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Organic photosensitizers with catechol groups for dye-sensitized photovoltaics

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Abstract

We have carried out a study on a number of organic dyes to identify photosensitizers for dye-sensitized photovoltaic applications with well matched redox potentials and good absorption characteristics. Triphenylmethyne, anthraquinone and xanthene dyes with catechol groups were chosen as the most promising dyes for fabrication of nanocrystalline TiO_2 based dye-sensitized photovoltaic (DSPV) cells using a liquid electrolyte. From our study, a xanthene dye, 9-phenyl-2,3,7-trihydroxy-6-fluorone is found to be efficient photosensitizer in DSPV cells compared to other dyes when a liquid electrolyte is used. Redox potentials, absorption and photovoltaic properties of these dyes are presented. Two possible ways of electron transfer, namely direct charge transfer via formation of strong charge transfer complexes and the conventional excited state electron injection through the HOMO–LUMO energy level matching are discussed.

Keywords: Organic dyes; Dye-sensitized solar cells; Xanthene; Catechol

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1. Introduction

Currently, the investigation of efficient molecular photosensitizers for the development of dye-sensitized nanocrystalline TiO_2 based dye-sensitized photovoltaic (DSPV) cells is a very active area of research. Presently, the most efficient and stable sensitizers are carboxylated polypyridyl ruthenium complexes [1]. Among them, $[Ru(dcbpy)_2(NCS)_2]$ (dcbpy = 4,4′-dicarboxylic bipyridyl), well known as the N3 dye, shows overall photoelectric conversion efficiency of 7–10% when a liquid electrolyte containing I_3^-/I^- solution is used [2,3]. There has also been potential interest in the investigation to find pure organic dye sensitizers for dye-sensitized photovoltaic cells. For example, perylene dyes [4,5], cyanine dyes [6–9], anthocyanine dyes [10], triphenylmethyne dyes [11], alizarine [12] and coumarin dyes [13] have been studied for their photosensitization in DSPV cells. Hara et al [14a] modified a coumarin 343 dye by extended π-conjugation which showed a very high photo-conversion efficiency of 5.6% in a DSPV cell. Recently, they also reported a class of polyene dyes [14b] which showed conversion efficiencies up to 6.8%.

The advantages of pure organic dyes over inorganic/organometallic dyes could be generalized as follows: (i) several commercial dyes are available with a variety of chelating groups that have good absorption profiles and very high molar extinction coefficients; (ii) simple modeling using semi-empirical quantum chemical methods for screening and structural modifications is possible; (iii) the absorption energies can be easily modified with extended conjugation; (iv) versatile functionalization onto polymers for preparation of dye-incorporated solid state poly electrolytes; (v) low cost compared to inorganic/organometallic dyes. Although pure organic dyes to date are less efficient than inorganic/organometallic dyes, further development of these types of dyes is critical to the emerging field of organic solar cell technology.

In this paper, we report the redox properties, absorption and photovoltaic measurements on a class of organic dyes. We chose several commercially available dyes with catechols for chelating onto titanium dioxide. These dyes were then screened (Fig. 1; Pyrocatechol Violet, **1**; Purpurin, **2**; Pyrogallol Red, **3**; 9-methyl-2,3,7-trihydroxy-6-fluorone, **4**; 9-phenyl-2,3,7-trihydroxy-6-fluorone, **5**) on the basis of their closest redox properties compared to the standard dye, N3. We discuss the concepts of direct charge transfer and the excited state electron transfer through the HOMO–LUMO energy level matching in these dyes.

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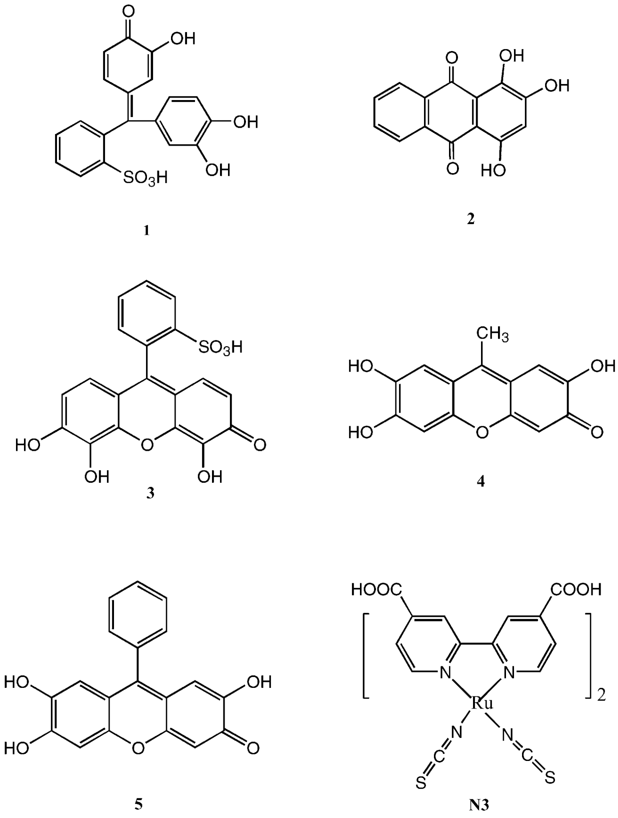

