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Poly-5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin as a material for photovoltaic devices

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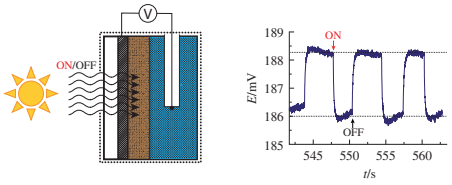
Superoxide-initiated anion-radical electrodeposition from solutions in DMSO was used to obtain smooth compact films of poly-5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin having a photovoltaic response.



Keywords: electropolymerization, superoxide radical anion, polyporphyrin films, photovoltaic response.

The development of new materials for devices that convert light into an electrical signal is of fundamental importance. Commercial photodetectors are based on inorganic semiconductors, though organic semiconductors typically have higher light absorption coefficients, and they are suitable for the production of flexible thin-film devices by low-cost liquid-phase technologies.[1–3] Porphyrin compounds are attractive for the development of optoelectronic devices due to the excellent chromophore characteristics of π-conjugated macrocycle systems,[4–7] diverse supramolecular behaviors of porphyrin ensembles[8–10] and high thermal and chemical stability of macrocyclic rings.[11–13] Porphyrin films can be deposited onto substrates using gas-phase (vacuum)[14,15] and liquid-phase methods. As a rule, higher porphyrin concentrations are achieved in a liquid phase, and solvation allows one to stabilize the ionic state of porphyrins in solutions and hence to prepare electrostatically stabilized materials.[16] Electrochemical methods make it possible to obtain materials with covalent-bound porphyrin moieties under mild conditions without hazardous reagents and to affect their properties by changing the working electrode potential[17] or by using potentiodynamic deposition.[18] Previously,[19–22] we found that substituted tetraphenylporphyrins in dimethyl sulfoxide (DMSO) solutions can form films with semiconductive and electrocatalytic properties on electrode surfaces with process initiation by an electrochemically synthesized superoxide radical anion.

In this work, we obtained a smooth compact film with a photovoltaic response, which is sufficient for practical use as a power-free photosensor, using superoxide-initiated anion anion precipitation from solutions of 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin [H_2T(4-HOPh)P] in DMSO.

The synthesis of H_2T(4-HOPh)P was reported previously,[23] the experimental details see in footnote.†

On the potential cycling of an ITO working electrode in a range from –2.0 to +1.5 V (Figure 1) in oxygen-saturated solutions of H_2T(4-HOPh)P, a polyporphyrin film was formed on it (Figure 2). The process was accompanied by changes in the positions and amplitudes of electrochemical responses on the CV curves from

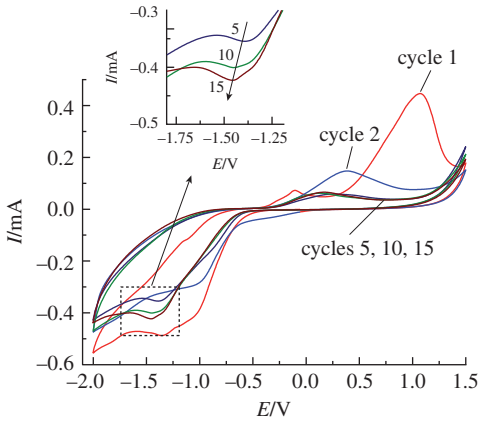
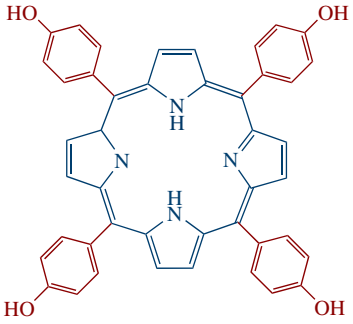


Figure 1 Changes in the shape of CV curves in the course of potential cycling (cycles 1, 2, 5, 10 and 15 are shown).



