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Journal of Photochemistry and Photobiology A: Chemistry 140 (2001) 173–177

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Nanoporous TiO_2 solar cells sensitized with iron(II) complexes of bromopyrogallol red ligand

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Received 2 November 2000; accepted 16 January 2001

Abstract

Complexation of bromopyrogallol ligand with di(aqua)bis(oxalato)iron(II) moiety, $[Fe(II)(H_2O)_2(C_2O_4)_1]^{2-}$, shows enhanced photovoltaic properties when compared with the photovoltaic cells coated by bromopyrogallol ligand only. Electrochemical and absorption spectroscopic data suggest the nature of the lowest electronic transition of iron(II) complex as a $\pi^*_{(\mathrm{bpr})} \leftarrow d\pi_{(\mathrm{Fe})}$, metal to ligand charge transfer transition. Photovoltaic cells coated with bromopyrogallol ligand complexed with iron(II) shows higher stability for photodegradation and incident photocurrent conversion efficiency with a UV radiation blocking filter.

Keywords: Dye sensitization; Photovoltaic cells; Titanium dioxide; Bromopyrogallol; Iron(II) complexes

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1. Introduction

Metallochromic triphenylmethane type dyes attracted many scientists due to their potential ability to chelate with a number of metal centers [1,2]. Recently, we have shown [3] that the dye materials belonging to this class is capable of producing high photocurrents and photovoltages when used as sensitizers in nano-pourous TiO_2 photovoltaic cells. However, slow photodegradation of dye molecules and low photocurrent conversion efficiencies have been the major problem faced by the scientists. Photo-excitation of these type of ligands involve ligand centered (LC) transitions and often strongly allowed transitions are well into the UV side of the spectrum. Hence, direct irradiation will cause the photodegradation of dye molecules, blocking the UV radiation results in low photocurrent conversion efficiencies. Furthermore, solar energy conversion schemes based on LC transitions do not involve an energy capture through a charge separation process. Therefore, in addition to photodegradation, charge recombination reduces the cell efficiency of photocells sensitized through an LC mechanism (Scheme 1a). A more efficient system would be a cell sensitized through a charge capturing mechanism [4], such as a metal–ligand charge transfer (MLCT) transition where charge recombination is much less probable (Scheme 1b).

In the present study we have found that when a iron(II) moiety is complexed with bromopyrogallol ligand and used as the sensitizing dye material, enhanced values for the observed cell photocurrents and photovoltages are obtained. In addition, cells coated with these iron(II) bromopyrogallol complexes have shown high stability for photodegradation of dye material with a higher value for the observed photocurrent.

2. Experimental

Nano-porous layers of TiO_2 were coated on CTO glasses (1.5 cm × 2 cm, sheet resistance approx. 20 Ω/cm^2) by following the methods described elsewhere [5]. Iron(II) ligand complexes were prepared by following the procedure given below: bromopyrogallol ligand and di(aqua)bis(oxalato) iron(II) (which was prepared by precipitating the complex in aqueous medium by adding oxalic acid to an aqueous solution of ferrous ammonium sulfate) were mixed (1:1 molar ratio) and refluxed for 2 h in methanol. The resultant mixture was evaporated and the dark black solid compound obtained was washed several times with acetone to remove any unreacted bromopyrogallol ligand.

TiO_2 plates were coated with dye materials by boiling them in methanolic solutions. Liquid state photovoltaic cells were fabricated by sandwiching a film of electrolyte (8:2 ethylene carbonate and acetonitrile), 0.5 M tetrapropyl ammonium iodide and 0.05 M I_2 in between dye coated TiO_2

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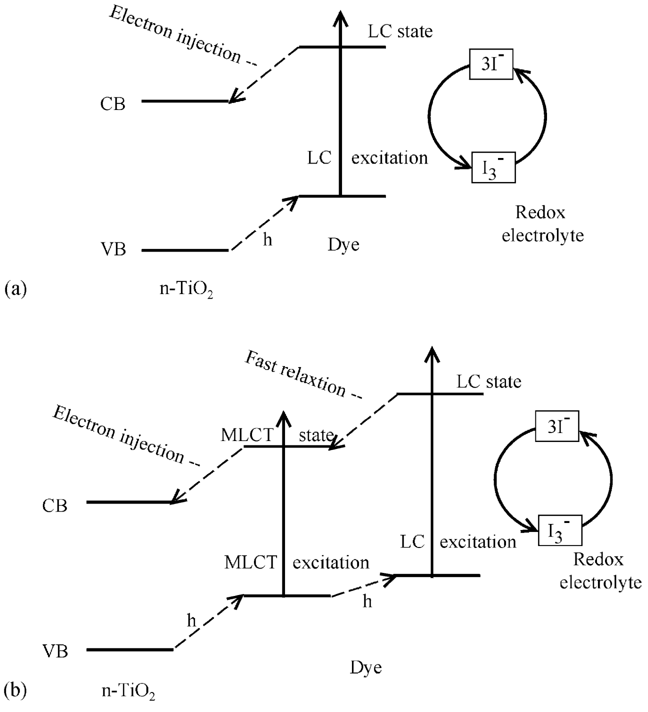
1010-6030/01/$ – see front matter
PII: S1010-6030(01)00392-6



