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Quenching of Semiconductor Quantum Dot Photoluminescence by a π -Conjugated Polymer

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In this communication we discuss the possibility of hole transfer between a photoexcited semiconductor quantum dot and a π -conjugated polymer. This charge-transfer event will be investigated (exploited) on the basis of its implication toward a solar energy conversion scheme. Experimentally, we show that the steady-state photoluminescence (PL) of a solution of InP quantum dots is quenched by the introduction of solvated poly-(3-hexylthiophene). Time-resolved PL experiments on these solutions are also presented. It was observed that the PL transients did not significantly change upon the addition of the conductive polymer. These new results indicate that said PL quenching is static in nature. This suggests that in solution, the quantum dot and the polymer exhibit a strong intermolecular interaction. As the two species encounter each other through diffusion, the polymer quenches the quantum dot photoluminescence without altering the population's PL lifetime. This new evidence suggests that the polymer and the quantum dot form a relatively stable complex.

Introduction

Little is understood about the interactions between nanocrystalline semiconductor quantum dots and π -conjugated polymers. Ever since the effect of quantum confinement was first realized, quantum dots have received a great deal of attention in the scientific community. Quantum dots are of scientific interest for several reasons. Due to the quantum confinement effect, their energetics are tunable by changing their size.¹ This provides a method for optimization of charge transfer² between quantum dots and other species. Quantum-confined structures exhibit a stronger oscillator strength than the bulk material, leading to the possibility of very large optical absorption coefficients ($>10^6$ cm⁻¹). Quantum dots also exhibit the photoluminescence (PL) up-conversion effect,³ and may be candidates for manifesting such phenomena as impact ionization and hot electron transfer.⁴ Synthetic techniques for dot preparation have been improved recently and the time necessary to produce samples has been reduced.⁵ Also, semiconductor quantum dots have been shown to interact with other semiconductor systems in a charge-transfer reaction.⁶

π -conjugated polymers are receiving a great deal of research interest⁷ and are both scientifically and industrially interesting for many reasons. Their mechanism of conduction is different than in bulk crystalline semiconductors.^{8,9} Because of the ability to process them in solution they present the possibility of low-cost devices to the marketplace. The low temperatures involved in their processing allow for the use of plastic substrates, and high-throughput printing techniques allow for the possibility of roll-to-roll production of devices. Their electronic properties are tunable through functionalization and derivatization.

Novel optoelectronic devices can be realized by blending quantum dots and conjugated polymers, in particular photovoltaic devices¹⁰ and organic light-emitting devices (OLEDs).¹¹ However, there is much to be learned to determine how these

two materials will behave when placed in contact, particularly with regard to interfacial energetics and charge-transfer reactions, and how the two are related.

In one focused avenue of interest with regard to solar energy conversion, researchers are working on developing practical dye-sensitized cells, in which a layer of light-absorbing species (or material) is adsorbed onto a high surface area, nanocrystalline, metal oxide semiconductor such as TiO₂.¹² This is typically sensitized to the terrestrial solar spectrum with a "Ru-trisbipy" or similar dye; however, recent work has also addressed the use of inorganic semiconductors as sensitizers.¹³ These materials inject electrons into the metal oxide semiconductors upon illumination. The complete device is made by filling the porous voids of the sensitized oxide with a nonvolatile material that acts as a hole transporter. This can be, for instance, a polymer based on a common hole transport moiety such as triphenylamine, that is potentially doped with an ionic species, or even a *p*-type semiconductor.¹⁴

An approach that we are exploring is to create a quantum-confined layer of inorganic semiconductor, such as InP, on the oxide surface to act as the light-absorbing species. This would confer the advantage of energetic tunability, high absorbance, and the possibility of hot electron transfer, impact ionization, and up-conversion. Vital to the operation of this cell would be multiple, unique charge-transfer events. Specifically, the charge-transfer events are electron transfer from the sensitizer to the conduction band of TiO₂ and hole transfer from the sensitizer to the valence band of the hole transport layer. Previously, we have shown that electron transfer from the sensitizing quantum dot to the TiO₂ conduction band does occur.⁶ Here, we investigate the hole transfer from the semiconductor quantum dot to poly(3-hexylthiophene) (P3HT). The hole-transfer step in this quantum dot/polymer system is interrogated by monitoring the photoluminescence of capped, solvated InP quantum dots and observing how this PL intensity is affected by the addition of a conductive polymer to the solution.

