

One-dimensional self-assembly of a water soluble perylene diimide molecule by pH triggered hydrogelation†

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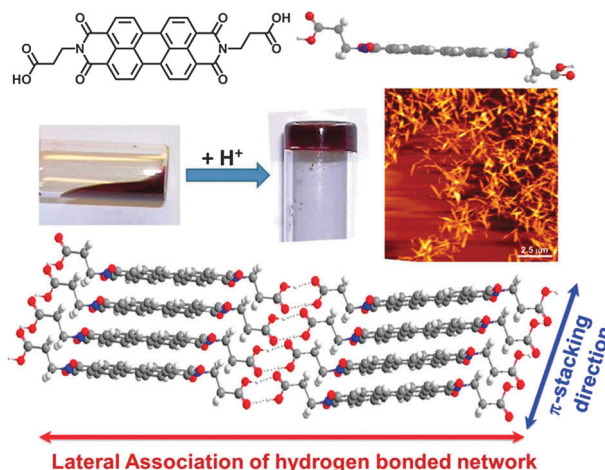
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Aniket Datar,^a Kaushik Balakrishnan^{ab} and Ling Zang^{*ac}

A water soluble perylene diimide molecule has been fabricated into nanofibers *via* a pH triggered hydrogelation route. The one-dimensional self-assembly is dominated by the intermolecular π - π stacking interactions in concert with the hydrogen bonding between the carboxylic acid side chains. The anisotropic electronic and optical properties observed for the nanofibers are consistent with the one-dimensional intermolecular π - π arrangement.

The control of molecular organization into well-defined nanostructures from electronically and optically active small molecules is considered an important approach to fabricate next generation nanoscale electronic devices.¹ The molecules of perylene tetracarboxylic diimide (PTCDI) belong to the n-type (electron accepting) semiconducting family and possess high photo and thermal stability along with chemical inertness. These properties have made PTCDI derivatives ideal materials for application in the field of organic electronics² and, already, the bulk phase materials of PTCDI have been utilized to fabricate various optoelectronic devices.^{3,4} The ability to achieve one-dimensional (1D) nanostructures from PTCDIs modified with alkyl and alkyloxy side-chains (at both imide and bay positions) in various organic solvents has been well documented by us⁵⁻¹⁰ and others.^{11,12} However, obtaining 1D nanostructures from side-chains favouring high solubility in aqueous solvent remains elusive. Recently, some water soluble PTCDI derivatives have been used for formation of micelles, vesicles and rod shaped aggregates and such self-assembled structures have been employed as fluorescent markers for biological systems.¹³⁻¹⁷

Processing PTCDI derivatives in aqueous solutions is highly challenging due to the strong hydrophobic interactions



Scheme 1 (top) Molecular structure and configuration of building block molecule PA-PTCDI. (center) Addition of acid to the basic aqueous solution of PA-PTCDI leads to formation of hydrogels composed of uniform nanofibers as imaged using AFM. (bottom) Schematic diagram showing the concerted intermolecular π - π stacking and hydrogen bonding interactions that form the nanofibril structure.

between the perylene backbones. Additionally, such molecules tend to form dimers in aqueous solutions.¹⁸ Thus, self-assembly processing developed for hydrophobic molecules in organic solvents may no longer be effective in water.¹⁹ In this communication, we report on a PTCDI derivative, *N,N'*-di(propanoic acid)-perylene-3,4,9,10-tetracarboxylic diimide (PA-PTCDI, shown in Scheme 1), which is soluble in water, and can be self-assembled into 1D nanostructure upon adjustment of solution pH. The short side chain, propanoic acid, provides a high degree of hydrophilicity, thus enabling sufficient water solubility, particularly in basic medium (*e.g.*, pH 9.0 buffer solution). Meanwhile, the small size of side chains causes minimal steric hindrance, thereby facilitating the columnar staking between the perylene backbones. Furthermore, the hydrogen bonding between protonated carboxylic acids provides additional directional control over lateral association of the molecule along with inherent π -stacking interaction of the perylene cores (Scheme 1). Such an approach is anticipated to provide a new self-assembly pathway for producing robust 1D

