Organic Microstructures

DOI: 10.1002/anie.200604359

Single-Crystal Organic Microtubes with a Rectangular Cross Section**

Xiujuan Zhang, Xiaohong Zhang, Wensheng Shi, Xiangmin Meng, Chunsing Lee, and Shuittong Lee**

Hollow tubular nanostructures can perform diverse functions such as nanoscale fluidic transport systems, closed reaction chambers, molecular sieves, specific ionic sensors, and so on.[1] Micro- and nanotubes also have a variety of applications in chemistry, biochemistry, and materials science. Since the discovery of carbon nanotubes, considerable attention has been directed towards hollow tubular nanostructures because of their novel properties and potential applications.[2] Most studies, however, have focused on inorganic nanotubes such as GaN, SnO_2, and TiO_2, and relatively few on nanotubes of organic/polymeric and biological systems.[3–7] Preparation of single-crystal nanotubes of organic compounds of low molecular weight has gained little success, although these compounds offer great variety and flexibility in molecular design and tunability of electronic and optical properties. Up to now, the synthesis of only a few systems by employing the typical self-assembly and template-based methods has been reported.[8,9] In general, organic nanotubes prepared thus far are either amorphous or moderately polycrystalline and have a circular cross section.

Herein we report a facile route to fabricate single-crystal [2-(*p*-dimethylaminophenyl)ethenyl]phenylmethylenepro panedinitrile (DAPMP; see Figure 1 d) microtubes with a distinctive rectangular cross section. DAPMP is a typical intramolecular-charge-transfer (ICT) compound and is regarded as an ideal candidate for nonlinear optical materials.[10] In ICT compounds electron-donor (D) and electron-acceptor (A) groups are connected through π conjugation.[11,12] Our approach utilizes the strong D–A dipole–dipole interaction between adjacent DAPMP molecules as the main driving force to direct the growth of DAPMP microtubes in aqueous solution. The process is simple and can be performed at room temperature without any templates or catalysts. The size of the microtubes can be tuned over a range by means of the concentration of the initial solution. Significantly, the remarkable tubular microstructures with rectangular cross section may exhibit exceptional optical and mechanical properties that are not achievable in circular nanotubes or other nanostructures.

A solution of DAPMP in THF (2×10^{-3} M, 200 μL) was injected into high-purity water (5 mL) with vigorous stirring. After stirring for 3 min, the sample was left undisturbed for about 4 h to stabilize the microstructures. Figure 1 shows SEM and TEM images of the as-prepared microtubes. The SEM images reveal that the microtubes have high morphological purity, and microstructures of other morphologies are not observed in the sample. No surfactant, template, or

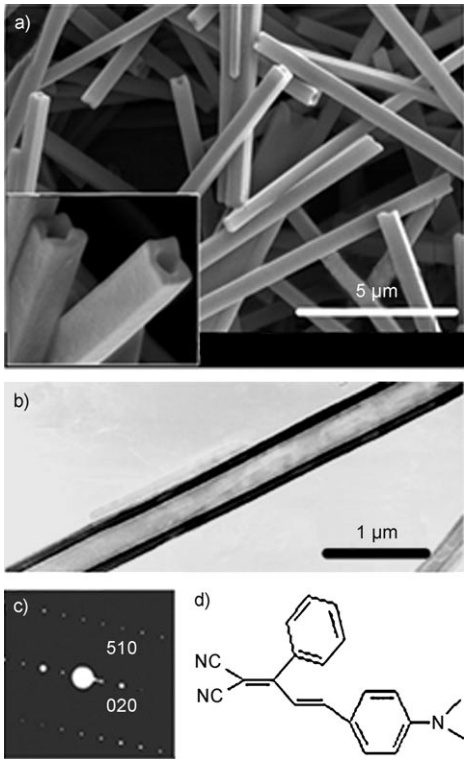

Figure 1. a) SEM image of DAPMP microtubes. Inset: enlarged SEM image showing the open tip and rectangular cross section. b) TEM image of DAPMP microtubes. c) Corresponding electron diffraction pattern of the microtube. d) Molecular structure of DAPMP.

