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Thermally stable porous supramolecular frameworks based on the metal and $\pi-\pi$ stacking directed self-assembly of 2,6-pyridyldicarboxylic acid bis-4-pyridylamide

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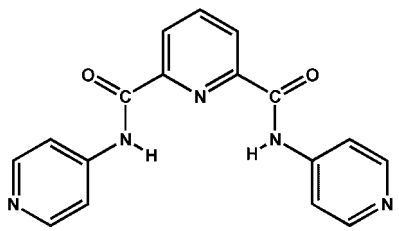
ABSTRACT: We report the formation of two thermally stable supramolecular structures based on 2,6-pyridyldicarboxylic acid bis-4-pyridylamide (PyI) and bis(hexafluoroacetylacetonato)manganese(II) that exhibits a microporous structure with cavities bearing hydrogen bonding motifs that can enclathrate acetone and methanol molecules via well-positioned hydrogen bonding interactions. Single-crystal x-ray diffraction in combination with thermogravimetric analysis and X-ray powder diffraction (XRPD) studies were utilized to study the structure and thermal behavior of *trans*-$[Mn(hfacac)_2(PyI)_2]\cdot 2(CH_3)_2CO$ (**1**) and *trans*-$[Mn(hfacac)_2(PyI)_2]\cdot 2CH_3OH$ (**2**). Our studies indicated that **1** and **2** are isostructural with respect to their supramolecular assembly and trap solvent molecules along the crystallographic *b* direction via the inwardly directed hydrogen bonding motifs of the PyI component. These solvent molecules can be thermally removed to generate a crystalline material with micropores bearing hydrogen bonding rich sites within an overall supramolecular matrix similar to **1** and **2**. The removal of the guest solvent molecules is reversible and can be followed with XRPD. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: thermally stable supramolecular frameworks; self-assembly; 2,6-pyridylcarboxylic acid bis-4-pyridylamide; bis(hexafluoroacetylacetonato)manganese(II); clathration; inclusion

INTRODUCTION

The construction of supramolecular framework solids that exhibit zeolite-like behavior is currently attracting great interest owing to their potential applications in catalysis and chemo-selective adsorption phenomena.[1–3] The development of molecular-based materials that are stable upon removal of enclathrated solvent represents an important goal towards the development of a new class of microporous materials. However, in typical molecular inclusion compounds, removal of the guest molecules cause the irreversible lost of crystallinity.[4,5] In other cases, although the solids can readily exchange the inclusion compounds or counterions while maintaining their crystal integrity,[6–11] the removal of guest species without their simultaneous replacement with a substitute leads to the collapse of the host structure. In recent years, special attention has been given to the use of coordination directed self-assembly as a synthetic strategy for the formation of robust porous structures.[12–21] This approach offers the advantage of forming supramolecular ensembles that retain the structure and function of their building units, thus offering the potential to modify the sorption properties of the resulting materials in a rational way.

As part of our efforts to investigate the design of functional self-assembled supramolecular structures with rigid or flexible bridging scaffolds, we prepared 2,6-pyridyldicarboxylic acid bis-4-pyridylamide (PyI), which in combination with metal ditopic linkers could potentially generate assemblies with inwardly directed hydrogen bonding motifs for guest-specific enclathration of small molecules in a supramolecular matrix. Here we report a new type of molecular ensemble formed via the coordination and $\pi-\pi$ stacking interactions of PyI and bis(hexafluoroacetylacetonato)manganese(II), which under the appropriate conditions afford a structure that retains its crystallinity during the thermal loss of the enclathrated guest species and results in a porous supramolecular structure with cavities bearing hydrogen bonding motifs.



PyI

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Table 1. Crystal data and structure refinement

	Complex **1**	Complex **2**
Empirical formula	$C_{50}H_{40}F_{12}MnN_{10}O_{10}$	$C_{46}H_{36}F_{12}MnN_{10}O_{10}$
Formula weight	1223.86	1171.79
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions:		
a (Å)	8.9703(2)	8.4731(2)
b (Å)	11.6952(3)	11.2014(4)
c (Å)	12.9494(4)	13.8151(6)
α (°)	101.4204(16)	103.0260(10)
β (°)	97.1535(16)	100.4820(10)
γ (°)	92.9771(13)	90.153(2)
Volume (Å^3)	1317.15(6)	1254.83(8)
Independent reflections	5871	5592
Goodness-of-fit on F^2	1.027	1.029
R_1[a], wR_2[b]	0.0471, 0.1053	0.0571, 0.1240

