



Electronic Structure Mechanism of Axial Ligands on Itinerant Electrons and Negative Magnetoresistance in Axially-Ligated Iron(III) Phthalocyanine Molecular Conductors

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ABSTRACT

Partially-oxidized Iron(III) phthalocyanine ($\text{Fe}^{\text{III}}\text{Pc}$) with axial CN or Br ligands are molecular conductors with giant negative magnetoresistance. Electron conduction occurs via intermolecular overlapping of Pc π -orbitals, while negative magnetoresistance is brought about by intramolecular interaction between Fe-d and Pc- π orbitals. Aside from permitting slip-stacked solid-state arrangement, axial ligands can further enhance the π -d interaction of $\text{Fe}^{\text{III}}(\text{Pc})$ depending on the strength of ligand field energies that proportionally leads to larger negative magnetoresistance. However, the strong ligand field of CN results in conductivity reduction due to the π -accepting nature of the ligand which enhances electron gradient in the oxidized Fe^{3+} , thereby localizing itinerant electrons in Pc, as evidenced by charge transfers between Fe-d and CN- π orbitals. In contrast, the π -donating nature of Br ligands complements the electron deficiency of Fe^{3+} , resulting in the delocalization of itinerant electrons in the Pc system, thus creating a highly conducting molecular system with giant negative magnetoresistance.

Keywords: π -d interaction, Axially-ligated iron(III) phthalocyanine, Molecular conductor, Giant negative magnetoresistance.

INTRODUCTION

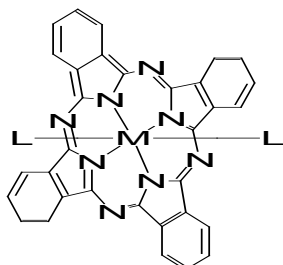
Phthalocyanine (Pc) is a planar molecule composed of four circular N-linked isoindole rings forming a fully-conjugated 18 π -electron system –ideal structural and chemical characteristics as building blocks of functional materials. In recent years, molecular engineering has been employed

to the Pc moiety to utilize its potential solid-state applications, particularly as organic conductors. Octahedral-coordinating central metal such as $\text{Co}^{3+}(\text{d}^6)$ and $\text{Fe}^{3+}(\text{d}^5)$ are incorporated to Pc to enable the attachment of linear axial ligands such as CN, thereby forming slip-stacked solid-state arrangement between adjacent $\text{Co}^{\text{II}}/\text{Fe}^{\text{III}}(\text{Pc})(\text{CN})_2$ units, resulting in the intermolecular overlapping



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of π -orbitals between Pc rings (HOMO), and thus generating electron conduction path/band upon partial-oxidization of the Pc system (electron hole transport)¹.



Scheme 1. Structure of Metallophthalocyanine with di-axial ligands (M = Fe³⁺, Co³⁺; L = CN, Cl, Br)

Axial ligands can further modify the properties of the metal phthalocyanine system. For Co^{III}(Pc)L₂ system, electrical conductivity are correlated to the effectiveness of intermolecular Pc π - π orbital overlap emanating from the bulkiness/steric effect of the axial ligands which are in the order: L = CN > Cl > Br².

The incorporation of magnetic Fe³⁺ (s = 1/2) central metal produces highly conducting Fe^{III}(Pc)L₂ (L = CN, Cl, Br) series with anisotropic giant negative magnetoresistance (GNMR).

The GNMR is brought about by the interaction between the d-orbital of Fe³⁺ and the π -orbital of the Pc moiety. Interestingly, it was observed that the intensity of π -d interaction is affected and can be modulated by the varying magnitudes of axial ligand field energy³.

Axial ligands affect the electronic structure of the Fe^{III}(Pc) system resulting in the modulation of orbital interactions. Ab initio calculations derived the differences (proximity) between the π and d orbital energies which correspond to the intensity of π -d interaction as 8.5450 eV and 7.8655 eV for L = Br and CN, respectively⁴. It was established that the axial ligand correspondingly lifts Fe-d orbitals nearer to Pc- π orbitals depending on its field energy, thereby intensifying π -d interaction. Moreover, the extent of the π -orbitals of the axial ligands results into stronger d-d interactions^{5,6}. Thus, higher axial ligand field energy equates to stronger π -d orbital interaction.

