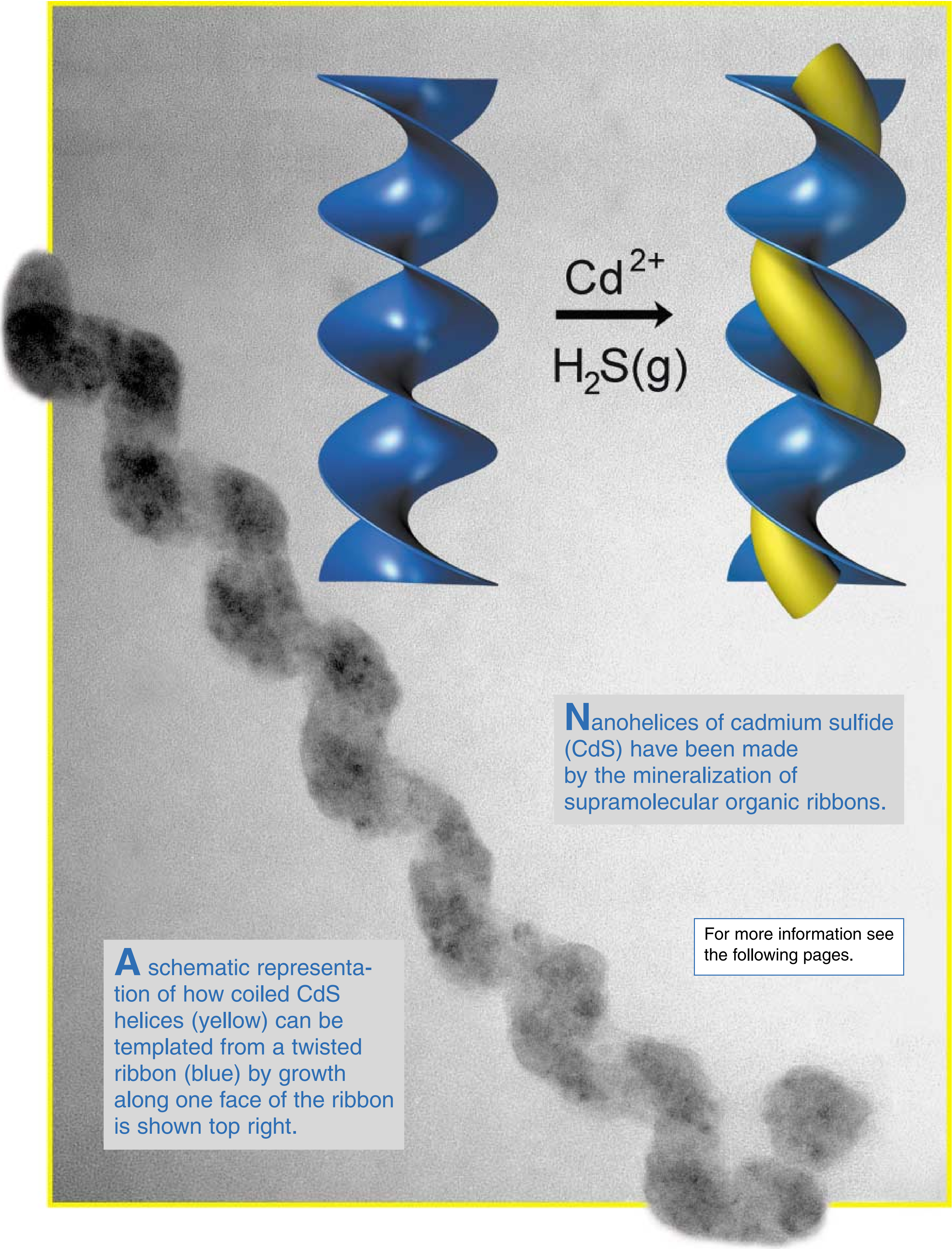

Nanohelices of cadmium sulfide (CdS) have been made by the mineralization of supramolecular organic ribbons.

