JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Subscriber access provided by American Chemical Society

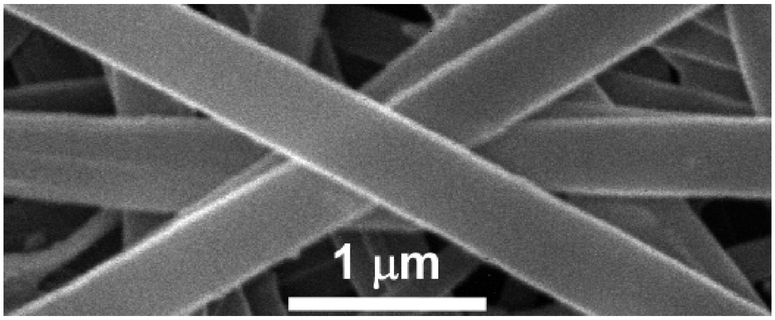
Communication

Nanobelt Self-Assembly from an Organic n-Type Semiconductor: Propoxyethyl-PTCDI

Kaushik Balakrishnan, Aniket Datar, Randy Oitker, Hao Chen, Jianmin Zuo, and Ling Zang

J. Am. Chem. Soc., **2005**, 127 (30), 10496-10497• DOI: 10.1021/ja052940v • Publication Date (Web): 12 July 2005

Downloaded from http://pubs.acs.org on March 25, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 43 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications High quality. High impact.

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 07/12/2005

Nanobelt Self-Assembly from an Organic n-Type Semiconductor: Propoxyethyl-PTCDI

Kaushik Balakrishnan,[†] Aniket Datar,[†] Randy Oitker,[†] Hao Chen,[‡] Jianmin Zuo,[‡] and Ling Zang*,[†]

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901,
and Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign,
Urbana, Illinois 61801

Received May 5, 2005; E-mail: lzang@chem.siu.edu

One-dimensional nanostructures (such as nanowires) of semiconductor materials have attracted increased interest in recent years due to their promising applications in optical and electronic nanodevices.[1] However, most nanowires reported to date are based on inorganic materials. Fewer studies have been performed on organic semiconductors, while they have been widely used in thin-film-based optoelectronic devices such as transistors, light-emitting diodes, and photovoltaic cells. Some one-dimensional nanostructures (e.g., nanofibers) have been fabricated with conducting polymers such as polyaniline[2,3] and polyacetylene,[4] but the crystalline structure of polymer nanofibers is often difficult to control due to the complicated intermolecular interaction. Recently, some works have proven that self-assembly through strong $\pi-\pi$ stacking is an effective approach to one-dimensional nanostructures for aromatic organic molecules,[5] particularly the larger macrocyclic aromatic molecules such as hexabenzocoronene.[6,7] This implies a potential way to enhance the charge carrier mobility, which is believed to be favored along the $\pi-\pi$ stacking direction.[8,9]

In this communication, we report on a simple method for fabricating nanobelt structures from organic semiconductor molecules. The molecule used is a derivative of perylene tetracarboxylic diimide (PTCDI), which forms an extremely robust class of materials with high photo and thermal stability. More interestingly, PTCDI materials are of *n-type* semiconductors, in contrast to the more common p-type counterparts in organic semiconductors,[10−12] making PTCDI molecules unique candidates for fabrication as various optoelectronic devices.

Self-assembling PTCDI molecules into one-dimensional structures represents a balance between molecular stacking and solubility. On one hand, a sufficient solubility in some solvents is crucial for processing the self-assembly from individual molecules, and this requires appropriate side chains (e.g., long and/or branched alkanes) to hinder the $\pi-\pi$ stacking of perylene backbones.[13] However, on the other hand, such a weakened $\pi-\pi$ stacking prevents the effective packing of PTCDI molecules along one dimension. One way to enhance the molecular packing is to increase the size of the core aromatic system, i.e., to change the PTCDI monomer to a trimer, tetramer, or pentamer.[14,15] In some cases, the enlarged PTCDI molecules favor the formation of fibril structures, whereas the molecular packing is not highly optimized. The twisting between the PTCDI units (energy minimization) in the supramolecules weakens the $\pi-\pi$ interaction between molecules and thus distorts the packing from the ideal face-to-face conformation. Indeed, red-shifted emission was often observed from the self-assembled crystals of the supra-PTCDI molecules, which implies distorted $\pi-\pi$ stacking.[8]

