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Journal Name

An Intermediate Band Dye-sensitised Solar Cell Using Triplet-Triplet Annihilation

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A new mechanism of charge photogeneration is demonstrated for the first time, based on organic molecular structures. This intermediate band approach, integrated into a Dye-sensitised Solar Cell configuration is shown to generate charges upon illumination with low energy photons. Specifically 610 nm photoexcitation of Pt porphyrins, through a series of energy transfer steps and triplet-triplet annihilation, excites a higher energy absorption onset molecule, which is then capable of charge injection into TiO_2. Transient absorption measurements reveal further detail of the processes involved.

Introduction

Intermediate band (IB) solar cells are a compelling third-generation photovoltaic technology[1,2] in which the inclusion of an intermediate band between the valence and conduction bands allows for photovoltaic efficiencies potentially exceeding the Shockley-Queisser limit.[3] IB technology is however in its infancy, with only a handful of proof-of-concept devices reported to date.[4-7] Herein we report a novel IB device, based on triplet-triplet annihilation[8, 9] incorporated into a dye-sensitised solar cell.[10, 11] This device architecture can overcome impediments presently faced by other IB technologies, particularly the complex manufacturing requirements and is shown to provide photocurrent from sub-band gap light under non-concentrated solar illumination.

Conventional solar cells are defined here as possessing a single energy gap between the hole- and electron-conducting bands. In these devices, the greatest sources of inefficiency typically result from the transmission of sub-bandgap photons and charge thermalisation back to the band edges following the absorption of high energy photons.

In IB devices, a third absorbing band or state is introduced between the valence and conduction bands, where photoexcitation into the conduction band may now occur through two means: directly by the absorption of high energy photons or by the sequential absorption of two lower-energy photons via the intermediate state. This dual gap behaviour

significantly improves the limiting efficiency of a PV device from 31% to 41% under AM1.5 illumination.[12] To date, IB solar cells have been reported using quantum dots, deep level impurities, or highly mismatched alloys to generate the intermediate band.[13-17] Here we report a new IB solar cell based on organic light absorbers, proposed by Ekins-Daukes and Schmidt in 2008,[12] where the intermediate band effect is achieved by energy pooling in long-lived triplet excited states, shown schematically in Fig. 1 and in a step-by-step manner in Fig. S1. Furthermore, this is achieved in a simple device based on the dye-sensitised solar cell (DSC) architecture.

The device is comprised of two electrodes, prepared on conductive glass substrates, internally connected with a liquid electrolyte. In conventional DSCs a photoexcited dye (dye 1) can inject an electron into a semiconductor to which it is bound. The resultant cationic dye is subsequently regenerated by a redox electrolyte while the injected charge is removed to an external circuit before being recombined at the counter electrode, restoring the redox mediator. The IB DSC reported here builds on the standard DSC design by incorporating elements of triplet-triplet annihilation upconversion (TTA-UC) to afford IB behaviour. In TTA-UC systems, two independent donor molecules (dye 2) are photoexcited and intersystem cross to their respective first excited triplet states, T_1. The interaction between an excited dye 2 and a ground-state dye 1 molecule can lead to transferral of dye 2's energy and spin multiplicity to dye 1 through a Dexter mechanism, leading to a triplet state dye 1. Upon collision of two such triplet-excited dye 1 molecules, an encounter complex is formed in which one partner is promoted to the first excited singlet state, while the other is deactivated to the ground state, with preservation of net spin multiplicity. In essence, the energies of two low-energy photons are combined through TTA to form one higher energy excited state. A review further discussing TTA-UC systems can be found in Ref [8].

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For the purposes of incorporating TTA-UC elements into a standard DSC, dye 2, capable of absorbing lower-energy photons than the tethered dye 1, is introduced to the electrolyte solution. Photoexcitation of dye 2, is followed by rapid intersystem crossing to the first excited triplet state, T_1. As in TTA-UC systems, a suitable arrangement of energy levels in the dyes leads to efficient triplet energy transfer to dye 1, where TTA-UC itself may occur to generate a higher-energy injecting state. Thus, IB behaviour is achieved by energy pooling in the triplet state of the dye 1, allowing the absorption and harnessing of otherwise-wasted photons.

