

## From Diamondoid Network to (4,4) Net: Effect of Ligand Topology on the Supramolecular Structural Diversity

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While *N,N*-bis(4-pyridyl)urea affords a 5-fold interpenetrated diamondoid network, its positional isomer *N,N*-bis(3-pyridyl)urea gave a net-to-net hydrogen-bonded (4,4) net (square grid network) displaying temperature-dependent anion-induced reversible single-crystal-to-single-crystal disorder–order phase transition, when the ligands are reacted with zinc perchlorate.

Building solid-state structures with a predefined molecular organization constitutes the ultimate goal of crystal engineering,<sup>1</sup> a subdiscipline of supramolecular chemistry.<sup>2</sup> Although criticized rather severely,<sup>3</sup> crystal engineering, in general, and crystal engineering of metal–ligand coordination (MLC) polymers, in particular, have emerged as highly challenging as well as rewarding areas of research because of their various potential applications.<sup>4</sup> Intelligent ligand design and the proper choice of a metal center are the main keys to the design of intriguing and useful coordination polymers.<sup>5</sup> On the other hand, crystal engineering of organic solids<sup>6</sup> is mainly governed by strong and directional hydrogen bonding.<sup>7</sup> The combination of both MLC and hydrogen bonding in the design of various supramolecular architectures should

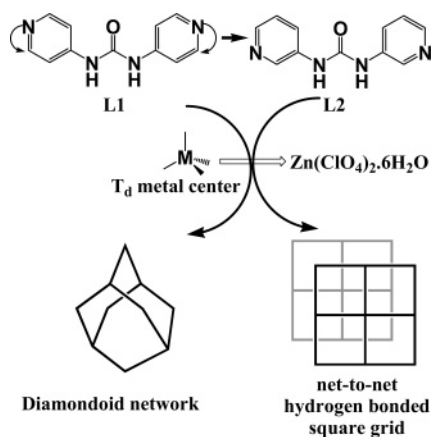
be considered an attractive design strategy because of the possibility of structural variations and guest entrapment induced by specific hydrogen-bonding interactions. Among the various coordination polymers, square grid (SG) coordination polymers<sup>8</sup> and diamondoid networks<sup>9</sup> have gained widespread interest because of their potential applications. A diamondoid network is formed by propagating a tetrahedral ( $T_d$ ) nodal point in all four directions by coordinating a topologically linear bidentate ligand, whereas a SG, a two-dimensional (2D) sheet-type structure, is formed when a square-planar nodal point is propagated in all four directions via MLC with a topologically linear bidentate ligand.

To create a novel supramolecular network using both MLC and hydrogen bonding as the design strategy, we have synthesized two new ligands, namely, *N,N*-bis(4-pyridyl)urea (**L1**) and *N,N*-bis(3-pyridyl)urea (**L2**). **L1** displays more linear ligating topology compared to its positional isomer **L2**. The backbone of the ligands is a urea moiety, which is eminent for its typical hydrogen-bonding network and potential applications.<sup>10</sup> Thus, the coordination polymers derived from these ligands are expected to self-assemble further via complementary hydrogen bonding involving a urea backbone. By keeping the metal coordination geometry fixed as  $T_d$  (such as Zn(II)),<sup>11</sup> we want to explore the resulting supramolecular structures of the solids obtained by reacting  $Zn(ClO_4)_2 \cdot 6H_2O$  in a 1:2 (metal–ligand) ratio with the cor-

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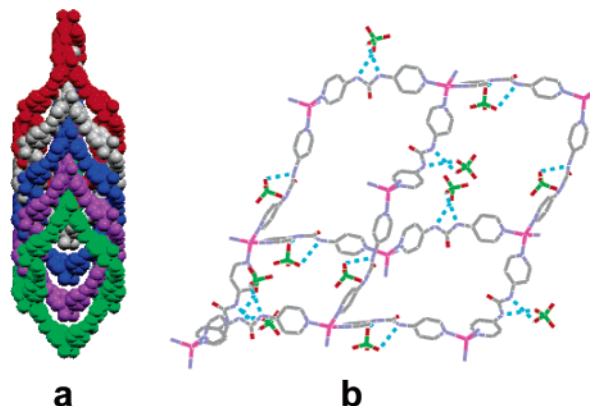
Scheme 1



responding topologically different ligands such as **L1** and **L2**. In this Communication, we report a novel supramolecular structural diversity in the form of a journey from a diamondoid network to a SG network by changing the ligating topology of the ligand (Scheme 1).

