# Understanding and Promoting Molecular Interactions and Charge Transfer in Dye-Mediated Hybrid Photovoltaic Materials

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# Supporting Information



ABSTRACT: The performances of hybrid organic-inorganic photovoltaics composed of conjugated polymers and metal oxides are generally limited by poor electronic coupling at hybrid interfaces. In this study, physicochemical interactions and bonding at the organic-inorganic interfaces are promoted by incorporating organoruthenium dye molecules into self-assembled mesostructured conjugated polymer-titania composites. These materials are synthesized from solution in the presence of surfactant structure-directing agents (SDA) that solubilize and direct the nanoscale compositions and structures of the conjugated polymer, dye, and inorganic precursor species. Judicious selection of the SDA and dye species, in particular, exploits interactions that direct the dye species to the inorganic-organic interfaces, leading to significantly enhanced electronic coupling, as well as increased photoabsorption efficiency. This is demonstrated for the hydrophilic organoruthenium dye N3, used in conjunction with alkyleneoxide triblock copolymer SDA, polythiophene conjugated polymer, and titania species, in which the N3 dye species are localized in molecular proximity to and interact strongly with the titania framework, as established by solid-state NMR spectroscopy. In contrast, a closely related but more hydrophobic organoruthenium dye, Z907, is shown to interact more weakly with the titania framework, yielding significantly lower photocurrent generation. The strong SDA-directed N3-TiO<sub>x</sub> interactions result in a significant reduction of the lifetime of the photoexcited state and enhanced macroscopic photocurrent generation in photovoltaic devices. This study demonstrates that multicomponent self-assembly can be harnessed for the fabrication of hierarchical materials and devices with nanoscale control of chemical compositions and surface interactions to improve photovoltaic properties.

## INTRODUCTION

In photosynthesis, plants, and organisms use dye and pigment molecules to harvest sunlight and convert solar energy to chemical energy for their growth and activities. Inspired by nature, extensive efforts in the scientific community focus on harnessing the photoexcitation of dye molecules and sequential charge transfer for renewable energy applications, including artificial photosynthesis,<sup>1,2</sup> water splitting and fuel cells,<sup>3–5</sup> and photovoltaics (PVs).<sup>6–9</sup> In photovoltaics, dye molecules or conjugated polymers can be combined with inorganic electronaccepting materials, creating a hybrid organic-inorganic material that combines solution-processability endowed by the organic donor, with the environmental, mechanical, and thermal stabilities of the inorganic acceptor. Among the numerous possible inorganic acceptors, metal oxides and, in particular, TiO<sub>2</sub>, have been widely investigated due to their low toxicities, good electron conductivities, and electron-accepting characters with respect to common organic donors.<sup>10,11</sup> Generally, organic/metal oxide PV device structures can be divided into two types: (i) dye-sensitized solar cells (DSSC), where a nanostructured porous metal oxide electrode accepts

Received: September 15, 2014 Published: September 19, 2014 excited electrons from the light-absorbing dye and an electrolyte is used for dye regeneration and hole transport; and (ii) conjugated polymer/metal oxide devices, where the polymer is both the light absorber and the hole conductor. Absorption of light by a conjugated polymer or dye molecule results in the formation of a bound electron—hole pair, an exciton. The excitonic nature of the photoexcited state requires high organic/inorganic interfacial areas to promote exciton dissociation and electron transfer from the conjugated polymer to the metal oxide.<sup>12,13</sup> Transport of the charges to the respective electrodes also requires continuity of each phase through the active layer. The combination of nanoscale phase separation with a continuous network of each phase is termed a "bulk hetero-junction" (BHJ).

BHJ-type morphologies in conjugated polymer/metal oxide films can be achieved by fabricating a nanostructured metal oxide layer, followed by infiltration of the conjugated polymer,<sup>12,14,15</sup> blending conjugated polymer with metal oxide nanoparticles,<sup>16–18</sup> or the coassembly of the conjugated polymer species with suitable metal oxide precursors.<sup>19,20</sup> Recently, we have shown that highly ordered BHJ morphologies can be achieved by incorporating various conjugated polymers from solutions containing surfactant species as structure-directing agents (SDAs) and soluble titania precursors into mesostructured TiO, nanocomposites.<sup>21-23</sup> In this methodology, the surfactant species self-assemble as the solvent evaporates, directing the formation of the cross-linking titania framework and providing a solubilizing environment for the incorporation of the relatively hydrophobic conjugated polymer. This results in a highly ordered conjugated polymer-containing mesostructured titania-SDA hybrid film.

Moreover, judicious selection of the SDA allows control over the proximity between the conjugated polymer and the TiO<sub>x</sub> framework and, hence, the charge generation efficiency.<sup>21</sup> The BHJ hybrid films are typically ~200 nm thick and absorb strongly in the visible region of the electromagnetic spectrum. Yet, most studies report poor photovoltaic performance with power conversion efficiencies below 2%.<sup>24</sup> Recent investigations have shown that one of the main reasons for the low charge generation efficiency in conjugated polymer/metal oxide PV cells is the relatively low extent of electronic coupling between the organic conjugated polymer and the inorganic metal oxide.<sup>23,25</sup> In DSSC-type materials, on the other hand, the dye and titania are strongly coupled through bridging coordination bonding, leading to the overlap of the  $\pi^*$  orbitals of the dye and the titanium 3d orbitals, which results in fast and efficient electron injection from the dye's excited state to the titania,<sup>10,26</sup> and in efficient charge generation with over 12% device efficiency.<sup>8</sup> Indeed, incident photon-to-current efficiency measurements of solid-state DSSCs using a conjugated polymer as the hole conductor have shown that the majority of photocurrent is created by dye excitation, reflecting the dye's efficient electron injection.<sup>27-29</sup> The bonding between the dye and the titania occurs via anchoring moieties, such as carboxylic acid groups, which promote electronic coupling between the dye species and the titania framework. However, in contrast to carboxylic-terminated dyes, the structures of most conjugated polymers do not yield direct covalent bonding to metal oxide frameworks.

The introduction of dye molecules into conjugated polymer/ metal oxide BHJ materials can enhance device performances, due to improved dye/metal oxide coupling, while maintaining the simplicity of polymer-based device processing and fabrication.<sup>30-32</sup> To benefit from dye integration into conjugated polymer/metal oxide BHJ materials and devices, control over the dye's location and chemical interactions is required. More specifically, the dye molecules must be directed to the hybrid inorganic-organic interface, so that dye/metal oxide interactions generate the electronic coupling necessary for harvesting the electron associated with the dye's photoexcited state. The contribution of dye molecules to the efficiency of a conjugated polymer/metal oxide device was demonstrated by Goh et al. for bilayer devices.<sup>33</sup> Depositing a monolayer of dye molecules between the TiO<sub>2</sub> and the conjugated polymer layers resulted in the enhancement of lightharvesting and suppression of charge recombination, effectively doubling device efficiency. For BHJ devices, several methodologies have been demonstrated for dye integration into conjugated polymer/metal oxide BHJ devices, including dye grafting onto  $TiO_2$  nanorods<sup>30–32,34</sup> or ZnO nanorods,<sup>35</sup> blending dye molecules into a conjugated polymer/ZnO blend,<sup>36</sup> and grafting short oligomers onto ZnO nanorods.<sup>37</sup> Although photocurrent generation was improved by using these methodologies, poor electron transport between nanoparticles or nanorods typically limits device performances.

Amphiphilic surfactants are known to direct the formation of mesostructured metal oxide materials with various structures (e.g., lamellar, hexagonal, cubic) and periodicities (2-50 nm) that can be controlled by the solution composition and processing conditions.<sup>38-40</sup> Mesostructured thin films are deposited from precursor solutions that contain a soluble metal oxide precursor, surfactant (SDA), conjugated polymer, and dye species that coassemble into liquid crystalline-like mesophases as volatile solvent species evaporate and the metal oxide network cross-links.<sup>41,42</sup> The coassembly of dye guest molecules within SDA-directed mesostructured films is appealing for optical applications, because high dye concentrations can be included, while avoiding undesirable aggregation of the dye molecules.<sup>43,44</sup> Furthermore, incorporation of dye molecules into SDA-directed mesostructured metal oxides enables the fabrication of hybrid dye/SDA/metal oxide composites, where properties of both the dye and the metal oxide can be exploited in optoelectronic devices. In situ dye incorporation within mesostructured metal oxide materials during the self-assembly process has been used in applications such as  $asers^{45-47}$  and LEDs, <sup>48,49</sup> but to the best of our knowledge, this has not been demonstrated yet for solar cells.

In this study, we use co-self-assembly of organoruthenium dye molecules with conjugated polymer, SDA, and TiO<sub>x</sub> precursor species to form highly ordered hybrid BHJ films with increased electronic coupling at the organic-inorganic interface and improved photovoltaic properties. Importantly, we show that in addition to directing the structure of the nanocomposite BHJ material, the SDA also directs the distributions of different dye species with respect to the conjugated polymer and the TiO<sub>x</sub> framework, according to their relative hydrophobicities and hydrophilicities. The interactions between the SDA and dye functional groups can be used to direct the dye to the hybrid interface and thereby promote covalent bonding with the titania surface. The covalent bonding and intimate proximities between the dye and the TiO<sub>x</sub> framework, as established by solid-state nuclear magnetic resonance (NMR) spectroscopy and energy-filtered transmission electron microscopy (TEM; see below), are reflected in photoluminescence lifetime measurements and macroscopic device performances.



Figure 1. Structural formulas of (A) the conjugated polymer, P3PBT, poly[3-(potassium-4-butanoate)thiophene-2,5-diyl], (B) the triblock copolymer Pluronic F127 structure-directing agent, (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>), (C) the N3 dye, *cis*-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II), and (D) the Z907 dye, *cis*-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarboxylato)(4,4'-dicarbo



**Figure 2.** Transmission electron micrographs of F127-directed cubic mesostructured  $TiO_x$  films containing (A) 6 wt % P3PBT with 3 wt % N3 or (B) 6 wt % P3PBT with 3 wt % Z907. Insets show 2D glancing-incidence SAXS patterns with assigned plane reflections.

# RESULTS AND DISCUSSION

Co-assembled conjugated polymer and dye-containing titaniasurfactant nanocomposite materials are shown to form hybrid bulk heterojunction films that exhibit photovoltaic properties that depend strongly on the structures and hydrophilicities of the dye and surfactant molecules. The conjugated polymer, a water-soluble polythiophene (P3PBT, Figure 1A), in combination with the metal oxide,  $TiO_x$ , have already been demonstrated to have photovoltaic properties.<sup>23</sup> The triblock copolymer Pluronic F127 (EO<sub>106</sub>PO<sub>70-</sub>EO<sub>106</sub>, Figure 1B) was chosen as the SDA because it is known to direct the deposition of a 3D cubic TiO<sub>x</sub> mesophase with continuous through-film channels that exhibit favorable contact between included conjugated polymers and the TiO<sub>x</sub> framework.<sup>21,23</sup> Two organoruthenium dyes, N3 and Z907 (Figure 1C,D) were selected for comparison, because they have both been thoroughly investigated in DSSC systems and have similar chemical structures, but with different hydrophilicities: N3 has four carboxylic moieties that render it hydrophilic, while Z907 has two carboxylic moieties and two nine-carbon atom alkyl chains that make it more hydrophobic than N3. We

hypothesize that these differences in chemical structure and hydrophilicity between the dyes will result in different interactions with the titania framework, SDA, and conjugated polymer species that will affect their relative distributions. In particular, the increased hydrophilicity of the N3 dye is expected to lead it to close proximities and stronger interactions with the titania framework that will be manifested by increased photocurrent generation.

