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A Molecular Conductor Based on Axially CN-Substituted Cobalt Tetrabenzoporphyrin

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A molecular conductor based on axially CN-substituted cobalt tetrabenzoporphyrin is reported. The crystal structure is isomorphous with a phthalocyanine-based conductor, however, estimation of effectiveness of π–π overlap and electrical transport measurement reveal that a slight change in molecular structure of macrocyclic π-conjugated ligands has significant influence on intermolecular interaction and electrical properties.

Phthalocyanine (Pc), a well-known macrocyclic π-conjugated ligand, is widely used in molecular electronics as a donor molecule or a p-type semiconductor,[1] and axially CN-substituted metallophthalocyanine complexes of $[\mathrm{M^{III}(Pc)(CN)_2}]^-$ (M = Co or Fe) are known as versatile building blocks for molecular conductors showing various crystal structure, electronic structure, and fascinating phenomena such as giant negative magnetoresistance.[2] Since to control and understand intermolecular interaction is a most important subject in the study of molecular conductors, there are several reports on using other axial ligands of Cl or Br as well as other macrocyclic π-conjugated ligands of 1,2- or 2,3-naphthalocyanines. Such substitution with bulky ligands can surely modulate π–π overlapping and electrical and magnetic properties.[3–5]

Herein, we present a molecular conductor of TPP[Co(tbp)(CN)$_2$]$_2$ (TPP: tetraphenylphosphonium), based on a macrocyclic π-conjugated ligand of tetrabenzoporphyrin (tbp) (Chart 1). The difference in molecular structure of tbp and Pc is only atoms at the meso positions bridging four pyrrole rings; substitution of the bridging nitrogen atoms of Pc with less electronegative methine groups forms tbp. In addition, the extended Hückel calculation shows that the distribution of HOMO coefficients of tbp and Pc are similar to each other. These features suggest that the crystal structure of the molecular conductor based on tbp is isostructural with that based on Pc, and comparison of the π–π overlap and electrical transport properties of the tbp-based molecular conductor with those of the Pc-based one is meaningful because we can understand influence on electrical transport properties caused by the slight change in the molecular structure of macrocyclic π-conjugated ligand. However, no report is available on molecular conductors composed of axially CN-substituted [M(tbp)] complex because of difficult and complicated preparation procedures.

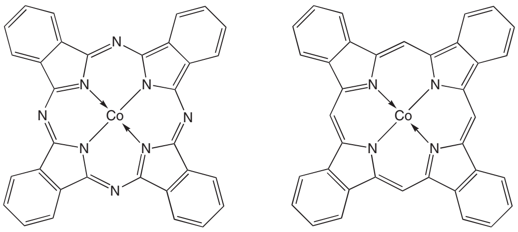

Chart 1.

In this study, first [Zn(tbp)] was synthesized by the template cyclization of isoindoline-3-acetic acid with zinc acetate reported by Edwards et al.[6] Second $\mathrm{H_2(tbp)}$ was obtained by demetalation of [Zn(tbp)] in concentrated sulfuric acid, and [Co(tbp)] was prepared from $\mathrm{H_2(tbp)}$ and bis(acetylacetonato)-cobalt(II) in refluxing 1-chloronaphthalene. The obtained [Co(tbp)] was stirred with NaCN in ethanol at room temperature, leading to Na[Co(tbp)(CN)$_2$], and the cation exchange was carried out by metathesis using tetraphenylphosphonium (TPP) iodide. The molecular conductor TPP[Co(tbp)(CN)$_2$]$_2$ was fabricated by electrochemical oxidation of obtained TPP[Co(tbp)-(CN)$_2$] in acetonitrile under the constant current of 1 µA. TPP[Co(tbp)(CN)$_2$]$_2$ could be also obtained by electrolysis of [Co(tbp)] with tetraphenylphosphonium iodide in propionitrile, as in the case of the preparation of TPP[Co(Pc)(CN)$_2$]$_2$.[3]

The crystal structure of TPP[Co(tbp)(CN)$_2$]$_2$ determined by X-ray diffraction is shown in Figure 1a.[7] As expected, TPP[Co(tbp)(CN)$_2$]$_2$ is isostructural with TPP[Co(Pc)(CN)$_2$]$_2$,[8] and the 1:2 ratio of cation:[Co(tbp)(CN)$_2$] units gives an effective charge of −0.5 for one [Co(tbp)(CN)$_2$] unit; each tbp ring is formally oxidized by 0.5e from the initial closed-shell tbp^{2-}. Along the *c* axis, the [Co(tbp)(CN)$_2$] units uniformly stack with the π–π overlapping of peripheral benzene rings, meaning that HOMOs of [Co(tbp)(CN)$_2$] units are expected to form a one-dimensional 3/4-filled band.