While the coordination polymeric compound  $[\text{Zn}(\text{L1})_2(\text{ClO}_4)_2]$  (**1**) obtained from **L1** displays a 5-fold interpenetrated diamondoid network, **L2** produces another coordination polymer  $[\text{Zn}(\text{L2})_2(\text{ClO}_4)_2]$  (**2a**) at room temperature, showing a net-to-net hydrogen-bonded SG network (involving complementary urea hydrogen bonding) having a disordered counterion. **2a** also shows a rare anion-induced temperature-dependent single-crystal-to-single-crystal disorder–order phase transition, producing a polymorph  $[\text{Zn}(\text{L2})_2(\text{ClO}_4)_2]$  (**2b**) at low temperature (100 K).

When topologically linear ligand **L1** is reacted with zinc perchlorate, colorless X-ray-quality single crystals are obtained over a period of 2 weeks (see the Supporting Information). The crystals of **1** belong to a centrosymmetric tetragonal crystal system (space group  $I4$ ), and the asymmetric unit is comprised of a full molecule of **L1**, two Zn(II) ions sitting on a 4-fold symmetry, and a full perchlorate ion.<sup>12</sup> The molecular geometry of ligand **L1** appears to be



**Figure 1.** (a) 5-fold interpenetrated diamondoid network in **1** in a space-filling model; (b) View of a single adamantanoid cage of the diamondoid network in **1** displaying how the hydrogen-bonding backbone of the spacer is holding the perchlorate counterion.

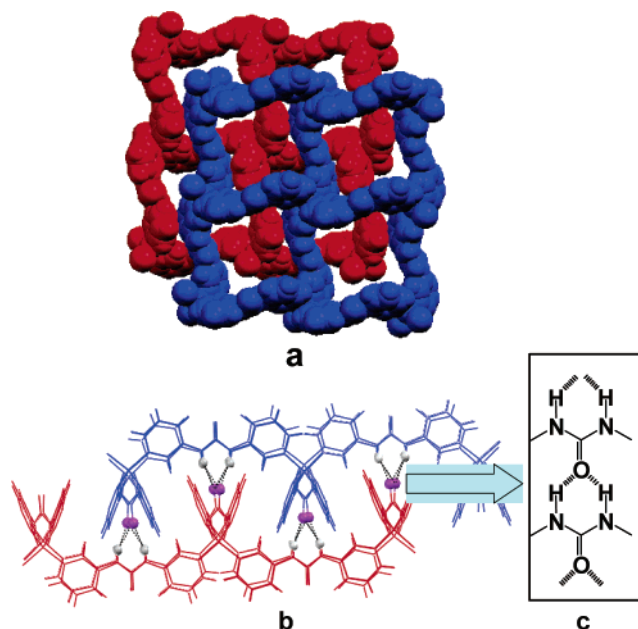
significantly nonplanar, displaying angular deviations of about  $22.8\text{--}26.8^\circ$  when the angle between the plane passing through the urea moiety and the corresponding pyridine rings is considered. The coordinating distance (N–Zn) is found to be 2.003 Å, indicating a strong coordination between the ligand and the metal center. The metal center Zn(II) displays a slightly distorted tetrahedral geometry ( $\angle\text{N–Zn–N} = 99.3(2)\text{--}114.7(1)^\circ$ ). In the crystal structure, the nearly tetrahedral metal center Zn(II) propagates into a diamondoid network by MLC with the ligand **L1**. Various intracage Zn $\cdots$ Zn distances are 13.652, 32.218, and 41.270 Å, indicating a significantly large void space of the diamondoid network. The void space is filled in the crystal structure by a 5-fold interpenetration of the diamondoid network (Figure 1a,b).

It is significant that the urea moiety of the ligand **L1** does not display its typical hydrogen-bonding network in the crystal structure of **1**. Instead, the protons attached to the urea nitrogen atoms form a hydrogen bond with the perchlorate counterion. The oxygen atom of the urea moiety remains free from hydrogen bonding (Figure 1b).

