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# A Noninterpenetrated 1D Molecular Ladder and 2D Butterfly Network: Effect of Positional Isomerism of Semirigid Bis(pyridylmethyl)pyromellitic Diimide Ligands on the Architecture of Their Metal(II) Complexes

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Three new complexes [Cd(4-pmpmd)$_{1.5}$(NO$_3$)$_2$]•CHCl$_3$ (**1**), [Cd(3-pmpmd)$_{1.5}$(NO$_3$)$_2$]•EtOH (**2**), and [Zn(3-pmpmd)$_{1.5}$(NO$_3$)$_2$]•MeOH (**3**) (3- or 4-pmpmd = *N*,*N*′-bis(3- or 4-pyridylmethyl)pyromellitic diimide) containing T-shaped building blocks have been obtained from reactions between the long semirigid ligands 3- or 4-pmpmd and either cadmium or zinc nitrate. **1** forms noninterpenetrated 1D molecular ladders that are linked via multiple, complementary intermolecular C–H•••O hydrogen bonds that effect the 3D alignment. **2** and **3** are isostructural and feature a noninterpenetrated 2D butterfly-shaped network with (6,3) topology. Multiple intermolecular C–H•••O hydrogen bonds exist between the 2D layers and generate the 3D framework. The structural differences between **1** and **2** or **3** are attributed to the different conformations adopted by the ligands, which illustrate the influence of positional isomerism on the resultant supramolecular architectures of metal complexes.

## Introduction

The design and synthesis of functional polymers via the rational combination of bridging, multidentate ligands with transition metal ions is of current interest in the field of supramolecular coordination chemistry, and many, varied network topologies have been identified.[1−4] Many complexes exhibiting encouraging properties, including magnetism, photoluminescence, catalytic properties, and gas storage, have been reported[5−8] during the past decade. On the basis of this extensive body of work, it is now generally accepted that the diverse framework structures are greatly dependent upon the functionality and the geometry of the organic ligands used in their assembly. Interestingly, compared to the vast amount of effort targeted at the development of complexes containing rigid bipyridyl ligands,[9−10] flexible bis(pyridyl)-

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substituted ligands have not been researched nearly as extensively.[11] Nonetheless, numerous multidentate ligands with diverse spacers linking terminal coordinating groups have already been synthesized and used to generate a large number of 0D to 3D functional supramolecular structures.[12−14] These ligands have attracted increased attention because the flexibility and conformational freedom of such multifunctional ligands promises greater possibilities for constructing novel frameworks and, potentially, for the fine-tuning of such structures.

The combination of an $M(NO_3)_2$ node with a bipyridyl ligand is known to often result in a T-shaped building block that, subsequently, can assemble into a variety of feasible network topologies and structural motifs[11] including 1D ladders, 2D brick walls, parquet (herringbone) patterns, molecular bilayers, and 3D frameworks.[15] It is noteworthy that while the early work involving T-shaped building blocks relied on $M(NO_3)_2$ nodes and *flexible* bipyridyl ligands, such as 1,4-bis(4-pyridylmethyl)benzene and 1,2-bis(4-pyridyl)ethane,[16] the enormous growth and development in this area was, in fact, based on the use of *rigid* bipyridyl ligands.[11,15] However, when long, rigid ligands form 1D molecular ladders or 2D networks, they contain large metallacyclic rings because of the lengthy nature of the ligands, and these metallacyclic rings are often interpenetrated to form higher dimensional structures. On the other hand, the judicious design of flexible ligands can take advantage of the fact that the spacer part of the ligands can be readily functionalized, and structures of the complexes can thus be deliberately altered to avoid further interpenetration.

We have been focusing our efforts on the design of suitable ligands capable of assembling preselected molecular architectures and have observed that ligands constructed around central arene groups and extended with imidazolyl (Im) or benzimidazolyl (Bim) pendants (arms) can form discrete cyclic or cage structures as well as infinite polymeric structures.[17] We prefer to classify this type of ligand as a *semirigid* ligand,[18] because both the spacer and the arms are rigid, and the flexibility arises strictly from the freely rotatable methylene ($-CH_2-$) joints. These semirigid ligands are quite different from highly flexible linear ligands containing soft aliphatic or oligoglycol chains as spacers.[13] The restricted flexibility of semirigid ligands, in contrast with completely flexible ligands, provides us with more control for directing the formation of target structures. This has enabled us to use semirigid ligands specifically for the preparation of both *closed* and *polymeric* structures, and we have termed the structural interconversion process between the closed and polymeric structures as *ring-opening isomerism*.[18] In this paper we report the assembly of a 1D molecular ladder $[Cd(4\text{-pmpmd})_{1.5}(NO_3)_2]\cdot CHCl_3$ (**1**) and two 2D butterfly networks $[Cd(3\text{-pmpmd})_{1.5}(NO_3)_2]\cdot EtOH$ (**2**) and $[Zn(3\text{-pmpmd})_{1.5}(NO_3)_2]\cdot MeOH$ (**3**) (4-pmpmd = *N,N′*-bis(4-pyridylmethyl)pyromellitic diimide; 3-pmpmd = *N,N′*-bis(3-pyridylmethyl)pyromellitic diimide) containing similar T-shaped connecting units. For these examples, the formation of two distinct structural topologies appears to be related to the *positional isomerism* of the two pyridyl arms (3- or 4-substituted), while the incorporation of pyromellitic diimide (pmd) as a spacer enables the formation of a hydrogen bond network that plays an important role in preventing the interpenetration that is often observed in polymeric structures containing long ligands.

## Experimental Section

All chemicals were commercial products of reagent grade and were used without further purification. Infrared spectra were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer in

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the region 4000−400 $cm^{-1}$ using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The XRD patterns were recorded on a D/Max-IIIA diffractometer with graphite-monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å). Thermogravimetric analyses were carried out on a NETZSCH TG 209 instrument under flowing nitrogen by heating the samples from 25 to 600 °C.

