

# Polyporphyrin Thin Films from the Interfacial Polymerization of Mercaptoporphyrins

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**Abstract:** Free-standing ultrathin films of a porphyrin homopolymer have been synthesized by interfacial polymerization of a mercaptoporphyrin. Coupling of 5,10,15,20-tetrakis( $\alpha$ -mercapto-*p*-tolyl)porphyrin at the water/chloroform interface by copper acetate yields continuous, flexible films after drying with supercritical CO<sub>2</sub>. These films are amorphous and retain many characteristics of the monomeric porphyrin, such as the property that they may be metalated. Spectroscopic evidence suggests efficient cross-linking of thiols through disulfide coupling occurs in these polyporphyrins to form a network. Polymerization is accompanied by the introduction of carbonyl functionality, probably the transformation of residual thiols to thioacetate by metal-mediated reaction with excess acetate ion. As an example of the catalytic properties of these polymers, they are shown to promote photooxidation of thietane to the corresponding sulfoxide by sensitizing singlet oxygen production.

## Introduction

Natural and artificial porphyrin-containing structures hold significant technological promise. For example, porphyrin derivatives play a key role in the catalysis of multielectron redox reactions involving small molecules<sup>1</sup> such as O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>. They promote light-induced charge separation<sup>2</sup> with charge transfer,<sup>3</sup> and the extended aromatic structure portends applications in the areas of optical<sup>4</sup> and molecular electronic<sup>5</sup> devices. Recent activity in the modular design of multiporphyrin arrays has yielded molecular “wires” where subunits are connected as ladder-type,<sup>5c</sup> cofacial,<sup>5f</sup> or acetylene-conjugated oligomers.<sup>4a,5g,h</sup> In pursuit of an appropriate material for studying the properties

of porphyrins such as their catalytic activity, a film of function-specific porphyrin is usually deposited or adsorbed on a support. Porphyrins have been incorporated into polymers as pendant groups,<sup>6</sup> in the backbone of networks<sup>7</sup> and linear polymers,<sup>4,8</sup> and as coordination polymers (“shish kebabs”).<sup>5d,9</sup> Thin films for catalysis studies have been prepared on electrodes by electropolymerization.<sup>10</sup> Free-floating films, synthesized by interfacial condensation,<sup>7</sup> can be supported on polymer membranes. However, robust films of porphyrin suitable for exploring many applications are not available.

We report here the synthesis of free-standing films of porphyrin homopolymer, for the first time, using disulfide bridges to cross-link monomers into a 3-dimensional network (Figure 1). The highly efficient polymerization is carried out at the liquid–liquid interface by oxidation of *p*-mercapto-porphyrins. Drying of films with supercritical carbon dioxide yields flexible material with thickness in the range 10–10000 nm. Our polymers are made by interfacial polymerization between a chloroform solution of the appropriate *p*-mercapto-porphyrin and a layer of aqueous oxidant, such as copper acetate. The highly-absorbing, shiny, purple polymer films are amorphous and retain their ability to be metalated, a valuable property for select catalytic applications. To provide an example of catalytic activity, we employed polyporphyrin films in the photosensitized oxidation of a cyclic thioether.

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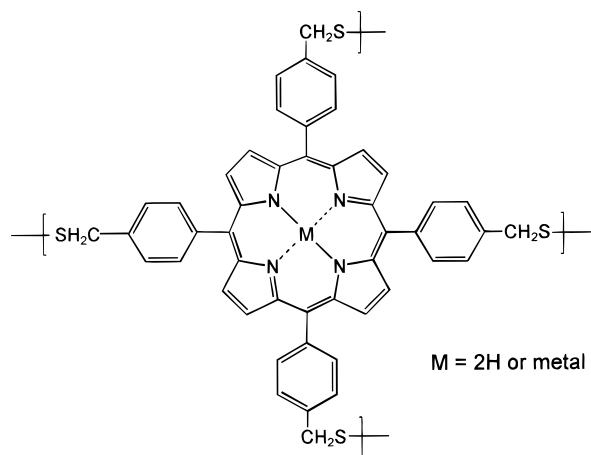
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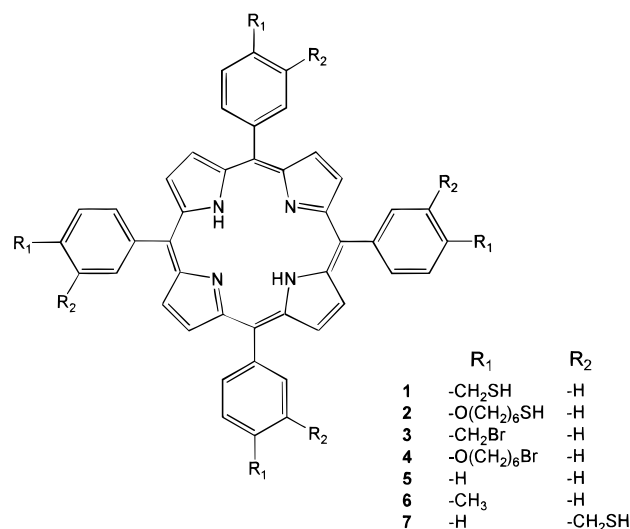
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**Figure 1.** Porphyrin polymer with disulfide links.

**Chart 1**



## Results and Discussion

Bromoporphyrins, made following the method of Bookser and Bruce,<sup>11</sup> were converted to thiols via the thiourea route<sup>12</sup> (see Chart 1 for structures). These thiols were initially used to study the formation of self-assembled monolayers on gold surfaces,<sup>12b</sup> but an attempt to metalate **1** in chloroform with a solution of cobalt(II) acetate in methanol led to the immediate formation of a dark brown precipitate, which, insoluble in all solvents, was presumed to be polymeric. When the thiol was replaced by the bromoporphyrin precursor **3**, no precipitate was observed, but a red cobalt porphyrin complex was obtained upon heating. We then adopted an interfacial polymerization scheme<sup>7</sup> and found that copper acetate was more effective at producing a film at the water/organic interface. In a typical optimized polymerization an excess of aqueous copper acetate was placed over a solution of monomer in chloroform. The end of this straightforward reaction was signaled by the disappearance of purple color from the organic phase. Colorimetric measurement of the organic phase before and after polymerization indicated 99.5% consumption of monomer.

A systematic study of the effect of oxidizer, temperature, concentration, and pH revealed that the chloroform/copper

acetate(aq) combination was distinctly superior for obtaining complete reaction and films with good mechanical integrity. Observations on the relative effect of aqueous phase constituents are summarized in Table 1. More extensive qualitative information on the role of copper salt, pH, temperature, and solvent is tabulated in the Supporting Information.

**Oxidation Reagents.** Various oxidizers/salts were examined for film formation. All the reactions were carried out in air at room temperature unless otherwise specified. All the reagents used in the aqueous layer were in excess with the concentration range 0.005–0.01 M. These reagents were divided into four types: (a) typical nonmetallic reagents including H<sub>2</sub>O<sub>2</sub>, I<sub>2</sub>, dilute H<sub>2</sub>SO<sub>4</sub>, dilute CH<sub>3</sub>COOH, TCBQ (tetrachlorobenzoquinone), and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>; (b) metal salts other than Cu<sup>2+</sup>, such as HgO + HCl, Cd(ClO<sub>4</sub>)<sub>2</sub>, AgNO<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, NaCl, and (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>4</sub>)<sub>4</sub>; (c) metal acetates other than Cu<sup>2+</sup> [Hg(OAc)<sub>2</sub>, Fe(OAc)<sub>3</sub>, Co(OAc)<sub>2</sub>, Cd(OAc)<sub>2</sub>, Zn(OAc)<sub>2</sub>, NaOAc, Mn(OAc)<sub>2</sub>]; (d) Cu<sup>2+</sup>-containing salts [Cu(OAc)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub>, Cu(SO<sub>4</sub>)<sub>2</sub>, Cu(BF<sub>4</sub>)<sub>2</sub>]. Qualitative results, using chloroform solutions of **1** for all experiments, are summarized in Table 1. A general observation is that some degree of film formation is seen with all systems, including water by itself. Ambient oxygen is assumed to be promoting slow disulfide cross-linking, as is typical with thiols. When acidic (0.1 M HCl), neutral (pure water), or basic (0.1 M NaOH) aqueous solutions were employed under N<sub>2</sub>, no film formation was detected. Metallic oxidizers appeared to be more effective at forming films, although some salts, such as those based on mercury and silver, quickly yielded black particles, which we assumed to be thiolates or sulfides. Other nonoxidizing metal salts, such as cadmium and zinc acetate, chosen because they have strong tendencies to form sulfides, produced thin films but no precipitate.

