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Block-Copolymer-Nanowires with Nanosized Domain Segregation and High Charge Mobilities as Stacked p/n Heterojunction Arrays for Repeatable Photocurrent Switching

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Development of materials for efficient photoenergy conversion is a subject of critical importance in current science and technology,[1] and where the use of organic materials becomes significant because of their structural flexibility and freedom of molecular design. Efficient materials performance requires controlled segregation of electron donor/acceptor moieties so that dimensions of components should be tailored for integration into devices. Although small molecular donor−acceptor dyads have been extensively studied in solution state or at surfaces,[2] donor/acceptor segregation cannot always be obtained. In contrast, block copolymers composed of appropriate segments often undergo molecular level phase segregation.[3] Therefore, dyads containing *polymeric* donors and acceptors might promote distinct donor/acceptor domain segregation, resulting in materials ideal for photoenergy conversion.[4] In this work, we prepared dimension-tailorable nanowires which undergo domain segregation by self-assembly. Films of the resulting 1D nanowires exhibit remarkably high charge mobility and can be fabricated by simple drop-casting into a device structure which allows persistent sequential photocurrent switching.

Block copolymers (**P1**−**P6**, in Figure 1) bearing both photoactive donor porphyrin (**D1** or **D2**) and acceptor fullerene (C_{60}) (**A1**, **A2**, or **A3**) units were synthesized using living ring-opening metathesis polymerization (ROMP).[5,6] ^{1}H NMR spectroscopy indicates the rigidity of the polymer backbone.[6]

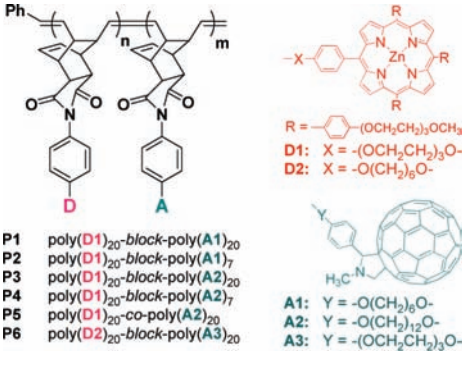

Figure 1. Structures of the investigated donor−acceptor copolymers.

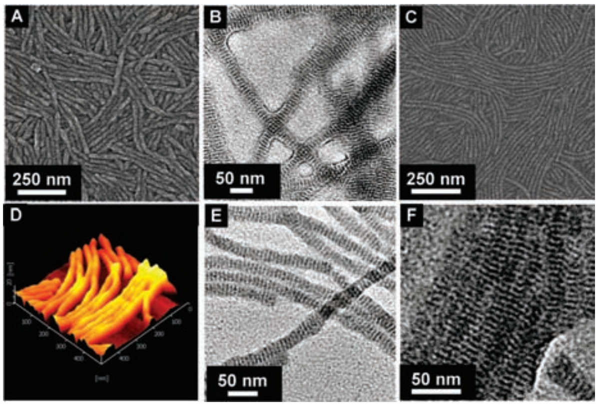

Figure 2. (A and B) SEM and TEM images respectively of **P1** nanowires dropcast from $CHCl_3$ solution. (C) SEM image of **P2** nanowires. (D and E) 3D-AFM and TEM images respectively of **P3** nanowires. (F) TEM image of **P3** nanowires with mutually aligned internal domains.

Remarkably, nanowire-like 1D nanostructures were formed by spin-coating or drop-casting their chloroform solutions onto silicon, mica, glass, or highly oriented pyrolitic graphite (HOPG) surfaces (**P1**, Figure 2A). The nanowires consist of regularly alternating domains arranged perpendicular to their long axes as shown by transmission electron microscopy (TEM) (**P1**, Figure 2B). The periodicity of this internal organization was confirmed by in-plane XRD analysis[6] where a domain width of 5.38 nm agrees well with the TEM images (5.45 nm width). Similar 1D nanostructures with a smaller 11 nm diameter were obtained by drop-casting a chloroform solution of **P2** (Figure 2C), while the spacing of the internal domains is similar (5.36 nm) to that of **P1**. **P3** and **P4**, containing the hydrophobic monomer **A2**, in which the fullerene unit is appended using a long C_{12} alkyl spacer, also gave homogeneous nanowires (**P3**, Figure 2D) but with a larger spacing of 6.24 nm between the internal domains (Figure 2E).[6] The diameter of the nanowires appears to be determined by the length of the copolymer chain while the width of the polymer building block defines the internal domain size. The random copolymer **P5** gave only an amorphous film by drop-casting.[6] Exchanging the respective chromophore spacers in **P1** (giving **P6**) led to spherical nano-objects with homogeneous dimensions.[6] Nanowires of 16 or 11 nm diameters were separately formed in films cast from a 1:1 mixture of **P1** and **P2**. Also, a 1:1 mixture of **P1** and **P3** provided separate nanowires with internal domains of 5.38 or 6.24 nm with no nanowires containing a mixture of both nanosized domains.[6] The current structural model entails block copolymers assembling into disks with porphyrins/fullerenes segregated respectively above/below the disks' planes due to their amphiphilicity. These disks further stack into fiber structures through self-recognition similar to that observed previously for other amphiphilic block copolymers.[7] High contrast in the TEM images is due to amphiphilic segregation of the chromophoric groups within the 1D nanostructures with dark

