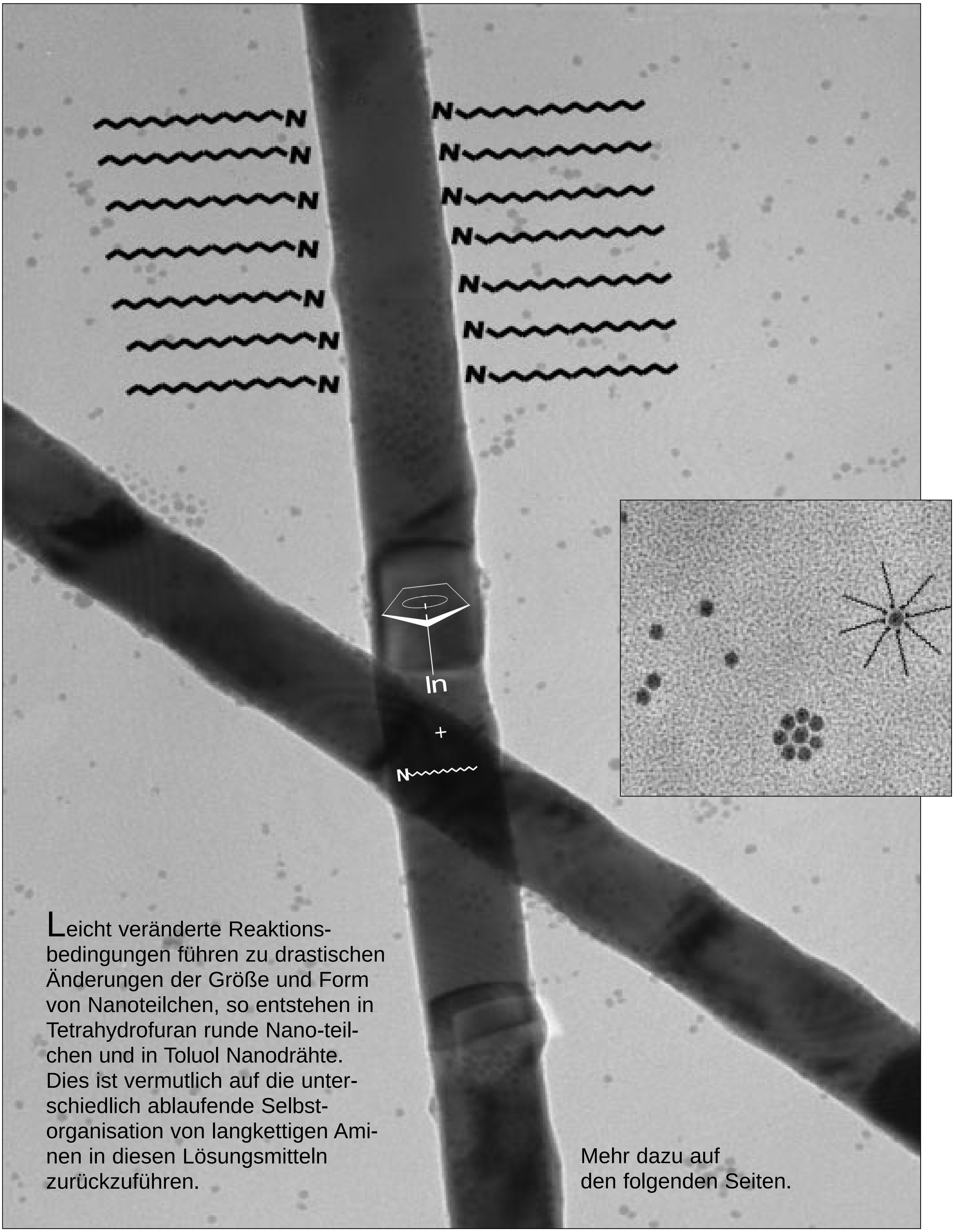

Leicht veränderte Reaktionsbedingungen führen zu drastischen Änderungen der Größe und Form von Nanoteilchen, so entstehen in Tetrahydrofuran runde Nano-teilchen und in Toluol Nanodrähte. Dies ist vermutlich auf die unterschiedlich ablaufende Selbstorganisation von langkettigen Aminen in diesen Lösungsmitteln zurückzuführen.

Mehr dazu auf den folgenden Seiten.

