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Assembly of large simple 1D and rare polycatenated 3D molecular ladders from T-shaped building blocks containing a new, long *N*,*N*′-bidentate ligand†

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Received (in Columbia, MO, USA) 23rd April 2004, Accepted 22nd July 2004
First published as an Advance Article on the web 20th August 2004

Molecular ladders $[Co_2(nbpy4)_3(NO_3)_4]\cdot$solvents and $[Cd_2(nbpy4)_3(NO_3)_4]$ (nbpy4 = *N*,*N*′-bis-(4-pyridinylmethylene)-1,5-naphthalenediamine) were synthesized *via* self-assembly; the former is a large, simple, noninterpenetrated 1D ladder that contains guest solvent molecules between the rungs, while the latter exists as 1D ladders in a rare four-fold interlocked 3D structure.

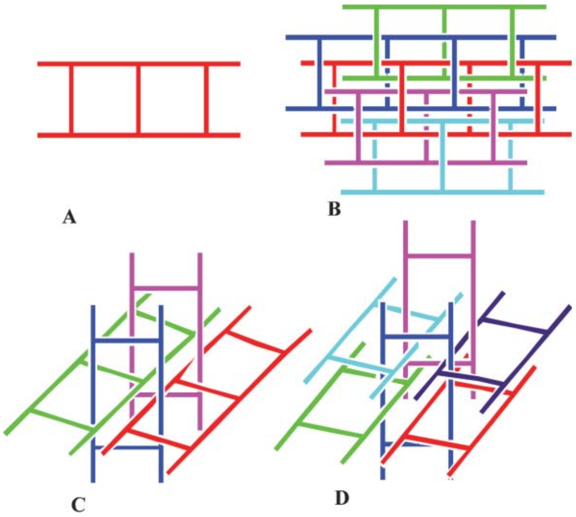
The enormous structural diversity exhibited by coordination polymers represents an opportunity and a challenge for the crystal engineering of materials with new structural motifs. One phenomenon that often contributes to this structural diversity is supramolecular isomerism[1] through the process of dimensional increase *via* interpenetration,[2] where from a topological point of view, architectures of higher dimensionality can be generated by polycatenation or polythreading of the constituent structures of lower dimensionality.[3]

T-shaped building blocks are one example that epitomizes the occurrence of structural diversity and polycatenation.[4,5] It has been documented by us and other groups that T-shaped units can assemble into various coordination polymers having different topologies, such as 1D ladders,[6,7] 2D brick walls,[8] parquet patterns,[9] molecular bilayers,[10] and 3D frameworks.[11,12] The simple 1D molecular ladders can, in addition, interpenetrate to form higher dimensional structures. To date, three structural motifs resulting from the polycatenation of molecular ladders have been identified and are shown in Scheme 1. The two-fold interlocked structure C is common and several well characterized ladder structures with this kind of polycatenation have been reported;[4,9,13,14] by contrast, structures formed *via* four-fold polycatenation, B and D, are rare and only one example is known for each.[15,16] Interestingly, it is quite unusual to find a ligand that generates a simple molecular ladder as well as a polycatenated ladder under different reaction conditions. Attempts to alter the degree of polycatenation, for example by changing the solvent system or metal center, often result instead in a completely different structural topology.[8,11,17]

We report herein a large, simple molecular ladder $[Co_2(nbpy4)_3(NO_3)_4]\cdot$solvents, **1**, and an inclined, four-fold catenated ladder structure $[Cd_2(nbpy4)_3(NO_3)_4]$, **2**, which were synthesized using the same bidentate ligand.

The new ligand, nbpy4, was prepared by the condensation of 1,5-naphthalenediamine and pyridine-4-carboxaldehyde, and features a long, rigid *exo*-bidentate character that resembles the familiar rod-like 4,4′-bipyridyl type ligands. Due to the presence of the napthalene group, however, there is an offset in the center of the ligand. Reaction of nbpy4 with $Co(NO_3)_2\cdot 6H_2O$ in a MeOH–CH_2Cl_2 mixture results in the rapid crystallization of complex **1**. The red brown crystals effloresce quickly when removed from the reaction solution, indicating that there are solvent molecules residing in the crystal that can easily escape. By contrast, the orange crystals of **2**, which grow slowly from the layering reaction of $Cd(NO_3)_2\cdot 4H_2O$ in MeOH and nbpy4 in CH_2Cl_2, are stable in air (see supplemental materials†).

