

MOLECULAR COMPLEXES BETWEEN OCTAETHYLTETRATHIAPORPHYRIN DICATION AND ELECTRON DONORS: A SPECTROSCOPIC AND ELECTROCHEMICAL STUDY

ATIF MAHAMMED, MORDECAI RABINOVITZ AND ITAMAR WILLNER

Institute of Chemistry, Hebrew University of Jerusalem, Jerusalem 91904, Israel

AND

EMANUEL VOGEL AND MICHAEL POHL

Institut für Organische Chemie der Universität Köln, D-50939 Cologne, Germany

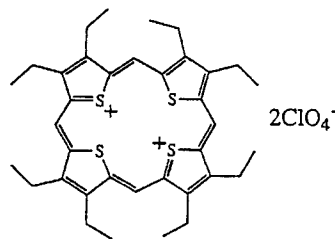
Octaethyltetrathiaporphyrin dication, OTP^{2+} , is electrochemically reduced by two successive electron-transfer processes to OPT^0 . OTP^{2+} forms intermolecular complexes with a series of π -donors. The association constants of the resulting complexes are controlled by the oxidation potentials of the π -donors and solvent properties. OTP^{2+} was incorporated into a Nafion membrane cast on a Pt electrode. Formation of OTP^{2+} - π -donor complexes in the polymer membrane was followed by electrochemical and spectroscopic means. The association constants of the OTP^{2+} - π -donor complexes in the Nafion membrane exhibit lower values than a homogeneous phase owing to the high ionic strength in the polyelectrolyte.

INTRODUCTION

Attractive intermolecular interactions between π -systems control the formation of diverse molecular complexes.^{1,2} Aggregation of organic dyes,³ stacking of aromatic molecules in crystals,⁴ host-guest complexes,⁵ intercalation of compounds in polymer media such as DNA⁶ or graphite⁷ and stabilization of the double helical DNA structure⁸ were attributed to attractive interactions between π -systems. Electron donor-acceptor interactions between π -systems provide an important driving force for the formation of molecular complexes.⁹ The formation of donor-acceptor complexes is controlled by the oxidation and reduction potentials of the components included in the complex, albeit other interactions such as attractive electrostatic forces could contribute to the stabilization of the resulting molecular complexes.¹⁰

Porphyrins provide macrocyclic π -conjugated systems, exhibiting poor electron-acceptor properties. Recent advances in organic synthesis accomplished the preparation of stable porphyrin analogues such as tetrathiaporphyrin dication,¹¹ tetraoxaporphyrin dication¹² and tetraoxaporphycene dication¹³ exhibiting aromatic character. These dications are expected to reveal enhanced electron-acceptor properties compared

with neutral porphyrins. In this paper, we describe the formation of molecular complexes of octaethyltetrathiaporphyrin dication, OTP^{2+} (**1**), with a series of π -donors; the formation of the complexes was followed by spectroscopic and electrochemical means.



(1)

EXPERIMENTAL

Absorption spectra were recorded on an Uvikon 860 spectrophotometer (Kontron) equipped with a thermostated cell. Cyclic voltammetric experiments were performed with a PAR Model 263 electroanalyser. The electrochemical cell consisted of a Pt voltammetric electrode (area 0.008 cm²) and a Pt wire as counter

electrode. Electrochemical measurements were performed in dichloromethane (CH_2Cl_2) or acetonitrile using $\text{Bu}_4\text{N}^+\text{BF}_4^-$ and $\text{Et}_4\text{N}^+\text{BF}_4^-$ as electrolytes, respectively. As reference electrodes Ag/AgCl or an SCE were applied. The reference electrodes were connected to the organic solvent working volume by a capillary. The reference electrodes were referenced separately to ferrocene solubilized in the respective organic solvent. Peak potentials were determined by complementary differential-pulse polarographic measurements. NMR spectra were recorded on an AMX 400 spectrometer (Bruker). All materials were obtained from commercial sources and of the highest purity available (Aldrich or Fluka).

Association constants of OTP^{2+} with the various π -donors in solution were determined spectroscopically. To a solution of OTP^{2+} in the respective solvent, increasing amounts of the respective π -donor were added. The resulting mixture was allowed to equilibrate for 10 min and the absorption spectra at different π -donor concentrations were recorded at 298 K. The difference spectra corresponding to the absorption spectra at any concentration of donor subtracted from the absorbance spectrum of pure OTP^{2+} solution were calculated. Association constants were derived from the absorbance differences ($\Delta\text{O.D.}$) and using the Benesi-Hildebrand relationship.

Nafion-modified electrodes were prepared by deposition of a 5% Nafion solution on the electrode surface ($20 \mu\text{m}^2$), followed by room-temperature evaporation of the solvent for *ca* 40 min. The resulting film thickness adsorbed on to the electrode was *ca* 1 μm .

OTP^{2+} was incorporated into the Nafion membrane by soaking the electrode in a deoxygenated CH_2Cl_2 solution of OTP^{2+} (1 mM) for 1 h. The resulting electrode was transferred into the electrochemical cell, which consisted of CH_2Cl_2 solution that contained tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte. No leakage of OTP^{2+} from the polyelectrolyte film to the solution could be detected over several hours. Cyclic voltammograms of OTP^{2+} incorporated in the Nafion film in the absence and presence of the π -donors (veratrole or 1,4-dimethoxybenzene) at different bulk concentrations in the electrolyte solution were recorded. The π -donor contents in the polyelectrolyte film were determined by integration of their anodic currents.

Spectroscopic measurements of OTP^{2+} incorporated in the Nafion membrane were performed by cutting a membrane, 0.018 cm thick, into 0.5×4 cm strips and incubating them in an OTP^{2+} - CH_2Cl_2 solution (1×10^{-3} M) for 1 h. The resulting membranes were washed with CH_2Cl_2 and positioned in a cuvette containing CH_2Cl_2 and the respective donor (veratrole or 1,4-dimethoxybenzene) (7×10^{-3} M). Absorption spectra were recorded at time intervals during treatment of the membrane with the π -donor solution.

