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Toward Templated Metal–Organic Frameworks: Synthesis, Structures, Thermal Properties, and Luminescence of Three Novel Lanthanide–Adipate Frameworks

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Three novel praseodymium–adipate frameworks were synthesized hydrothermally. GWMOF-3 ($[Pr_2(\text{adipic acid})_3(H_2O)_4]\cdot\text{adipic acid}\cdot 4H_2O$) and GWMOF-6 ($[Pr_2(\text{adipic acid})_3(H_2O)_2]\cdot$4,4′-dipyridyl) formed three-dimensional structures, whereas GWMOF-4 ($[Pr_2(\text{adipic acid})_3(H_2O)_2]\cdot H_2O$) produced a more dense, two-dimensional topology. Single-crystal X-ray and powder diffraction, IR spectroscopy, fluorescence spectroscopy, thermogravimetric analysis, and elemental analysis were employed to characterize all samples. GWMOF-6 represents an innovative step forward in metal–organic framework synthesis where a neutral molecular species not used in the construction of the framework is utilized as a structure-directing agent, or template. Furthermore, this template molecule (4,4′-dipyridyl) is shown to sensitize the fluorescence of lanthanide metal centers in a europium analogue of GWMOF-6.

Introduction

The study of porous framework materials in recent years has developed into a significant area of research.[1−6] Feasible applications in sensing, catalysis, ion exchange, separations, or gas storage have attracted considerable attention to these compounds.[7−13] Much of this interest stems from the ability of these materials to selectively sorb, occlude, and exchange species on an atomic or molecular size scale. Traditionally, zeolites and zeolite-like materials (e.g., aluminophosphates) represent the forefront of this line of research.[14−16] A more recent extension of this work has been the introduction of metal−organic framework materials (MOFs), which are porous materials constructed through highly directional covalent bonding between metal centers and organic "linkers" of varying dimensionality and functional group composition.[17−24]

MOFs offer the potential for extensive topological and functional control through judicious choice of the organic

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linker. The use of specific functional groups may influence which metals can be used, such as Zn^{2+} with carboxylate groups[25,26] or Cu^{2+} with pyridyl groups.[27−32] Further, the geometry of the organic component may influence the overall topology: more flexible aliphatic linkers have been shown to produce more dense structures,[33−37] whereas rigid, conjugated species may promote more open and robust topologies.[19,34,38−41] An exception to this allows for construction of open frameworks with a flexible ligand through selection of a metal center with a high coordination sphere, such as with the lanthanides and actinides.[18,22,42−47] An advantage of such a selection is that the flexibility of the ligand may aid in maintaining an open framework upon evacuation of any guest molecules present in the pores.[42,43] These few examples are by no means an exhaustive listing of the vast diversity of MOF materials but rather are representative of the philosophy of the construction of inorganic/organic hybrid frameworks. Readers are encouraged to explore more thorough reviews[6,7,9,17,48] to appreciate the breadth of compounds in these systems.

MOFs represent an incredible advancement in the field of framework materials and have in turn produced a host of novel topologies. Challenges remain, however, with respect to the tendency of some materials to lose porosity upon evacuation of guest molecules (usually solvent) from within the pores.[20,39] Interpenetration of adjacent layers and large pore frameworks occasionally poses a problem as well,[49−52] leading to essentially nonporous materials. Nonetheless, it is difficult to disregard the promise of a field featuring new and innovative materials, and novel routes to these and related compounds are thus necessary to advance our understanding of their formation and properties.

We have been exploring MOFs containing lanthanide and uranium metal centers due to the ability of these elements to have larger coordination spheres (vs transition metals), as well as their unique luminescent properties[53] and relevance to spent nuclear fuel issues.[54] Lanthanides in particular have an inherent affinity for oxygen-containing ligands over other functional groups and thus provide the potential for recognition and/or discrimination among a variety of linker and/or guest species on the basis of, for example, hard−soft acid−base considerations.[55,56] Of particular relevance to the current study are a number of adipate frameworks reported by our group[23,57] as well as others.[18,22,45−47,58] The extent to which this system has been explored through hydrothermal, sol−gel, and room-temperature synthetic approaches, as well as its structural diversity, actually provides an appropriate forum to explore novel routes to framework materials. In particular, the use of organic structure-directing agents, or “templates”, may be applied in an effort to promote formation of desirable compounds and structure types.

Templating can be broadly defined as the use of small organic molecules (or hydrated metal ions) to provide a support about which an inorganic host may crystallize. In general, “template” molecules may serve several different roles, including framework support and/or charge balance to their hosts. This approach has been widely successful in many systems, including zeolites,[59,60] phosphates,[61−65] and sulfates[66−69] and sulfides[70−79] yet remains less studied in MOF systems.[47,80]

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Expanding the applicability of templates to MOF systems is a logical extension of their structure-directing capabilities. MOF materials offer a tremendous range of topologies and compositions that in turn provide a number of opportunities to examine the role of incorporated guest molecules. In particular, the ability of metal centers to discriminate among functional groups (mentioned above) may allow for the use of multiple organic components (e.g. carboxylic and pyridyl) for use as hosts and guests, respectively.