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Experimental Section

Quantum Dot Synthesis. The procedure for the preparation of the high-quality InP quantum dots has been previously described in detail.¹⁵ It is essentially the method developed by Peng and Battaglia where octadecene was used as a noncoordinating solvent.

Polymer Fractionation. P3HT was purchased from Aldrich and fractionated using a multiple-step Soxhlet extraction process. In this process, different solvents are progressively employed, specifically, and in order, the solvents are changed for each Soxhlet extraction step from acetone to hexanes to dichloromethane to tetrahydrofuran and, finally, to chloroform. At each step, larger molecular weight fractions of the polymer are extracted. From the material received from Aldrich we were able to separate four usable fractions. These were characterized by gel permeation chromatography (GPC), UV-vis, and photoluminescence (steady state and time resolved). The GPC column was calibrated with a polystyrene standard. This provides only an approximate calibration to the measured molecular weights since the P3HT presents a different hydrodynamic radius to the column. More accurate measurements of molecular weight, by either light scattering or MALDI TOF, are underway.

Photoluminescence spectra were recorded using a Fluorolog-3 (JYHoriba) spectrometer that utilized a liquid N₂-cooled CCD detector. Monochromatic excitation light was generated by a Xe arc lamp with double monochromator. Fluorescence was collected at 90° relative to the excitation beam, passed through a single monochromator containing a 300 line/mm grating, and imaged on the liquid nitrogen-cooled CCD array. All PL spectra were corrected for the spectral output of the excitation source and for the spectral response of the detection optics. Linear absorption spectra were recorded on a Cary 500 double beam spectrophotometer at 1 nm spectral resolution.

Fluorescence decay signals were measured using the technique of time-correlated single photon counting (TCSPC). The spectrometer comprised a pulsed, picosecond diode laser (IBH NanoLED-10, having a pulse-width less than 200 ps) operating at a wavelength of 635 nm and a repetition rate of 1 MHz. Emission was detected at 90° to excitation by focusing the emission onto the slits of a 0.25 m monochromator (SPEX minimate) and subsequently detected by a photon counting photomultiplier tube (Hamamatsu H6279). No polarizing optics were positioned between the sample and the detector. The PMT output was amplified using a 1 GHz amplifier (Philips model 6954) and then shaped using a constant fraction discriminator (Ortec, Tennelec model 583) and fed into the start input of a time-to-amplitude converter (TAC, Ortec, model TC864), which was operated in reverse mode. The stop input to the TAC was supplied by an output directly from the pulsed laser diode controller (IBH NanoLED-C). The TAC output was fed to a multichannel analyzer (Oxford Instruments PCA3-8K) operating in pulse-height analysis mode. The instrument response function (IRF) from this system when scattering the excitation light from a dilute solution of colloidal silica was determined to be 220 ps. Using a nonlinear, least squares iterative deconvolution procedure employing the Marquardt minimization routine, the influence of the IRF could be removed from the measured luminescence decay curves to reproduce the true decay kinetics with a temporal resolution of less than 20% of the IRF (approximately 44 ps).

Results

Figure 1 shows the GPC results of the multistep Soxhlet extraction for the P3HT we obtained from Aldrich. During the

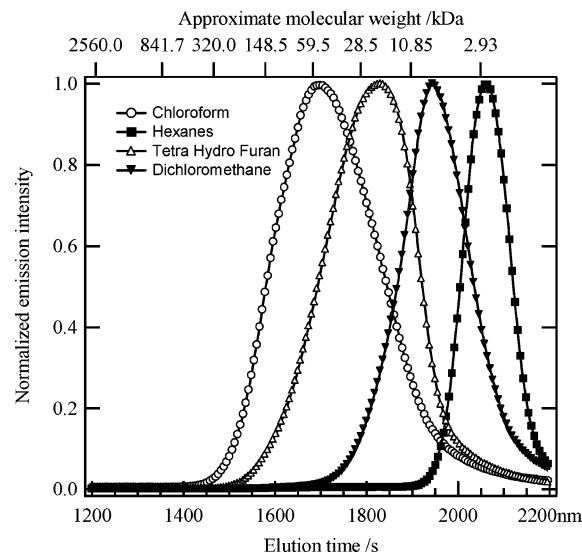


Figure 1. Gel permeation chromatography (GPC) results for Aldrich P3HT. Signal is emission intensity vs elution time. Different fractions shown have been extracted using the different solvents as discussed in the text.