The regular stacking of [Co(tbp)(CN)$_2$] units along the *c* axis, induced by special symmetry of TPP cation,[8] is the same as that of [Co(Pc)(CN)$_2$] units in TPP[Co(Pc)(CN)$_2$]$_2$, however, there are intermolecular N···H contacts within the sum of van der Waals radii between CN ligands and CH groups at the meso positions of adjacent two [Co(tbp)(CN)$_2$] units (Figure 1b). As seen in Figure 2, the molecular structure of the [Co(tbp)(CN)$_2$] unit is quite similar to that of [Co(Pc)(CN)$_2$] unit except for the meso positions. While nitrogen atoms at the meso positions of Pc repulse CN ligands of adjacent [Co(Pc)(CN)$_2$] units, the less electronegative methine groups make it possible to form the intermolecular N···H contacts with CN ligands of adjacent [Co(tbp)(CN)$_2$] units. As a result, CN ligands of the [Co(tbp)(CN)$_2$] unit become more linear.

The discrepancy of the intermolecular contacts strongly suggests changes in intermolecular interaction, therefore, we calculated angles between the *c* axis and the normal vector of the least-squares plane of 24 non-hydrogen atoms composing porphin for TPP[Co(tbp)(CN)$_2$]$_2$ and tetraazaporphyrin for TPP[Co(Pc)(CN)$_2$]$_2$, respectively. The angle in TPP[Co(tbp)-(CN)$_2$]$_2$ is 26.42°, which is about 3% larger than 25.59° in TPP[Co(Pc)(CN)$_2$]$_2$. The difference is reflected in interplanar

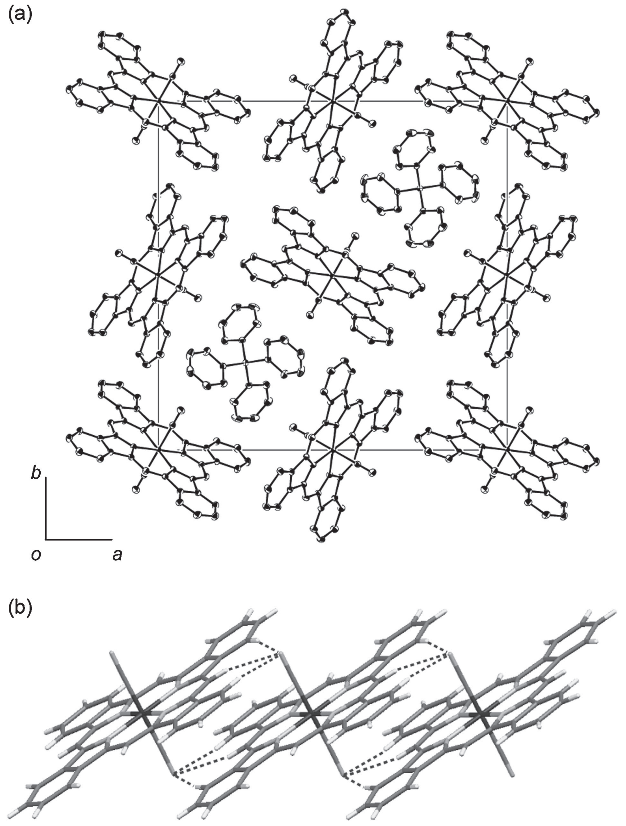

Figure 1. (a) Crystal structure of TPP[Co(tbp)(CN)$_2$]$_2$ and (b) molecular arrangement along the *c* axis. Dashed lines depict intermolecular N···H contacts.

distances of peripheral benzene rings; 3.44 and 3.50 Å for TPP[Co(tbp)(CN)$_2$]$_2$, and 3.40 and 3.46 Å for TPP[Co(Pc)(CN)$_2$]$_2$.[8] As a result, effectiveness of the π–π overlapping in TPP[Co(tbp)(CN)$_2$]$_2$ becomes reduced; the overlap integral between tbp rings estimated by extended Hückel calculation is 7.5×10^{-3}, which is 12% smaller than 8.5×10^{-3} of the overlap integral between Pc rings of TPP[Co(Pc)(CN)$_2$]$_2$.[8] The reduction of the π–π overlapping caused by the substitution of the bridging nitrogen atoms of Pc with less electronegative methine is more significant than that by steric repulsion observed in bulky axial ligand systems of TPP[Co(Pc)X$_2$]$_2$ (X = Cl or Br).[3]

Temperature dependence of electrical resistivity of TPP[Co(tbp)(CN)$_2$]$_2$, measured by using a four-probe method, is shown in Figure 3, together with that of TPP[Co(Pc)(CN)$_2$]$_2$. The resistivity at room temperature of $7.8 \times 10^{-2}\,\Omega\,\mathrm{cm}$ is ten times larger than that of TPP[Co(Pc)(CN)$_2$]$_2$ ($8.2 \times 10^{-3}\,\Omega\,\mathrm{cm}$).[8] In spite of the expected 3/4-filled band, the temperature dependence of resistivity of both conductors shows semiconducting behavior with small activation energies of 0.0185 and 0.01 eV for TPP[Co(tbp)(CN)$_2$]$_2$ and TPP[Co(Pc)(CN)$_2$]$_2$, respectively. In one-dimensional quarter-filled system, it is suggested that strong electron correlation should cause charge disproportionation, leading to an insulating ground state.[9] For TPP[Co(Pc)(CN)$_2$]$_2$, the charge disproportionation is certainly reported;[10] therefore, it seems that the ground state of TPP[Co(tbp)(CN)$_2$]$_2$ is also the charge-disproportionate state and that the electronic system becomes more sensitive to electron correlation owing to the reduction of bandwidth caused by the change in the intermolecular contacts.

