Violene/Cyanine Hybrids, Part 1

Violene/Cyanine Hybrids: A General Structure for Electrochromic Systems

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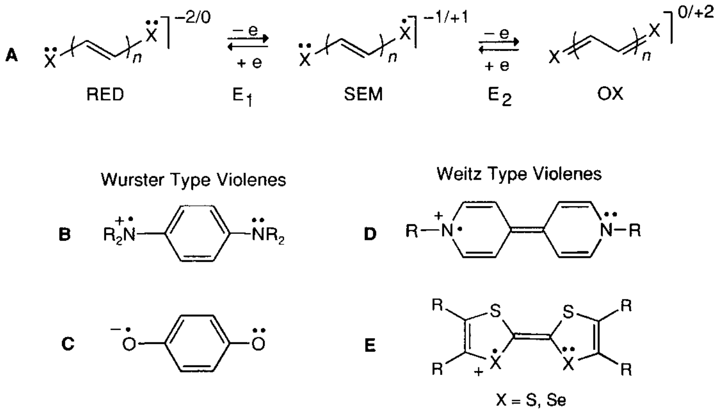
Abstract: Organic electrochromics are mainly based on two-step redox systems of the violene type, in which radical ions represent the long-wavelength-absorbing species. Since closed-shell systems are expected to be more persistent a new structural principle is developed that contains both the violene and the cyanine type. The latter provides the colored species. The scope of this new and general principle is demonstrated by several examples with oxidation levels ranging from −4 bis +4.

Keywords: cyanines · electrochemistry · electrochromics · redox chemistry · violenes



Introduction

Electrochromic behaviour is observed with reversible redox systems that display distinct changes of their absorption spectra in different oxidation states. This long-known phenomenon has gained rising importance in advanced materials and therefore both its theoretical background and its applications are actively investigated.[1]

Most of the organic electrochromic systems are based on the general structure A of two-step redox systems in which the radical ions SEM$^{+/-}$ are called violenes.[2] These radical ions, exemplified by **B – E**, always represent the species with the longest wavelength absorptions and highest extinction coefficients within the system.[2c] To achieve high color intensity these violenes must have high thermodynamic stability, for example $K_{\text{SEM}} = 2\,\text{SEM}/([\text{RED}] + [\text{OX}])$ has to be large.

Based on the appropriate combination of Wurster and Weitz type systems in an undivided electrochemical cell[3] highly efficient self-darkening rear-view mirrors for cars have been developed.[4] Nevertheless, open-shell systems tend to decompose more rapidly than similar closed-shell ones, since radical reactions are often connected to low activation energies. Therefore, electrochromic systems in which the colored forms also consist of closed shell moieties should, in principle, improve their persistency.

A new principle: We now propose the general structure **F** for these systems; this capitalizes on the well-documented reversibility of the violene-type redox system, but contains end groups that in the fully reduced or oxidized form represent delocalized closed-shell polymethine dyes (cyanines, oxonols, and merocyanines[5]). Owing to the strong thermodynamic stabilization of that delocalized polymethine type and also enforced by steric repulsions from planarity, the concentration of the radical ions SEM may even drop to zero, for example, the redox process may approach a two-electron transfer.

Owing to the great variability of both the violene- and cyanine-type structures, the general structure **F** can be found

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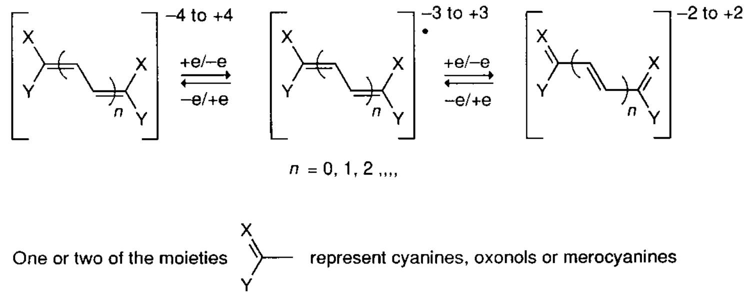
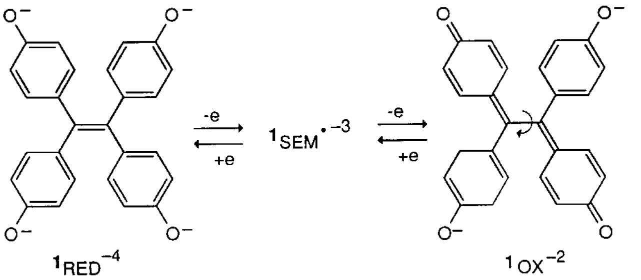
F



