further, the occluded cyclohexane molecules in **1a** can be removed by heating to give its porous guest-free form $[Cu_3(TP)_4(N_3)_2(DMF)_2]$ (**1g**). Particularly, in water, **1** can lose its coordinated N_3^- anions to generate $[Cu(TP)_2(H_2O)_4]\cdot 4H_2O$ (**1h**). More interestingly, the soft PCP (**1**) demonstrates the guest selectivity for the cycloalkane solvents, namely cyclohexane, cyclopentane, and decahydronaphthalene, in SCSC manners for the first time, attributed to the synergy effect between the size and geometry of the solvent and the shape of the framework cavity. Moreover, the desolvated samples of **1e** show the highly selective gas adsorption of CO_2 over N_2, indicating its potential application in the separation of the CO_2/N_2 mixture.

1. INTRODUCTION

Porous coordination polymers (PCPs) that exhibit a degree of flexibility or dynamic behaviors (soft porous crystals) have attracted significant attention because of their structural dynamics in recent years.[1−15] As compared to the rigid porous crystalline solids, the soft PCPs are sensitive to guest inclusion and removal due to their dynamic and flexible frameworks.[16−28] In other words, the soft PCPs can optimize their pore size in accordance with the type of guest molecule, while retaining high regularity.[29−31] As a result, the dynamic properties of these materials make them very useful for applications which are not easily accessible by rigid porous crystalline frameworks.[32−37] Accordingly, this can result in high selectivity or gated adsorption/desorption behavior for guest solvents.[38−45]

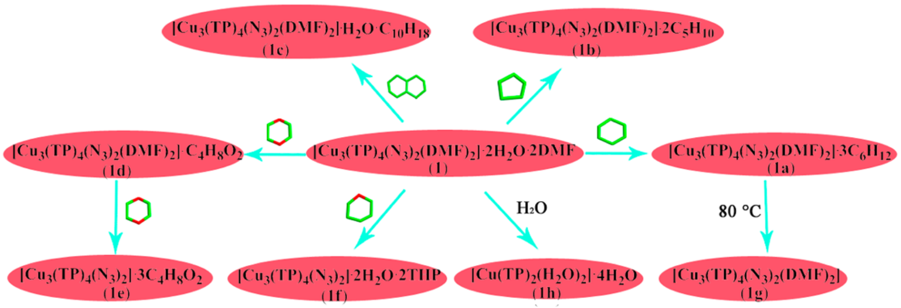
Examples for dynamic behaviors of the soft PCPs induced by altering the conventional volatile solvents, such as CH_3OH, CH_3CH_2OH, CH_3CN, CH_2Cl_2, $CHCl_3$, and CCl_4, or the component ratios of these mixed solvents have been reported through single-crystal to single-crystal (SCSC) transformations.[46−52] However, there are only very limited examples in which the solvents with rings, such as cycloalkanes and aromatic species, were utilized to investigate the dynamic behaviors of the soft PCPs through the SCSC transformations because of their relatively large sizes and geometries.[53−56] Very recently, the soft PCPs have been employed in liquid-phase adsorption and separation of C_6−C_8 aromatics, and solid-phase adsorption and separation of naphthalene and anthracene through the SCSC transformations.[53,54] However, we are not aware of any examples where the soft PCPs display guest selectivity for cycloalkane solvents through the SCSC transformations thus far.[46−56]

Cycloalkanes, such as the common cyclopentane (C_5H_{10}) and cyclohexane (C_6H_{12}), and the medium decahydronaphthalene ($C_{10}H_{18}$), are an important class of industrial mixed raw materials in petroleum and widely used as precursors in the synthesis of a variety of products.[57−59] In industry, such mixtures are normally purified by using a distillation process.[60−62] Microporous materials, such as the soft PCPs, are promising materials for the purity of such mixtures that involve selective adsorption.[63,64]

Herein we report the synthesis of a highly stable soft PCP, namely $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot 2H_2O\cdot 2DMF$ (**1**), via an *in situ* synthesis of 4-tetrazole pyridine (TP) (DMF = *N,N*′-dimethylformamide). Notably, the solvent molecules in **1** can be, respectively, exchanged by cyclohexane (C_6H_{12}), cyclopentane (C_5H_{10}), decahydronaphthalene ($C_{10}H_{18}$), 1,4-dioxane ($C_4H_8O_2$), and tetrahydropyrane ($C_5H_{10}O$) in SCSC manners to give $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot 3C_6H_{12}$ (**1a**), $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot 2C_5H_{10}$ (**1b**), $[Cu_3(TP)_4(N_3)_2$-

Received: April 10, 2014
Published: July 1, 2014

Scheme 1. Solvent Exchanged 1a−1h from 1 through SCSC Transformations



$(DMF)_2]\cdot H_2O\cdot C_{10}H_{18}$ (**1c**), $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot C_4H_8O_2$ (**1d**), $[Cu_3(TP)_4(N_3)_2]\cdot 3C_4H_8O_2$ (**1e**), and $[Cu_3(TP)_4(N_3)_2]\cdot 2H_2O\cdot C_5H_{10}O$ (**1f**) (Scheme 1). Further, the occluded cyclohexane molecules in **1a** can be removed by heating to give its porous guest-free form $[Cu_3(TP)_4(N_3)_2(DMF)_2]$ (**1g**). Compounds **1−1g** are stable in atmospheric conditions for several months, but they will decompose in methanol, ethanol, benzene, and toluene. Particularly, in water, **1** will lose its coordinated N_3^- anions to form $[Cu(TP)_2(H_2O)_4]\cdot 4H_2O$ (**1h**).[65] More importantly, the soft PCP (**1**) demonstrates the guest selectivity for the cycloalkane solvents, namely cyclopentane, cyclohexane, and decahydronaphthalene, through SCSC transformations for the first time. Moreover, the selective gas adsorption of CO_2/N_2 mixture was also investigated for the desolvated samples of **1e**.

