

A Polycationic Zinc-5,15-dichlorooctaethylporphyrinate-viologen Wire

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Abstract: Electropolymerization of zinc-10-bipyridinium-octaethyl-porphyrinate by cyclic scanning between -0.6 and $+1.6$ V yields a zigzag configured polymer, which appears as swollen, vesicular bilayer on atomic force micrographs. The same procedure leads to micrometer-long wire-shaped linear polymers, if the 5,15-methine bridge carbon atoms are blocked by chlorine substituents. The wires come in two parallel strands originating from antiparallel face-to-face dimers in the solution.

Introduction

Covalent or noncovalent oligomers and polymers of pigments may function as molecular photonic and/or electronic wires by supporting energy or electron transfer. Classic photonic wires are the micrometer-long noncovalent Scheibe or Jelly aggregates where excitons migrate up to 50 nm.¹ The most efficient electron conductors are cocrystals of quinone-type electron donors and acceptors in parallel arrangement² or polyacetylenes and polypyrroles.³ Covalent photonic wires containing porphyrin dye molecules were so far limited to a length of 9 nm.^{4–6} We introduce here an alternating polymer made of zinc porphyrin–viologen units synthesized by electrochemical oxidation of a single *meso*-viologen zinc porphyrinate monomer. The length-to-width ratio of $\geq 10^3$ and the novel dimer structure of the wire as demonstrated by transmission electron microscopy as well as the stereochemical enforcement of linear instead of zigzag polymerization prompted us to publish our results, although the material's properties could not be characterized so far.

Experimental Section

Materials. All solvents and 4,4'-bipyridine were of reagent grade quality and used without further purification. 5,15-Dichloro-octaethylporphyrin was prepared and purified by a known procedure. It was metalated with Zn(OAc)₂·H₂O in chloroform/methanol to give $\alpha\gamma$ -ZnOEP(Cl)₂ **2**.

Electrochemistry. A one side indium tin oxide (ITO)-coated electrode with a surface of about 1 cm² was applied (Delta Technology Limited, 100 Ω /square). All electrochemical measurements were carried out under argon at 20 °C on a dropping mercury electrode or on a platinum disk electrode. Voltammetric data were obtained with a standard three-electrode system using a Bruker E 130 M potentiostat

and a high-impedance millivoltmeter (minisys 6000, Tacussel). Current–potential curves were obtained from an Ifelec If 3802 X–Y recorder. The working electrodes were a platinum (EDI type, Solea Tacussel) of 3.14 mm² surface. ITO electrode served as optically transparent electrodes. A platinum wire was used as the auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). It was electrically connected to the solution by a junction bridge filled with the corresponding solvent containing the supporting electrolyte.

Zinc-10-[4,4'-bipyridinium-perchlorate]-porphyrinate (1a) was synthesized and characterized as described previously⁸ by electrochemical oxidation of ZnOEP in the presence of excess of 4,4'-bipyridine.

Zinc-5,15-dichloro-10-[4,4'-bipyridinium-hexafluorophosphate]-porphyrinate (2a). 4,4'-Bipyridine (187 mg, 1.20 mmol) was dissolved in 100 mL of a CH₂Cl₂/CH₃CN (4:1) solution containing 0.1 M tetraethylammonium hexafluorophosphate. After electrolyzing for 3 h at 1.0 V vs SCE, the initial violet solution turned green. The solvents were removed, and the residue was dissolved in a minimum of CH₂Cl₂. The solution was poured into water, and the organic layer was washed twice. The organic extract was concentrated (≈ 5 mL) and chromatographed on alumina. The first fraction (eluted with CH₂Cl₂/hexane (80:20)) was unreacted 5,15-ZnOEP(Cl)₂, the second fraction was excess of bipy. **2a** was eluted with a mixture of CH₂Cl₂/CH₃OH (99:1). The solvent was removed, and **2a** was recrystallized from CH₂Cl₂/n-hexane to give violet-green crystals (52 mg, 0.056 mmol, yield 94%).