**Organic Layer.** The choice of solvent for the organic layer is important in film growth. With the same oxidant, Cu(OAc)<sub>2</sub>, only chloroform can provide a medium for a complete reaction in comparison with toluene and dichlorobenzene. (Complete reaction is defined as consumption of >95% of monomer.) Film growth was especially slow with toluene. In more extensive experiments with chloroform we discovered that the small quantities of ethanol typically added to chloroform as a preservative were essential for complete reaction. For example, when chloroform with pentene (75 ppm) as preservative was employed as the organic medium, the reaction was incomplete after several days. If 1% ethanol was added to this chloroform, complete film formation was effected within 24 h. It is likely that ethanol complexes Cu(I), stabilizing this oxidation state and making Cu(OAc)<sub>2</sub> a more effective oxidizer. The addition of small amounts of acetonitrile also promotes complete reaction.

**Temperature Effects.** Increasing the reaction temperature over the range 25–65 °C was found to accelerate the film growth, but at temperatures higher than 45 °C the film was broken. Reactivity is better at higher temperature, but excessively high temperatures generate bubbling at the interface, disrupting the film.

**Type of Mercaptoporphyrimonomer.** The three free-base mercaptoporphyrimonomers **1**, **2**, and **7** all can form films of some kind with Cu(OAc)<sub>2</sub> in water through interfacial polymerization. However, only **1** and **2** demonstrated complete reaction; i.e., the organic layer turns colorless after the film formation. *Meta*-isomer **7** gave only very poor films, or more properly, small pieces of floating material at the interface, with the organic layer still strongly colored (i.e., unreacted porphyrin). **2** produced the best films in terms of processibility and physical appearance under the same conditions.

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**Table 1.** Effect of Nonmetals, Metal Reagents, and Acetate Salts on Film Formation<sup>a</sup>

aqueous layer	time	growing speed	film appearance
H <sub>2</sub> O <sub>2</sub>	2 d	very slow, incomplete	hardly seen
H <sub>2</sub> O	7 d	very slow, incomplete	ultrathin, <sup>b</sup> poor
I <sub>2</sub>	2 d	slow, I <sub>2</sub> moved into the organic layer	thin green <sup>b</sup> film, plus green slurry in CHCl <sub>3</sub>
TCBQ <sup>c</sup>	2 d	similar to I <sub>2</sub>	similar to I <sub>2</sub>
H <sub>2</sub> SO <sub>4</sub> (dil)	2 d	very slow, incomplete	ultrathin, green, poor
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	3 d	very slow, incomplete	hardly seen
HgO + HCl	16 h	fast, complete	thin green film, plus black suspension
AgNO <sub>3</sub>	16 h	fast, complete	suspension, no film
Cd(ClO <sub>4</sub> ) <sub>2</sub>	3 d	very slow, incomplete	ultrathin, poor
CdCl <sub>2</sub>	5 d	very slow, incomplete	hardly seen
Hg(OAc) <sub>2</sub>	2 h	very fast, complete	floating powder
Co(OAc) <sub>2</sub>	16 h	slow, incomplete	thin orange film
NaOAc	5 d	very slow, incomplete	extremely thin, poor
Mn(OAc) <sub>2</sub>	5 d	very slow, incomplete	ultrathin, poor
Fe(OAc) <sub>2</sub>	2 d	slow, incomplete	thin, broken
Cd(OAc) <sub>2</sub>	2 d	slow, incomplete	thin film, poor
Zn(OAc) <sub>2</sub>	5 d	very slow, incomplete	ultrathin, poor
HOAc	5 d	very slow, incomplete	ultrathin, green
Fe(OAc) <sub>3</sub>	20 h	fast, complete	thin film, metallic

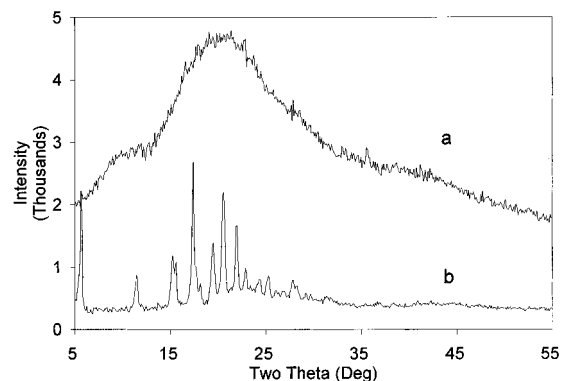
<sup>a</sup> The organic layer for all reactions was **1** in chloroform; all were done at room temperature under ambient conditions. <sup>b</sup> "Ultrathin" corresponds to ca. 1% consumption of monomer and "thin" to ca. 10%. <sup>c</sup> Tetrachlorobenzoquinone.

**Film Thickness.** Film thickness for the optimized copper acetate system could be controlled by reaction time for a fixed concentration, or by the total amount of porphyrin in the solution and the area of the liquid/liquid interface. For example, 1 mg of porphyrin consumed in film formation at a 4 cm diameter interface will give a film ca. 1 μm thick. The thickness was varied systematically in this way over the range 0.1–10 μm. The thinnest films obtained from oxidation with other systems were ca. 10 nm.

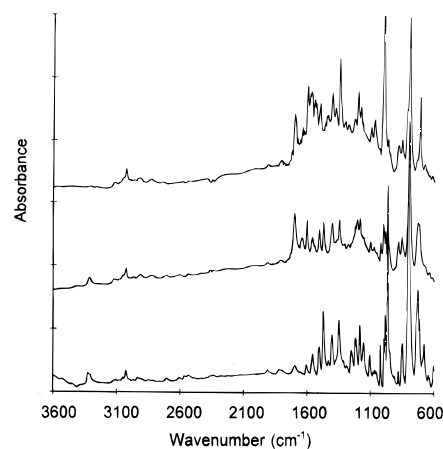
**Film Processing and Characterization.** A crucial step in the production of films with good structural integrity is drying with supercritical carbon dioxide. This technique (also known as critical point drying<sup>13</sup>) involves suspending the as-made film in a CO<sub>2</sub>-miscible solvent, such as acetone, exchanging the solvent with liquid CO<sub>2</sub>, warming to above the critical point, and venting off the gas. Critical point drying avoids the surface tension at the gas/liquid interface, which is capable of collapsing fragile structures. Films dried by simple solvent evaporation crumbled into dust. It is likely that association of planar porphyrin molecules assists the surface tension-induced disintegration of films. The longer alkane spacer group (thiol **2**, Chart 1) yielded films with improved mechanical properties compared to those made from (mercaptomethyl)porphyrin (thiol **1**). Films made from *meta*-isomers were significantly inferior to those from *p*-mercaptoporphyryns.

The films appeared brown-purple in reflected light and purple in transmitted light. They were smooth and shiny to the naked eye, although scanning electron microscopy revealed roughness on the 0.1–1 μm scale (causing some scattering in UV–vis and thus rising baselines toward lower wavelengths in the spectra in Figure 4). Thermal gravimetric analysis of films in nitrogen atmosphere indicated a weight loss of 5% up to 350 °C and significant loss at >350 °C. Films maintained integrity in concentrated sulfuric acid, in 28% aqueous ammonia, and under reflux in solvents such as water, dimethylformamide, and toluene.

