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Heterodyads: Electron Transfer at a Semiconductor Electrode–Liquid Electrolyte Interface Modified by an Adsorbed Spacer–Acceptor Complex

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Understanding of homogeneous electron transfer (ET) has advanced considerably in the past 3 decades.[1] Donor–spacer–acceptor complexes, referred to as homodyads, have played a central role in securing these advances.[2] Specifically, homodyads have permitted the distance and orientation of donor and acceptor to be fixed. This, in turn, has allowed important aspects of condensed-phase ET theory to be tested.[3] Typically, ET is initiated by photoexcitation of the donor and monitored by measuring evolution of an absorbance assigned to the reduced acceptor.

Heterogeneous ET has also been widely studied but remains less well understood.[4] This is particularly true of ET at the semiconductor electrode–liquid electrolyte interface (SLI).[5] In view of the importance of homodyads to the study of condensed-phase ET, it is surprising that no exactly analogous experiments have been reported for ET at the SLI,[6] specifically, experiments in which an acceptor is held at a fixed distance and orientation with respect to the semiconductor electrode by a molecular spacer. Such donor–spacer–acceptor complexes we would term heterodyads. Application of a sufficiently negative potential will result in ET to the acceptor positioned in the SLI by the spacer. Reoxidation of the acceptor may also be controlled potentiostatically.

Recent advances in preparative chemistry at the SLI permit realization of the experimental approach outlined above. Many of these advances are a consequence of successful work directed toward development of efficient regenerative photoelectrochemical cells based on transparent polycrystalline semiconductor films sensitized by chemisorbed dyes.[7,8] A transparent polycrystalline TiO_2 electrode (4 μm) supported on fluorine-doped tin oxide (TO) glass is used as the donor.[9] In the course of work directed at understanding sensitizer adsorption, it has been demonstrated that molecules such as salicylic acid are chemisorbed at TiO_2 by chelating to surface Ti^{4+} atoms while simultaneously eliminating intraband surface states.[10] Therefore, this and related molecules are used as spacer molecules. Among the most widely used acceptors in homodyads are the viologens, having one of the lowest redox potentials of any organic molecule showing significant reversibility.[11] In addition, they exhibit a large change in the visible extinction coefficient following reduction[12] and possess a first reduction potential that is essentially pH independent.[13] Attachment of the viologens to a range of spacers which chelate to the semiconductor electrode has proved possible.

Consistent with the above, we have prepared the spacer–acceptor complex 1-ethyl-1′-[(4-carboxy-3-hydroxyphenyl)-methyl]-4,4′-bipyridinium perchlorate **I** (Scheme 1). This complex was adsorbed from a 2×10^{-3} mol dm^{-3} aqueous solution onto an activated TiO_2 film during 24 h.[14] Adsorption was monitored spectroscopically via a charge-transfer band assigned to salicylic acid chelated to TiO_2.[10a]

A TiO_2 film on which had been adsorbed the spacer–acceptor complex **I** was incorporated as the working electrode in a single compartment three-electrode cell. The counter and reference electrodes were platinum and saturated calomel (SCE), respectively, and the electrolyte an aqueous 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 0.00 V and −0.80 V, see Figure 1a.[15] Spectra measured under the same conditions for an untreated film agree well with those previously reported and assigned to absorbance by free conduction band and surface-trapped electrons.[9a] Spectra measured following adsorption of 4-methylsalicylic acid are similar to those measured for the untreated film; however, absorbance by surface-trapped species is absent.[16] The latter observation is consistent with recently reported findings concerning the effect of such chelates on the energy of the intraband states associated with the surface defects at which they are adsorbed.[10] The absorbance by spacer–acceptor complex **I** at 550 nm is plotted against potential, see Figure 1b. We note, following addition of 2×10^{-3} mol dm^{-3} methylviologen, no spectrum which could be assigned to reduced viologen was detected at applied potentials as negative as −0.80 V. In short, in the absence of either spacer or acceptor, no reduction of viologen was detected spectroscopically at the applied potentials.

