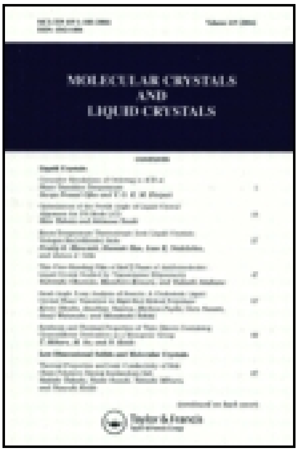

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Bridged Macrocyclic Metal Complexes as Semi-Conducting Materials

Michael Hanack [a]

[a] Institut für Organische Chemie, Lehrstuhl für Organische Chemie II der Universität Tübingen, Auf der Morgenstelle 18, D-7400, Tübingen, West Germany

Version of record first published: 28 Mar 2007.

To cite this article: Michael Hanack (1988): Bridged Macrocyclic Metal Complexes as Semi-Conducting Materials, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 160:1, 133-137

To link to this article: http://dx.doi.org/10.1080/15421408808083008

Mol. Cryst. Liq. Cryst., 1988, Vol. 160, pp. 133–137
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Bridged Macrocyclic Metal Complexes as Semi-Conducting Materials

MICHAEL HANACK

Institut für Organische Chemie, Lehrstuhl für Organische Chemie II der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, West Germany

Bridged macrocyclic transition metal complexes using phthalocyanine, tetrabenzoporphyrine and naphthalocyanine as macrocycles e.g. $[PcML]_n$ with M = Fe, Ru, Co and L = e.g. pyz, dib, tz, SCN^-, CN^- have been synthesized and their electrical properties were studied in detail. Regardless of the bridging ligand stable semi-conducting compounds are formed after doping with iodine or electrochemical doping. Some of these shish-kebab polymers e.g. $[PcM(tz)]_n$, M = Fe, Ru or e.g. $[PcML]_n$, M = Fe, Co; L = CN^-, SCN^- exhibit good semi-conducting properties without additional external doping. Their conductivities are comparable to the iodine doped bridged metallomacrocycles $[MacMLI_y]_n$. The mechanism of the formation of the bridged shish-kebab macrocyclic metal complexes has been studied by spectroscopic methods, mostly using ^{1}H-NMR spectroscopy.

Transition metal complexes, which are linked by linear bridging ligands L containing delocalizable π-electrons to form polymeric stacked arrangements $[MacML]_n$ have been synthesized. As macrocycle Mac phthalocyanine (Pc), tetrabenzoporphyrine (TBP), 2,3-naphthalocyanine (2,3-Nc) and 2,3-tetranaphthoporphyrine (2,3-TNP) have been employed. We have used Fe, Ru, Co, Rh and others as central metals and as bridging ligands e.g. pyrazine (pyz), diisocyanobenzene (dib), tetrazine (tz), cyanide (CN^-) and isothiocyanate (SCN^-). Depending on the macrocycle and the bridging ligand L these types of compounds are with and without additional oxydative doping good semi-conducting materials.[1]

The characterization of the bridged macrocyclic metal compounds was mostly done by IR spectroscopy or thermogravimetric methods. However NMR studies to investigate the mechanism of formation of the bridged metal complexes have also been carried out. For this purpose the monomeric and bridged phthalocyaninatoiron(II) and

-ruthenium(II) compounds $\mathrm{PcM(Me_4dib)_2}$ and $[\mathrm{PcM(Me_4dib)}]_n$, M = Fe, Ru were synthesized.[2]

The monomeric compounds $\mathrm{PcM(Me_4dib)_2}$, M = Fe (1), M = Ru (2) are characterized by their ^{1}H-NMR spectra. When recorded after some time the ^{1}H-NMR spectra of 1 and 2 show beside the original monomer signals of 1 and 2 two groups of signals shifted to higher field. The additional signals intensify the longer the monomers stay in solution. For the peripheric phthalocyaninato-protons an upfield shift of about 0.4 ppm is observed, which definitely shows the formation of dimers, trimers and oligomers. The polymerization can also be followed by observing the upfield shift of the methyl protons of the axial ligands in 1 and 2. From the ^{1}H-NMR investigations the mechanism of the formation of the oligomers as shown in Scheme 1 can be derived.