As expected for a cross-linked polymer, the polyporphyrins are amorphous. X-ray diffraction (Figure 2) of powdered film showed no resolved structure although broad features were observed at *d*-spacings of 2.1 and 4.4 Å. Interplanar distances in porphyrin stacks have been found to fall in the range of 4



**Figure 2.** X-ray powder diffraction pattern of (a) poly-**1** and (b) the corresponding monomer **1**. Both samples were ground into powder before measurement.



**Figure 3.** FTIR absorption spectra of mercaptoporphyrin **1** (lower spectrum), the nascent polymer from **1** containing cobalt (upper), and demetalated poly-**1** (middle).

Å.<sup>14</sup> Transmission FTIR spectra of **1** and poly-**1** (Figure 3) show that the complex vibrational behavior of the monomer is reproduced in the film. Band assignments are provided in Table 2. The most significant difference is the appearance of a strong peak at ca. 1700 cm<sup>-1</sup>, attributed to C=O, which is discussed below. In addition, the pyrrole N–H stretching for **1** has twin

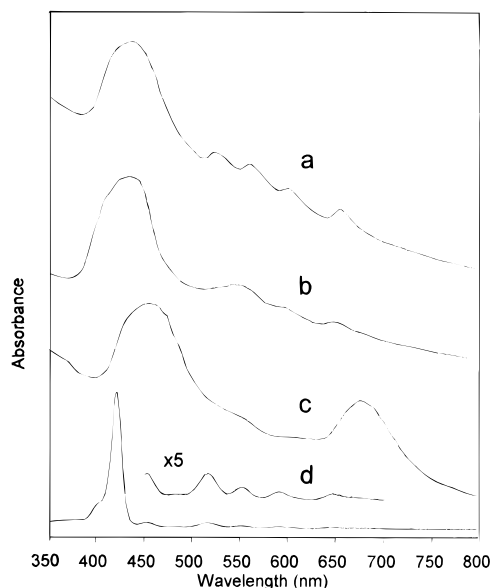
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**Table 2.** IR Assignments for **1** and poly-**1**<sup>a</sup>

assignment	<b>1</b>	poly- <b>1</b>	assignment	<b>1</b>	poly- <b>1</b>
$\nu(\text{N-H})$ ( $\text{cm}^{-1}$ )	3313 (m) + 3327 (m)	3320 (m)	$\nu(\text{pyrrole})$ ( $\text{cm}^{-1}$ )	1402 (s)	1405 (m)
$\nu(\text{C-H})_{\text{phenyl}}$ ( $\text{cm}^{-1}$ )	3025 (m)	3028 (m)	$\nu(\text{pyrrole})$ ( $\text{cm}^{-1}$ )	1348 (s)	1349 (m)
$\nu(\text{S-H})$ ( $\text{cm}^{-1}$ )	2565 (w)		$\nu(\text{C}_\alpha\text{-N})$ ( $\text{cm}^{-1}$ ) + $\nu(\text{C}_\alpha\text{-H})$ ( $\text{cm}^{-1}$ )	1222 (m) + 1213 (m)	1221 (w) + 1207 (m)
$\nu(\text{C=O})$ ( $\text{cm}^{-1}$ )		1701 (s)	B-phenyl ( $\text{cm}^{-1}$ )	1022 (m)	1022 (m)
A-phenyl ( $\text{cm}^{-1}$ )	1604 (m)	1603 (m)	C-phenyl ( $\text{cm}^{-1}$ )	966 (vs)	967 (vs)
$\nu(\text{C}_\alpha\text{-C}_m)$ ( $\text{cm}^{-1}$ )	1555 (m)	1559 (s)	$\delta(\text{pyrrole})$ ( $\text{cm}^{-1}$ )	801 (vs)	800 (vs)
$\nu(\text{C}_\alpha\text{-C}_m)$ ( $\text{cm}^{-1}$ )	1503 (m)	1507 (m)	$\nu(\text{C-S})$ ( $\text{cm}^{-1}$ )	678 (vs)	675 (w)
$\nu(\text{C}_\beta\text{-C}_\beta)$ ( $\text{cm}^{-1}$ )	1472 (s)	1473 (s)			

<sup>a</sup> Note, references include the following: (a) Baran, E. J.; Jubert, A. H.; Ferrer, E. G. *J. Raman Spectrosc.* **1992**, *23*, 489. <sup>b</sup> Hu, S.; Spiro, T. G. *J. Am. Chem. Soc.* **1993**, *115*, 12029. <sup>c</sup> Li, X.-Y.; Zgierski, M. Z. *J. Phys. Chem.* **1991**, *95*, 4268.



**Figure 4.** UV-vis absorption spectra of polymercaptoporphyrin films of thickness ca. 100 nm. Spectra have been normalized to the Soret band at 425–475 nm. (a) Neutral, unmetalated film (Figure 1,  $M = 2H$ ). (b) Metalated with copper ( $M = \text{Cu}^{2+}$ ). (c) Protonated polymer ( $M = 4H$ ). (d) Solution of the corresponding monomer in chloroform. Soret band extinction coefficients for the monomer were  $4.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$  and for the polymer ca.  $1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ .

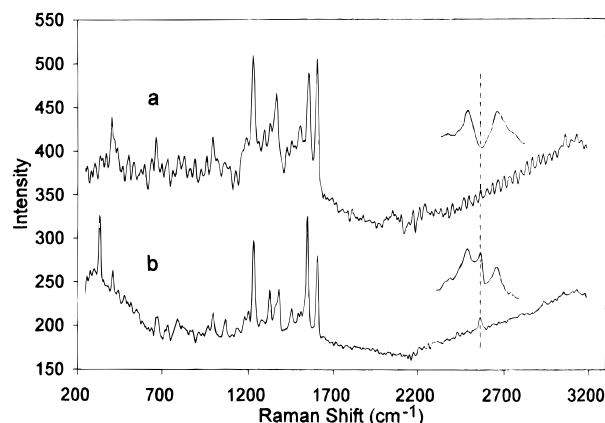
peaks at 3312 and 3327  $\text{cm}^{-1}$  for two possible isomeric structures, which coalesce into a single peak at 3320  $\text{cm}^{-1}$  in the polymer due to increased symmetry.

Porphyrin units incorporated into these films retain properties of unpolymerized porphyrins, including the ability to be metalated.<sup>15</sup> In Figure 4 the UV-vis absorption spectra of neutral, metalated ( $M = \text{metal}$ , Figure 1), and protonated ( $M = 4H$ , Figure 1) polyporphyrin ultrathin films are compared with the solution spectrum of the neutral monomer. Compared to the solution spectrum, the Soret band (ca. 450 nm) in the porphyrin polymer is red-shifted and broadened due to exciton interaction between  $B \pi\pi^*$  states. Such red-shifting has been observed in Langmuir-Blodgett monolayer films of porphyrins,<sup>16</sup> and severe broadening was observed in porphyrin aggregates.<sup>17</sup> Evidence for complete metalation, for example, by  $\text{Co}^{2+}$ , is provided by the complete disappearance of the 3320  $\text{cm}^{-1}$  band ( $\text{N-H}$  stretch on pyrroles) in the infrared transmission spectra (Figure 3) and a S:Co atomic ratio of 4.2:1 (theoretical 4:1), determined by energy dispersive X-ray analysis (EDX).

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**Figure 5.** Fourier transform (FT) Raman spectrum of (a) the polymer from 5,10,15,20-tetrakis( $\alpha$ -mercapto-*p*-tolyl)porphyrin monomer, poly-**1**, and (b) monomer **1**. Inset: FT-infrared spectra from 2450 to 2660  $\text{cm}^{-1}$  showing the disappearance of the 2465  $\text{cm}^{-1}$  S-H stretch on polymerization.

