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Electrochemically Induced Metalation of Polymeric Phthalocyanines

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Phthalocyanines (Pc's) have been of interest for many years and are used in a wide array of chemical[1] and materials[2] related processes as catalysts,[3] sensors,[4] and nonlinear optical devices.[1,2,5] Synthetic methods used to prepare both metallo (MPc) and nonmetallo (H$_2$Pc) phthalocyanines are extremely diverse and typically involve heating phthalonitrile[6] or related 1,3-diiminoisoindoline compounds[7] in the presence of either a templating transition metal salt or Li and Mg alkoxides.[8] These slow autocondensation reactions are generally carried out in high boiling solvents and result in the isolation of variable quantities of MPc or H$_2$Pc products after extensive purification.[6] Less frequently used methods of preparing MPc complexes involve the metalation of H$_2$Pc ligands with metal alkoxide complexes[9] in refluxing DMF and the electrolysis[10] of phthalonitrile in the presence of metal salts in ethanol.

During the course of our studies investigating the electrocatalytic properties of electropolymerizable tetraaminophthalocyanine (TAPc) compounds,[11,12] we have discovered a new way of metallating electropolymerized metal-free poly-H$_2$TAPc films by cyclic potential scanning in the presence of cobalt(II) salts. The resulting cobalt-exchanged poly-Co$_{\text{ex}}$TAPc films display spectroscopic and catalytic properties identical to films produced directly by the electropolymerization of CoTAPc.[11]

Tetraaminophthalocyanine (H$_2$TAPc) was synthesized by reducing tetranitrophthalocyanine[13] with aqueous Na$_2$S[14] according to the method of Achar *et al.*[15] The resulting blue-green solid is soluble in DMF and DMSO but generally insoluble in other common organic solvents and water. As with metallo-TAPc compounds,[11,16] H$_2$TAPc can be oxidatively electropolymerized in DMSO[17] or DMF solutions by repeatedly cycling between −0.20 and +0.90 V vs Ag/AgCl (see Supporting Information). Figure 1a illustrates typical changes observed in the UV−visible spectra of a thin film of poly-H$_2$TAPc coated on an indium−tin oxide ITO electrode at different applied potentials.[18] At 0.0 V the spectrum of the film resembles that of H$_2$TAPc dissolved in DMSO.[14] Several notable changes in the spectrum of poly-H$_2$TAPc films, however, are observed as the applied potential is made more cathodic. In particular, the E band initially centered at 342 nm is red shifted, while the Q-band initially centered at 748 nm increases in intensity and also is red shifted. Interestingly, the spectroelectrochemical behavior of poly-CoTAPc films[12,16] differs from that of poly-H$_2$TAPc films (Figure 1b) in that an additional peak is observed at 464 nm for poly-CoTAPc at −1.0 V. Guarr *et al.* have assigned this band to a Co(I)→TAPc metal-to-ligand charge-transfer transition.[16]

Figure 1c displays the spectrum of a cobalt-exchanged poly-H$_2$TAPc film (poly-Co$_{\text{ex}}$-TAPc) coated onto an ITO electrode. Metalation of the film is accomplished[10] by repeatedly cycling the poly-H$_2$TAPc coated electrode from +0.25 to −1.0 V vs Ag/AgCl in a degassed 0.1 M TBAP/DMSO solution containing either 10 mM CoCl$_2$ or 10 mM Co(ClO$_4$)$_2$ (see Supporting Information). Changes in the spectra of the cobalt-exchanged film at various potentials are virtually identical to those observed above for the poly-CoTAPc modified electrode, and the appearance of a band at 464 nm at −1.0 V appears to be diagnostic of the presence of CoTAPc in the polymer film. This result suggests that cobalt(II) ions in solution are not only penetrating the poly-TAPc film at potentials more negative than −0.7 V but are also incorporated into the phthalocyanine macrocycle producing poly-Co$_{\text{ex}}$TAPc.

To test this hypothesis, we poised a poly-H$_2$TAPc modified ITO electrode in a stirred degassed 0.1 M TBAP/DMSO solution containing 10 mM CoCl$_2$ at 0.0 V vs Ag/AgCl for ∼3 h. The spectroelectrochemical behavior of the film was then evaluated in a fresh 0.1 M TBAP/DMSO solution and found to be unchanged, confirming that no poly-Co$_{\text{ex}}$TAPc is formed at 0.0 V. In addition, no significant Co exchange was detected for the polymer coated electrode upon cycling between +0.25 and −0.60 V. However, for potential scans beyond −0.70 V, cobalt was found to readily exchange into the poly-H$_2$TAPc film and bond

