Light-Controlled Self-Assembly and Conductance: From Nanoribbons to Nanospheres

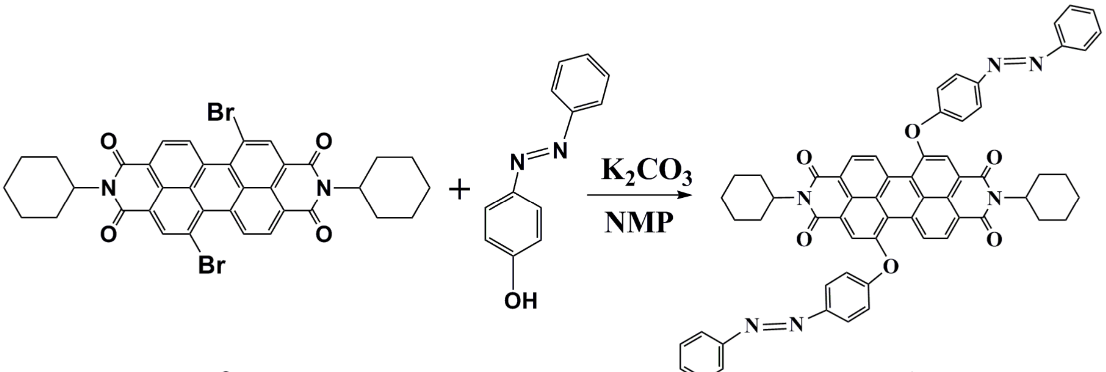
Lulu Ma,[a] Jiong Jia,[c] Tieying Yang,[d] Guangzhi Yin,[d] Yang Liu,[a] Xuan Sun,*[b] Xutang Tao*[a]

[a] *State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, P. R. China,* [b] *Key laboratory of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China,* [c] *School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, P. R. China,* [d] *Shanghai Institute of Applied Physic, Chinese Academy of Science , Shanghai 201204, P. R. China*

Email: txt@icm.sdu.edu.cn; sunxuan@sdu.edu.cn

Supporting Information

1. Synthesis



2

1

Scheme S1. Synthesis of **AZO-PDI 1**

Chemicals. All the chemicals were used as received without further purification and drying except noted. N,N′-dicyclohexyl-1,7-dibromoperylene bisimide **2** was prepared following the literature[1].

Synthesis of compound 1.

4-Phenylazophenol (0.99g) and N,N′-dicyclohexyl-1,7-dibromoperylene bisimide **2** (0.71g) were mixed with K_2CO_3 (0.83 g) in NMP (30 mL, chromatography grad). The reaction mixture was stirred at 145°C for 20 min. After the solvent was evaporated under reduced pressure, the crude product was purified by silica gel column chromatography (chloroform as eluent) to give 230 mg (24 %) of compound **1** as a red solid. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.54 (d, 2H, J=8.4 Hz), 8.63 (d, 2H, *J*= 8.4 Hz), 8.38 (s, 2H), 8.03 (d, 4H, *J*= 8.7 Hz), 7.92 (d, 4H, *J*= 6.9Hz), 7. 56-7.49 (m, 6H), 7.29 (m, 4H), 5.03-4.95 (m, 2H), 2.56-2.45 (m, 4H), 1.90-1.26 (m, 16H). MALDI-TOF, m/z: Calcd for $C_{60}H_{46}N_6O_6$, 947.04; Found, 947.3. Analysis calculated for $C_{60}H_{46}N_6O_6$ (%): C, 76.09; H, 4.90; N, 8.87. Found: C, 75.97; H, 4.89; N,8. 53.