[a] $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(F_o^2)^2]^{1/2}$, ans S = goodness-of-fit on $F^2 = [\Sigma(w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

RESULTS AND DISCUSSION

Design principles

We are exploring the supramolecular trends exhibited by molecules that can engage simultaneously in metal–ligand coordination, hydrogen bonding and π–π stacking interactions. Benzylic and pyridyl amide moieties with inwardly directed hydrogen bonding motifs have been shown in the past to serve as chemoselective molecular recognitions receptors,[22,23] hence we hypothesized that their incorporation into supramolecular designs could result in interesting functional superstructures. The ligand PyI contains these three basic structural features: (1) pyridyl groups that can coordinate to a metals, (2) carboxamide groups, which can have inwardly directed hydrogen bonding interactions, and (3) conjugation throughout the pyridyl groups, which can be involved in π–π stacking interactions. We explored the metal-coordination reactivity of PyI with the hydrated form of bis(hexafluoroacethylacetonato)manganese(II), a ditopic acceptor unit that has been used as a supramolecular scaffold in the past by us[24,25] and others,[26–28] and obtained the mononuclear complexes *trans*-$[Mn(hfacac)_2(PyI)_2]\cdot 2(CH_3)_2CO$ (**1**) and *trans*-$[Mn(hfacac)_2(PyI)_2]\cdot 2CH_3OH$ (**2**) that crystallize with open channel frameworks that are stabilized via π–π stacking interactions.

Synthesis

The ligand precursor 2,6-pyridyldicarboxylic acid bis-4-pyridylamide (PyI) was synthesized from the coupling of 4-aminopyridine and 2,6-pyridinedicarbonyl dichloride in chloroform in the presence of triethylamine and recrystallized from methanol (yield 75%).

The complexes *trans*-$[Mn(hfacac)_2(PyI)_2]\cdot 2(CH_3)_2CO$ (**1**) and *trans*-$[Mn(hfacac)_2(PyI)_2]\cdot 2CH_3OH$ (**2**) were synthesized from the reaction of 2 equiv. of PyI and 1 equiv. of the manganese ditopic unit in methanol and acetone, respectively. Slow evaporation of the solvent leads to the formation of crystals of **1** and **2** in 77 and 92% yield, respectively. Although PyI contains, in principle, three N donors that can potentially coordinate to metals, only one of them actually forms a dative coordination bond with manganese. Attempts to prepare infinite networks with PyI and $Mn(hfacac)_2$ led only to the assembly of the mononuclear complexes **1** or **2**, a behavior which suggests that the supramolecular structures formed by **1** and **2** dominate the self-assembly process during crystallization.

X-ray structures

Single-crystal x-ray diffraction studies reveal that **1** and **2** are mononuclear complexes in which the Mn^{2+} centers exist in an octahedral configuration with two molecules of PyI ligated in a *trans* configuration along the axial direction and two molecules of hexafluoroacetylacetonato ligated along the equatorial plane of the metal, overall giving rise to a N_2O_4 coordination sphere (Fig. 1). Only one of the pyridyl groups of each of the PyI molecules is coordinated to the Mn^{2+} center. The average Mn(II)—N_{py} bond distance in **1** and **2** is 2.25 Å (see Table 2) and compares well with the corresponding distances reported for similar structures.[6] The N_{py}—Mn(II)—N_{py} bond angle is 180° in both structures and the PyI ligands adopt an *anti* configuration with respect to the metal center, which gives rise to complexes with a planar *Z* shape topology (Fig. 1).

