## Synthesis of Partially-Oxidized Salts of Metal Phthalocyanine with Axial Halides

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Axially-ligated metal phthalocyanines (MPc's) are promising candidates as a component of molecular conductors. Their outstanding feature is the variation of the π-π stacking structure in their molecular assemblies. Without axial ligands, the planar MPc molecules are expected to form a face-to-face stacking one-dimensional column. Any inter-columnar interaction may be negligible, since their π-orbitals are not overlapped between the columns. On the other hand, axially substituted species form completely different stacking structure. The adjacent π-ligands shift away from the protruding axial ligands and overlap with the planar parts where the charge carriers are accommodated in a variety of π-π stacking networks.
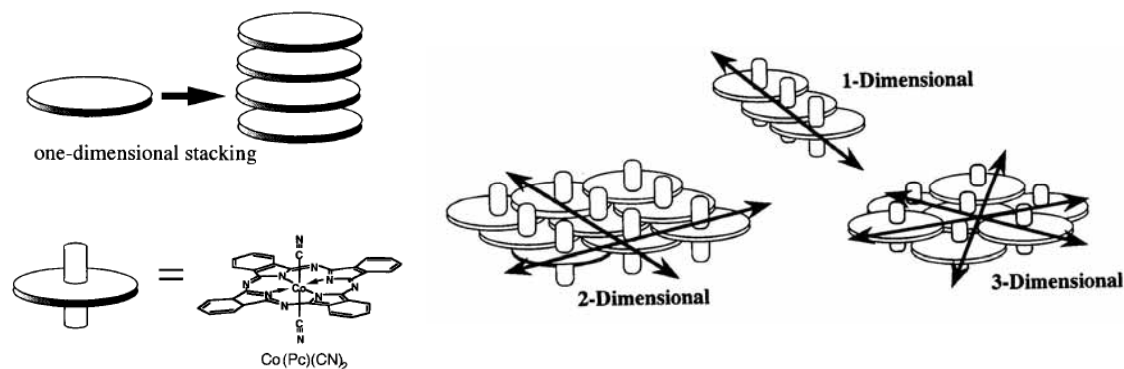
Axially-substituted metal phthalocyanines (Cyano-ligated; M = Co, Fe) have been found to form conducting species upon oxidation. Studies have shown that the axial substitution plays a major role in the effectiveness of π-π stacking and consequently on the solid state properties.

The development of phthalocyanines (Pc), particularly in the field of materials science hinges largely on the synthesis of new Pc derivatives. Employing halogens as axial ligands opens a new avenue for this exploration, due to some of the distinct and variable properties of this group in contrast with other known axially-ligated MPc's, particularly the dicyano-MPc.

We report herein the syntheses (multi-step and one-pot) of partially-oxidized crystalline salts of MPc's (M = Co, Fe) with axial halides (X = Cl, Br), utilizing tetraphenylphosphonium (TPP) as the cation, $TPP[M(Pc)X_2]_2$. Their crystal structures have been found to be isomorphous with $TPP[Co(Pc)(CN)_2]_2$.

$TPP[M(Pc)X_2]_2$ is synthesized by electrochemical oxidation of $K[M(Pc)(SCN)_2]$ and TPPX, or by direct one-pot electrochemical oxidation of MPc and TPPX. The first method involves initial chloro axial ligation by reacting MPc with thionyl chloride ($SOCl_2$) thereby producing the hardly soluble $M(Pc)Cl_2$. The proceeding step is axial ligand substitution by utilizing potassium thiocyanide (KSCN) to afford $K[M(Pc)(SCN)_2]$ salt which can be oxidized with TPPX to get $TPP[M(Pc)X_2]_2$ using acetone as solvent. The electrochemical crystallization process usually takes 2-3 weeks. The current also influences crystal quality, usually 1-3 μA yields good crystals.

The second procedure is a one-pot synthesis involving direct electrochemical reaction between MPc and TPPX. This method is more delicate in terms of solvent utilization. Some organic solvents were able to generate neutral radicals [M(Pc)X$_2$]. Tetrahydrofuran (THF) gave TPP[Co(Pc)X$_2$]$_2$, while an acetone-dimethylformamide (DMF) solvent system provided TPP[Fe(Pc)X$_2$]$_2$. Both partially-oxidized salts form dark green needle-like crystals.

As indicated by x-ray structure analysis, TPP[M(Pc)X$_2$]$_2$ forms one-dimensional π-π stacking network that results in a tetragonal crystal system. The MPc unit is formally oxidized by 0.5e, which translates into one MPc unit per TPP counter ion.

Since differing thickness of the axial ligands results into varying distances between neighboring molecules, as further evidenced by their overlap integrals (*s*) which indicated lower value for bulkier axial ligands (TPP[Co(Pc)(CN)$_2$]$_2$: $s = 10.0 \times 10^{-3}$, TPP[Co(Pc)Cl$_2$]$_2$: $s = 9.0 \times 10^{-3}$, TPP[Co(Pc)Br$_2$]$_2$: $s = 8.1 \times 10^{-3}$). This variation influences the electrical and magnetic properties of the system.
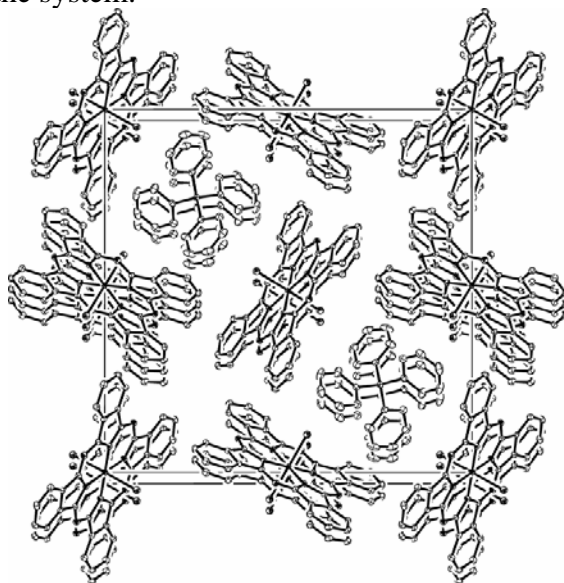
Crystal Structure of TPP[M(Pc)X$_2$]$_2$; Space group = $P4_2/n$; Crystal system = Tetragonal
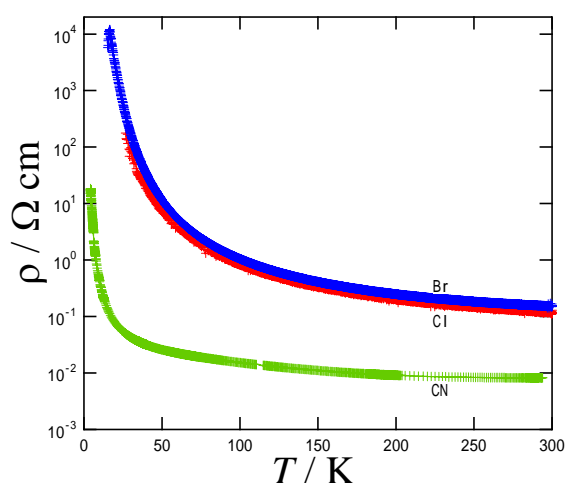
Temperature dependence of the electrical resistivity

Compared with its partially metallic dicyano-ligated counterpart, TPP[Co(Pc)X$_2$]$_2$ record one-order lower conductivity because of the lesser π-π overlap interaction, and they exhibit semiconducting properties.

A detailed characterization of TPP[M(Pc)X$_2$]$_2$ will be presented at the conference.