1. F. Würthner, V. Stepanenko, *J. Org. Chem.* 2004, *69*, 7933.

2. Spectroscopic and electrochemical characterization of the photochromic properties of the monomeric AZO-PDI.

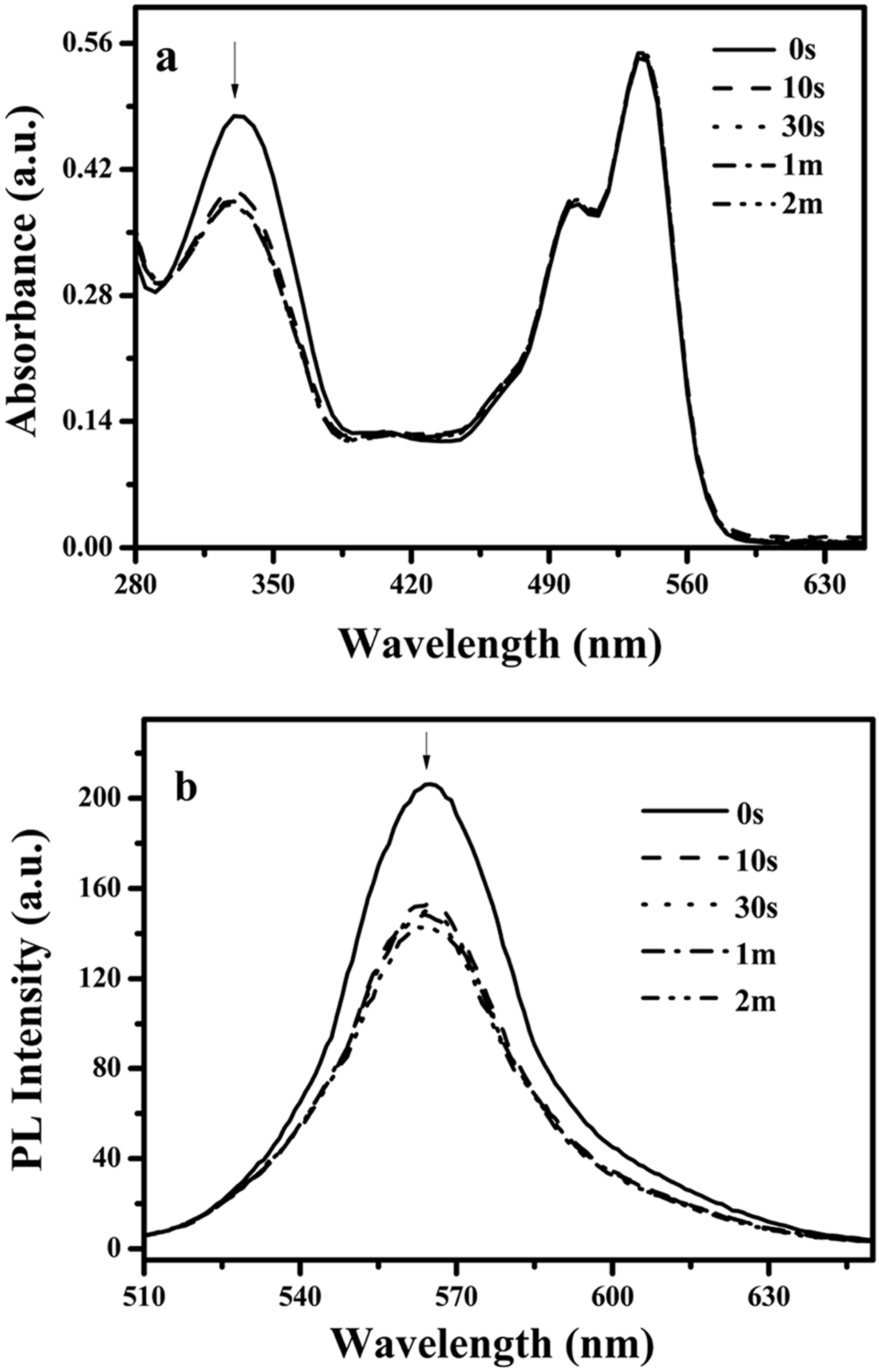


Figure S1. Time-dependent (a) Electronic absorption and (b) Steady State Fluorescence spectrum of **AZO-PDI** dissolved in $CHCl_3$ (10^{-5}mol•dm^{-3}) under the 365 nm light irradiation.

