

Self-Organized Perylene Diimide Nanofibers

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Received: August 26, 2004; In Final Form: October 22, 2004

A propeller-shaped perylene diimide trimer was synthesized and a simple evaporation method was used for the self-organization of trimer molecules into fluorescent nanofibers. The sizes of these fibers—from 4 to 150 nm in diameter—were measured by atomic force microscopy and can be controlled by adjusting the concentration of the initial solution. The aspect ratios (length/height) are around 500. The plane of the trimer was determined by polarized scanning confocal microscopy to be perpendicular to the axis of the fibers, in agreement with molecular mechanics calculations. UV/vis and NMR spectroscopies were used to monitor concentration-dependent π - π stacking in solution. Single-fiber fluorescence imaging and spectroscopy were performed using a total internal reflection fluorescence microscope equipped with a digital color camera and imaging CCD spectrometer. Strongly red-shifted fluorescence from these fibers indicates a high degree of electronic delocalization, and breaking up this delocalization by photobleaching blue-shifts the emission toward that of an isolated noninteracting molecule. The delocalization along these nanofibers and the ability to study the electronic structure using fluorescence make them potentially useful in nanoscale devices, such as field effect transistors and photoconductors.

Introduction

During the past decade, self-organization has received increased attention as a tool for the design and synthesis of well-defined organic nanostructures.^{1–9} Organic nanotubes and nanofibers are structures of particular interest, since, complementary to carbon nanotubes^{10,11} and inorganic semiconductor nanowires,¹² they can potentially be formed by low-cost processes such as spin-coating, printing, and evaporating and are compatible with plastic substrates.¹³ To date, several organic systems have been found which self-organize into nanofibers and nanotubes, including cyclic peptides,^{14,15} amphiphilic peptides,^{16,17} crowded aromatics,^{18–21} hexa-*peri*-hexabenzocoronenes,^{22,23} porphyrins,^{24–26} polyanilines,^{27–29} phthalocyanines,³⁰ cyanines,^{31,32} and merocyanines.^{33,34}

It has been shown that single crystals of organic materials can have high charge carrier mobilities,^{35–37} but single crystals are generally difficult to obtain, so self-organization provides an alternative route to creating molecular electronic materials at low cost.^{38–40} Although the relationship between molecular packing and charge carrier mobility is complex,^{41,42} strong π - π interactions are generally considered desirable for charge transport.^{43–47} Perylene diimides are excellent candidates for creating a self-organized molecular electronic material, since they are one of few n-type organic semiconductor systems that have demonstrated high charge carrier mobilities in thin film devices and structures^{13,47,48} and since perylene diimides have strong, well-studied π - π interactions which can be used to direct self-organization.^{49–64}

In this paper we report the self-organization of discrete nanofibers from a perylene diimide trimer (**1**), shown in Figure 1A. The three perylene diimide subunits strengthen the π - π interactions and are arranged around a central core to give the molecule a propeller-like shape which directs one-dimensional

self-organization,^{65,66} as seen in molecular mechanics calculations on a group of six trimers (Figure 1B,C). The phenylene linkers between the central benzene and three perylene diimide subunits allow some free rotation for the perylene diimide subunits to achieve ideal π - π stacking. The secondary alkyl chains improve solubility in organic solvents, which makes the synthesis and self-organization from solution phase feasible, and likely provide additional van der Waals attractions between adjacent molecules within the stacks and between adjacent stacks in larger nanostructures. Self-organization depends on the delicate balance between molecule–molecule and molecule–solvent interactions,⁶⁷ and hence solvents always play crucial roles in these systems. Trimer **1** is highly soluble in CH₂Cl₂ and CHCl₃ but not in MeOH, so solvent mixtures were used to tune the solubility for solution studies and for self-organization.

Results and Discussion

Synthesis. As shown in Scheme 1, the trimer (**1**) was obtained in satisfactory yield (64%) by triple condensation between anhydride **4** and triamine **7**. It should be noted that direct condensation between a similar triamine, 1,3,5-triaminobenzene, and **4** only gave monochromophoric derivatives.⁶⁸ Anhydride **4** in turn was synthesized by a two-step procedure:⁶⁹ condensation between 1-hexylheptylamine and perylene-3,4:9,10-tetracarboxyldianhydride gave the symmetric diimide **3**, followed by partial saponification. Triamine **7** was also synthesized by a two-step procedure:⁷⁰ acid-catalyzed triple condensation of 4-nitroacetophenone gave 1,3,5-tris(4-nitrophenyl)benzene, followed by reduction with hydrazine.