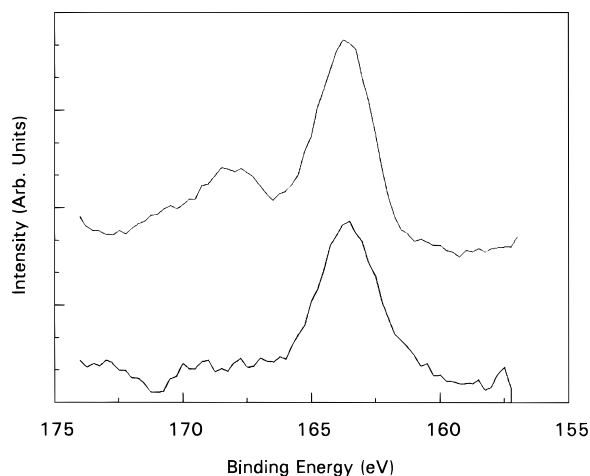
The structure for the polyporphyrin in Figure 1 involves cross-linking *via* disulfide bridges. This model for connecting monomers to make a film is one of several that employ sulfur bridges in various oxidation states (thioethers, sulfones, sulfoxides, metal thiolates). The Raman spectrum of poly(5,10,15,20-tetrakis( $\alpha$ -mercapto-*p*-tolyl)porphyrin), poly-**1**, (Figure 5) although it contains the strong C-S stretch at 667  $\text{cm}^{-1}$ , does not show the S-S vibration, which is usually intense.<sup>18</sup> This is because the S-S stretch in benzyl-type disulfides is abnormally weak.<sup>19</sup> However, several pieces of evidence support the existence of disulfide bridges: polymerization conditions mirror those known to promote oxidation of thiols to disulfides.<sup>20,21</sup> Of the several oxidizing agents employed (iodine,  $\text{H}_2\text{O}_2$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{AgNO}_3$ ,  $\text{HgO}$ ,  $\text{FeCl}_3$ ,  $\text{O}_2$ ), copper acetate was found to be the most effective in promoting complete polymerization to give rugged films. Interestingly, some of the most effective catalysts for disulfide formation are copper and iron porphyrins.<sup>21</sup> Thus, the reaction is probably autocatalytic. In addition, X-ray photoelectron spectroscopy (XPS) of thin polyporphyrin films confirmed the theoretical (experimental) N:S:Co ratio of 4:4:1 (3.9:4.0:1.0) on cobalt-metalated films. The sulfur  $\text{S}_{2p}$  photoelectron is sensitive to the oxidation state of the sulfur and yields well-resolved peaks of characteristic binding energy. A binding energy of 163.3 eV (Figure 6) is found for thiols and disulfides ( $163.3 \pm 0.5 \text{ eV}$ ) and is distinct from those of metal sulfides ( $161 \pm 0.5 \text{ eV}$ ) and more highly oxidized sulfur, such as sulfonate (168 eV) or sulfoxide (166 eV).<sup>22</sup>

(18) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press, San Diego, 1991; Chapter 14.

(19) Allum, K. G.; Creighton, J. A.; Green, J. H. S.; Minkoff, G. J.; Prince, J. L. S. *Spectrochim. Acta* **1968**, *24A*, 927–941.

(20) Harrison, D. C. *Biochem. J.* **1927**, *21*, 335–346.

(21) Barron, E. S. G.; Miller, Z. B.; Kalnitsky, G. *Biochem. J.* **1947**, *41*, 62–68.



**Figure 6.** X-ray photoelectron spectrum in the  $S_{2p}$  region of a thin film of poly-1 as-made (upper) and after ca. 10 nm of material had been etched away with an ion gun (lower).

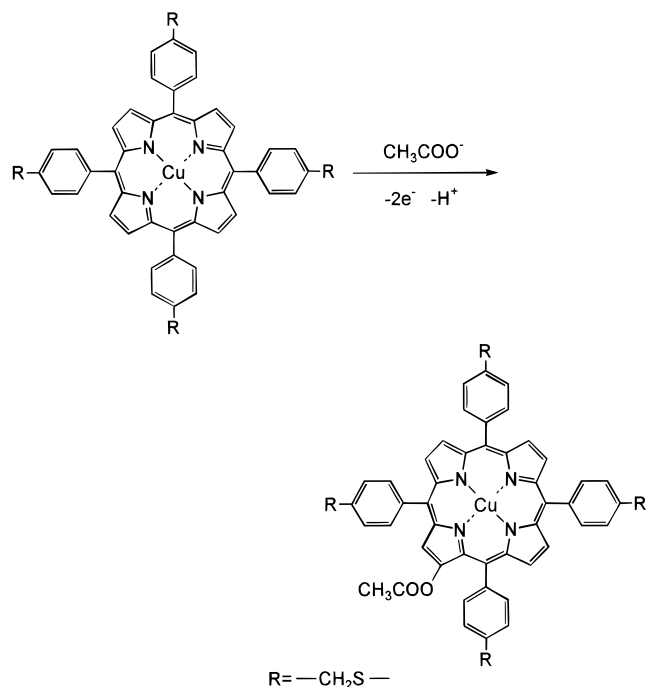
Sulfur from thioether bridges would yield an XPS photoelectron at 162.6 binding energy (aliphatic sulfide<sup>22</sup>), which would produce a shoulder on the observed peak in Figure 6. We are able to rule out the existence of bridging thiolates such as  $-S-Cu-S-$ , since copper is not seen in XPS of demetalated thin films and two Cu atoms would be required for every porphyrin.

If network formation occurred *via* disulfides, one would expect reducing agents to regenerate the thiol, leading to depolymerization of the polymer. When porphyrin films suspended in chloroform were treated with aqueous dithiothreitol in ammonia, a mild disulfide reducing agent, the porphyrin color in the organic phase was slowly regenerated. The solution UV-vis spectrum of this product was almost identical to that of metalated (with  $Cu^{2+}$ ) **5** (tetraphenylporphyrin).

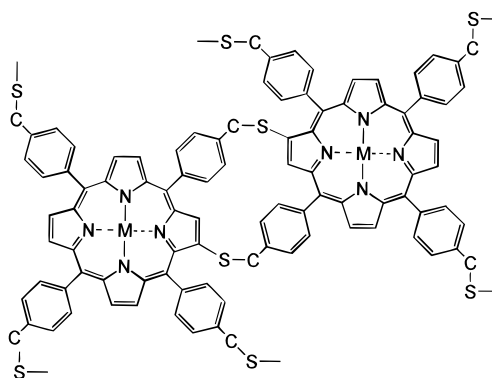
In addition to yielding the theoretical (experimental) C:N:S ratio of 48:4:4 (46:4.0:4.0), XPS of films also indicated partial oxidation of sulfur at the surface: a small peak at 168 eV binding energy, attributed to sulfonate ( $-SO_3^-$ ),<sup>22</sup> was well resolved from the major  $S_{2p}$  disulfide peak (Figure 6). The sulfonate signal disappeared after a few nanometers of the surface was etched away with an ion gun. At the organic/aqueous and air/water interfaces the polyporphyrin films have a propensity to spontaneously flip over to favor contact of water with the side of the film that was originally exposed to the aqueous oxidizer. This gradient in hydrophobicity results from differential surface oxidation, as more sulfonates impart greater hydrophilic character.

The strong IR absorption band at  $1701\text{ cm}^{-1}$  in the spectrum of the film (Figure 3) suggests the presence of  $C=O$ . When the film was treated with diphenyl hydrazine, no significant change in the intensity of the  $C=O$  stretch was observed, and the band was also insensitive to treatment with dilute acid or base. These tests indicate the absence of aldehyde and carboxylate, respectively. It is possible that this band results from  $C=O$  of a methyl ester. Giraudeau *et al.* have recently elaborated on the synthesis of  $\beta$ -substituted porphyrins by electrochemical oxidation of porphyrins with subsequent nucleophilic attack on the porphyrin  $\pi$ -cation radical.<sup>23</sup> Since an oxidizer is employed in our experiments in large excess, it may be argued that acetate adds to the porphyrin ring according to Scheme 1.<sup>23a</sup> The  $\pi$ -conjugation of the porphyrin is not

### Scheme 1



### Chart 2



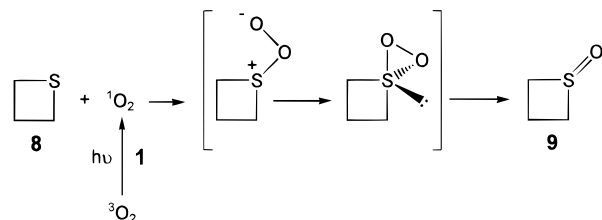
disrupted as a result of this reaction and the electronic properties of the monomer are thus preserved in the polymer. Another possible nucleophile would be thiol (as thiolate), producing thioether bridges as depicted in Chart 2.

