Inorg. Chem. **2009**, *48*, 2723−2725

Inorganic Chemistry
Communication

A Chiral Luminescent Coordination Polymer Featuring a Unique 4-Connected Self-Catenated Topology Built from Helical Motifs

Eric Shyu,[†] **Ronald M. Supkowski,**[‡] **and Robert L. LaDuca***[,§]

Illinois Mathematics and Science Academy, Aurora, Illinois 60506, Department of Chemistry and Physics, King's College, Wilkes-Barre, Pennsylvania 18711, and Lyman Briggs College and Department of Chemistry, Michigan State University, East Lansing, Michigan 48825

Received February 5, 2009

The luminescent chiral coordination polymer $\{[Cd(pht)(dpa)(H_2O)]\cdot 4H_2O\}_n$ (pht = phthalate; dpa = 4,4′-dipyridylamine) possesses an unprecedented 4-connected uninodal self-catenated three-dimensional 7^48^2 network topology, constructed from the interlocking of $[Cd(dpa)]_n$ double helices with $[Cd(pht)]_n$ single helices.

The mutual interpenetration of three-dimensional (3D) networks is a common feature of coordination polymer structures.[1] These aesthetic networks can often possess topologies mimicking those of known structure types (e.g., α-Po, PtS, $SrAl_2$), with longer tethering ligands promoting higher degrees of interpenetration.[2] In comparison, coordination polymers manifesting self-catenation, in which connecting rods of the network penetrate through the shortest circuits of the same network, are more limited in scope.[3−11] Self-catenated topologies can be deceptively simple, for example, in the regular (12,3)-**twt** net evident in the cationic $[Ni(tpt)]_n^{2n+}$ framework (tpt = tri-4-pyridyl-1,3,5-triazine).[3] On the other hand, these networks can be quite complex and highly connected, for example, in $\{[Ni(oba)(4,4'\text{-bipyridine})]\cdot H_2O\}_n$ (oba = oxybisbenzoate), which has a $(4.8^2)(4.6^4.8^4.10)$ 3,5-connected self-catenated binodal topology,[4] or in $[Co_3(oba)_3(bpmp)_2]_n$ [bpmp = bis(4-pyridylmethyl)piperazine], which presents a uninodal 8-connected self-catenated net with a unique $4^45^{17}6^7$ topology.[5]

Recently, we have been successful in inducing the self-assembly of self-catenated networks by employing the kinked and hydrogen-bonding-capable diimine 4,4′-dipyridylamine (dpa) as a neutral coligand in divalent metal dicarboxylate coordination polymers. $\{[Ni(dpa)_2(succinate)_{0.5}]Cl\}_n$ is the only example to date of a uniform 6^{10} topology self-catenated network,[6] while $\{[Co(oba)(dpa)]\cdot H_2O\}_n$ and its nickel congener represent unprecedented two-dimensional self-catenated layers with 6^6 topology.[7]

Herein we report the synthesis, structural characterization, topological analysis, and luminescent properties of the self-catenated coordination polymer $\{[Cd(pht)(dpa)(H_2O)]\cdot 4H_2O\}_n$ (**1**, pht = phthalate). The neutral network of compound **1** manifests the covalent linkage of helical submotifs into an elegant uninodal 4-connected self-catenated 3D framework.

Hydrothermal treatment of a mixture of cadmium perchlorate, phthalic acid, and dpa in a 1:1.3:2.75 molar ratio at 120 °C for 48 h generated monophasic yellow crystals of **1** in moderate yield.[12] Single-crystal X-ray diffraction[13] indicated that **1** crystallized in the chiral hexagonal space

---

* To whom correspondence should be addressed. E-mail: laduca@msu.edu.

[†] Illinois Mathematics and Science Academy.

[‡] King's College.

[§] Michigan State University.

(1) (a) Batten, S. R. *CrystEngComm* **2001**, *3*, 67–73. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247–289.

(2) Blatov, V. A.; Carlucci, L.; Ciani, G.; Proserpio, D. M. *CrystEngComm* **2004**, *6*, 377–395.

(3) Abraham, B. F.; Batten, S. R.; Grannas, M. J.; Hamit, H.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 1475–1477.

