Synthesis and Photoactivity of Chemically Asymmetric Polymeric Porphyrin Films Made by Interfacial Polymerization[†]

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Abstract: Thin polymeric porphyrin films have been prepared by interfacial polymerization of a pair of reactive comonomers, one or both of which are derivatized tetraphenylporphyrins. Combinations that have successfully yielded polymeric films include the following: tetrakis(4-aminophenyl)porphyrin (TAPP) in DMSO with tetrakis[4-(chlorocarbonyl)phenyl]porphyrin (TCCPP) in ethyl acetate, various aliphatic diamines in water with TCCPP in chloroform, various aliphatic diacyl chlorides in hexane with TAPP in DMSO, tetrakis(4-hydroxyphenyl)porphyrin (THPP) in aqueous base with TCCPP in chloroform, and ZnTHPP in aqueous base with CuTCCPP in chloroform. Typical film thicknesses are in the range 0.01–10 μm, depending on the particular monomers, reaction time, and reaction conditions. 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 functional groups that are present, demonstrated by X-ray photoelectron spectroscopy (XPS) and by contact angle studies. This asymmetry is a consequence of the interfacial polymerization method; for example, the surface formed in contact with TAPP solution has an excess of unreacted amine groups, while the surface formed in contact with TCCPP solution has an excess of unreacted acid chloride groups, which become carboxylic acid groups after the usual aqueous workup. When placed between identical semitransparent electrodes and irradiated with either broad-band light or a pulsed laser, these films develop directional photopotentials, whereby the film surface that was prepared in contact with the TCCPP solution (the acid surface) develops a more negative potential than the opposite (amine or hydroxyl) surface. Maximum photopotentials are currently about 25 mV. Films that are optically dense at the irradiation wavelength display photopotentials from a competing hole-injection mechanism; these effects are smaller, but occasionally they prevent the observation of the inherent photopotential asymmetry, which is seen consistently in thinner films. We consider the directionality of the photopotentials to be a manifestation of the chemical asymmetry of these interfacial films—that is, photoinduced charge separation involves electron transfer toward 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.

Photoinduced electron-transfer processes have been investigated extensively from both theoretical and experimental standpoints,[1] as well as with a view toward potential applications for solar energy conversion.[2] Efficient photoinduced electron transfer requires extremely rapid forward reactions to compete effectively with reverse reactions that are usually highly favorable, such as excited-state deactivation or charge recombination. In a typical approach, the forward reactions are driven by a moderate driving force, while the reverse reactions are rendered relatively less favorable initially by the excessively high driving force (the Marcus inverted region) and ultimately by an increasing physical separation of the reactant pair. Many such approaches have been modeled after the operation of the photosynthetic reaction center;[3] carefully constructed model linked donor–acceptor systems have been remarkably successful in imitating photosynthetic charge separation.[4] We report here the synthesis and properties of a novel type of system for photoinduced electron transport, namely thin polymer films of closely linked porphyrin monomers in which the film structure is asymmetric for purposes of directing charge transport.[5]

Thin polymeric films can be prepared by interfacial polymerization, a technique in which reactive comonomers are dissolved in separate immiscible solutions and thereby constrained to react only at the interface between the two solutions.[6] The films are typically very thin because the growing interfacial polymer film becomes a barrier to diffusional encounter of the two monomers; eventually the rate of the polymerization process levels off with a limiting polymer thickness of about 1 μm or less. To provide durability to the fragile films, the interfacial polymerization is frequently carried out at the surface of a microporous substrate, in which case the result is called a thin-film composite membrane.[7]

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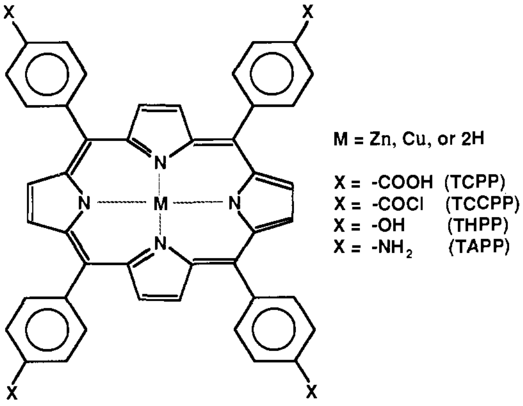

Figure 1. Structures and abbreviations for porphyrins.

We have applied the interfacial polymerization approach to the preparation of thin polymeric porphyrin films using a variety of monomer types, generally including one acid chloride derivative and either an amine or phenol comonomer. The porphyrin monomers and their standard abbreviations are shown in Figure 1.

Experimental Section

Materials. Tetrakis(4-carboxyphenyl)porphyrin (TCPP) was purchased from Porphyrin Products (Logan, UT) and converted to its acid chloride derivative (TCCPP) by refluxing in thionyl chloride (Aldrich Gold Label) followed by complete removal of solvent by distillation and vacuum drying. Tetrakis(4-aminophenyl)porphyrin (TAPP) was either purchased from Mid-Century Chemical (Posen, IL) or prepared by stannous chloride reduction of tetrakis(4-nitrophenyl)porphyrin (TNPP).[8] Tetrakis(4-methoxyphenyl)porphyrin (TMPP) was purchased from Aldrich and demethylated with pyridinium chloride to produce tetrakis(4-hydroxyphenyl)porphyrin (THPP).[9] Metalloporphyrins were prepared by refluxing the porphyrin with the corresponding metal acetate in methanol or methanol/DMSO solution.[10] Celgard 2500, which was used as a microporous substrate for interfacial polymerizations, was donated by Questar Division of Celanese Corp. Celgard 2500 is microporous polypropylene, having a porosity of 45% and stretch pores that are approximately elliptical with dimensions of 40 × 400 nm. The Celgard was cut to an appropriate size and washed with tetrahydrofuran (THF) before use.