RESULTS AND DISCUSSION

The cyclic voltammogram of OTP^{2+} is shown in Figure 1. It consists of two quasi-reversible waves at $E_{\text{pc}1} = +0.32$ V, $E_{\text{pc}2} = -0.04$ V. Although the peak-to-peak separation of the two waves is slightly higher than

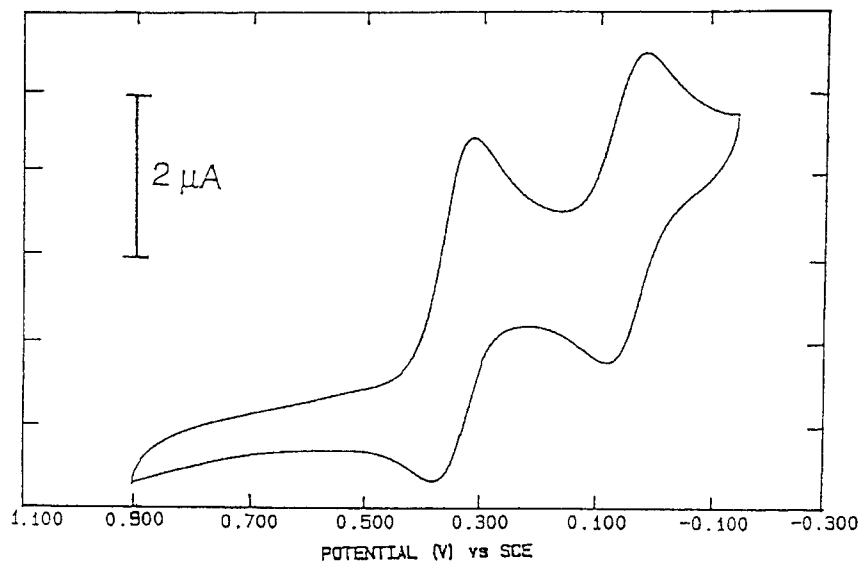
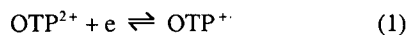


Figure 1. Cyclic voltammogram of OTP^{2+} (2×10^{-4} M) in CH_2Cl_2 . Tetrabutylammonium tetrafluoroborate (0.01 M) was used as electrolyte; scan rate = 100 mV s^{-1} .

for single electron-transfer reactions (*ca* 110 mV), RDE electrochemical measurements¹⁴ confirm that these redox reactions correspond to $1e^-$ processes:



The relatively positive reduction potential of OTP^{2+} indicates that the system could act as an electron acceptor and hence the formation of molecular complexes with π -donors seems feasible.

We examined the formation of complexes between

OTP^{2+} and a series of electron donors (Table 1). Upon addition of benzene in acetonitrile as solvent, a new charge-transfer (CT) band is observed at 740 nm as a result of the formation of the complex. A concerted decrease in the OTP^{2+} absorbance at $\lambda = 450$ nm, Figure 2, and increase in the CT absorbance at $\lambda = 740$ nm was observed on adding benzene. No spectral changes in the OTP^{2+} spectrum could be detected on addition of a non-polar solvent (hexane) to an OTP solution in acetonitrile. The formation of a single type of OTP^{2+} -benzene complex is supported by the appearance of isosbestic points. The association

Table 1. Association constants of OTP^{2+} - π -donor^a and donor-acceptor half-wave potential differences^b

Substrate	K_a (M^{-1})	$\text{Ln}[K_a$ (M^{-1})]	$\Delta E_{1/2}$ (V)
Hydroquinone	5904.0	8.683	0.52
Catechol	3457.8	8.150	0.74
1,4-Dimethoxybenzene	534.0	6.280	1.18
Veratrole	114.5	4.741	1.29
<i>p</i> -Xylene	22.85	3.130	1.61
Toluene	8.54	2.144	2.12
Benzene	22.81	3.127	2.22

^a Values in acetonitrile.

^b $\Delta E_{1/2} = E_{1/2}(\pi\text{-donor}) - E_{1/2}(\text{electron acceptor})$. $E_{1/2}$ for the electron acceptor, OTP^{2+} , corresponds to 0.28 V vs. SCE in acetonitrile. Values of $E_{1/2}(\pi\text{-donor})$ vs SCE in acetonitrile were taken from Ref. 23.

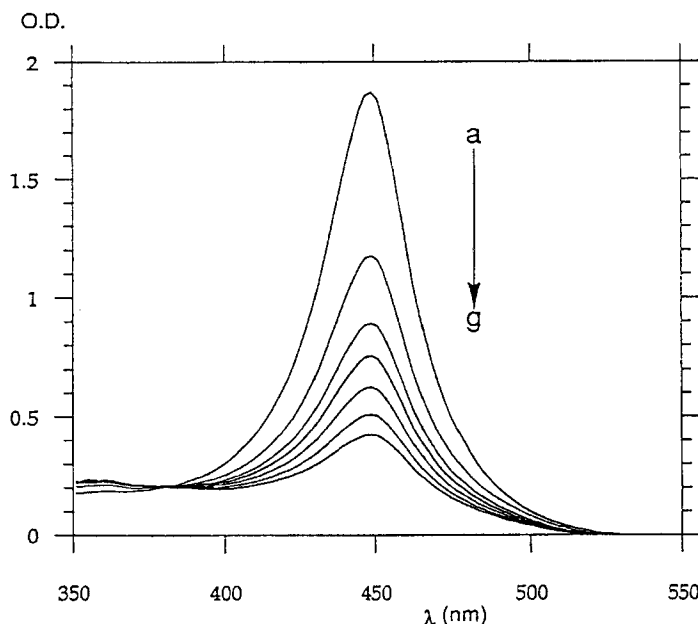
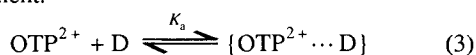


