

MIXED LIGAND METAL-ORGANIC FRAMEWORKS OF SELECTED METAL IONS: SYNTHESIS AND CRYSTAL STRUCTURAL INVESTIGATION

Busi Anil Kumar,

Government City College (A), Nayapul, Hyderabad.

Abstract:

In the pursuit of designing Metal-Organic Frameworks (MOFs) with precisely predictable network topologies, our research has focused on the synthesis of novel multidentate ligands. These ligands, in combination with commercially available multidentate ligands, have enabled the construction of MOF structures. We have successfully complexed these MOFs with transition metal ions and alkaline earth metals, resulting in the formation of coordination polymeric structures with potential applications as porous materials. The design of our ligands is unique in that it prevents the formation of homoleptic metal complexes, instead facilitating the coordination of multiple metal atoms to create open framework structures replete with void spaces. The MOFs synthesized in our studies currently contain solvents and ligands within their cavities, suggesting their potential as host-guest systems. These frameworks hold promise in selectively capturing harmful compounds such as pollutants and toxicants. To further enhance the functionality of these MOFs, we are exploring the functionalization of the organic ligands. This endeavor aims to introduce specific reactive or binding sites at well-defined and controllable positions within the network topology.

1. INTRODUCTION

1.1. Metal Organic Frameworks:

Metal organic frameworks or coordination polymers are organic-inorganic hybrid infinite structures based upon coordination bonds between a transition metal and the heteroatom of an organic molecule called ligand or spacer. These are formed by self-assembly process — a facile approach to materials of useful properties 30 . Thus, the physical property of individual constituents, such as luminescence, chemical functionality, and chirality, can be translated into that of the assembled MOFs. In coordination polymers. metal-ligand modules are linked infinitely into one, two three dimensions via metal-ligand or covalent bonds and the ligand must contain bridging moieties. They are also assemblies of metal ions or clusters functioning as nodes and organic ligands as the linkers. The cavities of as-synthesized MOFs are often filled with solvent molecules or counter ions. MOFs are thus essentially host-guest systems.

The functions of materials are largely determined by their solid-state structures³¹. This theorem is in turn the driving force for the desire to rationally design and control the assembly of MOF building blocks.

1.1.1. Secondary Building Unit (SBU):

As pioneers in the field of MOF, Yaghi and coworkers have coined the term secondary building unit or SBU which refers to molecular complexes or clusters that can be extended into porous networks using



polytopic linkers³². SBU is a useful tool for the overall topology prediction for MOFs. As illustrated in Figure 1, the four carbon atoms of the paddle wheel form square secondary building units, which in turn can, by means of linkers, form polyhedra, 2D sheets and 3D networks³⁴. Factors such as solvent templating, metal ion solvation, linkers' geometries, temperature, pH, presence and nature of available anions may play decisive roles in the formation of various structures^{33, 35}.



Figure 1: Illustration of Secondary Building Unit (SBU)

Utilizing SBUs and the linkers of well-known geometry and chemical properties can lead to better predictions. For a given shape of the building blocks, only few simple, high symmetry network of general importance are most likely to form from these subunits³⁵.

1.1.2. Metallic Nodes:

The metal atoms in MOFs can be thought of as templating joints for bridging ligands. Late transition metals are often used in MOF construction. Lanthanide metals are also used to impart luminescence properties to the framework. Although frameworks made of light main group metal cations such as Li⁺, Na⁺, and Al³⁺ would be lighter, they have not been observed to date. Metal ions can be introduced to the nodal positions of MOFs as single metal centers or as metal clusters. Group 2 MOF are rare, having few reports on Mg, Ca, Ba, Sr – containing structures^{35, 36}. Among metal clusters at nodes, Zn cluster are most often encountered³⁷.

Utilizing metal clusters as nodes of MOFs can be an effective approach to circumvent the lack of coordination sites that is often experienced with transition metals (i.e. Cu, Zn, Cd etc.) largely because metal clusters can accommodate sterically demanding organic ligands. This is also one of the strategies to obtain rigid structure without a tendency to interpenetrate.

1.1.3. Linkers:

The ability to derivatize and modify organic linkers gives chemists limitless access to various linkers. Oxygen- and nitrogen-donor ligands are often used in MOF synthesis. Polytopic ligands⁴³ such as 4, 4'-(ethyne-1, 2-diyl) dibenzoic acid are widely used as ligands due to their ability to bind to various metals with versatile binding modes.