A schematic representation of how coiled CdS helices (yellow) can be templated from a twisted ribbon (blue) by growth along one face of the ribbon is shown top right.

For more information see the following pages.

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Semiconductor Nanohelices Templated by Supramolecular Ribbons**

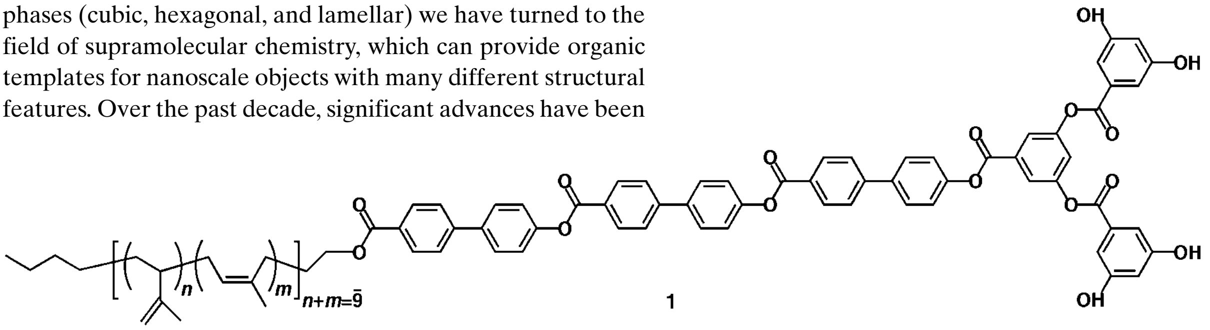
Eli D. Sone, Eugene R. Zubarev, and Samuel I. Stupp*

The synthesis of inorganic nanoobjects[1–15] and materials with nanoscale features[16–23] that are inaccessible by conventional synthetic or lithographic techniques is an important goal for chemistry. The ability to control the morphology of inorganic compounds on the nanoscale could provide systems for the study of quantum-confined behavior and may also have profound implications for a wide variety of technologies.[4, 24] Thus far, aside from extensive work on quantum dots[4, 5] and nanowires,[3, 8, 9, 24] progress has been greater for oxides than for non-oxides, with the latter including many semiconductors of interest for optoelectronic applications. For cadmium sulfide (CdS), for example, a semiconductor potentially suited for photovoltaic applications,[25] the nanoscale morphologies accessible so far have been largely limited to fairly basic shapes.[5–12] Here we report on the use of a self-assembled organic object to template the first example of a nanoscale helical morphology of cadmium sulfide. The CdS helices grow on supramolecular nanoribbons that are themselves found to be helical. The inorganic nanostructures have a coiled morphology with a pitch of 40–60 nm, which can be rationalized in terms of the period of the twisted organic ribbons.

Organic molecules that self-assemble into nanostructures have great potential as templates for the growth of inorganic materials.[14, 16–20, 22, 23] In the last few years, we have developed a methodology for the synthesis of nanostructured CdS in which lyotropic liquid crystals act as direct templates for the mineral phase by confining the precursor ions to the hydrophilic regions of the mesophase.[22, 23] In order to progress beyond the morphologies obtainable through typical lyotropic phases (cubic, hexagonal, and lamellar) we have turned to the field of supramolecular chemistry, which can provide organic templates for nanoscale objects with many different structural features. Over the past decade, significant advances have been made on how to organize molecules into new shapes through noncovalent bonds.[26–33] We have recently reported on molecules with a triblock architecture termed "dendron rodcoils" (DRC, **1**).[32, 33]

The DRC molecules (**1**) investigated can hydrogen bond in head-to-head fashion through dendron segments and self-assemble into nanoribbons, thus causing the gelation of various organic solvents. From crystallographic studies on model compounds it can be inferred that each ribbon is held together by hydrogen bonds between hydroxy and carbonyl groups of the hydrophilic dendron segments and $\pi-\pi$ stacking interactions of the aromatic rod segments.[32] We reported previously that the DRC nanoribbons tend to be flat in dichloromethane, with a consistent width of 10 nm and a thickness of 2 nm.[32]

