Electrochimica Acta 56 (2011) 10454–10463

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Easy methods for the electropolymerization of porphyrins based on the oxidation of the macrocycles

Delphine Schaming[a], Iftikhar Ahmed[a], Jian Hao[a], Valérie Alain-Rizzo[b], Rana Farha[c,d], Michel Goldmann[c,e], Hualong Xu[f], Alain Giraudeau[g], Pierre Audebert[b], Laurent Ruhlmann[a,*]

[a] Laboratoire de Chimie Physique, Groupe TEMiC, UMR 8000 au CNRS, Université Paris-Sud (11), Bâtiment 349, 91405 Orsay, France
[b] Laboratoire de Photophysique et Photochimie Supramoléculaires et Macromoléculaires, UMR 8531 au CNRS, Ecole Normale Supérieure de Cachan, Bâtiment d'Alembert, 61 avenue du Président Wilson, 94235 Cachan, France
[c] Institut des NanoSciences de Paris, UMR 7588 au CNRS, Université Paris 6, 4 place Jussieu, Boîte courrier 840, 75252 Cedex 05 Paris, France
[d] Laboratoire d'Analyse et Contrôle des Systèmes Complexes – LACSC, ECE Paris Ecole d'Ingénieurs, 37 Quai de Grenelle, 75015 Paris, France
[e] Université Paris Descartes, 45 rue des Saint Pères, 75006 Paris, France
[f] Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials and Laboratory of Advanced Materials, Fudan University, Shanghai 200433, PR China
[g] Laboratoire d'Electrochimie et de Chimie-Physique du Corps Solide, UMR 7177 au CNRS, Université de Strasbourg, 4 rue Blaise Pascal, 67070 Strasbourg, France

ARTICLE INFO

Article history:
Received 12 November 2010
Received in revised form 16 February 2011
Accepted 16 February 2011
Available online 23 February 2011

Keywords:
Electropolymerization
Porphyrin
Pyridinium
Viologen
Tetrazine

ABSTRACT

Two different methods of electropolymerization of porphyrins have been investigated and compared. They consist in the nucleophilic attack of Lewis bases onto electrogenerated dications of octaethylporphyrins. In the first method, a nucleophilic group has been directly grafted onto the macrocycle (ZnOEP-*meso*-bpy$^+$), while in the second one, free di-nucleophilic compounds (Nu–Nu) have been used in presence of a non-substituted porphyrin (ZnOEP). The advantage of the second method is to easily modify the nature of the bridging spacer between the macrocycles. Characterizations of the polymer obtained from the second method in the case of dipyridinium-tetrazine spacer are presented.

1. Introduction

Oligomers and polymers of porphyrins have attracted a considerable attention these last decades because of their potential applications as molecular wires, nonlinear optical materials, electronic devices, potentiometric or amperometric sensors, solar energy transformation cells [1–6].

Different strategies allowing the formation of porphyrins polymers (principally coordination and covalent polymers) have been already described in the literature.

A first common method to polymerize porphyrins consists in the use of bridging ligands which can coordinate the metal center of metalloporphyrins. For instance, such coordination polymers have been obtained by coordination of nitrogenous ligands with ruthenium, osmium or iron porphyrins [7,8].

Nevertheless, more frequently, covalent polymers have been synthesized. They can be obtained either by classical chemical way or by electrochemical way. For example, several works have shown the possibility to obtain direct polymerization of porphyrins by *meso*–*meso* coupling. Indeed, Osuka et al. have proposed a method based on the chemical oxidation of zinc diarylporphyrins by $Ag^{I}PF_6$ [9,10], but a similar *meso*–*meso* coupled polymer has been also recently obtained by electrooxidation of the magnesium porphine at a potential corresponding to the first oxidation of the macrocycle [11].

However, more currently, the formation of covalent polymers relies on the use of porphyrins with polymerisable substituents attached on the ring periphery. For example, polymerization of thiophene-substituted porphyrins has been allowed by a chemical oxidation with iron(III) chloride [12].

Electrooxidation can be also performed to obtain polymers from substituted porphyrins. This electrochemical strategy has been initially developed by Macor and Spiro, who have polymerized porphyrins by coupling of electrogenerated radical vinyl substituents [13]. Afterwards, other methods of electropolymerization have

---

[*] Corresponding author. Tel.: +33 1 69 15 44 38; fax: +33 1 69 15 61 88.
E-mail address: laurent.ruhlmann@u-psud.fr (L. Ruhlmann).

0013-4686/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2011.02.064

been published, for example from amine, pyrrole or thiophene-substituted porphyrins [5,14–18].

The main advantage of the electrochemical polymerization lies in the non-manual addressing of polymers allowing formation of films with a good reproducibility and a controlled thickness. Electropolymerization is also an easy way to functionalize conductive surfaces with a great precision. Moreover, electropolymerization of porphyrins provides densely packed layers that facilitate the electron hopping process between macrocycles [19,20].

In this context, we have also previously developed a method of electropolymerization based on nucleophilic attacks of bipyridinium-substituted porphyrins onto electrogenerated porphyrin dications [21,22].