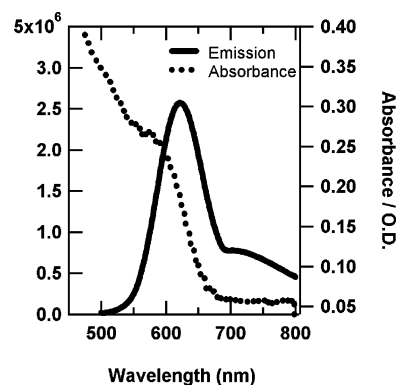


Figure 2. Electronic absorption (dotted line) and emission (solid line) spectra for solvated InP quantum dots.

GPC measurement, the PL intensity of the conjugated polymer was recorded as a function of elution time. It can be seen that different solvents used in the extraction gave different molecular weight fractions. With the better solvents, higher molecular weight fractions were extracted. It should be noted that a literature comparison of GPC vs MOLBI TOFMS data shows the GPC technique to overestimate the molecular weight of P3HT.¹⁶ The dichloromethane extraction fraction was the one we chose for the PL quenching experiments; its molecular weight is approximately 11 kDa.

Figure 2 shows the electronic absorbance and emission spectra of the InP quantum dots solvated in chloroform. A more thorough discussion of these spectra has previously been published and is not within the scope of this brief discussion.¹⁷ Figure 3 shows the electronic absorbance and emission spectra of the P3HT fraction used in the PL quenching experiment. This figure is presented as an illustration to show that the experimental conditions in the quenching exercise were such that the signal was from the dots and not from the polymer (which has negligible absorbance at the wavelength of excitation). It should be noted that the polymer does not have a significant PL signal when excited at 600 nm, which was the excitation wavelength chosen for the subsequent InP quantum dot quenching experiments. It is important that the polymer remains optically inert

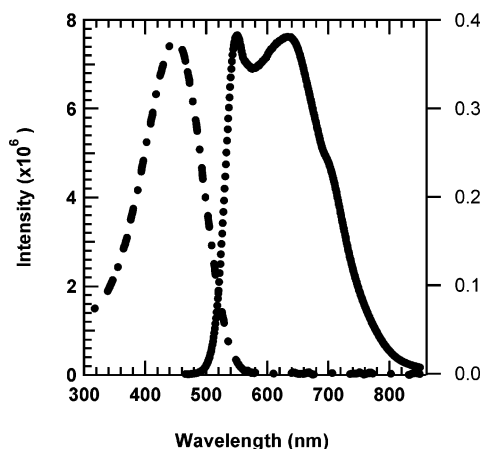


Figure 3. Electronic absorbance (dot dashed line) and emission (dotted line) spectra for P3HT. The dotted emission curve was excited at 440 nm.

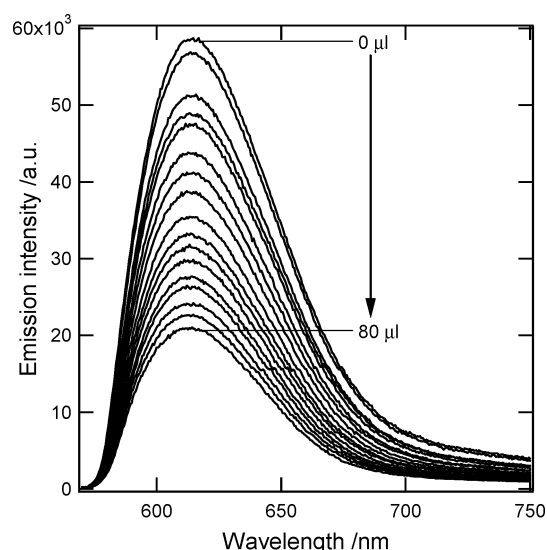


Figure 4. Steady-state PL measurement of a quantum dot solution (1.52×10^{-6} M) as aliquots of P3HT (0.8 g/L) are titrated in.

in this experiment. This is why we chose these particular InP quantum dots as they have a good optical absorption at 600 nm.

The PL quenching experiment was designed in such a way that we could expose the system (the cuvette) to visible light of the wavelength of 600 nm. This would selectively excite the InP quantum dots (which have a strong absorption at that wavelength), and not the P3HT. This has been experimentally confirmed by collecting emission spectra of the polymer excited at 440 nm and comparing that to spectra collected with 600 nm excitation. The amount of emitted light from the 600 nm excitation case is negligible. Therefore, when exciting at 600 nm, any emission that we observe would only be originating from the quantum dots. This experimental consideration should make interpretation of the results as straightforward as possible.