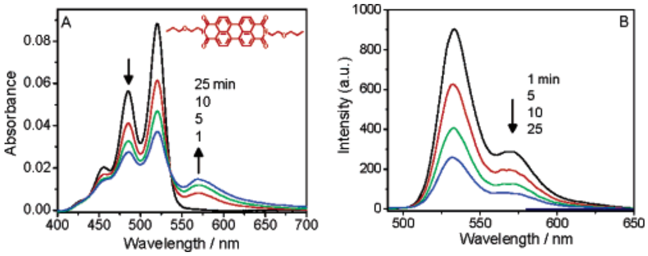


Figure 1. Crystal formation of propoxyethyl-PTCDI in methanol: absorption (A) and fluorescence (B) spectra recorded at different time intervals following injection of a minimal volume of chloroform solution. Excitation of the free molecules at 450 nm produces decreased emission due to the conversion into crystal phase, while excitation of the crystal phase at 570 nm results in no emission as evidenced by the zero intensity scanning line (580−650 nm, shown in B).

For the molecule used in this study (inset of Figure 1A), the greater conformational flexibility of the propoxyethyl side chain (compared to alkyl chains) affords sufficient solubility for the PTCDI molecule in hydrophobic solvents such as chloroform,[16] while the small size and increased density of the side chain allows for tight packing of the perylene backbones to maximize the $\pi-\pi$ interaction. As a result, the molecule becomes insoluble in more polar solvents, such as methanol. Injection of a minimum volume of concentrated chloroform solution of the molecule into methanol leads to formation of nanocrystal phase through self-assembly (more details in Supporting Information). Figure 1A shows the absorption spectral monitoring of such a self-assembling process. Right after the injection, the absorption bands (0−0, 0−1, 0−2, and 0−3 at 520, 485, 455, and 426, respectively) of the molecule decreased gradually with time, while a new band corresponding to the crystal phase appeared at longer wavelength. The isobestic point at 536 nm confirms a stoichiometric conversion from free molecules to single crystals. Normalization of the absorption spectra reveals the relative enhancement of the 0−1, 0−2, and 0−3 transitions (Figure S3), which implies strong excitonic interactions between the stacked PTCDI chromophores.[17,18]

Strong $\pi-\pi$ stacking normally leads to nonemitting crystal phase due to the forbidden low-energy excitonic transition.[8] This is consistent with the results shown in Figure 2B, where the emission of free molecules (excited at 450 nm) decreased gradually with the crystallization process, and excitation of the crystal phase at 570 nm resulted in no emission (Figure 1A). The measurement of differential scanning calorimetry (DSC) also suggested strong molecular packing through $\pi-\pi$ interaction (Supporting Information). The melting point of propoxyethyl-PTCDI (242 °C) is much higher than that of nonyldecyl-PTCDI (84 °C). The long and branched side chain of the latter diminishes the $\pi-\pi$ interaction between molecules and thus weakens the molecular packing, leading to a lower melting point. The weakened (distorted) $\pi-\pi$ stacking makes the low-energy excitonic transition allowable, resulting in red-shifted emission for the crystal phase (Supporting Information).

[†] Southern Illinois University.
[‡] University of Illinois at Urbana-Champaign.

