Kinetic competition in liquid electrolyte and solid-state cyanine dye sensitized solar cells †‡

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The photovoltaic performance of liquid electrolyte and solid-state dye sensitized solar cells, employing a squarilium methoxy cyanide dye, are evaluated in terms of interfacial electron transfer kinetics. Dye adsorption to the metal oxide film resulted in a mixed population of aggregated and monomeric sensitizer dyes. Emission quenching data, coupled with transient absorption studies, indicate that efficient electron injection was only achieved by the monomeric dyes, with the aggregated dye population having an injection yield an order of magnitude lower. In liquid electrolyte devices, transient absorption studies indicate that photocurrent generation is further limited by slow kinetics of the regeneration of monomeric dye cations by the iodide/iodine redox couple. The regeneration dynamics are observed to be too slow (\gg 100 µs) to compete effectively with the recombination of injected electrons with dye cations. In contrast, for solid-state devices employing the organic hole conductor spiro-OMeTAD, the regeneration dynamics are fast enough (\ll 1 µs) to compete effectively with this recombination reaction, resulting in enhanced photocurrent generation.

Introduction

Ruthenium complexes have attracted much interest in the area of molecular solar cells due to their exceptional photophysical properties.¹ Dye sensitized solar cells (DSSCs) based on ruthenium polypiridine complexes such as cis-dithiocyanatobis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (called N3) and trithiocyanato(4,4',4"-tricarboxy-2,2':6',2"-terpyridine) ruthenium(II) (black dye) have given the best light-to-energy conversion efficiencies.² Over the past decade, most studies have focused on changes in the electrochemical and photophysical properties of the complexes affected by the substitution or replacement of the pyridine rings by electron donor or aliphatic ligands, in order to control the electrochemical and photophysical properties of the complex and, thereby, improve the device performance.³ However, despite the broad metal-toligand charge transfer (MLCT) absorption band of these ruthenium complexes, which covers a wide spectral range from the UV to the visible region of the solar spectra, the lack of absorption in the near infrared region and the need for higher

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^dCatalan Institution for Research and Advanced Studies (ICREA) ^eInstitute of Chemical Research of Catalonia (ICIQ), Avgda, Països Catalans 16, 43007 Tarragona, Spain. E-mail: epalomares@iciq.es; Fax: +349770920220; Tel: +34977920241 molecular extinction coefficients in the visible are still major challenges for researchers.

Recently there has been an increasing interest in the development of organic dyes,⁴ which appear to be also promising due to their outstanding photophysical properties. Organic dyes present higher molar extinction coefficients when compared with ruthenium complexes. This property allows efficient light harvesting to be achieved with thinner mesoporous metal oxide films. This advantage is particularly important for DSSCs employing solid-state hole transport materials, where efficient charge collection has only been demonstrated for film thickness of the order of 2 μ m.⁴ For this reason organic dyes are an interesting approach for solid-state dye sensitized solar cells. Several groups have focused on the development of pure organic dyes⁴ such as coumarines, merocyanines, perylenes, hemicyanines, indolines and polyene dyes. Among them, indoline and thiophene dyes with an outstanding efficiency of ca. 8%, are so far the most efficient organic dyes for DSSCs.^{4a,4c} However, many organic dyes have a tendency of forming molecular aggregates on the surface of the semiconductor nanoparticles, which it has been suggested can result in a decrease in device efficiency. While the formation of molecular aggregates has been intensively studied and the low photocurrent has been usually assigned to intermolcular quenching,⁵ rather little attention has been placed on interfacial electron transfer kinetics of such organic DSSC devices. For example, cyanine dyes have been extensively explored as near infrared dyes for DSSCs^{5c,6} alongside other optoelectronic applications such as optical data storage⁷ and xerography.⁸ In fact, during our investigation, similar cyanine molecules were used as sensitizers for DSSCs.⁹

In this paper, we report the synthesis and study of the interfacial electron transfer dynamics for a cyanine dye

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derivative (MSqb) (Scheme 1) adsorbed onto a nanocrystalline TiO₂ film. The organic dye shows an absorption band edge shifted to the red region (~700 nm), obtained by expanding the π -conjugation system, and in addition the insertion of methoxy groups on the molecular structure to achieve the appropriate redox potentials to allow efficient charge regeneration from the electrolyte. Our aim is not only to study the effect of the dye structure upon the electron injection yield but also on the dye regeneration dynamics. Our data indicates that the efficiency of this regeneration may be a critical factor in limiting the efficiency in organic dye sensitized solar cells.

