

System-pH-dependent supramolecular isomers of puckered three-dimensional layered hydrogen-bonded networks: Syntheses, characterization and fluorescent properties

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Abstract

Two true supramolecular isomers (**1** and **2**) formulated as $[\text{Zn}(\text{bipy})(\text{H}_2\text{btc})_2]_n$ (bipy = 2,2'-bipyridine, H_3btc = benzene-1,3,5-tricarboxylic acid) have been hydrothermally prepared through systematically changing the pH value of reaction mixture, and characterized by single-crystal X-ray diffraction, element analysis, infrared spectra (IR), and differential scanning calorimetry (DSC). Isomer **1** crystallizes in triclinic space group $P\bar{1}$, tetrahedral Zn(II) ions possess four-coordinated environment, while isomer **2** crystallizes in monoclinic space group $C2/c$ and the distorted octahedral Zn(II) ions adopt six-coordinated fashion. **1** and **2** can be regarded as supramolecular structural isomers, the formation of which should be undoubtedly attributed to the preference for pH-dependent crystallization leading to multiple connectivity (monodentate and chelating bidentate) of organic ligand despite the same stoichiometry employed. The supramolecular chemistry, which organizes the coordination complexes into three-dimensional (3D) layered open structure, is driven by a combination of hydrogen-bond and π - π interactions. Moreover, **1** emits fluorescence at 350.1 nm ($\lambda_{\text{ex}} = 310.0$ nm) and **2** exhibits fluorescent property at about 351.4 nm ($\lambda_{\text{ex}} = 302.0$ nm).

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1. Introduction

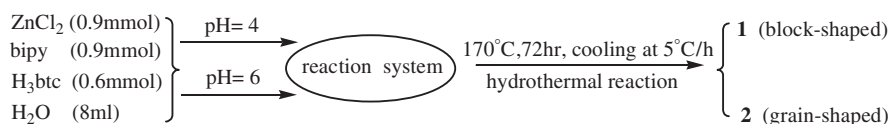
Long time ago, isomer was extensively investigated in the field of organic chemistry. Importantly, when the difference between coordination polymers [1] and supramolecular architectures [2] became unobvious, the concept of supramolecular isomerism [3] was introduced into crystal engineering by Zaworotko and coworkers to interpret their synthetic and structural relationship. For given metal centers and multifunctional bridging ligands, various connectivity manners can result in a series of supramolecular isomers which were defined as the occurrence of more than one superstructure arising from the same reagent. The final arrangements of supramolecule are significantly influenced by comprehensive factors such as reaction time, temperature, pH value, medium and the metal-to-ligand

ratio. Therefore, it is still a formidable challenge to predict the precise superstructure of those high-dimensional polymers with complicated ligands.

Much attentions [4–14] have been recently paid to the deliberate design and controlled synthesis of supramolecular isomerism owing to their potential applications as well as abundant structural information. Taking into account the different structure characteristic, several cases of structural isomerism [5,7] conformational isomerism [10,13] and optical isomerism [14] have been reported previously. Based on the cause to isomerism, some examples tuned via template molecules (solvent guest) [6–8], conformational conversion of ligand [10,13], ring-opening polymerization [6b,9,10a,14] and reaction-temperature-induced isomerism [12b,12c], have been published in the literature. Because different solvent molecules were involved in the corresponding coordination networks, most of those mentioned above should be classified as pseudo-polymorphism [5,6]. Strictly speaking, only several cases of

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Scheme 1. The synthetic procedure of isomers **1** and **2**.

true supramolecular isomerism with a fixed stoichiometry for all components were documented [10c,11,12a,12b] so far, which can be further categorized into two types, namely the building blocks intrinsic-nature-induced (conformational ligand) and extrinsic-stimulation-induced (temperature and acidity/basicity) isomers.

Aromatic polycarboxylic acids are widely used as space ligands because of their sterical rigidity and chemical robustness, in which multiple coordination fashions of carboxyl such as monodentate, bidentate (bridging) and chelating, can likely yield structural isomers. As illustrated in the two compounds α -[Co(dcbp)(H₂O)₂] and β -[Co(dcbp)(H₂O)₂] (dcbp = 4,4'-dicarboxy-2,2'-bipyridine) [12a], they display different 3D architectures as a result of various coordination modes of carboxyl in dcbp ligand: the former is bis-monodentate while the latter have both bridging bidentate and noncoordinated carboxylate groups. Although three cases of pH-induced pseudo-polymorphs Co₃(TMA)₂ (TMA = benzene-1,3,5-tricarboxylate) with solvent molecules were ever described [15], we select polycarboxylic H₃btc to synthesize true supramolecular isomer through changing the pH value of reaction system.

