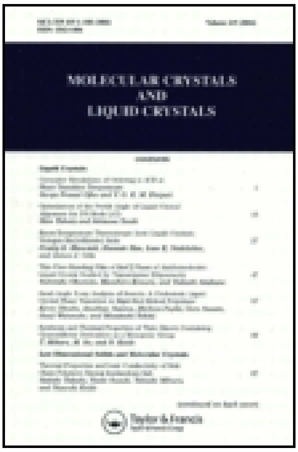

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ASYMMETRIC POLYPORPHYRIN FILMS BY INTERFACIAL POLYMERIZATION

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Abstract Interfacial polymerization of porphyrins derivatized with appropriate reactive functional groups yields thin polymeric films consisting of a network of linked porphyrins. A typical example is the reaction of tetra(p-chlorocarbonylphenyl)porphyrin (TCCPP) in chloroform with tetra(p-hydroxyphenyl)porphyrin (THPP) in aqueous base. The films display a unique chemical asymmetry, in the sense that opposite surfaces of the films show distinctive differences in the concentration and type of unreacted functional groups that are present. When placed between semitransparent electrodes and irradiated with either steady-state broad-band light or a pulsed laser, these films develop directional photopotentials (up to 25 mV), whereby the film surface that was prepared in contact with the TCCPP solution (the acid surface) develops a more negative potential than the opposite surface. We consider the directional photopotentials to be a manifestation of the chemical asymmetry of these interfacial films - that is, photoinduced charge separation involves electron transfer towards the acid surface of the film, which corresponds to the predicted trends of oxidation and reduction potentials of the various porphyrins within the polymer film.

Keywords: Polymer film, porphyrin, interfacial polymerization, asymmetric, artificial photosynthesis

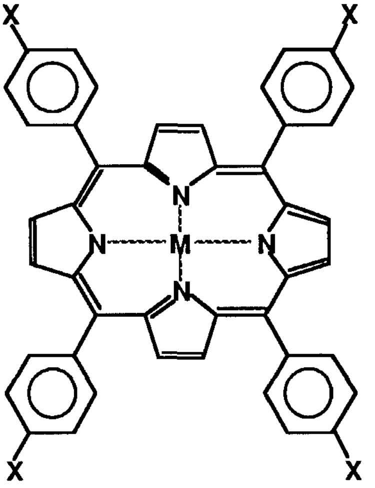
INTRODUCTION

One of the major applications envisioned for photoinduced charge transfer processes is solar energy conversion.[1] Artificial photosynthesis describes the approach that builds upon Nature's strategy for solar energy conversion, generally attempting to mimic the initial light-induced charge separation steps of photosynthesis. In recent years, much has been learned about the early steps in photosynthesis, in particular the importance of the orientation of the various components in directing efficient charge transfer.[2] In addition, impressive synthetic models have been created that display some of the remarkable features of the photosynthetic reaction center.[3] The fundamental requirement for efficient charge transfer is rapid kinetics for the forward electron transfer steps, so that they may effectively eliminate the energy-wasting back reaction steps (charge recombinations). In order to achieve rapid forward reactions, the principal parameters are the energetics, separation distance, and relative orientation of the various groups involved in the electron transfer processes.[4] In some cases, energy transfer processes can also be usefully adjusted to help control the location of the initial charge transfer step, analogous to the light harvesting properties of natural photosynthesis.[5]

Although the most efficient solar devices are still the solid-state devices, a number of molecular systems have made significant strides in modelling the high efficiency of the natural system. Generally, these synthetic systems fall into two categories. Delocalized model systems, such as Langmuir-Blodgett films and multilayers, mimic the basic membrane structure of the photosynthetic reaction center and some of the light harvesting properties.[6] Localized molecular systems involve a collection of photosensitizers and electron transfer relays, either covalently bound together or arranged to be in proximity by means of some organized assembly. The most complex and most efficient such system is currently the "pentad" molecule ($C\text{-}P_1\text{-}P_2\text{-}Q_1\text{-}Q_2$) that links two porphyrins as photosensitizers with two quinones as electron acceptors and a carotenoid as an electron donor.[3a] We consider our work to be an extension of this general approach. We have developed methods for creation of thin polymer films that consist of three-dimensional arrays of porphyrins.[7] The resultant films represent an asymmetric organized assembly because the porphyrins within the film have variable substituent patterns that create a distinctive gradient of redox properties across the film thickness.

