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Intrinsic Semiconducting Materials on Phthalocyanine Basis

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Stacked transition metal macrocycles $[\text{MacM(L)}]_n$ with M e.g. Fe, Ru, Os, Co, Rh and Mac = phthalocyanine (Pc) 1,2- or 2,3-naphthalocyanine (1,2-, 2,3-Nc) were synthesized. The bridging ligands (L) may be e.g. pyrazine (pyz) or *s*-tetrazine (tz). In general, these complexes $[\text{MacM(L)}]_n$ are insoluble in organic solvents; however, soluble oligomers $[\text{R}_4\text{PcM(L)}]_n$ can be prepared using metallomacrocycles R_nPcM , R = *t*-bu, et, OR, M = Fe, Ru, which are substituted in the peripheric positions. A systematic investigation of the influence of the bridging ligands on the semiconducting properties in $[\text{MacM(L)}]_n$ reveals that changing L, e.g., from dabco over pyz to tz leads to a steady increase of the semiconducting properties without external oxidative doping. Powder conductivities in the order of 0.1 S/cm can be reached by using *s*-tetrazine, 3,6-dimethyl-*s*-tetrazine (me_2tz) and others, e.g. fumarodinitrile, as the bridging ligands. The intrinsic conductivities are a result of the low oxidation potential of tz and me_2tz and due to the low lying LUMO in the corresponding bridged systems $[\text{MacM(tz)}]_n$.

Introduction

Phthalocyanines and their metal complexes have been investigated for many years in great detail. While in former times phthalocyanines were mostly used as dyes and catalysts¹, lately phthalocyanine chemistry has been undergoing a revival, because phthalocyanines and many of its derivatives exhibit properties which are of interest for applications in material science. Many metallophthalocyanines can be easily synthesized in high yields and purity, and also exhibit a high thermal stability.

Phthalocyanines and structurally related compounds are of interest in non-linear optics,² as liquid crystals,³ as Langmuir-Blodgett (LB) films,^{4,5} in optical data storage,⁶ as electrochromic substances,⁷ as low dimensional metals,^{5,8,9} in rectifying devices,¹⁰ as gas sensors,¹¹ as photosensitizers¹² and as carrier generation materials in NIR.¹³ The substituted derivatives of phthalocyanines function as active components in various processes driven by visible light: photoredox reactions and photooxidations in solution,^{1,14} activity in the therapy of cancer,^{1,15,16} photoelectrochemical cells,^{17,18} photovoltaic cells^{19,20} and electrophotographic applications.^{21,22}

Bridges Transition Metal Complexes $[\text{MacM}(\text{L})]_n$

A few years ago we developed a new concept to obtain a stacked arrangement of phthalocyaninato and naphthalocyaninato transition metal compounds, leading to coordination polymers where the macrocycle, the central metal atom and the bridging ligand can be varied systematically. Stacking is achieved by biaxially connecting the central transition metal atoms of the macrocycles with bidentate bridging ligands (L). We have previously synthesized and investigated such bridged macrocyclic metal compounds $[\text{MacM}(\text{L})]_n$ in detail with respect to their physical properties.^{5,8} A schematic structure of this type of compounds is shown in Figure 1.

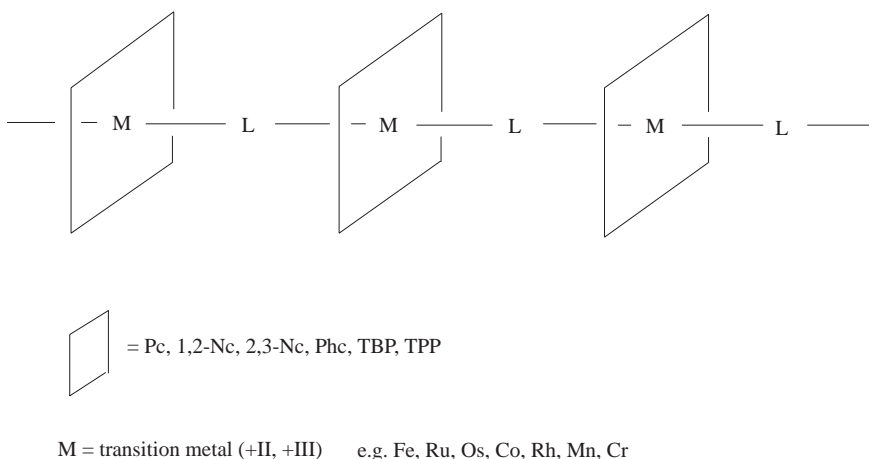


Figure 1. Bridged Transition Metal Complexes $[\text{MacM}(\text{L})]_n$
 L = pyz, tz, bpy, dip, me₂dib, me₄dib, CN⁻, SCN⁻

