use of the thin silvered graphite fibers, we now find the conductivity typically continues to increase well below 50 K, as shown in a data set terminating at ca. 20 K (Figure 1) and then reaches a gentle maximum having $\sigma(T_m) \sim 2000$–$5000\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at $T_m \lesssim 25$ K (Figure 1, inset). Both T_m and the relative conductivity show some variability with crystal, part of which undoubtedly reflects crystal quality and probably also residual stress in the mounts.[12] Upon further cooling, the conductivity at first decreases gradually, but it does not become vanishingly small as in most molecular crystals. Instead, it levels off to a high asymptotic ($T \rightarrow 0$) value (Figure 1, inset) that varies from about $^1/_2$ to 2 times that at room temperature. For comparison (Table I), the asymptotic low temperature to ambient conductivity ratio for the first low-temperature molecular conductor, HMTSeF-TCNQ,[2] is $\sigma(1.1)/\sigma(\text{room temp}) \sim {}^1/_2$.

The NiPcI charge carriers are associated with delocalized π orbitals on the macrocycle, with an additional small spin density ($\lesssim 0.5\%$) on iodine,[8] and have a narrow line width at room temperature ($\Gamma_{\parallel} = 2.4$ G, $\Gamma_{\perp} = 2.0$ G) that decreases upon cooling. In contrast, among the other molecular crystals that remain highly conducting at the lowest temperatures, scattering processes associated with two or three dimensionality cause the EPR line to be broad (e.g., $(\mathrm{TMTSeF})_2\mathrm{ClO}_4$),[13] even unobservably so (e.g., HMTSeF-TCNQ).[14] The spin susceptibility of NiPcI is metal-like, being virtually temperature independent down to the lowest accessible temperature, 2 K.[10b] The thermoelectric power of NiPcI single crystals is positive, confirming the hole conduction mechanism expected for the oxidized NiPc stacks, and varies linearly with temperature with a nearly zero intercept, consistent with metallic behavior down to the lowest measured temperature of ~10 K.[15] Fitting the data yields a tight-binding bandwidth of $4t \sim 0.44$ eV, in good agreement with $4t = 0.37$ eV, deduced from the susceptibility.[8]

The temperature-independent susceptibility, the thermoelectric power proportional to temperature, and the high conductivity as $T \rightarrow 0$ K are all precisely as expected if NiPcI is a truly metallic conductor. In addition, the weak interstack contacts, the narrow EPR line width, and a weak magnetoresistance[16] indicate that the carriers are strongly one dimensional. However, upon cooling, a conductive one-dimensional system normally is expected to undergo a metal–insulator transition[1] that is correlated with a periodic (Peierls) distortion (in this case in the conducting NiPc stack).[17] This in turn would lead to a vanishingly small conductivity as $T \rightarrow 0$, contrary to observation. The conductivity maximum at T_m perhaps reflects a tendency of NiPcI to undergo a metal–insulator phase transition that is suppressed by the disorder potential from the iodine chains. Disorder might produce a sufficient number of states at the Fermi level to give a metallic-like temperature variation of the susceptibility and thermoelectric power yet cause the conductivity to have a quasi-metallic behavior at low temperature. Intermolecular forces between the large NiPcI metallomacrocycles might also introduce geometric constraints not operative in the conductive crystals prepared from smaller building blocks (Table I) and may play a part, along with the disorder in the triiodide chains, in stabilizing the NiPcI metallic state. In any event, the present results pose new questions and present new opportunities in the study of charge transport in molecular crystals.

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(12) Detailed contactless microwave conductivity measurements, to be performed in collaboration with Prof. T. O. Poehler, will address this issue.

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(15) A linear least-squares fit between 10 and 60 K gives $S(T) = 0.184 + 0.384\ T$ (μV/K). Within the confines of the tight-binding model, the thermoelectric power of a one-dimensional metal is proportional to T:

$$S = \left(\frac{-\pi^2 k_B{}^2}{6|e|t} \frac{\cos(\pi\nu/2)}{\sin^2(\pi\nu/2)} \right) T$$

where t is the transfer integral and $\nu = 2 - \rho$ is the number of conduction electrons per molecule (1.67). See: Khanna, S. K.; Yen, S. P. S.; Samoano, R. B.; Chaikin, P. M.; Ma, C. L.; Williams, R.; Samson, S. *Phys. Rev. B* **1979**, *19*, 655–663.

(16) Magnetoresistance measurements on NiPcI performed at 4.2 K showed a positive $\Delta\rho/\rho$ of order 5% in a 50-kG field. Thus NiPcI is similar to HMTSeF-TCNQ, which has no detectable magnetoresistance above 100 K but does have a modest positive effect ($\Delta\rho/\rho \simeq 3\%$ at 28 kG) at 4.2 K. See: Cooper, J. R.; Weger, M.; Jerome, D.; Lefur, D.; Bechgaard, K.; Bloch, A. N.; Cowan, D. O. *Solid State Commun.* **1976**, *19*, 749–754.

