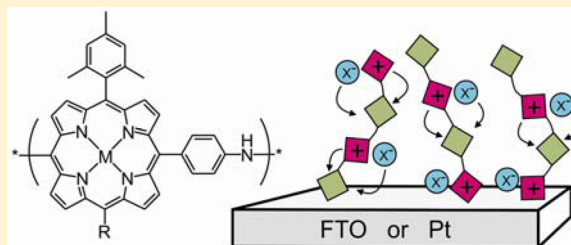


Hole Mobility in Porphyrin- and Porphyrin-Fullerene Electropolymers

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S Supporting Information

ABSTRACT: Charge transport within films of several new types of electropolymerized porphyrin and porphyrin-fullerene dyad polymers was studied in order to obtain information on the suitability of these organic semiconductors for applications in solar energy conversion, sensor devices, etc. The films, prepared by electropolymerization on a conductive substrate, were immersed in acetonitrile and studied using chronocoulometric and cyclic voltammetric electrochemical methods. The charge diffusion coefficients were found to be dependent upon the electrolytic medium. Electrolyte anion size plays a significant role in determining the rate of migration of charge through the polymers, demonstrating that migration of positive charge is accompanied by migration of negative counterions. Bulkier anions markedly decrease the charge diffusion coefficient. This strong dependence suggests that anion mobility is the rate-limiting process for diffusional charge transport within the porphyrin polymer films and that the largest rates obtained are lower limits to the intrinsic cation mobility. With electrolytes containing the relatively small perchlorate anion, charge diffusion coefficients of the porphyrin polymers were similar to those reported for polyaniline under acidic conditions. The charge diffusion coefficient for a zinc porphyrin polymer was found to decrease 2 orders of magnitude in the presence of pyridine, suggesting that metal-containing porphyrins polymer films may have sensor applications. Cation (hole) mobilities previously reported in the literature for porphyrin-containing polymers with chemical structures quite different from those investigated here were much smaller than those found for the polymers in this study, but further investigation suggests that the differences are due to choice of electrode size and material.



■ INTRODUCTION

Porphyrins are important carriers of redox potential in biology and chemistry. Their redox properties make them useful in molecular electronic applications. In part because porphyrins and their relatives absorb light strongly in the visible, they have uses in solar energy conversion, medicine, and photonics. The ability of metalated porphyrins to bind axial ligands leads to applications in sensing. Some of these functions require that porphyrins be oxidized or reduced and then transport charge to an electrode for collection. In principle, electrically conducting or semiconducting porphyrin polymers are particularly attractive for this application.

Recently, we reported the preparation and characterization of polymer films **1** and **2** formed by electropolymerization of *meso*-(4-aminophenyl)porphyrin or *meso*-(4-aminophenyl)-porphyrin-fullerene monomers (Figure 1).^{1,2} These films on electrodes were found to be *p*-type semiconductors that readily conduct positive charge (holes) to the attached electrode. The films absorb strongly in the visible and are of potential utility in solar energy conversion, sensors and related areas. There are a number of reports in the literature of electropolymerization of porphyrins on electrodes.^{1–16} However, polymers **1** and **2** differ significantly in structure from those produced previously. For example, in one widely studied class of polymers, the polymer chain is a substituted polyaniline, and the porphyrin macrocycles are present as pendant groups.^{3,9,10,14,17} Similarly, polymerization of vinyl groups^{4,11,12} and pyrroles^{4,18} with

porphyrins as pendant substituents has been reported. Porphyrins polymerized via linkage of two *meso*-aryl groups bearing amino¹⁶ or hydroxyl^{4,13,15} groups are also known. In none of these polymers is there a strong conjugated, conducting path that includes the porphyrin macrocycle. In some, the polymeric backbone is not conjugated, and charge transport must be by hopping between porphyrins. In others, the backbone may display conjugation, but the porphyrin macrocycles are simply pendant groups. Yet others feature two *meso*-aryl groups linked through chemical bonds to other atoms. Both of these aryl groups reside at steep dihedral angles to the porphyrin plane, and this limits conjugation at both ends of the diaryl system. With porphyrin polymer **1**, on the other hand, it is possible to draw resonance structures within the polymer similar to those reported for polyaniline that delocalize charge among more than one porphyrin unit.² The interporphyrin linkage contains only a single aryl ring, which limits conjugation enough to prevent undesirably large absorbance shifts to long wavelengths, but will still allow some conjugation between macrocyclic units. In addition, polymer **2** contains a fullerene moiety, which can in principle act as an electron-transporting unit. Given these unique features, we have investigated charge transport within films of