Such a cross-linking mechanism would be accelerated by higher pH, which is observed (at the expense of film integrity), but we saw no decrease in the overall rate under very acidic conditions, contrary to expectations for thiolate as nucleophile. Furthermore, the XPS valence electron data are more consistent with sulfur in the disulfide form. In addition, the thioester bridging scheme above would require eight (sterically hindered) bridges to each porphyrin unit in order to consume all thiol functionality on polymerization. Since copper is an insufficiently strong oxidizer to produce the cation radical ( $E = +1.05\text{ V vs SCE}$ ), we consider this nucleophilic substitution/cross-linking mechanism to be unlikely for our system. Indeed, acetate salts are commonly used to metalate porphyrins and nucleophilic addition is not observed. When tetraphenylporphyrin, **5**, or tetratolylporphyrin, **6**, were subjected to the same conditions (chloroform/water, copper(II) acetate), no evidence

(22) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer Inc.: Minneapolis, MN, 1979; p 56.

(23) (a) Giraudeau, A.; Ruhlmann, L.; El Kahef, L.; Gross, M. *J. Am. Chem. Soc.* **1996**, *118*, 2969–2979. (b) El Kahef, L.; El Meray, M.; Gross, M.; Giraudeau, A. *J. Chem. Soc., Chem. Commun.* **1986**, 621–622. (c) Giraudeau, A.; El Kahef, L. *Can. J. Chem.* **1991**, *69*, 1161–1165. (d) El Kahef, L.; Gross, M.; Giraudeau, A. *J. Chem. Soc., Chem. Commun.* **1989**, 963.

## Scheme 2

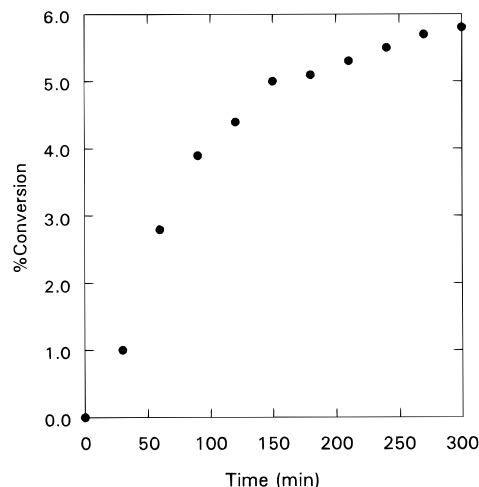


for reaction as in Scheme 1 was found. The same experiment, repeated in the presence of benzyl mercaptan, also yielded no reaction that would correspond to Chart 2. Thus, we believe disulfide to be the most likely bridging unit.

The use of disulfide bonds to connect monomer units has key advantages to synthetic schemes based on condensation between dissimilar functional groups. For example, Wamsler *et al.* describe interfacially polymerized porphyrins requiring coupling between acid chloride and alcohol or amine (yielding the corresponding ester or amide).<sup>7</sup> A tetrafunctional monomer must encounter the complementary functional group, reducing the probability of complete reaction and compromising physical properties. Unsupported films were not obtained.<sup>7</sup> The polymerization described here appeared to demonstrate remarkable economy in the consumption of sulfhydryl (thiol) groups, since no  $-SH$  was detected by Raman (Figure 5) or infrared spectroscopy ( $S-H$  stretch at  $2565\text{ cm}^{-1}$ ). One might expect unreacted thiol to remain on formation of the network depicted in Figure 1, but FTIR spectroscopy revealed less than 10% residual  $-SH$ .<sup>24</sup> In addition, Ellman's reagent,<sup>25,26</sup> a versatile test for thiols, gave a negative result. It is likely that residual thiol is scavenged by metal-mediated esterification by acetate ion. The resulting thioester,  $-R-S-CO-CH_3$ , would then yield the  $C=O$  stretch observed at  $1701\text{ cm}^{-1}$  (IR). The  $402\text{ cm}^{-1}$  Raman band might be attributable to the  $O=C-S$  bending mode.<sup>18</sup>

**Photosensitized Oxidation of Thietane.** A myriad of natural and synthetic processes employ porphyrins in catalytic and/or photochemical processes. We examined the use of our polyporphyrin films as a photooxidation catalyst. The system chosen was the self-catalyzed reaction of oxygen with thietane, **8**. Clennan *et al.*, in a recent study of this reaction using porphyrin as triplet sensitizer, have provided evidence for a thiadioxirane intermediate,<sup>27</sup> Scheme 2. Thin films of poly-**1** were used to promote photooxidation of thietane in  $CHCl_3$  under conditions where the molar ratio of thietane to porphyrin was *ca.* 2000:1. The conversion of **8** to sulfoxide as a function of time, determined using gas chromatography, is presented in Figure 7. Blank experiments, run under identical conditions but with no porphyrin film, yielded no detectable sulfoxide (the detection limit is 0.002% conversion on the scale used in Figure 7). Integration of all the peaks in the GC provided an estimate that the efficiency of conversion of **8** to **9** was 85%.

Figure 7 also shows that the conversion efficiency is not linear with time, as one would expect for low conversion and a pseudo-first-order reaction where thietane is in excess. It is probable that the porphyrin film itself is undergoing photodegradation. One would expect the disulfide bonds to be susceptible to oxidation, leading to eventual rupture of the network. Some yellowing of the solution was observed over the course of the



**Figure 7.** Conversion *vs* time for the poly-**1**-sensitized photooxidation of thietane in chloroform, monitored by GC. A system identical, except for the presence of poly-**1**, gave less than 0.002% conversion after 300 min.

experiment—a possible reason for the decrease in efficiency. Porphyrin films irradiated under ambient conditions with and without thietane remained intact under conditions of gentle stirring. Since no detailed studies on the structure or composition of the irradiated films have been made for these preliminary experiments, we have no explanation as to why the porphyrin disulfides are unexpectedly hardy.

In conclusion, we have used disulfide cross-links, pervasive in natural systems, efficiently to produce robust, free-standing porphyrin polymer films. Such a material should help bridge the gap between the remarkably versatile biochemistry of porphyrins and projected applications of synthetic porphyrin materials in the areas of catalysis, photochemistry, and separations.

## Experimental Section

Solvents were reagent- or HPLC-grade from Fisher Scientific and used as received. Most starting materials were from Aldrich and were used without further treatment. DIBAL-H stock solution (1.08 M) was prepared by diluting DIBAL-H (Aldrich) into HPLC grade hexane under inert atmosphere and was stored under  $N_2$ . Thietane was used as received from Aldrich, and thietane sulfoxide for chromatography standards was a generous gift from E. L. Clennan. Flash chromatography was performed on silica gel (EM Science), 60–200 mesh. Dichloromethane, chloroform, toluene, or mixtures of chloroform and methanol were used as eluent.

NMR spectra were recorded on a Varian Gemini 300 spectrometer. Chemical shifts are in parts per million from tetramethylsilane. The solvent for NMR was  $CDCl_3$  if not specified. Coupling constants are reported in hertz. Infrared spectra were obtained on a Nicolet 520 FTIR spectrometer with a DTGS detector. UV–vis spectra were taken on a Cary-14 or a Cary 13 spectrometer. Melting points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories (Knoxville, TN) or Atlantic Microlab (Norcross, GA). Mass spectra were run on a liquid secondary ion mass spectrometer using a cesium primary ion beam of 15 000 V on a Finnigan MAT95Q instrument (with thanks to Dr. David Powell, University of Florida). Raman spectra were acquired on a Bomem DA8 spectrometer with Raman accessory using a Lee Laser Nd:YAG laser source at 1064 nm and a  $N_2$ -cooled Ge avalanche detector.

