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High photo-currents with a zwitterionic thiocyanate-free dye in aqueous-based dye sensitized solar cells†

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We report a new water soluble and stable thiolate/disulfide redox couple (T^-/DS) and its use with a new zwitterionic and thiocyanate-free dye (**T169**) in a 100% aqueous electrolyte system. A DSSC incorporating **T169** and the T^-/DS showed the highest photocurrents ($J_{sc} = 13.30 \text{ mA cm}^{-2}$) and IPCE% (84%) values reported to date. In addition, a 2000 h long-term stability measurement was performed, where J_{sc} and V_{oc} of the above mentioned DSSC stayed somehow the same except for the fill factor (FF) which decreased from 0.62 to 0.48 and consequently lowered the total efficiency (from $\eta = 4.5\%$ on day 1 to $\eta = 3.3\%$ after 2000 h).

Introduction

A dye-sensitized solar cell (DSSC) has attracted much attention due to its relatively low cost, acceptable conversion efficiency and ease of fabrication.¹ Most of the research on DSSCs is focused on organic solvent-based electrolytes employing the widely used I^-/I_3^- redox couple. However, recently a number of research groups has started investigating water-based DSSCs.² For quite a long time, inclusion of water in the cell has been thought to have deadly effects.² Lindquist *et al.* proposed that water molecules get adsorbed onto the TiO_2 surface and coordinate with Ti atoms blocking the reaction of I_3^- with the electrons in the TiO_2 conduction band (CB) and hence causing severe reductions in photocurrent (J_{sc}) and efficiency (η).³ It was also confirmed that water molecules (and/or OH^-) can replace the weakly coordinated thiocyanate groups on the dye resulting in dye degradation.^{4,5} Water was shown to also interact with the redox mediator, where Tributsch *et al.* observed bleaching in the electrolyte as a result of transformation of I_3^- to IO_3^- and therefore depleting the cell from I_3^- and increasing the resistance at the counter electrode.⁶ This is in addition to weakening of TiO_2 -dye interaction and undesirable interactions with additives used in the electrolyte systems such as *tert*-butylpyridine (TBP).⁷

Recently, O'Regan *et al.* showed that the presence of water in a cell does not by itself cause these destructive effects.⁸ An iodine-based redox mediator in water achieved efficiencies

between $\eta = 2.4\%$ and 6.0% with different hydrophobic dyes.^{8–10} In addition, various water based redox systems were recently investigated. Sun and coworkers reported an efficiency of 3.5% in an aqueous thiolate/disulfide redox mediator and D51 dye.¹¹ Spiccia and co-workers achieved an efficiency of 4.1% when using the MK-2 sensitizer in conjunction with the $Fe(CN)_6^{4-/3-}$ redox mediator in water.¹² A 5.1% efficiency was achieved when using a cobalt(II)/(III) tris(2,2'-bipyridine) redox couple and an MK-2 dye,¹³ and a 5.6% efficiency was reported upon surface treatment with octadecyltrichlorosilane.¹⁴ Boschloo and coworkers reported an efficiency of 4.3% in LEG4 sensitized TiO_2 and a water-soluble TEMPO redox couple.¹⁵ However, in all of these reports the J_{sc} values were $\leq 11 \text{ mA cm}^{-2}$ at one Sun illumination, and again this might be due to diminished pores wetting and/or phase separation that is inflicted by the use of highly hydrophobic dyes.

DSSCs can operate efficiently in aqueous media if the suitable materials are employed. The components that need to be carefully sought for are: (1) a suitable dye that is not too hydrophobic to avoid diminished pore wetting and thus not allowing the redox mediator to efficiently regenerate the oxidized dye, (2) and not too hydrophilic to prevent its desorption from the TiO_2 surface at pH values higher than 5.0, (3) an appropriate dye that does not contain labile ligands in aqueous media (such as thiocyanate ligands^{16–23}) and (4) finally a photo-stable redox mediator exhibiting a suitable redox potential, facile kinetics to efficiently regenerate the dye and low absorbance in the visible spectrum. Herein, we report a new water soluble and stable thiolate/disulfide redox couple and its use with a new zwitterionic and thiocyanate-free dye in a 100% aqueous and Lewis-base free DSSC that show high photocurrents and IPCE%.

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Experimental

Materials and instrumentation

All chemicals and Z907 dye were purchased from Sigma-Aldrich and used as supplied. 1-(2-Hydroxyethyl)-5-mercaptopotetrazole was purchased from Carbosynth. The D35, Y123, and YD2 dyes were purchased from Dyenamo (Sweden). C106 and titania pastes (18NR-T Transparent and WER2-O Reflector titania pastes) were purchased from Dyesol (Australia). 5,5-Bis-(1*H*-tetrazol-5-yl)nonane²⁴ and 4,4'-bis(5-hexylthiophen-2-yl)-2,2'-bipyridine²⁵ were synthesized according to procedures found in the literature.