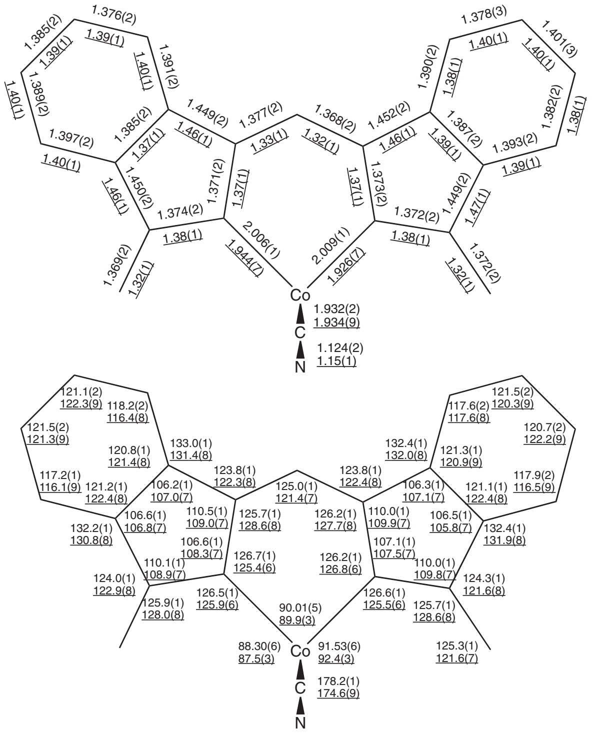

Figure 2. Bond lengths (Å) and angles (degree) of [Co(tbp)(CN)$_2$] and [Co(Pc)(CN)$_2$] units in TPP[Co(tbp)(CN)$_2$]$_2$ and TPP[Co(Pc)(CN)$_2$]$_2$. The values for TPP[Co(Pc)(CN)$_2$]$_2$ are cited from ref 8 and underlined.

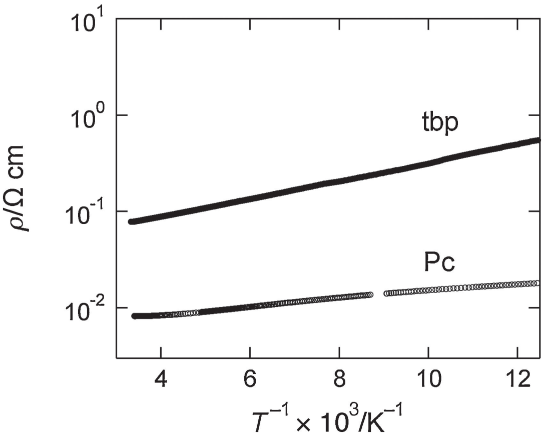

Figure 3. Temperature dependence of electrical resistivity along the *c* axis of TPP[Co(tbp)(CN)$_2$]$_2$ and TPP[Co(Pc)(CN)$_2$]$_2$.

In conclusion, by using a macrocyclic π-conjugated ligand of tbp, we have succeeded in fabricating a molecular conductor of TPP[Co(tbp)(CN)$_2$]$_2$. Although the molecular structure of tbp is similar to that of Pc and crystal structure of the obtained TPP[Co(tbp)(CN)$_2$]$_2$ was isostructural with TPP[Co(Pc)(CN)$_2$]$_2$, substitution of nitrogen atoms at meso positions with CH groups significantly affected π–π overlapping and electrical conductivity, suggesting that a slight change in molecular structure of macrocyclic π-conjugated ligands can effectively control intermolecular interaction. These results lead to new developments of molecular functional materials.

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7 Crystal data for TPP[Co(tbp)(CN)$_2$]$_2$: $C_{100}H_{60}N_{12}PCo_2$, fw 1578.49, tetragonal, $P4_2/n$, $a = 21.687(3)$, $c = 7.5462(2)$ Å, $V = 3547.11$ Å^3, $D_{\text{calcd}} = 1.48\,\text{g cm}^{-3}$. The intensity data were collected on a Bruker SMART APEX difractometer with graphite monochromated Mo Kα radiation ($\lambda =$ 0.7107 Å), μ(Mo Kα) $= 0.556\,\text{cm}^{-1}$, 3429 reflections with $I > 2.0\sigma(I)$, $R = 0.0555$, $R_w = 0.1690$ (262 variables). CCDC-843883.

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