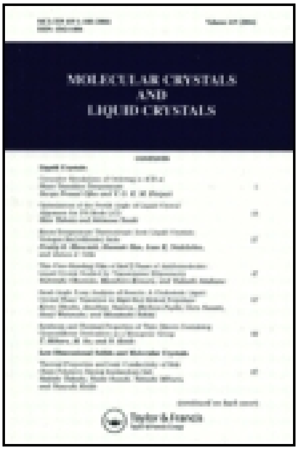

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: Carola Hedtmann-rein , Uwe Keppeler , Xaver Münz & Michael Hanack (1985): Doped and Nondoped Polymeric Bridged Macrocyclic Transition Metal Complexes, Molecular Crystals and Liquid Crystals, 118:1, 361-364

To link to this article: http://dx.doi.org/10.1080/00268948508076241

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 361-364
0026-8941/85/1184-0361/$10.00/0

Printed in the United States of America

DOPED AND NONDOPED POLYMERIC BRIDGED MACROCYCLIC TRANSITION METAL COMPLEXES

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Abstract Polymeric bridged macrocyclic transition metal complexes are prepared and characterized. Conductivities of doped and nondoped species are given.

INTRODUCTION

Macrocyclic transition metal complexes $\boxed{M}$ can be linked together by linear bridging ligands L containing delocalizable π-electrons to form a polymeric stacked arrangement (Fig. 1).[1]

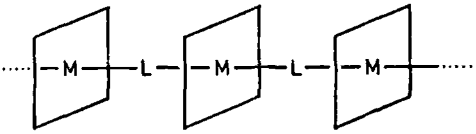

FIGURE 1 Polymeric bridged macrocyclic transition metal complexes.

The band structure of stacked metal phthalocyanines $[PcML]_n$ can be altered by changing the bridging ligand L. The band gap can depend, in addition to the central metal atom on the bridging ligand.[2]

DOPED POLYMERS CONTAINING COORDINATING BRIDGING LIGANDS

In addition to the already reported $[PcFe(pyz)]_n$,[3] the PcFe-polymers with coordinating ligands such as $[PcFe(dib)]_n$, $[Me_8PcFe(dib)]_n$, $[Cl_{16}PcFe(dib)]_n$, $[PcFe(Me_4dib)]_n$ and $[PcFe(Cl_4dib]_n$[4] also are easily dopable with iodine yielding $[R_mPcFe(X_4dib)I_y]_n$ (Table I). They can be synthesized either by treating the suspended undoped polymer with iodine in benzene (a) or by simultaneous doping and polymerisation in chlorobenzene (b):

$$\text{(a)}\ [R_mPcFe(X_4dib)]_n + n\ y/2\ I_2 \xrightarrow{\text{benzene}} [R_mPcFe(X_4dib)I_y]_n$$

$$\text{(b)}\ n\ R_mPcFe + n\ X_4dib + n\ y/2\ I_2 \xrightarrow[\text{benzene}]{\text{chloro-}} [R_mPcFe(X_4dib)I_y]_n$$

Only $[Cl_{16}PcFe(dib)]_n$ is not dopable. The compositions of the doped polymers were established by microanalysis. They are stable up to 100°C. Above this temperature iodine is lost.

Mössbauer spectra of the doped polymers prove, that the polymeric structure is preserved. Resonance Raman spectra show, that the counterions are I_3^- and I_5^-. The NC-valence frequencies in the IR-spectra shift to higher energies with increasing iodine doping level, which indicates an oxidation of the macrocycle. The doping process is reversible; iodine can be removed by extraction with benzene. The dark conductivity increases with the doping level.

Despite the rather large interplanar phthalocyanine-phthalocyanine spacings in a single $[R_mPcFe(X_4dib)I_y]_n$ chain (∿1190 ppm) the highest conductivities of polycrystalline samples are comparable to those of polycrystalline $[PcMOI_y]_n$ specimens (interring spacing ∿330 ppm).[5] So all evidence points, as in the case of the pyrazine compounds,[3] to an iodine oxidation process which does not produce the type of π-electron band structure found in the partially oxidized group IV $[PcMOI_y]_n$-polymers.

TABLE I IR-data, pressed-powder electrical conductivity data at room temperature and activation energies of polymers doped by the method of eq.(a).