**Coassembly of SDA-Directed Mesostructured TiO**<sub>x</sub>-**Dye-Conjugated Polymer Films.** Self-assembly of the mesostructured hybrid films occurs from isotropic micellar precursor solutions that contain the titania precursor species, the SDA, and the photoresponsive dye molecules and/or conjugated polymers. During dip-coating, solvent evaporation induces SDA self-assembly into liquid-crystal-like mesophases concurrently with titania condensation. The organic optical materials are hence incorporated into the SDA-directed mesostructured TiO<sub>x</sub> during its formation.<sup>21–23</sup> The relatively slow rate of the condensation of the TiO<sub>x</sub> allows the structuredirecting F127 triblock copolymer species to self-assemble into ordered mesophases before the TiO<sub>x</sub> condensation is

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completed. During this time, the N3 and P3PBT species are expected to retain sufficient local molecular mobilities to partition and adsorb to the  $\text{TiO}_{x}$ , leading to the surface compositions and interactions of these species that are established by the scattering and spectroscopic analyses below. Previous studies of dye-incorporated metal oxide nanocomposites have shown that coassembly of up to 1 wt % dye molecules in the precursor solution does not alter the overall extent and type of mesostructural ordering.<sup>46,47,50</sup> For solar cell applications, much higher contents of photoresponsive components are required to absorb a significant fraction of the incident solar radiation. Consequently, it is advantageous to incorporate dye molecules in much higher concentrations, which we demonstrate up to 15 wt %, together with up to 6 wt % conjugated polymer.

Interestingly, despite high loading of both conjugated polymer and dye molecules, cubic mesostructural order is maintained, with only a minor decrease in the degree of order, as evidenced by the 2D glancing-incidence SAXS (GISAXS) patterns and transmission electron microscopy (TEM) images of F127-directed TiO<sub>x</sub>-P3PBT-N3 and TiO<sub>x</sub>-P3PBT-Z907 films shown in Figure 2. Both GISAXS patterns acquired from F127-directed mesostructured titania films with 6 wt % P3PBT and 3 wt % N3 dye (Figure 2A, inset), or with 6 wt % P3PBT and 5 wt % Z907 dye (Figure 2B, inset), exhibit intense spots that are assigned to the (110), (101), and (110)reflections of a distorted body-centered cubic structure (*Im3m*), with the (110) plane parallel to the substrate surface.<sup>41,51</sup> The lattice parameters calculated from the GISAXS patterns are 17.2  $\pm$  0.5 nm for the F127-directed TiO<sub>x</sub>-P3PBT-N3 film and 16.9  $\pm$  0.5 nm for the F127-directed TiO<sub>x</sub>-P3PBT-Z907 film. Furthermore, these values are similar to those obtained for F127-directed cubic TiO<sub>x</sub> nanocomposite films synthesized under the same conditions, but without incorporation of photoresponsive guest species (16.6  $\pm$  0.5 nm, Supporting Information, Figure S1), and are in good agreement with previous studies of SDA-directed TiOx-conjugated polymer films.<sup>21,23</sup> The cubic-like mesostructural order of F127-directed titania films containing conjugated polymer and N3 or Z907 dye molecules is similarly observed in TEM images, as shown in Figure 2A and B, respectively. In the micrographs, the gray regions are associated with scattering from the TiO<sub>x</sub> frameworks, and the light regions are from the weakly scattering organic regions. Highly ordered cubic mesostructured regions are observed, with  $11.0 \pm 0.3$  nm between the centers of the gray organic regions, corresponding to a cubic lattice viewed along the (110) plane, with a lattice parameter of  $15.6 \pm 0.3$ nm. The slightly lower lattice parameters obtained from the TEM images, compared with those obtained from SAXS, are consistent with modest contraction of the TiO<sub>x</sub> framework under the intense electron beam and from tilting and focusing effects associated with the TEM analyses.<sup>41</sup> These results indicate the incorporation of relatively high concentrations of photoresponsive guests within the SDA-directed cubic mesostructured titania films.

During preparation of thin films by dip-coating, both the conjugated polymer and dye molecules were incorporated into the mesostructured titania-F127 films, as evidenced by UV–vis absorption spectra. For example, Figure 3A,B shows the optical absorption spectrum of a F127-directed mesostructured titania film containing 6 wt % P3PBT (black ×, Figure 3A), which is centered at 506 nm with no additional features, as typical of incorporated P3PBT.<sup>23</sup> The reflectance spectrum of the same



Figure 3. UV-visible absorption spectra of 200 nm thick F127directed mesostructured titania films containing (A) 6 wt % P3PBT (black  $\times$ ), 5 wt % N3 (orange triangles), or 6 wt % P3PBT together with 3 wt % N3 (red circles) and (B) 6 wt % P3PBT (black  $\times$ ), 6.6 wt % Z907 (light blue triangles), or 6 wt % P3PBT together with 3 wt % Z907 (blue circles).

sample (Supporting Information, Figure S2) shows that, although ~10% of the photons are scattered, the scattering intensity is nearly constant in the visible hence does not affect the absorption measurements. When only N3 molecules are incorporated (orange triangles, Figure 3A), the absorption spectrum exhibits the two  $t_2 \rightarrow \pi^*$  metal-to-ligand charge transfer (MLCT) bands centered at 410 and 546 nm that are typical for N3.<sup>52</sup> The inclusion of both photoresponsive P3PBT and N3 species in a F127-directed mesostructured TiO<sub>x</sub> film yields an absorption spectrum (red circles, Figure 3A) with distinct P3PBT and N3 bands and comparable intensities that reflect their similar contents in the films. Furthermore, the overall absorption of the film with both photoresponsive species is substantially higher, compared to those of the films with comparable film thicknesses, but containing the N3 dye or P3PBT species alone.

Similarly, the amphiphilic dye Z907, with its two long alkyl chains, is also easily incorporated into F127-directed meso-structured titania composites. The absorption spectrum of F127-directed titania containing 6 wt % Z907 (light blue triangles, Figure 3B) exhibits the two  $t_2 \rightarrow \pi^*$  MLCT bands



**Figure 4.** High-resolution cross-sectional TEM images of a 1  $\mu$ m F127-directed mesostructured TiO<sub>x</sub> films containing 15 wt % N3 (A, D), and corresponding energy-filtered TEM images of the same sample region using the sulfur  $L_{2,3}$  edge transition (165 eV; B, E). For clarity, an overlay of (A, D) and (B, E) is presented in (C, F), respectively, where titanium-rich regions are red and sulfur-rich regions are blue. The scale bar corresponds to 50 nm.

centered at 434 and 555 nm that are typical of Z907.<sup>53</sup> When both P3PBT and Z907 are incorporated together (blue circles, Figure 3B), a broad absorption spectrum centered at 512 nm is obtained, consistent with collective incorporation of the P3PBT and Z907 into the film. Here too, the absorption of the film with both electron-donating species is substantially higher than that of the films incorporating only one of the photoresponsive guests, while the thickness is only slightly increased. Thus, for the synthesis conditions used here, coassembly resulted in films with relatively high concentrations of photoresponsive guest species and enhanced light absorption properties.

Distributions of Guest Species in F127-Directed TiO<sub>v</sub>-Dye-Conjugated Polymer Films. In hybrid photovoltaic films, exciton dissociation and electron-transfer processes that occur at the donor/acceptor interfaces are critical to device performance. We hypothesize that macroscale photocurrent outputs in these BHJ materials can be understood and improved by measuring and correlating the molecular-level compositions and structures at their respective inorganicorganic interfaces. In this study, the interactions and distributions of the conjugated polymer, dye, SDA, and  $TiO_x$ framework species are established by using the complementary techniques of energy-filtered TEM (EF-TEM) and solid-state 2D NMR spectroscopy. In EF-TEM, elementally distinct signals are measured and spatially resolved to sub-eV-resolution by electron energy loss spectroscopy (EELS), providing a nanoscale distribution map of the elements within a material. Sulfur atoms, for example, have a strong EELS signature centered at 165 eV, corresponding to the  $L_{2/3}$  loss edge, and hence can be used to map the distribution of the sulfur-bearing conjugated polymer or dye guest molecules in the mesostructured films. To increase the signal-to-noise ratio in the elemental map, high dye loadings (15 wt %) were incorporated

into the titania nanocomposite, and the film was thinly crosssectioned (<50 nm) using a focused-ion-beam (FIB). Brightfield TEM micrographs of a F127-directed mesostructured titania film containing 15 wt % N3 dye are shown in low and high magnification in Figure 4A and D, respectively, where the gray regions are from the highly scattering  $TiO_x$  framework, and the bright spots are from the weakly scattering organic domains. Notably, the high dye loading led to an increase in film thickness, due in part to the higher viscosity of the precursor solution, though the highly ordered cubic mesostructure was maintained. The EF-TEM images of the same area and same magnification in Figure 4B,E, show bright, that is, sulfur-containing, spots that are associated with the organic regions and appear to be well distributed across the vertical dimension of the film. As N3 is the only sulfur-containing component in this film, the spatial distribution of the sulfur reflects the location of the N3 molecules in the nanocomposite. The N3 dye distribution relative to the  $TiO_x$  framework is analyzed by overlaying the sulfur elemental maps and the bright-field images, as shown in Figure 4C,F, where, for clarity, the titanium-rich regions are indicated in red and sulfur-rich regions in blue. This analysis clearly shows that the N3 dye molecules are incorporated within the SDA domains. The highmagnification sulfur elemental map (Figure 4E) further reveals that the N3 molecules appear to be distributed in the SDA domains, providing evidence for N3 incorporation into both the hydrophilic PEO-corona and hydrophobic PPO-core regions of the F127-filled mesochannels. Similar results (not shown here) establish that the Z907 dye species are also incorporated into the SDA domains of F127-directed TiOx/ Z907 films. Previously reported EF-TEM analyses of P3PBT incorporated into F127-directed mesostructured TiO<sub>x</sub> showed that, like the N3 and Z907 dyes, P3PBT is incorporated into



**Figure 5.** Aromatic regions of the solid-state 1D  ${}^{13}C{}^{1}H$  CPMAS spectra (left) and schematic diagrams (right) of (A) N3 dye adsorbed on TiO<sub>2</sub> nanoparticles, (B) 9 wt % N3 dye within a mesostructured TiO<sub>x</sub>-F127 host, and (C) 9 wt % Z907 dye within a mesostructured TiO<sub>x</sub>-F127 host. The spectra were acquired at room temperature and at 12.5 kHz MAS with a 2 ms contact time. In (A) and (B), a  ${}^{13}C$  signal at 169 ppm is observed that is indicative of N3 carboxylic acid groups strongly adsorbed to the TiO<sub>x</sub> surface, as depicted in the accompanying schematic diagrams. In (C), narrower signals are observed, indicating that the more hydrophobic Z907 molecules interact significantly less strongly than the hydrophilic N3 dyes with the TiO<sub>x</sub> framework, as depicted in the schematic.

the SDA domains, which form an interconnected organic network through the film.<sup>23</sup> The EF-TEM analyses of F127directed mesostructured  $\text{TiO}_x$  containing N3, Z907, or P3PBT, thus, suggest that both types of dye and the conjugated polymer molecules form nanoscale-separated regions of donor-acceptor species that are governed by their interactions with the SDA species and each other during self-assembly.