in already known compounds and allows to design a wealth of new systems. This communication illustrates the general structural principle with some representative examples of **F** with charges ranging from −4 to +4 emphasizing on their redox and electrochromic properties.

Results and Discussion

System 1: The long-known tetrakis(4-hydroxyphenyl)ethene[6] has been found to turn blue in basic solution. Later,[7] the blue color was ascribed to $\mathbf{1}_{\mathrm{OX}}^{-2}$, which consists of two oxonol systems connected through the central carbon atoms. System **1** can be depicted as the redox system in Scheme 1. We prepared the deep blue dipotassium salt of $\mathbf{1}_{\mathrm{OX}}^{-2}$, which showed reversible transfer of two electrons at rather negative potentials and two irreversible oxidation waves at positive potentials (Figure 1). Reduction of $\mathbf{1}_{\mathrm{OX}}^{-2}$ to $\mathbf{1}_{\mathrm{RED}}^{-4}$ is confirmed by the spectroelectrogram of Figure 2. Since $\mathbf{1}_{\mathrm{OX}}^{-2}$ is reversibly decolorized by reduction and diplays a sharp isosbestic, point there is no room for substantial amounts of (colored) $\mathbf{1}_{\mathrm{SEM}}^{-3}$.



Scheme 1. The redox system for **1**.

Abstract in German: *Organische elektrochrome Verbindungen leiten sich vorwiegend von zweistufigen Redoxsystemen vom Violentyp ab, in denen die langwellig absorbierende Spezies ein Radikalion ist. Da von Closed-shell-Systemen eine höhere Persistenz zu erwarten ist, wurde ein neues Strukturprinzip entwickelt, das sowohl den Violen- als auch den Cyanintyp enthält. Letzterer stellt die farbige Spezies. Die Anwendungsbreite dieses neuen, allgemeinen Prinzips wird an Beispielen demonstriert, deren Oxidationsstufen von −4 bis +4 reichen.*

System 2: Tetrakis(dimethylaminophenyl)ethene ($\mathbf{2}_{\mathrm{RED}}$) is known since 1906[8] and has been chemically oxidized to its dication.[8, 9] Cyclic voltammetry (CV) reveals two completely reversible redox potentials at about −0.30 V and +0.67 V (Figure 3). These potentials, however, again do not repre-

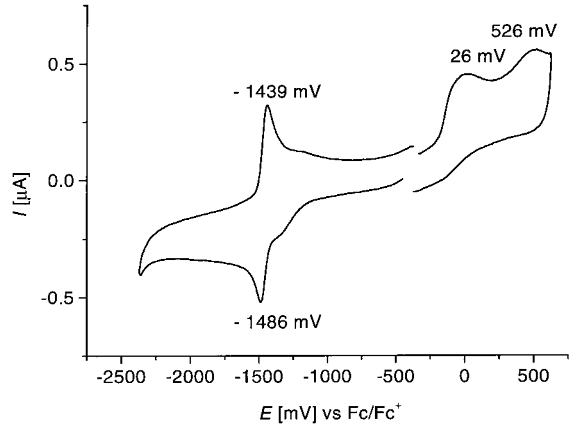


Figure 1. Cyclic voltammogram of $\mathbf{1}_{\mathrm{OX}}^{-2}\cdot 2\,\mathrm{K}^+$ in MeCN vs. $\mathrm{Fc}^0/\mathrm{Fc}^+$ ($\mathrm{Fc}^0/\mathrm{Fc}^+ = +\ 0.39$ V vs. Ag/AgCl), $n\mathrm{Bu}_4\mathrm{N}^+\mathrm{BF}_4^-$, scan rate 100 mV s^{-1}.

