

Surface-assisted one-dimensional self-assembly of a perylene based semiconductor molecule†

Aniket Datar, Randy Oitker and Ling Zang*

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Chloroform-vapor annealing of thin films of propoxyethyl perylene tetracarboxylic diimide (PE-PTCDI, an n-type semiconductor) deposited on glass or mica leads to formation of well-defined one-dimensional self-assemblies (e.g. nanobelts), which show optically uniaxial properties as demonstrated by the linearly polarized emission.

Self-assembling organic semiconductors into one-dimensional (1D) nanostructures has raised increasing interest in the design and development of organic optoelectronics,^{1–4} particularly those involving channel materials in the size scale of nanometres. However, most of the materials exploited so far are p-type semiconductors including the conducting polymers,^{3,4} conjugate oligomers⁵ and large disc-shaped aromatic molecules^{6–8}. In contrast, n-type molecules have been employed much less to achieve 1D self-assembly. Indeed, n-type organic semiconductors are not as common as the p-type counterparts among the available molecules with semiconductor characteristics. Recent research suggests that derivatives of perylene tetracarboxylic diimide (PTCDI) are one of a few classes of molecules that show typical n-type characteristics and high thermal and photo-stability.^{9–11}

While PTCDI molecules have successfully been used in the fabrication of a variety of optoelectronic devices, it turns out to be challenging to assemble PTCDI molecules into 1D nanostructures such as nanowires or nanofibers. This is partially due to the limited solubility of PTCDI. Effective solution processing of self-assembly requires sufficient solubility of molecules, and this in turn demands modification of the molecule with sterically bulky side chains.¹² However, in most of the cases the steric bulk of the side chains distorts the π - π interactions between molecules and thus leads to weakened molecular stacking. As a result, self-assembly of such molecules in solutions can hardly produce well-defined 1D morphology. In a recent work,¹³ we reported the effective fabrication of highly uniform nanobelts from a PTCDI molecule, which is modified with a short, flexible side chain, propoxyethyl (PE). Such a unique side chain provides the molecule with an ideal balance between the solubility and π - π stacking: the greater conformational flexibility of the propoxyethyl chain (compared to alkyl chains) affords PTCDI sufficient solubility in hydrophobic solvents like chloroform,¹⁴ but the small size and increased density

of the ether chain enable tight packing of the PTCDI backbones to maximize the π - π stacking.

Based on our initial success of 1D self-assembly, we move on in this communication to fabricate the nanobelt structures directly on a surface. Such *in situ* fabrication on a substrate will provide potential convenience for the future development of electronic devices (particularly at the nanoscale), which normally require surface deposition of nanomaterials. To this end, we chose glass (cover slip) as the main substrate to explore the surface-assisted self-assembly, aiming to present direct guidance for the nanoscale device fabrication on the surface of oxidized silicon, which possesses similar properties (e.g. composition and polarity) to glass. Moreover, a transparent substrate like glass will make the sample system highly adaptable and compatible for investigation with various optical microscopes, such as confocal and near-field scanning optical microscopes (NSOM), which are particularly useful for measurement at the single-wire level.¹⁵

The surface-assisted solvent-vapor annealing was performed in a closed chamber saturated with an appropriate solvent vapor (details can be found in the Supplementary Information†). The solvent was chosen mainly depending on the surface properties of the substrate. Factors that influence solvent choice include: (1) solubility in order to allow free molecules to be transported with the solvent on the surface; (2) minimum affinity to the surface, thus allowing high mobility on the surface. As a good solvent for PE-PTCDI, chloroform was chosen as the major solvent to carry out the vapor annealing of the sample cast on the surface of glass or mica (both are highly polar). The hydrophobic characteristic of chloroform should enable effective molecular dynamics (and thus the packing) on the hydrophilic surface. Such a solvent-vapor annealing process takes advantages of both the slow crystallization process (taking place in the minimal amount of solvent condensed on the surface) and the flat substrate (which confines the random walk of molecules from 3D in solutions to 2D on a surface, and thus facilitates the spatial-organization of the molecules).

The thin film samples to be annealed were prepared by drop-casting or spin-coating a concentrated chloroform solution of PTCDI onto the surface of mica or glass, respectively. Before solvent-vapor annealing, the film on glass showed a partially dewetted pattern (but no structured or ordered morphology, Fig. 1A). After extended annealing in the vapor of chloroform, a prolonged 1D assembly was formed (Fig. 1B). As indicated by the profile of the line scanning, the morphology of the fibrils was actually in a belt-shape, with height (thickness) and width measured at *ca.* 30 nm and 1 μ m, respectively. The average length of the fibrils was above 10 μ m, leading to an aspect ratio (length

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA. E-mail: lzang@chem.siu.edu; Fax: +1 618-453-6408; Tel: +1 618-453-6483