The use of molecular rather than monatomic bridges leads to the desirable outcome of enlarging the void space of MOFs by means of further extending the distance between metal nodes³⁶. Expansion of the network can be achieved by using long or polytopic ligands, which effectively enlarge the pore of the framework cavity³³. However, this strategy is not always preferable, especially when MOFs are to be functioning in gas inclusion.

1.1.4. MOF Synthesis:

In MOF synthesis, what essentially happens is the assembly of discrete molecular units into extended network³³. This synthetic approach allows reactions to take place at room temperature. Generally, little is known about the M-L species preformed in solution before the assembling process. MOFs are typically obtained by means of slow vapor diffusion and solvothermal synthesis. In the former synthetic condition, the materials can be obtained in one-pot synthesis, often under mild conditions^{34, 36}. A solvo-thermal reaction follows a liquid nucleation model in which a fast kinetics of nucleation and crystal growth or the reversible nature of the process can lead to formation of good quality crystals. Heating helps lower barrier to rotation of the linkers, which can result in more stable MOF structures. Solvent switching in synthesis may also produce novel structures³⁵.

In order for a pre-determined MOFs structure to be attained, MOFs constituents need to be able to self-correct; that is, to assemble in a reversible manner. This is also an inherently prominent feature of selfassembly process.

1.2. Applications of Metal Organic Frameworks:

As the unrenewable fossil fuel becomes increasingly depleted, hydrogen comes into play as one of the best alternative fuels due to its highest energy density among all common fuels (e.g. three times the energy density of gasoline). For hydrogen economy to be feasible, a light material with high capacity is required for the safe storage of hydrogen. This remains challenging in realizing а hydrogen economy. Research in H₂ storage still awaits material. a breakthrough То reduce mechanical requirements of pressurized vessels, MOFs have been investigated for their ability to physically absorb H₂.

Metal organic framework (MOF) is a class of microscale, crystalline inorganicorganic hybrid that has first captured the research attention as a new candidate for hydrogen storage materials. MOFs have many attributes, including high porosity and facile synthesis, making them the focus of hydrogen storage research³⁶.

1.2.1. MOFs as attractive H₂ storage system:

The purpose of this section is to highlight MOFs' applications as H₂ storage systems. Among the reported structures, MOF-177 by Yaghi and coworker exhibits the highest uptake of N₂ among all materials to date. It has a surface area of 4500 m^2/g and a pore volume of $0.69 \text{ cm}^3 \text{ per cm}^3$. This translates to an uptake of up to 7 weight percent H₂. However, measurements for a large set of Zn₄O-based MOFs revealed that only a small fraction of the surface is occupied by the guests. This then necessitated a need for pore optimization.

Surface area and pore volume can be determined by gas absorption isotherms. All porous MOFs so far are microporous by IUPAC definition, having pore size of less than 2 nm and displaying type I absorption isotherm (Figure 2). The assumption taken in such measurements is that a homogeneous



monolayer of the absorbate is formed on the walls of the absorbent. The apparent surface area is then the product of the number of molecules uptaken and an accepted value for the area occupied by an adsorbate molecule³⁶.



Figure 2: Type I gas absorption isotherm.

In fact, many reported MOFs to date have cavities that are too large for effective H₂ storage. For example, MOF-5 structure has a pore diameter of 15.2 Å, which is much larger than the 2.89 Å kinetic diameter of H_2^{36} . If a shorter linker isn't used to reduce the pore size, MOF-5 is simply too leaky to store H₂. MOFs with constricted appear non-porous with pores might absorption isotherm measurements as their small pores could not admit N₂ but allow the passage of H₂. Another case where this can happen is that the as-synthesized MOFs contain solvent molecules in the cavities that occlude entrance of other targeted guest molecules (i.e. H₂, N₂, CO etc.)³⁷. Decreased pore size might translate to a decrease in gravimetric density of hydrogen uptake; however, their volumetric capacities might be enhanced. There will always be a compromise to make along the line of MOFs structural design.