^a Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA. E-mail: lzang@eng.utah.edu; Fax: +1 801-585-0625; Tel: +1 801-587-1551

^b College of Optical Sciences, University of Arizona, Tucson, AZ 8572, USA

^c Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT 84112, USA

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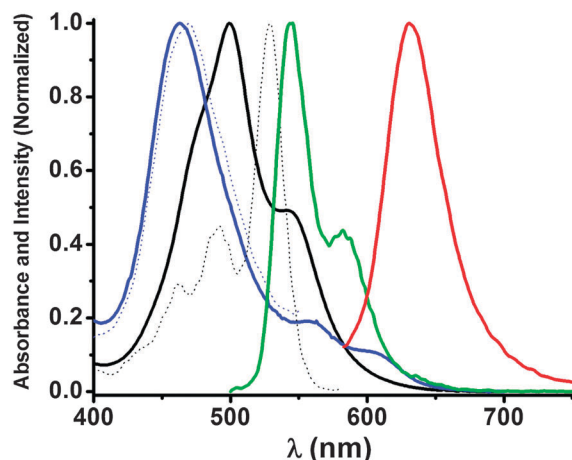


Fig. 1 UV-vis absorption (black), fluorescence excitation (black dotted) and emission spectra (green) of pH 9.0 aqueous solution of PA-PTCDI (8.0 μM). UV-vis absorption (blue), fluorescence excitation (blue dotted) and emission spectra (red) of pH 4.0 aqueous solution of PA-PTCDI (8.0 μM). Emission spectra were recorded at an excitation wavelength of 490 nm (green) for pH 9.0 solution and 460 nm for pH 4.0 solution. Excitation spectra were recorded at an emission wavelength of 590 nm for pH 9.0 solution and 630 nm for pH 4.0 solution.

nanostructures that possess optical and electrical properties intrinsic to the directional intermolecular arrangement.

Effects of protonation and deprotonation on aggregation of PA-PTCDI molecules were investigated using UV-vis absorption and fluorescence emission and excitation spectroscopy (Fig. 1). Complete dissolution of the molecule was achieved in pH 9.0 buffer (carbonate/bicarbonate) solution, which resulted in homogeneous solution of clear red colour. The UV-vis absorption spectrum showed a characteristic dimeric peak at 499 nm and a shoulder close to 544 nm (Fig. 1, black curve), for which the relative intensity between the vibronic $0 \rightarrow 0$ band and $0 \rightarrow 1$ band in the $\pi \rightarrow \pi^*$ electronic transition ($A^{0 \rightarrow 0}/A^{0 \rightarrow 1} \leq 0.6$) is reversal of that of monomeric PTCDis (for which $A^{0 \rightarrow 0}/A^{0 \rightarrow 1} > 1$). However, the corresponding fluorescence emission spectrum showed peaks at 548 and 589 nm typically characteristic of PTCDis in solutions. Such an observation indicates that PA-PTCDI exists in both monomeric and dimeric states in pH 9.0 solution, and only the monomeric component is fluorescent.^{20–22} This observation is further corroborated by the excitation spectrum, which shows the typical absorption profile of molecular PTCDis species (black dotted curve). On the other hand, the UV-Vis absorption spectrum in pH 4.0 buffer (phthalate) solution showed a broad peak with maxima near 461 nm (blue curve), and the corresponding fluorescence spectrum showed a significantly red shifted emission peak at 631 nm. The excitation spectrum (blue dotted curve) of the same PA-PTCDI solution matches the absorption spectrum. Such an observation indicates that the observed fluorescence emission resulted from higher order aggregates of PA-PTCDI under acidic conditions.²³ An emission peak at around 630 nm is usually attributed to the cofacial π -stacking in the molecular assembly of PTCDis.^{9,24} Transition from molecularly dispersed PA-PTCDI (monomeric and dimeric) to higher order aggregates observed in Fig. 1 was instantaneous, incorporating deprotonation–protonation of carboxylic acid groups, strong π - π stacking and hydrogen bonding interactions between the molecules. This implies feasible

control of the intermolecular arrangement and self-assembly through adjustment of solution pH.

