Rhodanine dyes for dye-sensitized solar cells: spectroscopy, energy levels and photovoltaic performance[†]

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Three new sensitizers for photoelectrochemical solar cells were synthesized consisting of a triphenylamine donor, a rhodanine-3-acetic acid acceptor and a polyene connection. The conjugation length was systematically increased, which resulted in two effects: first, it led to a red-shift of the optical absorption of the dyes, resulting in an improved spectral overlap with the solar spectrum. Secondly, the oxidation potential decreased systematically. The excited state levels were, however, calculated to be nearly stationary. The experimental trends were in excellent agreement with density functional theory (DFT) computations. The photovoltaic performance of this set of dyes as sensitizers in mesoporous TiO_2 solar cells was investigated using electrolytes containing the iodide/triiodide redox couple. The dye with the best absorption characteristics showed the poorest solar cell efficiency, due to losses by recombination of electrons in TiO_2 with triiodide. Addition of 4-*tert* butylpyridine to the electrolyte led to a strongly reduced photocurrent for all dyes due to a reduced electron injection efficiency, caused by a 0.15 V negative shift of the TiO_2 conduction band potential.

1. Introduction

At present there is a strong interest in developing metal free sensitizers for substitution of conventional ruthenium complexes¹⁻⁵ in dye sensitized solar cells (DSCs). Organic sensitizers have the advantage of high extinction coefficients and can thus also meet the demand of good light harvesting efficiency with thinner TiO₂ films. New less volatile redox systems such as ionic liquids⁶⁻⁹ and hole conductors¹⁰⁻¹² demand thinner TiO₂ films because of mass transport limitations or insufficient pore filling. A great variety of organic sensitizers based on polyene- triphenylamine,¹³⁻¹⁹ coumarin,²⁰⁻²² and indoline²³⁻²⁶ moieties give respectable conversion efficiencies of 5-9% with the traditional iodide/triiodide redox system. However, still a better fundamental understanding of the energetic, kinetic and geometric interplay between the oxide/dye/ electrolyte constituents is needed to be able to design new efficient and stable organic sensitizers for future devices.

Here we present a study on three sensitizers, with a general structure donor–linker–acceptor, D–L–A, where the triphenylamine moiety acts as an electron donor and rhodanine-3-acetic acid moiety as an acceptor. The linker conjugation is systematically changed with methine and thiophene units to increase the spectral response. The dyes will be referred to as L0, L1 and L2, respectively, according to the linker length, see Fig. 1. The rhodanine-3-acetic acid anchoring group has shown very promising efficiencies for coumarin and indoline dyes^{23–25} and also recently for triphenylamine based dyes by Liang and Tian *et al.*^{27,28}

Spectroscopic and electrochemical properties were characterized experimentally and by density functional theory (DFT) computations. Photoelectron spectroscopy (PES) was used for element specific information on the electronic and molecular structure of the dye sensitized surface.^{29–32} The behavior of the dyes in functional solar cell devices was further investigated by current–voltage (IV), incident-photon-to-current-efficiency (IPCE), charge extraction, voltage and current decay measurements. For this series of dyes used in DSCs two main effects were studied and discussed: (i) the dependence of the linker conjugation length and (ii) the influence of the additive 4-*tert*butylpyridine (4-TBP) on the overall solar cell performance for this series of dyes.

2. Experimental

2.1 Synthesis

The dyes were synthesized according to well known reactions; the detailed synthetic procedures are described in the ESI. \dagger As a representative, the synthesis of L1 is illustrated in Scheme 1. Suzuki coupling of 4-(diphenylamino) bromobenzene and

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Fig. 1 Molecular structure of the sensitizers used in this study: L0, L1 and L2. The number is related to the length of the conjugated linker between the triphenylamine and the rhodanine-3-acetic acid moieties.



Scheme 1 Synthetic route to dye L1.

5-formyl-2-thiophene-boronic acid under microwave irradiation provided compound **1**. Condensation of the aldehyde moiety with rhodanine-3-acetic acid by the Knoevenagel reaction with excess amount of piperidine yielded **L1**' as a precipitate which was filtered and washed with acetonitrile and water. The carboxylate-salt **L1**' was dissolved in dichloromethane (DCM), washed with aq. HCl (1 M) and converted to the corresponding carboxylic acid **L1**.

2.2 Dye-sensitized solar cells

Mesoporous TiO₂ films (*ca.* 10 μ m thick) were immersed in 500 μ M dye solutions in acetonitrile for 12–14 h in room temperature, followed by immersion in pure acetonitrile for a

few minutes and drying in an air flow. DSCs were further prepared using standard methods given in the ESI[†] and characterized using methods given there.

3. Results and discussion

3.1 Spectroscopic and electrochemical characterization

The optical and electrochemical properties of the dyes in solution and adsorbed onto TiO_2 are summarized in Table 1. A red-shift is observed with increasing the linker conjugation length; the absorption maxima in acetonitrile solution were observed at 459, 476 and 501 nm, for L0, L1 and L2, respectively. The corresponding molar extinction coefficients (ϵ_{max}) were approximately 44 000, 38 000 and 39 000 M⁻¹ cm⁻¹ for L0, L1 and L2, respectively, at absorption maximum. The high extinction coefficients of these dyes meet the requirements for solid state dye-sensitized solar cells, where thinner TiO₂ films are used to obtain efficient devices.¹⁰

