Charge transfer between acenes and PbS nanocrystals

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Abstract
Organic–inorganic hybrid heterojunctions have potential as the basis for future photovoltaic
devices. Herein, we report the results of investigations exploring the possibility of using
pentacene and tetracene as photoelectron donors in conjunction with PbS nanocrystals
(PbS-NCs). Photoinduced charge transfer was probed using external quantum efficiency
measurements on acene:PbS-NC hybrid photovoltaic devices in conjunction with
photoluminescence studies of the corresponding bilayer films. It is shown that photoelectron
transfer from pentacene to the PbS-NCs is inefficient as compared to that between tetracene and
PbS-NCs. The latter case can be rationalized in terms of the energy level alignment at the
heterojunction assuming a common vacuum level. However, in the case of pentacene:PbS-NC
junctions an interfacial energy level shift must be considered in order to explain the
observations.

1. Introduction

Narrow band gap semiconductor nanocrystals and organic
semiconductors (both polymer and small molecule) can
be used in combination to fabricate hybrid heterojunction
photovoltaic (PV) devices [1, 2]. To this end we
have recently demonstrated a promising PV system based
on PbS nanocrystals (PbS-NCs) and C_{60} which exhibited
photocurrents up to $\sim$5 mA cm^{-2} under AM1.5G [3]. In this
bilayer PV system the PbS-NCs functioned as the primary
light harvester and electron donor. Notably the contribution
to the photocurrent made by the C_{60} acceptor was found to be
much smaller than the PbS-NCs, consistent with the lower light
absorption coefficient (α) of C_{60} [4]. Utilization of an organic
component with greater light harvesting capability than C_{60}
has potential to increase the photocurrent in a PbS-NC based
hybrid PV device. This paper reports investigations exploring
the use of small molecule organic semiconductors pentacene
and tetracene (acenes) as the organic counterpart with PbS-
NCs in hybrid PV devices. Pentacene and tetracene absorb
visible light strongly ($\alpha \sim 10^5$ cm^{-1}) (.ibid), exhibit higher
hole mobilities (0.1–1 cm^2 V^{-1} s^{-1} [5]) and are promising

donor materials when used in conjunction with C_{60} [6, 7].
Photoinduced charge transfer between the acenes and the PbS-
NCs are studied and rationalized using energy band diagrams
formulated from direct measurements. The objective of the
work carried out is the identification of suitable acenes which
potentially would function as efficient electron donors to PbS-
NCs to fabricate hybrid photovoltaic devices.

2. Experimental details

Oleic acid ligand capped PbS-NCs were synthesized according
to a method reported elsewhere [8]. All chemicals were
analytical reagent grade and were used as received. 900 mg
of lead oxide (Sigma-Aldrich, 99.9%) was mixed with 1.6 g
of oleic acid (Sigma-Aldrich, tech. 90%) and 40 ml of 1-
octadecene (Fluka, $\geqslant$95%), and the mixture was heated to
130 °C under nitrogen and maintained at this temperature for
30 min. 20 ml of a stock solution, obtained by mixing
5 ml of hexamethyldisilthiane (Fluka) and 240 ml of 1-
octadecene, was rapidly injected into the lead oleate precursor
and kept at 70 °C for 20 min. Following this the PbS-NCs

were precipitated out by adding acetone and suspended in anhydrous chloroform. Prior to device fabrication the oleic acid ligands of PbS-NC were exchanged to shorter butylamine ligands. To perform ligand exchange, the PbS-NCs were dried under nitrogen and then resuspended in an excess of butylamine (Fluka, 99.5%) [9]. After standing for 72 h the PbS-NCs were precipitated out by addition of an excess of isopropanol and re-dispersed in chloroform. This process was repeated several times for purification purposes. Subsequently the PbS-NCs were dissolved in toluene at a concentration of 70 mg ml^{-1} for device fabrication. Approximate nanocrystal size was measured as 4 nm by transmission electron microscopy. Optical absorption characterization of the active layers was performed using a Varian Cary 5000 UV–vis–IR spectrophotometer. Photoluminescence (PL) of tetracene thin films deposited on glass was carried out using a Varian Eclipse Fluorescence spectrophotometer. PL of pentacene thin films, deposited on cleaned silicon wafer, was measured using an argon ion laser operating in multiline ultraviolet (UV) wavelengths (80 mW). For all acene single layer and bilayer samples the PL was obtained by optically exciting the samples at an angle to the plane of the substrate from the top side where the acene layers were deposited. Subsequently the PL emission, normal to the plane of the substrate, was collected through the same side and focused on to the entry slit of the monochromator. Using the absorption coefficients of the respective acenes it is found that teteracene and petacene layers absorb approximately 46% and 7% of the excitation, incident normal to the substrate, at 510 nm and 360 nm, respectively. PL measurements of PbS-NC thin films deposited on glass substrates were carried out using a laser diode operating at 658 nm following identical procedure as above.