Recently several carboxylic acid based molecules have been successfully gelled through hydrogen bonding, producing well-defined nanofibers in water.^{25–28} Since PA-PTCDI has two carboxylic acid groups at both ends, we expected that the intermolecular hydrogen bonding can be maximized by adjusting the pH to a value that affords the neutral state to the carboxylic acid group. To firstly dissolve PA-PTCDI in water, an organic base, triethylamine (TEA), was employed to adjust the pH above 9.0. It was found that PA-PTCDI can be well dissolved in water up to 10 mM in the presence of 6 molar fold of TEA. The pH was found to be in the range of 9.0–10.0 for the 1 : 6 (molar ratio) PA-PTCDI : TEA solutions with the concentration of PA-PTCDI varying between 0.8–8.0 μM ; UV-Vis spectral measurement of these solutions showed almost identical characteristics to those of the PA-PTCDI solution in pH 9.0 buffer (Fig. S1, ESI[†]). Upon addition of hydrochloric acid (HCl), a 4.4 mM solution of PA-PTCDI (in the presence of 26.4 mM TEA) gradually turned into a solid gel of dark red colour (Scheme 1). This gel was washed thoroughly with water to remove excess of HCl and triethylamine hydrochloride. The gel sample thus prepared was investigated using TEM as shown in Fig. 2A and B, which clearly indicates the formation of nanofibers with the length ranging from 3 to 5 μm and a width of 20–30 nm.

To further investigate the self-assembly of PA-PTCDI, nanofibers of this molecule were also fabricated using the phase transfer method previously developed in our lab for other PTCDis molecules.¹ Briefly, a larger amount (10 : 1 vol) of poor solvent (methanol or THF) was transferred atop a concentrated water solution of PA-PTCDI (4.4 mM, in the presence of 26.4 mM TEA) in a test tube. The precipitation driven phase transfer of PA-PTCDI occurs through diffusion and self-assembly of the molecule in the poor solvent. Nanofibers were formed in both methanol and THF solvents, with length ranging from 10–30 μm and width ranging from 100–200 nm as shown in the TEM image (Fig. S2, ESI[†]). Overall, these nanofibers are significantly larger than those produced from hydrogelation as shown in Fig. 2. The increase in size is largely due to the Ostwald ripening during the phase transfer processing, in which the extensive, long range molecular diffusion dictates the phase growth. The larger nanofibers obtained are conducive for fluorescence microscopy imaging and polarization study. A single PA-PTCDI nanofiber demonstrated strong fluorescence emission under excitation of 530–560 nm light, and the emission intensity is uniform along the nanofiber, consistent with the homogeneous single crystal phase throughout the nanofiber. The emission intensity was maximized when the excitation polarization was aligned about parallel to the long axis of the nanofiber and the emission intensity became minimal when the polarization was aligned about perpendicular to the nanofiber (Fig. S3, ESI[†]). Similar polarization dependence was found before for other PTCDis nanofibers.⁹ The observed fluorescence polarization along the long axis of the nanofiber is consistent with the columnar stacking of molecules. Because the π -planes of molecules often stack at a tilted angle from the completely perpendicular orientation relative to the long axis of the nanofiber,¹ the maximized intensity of polarized emission was not observed exactly along the nanofiber.

