

Synthesis and Structural Flexibility of a Series of Copper(II) Azolate-Based Metal–Organic Frameworks

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Keywords: Metal–organic frameworks / Porous materials / N ligands / Copper

The reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with three novel ditopic ligands, 2-methyl-1,4-benzenedinitetrazolate (MeBDT^{2-}), 4,4'-biphenyldinitetrazolate (BPDT^{2-}), and 2,3,5,6-tetrafluoro-1,4-benzenedinitetrazolate (TFBDTri^{2-}), affords the metal–organic frameworks $\text{Cu}(\text{MeBDT})(\text{dmf})$ (**1**), $\text{Cu}(\text{BPDT})(\text{dmf})$ (**2**), and $\text{Cu}(\text{TFBDTri})(\text{dmf})$ (**3**), respectively. These materials feature a common network topology in which octahedral Cu^{2+} ions are bridged by azolate ligands and dmf molecules to form one-dimensional chains. The individual chains are connected by the organic bridging units to form diamond-shaped channels, in which the solvent molecules project into the pores.

The bridging dmf molecules in **1** are readily displaced by other coordinating solvent molecules, which leads to a change in the pore dimensions according to the steric bulk of the solvent. Interestingly, attempts to exchange the analogous solvent molecules in the expanded framework **2** induced no change in the pore size, revealing the rigidity of the framework. Meanwhile, **3** exhibits modest flexibility and an improved thermal stability consistent with its chemical functionality. The marked difference in flexibility highlights the considerable impact the organic linker can have on the dynamic framework properties.

Introduction

Metal–organic frameworks have attracted much recent investigation because of their high permanent porosity, convenient modular synthesis, and chemical tunability.^[1] The ability to judiciously select the metal ion and organic linker suggests that if the appropriate components are combined, frameworks that are tailor-made for specific applications, such as gas storage^[2] and separation,^[3] may be prepared. However, significant improvements in the understanding of structure–property relationships within this class of material are still needed in order to fulfill their great potential. Indeed, despite the large number of frameworks studied for their gas sorption behavior, flexibility, and chemical stability, it still remains difficult to predict how changes to the framework constituents or network structure might affect the observed properties. Thus, improvements in this regard would greatly aid in materials design, and from a practical point of view, dramatically reduce the number of compounds that need to be studied for the discovery of high-performance materials.

The systematic investigation of the adsorptive and dynamic properties of materials exhibiting a common network topology may allow the effect of subtle changes to the framework, such as the metal node or the functionality or length of the organic bridging unit, to be elucidated. For

example, the IRMOF series of frameworks, which feature a cubic network of tetrahedral $[\text{Zn}_4\text{O}]^{6+}$ clusters bridged by dicarboxylate linkers, demonstrates that a common network type can be adopted despite the use of a diverse range of ligands.^[1a,4] Meanwhile, in the $\text{M}_2(\text{DOBDC})$ ($\text{M} = \text{Mg}, \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}$; $\text{DOBDC}^{4-} = 2,5\text{-dioxido-1,4-benzenedicarboxylate}$) and the $\text{M}_3[(\text{M}_4\text{Cl})_3(\text{BTT})_8]_2$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Cu}$; $\text{BTT}^{3-} = 1,3,5\text{-benzenetristetrazolate}$) frameworks, the same network connectivity is facilitated by a variety of metals.^[5,6] These materials are of significant interest due to the presence of unsaturated coordination sites on the pore surface, and depending on the metal employed, the frameworks can exhibit enhanced affinities or selectivities for certain gas molecules, which is crucial for the development of high-performance materials for hydrogen storage and carbon dioxide capture.

In addition to variations in the composition of the materials, metal–organic frameworks exhibiting reversible structural flexibility have also received significant attention due to their structural dynamics and unusual response to the adsorption of guest molecules.^[7] These materials frequently exhibit stepwise or hysteretic adsorption phenomena owing to transitions in the framework structure, which can be of benefit for gas storage and separation applications. For instance, in the separation of gases of very similar kinetic diameters, such as O_2 and N_2 , a potentially viable approach might be to modulate the gate-opening pressure by tuning the internal pore surface of the material. Thus, the two strategies mentioned above, namely modification of the metal or ligand component of the framework, are potential avenues for the preparation of optimized materials.