UV/Vis and emission spectra were recorded on a Jasco V-570 UV/vis/NIR and Jobin-Yvon-Horiba Fluorolog 3 spectrometers, respectively. All of the electrochemical measurements were performed with a CH Instruments 760B potentiostat (USA). The electrochemical setup consisted of a three-electrode cell, with a stained TiO₂ on FTO with the respective dye as the working electrode, a Pt wire 1 mm diameter as the counter electrode, and Ag/Ag⁺ (10 mM AgNO₃) in 0.1 M LiClO₄ in acetonitrile, and Fc/Fc⁺ standard (0.63 vs. NHE in acetonitrile) was used as a reference. Aqueous electrochemical measurements were performed using the same setup but with an Ag/AgCl reference electrode in saturated M KCl and K₃Fe(CN)₆/K₄Fe(CN)₆ standard (0.57 vs. NHE). Electrochemical impedance spectra (EIS) of the DSSCs were performed at 0 V in the frequency range 0.1 Hz–10⁵ Hz with oscillation potential amplitudes of 10 mV at RT. The obtained impedance spectra were fitted with the Z-view software (v2.8b, Scribner Associates Inc.). IPCE% spectra were recorded using a Newport 74000 Cornerstone™ monochromator and a solar simulator illuminated by a 300 watt xenon arc lamp (Oriel) through an AM 1.5 simulation filter (ScienceTech). Photocurrent vs. voltage characteristics were measured with a Keithley 2400 source meter. The irradiated area of the cell was 0.126 cm². Long-term stability measurements were performed under 1 Sun irradiation from a high-power white LED lamp during the first 15 days and after that cells were kept under ambient light at RT.

Solar cell fabrication

The dye sensitized solar cells were fabricated using standard procedures. The TiO₂ films were made from colloidal solutions using the doctor blading method (2× times) on “Tec15” and then heated to 480 °C for 30 min, resulted in a 14 μm thick TiO₂ film, on top of which a 6 μm TiO₂ scattering layer (150 nm–250 nm TiO₂ particles) was deposited and reheated at 480 °C for 30 min. TiCl₄ pre- and post-treatments were carried out on the FTO and titania films, respectively, following reported procedures in the literature.²⁶ These films were then reheated at 480 °C for 30 min. The TiO₂ films were stained by the respective dye solution (0.3 mM) in 1:1 *t*-butanol:acetonitrile for 18 h. The PEDOT counter electrodes were prepared by electro-polymerization of the EDOT (3,4-ethylenedioxythiophene) monomer by a periodic reversal potential technique.²⁷ The electrodeposition bath contained an aqueous

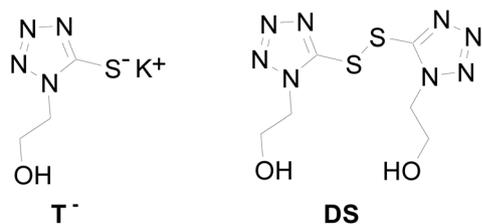
solution of 0.01 M EDOT and 0.1 M LiClO₄ with a 24 s pulse at a potential of 1.2 V and 12 s of –0.6 V vs. Ag/AgCl. Cell assembly was performed by sealing the counter electrode to the TiO₂ electrode with a 60 mm Surlyn (Dupont) spacer at 100 °C for 3 min. The electrolyte was introduced through two small holes, previously drilled through the counter electrode, which were then sealed with epoxy glue. The DSSC was then covered with an anti-reflection and UV-filter (Arktop, Asahi Glass, Japan).

Preparation of DS. To an aqueous solution of 1-(2-hydroxyethyl)-5-mercaptopotetrazole (TH) (5.0 g, 34 mmol) and a catalytic amount of NaI (10 mg), 3.2 ml (37.4 mmol) of 42% H₂O₂ was added drop-wise over a period of 30 min. The solution was left stirring for 2 h at RT, before it was concentrated under vacuum. The crystalline solid obtained upon cooling was filtered and washed with a small amount of ice-cold water and air dried. This yielded 2.5 g of the disulfide product as a pure white solid (50% yield). ¹H NMR (D₂O, 500 MHz) δ_{ppm}: 4.49 (t, 2H, *J* = 2.0 Hz), 3.85 (t, 2H, *J* = 2.0 Hz). ¹³C NMR: 153.82, 59.35, 50.73. Atmospheric pressure photoionization (APPI) MS (*m/z*): calculated for C₆H₁₁N₈O₂S₂ [M + H]⁺, 291.3; found, 291.1.

