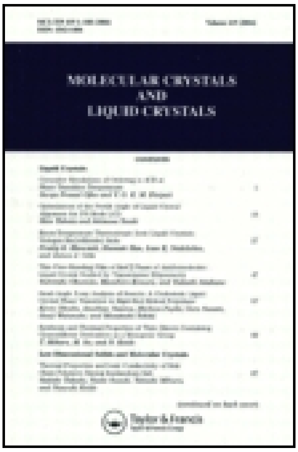

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# Controlled π–π Stacking Structure in Phthalocyanine-based Conductors

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**Abstract** Axially substituted metal-phthalocyanines are utilized for constructing molecular conductors. The starting component, $[M(Pc)(CN)_2]^-$ (Pc = phthalocyaninato), has been designed to achieve the multi-dimensional π–π interaction, and the conducting crystals have been obtained by the electrochemical oxidation. A variety of the π–π stacking structures, ranging from one- to three-dimensions, have been obtained depending on the crystal solvent for the neutral radical crystals of $Co(Pc)(CN)_2$. They are semiconducting with relatively high conductivity ($10^{-2}$—$10^{0}$ S cm$^{-1}$) at room temperature. The partially oxidized salt crystals obtained have a narrow one-dimensional metallic band. The metallic nature has been confirmed by the thermoelectric power measurements, though the conductivity is not always clearly metallic. A dramatic change in the conductivity and magnetic properties has been observed by the replacement of the central metal ion from non-magnetic Co$^{III}$ to magnetic Fe$^{III}$.

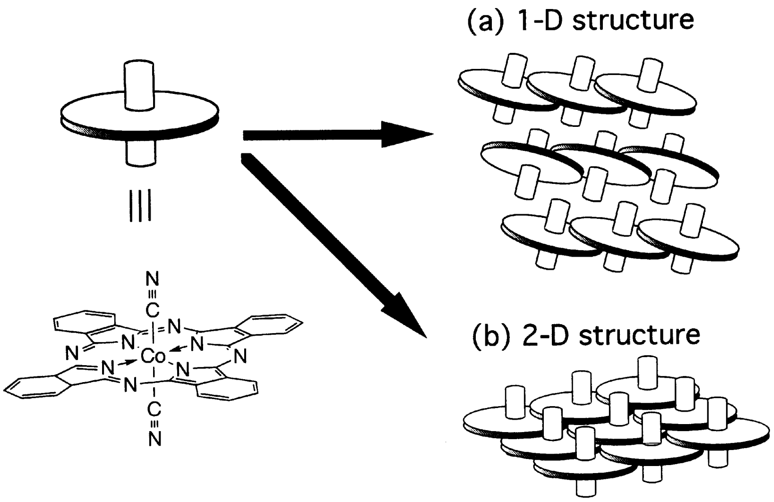
Keywords phthalocyanine; molecular conductor; crystal structure; dimensionality; neutral radical

## INTRODUCTION

Molecular design for controlling the molecular arrangement in their assemblies is important to attain the desired properties. Especially, for molecular conductors, the dimensionality of the electronic system, which results from the π–π interaction in the lattice, seriously affects the electronic properties. Ordinary π-conjugated planar molecules are packed in the lattice with face-to-face stacking structure. This always leads to a simple one-dimensional electronic system. The increased dimensionality appears when the planar molecule can interact with the adjacent molecules with a side-by-side interaction in addition to the ordinary face-to-face interaction. From this view, BEDT-TTF is an excellent molecule.

We have approached to this subject from a different point of view. If a π-conjugated planar molecule has projections at its center, the molecule cannot form a simple face-to-face stacked one-dimensional column. To achieve the intermolecular π–π stacking interaction, the molecule needs to slip a large distance, as shown in Scheme 1. The resultant one-dimensional chain now can interact with the adjacent chains by extra π–π stacking interaction. This situation leads to the formation of a two-dimensional sheet in which the π–π stacking interaction is extended two-dimensionally.