UV–Vis (CH₂Cl₂) λ_{\max} (nm) (ϵ , M⁻¹ cm⁻¹) 436 (151 200), 573 (11 400).

¹H NMR (300 MHz, DMSO-*d*₆, 25 °C) δ = 10.72 (d, J_o = 8.0 Hz, 2H, -bipy⁺), 9.75 (s, 1H, *meso*-H), 9.20 (d, J_o = 8.0 Hz, 2H, -bipy⁺), 8.48 (d, J_o = 8.0 Hz, 2H, -bipy⁺), 4.04 (q, J^3 = 7.5 Hz, 4H, CH₂ of Et), 3.97 (q, J^3 = 7.5 Hz, 4H, CH₂ of Et), 3.81 (q, J^3 = 7.5 Hz, 4H, CH₂ of Et), 2.16 (q, J^3 = 7.5 Hz, 4H, CH₂ of Et), 1.73 (t, J^3 = 7.5 Hz, 12H, CH₃ of Et), 1.62 (t, J^3 = 7.5 Hz, 6H, CH₃ of Et), 0.73 (t, J^3 = 7.5 Hz, 6H, CH₃ of Et). FAB-MS (NBA) m/z = 821.7 (C₄₆H₅₀N₆Cl₂Zn)⁺, 100%. Elemental analysis (C₄₆H₅₀N₆Cl₂ZnClO₄) calcd C 59.92, H 5.47, N 9.12; found C 60.27, H 5.62, N 8.87.

Cyclic voltammetry results are shown in Table 1. The half wave potential is equal to $E_{1/2} = (E_p^a + E_p^c)/2$, where E_p^a and E_p^c are the positive and the negative peak potentials measured on the first scan;

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Table 1. Half-wave Potentials ($E_{1/2}$ vs SCE) of Compounds 1 and 2 in $\text{CH}_3\text{CN}/1,2\text{-C}_2\text{H}_4\text{Cl}_2$ (1:4) Containing 0.1 M $(\text{Net}_4)\text{PF}_6^a$

porphyrins	ring oxidation		reduction of bipy ⁺ or V ²⁺		ring reduction
ZnOEP	0.94 (75)	0.68 (70)			-1.60 (65)
ZnOEP- <i>m</i> -bipy ⁺ (1a)	1.20 ^{irr} 1.37 (63)	0.91 (65)	-0.65 (63)		-1.31 (137)
Polymer 1b (20 scans)			0.02 (88)	-0.58 (105)	
5,15-ZnOEP(Cl) ₂	0.95 (105)	0.73 (85)			-1.41 ^{irr}
5,15-ZnOEP(Cl) ₂ bipy ⁺ (2a)		0.97 ^{irr}	-0.58 (65)		-1.28 ^{irr}
Polymer 2b (20 scans)			0.02 (114)	-0.058 (98)	

^a Scan rate = 0.1 V s⁻¹; working electrode, Pt; see text. 18 references have been flagged (there are apparently 18 references)

the numbers in brackets indicate their difference. Values for oxidation are only obtained on the first scan, because polymerization accompanies oxidation of **1a** or **2a**.

Polymer 1b. Electropolymerization was accomplished under an argon atmosphere in a 0.1 M solution of tetraethylammonium hexafluorophosphate in $\text{CH}_3\text{CN}/1,2\text{-C}_2\text{H}_4\text{Cl}_2$ (1:4) containing the monoperochlorate of **1** (1 mM). Cyclic scanning (100 mV s⁻¹) the working electrode potential was performed in the potential range between -0.60 and +1.60 V vs SCE. During anodic oxidation, the electrolyzed solution was continuously maintained under argon. After electrolysis, the electrode was washed five times with 10 mL of CH_3CN to remove the conducting salt present on the conducting film and finally dried under argon.