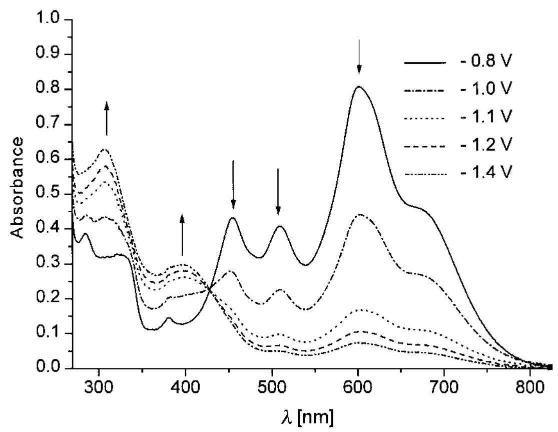


Figure 2. Spectroelectrogram of $\mathbf{1}_{\mathrm{OX}}^{-2}\cdot 2\,\mathrm{K}^+$ in MeCN; potentials are given vs. Ag/AgCl; supporting electrolyte $n\mathrm{Bu}_4\mathrm{NPF}_6$.

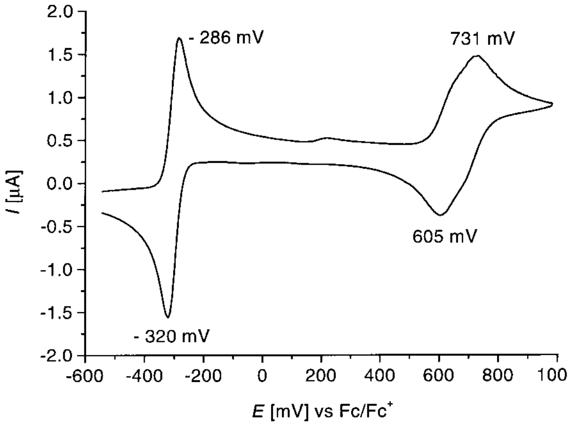
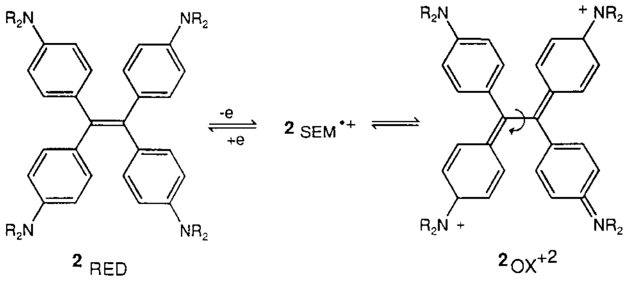


Figure 3. Cyclic voltammogram of $\mathbf{2}_{\mathrm{RED}}$ in MeCN vs. $\mathrm{Fc}^0/\mathrm{Fc}^+$, $n\mathrm{Bu}_4\mathrm{N}^+\mathrm{BF}_4^-$, scan rate 100 mV s^{-1}.

sent the presumed two-step redox system $\mathbf{2}_{\mathbf{RED}} \rightleftharpoons \mathbf{2}_{\mathbf{SEM}}{}^{\bullet+} \rightleftharpoons \mathbf{2}_{\mathbf{OX}}{}^{+3}$ (Scheme 2).

Instead, the first redox process already comprises transfer of two electrons. The spectroelectrogram (Figure 4) again reveals a sharp isosbestic point. The formation of the two broad absorption bands in the visible region must be ascribed to $\mathbf{2}_{\mathbf{OX}}{}^{+2}$, since ESR spectroscopy reveals only traces of $\mathbf{2}_{\mathbf{SEM}}{}^{\bullet+}$. The dication $\mathbf{2}_{\mathbf{OX}}{}^{+2}$ can be desribed as two directly connected moieties of Michlers hydrol blue.



Scheme 2. The redox system for **2**.