In this contribution, we explore the potential for the formation of templated MOFs by examining several frameworks within the Ln−adipate system. Modification of their synthetic parameters to incorporate 4,4′-dipyridyl guest molecules has resulted in a new family of MOF compounds with structures clearly influenced by the presence of these templating species. As such, we report the synthesis, structures, and thermal and luminescent properties of GWMOF-3 ($[Pr_2(C_6H_8O_4)_3(H_2O)_4]\cdot C_6H_8O_4\cdot 4H_2O$), GWMOF-4 ($[Pr_2(C_6H_8O_4)_3(H_2O)_2]\cdot H_2O$), and GWMOF-6 ($[Pr_2(C_6H_8O_4)_3(H_2O)_2]\cdot C_{10}H_8N_2$), the latter of which represents the first example of a templated lanthanide metal−organic framework material.

Experimental Section

Synthesis. GWMOF-3 ($[Pr_2(C_6H_8O_4)_3(H_2O)_4]\cdot C_6H_8O_4\cdot 4H_2O$) was synthesized hydrothermally in a 23-mL Teflon-lined Parr bomb. A solution of praseodymium chloride heptahydrate ($PrCl_3\cdot 7H_2O$), adipic acid ($C_6H_{10}O_4$, Aldrich), concentrated ammonium hydroxide (NH_4OH, Fisher Scientific), and water (molar ratio of 1:1:2:150) was made (pH = 4.04) and heated at 180 °C for 72 h under autogenous pressure. After 3 days, the reaction vessel was allowed to cool to room temperature. Green crystals were obtained after decanting the solution (pH = 4.99, 23% yield based on Pr), washed with water and ethanol, and dried in air at room temperature.

GWMOF-4 ($[Pr_2(C_6H_8O_4)_3(H_2O)_2]\cdot H_2O$) was synthesized by halving the amount of adipic acid in GWMOF-3 (molar ratio of 1:0.5:2:150 ($PrCl_3\cdot 7H_2O$:adipic acid:concentrated ammonium hydroxide:water), pH = 6.70). After 3 days at 180 °C, the supernatant liquid was decanted and green crystals were obtained (pH = 6.43, 30% yield based on Pr). The crystals were washed with water and ethanol and allowed to air-dry at room temperature.

GWMOF-6 ($[Pr_2(C_6H_8O_4)_3(H_2O)_2]\cdot C_{10}H_8N_2$) was prepared in a fashion similar to that for GWMOF-3. A solution of praseodymium chloride heptahydrate ($PrCl_3\cdot 7H_2O$), adipic acid ($C_6H_{10}O_4$, Aldrich), 4,4′-dipyridyl ($C_{10}H_8N_2$, Maybridge), ammonium hydroxide (NH_4OH, Fisher Scientific), and water (molar ratio of 1:1:1:2:150) was made (pH = 8.02). After being heated at 120 °C for 72 h, the solution (pH = 4.75) was decanted and green crystals (25% yield based on Pr) were obtained, which were washed with water and ethanol and allowed to air-dry at room temperature. GWMOF-6 was also successfully prepared with Nd^{3+}, Ce^{3+}, Sm^{3+}, and Eu^{3+}, yet these reactions (except Nd^{3+}) did not produce crystals suitable for single-crystal studies. Comparison of their powder X-ray diffraction patterns (PXRD), however, to the calculated pattern of GWMOF-6 shows that they are indeed isostructural.

Characterization of the samples was done using X-ray diffraction, thermogravimetric analysis (TGA), IR, and elemental analysis. Powder X-ray diffraction data were collected on a Scintag XDS 2000 diffractometer (Cu Kα, 3−60°, 0.05° step, 1.0 s/step) and manipulated using the JADE software package.[81] TGA was performed on a Perkin-Elmer Pyris1 at a temperature range of 30−600 °C (10 deg/min) with flowing $N_2(g)$. A Perkin-Elmer Spectrum RX I FT-IR was used to gather IR spectra using KBr pellets. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN. Fluorescence data for GWMOF-6 were collected on a Shimadzu RF-5301 PC spectrofluorophotometer with a Xe arc lamp source and 1.5/3.0 nm excitation and emission slit widths (respectively).

Single-Crystal X-ray Diffraction. Single crystals of GWMOF-3, -4, and -6 were isolated from the bulk reaction products and mounted on glass fibers for data collection at room temperature on a Bruker P4 diffractometer utilizing Mo Kα radiation and an APEX CCD detector. Nearly a hemisphere of data was collected for each material using a combination of ϕ and ω scans and 20 s exposures (Table 1). Data were integrated and corrected for absorption using the Bruker programs SAINT[82] and SADABS.[83] The structure of GWMOF-3 solved readily in both $P1$ and $P\bar{1}$ using direct methods (SIR92)[84] and refined using SHELXL-97[85] within the WINGX software suite.[86] The praseodymium, oxygen, and carbon atom positions were identified immediately, whereas hydrogen atom positions were either located in difference Fourier maps or placed in calculated positions and allowed to ride on the coordinates of the parent atom. Refinement in $P1$ proved unsatisfactory (several nonpositive definite displacement parameters as well as missing symmetry located with PLATON[87]), thus concluding the centric space group to be the correct choice.

