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Electrochemical synthesis and properties of polyporphyrin films based on 5,10,15,20-tetra(4-pyridyl)porphyrin

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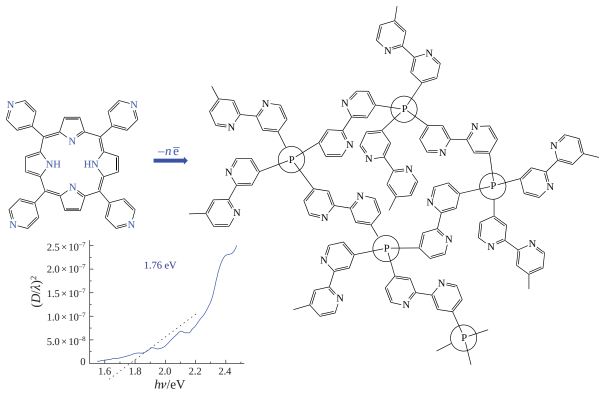
Polyporphyrin films were obtained by electrooxidative polymerization of 5,10,15,20-tetra(4-pyridyl)porphyrin which, in turn, was obtained by condensation of pyrrole with pyridine-4-carboxaldehyde. The polymer formation involved the side substituents, with the π-conjugated porphyrin platform being preserved. The obtained polyporphyrin forms an electroconductive coating possessing semiconductor properties with the band gap of 1.76 eV.



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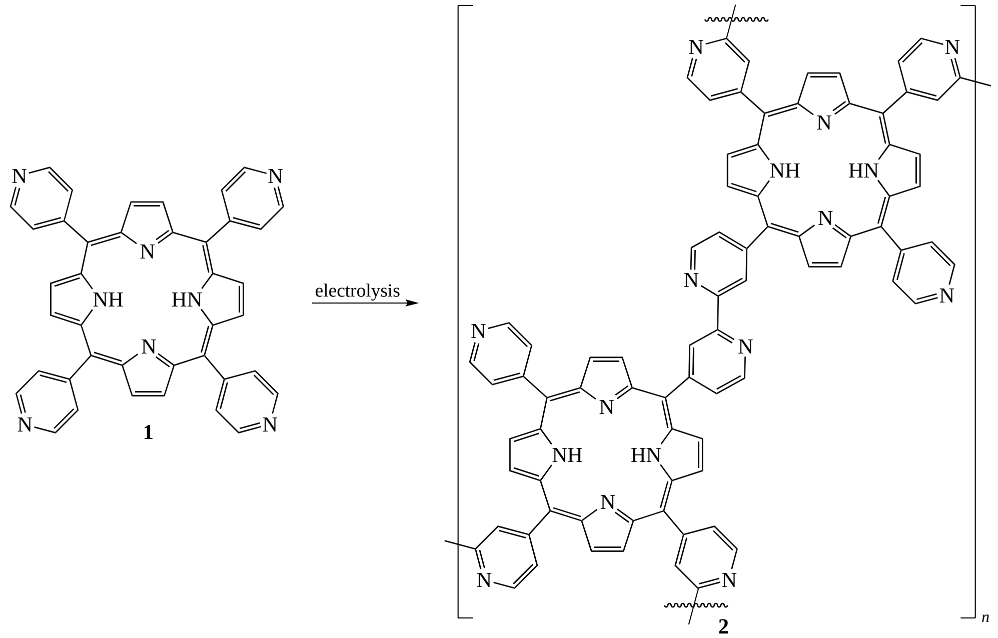
Porphyrins, tetrapyrrole macroheterocyclic compounds with a unique combination of physicochemical properties, are of great interest in materials science.[1–4] Natural and artificial porphyrin structures have a great engineering potential. Macroheterocyclic compounds catalyze oxidation or reduction reactions involving dioxygen,[5–7] nitric oxide,[8,9] alcohols[10] or thiols.[11] They facilitate photo-induced charge separation, and can be used in optics[12] and molecular electronics.[13] In practice, thin porphyrin films are normally deposited or adsorbed on a substrate.[14–16] One of the most common methods of conductive substrate surface modification with polymer films is electrochemical polymerization of a suitable monomer.[17,18] In this study, we synthesized 5,10,15,20-tetra(4-pyridyl)porphyrin $H_2T(4\text{-}Py)P$ **1** and then used it as the basis to obtain polyporphyrin films **2** by the electrochemical method (Scheme 1). A comprehensive study of the physicochemical properties of the prepared polyporphyrin films was conducted.



