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# FUNCTIONALIZED CONDUCTING POLYMERS WITH POLYAZULENE BACKBONE [1]

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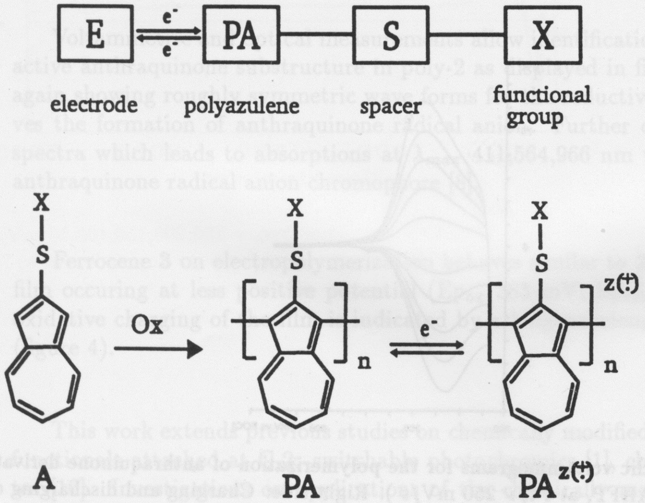
## ABSTRACT

Redox-active anthraquinone and ferrocene functional groups covalently linked to electronically conducting polyazulenes (PA) are accessible by electropolymerization of the C-2 substituted azulenes **1** and **2**. The polymer films were characterized by electrochemical and spectroelectrochemical methods.

## INTRODUCTION

Compared to the multitude of investigations reported on conducting organic polymers and its potential technical application and utilization for example in chemically modified electrode chemistry the publications on polyazulenes **PA** are less frequently, this particularly applies to functionalized compounds [1,2]. Nevertheless, polyazulenes as likewise azulenes are expected to have a distinctive electron transfer characteristics in consequence of the nonalternant topology of the molecular frame [3]. With an efficient synthesis of C-2 substituted azulenes in hand [4] we started a program to investigate C-2 functionalized azulenes in order to incorporate them into polyfunctional molecular components with a general setup as shown in scheme 1.



scheme 1.

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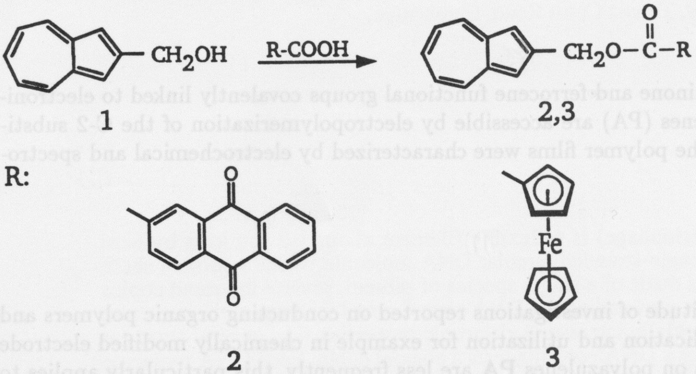
9,10-Anthraquinone and ferrocene azulene-conjugates **2** and **3** were subjected to electropolymerization and the polymeric films were characterized by electrochemical and spectroscopic methods [5].

## RESULTS

### Syntheses

The complete synthetic routes to the monomeric compounds are described elsewhere [4,5]. Azulenes **2** and **3** were synthesized by esterification of hydroxymethylazulene **1** and the corresponding carboxylic acids.



### Electropolymerization and electrochemical and optical properties of the polymer films

The first voltammetric cycle of **2** in fig. 1 (left side) clearly indicates the fast irreversible dimerization or coupling of azulene radical cation $2^{\cdot+}$ formed by oxidation. The nucleation and growth of the polymer film is demonstrated by multisweep cyclic voltammetry. The charging

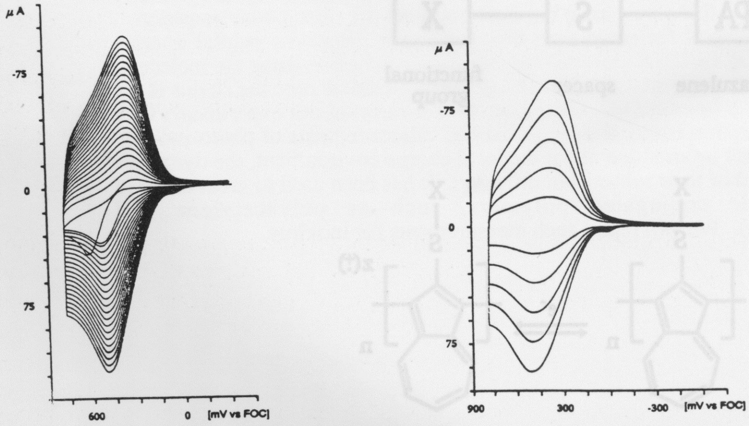


Fig. 1. **Left side: Multisweep cyclic voltammograms for the polymerization of anthraquinone derivative 2** (acetonitrile, 0.1M TBAHFP, **at Pt, $\nu$ 250** mV/s ). Right side: Charging and discharging of a polymer film ( acetonitrile, 0.1 M TBAHFP, monomer free, $\nu$ 250,200,150,100,50 mV/s).