Experimental section

Materials and reagents

All reagents were purchased from Sigma-Aldrich. The solvents used were of HPLC degree and those for electrochemical measurements were previously degassed with argon. Transparent conducting glass (TCO, F-doped SnO₂, 14Ω cm⁻²) was purchased from Hartford Glass Company Inc. and washed with water and soap, ethanol and acetone successively under sonication for at least 10 min prior to utilization.

Synthesis of the squarilium methoxy cyanide dye

The squarilium methoxy cyanide dye was obtained following previous literature reports.^{9a} All reagents were commercially available and used without further purification. A brief description of the procedure is described as follows:

5-Methoxy-2,3,3-trimethyl-3H-indol (1). 4-Methoxyphenylhydrazine hydrochloride (4.37 g, 25 mmol) and 3-methyl-2butanone (6.5 mL, 60 mmol) were refluxed in CH₃COOH (80 mL) for 5 h. The red solution was neutralized with KOH at 0 °C. The mixture was then extracted with Et₂O. The organic phase was dried over Na₂SO₄ and the solvent was removed under reduced pressure. The resulting oil was purified by column chromatography (SiO₂, Hexane–Et₂O) to afford **1** (3,78 g, 80%) as a yellow solid. ¹H NMR (CDCl₃, 300 MHz): d 7.42 (d, J = 8.5 Hz, 1H), 6.83 (m, 1H), 6.80 (d, J = 2.6 Hz, 1H), 3.82 (s, 3H), 2.24 (s, 3H), 1.28 (s, 6HH).

HRMS (FAB): Calc. for $C_{12}H_{15}NO$ 190.1232; found 190.1235.

N-(p-Carboxybenzyl)-5-methoxy-2,3,3-trimethyl-3H-indol quaternary salt (2). A mixture of 1 (1.89 g, 10 mmol), *p*-chloromethyl benzoic acid (1.76 g, 10.1 mmol) and *o*-dichlorobenzene was refluxed under argon at 110° for 12 h. The solvent was evaporated under reduced pressure and the resulting solid was re-dissolved in the minimum amount of acetonitrile. A black dense oil was obtained. Acetone was then added until a precipitate appeared. The solid was then filtered off and washed with acetone to yield the pure product as a brown solid (1.4 g, 38%).

¹H NMR (acetonitrile-d3, 300 MHz): d 7.92 (d, *J* = 8.1 Hz, 1H), 6.83 (s, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 3.82 (s, 3H), 2.24 (s, 3H), 1.28 (s, 6H).

HRMS (FAB): Calc. for $C_{20}H_{22}NO_3$ 324.1600; found 324.1601.

MSqb. Compound **2** (0.72 g, 2 mmol) and squaric acid (0.115 g, 1 mmol) were heated in an mixture of butanol (9 mL)-toluene (9 mL) with pyridine as a catalyst for 6 h. The solvent was evaporated and acetonitrile was added until a precipitate appeared. The precipitate was then filtered to obtain the pure product without further purification (green solid, 0.42 g, 58%). MP = 278 °C.

¹H NMR (dmso-d6, 300 MHz): d 7.92 (d, J = 7.9 Hz, 4H), 7.29 (d, J = 7.9 Hz, 4H), 7.22 (d, J = 2.5 Hz, 2H), 7.19 (d, J =8.8 Hz, 2H), 6.86 (dd, J = 8.8 and 2.5 Hz, 2H), 5.66 (s, 2H), 5.43 (br. s, 4H), 3.77 (s, 6H) and 1.71 (s, 12H). HRMS (FAB): Calc. for C₄₄H₄₀N₂O₈ 724.278; found 724.280.

Instruments

UV-Vis absorption spectra were recorded on a Shimadzu spectrophotometer model 2101 PC. In the case of transparent 4 μ m methoxy cyanide dye sensitized TiO₂ films



Scheme 1

(MSqb/TiO₂), the blank was obtained using identical dyefree mesoporous TiO_2 films to correct the light scatter phenomena.