Even if electropolymerization can be considered as an easy process to obtain such porphyrins wires, this possibility is often counterbalanced by the complicated synthesis of the starting monomeric subunits bearing appropriate substituents. In order to overcome this issue, we have recently proposed an easier way for the electropolymerization of porphyrins, based on the oxidation of porphyrin rings without key electroactive substituent but in the presence of appropriate nucleophilic compounds in the solution [23]. Moreover, this strategy of polymerization allows to easily modulate the nature of the bridging spacer between the macrocycles. For instance, we can insert by this way compounds with photocatalytic properties (such as polyoxometalates) into the porphyrins chains [24].

In this paper, we propose in the first three parts a detailed comparison between our two previous described methods of electropolymerization, using either a bipyridinium-substituted porphyrin (named method A, see Fig. 1A) or a porphyrin without nucleophilic substituent in the presence of 4,4′-bipyridine (named method B, see Fig. 1B). In the last part, characterizations of the polymer obtained from the method B are presented in the case of the use of dipyridyl-tetrazine nucleophile.

2. Experimental

2.1. Chemicals

The zinc β-octaethylporphyrin (ZnOEP) and the 4,4′-bipyridine (bpy) were purchased from Sigma–Aldrich.

The zinc *meso*-bipyridinium-β-octaethylporphyrin (ZnOEP-*meso*-bpy$^+$, ClO_4^-) was synthesized and characterized as described previously by electrochemical oxidation of ZnOEP in the presence of an excess of bpy [21].

The 3,6-di(pyridin-4-yl)-*s*-tetrazine (py-Tz-py) was synthesized according to a published method [25]. UV–vis (1,2-$C_2H_4Cl_2$): λ_{max} (nm) (ε, $M^{-1}\,cm^{-1}$) 271 (25,000). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.96 (d, 4H, J = 4.8 Hz), 8.52 (d, 4H, J = 4.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 163.93 (Tz), 151.48 (Py), 138.79 (Py), 121.56 (Py).

2.2. Electropolymerizations

Electropolymerizations were carried out with a three-electrode system using a PARSTAT 2273 potentiostat. One-side indium tin oxide electrodes (ITO, Sigma–Aldrich, 8–12 Ω/square) were used as working electrodes. A platinum wire was used as auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). It was electrically connected to the solution by a junction bridge filled with CH_3CN containing 0.1 mol dm^{-3} of tetraethylammonium hexafluorophosphate (NEt_4PF_6).

For each polymer, 25 iterative scans were carried out. After electropolymerization, the working electrodes were washed in CH_3CN to remove traces of the conducting salt present on the deposited films.

2.2.1. Method A

The method A of electropolymerization was carried out under argon atmosphere in a 0.1 mol dm^{-3} solution of NEt_4PF_6 in 1,2-$C_2H_4Cl_2$ containing 2.5×10^{-4} mol dm^{-3} of ZnOEP-*meso*-bpy$^+$, ClO_4^-. Cyclic scans (0.2 V s^{-1}) of the working electrode were applied between −0.90 and +1.60 V/SCE.

2.2.2. Method B

The method B of electropolymerization was carried out as described above in the same medium and in the same conditions, but using 2.5×10^{-4} mol dm^{-3} of ZnOEP and 2.5×10^{-4} mol dm^{-3} of Nu–Nu (bpy or py-Tz-py) instead of the substituted porphyrin.

2.3. UV–visible spectroscopic measurements

UV–visible absorption spectra were recorded with a double beam Perkin Elmer Lambda 9 spectrophotometer.

2.4. Atomic force microscopy (AFM)

AFM was performed directly on the surface of the ITO electrode using a Dimension 3100 (Veeco) in the tapping mode under ambient conditions. Silicon cantilevers (Veeco probes) with a spring constant of 300 N m^{-1} and a resonance frequency in the range of 120–139 kHz were used. The scanning rate was 1.0 Hz.

2.5. X-ray photoelectron spectroscopy (XPS)

XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation ($h\nu$ = 1253.6 eV) or Al Kα radiation ($h\nu$ = 1486.6 eV). In general, the X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The pass energy was fixed at 23.50, 46.95 or 93.90 eV to ensure sufficient resolution and sensitivity. The base pressure of the analyzer chamber was about 5×10^{-8} Pa. The sample was directly pressed to a self-supported disk (10 mm × 10 mm) and mounted on a sample holder then transferred into the analyzer chamber. The global spectra (0–1100 eV) and the narrow spectra of all the elements with higher resolution were both recorded by using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated by using the residual carbon (C1s = 284.6 eV). The data analysis was carried out by using the RBD AugerScan 3.21 software provided by RBD Enterprises or XPSPeak4.1 provided by Raymund W.M. Kwok (The Chinese University of Hongkong, China).

3. Results and discussion

3.1. Two different ways of electropolymerization of porphyrins

The electrochemical properties of porphyrins are now well established. Indeed, it is well known that the oxidation of the π-ring of a porphyrin proceeds via two one-electron steps generating respectively the π-radical cation and the dication [1].

The reactivity of porphyrin π-radical cations and dications with nucleophilic compounds has been also well studied. Indeed, Dolphin and Felton have observed for the first time the reactivity of oxidized porphyrins with nucleophilic solvents [26]. Afterwards, several groups have studied the nucleophilic attack of nitrogenous, phosphorous or sulfurous nucleophiles (nitrite ion, pyridine, phosphine, thiocyanate, ...) onto π-radical cations in *meso*-position of β-octaethylporphyrins or in β-position of *meso*-tetraphenylporphyrins [27–30]. Nevertheless, the π-radical cations have been in most cases prepared by chemical ways, principally by oxidation of macrocycles with iodine.