

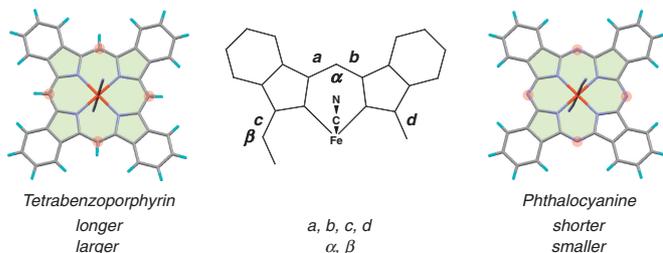
Comparison of Structural and Electrical Characteristics between Tetrabenzoporphyrin- and Phthalocyanine-based Charge-transfer Complexes

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Comparison of the molecular structures of isostructural tetrabenzoporphyrin (tbp) and phthalocyanine (Pc) complexes reveals that the distances and angles between the pyrroles and the atoms at the *meso* positions in tbp are greater than those of Pc, indicating that the differences around the *meso* positions are substantial between the porphin and porphyrazine frameworks.

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A charge-transfer complex based on axially CN-substituted iron tetrabenzoporphyrin has been fabricated. X-ray structure analysis reveals that the differences in the distances and angles around the *meso* positions between tetrabenzoporphyrin and phthalocyanine are substantial between the porphyrin and porphyrazine frameworks. Electrical transport measurements reveal semiconducting behavior with higher activation energy due to the reduction in π - π overlapping, compared to an isostructural phthalocyanine complex.

Phthalocyanine (Pc) (Chart 1) has been widely used as a donor molecule or p-type semiconductor.¹ Tetrabenzoporphyrin (tbp), a macrocyclic ligand similar to Pc, has recently attracted considerable interest in molecular electronics because of its high performance in organic thin film devices.² The only difference in the molecular structures of tbp and Pc lies in the atoms at the *meso* positions bridging four pyrrole rings; substitution of the bridging nitrogen atoms of Pc with less-electronegative methin groups affords tbp. Although the distribution of the HOMO coefficients of tbp and Pc is similar,³ the HOMO and LUMO levels of tbp are about 0.4 and 0.5 eV higher than those of Pc, respectively,⁴ suggesting that even a slight difference in molecular structure affects the electronic properties. Moreover, in a previous study on charge-transfer complexes composed of [Co^{III}(tbp)(CN)₂] and [Co^{III}(Pc)(CN)₂], we reported that intermolecular interactions and charge-transport properties can be effectively controlled by slightly modifying the molecular structure of macrocyclic π -conjugated ligands.³

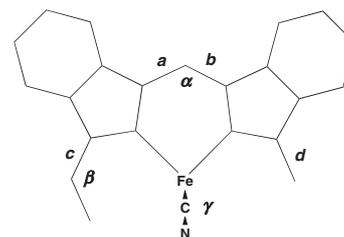
Herein, we employ a newly fabricated charge-transfer complex TPP[Fe^{III}(tbp)(CN)₂]₂ (TPP: tetraphenylphosphonium) and report the structural differences between tbp and Pc, along with the electrical transport properties of charge-transfer complexes based on these molecules. Both porphyrin and Pc are useful modeling compounds for biomaterials, and there are numerous structural reports on them. However, comparison of Pc to porphyrin is essentially ineffective owing to the difference

in their frameworks. On the other hand, as mentioned above, since the molecular structure of tbp resembles that of Pc, comparisons between them make it possible to consider the subtle structural differences between tbp and Pc, equivalent to the differences between the porphyrin and porphyrazine frameworks. Furthermore, as charge-transfer complexes generally involve strong intermolecular π - π interactions, comparison of the molecular arrangement and electrical properties between tbp- and Pc-based charge-transfer complexes provides insights into the difference in intermolecular interactions, which would be useful in comprehending the molecular electronics of macrocyclic complexes.

H₂(tbp) was prepared following the reported procedure,³ and Fe(tbp) was synthesized from H₂(tbp) and iron(II) chloride in refluxing 1-chloronaphthalene. The obtained Fe(tbp) was stirred with KCN in ethanol to afford K[Fe(tbp)(CN)₂]; cation exchange was carried out by metathesis using tetraphenylphosphonium (TPP) bromide. The charge-transfer complex, TPP[Fe(tbp)(CN)₂]₂, was fabricated by the electrochemical oxidation of TPP[Fe(tbp)(CN)₂] in acetonitrile, under a constant current of 0.3 μ A in an Ar atmosphere.