**Preparation of *N,N′*-Bis(3-pyridylmethyl)pyromellitic Diimide (3-pmpmd).** A mixture of pyromellitic dianhydride (4.4 g, 20 mmol) and 3-(aminomethyl)pyridine (4.3 g, 41 mmol) in DMF (40 mL) was heated to reflux with stirring for 5 h. On cooling, the yellow solution was filtered and the off-white crude solid was collected and washed with cold DMF. A white powder was obtained by recrystallization of the solid from DMF/$CH_3CH_2OH$ (20 mL/5 mL). Yield: 78%. Anal. Calcd for $C_{22}H_{14}O_4N_4$: C, 66.33; H, 3.52; N, 14.07. Found: C, 66.53; H, 3.67; N, 14.36%. IR (KBr, $cm^{-1}$): 3461 (w), 3001 (m), 2975 (m), 1767 (s), 1706 (vs), 1576 (w), 1429 (s), 1391 (vs), 1344 (s), 1307 (m), 1091 (s), 1024 (m), 923 (m), 736 (s), 712 (m), 628 (m).

***N,N′*-Bis(4-pyridylmethyl)pyromellitic Diimide (4-pmpmd).** A mixture of pyromellitic dianhydride (4.4 g, 20 mmol) and 4-(aminomethyl)pyridine (4.3 g, 41 mmol) in DMF (50 $mL^3$) was heated to reflux with stirring for 6 h. On cooling, the yellow mixture was filtered and the crude product was collected. Light brown crystals were obtained by recrystallization of the precipitate from DMF. Yield: 84%. Anal. Calcd for $C_{22}H_{14}O_4N_4$: C, 66.33; H, 3.52; N, 14.07. Found: C, 66.38; H, 3.68; N, 14.30. IR (KBr, $cm^{-1}$): 3461 (w), 3031 (m), 2980 (w), 1765 (s), 1707 (vs), 1599 (s), 1562 (m), 1422 (s), 1394 (vs), 1352 (vs), 1109 (s), 933 (s), 726. (s), 626 (w).

**[Cd(4-pmpmd)$_{1.5}$($NO_3$)$_2$]·$CHCl_3$ (1).** A solution of $Cd(NO_3)_2 \cdot 4H_2O$ (15.4 mg, 0.05 mmol) in EtOH (5 mL) was layered onto a solution of 4-pmpmd (39.8 mg, 0.1 mmol) in $CHCl_3$ (6 mL) in a test tube. The solutions were left to stand for 3 days at room temperature, and colorless block crystals were obtained. Yield: 57%. Anal. Calcd for $C_{34}H_{22}$ $CdCl_3N_8O_{12}$: C, 42.84, H, 2.33, N, 11.75. Found: C, 42.69, H, 2.63, N, 11.90. IR (KBr, $cm^{-1}$): 3540 (w), 3099 (w), 1773 (s), 1717 (vs), 1615 (s), 1452 (s), 1428 (s), 1391 (vs), 1347 (s), 1305 (s), 1225 (m), 1120 (m), 1086 (m), 1019 (w), 934 (m), 751 (m), 726 (s), 630 (w), 558 (w), 486 (w).

**[Cd(3-pmpmd)$_{1.5}$($NO_3$)$_2$]·EtOH (2).** The complex was prepared in the same way as **1** except that 3-pmpmd was used instead of 4-pmpmd. Yield: 63%. Anal. Calcd for $C_{35}H_{27}CdN_8O_{13}$: C, 47.77, H, 3.09, N, 12.73. Found: C, 47.89, H, 3.18, N, 13.08. IR (KBr, $cm^{-1}$): 3544 (w), 3476 (b), 3042 (w), 1774 (s), 1723 (vs), 1607 (w), 1461 (s), 1438 (s), 1390 (vs), 1361 (s), 1294 (s), 1118 (m), 1096 (m), 1030 (w), 927 (w), 734 (s), 707 (m), 644 (w), 559 (w).

**[Zn(3-pmpmd)$_{1.5}$($NO_3$)$_2$]·$CH_3OH$ (3).** The complex was prepared in the same way as that for **2** except that $Zn(NO_3)_2 \cdot 6H_2O$ in $CH_3OH$ (5 mL) was used instead of $Cd(NO_3)_2 \cdot 4H_2O$ in EtOH. Yield: 69%. Anal. Calcd for $C_{34}H_{26}ZnN_8O_{13}$: C, 49.80, H, 3.20, N, 13.66. Found: C, 49.13, H, 3.07, N, 13.61. IR (KBr, $cm^{-1}$): 3543 (w), 3506 (b), 3015 (w), 1774 (s), 1723 (vs), 1609 (w), 1468 (s), 1432 (s), 1390 (vs), 1361 (s), 1308 (s), 1118 (m), 1100 (m), 1024 (w), 926 (w), 735 (s), 708 (m), 647 (w), 558 (w).

**X-ray Crystallography.** Single crystals of **1**−**3** of suitable dimensions were mounted onto thin glass fibers. All the intensity data were collected on a Bruker SMART CCD diffractometer (Mo Kα radiation, $\lambda = 0.710\ 73$ Å) in Φ and ω scan modes. Structures were solved by Patterson methods followed by difference Fourier syntheses and then refined by full-matrix least-squares techniques against $F^2$ using SHELXTL.[19a] Except for atoms belonging to disordered solvate molecules, all other non-hydrogen atoms were refined with anisotropic thermal parameters. The solvate EtOH molecules in **2** are disordered over two positions and were refined with fractional site occupancy. Absorption corrections were applied using SADABS.[19b] All hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Crystallographic data and refinement parameters for the complexes are presented in Table 1. Relevant atomic distances and bond angles are collected in Table 2. CCDC reference nos.: 238372 (**1**); 238370 (**2**); (**3**) 246733.