Experimental

Dye synthesis

4,4'-(anthracene-9,10-diylbis(ethyne-2,1-diyl))dibenzoic acid (BDCA) was synthesised based on the method presented by Yu *et. al.* (detail in section S3),[18] while tetrabenzotetraphenylporphyrin platinum (II) (PtTBPP) was acquired from Frontier Scientific.

Electrochemistry

Square wave voltammetry was performed on BDCA in a 0.3 mM solution with 0.1 M tetrabutylammonium perchlorate (TBAP) supporting electrolyte in N,N-dimethylformamide(DMF). Glassy carbon working, platinum mesh counter and silver wire pseudo reference electrodes were used and measured values calibrated against 1 mM ferrocene.

Optical characterisation

Absorption measurements were made on solutions using a Shimadzu 1800 photospectrometer. Photoluminescence measurements were completed on a customised Horiba Fluorolog FL3-221, using monochromated Xe lamp light and a PMT detector.

Transient Absorption Spectroscopy

Photoinduced changes in absorption were measured using a tuneable pulsed Nd:YAG laser pump (<5 mJ/mm^2, Spectra Physics Quanta Ray) and Xe white light probe (Edinburgh Instruments, Xe900), in conjunction with a monochromator and silicon photodetector (Femto, HCA-S-200M-SI).

DSC devices

A dense layer of TiO_2 was deposited on cleaned F:SnO$_2$ glass by a spray pyrolysis method . Onto this a commercial TiO_2 paste (Dyesol NR 18T) was screen printed, followed by sintering at 500°C. This was stained with 0.2 mM BDCA in 50:50 acetonitrile:ethanol overnight and rinsed extensively prior to being sandwiched into a device with a counter electrode of a platinised F:SnO$_2$ glass slide, using a 25 μm Surlyn® gasket. This was back filled with an electrolyte of $Co^{2+}(bpy)3(NTf)_2$ in DMF (with PtTBPP at saturation) and sealed with Surlyn backed aluminium foil. The device was measured using a 560 - 640 nm filter (Andover 600FS40-50), with current measured on a Keithley 2400 sourcemeter. Detailed construction protocols are in section S6.

Results and Discussion

Dye 1, the injecting species, is based on 9,10-Bis(phenylethynyl)anthracene (BPEA), after preliminary electrochemical measurements (Fig S2) showed that charge injection from BPEA into TiO_2 is electronically favourable from the S_1 state, but forbidden from the T_1 state, making the chromophore a good candidate for use in an IB system. In order to facilitate binding to TiO_2, a functionalised derivative, BDCA [18] (structure in Fig 1) was employed. Dye 2, the donor, was PtTBPP(Fig 1a), a commonly-employed triplet sensitizer in photon UC systems with BPEA,[19] on account of good spectral and electronic complementarity.

The energetics of the two chromophores were studied prior to device fabrication. Square wave voltammetry measurements of BDCA (Figure S4) confirmed that the addition of carboxylate linkers to the central BPEA structure has minimal effect on the redox potentials of the chromophore (S*/S$^+$ = -0.64 V vs. NHE). PtTBPP is phosphorescent in a deoxygenated solution (measured in DMF at room temperature), and the first excited triplet energy level was estimated at 1.72 eV from the phosphorescence spectrum (Fig S5.1). Photon UC is observed in deoxygenated solutions of PtTBPP and BDCA, as well as when BDCA is bound to an Al_2O_3 surface, which is structurally similar to TiO_2 however prohibits electron injection (Fig S5.1, S5.2). Hence we deduce that triplet energy transfer from PtTBPP to BDCA is energetically favourable, placing the BDCA triplet state in the range of $1.07 \leq T_1 \leq 1.72$ eV, where 1.07 eV is half the energy of the BDCA first excited singlet state.[15] The upper limit of BDCA(T_1) is therefore determined to be -0.15 V (vs. NHE), well below the conduction band edge of TiO_2. Previously BPEA(T_1) has been reported to be at ~ 1.53 eV.[21]