Figure 2. Absorption spectra of OTP^{2+} in acetonitrile (2.8×10^{-5} M) at different concentrations of benzene: (a) 0; (b) 0.037; (c) 0.075; (d) 0.11; (e) 0.15; (f) 0.30; (g) 0.52 M

constant (K_a) of the complex [equation (3)] was calculated using the Benesi–Hildebrand relationship¹⁵ [equation (4)], which assumes the formation of a 1:1 complex, where $\Delta O.D.$ is the difference in the absorbance of the complex and the free electron acceptor at any analytical concentrations of $[OTP^{2+}]_0$ and electron donor, $[D]_0$, respectively, and $\Delta\epsilon$ is the difference in the extinction coefficient of the complex and free electron acceptor at the wavelength of absorbance measurement.



$$[OTP^{2+}]_0[D]_0/\Delta O.D. = 1/(K_a\Delta\epsilon) + ([OTP^{2+}]_0 + [D]_0)/\Delta\epsilon \quad (4)$$

Figure 3 shows the expression for the spectral changes of OTP^{2+} on addition of benzene in terms of equation (4). The extracted association constant corresponds to $K_a = 22.81 \text{ M}^{-1}$. Analysis of the built-up CT band, $\lambda = 740 \text{ nm}$, by equation (4) gave an association constant of similar value.

NMR studies revealed that the spectral changes of OTP^{2+} on addition of the electron donors indeed correspond to the formation of intermolecular complexes and do not represent any degradation or chemical reaction of OTP^{2+} . We examined the ^1H NMR spectra of OTP^{2+} on addition of 1,4-dimethoxybenzene in a CD_3CN solution. We found that the proton chemical shifts of OTP^{2+} and of the π -donor are influenced (shifted) as a result of the formation of the intermolecular complex, but the pattern of OTP^{2+} bands is not changed. In a CD_3CN solution consisting of OTP^{2+}

(3.7 mM) and 1,4-dimethoxybenzene (29 mM), we found the following shifts in the ^1H NMR bands: for OTP^{2+} , H_{meso} $\Delta\delta = -0.003 \text{ ppm}$, CH_2 $\Delta\delta = -0.002 \text{ ppm}$ and CH_3 $\Delta\delta = -0.007 \text{ ppm}$. For the π -donor, $\text{H}_{\text{aromatic}}$ $\Delta\delta = 0.015 \text{ ppm}$ and CH_3 $\Delta\delta = 0.009 \text{ ppm}$. The shifts in the ^1H NMR bands are sensitive to the concentration of the π -donor; as the concentration of the π -donor is increased, the $\Delta\delta$ values become larger. The fact that the protons associated with the π -donor are shifted upfield whereas those of OTP^{2+} are shifted downfield suggests that stacking of the π -donor above the OTP^{2+} plane takes place. The changes in the chemical shifts of the π -donor and OTP^{2+} on formation of the intermolecular complex are, however, small in magnitude. As the association constant of OTP^{2+} to 1,4-dimethoxybenzene is low, $K_a = 534 \text{ M}^{-1}$ (see below), averaging of the ^1H NMR signals of the free and bound π -donor gives rise to small $\Delta\delta$ values. Owing to these small changes in $\Delta\delta$ and the limited amounts of OTP^{2+} , quantitative determination of K_a by ^1H NMR spectroscopy for OTP^{2+} and the series of π -donors was difficult and the association constants were followed by absorption spectroscopy.

The derived values of the association constants of OTP^{2+} and the series of electron donors are summarized in Table 1, where the oxidation potentials of the electron donors are also detailed. Evidently, as the oxidation potential of the electron donor decreases, the association constant of the OTP^{2+} -donor complex increases. That is, the resulting OTP^{2+} complex exhibits higher stability as the oxidation of the encounter electron donor is thermodynamically favoured.

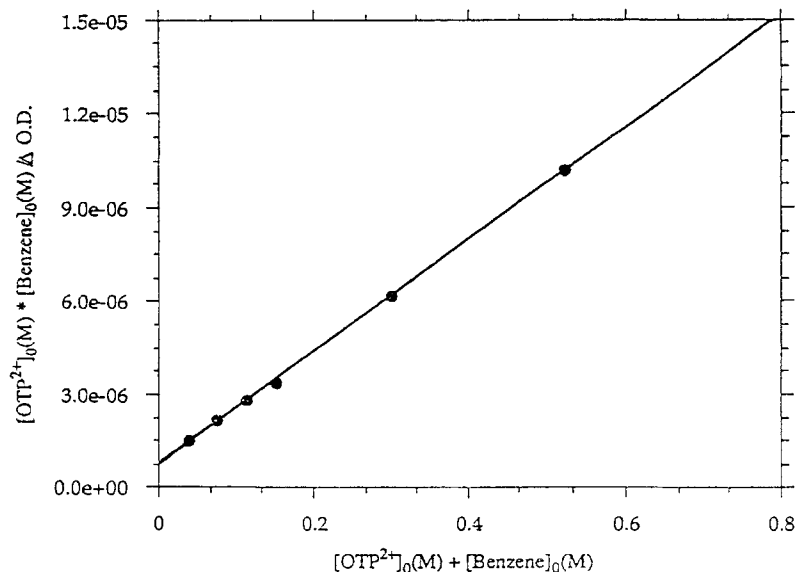


Figure 3. Benesi–Hildebrand plot for the association of benzene with OTP^{2+} , according to equation (4) and using data from Figure 2

