

Photoinduced electron transfer in arranged media and on semiconductor surfaces

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Abstract - Photoinduced electron transfer can be achieved in absorptive polymeric coatings and in self-organizing liquid crystalline porphyrins. The efficiency of sensitized photocurrent generation by pendent 10-substituted anthrylethyl derivatives of methacrylate can be related to the photophysical properties of monomeric and dimeric model compounds and to the proximity of approach of nearest-neighbor chromophores. Irradiation of a thin film of liquid crystalline porphyrin sandwiched between indium tin oxide electrodes results in induced asymmetry in the cell and to efficient photocurrent production.

INTRODUCTION

The control of photoinduced electron transfer between donor and acceptors has long been a significant goal of photochemists working in any of several subdisciplines. The basis for the interest in this transformation, eqn 1,



lies in controlling the directionality of the electron transfer, in activating the respective electron rich and electron deficient components, and in accessing an easy route to the radical ions. Important advances toward this objective have been made recently by defining the effect of distance, orbital orientation, solvation, and thermicity of the requisite electron exchange on the forward and backward rates (ref. 1).

An alternate approach is to construct a supramolecular array, Figure 1, in which a physical barrier permeable to electrons, and hence permissive to electron transfer, allows for the physical separation of the donor and acceptor. The radical ions formed via photoinduced electron transfer are then held at spatially distinct sites so that the subsequent dark chemistry of the oxidized and reduced species can be more easily controlled.

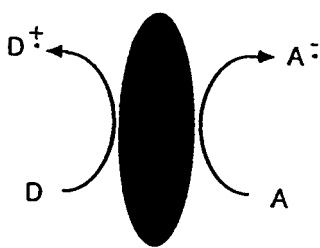


Figure 1. A supramolecular array for spatially controlled photoinduced electron transfer

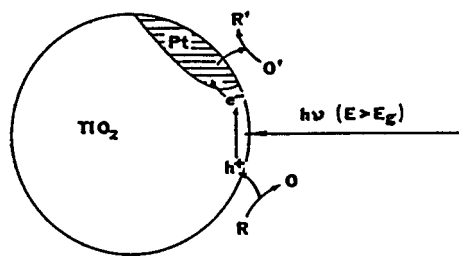


Figure 2. Electron-hole generation on an irradiated semiconductor particle (ref. 2)

One simple method for constructing such a barrier involves the adsorption of donor and acceptor molecules on the surface of a semiconductor particle. Photoexcitation of a semiconductor causes the promotion of an electron from the valence band to the conduction band, where it becomes highly mobile and can migrate to an accumulation (defect) site or to a specifically introduced metal center. The photogenerated electron-hole pair is thus confined to spatially distinct positions where, respectively, reduction and oxidation can occur, Figure 2. The irradiated metallized semiconductor particle can thus be thought of as a microelectrochemical cell (ref. 2).

If oxygen is employed for the reductive half reaction and an organic electron donor participates as the oxidative half reaction, chemical reaction between the components of the radical ion pair can lead to synthetically important oxygenation pathways. A wide variety of functional group transformations have been discovered and mechanisms for their operation have been suggested (ref. 3).

Although transition metal oxide semiconductors are most active and most stable in long term photocatalytic operation, they absorb light efficiently only in the long wavelength

ultraviolet. Their utility could be greatly expanded if their surfaces were modified by attachment of highly absorptive sensitizers whose absorption maxima were shifted to the visible. Indeed, with highly porous semiconductor layers, extremely efficient photosensitization by adsorbed metal complexes has been recently reported (ref. 4). Only monolayer coverage by the sensitizer is effective in this mode, however.

An alternate approach is to configure organic layers through which either electrons or excitons could migrate upon photostimulation. In principle, such polymeric coating would allow for chemical manipulation of the environment at the interface with the semiconductor surface, enhance physical separation of the electron and hole, and provide a vehicle for light collection and sensitization. We discuss here two such coatings for efficient light harvesting and energy migration: (1) a polymer with pendent chromophores, and (2) a self-organized absorptive liquid crystal.