On the other hand, d^{10} electron configuration transition metal complexes possibly possess luminescent properties. The aforementioned ideas prompt us to employ multi-dentate H₃btc as organic linkers and chelated bipy as an auxiliary ligand. In this contribution, we present two true supramolecular isomers without guest molecules, the formation of which were found to be extremely sensitive to the pH values of the reaction mixture (see Scheme 1). Of particular interest is that they both possess extended open structures, which evidently differ from the interconversion between polymeric chain and closed ring. Another feature is that the 3D frameworks are mainly sustained by hydrogen-bond interactions.

2. Experimental

2.1. Materials and general procedures

All chemicals were of reagent grade and were used as purchased from the Rgent company of chemical reagent in Tianjin without further purification. The IR spectra were recorded as KBr pellets on a FT-IR 170SX (Nicolet) spectrometer in the 4000–400 cm⁻¹ region. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240 analyzer. Fluorescent analyses were carried out on an Edinburgh Instruments analyzer model FL920. The DSC measurements were performed on a NETZSCH DSC

204 with a heating rate of 10 °C/min in the temperature range of 25–590 °C.

2.2. Syntheses

Two same mixtures of ZnCl₂ (0.123 g, 0.9 mmol), bipy (0.140 g, 0.9 mmol), and H₃btc (0.126 g, 0.6 mmol) in the molar ratio of 3:3:2 were both dissolved in 8 ml distilled water. The pH values were adjusted to 4(**1**) and 6(**2**) with 2 M KOH, respectively. Then, the resulting solution were transferred and sealed in two 25 mL Teflon-lined stainless-steel vessels, which were heated at 170 °C for 3 days. After the reactors were slowly cooled to room temperature at a rate of 5 °C/h, colorless block-shaped (**1**) and grain-shaped (**2**) crystals were filtered off, washed with distilled water and dried in air (yield: 52% and 56% based on ZnCl₂, respectively). Anal. Calcd. (%) for [Zn(bipy)(H₂btc)₂] (Mr = 639.81): C, 52.56; H, 2.84; N, 4.38. Found (**1**): C, 52.11; H, 2.93; N, 4.42. Found (**2**): C, 52.20; H, 2.97; N, 4.34. Selected IR spectra for **1**: ν (cm⁻¹) = 1715, 1698 s, 1614, 1558, 1541, 1442 m, 1252 s, 700 m; and for **2**: ν (cm⁻¹) = 1717 s, 1698, 1613, 1444 m, 1221 s, 764, 753 m.

2.3. Crystal structure determinations

Crystal data and experimental details are summarized in Table 1. Single crystal analyses were performed at 293(2) K with a Bruker SMART 1000 CCD diffractometer with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) by the $\omega - 2\theta$ scan technique. All data were collected for absorption by semi-empirical method using SADABS program. The program SAIN [16] was applied for integration of the diffraction profiles. Data analysis was carried out with program XPREP. The structure was solved with direct method using SHELXS-97 followed by structure refinement on F^2 with program SHELXL-97 [17]. All nonhydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were assigned to calculated positions with isotropic thermal parameters. Carboxylic acid hydrogen atoms were placed from different maps and refined subject to O–H distance restraints. The CCDC reference numbers are 281580 (**1**) and 281579 (**2**). Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

3.1. Description of crystal structures

Single-crystal X-ray diffraction analysis reveals that **1** and **2** are structural isomers without any guest molecules in

