

# Porphine-Based Electroactive Materials

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The general goal of our studies has been to synthesize homopolymers on the basis of (metallo)porphines, i.e. non-substituted (metallo)porphyrins. Several years ago [1] we discovered that the electrooxidation of the Mg(II) porphine (MgP, Fig. 1a) in acetonitrile (AN) solution resulted in an electroactive polymer film on the electrode surface. It has been established [1-4] that the film is composed of poly(Mg(II)porphine) of type I (pMgP-I, Fig. 1b, M = Mg(II)), i.e. of polymer chains where MgP units are linked by bonds in *meso*-positions of the macrocycle. This system represented the very first example of a homopolymer composed solely of porphyrin units.

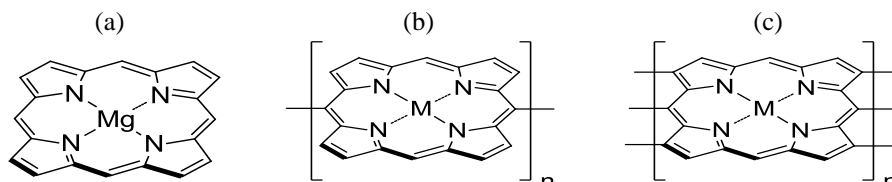


Fig. 1 Starting monomer, Mg(II) porphine (a). Poly(metallo)porphines of type I (b) and of type II (c). Central ion(s), M, may be Mg(II), 2 H<sup>+</sup>, Zn(II) or Co(II).

As we demonstrated later [5] such a molecular structure, pMgP-I, is formed only for a very low oxidation potentials (e.g. lower than 0.4 V vs. Ag/0.01 M AgNO<sub>3</sub> in AN for the potentiostatic regime). Materials with different properties are formed for higher oxidation potentials. Moreover, pMgP-I polymer is subjected an oxidative transformation in contact with a monomer-free AN solution if the potential is kept (or cycled) within the range over 0.4 V, the transformation rate increasing for higher potentials. It results in generation of quite a different molecular structure, pMgP-II (Fig. 1c, M = Mg(II)) where the neighboring porphine units are linked by one *meso-meso* bond and two *beta-beta* bonds.

More recently, this poly(Mg(II)porphine) of type I, pMgP-I, has been used to synthesize a novel series of porphine based polymers [6-8]. First, "free-base polyporphine of type I", pH<sub>2</sub>P-I (Fig.1b, M = 2H<sup>+</sup>), was obtained by means of acid treatment. Then, the ion-exchange method was applied to transform this metal-free polymer, pH<sub>2</sub>P-I, into novel polymetalloporphines of type I, pZnP-I and pCoP-I, having the same molecular structure (Fig.1b) but with M = Zn(II) or Co(II), respectively.

All these poly(metallo)porphines of type I, pMP-I (Fig.1b), have been transformed [6-8] into corresponding poly(metallo)porphines of type II, pMP-II (Fig.1c), M = Mg(II), 2 H<sup>+</sup>, Zn(II) or Co(II) by electrochemical oxidation of the polymer film.

All these polymers of type I and II demonstrate a pronounced electroactivity. The polymers of type I may be in a neutral (insulating) or in a positively or negatively charged (conducting) state, depending on the electrode potential. On the contrary, all polymers of type II show a strong redox response and a high electronic conductivity within the whole potential range of their stability (over 3 V wide).

Polyporphines of Co(II) have revealed a high electrocatalytic effect for oxygen reduction reaction, its potential being close to that for Pt electrode in both acidic and alkali solutions.

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