Selective Adsorption of Water, Methanol, and Ethanol by Naphthalene Diimide-Based Coordination Polymers with Constructed Open Cu²⁺ Metal Sites and Separation of Ethanol/Acetonitrile

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Supporting Information

ABSTRACT: The selective separation of ethanol/acetonitrile by porous materials has rarely been observed owing to their similar physicochemical properties. In this work, we report a new coordination network, [Cu₂(4-pmntd)₂(opd)₂] (4-pmntd = N,N’-bis(4-pyridymethyl)naphthalene diimide, opd = disodium 1,2-benzenedicarboxylate), which exhibits selective separation of ethanol over acetonitrile. The weak coordination bonds formed by unsaturated Cu²⁺ sites and hydroxyl groups are the key to such performance.

INTRODUCTION

Acetonitrile (CH₃CN) is an important organic solvent in the chemical industry, for example, acetonitrile is usually used in the manufacture of pharmaceuticals and photographic films.¹ Acetonitrile was also found to play an important role in the field of liquid chromatography because of its low viscosity and low chemical reactivity.²,³ Catalytic dehydrogenation from ammonia and ethanol is generally used in acetonitrile production.⁴ This method usually introduces some contaminants, such as unreacted ethanol. Thus, it is important to capture and separate ethanol from acetonitrile to use acetonitrile as the chemical feedback.⁵–⁸ In industry, acetonitrile was purified by membrane distillation. This process is energy-intensive and inefficient because of the formation of azetropes at a specific concentration because of the similar boiling points (acetonitrile, 81.1 °C; ethanol, 78.4 °C). Therefore, it is urgent to develop a new method for efficiently separating small molecules with similar physicochemical properties.

Recent studies have shown that porous material adsorption and separation has the advantage of high energy efficiency and low regeneration cost.⁹–¹² As a new generation of porous materials, coordination networks [also known as coordination polymers,¹³,¹⁴ metal–organic frameworks,¹⁵,¹⁶ or metal–organic materials (MOMs)¹⁷,¹⁸], have attracted much attention because of their unique porosity and chemical diversity.¹⁹–²⁵ In the past decades, a great number of MOMs have been already investigated for gas storage²⁶–²⁸ and separations (e.g., CO₂/N₂,²⁹ CO₂/CH₄,³⁰ CO₂/CO,³¹ CO₂/C₃H₆,³₂,³³ and C₃H₆/C₄H₁₀). However, to the best of our knowledge, current MOMs did not exhibit promising liquid mixture separation, such as acetonitrile/ethanol. Thus, how to achieve efficient separation of liquid mixture (such as acetonitrile/ethanol) by MOMs is still a challenge. The naphthalene diimides containing naphthalene π-unit and imide region in forming weak supramolecular interactions are an organic electron deficient system with excellent thermal, light, and air stability.³⁶–⁴¹ The LUMO level of pyridine ring naphthalene diimides is ≈-4.24 eV and the maximum absorption wavelength is 361 nm.³⁸ The naphthalene diimide-based coordination polymers could have abundant electronic properties that are beneficial for selective adsorption. In this study, we introduce a new coordination network constructed by a naphthalene diimide ligand, [Cu₂(4-pmntd)₂(CH₃OH)₄(opd)₂], which displays selective adsorp-
tion water, methanol, ethanol, and separation ability of acetonitrile/ethanol.