The ground state oxidation potential (E_{D/D^+}) of the dye is an important parameter when evaluating the driving force for regeneration of the oxidized dye via the redox system. The oxidation potential must be sufficiently more positive than the potential of the redox couple iodide/triiodide to obtain fast regeneration kinetics. Sluggish regeneration kinetics are unfavorable for the overall solar cell efficiency.^{31,33,34} The oxidation potentials of the dyes in solution were measured by differential pulse voltammetry (DVP) and showed a clear dependence on the conjugation length: $E_{L0/L0+} > E_{L1/L1+}$ > $E_{L2/L2+}$ see Table 1. Although the absolute values might differ slightly when the dyes are adsorbed onto TiO₂, the internal trend is expected to be similar. As the redox potential of the iodide/triiodide electrolyte is about 0.3 V vs. NHE, the regeneration driving force can be calculated to 0.69, 0.85 and 0.97 V, for L2, L1 and L0, respectively. This may be compared to 0.70 V for the conventional N719 ruthenium complex (oxidation potential of 1 V vs. NHE).² The estimated excited state potential, E_{D^*/D^+} , calculated from $E_{D/D^+}-E_{0-0}$, seems to be sufficiently more negative than the TiO_2 CB edge for all three dyes and hence should in theory have enough driving force for effective injection, as reported in Table 1.

PES measurements of the valence structure of sensitized TiO_2 reveals the HOMO energy levels of the adsorbed organic dyes, see Fig. 2. The results support the trend observed in the electrochemical measurements. When compared to PES data from adsorbed N719,³⁰ the peak positions of the HOMO energy levels of L2, L1 and L0 are shifted towards higher binding energy by approximately 0.2, 0.3 and 0.4 eV,

Table 1 Experimental spectral and electrochemical properties of the dyes

Dye	λ_{max}/nm	$\epsilon^b/\mathrm{M}^{-1}~\mathrm{cm}^{-1}$	$\lambda_{\rm em}{}^a/{\rm nm}$	$E_{\mathrm{D/D}+}^{c}/\mathrm{V}$ vs. NHE	$E_{(o-o)}^{d}/eV$	$E_{\mathbf{D}^*/\mathbf{D}^+}^{e}/\mathbf{V}$ vs. NHE
LO	459 ⁱ , 438 ⁱⁱ	44 000	607	1.27	2.38	-1.11
L1	476 ⁱ , 459 ⁱⁱ	38 000	668	1.15	2.19	-1.04
L2	501 ⁱ , 469 ⁱⁱ	39 000	726	0.98	2.08	-1.10

^{*a*} Absorption of dyes in acetonitrile solution^{*i*}, adsorbed onto TiO₂^{*ii*}, and emission spectra in acetonitrile. ^{*b*} Absorption coefficient in THF. ^{*c*} The ground state oxidation potential, E_{D/D^+} , of the dyes were measured with DPV under following conditions: working electrode; Pt, electrolyte; 0.1 M tetrabutylammonium hexafluorophosphate, TBA(PF₆) in acetonitrile. Potentials measured *vs*. Fc⁺/Fc were converted to NHE by addition of +0.63 V.⁴⁸ ^{*d*} $E_{(o-o)}$ is estimated from the intercept of the normalized absorption and emission spectra in acetonitrile. ^{*e*} E_{D^*/D^+} is estimated by subtracting $E_{(o-o)}$ to E_{D/D^+} .





Fig. 2 Photoelectron spectroscopy (PES) valence electronic structure of TiO₂ sensitized with L0, L1 and L2. The measurement was performed with a photon energy of 100 eV. The energy scale was calibrated using the Ti3p peak of the TiO₂ substrate.

respectively. While only one feature can be resolved in the HOMO level measured for L0 and L1, the less symmetric peak obtained in the measurements of L2 indicates that more than one state may be involved in the HOMO level of L2.

3.2 **Quantum chemical calculations**

In Table 2 we report experimental and computed absorption maxima for the lowest energy electronic transitions. Details of the quantum chemical calculations are given in the ESI.[†] Starting with the B3LYP and PBE1PBE gas phase results, we note that both methods provide a good prediction for λ_{max} of the shortest dye, L0; the calculated wavelengths are 466 and 440 nm, respectively, which compares well with the experimental λ_{max} of 459 nm for L0 in acetonitrile. However, the computations are not able to correctly predict the magnitude of the change in λ_{max} going towards longer dyes. In going from L0 to L2 the energy of the absorption maximum decreases by 0.23 eV experimentally, whereas the computational methods predict a decrease of 0.53-0.54 eV. For example, our B3LYP

calculation overestimates the energy of the absorption maximum of L2 in solution by 0.36 eV, whereas the PBE1PBE method does better with an overestimation of only 0.19 eV. The results are not surprising since TDDFT methods are known to underestimate the energies for charge-transfer states, and the underestimation generally increases with the distance of charge separation. The error can be partly reduced by the inclusion of Hartree-Fock exchange, which explains the slightly better performance of the PBE1PBE functional, as the latter includes more Hartree-Fock exchange than B3LYP. However, using the full Hartree-Fock exchange in the TDHF method leads to energies of the absorption maximum that are too low by 0.7-1.3 eV (data not shown here). Inclusion of solvent at the B3LYP and PBE1PBE levels using the PCM (polar continuum model) method generally reduces the transition energy by 0.21-0.23 eV. The gas phase results are, however, in better agreement with the experiments than the PCM results, for both the B3LYP and PBE1PBE methods. The reason for this is most likely a cancellation of errors; the underestimation of transition energies in the DFT calculations are partly compensated for by the higher transition energies in gas phase compared to solution. The computed oscillator strengths decrease slightly on going from L0 to the longer L1, which is in qualitative agreement with the experiments. The strong absorption calculated for L2 is not, however, supported by the experiments.