We have investigated the formation of nanoribbons in other solvents and found that in some cases they were not flat. Transmission electron microscopy (TEM) studies on a sample prepared from a DRC gel in ethyl methacrylate (EMA) reveals that the self-assembled ribbons adopt a helical structure in this solvent (Figure 1 a). Most of the ribbons in the micrograph show dark parallel bands across the width of the structure, spaced 15–25 nm apart. This pattern is consistent with the density projection of a twisted ribbon, as opposed to a coiled structure (Figure 1 a, inset). One would expect to see a zigzag pattern in projection for a coiled structure. Furthermore, the width of the parallel stripes in the TEM image is approximately 3 nm, which corresponds more closely to the thickness rather than to the width of the flat ribbons in CH_2Cl_2. As expected, both right-handed and left-handed helices are observed. The ribbons which do not show parallel stripes may represent flat structures, as had been observed in CH_2Cl_2, or they may be more tightly twisted helices in which there is not enough density contrast along the length of the ribbon to be visible by TEM. The helical nature of the ribbons remains intact after the addition of a cadmium nitrate ($Cd(NO_3)_2 \cdot 4\,H_2O$) solution in THF as a precursor to CdS mineralization (Figure 1 b). In other solvents, such as 2-ethylhexyl methacrylate (EHMA), we also found TEM evidence for some helical nanoribbons with similar pitch to those formed in EMA, although the striped pattern was not visible for all of the ribbons (see Supporting Information).



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We investigated the possibility of producing novel inorganic structures by mineralizing nanoribbons in both EHMA and EMA. Figure 2 shows TEM images of CdS which was isolated from a 1 wt.% gel of the DRC in EHMA to which a solution of cadmium nitrate in THF had been added prior to exposure to hydrogen sulfide gas. The structure in Figure 2 a shows the

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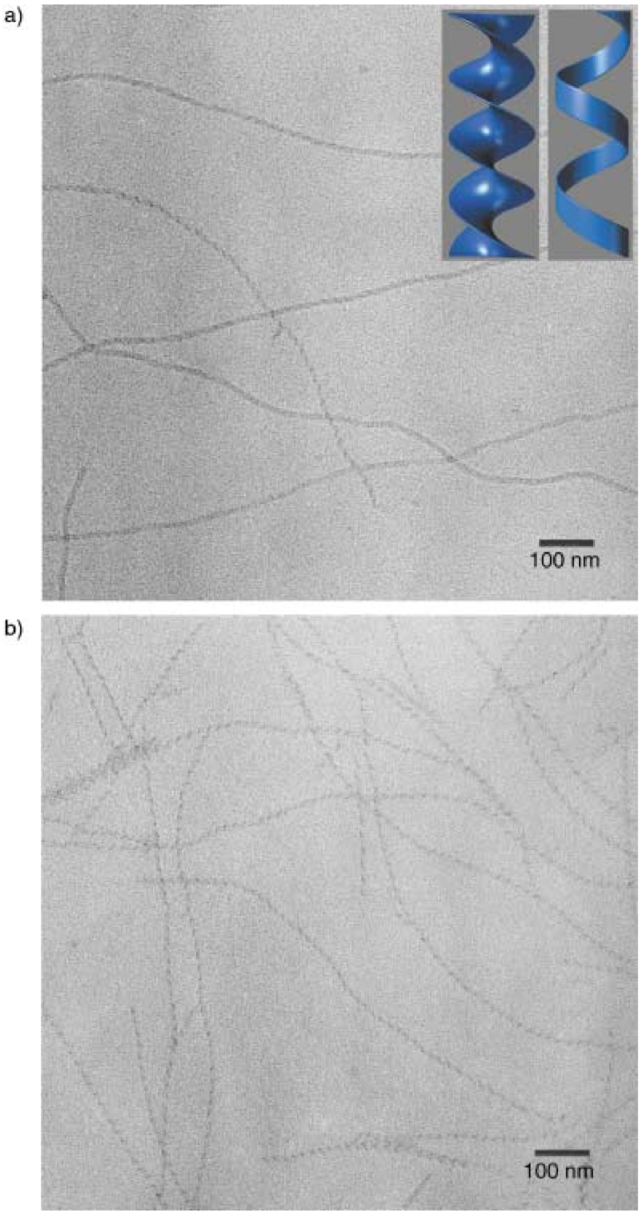