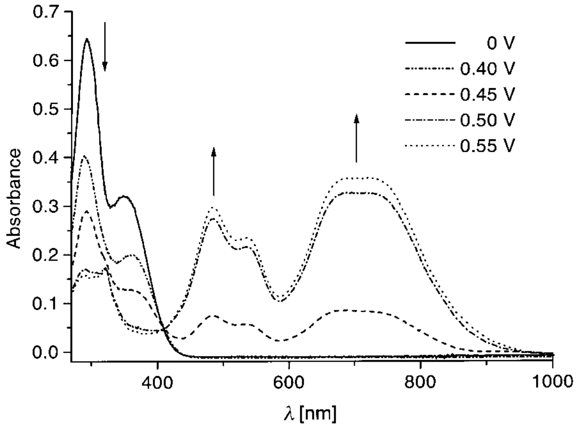


Figure 4. Spectroelectrogram of $\mathbf{2}_{\mathbf{RED}}$ in MeCN; potentials are given vs. Ag/AgCl; supporting electrolyte $n\mathrm{Bu_4NPF_6}$.

System 3: Several variations of violene/cyanine hybrids are demonstrated by system **3**: a) the oxidation level can be raised to +4, b) vinyl analogues of the basic ethene core in **F** can be employed, and c) aza substitution of the olefinic core is allowed. The colorless salt $\mathbf{3}_{\mathbf{OX}}{}^{+4}\cdot 4\,\mathrm{BF_4}^-$ was prepared from 4,4′-dipyridyl ketone[10] and hydrazine, and subsequent alkylation of the azine by triethyl oxonium tetrafluoroborate.[11] Reduction of $\mathbf{3}_{\mathbf{OX}}{}^{+4}$ (Scheme 3) finally yields $\mathbf{3}_{\mathbf{RED}}{}^{+2}$, in which two cyanine moieties are linked by an azo group.

As can be judged from the cyclic voltammogram the relevant nearly reversible process occurs already at about 0.5 V versus Fc^0/Fc$^+$ (Figure 5). The two peak potentials at −518 mV and −609 mV may indicate stepwise transfer of two electrons; however, this is not to be seen on reoxidation with only one peak potential at −458 mV. Only at very negative potentials (ca. −2 V vs. Fc^0/Fc$^+$) is another electron transfer indicated (Figure 5). On reduction of colorless $\mathbf{3}_{\mathbf{OX}}{}^{+4}$ the solution develops a strong violet color, which must be attributed to $\mathbf{3}_{\mathbf{RED}}{}^{+2}$, due to a rather well-developed isosbestic point (Figure 6). If the two peak potentials in Figure 5 result from kinetic control (time scale: seconds) the intermediate radical species $\mathbf{3}_{\mathbf{SEM}}{}^{+3}$ will hardly show up in the spectroelectrogram owing to the time scale of minutes to hours for each plot.

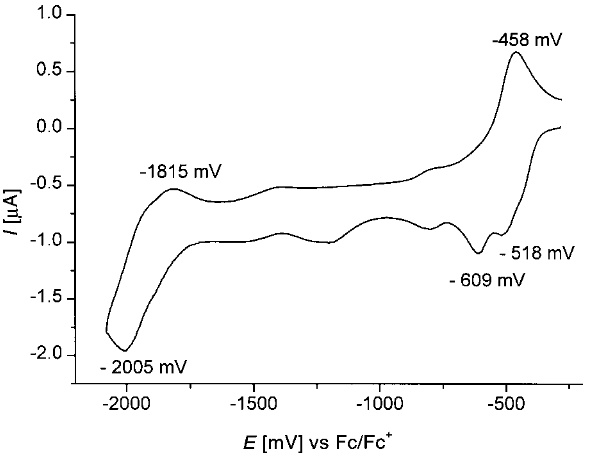


Figure 5. Cyclic voltammogram of $\mathbf{3}_{\mathbf{OX}}{}^{+4}\cdot 4\,\mathrm{BF_4}^-$ in PhCN vs. Fc^0/Fc$^+$, $n\mathrm{Bu_4N^+BF_4}^-$, scan rate 100 mV s^{-1}.