The selected bond lengths and bond angles of the [Fe(tbp)(CN)₂] unit in TPP[Fe(tbp)(CN)₂]₂, determined by X-ray crystal structure analysis at 300 K,⁵ with those of the [Fe(Pc)(CN)₂] unit in TPP[Fe(Pc)(CN)₂]₂,⁶ are shown in Table 1.⁷ Although the molecular structures of Pc and tbp are almost same, the bond lengths and angles around the *meso* positions and the Co–C \equiv N

Table 1. Selected bond lengths (\AA) and angles (degree) of [Fe(tbp)(CN)₂] and [Fe(Pc)(CN)₂] units in TPP[Fe(tbp)(CN)₂]₂ and TPP[Fe(Pc)(CN)₂]₂, respectively^a



	TPP[Fe(tbp)(CN) ₂] ₂	TPP[Fe(Pc)(CN) ₂] ₂
<i>a</i> / \AA	1.377(3)	1.323(3)
<i>b</i> / \AA	1.376(3)	1.325(3)
<i>c</i> / \AA	1.374(3)	1.323(1)
<i>d</i> / \AA	1.377(3)	1.322(3)
α / $^\circ$	125.8(2)	121.8(2)
β / $^\circ$	125.9(2)	121.9(2)
γ / $^\circ$	179.2(3)	174.9(2)

^aFe^{III} ion of [Fe(tbp)(CN)₂] and [Fe(Pc)(CN)₂] units lies on inversion center.

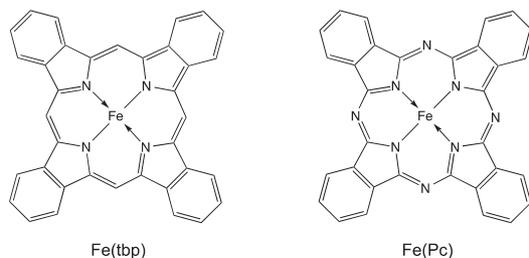


Chart 1.

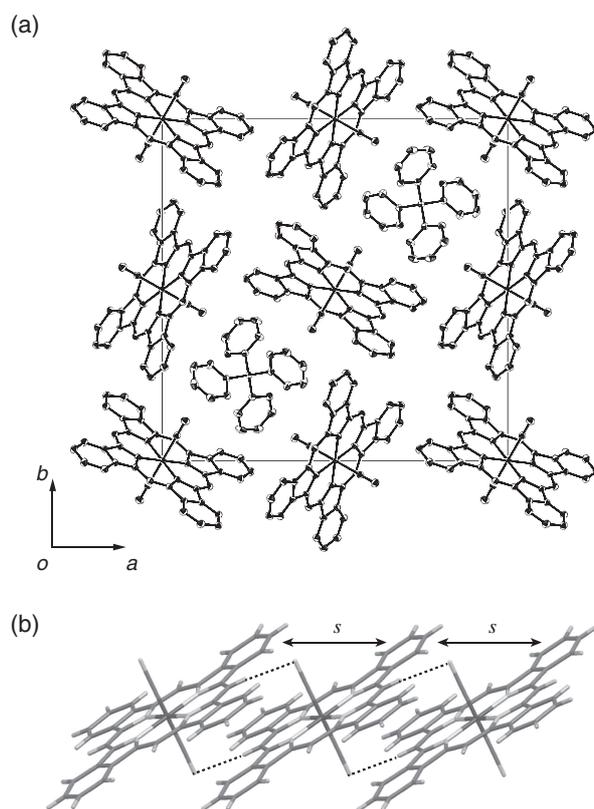
Table 2. Lattice parameters and overlap integrals (*s*) of TPP[Fe(tbp)(CN)₂]₂, TPP[Fe(Pc)(CN)₂]₂, TPP[Co(tbp)(CN)₂]₂, and TPP[Co(Pc)(CN)₂]₂ at room temperature and 120 K