H_2T(4-HOPh)P

† The film was deposited on a surface from a 10^{-3} M solution of H_2T(4-HOPh)P in DMSO containing 0.02 M tetrabutylammonium perchlorate in a three-electrode electrochemical cell. The working electrode was a glass plate with an ITO coating (the surface resistance was about 100 Ω per square). A Hg/Hg_2Cl_2, Cl^- (1 M LiCl) calomel electrode with a Luggin capillary was used as the reference electrode, and a platinized platinum disk (2.5 cm in diameter) was used as the auxiliary electrode. The solution was saturated with oxygen by passing it through a capillary tube for 30 min. A film was formed by potential cycling in a range from –2.0 to +1.5 V (sweep rate, 20 mV s^{-1}) using an SP-150 potentiostat (Bio-Logic Science Instruments, France). The structure of films was studied by atomic force microscopy (Solver 47 Pro, NT-MDT, Russia) and electron scanning microscopy (Hitachi TM4000 Plus). To study the photoresponse

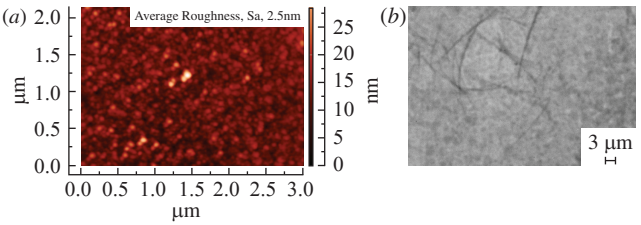


Figure 2 Micrographs of the surface of a poly-H_2T(4-HOPh)P film made by (*a*) atomic force microscopy and (*b*) scanning electron microscopy.

one cycle to the next one. The largest changes occurred during the first two cycles with the greatest increase in the film weight.[20] Note that, starting from the fifth cycle, the oxidation of porphyrin did not significantly contribute to the film deposition.[20] Figure 1 shows an increase in the peak intensity at –1.4 V when poly-H_2T(4-HOPh)P was deposited on an ITO electrode, indicating that the film growth continued after the fifth cycle (Figure 1, inset).

Microscopic studies of poly-H_2T(4-HOPh)P deposited on ITO in 15 potential cycles (see Figure 2) exhibited a compact film with a fairly smooth surface. The mean sample roughness [Figure 2(*a*)] was 2–3 nm. The film is formed by globular particles with a lateral size of about 40 nm. An electron micrograph [Figure 2(*b*)] demonstrates the uniformity of the film and the absence of defects and pronounced structural elements.

We found that the photoresponse of an ITO electrode modified with a polyporphyrin film differed significantly from that of pure ITO (Figure 3, curves *2* and *1*, respectively). Pure ITO manifested a long-term (>1 h) variation in the potential after the electrode was immersed in solution and a drift of the ON and OFF potentials [Figure 3(*a*), curve *1*]. Illumination of an ITO electrode that was kept under dark conditions resulted in slow changes in the potential [Figure 3(*b*), curve *1*], which are consistent with published data.[24] In contrast, a steady-state potential of the modified electrode was achieved within <30 min after immersion into solution. After that, the potential reversibly changed upon illumination.

The steady working electrode potentials under dark conditions and under illumination differed by 1.3 mV [Figure 3(*a*), curve *2*]. Moreover, the time dependence of the electrode potential passed through an extremum when the light was switched on or off. In the ON/OFF and OFF/ON processes on a modified electrode, the time of reaching an extremum potential was about 1 s [Figure 3(*b*), curve *2*], which is comparable with the duration of transient processes in the radiation source. The amplitude of a potential change upon an OFF/ON transition after a long stay under dark conditions exceeded 4 mV. Upon a short-term OFF/ON/..../OFF/ON switching [Figure 3(*c*)], the potential–time curve had a U-shaped profile, and the potential change on switching from OFF to ON state was about 2.3 mV. Thus, a poly-H_2T(4-HOPh)P film on an ITO surface led to a substantial increase in the working electrode potential amplitude and the rate of its variation upon the ON/OFF illumination switching.