Figure 1. Bright-field TEM micrographs of DRC nanoribbons formed in EMA: a) unstained sample prepared from a 5 wt.% gel of the DRC in EMA; b) helical nanoribbons after addition of mineralization precursor (1.5 wt.% of a 0.2 M solution of $Cd(NO_3)_2 \cdot 4H_2O$ in THF). The inset shows schematic representations of twisted (left) and coiled (right) helical morphologies.

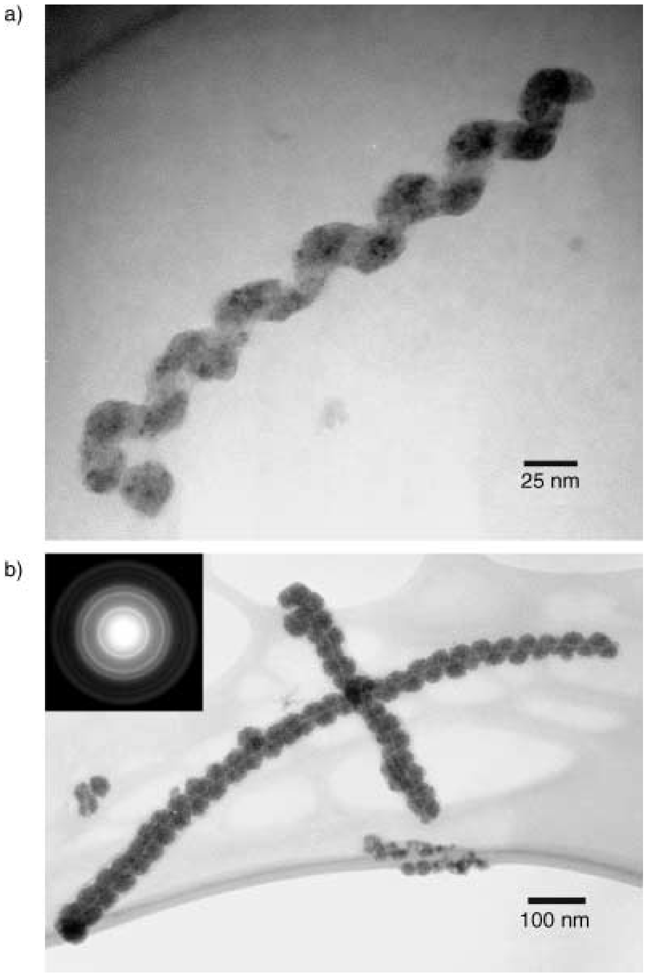

Figure 2. TEM micrographs of CdS precipitated in gels of the DRC in EHMA: a) helical nanostructure of CdS with a pitch of 40–50 nm; b) thicker helical structures with approximately the same pitch as the helix in Figure 2a. The inset shows the electron diffraction pattern corresponding to the CdS zinc blende structure. The lighter stripe visible along the axis of these helices may be the result of the lower contrast generated by the core of the helix.