Polymer 2b. Electropolymerization occurred in the same solvent as described above and containing 1 mM **2a**. Cyclic scanning (100 mV s⁻¹) of the working electrode was applied at potentials between -0.90 and +1.90 V vs SCE.

Spectroscopy. UV-Vis spectra were recorded on a Shimadzu UV-260 spectrophotometer. Glass plates covered with indium and tin oxide (ITO) and electrochemically deposited polymer of porphyrin were used to obtain UV-vis spectra of polymeric film.

Atomic Force (AFM) and Transmission Electron (TEM) Microscopy. AFM was performed directly on the surfaces of the ITO and gold electrodes using a Nanoscope IIIa (Digital Instruments, Santa Barbara, CA) in the tapping mode under ambient conditions. Silicon Cantilevers (Nanosensors, Wetzlar/Germany) with a spring constant between 31 and 77 N/m and a resonance frequency in the range of 299–402 kHz were used. The scanning rate was 1.0 Hz. Roughness analysis was performed with the Software 4.23r2 by Digital Instruments. An ITO electrode after 70 cycles of electropolymerization was then used to isolate polymers **1b** and **2b**. DMF removes most of the porphyrin polymer, but a red shining residue remains on the ITO surface. This residue was only removed by a mixture of concentrated HCl/ CH_3CN (9:1). To transfer the material from the ITO electrode to the TEM carbon grid, we first positioned the electrode in a glass vessel. Ten microliters of DMF was then applied to rinse ITO electrode from its top and collected on the bottom of the glass vessel. The resulting solution was collected on the bottom of the glass vessel and then applied four times in the same way in order to collect as much of polymers **1b** or **2b** in the smallest possible DMF volume. The ITO electrode was removed and the DMF sludge diluted very slowly with 2 mL of water. Rapid addition of water led to immediate precipitation of the porphyrin polymers and had to be avoided. A drop of the resulting aqueous suspension was then transferred to a carbon-coated electron microscope grid, negatively stained with phosphotungstate (2% w/v), and blotted with filter paper.

Results

One-electron oxidations of zinc β -octaethyl porphyrinate (ZnOEP) yield first the π -cation radical at a half-potential of 0.68 V (SCE) and then the dication at 0.94 V (SCE) in often fully reversible reactions.¹⁰ Already the monocationic radical may add nucleophiles to the methine bridge to yield isoporphyrins^{11–13} containing a saturated carbon bridge. In the case

of 4,4'-bipyridine (4,4'-bipy) as nucleophile one obtains labile isoporphyrin radicals with a monocationic bipyridyl substituent. At the given potential of 0.91 V, the isoporphyrin radical macrocycle is then spontaneously oxidized to the porphyrin π -cation and a proton is released to give the zinc porphyrinate **1** with a monocationic bipyridinium substituent. This product is stable and has been isolated in 70% yield.⁸

The cyclic voltammograms of **1a** monomer recorded in acetonitrile/1,2-ethylenedichloride (1:4) are shown in Figure 1a,b. A table of reduction and oxidation potentials is given in the Experimental Section. Upon reductive scanning, the voltammograms produce one reversible and one quasi-reversible one-electron peak. The first one-electron transfer at -0.65 V vs SCE corresponds to the reduction of 4,4'-bipyridinium, the second one at -1.31 V vs SCE, to the first reduction of the porphyrin π -system. Oxidative scanning yields two reversible and one irreversible one-electron peaks at 0.91, 1.20 (irrev.), and 1.37 V vs SCE. The first and the second peak correspond to π -cation radical and dication formation of the porphyrin ring, the third peak to the reversible oxidation of the isoporphyrin. The 4,4'-bipyridinium *meso*-substituent induced a positive potential shift of about 300 mV. The Soret band of the desorbed polymers in acetonitrile/HCl was red-shifted by 20 nm with respect to the monomers, the half-line width broadened from 20 to 70 nm.