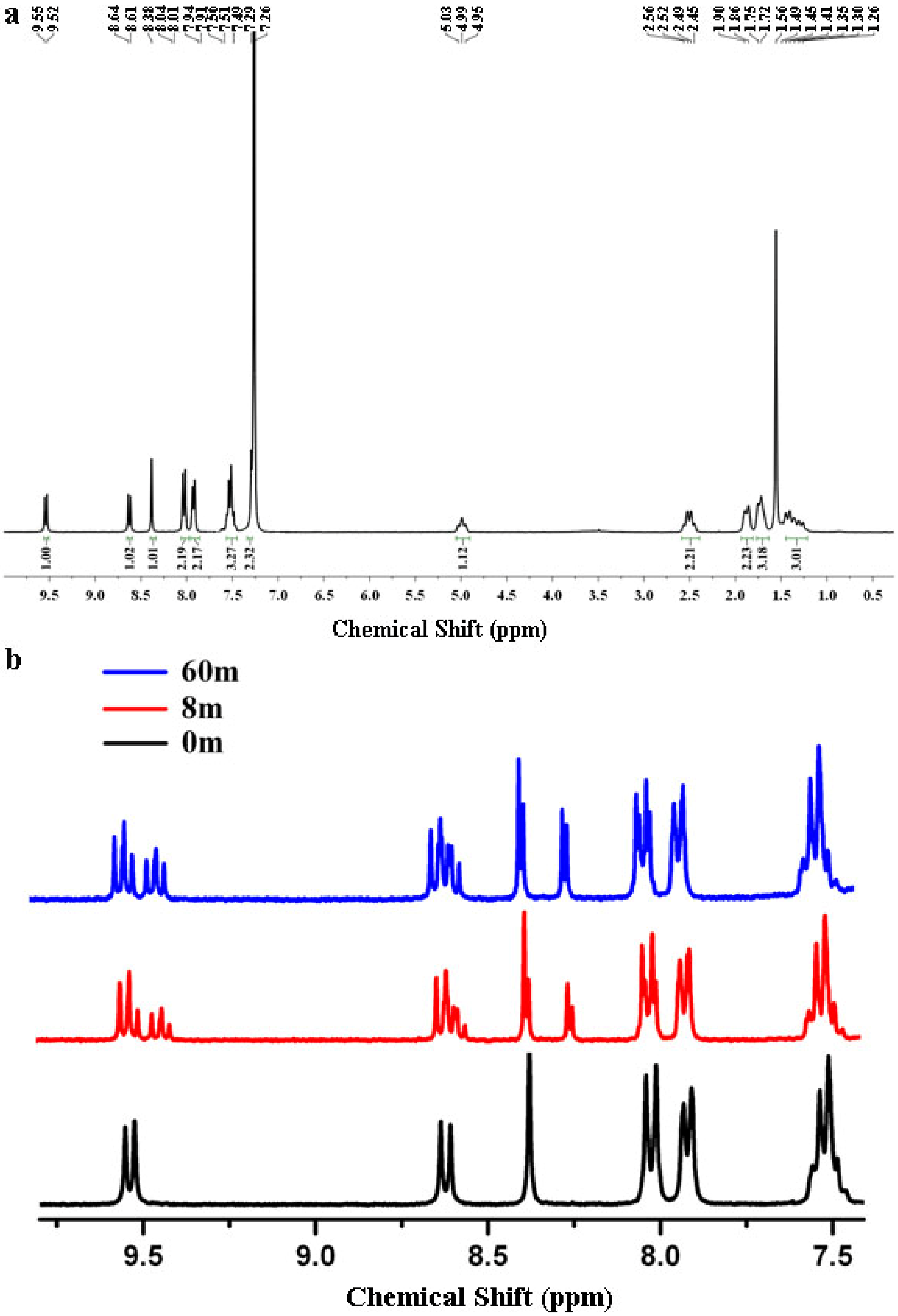


Figure S2. ^{1}H-NMR spectra of (a) **AZO-PDI**; (b) the photoisomerization of **AZO-PDI** in $CDCl_3$: before light irradiation (black), upon 365 nm light irradiation for 8 min (red), and upon 365 nm light irradiation for 60 min (blue).