Figure 4(*a*) shows the proposed structure of the polymer chain formed.[25] The working electrode potential varied due to the photogeneration of charge carriers[26,27] [Figure 4(*b*)] and their redistribution. The steady potential of a modified electrode in the

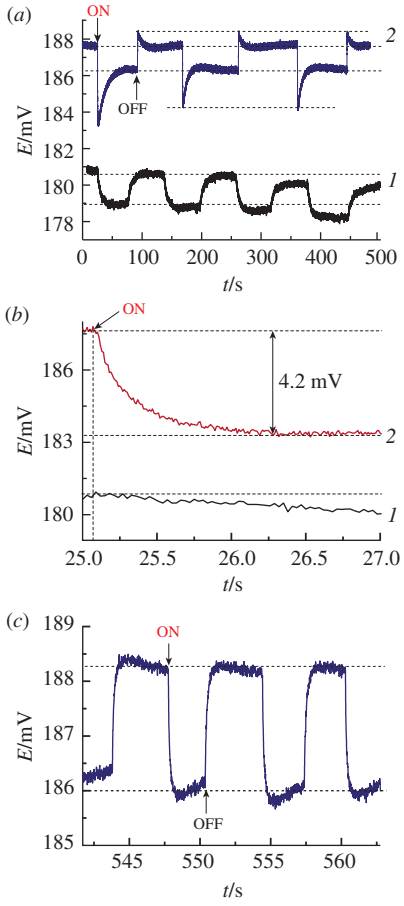


Figure 3 Photovoltaic response of (*1*) an ITO electrode and (*2*) a device prototype: (*a*) OFF/ON/..../OFF/ON switching with prolonged exposure under dark and illuminated conditions followed by attainment of a quasi-steady potential value, (*b*) potential variation after OFF/ON switching; (*c*) potential variation upon short-term OFF/ON switching. Solution, 0.5 M KCl + 0.001 M K_3[Fe(CN)$_6$]; lamp ON/OFF time, ~100 ms.

absence of illumination is determined by redox processes involving the ferrocyanide ion and the polymer film [Figure 4(*c*), processes I and II]. Upon illumination, the chromophore system of porphyrin polymer is excited to result in electron transfer from a donor moiety to an acceptor one or to the bulk polymer (exciton or electron–hole pair formation. As a result, electrons in the conduction band of semiconductor as well as positively charged (radical cation) and negatively charged (radical anion) centers arise. High electrical conductivity of the film[25] indicates that the diffusion of charge states to the interfaces is possible. A positively charged center can withdraw an electron from ITO [Figure 4(*c*), processes III], which is an n-type semiconductor.[28] An anion-radical polymer moiety can pass an electron to the depleted ITO layer [Figure 4(*c*), processes IV] or to a ferricyanide ion (processes I). In this case, the ferricyanide ion turns into a ferrocyanide ion and diffuses into the bulk of solution. We suppose that the photogenerated conductivity electrons are also involved in interfacial processes. The potential shift to negative values allows one to assume that an excess of anion-radical polymer moieties and electrons in the conduction band is formed in the film bulk under illumination due to the above processes.

The difference in the time dependences of potentials at long [Figure 3(*a*)] and short [Figure 3(*c*)] exposures can be explained as follows. At long exposure times, the steady-state potential of the film is influenced by the diffusion and recombination of all photogenerated charge states: excitons, electrons in the conduction band, holes and anion radicals. At short exposure times, the potentials mainly change due to processes with the charge states of the highest mobility (apparently, due to photogenerated electrons

of poly-H_2T(4-HOPh)P films, ITO electrodes with deposited photoactive poly-H_2T(4-HOPh)P layers were placed in a spectrophotometric cell filled with an aqueous solution of 0.5 M KCl + 0.001 M K_3[Fe(CN)$_6$]. The photoactive electrode potential was measured relative to an Ag/Ag^+ quasi-reference electrode of silver wire with the Teflon-coated side surface. A LED-A60 11 W lamp from ASD (spectral temperature, 4000 K; luminous flux, 990 lm; in a spectral range from 400 to 750 nm) was used as a light source.

