

Conjugated organic dyes for dye-sensitized solar cells†

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A new metal-free sensitizer 2-[3-(4-dimethylamino-phenyl)-allylidene]-malonic acid (**2**) has been synthesized by the condensation of *N,N'*-dimethylaminocinnaldehyde and malonic acid. This dye has two carboxyl groups on the same carbon atom, which act as better electron withdrawing groups in addition to providing effective anchoring to titanium dioxide. The new dye has characterized by UV-Vis, ¹H NMR and CHN analysis. Dye-sensitized nanocrystalline-titanium dioxide-semiconductor solar cells (DSSC) have been tested in a stable and durable redox electrolyte. The efficiency of dye is as high as 1.38%. The dye molecule is thermally stable up to 100°C.

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In the last decade, interest in dye-sensitized nanocrystalline-titanium dioxide-semiconductor solar cells (DSSCs) as non-conventional solar cells has increased due to their high performance and possibility of their low-cost production. Gratzel and co-workers¹ have first reported that DSSCs based on a nanocrystalline-TiO₂ film and Ru-complex photosensitizers, e.g. RuL₂(NCS)₂ complex, *cis*-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (the **N719** dye) and RuL'(NCS)₃ complex, trithiocyanato 4,4'4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (the black dye), produced solar-energy-to-electricity conversion efficiencies (η) up to 11% under AM 1.5 irradiation¹. The development of efficient Ru-complex photosensitizers is one factor in achieving highly efficient solar-cell performance. However, Ru dyes are very expensive owing to the rarity of the metal. As Ru dyes are exclusive, metal-free sensitizers such as synthetic organic dyes and natural dyes are important for DSSCs applications. Metal-free sensitizers, such as organic dyes², porphyrin dyes³, phthalocyanine dyes⁴ and natural dyes⁵ have been studied and developed. These metal-free sensitizers belong to typical D- π -A structures with both electron donor (D) and electron acceptor (A) linked by a π -conjugation

bridge, which can effectively produce a charge-separation excited state upon photoinduced intramolecular charge transfer (ICT). The ICT process in D- π -A structures strongly depends on the electron-donating ability of D, electron-withdrawing ability of A, as well as the electronic characteristics of the π bridge. These metal-free sensitizers are easy to synthesize, purify and also have high molar extinction coefficients.

The schematic representation of a DSSC is shown in Fig. 1. Briefly, the working phenomenon of DSSCs is the photoexcitation of a photosensitizer, followed by an electron transfer from an excited photosensitizer to the conduction band of TiO₂ in the ultrafast time

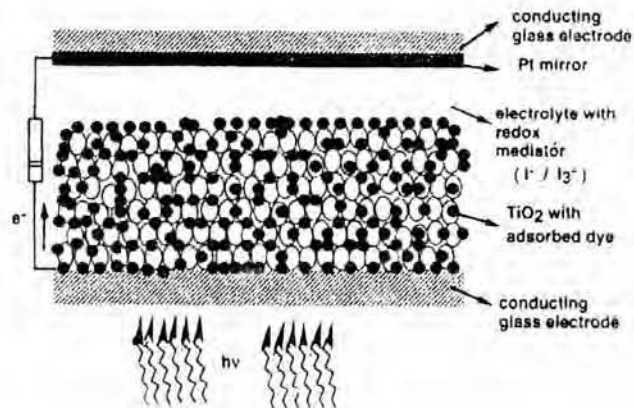
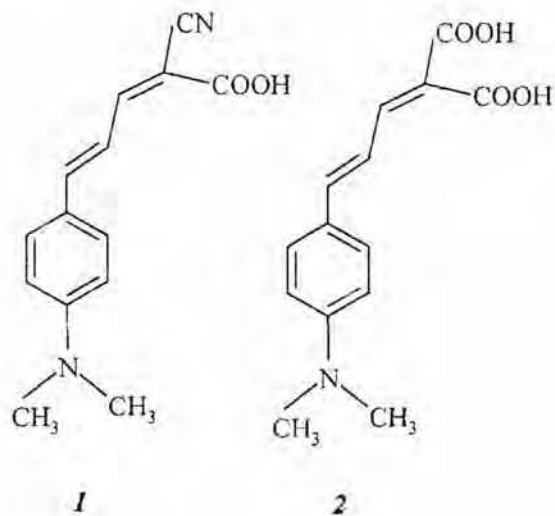


Fig. 1 — Cartoon of the make-up of the dye sensitized solar cell.