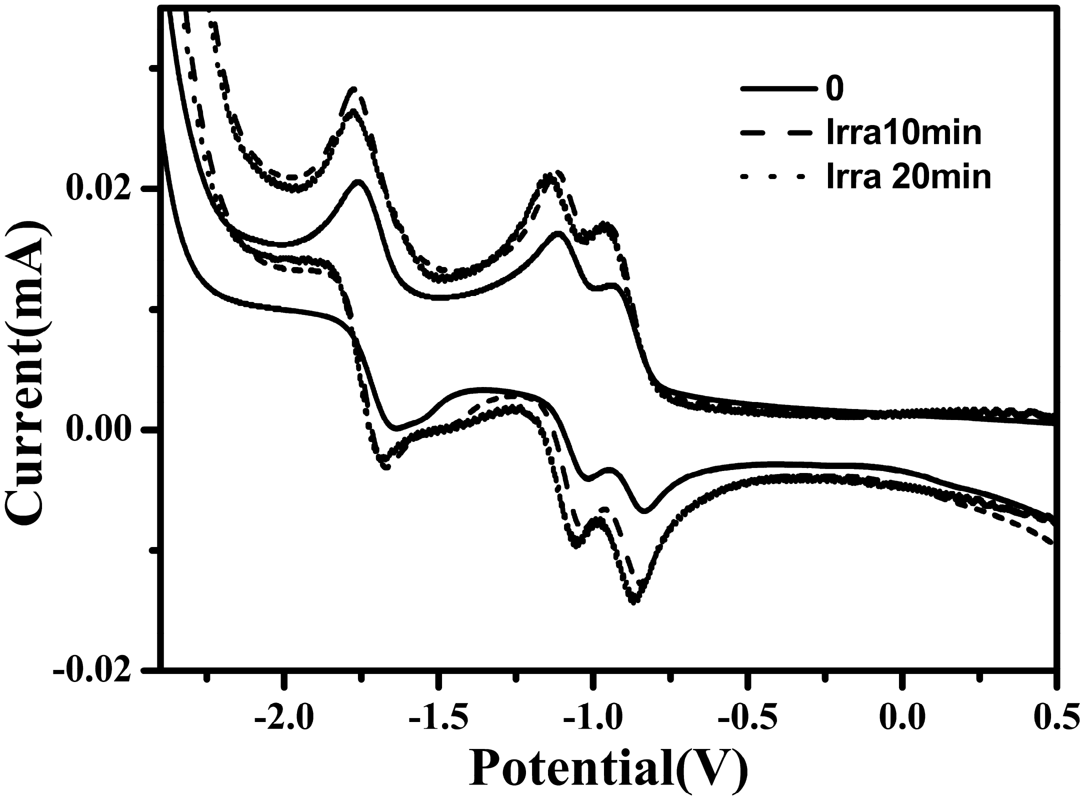


Figure S3. Cyclic voltammetry measurements of **AZO-PDI** in CH_2Cl_2 with tetrabutylammonium perchlorate (Bu4NClO4) as electrolyte (solid line) and those upon UV-irradiation for 10 min (dashed line); for 20 min (dotted line).

