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Highly Efficient Separation of a Solid Mixture of Naphthalene and Anthracene by a Reusable Porous Metal–Organic Framework through a Single-Crystal-to-Single-Crystal Transformation

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S *Supporting Information*

ABSTRACT: The three-dimensional crystalline porous metal–organic framework $[Ni_2(\mu_2\text{-}OH_2)(1,3\text{-}BDC)_2(tpcb)]_n$ (**1**) [1,3-H_2BDC = 1,3-benzenedicarboxylic acid; tpcb = tetrakis(4-pyridyl)cyclobutane] was used to separate a solid mixture of naphthalene and anthracene at room temperature via selective adsorption of naphthalene. The process involved a single-crystal-to-single-crystal transformation. The guest naphthalene molecules could be exchanged with ethanol, and the host, **1**, could be regenerated by removal of the guest ethanol molecules.

Porous metal–organic frameworks (MOFs) are the focus of considerable interest because of their potential applications in the areas of separation, adsorption, catalysis, and molecular recognition.[1−6] In much of this work, the aim has been to create robust materials that are able to retain an open-type network throughout cycles of sorption and desorption of guest molecules. The size and shape of the framework channels and voids allow the possibility of discrimination in regard to the types of guest that may be sorbed into the network, and thus, such materials are able to act as molecular sieves.[4−6] To date, much of the work exploring the ability of MOFs to separate mixtures relates to the separation of gas- or liquid-phase compounds.[4,5] It has recently been demonstrated that porous MOFs may be employed in the separation of species such as fullerenes, polycyclic dyes, organosulfur compounds, and aromatic hydrocarbons from solutions.[6] To the best of our knowledge, no examples of the utilization of porous MOFs in the separation of solid mixtures have been reported.

Naphthalene and anthracene are important raw chemicals that are produced in the coal tar industry and widely used as precursors in the synthesis of a variety of products, including pesticides and synthetic dyes. In industry, naphthalene and anthracene are normally purified using a distillation or crystallization process; this generally leads to purities of less than 95%.[7] These methods usually consume large amounts of energy or solvents. In the laboratory, naphthalene and anthracene can be separated using liquid chromatography.[6e] This method also requires large quantities of eluents. Thus, the separation of naphthalene and anthracene in an environmentally friendly manner represents a significant challenge. A strategy for the separation of such mixtures that we have been exploring involves selective sorption of one of the compounds in the vapor phase by a porous MOF. In comparison with traditional methods, this process would reduce the energy cost and the amount of eluent used.

Herein we report the synthesis of a stable MOF of composition $\{[Ni_2(\mu_2\text{-}OH_2)(1,3\text{-}BDC)_2(tpcb)]\cdot 12H_2O\}_n$ ($\mathbf{1}\cdot 12H_2O$) and its porous guest-free form $[Ni_2(\mu_2\text{-}OH_2)(1,3\text{-}BDC)_2(tpcb)]_n$ (**1**) and its application in the separation of a solid mixture of naphthalene and anthracene. This process, which involves a single-crystal-to-single-crystal (SCSC) transformation, does not lead to the deterioration of the coordination network, allowing the host network to be reused.

Green blocks of $\mathbf{1}\cdot 12H_2O$ were hydrothermally prepared from a mixture of $NiCl_2\cdot 6H_2O$, 1,3-H_2BDC (**2**), and tpcb (**3**) in 86% yield. Single-crystal X-ray diffraction analysis[8] revealed that $\mathbf{1}\cdot 12H_2O$ crystallizes in the orthorhombic space group *Fdd*2. The framework is constructed from $[Ni_2(\mu_2\text{-}OH_2)]$ units interconnected by the 1,3-BDC and tpcb linkers. A $[Ni_2(\mu_2\text{-}OH_2)]$ unit with its coordinated carboxylate and pyridyl-based ligands is shown in Figure S1a in the Supporting Information. The Ni centers, which are symmetry-related by a twofold axis, are bridged by a pair of carboxylate anions and a water molecule. The coordination environment of each Ni center is completed by a monodentate carboxylate O atom and a pair of *cis*-pyridyl N atoms. This results in an octahedral environment for each Ni center. The two noncoordinated carboxylate oxygen atoms form hydrogen bonds with the bridging water molecule.

