One-step Synthesis of Partially Oxidized Cobalt(III) Phthalocyanine Salts with Axial Ligands

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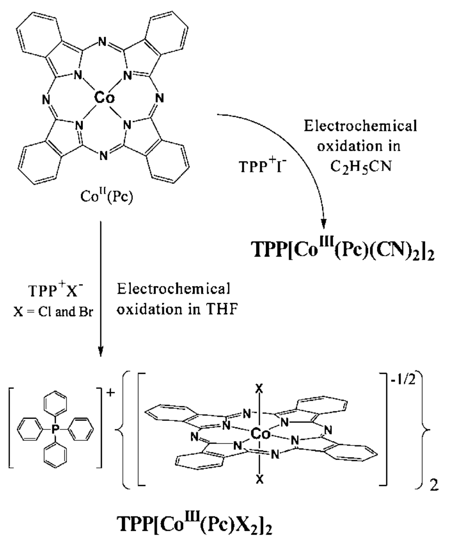
The one-pot syntheses of partially oxidized cobalt(III) phthalocyanine salts with axial halides, as well as a shorter route (single-step) for the axial dicyano counterpart are reported. The method utilizes an electrolytic reaction, and appears to be solvent dependent. Overlap integral calculations and electrical transport measurements indicate axial ligand effects on the molecular stacking of the cobalt phthalocyanine.

Partially-oxidized cobalt phthalocyanine salts with axial CN ligands, $Co^{III}(Pc)(CN)_2$, are known conductors, primarily because their π-ligands are oxidized.[1] This type of $M(Pc)L_2$ compound can be a vital component due to the possibility of introducing different ligands and central metal atoms. This leads to a variation in the π–π stacking structure of its molecular assemblies.[2] Compared with L = CN compounds, L = X (halides) compounds have not been studied in detail because the labile nature of halides makes it difficult to prepare the starting complexes. Herein, we present synthetic methodologies to synthesize new partially oxidized cobalt(III) phthalocyanine salts with axial halides.

A direct reaction to oxidize $Co^{II}(Pc)$ to $[Co^{III}(Pc)X_2]^-$ for X = Cl and Br is not known; therefore, a general method involving a multi-step synthesis[3,4] has to be utilized to prepare the partially oxidized salts. However, in this study, direct electrolysis of $Co^{II}(Pc)$ with TPP^+X^- (TPP = tetraphenylphosphonium; X = Cl or Br) has been determined to give the partially oxidized salts of $TPP[Co^{III}(Pc)X_2]_2$. Furthermore, electrolysis with TPP^+I^- in certain solvents has been found to give $TPP[Co^{III}(Pc)(CN)_2]_2$ in one-step. The series of crystals obtained are isomorphous, and their electrical properties are presented.

In our multi-step synthesis, $Co^{II}(Pc)$ was first allowed to react with thionyl chloride, thus producing the hardly soluble $Co^{III}(Pc)Cl_2$.[5] The proceeding step involves reduction of the Pc ligand as well as axial ligand substitution utilizing potassium thiocyanide to afford the $K[Co^{III}(Pc)(SCN)_2]$ salt.[4] The salt was then electrooxidized in acetone with TPP^+X^- to obtain the partially-oxidized $TPP[Co^{III}(Pc)X_2]_2$.

The one-pot synthesis of the partially oxidized $TPP[Co^{III}(Pc)X_2]_2$ salts involves the direct electrochemical reaction between $Co^{II}(Pc)$ and TPP^+X^- (Scheme 1). This method was initiated based on a report of the one-step electrocrystallization synthesis of the neutral radical $Co^{III}(Pc)Cl_2$.[6] Thus, we investigated whether this single-step procedure would be applicable to partially oxidized salts. This method was determined to be effective; however, more delicate in terms of solvent effects; only tetrahydrofuran (THF) gave $TPP[Co^{III}(Pc)X_2]_2$. Alternative organic solvents (dimethyl formamide, dichloromethane, dimethyl sulfoxide, acetone, and ethanol) only generated the neutral radical $Co^{III}(Pc)X_2$ crystals.



