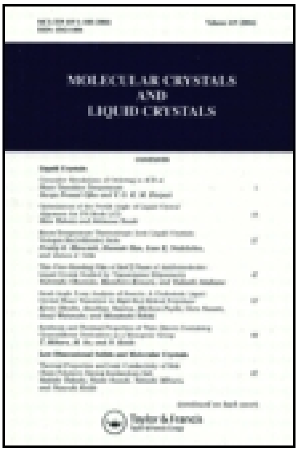

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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High-Pressure Optical Study of Partially Oxidized Metallophthalocyanines and Metallotetrabenzo-Porphyrins

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HIGH-PRESSURE OPTICAL STUDY OF PARTIALLY OXIDIZED METALLOPHTHALOCYANINES AND METALLOTETRABENZO-PORPHYRINS

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Abstract The reflectance spectra of (phthalocyaninato)-nickel(II) hexafluoroarsenate ($[Ni(pc)]_2AsF_6$) and (tetrabenzoporphyrinato)nickel(II) hexafluoroarsenate ($[Ni(tbp)]_3(AsF_6)(C_{10}H_7Cl)$) were measured at high pressures. The pressure dependence of the reflectance spectrum of $[Ni(pc)]_2AsF_6$ suggests that the charge-carrying hole moves from the organic ligand to the central metal ion under high pressure.

INTRODUCTION

Metallophthalocyanines ([M(pc)]) and metallotetrabenzoporphyrins ([M(tbp)]) form partially oxidized charge-transfer salts with a variety of counter anions.[1-14] The electrical properties of these salts vary from metallic ones to semiconductive ones, depending not only on the crystal structure or the degree of partial oxidization, but also on whether the central metal is oxidized or the organic ligands are oxidized. A typical example of the latter is (phthalocyaninato)cobalt triiodide ($[Co(pc)]_3I_3$). The group of Northwestern University has been reported[6] that $[Co(pc)]_3I_3$ behaves like a semiconductor, though 1/3-oxidized salts are generally metallic unless the lattice distorts with a commensurate periodicity. They have suggested that the central Co(II) ion is partially oxidized in this salt. Similar situation has been reported by the same group about (tetrabenzoporphyrinato)nickel triiodide ($[Ni(tbp)]_3I_3$),[3] but it is still ambiguous whether the central metal is oxidized or not in this complex.[15]

In the present study, we perform the high-pressure optical measurement of $[Ni(pc)]_2AsF_6$ and $[Ni(tbp)]_3(AsF_6)_2(C_{10}H_7Cl)$ to investigate how the lattice contraction affect the electronic structures of these partially oxidized phthalocyanine and tetrabenzoporphyrin salts. As a topic of the pressure effect, we discuss the possibility that high pressure might change the oxidation part in these macrocyclic molecules.

EXPERIMENTAL

$[Ni(pc)]_2AsF_6$ and $[Ni(tbp)]_3(AsF_6)_2(C_{10}H_7Cl)$ were synthesized by electrochemical method as we have previously reported.[11,12] The high pressure reflectance measurements were done on single crystals of a typical dimension of 0.1x0.2x0.05 mm^3.

High pressure was applied to the sample crystal using a diamond anvil cell. The details of the experimental procedure has been described elsewhere.[16] We used pentane-isopentane (1:1) and methanol-ethanol (4:1) mixtures as pressure media in the measurements of $[Ni(pc)]_2AsF_6$ and $[Ni(tbp)]_3(AsF_6)_2(C_{10}H_7Cl)$, respectively.

RESULTS AND DISCUSSIONS

$[Ni(pc)]_2AsF_6$

The polarized reflectance spectra of $[Ni(pc)]_2AsF_6$ at ambient pressure are shown in Fig. 1. In this material, planer [Ni(pc)] molecules are stacked along the *c*-axis.[12] The //*c* spectrum shows a Drude-type dispersion in the IR region, which is characteristic of a metal. In contrast the ⊥ *c*-spectrum exhibits the dispersion primarily ascribed to the *intra*-molecular excitation. This spectroscopic anisotropy indicates that the charge carrier of this complex has a quasi-one-dimensional character.

