

NMR (125 MHz, CD₂Cl₂, rt): δ =200.0, 144.9, 142.3, 141.9, 141.7, 141.5, 141.2, 140.7, 140.6, 140.2, 140.0, 139.8, 139.7, 139.2, 138.9, 138.6, 135.2, 134.8, 132.5, 132.4, 132.0, 131.6, 130.7, 130.4, 129.4, 129.1, 128.8, 128.0, 127.3, 126.8, 126.1, 90.7 (C_{cluster}), 90.6 (C_{cluster}), 73.1 (C_{cluster}), 73.0 (C_{cluster}).

¹H and ¹³C NMR spectra were recorded in deuterated solvents, such as CD₂Cl₂, on a Bruker DPX 250 and a Bruker DRX 500 spectrometer, using the proton or carbon signal of the solvent as an internal standard. The thermolysis reactions were carried out in sealed quartz tubes in a temperature controlled electromagnetic oven. SEM measurements were performed on a LEO 1530 field-emission scanning electron microscope. High-resolution TEM studies were conducted on a Philips Tecnai F30 analytical TEM at an operating voltage of 300 kV and on a TEM EM420 electron microscope at an operating voltage of 120 kV. The samples were dispersed in ethanol under ultrasonic irradiation and the suspension was dropped onto a TEM copper grid with a carbon film. TGA measurements were performed on a Mettler Toledo TS0801R0 device at a heating rate of 10 °C min⁻¹ between 0 and 900 °C under an inert atmosphere.

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Using Resonance Energy Transfer to Improve Exciton Harvesting in Organic–Inorganic Hybrid Photovoltaic Cells**

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Polymer-based solar cells^[1,2] share many common features with other types of organic solar cells,^[3] which are collectively called “excitonic solar cells”.^[4] The operation of excitonic solar cells is fundamentally different from that of conventional solar cells in that the absorption of photons creates Frenkel-type excitons with a binding energy around 0.4–1 eV.^[5] Because of the large binding energy, excitons can only efficiently dissociate at a heterojunction interface with favorably offset energy levels. The exciton diffusion length of most conjugated polymers is less than 10 nm,^[6,7] which is much smaller than the optical absorption path length, even at the maximum absorption wavelength. To use materials with small exciton diffusion lengths and make reasonably efficient cells, electron donor and acceptor materials have been blended into bicontinuous structures known as bulk heterojunctions.^[8–21] In these cells, the size of each phase should be comparable to or less than the exciton diffusion length so that excitons can reach the interface before geminate recombination. However, for organic semiconductors that are highly immiscible, controlling

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the kinetics of phase separation to yield phase separation of the proper dimensions (≤ 10 nm) is difficult. Therefore, there is a need to improve the transport of excitons to interfaces. In this communication, we show that excitons can be harvested more efficiently by using resonance energy transfer (RET) to transport excitons in a non-random manner from one semiconductor to the other. In resonance energy transfer processes, excitons in the donor (D) material transfer their energy to the closest acceptor (A) molecules, which are near the D/A interface. Consequently, if exciton dissociation can happen at the D/A interface (whether in a bulk heterojunction cell or flat device), RET will selectively place excitons at the dissociation interface, improving the probability for electron transfer to occur. We show that inserting a thin layer of a low band-gap polymer at the interface can triple the efficiency of a flat poly(3-hexylthiophene) (P3HT)/titania solar cell.

We use poly(*N*-dodecyl-2,5-bis(2'-thienyl)pyrrole-2,1,3-benzothiadiazole) (PTPTB)^[22,23] and P3HT as the energy-acceptor and energy-donor materials, respectively. The chemical structures of PTPTB and P3HT are shown in Figure 1a. Figure 1b shows the absorption spectrum of PTPTB and the emission spectrum of P3HT. Since the absorption of PTPTB has a large spectral overlap with the emission of P3HT, photon absorption by the P3HT molecules is accompanied by efficient energy transfer to the PTPTB molecules through directional RET.