Up to applied potentials of −0.80 V, 0.22 V negative of V_{fb} for the semiconductor electrode at pH 3.0,[17] the measured spectroscopy is reversible, see Figure 1a. Examination of the cyclic voltammogram (SCE reference electrode) shown in Figure 2 confirms the above. Specifically, we find that reduction of the acceptor is chemically reversible and electrochemically quasireversible. The formal potential $E^{\circ\prime}$ is determined to be −0.56 V, in good agreement with literature values for closely related compounds.[18] Further, we note that at potentials close to −0.8 V, the increase in absorbance at 550 nm for an increment in applied potential is small, see Figure 1b. This is consistent with the low currents observed at the same potentials in Figure 2, indicating that all adsorbed spacer–acceptor complex **I** has been reduced.

The absorbance at 550 nm of the fully reduced acceptor in Figure 1a is 0.82. Assuming an extinction coefficient for the reduced acceptor of 21 000 mol^{-1} cm^{-1} [12a] and the surface roughness factor for the polycrystalline TiO^2 film of 780,[7] we

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(16) Detailed spectra supporting this assertion will be presented in a paper currently being prepared.

(17) The relationship between V_{fb} and pH for polycrystalline TiO_2 films for which results are reported is V_{fb}(V, SCE) = −0.40 − (pH × 0.06), according to ref 9a.

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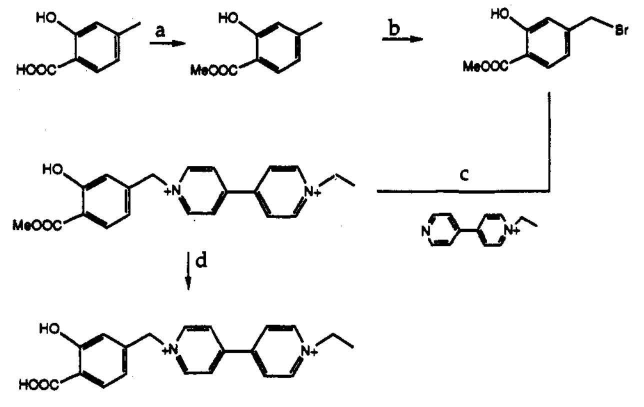
Scheme 1



I

[a] Reaction conditions: (a) MeOH, concentrated H_2SO_4, 70 °C, 85%. (b) CCl_4, NBS, catalyst $(PhCO_2)_2$, 70 °C, 88%. (c) MeCN, 80 °C, 70% (coreagent prepared as described in ref 22). (d) H_2O, 10% concentrated $HClO_4$, 95 °C, 90%. Anal. Calcd for I ($C_{20}H_{20}N_2O_{11}Cl_2$): C, 44.87; H, 3.77; N, 5.23; Cl, 13.24. Found: C, 44.99; H, 3.64; N, 4.76; Cl, 13.33. H^1 NMR (DMSO-d_6): δ 1.57–1.62 (t, J = 7.31 Hz, 3H), 4.67–4.75 (q, J = 7.31 Hz, 2H), 5.92 (s, 2H), 7.07–7.10 (d, J = 8.16 Hz, 1H, unresolved meta-coupling), 7.16 (s, J = 1H, unresolved meta-coupling), 7.84–7.87 (d, J = 8.16 Hz, 1H), 8.71–8.75 (d, J = 9.29 Hz, 2H), 8.74–8.77 (d, J = 9.29 Hz, 2H), 9.34–9.37 (d, J = 7.04 Hz, 2H), 9.45–9.48 (d, J = 7.03 Hz, 2H).

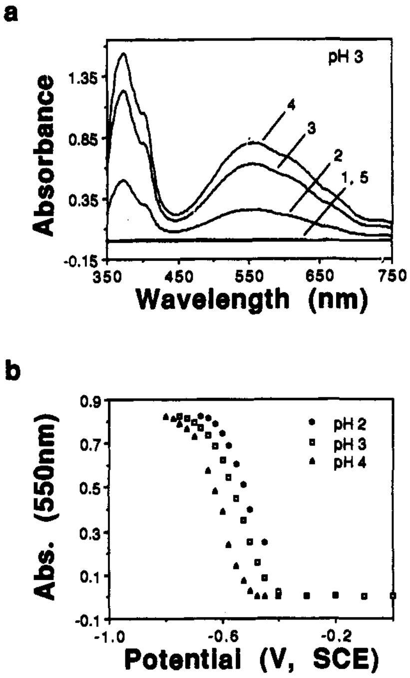


Figure 1. (a) Absorbance spectra for a transparent polycrystalline TiO_2 film derivatized by spacer–acceptor I adsorbed during 24 h from aqueous solution (2 × 10^{-3} mol dm^{-3}, pH 3.0) measured at the following potentials (V, SCE): (1) 0.00; (2) 0.50; (3) 0.60; (4) 0.70; (5) 0.00 (following 1–4). (b) Absorbance at 550 nm for derivatized semiconductor film (pH 3.0) in spectra a plotted against potential. Also shown are results of a similar experiments at pH 2.0 and 4.0.