PV devices were fabricated on indium tin oxide (ITO) (20 Ω/□) coated glass cleaned using a three stage ultrasonic bath treatment in toluene, an aqueous surfactant solution and acetone. Immediately prior to use, the ITO substrates were subjected to oxygen plasma treatment for 5 min. Discrete heterojunction PV devices were fabricated by evaporation of 50 nm of the organic layers (pentacene or tetracene) under vacuum (10^{-5} Torr) at a deposition rate of ∼0.1 nm s^{-1} onto the ITO substrates. PbS-NCs were spin coated at 2000 rpm for 60 s on pre-deposited acene films. Thickness of the PbS-NC film was measured as ∼100 nm using atomic force microscopy measurements. Higher spin speeds (2000 rpm) were used to minimize damage to the underlying acene layers, which were observed to be weakly soluble in toluene. An Al top contact was deposited through a shadow mask to fabricate PV devices with ∼10 mm^2 active areas. Current density–voltage (JV) measurements were carried out using a Keithley 2400 source meter under AM1.5G solar irradiation using an Oriel 81160 class B solar simulator. External quantum efficiency (EQE) measurements were carried out using an automated setup including a Bentham IL1 (100 W) quartz halogen light source, a Bentham TMc 300 monochromator, Keithley 487 picoammeter, a Newport 1830C optical power meter, and 818-SL, 818-IG photodetectors.
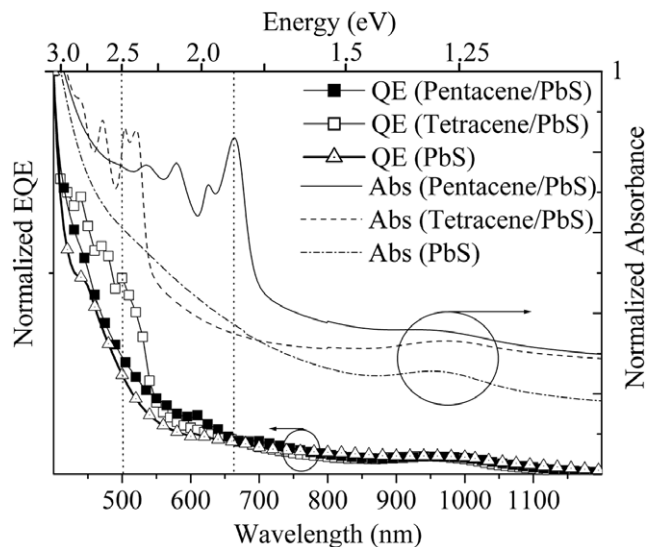

Figure 1. Absorbance (normalized) spectra of pentacene (50 nm)/PbS-NC (100 nm) (black line), tetracene (50 nm)/PbS-NC (100 nm) (dashed line) and PbS-NC (100 nm) single layer (dash–dot–dash line). Normalized EQE measurements of pentacene (50 nm)/PbS-NC (100 nm) (black squares), tetracene (50 nm)/PbS-NC (100 nm) (white squares) and PbS-NC (100 nm) single layer device (white triangles). Each spectrum is normalized by dividing the points by the maximum signal.