3. Characterization and conductivity of the self-assembled nanostructures formed from AZO-PDI molecules.

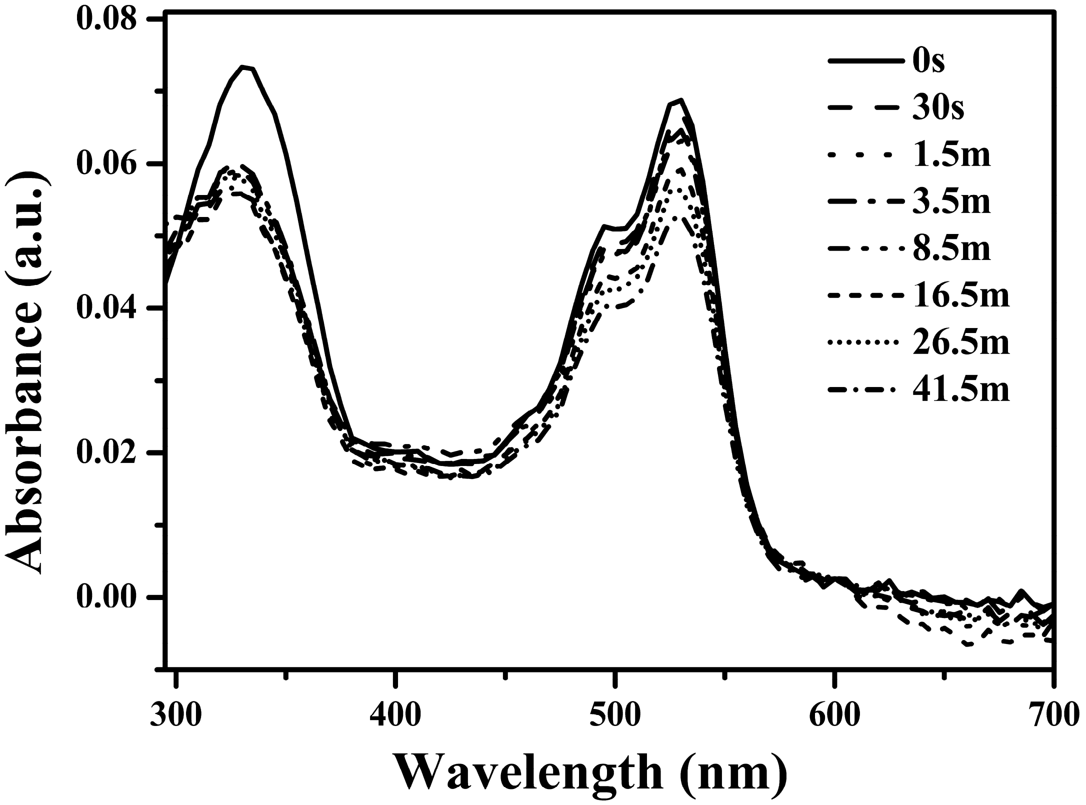


Figure S4. Electronic absorption spectra of the **AZO-PDI** nanoaggregates obtained in the $CHCl_3/CH_3OH$ (v/v = 3/200) binary solvents (solid line); and upon 365 nm light irradiation along with time (dashed lines).

