Interface engineering for solid-state dye-sensitised nanocrystalline solar cells: the use of an organic redox cascade†

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We demonstrate the formation of a charge transfer cascade at a nanostructured TiO_2/dye/polymer/molecular hole transport multilayer interface. Charge recombination dynamics at this interface are shown to be retarded when the ionisation potential of the polymer layer exceeds that of the molecular hole transport layer.

Nanocomposites of inorganic and organic semiconductors are currently receiving extensive interest for both organic light emitting diodes and photovoltaic device applications.[1–3] The efficient operation of such devices ultimately depends on the ability to control the charge transfer at the device heterojunction. We, and others, have recently been focusing upon a range of 'interface engineering' strategies to control electron transfer dynamics at nanostructured inorganic/organic interfaces.[4–8] Such dynamics are of particular interest for the development of solid-state dye-sensitised solar cells (DSSCs).[9–12] In this study we demonstrate a novel strategy to retard interfacial charge recombination in such devices, employing an organic redox cascade to increase the spatial separation of photogenerated electrons and holes, as illustrated in Fig. 1.

Solid-state DSSCs employing the organic hole transporter spiro-OMeTAD (2,2′–7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenyl-amine) 9,9′-spirobifluorene) have recently been reported with efficiencies of up to 4%.[13] This efficiency, whilst promising, remains however significantly below those reported for analogous devices employing iodide/iodine-based redox electrolytes. A key factor limiting the performance of devices of spiro-OMeTAD DSSCs is their fast interfacial charge recombination dynamics relative to liquid electrolyte devices.

Fig. 2 illustrates this point, showing typical recombination dynamics for these two device types employing the sensitiser dye $RuL_2(NCS)_2$ (*cis*-isothiocyanato bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)). It is apparent that the charge recombination dynamics for the spiro-OMeTAD device are two orders of magnitude faster then those observed for the liquid electrolyte device, consistent with previous observations. These faster recombination dynamics limit the diffusion length of photogenerated charges within the device, and therefore limit the maximum device thickness (and therefore light absorption) compatible with efficient charge collection.

Fig. 2 also shows the corresponding charge recombination dynamics of injected TiO_2 electrons with dye cations, observed in the absence of any organic hole conductor or redox couple. It is striking that charge recombination dynamics to dye cations and spiro-OMeTAD cations are indistinguishable. We have previously shown that recombination dynamics to dye cations are dependent upon both the dynamics of electron transport in the TiO_2 film and

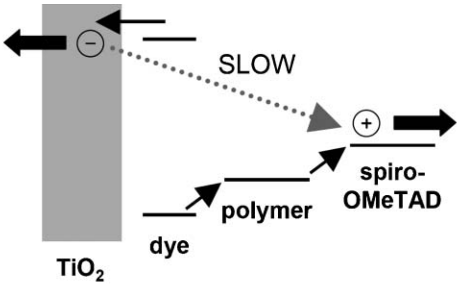

Fig. 1 Illustration of the organic redox cascade strategy addressed in this study to retard interfacial charge recombination.

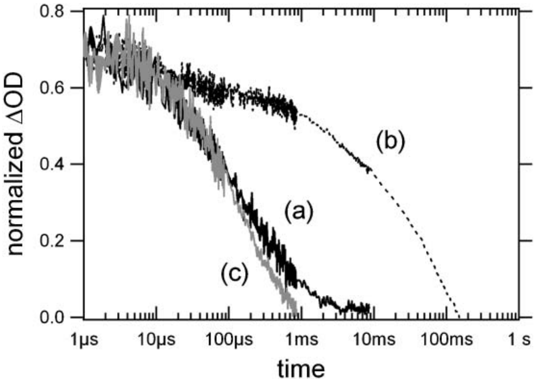

Fig. 2 Transient absorption data monitoring charge recombination dynamics of (a) a $RuL_2(NCS)_2$-sensitised TiO_2 film, (b) the same film covered in redox electrolyte and (c) the same film following addition of spiro-OMeTAD. Data collected monitoring TiO_2 electron absorption at 1000 nm following optical excitation at 530 nm, with 25 mW cm^{-2} continuous white light bias. The spiro-OMeTAD was spin coated from chlorobenzene with no additives. The redox electrolyte comprised 0.1 M lithium iodide, 0.8 M tetra butyl ammonium iodide, 0.5 M *tert*-butylpyridine and 0.05 M iodine in acetonitrile.