In Table 3, the experimental oxidation potentials are listed together with the computed oxidation potentials and reorganization energies. It can first be noted that the B3LYP and PBE1PBE methods yield oxidation potentials for all three dyes that are too positive by approximately 0.6 and 0.5 V, respectively. The relative position of the oxidation potentials within this group of dyes that are calculated are, however, in very good agreement with experiment. This indicates that the computations are able to reproduce differences in the oxidation properties between the dyes. It is interesting that the computed reorganization energy is almost identical for the three dyes. It is noted that the polyene diphenyl aniline cyanoacetic acid (D5), which showed high performance in solar cells reported by our group¹⁴ has a very similar calculated reorganization energy (0.97 eV).

Fig. 3 depicts the B3LYP computed LUMO orbitals of the dyes. In all three dyes the strongest absorption band is dominantly of HOMO-LUMO character, i.e. the expansion coefficient for the HOMO-LUMO transition is higher than 0.65. The electron redistribution of the orbitals indicates a charge separation upon electronic excitation. Both HOMO

Table 2 Experimental and computed spectral properties of the lowest energy absorption band of the dyes

Dye	λ_{\max}^{a}/nm Exp.	$arepsilon^b/\mathbf{M}^{-1}\mathbf{cm}^{-1}$ Exp.	λ_{\max}^{c}/nm B3LYP	f ^d B3LYP	λ_{\max}^{e}/nm PBE1PBE	f ^f PBE1PBE
L0 L1	459 476	44 000 38 000	466, 510 ⁱ 543, 605 ⁱ	$\begin{array}{c} 0.89,\ 0.93^{\rm i}\\ 0.88,\ 0.89^{\rm i} \end{array}$	440, 476 ⁱ 503, 553 ⁱ	$0.95, 0.99^{i}$ $0.94, 0.93^{i}$
L2	501	39 000	586, 653 ⁱ	1.22, 1.23 ⁱ	542, 596 ⁱ	1.35, 1.34 ⁱ

^a Absorption maxima of dyes in acetonitrile solution at room temperature. ^b Absorption coefficient in THF. ^c TDDFT-B3LYP/6-31+G (d) computed vertical excitation wavelengths. (i) in acetonitrile using the PCM approach. d TDDFT-B3LYP/6-31+G (d) computed oscillator strengths. e TDDFT-PBE1PBE/6-31+G (d) computed vertical excitation wavelengths. f TDDFT-PBE1PBE /6-31+G (d) computed oscillator strengths.

 Table 3 Experimental and computed electrochemical properties of the dyes

Dye	$\frac{\Delta E_{D/D}}{E_{D/D}} + [V vs. \text{ NHE}]^{ii}$ Exp.	$\frac{\Delta E_{D/D}}{E_{D/D}} + \begin{bmatrix} b \\ vs. & \text{NHE} \end{bmatrix}^{\text{ii}} \\ \text{B3LYP}$	$\frac{\Delta E_{D/D}}{(E_{D/D}+[V vs. NHE]^{ii})}$ PBE1PBE	λ_{o}^{d}/eV (kcal mol ⁻¹)
L0 L1 L2	$\begin{array}{c} 0^{i} \ (1.27)^{ii} \\ -0.12^{i} \ (1.15)^{ii} \\ -0.29^{i} \ (0.98)^{ii} \end{array}$	$\begin{array}{c} 0^{i} \ (0.73)^{ii} \\ -0.20^{i} \ (0.53)^{ii} \\ -0.33^{i} \ (0.40) \end{array}$	$\begin{array}{c} 0^{i} \ (0.81)^{ii} \\ -0.19^{i} \ (0.62)^{ii} \\ -0.30^{i} \ (0.51)^{ii} \end{array}$	0.96 (22.1) 0.95 (22.0) 0.94 (21.6)

(i) The relative difference in ground oxidation potential, $\Delta E_{D/D^+}$, between the dyes normalized to the value for L0 and (ii) the absolute ground state oxidation potential, E_{D/D^+} vs. NHE of^{*u*} (exp) Dyes measured under following conditions; Working electrode; Pt, Electrolyte; 0.1 M tetrabutylammonium hexafluorophosphate, TBA(PF₆) in acetonitrile. Potentials measured vs. Fc⁺/Fc were converted to NHE by addition of +0.63 V.^{48 b} (B3LYP) Values computed using equation. 1. at the *PCM-B3LYP/6-31+G(d)* level. ^{*c*} (PBE1PBE) Values computed at the *PCM-PBE1PBE/6-31+G(d)* level. ^{*d*} The electron-transfer reorganization energy computed using equation. 2 at the *PCM-B3LYP/6-31+G(d)* level.



Fig. 3 The frontier molecular orbitals of the HOMO (bottom) and LUMO (top) calculated with PCM-PBE1PBE/6-31 + G(d) level. The electron redistribution of the orbitals shows a clear charge separation upon electronic excitation.

and LUMO are partially located on the conjugated system which supports the observed dependence of the oxidation potential upon the linker conjugation length. The LUMO orbital does not extend out to the carboxylate group that links the dye to the TiO₂ surface, indicating a less strong electronic coupling between the dye LUMO and the acceptor states of TiO₂ in comparison to for example cyanoacetic acid as anchoring group where the conjugation is extended out on the carboxylic group. In this context, it is also interesting to compare our results with the high efficiency indoline dye reported by Hourichi et al. using the same rhodanine-3-acetic acid anchoring group as in the present study.23,25,26 Our calculation of the indoline dye (not shown here) shows a lack of electron density of the LUMO on the anchoring group, which also suggests a less strong electronic coupling with TiO2 acceptor states.