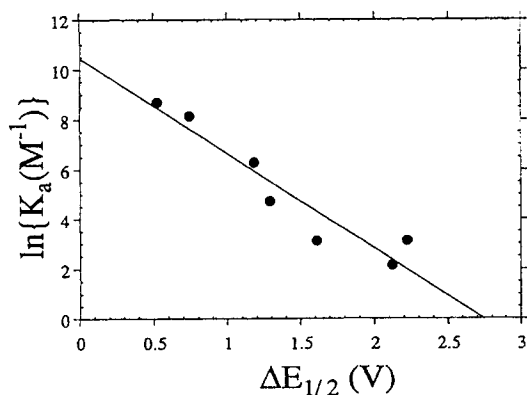
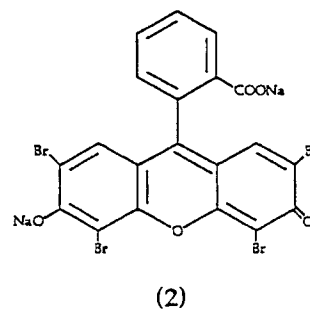


Figure 4. Correlation of $\text{OTP}^{2+}-\pi$ -donor association constants and the difference in half-wave potential of donor-acceptor components

Figure 4 shows the relationship between $\Delta E_{1/2} = [E_{1/2}(\text{donor}) - E_{1/2}(\text{OTP}^{2+})]$ and the logarithm of the association constants. A linear relationship is obtained, implying that the stability of the complexes is controlled by CT interactions in the assembly. Nonetheless, when the electron donor includes additional electrostatic interactions with OTP^{2+} , a synergistic effect on the association constant is observed. Eosin Y (2) includes, in addition to electron-donating properties ($E_{1/2} = 0.72$ V vs SCE in acetonitrile) also two negative charges. The association constant exhibits a substantially higher value, $K_a = 4.6 \times 10^5 \text{ M}^{-1}$.

The polarity of the solvent is expected to affect intermolecular complexes stabilized by CT interactions.⁹ An increase in the solvent dielectric constant or its dipole moment would stabilize the CT interactions. Table 2 summarizes the experimental values of the association constants (K_a) of OTP^{2+} with two electron donors, veratrole and 1,4-dimethoxybenzene, in a series of solvents. The association constants increase as the dipole moment (or dielectric constant) of the solvent increases. Hence a linear relationship between the association constants of OTP^{2+} with various electron



donors and their dependence on the solvent dipole moment is imperative so that CT interactions provide the driving force for stabilization of the $\text{OTP}^{2+}-\pi$ -donor complexes.

A further insight into the formation of CT complexes between OTP^{2+} and the electron donors was obtained by an electrochemical study, in which OTP^{2+} was immobilized into a Nafion membrane cast on an electrode.¹⁶ We selected the perfluorinated polyelectrolyte Nafion as the polymer matrix to characterize electrochemically the OTP^{2+} -donor complexes, since a Nafion cast film on an electrode provides an ionically conducting microenvironment that incorporates and retains hydrophobic, positively charged electroactive species such as OTP^{2+} .¹⁷ Furthermore, the transparency of Nafion films enables one to correlate the electrochemical behaviour of OTP^{2+} -donor complexes with their spectroscopic properties. Figure 5 shows the cyclic voltammogram of OTP^{2+} incorporated in the Nafion membrane cast on a Pt electrode. In contrast to the quasi-reversible stepwise reduction of OTP^{2+} in a homogeneous phase, the electrochemical reduction of OTP^{2+} in the Nafion membrane reveals only one reversible wave, $E_{pc} = 0.56$ V, corresponding to the $1e^-$ reduction of OTP^{2+} (Figure 5). The electrochemical response of OTP^{2+} in the Nafion film reveals several interesting features: the first reduction potential of OTP^{2+} [equation (1)] is shifted to positive potentials by ca 240 mV as compared with a homogeneous dichloromethane solution. This shift to positive potentials

Table 2. Association constants of $\text{OTP}^{2+}-\pi$ -donor complexation as a function of solvent polarity

Substrate	Solvent	K_a (M^{-1})	ϵ^a	μ^a
Veratrole	CH_3CN	114.5	36.2	3.92
	CH_2Cl_2	25.72	8.9	1.60
	$\text{Cl}_2\text{CHCHCl}_2$	0.35	8.2	1.32
1,4-Dimethoxybenzene	CH_3CN	534.0		
	CH_2Cl_2	56.8		
	$\text{Cl}_2\text{CHCHCl}_2$	0.54		

^a Taken from Ref. 24.

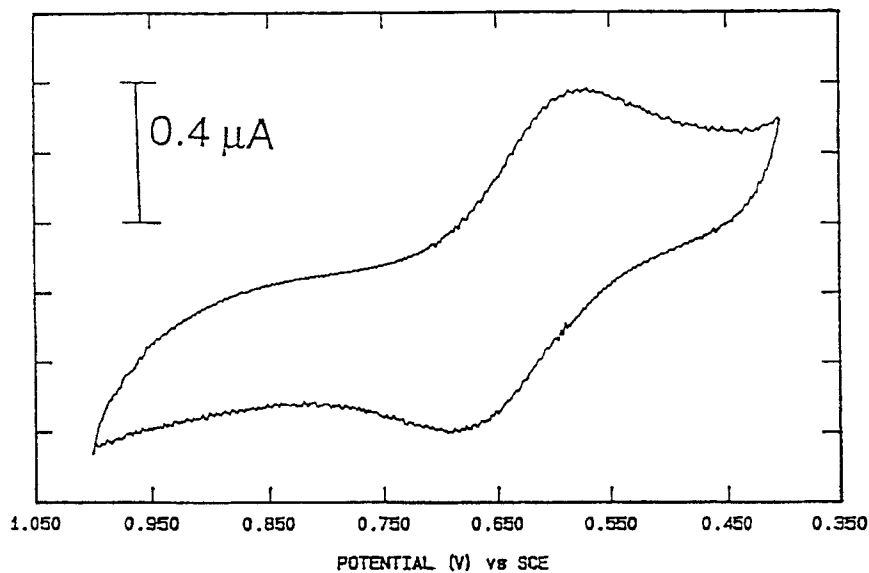


Figure 5. Cyclic voltammograms of OTP^{2+} incorporated in the Nafion membrane cast on a Pt electrode. Potential range 1–0.4 V. The experiment was performed in CH_2Cl_2 , with tetrabutylammonium tetrafluoroborate (0.1 M) as electrolyte; scan rate = 100 mV s^{-1} .

might be attributed to the change in the medium polarity in the Nafion film, neutralization of OTP^{2+} by the Nafion film counter ions and steric distortion of non-planar OTP^{2+} to a planar configuration in the polyelectrolyte film.