The bridging ligands (L) are linear organic molecules containing a conjugated π -electron system, e.g. pyrazine (pyz), *p*-diisocyanobenzene (dib) and substituted *p*-diisocyanobenzenes, tetrazine (tz), and substituted tetrazines. If the oxidation state of the central metal atom is +3 (e.g. Co^{3+} , Fe^{3+}), charged bridging ligands such as cyanide (CN^-), thiocyanate (SCN^-) and others also can be utilized. As macrocycles, phthalocyanines, substituted phthalocyanines, 1,2- and 2,3-naphthalocyanines, phenanthrocyanines, tetrabenzoporphyrins and tetranaphthoporphyrins have been used.^{5,8}

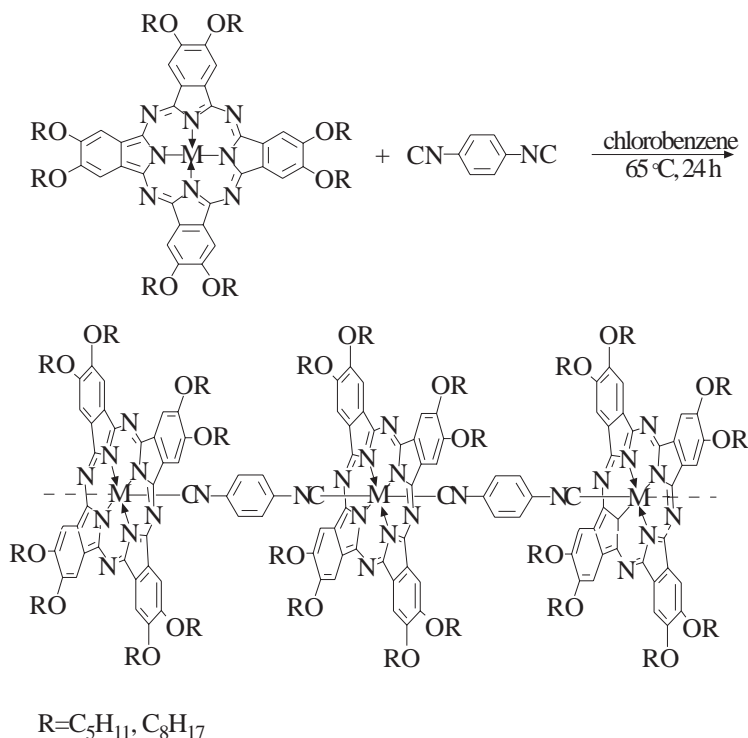
Many of the bridged macrocyclic metal complexes $[\text{MacM}(\text{L})]_n$ (“shish-kebab polymers”) can be prepared in high yields and high purity by treating the metallomacrocycle MacM either with pure ligand or with the ligand in an appropriate solvent, e.g. acetone, chloroform, or benzene. For example, $[\text{PcFe}(\text{pyz})]_n$ is obtained as a dark violet solid from PcFe and pyrazine in benzene or directly by reacting PcFe in a melt of pyrazine.²³ $[\text{PcFe}(\text{dib})]_n$ is formed quantitatively by refluxing PcFe with 1,4-diisocyanobenzene in acetone. Powder diffraction data indicate a high crystallinity for many of the coordination polymers obtained in this manner.

The bridged structure shown in Figure 1 has been proved for many compounds using a variety of physical methods⁵ including thermogravimetry, detailed IR-investigations²⁴ Mössbauer spectroscopy,²⁵ ¹H- and ¹³C-NMR spectroscopy²⁶ as well as scanning tunnel microscopy (STM).²⁷ The crystal structure of a very similar compound $[\text{DMGCo}(\text{pyz})]_n$ (DMG = dimethylglyoximato) shows that the pyrazine molecules within the chain are all arranged within a plane perpendicular to that of the planar DMGCo-units.²⁸ The mechanism for the formation of this kind of coordination polymer has also been investigated using spectroscopic methods.²⁹

