Molecular Crystals and Liquid Crystals

Synthesis and Properties of Conducting Bridged Macrocyclic Metal Complexes

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SYNTHESIS AND PROPERTIES OF CONDUCTING BRIDGED
MACROCYCLIC METAL COMPLEXES

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Abstract

Stacked bridged macrocyclic metal complexes of the
type shown in Fig. 1B with pyrazine and 1,4-diiso-
cyanobenzene as the bridging ligands L, Pc and TBP as
the macrocycle (Mac) and Fe and Ru as the central
metal atoms M are doped with iodine. The properties
and conductivities of the doped compounds $[MacML]_n$
are reported. The synthesis and properties of type
C-polymers (Fig. 1) ($[PcMCN]_n$, M = Co, Fe, Mn, Cr)
with CN as the bridging ligand are described. With Co
and Fe these polymers show room temperature con-
ductivities around 10^{-2} S/cm without doping, which
are in the same range as the iodine doped
$[PcML]_n$-compounds.

Stacked bridged macrocyclic metal complexes e.g.
phthalocyaninato metal complexes $[PcMO]_n$, (M = Si, Ge) can
be synthesized using the Kenney-Marks approach by thermal
dehydration of the phthalocyaninato metal dihydroxides
$PcM(OH)_2$ (M = Si, Ge)[1]. After doping with iodine well

characterized compounds $[(PcMO)I_y]_n$ are formed which
exhibit room temperature conductivities up to 1 S/cm.

Recently the synthesis of the peripherally sub-
stituted μ-oxo-polymers $[R_4PcMO]_n$, R = t-Bu, Tms; M = Si,
Ge, Sn were carried out in our laboratories[2]. The presence
of the bulky substituents in these compounds gives rise to
high solubilities in common organic solvents, like chloro-
form, methylenechloride and tetrahydrofurane etc. The
soluble μ-oxo-polymers are also dopable with iodine.

Phthalocyaninatogermaniumsulfur polymers $[PcGeS]_n$
were also synthesized, doping with iodine however led to
destruction of the Ge-S-bonds[3].

Instead of oxygen and sulfur also fluorine was used
as the bridging ligand to form $[PcMF]_n$ (M = Al, Ga, Cr).
After doping with iodine $[(PcMF)I_y]_n$ is formed which show
conductivities in the same range as the doped μ-oxo-
polymers[4].

We reported several times about the synthesis of
stacked bridged macrocyclic metal complexes using our
approach: Here instead of the main group elements Si or Ge
transition metals which prefer an octahedral configuration
e.g. Fe, Ru, Co, Mn or Cr are the central metal atoms. The
macrocycles used mostly are phthalocyanine (Pc) and
tetrabenzporphirine (TBP), other macrocycles have also
been applied. The bridging ligands are linear, π-electron
containing molecules[5]. In stacked structures of this type
the macrocycle, the central metal atom M and the bridging
ligand L can be varied systematically, leading to polymeric
structures of quite different physical properties, in-

cluding different conductivities. The large flexibility of this approach is shown in Fig. 1 only using different bridging ligands, thereby leading to different interring distances but also to an electron pathway along the central axis of the polymer:

The bridging ligand L in Fig. 1 can be axially linked to the central transition metal of the macrocycle in three different ways:

A. By two σ-bonds as shown in Fig. 1A. A possible bridging molecule for this type would be the acetyliddianion $C\equiv C^{2-}$.

B. With two coordinative bonds as shown in Fig. 1B. The bridging ligand here can be e.g. pyrazine (pyz), bipyridine (bpy) or 1,4-diisocyanobenzene (dib).