INTERFACIAL POLYMERIZATION

The technique of interfacial polymerization involves copolymerization of two reactive monomers contained in immiscible solutions and constrained to react only at the interface of those solutions.[8] The resultant films are typically very thin because the growing interfacial polymer becomes a barrier to diffusion of the two monomers, and the polymerization levels off at a limiting thickness, typically of the order of 1 μm or less. We have adapted this general technique to the preparation of polymeric porphyrin films, where the monomers are typically derivatized tetraphenylporphyrins (Figure 1). One monomer has always been the acid chloride derivative (TCCPP or a metalloporphyrin analog), and a variety of comonomers have been used, including the amino porphyrin or metalloporphyrin derivative (TAPP), the phenolic porphyrin or metalloporphyrin derivative (THPP), and various aliphatic polyamines, such as ethylene diamine (EDA), diethylenetriamine (DETA), or polyethylenimine (PEI). The resultant films are either polyamides or polyesters, and are expected to be highly crosslinked because of the high functionality of the monomers. Film thicknesses are of the order of a few hundred Ångstroms up to several μm, depending on the particular monomers and reaction conditions. The thinnest films arise from copolymerization of two porphyrin monomers, presumably because their diffusion becomes seriously hindered relatively early in the polymerization process.



M = Zn, Cu, Ni, Pd, or 2H

X = -COOH (TCPP)
X = -COCl (TCCPP)
X = -OH (THPP)
X = -NH$_2$ (TAPP)

FIGURE 1. Tetraphenylporphyrin monomers. TXPP is used to represent a free-base porphyrin and MTXPP represents a metalloporphyrin.

EXPERIMENTAL

The procedures for preparation of the interfacial polymeric porphyrin films have been reported.[7] Related metalloporphyrin polymer films were always prepared from metalloporphyrin monomers, although preliminary experiments suggested that at least partial metallation of a finished polymer film could be accomplished. Metalloporphyrin monomers were prepared by metal insertion into the corresponding porphyrin using the metal acetate in refluxing methanol or methanol/DMSO. Cu, Pd, and Ni metalloporphyrins remained metallated after the conversion to acid chloride (conversion of MTCPP to MTCCPP involves refluxing thionyl chloride), while the Zn derivative was demetallated under those reaction conditions.

Photopotential measurements were taken in two fundamentally different ways. Using pulsed laser irradiation (PTI 2300/201 dye laser), the photopotential was fed directly into an oscilloscope (Tektronix 11402, using a 1 MΩ input impedance); typical measurements included rise and fall times and maximum photopotential (usually a few mV). Larger photopotentials were obtained using broad-band irradiation from a continuous light source (150 W Xe lamp, with UV and IR filtered out by a water-filled Pyrex cell); in these cases, the photopotential was monitored by a high-impedance electrometer (Keithley 616). A similar arrangement was used to measure photocurrents. The ITO sandwich cell and the measurement methods have been described in greater detail previously.[7]

STRUCTURAL ASYMMETRY

We have proposed that the interfacial polymerization method inherently leads to structurally asymmetric polymer films, since the two film surfaces ultimately finish their polymerization in the presence of an excess of only one of the two monomers. For example, the film surface formed in the presence of an excess of TCCPP monomer shows an excess of carboxyl groups (the films are washed in aqueous solutions that hydrolyze any unreacted acid chlorides). Thus each interfacial polymer film has two distinct sides, which we typically call the carboxy (C) surface and the amino (N) or hydroxy (H) surface. The differences between these two sides have been characterized by contact angle pH titrations and by XPS surface analyses of metalloporphyrin films made from CuTCCPP and ZnTHPP.[7]