Powder Conductivities and Doping of $[\text{MacM}(\text{L})]_n$ -Compounds

The powder conductivities of most of the bridged phthalocyaninato transition metal complexes $[\text{PcM}(\text{L})]_n$ for $\text{M} = \text{e.g. Fe, Ru, Os, Co, Rh}$ and $\text{L} = \text{pyz, dib etc.}$, are low in the range of $10^{-6} - 10^{-7}$ S/cm. However, many of these compounds can be doped either chemically or electrochemically. Table 1 shows a selection of compounds which have been doped chemically (with iodine) or electrochemically (with BF_4^- , PF_6^- , HSO_4^- , ClO_4^-) leading to good semiconducting properties ($\sigma_{RT} = 10^{-5} - 10^{-1}$ S/cm) with thermal stabilities up to 120-130°C. The chemically doped compounds $[\text{PcM}(\text{L})\text{I}_y]_n$ are obtained by heterogeneous doping either in benzene or in CHCl_3 . $[\text{PcFe}(\text{pyz})]_n$ can be doped also electrochemically. With $\text{X} = \text{BF}_4^-$, PF_6^- , HSO_4^- , ClO_4^- , stable compounds $[\text{PcM}(\text{L})\text{X}_y]_n$ are obtained. The composition of the doped polymers was established by elemental analysis and TG/DTA. The results of ^{57}Fe -Mössbauer-spectroscopy prove that doping does not destroy the bridged structure of the polymers.²⁵

In general, the complexes $[\text{MacM}(\text{L})]_n$ show only very low solubility in organic solvents. However, soluble oligomers $[\text{R}_4\text{PcM}(\text{L})]_n$ and $[\text{R}_8\text{PcM}(\text{L})]_n$ ^{30,31,32} have been prepared using substituted metallomacrocycles R_4PcM , in which $\text{R} = t\text{-Bu, Et, OR}'$ ($\text{R}' = -\text{C}_5\text{H}_{11}, -\text{C}_{12}\text{H}_{25}$) and R_8PcM ($\text{R} = -\text{C}_5\text{H}_{11}, -\text{C}_{12}\text{H}_{25}, -\text{OC}_5\text{H}_{11}, -\text{OC}_{12}\text{H}_{25}$) and $\text{M} = \text{Fe, Ru}$.^{33,34,35} These types of oligomers are soluble in most common organic solvents, thereby allowing the determination of chain lengths by the usual methods, e.g., $^1\text{H-NMR}$ spectroscopy.³⁰ Depending upon the method of preparation, oligomers which contain 20-50 MacM-subunits can be obtained. Scheme 1 shows one of the ways of synthesizing soluble bridged coordination polymers.³⁶ The soluble octasubstituted phthalocyaninatometal compounds can be obtained as described above.



Scheme 1. Syntheses of Soluble $[\text{R}_8\text{MacM}(\text{L})]_n$ Complexes

Doping of the soluble oligomers with iodine also leads to semiconductive systems, as can be seen in Table 1. As in the case of peripherally unsubstituted systems, the composition of the doped polymers was determined by elemental analysis.³⁷

Table 1. Room Temperature Powder Conductivities of Some Undoped and Doped [MacML]_n Compounds.⁵

Compound	σ_{RT} [S/cm]
[PcFe(pyz)] _n	$1 \cdot 10^{-6}$
[PcFe(pyz)I _{2.5}] _n	$2 \cdot 10^{-1}$
[(EHO) ₄ PcFe(pyz)] _n	$< 10^{-12}$
[(EHO) ₄ PcFe(pyz)I _{1.3}] _n	$6 \cdot 10^{-5}$
[PcRu(pyz)] _n	$1 \cdot 10^{-7}$
[PcRu(pyz)I _{2.0}] _n	$2 \cdot 10^{-2}$
[PcRu(dib)] _n	$2 \cdot 10^{-6}$
[PcRu(dib)I _{2.0}] _n	$7 \cdot 10^{-3}$
[<i>t</i> -Bu ₄ PcRu(dib)] _n	$2 \cdot 10^{-7}$
[<i>t</i> -Bu ₄ PcRu(dib)I _{1.2}] _n	$1 \cdot 10^{-4}$
[PcFe(dib)] _n	$2 \cdot 10^{-5}$
[PcFe(dib)I _{3.0}] _n	$3 \cdot 10^{-2}$
[PcFe(Me ₄ dib)] _n	$1 \cdot 10^{-7}$
[PcFe(Me ₄ dib)I _{3.0}] _n	$2 \cdot 10^{-2}$
[(<i>n</i> -C ₅ H ₁₁) ₈ PcFe(Me ₄ dib)] _n	$< 10^{-12}$
[(<i>n</i> -C ₅ H ₁₁) ₈ PcFe(Me ₄ dib)I _{1.8}] _n	$9 \cdot 10^{-7}$
[(EHO) ₄ PcFe(Me ₄ dib)] _n	$< 10^{-12}$
[(EHO) ₄ PcFe(Me ₄ dib)I _{2.5}] _n	$2 \cdot 10^{-10}$