zigzag pattern one would expect from a 2D density projection of a coiled helix (Figure 1a, inset), with a pitch of approximately 40–50 nm. Furthermore, the peaks and valleys of the periodic pattern are darker than the rest of the material. This pattern is consistent with what one would expect to see for the coiled form of a helix, since the strand loops below itself at the turns of the helix. These turns would show up as regions of higher electron density in a TEM image, and thus appear darker, as is observed here. Thicker helical structures, with widths ranging from 35–100 nm and lengths of up to two microns were also found (Figure 2b). The period of these structures is also 40–50 nm, which suggests that they result when structures such as the one shown in Figure 2a mineralize further. Electron diffraction studies (Figure 2b, inset) confirmed that the mineral is CdS with the zinc blende structure, as characterized by rings corresponding to the {111}, {220}, and {311} reflections. High resolution TEM studies (see Supporting Information) revealed that the polycrystalline CdS is made up of small domains with grain sizes of about 4–8 nm. We note that not all of the CdS isolated from the EHMA gels was helical in morphology; there was a significant amount of material which appeared to be untemplated, probably as a result of some nucleation and growth in the bulk solvent, or from single DRC molecules not part of ribbons.

We found that nanoribbons did not need to be in the gelled state to produce helical nanostructures of CdS when mineralized. EMA gels containing 3 or 5 wt.% DRC could be diluted in additional EMA to form a suspension of nanoribbons. Cadmium nitrate in THF was then added to this suspension and the sample was exposed to $H_2S(g)$. This method allowed TEM observation of a drop deposited directly from the suspension onto a holey carbon grid (after exposure to gas). By eliminating the work-up in THF, which was necessary for the gel-mineralized samples, we were able to simultaneously observe the CdS and the organic ribbons in the suspension-mineralized samples. Furthermore, the early stages of mineralization were more readily observed. Figure 3a shows a CdS helix at an early stage of its growth on a DRC nanoribbon in EMA. The pitch of this helix is about 60 nm. As is evident in the inset, there are gaps between sections of the growing mineral in which the organic ribbon is visible (indicated by the arrow). A lower magnification micrograph in which a number of helical structures are visible is shown in Figure 3b.

We propose that the ribbons act as templates for the CdS because of the likely preferred affinity of Cd^{2+} ions (solvated in THF) for the hydrophilic region of the ribbon (the hydroxy-containing dendron portion) over the relatively hydrophobic solvent. This would produce a local supersaturation of ions around the DRC ribbon, which would lead to nucleation and growth of CdS crystals localized at the ribbon after exposure to $H_2S(g)$. The existence of gaps between sections of the mineral at the early stages of its growth (Figure 3a) suggest that there are many nucleation sites along the length of the ribbon. These nuclei grow until they eventually join to form a continuous solid, rather than the entire structure emanating from a single nucleation event on the ribbon.

