

# Morphology control of nanofibril donor-acceptor heterojunction to achieve high photoconductivity: exploration of new molecular design rule

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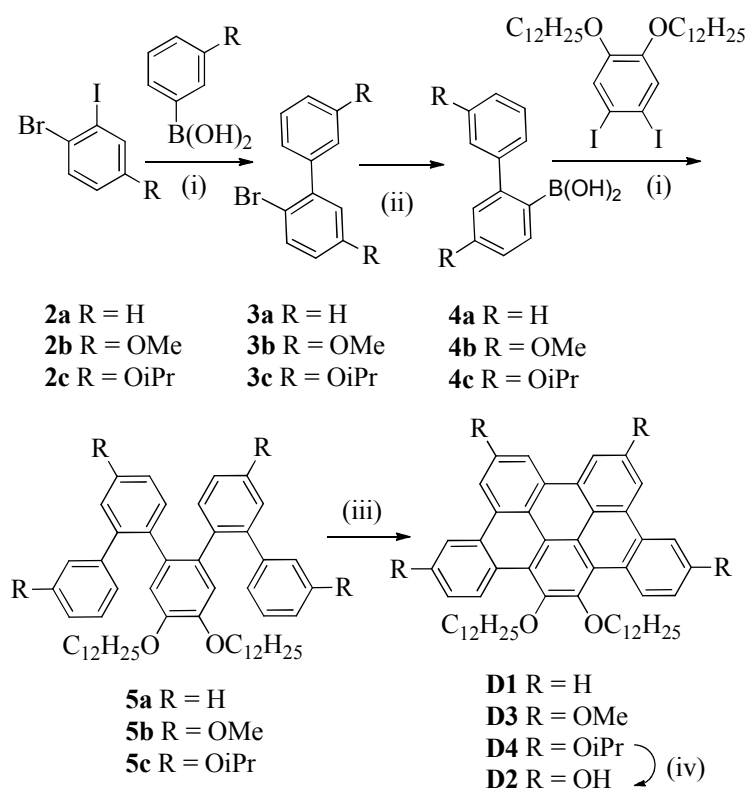
## Materials

Synthesis of PTCDI and the nanofibril fabrication were followed the previous reported methods.<sup>1,2</sup> Synthesis of **D1-D4** was shown in Scheme S1. Detailed synthesis and structural characterization of **D1-D4** were published elsewhere.<sup>3</sup> A brief description of the synthesis is described here as the following: As shown in Scheme S1, the key steps are the Suzuki-Miyaura coupling of biarylboronic acid derivatives (**4a**, **4b**, **4c**) with 1,2-bis(dodecyloxy)-4,5-diiodobenzene to form o-quinquephenyls (**5a**, **5b**, **5c**) and the subsequent Scholl oxidative cyclization to yield the TBP cores. The Suzuki-Miyaura coupling went smoothly and could proceed directly from 2-bromobiaryl derivatives (**3a**, **3b**, **3c**) as a one-pot synthesis with good overall yields (around 50%). The Scholl

reactions were carried out using 5-10 equivalents of  $\text{FeCl}_3$  in a nitromethane/dichloromethane solvent mixture at 0 °C. Under these conditions, compounds **D1**, **D3** and **D4** were obtained in 15-30% yields. Compound **D2** was synthesized from **D4** in excellent yields using B-bromo-9-BBN as the dealkylation reagent. The structures and purity of all four donor molecules (**D1-D4**) have been characterized and confirmed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, 2D COSY NMR, MALDI-TOF mass spectrometry measurements and elemental analysis.

To coat the PTCDI nanofibers with D molecules, 7 nmol of nanofibers were deposited onto a 5mm  $\times$  5 mm silicon wafer covered with 300-nm thick  $\text{SiO}_2$ , followed by drop-casting of 4 nmol of **D1-D4** dissolved in a 0.1 mM ethanol solution.

#### Scheme S1



i)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{Na}_2\text{CO}_3$ , Toluene, reflux ; ii)  $n\text{-BuLi}$ ,  $\text{B}(\text{OCH}_3)_3$ , THF ;  
 iii)  $\text{FeCl}_3$ ,  $\text{MeNO}_2$ , DCM, 0 °C; (iv) B-Br-BBN,  $\text{CH}_2\text{Cl}_2$

## **General Characterization**

UV-vis absorption spectra were measured on a PerkinElmer Lambda 25 spectrophotometer. The fluorescence spectra were taken on a PerkinElmer LS 55 spectrophotometer. Bright field and fluorescence optical microscopy images were obtained with Leica DMI4000B inverted microscope equipped with Acton SP-2356 Imaging Spectrograph system and Princeton Instrument Acton PIXIS:400B Digital CCD Camera System for high resolution full spectral recording. AFM measurement was performed in tapping mode on a Veeco MultiMode V scanning probe microscope, for which samples were directly drop-cast on a silicon wafer covered with 300-nm thick SiO<sub>2</sub> layer. The electrical conductivity were measured using a two-probe method on a Signatone S-1160 Probe Station combined with an Agilent 4156C Precision Semiconductor Analyzer. A tungsten lamp was used as the light source with a light intensity of 0.17 mW/mm<sup>2</sup> on the testbed. The gold-electrode pair used was 14 μm in width and 5 μm in gap.

## **Kelvin Probe Force Microscopy (KPFM)**

Indium-doped tin oxide (ITO) coated glass slides (Delta Technology, R = 5-15 Ω) were used as substrates for KPFM measurements. Before use, ITO glass substrates were rinsed thoroughly with distilled water and ethanol, followed by drying with nitrogen blowing. Donor coated PTCDI nanofibers were deposited onto the ITO glass via drop casting. KPFM experiments were performed with Bruker Dimension Icon equipped with Extender Electronics module. Conductive antimony (n) doped silicon tips (SCM-PIT, Bruker) were used along with a cantilever coated with 20 nm Pt/Ir on both sides. Surface potential was measured using Lift Mode.<sup>4</sup> Briefly, a topographic line scan was first recorded with

Tapping Mode, and then the same line was rescanned in Lift Mode with 20 nm constant distance between the tip and substrate. The white light illumination was provided by a tungsten lamp, which delivered a light intensity of  $10 \text{ mW/cm}^2$  on the substrate.