“Intrinsic” Semiconductive Polymers

PcFe, PcRu and 2,3-NcFe react easily with 1,2,4,5-tetrazine (tz) and 1,2,4-triazine (tri) to the corresponding monomers MacM(L)₂ (L = tz, tri) and under somewhat different conditions to the bridged systems [MacM(L)]_n (L = tz, tri), respectively. The tetrazine bridged macrocycles, in contrast to other bridged compounds [MacM(L)]_n (M = Fe or Ru and L = pyz or dib) show good semiconducting properties already without external oxidative doping ($\sigma_{RT} = 0.05 - 0.3$ S/cm).⁵

The powder conductivities of a selection of monomeric and bridged macrocycles (mostly phthalocyanines) in the non-doped state are listed in Table 2. All the bridged complexes [MacM(L)]_n (M = Fe, Ru, Co; L = pyz, tz, dabco) consist of cofacially arranged macrocycles which are separated by approximately the same distance (about 600 pm) (see Figure 1).

Systematic investigations of the influence of the bridging ligands on the semiconducting properties in [MacM(L)]_n reveal that changing L from diazabicyclo[2.2.2]octane (dabco) to pyrazine (pyz) to *s*-tetrazine (tz) leads to a steady increase of the semiconducting properties without external oxidative doping. Powder conductivities in the order of 0.1 S/cm can be reached by using *s*-tetrazine as the bridging ligand.

Although the monomeric complexes PcM(L)₂ (L = pyz, dabco, tz; M = Fe, Ru, Os) show insulating behaviour (Table 2), it can be seen that the ligand L has a significant effect on the conductivity of the bridged complexes [MacM(L)]_n. As dabco is a ligand containing no π -orbitals to interact with the metallomacrocycle, the complex [PcFe(dabco)]_n is an insulator. An increase in conductivity is observed for the pyrazine-bridged compounds [MacM(pyz)]_n, which exhibit conductivities in the low semiconducting region. However, by changing the bridging ligand from pyrazine to *s*-tetrazine the conductivity is increased by 3 to 5 orders of magnitude without external oxidative doping.

Table 2. Room Temperature Powder Conductivities of Monomeric and Bridged Macrocyclic Transition Metal Complexes (pressed pellets, 10^8 Pa).⁵