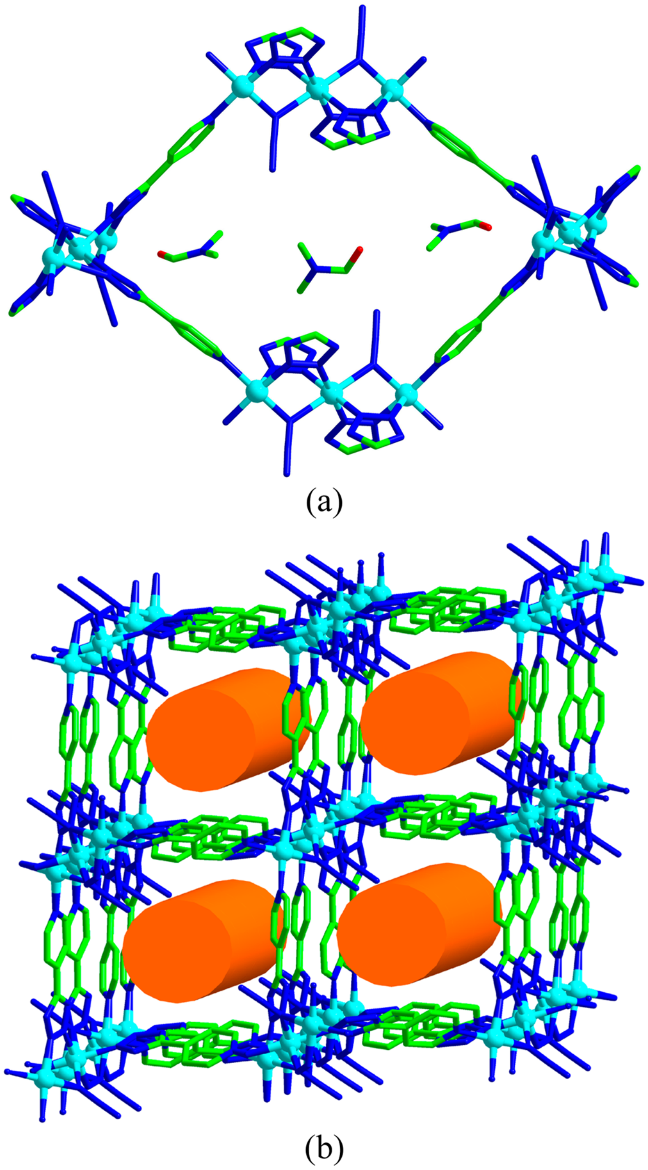
2. RESULTS AND DISCUSSION

2.1. Structure Description of (1).

Compound (**1**) was prepared by "one pot" method with $Cu(NO_3)_2\cdot 3H_2O$, NaN_3, and 4-cyanopyridine in DMF at 80 °C for 1 day. Single-crystal X-ray analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/n$ (Supporting Information Table S1). The asymmetric unit of **1** consists of one and a half Cu(II) atoms, two TP anions, and one azide anion. The two Cu(II) atoms (Cu1 and Cu2) are six-coordinated in octahedral geometries, but they show different coordination environments (Supporting Information Figure S1a). Cu1 atom, sitting on an inversion center, is coordinated by six nitrogen atoms (Cu1−N4 = 2.020(3), Cu1−N8 = 2.024(3), and Cu1−N11 = 2.296(3) Å) from four different TP anions and two distinct azide anions in an octahedral environment (Supporting Information Tables S2−S10). Nevertheless, Cu2 atom is coordinated by five nitrogen atoms (Cu2−N1 = 2.012(3), Cu2−N3 = 2.022(3), Cu2−N6 = 2.017(3), and Cu2−N11 = 1.989(3) Å) from four different TP anions and one azide anion, and one oxygen atom (Cu2−O1 = 2.492(14) Å) from one DMF molecule in an octahedral sphere. Both the Cu−N and Cu−O bond distances fall into the range of normal values of the related complexes.[66−69] Two neighboring Cu1 and Cu2 atoms are linked by one end-on (EO) single azido bridge and two deprotonated TP bridges, with the Cu···Cu separation of 3.444(5) Å. Further, Cu1, Cu2, and a symmetry-related $Cu2^{\#1}$ (symmetry code: $-x + 1, -y, -z + 1$) are joined together via two N_3^- anions and two DMF molecules to yield a unique trinuclear Cu(II) cluster $[Cu_3(N_3)_2(DMF)_2]$. Moreover, each trinuclear cluster is linked by eight neighboring ones through the bridging TP anions, resulting in a 3D porous CsCl-type framework with square windows of ca. 13.135 Å × 21.390 Å (Figure 1a,b and Supporting Information Figure S1b−d). The free water and DMF molecules are included in the channels. The calculated free volume in fully desolvated (**1**) is 56.2% by PLATON.[70]

2.2. Single-Crystal to Single-Crystal Transformations.

Inspired by the relatively open framework and the presence of


(a)

(b)

Figure 1. (a) View of the square window of **1**. (b) View of the 3D porous framework of **1**.

guest solvents (DMF and H_2O) in **1**, we tried to investigate its SCSC properties through a solvent exchange method. The crystalline samples of **1** were, respectively, immersed in several solvents with 5-, 6-, or 10-membered rings, namely, cyclopentane, cyclohexane, decahydronaphthalene, 1,4-dioxane, and tetrahydropyrane. Strikingly, the guest molecules in **1** can be replaced with the solvents to yield their corresponding exchanged compounds, namely $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot 3C_6H_{12}$ (**1a**), $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot 2C_5H_{10}$ (**1b**), $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot H_2O\cdot C_{10}H_{18}$ (**1c**), $[Cu_3(TP)_4(N_3)_2(DMF)_2]\cdot C_4H_8O_2$ (**1d**), $[Cu_3(TP)_4(N_3)_2]\cdot 3C_4H_8O_2$ (**1e**), and $[Cu_3(TP)_4(N_3)_2]\cdot 2H_2O\cdot C_5H_{10}O$ (**1f**), without destroying its single-crystal nature (Scheme 1 and Figure 2).

