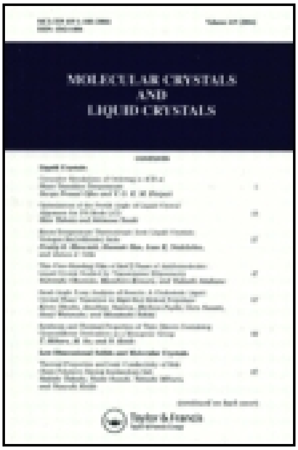

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 14 Oct 2011.

To cite this article: O. Schneider , J. Metz & M. Hanack (1982): Synthesis and Properties of a New Kind of One-Dimensional Conductors 17. Studies on monomeric and polymeric phthalocyaninato-iron(II) and -cobalt(II) complexes, Molecular Crystals and Liquid Crystals, 81:1, 273-284

To link to this article: http://dx.doi.org/10.1080/00268948208072574

Mol. Cryst. Liq. Cryst., 1982, Vol. 81, pp. 273–284
0026-8941/82/8101-0273$06.50/0

Printed in the United States of America

(Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, Colorado, August 1981)

SYNTHESIS AND PROPERTIES OF A NEW KIND OF ONE-DIMENSIONAL CONDUCTORS

17. Studies on monomeric and polymeric phthalocyaninato-iron(II) and -cobalt(II) complexes*

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Submitted for publication August 22, 1981

A new approach for a one-dimensional organic conductor with a chemically bonded backbone is presented. The proposed compounds consist of a linear arrangement of transition metal atoms, e.g. Fe, Co, bridged by linear bidentate π-electron containing ligands, e.g. pyrazine, 4,4'-bipyridine, and 1,4-diisocyanobenzene. This structure is stabilized by the tetradentate planar phthalocyanine molecule complexing each octahedrally coordinated central atom in its equatorial plane. The synthesis and characterization of the monomeric, dimeric and polymeric compounds PcML/PcML$_2$, PcM-L-PcM and [PcML]$_n$ are described and a comparison of their electrical conductivity as a function of their structural features is given in detail. The electrical conduction of the monomeric units increases after polymerisation by a factor of 10^7 without doping. In the second part soluble tetrasubstituted phthalocyaninato(IVB)-metalloxanes are described and the effect of homogeneous and heterogeneous iodination on conductivity is discussed.

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*This work was supported by the Stiftung Volkswagenwerk.

In the last ten years particular interest is placed on the development of organic materials with metal-like conductivity. A basic principle on designing such compounds is the existence of a mixed valence state combined with a stacked structure. Several routes were worked out to establish these features in different types of compounds [1].

One approach generating a linear chain structure is to build up a chemically bonded backbone consisting of an alternating metal-ligand arrangement. The one-dimensionality is stabilized by a tetradentate, planar ligand complexing the octahedrally coordinated metal atom in its equatorial plane*. Compounds of the described composition are the well known polyphthalocyaninatosiloxane, -germoxane and -stannoxane, which behave like insulators in the undoped state [2]. In case of the silicon and germanium derivatives an increase of conductivity up to 1 S/cm is reported after doping with iodine [4]. The isoelectronic fluorophthalocyaninatometal-polymers of aluminum, gallium, and chromium are also described as highly conducting materials with $\sigma = 0.01$ to 1 S/cm [5]. Partially oxidized stacked metallomacrocycles with direct metal-metal contact were also examined [6]. In these compounds the interplanar spacing of the phthalocyanine molecules presumably is the dominating factor for conduction.

Our concept [7] deviates from the above mentioned systems in using the backbone-approach with a conductivity along the central chain excluding π-π-interaction by long

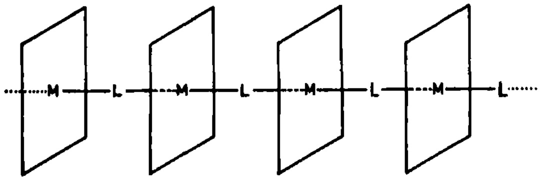

FIGURE 1 Generalized structure of a linear system with a chemically bonded backbone, □=tetradentate ligand, M = metal, L = bridging ligand

