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Heterosupramolecular Chemistry: Long-Lived Charge Trapping by Vectorial Electron Flow in a Heterotriad

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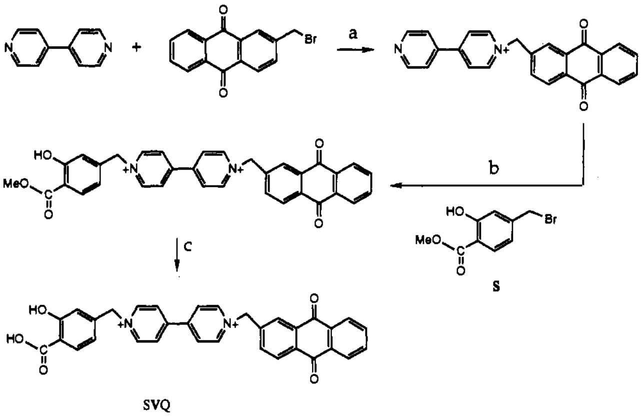
Artificial systems that achieve long-lived light-induced charge separation are of general interest.[1] Potential applications include photocatalysis and optoelectronics. Of particular interest are systems based on nanocrystalline semiconductor particles.[2] Efficient operation of such devices requires spatial separation of the photogenerated electron and hole on a time scale fast compared with recombination. Additionally, the potential gradient used to achieve charge separation should dissipate a minimum of the absorbed photon's energy. Bringing together recent advances in the preparation of dye-sensitized transparent polycrystalline semiconductor films[3] and synthesis of supermolecules containing multiple redox components,[4] a modified semiconductor electrode–liquid electrolyte interface (SLI) has been prepared at which potentiostatically controlled vectorial electron flow leads to long-lived charge trapping. Vectorial electron flow, initiated by bandgap irradiation of the semiconductor substrate, also leads to long-lived charge separation and will be described in a forthcoming paper.[5]

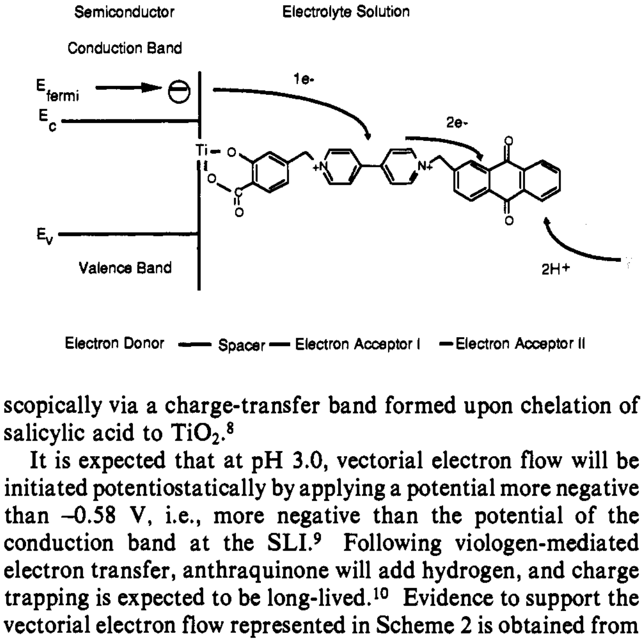
Recently, we described attachment of a redox species to a semiconductor electrode using a chelate (spacer).[6] Application of a sufficiently negative potential results in electron transfer (ET) from the semiconductor conduction band (donor) to the redox species (acceptor) positioned at the SLI. Such heterogeneous donor–spacer–acceptor complexes were termed heterodyads. Subsequently, we have modified the SLI by adsorption of a spacer–acceptor I–acceptor II complex to form a heterotriad (acceptor II having a more positive formal electrode potential than acceptor I). Specifically, a transparent polycrystalline TiO_2 film prepared on conducting tin oxide glass (fluorine doped) acts as the donor.[7] Salicylic acid chemisorbed at TiO_2 by chelation to surface Ti^{4+} atoms is used as a spacer.[8] Attachment of a viologen to the above spacer has proved possible. The second acceptor of the heterotriad, anthraquinone, is linked to the viologen.[9] Preparation of the perchlorate salt of the above spacer–acceptor I–acceptor II complex (SVQ) is summarized in Scheme 1. SVQ was adsorbed from a 1×10^{-3} mol dm^{-3} aqueous solution onto a TiO_2 film during 36 h. Adsorption was monitored spectroscopically via a charge-transfer band formed upon chelation of salicylic acid to TiO_2.[8]