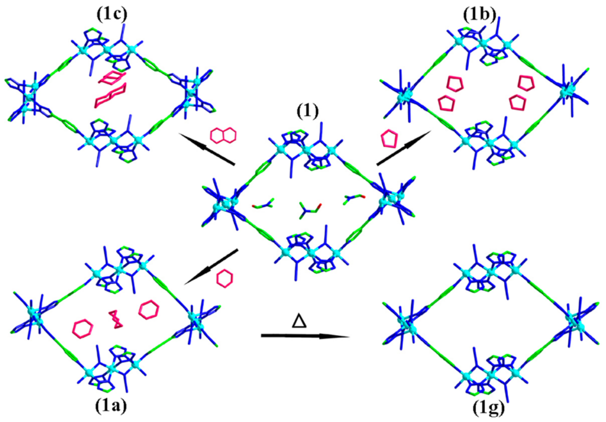


Figure 2. Structural transformations from **1** to **1a**−**1c** and **1g** in SCSC manners.

Typically, the complete removal of free guest DMF and water molecules could be achieved to give cyclohexane-exchanged crystalline samples of **1a** after the crystalline samples of **1** were suspended in cyclohexane for 7 days (Figure 2). Single-crystal X-ray analysis reveals that **1a** still maintains the original monoclinic space group $P2_1/n$ (Supporting Information Table S1). There is only a little expansion of *a*, *b*, and *c* axes (Δa = 0.96%, Δb = 1.89%, and Δc = 1.02%), which consequently results in a small expansion of the cell volume (ΔV = 3.74%) (Supporting Information Table S11). The overall framework structure of **1a** is the same as that of **1** (Supporting Information Figure S2). However, the sizes of the square windows have obvious variations from ca.13.135 Å × 21.390 Å in **1** to ca.13.261 Å × 21.697 Å in **1a** (Supporting Information Figure S2b). In addition, the separations of the weak Cu···O(DMF) interactions were significantly elongated from 2.492 Å in **1** to 2.853 Å in **1a**.

It is interesting to note that the guest cyclohexane molecules in the crystalline samples of **1a** can be further removable after heating at 80 °C for 3 h under a dynamic vacuum, which led to the porous guest-free form $[Cu_3(TP)_4(N_3)_2(DMF)_2]$ (**1g**) (Supporting Information Figure S3). Compounds **1g** and **1a** have the identical monoclinic space group $P2_1/n$ (Supporting Information Table S1). In comparison with **1**, the unit cell parameters of **1g**, such as *a*, *b*, and volume, contracted by 1.29%, 2.58%, and 2.16%, respectively. Accordingly, the sizes of the square windows reduce from ca.13.261 Å × 21.697 Å in **1a** to ca. 13.090 Å × 21.447 Å in **1g** because of the removal of the guest-free cyclohexane molecules. The distances of the weak Cu···O(DMF) interactions decreased from 2.853 Å in **1a** to 2.599 Å in **1g** (Supporting Information Table S4). It is noteworthy that the porous guest-free form (**1g**) could not be directly obtained from **1** by heating under a dynamic vacuum, which may be attributed to the involatility of the guest DMF molecules relative to the cyclohexane solvents.

Similarly, **1b** and **1c** also can be achieved by soaking the crystalline samples of **1** in cyclopentane for 7 days and decahydronaphthalene for 20 days, respectively (Figure 2). Single-crystal X-ray analysis shows that **1b** and **1c** also remain in the monoclinic space group $P2_1/n$ (Supporting Information Figures S4 and S5). However, contractions of *a* and *b* axes (Δa = −0.18% and Δb = −0.43% for **1b**, and Δa = −2.36% and Δb = −0.43% for **1c**) and expansions of *c* axis (Δc = 1.83% for **1b** and Δc = 3.72% for **1c**) led to small expansions of the cell volumes (ΔV = 1.12% for **1b** and ΔV = 1.50% for **1c**) (Supporting Information Table S11). The sizes of the square windows for **1b** and **1c** are ca.13.111 Å × 21.549 Å and ca. 12.825 Å × 21.838 Å, respectively (Supporting Information Figures S4b and S5b). The distances of the weak Cu···O(DMF) interactions range from 2.492 Å in **1** to 2.754 Å in **1b** and 2.745 Å in **1c**. Noteworthy, in **1b**, the guest-free DMF and water molecules are completely exchanged by cyclopentane molecules. Nevertheless, in **1c**, partial waters still remain in the porous framework after the exchange of **1** by the decahydronaphthalene, which may arise from the relatively large shape and geometry of the decahydronaphthalene molecule.

To further investigate the SCSC transformations of **1** in polar solvents, the 1,4-dioxane and tetrahydropyrane were employed to replace the water and DMF solvents of **1** (Figure 3).

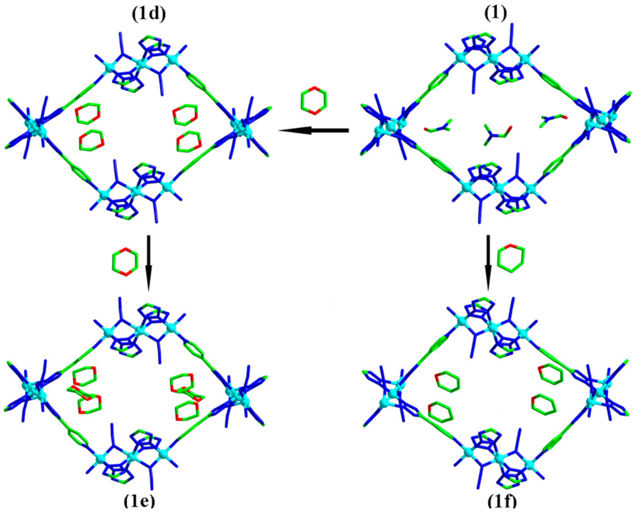


Figure 3. Structural transformations from **1** to **1d**−**f** in SCSC manners.

