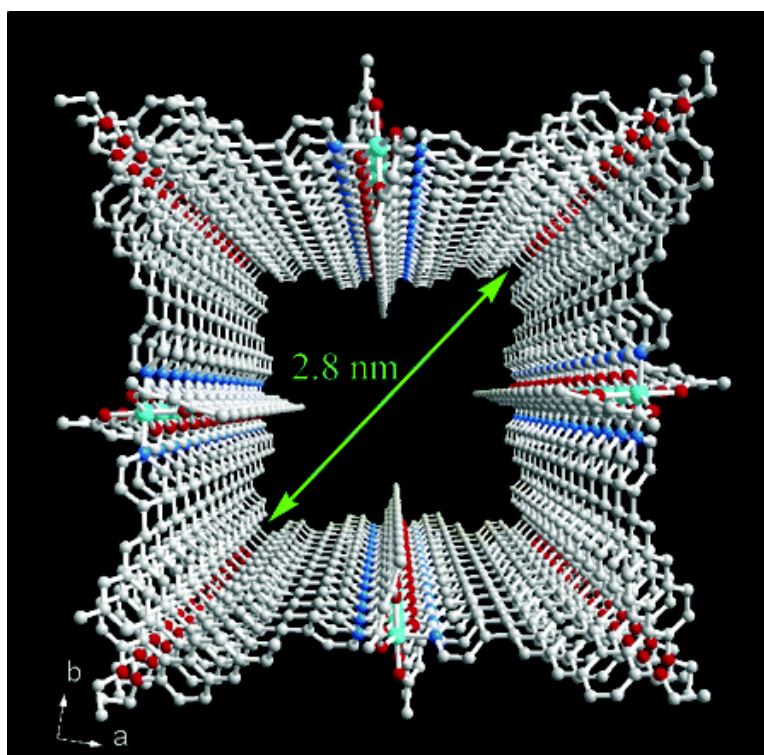


Interlocked Chiral Nanotubes Assembled from Quintuple Helices

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J. Am. Chem. Soc., **2003**, 125 (20), 6014-6015 • DOI: 10.1021/ja029926s • Publication Date (Web): 24 April 2003

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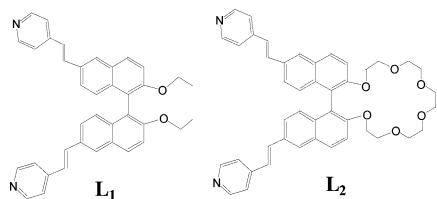
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Inorganic and organic nanotubes have received much attention due to their potential applications in nanoelectronics, molecular devices and sensors, ion exchange, and catalysis.¹ It is well established that single-walled carbon nanotubes (SWNTs) exist in chiral forms because of the helical wind of the graphitic sheets around the tube axis.² Recent theoretical studies indicated that chiral SWNTs cannot be used as enantiospecific adsorbents because of the lack of functional groups.³ On the other hand, it is conceivable to construct nanotubular structures using intrinsically chiral organic and metal-organic helices as the building blocks. The ability to incorporate other functionalities into such nanotubular structures will expand their utility in enantioselective processes. Metal-containing helical chains⁴ are ideally suited for the hierarchical assembly into nanotubular architectures. Atwood et al. reported the only example of a nanometer-scale helical tubule formed by linking *p*-sulfonatocalix[4]arene with lanthanide ions.^{5,6} We rationalize that the twisted binding sites of chiral rigid ditopic bridging ligands based on the 1,1'-binaphthyl unit will induce the formation of helical structures when linked by a linear metal-connecting point.⁷ Such homochiral helices can hierarchically assemble into nanotubular architectures with utilizable functional groups. We report here the synthesis and characterization of periodically ordered homochiral nanotubes assembled via interlocking quintuple helices formed from Ni(acac)₂ and C₂-symmetric 1,1'-binaphthyl-6,6'-bipyridines **L**₁ and **L**₂.⁸

Enantiopure **L**₁ and **L**₂ were synthesized by Heck coupling between 4-vinylpyridine and 6,6'-dibromo-2,2-diethoxy-1,1'-binaphthalene and 6,6'-dibromo-2,2'-(pentaethylene glycol)-1,1'-binaphthalene⁹ in 94% and 72% yield, respectively. Single crystals of [Ni(acac)₂(**L**₁)]·3CH₃CN·6H₂O, **1**, and [Ni(acac)₂(**L**₂)]·2CH₃CN·5H₂O, **2**, were synthesized in good yields by heating a mixture of Ni(acac)₂(H₂O)₂ and **L**₁ or **L**₂ in CH₃CN and CH₂Cl₂ at 70 °C for 2 days, respectively. **1** and **2** were formulated on the basis of microanalysis, IR, and thermogravimetric analyses.¹⁰