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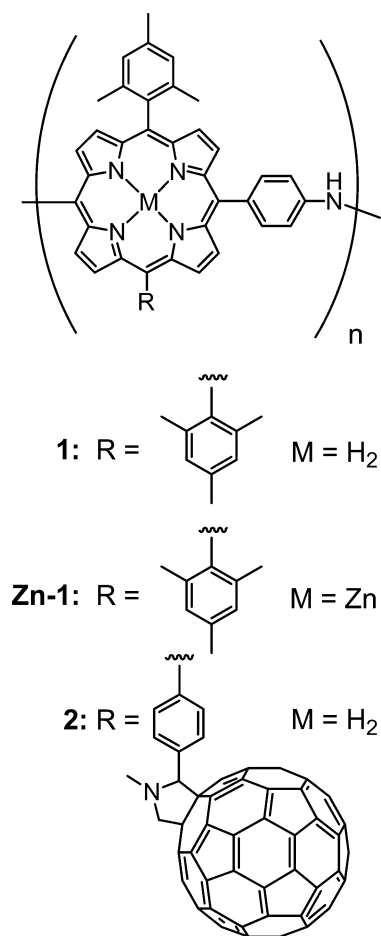


Figure 1. Structures of porphyrin electropolymer **1**, the zinc analog of **1**, **Zn-1**, and porphyrin-fullerene dyad electropolymer **2**.

these polymers using electrochemical techniques in order to compare their properties with those of previously reported porphyrin polymers and to begin to evaluate their suitability for applications in photovoltaics, sensors, and similar applications.

Charge transfer within the porphyrin polymer films is presumably via a self-exchange process where oxidized porphyrin macrocycles within the film can transfer their holes to other porphyrins in the same or nearby polymer chains. This transfer may occur either by “through-space” hopping to a porphyrin in the same or a different chain or via involvement of the partially conjugated linkage joining the porphyrins within a chain. In order to investigate these effects, films of the porphyrin polymers in Figure 1 were analyzed using electrochemical techniques to determine charge diffusion coefficients (D_{CT}). In addition, films of a previously reported porphyrin electropolymer, **3**,⁷ which was obtained from polymerization of monomer **4** (Figure 2), were studied for purposes of comparison of the new porphyrins with existing materials.

Although charge transport through a conducting polymer film will ultimately be limited by the maximum, intrinsic rate of electron movement between sites, transport may be further limited in some cases by diffusion of counterions through the film. The counteranions accompany the moving charges in order to maintain electrical neutrality. This counterion diffusion rate can depend on the size of the anion and the structure of the polymer film.^{19–22} This counterion effect can be very significant and important. For example, formation of the films by cationic electropolymerization using multiple voltammetric

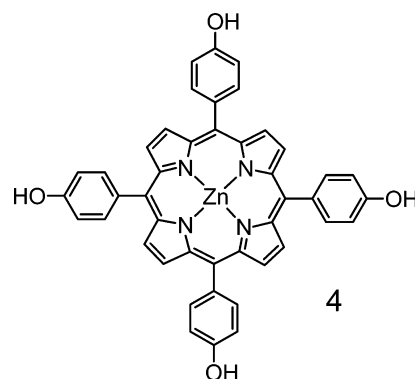


Figure 2. Structure of monomeric porphyrin **4**, electropolymerization of which gives porphyrin polymer **3**.⁷

cycles typically requires essentially complete oxidation of the existing film during each cycle before additional polymerization can take place at the ends of the growing chains because the polymer is more easily oxidized than the monomer in solution. Also, the applicability of semiconducting polymers in photovoltaics, light-emitting diodes, molecular electronics, and related areas depends in part upon the rate of charge transport through the film. In previous work, we observed that oxidation of a film of **1** in a solution containing hexafluorophosphate ions is accompanied by migration of hexafluorophosphate into the film.² Thus, our electrochemical studies were designed to evaluate any role of counteranion size on the measured D_{CT} values. In addition, metalated porphyrins such as **Zn-1** can bind anions or neutral species via coordination to the metal, and this might be expected to have an effect on charge transport as well. For this reason, **Zn-1** was included in the study.

EXPERIMENTAL SECTION

Materials. Acetonitrile (Omnisolv grade), lithium perchlorate, and sodium tetrakis-(3,5-bis-trifluoromethylphenyl)borate (NaBARF₄) were obtained from Alfa Aesar. Lithium bis-(trifluoromethane)sulfonamide (LiNTf₂), tetra-*n*-butylammonium *p*-toluene sulfonate (TBAPTS), tetra-*n*-butylammonium hexafluorophosphate, and 2,6-di-*tert*-butylpyridine were obtained from Sigma-Aldrich. Dichloromethane was distilled prior to use. All other solvents were commercially obtained and used as received.