### **Solvent Vapor Annealing Process**

Solvent vapor annealing was performed by putting the nanofiber sample (deposited on a substrate) into a sealed 50 mL jar, which contained 5 mL of ethanol at bottom to maintain the saturated vapor of ethanol. The annealing was kept for 3 hours.

### **Preparation of Surface Modified Glass slides**

The glass slides were first thoroughly cleaned in acetone and isopropanol for 3 min each in an ultrasonic bath, and then cleaned with a piranha solution (70 vol%  $\text{H}_2\text{SO}_4$ : 30 vol% 30%  $\text{H}_2\text{O}_2$ ) for 20 min, followed by rinsing with deionized water and drying in air flow. To form monolayer of octadecyl-trichlorosilane (OTS) on the surface, the glass slides were immersed in an anhydrous toluene solution of OTS (3 mM) for 3 h, followed by ultrasonic cleaning in fresh toluene solvent for 2 min to remove the excessive OTS residues. The glass slides were then baked on a  $150^\circ\text{C}$  hot plate for 1 h to enhance the surface crosslinking.

### **Other Supporting Figures**

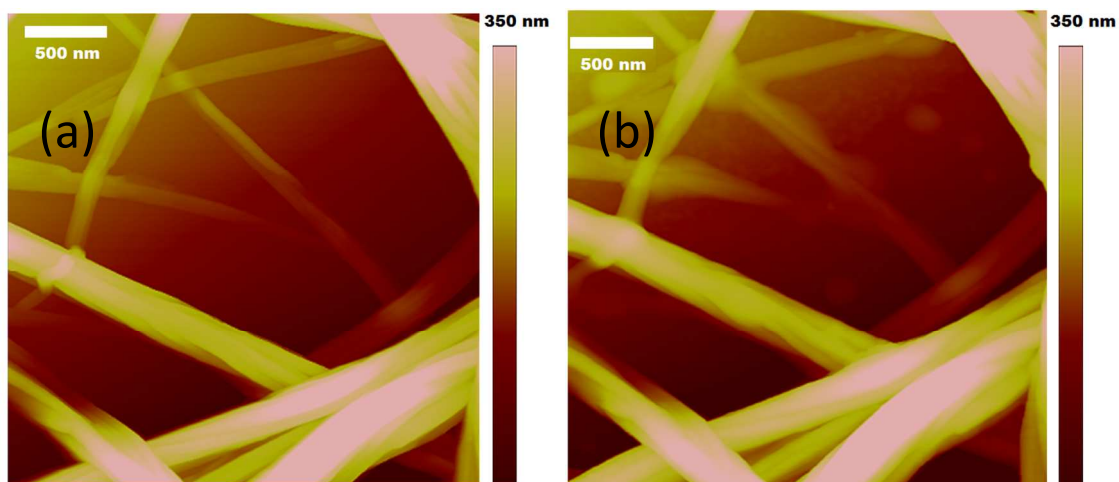


Figure S1. AFM images of PTCDI nanofibers drop-cast on the surface of silicon wafer covered with 300-nm thick SiO<sub>2</sub> before (a) and after (b) coating with **D2**.

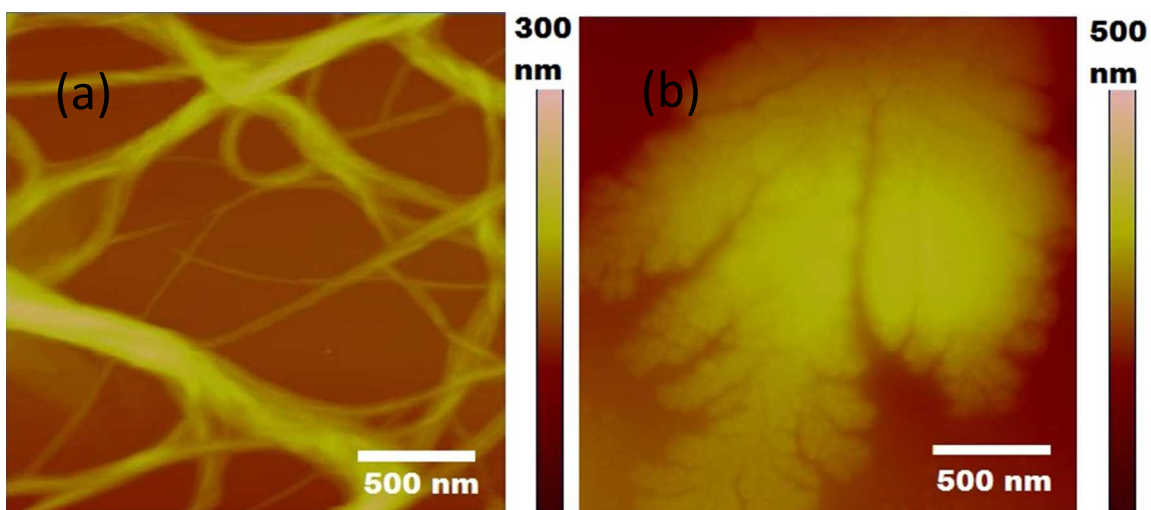


Figure S2. AFM images of **D1** (a) and **D2** (b) drop-cast on the surface of silicon wafer covered with 300-nm thick SiO<sub>2</sub>.

