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New Rigid Angular Dicarboxylic Acid for the Construction of Nanoscopic Supramolecules: From a Molecular Rectangle to a 1-D Coordination Polymer

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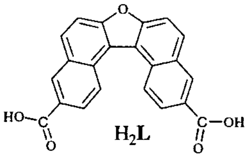
A new rigid angular bridging ligand, 7-oxa-dibenzofluorene-3,11-dicarboxylic acid (H_2**L**), was synthesized by cyanation of known *rac*-6,6′-dibromo-1,1′-bi-2-naphthol followed by ring closure and hydrolysis with concentrated sulfuric acid and used for the self-assembly of nanoscopic molecular rectangle $[Cu_4(\mathbf{L})_4(Py)_8]\cdot 2DMF\cdot 10H_2O$, **1**, and 1-D coordination polymer $[Co_2(\mathbf{L})_2(Py)_4]\cdot 2DMF\cdot 2H_2O$, **2**. Both **1** and **2** contain open channels occupied by DMF and water guest molecules. Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 8.869(2)$ Å, $b = 16.437(3)$ Å, $c = 21.586(4)$ Å, $\alpha = 78.18(3)°$, $\beta = 79.19(3)°$, $\gamma = 83.66(3)°$, $U = 3017.0(11)$ Å^3, and $Z = 1$. Crystal data for **2**: triclinic, space group $P\bar{1}$, $a = 8.254(2)$ Å, $b = 12.154(2)$ Å, $c = 15.348(3)$ Å, $\alpha = 95.34(3)°$, $\beta = 93.38(3)°$, $\gamma = 94.37(3)°$, $U = 1525.1(5)$ Å^3, and $Z = 1$.

The synthesis and characterization of organized supramolecular architectures such as metallamacrocycles and 1-, 2-, and 3-D extended porous frameworks have attracted considerable attention because of their intrinsic aesthetic appeal and potentially exploitable properties.[1,2] In particular, Yaghi and co-workers have demonstrated the construction of highly porous metal-organic frameworks based on rigid linear dicarboxylate linkers.[3] More recently, Yaghi et al.[4] and Zaworotko et al.[5] independently reported the use of 1,3-benzenedicarboxylate with a 120° angle between two functional groups to produce discrete nanometer-sized polygons as well as the use of these polygonal secondary building units in the construction of extended coordination networks. We have designed a new rigid ligand with a roughly 90° angle between the two carboxylate functional groups, 7-oxa-dibenzofluorene-3,11-dicarboxylic acid (H_2**L**). We believe that this ligand geometry would be ideal for building nanoscopic metallamacrocycles and extended coordination networks. Herein, we wish to report the self-assembly and single-crystal X-ray structures of a discrete molecular rectangle based on the Cu_4**L**$_4$ building unit and a 1-D coordination polymer based on the Co_2**L**$_2$ building unit.


H_2**L**

H_2**L** was synthesized by cyanation of known *rac*-6,6′-dibromo-1,1′-bi-2-naphthol followed by ring closure and hydrolysis with concentrated sulfuric acid.[6] The copper and cobalt complexes $[Cu_4(\mathbf{L})_4(Py)_8]\cdot 2DMF\cdot 10H_2O$, **1**, and $[Co_2(\mathbf{L})_2(Py)_4]\cdot 2DMF\cdot 2H_2O$, **2**, were obtained in 55% and 60% yield, respectively, by treating the corresponding metal nitrates and H_2**L** in a mixture of DMF, MeOH, and Py at 60 °C. Both **1** and **2** are stable in air and insoluble in water and common organic solvents. The IR spectra of **1** and **2** exhibited bands characteristic of carboxylate groups at 1660−

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(1) For reviews on discrete metallamacrocycles and polygons, see: (a) Keefe, M. H.; Benkstein, K. D.; Hupp, J. T. *Coord. Chem. Rev.* **2000**, *205*, 201−228. (b) Fijita, M.; Ogura, K. *Coord. Chem. Rev.* **1996**, *148*, 249−264. (c) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502−518. (d) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−907.

