

Supporting information for “Electronic Structure and Properties of Poly- and Oligoazulenes”

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Experimental Part

Synthesis

The 1,3-azulene oligomers **Az₂** - **Az₆** were synthesized from 1-bromoazulene and 1,3-dibromoazulene by a Ni-catalyzed coupling reaction according to ref.¹.

Az₂: C₂₀H₁₄ (254.33 g·mol⁻¹), m.p.: 103-104 °C; EI-MS (70eV): M⁺: 254 (100%), M²⁺: 127 (17 %).

Az₃: C₃₀H₂₀ (380.49 g·mol⁻¹), m.p.: 115 °C; EI-MS (70eV): M⁺: 380 (100%), M²⁺: 190 (11 %).

Az₄: C₄₀H₂₆ (506.65 g·mol⁻¹), m.p.: 193-196 °C; EI-MS (70eV): M⁺: 506 (100%), M²⁺: 253 (23 %).

Az₅: C₅₀H₃₂ (632.80 g·mol⁻¹), degr. at 150 °C; EI-MS (70eV): M⁺: 632 (100%), M²⁺: 316 (21 %).

Az₆: C₆₀H₃₈ (758.96 g·mol⁻¹), degr. at 180 °C; EI-MS (70eV): M⁺: 758 (57%), M²⁺: 379 (17 %).

Soluble chemically synthesized polyazulene (**PAz chem**) was prepared from 1,3-dibromoazulene by a dehalogenative polycondensation catalyzed by the zero-valent nickel complex Ni(COD)₂ as described in ref.².

Electrochemical Setup

Cyclic voltammetry measurements were performed at room temperature using an undivided electrochemical cell with a three-electrode arrangement and a computer controlled EG&G potentiostat/galvanostat 283 A or an Amel 5000 electrochemistry system connected with a plotter. As working electrode we used a home-made platinum disk electrode together with a Ag/AgCl pseudo-reference- and a platinum counter electrode. As supporting electrolyte tetrabutyl-ammonium hexafluorophosphate (TBAH) was used. For electrochemical experiments 5 mg of the compounds were dissolved in 5-8 ml of the solvent. Spectroelectrochemistry of the polymer films was measured in reflection at a home-made platinum disk electrode. Spectroelectrochemistry of the oligomers was carried out in transmission with an electrochemical cell that has been described already in detail.³

The CVs were calibrated by addition of ferrocene as internal standard. According to refs^{4,5}, the redox potential E_{Fc/Fc⁺} in MeCN is -5.15 eV vs. vacuum (by NHE = - 4.75 eV vs. vacuum and E_{Fc/Fc⁺} = 400 mV vs. NHE). For comparison of the Fc/Fc⁺ redox potential in different solvents refs.^{6,7} can be

consulted. Nevertheless, these values have to be handled with care because the use of aqueous reference electrodes in nonaqueous solutions is questionable.⁸ *Jenekhe et al.* proposed a value of $SCE = -4.4$ eV vs. vacuum level.⁹ With $E_{Fc/Fc^+} = 400$ mV vs. SCE⁷ this results in E_{Fc/Fc^+} in MeCN = -4.8 eV vs. vacuum. Since these differences are of more than 0.3 eV, we adjust our data solely vs. Fc/Fc^+ .

DFT Calculations

The density functional theory (DFT) calculations were carried out using the Gaussian03 program.¹⁰ In our study we used the BHandHLYP hybrid functional at the 3-21G basis set. The geometries of all derivatives were optimized imposing C_2 symmetry. The transition energies and oscillator strengths were calculated with the time dependent DFT formalism.

Electrochemistry of azulene and PAz chem

First we elucidated whether chemically polymerized azulene **PAz chem** undergoes a reversible oxidation process or further polymerization is possible. For this reason we compared the electrochemical behavior of monomeric azulene and **PAz chem** in dichloromethane because both materials are highly soluble in this solvent. **Figure S1** shows the potentiodynamic polymerization of azulene (**a**) and the cyclic voltammogram (CV) of **PAz chem** (**b**) under equal conditions but at different potential ranges. The polymerization of azulene was initiated by an oxidative wave at 800 mV (vs. Ag/AgCl pseudo-reference electrode) in the first cycle leading to the formation of polyazulene (**PAz el**). When ferrocene was added as internal standard before the polymerization was started, the initial oxidative wave was at about 600 mV vs. Fc/Fc^+ . The current-potential behavior in the next cycles differed remarkably from the initiating cycle. The current between 0 and 1000 mV increased with each cycle because an additional polymer layer at the electrode surface had to be charged and discharged again. In contrast to this behavior the cathodic current peak between -200 and -600 mV decreased. This current could be assigned to the reduction of protons at the platinum electrode being released during the polymerization.