$$
\begin{array}{llllll}
\mathrm{I} & m\ \mathrm{PcM} & +\ 2m\ \mathrm{L} & \rightleftharpoons & m\ \mathrm{PcML_2} & \\
\mathrm{II} & m\ \mathrm{PcML_2} & & \rightleftharpoons & m\ [\mathrm{PcML}] & +\ m\ \mathrm{L} \\
\hline
\mathrm{III} & m\ [\mathrm{PcML}] & +\ \mathrm{PcML_2} & \rightleftharpoons & m\ \mathrm{L{-}PcM{-}L{-}PcM{-}L} & +\ m\ \mathrm{L} \\
\mathrm{IV} & m\ \mathrm{L{-}PcM{-}L{-}PcM{-}L} & & \rightleftharpoons & m\ [\mathrm{L{-}PcM{-}L{-}PcM}] & +\ m\ \mathrm{L} \\
\mathrm{V} & m\ [\mathrm{L{-}PcM{-}L{-}PcM}] & +\ \mathrm{PcML_2} & \rightleftharpoons & m\ \mathrm{L{-}PcM{-}L{-}PcM{-}L{-}PcM{-}L} & +\ m\ \mathrm{L}
\end{array}
$$

SCHEME 1

Mößbauer spectroscopy is another important method to obtain additional information about the structure of the bridged macrocyclic iron compounds. The isomer shift (δ) and the quadrupol splitting (ΔE_Q) have been measured for a variety of monomeric and polymeric phthalocyaninato-, tetranaphthoporphyrinato- and naphthalocyaninatoiron compounds. From these data an independent proof for the hexacoordination of the bridged compounds was obtained.

The bridged systems $[\mathrm{MacFeL}]_n$, Mac = Pc, TBP, 2,3-Nc and 2,3-TNP, L = e.g. pyz, dib, have been oxidatively doped with iodine. Incremental doping results in the formation of stoichiometric compounds $[\mathrm{MacMLI}_y]_n$ which are stable up to 120°C.[3–4]

The influence of the length of the bridging ligand L on the electrical conductivity has been studied systematically. By changing the bridging ligand L the distance of the cofacial macrocycles in $[\mathrm{MacMLI}_y]_n$ can be varied ranging from ~700 pm for pyz to ~1150 pm for dib. The powder conductivities of the corresponding polymers $[\mathrm{PcFeLI}_y]_n$ at the maximum doping level did not change (maximum conductivity

TABLE I

Electrochemical doping of $[PcFe(pyz)]_n$ using a current density of 120 μA/cm²

Supporting electrolyte	Solvent	σ_{RT}[S/cm][a]
$(Bu_4N)BF_4$	CH_2Cl_2	4×10^{-2}
$(Bu_4N)PF_6$	CH_2Cl_2	3×10^{-2}
$(Bu_4N)B(Ph)_4$	CH_2Cl_2	2×10^{-6}
$LiClO_4$	H_2O	3×10^{-3}

[a] Four-probe-techique.