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejic.201000490> or from the author.

Recently, we have reported two copper-based frameworks: Cu(BDT)(dmf) (BDT^{2-} = 1,4-benzeneditetrazolate) and Cu(BDTri)(L) (L = dmf, def; BDTri^{2-} = 1,4-benzeneditriazolate).^[8,9] Despite the use of different azolate functional groups, the frameworks are isostructural to each other, and in the case of the triazolate-based materials, the same network topology is adopted despite a different bridging solvent molecule being present in the structure. Interestingly, these materials exhibit reversible changes in the pore dimensions depending on the quantity of guest solvent in the pores. In the case of the evacuated frameworks, a state in which the pore apertures are closed, a high selectivity of O_2 over N_2 is observed due to a kinetic sieving effect based on the slightly smaller kinetic diameter of O_2 (3.46 Å) relative to N_2 (3.64 Å).^[10] Here, we extend this library of metal-organic frameworks based on copper(II) azolate derived from three new organic linkers depicted in Figure 1: 2-methyl-1,4-benzeneditetrazolate (MeBDT^{2-}), 4,4'-biphenylditetrazolate (BPDT^{2-}), and 2,3,5,6-tetrafluoro-1,4-benzeneditriazolate (TFBDTri^{2-}). The ligands have been synthesized for their different functionalities and lengths, which are anticipated to allow access to unique dynamic properties within the resulting frameworks. Indeed, while the resulting frameworks exhibit the same network topology, they possess significantly different flexibility and chemical stability profiles with respect to exchange of the bridging ligand, demonstrating the exquisite dependence of the framework properties on the organic linker.

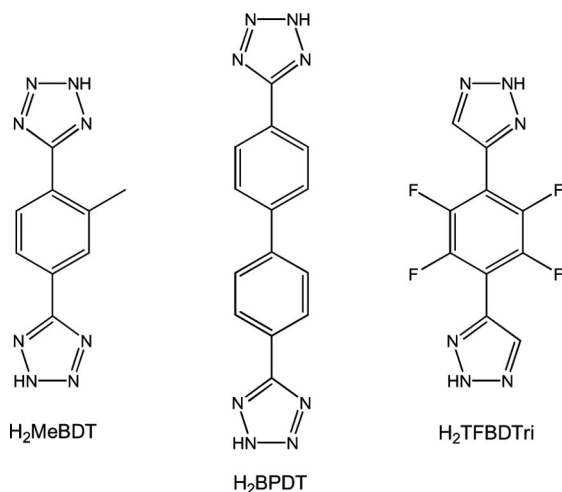


Figure 1. Protonated forms of the organic bridging units employed in the present work: 2-methyl-1,4-benzeneditetrazolate (MeBDT^{2-}), 4,4'-biphenylditetrazolate (BPDT^{2-}), and 2,3,5,6-tetrafluoro-1,4-benzeneditriazolate (TFBDTri^{2-}).

Results and Discussion

The combination of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and H_2MeBDT in an acidified mixture of dmf and methanol at room temperature yielded blue-green, block-shaped single crystals of the solvated form of Cu(MeBDT)(dmf) (**1-AS**). X-ray diffraction analysis of the crystals revealed an orthorhombic network

crystallizing in the space group *Imma* (Figure 2), which is isostructural to both Cu(BDT)(dmf)^[8] and Cu(BDTri)(L) (L = dmf, def).^[9] The network consists of octahedral Cu^{2+} ions, in which the four equatorial coordination sites are coordinated by nitrogen atoms of four different tetrazolate groups, while the axial sites are occupied by bridging dmf molecules resulting in one-dimensional chains in the [010] direction. The individual chains are linked by the MeBDT^{2-} ligands, creating diamond-shaped one-dimensional channels that run parallel to the Cu^{2+} chains. Note that the methyl substituent on the bridging ligand was crystallographically disordered over the four possible sites on the benzene ring. Thermogravimetric analysis of a sample of **1-AS** following immersion in dichloromethane revealed that, following the initial evaporation of dichloromethane up to approximately 50 °C, the material maintains its structure until approximately 200 °C, above which the bound dmf molecules are lost, resulting in decomposition of the framework. The thermal stability is indeed comparable to that of other tetrazolate-based frameworks reported recently.^[6,8]