C. By one σ-and one coordinative bond, a possible bridging ligand would be the cyano group CN^-.

Fig.1
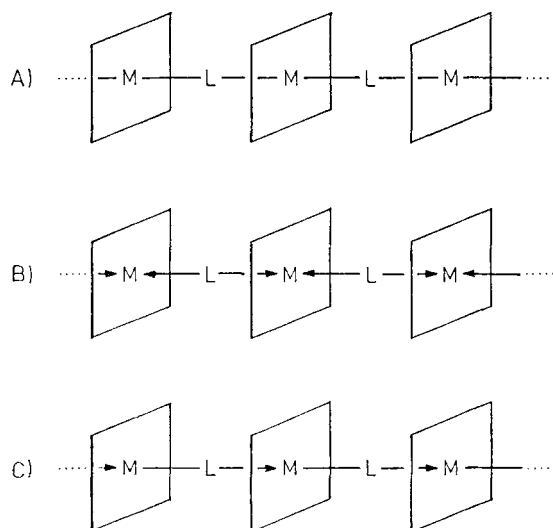
We have shown[5] that type B-polymers with two co-
ordinative bonds from the bridging ligand L to the central
metal atom M of the macrocycle are stable compounds which
have been well characterized[5]: A prototype is shown in
Fig. 2.

Fig.2
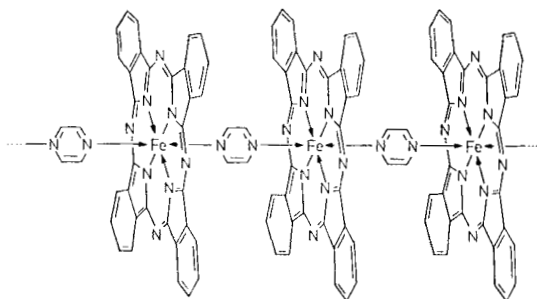
All type B-polymers with L = pyz, dib and bpy, with
M = Fe, Ru, and Co and phthalocyanine as the macrocycle
show typical semiconducting behavior with room temperature
powder conductivities of 10^{-6} - 10^{-5} S/cm and activation
energies of 0.4 eV without doping. The conductivities are
10^5 - 10^6 times higher than the corresponding monomers
$PcML_2$.

In the following we report about two topics:

About the doping of the type B coordination polymers
with iodine.

On the type C-polymers with one σ- and one coordinative
bond, which exhibit unusual high conductivities already
without additional doping.

As in case of the afore mentioned phthalocyaninato-μ-oxo-
and fluorine polymers $[PcMO]_n$ and $[PcMF]_n$ the phthalo-
cyaninatoironpyrazine polymer $[PcFe(pyz)]_n$ is also dopable
with iodine and yields compounds with the stoichiometry
$[PcFe(pyz)I_y]_n$ (y = 0 to 2.6)[6]. The materials can be
synthesized either by treating the suspended undoped
polymer with iodine in benzene (eq. 1, heterogeneous
doping) or by precipitating the polymer from a $PcFe(pyz)_2$
slurry containing iodine (eq. 2, homogeneous doping).

$$[PcFe(pyz)]_n + n\ y/2\ I_2 \xrightarrow{\text{benzene}} [PcFe(pyz)I_y]_n \quad (1)$$

$$n\ PcFe(pyz)_2 + n\ y/2\ I_2 \xrightarrow{\text{CHCl}_3} [PcFe(pyz)I_y]_n + n\ pyz \quad (2)$$
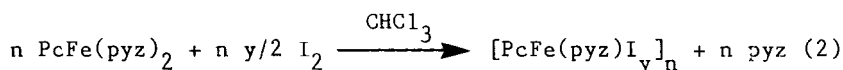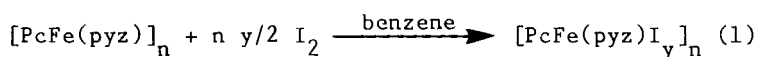
The compositions of the doped pyrazine polymers were
established both by microanalysis and TG/DTA. The TG data
reveal three well-defined stages of mass loss. The first
and second correspond well to initial iodine loss (120 –
200°C), followed by pyrazine loss (230 – 290°C). The third
mass loss is generally rather small. The infrared spectrum
of the thermal residue after the first stage is identical
to that from an authentic sample of $[PcFe(pyz)]_n$. The
thermal stability of $[PcFe(pyz)I_y]_n$ is therefore in the
same range as for iodine doped $[(PcSiO)I_y]_n$ and
$[(PcAlF)I_y]_n$[4].