GWMOF-4 also solved readily with direct methods (SIR92) in both $P1$ and $P\bar{1}$, with $P\bar{1}$ giving a lower initial R factor. Refinement with SHELXL-97 within WINGX proceeded for both models, yet tests for missing symmetry using PLATON clearly indicated $P\bar{1}$ to be the correct assignment. Heavy atoms (Pr, C, O) were located in difference Fourier maps, whereas H atom positions on the carbon atoms were placed in idealized locations and allowed to ride on the parent atoms. H atoms on O2W were located in a difference map and allowed to refine freely. No satisfactory H atom positions could be found near O1W and were thus not included in the

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Table 1. Crystal Data and Structure Refinement for GWMOF-3, -4, and -6

	GWMOF-3 ($C_{12}H_{21}O_{12}Pr$)	GWMOF-4 ($C_{18}H_{30}O_{15}Pr_2$)	GWMOF-6 ($C_{14}H_{18}NO_7Pr$)
fw	498.20	760.98	453.20
temp (K)	293(2)	293(2)	293(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst system	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	*Pbcn* (No. 60)
a (Å)	8.6550(5)	8.67860(10)	21.9415(10)
b (Å)	9.9366(6)	10.38310(10)	7.7878(3)
c (Å)	11.7170(6)	13.6693(2)	19.6649(9)
α (deg)	74.7100(10)	101.3547(7)	90.00
β (deg)	69.7950(10)	106.1204(7)	90.00
γ (deg)	85.9590(10)	93.9593(5)	90.00
V (Å^3)	911.96(9)	1150.11(2)	3360.3(3)
Z	2	2	8
D_c (Mg/m^3)	1.814	2.1821	1.792
μ (mm^{-1})	2.728	4.260	2.933
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0360	0.0283	0.0434
$wR_2{}^a$	0.0778	0.0549	0.0907

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

refinement. O3W is a partially occupied, uncoordinated water molecule residing in the void spaces of GWMOF-4, and H atoms for this location could not be refined. No attempt was made to impart constraints. Details of the treatment of these sites can be found in the Supporting Information (CIF).

GWMOF-6 solved readily in *Pbcn* and proceeded in a fashion analogous to that for GWMOF-3 and -4 (above). Disorder is present in one adipic acid chain (C3, C4, and C5) and was thus handled by splitting the sites, constraining their distances to 1.0 Å, and fixing the occupancies to 0.5. No attempts to place H atoms at these locations were made. H atoms were, however, placed in idealized positions for all carbon atoms and although located in a difference map constrained to ride on the parent oxygen atom for the bound water molecule (O7). Further details on the treatment of the disorder and H atom can be found in the Supporting Information (CIF). Details of the data collection and refinement for all structures can be found in Table 1 and Supporting Information in CIF format is available via the Internet at http://pubs.acs.org. Crystallographic data for compounds GWMOF-3, -4, and -6 have also been deposited with the Cambridge Crystallographic Data Centre (CCDC) and may be obtained at http://www.ccdc.cam.ac.uk/ by citing nos. 253574, 253575, and 253576 for -3,-4, and -6, respectively.

Structural Description

The formation of a Ce^{3+} analogue of GWMOF-3 via sol−gel synthesis has recently been reported in the literature;[47] therefore, only a brief structural description will be given here. GWMOF-3 (Figure 1) consists of one-dimensional chains of PrO_{10} polyhedra that propagate along [100].

These chains are linked to one another through adipic acid backbones in two directions ([001] and [010]) to form a three-dimensional framework. Their connectivity gives rise to three distinct sets of channels along each of the primary crystallographic directions, with those along [001] being the most pronounced. Within the coordination sphere of the single unique Pr^{3+} site, there are two types of oxygen-containing ligands: two bound water molecules and eight carboxylate oxygen anions that result in a bicapped square antiprism coordination geometry (Figure 2).

The bound H_2O groups (O6 and O7) are adjacent to each other and are at an average distance of 2.670(3) Å from the metal center (Table 2). Two of the carboxylate oxygens (O8 and O9) are in bidentate coordination as part of an adipic acid molecule that connects adjoining PrO_{10} chains along the [010] direction. Of the remaining six carboxylate oxygens, O2 and O3 (and their symmetry pairs) are in bridging tridentate coordination and thus participate in the edge sharing within the chains. Last, O4 and O5 are the other halves of the O1 and O6 carboxylic groups, respectively. Bond lengths and angles for this geometry are typical, and

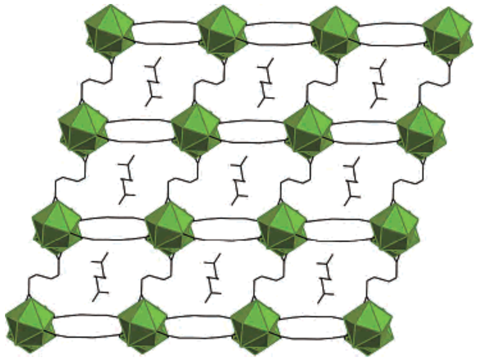

Figure 1. Extended framework structure of GWMOF-3 viewed down [100]. Green polyhedra represent the praseodymium, and the black lines represent adipic acid ligands and guest molecules.