(2) For reviews on extended coordination networks, see: (a) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638−2684. (b) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173−304. (c) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1461−1494. (d) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319−330. (e) Zaworotko, M. J.; Moulton, B. *Chem. Rev.* **2001**, *101*, 1629−1658.

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(5) (a) Lu, J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2113−2116. (b) Bourne, S. A.; Lu, J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2111−2113. (c) Moulton, B.; Lu, J.; Mondal, A.; Zaworotko, M. J. *Chem. Commun.* **2001**, 863−864.

(6) Spectroscopic data for H_2**L**. ^1H NMR (DMSO-d_6): δ 13.2 (s), 9.13 (d, $^3J_{H-H} = 8.6$ Hz), 8.89 (s), 8.38 (d, $^3J_{H-H} = 8.6$ Hz), 8.32 (d, $^3J_{H-H} = 7.1$ Hz), 8.15 (d, $^3J_{H-H} = 7.1$ Hz). $^{13}C\{^1H\}$ NMR(DMSO-d_6): δ 167.2, 155.0, 132.0, 130.4, 130.1, 129.7, 126.8, 126.3, 125.3, 118.1, 113.5.

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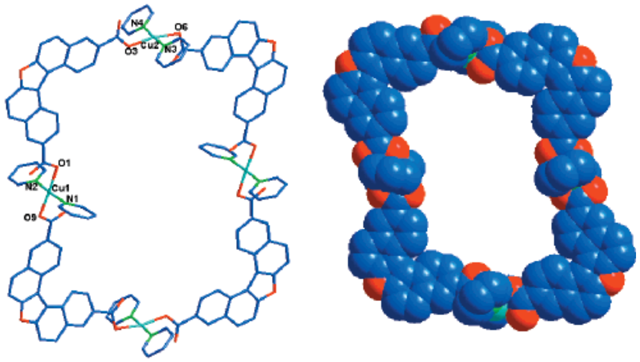

Figure 1. Left: molecular rectangle of **1**. Key bond distances (Å): Cu1−O1, 1.999(4); Cu1−N1, 2.002(5); Cu1−N2, 1.996(5); Cu1−O9, 1.963(4); Cu2−O3, 1.959(4); Cu2−O6, 1.971(4); Cu2−N3, 2.008(5); Cu2−N4, 2.015(5). Right: space-filling model showing the nanoscale cavity of $\sim$1.1 × 1.7 nm^2 within the molecular rectangle of **1**.

1320 cm^{-1}.[7] Thermogravimetric analyses (TGA) show that **1** loses 12.4% of total weight in the 35−150 °C temperature range, corresponding to the loss of 10 water molecules and two DMF molecules per formula unit (expected 12.8%). Compound **2** exhibits a weight loss of 12.6% in the 30−200 °C temperature range, corresponding to the loss of two water and two DMF molecules per formula unit (expected 13.7%).[8] Phase purities of **1** and **2** have also been supported by powder diffraction patterns of their bulk samples which are consistent with the theoretical patterns generated from their single-crystal X-ray diffraction data.