$\sigma_{RT} = 10^{-2} - 10^{-1}$ S/cm) using both pyz and dib as the bridging ligand L.[3] This points to a different conductivity mechanism for the transition metal polymers in comparison with e.g. iodine doped $[PcSiO]_n$.[5-6]

Electrochemical doping of $[MacML]_n$ compounds is also possible. As an example electrochemical doping of $[PcFe(pyz)]_n$ ($\sigma_{RT} = 2 \times 10^{-6}$ S/cm) with a variety of counterions BF_4^-, $B(Ph)_4^-$, PF_6^- and ClO_4^- is described (Table I).[7] The doping experiments are done in CH_2Cl_2 or H_2O with current densities about 90–200 μA/cm² and a

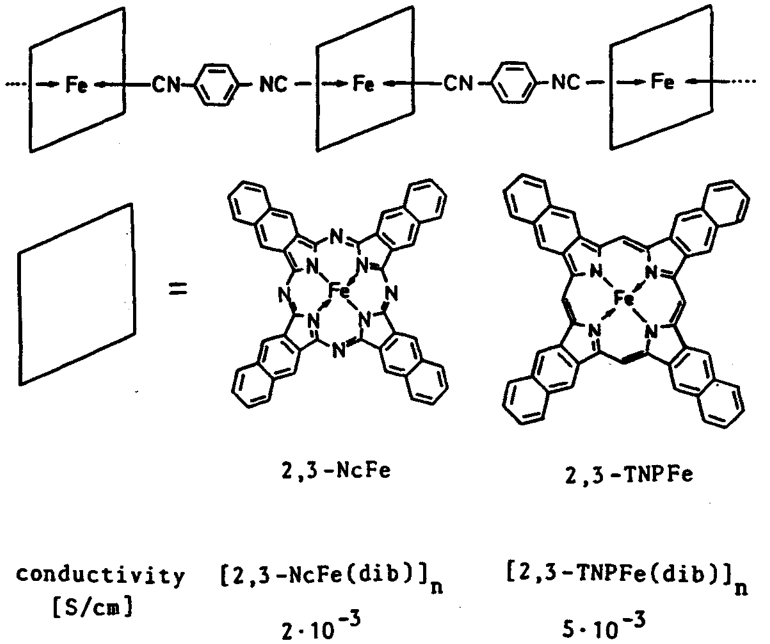

FIGURE 1 Schematic drawing of $[2,3\text{-}NcFe(dib)]_n$, $[2,3\text{-}TNPFe(dib)]_n$ and powder conductivities.

TABLE II

Conductivity data of monomeric and s-tetrazine bridged metal macrocycles

Compound	σ_{RT}[S/cm]	E_a [eV]
$PcFe(tz)_2$	$> 10^{-9}$ [a]	—
$[PcFe(tz)]_n$	2×10^{-2} [b]	0.10
$PcRu(tz)_2$	$< 10^{-11}$ [a]	—
$[PcRu(tz)]_n$	1×10^{-2} [b]	0.10
$[2,3\text{-}NcFe(tz)]_n$	3×10^{-1} [b]	0.07

[a] Two-probe-technique.
[b] Four-probe-technique.

0.1 mol/1 solution of the supporting electrolytes (except $(Bu_4N)B(Ph)_4$:0.05 mol/1). The electrolysis is stopped between 0.25 and 1.0 F/mol (of constitutive unit of the polymer); best conductivities were reached at 0.5 F/mol. IR spectra of the doped species show a broad electronic absorption.

Using 2,3-naphthalocyanine and 2,3-tetranaphthoporphyrine as the macrocycles the corresponding polymers $[MacFe(dib)]_n$ (Mac = 2,3-Nc, 2,3-TNP) have been prepared.[8]

Due to the low oxidation potential of the macrocycles, both types of polymers show conductivities of $\sim 10^{-3}$ S/cm, caused already by oxygen doping.[8]

Table II shows the conductivity data of s-tetrazine bridged metal macrocycles in comparison with the corresponding bisaxially substituted monomers. In spite of the fact that the monomers e.g. $PcFe(tz)_2$ show clearly insulating behavior, the s-tetrazine bridged macrocyclic compounds show in general comparatively high conductivities (Table II) without additional external oxidative doping.[9]

The reason for the high conductivities of the s-tetrazine bridged metallomacrocycles is not yet completely understood. The electronic structure of $[PcFe(pyz)]_n$ has been studied by means of the tight-binding (LCAO) method. As a result a band gap of about 0.7 eV and semi-conducting behavior was predicted.[10] The band gap according to these calculations is mostly determined by the difference

TABLE III

Conductivity data of cyano- and thiocyanato-bridged cobalt macrocycles.