The ability of excitons to diffuse in P3HT was characterized by comparing the luminescence of films of P3HT of varying thickness on titania, which can quench excitons by electron transfer, to that of similar films on glass, which cannot quench excitons.^[24] The photoluminescence (PL) quenching efficiency was determined by subtracting the PL on titania from the PL on glass and dividing by the PL on glass. The ability of PTPTB to accept excitons from P3HT by either RET or exciton diffusion was characterized by performing the same experiment with a layer of PTPTB inserted between the P3HT and glass substrate. We used the high-molecular-weight fraction of

PTPTB for PL measurements and device fabrication, since it is insoluble even in boiling tetrahydrofuran (THF), and therefore intermixing of PTPTB and P3HT did not occur when we spin-cast P3HT from THF on top of the PTPTB layer. When using PL quenching measurements of this type to determine the distance over which excitons can be harvested, it is very important to account for the possibility that the number of excitons formed in P3HT films cast on different substrates might vary due to the effects of optical interference caused by the thin-layer stacks used in these measurements. The refractive index of the titania used in this study measured by ellipsometry was found to be approximately 2.1 at 632 nm. By contrast, the refractive index of the glass substrate is only 1.5. A consequence of the high refractive index of titania is that incoming light can be reflected by the titania/P3HT and titania/glass interfaces. The reflected light interferes with the incoming light and strongly modifies the local optical field and therefore the absorption of P3HT. The presence of titania close to P3HT also changes the external PL efficiency of P3HT due to the change in density of photonic modes.^[25,26] According to our numerical modeling, these interference problems, which can result in misleading PL quenching results, can be avoided by using a very thin layer of titania. For our experiments, the incident angle of the pumping light (442 nm) was 27° from the normal direction, and the photoluminescence was collected in the front-face mode. A transfer-matrix numerical model^[3] showed that the presence of a 4 nm titania layer reduced the local light intensity by less than 5 % for both transverse electric (TE) and transverse magnetic (TM) modes, as opposed to a more than 60 % reduction of light intensity with a 50 nm thick film of titania. Thus, 4 nm titania films were used for the optical measurements performed for this study. The roughness of the titania and PTPTB films were found to be less than 1 nm and 2 nm, respectively. Figure 2 shows the dependence of PL quenching efficiency on the thickness of P3HT for glass/TiO₂/P3HT and glass/TiO₂/PTPTB/P3HT samples. For 8 nm thick P3HT films, energy transfer to PTPTB more than

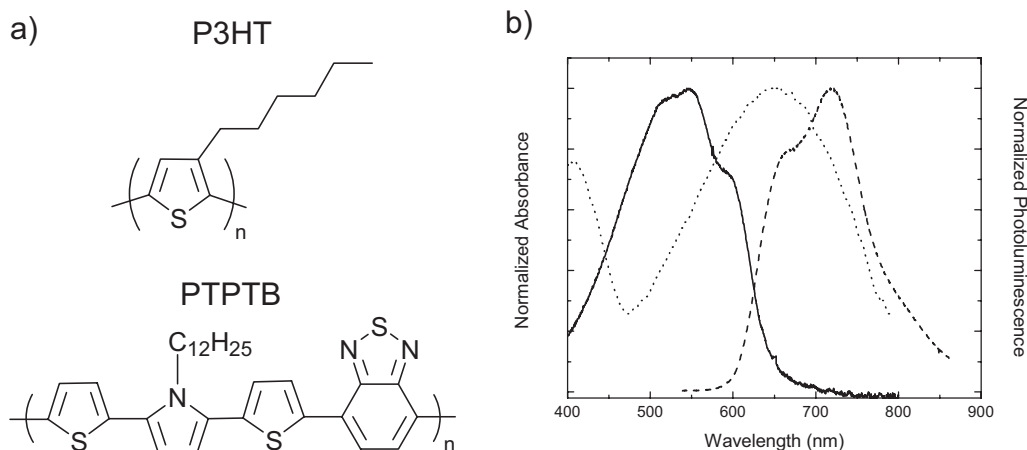


Figure 1. a) Chemical structures of P3HT and PTPTB. b) Absorption spectrum of P3HT (solid), emission spectrum of P3HT (dash), and absorption spectrum of PTPTB (dot).