Film Preparations. A typical procedure for preparation of a free-floating interfacial film is as follows. A 1 mM solution of TCCPP in chloroform is added to a Petri dish, and an equal volume of 1 mM THPP in pH 11 carbonate buffer is carefully layered on top. After 1–3-h reaction time, the aqueous layer is removed by pipet until the interfacial film breaks and folds over the retreating aqueous solution. A portion of the film is removed with a large spoon and subjected to a series of washes, initially the reaction solvents and ultimately aqueous buffer solutions. The wet film is then deposited onto an appropriate substrate for subsequent analyses, wet with 2-propanol, and allowed to air-dry overnight. The same technique provides polyporphyrin films made from TCCPP and aliphatic polyamines such as ethylenediamine (EDA), diethylenetriamine (DETA), and polyethyleneimine (PEI), although significantly shorter reaction times (several minutes) are sufficient and substantially thicker films result.

In a typical procedure for preparation of a supported polymeric porphyrin membrane, a 1% (w/v) solution of TAPP in DMSO is soaked overnight into a piece of microporous polypropylene (Celgard), after which a 1% (w/v) solution of TCCPP in ethyl acetate containing 1% (v/v) pyridine as catalyst[11] is applied at the top surface of the support. The polymerization is allowed to proceed undisturbed for at least 2 h, after which the composite membrane (i.e., the microporous support plus the polymeric porphyrin film) is thoroughly washed as described above. This procedure creates the polymeric porphyrin film at one surface of the microporous support, such that the exposed surface is the one that had been in contact with the acid chloride (TCCPP) solution during its formation (the carboxyl or C-surface). A slight modification of the procedure allows the opposite surface (the amine or N-surface) to be exposed. In such a case, the TCCPP/pyridine/ethyl acetate solution is first soaked into the microporous support and then laid atop the TAPP/DMSO solution. Experiments that characterize the surfaces of the polymeric porphyrin films, described below, were performed on composite membranes with the appropriate surface exposed.

Electron Microscopy. Scanning electron microscopy was performed with an International Scientific Instruments Model Alpha-9; films were visualized by vacuum sputtering with Au/Pd. Transmission electron microscopy was performed on washed but otherwise untreated film samples with a Hitachi HS-7S instrument and 50-kV electron beam energy.

Contact Angle Studies. Contact angle measurements on TAPP/TCCPP films were performed on films prepared on Celgard as a microporous, hydrophobic support. For comparison of opposite surfaces of these films, nominally identical films were prepared with either the acid or amine side exposed, as described above. For DETA/TCCPP films, free-floating films were prepared, washed, and deposited onto clean Celgard such that either the acid or amine surface was exposed. It was necessary to have a hydrophobic support for the contact angle measurements; if a film was picked up onto glass, the aqueous drop frequently wicked through the film and wet the glass beneath. To keep the Celgard support flat, it was attached to a glass slide with double-stick tape. Contact angle measurements were performed essentially as described by Whitesides and co-workers.[12] A 1-μL drop of aqueous buffer solution was placed on the film surface by syringe, and the contact angle was measured as the angle made by the tangent to the liquid phase at the point of contact. The angle was determined either directly by using a Rame-Hart Model 100 contact angle apparatus or indirectly by photography of the drop and measurement from an enlarged photograph. Typical reproducibility of angle measurements on nominally identical samples was ±5°.

X-ray Photoelectron Spectroscopy. Samples for XPS studies were prepared from ZnTHPP and CuTCCPP monomers so that the different metals would serve as markers for the different porphyrin monomers. Free-floating interfacial films were prepared and washed thoroughly as described above and then deposited onto either a glass or Celgard support such that either the acid surface or the hydroxy surface was exposed. XPS experiments were performed with a Perkin-Elmer PHI 560 system using Kα X-rays from either a Mg anode (X-ray energy 1253.6 eV) or an Al anode (1486.6 eV) and a constant pass energy of either 25 or 50 V. Integrated areas were determined for several characteristic atomic photolines and converted to atomic ratios by standard atomic sensitivity factors for each element and orbital[13] [element (orbital), binding energy, atomic sensitivity factor]: Zn ($2p_{3/2}$), 1023 eV, 4.8; Cu ($2p_{3/2}$), 936, 946 eV, 4.2; N (1s), 400 eV, 0.42; Zn (3p), 90 eV, 0.75; Cu (3p), 78 eV, 0.65. There was no correction for differing escape depths for emissions from different elements. However, comparisons were always made with photolines of comparable binding energy in order to minimize the influences of surface contamination or nonuniform elemental distribution on the observed metal atom ratios.

Atomic Absorption Spectroscopy. A sample of ZnTHPP/CuTCCPP film from the same preparation as the XPS studies (Table I, film A) was dissolved completely in 1 M nitric acid at 60 °C, filtered, and the atomic ratio of Zn to Cu was determined by atomic absorption spectrophotometry. The instrument was a Perkin-Elmer Model 305B, and the observed elemental ratio was calculated by adding standard additions with known amounts of Zn and Cu to the original sample.