Scheme 1



[a] Reaction conditions: (a) toluene, 110 °C, 85%; (b) MeCN, 80 °C, 70% (S prepared as described in ref 6); (c) 1.0 mol dm^{-3} $HClO_4$ (50% by vol DMSO), 95 °C, 80%. Anal. Calcd. for perchlorate salt of SVQ ($C_{33}H_{24}N_2O_{13}Cl_2$): C, 54.45; H, 3.31; N, 3.85; Cl, 9.77. Found: C, 54.34; H, 3.32; N, 3.87; Cl, 9.65. Partial ^1H NMR (DMSO-d_6): δ 5.96 (s, 2H), 6.19 (s, 2H). These singlets are diagnostic for linkage of the redox components of SVQ. Disappearance of a singlet at δ 3.87 (s, 3H) is diagnostic for conversion of the ester precursor of SVQ to the active acid (the ester form of SVQ is not adsorbed at TiO_2).

Scheme 2



It is expected that at pH 3.0, vectorial electron flow will be initiated potentiostatically by applying a potential more negative than −0.58 V, i.e., more negative than the potential of the conduction band at the SLI.[9] Following viologen-mediated electron transfer, anthraquinone will add hydrogen, and charge trapping is expected to be long-lived.[10] Evidence to support the vectorial electron flow represented in Scheme 2 is obtained from cyclic voltammetry and potential-dependent optical absorbance spectroscopy.

Cyclic voltammograms (CVs) recorded for a modified TiO_2 film at pH 3.0 are shown in Figure 1. The isolated counter and reference electrodes were platinum and saturated calomel (SCE), respectively, and the electrolyte an aqueous (deoxgenated) solution of $LiClO_4$ (0.2 mol dm^{-3}, pH adjusted to 3.0 using $HClO_4$). The first cathodic scan shows a large wave at −0.6 V due to $1e^-$ reduction of viologen (acceptor I) and $2e^-/2H^+$ viologen-mediated reduction of anthraquinone (acceptor II), see Figure 1a. (Part of this cathodic wave is due to direct reduction of anthraquinone at −0.4 V, presumed to be a consequence of either a cisoid conformation of the spacer–acceptor I–acceptor II complex or chelation within the microporous electrode in a manner that favors such a process.) The first anodic scan shows a wave at −0.5 V, the result of $1e^-$ oxidation of viologen. There is also a residual

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(1) Graetzel, M. *Nature* **1993**, *366*, 206–207.

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(3) O'Regan, B.; Graetzel, M. *Nature* **1991**, *353*, 737–740.

(4) Examples of work of this type include the following: (a) Shafirovich, V.; Amouyal, E.; Delaire, J. *Chem. Phys. Lett.* **1991**, *178*, 24–30. (b) Cormier, A.; Posey, M.; Bell, W.; Fonda, H.; Connolly, J. *Tetrahedron* **1989**, *45*, 4831–4842.

(5) Marguerettaz, X.; Redmond, G.; Rao, R.; Fitzmaurice, D., paper in preparation.

(6) Marguerettaz, X.; O'Neill, R.; Fitzmaurice, D. *J. Am. Chem. Soc.* **1994**, *116*, 2629.

(7) O'Regan, B.; Moser, J.; Anderson, M.; Graetzel, M. *J. Phys. Chem.* **1990**, *94*, 8720–8726.

(8) (a) Frei, H.; Fitzmaurice, D.; Graetzel, M. *Langmuir* **1990**, *6*, 198–206. (b) Moser, J.; Punchihewa, S.; Infelta, P.; Graetzel, M. *Langmuir* **1991**, *7*, 3012–3018. (c) Redmond, G.; Graetzel, M.; Fitzmaurice, D. *J. Phys. Chem.* **1993**, *97*, 6951-6954.