Preparation of T169. In an argon-degassed anhydrous DMF, a mixture of 4,4'-bis(5-hexylthiophen-2-yl)-2,2'-bipyridine (200 mg, 0.41 mmol) and di-μ-chloro-bis[η⁶-*p*-cymene]chlororuthenium(II) (125 mg, 0.20 mmol) were heated at 100 °C for 4 h. Then, 4,4'-dicarboxy-2,2'-bipyridine (100 mg, 0.41 mmol) was added and the temperature was raised to 140 °C for 4 h in the dark. The solution was heated for an additional 4 h at 140 °C after adding 5,5-bis-(1*H*-tetrazol-5-yl)nonane (108 mg, 0.41 mmol). Finally, the DMF was evaporated under vacuum and the crude product was dissolved in water at pH = 7.0 (adjusting pH using NaOH/HCl). The dissolved product was purified on a preparative C-18 column using water: methanol as the eluting solvent. The main band was collected and the solution pH was lowered to 4.2 by the addition of 0.02 M HCl. The precipitated product was filtered and washed with water and diethyl ether successively to afford T169 as a pure dark solid (402 mg, 87% yield). ¹H NMR (d₆-DMSO, 500 MHz) δ_{ppm}: 9.05 (s, 2H), 9.00 (d, 2H, *J* = 3.5 Hz), 8.17 (d, 1H, *J* = 5.5 Hz), 8.05 (d, 1H, *J* = 3.5 Hz), 8.03 (d, 1H, *J* = 3.5 Hz), 7.91 (d, 1H, *J* = 5.5 Hz), 7.84–7.81 (m, 2H), 7.74 (dd, 1H, *J*₁ = 6.0 Hz, *J*₂ = 2 Hz), 7.70 (d, 1H, *J* = 6.0 Hz), 7.56 (dd, 1H, *J*₁ = 6.0 Hz, *J*₂ = 2 Hz), 7.52 (d, 1H, *J* = 6.0 Hz), 7.12 (t, 2H), 2.95 (t, 4H), 2.21 (m, 2H), 2.06 (m, 2H), 1.74–1.72 (m, 4H), 1.40–1.36 (m, 12H), 1.05–0.88 (m, 14H), 0.6 (m, 6H). APPI MS (*m/z*): calculated for C₅₅H₆₉N₁₂O₄RuS₂ [M + H]⁺, 1127.4; found, 1127.1.

Results and discussion

The water soluble thiolate, 1-(2-hydroxyethyl)-5-mercaptopotetrazole potassium salt (T[−]) and the oxidized disulfide dimer form (DS) were used as an aqueous redox couple in the present study, Scheme 1. DS was obtained from the commercially available thiol [1-(2-hydroxyethyl)-5-mercaptopotetrazole, TH] by



Scheme 1 Structure of the thiolate/disulfide (T^-/DS) redox couple.

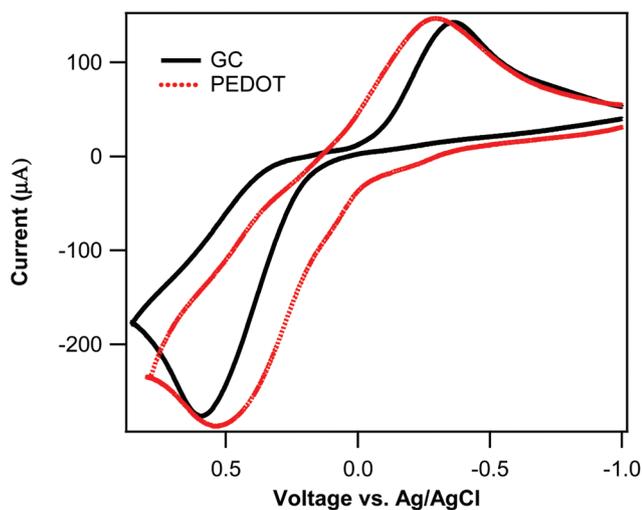


Fig. 1 Cyclic voltammograms (0.1 M KCl) scan for T^-/DS at a scan rate = 100 mV s^{-1} with a GC (solid-black) and PEDOT (dotted-red) working electrodes.

oxidation with H_2O_2 in the presence of a catalytic amount of NaI in water.²⁸ The redox potential of the T^-/DS redox couple was determined to be 0.325 V vs. NHE in water, Fig. 1. The T^-/DS showed high redox over-potential at Pt and glassy carbon electrodes (GC), however, by using a PEDOT based electrode the over-potential was lowered as can be seen in Fig. 1. Therefore, all the assembled DSSCs in this work consisted of PEDOT based counter electrodes (CE) prepared by periodic reversal potential techniques²⁷ that showed good stabilities and charge transfer impedances at the T^-/DS electrolyte/CE interface as deduced from electrochemical impedance spectroscopy (EIS) measurements performed with symmetrical cells of the structure CE/electrolyte/CE, Fig. 2.