An IB DSC device, shown schematically in Fig 1b, was constructed with a BDCA-sensitized TiO_2 electrode and a solution with both PtTBPP and a cobalt-based electrolyte. Operation of the IB process in the device was demonstrated through two means: a photocurrent response when photoexcitation occurs via the IB mechanism, and pump-probe transient absorbance measurements of the BDCA-PtTBPP kinetics. For the former, the photocurrent response to excitation below the absorption threshold of BDCA was measured using incoherent light that was bandpass and neutral-density filtered to provide a 560 - 640 nm excitation source of variable intensity. A plot of photocurrent against excitation intensity (Fig 2b) shows a superlinear relationship with an exponent of 1.47, signifying multiple absorptions with energy pooling in the intermediate triplet state are required to generate injected charge. On the other hand, direct excitation of BDCA with different light intensities to yield similar current densities showed a near perfect linear regression (see Fig S7.2). Superlinearity arises from competition between TTA, which generates the injecting state, and nonradiative deactivation of the BDCA triplet state, such that at higher light intensities a larger triplet population exists to improve the quantum efficiency of TTA.[17] Unfortunately the comparatively low shunt resistances, in concert with low current densities, of the devices dominates the current-voltage responses under 560 - 640 nm illumination (see Fig S7.3).

Control devices made without BDCA showed no current response under the same conditions. Devices containing TiO_2-tethered BDCA

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but no PtTBTPP likewise exhibited no response, confirming the centrality of PtTBTPP in the first step of the IB DSC process (Fig S8.3). The near-linear light intensity dependence of photocurrent for directly excited BDCA eliminates trap-filling as a cause for superlinearity in the IB device under long wavelength illumination.

The IB mechanism shown in Fig 1 describes how photoexcitation of PtTBTPP with low energy photons can, after intersystem crossing, triplet energy transfer and TTA, produce $BDCA(S_1)$, which then yields $BDCA^+$ upon charge injection into TiO_2. Thus the rate of the appearance of this cationic species signifies the kinetics of processes leading to the generation of the injecting state. To this end, broadband pump-probe transient absorption (TA) measurements of PtTBTPP solution, BDCA on TiO_2, and the combined system were carried out, as shown in Fig. 3a. $BDCA^+$ was also prepared electrochemically for reference (Fig. S9.2). TA experiments were carried out in the absence of redox mediator, as this would rapidly regenerate $BDCA^+$ to neutral BDCA.

Upon 610 nm excitation, deoxygenated PtTBTPP solution shows positive TA features (i.e. induced absorbance) from 650-730 nm and at wavelengths beyond 820 nm, corresponding to absorption within the triplet manifold, as well as a negative feature at 770 nm assigned to phosphorescence (Fig 3a, Fig. S8.2). Excitation of BDCA at 500 nm revealed the TA spectrum of $BDCA^+$, which was in good agreement with the spectroelectrochemically produced species (Fig S9.2) with its decay due to recombination with injected electrons. $BDCA^+$ absorption is centred around 700 nm, but is quite broad and featureless, making direct spectral analysis somewhat challenging.

After excitation at 610 nm, the mixed system reveals the spectral feature of the 610 nm excited PtTBTPP at shorter times, while at t > 10 µs the shape more closely resembles that of 500 nm excited BDCA.

This was further explored in Figs 3d-f by monitoring induced changes in absorption (ΔOD) at 720 nm (where phosphorescence does not complicate analysis - see Section S8). The decay of $PtTBTPP(T_1)$ in neat solution is well-fitted by a single exponential model with τ = 17.2 µs, while $BDCA^+$ on TiO_2 is fitted with a stretched exponential decay (τ = 4.49 µs, β = 0.318), in line with reports from Anderson *et al.*.[23] The combined system, which is expected to exhibit IB behaviour, shows a more complicated transient with three identifiable features. The first, a relatively fast decay ($τ_1$ = 2 µs), is followed by a rising component ($τ_{rise}$ = 8.11 µs). The second decay displays the same behaviour as the BDCA (500 nm excitation) and is fitted with the same time constant and stretching factor. Further details of the fitting process can be found in section S8.