[*] X. Zhang, Prof. X. Zhang, Prof. W. Shi, Prof. X. Meng
Nano-organic Photoelectronic Laboratory and
Laboratory of Organic Optoelectronic
Functional Materials and Molecular Engineering
Technical Institute of Physics and Chemistry
Chinese Academy of Science
Beijing 100101 (P.R. China)
Fax: (+86) 10-6487-9375
E-mail: xhzhang@mail.ipc.ac.cn
Prof. C. Lee, Prof. S. Lee
Center of Super-Diamond and Advanced Film (COSDAF)
Department of Physics and Materials Science
City University of Hong Kong
Hong Kong SAR (P.R. China)
Fax: (+852) 2784-4696
E-mail: apannale@cityu.edu.hk

[**] This work is supported by the Chinese Academy of Sciences, China and CAS-Croucher Joint Laboratory. S.T.L. thanks the support (project no. CityU 2/02C) of the Research Grants Council of Hong Kong SAR, China. We thank Dr. Kai Zou for TEM characterization and Prof. Jack Chang for discussions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

catalyst is employed in the present method. In fact, other than the organic source material, only two solvents (water and an extremely small amount of THF) are used in the process. As DAPMP is virtually insoluble in water, it is expected that practically all DAPMP molecules segregated from THF should have been organized to form microtubes in water. Figure 1c shows the corresponding selected-area diffraction (SAD) pattern of the microtube. The sharp spots clearly demonstrate that the microtube is single-crystalline. The microtubes were also characterized by X-ray diffraction (XRD) (Figure 2). The crystal structure is tetragonal (see the Supporting Information).[13]

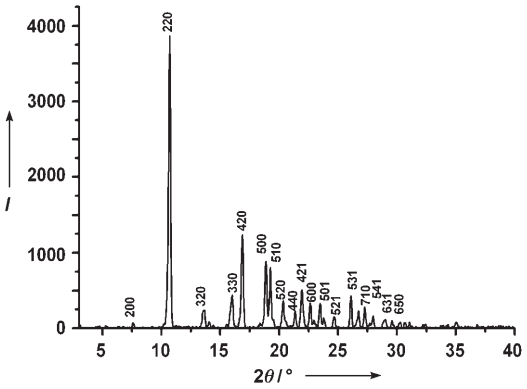

Figure 2. XRD pattern of DAPMP microtubes.

The optical properties of the microstructure provide information on the formation process. Figure 3 shows the UV/Vis absorption spectra of the as-prepared microstructures in water suspension and the dilute THF solution of DAPMP. The spectrum of the dilute DAPMP/THF solution (1×10^{-5} M, curve m in Figure 3) exhibits only one peak at 486 nm, which originates from intramolecular charge transfer (CT) from the HOMO of the donor to the LUMO of the acceptor.[14,15] The spectra of the suspension of microstructures show that the intramolecular CT band is subject to gradually increasing red shift with increasing aging time. Moreover, a new band originating from intermolecular CT transition between adjacent molecules appears at about 550 nm and is gradually red-shifted to approximately 603 nm with increasing aging time. The new band gradually becomes predominant at the expense of the intramolecular CT band, and this suggests that on formation of microstructures the main interaction changes from intramolecular to intermolecular CT.

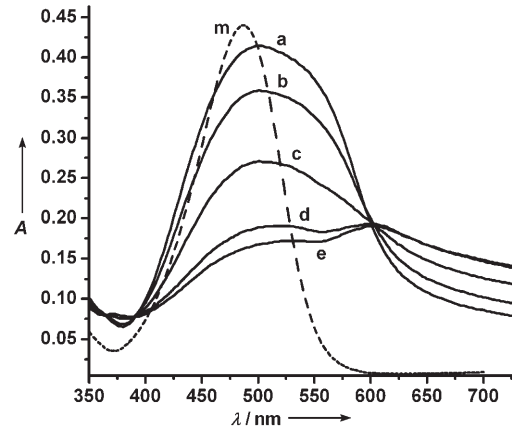

Figure 3. UV absorption spectra of DAPMP microstructures in water at different aging times; a) 10 min, b) 1 h, c) 2 h, d) 4 h, e) 24 h. Curve m is the spectrum of the dilute DAPMP/THF solution (1×10^{-5} M).

