

## SHAPE-MEMORY EFFECT IN A FLEXIBLE POLYDENTATE PYRIDINE CONTAIN METAL–ORGANIC FRAMEWORK

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**Abstract.** In the past few decades, due to human activities such as fossil fuel power generation, more and more CO<sub>2</sub> in the atmosphere has been caused, and the greenhouse effect has become more and more obvious. This poses a huge threat to human and global security. At present, the CO<sub>2</sub> concentration in the atmosphere has exceeded 400 ppm, which is about 40% higher than before industrialization, and the surface temperature has increased by about 0.8 °C [1]. In work, we illustrate deliberate design strategy based on a switchable porous new systems as member of a representative class of flexible MOFs via combination of Zn(II) as a metal ions with polydentate pyridine contain ligands and carboxylic contain compounds at different reaction conditions that will depend on mole ration of starting materials, solvent systems and temperature to comprise with reported structures in the literature. Based on in situ experimental like (SC-XRD and PXRD) that will combined with literature reports to find responsive and nonresponsive, depending on the transformability of the gas-free reopened pore phase into the collapsed phase. To the best of our knowledge, a few flexible frameworks are known to exhibit permanent porosity even in the absence of gas molecules.

**Keywords:** Coordination polymer, Crystal engineering, Hydrogen bonds, Self-assembly and Solvent effects

### 1 Introduction

The rational design and assembly of coordination polymers are of current interest due to their fascinating architectures and potential applications in gas storage, luminescence, separation, catalysis, drug delivery, and so on [1-6]. Among the various N-donor bridging ligands, the 4,4'-bipyridine type rigid linear ligands have afforded many noteworthy 2-D and 3-D frameworks whit different metal ions. When rigid bifunctional ligands are used as spacers to connect metal centers, the topology of the network is usually determined by the coordination geometry of the central metal preference. Contrary to rigid ligands, the bifunctional flexible ligands with conformational flexibility can induce variety of structures and may lead to the formation of the supramolecular isomers. Many factors such as the coordination environment of metal centers, the donor sets of ligands, solvent molecules, temperature, templates, counteranions, etc. can affect the final architectures . Supramolecular isomerism is an essential element in the crystal engineering of coordination polymer frameworks [7-9]. Supramolecular isomerism often results from the existence of several different building block units with little or no difference in formation energy, making it difficult to accurately predict final topologies. The study of supramolecular isomerism is not only important in producing novel functional materials with a variety of topologies and

interesting properties, but may also be helpful in developing a fundamental understanding of the factors influencing crystal growth. However, the rational design and synthesis of supramolecular isomers are still challenging topics [11-13]. Taking into account that systematic investigation of the influence of the rigid spacer and substituent position of N-donor ligands on the formation of coordination frameworks is scarce so far, to investigate the impact of substituent position of N-donor ligands on the structural diversity of the assembled frameworks, L2 instead of L1, which have different substituent groups and same spacer (Scheme 1), in an effort to investigate their supramolecular coordination chemistry, was used in the reaction and complexes 1-4 were successfully isolated

## 2. Experimental

### 2.1 Materials

The solvents and reagents used in these studies were obtained from commercial sources and were used as received.

### 2.2 Physical measurements

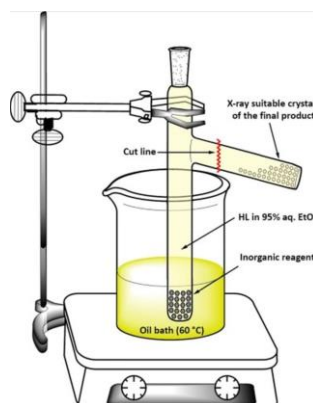
The IR absorption spectra were recorded in the range of 400–4000  $\text{cm}^{-1}$  by means of a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. Microanalyses were performed using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

### 2.3 X-ray crystallography

X-ray data for complexes 1 and 2 were collected at 100 K on a Bruker AXS SMART APEX – and complex 3 on an APEX II CCD diffractometer, using Mo K $\alpha$  radiation ( $K\alpha = 0.71073 \text{ \AA}$ ) in the x-scan mode. The structures were determined by direct methods and refined by full-matrix least-squares procedures using SHELXTL.

### 2.3 Syntheses

The compounds were prepared following branched tube methods as showed in fig.1.



**Fig. 2.** Graphical representation of the apparatus used in the syntheses of 1-4

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## 2.4 Results and discussion

The apparatus used in this work is shown in Fig. 1, and consists of a glass tube fitted with a side branched arm, which forms an angle of  $85^\circ$  with the main reaction tube. The Mn(II) salts are typically added to the main reaction tube, and the ligand is added as a ethanol solution (0.5 mmol of the ligand L in 25 ml of ethanol). Alternately, all solid reactants may be added to the main reaction tube and neat ethanol (25 ml) is added to fill the apparatus. Then, the main reaction tube is sealed and it is immersed in a  $60^\circ\text{C}$  oil bath, with the branched arm remaining at room temperature (not immersed in the oil bath). The temperature differential between the reaction tube and the angle-mount arm is believed to allow for the formation of single crystals suitable for X-ray crystallography. It is noted that one-pot reactions in a flask often do not produce single crystals, and the use of the unique apparatus described herein is advantageous in such cases.