Fig. 1. Organic molecular dyes considered in this study and N3.

2. Materials and methods

UV-Vis spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. All the dyes studied in this paper were purchased from Aldrich and used without further purification. N3 was purchased from Solaronix (Switzerland). TiO_2 films of approximately 6 μm thickness were prepared using commercial colloidal TiO_2 powder (Degussa, P25, average size 10–50 nm) by spin coating onto SnO_2:F, (TEC-15, 15 Ω/sq) coated glass plates. For absorption measurements, transparent TiO_2 films of approximately 2 μm thickness were prepared and then sintered at 500 °C for 1 h. Adsorption of the dye was carried out by placing the sintered, hot (about 80 °C), TiO_2 film into the dye solution (10^{-4} M) in ethanol and soaking it overnight. After completion of the dye adsorption, the film was rinsed with ethanol and dried. The PV measurements were performed immediately after the preparation of the dye-adsorbed films. DSPV cells were assembled by clamping together the platinum coated SnO_2 counter electrode and the dye adsorbed TiO_2 working electrode with an active area of 0.25 cm^2. A liquid electrolyte consisting of 1.0 M LiI, 0.1 M I_2 in acetonitrile was introduced in between two plates. The DSPV cells were exposed to simulated AM1.5 solar light at 1 sun of 100 mW/cm^2 light intensity using an Oriel 1000 W xenon lamp and appropriate filters. Photocurrents and photovoltages were measured using a Keithley 2400 source meter in conjunction with a personal computer. Photoaction spectrum was obtained with a 150 W Xe lamp (Photon Technology Int. model, A-1010B) coupled to a Digikrom 240 monochromator. Incident irradiance was measured with a newport optical power meter, model 835 coupled to a photodiode and the photocurrent was collected on a Keithley digital multimeter, model 169 DMM. Redox potentials of the dyes were measured by cyclic voltammetry using a VoltaLab-40 potentiostat in a standard three-cell electrode arrangement. Voltammograms were recorded using a platinum (area 0.64 cm^2) in a 2 mM solution of the dyes containing 0.1 M supporting electrolyte.

All the geometries were fully optimized using the PRECISE keyword by a semi-empirical method AM1 (Austin Model 1) [15] and the HOMO–LUMO orbital surfaces were calculated by ZINDO [16] (single point) using Hyperchem computational software. All the calculations were performed under gas phase conditions.

3. Results and discussion

The transfer of an electron from the LUMO of the dye to the conduction band of TiO_2 and reduction of the dye back to the ground state by the electrolyte are essential for efficient energy conversion in a DSPV cell. For this, the energy level matching between the dye and semiconductor is very important and the knowledge of redox potentials of the dye is crucial to optimize the cell efficiency. The direct charge transfer between the TiO_2 and the dye via formation of strong charge transfer complexes is also an alternative way for the energy conversion. We believe that both excited state injection as well as direct charge transfer processes are contributing for energy conversion in our DSPV cells. We discuss both the processes in detail below.

We have studied three types of organic dyes, namely, triphenylmethyne dye (**1**), anthraquinone dye (**2**), and xanthene dyes (**3**–**5**) (Fig. 1). Each of these dyes was chosen because they have catechols as chelating groups. The three xanthene dyes (**3**–**5**) have higher molar extinction coefficients compared to **1** and **2**. The UV-Vis absorption spectra of the dye, **5** measured from ethanol solution is shown in Fig. 2. The absorption spectra of this dye adsorbed onto TiO_2 films is also shown in the figure. The absorption maxima and extinction coefficients at maximum wavelengths for all the dyes measured in ethanol solution are provided in Table 1.

