

Synthesis and Characterization of Phthalocyaninatometal (PcM, M=Fe²⁺, Co²⁺) Complexes with Monodentate Aromatic Isocyanide Ligands

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Metallophthalocyanines [PcM, Pc: phthalocyanine, M: Fe²⁺, Co²⁺] were reacted with α -isocyanonaphthalene (α -in) and α -isocyananthracene (α -ia) to form monomeric complexes. The synthesis and coordination behaviour of the isocyanides as a ligand (L) are discussed. All the products were characterized by spectroscopic methods and instrumental analysis. The electrical conductivities of these complexes, which were not treated with dopant, were attributed to the metal-ligand electron delocalization in the PcML₂ complexes. The complexes have an enlarged macrocycle where the π -electron back donating ability of PcM is stronger than the σ -electron coordinating ability of the isonitrile ligands. Their electrical conductivities were measured as $\sigma_{RT} = 2.1 \times 10^{-9} \sim 3 \times 10^{-10}$ S/cm. Also thermal stability was investigated in this study.

Introduction

Many conducting and semiconducting organic compounds, such as charge-transfer complexes, doped polyacetylene (PA), polypyrrole (PP), polythiophene (PTP), polyaniline and others, have been developed during the last twenty three years.¹ Some of them, however, have serious disadvantages, including low thermal and chemical stability, which restrict their practical applications. Thus, the search for conducting or semiconducting compounds with high thermal and chemical stability is an important task for chemists, physicists and materials engineers. Figure 1 shows electrical conductivities of various metallic, semiconductor and insulating materials.

Organic conductors based on organometallic compounds have received special attention. In 1979, Hanack *et al.*² reported a new type of conductor, square-planar metal complexes polymerized to linear chains by means of bridging ligands. This type of one-dimensional conductor is to be distinguished from charge-transfer complexes, in which strong electron donors like tetrathiafulvalene are combined with strong electron acceptors such as 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).³ The transition of one electron from donor to acceptor leads to the formation of cation and anion radicals, which stack together as alternating columns within the crystal. The direction of conductivity is along the columns, which results from the overlaps of π -orbitals on neighboring radicals.

Phthalocyanine (Pc) and metallophthalocyanines (PcM) have been investigated for many years. They have been mostly used as dyes and catalysts.⁵ Recently, metallophthalocyanine chemistry has been undergoing a revolution because phthalocyanine and many of its derivatives exhibit

interesting properties applicable to materials science. Phthalocyanines and their related compounds are of interest, for

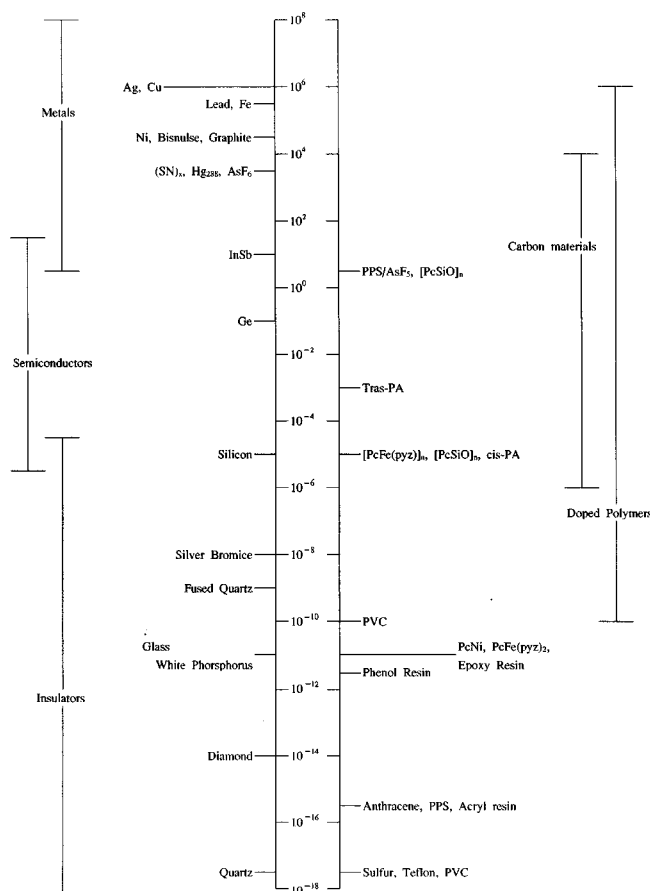


Figure 1. Electrical conductivities of various metallic, semiconductor and insulating materials.⁴