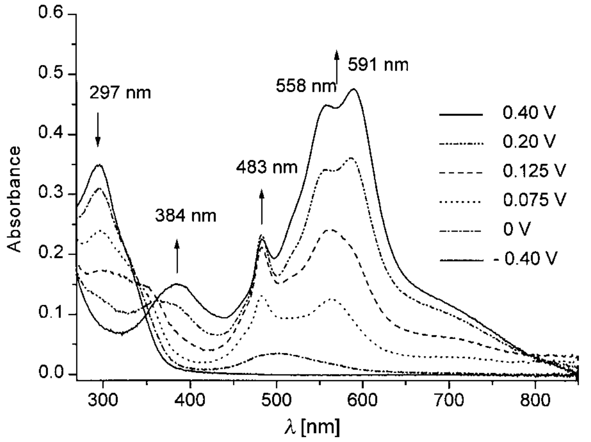
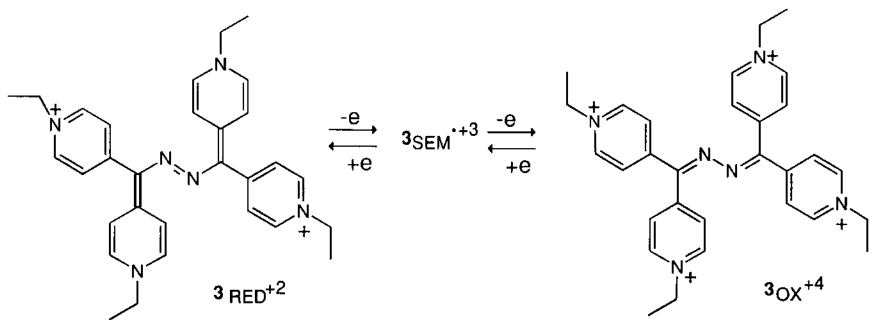


Figure 6. Spectroelectrogram of $\mathbf{3}_{\mathbf{OX}}{}^{+4}\cdot 4\,\mathrm{BF_4}^-$ in MeCN; potentials are given vs. Ag/AgCl; supporting electrolyte $n\mathrm{Bu_4NPF_6}$.

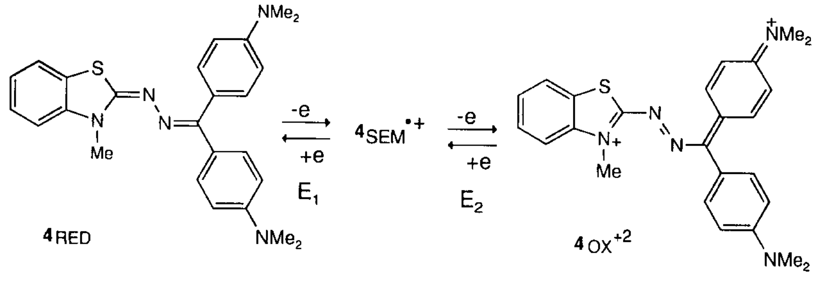
System 4: This example was selected to demonstrate hybridization of the violene system



Scheme 3. The redox system for **3**.

with a cyanine type structure at one end of the molecule only. From thio-Michlers ketone[12] and *N*-methylbenzothiazolone hydrazone[12] $\mathbf{4}_{\mathrm{RED}}$[11] is easily available (Scheme 4).

The cyclic voltammogram of $\mathbf{4}_{\mathrm{RED}}$ (Figure 7) now reveals two completely reversible redox waves that correspond to two single-electron transfers (comparison with one equivalent of ferrocene). Another nearly irreversible peak at about 0.80 V (scan rate $100\,\mathrm{mV\,s^{-1}}$) is not shown. Thus **4** behaves as a typical violene system with $K_{\mathrm{SEM}} = 4.6 \times 10^3\,\mathrm{L\,mol^{-1}}$ thereby resembling the symmetrical violene system *N*-methylbenzothiazolone azine ($K_{\mathrm{SEM}} = 9.3 \times 10^6\,\mathrm{L\,mol^{-1}}$).[13] As a result of its stepwise electron transfer, the spectroelectrogram of **4** is more complex (Figure 8) than those of systems **1**–**3**. Whereas $\mathbf{4}_{\mathrm{RED}}$ shows no absorption above about 430 nm, on slight oxidation a sharp band develops at 450 nm together with a very broad one at about 700–1200 nm, typically observed in violene radical cations.[2c]



Scheme 4. The redox system for **4**.