On the other hand, when **L2**, the topologically more angular analogue of **L1**, is reacted with zinc perchlorate (see the Supporting Information), block-shaped golden-colored single crystals suitable for X-ray diffraction are obtained. Crystal structure analysis of **2a** at room temperature reveals that the crystal belongs to a primitive tetragonal crystal system (space group  $P4_2/n$ ) and the asymmetric unit, of which is comprised of a half-ligand molecule sitting on a 2-fold symmetry, a Zn(II) ion sitting on a 4-fold symmetry, and a perchlorate counterion having disordered oxygen atoms.<sup>12</sup> When the data of the same crystal of **2a** are collected at low temperature (100 K) with the hope of reducing the disorder of the counterion, a new crystal phase **2b** emerged. Crystal **2b** belongs to a body-centered tetragonal  $I4_1/a$  space group contrary to the tetragonal primitive ( $P4_2/n$ ) crystal system obtained at room temperature.<sup>12</sup> The asymmetric unit of **2b** contains one Zn(II) ion center sitting on a center of symmetry, one full molecule of the ligand, and a full ordered perchlorate counterion. The reversible nature of the phase transition is confirmed by collecting diffraction data several times on the same crystal at both temperatures. This phenomenon can be regarded as an example of a reversible anion-induced single-crystal-to-single-crystal disorder–order polymorphism<sup>13</sup> triggered by

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(12) X-ray diffraction data for **1**, **2a**, and **2b** are collected using Mo K $\alpha$  ( $\lambda = 0.7107$  Å) radiation on a SMART APEX diffractometer equipped with a CCD area detector. Data collection, data reduction, and structure solution/refinement are carried out using the software package of SMART APEX. All of the structures are solved by direct methods and refined in a routine manner. In all cases, non-hydrogen atoms are treated anisotropically. Whenever possible, the hydrogen atoms are located on a difference Fourier map and refined. In other cases, the hydrogen atoms are geometrically fixed. Crystal data for **1**:  $\text{C}_{11}\text{H}_{10}\text{Cl}_1\text{N}_4\text{O}_5\text{Zn}_{0.50}$ , FW = 346.37, tetragonal,  $I4$ ,  $a = b = 17.880(5)$  Å,  $c = 8.254(4)$  Å,  $V = 2638.5(17)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.744$  g/cm<sup>3</sup>,  $F(000) = 1408$ ,  $T = 100$  K. Final residuals (for 202 parameters) were  $R1 = 0.0443$  for 2709 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.0545$ ,  $wR2 = 0.0909$ , and  $\text{GOF} = 1.025$  for all 3082 reflections. Crystal data for **2a**:  $\text{C}_{5.50}\text{H}_5\text{Cl}_{0.50}\text{N}_2\text{O}_{2.02}\text{Zn}_{0.25}$ , FW = 165.54, tetragonal,  $P4_2/n$ ,  $a = b = 12.0544(10)$  Å,  $c = 9.2802(15)$  Å,  $V = 1348.5(3)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.631$  g/cm<sup>3</sup>,  $F(000) = 673$ ,  $T = 298$  K. Final residuals (for 126 parameters) were  $R1 = 0.0580$  for 1480 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.0605$ ,  $wR2 = 0.1813$ , and  $\text{GOF} = 1.103$  for all 1601 reflections. Crystal data for **2b**:  $\text{C}_{11}\text{H}_{10}\text{Cl}_1\text{N}_4\text{O}_5\text{Zn}_{0.50}$ , FW = 346.37, tetragonal,  $I4_1/a$ ,  $a = b = 16.8992(7)$  Å,  $c = 18.4603(14)$  Å,  $V = 5271.9(5)$  Å<sup>3</sup>,  $Z = 16$ ,  $D_c = 1.746$  g/cm<sup>3</sup>,  $F(000) = 2816$ ,  $T = 100$  K. Final residuals (for 235 parameters) were  $R1 = 0.0251$  for 2766 reflections with  $I > 2\sigma(I)$ , and  $R1 = 0.0294$ ,  $wR2 = 0.0675$ , and  $\text{GOF} = 1.058$  for all 3089 reflections.



