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Electrochemically synthesized superoxide radical anion as an activator of electrodeposition of polyporphyrin films

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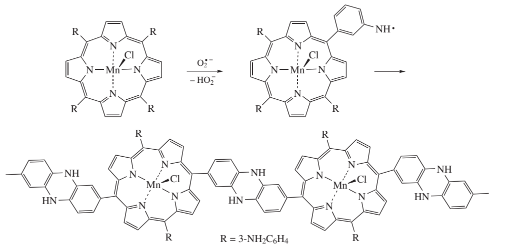
The electrochemical deposition of polyporphyrin films was activated by the superoxide radical anion generated in solution upon electrochemical reduction of dissolved oxygen.



Elaboration of new functional materials is among the prior directions in the development of society, technology, and chemical science. The principles of porphyrin-based materials formation are discussed by many authors.[1–5] Film materials based on porphyrins may be used as efficient catalysts,[6,7] active elements in sensor devices,[8] organic transistors,[9] light emitting diodes,[10] nonlinear optical converters,[11] and electrochromic devices.[12] Among the various methods for creating porphyrin films,[13–15] electrochemical polymerization deserves attention as it allows one to obtain well reproducible films using simple and inexpensive facilities. By varying the deposition mode, composition of the electrolyte, temperature and other factors, it is possible to alter the characteristics of the resulting material in a broad range.[16,17] The nature of the solvent used in the electrodeposition affects the adsorption of electroactive components on the electrode surface, transportation of reagents, their energy, and sometimes hinders the formation of the film on the electrode. As our experiments have revealed, the deposition rate of polyporphyrin films in degassed DMSO is very low.[18]

Here, we have shown that efficient electrodeposition of polyporphyrin films from trichloro[5,10,15,20-tetrakis(*m*-aminophenyl)porphyrin]manganese(III) [MnClT(*m*-NH$_2$Ph)P] in DMSO solutions is possible in the presence of dissolved oxygen.

The films were deposited by potential cycling in the range corresponding to the electrochemical window of DMSO for the working electrode material selected (Figure 1).[†]

The redox behaviour of MnClT(*m*-NH$_2$Ph)P in the degassed solution [Figure 1(*a*), curve *1*] includes a quasi-reversible valence change of the central metal ion Mn^{III}/Mn^{II} under potential of about 0 V *vs.* the Ag/Ag$^+$ reference quasi-electrode. Two processes of macrocycle reduction are observed in the negative potential region, electrooxidation of the macrocycle is observed in the positive potential region. Repeated potential cycling (25 cycles) in degassed porphyrin solutions did not considerably change the

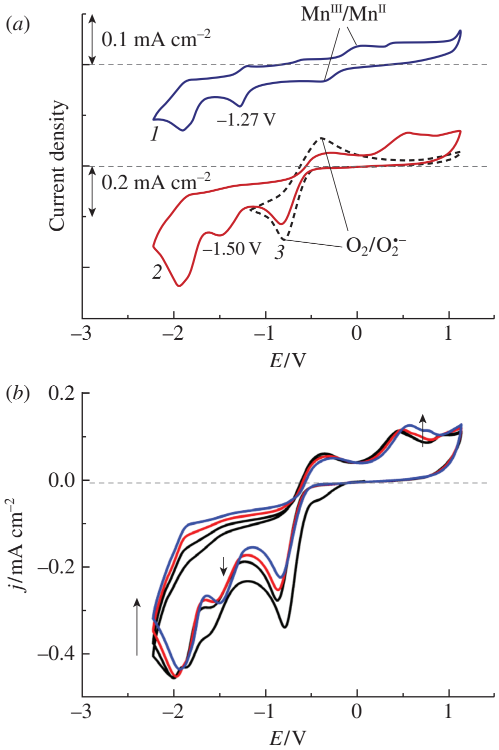


Figure 1 Electrochemical responses on glassy carbon electrode in DMSO solutions (*a*) of MnClT(*m*-NH$_2$Ph)P in (*1*) degassed solution and (*2*) oxygen-saturated one, (*3*) of oxygen in the absence of MnClT(*m*-NH$_2$Ph)P; (*b*) of MnClT(*m*-NH$_2$Ph)P in oxygen-saturated solution during film deposition. Tendency in change of CV curve is indicated by arrows, scan rate was 20 mV s^{-1}.

[†] Electrochemical deposition of films was carried out from freshly prepared 1 mM solution of MnClT(*m*-NH$_2$Ph)P in DMSO. Additional purification (DMSO >99.5%, Aldrich) was performed by zone melting. According to the Fischer method, the residual water content was below 0.02%. Pure tetrabutylammonium perchlorate (>98.0 %, Aldrich) was recrystallized from ethanol and used as the background electrolyte (0.02 M). Electrochemical studies and film deposition were performed using an SP-150 potentiostat (Bio-Logic Science Instruments).