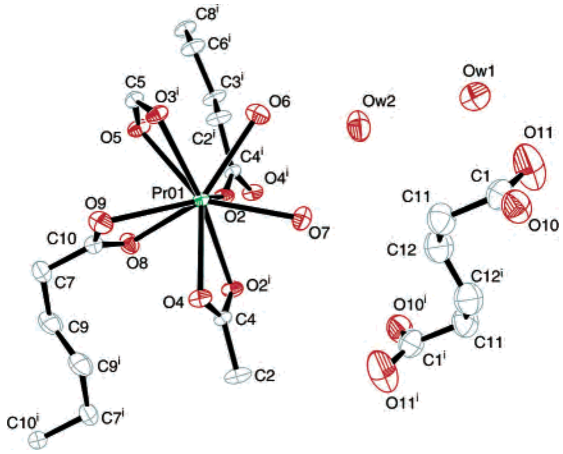

Figure 2. ORTEP drawing of GWMOF-3. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. The superscript indicates the following symmetry transformation: i = $-x$, $-y$, $-z$.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	GWMOF-3 ($C_{12}H_{21}O_{12}Pr$)[a]		
Pr(1)−O(6)	2.460(2)	Pr(1)−O(3)	2.496(2)
Pr(1)−O(7)	2.591(3)	C(12)^{i}−C(12)−C(11)	114.9(5)
Pr(1)−O(2)	2.571(2)	C(1)−C(11)−C(12)	115.4(4)
	GWMOF-4 ($C_{18}H_{30}O_{15}Pr_2$)[b]		
Pr(1)−O(7)	2.843(3)	Pr(2)−O(10)	2.486(2)
Pr(2)−O(7)	2.465(3)	Pr(1)−O(7)−Pr(2)^{i}	115.26(11)
Pr(1)−O(8)	2.847(3)	Pr(1)−O(8)−Pr(2)^{i}	113.95(10)
Pr(2)−O(8)	2.500(3)	Pr(1)−O(3)−Pr(1)^{ii}	116.73(10)
Pr(1)−O(3)	2.595(3)	Pr(2)^{iii}−O(10)−Pr(2)^{iv}	116.65(10)
	GWMOF-6 ($C_{14}H_{18}NO_7Pr$)[c]		
Pr(1)−O(2)	2.573(3)	Pr(1)^{i}−O(2)−Pr(1)	108.94(11)
Pr(1)−O(5)	2.544(3)	Pr(1)^{ii}−O(5)−Pr(1)	111.49(11)
Pr(1)−O(7)	2.489(3)		

[a] i = $-x, -y + 1, -z + 1$. [b] i = $x, y + 1, z$; ii = $-x + 1, -y + 2, -z + 1$; iii = $x, y + 2, z$; iv = $-x + 1, -y + 2, -z$. [c] i = $-x + 1/2, y + 1/2, z$; ii = $-x + 1/2, y - 1/2, z$.

similar Pr^{3+} coordination and chain motifs have been observed in related Ln−carboxylate MOF materials.

Within the channels of GWMOF-3, there are two unique water sites (OW1 and OW2) and a complete neutral, adipic acid molecule. The H_2O sites are at an average distance of 2.83 and 2.79 Å, respectively, from H-bond acceptors either on the Pr−carboxylate framework itself or the guest adipic acid molecule. These water molecules sit in the center of the channels running along [001] (OW2) and in the corners of the channels along [100] (OW1) and are 2.917(3) Å from each other. The adipic acid molecules are protonated (as suggested by charge balance requirements, IR spectroscopy, and location of H atoms in the X-ray structure refinement) and reside in the center of the channels that propagate along [001]. Bond lengths and angles for this molecule are as expected when compared to those found in pure adipic acid.[88] The disposition of those found in the channels of GWMOF-3, however, are markedly kinked as a result of rotation around the C11−C12 bond. This arrangement may be a steric effect resulting from the confined channel region within which the molecules reside, as well as from the influence of neighboring water molecules, both bound and extraframework. Other MOF structures showing considerable flexibility of adipic acid groups can be found in other Ln−adipates[18,22,23,45−47,58] as well as in $UO_2(C_6H_8O_4)$.[57]

GWMOF-3 exhibits interesting dehydration behavior in that both the bound and extraframework water molecules may be removed. Thermogravimetric analysis shows an initial weight loss at approximately 55 °C (14.3%) and is attributed to loss of both the bound and extraframework water molecules. This occurs at a slightly lower than usual temperature but is consistent with other Ln−adipate materials.[47] Loss of the guest adipic acid molecule occurs next at 210 °C (14.6%), followed by a final weight loss at approximately 330 °C attributed to decomposition of the framework. Note that the calculated weight percentages of the H_2O and guest adipic acid are 14.3% and 14.6%, respectively. Given the proximity of these values and the inherent estimations made in TGA calculations, loss of H_2O and retention of adipic acid after the first weight loss event was confirmed with IR spectroscopy. PXRD confirmed that the structure is maintained upon removal of the water molecules yet collapses upon removal of the adipic acid guest molecules. Elemental analysis confirmed the purity of the as synthesized sample [Anal. Found (calcd): C, 28.87 (28.69); H, 5.15 (5.02)].