Synthesis. Porphyrin monomers for preparation of **1** and **2** were synthesized according to previously established methods.^{1,2} The monomer necessary to prepare **Zn-1**, zinc 5-(4-aminophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin, was synthesized from 5-(4-aminophenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin² **1** by stirring a solution of the porphyrin overnight in 5:1 dichloromethane:methanol with 10 equivalents of zinc(II) acetate. The organic layer was washed with distilled water, saturated aqueous sodium bicarbonate, and again with distilled water, and the solvent was removed under reduced pressure. Tetra-*p*-hydroxyphenyl porphyrin was obtained from Sigma-Aldrich, and zinc was inserted according to Smeets et al.²³ to produce monomer **4**.

Electrochemistry. CH Instruments 650C or 760D electrochemical workstations were used in a 3-electrode experimental configuration with a platinum gauze counter electrode and pseudo Ag/AgCl reference electrode. All potentials were converted to SCE using ferrocene as an internal reference

(Fc⁺/Fc ~0.46 V vs SCE).²⁴ Compensation for *iR* voltage drop was applied when needed.

Monomers were electropolymerized on a 25 μm diameter platinum working electrode (CH Instruments) or a fluorinated tin oxide electrode (FTO, Hartford Glass, TEC-15) by cyclic voltammetry. Unless cited, solutions for polymerization consisted of the following: Monomer for **1**, 0.60 mM in acetonitrile containing 100 mM LiClO₄; monomer for **Zn-1**, 0.53 mM in acetonitrile:dimethylformamide 14:1 containing 100 mM LiClO₄; monomer for **2**, 0.22 mM in dichloromethane containing 100 mM tetra-*n*-butylammonium hexafluorophosphate; monomer for **3**, 1.1 mM in acetonitrile containing 100 mM LiClO₄ and 50 mM 2,6-di-*tert*-butylpyridine.⁷ Polymer films of various thicknesses were obtained by repeated CV cycles at 200 mV/s. The scans were anodic from 0.2 to ~1.3 V vs SCE for monomers giving **1** and **2** and from -0.1 to ~1.1 V vs SCE for monomers giving **Zn-1** and **3**.

Chronocoulometry was performed in acetonitrile containing 100 mM LiClO₄, lithium bis(trifluoromethane)sulfonamide (LiNTf₂), tetra-*n*-butylammonium *p*-toluenesulfonate (TBAPTS), or sodium tetrakis-(3,5-bis-trifluoromethylphenyl)-borate (NaBARF₄) as supporting electrolyte. Chronocoulometric experiments were performed with increasingly anodic step potentials using a 100 ms pulse applied from ~0.2 V vs SCE for **1**, **2**, and **3** and ~-0.1 V vs SCE for **Zn-1**.

Cyclic voltammetry of polymer films to determine D_{CT} was performed in acetonitrile containing 100 mM LiClO₄ as supporting electrolyte. Scan rates were increased in successive cycles until no anodic peak current could be determined.

RESULTS

Chronocoulometric Studies. One method for studying the migration of charge through a material on an electrode is chronocoulometry and application of the Cottrell equation,^{7,14,22,25–27} which is shown in integrated form as eq 1. Here, Q is the charge in coulombs passed through the film to or from the electrode at time t , n is the number of electrons per site involved in the redox process, F is the Faraday constant, A is the geometric electrode area, D_{CT} is the charge diffusion coefficient, and C is the concentration of oxidized species (mol/cm³).

$$Q = 2nFAD_{\text{CT}}^{1/2}C\pi^{-1/2}t^{1/2} \quad (1)$$

In the Cottrell-based experiments, a potential is applied to the electrode-immobilized semiconductive porphyrin material immersed in an electrolyte solution. The potential is stepped from a point where the material is in the neutral redox state to one in which the redox state is changed. In this case, the potential is made increasingly more oxidizing, thereby removing electrons from the porphyrin macrocycles. Upon the change in applied potential, charge flows within the film to convert some of the porphyrins to the new redox state, and this process is detected in the electrochemical cell as a function of time. The Q vs $t^{1/2}$ plot at each potential value consists of a linear region at earlier times, and then a leveling off as oxidation of the film is completed. Given the value of n , the Faraday constant, and the electrode area, the value of $D_{\text{CT}}^{1/2}C$ at each potential may be extracted from the slope of this linear area. At potentials where all porphyrins have been oxidized, the value of the diffusion constant D_{CT} may be calculated if the concentration of oxidized species is known from an independent measurement.