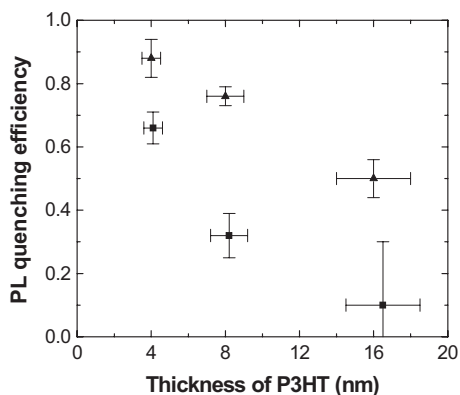


Figure 2. Dependence of PL quenching efficiency on the thickness of P3HT for glass/TiO₂/P3HT (■) and glass/PTPTB/P3HT (▲). The thickness of the PTPTB and titania layers were 8 nm and 4 nm, respectively.

doubles the fraction of quenched excitons, compared to exciton diffusion to titania. The 8 nm P3HT PL is quenched equally regardless of whether the PTPTB layer (5 nm) is deposited on TiO₂ or glass, demonstrating that ~5 nm PTPTB fully coats TiO₂.

The energy diagram and device structure of solar cells made with TiO₂, PTPTB, and P3HT are shown in Figures 3a,b.^[22] Figure 3c shows the current–voltage (*I*–*V*) characteristics of a

fluorinated tin oxide (FTO)/TiO₂/PTPTB/P3HT/Ag device and an FTO/TiO₂/P3HT/Ag control device tested under 100 mW cm⁻² simulated air mass (AM) 1.5 radiation. The control device without the PTPTB layer has a short circuit current density (*J*_{sc}) of 0.46 mA cm⁻², an open-circuit voltage (*V*_{oc}) of 0.64 V, a fill factor (*FF*) of 0.63, and an overall power conversion efficiency η_p of 0.19%. The device with PTPTB is nearly three times better, with *J*_{sc} of 1.33 mA cm⁻², *V*_{oc} of 0.67 V, *FF* of 0.63, and η_p of 0.56%. The photocurrent action spectrum of the FTO/TiO₂/PTPTB/P3HT/Ag device matches the absorption of P3HT (Fig. 3d) and shows that the contribution from the direct optical absorption of PTPTB is almost negligible. Thus, the tripling of the photocurrent by the thin PTPTB layer can be attributed to the energy transfer from P3HT to PTPTB. Increasing the thickness of the PTPTB layer to 20 nm led to a decrease in the photocurrent, which is likely due to a low electron mobility in PTPTB. Decreasing the PTPTB thickness to 2 nm also led to a slight decrease in photocurrent, which we attribute to a discontinuous PTPTB layer.

Since the resonance energy transfer rate constant decays with distance *r* as 1/*r*⁶ (or 1/*r*⁴, assuming a plane of PTPTB energy-acceptor molecules), simple calculations show that energy transfer places almost all of the excitons that end up in PTPTB within approximately 1–2 nm from the PTPTB/P3HT interface. Although the energy diagram suggests that both