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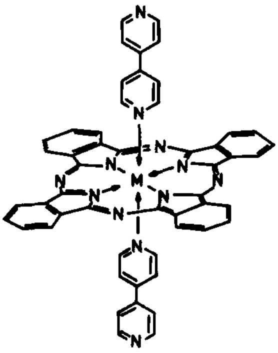
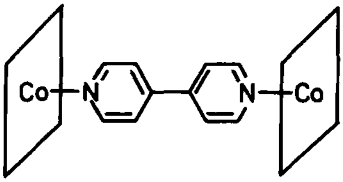
*A recent publication shows by X-ray analysis of $[\mathrm{TPPMn(III)im}]_{\infty}$ that an analogous zig-zag chain is possible, if a non-linear bridging ligand like the imidazolate-anion(im) is used [3].

interplanar distances. The backbone itself consists of transition metal atoms M = Fe, Co bridged by linear bidentate π-electron containing ligands L = pyrazine (pyz), 4,4'-bipyridine (bipy), 1,4-diisocyanobenzene (dib). EHMO-calculations show for M = Fe^{2+} and L = $|C\equiv C|^{2-}$ partly occupied



1 M = Fe
2 M = Co



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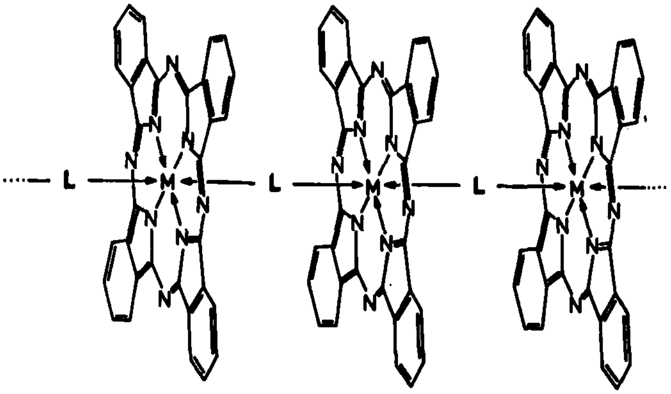

4 M = Fe
5 M = Co

a L = pyz
b L = bipy
c L = dib

FIGURE 2 Monomeric, dimeric and polymeric phthalocyaninatometal complexes of iron and cobalt energy bands (crossed by the approximate Fermi level) which is a necessary condition for metal-like electrical conductivity. This partial band-occupation is solely caused by band-overlaps and neither by unpaired electrons in the unit cell nor by any doping process.

In this conference we present the preparation, chemical and physical properties of monomeric, dimeric and polymeric compounds, Fig. 2, with Fe^{2+} and Co^{2+} as metal ions, phthalocyanine dianion (Pc^{2-}) as macrocycle and pyrazine (pyz), 4,4'-bipyridine (bipy) and 1,4-diisocyanobenzene (dib) as bridging ligands.

All compounds used for conductivity measurements were synthesized under nitrogen with purified materials and solvents. Fig. 3 gives a brief survey of the generalized reaction conditions leading to compounds as shown in Fig. 2. Detailed information is given elsewhere [8,9]. The colour of the semicrystalline powders varies from blue or violet for the monomeric species to dark blue with a violet reflex for the polymeric solids.

As shown in Fig. 3, there is a distinct difference in the coordination behavior of iron(II)- and cobalt(II)-ion incorporated in the phthalocyaninato-moiety. To our knowledge only hexacoordinated $PcFeL_2$-compounds are isolated and characterized [10], whereas for cobalt the existence of penta-(PcCoL) and hexacoordinated ($PcCoL_2$) complexes is proved [11]. A pentacoordinated PcFeL-compound is predicted by some workers [10a,12] from UV-spectroscopic data as an intermediate in the reaction of pyridine with PcFe to the hexacoordinated $PcFe(py)_2$.