UV/Vis Spectroscopy. UV/vis absorption spectra are sensitive to interchromophore distance and orientation^{71,72} and have been widely used to study π - π stacking of perylene dyes.^{53,54,57,61,73} Figure 2 shows absorption spectra of **1** at different concentrations in 1:1 MeOH/CHCl₃. At low concentration (0.067 μ M) the spectra are similar to that of monomeric perylene diimide **3**,⁷⁴ while at higher concentration (0.67 μ M)

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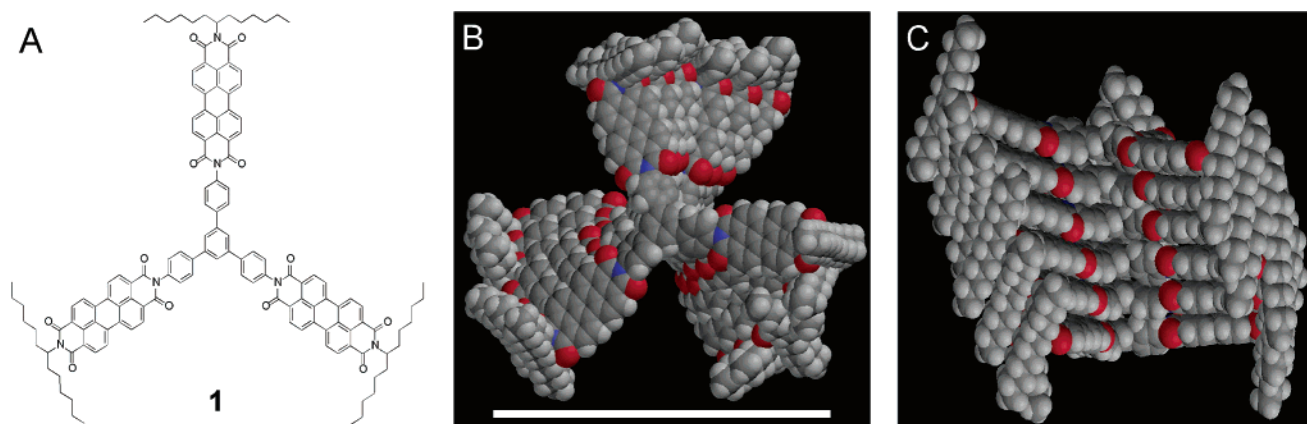
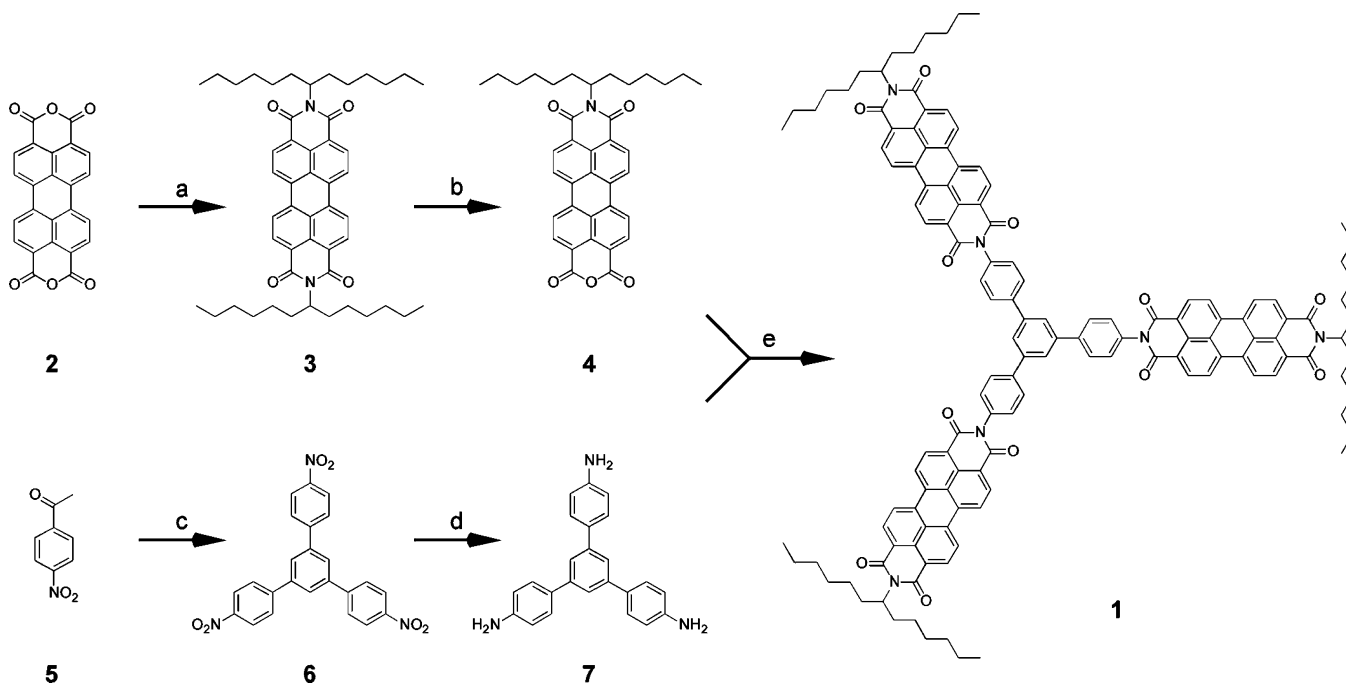