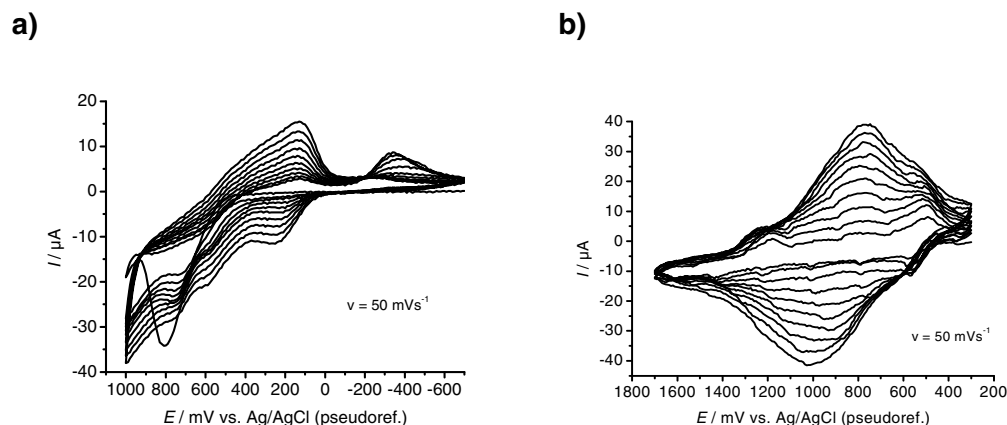


Figure S1. CVs of azulene (a) and **PAz chem** (b) in CH_2Cl_2 with TBAH (0.2 M) as supporting electrolyte. In both CVs 10 cycles were measured with a scan rate of $v = 50 \text{ mV s}^{-1}$. In contrast to azulene that underwent electrochemical polymerization **PAz chem** crystallized at the electrode surface.

The CV of the electrochemical polymerization of azulene in CH_2Cl_2 looks similar to the CV reported for electrochemical polymerization in acetonitrile.¹¹ In acetonitrile the initial oxidative wave was at about 670 mV vs. Fc/Fc^+ .¹² When **PAz chem** was investigated under potentiodynamic conditions (**Figure S1b**), no initiating cycle could be observed that clearly differed from the following cycles. The shape of the first cycle was formed by some oxidative sub-waves. At further cycles the shape of each cycle changed marginally compared to the previous which eventually lead to only one mayor oxidative wave dominating the tenth cycle. This linear change was less intense at lower concentration of **PAz chem** or at lower scan rate v . Therefore, this behavior might not be caused by any electrochemical reaction but by the charging and discharging process that depends on the thickness of the polymer layer and scan rate. These results imply that, as opposed to azulene, **PAz chem** did not undergo any further electropolymerization but crystallized at the electrode surface. This interpretation is reasonable because the charge as well as the electronic spin should be at least partially delocalized in an oligomer or even more in a polymer chain which should lead to a drastically decreased reactivity. When ferrocene was added as internal standard before the crystallization was started, the first oxidative subwave of **PAz chem** was found to be about -40 mV vs. Fc/Fc^+ . As expected for highly conjugated systems, the

oxidation of **PAz chem** (at -40 mV vs. Fc/Fc⁺) was possible at a significantly lower potential than the oxidation of the monomer (at 600 mV vs. Fc/Fc⁺). In **Figure S2** the CVs of films of **PAz el** and **PAz chem** in monomer free solution at different scan rates are depicted. In both cases the oxidation (doping) of the polymer films was reversible in the displayed potential range and the current increased linearly with scan rate as expected for a process without limiting diffusion. When the oxidation was carried out up to higher doping levels (i.e. to higher potentials), particularly the CVs of **PAz el** showed some decrease in current with each cycle (data not shown).

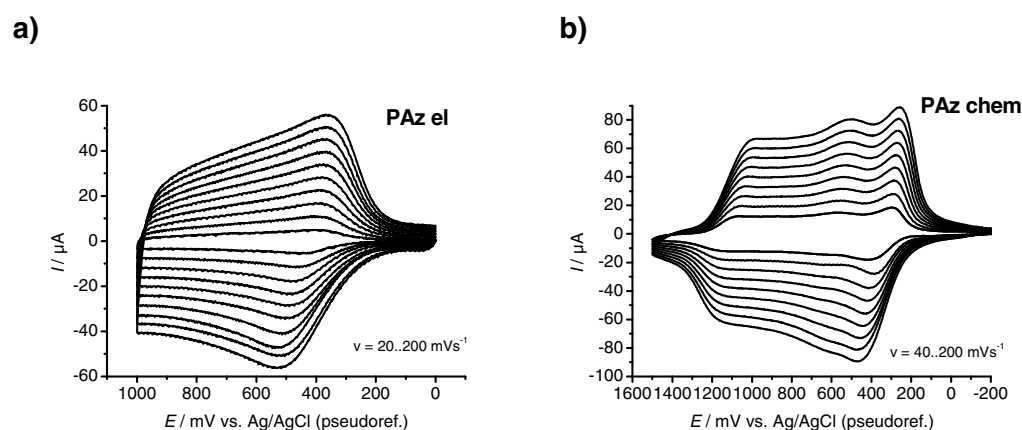


Figure S2. CVs of films of **PAz el** (a) and **PAz chem** (b) in monomer free solution (CH₂Cl₂ with TBAH, 0.2 M as supporting electrolyte) at different scan rates up to $\nu = 200 \text{ mV s}^{-1}$. The scan rate was increased in steps of 20 mV s^{-1} (smallest to largest cycle).