The intensity of the π -d interaction has a direct correlation effect on the GNMR of the

Fe^{III}(Pc)L₂ system. At magnetic field of 15 Tesla, Fe^{III}(Pc)(CN)₂ and Fe^{III}(Pc)Br₂ have exhibited 93% and 67% reduction of electrical resistivity (GNMR), respectively. However, the intensity of GNMR in Fe^{III}(Pc)L₂ (L = CN > Br) have an inverse effect on the normal electrical conductivity (at ambient temperature and magnetic field) of the Fe^{III}(Pc)L₂ series which resulted in the order: L = CN < Br, wherein a 2-order electrical conductivity decrease in Fe^{III}(Pc)(CN)₂ attributed to π -d interaction, and no decrease in the electron transport of Fe^{III}(Pc)Br₂ were observed, even as the Br-ligated species also has a relatively strong π -d interaction as demonstrated by its GNMR profile³.

For years, there was a prevailing concept that the existence of π -d interaction in the Fe^{III}(Pc)L₂ system will always consequently equate to electron localization (decrease in conductivity). However, an absence of electron localization was observed in the Fe^{III}(Pc)Br₂ system, where its electrical conductivity is in the same order as its Co homologue, Co^{III}(Pc)Br₂, in which there is no π -d interaction. In terms of molecular structure, the electronic conduction band width of Fe^{III}(Pc)L₂ stood unaffected by the π -d and GNMR interplay, as it remained to be based on the effectiveness of the intermolecular Pc π - π orbital overlap brought about by the steric effect of the axial ligands⁷. Thus, the origin of the π -d interaction– electron localization – GNMR interplay phenomenon in the Fe^{III}(Pc)L₂ system may be traced to its electronic structure. And the elucidation of the electronic structure mechanism of Fe^{III}(Pc)L₂ may provide new prospects in the design of functional highly conducting molecular systems with GNMR.

MATERIALS AND METHODS

Tetraphenylphosphonium (TPP) salts of axially-ligated metallophthalocyanines: TPP[Fe^{III}(Pc)(CN)₂]₂⁺, TPP[Fe^{III}(Pc)Br₂]₂⁺ and TPP[Co^{III}(Pc)(CN)₂]₂⁺ were synthesized using previously reported methods^{2,3}. For TPP[Co^{III}(Pc)(CN)₂]₂⁺ and TPP[Fe^{III}(Pc)(CN)₂]₂⁺: 30 mg Co^{II}(Pc)/Fe^{II}(Pc) and 60 mg tetraphenylphosphonium iodide (TPPI) was dissolved in 40 mL propionitrile (CH₃CH₂CN) in a two-compartment electrochemical cell. Applied current was set at 10 μ A. Partially-oxidized TPP[Co^{III}(Pc)(CN)₂]₂⁺ and TPP[Fe^{III}(Pc)(CN)₂]₂⁺ took 6-8 weeks to crystallize with a yield of about 10-15%. For TPP[Fe^{III}(Pc)Br₂]₂⁺: 30 mg Fe^{II}(Pc) and 60 mg TPPBr

were suspended in 40 mL 1:3 dimethylformamide (DMF) : acetone solvent system and subsequently mixed via a sonicator. A current of 5 μ A was then applied to the system. Electrocrystallization of the partially-oxidized TPP[Fe(Pc)Br₂]₂ takes 2-3 weeks to accomplish. The product conversion is between 60-70%.

UV-Vis solution absorption spectra of TPP[Fe^{III}(Pc)(CN)₂]₂, TPP[Fe^{III}(Pc)Br₂]₂ and TPP[Co^{III}(Pc)(CN)₂]₂ in Dimethylformamide were measured from 13000 cm⁻¹ to 30000 cm⁻¹ using a JASCO Ubest V570 spectrophotometer.

RESULTS AND DISCUSSION

The electronic absorption spectra is an effective method to experimentally describe the electronic structure and corresponding orbital interactions of the Fe^{III}(Pc)L₂, which is a unique single molecule π -d system.