Typically, after crystalline samples of **1** were immersed in 1,4-dioxane solvent for 4 days, the guest-free DMF and water molecules could be completely replaced by 1,4-dioxane to give the corresponding exchanged crystalline **1d** (Supporting Information Figure S6). Single-crystal X-ray analysis indicates that **1d** still reserves the monoclinic space group $P2_1/n$ (Supporting Information Table S1). There are expansions of *a* and *c* axes (Δa = 1.2% and Δc = 1.9%) and a contraction of *b* axis (Δb = −1.0%), which finally result in a small expansion of the cell volume (ΔV = 2.1%) (Supporting Information Table S11). The size of the square window of **1d** is ca. 13.299 Å × 21.506 Å (Supporting Information Figure S6b). Obviously, the guest exchange is accompanied by a small expansion in the size of the square window relative to that of **1** (ca.13.135 Å × 21.390 Å). The overall framework structure of **1d** is also identical to that of **1** (Supporting Information Figure S6c). It is noteworthy that the distances of the weak Cu···O(DMF) interactions vary from 2.492 Å in **1** to 3.028 Å in **1d**, indicating that the coordinated DMF molecules in **1** have become the guest-free molecules in **1d**. As a result, it is possible that the DMF molecules in **1d** could be further exchanged by 1,4-dioxane. After crystalline samples of **1d** were further suspended in 1,4-dioxane solvent for an additional 3 days, its DMF molecules can be completely exchanged by 1,4-dioxane to yield crystalline samples of **1e** (Supporting Information Figure S7). Compound **1e** also crystallizes in the monoclinic space group $P2_1/n$ (Supporting Information Table S1). In comparison with those of **1**, *a* and *c* axes expand to 0.83% and 1.98%, and *b* axis shrinks to 2.25% in **1e**, which finally results in a small expansion of the cell volume (ΔV = 0.42%). The sizes of the square windows vary from ca.13.135 Å × 21.390 Å in **1** to ca.13.244 Å × 21.382 Å in **1e** (Supporting Information Figure S7b). Similarly, the DMF molecules in **1** can also be completely exchanged by the polar tetrahydropyrane to give **1f** after the crystalline samples of **1** were soaked in tetrahydropyrane for 7 days (Supporting Information Figure S8). In contrast to those of **1** (ca.13.135 Å × 21.390 Å) and **1e** (ca.13.244 Å × 21.382 Å), there is a small expansion of the size of the square window of **1f** (ca.13.596 Å × 21.456 Å) (Supporting Information Figure S8b). Apparently, the two examples indicate that the SCSC transformations of **1** also can occur in polar solvents through the exchange of the DMF and water molecules. Different from the no-polar solvents, the polar ones can completely replace all the solvents including the coordinated DMF molecules of the crystalline samples of **1**, which may be generated from the polar effect of the solvents.

Notably, a distinct SCSC transformation takes place by putting compound **1** in water, and a mononuclear compound (**1h**) was obtained.[65] In **1h**, each Cu(II) atom is coordinated by two TP anions and four water molecules (Supporting Information Figure S9). We presume that azide anion of **1** was unstable in water, and can react with water to form azoimide and hydroxyl ions. So the trinuclear Cu(II) cluster $[Cu_3(N_3)_2(DMF)_2]$ in **1** disaggregates, leading to transformation from **1** to **1h**. In addition, if compounds **1a**−**g** were soaked in water, the same results can be observed.

2.3. Guest Selectivity of Cyclohexane, Cyclopentane, and Decahydronaphthalene in Liquid State.

Of special interest, crystalline samples of **1** show guest selectivity for a mixture of cyclohexane and cyclopentane, cyclohexane and decahydronaphthalene, or cyclopentane and decahydronaphthalene (Figure 4). Typically, when crystalline samples of **1** were immersed in the mixture of cyclohexane and cyclopentane with a volume ratio of 1:1, **1a** was always obtained as the only product, which was proven by single-crystal X-ray diffraction (Figure 4). The result demonstrates that crystalline samples of **1** could be a potential absorbent for the separation of cyclohexane and cyclopentane in liquid phase. Further, when crystalline samples of **1** were soaked in the mixture of cyclopentane and decahydronaphthalene, only cyclopentane could be selectively adsorbed to give **1b** (Figure 4). Similarly, a guest selectivity for cyclohexane over decahydronaphthalene was also observed in a process similar to that using cyclopentane and decahydronaphthalene. The results clearly exhibit a different capability for selective absorption in a sequence of cyclohexane > cyclopentane > decahydronaphthalene. Notably, for guest selectivity for cyclohexane, cyclopentane, and decahydronaphthalene using **1** as absorbents may be the result of the synergy effect between the size and geometry of the solvent and the shape of the framework cavity.[53] In terms of the guest selectivity for cyclohexane or cyclopentane in the mixed solvent of cyclopentane and decahydronaphthalene, or cyclohexane and decahydronaphthalene, the size of the solvent is critical for the structural transformation. In these corresponding mixtures, crystalline samples of **1** prefer to selectively absorb the solvents with smaller sizes, such as cyclohexane and cyclopentane. Nevertheless, the guest selectivity for cyclohexane in the mixture of cyclohexane and cyclopentane may be attributed to the synergy effect between the size and geometry of the solvent and the shape of the framework cavity. In other words, the shape of the cavity of **1** only allows the preferential diffusion of the solvents with suitable size and geometry into the framework.