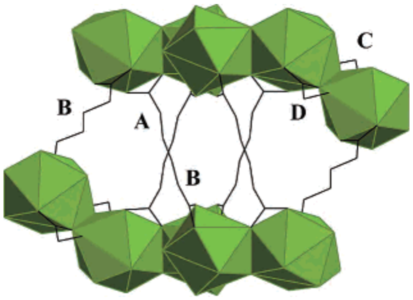

Figure 3. Extended framework structure of GWMOF-4, viewed down [100]. Adipic acid chains A and B represent interlayer linkage. Adipic acid chains C and D run along [010] and represents intralayer linkage. Green polyhedra represent the praseodymium, and the black lines represent adipic acid ligands.

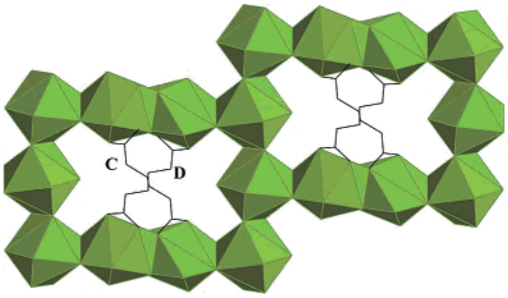

Figure 4. Extended framework structure of GWMOF-4, viewed down [010]. Note the intralayer adipic acid chains (C and D) that bridge the intralayer pores. Green polyhedra represent the praseodymium, and the black lines represent adipic acid ligands.

The structure of GWMOF-4 is slightly more complicated than that of GWMOF-3 and may be thought of as consisting of tethered two-dimensional slabs of PrO_9 and PrO_{10} polyhedra (Figure 3).

For discussion purposes, we first describe this slab motif as consisting of parallel chains of PrO_9 polyhedra that propagate along [100] (Figure 4).

These chains are stitched together through edge-shared $[Pr_2O_{18}]$ dimers to form layers in the (010) plane. Pores within the layers resulting from this connectivity measure approximately 11.0 Å by 4.6 Å as determined from the shortest O−O atom position distances (O3−O3 and O2−O4, respectively). Subsequent layers are stacked along [010] and are tethered through two unique adipic acid molecules. The pore regions of each layer are in fact aligned throughout this stacking sequence. Four crystallographically distinct adipic acid groups are involved in this linking of the layers: two interslab linkages that effectively “cross-link” layers to one another (represented as A and B in Figure 3) and two strictly intraslab linkages (represented as C and D in Figures 3 and 4) that bridge the pores within the (010) slabs. Adipic acid chains A and B bridge the holes between the slabs of praseodymium polyhedra (Pr1−Pr2 polyhedra) and consist

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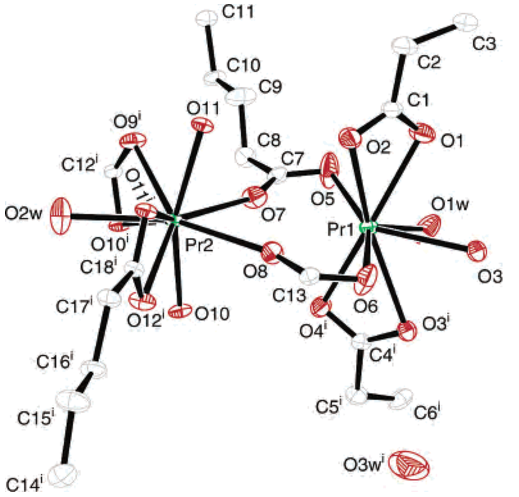

Figure 5. ORTEP drawing of GWMOF-4. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. The superscript indicates the following symmetry transformation: $\mathrm{i} = -x, -y, -z$.

of C7−C12 and C13−C18, respectively. They share the same connectivity and appear to crisscross one another when viewed down [100]. Each chain connects a Pr1 polyhedron in one layer with a Pr2 polyhedron in the next layer. Although Pr2−Pr2 polyhedra are edge-shared within the slabs, they are also linked across the channels in the [010] direction via chains C and D, constructed by C1, C2, C3, C3^{i}, C2^{i}, and C1^{i} and C4, C5, C6, C6^{i}, C5^{i}, and C4^{i}, respectively.

There are two crystallographically unique Pr^{3+} sites in GWMOF-4: Pr1 in 9-fold coordination with one H_2O group (O8) and eight carboxylic oxygen atoms and Pr2 in 10-fold coordination with one H_2O group (O11) and nine carboxylic oxygen atoms. Two of these (O4 and O7) are in bridging tridentate coordination with Pr1, with their symmetry pairs in bridging tridentate coordination with Pr2. Oxygen atoms O2 and O5 are responsible for the edge sharing within the $[Pr_2O_{18}]$ dimers. The other halves of these carboxylic groups (O12, O13, and O10, respectively) are coordinated to Pr2. Finally, there exists a bidentate carboxylic group containing O6 and O14 (Figure 5).

Thermal analysis of GWMOF-4 showed a single weight loss event beginning at approximately ∼150 °C (5.3%, presumably the onset of dehydration) that merges with a sharp, terminal decrease beginning at approximately 325 °C. The latter event is presumably the decomposition of the framework structure. No further characterization of the thermally treated material was attempted.