Scheme 1.

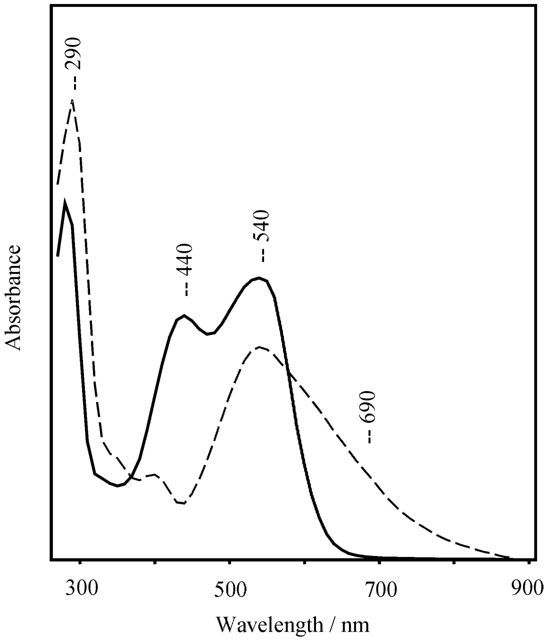


Fig. 1. Absorption spectra of di(aqua)bis(oxalato)iron(II) bromopyrogallol (-----) and bromopyrogallol red (—) in aqueous media.

plate and Pt plate deposited on conducting SnO_2 glass. Pt coated surface on SnO_2 was prepared either by thermal evaporation or by cathodically electrolyzing a solution of hexachloroplatinic acid.

Absorption spectra of the compounds in aqueous solutions were recorded using Perkin-Elmer 551 double beam spectrophotometer. Photocurrent action spectra (i.e. dependency of the observed photocurrent as a function of the wavelength) were monitored using Nikon monochromator Auto-scanner AS-C 101 equipped with Stanford Research lock-in amplifier.

Cyclic voltammograms were recorded using an EG&E Princeton applied research instrument potentio/galvanostat, model: Versastat II. Solutions were degassed for 20 min by bubbling N_2 prior to the scans.

3. Results and discussion

Metallochromic triphenylmethane type dyes have been subjected for many studies in the area of trace metal analysis due to its potential ability to chelate with the number of metal ions. However, these molecules have received very little attention as potential solar energy capturing pigments in dye sensitized nano-porous photovoltaic cells. Intense absorption band centered in the visible range of the spectrum at ca. 540 nm and strong ability to bind with nano-porous TiO_2 semiconductor surfaces have made these molecules as promising pigments in light harvesting mechanisms. Simple complexation of bromopyrogallol ligand with iron(II) moiety changes its deep reddish color to very intense blue color retaining the ability to adsorb on to a nano-porous TiO_2 surface.

The compounds are readily soluble in water and electronic absorption spectra of bromopyrogallol ligand and its iron(II) bisoxalato complex in aqueous medium are shown in Fig. 1. Absorption spectrum of the ligand shows $\pi^* \leftarrow \pi$ transition in the 540 nm region. When the absorption spectrum of bromopyrogallol is compared with the absorption spectrum of iron(II) complex, the striking feature is the appearance of a new peak around 690 nm. The band at 690 nm is well extended to the 900 nm region of the spectrum. This suggests that the nature of the lowest transition state of iron(II) bromopyrogallol complex is different from the free bromopyrogallol ligand. One of the major advantages of using di(aqua)bis(oxalato)iron(II) as the complexing unit (i.e. oxalato ligand as the spectator ligand) is the absence of chromophores in the visible range for this moiety, hence allowing us to interpret spectroscopic properties more readily.