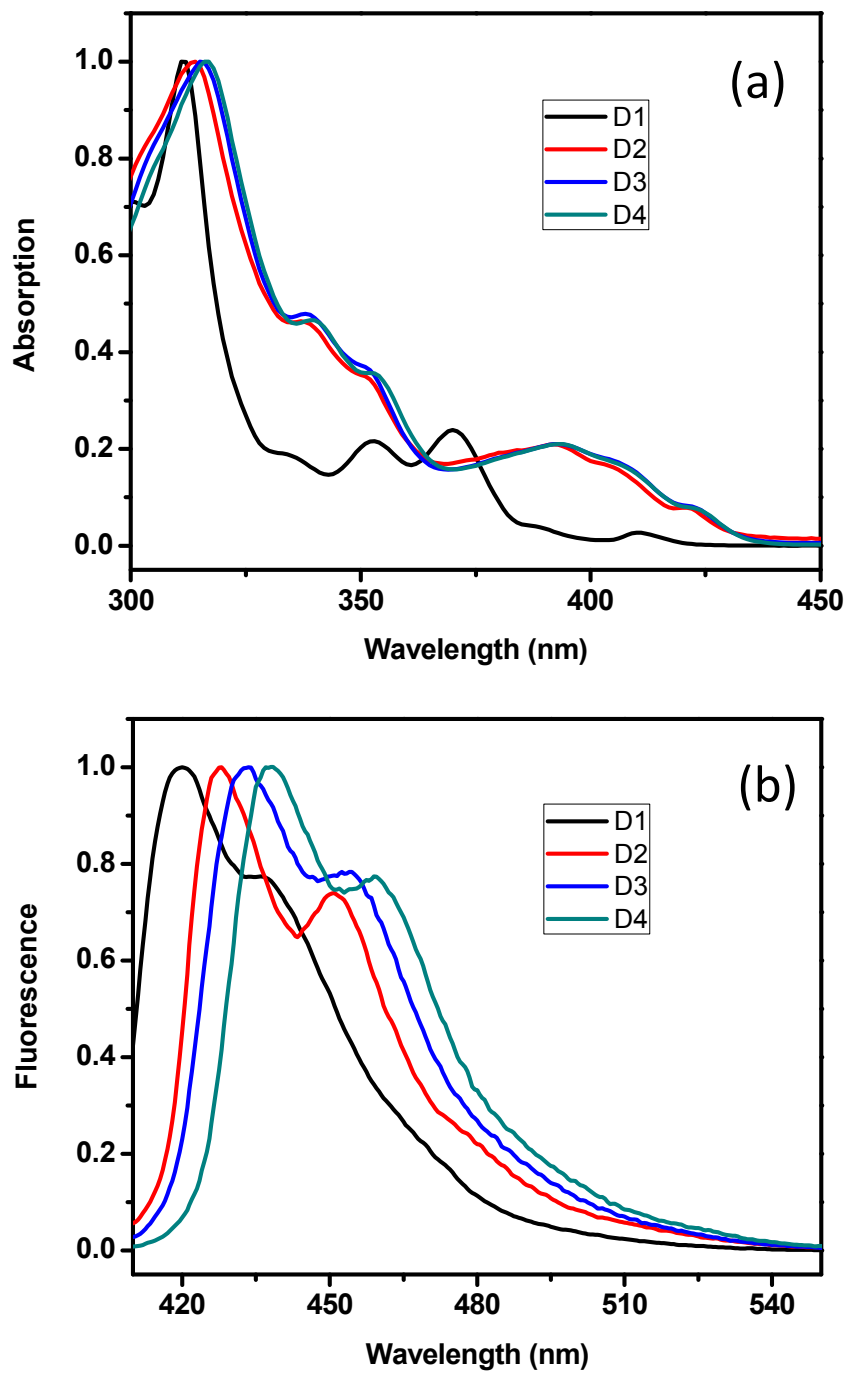


Figure S3 Normalized absorption (a) and fluorescence spectra (b) of **D1-D4** in ethanol solution.

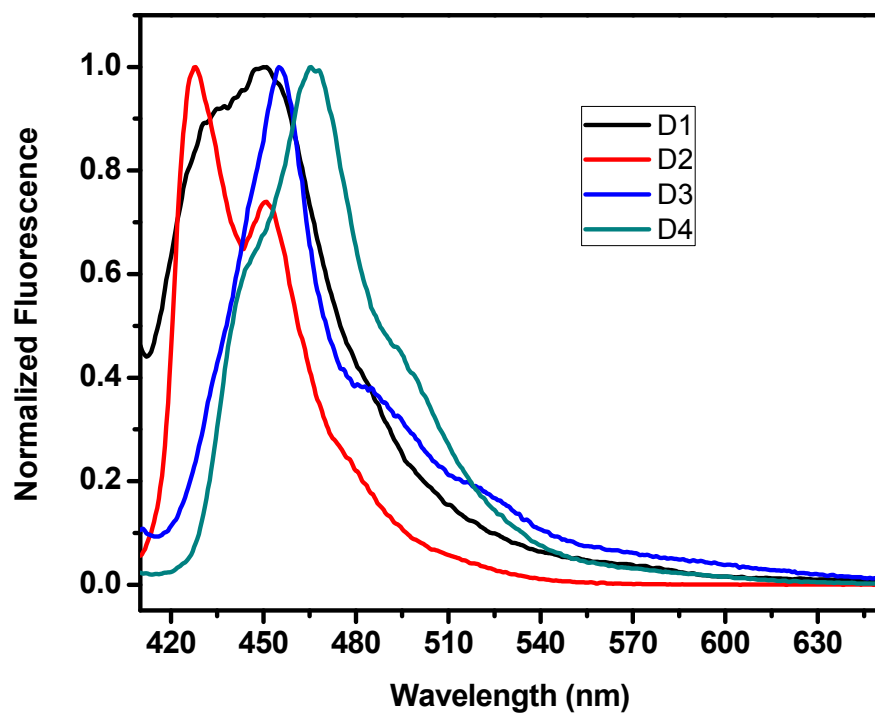
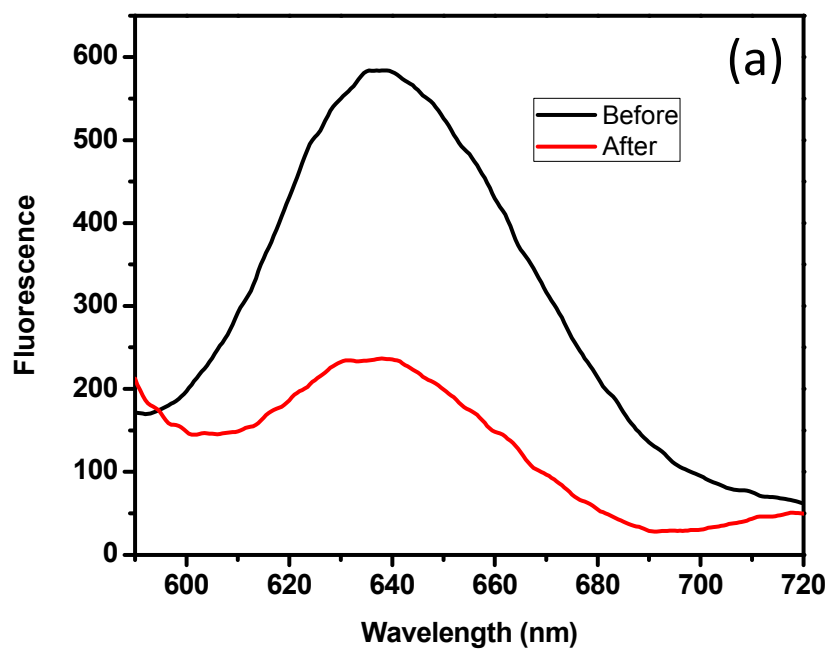