GWMOF-6 is composed of edge-shared PrO_9 polyhedra that run along the [010] direction, linked by adipic acid chains in the [100] and [001] directions to form a three-dimensional framework (Figure 6).

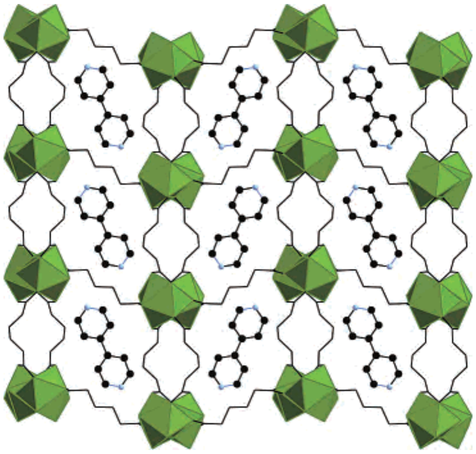

Figure 6. Extended framework structure of GWMOF-6, viewed down [010]. Green polyhedra represent praseodymium, and black lines represent the adipic acid ligands. The ball-and-stick figure represents 4,4′-dipyridyl (black spheres are carbon, and blue spheres are nitrogen).

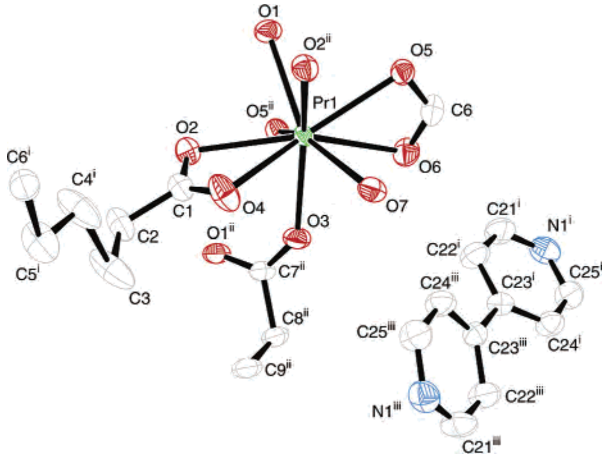

Figure 7. ORTEP drawing of GWMOF-6. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Superscripts indicate the following symmetry transformations: $\mathrm{i} = x, -y, z + 1/2$; $\mathrm{ii} = -x + 1/2, y + 1/2, z$; $\mathrm{iii} = -x, -y, -z$.

Within the structure there is one crystallographically distinct Pr^{3+} surrounded by nine oxygens, seven of which are crystallographically unique. Oxygen atoms O1 through O6 are associated with three carboxylic acid groups. Bridging tridentate ligands between one carbon and two praseodymium metal centers are formed by O2 and O5, whereas O1, O3, O4, and O6 are bridging bidentate ligands. There is one water molecule (O7) bound to the Pr^{3+} center (Figure 7).

The channel region is host to a neutral 4,4′-dipyridyl molecule. The 4,4′-dipyridyl molecule is slightly twisted with a torsion angle between the two aromatic rings of approximately 27.0°. The distances between the nitrogen in the 4,4′-dipyridyl and the hydrogen atoms of the bound water molecule is 2.770 Å, and thus, they participate in hydrogen bonding, which in turn may contribute to framework stability.

Powder X-ray diffraction and TGA was used in conjunction with IR to study the thermal properties of GWMOF-6. GWMOF-6 revealed weight losses at 205 °C (5%) and 305 °C (16%); IR confirmed that these assignments could be attributed to the loss of both bound water molecules (205 °C) and the second to loss of the 4,4′-dipyridyl guest (305 °C), followed by decomposition of the framework (380 °C). After removal of the bound water molecule, GWMOF-6 retained its original structure with no new crystalline phases forming. The PXRD pattern of the dehydrated GWMOF-6 matched the calculated pattern, with only a slight broadening of the peaks occurring. IR confirmed that the water was removed by a significant decrease of the broad −OH peak

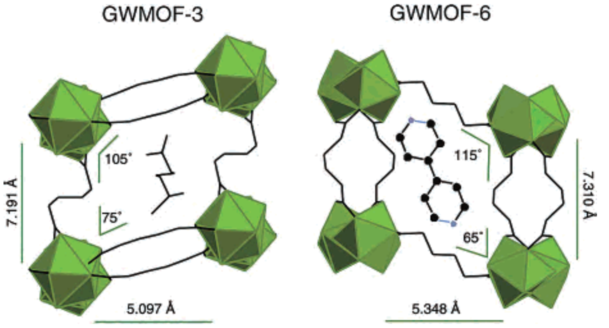

Figure 8. Comparison of GWMOF-3 pore topology to GWMOF-6 pore topology. Distances and angles are measured from the shortest O−O distances. Note the increase in pore size and angles when the more rigid 4,4′-dipyridyl is introduced as the guest molecule over the more flexible adipic acid. Green polyhedra represent praseodymium, black represents carbon, and blue represents nitrogen.

between 3000 and 3500 cm^{-1}. GWMOF-6 was rehydrated at saturated humidity for 7 days, as confirmed by IR. After rehydration, PXRD showed that the original structure was maintained. An unidentified crystalline phase was formed upon removal at 305 °C of the 4,4′-dipyridyl guest, however, which is suggestive of the 4,4′-dipyridyl's function in supporting the framework. Further attempts to characterize this new phase have not been successful. Elemental analysis confirmed the purity of the as synthesized sample [Anal. Found (calcd): C, 37.1 (36.44); H, 4.01 (4.06); N, 3.08 (3.50)].