REDOX ASYMMETRY

The structural asymmetry of these films leads to an asymmetry in redox potentials that can be useful for directing charge transport across the film. The films contain porphyrins with a variety of substitution patterns, based on the original type of porphyrin (e.g. TCCPP or TAPP) and based on the number of linkages made (e.g. from one to four amide bonds can be made between TCCPP and TAPP units). We define the various types of porphyrins as X_n, where X represents the original monomer and the subscript represents the number of linkages, e.g. C_3 represents a porphyrin that was originally TCCPP but exists within the polymer film with three bonds to neighboring monomers and one unreacted carboxyl group. Thus a polymer film made from two porphyrin monomers can contain porphyrins substituted with eight different patterns. The effect of substituents on the redox properties of porphyrins has been well-established,[9] and we have demonstrated that the Hammett equation can be used to effectively predict the redox potentials of the monomers used in our studies.[7,10] In an optimum case, the redox potentials of the various porphyrins expected to be found within a typical film generate a relatively smooth potential gradient across the film, as illustrated in Figure 2 for TCCPP and TAPP as the comonomers. For TCCPP and THPP, the calculated gradient is somewhat smaller but in the same direction; for esters, C_1 to C_4 are calculated to be essentially indistinguishable (-0.70 and +1.38 V), while H_1 to H_4 span the ranges from -0.86 to -0.77 V and +1.18 to +1.31 V. For aliphatic polyamines as the comonomer, the only redox asymmetry is that illustrated by C_1 to C_4 in Figure 2 (about 10 mV).

PHOTOPOTENTIALS

Asymmetric photoresponses of the films were determined by measuring photopotentials and photocurrents of the porphyrin polymer films in a symmetrical sandwich cell. The direction of irradiation and the arrangement of the detection system were varied in all of the possible

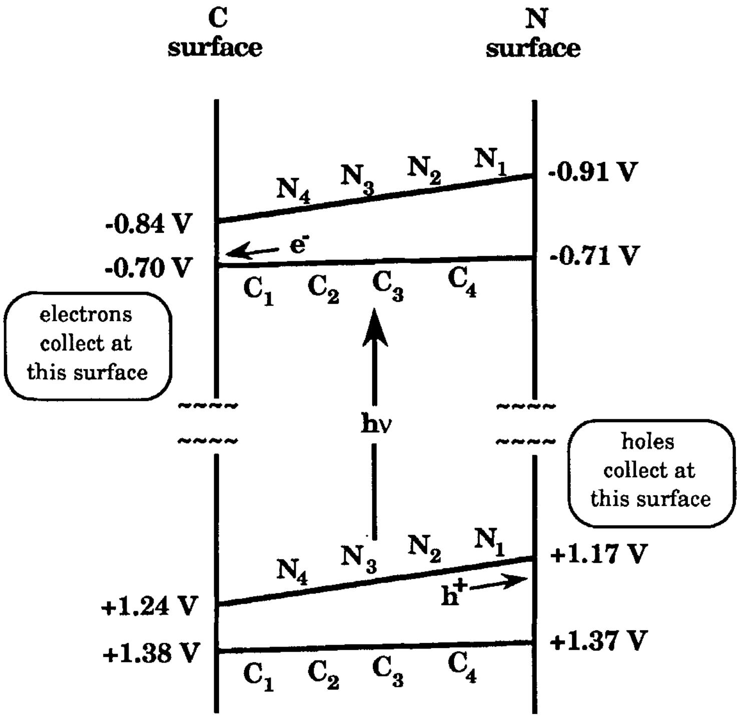


FIGURE 2. Representation of the redox potential gradient predicted based upon the different patterns of porphyrin substituent patterns expected in a TCCPP/TAPP interfacial polymer film.

combinations, as illustrated in Figure 3. The light source was either a pulsed laser or a steady-state broad-band source.

Pulsed laser experiments demonstrate that the photopotential rises very rapidly, generally within 10 nsec after a subnanosecond pulse. A significant portion of the photopotential decays relatively rapidly, within about 1 μsec, while the majority of the photopotential exhibits a very long decay that is limited by the response time of the instrument (about 150-200 μsec for the Tek 11402 when connected to a typical cell). A typical laser photopotential profile is shown in Figure 4, which illustrates the usual features observed, including the rapid rise, partial rapid decay, and the long-lived decay.