Framework catenation has long been recognized in the MOF research and is often encountered when long linkers are used^{33, 36}. In some cases catenation can lead to undesirably nonporous networks. Nevertheless, some materials have been reported to display porosity while possessing interpenetrating networks^{37a}.

Catenation takes the form of interpenetration and interweaving. The occurs when two former or more frameworks have the maximal offset from each other (Figure 3b) while the latter occurs when the frameworks have the minimal offset and exhibit many close contacts (Figure 3c). Interpenetration is desirable as it maximizes the exposed MOFs surface of catenated while interweaving results in blockage of potential absorption sites³⁶. Depending upon the the degree of penetration, resulting framework still can exhibit void space for selectively trapping of small molecules.



Figure 3: Interpenetration and Interweaving MOFs a) Repeating Unit of MOFs with SBU showed as cubes and linkers as rods; b) Interpenetrating Frameworks: c) Interweaving Framework³⁶.

1.2.2. MOFs as Catalysts:



Application of MOFs in this domain has been met with limited success, mainly because the metals in **MOFs** are coordinatively Nevertheless. saturated. useful catalytic systems have been achieved with **MOFs** in the catalysis of aldehydes^{38a}, cyanosilylation of hydrogenation of nitro aromatics, and oxidation of alkylphenylsulfides etc^{20b}. Hill and coworkers have recently reported a redox active vanadium- and terbiumcontaining MOF that can catalyze the oxidation of PrSH to PrSSRPr using only ambient air under mild conditions.

1.2.3. MOFs Functioning in Chromatography:

The petroleum industry relies on the important process of separating linear from branched alkanes in order to boost octane ratings of gasoline. MOFs can be useful for such purposes due to their selective sorption and high thermal stability. Good GC separation of mixture of linear and branched alkanes has been reported when MOF-508 was used as the stationary phase. Overall, MOF applications originate from their abilities to function as host-guest systems.

1.2.4. Luminescence in MOFs:

Luminescence is a light-emitting phenomenon from any emissive substance. It involves electronic transitions from excited states to the ground state. Luminescence classified can be into fluorescence and phosphorescence depending on the nature of the excited state. Supramolecular luminescent materials are mostly small organic and coordination compounds. The most important application of the latter is their use as sensors and lightemitting diodes (LEDs). Luminescent materials then can be classified based on the origin of emission; i.e. whether it is ligandbased or metal-based emission. The role of the ligand is to harvest photon energy and effectively transfer that energy to the emissive metal centers. Such phenomenon is often termed the antenna effect and is describe in Figure 4.



Figure 4: Antenna Effect in Lanthanide Luminescence.

Ligand based luminescence often in organic occurs molecules and coordination compound. It involves the electronic transitions of the ligands. Many luminescent organic molecules contain aromatic moieties. Both of the organic ligands employed in current study are luminescent and are examples of such molecules. Often, formation of complex involving luminescent ligand enhances the emission of the resulting complex as compared to that of free ligands. Quite a number of Zn (II) complexes, including the Zn framework generated from this study, are luminescent.



2. <u>SCOPE OF THE PRESENT WORK</u>

Metal organic framework (MOF) has emerged as a new class of porous, thermally stable material which has attracted great attention due to their wide applications in gas storage, separation, catalysis etc. Selfassembly is the operative mechanism of MOFs syntheses. Although the outcome of these self-assembly processes are often unpredictable, the formation of one product in high yield typically can be rationalized on the basis of the interplay between kinetic and thermodynamic factors. The factors which we can control to reduce the unpredictability of the outcome can be enlisted as follows:

- Stereo electronic molecular information encoded in the ligand(s),
- Reading-out this information by metal ions having a set of coordination numbers and stereo chemical preferences depending on their size, charge and electronic structures,
- The counter ions present in the reaction system, and
- The external conditions used for the recognition and its expression in the final supramolecular entities.

The methods used to synthesize MOFs include Diffusion methods, Saturation methods, hydro (solvo) thermal methods, and microwave and ultrasonic methods. The goal of the research is to arrive at multidimensional, highly porous and functional MOFs via hierarchical assembly of smaller molecular building blocks and, at the same time, to examine the possibilities for different interesting molecular textures by tuning the reaction conditions. This goal is to be accomplished by the knowledge of ligand coordination mode, and geometry as well as logical choices of ligands and metals from which the MOFs are to be constructed from.