Figure 4 shows the PL results of our quenching experiment. We start with 100 μ L of quantum dot solution (1.52×10^{-6} M¹⁸); the peak for this scan exhibits the strongest PL intensity. Subsequently, we iteratively titrate in 5 μ L of the P3HT solution (0.8 g/L solution). The data presented in Figure 4 have been corrected for the dilution factor experienced by the quantum dots PL with each 5 μ L addition. It can clearly be seen that the presence of the conductive polymer decreases the intensity of the quantum dots' steady-state PL spectra. We suggest that the

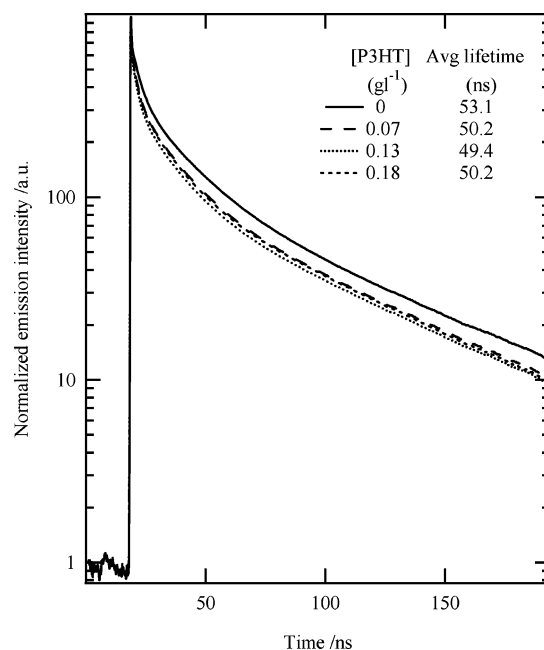


Figure 5. Time-resolved PL measurements of an InP quantum dot sample as aliquots of P3HT are titrated in; the Y-axis is shown in the log scale.

observed PL quenching may arise from hole transfer from the excited quantum dot to the polymer after a diffusion-controlled encounter. We will attempt to establish this in the discussion section.

We also conducted TRPL experiments on this system as the polymer was titrated into the solution. The results are shown in Figure 5. Here the sample was excited with 632 nm (pulsed) light and the emission was monitored at 650 nm. These transients were fit using eqs 1 and 2, this fitting is discussed

$$I(t) = \sum_{i=1}^n \alpha_i \exp(-t/\tau_i) \quad (1)$$

$$\tau_{\text{avg}} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2 + \alpha_3 \tau_3^2 + \alpha_4 \tau_4^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3 + \alpha_4 \tau_4} \quad (2)$$

below. Here, it can be seen that the addition of polymer does not have a dramatic effect on the average lifetime of the quantum dots. This suggests that we are observing static quenching. Thus, when the quenching species encounters the lumophore (and eliminates the PL) it "sticks" and pulls that particular dot from the rest of the emitting population. To the author's knowledge, this is the first report of this sort of behavior between semiconductor quantum dots and π -conjugated organic systems. This may shed some light on the overall mechanism of quenching, and may have an impact on our understanding of the dot-polymer intermolecular interaction.

The average lifetimes were determined by allowing α_i and τ_i to vary, and then convoluting eq 1 with the instrument response function. This was then iteratively fitted to the data (this is described in the Experimental Section). It is clear from Figure 4 that the decays could not be fitted to a single exponential. The data were successfully modeled using four exponentials, and the average lifetime was determined using eq 2. In both equations t is time, τ is lifetime, and α is a pre-exponential factor. The use of a sum of exponentials (up to four) to model the luminescence decay of the photoluminescence of semiconductor quantum dots is not uncommon. This is due to the

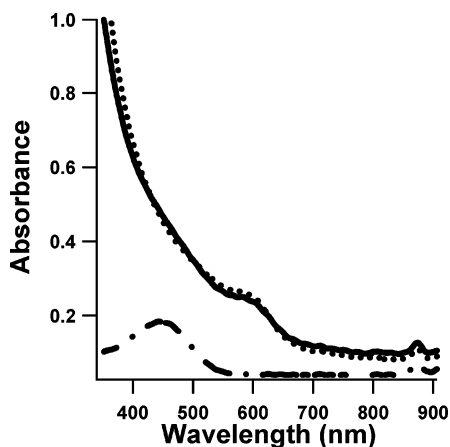


Figure 6. Electronic absorption spectra for the polymer solution (dot dashed line), the InP quantum dot solution (dotted line), and the mixture of dots and polymer (solid line).

numerous decay paths that can influence the nonradiative decay mechanisms of the exciton. The population and depopulation of variable-depth trap states is one such example. Recent studies on CdSe quantum dots have shown that monoexponential decays can only be observed for isolated quantum dots, and then, only measured when the dots, which blink, are >95% in their full “on” state.¹⁹ The use of multiexponentials in this fitting does not give us the strongest sense of the true lifetime of these dots. However, the main idea to be learned from this experiment is that the lifetime is *relatively* unchanged by the addition of the polymer.