The absorption maxima of these dyes ranges from 470 to 570 nm with cutoff wavelengths at around 700 nm which, makes them potential candidates for light harvesting in DSPV cells. Interestingly, the dye **5** adsorbed onto TiO_2 shows a large blue shift (51 nm) compared to other dyes with enormous broadening (Fig. 2). The orange color of the xanthene dye solutions (**3**, **4** and **5**) in ethanol become deep reddish upon the adsorption onto TiO_2 which indicates the formation of a new charge transfer complex between TiO_2

Table 1
UV-Vis absorption maximum, oxidation potentials and estimated LUMO values for the dyes **1**–**5** along with reported values of N3

Dye	Abs. max. (nm)[a]	$E^0(S^{+/0})$ (V)[b] vs. (SCE)	E^{0-0} (eV)[c]	$E^0(S^{+/*})$ (V)[d] vs. (SCE)	LUMO (eV)
1	571 (7.7)	+0.82	2.09	−1.27	−2.98
2	485 (8.0)	+0.59	2.32	−1.73	−2.52
3	510 (27.0)	+0.89	1.98	−1.09	−3.17
4	483 (72.5)	+0.97	2.42	−1.45	−2.81
5	517 (67.2)	+0.90	2.39	−1.49	−2.77
N3[e]	532 (13.7)	+0.85	1.85	−1.0	−3.85

[a] The values in parentheses are extinction coefficients ($\epsilon/10^3\,M^{-1}\,cm^{-1}$) measured in ethanol solution.
[b] From ref. [3].
[c] Oxidation potentials measured in 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as supporting electrolyte at scan rate 100 mV/s^{-1}.
[d] E^{0-0} values were estimated from crossing point of the emission and absorption spectra.
[e] $E^0(S^{+/*})$ values were calculated from $E^0(S^{+/*}) = E^0(S^{+/0}) - E^{0-0}$.

and the dyes. Thus dye-adsorbed TiO_2 films show different absorption characteristics compared to the solutions. The experimental observation of surface chelation by catechol groups in **5** was earlier reported by Gratzel et al [17]. They also observed that the shift in the visible absorption is pH dependent and solutions at acidic pH, the absorption band is red shifted greatly which was attributed to the deprotonation of OH groups that do not participate in the chelation of the metal ion. The blue shift in absorption maximum in TiO_2 films compared to solution was also previously observed in hemicyanine dyes [9] and was explained by the high polarity of TiO_2 surface and the formation of a new charge transfer state at the TiO_2 due to good electronic coupling between TiO_2 and catechol groups. The broadening of the spectra could be due to the interaction of neighboring dye molecules and formation of aggregates. Earlier studies also showed the broadening of the absorption spectrum of organic dyes in TiO_2 compared to ethanol solution [6,14a]. The feature of broadening in TiO_2 films is in fact advantageous in these systems for covering wider range of the solar spectrum for better light harvesting properties.

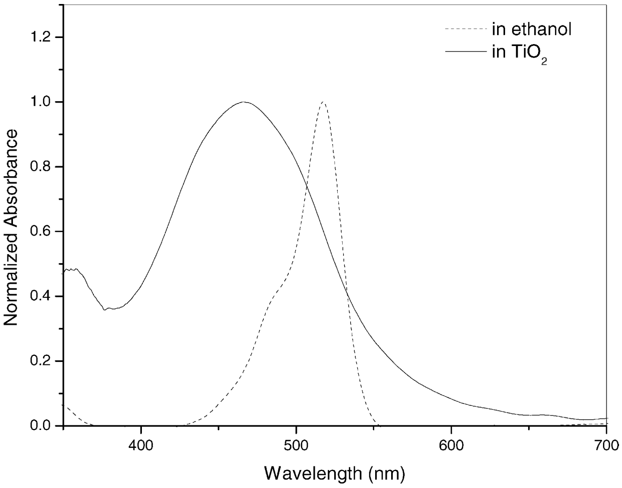

Fig. 2. UV-Vis absorption spectra measured in ethanol solution and adsorbed onto TiO_2 films for the dye **5**.