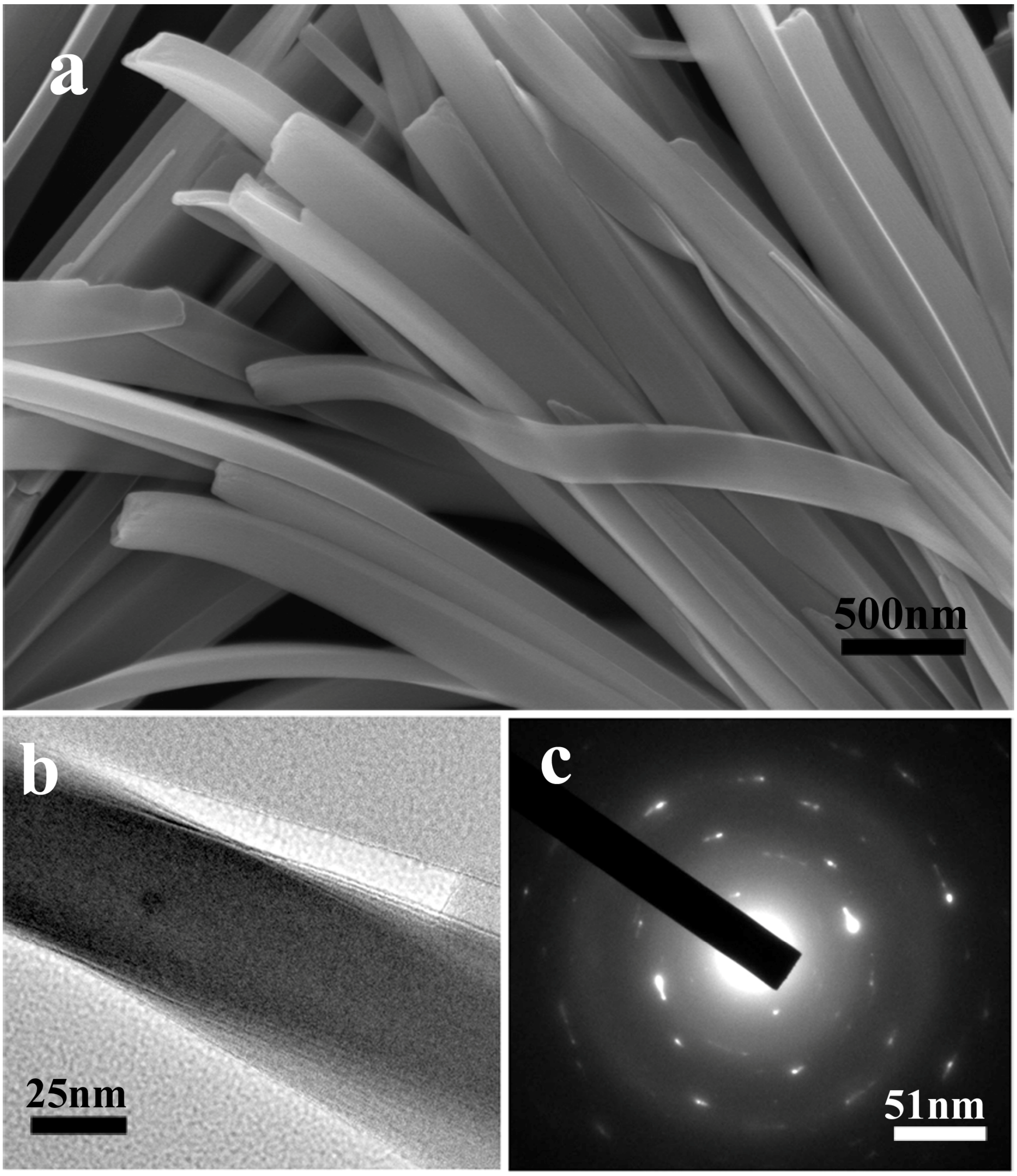


Figure S5. (a) SEM image of the nanoribbons, (b) HR-TEM of a single nanoribbon and (c) corresponding electron diffraction pattern from a nanoribbon.