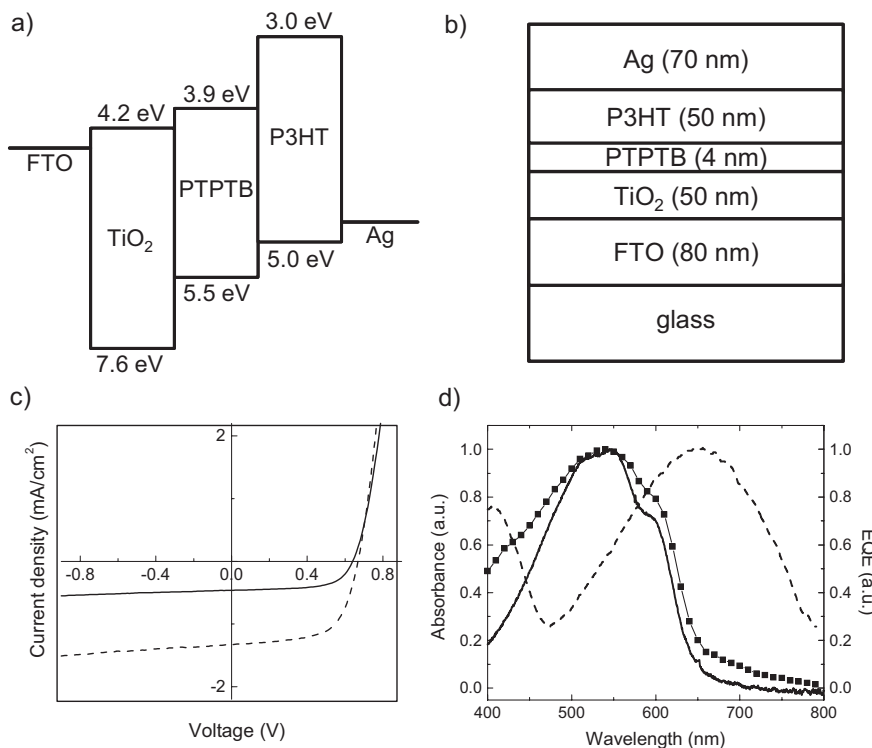


Figure 3. a) Device structure and b) energy diagram of photovoltaic cells. PTPTB energy levels are from [20]; P3HT energy levels were measured by cyclic voltammetry. c) Current–voltage (*I*–*V*) characteristics of fluorine-doped tin oxide (FTO)/TiO₂/P3HT/Ag (solid) and FTO/TiO₂/PTPTB/P3HT/Ag (dashed) cells tested under 100 mW cm⁻² simulated air mass (AM) 1.5. The thicknesses of titania, PTPTB, and P3HT are 50 nm, 4 nm, and 50 nm, respectively. d) Comparison between the photocurrent action spectrum of an FTO/TiO₂/PTPTB/P3HT/Ag photovoltaic cell with a 4 nm thick layer of PTPTB (square), and the absorption spectra of P3HT (solid) and PTPTB (dashed). EQE: external quantum efficiency.

electron transfer from PTPTB to titania and hole transfer from PTPTB to P3HT are possible, electron transfer from PTPTB to titania has been reported to be inefficient and has been attributed to an insufficient band offset between PTPTB and titania.^[27] By contrast, the larger driving force for hole transfer (0.5 eV) from PTPTB to P3HT apparently leads to a much faster hole transfer. Similar experiments performed with poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylenevinylene) (MDMO-PPV) on PTPTB found that energy transfer to the PTPTB occurred even more effectively due to the higher luminescence efficiency of MDMO-PPV compared to P3HT. However, the device with a PTPTB layer did not show any enhancement of photocurrent compared to the device without PTPTB. This result indicates that excitons are not split as efficiently at the MDMO-PPV/PTPTB interface, which is not surprising because the offset in highest occupied molecular orbital (HOMO) between these two materials is less than 0.3 eV and hence smaller than the offset in HOMO between PTPTB and P3HT (0.5 eV). We conclude that P3HT/PTPTB is a good system to use for photovoltaic applications because it enables not only directional RET, but also exciton splitting. It is important to note, however, that only some of the PTPTB luminescence is quenched by hole transfer and that a better combination of materials could lead to PV cells with higher efficiency. Although titania is not the electron acceptor in these devices, it performs several important tasks. Because PTPTB is virtually insoluble and difficult to process, it must be deposited first. The titania serves as a hole-blocking layer, and modifies the workfunction of the bottom contact from 4.9 eV (FTO) to 4.5 eV (TiO₂), which makes it a suitable electron-withdrawing contact. A titania overlayer also reduces the surface roughness, which prevents shorting and ensures uniform polymer film thicknesses. Finally, titania is a target for nanostructuring, and could serve as a template for a bulk heterojunction device incorporating the energy-transfer approach.