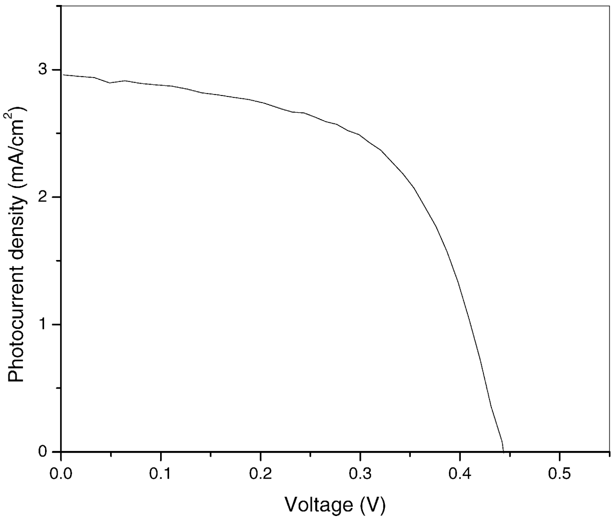

Fig. 3. Current–voltage (*I*–*V*) curve for the efficient dye **5** in nanocrystalline TiO_2 based DSPV cell containing 1.0 M LiI, 0.1 M I_2 in acetonitrile as redox electrolyte.

Fig. 3 shows typical *I*–*V* curve measured for the dye **5**. The short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and overall efficiency (η_e) for all the dyes are presented in Table 2. The J_{sc}, V_{oc} are obtained from *I*–*V* curves and FF (squareness of the *I*–*V* curve) and η_e are calculated using the following equations.

$$FF = \frac{V_{max} I_{max}}{V_{oc} J_{sc}}$$

Table 2
Photovoltaic properties measured for the dyes **1**–**5** along with N3

Dye	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF	η_e (%)
1	3.59	170	0.33	0.20
2	2.60	290	0.43	0.33
3	1.5	404	0.52	0.31
4	1.7	424	0.49	0.36
5	3.0	443	0.33	0.74
N3	18.75	592	0.56	4.71

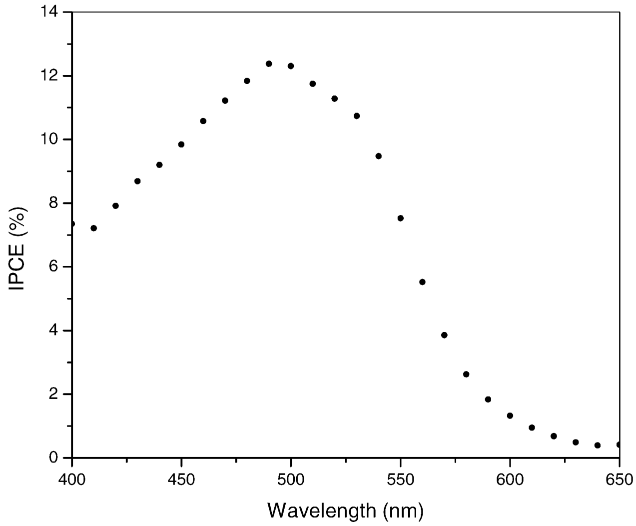

Fig. 4. Photocurrent action spectra obtained for **5** adsorbed onto nanocrystalline TiO_2 based DSPV cell.

and

$$\eta_{\mathrm{e}} = \frac{V_{\mathrm{oc}} J_{\mathrm{sc}} \mathrm{FF}}{I_{\mathrm{s}}}$$

where $V_{\max}$ and $I_{\max}$ are the maximum voltage and current at the maximum power output and I_s is the intensity of illuminated light. The PV values presented in Table 2 are the averages of **3**–**5** measurements each from three different sample cells. Fig. 4 presents the photoaction spectrum of the cell with the efficient xanthene dye **5**, where the incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength and the IPCE values were calculated by using the equation,

$$\mathrm{IPCE\%} = \frac{1240 \times \text{photocurrent} \times \text{density}\,(\mathrm{mA/cm^2})}{\text{Wavelength}\,(\mathrm{nm}) \times \text{irradiance}\,(\mathrm{mW/cm^2})} \times 100$$

It is interesting to note that **5** showed good photovoltaic efficiency compared to other dyes. The short-circuit photocurrent of $3\,\mathrm{mA/cm^2}$, photovoltage of 0.44 V and overall conversion efficiency of 0.74% for such a simple system without any metal centers is promising and suggest efficient charge carrier injection. The IPCE at maximum absorption wavelength was found to be 12% in **5** compared to N3 of 52% from our measurements. In a recent report on catechol sensitized TiO_2 nanoparticles, it has been suggested that the electron transfer process takes place due to the excitation of catechol to titanium charge transfer complex rather than the conventional way of dye excitation followed by electron transfer [18]. The earlier study by Ramakrishna et al. [19] on xanthene dyes with carboxylic groups also showed that a portion of the dye molecules form strong charge transfer complexes with TiO_2 and inject electrons directly into the conduction band of the TiO_2. Although the direct charge transfer is playing a crucial role in the energy conversion process in these dyes, the conventional way of electron injection through the HOMO–LUMO energy level matching with TiO_2 is also contributing in the energy conversion and is discussed in detail below.