**Dye-TiO<sub>x</sub> Distributions.** Efficient photocurrent generation in hybrid PV materials requires not only spatial proximity between the organic electron-donor and inorganic electronacceptor species, but also electronic coupling at their mutual organic-inorganic interface. Indeed, it has been established that the efficiency of electron injection from the photoexcited dye to titania in DSSC is nearly unity, due to the electronic coupling endowed by anchoring the dye to the titania surface.<sup>26,54,5</sup> Therefore, in addition to promoting distribution of the dye species in the SDA domains near the TiO<sub>r</sub> framework, dye adsorption or interactions with the TiO, framework surface during coassembly is desired. Such adsorption of N3 or Z907 dye molecules at the TiO<sub>x</sub> surface can be achieved through bridging coordination involving two carboxylic acid groups.<sup>2</sup> Fourier transform IR (FTIR) spectroscopy is often used to establish the bonding interactions between dye molecules and metal oxides, though here, the FTIR bands of the F127 SDA, the  $TiO_{xy}$  and those of the dye species in the region of the

carboxylic groups (~1500-1700 cm<sup>-1</sup>) overlap and thus preclude meaningful FTIR analysis. Alternatively, solid-state NMR is a powerful method for characterizing and identifying interactions and bonding between molecular species, including dye-titania interactions.<sup>56</sup> For example, a 1D  $^{13}C{^1H}$  CPMAS NMR spectrum is shown in Figure 5A for standard 22 nm diameter titania nanoparticles with adsorbed N3 molecules, similar to those used in DSSCs. This spectrum exhibits similar signals to those in a solution-state <sup>13</sup>C NMR spectrum of N3 in perdeuterated methanol (peak positions reported in the Experimental Section). The signals are also similar to those in the solid-state <sup>13</sup>C{<sup>1</sup>H} CPMAS spectrum of F127-directed mesostructured TiO<sub>x</sub>-N3 (Figure 5B), although as expected, there is increased inhomogeneous broadening, due to a distribution of local N3 adsorption environments, as well as contributions from <sup>1</sup>H-<sup>1</sup>H dipole-dipole couplings. The <sup>13</sup>C signals corresponding to the various aromatic and isothiocyanato (NCS) moieties can be mostly resolved at ca. 126, 137, 141, 153, and 159 ppm and assigned to the <sup>13</sup>C atoms labeled "3/5", "8", "4", "6", and "2", respectively, in the schematic diagram of Figure 5A, right. As these moieties do not form covalent bonds directly to the titania surface, they are not strongly affected by adsorption on the surface, as manifested by their unchanged isotropic <sup>13</sup>C chemical shifts. In contrast to these <sup>13</sup>C moieties, the carboxylic acid groups interact via



**Figure 6.** Solid-state 2D <sup>13</sup>C{<sup>1</sup>H} dipolar-mediated heteronuclear correlation (HETCOR) NMR spectrum acquired at room temperature over 60 h for mesostructured TiO<sub>x</sub>-F127 containing 9 wt % N3 under MAS conditions of 12.5 kHz, with a 2 ms CP contact time. 1D <sup>13</sup>C{<sup>1</sup>H} CPMAS and single-pulse <sup>1</sup>H MAS spectra are shown along the top horizontal axis and the left vertical axis, respectively. Correlated 2D signals associated with the triblock copolymer F127, TiO<sub>x</sub> surface, and N3 dye species are resolved. The structure of the N3 dye is shown in the upper left with its various carbon moieties labeled. The schematic diagram in the upper right depicts the relative distributions of N3 molecules within a single F127-directed TiO<sub>x</sub> mesochannel, as viewed along the (*111*) axis of a cubic structure, and the dye's interaction with the titania framework, which are consistent with the NMR and EF-TEM results. N3 molecules are dispersed in the mesochannels such that they interact with PEO (blue) and PPO (yellow) segments predominantly.

electrostatic or hydrogen-bonding interactions at the titania surface, such that several new <sup>13</sup>C signals are observed between 166 and 171 ppm in the region that is typical for carboxylate moieties. The most intense signal at 167 ppm, which is also observed in the solution-state <sup>13</sup>C NMR spectrum (see Experimental Section), corresponds to protonated carboxylic groups that are not directly bound to the titania surface. Notably, however, there is additional <sup>13</sup>C signal intensity at 169-170 ppm that is not observed in the solution-state spectrum and does not correspond to a deprotonated carboxylate group (which would yield a signal at ca. 173 ppm<sup>26,57</sup>). This additional peak and its displacement by about 2 ppm from the solution value are similar to recent observations reported for carboxylic acid moieties of similar dye molecules adsorbed on TiO<sub>2</sub> nanoparticles.<sup>56</sup> The signal intensity at 169-170 ppm is thus attributed to carboxylic moieties adsorbed at the titania nanoparticle surfaces.

The aromatic region of the 1D  ${}^{13}C{}^{1}H$  CPMAS spectrum in Figure 5B corresponds to the N3 dye species incorporated in mesostructured F127-TiO<sub>x</sub> and has similar spectral features to the N3 dye adsorbed on the titania nanoparticles (Figure 5A). Importantly, the broad signal at about 170 ppm corresponding to surface-bound carboxylate moieties, reflects a distribution of local adsorption environments and low dye mobility at the disordered titania surface; similarly broad  ${}^{13}C$  and  ${}^{1}H$  signals are observed for the N3 dye moieties in both the mesostructured composite and on the titania nanoparticles (Figure 5A). A <sup>13</sup>C{<sup>1</sup>H} CPMAS spectrum acquired for a cubic mesostructured F127-TiO<sub>x</sub> composite containing 9 wt % of both the N3 dye and the P3PBT (Supporting Information, Figure S3) similarly exhibits significant <sup>13</sup>C signal intensity at 169-170 ppm, indicating that the N3 dye species adsorb on titania also in the presence of the conjugated polymer species. A schematic diagram is shown (Figure 5B, right) that depicts the adsorption of N3 carboxylic acid moieties at the titania surface of a single F127-TiO<sub>x</sub> mesochannel. While the EFTEM results in Figure 4 show selective partitioning of the N3 molecules into the organic domains, the 1D <sup>13</sup>C CPMAS NMR results indicate that a substantial fraction of those N3 molecules are also in close proximity to and interact strongly with the  $TiO_x$ framework, where they can facilitate charge transfer from the dye and conjugated polymer species to the  $TiO_x$ .

Compared to the hydrophilic N3 dye species, however, the more hydrophobic organoruthenium dye Z907 is distributed significantly differently in an otherwise identical F127-directed TiO<sub>x</sub> film. The molecular structure of Z907 is similar to that of the N3 dye, except for the substitution of two carboxylic acid groups with nine-carbon alkyl chains, which make the Z907 molecules significantly more hydrophobic and bulkier than the N3 dye. Figure SC shows the aromatic region of a 1D  $^{13}C{^1H}$ 

CPMAS spectrum acquired for a F127-directed mesostructured TiO<sub>x</sub> film containing 9 wt % Z907, which exhibits several key differences from that of the N3-containing film in Figure 5B. Specifically, many of the <sup>13</sup>C signals for the Z907 dye (Figure 5C) are significantly narrower than those for the N3 species (Figure 5B), indicating that a substantial fraction of the Z907 dye species are in more uniform averaged local environments, consistent with greater molecular mobility and weaker interactions with the titania framework. This allows for the partial resolution of additional <sup>13</sup>C signals present at 160, 156, and 130 ppm that can be assigned to <sup>13</sup>C atoms "2\*", "6\*", and "3\*/5\*", respectively, which reflect the lower molecular symmetry of the Z907 molecule. This is in contrast to the F127-directed TiO<sub>x</sub>-N3 composite, where the breadths of the <sup>13</sup>C signals indicate that a significant fraction of N3 molecules are adsorbed at the  $TiO_x$  surfaces. Also, in the spectrum of the F127-directed TiO<sub>x</sub>-Z907 film material, two sharp <sup>13</sup>C signals are observed at 168 and 172 ppm, denoted as 7 and 7", respectively, which are assigned to protonated and deprotonated carboxylic acid groups, respectively, based on a solutionstate <sup>13</sup>C NMR spectrum (see Experimental Section). Only weak signal intensity is evident at 169-170 ppm from carboxylic acid moieties directly bound to TiO<sub>x</sub>, which together with the strong and relatively narrow signals at 168 and 172 ppm, indicate that the majority of Z907 dye molecules do not adsorb or interact strongly with the titania framework. The schematic diagram shown in Figure 5C (right) depicts Z907 dye molecules near but not interacting strongly with the titania surfaces of a single F127-TiO<sub>x</sub> mesochannel, consistent with the NMR results.

Molecular Interactions and Compositions near the Organic-Titania Interfaces. Detailed insights into the local compositions and molecular distributions of the guest species within the mesostructured composites can be obtained by using solid-state NMR to probe their mutual proximities. 2D heteronuclear correlation (HETCOR) NMR techniques, in particular, correlate the chemical shifts of molecularly proximate <sup>13</sup>C and <sup>1</sup>H nuclei through their heteronuclear dipole-dipole couplings. Specifically, 2D <sup>13</sup>C{<sup>1</sup>H} HETCOR spectra allow signals associated with the various <sup>1</sup>H and <sup>13</sup>C nuclei of the dye and conjugated polymer guests and triblock copolymer species to be resolved and correlated. This provides information about the relative distributions of the various moieties. For example, a 2D <sup>13</sup>C{<sup>1</sup>H} HETCOR spectrum acquired at room temperature for a cubic mesostructured F127directed TiO<sub>x</sub>-N3 nanocomposite containing 9 wt % N3 is shown in Figure 6. 1D single-pulse <sup>1</sup>H MAS and 1D  $^{13}C{^{1}H}$ CPMAS spectra acquired on the same material are shown along the left vertical and top horizontal axes, respectively, to aid interpretation of the 2D HETCOR spectrum. A number of strong intensity correlations are observed between the <sup>1</sup>H and <sup>13</sup>C nuclei associated with the PEO and PPO blocks of the F127 structure-directing agent. The intense <sup>13</sup>C signal at 71 ppm associated with  $-OCH_2$ - groups of the PEO is correlated with a <sup>1</sup>H signal at 3.8 ppm corresponding to their <sup>1</sup>H moieties. Similarly, the <sup>13</sup>C signals at 73 and 75 ppm associated with the -OCH<sub>2</sub>- and -OCH- moieties, respectively, of the PPO are correlated with their <sup>1</sup>H signals at 3.6 and 3.4 ppm. Finally, the <sup>1</sup>H signal at 1.1 ppm is strongly correlated with the <sup>13</sup>C signal at 18 ppm, both associated with the  $-CH_3$  groups of the PPO. The narrow (<0.5 ppm full-width-half-maximum, fwhm) line widths of the <sup>13</sup>C signals reflect the relatively high molecular

mobilities of the majority of triblock copolymer segments associated with the F127 structure-directing species at room temperature.