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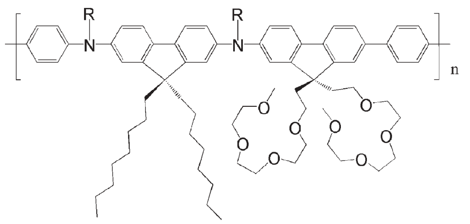
the spatial separation of the cation from the TiO_2 surface.[14,15] The observation of indistinguishable recombination dynamics to both the dye and spiro-OMeTAD cations indicates that hole transfer from the dye to spiro-OMeTAD does not result in a significant movement of the cation away from the TiO_2 surface. In other words, despite the spiro-OMeTAD largely filling the pores of the mesoporous film, in these films the photogenerated spiro-OMeTAD cations remain localised close to the dye-sensitised TiO_2 surface.

The localisation of the spiro-OMeTAD cations ('holes') on the TiO_2 surface can be readily understood in terms of local electric fields at TiO_2/dye/spiro-OMeTAD interface. Such electric fields may derive both from interface dipoles and from coulombic interactions of the photogenerated charges.[16,17] One strategy to overcome this localisation of the spiro-OMeTAD cations is the introduction of mobile ions to the organic phase, such as lithium triflamide salts, to screen these electrostatic interactions. The addition of such salts results in a significant retardation of recombination dynamics, consistent with an increased spatial separation of the spiro-OMeTAD cations from the TiO_2 surface, and results in an improvement in device efficiencies by up to an order of magnitude.[9] One limitation to this approach is however the requirement of the addition of volatile pyridine to the hole-transport layer to solubilise the lithium salt. We have recently demonstrated an alternative solubilisation strategy based upon the attachment of tetraethylene glycol (TEG) side groups to the organic hole transporter to ligate the lithium ions.[12,18] We have furthermore employed this strategy to achieve an organic multilayer structure, depositing the dual function ion ligating and hole transport polymer between the sensitiser dye and spiro-OMeTAD to achieve a localised ionic screening of the interfacial electric fields.[12] In this study we extend this multilayer approach, modulating the ionisation potential of the polymer layer to achieve an energetic redox cascade, as illustrated in Fig. 1, and resulting in a further retardation of the interfacial charge recombination dynamics.

The ion-ligating, hole-transporting polymers employed in this study are shown in Fig. 3. We have previously demonstrated that polymer **P1** can be adsorbed by dip-coating to form a conformal monolayer on dye-sensitised nanocrystalline TiO_2 films. Subsequent spin-coating of a spiro-OMeTAD bulk hole transport layer did not result in dissolution of this layer. In this study we vary the substituents to the phenyl side group of the polymer, modulating its ionisation potential from 4.73 to 5.05 eV (see Fig. 3). It is apparent that this range overlaps the ionisation potential of spiro-OMeTAD (4.77 eV).

Fig. 4 shows typical charge recombination dynamics for multilayer structures employing polymers **P1** to **P4** obtained, as for Fig. 2, by monitoring the decay of photoinduced absorption of electrons injected into the TiO_2 electrode. In each case, the polymer layer was deposited by immersing dye-sensitized nanocrystalline TiO_2 films in a 1 : 9 acetonitrile–chlorobenzene solution containing 1.5 mM of **P1** to **P4** and 18 mM lithium triflamide ($Li[CF_3SO_2]_2N$) at 70 °C for 30 min, followed by drying under ambient conditions. Spiro-OMeTAD was subsequently deposited by spin coating a 0.17 M solution of spiro-OMeTAD in chlorobenzene. Control data were also obtained by omitting the polymer layer. It is apparent that, depending upon which polymer is employed, the deposition of the polymer layer can result in a significant retardation of the interfacial charge recombination relative to the polymer-free control.



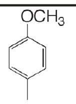
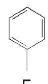
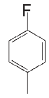
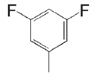
	R	Ionization potential (eV)
P1		4.82
P2		4.73
P3		4.76
P4		5.05
spiro-OMeTAD	-	4.77

Fig. 3 Chemical structures of the ion-ligating hole transport polymers employed in this study, and corresponding ionisation potentials determined by cyclic voltammetry.

