Promoting charge-separation in p-type dye-sensitized solar cells using bodipy†

Jean-François Lefebvre, Xue-Zhong Sun, James A. Calladine, Michael W. George and Elizabeth A. Gibson*

The viability of applying bodipy sensitisers to NiO-based p-type dye-sensitised solar cells (p-DSCs) has been successfully demonstrated. The triphenylamine donor–bodipy acceptor design promotes a long-lived charge-separated state which is difficult to achieve with NiO-based devices. The current was above 3 mA cm⁻² and the IPCE was 28%.

The dye was prepared by reacting 4-carboxy-4'-00-di(5-formyl-2-thienyl)triphenylamine with 2,4-dimethyl-3-ethylpyrrole in the presence of trifluoroacetic acid (see ESI† for details). The resulting dipyrane was oxidised with p-chloranil before reacting with boron trifluoride etherate to give 1.

The optical and electrochemical properties are summarised in Table S1 (ESI†). The electronic spectrum of 1 contains absorption maxima at 365 nm (ε = 56 000 L mol⁻¹ cm⁻¹) and 540 nm (ε = 112 000 L mol⁻¹ cm⁻¹), almost double that of the push–pull sensitisers (“P1”) coupled to a highly substituted bodipy (Fig. 1). The dye was prepared by reacting 4-carboxy-4'-A4-dii(5-formyl-2-thienyl)triphenylamine with 2,4-dimethyl-3-ethylpyrrole in the presence of trifluoroacetic acid (see ESI† for details). The resulting dipyrane was oxidised with p-chloranil before reacting with boron trifluoride etherate to give 1.

The optical and electrochemical properties are summarised in Table S1 (ESI†). The electronic spectrum of 1 contains absorption maxima at 365 nm (ε = 56 000 L mol⁻¹ cm⁻¹) and 540 nm (ε = 112 000 L mol⁻¹ cm⁻¹), almost double that of the push–pull sensitisers (“P1”) coupled to a highly substituted bodipy (Fig. 1). The dye was prepared by reacting 4-carboxy-4'-A4-dii(5-formyl-2-thienyl)triphenylamine with 2,4-dimethyl-3-ethylpyrrole in the presence of trifluoroacetic acid (see ESI† for details). The resulting dipyrane was oxidised with p-chloranil before reacting with boron trifluoride etherate to give 1.

The optical and electrochemical properties are summarised in Table S1 (ESI†). The electronic spectrum of 1 contains absorption maxima at 365 nm (ε = 56 000 L mol⁻¹ cm⁻¹) and 540 nm (ε = 112 000 L mol⁻¹ cm⁻¹), almost double that of the push–pull sensitisers (“P1”) coupled to a highly substituted bodipy (Fig. 1). The dye was prepared by reacting 4-carboxy-4'-A4-dii(5-formyl-2-thienyl)triphenylamine with 2,4-dimethyl-3-ethylpyrrole in the presence of trifluoroacetic acid (see ESI† for details). The resulting dipyrane was oxidised with p-chloranil before reacting with boron trifluoride etherate to give 1.

The optical and electrochemical properties are summarised in Table S1 (ESI†). The electronic spectrum of 1 contains absorption maxima at 365 nm (ε = 56 000 L mol⁻¹ cm⁻¹) and 540 nm (ε = 112 000 L mol⁻¹ cm⁻¹), almost double that of the push–pull sensitisers (“P1”) coupled to a highly substituted bodipy (Fig. 1). The dye was prepared by reacting 4-carboxy-4'-A4-dii(5-formyl-2-thienyl)triphenylamine with 2,4-dimethyl-3-ethylpyrrole in the presence of trifluoroacetic acid (see ESI† for details). The resulting dipyrane was oxidised with p-chloranil before reacting with boron trifluoride etherate to give 1.

The optical and electrochemical properties are summarised in Table S1 (ESI†). The electronic spectrum of 1 contains absorption maxima at 365 nm (ε = 56 000 L mol⁻¹ cm⁻¹) and 540 nm (ε = 112 000 L mol⁻¹ cm⁻¹), almost double that of the push–pull sensitisers (“P1”) coupled to a highly substituted bodipy (Fig. 1). The dye was prepared by reacting 4-carboxy-4'-A4-dii(5-formyl-2-thienyl)triphenylamine with 2,4-dimethyl-3-ethylpyrrole in the presence of trifluoroacetic acid (see ESI† for details). The resulting dipyrane was oxidised with p-chloranil before reacting with boron trifluoride etherate to give 1.
electronic properties of the chromophore were unchanged on binding. However, when 1 was excited in the higher energy band (406 nm) the emission spectrum was solvent dependent: emitting from the higher energy triphenylamine (475 nm) when in CH$_2$CN; emitting from the lower energy bodipy (560 nm) when in CH$_2$Cl$_2$.