**Figure 2.** Structure of **2b**: (a) two SG networks (red and blue) sitting on top of each other displaying a slipped packing; (b) edge view of the assembly of two SG networks displaying net-to-net hydrogen bonding through typical urea hydrogen bonding; the interacting oxygen and hydrogen atoms (represented by a ball-and-stick model) of the urea moiety are shown in purple and gray, respectively; (c) schematic representation of the typical urea hydrogen bonding.

the degree of order of the counterion. It may be noted that the X-ray structure of **1** at room temperature shows a disordered perchlorate ion, which becomes ordered at low temperature (100 K) without any phase transition.

The molecular geometry of the ligand is found to be significantly nonplanar in both crystal forms. The angular twists are  $31.0^\circ$  and  $28.7\text{--}34.5^\circ$  in **2a** and **2b**, respectively, when the angle between the plane passing through the urea moiety and the corresponding pyridine rings is considered. The metal–ligand coordinating distance is found to be in the close range of  $2.005(1)\text{--}2.012(2)$  Å in both **2a** and **2b**, which is comparable to that obtained in **1**. The metal center in both forms displays a slightly distorted tetrahedral geometry ( $\angle\text{N–Zn–N} = 102.8(1)\text{--}114.1(1)^\circ$ ). The overall supramolecular networks in both **2a** and **2b** are identical, displaying a (4,4) net triggered by the MLC of the topologically more angular ligand **L2** with the tetrahedral metal center. The metal–metal separation distances are 12.054 and 11.958 Å in **2a** and **2b**, respectively. The intranet angles involving the metal centers are  $90^\circ$  and  $89.9^\circ$  in **2a** and **2b**, respectively, displaying the SG nature of the net. The (4,4) nets are found to pack on top of each other, displaying a slipped geometry stabilized through typical urea hydrogen bonding involving N–H $\cdots$ O interactions ( $\text{N}\cdots\text{O} = 2.893(3)$  Å;  $\angle\text{N–H}\cdots\text{O} = 160.1(5)^\circ$  in **2a**;  $\text{N}\cdots\text{O} = 2.842(2)\text{--}2.905(2)$  Å;  $\angle\text{N–H}\cdots\text{O} = 155.8(2)\text{--}160.7(2)^\circ$  in **2b**; Figure 2).

The size of the grid (taking into account the van der Waals radii) within the net in both crystal forms is  $\sim 9 \times 9$  Å. It is interesting to note that no interpenetration of the network is observed in these crystal forms despite having such a large grid size. Instead, the available void space of the grid is occupied by the counterion as well as by some part of the ligand molecule protruding from the adjacent hydrogen-bonded net. To the best of our knowledge, examples of a net-to-net hydrogen-bonded SG coordination polymer are rare.<sup>14</sup> It may be noted that the major peak positions of the powder X-ray diffraction patterns of the bulk solids of **1** and **2a** match well with those of the simulated patterns obtained from respective single-crystal data, indicating the presence of mainly one crystalline phase in the corresponding coordination polymers **1** and **2a** (see the Supporting Information).

In summary, two fascinating coordination polymeric networks (a 5-fold diamondoid network and a rare net-to-net hydrogen-bonded SG network) derived from two newly synthesized topologically variant pyridylurea-based bidentate ligands and tetrahedral metal nodes Zn(II) have been reported. While the hydrogen-bonding backbone in the diamondoid network is holding the counterion (perchlorate) by hydrogen-bonding interactions, the SG network shows rare net-to-net hydrogen bonding displaying propagation of the polymer in 2D (SG) via MLC and self-assembly of the polymeric (4,4) net in 3D via a strong and self-complementary classical urea hydrogen bond. The temperature-dependent anion-induced reversible single-crystal-to-single-crystal disorder–order phase transition is also a new phenomenon in coordination polymers. The overall supramolecular structural diversity in going from a diamondoid network to a (4,4) net architecture is attributed to the ligating topology of the ligands. Engineering of these ligands at the molecular level in order to create microporous coordination polymers is underway.

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**Supporting Information Available:** Syntheses and analytical data for ligands **L1** and **L2**, coordination polymers **1** and **2**, hydrogen bonding parameters for **1**, **2a**, and **2b**, and a powder X-ray diffraction comparison plot (simulated and bulk solid) in PDF format; crystallographic data for **1**, **2a**, and **2b** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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