The reversible first reduction wave of OTP^{2+} shows a large peak-to-peak separation, $E_{\text{pc}} - E_{\text{pa}} = 108 \text{ mV}$. Also the cathodic peak current (i_{pc}) is linearly dependent on the square root of the scan rate. These observations indicate that the voltammetric response is controlled by the diffusion of OTP^{2+} within the polyelectrolyte film. This suggests that electron transfer from the electrode to OTP^{2+} is slow, even though the thickness of the Nafion film is $1 \mu\text{m}$. The diffusion coefficient of OTP^{2+} in the Nafion film was determined by a potential-step chronoamperometric experiment [Figure 6(A)]. The diffusion coefficient was calculated from the graphical analysis of the current decay [Figure 6(B)], using equation (5), to give $D = (8.5 \pm 0.4) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$:

$$i = nFAD^{1/2}C/(\pi t)^{1/2} \quad (5)$$

A similar potential-step chronoamperometric experiment in a homogeneous dichloromethane solution revealed a diffusion coefficient corresponding to $D = (2.2 \pm 0.2) \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ for OTP^{2+} . The substantially lower diffusion coefficient of OTP^{2+} in the Nafion membrane suggests that the electrical interactions between the polyelectrolyte and OTP^{2+} limit diffusion of the electroactive species within the polymer. The electron transfer rate constant from OTP^{2+} to the electrode corresponds to $k_{\text{et}} = 2.93 \times 10^{-4} \text{ cm s}^{-1}$. By

assuming that all OTP^{2+} incorporated in the Nafion film communicates with the electrode, and by calculating the total charge associated with the reduction wave of OTP^{2+} , we estimate that the amount of OTP^{2+} incorporated in the polymer film corresponds to $0.43 \times 10^{-11} \text{ mol}$. The electrode surface area is 0.008 cm^2 and the polymer thickness is $1 \mu\text{m}$. Hence the volume of polymer film corresponds to $8 \times 10^{-7} \text{ cm}^3$ and the total number of polyelectrolyte sulphonated groups is $2.9 \times 10^{-8} \text{ equiv. cm}^{-2}$. We thus estimate that ca 4% of the Nafion anionic groups are electrostatically bound to OTP^{2+} .

The cyclic voltammograms of the Nafion cast electrode that includes OTP^{2+} were recorded in the presence of various concentrations of 1,4-dimethoxybenzene or veratrole. In these experiments, the Nafion membrane is fully loaded with OTP^{2+} . Under these conditions, ca $5.2 \times 10^{-11} \text{ mol}$ of OTP^{2+} are associated with the membrane and ca 45% of the polymer anionic groups are neutralized by OTP^{2+} . Figure 7 shows the voltammogram of OTP^{2+} in the presence of different concentrations of veratrole. The peak potential is negatively shifted as the concentration of the electron donor increases. Figure 8 shows the change in half-wave potential of OTP^{2+} as a function of 1,4-dimethoxybenzene and veratrole concentrations. The curves reveal a saturation profile. These results are consistent with a complexation process of the respective electron donors to polymer-incorporated OTP^{2+} (Scheme 1). The negative shifts in the half-wave potentials of OTP^{2+} are attributed to association of the