Table 1
Crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	C ₂₈ H ₁₈ N ₂ O ₁₂ Zn	C ₂₈ H ₁₈ N ₂ O ₁₂ Zn
Formula weight	639.81	639.81
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	8.0794(10)	9.9352(9)
<i>b</i> (Å)	8.8464(11)	15.6901(15)
<i>c</i> (Å)	19.628(3)	16.6642(16)
α (°)	90.859(2)	
β (°)	98.774(2)	92.9490(10)
γ (°)	108.913(2)	
<i>V</i> (Å ³)	1308.5(3)	2594.2(4)
<i>Z</i>	2	4
<i>D</i> _{calc} (mg m ⁻³)	1.624	1.638
μ (mm ⁻¹)	1.012	1.021
<i>F</i> (000)	652	1304
Θ range (°)	2.10–25.03	2.43–25.03
Limiting indices	$-9 \leq h \leq 9, -10 \leq k \leq 10,$ $-22 \leq l \leq 23$	$-11 \leq h \leq 11, -16 \leq k \leq 18,$ $-19 \leq l \leq 19$
Reflections collected/unique	7168/4575 [<i>R</i> _(int) = 0.0150]	6905/2281 [<i>R</i> _(int) = 0.0266]
Completeness to $\theta = 25.03$	98.6%	100.0%
Goodness-of-fit on <i>F</i> ²	1.038	1.086
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> ₁ = 0.0360, <i>wR</i> ₂ = 0.0944	<i>R</i> ₁ = 0.0319, <i>wR</i> ₂ = 0.0859
Largest diff. peak and hole (e Å ⁻³)	0.533, -0.271	0.370, -0.463

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

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

1			
Zn(1)–O(7)	1.9450(18)	Zn(1)–O(2)	1.9650(17)
Zn(1)–N(2)	2.043(2)	Zn(1)–N(1)	2.054(2)
O(1)–C(17)	1.250(3)	O(2)–C(17)	1.268(3)
O(3)–C(18)	1.223(3)	O(4)–C(18)	1.301(3)
O(5)–C(19)	1.194(3)	O(6)–C(19)	1.314(3)
O(7)–Zn(1)–O(2)	119.00(8)	O(7)–Zn(1)–N(2)	104.19(9)
O(2)–Zn(1)–N(2)	119.98(8)	O(7)–Zn(1)–N(1)	126.77(8)
O(2)–Zn(1)–N(1)	101.60(8)	N(2)–Zn(1)–N(1)	80.47(9)
2			
Zn(1)–N(1)	2.0606(17)	Zn(1)–N(1)#1	2.0606(17)
Zn(1)–O(2)	2.0801(15)	Zn(1)–O(2)#1	2.0801(15)
Zn(1)–O(1)#1	2.3341(17)	Zn(1)–O(1)	2.3341(17)
N(1)–Zn(1)–N(1)#1	79.69(9)	N(1)–Zn(1)–O(2)	113.56(6)
N(1)#1–Zn(1)–O(2)	107.52(6)	N(1)–Zn(1)–O(2)#1	107.52(6)
N(1)#1–Zn(1)–O(2)#1	113.56(6)	O(2)–Zn(1)–O(2)#1	125.70(9)
N(1)–Zn(1)–O(1)#1	158.97(7)	N(1)#1–Zn(1)–O(1)#1	91.06(7)
O(2)–Zn(1)–O(1)#1	87.18(6)	O(2)#1–Zn(1)–O(1)#1	58.91(6)
N(1)–Zn(1)–O(1)	91.06(7)	N(1)#1–Zn(1)–O(1)	158.97(7)
O(2)–Zn(1)–O(1)	58.91(6)	O(2)#1–Zn(1)–O(1)	87.18(6)
O(1)#1–Zn(1)–O(1)	103.39(9)		

the coordination networks. Isomer **1** belongs to triclinic space group *P*-1, and **2** belongs to monoclinic space group *C*2/*c*. The atomic numbering scheme and atom connectivity are shown in Fig. 1. Each unit cell contains two

[Zn(bipy)(H₂btc)₂] molecules in **1**, and four [Zn(bipy)(H₂btc)₂] molecules in **2**. Although isomers **1** and **2** consist of the same building block [Zn(bipy)(H₂btc)₂], they display different 3D hydrogen-bonded supramolecular framework.