Cyclic voltammograms recorded for bromopyrogallol ligand and iron complexes in 1×10^{-3} M KNO_3 solutions [6] are shown in Fig. 2. Quasi-reversible reduction waves were observed for both molecules, bromopyrogallol ligand and iron(II) complex of the same at a potential of −430 mV with reference to a Ag/AgCl electrode. Irreversible oxidation which occurred at 628 mV of free bromopyrogallol ligand is absent for the iron(II) complex in the scan range. Binding of the bromopyrogallol ligand with iron(II) bisoxalato moiety shows no effect on reduction potential and hence reductions of free ligand and iron(II) complex can be assigned as ligand based. Therefore, the electronic transition tailing out to 900 nm region of the spectrum for the iron(II)

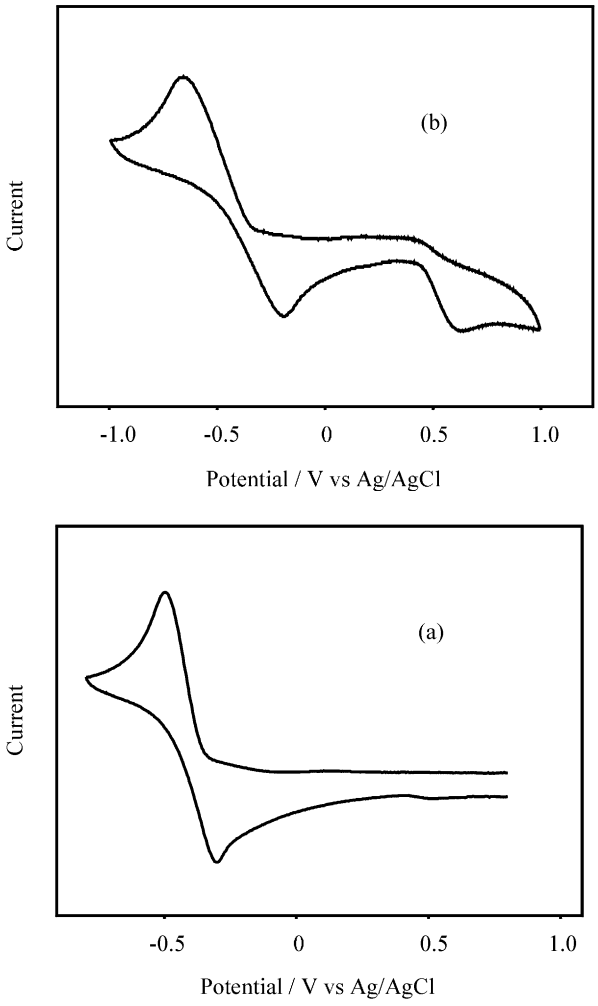


Fig. 2. Cyclic voltammograms of (a) iron(II) bisoxalato bromopyrogallol and (b) bromopyrogallol red in aqueous solution containing 1×10^{-3} M KNO_3 as supporting electrolyte. Working electrode: Teflon shrouded Pt electrode; scan rate: $100\,mV\,s^{-1}$.

complex is most likely to be a $\pi^*_{(bpr)} \leftarrow d\pi_{(Fe)}$, MLCT transition.

Photocurrent action spectra recorded for two dye molecules are shown in Fig. 3. Bromopyrogallol shows two peaks at 362 and 625 nm, respectively. The band appearing at 362 nm has been attributed [7] to the sensitization through TiO_2 band gap excitation and the peak at 625 nm to the dye sensitization. In the photocurrent action spectrum of iron(II) bromopyrogallol complex, the peak at 362 nm due to TiO_2 sensitization has disappeared indicating a large surface dye concentration [8]. Furthermore, photocurrent action spectrum has a shoulder at 698 nm, while the absorption peak in aqueous medium has a maximum at around 690 nm. The observed red shift can be interpreted by the increased delocalization of π^* orbitals of the bromopyrogallol ligand upon chealation to the Ti^{4+} ion. A similar red shift has been observed for bis(bipyridyl)Ru(II) complexes and the effect was attributed to the lower of the energy π^* orbitals due to delocalization [9].