Films of porphyrin polymers **1**, **Zn-1**, **2**, and **3** were prepared on 25 μm diameter platinum microelectrodes as described in the Experimental Section, and cyclic voltammograms were obtained in acetonitrile containing 100 mM LiClO₄ (Figure 3).

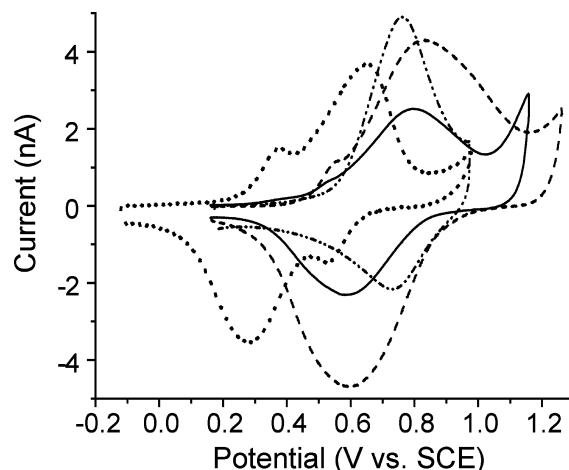


Figure 3. Cyclic voltammograms in acetonitrile of polymer films of **1** (solid), **2** (dashed), **Zn-1** (dotted), and **3** (dash-dot) grown on 25 μm platinum disc electrodes. The solution contained 100 mM LiClO₄, and the voltammograms were scanned at 200 mV/s.

The voltammograms for **1**, **Zn-1**, and **2** are consistent with those reported previously,^{1,2} and that for **3** is consistent with literature reports.⁷ Reversible behavior was observed for all films. Chronocoulometry was performed in acetonitrile containing 100 mM LiClO₄ as supporting electrolyte. The experiments were performed by applying an anodic potential step using a 100 ms pulse. The electrode potential before each voltage step was 0.2 V vs SCE for **1**, **2**, and **3**, and -0.1 V vs SCE for **Zn-1**. Values of $D_{\text{CT}}^{1/2}C$ were calculated at each potential as discussed above, and these were plotted on a logarithmic scale vs the potential after each voltage step as shown in Figure 4. When the polymers are fully oxidized at potentials beyond their anodic peaks shown in Figure 3, the values of $D_{\text{CT}}^{1/2}C$ plateau at a limiting value. At this plateau, D_{CT} can be determined if C is known. The film density and thus concentration of porphyrin sites has been reported for **1** (1.42 g/cm³) and **2** (1.56 g/cm³).^{1,2} At the plateau, it is assumed that all porphyrin sites are oxidized, and this allows calculation of D_{CT} . In the calculations, n was taken as 1 for **1**, **2**, and **Zn-1**, as it is assumed that each porphyrin undergoes 1-electron oxidation. For **3** a value of $n = 0.49$ was taken from the published data.⁷ It is assumed that the value of C for **Zn-1** is the same as that for **1**. The value of C for **3** has been reported (1.35 g/cm³).¹⁵ The results are shown in Table 1. The variability in D_{CT} measurements repeated on a single film type was $\leq \pm 30\%$.

Anion Effects on Polymer Charge Diffusion. As discussed above, the properties of the counteranion, and in particular its size, can limit the experimentally observed D_{CT} in some cases. In order to determine whether or not the values in Table 1 are limited in this way, the chronocoulometry experiment was performed on acetonitrile solutions of **1** using inert salts with anions of different sizes. The salts investigated were lithium perchlorate, tetra-*n*-butylammonium *p*-toluenesulfonate (TBAPTS), lithium bis(trifluoromethane)sulfonamide (LiNTf₂), and sodium tetrakis-(3,5-bis-trifluoromethylphenyl)borate (NaBARF₄).