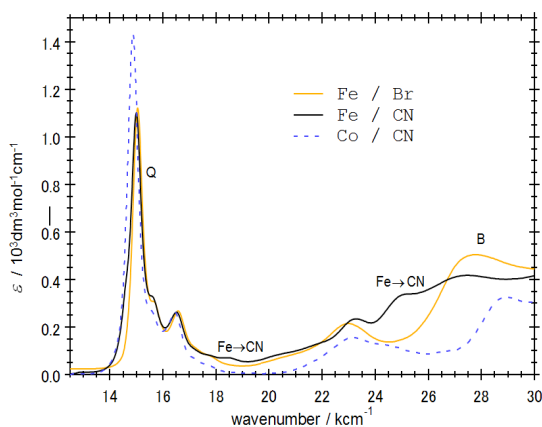


Fig. 1. UV-Vis spectra of TPP[Fe^{III}(Pc)(CN)₂]₂, TPP[Fe^{III}(Pc)Br₂]₂ and TPP[Co^{III}(Pc)(CN)₂]₂

Figure 1 displays the UV-Vis absorption spectra of TPP[Fe^{III}(Pc)(CN)₂]₂, TPP[Fe^{III}(Pc)Br₂]₂ and TPP[Co^{III}(Pc)(CN)₂]₂ from 13000 to 30000 cm⁻¹. The characteristic intra-Pc ring $\pi \rightarrow \pi^*$ transitions: Q ($1a_{1u}(\pi) \rightarrow 1e_g(\pi^*)$) at around 15000 cm⁻¹ (665 nm), and B/Soret: ($1a_{2u}(\pi) \rightarrow 1e_g(\pi^*)$) at around 27500 cm⁻¹ (365 nm) were observed for all species. Also, for the Fe^{III}(Pc)(CN)₂ species, two metal to axial ligand charge transfers (MLCT) were detected:

MLCT₁ = ($e_g(d\pi) \rightarrow 1b_{1u}(\pi^*)$) at around 18500 cm⁻¹ (540 nm), and MLCT₂ = ($e_g(d\pi) \rightarrow 1b_{2u}(\pi^*)$) at around 25000 cm⁻¹ (400 nm)⁸.

The charge transfer (CT) between Fe³⁺ and CN ligands in Fe^{III}(Pc)(CN)₂ and the absence of CT between Fe³⁺ and Br ligands in Fe^{III}(Pc)Br₂, despite having π -d interactions, points to the axial ligands as the origin of the electron localization/delocalization mechanism in the Fe^{III}(Pc)L₂ system. That is, the oxidized state of Fe³⁺ (vacancy in $e_g(d\pi)$) enables the attraction of electron density from electron-rich Pc (Fe- d_{yz} to Pc- p_z), while axial CN which is a strong π -acceptor further intensifies the withdrawal of electron density from Fe³⁺ (to CN p_x -orbital), thereby resulting to the localization of itinerant electrons in Pc. In contrast, the strong π -donor character of Br appears to compensate for the electron deficiency of Fe³⁺, thereby favoring electron delocalization that results in the easing of electron transport on the part of the Pc moiety. Moreover, the absence of the MLCT peaks in Co^{III}(Pc)(CN)₂ system (Fig. 1) further ascertains that the nature of MLCT₁ and MLCT₂ are induced by the π -d electron interplay in the Fe^{III}(Pc)(CN)₂ species.

CONCLUSION

The strong π -d interaction in Fe^{III}(Pc)L₂ system always result in GNMR. Axial ligands enhance the π -d interaction depending on their field energy. It is established that the π -d interaction in Fe^{III}(Pc)L₂ does not always result in electron localization. Electron localization is not dependent on the π -d but on the electronic character of the axial ligands.

Employing axial ligands that are π -donor (weak field energies) by nature will still significantly enhance the π -d interaction of Fe^{III}(Pc) to produce GNMR with the absence electron localization. π -donor ligand such as Br compensates for the electron deficiency of the oxidized Fe³⁺, thereby easing itinerant electrons in Pc to favor electron delocalization. Thus, it is possible to create a highly conducting magnetic molecular system with GNMR such as Fe^{III}(Pc)Br₂ which has strong π -d interaction and unhampered electron transport.

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