Both complexes of **1** and **2** crystallize in the triclinic

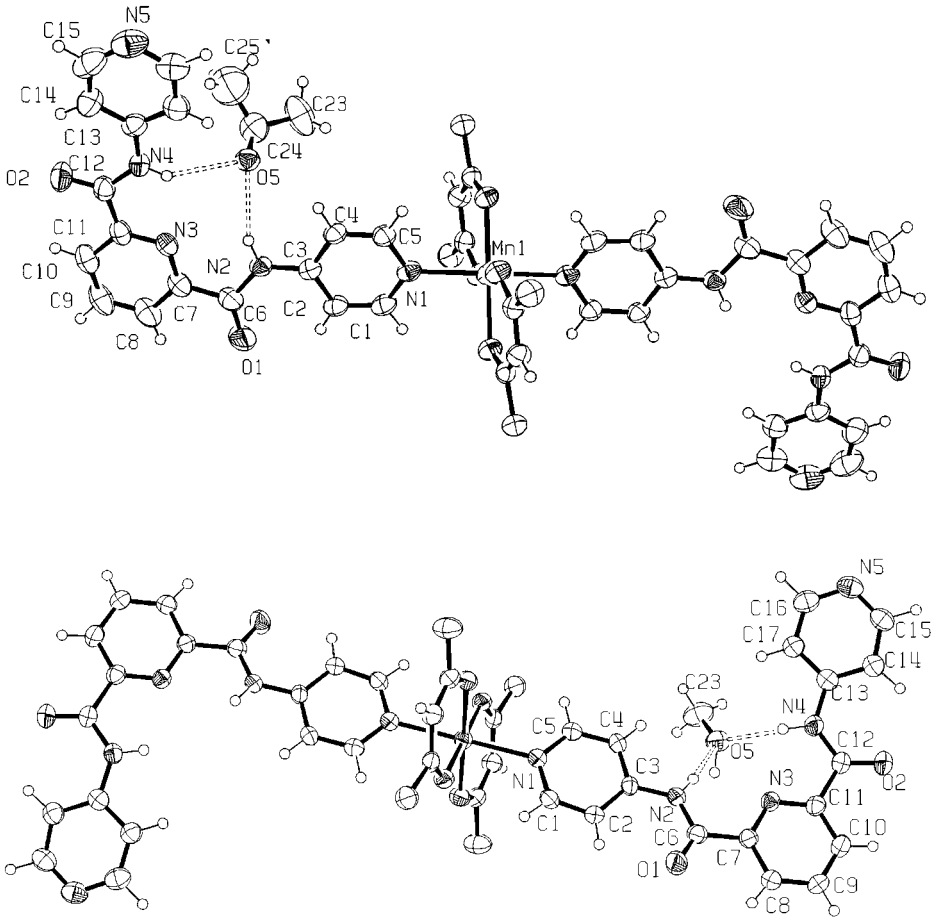

Figure 1. Structures of *trans*-$[Mn(hfacac)_2(PyI)_2]\cdot 2(CH_3)_2CO$ (**1**) (top) and *trans*-$[Mn(hfacac)_2(PyI)_2]\cdot 2CH_3OH$ (**2**) (bottom)

Table 2. Selected bond lengths (Å) and angles (°)

Complex **1**	Mn(1)—O(3)	2.1530(14)
	Mn(1)—O(4)	2.1677(14)
	Mn(1)—N(1)	2.2522(17)
	O(4)—Mn(1)—O(4)	180.00(9)
	O(3)—Mn(1)—N(1)	87.09(6)
	O(3)—Mn(1)—N(1)	92.91(6)
	O(4)—Mn(1)—N(1)	92.46(6)
	O(4)—Mn(1)—N(1)	87.54(6)
	O(4)—Mn(1)—N(1)	92.46(6)
Complex **2**	O(3)—Mn(1)	2.1567(19)
	O(4)—Mn(1)	2.1572(19)
	N(1)—Mn(1)	2.243(2)
	O(5)—H(3O)	0.98(6)
	Mn(1)—O(3)	2.1567(19)
	Mn(1)—O(4)	2.1572(19)
	Mn(1)—N(1)	2.243(2)
	O(3)—Mn(1)—O(3)	180.00(13)
	O(3)—Mn(1)—O(4)	85.40(7)
	O(3)—Mn(1)—O(4)	94.60(7)
	O(3)—Mn(1)—N(1)	93.62(8)
	O(3)—Mn(1)—N(1)	86.38(8)
	O(4)—Mn(1)—N(1)	90.74(8)

$P\bar{1}$ space group. The planar structures adopted by **1** and **2** promote the formation of extensive π–π stacking interactions between the molecular building units. This results in stacked sheets along the crystallographic *b* direction and the generation of open channels that are filled with acetone and methanol molecules, respectively (see below) (Plate 1). Two principal π–π stacking interactions occur between the building units along *b*. One involves the stacking of the non-coordinating pyridyl groups and one of the carboxamide groups of the next adjacent building unit along the *a* direction and the other involves π–π stacking interactions between half of the ligand frames in adjacent building units along the *a* direction as well (see Plate 2).

