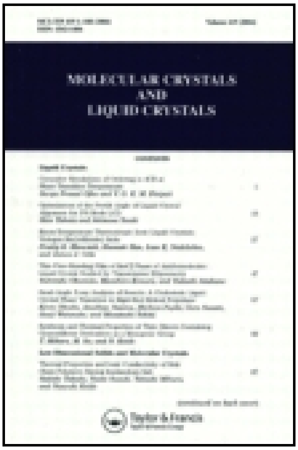

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Phthalocyanine Conductors: New Trend for Crystal and Functionality Design

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Conductors obtained from axially substituted phthalocyanine units are presented. In contrast to face-to-face one-dimensional stacking in conductors with planar phthalocyanins, various types of π–π stacking structures can be obtained owing to the slipped stacking.

Keywords: crystal structures; organic conductors; phthalocyanine; π–π stacking structure

INTRODUCTION

Phthalocyanines are well-known functional dye, and many studies on their electronic applications have been carried out. The metallic

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conductors were found about 25 years ago [1,2], and their electrical properties were recognized as promising functionality. The early conductors are represented as $M^{II}(Pc)X_y$, where M = Ni, Cu, Co, etc., Pc is phthalocyaninato, X is closed-shell anions such as I_3^-, PF_6^-, etc., and $1/3 < y < 2/3$. The partially oxidized M(Pc) units form a face-to-face stacked one-dimensional (1-D) column, and charge transport occurs through the π–π overlaps in this column.

About 10 years ago, we proposed different types of the conductors based on the axially substituted $M^{III}(Pc)(CN)_2$ units [3]. The axial CN groups now prevent direct metal-over-metal type stacking, and resultant slipped stacking can lead to various molecular arrangements with 1-D through 3-D π–π overlaps. The conductors obtained by electrochemical oxidation of the starting $[M^{III}(Pc)(CN)_2]^-$ anion can be classified into two groups; neutral radicals and partially oxidized salts. In each case, the π–π stacking structure varied by the second component of the crystal, i.e., crystal solvents and/or cations. The $M^{III}(Pc)(CN)_2$ unit also has flexibility of replacement of the M species, and conductors with local magnetic moments, which show unique magnetic and electrical properties arising from the π-d interaction, have been obtained [4]. In the following sections, their unique structural characteristics are described.

NEUTRAL RADICAL CRYSTALS

The neutral radical crystals obtained usually contain crystal solvents and the π–π stacking network depends on the solvent species. As shown in Figure 1, there are three kinds of networks. Furthermore, there are two different types of π–π overlaps. Though the 1-D network can be formed by ether type-A or type-B overlap, only 1-D with type-A has been obtained so far. The 2-D sheet can be constructed with mixing of A and B (2-D with A and B) or with solely B (2-D with B). The 3-D network always contains both A and B. The network pattern and the resistivity at room temperature of the neutral radical crystals [1,5] are summarized in Table 1, with those of axial Cl ligand and 2,3-naphthalocyanine (2,3-Nc) [6] systems.

Though they are all semiconductors, it is worth noting that the resistivity values are rather low for the solvent-inclusive crystals. The solvent-free Pc crystal in which intermolecular π–π interaction is very poor shows the value comparable to those of the Li(Pc) and $Lu(Pc)_2$ neutral radical crystals [7]. The resistivity of the same Pc unit tends to decrease with increasing the dimensionality of the network, except for the CH_3OH-inclusive $Co(Pc)(CN)_2$. This trend may be reasonable, since the Coulomb repulsion energy that causes the thermal activation

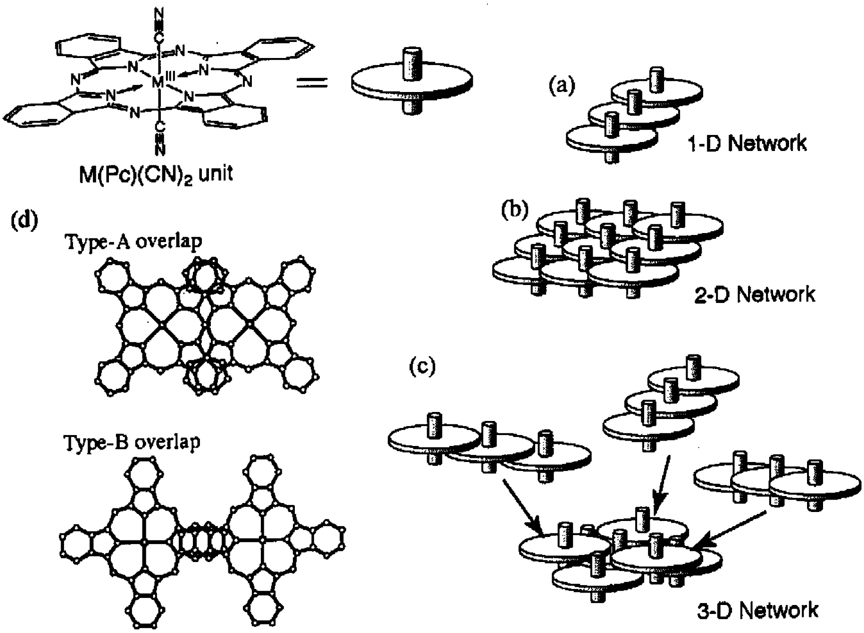

FIGURE 1 π–π stacking structures in the M(Pc)(CN)$_2$ system; (a) 1-D π–π stacking network, (b) 2-D π–π stacking network, and (c) 3-D π–π stacking network composed of three different 1-D networks, and (d) two types of π–π overlap modes.

behavior in these neutral radical crystals depends on the dimensionality of the charge carrier pathway. However, since the degree of the π–π interaction in each crystal varies and some crystals are not stable due to the exclusion of the crystal solvent, the detailed systematic comparison is rather difficult. Especially, the exceptional trend of CH_3OH-inclusive crystal is remarkable, and further characterization is required. The resistivity of the Fe compound is always higher than that of the corresponding Co compound. As shown later, the paramagnetic Fe^{III}-centered species generally show higher resistivity than the corresponding diamagnetic Co^{III}-centered species.