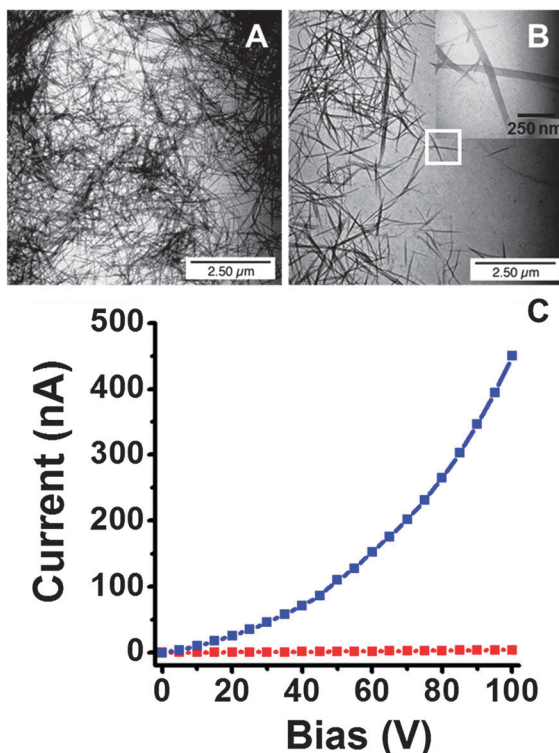


Fig. 2 (A and B) Large-area TEM image of densely packed PA-PTCDI nanofibril networks, which were synthesized by the gelation method and (inset B) a higher-magnification image showing discrete, straight nanofibers. (C) *I*-*V* curves for the nanofibers (red curve) before and (blue curve) after exposure to diethylamine vapor (device fabrication scheme and conductivity of pristine nanofibers (red curve) are shown in Fig. S5, ESI[†]).

The intermolecular π - π stacking within the nanofibers was also evidenced by wide angle X-ray diffraction (XRD) measurement (Fig. S4, ESI[†]). For the nanofibers prepared from gelation, the XRD spectrum clearly revealed the *d*-spacing of 3.4 Å, which is characteristic of the cofacial stacking between π -conjugated molecules.¹ Extended π - π stacking along the nanofiber has been proven to be effective for mediating charge transfer through π -electron delocalization.²⁹ Indeed, when connected between two electrodes, PA-PTCDI nanofibers demonstrated measurable electrical conductivity (Fig. S5, ESI[†]). Upon exposure to the saturated vapor of diethylamine (a strong electron donor), the conductivity of the nanofibers increased by almost two orders of magnitude as shown in Fig. 2C. A similar observation was reported for other volatile organic amines such as isobutyl amine. The large electrical modulation thus observed is largely due to the interfacial electron doping from the amine, followed by efficient long range electron transport through the π - π stacking.^{7,30} It should be noted that the carboxylic side chain may also contribute to the large electrical modulation by strong chemical binding with amines. Moreover, the carboxylic group also forms strong electrical contact with the gold electrode as previously evidenced in single molecule electronic break-junction studies.³¹ Considering all these features together, the PA-PTCDI nanofibers obtained from the gelation may find potential application in chemiresistor sensors for trace vapor detection of organic amines.

In conclusion, we report on a simple pH triggered gelation approach to fabricate well-defined nanofibers from a PTCDI

based molecule in aqueous media. The nanofibers as prepared exhibit strong fluorescence polarization and one-dimensional enhanced charge transport, both of which result from the anisotropic and enhanced electronic coupling between the intermolecular π - π stacking along the nanofiber. The reported work represents a green methodology for preparing organic semiconductor nanomaterials, for which no organic solvents are employed.