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(13) Tetranitrophthalocyanine (H$_2$TNPc) was prepared by the method of Oliver and Smith[8] and likely exists as a mixture of positional isomers. The resulting blue-green mixture was washed repeatedly with water and acetone; yield 55%. Anal. Calcd for C$_{32}$ H$_{14}$N$_{12}$ O$_8$·C$_4$H$_{10}$O: C, 56.25; H, 3.10; N, 21.90. Found: C, 56.76; H, 2.50; N, 21.96. UV−vis (DMSO); $\lambda_{\max} = 312$, 392 (sh), 654 (sh) 698, 714 nm. FTIR (DRIFTS, KBr, 4000−500 cm^{-1}): 3300 ($\nu_{\text{N−H}}$), 1525 ($\nu_{\text{C=N}}$), 1340($\nu_{\text{N−O}}$), 1138, 1109, 1019, 845 and 742.

(14) In a typical experiment, 0.10 g (0.14 mmol) of H$_2$TNPc was added to a flask containing 0.5 g (2 mmol) of Na$_2$S·9H$_2$O in 3 mL of degassed water. The mixture was refluxed for 5 h, cooled to room temperature and filtered producing a green precipitate. The H$_2$TAPC sample was washed with 1 M HCl, 1 M NaOH, and water until the pH of the final washings was neutral. Anal. Calcd for C$_{32}$ H$_{22}$ N$_{12}$·2H$_2$O: C, 64.64; H, 4.41; N, 28.25. Found: C, 64.25; H, 4.38; N, 28.00. UV−vis (DMSO); $\lambda_{\max} = 312$(sh), 342, 492, 446(sh), 672(sh), and 736 nm. FT-IR (DRIFTS, KBr, 4000−500 cm^{-1}): 3350−3200 ($\nu_{\text{N−H}}$), 1616 ($\nu_{\text{C=N}}$), 1500($\nu_{\text{C=C}}$), 1351, 1325, 1103, 1018, 823 and 748 cm^{-1}. ^{1}H NMR (DMSO-d_6, δ, ppm): 9.02 (m, 1H), 8.48 (m, 1H), 7.50 (m, 1H), and 6.55 (m, 2H).

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(17) H$_2$TAPc solutions (1 mM) in degassed DMSO (20 mL) containing 0.1 M TBAP generally were used in electropolymerization studies (see Supporting Information). H$_2$TAPC electropolymerizes at potentials >+0.60 V vs Ag/AgCl, whereas no film is formed at potentials less than +0.60 V. A scan rate of 150 mV/s was used during the electropolymerization process which was stopped after 50 cycles. The onset of film formation for CoTAPc occurs at ∼+0.80 V. Glassy carbon electrodes were cleaned and polished by the following method: sonication in DMF (5 min), washing with water, polishing with alumina, and sonication in water (5 min).

(18) Poly-H$_2$TAPc modified ITO electrodes were cycled 100 times at 150 mV/s in the presence of 10 mM Co(ClO$_4$)$_2$·6H$_2$O or CoCl$_2$ and the spectroelectrochemical behavior of the resulting films was evaluated using a HP 8452A diode array spectrophotometer and a BAS CV-1B potentiostat.

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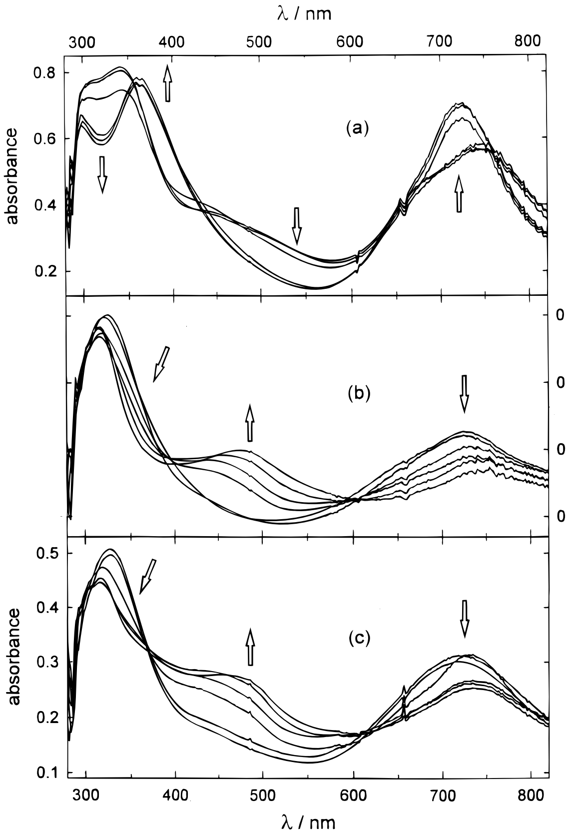

Figure 1. *In situ* UV−visible spectra at potentials from 0.00 to −1.25 V (0.25 V increments) in 0.1 M TBAP/DMSO solution for (a) poly-H_2TAPc, (b) poly-CoTAPc, and (c) poly Co_{ex}TAPc on ITO electrodes. Arrows denote direction of absorbance change with increasingly negative potential. Polymer films were made under standard conditions using 50 oxidation−reduction cycles (see Supporting Information and ref 18).

