1P014

Electronic Structures and Correlating Properties of Axially-Ligated Metallophthalocyanine Molecular Conductors

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Metallophthalocyanines [M(Pc)] become conductors when their HOMO which is located on the Pc-π, is oxidized in any extent. Moreover, axial ligands can be attached to its central metal thereby enabling the control and design of its solid-state crystallographic arrangement. The orientation of M(Pc) particularly its intermolecular distances, positions, and dimensionality, plays an important factor on its physical characteristics, especially on its electrical conductivity (**Figure 1**) [1].

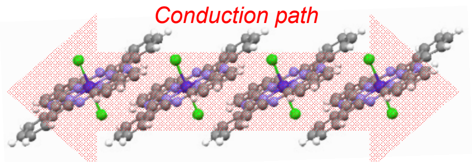

Figure 1. M(Pc)L_2 slipped-stack 1-D formation.

The varying physico-chemical properties of the central metal and ligands influence the intramolecular π-d and the intermolecular π-π interactions which eventually affects the electronic character and thus, the solid-state properties of the system (**Figure 2**). The electronic structures of the non-magnetic Co^{3+} and the magnetic Fe^{3+} π-conjugated phthalocyanines with various sets of axial ligands of different sizes and ligand field strengths can contribute an important role in better understanding the nature of molecular conductors, more specifically their inherent correlation effects which are of importance for future multifunctional conducting materials.

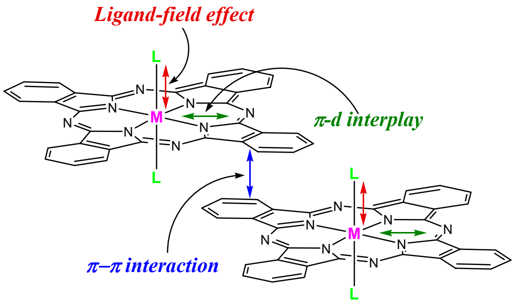

Figure 2. Inter-/intra-molecular M(Pc)L_2 interactions.

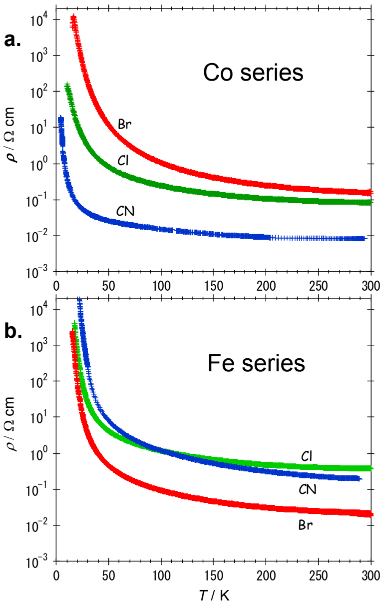

Figure 4. Electrical resistivity profile.

As appropriate representative model compounds for this study, we have synthesized partially-oxidized salts of Co^{III} and Fe^{III} phthalocyanines with axial cyanide, chloride, and bromide, with tetraphenylphosphonium (TPP) as counter cation - TPP[$M^{III}(Pc)L_2]_2$ - via multi-step and single-step procedures. The resulting crystal structure reveals one-dimensional formation of M(Pc)L_2 along with TPP which also forms in single profiles in-between the interstitial spaces. Intermolecular overlap between M(Pc) units takes place among their two adjacent benzene rings (**Figure 3**). The axial ligand thickness (bulkiness) is a key factor in the effectiveness of the π-π interaction between M(Pc)L_2 units. Thus, the expected trend in the conductivity (L = CN > Cl > Br) due to the varying band widths related to the effective π-π overlap caused by the different axial ligand

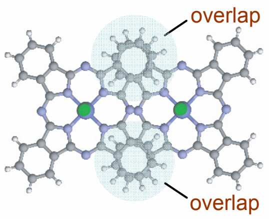

Figure 3. Inter-M(Pc) overlap.

sizes (Br > Cl > CN) in M(Pc)L_2 compounds is observed in the TPP[Co^{III}(Pc)L_2]$_2$ series (**Figure 4a**) [2]. As for the TPP[Fe^{III}(Pc)L_2]$_2$ series, an unusual conductivity profile is observed (L = Br > Cl ≈ CN) (**Figure 4b**). This is thought to be due to factors relating to the varying π-*d* interactions in the system – a phenomenon which can be attributed to the interaction between conduction π-electrons of the Pc and localized *d*-spins of the central metal, and the effect of the chemical species of the axial ligands on the Pc-metal π-*d* system.