Figure S4. Normalized fluorescence spectra of **D1-D4** on drop-cast on glass surface.



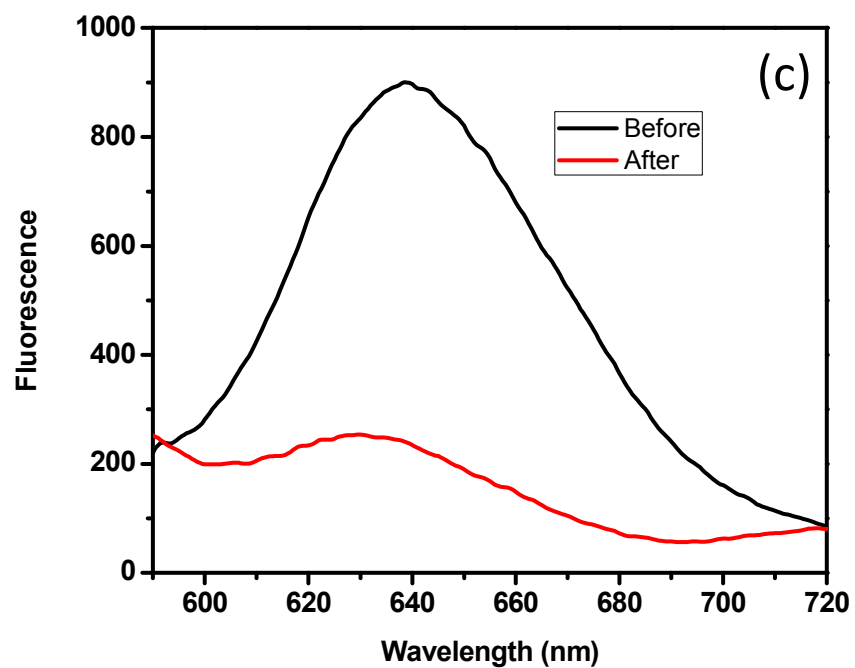
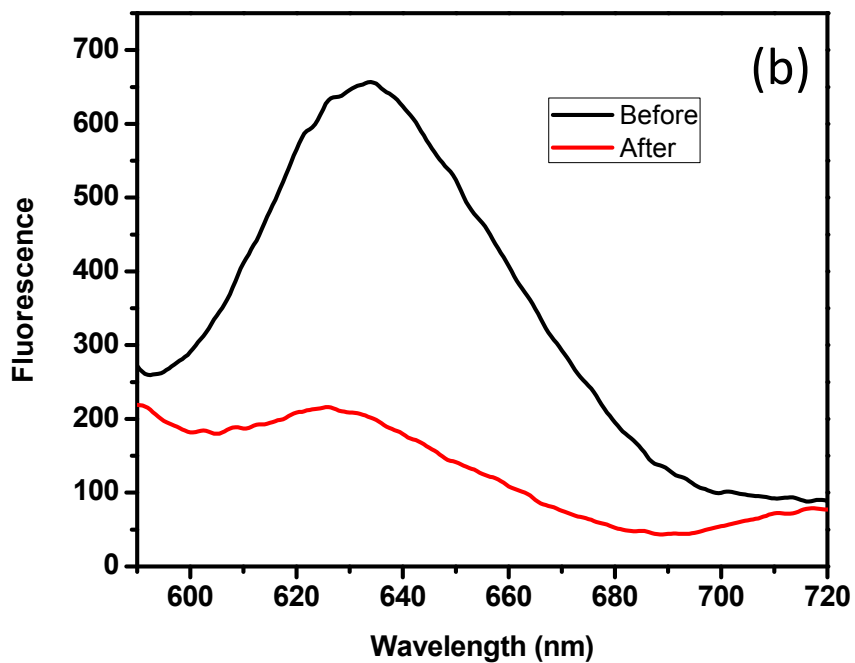
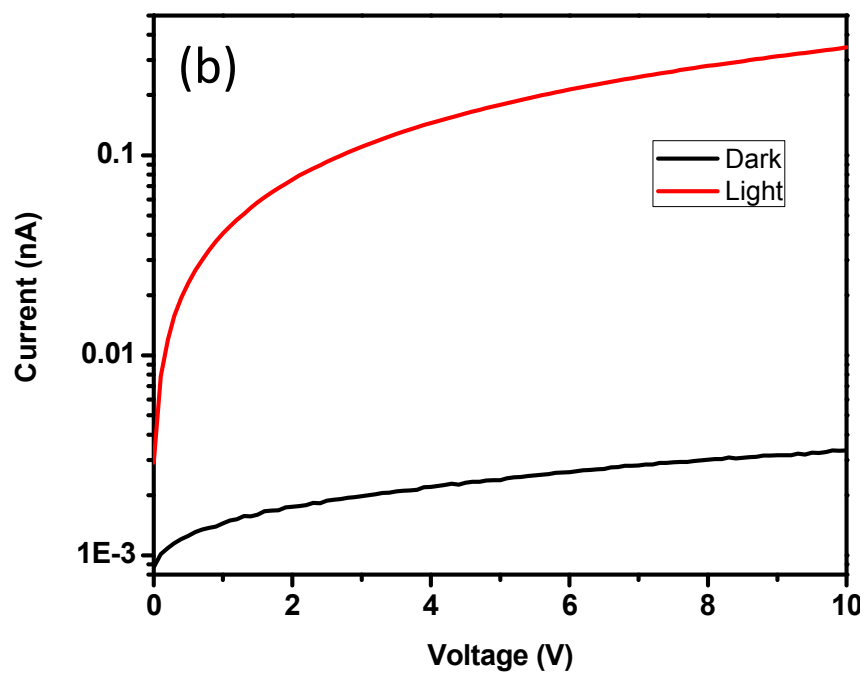
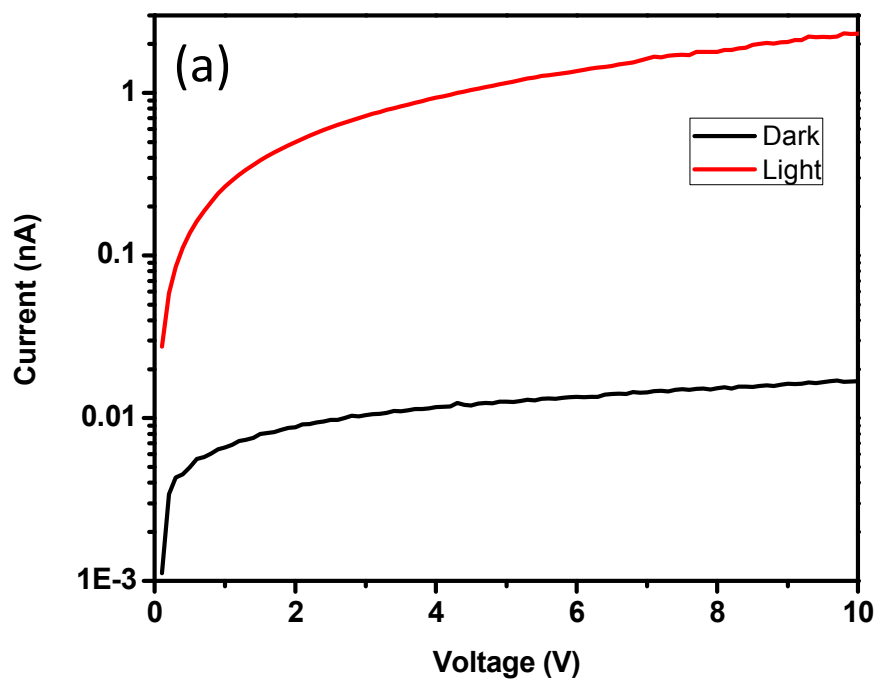