The complex structure is perhaps best described by considering first the network generated by the combination of the $[Ni_2(\mu_2\text{-}OH_2)]$ units with the 1,3-BDC anions. Each $[Ni_2(\mu_2\text{-}OH_2)]$ unit is linked to four equivalent units through the bridging BDC ligands. The resulting network of composition $[Ni_2(\mu_2\text{-}OH_2)](1,3\text{-}BDC)_2$ has the topology of the diamond net. The neutral four-connecting ligand tpcb supports this framework. Each $[Ni_2(\mu_2\text{-}OH_2)]$ unit is bound to four separate tpcb ligands and each tpcb ligand is bound to four $[Ni_2(\mu_2\text{-}OH_2)]$ units within a single adamantane-type unit of the $[Ni_2(\mu_2\text{-}OH_2)](1,3\text{-}BDC)_2$ network, as shown in Figure S1b.

Examination of the extended structure reveals infinite channels that extend parallel to the *a* axis (Figure 1). In $\mathbf{1}\cdot 12H_2O$, uncoordinated water molecules occupy these channels (Figure S1c,d). The shape of the one-dimensional channels is irregular, with relatively small kite-shaped windows apparent when viewed

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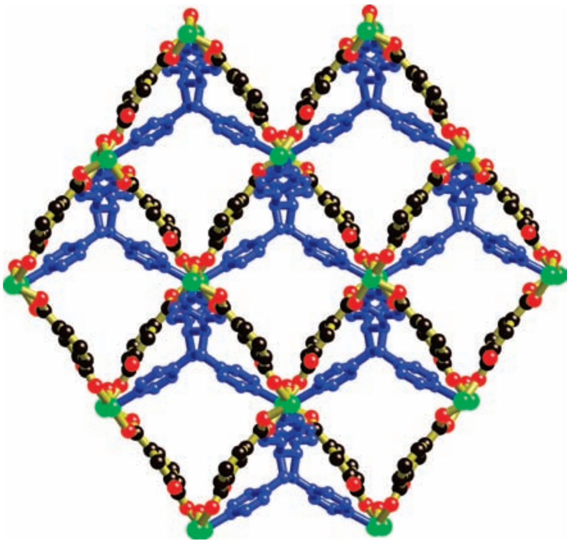

Figure 1. View of the coordination network of $1 \cdot 12H_2O$ along the *a* axis. All of the guest molecules and hydrogen atoms have been omitted for clarity.

along the *a* axis. These windows open up into larger chambers along the channels. Without guest molecules, the total potential void volume of the open channels in $1 \cdot 12H_2O$ was calculated by PLATON analysis to be 50.9% of the crystal volume (5972 $Å^3$ of the 11 727 $Å^3$ unit cell volume).[9]

Upon exposure to air over several days, single crystals of $1 \cdot 12H_2O$ gradually lose the uncoordinated water molecules but retain their single-crystal character (Figure S2). Thermogravimetric analysis (TGA) indicated that **1** is stable up to 218 °C (Figure S3). Guest-free crystals of **1** could be obtained by heating crystals of $1 \cdot 12H_2O$ in air at 170 °C or under vacuum at 100 °C for ~12 h. Although the loss of the uncoordinated water is accompanied by a contraction of the cell volume from 11 727 $Å^3$ to 11 597 $Å^3$, the framework structure of **1** is essentially unchanged (Figures S1 and S4). The aperture size of **1** is approximately 10.0 Å × 6.4 Å. The permanent porosity of **1** was confirmed by N_2 sorption measurements at 77 K (Figure S5), which revealed a Brunauer–Emmett–Teller (BET) surface area of 1029 $m^2\ g^{-1}$ and a pore volume of 0.36 $cm^3\ g^{-1}$. The stability of this robust porous MOF and the presence of relatively large intraframework voids prompted us to investigate whether the network would be able to exhibit selective adsorption of guest molecules with retention of single-crystal character.

