One-dimensional Self-assembly of a Water Soluble Perylene Diimide Molecule by pH Triggered Hydrogelation

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I. Materials and methods

N,N’-di(propanoic acid)-perylene-3,4,9,10-tetracarboxylic diimide (PA-PTCDI).

This compound was synthesized following the standard condensation method developed by Langhals. Briefly, 1.376 g (3.507 mmol) perylene-3,4,9,10-tetracarboxylic dianhydride (Aldrich), 2.5 g (28.06 mmol) 3-aminopropanoic acid (Aldrich), and 18 g imidazole were heated under argon at 100 °C for 4 h. The reaction mixture was cooled to room temperature and dispersed in 100 mL ethanol followed by addition of 300 mL 2 M HCl. The mixture was stirred overnight. The resulting red solid was collected by vacuum filtration through a 0.45 μm membrane filter (Osmonics). It was washed thoroughly with distilled water until the pH of washings turned to be neutral. The collected solid was dried in vacuum at 60 °C. TLC: Rf (silica gel/CHCl₃:n-butanol 95:5) = 0.68.

pH 9.0 and pH 4.0 solutions were prepared with buffer capsules acquired from Hydrion Buffer Capsules. UV-vis absorption and fluorescence spectra were measured on a PerkinElmer Lambda 25 spectrophotometer and LS 55 fluorometer, respectively. Pyrex glass cover slips (from
Corning Inc.) were used as the support substrate for AFM measurement of the self-assembled nanostructures. Prior to use, the cover slip was cleaned with piranha reagent (30:70 H₂O₂ (35%):H₂SO₄), followed by rinsing with water and methanol. Caution: Piranha solution is an extremely strong oxidizing reagent.

II. Preparation of nanofibers

1. pH triggered gelation

4.0 mL stock solution of PA-PTCDI (4.4 mM) was prepared with addition of 14.68 μL of TEA, which gave a molar ratio of PA-PTCDI:TEA of 1:6. The solution thus prepared looked clear, in red color. 1.0 mL of this solution was added to a test tube, followed by addition of 120 μL of 4.0 M HCl. Gel was formed within 5 minutes after addition of HCl. The gel thus formed was then washed (through centrifugation) with 2.0 mL of deionized, distilled water for at least 8 times until the pH of supernatant water became 4.0-5.0. The gel obtained was then dispersed in 2.0 mL deionized, distilled water ready for experimental investigation.

2. Phase transfer method

Briefly, the molecular self-assembly of PA-PTCDI was processed through slow crystallization at the interface between a ‘good’ and a ‘poor’ solvent, where the slow ‘phase transfer’ between the two solvents decreases the solubility at the interface. The poor solvent (e.g., methanol, THF in this case) is normally quite different (e.g., in term of polarity, density) from the good solvent (e.g., water in this case), thus providing the possibility to keep the two solvents in separate phases for an extended period. Typically, a larger amount (10:1 vol) of poor solvent was transferred carefully atop a concentrated water solution of PA-PTCDI (4.4 mM) in a test tube. The solution was kept overnight without disturbing. Red crystals formed at the interface,
followed by slow diffusion into the upper phase of poor solvent. The nanofibers thus formed can be transferred and cast onto TEM grid by pipetting.

III. Spectral Characterization

**Figure S1.** UV-vis absorption spectra of PA-PTCDI dispersed in TEA (A) and pH 9 buffer solution (B). (C) Plot of Absorbance (A) at 499 nm vs. concentration of PA-PTCDI. (D) Plot of ratio of A$_{0\rightarrow0}$ / A$_{0\rightarrow1}$ vs. concentration of PA-PTCDI. Concentration of PA-PTCDI in both solutions was increased from 0.8 to 8.0 µM.

Concentration dependence studies for PA-PTCDI in pH 9.0 buffer solution showed typical dimer like characteristics, as evidenced from the absorption spectra, where appeared a dominant peak at
499 nm along with a shoulder around 544 nm, for which the relative intensity between the vibronic 0→0 band and 0→1 band in the electronic $\pi \rightarrow \pi^*$ transition ($A_0^{0→0}/A_0^{0→1} \leq 0.6$) is reversal to that of monomeric PTCDIs. Molar absorptivity of the dimer at $\lambda_{\text{max}} = 499$ nm was measured to be ca. 74,000 M$^{-1}$ cm$^{-1}$. $A_0^{0→0}/A_0^{0→1}$ ratio varied only slightly between 0.6 to 0.53 within the concentration range tested, further confirming dimer state.$^{3-7}$