Scheme 1. One-step synthesis of $TPP[Co^{III}(Pc)L_2]_2$.

Interestingly, when propiononitrile was used as the solvent under the same single-step reaction conditions, a different product was observed. Propiononitrile produced a mixture of cyanide and halide ligands, $TPP[Co^{III}(Pc)(CN/X)_2]_2$; whereas propiononitrile with TPP^+I^- gave $TPP[Co^{III}(Pc)(CN)_2]_2$. Halides can act as nucleophilic reagents; therefore, the following equilibrium may be realized during electrolysis, $R–CN + X^- \rightleftharpoons R–X + CN^-$. For X = Cl or Br, both X^- and CN^- can be incorporated in the products, whereas only the $Co^{III}(Pc)(CN)_2$ species is selectively incorporated when I^- is used. This is thought to be due to the reducing ability of I^-, which makes it difficult to stabilize the I^--coordinated $Co^{III}(Pc)$. This one-step electrocrystallization method for synthesizing $Co^{III}(Pc)(CN)_2$ salts is desirable compared with the conventional multi-step route, which uses massive amounts of toxic cyanide reagents.

The electrocrystallization process varies depending on the method. The one-step synthesis usually takes 2–8 weeks, whereas the electrochemical reaction between $K[Co^{III}(Pc)(SCN)_2]$ and TPP^+X^- takes 1–3 weeks (current of 1–3 μA). Furthermore, a homogenous acetone solution of the $K[Co^{III}(Pc)(SCN)_2]$ with the TPP^+X^- system produced purely $TPP[Co^{III}(Pc)X_2]_2$. On the other hand, $Co^{II}(Pc)$ in the one-step synthesis did not completely dissolved in THF, and the electrolysis gave a mixture of crystals of $Co^{III}(Pc)X_2$ and $TPP[Co^{III}(Pc)X_2]_2$; they could be readily separated based on their different appearances. For the crystal growth of the partially oxidized salt, both $Co^{III}(Pc)X_2$ neutral radical and $[Co^{III}(Pc)X_2]^-$ anionic species have to coexist in the solution. Probably, this condition is satisfied only in THF in the one-step synthesis.

The single-crystal X-ray structural measurements revealed that the series of $TPP[Co^{III}(Pc)L_2]_2$[7–9] (L = CN, Cl, and Br)

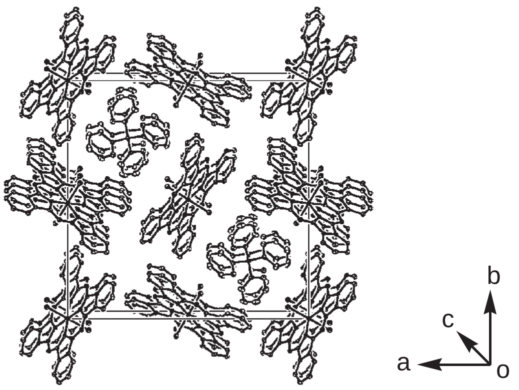
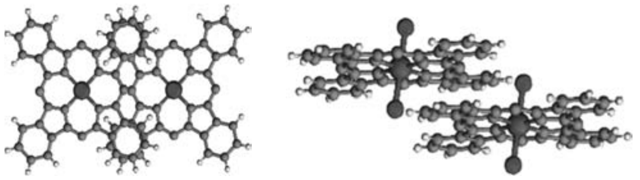


Figure 1. Crystal Structure of TPP[$Co^{III}(Pc)Cl_2]_2$.



(a) (b)

Figure 2. Computational graphical representation of the π–π overlap between the $Co^{III}(Pc)L_2$ moieties: top (a), and side (b) perspectives.

crystals was isomorphous (Figure 1). The $Co^{III}(Pc)L_2$ units form a one-dimensional π–π stacking network. In addition, TPP stacks one-dimensionally and is surrounded by the $Co^{III}(Pc)L_2$ formation. The $Co^{III}(Pc)L_2$ unit is formally oxidized by 0.5e, which translates into two $Co^{III}(Pc)L_2$ units per TPP counter cation, resulting in a tetragonal crystal system.