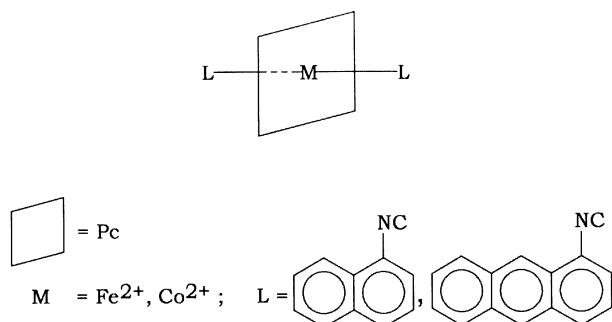


Figure 2. Types of organic semiconductors in this study.

example, in non-linear optics,⁶ Langmuir-Blodgett (LB) films,^{7,8} optical data storage⁹ and gas sensors.¹⁰ The substituted derivatives of phthalocyanines function as active components in various processes driven by visible light⁶: photoredox reactions and photooxidations in solution,^{5,11} photoelectrochemical cells and photovoltaic cells.¹²

Phthalocyanine and its metal compounds (PcM) are interesting for many reasons. They possess electronic and morphologic characteristics that are very favorable or necessary for semiconductive or conductive properties. Moreover, metallophthalocyanines are very thermally stable and many of them can be easily synthesized in high yield and purity.

In this study, we report the synthesis and characterization of metallophthalocyanine, PcM ($M = \text{Fe}^{2+}, \text{Co}^{2+}$) complexes with monodentate aromatic isocyanide ligands. PcM and isocyanide ligands form a new class of low-dimensional organic semiconductors. The monomer-type complexes consisted of 1 molecule of PcM and 2 molecules of ligand. The products were analyzed by spectroscopic methods and their electrical and thermal properties are also studied in this paper.

Experimental Section

All solid chemicals were recrystallized and purified by sublimation. Solvents were dried with molecular sieves, and distilled before use. All other chemicals were used as received from Aldrich Chemicals Co. Ltd.

FTIR spectra were recorded on a Nicolet 510P spectrophotometer, using NaCl-cell and KBr disc. Elemental analyses were performed with a CE instrument EA-1110 elementary analyser at combustion temperatures of 1030°C and Helium gas was used as a carrier gas. UV/vis spectra of all the complexes were obtained with a Shimadzu UV-365 spectrophotometer using Nujol mulls between quartz plates. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AMX-500 spectrometer operating at 500 MHz and 125 MHz, respectively. All spectra were recorded in CDCl₃ solution with TMS as a reference. Mass spectra of all products were recorded with a JEOL JMS-DX 303 Mass Spectrometer at an ionization temperature of 220 °C and electron energy of 70 eV. TG/DTA measurements were taken using the TG-DTA_92 (SETARAM Co.). Conductivity measurements were recorded on a KEITHLEY 195A Digital Multimeter in

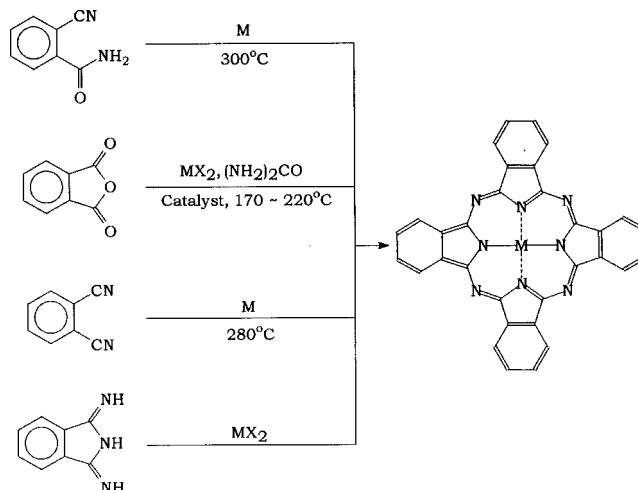


Figure 3. General synthetic routes of metallophthalocyanines.

the usual four-probe geometry in compact powders at a pressure of 4 tons.

Synthesis of metal macrocycles: A summary of basic methods for the synthesized phthalocyanines is shown in Figure 3. Various starting materials can be used to prepare phthalocyaninatometal compounds. Most of these complexes can be synthesized from phthalonitrile or its derivatives and the corresponding metals or metal salts in boiling solvents, such quinoline or 1-chloronaphthalene. They also can be obtained by metal insertion into the metal-free phthalocyanine.