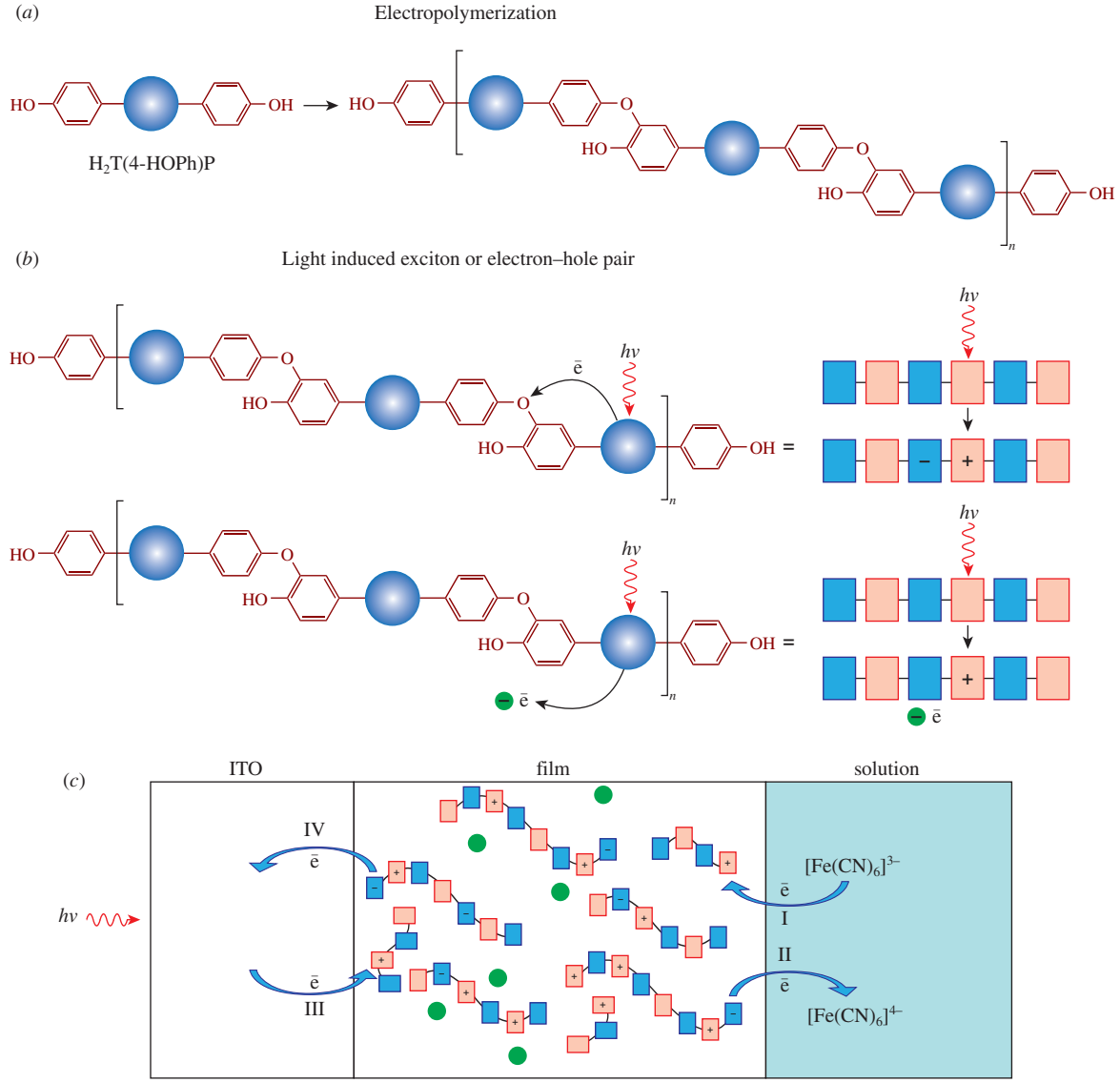


Figure 4 (*a*) Electropolymerization of the porphyrin used, (*b*) photogenerated exciton or electron–hole pair, and (*c*) electron transfer processes at the interfaces.

in the conduction band). Additionally, upon short-term switching, the ferrocyanide ion does not have enough time to diffuse into the bulk of solution; when the illumination is turned off, reverse electron transfer occurs, and the system returns to its previous state.

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