In addition to the signals arising from the triblock copolymer SDA species, a number of intensity correlations in Figure 6 are associated with intramolecular dye interactions. Specifically, signals at 126, 137, 141, 153, 159, and 167 ppm are assigned to the aromatic  ${}^{13}$ C nuclei of the N3 dye labeled in Figure 5 as "3/ 5", "8", "4", "6", "2", and "7", respectively. These <sup>13</sup>C signals are all correlated with <sup>1</sup>H signal intensity centered at 8.4 ppm from the aromatic or carboxylic <sup>1</sup>H nuclei, which are known to occur between 7.5 and 9.5 ppm in solution-state <sup>1</sup>H NMR spectra.<sup>57</sup> The additional broadening of the correlated intensity in the <sup>1</sup>H dimension of the 2D spectrum, compared to solution-state measurements, likely results from a distribution of local N3 environments that are not averaged on the time scale of the NMR measurement. This includes correlated 2D signal intensity observed at 169-170 ppm in the <sup>13</sup>C dimension and 8.4 ppm in the <sup>1</sup>H dimension (Figure 6, blue shading), which is attributed to carboxylic acid moieties that are bound to the titania framework.

The distribution of the dye molecules within the mesostructured F127-titania host can be established from measurements of their intermolecular interactions, as evidenced in 2D  ${}^{13}C{}^{1}H$  HETCOR spectra (Figure 6). In particular, the <sup>1</sup>H signal at ca. 8.4 ppm from the aromatic and carboxylic acid moieties of the N3 dye exhibits correlated intensity not only with the  $^{13}\mathrm{C}$  moieties of the N3 molecules, but also with the <sup>13</sup>C signals at 71 ppm from the PEO –OCH<sub>2</sub>– groups and at 73 and 75 ppm from the  $-OCH_2$  and -OCH moieties, respectively, of the PPO segments. These intensity correlations unambiguously establish that the N3 dye molecules are in close (<1 nm) proximity to both the PEO and PPO moieties of the F127 triblock copolymer SDA, a result that is consistent with the EF-TEM analysis (Figure 4). This is further supported by evidence of ring-current effects associated with the aromatic groups of the dye molecules on nearby PEO and PPO moieties. Ring currents arise from delocalized electrons in  $\pi$ -orbitals that, in large magnetic fields, can induce local fields that alter the isotropic chemical shifts of nearby <sup>1</sup>H or <sup>13</sup>C nuclei. The effects of such ring currents are highly local and depend on the distances and relative orientations of a nearby molecular moiety to the aromatic rings. In similar mesostructured materials, they have been shown to induce broadening of <sup>1</sup>H signals to lower frequencies.<sup>21,58</sup> This is similarly observed in Figure 6 for the <sup>1</sup>H signals associated with both the PEO -OCH<sub>2</sub>- and the PPO -OCH<sub>2</sub>- and -OCH- species, compared to their signals in an otherwise identical mesostructured F127-titania composite without conjugated polymer or dye species (Supporting Information, Figure S4). Furthermore, the N3 species in the PEO corona regions are expected to be in close proximity to and interact strongly with the TiO<sub>x</sub> framework, which is consistent with weak 2D intensity correlations between the <sup>13</sup>C signals from N3 carbon atoms "3/5" and "2" and the <sup>1</sup>H signal near 6.0 ppm, the region associated with TiOH (Figure 6, maroon shading). These results collectively provide corroborative evidence that the N3 dye molecules are distributed in regions of the mesochannels containing PEO and PPO blocks associated with the F127 SDA species, as depicted schematically in the inset of Figure 6 (upper right). Such a distribution of the hydrophilic N3 dye molecules is consistent with the EF-TEM and 1D NMR results, though much more detailed.



**Figure 7.** Solid-state <sup>13</sup>C dynamic-nuclear-polarization-enhanced (DNP) HETCOR NMR spectra acquired at 105 K for mesostructured  $TiO_x$ -F127 containing 9 wt % P3PBT and 9 wt % N3 under MAS conditions of 12.5 kHz, with a 1 ms CP contact time. (A) 1D <sup>13</sup>C{<sup>1</sup>H} CPMAS spectra with (red) and without (black) microwave illumination, demonstrating the enhancements achieved using DNP. (B) 2D <sup>13</sup>C{<sup>1</sup>H} dipolar-mediated DNP-HETCOR NMR spectrum acquired in 12 h under the same conditions as in (A), with a 1D <sup>13</sup>C{<sup>1</sup>H} CPMAS spectrum and a <sup>1</sup>H projection shown along the top horizontal axis and the left vertical axis, respectively. Correlated 2D signals associated with the F127 triblock copolymer, TiO<sub>x</sub> surface, N3 dye, and P3PBT species are resolved. The structures of the guest species are shown in the upper left with the various carbon moieties labeled. A schematic structural diagram is shown in the inset that depicts the relative distributions of the guest species within both the PEO (blue) and PPO (yellow) regions of a single F127-directed TiO<sub>x</sub> mesochannel, as viewed along the (*111*) axis of a cubic structure, which are consistent with the NMR and EF-TEM results.

Similar 2D  $^{13}C{^1H}$  HETCOR measurements were conducted on F127-directed cubic mesostructured titania composites containing either amphiphilic Z907 dye molecules or hydrophobic P3PBT conjugated polymer macromolecules to establish their respective interactions with the host material. The 2D NMR spectra are shown in Supporting Information (Figures S5 and S6) and exhibit similar correlated signal intensities between the guest species and triblock copolymer moieties, as well as similar ring-current influences on the latter. These allow the distributions of the Z907 dye and the P3PBT conjugated polymer also to be established within the mesostructured titania host, which in both cases are similar to the distribution observed for the N3 species. Each is distributed within the mesochannel regions, such that they are in close proximity to both the PEO and the PPO segments, which are expected to segregate at the nanoscale into principally corona and core regions, respectively, of the F127directed mesochannels. Under the conditions used here, both the PEO and PPO segments interact similarly with the different photoresponsive species and do not exert distinct structuredirecting influences on them. For the material compositions and conditions employed, the photoresponsive dyes and conjugated polymer guest species are thus distributed within the relatively hydrophobic titania mesochannels where they interact with both the PEO and PPO moieties.

As shown below for F127-TiO<sub>x</sub> materials containing both the N3 dye and P3PBT conjugated polymer, their respective interactions and spatial distributions are altered by the presence of each other. Given the challenge of applying conventional 2D NMR techniques to materials with natural <sup>13</sup>C isotopic abundances, dynamic nuclear polarization (DNP) was used to enhance the NMR signals of the relatively dilute N3 dye and P3PBT species in order to establish their mutual interactions with each other in the F127-directed TiO<sub>x</sub>-N3-P3PBT composite. In a DNP-NMR experiment, the high polarization of unpaired electrons of paramagnetic moieties is transferred to nearby NMR-active nuclei (usually <sup>1</sup>H). At high fields, this is accomplished by applying high power continuous-wave irradiation from a gyroton microwave source to saturate the transitions of the paramagnetic electron spins.<sup>59</sup> Usually unpaired electrons are introduced via stable exogenous nitroxide biradicals in an appropriate solvent.<sup>60</sup> With state-ofthe-art biradical polarizing agents and sample temperatures in the range of 80-110 K, <sup>1</sup>H DNP-NMR signal enhancements of up to 250 have been reported.<sup>61-66</sup> The resulting DNPenhanced <sup>1</sup>H polarization can then be easily transferred to heteronuclei (i.e., <sup>13</sup>C, <sup>15</sup>N, etc.) by conventional crosspolarization.

Here, DNP-NMR experiments were conducted by incipiently impregnating<sup>67</sup> 44 mg of F127-directed TiO<sub>x</sub>-N3-P3PBT material with 9  $\mu$ L of 16 mM TEKPol in 1,1,2,2-tetrachloro-ethane (TCE) solution. The TEKPol nitroxide biradical was selected, as it provides <sup>1</sup>H DNP-NMR enhancements ( $\varepsilon_{\rm H}$ ) up to 200 in bulk TCE solutions under similar experimental conditions.<sup>62</sup> As TCE and TEKPol are both hydrophobic, it is expected that the TCE swells the F127 triblock copolymer and disperses the TEKPol biradical within the mesostructured composite. With DNP, the highly polarized unpaired electrons of the TEKPoL transfer their polarization to <sup>1</sup>H nuclei of nearby (<1 nm) organic functionalities. <sup>1</sup>H–<sup>1</sup>H spin-diffusion then distributes the enhanced polarization to the exterior surfaces and into the interior mesochannels of the inorganic–organic hybrid materials.<sup>68–70</sup>

Figure 7A shows the 1D <sup>13</sup>C{<sup>1</sup>H} CPMAS spectrum acquired at 110 K of the TEKPol-impregnated cubic mesostructured F127-directed TiOx-N3-P3PBT composite containing 9 wt % P3PBT and 9 wt % N3. The <sup>13</sup>C DNP enhancements ( $\varepsilon_c$ ) for each of the different components were measured by comparing the intensities of the different <sup>13</sup>C resonances in the spectra acquired with and without microwave irradiation under otherwise identical conditions. As all of the magnetization in a <sup>13</sup>C{<sup>1</sup>H} CPMAS experiment is derived from <sup>1</sup>H nuclei, the measured values of  $\varepsilon_c$  correspond to the <sup>1</sup>H DNP-NMR enhancements for the individual components, which interestingly were different for the different moieties. Specifically, <sup>13</sup>C CPMAS DNP signal enhancements  $\varepsilon_c$  of about 3 were obtained for the N3 dye and P3PBT species, about 6 for the PEO moieties and TCE solvent, and about 12 for the PPO moieties. All of these DNP enhancements are relatively low, likely due to the relatively low bulk biradical concentration in the composite (ca. 3 mM, dilution of TEKPoL in the SDA/P3PBT/N3-filled mesochannels), high concentration of <sup>1</sup>H-containing moieties in the mesochannels), and short <sup>1</sup>H longitudinal spin-lattice  $(T_1)$  relaxation times. Keeping in mind that <sup>1</sup>H spin diffusion tends to equalize the <sup>1</sup>H polarization throughout the

sample,<sup>68–70</sup> the observation of distinct <sup>13</sup>C CPMAS DNP signal enhancements for the different species indicates that they are spatially separated. The measured DNP-NMR enhancements likely reflect the relative concentrations of TEKPol near the different species. This suggests that the TEKPol biradicals are preferentially partitioned within the mesochannels in the PPO cores ( $\varepsilon_c \sim 12$ ) and near the PEO coronas ( $\varepsilon_c \sim 6$ ). The similar DNP enhancements ( $\varepsilon_c \sim 3$ ) for the N3 dye and P3PBT species indicate that these two species are spatially proximate, with their relatively low  $\varepsilon_c$  values being consistent with locations near the TiO<sub>x</sub> surfaces and relatively distant from the PPO moieties in the mesochannel cores.

