Novel Phthalocyanine Conductor Containing Two-dimensional Pc Stacks, $[PXX]_2[Co(Pc)(CN)_2]$ (PXX = *peri*-Xanthenoxanthene, $Co(Pc)(CN)_2$ = Dicyano(phthalocyaninato)cobalt(III))

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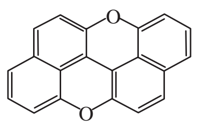
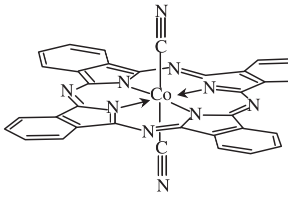
A novel phthalocyanine conductor containing 2-D π–π stacks of the partially oxidized $Co(Pc)(CN)_2$ units has been obtained by the electrochemical oxidation method with PXX. The crystal is highly conductive ($>10^3\,S\,cm^{-1}$) at all the temperatures measured ($5\,K < T < 300\,K$). Though the metallic character becomes clearer compared with the single chain or ladder chain conductors, the 2-D sheet has been found to be still anisotropic.

In order to construct molecular conductors with multi-dimensional π–π stacking structures we have been utilizing axially substituted phthalocyanines, $M^{III}(Pc)(CN)_2$ (M = Co, Fe). Most of the conducting crystals with multi-dimensional arrangements of the $Co(Pc)(CN)_2$ units are neutral radical crystals in which the Pc ligand is fully oxidized.[1] The partially oxidized salts with higher conductivities so far obtained are the following; the 1-D single chain conductors of $TPP[Co(Pc)(CN)_2]_2$ (TPP = tetraphenylphosphonium)[2] and $(PTMA)_x[Co(Pc)(CN)_2]\cdot y$(solvent) (PTMA = phenyltrimethylammonium),[3] the two-leg ladder conductor of $[PXX][Co(Pc)(CN)_2]$,[4] and $K[Co(Pc)(CN)_2]_2\cdot 5CH_3CN$[5] in which the $Co(Pc)(CN)_2$ units form 2-D sheets. Unfortunately, the last crystal with the highest dimensionality was unstable, so the dimensionality of the electronic structure in the 2-D Pc stacks has not been examined. We have recently obtained the partially oxidized salt of $[PXX]_2[Co(Pc)(CN)_2]$ with the 2-D Pc stacks. The anisotropy of the 2-D Pc π–π stacking sheet has been studied experimentally for the first time.



PXX



$Co(Pc)(CN)_2$

Single crystals were grown by electrochemical oxidation of $K^+[Co(Pc)(CN)_2]^-$ (ca. 20 mg) with PXX (ca. 10 mg) in acetonitrile (ca. 30 mL). In the previous paper,[4] this method was reported to give two kinds of crystals,[6] needles, and plates. Careful inspection of the needle crystals made us notice that there were two kinds of needles; one is the major species and corresponds to the previously reported ladder conductor, $[PXX][Co(Pc)(CN)_2]$, and the other is the title compound, $[PXX]_2[Co(Pc)(CN)_2]$, of which existence was not detected frequently. The crystal shapes are practically identical but they are distinguishable by surface luster. The crystal structure of $[PXX]_2[Co(Pc)(CN)_2]$ determined by X-ray analysis is shown in Figure 1a.[7] The cobalt atom of the $Co(Pc)(CN)_2$ unit is located on an inversion center and PXX is on a general position. The stoichiometry is found to be 2:1, and PXX forms a 1-D chain along the *c* axis. On the other hand, the $Co(Pc)(CN)_2$ units form a 2-D sheet parallel to the *ac* plane with the type A π–π overlap[1] along the *c* axis and the type B overlap[1] along [1 0 1] (Figure 1b). The effectiveness of the π–π interaction can be evaluated from the extended Hückel calculation. The HOMO–HOMO overlap integrals between the Pc rings are 9.9×10^{-3} along the *c* axis (s_A) (interplanar distance = 3.36 Å), and -1.8×10^{-3} along [1 0 1] (s_B) (3.51 Å). The periodicity of the PXX 1-D column is two-fold and there are two kinds of overlap integrals, 9.4×10^{-3} (3.45 Å) and -7.0×10^{-3} (3.41 Å) between PXX's. The effective charge δ in $[PXX^{+\delta}]_2[Co(Pc)(CN)_2]^{-2\delta}$ can be estimated from the molecular geometry of PXX[8] and is found to be 0.25. The oxidation state of the $Co(Pc)(CN)_2$ unit, therefore, is 0.5 from the stoichiometry; the chemical formula is $[PXX^{+0.25}]_2[Co(Pc)(CN)_2]^{-0.5}$. The calculated Fermi surface is shown in Figure 1c. There are two kinds of 1-D pairs along the *c* axis; one is the purely 1-D part formed by the PXX 1-D column and the other is the quasi-1-D part modulated by the dispersion along the k_a direction in the 2-D stacks of the $Co(Pc)(CN)_2$ units.

