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A supramolecular approach to lithium ion solvation at nanostructured dye sensitised inorganic/organic heterojunctions†

Taiho Park,[a] Saif A. Haque,[b] Robert J. Potter,[c] Andrew B. Holmes*[a] and James R. Durrant*[b]
[a] *Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: abh1@cam.ac.uk; Fax: ++44 (0) 1223 334866; Tel: ++44 (0) 1223 334370*
[b] *Centre for Electronic Materials and Devices, Department of Chemistry, Imperial College of Science Technology and Medicine, London, UK SW7 2AZ. E-mail: j.durrant@imperial.ac.uk; Fax: ++44 (0) 207 5945801; Tel: ++44 (0) 207 5945321*
[c] *Innovations Group, Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, UK RG4 9NH*

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A novel arylamine based hole transporting material (HTM) with tetraethylene glycol (TEG) side groups is reported. Lithium ions solubilised by the TEG groups are employed to modulate interfacial electron transfer reactions at a dye sensitised TiO_2/HTM interface.

Nanocomposites of inorganic and organic semiconductors are currently receiving extensive interest for both OLED 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. Recently several studies have focused on the utilization of mobile lithium ions in active device layers to control interfacial charge transfer. Such an approach has been successfully employed to control charge transfer at metal/organic and inorganic/organic semiconductor interfaces for light emitting electrochemical cells and dye sensitised nanocrystalline semiconductor solar cells respectively.[4,5,6] However the use of this approach has been limited to date since ionic salts are not soluble in most organic semiconductors, and has therefore required the addition of co-solvents such as polyethylene oxide or *tert*-butylpyridine (^tBP).[5,6] Herein we report an alternative approach based on hole transporting oligomers comprising ion solvating and transporting tetraethylene glycol (TEG) side groups. Such materials have recently been employed to control charge transfer at a metal/organic semiconductor interface for light emitting electrochemical cells.[7] In this paper we demonstrate that such type materials can be used to control charge transfer at a nanostructured dye sensitised inorganic/organic semiconductor heterojunction. †

A configuration of particular interest is the dye sensitised nanocrystalline solar cell (DSSC). A typical DSSC comprises a dye sensitised nanocrystalline mesoporous TiO_2 film interpenetrated by an organic hole transporting material (HTM). Visible light is absorbed by the sensitizer dye $RuL_2(NCS)_2$ (chemical name: *cis*-isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II). Electron injection from the excited-state of the dye into the conduction band of TiO_2 is followed by subsequent hole-injection from the photo-oxidised dye to the HOMO of the HTM, regenerating the dye's original state. This double-charge injection process generates mobile electrons and holes in the TiO_2 and organic semiconductor phases respectively, which are subsequently collected at the device contacts. The efficient operation of the device requires both high yields of charge separation and the minimization of charge recombination between the photo-generated electrons in the TiO_2 and holes in the HTM. In this paper we demonstrate that novel HTMs bearing TEG chains can be used to solvate lithium ions and control charge transfer at the dye sensitised nanocrystalline TiO_2/organic semiconductor heterojunction.

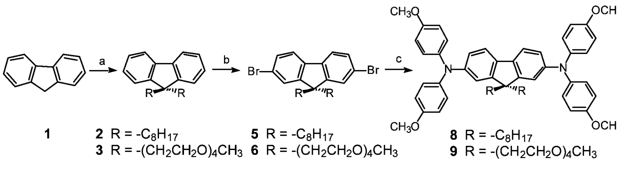
The chemical structure of the novel hole transporting materials is shown in Scheme 1. The HTMs are based on arylamine TPD structures (TDP = *N,N*′-diphenyl-*N,N*′-(*m*-tolyl)-benzidine) and comprise tetraethylene glycol groups on the 9-position of a fluorene unit (**9** in Scheme 1) to solvate lithium ions in the HTM domain. The novel compound **9** and its analogue **8** having octyl side chains for comparison were synthesized by employing a Pd-catalyzed *C–N* coupling reaction.[8]

The dioctyl substituted fluorene **5** was synthesised by substitution reactions of the fluorene **1** carbanion and octyl bromides with 2 equivalents of *n*-BuLi, followed by bromination in the presence of bromine, employing iodine as a catalyst, giving an 87% overall yield.[9a] Similar reactions were carried out to synthesise the dibromofluorene bearing tetraethylene glycol groups **6**. In this case, two repeated substitution reactions[9b] of **1** and the tosylated alcohol **4** gave the fluorene **3** with tetraethylene glycol groups in high yields (89%). The same bromination as above gave the dibromo fluorene **6** with tetraethylene glycol groups in 94% yield. Details of chemical analyses of **8** and **9** are described in the ESI.†

Methoxy substituents have been introduced onto the TPD structure to provide a sufficient driving force for a high hole transfer from the $Ru(L)_2(NCS)_2$ dye cation to the highest occupied molecular orbitals of the HTM. Oxidation mid-point potentials for **8** and **9** were determined from cyclic voltammetry (CV) in CH_2Cl_2 solution to be +0.42 and +0.41 V *vs*. Ag^+/AgCl, respectively, indicating the substitution of the octyl side groups of the fluorene unit with TEG groups had negligible effect on the HTM oxidation potential.

