# Redox-Switchable Squaraines with Extended Conjugation

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**ABSTRACT**
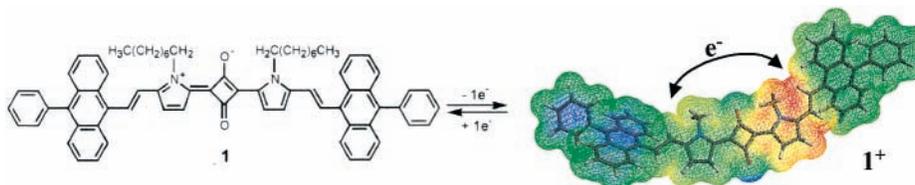


The redox chemistry of $\pi$-extended squaraines is investigated using cyclic voltammetry, in-situ spectroelectrochemistry and quantum chemical calculations. Squaraine 1 is reversibly oxidized to the radical cation and dication whereas reduction shows limited electrochemical but fully chemical reversibility. The radical cation of 1 reveals absorption bands at 1000 nm and a "two-band feature" at 1600 nm. Their implications on the intramolecular electron transfer are discussed.

Low-molecular-weight functional $\pi$-conjugated systems have attracted considerable interest in the design strategy of molecule-based optoelectronic devices since they can be encoded with application-oriented and selectively addressable optoelectronic properties.[1,2] Especially for a single-electron-based approach, molecular wires and donor−bridge−acceptor systems are of basic necessity. To understand their electronic properties, the study of smaller conjugated $\pi$-segments seems advisable, especially if assembled through arrays of organic dye molecules with novel optical properties.

We report here the synthesis and the redox switching properties of squaraine conjugates comprising a central squaraine unit and peripheral arylethenes. Both components are widely seen in several functional molecular materials. For example, squaraines are extensively used in applications such as xerography, imaging, optical recording, organic solar cells, and nonlinear optics.[3] Stilbenoid systems and phenylenvinylene based materials are main components in the wide field of molecular switching, in light-emitting devices, and in semiconducting organic materials.[4]

In recent years, several reports on the synthesis of $\pi$-extended squaraine dyes,[5] low-band-gap polysquaraines,[6] and squaraine-based chemosensors[7] were published. For

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anilino and indolenium squaraines, electrochemical as well as spectroelectrochemical investigations were hampered by the insufficient stability of the charged donor−acceptor bridge systems.[8] In the present work, the redox chemistry of the $\pi$-extended squaraines **1−3** is studied in detail. Optical properties of the electrochemically generated species are also discussed. Cyclic voltammetry and spectroelectrochemistry are used as analytical tools.[9]
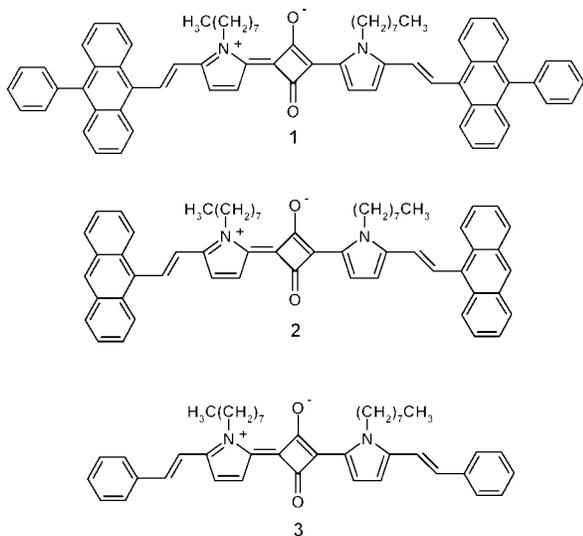