Irradiation Studies. Photoactivities of the polymeric porphyrin films were measured in a dry sandwich cell consisting of two identical transparent or semitransparent electrodes. The active area of the electrodes was a square 5 mm on a side, and the material was either indium tin oxide (100 Ω/square) on glass, inscribed in an L-shape to overlap only the active areas on opposite electrodes, or semitransparent 5-mm strips of evaporated Au/Pd, crossed on opposite electrodes. A piece of freshly prepared and washed film greater than the active area was placed on one electrode, and the second electrode was clamped on top of it. The film was generally allowed to dry under ambient conditions for 2 days, but no significant differences were noted if it was dried in a vacuum desiccator for 5 min. Only rarely were the cells short-circuited, which could be easily detected by measuring the resistance between the two electrodes, which was ordinarily very high (>10 MΩ). Photopotentials and photocurrents were measured with a Keithley 616 electrometer, a Tektronix 11402 digital oscilloscope, or a custom-designed high-impedance voltage

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follower. Steady-state irradiation was with a 150-W light source, either xenon or quartz–halogen. Pulsed irradiation was with a PTI 2300 nitrogen laser (337 nm, 1.4 mJ/pulse, pulse width at half-height 0.6 ns), a PTI 201 dye laser (450 nm, 0.2 mJ, 0.5 ns), or a Phase-R dye laser (650 nm, 150 mJ, 400 ns). The films were irradiated in each of the possible orientations with respect to the direction of the light and the connection of the electrical probes. The four combinations are abbreviated with two-letter codes, where the first letter indicates the surface facing the light and the second letter indicates the electrode probed by the detection system (with the other electrode grounded); e.g., CC indicates that the acid surface of the film was facing the irradiation source and the electrodes were connected such that the electrode next to the acid surface was connected to the oscilloscope and the electrode next to the opposite (amine or hydroxyl) surface was grounded.

Electrical and Electrochemical Studies. A typical DETA/TCCPP film in a photopotential sandwich cell was observed to follow Ohm's law, with a resistance greater than 10^{11} Ω. Electrical or electrochemical properties of polyporphyrin films in contact with aqueous solution were particularly difficult to evaluate because the films always displayed extremely low electrical resistance under such circumstances. A TAPP/TCCPP film supported on Celgard was clamped in a standard two-compartment membrane cell between two aqueous solutions. The electrical resistance of the cell with the membrane present was always indistinguishable from the resistance in the absence of the membrane. In the most sensitive experiment, Ag/AgCl electrodes were placed within 2 cm of each side of the membrane in a 1.0 M KCl solution in 30% aqueous ethylene glycol. Ohm's law plots gave identical resistance values of 35 ± 1 Ω with and without a membrane present on the support.

Results

Synthesis and Thickness of Polyporphyrin Films. We have demonstrated that the technique of interfacial polymerization can be used to prepare thin polymeric films built from porphyrins as monomers. The polyporphyrin films may be prepared either as free-floating interfacial films or on microporous supports in the standard manner for thin-film composite membranes. The polymerization reactions investigated so far are either between amines and acid chlorides, forming polyamides, or between phenols and acid chlorides, forming polyesters. The derivatized porphyrin monomers are all tetrasubstituted with reactive functional groups so the polymers are expected to be highly cross-linked network polymers. The fastest reactions (requiring only minutes) and the thickest films (0.1–10 μm, depending on reaction time) arise with the use of aqueous aliphatic polyamines. Films made from two porphyrin monomers form more slowly, typically requiring hours, and have much thinner limiting thicknesses (0.01–0.1 μm). The difference is apparently caused by the ability of the small aliphatic monomers to continue diffusing through the growing polymer film much longer than the bulky porphyrin monomers. This is consistent with the normal view of the mechanism of interfacial polymerization, in which the polymer growth primarily takes place in the organic phase, rather than in the aqueous phase.[6]

The visual appearance of the polymeric porphyrin films varies from pale yellow to red-purple depending on thickness, which is a function of the specific monomers used and the reaction time. The visible absorption spectra are similar to those of the original porphyrin monomers but significantly broadened and somewhat red-shifted at the Soret (B) band, indicating aggregation of the porphyrin units.[14] The observed absorbance of a film can be correlated with an approximate thickness, assuming that the density of the porphyrin polymer is about 1 g/cm^3 and the extinction coefficients of the visible (Q) bands are comparable to those of the porphyrin monomers. For many of the films, confirming values of thickness were obtained by weighing films of known area, assuming the same density, and by scanning and transmission electron microscopy. Besides revealing the approximate film thicknesses (Figure 2A,B), the electron micrographs illustrate that the films have different textures on opposite surfaces (Figure 2C,D).

Characterization of Surface Asymmetry by XPS. Opposite surfaces of polymeric metalloporphyrin films (from ZnTHPP and CuTCCPP) were characterized by X-ray photoelectron spectroscopy (XPS). The data shown in Table I reveal distinctly different ratios of Zn and Cu, depending upon whether the surface exposed is the one that had been prepared in contact with ZnTHPP monomer solution or CuTCCPP monomer solution. For one film (film A) that was studied on both sides, the Zn/Cu ratio varied from 1.3 (on the ZnTHPP side) to 0.4 (on the CuTCCPP side). The bulk ratio of Zn/Cu in this film was measured by atomic absorption spectrophotometry to be 0.7, indicating that both surfaces differ from the bulk distribution. The specific Zn/Cu ratios show significant variations even for nominally identical films; for example, films B and C show significantly greater surface asymmetries than film A.