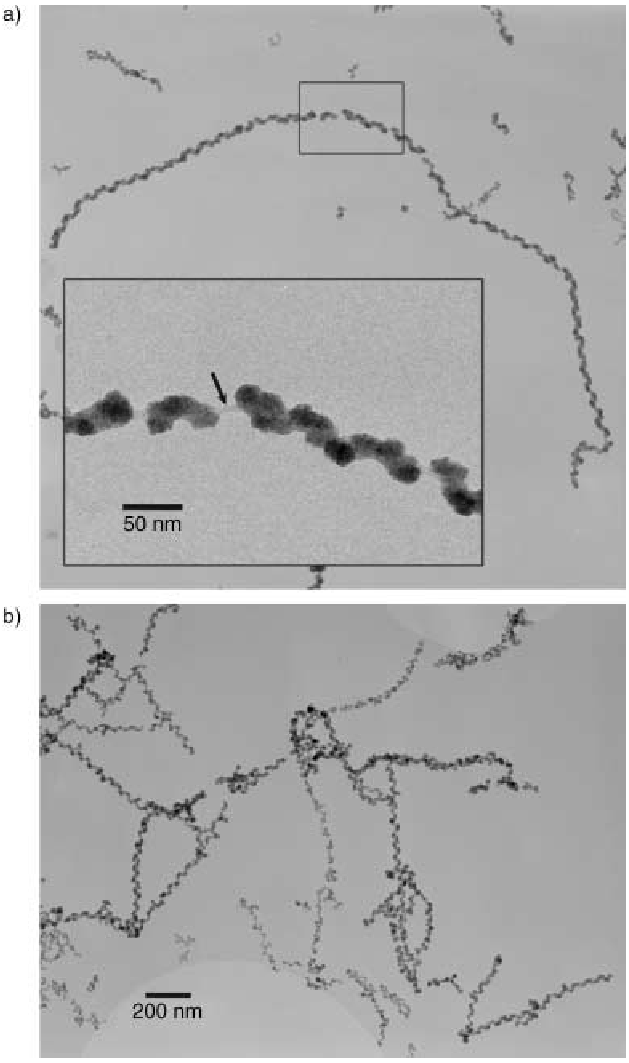

Figure 3. TEM micrographs of CdS precipitated in a suspension of DRC nanoribbons in EMA: a) CdS helix at an early stage of growth. The inset shows an enlargement of the boxed section and highlights the visibility of the organic ribbon in between sections of CdS (indicated by arrow); b) Lower magnification view showing a number of CdS helices.

We note that while the DRC ribbons have a twisted form, the CdS which is templated by these ribbons has a coiled helical structure. This apparent inconsistency could be explained by a templating scheme in which the CdS grows along only one face of the twisted ribbon template (Figure 4). The result would be a coiled helix of CdS with a pitch twice that of the twisted ribbons; in our case the pitch of the CdS (about 50 nm) is a little more than twice the pitch of the twisted ribbons (about 20 nm). The slightly larger than expected pitch of the CdS helices could result from distortions of the nanoribbon structure during mineralization. If the CdS helices are indeed produced by the templating scheme shown in Figure 4, it would suggest that the two faces of the DRC ribbons are not equivalent in terms of their ability to nucleate CdS, since nucleation and growth would have to be favored on one face to produce coiled structures. Twisted ribbons with a slightly coiled axis would have one face that was more exposed to the solvent, thus making it more favorable for mineral nucleation and growth. Alternatively, a nucleation event on one face of the ribbon could distort the ribbon in such a way as to make the two faces inequivalent. We note that while most of the CdS helices are single coils, we do observe some objects that appear to be double coils, which might result from mineralization along both faces of a ribbon. More details of the DRC nanoribbon structure need to be elucidated to gain further insight into the templating mechanism.

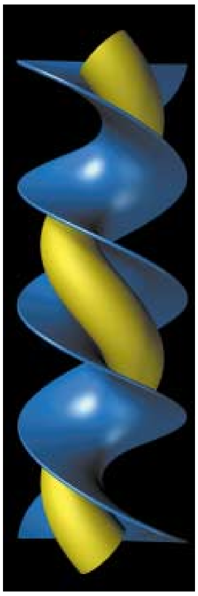

Figure 4. Schematic representation of a possible templating mechanism in which a coiled CdS helix is produced from a twisted helical template through growth along one face of the template. The resulting yellow mineral (shown at an early stage of growth so as not to obscure ribbon) would have a pitch twice that of the ribbon template (blue).

The semiconductor helical structures reported possess a unique morphology for CdS that may have interesting electronic or photonic properties. Perhaps more importantly, the structures represent a step towards the goal of harnessing the power of supramolecular organic chemistry to build inorganic structures for nanotechnology, beyond what has been accomplished with liquid crystals. Our results suggest that by using extremely uniform, stable, nonaggregated supramolecular objects as templates one can achieve good control over the morphology of the templated product.

Experimental Section

EMA gels were prepared by dissolving the DRC (30–50 mg) in EMA (1 g) through sonication, and heating in a sealed vial to about 75 °C for 5 minutes. Gels typically formed overnight. TEM samples of the gels were prepared by suspending a portion of the gel in EMA, casting it onto a holey carboncoated Cu grid, and wicking away the excess. TEM was performed on a Hitachi H-8100 microscope operating at 100 kV.