Selective Synthesis of Novel In and In_3Sn Nanowires by an Organometallic Route at Room Temperature**

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Marie-José Casanove, and Bruno Chaudret*

Controlling the shape of nanostructures at the mesoscopic level is one of the most challenging issues presently faced by synthetic inorganic chemists.[1] This is especially true of nanowires, which are one-dimensional objects, for which the control of growth at the molecular level seems particularly difficult.[2–7] Several methods have been used to grow nanowires, such as laser-assisted catalytic growth[2] and the analogous SLS (solution–liquid–solid) method.[3] Alternative methods use templating materials (mesoporous silica, alumina membranes, polymers, nanochannel glass, carbon nanotubes).[4, 5] Some recent papers propose the use of chelating agents to control the direction of nanowire growth in solution.[6] Finally an elegant study by Alivisatos et al.[7] emphasizes the importance of reaction conditions and, in particular, the concentration of the precursors and the ratio of surfactants for preparing CdSe nanocrystals of various shapes, including nanorods.

We have been interested for several years in using the tools of organometallic chemistry for preparing nanostructures.[8] The next challenge appears to be the control of the mesoscopic structure. This can be achieved by self-assembly of spherical nanoparticles in one, two, or three dimensions, or by growing nanocrystals of controlled shapes (nanorods, nanowires, cubes, pyramids, etc.).[1, 7, 9] We recently reported the synthesis of indium nanoparticles from the organometallic precursor InCp ($\mathrm{Cp} = \mathrm{C_5H_5^-}$) and the two- and three-dimensional assembly of the particles by using trioctylphosphane oxide (TOPO) as a ligand.[10] Here we report on the use of long-chain amines as templates for the synthesis of indium nanowhiskers[11] from InCp (**1**) and the extension of this work to the preparation of unprecedented nanowires of In_3Sn.

In a typical experiment **1** (90 mg, 0.5 mmol) was dissolved in distilled and degassed toluene or THF (11 mL) containing hexadecylamine (HDA; 60 mg, 0.25 mmol). The reaction mixture was then allowed to react in a Schlenk tube in the absence of light or in a quartz cell in the presence of UV light ($\lambda = 365$ nm) and without stirring.

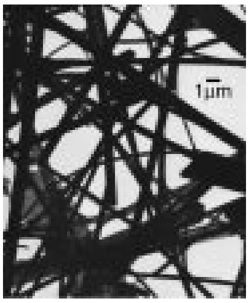

Figure 1. TEM micrograph of indium nanowires prepared in the presence of 0.5 equiv HDA (4-d reaction).

After irradiation for four days at room temperature, examination of a transmission electron microscopy (TEM) grid prepared from a drop of the crude solution revealed the presence of straight nanowires (or ribbons) with a high aspect ratio. The length of nanowires is difficult to estimate, but some were definitely longer than 40 µm, the distance between two copper wires of the grid, and others even exceeded 200 µm. The width of the nanowires was not controlled (most ranged between 100 nm and 1 µm; Figure 1). These wires were shown by high-resolution electron microscopy (HREM) and X-ray diffraction (XRD) to consist exclusively of bct indium (Figure 2).

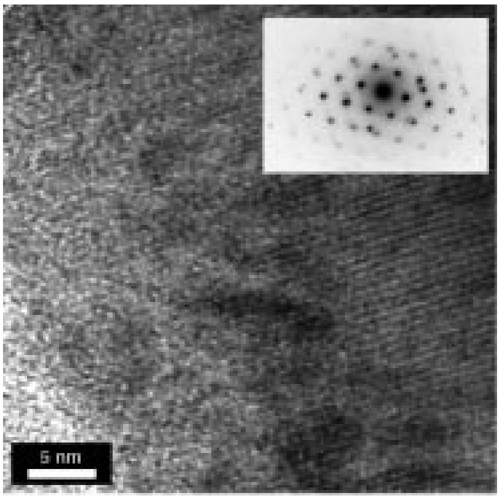

Figure 2. HREM micrograph of an indium nanowire revealing its monocrystalline (bct) structure. Inset: electron diffraction pattern of one wire corresponding to bct In (zone axis [100]).

Besides the wires, some nanoparticles were detected by TEM; they have the same size and shape as those prepared in the absence of UV irradiation (see below). Monitoring the reaction by NMR spectroscopy revealed decreasing intensity of the signal for **1** in solution and the production of CpH, and microscopy showed the predominant formation of wires.

Several parameters can affect the outcome of this decomposition reaction. To understand the formation of the wires and to achieve a better control over their diameter, we examined the influence of several parameters: nature of the amine and concentration relative to indium, rate of decomposition (UV irradiation), and the surrounding medium (nature of the solvent, concentration of the reagents in solution, and presence of water).

