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Highly Fluorescent Rigid Supramolecular Polymeric Nanowires Constructed Through Multiple Hydrogen Bonds

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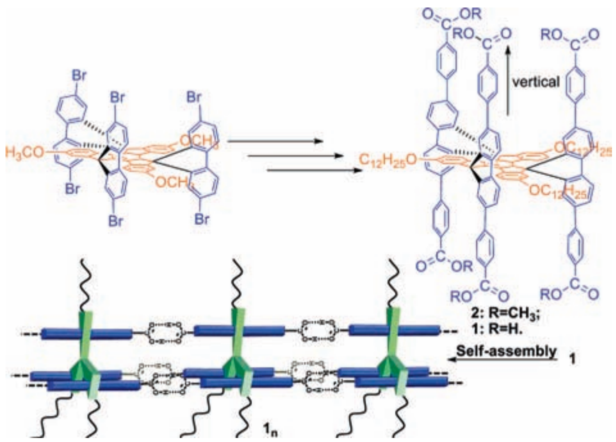
One-dimensional (1D) noncovalent supramolecular polymeric nanostructures[1] self-assembled from low-molecular-weight building blocks have attracted considerable interest for applications in material science as a *bottom-up* approach to fabricate optoelectronic devices.[2] Recently, the fabrication of devices utilizing nanowires based on $\pi-\pi$ interaction has been intensively explored as an effective tool. Differently, geometrical matching and directionality of hydrogen bonding provides another method to form 1D nanowires with various properties.[1c,g] From another perspective, because of serious self-quenching in $\pi-\pi$ interacted systems, it is challenging to obtain highly florescent nanowires after self-assembly.[3] Therefore, hydrogen bonding can be considered as a potential solution, which may pave the way to optoelectronic applications in the chemical and biological fields.

In our previous work, a readily modifiable shape-persistent three-dimensional (3D) skeleton was facilely developed for organic light-emitting diodes and the construction of nanocages.[4] Herein, we report a supramolecular polymer constructed by multiple hydrogen bonds, which can form uniform nanowires with high aspect ratio and high solid quantum efficiency (22%). Scheme 1 outlines the structure of **1**, which was synthesized in 67% overall yield, starting from the corresponding hexabromide.[7] **1** can self-assemble to a novel supramolecular polymer **1**$_n$. The introduction of multiple hydrogen bonds not only provides the strong tendency of self-assembly in the vertical direction,[5] but also lowers the possibility of the mismatch of hydrogen bonds;[6] moreover, the rigid 3D structure effectively reduces the self-quenching in the solid state and aggregation to achieve the high fluorescence efficiency in the solid state.[4a]

When hexane vapor diffused into the THF solution of **1** (1.2×10^{-3} M), the clear solution gradually turned opaque and some white flocs precipitated, which indicated the formation of certain aggregates. As illustrated in Figure 1a,b, scanning electron microscopy (SEM) images demonstrated that uniform and well-dispersed nanowires with diameters ranging from 100 to 200 nm and length achieving several hundred micrometers were formed. Transmission electron microscopy (TEM) images (Figure 1c) indicated the straight shape and uniform inner structure of these nanowires. Tapping-mode atomic force microscopy (TM-AFM) images showed the height distribution of nanowires with about 120 nm on average. However, once water was added into THF solution of **1**, only solids or short bulks were obtained.[7] All results confirmed the construction of **1**$_n$ through hydrogen-bonding.

Considering the strong multivalent interaction in such a system,[4b,6] we also investigated self-assembly behaviors on a mica surface by the evaporation of a highly dilute solution of **1** (2.4×10^{-6} M) in THF/$C_2H_2Cl_4$ (1:1). It is exciting that the TM-AFM showed the presence of monodispersed lines with a uniform height of 1.3~1.6 nm, which corresponds remarkably well to the planar diameter of **1** (ca. 1.4 nm without side chains[7]), indicating that the shape-persistent structure existed with strong interactions in merely one direction. We rationally deduced that such *monomolecular* nanofibers were formed with **1** connected to each other along the direction of hydrogen bonds, and possibly they were subunits of larger nanowires precipitated from concentrated solution.