POLYMERIC SENSITIZING COATINGS

Conceptually, excitation of an absorptive polymer layer should be effective in generating an electron-hole pair at the surface of a semiconductor particle to which it is attached if a mechanism exists for efficient migration of either energy or electrons through the layer, Figure 3.

If the monomeric constituents of this layer comprise a chromophore of reasonably high absorptivity, the polymer will be an efficient light harvester since the local concentration, and hence optical density, will be quite high in the film. In practice, this result is difficult to achieve because self-quenching routes and the presence of energy traps or polymer defect sites limit electron or exciton mobility. Relatively little data is available which correlate the efficiency of exciton migration through a polymeric layer with the structure of the pendent chromophore.

We have therefore synthesized poly-(10-substituted anthrylethyl)methacrylates **1** in which the steric bulk of the 10-substituent is varied (X = H, Et, Bu, i-Pr, Ph).

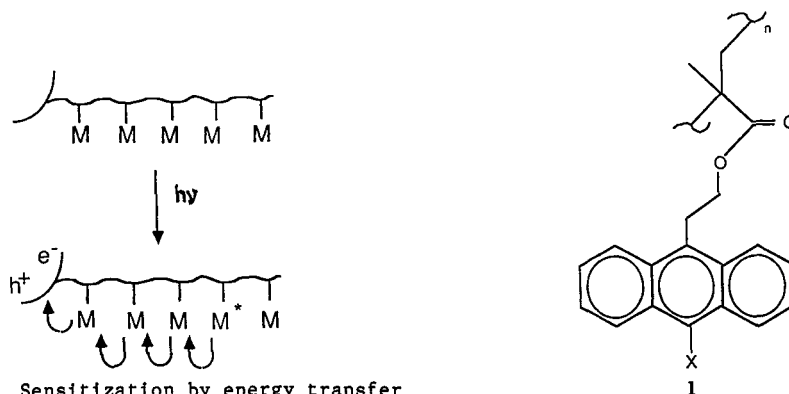


Figure 3. Sensitization by energy transfer through a polymeric coating

The fluorescence spectrum of the ethyl-substituted polymer is characterized by a strong blue-shifted band (ca. 550 nm) attributable to excimer-like interactions between pendent groups. This band is absent in dilute solutions of the pivalate ester of 10-ethylanthryl ethanol, Figure 4 (ref. 5).

Such nearest neighbor interactions can be modeled by comparing the emission spectra of glutarate and pivalate esters of related derivatives, as shown in Figure 5 for the parent anthrylethylesters (ref. 5).

By observing the rate and quantum efficiency for emission for the monomeric and dimeric components of the model systems, it has proved possible to calculate the thermodynamic parameters for intramolecular excimer formation in a series of the model compounds, Table 1.

A comparison of this kinetic analysis with the results of steady state photolysis of the model compounds allows for prediction of the optimal structural parameters for the monomeric unit in a sensitizing polymer layer: sterically blocking groups should allow for sufficiently close approach of neighboring units so that exciton migration can occur, while simultaneously blocking bond formation through dimerization. These predictions can be verified by observing sensitized photocurrent response attainable with the 10-butyl substituted polymer (ref. 6).

A further elaboration of the photochemical and photophysical features which influence sensitization efficiency on polymer-coated semiconductor electrodes in photoelectrochemical cells will be forthcoming.

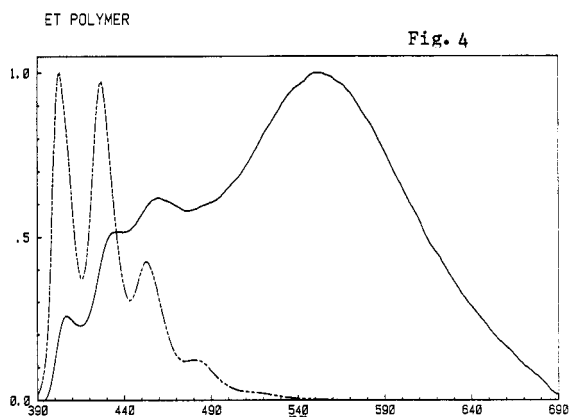


Figure 4. Fluorescence spectra of poly-(10-ethylanthrylethyl)methacrylate (solid line) and its analogous pivalate ester (dotted line) (ref. 5).