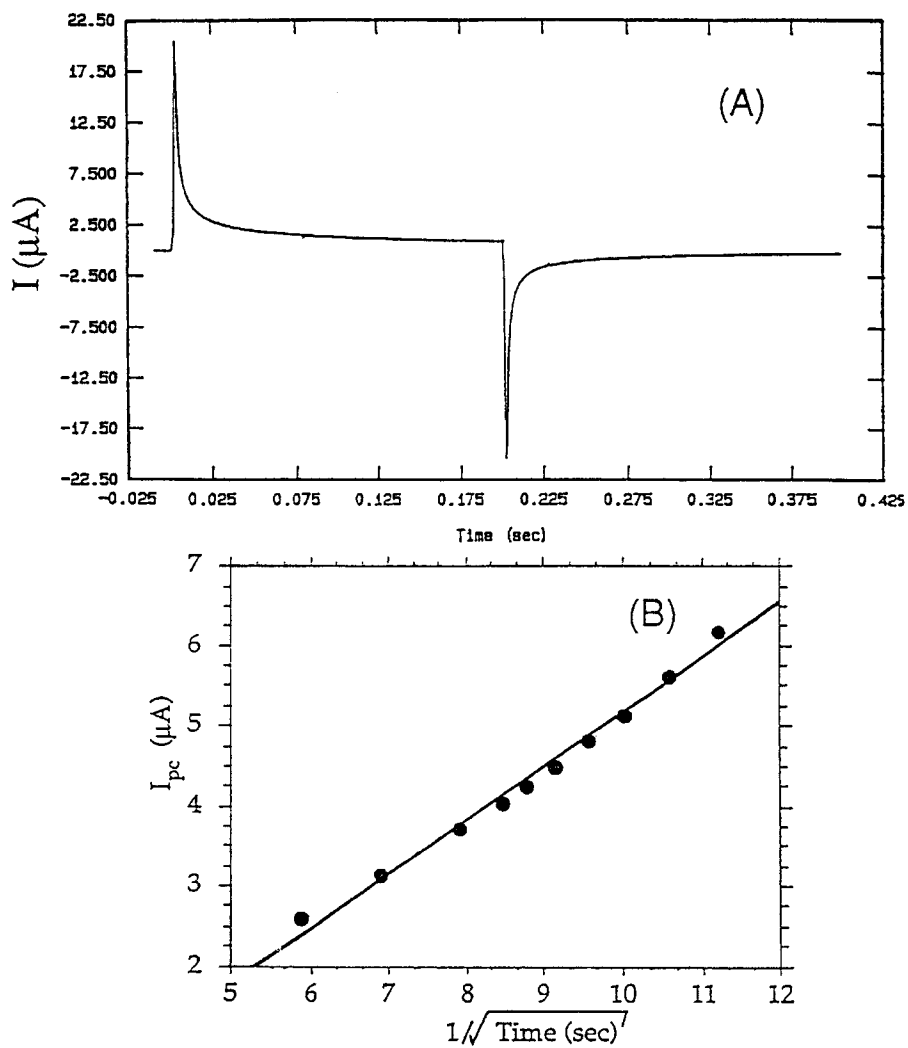


Figure 6. (A) Chronoamperometric current vs time for OTP^{2+} incorporated in the Pt-Nafion membrane in CH_2Cl_2 , with tetrabutylammonium tetrafluoroborate (0.1 M) as electrolyte. The potential step applied was from 0.8 to 0.5 V and back. (B) Cottrell plot (I vs $t^{1/2}$) for the current transient shown in (A)

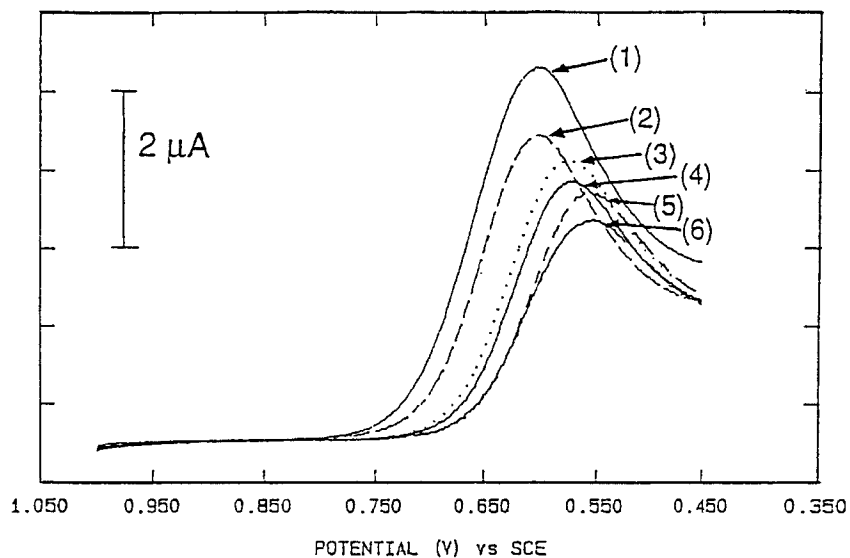


Figure 7. Linear-sweep voltammograms of OTP^{2+} incorporated in the Pt-Nafion electrode in the presence of different concentrations of veratrole: (1) 0; (2) 4×10^{-3} ; (3) 8×10^{-3} ; (4) 1.2×10^{-2} ; (5) 1.6×10^{-2} ; (6) 2×10^{-2} M. All experiments were performed in CH_2Cl_2 , with tetrabutylammonium tetrafluoroborate (0.1 M) as electrolyte. Scan rate = 100 mV s^{-1}

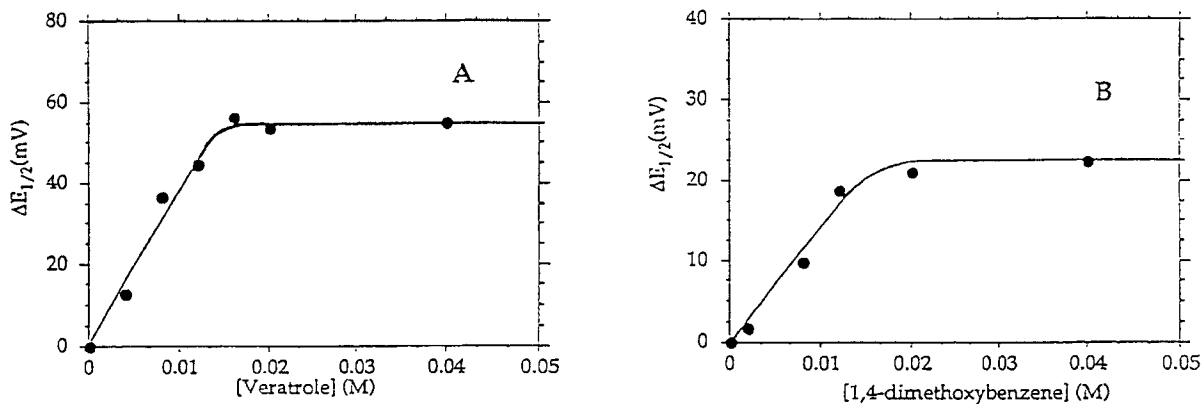
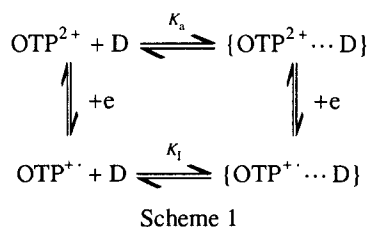