(4) Wang, X.-L.; Qin, C.; Wang, E.-B.; Su, Z.-M. *Chem.—Eur. J.* **2006**, *12*, 2680–2691.

(5) Martin, D. P.; LaDuca, R. L. *Inorg. Chem.* **2008**, *47*, 9754–9756.

(6) Montney, M. R.; Mallika Krishnan, S.; Patel, N. M.; Supkowski, R. M.; LaDuca, R. L. *Cryst. Growth Des.* **2007**, *7*, 1145–1153.

(7) Martin, D. P.; Supkowski, R. M.; LaDuca, R. L. *Inorg. Chem.* **2007**, *46*, 7917–7922.

(8) Wang, X. L.; Qin, C.; Wang, E.-B.; Li, Y.-G.; Su, Z.-M.; Xu, L.; Carlucci, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 5824–5827.

(9) Lloyd, G. O.; Atwood, J. L.; Barbour, L. J. *Chem. Commun.* **2005**, 1845–1847.

(10) Niel, V.; Thompson, A. L.; Goeta, A. E.; Enachescu, C.; Hauser, A.; Galet, A.; Munoz, M. C.; Real, J. A. *Chem.—Eur. J.* **2005**, *11*, 2047–2060.

(11) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D.; Rizatto, S. *Chem.—Eur. J.* **1999**, *5*, 237–243.

(12) $Cd(ClO_4)_2\cdot 6H_2O$ (100 mg, 0.233 mmol), dpa (110 mg, 0.642 mmol), and phthalic acid (53 mg, 0.30 mmol) were mixed with 10 mL of deionized water in a 23 mL Teflon-lined Parr acid digestion bomb. The bomb was sealed and heated at 120 °C for 48 h, whereupon it was cooled slowly to 25 °C. Yellow blocks of **1** (73 mg, 58% yield based on Cd) were isolated after washing with deionized water and hot ethanol and drying in air. Anal. Calcd for $C_{18}H_{23}CdN_3O_9$: C, 40.20; H, 4.31; N, 7.81. Found: C, 39.86; H, 4.24; N, 7.69. IR (powder): ν (cm^{-1}) 3200(w, br), 1637(w), 1596(m), 1552(s), 1522(s), 1490(m), 1442(m), 1402(s), 1361(s), 1218(s), 1146(w), 1084(w), 1073(w), 1058(w), 1017(s), 914(m), 867(m), 845(m), 821(m), 808(w), 751(s), 703(m), 663(w), 652(m).

(13) Crystal data for **1**: $C_{18}H_{23}CdN_3O_9$, fw = 537.80 g/mol, hexagonal, space group $P6_122$, $a = b = 11.5693(10)$ Å, $c = 56.235(10)$ Å, $V = 6518.6(14)$ Å^3, $Z = 12$, $\rho_{calcd} = 1.638$ g/cm^3, μ(Mo Kα) = 1.059 mm^{-1}, $F(000) = 4590$, R [$I > 2\sigma(I)$] = 0.0374, wR [$I > 2\sigma(I)$] = 0.0864, GOF = 1.205, T = 173(2) K, CCDC No. 714712.

10.1021/ic900241q CCC: $40.75

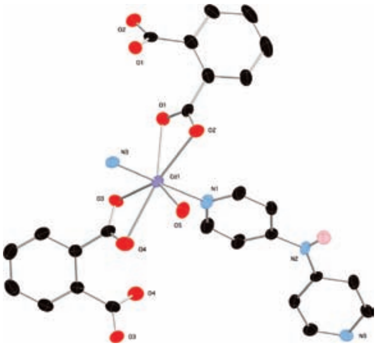

Figure 1. Coordination environment of **1** with thermal ellipsoids shown at 50% probability. Complete pht-A and pht-B ligands are shown.