Scheme 1

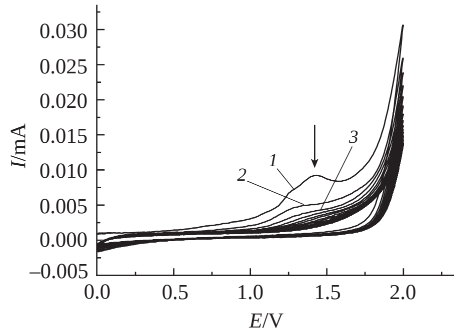


Figure 1 CV of $H_2T(4\text{-}Py)P$ **1** electropolymerization in dichloromethane on a GC electrode at a potential scan rate of 20 mV s^{-1} in the range from 0 to 2 V (*1, 2, 3* are the cycle numbers, total number of cycles is 20).

The electrosynthesis of polyporphyrin films was carried out in a three electrode electrochemical cell. A glassy carbon (GC) rod and ITO-coated glass plates were used as the working electrodes. The reference electrode was a saturated calomel electrode. The counter electrode was a platinum wire. The electropolymerization was performed from freshly made porphyrin solutions in dichloromethane with tetrabutylammonium perchlorate (0.02 mol dm^{-3}) as the supporting electrolyte. The porphyrin concentration in the solution was 10^{-3} mol dm^{-3}. The cyclic voltammograms (CVs) were recorded at the scan rate of 20 mV s^{-1}.

The CVs of the 5,10,15,20-tetra(4-pyridyl)porphyrin **1** solution in the region of positive potentials have a double peak corresponding to the irreversible porphyrin oxidation accompanied by polyporphyrin film deposition on the electrode (Figure 1). The prepared film evenly covers the electrode, is not washed off by the solvent used in the process, and is not erased by mechanical action. The first peak of the maximum corresponds to the pyridyl fragment oxidation and formation of π-radical cations and shows the onset of electropolymerization of **1**. We attributed the further current growth at a higher electrode anode potential value to the polymer chain increase. The second peak around 1.4 V is evidently associated with the polymer chain breakage and completion of the electropolymerization process (see Figure 1).

The UV-VIS spectrum of the poly-$H_2T(4\text{-}Py)P$ film **2** is similar to the porphyrin monomer **1** spectrum in the solution (Figure 2). The spectrum has a Soret band characteristic of porphyrins and four bands in the long-wave region. The Soret band of the polyporphyrin becomes broader and is shifted from 416 nm (the porphyrin monomer spectrum in the solution) to 426 nm. This Soret band shift to the longer wavelength region and broadening are associated with the polyporphyrin formation. Such changes in the spectrum were observed when aggregates were formed.[19] The unchanged four-band spectrum of the polyporphyrin film indicates that the π-conjugated porphyrin platform was not affected by the electropolymerization.

For the IR-spectroscopy studies, the polyporphyrin films deposited on a Pt-electrode were taken off the electrode surface, and tablets with KBr were formed. The IR spectra of the $H_2T(4\text{-}Py)P$ polyporphyrin **2** film are extremely close to the porphyrin monomer **1** spectrum, with small differences observed in the shortwave region. There are bands of the bending vibrations of the macroheterocycle pyrrole ring N–H bond in the region of 3200–2800 cm^{-1}. The reported[20] polyporphryin spectrum contains similar bands.