(17) We note that a possible trimerization of the NiPc stacks in response to the trimerization of iodine to form $\mathrm{I_3^-}$ is not a Peierl's distortion, does not cause a gap at the Fermi surface, ($k_F = 5\pi/6a$, where a is the interplanar spacing, for $\rho = 0.33$) and should not lead to a metal-to-insulator transition.

Resonance Raman Excitation of O_2 Stretching Vibrations of Oxy(tetraphenylporphinato)cobalt(II) at 457.9 nm

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The intense current interest in dioxygen adducts of metalloporphyrins stems from their obvious importance to the study of biological oxygen carriers and heme-containing oxidoreductases as well as their relevance to recent investigations of metalloporphyrin-based oxidation catalysts.[1-3] For this reason, it is essential to develop and demonstrate readily accessible and effective probes for characterization of these important adducts.

The O_2 stretching ($\nu(O_2)$) vibrations of dioxygen adducts of metal complexes provide valuable information about the nature of the metal–O_2 bond (superoxo/peroxo) and the geometry of the metal–O_2 moiety (end on/side on). The $\nu(O_2)$ of Co(II) Schiff base complexes can be resonance enhanced by laser lines in the visible region because their Co(II)–O_2 charge-transfer (CT) bands are located in the 500–600-nm region.[4-6] In contrast, resonance enhancement of $\nu(O_2)$ of Co(II) porphyrins by "visible" laser lines (450–700 nm) has not been observed[7,8] since their Co(II)–O_2 CT bands are in the UV region. Only recently, Tsubaki and Yu[9] were able to observe the $\nu(O_2)$ of oxycobalt myoglobin and oxycobalt hemoglobin by usng the 406.7-nm line of a Krypton ion laser. In this communication, we show that the $\nu(O_2)$ of a Co(II) porphyrin, $\mathrm{Co(TPP)(py)O_2}$, can be observed by using the 457.9-nm line of a conventional argon ion laser if proper experimental conditions are met.

As is well-known,[6] the concentration of the 1:1 O_2/Co adduct in solution equilibria increases as the temperature is lowered and

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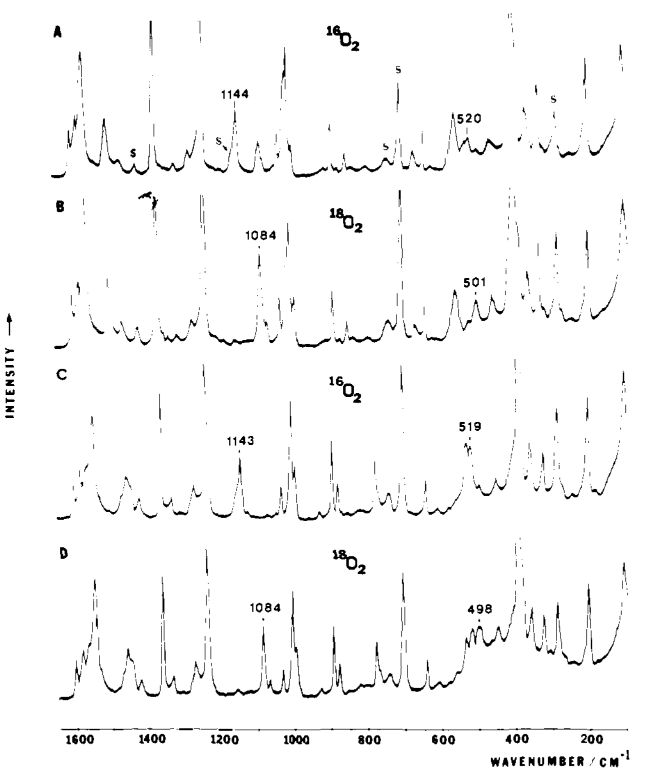

Figure 1. Resonance Raman spectra (457.9-nm excitation) of dioxygen adducts of Co(TPP) and Co(TPP-d_8) in CH_2Cl_2 containing 3% pyridine at ~−70 °C under ~4 atm of O_2 pressure: (A) Co(TPP) + $^{16}O_2$; (B) Co(TPP) + $^{18}O_2$; (C) Co(TPP-d_8) + $^{16}O_2$; (D) Co(TPP-d_8) + $^{18}O_2$. S denotes the solvent band.

as the O_2 pressure is increased. The "minibulb" method that we reported previously enables us to measure the resonance Raman (RR) spectra of dioxygen adducts of Co(II) Schiff base complexes in solution equilibria at ~−80 °C under ~3 atm of O_2 pressure. Thus, this method is ideal for RR studies of $\nu(O_2)$ of Co(II) porphyrins under "preresonance conditions". All the spectra shown below were obtained by using this method in conjunction with a Spectra-Physics Model 164 Ar ion laser (457.9-nm excitation, ~30 mW) and a Spex Model 1401 double monochromator.