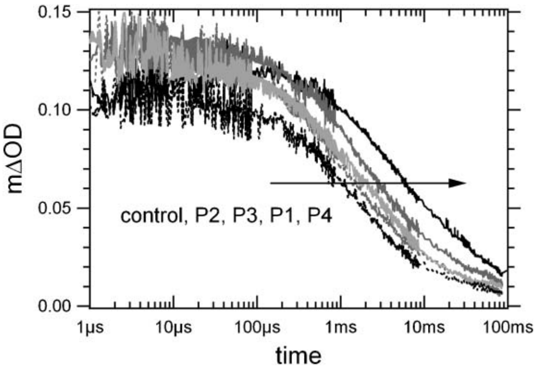


Fig. 4 Transient absorption data monitoring charge recombination dynamics of TiO_2/dye/polymer/spiro-OMeTAD films as a function of polymer employed. Data collected in the dark monitoring TiO_2 electron absorption at 1000 nm following optical excitation at 530 nm. All data collected with lithium triflamide in the polymer deposition solutions, and without any additives to the spiro-OMeTAD spin coating solution. Control data collected without any polymer layer.

The retardation of the recombination dynamics observed for polymers **P1** to **P4** shows excellent correlation with the ionisation potential of these polymers, as shown in Fig. 5. The recombination dynamics are becoming progressively slower with increasing polymer ionisation potential. This behaviour is consistent with our redox cascade strategy, as illustrated in Fig. 1. For polymer ionisation potentials close to that of spiro-OMeTAD, a significant proportion of photogenerated holes are likely to remain on the polymer layer. However, polymer ionisation potentials greater than spiro-OMeTAD may allow the formation of a redox cascade

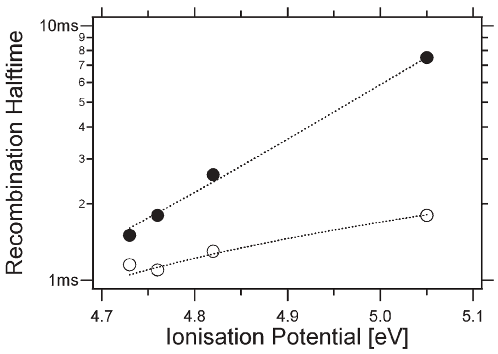


Fig. 5 Recombination halftimes determined from transient absorption data such as that shown in Fig. 4 as a function of polymer ionisation potential. Data shown with the inclusion (●) and omission (○) of lithium triflamide from the polymer dipping solution.

as illustrated in Fig. 1, increasing hole transfer from the polymer to the spiro-OMeTAD. This would increase the spatial separation of photogenerated holes from the TiO_2 surface and consequently result in slower charge recombination dynamics, as observed experimentally.

We note that the retardation of recombination dynamics observed due to the insertion of the polymer layer is dependent upon the inclusion of lithium triflamide in the polymer deposition solution. A retardation of recombination dynamics with increasing polymer ionisation potential is also observed in the absence of the salt (Fig. 5, open symbols) but the effect is small compared to that observed in the presence of the salts. This observation is consistent with our conclusion (*see above*) that the formation of an energetic redox cascade will be dependent not only upon the relative ionisation potentials of the materials employed but also upon the interfacial dipoles and coulombic attractions between the photogenerated charges. In the absence of ionic screening, these electrostatic interactions can be expected to dominate the interfacial energetics, and therefore prevent significant formation of an energetic redox cascade. However, the presence of the co-deposited lithium triflamide can be expected to screen these electrostatic interactions, allowing the formation of an energetic redox cascade based upon the differing ionisation potentials of the polymer and spiro-OMeTAD layers, consistent with our experimental observations.

The solution processing of organic multilayer nanostructures is a key challenge for a range of organic electronic and optoelectronic devices, including not only dye-sensitised solar cells, but also polymer-based devices and light-emitting diodes. We report here the successful fabrication of such a multilayer structure, employing organic semiconducting materials with different ionisation potentials to achieve an energetic redox cascade at a dye-sensitised nanostructured interface. The application of this strategy to the optimisation of solid-state dye-sensitised solar cells is currently ongoing.

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