Fluorescence emission and excitation spectra were measured using an Aminco Bowman spectrofluorometer model with a support for solid films. Fluorescence emission decays were recorded using an Edinburgh Instrument picosecond pulsed laser diode with a nominal wavelength of 635 nm (instrument response 350 ps). Transient absorption measurements were recorded as reported before.¹⁰ Cyclic voltammetry was conducted in dry solvents containing 1 mM of the cyanide dye and 0.1 M of dry tetrabutyl ammonium perchlorate as the supporting electrolyte. Reference electrode Ag/AgCl; working electrode and counter electrode, Pt; scan rate 100 mV s⁻¹; temperature 25 °C.

Squarilium methoxy cyanide dye sensitized TiO₂ films (MSqb/TiO₂)

Nanocrystalline TiO₂ and ZrO₂ particles and the mesoporous TiO₂ and ZrO₂ films were prepared as reported before.¹⁰ The 4 µm thick transparent TiO₂ films were used for characterizations such as spectroscopic and electrochemical measurements. Double-layer mesoporous TiO₂ films (8 µm) were employed for photovoltaic measurements with an additional layer of 4 µm thick scatter TiO₂ particles (diameter *ca.* 100 nm). The TiO₂ films were calcined at 450 $^{\circ}$ C for 30 min. The film thicknesses were measured using a surface profiler model XP1 profilometer, Ambios Technology. The films were cut into pieces of 1 cm^2 with an active area of 0.160 cm^2 and immersed in a dye solution for at least 5 h. The dye solution (0.5 mM) was prepared in a mixed solvent of acetonitrile-4-tert-butyl alcohol with a volume ratio of 1 : 1. The electrolyte for MSqb liquid dye sensitized solar cells (Msqb/DSSCs) comprised tetra-butyl ammonium iodide 0.6 M (2.216 g), LiI 0.1 M (0.134 g), I₂ 0.1 M (0.253 g), and 4-tert-butyl pyridine 0.5 M (0.676 g) in 10 mL of acetonitrile, HPLC degree. This electrolyte was introduced through holes drilled in the counter electrode, which were sealed immediately with a microscope cover slide. For solid-state Msqb devices (MSqb/s-DSSCs) we employed spiro-OMeTAD hole conductor [chemical name: 2,2',7,7'-tetrakis(N,N-di-p-methyloxyphenylamine)9,9'spirobifluoreno]. Several salts and additives such as tert-butyl pyridine, lithium bis-trifluorosulfinimid $[Li(CF_3SO_2)_2N]$ and the chemical dopant tris(*p*-bromophenyl) ammoniumyl hexachloroantimonate, [N(p-C₆H₄Br)₃][SbCl₆]. A thin layer of evaporated gold was used as the counter electrode.

Light-to-energy conversion measurements

The *I*–*V* measurements for liquid based MSqb/DSSCs were realized using an Oriel[®] 250 W Xenon lamp with the appropriate Oriel[®] filters to simulate the desired 1.5 AM solar spectrum and a Keithley[®] 2400 source meter. *I*–*V* measurements for solid-state DSSCs have been carried out using a Steuernagel[®] constant 575 solar simulator and a Keithley[®] 2400 source meter. Calibration of this system has been carried out by comparative measurements of DSSCs with a Spectrolab[®] X-10 solar.

Results and discussion

UV-Vis absorption spectra

The absorption spectra of MSqb in solution and for the $MSqb/TiO_2$ film are shown in Fig. 1. It can be seen that the MSqb has a well-defined spectrum with a maximum at $\lambda = 655$ nm and a shoulder at $\lambda = 600$ nm when dry pure acetonitrile (ACN) is used as a solvent. As reported before,^{5a} we assign this spectrum to the non-aggregated form of MSqb. The use of other solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or dichloromethane (DCM) induces the formation of J- and H-aggregated dimers for MSqb dye (data not shown).

The absorption spectrum of the MSqb sensitized TiO₂ film shows clear evidence for significant aggregation of the MSqb dye. It is apparent that the absorption of the MSqb/TiO₂ film has an absorption peak at $\lambda = 600$ nm unlike the MSqb dye in ACN. This spectrum is indicative of the presence of H-type MSqb aggregates. The residual peak at 650 nm is assigned to a sub-population of monomeric dyes adsorbed onto the TiO₂, as evidenced by emission data shown below.

