

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

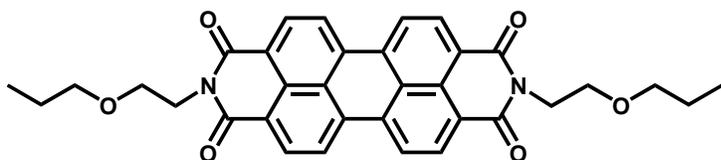
Aniket Datar, Randy Oitker and Ling Zang*

Department of Chemistry and Biochemistry, Southern Illinois University,
Carbondale, IL 62901, USA.

Electronic Supplemental Information

I. Materials

a. PE-PTCDI:



N,N'-di(propoxyethyl)-perylene-3,4,9,10-tetracarboxylic diimide (PE-PTCDI)
Synthesis and characterization was followed the same process described elsewhere.¹

b. Mica:

Mica discs (9.9 mm, quality grade V1, muscovite) were obtained from Ted Pella. Fresh surface was created simply by cleavage with Scotch tape.

c. Glass cover slip:

Pyrex glass cover slips were obtained from Corning Inc. Prior to use, the cover slips were cleaned with piranha reagent (30:70 H₂O₂(35%):H₂SO₄), followed by rinsing with water and methanol.² *Caution: Piranha solution is an extremely strong oxidizing reagent.* The roughness of the glass surface thus cleaned was about 0.8 nm as confirmed by the shear-force mode AFM measurement performed with a NSOM (Figure S1). The sub-nanometer resolution obtained for the z-height measurement implies the flat top-surface of the probe (tip) and the optimum scanning feedback, both of which are crucial for high quality NSOM measurement (*vide infra*).

d. Surface polarity of mica and glass:

Surface polarity of mica and glass was characterized by measuring the contact angle of water on the substrate. The measurement was carried out on a Tanteq contact angle meter using a drop volume of 1 μ L. As observed (Table S1), mica demonstrated higher polarity than glass, consistent with the stronger dewetting property observed for the thin-films deposited on mica.