3. EXPERIMENTAL SECTION

3.1. Materials:

Reagent grade Calcium (II) nitrate, Magnesium (II) nitrate, Cadmium (II) nitrate, Cobalt (II) nitrate were purchased from Qualigens chemicals, India, while pyridine-3-carboxaldehyde, hydrazine, oxobis benzoic acid (obaH₂), 4,4'-bipyridine were acquired from Aldrich chemical company (U.S.). Other chemical like Formic Ethanol. acid. Methanol, Dimethylformamide (DMF), triethylamine and other solvents acquired from S. D. Fine chemicals. All the solvents were freshly distilled following the standard literature procedure.

3.2. Analysis and Measurements:

¹H-NMR spectra were recorded on a JEOL JNM-LA 400 FT (400 and 80 MHz respectively) instrument in d⁶-DMSO with Me₄Si as the internal standard. Melting points were determined with an electrical melting point apparatus by PERFIT, India and were uncorrected. The IR spectra (KBr pellets) were recorded on a Perkin-Elmer Model 1320 spectrometer in the 4000-400 cm⁻¹ spectral regions. Elemental analyses (C, H, and N) were performed on a LECO CHNS-932 micro-analytical analyzer at Lucknow. TG analysis CDRI, was performed on a Perkin-Elmer TGA7 instrument in flowing N2 with a heating rate of 5 °C/min.

3.3. X-ray Structural Studies:

Single crystal X-ray data were collected at 100K, on a Bruker SMART APEX CCD diffractometer using graphite monochromatic MoK_{α} radiation (λ = 0.71073 Å) at IIT Kanpur. The linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography³⁹. The data integration and reduction were processed with SAINT⁴⁰ software. An empirical absorption correction was applied to the collected reflections with SADABS using XPREP⁴¹. The structure was solved by the direct method using SHELXTL and refined on F^2 by full-matrix least-squares technique using the SHELXL-97⁴² program package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps and they were treated as riding atoms using SHELXL default parameters. The crystal and refinement data are collected in Table 3.1.

TABLE 3.1:

	Complex
Empirical	$C_{28}H_{32}Mg_2O_{18}$
Formula	
Formula	705.16
Weight	
Temperature,	100 (1)
Κ	
Radiation	Μο Κα
Wavelength, Å	0.71069
Crystal System	Monoclinic

Space Group	P21
<i>a</i> , Å	8.974 (5)
b, Å	10.327 (5)
<i>c</i> , Å	16.737 (5)
α, (°)	90.00
β, (°)	94.331 (5)
γ, (°)	90.00
<i>V</i> , Å ³	1546.7 (12)
Ζ	2
$\rho_{calc} \ mg/m^3$	1.514
μ , mm ⁻¹	0.163
F(000)	736
Independent	4441
Refl.	
Refl.used	5289
$(I>2\sigma(I))$	
<i>R</i> _{int} Value	0.0345
GOOF	1.094
Final R indices	R1 = 0.0539
$[I > 2\sigma(I)]$	wR2 = 0.1069
R indices	R1 = 0.0709
(all data)	wR2 = 0.1350

3.4. Synthesis:

3.4.1. Synthesis of 1,4-bis(3-pyridyl)-2,3diaza-1,3-butadiene, (L₁)

3-Pyridine carboxalidehyde (2.2 mL, 22 mmol) was dissolved in ethanol (15 mL), followed by dropwise addition of hydrazine (35 wt % solution in water, 1 mL, 11 mmol). After addition of one drop of formic acid, the mixture was stirred at room temperature for 24 h and filtered, and the resulting yellow crystalline solid was washed with



ethanol/ether (1:1) several times and dried in air. Yield: 75%. ¹H NMR (CDCl₃, ppm): 8.98 (s, 2H, pyridyl), 8.70 (d, 2H, pyridyl), 8.66 (s, 2H, H-C=N), 8.21, 8.19 (t, t, 2H, pyridyl), 7.39 (q, 2H, pyridyl). IR (KBr, cm⁻¹): 1644.5 (s), 1615.3 (s), 1585.7 (s), 1482.1 (s), 1410.6 (s), 1335.0 (s), 1302.6 (s). Anal. Calcd. for C₁₂H₁₀N₄: C, 68.57%; H, 4.76%. Found: C, 68.26%; H, 4.59%.

