

Photoinduced Charge Separation and Charge Transport in Carbon Nanostructure-based Devices

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Organic materials have attracted much attention due to their potential applications in organic electronics. In this regard, charge-transporting (CT) properties of organic thin films have found to be important in organic transistors, whereas excellent charge separation (CS) and CT properties of organic thin films are essential for organic photovoltaics (OPVs). In this talk I will present some of our examples relating to organic electronics and devices.¹⁻³

Organic/inorganic hybrid nanostructures are a new class of nanomaterials in which organic and inorganic components are integrated and exhibit unique properties that cannot be derived from the individual components or their bulk composites. In particular, research in one-dimensional (1D) organic/inorganic hybrid nanomaterials has focused on controlling the morphology of nanomaterials to generate structures with novel function and properties. However, although there are some reports of nanoscale organic/inorganic or organic/organic p-n junctions possessing unique electric and photoelectric properties, there are still challenges in connecting 1D organic/inorganic nanomaterials in a controllable and functional manner. We have developed the first example of p-n double-cable polymer nanorods that exhibit photoconductivity.² We used ordered anodic aluminum oxide (AAO) templates and chose 3-hexylthiophene (3HT) and C₆₀, as our p-type and n-type organic components, respectively. To achieve the formation of a “bulk heterojunction (BHJ)” nanorod composed of 3HT and C₆₀, thiophene tethered to C₆₀ (TC₆₀) was prepared and copolymerized with 3HT to yield the corresponding copolymer exhibiting the covalent incorporation of C₆₀ into the thiophene polymer (denoted P(3HT+TC₆₀)). In a typical experiment, segmented metal-polymer-metal nanorods were synthesized by electrochemical deposition of gold into an AAO template, followed by electrochemical copolymerization of 3HT and TC₆₀ with a molar ratio of 4:1 (weight ratio of thiophene:C₆₀ unit \approx 1:1) and final electrochemical deposition of gold (denoted Au/P(3HT+TC₆₀)/Au). The Au segments were introduced to create electrical connections between the P(3HT+TC₆₀) segments and Au microelectrode. We expected that illumination of the Au/P(3HT+TC₆₀)/Au nanorod would lead to CS within the P(3HT+TC₆₀) segment and subsequent hole and electron transport to the respective Au segments of the rod to which external bias voltage was applied. An analogous three-segment nanorod without TC₆₀ (denoted Au/P3HT/Au) was also prepared as a

control using similar conditions. The photoelectric properties of the Au/P(3HT+TC₆₀)/Au and Au/P3HT/Au nanorods were probed by current (*I*) versus bias voltage (*V*) measurements. Single nanorod devices were prepared by depositing multicomponent nanorods on top of a microelectrode array. The *I-V* curve of an individual Au/P(3HT+TC₆₀)/Au nanorod shows that the nanorods are highly insulating in the dark with resistivity of 1.2×10^5 W•cm. However when illuminated, a photoresponse is detected along with an increase in bias voltage. In this case, a typical *I-V* curve shows that the Au/P(3HT+TC₆₀)/Au nanorod serves as a semiconductor with a resistivity of 8.4×10^3 W•cm. On the other hand, the Au/P3HT/Au nanorods are highly insulating both in the dark (1.6×10^5 W•cm) and under illumination (1.2×10^5 W•cm). These results therefore show that the p-n double-cable structure contributes to the enhanced photoconductivity of the hybrid nanostructure.

Recently liquid crystals (LCs) have drawn much attention as a promising type of molecular semiconductor because of the potential utility in organic electronics including organic thin-film transistors, organic light-emitting diodes, and OPVs. Disc-like molecules functionalized with alkyl groups self-assemble into supramolecular 1D columns that further self-organize into hexagonal, rectangular, and nematic phases as discotic liquid crystals (DLCs). Hierarchical self-assembly from simple disc-like molecules to DLCs through the formation of 1D columns is a highly appealing strategy to organize donor-acceptor (D-A) molecules, i.e., forming p-n heterojunction structures exhibiting ambipolar CT properties and efficient photocurrent generation. Herein we report the synthesis and LC and CT properties of a zinc phthalocyanine (ZnPc)-C₆₀ dyad. Six 4-dodecyloxyphenoxy groups were introduced into the periphery of the central core to form discotic columnar structure of the ZnPc. C₆₀ was also tethered to the ZnPc core via a short semiflexible bridge. As expected, due to the strong π - π interaction between the C₆₀ molecules and the covalent linkage, the C₆₀ molecules were arranged successively along the ZnPc 1D column, leading to D-A bicontinuous structure in the LCs. The D-A heterojunction structure of ZnP-C₆₀ molecules was found to exhibit highly efficient ambipolar CT properties. Such relationship between the LC structures and CT properties will provide basic and fundamental information on the rational design of high-performance LC materials in organic electronics.

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