The first, rapidly decaying component of the transient is attributed to the loss of triplet-excited porphyrin, which is accelerated roughly an order of magnitude by favourable triplet energy transfer to the TiO_2-tethered BDCA. Following near-complete porphyrin quenching, the slowly rising component is assigned to the generation of cationic BDCA. As discussed by Lissau *et al.*[24], this slow onset is due to the necessary build-up of triplet-excited BDCA prior to TTA occurring, which generates the injection-active BDCA singlet state. The decay of the final long-lived feature following the completion of this rise is ascribed to the recombination of $BDCA^+$ with injected electrons, as per Fig 3b. This strongly supports the proposed mechanism (Fig 1 & Fig S1), with excitation of two donor molecules at 610 nm, *i.e.* beyond the absorption onset of the acceptor, ultimately leading to charge injection from the acceptor, in accordance with IB functionality.

Conclusions

For the first time, an intermediate band solar cell was produced and demonstrated using organic and organometallic compounds as the active materials, with sub bandgap photocurrent demonstrated. This simple and scalable technology demonstrates IB behaviour with superlinear current response to illumination intensities below 1 sun. The IB mechanism functions through low energy excitation of a porphyrin absorber, followed by intersystem crossing and triplet energy transfer to a bound (acceptor/injector) molecule. Triplet-triplet annihilation in the bound (acceptor/injector) population upon reception of two or more triplet excitations can generate the singlet-excited bound (acceptor/injector), allowing the acceptor to inject charge into the semiconductor where it is transported to an external circuit. The observation of $BDCA^+$ and $PtTBTPP(T_1)$ quenching from TA measurements offers clear evidence of this IB mechanism in practice, with charge generation resulting from low energy (sub absorption onset) photons. This represents both a new approach to the implementation of IB technology, and strategy for the improvement of DSC solar-to-electric conversion efficiencies.

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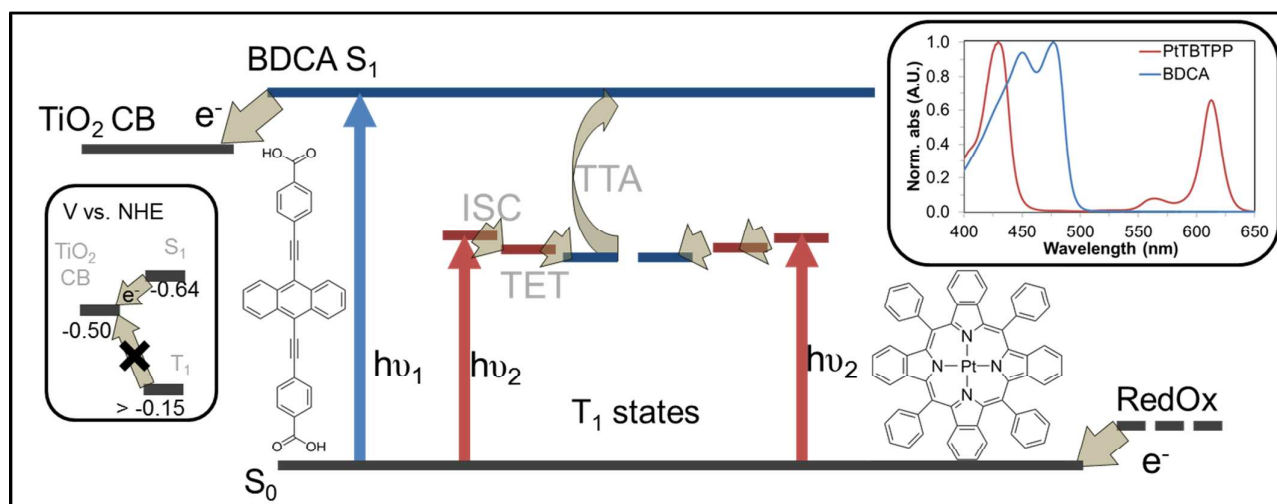
Figure 1. Energy level diagram of IB DSC, with excitation of BDCA (left structure, blue states) occurring either by direct excitation with a single high energy photon ($h\upsilon_1$) or by two low-energy photon ($h\upsilon_2$), absorptions, commencing with photoexcitation of PtTBTPBP (right structure, red states). Left inset demonstrates energetically favourable electron injection into the TiO_2 conduction band from BDCA(S_1) but not BDCA(T_1), while the right inset shows the absorption spectra of PtTBTPP and BDCA (measured in DMF).
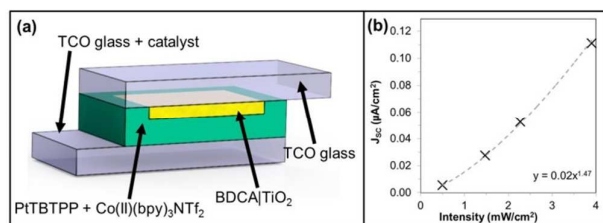
Figure 2. (a) Physical construction of an IB DSC device and (b) Superlinear current density response of an IB DSC device to PtTBTPP excitation (λ = 560 - 640 nm).