Phthalocyaninatoiron(II), PcFe(II). Yield: 67.4%, dark green powder. FTIR (KBr, cm⁻¹): 3043, 1608, 1510, 1500, 1412, 1331, 1292, 1165 (-CH), 1127 (-CH), 1085 (-C-N), 662, 627, 605. MS (70 eV, m/e, %): 569, 568 (M⁺ 100), 284 (M²⁺ 28), 184 (61), 156 (58), 128 (66), 69 (40), 56 (68). Anal. calc. for C₃₂H₁₆N₈Fe (M = 568.38): C 67.62, H 2.84, N 19.71; found: C 66.92, H 2.93, N 19.11%.

Phthalocyaninatocobalt(II), PcCo(II). Yield: 87%, violet powder. FTIR (KBr, cm⁻¹): 3065, 1607, 1520, 1466, 1421, 1331, 1289, 1164, 1120 (-CH), 1087 (-C-N), 1071, 912, 873, 782, 757, 733. MS (70 eV, m/e, %): 571 (M⁺ 100), 568 (15), 355 (10), 281 (41), 207 (58), 191 (10), 96 (15), 44 (18). Anal. calc. for C₃₂H₁₆N₈Co (M = 571.47): C 67.26, H 2.82, N 19.61; found: C 66.95, H 2.50, N 18.99%.

Synthesis of Ligands;

Synthesis of formamides: general procedures. Formamides, α -N-formylamino-naphthalene (α -N-n) and α -N-formylaminoanthracene (α -N-a) were prepared by the reaction of corresponding amines with formic acid or with phenylformate under reflux for 24-72 hrs.¹³ The solids obtained by filtration were washed with Et₂O and water and dried in vacuum. The soluble powder α -N-a was boiled with alcohol to remove impurities, filtered, washed with Et₂O and dried.

α -N-formylaminonaphthalene (1). Pink powder. FTIR (KBr, cm⁻¹): 3225 (NH), 1657 (C = O). ¹H NMR (500 MHz, CDCl₃): δ = 9.03, 8.64, 8.02 (2d, 1H, J = 7.34, 7.52 Hz (isomer)), 7.84-7.91, 7.76 (2d, 1H, J = 8.29, 8.27 Hz (isomer)), 7.50-7.62, 7.46, 7.30. ¹³C NMR (125 MHz, CDCl₃): δ =

164.21 (CHO), 159.71 (CHO, isomer), 134.32, 132.23, 127.82, 127.01, 126.80, 126.50, 126.12, 125.70, 121.37, 119.03. Anal. calc. for $C_{11}H_9NO$ ($M = 171.2$): C 77.19, H 5.26, N 8.19; found: C 77.29, H 5.41, N 8.28%.

α -N-formylaminoanthracene (2). Gray powder. FTIR (KBr, cm^{-1}): 3225 (NH), 1658 (C = O). 1H NMR (500 MHz, $CDCl_3$): $\delta = 8.70, 8.53, 8.48, 8.00-8.06, 7.92$ (2d, 1H, $J = 8.71, 8.58$ Hz (isomer)), 7.54, 7.44, 7.31. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 163.66, 159.56, 132.00, 128.46, 128.24, 127.96, 127.50, 127.41, 127.22, 126.31, 125.94, 124.93, 124.51, 120.14, 119.75, 118.31$. Anal. calc. for $C_{15}H_{11}NO$ ($M = 221.3$): C 81.42, H 5.01, N 6.33; found: C 81.94, H 5.25, N 6.30%.

Synthesis of isocyanides: general procedure. A solution of diphosgene in dry CH_2Cl_2 was added to a boiling suspension of the appropriate formamide in Et_3N and CH_2Cl_2 for 2 hrs. After an additional 1 hr, the mixture was allowed to cool to ambient temperature. The solution was filtered and washed several times with 10% Na_2CO_3 solution. The organic layer was dried over anhydrous $MgSO_4$. The crude product was purified by chromatography on Al_2O_3 (neutral, CH_2Cl_2/n -hexane 1:1 vol %), followed by distillation under vacuo.

α -isocyanonaphthalene (α -in) (3). Dark brown liquid. FTIR (film, cm^{-1}): 2119 (N \equiv C), 1H NMR (500 MHz, $CDCl_3$): $\delta = 8.19, 7.92, 7.89, 7.69, 7.64, 7.57-7.62, 7.45$. ^{13}C NMR (125 MHz, $CDCl_3$): 187.50(NC), 133.67, 129.72, 128.31, 128.03, 127.46, 124.94, 124.56, 122.95. MS (70 eV, m/e, %): 151 ($M^+ 100$), 125 (30), 100, 87, 76, 63, 50.