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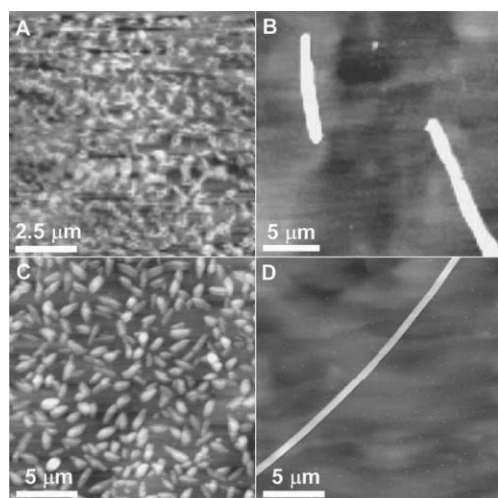


Fig. 1 Tapping-mode AFM images of PE-PTCDI thin film spin-coated on glass (0.25 mM chloroform solution, at 1500 rpm) after various surface treatments: (A) dried in air for 1 h; (B) annealed in chloroform vapor for 24 h; (C) annealed in methanol vapor for 24 h; (D) a film spin-coated from a 0.44 mM chloroform solution and annealed in chloroform vapor for 24 h. The total z -heights for A–D are 25, 30, 41 and 32 nm, respectively.

over thickness) larger than 300. To examine the effect of film thickness on the dimensional size of the final nano-assembly, a thicker film was prepared from a higher concentration chloroform solution. Interestingly, under the same conditions of annealing, the thicker film did not lead to formation of thicker or wider nanobelts; rather the length of the belt was significantly extended (Fig. 1D). This observation implies that the self-assembly in the presence of chloroform is likely to proceed through the vapor-induced swelling and dissolution of the film, followed by the delocalization and reorganization of the ‘dissolved molecules’. Such a hypothesis is also consistent with the hydrophobic characteristics of chloroform, which enable the solvent vapor to be condensed on a polar surface (like glass) as a droplet (with sufficient thickness for dissolving the molecules) rather than an extremely thin layer of liquid completely spread out on the surface (like the case of methanol). The observation shown in Fig. 1 demonstrates the feasibility of controlling the length of nanobelt assembly through changing the processing conditions (*e.g.*, the concentration of the starting solution used for casting the film). The length-adjustable 1D nanomaterials are highly desired for fabricating nanowire-based optoelectronic devices which often require a wide variety of channel lengths to achieve the optimum gate or optical modulation.

As a control, methanol (a poor solvent for PE-PTCDI) was also used to repeat the same annealing process as carried out for chloroform. Due to the limited solubility, the presence of methanol did not provide the molecules with sufficient mobility to achieve the self-organization (*e.g.* 1D packing through molecular π - π packing). However, the strong affinity (hydrogen bonding) of methanol for the glass surface may facilitate the dewetting of the thin film of PE-PTCDI (which is predominantly hydrophobic compared to the glass surface).¹⁶ Indeed, as shown in Fig. 1C, typical dewetting patterns were formed from the methanol annealing, where approximately uniform, slightly-prolonged nanocrystals were produced. As will be demonstrated later, such

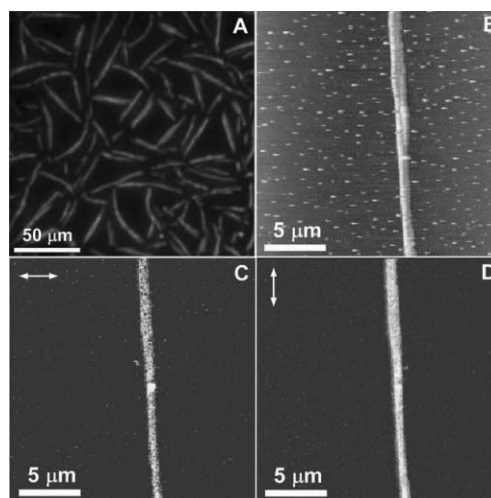
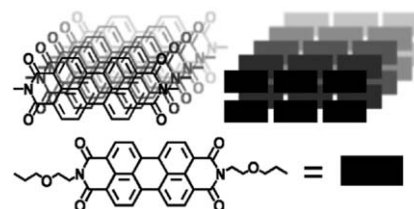


Fig. 2 (A) Fluorescence microscopy and (B) NSOM topography and (C, D) emission images of PE-PTCDI nanobelts fabricated on glass following the same procedure as in Fig. 1D. NSOM topography image (B) was measured by shear force mode scanning (total z -height, 33 nm), and the emission was collected after a polarizer at both horizontal (C) and vertical (D) positions. The emission count ranges for C and D are 85–159 and 49–208, respectively.

dewetting-induced structural organization is even facilitated when a more polar and smooth substrate (such as mica) is used.