The amine/In ratio was varied while keeping the InCp concentration in solution and the reaction time (24 h) constant. In the absence of amine, the decomposition led to nanoparticles of about 11 nm in size without any formation of wires. However, most of these particles have an elongated

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shape, perhaps because of a preferred axis of growth. A small quantity of amine (amine/In 0.1/1) is sufficient for the formation, besides nanoparticles, of some nanowires with sizes between 100 and 800 nm. Increasing the amine/In ratio increases the yield of the reaction and leads to a better width distribution (most sizes lay between 150 and 350 nm and between 150 and 250 nm for amine/In ratios of 0.5 and 2, respectively; see Figure 3). With an amine/In ratio of 5, a width distribution centered at 250 nm was obtained.

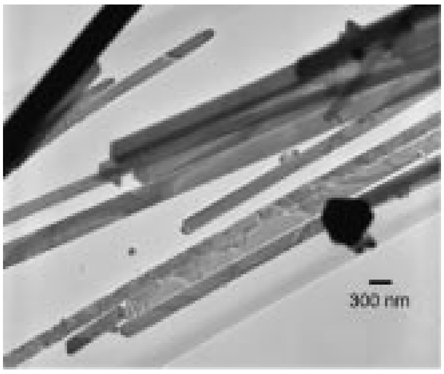

Figure 3. TEM micrograph of indium nanowires prepared in the presence of HDA (0.5 equiv).

For an amine/In ratio of 2, a microscopy grid was prepared after 90 min and after 24 h. The mean diameter of the wires was 150 – 200 nm and 200 – 250 nm, respectively. This suggests that increasing the time of the reaction increases the mean diameter of the wires, but not drastically. Changing the length of the alkyl chain from hexadecyl to dodecyl leads to the formation of thinner wires (diameter ca. 50 – 100 nm after 1.5 h of irradiation, and 100 – 150 nm after 24 h).

We compared reactions in the presence and in the absence of UV irradiation. In toluene at room temperature in the absence of UV irradiation, the reaction between **1** and 0.5 equiv HDA proceeded slowly to yield In particles of regular size centered near 3 nm. In addition to these particles, some larger crystals (10 – 20 nm) of various shapes were produced. However, for amine/In ratios greater than 2 in the absence of light, a few wires were obtained together with particles. Nevertheless, these experiments suggest that irradiation is crucial for the formation of the wires.

On decreasing the InCp concentration in toluene by a factor of five at an amine/In ratio of 0.5 or 2.5 nanoparticles of very narrow size distribution, centered at 6.7 and near 4.7 nm, respectively, were obtained. These particles, like the previously reported TOPO-stabilized particles, self-organize into hexagonal superlattices.[10]

The water content of the reaction solution was previously demonstrated to play an important role in the regulation of the size of nanoparticles of indium or tin.[8e, 10] In the present case, the water content of distilled toluene, measured by the Karl Fischer technique before experiments, was around 50 ppm. Increasing the water content to 250 or 450 ppm at an amine/In ratio of 2 led to the formation of nanoparticles and almost no wires. Carrying out the reaction in THF instead of toluene, either in the presence or in the absence of UV light, does not produce wires, but nearly monodisperse nanoparticles of spherical shape and size centered near 7 nm (Figure 4). These particles also self-organize in two and three dimensions (see above and ref. [10]).

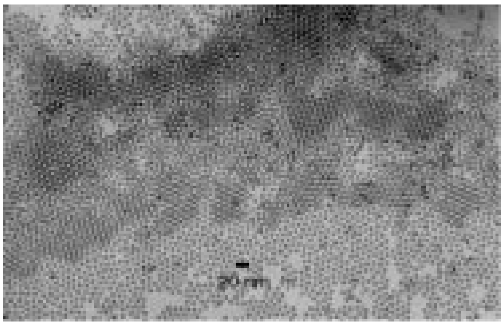

Figure 4. Mono- and multilayers of indium nanoparticles prepared in THF in the presence of 0.5 equiv HDA.

Finally, we previously reported that for late transition metals, the use of two organometallic precursors allowed the synthesis of bimetallic nanoparticles.[8c,d] Since indium tin oxide wires appeared to be an attractive target, we investigated the co-decomposition of InCp and $[Sn(NMe_2)_2]_2$.[12] In toluene at room temperature, with UV irradiation and in the presence of HDA (InCp/$[Sn(NMe_2)_2]_2$/HDA 1/0.41/0.5), nanowires were produced and were shown by XRD, HREM, and electron diffraction (ED) to consist exclusively of tetragonal β-In_3Sn. The mean diameter is smaller than in the case of pure In and lies near 100 nm (Figure 5).

