

A Molecular Conductor Based on Axially CN-Substituted Cobalt Tetrabenzoporphyrin

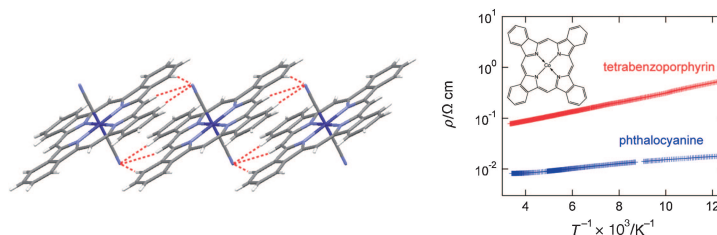
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A molecular conductor based on axially CN-substituted cobalt tetrabenzoporphyrin is reported. The crystal structure is isomorphous with a phthalocyanine-based conductor, however, estimation of effectiveness of π - π overlap and electrical transport 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 $[M^{III}(Pc)(CN)_2]^-$ ($M = Co$ 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.

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 $H_2(tbp)$ was obtained by demetalation of $[Zn(tbp)]$ in concentrated sulfuric acid, and $[Co(tbp)]$ was prepared from $H_2(tbp)$ 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 porphyrin 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

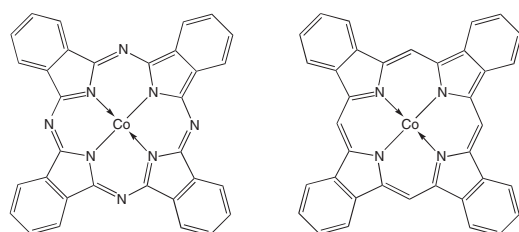


Chart 1.

molecular 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: C₁₀₀H₆₀N₁₂PCo₂, fw 1578.49, tetragonal, *P*4₂/*n*, *a* = 21.687(3), *c* = 7.5462(2) Å, *V* = 3547.11 Å³, *D*_{calcd} = 1.48 g cm⁻³. The intensity data were collected on a Bruker SMART APEX diffractometer with graphite monochromated Mo Kα radiation (*λ* = 0.7107 Å), *μ*(Mo Kα) = 0.556 cm⁻¹, 3429 reflections with *I* > 2.0σ(*I*), *R* = 0.0555, *R*_w = 0.1690 (262 variables). CCDC-843883.
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