GWMOF-6 shares a topology similar to that of GWMOF-3, with the primary differences in topology (i.e., pore shape and size) between the two caused by the different host molecules residing in the channels. We see that the overall shapes of the pores in both structures resemble a parallelogram. However, the angles in GWMOF-6 are slightly more acute. The pore size in GWMOF-6 also appears to be slightly larger than those in GWMOF-3 on the basis of the distance measured between the shortest O−O positions in each structure. These distances and angles are represented in Figure 8 and demonstrate the effect that a bulkier, more rigid molecule has on the resulting topology.

Discussion

The results described herein represent an extension of our previous work on Ln−adipates. GWMOF-1 and GWMOF-2[23] were synthesized in a fashion identical with that for GWMOF-3. However, by movement across the lanthanide series from Nd^{3+} to Pr^{3+} and Ce^{3+}, different, more open topologies are seen. Further, the presence of an uncoordinated adipic acid molecule in the channels of GWMOF-3 suggests that it may play a role as a structure-directing agent in the formation of the framework. In an effort to explore this phenomenon and hence the possibility of templating, a reaction was prepared using half of the adipic acid ratio as in GWMOF-3 resulting in the formation of GWMOF-4 (a two-dimensional slab phase was thereby synthesized). Despite the formation of a unique topology, it is conceivable that a more dense phase with increased building unit dimensionality (2-dimensional slabs verses 1-dimensional chains) occurs when less adipic acid (and thus an increased metal concentration) is used. Consequently, this result in itself is suggestive yet inconclusive with regard to structure direction.

To further explore the possible templating mechanism, a molecule different from the ligand was chosen in an attempt to direct the formation of an open framework. Thus, we used 4,4′-dipyridyl with the idea that the nitrogen groups would not coordinate to the Pr^{3+} centers in the presence of carboxylate groups on the basis of hard−soft acid−base preferences.[55,56] This was realized in that the 4,4′-dipyridyl molecules in GWMOF-6 remain neutral and uncoordinated to the Pr^{3+} and are instead hydrogen bound to the water groups on the metal centers. Other considerations supporting our choice of this "template molecule" include the fact that 4,4′-dipyridyl is a rigid molecule and is approximately the same length as an adipic chain. This allows for observations of the effects these attributes have on the resulting topology. Further, 4,4′-dipyridyl is potentially chromophoric considering its delocalized π-electron system stemming from its aromaticity. These properties suggest that the 4,4′-dipyridyl may act as a sensitizing molecule (below) in luminescent behavior.

Davis and Lobo address templating in zeolites in great detail,[59] and their discussion can be further extended to templates in metal−organic framework (MOF) systems. Their definition defines templating in a framework material as "the phenomenon occurring during ... the nucleation process whereby the organic species organizes ... [poly]hedra into a particular geometric topology around itself and thus provides the initial building blocks for a particular structure." In this definition, the organic guest molecules act in one of three roles as space-filling species, structure-directing agents, or true templates. In both GWMOF-3 and GWMOF-6, the guest molecules are clearly space-filling species and quite arguably structure-directing agents. By a change of the molecular species residing in the channels of GWMOF-3 and GWMOF-6, a distinct change in topology is seen, supporting the role of the species as a structure-directing agent. It is a bit more difficult to define whether either structure is an example of a "true template". To act as a true template, the organic species must create a unique topology that is irreproducible when another similar molecule is used. In effect, the topology is dependent on and structurally reflective of which species is used. Davis and Lobo also assert further that in true templating, free rotation of the guest molecule must not occur, as the molecule itself does not induce the topology of the overall structure but rather the volume needed to allow molecular rotation. The ordering and fixed positions of the adipic acid and 4,4′-dipyridyl molecules in GWMOF-3 and GWMOF-6, respectively, may in fact support a "true templating model."

We are aware of only one other MOF system in which guest molecules have been considered "templates": $Zn_2(OH)(btc)]_2(4,4'\text{-bipy})$ was synthesized by Feng et al.,[80] as part of an exploration of the "mixed-ligand systems of Zn−carboxylate−amine". In this compound, the dipyridyl guest molecules may in fact influence the resulting topology yet appear to have been included in the syntheses as linker molecules for the assembly of framework building units.

As a side note to the synthesis of GWMOF-6, it is interesting to comment on the effects certain variations of temperature and molar ratio variations had on its formation. GWMOF-6 was initially synthesized using the same molar ratios of GWMOF-3 (except for the addition of the 4,4′-dipyridyl). Comparison of the PXRD pattern of this first attempt to the calculated pattern matched exactly save for one extra unidentified peak around 7.0° in 2θ. This peak hints to the formation of a second crystalline phase in the initial reaction. By variation of the starting molar ratios, however, it was found that a molar ratio of 1.5:2:1:2:320 ($PrCl_3 \cdot 7H_2O$:adipic acid:4,4′-dipyridyl:concentrated ammonium hydroxide:water) gave the pure phase of GWMOF-6. Variation of the starting salt to the nitrate analogue ($Pr(NO_3)_3 \cdot 6H_2O$, Strem Chemicals) had no effect on the products.