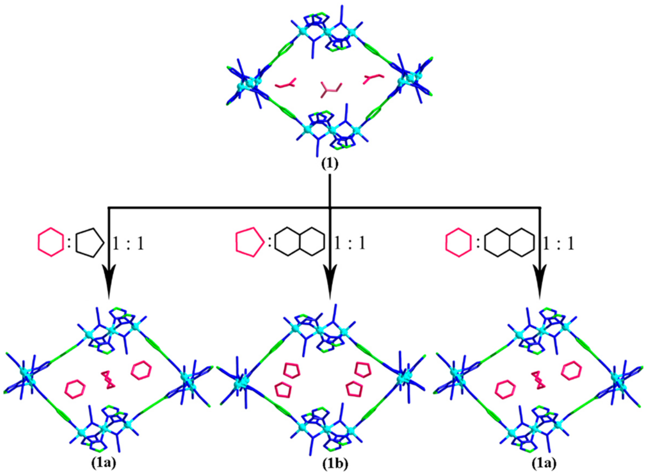
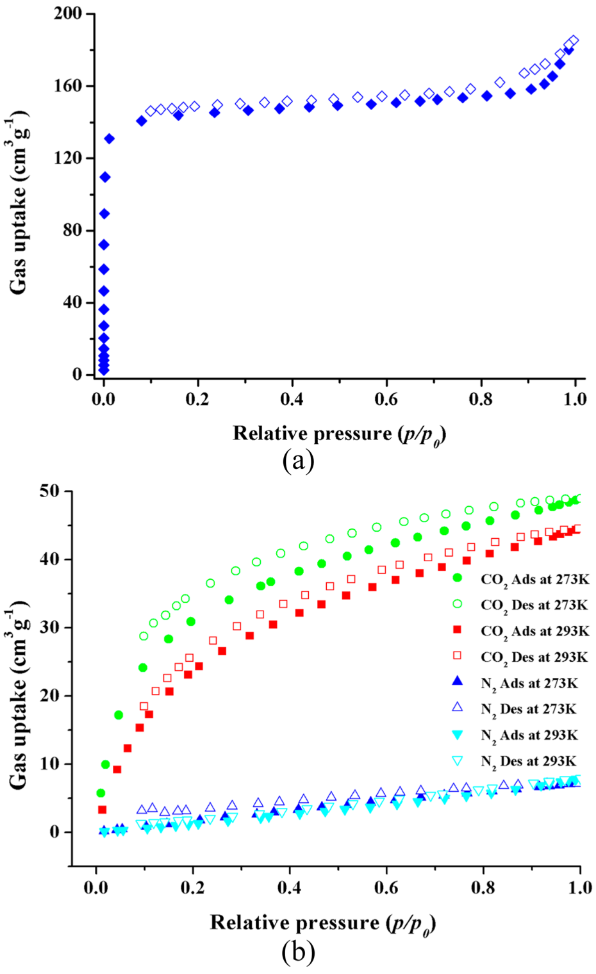


Figure 4. Selective absorption of cyclohexane, cyclopentane, and decahydronaphthalene by **1**.

2.4. Gas Adsorption Properties.

As described above, the coordinated DMF in **1** can be completely exchanged by 1,4-dioxane and tetrahydropyrane to give **1e** and **1f**, respectively. Thus, open metal sites will be created within the pores of **1e** and **1f**.[41,43] It prompted us to investigate the adsorption properties of this system. Typically, the activated samples of **1e** were prepared by heating at 120 °C for 5 h under a dynamic vacuum, and its X-ray powder diffraction (XRPD) pattern indicated the maintenance of the original framework (Supporting Information Figures S10 and S11). As shown in Figure 5a, the N_2 adsorption at 77 K showed a type I behavior with a slight hysteresis between adsorption and desorption. The result suggests that the samples were typical crystalline microporous materials and the framework showed the dynamic feature.[71−73] From the N_2 adsorption isotherm, we can see that the activated samples of **1e** can store up to 195.2 $cm^3\ g^{-1}$, which corresponds to a BET specific surface area of 459.8 $m^2\ g^{-1}$ and a Langmuir surface area of 641.5 $m^2\ g^{-1}$, respectively.

It is well-known that the CO_2 capture and separation are of great significance in industrial and environmental aspects.[74,75] Due to the presence of open metal sites in **1e**, it will be interesting to evaluate its capability for CO_2/N_2 selectivity. As a result, the CO_2 and N_2 sorption isotherms of **1e** were measured at 273 and 293 K, respectively. As shown in Figure 5b, the adsorption amounts of CO_2 at saturation are 48.7 $cm^3\ g^{-1}$ at 273 K and 44.5 $cm^3\ g^{-1}$ at 293 K, respectively, whereas almost



(a)

(b)

Figure 5. (a) N_2 adsorption isotherms at 77 K of the activated samples of **1e**. (b) N_2 and CO_2 adsorption isotherms at 293 and 273 K of the activated samples of **1e**.

no uptake was observed for the adsorption isotherms of N_2. So the activated samples of **1e** show a high CO_2/N_2 adsorption selectivity of 25 at 273 K and 20 at 293 K, respectively.[74,75] To further study the cyclability of CO_2 adsorption in the activated samples of **1e**, the CO_2 sorption isotherms were measured for five cycles at 293 K with the material just by evacuation without heating. As shown in Figure 6, no apparent decreases in capacity of CO_2 were observed over five cycles. Thus, the activated samples of **1e** have potential applications in the storage of CO_2 and separation of CO_2/N_2 mixture.

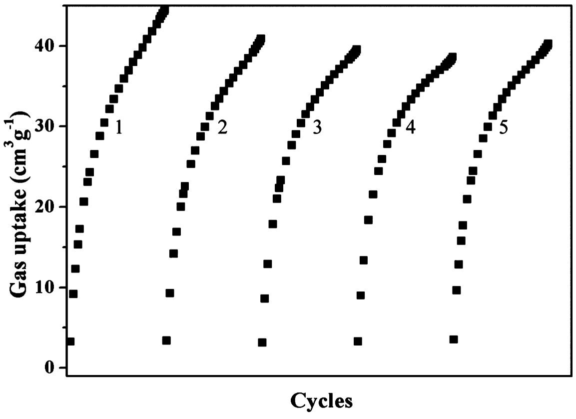


Figure 6. Five cycles of CO_2 uptake of the activated samples of **1e** at 293 K and 1 atm without the reactivation process between the cycles.

3. CONCLUSIONS

In summary, we have prepared a highly stable soft 3D PCP (**1**) via the facile *in situ* synthesis of the 4-tetrazole pyridine. The fascinating feature of **1** is that its solid-state conversion reactions induced by solvent exchanges, such as cyclohexane, cyclopentane, decahydronaphthalene, 1,4-dioxane, and tetrahydropyrane, occurred in SCSC manners to yield a series of PCPs (**1a**−**f**) with identical structural patterns. The occluded cyclohexane molecules in **1a** can be further removed by heating to give the porous guest-free form (**1g**). Of further importance, the soft PCP (**1**) demonstrates the guest selectivity for the cyclohexane, cyclopentane, and decahydronaphthalene through SCSC transformations for the first time, which may be the result of the synergy effect between the size and geometry of the solvent and the shape of the framework cavity. Remarkably, the highly selective gas adsorption of CO_2 over N_2 for the desolvated samples of **1e** indicates its potential application in the separation of CO_2/N_2 mixture. Further SCSC transformation study induced by solvents is underway in our lab, with the aim of producing new soft PCP crystalline materials with interesting properties and applications.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. All chemicals and solvents were obtained from commercial sources, and were used without further purification. The FT-IR spectra of the compounds were performed in the range 4000−400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. The C, H, and N elemental analyses were measured on a Perkin−Elmer 2400CHN elemental analyzer. PXRD patterns were carried out on a Rigaku Dmax 2000 X-ray diffractometer. Thermogravimetric analyses were performed on a PerkinElmer TG-7 analyzer heated from room temperature to 600 °C under nitrogen.