Single crystal X-ray diffraction studies§ revealed that 1D infinite molecular ladders are formed in both **1** and **2**, as shown in Fig. 1. The metal centers (Co or Cd) adopt a heptacoordinated geometry: three nbpy4 ligands form a "T-joint" at the metal center whose remaining coordination sites are occupied by two bidentate nitrates. The 1D ladders are generated from the T-shaped building blocks, with nbpy4 acting as rungs and side rails. As is often observed in ladder structures, the T-joints deviate from the ideal T-shape and thus generate rhombic cavities that show much more distortion in **1** than in **2**. In **1**, simple ladders run parallelly and stack in an offset way in the *bc* plane. Several severely disordered CH_2Cl_2 and MeOH molecules are accommodated inside the cavities, which explains why the crystals quickly turn cloudy upon removal form the mother liquor. By comparison, no solvent molecules are present in the crystal structure of **2** where, instead, the



Scheme 1 Schemetic representation of a simple molecular ladder A, four-fold parallel polycatenation B, two-fold inclined polycatenation C, and four-fold inclined polycatenation D.

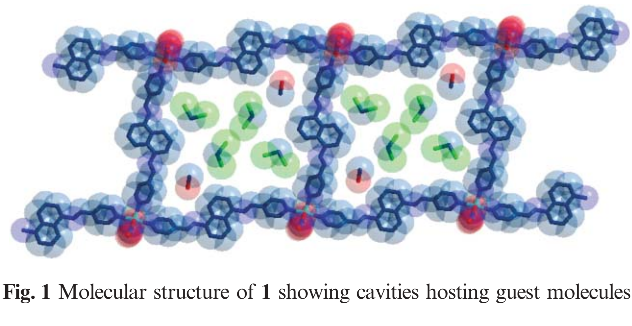


Fig. 1 Molecular structure of **1** showing cavities hosting guest molecules.

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† Electronic supplementary information (ESI) available: synthesis and characterization details are available. See http://www.rsc.org/suppdata/cc/b4/b406126h/

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DOI: 10.1039/b406126h

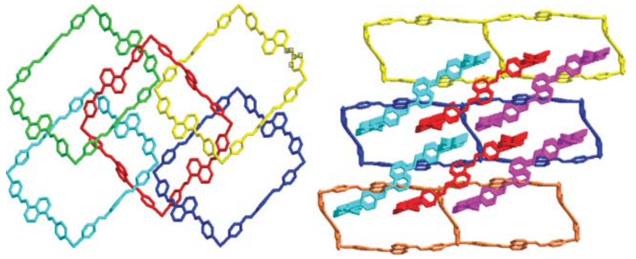

Fig. 2 Structural view of **2** showing four-fold catenation (left) and the simplified staggered polycatenation (right).

rhombic cavity is filled due to the catenation with four other ladders, as illustrated in Fig. 2. One of the important features of **2** is that the four-fold polycatenation is offset by 1/2, thus every ring is interlocked by two parallel ladders above and by two parallel ladders below the ring (Fig. 2). This staggered interpenetration by the inclined ladders results in the 1D → 3D expansion shown in Fig. 3.

The simple, noninterpenetrated ladder motif of **1** is quite common for 1D coordination polymers;[6,7] however, no simple, noninterpenetrated ladder with very long rungs (M···M separations of 21–22 Å)[18] has, to the best of our knowledge, been reported. Furthermore, the rarity of identifying a ligand that forms both interpenetrated and noninterpenetrated ladders is of significant interest. It is generally true that changing the solvent system for a specific combination of metal and ligand usually results in structural diversification, such as brick walls, *etc.*, rather than in a polycatenation of ladders.[8,11,17] For the present two cases, a complicated combination of kinetic and thermodynamic factors, as well as the use of different metal centers, are primarily responsible for the occurence of the different structures (see supplemental materials†).