(*S*)-**1** adopts a chiral framework assembled from interlocking nanotubes that are constructed from quintuple helices. (*S*)-**1** crystallizes in the chiral space group *P*4₁2₁,¹¹ with one Ni(acac)₂ unit, one **L**₁ ligand, three CH₃CN, and six water guest molecules in the asymmetric unit. The Ni center coordinates to two acac anions in the equatorial plane and to two pyridyl groups of two different **L**₁ in trans fashion with an N–Ni–N angle of 177.6(2)°. The Ni(acac)₂ units are bridged by binaphthyl backbones of **L**₁ to form an infinite helical chain running along the *c*-axis (Figure 1a). The left-handed helix is generated around the crystallographic 4₁ axis

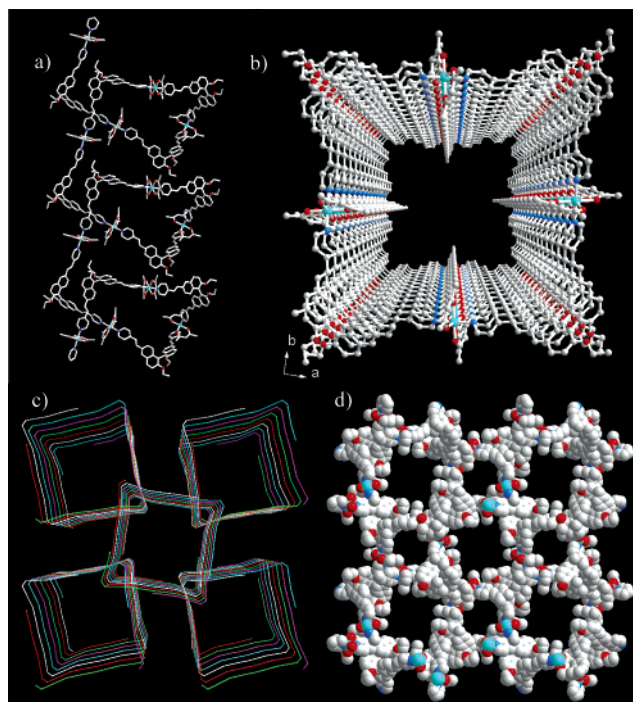


Figure 1. (a) Left-handed 4₁ helical chain of **1** built from alternating Ni(acac)₂ and **L**₁. (b) Parallel association of five helices into a chiral nanotube with an opening of ~2 × 2 nm. (c) A schematic illustrating the interlocking of adjacent helical chains. (d) A space-filling model showing the open channels within the 3D chiral framework of **1**. The included solvent molecules have been omitted.

with a pitch of 47.35(1) Å. The naphthyl rings of **L**₁ have a dihedral angle of 84.4°. The bulk of the naphthyl moieties are pointing away from the helical axis to generate a hollow cylinder. Interestingly, five infinite helical chains associate in parallel to form the wall of a tetragonal nanotube with an opening of ~2 × 2 nm (Figure 1b). Each helix further intertwines with four other helices from four different nanotubes to give a periodically ordered interlocked architecture (Figure 1c). The framework is stabilized by two types of strong π···π stacking interactions among the intertwined vinylnaphthyl groups: parallel stacking with face to face separations of 3.24 and 3.26 Å and nonparallel stacking with the nearest carbon to carbon separations of 3.49 and 3.68 Å. Interlocking of the nanotubes leads to a 3D chiral framework with the eclipsing of nanotube corners. Partially eclipsed nanotubes have open channels of 1.7 × 1.7 nm in dimensions which are filled with CH₃CN and water guest molecules. The packing of adjacent tubes along the *c*-axis also leads to smaller open channels of ~7 × 11 Å that are occupied by water molecules. Calculations using PLATON show that the effective volume for inclusion is greater than 6242 Å³, comprising 45.4% of the crystal volume.¹²

We have successfully incorporated chiral crown ethers into the walls of nanotubes by modifying the 1,1'-positions of **L**₁. (*R*)-**2**

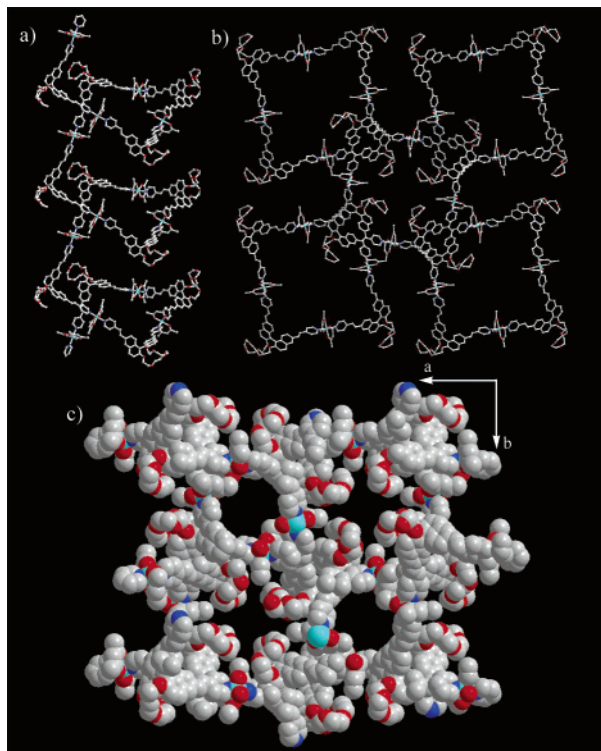


Figure 2. (a) Right-handed helical chain of **2** built from Ni(acac)₂ and **L**₂. (b) Interlocking of each nanotube with four other nanotubes. (c) A space-filling model showing the open channels within the 3D chiral framework of **2**. The included solvent molecules have been omitted.