A single-crystal X-ray diffraction study performed on **1**[9] reveals a rectangular macrocycle with a crystallographic inversion center located at the center of the molecule, as shown in Figure 1. The asymmetric unit consists of two Cu(II) centers, two **L** ligands, four pyridine molecules, and one DMF and five water guest molecules. Both Cu(II) centers adopt a square planar geometry by coordinating to two *trans*-pyridine N atoms and two *trans*-carboxylate O atoms of two L ligands, with *cis*-angles ranging from 89.5° to 90.9° for the Cu1 center, and from 89.4° to 90.9° for the Cu2 center, respectively. Each L ligand coordinates to two Cu atoms through its two carboxylate groups in a monodentate fashion leading to a metallamacrocycle, with metal centers as linear connectors and L ligands as 90° corners. Because the O3−Cu2−O6 angle of 166.6(2)° deviates more significantly from 180° than the O1−Cu1−O9 angle (176.7(2)°), the tetracopper cycle adopts a rectangular geometry (rather than a molecular square expected from the combination of a 90° angular unit and a linear spacer). The **L** ligand containing O1 and O3 atoms has an *S* configuration with a dihedral angle of 7.53° between the two naphthyl rings, while the **L** ligand containing O6 and O9 atoms has an *R* configuration with a dihedral angle of 13.77° between the two naphthyl rings.[10] The macrocyclic skeleton of Cu atoms, coordinating carboxylate O atoms, and carbon atoms of the naphthyl rings is nearly planar with the largest deviation of 0.88 Å from the plane. A space-filling representation of **1** illustrated in Figure 1 clearly demonstrates the formation of nanoscopic rectangular cavity with a dimension of $\sim$1.1 × 1.7 nm^2 which is occupied by DMF and H_2O solvent molecules (the Cu−Cu distances in the rectangle are 1.63 and 2.33 nm). There are significant hydrogen bonding interactions between water guest molecules and noncoordinating O atoms of the carboxylate groups, as indicated by the O···O distances of 2.642(1) and 2.621(1) Å. The molecular rectangles partially eclipse to form a nanoscale channel with dimensions of $\sim$0.85 × 1.1 nm^2 (Figure 2).

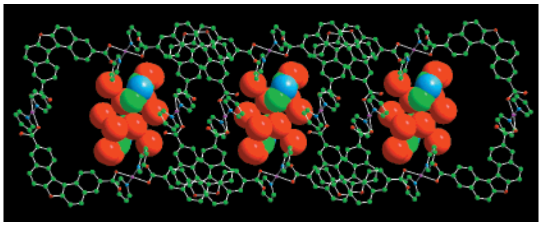

Figure 2. Molecular rectangles of **1** partially eclipse to result in nanoscale channels of $\sim$0.85 × 1.1 nm^2 which are filled with DMF and water guest molecules.

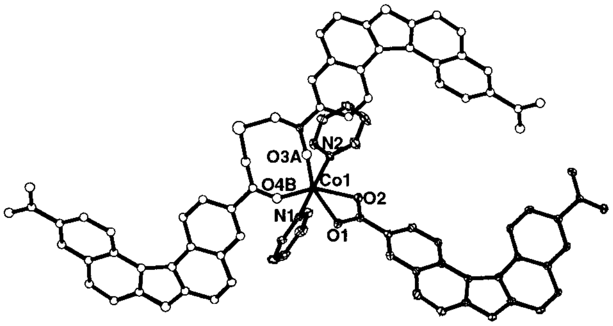

Figure 3. Coordination environment of **2**. The asymmetric unit is shown in ellipsoids at 40% probability. Key bond distances (Å): Co1−O1, 2.178(3); Co1−O2, 2.215(3); Co1−N1, 2.149(4); Co1−N2, 2.166(4); Co1−O3A, 2.022(3); Co1−O4B, 2.024(3).

A single-crystal X-ray analysis of **2**[11] reveals a 1-D coordination polymeric structure with the Co_2**L**$_2$ macrocyclic building block, which has a crystallographic inversion center residing on the midpoint of the Co−Co vector (Figure 3).[12] The asymmetric unit consists of one Co center, one **L** group,

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(7) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic Press: New York, 1983.

(8) Anal. Calcd for $C_{134}H_{114}N_{10}O_{32}Cu_4$, **1**: C, 61.2; H, 4.37; N, 5.32. Found: C, 60.5; H, 3.62; N, 4.19. Anal. Calcd for $C_{70}H_{58}N_6O_{14}Co_2$, **2**: C, 63.5; H, 4.41; N, 6.34. Found: C, 63.7; H, 3.54; N, 4.78. Despite several attempts, the nitrogen contents of **1** and **2** are consistently lower than expected. The low nitrogen contents of **1** and **2** are probably a result of facile loss of DMF guest molecules, which is consistent with the broadened X-ray powder diffraction patterns of **1** and **2**.