	TPP[Fe(tbp)(CN) ₂] ₂		TPP[Fe(Pc)(CN) ₂] ₂		TPP[Co(tbp)(CN) ₂] ₂		TPP[Co(Pc)(CN) ₂] ₂	
Temperature/K	300	120	293	120	RT	120	296	120
Space group	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> 4 ₂ / <i>n</i>	<i>P</i> 4 ₂ / <i>n</i>
<i>a</i> /Å	21.7632(4)	21.6330(4)	21.722(2)	21.5807(4)	21.6807(3)	21.6002(3)	21.676(8)	21.5342(3)
<i>c</i> /Å	7.5449(1)	7.4887(1)	7.448(2)	7.3931(1)	7.5462(2)	7.4940(1)	7.474(4)	7.4020(1)
Volume/Å ³	3573.5(1)	3504.6(1)	3514.4(5)	3443.2(1)	3547.1(1)	3496.5(1)	3511(3)	3432.5(1)
<i>s</i> (×10 ⁻³)	7.6	8.4	8.7	9.7	7.5	8.2	8.5	9.7
Ref.	This study	This study	6	This study	3	4	17	4

angle in the [Co(tbp)(CN)₂] unit are significantly different from those in the [Co(Pc)(CN)₂] unit.^{3,4} As shown in Table 1, the same tendency was maintained between TPP[Fe(tbp)(CN)₂]₂ and TPP[Fe(Pc)(CN)₂]₂. Distances between the pyrrole units and atoms at the *meso* positions are longer in the *tbp* unit; angles between the pyrrole units and atoms at the *meso* positions are larger in the *tbp* unit. The Fe–C≡N angle in the *tbp* unit is more linear than that in the *Pc* unit. Comparing the reported porphyrinatoiron(III) compounds with Fe(*Pc*) and Fe(*Pc*)X units (X = Cl and I),^{8–13} it is found that the bond lengths and angles around the *meso* position in porphyrin are also longer and larger than those in phthalocyanine. Thus, the shorter bond lengths and smaller bond angles around the *meso* position in *Pc* than in *tbp* are substantial, and can be attributed to the smaller atomic radius and lone pair of nitrogen atoms at the *meso* positions. Further, the differences are substantial in the molecular framework between porphyrin and porphyrazine, which are less affected by the introduction of a central metal and axial ligands as well as by substitutions on macrocyclic ligands.^{14–16}

Figure 1 shows the crystal structure of TPP[Fe(tbp)(CN)₂]₂, which is isostructural with TPP[Co(tbp)(CN)₂]₂, TPP[Fe(Pc)(CN)₂]₂, and TPP[Co(Pc)(CN)₂]₂.^{3,6,17} The [Fe(tbp)(CN)₂] units uniformly stack along the *c* axis, with overlapping peripheral benzene rings with interplanar distances of 3.46 and 3.52 Å, leading to the formation of a one-dimensional electronic system with a 3/4-filled HOMO band, as well as the other three compounds. The intermolecular N...H contacts (2.69 Å) are within the sum of the van der Waals radii between the CN ligands and the CH groups at the *meso* positions of the two adjacent [Fe(tbp)(CN)₂] units (Figure 1b). Similar contacts are observed for TPP[Co(tbp)(CN)₂]₂,³ suggesting that the intermolecular contacts, weak C–H...N-type hydrogen bonds, make the M–C≡N angle in the [M(tbp)(CN)₂] unit more linear than that in the [M(Pc)(CN)₂] unit. In other words, the lone pair of the nitrogen atom at the *meso* position in the [M(Pc)(CN)₂] unit repulses the CN ligands of the adjacent units.

X-ray crystal structure analyses for TPP[Fe(tbp)(CN)₂]₂ and TPP[Fe(Pc)(CN)₂]₂ at 120 K were also performed.¹⁸ Table 2 summarizes their cell parameters and overlap integral (vide infra) at room temperature and 120 K, together with those of TPP[Co(tbp)(CN)₂]₂ and TPP[Co(Pc)(CN)₂]₂.^{3,4,6,17} As seen in Figure 2, thermal variations in the lattice parameters of all the compounds show the same trend, i.e., contraction of the *c* axis is larger than that of the *a* axis; however, the Co salts are more anisotropic than the Fe salts. To evaluate the influence of anisotropy on changes in the effectiveness of the intermolecular interaction, the overlap integrals between the *tbp* rings or *Pc* rings along the *c* axis were estimated by extended Hückel

**Figure 1.** (a) Crystal structure of TPP[Fe(tbp)(CN)₂]₂ and (b) molecular arrangement along the *c* axis. Dashed lines depict intermolecular N...H contacts. The overlap integral (*s*) along the *c* axis is estimated by extended Hückel calculation (see main text).