Figure 1. (A) Chemical structure of the perylene diimide trimer (**1**); (B) top view and (C) side view of self-organized structure according to molecular mechanics calculations. Scale bar, 4 nm.

SCHEME 1. Synthesis of Perylene Diimide Trimer **1**^a



^a Conditions: (a) 1-hexylheptylamine, imidazole, 130 °C; (b) *t*-BuOH, KOH, reflux; (c) toluene, CF₃SO₃H, reflux; (d) hydrazine hydrate, Raney Ni, THF, 85 °C; (e) imidazole, 130 °C.

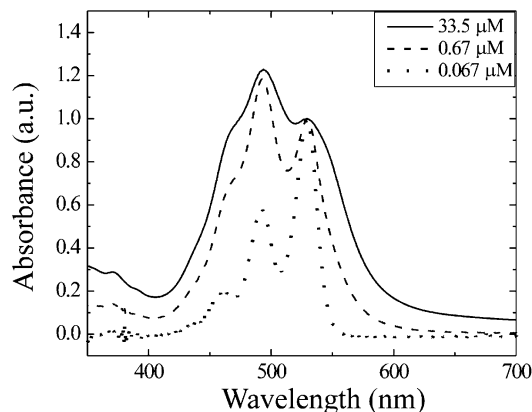


Figure 2. Concentration-dependent absorption spectra of **1** in 1:1 MeOH/CHCl₃. All spectra were normalized at the peak at 529 nm. the order of intensity for 0→0 (530 nm) and 0→1 (493 nm) vibronic transitions (Figure 2) is reversed, which is indicative of π - π stacking in perylene diimides.^{54,55,61-63,73} Model compounds with two perylene diimides facing each other also

show the same feature in their absorption spectra.^{73,75,76} Monomeric perylene diimide **3** does not show such evidence of stacking even at much higher concentrations (30 μ M), indicating that the trimer structure is encouraging self-organization.

NMR and Self-Organization. ¹H NMR is an established method for the evaluation of π - π stacking of aromatic rings,⁷⁷ first in biopolymers⁷⁸ and recently in synthetic oligomers and self-organizing small molecules.^{55,79,80} ¹H NMR spectra of trimer **1** at different concentrations in CDCl₃ are shown in Figure 3. When the concentration is increased from 0.12 to 0.81 mM, there is clear upfield shift and broadening of the peaks. The upfield shift is due to shielding effects of the aromatic ring above the respective protons and thus directly indicates π - π stacking.⁷⁸ The relative magnitude of the shifts, H-1 ($\Delta\delta$ = 0.07 ppm) > H-2 ($\Delta\delta$ = 0.04 ppm) > H-3 ($\Delta\delta$ = 0.01 ppm), reflects the larger ring current experienced by protons closer to the center.

Self-Organization and Atomic Force Microscopy (AFM). In a typical experiment, a solution of **1** (1–50 μ M) in 9:2 CH₂-Cl₂/MeOH solvent mixture, where there is no aggregation, is

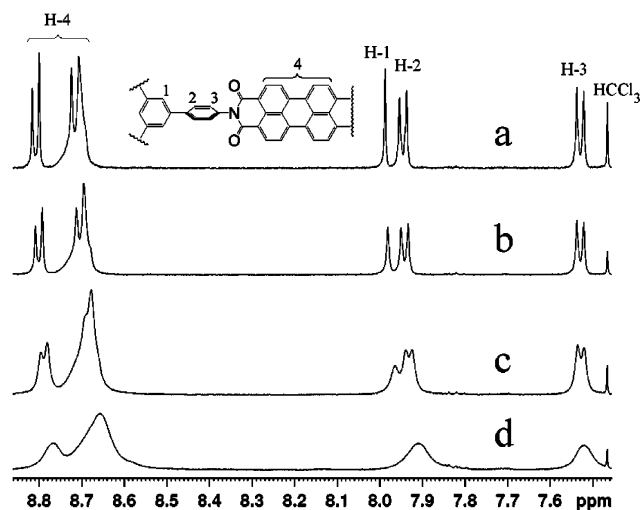


Figure 3. ^1H NMR spectra of trimer **1** in CDCl_3 at different concentrations: (a) 0.12; (b) 0.24; (c) 0.43; (d) 0.81 mM.

