Skewered Cyano-Bridged Cobalt Naphthalocyanine Polymer: An Electron Transport Engineering

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Naphthalocyanines (Nc) are ideal molecular conductors due to their flat and fully-conjugated structures. Attachment of a central metal (Co) and dicyano (CN) axial ligands to Nc produced CN-bridged cobalt naphthalocyanine, a skewered-type polymer complex. The polymeric species enabled intra-chain electron transport through the CN bridge by which, coupled with the interchain π - π overlaps, produced a multi-dimensional electronic system. This molecular design has decreased the electrical resistivity by 5 orders relative to the monomeric Co(Nc) with di-axial CN complex.

Keywords: molecular conductors, naphthalocyanine, molecular engineering

1. INTRODUCTION

Molecular conductors are electrical conductors based on organic components/ compounds. The principal rationale and motivation for the study of this class of compounds are: the lower density of organic compounds than classical metal conductors; and the versatility of organic systems which enables materials engineering. In this variety of conducting materials, the orbital overlapping between the organic π -systems $(\pi - \pi \text{ interaction})$ is the primary factor for the electron transport [Scheme 1].



Scheme 1. Electron-Transport Via the π - π Orbital Overlaps in Molecular Systems (rectangles represent molecular units ideally flat).

In designing a suitable molecular conductor, it is necessary to increase the electron transport path and dimensionality in order to achieve optimal π - π orbital interactions between molecular units (Marks, 1990).

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Naphthalocyanine (Nc) is a structurallyideal component for molecular conductors [Figure 1a]. Its flat structure enables solid-state design flexibility, and its extensive fullyconjugated π -system permits optimal electron path and mobility (delocalization). Nc is a π extended derivative of a contemporary and important molecular conductor called phthalocyanine (Pc) [Figure 1b]. Furthermore, Nc also share the structural versatility of Pc, i.e., the incorporation of central metal and corresponding axial and peripheral substitution for the eventual modulation of properties (Inabe and Tajima, 2004).



(b)

Figure 1. (a) 1,2-naphthalocyanine, a π -Extended Derivative of Phthalocyanine, (b).

The facile insertion of cobalt as central atom in Pc results in an octahedral configuration that eventually enables di-axial (CN) ligand attachment makes cobalt an ideal central metal. And since polymerization can occur through axial ligands in Co(Pc) (Metz and Hanack, 1983), the same is considered true with Co(Nc). In effect, the utilization of Nc produce a more extended molecular π -system, thus, a more reduced HOMO-LUMO band gap that is likely to result in a better electrical conductivity (Orti et al., 1996).

It has been established that electron transport occurs through the CN-bridge between molecular π -systems. Thus, it would be suitable to explore the CN-bridge factor in optimizing the avenues for electron transport in Nc systems. And as an additional possibility, the skewered-type conformation produced by the CN-bridged Nc is also deem to generate intra- and inter-(skewer) chain π -orbital interactions that may additionally increase electrical conductivity [Scheme 2].



Scheme 2. Multidimensional Intra-Chain and Inter-Chain Electron Transport in a Skewered-Type (CN-bridged Nc) Molecular Conductor Design.

2. METHODOLOGY

The $[Co^{III}(1,2-Nc)CN]_n$ precursors - 1,2-Naphthalocyaninatocobalt(II) and Potassium dicyano-1,2-naphthalocyaninatocobalt(III) were previously synthesized and characterized. $Co^{II}(1,2-Nc)$ was synthesized from the reaction of dicobalt octacarbonyl and 1.2naphthalenedicarbonitrile in ethylene glycol at 200°C under N₂ atmosphere with ammonium molybdate as catalyst. Separation of Nc isomers done chromatography were by and crystallization. Attachment of axial CN ligands and the simultaneous oxidation of Co^{2+} into Co^{3+} was done with potassium cyanide (KCN) in acetone stirred at 60°C in air to produce K[Co^{III}(1,2-Nc)(CN)₂] (Gacho et al., 2001, 2006).