To start, we fabricated DSSCs with hydrophobic dyes such as D35,²⁹ Y123,³⁰ YD2,³¹ Z907,³² TG6³³ and C106³⁴ (the structures are found in ESI Scheme S1†) and evaluated the performance of the T^-/DS redox couple as the electroactive component. The best performing dye out of the above mentioned ones was C106 and therefore we decided to optimize the T^-/DS with it. The concentration ratio of the T^- and DS was first optimized in a Lewis-base free aqueous electrolyte system with 0.1% TritonX-100® as the only additives at pH = 5.0. TritonX-100® is a non-ionic surfactant that lowers the

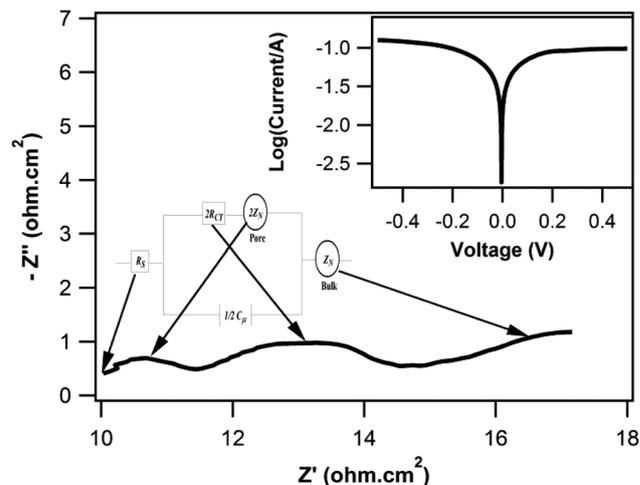


Fig. 2 Impedance spectra of the dummy device PEDOT/electrolyte/PEDOT as Nyquist plots including the transmission line model. (Inset) A Tafel plot of the dummy device.

surface tension of water (~ 30 dynes per cm at 0.1% for TritonX-100®) and thus enables better wetting of the titania pores.³⁵ The use of a surfactant is of high importance in aqueous based DSSCs due to the diminished wetting of the titania pores especially when using hydrophobic dyes such as C106.^{8,36} Interestingly, the optimized concentration ratio of T^-/DS was found to be 0.4/0.4 M which is similar to the analogous organic based thiolate/disulfide (T^-/T_2) electrolyte system reported by Grätzel *et al.*³⁷ Using this optimized concentration resulted in diffusion-limited photocurrents $J_{DL} > 20 \text{ mA cm}^{-2}$, Fig. 3A. The photovoltaic parameters were measured to be: photocurrent $J_{SC} = 10.0 \text{ mA cm}^{-2}$, photovoltage $V_{OC} = 515 \text{ mV}$, fill factor $FF = 0.61$ and efficiency $\eta = 3.17\%$, Table 1. The maximum incident photon to current efficiency at 500 nm was 54%, Fig. 3B.

We started investigating the commonly used Lewis base *N*-methylbenzimidazole (NMB) as an electrolyte additive that would give better DSSC performance (increased photocurrents and/or photovoltages). In general, the use of Lewis bases as additives in organic based electrolyte systems has been studied by different groups who showed that their use can have positive effects on the semiconductor surface states, upward shifts in the conduction band edge (CB), deceleration of recombination kinetics, as well as on the photovoltaic parameters of DSSCs.^{7,38,39} To our surprise there were no positive effects on the DSSC performance that were detected with the use of NMB up to concentrations of 0.8 M while keeping the pH at 5.0, Fig. 3A, rather a slight decrease in the fill factor was seen ($FF = 0.53$). This might be due to the fact that at pH 5.0, NMB would be mostly in the protonated form (conjugate acid $pK_a = 5.6$) and thus it might neither adsorb to the Lewis-acid sites (Ti^{+4}) in the TiO_2 film nor would it decrease the amount of adsorbed protons and in turn won't have any effects on CB. A somehow related finding is already known about lithium cations, where its use as an additive in non-aqueous aprotic electrolyte