3.4.2. Synthesis of $\{Mg_2(oba)_2.8H_2O\}_n$,

This compound was synthesized by mixing 1 mmol of obaH₂ and 2 mmol of Mg(NO₃)₂.6H₂O in 4 ml of water in teflonlined autoclave, which was heated under autogenous pressure to 180 °C for 84 h. Upon cooling to room temperature the desired product appeared as colorless cubic in ca. 70% yield. The same crystalline product could be obtained when chloride salt of Mg (II) is used in place of nitrate salt. Anal. Calcd. for C₂₈H₃₂Mg₂O₁₈: C, 47.6%; H, 4.53%; O, 40.8%. Found: C, 47.5%; H, 4.43%; O, 40.7%. Main IR features (cm⁻¹, KBr pellet): 3381 vs for v(O-H); 3050 w for v(C-H); 1608 vs, 1556 s for $[v_{as}(O-C-O) +$ v(C=C + C=N)]; 1455 m for $v(C_{ar}-C)$; 1367 vs, 1278 m for v_s(O-C-O); 1226 m, 1105 w, 1025 w for δ_{ip} (C-H); 944 w for δ_{ring} ; 747 m for $\delta_{op}(C-H)$; 618 w for $\pi(CO_2)$; 498 w, 467 w for v(M-O + M-N).

Table 3.2.: Selected Bond Lengths (Å) and Bond Angles (deg) for Complex :

Mg2-O4	2.044	l (8)	
Mg2	-OW2	2.130 (9)	
Mg2-OW3	2.079	9 (8)	
Mg2	-OW1	2.123 (8)	
Mg2-O6	2.05	(1)	
Mg2	-08	2.206 (8)	

O1-Mg1 2.061 (9) O9-Mg1 2.049 (8) 2.026 (8) **O8-Mg2** Mg1-OW4 2.06(1)Mg1-OW5 2.144 (8) Mg1-OW6 2.071 (8) Mg1-01 2.061 (9) Mg1-09 2.049 (8)

O4-Mg2-OW2 92.9 (3) OW3-Mg2-O6 87.3 (3) O4-Mg2-OW3 173.8 (4) OW3-Mg2-O8 90.2 (3) O4-Mg2-OW1 86.7 (3) OW1-Mg2-O6 92.5 (3) O4-Mg2-O6 93.0 (3) OW1-Mg2-O8 175.1 (4) O4-Mg2-O8 95.9 (3) O6-Mg2-O8 91.5 (3) OW2-Mg2-OW3 86.9 (3) C7-O1-Mg1 129.9 (7) OW2-Mg2-OW1 88.1 (3) C14-O3-Mg1 152.7 (8) OW2-Mg2-O6 174.1 (4) Mg2-O4-C14 129.9(7) OW2-Mg2-O8 87.7 (3) Mg2-OW2-H2W2 111.1 (6) OW3-mg2-OW1 87.2 (3) Mg2-OW2-H1W2 62.3 (5)

4. RESULTS AND DISCUSSION

Due to the potential applications and unusual topologies of metal organic frameworks (MOFs), syntheses of these materials have attracted a lot interest in recent years. Our research efforts in the synthesis of MOFs were directed to



construct open frameworks with high porosity.

For this we designed and synthesized multi-armed ligand L_1 so that they can form coordination complexes with high porosity. The long rigid bidentate ligand 1,4-bis (3-pyridyl)-2,3-diaza-1,3-butadiene (L_1) was prepared in 75% yield by the Schiff-base condensation reaction of 3-pyridine carboxalidehyde with hydrazine (35 wt % solution in water) in ethanol by maintain acidic condition at room temperature.