Another interesting side note is that attempts to synthesize GWMOF-6 with these optimized molar ratios (1.5:2:1:2:320) at 180 °C produced GWMOF-4. When using the GWMOF-3 ratios (1:1:1:2:150), however, the structure for GWMOF-6 (with the extra PXRD peak) is obtained at both 120 and 180 °C. The implications of these data are yet unclear but may eventually provide additional insight into the mechanism through which these frameworks are formed.

Fluorescence. The fluorescence of Ln−MOFs has not been explored extensively.[42,44,46,89] Yaghi et al. have indeed surveyed the fluorescent properties of a terbium-containing MOF and show that this property could suggest useful sensing applications for these materials.[41] A characteristic of lanthanide fluorescence is their low absorbance coefficients, and a coordinated organic ligand with a delocalized π-system is often used to transfer energy to the metal center to stimulate sensitized emission via an intramolecular pathway (often referred as the antenna effect).[90] This "antenna effect" is quite effective, even over relatively large distances. The critical transfer distance is the separation distance between the donor and acceptor required for 50% energy transfer efficiency and has been estimated as high as 10 Å for Eu^{3+} and 3−4 Å for Tb^{3+}.[91] The Eu^{3+} analogue of GWMOF-6 was excited at the maximum absorption wavelength of the 4,4′-dipyridyl (236 nm)[92] to see if it were possible to excite the Eu through the 4,4′-dipyridyl. Peaks were observed at 595 and 615 nm (Figure 9).

Exciting $Eu(NO_3)_3$ (the starting salt) at this wavelength produced no fluorescence features, confirming that the energy transfer causing these transitions is coming from the 4,4′-dipyridyl.

Often the presence of bound water will quench fluorescence due to loss of excited-state energy to vibrational energy of an OH oscillator of close proximity.[93] However, due to the proximity of the 4,4′-dipyridyl to the Eu^{3+}, fluorescence is still observed despite the presence of the bound water. When the bound water is removed through heating (TGA), however, a noticeable increase (~3 times) in the relative intensity of the europium fluorescence is observed. Though we see an increase in the relative intensities, we have yet to conduct any substantial quantitative measurements. The exploration of the fluorescent properties of this MOF represents the first step in the development of new fluorescent MOFs. For example, it may be feasible to incorporate an unsaturated ligand (linker) that will excite the lanthanide at one range of wavelengths and then have a guest molecule that will span another range of wavelengths, therefore expanding the effective range of excitation. Influence over the quantum efficiency and/or lifetime of the fluorescence may be viable by incorporating a ligand and a template that have similar excitation wavelengths. Incorporation of multiple lanthanides into these frameworks could provide additional sensing applications. Attempts to induce fluorescence in the other lanthanide analogues of GWMOF-6 (Pr^{3+}, Nd^{3+}, Ce^{3+}, and Sm^{3+}) were unsuccessful yet not surprising considering that these lanthanides fluoresce less effectively.[53]

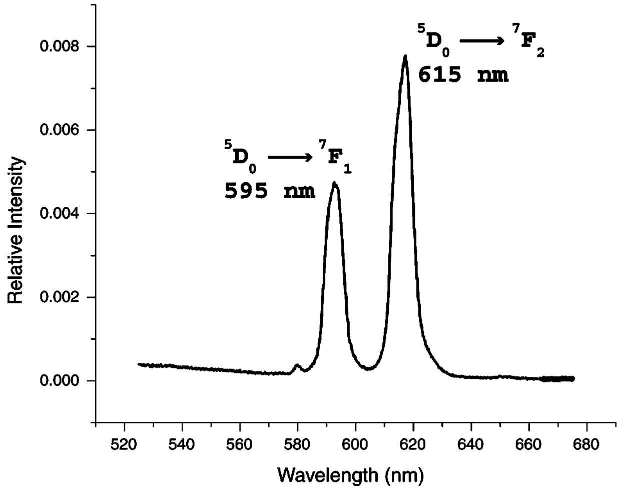

Figure 9. Fluorescence spectra of the europium analogue of GWMOF-6. An excitation wavelength of 236 nm was used. The relative intensity is given in arbitrary units.

Conclusion

The syntheses of three praseodymium−adipate frameworks are reported. GWMOF-3 and GWMOF-6 demonstrate the effects a template has on overall framework topology. Despite the number of lanthanide−adipate frameworks, these structures specifically demonstrate the conditions under which a molecule may be introduced as a neutral guest. The inclusion of other neutral guest molecules into metal−organic frameworks is currently being explored. GWMOF-6 also demonstrated fluorescence of the metal center by guest−host energy transfer after excitation of the guest molecule. Guest molecule and ligand contributions to the antenna effect will be an important focus in future studies, as well as the use of multiple lanthanide elements in framework construction. Further, sorption studies are planned to explore the influence of the guest molecules on sorption behavior.

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Supporting Information Available: A file of X-ray crystallographic data in CIF format for GWMOF-3, -4, and -6. This material is available free of charge via the Internet at http://pubs.acs.org.

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