Table S1

Contact angle	mica	glass
water	12°	18°

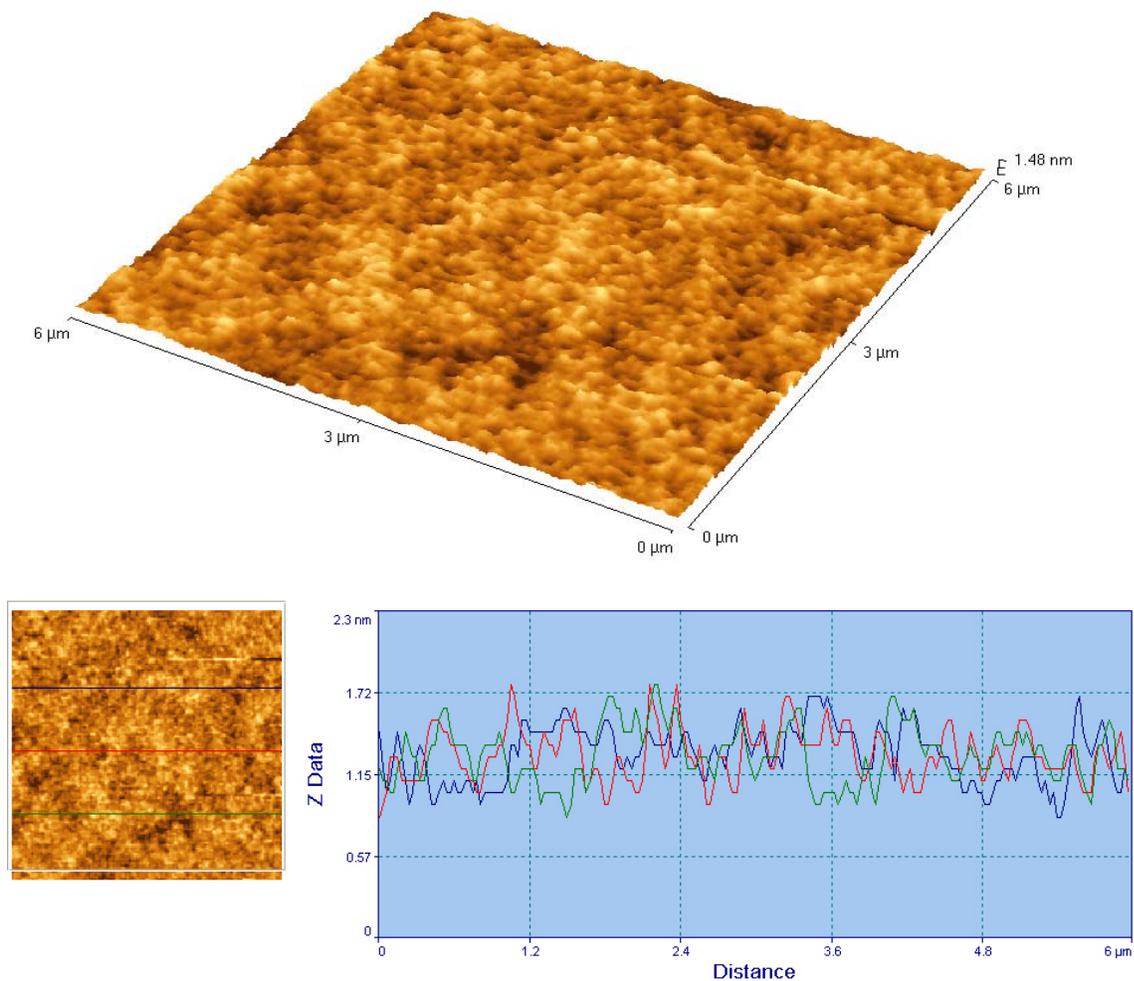


Figure S1. (top) 3D AFM image of a glass surface cleaned by piranha reagent; (bottom) the same image with three line-scan profiles showing the roughness (~ 0.8 nm) of the surface.

II. Sample Preparation:

a. drop-casting on mica:

Two drops of chloroform solution of PE-PTCDI (25 or 100 μ M) were cast on freshly cleaved mica substrate using a glass micro-pipette (Fisher SMI Micro/Pettor capillary). The thin-film thus prepared was subject to drying in air, aging in an oven at 60 °C or annealing with a solvent-vapor (chloroform or methanol) in a sealed chamber (*vide infra*).

b. spin-coating on glass:

Uniform thin-film on glass was prepared by spin-coating three drops (Fisher disposable glass pipette) of chloroform solution of PE-PTCDI (0.25 or 0.44 mM) on a cleaned glass cover slip at 1500 rpm. The thin-film thus prepared was subject to drying in air, followed by annealing in a sealed chamber saturated with solvent-vapor (chloroform or methanol) (*vide infra*).

c. solvent-vapor annealing:

The solvent-vapor annealing was carried out in a desiccator having a lid with valve-controlled vent, which was connected to a vacuum pump. About 30 mL of solvent in a beaker was put in the chamber, followed by vacuum-pumping for about 5 min. The chamber was then sealed by closing the vent, leading to saturation of the solvent vapor inside the chamber. The sample was kept in the vapor environment for an extended period (normally 24 h) to complete the annealing process. The annealing was performed separately for different samples. When switching between different solvents, the chamber was cleaned by repeated vacuum pumping (about three times) before putting in a new beaker of solvent.

III. AFM Measurement:

AFM measurement was carried out in tapping mode on a TopoMetrix Explorer using antimony doped silicon tip. The largest scanning area is $80 \times 80 \mu\text{m}$, and the highest z-resolution is about 0.2 nm. The high resolution in z-height makes AFM especially useful for measuring the thickness of the 1D nanostructures fabricated in this study.

IV. NSOM Measurement:

The near-field scanning optical microscope (NSOM) used in this study was set up mainly based on the prototype NSOM obtained from Veeco (Aurora III) (Figure S2). The central part of NSOM is the tapered, aluminum coated, single-mode optical fiber probe (Veeco, model 1640-00), which is ended with a tiny aperture of 50-80 nm. High optical resolution is achieved by illuminating a sample through the subwavelength aperture while the sample is held in close proximity (namely near-field region) to the probe. Within the near-field the optical resolution is limited only by the probe aperture size, breaking the diffraction limit ($\lambda/2$) to the resolution of ordinary optical microscopy. The NSOM tip-sample distance is regulated by feedback mechanisms similarly to those used in AFM. Simultaneous high-resolution optical (50-80 nm) and topographical ($\sim 10 \text{ nm } x, y$ -resolution, $\leq 1 \text{ nm } z$ -resolution) images were obtained by scanning the sample. Thus, with NSOM the spectral properties (e.g. emission intensity) of a nanostructure can be

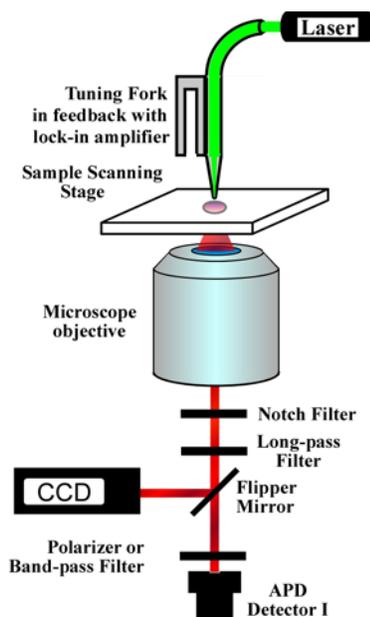


Figure S2. Schematic diagram showing the basic working principle of the NSOM used in this study.

directly correlated to the topography features (e.g. size and shape).