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scale. The oxidized form of the dye is restored by an electron donation from the electrolyte, usually an organic solvent containing redox system, such as the iodide/triiodide couple. The most favoured organic solvents used in the redox electrolyte are either acetonitrile or methoxy propionitrile. Among several factors which govern the η of DSSCs, the durability of redox electrolyte plays an important role. As these organic solvents are highly volatile, low viscous and leading to leakage of electrolyte and less durability, it is necessary to use high-boiling and high-viscous solvents so as to improve the durability. It has been widely reported that the change of electrolytic solvent will influence η . The dye molecule 2-cyano-5-(4-dimethylamino-phenyl)-penta-2,4-dienoic acid (**1**) shows η 5.5% in the electrolytic system 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI) / 0.1 mL LiI-0.05 M I₂ solution in methoxy propionitrile (MAN) and with 0.6 M *tert*-butyl pyridine (TBP)^{2d}. It has been reported that the TBP provides increased cell voltage and efficiency η and at the same time the durability of the cell was reduced due to the reactivity of TBP with dye molecule^{2b}. In order to make durable DSSCs, it is necessary to avoid TBP and also use as high boiling organic solvents. The present DSSC based on a new organic dye **2**, has two carboxyl groups on same carbon atoms providing better anchoring group than dye **1**. Both dyes **1** and **2** were studied in a stable redox electrolyte 0.1 M I₂, 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI) and 0.5 M *n*-methylbenzimidazolium iodide (NMBI) in γ -butyrolactone (AHI), which has high boiling point and more durable.



Materials and Methods

Optically transparent conducting glass (CTO glass, fluorine-doped SnO₂ overlayer, transmission > 85% in the visible, sheet resistance 10 Ω/cm^2) was obtained from ASAHI, Japan. Titanium tetraisopropoxide, 4-dimethylaminocinnamaldehyde, malonic acid and cyanoacetic acid were procured from Acros Chemicals. TiO₂ nanoparticles and an organic TiO₂ paste were supplied by AISIN SEIKI, Japan. All other solvents and chemicals used in this work were of reagent grade (S.D. Fine Chemicals, India) and used without further purification.

UV-vis spectra were measured with Shimadzu model 1700 spectrophotometer. The concentration of the compounds was maintained at 0.1×10^{-3} M. ¹H NMR spectra were recorded on a Bruker NR-300 AF-FT NMR.

Preparation of DSSC test cells

Preparation of nanocrystalline TiO₂ thin films

TiO₂ photoelectrode (area: ca. 0.5 cm \times 0.9 cm) was prepared by screen-printing. TiO₂ nanoparticles and an organic TiO₂ paste for screen-printing were prepared by methods reported by Gratzel and co-workers⁶. The TiO₂ paste consisted of the TiO₂ nanoparticles, large TiO₂ particles (average diameter 19 nm). The TiO₂ paste was printed on a glass substrate coated with transparent conducting oxide (F-doped SnO₂) and subsequently sintered at 450°C in air for 30 min. Thickness of the TiO₂ thin films, measured by Scanning Electron Microscopy was ca. 6 μm . The dye was dissolved in ethanol at a concentration of 0.1×10^{-3} M. The TiO₂ thin films were soaked in the dye solution and then kept at room temperature for 13 h so that the dye was adsorbed onto TiO₂ films. The dye coating was done immediately after the high temperature annealing in order to avoid rehydration of the TiO₂ surface or capillary condensation of water vapors from ambient air inside the nanopores of the film. The presence of water in the pores decreases the injection efficiency of the dye. The electrode was dipped into the dye solution while it was still hot, i.e. its temperature was ca. 80°C. After completion of the dye adsorption, the photo electrode was withdrawn from the solution and washed thoroughly with ethanol to remove non-adsorbed dye under a stream of dry air or argon.