Each asymmetric unit in **1** is composed of one crystallographic independent [Zn(bipy)(H₂btc)₂] molecule, in which the tetrahedral Zn(II) center is coordinated to two *N,N'*-chelating sites of bipy ligand (Zn–N = 2.043(2)–2.054(2) Å) and two oxygen atoms from two different carboxylate group (Zn–O = 1.945(18)–1.965(17) Å). Two aromatic rings of bipy are noncoplanar with a dihedral angle of 10.70°. Isomer **1** possesses two types of unique hydrogen-bond and details of these are given in Table 3. One is intrachain hydrogen-bond interactions (O11...O12 = 2.619 Å, H11...O12 = 1.810 Å, and \angle O11–H11...O12 = 168.71°), adjoining the discrete molecules [Zn(bipy)(H₂btc)₂] into a zigzag-chain (see Fig. 2a), at two sides of which those bipy ligands were alternately located. The other interchain hydrogen-bond (O6...O1 = 2.630 Å, H6...O1 = 1.871 Å and \angle O6–H6...O1 = 153.41°) bridges two adjacent zigzag-like chains to give a 2D undulate sheet (see Fig. 3a). According to the hydrogen-acceptor distances, these hydrogen-bonds are quite strong because they are shorter than the typical length [18] of 1.9–2.1 Å. In addition, two edge-sharing hydrogen-bonded 40- and 16-membered rings were generated in the 2D sheet (Fig. 3a). The whole 3D-layered puckered motif (see Fig. 4a) was basically dominated by face-to-face π – π stacking

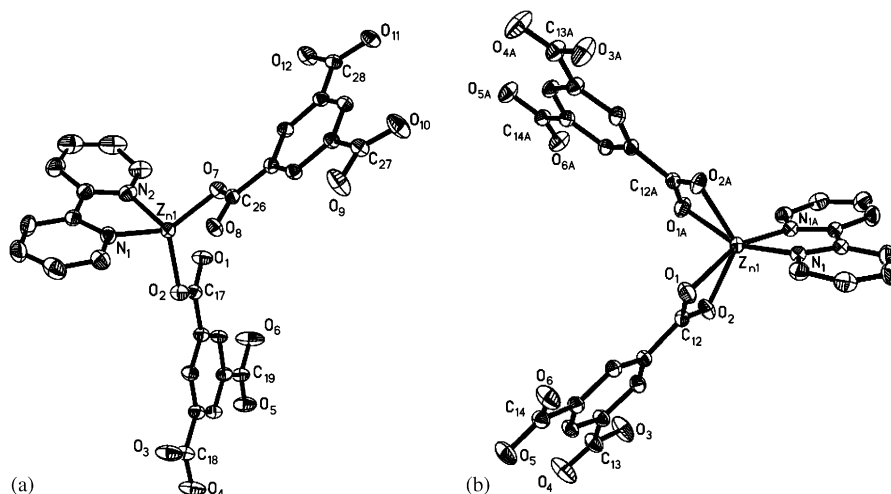


Fig. 1. Molecular structures of **1** (a) and **2** (b) showing the metal coordination environment (ORTEP plot with 30% thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Table 3
Parameters of hydrogen-bond interaction in **1** and **2**

D–H...A	$d(\text{D–H})$ (Å)	$d(\text{H...A})$ (Å)	$d(\text{D...A})$ (Å)	$\angle(\text{D–H...A})$ (deg)
1				
O4–H4...O ⁱ	0.820	1.833	2.650	175.09
O6–H6...O1 ⁱⁱ	0.820	1.871	2.630	153.41
O9–H9...O8 ⁱⁱⁱ	0.820	1.899	2.664	154.71
O11–H11...O12 ^{iv}	0.820	1.810	2.619	168.71
2				
O3–H3...O2 ^v	0.820	1.942	2.699	153.20
O6–H6...O5 ^{vi}	0.820	1.830	2.618	160.78

$i = -x, -y, -z$; $ii = -x+1, -y+2, -z$; $iii = -x+1, -y+1, -z+1$; $iv = -x+2, -y+3, -z+1$; $v = -x+3/2, -y+1/2, -z$; $vi = -x, -y+1, -z$.

(interlayer centroid–centroid separation of 3.400 Å) besides O–H... π (3.151 Å) and C–H... π (2.259 and 2.903 Å) interactions.