## 2.5 Crystal structures of 1–4

Crystal structures data summarized in table 1 and structures described below

**Complex 1:** The crystal structure of **1** with the atom labeling is shown in Fig. 1 Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in triclinic space group  $P-1$ . The asymmetric unit of **1** consists of four Mn(II) centers, two deprotonated L1 ligands, two thiocyanate ligands without any solvnt. The Mn(II) centers bridges by four  $\mu$ -nitrogen atoms and the complex **1** exhibits a square grid-like structure.

### Complex 2

The asymmetric unit of **2** contain two Mn(II) ion, one L2 ligand, three thiocyanate ligands. The complex **2** consists of a centrosymmetric structure with two types of Mn(II) centers. The coordination environments around Mn(II) ions are distorted octahedral geometries and each manganese(II) ions are coordinated with two nitrogen and one oxygene atoms from the L2 ligand and two end-on (EO) bridging thiocyanate groups. The distorted octahedral geometries of Mn1 and Mn2 centers are completed by one terminal azido and methanol ligands, respectively. Two Mn(II) centers are bridged by the L5 ligand through one oxygen atom and four nitrogen atoms with Mn1 $\cdots$ Mn2 distance 3.972(1) Å.

### Complex 3

Complex **3** crystallizes in the monoclinic crystal system and  $P2_1/c$  space group. the asymmetric unit of **3** consists of symmetry related four Mn(II) ions, four pentadentate L1 and four terminale thiocyanate ligands. Each Mn(II) ion is connected to the other two Mn(II) ions through bridging oxygen atoms from L1 ligands to form a square grid-like structure. Each Mn(II) ions are coordinated by three nitrogen atom from two different L1 ligand, one nitrogen atom from terminale azide ligand. The coordination geometry around the all Mn(II) ions can be described as a distorted octahedral geometries.

### Complex 4

The structure of **4** Mn(II) ions bridged by two L1 ligands. The molecular structure of **4** is very similar to that of **3**, with the difference being that the distorted octahedral geometries of Mn(II) ions are completed with thiocyanate. Furthermore, crystal structure of **4** is interpenetrated lattice.

**Table 2.** Crystal data and structure refinement parameters for complexes **1-4**.

Crystal data	1	2	3	4
Temperature (K)	100 (2)	<a href="http://../User/Desktop/Ghodrairan/M4/grat011_cell_measurement_temperature">../User/Desktop/Ghodrairan/M4/grat011_cell_measurement_temperature</a> <sup>293</sup> (2)	110 (2)	100 (2)
Formula weight	1376.95	1435	1790.49	3507
Crystal system	triclinic	Triclinic	monoclinic	triclinic
Space group	P-1	P-1	P21/c	P-1
a (Å)	12.7720 (7)	9.743 (2)	14.1532 (13)	13.4149 (16)
b (Å)	12.9943 (7)	12.392 (2)	43.808 (4)	14.0300 (15)
c (Å)	19.9873 (11)	14.5990 (19)	14.0851 (14)	24.147 (3)
$\alpha$ (°)	85.019 (2)	81.677 (14)	90	98.319 (7)
$\beta$ (°)	87.169 (2)	73.422 (15)	110.454 (4)	91.437 (7)
$\gamma$ (°)	66.460 (2)	69.467 (19)	90	117.846 (6)
V (Å <sup>3</sup> )	3029.2 (3)	1580.1 (5)	8182.5 (14)	3953.8 (8)
Z	2	1	4	1
D <sub>c</sub> (g cm <sup>-3</sup> )	1.510	1.508	1.453	1.473
$\mu$ (mm <sup>-1</sup> )	0.89	0.86	0.73	0.80
$\theta$ max. (°)	35.9	29.3	33.3	26.1
Measured refls.	76101	10574	92040	53067
Independent refls.	25061	7060	24646	14663
R <sub>int</sub>	0.057	0.064	0.061	0.190
S	1.01	0.94	1.06	0.96
R1/wR2	0.050/0.112	0.066/0.201	0.079/0.230	0.083/0.238
$\Delta\rho$ max/ $\Delta\rho$ min (eÅ <sup>-3</sup> )	0.56/-0.60	0.73/-0.48	3.62/-1.14	0.83/-0.68