X-ray diffraction powder patterns were acquired with a Siemens D5000 X-ray diffractometer using a  $Cu\ K\alpha$  ( $1.54\text{ \AA}$ ) X-ray source excited at 40 kV and 30 mA. The samples were ground to fine powders before measurements. X-ray diffraction analysis of the free-standing films revealed an amorphous structure. Energy dispersive X-ray analysis (EDX) was performed with a JEOL JXA-840A electron probe microanalyzer using a beam energy of 15 kV and an acquisition time

(24) Samples allowed to react for a short time or polymerized at low concentration showed some residual thiols.

(25) Ellman, G. L. *Arch. Biochem. Biophys.* **1959**, *82*, 70–77.

(26) Bardwell, J. C. A. *Mol. Biol.* **1994**, *14*, 199–205.

(27) Clennan, E. L.; Dobrowolski, P.; Greer, A. *J. Am. Chem. Soc.* **1995**, *117*, 9800–9803.

of 100 s. X-ray photoelectron spectroscopy (XPS) was performed with a Perkin-Elmer PHI5100 system employing a 10-360 precision energy analyzer, and a Mg K $\alpha$  source. The takeoff angle for photoelectrons was 75°, the base vacuum was better than  $1 \times 10^{-8}$  Torr, and pass energies for elements were as follows: C<sub>1s</sub>, 17.9 eV; Cu<sub>2p</sub>, 44.75 eV; N<sub>1s</sub>, 17.9 eV; S<sub>2p</sub>, 44.75 eV; Co<sub>2p</sub>, 44.75 eV. Polymer film thickness was measured with a digital micrometer for films in the micrometer range. Thinner films were measured by weighing them on a microbalance, determining their area, and assuming a density of 1.2 g cm<sup>-3</sup>. As-made films contained metal (e.g., Cu<sup>2+</sup>) ion. Demetalation was performed by exposing films to aqueous solutions of mineral acids, and films were metalated by heating under reflux in a solution of metal acetate in 40:60 (v/v) methanol/chloroform.

Triplet-sensitized oxidation of thietane, as described by Clennan *et al.*,<sup>27</sup> was performed using films of poly-1 approximately 1  $\mu$ m thick and 4 cm in diameter, prepared as described below. Films were treated with 10 M HCl in 1:1 water/acetone for 2 h at room temperature to remove copper and then sequentially rinsed in water, 0.1 M NH<sub>4</sub>OH, acetone, and chloroform. Photochemistry was carried out by irradiating 20 mL of a 1 wt % solution of thietane in chloroform under ambient conditions. The light source was a 100 W xenon arc lamp (Varian P-1505-71) filtered through 1 cm of 12 M NaNO<sub>2</sub>(aq). Reaction products were determined at intervals using a Varian 3300 gas chromatograph equipped with a DB-5MS (J&W Scientific) capillary column and a flame ionization detector.

**$\alpha$ -Bromo-*p*-tolunitrile.**<sup>28</sup> *p*-tolunitrile (10.0 g, 85.4 mmol), *n*-bromosuccinimide, (15.2 g, 85.5 mmol), and benzoyl peroxide (0.2 g) were added to 60 mL of CCl<sub>4</sub>. This mixture was heated under reflux for 7 h, after which time all solids floated to the surface. The mixture was filtered when hot, washed with hot and CCl<sub>4</sub>, and the solvent was removed from the filtrate under reduced pressure. The product was recrystallized twice from cyclohexane and dried under vacuum at 50 °C for 6 h. Yield: 8.05 g (48.1%). The product appeared as white crystals. <sup>1</sup>H NMR:  $\delta$  4.45 (s, 1, CH<sub>2</sub>Br), 7.48 (d, 1,  $J$  = Hz, H-3,5), 7.64 (d, 1,  $J$  = Hz, H-2,6). Mp: 113–116 °C (lit. 114–116 °C).<sup>28</sup> Anal. Found: C, 49.02; H, 3.09; N, 7.14; Br, 40.77. Calcd: C, 48.98; H, 3.06; N, 7.14; Br, 40.81.

**$\alpha$ -Bromo-*p*-tolualdehyde.**<sup>11</sup> This was a modified version of Bookser and Bruce's method.<sup>11</sup> Toluene was used as solvent instead of chlorobenzene for easier workup. A 6.00 g (30.6 mmol) sample of  $\alpha$ -bromo-*p*-tolunitrile was dissolved in 60 mL of toluene and cooled to 0 °C. A 40 mL (43.2 mmol) portion of 1.08 M DIBAL-H in hexane was added dropwise under N<sub>2</sub>. The solution was stirred for another hour at 0 °C. An 80 mL sample of chloroform was then added followed by ca. 200 mL of 10% HCl, and the solution was stirred at room temperature for 1 h. The organic layer was separated, washed with distilled water, dried over anhydrous MgSO<sub>4</sub>, and filtered. The solvent was almost completely removed from the filtrate under reduced pressure, and the residue was cooled, filtered, washed with cold hexane, and dried at 50 °C under vacuum. Yield: 5.21 g (85%). The product appeared as white crystals. Mp: 97–100 °C (lit. 97–99 °C). Anal. Found: C, 48.78; H, 3.58; N, 0, Br, 39.57. Calcd: C, 48.27; H, 3.54; N, 0; Br, 40.14. IR:  $\nu$  (cm<sup>-1</sup>) 1711 (s, C=O), 2745 and 2824 (m, CHO), 1585 and 1610 (m, C=C). <sup>1</sup>H NMR:  $\delta$  4.50 (s, 2, CH<sub>2</sub>Br),  $\delta$  7.55 (d, 2,  $J$  = 8.2 Hz, H-3,5), 7.85 (d, 2,  $J$  = 8.2 Hz, H-2,6),  $\delta$  10.04 (s, 1, CHO).

**$\alpha$ -Bromo-*m*-tolualdehyde.** Procedures were similar to those for  $\alpha$ -bromo-*p*-tolualdehyde. A 5.00 g (25.5 mmol) sample of  $\alpha$ -bromo-*m*-tolunitrile was dissolved in 50 mL of chlorobenzene and cooled to 0 °C under N<sub>2</sub>. A 34 mL (36 mmol) portion of the DIBAL-H stock solution was added dropwise. The reaction was completed and worked up as for  $\alpha$ -bromo-*p*-tolualdehyde. Yield: 3.80 g (75%). Mp: 45–47 °C (lit. 46–49 °C). <sup>1</sup>H NMR:  $\delta$  4.52 (s, 2, CH<sub>2</sub>Br), 7.53 (t, 1,  $J$  = 8 Hz, H-5), 7.65 (d, 1,  $J$  = 8 Hz, H-4), 7.83 (d, 1,  $J$  = 8 Hz, H-6), 7.91 (s, 1, H-2), 10.02 (s, 1, CHO). IR:  $\nu$  (cm<sup>-1</sup>) 1712 (s, C=O), 2743 and 2822 (m, CHO), 1596 and 1608 (m, C=C).

**( $\omega$ -Bromo-*p*-hexoxyl)benzaldehyde.**<sup>29</sup> To a mixture of 7.32 g (0.03 mol) of Br(CH<sub>2</sub>)<sub>6</sub>Br, 1.4 g (0.01 mol) of K<sub>2</sub>CO<sub>3</sub>, and a catalytic amount

of KI in 20 mL of dry acetone was added 1.22 g (0.01 mol) of 4-hydroxybenzaldehyde dissolved in 20 mL of acetone dropwise, under N<sub>2</sub>. The mixture was heated under reflux for 18 h. The solution was poured into ice-water, and the precipitate filtered and then washed with hexane. Yield: 2.02 g (71%). <sup>1</sup>H NMR:  $\delta$  4.04 (t, 2,  $J$  = 6 Hz, -OCH<sub>2</sub>-), 6.99 (d, 2,  $J$  = 9 Hz, H-3,5), 7.83 (d, 2,  $J$  = 9 Hz, H-2,4), 9.88 (s, 1, CHO), 3.43 (t, 2,  $J$  = 6 Hz, -CH<sub>2</sub>Br), 1.85 (m, 4, -OCCH<sub>2</sub>- and -CH<sub>2</sub>CBr), 1.55 (m, 4, -OCCCH<sub>2</sub>- and -CH<sub>2</sub>CCBr).