3. Results and discussion

Figure 1 shows the normalized EQE and absorbance spectra of pentacene (50 nm)/PbS-NC (100 nm) and tetracene (50 nm)/PbS-NC (100 nm) devices. The absorbance of pentacene/PbS-NC comprises the superposition of pentacene absorption (665–535 nm) with that of the PbS-NCs. Similarly, the absorbance of the tetracene/PbS-NC bilayer consists of the absorption of tetracene (525–450 nm) together with the contribution from PbS-NCs. The EQE measurement is used to probe the ratio between the number of photo-generated electrons collected at the contacts to the number of incident photons and is used as a standard technique to quantify contributions from the different light harvesting components comprising a PV device. The tetracene/PbS-NC device exhibits a response in the 525–450 nm region not present in the single layer PbS-NC device. This increase in EQE, indicated by the vertical dotted line at 500 nm in figure 1, correlates with the primary excitonic absorption of tetracene at 500 nm (2.5 eV). This is compelling evidence that excitons created by photo-absorption in tetracene dissociate at the tetracene/PbS-NC interface contributing to the photocurrent generated from the device. Conversely, for the pentacene/PbS-NC system, the increase in the EQE, relative to the EQE of PbS-NC single layer device is very small at the primary excitonic absorption of pentacene—indicated by the dotted line in figure 1 at 663 nm (1.9 eV)—evidence that pentacene does not contribute to the photocurrent.

To corroborate the EQE measurements, PL studies were carried out for the pentacene (50 nm)/PbS-NC (100 nm) and tetracene (50 nm)/PbS-NC (100 nm) bilayer samples. A commensurate reduction of the donor PL intensity generally
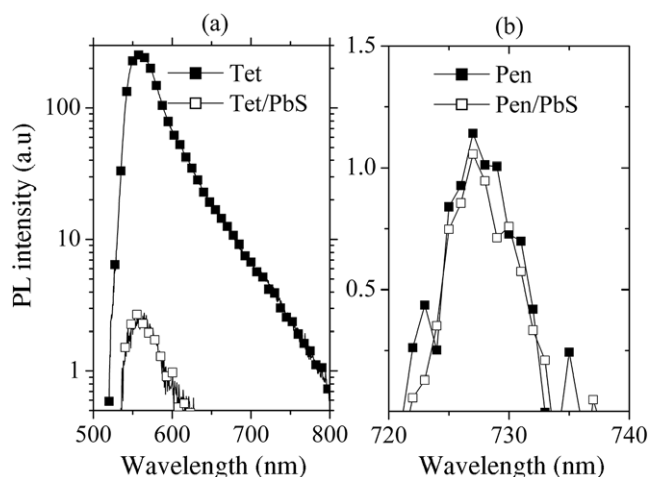
Figure 2. (a) PL of tetracene (50 nm) (black squares) and tetracene (50 nm)/PbS-NC (100 nm) (white squares) measured by exciting at 510 nm. (b) PL intensity of pentacene (50 nm) (line with black squares) and pentacene (50 nm)/PbS-NC (100 nm) (line with white squares) excited in multiline UV.


Figure 3. (a) EQE of the PV devices: pentacene (50 nm)/PbS-NC (100 nm) (white squares), tetracene (50 nm)/PbS-NC (100 nm) (dark squares) and PbS-NC (100 nm) single layer device (white triangles). (b) PL intensity of PbS-NC (white triangles), pentacene/PbS-NC (white squares) and tetracene/PbS-NC (dark squares) excited at 658 nm.

indicates the presence of a dominant photoinduced charge transfer process between donor–acceptor species [10]. In order to clearly observe any PL quenching effects within the acene/PbS-NC bilayer systems the acene film thickness deposited taking to account their exciton diffusion lengths (pentacene: 65 ± 16 nm [6] and tetracene: 12 ± 1 nm [11]).