Given that excitons can only be harvested from approximately the first 8 nm of the P3HT and that the PTPTB thickness is itself 4 nm thick, it is surprising that the PTPTB does not generate more photocurrent by directly absorbing light (although it does provide a small contribution to the photocurrent action spectrum at 650 nm, where a P3HT-only device has no absorption). Since it is clear that excitons can be split at the PTPTB/P3HT interface, the exciton diffusion length in PTPTB must be smaller than 4 nm. Steady-state photoluminescence experiments showed that the PL of 4 nm PTPTB was not significantly quenched in the presence of a solid layer of titania, which is attributed to the combination of a very small exciton diffusion length in PTPTB and inefficient electron transfer from PTPTB to titania.

In addition to improving exciton harvesting, it is also possible that the PTPTB improves the photocurrent by preventing geminate or non-geminate recombination.^[28,29] However, when reverse-biased at -1 V, the photocurrents of the FTO/TiO₂/PTPTB/P3HT/Ag device and the FTO/TiO₂/P3HT/Ag control device only increased by 11 % and 16 %, respectively,

after subtraction of the dark currents. The fact that the photocurrent does not increase very much with reverse biasing suggests that geminate (and/or non-geminate) recombination is not that important and that the threefold increase in photocurrent with PTPTB is not entirely attributable to a reduction in the recombination of photogenerated carriers.

In conclusion, we have shown that resonance energy transfer can be used to transport excitons in organic photovoltaic cells from the light-absorbing donor layer to the acceptor layer. This method is powerful for several reasons. First, it places excitons right at the donor/acceptor interface, where they can be split by hole transfer. Second, it is faster than exciton diffusion and thereby enables harvesting of excitons before geminate recombination occurs. Third, it provides a mechanism for excitons to overcome low-energy sites in the absorbing layer that could prevent them from diffusing to the D/A interface. We believe that the RET strategy is essential to efficiently harvesting excitons in many types of bulk heterojunction PV cells. Finally, we would like to point out that if RET had not been accounted for when we interpreted the PL quenching of P3HT on PTPTB, we would have concluded that the exciton diffusion length was larger than it really is. We hypothesize that the neglect of RET has led to overestimations of exciton diffusion lengths in several materials. Finally, while planar device architectures were used, it is clear that even higher conversion efficiencies could be obtained by nanostructuring the titania substrate in these devices.

Experimental

Polymer Synthesis and Purification: Poly(*N*-dodecyl-2,5-bis(2'-thienyl)pyrrole-2,1,3-benzothiadiazole) (PTPTB) [22] was synthesized by standard Suzuki-coupling polymerization of 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-dodecylpyrrole and 4,7-di-2'-(5'-bromo)thienyl-2,1,3-benzothiadiazole [30]. The high-molecular-weight fraction was isolated by Soxhlet purification, as described by Dhana-balan et al. [22]. This fraction was insoluble in dichloromethane and tetrahydrofuran (THF), but moderately soluble in hot *o*-dichlorobenzene (ODCB). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy (PerSeptive Biosystems Voyager-DE instrument in positive ion mode using *trans*-3-indole acetic acid as the matrix): 2435 (H-TBT(PTBT)₄-H), 2668 (H-(PTBT)₅-H), 2968 (H-TBT(PTBT)₅-H), 3201 (H-(PTBT)₆-H), 3501 (H-TBT(PTBT)₆-H), 3736 (H-(PTBT)₇-H), 4032 (H-TBT(PTBT)₇-H), 4267 (H-(PTBT)₈-H), 4565 (H-TBT(PTBT)₈-H). UV-vis (Cary 50 UV-vis spectrometer, in ODCB): 370, and 570 nm. UV-vis (spin-coated on glass from ODCB solution): 420 and 675 nm. P3HT was purchased from Aldrich and purified with Soxhlet extraction; first with methanol, then with heptane, and finally with tetrahydrofuran (THF).