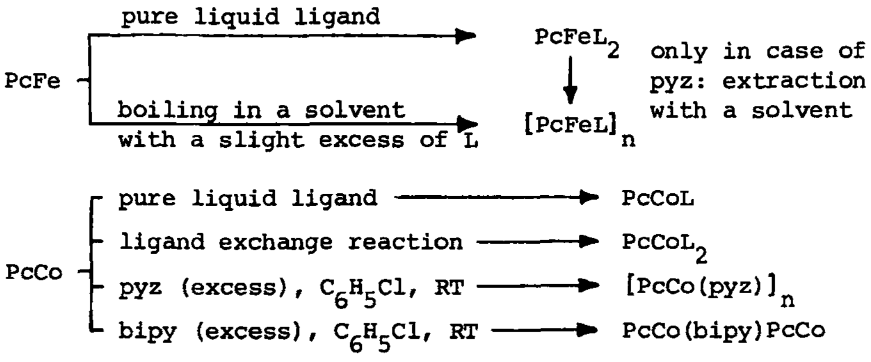

FIGURE 3 General procedures for the preparation of the described compounds

The synthesized materials where thoroughly examined for their stoichiometry, and with respect to conductivity measurements, for their purity. As a helpful tool we used the combined thermogravimetric and differential-thermal analysis (TGA/DTA), assisted by elemental analysis. Magnetic susceptibility measurements gave information on the spatial environment of the metal ions. The polymeric iron complexes *4a-c* were found in the expected low-spin-state with a small paramagnetic contribution, not uncommon for diamagnetic iron-compounds. All examined PcCoL and $PcCoL_2$ adducts are low-spin complexes with $\mu eff \approx 2$ B.M. [8]. Soluble cobalt-compounds were investigated by EPR-measurements.To gain further information the different physical behavior of monomeric and polymeric species was studied by UV/VIS/NIR/IR and FIR spectra [13]. Especially NIR-spectroscopy was established to distinguish penta- and hexacoordinated cobalt [8].

These methods point out the composition, purity and properties of the examined materials. Works are in progress to get information on the degree of polymerisation of our one-dimensional systems.

An astonishing result of our synthetic efforts was the ease of polymerisation, especially of *4a*. In contrast $PcFe(pyz)_2$ could only be isolated, if the excess pyrazine was sublimed or washed out with methanol or ethanol. Washings with chloroform, benzene or chlorobenzene lead to loss of pyrazine yielding the polymeric *4a*. This observation was proved by visible spectroscopy: only in the presence of a 10^6-fold excess of pyrazine in the solvent used, it was possible to record the pure spectrum of $PcFe(pyz)_2$. Without excess pyrazine, the polymerisation of $PcFe(pyz)_2$ to *4a* could be followed spectroscopically.

A solution of the analogous cobalt complex is not stable. Without excess ligand the $PcCoL_2$-complex dissociates immediately and insoluble PcCo precipitates. The higher inertness in solution for the iron-complexes in contrast to the cobalt adducts have a counterpart in their thermal stability (TGA). The thermal stability increases in the following sequence, and ranges from 80°C for $PcCo(pyz)_2$ up

$$\begin{aligned} & PcCo(pyz)_2 < [PcCo(pyz)]_n < PcCo(bipy)PcCo \\ & \approx PcCo(pyz) \approx PcCo(bipy)_2 < PcFe(pyz)_2 \\ & < PcFe(bzNC)^{*}_2 < PcFe(bipy)_2 \approx [PcFe(bipy)]_n \\ & < [PcFe(dib)]_n \approx [PcFe(pyz)]_n \end{aligned}$$

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*bzNC = benzylisocyanid

to 240°C for $[PcFe(pyz)]_n$ for the beginning thermal dissociation:

$$PcML_{x;x=1,2} \xrightarrow{\Delta} PcM + L\uparrow$$

The reduced thermal stability of the hexacoordinated cobalt-compounds compared with the pentacoordinated derivatives seems to be a consequence of the unpaired electron of the cobalt atom occupying a d_{z^2}-orbital and therefore preventing the formation of two strong coordinative bonds perpendicular to the planar macrocycle.

An X-ray analysis carried out on $PcFe(4\text{-}Mepy)_2$ and $PcCo(4\text{-}Mepy)_2$ shows a significant longer M-N bond distance to the axial 4-methylpyridine in the cobalt-(232 pm) than in the iron-complex (204 pm) [14]. Recently the structure of the polymeric bis(dimethylglyoximato)pyrazinecobalt(II), $[Co(dmgH)_2pyz]_\infty$, [15] was determined. The long $Co\text{-}N_{pyz}$ distance (224 pm) reported for this one-dimensional system presumably gives rise to the found low electrical conductivity.

