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Reversible Complexation of O_2 to (*meso*-Tetraphenylporphyrinato)cobalt(II) Plasma Polymer and Sublimed Films at Room Temperature

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Introduction

As a part of our overall program of synthesizing and characterizing metal-containing plasma polymers,[2] we have been investigating the incorporation of (*meso*-tetraphenylporphyrinato)cobalt(II) (CoTPP) into plasma polymer thin films for use as O_2 permselective membranes. Cobalt porphyrin systems have become increasingly important in the study of biological processes.[3] We have made a preliminary report of the reversible binding of O_2 to CoTPP in plasma polymer films at room temperature.[2g,h] CoTPP has been shown in the literature to reversibly bind O_2 in Ar matrices[4] and in solutions at low temperature (<200 K) when coordinated to axial bases such as 1-methylimidazole (1-MeIm).[5-7] ESR evidence for O_2 binding by CoTPP·1-MeIm has been detected at temperatures as high as 270 K.[8] We report here spectral evidence for the reversible binding of O_2 to CoTPP·1-MeIm at 298 K when prepared as a thin sublimed film and compare this evidence to that found for CoTPP incorporated into plasma polymer films.

Experimental Section

Thin plasma polymer film preparations were carried out in a continuous-flow, inductively coupled plasma reaction chamber described earlier.[2g,h] The bottom of the chamber was sealed to an aluminum base plate by means of an O-ring. A tantalum heating boat, inside the reactor, was connected to two copper wire terminals which passed through two ports in the base plate. Current to the copper terminals was regulated using a Variac. Two threaded ceramic plugs insulated the copper terminals from the base plate, and a series of Swagelok and Cajon-ultratorr fittings provided a vacuum-tight seal around the terminals. A molybdenum shield could be moved over the heating boat to prevent sublimation into the plasma and thereby provide precise deposition times.

The equipment used for plasma generation was a Tegal 300-W RF generator, operating at 13.56 MHz, with a matching network and a Bird Electronics Model 4410 wattmeter. Tantalum heating boats were purchased from R. D. Mathis Co. Infrared spectra were obtained using an Analect FX-6200 FTIR spectrophotometer. UV–vis spectra were obtained using a Beckman Acta III spectrophotometer. Pressure in the vacuum line was measured using an MKS Baratron differential pressure transducer with a 1-Torr pressure range.

O_2, N_2, and *trans*-2-butene (99.0%) were purchased from Linde Industrial Gases and used without further purification. 1-Methylimidazole (1-MeIm) (99%) was purchased from Aldrich Chemical Co. and distilled prior to use (198 °C). CoTPP (λ_{max} = 409 and 523 nm) was used as purchased from Strem Chemical Co. (Anal. Calcd for $C_{44}H_{28}N_4Co$: C, 78.68; H, 4.20; N, 8.34. Found: C, 78.96; H, 4.29; N, 8.40.)

Plasma polymer thin films were prepared as follows. CoTPP (ca. 100 mg) was added to the heating boat and the reactor sealed and evacuated. After the reactor had reached a constant base pressure (ca. 1 mTorr), *trans*-2-butene was introduced at the desired flow rate (0.5–0.6 cm^3/min) and CoTPP was heated in the tantalum heating boat. Both current and potential through the tantalum heating boat were monitored during polymerization and could be used to regulate the sublimation rate of the metal complex. When the desired sublimation rate (e.g. 1 (μg/cm^2)/min; the desired sublimation rate depends on the desired film loading) of the sample was achieved, the rf power supply was turned on (7–8-W rf power), initiating a glow discharge (plasma). The molybdenum shield was then removed, allowing the CoTPP to sublime into the plasma. CoTPP/*trans*-2-butene plasma polymer was allowed to deposit for several minutes (15–20 min). The amount of plasma polymer deposited ranged from 20 to 100 μg/cm^2. After the deposition period (15–20 min), the molybdenum shield was moved over the heating boat again and the plasma generator was turned off. Film samples prepared by the above method are referred to as plasma polymer films, while those prepared similarly but in the absence of plasma and of *trans*-2-butene are referred to as sublimed films.

Thin films were deposited onto NaCl windows and glass or quartz slides to obtain FTIR and UV–vis spectra, respectively, under a controlled atmosphere. Thin films prepared on NaCl windows were mounted in an IR gas cell (Buck Scientific) which could be purged with the desired gases or vapors. Spectra of the film samples were recorded under Ar and O_2 separately. The spectra were then recorded after exposing the films to 1-MeIm vapor by passing Ar through a bubbling tube containing 1-MeIm prior to entering the FTIR cell. The cell was then flushed with pure O_2 or Ar, and spectra were again recorded between 600 and 4200 cm^{-1} (3.8-cm^{-1} resolution). The removal of the 1-MeIm vapor was monitored spectroscopically, and flushing was continued until no further changes in IR spectra were detected. Background IR spectra of the pure gases were also recorded. Films on glass slides, used for UV–vis spectra, were placed in a UV–vis gas cell described earlier[9] and treated similarly to the samples in the IR cell.