**Table 1.** Crystallographic Data for Complexes **1**−**3**

| param | 1 | 2 | 3 |
|---|---|---|---|
| formula | $C_{34}H_{22}CdCl_3N_8O_{12}$ | $C_{35}H_{27}CdN_8O_{13}$ | $C_{34}H_{26}ZnN_8O_{13}$ |
| fw | 953.35 | 880.05 | 820.00 |
| cryst system | triclinic | monoclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/a$ | $P2_1/a$ |
| $a$/Å | 11.012(1) | 15.403(2) | 15.361(4) |
| $b$/Å | 13.190(2) | 13.614(2) | 13.388(4) |
| $c$/Å | 13.934(2) | 17.400(2) | 17.105(5) |
| α/deg | 95.099(2) | 90 | 90 |
| $\beta$/deg | 106.142(2) | 103.251(2) | 103.427(5) |
| $\gamma$/deg | 99.003(2) | 90 | 90 |
| $V$/Å$^3$ | 1901.3(4) | 3551.4(7) | 3421.6(17) |
| Z | 2 | 4 | 4 |
| $D_{calcd}$/g cm$^{-3}$ | 1.665 | 1.646 | 1.592 |
| cryst size, mm | 0.42 × 0.40 × 0.27 | 0.50 × 0.25 × 0.05 | 0.45 × 0.30 × 0.15 |
| $\mu$(Mo Kα)/mm$^{-1}$ | 0.859 | 0.696 | 0.800 |
| $T$/K | 298(2) | 293(2) | 293(2) |
| no. of unique reflcns | 16 303 | 21 863 | 20 845 |
| reflcns used [$I > 2\sigma(I)$] | 8189 | 7794 | 7460 |
| R$_1$ [a] | 0.0403 | 0.0393 | 0.0409 |
| wR$_2$ [b] | 0.1215 | 0.0718 | 0.0996 |

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

## Results and Discussion

**Syntheses and Characterization.** As shown in Scheme 1, two semirigid ligands that are positional isomers have been prepared and employed for the syntheses of complexes **1**−**3**. The ligand 4-pmpmd was obtained in about 80% yield by improving on a procedure from the literature.[19e,20] The ligand 3-pmpmd is a new compound that was obtained using a similar reaction of pyromellitic dianhydride with 3-aminomethylpyridine in a 1:2 molar ratio in DMF at reflux (Scheme 1). The two ligands are insoluble in water and most of the common solvents, but both are moderately soluble in hot DMF and $CHCl_3$. When the desired ligand in $CHCl_3$ was allowed to react slowly with $M(NO_3)_2$ in EtOH (M = Cd) or MeOH (M = Zn) in either a 2:1 or a 1:1 molar ratio by the layering method, crystalline products suitable for X-ray diffraction analysis were obtained after letting the solutions sit for several days at room temperature; this suggests that the composition of the product is insensitive to the reactant concentration ratios.

The ligands 3-pmpmd and 4-pmpmd have the same long, rigid pyromellitic diimide (pmd) spacer, which provides

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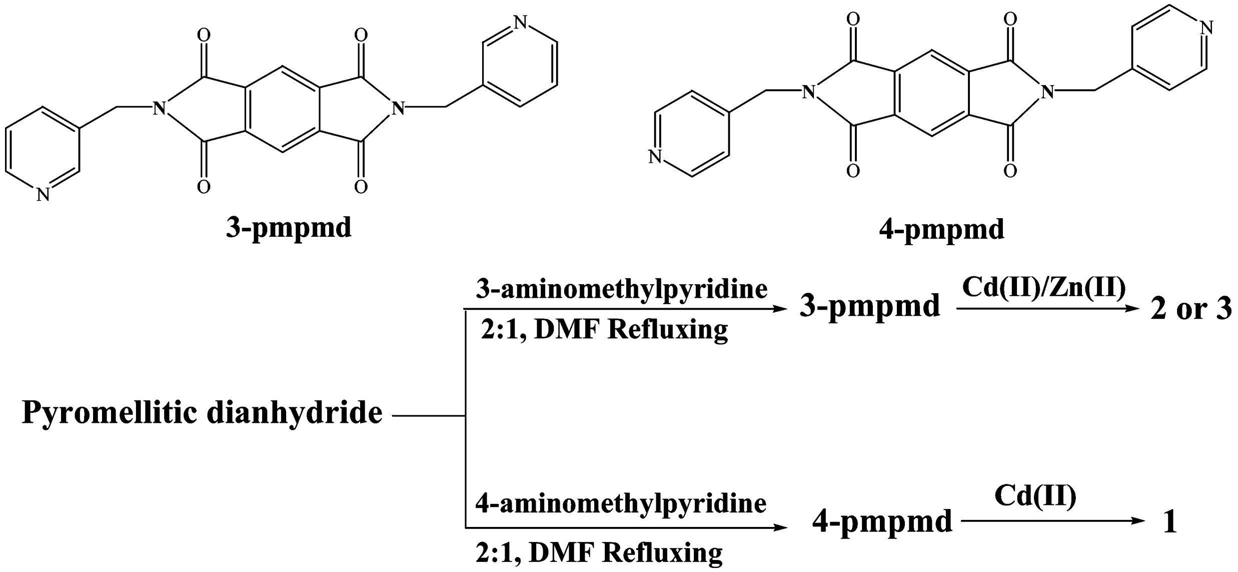
**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Compounds **1**−**3**[a]