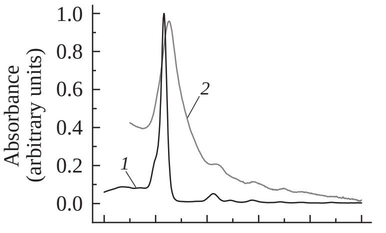


Figure 2 UV-VIS spectra of (*1*) monomer **1** in DCM and (*2*) poly-$H_2T(4\text{-}Py)P$ **2** film.

The peak at 3310 cm^{-1} corresponding to the stretching vibrations of N–H bond in the tetrapyrrole cycle is also found in the poly-$H_2T(4\text{-}Py)P$ **2** spectrum. The pronounced bands of the unprotonated pyridine ring at 1590–1650 cm^{-1} change their intensity in case of polyporphyrin. The intensity of the band at 1592 cm^{-1} becomes lower and the peak of the pyridine ring vibrations at 1650 cm^{-1} disappears. The film spectrum has a new peak at 1554 cm^{-1} that can be attributed to the C=N bipyridine fragment vibrations (Figure 3). Similar vibrations are observed in the 2,2′-bipyridine spectrum.[21] Based on the spectral studies, it can be suggested that the electropolymerization consists in interaction of the pyridyl substituents with each other with the formation of bipyridine fragments.

The IR spectrum of the film has a band characteristic of ClO_4^- in the region of 1140–1015 cm^{-1}, which indicates inclusion of the supporting electrolyte anions into the polymer[22] (such band in the monomer **1** spectrum is absent). The bands of bending vibrations of the pyridine ring C–H bonds of the film spectrum in the region of 900–700 cm^{-1} are the same as in the monomer spectrum, the triplet with the maxima at 881, 841 and 783 cm^{-1} is found both in the porphyrin monomer and polyporphyrin film spectra.[23]

The film semiconductor properties were evaluated based on the optical band gap calculated from the film electronic absorption spectra. The optical band gap was determined based on the spectra analysis of the film absorption near the long-wavelength absorption edge.[24–26] The band gap values were determined by linearly extrapolating the spectral characteristics of the obtained material represented in Tauc coordinates (Figure 4)[27–31] to the zero value of optical density $[(D/\lambda)^2 = 0]$.[32]

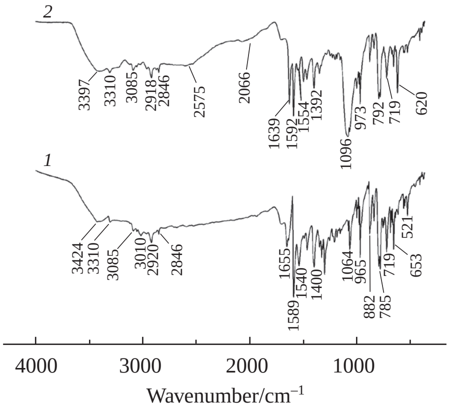


Figure 3 IR spectra of (*1*) monomer **1** and (*2*) polymer poly-$H_2T(4\text{-}Py)P$ **2**.

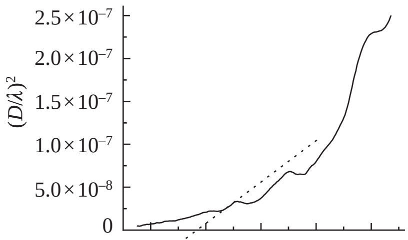


Figure 4 Spectral dependences of polyporphyrin film absorption near the absorption edge in Tauc coordinates.

The lower the obtained band gap value, the higher the film conductivity. The optical band gap of the poly-H_2T(4-Py)P **2** film was found to be 1.76 ± 0.05 eV.

To conclude, new polyporphyrin films based on 5,10,15,20-tetra(4-pyridyl)porphyrin were obtained by electrochemical polymerization from a solution in dichloromethane. The novelty and prospects of the study are to determine the practically useful properties of the obtained material. In particular, the synthesized films have semiconductor properties, which makes it possible to use them as elements in various types of electrochemical devices.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.01.028.

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