Fig. 2A shows the fluorescence microscopy image of the nanobelts fabricated on a glass cover slip. With different excitation wavelengths (450–490 nm for the higher energy transition band and 530–560 nm for the lower energy transition band), the emission color was found to be the same, implying that the emission of the assembled crystal was only from the lowest excimer-like state (which is formed mainly due to the strong electronic coupling between the π -orbitals).¹⁷ The uniform intensity observed over a large area of sample suggests a well-defined morphology (*e.g.* size and shape) of the nanobelts. As previously observed, strong π - π stacking normally leads to a weakly-emitting crystal phase due to the forbidden low energy excitonic transition,^{2,13} thus making it difficult to detect the emission from a diluted suspension of the assemblies. With a fluorescence microscope, the dense excitation beam can be highly focused onto a small area, enabling detectable emission by the CCD camera. Additionally, detection of emission at the dry state can exclude the potential influence of solvent on the fluorescence quantum yield.¹⁷

The 1D molecular packing within the self-assembly may produce linearly polarized emission (Scheme 1), as implied from



Scheme 1 Molecular structure of PE-PTCDI and schematic diagram of the 1D self-assembly induced by π - π stacking.

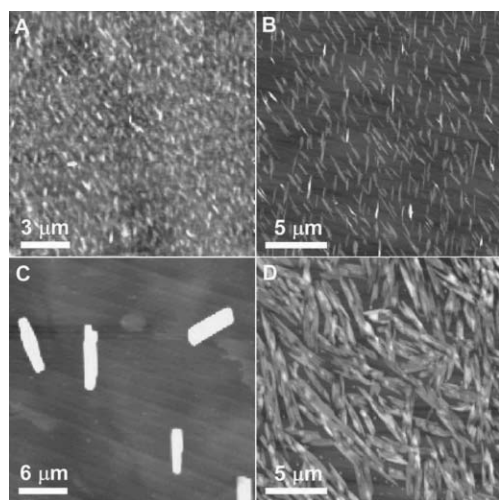


Fig. 3 Tapping-mode AFM images of PE-PTCDI thin film drop-cast on mica after various surface treatments: (A) dried in air for 1 h; (B) aged in an oven at 60 °C for 56 h; (C) annealed in chloroform vapor for 24 h; (D) annealed in methanol vapor for 24 h. The concentrations of the chloroform solutions used for casting were 25 μM for A–C, and 100 μM for D. The total z -heights for A–D are 30, 35, 70 and 44 nm, respectively.

the previously observed uniaxial optical behaviour with cross-polarized microscopy.¹³ This is confirmed by the results shown in Fig. 2C–D, where the emission (collected after a plane polarizer) was measured at two configurations for the polarizer, close to parallel and perpendicular to the long-axis of the belt. It is clearly seen that the emission intensity detected with the parallel polarizer was more than two times higher than that detected with the perpendicular polarizer. Such an observation implies that the emission transition dipole moment is approximately along the 1D molecular stacking direction, which is consistent with the excimer-like electronic coupling resulting from the π – π interactions.¹⁷ A similar observation has recently been reported on the π – π stacked dimer of phenalene,¹⁸ for which the orientation of the electronic transition dipole changes from in-plane (for an individual molecule) to perpendicular to the molecular plane (for the dimer).

The same annealing process was also performed using mica as the substrate. Mica possesses a similar polar surface to glass, and more importantly, it provides an atomically smooth surface (by fresh cleavage) suitable for AFM imaging, leading to an option to clarify whether the dewetting property observed for the methanol-annealed glass sample is due to the surface polarity or the surface roughness¹⁶ (the glass used in this study possessed a surface roughness of about 0.8 nm as measured by the AFM, see Supplementary Information†). Fig. 3A shows the AFM image of a PE-PTCDI film drop-cast on mica after drying in air for 1 h. Clearly, the film underwent significant dewetting, likely due to the highly polar surface of mica (compared to the hydrophobic characteristic of PE-PTCDI). Upon aging in an oven at 60 °C for 56 h, an improved dewetting pattern was attained, with generation of more discrete, rod-shaped nanocrystalline phases (Fig. 3B). Annealing the freshly prepared film in a vapor of chloroform generated nanobelts (Fig. 3C) with a smaller aspect ratio (compared to those formed on glass, Fig. 1B and D). Moreover, the size (e.g., the thickness) of the nanobelts assembled on mica

was around 70 nm (Fig. 3C), larger than those formed on glass (~ 30 nm, Fig. 1B and D). This is likely due to the thicker film prepared by drop-casting on the mica surface. The discrete pattern of the assembled crystals (compared to Fig. 3D) was mainly due to the poor wetting of chloroform on the polar surface of mica, which produces more localized (non-continuous) spreading of solvent on the surface (as discussed above for the case of glass). Annealing the mica sample with methanol vapor produced a similar dewetting pattern as observed on the glass surface. The slightly higher density of the nanocrystals obtained on mica (Fig. 3D) was likely due to the thicker film prepared by drop-casting (compared to spin-coating). These observations suggest that the dewetting property of the PTCDI film on mica and glass is predominantly a result of the surface polarity, which is highly non-compatible with the hydrophobic phase of PTCDI.

In summary we have successfully fabricated 1D self-assembly of a perylene based n-type semiconductor molecule on both glass and mica surfaces with solvent-vapor annealing. Particularly on glass, the 1D assembly can be extended to a few tens of micrometres, providing potentially convenient applications in nanowire-based optoelectronic devices. The charge carrier mobility is expected to be optimal along the 1D molecular packing.

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