Compound	σ_{RT}[S/cm][a]	E_a[eV]
$[PcCoCN]_n$	2×10^{-2}	0.10
$[TBPCoCN]_n$	4×10^{-2}	0.11
$[PcCoSCN]_n$	6×10^{-3}	0.22

[a] Four-probe-technique.

in energies between the LUMO of the bridging ligand and the HOMO of the transition metal d_{xy} orbital. The higher conductivities of the s-tetrazine bridged compounds $[PcFe(tz)]_n$, $[PcRu(tz)]_n$ and $[2,3\text{-}NcFe(tz)]_n$ are thereby explainable by the low lying LUMO of this ligand.

Cyanide bridged phthalocyaninato (Pc)- and tetrabenzoporphyrinato (TBP) metal compounds, (M = Co, Fe) form a second class of macrocyclic metal complexes with comparatively high semi-conducting behavior. $[PcCoCN]_n$ is well investigated[11] and preparation methods have been extended to the analogus $[TBPCoCN]_n$[12] and $[PcCoSCN]_n$[13] which all show comparable electrical properties (Table III).

$[PcCoCN]_n$ can be dissolved in conc. H_2SO_4 and CF_3SO_3H. From sulfuric acid solution of $[PcCoCN]_n$ containing e.g. polyamide Kevlar, flexible fibers can be spun showing good antistatic properties without doping.

Acknowledgments

This work was supported by the Stiftung Volkswagenwerk, the Bundesministerium für Forschung und Technologie and the "Forschungsschwerpunkt Nr. 39, Neue Materialien" at the University of Tübingen

References

1. (a) M. Hanack, *Chimia*, **37**, 238 (1983); (b) M. Hanack, A. Datz, R. Fay, K. Fischer, U. Keppeler, J. Koch, J. Metz, M. Mezger, O. Schneider and H.-J. Schulze in T. Skotheim (ed.), *Handbook on Conducting Polymers*, Marcel Dekker, New York 1985.
2. U. Keppeler and M. Hanack, *Chem. Ber.*, **119**, 3363 (1986).
3. M. Hanack, U. Keppeler and H.-J. Schulze, *Synth. Met.*, **20**, 347 (1987).
4. B. N. Diel, T. Inabe, K. K. Jaggi, J. W. Lyding, O. Schneider, M. Hanack, C. R. Kannewurf, T. J. Marks and C. H. Schwartz, *J. Am. Chem. Soc.*, **106**, 3207 (1984).
5. M.-H. Whangbo and K. R. Stewart, *Isr. J. Chem.*, **23**, 133 (1983).
6. T. Inabe, J. G. Gaudiello, M. K. Moguel, J. W. Lyding, R. L. Burton, W. J. McCarthy, C. R. Kannewurf and T. J. Marks, *J. Am. Chem. Soc.*, **108**, 7595 (1986).
7. M. Hanack and A. Leverenz, *Synth. Met.*, **22**, 9 (1987).
8. S. Deger and M. Hanack, *Isr. J. Chem.*, **27**, 347 (1986). M. Rein and M. Hanack, unpublished.
9. U. Keppeler, S. Deger, A. Lange, and M. Hanack, *Angew. Chem.*, **99**, 349 (1987).
10. E. Canadell and S. Alvarez, *Inorg. Chem.*, **23**, 573 (1984).
11. J. Metz and M. Hanack, *J. Am. Chem. Soc.*, **105**, 828 (1983).
12. M. Hanack and C. Hedtmann-Rein, *Z. Naturforsch.*, **40b**, 1087 (1985).
13. M. Hanack and C. Hedtmann-Rein, *Inorg. Chem.*, **26**, 2649 (1987).