The varying thickness of the axial ligands[10] results in different distances between the $Co^{III}(Pc)L_2$ moieties, thereby affecting the effectiveness of the π–π overlap (Figure 2). This hypothesis was confirmed by overlap integral (S) calculation using the extended Hückel method.

The computed values obtained are as follows: for TPP-[$Co^{III}(Pc)(CN)_2]_2$, $S = 0.0085$;[7] for TPP[$Co^{III}(Pc)Cl_2]_2$, $S = 0.0090$; and for TPP[$Co^{III}(Pc)Br_2]_2$, $S = 0.0081$. These results indicate that as the ligand gets bulkier, the overlap integral decreases, and the band width becomes narrower.

Electrical resistivity measurements using a 4-probe technique further confirmed this relationship. As can be seen in Figure 3, the Br-ligated species, which has the least effective π–π overlap due to the bulky ligand, has the highest electrical resistivity. This series of crystals is expected to have a 3/4-filled metallic band, since the one-dimensional chain composed of Pc units formally oxidized by 0.5e is uniform. However, all of them exhibited an apparent semiconducting temperature dependence with a small activation energy ($E_A < 0.01$ eV for L = CN,[7] 0.008–0.015 eV for L = Cl, and 0.015–0.026 eV for L = Br). All of the systems have rather narrow bands, making the electronic system sensitive to the correlation effects; therefore, the semiconducting transport property may be related to the charge ordered instability suggested for quarter-filled one-dimensional molecular conductors.[11]

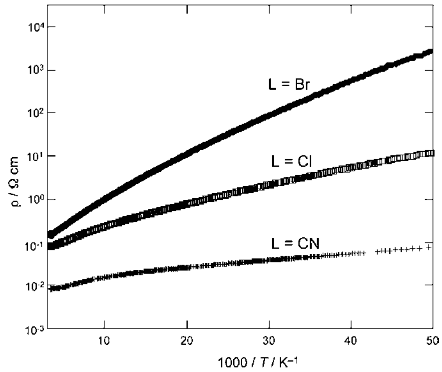


Figure 3. Electrical resistivity plot of TPP[$Co^{III}(Pc)L_2]_2$.

In conclusion, we were able to synthesize the partially oxidized $Co^{III}(Pc)L_2$ salts by a one-pot synthetic route. This methodology may be applied to other M(Pc) species, and useful for systematic extension of a variety of the conductors.

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8 Crystal data for TPP[$Co(Pc)Cl_2]_2$: $C_{88}H_{52}Co_2Cl_4N_{16}P$, fw 1624.14, tetragonal, space group $P4_2/n$, $a = 21.501(11)$, $c = 7.537(4)$ Å, $V = 3484.4(30)$ Å^3, $Z = 2$, $D_{calcd} = 1.548$ g cm^{-3}, Rigaku RAXIS-RAPID at 123 K, Mo Kα, μ (Mo Kα) = 7.175 cm^{-1}, No. of unique reflections = 3984, 265 variables, $R1 = 0.0309$ ($I \geq 2\sigma(I)$), $R_W = 0.0869$ (F^2, all data). CCDC-604220.
9 Crystal data for TPP[$Co(Pc)Br_2]_2$: $C_{88}H_{52}Co_2Br_4N_{16}P$, fw 1801.94, tetragonal, space group $P4_2/n$, $a = 21.4119(19)$, $c = 7.6088(7)$ Å, $V = 3488.4(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.715$ g cm^{-3}, Rigaku RAXIS-RAPID at 123 K, Mo Kα, μ (Mo Kα) = 28.616 cm^{-1}, No. of unique reflections = 3993, 265 variables, $R1 = 0.0481$ ($I \geq 2\sigma(I)$), $R_W = 0.1096$ (F^2, all data). CCDC-604221.
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