## RESULTS AND DISCUSSION

**Crystal Structures and Characterizations.** Solvothermal reaction of diimide-based ligand 42-44 4-pmntd and carboxyl ligand opd with Cu(NO3)2·6H2O in the mixture solvents of CHCl3/CH3OH/H2O at 70 °C afforded green crystals of [{[Cu2(4-pmntd)2(CH3OH)4(opd)2]}6 (1·MeOH)]. Single-crystal X-ray diffraction (SCXRD) revealed that compound 1·MeOH crystallized in orthorhombic space group Ccma. In 1·MeOH, each Cu2+ was coordinated by two nitrogen atoms from two 4-pmntd ligands and two oxygen atoms from two opd ligands (Figure 1). It was noted that the Cu2+ was also bonded by two apical oxygen atoms from methanol molecules and the Cu–O bond length is 2.629 Å, indicating that there was weak interaction between Cu2+ and methanol molecules. Consequently, the Cu2+ cations of 1·MeOH adopt an octahedral coordination geometry and serve as 4-connected nodes. The topology of this compound is a noninterpenetrated uninodal 2D network, which was revealed by the TOPOS45 software (Figure 2). The point symbol of the framework is (4.6.8) with a 4L1 (TotUMod) topological type in the reticulum chemistry structure resource. The independent 2D networks are staggered relatively to each other to form rectangular-shaped tubular channels occupied by guest molecules. Thermogravimetric analysis (TGA) revealed that the as-synthesized 1·MeOH loses guest molecules below 110 °C and retains stability until to 220 °C (Figure S3).

Compound 1·MeOH underwent single-crystal-to-single-crystal (SCSC) transformation after the coordinated methanol desolvated phase, [Cu(4-pmntd)(opd)]n (1·dry). Although the crystal system and space group remain unchanged, the copper center in 1·dry became tetra-coordinated with a quadrilateral coordination environment. Such coordination change is accompanied by apparent color change from green (1·MeOH) to violet (1·dry). Therefore, the unsaturated metal sites were formed in 1·dry and could have potential applications for selective gas/vapor separation because of the metal–guest interactions. Interestingly, a single crystal of 1·dry can revert to 1·MeOH when soaked in methanol at room temperature and the color can return to green, indicating that the structural transformation is reversible. Further, 1·dry was shown to exhibit SCSC structural change after the immersion of the single crystal into water or ethanol to form 1·H2O and 1·EtOH. SCXRD revealed that the coordination geometry of Cu2+ in 1·H2O and 1·EtOH is octahedral with coordinated solvent molecules (Figure 3).

**Vapor Adsorption Studies.** To investigate vapor sorption properties, samples of the as-synthesized 1·MeOH were first activated to afford 1·dry and the vapor sorption performance of 1·dry was investigated at 298 K. For water (H2O) adsorption, a rapid increase in the amount of adsorbed vapor under low pressure (0 < P/P0 < 0.02) was observed, indicating initial adsorption with two molecules of water per unit pore. Further, at the pressure range of 0.03 < P/P0 < 0.3, an increase of adsorption corresponding to one molecule of water per unit pore. The third stepwise sorption was occurred at 0.3 < P/P0 < 0.4, revealing the adsorption of two water molecules per unit pore. H2O adsorption reached the saturation uptake (ca. 125 cm3 g−1) when the pressure over P/P0 > 0.4. According to the interesting stepped isotherm, we assumed that two water molecules were first adsorbed on the unsaturated Cu2+ sites, followed by three water molecules entering the pores of the network. The above assumption is consistent with the results of single crystal X-ray diffraction analysis, which indicates that 1·dry could adsorb two water molecules at the unsaturated Cu2+ metal site and three water molecules in the pores. Such different binding sites result in the stepped isotherm (Figure 4a). In addition, we also studied the methanol (CH3OH) sorption of 1·dry. Similar to water sorption, 1·dry exhibited an initial adsorption at 0 < P/P0 < 0.2, which corresponding to about two methanol molecules per unit pore, and then one methanol molecule was adsorbed into the pores at 0.2 < P/P0 < 0.8 (Figure 4a).