The one-electron oxidations at potentials above 1 V were essentially irreversible (Figure 1a). That should be related to an intermolecular reaction between the dication porphyrin and the 4,4'-bipyridinium nucleophile to generate the corresponding isoporphyrin dimer and further oxidation to an isoporphyrin-porphyrin dimer. This dimer may, to a small extent, undergo a two-electron reduction upon cycling to give the starting material¹⁴ or preferably lose a proton to rearomatize and to give a porphyrin dimer with a viologen spacer. Repetitions finally yield the alternating porphyrin-viologen copolymers (Figures 2 and 3). Preparative cyclic scanning voltammetry (100 mV/s) of platinum, glassy carbon gold, or ITO working electrodes between -0.80 and 1.60 V (SCE) then led to a continuous increase of the height of the voltammetric peaks at 0.02 and -0.58 V (SCE) for the electroactive viologen spacers (Figure 1b). This was taken as an indication for the growth of a polymeric porphyrin-viologen **1b** film on the platinum electrode.^{11,15} The most successful system for the preparation of the polymer consisted of concentrated solutions of porphyrin **1** (>10⁻³ M) in mixtures of acetonitrile and 1,2-dichloroethane (1:4). Less concentrated solutions did not lead to polymers.

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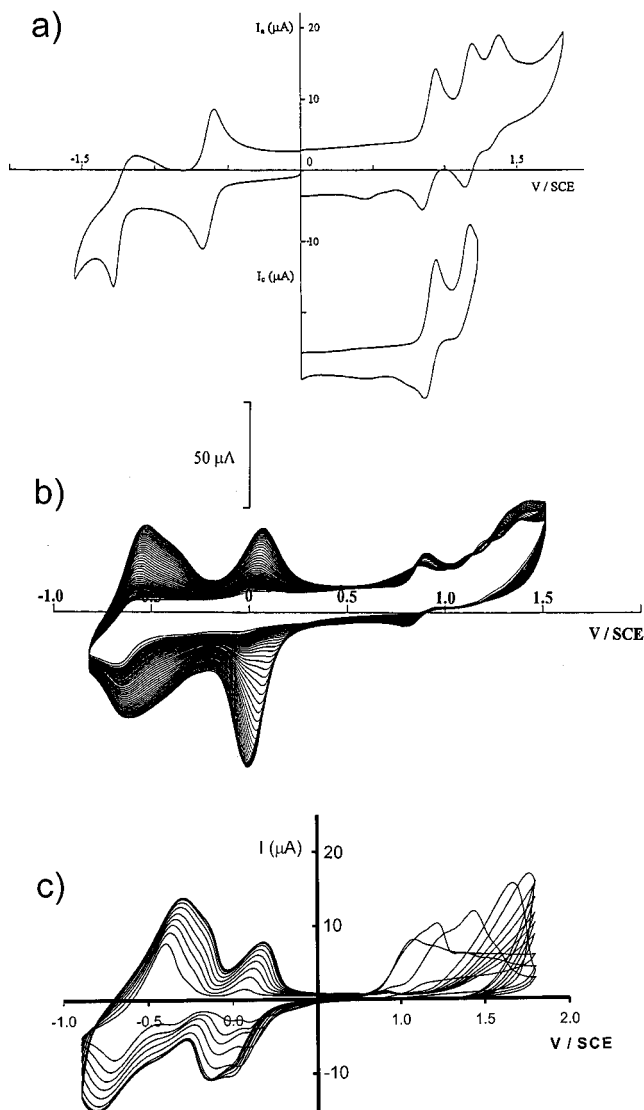


Figure 1. (a) Cyclic voltammetry of **1a**. Time-dependent cyclic voltammetry of (b) zinc porphyrinate **1a** and (c) the 5,15-dichloro derivative **2**. Working electrode: Pt, $\nu = 100 \text{ mV s}^{-1}$.