Results and Discussion

Sublimed CoTPP Films. Infrared spectra of sublimed CoTPP films on NaCl matched those of nonsublimed CoTPP samples prepared as KBr disks, as well as published spectra.[4,10] This indicates retention of structure upon sublimation. Prior to exposure to 1-MeIm vapor, IR spectra of the films measured under O_2 were identical to those measured under N_2. After exposure to 1-MeIm vapor in an Ar stream and subsequent purging with pure Ar, IR spectra of the CoTPP sublimed films contained absorption bands associated with 1-MeIm, indicating the presence of 1-MeIm bound within the film. Subsequent exposure to O_2 at room temperature caused additional changes in IR spectra. As seen in Figure 1, absorption bands at 1143, 1103, and 1087 cm^{-1} are present in the spectrum recorded in O_2 but absent in the spectrum obtained under Ar. These absorption bands were not

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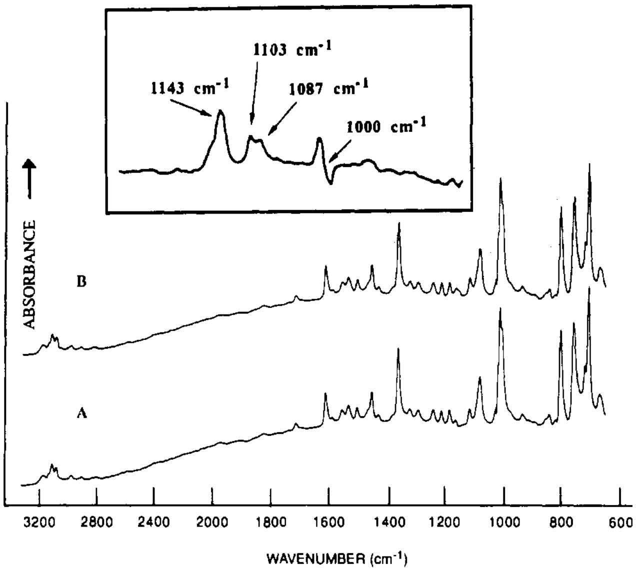

Figure 1. FTIR absorbance spectra of a CoTPP sublimed film (mass thickness = 75.27 μg/cm^2) exposed to (A) 1-MeIm-saturated Ar (1 atm, 30 min) and subsequent purging with Ar (1 atm, 15 h) and then (B) O_2 (1 atm, 30 min). The inset is a difference spectrum (B minus A) showing an expanded view of relevent peak positions.

present in background spectra of Ar or O_2. The changes in the IR spectrum due to O_2 were reversed by flushing the IR cell with Ar for 30 min. These spectral changes are indicative of reversible O_2 binding by the CoTPP·1-MeIm complex at room temperature.

UV–vis spectra of CoTPP sublimed films on quartz slides were also recorded at room temperature. These spectra exhibit λ_{max} values of 412, 530, and 612 nm. These values are similar to those in literature reports of toluene solution spectra of CoTPP in which λ_{max} values of 410 and 526 nm are observed[6,11] and indicate retention of structure upon sublimation. The band at 612 nm was very weak and it was difficult to assign it a λ_{max} value, but it has been attributed to trace chlorin impurities.[12] The treatment of these films with 1-MeIm vapor in a N_2 stream for 15 min caused the band at 530 nm to shift to 534 nm. Subsequent exposure to O_2 did not cause additional spectral changes. The change in the spectra due to 1-MeIm was reversed by heating the film to 130 °C under vacuum for 1 h. The spectral change due to exposure to 1-MeIm vapor suggests that 1-MeIm is coordinating to the cobalt center and that the inner coordination sphere is preserved upon sublimation.

The reversible IR spectral changes, observed during the interaction between sublimed CoTPP films (after exposure to 1-MeIm) and O_2, suggest that our CoTPP sublimed films reversibly bind O_2 at room temperature. The absorption bands in the IR spectrum of the sublimed films measured under O_2 at 1143, 1103, and 1087 cm^{-1} are all consistent with an O–O stretching frequency for O_2 bound to cobalt complexes.[13-15] The IR band at 1143 cm^{-1} is in agreement with the O–O IR stretching frequency for O_2 bound to the Co center of the CoTPP·1-MeIm complex (at 195 K), which is reported to be at 1142 cm^{-1}.[14]

Literature reports indicate that the CoTPP·1-MeIm complex has a very low affinity for O_2 at room temperature in solution.[7] In at least one case, however, ESR evidence for O_2 binding to the CoTPP·1-MeIm complex has been reported at temperatures as high as 270 K in toluene.[8] It should also be noted that to our knowledge there are no literature reports of room-temperature O_2-binding studies of thin sublimed films of CoTPP. The apparent interaction observed here between O_2 and CoTPP sublimed films may be a surface effect and therefore may be restricted to thin films.