In contrast to **PAz el** the CVs of **PAz chem** showed a fine structure formed by some oxidative sub-waves almost with the same shape as in the first cycle of the electrochemical crystallization process. This might be explained by the presence of different oxidation potentials within the polymer strands going along with the formation of polarons or bipolarons (or polaron pairs) depending on the doping level.¹³ The absence of any fine structure in the CVs of **PAz el** enforces the assumption that an oligomer mixture or polydisperse polymers were formed. We mention here that we have not been able to determine the exact molecular weight distribution of **PAz el** or **PAz chem** with the experimental

techniques which were available to us. Therefore, we could not go further into detail. However, the absolute length of the chemically synthesized polymer chains should not be a crucial parameter because even in the doped state the absolute conjugation length of **PAz chem** is not expected to be beyond 10 monomer units.

Spectroelectrochemistry of films of **PAz₂** and **PAz₃** in monomer free solution

When **Az₂** and **Az₃**, were polymerized electrochemically, the spectra of the resulting polymer films exhibited somewhat more homogeneous absorption spectra upon stepwise oxidation than those of **PAzel** in **Figure 3b** in the main manuscript.

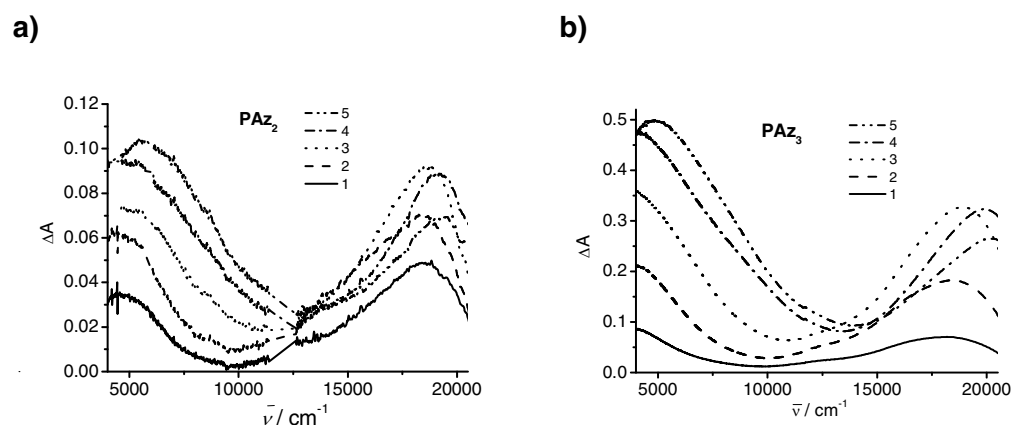


Figure S3. Spectroelectrochemistry of films of **PAz₂** (a) and **PAz₃** (b) in monomer free solution (solvent: CH₂Cl₂, supporting electrolyte: 0.2 M TBAH). Difference spectra presenting the optical changes collected during the stepwise oxidation (increased doping level from 1 to 5).

Bond distances and the dihedral angles for neutral Az₈

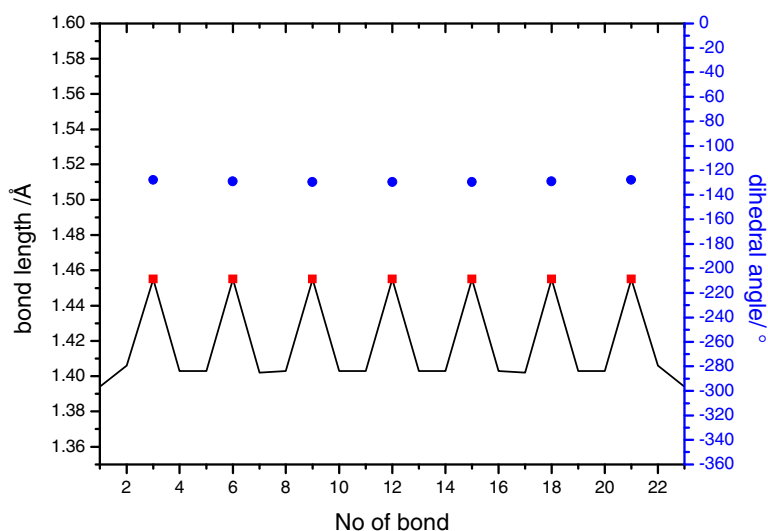


Figure S4. Bond distances and dihedral angle between two adjacent azulene monomers for neutral Az₈.

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