Self-directed Assembly of Photoactive Perylenediimide-Bridged Silsesquioxane into a Superlong Tubular Structure

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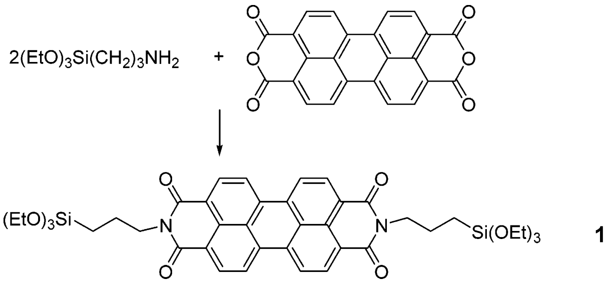
Hybrid silicate materials derived from the hydrolytic polycondensation of organo-bridged silsesquioxane precursors, $(RO)_3{-}Si{-}R'{-}Si{-}(OR)_3$, where R and R′ are organic groups, have received increasing attention over the past decade.[1] Recently, efforts are being made to better control their structure to create new diverse functional materials. Surfactant-directed self-assembly[2] and self-directed assembly[3] methods have been successfully developed for the fabrication of bridged silsesquioxanes with well-organized structure. Self-directed assembly that takes advantage of the weak interactions, such as hydrogen bonding, $\pi-\pi$, and/or hydrophobic interactions between the R′, provides a very easy method for fabricating the hierarchical structure. By judicious choice of the organic substructure R′ in the precursor, new intrinsic nanomaterials including both the nature of the molecules and their collective properties within the aggregate will be realized. Recent efforts on such materials have shown their infinite applications and will agitate a new challenge in this area.[4]

Substituted perylenediimide is one of the most extensively studied classes of organic semiconductors and has enjoyed possible applications in optical and electronic devices.[5] Recent investigations on the self-organization of perylenediimide have shown that the photoluminescence properties depend strongly on the molecular interactions and their relative orientations.[6] Introduction of photoactive perylenediimide into supramolecular silsesquioxane via its large π systems will achieve organized multichromophoric systems with new collective effects.

Scheme 1. Structure of the Precursor Perylenediimide Monomer 1



Herein, we report the synthesis and self-directed assembly of photoactive perylenediimide-bridged silsequioxane **1** into a superlong tubular structure with highly ordered lamellar mesostructure in the tube walls. The $\pi-\pi$ interactions between the perylenediimide cores combined with the solvophobic interactions of the perylenediimide cores and the solvophilic interactions of the (propyl)triethoxysilane parts are responsible for the self-assembly of **1** into the tubular superstructure. The optical behaviors of the resulting anisotropic ordered tubes of **1** have been characterized by UV−vis absorption and photoluminescence spectra.

Scheme 1 shows the structure of the precursor perylenediimide monomer **1**, which is very stable in the open air. It was synthesized in a single step from the commercially available starting materials, (3-aminopropyl)triethoxysilane and 3,4,9,10-perylenetetracaboxylic dianhydride (see the Supporting Information). Slower evaporation of **1**'s acetone/petroleum ether (v/v = 1:5) solution in air yielded shiny needlelike red precipitate of **1**.

Figure 1 shows the typical FESEM (field emission scanning electron microscopy) images of material **1** precipitate. Low-magnification FESEM images reveal that the material **1** consists of needlelike fibers with a clean and smooth surface, and the fibers have length of several hundred micrometers (Figure 1A) and outside diameters ranging from 1 to 9 μm (most of them range from 1 to 4 μm, Figure 1B,E). High-magnification FESEM images (Figure 1C,D) demonstrate that the centers of the fibers are empty; i.e., the fibers have tubular morphology. Typically, the tube (Figure 1D) has an outside diameter of 2.8 μm and inside diameter of 1.5 μm with a wall thickness of 0.65 μm.

To gain insight into the molecular orientation and packing profile within the assembled morphologies, we examined the X-ray diffraction (XRD) of **1**, as shown in Figure 2. The XRD pattern shows multiple orders of (00*l*) (l = 1, 2, 3, 4,.....) peaks, indicative of highly ordered lamellar stacks with *d* spacing of 2.94 nm and with the lamellar sheets running

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(1) (a) Shea, K. J.; Loy, D. A.; Webster, O. W. *J. Am. Chem. Soc.* **1992**, *114*, 6700−6710. (b) Corriu, R. J. P.; Moreau, J. J. E.; Thepot, P.; Wong Chi Man, M. *Chem. Mater.* **1992**, *4*, 1217−1224.

(2) (a) Kapoor, M. P.; Yang, Q.; Inagaki, S. *J. Am. Chem. Soc.* **2002**, *124*, 15176−15177. (b) Guan, S.; Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 5660−5661. (c) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304−307. (d) Lu, Y.; Fan, H.; Doke, N.; Loy, D. A.; Assink, R. A.; LaVan, D. A.; Brinker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 5258−5261.