The nature of the iodine doping process was also
investigated by X-ray powder diffractometry, resonance
Raman and ^{57}Fe Mößbauer spectroscopy[6]. The doped polymers
in contrast to undoped $[PcFe(pyz)]_n$ show only a diffuse
X-ray diffraction pattern. Resonance Raman studies reveal
strong scattering about 170 cm^{-1}, which is essentially

invariant with iodine content in $[PcFe(pyz)I_y]_n$. This band has been associated (on the basis of structurally well-characterized model compounds) with polyiodides having I_2 units coordinated to I_3^- [7]) and therefore can be assigned as I_5^-. ^{57}Fe Mößbauer spectroscopy on $[PcFe(pyz)I_y]_n$ unambigiously shows, that doping does not destroy the polymeric structure of the compound. Isomer shifts and quadrupole splitting of $PcFe(pyz)_2$, $[PcFe(pyz)]_n$, and $[PcFe(pyz)I_y]_n$ are nearly identical, supporting hexaco-ordinated iron ions in all three compounds. The presence of I_5^-, as indicated by the resonance Raman results, clearly demonstrates that oxidation takes place in the linear chain compound $[PcFe(pyz)]_n$. The ^{57}Fe Mößbauer data, however, suggest that the oxidation involves orbitals that are not predominantly metallic in character.

Electrical conductivity measurements on heterogeneously (eq. 1) and homogeneously (eq. 2) doped $[PcFe(pyz)I_y]_n$ show that the conductivity versus dopant level relationship is rather similar to that of the $[(PcMO)I_y]_n$ compounds. The highest conductivities, measured for compressed polycrystalline samples, was found for $[PcFe(pyz)I_{2.54}]_n$ which was doped via the synthetic route indicated in eq. 1. This sample shows a room temperature conductivity of $\sigma_{RT} = 0.2$ S/cm. The temperature dependence of the doped polymer conductivity can be fit to a model of thermal activation. The derived activation energies E_a decrease with increasing conductivity. Compared with the activation energy of the undoped $[PcFe(pyz)]_n$, the E_a of the highly conducting $[PcFe(pyz)I_{2.54}]_n$ is significantly lower. The observation of increasing conductivities and decreasing activation energies, with increasing iodine

content, has been noted for the $[(PcMO)I_y]_n$ materials[7] and several other conductive phthalocyanine polymer systems[4].

Several other type B-polymers have been doped with iodine, leading also to stable iodine containing compounds. The data are summarized in Table 1. For the first time TBP was used as a macrocycle in these type of compounds, leading to $[TBPFe(dib)I_y]_n$ with a room temperature conductivity of 10^{-2} S/cm.

TABLE 1   Electrical Conductivity Data for Iodine-
doped Polymers $[MacML]_n$

|	y	σ_{RT} [S/cm]
$[PcFe(pyz)I_y]_n$	0	$2 \cdot 10^{-6}$
	0.38	$4 \cdot 10^{-4}$
	1.49	$6 \cdot 10^{-3}$
	2.54	$2 \cdot 10^{-1}$
$[PcFe(dib)I_y]_n$	1.5	10^{-2}
$[PcFe(Me_4dib)I_y]_n$	0	$1 \cdot 10^{-7}$
	1	$2 \cdot 10^{-4}$
	2	$6 \cdot 10^{-3}$
	3	$3 \cdot 10^{-2}$
$[PcFe(Cl_4dib)I_y]_n$	0	$4 \cdot 10^{-6}$
	1.66	$2 \cdot 10^{-2}$
	2.64	$5 \cdot 10^{-2}$
$[TBPFe(dib)I_y]_n$	0	$2 \cdot 10^{-6}$
	1.7	$9 \cdot 10^{-3}$
$[PcRu(dib)I_y]_n$	2	$1 \cdot 10^{-2}$

From the data in Table 1 it is evident, that the bridged transition metal macrocycles are dopable with iodine, leading two stable compounds of conductivities which are in the same range as $[(PcMO)I_y]_n$ and $[(PcMF)I_y]_n$. In spite of the rather large interplanar spacings in a single chain of the type B-polymers doping leads to a large increase in electrical conductivity.