Being different with water, ethanol adsorption of 1·dry displays the one-step isotherm with uptake around 50 cm3 g−1 at 100 kPa (Figure 4b). Single-crystal X-ray diffraction of 1·
EtOH revealed that two ethanol molecules were coordinated with unsaturated Cu$^{2+}$. Remarkably, the acetonitrile (CH$_3$CN) uptake of 1·dry at 298 K was found to be negligible (ca. 10 cm$^3$ g$^{-1}$ at 100 kPa). The naphthalene diimide-based coordination polymers are hydrogen-bonded frameworks for the imide carbonyl groups being the acceptor of hydrogen-bonded. 1·dry selective adsorption of water, methanol, and ethanol for them contain the hydroxyl groups as hydrogen-bonded donors and interact with unsaturated Cu$^{2+}$ sites. The big molecular size and no hydroxyl group of acetonitrile can neither interact with unsaturated Cu$^{2+}$ sites nor enter the pores (Figure 5). The mixed solvents, ethanol and acetonitrile, are commonly used such as in phase chromatography of biomolecules and the ethanol/acetonitrile separation and recycling, which are of great significance. The high ethanol uptake and low acetonitrile uptake of 1·dry at 100 kPa are beneficial for the ethanol/acetonitrile separation at ambient temperature.

**Ethanol/Acetonitrile Separation.** Given the differences in the adsorption behaviors of the 1·dry for ethanol and acetonitrile, we utilized 1·dry as a stationary phase to discover the separation performance of ethanol/acetonitrile binary mixtures. A column (10 × 10 × 100 mm) was packed with 1·dry (ca. 10 g) and let 1 mL ethanol and 1 mL acetonitrile binary mixtures pass through the column. Evolved solvent components were monitored by NMR (integrating the peak area). In the experiment, C$_2$H$_5$OH and CH$_3$CN were initially coadsorbed before CH$_3$CN was replaced by C$_2$H$_5$OH. An acetonitrile outlet purity was increased from 50 to 70% (Figure 6). We assume that the specific interaction between unsaturated metal sites and hydroxyl guest (ethanol) plays a vital role for such real ethanol/acetonitrile separation performance. Furthermore, the TGA studies indicate that the coordinated ethanol molecules in the pores of 1·EtOH could be removed by heating up to 110 °C and readsobered by dispersing the material to ethanol vapor at room temperature. These procedures can be repeated for five cycles, validating the reversibility of the process (Figure S4).

**CONCLUSIONS**

In summary, this work demonstrates a strategy that constructed open metal sites in coordination networks and could improve the selective sorption between hydroxyl guests and nonhydroxyl guests. This new naphthalene diimide-based coordination polymer is the first example that exhibits selective separation of ethanol/acetonitrile at ambient temperature.

**EXPERIMENTAL SECTION**

**Physical Measurements.** Elemental analyses (C, H, and N) were carried out with a PerkinElmer 240C elemental analyzer. FT-IR spectra were obtained from KBr pellets in the range of 4000–400 cm$^{-1}$ on a VECTOR 22 spectrometer. Powder X-ray diffraction (PXRD) was performed on a Bruker D8 ADVANCE diffractometer (Cu K$_\alpha$, 1.5418 Å) at 40 kV and 40 mA. Thermal analyses were performed on a TGA V5.1A Dupont 2100 instrument from room temperature to
and 1 IR (KBr, cm⁻¹; H, 2.49; N, 6.58%. Found: C, 51.85; H, 2.16; N, 6.69%.

was stirred and then sealed in a 20 mL Teflon-lined autoclave. The autoclave was heated to 70 °C and held at that temperature for 7 days, followed by further cooling to room temperature. Green crystals of 1 were collected in 32% yield based on the ligand. Anal. Calcd for C₃₇H₂₁Cl₃CuN₄O₁₀: C, 51.85; H, 2.16; N, 6.69%. Found: C, 51.85; H, 2.16; N, 6.69%.