The structures of **1** and **2** are almost identical and vary only in the local alteration caused by the stoichiometrical enclathration of acetone or methanol, respectively. In complex **1**, acetone molecules are trapped in the cavity formed by the pyridyl amide moieties of PyI. Both of the carboxamide NH groups are hydrogen bonding to the carbonyl group of acetone with $NH—O_{C=O}$ bond

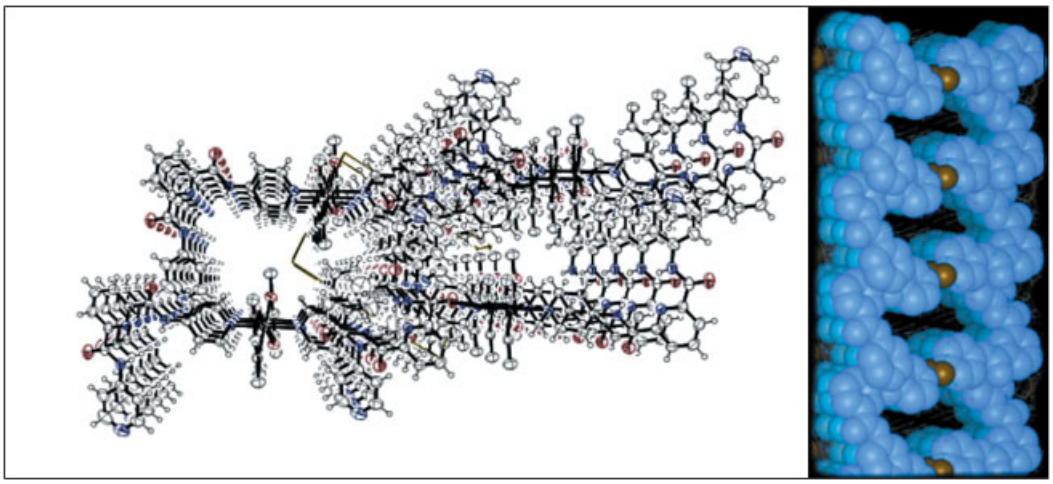

Plate 1. Crystal lattice of **1** as seen from the crystallographic *b* direction

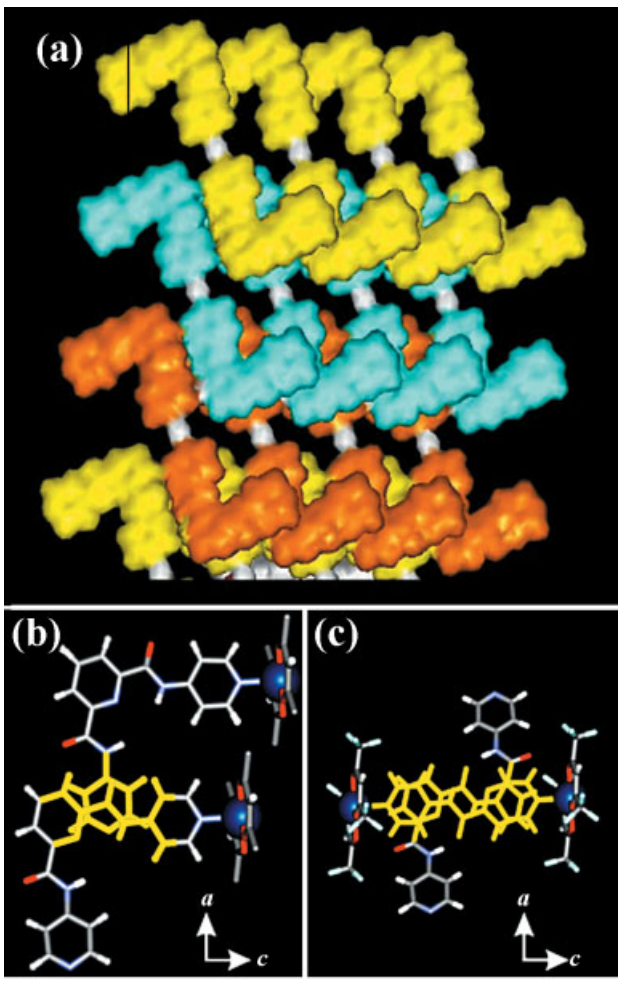

Plate 2. π–π stacking of **1** and **2**. (a) View from *b* direction; (b) and (c) two types of π–π stacking interaction between the Pyl groups