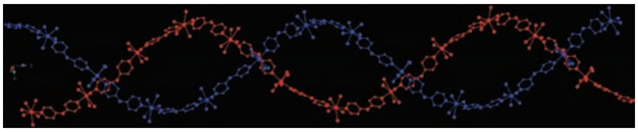

Figure 2. Transverse view of the $[Cd(H_2O)(dpa)]_n^{2n+}$ right-handed double-helix motif in **1**.

group $P6_122$ with a Flack parameter[14] of 0.01(3), indicating enantiomeric purity within the single crystal despite the use of achiral starting materials. The asymmetric unit of **1** (Figure 1) contains a divalent Cd atom, two halves of two distinct pht ligands situated across crystallographic 2-fold rotation axes (pht-A, O1−O2; pht-B, O3−O4), one dpa ligand, and one bound water molecule, along with four total water molecules of crystallization. The coordination environment at cadmium is best described as a $\{CdN_2O_5\}$ distorted pentagonal bipyramid, with the axial positions occupied by N donor atoms from two dpa ligands. The equatorial plane consists of chelating carboxylate groups from pht-A and pht-B and an aqua ligand. The chelation of the carboxylate O atoms in pht-B [Cd−O bond distances = 2.366(3) and 2.606(3) Å] is much less symmetric than the chelation in pht-A [Cd−O bond distances = 2.486(3) and 2.514(3) Å].

Extension of the structure through the tethering dpa ligands and the crystallographic symmetry generates 6-fold homochiral right-handed $[Cd(H_2O)(dpa)]_n^{2n+}$ double helices that are oriented along the *c* crystal direction (Figure 2). The Cd···Cd distances through the dpa ligands measure 12.223 Å. The slight twist between the pyridyl rings of the dpa ligands (15.0°) promotes the long 56.235 Å pitch of the double-helix motif, which defines the *c* lattice parameter. The inner diameter of a single double-helix pattern is approximately 16 Å, neglecting van der Waals radii.

Neighboring homochiral $[Cd(H_2O)(dpa)]_n^{2n+}$ double helices aggregate to create a striking pattern (Figure 3) wherein each double helix is interdigitated by six others, arranged in a hexagonal pattern. Each double-helix unit is covalently connected to both helices in six other double-helix units via bis(chelating) pht-A and pht-B ligands with a Cd···Cd through ligand distances of 7.036 and 6.791 Å, respectively. The carboxylate groups of pht-A and pht-B are twisted by 52° and 56° relative to the plane of the ligand's aromatic ring. The Cd atoms and pht-A and pht-B ligands construct homochiral 6-fold $[Cd(pht)]_n$ single helices (Figure 4). Each Cd atom is thus bridged to four others via the dpa, pht-A, and pht-B ligands, establishing a 4-connected 3D $[Cd(pht)(dpa)(H_2O)]_n$ coordination polymer network within the structure of **1**.

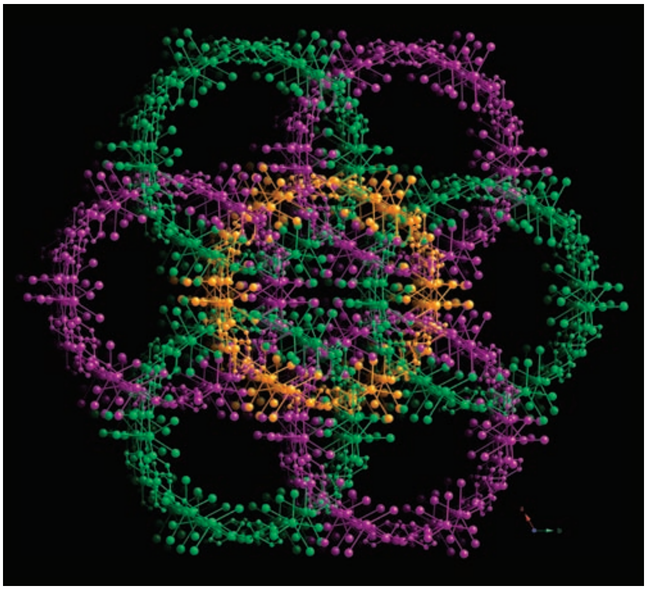

Figure 3. Interdigitation of $[Cd(H_2O)(dpa)]_n^{2n+}$ homochiral double-helix motifs in **1**.

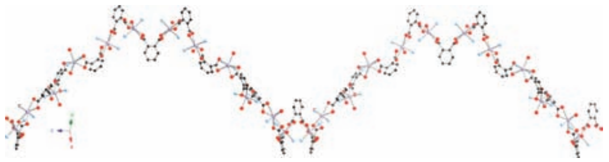

Figure 4. Side view of a $[Cd(H_2O)(pht)]_n$ homochiral single-helix motif in **1**.