Type C-polymers

For the first time phthalocyaninatometal polymers with a bridging ligand linked by one σ- and one coordinative bond to the central metal have been synthesized. These are the (μ-cyano)phthalocyaninatometal compounds shown in Fig. 3. The most interesting property of these type of (μ-cyano)-phthalocyaninatometal compounds is, that with Co and Fe as the central metal atom, they exhibit DC room temperature conductivities around 10^{-2} S/cm without doping, therewith showing conductivities which are in the same range as the iodine doped $[PcMO]_n$ (M = Si, Ge) and $[PcML]_n$ (M = Fe, Ru, L = pyz, dib).

Fig. 3


2a-d

a: M = Co   c: M = Mn
b: M = Fe   d: M = Cr
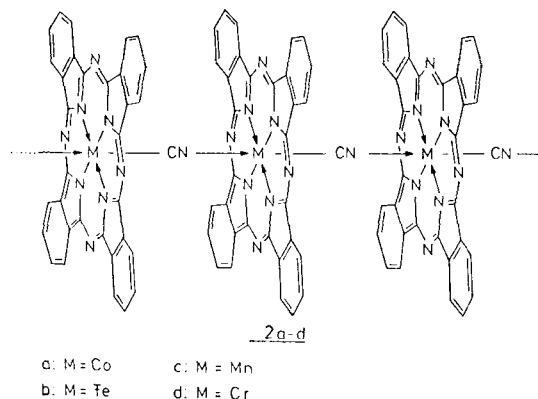
Compounds of this type have been synthesized in addition to Co and Fe with Mn and Cr as the central metal atoms (Fig. 3).

A general route leading to the cyano bridged polymers $[PcMCN]_n$ is the splitting off of alkali-metal cyanide from alkali-metal-dicyano(phthalocyaninato)transition-metal(III) complexes $M'[PcM(CN)_2]$ $(\underline{1})$ (Fig. 4). The complexes $M'[PcM(CN)_2]$ $(\underline{1})$ were synthesized either by <u>in situ</u> oxidation of PcM (M = Co, Mn, Cr) $(\underline{5})$ with oxygen in the presence of excess cyanide or by reaction of $PcMCl_2$ (M = Co, Cr) $(\underline{4})$ and PcMCl (M = Mn, Fe) $(\underline{3})$ with alkali-metal cyanide in ethanol. The polymers $[PcMCN]_n$ $(\underline{2})$ are formed during extraction of the monomeric complexes $M'[PcM(CN)_2]$ $(\underline{1})$ with water[8,9]. This also suggests the intermediate formation of $M'[PcM(CN)_2]$ in the reaction of $PcMCl_2$ (M = Co, Cr) with aqueous alkali-metal cyanide solution which lead to the corresponding polymers $[PcMCN]_n$.

Fig.4 Syntheses of Monomeric and Polymeric Phthalocyaninatometal(III) Cyano-Derivatives
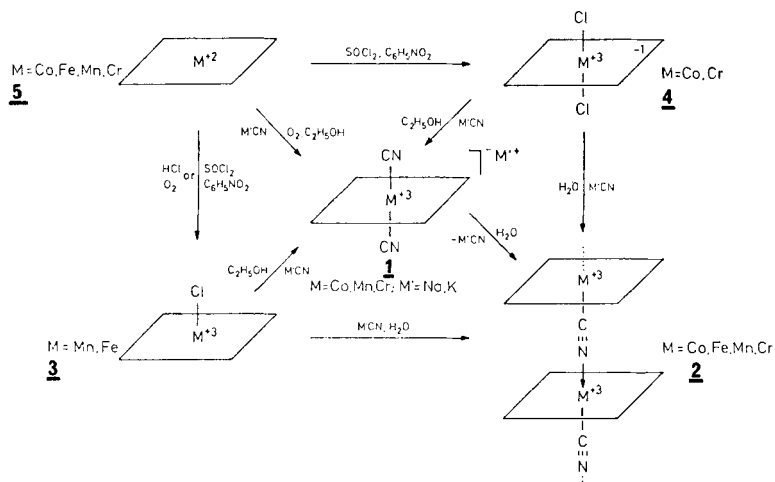
A possible other route for the synthesis of polymeric
$[PcMCN]_n$ is the displacement of the axial anion X^- by CN^-
in a coordinatively unsaturated compound PcMX (X = halide).
This method was successfully applied for the synthesis of
$[PcFeCN]_n$ (2b) and $[PcMnCN]_n$ (2c) (Fig. 4) The starting
materials PcFeCl (3b) and PcMnCl (3c)[10,11] were syn-
thesized by oxidative chlorination of the parent phthalo-
cyanines (see Fig. 4). Treatment of both chlorides with
aqueous alkali-metal cyanide solution yields the polymers
2b,c respectively.