3.3 Solar cell performance

The photovoltaic performance of solar cells based on L0, L1 and L2 dyes under AM 1.5G illumination, 100 mW cm⁻², is summarized in Table 4. The efficiencies obtained with solar cells with electrolyte 1 (0.5 M LiI and 0.05 M I₂ in acetonitrile) were $\eta = 2.7\%$ for L0, $\eta = 2.3\%$ for L1 and $\eta = 1.7\%$ for L2, showing that higher efficiencies were obtained for the dyes with a shorter conjugation length. In order to improve the open-circuit potential (V_{OC}), 0.5 M 4-tertbutylpyridine (4-TBP) was added to the electrolyte. Although this gave

Table 4 Solar cell characteristics of DSCs based on the L0, L1 and L2 under AM 1.5G illumination (100 mW cm⁻²). The electrolytes used were: (1) 0.5 M LiI and 0.05 M I₂ in acetonitrile; (2) same, but with 0.5 M 4-*tert*-butylpyridine added

Conditions ^a	$\eta/\%$	$V_{\rm oc}/{ m V}$	$J_{\rm SC}/{ m mA~cm^{-2}}$	ff
L0, electrolyte 1	2.7	0.50	10.0	0.54
L0, electrolyte 2	1.3	0.61	3.7	0.58
L1, electrolyte 1	2.3	0.44	10.5	0.50
L1, electrolyte 2	2.0	0.58	5.9	0.58
L2, electrolyte 1	1.7	0.41	7.7	0.54
L2, electrolyte 2	0.8	0.49	2.9	0.56

^{*a*} The TiO₂ film thickness was $\sim 10 \ \mu$ m. Electrodes were dyed during 15 h in 500 μ M dye solutions in acetonitrile. The active area was 0.48 cm².

rise to a modest increase of $V_{\rm OC}$ by about 0.1 V, a dramatic decrease of the short-circuit current density ($J_{\rm SC}$) was observed, resulting in lower overall solar cell efficiencies.

Spectra of the incident photon-to-current-conversion efficiency (IPCE) for L0, L1 and L2-based solar cells with electrolyte 1 (no 4-TBP) are shown in Fig. 4. In the range 500–550 nm, IPCE maxima of up to 84%, 74% and 50% were found for L0, L1 and L2, respectively. The effect of 4-TBP addition to the electrolyte is pronounced in the IPCE spectra.



Fig. 4 Spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for DSC based on L0 (\bullet), L1 (\blacksquare) and L2 (\triangleright), respectively. Electrolyte: 0.5 M LiI and 0.05 M I₂ in acetonitrile.



Fig. 5 Spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for DSCs based on (a) L0 (b) L1 and (c) L2; with (- - -) and without (—) 4-TBP in the electrolyte, (d) normalized IPCE spectra for DSC based on L0.

Fig. 5a–c shows IPCE spectra of L0, L1 and L2 using electrolyte with and without 4-TBP. Fig. 5d shows normalized IPCE spectra of L0 based solar cells with the two electrolytes. A pronounced blue shift of the IPCE spectrum is observed for L0. Similar blue shifts are found for L1 and L2.

3.4 Origin of differences in photovoltaic performance of L0, L1 and L2

We will divide this section in two parts: First, we will discuss the internal differences observed in electrolyte without 4-TBP, and second we will discuss the effect of 4-TBP on the solar cell performance.

3.4.1 Performance of L0, L1 and L2 sensitizers in absence of 4-TBP. Dve-load: Although the organic sensitizers differ only slightly in chemical structure, there are significant differences in dye load, photocurrent generation, charge recombination kinetics and energy levels in the DSC. The dye load was determined by desorbing the dye from the TiO₂ film using an alkaline solution and recording the UV-Vis spectrum. The L2 dye load was equal or higher than the L0 dye load. This was unexpected as L2 is a larger molecule, and this could be an indication of aggregation of L2. The coverage of dye on the sensitized TiO₂ samples can also be estimated by PES measurement by a comparison between the intensity of a dye specific core level peak and a substrate (TiO₂) specific peak. The coverage of dye on the sensitized TiO₂ surface was found to vary between the sensitizers. The relative intensity ratio of the S2p from the double bonded sulfur in the anchor group and Ti2p peak originating from the TiO_2 is 0.66, 0.73 and 1 for L0, L1 and L2, respectively. This result is a further indication that more L2 than L0 is adsorbed on the TiO₂ surface. It should be noted that PES is a surface sensitive techniques, probing only a few angströms into the material.

Dye orientation: The dye orientation on the surface was further investigated by analyzing N1s (nitrogen) and S2p core-level PES. For a randomly ordered molecular layer (dye powder on conducting glass), the PES N1s intensities should show a 1:1 ratio of the peak originating from the triphenylamine moiety (N1s_{TPA}) and that from the rhodanine-3-acetic acid moiety (N1s_{R3A}). As observed in Fig. 6, the N1s signal from these samples can indeed be reasonably well curve



Fig. 6 N1s PES spectra of L0 (top figure), L1 (middle figure) and L2 (lower figure). Both spectra of multilayers (ML) and spectra of dyesensitized TiO_2 are shown for the different dyes. The measurements were performed with a photon energy of 1487 eV for the ML and both 1487 and 758 eV for the dye-sensitized TiO_2 .