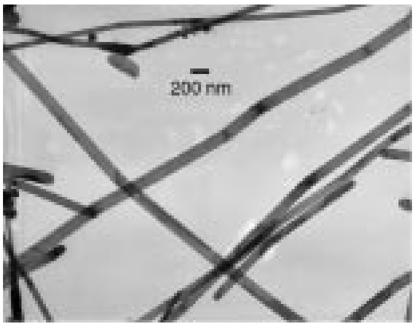

Figure 5. TEM micrograph of In_3Sn nanowires prepared in the presence of HDA.

In conclusion, we have described a simple method for obtaining indium nanowires at room temperature. This method can be easily extended to the controlled synthesis of nanowires of In_3Sn. The diameters of the wires are relatively large, near 200 nm for In and 100 nm for In_3Sn, but relatively narrow width distributions can be obtained. Clearly, the amine ligand is crucial for the formation of nanowires. However, the experiments varying the relative and absolute concentrations of InCp and the amine suggest that two other factors are important: the organization of the amine molecules in solution and the availability of indium atoms in the vicinity of the growing wire. These factors may explain the negative role of water, which may change both the organization of amine molecules in solution and cover the surface of growing indium particles, as suggested previously for indium colloids in polyvinylpyrrolidone (PVP).[10] The second factor is also in agreement with the need for photochemical decomposition of InCp, which presumably results in rapid production of indium atoms. The organization probably occurs in a similar way to that previously observed for gold–amine complexes.[13] In contrast to other recently reported processes of nanowire growth, this process does not need a catalyst or even a continuous injection of precursors for growth to proceed. Hence, no seeds are visible at the ends of the wires. However, indium is a low-melting element, and a process involving "molten" indium may be operative. Amorphous, pseudomolten particles, such as those previously observed in PVP,[10] may condense onto a preferred face of a preformed crystal. Finally, it is noteworthy that small changes in the reaction conditions allow the formation of spherical nanoparticles whose size depends upon the precise conditions, but which are uniform in each case and self-assemble in two and three dimensions.