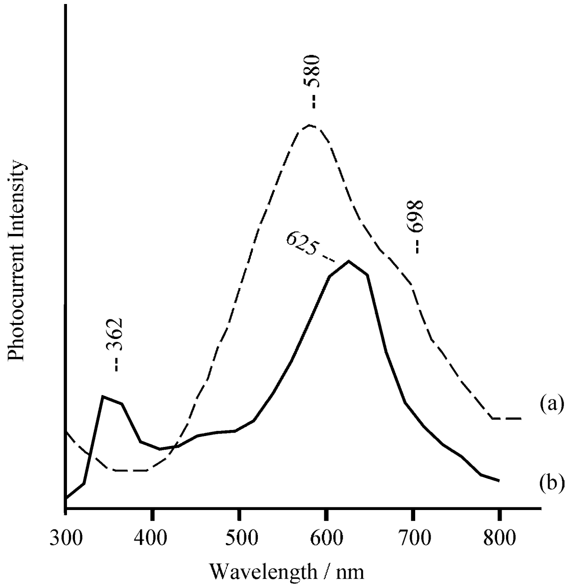


Fig. 3. Photocurrent action spectra for nanocrystalline TiO_2 films coated with (a) iron(II) bisoxalato bromopyrogallol and (b) bromopyrogallol red. Front wall illumination.

Average short circuit photocurrents (I_{SC}), open circuit photovoltages (V_{OC}) and cell efficiencies are given in Table 1. Photocurrent–voltage characteristics (I/V curves) are shown in Fig. 4. Complexation of bromopyrogallol ligand with di(aqua)bis(oxalato)iron(II) moiety has increased the cell efficiency from 0.2 to 0.3. However, when efficiencies are compared with values obtained by blocking the UV radiation ($\lambda \leq 348$ nm), reduction is approximately equal for the two dye materials. Efficiency of the cell constructed coating iron(II) bromopyrogallol complex and the bromopyrogallol coated cells show about 0.6% reduction when UV light was blocked. This can be attributed to the fact that iron(II) bisoxalato bromopyrogallol and bromopyrogallol have a similar action spectra in the visible region. It is

Table 1
Average photocurrent, voltage and cell efficiency values for the two dye materials: $750\,W\,m^{-2}$ solar simulator. Values in brackets are when the cell is exposed to afternoon sunshine[a]

Compound	Photocurrent ($mA\,cm^{-2}$)	Photovoltage ($mV\,cm^{-2}$)	Cell efficiency
Bromopyrogallol	0.83 (0.89)	411 (419)	0.20 (0.14)[a]
Iron(II) complex	1.23 (1.32)	423 (471)	0.29 (0.24)[a]

[a] Cell efficiency values obtained by blocking UV radiation ($\lambda \leq 348$ nm).

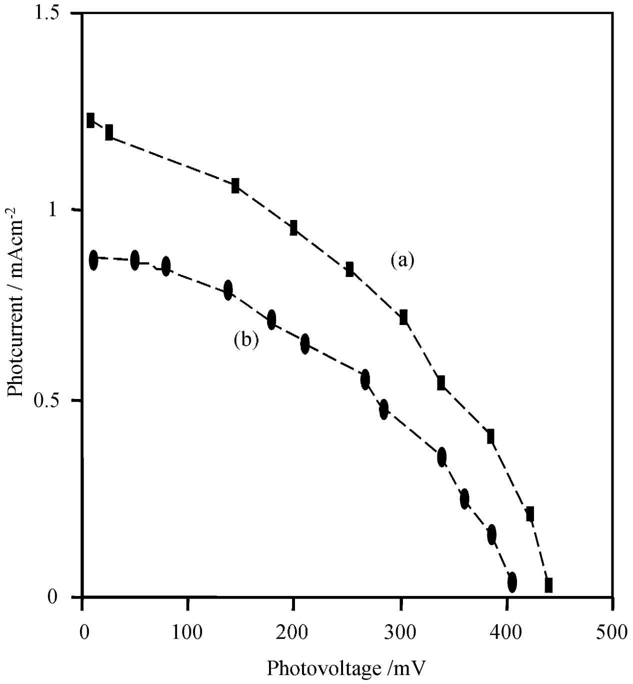


Fig. 4. Photocurrent–voltage curves for (a) iron(II) bisoxalato bromopyrogallol and (b) bromopyrogallol red.

noteworthy to mention that when bromopyrogallol ligand is complexed with ferrous ammonium sulfate, values obtained for photocurrents and photovoltages are comparable to the values obtained by coating iron(II) bisoxalato bromopyrogallol dye. This indicates that there is no significant role of the spectator, oxalato ligand on the current–voltage properties of the constructed photocells. Results clearly suggest that the enhancement of cell efficiency of iron(II) bisoxalato bromopyrogallol is a result of the MLCT character.