(9) The potential of the conduction band of the nanocrystalline TiO_2 film at the SLI has been determined to be −0.58 V (SCE) at pH 3.0, see: Rothenberger, G.; Fitzmaurice, D.; Graetzel, M. *J. Phys. Chem.* **1992**, *96*, 5983-5396. The formal electrode potential of the viologen component of the heterotriad was determined to be −0.56 V (SCE), see ref 6. The peak reduction potential of anthraquinone was determined to be −0.44 V (SCE), see Figure 2b.

(10) (a) Hable, C. T.; Crooks, R. M.; Wrighton, M. S. *J. Phys. Chem.* **1989**, *93*, 1190–1192.

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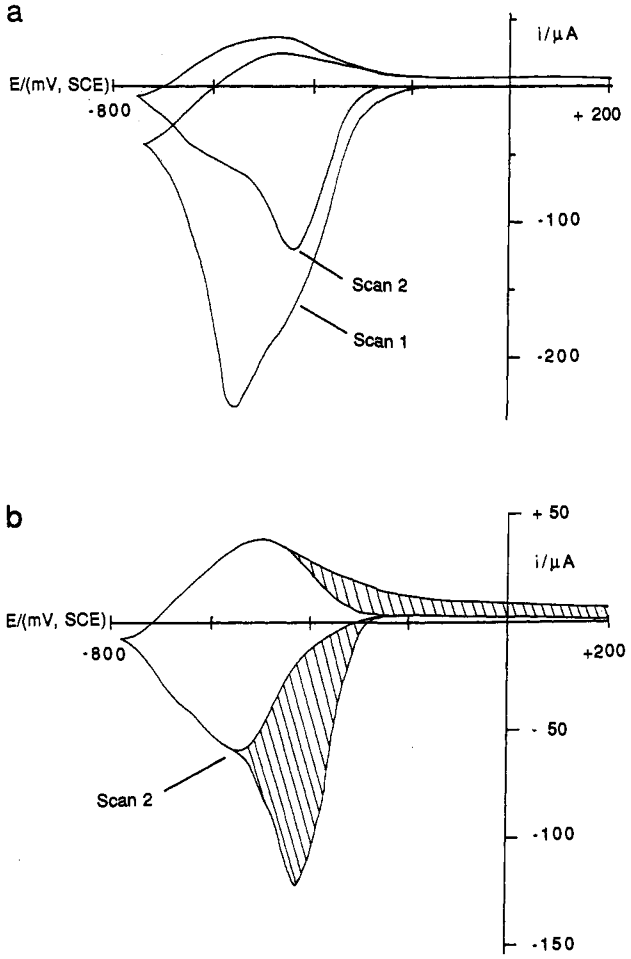

Figure 1. (a) Cyclic voltammogram of polycrystalline TiO_2 film derivitized by SVQ adsorbed during 36 h from aqueous solution (1×10^{-3} mol dm^{-3}). Conditions: 0.050 V s^{-1} scan rate (0.005-V step). (Background voltammogram measured for underivitized film has been subtracted.) (b) Scan 2 in (a) has been deconvolved into a contribution due to reduction and oxidation of the viologen acceptor and a contribution (shaded area) due to direct reduction and oxidation of the anthraquinone acceptor.

anodic current at potentials more positive than −0.3 V due to reoxidation of reduced anthraquinone. Consistent with the above, subsequent cathodic scans show waves at −0.4 V due to direct reduction of anthraquinone and at −0.6 V due to reduction of viologen. No current due to viologen-mediated reduction of anthraquinone is apparent. Further, the cathodic current in Figure 1b, due to reduction of viologen, is about half that due to viologen-mediated reduction of anthraquinone. Similar CVs have been reported by Wrighton and co-workers at low pH for polymeric viologens charge compensated by anthraquinone.[10]