α -isocyananthracene (α -ia) (4). Yield 72.3%, dark brown powder. FTIR (KBr, cm^{-1}): 2118 (N \equiv C). 1H NMR (500 MHz, $CDCl_3$): $\delta = 8.62, 8.37, 8.01, 7.99, 7.98, 7.96, 7.94, 7.93, 7.51, 7.49, 7.48, 7.46, 7.45, 7.32, 7.30, 7.29$. ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 167.30$ (NC), 133.38, 132.26, 130.97, 130.24, 128.48, 127.97, 127.23, 126.69, 126.55, 125.59, 124.19, 123.68, 121.93. MS (70 eV, m/e, %): 203 ($M^+ 100$), 176 (14), 102 (7), 90 (17), 75 (7). Anal. calc. for $C_{15}H_9N$ ($M = 203.24$): C 88.67, H 4.43, N 6.90; found: C 87.99, H 4.30, N 6.03%.

Synthesis of monomeric metallophthalocyanine complexes with monodentate isocyanide ligands: General procedure. A mixture of PcM and 20 times excess of the appropriate isocyanide ligand (3, 4) in $CHCl_3$ or 1-chlorobenzene was refluxed in an ampule with stirring for 3-7 days. The mixture was then diluted with MeOH and the precipitation was isolated by centrifugation. The precipitate was washed with n -hexane and MeOH and dried under vacuum.

Bis(α -isocyanonaphthalene)phthalocyaninatoiron(II), $PcFe(\alpha$ -in) $_2$ (5). Yield 91%; green powder. FTIR (KBr, cm^{-1}): 2122 (N \equiv C). UV (Nujol, λ_{max} , nm); 665, 604_{sh}, 394_{sh}, 312. Anal. calc. for $C_{54}H_{30}N_{10}Fe$ ($M = 874.75$): C 74.15, H 3.46, N 16.01; found: C 73.18, H 3.41, N 15.95%

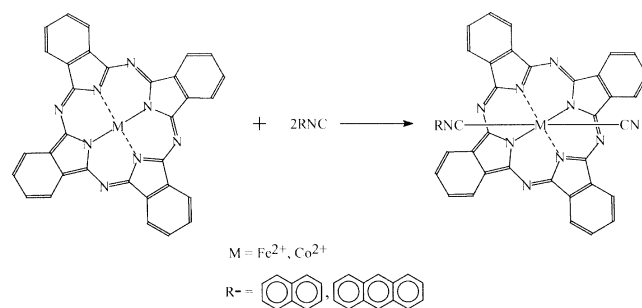
Bis(α -isocyananthracene)phthalocyaninatoiron(II), $PcFe(\alpha$ -ia) $_2$ (6). Yield 53%; dark green powder. FTIR (KBr, cm^{-1}): 2116 (N \equiv C). UV (Nujol, λ_{max} , nm); 792, 669_{sh}, 604_{sh}, 480_{sh}, 403. Anal. calc. for $C_{62}H_{34}N_{10}Fe$ ($M = 974.87$): C 76.39, H 3.52, N 14.37; found: C 75.57, H 3.55, N 13.69%.

Bis(α -isocyanonaphthalene)phthalocyaninatocobalt(II), $PcCo(\alpha$ -in) $_2$ (7). Yield 47%; violet powder. FTIR (KBr, cm^{-1}): 2117 (N \equiv C). UV (Nujol, λ_{max} , nm); 755, 671, 645_{sh}, 362. Anal. calc. for $C_{54}H_{30}N_{10}Co$ ($M = 877.83$): C 73.88, H 3.44, N 15.96; found: C 73.21, H 3.25, N 15.02%.

Bis(α -isocyananthracene)phthalocyaninatocobalt(II), $PcCo(\alpha$ -ia) $_2$ (8). Yield 51%; violet powder. FTIR (KBr, cm^{-1}): 2115 (N \equiv C). UV (Nujol, λ_{max} , nm); 727, 653, 631_{sh}, 342. Anal. calc. for $C_{62}H_{34}N_{10}Co$ ($M = 977.95$): C 76.15, H 3.50, N 14.32; found: C 75.23, H 3.27, N 13.99%.