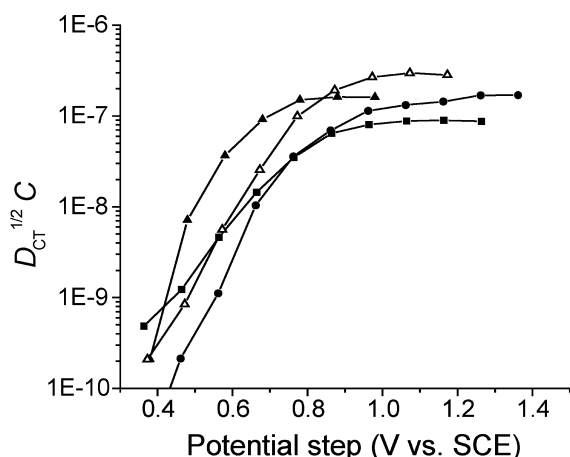


Figure 4. Chronocoulometric results. The $D_{CT}^{1/2}C$ values were obtained from eq 1 as described in the text and are plotted here on a logarithmic scale vs the applied potential after each potential step. Results are shown for **1** (solid squares), **2** (solid circles), **Zn-1** (solid triangles), and **3** (hollow triangles). For application of eq 1, $n = 1$ for **1**, **2**, and **Zn-1** and 0.49 for **3**.⁷ The potential before application of the voltage step was 0.2 V vs SCE for **1**, **2**, and **3** and -0.1 V vs SCE for **Zn-1**.

Table 1. Values of D_{CT} from Chronocoulometry with LiClO_4 as Electrolyte

polymer	limiting $D_{CT}^{1/2}C$ ($\text{mol cm}^{-2} \text{s}^{-1/2}$)	D_{CT} ($\text{cm}^2 \text{s}^{-1}$)
1	9.2×10^{-8}	1.7×10^{-9}
2	1.4×10^{-7}	1.7×10^{-8}
Zn-1	2.3×10^{-7}	1.0×10^{-8}
3	2.7×10^{-7}	2.3×10^{-8}

For these experiments, films of **1** were electrochemically prepared by a method identical to that used in the previous experiments, with lithium perchlorate as the supporting electrolyte. Chronocoulometry experiments were performed in acetonitrile solvent containing 100 mM electrolyte salt. The D_{CT} values obtained using eq 1 are shown in Table 2. The

Table 2. Values of D_{CT} for **1** from Chronocoulometry with Various Salts

electrolyte	limiting $D_{CT}^{1/2}C$ ($\text{mol cm}^{-2} \text{s}^{-1/2}$)	D_{CT} ($\text{cm}^2 \text{s}^{-1}$)
LiClO_4	9.2×10^{-8}	1.7×10^{-9}
TBAPTS	7.0×10^{-8}	9.8×10^{-10}
LiNTf_2	1.2×10^{-8}	2.9×10^{-11}
NaBArF_4^a	2.6×10^{-9}	1.4×10^{-12}

^aValues could only be determined using a very thin film.

variability in D_{CT} measurements repeated with a film/electrolyte combination was $\pm 50\%$. With NaBArF_4 , relatively thick samples similar to those used with the other salts did not conduct appreciably and essentially no current was detected. For this salt, $D_{CT}^{1/2}C$ could be obtained only on very thin films, and these films may contain defects allowing the electrolyte to directly approach the platinum electrode. Thus, the reported value is a maximum. It is clear from the table that anion size has a dramatic effect on D_{CT} .

The results in Table 2 suggest that charge diffusion is being limited by steric interference between the counteranion and the polymer framework. If counteranions cannot enter the voids in the film to neutralize charge, significant oxidation cannot take

place. Thus, not only counteranion size but also the structures of the pores within the polymer film will affect diffusion. We therefore investigated whether the charge transfer process would be affected if the film were electropolymerized using a salt with a larger anion as the electrolyte. Polymer **1** was electrosynthesized on a $25 \mu\text{m}$ platinum microelectrode using 100 mM LiNTf_2 as the electrolyte and then studied by chronocoulometry with 100 mM LiClO_4 or with 100 mM LiNTf_2 as the electrolyte in acetonitrile solvent as described above. Analysis of the chronocoulometric data yielded limiting $D_{CT}^{1/2}C$ values at full film oxidation of 1.4×10^{-7} and $1.5 \times 10^{-7} \text{ mol cm}^{-2} \text{s}^{-1/2}$ for ClO_4^- and NTf_2^- , respectively. This small discrepancy is within the experimental error, and if film concentrations C are comparable, the values of D_{CT} are approximately the same. This contrasts with the results given above where electropolymerization was carried out in the presence of the smaller perchlorate anion: $D_{CT}^{1/2}$ values of $9.2 \times 10^{-8} \text{ mol cm}^{-2} \text{s}^{-1/2}$ with a ClO_4^- anion and $1.2 \times 10^{-8} \text{ mol cm}^{-2} \text{s}^{-1/2}$ using the NTf_2^- electrolyte.