Table I. Atomic Ratios Determined by XPS for ZnTHPP/CuTCCPP Films[a]

sample	anode	Zn/Cu ratio		N 1s/ (Zn + Cu)[b]
		$2p_{3/2}$ lines	3p lines	
ZnTHPP monomer	Mg			3.3 (4.3)
CuTCCPP monomer	Mg			2.9 (6.3)
polyporphyrin film A				
ZnTHPP side	Mg	0.86	1.34	2.6 (3.6)
	Al	1.09	1.10	2.4 (2.6)
CuTCCPP side	Mg	0.42	0.67	2.1 (3.0)
	Al	0.41	0.57	1.9 (2.1)
polyporphyrin film B				
ZnTHPP side	Mg	6.76	4.66	2.7 (3.3)
	Al	5.04	4.44	2.5 (2.7)
polyporphyrin film C				
CuTCCPP side	Mg	0.07	<0.05	3.3 (4.4)
	Al	0.11	0.09	2.9 (2.9)

[a] Films A–C were prepared separately but under nominally identical conditions, as described in the Experimental Section for free-floating films. Films A and B were deposited onto glass, and film C was deposited onto Celgard. [b] Ratio of N 1s to total Cu + Zn, where the first value represents the metal $2p_{3/2}$ lines and the parenthetical value represents the 3p lines.

Some of the variations in Table I are systematic, reflecting expected differences of escape depths for photoelectrons from different orbitals ejected by different X-ray energies. For example, the 3p lines generally show less asymmetry than the $2p_{3/2}$ lines; electrons ejected from 3p orbitals have significantly greater kinetic energy (lower binding energy) and represent a greater sampling depth within the film. A simple calculation for escape depth as a function of kinetic energy[15] predicts escape depths of 1.7 and 1.9 nm for the Zn and Cu $2p_{3/2}$ lines, respectively, and 3.8 nm for the Zn or Cu 3p lines (Mg X-rays). Similarly, less asymmetry is typically observed when the X-rays are from the Al anode; since the X-rays are of higher energy, electrons are ejected with higher kinetic energy. The corresponding escape depth calculations are 2.4 and 2.6 nm for Zn and Cu $2p_{3/2}$ lines and 4.1 nm for the Zn and Cu 3p lines. The trend therefore indicates that there is a surface asymmetry and the extent of asymmetry becomes less as increasing depths of the film are sampled. It is important to note that the escape depths are comparable for Zn and Cu, since we only compare lines from their corresponding orbitals, so that escape depth differences could not be an artificial cause of the apparent asymmetry. We are pursuing further experiments that could lead to a more complete depth profiling of these films.

Ratios of nitrogen to the sum of the metals are also shown in Table I. Since every metal should be complexed to a porphyrin and there should be no other sources of metal or nitrogen in these films, the ratios should be 4/1 uniformly. The values are typically lower than 4, either because the atomic sensitivity factors are not appropriate for porphyrins (similar ratios are observed with the porphyrin monomers) or because there is slow decomposition of the organic material during the experiment, with loss of nitrogen faster than loss of metals. The latter explanation is supported by the observation that higher ratios are observed for the 3p lines, which represent sampling of a greater escape depth. Furthermore, a more rapid loss of nitrogen (relative to the metals) was observed when the original monomers (ZnTHPP and CuTCCPP) were

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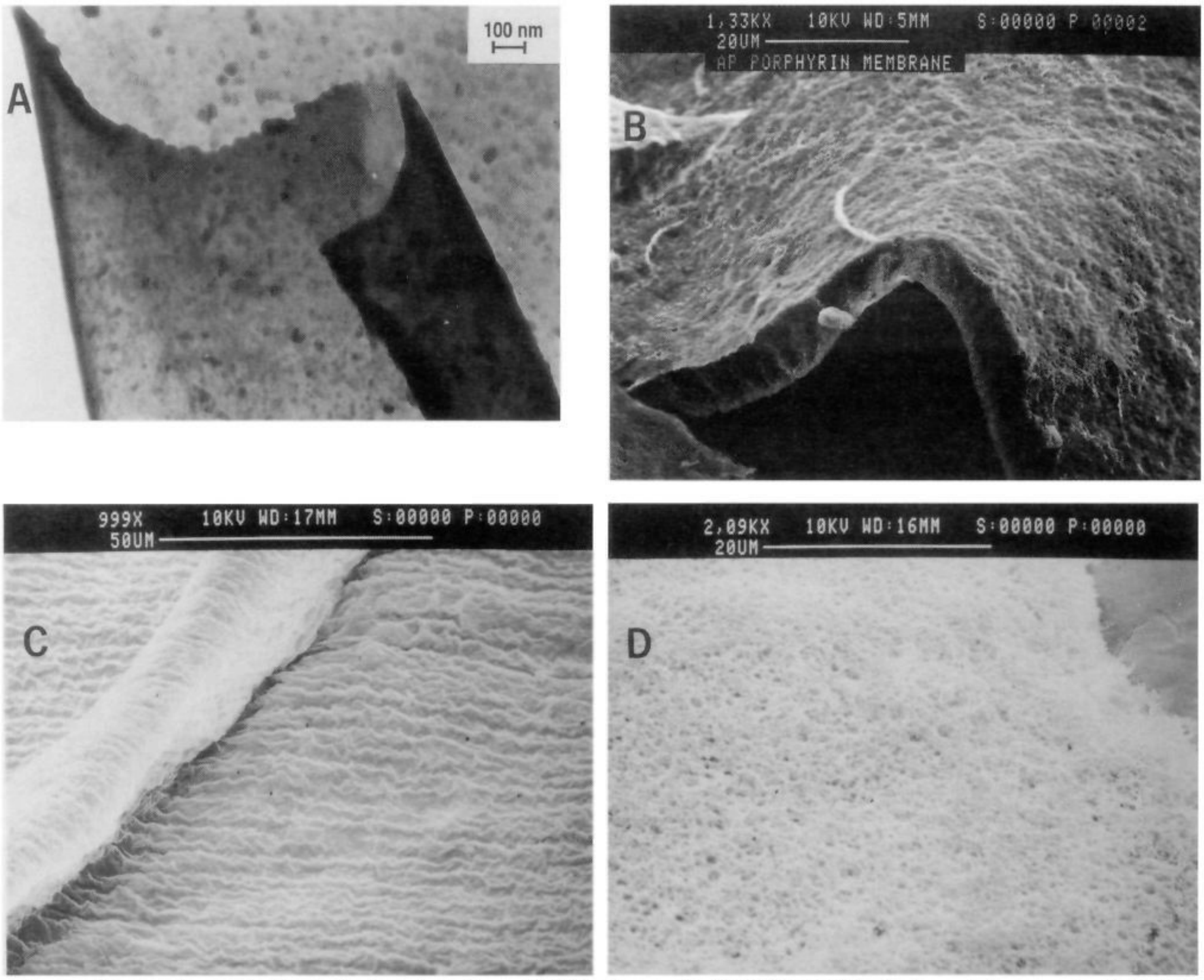