As determined by *TOPOS* software,[15] the Schäfli symbol for this 4-connected uninodal network is 7^48^2, representing a relatively simple yet unprecedented self-catenated topology (Figure 5). The Long vertex symbol is $7.7.7_2.7_3.8_2.8_3$ with a coordination sequence of 4, 12, 36, 73, 136, 213, 296, 395, 514, and 648. The eight-membered circuits within this net are responsible for the self-catenation (Figure 6). Chirality of the overall self-catenated network is imposed by the homochiral $[Cd(H_2O)(dpa)]_n^{2n+}$ and $[Cd(pht)]_n$ helical submotifs. If the pht-A ligands are neglected and each Cd atom is treated as a 3-connected node, a triply interpenetrated system of self-catenated regular (12,3)-**twt** networks can be invoked as a subnet (Figure S1 in the Supporting Information).[16] There has only been one prior report of an interpenetrated self-catenated uninodal lattice: the doubly interpenetrated (12,3)-**twt** networks within the structure of $[Co(2,2'\text{-bipyridine-}4,4'\text{-dicarboxylate})(H_2O)_2]_n$,[17] identified by Ciani et al.[1b] Nevertheless, there is no true system of mutually interpenetrated networks in the structure of **1** because of the

---

[14] Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *29*, 876–881.

[15] Blatov, V. A.; Shevchenko, A. P.; Serezhkin, V. N. *J. Appl. Crystallogr.* **2000**, *33*, 1193.

[16] Blatov, V. A. *Acta Crystallogr., Sect. A* **2007**, *63*, 329–343.

[17] Schareina, T.; Schick, C.; Abrahams, B. F.; Kempe, R. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1711–1713.

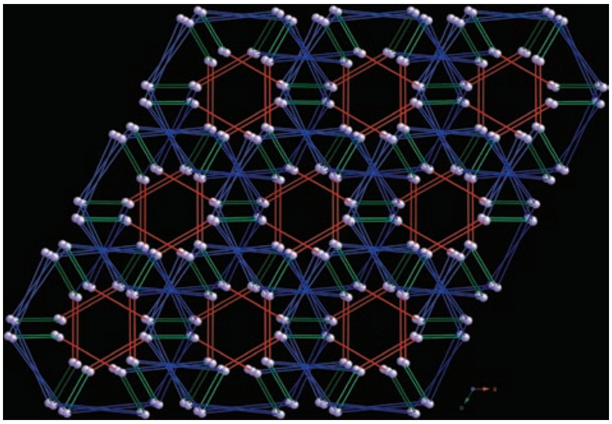

Figure 5. Network perspective of the $7^4 8^2$ self-catenated 4-connected topology of **1**. pht-A, pht-B, and dpa ligands are shown as green, red, and blue rods, respectively.

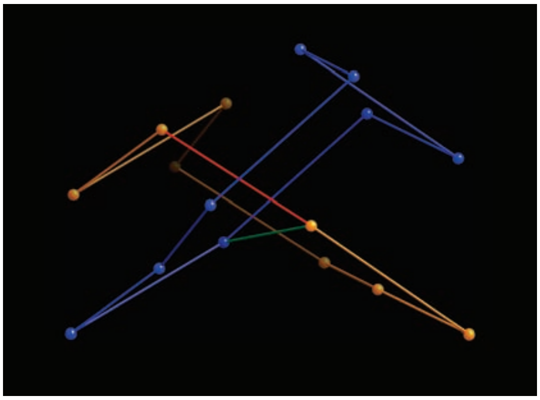

Figure 6. Closeup of the self-catenation of eight-membered rings in **1**. The Cd atoms within the self-catenated rings are shown in blue and orange. The red rod indicates the dpa ligand that causes the self-catenation; the green rod denotes the pht-A ligand that connects the two rings.

overall self-catenation of the 4-connected coordination polymer framework.