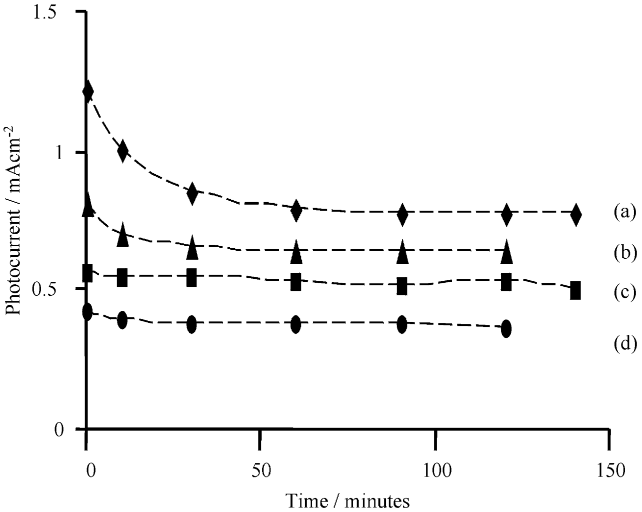


Fig. 5. The time development of the photocurrent when cells were illuminated with 750 W m^{-2} solar simulator for: (a) iron(II) bisoxalato bromopyrogallol; (b) bromopyrogallol red; (c) iron(II) bisoxalato bromopyrogallol with a UV blocking filter; (d) bromopyrogallol red with a UV filter.

Fig. 5 shows the time development curves for the photocurrent of the cell coated with the two dye materials when exposed to a 750 W m^{-2} solar simulator. TiO_2 band gap excitation by UV light generates electrons and holes which are readily accepted by oxygen atoms to form peroxides. This leads to a rapid photodegradation of coated dye material and it is prominent when using liquid redox couple (I^-/I_3^-) as a regenerator for the dye material. Rapid reduction of observed photocurrent during the initial times shows this effect. Factors affecting photodegradation have been extensively studied [10] and have shown remarkable photostability when cells are prepared under an inert atmosphere.

4. Conclusion

Complexation of bromopyrogallol red with iron(II) compounds show increased cell efficiency, when comparing with similar cell constructed by coating bromopyrogallol ligand. Cyclic voltammetric and absorption data suggest that the lowest transition has a MLCT character. However, complexation of bromopyrogallol ligand with iron(II) bisoxalato moiety was unable to increase the cell efficiency to a higher level to be considered for any practical application. One of the reasons could be the lack of the other light harvesting chromophore units in the complex. Nevertheless, the present study clearly indicates to us that the way forward in developing dye sensitized solar photovoltaic cells is by harvesting solar energy through a charge capturing mechanism. In any such mechanism, lowest electronic transition should have a charge transfer character to the chromophore that binds with n-type semiconductor.

Acknowledgements

National Science Foundation in Sri Lanka (Grant No. RG/98/C/05) and University of Sri Jayewardenepura research Grant ASP/6/R/97/05 are greatly acknowledged for the financial support for this project. PMJ acknowledges the support of Uppsala University in Sweden for donating an EG&G Prac microcell kit (model No. K0264) through IPICS program.

References

[1] D.T. Burns, D. Dadger, Analyst 105 (1980) 1082.
[2] Z. Hausenblasova, S.V. Nemcova, J. Microchem. 26 (1981) 262.
[3] P.M. Jayaweera, A.R. Kumarasinghe, K. Tennakone, J. Photochem. Photobiol. A 126 (1999) 111.
[4] M.R. Waterland, K.C. Gordon, J.J. McGarvey, P.M. Jayaweera, J. Chem. Soc., Dalton Trans. (1998) 609.
[5] K. Tennakone, G.R.R.A. Kumara, K.G.U. Wijayantha, I.R.M. Kottegoda, V.S.P. Perera, G.L.M. Aponsu, J. Photochem. Photobiol. A 108 (1997) 175.
[6] G.P. Sahu, S.C. Lavale, Asian J. Chem. 12 (2000) 203.

[7] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos, M. Gratzel, J. Am. Chem. Soc. 115 (1993) 6382.

[8] K. Tennakone, G.R.R.A. Kumara, K.G.U. Wijayantha, J. Semicond. Sci. Technol. 11 (1996) 1737.

[9] M.K. Nazeeruddin, A.K.I. Rodicio, R.H. Baker, M.P. Liska, N. Vlachopoulos, M. Gratzel, J. Am. Chem. Soc. 115 (1993) 6382.

[10] K. Tennaknoe, G.R.R.A. Kumara, I.R.M. Kottegoda, K.G.U. Wijayantha, J. Semicond. Sci. Technol. 12 (1997) 128.