

Synthesis and Properties of Axially-Ligated Co and Fe Phthalocyanines Partially-Oxidized Salts

○Derrick Ethelbhart C. Yu,¹ Toshio Naito,^{1,2} Tamotsu Inabe,¹ Akira Kikuchi,¹ Tetsuya Taketsugu,¹ Masaki Matsuda,³ and Hiroyuki Tajima³

¹ Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo

² Creative Research Initiative, Hokkaido University, Sapporo

³ Institute for Solid-State Physics, University of Tokyo, Kashiwa, Chiba

Partially-oxidized cobalt phthalocyanine salts with axial CN ligands, $\text{Co}^{\text{III}}(\text{Pc})(\text{CN})_2$, are known conductors primarily because their π -ligands are oxidized.¹ This type of $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ compound can be a vital component of molecular conductors due to the possibility of introducing different ligands and central metal atoms. These factors can lead to a variation in the π - π stacking structure of the molecular assemblies of the resulting compounds.² Compared with $\text{L} = \text{CN}$ compounds, $\text{L} = \text{X}$ (halides) compounds have not been studied in detail because the labile nature of halides makes it difficult to prepare the starting complexes.³

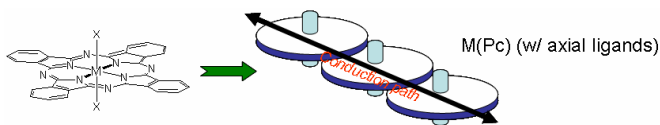
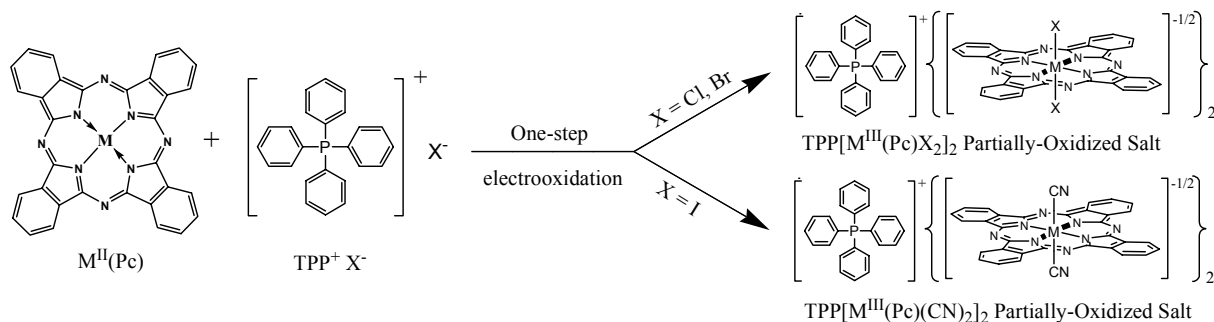


Figure 1. 1-D stacking arrangements of metal phthalocyanines.

A direct reaction to oxidize $\text{M}^{\text{II}}(\text{Pc})$ to $[\text{M}^{\text{III}}(\text{Pc})\text{X}_2]^-$ for $\text{M} = \text{Co}$ and Fe , and $\text{X} = \text{Cl}$ and Br is not known; hence, a multi-step synthesis involving a series of general methods is utilized to prepare the partially oxidized salts.^{4,5} However, this study has shown that the direct electrolysis of $\text{M}^{\text{II}}(\text{Pc})$ with TPP^+X^- (TPP = tetraphenylphosphonium; $\text{X} = \text{Cl}$ or Br) can result to produce the partially oxidized salts of $\text{TPP}[\text{M}^{\text{III}}(\text{Pc})\text{X}_2]_2$ (**Scheme 1**). Furthermore, electrolysis with TPP^+I^- in certain solvents has been found to give $\text{TPP}[\text{M}^{\text{III}}(\text{Pc})(\text{CN})_2]_2$ in one-step.



Scheme 1. General pathway for the one-step synthesis of $\text{TPP}[\text{M}^{\text{III}}(\text{Pc})\text{L}_2]_2$.

The series of crystals obtained are isomorphous (**Figure 2a**). The $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ units form a one-dimensional π - π stacking network. TPP stacks one-dimensionally and is surrounded by the $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ formation. The $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ unit is formally oxidized by $0.5e$, which translates into two $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ units per TPP counter cation. π - π overlaps are between two benzene rings from each adjacent $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ moiety (**Figures 2b** and **2c**).

The varying thickness of the axial ligands (twice of the van der Waals radii: $\text{CN} = 3.4\text{\AA}$, $\text{Cl} = 3.5\text{\AA}$, and $\text{Br} = 3.7\text{\AA}$) results in different distances between the $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ moieties, thereby affecting the effectiveness of the π - π overlap. This hypothesis was confirmed by the concurring results of the overlap integral calculations using the extended Hückel method, thermoelectric power, magnetic susceptibility, and electrical conductivity measurements, which translate to the relative band widths ($\text{CN} > \text{Cl} > \text{Br}$) of the $\text{M}^{\text{III}}(\text{Pc})\text{L}_2$ moieties.