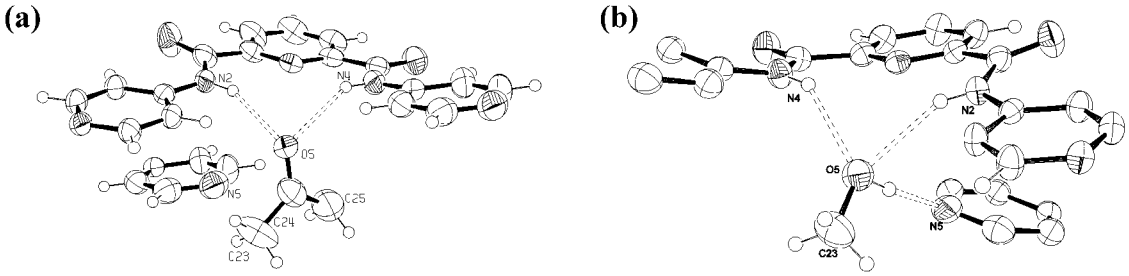

Figure 2. Contacts between guest species and the PyI groups of (a) **1** and (b) **2**

distances averaging 2.32 Å and with an average NH—O(5) bond angle of 158° (Fig. 2). The crystal structure of **1** reveals that the methyl groups of acetone guest molecules are distorted, which suggests that the space where the guest molecules are trapped is ample and may potentially be exploited for further guest-specific receptor design.

Complex **2** entraps molecules of methanol similarly to the acetone–PyI complex in **1**. Interestingly, the methanol guest molecules form three hydrogen bonds with their host structure. Two of them are with the carboxamide NH groups, similarly to complex **1**, and the third is with a non-coordinating pyridyl group from an adjacent building unit located along the *a* direction and which is located underneath of the carboxamide moieties of the PyI groups of the complex (see Fig. 2). The average bond distance NH—O_{MeOH} is 2.36 Å and $N(5')_{Py}$—HO(5)Me is 3.06 Å. The average bond angle NH—O(5) is 158° and for $N_{py}(5')$—HO(5)Me is 175°.

The microporous nature of **1** and **2** combined with the presence of carboxamide groups in the cavities of these structures merits attention, since only a few examples exist in the literature that combine these features.[29–32] The cavities where the guest solvent molecules reside in **1** and **2** contain two hydrogen bond donors, N(2)H and N(4)H, and two hydrogen bond acceptors, N(3) and N(5′) within a proper distance to bind cooperatively to guest species (Plate 3). The incorporation of simple functional groups such as carboxamide moieties within the matrix of porous solid-state structures can serve as model examples in the design of much more complex systems that target chemical sensing and catalytic functions.[12]

Guest desorption and formation of porous phase in 1 and 2

The single-crystal x-ray structures of **1** and **2** clearly indicate that open channels occupied by guest solvent molecules, acetone in **1** and methanol in **2**, exist along the *b* direction. The removal of solvent from crystalline samples of **1** and **2** was studied with thermogravimetric analysis (TGA) and x-ray powder diffraction (XRPD). The TGA behavior of **1** and **2** and accompanying changes in the XRPD on thermal lost of bound solvent are shown in Plate 4.

For complex **1**, the weight loss observed at 130 °C is consistent with the loss of all the cavity solvent (calculated 9.47%, found 9.63%). The wide plateau area above 170 and below 260 °C in the TGA trace suggests that the guest-free compound is stable and only decomposes irreversibly at temperatures higher than 260 °C. XRPD data for **1** before and after desolvation show strong diffraction signals and is indicative that the desolvated form of **1** conserves its original supramolecular structure. Further confirmation that the desolvated form of **1** remains crystalline is the retention of the macroscopic crystal shape of single crystals before and after removal of the guest molecules, as shown in Plate 4(d).