Significantly larger photopotentials are observed using broad-band steady-state irradiation, since this allows significantly more light to impinge upon the sample (the laser provides only 0.2 mJ per pulse at 450 nm). The maximum steady-state photopotential is typically 3-4 times larger than that observed in pulsed laser studies. Presumably this represents the cumulation of the long-lived charge separation that is observed to decay slowly after each laser pulse.

Using steady-state irradiation, the effects of light intensity were investigated, as illustrated in Figure 5. The effects rise roughly in

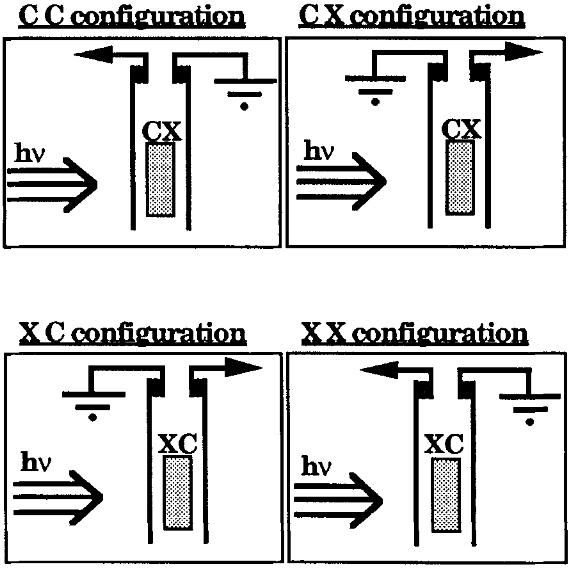


FIGURE 3. Configurations for measurement of asymmetric photoresponses. The first letter represents the film surface towards the light source and the second letter represents the film surface connected to the detection system. C represents the carboxy side (from TCCPP) and X represents the opposite side (N from TAPP or aliphatic amines or H from THPP).

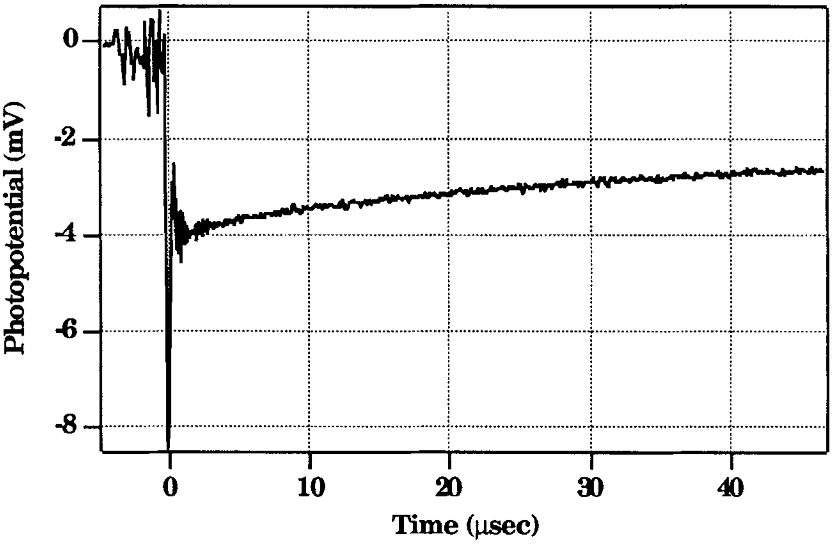


FIGURE 4. Photopotential of a TCCPP/THPP film in the HC configuration after irradiation by a 450 nm laser pulse (<1 nsec).

proportion to light intensity at low levels and eventually begin to level off at higher light intensities. This type of saturation effect is commonly observed for photovoltaic systems.[11]

