Table 2. Magnetoresistance along and perpendicular to the layer planes at 10 K and 80 K

Crystal direction	$\Delta\rho/\rho$ (in %) $T = 10$ K	$\Delta\rho/\rho$ (in %) $T = 80$ K
Parallel to layer plane	− 7.14	+ 11.5
Perpendicular to layer plane	− 5.18	+ 8.3

rison is given in Table 2. The presence of stacking faults also gave rise to nonlinear I–V characteristics across the layer planes, similar to those due to tunnelling between quantum wells at 10 K, which disappeared at higher temperatures.

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Enhancement of the energy and quantum conversion efficiencies of a photoelectrochemical cell sensitized with a combination of cationic and anionic dyes

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The dye bromopyrogallol red surface complexes to TiO$_2$ and adsorbs the electron-donating cationic dye, acridine orange, binding it to the anionic sulphonate site. The resulting double dye film, when used in a photoelectrochemical cell, shows enhanced incident photon to current and energy conversion efficiencies and a broadened spectral response owing to charge transfer between the dyes and utilization of light absorbed by both the dyes.

SOLAR energy conversion that mimics photosynthesis in utilizing pigments for light harvesting continues to receive much attention and different types of pigment-based artificial light-harvesting systems have been reported[1–9]. One approach to the problem attempts to create reaction centres, linking chromophores, electron donors and/or acceptors by covalent or coordinate bonds. The other, the

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practically more successful method, is dye-sensitization of semiconductor nanostructures[2,4]. Attempts have also been made to use coupled electron donor and/or acceptor units to sensitize semiconductors, hoping that this would facilitate the charge separation. The intimate contact between different units, considered necessary for charge transfer is realized via covalent linkages[5,6,10,11]. In this communication, we describe a simple model system where the broadening of the spectral response enhanced charge separation and the consequent increase in the energy and incident photon to current efficiencies (η and IPCE) are more explicitly demonstrated in a photoelectrochemical cell (PEC) by ionic linkage of bromopyrogallol red (B) anions surface-complexed to TiO$_2$ with the acridine orange (A) cations.

TiO$_2$ films were deposited by spraying a dispersion of Degussa P25 (particle size $\sim$ 30 nm) onto conducting tin oxide (CTO) glass plates and sintering at 450°C. On soaking the plate in a solution of the anionic dye, bromopyrogallol red (5,5′-dibromopyrogallol sulphonephthalien) in ethanol (1×10^{-4} M), the dye anchors firmly to TiO$_2$ by complexation involving two of its hydroxyl groups (Figure 1 a). Estimated dye surface concentration (SC) was $\sim$ 90% of the monolayer coverage (dye on the plate is desorbed into a measured volume of 0.02 M NaOH in 80% ethanol and its concentration estimated spectrophotometrically). The second dye, acridine orange (3,6-bis(dimethylamino) acridine hydrochloride), which is cationic gets deposited on top of the first dye, when the plate is soaked in a solution of this dye (1×10^{-4} M in ethanol) or by spreading a measured quantity of the dye solution (0.05 M) on the film. The dye A cation binds to the anionic sulphonate site of B (Figure 1 a), replacing H$^+$ and eliminating HCl. PECs were made from TiO$_2$ films coated with B, A and A–B (A coated on top of B) in the usual manner, interposing the electrolyte (0.5 M tetrapropyl ammonium iodide + 0.03 M I$_2$ in acetonitrile containing 10% ethylene carbonate) between the film and the platinized CTO glass counter electrode. Table 1 gives the
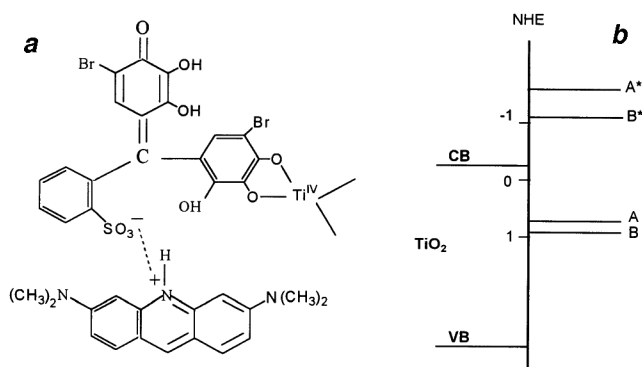

Figure 1. a, Schematic structural diagram showing the surface complexation of bromopyrogallol red (B) to TiO$_2$ and ionic binding of acridine orange (A) cation to the anionic sulphonate group of bromopyrogallol red; b, Energy level diagram indicating the band positions of TiO$_2$, ground and excited levels of the two dyes. VB, Valence band; CB, Conduction band.