Figure 2(a) shows a comparison of the PL intensity of a tetracene film as compared to a tetracene/PbS-NC bilayer. The PL intensity at 560 nm from tetracene in the bilayer is two orders of magnitude lower than that from the single layer. Such strong quenching of the PL intensity can be attributed to efficient photoinduced charge transfer from the tetracene layer to PbS-NCs and is consistent with the peaks in the EQE data (figure 1). To rationalize the magnitude of quenching (>100 folds) of the 50 nm film of tetracene, taking in to account its small exciton diffusion length (12 nm), we postulate that a large exciton population has to be generated close to the heterojunction. This type of spatial distribution of excitons can originate as a result of the excitation angle as well the surface roughness of the interface. Similarly, a PL study was carried out on pentacene/PbS-NC bilayer and pentacene single layer thin films. High energy photon excitation (Ar ion laser operating at multiline UV at 80 mW) was utilized for the pentacene samples due to the low PL yield of thin film pentacene [12]. Figure 2(b) shows the PL intensities of pentacene/PbS-NC bilayer and pentacene single layer films which demonstrates PL with similar magnitudes without any significant quenching. This provides evidence that excitons formed in the pentacene layer are not quenched at the heterojunction with PbS-NC, although the intrinsically low PL intensity from the pentacene films is characteristic of extremely short lived singlet states which rapidly convert to non-emissive states such as charge transfer or triplet states. Whilst the latter two could also contribute to photocurrent generation in the device, the shape similarity between the EQE response of devices with and without pentacene (figure 1) supports the
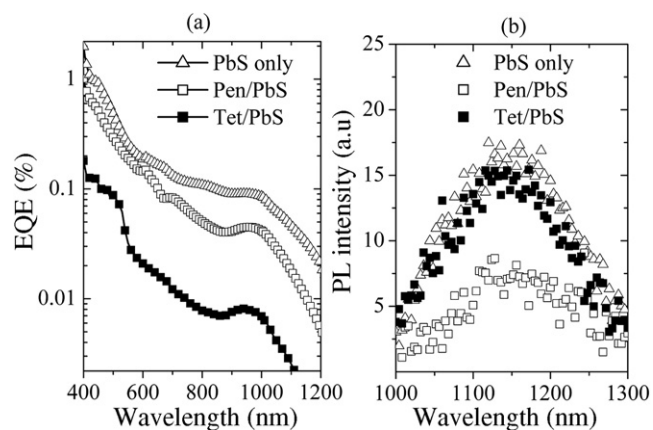
conclusion that excitons formed in the pentacene layer are not efficiently quenched at the heterojunction with PbS-NCs.

Similarly, experiments were carried out to investigate the photoinduced charge transfer from the PbS-NCs to the acene layers. Figure 3(a) shows the EQE measurements for pentacene (50 nm)/PbS-NC (100 nm) and tetracene (50 nm)/PbS-NC (100 nm) bilayer and PbS-NC (100 nm) single layer devices. An EQE peak in the spectral range between 950 and 1000 nm is seen for all three device structures. This peak correlates with the primary excitonic optical transition in the PbS-NCs (figure 1) and is evidence that excitons formed in the PbS-NCs are contributing to the generated photocurrent in these systems. PL emission from the PbS-NC layers were measured in pentacene/PbS-NC and tetracene/PbS-NC bilayers and compared to that of PbS-NC single layer films (figure 3(b)). It is evident that PL emission from PbS-NCs in pentacene/PbS-NC bilayer is lower than the PbS-NC single layer, indicating quenching of excitons in PbS-NC layer at the heterojunction. Conversely, tetracene/PbS-NC showed similar PL intensity to pristine PbS-NC single layer film, indicating that excitons formed in the PbS-NC are not quenched at the heterojunction with tetracene. Furthermore, it is also evident from figure 3(a) that the tetracene layer seriously deteriorates the efficiency with which charge carriers are extracted to the external circuit.

In order to rationalize the EQE and PL measurements a schematic zero field energy level diagrams, shown in figure 4, are constructed using the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energies of the active materials. LUMO and HOMO values of pentacene (3.0 and 4.9 eV [6]) and tetracene (3.0 and 5.4 eV [13]) were obtained from literature. The ionization potential (HOMO) of the PbS-NCs were measured as 5.2 eV using cyclicvoltammetry techniques described in our previous work [14]. The electron affinity (LUMO) of the PbS-NC is calculated as 4.2 eV by subtracting the optical bandgap (1 eV),
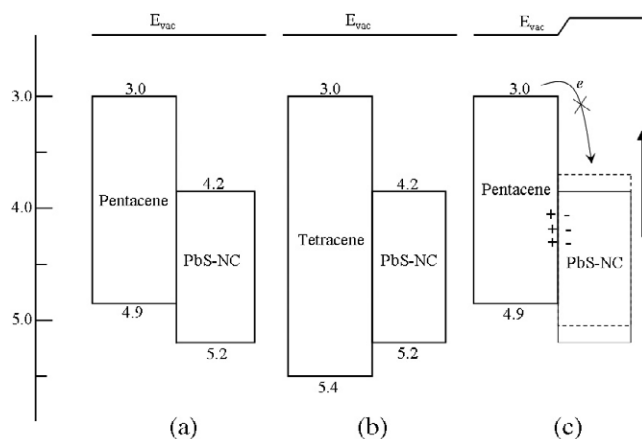
Figure 4. (a) Pentacene/PbS-NC, (b) tetracene/PbS-NC flat band energy diagrams. (c) shows the interfacial vacuum level shift at pentacene and PbS-NCs.