Luminescence and electrochemistry measurements

Emission data for the MSqb dye were obtained employing non-injecting mesporous ZrO₂ films. Absorption spectra for MSqb/TiO₂ and MSqb/ZrO₂ were indistinguishable. The emission spectra of MSqb/ZrO₂ films revealed a $\lambda_{em}^{max} = 706$ nm. The corresponding excitation spectrum for this film exhibits a well defined band at 650 nm, corresponding to the absorption maximum of monomeric MSqb dyes, but a negligible contribution from the aggregated dye absorption band indicative of rapid non-radiative quenching of photogenerated excited states in the dye aggregates.

The emission properties of the MSqb are summarized in Table 1.

The transient luminescence studies confirmed efficient electron injection for the MSqb sensitized TiO_2 films, as shown in Fig. 2.



Fig. 1 The UV-Vis absorption spectra of the monomer as the aggregated form of the MSqb (H-aggregate).

	Absorption/a u	Emission/a u	Emission lifetime/ng	$E (dya^{+}/dya)^{a}$
	Absolption/a.u.	Emission/a.u.	Emission methic/iis	$L_{\rm m}$ (uye /uye)
MSqb/ACN	600, 655	670	$\tau_1 = 0.64 \ (0.25) \ \tau_2 = 2.1 \ (0.75)$	0.451
MSqb/ZrO ₂	615,660	700	$\tau_1 = 0.23 \ (0.80) \ \tau_2 = 0.95 \ (0.20)$	_
MSqb/TiO ₂	615, 660	706	$\tau < \mathrm{IRF}^b$	
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" V vs. SCE." The emission lifetime was within the instrument response of the apparatus measured using a TiO_2 film as a blank. The excitation wavelength was 635 nm. IRF = Instrument response file.

This comparison shows the transient luminescence decay of MSqb sensitized TiO₂ and ZrO₂ films, normalized to the same number of absorbed photons. ZrO2 film was employed as a control film, as the relatively high conduction band edge of this material prevents electron injection, consistent with the long excited lifetime observed for dyes adsorbed to this film. It can be noted that when compared to the control ZrO₂ films, the MSqb luminescence is strongly quenched on the TiO₂ film, consistent with efficient electron injection. In addition, despite the lower emission quantum yield of the MSqb/ZrO₂ films, when compared to acetonitrile solution, a double exponential decay with a component of $\tau_1 = 0.71$ ns and $\tau_2 = 1.2$ ns was measured, which is in agreement with MSqb in ACN solution that also shows multi-exponential behaviour with $\tau_1 = 0.6$ ns and $\tau_2 = 2.1$ ns (Table 1). According to the steady-state emission spectra of the MSqb/ZrO₂ film illustrated in Fig. 3, we have assigned the emission decay to the non-aggregated forms on the MSqb/ZrO₂. We are aware that lower excitation wavelengths ($\lambda_{ex} < 635$ nm) will be desirable to further prove our hypothesis by exciting the aggregates. Unfortunately, fastpulsed laser diodes between 550 to 620 nm were not available in our instrument. Nonetheless, as illustrated elsewhere on the manuscript, we demonstrated that electron injection mainly occurs from monomers by using incident photon-to-current conversion efficiency (IPCE) measurements.

Cyclic voltammograms were performed to determine the ground state oxidation potential for the MSqb dye. The oxidation potential of MSqb was found to be 0.451 V vs. SCE. From the MSqb/ZrO₂ emission spectra we can consider that



Fig. 2 Time resolved single photon counting decays of emission from MSqb sensitized on ZrO₂ [black, (a)] and TiO₂[grey, (b)]. The acquisition time for both samples was 600 seconds, $\lambda_{ex} = 635$ nm and $\lambda_{em} = 710$ nm. Laser power at $\lambda_{ex} = 635$ nm, 20 nJ cm⁻².

 $E_{0-0} = 1.8$ eV which is the energy difference between the ground state oxidation potential $[E^0 (D^+/D)]$ and the excited-state oxidation potential $[E^0 (D^*/D^+)]$ of the MSqb dye.

From this numbers we can estimated the excited-state oxidation potential to be ~ -1.35 vs. SCE, which is more negative than the energy level of the TiO₂ conduction band edge^{4b} estimated to be located at ~ -0.74 V vs. SCE suggesting that electron injection should be possible.