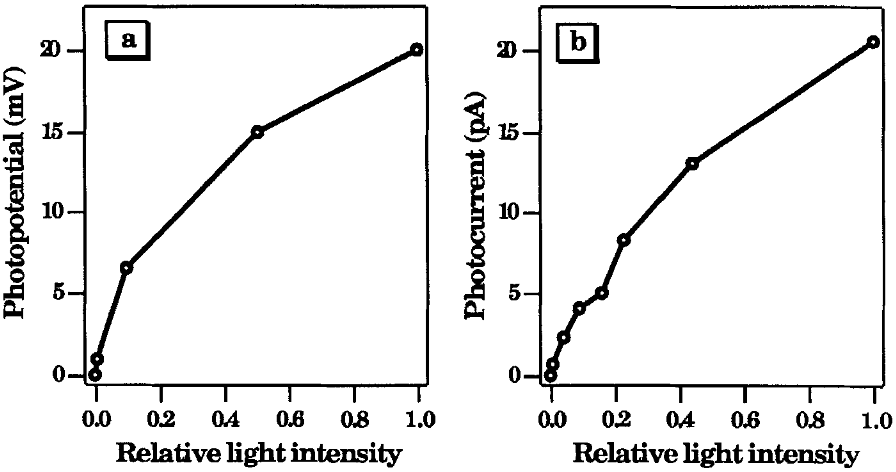


FIGURE 5. (a) Steady-state photopotential of a TCCPP/DETA film under broad-band irradiation; (b) Steady-state photocurrents of a TCCPP/THPP film under monochromatic irradiation at 450 nm.

In the sandwich cells, the films follow Ohm's Law up to at least 2 V, with typical resistance values of 10^{11} to 10^{12} Ω. Since the films are deposited wet onto the electrodes and air-dried in the sandwich cell, electrical contact between the film and the electrodes is far from optimized. Thus, observations of photocurrents are irreproducible from cell to cell at present, and they are generally very low (in the picoampere range).

We have not performed a complete action spectrum for the photopotentials and photocurrents, but approximately comparable effects are observed at all the wavelengths absorbed by the porphyrin films.

A variety of metalloporphyrins were investigated as comonomers for preparation of polymeric porphyrin films. Although the central metal ions have distinctive effects on the redox properties of the porphyrins,[12] no distinctive trends could be detected in the photopotentials from the metalloporphyrin films, and none provided photopotentials significantly larger than were observed for the free-base porphyrin films (Table 1). It is possible that the shorter singlet lifetimes of the metalloporphyrins tend to lower the effectiveness of charge separation in these systems.

Additives to the films can create significant changes in the observed photopotentials. Soaking a TCCPP/DETA film in an aqueous solution of methyl viologen (MV), either before or after depositing it onto the electrodes, leads to a great increase in photopotential (Table 1, entry 10).

TABLE 1. Representative photopotentials from various types of polymeric porphyrin and metalloporphyrin films.

Entry	Comonomers	Light Source	Maximum Photopotential (mV)			
			CC	CH	HC	HH
1	TCCPP/THPP	broad-band		+18	-20	
2	TCCPP/THPP	450 nm laser	-7.0	+7.0	-5.3	+5.3
3	TCCPP/THPP	450 nm laser	-2.4	+2.5	+2.2	-3.0
4	CuTCCPP/THPP	450 nm laser	-3.6	+4.1	-4.5	+4.8
5	TCCPP/ZnTHPP	450 nm laser	-0.7	+0.6	-0.2	+0.2
6	CuTCCPP/ZnTHPP	450 nm laser	-7.8	+6.3	-1.8	+1.3
7	PdTCCPP/THPP	450 nm laser	-0.7	+0.8	-1.4	+0.8
8	PdTCCPP/ZnTHPP	450 nm laser	-0.6	+0.7	-0.3	+0.4
9	TCCPP/DETA	broad-band		+23	-18	
10	TCCPP/DETA/MV	broad-band		+140		

In numerous cases, we observed asymmetric photoresponses that correlated with the direction of irradiation rather than with the side of the film (Table 1, entry 3, is an example). These cases correspond to films that are relatively thick (highly absorbing); for example, entry 3 is a film with $A > 2$ at 450 nm, while typical films have $A < 1$ at the irradiation wavelength. The observation in such cases is that whichever side is towards the light develops a negative photopotential. This effect has been documented in symmetrical photocells of liquid crystal porphyrins.[11a] The root cause is uneven light absorption through the film; since excited porphyrins inject electrons into the electrode, the electrode closer to the light source will develop a significantly greater negative charge. This effect dominates whenever the film thickness is significantly greater than the exciton diffusion length. The most typical TCCPP/THPP films are of the order of a few hundred Ångstroms, and these display the asymmetric photopotentials that reflect the structural asymmetry.

ACKNOWLEDGEMENTS

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