The DNP-enhanced 2D <sup>13</sup>C{<sup>1</sup>H} HETCOR spectrum in Figure 7B acquired for a cubic mesostructured F127-directed TiO<sub>x</sub> composite containing 9 wt % P3PBT and 9 wt % N3 supports these hypotheses. A number of differences are observed with respect to a conventional 2D HETCOR spectrum (Supporting Information, Figure S7). In particular, the low temperatures (110 K) required for these DNP-NMR experiments result in significant broadening of the signals and modest displacements of the <sup>1</sup>H signals of the alkyleneoxide moieties of the triblock copolymer to lower frequencies (to 2.9 ppm for the  $-OCH_2 - / -OCH -$  moieties and to 0.0 ppm for the  $-CH_3$  groups). In addition, the TCE solvent used to solubilize the TEKPol biradical contributes additional, correlated signal intensity near 6 ppm in the <sup>1</sup>H dimension and 75 ppm in the <sup>13</sup>C dimension. Partially resolved <sup>13</sup>C signals are present at 126, 140, 153, and 159 from aromatic moieties "3/5", "4/8", "6", and "2" of the N3 dye species, along with a <sup>13</sup>C shoulder at 131 ppm that may be associated with the polythiophene backbone moiety "A" of the P3PBT. Each of these aromatic <sup>13</sup>C signals exhibits an intensity correlation with the <sup>1</sup>H signal centered at about 8.7 ppm from their respective aromatic protons. Additionally, correlated signals from the P3PBT alkyl moieties "B", "C", and "D" are observed between 25-35 ppm in the <sup>13</sup>C dimension and between 0–4 ppm in the <sup>1</sup>H dimension, along with strong though broadened intensity correlations associated with the triblock copolymer SDA moieties, as labeled. These 2D intensity correlations represent intramolecular interactions that allow the signals from the otherwise similar dye and conjugated polymer moieties to be resolved and identified.

More importantly, the enhanced signal sensitivity provided by DNP-NMR allows intermolecular interactions between the N3 dye, P3PBT conjugated polymer, F127 structure-directing species, and the TiOH surface moieties to be directly measured and analyzed. For example, in the 2D <sup>13</sup>C{<sup>1</sup>H} DNP-HETCOR spectrum of Figure 7B, correlated signal intensity (maroon shading) is observed between the <sup>13</sup>C signal at 126 ppm arising from <sup>13</sup>C atoms "3" and "5" of the N3 dye and the <sup>1</sup>H signal at 6.5-7 ppm from surface TiOH moieties of the  $TiO_r$ framework. Such correlated intensity is consistent with the proximities of carbon atoms "3" and "5" to the carboxylic acid groups of the N3 dye, which are expected to have favorable interactions with the TiO<sub>x</sub> framework. (Weak correlated intensity also appears to be present in this region in the conventional 2D<sup>13</sup>C{<sup>1</sup>H} HETCOR spectrum in Figure 6, which can now be more confidently attributed.) In addition, the <sup>13</sup>C signal at 131 ppm appears to exhibit correlated intensity with the same TiOH <sup>1</sup>H signal at 6.5 ppm (Figure 7B, maroon shading). In addition, solid-state  $2D^{-1}H{}^{1}H{}$  homonuclear spin-diffusion and double-quantum correlation NMR spectra (Supporting Information, Figures S8 and S9) provide separate



**Figure 8.** Photoluminescence lifetime measurements of N3 and Z907 dyes in neat films (100 nm thick) and incorporated into mesostructured  $\text{TiO}_x$  films (200 nm thick): neat N3 film (red  $\blacktriangle$ ), neat Z907 film (blue  $\blacksquare$ ), F127-directed mesostructured  $\text{TiO}_x$  film containing 6 wt % N3 (red  $\triangle$ ), and F127-directed mesostructured  $\text{TiO}_x$  film containing 6 wt % Z907 (blue  $\Box$ ). The instrument response function is denoted by the black circles,  $\bullet$ . The excitation wavelength was 515 nm, and detection was at wavelengths above 532 nm.

and direct corroborative evidence for the proximities (<1 nm) of the aromatic protons of the N3 dye molecules, the alkyl protons of the P3PBT, and the TiOH moieties of the framework surface. A schematic diagram of the distributions of the N3 dye and P3PBT conjugated polymer species within both PEO and PPO regions and near the surface of a single titania mesochannel is shown in the inset of Figure 7B (upper right), which are consistent with the 2D NMR and EF-TEM (Figure 4) results. In summary, the distribution of the N3 dye and P3PBT species in the mesostructured composite containing both components is significantly different from that observed in otherwise identical composite materials containing only one of the individual components. The observation of similar DNP enhancements for the electrondonating N3 dye and P3PBT guest species establishes their mutual proximities (<1 nm) and their close proximities to the electron-accepting TiO<sub>x</sub> framework away from the PPO core. The intensity correlations observed in the high quality DNPenhanced 2D HETCOR spectrum are consistent with this analysis. The 2D DNP-NMR capabilities permit, for the first time, a direct and detailed investigation of dilute dye and conjugated polymer guest species with <sup>13</sup>C in natural abundance in hybrid photovoltaic materials.

Optical and Photovoltaic Properties of Mesostructured Titania-SDA-Dye-Conjugated Polymer Films. We expect that the differences in the chemical compositions and structures at the inorganic-organic interfaces of the different dye-containing materials should influence the respective efficiencies by which charge is transferred from the dyes and conjugated polymer species to the TiO<sub>x</sub>. Indeed, the different distributions of the N3 and Z907 dye species in the selforganized hybrid films and their interactions with the P3PBT conjugated polymer and  $TiO_x$  framework are manifested by their different macroscopic photoresponse properties. For example, time-resolved photoluminescence (PL) measurements are sensitive to quenching and excited-state lifetimes, which are modified by donor-acceptor interactions in the self-organized dye-mediated photovoltaic films. Importantly, there is little to no overlap between the absorption and emission spectra of

different species ensuring that energy transfer does not contribute to the photophysical processes and the PL quenching could be associated solely with charge transfer. More specifically, photoexcitation of N3 and Z907 dye molecules create metal-ligand charge transfer states with typical lifetimes of 50 and 45 ns, respectively, when measured in solution.<sup>52,71</sup> Proximity and electronic coupling of the dye species to the TiO<sub>x</sub> surfaces can induce exciton dissociation and electron transfer to the TiO<sub>x</sub> network, effectively reducing the lifetime of the excited state.<sup>72,73</sup> To analyze quantitatively the decay lifetimes, time-resolved PL spectra were measured for neat-dye and F127-directed mesostructured TiO<sub>x</sub>-SDA-dye/ conjugated polymer films, and decay curves fitted to the respective transient PL data. For the neat-dye films, a good fit was obtained with a monoexponential decay curve and the lifetime extracted from it. However, for the mesostructured TiO<sub>x</sub>-SDA films incorporated with dye, conjugated polymer, or both, a monoexponential fit was unsatisfactory, and the average emission lifetimes were analyzed using biexponential decay kinetics, as expressed by eqs 1 and 2:

$$I(t) = \sum_{i=1}^{2} A_i e^{-t/\tau_i}$$
(1)

where

$$\tau_{\rm AV} = \frac{\sum_{i=1}^{2} A_i \tau_i}{\sum_{i=1}^{2} A_i}$$
(2)

Multiexponential decay is typical for dyes adsorbed on metal oxides, due to surface defects or trapped states. This is especially true for dyes near amorphous metal oxide surfaces, similar to those present in the mesostructured F127-TiO<sub>x</sub> films.<sup>74,75</sup>

PL lifetime shortening, due to the closer proximities of dye molecules bound to or near the mesostructured titania surfaces, is clearly evident in Figure 8 and is summarized in Table 1. The PL decay curves of the neat-dye films exhibit behaviors that are typical of ruthenium-based dyes, <sup>52,72,73,76</sup> with lifetimes of 23 and 15 ns, for neat N3 (filled red triangles) and Z907 (filled

Table 1. Photoluminescence Lifetimes of 100 nm Thick Neat-Dye Films and 200 nm Thick F127-Directed Mesostructured  $TiO_x$  Films Containing Either 9 wt % N3 or Z907 Dye Molecules

layer's composition	lifetime $(\tau, ns)$	$\chi^2$
N3	23	$2.2 \times 10^{-4}$
Z907	15	$4.0 \times 10^{-4}$
TiO <sub>x</sub> -F127-N3	0.97	$5.3 \times 10^{-4}$
TiO <sub>x</sub> -F127-Z907	5.6	$1.7 \times 10^{-3}$

blue squares) films, respectively. Incorporating the dyes into F127-directed mesostructured titania films yields large differences in the PL decay behaviors for the two dyes (open symbols). For example, N3 dye species incorporated at a loading of 6 wt % exhibits more than a 20-fold decrease in its PL lifetime (down to 1 ns), relative to that of the neat N3 film. This significant decrease in the PL lifetime of the N3 dye reflects the charge transfer that takes place between photoexcited N3 molecules and the titania, consistent with their close molecular proximities and interactions, as established by the NMR analyses. On the other hand, Z907 dye species incorporated at the same loading of 6 wt % in an otherwise identical F127-directed TiO<sub>x</sub>-Z907 mesostructured film shows only a moderate decrease in PL lifetime, to 5.6 ns, indicating less efficient electron transfer from the dye to the titania, compared to that in the N3-containing film. These results are consistent with those reported by Durant et al.<sup>72</sup> and Palomares et al.,<sup>73</sup> who studied the charge transfer dynamics by measuring the PL lifetimes of ruthenium-based dyes on mesoporous TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> substrates. In particular, the dye-Al<sub>2</sub>O<sub>3</sub> films exhibited relatively long lifetimes of ~20 ns, because the excited state of the dye is below the conduction band of alumina and, therefore, no electron injection occurs. By comparison, the dye-TiO<sub>2</sub> films exhibited much faster decay kinetics, with lifetimes of usually less than 1 ns, which indicates efficient electron injection to the conduction band of the TiO<sub>2</sub> semiconductor. In the high-surface-area SDA-directed dyecontaining mesostructured titania films being analyzed here, however, the decrease in the PL lifetime of the N3 dye is

governed not by the type of electron-accepting substrate used, but rather by the proximities and interactions of the electrondonor and electron-acceptor species. The PL lifetime measurements, therefore, confirm that coassembled N3 molecules are molecularly close to and interact strongly with the mesostructured titania framework, resulting in a short PL lifetime. This is in contrast to the Z907 dye molecules, whose relatively long hydrophobic alkyl chains disfavor interactions with the polar titania surface, resulting in only a slight reduction in the measured PL lifetime in the F127-directed mesostructured Z907-TiO<sub>x</sub> composite.