Naphthalene and anthracene both have a kinetic diameter of 6.55 Å,[6e] and on this basis one may reasonably expect both to be able to enter the channels. However, in view of the difference in the sizes and shapes of these two aromatic molecules, it is also reasonable to expect that they would interact differently with the host framework. Since both naphthalene and anthracene are able to sublime, we speculated that one of these compounds might be preferentially adsorbed in the vapor phase by **1** when a mixture of anthracene and naphthalene was sealed with **1** in a vessel. To test our hypothesis, we placed a sample of **1** (0.415 g, 0.5 mmol) in one tube (4 cm in length and 0.7 cm in inner diameter) and placed a 1:1 molar ratio mixture of naphthalene (0.256 g, 2 mmol) and anthracene (0.356 g, 2 mmol) in a second tube. These tubes were placed in a 50 mL Erlenmeyer flask that was subsequently sealed. After ~5 h at room temperature, the amount of white powder in the tube containing the naphthalene/anthracene mixture had been visibly reduced.

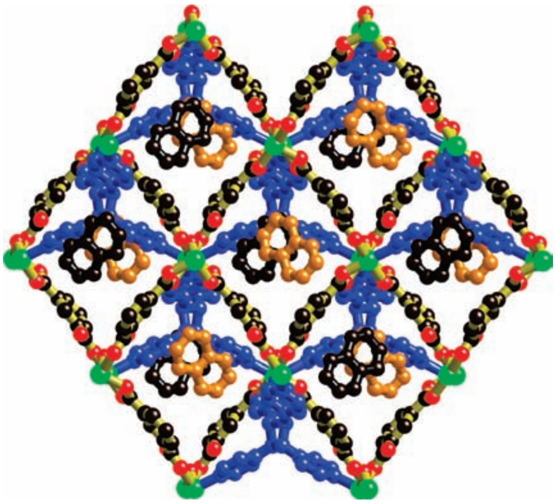

Figure 2. View of the structure of $1 \cdot 2C_{10}H_8$. Hydrogen atoms have been omitted for clarity.

The sample in the tube that originally contained **1** was investigated using single-crystal X-ray diffraction. The structure determination indicated the sorption of two naphthalene molecules per $Ni_2(\mu_2\text{-}OH_2)$ unit (Figure 2). Unlike many examples of guest inclusion in coordination networks, the naphthalene molecules are ordered and well-defined. The crystals are formulated as $\{[Ni_2(\mu_2\text{-}OH_2)(1,3\text{-}BDC)_2(tpcb)] \cdot 2C_{10}H_8\}_n$, ($1 \cdot 2C_{10}H_8$), which corresponds to a naphthalene uptake of ~0.309 g/g of **1**. The UV–vis spectrum further confirmed the formula (Figure S6). We note that there are $C{-}H \cdots Cg$ (π-ring) interactions[10] ($C9{-}H9 \cdots Cg_{C25-C30}$, with $H9 \cdots Cg_{C25-C30}$ = 2.69 Å and $C9 \cdots Cg_{C25-C30}$ = 3.57 Å) between the framework of **1** and the naphthalene molecules (Figure S7). We thus presume that the absorption of naphthalene molecules by **1** is driven largely by these $C{-}H \cdots Cg$ interactions. $1 \cdot 2C_{10}H_8$ is unable to adsorb any further naphthalene, despite the fact that there is an estimated void volume that represents 20.3% of the crystal volume (2367 $Å^3$ of the 11 668 $Å^3$ unit cell volume).[9] In view of the relatively high void volume, the failure of the network to adsorb additional naphthalene may reflect favorable host–guest and guest–guest interactions when the crystals are formulated as $1 \cdot 2C_{10}H_8$.

The results of powder X-ray diffraction (PXRD) analysis of $1 \cdot 2C_{10}H_8$ were in agreement with the simulated pattern generated from the single-crystal structure (Figure S8). When superfluous quantities of **1** were used (more than 0.830 g), the naphthalene in the mixture was completely adsorbed, leaving only anthracene in the second glass tube. The ^1H NMR spectrum of the residual white powder in the tube showed chemical shifts at 8.59, 8.09, and 7.53 ppm, indicating the presence of pure anthracene (Figure S9). Chromatography with UV detection (HPLC-UV) measurements on this sample further indicated that no naphthalene was present in this powder and that the purity of the anthracene was 99.5% (Figure S10). Naphthalene/anthracene mixtures with other molar ratios (e.g., 1:2 or 2:1) could also be separated by **1** (Figure S11). For the purpose of comparison, we investigated the ability of activated carbon to sorb naphthalene under similar conditions. In this experiment, 10 g of activated carbon and naphthalene were used. After absorption for

5 days, the activated carbon was subjected to Soxhlet extraction for 20 h using 100 mL of ethanol. UV−vis measurements indicated that 1 g of activated carbon could absorb ~8 mg of naphthalene (Figure S12).