Syntheses of the dyes **1−3** were accomplished by condensation of appropriate pyrrol derivatives with squaric acid according to known procedures.[10] The cyclic voltammograms of compounds **1−3** are shown in Figure 1. It is shown that
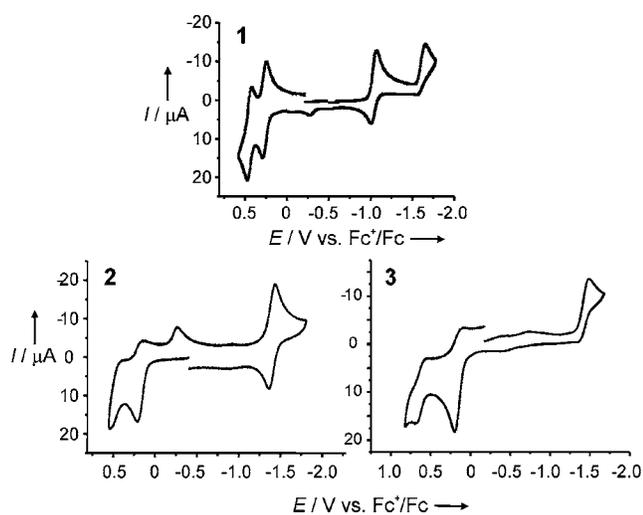


**Figure 1.** Cyclic voltammograms of **1−3** in CH$_2$Cl$_2$: 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte; scan rate, 250 mV/s.

compound **1** exhibits the highest degree of reversibility (two reversible oxidation steps, and a one-electron reduction with limited reversibility) clearly indicating that the higher

stabilization of the radical ions and the dication is ensured by the phenylanthracenyl unit. It is shown that blocking the meso (C-10) position of the anthracene unit increases reversibility.

The half-wave potentials of squaraines **1−3** are shown in Table 1. The almost equal reduction potentials of all three

**Table 1.** Comparison of the Half-Wave Potentials (mV vs Fc$^+$/Fc) of **1−3** in Dichloromethane with Tetrabutylammonium Hexafluorophosphate as the Supporting Electrolyte (Peak Potential Separation in Parentheses)

|   | $E_{1/2}^{ox1}$ | $E_{1/2}^{ox2}$ | $E_{1/2}^{red}$ |
|---|---|---|---|
| 1 | 250 (60) | 460 (65) | −1300 (75) |
| 2 | 235[a] | 540[a] | −1380 (70) |
| 3 | 195[a] | 680[a] | −1355[a] |

[a] Peak potentials $E^p$.

dyes account for only minor contribution of the peripheral substituents (phenyl, anthracenyl, and phenylanthracenyl, respectively) to the LUMO-dominated radical anion formation. The negative charge is therefore localized at the central pyrrole−squaraine−pyrrole unit.

Quantum chemical calculations of the geometries and charge distributions of **1** in different oxidation states were performed at the AM1 level.[11] This is supported by DFT[12] calculations (B3LYP-6-31G*) of geometries and IR spectra of a pyrrole appended squaric acid, which lacks the peripheral substituents.[13] One of the results of these calculations is that the pyrrole−vinyl subunits have to be regarded as the effective redox centers in the oxidative process (see Figure 2).[14] Second, the calculations also predict that the spreading of the positive charges is extended further to the anthracene substructures. This is in agreement with the finding of reduced stability of the oxidized forms of compounds **2** and **3**. The oxidation to the radical cation disintegrates obviously the conjugated $\pi$-systems of **1−3** into an donor−bridge−acceptor system comprising positively charged and neutral stilbenoids as acceptor and donor subunits, respectively, and the squaraine as the bridge.

Upon one-electron reduction, the absorption at 680 nm of **1** decreases leading to new absorption bands with low

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(14) Calculated reorganisation energies (upon oxidation) of 0.567 eV are significantly high; see also: Knorr, A.; Daub, J. *Angew. Chem., Int. Ed.* **1997**, *36*, 2817.
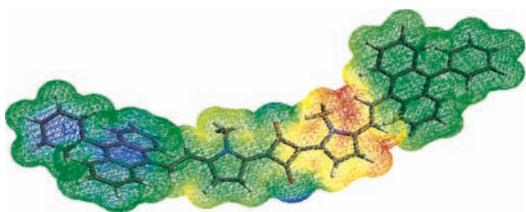
**Figure 2.** Calculated charge distribution in $1^+$.