estimate an adsorbate concentration of about 5 × 10^{-11} mol cm^{-2}. This is equivalent to 3 × 10^{13} adsorbed spacer–acceptor complexes I per square centimeter, in excellent agreement with the reported density of states assigned to surface Ti^{4+} sites[19] at which salicylic acid and related molecules are adsorbed.[10] We conclude that there is close to monolayer coverage of the spacer–acceptor complex I due to adsorption at surface Ti^{4+} sites.

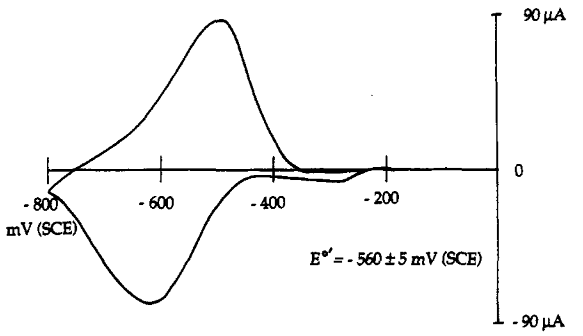
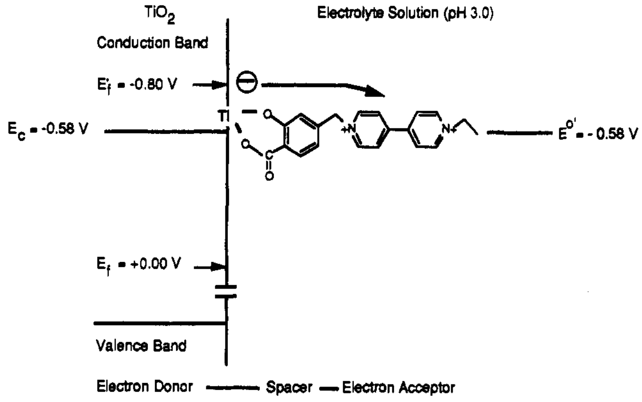


Figure 2. Cyclic voltammogram of polycrystalline TiO_2 film derivatized by adsorbed spacer–acceptor I as described in caption of Figure 1. Conditions: 0.050 V s^{-1} scan rate; 0.005 V step; aqueous $LiClO_4$ (2 × 10^{-3} mol dm^{-3}, pH 3.0), isolated Pt counter electrode; SCE reference. (Background voltammogram measured for underivatized film has been subtracted.)

Scheme 2



To account for the results presented in Figure 1b, we have prepared an energy level diagram for the heterodyad in question (Scheme 2). Ideally, the acceptor will be reduced at potentials more negative than V_{fb} for the conduction band, i.e., −0.58 V. The absorbance assigned to the reduced viologen in Figure 1a increases significantly at potentials more negative than about −0.5 V, consistent with rectified electron transfer at this interface. To further support the above conclusion, the experiment represented in Figure 1a was repeated at pHs 2.0 and 4.0. Results are plotted in Figure 1b. The average shift in the absorbance onset is 0.057 V/pH unit, in accord with expected Nernstian behavior at a TiO_2 electrode.[20] Reoxidation of the reduced acceptor is complete at all the above pHs. At pHs greater than 8, the V_{fb} of the conduction band is at potentials more negative than −0.88 V, and electron transfer is expected to result in a two-electron reduction of the viologen acceptor.[11] Irreversible reduction is observed under such conditions.

Results presented demonstrate that behavior of the above heterodyad is analogous to that of donor–spacer–acceptor complexes in the condensed phase. Heterodyads are therefore be expected to prove useful in achieving an improved understanding of ET at the SLI. Currently the dependence of the rate constant for interfacial electron transfer on the concentration of electrons in the conduction band, the distance of the acceptor from the surface, and the driving force for the reaction are being studied.[21]

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