4.2. Gas Adsorption Experiments. The gas adsorption−desorption experiments were performed on an automatic volumetric adsorption equipment (V-Sorb 2800S). The samples of **1e** were heated at 120 °C for 5 h under a dynamic vacuum. Gas adsorption isotherms for N_2 were monitored at 77, 273, and 293 K, and CO_2 gas adsorption isotherms were conducted at 273 and 293 K.

4.3. X-ray Crystallography. Single-crystal X-ray diffraction data was recorded at a temperature of 293(2) K on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures of **1**−**1h** were solved by Direct Method of SHELXS-97[76] and refined by full-matrix least-squares techniques using the SHELXL-97 program.[77] Non-hydrogen atoms were refined with anisotropic temperature parameters. Some atoms in **1c** (C16−C20) and **1f** (C13−C20 and O1−O4) were not refined with anisotropic temperature parameters. The disordered atoms in **1e** (C17−C20, O3 and O4) were refined using C and O split over two sites. All hydrogen atoms on carbon atoms were generated geometrically. Some methylene hydrogen atoms of **1a**, **1b**, **1c**, **1e**, **1f**, and **1g** could not be positioned. The aqua hydrogen atoms were not included in the model. The detailed crystallographic data and structure refinement parameters for **1**−**1h** are summarized in Supporting Information Table S1.

4.4. Synthesis of (1) and Its Solvent Exchange in SCSC Manners. *4.4.1. Synthesis of 1.* A mixture of $Cu(NO_3)_2·3H_2O$ (0.181 g, 0.75 mmol), 4-cyanopyridine (0.104 g, 1 mmol), NaN_3 (0.097 g, 1.5 mmol), and DMF (10 mL) was placed in a 15 mL Teflon reactor and kept under autogenous pressure at 80 °C for 1 day. Then the mixture was cooled to room temperature, and the resulting dark green block crystals were obtained in 65% yield. Anal. Calcd (%) for **1**: C, 36.41; H, 4.07; N, 35.38. Found: C, 36.80; H, 4.33; N, 35.63. IR data (KBr, cm^{-1}): 3393s, 3088s, 2064w, 1679w, 1657s, 1559m, 1303s, 1063m, 849m, 759w.

*4.4.2. Solvent Exchange from **1** to **1a**.* The crystalline samples of **1** were immersed in cyclohexane for 7 days to give **1a**. Anal. Calcd (%) for **1a**: C, 45.83; H, 5.29; N, 31.18. Found: C, 46.01; H, 5.39; N, 30.98. IR data (KBr, cm^{-1}): 3354s, 3044s, 2080w, 1657w, 1626w, 1561m, 1538s, 1350s, 1134s, 1096m, 871s, 849m.

*4.4.3. Solvent Exchange from **1** to **1b**.* Compound **1b** was prepared by a method similar to that of **1a** except that cyclopentane was used instead of cyclohexane. Anal. Calcd (%) for **1b**: C, 41.94; H, 4.40; N, 34.23. Found: C, 42.01; H, 4.57; N, 34.10. IR data (KBr, cm^{-1}): 3356m, 3090s, 2080w, 2058w, 1626w, 1561m, 1539s, 1388s, 1134s, 1065m, 905s, 758m.

*4.4.4. Solvent Exchange from **1** to **1c**.* Compound **1c** was obtained by soaking **1** in decahydronaphthalene for 20 days. Anal. Calcd (%) for **1c**: C, 41.36; H, 4.34; N, 33.76. Found: C, 41.53; H, 4.52; N, 33.57. IR data (KBr, cm^{-1}): 3338s, 3087s, 2078w, 2059w, 1624w, 1560s, 1388m, 1349s, 1133s, 1033s, 759m, 721m.

*4.4.5. Solvent Exchange from **1** to **1d** and **1d** to **1e**.* Compound **1d** was prepared by soaking **1** in 1,4-dioxane for 4 days. IR data (KBr, cm^{-1}) for **1d**: 3334s, 3042m, 2850s, 2080w, 1624w, 1374m, 1217m, 1099s, 844m, 719w. The crystalline samples of **1d** were kept soaking in 1,4-dioxane for another 3 days, yielding crystalline samples of **1e**. Anal. Calcd (%) for **1e**: C, 38.49; H, 3.59; N, 32.41. Found: C, 38.66; H, 3.70; N, 32.59. IR data (KBr, cm^{-1}): 3362m, 3044s, 2082w, 1655w, 1625w, 1560s, 1119m, 1014s, 758s, 722m.

*4.4.6. Solvent Exchange from **1** to **1f**.* Compound **1f** was prepared by a method similar to to that of **1a** except that tetrahydropyrane was used instead of cyclohexane. Anal. Calcd (%) for **1f**: C, 38.26; H, 3.78; N, 34.11. Found: C, 38.02; H, 3.63; N, 34.28. IR data (KBr, cm^{-1}): 3359m, 3093s, 2080w, 1717s, 1657w, 1625w, 1561m, 1539s, 1382m, 1195m, 1134s, 848m, 758w.

*4.4.7. Solvent Removal from **1a** to **1g**.* The crystalline samples of **1a** were heated at 80 °C for 3 h under a dynamic vacuum, which led to crystals of **1g**. Anal. Calcd (%) for **1g**: C, 35.84; H, 3.01; N, 39.01. Found: C, 35.99; H, 3.22; N, 38.79. IR data (KBr, cm^{-1}): 3344s, 3088s, 2081w, 1656w, 1624w, 1560m, 1522s, 1386m, 1133s, 1034s, 848m, 758m.