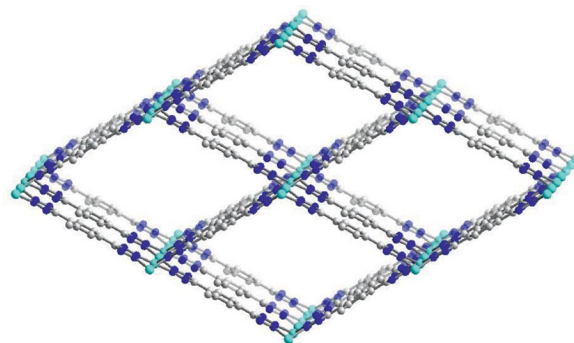


Figure 2. A portion of the crystal structure of as-synthesized Cu(MeBDT)(dmf) (**1-AS**) as viewed down the [010] direction. Turquoise, gray, and blue spheres represent Cu, C, and N atoms, respectively. Hydrogen atoms and bridging dmf molecules have been omitted for clarity.

Surprisingly, the single-crystallinity of the as-synthesized material was lost after evacuation of the pores by immersing the crystals in dichloromethane and evaporating the solvent within the pores under a slow flow of dinitrogen. This is presumably due to the mechanical stress generated by the significant changes in the dimensions of the channels within the framework. Indeed, comparison of the powder X-ray diffraction pattern of **1-AS** (Figure 3a) with that of the desolvated material (**1-dmf**, Figure 3b) revealed a significant shift in several of the predominant reflections, most notably the (101) reflection. Furthermore, full indexing of the powder pattern was possible to a significantly smaller unit cell within the same space group, *Imma*, wherein the cell parameter *c* was significantly contracted relative to the solvated structure, indicating partial collapse of the one-dimensional channels upon removal of the non-coordinated solvent molecules. Infrared spectroscopy confirmed that the bridging dmf molecules, and hence the original network connectivity, had been retained in **1-dmf**. Moreover, after solvation of

the pores of **1**-dmf by soaking in neat dmf, a powder X-ray diffraction pattern matching that of **1**-AS was obtained, indicating the opening of the pore aperture.

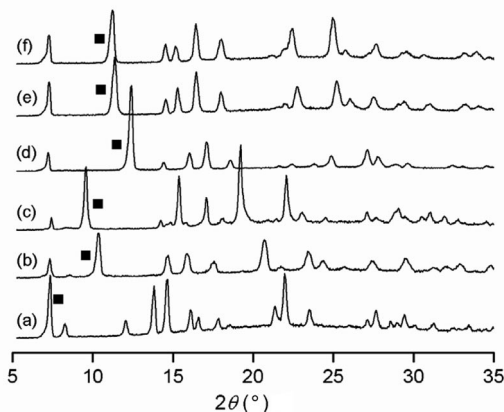


Figure 3. Powder X-ray diffraction patterns for (a) as-synthesized Cu(MeBDT)(dmf) (**1**-AS), (b) evacuated Cu(MeBDT)(dmf) (**1**-dmf), (c) Cu(MeBDT)(def) (**1**-def), (d) Cu(MeBDT)(MeOH) (**1**-MeOH), (e) Cu(MeBDT)(EtOH) (**1**-EtOH), (f) Cu(MeBDT)(dmsO) (**1**-dmsO). The filled square symbol indicates the (101) reflection, which readily evolves upon solvent exchange.