PARTIALLY OXIDIZED SALT CRYSTALS

The structural and electrical features of the partially oxidized salt crystals are summarized in Table 2. Excepting the 3-D network, various network structures have been obtained depending on the cationic species.

TABLE 1 Structural and Physical Properties of the Neutral Radical Crystals

Pc unit	Dimensionality of π–π stacking network	Crystal solvent	$\rho_{\mathrm{RT}}/\Omega\,\mathrm{cm}$
Co(Pc)(CN)$_2$	Discrete	None	10^4
	1-D with A	CHBr$_3$	10^2
		CH$_2$Cl$_2$	10^3
		CH$_3$OH	10^{-1}
	2-D with A and B	CHCl$_3$	10^1
		DMSO	10^0
		DMF	10^1
		CH$_3$CN	10^2
		Acetone	10^1
	3-D	H$_2$O	10^0
		EtOH	10^1
Co(Pc)Cl$_2$	2-D with A and B	Acetone	10^2
	3-D	EtOH	10^2
Fe(Pc)(CN)$_2$	2-D with A and B	CHCl$_3$	10^3
Fe(Pc)Cl$_2$	2-D with A and B	Acetone	10^4
Co(2,3-Nc)(CN)$_2$	1-D with A	None	10^2
	2-D with A and B	*o*-Dichlorobenzene	10^1
	3-D	CH$_3$CN	10^0

The potassium salt is the very first conductor of this Pc unit [8]. However, due to the instability of the crystal, the detailed physical properties are unknown. In the other closed-shell cation salts

TABLE 2 Structural and Physical Properties of the Partially Oxidized Salt Crystals

Composition	Dimensionality of π–π stacking network	M	$\rho_{\mathrm{RT}}/\Omega\,\mathrm{cm}$	Temperature dependence
K[M(Pc)(CN)$_2$]$_2$ · 5CH$_3$CN	2-D with A and B	Co	$\sim10^{-1}$	unstable
TPP[M(Pc)(CN)$_2$]$_2$	1-D with A	Co	10^{-2}	metallic $>$ 300 K
		Fe	10^{-1}	semiconducting
PTMA$_x$[M(Pc)(CN)$_2$] · y(solvent)	1-D with A	Co	10^{-2}	metallic $>$ 250 K
		Fe	10^{-2}	metallic $>$ 280 K
[PXX][M(Pc)(CN)$_2$] (PXX-I)	Two-leg ladder with A and B	Co	10^{-2}	metallic $>$ 120 K
		Fe	10^{-1}	semiconducting
[PXX]$_2$[M(Pc)(CN)$_2$] (PXX-II)	2-D with A and B	Co	10^{-3}	metallic $>$ 100 K
[PXX]$_2$[M(Pc)(CN)$_2$] · CH$_3$CN (PXX-III)	2-D with B (double sheet by A)	Co	10^{-1}	semiconducting (metallic $>$ 5 K at 9 kbar)
[PXX]$_4$[M(Pc)(CN)$_2$] · CH$_3$CN (PXX-IV)	2-D with B (single sheet)	Co	10^4	semiconducting

(TPP = tetraphenylphosphonium and PTMA = phenyltrimethylammonium), the 1-D network of the Pc unit is formed [9,10]. On the other hand, PXX (*peri*-xanthenoxanthene) is an open-shell cation, and forms a one-dimensional column in the salt crystals. Though PXX is partially oxidized states, the columns are not conducting due to their periodic distortion or charge disproportionation. The Pc unit is also in partially oxidized states (each Pc ring is oxidized by about 1/2e) except for PXX-IV in which the ring is unoxidized. In PXX-I, the neighboring two 1-D with A chains interact by type B overlaps (two-leg ladder) [11]. In the other PXX compounds, the π–π stacking network becomes 2-D. In PXX-II, the 2-D sheet is constructed with both type A and B overlaps. Since these two overlap modes have different π–π interaction (overlap integral), the electronic structure of the 2-D sheet is anisotropic [12]. Nevertheless, the crystal is highly conducting and shows clear metallic behavior in a wider temperature range compared with those with simple 1-D network.

Contrary to PXX-II, PXX-III has a 2-D sheet constructed with solely type-B overlaps, resulting in nearly isotropic electronic structure [13]. Two of the neighboring sheets interact by type-A overlaps, forming double sheet structure. Since the π–π interaction in type-B overlap is much weaker than in type-A, the resistivity is rather high. However, by applying high pressure, the crystal shows metallic behavior down to 5 K. Though PXX-IV has the same isotropic 2-D sheet, it is not conductive because the Pc ligand is not oxidized.

The Fe salts studied in detail so far are of 1-D and ladder systems. In general, replacement of Co to Fe results in slight increase of resistivity at room temperature. This supposed to be due to the paramagnetic center in the π-ligand. The effect is more pronounced at lower temperature; the difference becomes more than several orders at around 20 K. The giant negative magnetoresistance observed around this temperature suggests π-d interactions in this system [4,14] and this feature may lead to the possibility of designing novel magneto-conductors.

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