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[1] A. P. Alivisatos, *Science* **1996**, *271*, 933.
[2] a) A. M. Morales, C. M. Lieber, *Science* **1998**, *279*, 208; b) C. M. Lieber, *Solid State Commun.* **1998**, *107*, 607; c) J. Hu, T. W. Odom, C. M. Lieber, *Acc. Chem. Res.* **1999**, *32*, 435; d) X. Duan, C. M. Lieber, *Adv. Mater.* **2000**, *12*, 298; e) M. S. Gudiksen, C. M. Lieber, *J. Am. Chem. Soc.* **2000**, *122*, 8801; f) C.-C. Chen, C.-C. Yeh, *Adv. Mater.* **2000**, *12*, 738.
[3] a) T. J. Trentler, K. M. Hickman, S. C. Goel, A. M. Viano, P. C. Gibbons, W. E. Buhro, *Science* **1995**, *270*, 1791; b) W. E. Buhro, K. M. Hickman, T. J. Trentler, *Adv. Mater.* **1996**, *8*, 685; c) T. J. Trentler, S. C. Goel, K. M. Hickman, A. M. Viano, M. Y. Chiang, A. M. Beatty, P. C. Gibbons, W. E. Buhro, *J. Am. Chem. Soc.* **1997**, *119*, 2172; d) S. D. Dingman, N. P. Rath, P. D. Markowitz, P. C. Gibbons, W. E. Buhro, *Angew. Chem.* **2000**, *112*, 1530; *Angew. Chem. Int. Ed.* **2000**, *39*, 1470.
[4] a) C. R. Martin, *Science* **1994**, *266*, 1961; b) C. R. Martin, *Chem. Mater.* **1996**, *8*, 1739; c) S. A. Sapp, B. B. Lakshmi, C. R. Martin, *Adv. Mater.* **1999**, *11*, 402.
[5] a) T. M. Whitney, J. S. Jiang, P. C. Searson, C. L. Chien, *Science* **1993**, *261*, 1316; b) A. D. Berry, R. J. Tonucci, M. Fatemi, *Appl. Phys. Lett.* **1996**, *69*, 2846; c) Z. Zhang, D. Gaekhtman, M. S. Dresselhaus, J. Y. Ying, *Chem. Mater.* **1999**, *11*, 1659; d) T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, T. P. Russel, *Science* **2000**, *290*, 2126; e) C. Tang, S. Fan, M. Lamy de la Chapelle, H. Dang, P. Li, *Adv. Mater.* **2000**, *12*, 1346.
[6] a) W. Wang, Y. Geng, Y. Qian, M. Ji, X. Liu, *Adv. Mater.* **1998**, *10*, 1479; b) Y. Li, Y. Ding, Z. Wang, *Adv. Mater.* **1999**, *11*, 847; c) Y. Li, H. Liao, Y. Fan, Y. Zhang, Y. Qian, *Inorg. Chem.* **1999**, *38*, 1382.
[7] a) L. Manna, E. C. Scher, A. P. Alivisatos, *J. Am. Chem. Soc.* **2000**, *122*, 12700; b) X. Peng, L. Manna, W. Yang, J. Wickham, E. Scher, A. Kadavanich, A. P. Alivisatos, *Nature* **2000**, *404*, 59.
[8] a) A. Rodriguez, C. Amiens, B. Chaudret, M.-J. Casanove, P. Lecante, J. S. Bradley, *Chem. Mater.* **1996**, *8*, 1978; b) O. Vidoni, K. Philippot, C. Amiens, B. Chaudret, O. Balmes, J.-O. Malm, J.-O. Bovin, F. Senocq, M.-J. Casanove, *Angew. Chem.* **1999**, *111*, 3950; *Angew. Chem. Int. Ed.* **1999**, *38*, 3736; c) C. Pan, F. Dassenoy, M.-J. Casanove, K. Philippot, C. Amiens, P. Lecante, A. Mosset, B. Chaudret, *J. Phys. Chem. B* **1999**, *103*, 10098; d) T. Ould Ely, C. Pan, C. Amiens, B. Chaudret, F. Dassenoy, P. Lecante, M.-J. Casanove, A. Mosset, M. Respaud, J.-M. Broto, *J. Phys. Chem. B* **2000**, *104*, 695; e) C. Nayral, E. Viala, P. Fau, F. Senocq, J.-C. Jumas, A. Maisonnat, B. Chaudret, *Chem. Eur. J.* **2000**, *6*, 4082.
[9] T. S. Ahmadi, Z. L. Wang, T. C. Green, A. Henglein, M. A. El-Sayed, *Science* **1996**, *272*, 1924.
[10] K. Soulantica, A. Maisonnat, M.-C. Fromen, M.-J. Casanove, P. Lecante, B. Chaudret, *Angew. Chem.* **2001**, *113*, 462; *Angew. Chem. Int. Ed.* **2001**, *40*, 448.
[11] Indium nanowires were recently proposed as by-products of the synthesis of InGaN layers: A. Krost, J. Bläsing, H. Protzmann, M. Lünenbürger, M. Heuken, *Appl. Phys. Lett.* **2000**, *76*, 1395.
[12] M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1984**, *23*, 413.
[13] S. Gomez, K. Philippot, V. Collière, B. Chaudret, F. Senocq, P. Lecante, *Chem. Commun.* **2000**, 1945.

[2.2]Paracyclophane/Dehydrobenzoannulene Hybrids: Transannular Delocalization in Open-Circuited Conjugated Macrocycles**

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Timothy J. R. Weakley, Henning Hopf,* and
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In memoriam Donald J. Cram

A variety of factors, such as conjugation length, planarity versus nonplanarity, double versus triple bonds, and introduction of donor and/or acceptor groups, can control the physical and chemical properties of an [*n*]annulene.[1] We have been involved extensively in developing the chemistry of a particular subset, namely dehydrobenzo[*n*]annulenes (DBAs),[2] and have shown the influence of many of the above-listed factors on DBA properties.[3] Although the transmission of "electronic information" is easily accomplished throughout the macrocycle because of the closed circuit of conjugated π electrons, how would this transmission be affected if a small yet electronically bridgeable "gap" were installed? Inclusion in the DBA skeleton of a moiety capable of transannular interactions would provide such a test case. One particular segment that could provide a possible answer is a cyclophane.[4] Small-sized cyclophanes are fascinating structures for annelation to a DBA skeleton in order to study transannular interactions in large macrocycles. Since the aromatic rings of a cyclophane can be fixed in a forced proximity and in a desired orientation, [2.2]paracyclophane

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