For such a purpose, phthalocyanine is a desirable component, since the existence of the central metal ion allows us to introduce axial



**Scheme 1**

ligands without difficulty. We have thus performed the electrocrystallization of $[Co(Pc)(CN)_2]^-$ (dicyano(phthalocyaninato)cobalt(III) anion).[1,2] The oxidation process preferentially occurs at the π-ligand, and the obtained crystals can be divided into two classes; one is the neutral radical crystals in which each Pc π–ligand is completely oxidized and the other is the partially oxidized salt crystals in which fractional oxidation occurs for each Pc π–ligand.

## NEUTRAL RADICAL CRYSTALS

When the neutral radical, $Co(Pc)(CN)_2$, crystallizes as a single component crystal,[3] the Pc π-planes cannot be parallel with each other as shown in Fig. 1. Consequently, the π–π stacking interaction becomes insufficient, resulting in a poor electrical conductor ($10^{-4}$ S $cm^{-1}$ at room temperature). The situation dramatically changes by incorporation of crystal solvents. As shown below, crystal solvents lead to the efficient π–π stacking structure. Furthermore, the dimensionality of the π–π stacking structure can be tuned by the species of the crystal solvents.

The neutral radical crystals with one-dimensional π–π stacking interaction have been obtained when the electrocrystallization was performed in the presence of $CHBr_3$[1] or $CH_2Cl_2$. The resultant crystals contain these molecules as the crystal solvent. In both cases, the Pc planes are parallel within a chain but not parallel to those in the adjacent chains, as shown in Scheme 1(a). The crystal solvents occupy the cavity formed between the Pc chains with ($CHBr_3$) or without ($CH_2Cl_2$) specific interactions with the axial CN ligands.

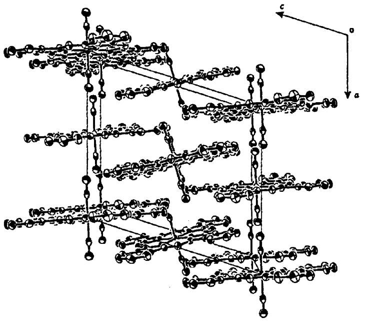


FIGURE 1 Crystal structure of $Co(Pc)(CN)_2$.

When the crystal solvent is $CHCl_3$,[4] acetone, DMSO,[3] or $CH_3CN$, two-dimensional π–π stacking structure (Scheme 1(b)) occurs. In all the cases, the crystal solvents are packed in the space formed between the two-dimensional Pc sheets. Orientation of the Pc planes in the neighboring sheets is parallel in the $CHCl_3$, acetone, and DMSO inclusive crystals (Fig. 2(a)), while it is alternately changed in the $CH_3CN$ inclusive crystal (Fig. 2(b)). Except for $CHCl_3$, which forms a hydrogen bond with the axial CN ligand, the crystal solvents have no specific interactions with the Pc units. The spacing between the Pc sheets in these crystals is so large that any electronic interaction between them is very weak.

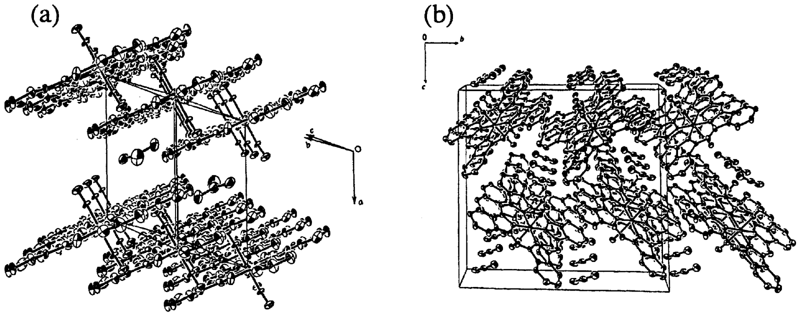


FIGURE 2 Crystal structures of $Co(Pc)(CN)_2{\cdot}2(acetone)$ (a) and $Co(Pc)(CN)_2{\cdot}CH_3CN$ (b).

In some special cases, the distance between the Pc sheets becomes very short so that the electronic interaction between them is comparable to that within the sheet. Such crystals have been obtained when the crystal solvent is $H_2O$[2,4] or EtOH. In these crystals, the solvent molecules occupy the space formed in the complicated three-dimensional π–π stacking network of the Pc units. Each solvent molecule is bound to the Pc unit with hydrogen-bonding interaction in common.