extinction coefficients beyond 300 nm (Figure 3). After reoxidation, the initial spectrum is fully restored. Compound
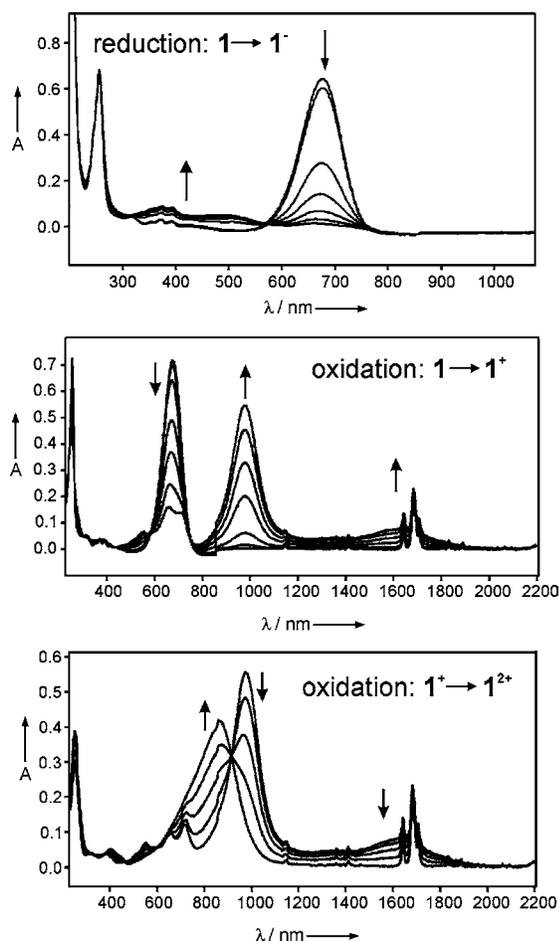


**Figure 3.** UV/vis/NIR spectroelectroelectrograms of **1**.

**1** can therefore be considered as an electrochemically driven on/off switch of the NIR absorption.[15] The complete loss of the charge-transfer transition indicates a severe change in the electronic properties of the central squaraine. Dimerization under C−C bond formation may rationalize the spec-

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troscopic findings.[16] The feature of the cyclic voltammogram can also be taken as an indication for a fast dimerization step leading to cathodic and anodic peak currents with unequal magnitude. This assumption is also supported by the fact that the carbonyl stretching frequency of **1** (neutral form of **1**: $\bar{\nu} = 1620$ cm$^{-1}$) is shifted toward lower wavenumbers on reduction (**1**: $\bar{\nu} = 1590$ cm$^{-1}$).

Upon oxidation of **1**, new electronic absorptions at about 1000 and 1600 nm appear, which are ascribed to the radical cation $1^+$ (Figure 3). Further oxidation leads to a decrease of the radical cation absorptions. A new absorption band arises at 850 nm, which is in agreement with the formation of the dication $1^{2+}$. After back-reduction to the neutral dye the initial spectrum is fully recovered.

The two reversible couples of oxidation yield a potential difference $\Delta E = 210$ mV from which a comproportionation constant $K_{co} = 3560$ can be derived. According to Robin/Day classification, radical cation $1^+$ is assigned as a class III system with strongly coupled donor/acceptor units.[17]

Analysis of the UV/vis/NIR spectra of radical cation $1^+$ provided further insight into the electronic structure. Figure 4 displays a plot of the NIR absorption vs wavenumbers,
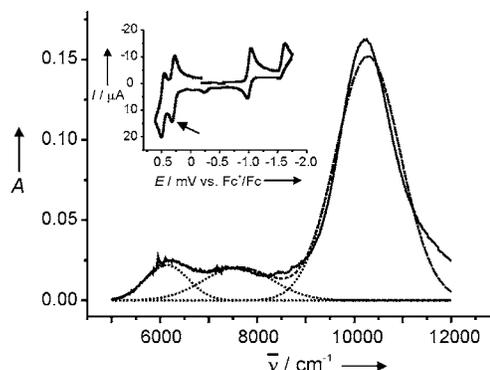