Table 1 Redox processes of MnClT(*m*-NH_2Ph)P and its oxo complexes in DMSO on glassy carbon. The potentials were measured relative to an Ag/Ag^+ reference quasi-electrode, scan rate of 20 mV s^{-1}.

Complex	Red_4/V	Red_3/V	Red_2/V	Red_1/V	Red–Ox/V	Ox_1/V	Ox_2/V
MnClT(*m*-NH_2Ph)P in DMSO	–/–	–/–1.93	–1.17/–1.27	–0.54/–0.63 (low intensity)	0.05/–0.34 Mn^{III}/Mn^{II}	0.47/–	–/–
Oxo complexes		–/–1.95	–/–1.50	–/–	–0.28/–0.82 $O_2/O_2^{\bullet-}$	0.56/–	0.76/– (low intensity)

electrochemical responses. No polyporphyrin film was revealed on the surface of the working electrode after its withdrawal from the cell.

CV signal recorded in oxygen-saturated DMSO solution [Figure 1(*a*), curve *3*] shows that one-electron electroreduction of oxygen occurs to give the superoxide radical anion ($O_2^{\bullet-}$):[19]

$$O_2 + e^- \rightarrow O_2^{\bullet-} \quad (1)$$

According to Nicholson's formula,[20] the ratio of the limiting anodic peak current to the cathodic one for the $O_2/O_2^{\bullet-}$ redox couple on glassy carbon is 0.77, indicating that $O_2^{\bullet-}$ participates in homogeneous or heterogeneous chemical reactions. The similar conclusion was made by us previously in a discussion of the electrochemical behaviour of the $O_2/O_2^{\bullet-}$ redox couple on Pt electrode in DMSO.[21] The electrochemical response of $O_2^{\bullet-}$ reduction may be affected by (i) the disproportionation of the superoxide radical anion [equation (2)],[22] (ii) its reaction with water [equation (3)],[23] (iii) reactions of the superoxide radical anion and its transformation products with the solvent[24] [equations (4), (5)]:

$$2\,O_2^{\bullet-} \rightarrow O_2 + O_2^{2-},\ k = 4.38\times10^3\ \text{mol}^{-1}\ \text{s}^{-1}\ (25\,^\circ\text{C, DMSO}) \quad (2)$$

$$2\,O_2^{\bullet-} + H_2O \rightarrow HO_2^- + OH^- + O_2, \quad (3)$$
$$k = (0.5\text{–}3.5)\times10^{-3}\ \text{mol}^{-1}\ \text{s}^{-1}\ (25\,^\circ\text{C, DMF})$$

$$Me_2SO + O_2^{\bullet-} \rightarrow Me^{\bullet} + MeS(O)OO^- \quad (4)$$

$$Me_2SO + HO_2^{\bullet} \rightarrow H_2O_2 + {}^{\bullet}CH_2(Me)SO \quad (5)$$

The rates of reactions (2)–(4) are rather low, which allows one to prepare long-living superoxide radical anions electrochemically in aprotic solvents[25] and study their reactions with porphyrins.[21,26–28]

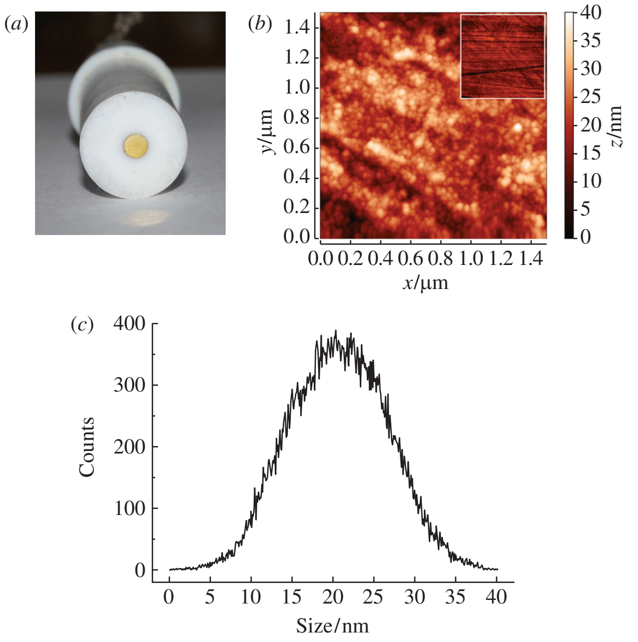


Figure 2 The polyporphyrin film deposited from a MnClT(*m*-NH_2Ph)P solution in DMSO on Pt electrode: (*a*) photo, (*b*) AFM image (Solver 47 Pro, NT-MDT) and bare Pt (inset), (*c*) roughness distribution.

Once MnClT(*m*-NH_2Ph)P solution is saturated with oxygen, the redox responses of the central ion in the Mn^{III}/Mn^{II} metal complex disappear in the CV curves [Figure 1(*a*), curve *2*], and the macrocycle oxidation and reduction potentials transmute. These changes may be explained by the formation of oxo complexes, where the metal acquires a stable oxidation state. The potentials of electrochemical response of MnClT(*m*-NH_2Ph)P and its oxo complexes are given in Table 1.