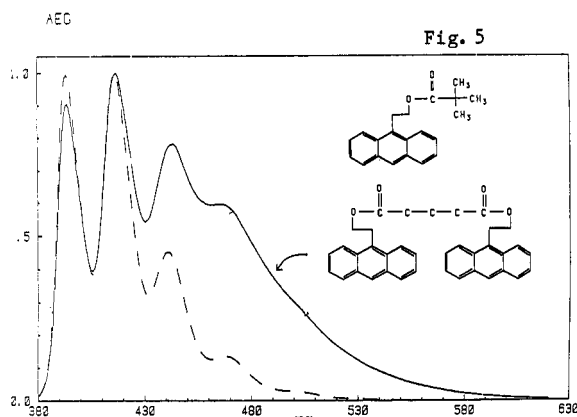
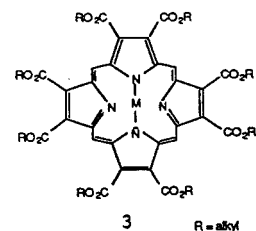
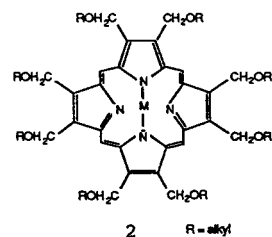


Figure 5. Models for nearest neighbor interactions: anthrylethylglutarate (solid) and anthrylethylpivalate (dashed) (ref. 5).

Table 1. Thermodynamic Parameters for Intramolecular Excimer Formation in Anthrylethylglutarates

R	$M_0-D_H(\text{cm}^{-1})$	E_p (kcal/mole)	ΔH (kcal/mole)	E_p (kcal/mole)	ΔS (cal/mol deg)	K_e (382°C)
H	3809	4.61	-5.19	5.70	-14.7	1.72
Et	3140	6.40	-3.62	5.36	-14.4	0.185
Bu	3125	6.99	-3.30	5.60	-14.3	0.123
IP	1701	3.13	-	-	-	-

(With the bulky phenyl-substituted glutarate, so little excimer emission could be observed that calculation of its physical properties proved to be impossible.)



LIQUID CRYSTALLINE PORPHYRIN PHOTOCELLS

Liquid crystalline discotic mesophases have been proposed as units for the construction of one-dimensional conductors (ref. 7). We have recently synthesized a series of octaether 2 and octaester 3 substituted porphyrins which exhibit reasonably broad liquid crystalline temperature ranges (ref. 8).

Our interest in such materials derives from the simple idea that the partial molecular alignment afforded by the liquid crystalline phase might suffice for the ordering of large area organic materials which might act effectively as a new type of ordered organic semiconductor.

The specific physical properties of a given liquid crystal depend significantly on molecular structure. Greater enthalpy changes are encountered in the transition to the isotropic melt with the esters than with the ethers. Specific phase transition temperatures are sensitive to the length and functional identity of the central metal. Although two liquid crystalline regimes are sometimes observed with the esters, none of the compounds appear to have nematic phases. Both the lack of a phase with a Schlieren texture under a polarizing microscope and the observation that the crystal, on first heating, does not deform until it melts to an isotropic liquid suggest that the liquid crystal is discotic and that the approach to alignment might be best accomplished from careful cooling from the isotropic melt.

Spectroscopic characterization of these compounds indicate that in a film appreciable excitation delocalization occurs and that excitation migration can proceed over long distances (on a molecular scale) (ref. 9). For example, in a film of the zinc octaether 2 containing 4% of the free base, emission is observed almost entirely from the minor component, Figure 6.

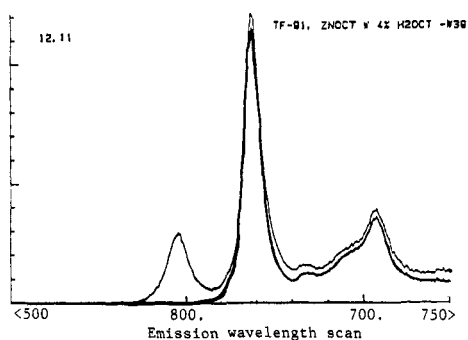


Figure 6. Fluorescence of a Thin Film of 2-Zn containing 4% 2-H₂. Bottom curve represents net emission after subtraction of the emissive component from Zn porphyrin (ref. 9).