An analysis of the electronic structure of MSqb *in vacuo* was undertaken employing DFT calculations using the Spartan[®] 06 program package. A schematic representation of the molecular orbitals is illustrated in Fig. 4. The calculated energy for the highest occupied molecular orbital (HOMO) of Msqb was -4.47 eV while for the lowest unoccupied molecular orbital (LUMO) the energy value found was -2.26 eV. Hence, as a result of these calculations, a HOMO–LUMO gap of 2.2 eV can be determined, which is in reasonable agreement with the experimental value obtained for E_{0-0} .

Photovoltaic performances of MSqb/TiO₂ solar cells

The photovoltaic performances of the different DSSCs based on MSqb under AM 1.5 irradiation (100 mW cm⁻²) are shown in Table 2.

Despite the high emission quenching observed in the luminescence experiments described above, the efficiencies of the liquid MSqb based DSSCs are low. We investigate such



Fig. 3 The excitation in black ($\lambda_{em} = 730$ nm) and the singlet excited emission spectra in grey ($\lambda_{ex} = 650$ nm) under standard conditions for a 4 μ m thick MSqb/ZrO₂ film.



Fig. 4 Optimised molecular structures of Msqb by DFT calculations and the graphical representation of the HOMO (a) and LUMO (b) orbitals.

issues further measuring incident photon-to-current conversion efficiency (IPCE) spectra.

As can be observed in Fig. 5, the IPCE shows mainly injection of electrons from the non-aggregated dyes of the MSqb/TiO₂ film ($\lambda_{max} = 670$ nm). On the other hand, it is well established that to achieve high electron injection yields, the electron injection rate must be fast enough to avoid kinetic competition with the de-excitation of the excited states (Fig. 6).

Katoh *et al.* have studied the electron transfer kinetics in TiO_2 and ZnO sensitized films with coumarine dyes and they have observed ultra-fast (<150 fs) kinetics for the electron injection reaction.¹¹ We have shown a high electron injection yield from the non-aggregated MSqb into the CB (conductive band) of TiO₂. Moreover, the redox potential of the oxidized dye should accept electrons from the I⁻ ions regenerating the ground state of the dye (Fig. 6) as the energetic driving force for the regeneration of the dye ground state is adequate. In order to seek further, we decided to perform laser transient

Table 2 Photovoltaic performance of MSqb DSSCs

	$I_{\rm sc}/{\rm mA~cm}^{-2}$	$V_{\rm oc}/{ m V}$	FF	η (%)
MSqb/DSSC	0.75	0.460	0.710	0.24
N719/DSSC ^a	14.8	0.702	0.68	7.0
MSqb/s-DSSC ^b	1.0	0.59	0.44	0.26
N719/s-DSSC	2.5	0.845	0.670	1.43

^{*a*} DSSCs employing N719 [chemical name *cis*-bis (thiocyanato)bis-(2,2'-bipiridine-4,4'-dicarboxylato)ruthenium ditetrabutylammonium salt] dye were employed for comparison purposes. ^{*b*} The samples were annealed at 80 °C for 1 min. The results are the average of four devices. I_{sc} = Current at short circuit, V_{oc} = voltage at open circuit, FF = fill factor, η = efficiency.



Fig. 5 Photocurrent action spectrum obtained with a $Msqb/TiO_2$ DSSC. The redox electrolyte comprised tetra-butylammonium iodide 0.6 M (2.216 g), LiI 0.1 M (0.134 g), I₂ 0.1 M (0.253 g), and 4-*tert*-butyl pyridine 0.5 M (0.676 g) in acetonitrile.



Fig. 6 Schematic energy diagram for a MSqb DSSC with iodine/ iodide electrolyte. (1) Light excitation, (2) emission back electron transfer reaction, (3) electron injection process, (4) electron recombination with the oxidized dye. $k_{\rm RC}$ represents the kinetic rate for electron recombination and $k_{\rm RG}$ the kinetic rate for dye regeneration.

absorption studies to investigate: (1) the electron recombination dynamics between the light induced MSqb cation and the injected electrons at the TiO_2 surface and (2) the regeneration reaction between the electrolyte and the oxidized MSqb dye in the device.