The electrical conductivities of monomeric and dimeric complexes are compared to the analogous polymeric compounds as shown in Tab. 1 and 2. Electrical conductivity data were aquired depending on their order of magnitude with a two-

TABLE 1 Conductivity measurements of monomeric and polymeric phthalocyaninatoiron(II) complexes*

	$\sigma_{295\,K}$ $[\frac{1}{\Omega \cdot cm}]$	
β-PcFe	$4 \cdot 10^{-11}$	
$PcFe(pyz)_2$	$2 \cdot 10^{-12}$	
$[PcFe(pyz)]_n$	$2 \cdot 10^{-5}$	**
$PcFe(bipy)_2$	$5 \cdot 10^{-13}$	
$[PcFe(bipy)]_n$	$2 \cdot 10^{-8}$	
$PcFe(bzNC)_2$	$2 \cdot 10^{-12}$	
$[PcFe(dib)]_n$	$2 \cdot 10^{-5}$	**

*two-probe technique, polycrystalline samples

**four-probe technique, polycrystalline samples

TABLE 2 Conductivity measurements of monomeric, dimeric, and polymeric phthalocyaninatocobalt(II) complexes*

	σ_{295K} $[\frac{1}{\Omega \cdot cm}]$
β-PcCo	$2 \cdot 10^{-11}$
PcCo(pyz)	$7 \cdot 10^{-12}$
$[PcCo(pyz)]_n$	$1 \cdot 10^{-9}$
$PcCo(bipy)_2$	$2 \cdot 10^{-11}$
PcCo(bipy)PcCo	$3 \cdot 10^{-11}$

*two-probe technique, polycrystalline samples

probe apparatus [16] or by the square four-probe van der Pauw technique [17]. The apparatus employed was developed in our laboratory [18] for the special requirements of the polycrystalline materials. Measurements were carried out at ambient temperature under 2 kbar (two-probe) and 1 kbar (four-probe) pressure. Samples were pressed in cylindrical pellets 13 mm in diameter and ca 0.5 - 1.2 mm thick. DC-measurements in the range from 10^{-6} A to 10^{-2} A show ohmic behaviour for all examined materials.

Polymerisation of the phthalocyaninatoiron(II) via π-electron-containing bridging ligands like pyrazine, 4,4'-bipyridine and 1,4-diisocyanobenzene yield an increasing conductivity over 7 orders of magnitude, without doping. Polymerisation of the phthalocyaninatocobalt(II) improves conductivity too, however not to such a great extent as for the iron-compounds. A limitation in the case of cobalt possibly is the long Co-N(ligand)-distance, which prevents π-overlapping along the chain, a necessary condition for electron motion from metal to metal via bridging ligands.

Electron transport through bridging molecules is discussed in a great variety, e.g. for dimeric mixed valence Ru(II)/Ru(III) compounds [19] or recently in a dimeric heme-pyz-heme compound [20]. This system shows a strong NIR-band around 800 nm, which is interpreted in sence of an electron exchange between the two iron ions.

In this work we prove the possibility of electron transport via bridging molecules in a one-dimensional organometallic polymer by electrical conductivity measurements. It is emphasized, that in the described polymers (4,5), any direct Pc-Pc-interaction within the one-dimensional chain is excluded, due to the great interplanar distances (700 or 1200 pm, respectively), according to the metals and bridging ligands involved. Despite a Fe-Fe-distance of about 1150 pm in *4c* compared to 700 pm in *4a* the same conductivity for both materials was observed.

This is in contrast to the results of Marks and coworkers , who found for $[(PcSi\text{-}ORO)I_x]_n$ by variation of R that the interplanar spacing correlates inversely with the electrical conductivity of the iodine-doped materials [21]. The conductivity of $[(PcSi\text{-}O\text{-}⌬\text{-}O)I_{0.85}]_n$ in which the Pc-moieties are separated roughly by the same distance as in *4b* or *4c* , is one order of magnitude lower than in our compounds, although the silicon derivative is a doped solid.