Figure 2. Electron micrographs of typical polyporphyrin films: (A) TEM of a very thin THPP/TCCPP film that has curled over onto itself; (B) SEM of a thick DETA/TCCPP film with a fold that exposes a cross section; (C) SEM of the N-surface of a DETA/TCCPP film; (D) SEM of the C-surface of a DETA/TCCPP film.

subjected to extended irradiation (400 min, as compared to 30 min for a typical analytical run). Escape depth calculated for the N 1s line is 3.2 nm (Mg X-rays) or 3.6 nm (Al X-rays), which is between the values for the metal $2p_{3/2}$ and 3p lines.

Characterization of Surface Asymmetry by Contact Angle pH Titrations. Opposite surfaces of the polymeric porphyrin films were also characterized by measurements of the contact angles between the surfaces and aqueous buffer solutions of various pH values (Figure 3). The measured contact angles trace the relative hydrophilicity of the membrane surface, which is affected by the state of ionization of the functional groups present at the surface, called contact angle titration.[12] Aqueous titrations of model monomer porphyrins indicate that the solution pK_a values for the carboxylic acid groups of TCPP lie in the range pH 5–7 and that the amine groups of TAPP protonate in the range pH 1–3; the central nitrogens of the porphyrin rings also protonate at about pH 1, which is detectable by a distinctive color change from purple to green. The contact angle measurements show that the polypropylene support material (Celgard) is hydrophobic (high contact angle) but becomes distinctly more hydrophilic when a polymeric porphyrin film is present. When the N-surface is exposed to the aqueous buffer, little change in contact angle is observed as a function of pH, except at pH 1, where the porphyrin ring protonates (the film turns green where the acid drop contacts it). The C-surface, on the other hand, reflects a distinct change in contact angle both at low pH, where the porphyrin ring protonates, and at high pH, where the carboxylic acid groups deprotonate.

Photochemical Asymmetry. Upon laser irradiation, the polyporphyrin films display photopotentials that are distinctly directional (Table II). The photopotentials are relatively small, up to 25 mV on broad-band, steady-state irradiation and up to 7 mV on pulsed laser irradiation. The general pattern is that the C-surface develops a more negative charge while the opposite surface (the N- or H-surface) develops a more positive charge. In two of the cases cited in Table II the films give inconsistent results in the XC and XX configurations; an explanation is offered in the Discussion.

The rise times of the photopotentials are very rapid, less than 10 ns after a subnanosecond pulse. Upon steady-state irradiation, the observed photopotentials rise to a saturation level,[16] which are the values indicated in Table II. Decay times for both laser and steady-state irradiation generally approximate the RC time constant of the detection system.

Under short-circuit conditions, small photocurrents have been observed (up to 2 pA), which follow the same directional pattern as the photopotentials. Work is in progress to optimize the photopotentials and photocurrents by developing better ohmic contacts between the films and electrodes.

In contact with electrolyte solution, these polymeric films are highly permeable to ions, with an apparent resistance of less than

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Table II. Photopotentials from Polyporphyrin Films

			confign,[a] max potential (mV)			
entry	film (thickness,[b] μm)	irrad source	CC	CX	XC	XX
1	THPP/TCCPP (0.01)	broad-band		+18	−20	
2	THPP/TCCPP (0.01)	450-nm laser	−7.0	+7.0	−5.3	+5.3
3	THPP/TCCPP (0.1)	450-nm laser	−2.4	+2.5	+2.2	−3.0
4	DETA/TCCPP (1)	broad-band		+23	−18	
5	DETA/TCCPP (1)	337-nm laser	−2.5	+2.5	+3.0	−3.0
6	TAPP/TCCPP[c] (0.1)	648-nm laser	−1.4	+0.9	−0.7	+0.7

[a] The two-letter abbreviation indicates (1) the surface facing the light source and (2) the electrode connected to the detection system (with the opposite electrode grounded). C represents the acid (TCCPP) side of the film and X represents the opposite (amine or hydroxyl) side. [b] Order of magnitude thickness estimated from the visible absorption intensity. [c] All films were prepared as free-floating films, except TAPP/TCCPP films, which were on Celgard supports, a necessity of their preparation. The support gave a consistent blank of −0.5 mV, which was subtracted from the observed photopotentials to give the listed values. No other samples gave significant blanks.