calculations for all the compounds at room temperature and 120 K. At room temperature, the estimated value for TPP[Fe(tbp)(CN)₂]₂ was 7.6×10^{-3} , which was almost identical to that of TPP[Co(tbp)(CN)₂]₂ (7.5×10^{-3}) and smaller than that of TPP[Fe(Pc)(CN)₂]₂ and TPP[Co(Pc)(CN)₂]₂ (8.7×10^{-3} and 8.5×10^{-3} , respectively).^{3,6,17} At 120 K, the overlap integrals of TPP[Fe(tbp)(CN)₂]₂ and TPP[Co(tbp)(CN)₂]₂ were 8.4×10^{-3} and 8.2×10^{-3} , respectively, while that of both TPP[Fe(Pc)(CN)₂]₂ and TPP[Co(Pc)(CN)₂]₂ was 9.7×10^{-3} . These results indicate that although the effectiveness of π - π overlapping in both [M(tbp)(CN)₂] and [M(Pc)(CN)₂] units is enhanced as temperature decreases, the anisotropies observed in the contraction of cell axes are insignificant for π - π overlapping.

Figure 3 shows the temperature dependence of the electrical resistivity of TPP[Fe(tbp)(CN)₂]₂, together with that of

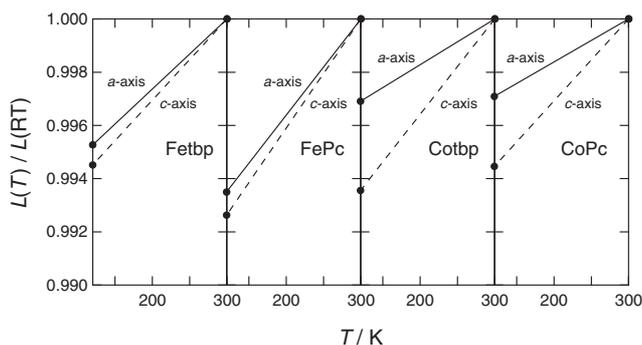


Figure 2. Temperature dependence of length (L) of a axis (solid line) and c axis (dashed line) for (a) TPP[Fe(tbp)(CN)₂]₂, (b) TPP[Fe(Pc)(CN)₂]₂, (c) TPP[Co(tbp)(CN)₂]₂, and (d) TPP[Co(Pc)(CN)₂]₂.

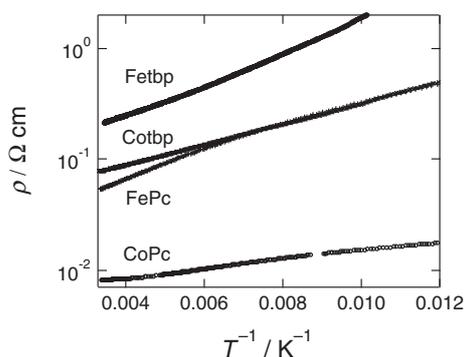


Figure 3. Temperature dependence of electrical resistivity of TPP[Fe(tbp)(CN)₂]₂, TPP[Co(tbp)(CN)₂]₂, TPP[Fe(Pc)(CN)₂]₂, and TPP[Co(Pc)(CN)₂]₂.

TPP[Fe(Pc)(CN)₂]₂, TPP[Co(tbp)(CN)₂]₂, and TPP[Co(Pc)(CN)₂]₂, measured using a four-probe method. Similar to the other three compounds, TPP[Fe(tbp)(CN)₂]₂ showed semiconducting behavior with an activation energy of 0.028 eV, which was the largest among those for the compounds studied. Substitution of Pc to tbp and the nonmagnetic Co^{III} to the magnetic Fe^{III} ($S = 1/2$) enhances the semiconducting behavior, owing to the reduction in π - π overlapping and spin scattering, respectively.^{3,19} Therefore, the largest activation energy and resistivity observed for TPP[Fe(tbp)(CN)₂]₂ is reasonable. The suppression of magnetic scattering by the magnetic field would enable us to observe a giant negative-magnetoresistance effect in TPP[Fe(tbp)(CN)₂]₂.

In conclusion, we performed X-ray crystal structure analysis on a newly fabricated charge-transfer complex of TPP[Fe(tbp)(CN)₂]₂. Comparison of the molecular structures of TPP[Fe(tbp)(CN)₂]₂ with those of isomorphous Co(tbp), Fe(Pc), and Co(Pc) compounds revealed that the distances and angles between the pyrroles and atoms at the *meso* positions in tbp compounds were greater than those in Pc, indicating that the differences around the *meso* positions are substantial between the porphyrin and porphyrazine frameworks. The differences in the *meso* position also affect the intermolecular π - π overlapping, leading to changes in the electrical properties. These results would provide valuable information for improving the molecular electronics of macrocyclic complexes.

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Supporting Information is available electronically on J-STAGE.

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