Figure S5. Fluorescence spectra recorded on the PTCDI nanofibers deposited on glass before (black) and after (red) drop-casting of **D1** (a), **D2** (b), **D3** (c).





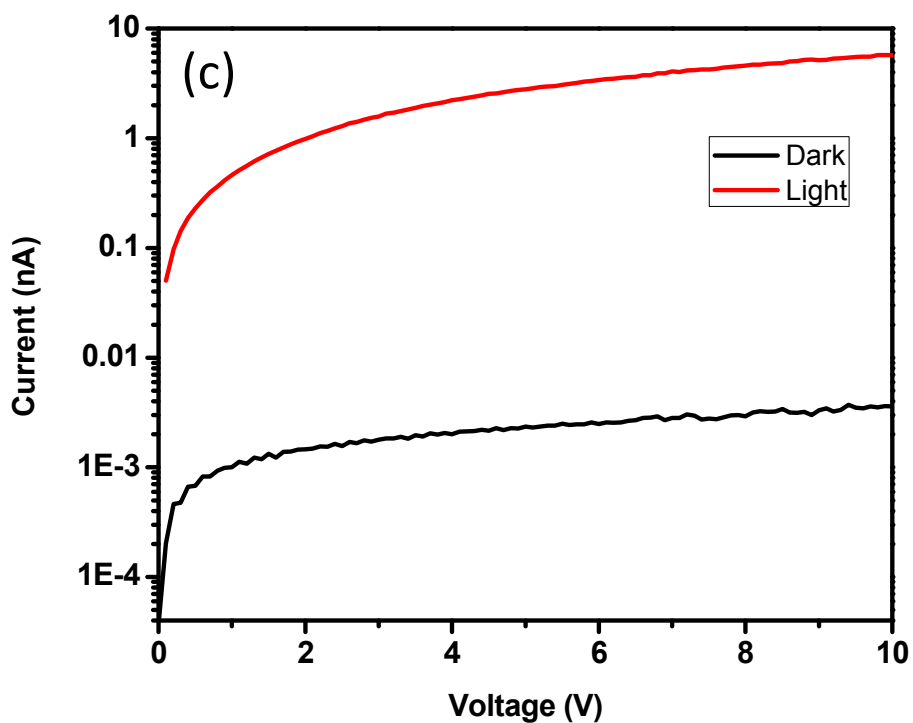


Figure S6. Example I-V curves of PTCDI nanofibers coated with **D1** (a), **D2** (b), **D3** (c) measured in dark (black) and under white light illumination of  $0.17 \text{ mW/cm}^2$  (red).