Finally, photovoltaic device measurements show the effects of incorporating both conjugated polymer and dye molecules in the SDA domains of mesostructured titania, and especially demonstrate the importance of controlling the chemical composition at the donor–acceptor interfaces by judicious selection of the dye species and architecture. In organic–inorganic donor–acceptor photovoltaic devices, such as DSSCs or hybrid conjugated polymer–metal oxide solar cells, the electron transfer from the donor to the acceptor is a crucial step in photocurrent generation.<sup>10,77</sup> In the hybrid systems being examined here, both the conjugated polymer and the dye molecules can act as donors, with electron transfer from each of them to the titania acceptor being highly dependent on their molecular proximities and their electronic coupling.

Consequently, the different compositions and structures of the organic—inorganic interfaces in the N3- and Z907containing mesostructured titania PV films, as elucidated by solid-state NMR, are expected to affect the macroscopic photocurrents that they respectively generate, as manifested principally by the short-circuit current ( $J_{sc}$ ). F127-directed cubic mesostructured titania films containing P3PBT conjugated polymer and either N3 or Z907 dye species were fabricated and integrated as the active layers in photovoltaic devices, as described in the Experimental Section and as illustrated schematically in Figure 9A. The performances of photovoltaic devices, with either P3PBT alone, P3PBT-N3, or P3PBT-Z907 as the organic electron-donor species were characterized according to their current—voltage behaviors. As shown in Figure 9B and summarized in Table 2, the open-



**Figure 9.** (A) Schematic diagram of PV devices fabricated with a 200 nm F127-directed mesostructured  $TiO_x/P3PBT/Z907$  or N3 film as the active layer, and (B) Current density–voltage characteristics (*J*–*V*) measured under 1.5 AM illumination of PV devices with an active layer based on F127-directed mesostructured  $TiO_x$  films containing 6 wt % P3PBT without dyes (black ×), 6 wt % P3PBT with 3 wt % N3 (red O), or 6 wt % P3PBT without dyes (black ×), 6 wt % P3PBT with 3 wt % N3 (red O).

Table 2. Summary of Photovoltaic Characteristics of Devices Based on 200 nm Thick F127-Directed Mesostructured  $TiO_x$ Films Containing 6 wt % P3PBT without Dyes, or 6 wt % P3PBT with Either 3 wt % N3 or Z907 Dye Molecules

device active layer composition	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}~({\rm V})$	fill factor
TiO <sub>x</sub> -F127-P3PBT	0.037	0.71	0.27
TiO <sub>x</sub> -F127-P3PBT-N3	0.066	0.65	0.29
TiO <sub>x</sub> -F127-P3PBT-Z907	0.007	0.69	0.27

circuit voltage (x-axis intercept,  $V_{oc}$ ) is similar in all devices, varying over the narrow range of 0.65-0.71 V, in agreement with previously reported TiO<sub>x</sub>-P3PBT devices,<sup>23,78</sup> TiO<sub>x</sub>-N3-P3HT devices,<sup>31</sup> and TiO<sub>x</sub>-Z907-P3HT devices.<sup>30</sup> Generally in bulk heterojunction devices, the V<sub>oc</sub> depends on the donoracceptor band offset and the metal-electrode work functions,<sup>3</sup> while in DSSCs the  $V_{\rm oc}$  depends on the band offset between the electron acceptor and the hole-transporting material.<sup>79</sup> Hence, the similar  $V_{\rm oc}$  values in all three devices indicate that indeed P3PBT acts as both the electron donor and the holetransporting material in all three types of devices. In contrast to the similar  $V_{oc}$  values, the short-circuit current densities (yaxis intercept,  $J_{sc}$ ) are significantly different in the three types of devices, as evident from Figure 9B. While the magnitudes of the J<sub>sc</sub> values are low compared with other conjugated polymertitania devices,<sup>14,15</sup> due to the low donor loadings and low carrier mobilities in both the organic and amorphous inorganic regions, the trend in the  $J_{sc}$  values is nevertheless directly correlated with the molecular compositions and structures at the organic-inorganic interfaces.

The effects of dye species on the short-circuit current densities Jsc of the mesostructured P3PBT-titania hybrid films depend strongly on the type of dye incorporated. Figure 9B shows that the  $J_{sc}$  value measured for the F127-directed TiO<sub>x</sub>-P3PBT device is 0.037 mA/cm<sup>2</sup>, in good agreement with previous reports.<sup>23</sup> The  $J_{sc}$  is doubled for devices fabricated with mesostructured titania active layers containing both P3PBT and N3 donor species, while it is dramatically reduced for devices based on similar mesostructured TiO<sub>x</sub>-P3PBT-Z907 active layers. Importantly, all devices contained the same amounts of P3PBT and dye species, and the optical absorption of the films increased for both devices containing the respective dyes, relative to films containing only P3PBT (Figure 3). Hence, the significant differences in the photocurrents are correlated with the organic-inorganic interfacial interactions, which are promoted by the N3 (or hindered by Z907) dye species, as elucidated by the NMR analyses.

In devices based on F127-directed mesostructured titania films containing P3PBT as the only donor (black crosses), photocurrents are generated by photoexcitation of the P3PBT conjugated polymer, followed by electron transfer to the titania framework. The incorporation of dye molecules (along with the P3PBT) enables additional photocurrent to be generated from dye photoexcitation and electron transfer to titania. However, this requires close proximities and electronic coupling between the dye species and titania framework, as discussed above. Notably, the relatively hydrophobic Z907 dye molecule does not associate closely to or interact strongly with the titania framework. Accordingly, the presence of Z907 in a mesostructured TiO<sub>x</sub>-P3PBT film does not contribute appreciably to the generation of photocurrent (Figure 9B) and, in fact, its presence actually reduces the photocurrent, compared to the mesostructured TiOx-P3PBT device. The reduction in the

photocurrent in the presence of Z907 is attributed to Z907 molecules that are too distant from the  $TiO_x$  framework to transfer electrons efficiently, but which undesirably act as exciton quenching sites.

In contrast to the deleterious influence of Z907 dye species on photovoltaic performance, the hydrophilic N3 dye species coassemble near and interact strongly with the mesostructured titania framework (Figures 6 and 7), resulting in improved photovoltaic device performance. As shown in Figure 9B, a factor of 2 higher short-circuit current density is achieved in the presence of both N3 and P3PBT donor species, compared to that of a device based on an active layer containing P3PBT alone. A factor of 8 higher  $J_{sc}$  is obtained than that measured for an otherwise identical film containing the Z907 dye. An even higher value of  $J_{sc}$  would likely be possible, if all N3 molecules were bound to the titania interface. However, the N3 is distributed in both the PEO and the PPO regions of the F127directed mesochannels, as established by the EFTEM (Figure 4) and NMR (Figure 6) results, indicating that a significant fraction of the N3 dye species still remains relatively far (>1 nm) from the titania framework. Only the N3 molecules that are adsorbed on or strongly interacting with the electronaccepting titania are expected to contribute to the photocurrent, so that the increase in  $J_{sc}$  could be substantially higher.

The contribution of N3 molecules to the photocurrent and efficiency can also be seen in the incident photon-to-current efficiency (IPCE) plot presented in Figure 10. The IPCE of the



**Figure 10.** Incident photon-to-current efficiency (IPCE) curves of photovoltaic devices based on 200 nm thick F127-directed mesostructured titania films containing 6 wt % P3PBT without dyes (black crosses), and 6 wt % P3PBT with 3 wt % N3 (red circles).

device based on F127-directed mesostructured  $TiO_x$ -N3-P3BT film containing 6 wt % P3PBT and 3 wt % N3 (red circles) exhibits increased efficiency at wavelengths between 420 and 600 nm, compared to similar devices based on mesostructured F127-titania active layers containing only P3PBT donor species (black crosses). Moreover, the maximum of the IPCE curve for the device based on active layers containing both N3 and P3PBT donor species is red-shifted by 20 nm with respect to the maximum for the device containing P3PBT only. This shift is direct evidence of the contribution from photoexcitation of the N3 dye species to the photocurrent, which arises from the increased efficiency at higher wavelengths associated with the 546 nm MLCT band of N3 (Figure 3). Therefore, the

molecular-level compositions and structures of the electrondonor and electron-acceptor species at the organic—inorganic interface are mediated by the dye species and their interactions with the SDA and network-forming titania framework, which directly influence the macroscopic photoluminescence and photovoltaic properties of the hybrid organic—inorganic films.

# CONCLUSIONS

In this study, the chemical compositions and molecular interactions of electron-donor and electron-acceptor species were measured and analyzed for dye-mediated conjugated polymer-titania interfaces in SDA-directed mesostructured hybrid photovoltaic materials. Incorporation of the organoruthenium dyes N3 or Z907 with different hydrophilicities, together with the polythiophene conjugated polymer P3PBT, into mesostructured titania were shown to lead to dramatically different photovoltaic properties. Highly ordered cubic mesostructured titania films were obtained that contained relatively high loadings (up to 9 wt % each) of the dye molecules and the conjugated polymer. These were distributed principally in the mesochannels, though with different proximities to the organic-inorganic interface, which depended on the architectures of the dye species. The differences are due to the different architectures of the N3 and Z907 dye molecules, which influence their distributions and interactions with the titania framework, along with those of the conjugated polymer species, within the mesostructured F127-TiO, composites. For the N3 dve, its four carboxylic moieties impart a high degree of hydrophilicity that promotes its interactions with the titania surface, as manifested by solid-state NMR analyses. In contrast, the Z907 dye has two long alkyl chains that render the molecules more hydrophobic and disfavor its interactions with the titania surface, which are much weaker than for N3. The strong N3-titania interactions promote electron transfer from photoexcited N3 dye species to the titania framework, as reflected in a reduction of the photoluminescence decay rates and higher photocurrent generation in corresponding photovoltaic devices. The correlations between the molecular-level compositions and interactions at the organic-inorganic interfaces with the macroscopic optoelectronic properties of the photovoltaic films and devices provides new insights into the relationships between structure and function in dye-mediated optoelectronic materials in general and in hybrid organic-inorganic materials specifically. These results and the detailed understanding that they provide open new opportunities for better control of physicochemical interactions at heterojunction interfaces, yielding molecularlevel criteria for the design, syntheses, and properties of hybrid functional materials.