We have shown earlier that the disubstitution of meso-pyridinium porphyrins occurs statistically at position 5,10 or 5,15 at high potential.^{8a,b} The bipyridine unit of one porphyrin **1a** may therefore either add to the methine bridge next to the substituted bridge of the other porphyrin, for example, at C10 if the bipyridine unit is at C5, or to the opposite methine bridge, for example, C15 in this case. As a result linear or orthogonal dimer units may occur and a disordered zigzag polymer is formed after several consecutive oxidation–reduction cycles. Furthermore, since ZnOEP and its π -cation radical occur as dimers in solution¹⁷ and in the solid state,¹⁸ two irregular chains of undefined length will grow independently at each step. The final polymerization product on the electrode surface is therefore an irregular porphyrin bilayer. In scanning force micrographs taken directly on the surface of an ITO electrode the polyelectrolyte with two positive charges on each unit appears in the form of tightly packed micellar spheres. The corresponding films could be partly dissolved by treatment with dimethyl formamide

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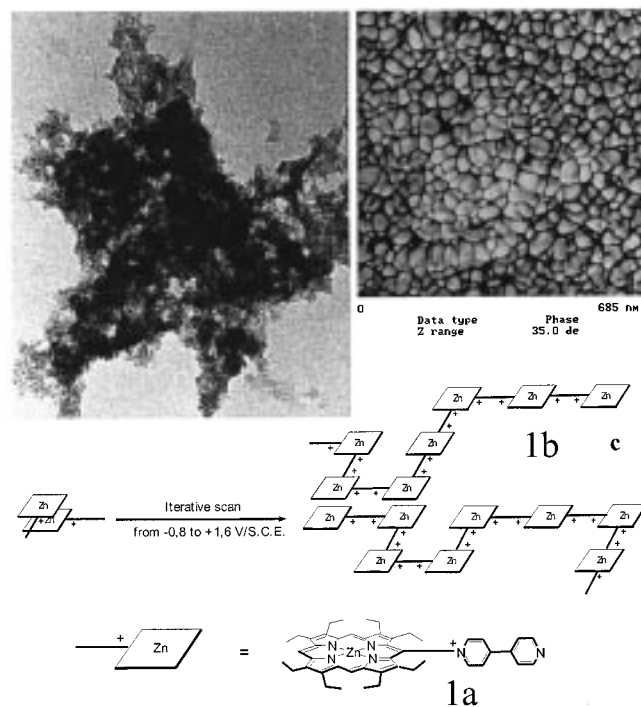


Figure 2. (a) The transmission electron micrograph (TEM) after transfer onto a carbon grid (left, phosphotungstate stained), (b) the atomic force micrograph (AFM) of the polymer **1b** on an ITO electrode, and (c) schematic polymerization scheme of a $(\text{ZnOEP-4,4'-bipy})^+$ **1a**.

