

## Synthesis and Electrical Conductive Properties of Polymeric Metalloporphyrins

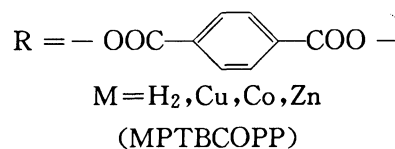
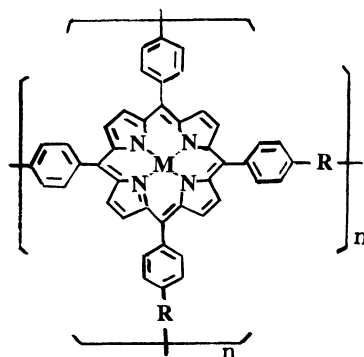
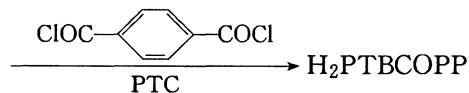
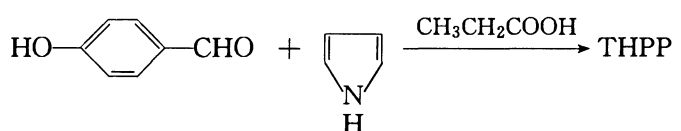
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The polymeric porphyrin film has been prepared by interfacial polymerization of tetrakis (4-hydroxy phenyl) porphyrin (THPP) with terephthalyl chloride. The spectra and electrical properties of its complexes with transition metal (Cu, Co, Zn) have been studied. The polymer exhibits semi-conducting property ( $\sigma_{RT} = 4.83 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ ) 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.<sup>1)</sup> Axially bridged porphyrinic metal complexes, which are linked by linear bridging ligands containing delocalizable  $\pi$ -electrons to form one-dimensional system have high conductivity.<sup>2-4)</sup> However, so far very few investigation<sup>5)</sup> have been done concerning the preparation and the property of the porphyrinic sheet polymer. In this paper, the thin polymeric film of porphyrin ( $\text{H}_2\text{PTBCOPP}$ ) 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.

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 ( $\text{H}_2\text{PTBCOPP}$ )  $\lambda_{\text{max}}$  (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  $3312\text{ cm}^{-1}$  and  $\delta_{\text{NH}}$  near  $965\text{ cm}^{-1}$  for the ligand disappear in the complexes. The strong absorption near  $1000\text{ cm}^{-1}$  appears to be a characteristic absorption of all metalloporphyrins, and  $\nu_{\text{C=O}}$  appears near  $1734\text{ cm}^{-1}$ . Anal. Found (calcd. for  $\text{H}_2\text{PTBCOPP} \cdot 4\text{H}_2\text{O}$ ): 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 measurement is performed on compacted disks of the pristine and iodine-doped polymers. The conductivity of each undoped polymer is less than  $10 \times 10^{-9} (\text{S} \cdot \text{cm}^{-1})$ , and other results are summarized in the table 1. Iodine-doped ZnPTBCOPP shows an electrical conductivity of  $4.83 \times 10^{-4} (\text{S} \cdot \text{cm}^{-1})$ , which is 5 orders of magnitude greater than ZnPTBCOPP. The conductivity of doped polymers increases in the order  $\text{H}_2\text{PTBCOPP}:\text{I}_2 < \text{CuPTBCOPP}:\text{I}_2 < \text{CoPTBCOPP}:\text{I}_2 < \text{ZnPTBCOPP}:\text{I}_2$ . The doped polymers are air-stable.

Table 1. Conductivity data of iodine-doped polymeric porphyrins

| Compound                   | Dopant       | Molar ratio | $\sigma_{\text{RT}} (\text{S} \cdot \text{cm}^{-1})$ |
|----------------------------|--------------|-------------|------------------------------------------------------|
| $\text{H}_2\text{PTBCOPP}$ | $\text{I}_2$ | 1 : 1       | $4.63 \times 10^{-6}$                                |
| $\text{CuPTBCOPP}$         | $\text{I}_2$ | 1 : 1       | $4.05 \times 10^{-5}$                                |
| $\text{CoPTBCOPP}$         | $\text{I}_2$ | 1 : 1       | $5.08 \times 10^{-5}$                                |
| $\text{ZnPTBCOPP}$         | $\text{I}_2$ | 1 : 1       | $4.83 \times 10^{-4}$                                |

## References

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