Mineralized gels in EHMA were prepared by placing the DRC (10 mg) and EHMA (1 g, in some cases containing 1 mg mL^{-1} of divinylbenzene) in a sealed vial and heating to about 75 °C to dissolve the DRC. A 0.2 M solution (20 mg) $Cd(NO_3)_2 \cdot 4H_2O$ in THF was then added to the solution, and the vial was capped and allowed to cool to room temperature and gel. We note that some of cadmium nitrate precipitated and settled to the bottom of the vial prior to gelation, thus reducing the actual concentration of available cadmium ions. This precipitate was avoided when working up the gels after exposure to H_2S(g). Gels were aged for approximately one week prior to exposure to H_2S(g) for 30 min, after which time the gas had diffused through most of the gel, as evidenced by a change to a yellow color. After aging the samples again (typically one week). TEM samples were prepared by removing excess organic material by dissolution of the gel in THF (the DRC is soluble in THF) and isolation of the inorganic product by centrifugation. The CdS was resuspended in THF, cast onto a TEM grid, and imaged at 200 kV.

DRC ribbons from EMA gels were mineralized from a suspension of a 3 or 5 wt. % gel (about 100 mg) in EMA (2 g). A 0.2 M solution (20 mg) of $Cd(NO_3)_2 \cdot 4H_2O$ in THF was added to this suspension, and after one hour the sample was exposed to H_2S(g) for 15 min. TEM samples were prepared 5 min after exposure by depositing a drop of the suspension onto a holey carbon grid and wicking away the excess.

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[1] S. Iijima, *Nature* **1991**, *354*, 56.
[2] R. Tenne, L. Margulis, M. Genut, G. Hodes, *Nature* **1992**, *360*, 444.
[3] J. T. Hu, O. Y. Min, P. D. Yang, C. M. Lieber, *Nature* **1999**, *399*, 48.
[4] A. P. Alivisatos, *Science* **1996**, *271*, 933.
[5] A. D. Yoffe, *Adv. Phys.* **2001**, *50*, 1.
[6] P. V. Braun, S. I. Stupp, *Mater. Res. Bull.* **1999**, *34*, 463.
[7] J. Huang, Y. Xie, B. Li, Y. Liu, Y. Qian, S. Zhang, *Adv. Mater.* **2000**, *12*, 808.
[8] D. Routkevitch, T. Bigioni, M. Moskovits, J. M. Xu, *J. Phys. Chem.* **1996**, *100*, 14037.
[9] Y. Li, J. H. Wan, Z. N. Gu, *Acta Phys. Chim. Sin.* **1999**, *15*, 1.
[10] C.-C. Chen, J.-J. Lin, *Adv. Mater.* **2001**, *13*, 136.
[11] J. H. Adair, E. Suvaci, *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 160.
[12] N. Pinna, K. Weiss, J. Urban, M.-P. Pileni, *Adv. Mater.* **2001**, *13*, 261.
[13] L. Manna, E. C. Scher, A. P. Alivisatos, *J. Am. Chem. Soc.* **2000**, *122*, 12700.
[14] J. H. Jung, Y. Ono, K. Hanabusa, S. Shinkai, *J. Am. Chem. Soc.* **2000**, *122*, 5008.
[15] R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz, J. G. Zheng, *Science* **2001**, *294*, 1901.
[16] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.
[17] S. Mann, G. A. Ozin, *Nature* **1996**, *382*, 313.
[18] H. Yang, N. Coombs, G. A. Ozin, *Nature* **1997**, *386*, 692.
[19] P. D. Yang, D. Y. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, *Nature* **1998**, *396*, 152.
[20] M. E. Raimondi, J. M. Seddon, *Liq. Cryst.* **1999**, *26*, 305.
[21] C. B. Murray, C. R. Kagan, M. G. Bawendi, *Science* **1995**, *270*, 1335.
[22] P. V. Braun, P. Osenar, S. I. Stupp, *Nature* **1996**, *380*, 325.
[23] P. V. Braun, P. Osenar, V. Tohver, S. B. Kennedy, S. I. Stupp, *J. Am. Chem. Soc.* **1999**, *121*, 7302.
[24] C. M. Lieber, *Solid State Commun.* **1998**, *107*, 607.
[25] O. Savadogo, *Sol. Energy Mater. Sol. Cells* **1998**, *52*, 361.
[26] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312.
[27] J.-M. Lehn, *Supramolecular Chemistry*, VCH, New York, **1995**.
[28] S. I. Stupp, Y. LeBonheur, K. Walker, L. S. Li, K. E. Huggins, M. Keser, A. Amstutz, *Science* **1997**, *276*, 384.
[29] E. R. Zubarev, M. U. Pralle, L. Li, S. I. Stupp, *Science* **1999**, *283*, 523.
[30] J. S. Moore (Ed.), *MRS Bull.* **2000**, *25*, special issue.
[31] G. N. Tew, M. U. Pralle, S. I. Stupp, *J. Am. Chem. Soc.* **1999**, *121*, 9852.
[32] E. R. Zubarev, M. U. Pralle, E. D. Sone, S. I. Stupp, *J. Am. Chem. Soc.* **2001**, *123*, 4105.
[33] E. R. Zubarev, M. U. Pralle, E. D. Sòne, S. I. Stupp, *Adv. Mater.* **2002**, *14*, 198.