The composition of asymmetric unit of isomer **2** resemble isomer **1**. Unlike, the central Zn(II) ion is six-coordinate with a highly twisted ZnN₂O₄ octahedron, which is chelated by two N_{pyridyl} (Zn–N = 2.061(17) Å), and the remaining coordination sites are occupied by four oxygen atoms from two COO[−] ligands (Zn–O = 2.080(15)–2.334(17) Å). The bond angle N–Zn–N of 79.69(9)° is well consistent with that of 80.47(9)° in **1**. Two pyridine rings are twisted with the deviation (7.85°) from the ideal value. One deprotonated carboxyl (−COO[−]) adopts chelating bidentate pattern (monodentate mode in **1**) and the other two neutral carboxyl (−COOH) are noncoordinated and favor their participation in hydrogen bonding interaction. Isomer **2** was connected into a Z-shaped chain (see Fig. 2b) by intrachain hydrogen-bond (O6...O5 = 2.618 Å, H6...O5 = 1.830 Å and \angle O6–H6...O5 = 160.78°). Neighboring chains interlink each other to furnish a 2D-stepped sheet (see Fig. 3b), in which those 68-membered hydrogen-bonded rings containing quasi-rhom-

bus grids with dimension of 17.938 × 16.842 Å based on the Zn...Zn distances, are fused together via a 16-membered ring. The formation of the 2D sheet should be attributed to another hydrogen-bond (O3...O2 = 2.699 Å, H3...O2 = 1.942 Å, \angle O3–H3...O2 = 153.20°). In contrast, the 3D-layered puckered structure (see Fig. 4b) in **2** was mainly stabilized by other O6–H6...O5 hydrogen bonds pointing above and below the rhombus grids, not by π – π stacking interactions. The most striking feature different from isomer **1** is the presence of 1D void channel with the size of ca. 31.106 × 12.975 Å. According to the O...O separation (2.62 Å), this interaction is very strong. Finally, the configurations of isomers **1** and **2** completely differ from those complexes [Zn_{3.5}(μ_3 -OH)(btc)₂(bipy)₂·H₂O]_n and [Zn₂(H₂O)₃(2,2'-bipy)₂(btc)] [Zn(H₂O)(2,2'-bipy)(btc)]·8H₂O reported [19] previously. The former consists of single metal center and pentanuclear clusters, while the latter is composed of independent cationic and anionic chains.

It is to be noted that the analogous reactions were synchronously carried out at pH = 2, 8 and 10, respectively. Unfortunately, we failed to obtain the desired products, suggesting that the crystallization and growth

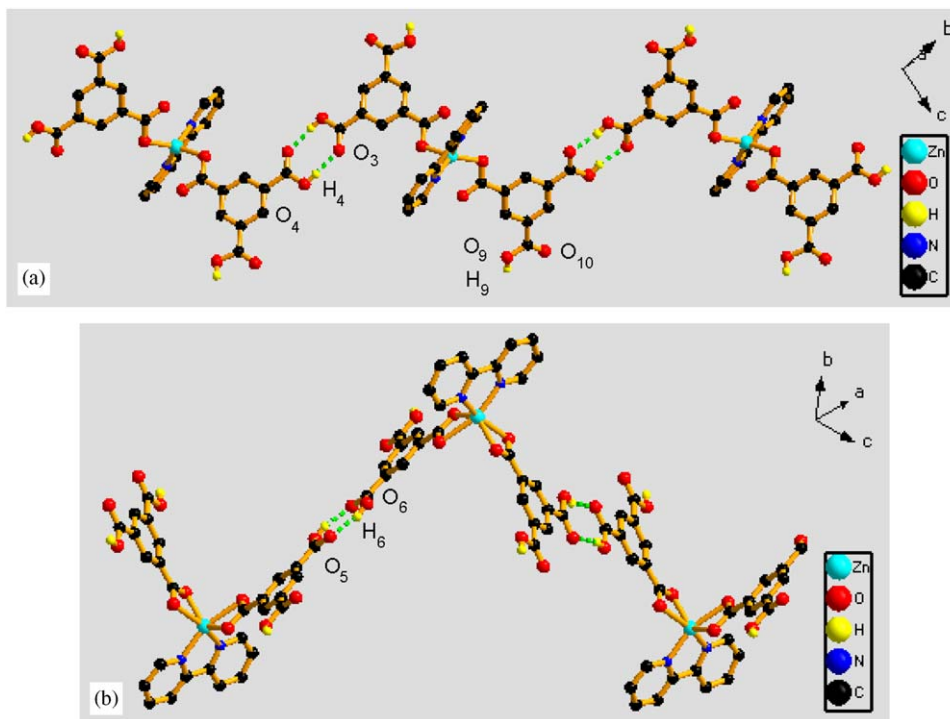


Fig. 2. (a) 1D zigzag chains generated through the hydrogen bond (O11–H11···O12) in **1** and (b) 1D Z-shaped chains generated via hydrogen bond (O6–H6···O5) in **2**.