For complex **2**, the TGA trace shows a weight loss between 40 and 175 °C that corresponds well with the removal of all the methanol guest molecules in the structure (calculated 5.46%, found 5.50%). The plateau range of thermal stability after desolvation coincides exactly with that of the product generated from the thermal loss of **1** (170–260 °C). Additionally, the XRPD on the desolvated form of **2** is identical to the diffraction pattern of the desolvated form of **1**, a fact that further supports the retention of supramolecular structure in the guest-free state of these complexes. The slight shift and splitting of some peaks may be attributed to the subtle change of the relative positions of some of the atoms in the crystal lattice.[33] This phenomenon is commonly observed in zeolites,[34] which indicates the distortion of micropores but does not preclude porosity of the compound. To investigate this question further, we exposed the desolvated crystalline material to small amounts of methanol solvent and observed the reintroduction of the guest molecules into the structure by the reconstitution of the XRPD pattern of the complex **2**. A similar behavior is observed when replacing acetone for methanol. These results demonstrate that removal of the enclatherated solvent molecules in **1** and **2** generate a microporous material with hydrogen bond rich cavities that can bind to acetone or methanol reversibly in the solid state.

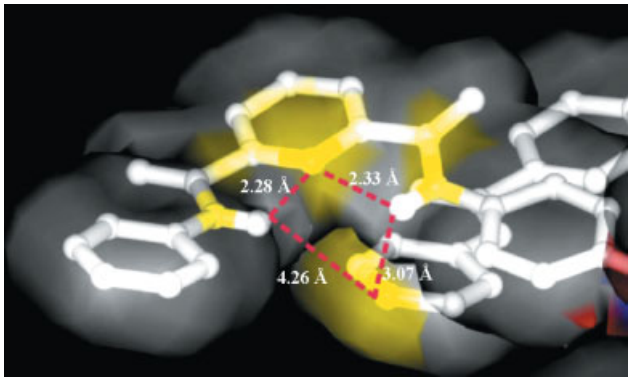

Plate 3. Representation of the van der Waals surfaces of the H-bonding rich pocket formed by two groups of Pyl in **1** and **2**

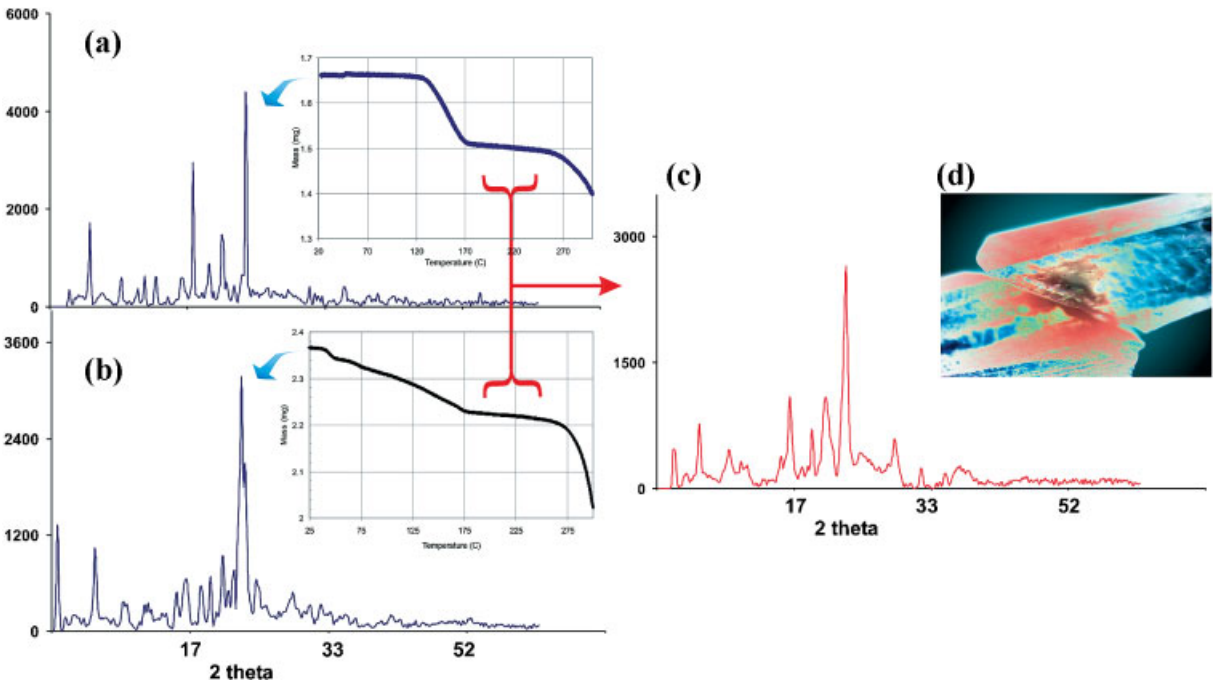

Plate 4. TGA and XRDP patterns of (a) **1** and (b) **2**. (c) XRDP pattern after removal of guest acetone and methanol molecules from the structures of **1** or **2**. (d) Microscopy image of crystals of **1** before (left) and after desolvation (right)