allowed to evaporate slowly and the preferential evaporation of CH_2Cl_2 (bp = 40 °C) over MeOH (bp = 64.7 °C) gradually lowers the solubility and favors self-organization into thermodynamically stable structures. Nanofibers on glass cover slides can be obtained simply by immersing the cover slides in the solution as it is evaporated. The final morphology is very sensitive to the solvent mixture: too little CH_2Cl_2 results in fast precipitation and lowered aspect ratio (length/height), while too much CH_2Cl_2 results in less organized fibers. For example, slow evaporation of a solution of the trimer in pure CH_2Cl_2 or CHCl_3 gives only an oily residue and no discrete fibers.

Figure 4A–G shows the topographic features observed by noncontact AFM for samples self-organized from different concentrations. Self-organization from a more concentrated solution (50 μM) of **1** results in a dense packing of fiber structures, which can often be tens of micrometers in length (Figure 4A) with high aspect ratios (length/height \sim 500). These

fibers can also be formed on a surface patterned with gold (Figure 4B). No abrupt change in direction or diameter of the fibers is observed at the glass and gold boundary, indicating that the fibers self-organize in solution and then precipitate onto the surface.

The diameters and the morphologies of the fibers can be controlled by changing the solution concentration. Generally the higher the concentration, the larger the diameter and the denser the fibers. Parts A and B of Figure 4 show fibers formed from a 50 μM solution of **1**; parts C–F of Figure 4 show fibers formed from 25 μM solution, and Figure 4G shows fibers formed from a 1 μM solution. Note that the smallest fibers formed (line scan, Figure 4H) are \sim 4 nm in height, as would be expected from a single column of trimer molecules stacked as predicted from the molecular mechanics calculations (Figure 1B). Parts D and E of Figure 4 also show that these fibers readily form junctions, bends, rings, and other unique topologies.

Polarized Scanning Confocal Microscopy and Chromophore Orientation. Absorption and emission spectra of perylene diimides with different substitutes R_1 and R_2 (Figure 5A) are virtually identical,^{81,82} and the electronic transition has been shown to be polarized along one direction by fluorescence anisotropy measurements.⁸³ The transition dipole moment is along the long axis according to semiempirical MO INDO/S calculations (the z -axis in Figure 5A).⁸⁴ In the trimer **1** the transition dipoles of three subunits form a transition dipole plane, which is perpendicular to the self-organization direction according to computer modeling (Figure 5A).

Polarized fluorescence imaging confirms that the absorption transition dipole of the molecules in the fibers is perpendicular to the long axis of the fibers, further corroborating the stacking model shown in Figure 1B,C. Figure 5 shows scanning confocal microscopy (SCM) images of the same crossed fibers, taken with the excitation laser polarized vertically (Figure 5B) and horizontally (Figure 5C) relative to the page. Whether the laser is polarized vertically or horizontally, the fiber perpendicular to the excitation laser polarization direction is brighter than the