**5,10,15,20-Tetratolylporphyrin, 6.**<sup>30</sup> A 5.00 g (41.6 mmol) sample of tolualdehyde and 100 mL of propionic acid was added to a 250 mL flask. The solution was stirred and heated to reflux for 20 min. A 2.79 g (41.6 mmol) portion pyrrole was then added, and heating was continued for another 30 min. The mixture was cooled to 4 °C and filtered. The purple shiny crystals were washed with methanol three times and dried under vacuum. Yield: 1.33 g (19.1%). <sup>1</sup>H NMR:  $\delta$  2.66 (s, 12, -CH<sub>3</sub>), 7.41 (d, 8,  $J$  = 8 Hz, H-3',5'), 7.94 (d, 8,  $J$  = 8 Hz, H-2',4'), 8.66 (s, 8, pyrrolic  $\beta$ -H), -2.78 (s, 2, =NH). UV-vis (in chloroform):  $\lambda_{\max}$  420 nm ( $\epsilon$  4.8  $\times$  10<sup>5</sup> mol<sup>-1</sup>·L·cm<sup>-1</sup>), 516 (1.9  $\times$  10<sup>4</sup>), 551 (9.7  $\times$  10<sup>3</sup>), 590 (5.7  $\times$  10<sup>3</sup>), 649 (6.2  $\times$  10<sup>3</sup>).

**5,10,15,20-tetrakis( $\alpha$ -bromo-*p*-tolyl)porphyrin, 3.**<sup>11</sup> To 1.5 L of chloroform were added 3.00 g (15 mmol) of  $\alpha$ -bromo-*p*-tolualdehyde and 1.05 g (15 mmol) of pyrrole. During stirring, 0.71 g (5.0 mmol) of Et<sub>2</sub>O·BF<sub>3</sub> was added to the mixture. Stirring was continued for 1 h more at room temperature followed by the addition of 0.61 g (6.0 mmol) of triethylamine and 2.77 g (11.3 mmol) of TCBQ, and the temperature was raised to reflux and kept under reflux for 1 h. The volume of the mixture was then reduced to ca. 200 mL and filtered through silica gel (neutral). After the filtrate was dried under reduced pressure, the purple sediment was redissolved in toluene. The solution was passed over silica gel, eluting with toluene. After the toluene was removed, the sediment was washed with methanol again, giving shiny purple fine crystals. The product was dried at 100 °C under vacuum. Yield: 2.23 g (60%). Anal. Found: C, 58.57; H, 3.51; N, 5.73; Br, 32.16. Calcd: C, 58.44; H, 3.47; N, 5.68; Br, 32.40. <sup>1</sup>H NMR:  $\delta$  -2.8 (s, 2, NH), 4.84 (s, 8, CH<sub>2</sub>Br), 7.82 (d, 8,  $J$  = 8 Hz, H-3',5'), 8.19 (d, 8,  $J$  = 8 Hz, H-2',6'), 8.85 (s, 8,  $\beta$ -pyrrolic H). IR (KBr):  $\nu$  (cm<sup>-1</sup>) 3325 and 3308 (m, =NH), 3027 (m, C-H on phenyl and pyrroles), 1614, 1575, 1540 (m, C=C), 1221 (s, -CH<sub>2</sub>Br), 595 (s, -CBr). UV-vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  420 nm ( $\epsilon$  3.9  $\times$  10<sup>5</sup> mol<sup>-1</sup>·L·cm<sup>-1</sup>), 516 (1.6  $\times$  10<sup>4</sup>), 551 (8.4  $\times$  10<sup>3</sup>), 589 (5.8  $\times$  10<sup>3</sup>), 646 (4.9  $\times$  10<sup>3</sup>).

**5,10,15,20-Tetrakis( $\alpha$ -bromo-*m*-tolyl)porphyrin.**  $\alpha$ -Bromo-*m*-tolylaldehyde (2.80 g, 14.0 mmol) and pyrrole (0.98 g, 14.0 mmol) were dissolved in 1500 mL of dry chloroform; after 0.71 g (5.0 mmol) of Et<sub>2</sub>O·BF<sub>3</sub> was added, the mixture was stirred at room temperature for 1 h. Triethylamine (0.61 g, 6.0 mmol) and TCBQ (2.80 g, 11.4 mmol) were then added and heated under reflux for 1 h. The volume was reduced to 200 mL under vacuum and the solution filtered through 60 g of silica gel. The filtrate and the CH<sub>2</sub>Cl<sub>2</sub> washing were combined and dried under reduced pressure. The solid was washed with toluene and methanol. The product was recrystallized from MeOH/CH<sub>2</sub>Cl<sub>2</sub> and dried under vacuum. Yield: 1.54 g (42%). <sup>1</sup>H NMR:  $\delta$  -2.8 (s, 2, NH), 4.78 (s, 8, CH<sub>2</sub>Br), 7.74 (t, 4,  $J$  = 7.6 Hz, H-5'), 7.82 (d, 4,  $J$  = 7.6 Hz, H-6'), 8.15 (d, 4,  $J$  = 7.6 Hz, H-4'),  $\delta$  8.25 (s, 4, H-2'), 8.88 (s, 8,  $\beta$ -pyrrolic H). IR (KBr):  $\nu$  (cm<sup>-1</sup>) 3331 (w, =NH), 3037 (m, C-H on phenyl and pyrroles), 1610, 1592, 1559 (m, C=C). UV-vis (in chloroform):  $\lambda_{\max}$  419 nm ( $\epsilon$  2.4  $\times$  10<sup>5</sup> mol<sup>-1</sup>·L·cm<sup>-1</sup>), 516 (1.1  $\times$  10<sup>4</sup>), 551 (5.8  $\times$  10<sup>3</sup>), 590 (5.3  $\times$  10<sup>3</sup>), 666 (1.4  $\times$  10<sup>4</sup>).

**5,10,15,20-Tetrakis( $\omega$ -bromo-*p*-hexoxy)phenyl)porphyrin, 4.** ( $\omega$ -Bromo-*p*-hexoxy)benzaldehyde, (3.00 g, 10.5 mmol), pyrrole (0.74 g, 10.5 mmol), and BF<sub>3</sub> etherate (0.50 g) were mixed in 1100 mL of chloroform. After the mixture was stirred at room temperature for 1 h, 0.43 g of triethylamine and 1.95 g of TCBQ were added, and the resulting mixture was heated under reflux for 1 h. The product was worked up the same way as for 3. Yield: 1.95 g (57%). Anal. Found: C, 61.44; H, 5.45; N, 4.23; Br, 24.15. Calcd: C, 60.99; H, 6.17; N, 4.19; Br, 23.87. <sup>1</sup>H NMR:  $\delta$  -2.76 (s, 2, NH), 4.26 (t, 8,  $J$  = 6 Hz, -OCH<sub>2</sub>-), 7.27 (d, 8,  $J$  = 7.2 Hz, H-3', 5'), 8.11 (d, 8,  $J$  = 7.2 Hz, H-2',6'), 3.51 (t, 8,  $J$  = 6.6 Hz, -CH<sub>2</sub>Br), 2.01 (m, 16, -OCCH<sub>2</sub>- and -CH<sub>2</sub>CBr), 1.67 (m, 16, -OCCCH<sub>2</sub>- and -CH<sub>2</sub>-

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CCBr), 8.86 (s, 8,  $\beta$ -pyrrolic H). UV-vis (in chloroform):  $\lambda_{\max}$  423 nm ( $\epsilon$   $4.5 \times 10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ), 518 ( $1.8 \times 10^4$ ), 556 ( $1.2 \times 10^4$ ), 593 ( $6.7 \times 10^3$ ), 649 ( $6.5 \times 10^3$ ).