(9) X-ray single-crystal diffraction data for **1** was collected on a Siemens SMART CCD diffractometer. Crystal data for **1**: triclinic, space group $P\bar{1}$, $a = 8.869(2)$ Å, $b = 16.437(3)$ Å, $c = 21.586(4)$ Å, $\alpha = 78.18(3)°$, $\beta = 79.19(3)°$, $\gamma = 83.66(3)°$, $U = 3017.0(11)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.45$ g cm^{-3}, μ(Mo Kα) = 0.781 mm^{-1}. Least-squares refinement based on 12207 reflections with $I > 2\sigma(I)$ and 812 parameters led to convergence, with a final R1 = 0.072, wR2 = 0.169, and GOF = 1.01.

(10) A crystallographic inversion center generates opposite enantiomers of both **L** ligands which completes the molecular rectangle.

(11) Crystal data for **2**: triclinic, space group $P\bar{1}$, $a = 8.254(2)$ Å, $b = 12.154(2)$ Å, $c = 15.348(3)$ Å, $\alpha = 95.34(3)°$, $\beta = 93.38(3)°$, $\gamma = 94.37(3)°$, $U = 1525.1(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.44$ g cm^{-3}, μ(Mo Kα) = 0.619 mm^{-1}. Least-squares refinement based on 5342 reflections with $I > 2\sigma(I)$ and 411 parameters led to convergence, with a final R1 = 0.074, wR2 = 0.175, and GOF = 1.08.

(12) The crystallographic inversion center generates the opposite enantiomer of **L**, and **2** contains racemic forms of **L** ligands.

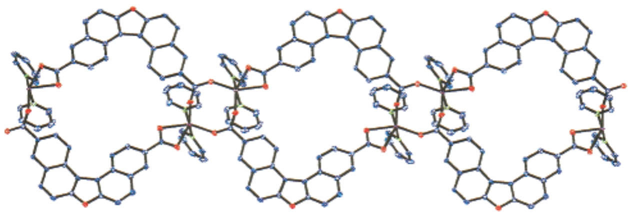

Figure 4. 1-D polymeric chain based on the $Co_2\mathbf{L}_2$ building unit. The DMF guest molecules reside inside the open channels formed by the $Co_2\mathbf{L}_2$ macrocycles, while the water guest molecules are located inside the smaller channels formed between the adjacent 1D chains.

two pyridine molecules, one DMF, and one water molecule. The Co atom coordinates to four O atoms of one chelating carboxylate group and of two bridging carboxylate groups from three different **L** ligands and two *trans*-pyridine N atoms to result in a highly distorted octahedral geometry. The *cis*-bond angles range from 60.0° to 96.6° while the *trans*-bond angles range from 112.5° to 172.6°. The two naphthyl rings of ligand **L** have a dihedral angle of 16.66°. Each **L** ligand uses one of the carboxylate groups to chelate to one Co center and uses the other carboxylate group to bridge two other Co centers. The bent configuration of **L** has thus accommodated the formation of 1-D polymeric chains running along the *c*-axis and containing both doubly carboxylate-bridged dicobalt units and the $Co_2\mathbf{L}_2$ metallamacrocycles (Figure 4). The adjacent Co−Co distances are 4.38(6) Å, while the separations between the Co(II) centers across ligand **L** are 12.25(8) Å. The 1-D polymeric chains stack on top of each other along the *a*-axis to result in open channels that are occupied by DMF molecules. Adjacent 1-D polymeric chains stack along the *b*-axis to form smaller open channels that are occupied by water molecules which form hydrogen bonds with carboxylate O atoms.

In summary, we have demonstrated the self-assembly of a nanoscopic molecular rectangle and a 1-D coordination polymer composed of metallamacrocycles using a novel rigid angular dicarboxylate ligand. A systematic investigation on the use of the angular dicarboxylate linkers in the synthesis of metallamacrocycles and related architectures as well as their inclusion properties and guest exchange phenomena is currently under way.

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Supporting Information Available: Experimental procedures, TGA curves, powder diffraction patterns, two tables, and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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