#### EXPERIMENTAL SECTION

**Materials.** Analytical grade absolute methanol (AR, BioLab/ Gadot, Israel), hydrochloric acid (HCl 37%, Carlo Erba, Italy), dichlorobenzene (DCB AR, BioLab, Israel), and titanium tetraethoxide (TEOT, technical grade, Aldrich) were used asreceived. The structure-directing agent was the triblock copolymer, Pluronic F127 ( $M_n = 12600$ ), with the chemical formula (ethylene oxide)<sub>106</sub>-(propylene oxide)<sub>70</sub>-(ethylene oxide)<sub>106</sub>; it was received from the BASF corporation as a gift and used as-received. Two types of conjugated polymers were purchased from Reike Metals, Inc., U.S.A., and used asreceived: poly[3-(potassium-4-butanoate)thiophene-2,5-diyl] (P3PBT,  $M_w = 19000 \text{ g/mol}$ , 90-94% regioregularity), and poly(3-hexylthiophene-2,5-diyl) (P3HT,  $M_w = 50000 \text{ g/mol}$ , 95% regioregularity). Two organoruthenium dyes were purchased from Sigma-Aldrich, and used as-received: N3 dye (*cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)), and Z907 dye (*cis*-bis(isothiocyanato)(2,2'bipyridyl-4,4'-dicarboxylato)(4,4'-dinonyl-2'-bipyridyl) ruthenium(II)). The molecular structures of the F127 SDA, P3PBT conjugated polymer, N3 dye, and Z907 dye used in this study are shown in Figure 1A–D, respectively. For characterization of dye adsorption, TiO<sub>2</sub> nanoparticles (P25 powder) with an average diameter of 22 nm were purchased from Degussa Inc. Perdeuterated solvents, CD<sub>4</sub>O (99.96%), D<sub>2</sub>O (D, 99.9%), and DCl (D, 99.5%, 35 wt % in D<sub>2</sub>O), were purchased from Sigma-Aldrich, and used as-received.

Materials Syntheses. In a typical synthesis, TEOT was hydrolyzed by addition of 0.18 mL of 12 M HCl to 0.5 mL of liquid TEOT, after which the mixture was vigorously stirred for 60 min or until the solution was clear. Simultaneously, 0.095 g of Pluronic F127 was dissolved in 1 or 2 mL of methanol, depending on whether the precursor solution was prepared with or without additional methanol from the dye solution, respectively. Since the final precursor solution contained mainly two volatile solvents, water, and methanol, it was important to keep the volume ratio between the two solvents constant in order not to affect the viscosity of the solution, which is known to influence film thickness. After dissolution, which was achieved after an hour of stirring, the F127/alcohol solution was added to the hydrolyzed titanium ethoxide, and the mixture was left for further stirring for at least 2 h. The P3PBT to be incorporated into the hybrid film was dissolved in deionized water at concentrations ranging from 5 to 7 mg/mL. The solution was heated to 60 °C and stirred for an hour to fully dissolve the polymer and then cooled to room temperature. The dye solution was prepared by dissolving the required amount of dye (ranging from 5 to 15 mg) in 0.5 mL of methanol. The final precursor solution was prepared by adding the polymer solution to the  $TiO_r/SDA$  solution in 1:1 volume ratio for films with only the conjugated polymer incorporated. In the case where both the dye and the conjugated polymer were incorporated, the dye solution and the polymer solution were mixed with the  $TiO_r/SDA$  solution in 1:3:2 volume ratio, respectively. Thin films were prepared by dip-coating on glass, silicon, polyimide, or on thin (7 nm) TiO<sub>2</sub> layer deposited by atomic layer deposition (ALD) on indium-tin-oxide (ITO) substrates. The dip-coating was performed at speeds of 2-5 mm/s in an environmentally controlled chamber with a relative humidity of 50%, yielding mesostructured films composed of disordered titania frameworks, surfactant SDA species, and dye and conjugated polymer guest molecules.

The loadings of conjugated polymer and dye species in the mesostructured titania films were estimated based on the relative amounts of the components in the precursor solutions. The molar ratios of components in the precursor solutions used for preparing the photovoltaic devices are shown in Table 3. Precise determination of the conjugated polymer and dye loading is challenging due to the low concentration of these species in the films, and their small total masses. Nevertheless, in order to estimate the concentrations of the photoresponsive components, the mesostructured films were dissolved in MeOH and  $H_2O$  and absorption of each dissolved film was compared to known concentrations in standard solutions.

Table 3. Molar Ratios of Components in the Precursor Solutions Used to Prepare the F127-Directed Mesostructured  $TiO_x$  Films Containing 6 wt % P3PBT without Dyes, or 6 wt % P3PBT with Either 3 wt % N3 or Z907 Dye Molecules

layer's composition	TEOT	F127	P3PBT	N3	Z907
TiO <sub>x</sub> -F127-P3PBT	1	0.0032	0.0005		
TiO <sub>x</sub> -F127-P3PBT-N3	1	0.0032	0.0006	0.0060	
TiO <sub><i>x</i></sub> -F127-P3PBT- Z907	1	0.0032	0.0006		0.0055

Samples for NMR characterization were synthesized using the perdeuterated solvents  $D_2O$ , DCl, and MeOD. The final precursor solutions with the same composition as described above were drop-cast on Teflon substrates and allowed to dry over 30 days in relative humidity of 50%.

**Device Preparation.** PV devices were fabricated on  $12 \times$ 12 mm<sup>2</sup> glass plates covered with patterned tin-doped indium oxide (ITO), designed as inverted PV cells. The substrates were thoroughly cleaned by sonication in acetone, methanol, and isopropanol. Then, a 7  $\pm$  0.5 nm dense TiO<sub>2</sub> layer was deposited by atomic layer deposition (ALD) using tetrakisdimethyl amino titanium and H2O as precursors, to function as an electron transporting layer (ETL). Before the deposition of the mesostructured titania conjugated polymer-dye films, the substrates were cleaned by exposure to an oxygen plasma for 5 min at 50% power using a Diener Femto-PCCE RIE plasma. Following deposition of the cubic mesostructured films (170-200 nm thick) on the ITO/TiO<sub>2</sub> substrates using the procedure described above, the films were dried in a glovebox, and a  $\sim$ 30 nm layer of neat P3HT was deposited on top from a 20 mg/mL DCB solution by spin-coating at 1500 rpm in an nitrogen atmosphere, to function as a hole-transporting layer (HTL). All the devices were heat treated at 90 °C under vacuum for 3 h for final drying. The top contact was deposited by thermal evaporation of a 100 nm thick gold layer through an eightpixel shadow mask, creating eight 2.4 mm<sup>2</sup> devices. Device fabrication was completed by postevaporation annealing for 5 min at 90 °C in a nitrogen atmosphere.

**Characterization.** Small-angle X-ray scattering (SAXS) patterns were acquired on films deposited onto polyimide substrates that were measured using Rigaku SMAX-300 with Cu K $\alpha$  radiation,  $\lambda = 1.5405$  Å and a pinhole collimation yielding a beam of 400  $\mu$ m (fwhm). A two-dimensional position-sensitive gas detector (200 mm diameter) positioned 1500 mm behind the sample was used. The patterns were recorded using a microfocus X-ray tube (45 kV/0.9 mA) coupled to a side-by-side Kirkpatrick Baez multilayer monochromator. Each sample was laid horizontally in a glancing incidence configuration (GISAXS), where the angle between the beam and the sample was around 2°.

High-resolution (HR) transmission electron microscopy (TEM) measurements were conducted using a FEI Tecnai G2 T20 S-Twin microscope operating at 200 keV. Energy-filtered (EF) TEM measurements were performed using a FEI Titan 80–300 keV S/TEM operating at 200 keV with filters set to sulfur  $L_{2,3}$  edge (165 eV). Samples for EF-TEM examination were thinned by using a Focused Ion Beam integrated within the Strata 400 STEM Dual Beam system of a Field-Emission Scanning Electron Microscope (FE-SEM).

The absorption spectra were measured using a Varian Cary 100 Scan UV–vis spectrophotometer over a wavelength range of 300–800 nm.

Solid-state two-dimensional (2D) <sup>13</sup>C{<sup>1</sup>H} heteronuclear correlation NMR experiments were conducted at 11.7 T using a Bruker AVANCE II NMR spectrometer operating at frequencies of 500.24 MHz for <sup>1</sup>H and 125.79 MHz for <sup>13</sup>C. The experiments were performed at room temperature under magic-angle-spinning (MAS) conditions using a 4 mm doubleresonance variable-temperature Bruker MAS probehead. Crosspolarization (CP) was used to transfer magnetization from <sup>1</sup>H to <sup>13</sup>C nuclei by adiabatic passage through the Hartmann-Hahn condition.<sup>80</sup> Heteronuclear <sup>1</sup>H decoupling was applied during signal acquisition at a <sup>1</sup>H nutation frequency of 100 kHz by using the pulse sequence SPINAL-64.81 Quadrature detection in the indirect <sup>1</sup>H dimension was achieved by using time-proportional-phase-incrementation (TPPI).<sup>82</sup> The 2D spectra were acquired by using a 1 s recycle delay and under MAS conditions of 12.5 kHz with a 2 ms CP contact time. Additionally, high power  ${}^{1}H-{}^{1}H$  homonuclear decoupling using the eDUMBO-1<sub>22</sub> sequence was applied during the <sup>1</sup>H evolution time with a phase-modulated radio frequency pulse of constant amplitude (100 kHz).<sup>83</sup> In the indirect (<sup>1</sup>H) dimension, a scaling factor of  $\lambda = 0.623 - 0.638$  was calibrated from separate  $2D^{-1}H^{-1}H$  spin diffusion NMR experiments. Contour levels shown in the 2D NMR spectrum correspond to 5, 10, 25, 40, 55, 70, and 85% of the maximum signal intensity. <sup>13</sup>C and <sup>1</sup>H chemical shifts were referenced to neat tetramethylsilane (TMS, 0 ppm), using tetrakis-methylsilane as an external secondary reference (<sup>13</sup>C and <sup>1</sup>H chemical shifts of 3.52 and 0.25 ppm relative to TMS, respectively).84

Dynamic nuclear polarization (DNP)-enhanced solid-state NMR experiments were performed at 9.4 T using a Bruker Avance III DNP-NMR spectrometer operating at 400.3 MHz for <sup>1</sup>H and 100.7 MHz for <sup>13</sup>C.<sup>61</sup> The experiments were conducted with sample temperatures of about 110 K using a 3.2 mm triple resonance <sup>1</sup>H/<sup>13</sup>C/<sup>15</sup>N variable temperature CPMAS probehead. DNP was achieved by irradiating the sample with high-power 263 GHz microwaves from a gyrotron and delivered to the sample by a corrugated waveguide with about 4 W of power reaching the sample. Samples were prepared for DNP-NMR experiments by incipient wetness impregnation.<sup>85</sup> The composite film was impregnated with a 16 mM TEKPol<sup>62</sup> solution of 1,1,2,2-tetrachloroethane (TCE).<sup>86</sup> Samples were then packed into 3.2 mm sapphire rotors for all DNP experiments. Additional details on sample preparation are provided in the main text.