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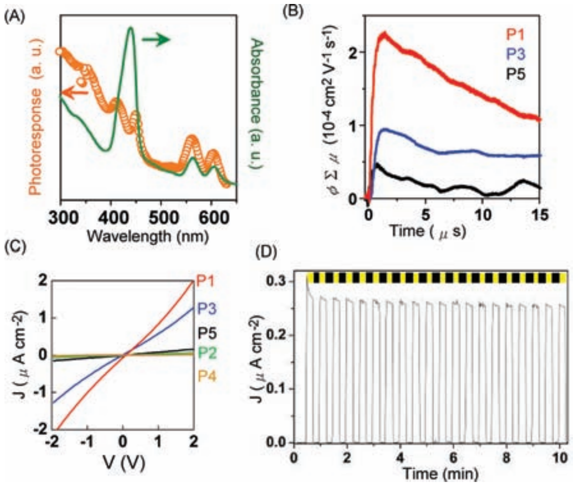

Figure 3. (A) Electronic absorption spectrum and photocurrent action spectrum of a cast film of **P1** nanowires. (B) FP-TRMC profiles for **P1** nanowires, **P3** nanowires, and amorphous **P5** deposit; (C) Current density−voltage profiles of a cast film of **P1**−**P4** nanowires and **P5** polymer (photoirradiation at 550 nm). (D) Changes in electric current density of a cast film of **P1** nanowires in response to on (yellow) or off (black) white light irradiation. The applied power density and voltage were 20 mW·cm^{-2} and +0.5 V, respectively.

regions due to fullerene-rich domains. Self-recognition properties of different polymers account for their separation during fiber formation from solutions containing two different polymers. Self-assembly processes of the wires continue when the fibers are deposited out of solution (onto TEM grid or electrode substrates). Nanowires cast from solution tend to aggregate with internal domains also aligned between them (Figure 2F).

Overlaps in the electronic and photoaction spectra of **P1** nanowires (Figure 3A) indicate that photoactivity is due to excitation of the porphyrins while quenching of the porphyrin fluorescence emission in nanostructured films of **P1** and **P3** by 77 and 72%, respectively, relative to the porphyrin only homopolymer[6] suggests strongly that photoinduced electron transfer from porphyrins to C_{60} moieties occurs.[4k] Also, UV−vis spectra confirm a lack of aggregative electronic interactions between porphyrins and fullerenes in nanostructured **P1** and **P3**.[6] Thus we believe that each nanowire is formed from orderly stacked supramolecular p/n heterojunctions (which are further ordered between fibers when deposited on a substrate; see Figure 2F). Flash photolysis time-resolved microwave conductivity (FP-TRMC) upon excitation with a 355-nm laser pulse provided overall conductivity $(\Phi\Sigma\mu)$ as high as 6.4×10^{-4} cm^2 V^{-1} s^{-1} for the **P1** nanowires, a response double in magnitude to that of the **P3** nanowires, while conductivity from deposited **P5** was remarkably 1 order of magnitude weaker (Figure 3B). An overall charge mobility as high as 0.26 cm^2 V^{-1} s^{-1} was calculated for **P1** nanowires, more than 1 order of magnitude larger than **P3** nanowires (0.01 cm^2 V^{-1} s^{-1}). Mobilities are in the range of those often obtained for highly ordered columnar assemblies of organic discotic materials.[8] Figure 3C shows the current density−voltage characteristics of films of **P1** and **P3** nanowires and **P5** film. These characteristics of the **P1** (and **P3**) nanowire films led to the observation of persistent photocurrent switching with sharp on/off responses upon alternating white light irradiation and darkness for nanowires of **P1** assembled on gold gap electrodes (1-μm spaced and 1-mm long) (Figure 3D).

Ambipolar charge transport in nanostructured films of **P1** and **P3** characterized by the current-mode time-of-flight (TOF) technique revealed a similarity in their electron mobilities ($\sim 3 \times 10^{-3}$ cm^2 V^{-1} s^{-1}) but a considerable difference in hole mobility (**P1**, 3.7×10^{-2} cm^2 V^{-1} s^{-1}; **P3**, 3.7×10^{-3} cm^2 V^{-1} s^{-1}) at an electric field of 4×10^4 V m^{-1}.[6] Packing state or spacer identity might be responsible for differences in hole mobility. It is important to note that, while it is likely that charge carriers are generated at the nanosized interface between porphyrin and fullerene domains through photoinduced electron transfer from porphyrins to fullerenes,[4k] these charge carriers should result in a photocurrent by their propagation through *interwire* carrier transfer between domains of similar chromophores rather than by moving along the 1D nanowires. This can only be permitted by the close alignment of domains between chromophores and suggests a method for improving our device properties by better aligning the fibers. Thus, our results illustrate the close relationship that exists between charge carrier mobility and nanostructure design.[9]

In conclusion, we have fabricated photoconductive films of domain-segregated self-assembled nanowires with tailorable dimensions from block copolymers appended with hydrophilic porphyrin donor and fullerene acceptor side chains. These 1D nanostructured organic materials are interesting candidates for applications in photovoltaic or electronic devices and provide insight into the preparation of functional organic materials.

Acknowledgment. This work was in part financed by the World Premier International Research Center (WPI) Initiative on Materials Nanoarchitectonics and the Nanotechnology Network Project, MEXT, Japan. We thank Dr. Toshifumi Satoh at Hokkaido University for performing the SEC analysis.

Supporting Information Available: Synthetic details and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA907414Z