The PcMX precursors for the cobalt and chromium poly-
mers 2a,d were not known. The reported synthesis for
$PcCoCl$[11,12] only produces impure $PcCoCl_2$ (4a), which
undergoes thermal decomposition above 300°C followed by a
peripheral chlorine-substitution yielding ClPcCo.

A method for the introduction of the $Pc^{2-}M^{3+}$-unit
into the reaction path, using as starting materials
$PcCoCl_2$ (4a) and $PcCrCl_2$ (4d) in protic solvents, has been
developed (see Fig. 4). Again $PcCoCl_2$ and $PcCrCl_2$ were
converted into the corresponding polymers 2a,d in an
aqueous alkali-metal cyanide solution. $Pc^{1-}M^{3+}$ is simul-
taneously reduced and polymerized under the reaction
conditions[13,14]. Possible intermediates in this reaction
are the monomeric complexes $M'[PcM(CN)_2]$ (1a,d) (M = Co,
Cr; M' = Na, K).

The monomeric complexes $M'[PcM(CN)_2]$ (1) were
characterized through IR, far-IR, UV-VIS and, in some
cases, by ^1H-NMR spectroscopy. The IR spectra of 1a,d
(Table 2) exhibit CN-valence frequencies around 2130 cm^{-1},

which is in the anticipated region for terminal Co(III) and Cr(III)-cyano groups[15]. The absorption of the Mn-derivative (ν_{CN}: 2114 cm^{-1}) and the Fe-derivative (ν_{CN}: 2112 cm^{-1}) also correlates with reported data[15]. These observations support the structure $\underline{1}$ for the complex anion, in the case of (1a) this structure has been confirmed by the ^{1}H-NMR-spectrum (δ [ppm]: 8.2 m, aromatic H; 9.5 m, aromatic H). $K_2[PcFe(CN)_2]$[16], with iron in the +2 formal oxidation state, shows the CN-band near the absorption of free CN$^-$. The mass spectra and the elemental analyses of (1a,c,d) are in accordance with the stoichiometry suggested.

The polymers 2a-d were characterized by IR and far-IR spectroscopy, magnetic measurements, thermogravimetrical and microanalytical analyses and chemical decomposition. The CN valence frequencies of 2a,c,d compared with the monomeric complexes $\underline{1}$, (Table 2) are shifted about 30 cm^{-1} (M = Co) and 20 cm^{-1} (M = Cr, Mn) to higher energy. This increase in CN-valence frequency is evidence for the presence of a cyano bridge [15] in 2a-d. The polymers exhibit thermal stabilities up to 250°C and are insoluble in noncoordinating solvents.

TABLE 2   Infrared and Thermoanalytical Data for Monomeric and Polymeric Cyano Complexes.

	ν_{CN} $[cm^{-1}]$[a]	Dissociation range of the cyano group $[°C]$[b]
$NaPcCo(CN)_2 \cdot 5\ H_2O$	2130	280 - 310
$Na(H_3C)_8PcCo(CN)_2 \cdot 3\ H_2O$	2132	170 - 300
$KPcMn(CN)_2 \cdot 2\ EtOH$	2114	250 - 380
$NaPcCr(CN)_2\ EtOH, 2H_2O$	2133	310 - 455
$PcCo(py)CN$	2147	180 decomp.
$[PcCoCN]_n$	2158	220 - 300
$[(H_3C)_8PcCoCN]_n$	2142	150 - 270
$[PcFeCN]_n$	2133	170 - 230
$[PcMnCN]_n$	2133	250[c]
$[PcCrCN]_n$	2150	170 - 300

a) Nujol mull

b) Heating rate 2°/min. N_2

c) Endothermic weightloss.