Fabrication of test cell

The electrochemical cell (two-electrode type) used for photovoltaic measurements consisted of a dye-

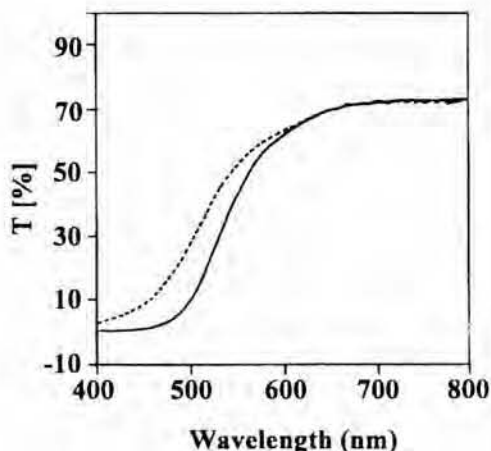


Fig. 2 — Transmittance spectra in UV-Vis region of the dyes: (—) 1 and (---) 2.

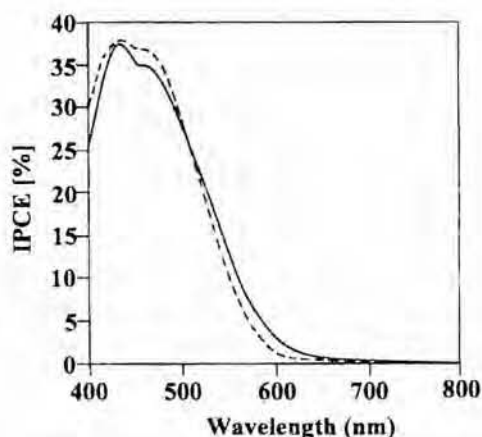


Fig. 3 — Spectra of monochromatic incident-photon-to-current conversion efficiencies (IPCEs) for DSSCs based on the conjugated dyes: (—) 1, (---) 2. The electrolyte was a solution of 0.1 M I_2 , 0.9 M DMPImI and 0.5 M NMBI in γ -butyrolactone.

sensitized semiconductor electrode, a counter electrode, a polyethylene film spacer (100 μ m thick), and an organic electrolyte. The counter electrode was a Pt film on a TCO-coated glass plate by means of spin coating technique. The active surface area of the TiO_2 film electrode was *ca.* 0.45 cm^2 (0.5 $cm \times 0.9$ cm). The electrolyte was a 0.1 M I_2 , 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI) and 0.5 M *n*-methylbenzimidazolium iodide (NMBI) in γ -butyrolactone (AHI). The electrolyte was introduced into the cell by pre-drilled whole of the counter electrode and later closed by cover glass. The photovoltaic performance of the solar cells was measured with a source meter (Keithley 2000). We employed an AM 1.5 solar simulator (home built) as the light source. The incident light intensity was calibrated by using a standard test cell of polycrystalline silicon solar cell

obtained from Solarinox. Action spectra of the monochromatic IPCE for the solar cell were measured with the solar simulator (home built).

Synthesis of 2-cyano-5-(4-dimethylamino-phenyl)-penta-2,4-dienoic acid (**1**) was done according to the reported procedure^{2d}.