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Notes and references

- 1 L. Zang, Y. Che and J. S. Moore, *Acc. Chem. Res.*, 2008, **41**, 1596–1608.
- 2 F. Würthner, *Chem. Commun.*, 2004, 1564–1579.
- 3 A. C. Grimsdale and K. Müllen, *Angew. Chem., Int. Ed.*, 2005, **44**, 5592–5629.
- 4 A. P. H. J. Schenning and E. W. Meijer, *Chem. Commun.*, 2005, 3245–3258.
- 5 K. Balakrishnan, A. Datar, R. Oitker, H. Chen, J. Zuo and L. Zang, *J. Am. Chem. Soc.*, 2005, **127**, 10496–10497.
- 6 Y. Che, A. Datar, K. Balakrishnan and L. Zang, *J. Am. Chem. Soc.*, 2007, **129**, 7234–7235.
- 7 Y. Che, A. Datar, X. Yang, T. Naddo, J. Zhao and L. Zang, *J. Am. Chem. Soc.*, 2007, **129**, 6354–6355.
- 8 Y. Che, X. Yang, S. Loser and L. Zang, *Nano Lett.*, 2008, **8**, 2219–2223.
- 9 A. Datar, K. Balakrishnan, X. Yang, X. Zuo, J. Huang, R. Oitker, M. Yen, J. Zhao, D. M. Tiede and L. Zang, *J. Phys. Chem. B*, 2006, **110**, 12327–12332.
- 10 A. Datar, R. Oitker and L. Zang, *Chem. Commun.*, 2006, 1649–1651.
- 11 A. L. Briseno, S. C. B. Mannsfeld, C. Reese, J. M. Hancock, Y. Xiong, S. A. Jenekhe, Z. Bao and Y. Xia, *Nano Lett.*, 2007, **7**, 2847–2853.
- 12 F. Würthner, B. Hanke, M. Lysetska, G. Lambright and G. S. Harms, *Org. Lett.*, 2005, **7**, 967–970.
- 13 Y. Huang, Y. Yan, B. M. Smarsly, Z. Wei and C. F. J. Faul, *J. Mater. Chem.*, 2009, **19**, 2356–2362.
- 14 C. D. Schmidt, C. Böttcher and A. Hirsch, *Eur. J. Org. Chem.*, 2007, **2007**, 5497–5505.
- 15 X. Zhang, Z. Chen and F. Würthner, *J. Am. Chem. Soc.*, 2007, **129**, 4886–4887.
- 16 X. Zhang, S. Rehm, M. M. Safont-Sempere and F. Würthner, *Nat. Chem.*, 2009, **1**, 623–629.
- 17 D. Görl, X. Zhang and F. Würthner, *Angew. Chem., Int. Ed.*, 2012, **51**, 6328–6348.
- 18 Z. Chen, A. Lohr, C. R. Saha-Moller and F. Würthner, *Chem. Soc. Rev.*, 2009, **38**, 564–584.
- 19 T. H. Rehm and C. Schmuck, *Chem. Soc. Rev.*, 2010, **39**, 3597–3611.
- 20 W. Wang, L. Wang, B. J. Palmer, G. J. Exarhos and A. D. Q. Li, *J. Am. Chem. Soc.*, 2006, **128**, 11150–11159.
- 21 J. J. Han, A. D. Shaller, W. Wang and A. D. Q. Li, *J. Am. Chem. Soc.*, 2008, **130**, 6974–6982.
- 22 C. Backes, J. Schunk, F. Hauke and A. Hirsch, *J. Mater. Chem.*, 2011, **21**, 3554–3557.
- 23 W. E. Ford, *J. Photochem.*, 1987, **37**, 189–204.
- 24 K. Balakrishnan, A. Datar, T. Naddo, J. Huang, R. Oitker, M. Yen, J. Zhao and L. Zang, *J. Am. Chem. Soc.*, 2006, **128**, 7390–7398.
- 25 M. D. Segarra-Maset, V. J. Nebot, J. F. Miravet and B. Escuder, *Chem. Soc. Rev.*, 2013, DOI: 10.1039/C2CS35436E.
- 26 R. C. Howe, A. P. Smalley, A. P. Guttenplan, M. W. Doggett, M. D. Eddleston, J. C. Tan and G. O. Lloyd, *Chem. Commun.*, 2013, **49**, 4268–4270.
- 27 Z. He, H. Wang, Y. Wang, Y. Wu, H. Li, L. Bi and L. Wu, *Soft Matter*, 2012, **8**, 3315.
- 28 R. Iwaura and M. Ohnishi-Kameyama, *Chem. Commun.*, 2012, **48**, 6633–6635.
- 29 V. Coropceanu, J. C. r. m. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J.-L. Bredas, *Chem. Rev.*, 2007, **107**, 926–952.
- 30 Y. Huang, B. Quan, Z. Wei, G. Liu and L. Sun, *J. Phys. Chem. C*, 2009, **113**, 3929–3933.
- 31 F. Chen, X. Li, J. Hihath, Z. Huang and N. Tao, *J. Am. Chem. Soc.*, 2006, **128**, 15874–15881.