Results and Discussion

The synthesis of monomeric bis-adduct, $PcM(RNC)_2$ (5~8), was carried out by reacting PcM(II) with the isocyanide ligands (3, 4) either in solution or as a melt (Scheme 1).



Scheme 1

All the monomeric complexes 5~8 were characterized by Fourier Transform Infrared and Ultraviolet spectroscopic methods. The characteristic NC-stretching vibration of the isocyanide ligands appears as intensive bands at 2115-2122 cm^{-1} . Comparison of the NC-stretching vibration of the $PcFe(RNC)_2$ complexes with the NC-stretching vibration of the free ligand confirms the expected aryl-substituted isocyanides with respect to the π -acceptor properties.

Investigations of ligand field spectra in the UV/vis region, magnetic susceptibilities and electron spin resonance provide the basis for the assignment of electronic configurations of macrocyclic complexes with transition metal ions. In the UV/vis spectra of phthalocyanine complexes, the frequency of maximum absorption often is not strongly changed with solvents.¹⁴

The $a_{1u}-e_g^*$ transition (Q-band) of phthalocyanine causes a charge transfer from the center of the complex toward the periphery and is influenced by the electronic properties of the central metal atom.

The nearly same Q-band energies of monomeric [$PcM(L)_2$] complexes are clearly observed, as shown from

Table 1. Infrared Data of $\nu_{N \equiv C}$ Vibration of $PcM(L)_2$ Complexes

Compound	Ligand	
	α -in (8)	α -ia (9)
Free Ligand	2119	2118
$PcFe(L)_2$	2122	2116
$PcCo(L)_2$	2117	2115

Table 2. The UV/Vis Data of PcM(L)₂ Complexes

Compound	λ_{max} (nm)			
PcFe(α -in) ₂ (5)	665	604 _{sh}	394 _{sh}	312
PcFe(α -ia) ₂ (6)	792	669 _{sh}	604 _{sh}	480 _{sh} 403
PcCo(α -in) ₂ (7)	755	671	645 _{sh}	362
PcCo(α -ia) ₂ (8)	727	653	631 _{sh}	342

Table 3. TG/DTA Data of PcM(L)₂ Compounds

Compound	Temp. range (°C)	Mass loss (%) calc./found	DTA signal T_{max} (°C)
PcFe(II)	380-693	-	-
PcCo(II)	490-587	-	-
PcFe(α -in) ₂ (5)	230-308	35.02/33.28	305 end.
PcFe(α -ia) ₂ (6)	290-346	41.70/40.05	340 end.
PcCo(α -in) ₂ (7)	244-323	34.90/32.81	314 end.
PcCo(α -ia) ₂ (8)	285-321	41.56/42/00	320 end.

Table 4. Electrical Conductivities of Monomeric Complexes

Compound	RT (S/cm)
PcFe(α -in) ₂ (5)	2×10^{-10}
PcFe(α -ia) ₂ (6)	1×10^{-10}
PcCo(α -in) ₂ (7)	2.1×10^{-9}
PcCo(α -ia) ₂ (8)	3×10^{-10}

the data Table 2. The spectra of **5-8** have similar Soret bands between 312 nm and 342 nm and Q-bands between 665 nm and 792 nm.

TG/DTA experiments on **5-8** (Table 3) show decomposition proceeds in a the range between 230°C and 346°C. The isocyanide ligands were dissociated at these temperatures. Thermal stability is one of the most important properties of phthalocyanine complexes. But PcM is superior to PcM(L)₂ complexes in this characteristics. Table 3 shows TG/DTA analysis data of monomeric phthalocyaninatometal complexes.

The electrical conductivity was measured by the van der Pouw method on a pressed polycrystalline powder. The electrical conductivities for complexes are given in Table 4. The conductivities of monomeric complexes are found to be in the range of $1 \times 10^{10} \sim 2 \times 10^9$ S/cm.

The oligomeric complexes, [PcML]_n, which are composed

of PcMs and ligands like polymers, increased by $10^3 \sim 10^5$ times compared with the corresponding monomeric complexes without doping. The reason is that oligomeric complexes have a weak π -bonding configuration (easy removing an electron along the axis) between Mac-L[Mac; Pc], with the oligomer system having a oxidation potential lower than that of monomeric complexes. The π -electron energy calculated by valence effective Hamiltonian method is -5.93 eV (HOMO) in 2,3-naphthalocyanine (2,3-NcH₂) and -6.32 eV (HOMO) in PcH₂, respectively.^{4,15}

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