Figure 8. Changes in the $\text{OTP}^{2+}/\text{OTP}^+$ half-wave potential as a function of π -donor concentrations in the electrolyte solutions: (A) veratrole and (B) 1,4-dimethoxybenzene, as π -donors



donors, whereby the reduction of OTP^{2+} is thermodynamically less favoured. The association constant of an electroactive species that forms a complex with a donor compound according to Scheme 1 is given by equation (6):

$$\Delta E_{1/2} = E_{1/2}^{\text{Free}} - E_{1/2} = \frac{RT}{nF} \ln \left(\frac{1 + K_a[\text{D}]}{1 + K_1[\text{D}]} \right) \quad (6)$$

where $E_{1/2}^{\text{Free}}$ and $E_{1/2}$ represent the half-wave potentials of the electroactive species in the absence of donor and in the presence of the donor, respectively, and $[\text{D}]$ is the concentration of the electron donor in the polymer membrane. K_a and K_1 are the association constants of the electroactive species in the two redox states.¹⁸ As the association constant of the donors to the reduced acceptor can be assumed¹⁹ to be negligibly small, $K_1 \approx 0$, equation (6) can be rearranged in terms of equation (7):

$$\Delta E_{1/2} = \frac{RT}{nF} \ln(1 + K_a[\text{D}]) \quad (7)$$

Figure 8 shows graphically the dependence of $\Delta E_{1/2}$ of OTP^{2+} on the bulk concentration of veratrole and 1,4-dimethoxybenzene. For 1,4-dimethoxybenzene, $\Delta E_{1/2}$ of OTP^{2+} increases up to a bulk concentration of *ca* 2.2×10^{-2} M and then levels off to a constant value. For veratrole, $\Delta E_{1/2}$ increases up to a bulk concentration corresponding to *ca* 1.8×10^{-2} M. The saturated values of $\Delta E_{1/2}$ are consistent with the complete complexation of OTP^{2+} within the polymer.

Figure 9 shows the linear relationship of $\Delta E_{1/2}$ and the bulk concentration of electron-donor according to Equation (8) and the suggested model of complexation within the polymer.

Further quantitative determination of the association constants of OTP^{2+} with veratrole and 1,4-dimethoxybenzene in the Nafion film, according to this model, can be achieved by following the oxidation waves of the electron donor incorporated in the polyelectrolyte film. Figure 10 shows the anodic currents associated with the oxidation of veratrole in the Nafion film at different bulk concentration of the electron donor. By integration of the anodic peaks, the charge associated with the oxidation of the π -donor was estimated, and the total concentration of the π -donor in the Nafion membrane

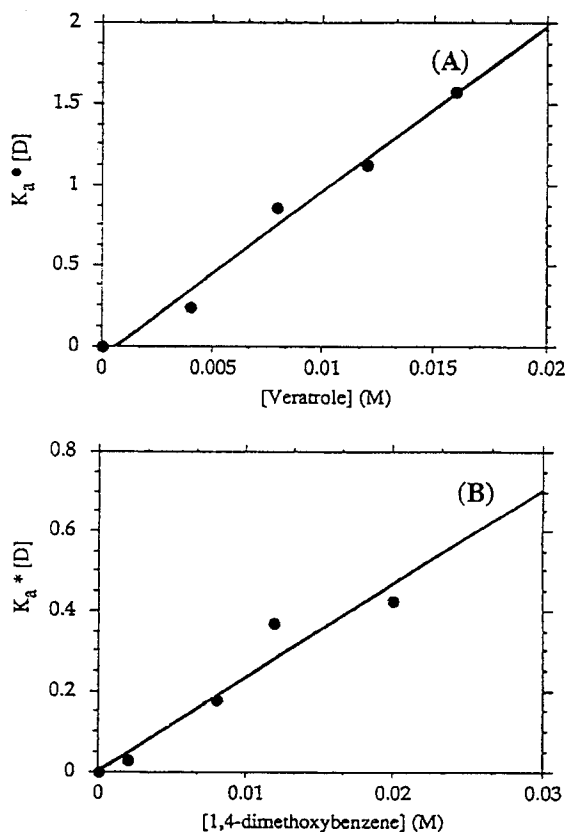


Figure 9. Plots of the product $K_a[\text{D}]$ as a function of π -donor concentrations in the bulk electrolyte solution, according to equation (7): (A) for veratrole and (B) for 1,4-dimethoxybenzene

was determined. Equation (7) is rearranged in terms of equation (8):

$$\Delta E_{1/2} = \frac{RT}{nF} \ln \left(1 + \frac{[\{\text{A} \cdots \text{D}\}]}{[\text{A}]_0 - [\{\text{A} \cdots \text{D}\}]} \right) \quad (8)$$

where $[\{\text{A} \cdots \text{D}\}]$ and $[\text{A}]_0$ correspond to the concentration of the complex and total concentration of OTP^{2+} in the Nafion film. By integration of the cathodic peaks provided in Figure 6 and using the $\Delta E_{1/2}$ values, the concentrations of the complex $[\{\text{A} \cdots \text{D}\}]$, at each bulk concentration of the donors, was determined. From these data, and realizing that the concentration of free donor in the Nafion film corresponds to $[\text{D}]_0 - [\{\text{A} \cdots \text{D}\}]$, the association constants of veratrole and 1,4-dimethoxybenzene to OTP^{2+} are $K_a = 3.13$ and 8.27 M^{-1} , respectively. We realize that the trend in the value of the association constants, observed in the homogeneous phase, is preserved in the Nafion membrane. That is, 1,4-dimethoxybenzene has a *ca* 2.5-fold