Synthesis of 2-[3-(4-dimethylamino-phenyl)-allylidene]-malonic acid (**2**)

An acetonitrile solution of 4-dimethylaminocinnamaldehyde (2.5 g) and malonic acid (1.8 g) was refluxed in the presence of piperidine (0.5 mL) for 4 h. The solvent was evaporated under reduced pressure. The obtained solid material was subjected to silica gel column and was eluted with chloroform. The front running orange colour band was collected and solvent was evaporated (Yield: 80%). Melting point (m.pt.) 230-233. 1H NMR ($CDCl_3$): δ 3.40 (6H, s), 6.75 (2H, d), 7.15 (1H, dd), 7.55 (1H, d), 8.05 (1H, d). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36; O, 24.49. Found: C, 64.27; H, 5.85; N, 5.39; O, 24.52. UV-Vis spectrum in ethanol [λ_{max} , nm (10^{-3} ϵ , $mol^{-1} L cm^{-1}$): 416 (4.11)].

Results and Discussion

Compound **1** was synthesized as reported^{2d}. Compound **2** was synthesized by condensation of 4-dimethylaminocinnamaldehyde and malonic acid in acetonitrile solvent. The compound was purified by silica gel column chromatography with chloroform as eluent and characterized by UV-Vis, 1H NMR and CHN analysis. The dye **2** has two carboxyl groups that are better anchoring group than in the previous dye **1**. The two-carboxyl groups in dye **2** are better electron withdrawing groups than the cyano and carboxyl groups in dye **1** and expecting enhanced performance of dye **2** in DSSC. The absorption spectra of dyes **1** and **2** were measured in ethanol solvent and λ_{max} of dyes **1** and **2** were found at 420 and 422 nm, respectively. The transmittance spectrum of UV-Vis region of dyes **1** and **2** is shown in Fig. 2. Both dyes have 70% transmittance, which anticipates a broader spectral response and fine performance of these dyes in DSSCs.

The photocurrent action spectrum of DSSCs composed of nanocrystalline TiO_2 , a dye photosensitizer, and redox electrolyte (AHI) is shown in Fig. 3, where the photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The photoreponse of thin films extends up to 600 nm. The IPCE is represented by the following equation:

Table 1 — Photovoltaic performance of DSSCs based on different dyes^a

Dye	J_{SC} [mA cm ⁻²]	V_{OC} [V]	Fill factor (<i>ff</i>)	η [%]
1	2.84	0.64	0.73	1.33
2	2.90	0.64	0.74	1.38
N719	6.50	0.78	0.72	3.66

^aConditions: irradiated light AM 1.5 (1000 W m⁻²); photoelectrode: TiO₂ (6 μ m thickness and 0.5 cm \times 0.9 cm); electrolyte: 0.1 M I₂/0.9 M 1,2-dimethyl-3-*n*-propylimidazolium iodide/0.5 M methylbenzimidazolium iodide in γ -butyrolactone.

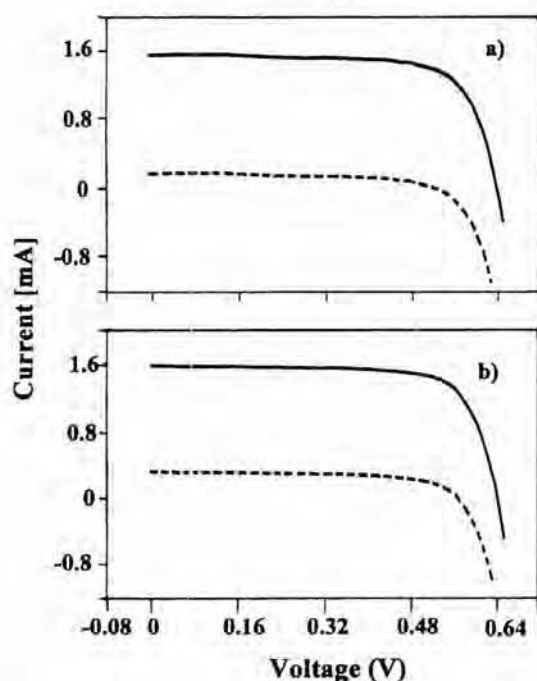


Fig. 4 — Photocurrent-voltage curves (a) dye **1** (—) AM 1.5, (---) dark, and (b) dye **2** (—) AM 1.5, (---) dark. Conditions as in Table 1.