During potential cycling in oxygen-saturated MnClT(*m*-NH_2Ph)P solution in DMSO, the shape of CV curves changes from one cycle to another [Figure 1(*b*)]. This is accompanied by the formation of a film on the working electrode surface. The appearance of the polyporphyrin film deposited from a MnClT(*m*-NH_2Ph)P solution in DMSO is illustrated by Figure 2(*a*). The resulting film is shiny with a golden shade, strongly adheres to the working electrode surface, and is insoluble in water, ethanol, and dichloromethane. According to atomic force microscopy data, the film is formed of round globules with similar sizes and with lateral sizes ranging within 20–50 nm [Figure 2(*b*)]. The roughness distribution is close to Gaussian one [Figure 2(*c*)].

The spectral characteristics of the polyporphyrin films deposited on transparent indium–tin oxide (ITO) were studied (Figure 3). The absorption spectrum of the resulting film (curve *2*) contains the main bands of the starting MnClT(*m*-NH_2Ph)P solution (curve *1*).

The Soret band (~420 nm), charge transfer band (~473 nm) and Q-bands (~572 and ~606 nm) shift bathochromically and broaden in the film spectrum. Retention of the charge transfer band and Q-bands in the spectrum indicates the presence of the intact porphyrin metal complex in the film. A broadening of bands and a bathochromic shift were observed upon formation of a linear porphyrin polymer.[29] The absorption band at ~770 nm in the spectra of films may be due to protonation of porphyrin moieties.[30]

Activation of the electrochemical deposition of a polyporphyrin film in the presence of oxygen may be explained by electrochemical synthesis of superoxide radical anion ($O_2^{\bullet-}$), whose affinities to a hydrogen atom and to a proton are high. Reactions of $O_2^{\bullet-}$ with saturated tetraphenylporphyrins result in porphyrin radicals.[21,26–28] Recombination of the latter affords a porphyrin dimer (Scheme 1). The significant decrease in the reactivity of

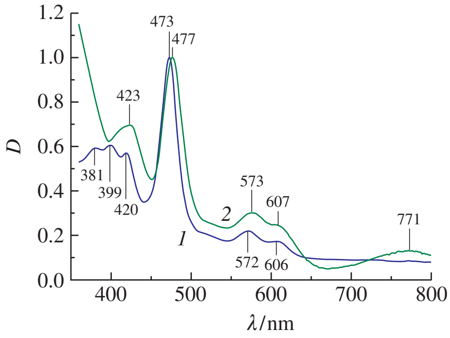
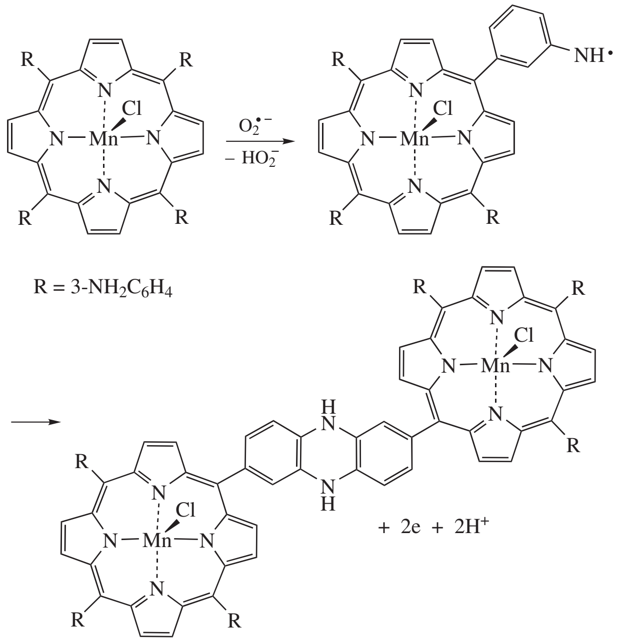


Figure 3 Absorption spectra of (*1*) MnClT(*m*-NH_2Ph)P solution in DMSO and (*2*) polyporphyrin film deposited. The spectrum was normalized relative to the charge transfer band (*ca.* 475 nm).



Scheme 1 The porphyrin radical generation upon the action of the superoxide radical anion and its recombination, which gives rise to the dimeric (then polymeric) chain.

aminophenyl side groups after porphyrin dimer formation is not described in the literature. Therefore, we can suggest the high probability of interaction between the superoxide and the dimeric form of aminophenyl porphyrin. Dimeric form of radical leads to trimers and tetramers *via* radical recombination. In this way, increasing in chain length should be expected due to recombination of radicals produced by interaction of superoxide with mono-, di-, tri-, tetra- and, probably, oligo- or polymer forms of porphyrin. The reaction of $O_2^{\bullet-}$ with protons gives the $HO_2^{\bullet}$ radical, which is a strong oxidant and can give rise to the chemical oxidation of side groups and further evolution of the polymerization process.

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