(3) (a) Moreau, J. J. E.; Vellutini, L.; Wong Chi Man, M.; Bied, C.; Bantignies, J.-L.; Dieudonne, P.; Sauvajol, J.-L. *J. Am. Chem. Soc.* **2001**, *123*, 7957−7958. (b) Moreau, J. J. E.; Pichon, B. P.; Wong Chi Man, M.; Bied, C.; Pritzkow, H.; Bantignies, J.-L.; Diudonne, P.; Sauvajol, J.-L. *Angew. Chem., Int. Ed.* **2004**, *13*, 203−206.

(4) (a) Liu, N.; Yu, K.; Smarsly, B.; Dunphy, D. R.; Jiang, Y.-B.; Brinker, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 14540−14541. (b) Barboiu, M.; Cerneaux, S.; van der Lee, A.; Vaughan, G. *J. Am. Chem. Soc.* **2004**, *126*, 3545−3550.

(5) Würthner, F. *Chem. Commun.* **2004**, 1564−1579, and references therein.

(6) Liu, S.-G.; Sui, G.; Cormier, R. A.; Leblanc, R. M.; Gregg, B. A. *J. Phys. Chem, B* **2002**, *106*, 1307−1315.

10.1021/cm050275j CCC: $30.25

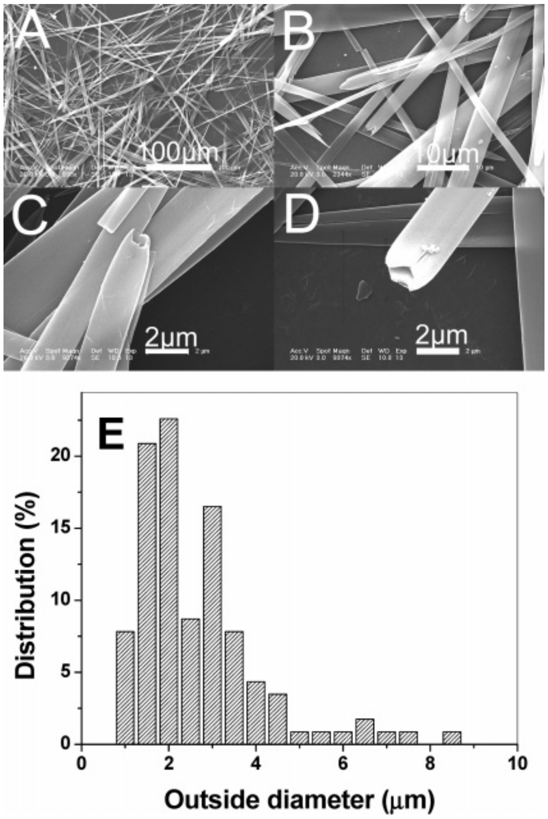

Figure 1. Low (A, B) and high (C, D) magnification FESEM images of **1** precipitate as well as the histogram (E) for the distribution of the outside diameters of the tubes.

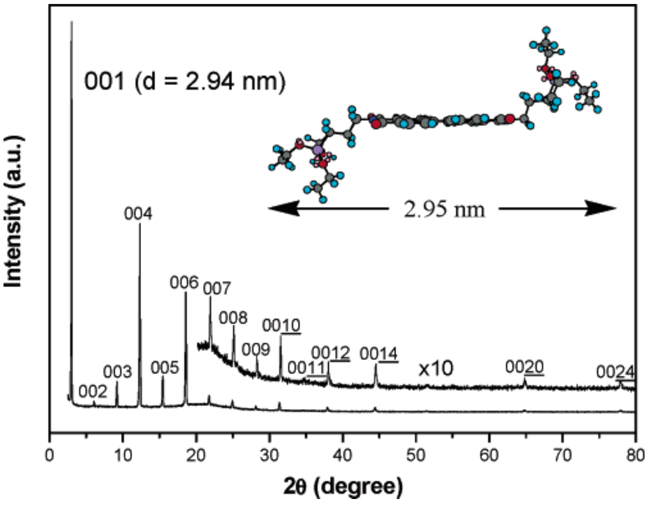

Figure 2. XRD pattern of **1**'s superlong tubes. Inset: molecular model of **1** which is in trans-form. Atomic legend: gray (C), dark blue (N), red (O), purple (Si), and green (H).

parallel to the axial of the superlong tube (Figure S1). Molecular models of **1** (using Gaussian 03 Pro, AM1 method) estimate the molecular lengths of **1** to be ca. 2.95 nm, indicating that **1**'s monomer packed at an angle of almost 90° relative to the plane of the lamellar.