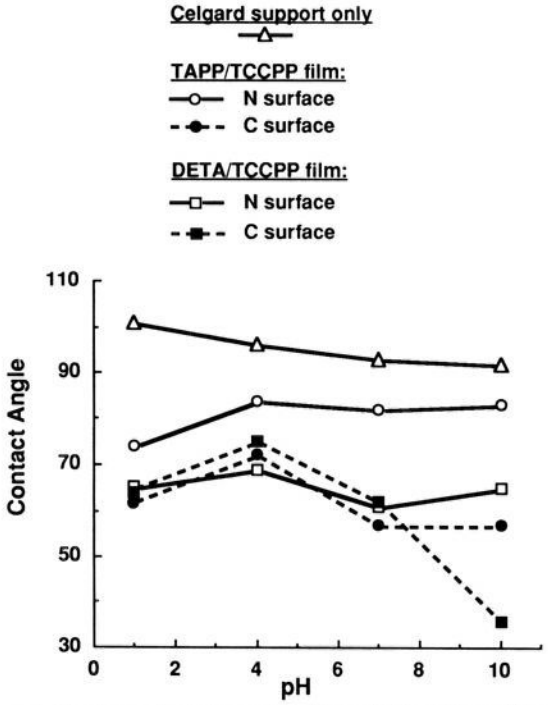

Figure 3. Contact angles between the surfaces of polyporphyrin films and aqueous buffer solutions of various pH values. Films were cast on Celgard 2500, a microporous polypropylene support.

5 Ω. Nevertheless, they are capable of heterogeneous photosensitization of the reduction of viologens in the presence of sacrificial donors such as EDTA. Development of solution-phase photochemistry of these membranes is also in progress.

Discussion

We believe the results described above represent the first documentation of chemical asymmetry in a polymer film or membrane in which the asymmetry is generated during the polymerization process. Membranes normally referred to as "asymmetric" are typically asymmetric in their physical structure or morphology, or the membranes are subjected to some type of posttreatment that renders them asymmetric.[7] Enkelmann and Wegner have used interfacial polymerization to create an asymmetric polyamide membrane, but the asymmetry was induced by the replacement of one monomer by another during the interfacial polymerization process.[17] Although Enkelmann and Wegner describe the general concept of end-group asymmetry in interfacial polymer films, the presence of asymmetry could only be inferred from transport experiments.

The source of the functional group asymmetry is readily visualized from a description of the interfacial polymerization process.

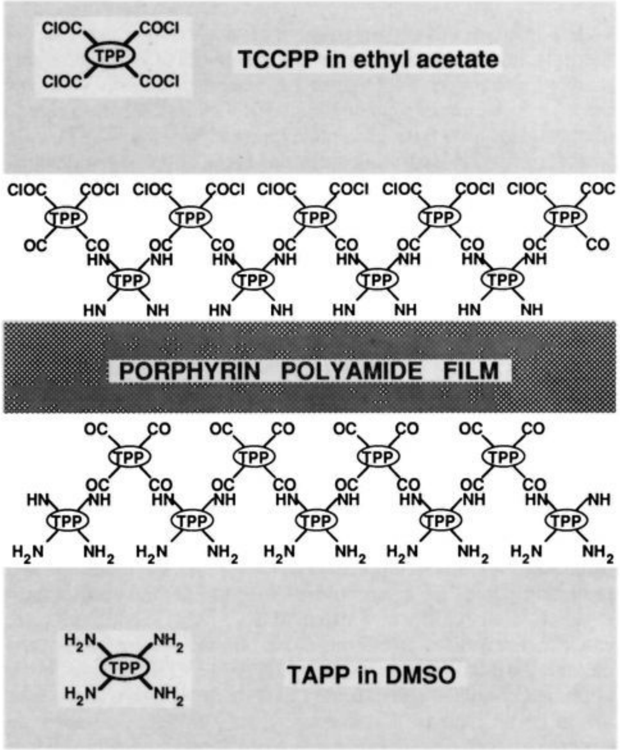

Figure 4. Idealized structure for an asymmetric polyamide porphyrin film made from TAPP/TCCPP by interfacial polymerization. (TPP represents tetraphenylporphyrin.)

Each of the two monomers approaches the polymerization reaction at the interface from different directions because of their confinement (at least initially) to separate immiscible solutions. The growing polymer film creates a barrier at the interface that gradually slows the reaction between the two monomers. As the polymerization reaction subsides, each surface of the polymer film is in contact with a different monomer solution so that any unreacted functional groups on the polymer surfaces are terminated by the monomer in excess at that time. In our example of amine and acid chloride substituted porphyrins, the surface in contact with the amine solution will have mainly unreacted amine groups (the N-surface) and the opposite surface will have mainly unreacted acid chloride groups (the C-surface). Figure 4 presents an idealized picture of the polymer structure, illustrating the surface functional group asymmetry. It is important to note that this type of asymmetry should be very slight in most of the common examples of interfacial polymerization where both monomers are difunctional and the polymerization leads to high polymers. In such cases, the relative concentration of unreacted functional groups is very small, limited to end groups at the termini of long polymer chains. With tetrafunctional monomers, high concentrations of functional groups may remain unreacted, and this can lead to a high degree of functional group asymmetry.