Scheme 1. The Structure of Hexaacid **1** and the Schematic Diagram of Its Assembly **1**$_n$



To further elucidate the structure of the nanowires, Fourier transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD), and selected area electron diffraction (SAED) were implemented. FTIR showed the characteristic stretching vibration absorption bands of typical dimerized carboxylic acids at 3448 (O−H) and 1691 cm^{-1} (C=O),[7] which were lower than those of dissociated ones (ca. 3550 and 1725 cm^{-1}).[5c] Moreover, the associated hydrogen bonds led to a broad absorption of the stretching vibration of O−H bond centered at 3448 cm^{-1}. In sharp contrast with the solid deposited from THF, only one broad peak was observed in nanowires at a *d* spacing of 4.3 Å in the XRD pattern (Supporting Information, Figure S8b),[7] which was reported to be the result of interactions of alkyl chains.[3b] However, SAED exhibited a series of diffraction rings, indicating that certain extent ordered arrangements existed along the nanowires (Figure 1d). Therefore, we envisaged that our nanowires were constructed with lots of single molecular wires via weak lateral interactions from alkyl chains and arranged parallel to the substrate in a less ordered way, which resulted in the disappearance of periodicity of long axis in XRD (Figure S10).[2e] However, the orientation of hydrogen bonds, the shape-persistent

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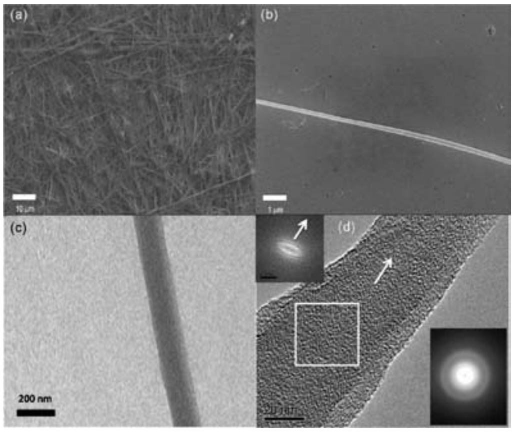

Figure 1. (a, b) SEM, (c) TEM, (d) HR-TEM images of nanowires; the upper left inset of panel d is a FFT image of the white square zone and the lower right is a SAED pattern. The arrows indicate the long axis of a single nanowire.

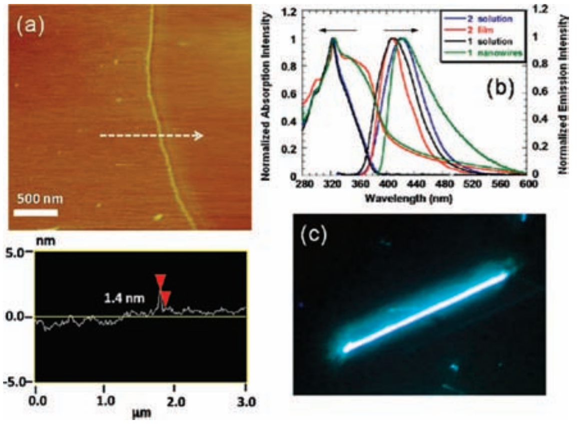

Figure 2. (a) AFM images of an air-dried sample of the highly dilute solution of **1** (2.4×10^{-6} M) in THF/$C_2H_2Cl_4$ (1:1) deposited on a mica substrate; (b) UV−vis and PL spectra of **2** and **1** both in THF solution and in solid states; (c) fluorescence micrograph of supramolecular nanowires (400 magnitude).

structure, and even the weak lateral interactions also together guaranteed the intensively one-dimensional growth tendency of the nanowires, further confirmed by analysis of high resolution TEM images using fast Fourier transformation (FFT) and filtered inverse FFT (Figure 1d).[7]

Figure 2b compares absorption and photoluminescence (PL) spectra of ester **2** and monomer **1** both in THF solution (1.0×10^{-6} M) and in solid states. In dilute solution, both **1** and **2** showed the identical absorption features peaking at 324 nm due to the similar effective conjugation length (2,7-diphenylspirofluorene fragment) of these molecules in the ground state.[4b] However, the emission peak of **1** (411 nm) resulted in a 12 nm blue-shift in comparison with that of **2** (423 nm), which resulted from the solvent effect. In thin film, except for the identical absorption maximum, both **2** and **1** exhibited a shoulder around 350 nm with obvious absorbance enhancement; however, to our surprise, the emission λ_{max} of **2** in thin film resulted a 15 nm blue-shift (408 nm) from their solution, and oppositely a 13 nm red-shift was observed in nanowires of **1**, possibly caused by a different solid state conformation and the formation of H-bonds. Figure 2c shows the greenish blue emitting nanowires under fluorescence microscope. Their absolute photoluminescence (PL) efficiency was measured to be 22% by an integrating sphere system, which was quite high among organic nanowires.[3b,8] In comparison with the solvent efficiency of **1** (32%), only 10% efficiency was lost in the solid state.[7] Our design provided a method to obtain 1D nanowires with relatively high solid quantum efficiency.

In conclusion, we have developed a novel supramolecular polymeric nanowires constructed by a 3D shape-persistent hexaacid **1** through multiple hydrogen bonding. We also obtain a single molecular nanowire from highly dilute solution. Detailed results demonstrate that self-assembly of **1** through such an approach successfully led to high fluorescent nanowires by the obvious reduction of self-quenching in the solid state. We are currently investigating the development of nanoscale devices using these nanowires.

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Supporting Information Available: Detailed experimental procedures and characterization data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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