10.1021/ja052940v CCC: $30.25 © 2005 American Chemical Society

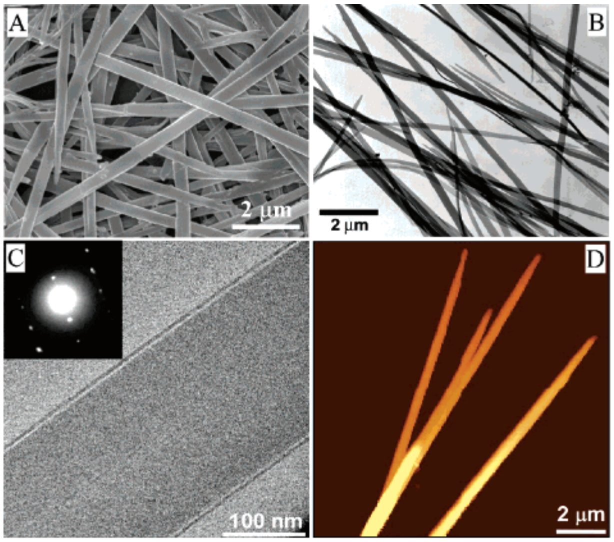


Figure 2. (A) SEM image of propoxyethyl-PTCDI nanobelts (gold-stained) cast on glass; (B) TEM image of nanobelts cast on SiO_2 film; (C) zoom-in TEM image of a nanobelt cast on SiO_2 film ([Inset] Electron diffraction over a nanobelt cast on carbon film.); (D) AFM image of nanobelts cast on mica (*z*-scale: 0−140 nm); average thickness, 100 nm.

Optimized $\pi-\pi$ stacking favors the one-dimensional growth of crystals. SEM measurement of the self-assembly of propoxyethyl-PTCDI in methanol reveals well-defined beltlike nanostructures as shown in Figure 2A. The close-to-rectangular shape of the cross section can be seen either from the broken nanobelts or the belts twisted in the middle with one edge facing upward (Supporting Information). TEM and AFM measurements of the sample also revealed the uniform nanobelt structures (Figure 2B, D). High-magnification TEM imaging over a single belt showed even contrast across the whole surface (Figure 2C), consistent with the beltlike structure. Electron diffraction of the nanobelt showed a typical crystalline pattern with sharp diffraction spots (inset of Figure 2C). Two distinct reciprocal lattice vectors can be obtained from the diffraction pattern, giving two *d* spacings, *d*1 0.865 and *d*2 0.466 nm. The *d*1 is perpendicular to the belt direction. These spacing values are consistent with the X-ray measurement of bulk crystals of the similar PTCDI molecules.[19] As a comparison, we have also imaged the self-assembled nanostructure of nonyldecyl-PTCDI, for which only spherical shape (zero-dimension) nanocrystals were found (Supporting Information). The lack of one-dimensional self-assembly is consistent with the distorted $\pi-\pi$ stacking due to the steric hindrance of branched side chains as discussed above.

Considering the parallel conformation between packed molecules, the anisotropy in the cross-sectional plane is expected to be small compared to the anisotropy along the $\pi-\pi$ stacking, i.e. the one-dimensional nanostructure obtained would be approximately optically uniaxial.[20] This is similar to the uniaxial columnar packing of discotic liquid crystal molecules. Figure 3 shows the consecutive rotating microscopy imaging of a nanobelt under crossed polarization, where the central image was taken in the bright field. Only when the nanobelt was aligned 45° to the direction of the polarizer was the anisotropy birefringence maximized. At a position parallel to the polarizer, the birefringence of the nanobelt became minimal (hardly detectable). This implies that the optical axis is indeed along the direction of $\pi-\pi$ stacking.

In summary, an n-type semiconductor nanobelt structure has been successfully fabricated through a simple self-assembling process in methanol solution. Both electron and optical microscopy measurements suggest the uniaxial crystal structure of the nanobelt. The uniform nanobelts could be an ideal system for exploring the dimensionally confined optoelectronic properties (e.g., charge carrier mobility) of organic semiconductor materials. We are currently in the process of fabricating such nanobelts into field effect transistors (FET) on oxidized silicon wafers.