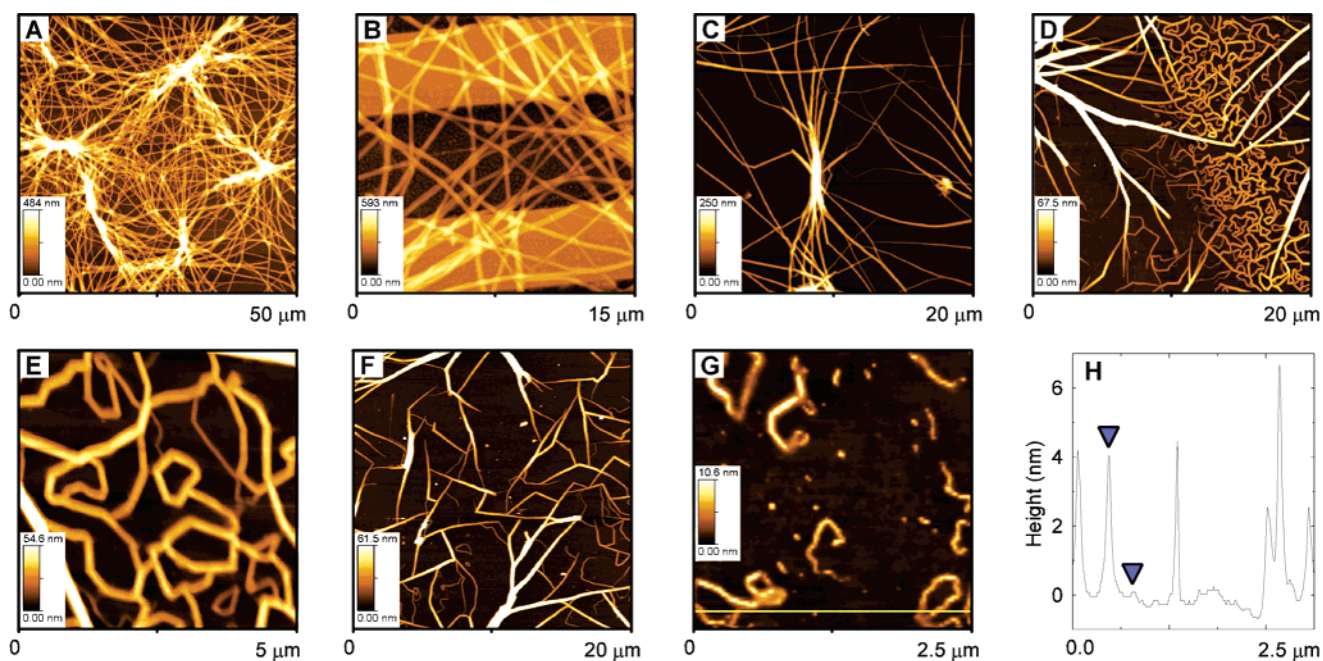


Figure 4. Topographic features covering wide size range: (A) large area overview, diameters \approx 100 nm; (B) fibers on surface patterned with gold, diameters \approx 100 nm; (C) a single spiderlike cluster, diameters \approx 60 nm; (D) transition between big and medium fibers; (E) medium-sized fibers featuring pentagon structures, diameters \approx 25 nm; (F) medium-sized fibers featuring different microstructures, diameters \approx 30 nm; (G) small fibers, diameters \approx 4 nm; and (H) height-profile corresponding to the yellow line in G. The fibers are formed on glass substrate by slowly evaporating a solution of **1** in 2:9 MeOH/ CH_2Cl_2 . The initial concentrations are 50 μM for A,B; 25 μM for C–F; and 1 μM for G.

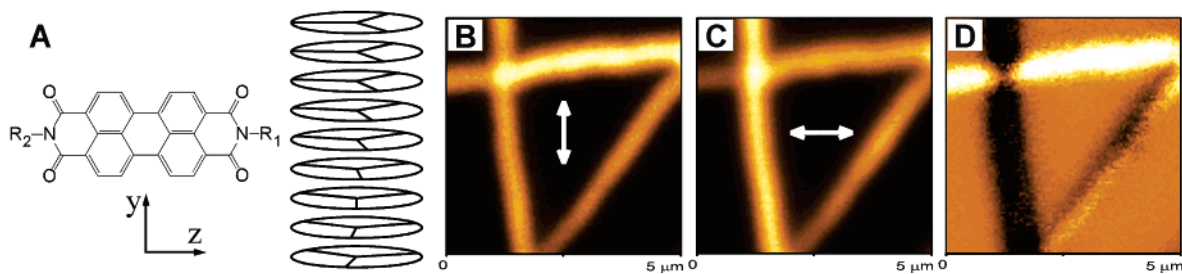


Figure 5. (A) Electronic transition dipole moment of perylene diimide monomer is along the z direction and the transition dipole plane, formed by the three perylene subunits in trimer **1**, is perpendicular to the self-organization direction. (B and C) Scanning confocal microscopic images under plane polarized laser excitation as indicated by the arrows. (D) Difference image between B and C.

fiber parallel to the polarization direction. The difference image Figure 5D, obtained by subtracting Figure 5C from Figure 5B, provides higher contrast, showing positive difference for the horizontal fiber and negative difference for the vertical fiber. Another fiber, about 45° to both polarization directions, shows similar fluorescence intensity in Figure 5B,C and largely cancels out in the difference image Figure 5D. Polarized emission images taken by using circularly polarized excitation light, separating the fluorescence by polarizing beam splitter and detecting with two single-photon-counting avalanche photodiode (APD) detectors, give similar results (see Supporting Information), showing that the emission dipole is also perpendicular to the long axis of the fibers.

Single Nanofiber Imaging and Spectroscopy. High-contrast true-color fluorescence images were obtained using a total internal reflection fluorescence (TIRF) microscope equipped with a digital camera. A true-color image of a sample made by allowing a $50 \mu\text{M}$ solution of trimer **1** to evaporate quickly (~ 10 min) inside a glass-bottom microwell dish (MatTek, Ashland, MA) is shown in Figure 6A. The trimer **1** in solution emits in the green ($\lambda_{\text{max}} \sim 540$ nm), but, as seen in the color image, the fluorescence from the self-organized nanofibers is red, though some green spots are seen due to unorganized (non π -stacking) molecules. Samples prepared, like those in Figure 4, through slow evaporation (~ 10 h) on glass slides show only red emission from well-organized fibers. Red emission is well-known for π -stacked perylene diimides^{52,63} and a cofacial perylene model compound.⁷⁵ A large red shift in emission indicates strong intermolecular electronic interaction and high degree of order,⁵² which are associated with large exciton diffusion lengths^{49,51,85,86} and high charge carrier mobilities.^{37,43}