A similar quenching experiment was conducted with the same quantum dots and poly(vinylcarbazole) (PVK) as the polymer for a control. Due to the large band-gap of the PVK, we expect the alignment of the valence bands of the two semiconductors to be unfavorable for hole transfer from the valence band of the quantum dot to the highest occupied molecular orbital (HOMO) of the PVK (5.8 eV). We observed no change in the PL signature (after dilution correction) of the quantum dots when the solvated PVK was added to the solution.

We collected the electronic absorption spectrum of the solution containing both the InP quantum dots and the P3HT. This spectrum is shown in Figure 6, with the absorption spectra for individual components shown for comparison. It can be seen that there are no new peaks or significant shifts in this spectrum of the mixture.

Discussion

With regard to the solar energy conversion scheme mentioned in the Introduction, the materials chosen for these studies are quite promising. For a good device we need charge generation, separation, and collection. The InP quantum dots generate the charge carriers by the absorption of a visible photon. It has been shown that the electron can effectively be transferred to a metal oxide,⁶ illustrating one-half of the charge-separation step. The question that needs to be addressed here is: does the new data presented here illustrate a hole transfer event that would constitute the completion of charge-separation in a solar energy conversion scheme?

It has been shown that a hole can be transferred from an excited semiconductor quantum dot to an organic donor molecule with experimental techniques such as PL quenching and transient absorption spectroscopy.²⁰ Other groups have demonstrated a working solar cell with hybrid quantum dot/

organic polymeric devices (indirectly inferring that the quantum dot transfers the photoexcited hole to the p-type polymer).²¹ The work presented here aims to use carefully chosen straightforward experiments to fundamentally show that the photoexcited hole in the sensitizing dots can, potentially, be transferred to the organic polymeric hole-conducting material.

Because the steady-state PL of the quantum dot is quenched by the addition of the P3HT (Figure 4), we can say that there is some kind of interaction between the two. To the author’s knowledge, this is the first time that a solution phase experiment has been conducted on an InP quantum dot/P3HT matrix. That the time-resolved PL lifetime is independent of the concentration of the P3HT tells us that the interaction is not diffusion limited. This suggests the possibility that the quantum dot and polymer irreversibly interact in such a way that the product of said interaction no longer emits. This could be through a chemical reaction or a strong adsorption.

An initial consideration would be to ask if the product of a quantum dot/polymer encounter is even photoexcited in this investigation, i.e., is the quantum dot/P3HT complex transparent to the 600 nm light used in the quenching experiment? By considering the absorption spectrum shown in Figure 6, we can discount this concern. Because the first excitonic peak for the quantum dot is not diminished or shifted in energy when the dots are in the presence of the polymer, we suggest that there is no change in the electronic structure of the InP quantum dot. This implies that when the dots are excited by 600 nm light, photons are absorbed by the quantum dot. Therefore in this quenching experiment, the quantum dots are photoexcited.

We will now address the challenge of assigning a reasonable mechanism to this quenching event. We shall put forward four possible routes: chemical passivation of the radiative recombination center, the existence of a long-lived photoinduced charge-transfer complex, energy transfer, and excited-state charge transfer.

The case of chemical passivation involves the polymer undergoing a chemical reaction with the InP dots when introduced to the solution. This reaction could proceed without photoexcitation. There is a literature precedent for such quenching to occur.²² If it were the case that there was a chemical reaction between the two, it might be that the breaking and making of a chemical bond would have an impact on the absorption spectrum, shifting the absorbance such that the product did not adsorb the light used in our experiment. Without photoexcitation, there can be no PL; thus, quenching would be the observed outcome. However, since there is no significant change in the electronic absorbance spectrum when the two species are blended (as seen in Figure 6), the case of a nonphotochemical reaction leading to quenching in this system is not a strong one.