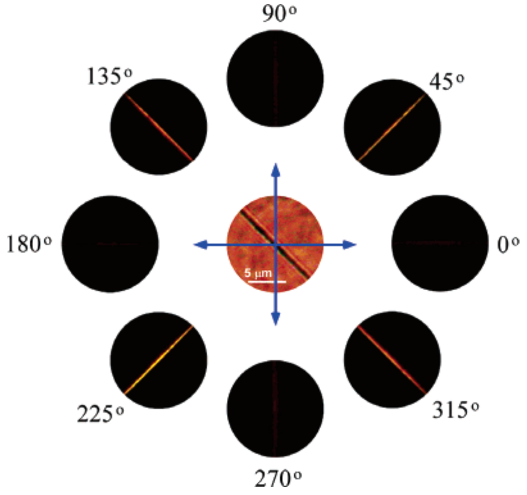


Figure 3. Single nanobelt under cross-polarized microscope (homemade based on Veeco Aurora III NSOM, using a 100 × NA1.25 oil immersion polarization objective and 36× zoom CCD camera): consecutive rotation of the sample showed an alternate appearance of birefringence as the nanobelt was aligned at 45° to the polarizer.

Acknowledgment. This work was supported by Consortium for Advanced Radiation Sources (CARS), and ORDA, COS, and MTC at SIUC. We thank Prof. Dan Dyer for DSC measurement.

Supporting Information Available: Experimental details of synthesis, spectroscopy and microscopy measurements; complete refs 4, 7, 10, and 14. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Law, M.; Goldberger, J.; Yang, P. *Annu. Rev. Mater. Res.* **2004**, *34*, 83.
(2) Huang, J. X.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314.
(3) Zhou, Y.; Freitag, M.; Hone, J.; Staii, C.; Johnson, J. A. T. *Appl. Phys. Lett.* **2003**, *83*, 3800.
(4) Lee, H. J. et al. *J. Am. Chem. Soc.* **2004**, *126*, 16722.
(5) Nguyen, T.-Q.; Martel, R.; Avouris, P.; Bushey, M. L.; Brus, L.; Nuckolls, C. *J. Am. Chem. Soc.* **2004**, *126*, 5234.
(6) Kastler, M.; Pisula, W.; Wasserfallen, D.; Pakula, T.; Mullen, K. *J. Am. Chem. Soc.* **2005**, *127*, 4286.
(7) Hill, J. P. et al. *Science* **2004**, *304*, 1481.
(8) Wurthner, F. *Chem. Commun.* **2004**, 1564.
(9) Guillon, D. *Struct. Bonding* **1999**, *95*, 41.
(10) Katz, H. E. et al. *Nature* **2000**, *404*, 478.
(11) Newman, C. R.; Frisbie, C. D.; da Silva Filho, D. A.; Bredas, J.-L.; Ewbank, P. C.; Mann, K. R. *Chem. Mater.* **2004**, *16*, 4436.
(12) Xu, B. Q.; Xiao, X.; Yang, X.; Zang, L.; Tao, N. J. *J. Am. Chem. Soc.* **2005**, *127*, 2386.
(13) Langhals, H. *Heterocycles* **1995**, *40*, 477−500.
(14) Wasielewski, M. R. et al. *J. Am. Chem. Soc.* **2004**, *126*, 8284−8294.
(15) Yan, P.; Chowdhury, A.; Holman, M. W.; Adams, D. M. *J. Phys. Chem. B* **2005**, *109*, 724.
(16) Cormier, R. A.; Gregg, B. A. *Chem. Mater.* **1998**, *10*, 1309−1319.
(17) Van Herrikhuyzen, J.; Syamakumari, A.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 10021.
(18) Rybtchinski, B.; Sinks, L. E.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, *126*, 12268.
(19) Hadicke, E. H.; Graser, F. *Acta Crystallogr.* **1986**, *C42*, 189.
(20) Friedrich, M.; Wagner, Th.; Salvan, G.; Park, S.; Kampen, T. U.; Zahn, D. R. T. *Appl. Phys., A* **2002**, *75*, 501.

JA052940V