The polymeric structure of $\underline{2}$ (Fig. 3) is destroyed when the material is treated with a competing ligand. This confirms the proposed chain structure[8] thus being exemplified for $[PcCoCN]_n$: When $[PcCoCN]_n$ is treated with bases (L) such as pyridine (py), 2-methylpyrazine (mepyz), piperidine (pip), and $\underline{n}$-butylamine (ba), monomeric complexes are obtained with the composition $PcCo(CN)L$ $(\underline{6})$ (Fig. 5). These compounds were characterized through IR and mass spectroscopy as well as by elemental and thermal analyses.

Fig. 5
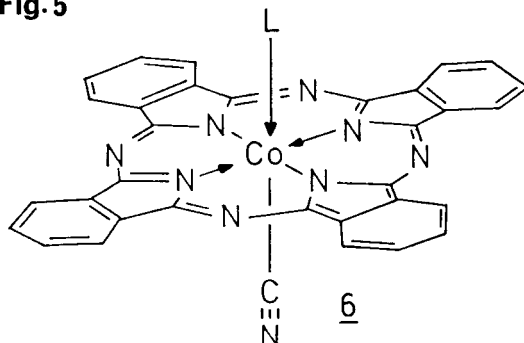
Although the main emphasis of spectroscopic and chemical characterization of $[PcMCN]_n$ polymers has been directed toward the cobalt derivative $\underline{\underline{2a}}$ the results are generalizable. The compounds $\underline{\underline{2b,c,d}}$ and the iron derivative $[HPcFeCN]_n$[9] are found by powder X-ray diffraction studies to be isostructural to $[PcCoCN]_n$.

$[PcCoCN]_n$ $(\underline{\underline{2a}})$ exhibits electrical conductivities around 10^{-2} S/cm (Table 3) without additional doping, which are in the same range as those obtained for doped

samples of the μ-oxo and μ-fluoro polymers $[R_4PcMX]_n$. When the polymeric structure of $[PcCoCN]_n$ was destroyed by treatment with a competing ligand e.g. py, pip, ba, mepyz to form PcCo(L)CN, (6), the conductivity was diminished by 6 - 10 orders of magnitude (Table 3).

TABLE 3   Dc-Dark Conductivities for Polymeric
           Phthalocyaninatometal(III) Cyano-Derivatives

Compound	S/cm	Activation Energy eV
$[PcCoCN]_n$	2×10^{-2} b)	0.1
$[(H_3C)_8PcCoCN]_n$	5×10^{-5} b)	
$[PcFeCN]_n$	6×10^{-3} b)	0.1
$[PcMnCN]_n$	1×10^{-5} a)	
$[PcCrCN]_n$	3×10^{-6} a)	

a) Two-probe technique, 1 kbar.
b) Four-probe technique, 1 kbar.

The iron cyano polymer $[PcFeCN]_n$ (2b) shows a conductivity comparable to that of the cobalt polymer. The corresponding monomeric derivatives of the type PcFe(L)CN are not as yet known. Lower values for the (μ-cyano)-phthalocyaninatomanganese and chromium compounds (2c,d) (Table 3) in the range of 10^{-5} - 10^{-6} S/cm were obtained. $[PcCoCN]_n$ and $[PcFeCN]_n$ show a semiconducting behavior, the activation energy was found to be 0.1 eV[17]. Homogeneous doping of $[PcCoCN]_n$ with iodine, starting with Na[PcCo(CN)$_2$] and using a special technique[18], led to stable compounds $[(PcCoCN)I_y]_n$ e.g. with y = 1.6. The

conductivity was only slightly increased by the doping
process to σ_{RT} = 0.6 S/cm.

No final explanation for the comparable high con-
ductivity of $[PcCoCN]_n$ and $[PcFeCN]_n$ can be given at this
time. EPR spectra obtained from polycrystalline samples of
$[PcCoCN]_n$ exhibit two signals, one at the free electron
value and the other at g = 2.3. While the signal at g =
2.0028 suggests an oxidation centered on the macrocyclic
ligand, the weak signal at g = 2.3 is ascribed to the $g\perp$
branch of a pentacoordinated PcCo(II) unit[14], which
corresponds to a partial reduction of the back bone.

Acknowledgment

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