Compound	σ_{RT} [S/cm]
PcFe(dabco) ₂	$1 \cdot 10^{-10}$
[PcFe(dabco)] _n	$1 \cdot 10^{-9}$
PcFe(py ₂ z) ₂	$3 \cdot 10^{-12}$
[PcFe(py ₂ z)] _n	$1 \cdot 10^{-6}$
PcFe(tz) ₂	$< 10^{-9}$
[PcFe(tz)] _n	$2 \cdot 10^{-2}$
[PcFe(Me ₂ tz)] _n	$4 \cdot 10^{-3}$
[PcRu(py ₂ z)] _n	$1 \cdot 10^{-7}$
PcRu(tz) ₂	$< 10^{-11}$
[PcRu(tz)] _n	$1 \cdot 10^{-2}$
[PcRu(tri)] _n	$2 \cdot 10^{-4}$
[PcRu((NH ₂) ₂ tz)] _n	$4 \cdot 10^{-3}$
[PcRu(Cl ₂ tz)] _n	$3 \cdot 10^{-3}$
[PcRu(Me ₂ tz)] _n	$4 \cdot 10^{-3}$
[PcRu(<i>p</i> -(NH ₂) ₂ C ₆ H ₄)] _n	$5 \cdot 10^{-9}$
[PcRu(CN) ₂ C ₆ F ₄]] _n	$1 \cdot 10^{-3}$
[2,3-NcFe(py ₂ z)] _n	$5 \cdot 10^{-5}$
[2,3-NcFe(tz)] _n	$3 \cdot 10^{-1}$
[(CN) ₄ PcFe(py ₂ z)] _n	$5 \cdot 10^{-9}$
[(CN) ₄ PcFe(tz)] _n	$1 \cdot 10^{-6}$
[<i>t</i> -Bu ₄ PcFe(py ₂ z)] _n	$5 \cdot 10^{-11}$
[<i>t</i> -Bu ₄ PcFe(tz)] _n	$9 \cdot 10^{-9}$
[Et ₄ PcFe(py ₂ z)] _n	$8 \cdot 10^{-9}$
[Et ₄ PcFe(tz)] _n	$2 \cdot 10^{-4}$
[Et ₄ PcFe(tri)] _n	$5 \cdot 10^{-9}$
[(EHO) ₄ PcFe(py ₂ z)] _n	$< 10^{-12}$
[(EHO) ₄ PcFe(tz)] _n	$3 \cdot 10^{-6}$
[Et ₄ PcRu(py ₂ z)] _n	$5 \cdot 10^{-10}$
[Et ₄ PcRu(tri)] _n	$2 \cdot 10^{-8}$
[Et ₄ PcRu(tz)] _n	$5 \cdot 10^{-9}$
[<i>t</i> -Bu ₄ PcRu(py ₂ z)] _n	$7 \cdot 10^{-8}$
[<i>t</i> -Bu ₄ PcRu(tz)] _n	$1 \cdot 10^{-6}$

One of the factors responsible for the electrical conductivities in bridged macrocyclic transition metal complexes [MacM(L)]_n is the band gap, which has been shown by theoretical calculations to be determined by the energy difference between the LUMO of the bridging ligand and the HOMO of the transition metallomacrocyclic.³⁸ Therefore, to achieve semiconducting properties, the metallomacrocyclic should contain a high lying HOMO, whereas a bridging ligand with a low lying LUMO should be used. The ligands used for the preparation of the bridged macrocyclic transition metal complexes listed in Table 2 were selected because they possess a low lying LUMO. In addition to *s*-tetrazine and its derivatives, some other interesting attempts to achieve intrinsic conductivity in such systems will be described as follows: The *p*-diaminotetrazine bridged polymer [PcRu(NH₂)₂tz] shows a powder conductivity which is about 6

orders of magnitude higher than that of $[\text{PcRu}(p\text{-(NH}_2)_2\text{C}_6\text{H}_4)]_n$, due to the fact that *p*-phenylenediamine contains no hetero atoms in the aromatic ring (Table 3). Furthermore, soluble (peripherally substituted) tetrazine-bridged phthalocyaninatotransition metal complexes were synthesized using a variety of tetraalkyl- and alkoxy-substituted phthalocyaninatoiron and -ruthenium complexes. These tetrazine-bridged systems again show higher conductivities than the corresponding pyrazine analogues, albeit to a lesser extent than the peripherally unsubstituted ones (Table 2).

Different bidentate nitriles also have been used for the preparation of bridged phthalocyaninoruthenium complexes.³⁹ Tetrafluoroterephthalic acid dinitrile $(\text{CN})_2\text{C}_6\text{F}_4$ reacts with PcRu to give the bridged compound $[\text{PcRu}(\text{CN})_2\text{C}_6\text{F}_4]_n$, which exhibits a powder conductivity of $\sigma_{RT} = 10^{-3}$ S/cm without external oxidative doping. Fumarodinitrile (NC-CH = CH-CN), dicyanoacetylene and even dicyan have been used to prepare the corresponding bridged phthalocyaninoruthenium complexes. All compounds show intrinsic conductivities in the range of $\sigma_{RT} = 10^{-3}$ S/cm.³⁹

Electron-withdrawing substituents in the peripheric positions of the phthalocyanine macrocycle show the expected effect: for example, $[(\text{CN})_4\text{PcFe}(\text{tz})]_n$ exhibits a conductivity which is at least 3 orders of magnitude less than the conductivities of other tetrazine-bridged compounds investigated so far (Table 2).⁴⁰

