

Effect of Interface on Charge Transfer Dynamics in Hybrid Polymer:CdSe Photovoltaics

Elsa Couderc^{1,2}, Matthew J. Greaney^{1,2}, Stephen E. Bradforth^{1,2}, and Richard L. Brutchey^{1,2}

¹Department of Chemistry, University of Southern California, Los Angeles, CA 90089, United States

²Center for Energy Nanoscience, University of Southern California, Los Angeles, CA 90089, United States

Email: brutchey@usc.edu

Introduction. In 2002, Alivisatos and co-workers reported the first example of a hybrid BHJ solar cell by blending poly(3-hexylthiophene) (P3HT) with CdSe nanocrystals.¹ Semiconductor nanocrystals possess several attributes that make them attractive substitutes for fullerene acceptors; namely, (i) tunable band gaps, (ii) strong, broad absorption, (iii) high dielectric constants to help overcome the strong exciton binding energy of conjugated polymers, and (iv) high electron mobilities.² Furthermore, the ability to tune the morphology of semiconductor nanocrystals can be used to improve device performance, with anisotropic nanorod acceptors facilitating directional electron transport along their principal rod axis, thereby reducing the number of electron hopping events required for charge collection. While power conversion efficiencies for hybrid BHJ solar cells have reached ~5-6% after just one decade of research,³ their device performance still lags behind both calculated predictions and that of their all-organic counterparts utilizing fullerene acceptors.

Interface Engineering with Organic Ligands. It is generally thought that a major contributor to the efficiency gap in hybrid BHJ solar cells is the intrinsic surface states on semiconductor nanocrystals.⁴ We have focused on a design criterion to improve hybrid BHJ solar cells that is unique to these systems and that can also directly address this issue of surface states; that is, the ability to molecularly tune the donor/acceptor interface with organic ligands. Prior to our work, the principal rationale behind this concept had been to remove the native insulating ligands from the nanocrystal surface to better facilitate charge transfer and charge collection. We introduced another effect within this context, which is the ability for ligands to contribute to the HOMO/LUMO energies of the semiconductor nanocrystal and consequently affect the energy offset (ΔE_{DA}) between the HOMO of the donor and the LUMO of the nanocrystal acceptor. As the LUMO energy of the semiconductor nanocrystal is increased relative to the HOMO of the donor *via* ligand exchange, the open circuit potential (V_{OC}) of the device can be maximized to increase the device performance of the hybrid BHJ solar cells.

Rationally introducing small, strongly binding, electron-donating ligands such as *tert*-butylthiol enables improvement in the open circuit potential of hybrid BHJ solar cells by raising the LUMO energy level of the nanocrystal acceptor phase.^{5,6} Hybrid BHJ solar cells fabricated from blends of *tert*-butylthiol-exchanged CdSe nanocrystals and P3HT achieved power conversion efficiencies of 2.0%. Compared to devices made from pyridine-exchanged ($V_{OC} = 0.57$ V) and non-ligand exchanged CdSe ($V_{OC} = 0.70$ V), the thiol-exchanged CdSe nanocrystals were found to consistently exhibit the highest open circuit potentials with $V_{OC} = 0.80$ V. The high open circuit potential associated with devices using

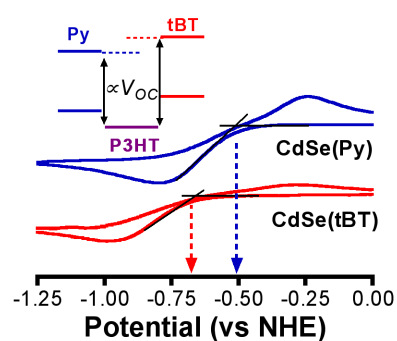


Fig 1. Cyclic voltammograms for CdSe nanocrystals exchanged with *tert*-butylthiol and pyridine demonstrating a higher lying LUMO for the thiol-exchanged nanocrystals.

the *tert*-butylthiol-exchanged acceptors is attributed to an elevated nanocrystal LUMO energy relative to the HOMO energy of P3HT, which produces the greatest ΔE_{DA} of the three ligand types investigated (**Fig. 1**). The highest power conversion efficiency that has been achieved using this ligand construct is with the low band gap PCPDTBT donor polymer ($\eta_{\text{champ}} = 4.1\%$).⁷

Despite improving device performance in hybrid BHJ solar cells, the physical mechanisms that occur at the organic/inorganic interfaces are still poorly understood – in particular the formation and evolution of charge transfer states and of mobile charge carriers. Consequently, direct measurement of the charge transfer processes in hybrid blends is of particular interest. We explored a PCPDTBT:CdSe hybrid BHJ utilizing *tert*-butylthiol-exchanged CdSe nanocrystals by ultrafast transient absorption spectroscopy to probe the carrier dynamics.⁸ By selectively pumping the low band gap PCPDTBT polymer, we have been able to determine that electron transfer from the polymer to the nanocrystal happens on an ultrafast timescale < 65 fs through observation of an unambiguous spectral signature for the reduced quantum dot acceptor (**Fig. 2**). From this timescale, the coupling between the polymer chains and the quantum dots is estimated to be $J \geq 17$ meV. The amplitude of the unambiguous spectral bleach signature on the reduced quantum dot acceptors allows for the first direct calculation of the absolute electron transfer yield in a hybrid solar cell ($82 \pm 5\%$). We also demonstrated that a limitation of the hybrid BHJ is rapid and measurable geminate recombination due to the small separation of the initial charge pair. The fast recombination is consistent with the internal quantum efficiency of the corresponding solar cell. We therefore have identified and quantified a main loss mechanism in this type of third generation solar cell.

References

1. Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425-2427.
2. McGehee, M. D. *MRS. Bull.* **2009**, *34*, 95-100.
3. Liu, Z.; Sun, Y.; Yuan, J.; Wei, H.; Huang, X.; Han, L.; Wang, W.; Wang, H. Ma, W. *Adv. Mater.* **2013**, *25*, 5772-5778.
4. Moule, A. J.; Chang, L.; Thambidurai, C.; Vidu, R. Stroeve, P. Hybrid Solar Cells: Basic Principles and the Role of Ligands. *J. Mater. Chem.* **2012**, *22*, 2351-2368.
5. Greaney, M. J.; Das, S.; Webber, D. H.; Bradforth, S. E.; Brutchey, R. L. *ACS Nano*, **2012**, *6*, 4222–4230.
6. Webber, D. H.; Brutchey, R. L. *J. Am. Chem. Soc.* **2012**, *134*, 1085-1092.
7. Greaney, M. J.; Araujo, J.; Burkhart, B.; Thompson, B. C.; Brutchey, R. L. *Chem. Commun.* **2013**, *49*, 8602-8604.
8. Couderc, E.; Greaney, M. J.; Brutchey, R. L.; Bradforth, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 18418-18426.