Table 1. Short-circuit photocurrent, open-circuit voltage and efficiency of the cells where TiO_2 films are sensitized with: A, acridine orange; B, bromopyrogallol red; A–B, acridine orange on bromopyrogallol red (Illumination, 750 W m^{-2} from a solar simulator)

Dye	I_{sc} (mA/cm^2)	V_{oc} (mV)	$\eta\%$
A	0.98 ± 0.69	250 ± 12	0.2 ± 0.07
B	4.09 ± 0.59	233 ± 12	0.4 ± 0.07
A–B	6.32 ± 0.56	249 ± 9	0.8 ± 0.05

short-circuit photocurrent (I_{sc}), open-circuit voltage (V_{oc}) and efficiency (η) of these cells at 750 W m^{-2} illumination from a solar simulator. It is seen that the double-dye system yields higher values for I_{sc}, V_{oc} and η. Again the photocurrent action spectra (Figure 2), clearly show the responsiveness of the double-dye cell to light absorbed by both the dyes and the two dyes synergistically promote the IPCEs of each other. The IPCEs (~ 28%, 29%) at peak absorption positions (~ 595 nm, 502 nm) of B and A are higher in the double-dye cell and exceed the contributions from the individual dyes (~ 15%, 1%) at the same SC. It is interesting to note that although A is very inefficient in injecting electrons to TiO_2 directly, the excited state in the combination A–B (i.e. A*–B) efficiently sensitizes TiO_2. As expected, the performance of the A–B cell was found to be optimum when the molar SC of the outer dye A is same as that of the inner dye (cation–anion combination requires this stoichiometry). An increase of SC beyond the optimum value drastically reduces the IPCE, undoubtedly because of the intermolecular quenching between excited molecules of A. Again in the cells made from the individual dyes, the optimum IPCEs corresponded to the monolayer dye coverage.

The above observations can be understood on basis of the mechanism explained below. On excitation of an outer dye molecule A (which is a good electron donor), an electron transfers to the inner dye molecule B and then to the conduction band (CB) of TiO_2, i.e.

$$A^*\text{–}B\text{–}TiO_2 \rightarrow A^+\text{–}B^-\text{–}TqiO_2 \rightarrow A^+\text{–}B\text{–}TiO_2(e^-). \quad (1)$$

Similarly, when an inner dye molecule gets excited, an electron transfers from B to CB of TiO_2 and from donor A to the cationic intermediate of B, i.e.

$$A\text{–}B^*\text{–}TiO_2 \rightarrow A\text{–}B^+\text{–}TiO_2(e^-) \rightarrow A^+\text{–}B\text{–}TiO_2(e^-). \quad (2)$$
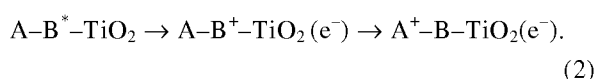
The location of the energy levels of the dye indicated in Figure 1 *b* (determined from cyclic voltammetry and optical absorption data) shows that the above electron transfers are energetically permitted. Both processes (1) and (2) widen the charge separation and the consequent increase of the charge injection efficiency and/or suppression of recombination of the germinate pair increases η and IPCE. Overlapping of the fluorescent and absorption spectra of A with the absorption spectrum of B (Figure 2) facilitates Dexter-type[12] electron transfer from A to B (we
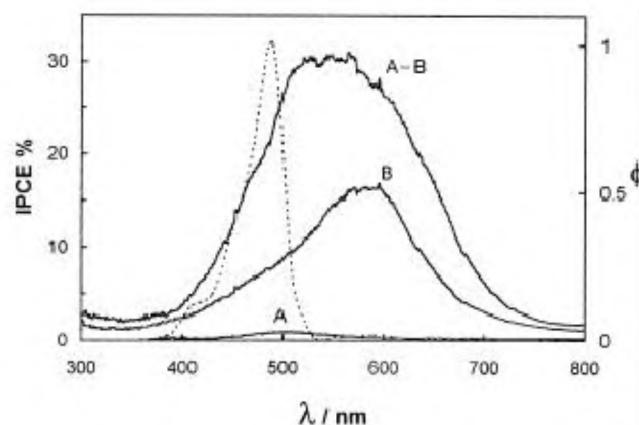

Figure 2. Photocurrent action spectra of PECs made from TiO_2 film coated with: A, acridine orange; B, bromopyrogallol red; and A–B, acridine orange on bromopyrogallol red. (Broken line), Variation of the fluorescent quantum yield ϕ (normalized) of acridine orange (5×10^{-7} M) aqueous solution with the excitation wavelength.

have also noted that the fluorescence of A is quenched by B as expected). The ionic binding of the two dyes provides the close interaction necessary for the electron transfer. The dyes we have selected are not the best sensitizers, but serve to illustrate the strategy of using cationic and anionic dyes with requisite donor–acceptor, spectral and anchoring properties to increase the efficiency of dye-sensitized solar cells. Dyes developed for the sensitization of oxide semiconductors (e.g. Ru-bipyridyl complexes) may be modified to meet the above requirements. The use of two pigments for sensitization of nanocrystalline semiconductor films in the manner we have described, brings dye-sensitized solar cells even closer to natural photosynthesis, where inter-pigment charge and/or energy transfer[13] play a crucial role.

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