The fluorescence emission spectra of a single spot in the image can be obtained by passing fluorescence through a narrow slit and directing it onto a LN₂-cooled CCD camera via a diffraction grating.^{87,88} Figure 6B shows the emission spectra of red fibers with and without a green component. As expected, the green emission shows the typical spectrum of nonaggregated perylene diimide with peaks at 544 and 588 nm, while the red emission from the fibers shows a broad peak around 650 nm, with shoulders at 688 and 720 nm, typical for highly ordered thin films. The absorption spectrum of the fibers in Figure 6A is also shown in Figure 6B and is similar to that of aggregates formed in solution (Figure 2).

We also observed distinct emission color changes over time for fluorescent nanofibers formed on glass surfaces. Figure 7A–C shows the TIRF images and the corresponding fluorescence spectra for the nanofibers during the course of photobleaching. Under continuous photoexcitation the fluorescence intensity decreases, but, more interestingly, the color steadily changes over time from red to yellow-green and the emission peak shifts from 650 to 580 nm. Perylene diimides, like all chromophores, undergo eventual photodestruction (photobleach-

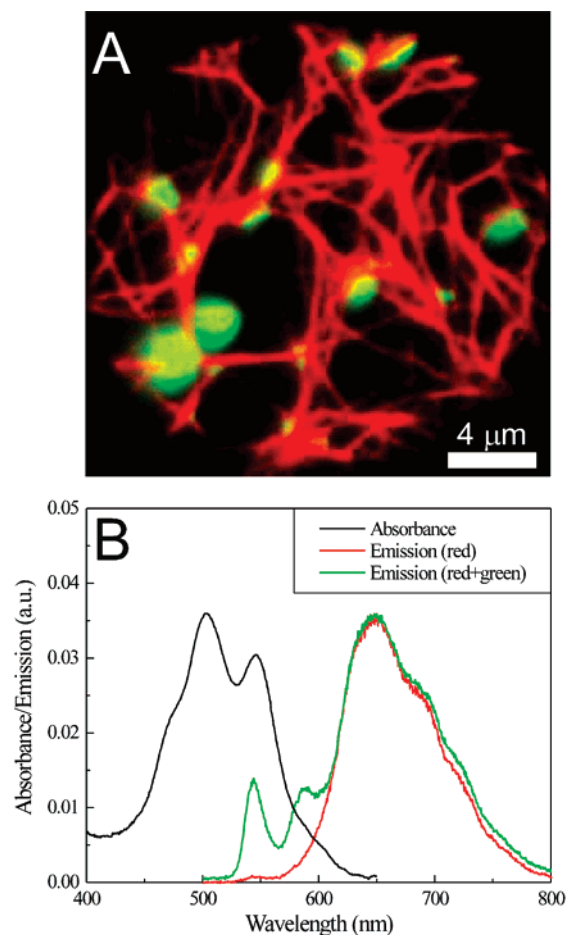


Figure 6. Single nanofiber imaging and spectroscopy. (A) TIRF image of self-organized fibers together with free molecules. (B) Emission spectra of red fibers with (green line) or without (red line) a green component and bulk absorption spectra (black line) of the solid sample. The spectra are normalized at the peaks. Excitation wavelength: 488 nm.

ing) under illumination in air,⁸⁹ and, as individual chromophores along the fibers are bleached, the π - π interactions and electronic delocalization along the fibers are broken up (Figure 7D), and the emission shifts toward the green emission of isolated perylene diimides.

Conclusion

A perylene diimide trimer was synthesized and a simple evaporation method was used for self-organization of trimer molecules into fluorescent nanofibers. Organization and π - π stacking of the perylene diimide chromophores in solution was evident from upfield shifts in the NMR and reversed intensity order for $0 \rightarrow 0$ and $0 \rightarrow 1$ vibronic transitions in the UV/vis