Solution-state NMR experiments were conducted at 14.1 T using a Varian VNMRS spectrometer operating at frequencies of 600 MHz for <sup>1</sup>H and 150.9 MHz for <sup>13</sup>C. <sup>13</sup>C NMR spectra were acquired on the N3 and Z907 dyes using methanol (d-4) and a 1:1 mixture by volume of acetonitrile (d-3) with *tert*-butanol (d-10) as solvents, respectively. For the N3 dye, <sup>13</sup>C NMR signals were observed at 167.0, 166.6 161.0, 159.5, 155.4, 154.3, 140.5, 139.9, 135.8, 127.6, 126.8, and 124.3 ppm. For the Z907, the <sup>13</sup>C NMR signals were observed at 167.6, 167.2, 162, 160.5, 160.3, 158.9, 156.6, 155.6, 154.9, 153.4, 140.2, 139.5, 137.4, 136.1, 131.3, 129.4, 128.4, 128.3, 127.2, 125.6, 125.5, 124.8, 124.6, 37.4, 37.0, 34.0, 33.9, 32.5, 32.3, 31.4, 24.8, 24.7, 19.9, 15.8, and 15.7 ppm. For both spectra, the signals were referenced using <sup>13</sup>C signals from the solvents as secondary internal standards.

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For the photoluminescence decay measurements, the samples were illuminated by a tunable pulsed laser (Coherent Chameleon Ultra II), passing through an OPO (Coherent) and a harmonic generator (Coherent), to produce 515 nm excitation of 100 fs pulses at a repetition rate of 80 MHz. The laser was focused on each sample, while PL was detected from the side, through an optical fiber, by a single-photon counting avalanche photodiode (ID Quantique Ultralow Noise id-100) connected to a time-correlated single photon counter (Picoquant Hydraharp 400) for transient emission measurements. To make sure no laser light was scattered into the detector, a long-pass filter (Semrock 532LP Edgebasic) was used together with red-colored glass (CGRG 610 nm).

Film thicknesses were determined by measuring the cross sections of the final films or devices, using the Dual Beam system of the FE-SEM and were found to be ~200 nm for the mesostructured hybrid films, and ~100 nm for the neat dye films. The device architecture is described in the text. Device current-density-voltage (J-V) curves were measured in inert atmosphere under 100 mW/cm<sup>2</sup> AM 1.5G illumination (Newport Inc. 67005 solar simulator; lamp power, 150 W) using a Keithley 2400 source meter. Incident photon-to-current efficiency (IPCE) measurements were conducted using an EQE system (Oriel QE-PV-SI, Newport Inc.), with a Cornerstone 260 monochromator with a Merlin and a preamplifier.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

GISAXS pattern of F127-directed TiO, mesostructured film; Reflectance spectrum of F127-directed mesostructured titania film containing 6 wt % P3PBT measured in an integrating sphere; Solid-state <sup>13</sup>C{<sup>1</sup>H} DNP-CPMAS spectrum of mesostructured titania-F127 host containing 9 wt % P3PBT and 9 wt % N3 dye; Solid-state 2D HETCOR NMR spectrum of mesostructured titania-F127 nanocomposite; Solid-state 2D HETCOR NMR spectrum of mesostructured titania-F127 containing 9 wt % Z907; Solid-state 2D HETCOR NMR spectrum of mesostructured titania-F127 containing 9 wt % P3PBT; Solid-state 2D HETCOR NMR spectrum of mesostructured titania-F127 containing 9 wt % P3PBT and 9 wt % N3; Solid-state 2D <sup>1</sup>H{<sup>1</sup>H} homonuclear spin-diffusion correlation NMR spectra of the TiO<sub>2</sub>/N3 dye/P3PBT nanocomposite; Solid-state 2D <sup>1</sup>H{<sup>1</sup>H} single-quantum double-quantum (SQ-DQ) homonuclear correlation solid-state NMR spectrum of the TiO<sub>2</sub>/N3 dye/P3PBT nanocomposite. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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# **Supporting Information**

# Understanding and promoting molecular interactions and charge transfer in dye-mediated hybrid photovoltaic materials

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**Figure S1:** 2D glancing-incidence SAXS pattern with assigned plane reflections of a 200 nm F127-directed  $TiO_x$  mesostructured film.



**Figure S2:** Reflectance spectrum of a 200 nm thick F127-directed mesostructured titania film containing 6 wt% P3PBT measured in an integrating sphere.



**Figure S3:** Solid-state <sup>13</sup>C{<sup>1</sup>H} DNP-CPMAS spectrum acquired at 105 K and at 12.5 kHz MAS on a mesostructured titania-F127 host containing 9 wt% P3PBT and 9 wt% N3 dye. Significant signal intensity is observed at ca. 169 ppm that is attributed to carboxylic acid moieties that are bound to the titania framework. The spectrum was acquired in 25 min with a 1 ms contact time.



**Figure S4:** Solid-state 2D <sup>13</sup>C{<sup>1</sup>H} dipolar-mediated heteronuclear correlation (HETCOR) NMR spectrum acquired at room temperature for mesostructured titania-F127 containing no dye or conjugated polymer species under MAS conditions of 12.5 kHz, with a 2-ms CP contact time. 1D <sup>13</sup>C{<sup>1</sup>H} CPMAS and single-pulse <sup>1</sup>H MAS spectra are shown along the top horizontal axis and the left vertical axis, respectively. No asymmetric broadening to lower ppm in the <sup>1</sup>H dimension of the 2D spectrum is observed for any of the <sup>1</sup>H signals associated with the PEO or PPO moieties. This is in contrast to 2D HETCOR spectra (Figs. 6, S5 and S6) acquired on similar mesostructured composites containing dye or conjugated polymer species, for which broadening is clearly observed and attributed to ring-current effects arising from molecularly proximate dye or conjugated species.<sup>21</sup>



**Figure S5:** Solid-state 2D <sup>13</sup>C{<sup>1</sup>H} dipolar-mediated heteronuclear correlation (HETCOR) NMR spectrum acquired at room temperature for mesostructured titania-F127 containing 9 wt% Z907 under MAS conditions of 12.5 kHz, with a 2-ms CP contact time. 1D <sup>13</sup>C{<sup>1</sup>H} CPMAS and single-pulse <sup>1</sup>H MAS spectra are shown along the top horizontal axis and the left vertical axis, respectively. <sup>13</sup>C signals at 71 and 75 ppm from both the PEO and PPO –OCH<sub>2</sub>– moieties are correlated with the <sup>1</sup>H signal at ca. 8 ppm (which is also broadened to higher frequency by ring-current effects) from the aromatic protons of the Z907 dye, indicating that the guest species are in close proximities to and distributed among the PEO and PPO segments. The schematic diagram shows the distribution of Z907 molecules within PEO (blue) and PPO (yellow) regions of a single mesochannel, as viewed along the (*111*) axis of a cubic mesostructure.



**Figure S6:** Solid-state 2D <sup>13</sup>C{<sup>1</sup>H} dipolar-mediated HETCOR NMR spectrum acquired at room temperature for mesostructured titania-F127 containing 9 wt% P3PBT under MAS conditions of 12.5 kHz, with a 2-ms CP contact time. 1D <sup>13</sup>C{<sup>1</sup>H} CPMAS and single-pulse <sup>1</sup>H MAS spectra are shown along the top horizontal axis and the left vertical axis, respectively. Ring-current broadening to lower frequency is observed for the <sup>1</sup>H signals associated with the  $-OCH_2$ - moieties of PEO and the  $-OCH_2$ - and -OCH- moieties of PPO, indicating that the P3PBT is distributed among both. A schematic diagram depicts the relative distributions of the P3PBT within PEO (blue) and PPO (yellow) regions of a single mesochannel, as viewed along the (*111*) axis of a cubic structure, which are consistent with the NMR results.



**Figure S7:** Solid-state 2D <sup>13</sup>C{<sup>1</sup>H} dipolar-mediated HETCOR NMR spectrum acquired at room temperature for mesostructured titania-F127 containing 9 wt% P3PBT and 9 wt% N3 under MAS conditions of 12.5 kHz, with a 2-ms CP contact time. 1D <sup>13</sup>C{<sup>1</sup>H} CPMAS and single-pulse <sup>1</sup>H MAS spectra are shown along the top horizontal axis and the left vertical axis, respectively. Narrow signals are observed for most species, especially in the <sup>13</sup>C dimension, in contrast to the DNP-enhanced spectra acquired on the same sample at 105 K.



Figure S8. Solid-state 2D <sup>1</sup>H{<sup>1</sup>H} homonuclear spin-diffusion correlation NMR spectra of the TiO<sub>2</sub>/N3 dye/P3PBT nanocomposite material acquired at 17 Tesla (700 MHz) and 22 kHz MAS with spin-diffusion mixing periods ( $\tau_{mix}$ ) of (A) 2 µs and (B) 20 ms. The red diagonal lines indicate correlations between signals that correspond to <sup>1</sup>H species with identical chemical shifts. Slices from each 2D spectrum (green,  $\tau_{mix}=20$  ms; blue,  $\tau_{mix}=2$  µs) taken parallel to the  $F_2$ (directly detected) dimension are shown for <sup>1</sup>H chemical shifts of (C) 1.2 ppm and (D) 9.0 ppm in the indirect dimension, corresponding to the PPO methyl protons and aromatic/carboxylic acid protons, respectively. The slices of the 2D spectra indicate that the protons of the PPO methyl groups at 1.2 ppm show only weak intensity correlations with the aromatic or carboxylic acid protons of the N3 dye, even after a long 20 ms spin-diffusion period. Similarly, the carboxylic acid/aromatic protons at 9.0 ppm exhibit very weak correlated signal intensity with the PPO methyl group protons at 1.2 ppm after a 20 ms spin-diffusion period. In both cases, strong correlated signals are observed at 3.5 ppm associated with the PEO protons. These results are consistent with the DNP-enhanced HETCOR experiments and analysis of the DNP enhancements, which indicate that the N3 dye molecules are distant from the PPO cores of the SDA and proximate to the TiO<sub>2</sub> surface within the mesochannels of the nanocomposite. During the  $t_1$  evolution period, e-DUMBO-1<sub>22</sub> homonuclear decoupling was applied and the chemical shifts in the indirect dimension were corrected by applying a scaling factor of 0.57.



**Figure S9**. (A) Solid-state 2D <sup>1</sup>H{<sup>1</sup>H} single-quantum double-quantum (SQ-DQ) homonuclear correlation solid-state NMR spectrum of the TiO<sub>2</sub>/N3 dye/P3PBT nanocomposite material at 17 Tesla (700 MHz) and 25 kHz MAS. A single rotor cycle was employed for excitation and reconversion of the DQ coherences. The intensity correlation at 9.8 ppm in the indirect (DQ) dimension and 7.0 ppm in the direct (SQ) dimension indicates dipolar coupling between protons with chemical shifts of 7.0 ppm and 2.8 ppm. This is consistent with the close spatial proximities of the aromatic protons of the N3 dye molecules and the alkyl protons of the P3PBT. (B) Rotor-synchronized <sup>1</sup>H spin-echo spectrum. (C) The projection of the 2D DQ-SQ correlation spectrum. <sup>1</sup>H signals from mobile PPO and PEO proton moieties are suppressed in the DQ-filtered spectrum, while signals from the N3 dye and P3PBT conjugated polymer are clearly visible. The DQ-SQ correlation spectrum was acquired with a rotor-synchronized BABA pulse sequence.<sup>87</sup>