**Mercaptoporphyrins.** All three mercaptoporphyrins, 5,10,15,20-tetrakis( $\alpha$ -mercapto-*p*-tolyl)porphyrin (**1**), 5,10,15,20-tetrakis( $\alpha$ -mercapto-*m*-tolyl)porphyrin (**7**), and 5,10,15,20-tetrakis[( $\omega$ -mercapto-*p*-hexoxy)phenyl]porphyrin (**2**), were prepared via the thiourea route.<sup>12a</sup>

**5,10,15,20-Tetrakis( $\alpha$ -mercapto-*p*-tolyl)porphyrin, **1**.** **3** (0.22 g, 0.2 mmol) and thiourea (1.0 g, 13 mmol) were dissolved in 80 mL of toluene and 15 mL of methanol. The mixture was purged with N<sub>2</sub> and heated under reflux for 50 h in the dark. After mixture was cooled to 40–50 °C, a solution of 0.1 g of NaOH in 30 mL of boiled distilled water was transferred carefully under N<sub>2</sub> into the mixture, and stirring was continued for 12 h under nitrogen. The solution was cooled to room temperature, and the reaction was terminated by adding 20 mL of diluted HCl (about 3 mmol, deoxygenated). The organic layer was collected and washed with distilled water to pH 7. The solvent was removed under reduced pressure. The sediment was sonicated with methanol, filtered, washed with methanol, and dried. Recrystallization was performed with toluene/methanol. Yield: 0.16 g (88%). MS (LSIMS):  $m/z$  799.197 (M + H)<sup>+</sup> (theoretical 799.206 for C<sub>48</sub>H<sub>39</sub>N<sub>4</sub>S<sub>4</sub>). <sup>1</sup>H NMR:  $\delta$  -2.75 (s, 2, NH), 2.08 (t, 4,  $J = 7.2$  Hz, SH), 4.11 (d, 8,  $J = 7.6$  Hz, -CH<sub>2</sub>S-), 7.71 (d, 8,  $J = 8$  Hz, H-3',5'), 8.16 (d, 8,  $J = 8$  Hz, H-2',6'), 8.85 (s, 8,  $\beta$ -pyrrolic H), and no CH<sub>2</sub>Br residue was detected in NMR. IR (KBr):  $\nu$  (cm<sup>-1</sup>) 3313 and 3327 (m, =NH), 3121 (w) and 3025 (m, C-H on phenyl and pyrroles), 2564 (w, S-H), 1604, 1555, 1503 (m, C=C), 1249 (m, -CH<sub>2</sub>S-). UV-vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  423 nm ( $\epsilon$   $4.4 \times 10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ), 519 ( $1.7 \times 10^4$ ), 556 ( $1.2 \times 10^3$ ), 593 ( $5.8 \times 10^3$ ), 653 ( $5.9 \times 10^3$ ).

**5,10,15,20-Tetrakis( $\alpha$ -mercapto-*m*-tolyl)porphyrin, **7**.** By following the same method used in the synthesis of **1**, **7** was obtained in a yield of 74%. It was also found that this mercaptoporphyrin is less sensitive to air than **1** in solution (there was no precipitate observed even after its solution was exposed to air for three days). <sup>1</sup>H NMR:  $\delta$  -2.81 (s, 2, NH),  $\delta$  1.98 (t, 4,  $J = 7.2$  Hz, SH), 4.04 (d, 8,  $J = 7.6$  Hz, CH<sub>2</sub>S),  $\delta$  7.70 (m, 8, H-4',5'), 8.05 (d, 4,  $J = 8$  Hz, H-6'), 8.18 (s, 4, H-2'), 8.84 (s, 8,  $\beta$ -pyrrolic H). UV-vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  420 nm ( $\epsilon$   $2.6 \times 10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ), 516 ( $1.2 \times 10^4$ ), 551 ( $5.8 \times 10^3$ ), 590 ( $4.5 \times 10^3$ ), 646 ( $4.0 \times 10^3$ ).

**5,10,15,20-Tetrakis[( $\omega$ -mercapto-*p*-hexoxy)phenyl]porphyrin, **2**.** Due to the less active C-Br group in this starting material, no complete conversion of C-Br to C-SH was observed even after prolonged heating under reflux (estimated as 75% conversion from <sup>1</sup>H NMR). Recovery was 82%. <sup>1</sup>H NMR:  $\delta$  -2.77 (s, 2, NH), 1.40 (t, 4,  $J = 7.4$  Hz, SH), 2.61 (m, 8, CH<sub>2</sub>S), 4.24 (t, 8,  $J = 6$  Hz, -OCH<sub>2</sub>-), 7.26 (d, 8,  $J = 7.2$  Hz, H-3', 5'), 8.10 (d, 8,  $J = 7.2$  Hz, H-2', 6'), 1.90 (m, 8, -OCCH<sub>2</sub>-),  $\delta$  1.74 (m, 8, -CH<sub>2</sub>CSH), 1.62 (m, 16, -OCCCH<sub>2</sub>- and -CH<sub>2</sub>CCSH), 8.86 (s, 8,  $\beta$ -pyrrolic H). UV-vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  423 nm ( $\epsilon$   $4.4 \times 10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$ ), 519 ( $1.7 \times 10^4$ ), 556 ( $1.2 \times 10^4$ ), 593 ( $5.8 \times 10^3$ ), 653 ( $5.9 \times 10^3$ ).

**Interfacial Polymerization.** A 20 mL sample of an aqueous solution of copper acetate (ca. 0.005 M) was placed over 15 mL of **1** (ca. 0.0003 M) in chloroform in a beaker which was wrapped with aluminum foil. A film was obtained after a few hours of reaction at room temperature.

Thiol-free porphyrins were tested under the same condition. **3**, **4**, **5**, and **6** all gave negative results; i.e., no film was observed for time intervals up to 72 h.

Non-porphyrinthiols were also tested. None of *n*-C<sub>18</sub>-SH, H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>-SH, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SH, or HS(CH<sub>2</sub>)<sub>9</sub>SH formed a film at the interface, but some white slurry was seen near the interface for HS(CH<sub>2</sub>)<sub>9</sub>SH. When silver nitrate or mercury acetate was used instead of copper acetate in the aqueous layer, all of the above thiols produced a yellow to black slurry in the organic layer near the interface.

**Supercritical Drying.** The wet films, which contain solvent, collapse upon drying in air because of relatively large liquid-vapor interfacial forces which act to disrupt the delicate structure during an evaporative drying process. At the same time, porphyrin molecules have a tendency to stack, which will further promote collapse when solvents evaporate. Thus, it is an advantage to employ supercritical drying for these films.

The cleaned and acetone-soaked films were loaded between flat Teflon films in a porous glass drying cell which was full of acetone. The drying cell was transferred into a drying chamber having temperature and pressure control. Liquid CO<sub>2</sub> at about 1200 psi was then pumped into the drying chamber. Every 15 min the liquid was carefully vented while the CO<sub>2</sub> cylinder was kept open to the cell. After about 8–10 such exchanges, the drying chamber was heated to above the supercritical temperature and pressure, typically 40 °C and 1300 psi, and kept under these conditions for several minutes. The system was then vented and cooled to room temperature before the sample was removed. The films treated this way have significantly enhanced mechanical stability. There was no cracking or damage during drying. Elemental analysis (10 mm thick films): found (calcd for C<sub>50</sub>H<sub>36</sub>N<sub>4</sub>S<sub>4</sub>O<sub>2</sub>-Cu, which corresponds to M = Cu<sup>2+</sup> in Figure 1 plus one thioacetate group per porphyrin) C, 60.7 (65.5); H, 3.80 (3.93); N, 5.70 (5.11); S, 12.76 (13.98); Cu, 5.35 (6.94). Metal was difficult to remove completely from thicker (>10  $\mu\text{m}$ ) films.

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**Supporting Information Available:** Tables describing qualitative results of mercaptoporphyrin polymerization under various conditions (4 pages). See any current masthead page for ordering and Internet access instructions.

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