The ability of the bridging solvent to be modified in the Cu(BDTri)(L) (L = dmf, def) system prompted our efforts to probe the extent to which this is possible for **1**. In our hands, while the framework could not be prepared directly within other solvents, we found that the as-synthesized material **1**-AS could be immersed in def to generate Cu(MeBDT)(def) (**1**-def), in which the bridging dmf solvent molecules were fully displaced by def. Furthermore, indexing of the powder X-ray pattern of the dried form of **1**-def (Figure 3c) was possible within the space group *Imma* by using a unit cell larger than that observed for **1**-dmf, which is consistent with the slightly greater steric bulk of def relative to dmf.

The generality of the substitution of the bridging solvent was tested by submerging samples of **1**-AS within a number of common organic solvents. Indeed, dmf could be displaced by a broad range of other coordinating solvents, such as methanol, ethanol, and dmsO, to generate Cu(MeBDT)(MeOH) (**1**-MeOH), Cu(MeBDT)(EtOH) (**1**-EtOH), and Cu(MeBDT)(dmsO) (**1**-dmsO), respectively. Immersion of single crystals of **1**-AS within these coordinating solvents resulted in rapid cracking of the crystals, which is consistent with the significant mechanical stress imparted

by the changes in the dimensions of the one-dimensional channels. However, the powder X-ray diffraction patterns (Figure 3d–f) could be fully indexed within the space group *Imma* in all cases, affording the unit cell parameters tabulated in Table 1. Comparison of the unit cell volumes reveals that the pore dimensions follow that of the steric bulk of the coordinated solvent, suggesting the possibility for tuning the porosity and the surface chemistry by use of the appropriate solvent molecule. Notably, the use of solvent molecules larger than the size of the pores, such as 1-butanol and benzyl alcohol, resulted in no displacement of the bridging solvent, as evidenced by the unchanged powder X-ray pattern after drying the sample.

The reaction of CuCl₂·2H₂O and H₂BPDT in an acidified dmf and EtOH mixture at room temperature yielded blue, block-shaped crystals of the solvated form of Cu(BPDT)(dmf) (**2**-AS). Indexing of the powder X-ray diffraction within the space group *Imma* revealed that the framework is indeed an expanded version of **1**. The unit cell parameter *a* [31.559(4) Å] is significantly larger than the corresponding value observed in **1**-AS [22.709(5) Å], which is consistent with the use of a longer organic linker and the formation of wider channels. Interestingly, in contrast to **1**, samples of **2** that were washed with dichloromethane and air-dried retained the same powder X-ray diffraction pattern (Figure S1), indicating structural rigidity upon evacuation of the pores of the framework. The flexibility of **2** and its solvent exchange properties were further assessed by submerging crystals of **2** within the same organic solvents as those successfully incorporated into **1**. Surprisingly, under all conditions, the framework structure remained rigid, and no changes to the powder X-ray diffraction pattern were detected.

The solvothermal reaction of CuCl₂·2H₂O and the fluorinated ligand H₂TFBDTri at 80 °C in dmf over four days resulted in the precipitation of Cu(TFBDTri)(dmf) (**3**-AS) as a blue-purple powder. Analysis of the powder X-ray diffraction pattern revealed that the material is indeed isostructural to **1**. Note that, in the case of perfluorinated ligands bearing carboxylate functionalities, materials that are isostructural to their non-fluorinated counterparts have not yet been reported.^[11] As expected from the higher coordination strength of the ligand, thermogravimetric analysis revealed a modest increase in the thermal stability of the framework over **1** and **2** (Figures S4–S6), which may be attributed to the higher thermal stability of the triazole functionality^[12] and/or aryl carbon–fluorine bonds.^[13] A similar

Table 1. Unit cell parameters of as-synthesized and solvent-exchanged forms of **1**–**3** as determined from indexing^[a] of the powder X-ray diffraction patterns.