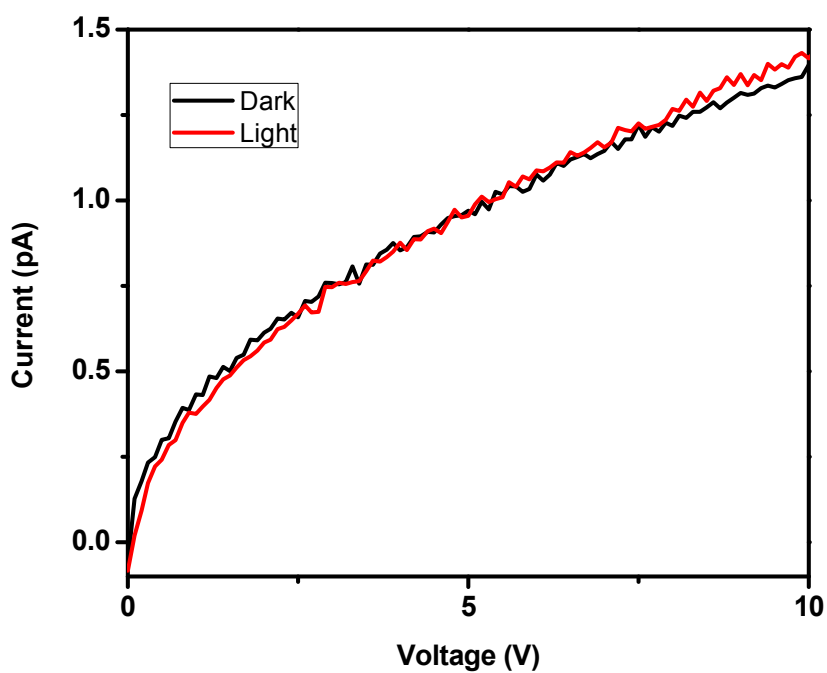


Figure S7. I-V curves measured for **D4** film in dark (black) and under light illumination (red). Experimental conditions are the same as in Figure S6.

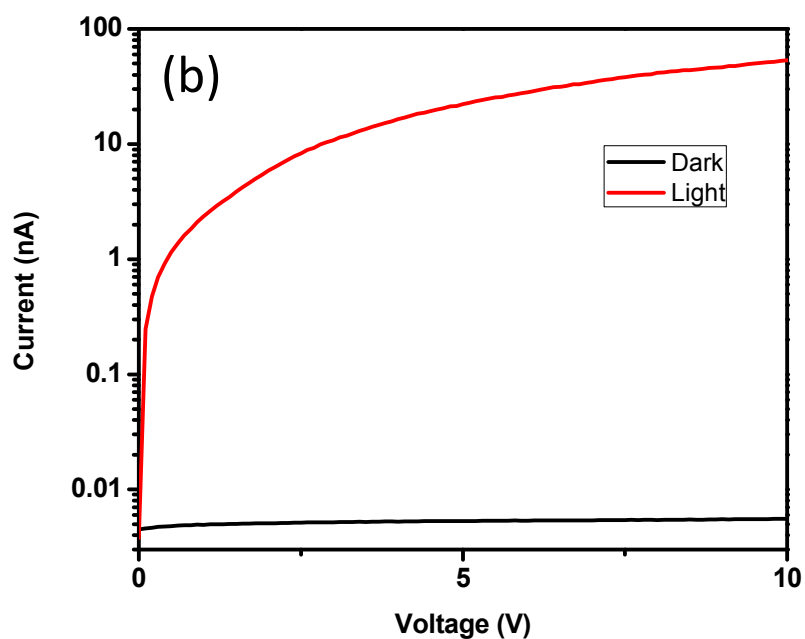
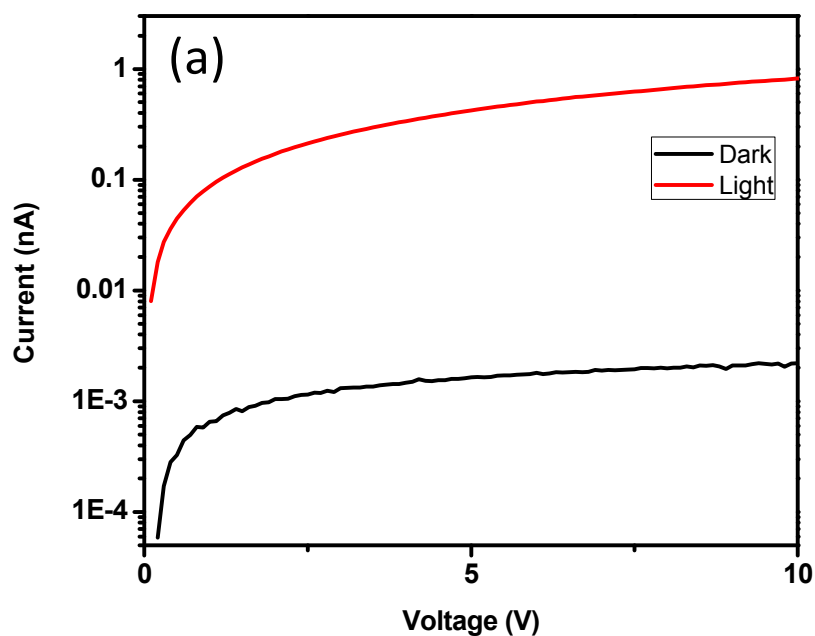


Figure S8. I-V curves measured for **D3** (a) and **D4** (b) coated nanofibers after solvent vapor annealing in dark (black) and under light illumination (red). Photocurrent measurement conditions are the same as in Figure S6.

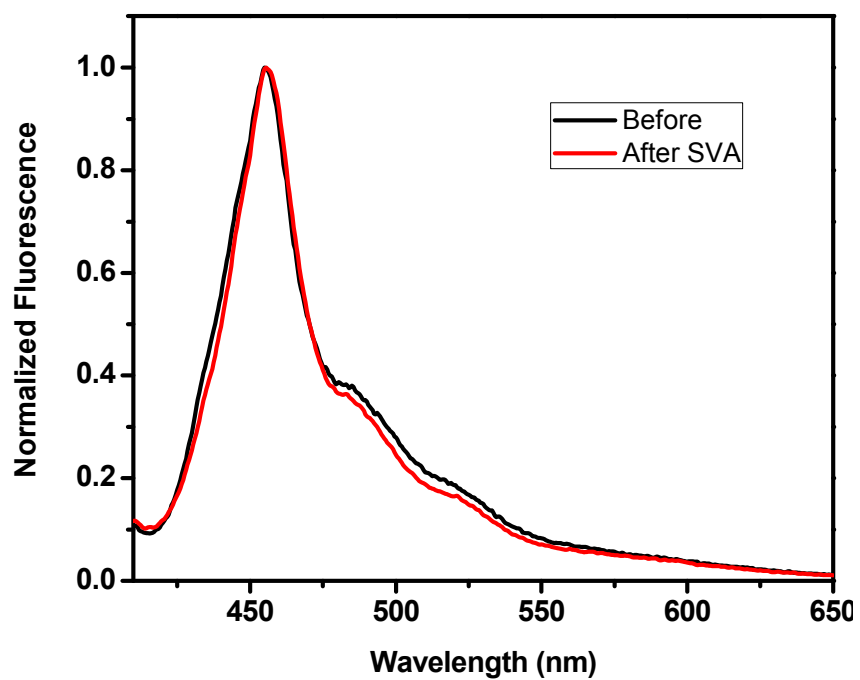


Figure S9. Fluorescence spectra recorded on **D3** film deposited on OTS modified glass surface before (black) and after (red) solvent vapor annealing.