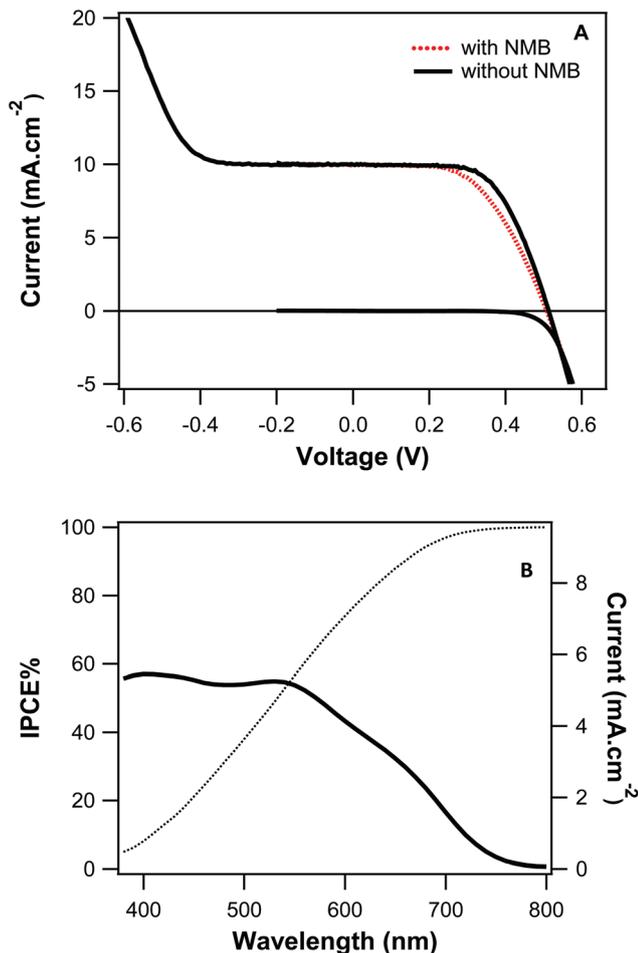


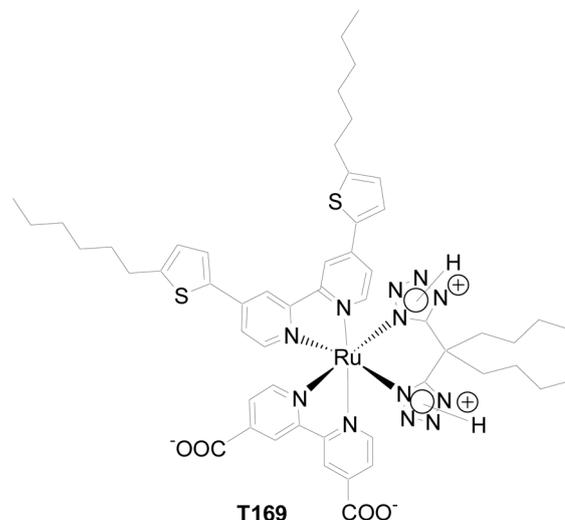
Fig. 3 (A) Photocurrent–voltage characteristics of DSSCs sensitized with C106 with (solid-black) and without (dotted-red) NMB in the T⁻/DS electrolyte and measured under 100 mW cm⁻² simulated AM1.5 spectrum with an active area = 0.126 cm². (B) IPCE% (solid) and integrated current spectra (AM 1.5 G) (dotted) of the corresponding DSSC.

Table 1 DSSCs' performance of T169 and C106 dyes with T⁻/DS electrolyte

	Time (h)	J_{SC} , mA cm ⁻²	V_{OC} , mV	FF	η^b (%)
T169	24	13.3 (13.0 ^a)	545	0.62	4.50
	200	13.1 (13.0)	544	0.56	3.99
	500	13.1 (12.9 ^b)	543	0.55	3.92
	2000	13.0 (12.8)	540	0.48	3.37
C106	24	10.0 (9.8)	515	0.61	3.17
	200	9.9 (9.7)	485	0.58	2.80
	500	8.8 (8.5 ^b)	475	0.57	2.40
	2000	8.0 (7.7)	465	0.54	2.02

^a Integrated photocurrent (AM1.5 Global). ^b Measured under 100 mW cm⁻² simulated AM1.5 spectrum with an active area = 0.126 cm².

systems downshifts the titania flat-band potential (E_{FB}), however, it does not have any effect on E_{FB} when used in protic solvents such as water.^{40,41} Therefore, our optimized redox



Scheme 2 Structure of T169 as a zwitterion at pH = 5.0.

system lacked any additives such as the ones used for non-aqueous DSSC's (lithium salts and Lewis bases).