### Table 1. Crystallographic Data and Structure Refinement for 1

| complex | 1-MeOH | 1-dry | 1-H₂O | 1-EtOH |
|---------|--------|-------|-------|--------|
| formula | C₉Ｈ₁₂ClCuN₄O₁₀ | C₉Ｈ₁₂ClCuN₄O₁₁ | C₉H₁₂CuN₄O₁₄ | C₉H₁₂CuN₄O₁₄ |
| P₀     | 851.47 | 724.08 | 770.06 | 820.12 |
| T (K)  | 150(2) | 373(2) | 293(2) | 150(2) |
| wavelength (Å) | 1.54178 | 0.71073 | 0.71073 | 1.54178 |
| crystal system | orthorhombic | orthorhombic | orthorhombic | orthorhombic |
| space group | Cc ca | Cc ca | Cc ca | Cc ca |
| a (Å)  | 17.1736(6) | 17.354(2) | 17.033(2) | 17.2256(10) |
| b (Å)  | 28.5197(11) | 28.747(5) | 28.521(6) | 28.4486(16) |
| c (Å)  | 15.4911(5) | 15.0069(19) | 15.290(2) | 15.7432(19) |
| α (deg) | 90 | 90 | 90 | 90 |
| β (deg) | 90 | 90 | 90 | 90 |
| γ (deg) | 90 | 90 | 90 | 90 |
| V (Å³) | 7587.3(5) | 7486.4(18) | 7428(2) | 7714.9(11) |
| Z | 8 | 8 | 8 | 8 |
| μ (mm⁻¹) | 3.296 | 0.643 | 0.659 | 1.436 |
| F (000) | 3448 | 2952 | 3128 | 3336 |
| reflections collected/unique | 7807/2819 | 10365/3622 | 18800/3582 | 7019/2869 |
| GOF | 1.051 | 1.004 | 1.938 | 1.024 |
| R₁, R₂ [t > 2σ(t)] | 0.0832, 0.2568 | 0.0841, 0.2178 | 0.1284, 0.3211 | 0.1009, 0.2883 |
| R₁, R₂ [all data] | 0.0936, 0.2659 | 0.1937, 0.2775 | 0.1795, 0.3441 | 0.1353, 0.3315 |

800 °C with a heating rate of 10 °C min⁻¹ in the air, and the data are consistent with the structures. The vapor adsorption isotherms (at 298 K) were measured by using the BELSORP-max automatic volumetric sorption apparatus.

### General Procedures

Chemicals were purchased from commercial sources and used without further purification.

**Synthesis.** ([Cu(4-pmntd)(CH₃OH)₂(opd)]·CHCl₃)n (1-MeOH). A mixture of 4-pmntd (6 mg, 0.0125 mmol), Cu(NO₃)₂·6H₂O (8 mg, 0.025 mmol), and Na₂[opd] (21 mg, 0.1 mmol) in H₂O/CH₃OH/CHCl₃ (1 mL/3 mL/10 mL) was stirred and then sealed in a 20 mL Teflon-lined autoclave. The autoclave was heated to 70 °C and held at that temperature for 7 days, followed by further cooling to room temperature. Green crystals of 1 were collected in 32% yield based on the ligand. Anal. Calcd for C₃₇H₂₁Cl₃CuN₄O₁₀·C, 52.19; H, 2.49; N, 6.58%. Found: C, 51.85; H, 2.16; N, 6.69%.

**X-ray Crystallography.** The diffraction data were collected on an Oxford Gemini S Ultra diffractometer equipped with Cu Kα radiation (λ = 1.54178 Å) for complex 1-MeOH and 1-EtOH, or on the same diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) for complexes 1-dry and 1-H₂O by using φ and ω scans. Multiscan adsorption corrections were applied for all complexes. The structures were solved by the direct methods (SHELXS) and refined by the full matrix least-squares method against F² using the SHELXL software. The coordinates of the nonhydrogen atoms were refined anisotropically. Most of hydrogen atoms have not been added. Details of the crystal parameters, data collections, and refinement for all compounds are summarized in Table 1. Further details are provided in the Supporting Information. CCDC numbers 966848 (1-MeOH), 966849 (1-dry), 966850 (1-H₂O), and 1861423 (1-EtOH).

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