obtained from the absorption onset, from the above ionization potential value of PbS-NCs.

It is possible to rationalize all of the observations pertaining to the tetracene/PbS-NC heterojunction based on the figure 4(b), which assumes a common vacuum level across the junction. Strong PL quenching of the tetracene seen in figure 2(a) is driven by the large offset in the LUMO of the tetracene and the conduction band of the PbS-NCs (>1 eV). Conversely, quenching of the excitons formed in PbS-NCs is not facilitated (figure 3(b)) by the tetracene layer since the PbS-NC band gap is positioned within the HOMO–LUMO gap of tetracene. The low EQE in devices employing tetracene can therefore be understood from the existence of the offset between the PbS-NC valance band and the HOMO of tetracene, which impedes extraction of holes deteriorating the efficiency with which free carriers are extracted to the external circuit.

Contrary to the tetracene/PbS-NC system discussed above, the charge transfer phenomenon, observed from figures 1 and 2(b), occurring at the pentacene/PbS-NC heterojunction is more difficult to rationalize based on the band diagram proposed in figure 4(a). It is seen that excitons formed in pentacene, which is reported to have lower exciton binding energy relative to tetracene [15], do not contribute to photocurrent generation despite a favourable frontier molecular offset at the heterojunction. A phenomenological explanation is provided to understand the above, postulating a hitherto unknown interfacial effect between pentacene/PbS-NCs. It is now well established that the assumption of a common vacuum level across organic–organic and organic–inorganic interfaces is often invalid due to the spontaneous formation of a dipole layer at the heterojunction [16–18]. Whilst there are a number of possible mechanisms for dipole layer formation, including ground state charge transfer, chemical bond formation or electron cloud push-back effects [16] the result is an abrupt shift in the relative position of the energy levels of the two materials comprising the heterojunction. We propose that such a dipole layer exists at the interface between pentacene and PbS-NC as a result of ground state charge transfer from the HOMO of pentacene into surface states in the band gap of PbS-NC (figure 4(c)). The existence of surface states with energies in the band gap of inorganic semiconductors is well documented and gives rise to the phenomena of Fermi level pinning [19, 20]. In this case the resulting dipole would raise the energy levels of the PbS-NC with respect to the pentacene, as depicted in figure 4(c). Whilst it remains thermodynamically favourable for electrons in the LUMO of pentacene to transfer to the conduction band of PbS-NCs, the interfacial dipole would act to impede charge transfer such that relaxation to the ground state occurs preferentially to exciton dissociation. Under these circumstances the pentacene layer would not contribute to light harvesting consistent with the experimental finds. Notably this mechanism would not be operative at the tetracene/PbS-NC interface since the band gap of PbS-NC lies between the HOMO and LUMO levels of tetracene (figure 4(b)). Whilst this model offers a simple explanation for the failure of pentacene to contribute to the photocurrent in PbS-NC/pentacene photovoltaics, more complex explanations cannot however be ruled out.

4. Conclusion

In summary, the results of investigations exploring the possibility of using pentacene and tetracene as light harvesting donor materials in conjunction with PbS nanocrystal films are reported. It is shown that photoelectron transfer from pentacene to the PbS-NCs is inefficient as compared to that between tetracene and PbS-NCs. Whilst, the latter can be rationalized in terms of the interfacial energy level alignment assuming a common vacuum level, the former cannot be explained without considering the role of trap states at the PbS-NC surfaces. This work serves to highlight the complexities that can arise at organic–inorganic semiconductor interfaces and is significant for design and fabrication of hybrid photovoltaic devices.

Acknowledgments

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