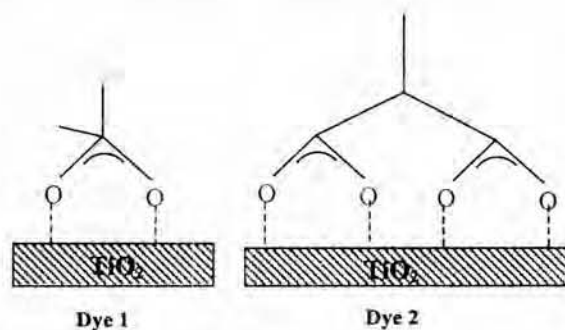


Fig. 5 — Mode of adsorption of dyes **1** and **2** on nanocrystalline TiO₂.

$$\text{IPCE [\%]} = \frac{1240[eVnm] \times J_{SC}[\text{mAcm}^{-2}]}{\lambda[\text{nm}] \times \phi[\text{WM}^{-2}]} \times 100 \quad \dots (1)$$

where J_{SC} is the short-circuit photocurrent density for monochromatic irradiation and λ and ϕ are the wavelength and the intensity, respectively, of the monochromatic light. Both the organic dyes **1** and **2** have maximum IPCEs values of 38% at around 420 nm.

The photovoltaic performance of DSSCs based on **1** and **2** under AM 1.5 irradiation (1000 W m⁻²) are shown in Table 1. The solar energy-to-electricity conversion efficiency, η , under white-light irradiation (e.g. AM 1.5) can be obtained from the following equation.

$$\eta [\%] = \frac{J_{SC}[\text{mAcm}^{-2}] \times V_{OC}[\text{V}] \times ff}{I_0[\text{WM}^{-2}]} \times 100 \quad \dots (2)$$

where I_0 is the photon flux (e.g., 1000 W m⁻² for AM 1.5). J_{SC} is the short-circuit photocurrent density under irradiation, V_{OC} is the open-circuit voltage, and ff represents the fill factor. The fill factor is defined by:

$$ff = \frac{J_{PH(\text{max})} \times V_{PH(\text{max})}}{J_{SC} \times V_{OC}} \quad \dots (3)$$

where $J_{PH(\text{max})}$ and $V_{PH(\text{max})}$ are the photocurrent and photovoltage for maximum power output and J_{SC} and V_{OC} are the short-circuit photocurrent density and open-circuit photovoltage. The photovoltaic performance data of dyes **1**, **2** along with the standard **N719** dye are given in Table 1. Fig. 4 shows the photocurrent-voltage characteristics obtained with a DSSC under illumination of simulated AM1.5 solar light. The I - V curves in Fig. 4 refer to the two respective dye-coated TiO₂ films, and related parameters are listed in Table 1. The maximum η , 1.38%, was achieved under AM 1.5 irradiation with a DSSC based on dye **2** ($J_{SC} = 2.9$ mA cm⁻², $V_{OC} = 0.64$ V, $ff = 0.74$). Under similar conditions, **N719** has shown the η of 3.5 – 3.7%⁷. These results strongly indicate that the application of these metal free sensitizers in DSSCs is promising.

It is clear that dye **2** has better performance than dye **1**. This is because the two carboxyl groups in dye **2** not only act as electron withdrawing groups, but also provide better anchoring groups to nanocrystalline TiO₂⁸. The binding mode of dyes **1** and **2** has shown in Fig. 5. Hence, the dye **2** has more sites to bind TiO₂ and more electron withdrawing nature and can inject the excited electron into the conduction band of TiO₂ efficiently.