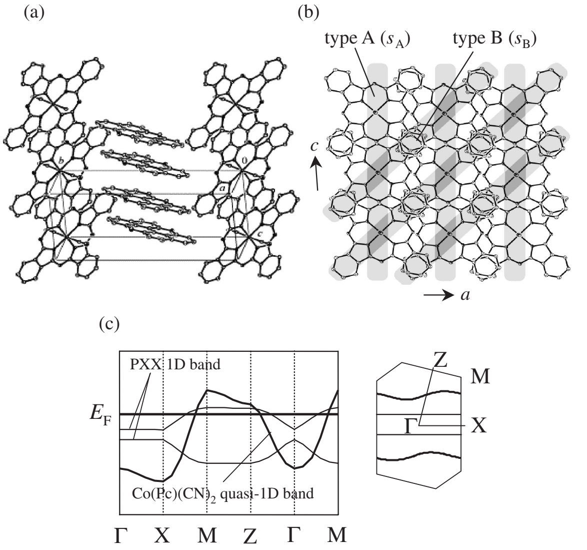


Figure 1. Crystal structure of $[PXX]_2[Co(Pc)(CN)_2]$ (a), the $Co(Pc)(CN)_2$ units arrangement in the *ac* plane (b) and the calculated band structure and Fermi surface (c).

The temperature dependence of the electrical resistivity along the *c* axis, corresponding to the needle axis, measured by a four probe method is shown in Figure 2. Compared with $TPP[Co(Pc)(CN)_2]_2$ ($\rho_{rt} = 10^{-2}\,\Omega\,cm$) and [PXX][Co(Pc)-

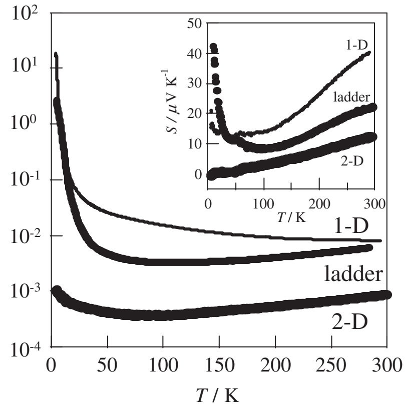


Figure 2. Temperature dependence of the electrical resistivity and the thermoelectric power (inset) of TPP[Co(Pc)$(CN)_2$]$_2$ (1-D), [PXX][Co(Pc)$(CN)_2$] (ladder) and $[PXX]_2$[Co(Pc)$(CN)_2$] (2-D).

$(CN)_2$] (10^{-2} Ω cm), the electrical resistivity in $[PXX]_2$[Co(Pc)-$(CN)_2$] is quite low (10^{-3} Ω cm) and the low resistivity is retained even at 5 K. The contribution from the PXX 1-D columns to the charge conduction must be negligibly small because of the two-fold periodicity and the narrow band width. Since the overlap integrals between the Pc rings in $[PXX]_2$[Co(Pc)$(CN)_2$] (9.9×10^{-3} and 1.8×10^{-3}) are the same order as in [PXX]-[Co(Pc)$(CN)_2$] (6.7×10^{-3} and 2.8×10^{-3}), and in TPP-[Co(Pc)$(CN)_2$]$_2$ (8.5×10^{-3}), the difference in the π–π stacking network structure is responsible for the difference in the transport properties. The temperature dependence of the thermoelectric power in $[PXX]_2$[Co(Pc)$(CN)_2$] clearly indicates the metallic behavior (Figure 2 (inset)); the thermoelectric power correlates linearly with temperature above 5 K, in contrast to [PXX][Co(Pc)$(CN)_2$] which shows metallic behavior only above 100 K. The positive values are consistent with the hole conduction in the partially oxidized Pc π systems.