The electrochemical properties of 1 were determined by cyclic and square wave voltammetry and calibrated vs. FeCp$_2$/FeCp$_3$ (Fig. S13 and S14, ESI†). A reversible reduction process at $-1.46$ V and two closely spaced irreversible oxidation processes at 0.65 and 0.75 V were observed. The estimated driving forces‡ for both injection ($\Delta G_{\text{inj}}$) and regeneration ($\Delta G_{\text{reg}}$) are both negative, indicating that 1 is a suitable NiO sensitisers. DFT calculations were also performed on 1 to further explore the geometry and electronic properties. $E_{\text{DFT}}$ is 0.81 V, is suitably positive to allow for efficient charge-separation between geometry and electronic properties. The results supported experimental evidence that the bodipy was decoupled from the triphenylamine–thiophene donor and the calculated optimised geometry placed the two at an angle of $84 \pm 0.4\, ^\circ$. Fig. S16 (ESI†) shows the electronic distribution in the frontier orbitals: the HOMO level of 1 is located on the triphenylamine; two degenerate HOMO – $1(-2)$ orbitals and two degenerate LUMO($\pm1$) levels are located on the bodipy. TD-DFT suggested that the lowest energy electronic transitions were bodipy-localised $\pi-\pi^*$ in nature, with some contribution from a charge shift from the HOMO to the LUMO.

NiO p-DSCs were assembled with 1 as the sensitisier and a $1^+//I^-$/redox shuttle (see ESI† for details). The photocurrent density–photo-voltage curve and spectral response of a typical cell are given in Fig. 2. The cell parameters were $J_{SC} = 3.15$ mA cm$^{-2}$, $V_{OC} = 79$ mV, $FF = 0.31$, $\eta = 0.08\%$. The maximum incident photon-to-current conversion efficiency (IPCE) was 28%. These values are superior to related triphenylamine-based dyes reported previously, but fall short of those achieved with the most successful dye, P1, ($J_{SC} = 5.48$ mA cm$^{-2}$, IPCE = 64%). The photocurrents obtained with our bodipy-based dyes are extremely encouraging compared to bodipy-sensitised TiO$_2$ devices. TiO$_2$-DSCs are usually more efficient than p-DSCs, but to our knowledge the highest IPCE for a bodipy-sensitised n-DSC is less than 30%. This suggests that the bodipy chromophore may be better suited to the NiO system than conventional TiO$_2$-DSCs. Further improvements in efficiency are likely to come from broadening the absorption band by increasing the electronic coupling between the $\pi$-linker and the bodipy and extending the conjugation by functionalising the dye periphery.

To probe the charge-transfer dynamics of this new dye–NiO system, we performed ps- and ns-transient absorption spectroscopy (TA) both with 1 in CH$_2$Cl$_2$ and adsorbed on NiO. Excitation of 1 in solution (Fig. 3 black line) at 532 nm generated an excited state which absorbed between 400–500 nm and decayed over ca. 400 ps to form a new intermediate with narrower absorption bands at 425 and 650 nm which decayed much more slowly ($\tau_{425} \approx 300 (\pm 10)$ ns in air, $\tau_{425} \approx 860$ ns, $\tau_{650} \approx 730$ ns in Ar) to the ground state. We have assigned this long-lived transient to a triplet bodipy ($^{1}T^*$) excited state (see ESI† for further details).

The transient absorption results were different for 1 adsorbed on NiO (Fig. 3 red dashed line). On the ps timescale, the broad features between 400–470 nm corresponding to $^{1}T^*$ that were observed in CH$_2$Cl$_2$ were less intense. Instead a peak at 575 nm formed rapidly ($\tau_{\text{rise}} \approx 1$ ps) which was characteristic of $^{1}T^*$ by comparison with our spectroelectro-chemistry experiments (Fig. S26, ESI†). A broad featureless absorption persisted throughout the ps- and ns-transient spectra. This is attributed to oxidised NiO and indicates that the charge-separated state (NiO$^+/I^-$) had formed. The dynamics for each band were characteristically heterogeneous and we have fitted the rise and decay in each experiment to first order kinetics giving a short ($\tau_{\text{ps}}$) and long ($\tau_{\text{ns}}$) time constant (Table S4, ESI†) to enable us to compare the general behaviour of the intermediates. The rapid time constant for the formation of NiO$^+/I^-$ can be compared to the lifetime of $^{1}T^*$ recorded in solution to give an estimate of the injection efficiency.‡ Using this approach gives a very high efficiency of 99% but it should be noted that any slower injection processes were masked by the subsequent decay of this peak. To try and provide a more realistic value for this process we have compared...
the relative amplitudes after excitation of the signals at 425 nm (which contains contributions from both 1\(^{+}\) and 1\(-\)) and 575 nm (NiO\(^+\)/I\(^-\) only) at early (2 ps) and late (2 ns) times. This analysis suggests that the charge-separation efficiency is closer to 50% and this result is more in agreement with the maximum IPCE for the solar cells. The peak attributed to NiO\(^+\)/I\(^-\) at 575 nm (\(\tau_2 \approx 180\) ns) lived three orders of magnitude longer than the charge-separated state of the widely studied P1 dye.\(^6\)