The low band gaps of all tetrazine-bridged coordination polymers with group VIII transition metals $[\text{MacM}(\text{L})]_n$ [Mac = Pc; M = Fe, Ru, Os; Mac = 2,3-Nc; M = Fe; L = e.g. tz, Me₂tz, (NH₂)₂tz] can be demonstrated by physical properties which are not shown by the corresponding system $[\text{MacM}(\text{L})]_n$ with L = pyz or dib: all polymers with group VIII transition metals containing tetrazine or related compounds as bridging ligands $[\text{MacM}(\text{L})]_n$ (L = tz, tri, $(\text{CN})_2\text{C}_6\text{F}_4$, NC-CH = CH-CN, *p*-(NH₂)₂tz) show broad bands in the UV/Vis/NIR spectra between with different maxima, e.g. for $[\text{PcFe}(\text{tz})]_n$ at 1650 nm (0.75 eV) and for $[\text{PcRu}(\text{tz})]_n$ at about 1300 nm (0.95 eV). The corresponding pyrazine-bridged systems $[\text{PcM}(\text{pyz})]_n$ (M = Fe, Ru, Os) exhibit “normal” UV/Vis spectra with Soret- and Q-bands between 245 and 700 nm, respectively. The results from the UV/Vis spectra obtained with $[\text{PcFe}(\text{tz})]_n$ and the other systems mentioned above are supported by UPS data of $\text{PcFe}(\text{tz})_2$ and $[\text{PcFe}(\text{tz})]_n$, which also show that $[\text{PcFe}(\text{tz})]_n$ exhibits a small band gap.⁴¹ With the help of XPS it was possible to demonstrate that for $\text{PcFe}(\text{tz})_2$, $[\text{PcFe}(\text{pyz})]_n$ and $[\text{PcFe}(\text{tz})]_n$ oxygen has only a negligible influence on the conductivity of these compounds; in other words, oxygen is not a doping agent.⁴¹ On the other hand, it should be mentioned that the conductivities very much depend on the substituents on the peripheric positions: $[(\text{t-Bu})_4\text{PcFe}(\text{tz})]_n$ and $[(\text{Et})_4\text{PcFe}(\text{tz})]_n$ both show CT bands in the UV/VIS/NIR spectra. The conductivities of these compounds, however, are low in comparison with $[\text{PcFe}(\text{tz})]_n$. The large *t*-butyl groups in $[(\text{t-Bu})_4\text{PcFe}(\text{tz})]_n$ hinder an electron transfer from chain to chain, thereby decreasing the macroscopic measured conductivities.⁴¹

The absorption bands in the near infrared correlate well with the electrochemically estimated energy gap between the HOMOs of the different metallomacrocycles and the LUMO of *s*-tetrazine in all the tetrazine-bridged systems described here. The broad band observed in the absorption spectra of these and other described bridged complexes can be assigned to charge transfer processes from the metallomacrocycle to the π^* -orbital of the bridging ligand (e.g., tz, tri, etc.).

Bridged Macrocyclic Complexes with Trivalent Transition Metal Ions

As described above, the central transition metals within the macrocycles may also have the oxidation number +3. An octahedral configuration of the metal in the macrocycles is also possible, for instance for Fe^{3+} , Co^{3+}

and Rh^{3+} . For the formation of the corresponding polymers, CN^- , SCN^- , or N_3^- are suitable bridging ligands.^{42–45}

Figure 2 schematically shows a cyano-bridged intrinsic semiconductive phthalocyanine complex which can be synthesized by the displacement of the axial anion X^- by CN^- in a coordinatively unsaturated compound PcMX .