Figure 1A shows the RR spectrum of Co(TPP) dissolved in CH_2Cl_2 (~10^{-2} mol/L) containing 3% pyridine and saturated with $^{16}O_2$ gas at ~4 atm of O_2 pressure. The temperature of the minibulb was kept at ~−70 °C by using a CTI Model 21 closed-cycle helium refrigerator. As expected, this spectrum is very similar to that of Co(TPP) (457.9-nm excitation) reported previously[7] except that an additional band of medium intensity appears at 1144 cm^{-1}. As is shown in Figure 1B, this new band disappears completely, and the Co(TPP) band at 1084 cm^{-1} becomes much stronger when the solution is saturated with $^{18}O_2$. These results clearly indicate that the $\nu(^{16}O_2)$ of Co(TPP)(py)O_2 is at 1144 cm^{-1} and that this band has shifted and accidentally overlaps the 1082-cm^{-1} band of Co(TPP) upon $^{16}O_2$–$^{18}O_2$ substitution. In fact, the $\nu(^{16}O_2)$ of Co(TPP)(py)O_2 obtained here is very close to that of Co(TPP)(1-MeIm)O_2 at 1142 cm^{-1} reported previously by using IR difference spectroscopy.[10] To further confirm our interpretation, we have carried out similar experiments with Co(TPP-d_8) in which the eight β-pyrrole hydrogens are substituted by deuterium. As is seen in Figure 1C, the $\nu(^{16}O_2)$ of Co(TPP-d_8)(py)O_2 is at 1143 cm^{-1}. However, the band at 1082 cm^{-1} of Co(TPP) is now shifted under the strong band near 1000 cm^{-1}. As a result, the $\nu(^{18}O_2)$ of Co(TPP-d_8)(py)O_2 is observed at 1084 cm^{-1} without any interference from other bands. The observed $\nu(O_2)$ shift from 1144 to 1084 cm^{-1} (60 cm^{-1}) is close to that of a perturbed diatomic molecule (65 cm^{-1}). As discussed previously,[7] the large shift of the $\nu(O_2)$ in going from "base-free" Co(TPP)O_2 (1278 cm^{-1}) to "base-bound" Co(TPP)(py)O_2 (1144 cm^{-1}) is attributed to the effect of the pyridine ligand, which donates the electrons to the O_2 via σ and/or π bonding to the Co atom.

Careful inspection of these spectra also reveals the presence of the ν(Co–O_2) in the low-frequency region. The band at 520 cm^{-1} in Figure 1A has shifted to 501 cm^{-1} (Figure 1B) by $^{16}O_2$–$^{18}O_2$ substitution. In the case of Co(TPP-d_8), this band shifts from 519 to 498 cm^{-1} by oxygenation (Figure 1C and D). The RR spectrum of Co(TPP)(py) obtained under similar conditions shows no appreciable bands in the 600–500- and 1200–1100-cm^{-1} regions.

Previously, Nozawa et al.[11] observed the anomalous broadening of the MCD Soret band upon oxygenation of the Co(II) complex of mesoporphyrin IX dimethyl ester and suggested the presence of the Co(II)–O_2 CT transition in the Soret region near 400 nm. Wayland et al.[12] also suggested the possibility of assigning a similar transition of Co(TPP)O_2 in the Soret region. Our RR observation together with those of Tsubaki and Yu[9] definitely supports these suggestions.

Finally, it is interesting to note that O_2 adducts of cobalt hemoglobin exhibit two $\nu(O_2)$ at ~1153 and ~1122 cm^{-1},[9] whereas that of an "unprotected" Co(TPP) shows only one $\nu(O_2)$ at 1144 cm^{-1}. A more detailed study including the effects of in-plane and axial ligands and the solvent (environment around the bound O_2) on $\nu(O_2)$ is now in progress.

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Reaction of Singlet Oxygen with Enol Esters: A New Path Implicating a Dipolar Intermediate

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The reactions of singlet oxygen ($^1\Delta_g$, $^1O_2$) with unsaturated organic compounds typically fall into one of three categories: [2 + 2] cycloaddition to form a dioxetane; [4 + 2] cycloaddition giving an endoperoxide; and the "ene" reaction yielding an allylic hydroperoxide.[1] The mechanism for this last transformation has proven to be enigmatic with suggestions of a concerted reaction[2] competing with proposed stepwise paths going through a biradical,[3] perepoxide,[4] or zwitterionic[5] intermediate. Herein we report the

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