

Magnetic and Electronic Transport Engineering of Metallophthalocyanine Molecular Conductors

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Phthalocyanines (Pc) are flat, π -conjugated structures ideal for molecular solid-state engineering. Various metals and axial ligands can be incorporated to the Pc unit – $M(Pc)L_2$, thereby enabling control and design of solid-state crystallographic arrangement. Furthermore, $M(Pc)L_2$ can become efficient conductors when their highest-occupied molecular orbital (Pc π -system) is oxidized. Particularly, variations in the intermolecular distances and dimensionalities of the $Co(Pc)L_2$ system result into modified electrical conductivities depending on the effectiveness of the intermolecular Pc π - π orbital overlaps.¹

The incorporation of a magnetic central metal (Fe^{3+}) into the $M(Pc)L_2$ system can result into further functionalization, producing magnetic molecular conductors. However, the inherent interaction between the d-metal orbital and the Pc π -system (π -d) causes the scattering of itinerant electrons thereby reducing electron transport. It was found out that the π -d interaction can be proportionally modulated by the strength of the ligand field energies of the axial ligands (CN, Cl, Br), enabling further tuning (intramolecular) of electrical conductivity. Moreover, it turned out that the π -d interaction also proportionally varies magnetotransport because the electronic state formed by the π -d interaction can be variably broken by external magnetic field, thus resulting in apparent controllable giant negative magnetoresistance (~65-95%).²

A closer look on the electronic structure of the partially-oxidized $M(Pc)L_2$ ($M = Co^{3+}$, Fe^{3+} ; $L = CN$, Cl, Br) system through optoelectronic and thermoelectric profiles reveals that the electronic conduction band (width) is determined exclusively by the effectiveness of the π - π orbital overlap of the Pc units ($L = CN > Cl > Br$). Furthermore, paramagnetic concentration derived from Curie-tail contribution deduced varying localized electron concentrations in the $M(Pc)L_2$ system which correlate the efficiency of electron transport and hence, their band width profile. Thus, the construction and establishment of stable and intrinsic electronic conduction band (width) further zero-in on the essential factors concerning the design of ideal multifunctional molecular conductors.

[1] T. Inabe et al., *Chem. Rev.* 104 (2004) 5503; D.E.C. Yu et al., *Chem. Lett.* 35 (2006) 602.

[2] D.E.C. Yu et al., *J. Chem. Mater.* 19 (2009) 718.