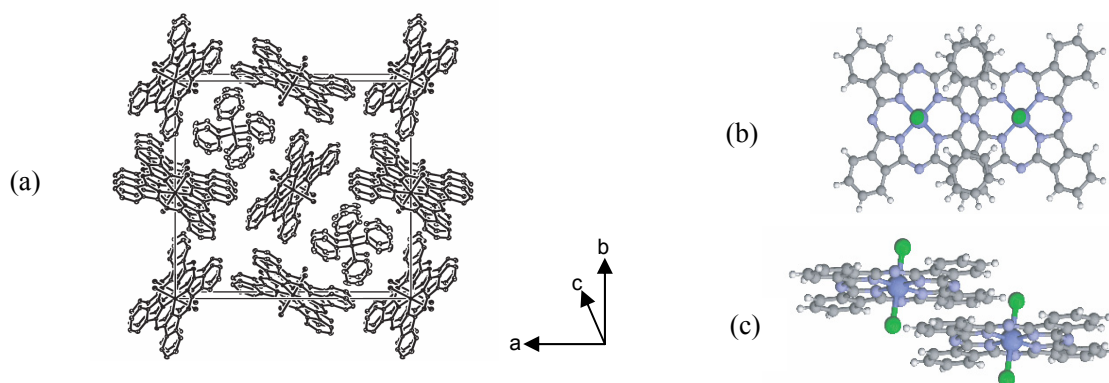


Figure 2. (a) Crystal structure of TPP[Co^{III}(Pc)Cl₂]₂. Space group = $P4_2/n$; Tetragonal; $Z=2$; And computational graphical representation of the π - π overlap between the Co^{III}(Pc)Cl₂ moieties: (b) top, and (c) side perspectives.

From the difference in axial ligand thickness, the effectiveness of the π -interaction between the

M(Pc) units is expected to be in the order CN>Cl>Br. However, the conductivity followed this trend only in the TPP[Co(Pc)L₂]₂ series. **Figure 3a** indicates that the Br-ligated species, which has the least effective π - π overlap, has the highest electrical resistivity.

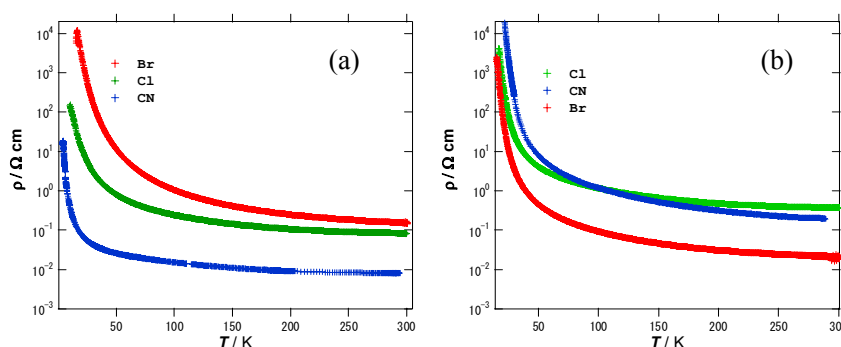


Figure 3. Electrical resistivity along the conduction path (c-axis) of (a) TPP[Co^{III}(Pc)L₂]₂, and (b) TPP[Fe^{III}(Pc)L₂]₂.

However, the Br species in the TPP[Fe(Pc)L₂]₂ series (**Figure 3b**) showed lower resistivity than its CN and Cl counterparts. One possible reason for this is since Fe³⁺ has magnetic spin, the ligand field energy (CN>>Cl>Br) variably splits the Fe³⁺ d -orbitals (d^5). Due to this, the degree of scattering of the conduction π -electrons by the magnetic moment may be altered by the d -orbital energy.

The magnetic susceptibility profile of the TPP[Fe(Pc)L₂]₂ series shown in **Figure 4**. It has been reported for L = CN that large anisotropy of susceptibility results from the very anisotropic g -tensor of the Fe(Pc)(CN)₂ unit. Such anisotropy is also observed for L = Cl and Br, but the degree seems to be smaller. The striking difference lies in the anomalies due to the antiferromagnetic interactions at low temperature (5-25K). The anomaly is supposed to be related to the magnitude of the π - d interaction, its lower degree and its occurrence at a lower temperature in TPP[Fe(Pc)X₂]₂ than in TPP[Fe(Pc)(CN)₂]₂ signifies that the former has a smaller π - d interaction than the latter.

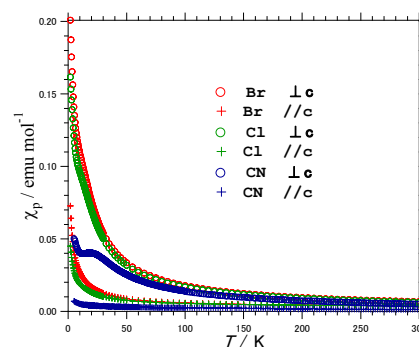


Figure 4. Magnetic susceptibility at 1T of TPP[Fe^{III}(Pc)L₂]₂.

Overall, this phenomenon can be attributed to the interaction between conduction π -electrons and localized d -spins in the [Fe^{III}(Pc)L₂]₂ units. Moreover, to further study these π - d systems, corroborating data from g -tensor anisotropy, magnetoresistance and magnetic torque measurements, as well as quantum chemical calculations for Fe^{III}(Pc)L₂ in order to evaluate the effect or influence of the axial ligands on the d -centered energy levels, are now in progress.

References 1) T. Inabe, *J. Porph. Phthal.* 2001, 5, 3; 2) T. Inabe, and H. Tajima, *Chem. Rev.* 2004, 104, 5503; 3) D.E.C. Yu, H. Imai, M. Ushio, S. Takeda, T. Naito, and T. Inabe, *Chem. Lett.* 2006, 35, 602; 4) J.F. Myers, G.W. Canham, and A.B.P. Lever, *Inorg. Chem.* 1975, 14, 461; 5) C. Hedtmann-Rein, M. Hanack, K. Peters, E. Peters, and H. G. von Schnering, *Inorg. Chem.* 1987, 26, 2647.