Whether the dimensionality of the π–π stacking structure really reflects the dimensionality of the electronic system has been confirmed by the overlap integral calculation of each crystal and by some anisotropic conductivity data. Compared with the solvent-free crystal, the solvent-inclusive crystals are much more conductive; $10^{-2}$ — $10^{0}$ S

$cm^{-1}$ at room temperature. Furthermore, there is a rough correlation between the dimensionality of the electronic system and the conductivity; the conductivity is higher in the crystals with higher dimensionality.

## PARTIALLY OXIDIZED SALT CRYSTALS

The partially oxidized salt crystals so far obtained have one-dimensional electronic systems. The TPP (tetraphenylphosphonium) salt is a single-chain one-dimensional conductor,[5] while the PXX (*peri*-xanthenoxanthene) salt is a ladder-chain one-dimensional conductor.[6]

The crystal structure of $TPP[Co(Pc)(CN)_2]_2$ is shown in Fig. 3. The regularly stacked one-dimensional Pc chains are arranged in a tetragonal fashion around the one-dimensional TPP array. Since TPP is a closed-shell cation with a charge +1*e*, one Pc unit is formally oxidized by 0.5*e*. This electronic state leads to a 3/4-filled metallic one-dimensional band for the single Pc chain. This band structure is supported by the thermoelectric power measurements; the positive thermoelectric power is linearly correlated with the temperature above 120 K. From its slope, one can deduce the band width of about 0.5 eV. This value is in good agreement with that estimated from the plasma frequency in the reflectance spectrum.[5,7] In contrast to the clear metallic behavior of the thermoelectric power, its electrical conductivity reveals faint metallic behavior only around room temperature ($\sigma_{rt} = 120$ S $cm^{-1}$, Fig. 4(a)).

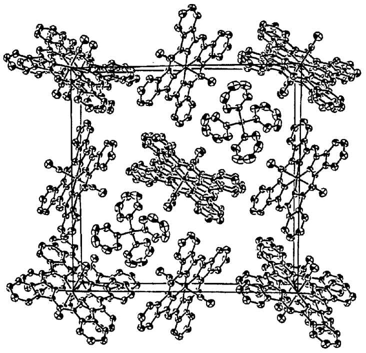


FIGURE 3
Crystal structure of $TPP[Co(Pc)(CN)_2]_2$.

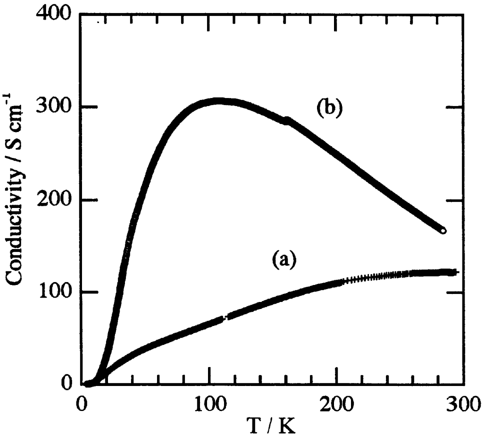


FIGURE 4
Temperature dependence of the conductivity of TPP[Co(Pc)(CN)$_2$]$_2$ (a) and [PXX][Co(Pc)(CN)$_2$] (b).

The crystal structure of the ladder-chain conductor, [PXX]-[Co(Pc)(CN)$_2$] is shown in Fig. 5. The Pc units similarly form a one-dimensional chain along the *c*-axis, but there are extra π–π overlaps between these two chains. In this crystal, both components are oxidized by 0.5*e*; namely [PXX]$^{0.5+}$[Co(Pc)(CN)$_2$]$^{0.5-}$. PXX's are dimerized, and the charge is localized in each dimer unit. Therefore, the charge-transport in this crystal preferentially occurs in the Pc ladder chain. Though the overlap integral value for each Pc chain is comparable to that in the TPP salt, the temperature dependence of the conductivity is remarkably different from that of the TPP salt. The conductivity ($\sigma_{rt}$ = 160 S cm$^{-1}$) is clearly metallic above ~100 K, as shown in Fig. 4(b). Since the formal charge of the Pc unit is the same