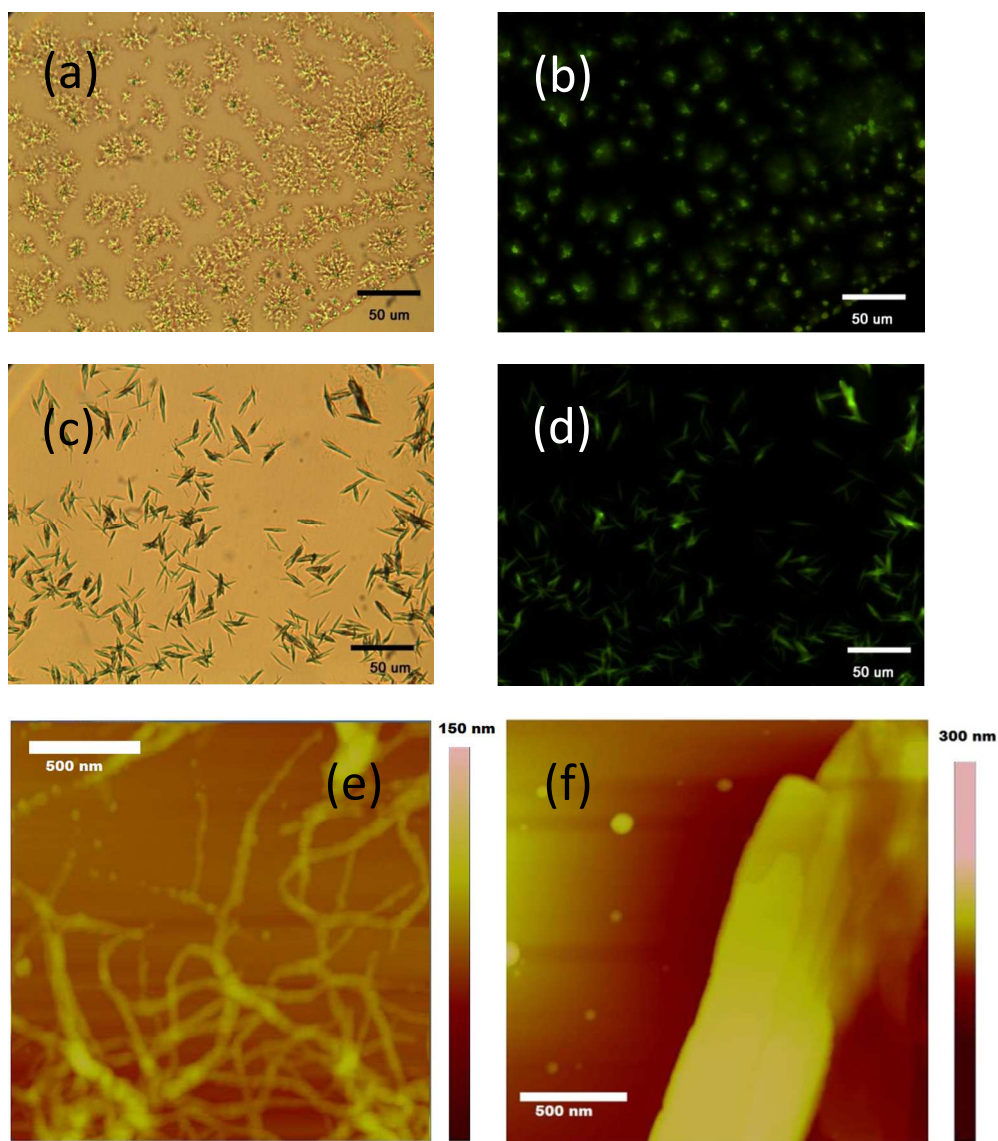


Figure S10. Bright field microscopy (a,c) and fluorescence microscopy images (b,d) of **D3** drop-cast on OTS modified glass surface before (a,b) and after (c,d) ethanol vapor annealing. AFM images of the same sample before (e) and after (f) ethanol vapor annealing.

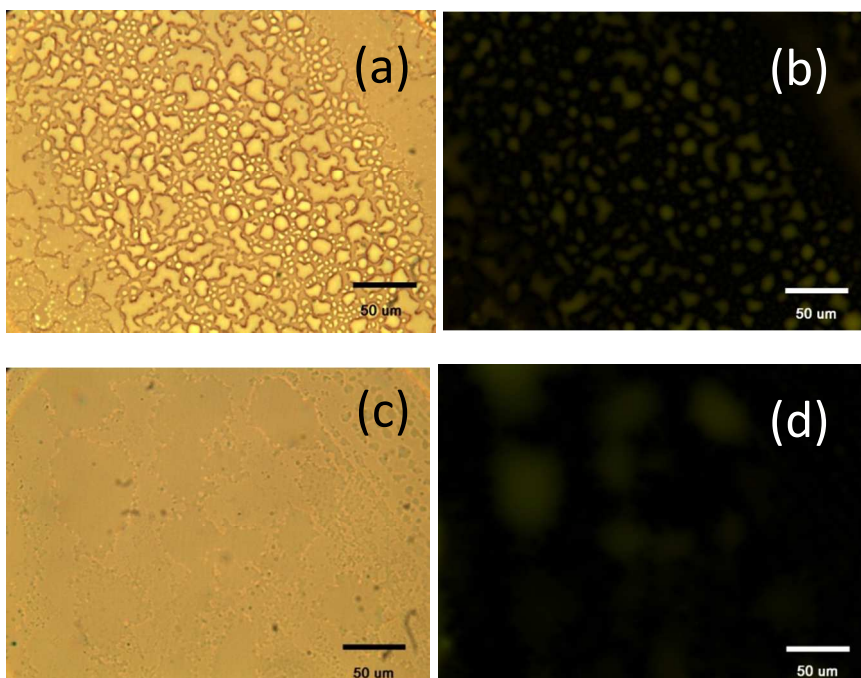


Figure S11. Bright field microscopy (a,c) and fluorescence microscopy images (b,d) of **D4** drop-cast on OTS modified glass surface before (a,b) and after (c,d) ethanol vapor annealing.