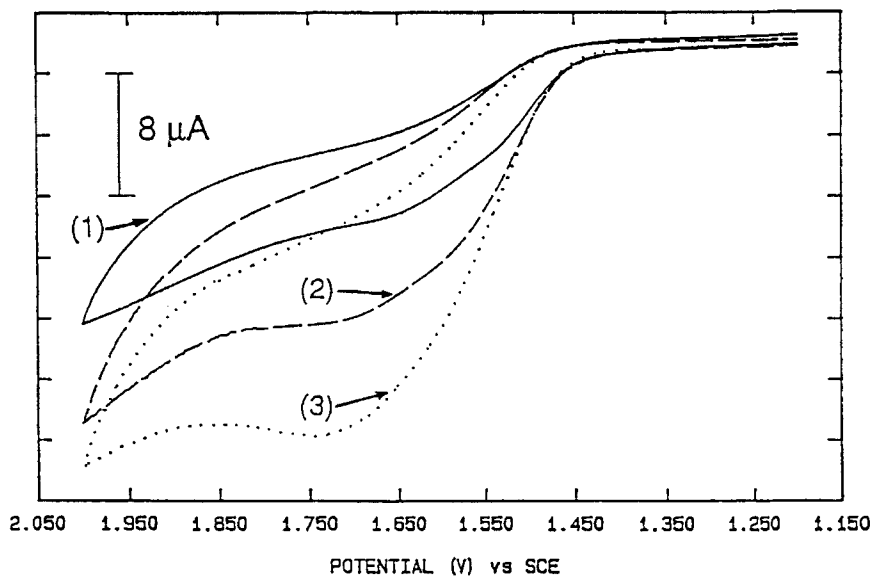


Figure 10. Cyclic voltammograms of veratrole incorporated in the OTP^{2+} -Pt-Nafion electrode at different bulk concentrations of veratrole in the electrolyte solution: (1) 4×10^{-3} ; (2) 8×10^{-3} ; (3) 1.2×10^{-3} M. Scan rate for all experiments = 100 mV s^{-1}

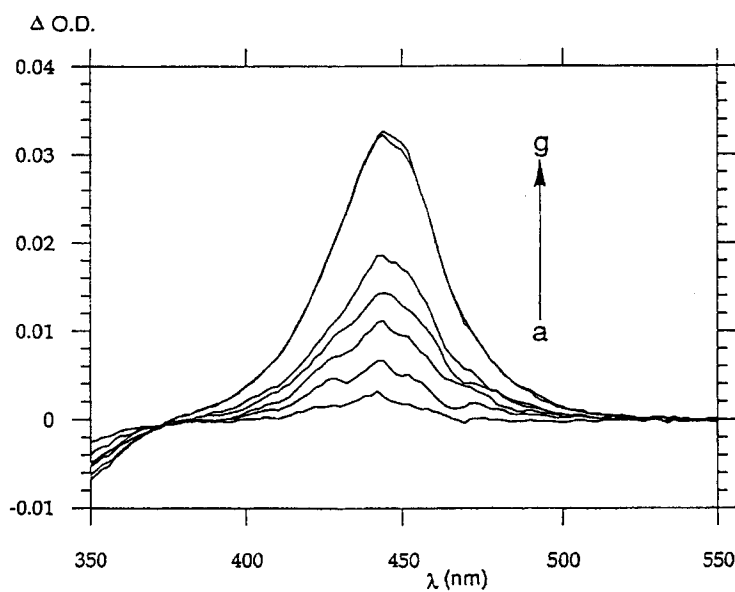


Figure 11. Difference absorbance spectra (spectrum of complex subtracted from the spectrum of OTP^{2+}) of OTP^{2+} incorporated in a Nafion membrane at time intervals during treatment with veratrole (7×10^{-3} M) in CH_2Cl_2 solution: (a) 4; (b) 8; (c) 12; (d) 16; (e) 21; (f) 53; (g) 67 min

higher association constant. Nonetheless, the values of the association constants for the intermolecular OTP^{2+} - π -donor complexes are lower in the Nafion film as compared with the homogeneous CH_2Cl_2 solution. This is rationalized in terms of the high ionic strength in the polyelectrolyte film, which weakens the stabilizing CT interactions.

Further support for the formation of OTP^{2+} - π -donor complexes in the Nafion membrane was obtained spectroscopically. The absorption spectrum of OTP^{2+} in the polymer is similar to that in CH_2Cl_2 solution. Treatment of the OTP^{2+} -loaded Nafion film with a CH_2Cl_2 solution of 1,4-dimethoxybenzene (7×10^{-3} M) or veratrole (7×10^{-3} M) results in time-dependent spectral changes in the absorption band of OTP^{2+} , consistent with the formation of intermolecular complexes. Figure 11 shows the difference spectra of the OTP^{2+} absorption band, $\lambda = 350$ – 550 nm, at different time intervals on treatment with a veratrole solution (7×10^{-3} M). The absorption band decreases in intensity, and the formation of an isosbestic point is visible. In contrast to a homogeneous phase, where the absorption changes of OTP^{2+} on addition of the π -donor are instantaneous, the spectral changes of OTP^{2+} in the Nafion film are time dependent. The absorption spectra reach a constant value after treatment of the OTP^{2+} -loaded film for ca 40 min with the π -donor solution. The time-dependent spectral changes of OTP^{2+} reflect the equilibration time constant of the π -donor between the bulk solution and the polyelectrolyte phase. These results imply that OTP^{2+} incorporated in the Nafion membrane forms a CT intermolecular complex with the solution solubilized π -donor.

CONCLUSIONS

We find that octaethyltetrathiaporphyrin dication, OTP^{2+} , forms intermolecular complexes with π -donors. The increase in the association constants of the complexes as a function of π -donor oxidation potentials and solvent dipole moment suggest that CT interactions are the major driving force for the stabilization of OTP^{2+} complexes. CT complexes of porphyrins and metalloporphyrins are well documented in the literature.^{20,21} We have found that the thia analogues of porphyrin ligands exhibit similarly the ability to form CT complexes. Indeed, OTP^{2+} forms intermolecular CT complexes with porphyrins and metalloporphyrins.²²

The electrochemistry of OTP^{2+} was followed in a homogeneous CH_2Cl_2 solution and in a Nafion film cast-electrode configuration. We found that the polyelectrolyte affects the electrochemical and electronic properties of the porphyrin. The stability of OTP^{2+} in the Nafion film enabled us to follow the formation of intermolecular complexes with π -donors within the polymer by electrochemical and spectroscopic means.

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