Table 5 Intensity ratios of N1s core level PES peaks for the dyes on ${\rm TiO}_2$

Dye	$\frac{N1s_{R3A}/N1s_{TPA}}{h\nu} = 1487 \text{ eV}$	$\frac{N1s_{R3A}}{N1s_{TPA}}$ $h\nu = 758 \text{ eV}$
LO	0.43	0.33
L1	0.41	0.28
L2	0.32	0.23
D5	0.37	0.23

fitted with two components having the same intensity. The peak at lower binding energy can be assigned to $N1s_{TPA}$ and the peak at higher binding energy to $N1s_{R3A}$.³⁵

In dye-sensitized TiO₂ electrodes the ratio between these two peaks changed. An intensity ratio between the N1s_{B3A} and $N1s_{TPA}$ peaks of about 0.5 was found at a photon energy of 1487 eV, which gives a strong evidence for a dominating orientation of the molecule having the triphenylamine moiety pointing out from the TiO₂ surface.³⁵ The surface sensitivity depends on the kinetic energy of the emitted electrons and can be improved by decreasing the photon energy. This explains why the intensity ratio between N1s_{R3A} and N1s_{TPA} decreasees further in the measurements performed at lower photon energy of 758 eV, see Table 5. Comparing the N1s ratios in more detail we observe that the intensity ratio decreases in the order L0, L1, L2. This change is in accordance with the decrease in the distance between the two nitrogen atoms in the different molecules. Previous measurements of the D5 molecule, also containing two spectroscopically distinguishable nitrogen atoms at a distance similar to that of L1, show very similar ratios.35 The PES analysis of the dye-sensitized samples therefore suggests that differences in molecular orientation among the L0, L1, L2 series is small and the preferred orientation is having the triphenylamine moiety pointing out from the surface and is similar to that of the D5 molecule. Additional measurements using the S2p signals confirm the results (see ESI).[†]

Light-harvesting efficiency: L2-sensitized TiO₂ films absorb more sunlight than L1 or L0-sensitized films. The lightharvesting efficiency (LHE = $(1 - 10^{-4})$, with A the absorbance of the film) was measured with dyes adsorbed on ~3 µm thick TiO₂ films, and is plotted in Fig. 7. As expected, L2 has the most red-shifted onset, followed by L1. Due to the high extinction coefficients, the LHE is 100% in the range 400–500 nm for all dyes. The IPCE in the same range was, however, significantly below 100%, see Fig. 4. IPCE can be expressed as follows:

$$IPCE(\lambda) = LHE(\lambda) \cdot \phi_{inj} \cdot \eta_{reg} \cdot \eta_{cc}$$
(1)

where ϕ_{inj} , η_{reg} and η_{cc} are the quantum yields of charge injection, dye regeneration and charge collection efficiency, respectively. For L0 an IPCE of 84% was obtained. As reflection losses are estimated to be in the order of 15%, it appears that ϕ_{inj} , η_{reg} and η_{cc} are all nearly 100% for this dye. We will now establish which factors limit the IPCE of L1 and L2.

Injection efficiency: The injection efficiency is given by the ratio of the rate constant for electron injection and the sum of all deactivation rate constants for the excited dye molecule.



Fig. 7 UV-Vis absorption spectra converted to LHE(%) of L0 (\bullet), L1 (\blacksquare) and L2 (\triangleright) adsorbed onto TiO₂ in the presence of redox electrolyte. Inset: UV-Vis absorption spectra of L0, L1 and L2, respectively, adsorbed onto TiO₂ in the presence of electrolyte.

The calculated LUMO levels for dyes L0, L1 and L2 are similar, see Table 1, and located well above the TiO₂ conduction band edge. Furthermore, the dyes have identical binding groups and similar electronic structure, suggesting that electronic coupling to CB states will be similar. Therefore, no significant differences in ϕ_{inj} between the dyes are expected.

Regeneration of the oxidized dye: Photoinduced absorption (PIA) spectroscopy^{34,36} demonstrated clearly that the dyes were able to inject electrons into TiO₂ upon excitation, as spectral characteristic of the oxidized dye molecules were observed (see Supporting Information). The spectral characteristic of the oxidized dye disappeared from the PIA spectrum when the redox electrolyte was added (see ESI).[†] This suggests that the regeneration of the dye (reduction of the oxidized dye by iodide) is efficient. As the oxidation potentials for the dyes differ, rate constants for regeneration may differ, and, based on driving force, are expected to be decrease in the order L0 > L1 > L2. Ultrafast laser spectroscopy studies, to be published elsewhere, are presently being performed on the system to determine injection and recombination kinetics, and their impact on the photocurrent generation. Different limitations in the ultrafast kinetics can reduce the value of η_{reg} and may explain in part the observed differences in IPCE.

Charge collection efficiency: Losses of injected electrons during transport in the porous TiO_2 film are given by good approximation by the ratio of electron transport time and electron lifetime. These characteristic time constants were determined using photocurrent and photovoltage transients following small modulations of light intensity as previously described.^{37–41} No significant differences in electron transport times plotted against short-circuit charge density in the film are found (see ESI),† which can be expected as the transport is determined mostly by properties of the mesoporous TiO_2 electrode and not by the dye.³⁹ Electron lifetimes measured at the same light intensities, but under open-circuit conditions, differ significantly between the dyes, see Fig. 8a. Electron lifetimes under short-circuit conditions were estimated using



Fig. 8 (a) Electron lifetime as function of open-circuit voltage. Time constants were determined using time-resolved small modulation techniques. Solar cells based on L0 (\bullet), L1 (\blacksquare) and L2 (\triangleright), respectively, with 0.5 M LiI, 0.05 M I₂ in acetonitrile. (b) Extracted charge as a function of open-circuit potential in dye sensitized solar cells based on L0 (\bullet), L1 (\blacksquare) and L2 (\triangleright), respectively, with electrolyte (1) 0.5 M LiI, 0.05 M I₂ in acetonitrile. (c) Dark current-voltage characteristics of DSC based on L0 (\bullet), L1 (\blacksquare) and L2 (\triangleright), respectively.

the extracted charge under short-circuit conditions and the relation between charge and electron lifetime at open circuit condition that were measured separately (see ESI).† η_{cc} was estimated to be 0.9 for L2-sensitized solar cells and 1.0 for L1 and L0. In conclusion, the differences in IPCE as observed in Fig. 4 can be attributed to differences electron collection and possibly also to differences in dye regeneration efficiency.