On injecting the solution of organic molecules (DAPMP) in a good solvent (THF) into a poor solvent (water), the sudden change in the environment of the DAPMP molecules will induce molecular segregation from THF and precipitation in water to form seed crystals. In the subsequent growth process, the strong intermolecular D–A dipole–dipole interactions between adjacent DAPMP molecules become dominant and act as the driving force for the DAPMP molecules to aggregate. The limited solubility of DAPMP in the poor solvent water together with the strong intermolecular dipole–dipole interactions forces the DAPMP molecules to align orderly and assemble mainly along the direction of the dipole moment, and thus one-dimensional microstructures are formed.

To further elucidate the mechanism of formation of the tubular structures with rectangular cross section, the temporal evolution of morphology was studied by TEM. The products obtained immediately after stirring contained almost exclusively solid rectangular nanorods with a diameter of 300 nm (Figure 4a). After 10–20 min, the ends of some nanorods curved inwards (Figure 4b). A high proportion of semitubular microstructures had formed together with a mixture of microtubes and nanorods after 30 min (Figure 4c). After about 4 h, almost all the products had turned into hollow structures with diameters of about 600 nm (Figure 4d).

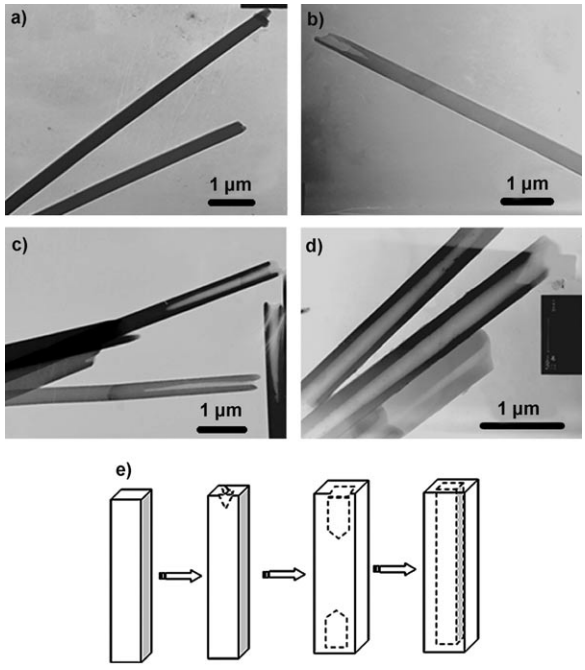

Figure 4. TEM images of DAPMP samples obtained after stirring for a) 1 min, b) 10 min, c) 30 min, d) 4 h, and e) proposed process of tube formation.

On the basis of on TEM analysis, the formation process of microtubes is proposed as follows: The etching or dissolution of DAPMP by THF starts at the center of the solid rectangular nanorods, continues towards the interior along the length axis, and thus gradually converts the solid nanorods to microsemitubes and finally to completely hollow tubular structures (Figure 4e). Similar to ZnO nanodisks, a high density of defects probably existed at the center of the rectangular nanorods and induced a high etching rate at the center and resulted in the formation of tubular structures.[16] On the other hand, the diameter of the final microtubes was larger than that of the initial nanorods, that is, recrystallization occurred concurrently with the etching process. The tube formation process is similar to the "dissolution" process proposed by Sun et al. to explain the formation of hematite nanotubes, in which the tips of the spindlelike nanorods dissolved to form hollow nanotubes.[17]

Studies with different concentrations of the DAPMP/THF solution for the preparation of the microstructures revealed a convenient way to control the size of the microtubes. For example, as the initial concentration increased from 1×10^{-3} to 2×10^{-3} and to 5×10^{-3} M, the outer diameter of the microtubes obtained changed from 450 to 600 nm and then to 1 μm, respectively (Figure 5). The inner diameter also increased correspondingly. This result indicates that by adjusting the initial concentration of DAPMP, it is possible to controllably obtain microstructures with desired diameters within a certain range. Clearly, a high concentration will increase the supply of source molecules (DAPMP) during seed formation and thus enhance the subsequent rate of crystallization and growth. All these conditions favor the formation of larger seeds and more defects in the initial nanorods. Consequently, a higher density of defects at the center will lead to a higher local etching rate and finally the formation of a larger hollow cavity at the center. The above analysis is supported by the SEM images in Figure 5, which show that the microtubes formed at a higher concentration have larger interior cavities and sharp open ends (Figure 5a), while microtubes formed at a lower concentration have flatter open ends and smaller inner diameters (Figure 5b).