This substantial increase in the charge-separated state lifetime prompted us to investigate the effect of substituting the I\(^2\)/I\(^-\) for the tris(4,4’-di-tert-butyl-2,2’-dipryridyl)cobalt(II/III) redox shuttle in our DSCs in an attempt to increase the photocurrent.\(^7\) Unfortunately the photocurrent was negligible in this case, suggesting that the lifetime was still not sufficient for re-oxidation of I\(^-\) by the cobalt electrolyte.\(^8\)

\(\tau_1\) for the NiO\(^+\)/I\(^-\/) signal differed little in the presence of I\(^2\)/I\(^-\) (Fig. 3 blue dotted line) and absence of I\(^2\)/I\(^-\) (Fig. 3 red dashed line, shifted to \(\lambda_{\text{max}} = 600\) nm) hence there was no measurable effect of the electrolyte on a short timescale. However, on a ns timescale the signal for NiO\(^+\)/I\(^-\/) decayed much more rapidly (\(\tau_1 \approx 23\) ns) in the presence of the electrolyte, indicating that interception of the electron by the redox shuttle efficiently competes with recombination. This re-oxidation is very fast compared to the \(\mu\)s timescale reported for re-reduction of dyes on TiO\(_2\).\(^22\) The mechanism for the dye regeneration pathway in n-DSCs is still under debate and it is currently believed that two equivalents of I\(^-\) per dye molecule are required.\(^22-24\) For p-DSCs, re-oxidation of the dye requires only one molecule of I\(^2\) per dye and this may be why we observe this process proceeding more quickly. Reported timescales for the regeneration reaction range from ps to \(\mu\)s.\(^9,25\) Reasons for the differing kinetics could be the different driving force for the reaction (reported \(\Delta G_{\text{reg}} < 200\) meV to 1 eV; \(\Delta G_{\text{reg}} = 640\) meV for 1) and the overlapping signals for reduced dye and I\(^2\)- produced from the reduction of I\(^2\) (\(\lambda = 420-475\) nm).

In our TA experiments on 1/NiO in the presence of electrolyte we also observed an additional peak centred at 425 nm which decayed with \(\tau = 500\) ns. At first we were concerned that the presence of the heavy atoms in the electrolyte had driven the S\(\text{I}^\text{I} \rightarrow \text{I}^\text{II}\) conversion as observed by Morandeira et al. for Coumarin 343/ NiO\(^+\) but the band at 650 nm that accompanied the higher energy peak for 1\(^+\) in CH\(_3\)Cl\(_2\) was absent in this sample. Instead, we have assigned this transient as I\(^2\). The extinction coefficient of I\(^2\) should be three times greater than that of the reduced bodipy. The different amplitudes at 420 nm vs. 600 nm in the TA spectrum 2 ns after excitation indicates that both reduced dye and reduced bodipy are present in similar quantities. Therefore we have compelling evidence that electron transfer from the photoreduced dye to I\(^2\) generating I\(^2\)- contributes to the photocurrent in p-DSCs.

In conclusion, the three orders of magnitude increase in charge-separated state lifetime is a significant breakthrough in our efforts to improve the efficiency of dye-sensitized photocathodes. We anticipate that tuning the electronic coupling by modifying the substituents on the bodipy will increase the charge-separated state yield and lifetime further. This will enable higher photocurrents to be obtained and alternative electrolytes to be used which increase the photovoltage. These results have wider implications to the field of “solar fuels” since photocatalysis requires long-lived charge-separated intermediates for the desired chemical reactions to take place.

We thank the University of Nottingham and The Royal Society for funding and MWG gratefully acknowledges receipt of a Wolfson Merit Award.

Notes and references