It is also worthwhile to compare **2** with other known catenated ladder structures. The degree of polycatenation is certainly influenced by the length and steric bulk of the ligand, which directly places a restriction on the extent of interpenetration that is physically possible. An easy comparison can be made using the ligand series of 4,4′-bipyridyl, 1,2-bis(4-pyridyl)ethyne and 1,4-bis(4-pyridyl)butadiyne, which form single,[6] two-fold catenated[9,13] and four-fold catenated[15] ladder structures as illustrated in Scheme 1A, 1C and 1B, respectively. The ligand nbpy4 is significantly longer than 1,4-bis(4-pyridyl)butadiyne, (16.1 Å *vs.* 12.2 Å) thus enabling each square to be catenated by more than four other ladders. However, the staggered structure of nbpy4 naturally divides each square into four segments, Fig. 1, which would seem to favor the four-fold polycatenation with each interlocked ladder occupying one segment. On the other hand, the mode of catenation rather than the extent of polycatenation determines the degree of dimensional increase. Thus, a 1D → 2D dimensional increase can be achieved by parallel catenation (Scheme 1B), whereas a 1D → 3D dimensional expansion inevitably results from inclined catenation. Most of the known 1D → 3D transformations are created by two-fold inclined catenation, where each square is interlocked by the other two ladders (Scheme 1C).[4,9,13,14]

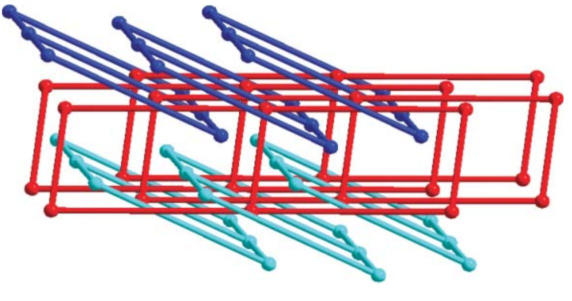

Fig. 3 1 to 3 Dimensional increase in **2** *via* inclined polycatenation.

In **2** each ring of the ladder is penetrated by four other ladders with perpendicular orientation to generate a 3D structure. A closely related example of 4-fold inclined catenation was reported by Fujita.[16] The only other known four-fold catenation is found in the coordination polymer $\{[Cu_2(MeCN)_2(1,4\text{-bis}(4\text{-pyridyl})\text{-butadiyne})_3](PF_6)_2\}$, which exhibits a parallel catenation to give a 1D → 2D dimensional increase.[15]

In summary, we successfully assembled a large, simple molecular ladder **1** and a polycatenated ladder coordination polymer **2** using the same long, rigid nbpy4 ligand. The former contains large cavities inside the ladder framework which host guest molecules, while the latter offers a new type of adaptation between the metal center and the ligand rigidity to accomplish a 1D → 3D dimensional expansion.

Acknowledgement for partial support is made to the Donors of the Petroleum Research fund, grant #36822 and to the National Science Foundation through grant CHE:0139143.

Notes and references

§ Crystal data for **1**: $Co_2C_{71.4}H_{61.2}Cl_{8.4}N_{16}O_{13.2}$, M = 1770.20, triclinic, space group $P\bar{1}$, a = 10.1474(6), b = 13.4825(7), c = 15.8374(9) Å, α = 85.401(1), β = 88.977(1), γ = 68.039(1), U = 2002.89(19) Å^3, T = 150 K, Z = 1, 7051 independent reflections measured, final $R1$ = 0.0588, and $wR2$ = 0.1446. **2**: $Cd_2C_{66}H_{48}N_{16}O_{12}$, M = 1482.0, monoclinic, space group $P2_1/n$, a = 15.6034(9), b = 13.5413(8), c = 15.8953(10) Å, β = 116.069(1), U = 3016.8(3) Å^3, T = 150 K, Z = 2, 5314 independent reflections measured, final $R1$ = 0.0496, and $wR2$ = 0.1113. CCDC 235891 and 235892. See http://www.rsc.org/suppdata/cc/b4/b406126h/ for crystallographic data in .cif or other electronic format.

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