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Table III. Calculated and Measured Redox Potentials of Various Substituted Tetraphenylporphyrins

		calculated[a]		experimental[b]	
substituent[c]	abbrev	*E*(redn)	*E*(oxidn)	*E*(redn)	*E*(oxidn)
COOH	TCPP	−0.70	+1.38	−0.77	+1.36
CONHR	$\mathbf{C}_4$	−0.71	+1.37	−0.74	+1.40
COOR	$\mathbf{C'}_4$	−0.70	+1.38	−0.69	+1.38
NH_2	TAPP	−0.93	+1.15	−0.94	+0.73
NHCOR	$\mathbf{N}_4$	−0.84	+1.24	−0.86[d]	
OH	THPP	−0.88	+1.20	−0.89	+0.99
OOCR	$\mathbf{H}_4$	−0.77	+1.31		

[a] Volts vs NHE, based on Hammett correlations: $E(\text{oxidn}) = +1.28 + 0.055\ (4\sigma)$; $E(\text{redn}) = -0.80 + 0.055\ (4\sigma)$. [b] Volts vs NHE, measured in DMSO solution.[18d] [c] Substituents are at all four para positions; σ constants are taken from ref 18e. [d] Reference 18b.

A second level of asymmetry can be visualized on the basis of the patterns of substituents found on the porphyrin monomers within the polymer. Each porphyrin monomer, initially with four reactive functional groups, will succeed in making from one to four covalent links with its comonomer. Thus, a DETA/TCCPP film may contain up to four different types of porphyrin, having one to four amide bonds and the remainder carboxylic acid groups from hydrolysis of unreacted acid chlorides. We abbreviate these as $\mathbf{C}_n$, where **C** represents a porphyrin that was originally TCCPP and *n* represents the number of amide linkages. Similarly, **N** is used to represent the aminoporphyrin TAPP, and **H** is used to represent the hydroxyporphyrin THPP. A TAPP/TCCPP film may contain up to eight kinds of porphyrins: $\mathbf{N}_1$–$\mathbf{N}_4$ and $\mathbf{C}_1$–$\mathbf{C}_4$. Similarly, a THPP/TCCPP film could include $\mathbf{H}_1$–$\mathbf{H}_4$ and $\mathbf{C'}_1$–$\mathbf{C'}_4$ porphyrin types, where $\mathbf{C'}_n$ represents TCCPP with *n* ester linkages.

The variously substituted porphyrins have different oxidation and reduction potentials that are predictable based on Hammett correlation.[18] Calculated and experimental values for some of the patterns of interest are shown in Table III. The data show that transformation of the carboxyl derivatives to their corresponding amides or esters results in only small differences in the oxidation and reduction potentials. In contrast, the oxidation and reduction potentials of porphyrins with amine or hydroxyl substituents are significantly affected when the substituents are converted to amides or esters. Table III also illustrates that the measured oxidation potentials for TAPP and THPP do not fit the Hammett correlation well, being much more readily oxidized than would be predicted. These porphyrins have been observed to undergo oxidative electropolymerization[19] and apparently undergo a different oxidation mechanism than the other porphyrins.

The various porphyrins are also expected to show differences in their relative concentrations and locations within the polymeric film: there are higher local concentrations of a porphyrin type near the surface formed in the presence of an excess of that monomer, for example, more N-type porphyrins near the surface in contact with the TAPP monomer solution (the N-surface). In addition to this concentration gradient, there is also a gradient of substitution patterns. Because each amide linkage necessarily connects porphyrins of opposite type, wherever N-type porphyrins predominate over C-type porphyrins the relative degree of substitution (number of amide bonds, *n*) of the N-type porphyrins will be lower than the degree of substitution of the C-types. Together with the redox potential differences of the different substitution patterns, these concentration gradients are predicted to generate a redox potential gradient across the membrane, illustrated in Figure 5.

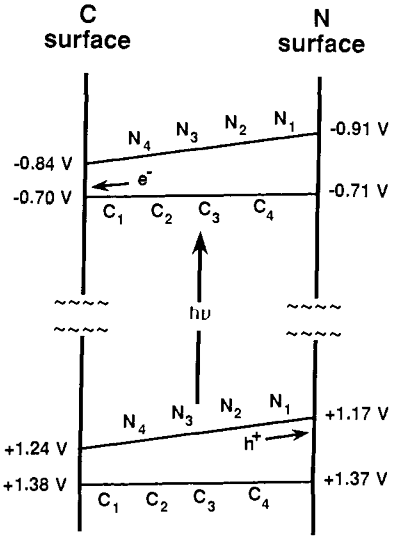

Figure 5. Schematic description of the porphyrin substitution patterns predicted within a TAPP/TCCPP film, their relative oxidation and reduction potentials, and the development of a photopotential by directional charge separation across the film. $\mathbf{C}_n$ represents a tetraphenylporphyrin with *n* amide linkages and 4 − *n* carboxyl groups. $\mathbf{N}_n$ represents a tetraphenylporphyrin with *n* amide linkages and 4 − *n* amino groups.

The photopotentials observed from the polymeric porphyrin films show a directionality that generally fits the predicted redox potential gradient across the membrane. This is in keeping with the relative redox potentials of the substituted tetraphenylporphyrins as shown in Table III and Figure 5; that is, electrons will have a tendency to be transferred toward the C-side of a film and holes will have a tendency to be transferred toward the opposite side of the film.