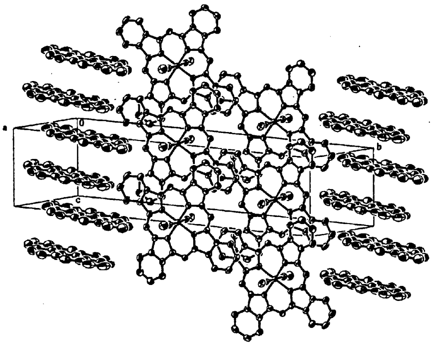


FIGURE 5
Crystal structure of [PXX][Co(Pc)(CN)$_2$].

as that in the TPP salt, the band is also 3/4-filled. However, the band now becomes two overlapping one-dimensional bands due to the chain doubling. This effectively increases the band width. The faint metallic behavior observed in the conductivity of TPP[Co(Pc)(CN)$_2$]$_2$ may be related to its narrow band width and highly one-dimensional nature.

When the central non-magnetic Co$^{\mathrm{III}}$ ion is replaced by the magnetic Fe$^{\mathrm{III}}$ ion, another effect appears. This replacement has been found to bring no influence on the crystal structure.[7] A marked difference however appears in the conductivity, as depicted in Fig. 6 for TPP[Fe(Pc)(CN)$_2$]$_2$. Though the room temperature resistivity (~$10^{-1}$ Ω cm) is only one order higher than that of TPP[Co(Pc)(CN)$_2$]$_2$, at lower temperature the difference becomes larger due to their different apparent activation energies, especially below ~40 K. On the other hand, the thermoelectric power above 100 K and reflectance spectra are almost the same for both Co and Fe salts; namely the same band width.[7] Also, it has been confirmed that there is no structural transition in the Fe salt down to 30 K. Therefore, the difference in the conductivity behavior must arise from the localized magnetic moment of $d^5$ Fe$^{\mathrm{III}}$. The magnetic susceptibility of the Fe salt is shown in Fig. 7, together with that of the Co salt. In contrast with the Pauli-like temperature independent susceptibility of the Co salt, the susceptibility of the Fe salt is strongly temperature dependent; the behavior is a

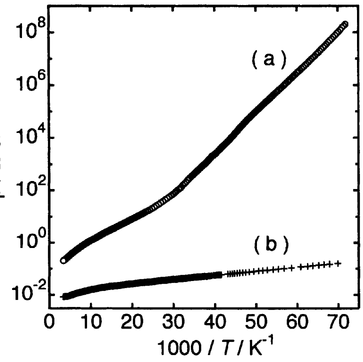


FIGURE 6 Temperature dependence of the resistivity of TPP[Fe(Pc)(CN)$_2$]$_2$ (a) and TPP[Co(Pc)(CN)$_2$]$_2$ (b).

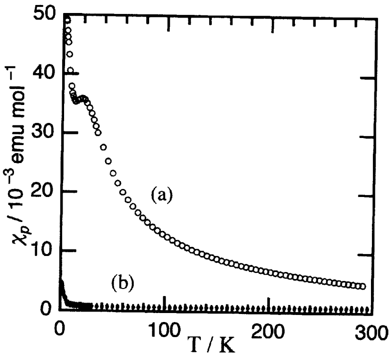


FIGURE 7 Magnetic susceptibility of TPP[Fe(Pc)(CN)$_2$]$_2$ (a) and TPP[Co(Pc)(CN)$_2$]$_2$ (b).

Curie-Weiss type with anomaly around 20 K. The susceptibility is also highly anisotropic; $\chi_p(\perp c) > \chi_p(//c)$. The large susceptibility value indicates that both $Fe^{III}$-centered and π-radical-centered spins are localized. This crystal also shows notable magnetoresistance behavior; giant negative magnetoresistance is observed below ~50 K.[8] The magnetoresistance is again anisotropic; the effect is much larger for $B\perp c$ than for $B//c$. The study on the detailed magnetic structure and mechanism of the negative magnetoresistance is now under way.

## ACKNOWLEDGEMENT

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