Electron lifetimes in dye-sensitized solar cells depend significantly on the type of sensitizing dye, as has been observed before in several studies.^{42,43} This is remarkable as the lifetime reflects the recombination between electrons in the TiO₂ and triiodide in the electrolyte. The relatively large differences in electron lifetime between the dyes used in this study are even more surprising, considering the similarity of the dyes. In Fig. 8a electron lifetimes of DSCs based on L0. L1 and L2 are shown as a function of open-circuit voltage. Lifetimes decrease in the order L0 > L1 > L2. Adsorbed dye can affect the position of the TiO_2 conduction band edge. The relation between charge and open-circuit voltage was therefore studied, see Fig. 8b. No significant differences in photovoltage-charge relation were found for the different dyes, indicating that the dyes affect the surface in a similar way. Differences in electron recombination are thus only due to the nature of the dye, and not due to band edge shifts.

It appears that dye molecules can catalyze the reduction of triiodide.⁴³ To confirm this, dark current–voltage characteristics were measured, see Fig. 8c. The dark current decreases in the order L2, L1 and L0, which agrees well with the electron lifetime results. The higher dye load of L2 in comparison to L1 and L0 does not protect electrons in TiO₂ from recombination with triiodide, but is in fact promoting this reaction. The origin of the catalysis of triiodide reduction may be the formation of a complex between the dye and iodine (or triiodide), as was recently suggested by O'Regan *et al.*⁴³ Differences in binding constants of dye and iodine (or triiodide) are possibly the origin of the differences in electron lifetimes and dark currents.

3.4.2 Influence of 4-TBP additive on the photovoltaic performance. Position of the conduction band: The position of the TiO₂ conduction band (CB) depends on the surface charge, which is affected by the electrolyte composition. Li⁺ ions adsorb relatively strongly at the TiO₂/electrolyte interface and cause thereby a positive shift of the conduction band edge potential. Adsorption of negatively charged ions or Lewis base molecules, such as 4-TBP, shifts the CB edge to more negative potential. 4-TBP has successfully been used to increase the efficiency of N719-sensitized TiO₂ solar cells as it improves the open-circuit voltage, while the short-circuit currents is hardly affected.^{2,37} To study the relation between charge and open-circuit voltage for DSCs with and without 4-TBP in the electrolyte, we applied a charge extraction method.44 Results are presented in Fig. 9 for L1-sensitized solar cells. For a given charge, a higher open-circuit voltage, $V_{\rm OC}$, is obtained when 4-TBP is present in the electrolyte. This implies that the conduction band edge is shifted to more negative potential, provided that distribution of traps is not affected.37

IPCE spectra are significantly lower and blue-shifted in the presence of 4-TBP, see Fig. 5. To explain these observations, we will again factorize the IPCE using eqn (1).

Light-harvesting efficiency: The absorption spectrum of the adsorbed dyes did not change in the presence of 4-TBP. Furthermore, no significant differences in dye-desorption was observed when sensitized films were exposed to redox



Fig. 9 Extracted charge as a function of open circuit potential in L1-sensitized solar cells with electrolyte 1 (\bullet) 0.5 M LiI, 0.05 M I₂ in acetonitrile and 2 (\Box) 0.5 M LiI, 0.05 M I₂, 0.5 M 4-TBP in acetonitrile.

electrolyte with and without 4-TBP. The blue-shift of the IPCE must originate from one of the other factors.

Regeneration of the oxidized dye: We do not expect that 4-TBP interferes significantly with the dye regeneration, although fast spectroscopic studies are needed to confirm this. η_{reg} is likely to be similar to the situation without 4-TBP in the electrolyte.

Charge collection efficiency: In contrast to N719-sensitized TiO₂ solar cells,^{45–47} 4-TBP did not increase the electron lifetime in L0, L1 and L2-sensitized solar cells. The collection efficiency is therefore not expected to be much affected. The presumed blocking effect of 4-TBP, by binding to uncovered TiO₂ surface will be less important for small dye molecules. Furthermore, if the main reaction pathway of recombination is through a possible dye-iodine (-triiodide) complex, the surface blocking will not have much effect.

Injection efficiency: The observed changes in the IPCE spectra are most likely due to changes in the injection efficiency upon addition of 4-TBP. As discussed above, addition of 4-TBP leads to a shift of the TiO₂ conduction band edge to higher energy. This will decrease the density of acceptor states in the TiO₂ which are located at the same energy as the excited dye levels. This will result in a decrease of the electron injection rate constant and the injection efficiency. The observed blue shift in the IPCE spectra suggests that the injection efficiency is wavelength dependent and is illustrated in Fig. 10. If electron injection occurs from hot (= not vibronically relaxed) excited states a wavelength-dependent injection rates and injection efficiency may be expected. The excited state resulting from absorption of a red photon has less energy than that resulting from a blue photon, and its energy may not be high enough for successful electron injection.