CONCLUSION

The preparation of supramolecular structures with tailored functional designs remains a considerable challenge at the forefront of nanochemistry. The current approach to this problem is based on the design and synthesis of molecular modules that upon self-assembly form supramolecular structures with coupled structural hierarchies that often exhibit novel chemical or physical properties. Additionally, this approach allows for the rational modification of the synthetic modules prior to the self-assembly process in order to promote useful properties and functions in the new molecular materials. Here we report a new supramolecular structure based on 2,6-pyridyldicarboxylic acid bis-4-pyridylamide (PyI) and bis(hexafluoroacetylacetonato)manganese(II) that is stabilized via coordination bonds, hydrogen bonding and π–π stacking interactions. Upon desolvation, these structures generate a microporous crystalline phase that contains internal cavities bearing inwardly directed carboxamide moieties that can bind to acetone or methanol molecules reversibly.

EXPERIMENTAL

General techniques. Room temperature x-ray powder diffraction patterns were collected on a Rigaku Miniflex x-ray diffractometer in the range $5° \leq 2\theta \leq 65°$ using a step size of 0.05° (40 s per step) and a wavelength of 1.5405 Å (Cu Kα). To perform the XRD studies on **1** and **2**, the samples were adhered to glass slides with high-vacuum grease and mounted vertically in an aluminum holder located in a laboratory-built cell with a Mylar window and filled with an N_2 atmosphere. Single-crystal x-ray diffraction data for all the compounds were collected on a Nonius Kappa CCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was carried out at 200(1) K. Data were corrected for absorption using the DENZO-SMN program. The structure was solved by a combination of direct methods and the heavy atom method using SIR 97. For the final structural refinement, SHELXL97 was used. Elemental analysis was performed by Oneida Research Service (Whitesboro, NY, USA) and Atlantic Microlab (Norcross, GA, USA). All chemicals were purchased from Aldrich (Milwankee, WI, USA) and used without further purification.

Synthesis of PyI. A solution of 2,6-pyridinedicarbonyl dichloride (7.12 mmol) and triethylamine (7.20 mmol) in 50 ml of chloroform was prepared and chilled to 4 °C in an ice-bath for 5 min, then 4-aminopyridine (7.12 mmol) was added slowly to the cold solution over a period of 10 min. The reaction mixture was stirred at room temperature overnight and upon concentration a white precipitate was obtained and identified as the product. The solid was recrystallized from methanol to remove trace impurities of triethylammonium chloride; yield 1.03 g (75%). ^{1}H NMR (DMSO-d_6, 300 MHz) from TMS: δ 7.96 (d, 4H), 8.34 (t, 1H), 8.44 (d, 2H), 8.58 (d, 4H), 11.26 (s, NH). ^{13}C NMR (DMSO-d_6, 62.5 MHz): δ 116.40, 128.09, 142.37, 146.87, 150.18, 152.53, 164.57.

Synthesis of trans-*[Mn(hfacac)$_2$(PyI)$_2$]·2(CH$_3$)$_2$CO (**1**).* Slow evaporation of an acetone–ethanol solution (80:20) of 61.7 mg (0.311 mmol) of Mn(hfacac)$_2\cdot 4H_2O$ and 100 mg (0.311 mmol) of PyI gave 185.7 mg (77%; yellow solid) of **1**. Calculated for $C_{50}H_{40}F_{12}MnN_{10}O_{10}$: C 49.07, H 3.26, N 11.44. Found: C 49.02, H 3.18, N 11.39%.

Synthesis of trans-*[Mn(hfacac)$_2$(PyI)$_2$]·2CH$_3$OH (**2**).* Slow evaporation of a methanol solution of 61.7 mg (0.311 mmol) of Mn(hfacac)$_2\cdot 4H_2O$ and 100 mg (0.311 mmol) of PyI gave 205.4 mg (92%; yellow solid) of **2**. Calculated for $C_{46}H_{36}F_{12}MnN_{10}O_{10}$: C 47.15, H 3.07, N 11.95. Found: C 47.21, H 3.12, N 11.93%.

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