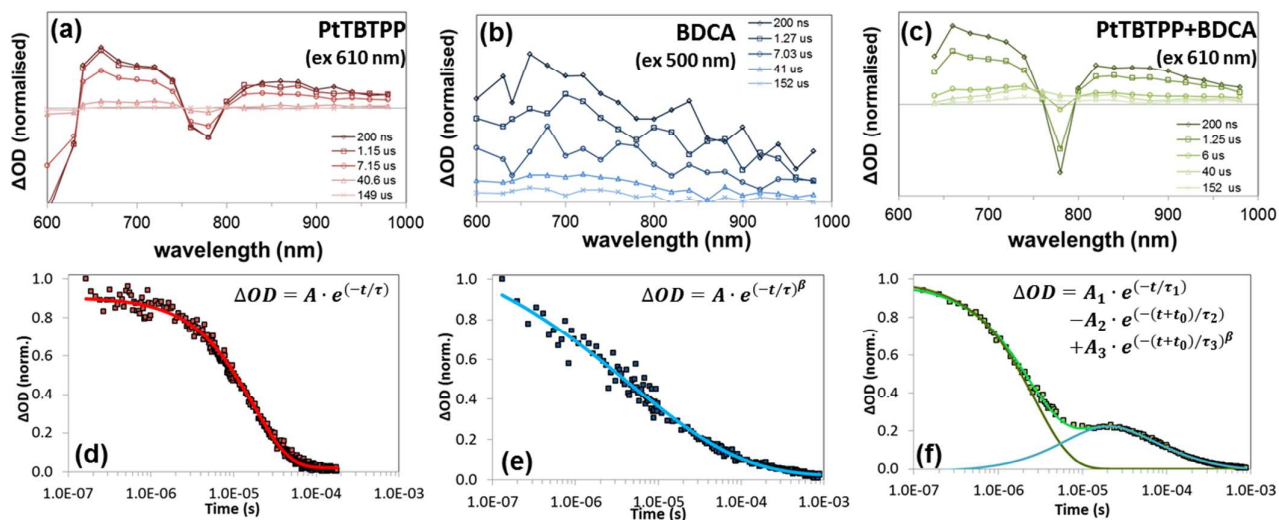Figure 3. TA spectroscopy (a) PtTPTBP, ex 610 nm, (b) BDCA|TiO$_2$, ex 500 nm (c) PtTPTBP+BDCA|TiO$_2$, ex 610 nm (d-e) Normalised ΔOD for systems at 720nm in (a-c) respectively, as functions of time.