Effects of Pyridine Ligation. The zinc atoms of **Zn-1** can coordinate a wide range of Lewis bases. The effect of such ligation on hole mobility was probed using pyridine, which coordinates to the zinc atom.²⁸ A film of **Zn-1** on a platinum electrode was prepared using LiClO_4 as the electrolyte and analyzed by chronocoulometry in a 100 mM LiClO_4 electrolyte containing 3% v/v pyridine in acetonitrile. Analysis as described above gave a value for D_{CT} of $2.3 \times 10^{-10} \text{ cm}^2 \text{s}^{-1}$, which is much less than the value of $1.0 \times 10^{-8} \text{ cm}^2 \text{s}^{-1}$ found for this polymer under the same conditions without pyridine present. Thus, the introduction of pyridine drastically alters the electrical conductivity of the film (see the Supporting Information).

Charge Diffusion Coefficients from Cyclic Voltammetry. In the chronocoulometric study, **3** was included in order to compare the charge diffusion coefficients of the new polymers with those of a known porphyrin polymer. The reported⁷ value of D_{CT} for **3** is $8.5 \times 10^{-11} \text{ cm}^2 \text{s}^{-1}$, whereas that found in our studies (Table 1) is $2.3 \times 10^{-8} \text{ cm}^2 \text{s}^{-1}$. The difference is striking and suggests either that the polymer **3** prepared in our laboratories is very different from that reported earlier or that there is a significant difference in the method of measurement of diffusion coefficients in the two studies. In order to discover the reasons for this discrepancy, we undertook measurement of D_{CT} for **3** and the other porphyrin polymers under conditions more similar to those reported previously for **3**. In the previous study, electropolymerization was carried out on indium tin oxide (ITO) conductive glass electrodes rather than platinum microelectrodes, and D_{CT} was determined by cyclic voltammetry using a variation of the Randles-Sevcik equation. The Randles-Sevcik equation at 298 K (eq 2)²⁹ relates the peak current in the cyclic voltammogram, i_p

$$i_p = 2.69 \times 10^5 n^{3/2} A D_{CT}^{1/2} C \nu^{1/2} \quad (2)$$

to the potential scan rate, ν , where n is the number of electrons per porphyrin unit in the oxidation process, A is the electrode area, and C is the concentration of redox species in the film (mol/cm^3). The equation indicates that at sufficiently high scan rates, a plot of i_p vs $\nu^{1/2}$ should be linear, in which case an estimate of D_{CT} may be calculated from the slope of this region.

Figure 5 shows plots of i_p vs $\nu^{1/2}$ for polymers **1**, **2**, and **3** determined in acetonitrile solvent containing 100 mM LiClO_4 . In Figure 5a, the polymers were prepared on fluorinated tin

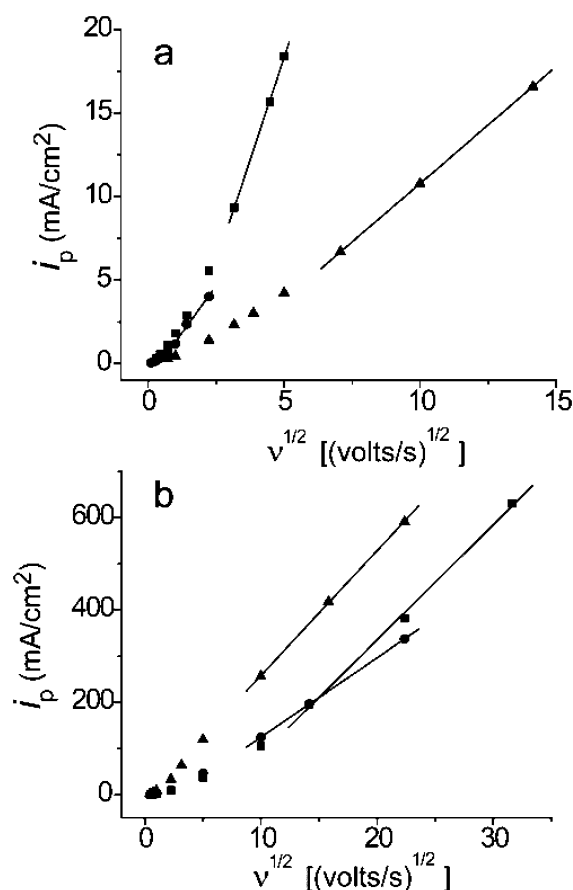


Figure 5. Dependence of maximum current density on scan rate: **1** (squares), **2** (circles), **3** (triangles). (a) Films deposited on a fluorinated tin oxide layer on glass. (b) Films deposited on 25 μm platinum electrodes. The lines are the linear least-squares best fits to the last three data points for each compound. The D_{CT} values in Table 3 were calculated from the slopes of these lines.

oxide conducting glass electrodes (polymer area 0.5–1.0 cm^2) as described in the Experimental Section. In Figure 5b, the polymers were prepared on 25 μm diameter platinum electrodes using the same solvents and supporting electrolytes.