V. Fluorescence Microscopy:

Fluorescence microscopy imaging was carried out with a Leitz Orthoplan II microscope equipped with a real-color CCD camera for catching the emission image. Two filter sets were available for exciting the sample at different wavelength regions: FITC filter set with excitation at 450-490 nm and emission collected at > 515 nm, and Rhodamine filter set with excitation at 530-560 nm and emission collected at > 580 nm. The former filter set provided excitation for the higher energy transition band of the crystal phase, while the later set enabled the excitation of the lower transition band.^{1, 3} Figure S3 shows the emission images taken from the PE-PTCDI nanobelts under excitation with the two wavelength sets. It is clearly seen that the emission color and intensity distribution (between different belts) are almost the same for the excitation at different wavelengths (although the absolute intensity could be different due to the different intensity of excitation with the two filter sets). This implies that the emission of the self-assembled crystals is likely from the lowest excimer-like state,^{3, 4} which is formed through the strong π - π stacking between PTCDI molecules.

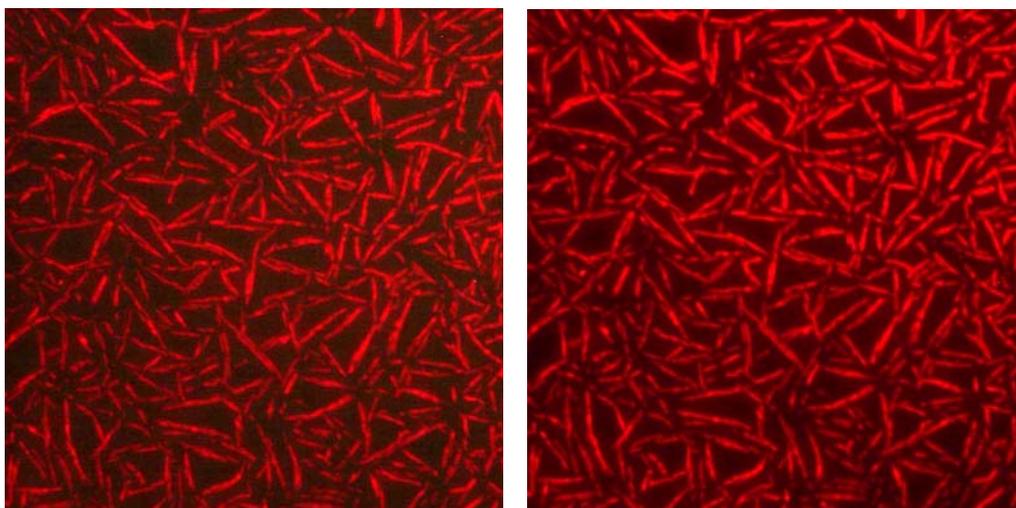


Figure S3. Fluorescence microscopy images taken from PE-PTCDI nanobelts on glass with two filter sets: (left) FITC filter set (excitation at 450-490 nm, emission collected at > 515 nm) and (right) Rhodamine filter set (excitation at 530-560 nm, emission collected at > 580 nm). The nanobelts were fabricated by solvent-vapor annealing (24 h) of a thin-film spin-cast from a chloroform solution (0.44 mM) of PE-PTCDI at 1500 rpm.

References:

1. K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. Zuo and L. Zang, *J. Am. Chem. Soc.*, 2005, **127**, 10496-10497.
2. L. Zang, R. Liu, M. W. Holman, K. T. Nguyen and D. M. Adams, *J. Am. Chem. Soc.*, 2002, **124**, 10640-10641.

3. M. J. Ahrens, L. E. Sinks, B. Rybtchinski, W. Liu, B. A. Jones, J. M. Giaimo, A. V. Gusev, A. J. Goshe, D. M. Tiede and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2004, **126**, 8284-8294.
4. F. Wurthner, *Chem. Commun.*, 2004, 1564-1579.