| 1 | | 2 | | 3 | |
|---|---|---|---|---|---|
| Cd(1)−N(1) | 2.319(3) | Cd(1)−N(1) | 2.329(3) | Zn(1)−N(1) | 2.164(2) |
| Cd(1)−N(4)$^1$ | 2.316(3) | Cd(1)−N(4)$^1$ | 2.319(3) | Zn(1)−N(4)$^1$ | 2.103(2) |
| Cd(1)−N(5) | 2.321(3) | Cd(1)−N(5) | 2.345(3) | Zn(1)−N(5) | 2.191(2) |
| Cd(1)−O(7) | 2.493(3) | Cd(1)−O(7) | 2.452(3) | Zn(1)−O(7) | 2.444(3) |
| Cd(1)−O(8) | 2.447(3) | Cd(1)−O(8) | 2.359(3) | Zn(1)−O(8) | 2.134(3) |
| Cd(1)−O(10) | 2.476(3) | Cd(1)−O(10) | 2.382(3) | Zn(1)−O(10) | 2.110(2) |
| Cd(1)−O(11) | 2.423(3) | Cd(1)−O(12) | 2.476(3) | | |
| N(1)−Cd(1)−N(5) | 95.09(9) | N(4)$^1$−Cd(1)−N(1) | 93.21(11) | N(4)$^1$−Zn(1)−N(1) | 94.09(11) |
| N(4)$^1$−Cd(1)−N(5) | 100.24(9) | N(4)$^1$−Cd(1)−N(5) | 92.37(10) | N(4)$^1$−Zn(1)−N(5) | 94.20(8) |
| N(4)$^1$−Cd(1)−N(1) | 163.84(9) | N(1)−Cd(1)−N(5) | 174.19(11) | N(1)−Zn(1)−N(5) | 171.68(8) |
| O(7)−Cd(1)−O(8) | 51.29(10) | O(7)−Cd(1)−O(8) | 52.49(12) | O(7)−Zn(1)−O(8) | 54.60(10) |
| O(10)−Cd(1)−O(11) | 51.82(10) | O(10)−Cd−O(12) | 52.24(12) | O(10)−Zn(1)−O(8) | 127.03(11) |
| C(3)−C(6)−N(2) | 114.1(3) | C(2)−C(6)−N(2) | 112.4(3) | C(2)−C(6)−N(2) | 113.3(2) |
| N(3)−C(17)−C(18) | 112.5(2) | N(3)−C(17)−C(18) | 111.3(3) | N(3)−C(17)−C(18) | 111.1(2) |
| C(25)−C(28)−N(6) | 111.4(3) | C(24)−C(28)−N(6) | 113.6(3) | C(24)−C(28)−N(6) | 112.9(2) |

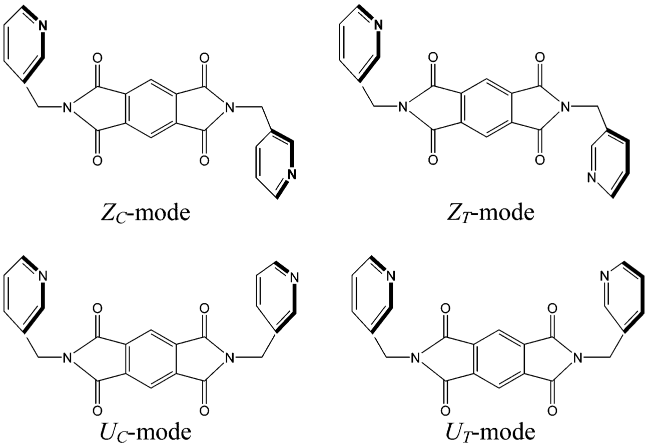
[a] Symmetry transformations indicated by a superscript 1 used to generate equivalent atoms: (1) $x + 1, y, z - 1$ for **1**; $-x + 1/2, y - 1/2, -z + 2$ for **2**; $-x + 1/2, y - 1/2, -z + 1$ for **3**.

**Scheme 1.** Molecular Structure of the Ligands 3- and 4-pmpmd and the Synthetic Procedures of the Ligands and Their Complexes



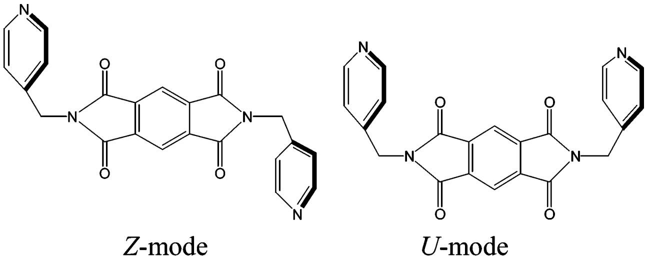
potential H-bond donors (C−H) and acceptors (C═O), and both ligands have the two pyridyl arms acting as nonchelating, coordinating donors. The functionalized central spacer of this semirigid ligand may lead to a coordination chemistry different from that of ligands containing a benzene-based spacer,[17a−d] which have been used by us previously; we are, therefore, interested in how the topology of the resultant metal complexes will be affected by the different functionality and structure of the central spacer. Furthermore, since the two pyridyl arms can rotate freely around the methylene groups (−$CH_2$−), a variety of conformations are possible for the two ligands. Theoretically, the ligand can take on any one of four possible conformations, $Z_T$-, $Z_C$-, $U_T$-, or $U_C$-mode, which are depicted in Chart 1. The two 3-pyridyl groups of 3-pmpmd can be located on either the same or opposite sides of the central pmd piece, and in each case, the nitrogen donors can point in either the same or opposite direction. By comparison, the 4-pyridyl groups of 4-pmpmd possess $C_2$ symmetry, which reduces the possible conformations to only two, namely the *U*- and *Z*-modes, as shown in Chart 2. Such symmetrical and conformational differences result from the different positions of the nitrogen atom on the pyridyl group of the two ligands; i.e., they are 3,3′- and 4,4′-positional isomers. Therefore, the reaction of the two

**Chart 1.** Possible Coordination Modes of the Ligand 3-pmpmd[a]



[a] *Z* for *anti*-orientation of the pyridyl rings, *U* for *syn*-orientation of the pyridyl rings, *C* for the N in pyridyls facing the same direction (*cis*), and *T* for the N in pyridyls opposing each other (*trans*).

**Chart 2.** Possible Coordination Modes of the Ligand 4-pmpmd[a]



[a] *Z* for *anti*-orientation of the pyridyl rings and *U* for *syn*-orientation of the pyridyl rings

ligands with the same metal ions may produce different structures, dictated by the conformational preference adopted by the individual ligand. Indeed in the noninterpenetrated polymeric ladder structure (**1**) containing the symmetrical 4-pmpmd, the ligand is found in the pure *anti*-conformation (*Z*-mode). By contrast, in **2** and **3**, which contain the less symmetrical 3-pmpmd ligand, the 2D noninterpenetrated butterfly-shaped (6,3) net displays both the $Z_T$- and $U_C$-mode ligand conformations. The latter structure forms with the $M(NO_3)_2$−tris(pyridyl) motif as the common building block and also exhibits intermolecular hydrogen bonding that helps to prevent structural interpenetration (see Crystal Structure section).