Support for the above interpretation is provided by potential dependent visible absorbance spectroscopy of a modified TiO_2 film incorporated as the working electrode of a three-electrode, single compartment cell.[11] The counter and reference electrodes were platinum and saturated calomel (SCE), respectively, and the electrolyte was an aqueous (deoxygenated) solution of $LiClO_4$ (0.2 mol dm^{-3}, pH adjusted to 3.0 using $HClO_4$). The applied potential was controlled using a Ministat Precision Potentiostat. Following incorporation of the above cell in a Hewlett-Packard 8452A diode array spectrophotometer, visible spectra were measured at 0.025-V intervals between 0.000 and −0.800 V. In Figure 2a, a spectrum measured at −0.400 V is assigned to anthraquinone reduced directly at the SLI.[12] At applied potentials

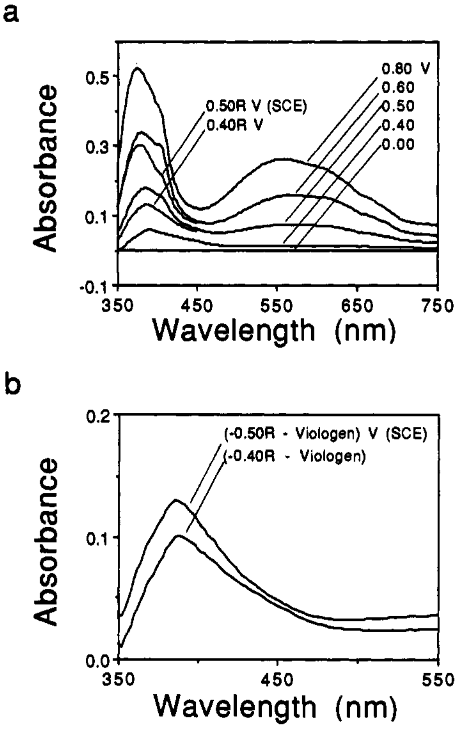

Figure 2. (a) Absorbance spectra of a transparent polycrystalline TiO_2 film derivitized by SVQ adsorbed during 36 h from aqueous solution (1×10^{-3} mol dm^{-3}) at the indicated potentials. (b) Spectra at indicated potentials corrected for absorption by reduced viologen.

more negative than that of the conduction band at the SLI, we measure an absorbance which may be assigned to the summed spectra of reduced viologen and reduced anthraquinone.[12,13] That this is the case is evident from spectra measured at −0.400 and −0.500 V as the applied potential is returned to 0.000 V. These spectra, corrected for absorption by reduced viologen, are shown in Figure 2b and agree well with that of reduced anthraquinone.[12] Significantly, at 0.000 V, the spectrum assigned to reduced anthraquinone persists for more than 5 min. Oxidation of the reduced anthraquinone due to reaction with residual dissolved molecular oxygen leads to the formation of peroxide.[14] The final spectrum is indistinguishable from that measured initially at 0.000 V. Further, we note that the potential-dependent spectroscopy shown in Figure 2 is reproducible over many cycles.

We have described a modified SLI at which long-lived charge trapping follows potentiostatically controlled vectorial electron flow. Generally, an important feature of this system is the novel combination of solid-state nanotechnology and supramolecular chemistry to form a heterotriad. Further development of such heterosupramolecular chemistry offers the prospect of combining the functionality of supramolecular assemblies with the addressability that is a consequence of their organization in the two-dimensional space defined by the semiconductor–liquid interface.

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[11] O'Regan, B.; Graetzel, M.; Fitzmaurice, D. *Chem. Phys. Lett.* **1991**, *183*, 89–93.

[12] Anthraquinone was adsorbed at a polycrystalline TiO_2 film and the absorbance spectrum of the reduced compound measured under the conditions in Figure 2. The corresponding cathodic wave, measured under the same conditions as in Figure 1, indicated a peak reduction potential of about −0.4 V, and that reduction is complete at about −0.6 V.

[13] Kok, B.; Rurainski, H.; Owens, O. *Biochim. Biophys. Acta* **1965**, *109*, 347–356.

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