**Figure 4.** UV/vis/NIR spectroelectrochemistry: plot of the intensity of the long wavelength absorption of $1^+$ vs wavenumbers.

extracted from the spectroelectrochemical experiment. Fitting the spectrum with Gaussian-shaped curves gives two absorption bands in the long wavelength region. This leads to the conclusion that the bridging squaraine unit may also participate in the intramolecular electron transfer on the radical cation state (hopping from the radical cation subunit to the bridge).[18]

FT-IR spectroelectrochemistry is also a useful method to characterize the oxidation process. In the neutral form of the squaraine dyes, the absorption at 1620 cm$^{-1}$ corresponds to the C−O stretching frequency of the $C_4O_2$ moiety.[19] The

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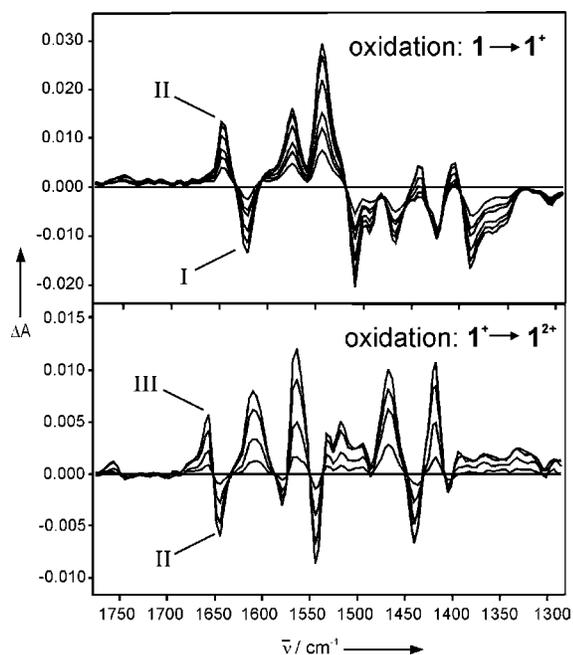
**Figure 5.** FT-IR spectroelectrochemistry of the oxidation processes of **1**: first (top) and second (bottom) oxidation; presented are the differential spectra with the initial spectrum as the zero line; indication of the $C_4O_2$ stretching vibration in **1** (I), **1$^+$** (II), and **1$^{2+}$** (III).

pyrrole vibration bands are expected in the region of 1600−1450 cm$^{-1}$. Upon oxidation of **1** to **1$^+$**, the maximum of the stretching frequency is shifted to higher wavenumbers by 25 cm$^{-1}$ accounting for a strengthening of the C=O bond. Thus, the squaraine bridge sensitively reports on positive charging. It is not surprising that on oxidation of **1$^+$** to **1$^{2+}$**

the band is shifted by an additional 29 cm$^{-1}$. In summary, we have shown that proper functionalization of squaraines, as, for example, compound **1**, are valuable probes for studying intermolecular interaction and molecular switching, depending on the redox state. Two reversible one-electron oxidations lead to a stable radical cation and dication with significant spectral changes. Reduction leads in a one-electron transfer to the radical anion, which has limited stability. From the spectroscopic properties, a dimerization of the radical anion is postulated. The overall process (electron transfer and chemical dimerization) is however chemically reversible. It is assumed that oxidation leads to an electronic situation at the mixed valent radical cation stage in which the positive charge primarily is localized on the vinylpyrrole subunits. However, exchange within the molecular entity may either occur to the squaraine bridge or the second peripheral vinylic unit. Studies in order to quantify these results are underway.

**Supporting Information Available:** Synthetic procedures for the preparation of **1−3**, electrochemical data for **1−3**, and calculated charge distributions of **1**, **1$^+$**, and **1$^{2+}$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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