The IR spectra of complexes **1**−**3** show two strong absorption bands at 1452−1468 and 1294−1308 $cm^{-1}$ attributed to $\nu(NO_3^-)$. The characteristic absorptions of the pyromellitic diimide carbonyl groups were observed at 1717 and 1773 $cm^{-1}$ for **1** and at 1723 and 1774 $cm^{-1}$ for **2** and **3**. These bands are all blue-shifted relative to those of the free ligands (1707 and 1765 $cm^{-1}$ for 4-pmpmd, and 1706 and 1767 $cm^{-1}$ for 3-pmpmd). It is worth pointing out that in a comparison of the carbonyl absorptions of **1** and **2** (or **3**), one notices that one of the $\nu(C{=}O)$ bands in **1** is less blue-shifted (by about 7 $cm^{-1}$) than the corresponding band in **2**, which may be related to the difference in hydrogen bond formation in **1** and **2** (vide infra). In the IR specta of **2** and **3**, the broad bands centered at 3476 and 3506 $cm^{-1}$, respectively, indicate the presence of hydroxyl groups from the solvate molecules. For **1**, the band appearing at 751 $cm^{-1}$ is tentatively assigned as a $\nu(C{-}Cl)$ vibration.

The bulk phase purity of the complexes was convincingly established by X-ray powder diffraction measurements. Figure S1 shows the observed powder diffraction pattern acquired on the as-prepared compound **1** together with the calculated pattern generated from the single-crystal X-ray diffraction data. The peak positions of the measured pattern closely match those of the simulated one, although the intensities differ slightly, probably due to preferred orientation effects. The diffraction patterns for complexes **2** and **3** are depicted in Figures S2 and S3, which demonstrate the close match between the observed and the calculated patterns, confirming that a single phase (greater than ~95% purity) is formed for each complex.

**Crystal Structure. $[Cd(4\text{-pmpmd})_{1.5}(NO_3)_2]\cdot CHCl_3$ (1).** This complex exhibits a ladderlike structure where the Cd(II) centers are heptacoordinated, as shown in Figure 1.

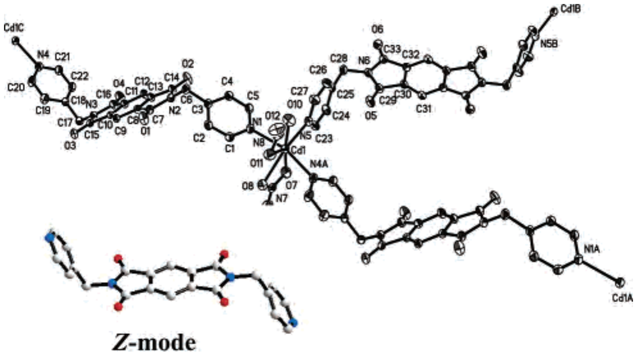


**Figure 1.** Thermal ellipsoid plot of the crystal structure in **1** drawn with 30% probability ellipsoids and ball-and-stick representation of the *Z*-mode of 4-pmpmd.

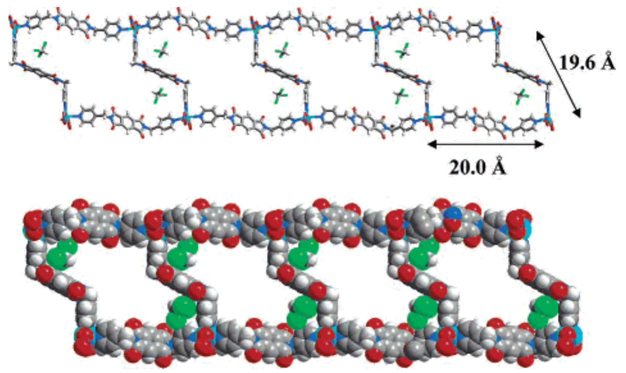


**Figure 2.** 1D molecular ladder in **1** showing enclathration of $CHCl_3$ and the staggered cavity.

This heptacoordinated $CdN_3O_4$ environment is composed of four oxygen atoms from two bidentate nitrate groups and three nitrogen atoms from three independent 4-pmpmd ligands bound to the metal ion in a distorted T-joint fashion. The Cd−N and Cd−O bond lengths ranging from 2.316(3) to 2.321(3) Å and 2.423(3) to 2.493(3) Å (Table 2), respectively, are comparable to the bond lengths in other Cd(II) coordinated complexes containing similar T-shaped building blocks.[11,15] The self-assembly of the T-shaped $Cd(4\text{-pmpmd})_3$ building blocks results in a 1D molecular ladder with remarkably large $Cd_4(4\text{-pmpmd})_4$ rings having dimensions of about 20 × 20 $Å^2$, estimated using the Cd···Cd separations on the edges as shown in Figure 2. All 4-pmpmd ligands in **1** take on the *Z*-mode conformation to constitute the rungs and side rails of the ladder, and this conformation is quite similar to that found in the first molecular ladder reported by Fujita[16a] in the complex obtained from the reaction of $Cd(NO_3)_2$ and 1,4-bis(4-pyridylmethy)lbenzene (bpmb) in a 2:3 molar ratio. A similar conformation was also observed in the 2D weave structure of $HgI_2(4\text{-pmpmd})$, which was synthesized using the same ligand.[17e] It is notable that this *Z*-mode conformation of the ligand causes the rungs of the ladder to be zigzag, rather than straight, such that the rhomboid cavity within the ladder is naturally divided into two segments. Two chloroform solvate molecules are held at the two opposite corners, leaving a spacious cavity in the middle, as shown in Figure 2.