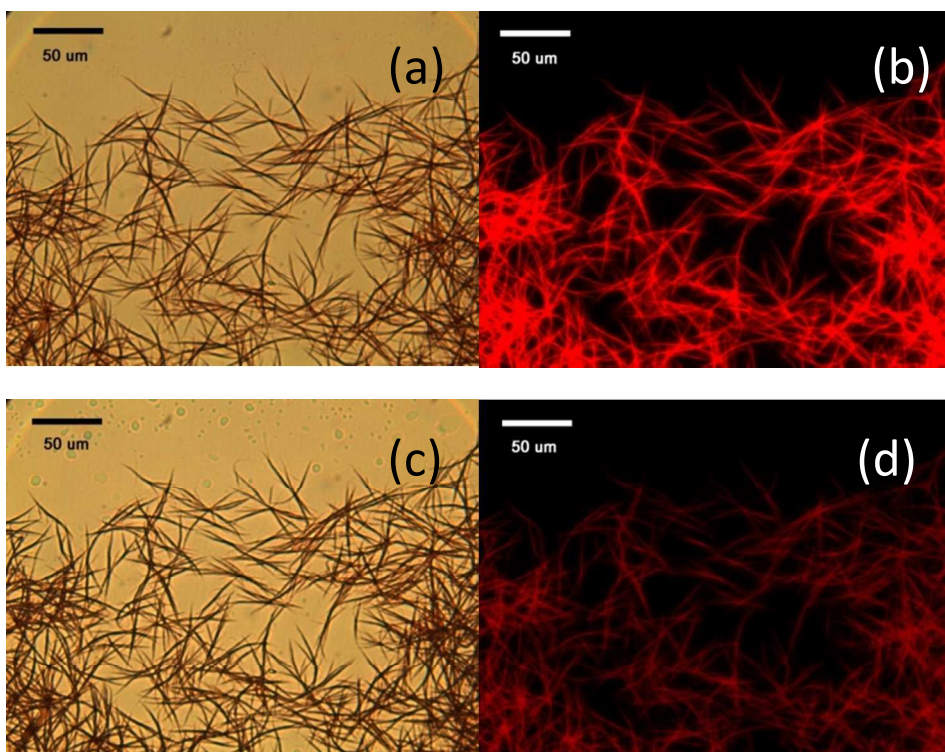


Figure S12. Bright field microscopy (a,c) and fluorescence microscopy images (b,d) measured over the PTCDI nanofibers before (a,b) and after (c,d) drop-casting of **D4**.

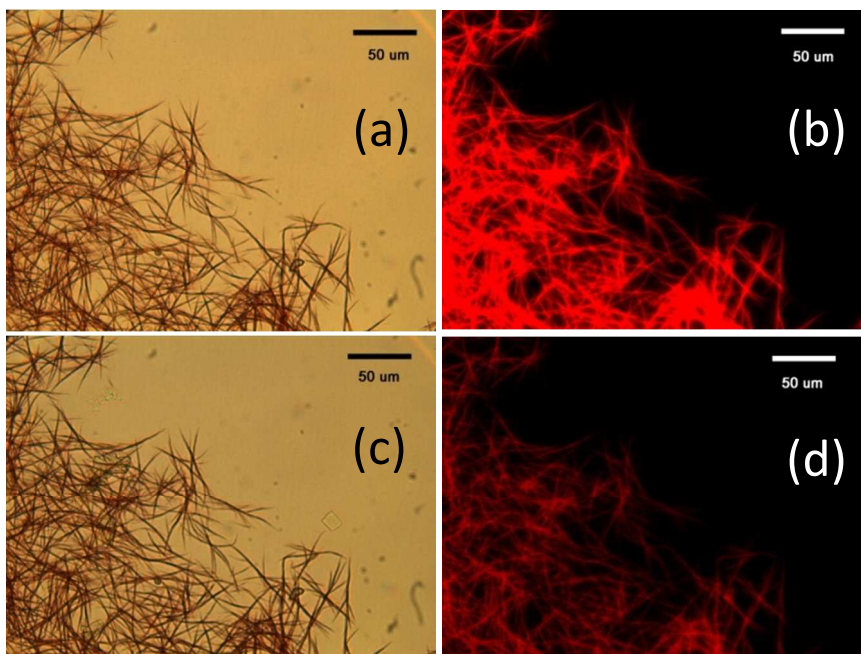


Figure S13 Bright field microscopy (a,c) and fluorescence microscopy images (b,d) measured over the PTCDI nanofibers before (a,b) and after (c,d) drop-casting of **D3**.

## References

- (1) Zang, L.; Che, Y.; Moore, J. S. *Acc. Chem. Res.* **2008**, *41*, 1596-1608.
- (2) Che, Y.; Huang, H.; Xu, M.; Zhang, C.; Bunes, B. R.; Yang, X.; Zang, L. *J. Am. Chem. Soc.* **2011**, *133*, 1087-1091.
- (3) Chou, C.-E.; Li, Y.; Che, Y.; Zang, L.; Peng, Z. *RSC Advances* **2013**, DOI: 10.1039/C1033RA43392G.
- (4) Palermo, V.; Palma, M.; Samorì, P. *Adv. Mater.* **2006**, *18*, 145-164.