The incipient voids within the $7^4 8^2$ network of **1** are occupied by the water molecules of crystallization, anchored to the coordination polymer matrix via hydrogen-bonding mechanisms involving the central amine groups of the dpa tethers, the carboxylate O atoms of the pht ligands, and the bound water molecules. Compound **1** contains a solvent-accessible void space of 22.1% of the unit cell volume according to a calculation performed using *PLATON*.[18] These voids are occupied by discrete chains of four cocrystallized water molecules (Figure S2 in the Supporting Information).

The desolvation and degradation behavior of **1** was investigated by thermogravimetric analysis (Figure S3 in the Supporting Information). Dehydration commenced at ~50 °C and was complete by ~120 °C. The 16.0% observed mass loss was consistent with the loss of the aqua ligands and all of the cocrystallized water (16.9% calcd). The mass remained largely steady between ~120 and ~230 °C, whereupon the likely destruction of the self-catenated coordination polymer net occurred. Elimination of the bound water and organic components was observed between ~230 and 650 °C. The final mass remnant of 31.8% at 650 °C corresponds to the likely deposition of $CdCO_3$ (31.9% calcd).

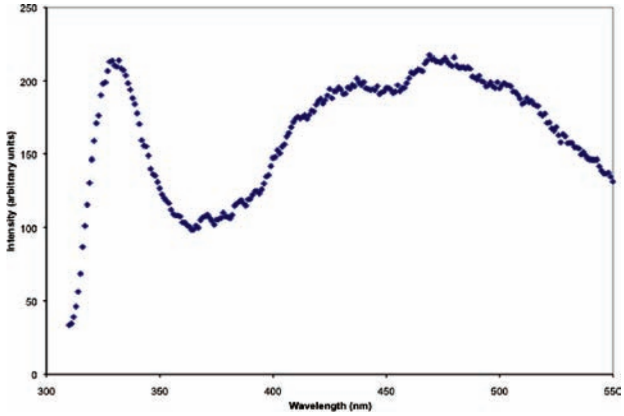

Figure 7. Luminescence spectrum of a polycrystalline sample of **1**.

Irradiation of a polycrystalline sample of **1** with ultraviolet light ($\lambda_{\text{ex}} = 300$ nm) resulted in a broad visible light emission spanning from violet to green wavelengths (400−550 nm), along with a narrower ultraviolet emission centered on 340 nm (Figure 7). To the naked eye, the emission appears bluish-white. Similar to other divalent cadmium-based coordination polymers incorporating aromatic ligands,[19] this emissive behavior is ascribed to $\pi \rightarrow \pi^*$ transitions within the molecular orbital manifolds of pyridyl and phenyl rings of the dpa and phthlate moieties, respectively.

In conclusion, the luminescent coordination polymer $\{[Cd(pht)(dpa)(H_2O)] \cdot 4H_2O\}_n$ displays an elegant, self-catenated unprecedented 4-connected chiral topology, constructed from interlocking homochiral $[Cd(H_2O)(dpa)]_n^{2n+}$ double helices and $[Cd(pht)]_n$ single helices. Efforts to prepare additional entries in the small class of self-catenated dicarboxylate coordination polymers, focusing on kinked or flexible hydrogen-bonding-capable neutral diimines, are ongoing in our laboratory.

Acknowledgment. This work was funded by the donors of the American Chemical Society Petroleum Research Fund. E.S. thanks Dr. Gail Richmond and the Michigan State University High School Science Honors Program for his participation in this work.

Supporting Information Available: Supplementary figures and a CIF file for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC900241Q

---

(18) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1998.

(19) (a) Dai, J. C.; Wu, X. T.; Fu, Z. Y.; Cui, C. P.; Hu, S. M.; Du, W. X.; Wu, L. M.; Zhang, H. H.; Sun, R. Q. *Inorg. Chem.* **2002**, *41*, 1391–1396. (b) Chen, W.; Wang, J. Y.; Chen, C.; Yue, Q.; Yuan, H. M.; Chen, J. S.; Wang, S. N. *Inorg. Chem.* **2003**, *42*, 944–946. (c) Hao, N.; Shen, E.; Li, Y. B.; Wang, E. B.; Hu, C. W.; Xu, L. *Eur. J. Inorg. Chem.* **2004**, 4102–4107.