Pressure dependence of the //*c* spectrum is shown in the left panel of Fig. 2. One should be careful in discussing the high-pressure reflectance spectrum, because reflectivity depends on the refractive index of the pressure medium surrounding a sample as well as the intrinsic dielectric properties of the sample. For instance, the reflectance of the higher-energy tail of the Drude-

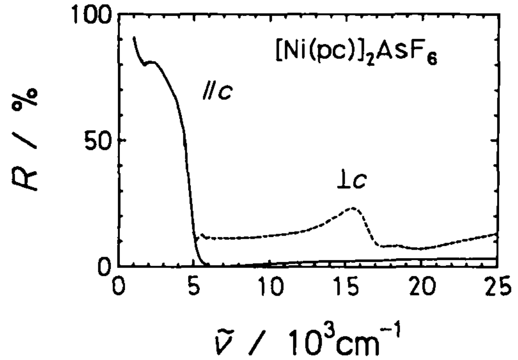

FIGURE 1 Polarized reflectance spectra of [Ni(pc)]$_2$AsF$_6$.

edge in Fig. 2 rises at high pressure, but this change is mainly attributable to the increase of the refractive index of the pressure medium. Another difficulty in high pressure reflectivity measurement is that conventional Kramers-Kronig transformation is not applicable to a reflectance spectrum in the medium the refractive index of which is not equal to 1.[17,18] To overcome this difficulty we calculated the reflectance spectrum which is expected to be observed when the sample is placed in the medium with the refractive index of n_0. The reflectivity was calculated using the refractive index of the medium and the complex refractive index of the sample which had been obtained from Kramers-Kronig transformation of the ambient-pressure reflectance spectrum. The Eq. (1) was used for this calculation,

$$R(\omega) = | n(\omega) - n_0 |^2 / | n(\omega) + n_0 |^2 \qquad (1)$$

where n(ω) denotes the complex refractive index of the sample and n_0 the refractive index of the pressure medium. The observed high-pressure spectra are shown in Fig. 2 by solid circles together with the ambient-pressure spectra thus calculated (broken lines). The difference of the observed spectrum from the calculated one is the intrinsic change of the sample due to the lattice contraction.

As mentioned in the preceding section, the slight rise of the reflectance of the higher-energy tail of the Drude-edge is ascribed to the increase of the refractive index of the pressure medium. The most important result is that the plasma edge does not show any large shift as compared with the broken lines, leading to the conclusion that the plasma-frequency (ω_p) of this material is scarcely dependent on pressure. Usually the bandwidth ($4t$) of an organic conductor remarkably increases by pressure, so that the plasma edge significantly shifts to a high-wavenumber side.[19] The shift of plasma frequency is evaluated by using Eq. (2) based on a simple one-dimensional tight-binding band model,

$$\hbar\omega_p = 4ed[Nt\sin(\pi\rho/2)]^{1/2} \qquad (2)$$

where d and N are intermolecular spacing and the density of phthalocyanine, respectively, and ρ is the degree of partial oxidation. Since the pressure dependence of the bandwidth of typical organic conductors is $d\ln t/dP = +2\sim 3$ % kbar^{-1}, the plasma frequency at 16 kbar is expected to show blue shift by 17~27 %. In contrast to this anticipation this material shows no significant pressure shift or possibly the slight shift to the reverse side in the high-pressure region. This experimental result is unusual.

The pressure dependence of $\perp c$ is shown in the right panel of Fig.2. The spectral profiles are considerably deformed at high pressures. The dispersion around 18000 cm^{-1} is suppressed and the peak at 15000 cm^{-1} becomes sharper on elevating pressure. The dispersion around 18000 cm^{-1} can be assigned to the *intra*-molecular excitation from the mixed orbital between metal 3dπ (e_g) and ligand second πHOMO(e_g) to the ligand πHOMO(a_{1u}).[20,21] This excitation is allowed only to a cation radical ($[\mathrm{M(II)(pc)^-}]^+$), because the π HOMO(a_{1u}) is fully occupied in a neutral molecule ($[\mathrm{M(II)(pc)^{2-}}]^0$). This salt has another *intra*-molecular excitation around 15000 cm^{-1}, which is assigned to a π-π^* (π HOMO(a_{1u})-π LUMO(e_g)) transition.[20,21] It is well known that the so-called Q-band of neutral phthalocyanine appears in the same spectral region. So we consider that the $\perp c$ spectrum of the $[Ni(pc)]_2AsF_6$ at ambient pressure can be reproduced by the superposition of the spectra of $(pc)^{2-}$ and $(pc)^-$, but the spectra at high pressures rather approach to the spectrum of $(pc)^{2-}$. This phenomenon is understandable if we assume that the oxidized site moves from the organic ligand $(pc)^{2-}$ to the central metal M(II), that is, $[Ni(II)(pc)^-]^+$ is converted to $[Ni(III)(pc)^{2-}]^+$ at high pressures. Since the bandwidth of the nickel $3d$-band is considered to be narrower than the ligand π-band, the conversion of the charge-carrying hole from the ligand to the metal would cancel the pressure effect of increasing t. This model is consistent with the pressure dependence of the $//c$ spectrum as well.