The studied C106 based DSSC attained a maximum J_{SC} and IPCE% at 500 nm of 10.0 mA cm⁻² and 54%, respectively. This J_{SC} is similar to that attained by O'Regan *et al.* with an organic dye (D149),⁸ and slightly lower than the one reported by Yan *et al.* ($J_{SC} = 10.97$ mA cm⁻²)³⁶ with N719 and Villarroya-Lidon ($J_{SC} = 11.01$ mA cm⁻²)⁴² with Z-907 and an iodine-based aqueous electrolyte systems. These values are among the highest attained photocurrents reported with aqueous based electrolyte systems in a handful number of reports,^{8,13,14,36} however, they are still lower than the ones reported in organic-based electrolyte systems. We and other research groups agree on the fact that the use of hydrophobic dyes, as is the case in most of the studied dyes in aqueous electrolytes, will decrease the TiO₂ wettability and hence would negatively affect the J_{SC} to a large extent. For this reason, we synthesized a new amphiphilic dye, T169, which is in a zwitterionic form at pH = 5.0, Scheme 2. The synthesis of T169 was based on our recent reports on tetrazolate based dyes that show good DSSC performance and long-term stability.^{24,43} T169 was characterized by electrochemistry, ¹H-NMR, UV/Vis, emission and APPI mass spectrometry.

The UV/Vis and emission spectra of T169 in ethanol are shown in Fig. 4. The lowest energy MLCT absorption band is at 522 nm ($\epsilon = 13\,500$ M⁻¹ cm⁻¹), while the emission maximum is at 700 nm. The electrochemical properties of T169 were evaluated by differential pulse and cyclic voltammetry in acetonitrile as anchored on a 7 μ m titania film (see ESI Fig. S1†). The RuII/III redox potential of T169 was measured to be $E_{1/2} = 1.11$ V vs. NHE. The excited-state oxidation potentials (E_{ox}^*) of T169, derived from both the redox potential ($E_{1/2}$) and the approximated optical energy gap (E_{0-0}) from the intersection of the corresponding absorption and emission spectra, was quantified to be -0.85 eV. The UV/Vis absorption spectra of T169 vs. pH (between pH = 8.6 and 3.5) in 10% ethanol in water

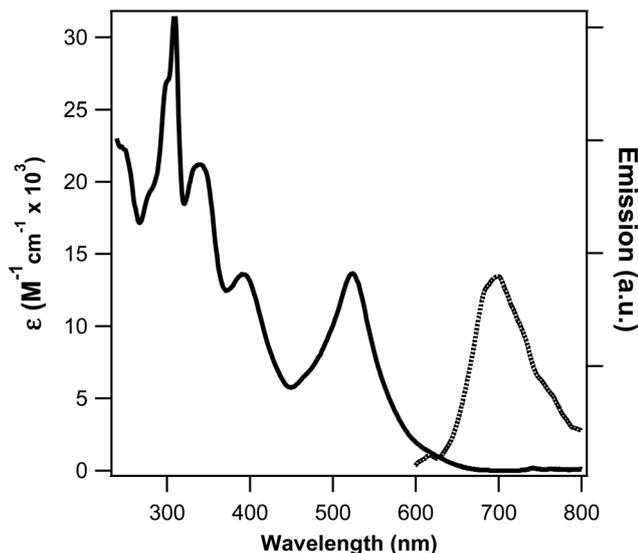


Fig. 4 Absorption (solid) and emission (dashed) spectra of T169 in ethanol.

showed a maximum change in absorbance (monitored at 522 nm and 310 nm) at pH = 6.0 and the dye crashed out from the solution at pH values below 3.5, Fig. 5, where the latter is believed to be due to the protonation of the carboxylic acid moieties (4,4'-dicarboxy-2,2'-bipyridine) as measured by different groups.^{44,45} Therefore from the above mentioned result we estimated the pK_a value of the protonated tetrazole groups to be $\sim 6.0 \pm 0.1$ (the pK_a of free tetrazole is 4.9),⁴⁶ and therefore T169 would be mostly in a zwitterionic form at pH = 5.0 as shown in Scheme 2.