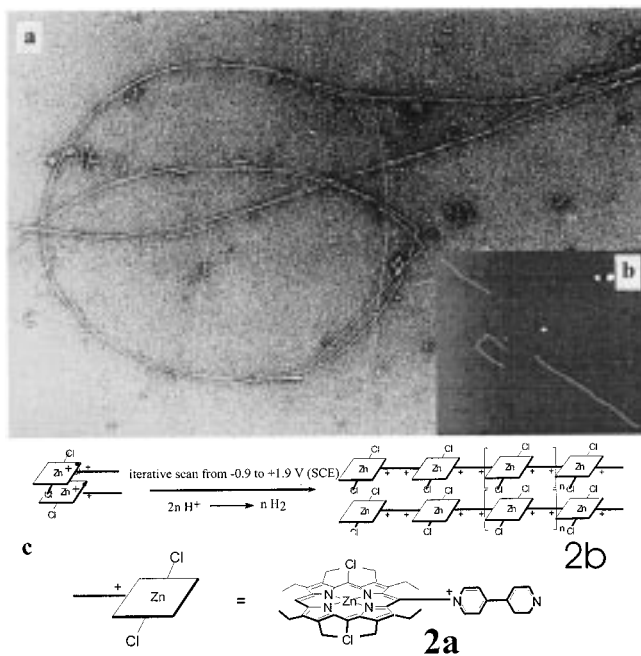


Figure 3. (a) Transmission electron micrograph of collected fibers on a carbon grid. Negative stain: 2% phosphotungstate, (b) scanning force micrograph of short fibers on the gold electrode, and (c) scheme of the linear chain growth of $\text{ZnOEP}(\text{bipy}^+)\text{Cl}_2$.

and were completely removed from the electrode with concentrated hydrochloric acid/acetonitrile (9:1) mixtures. Methanol, ethanol, acetonitrile, and chloroform did not remove the electrode coating. The transmission electron micrograph of a dried aqueous suspension only showed irregular layer structures; the micellar assemblies were obviously destroyed during the transfer process (Figure 2). AFM measurements of the same probe on mica yielded the similar irregular structures.

ZnOEP was then replaced by zinc-5,15-dichlorooctaethyl porphyrinate⁷ in order to enforce a linear polymerization on the electrode surface along opposite 5,15-methine bridges only. The same procedures as described above for **1b** were now applied to the polymer **2b**. The dichloro porphyrin **2a** is more difficult to oxidize than the non-chlorinated one, and it polymerizes much faster than **1a** (Figure 1c). TEM of the transferred polymer now showed fibers after negative staining. They had a length of several micrometers and a diameter of about 20 Å (Figure 3). This is in agreement with the 19 Å molecular width of an octaethylporphyrin molecule. The length of a typical fiber points to polymerization grades of at least 2000, which is to the best of our knowledge the largest defined dye polymer described so far. Furthermore, the fibers of **2b** appear in two parallel running strands originating from the noncovalent, stacked dimers of ZnOEP radical dimers,^{16,17} which are presumably also present in the case of the bipyridine derivative **2a** and its π -radical. The very high polymerization grade of the linear porphyrin fibers is probably related to the fact that two chains grow independently but next to each other. In this way, defects do not lead directly to a termination of chain growth, but one chain can act as a matrix for the second one. The fact that both chains grow parallel to each other also indicates a perfectly ordered dimer probably with both bipyridine units in an antiparallel order. Cross links between the upper and lower porphyrin fibers do not occur because of the rigidity of the building blocks. Attempts to detect the same porphyrin fibers on mica using the same transfer method were only partly successful. Small numbers of short fibers were found. Most of the fiber length was presumably buried in uncharacteristic oligomer material deposited on the mica surface. The lateral resolution of AFM was not good enough to detect two parallel strands. The low-yield, well-defined dimeric fiber of **2b** was essentially only found by TEM,

the primary surface micelles of **1b** only by AFM. Although the fibers of **2** are, of course, also buried in a large excess of low molecular weight porphyrins, they are detectable after negative staining in transmission electron microscopy. TEM is, on the other hand, not applicable for solid electrode surfaces. The estimated yield of the fibers is below 5% and is only reached in the given solvent mixture at high concentration of **2b**. Systematic experiments to improve the ordering of dimers and oligomers, for example, by variation of the porphyrin's central metal ions and their counterions, and thereby the yield of the linear polymerization are currently undertaken.

The porphyrin polymer described here is different from other porphyrin wires⁴⁻⁶ in the following respects: (i) it contains links, which form stable radicals, and (ii) the electrochemical polymerization procedure opens the way to the application of a large variety of metalloporphyrins. More electron-withdrawing central ions should also decrease the reaction rates between porphyrins, and a stepwise oligomerization may then lead to oligomers of defined lengths. The rich redox and photochemistry of both metalloporphyrins and viologens promises interesting conductivity properties of the giant polymer fibers. First experiments in this direction are under way, although only about ten of milligram are available yet.

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