The case of a photoinduced charge-transfer complex causing the quenching is interesting to consider after the above discussion. In this case, a different mechanism than discussed above would be responsible for the observed quenching. In the ground state, the quantum dot and the P3HT may be neighbors in solution, but they have not undergone a chemical reaction. When photons are incident on the donor–acceptor pair, the resultant electronic transition is very different from the electronic absorbance transition of the free quantum dots and polymers.^{23–25} That is to say, according to Mulliken theory, a charge-transfer complex exhibits a different absorbance spectrum than when the donor and acceptor are independent. So, like the case of chemical reactivity, we can use the absorbance spectrum of the mixture from Figure 6 to dismiss this case.

Energy transfer from the quantum dots to the larger band gap P3HT is not thermodynamically favorable. Below is a discussion and a possible energy diagram showing feasible relative band alignments; it will become apparent then, in any permutation of band alignment of the small band gap InP quantum dot and the large band gap P3HT, that both hole and electron transfer from the quantum dot to the polymer is not exothermic. By consideration of the electronic absorption and emission of the two species (Figures 3 and 2), one can see that any photons emitted by the InP dots will be transparent to the P3HT. If there were any sort of nonradiative energy-transfer mechanism in operation, one might expect to observe an increase in the number of photons emitted from the polymer. A pathway out of the quantum dot's excited state would lead to some number of polymer molecules being in the excited state (of which some fraction would result in radiative recombination). By considering Figure 4, we can see that, as polymer is added to the cell, there is no increase in the signal at 650 nm. We are currently investigating other contrasting systems of different semiconductor quantum dots and π -conjugated organics where this is not the case (i.e. different materials that do exhibit energy transfer instead of charge transfer). However, for these InP quantum dots and P3HT, energy transfer is not a likely mechanism by which the PL is quenched.

The final mechanism that will be covered in this discussion will be excited-state charge transfer. In this scenario, a photon of light is absorbed by the quantum dot and a pair of excited-state charge carriers is created. These may radiatively recombine, or there may exist a competing, nonradiative pathway out of the excited state. A charge-transfer event would be such a competing nonradiative pathway out of the excited state. This was the case reported by Blackburn et al. where excited InP quantum dots transferred an electron to TiO_2 .⁶ Whereas said study did involve InP as the sensitizer, it was a metal oxide that the quantum dots were paired with, which is different than what is presented here. Due to the relative conduction band edge alignment in that system, they observed electron transfer. In this article, we address a different pairing material (P3HT) with different valence band edge alignments. In any case, we bring up that literature example specifically to illustrate the idea of a charge transfer between quantum dots and other semiconducting materials. As we were able to dismiss the other mechanism options with our experimental observations, we feel that the excited-state charge-transfer event is the most reasonable mechanism for this quenching. More work is being conducted to clarify this contention (specifically transient absorbance studies).

It may also be of interest to consider an energy diagram of this system. Figure 7 shows a simple energy level diagram for the InP quantum dot/P3HT interface. This particular alignment would favor hole transfer.

In this instance hole transfer from the quantum dots to the polymer would be favorable. If the InP dots were photoexcited and P3HT were added, the hole transfer would result in the quenching of the PL of the quantum dots. The authors admit that there is a variety of different band edge offsets possible. However, the amount of effort needed to correctly address this issue is beyond the scope of our funding. We present this energy diagram only to illustrate that it is possible for hole transfer to occur in this system, and this diagram is not inconsistent with our experimental observations reported in this document.

Conclusions

The addition of P3HT to a solution of colloidal InP quenches the photoluminescent emission of the capped InP semiconductor

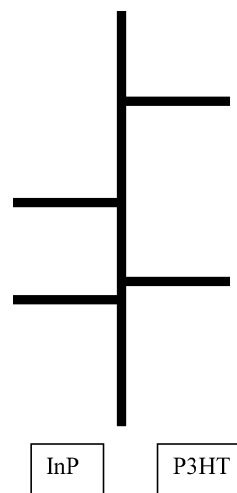


Figure 7. Cartoon energy level diagram illustrating a potential band-alignment configuration. The alignments shown are based on the results in this paper.

quantum dots. This suggests that the excited InP quantum dot transfers its hole to the conductive polymer. What we have presented here are proof-of-concept results that suggest that the proffered InP quantum dot/polymer composite may be a suitable candidate for a real world solar energy conversion device. The time-resolved PL experiments show that this emission is quenched statically. The fact that quantum dot/conjugated polymers composites make functional solar cells suggests that there is charge transfer between the two. These new results show that there is a strong interaction between the quantum dot and the polymer. Work is currently underway to more thoroughly understand this mechanism and its impact on solar energy conversion efficiency.

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