of these two isomers are highly sensitive to acidity/basicity of the reaction system. Curiously, although the pH values were dissimilar to each other, the deprotonated degree of carboxyl groups is equivalent, which is confirmed by the IR characteristic absorption at 1715 and 1717 cm^{-1} showing the existence of $-\text{COOH}$. The isomeric relationship stems from the different connectivity of H_3btc ligand, thus resulting in two types of 3D topologies. In isomer **1** the carboxyl coordinates in monodentate mode, whereas the carboxylate group in **2** adopts chelating coordination mode. Considering those previous complexes [20] where the BDC (BDC = 1,4-benzenedicarboxylate) ligands exhibit diverse connectivity, the variation of coordination fashions are profoundly impacted by the pH value of reaction system. The formation mechanisms of pH-dependent supramolecular isomerism need to be further explored.

3.2. Fluorescent properties and DSC analyses

Some zinc-containing coordination polymers [21] usually exhibit fluorescence, and in our study we also investigated the fluorescent properties of isomers **1** and **2** in the solid state. As shown in Fig. S1, **1** and **2** display fluorescence at room temperature with the emission maxima at 350.1 nm ($\lambda_{\text{ex}} = 310.0$ nm) and around 351.4 nm ($\lambda_{\text{ex}} = 302.0$ nm), respectively. It has been proved that the free bipy emits at 535.0 nm ($\lambda_{\text{ex}} = 347.0$ nm) [21b], and H_3btc molecule emits in the range of 370–400 nm [22]. Thus, the similar emission

spectra of these two complexes observed are likely assigned to intraligand $n \rightarrow \pi^*$ transitions [23] within H_3btc molecules. In comparison with the band for uncoordinated H_3btc , the emission spectra for polymers appear hypsochromic shift which should be contributed by the coordination of Zn^{2+} ions to the H_3btc ligands.

To evaluate the thermal stability of the isomers, DSC analyses were performed in the temperature range of 25–590 °C. As shown in Fig. S2, an endothermic peak was observed at 390.8 °C corresponding to the decomposition of framework **1**, while the lantern breakdown of **2** took place at 388.7 °C. The results suggest that isomer **1** is slightly stable than isomer **2**, which can be ascribed to the difference of aromatic interaction.

4. Conclusions

In summary, two open polymeric supramolecular isomers were unprecedentedly isolated and structurally characterized. We have demonstrated what to our knowledge represent the first paradigm of genuine pH-dependent structural isomerism without guest molecules and ligand conformational change and ring-opening process. Our work indicated that the resulting structures were closely tied to the conditions adopted, especially to the solution acidity/basicity. We believe that not only the modular building blocks but also the external chemical stimulation play a crucial role in the assembly process. As expected, such unusual phenomenon endow us with an effective