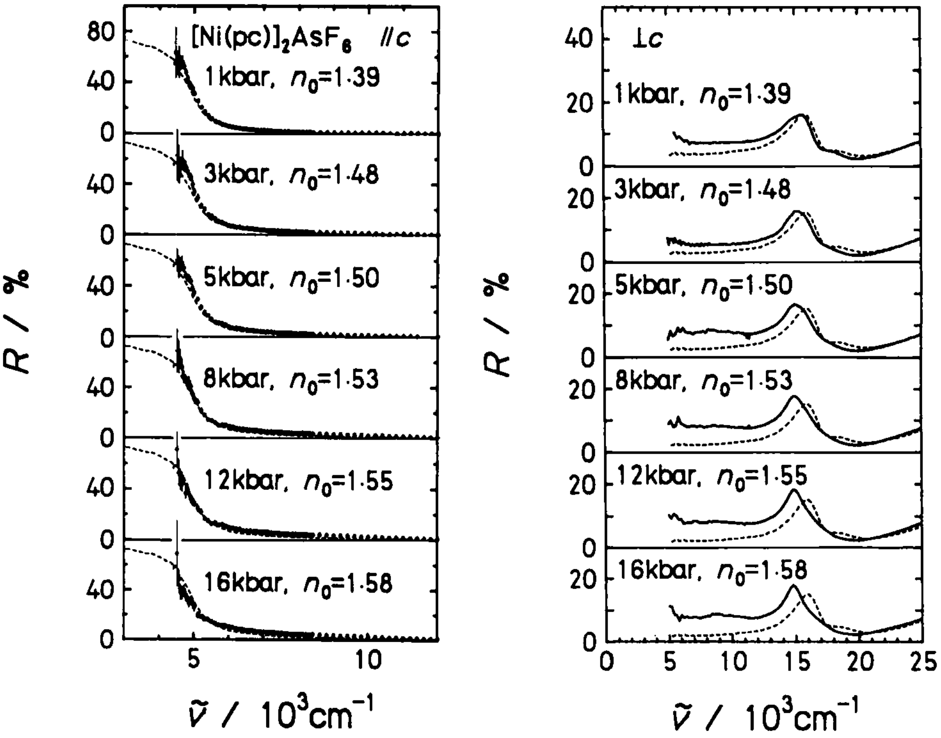

FIGURE 2. Pressure dependence of polarized reflectance spectra of $[Ni(pc)]_2AsF_6$.

$[Ni(tbp)]_3(AsF_6)_2(C_{10}H_7Cl)$

Figure 3 shows the reflectance and conductivity spectra of $[Ni(tbp)]_3(AsF_6)_2(C_{10}H_7Cl)$ at ambient pressure. The molecules are stacked approximately along the *c*-axis in this complex and the stacking column has a trimerized structure.[11] The intermolecular HOMO-HOMO overlap integrals calculated by using a MNDO wave function are $S = 0.022$ (*intra*-trimer) and $S = 0.002$ (*inter*-trimer). The //*c* conductivity spectrum exhibits a strong and sharp absorption band at 4200 cm^{-1} with an oscillator strength of 1.2 per a trimer unit. This absorption is safely assignable to the *intra*-trimer charge-transfer transition because of its polarization direction. The oscillator strength and the line shape of this absorption are unusually large and sharp for a charge-transfer transition. The absorption band in the ⊥ *c* spectrum naturally involves Q-band as well as the *intra*-molecular transition of tetrabenzoporphyrin cation radical. However, this spectrum shows complicated structure in contrast to the corresponding spectrum of $[Ni(pc)]_2AsF_6$.

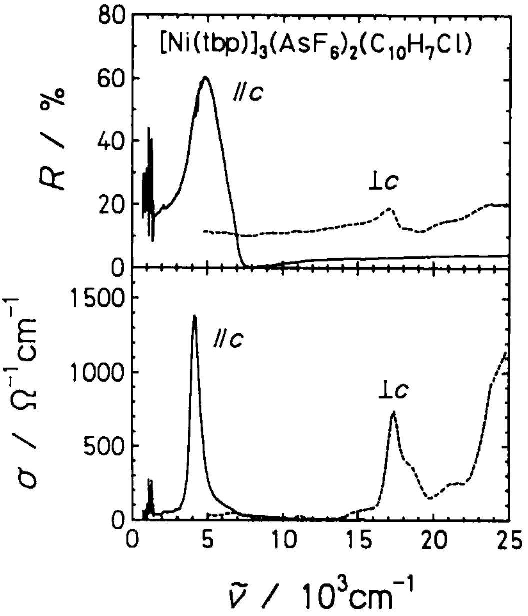

FIGURE 3 Polarized reflectance and conductivity spectra of $[Ni(tbp)]_3(AsF_6)(C_{10}H_7Cl)$ at ambient pressure.

The left panel of Fig.4 shows the pressure dependence of the //*c* spectrum. As compared with the broken line calculated by the method described in the preceding section, the blue shift of the charge-tansfer band is the intrinsic change by pressure. The rate of the blue shift against pressure is +0.5 - +0.7 % kbar^{-1}. In general high pressure stabilizes the charge-tansfer excited state due to the increase of the electrostatic energy[22] but unstabilizes it because of the enhancement of the transfer integral represented by t.[23] The blue shift indicates that the latter effect of increasing t is dominant in this complex.