Photovoltaic effects in porphyrin films have been noted in numerous reports, including monolayers,[20] bilayer membranes,[21] derivatized semiconductor electrodes,[22] and vacuum-deposited or spin-coated thin solid films.[23] Although our photopotentials are not large, our results offer the first evidence for asymmetric photopotentials arising from asymmetric polymeric porphyrin films. Since there is no external bias applied to the films, these films thus represent the equivalent of an organic polymer semiconductor.

Under pulsed laser irradiation, the films develop transient photopotentials that are smaller than under broad-band irradiation, presumably because there are fewer total photons impinging on the sample in the pulsed laser experiments. Furthermore, the pulsed laser results do not always correlate with the predicted film asymmetry. Thinner films (Table II, entries 2 and 6) show the same correlation as the broad-band irradiations (entries 1 and 4), while thicker films (entries 3 and 5) give a relatively negative potential on whichever surface is toward the irradiation source. The latter observation has been noted before[24] and interpreted with the concept that the excited porphyrins within the immediate vicinity of an electrode (determined by the exciton diffusion length) transfer electrons to the electrode (or equivalently, undergo hole injection from the electrode), a typical phenomenon for a p-type

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J. Am. Chem. Soc. **1989**, *111*, 8491–8493

semiconductor.[23] Excited porphyrins more distant from an electrode (in the bulk phase) are considered to act as charge carriers that simply lower the film resistance.[24a] In contrast, we consider that the bulk of our polyporphyrin films includes a redox potential gradient that contributes significantly to the observed photopotential.

Thus, we believe that there are at least two competing mechanisms for generation of photopotentials in our polyporphyrin films: (1) an electrode hole-injection mechanism, which is expected to be particularly important for films with a nonuniform distribution of excited states—that is, where the optical penetration depth is significantly less than the total film thickness, such as thick films irradiated at a wavelength of high absorptivity (e.g. near the Soret band); and (2) a bulk charge-separation mechanism based on an inherent asymmetry of the polymer structure, which can be most readily observed when the excitation is relatively uniformly distributed across the film, such as with thin films or films irradiated with broad-band light.

Conclusions. Polymeric thin films can be made from porphyrin monomers by the technique of interfacial polymerization. The method leads to a novel structural asymmetry in that opposite surfaces of the films have different concentrations of unreacted functional groups. The surface asymmetry was demonstrated by XPS studies of metalloporphyrin films and by contact angle titrations with aqueous buffers. The films also display a photochemical asymmetry in that irradiation leads to directional charge separation across the film, specifically involving transfer of electrons toward the acid-rich surface of the film. The directionality is consistent with the proposed asymmetric structure of the polymer film, since the redox potentials of the substituted porphyrins become more positive toward the acid side of the film.

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Reaction of Photochemically Generated Dibromocarbene with 1,2-Dimethylenecycloalkanes. 1,4 Addition Is Real[1]

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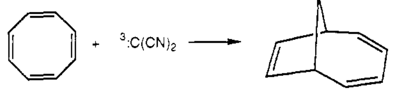
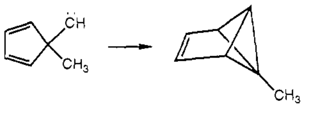
Abstract: Photochemically or thermally generated dibromocarbene adds to a variety of 1,2-dimethylenecycloalkanes and to norbornadiene to give both 1,2 and 1,4 addition products. The ratios of the products of the two addition types match those found from dibromocarbene generated from bromoform. Dibromocarbene is capable of 1,4 addition.

The reactions of carbenes with all manner of 1,3-dienes have been examined over the years in attempts to find 1,4 addition.[2] Despite this attention, only one intermolecular example has survived further scrutiny. This is the reaction of triplet dicyanocarbene with cyclooctatetraene to give, along with the product of 1,2 addition, 8,8-dicyanobicyclo[4.2.1]nona-2,4,6-triene.[3] It has been suggested[4] that this unique case depends upon the presence of *both* the cyclooctatetraene and the cyano groups. Certainly it is not general; dicarbomethoxycarbene gives only 1,2 addition to cyclooctatetraene,[2] and dicyanocarbene does not add in 1,4 fashion to other dienes. An exquisite labeling study from the laboratory of U. Burger revealed an intramolecular example of 1,4 addition in the reaction of cyclopentadienylcarbene to form benzvalene.[5]





One may legitimately wonder why this symmetry-allowed reaction appears so rarely. It has been suggested that the favorable HOMO–LUMO interaction between π_2 of the diene and the empty 2p orbital of the carbene is overwhelmed by the destabilizing interaction between the filled orbitals, π_1 of the diene and the carbene hybrid orbital.[6]

This short list exhausted the proven examples until recently, when it was discovered by two groups that 1,2-dimethylenecycloalkanes reacted with CHX_3 (X = Br, Cl) and alkali or with phenyl(trihalomethyl)mercury reagents to give modest amounts of 1,4 addition.[7,8] The obvious, and suggested, mechanisms were

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(2) For reviews, see: (a) Jones, M., Jr.; Moss, R. A. *React. Intermed.* **1978**, *1*, 78. (b) Moss, R. A.; Jones, M., Jr. *React. Intermed.* **1981**, *2*, 83. (c) Jones, M., Jr.; Moss, R. A. *React. Intermed.* **1985**, *3*, 62.

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