crystallizes in chiral space group $P4_32_12^{13}$ and adopts a tubular architecture similar to that of **1**. The right-handed helix consists of alternating Ni(acac)₂ and **L**₂ around the 4_3 axis with a pitch of 47.48- (1) Å (Figure 2a). The naphthyl rings of **L**₂ have a dihedral angle of 84.5°. Five helices associate in parallel to form a nanotube with an opening of $\sim 2 \times 2$ nm. These nanotubes interlock each other to form a chiral 3D framework with all of the crown ethers oriented into the adjacent tubes (Figure 2b). The framework of **2** is also stabilized by two types of $\pi \cdots \pi$ interactions among the intertwined vinyl naphthyl groups.¹⁴ The tubular channels of **2** are decorated with chiral crown ethers (Figure 2a), while the residual void space is filled with CH₃CN and water molecules. The effective volume for inclusion is ~ 5488.8 Å³, comprising $\sim 40\%$ of the crystal volume. The placement of chiral crown ethers inside the nanotubes promises to render **2** useful for enantioselective processes. Chiral crown ethers are well known for enantioselective interactions with organic cations such as protonated amino acids.¹⁵ It is interesting to note that the handedness of **1** and **2** is determined by the enantiomer of **L**₁ and **L**₂ used, as evidenced by the fact that (*S*)-**1** adopts a left-handed tubular structure, while (*R*)-**2** adopts a right-handed structure. CD spectra of both **1** and **2** made from *R*- and *S*-enantiomers of **L**₁ and **L**₂ are mirror images of each other, indicating their enantiomeric nature.

A combination of TGA and PXRD experiments indicates that the frameworks of **1** and **2** remain intact upon complete removal of all of the included CH₃CN and water molecules. PXRD patterns of the evacuated solids of **1** and **2** are similar to those of their pristine solids. Preliminary results indicated that **1** readily adsorbs

aromatic molecules such as toluene, xylenes, and nitrobenzene (Supporting Information). A systematic investigation is underway on the inclusion properties, guest exchange, and enantioselective interactions of **1** and **2**.

In conclusion, we have demonstrated the self-assembly of periodically ordered, interlocked homochiral nanotubes based on helical chains that are built from C_2 -symmetric bipyridyl ligands and linear metal-connecting points. The ability to incorporate chiral functionalities inside the interlocked nanotubes promises to lead to novel chiral zeolitic materials exploitable for enantioselective separations and catalysis.

Acknowledgment. We thank NSF (CHE-0208930) for financial support. We thank Dr. P. S. White for experimental help. W.L. is an A. P. Sloan Fellow, a Beckman Young Investigator, a Cottrell Scholar of Research Corp., and a Camille Dreyfus Teacher-Scholar.

Supporting Information Available: Experimental procedures, two tables, and 13 figures (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) 6,6'-Dibromo-2,2'-(pentaethylene glycol)-1,1'-binaphthalene was synthesized in 57% yield by treating 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalene with NaH, followed by pentaethylene glycol ditosylate.
- (10) Microanalysis, TGA, and XRPD data indicated that **1** and **2** readily lose their guest molecules upon exposure to air.
- (11) Crystal data for **1**: tetragonal, space group $P4_12_1$, with $a = 38.098(5)$, $b = 38.098(5)$, $c = 9.470(2)$ Å, $V = 13745(4)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.00$ g/cm³. $R_1 = 0.108$, $wR_2 = 0.269$, and GOF = 1.05. Flack parameter = 0.01(3).
- (12) A pstep value of 5 is used, which slightly underestimates the void volume. Spek, A. L. *PLATON*, Version 1.62, University of Utrecht, 1999.
- (13) Crystal data for **2**: tetragonal, space group $P4_32_1$, with $a = 38.031(5)$, $b = 38.031(5)$, $c = 9.495(2)$ Å, $V = 13734(4)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.09$ g/cm³. $R_1 = 0.148$, $wR_2 = 0.344$ and GOF = 1.23. Flack parameter = 0.10(5).
- (14) Parallel stacking has face-to-face separations of 3.26 and 3.34 Å, while nonparallel stacking has the nearest carbon to carbon distances of 3.62 and 3.74 Å.
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JA029926S