The right panel of Fig.6 shows the pressure dependence of the ⊥ *c* spectrum. The Q-band at 17000 cm^{-1} is remarkably suppressed at high pressure while the dispersion at 15000 cm^{-1} is enhanced. It is interesting to note that the spectral profile at high pressure resembles that of $[Co(tbp)]_3(ClO_4)_2(C_{10}H_7Cl)$ measured at ambient pressure shown in Fig. 7. However, the origin of this spectral change is not obvious at the moment.

CONCLUSIONS

High pressure significantly affected the reflectance spectra of $[Ni(pc)]_2AsF_6$ and $[Ni(tbp)]_3(AsF_6)_2(C_{10}H_7Cl)$. The pressure dependence of the spectra of $[Ni(pc)]_2AsF_6$ suggests that the oxidized site is replaced from the $(pc)^{2-}$ to Ni(II) under high pressure. In both materials, the excitations of a primarily *intra*-molecular character are considerably dependent on pressure. This kind of pressure effect has not been observed in the π-conjugated organic molecular crystal. The origin of this pressure effect is not clear at present. However, these experimental results indicate that the *intra*-molecular excitations are closely correlated to the the charge-transfer interactions in the partially oxidized phthalocyanine and tetrabenzoporphyrin salts.

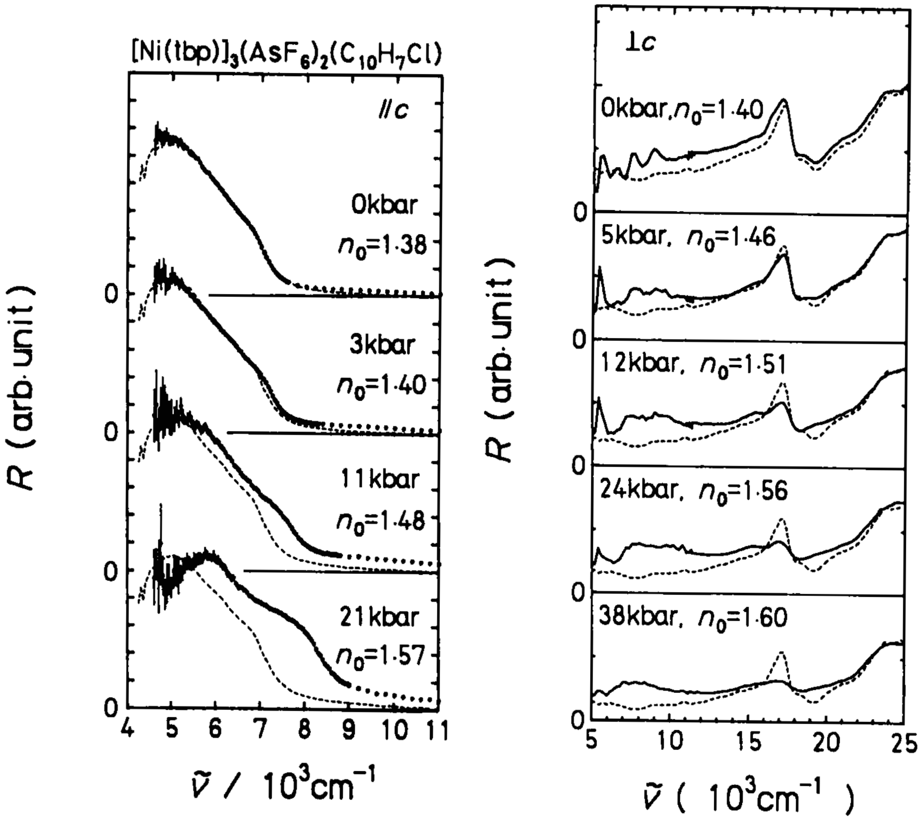

FIGURE 4 Pressure dependence of the polarized reflectance spectra of [Ni(tbp)]$_3$(AsF$_6$)$_2$(C$_{10}$H$_7$Cl).

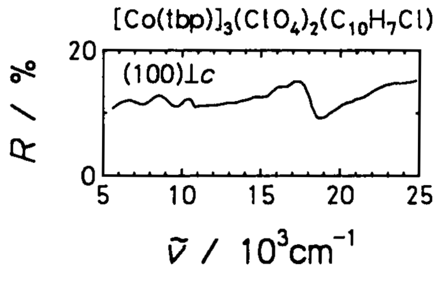

FIGURE 5 Reflectance spectrum of [Co(tbp)]$_3$(ClO$_4$)$_2$(C$_{10}$H$_7$Cl).

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