**Table 3.** Hydrogen Bonds Distances (Å) and Angles (deg) for Complexes **1**−**3**

| complex | donor−H···acceptor | D−H | H···A | H···A | D−H···A |
|---|---|---|---|---|---|
| 1 | C(4)−H(4a)···O(2) | 0.93 | 2.50 | 3.219(1) | 134 |
| | C(12)−H(12a)···O(4) | 0.93 | 2.37 | 3.284(1) | 166 |
| | C(19)−H(19a)···O(1) | 0.93 | 2.38 | 3.189(1) | 145 |
| 2 | C(1)−H(1a)···O(9) | 0.93 | 2.42 | 3.286(5) | 155 |
| | C(3)−H(3a)···O(11) | 0.93 | 2.51 | 3.408(5) | 162 |
| | C(6)−H(6a)···O(9) | 0.97 | 2.39 | 3.326(5) | 161 |
| | C(20)−H(20a)···O(6) | 0.93 | 2.50 | 3.227(5) | 135 |
| | C(26)−H(26a)···O(6) | 0.93 | 2.58 | 3.220(6) | 126 |
| 3 | C(3)−H(3a)···O(11) | 0.93 | 2.48 | 3.346(4) | 156 |
| | C(6)−H(6a)···O(9) | 0.97 | 2.33 | 3.277(4) | 167 |
| | C(9)−H(9a)···O(3) | 0.93 | 2.47 | 3.277(3) | 145 |
| | C(20)−H(20a)···O(5) | 0.93 | 2.45 | 3.202(4) | 138 |

A detailed examination of the crystal packing revealed that the remaining cavity inside the ladder is not empty. The side rails in **1** are involved in complex but well-ordered intermolecular hydrogen bonding interactions (Table 3), which dictate the arrangement of the ladders and which also prevent interpenetration though the cavities are quite large. As shown in Figure 3, two types of C−H···O hydrogen bonds[21] are present in the crystal packing. One is inside the cavity and the other is outside the cavity, and in both cases the distances between the hydrogen and oxygen atoms are well below the sum of the van der Waals radii of 2.72 Å (H = 1.20 and O = 1.52 Å). The outside C−H···O hydrogen bond exists between the O1 atom, belonging to the pmd spacer, and the C19 atom, belonging to the pyridyl group, connecting the molecular ladders into a 2D sheet (green). The hydrogen bonds between the sheets cause the sheets to stack in an offset fashion, thus blocking channels that could potentially house interpenetrating networks. These hydrogen bonds exist in two sets: one between O4 and C12, both part of the pmd piece; the other between O2 and C4, belonging to the pmd and pyridyl groups, respectively. Each set of C−H···O hydrogen bonds results in 2D stepped sheets running in different directions as shown in Figure 3. All 2D sheets described above are cross-linked, with each ladder bound to six neighboring ladders via C−H···O hydrogen bonds. A noticeable feature of these hydrogen bonds is that they are formed complementarily in pairs, thus generating a closely packed, well-arranged 3D framework.

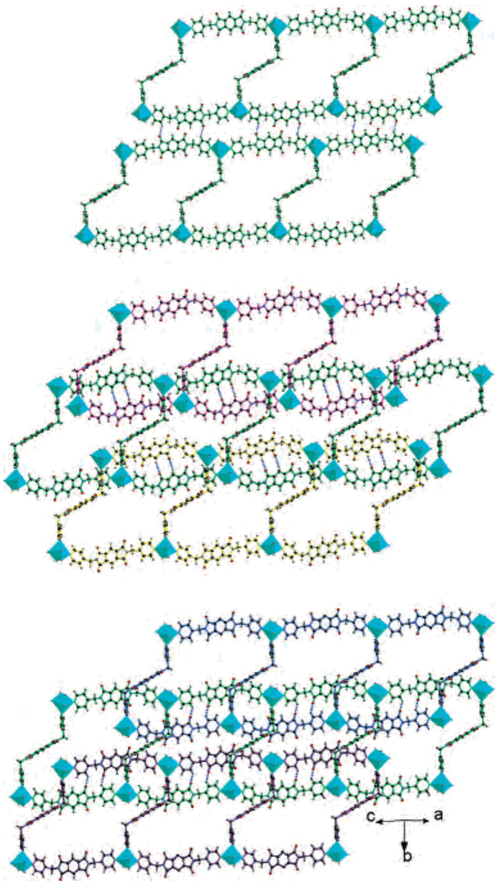


**Figure 3.** 2D sheets formed via complementary C−H···O hydrogen bonds between ladders in **1** running in different directions. Ladders are differentiated by color, and the metal coordination geometry is depicted in polyhedral representation.

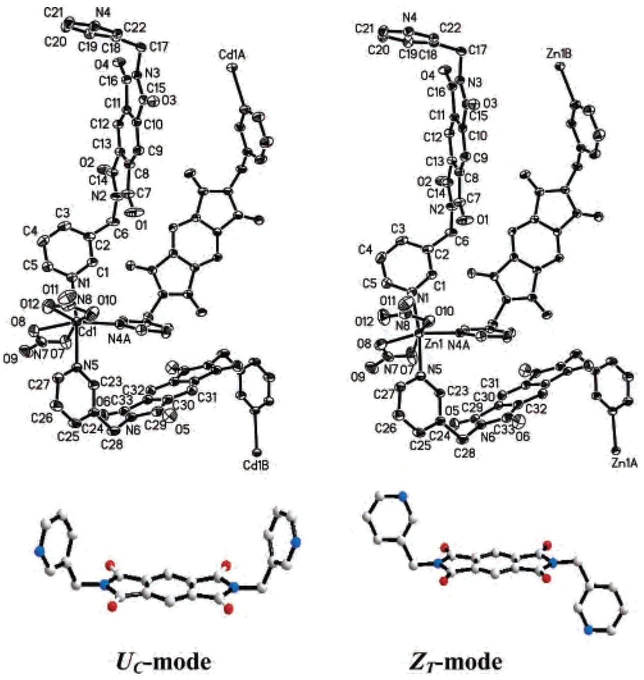


**Figure 4.** Thermal ellipsoid plot of the crystal structures in **2** and **3** drawn with 30% probability ellipsoids and ball-and-stick representation of the $Z_T$- and $U_C$-modes of 3-pmpmd.