	1 -AS	1 -dmf	1 -def	1 -MeOH	1 -EtOH	1 -dmsO	2	3 -dmf	3 -def	3 -dmsO
<i>a</i> (Å)	22.72	24.66	24.39	25.10	24.88	25.01	31.23	24.54	24.55	24.64
<i>b</i> (Å)	7.234	7.090	7.124	7.270	7.195	7.137	6.667	6.970	6.980	6.960
<i>c</i> (Å)	14.95	9.290	10.21	7.561	8.338	8.480	12.98	9.390	9.948	8.618
<i>V</i> (Å ³)	2349.0	1624.3	1773.0	1379.5	1494.0	1513.6	2702.6	1606.1	1705.0	1478.3

[a] Space group: *Imma*.

soaking of **3**-AS within def and dmsO generated the corresponding frameworks Cu(TFBDTri)(def) (**3**-def) and Cu(TFBDTri)(dmsO) (**3**-dmsO), respectively. As was observed for **1**, the powder X-ray diffraction patterns (Figures S2a–c) indicated the flexibility of the framework, and the resulting unit cell volumes correlate with the steric bulk of the solvent employed. Surprisingly, when samples of **3**-AS were submerged in water or methanol, significant broadening of the reflections in the powder pattern was observed, indicating a decrease in the crystallinity of the sample.

The significant difference in the framework flexibility between compounds **1**, **2**, and **3** is quite unexpected, because of the structural similarities and network connectivity of the materials. While the exact mechanism giving rise to the solvent substitution is currently unknown, one origin for the different behavior may lie in the strength of the binding of the bridging solvent molecules as a result of electronic effects and steric demands imposed by the various bridging ligands. Similar effects have been reported recently by Férey and co-workers for derivatives of the MIL-53(Fe) structure type,^[14] which exhibited linker-dependent flexibility upon immersion in a variety of organic solvents. Ongoing studies will be directed towards gaining a more detailed understanding of the mechanism of solvent substitution and effects on the resulting gas sorption properties.

Conclusions

The foregoing results demonstrate broad applicability of the Cu(BDT)(dmf) structure type, allowing for the generation of three isostructural materials from a variety of organic linkers. The flexibility within this series of framework is strongly influenced by the specific organic bridging unit that is employed, wherein **1** is readily flexible upon the incorporation of guest solvent molecules into the pores, while the **2** remains rigid under all conditions attempted in this study. Flexibility could also be demonstrated for **3**, in which def and dmsO could be exchanged for dmf. Studies directed towards elucidating the reasons for such a significant difference in the flexibility between these frameworks are currently underway. Furthermore, efforts to achieve a more detailed understanding of the chemical properties of the channels, such as polarity-dependent guest solubility, and the adsorptive properties of the frameworks, are also ongoing. We envisage that this structure type can be adopted by an even broader range of ligand functionalities, which should lead to an increased understanding of the structure–property relationships within this class of metal–organic framework.

Experimental Section

General: All ligand syntheses were performed under a nitrogen atmosphere by using standard Schlenk techniques. Azidomethyl pivalate^[15] and 1,4-diethynyl-2,3,5,6-tetrafluorobenzene^[16] were prepared as previously reported. All glassware was dried in an oven

set to a temperature of 150 °C for 24 h prior to use. Toluene was dried with activated 4 Å molecular sieves, passed through a column of activated alumina, and degassed with nitrogen. Methanol was dried with calcium hydride and then distilled. All other syntheses and manipulations were carried out in air. All reagents were obtained from commercial vendors and used without further purification.