Dye sensitized nanocrystalline TiO_2 films were prepared as previously described.[10] The dye–TiO_2 film pores were filled with the HTM by spin coating from a 0.17 M, 1 : 9 acetonitrile : chlorobenzene solution. Variation in lithium ion concentration in the HTM layers was achieved by adding an appropriate amount of lithium triflamide in the spin-coating solution with and without the co-addition of 0.11 M ^tBP.

Transient absorption spectroscopy was employed as previously[10] to study the influence of lithium ions upon the yield of



Scheme 1 *Reagents and conditions*: a) i) *n*-BuLi, THF, −65 °C, 1 h; ii) $C_8H_{17}Br$ or $Ts(CH_2CH_2O)_4CH_3$ **4**, THF, −65 °C, 30 min; b) Br_2, I_2, CH_2Cl_2, rt, overnight; c) di(*p*-methoxyphenyl)amine **7**, $Pd(OAc)_2$, $P(^tBu)_3$, toluene, 90 °C, overnight.

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† Electronic Supplementary Information (ESI) available: experimental details and absorption spectra. See http://www.rsc.org/suppdata/cc/b3/b306604e/

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hole transfer from the dye cation to the HTM (reaction 1) and the recombination dynamics between photo-injected electrons and HTM cations (reaction 2).

$$\mathrm{Dye^+ + HTM \rightarrow Dye + HTM^+} \qquad (1)$$

$$\mathrm{HTM^+ + e^-_{TiO2} \rightarrow HTM} \qquad (2)$$

Transient absorption data were collected following optical excitation of the $Ru(L)_2(NCS)_2$ sensitiser dye at 550 nm. In the absence of HTM, a broad positive absorption band was observed centred at 800 nm and a negative feature at 540 nm, spectral features assigned as previously to the formation of the $Ru(L)_2(NCS)_2$ cation following photoinduced electron injection.[10] In the presence of the HTM a reduction in the photoinduced dye cation signal at 800 nm is observed, along with the appearance of a positive feature with an absorption maximum at ~ 520 nm, a spectral feature we have previously assigned to the formation of the HTM radical cation.[10]

The yield of the hole transfer (reaction 1) was determined as a function of lithium ions in the presence and absence of t-butyl pyridine in the HTM domain for both HTMs **8** and **9**, as summarized in Table 1. In the absence of Li^+, the yield of hole transfer from the dye cation to HTMs **8** and **9** was determined as 79 and 88% respectively, consistent with the large free energy difference between the dye and HTM oxidation potentials, as we have discussed previously.[10] For HTM **8** in the absence of ^tBP, it is apparent that an increase in Li^+ from 0 to 0.04 M results in a reduction in the hole transfer yield from 88 to 74%. Increasing the lithium ion concentration beyond 0.04 M results in a rapid loss of hole transfer yield from the dye cation to the HTM **8** and an increase in the optical light scattering of the film. This observation can most reasonably be rationalized in terms of incomplete wetting of the dye sensitised TiO_2 film pores by HTM due to crystallization of the lithium triflamide salt during spin-coating. The addition of ^tBP to the HTM **8** solution reduced the sensitivity of the transient signal amplitude to lithium ion concentration, with significant loss of hole transfer yield only being observed for a Li^+ concentration of 0.25 M, consistent with previous reports that the co-addition of ^tBP increases the solubility of Li^+ ions in the HTM.[1] We note however that the addition of ^tBP is undesirable for technological applications due both to its volatility and carcinogenic properties.