The formation of tubular structures is also very sensitive to the growth temperature. At 60 °C or higher, no microtubes were formed, and only solid nanorods were produced. The lack of etching is due to rapid evaporation of THF at high temperatures.

Significantly, the as-synthesized organic microtubes, like the DAPAP molecule, show pronounced nonlinear optical properties in that they give a strong frequency-doubling up-conversion peak centered at 400 nm on excitation by an 800-nm laser (Figure 6). Such interesting optical properties suggest that the DAPMP microtubes may be a better form of DAPMP for novel device applications, such as optical computing, telecommunications, and optical information processing.[18] The frequency-doubling capability of DAPMP microtubes is interesting and warrants further work.

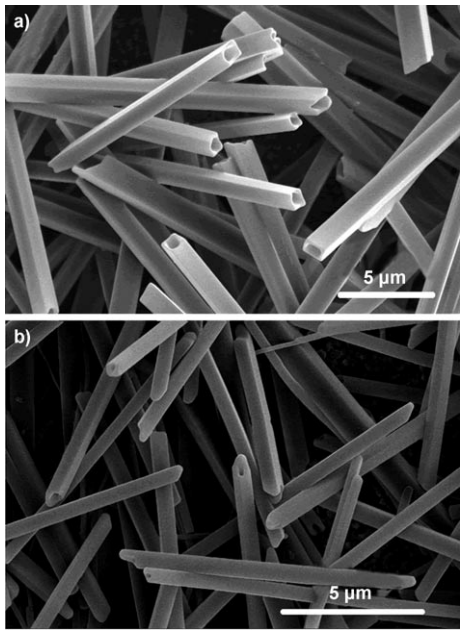

Figure 5. SEM images of microtubes with sizes of a) 1 μm and b) 450 nm.

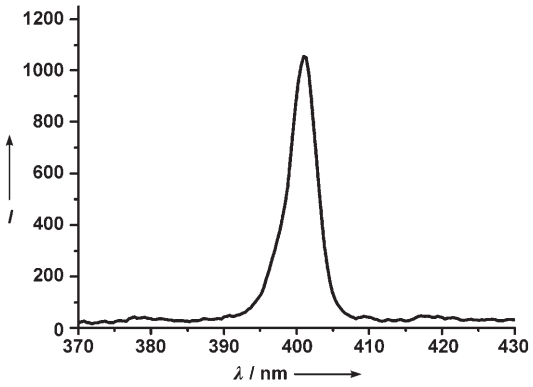

Figure 6. Room-temperature photoluminescence spectrum of the as-synthesized microtubes of DAPMP (excitation wavelength: 800 nm).

In summary, single-crystal DAPMP microtubes with rectangular cross sections have been prepared. It is considered that segregation from THF leads to nucleation of DAPMP microstructures in water, while the strong dipole–dipole interaction between neighboring DAPMP molecules induces one-dimensional growth, and the subsequent etching by THF contributes to the formation of tubular structures. The size of the microtubes can be tuned by varying the concentration of the DAPMP solution. The microtubes exhibit remarkable frequency-doubling up-conversion properties that may find applications in photonics.

Received: October 25, 2006
Published online: January 16, 2007

Keywords: donor–acceptor systems · microtubes · nonlinear optics · self-assembly

[1] D. T. Bong, T. D. Clark, J. R. Granja, M. R. Ghadiri, *Angew. Chem.* **2001**, *113*, 1016; *Angew. Chem. Int. Ed.* **2001**, *40*, 988.

[2] S. Iijima, *Nature* **1991**, *354*, 56; A. Nojeh, G. W. Lakatos, S. Peng, K. Cho, R. F. W. Pease, *Nano Lett.* **2003**, *3*, 1469; M. Zhang, W. Gorski, *J. Am. Chem. Soc.* **2005**, *127*, 2058.

[3] J. Q. Hu, Y. Bando, J. H. Zhan, F. F. Xu, T. Sekiguchi, D. Golberg, *Adv. Mater.* **2004**, *16*, 1465; L. Zhang, M. Wan, *J. Phys. Chem. B* **2003**, *107*, 6748; Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, H. Xu, *J. Am. Chem. Soc.* **2003**, *125*, 12384.

[4] Y. Liu, M. L. Liu, *Adv. Funct. Mater.* **2005**, *15*, 57.

[5] L. W. Yin, Y. Bando, J. H. Zhan, M. S. Li, D. Golberg, *Adv. Mater.* **2005**, *17*, 1972.

