

Manuscript Number : IC049641B

Supporting information

Organic cross-linked electropolymers as supported oxidation catalysts : poly(tetra-9,9'-spirobifluorenylporphyrinmanganese) films

Cyril Poriel^a, Yann Ferrand^a, Paul Le Maux^a, Joëlle Rault-Berthelot^{b*} and Gérard Simonneaux^{a*}

^aLaboratoire de Chimie Organométallique et Biologique, UMR CNRS 6509 and
^bLaboratoire d'Electrochimie Moléculaire et Macromoléculaire, UMR CNRS 6510,
Université de Rennes 1, 35042 Rennes cedex, France.

Electrochemistry

Microcoulometric measurements were performed during the polymerization reaction and then, directly on the thin deposits. The charge used for the polymerisation reaction was two electrons for the porphyrin oxidation and more than one electron for each position of the carbon-carbon coupling due to oxidation and doping. These values were compared to the charge consumed during the oxidation of the film. In this case, two electrons for metalloporphyrin oxidation and one electron for the doping of each polymerised fluorene units were detected. Comparison of the two experiments shows that both fluorenyl units of each spirofluorene are involved in the polymerisation reaction.

The comparison of the intensity of the E1 and E3 waves gives information on the number of spirobifluorene units being oxidized in the different monomers taking into account that the E1 wave corresponds to the monoelectronic oxidation of the porphyrin. Such a comparison shows

that the number of the spirobifluorene units oxidized in (TSP)H₂ is more important than in the case of (MSP)H₂. The ratio of the intensity of E³ by the intensity of E¹ is of 5.4 in the case of (MSP)H₂ (not shown) and of 10 in the case of (TSP)H₂. These values are not too far from the theoretical values of 5 and 14 respectively. Taking into account experimental mistakes, one observes that in the case of (MSP)H₂, the three carbon atoms are oxidized whereas oxidation of (TSP)H₂ concerns only 8 carbon atoms instead of 12 showing probably steric limitations. In fine, electroactive polymers are formed through carbon-carbon linkages between spirobifluorene units. As soon as the polymer is obtained under its p-doped state, positive charges are mobile along the aromatic chain and anions (PF₆⁻) are inserted in the polymer for neutrality. Electrodeposition is also performed along potentiostatic oxidation at E more positive than the potential at which occurs the oxidation of the fluorenyl units (E > 1.3 V). The polymeric film formed on the platinum electrode is conductive with a structure varying with the number of spirobifluorenyl units on the macrocycle ring (vide infra), the potential of formation and the thickness of the deposit.

Characterization of the polymer film

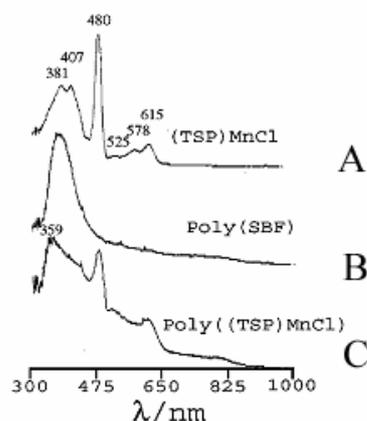


Figure S1. UV-Vis spectra of (TSP)Mn(Cl), poly(SBF) and poly((TSP)Mn(Cl)).

Figure S1 shows the UV-visible spectra of (TSP)MnCl and neutral poly((TSP)MnCl). The electronic spectrum of the monomer in solution in CH₂Cl₂ (Figure 3A) presents several absorption bands at 381, 407, 525, 578 and 615 nm and a main absorption band at 480 nm. The electronic spectrum of neutral poly((TSP)MnCl) obtained as a thin film on a platinum

surface (acting also as reflector for optical measurements) by anodic oxidation of a solution of (TSP)MnCl at 1.55 V and then undoping at 0.0V is presented in Figure S1. Two main bands are observed at 480 and 615 nm, with an additional absorption band which maximum is at 360 nm and fits with the main absorption of the poly(spirobifluorene) (Fig. 3B). This relatively large band hides the bands observed at 381 and 407 nm in the monomer.