The plots in Figure 5 become linear at the fastest scan rates, as expected, and the slope of each line was determined by a linear least-squares method using the final three data points. The slopes were used with eq 2 to calculate the D_{CT} values given in Table 3. The variability in D_{CT} measurements repeated on a single film type was $\leq \pm 50\%$. The values of n and C were the same as discussed above for the chronocoulometric approach.

DISCUSSION

The D_{CT} values for polymers **1**, **2**, and **3** were measured on platinum microelectrodes using both cyclic voltammetric and pulsed methods (eqs 1 and 2), and the results from the two methods are comparable, within experimental error (Tables 1

and 3). The D_{CT} values for all four polymers are roughly similar to one another and are comparable to the largest D_{CT} values reported by White and Murray¹⁴ for various metalloporphyrin electropolymers with structures different from those of **1**, **2**, and **Zn-1**. The D_{CT} values are also similar to or larger than those reported for a variety of other semiconductive organic polymers.^{22,26,30,31} Films of the well-known polyaniline were reported to have a D_{CT} value of $3.6 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ under aqueous acidic conditions as determined by rotating disk electrode methods.³² These results suggest that in this particular type of application, polymers **1**, **2**, and **Zn-1** display conductivities comparable to or better than other porphyrin polymers and organic polymers in general.

The question of whether the D_{CT} values measured here are indicative of the intrinsic hole transfer rate in the polymer or limited by the movement of counteranions through the film is addressed by the experiments with **1** using different supporting electrolytes (Table 3). The D_{CT} value for perchlorate is the largest, those for TBAPTS and LiNTf_2 are smaller and comparable, and that for NaBARF_4 the smallest. Although the effective size of anions in electrochemical experiments is difficult to quantify due to solvent effects, ion pairing, hydrogen bonding, shape anisotropy, etc.,^{33–36} the D_{CT} values in Table 3 indicate a decrease in charge mobility with increasing anion size. This suggests that the D_{CT} values reported here are reflective of the rate of migration of counteranions through voids in the polymer. This conclusion is bolstered by the observation that when **1** was electropolymerized in a solution containing LiNTf_2 rather than the smaller LiClO_4 , the limiting $D_{\text{CT}}^{1/2}C$ values measured for the resulting film with ClO_4^- and NTf_2^- were nearly identical. This suggests that the voids or pores in the film prepared with LiNTf_2 were larger than those in the film prepared with LiClO_4 , making the $D_{\text{CT}}^{1/2}C$ values less sensitive to the size of the anion in the range of sizes investigated. The limiting $D_{\text{CT}}^{1/2}C$ value obtained for perchlorate with the film polymerized with LiNTf_2 ($1.4 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-2}$) was larger than that obtained for perchlorate with the film polymerized with LiClO_4 ($9.2 \times 10^{-8} \text{ mol cm}^{-2} \text{ s}^{-2}$), suggesting that counteranion mobility is the limiting factor even when perchlorate is the anion.

Consistent with this conclusion, cyclic voltammetry of films of **1** on both the platinum microelectrode and FTO showed a dramatic increase in peak separation as the scan rate increased, regardless of the substrate (Supporting Information). This is consistent with a high ionic resistance within the polymer and slow movement of anions required to stabilize the oxidized porphyrin macrocycles. Thus, it appears that the intrinsic hole mobility in the porphyrin polymers is limited by anion migration in all of the results reported here and that the fastest charge migration rates found are lower limits for the intrinsic rates.

Polymer **2** differs from **1** in that each porphyrin bears a fullerene moiety. These fullerenes are not oxidized in the range of potentials studied here. Table 1 reports that the charge diffusion coefficient for **2** is 10 times larger than that for **1**. Table 2 also shows a larger D_{CT} for **2** than for **1**, although the difference is somewhat smaller. These results suggest that during polymerization the relatively large fullerene moiety prevents the porphyrin chains from approaching one another as closely as they do in **1**, leading to a more open structure for the films of **2**. This facilitates penetration of the counteranions into the film, thereby increasing hole mobility.