The vapor pressure of naphthalene is higher than that of anthracene at room temperature, so it may be reasonably argued that the preferential uptake of naphthalene over anthracene reflects the greater volatility of naphthalene. In order to determine whether the relative volatilities of the aromatic hydrocarbons were a factor in the selective adsorption, crystals of **1** and solid anthracene were heated in an evacuated flask at 150 °C for 10 h. After this time, the weight of **1** had not changed, and single-crystal X-ray crystallographic analysis revealed that no anthracene had been adsorbed by **1**. The UV−vis diffuse reflectance spectrum of these crystals was very similar to that of **1** (Figure S13). These results indicate that **1** is not a suitable host for anthracene and that the coordination network is truly able to discriminate between the aromatic hydrocarbons. Since anthracene and naphthalene have the same kinetic diameter, we assume that the failure of **1** to sorb results from the inability of the larger anthracene molecule to form favorable intermolecular interactions with the host network. We note that aromatics such as benzene, naphthalene, and anthracene, which have similar kinetic diameters, can be absorbed by open-framework compounds such as HKUST-1[11a] and MOF-5[11b] simultaneously. Thus, the ability of **1** to selectively sorb aromatics is different from that of HKUST-1 and MOF-5.[6e]

The naphthalene sorbed by the coordination network was recovered by soaking $\mathbf{1}\cdot 2C_{10}H_8$ in ethanol (4 × 3 mL). After the removal of **1** from the solution, a white precipitate was obtained upon the addition of 20 mL of water to the ethanol solution. The precipitate was separated by filtration and dried with anhydrous Na_2SO_4. ^1H NMR analysis of the precipitate showed signals for the naphthalene protons at 7.93 and 7.53 ppm (Figure S9). HPLC-UV measurements confirmed that anthracene was not present in this powder sample; the purity of the naphthalene was 99.1% (Figure S10). In the extraction of naphthalene from $\mathbf{1}\cdot 2C_{10}H_8$ using ethanol, we found that **1** had sorbed ethanol to form a compound having the formula $\{[Ni_2(\mu_2\text{-}OH_2)(1,3\text{-}BDC)_2(tpcb)]\cdot 3.5EtOH\}_n$ ($\mathbf{1}\cdot 3.5EtOH$) (Figures S14 and S15) with retention of single-crystal character. The porous guest-free coordination network **1** could be regenerated by either heating the sample of $\mathbf{1}\cdot 3.5EtOH$ or placing it under vacuum (Figure S16). All of the sorption and desorption processes involving **1** proceeded with retention of single-crystal character. Investigation of the sorption properties of the regenerated **1** indicated that it was able to sorb more than 90% of its original capacity of naphthalene. Further cycling did not result in further reduction of the capacity. In comparison with each previous cycle, the absorption capacities of **1** in the next five cycles were 92.3, 91.2, 91.7, 90.8, and 90.2%.

Traditionally, solid mixtures of compounds have been separated using porous MOFs by dissolving the mixtures in appropriate solvents and immersing the MOFs in the solution. Under these circumstances, preferential sorption of the solute mixture can be achieved.[6] As part of the present work, we employed a similar approach to investigate whether we could use **1** to separate a naphthalene/anthracene mixture that had been dissolved in benzene. Under these circumstances, we found that only benzene molecules were sorbed by **1** to form a compound of composition $\mathbf{1}\cdot 4C_6H_6$ (Figures S17−S19). When mesitylene was used as the solvent in place of benzene, the UV−vis diffuse reflectance spectrum indicated that neither solute nor solvent was absorbed by **1** (Figure S13). These results suggest that naphthalene absorption by **1** is favored in the sublimation process. We investigated whether **1** could absorb other volatile aromatic species such as ferrocene. Single-crystal X-ray diffraction analysis indicated that each $[Ni_2(\mu_2\text{-}OH_2)(1,3\text{-}BDC)_2(tpcb)]$ unit can absorb one ferrocene molecule to form $\{[Ni_2(\mu_2\text{-}OH_2)(1,3\text{-}BDC)_2(tpcb)]\cdot FeCp_2\}_n$ ($\mathbf{1}\cdot FeCp_2$) (Figures S20−S23).