1,4-Ditetrazol-5-yl-2-methylbenzene (H₂MeBDT): Toluene (20 mL) was added to a 100 mL round-bottom flask containing 2-methyl-terephthalonitrile (0.34 g, 2.4 mmol), sodium azide (0.95 g, 15 mmol), and triethylamine hydrochloride (2.0 g, 15 mmol). The reaction mixture was heated at reflux for three days, after which time a pale-brown solid was observed on the walls of the reaction vessel. The reaction mixture was dissolved in NaOH (30 mL, 1 M) and vigorously stirred for 30 min, then the aqueous phase was collected by phase separation. This fraction was treated with HCl (30 mL, 1 M) until the pH of the solution was ca. 1, and the resulting white solid was collected by filtration and dried overnight at 120 °C. The dried product was finely ground to yield a pale-yellow powder (0.43 g, 79%). IR (neat): $\tilde{\nu}$ = 3137 (m), 3065 (m), 3007 (m br), 2927 (m br), 2827 (m br), 2707 (s br), 2625 (s br), 2495 (s br), 1807 (m br), 1580 (s), 1496 (m), 1454 (m), 1435 (m), 1390 (s), 1350 (w), 1282 (w), 1238 (s), 1153 (m), 1109 (m), 1086 (m), 1030 (m), 986 (s), 920 (s), 887 (s), 835 (s), 741 (s), 705 (w br) cm⁻¹. ¹H NMR ([D₆]dmsO): δ = 17.10 (br. s, 2 H, -NH), 8.14 (s, 1 H, H_{Ph}), 8.07 (d, J = 8 Hz, 1 H, H_{Ph}), 7.96 (d, J = 8 Hz, 1 H, H_{Ph}), 2.61 (s, 3 H, -CH₃) ppm.

4,4'-Ditetrazol-5-yl-biphenyl (H₂BPDT): Toluene (20 mL) was added to a 100 mL round-bottom flask containing 4,4'-biphenyldicarbonitrile (0.50 g, 2.4 mmol), sodium azide (0.95 g, 15 mmol) and triethylamine hydrochloride (2.0 g, 15 mmol). A workup procedure analogous to H₂MeBDT was followed, yielding the pure product as an off-white powder (0.61 g, 87%). C₁₄H₁₀N₈ (290.28): C 57.93, H 3.47, N 38.60; found C 57.75, H 3.49, N 38.30. IR (neat): $\tilde{\nu}$ = 3130 (m br), 3064 (m br), 3005 (m br), 2853 (s br), 2731 (s br), 2645 (s br), 1612 (s), 1556 (m), 1486 (s), 1423 (s), 1158 (m), 1055 (m), 1034 (m), 987 (m), 847 (w), 823 (s), 741 (s), 698 (w) cm⁻¹. ¹H NMR ([D₆]dmsO): δ = 17.01 (br. s, 2 H, -NH), 8.21 (d, J = 8 Hz, 4 H, H_{Ph}), 8.04 (d, J = 8 Hz, 4 H, H_{Ph}) ppm. MS (FAB): m/z (%) = 289 (37) [M – H]⁺.

4,4'-(Perfluoro-1,4-phenylene)bis(1*H*-1,2,3-triazole-4,1-diyl)bis-(methylene)bis(2,2-dimethylpropanoate) (FBTriMP): Water (3 mL) and *tert*-butyl alcohol (6 mL) were added to a 50 mL round-bottom flask containing 4-diethynyl-2,3,5,6-tetrafluorobenzene (0.17 g, 0.83 mmol) and azidomethyl pivalate (0.29 g, 1.8 mmol). Sodium L-ascorbate (17 mg, 0.042 mmol) and CuSO₄ solution (42 μ L, 0.083 mmol, 1 M) were added under vigorous stirring. The reaction mixture was heated to 60 °C for 16 h, after which time an orange solid was observed. Ice water (10 mL) was added, followed by NH₃ solution (3 mL, 10%). The resultant suspension was stirred for 2 h, and the product was isolated by filtration, washing with water, and drying under vacuum to yield a pale orange powder (0.35 g, 82%). C₂₂H₂₄F₄N₆O₄ (512.46): C 51.56, H 4.72, N 16.40; found C 51.29, H 4.62, N 16.10. IR (neat): $\tilde{\nu}$ = 3093 (w), 2983 (w), 1743 (s), 1490 (s), 1435 (m), 1389 (m), 1355 (w), 1275 (m), 1232 (m), 1116 (vs), 1058 (m), 1035 (s), 999 (m), 972 (s), 915 (m), 873 (w), 826 (m), 790 (m), 763 (m), 725 (w), 674 (w), 631 (w), 584 (w), 532 (w) cm⁻¹. ¹H NMR ([D₆]dmsO): δ = 8.82 (s, 2 H, -CH), 6.46 (s, 4 H, -CH₂), 1.15 [s, 18 H, -C(CH₃)₃] ppm. ¹⁹F NMR ([D₆]dmsO): δ = -140 ppm.