CoTPP Plasma Polymer Films. Infrared spectra of CoTPP/*trans*-2-butene plasma polymer films matched those of CoTPP samples prepared as KBr disks or sublimed films, with the addition of absorption bands due to the *trans*-2-butene plasma polymer matrix. A more detailed description of the nature of the binding of CoTPP and other Co(II) complexes to the plasma polymer matrix is the subject of a subsequent publication.[16] Infrared spectra of CoTPP plasma polymer films changed significantly upon exposure both to 1-MeIm vapor in an Ar stream and to O_2 at room temperature. When films were exposed to 1-MeIm vapor in Ar and then subsequently exposed to O_2, IR spectra contained an absorption band at 1100 cm^{-1}, which was not present in spectra of sublimed films or 1-MeIm alone. This band was found to diminish when the film was heated at 130 °C under N_2 for 1 h. The band at 1100 cm^{-1} is consistent with the O–O stretching frequency of O_2 bound to a cobalt center[13-15] and indicates that O_2 is bound to the metal center when CoTPP is incorporated into a *trans*-2-butene plasma polymer thin film which has been exposed to 1-MeIm vapor.

UV–vis spectra of CoTPP/*trans*-2-butene plasma polymers were recorded under the same conditions as spectra of sublimed films. UV–vis spectra of CoTPP/*trans*-2-butene plasma polymers on glass slides exhibited λ_{max} values of 408, 526, and 612 nm. When the films were exposed to 1-MeIm vapor in N_2, and subsequently O_2, the band at 526 nm in the UV–vis spectrum reversibly shifted to 528 nm (1-MeIm in N_2) and then to 547 nm (O_2). This change was reversed by heating the sample under N_2 at 130 °C. A similar spectral change has been reported for CoTPP in toluene solution containing pyridine[6] and a 2-methyltetrahydrofuran solution[5] upon binding O_2 at low temperatures (below 200 K). Therefore, the spectral changes observed at room temperature for our plasma polymer films are considered to be indicative of O_2 binding.

The appearance of the band at 1100 cm^{-1} in IR spectra of CoTPP/*trans*-2-butene plasma polymer films at room temperature is consistent with an O–O stretching frequency for O_2 bound to a cobalt center.[13-15] No similar band appears when NiTPP/*trans*-2-butene or *trans*-2-butene plasma polymer films are exposed to 1-MeIm vapor followed by O_2. Although the CoTPP·1-MeIm complex bound to O_2 is reported[14] to have an O–O stretching frequency at 1142 cm^{-1} (measured at 195 K), one would expect there to be some shift in the position of this band due to the unique environment of the porphyrin complex in the plasma polymer film. Also, the absorption band at 1103 cm^{-1} in IR spectra of sublimed CoTPP films (attributed to O_2 binding) is in the same position as the band observed here for the corresponding plasma polymer.

The reversible UV–vis spectral changes due to 1-MeIm and O_2 suggest that O_2 reversibly binds to the cobalt center of CoTPP in the plasma polymer films. The λ_{max} shift upon exposure to O_2 (after exposure to 1-MeIm vapor in N_2) is the same shift observed when O_2 binds to CoTPP in solution.[5,6] Also, a similar shift is seen for the "picket fence" porphyrin [*meso*-$\alpha,\alpha,\alpha,\alpha$- tetrakis(*o*-pivalamidophenyl)porphyrinato]cobalt(II) (CoTpivPP).[17]

Several differences are apparent between the O_2 binding to CoTPP·1-MeIm in sublimed films and that in the plasma polymer films. (1) IR spectra of sublimed films yield three new peaks at 1143, 1103, and 1087 cm^{-1}, which indicate O_2 binding; IR spectra of plasma polymer films yield only one peak at 1103 cm^{-1}. (2) UV–vis spectra of sublimed films show no shift in λ_{max} values on

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exposure to O_2; a λ_{max} shift is observed for UV–vis spectra of the plasma polymer films. (3) Dioxygen binding in the sublimed films is reversible at room temperature; the plasma polymer films require heating to reverse the spectral changes associated with O_2 binding. These observations suggest that the different environments in which CoTPP is situated for the two cases (a crystalline lattice in the sublimed film and an amorphous matrix in the plasma polymer film) have two effects. First, item 1 above suggests that there exist a small number of distinguishable environments for CoTPP in the sublimed film but not in the plasma polymer. Second, the plasma polymer bound CoTPP has a higher affinity for O_2 than CoTPP prepared as a sublimed film. The latter is consistent with literature reports that CoTPP coordinated to polystyrene-bound imidazole has a higher affinity for O_2 at 25 °C than the CoTPP·1-MeIm complex in solution.[7] The only difference is that in our work CoTPP, rather than the axial base, 1-MeIm, is bound to a polymer matrix.

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