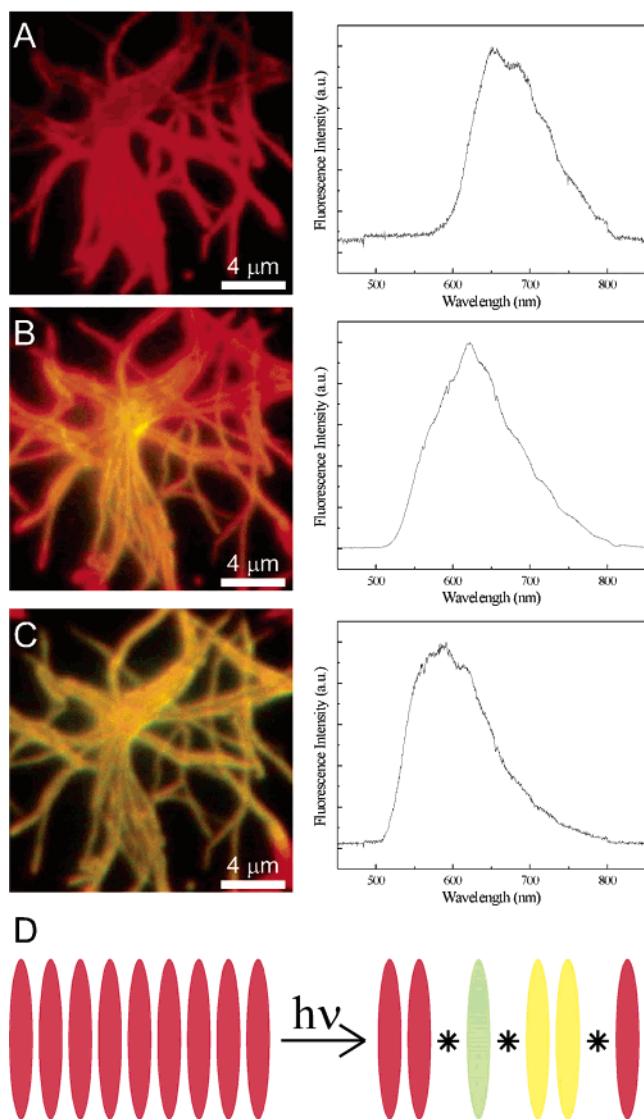


Figure 7. Nanofibers changing their color. TIR images and spectra of self-organized nanofibers: (A) before laser irradiation; (B) after 1 min laser irradiation at ~ 1000 W/cm²; (C) after 10 min laser irradiation; (D) proposed mechanism (photobleaching shortens the electronic interaction length). Excitation wavelength: 488 nm.

spectra. Evaporation of these solutions onto glass slides allowed the fibers to be studied by AFM and fluorescence microscopy. The sizes of these fibers, from 4 to 150 nm in diameter, can be controlled by changing the concentration of the initial solution, while the aspect ratios (length/height) are generally around 500. The plane of the trimer was determined by polarized SCM to be perpendicular to the axis of the fibers, consistent with molecular mechanics calculations. Single-fiber fluorescence images and spectra were collected in a TIRF microscope equipped with a digital color camera and imaging CCD spectrometer. Strongly red-shifted fluorescence from these fibers indicates a high degree of electronic delocalization along the fibers, and breaking up this delocalization by photobleaching blue-shifts the emission toward that of an isolated noninteracting molecule. The electronic communication between molecules in these nanofibers and the ability to study their electronic structure using fluorescence make them potentially useful for nanoscale devices, such as field effect transistors and photoconductors.

Experimental Section

Material and Methods. All chemicals were purchased from Aldrich and used without further purification unless otherwise

specified. *N*-(1-Hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide (**4**)^{69,87} and 1,3,5-tris(4-nitrophenyl)benzene (**6**)⁷⁰ were synthesized according to literature methods. Column chromatography was performed on SiliCycle ultrapure silica gel (70–230 mesh). Thin-layer chromatography (TLC) was carried out on Selecto Scientific silica gel 60 F-254 flexible TLC plates. NMR spectra were recorded on a Bruker 300, 400, or 500 MHz instrument as noted, and the chemical shifts were reported relative to tetramethylsilane (TMS) at 0 ppm (for ¹H NMR) and CDCl₃ at 77.16 ppm (for ¹³C NMR). Atmospheric pressure chemical ionization (APCI) mass spectra were taken on a JEOL JMS-LCmate mass spectrometer (JEOL Ltd., Tokyo, Japan); matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained on a Voyager DE mass spectrometer (AB Biosystems, Framingham, MA). UV/vis absorption spectra were recorded on a Perkin Elmer Lambda 25 UV/vis spectrometer and fluorescence emission spectra on a Perkin Elmer LS 55 fluorometer with excitation at 488 nm. Molecular mechanics calculations were performed using a Merck MMFF94 force field⁹⁰ in Spartan 5.1.1 (Wavefunction Inc.).