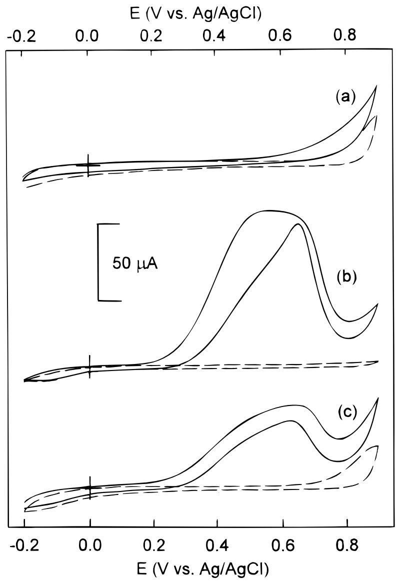

Figure 2. Cyclic voltammetry for (a) poly-H_2TAPc, (b) poly-CoTAPc, and (c) poly-Co_{ex}TAPc modified glassy carbon electrodes in aqueous 0.1 M KH_2PO_4, with (solid line) and without (dashed line) 12 mM cysteine. Polymer films were made under standard conditions using 50 oxidation−reduction cycles (see Supporting Information and ref 18).

to the phthalocyanine ligands. The ionophoric behavior of poly-MTAPc films has been noted by others,[11a,b] and poly-H_2TAPc films appear to behave in a similar manner.

Both H_2TAPc and poly-H_2TAPc display two one-electron redox processes in DMSO at −0.72 and −1.26 V vs Ag/AgCl (Supporting Information). It appears that the cobalt-exchange process involving poly-H_2TAPc films occurs at potentials close to the first of these, which is thought to involve the reduction of the Pc ring.[12] At the present time, we speculate that the mechanism of metal incorporation into the polymer involves reduction of occluded Co^{II} ions to Co^{I} by the reduced poly-H_2TAPc film. The Co^{I} ions in turn are stabilized by coordination to the phthalocyanine macrocyclic ligands. Similar electrochemically mediated reduction of metal ions such as Pt in conducting polymers has been observed for poly-viologen[19] and poly-Ru-bipy[20] coated electrodes. However, in these studies the occluded metal ions were reduced completely to the metallic state and formed aggregates of pure metal trapped in the polymer films. Interestingly, for the latter complexes, the metal leaches readily from the films upon oxidation in strongly acidic or basic solution. Poly-Co_{ex}TAPc films, on the other hand, are stable in both 0.05 M H_2SO_4 and 0.1 M NaOH solutions. Furthermore, these films are able to catalyze the reduction of O_2 to H_2O_2 and H_2O, identical to poly-CoTAPc films, thus providing further evidence that the exchanged cobalt is bound to the phthalocyanine ligands of the polymer.

To further confirm the metalation of the macrocyclic ligands in poly-H_2TAPc films, we examined the propensity of poly-Co_{ex}TAPc modified electrodes to electrocatalytically oxidize cysteine. As shown in Figure 2a, no oxidation current is detected for cysteine using the poly-H_2TAPc coated electrode, whereas both poly-CoTAPc and poly-Co_{ex}TAPc coated electrodes demonstrate the shifted onset of oxidation and the anodic current during cathodic sweeping that is characteristic of cysteine oxidation electrocatalyzed by CoTAPc films.[11d] Thus, the presence of CoTAPc in the film is crucial to the catalytic activity.

We are presently examining the generality of this new electrochemically induced metal exchange process with poly-H_2TAPc and related poly-aminophenylporphyrin films to determine other metal ions which exchange into the polymer films. This approach offers several potential advantages in preparing chemically modified electrodes such as (i) control of the quantity and dispersion of the active metal species in the polymer, (ii) regeneration of metal depleted polymers, and iii) doping more than one metal into metal-free polymer films.

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Supporting Information Available: Description of the materials and methods of synthesis and characterization as well as cyclic voltammograms illustrating the electropolymerization, metal exchange, and stability of electrodes (12 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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