When Triethylamine (TEA) was considered as a basic medium to dissolve PA-PTCDI in water, solutions were initially prepared at three different molar ratios of PA-PTCDI:TEA of 1:2, 1:4 and 1:6. Only the solution of PA-PTCDI:TEA at molar ratio of 1:6 gave complete dissolution of the molecule and resulted in clear red homogeneous solution. UV-vis measurements were performed for a series of concentrations of PA-PTCDI (0.8 – 8.0 μM), all fixed at a molar ratio of PA-PTCDI:TEA of 1:6. Absorption spectra of PA-PTCDI in TEA looks quite similar to those obtained in pH 9 buffer. For example, the molar absorptivity measured in TEA solutions was also ca. 74,000 M$^{-1}$ cm$^{-1}$ and $A_0^{0→0}/A_0^{0→1}$ ratio also varied between 0.6 to 0.53. These observations indicate that PA-PTCDI existed in dimeric state in basic aqueous solutions.

IV. TEM images of PA-PTCDI nanofibers fabricated by Phase transfer method

![Figure S2. Large-area TEM images of PA-PTCDI nanofibers synthesized by the phase transfer method in methanol (A) and THF (B).](image)
V. Fluorescence Microscopy Imaging of a Single Nanofiber fabricated by Phase transfer method

![Fluorescence Microscopy Imaging](image1)

**Figure S3.** Fluorescence microscopy imaging of a single nanofiber with polarized excitation (A and B). The direction of the excitation polarization is indicated by the arrow labelled at the top left in each figure. Excitation: 530-560 nm; emission collected at > 595 nm.

VI. Wide angle X-ray scattering (WAXS) studies on gel nanofibers

![Wide Angle X-ray Scattering](image2)

**Figure S4.** WAXS spectrum obtained for the nanofibers of PA-PTCDI gel.

Wide angle X-ray scattering (WAXS) shown in Fig. S3 was performed at 18-ID-BioCAT beamline at Argonne National Lab. The WAXS pattern was collected in the q-range of 0.1 to 3.0 Å⁻¹ and q= 4π/λ* sinθ; where λ is X-ray wavelength and θ is the X-ray scattering angle. Essentially this q range allows us to look at the characteristic peaks from not only the molecule but also from the intermolecular π-π stacking interaction due to the self-assembly. In general the
The $q$ value for the $\pi-\pi$ stacking is close to 1.8 which corresponds to 0.34 nm in $d$ spacing, in agreement with prior observations of such systems.\textsuperscript{8,9}

V. Electrode fabrication and I-V measurement

![Diagram of electrode fabrication and I-V measurement](image)

**Figure S5.** (A) Schematic presentation of electrode fabrication amine sensing experiment; (B) typical I-V data (red curve) obtained for Pristine PA-PTCDI nanofibers before exposure and (C) after exposed to the saturated vapor of diethylamine under ambient condition (blue curve). Down arrow with embedded captions indicates corresponding steps in (A) at which the data was collected.
The electrical conductivity characterization of the nanowires was based on direct current voltage (I-V) measurement, which was performed with a two-electrode device. PA-PTCDI nanofibers produced from the gelation were deposited onto the electrode pair by drop casting of the water suspension. The electrodes were fabricated by sputter deposition of gold (~8 nm thickness) onto glass substrate using a Denton DESK IV sputter coater, followed by scratching the gold film with a razor blade to create a pair of film-electrodes with gap close to 80 µm. The Pyrex glass substrate (from Corning Inc.) was pre-cleaned with piranha reagent (30:70 H₂O₂(35%):H₂SO₄), followed by rinsing with water and methanol. 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 AFM imaging. Such a flat surface is suitable for fabrication of flat electrodes and deposition of nanofibers.

The I-V measurement was carried out with a Keithley 638 Picoammeter equipped with a Voltage Source providing applied bias between 0–100 V. The device was placed in a sealed glass jar. After measuring the I-V curve for the pristine nanofibers as shown in Fig. S5 B, a small vial of diethylamine liquid was put into the jar, followed by I-V measurement at different time intervals. After ca. 5 min, the diethylamine vapor became saturated, and meanwhile the surface adsorption on nanofibers also reached the equilibrium as indicated by the saturation in current value. The maximal current thus obtained was plotted in Fig. S5 C to demonstrate the electrical modulation of the nanofiber upon exposure to amine vapor.

References: