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Porphyrin–acetylene–thiophene polymer wires†

Guangtao Li,[a,c] Tianyu Wang,[a] Andrea Schulz,[a] Sheshanath Bhosale,[a] Matthias Lauer,[a] Pamela Espindola,[b] Jürgen Heinze[b] and Jürgen-Hinrich Fuhrhop*[a]
[a] *Freie Universität Berlin, Institut für Organische Chemie, Takustr. 3, D-14195 Berlin, Germany. E-mail: fuhrhop@chemie.fu-berlin.de; Fax: +49 30 838 55589; Tel: +49 30 838 55394*
[b] *Universität Freiburg, Institut für Physikalische Chemie, Albertstr. 21a, D-79104 Freiburg i. Br, Germany*
[c] *Department of Chemistry, Tsinghua University, 100084 Beijing, China*

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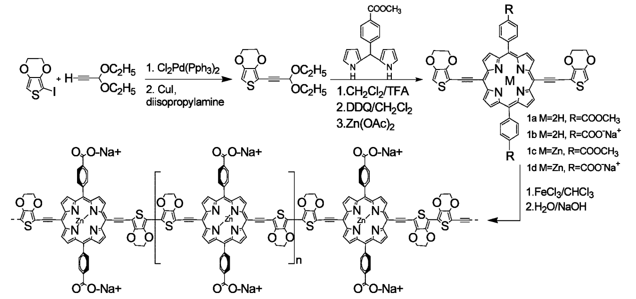
5,15-Bis[acetylene-4-(ethylenedioxy)thiophene]-10,20-bis(4-carboxyphenyl)porphyrin was synthesized by a Sonogashira coupling and polymerized to fibres; TEM and AFM images show uniform porphyrin wires with a length of several micrometers and a thickness of less than 4 nm.

Polymeric wires made of metalloporphyrins are of interest, because the porphyrin ligands can, depending on the central metal ions, be reversibly oxidized to cationic or anionic radicals[1] and because their excited states can be highly populated[2] So far, metalloporphyrin units have been connected in covalent polymers by acetylene,[3] thiophene,[4] phenylacetylene[4] and viologen[5] linkers. The typical width of a substituted porphyrin is 2 nm and strands with a length of about 50 nm or more are easily recognized as such in TEM or AFM images. So far only a porphyrin–viologen polymer was thus characterized,[5] and could only be obtained in minute quantities. A 128-mer of directly *meso–meso* coupled porphyrins has been analysed by HPLC and even MALDI-TOF mass spectrometry.[6]

We have now formulated and synthesized several acetylene–thiophene-substituted monomers (Scheme 1), after we had shown that micellar thiophene fibres gave covalent wires after oxidation.[7] Anderson and coworkers formulated a cumulene or “quinoid” structure of the excited state of such porphyrin–acetylene–arene triads.[8] Electron conduction may occur if both the dithiophene and the metalloporphyrin units are oxidized to π-radicals or to diamagnetic π–π dimers, with intense charge transfer bands in the near IR[9,10]

The synthesis of porphyrin monomers **1** started with a Sonogashira coupling of 2-iodo-3,4-(ethylenedioxy)thiophene with 3,3-diethoxypropyne. The product was cyclized[3] with 5-(4-methoxycarbonylphenyl)dipyrromethane in dichloromethane–trifluoroacetic acid containing dichlorodicyanobenzoquinone to yield porphyrin **1a** in a yield of 3% (Scheme 1). 10–20 mg Quantities were routinely obtained in one batch. The ^{1}H NMR and mass spectra of the dimethylester **1a** (parent peak at *m/z* 906.8, positive FAB) were as expected, but a large degree of fragmentation was observed in the latter.



Scheme 1

Polymerization of the zinc complex occurred either by chemical oxidation with iron(III) chloride in chloroform solution or by electrochemical oxidation of 10 mg of **1a** or **1c** on a platinum electrode. A black precipitate was formed. 10 mg of the polymerized esters **1a** or **1c** was at first dispersed in chloroform and filtered. The remaining solid was subsequently washed extensively with chloroform, water and finally with cyclohexane, until the filtrate was colorless and showed no fluorescence. Soluble oligomers of low molecular weight were thus removed and discarded. The red filtrate showing a visible porphyrin spectrum was tested for oligomers by positive FAB mass spectrometry. Only fragments with molecular masses below *m/z* 600 were observable. Similar observation were reported even for thiophene polymers without heavy porphyrin constituents.[7,11] Between 6 and 8 mg of a black, dry powder was obtained. Saponification of 8 mg of the polymeric esters was executed in 70 mL of 0.01 M NaOH in water (pH 13), which was diluted with 30 mL of ethanol and stirred for two weeks (!). The resulting slightly yellow dispersion was applied without further treatment to carbon grids for transmission electron microscopy (TEM). The solvent was blotted off with filter paper and the remaining sodium hydroxide was dissolved in a drop of water, which was again blotted off. Photographs were taken without staining under low-dose conditions and showed leaflets with a width and length of a few micrometers and a fibrous hyperfine structure (inset in Fig. 1(a)). The width of the fibers was about 2 nm, as deduced from the measurement of the width of bundles of ten distinguishable fibres. This value corresponds to the width of the porphyrin unit **1b** (Fig. 1(a)).

The monomeric zinc complex **1c** in dichloromethane absorbed at 460 nm (half width: 20 nm) and 656 nm, while a dispersion of the polymeric diester in DMSO showed peaks at 434, 570 and 670 nm. These data are comparable to those of Anderson’s corresponding dimer spectra.[8,12] Strong, single fluorescence peaks were found at 720 nm for the free base **1a** and at 680 nm for the zinc complex **1c**. The black platelets were dispersed in aqueous sodium hydroxide–ethanol (7:3) and stirred for two weeks in the dark. Green, slightly turbid solutions of the polymers of disodium dicarboxylate **1d** probably with an axial water ligand on the central zinc ion were thus obtained. Both colored dispersions produced two fluorescence

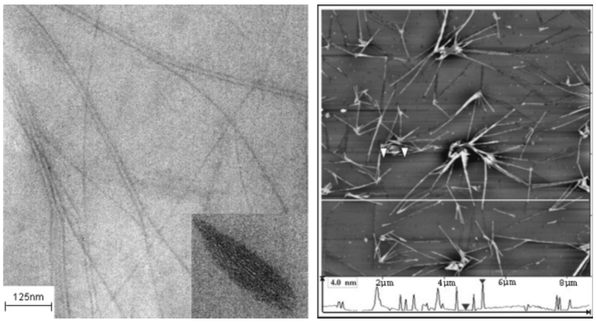


Fig. 1 (a) TEM of the leaflets of the polymer of the free porphyrin base **1b** (inset) and the zinc complex **1d**. The diameter of the fibres is about 2 nm and their lengths several μm. (b) AFM image of the fibrous polymers made of **1d**. The thin fibers have a height of 2.5 nm and a length of up to 3 μm.

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† Electronic supplementary information (ESI) available: Larger magnification image of Fig. 1(a); fuller version of the inset to Fig. 1(a), and magnified color image of Fig. 1(b). See http://www.rsc.org/suppdata/cc/b3/b313415f/

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bands at 650 and 720 nm for the **1b** polymer and at 620 and 660 nm for the polymer of zinc complex **1d**. Only the TEM images of the zinc complex **1d** produced the desired well-defined and separated fibers in the form of totally linear strands (Fig. 1(a)). Low contrast led to ill-defined contours, which did not allow exact measurements of their thickness (*ca*. 4 ± 2 nm) while negative staining produced ill-defined clusters. The uniform shape of the fibers over the length of a few micrometers clearly indicates that the polymer is of covalent nature. Aggregation of smaller stacks would always lead to steps caused by side-on adsorption as well as branching. The lengths of the fibers was up to 2.5 μm. This is longer than observed for the free base leaflets. Formation of stable zinc porphyrinate radicals[1] thus seems to help in the polymerization step. A single 2.5 μm fibre should contain about 1200 monomers corresponding to a hypothetical molecular weight of 1.3×10^6 Da. This is typical for non-covalent micellar fibers[13] and their covalent polymerization products.[5]

AFM images of the fibres originating from the same dispersion were taken with a 2 nm tip in the tapping mode on mica platelets. Heights between 3 and 4 nm and lengths between 500 and 3000 nm originating from bundles were found (Fig. 1(b)). The fibers were stable on mica for several hours, but rapidly disappeared under a beam of electrons or on graphite.

Voltammetric charging/discharging experiments of the material were carried out in connection with *in situ* conductivity measurements.[14] Cyclic voltammetry showed, in agreement with expectations, that the zinc porphyrin moiety was oxidized in the range of 0.6–0.9 V while the oxidation of the thiophene dimers starts at potentials higher than 1.0 V. The conductivity measurements of fibrous sheets made of hydrophobic zinc porphyrinate polymers on platinum electrodes gave upper values of 6×10^{-3} S cm^{-1} for the acetylene-linked polymer **1c**, and 8×10^{-4} S cm^{-1} for the same polymer with 1,4-phenylene spacers between the thiophene and porphyrin units (Fig. 2). This conductivity compares with 10^{-3} S cm^{-1} for charge transfer complexes of metalloporphyrins[15] and with 6–10 S cm^{-1} for polythiophenes.[16–20] The conductivity of the phenylene–porphyrin system at low charging potentials first increased above 0.6 V, reached a maximum, and then decreased again at potentials above 0.8 V. Electrons are obviously hopping between the porphyrin units in the half-oxidized ground state over a distance of about 1.5 nm. When all of the zinc-porphyrinate units are oxidized to cation radicals, conductivity is lost because all isoenergetic orbitals are occupied. The same effect was observed in the acetylene-porphyrin, but is not resolved due to the unfavourable measurement scale. The relatively low final conductivity at a charging potential of 1.2 V, where the thiophene as well as the porphyrin units are oxidized, indicates that the number of mobile charge carriers is drastically reduced with respect to polythiophene.[16–20] The oxidized dithiophene unit may act as an electron sink for the electrons of the porphyrin radicals. Adjustment of the oxidation potential of the metalloporphyrin by a change of metal ions should increase the conductivity. The finding, that the acetylene spacer allows a considerably higher rate of electron hopping than the 1,4-phenylene spacer, is probably related to the smaller distance between the dithiophene and porphyrin units as well as to the more favourable parallel orientation of the π-orbitals of different energy. Systematic investigations of the light-induced charge separation in the corresponding acetylene–thiophene connected porphyrin dimers containing other metal ions in addition to Zn(II) (*e.g.* Al(III) or Sn(IV)) are currently underway.

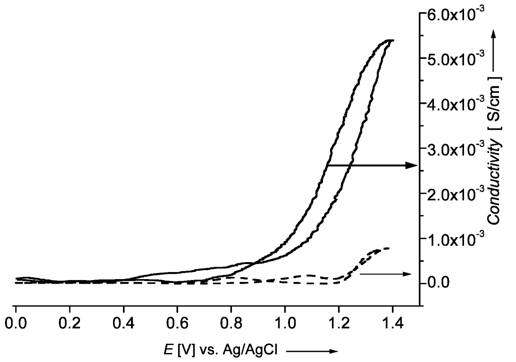

Fig. 2 Conductivity curves of the porphyrin–dithiophene polymer **1d** with an acetylene spacer (—) and the corresponding polymer with a 1,4-phenylene spacer (---). The polymer was formed on an ITO-electrode and the conductivity was measured *in situ* on a microarray working electrode (5 μm gap).[14]

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