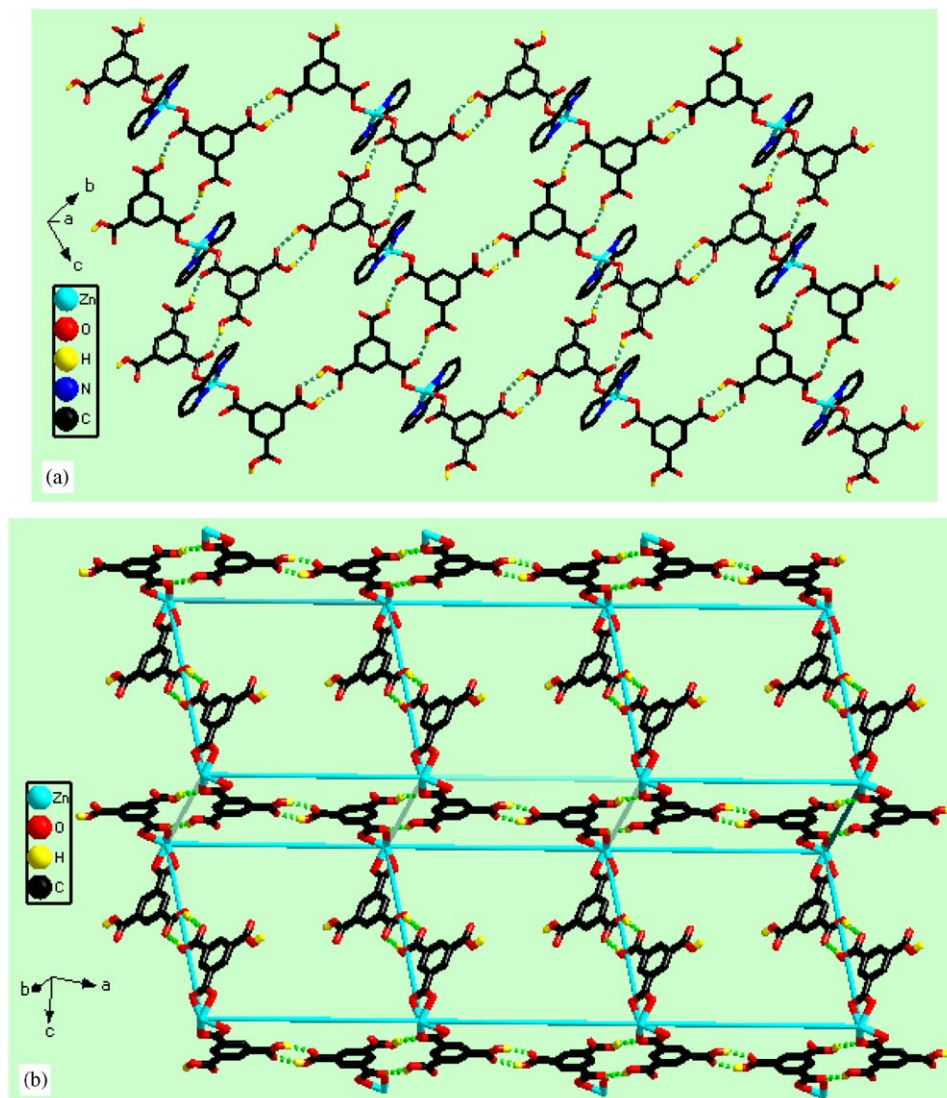


Fig. 3. (a) 2D undulated sheet extended through the hydrogen bond (O6–H6...O1) in **1** showing edge-sharing hydrogen-bonded 40- and 16-membered rings and (b) 2D-stepped sheet extended through hydrogen bond (O3–H3...O2) in **2** showing quasi-rhombus grids. Blue balls represent the Zn(II) atoms. The bipy rings have been omitted for clarity.

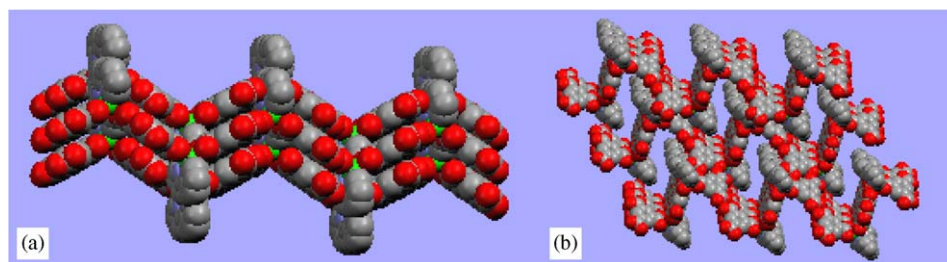


Fig. 4. (a) Side view of the puckered 3D-layered motif in **1** sustained by $\pi \cdots \pi$ stacking and (b) side view of the puckered 3D-layered motif in **2** driven by other hydrogen bond (O6–H6...O5) showing one channel.

strategy for the synthesis of supramolecular isome. Furthermore, this work will greatly advance our understanding of secondary noncovalent interactions (hydrogen-bonding and π – π stacking).

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Supporting information available

X-ray crystallographic files in CIF format, fluorescent spectra and DSC curves of **1** and **2**.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at: [doi:10.1016/j.jssc.2006.04.048](https://doi.org/10.1016/j.jssc.2006.04.048).

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