**[Cd(3-pmpmd)$_{1.5}$(NO$_3$)$_2$]·EtOH (2).** Complex **2** contains 2D networks composed of the neutral coordination framework and ethanol solvate molecules, which are hosted between the 2D networks. Figure 4 shows a fragment of the structure of **2**, where the Cd(II) ions are found in a heptacoordinated $CdN_3O_4$ environment. The three nitrogen atoms originate on the 3-pyridyl groups of three individual 3-pmpmd ligands, and the four oxygen atoms are from two bidentate, coordinated $NO_3^-$ anions. Two of the three 3-pmpmd ligands are in the $U_C$-mode with *syn*, *cis*-conformation, while the third is in the $Z_T$-mode with *anti*, *trans*-conformation (see Chart 1), thus forming a novel W-joint for the Cd(3-pmpmd)$_3$ building blocks as shown in Figure 4. Such W-joint modules can be regarded as being distorted T-joints that generate an undulated 2D network

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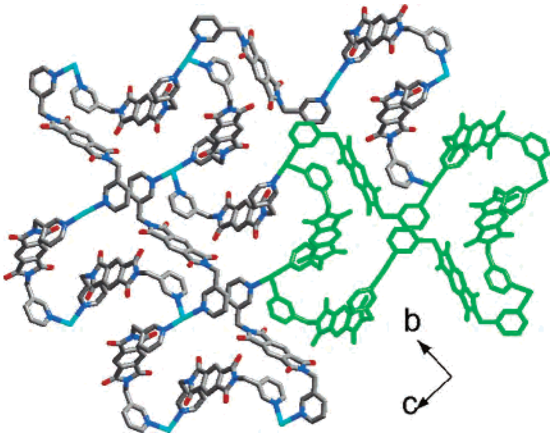

**Figure 5.** 2D network in **2** (or **3**) showing the butterfly-shaped metallacyclic $M_6$(3-pmpmd)$_6$ ring in green.

composed of butterfly-shaped $Cd_6$(3-pmpmd)$_6$ rings, as seen in Figure 5. The basic unit of the 12-membered $Cd_6$(3-pmpmd)$_6$ ring contains a very long Cd···Cd distance of about 16 Å for the $U_C$-mode linkage and about 14 Å for the $Z_T$-mode linkage. However, the existence of two types of ligand conformations makes the ring fold back to form a butterfly shape, with two 3-pyridyl groups from each butterfly ring interacting in weak $\pi\cdots\pi$ interactions (centroid-to-centroid distance 4.08 Å) to form the "body" part of each butterfly. Such an arrangement of the $U_C$- and $Z_T$-mode of ligands is unusual in comparison to the pure *trans*-conformation observed for the rigid 3,3′-bipyridyl ligands, such as 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene and 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene, in their polymeric structures.[22] Various C−H···O hydrogen bonds were formed between the 2D networks, involving oxygen atoms from both the pmd piece and the nitrate groups, as listed in Table 3. Thus, this 3D hydrogen bonded framework is based on noninterpenetrated 2D networks. The ethanol solvate molecules are located inside the cavities of the 3D framework and do not appear to interact with the host structure.

**[Zn(3-pmpmd)$_{1.5}$(NO$_3$)$_2$]·CH$_3$OH (3).** X-ray structural analysis indicated that complex **3** is isostructural with complex **2**, although they contain different solvent molecules. As shown in Figure 4, the distorted T-shaped building blocks that form the 2D network are the same, although the Zn(II) ion is in a hexacoordinate rather than a heptacoordinate environment, which is most likely due to the smaller size of Zn(II) compared to Cd(II). The hexacoordinate zinc environment, $ZnN_3O_3$, consists of 3 nitrogens that also originate from three different ligands; however, the nitrate anions are coordinated differently than in **2**: one is bidentate while the other is only monodentate. This difference causes a slight variation in the C−H···O hydrogen bonds in **3** (Table 3) but does not influence the topology of the 2D butterfly framework or the 3D hydrogen-bonded network. The methanol solvate molecules are not bound to the framework, and they exhibit no observable interactions with the host structure.

**Topological Analysis and Supramolecular Isomerism.** The ladder topology in complex **1** is clearly noninterpenetrated, although the ladder edges are offset due to the *Z*-mode conformation of the 4-pmpmd ligand. It is worth mentioning that such simple ladders with long *nonrigid* rungs (M···M separations of 19−20 Å) are, to the best of our knowledge, unprecedented. For comparison, we have obtained a noninterpenetrated 1D ladder structure with dimensions of 21 × 22 Å$^2$ by using the long, rigid, staggered ligand *N*,*N*′-bis(4-pyridinylmethylene)-1,5-naphthalenediamine with guest molecules occupying the square cavities.[23] Also, very recently, Fujita[24] reported on an even larger simple molecular ladder structure with dimensions of 24 × 24 Å$^2$ that was formed using a long rigid ligand with a spacer modified by bulky substituents, and the remaining portion of the cavities was occupied by guest molecules. As for the nonrigid ligands, the flexible 1,2-bis(4-pyridyl)ethane was found to form in a simple molecular ladder structure (10 × 10 Å$^2$),[16b] while the longer semirigid ligand 1,4-bis(4-pyridylmethyl)benzene resulted in a 4-fold interpenetrated molecular ladder.[16a] In our case, interpenetration was prevented by the formation of hydrogen bonds, suggesting a possible approach for preventing interpenetration via the incorporation of functional spacers into the ligands.