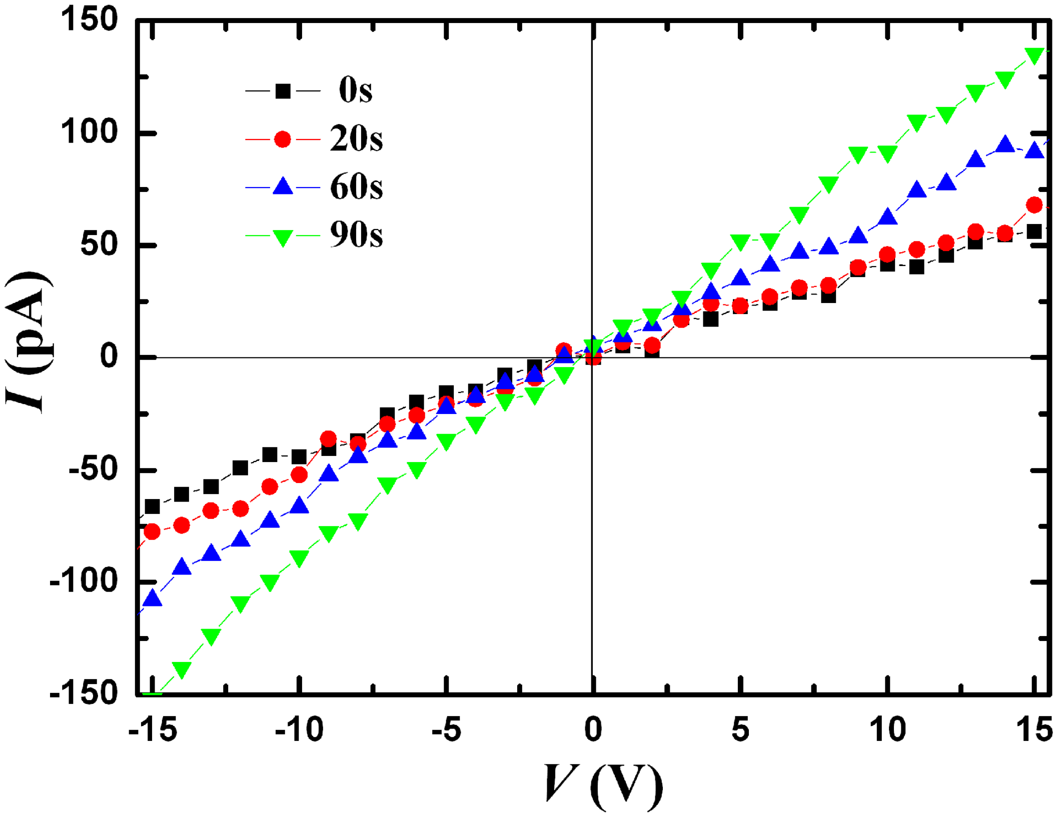


Figure S6. I-V curves for the nanoribbons of **AZO-PDI** under >500 nm light irradiation along with time.

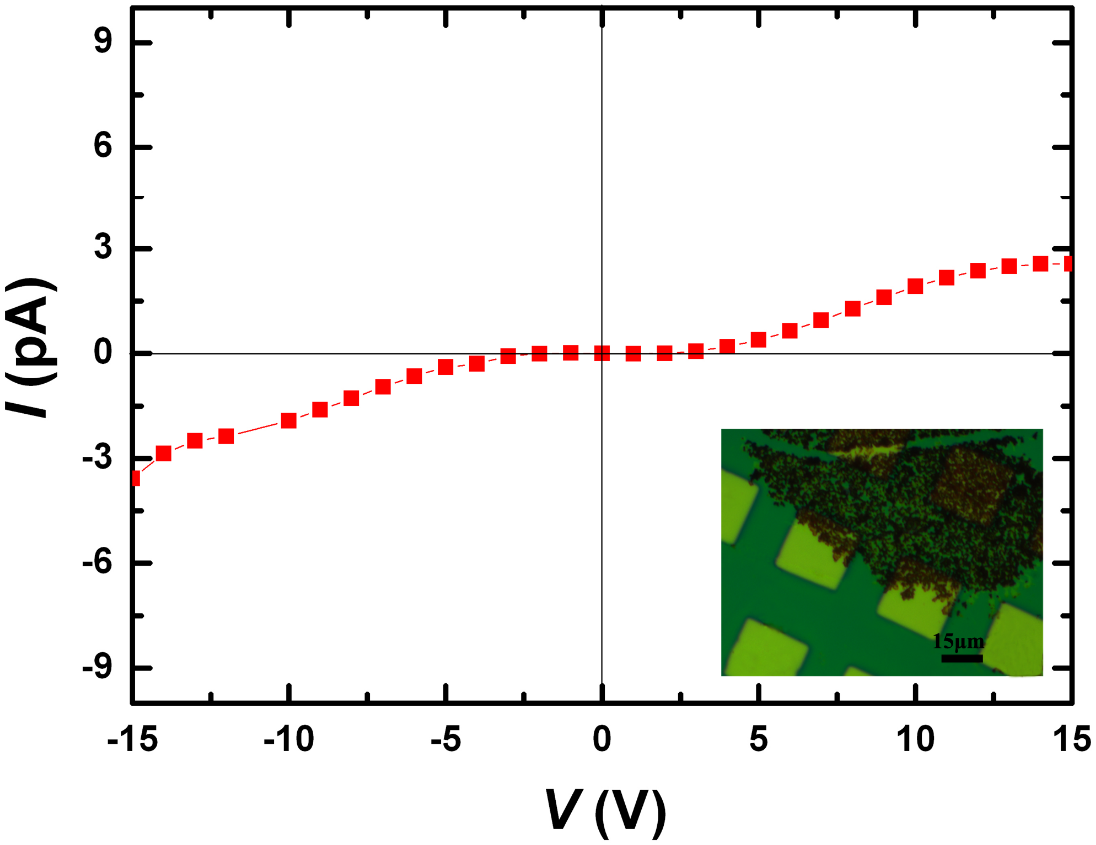


Figure S7. I-V curves for the nanospheres obtained by injecting the photoisomerized chloroform solution of **AZO-PDI** into methanol. Inset: microscope image showing the nanospheres lay out on the electrodes (yellow).