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Synthesis and Electrical Conductive Properties of Polymeric Metalloporphyrins

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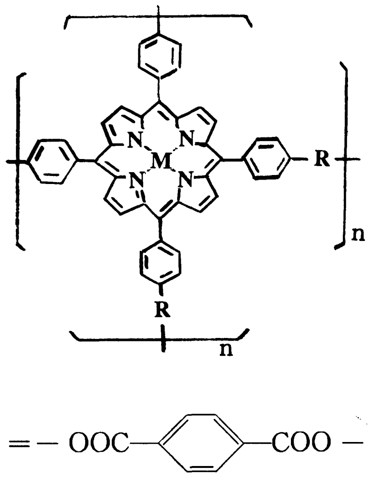
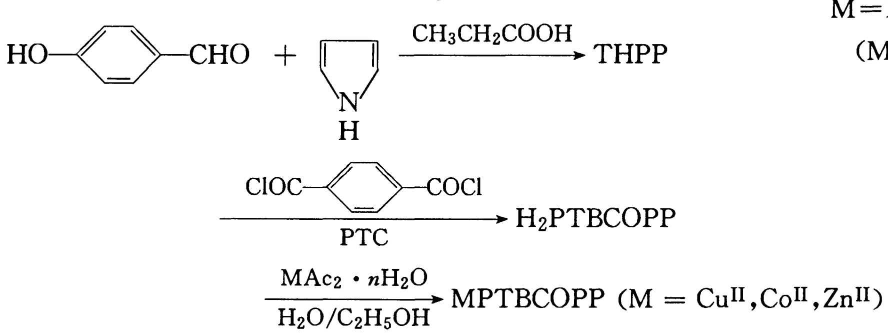
The polymeric porphyrin film has been prepared by interfacial polymerization of tetrakis (4-hydroxy phenyl) porphyrin (THPP) with terephthalyl chloride. The spectra and electrical properties of its complexes with transition metal (Cu, Co, Zn) have been studied. The polymer exhibits semi-conducting property ($\sigma_{RT}=4.83\times10^{-4}$ S · cm^{-1}) after doping with iodine.

During the past several years great progress has been made in the field of organic electrical conductive materials based on bridged macrocyclic metal complexes.[1] Axially bridged porphyrinic metal complexes, which are linked by linear bridging ligands containing delocalizable π-electrons to form one-dimensional system have high conductivity.[2-4] However, so far very few investigation[5] have been done concerning the preparation and the property of the porphyrinic sheet polymer. In this paper, the thin polymeric film of porphyrin (H_2PTBCOPP) which is linked by terephthalate to form two-dimensional arrangements and its complexes with copper, cobalt or zinc have been synthesized and their conductivities have been studied.



M = H_2, Cu, Co, Zn
(MPTBCOPP)

The polymeric porphyrin and its transition metal complexes are synthesized via the following route:



Crude products are washed several times respectively with water, alcohol and chloroform. Yields of 80% or better of MPTBCOPP are obtained after drying. The visible spectrum of ligand (H_2PTBCOPPO) λ_{max} (nm): 422.7 (Soret), 518.4, 555.5, 594.9, 650.9. The number of the absorption peak of the metal complexes decreases compared with the ligand because of increasing symmetry of porphine ring. IR spectra (KBr): the weak absorptions of N—H stretching vibration at 3312 cm^{-1} and δ_{NH} near 965 cm^{-1} for the ligand disappear in the complexes. The strong absorption near 1000 cm^{-1} appears to be a characteristic absorption of all metalloporphyrins, and $\gamma_{C=O}$ appears near 1734 cm^{-1}. Anal. Found (calcd. for H_2PTBCOPP • $4H_2O$): C, 71.02(71.29); H, 3.85(4.16); N, 4.79(5.54). The polymeric film of porphyrin and its metal complexes have also been characterized by thermal analysis, scanning electron microscope and fluorescence spectra.

Two-point probe conductivity measurment is performed on compacted disks of the pristine and iodine-doped polymers. The conductivity of each undoped polymer is less than 10×10^{-9} (S • cm^{-1}), and other results are summerized in the table 1. Iodine-doped ZnPTBCOPP shows an electrical conductivity of 4.83×10^{-4} (S • cm^{-1}), which is 5 orders of magnitude greater than ZnPTBCOPP. The conductivity of doped polymers increases in the order H_2PTBCOPP: I_2 < CuPTBCOPP: I_2 — CoPTBCOPP: I_2 < ZnPTBCOPP: I_2. The doped polymers are air-stable.

Table 1. Conductivity data of iodine-doped polymeric porphyrins

Compound	Dopant	Molar ratio	σ_{RT} (S • cm^{-1})
H_2PTBCOPP	I_2	1 : 1	4.63×10^{-6}
CuPTBCOPP	I_2	1 : 1	4.05×10^{-5}
CoPTBCOPP	I_2	1 : 1	5.08×10^{-5}
ZnPTBCOPP	I_2	1 : 1	4.83×10^{-4}

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