In contrast to the data we obtained for HTM **8**, we find that the hole transfer yield for HTM **9** (bearing TEG groups) is not reduced by Li^+ for all ion concentrations studied. Furthermore no recrystallisation of the lithium triflamide salt was observed. We thus conclude that HTM **9** solvates lithium ions readily; resulting in no crystallization of the lithium triflamide salt during the spin-coating procedure. It is also apparent from the data in Table 1 that, in the absence of ^tBP, the addition of Li^+ to the HTM **9** actually results in a small increase in HTM cation yield (from 79 to 96%). This small increase most probably arises from faster electron injection dynamics from the $RuL_2(NCS)_2$ excited state into the TiO_2 conduction band, consistent with our previous observations.[11]

Table 1 HTM cation yields determined by transient laser spectroscopy for $TiO_2/RuL_2(NCS)_2$/HTM films[a]

	Li^+	^tBP	Yield (%)	
[Cell][a]	$[Li^+]/[HTM]b^b$	$[^tBP]/[Li^+]^b$	HTM **9**	HTM **8**
[HTM]	—	—	79	88
[HTM + Li^+]	0.04	—	96	74
	0.13	—	96	—
	0.25	—	91	—
[HTM + Li^+ + ^tBP]	0.04	7.3	77	73
	0.13	2.2	78	71
	0.25	1.1	81	22

[a] The yield of hole transfer from the dye cation to the HTM was determined by comparing the amplitude of the dye cation band at 800 nm in the presence and absence of HTM, as detailed previously.[11]

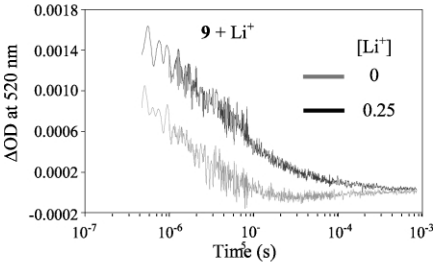

Fig. 1 Transient absorption data collected for $TiO_2/RuL_2(NCS)_2$/HTM **9** films as a function of lithium ion concentration added to the HTM deposition solution. Data collected at a probe wavelength of 520 nm, monitoring the appearance and decay of the HTM cation absorption band, assigned to the charge recombination reaction, eqn. (2).

The addition of Li ions to the HTM spiro-OMeTAD in the presence of ^tBP has previously been shown to increase the efficiency of dye sensitized photovoltaic cells.[6] This increase was attributed to a retardation of the interfacial recombination reaction (reaction 2) due to electrostatic screening of the photoinjected electron from the HTM cation. We consider therefore the influence of the lithium ions upon the interfacial recombination dynamics employing HTM **9** in the absence of ^tBP, as shown in Fig. 1. It is apparent that the addition of lithium ions results in a 5–10 fold retardation of the interfacial recombination dynamics, consistent with desired ionic screening of the charge separated species.

In conclusion we have demonstrated that an organic hole transporting material with TEG side chains can be used to solvate lithium ions without co-solvents such as *tert*-butylpyridine. We have employed such materials to control interfacial charge transfer at a dye sensitized nanocrystalline TiO_2/organic HTM heterojunction. Specifically we have demonstrated that lithium ion doped TEG-HTMs can be used to control interfacial charge recombination and simultaneously achieve a high yield of hole transfer from dye cations to HTM. Such materials therefore provide a novel approach to achieving ion solvation in organic HTM's for a wide range of potential device applications.

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Notes and references

1 U. Bach, D. Lupo, P. Compte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Gratzel, *Nature*, 1998, **395**, 583.
2 W. U. Huynh, J. J. Dittmer and A. P. Alivisatos, *Science*, 2002, **295**, 2425.
3 S. Coe, W-K. Woo, M. Bawendi and V. Bulovic, *Nature*, 2002, **420**, 800.
4 T. M. Brown, R. H. Friend, I. S. Millard, D. J. Lacey, J. H. Burroughes and F. Cacialli, *Appl. Phys. Lett.*, 2001, **79**()), 174; J. Kruger, U. Bach and M. Gratzel, *Adv. Mater.*, 2000, **12**(6), 447.
5 Q. Pei, Y. Yang, G. Yu, C. Zhang and A. J. Heeger, *Science*, 1995, **269**, 1086.
6 J. Kruger, R. Plass, L. Cevey, M. Piccirelli, M. Gratzel and U. Bach, *Appl. Phys. Lett.*, 2001, **79**(13), 2085.
7 J. Morgado, F. Cacialli, R. H. Friend, B. S. Chuah, H. Rost and A. B. Holmes, *Macromolecules*, 2001, **34**, 3094.
8 T. Yamamoto, M. Nishiyama and Y. Koie, *Tetrahedron Lett.*, 1998, **39**, 2367.
9 (*a*) M. Ranger and M. Leclerc, *Can. J. Chem.*, 1998, **76**, 1571; (*b*) Q. Pei and Y. Yang, *J. Am. Chem. Soc.*, 1996, **118**, 7416.
10 S. A. Haque, Taiho Park, Andrew B. Holmes and J. R. Durrant, *ChemPhysChem*, 2003, **1**, 89.
11 Y. Tachibana, S. A. Haque, I. Mercer, J. R. Durrant and D. R. Klug, *J. Phys. Chem. B*, 2001, **105**, 7424.