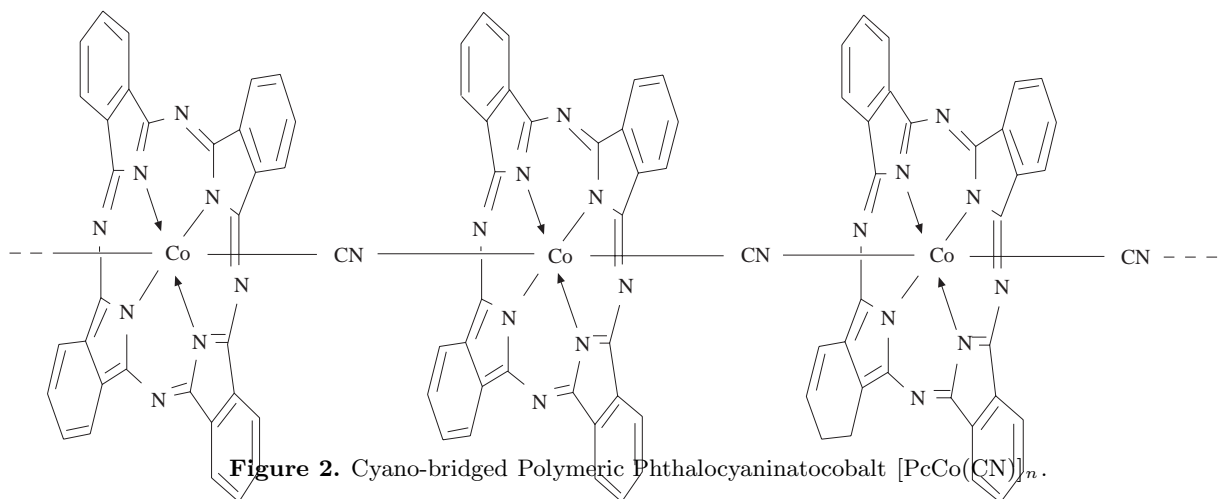


Figure 2. Cyano-bridged Polymeric Phthalocyaninatocobalt $[\text{PcCo}(\text{CN})]_n$.

A second general route also leading to cyano-bridged polymers $[\text{PcM}(\text{CN})]_n$ is the elimination of alkali metal cyanide from dicyano(phthalocyaninato)transitionmetal(III) complexes $\text{M}'[\text{PcM}(\text{CN})_2]$ ($\text{M}' = \text{Na}, \text{K}$; $\text{M} = \text{Co}, \text{Rh}, \text{Fe}, \text{Mn}, \text{Cr}$). These compounds can easily be obtained either by reaction of the chloro compounds PcMCl_2 ($\text{M} = \text{Co}, \text{Cr}$) with an excess of alkali metal cyanide in ethanol or by oxidation of PcM ($\text{M} = \text{Co}, \text{Fe}, \text{Mn}$) in the presence of cyanide with atmospheric oxygen. From the received mononuclear alkali metal dicyano(phthalocyaninato)transition metal(III) alkali metal cyanide is split off by treatment with boiling water. Thereby the polymer $[\text{PcM}(\text{CN})]_n$ is obtained in nearly quantitative yield. Peripherally substituted cobaltphthalocyanines also form soluble polymers. $[(\text{R})_x\text{PcCo}(\text{CN})]_n$ ($\text{R} = \text{t-Bu}$ for $x = 4$ and $\text{R} = \text{C}_7\text{H}_{15}$ for $x = 8$) have been prepared in this way.^{46–48}

The electrical conductivities of the polymers without additional doping are given in Table 3. When the bridged structure was destroyed by treatment with a competing ligand to form $\text{PcCo}(\text{L})(\text{CN})$, the conductivity was diminished by 6-10 orders of magnitude.⁴²

Table 3. Electrical Conductivities of Cyano Bridged Compounds⁵

Compound	$\sigma[\text{S/cm}]$
$[\text{PcCo}(\text{CN})]_n$	$2 \cdot 10^{-2}$
$[\text{PcFe}(\text{CN})]_n$	$6 \cdot 10^{-3}$
$[\text{PcMn}(\text{CN})]_n$	$1 \cdot 10^{-5}$
$[\text{PcCr}(\text{CN})]_n$	$3 \cdot 10^{-6}$
$[(\text{t-Bu})_4\text{PcCo}(\text{CN})]_n$	$2 \cdot 10^{-7}$
$[(2,3\text{-C}_7\text{H}_{15})_8\text{PcCo}(\text{CN})]_n$	$3 \cdot 10^{-9}$
$[(\text{t-Bu})_4\text{-2,3-NcCo}(\text{CN})]_n$	$8 \cdot 10^{-2}$
$[2,3\text{-NcCo}(\text{CN})]_n$	$1 \cdot 10^{-1}$

Outlook

As one of the first stable systems exhibiting intrinsic electrical conductivities, without external oxidative doping, the bridged transition metal complexes described hold a strong potential for future applications, e.g., as molecular wires in miniaturized machines. Because of their high thermal and chemical stability, they are also of interest for technical applications, like antistatically equipping foils and fibers.⁴⁹ Some of these complexes also possess excellent photoconductivities⁵⁰ and can be used in Xerox machines.

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