Laser transient absorption measurements

The primary reason to use the extended carboxylated π system was to increase the UV-Vis band edge in the infrared region of the spectra, but also to achieve a controlled separation of the organic dye from the TiO₂ surface. We have previously demonstrated, using ruthenium based dyes, the relationship between electron recombination dynamics and the HOMO distance of the anchored molecule.^{3a,12}

The presence of the benzene ring as a spacer on the MSqb dye results in a ~7 Å separation of the charged species to the nanoparticle surface. The DFT theoretical calculations described before illustrate that either the HOMO or the LUMO orbitals of MSqb are delocalised on the aromatic backbone of the molecule, in contrast with the ruthenium dye where the HOMO is situated mainly on the axial ligands and the LUMO orbital on the carboxyl bipyridine which anchor the dye to the TiO₂ surface. The decay upon induced light absorption was monitored following laser excitation of the dye sensitized TiO₂ film, in the absence of any applied bias or redox active electrolyte. Fig. 7 illustrates the charge recombination decay for MSqb on TiO₂. The estimated half time, $t_{50\%}$, for MSqb/TiO₂ is ~0.1 ms.

This result is in good agreement with the recombination *versus* HOMO distance dependence observed for the Ru(dcbpy)₂Cl₂ complex (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) with a distance of ~7.4 Å, reported previously by Clifford *et al.*^{12a} (ESI, Fig 1S‡). However, this value indicates that the electron recombination reaction is ~10 times faster when compared with the ruthenium based dye N719 (chemical name: *cis*-bis(thiocyanato)bis(2,2'-bipiridine-4,4'-dicarboxylato)ruthenium(II) ditetrabutylammonium salt). This faster recombination cannot by itself explain the unexpected low efficiency of liquid MSqb DSSCs, the 0.1 ms half time still being slower than the regeneration half time observed for N719 in typical acetonitrile based electrolytes (~1 µs).

This observation therefore raises the issue of whether the regeneration dynamics in MSqb DSSCs may be significantly slower than N719 based devices, potentially resulting in the observed cells' lower performance. We have previously demonstrated¹³ that the presence of the I^-/I_3^- redox electrolyte induces, upon light excitation of the dye sensitized TiO₂ film, a biphasic transient decay with a fast phase, assigned to the dye

0.005

-0,00

0.5

cation electron recombination kinetics, and a slow phase, assigned to the formation of I₂⁻, with an estimated half time of $t_{50\%} \approx 0.3$ s for N719 (ESI Fig. 2S‡). However, the transient absorption data observed following excitation of the Msqb/TiO₂ film in the presence the redox electrolyte strongly indicate a negligible yield of I₂⁻ (Fig. 8).

The absence of I_2^- yield in the kinetics can be understood in terms of kinetic competition between the recombination reaction [Fig. 6, reaction (4), $k_{\rm RC}$] and the electron regeneration of the oxidized dye by the redox couple [Fig. 6, reaction (5), k_{RG}]. Under normal conditions of device operation for N719 dye sensitized solar cells, $k_{\rm RG} \gg k_{\rm RC}$, avoiding the wasteful electron recombination reaction (4) and therefore, for liquid electrolyte devices, the charge recombination between injected electrons and oxidized dye molecules will not be an important loss mechanism limiting the device efficiency. However, in our case $k_{\rm RG} \approx k_{\rm RC}$ and hence the back electron transfer reaction (4) limits the device performance. We have recently suggested the presence of an intermediate mechanism for dye sensitized solar cells, resulting in complex formation between the dye cation and the electrolyte, potentially necessary for successful regeneration dynamics.¹⁴ Although it has been only demonstrated in the case of ruthenium based DSSCs, we would like to stress that, in the case of organic dyes, it is an important issue to take into account for the design of organic DSSCs since the cation is only formed on the nonaggregated dves as demonstrated in this work. Further to prove that the results described above are not mainly due to the lack of enough driving force between the oxidized dye and the redox electrolyte, we used an organic molecule as a hole conductor that has lower oxidation potential than our liquid redox electrolyte and we performed identical experiments. Schmidt-Mende et al. have reported a striking 4% solid-state solar cell using an indoline dye and spiro-OMeTAD as a molecular hole conductor which approaches the efficiencies obtained for such a dye when a liquid iodine/iodide electrolyte is employed ($\eta \approx 8\%$ under 100 mW cm⁻² 1.5 AM irradiation) and improves the efficiency reported for ruthenium based



Fig. / 1 ransient absorption data monitoring the electron recombination dynamics for the MSqb/TiO₂ film. The inset shows the transient absorption spectra for the MSqb/TiO₂ film monitored at 0.1 ms after excitation at 650 nm.