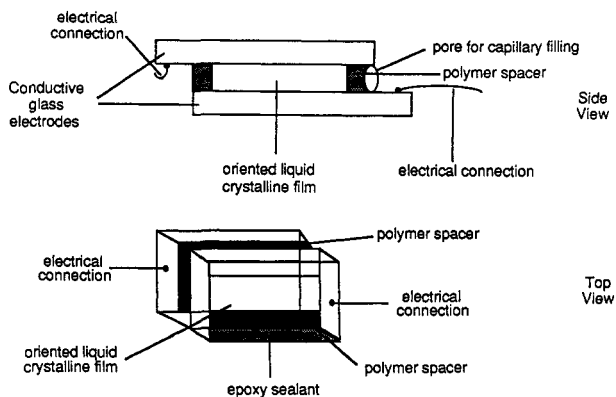


Figure 7. A Solid State Liquid Crystalline Photocell.

In addition, strong fluorescence is observed from the backside of a 40 micron thick film in which light is absorbed in the first 0.4 microns. Spectroscopic evidence for ordering is obvious from the appearance of additional absorption bands and from relative quenching of the Soret and Q bands in the ordered film, when compared with dilute solution samples.

The porphyrins can be capillary-filled into the space between conductive glass electrodes to form a solid state liquid crystalline photocell, Figure 7 (ref. 10).

When the porphyrin has been capillary filled between two sheets of indium tin oxide on glass with a 1-5 micron spacing, it can be cooled through the liquid crystalline phase into the solid state. Upon irradiation, either electrode will act as a photoanode with electrons flowing toward the light. The induced directionality of the cell can be reversed after short irradiation times. The open circuit photovoltage (between 120 and 250 mV) appears to be unaffected by the presence of oxidizing dopants. Both the short circuit current and open circuit voltage have rise and decay times less than 15 msec. The short circuit action spectrum and the fluorescence excitation spectra are identical, showing strong quenching of the Soret band. Under a voltage bias there are only subtle changes in the action and excitation spectra (ref. 10).

The observation of significant photocurrent and photovoltage in a purportedly symmetric sandwich cell was unanticipated and further work delineating its operation and physical optimization is in progress.

CONCLUSIONS

Photoinduced electron transfer through "thick" layers has been observed. Two types of structures have proved to be active: (1) adsorbed polymers constructed from monomeric units bearing a highly absorptive pendent group; and (2) liquid crystalline films spaced between semiconductive glasses. The incorporation of optimal structural features is rewarded with improved photocurrent and photovoltage production. Many unanswered questions remain in the general area of relating molecular structure to macroscopic properties in designed arrays. Continued investigation into the relationship between structure and photophysical characteristics is likely to be a profitable approach.

Acknowledgement

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REFERENCES

1. J.R. Miller, *New J. Chem.* 11, 83 (1987).
2. A.J. Bard, *J. Photochem.* 10, 50 (1979).
3. M.A. Fox, *Top. Curr. Chem.* 142, 72 (1987).
4. N. Vlachopoulos, P. Liska, J. Augustynski, and M. Graetzel, *J. Amer. Chem. Soc.* 110, 1216 (1988).
5. M.A. Fox and P. Britt, *J. Phys. Chem.*, submitted for publication, 1988.
6. M.A. Fox and P. Britt, *J. Electroanal. Chem.*, submitted for publication, 1988.
7. C. Piechocki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, *J. Amer. Chem. Soc.* 104, 5246 (1982).
8. B.A. Gregg, M.A. Fox, and A.J. Bard, *Chem. Commun.* 1134 (1987).
9. B.A. Gregg, M.A. Fox, and A.J. Bard, *J. Phys. Chem.*, submitted for publication, 1988.
10. B.A. Gregg, unpublished observations.