Figure 3 shows the reflectance spectra at room temperature for the polarization parallel and perpendicular to the *c* axis in the *ac* plane. The spectrum with the polarization parallel to the *c* axis, $E_{//}c$, exhibits a plasma edge at around 5800 cm^{-1}. On the other hand, the $E_{\perp}c$ spectrum shows no notable dispersion in the frequency range studied, suggesting that the electronic structure of the $[PXX]_2$[Co(Pc)$(CN)_2$] is rather a 1-D system as suggested by the band calculation (Figure 1c). According to the 1-D tight-binding model,[9] the band width, $4t$, of the $[PXX]_2$[Co(Pc)$(CN)_2$] is estimated to be 0.53 eV, which is comparable to that of TPP[Co(Pc)$(CN)_2$]$_2$ (0.62 eV).[10] This observation is consistent with the overlap integrals and again indicating that the large difference in conducting behaviors is caused by the difference in the stacking network structure. However, the experiments reveal that the 2-D Pc arrangement does not lead to isotropic electronic structure because of the difference in the overlap integrals between s_A and s_B ($s_A/s_B = 5.5$).

In summary a highly conducting crystal containing the Pc 2-D π–π stacks, $[PXX]_2$[Co(Pc)$(CN)_2$], has been newly obtained. The calculated Fermi surface is the quasi-1-D and is consistent with the reflectance spectra in the *ac* plane. This indicates that the 2-D arrangement of the Co(Pc)$(CN)_2$ units by combining both type A and type B overlap modes rather leads to anisotropic electronic structure. The anisotropy may be reduced by the application of the hydrostatic pressure and/or the uniaxial strain to the crystal.

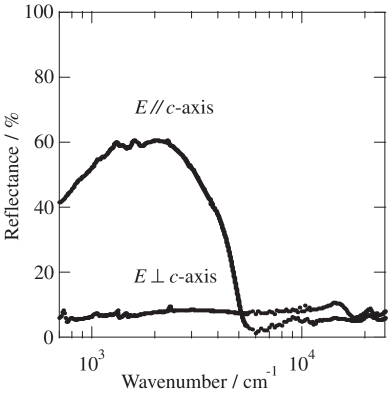


Figure 3. Single-crystal optical reflectance spectra of $[PXX]_2$-[Co(Pc)$(CN)_2$] with the polarization parallel and perpendicular to the *c*-axis.

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References and Notes

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6 The plates are $[PXX]_2$[Co(Pc)$(CN)_2$]·CH_3CN, and the study of the plates is now in progress.

7 Crystal data for $[PXX]_2$[Co(Pc)$(CN)_2$]: $C_{74}H_{36}O_4N_{10}Co$, triclinic, space group $P1$, $a = 9.8929(9)$ Å, $b = 18.175(2)$ Å, $c = 7.2949(8)$ Å, $\alpha = 95.175(2)°$, $\beta = 104.335(3)°$, $\gamma = 96.413(4)°$, $V = 1253.4(2)$ Å^3, $Z = 1$, $D_{calcd} = 1.574$ g cm^{-3}. The intensity data were collected on a Rigaku R-AXIS Rapid-imaging plate diffractometer at 123 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). A purplish black needle with dimensions of $0.65 \times 0.03 \times 0.10$ mm^3, μ(Mo Kα) = 4.16 cm^{-1}, 11484 reflections measured, 5622 unique reflections, 3861 reflections with $I > 3.00\sigma(I)$, $R = 0.043$, $R_w = 0.051$ (403 variables). Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication no. CCDC-224549. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html. Instruction for depositing the crystallographic data is available on the Web at http://www.ccdc.cam.ac.uk/conts/depositing.html.

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