Fig. 8 Transient absorption data monitoring at 750 nm for a MSqb/TiO₂ film (grey) and for a MSqb/TiO₂ open-cell (black). The open-cell electrolyte consisted of 0.1 M LiI, 0.05 M I₂ in propylene carbonate.



Fig. 9 Transient absorption kinetics obtained for MSqb/TiO₂/spiro-OMETAD film upon excitation at $\lambda_{ex} = 650$ nm (laser pulse intensity 25–50 µJ cm⁻²) and monitoring at $\lambda_{probe} = 570$ nm (black decay). As control sample an MSqb/TiO₂ was employed (grey decay).

solid-state DSSCs.¹⁵ Interested by these results and the fact that the solid-state MSqb DSSCs showed relative higher efficiencies for solid-state devices, we explored the kinetics for dye regeneration using the organic hole conductor molecule instead of the liquid redox electrolyte. Klug and coworkers have shown previously that the hole transfer from the oxidized dye to the organic hole conductor spiro-OMeTAD occurs on the 100 ps timescale regenerating the dye's original ground state.¹⁶ Fig. 9 shows the decay for the spiro-OMeTAD cation upon excitation of the MSqb/TiO₂/spiro-OMeTAD film.

As can be seen, a long-lived positive signal is observed when we probe at $\lambda = 570$ nm upon excitation at $\lambda = 650$ nm. This is in clear contrast with the spectrum recorded for MSqb/TiO₂ (Fig. 7 inset) where a broad negative feature can be observed which we have assigned to the bleaching of the MSqb ground state. Hence, the positive signal can only be due to the formation of the spiro-OMeTAD cation. Unfortunately, the hole injection kinetics are not resolved on the time scale employed in our experiments. It is obvious that $k_{\rm RG} \gg k_{\rm RC}$ when an organic molecule hole conductor is employed as a "solid electrolyte", solving the "kinetic competition" between reactions (4) and (5), despite the lower oxidation potential of the organic hole conductor.

Conclusions

In summary, we directly addressed the role of the molecular aggregates on the injection kinetics for a sensitized mesoporous TiO₂ film. We find that upon light excitation the electron injection only occurs from the monomers and the yield remains high (~95% of electrons are injected into the CB of TiO₂) despite the presence of H-aggregates on the film. Moreover, the steady-state luminescence and the IPCE experiments also showed that only the non-aggregated Msqb dyes are directly involved in the electron injection dynamics. On the other hand, kinetic competition between $k_{\rm RC}$ and $k_{\rm RG}$ is observed to be important when an iodine/iodide standard

electrolyte is used, resulting in a significant reduction in the vield of the regeneration reaction and therefore low device performance due to the fast electron recombination kinetics for MSqb/TiO₂ films. The laser transient spectroscopy data shows negligible changes due to the presence of the electrolyte on the Msqb recombination dynamics, indicating the lack of I_2^- formation in contrast to what it has been observed for other efficient dyes. However, an extensive interest in organic dye sensitized solar cells is currently under way and the use of solid hole conductor electrolytes where the regeneration dynamics (polymer electrolytes, small organic molecules, etc...) may result in significant improvement of device performance. Thus, our studies of charge recombination dynamics between the oxidized organic dye and the organic hole conductor spiro-OMeTAD, show a remarkable yield of hole transfer and hence, we expect that, for dyes which do not form a stable intermediate with the liquid electrolyte, it will be possible to achieve higher efficiencies for the solid-state version of the dye sensitized solar cells similar to the devices based on a liquid electrolyte.