During our experiments we noticed that acetone is a relatively good solvent ($\times 10^{-2}$ M) for **1**, while petroleum ether is not ($\times 10^{-6}$ M). To explore the formation process of the tubes, topologies of **1**'s small crystals grown in acetone under the same conditions were investigated. Only plates with lamellar structures were observed (Figure S2), indicating that petroleum ether plays an important role for the formation of the tubes. It is well-documented that the structure of organic molecules plays an important role in determining their stacking mode.[5] So the molecular structural features of **1** can provide a clue for the understanding of the possible formation mechanism of the tubes. Molecule **1** is composed of three parts, i.e., two (propyl)triethoxysilane parts which are very soluble in the petroleum ether and one rigid perylenediimide core with poor solubility in the petroleum ether. So we can consider **1** as an amphiphilic molecule relative to the petroleum ether. When an appropriate amount of **1** was diso1ved in acetone/petroleum ether (v/v = 1:5) mixing solution, single molecule or low aggregation of **1** was surrounded by the solvent molecules of acetone and petroleum ether. With the evaporation of lower boiling point solvent molecules of acetone (relatively good solvent for **1**), the concentration of **1** increased accompanied by its remarkable decrease of solubility. This resulted in the improvement of the energy in the system, in which the (propyl)triethoxysilane parts were absorbed by the solvent molecules of petroleum ether, while the perylenediimide cores were repelled by them. **1**'s molecules tended to escape out of the system to minimize the energy. To reach a relatively stable state, **1**'s molecules associated through the face-to-face $\pi-\pi$ interaction between the perylenediimide cores with the (propyl)triethoxysilane parts stretching out to the solution. With the evaporation of more and more petroleum ether, the concentration of the aggregates increased and arranged in lamellar structure until reaching a point where increased energy in the system could not be minimized by the association interactions. The sheets scrolled to the tubular topology with as much as (propyl)triethoxysilane parts extended to the petroleum ether while as little as the perylenediimide cores contacted with the petroleum ether, and the system reached a new balancing state with all parts located well at their favorite positions (Figure S3). While in acetone, due to the relative higher solubility of **1**, no such point existed for **1** to scroll into the tubular structure, leaving only the lamellar structure of **1** (Figure S2). On the basis of the above discussion, due to the amphiphilic nature of **1** relative to the solvent molecules**,** the cooperative $\pi-\pi$ interactions between the perylenediimide cores, the solvophobic interactions of the perylenediimide cores, and the solvophilic interactions of the (propyl)triethoxysilane parts were responsible for the self-assembly of **1** into the tubular superstructure.

We have checked the effects of partial hydrolysis and condensation on the morphology of the sample. Immersing **1**'s film (see Supporting Information, section 2) into the hydrochloric acid solution (pH = 2) for 15 days resulted in the formation of hybrid **H1**. It is obvious that **1**'s tubular structure collapsed to a crystalline plate with lamellar structure (Figure S4, FESEM images of **H1)**. The XRD pattern of **H1** (Figure S5) shows two distinct sets of (00*l*) peaks with *d* spacings of 2.94 and 2.46 nm, respectively. This can be attributed to the partial hydrolysis and condensation of the interlamellar triethoxysilane parts as also evidenced by the ^{29}Si CP-MAS NMR results (Figure S6). It is not difficult to understand that due to the hydrolysis and condensation of triethoxysilane parts of **(1)**, the distance between the interlamellar and intralamellar perylenediimide cores were pulled more closely, which crashed the tubes into more closely packed lamellar plates.

The effects of the self-directed closely packed structure on the optical behaviors of **1** are demonstrated by the UV−vis absorption and photoluminescence spectra (Figure S7). The absorption spectrum of dilute solution of **1** [Figure S7-(A)] shows four well-resolved, relatively narrow absorption peaks at 425, 454, 482, and 518 nm. However, line broadening was observed for **1**'s superlong tube film due to the significant intermolecular electronic interactions of the close-packed molecules. This agrees very well with those reported for red perylenediimide pigments in the crystalline state.[6] Figure S7(B) shows the photoluminescence (PL) spectra of dilute solution of **1**, **1**'s superlong tube film, and **H1** hybrid. Dilute solution of **1** shows two well-resolved peaks at 529 and 565 nm. Both emission spectra for **1**'s superlong tube film and **H1** hybrid consist of a broad band from 550 to 750 nm, significantly broadened and red-shifted with respect to that of dilute solution of **1**. Moreover, an obvious red shift has been observed for the emission band from **1**'s superlong tube film ($\lambda_{max} = 607$ nm) to **H1** hybrid ($\lambda_{max} = 625$ nm). This can be attributed to the closer packing of the perylenediimide molecules in the **H1** hybrid and indicates an increased intermolecular charge-transfer character in the excited state of **H1** hybrid.

In summary, we have synthesized supramolecular perylenediimide-bridged organosilane with tubular topology by self-directed assembly for the first time. A most interesting perspective of the tubular aggregates is the possibility to use them as nanometer-scale devices for energy transport. These studies should also cast light onto the contribution of controlled formation of the three-dimensional functional devices with targeted functionalities in silica through self-organization and creating systems of a variety of applications (molecular recognition, advanced catalysis, transport, optic, electronic or magnetism, etc.).

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Supporting Information Available: Experimental details, Figures S1−S7 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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