T169 based DSSCs employing a 14 μm thick TiO_2 layer plus a 6 μm scattering layer (150–250 nm) with the T^-/DS electrolyte were fabricated. The photocurrent *vs.* voltage (*IV*) response of T169 is shown in Fig. 6. T169 showed a surprising performance with $J_{sc} = 13.30 \text{ mA cm}^{-2}$, $V_{oc} = 545 \text{ mV}$, $\text{FF} = 0.62$ and $\eta = 4.50\%$, Table 1. In addition, the above cell showed an unprecedented maximum $\text{IPCE}\% = 84\%$ between 500 and 530 nm, Fig. 7. Such results suggest good injection, collection and regeneration efficiencies in the T169 based DSSC with the aqueous T^-/DS electrolyte system. Therefore, from these results we can safely conclude that T169 does not cause diminished wetting of the titania pores unlike most hydrophobic dyes used along with aqueous electrolytes reported in the literature. We believe that this is due to the presence of the positive charge(s) on the tetrazole groups at the working pH, which enhances the wetting in the vicinity of the photo-anode/electrolyte interface. Another reason behind these results might be due to better regeneration of T169 when compared to C106, since the positive charges of the protonated tetrazole moiety could facilitate the approach of T^- or even cause an association with the latter such as ion-pairing that would affect positively the rate of regeneration.

In order to test the robustness under light soaking of our aqueous based DSSCs, we performed a 2000 h long-term test

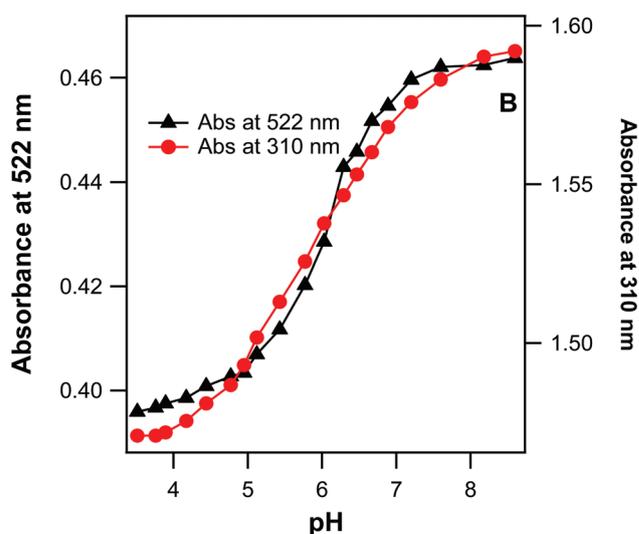
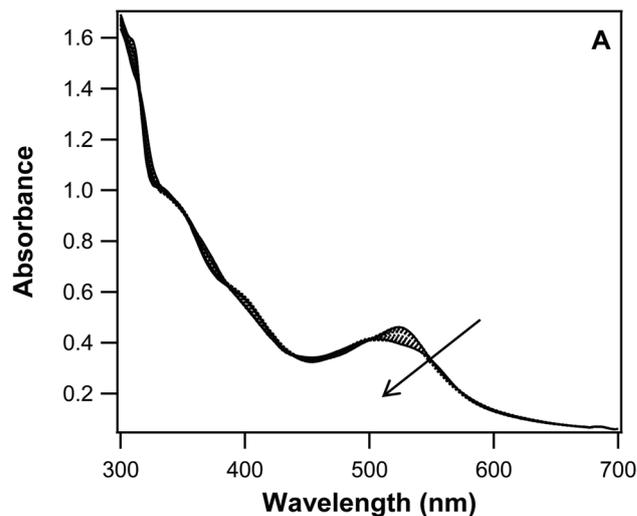


Fig. 5 (A) Change in T169 absorbance with pH between 8.6 and 3.5. (B) Change in T169 absorbance at 522 (black-triangles) and at 310 nm (red-circles).

at RT, and where the first 500 h was under one-Sun irradiation and between 500 h and 2000 h was under ambient light and temperature. Fig. 6 shows the *IV* curves evolution with time of T169 and C106 based cells with T^-/DS . As can be seen the J_{sc} and V_{oc} values diminished slightly with time for T169, however, the FF and $\eta\%$ decreased constantly from $\text{FF} = 0.62$ and $\eta = 4.50\%$ on day 1 to $\text{FF} = 0.48$ and $\eta = 3.37\%$ after 2000 h (data collected is presented in Table 1). As for C106, all the photovoltaic parameters decreased with time, where J_{sc} , V_{oc} , FF and $\eta\%$ decreased from 10 mA cm^{-2} , 515 mV, 0.61 and 3.17% to 8.0 mA cm^{-2} , 465 mV, 0.54 and 2.02% after 2000 h, respectively. These results are similar to our recently reported long-term measurements on N719 and thiocyanate-free tetrazolate based dyes (T162 and T147), where we found that the most probable reason behind the deterioration of J_{sc} in N719 is due to the labile thiocyanate ligands compared to the tetrazolate