	$\nu_{NC}[cm^{-1}]$	$\sigma_{RT}[S/cm]$[a]	Ea[eV][b]
$[PcFe(dib)]_n$	2102	$2\cdot10^{-5}$	0.25
$[PcFe(dib)I_{1.4}]_n$	2110	$7\cdot10^{-3}$	0.14
$[PcFe(dib)I_{3.0}]_n$	2124	$3\cdot10^{-2}$	0.10
$[Me_8PcFe(dib)]_n$	2098	$4\cdot10^{-4}$	0.22
$[Me_8PcFe(dib)I_{2.7}]_n$	2098,2122sh	$1\cdot10^{-2}$	0.12
$[Me_8PcFe(dib)I_{3.6}]_n$	2098,2126sh	$3\cdot10^{-2}$	0.11
$[Cl_{16}PcFe(dib)]_n$	2122	$3\cdot10^{-11}$	-
$[PcFe(Me_4dib)]_n$	2092	$1\cdot10^{-7}$	-
$[PcFe(Me_4dib)I_{1.5}]_n$	2100	$1\cdot10^{-3}$	0.17
$[PcFe(Me_4dib)I_{3.0}]_n$	2112	$2\cdot10^{-2}$	0.14
$[PcFe(Cl_4dib)]_n$	2058	$4\cdot10^{-6}$	-
$[PcFe(Cl_4dib)I_{0.5}]_n$	2067	$6\cdot10^{-4}$	0.21
$[PcFe(Cl_4dib)I_{2.6}]_n$	2073	$6\cdot10^{-2}$	0.13

[a] Four-probe technique (van der Pauw) at 10^8 Pa (1 kbar).

[b] Calculated from $\sigma_T = \sigma_o \cdot e^{-(E_a/kT)}$ for data from 96-300 K.

NONDOPED CYANO-BRIDGED POLYMERS

Polymers which already show without doping the same conductivities as the doped polymers described before are the μ-cyano(phthalocyaninato)metal compounds (Table II).

A general route leading to the cyano-bridged polymers is the removal of alkalimetal cyanide from alkalimetal-dicyano(phthalocyaninto)-metal(III) complexes $M'PcM(CN)_2$ (M' = Na,K; M = Cr,Mn, Fe,Co). The polymers were characterized by IR and FIR spectroscopy, magnetic measurements, thermogravimetrical and microanalytical analyses and chemical decomposition.[6]

TABLE II IR-data, pressed-powder electrical conductivity data at room temperature and activation energies.

	ν_{CN} [cm^{-1}][c]	σ_{RT} [S/cm][a]	Ea[eV][b]	Ref.
$[PcCoCN]_n$	2158 (2130)	$2 \cdot 10^{-2}$	0.1	6a,6c
$[PcFeCN]_n$	2133 (2112)	$6 \cdot 10^{-3}$	0.1	6b,6c
$[PcMnCN]_n$	2133 (2114)	$1 \cdot 10^{-5}$	-	6c
$[PcCrCN]_n$	2150 (2133)	$3 \cdot 10^{-6}$	-	6c
$[PcRhCN]_n$	2160 (2130)	$1 \cdot 10^{-4}$	-	-
$[TBPCoCN]_n$	2138 (2121)	$4 \cdot 10^{-2}$	0.2	-

[a],[b] See Table I.

[c] Values in parenthesis show the CN-valence frequencies for $M'PcM(CN)_2$-complexes.

As first example of a cyano-bridged polymer containing a 4d-transition-metal $[PcRhCN]_n$ was prepared. In addition to phthalocyanine, tetrabenzoporphyrine also can be used as macrocycle, shown by the synthesis of $[TBPCoCN]_n$ (Table II). The increase of CN-valence-frequencies going from $M'PcM(CN)_2$ to the polymer (Table II) in all cases is an evidence for the cyano bridged polymers.

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4. Abbreviations: R_mPcFe = peripherally substituted phthalocyaninatoiron(II)-macrocycle: m = 8, R = H, Me; m = 16, R = Cl. dib = 1,4-diisocyanobenzene; X_4dib = 2,3,5,6-substituted dib: X = Me,Cl.
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