Table 3. Values of D_{CT} from Cyclic Voltammetry

polymer	D_{CT} (Pt) ($\text{cm}^2 \text{ s}^{-1}$)	D_{CT} (FTO) ($\text{cm}^2 \text{ s}^{-1}$)
1	1.6×10^{-9}	4.2×10^{-11}
2	5.7×10^{-9}	3.5×10^{-11}
3	2.3×10^{-8}	7.1×10^{-11}

Turning to the results for the zinc polymer in Table 1, charge mobility for **Zn-1** was about 6 times greater than that for **1** itself. Although this difference is rather small, it may be the result of a more open pore structure for the zinc porphyrin polymer. Zinc porphyrins are 5-coordinate and will form complexes with Lewis bases. Even weak Lewis bases such as perchlorate are known to form complexes.³⁷ The presence of such complexes during the electropolymerization process may lead to less-dense packing of the porphyrin units in the polymer.

The results obtained for **Zn-1** with and without a stronger base, pyridine, in the electrolyte solution show that D_{CT} is over 40 times larger for the polymer without pyridine present. It seems likely that pyridine coordination in **Zn-1** partially fills the voids between polymer chains with relatively tightly bound ligands to zinc and therefore hinders movement of counteranions in the film. When pyridine is absent, counteranions may weakly bind to the zinc but can be readily displaced by other counteranions and thus migrate relatively freely through the polymer pores. In the presence of pyridine, counteranions cannot displace the strongly bound pyridine, and the number of viable diffusion pathways through the film is reduced.

The D_{CT} values obtained for films of **1**, **2**, and **3** prepared on FTO substrates are all much smaller than those measured on the platinum microelectrodes. This difference is likely due in part to the larger active surface area of the FTO electrode ($0.5\text{--}1.0\text{ cm}^2$) relative to that of the platinum microelectrode ($4.9 \times 10^{-6}\text{ cm}^2$). The orders of magnitude drop in electrode area bring a proportional decrease in electrochemical currents. The lower current makes the drop in applied potential due to current flow much smaller on the platinum microelectrode than on the FTO. Instrumental compensation for such drops (iR compensation) was incorporated into the experiments, but even a small percentage of uncompensated resistance can cause broadening in the voltammograms. This decreases the peak current values and gives artificially low values of D_{CT} from the Randles-Sevcik equation. To test this hypothesis, an experiment using a 1.6 mm-diameter platinum disk was performed and resulted in D_{CT} values intermediate between those from the FTO electrode and the platinum microelectrode. Thus, the platinum microelectrodes give a more accurate determination of D_{CT} due to the low currents obtained during the experiments.

In the earlier study⁷ on charge diffusion coefficients in **3** a lack of effect of changing the anion size on D_{CT} was noted, and it was concluded that the measured value reflected charge transport by hole hopping in the polymer, rather than counteranion diffusion. Clearly, D_{CT} in **1**, **2**, and **Zn-1** is limited by counteranion mobility, and the inherent hole mobility in these polymers is larger than the values in Tables 1–3.

CONCLUSION

For **1**, **2**, and **Zn-1**, charge mobility studies using chronocoulometry and cyclic voltammetry gave roughly similar values when polymers were formed electrochemically on platinum microelectrodes. The experiments using counteranions of various sizes show that the measured charge diffusion coefficients are limited by counteranion diffusion through the polymer and that intrinsic hopping rates of holes within the films are faster than those indicated in the tables. Small charge diffusion coefficients reported by others⁷ for **3** were found to be an artifact of their measurement on large electrodes, and

diffusion coefficients comparable to those found for **1**, **2**, and **Zn-1** were found for **3** on platinum microelectrodes. However, these measured mobilities for **3** may also be limited by counteranion diffusion. Given the results presented above, it is likely that hole mobilities in solvent-free films of porphyrin polymers and/or under conditions in which the entire film is not oxidized will be significantly different from the situation studied here, where the films are submerged in electrolyte and highly oxidized. Large charge mobilities are desirable for semiconducting polymer applications in photovoltaics and other photoelectric or photoelectrochemical devices, sensors, molecular electronics, etc. as they reduce the buildup of charge within the film during use and reduce the effects of processes competing with delivery of charge to electrodes. The fact that mobilities found here for the porphyrin polymers studies were as large or larger than those reported for other organic polymers suggests that the porphyrin polymers may be good candidates for such applications. In addition, the very large change in charge diffusion coefficient noted for **Zn-1** upon introduction of pyridine suggests that such polymers may have applications as chemical sensors. The diffusion coefficients measured for the porphyrin polymers are large enough that the use of such materials in sensor applications would be practical.

ASSOCIATED CONTENT

Supporting Information

Cyclic voltammetric results for **1** at various scan rates on FTO electrodes and on platinum microelectrodes and chronocoulometric results for **Zn-1** with and without pyridine. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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