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. 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 and polypyrrole, while the crystalline structure of polymer nanofibers is often difficult to control due to the complicated intermolecular interaction. Recent studies have proven that self-assembly through strong \( \pi-\pi \) stacking is an effective approach to one-dimensional nanostructures for aromatic organic molecules, particularly the larger macrocyclic aromatic molecules such as hexabenzocoronene. This implies a potential way to enhance the charge carrier mobility, which is believed to be favored along the \( \pi-\pi \) stacking direction.

In this communication, we report on a simple method for fabricating nanobelts 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 diimide (PTCDI), which forms an extremely robust class of materials with high photo and thermal stability. More interestingly, PTCDI materials are of particular interest due to their promising applications in optical and electronic devices. The structural flexibility of the propoxyethyl side chain allows for the fabrication of conducting polymers such as polyaniline and polypyrrole, while the crystalline structure of polymer nanofibers is often difficult to control due to the complicated intermolecular interaction. Recent studies have proven that self-assembly through strong \( \pi-\pi \) stacking is an effective approach to one-dimensional nanostructures for aromatic organic molecules, particularly the larger macrocyclic aromatic molecules such as hexabenzocoronene. This implies a potential way to enhance the charge carrier mobility, which is believed to be favored along the \( \pi-\pi \) stacking direction.

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 succeed, resulting in red-shifted emission for the crystal phase (Supporting Information).

Strong \( \pi-\pi \) stacking normally leads to nonemitting crystal phase due to the forbidden low-energy excitonic transition. This is consistent with the results shown in Figure 2B, where the emission of free molecules (excited at 450 nm) decreases gradually as the crystal phase at 570 nm results in no emission (Figure 1A). The measurement of direct bandgap 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 succeed, resulting in red-shifted emission for the crystal phase (Supporting Information).
Two distinct reciprocal lattice vectors can be obtained from the crystalline pattern with sharp diffraction spots (inset of Figure 2C). Electron diffraction of the nanobelt showed a typical structure. TEM and AFM measurements of the sample also twisted in the middle with one edge facing upward (Supporting Information). TEM and AFM measurements of the sample showed an alternate appearance of birefringence as the nanobelt was aligned at 45° to the polarizer.

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.

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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.

Figure 2. (A) SEM image of propoxyethyl-PTCDI nanobelts (gold-stained) cast on glass; (B) TEM image of nanobelts cast on SiO2 film; (C) zoom-in TEM image of a nanobelt cast on SiO2 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, \( d1 \) 0.865 and \( d2 \) 0.466 nm. The \( d1 \) 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

References


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