 (L_1)

Scheme 1: A Schematic Diagram for the Synthesis of L₁ via Schiff Base Reaction

4.1. Crystal Structure of Complex :

This complex crystallizes in monoclinic crystal system in P21 space group. In the asymmetric unit of this complex, two ligand oba²⁻, two Mg (II), eight water molecules are present. The structure of this complex consists of 2D coordination polymeric layers of octacoordinated obaH₂ bridged Mg (II) dimers. Each octa-coordinated Mg (II) ion is having distorted octahedral geometry with one axial and two equatorial ligation from three water molecules and remaining one axial and two equatorial ligation from three O atoms of the

three obaH₂ molecules. Each of the carboxylate group of the ligand coordinates through O atoms in a mono-dentate fashion (Fig. 5). The X-ray structure shows that there is a carboxylate bridged Mg (II) dimers (Fig. 5). All the Mg-O bond distances are in the normal range and are listed in Table 3.2. Two water molecules reside in between layers as guest molecules. The metal bound water molecules are involved in H-bonding interaction with other metal bound water molecules, guest water molecules and with O atoms of the carboxylate group of the ligand obaH₂. The H-bonding interactions extend the structure along all crystallographic axes (Fig. 6). A Hydrogen bonded 3-D packing diagram is depicted in Figure 6.



Fig. 5: Coordination mode of Mg (II) ion in Complex 1



Fig. 6: 3-D packing diagram in Complex 1

5. <u>CONCLUSION AND SCOPE OF</u> <u>FUTURE WORK</u>

It has been an ongoing challenge to absolutely predict the network topology of the designed MOFs; nevertheless, various novel and interesting molecular textures have been synthesized with the use of ligands and appropriate metals and characterized. In the present we have studied the synthesis of multidentate ligand and used ligand with other commercially this available multidentate ligands for the construction of Metal Organic Framework structures and their complexation with transition metal ions and with alkaline earth metals to obtain coordination polymeric structures for potential porous materials. The ligand was designed in such a way that it excludes the formation of homoleptic metal complexes and instead can coordinate more than one metal atom to form open framework structures with void spaces. The frameworks obtained in the present studies are having solvents and ligands occupying The ability their cavities. for these frameworks to function as useful host-guest systems is therefore very probable. Potentially they could selectively entrap deleterious compounds (pollutants, toxicants, etc.).

Further investigation towards functionalization of the organic ligands may be of interest towards the generation of networks containing specific functions as reactive or binding sites at well-defined and controllable positions within the network topology. However, more number of different multidentate rigid ligands has to be designed and synthesized. In addition to transition metals, lanthanide ions should also be tried for having metal organic framework of diverse topologies and porosity some of which are being investigated in our laboratory.

REFERENCES

- (1) Lehn, J. M. Science 1985, 227, 849.
- (2) Lehn, J. M. Science **1993**, 260, 1762.
- (3) Lehn, J. M. Supramolecular Chemistry: Concepts and Perspectives; VCH: Weinheim, 1995.

(4) Hofmann, K. A.; Kuspert, Z. Z. Anorg. Allg. Chem. **1897**, 69, 204.

(5) Powell, H. M. J. Chem. Soc. **1948**, 61.

(6) Powell, H. M.; Rayner, J. H. Nature **1949**, 163, 566.

(7) Williams, F. V. J. Am. Chem. Soc. **1957**, 79, 5876.

(8) Cram, D. J.; Steinberg, H. J. Am. Chem. Soc. **1951**, 73, 5691.

(9) Pedersen, C. J. J. Am. Chem. Soc. **1967**, 89, 7017.

(10) Dietrich, B.; Lehn, J. M.; Sauvage, J. P. Tetrahedron Lett. **1969**, 10, 2889.

(11) Ts'o, P. O. P. Basic Principles in Nucleic Acid Chemistry, Vols 1 and 2; Academic Press: London, 1974.