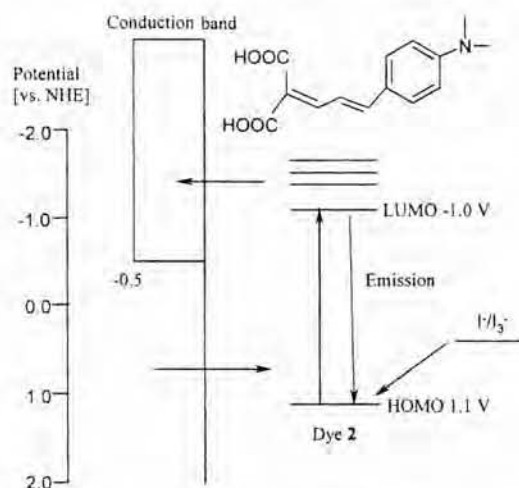


Fig. 6 — Schematic energy diagram for a DSSC based on dye **2** a nanocrystalline TiO_2 electrode.

Fig. 6 shows a typical energy diagram for a DSSC based on a nanocrystalline- TiO_2 electrode, dye **2** as the photosensitizer, and the I^-/I_3^- redox electrolyte. The HOMO and LUMO levels of the dye correspond to the E_{OX} (1.0 V versus NHE) and $E_{\text{OX}}-E_{0,0}$ (-1.1 V versus NHE) levels of the dye. However, the energy levels of the free dye might differ from the levels for the adsorbed dye.

The adsorbed dye first absorbs the incident photon flux and is then excited from the ground state to the excited state owing to the intramolecular $\pi-\pi^*$ transition. The excited electron in femtosecond lifetime can inject into the conduction band of TiO_2 and dye gets oxidized⁹. The oxidized dye must accept electrons from the I^- redox mediator, regenerating the ground state of the dye. The reduction of the N3 dye cations by I^- is reported to occur within 100 ns, which is electrons and the N3 dye cations¹⁰. In addition, when the energetic driving force for re-reduction of the dye, which is estimated from the difference in the oxidation potentials of the dye and I^- ions, is sufficiently large and the reaction yield is near 100%¹¹. Taking into consideration these points, re-reduction of the dye cations by I^- must occur effectively, just as in the N3 dye system.

The dyes **N719** and **1** have achieved η of 11 and 5.5 % respectively, with iodide/triiodide redox couple in acetonitrile solvent. The DSSC with photosensitizer **1**, TBP and co-adsorbate chenodeoxycholic acid was used in order to get η of 5.5 %. It was reported that with indoline and coumarin dyes, the addition of TBP will degrade the dye and lead to decreases in η as well as durability^{2b}. But for outdoor uses, DSSCs with io-

dide/triiodide redox couple in acetonitrile solvent are not suitable because the boiling point of acetonitrile is low and being highly volatile, it will not stand at high temperature for long time. In the present system, we have replaced acetonitrile solvent with γ -butyrolactone which has high boiling point as well as high viscous and can withstand at high temperatures. Hence, these DSSCs with redox systems in γ -butyrolactone solvent may be better for outdoor applications for long durability than the previous DSSC systems and can be used for long time. They are also possible alternative cells to normal fuel cells^{12,13}.

The thermal stability of dye also plays an important role in η and durability of DSSC. For this reason, we have carried out the thermal stability studies of dyes **1** and **2**. These dyes were heated at 100°C under aerial conditions for 10 h. The aerial heated samples were analyzed by UV-Vis, ^1H NMR and CHN analysis. The data were found exactly matched with room temperature sample data. Consequently, these meta-free sensitizers **1** and **2** were stable up to 100°C .

Conclusions

The newly synthesized dye **2** has two carboxyl groups, which are improved electron withdrawing groups as well as better anchoring groups than the previous dye **1**. These metal-free sensitizers are easy to synthesise and purify than metal-based sensitizers. Both dyes **1** and **2** are used in DSSCs studies with stable redox electrolytic system **AH1**. It has been found that η for dyes **1** and **2** is 1.33 and 1.38%, respectively. The dye is thermally stable up to 100°C . These DSSCs are better useful for outdoor purposes and can withstand up to 100°C .