*4.4.8. Structural Transformation from **1a** to **1h**.* Compound **1h** was obtained by a method similar to that of **1a** except that water was used instead of cyclohexane. Anal. Calcd (%) for **1h**: C, 28.83; H, 4.84; N, 28.02. Found: C, 28.66; H, 4.99; N, 28.25. IR data (KBr, cm^{-1}): 3615m, 3046m, 1616w, 1562s, 1525s, 1424w, 1255s, 1069s, 965sw, 801s, 709w.

CCDC-974744 (**1**), CCDC-974745 (**1a**), CCDC-974746 (**1b**), CCDC-974747 (**1c**), CCDC-974748 (**1d**), CCDC-974749 (**1e**), CCDC-974750 (**1f**), CCDC-974751 (**1g**), and CCDC-974752 (**1h**) 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, selected bond lengths and angles, structure illustrations for compounds **1**−**1h**, and PXRD patterns of compounds **1**−**1h**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: yangj808@nenu.edu.cn.
*E-mail: majf247@yahoo.com. Fax: +86-431-85098620.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants 21071028, 21001023, 21277022, 21371030, 21301026) and the Fundamental Research Funds for the Central Universities of China.

■ REFERENCES

(1) Kitagawa, S.; Uemura, K. *Chem. Soc. Rev.* **2005**, *34*, 109−119.

(2) Serre, C.; Millange, F.; Thouvenot, C.; Noguès, M.; Marsolier, G.; Louër, D.; Férey, G. *J. Am. Chem. Soc.* **2002**, *124*, 13519−13526.

(3) Lee, C. Y.; Bae, Y.-S.; Jeong, N. C.; Farha, O.; Sarjeant, A. A.; Stern, C. L.; Nickias, P.; Snurr, R. Q.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2011**, *133*, 5228−5231.

(4) Férey, G.; Serre, C. *Chem. Soc. Rev.* **2009**, *38*, 1380−1399.

(5) Kitaura, R.; Seki, K.; Akiyama, G.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 428−431.

(6) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739−1753.

(7) Zhou, H.-C.; Long, J.; Yaghi, O. *Chem. Rev.* **2012**, *112*, 673−674.

(8) Wei, Y.-S.; Chen, K.-J.; Liao, P.-Q.; Zhu, B.-Y.; Lin, R.-B.; Zhou, H.-L.; Wang, B.-Y.; Xue, W.; Zhang, J.-P.; Chen, X.-M. *Chem. Sci.* **2013**, *4*, 1539−1546.

(9) He, Y.-C.; Yang, J.; Yang, G.-C.; Kan, W.-Q.; Ma, J.-F. *Chem. Commun.* **2012**, *48*, 7859−7861.

(10) Li, M.; Li, D.; O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2014**, *114*, 1343−1370.

(11) Tian, D.; Chen, Q.; Li, Y.; Zhang, Y.-H.; Chang, Z.; Bu, X.-H. *Angew. Chem., Int. Ed.* **2014**, *53*, 837−841.

(12) Tong, X.-L.; Hu, T.-L.; Zhao, J.-P.; Wang, Y.-K.; Zhang, H.; Bu, X.-H. *Chem. Commun.* **2010**, *46*, 8543−8545.

(13) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734−777.

(14) Zeng, Y.-F.; Hu, X.; Liu, F.-C.; Bu, X.-H. *Chem. Soc. Rev.* **2009**, *38*, 469−480.

(15) Makal, T. A.; Li, J.-R.; Lu, W.; Zhou, H.-C. *Chem. Soc. Rev.* **2012**, *41*, 7761−7779.

(16) Kitagawa, S.; Kitaura, R.; Noro, S.-I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334−2375.

(17) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762−1765.

(18) Choi, H.-S.; Suh, M. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 6865−6869.

(19) Horcajada, P.; Serre, C.; Maurin, G.; Ramsahye, N. A.; Balas, F.; Vallet-Regí, M. A.; Sebban, M.; Taulelle, F.; Férey, G. *J. Am. Chem. Soc.* **2008**, *130*, 6774−6780.

(20) Demessence, A.; Long, J. R. *Chem.—Eur. J.* **2010**, *16*, 5902−5908.

(21) Li, C.-P.; Du, M. *Chem. Commun.* **2011**, *47*, 5958−5972.

(22) Chen, X.-D.; Zhao, X.-H.; Chen, M.; Du, M. *Chem.—Eur. J.* **2009**, *15*, 12974−12977.

(23) Xiao, J.; Wu, Y.; Li, M.; Liu, B.-Y.; Huang, X.-C.; Li, D. *Chem.—Eur. J.* **2013**, *19*, 1891−1895.

(24) Wang, J.-H.; Li, M.; Li, D. *Chem. Sci.* **2013**, *4*, 1793−1801.

(25) Zhang, H.-M.; Yang, J.; He, Y.-C.; Ma, J.-F. *Chem.—Asian J.* **2013**, *8*, 2787−2791.

(26) Li, J.-R.; Tao, Y.; Yu, Q.; Bu, X.-H.; Sakamoto, H.; Kitagawa, S. *Chem.—Eur. J.* **2008**, *14*, 2771−2776.

(27) Chaemchuen, S.; Kabir, N. A.; Zhou, K.; Verpoort, F. *Chem. Soc. Rev.* **2013**, *42*, 9304−9332.

(28) Zhang, S.-M.; Chang, Z.; Hu, T.-L.; Bu, X.-H. *Inorg. Chem.* **2010**, *49*, 11581−11586.

(29) Wu, C.-D.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 1958−1961.

(30) Das, M. C.; Bharadwaj, P. K. *J. Am. Chem. Soc.* **2009**, *131*, 10942−10949.

(31) Seo, J.; Bonneau, C.; Matsuda, R.; Takata, M.; Kitagawa, S. *J. Am. Chem. Soc.* **2011**, *133*, 9005−9013.

(32) Kawano, M.; Fujita, M. *Coord. Chem. Rev.* **2007**, *251*, 2592−2605.

(33) Kitagawa, S.; Matsuda, R. *Coord. Chem. Rev.* **2007**, *251*, 2490−2509.

(34) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 278−289.

(35) Ma, L.; Lin, W. *Top. Curr. Chem.* **2010**, *293*, 175−205.

(36) Li, B.; Wen, H.-M.; Wang, H.-L.; Wu, H.; Tyagi, M.; Yildirim, T.; Zhou, W.; Chen, B. *J. Am. Chem. Soc.* **2014**, *136*, 6207−6210.