It is interesting to compare the L2 sensitizer to the closely related D5 dye^{14,35} that differs in structure only by the acceptor group, cyanoacetic acid. This causes a difference in excited state potential, E_{D^*/D^+} : values of -1.04 V for L2 and -1.36 V for D5 vs. NHE are estimated under the same



dye donor state and TiO2 acceptor states is also shown.

- 1 B. O'Regan and M. Grätzel, Nature, 1991, 353(6346), 737-740.
- 2 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, J. Am. Chem. Soc., 1993, 115(14), 6382–6390.
- 3 M. A. Green, K. Emery, D. L. King, Y. Hishikawa and W. Warta, *Prog. Photovolt.*, 2007, **15**(1), 35–40.
- 4 J. M. Kroon, N. J. Bakker, H. J. P. Smit, P. Liska, K. R. Thampi, P. Wang, S. M. Zakeeruddin, M. Grätzel, A. Hinsch, S. Hore, U. Wurfel, R. Sastrawan, J. R. Durrant, E. Palomares,

conditions. In contrast to L2, high IPCE values are obtained for D5, even in the presence of 4-TBP, and significantly higher photovoltages are found. While the principle anchoring group to the TiO₂ is identical, *i.e.* carboxylic acid, computational results show that in case of D5 the LUMO is extended to this group, whereas it is not in case of the rhodanine-3-acetic acid of L2 (see Fig. 3). This suggests that a combination of reduced injection driving force (~0.2 V) and weaker coupling between the excited state level in L2 and TiO₂ CB levels result in slower injection kinetics and poorer injection efficiencies in cases where the TiO₂ CB levels are relatively close in energy to the excited state levels of the dye, *i.e.* when 4-TBP is present in the electrolyte.

4. Conclusions

A series of three closely related dyes has been designed, synthesized and investigated in dye-sensitized solar cells. The dyes consist of an electron donor moiety, triphenylamine, and an electron acceptor moiety, rhodanine-3-acetic acid, linked together using methine and thiophene moieties. Increase of the conjugation length resulted in a more red-shifted spectral response and less positive oxidation potentials. The calculated excited state levels were stationary. DFT calculations using PCM solvation corrected B3LYP and PBE1PBE was in good agreement with experimental electrochemical and optical data. The photovoltaic performance of this set of dyes as sensitizers in mesoporous TiO₂ solar cells was investigated using electrolytes containing the iodide/triiodide redox couple. The dye with the best absorption characteristics, L2, showed the poorest solar cell efficiency, due to insufficient dye regeneration and charge collection efficiencies. Addition of 4-tertbutylpyridine to the electrolyte led to a strongly reduced photocurrent for all dyes due to a reduced electron injection efficiency, caused by a 0.15 V negative shift of the TiO₂ conduction band potential.

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Fig. 10 Energy scheme of the dye sensitized TiO₂ solar cell, where the

shift in CB, influencing the photovoltage is illustrated for the cases

with and without 4-TBP. The possible variation in overlap between

- 5 S. Ito, M. K. Nazeeruddin, P. Liska, P. Comte, R. Charvet, P. Pechy, M. Jirousek, A. Kay, S. M. Zakeeruddin and M. Grätzel, *Prog. Photovolt.*, 2006, 14(7), 589-601.
- 6 S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Pechy, M. Takata, H. Miura, S. Uchida and M. Grätzel, *Adv. Mater.*, 2006, **18**(9), 1202.
- 7 N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhote, H. Pettersson, A. Azam and M. Grätzel, J. Electrochem. Soc., 1996, 143(10), 3099–3108.
- 8 P. Wang, S. M. Zakeeruddin, M. Grätzel, W. Kantlehner, J. Mezger, E. V. Stoyanov and O. Scherr, *Appl. Phys. A*, 2004, **79**(1), 73–77.
- 9 P. Wang, S. M. Zakeeruddin, J.-E. Moser, R. Humphry-Baker and M. Grätzel, J. Am. Chem. Soc., 2004, 126, 7164–7165.
- 10 L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, S. Uchida and M. Grätzel, *Adv. Mater.*, 2005, 17(7), 813.
- 11 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Grätzel, *Nature*, 1998, **395**(6702), 583–585.
- 12 J. Hagen, W. Schaffrath, P. Otschik, R. Fink, A. Bacher, H. W. Schmidt and D. Haarer, Synth. Met., 1997, 89(3), 215–220.
- 13 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. Grätzel, *J. Am. Chem. Soc.*, 2006, **128**(51), 16701–16707.
- 14 D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2006, (21), 2245–2247.
- 15 K. Hara, T. Sato, R. Katoh, A. Furube, T. Yoshihara, M. Murai, M. Kurashige, S. Ito, A. Shinpo, S. Suga and H. Arakawa, *Adv. Funct. Mater.*, 2005, **15**(2), 246–252.
- 16 T. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N. A. Anderson, X. Ai, T. Q. Lian and S. Yanagida, *Chem. Mater.*, 2004, **16**(9), 1806–1812.
- 17 D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt and L. Sun, *J. Org. Chem.*, 2007, **72**(25), 9550–9556.
- 18 D. P. Hagberg, J. H. Yum, H. Lee, F. De Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Gratzel and M. K. Nazeeruddin, J. Am. Chem. Soc., 2008, 130(19), 6259–6266.
- 19 H. Qin, S. Wenger, M. Xu, F. Gao, X. Jing, P. Wang, S. M. Zakeeruddin and M. Gratzel, *J. Am. Chem. Soc.*, 2008, 130(29), 9202.
- 20 K. Hara, Z. S. Wang, T. Sato, A. Furube, R. Katoh, H. Sugihara, Y. Dan-Oh, C. Kasada, A. Shinpo and S. Suga, *J. Phys. Chem. B*, 2005, **109**(32), 15476–15482.
- 21 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**(2), 597–606.
- 22 K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga and H. Arakawa, *Chem. Commun.*, 2001, (6), 569–570.
- 23 T. Horiuchi, H. Miura and S. Uchida, *Chem. Commun.*, 2003, (24), 3036–3037.
- 24 T. Horiuchi, H. Miura, K. Sumioka and S. Uchida, J. Am. Chem. Soc., 2004, 126(39), 12218–12219.