There are several ways of altering HOMO–LUMO energies or redox potentials by varying the structure in organic molecules. Though direct correlation of these properties with photovoltaic efficiencies is not possible, the qualitative comparison of relative performances of the dyes with standard dyes can be made. Oxidation potentials from cyclic voltametric studies are shown in Table 1. All the dyes showed a quasi reversible wave with oxidation potentials ranging from +0.6 to 0.9 V versus SCE. The E^{0-0} energy of the dyes which were estimated from the crossing point

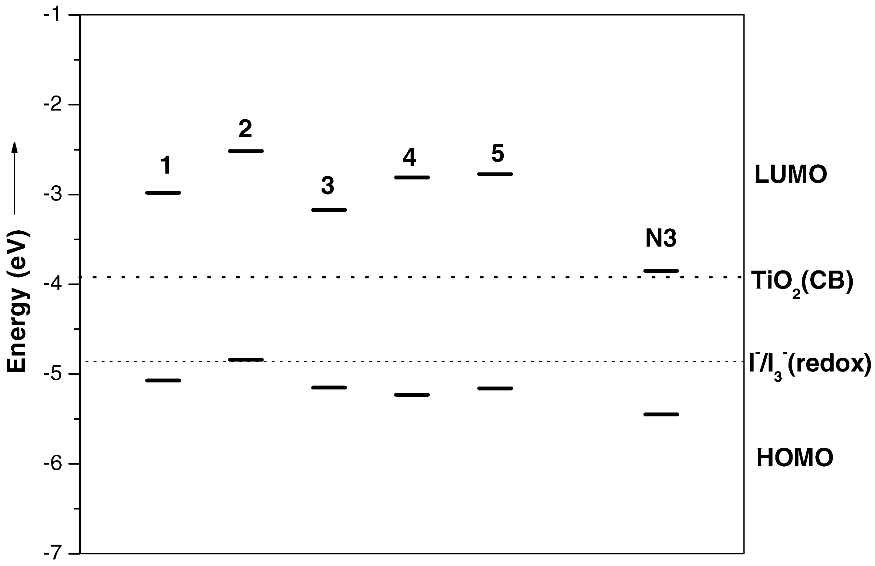

Fig. 5. A schematic energy level diagram of N3 and **1**–**5**. The reported experimental conduction band (CB) edge or LUMO of TiO_2 and HOMO of redox electrolyte, I^-/I^{3-} (dotted lines) are also shown.

of the absorption and emission spectra were used to calculate the excited state oxidation potentials from the equation, $E^0(S^{+/*}) = E^0(S^{+/0}) - E^{0\text{–}0}$ are also presented in the table. Although calculated excited state oxidation potentials of **3** is found to be −1.1 V and is close to the value of N3 (−1.0 V), the dye **5** showed higher photovoltaic efficiency. This could be due to its higher molar extinction coefficient. A schematic diagram which shows the LUMOs of all the dyes with respect to N3 and TiO_2 conduction band is depicted in Fig. 5. The excited state oxidation potentials were converted into LUMO energies in eV (Table 1) using the solid state scale that is available in the literature [20]. The comparison of LUMO values between the present dyes and N3 gives a qualitative explanation why these dyes show lower efficiencies. N3 has been chosen as standard dyes for comparison as this dye has optimum LUMO energy level matching with TiO_2. A reported value of conduction band edge level of TiO_2 (−4.3 eV) [1] measured in vacuum is provided in Fig. 5 as a guide. It is apparent from the figure that the LUMO values of these organic dyes are above the conduction band of TiO_2 and close to the LUMO value of N3 and are compatible for efficient electron transfer into the conduction band of TiO_2. Any dye with a LUMO energy level below TiO_2's conduction band edge would be incompatible for electron transfer and thus may not be useful for solar energy conversion. The HOMO levels of the dyes also plays an important role in reducing the dye back to its ground state by an electrolyte present in the device. As can be seen from the table and Fig. 5, the HOMO (ground state oxidation potentials) levels of all the dyes are compatible with the energy level of the redox electrolyte and thus they show photoconversion efficiency. From our study, **3**, **4** and **5** are found to have a better absorption coefficient, 27, 67 and 72 × $10^3\,M^{-1}\,cm^{-1}$ respectively compared to other dyes and N3 (13.1 × $10^3\,M^{-1}\,cm^{-1}$) [3]. However, low photoconversion efficiency observed in these dyes compared to N3 could be due to the electron recombination processes as well as other factors such as more negative LUMO energies and aggregation.