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## 2.6 Conclusions

In summary, a series of Mn complexes prepared via one pot simple method and final product received without any recrystallization. Using the classical bridging ligand which lacks potential hydrogen donor or acceptor groups (except the very weakly basic imine nitrogen atom which is only a modest hydrogen acceptor and often does not participate in intermolecular hydrogen bonding) yields complex 1 in all three tested solvents. In 4, the change from acetonitrile to methanol leads to a structure where the solvent molecules not only engage in extensive hydrogen bonding, but they also coordinate to the manganese ions. Each ion is coordinated in an all-trans manner by N-bound thiocyanate anions. Crystallization from solutions containing Mn<sup>2+</sup> and SCN<sup>-</sup> ions as well as bis(4-pyridyl) substituted hydrazone derivatives L normally leads to the formation of 2D [Mn(SCN)<sub>2</sub>L<sub>2</sub>]<sub>n</sub> MOFs. When a ligand L which cannot form hydrogen bonds with the solvent molecules is employed, the obtained product has an interpenetrated structure with the voids of each 2D network occupied by atoms of two neighboring networks. Adding an amide functional group, acting both as a hydrogen donor and acceptor, on the bridging ligands, thus allowing hydrogen bonding of the solvent molecules and, expectedly, preventing interpenetration, was found to have three possible effects: (1) formation of hydrogen bonded interpenetrated structures; (2) hydrogen bonding of solvent into the voids leading to noninterpenetrated 2D networks (as expected); and (3) replacement of one or more of the bridging ligands by solvent molecules.

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## TƏRKİBİ METAL-ÜZVİ KARKASDA OLAN EVALİ POLİDENTAT PİRİDİNDƏ FORMA-YADDAŞ TƏSİRİ

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**Abstrakt.** Son bir neçə onillikdə, qalıtq yanacaq enerjisi istehsalı kimi insan fəaliyyəti nəticəsində atmosferdə getdikcə daha çox CO<sub>2</sub> əmələ gəlir və istixana effekti getdikcə daha aydın görünür. Bu, insan və qlobal təhlükəsizliyə böyük təhlükə yaradır. Hazırda atmosferdə CO<sub>2</sub> konsentrasiyası 400 ppm-i keçib ki, bu da sənayeləşmədən əvvəlkindən təxminən 40% yüksəkdir və səthin temperaturu təxminən 0,8 °C artmışdır [1]. İşdə biz çevik MOF-ların təmsilçi sinfinin üzvü kimi dəyişdirilə bilən məsaməli yeni sistemlərə əsaslanan düşünülmüş dizayn strategiyasını təsvir edirik. Zn(II)-nin polidentat piridinlə metal ionları ilə birləşməsi nəticəsində müxtəlif reaksiya şəraitində liqandlar və karboksilik tərkibli birləşmələr var ki, bu da ədəbiyyatda bildirilmiş strukturlardan ibarət başlanğıc materialların, həlledici sistemlərin və temperaturun mol nisbətindən asılı olacaq. Qazsız yenidən açılmış məsamə fazasının çökmüş fazaya çevrilə bilməsindən asılı olaraq, cavab verən və reaksiya verməyənləri tapmaq üçün ədəbiyyat hesabatları ilə birləşdiriləcək in situ eksperimental (SC-XRD və PXR) əsasında. Bildiyimiz qədər, bir neçə çevik çərçivənin qaz molekulları olmadıqda belə daimi məsaməlik nümayiş etdirdiyi məlumdur.

**Açar sözlər:** koordinasiya polimeri, kristal mühəndisliyi, hidrogen rabitəsi, öz-özünə yığılma və solvent effektləri

## ЭФФЕКТ ПАМЯТИ ФОРМЫ В ГИБКОМ ПОЛИДЕНТАТНОМ ПИРИДИНЕ, СОДЕРЖАЩЕМ МЕТАЛЛООРГАНИЧЕСКИЙ КАРКАС

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За последние несколько десятилетий из-за деятельности человека, такой как производство электроэнергии на ископаемом топливе, в атмосфере появлялось все больше и больше CO<sub>2</sub>, а парниковый эффект становился все более и более очевидным. Это представляет собой огромную угрозу человеческой и глобальной безопасности. В настоящее время концентрация CO<sub>2</sub> в атмосфере превысила 400 ppm, что примерно на 40% выше, чем до индустриализации, а температура поверхности увеличилась примерно на 0,8 °C [1]. В работе мы иллюстрируем продуманную стратегию проектирования, основанную на переключаемых пористых новых системах как представителя представительного класса гибких MOF. За счет сочетания Zn(II) как ионов металла с полидентатными пиридинсодержащими лигандами и карбоксильными соединениями при различных условиях реакции, которые будут зависеть от мольного соотношения исходных материалов, систем растворителей и температуры соединения со структурами, указанными в литературе. На основе экспериментальных исследований на месте (SC-XRD и PXR), которые будут объединены с литературными отчетами, чтобы определить реагирующие и

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не реагирующие, в зависимости от способности к трансформации безгазовой фазы вновь открытых пор в сжатую фазу. Насколько нам известно, известно, что некоторые гибкие каркасы демонстрируют постоянную пористость даже в отсутствие молекул газа.