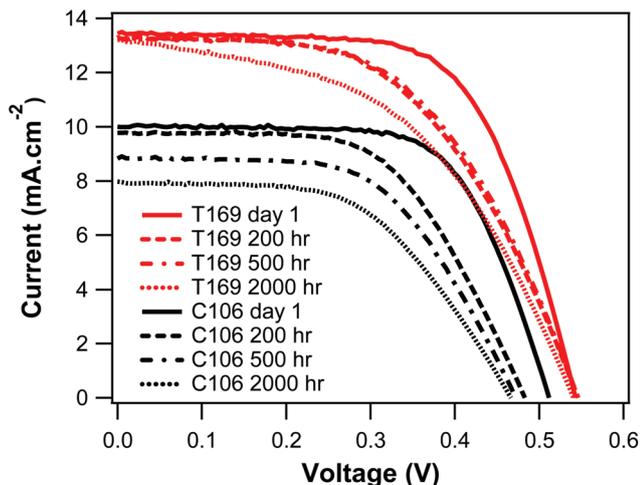


Fig. 6 Photocurrent–voltage characteristics of DSSCs sensitized with dyes: **T169** (solid-red) and **C106** (solid-black) assembled with T⁻/DS. The evolution of the *I/V* during visible-light soaking (100 mW cm⁻² simulated AM1.5) for the first 500 h at RT and at ambient light and temperature between 500 and 2000 h. At 200 h (dashed), at 500 h (dotted-dashed) and at 2000 h (dotted).

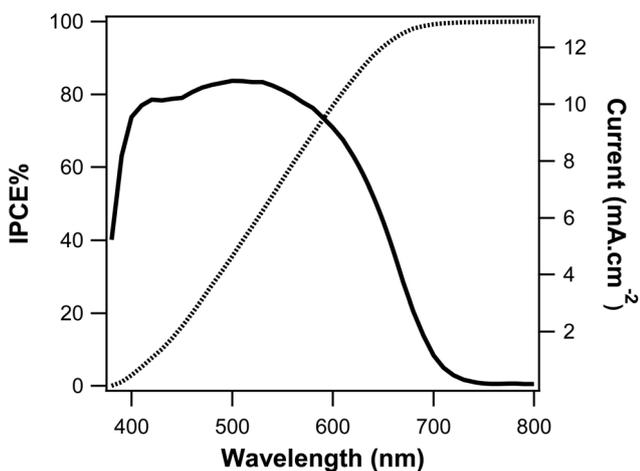


Fig. 7 IPCE% (solid) and integrated current spectra (AM 1.5 G) of **T169** (dotted) DSSC.

based dyes that did not show any decrease in J_{sc} up to 2000 h of 1 Sun irradiation at 70 °C.²⁴ Therefore, the aquation of the thiocyanate ligands in the case of **C106** might be the reason behind the gradual decrease in its photovoltaic parameters over time. As for **T169**, upon inspecting closely the cells during the course of the long-term measurement, we realized that both dyes started leaching slightly into the aqueous electrolyte but was more evident in the case of **T169** than **C106**. Performing a UV/Vis desorption *versus* time experiment in water at pH = 5.0 of titania films stained with both dyes, confirmed the faster rate of **T169** leaching into water than **C106** (Fig. S2 in the ESI†). Therefore, we correlate the decrease in FF for both cells to the desorption of both dyes with time, but more profound in the case of **T169**.

Conclusion

In summary, we were successful in synthesizing a water soluble and stable redox electrolyte system based on a thiolate/disulfide couple. An unexpected finding that we encountered was the fact that NMB as a Lewis-base additive that is conventionally used in organic based DSSCs did not add any enhancements to the efficiencies (current and voltage) of our aqueous based solar cells. We also engineered a tetrazolate based dye (**T169**) that exists in a zwitterionic form at pH 5.0. **T169** based DSSC incorporating the aqueous electrolyte T⁻/DS showed one of the highest currents and IPCE% values reported to date in aqueous based DSSCs. Therefore, the use of zwitterionic amphiphilic dyes might be a new venue to explore in fabricating efficient aqueous DSSCs that do not suffer from poor wetting and thus diminished efficiencies. As a last conclusion, the current results indicate that water as a solvent or additive to DSSC electrolytes might not “poison” a DSSC as has been thought until recently. However, more work is still needed for designing new dyes, electrolyte systems and even new additives that would enhance photocurrents and photovoltages of aqueous DSSCs, especially dyes that do not cause low TiO₂ wetting and do not desorb with time. Currently, we are working on the synthesis of such dyes to be evaluated with the T⁻/DS redox couple. Lastly, in principal we can also project that most reported dyes in the literature that contain azolate chelates^{47,48} can also be in a zwitterionic form in aqueous solutions of pH values higher than 3.5 but lower than the pK_a values of the corresponding azolate conjugate acid.

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