2,3,5,6-Tetrafluoro-1,4-benzeneditriazolate (H₂TFBDTri): Methanol (5 mL) and water (5 mL) were added to FBTriMP (0.55 g, 1.1 mmol) in a 50 mL glass round-bottom flask and vigorously

stirred for 5 h. Water (40 mL) was added, and the mixture was extracted with ether (4 × 20 mL). The aqueous layer was then acidified with an excess of HCl (1 M) to obtain an off-white precipitate. The product was filtered, copiously washed with water, ether, and dichloromethane, and dried under vacuum to afford an off-white powder (0.21 g, 70%). The product can be further purified if necessary from residual copper catalyst by dissolution in aqueous ethylenediamine (15%) followed by precipitation with HCl (1 M) and washing with water, ether, and dichloromethane. IR (neat): $\tilde{\nu}$ = 3098 (br. w), 2883 (br. m), 2784 (br. m), 2661 (br. m), 1474 (s), 1445 (m), 1404 (w), 1348 (w), 1245 (m), 1234 (m), 1203 (m), 1157 (m), 1147 (m), 1081 (m), 1018 (w), 976 (vs), 907 (m), 854 (m), 825 (m), 781 (m), 727 (w), 673 (w), 619 (w) cm^{-1} . ^1H NMR ($[\text{D}_6]\text{dmsO}$): δ = 15.73 (br. s, 2 H, -NH), 8.41 (br. s, 2 H, -CH) ppm. ^{13}C NMR ($[\text{D}_6]\text{dmsO}$): δ = 144 (d, $^1J_{\text{C,F}}$ = 254 Hz, -CF), 134 (s, -C_{Ar}), 125 (br. s, -CH), 110 (s, C_{Tri}) ppm. ^{19}F NMR ($[\text{D}_6]\text{dmsO}$): -135 ppm. MS (HR-ESI): m/z = 284.0438 (100.00%; $^{12}\text{C}_{10}\text{H}_4\text{N}_6\text{F}_4$), 285.0462 (12.16%; $^{12}\text{C}_9^{13}\text{CH}_4\text{N}_6\text{F}_4$).

Cu(MeBDT)(dmf) (1, Cu–MeBDT): H_2MeBDT (9.0 mg, 0.04 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (6.8 mg, 0.04 mmol) were added to a 4 mL scintillation vial. A 1:1 (v/v) mixture of dmf and ethanol (2 mL), and concentrated HCl (20 μL) were added to the solids, and the vial was placed on a hotplate set at 120 °C following tight sealing with a Teflon-lined cap. A blue-purple microcrystalline powder was collected after two days to afford 5.0 mg of product (37%). IR (neat): $\tilde{\nu}$ = 3305 (m, br), 3154 (w), 2977 (w), 1652 (s), 1568 (w), 1475 (w), 1438 (m), 1395 (m), 1364 (w), 1265 (w), 1213 (m), 1156 (m), 1119 (m), 1090 (m), 986 (s), 849 (m), 823 (s) cm^{-1} . Crystals appropriate for single-crystal X-ray diffraction analysis were prepared as follows: A solution of H_2MeBDT (9.0 mg, 0.042 mmol) in dmf (1 mL) was added to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (6.8 mg, 0.040 mmol) in methanol (1 mL) in a 4 mL scintillation vial. Concentrated HCl (20 μL , 12 M) was added to the reaction mixture to yield a green solution, which was kept at room temperature for five days. The resulting pale blue rod-shaped crystals were stored in the mother liquor.