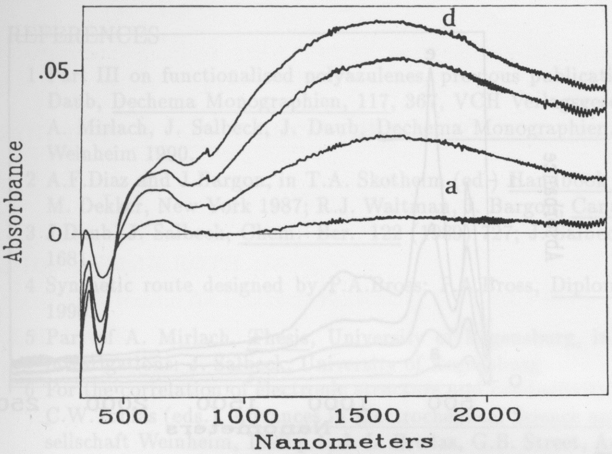


Fig. 2. **Absorption spectra ( difference spectra) of the polymer film of poly-2 taken during** the doping cycle at different voltages, curve a: 800 mV, curve d: 1200 mV (vs Ag/AgCl).

and discharging of the polymer film of poly-**2** (figure 1, right) shows almost mirror-symmetric oxidativ and reductive waves.

Spectroelectrochemistry using optically transparent electrodes (OTEs) allows to obtain the optical spectra during the process of p-type doping of the polymer film of poly-**2** (fig. 1). On oxidative charging a broad absorption band at $\lambda_{max}$ 1575 nm appears. On the nature of this transition will be reported separately [6]. Poly-**2** as do the other C-2 functionalized polyazulenes **exhibit electrochemichromism** .

Voltammetric and optical measurements allow identification and assignment of the electroactive anthraquinone substructure in poly-2 as displayed in fig. 3. The cyclic voltammogram again showing roughly symmetric wave forms for the reductive and oxidative scan clearly proves the formation of anthraquinone radical anion. Further confirmation comes from optical spectra which leads to absorptions at $\lambda_{max}$ 411,564,966 nm which are typically for the 9,10-anthraquinone radical anion chromophore [8].

Ferrocene **3** on electropolymerization behaves similar to **2** with the growth of the polymer film occuring at less positive potential ($Ep_{ox}$ 383 mV; $Ep_{red}$ 271 mV, vs FOC). Again, the oxidative charging of the film is indicated by a long-wavelength absorption at $\lambda_{max}$ 1685 nm (figure 4).

This work extends previous studies on chemically modified polyazulenes with the following functionals attached at C-2: switchable photochromics [1], chiral groups [9], and carbohydrates [10]. Investigations on applications of the chemically modified polyazulenes in electrode chemistry and in electrocatalysis are in progress.

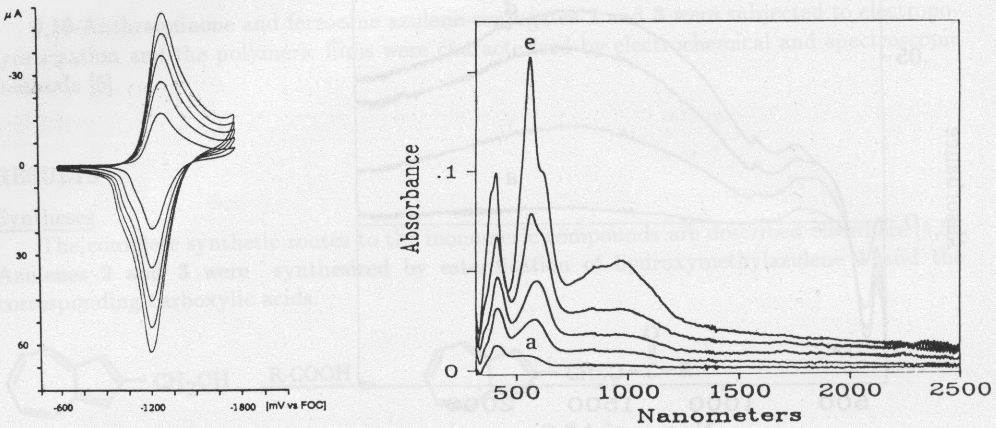


Fig. 3. Cyclic voltammograms in acetonitrile ,0.1M TBAHFP, monomer free, ν 250,200,150,100,50 mV/s) and spectroelectrochemistry of poly- **(2)** of the reductive domain ( a) -750 mV, e) -1150 mV vs Ag/AgCl).

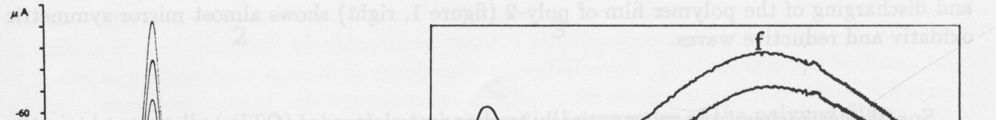


Fig. 4. Cyclic voltammogram (acetonitrile, 0.1M TBAHFP, monomer free, ν 250,200,150,100,50 mV/s) the polymer film of poly-3 (left) and absorption difference spectra at various doping levels, a) 700 mV, f) 1050 mV (vs Ag/AgCl) (right).

## ACKNOWLEDGEMENTS

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