Acknowledgements

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References

- (a) O'Regan & Gratzel M, *Nature*, 353 (1991) 737; (b) Nazeeruddin M K, Day A, Rodicio I, Humphry-Baker R, Muller-E, Liska P, Vlachopoulos N & Gratzel M, *J Am Chem Soc*, 115 (1993) 6382; (c) Hagfeldt A & Gratzel M, *Chem Rev*, 95 (1995) 49; (d) Hagfeldt A & Gratzel M, *Acc Chem Res*, 33 (2000) 269; (e) Gratzel M, *Nature*, 414 (2001) 338; (f) Wang P, Klein C, Humphry-Baker R, Zakeeruddin S M & Gratzel M, *J Am Chem Soc*, 127 (2005) 808.
- (a) Sayama K, Tsukagoshi S, Hara K, Ohga Y, Shimpou A, Abe Y, Suga S & Arakawa H, *J Phys Chem B*, 106 (2002)

- 1363; (b) Horiuchi T, Miura H & Uehida S, *J Chem Soc Chem Comm*, (2003) 3036; (c) Park S Y & Oh S, *Bull Korean Chem Soc*, 24 (2003) 569; (d) Hara K, Sato T, Katoh R, Furube A, Yoshihara T, Murai M, Kurashige M, Ito S, Shinpo A, Suga S & Arakawa H, *Adv Funct Mater*, 15 (2005) 247.
- 3 (a) Campbell W M, Burrell A K, Officer D L & Jolley K W, *Coord Chem Rev*, 248 (2004) 1363, (and references therein); (b) Nazeeruddin M K, Humphry-Baker R, Officer D L, Campbell W M, Burrell A K & Gratzel M, *Langmuir*, 20 (2004) 6515.
- 4 (a) Nazeeruddin M K, Humphry-Baker R, Gratzel M & Murrer B A, *J Chem Soc, Chem Comm*, (1998) 719; (b) Palmoraes E, Martinez-Diaz M, Haque S A, Torres T & Durrant J, *J Chem Soc, Chem Comm*, (2004) 2112.
- 5 (a) Tennakone K, Kumarasinghe R, Kumara G R R A, Wijayantha K G U & Srimannar P M, *J Photochem Photobiol A*, 108 (1997) 193; (b) Dai Q and Rabani J, *New J Chem*, 26 (2002) 421.
- 6 (a) Barbe C J, Arendse F, Comte P, Jirousek M, Lenzenmann F, Shklover V & Gratzel M, *J Am Chem Soc*, 80 (1997) 3157; (b) Wang P, Zakeeruddin S M, Comte P, Charvet R, Humphry-Baker R & Gratzel M, *J Phys Chem*, 100 (1996) 16502.
- 7 Reddy P Y (Unpublished results).
- 8 (a) Duffy N W, Dobson K D, Gordon K C, Robinson B H & McQuillan A J, *Chem Phys Lett*, 266 (1997) 451; (b) Ramamurthy V & Schanze K S, *Semiconductor Photochemistry and Photophysics* (New York, Basel), 2003.
- 9 Kitamura T, Ikeda M, Shigaki K, Inoue T, Anderson N A, Ai X, Lian T & Yanagida S, *Chem Mater*, 16 (2004) 1806.
- 10 Haque S A, Tachibana Y, Klug D R & Durrant J R, *J Phys Chem B*, 102 (1998) 1745.
- 11 Hague S A, Park T, Holmes A B & Durrant J R, *Chem Phys Chem*, 4 (2003) 89.
- 12 Chidambaram V, Srinivas B & Viswanathan B, *Ind J Chem*, 44A (2005) 456.
- 13 Han S D, Kim J D, Singh K C & Chaudhary R S, *Ind J Chem*, 43A (2004) 1599.