Cu(BPDT)(dmf) (2, Cu–BPDT): H_2BPDT (12 mg, 0.041 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (6.8 mg, 0.040 mmol) were added to a 4 mL glass scintillation vial. A 1:1 (v/v) mixture of dmf and methanol (2 mL), and concentrated HCl (20 μL) were added to the solids, and the vial was placed on a hotplate set at 90 °C following tight sealing with a Teflon-lined cap. A blue-purple microcrystalline powder was collected after two days to afford 6.0 mg (37%) of product. IR (neat): $\tilde{\nu}$ = 3317 (m br), 3074 (w), 2915 (w), 2539 (m br), 1673 (s), 1590 (s), 1545 (s), 1424 (m), 1369 (m), 1246 (s), 1126 (m), 1024 (s) cm^{-1} .

Cu(TFBDTri)(dmf) (3, Cu–TFBDTri): $\text{H}_2\text{TFBDTri}$ (8.5 mg, 0.029 mmol) and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (51 mg, 0.30 mmol) were added to a 4 mL glass scintillation vial. Then, dmf (3 mL) acidified with three drops of HNO_3 (0.2 M) was added to the solids, and the vial was placed on a hotplate set at 80 °C following tight sealing with a Teflon-lined cap. A blue-purple microcrystalline powder was collected after four days by filtration, washing with dmf, and evacuation under vacuum to afford 4 mg of product. This solid is isostructural to the $\text{CuBDTri}(\text{dmf})$ C phase,^[9] and its unit cell can be indexed with the same space group, *Imma*, with lattice parameters a = 24.53(2) Å, b = 6.959(7) Å, c = 9.393(7) Å. IR (neat): $\tilde{\nu}$ = 1643 (s), 1488 (s), 1384 (m), 1370 (sh), 1337 (w), 1245 (w), 1223 (w), 1106 (m), 1060 (w), 1021 (w), 974 (vs), 849 (m), 789 (s), 696 (w), 665 (w), 637 (w), 482 (m) cm^{-1} .

Crystal Data for 1-AS: $\text{C}_{13}\text{H}_4\text{CuN}_8\text{O}$, M = 351.79, orthorhombic, *Imma*, a = 22.709(5) Å, b = 7.1180(14) Å, c = 12.828(3) Å, V = 2073.6(8) Å³, T = 100(2) K, λ = 0.71073 Å, Z = 4, ρ = 1.127 g/cm³,

2554 data measured, 470 unique data, R_{int} = 0.0470, $R1$ = 0.0809, $wR2$ = 0.2241 for 470 contributing reflections [$I \geq 2\sigma(I)$], GOF = 0.902. A description of the refinement procedure can be found in the Supporting Information. CCDC-778563 contains the supplementary 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.

Other Physical Measurements: Powder X-ray diffraction data was collected by using $\text{Cu-K}\alpha$ radiation (λ = 1.5406 Å) with a Siemens D5000 diffractometer. Indexing of the diffraction patterns for 1–3 was performed within the Bruker EVA software. Single-crystal X-ray diffraction data were collected with a Siemens SMART 1000 diffractometer, and structures were subsequently solved using the SHELXTL 5.0^[17] software package following absorption corrections applied by SADABS.^[18] ^1H NMR spectra were recorded at ambient temperature with Bruker AV-300, AVQ-400, AVB-400, and AV-600 spectrometers, and all chemical shifts are given in relation to residual solvent peaks. Thermogravimetric analyses were carried out with a TA Instruments TGA 2950 instrument at a temperature ramping rate of 4 °C/min under a flow of nitrogen gas. Infrared spectra were collected by using a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory (ATR). Carbon, hydrogen, and nitrogen analyses were performed by the Microanalytical Laboratory at the University of California, Berkeley.

Supporting Information (see footnote on the first page of this article): Powder X-ray diffraction patterns, TGA profiles, and details of the structure refinement procedure.

Acknowledgments

This work was supported by the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award number DE-SC0001015, and the Korea Research Foundation Grant funded by the Korean Government (MEST) (KRF-2009-220-C00021). We thank Fulbright New Zealand for partial support of K. S., and Dr. A. G. DiPasquale for helpful discussions.

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Received: May 1, 2010

Published Online: July 5, 2010