The noninterpenetrated 2D networks in **2** and **3** are almost identical, composed of the same butterfly-shaped $M_6$(3-pmpmd)$_6$ unit. When the network is simplified to a node-and-connection representation, where the metal centers are the nodes and bridging ligands the connectors, a "polycyclohexane network"[16a] becomes apparent when the structure is viewed along the *a* axis. Such a polycyclohexane network can be convincingly represented as the well-known herringbone or parquet arrangement[11] of (6,3) topology, as shown in Figure 6. Representing one type of common polymeric architecture obtained from the T-shaped building blocks, the herringbone pattern has been observed in complexes constructed from either flexible[14c,25] or rigid ligands.[15d,26] It is interesting that all known herringbone networks are interpenetrated in either a triple or a 4-fold fashion. Long semirigid bipyridyl ligands with arylidene[27] or aryloxy[14f] central spacers have already been prepared to construct various supramolecular assemblies, but no polymeric structure containing the T-shaped building blocks has been generated so far with a semirigid ligand as long as 3-pmpmd. Furthermore, the Zn(II) containing M(NO$_3$)$_2$−tris(pyridyl) network is uncommon, although several ladder structures have been reported,[26a,28] suggesting a potential field awaiting exploration.

It is of special interest to compare the inherent relationship between the structural topologies of these three neutral coordination networks. If we ignore the solvated guest molecules and assume that they are not directly involved in

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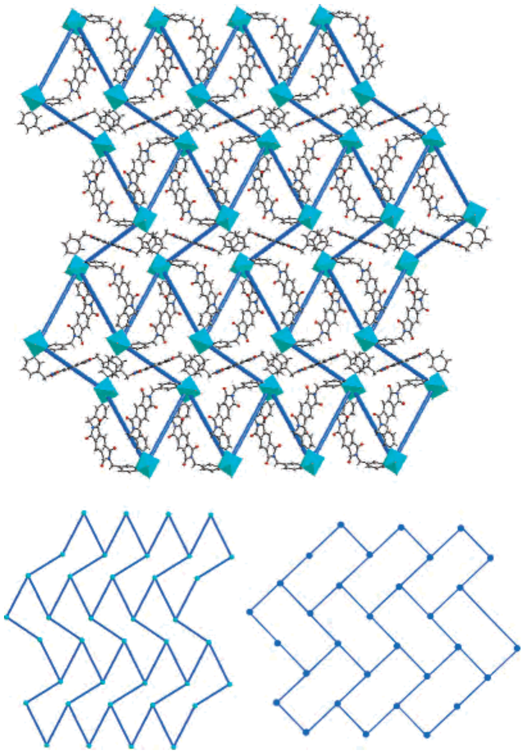

**Figure 6.** Schematic representation of the network in **2** (or **3**) showing the node-and-connection polycyclohexane net and the closely related herringbone (or parquet) structural motif.

network formation, then the networks in complexes **1** and **2** have the same molecular formula, $Cd(C_{33}H_{21}O_6N_6)(NO_3)_2$, composed of the same metal nitrate and one of the two isomeric ligands, 3-pmpmd or 4-pmpmd. More importantly, the building blocks responsible for the network formation display the same T-shaped feature, $CdL_{1.5}(NO_3)_2$ (L = 3-pmpmd or 4-pmpmd), with quite similar structural parameters around the metal ions. Therefore, complexes **1** and **2** are supramolecular isomers,[1a] which represent a new form of supramolecular isomerism created by the positional isomerism of the ligands. The ligand 4-pmpmd preferred the *Z*-mode conformation, while 3-pmpmd adopted both the $Z_T$- and the $U_C$-mode conformations, thus leading to different network topologies in **1** and **2**. A related supramolecular isomerism phenomenon may be found in Zaworotko's work,[16b] where $[Co(NO_3)_2(1,2\text{-bis}(4\text{-pyridyl})\text{ethane})_{1.5}]_n$ exhibited molecular ladder or bilayer topologies due to the different conformations of the same ligand. Although the two polymers contained different solvated molecules (MeCN or $CHCl_3$), the common T-shaped building block causes them to be supramolecular isomers, and this form of supramolecular isomerism was termed conformational isomerism.[1a] Other supramolecular isomerism phenomena, such as structural isomerism,[29] topological isomerism,[30] and ring-opening isomerism,[18] have also been documented, providing further insight and rationalization of the various synthetic influences in the field of crystal engineering. Positional isomerism differs from conformational isomerism in that the isomeric ligands provide easily distinguished but structurally related conformations and extend the scope of supramolecular isomerism.

**Thermal Analysis.** Thermogravimetric analysis (TGA) was performed by heating the complexes from 25 to 600 °C under flowing nitrogen. For **1**, a gradual weight loss (about 10%) occurred between 25 and 250 °C, indicative of the loss of the $CHCl_3$ molecules. The framework decomposed at about 270 °C where an abrupt weight loss was observed, followed by a final weight loss in the 340−600 °C range. **2** and **3** showed similar weight loss patterns: a slow weight loss (3−5%) between 25 and 300 °C indicative of the loss of solvated molecules, followed by a major weight loss in the 330−400 °C range for **2** and in the 300−440 °C range for **3**, corresponding to structure decomposition.

## Conclusion

The effect of position or orientation of the pyridyl pendant arms on the framework of coordination polymers with T-shaped connections has been studied by utilizing the two long semirigid isomeric ligands 3-pmpmd and 4-pmpmd. Reaction of $Cd(NO_3)_2$ with 4-pmpmd resulted in a 1D molecular ladder with an unprecedented staggered cavity formed by *Z*-mode 4-pmpmd edges. Formation of multiple, complementary C−H···O hydrogen bonds between the ladders successfully prevents interpenetration and generates a well-ordered 3D framework. Two butterfly-shaped networks have been assembled from the reaction of $Cd(NO_3)_2$ or $Zn(NO_3)_2$ with 3-pmpmd, which adopted both the $Z_T$- and the $U_C$-mode conformations. The network topology can be related to the well-known herringbone pattern of a (6,3) net. Adoption of mixed conformations in combination with the formation of multiple C−H···O hydrogen bonds leads to a unique network structure that avoids interpenetration. Supramolecular isomerism that arises from the positional isomerism of the ligands was discussed and compared with other known isomerism phenomena, suggesting a possible approach for the construction of variable polymeric structures based on similar building blocks.

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**Supporting Information Available:** Crystallographic data in CIF format, XRD patterns, and single-crystal diffraction simulations for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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