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References

- (a) N. Robertson, Angew. Chem., Int. Ed., 2006, 45, 2338; (b)
 M. K. Nazeeruddin, C. Klein, P. Liska and M. Graetzel, Coord. Chem. Rev., 2005, 249, 1460.
- 2 (a) M. Gratzel, Prog. Photovoltaics, 2006, **15**, 429; (b) Y. Chiba, A. Islam, R. Komiya, N. Koide and L. Han, Appl. Phys. Lett., 2006, **88**, 223505/1.
- 3 (a) S. A. Haque, S. Handa, K. Peter, E. Palomares, M. Thelakkat and J. R. Durrant, Angew. Chem., Int. Ed., 2005, 44, 5740; (b) C. Klein, M. K. Nazeeruddin, P. Liska, D. Di Censo, N. Hirata, E. Palomares, J. R. Durrant and M. Graetzel, Inorg. Chem., 2005, 44, 178; (c) M. Yanagida, T. Yamaguchi, M. Kurashige, K. Hara, R. Katoh, H. Sugiara and H. Arakawa, Inorg. Chem., 2003, 42, 7921; (d) N. Hirata, J.-J. Lagref, E. Palomares, J. R. Durrant, K. K. Nazeerddin, M. Gratzel and D. Di Censo, Chem.-Eur. J., 2004, 10, 595.
- 4 (a) S. Kim, J.-K. Lee, S.-O. Kang, J. Ko, J.-H. Yum, S. Fantacci, F. de Angelis, D. Di Censo, M. K. Nazeeruddin and M. Gratzel, J. Am. Chem. Soc., 2006, **128**, 16701; (b) K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara and H. Arakawa, J. Phys. Chem. B, 2003, **107**, 597; (c) T. Horiuchi, H. Miura, K. Sumikoa and S. Uchida, J. Am. Chem. Soc., 2004, **126**, 12218; (d) D. P. Hagberg, T. Edvisson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, Chem. Commun., 2006, 2245.
- 5 (a) W. West and S. Pearce, J. Phys. Chem., 1965, 69, 1894; (b)
 A. Ehret, L. Stuhl and M. T. Spitler, *Electrochim. Acta*, 2000, 45, 4553; (c)
 K. Takeshi, P. K. Sudeep and P. V. Kamat, J. Phys. Chem. B, 2006, 110, 16169.
- 6 K. Sayama, S. Tsukagoshi, K. Hara, Y. Ohga, A. Shinpou, Y. Abe, S. Suga and H. Arakawa, *J. Phys. Chem. B*, 2002, **106**, 1363.
- 7 J. Li and F. Gan, Appl. Opt., 2000, 39, 3525.
- 8 A. R. Tameev, A. V. Vannikov and H. F. M. Schoo, *Thin Solid Films*, 2004, **451–452**, 109.
- 9 (a) X. Chen, J. Guo, X. Peng, M. Guo, Y. Xu, L. Shi, C. Liang, L. Wang, Y. Gao, S. Sun and S. Cai, J. Photochem. Photobiol., A,

2005, **171**, 231; (*b*) S. Alex, U. Santhosh and S. Das, *J. Photochem. Photobiol.*, *A*, 2005, **172**, 63.

- 10 S. Hore, E. Palomares, H. Smit, N. J. Bakker, P. Comte, P. Liska, K. R. Thampi, J. M. Kroon, A. Hinsch and J. R. Durrant, *J. Mater. Chem.*, 2005, 15, 412.
- 11 T. Yoahihara, R. Katoh, A. Furube, M. Murai, Y. Tamaki, K. Hara, S. Murata, H. Arakawa and M. Tachiya, J. Phys. Chem. B, 2004, 108, 2643.
- 12 (a) J. N. Clifford, E. Palomares, M. K. Nazeeruddin, M. Gratzel, J. Nelson, X. Li, N. J. Long and J. R. Durrant, J. Am. Chem. Soc., 2004, **126**, 5225; (b) J. R. Durrant, S. A. Haque and E. Palomares, Chem. Commun., 2006, 3279; (c) E. Palomares, M. V. Martínez-Díaz,

S. A. Haque, T. Torres and J. R. Durrant, Chem. Commun., 2004, 2112.

- 13 A. N. M. Green, E. Palomares, S. A. Haque, J. M. Kroon and J. R. Durrant, J. Phys. Chem. B, 2005, 109, 12525.
- 14 J. N. Clifford, E. Palomares, M. K. Nazeruddin, M. Gratzel, W. R. Griffith and J. R. Durrant, *J. Phys, Chem. C*, 2007, **111**, 6561–6567.
- 15 L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida and M. Gratzel, *Adv. Mater.*, 2005, 17, 813.
- 16 U. Bach, Y. Tachibana, S. A. Haque, J.-E. Moser, J. R. Durrant, M. Gratzel and D. R. Klug, J. Am. Chem. Soc., 1999, 121, 7445.



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