Assignment of Stereochemistry of Facially Protected Bis-porphyrins by Use of a "Molecular Ruler"[**]

Maxwell J. Crossley* and Pall Thordarson

Herein we introduce a "molecular ruler" concept that can be used to unambiguously assign two stereoisomers of dizinc(II) bis(C_2-capped porphyrins) that could not otherwise be assigned by conventional techniques such as ^{1}H NMR spectroscopy. In essence the molecular ruler concept involves measurement of the distance between binding sites in a ditopic host molecule by determination of the binding of bidentate guest molecules in which the recognition groups are separated by spacers of different length. In a relatively rigid host molecule, the bidentate guest molecule that best fits the host should be most tightly bound. If the bidentate guest molecule is too short to span the binding sites, an energy penalty will have to be paid to distort either the host or the guest to achieve binding at both sites. The energy penalty will appear as a lower association constant. Similarly, when a host is too long it will have to distort itself to bind at both ends. Again this is at an energy cost.

In the present case we use a rigid dizinc(II) bis-porphyrin system and measure the distance between the zinc atoms by examining the molecular recognition of α,ω-diaminoalkanes. The molecular ruler concept is used here to discriminate between two structural isomers of a facially protected bis-porphyrin. Discrimination is possible because although the zinc(II)$\cdots$zinc(II) distance is the same in each case, the distances between the sites of complexation are very different. In the *syn* isomer **4** the capping superstructure of both porphyrin units lie on the same face of the conjugated bis-porphyrin skeleton (C_{2v} symmetry) and hence the sites of complexation of the bidentate ligand both lie on the other unprotected face. In the *anti* isomer **5** (C_{2h} symmetry), the capping superstructures lie on opposite faces of the conjugated bis-porphyrin skeleton, and, therefore, so do the diagonally opposed binding sites.

We sought the dizinc(II) *syn*- and *anti*-bis(7,8-C_2-capped porphyrins), **4** and **5**, respectively, for our studies towards self-replication of **4**. These stereoisomers were prepared by the sequence outlined in Scheme 1. The zinc(II) 7-nitro-C_2-capped porphyrin[1, 2] **1** prepared by Baldwin et al. was readily available from the unsubstituted C_2-capped porphyrin[3, 4] by our modified method for porphyrin synthesis.[5] Hydrogenation using sodium borohydride and palladium on active carbon[1, 2] gave the unstable zinc(II) 7-amino-C_2-capped porphyrin **2** that was immediately photooxidized following our methodology[6] to give the zinc(II) 7,8-C_2-capped porphy-

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