The polymeric $[Co^{III}(1,2-Nc)CN]_n$ [Figure 2] was prepared by heating $K[Co^{III}(1,2-$ Nc)(CN)₂] in water for 12 days at 95-100°C with constant stirring. The suspension was then filtered, dried in vacuo, and extracted with anhydrous acetone until the eluent became pale green then it was eventually washed with pyridine until the eluent became almost colorless. The resulting solid was then rinsed with acetone then air-dried. Yield: 130 mg (65%), blue powder with luster. Compound characterization was done using electrospray ionization (ESI) mass spectrometer (Finnigan MAT 95ST) in 7:3 methanol:chloroform matrix, and fourier-transform infrared (FT-IR) spectrophotometer (Nicolet Magna-IR 550) in KBr disc (Yu, 2002).



Figure 2. Skewered μ-cyanonaphthalocyaninato cobalt(III), [Co^{III}(1,2-Nc)CN]_n

The electrical resistivity profile was obtained via a conventional 4-probe van der Pauw technique utilizing dried hydraulically-pressed pellet of the sample connected by silver wires under a purged cryostat environment. The measurement was done in a slow cool-down condition with return sweep from ~280K – 85K (liquid nitrogen limit).

3. RESULTS AND DISCUSSION

The polymerization of $[Co^{III}(1,2-Nc)CN]_n$ is caused by the conventional splitting of potassium cyanide (KCN) with the treatment of water on the K $[Co^{III}(1,2-Nc)(CN)_2]$ complex. However, the right amount of heat (95-100°C) is needed to activate the reaction and prevent decomposition.

 $Co^{II}(1,2-Nc)$ the As precursors and $K[Co^{III}(1,2-Nc)(CN)_2]$ were already wellcharacterized by NMR, XRD, and elemental analyses (Gacho et al., 2001, 2006), hence, only mass and infrared spectroscopy are sufficient to confirm the monomeric attachment (polymerization) via the CN bridge of $[Co^{III}(1,2-Nc)CN]_n$. The mass spectrum of the polymeric $[Co^{III}(1,2-Nc)CN]_n$ indicated major fragment (ion) peaks corresponding to: (a) single CN-bridged Co(Nc) dimer - [(Co^{III}(1,2- $Nc_2(CN)$ ⁺ at m/z = 1569 (calculated m/z =1569), (b) mono axial CN-ligated Co(Nc) - $[Co^{III}(1,2-Nc)(CN)]^+$ at m/z = 797 (calculated m/z = 797), and (c) planar Co(Nc) without axial CN - $[Co^{II}(1,2-Nc)]^+$ at m/z = 771 (calculated m/z = 771). Moreover, the infrared spectra showed that the CN valence frequency of the polymeric species shifted to higher cm⁻¹) as compared with wavenumber (2142 the monomeric complex (2126cm⁻¹) [Figure **3a-b**] (Yu, 2002). The shift of the CN peak can be attributed to the presence of cyano bridges in the polymer, as reflected by Co-C and C-N bond strengths determined by the σ -donating ability of the CN (Gaus and Crumbliss, 1976).



Figure 3. Infrared Spectrum of (a) [Co^{III}(1,2-Nc)CN]_n and (b) K[Co^{III}(1,2-Nc)(CN)₂], Emphasizing on the CN Peak (encircled).

The electrical resistivity at around ambient temperature of $[Co^{III}(1,2-Nc)CN]_n$ registered at around $4x10^3$ ohm·cm [**Figure 4**], while the monomeric K[Co^{III}(1,2-Nc)(CN)₂] recorded around $2x10^8$ ohm·cm [**Figure 5**]. This figure translates to a 5-order decrease in electrical resistivity (higher electrical conductivity; better electron transport) for [Co^{III}(1,2-Nc)CN]_n. Moreover, a steep increase in the resistivity profile at lower temperature and electron transport saturation is reached at around 200 K for the monomeric complex, while a relatively stable profile down to 85 K is registered for the polymer species another preferred characteristic of molecular conducting materials. This phenomenon can be attributed to the increase in electron transport dimensionality as factored by the CN polymeric bridge and the effective π - π interaction between Nc units brought about by the more orderly skewered polymeric chain.



Figure 5. Electrical Resistivity of K[Co^{III}(1,2-Nc)(CN)₂].

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