The above described compounds were investigated as undoped species. Iodine-doping of $[PcFe(pyz)]_n$ yields unstable materials with permanent loss of the doping agent. The conductivity increased between two and three orders of magnitude depending on the iodine content. Iodinations were carried out in heterogeneous phase (vapor - solid) because of the low solubility of the polymers. In the course of our investigations on the synthesis of acetylene-bridged phthalocyaninatometals we tried to solve preparation problems by using soluble complexes [22]. It is known, that an introduction

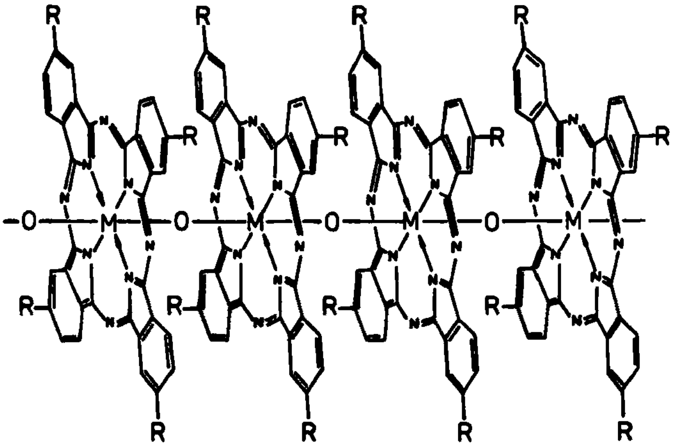

FIGURE 4 Tetrasubstituted μ-oxo-phthalocyaninato(IVB)-metalpolymers

of bulky substituents e.g. butylgroup in the periphery of the macrocycle causes solubility in common organic solvents like chloroform, acetone, toluene. Our work in this field lead to a variety of new phthalocyaninato(IVB) complexes including the soluble derivatives of the μ-oxo-phthalocyaninato(IVB)-metalpolymers cited above.

The undoped materials synthesized show an electrical conductivity comparable with the data of the unsubstituted compounds, Table 3. These compounds enable us now to compare doping methods like the heterogeneous solid - solid, vapor - solid and liquid - solid reactions with an iodination in homogeneous solution. Upon iodine uptake the blue sample changes to a black powder which appears as a deep brown solid at a maximum iodine content of 35%. These samples are air-stable and storable over several months without iodine loss. In Table 4 some data are collected for the silicon compound. There is no detectable variation in conductivity resulting from the doping method.

The tin-compound changes colour from blue to green after contamination with iodine vapor. The FIR-spectrum of a doped sample shows the appearence of the Sn-J-band at 154 cm^{-1}, which suggests a metal-iodination and a polymer-destruction process.

At present it is speculative to discuss the effekt of the M-O-backbone on conductivity. While O^{2-} in the μ-oxo-compound behaves like an electron trap in the chain, electron transport along the backbone should be supported by bridging S^{2-}. Recently the synthesis of the polymeric μ-thio-phthalocyaninatogermanium(IV) was successful [23]. We hope to get more information on that field by doping this thio-compound.

TABLE 3 Conductivity measurements of tetra-t-butyl-phthalocyaninato(IVB) metalloxanes*

	$\sigma_{295K}\ [\frac{1}{\Omega \cdot cm}]$
$[\underline{t}\text{-Bu}_4\text{PcSiO}]_n$	$2 \cdot 10^{-7}$
$[\underline{t}\text{-Bu}_4\text{PcGeO}]_n$	$6 \cdot 10^{-11}$
$[\underline{t}\text{-Bu}_4\text{PcSnO}]_n$	$4 \cdot 10^{-12}$

*two-probe technique, polycrystalline samples

TABLE 4 Conductivity measurements of iodine doped tetra-t-butylphthalocyaninatosiloxane*

$[(\underline{t}\text{-Bu}_4\text{PcSiO})\text{I}_x]_n$	x	σ_{295K} $[\frac{1}{\Omega \cdot cm}]$	doping method
	0.5	$2 \cdot 10^{-4}$	mull
	1.1	$7 \cdot 10^{-4}$	toluene 0.005 m
	1.6	$9 \cdot 10^{-4}$	ether 0.005 m
	1.7	$1 \cdot 10^{-3}$	ether 0.005 m
	2.0	$2 \cdot 10^{-3}$	vapor
	3.9	$2 \cdot 10^{-3}$	saturated n-hexane slurry

*four-probe technique, polycrystalline sample

We presented a new approach for a one-dimensional organic conductor. This concept will be furthermore investigated using other metals, e.g. Ru, macrocyclic systems, e.g. tetraphenylporphine, dihydrodibenzo[b,i] [1,4,8,11]tetraazacyclotetradecine and bridging ligands. Especially the up to now unsolved problem of synthesizing polymers containing M-C-σ-bonds of the type mentioned in the introduction is under investigation.

Main interest will be placed on growing single crystals of the described polymers and studying their morphology.

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