In summary, the present work has demonstrated the use of a novel reusable porous coordination polymer in the highly efficient separation of a solid mixture of naphthalene and anthracene at ambient temperature in a process that involves a SCSC transition. This separation is the result of a particularly favorable association between the host network and the naphthalene guest molecules. It is anticipated that a similar approach involving porous coordination networks may be employed in order to separate solid mixtures of substances that are able to sublime. We are hopeful that analogues of **1** whose preparations are currently underway in our laboratory may also be useful in the separation of solid mixtures.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Crystal data for $\mathbf{1}\cdot 12H_2O$, **1**, $\mathbf{1}\cdot 2C_{10}H_8$, $\mathbf{1}\cdot 3.5EtOH$, $\mathbf{1}\cdot 4C_6H_6$, and $\mathbf{1}\cdot FeCp_2$ (CIF); details of synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) (a) Crystal data for $\mathbf{1}\cdot 12H_2O$: orthorhombic; space group $Fdd2$; $a = 15.571(3)$ Å, $b = 23.296(5)$ Å, $c = 32.328(7)$ Å; $V = 11727(4)$ Å^3; $Z = 8$; $D_{calcd} = 1.156$ g/cm^3; μ(Mo Kα) = 0.708 cm^{-1}; $T = 223$ K; $R_1 = 0.0593$ [$I > 2\sigma(I)$], $wR_2 = 0.1559$ (all data); $S = 1.088$. (b) Crystal data for **1**: orthorhombic; space group $Fdd2$; $a = 15.526(3)$ Å, $b = 22.639(5)$ Å, $c = 32.994(7)$ Å; $V = 11597(4)$ Å^3; $Z = 8$; $D_{calcd} = 0.949$ g/cm^3; μ(Mo Kα) = 0.689 cm^{-1}; $T = 223$ K; $R_1 = 0.0598$ [$I > 2\sigma(I)$], $wR_2 = 0.1664$ (all data); $S = 1.089$. (c) Crystal data for $\mathbf{1}\cdot 2C_{10}H_8$: orthorhombic; space group $Fdd2$; $a = 15.322(3)$ Å, $b = 24.083(5)$ Å, $c = 31.621(6)$ Å; $V = 11668(4)$ Å^3; $Z = 8$; $D_c = 1.235$ g/cm^3; μ(Mo Kα) = 0.701 cm^{-1}; $T = 223$ K; $R_1 = 0.0547$ [$I > 2\sigma(I)$], $wR_2 = 0.1488$ (all data); $S = 1.063$. (d) Crystal data for $\mathbf{1}\cdot 3.5EtOH$: orthorhombic; space group $Fdd2$; $a = 15.483(3)$ Å, $b = 23.434(5)$ Å, $c = 32.448(7)$ Å; $V = 11773(4)$ Å^3; $Z = 4$; $D_{calcd} = 1.116$ g/cm^3; μ(Mo Kα) = 0.683 cm^{-1}; $T = 223$ K; $R_1 = 0.0861$ [$I > 2\sigma(I)$], $wR_2 = 0.2172$ (all data); $S = 1.176$. (e) Crystal data for $\mathbf{1}\cdot 4C_6H_6$: orthorhombic; space group $Fdd2$; $a = 15.477(3)$ Å, $b = 23.392(5)$ Å, $c = 32.321(7)$ Å; $V = 11701(4)$ Å^3; $Z = 8$; $D_{calcd} = 1.293$ g/cm^3; μ(Mo Kα) = 0.703 cm^{-1}; $T = 223$ K; $R_1 = 0.0687$ [$I > 2\sigma(I)$], $wR_2 = 0.1821$ (all data); $S = 1.197$. (f) Crystal data for $\mathbf{1}\cdot FeCp_2$: orthorhombic; space group $Fdd2$; $a = 15.417(3)$ Å, $b = 23.492(5)$ Å, $c = 32.648(7)$ Å; $V = 11824(4)$ Å^3; $Z = 8$; $D_{calcd} = 1.139$ g/cm^3; μ(Mo Kα) = 0.920 cm^{-1}; $T = 223$ K; $R_1 = 0.0890$ [$I > 2\sigma(I)$], $wR_2 = 0.2408$ (all data); $S = 1.197$.

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