[6] L. F. Zhang, K. Yu, A. Eisenberg, *Science* **1996**, *272*, 1777.

[7] H. Qiu, M. Wan, B. Matthews, L. Dai, *Macromolecules* **2001**, *34*, 675; B. H. Hong, J. Y. Lee, C. W. Lee, J. C. Kim, S. C. Bae, K. S. Kim, *J. Am. Chem. Soc.* **2001**, *123*, 10748; S. Hecht, A. Khan, *Angew. Chem.* **2003**, *115*, 6203; *Angew. Chem. Int. Ed.* **2003**, *42*, 6021.

[8] Z. C. Wang, C. J. Medforth, J. A. Shelnutt, *J. Am. Chem. Soc.* **2004**, *126*, 15954; M. R. Ghadiri, J. R. Granja, L. K. Buehler, *Nature* **1994**, *369*, 301; X. J. Zhang, X. H. Zhang, W. S. Shi, X. M. Meng, C. S. Lee, S. T. Lee, *J. Phys. Chem. B* **2005**, *109*, 18777; C. H. Gorbitz, *Chem. Commun.* **2006**, *34*, 2332; N. Ashkenasy, W. S. Home, M. R. Ghadiri, *Small* **2006**, *2*, 99–102; T. Q. Nguyen, R. Martel, P. Avouris, M. L. Bushey, L. Brus, C. Nuckolls, *J. Am. Chem. Soc.* **2004**, *126*, 5234.

[9] L. Y. Zhao, W. S. Yang, Y. Ma, J. N. Yao, Y. L. Li, H. B. Liu, *Chem. Commun.* **2003**, *31*, 2442; X. J. Zhang, W. G. Ju, M. M. Gu, X. H. Zhang, X. M. Meng, W. S. Shi, C. S. Lee, S. T. Lee, *Chem. Commun.* **2005**, *33*, 4202; K. Lu, J. Jacob, P. Thiyagarajan, V. P. Conticello, D. G. Lynn, *J. Am. Chem. Soc.* **2003**, *125*, 6391; Y. H. Sun, K. Q. Ye, H. Y. Zhang, J. H. Zhang, L. Zhao, B. Li, G. D. Yang, B. Yang, Y. Wang, S. W. Lai, C. M. Che, *Angew. Chem.* **2006**, *118*, 5738; *Angew. Chem. Int. Ed.* **2006**, *45*, 5610.

[10] H. Z. Wang, X. G. Zheng, W. D. Mao, Z. X. Yu, Z. L. Gao, G. Q. Yang, P. F. Wang, and S. K. Wu, *Appl. Phys. Lett.* **1995**, *66*, 2777.

[11] X. H. Zhang, B. J. Chen, X. Q. Lin, O. Y. Wong, C. S. Lee, H. L. Kwong, S. T. Lee, S. K. Wu, *Chem. Mater.* **2001**, *13*, 1565; J. Seo, S. Kim, S. Y. Park, *J. Am. Chem. Soc.* **2004**, *126*, 11154.

[12] R. Dworczak, W. M. F. Fabian, B. N. Pawar, H. Junek, *Dyes Pigm.* **1995**, *29*, 65; L. Horner, K. L. Kluepfel, *Justus Liebiegs Ann. Chem.* **1955**, *591*, 69.

[13] C. Dong, *J. Appl. Crystallogr.* **1999**, *32*, 838.

[14] E. Horiguchi, K. Shirai, M. Matsuoka, M. Matsui, *Dyes Pigm.* **2002**, *53*, 45.

[15] J. Y. Jaung, M. Matsuoka, K. Fukunishi, *Dyes Pigm.* **1996**, *31*, 141.

[16] F. Li, Y. Ding, P. X. Gao, X. Q. Xin, Z. L. Wang, *Angew. Chem.* **2004**, *116*, 5350; *Angew. Chem. Int. Ed.* **2004**, *43*, 5238.

[17] C. J. Jia, L. D. Sun, Z. G. Yan, L. P. You, F. Luo, X. D. Han, Y. C. Pang, Z. Zhang, C. H. Yan, *Angew. Chem.* **2005**, *117*, 4402; *Angew. Chem. Int. Ed.* **2005**, *44*, 4328.

[18] P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York, **1991**, pp. 160–174.