- (12) Saenger, W. Principles of Nucleic Acid Structure; Springler-Verlag: New York, 1984.
- (13) Jaenicke, R. Biochemistry **1991**, 30, 3147.
- (14) Alberts, B.; Bray, D.; Lewis, J.; Raff, M.; Roberts, K.; Watson, J. D. Molecular Biology of the Cell; 3rd ed. Garland Publishing: London, 1994.
- (15) Stupp, S. I.; Braun, P. V. Science **1997**, 277, 1242.
- (16) MacGillivray, L. R.; Atwood, J. L. Nature 1997, 389, 469.
- (17) Gutsche, C. D. Acc. Chem. Res. 1983, 16, 161.
- Berl, V.; Huc, I.; Khoury, R. G.; Krische, M. J.; Lehn, J. M. Nature 2000, 407, 720.
- (19) Oda, R.; Huc, I.; Schmutz, M.; Candau, S.
- J.; Mackintosh, F. C. Nature **1999**, 399, 566.
- (20) Barboiu, M.; Lehn, J. M. Proc. Natl. Acad. Sci. U. S. A. **2002**, 99, 5201.
- Barboiu, M.; Vaughan, G.; Graff, R.; Lehn,
 J. M. J. Am. Chem. Soc. 2003, 125, 10257.
- (22) Huc, I.; Lehn, J. M. Proc Natl Acad Sci U S A **1997**, 94, 2106.
- (23) Storhoff, J. J.; Mirkin, C. A. Chem. Rev. **1999**, 99, 1849.
- (24) Kirby, A. J. Angew. Chem., Int. Ed. Engl. **1996**, 35, 707.
- (25) Rakow, N. A.; Suslick, K. S. Nature 2000, 406, 710.
- (26) Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. Nature **1996**, 382, 607.
- (27) Lindoy, L.F., Atkinson, I.M., Editor Stoddart, J.F. Self-Assembly in supramolecular systems, RSC, UK, p4, 6, 2000.
- (28) Dodziuk, H. Introduction to Supramolecular Chemistry, Kluwer Academic Publishers, Netherlands, 2002, p1, 25-26.
- (29) Jones, W.; Rao. C.N.R. Supramolecular organization and materials design, Cambridge University Press, 2002, p 214, 391.
- (30) Fasina, T. M.; Collings, J.C.; JBurke, M.; Batsanov, A. S.; Ward, R. M.; Albesa-Jové,

D.; Porrès, L.; Beeby, A.; Howard, A. K.; Scott, A. J.; Clegg, W.; Watt, S. W.; Viney, C.; Marder, T. B. J. Mater. Chem. 2005, 15, 690.

- (31) Janiak, C.; Dalton Trans. 2003, 2781.
- (32) Carrano, C.J.; Santillan, G.A. Inorg. Chem. **2008**, 47 (3), 930.
- (33) Eddaoudi, M.; Moler, D.B.; Li,H., Chen, B.; Reineke, T. M.; O'Keeffe, and Yaghi, O.M. Acc. Chem. Res. **2001**, 34, 319.
- (34) Eddaoudi, M.; Kim, J.; Vodak, D.; Sudik, A.; Wachter, J.; O'Keeffe, M.; Yaghi, O.M. Proc. Natl. Aca. Sci. (USA), **2002**, 99, 4900.
- (35) Yang, Y.; Jiang, G.; Li, Y.-Z.; Bai, J.; Pan, You, X.-Z. Inorg. Chim., Acta. 2006, 359, 3257.
- (36) Yaghi, O.M.; Rowsell, J.L.C. Angew. Chem. Int. Ed. 2005, 44, 4670.
- (37) (a) Evans, O.R.; Ngo, H.L.; Lin, W. J. Am. Chem. Soc. 2001, 123, 10395. (b) Gomez-Lor, B.; Gutierrez-Puebla, E.; Iglasias, M.; Monge, A.; Ruiz-Valero, C.; Snejko, N. Inorg. Chem. 2002, 41, 2429.
- (38) (a) Evans, O.R.; Ngo, H.L.; Lin, W. J. Am. Chem. Soc. 2001, 123, 10395. (b) Gomez-Lor, B.; Gutierrez-Puebla, E.; Iglasias, M.; Monge, A.; Ruiz-Valero, C.; Snejko, N. Inorg. Chem. 2002, 41, 2429.
- (39) International Tables for X-ray Crystallography, Kynoch Press: Birmingham, England, 1974, Vol. IV.
- (40) SAINT+, 6.02ed.; Bruker AXS, Madison, WI, 1999.
- (41) XPREP, 5.1 ed. Siemens Industrial Automation Inc.: Madison, WI, 1995.
- (42) Sheldrick, G.M.; SHELXL-97: Program for Crystal Structure Refinement: University of Göttingen, Göttingen, Germany, 1997.



(43) (a) Neogi, S.; Savitha, G.; Bharadwaj, P. K. Inorg. Chem., 2004, 43, 3771. (b) Neogi, S.; Bharadwaj, P. K. Inorg. Chem., 2005, 44, 816. (c) Neogi, S.; Bharadwaj, P. K. Crystal Growth and Design, 2006, 6, 433.