Atomic force microscopy images were obtained on a Topo-Metrix Explorer AFM, using high resonance frequency silicon probes from Veeco (model no. 1650-00). A scanning confocal microscope was modified from a Veeco Aurora-2 near-field scanning optical microscope (NSOM), equipped with a 100 × 1.25 NA objective (Zeiss), holographic 488 nm supernotch filter (ThermoOriel), and single-photon-counting avalanche photodiode (APD) detectors (Perkin Elmer/EG&G SPCM-AQR-15). Samples were photoexcited with 488 nm light from an argon ion laser (Melles-Griot) at very low excitation powers (1–10 W/cm²). Polarized excitation was achieved by passing circularly polarized light through a polarizing beam splitter (Newport) before it entered the microscope. Polarized emission detection was performed by separating the fluorescence with the polarizing beam splitter and collecting both components simultaneously with two APD detectors. The fluorescence images were collected and processed using Veeco SPMLab software.

Total internal reflection fluorescence images were obtained using a Nikon 4500 color digital camera attached to the front port of a Nikon Diaphot 300 microscope, modified to be used as through-objective TIRF microscope.⁹¹ Evanescent wave excitation at 488 nm of the sample was achieved using off-axis illumination through a Nikon 1.4 NA 60× objective.⁹² The illuminated area of the sample was typically between 20 and 50 μm in diameter. To obtain the fluorescence spectra, an entrance slit was used to select the fluorescence originating from a vertical cross-section of the illuminated sample. The emission emerging from the specific cross-section was then dispersed using a monochromator (Spex 0.3m, 150 grooves/mm) and detected using a liquid-N₂-cooled CCD camera (Roper Scientific). The fluorescence emission spectra were obtained using a 10 s collection time at excitation powers between 5 and 100 W/cm².

Synthesis of 1,3,5-Tris(4-aminophenyl)benzene (7). A 1.5 g (3.4 mmol) amount of 1,3,5-tris(4-nitrophenyl)benzene (**6**),⁷⁰ 2 g (40 mmol) of hydrazine hydrate, 50 mL of tetrahydrofuran (THF), and 2 g of Raney nickel were stirred at 85 °C in a pressure vessel for 6 h. After cooling, the nickel was filtered off and washed with 50 mL of THF. The filtrate was concentrated to give 0.84 g of yellow solid, which was dissolved in a small amount of THF and purified by column chromatography (SiO₂, 2.5:97.5 MeOH/CH₂Cl₂). Yield: 385 mg (32%) of pale yellow powder. On TLC, the product can be identified by characteristic blue fluorescence under UV illumination (λ

= 254 nm) and turns dark slowly; R_f (silica gel, 5:95 MeOH/CH₂Cl₂) = 0.11. ¹H NMR (400 MHz, CDCl₃): δ 3.73 (s, 6 H, 3 NH₂), 6.78 (d, J = 8.6 Hz, 6 H, Ar), 7.50 (d, J = 8.6 Hz, 6 H, Ar), 7.59 (s, 3 H, Ar). ¹³C NMR (75 MHz, CDCl₃): δ 115.52, 123.06, 128.35, 132.06, 142.11, 146.00; MS (APCI+): m/z = 352 [M + H]⁺.

Synthesis of Perylene Diimide Trimer (1). A 3.5 mg (0.01 mmol) amount of 1,3,5-tris(4-aminophenyl)benzene (7), 22.9 mg (0.04 mmol) of *N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxyl-3,4-anhydride-9,10-imide (4), and 3.5 g of imidazole were stirred at 130 °C under argon for 6 h. After cooling, the mixture was dispersed in 6 mL of ethanol, acidified to pH < 1 with 2 N HCl, and stirred at room temperature for 30 min. The red precipitate was collected by filtration, washed with 30 mL of H₂O, redissolved in CH₂Cl₂, and purified by column chromatography (SiO₂, from CH₂Cl₂ to 0.5:99.5 MeOH/CH₂Cl₂). Yield: 13 mg (64%) of red powder. R_f (silica gel, 1:20 acetone/CHCl₃) = 0.57. ¹H NMR (500 MHz, CDCl₃): δ 0.84 (t, 18 H, 6 CH₃), 1.15–1.40 (m, 48 H, 24 CH₂), 1.88 (m, 6 H, α -CH₂), 2.26 (m, 6 H, α -CH₂), 5.20 (m, 3 H, CH 1-hexylheptyl), 7.53 (d, J = 8.4 Hz, 6 H, phenylene), 7.95 (d, J = 8.4 Hz, 6 H, phenylene), 7.99 (s, 3 H, central benzene), 8.65–8.84 (m, 24 H, perylene). MS (MALDI, negative): m/z = 2018.0 [M]⁻.

Acknowledgment. This work was supported primarily by the NSF MRSEC Grant DMR-0213574 and in part by the Department of Energy Office of Basic Energy Sciences under the Award Agency Project DE-FG02-02ER15375. D.M.A. thanks Research Corp. for a Cottrell Scholar Award RC No. CS0937.

Supporting Information Available: SCM images showing polarized emission from the fibers and ¹H NMR and MS spectra for 1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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