Taking a closer examination on the M(Pc)L_2 electronic system, unlike Co^{3+} which has a d^6 (S = 0) configuration, Fe^{3+} (d^5) has a magnetic spin (S = 1/2) and from which, based on molecular modeling calculation, an unpaired electron occupies one of doubly-degenerate d_{xz} and d_{yz} orbitals (**Figure 5**). Therefore, this makes the possibility for the different ligand field energies (CN >> Cl > Br) to variably split the Fe^{3+} *d*-orbitals. The *d*-level splitting thus affects the energy difference between the HOMO (Pc-π) and the doubly-degenerate d_{xz} and d_{yz} orbitals of the Fe^{3+}, which in turn modulates the π-*d* interaction in the M(Pc)L_2 complex, and eventually affects their physical properties. By employing theoretical quantum chemical calculations, corroboration to this hypothesis was observed (**Figure 6**).

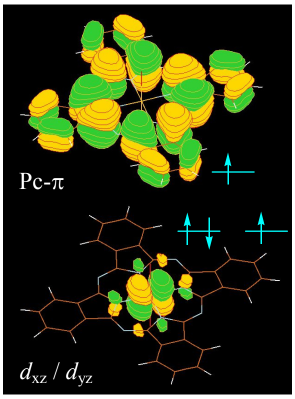

Figure 5. Electronic structure.

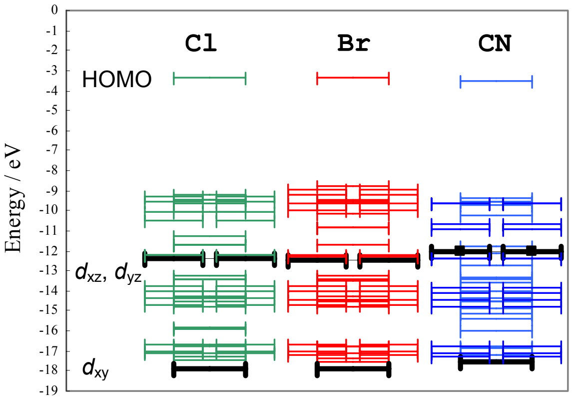

Figure 6. Calculated orbital energy diagram of Fe^{III}(Pc)L_2.

Magnetic anisotropy is a vital characteristic in consideration for conceptualizing and creating multifunctional conducting materials. The magnetic susceptibility feature of the Fe^{III}(Pc)L_2 series (**Figure 7**), as supported by the *g*-factor data (**Figure 8**) derived from electron paramagnetic resonance measurements reveals high magnetic anisotropy, moreover, it is hardly affected by the ligand manipulation scheme. However, the magnetic susceptibility anomaly due to some antiferromagnetic interaction occurs at lower temperature in the case of L = Cl & Br as compared with L = CN, signifying lesser π-*d* interaction. Thus, this magnetic property manifestation is in agreement with the conductivity as well as the electronic profile of the Fe series which has varying π-*d* interactions. They collectively suggest that the intensity of the π-*d* interplay can be strongly correlated with the conductivity of the system.

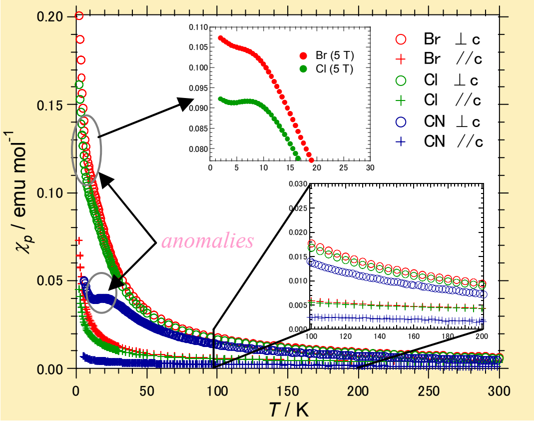

Figure 7. Magnetic susceptibility @ 1 T; top inset @ 5 T.

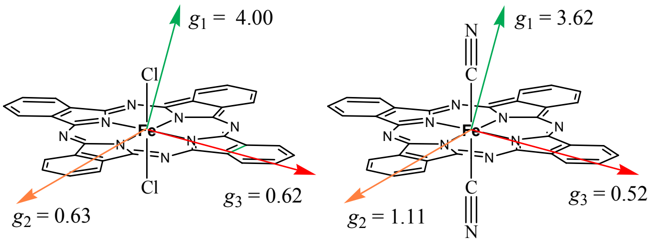

Figure 8. Schematic illustration of Fe^{III}(Pc)L_2 *g*-factor anisotropy.

Nevertheless, given that the basic criteria essential for multifunctional conductors are satisfied in the partially-oxidized Fe^{III}(Pc)L_2 system, further investigations are now being done to probe more thoroughly onto the extend of this correlation.

References

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2. D.E.C. Yu, H. Imai, M. Ushio, S. Takeda, T. Naito, and T. Inabe, *Chem. Lett.* **2006**, *35*, 602.