(37) Kanoo, P.; Sambhu, R.; Maji, T. K. *Inorg. Chem.* **2011**, *50*, 400−402.

(38) Culp, J. T.; Smith, M.; Bittner, E.; Bockroth, B. *J. Am. Chem. Soc.* **2008**, *130*, 12427−12434.

(39) Choi, H. J.; Dincă, M.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 7848−7850.

(40) Kitaura, R.; Fujimoto, K.; Noro, S.-I.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 133−135.

(41) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869−932.

(42) Li, J.-R.; Yu, J.; Lu, W.; Sculley, J.; Balbuena, P. B.; Zhou, H.-C. *Nat. Commun.* **2013**, *4*, 1538−1535.

(43) Thallapally, P. K.; Tian, J.; Radha-Kishan, M.; Fernandez, C. A.; Dalgarno, S. J.; Mcgrail, P. B.; Warren, J. E.; Atwood, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 16842−16843.

(44) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* **2012**, *112*, 782−835.

(45) Zhang, D.-S.; Chang, Z.; Li, Y.-F.; Jiang, Z.-Y.; Xuan, Z.-H.; Zhang, Y.-H.; Li, J.-R.; Chen, Q.; Hu, T.-L.; Bu, X.-H. *Sci. Rep.* **2013**, *3*, 3312−3318.

(46) Mir, M. H.; Koh, L. L.; Tan, G. K.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 390−393.

(47) Medishetty, R.; Koh, L. L.; Kole, G. K.; Vittal, J. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 10949−10952.

(48) Liu, Q.-K.; Ma, J.-P.; Dong, Y.-B. *Chem. Commun.* **2011**, *47*, 12343−12345.

(49) Tsolmon, B.; Sun, F.; Zhang, J.; Cai, J.; Ren, H.; Zhu, G. *Chem. Commun.* **2012**, *48*, 7613−7615.

(50) Li, J.; Huang, P.; Wu, X.-R.; Tao, J.; Huang, R.-B.; Zheng, L.-S. *Chem. Sci.* **2013**, *4*, 3232−3238.

(51) Zeng, M.-H.; Hu, S.; Chen, Q.; Xie, G.; Shuai, Q.; Gao, S.-L.; Tang, L.-Y. *Inorg. Chem.* **2009**, *48*, 7070−7079.

(52) Bloch, W. M.; Sumby, C. J. *Chem. Commun.* **2012**, *48*, 2534−2536.

(53) Xu, G.; Zhang, X.; Guo, P.; Pan, C.; Zhang, H.; Wang, C. *J. Am. Chem. Soc.* **2010**, *132*, 3656−3657.

(54) Liu, D.; Lang, J.-P.; Abrahams, B. F. *J. Am. Chem. Soc.* **2011**, *133*, 11042−11045.

(55) Ohmori, O.; Kawano, M.; Fujita, M. *J. Am. Chem. Soc.* **2004**, *126*, 16292−16293.

(56) Luo, X.-Z.; Jia, X.-J.; Deng, J.-H.; Zhong, J.-L.; Liu, H.-J.; Wang, K.-J.; Zhong, D.-C. *J. Am. Chem. Soc.* **2013**, *135*, 11684−11687.

(57) Wang, Z. D.; Fingas, M.; Landriaul, M.; Sigouin, L.; Xu, N. N. *Anal. Chem.* **1995**, *67*, 3491−3500.

(58) Xiao, Q.; Sun, Y.; Zhang, Y.; Chai, P. *Org. Geochem.* **2012**, *50*, 44−56.

(59) Dutta, T. K.; Harayama, S. *Anal. Chem.* **2001**, *73*, 864−869.

(60) Jensen, T. S.; Arvin, E.; Svensmark, B.; Wrang, P. *Soil Sediment Contam.* **2012**, *50*, 44−50.

(61) Dutta, T. K.; Harayama, S. *Anal. Chem.* **2001**, *73*, 864−869.

(62) Nocentini, M.; Pinelli, D.; Fava, F. *Chemosphere* **2007**, *41*, 1115−1311.

(63) Wang, X. L.; Liu, L. M.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6499−6503.

(64) Ranck, J. M.; Bowman, R. S.; Weeber, J. L.; Katz, L. E.; Sullivan, E. J. *J. Environ. Eng.* **2005**, *131*, 434−442.

(65) Wang, J.-W.; Guo, J.-X.; Fu, F.; Li, D.-S.; Wang, J.-J.; Zhang, M.-L. *Z. Kristallogr.—New Cryst. Struct.* **2007**, *222*, 55−56.

(66) Murdock, C. R.; Lu, Z.; Jenkins, D. M. *Inorg. Chem.* **2013**, *52*, 2182−2187.

(67) Wei, Z.; Lu, W.; Jiang, H.-L.; Zhou, H.-C. *Inorg. Chem.* **2013**, *52*, 1164−1166.

(68) Liu, B.; Yu, Z.-T.; Yang, J.; Hua, W.; Liu, Y.-Y.; Ma, J.-F. *Inorg. Chem.* **2011**, *50*, 8967−8972.

(69) Liu, B.; Yang, J.; Yang, G.-C.; Ma, J.-F. *Inorg. Chem.* **2013**, *52*, 84−94.

(70) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.

(71) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695−704.

(72) Procopio, E. Q.; Fukushima, T.; Barea, E.; Navarro, J. A. R.; Horike, S.; Kitagawa, S. *Chem.—Eur. J.* **2012**, *18*, 13117−13125.

(73) Qin, J. S.; Du, D. Y.; Li, W. L.; Zhang, J. P.; Li, S. L.; Su, Z. M.; Wang, X. L.; Xu, Q.; Shao, K. Z.; Lan, Y. Q. *Chem. Sci.* **2012**, 3, 2114−2118.

(74) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724−781.

(75) Bae, Y.-S.; Snuur, R. Q. *Angew. Chem., Int. Ed.* **2011**, *50*, 11586−11596.

(76) Sheldrick, G. M. *SHELXS-97, Programs for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(77) Sheldrick, G. M. *SHELXL-97, Programs for X-ray Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.