- 25 T. Horiuchi, H. Miura and S. Uchida, J. Photochem. Photobiol., A: Chem., 2004, 164(1-3), 29–32.
- 26 D. Kuang, S. Uchida, R. Humphry-Baker, S. M. Zakeeruddin and M. Gratzel, *Angew. Chem., Int. Ed.*, 2008, **47**(10), 1923–1927.
- 27 M. X. W. Liang, F. Cai, P. Chen, B. Peng, J. Chen and Z. Li, *J. Phys. Chem. C*, 2007, **111**, 4465–4472; M. X. W. Liang, F. Cai, P. Chen, B. Peng, J. Chen and Z. Li, *J. Phys. Chem. C*, 2007, **111**, 4465–4471.
- 28 H. N. Tian, X. C. Yang, R. K. Chen, R. Zhang, A. Hagfeldt and L. Sun, J. Phys. Chem. C, 2008, 112(29), 11023–11033.
- 29 H. Rensmo, K. Westermark, S. Sodergren, O. Kohle, P. Persson, S. Lunell and H. Siegbahn, J. Chem. Phys., 1999, 111(6), 2744–2750.
- 30 E. M. J. Johansson, M. Hedlund, H. Siegbahn and H. Rensmo, J. Phys. Chem. B, 2005, 109(47), 22256–22263.
- 31 E. M. J. Johansson, P. G. Karlsson, M. Hedlund, D. Ryan, H. Siegbahn and H. Rensmo, *Chem. Mater.*, 2007, **19**(8), 2071–2078.
- 32 K. Westermark, H. Rensmo, H. Siegbahn, K. Keis, A. Hagfeldt, L. Ojamae and P. Persson, J. Phys. Chem. B, 2002, 106(39), 10102–10107.
- 33 M. Alebbi, C. A. Bignozzi, T. A. Heimer, G. M. Hasselmann and G. J. Meyer, J. Phys. Chem. B, 1998, 102(39), 7577–7581.
- 34 P. Qin, X. Yang, R. Chen, L. Sun, T. Marinado, T. Edvinsson, G. Boschloo and A. Hagfeldt, *J. Phys. Chem. C*, 2007, **111**(4), 1853–1860.
- 35 E. M. J. Johansson, T. Edvinsson, M. Odelius, D. P. Hagberg, L. Sun, A. Hagfeldt, H. Siegbahn and H. Rensmo, *J. Phys. Chem. C*, 2007, **111**(24), 8580–8586.
- 36 G. Boschloo and A. Hagfeldt, Chem. Phys. Lett., 2003, 370(3-4), 381–386.
- 37 G. Boschloo, L. Häggman and A. Hagfeldt, J. Phys. Chem. B, 2006, 110(26), 13144–13150.
- 38 J. Nissfolk, K. Fredin, A. Hagfeldt and G. Boschloo, J. Phys. Chem. B, 2006, 110(36), 17715–17718, 22950.
- 39 S. Nakade, T. Kanzaki, W. Kubo, T. Kitamura, Y. Wada and S. Yanagida, J. Phys. Chem. B, 2005, 109(8), 3480–3487.
- 40 K. Hara, K. Miyamoto, Y. Abe and M. Yanagida, J. Phys. Chem. B, 2005, 109(50), 23776–23778.
- 41 B. C. O'Regan and F. Lenzmann, J. Phys. Chem. B, 2004, 108(14), 4342–4350.
- 42 N. Koumura, Z. S. Wang, S. Mori, M. Miyashita, E. Suzuki and K. Hara, J. Am. Chem. Soc., 2006, 128(44), 14256–14257.
- 43 B. C. O'Regan, I. Lopez-Duarte, M. V. Martinez-Diaz, A. Forneli, J. Albero, A. Morandeira, E. Palomares, T. Torres and J. R. Durrant, J. Am. Chem. Soc., 2008, 130(10), 2906–2907.
- 44 N. W. Duffy, L. M. Peter and K. G. U. Wijayantha, *Electrochem. Commun.*, 2000, 2(4), 262–266.
- 45 K. Hara, Y. Dan-Oh, C. Kasada, Y. Ohga, A. Shinpo, S. Suga, K. Sayama and H. Arakawa, *Langmuir*, 2004, 20(10), 4205–4210.
- 46 Z. P. Zhang, S. M. Zakeeruddin, B. C. O'Regan, R. Humphry-Baker and M. Grätzel, *J. Phys. Chem. B*, 2005, 109(46), 21818–21824.
- 47 N. R. Neale, N. Kopidakis, J. van de Lagemaat, M. Grätzel and A. J. Frank, J. Phys. Chem. B, 2005, **109**(49), 23183–23189.
- 48 V. V. Pavlishchuk and A. W. Addison, *Inorg. Chim. Acta*, 2000, 298(1), 97–102.