An insight into the charge transfer processes in dye attached TiO_2 systems can be gained by studying molecular orbital surfaces [10,11]. We have calculated molecular orbital surfaces of all the dyes by attaching them onto TiO_2. Typical HOMO–LUMO orbital surfaces of the efficient dye, **5** attached onto TiO_2 through its one catechol group are shown in Fig. 6. Though **5** has two different adsorbing sites at each end, as shown in Fig. 6, the delocalization renders the two sites equivalent. The formation of ruthenium dinuclear complexes of the dye **5** also suggests that two sites are open for chelating onto TiO_2 [21]. As expected, the LUMOs are localized on the chelating group and TiO_2 bonding orbitals which, clearly delineates the possibility of charge transfer from the dye to the Ti(IV) d-orbitals when it is photo-excited. Earlier studies showed that catechol groups in polypyridine complexes [22] and alizarine [10,12] molecule act as strong chelating moieties through the –OH groups to one surface Ti^{4+} ion and produce good photocurrents. Similar to earlier observation in anthocyanine dye [10], it is noteworthy that the adsorption of these dyes to the surface of TiO_2 is a rapid reaction displacing an OH^- counterion from Ti(IV) site that combines with a proton donated by these dyes, forming one molecule of H_2O and a strong complex. This proves that catechols are also efficient groups for adsorbing onto TiO_2 like carboxylic groups.

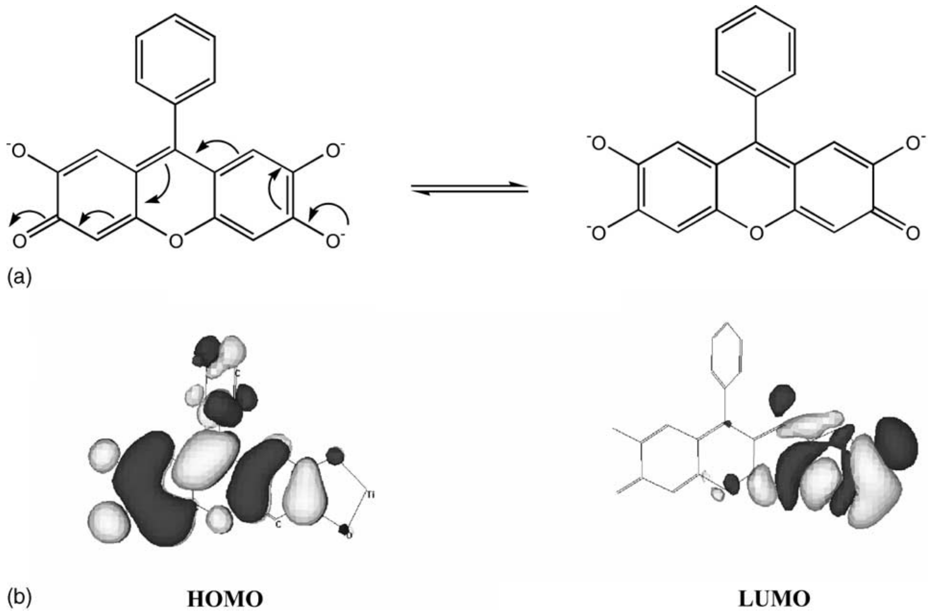

Fig. 6. (a) Delocalization in **5** (b) HOMO–LUMO orbital surfaces of the dye **5** complexed with Ti(IV).

4. Conclusion

We have identified and studied various commercially available organic dyes with catechol groups for their use in DSPV cells as photosensitizers and showed that xanthene dyes are efficient compared to triphenylmethyne and anthraquinone dyes due to their favorable absorption properties. A xanthene dye showed efficient photo-to-electric conversion efficiency compared to other dyes. We have demonstrated that the catechols are good chelating groups in organic molecules for their efficient adsorption onto TiO_2 via formation of strong complexes. Though photovoltaic efficiency is found to be low in these organic dyes for fabricating practical devices, this study suggests a promising alternative approach to dye selection from commercial sources for DSPV cells and for further investigation to identify more organic systems with improved efficiency. The two processes namely, direct electron transfer via formation of strong charge transfer complexes and the conventional excited state electron injection through HOMO–LUMO level matching may be contributing in the energy conversion in our cells. We are currently investigating the possibilities to improve the efficiencies in these dyes.

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