Device Fabrication and Testing: We used fluorine-doped SnO₂ (FTO, provided by AFG Industries, Inc., 100 Ω/□) as the bottom transparent electrode and spin cast a 50 nm thick solid titania film using a sol-gel method [31]. A 4 nm thick film of PTPTB was spin cast as described earlier. 50 nm thick P3HT films were cast from THF onto the PTPTB or TiO₂. Finally, a 70 nm thick Ag electrode was evaporated on top of the P3HT layer at a pressure of 10⁻⁶ torr (1 torr ~ 133 Pa). All devices were tested in a nitrogen environment with a Keithley 2400 SourceMeter under 100 mW cm⁻² simulated AM 1.5 illumination from a Spectra-Physics 300 W solar simulator (Model 81250). Once the power from the simulator was determined, a

400 nm cutoff filter was used to remove the UV light. The photocurrent action spectrum was obtained with a lock-in amplifier (Stanford Research Systems SR830) and the chopped output of a 75 W xenon lamp/monochromator (Acton) with a spectral resolution of 10 nm. The spectral mismatch of the device was found to be 0.70.

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A New Metastable Phase of Crystallized $V_2O_4 \cdot 0.25H_2O$ Nanowires: Synthesis and Electrochemical Measurements**

By Mingdeng Wei,* Hideki Sugihara, Itaru Honma, Masaki Ichihara, and Haoshen Zhou*

Nanoscale materials often exhibit physical and chemical properties that differ greatly from their bulk counterparts,^[1] and have attracted much attention because of their structural, electronic, and optical properties and their potential applications. One-dimensional (1D) nanostructures include nanotubes, nanorods, nanowires, nanofibers, nanobelts, and nanoribbons. In the past decade, a large number of 1D structural nanoscale materials have been reported, such as TiO_2 ,^[2–4] V_2O_5 ,^[5–7] VO_2 ,^[8–11] MnO_2 ,^[12–14] and ZnO .^[15–17] Among them, nanoscale V^{4+} oxides are particularly interesting because they have unique electrical and optical properties, which lead to a wide variety of potential applications including lithium batteries,^[18,19] temperature-sensing devices,^[20] optical switching devices,^[21] and optical data-storage media.^[22]

V^{4+} oxides, VO_2 and V_2O_4 , exhibit a semiconductor-to-metal transition (SMT) near the critical temperature, T_c , ~ 67 °C that is the result of an atomic structural rearrangement.^[23] Above the T_c , V^{4+} oxides have a tetragonal rutile structure and exhibit metallic properties. Below the T_c , V^{4+} oxides are narrow-gap semiconductors with a monoclinic structure.^[24] So far, more than ten phases of V^{4+} oxides have been reported. These V^{4+} oxides include rutile VO_2 ($P4/mmm$),^[25] monoclinic VO_2 ($P2_1/c$),^[26] triclinic VO_2 ($P^*(2)$, Joint Committee on Powder Diffraction Standards (JCPDS) 19-1401),^[27] tetragonal (A) VO_2 ($P4_2/nmc$),^[28–31] monoclinic (B) VO_2 ($C2/m$),^[31] (C) VO_2 ,^[32] orthorhombic $VO_2 \cdot H_2O$ ($P222$),^[33] tetragonal $VO_2 \cdot 0.5H_2O$ ($I4/mmm$),^[17] monoclinic V_2O_4 ($P21/c$, JCPDS 19-1398), and $V_2O_4 \cdot 2H_2O$ (JCPDS 13-0346, 23-0727).

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