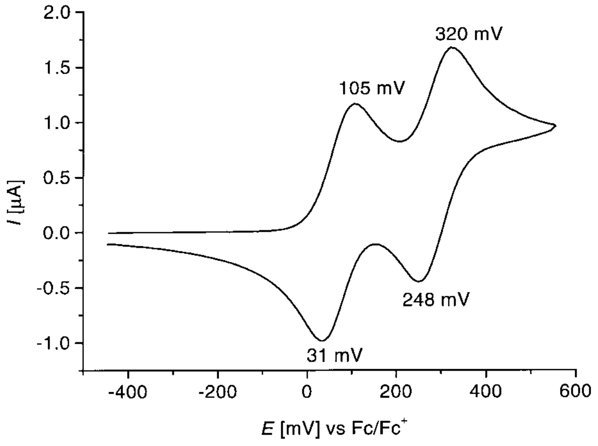


Figure 7. Cyclic voltammogram of $\mathbf{4}_{\mathrm{RED}}$ in MeCN vs. $\mathrm{Fc^0/Fc^+}$, $n\mathrm{Bu_4N^+BF_4^-}$, scan rate $100\,\mathrm{mV\,s^{-1}}$.

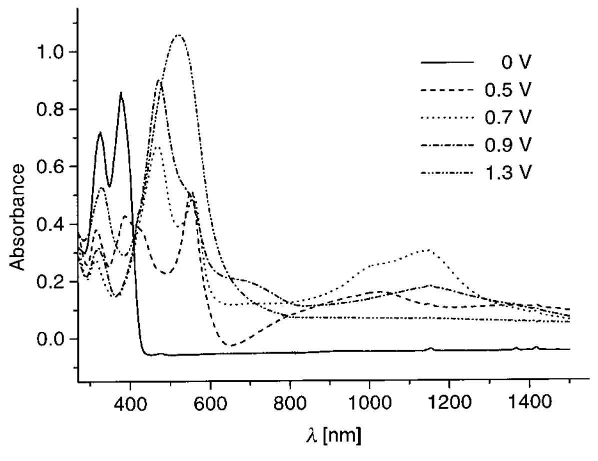


Figure 8. Spectroelectrogram of $\mathbf{4}_{\mathrm{RED}}$ in MeCN; potentials are given vs. Ag/AgCl; supporting electrolyte $n\mathrm{Bu_4NPF_6}$.

Therefore these bands are ascribed to $\mathbf{4}_{\mathrm{SEM}}^{+}$. On further oxidation the NIR band is first strengthened, but finally vanishes. This change is accompanied by a new absorption at 440 nm, which should be caused by $\mathbf{4}_{\mathrm{OX}}^{+2}$. The final somewhat broader band at about 550 nm may contain some higher oxidized species.

Proof of radical states in **2** and **4** (and some other systems)[14] was sought by ESR spectroscopy. As expected, only traces of $\mathbf{2}_{\mathrm{SEM}}^{\bullet+}$ were found in which the single electron is symmetrically distributed over the whole radical cation. In contrast, a much more higher concentration of $\mathbf{4}_{\mathrm{SEM}}^{\bullet+}$ was observed; however, the very broad signals could not be resolved.

Optimized structures (PM3) were calculated for oxidation levels 0 to +4 for **2** and **4** (together with other systems).[14] In all cases the geometries of $\mathrm{SEM}^{\bullet+}$ and SEM^{+3} on the one hand and OX^{+2} together with OX^{+4} on the other are very similar. Thereby, the radical states approach planarity as far as possible, whereas in OX^{+2} and OX^{+4} the two planarized cyanine moieties are arranged nearly perpendicular to one another. The latter situation is pictured in Figure 9 for $\mathbf{2}_{\mathrm{OX}}^{+2}$/$\mathbf{2}_{\mathrm{OX}}^{+4}$ and $\mathbf{4}_{\mathrm{OX}}^{+2}$/$\mathbf{4}_{\mathrm{OX}}^{+4}$.

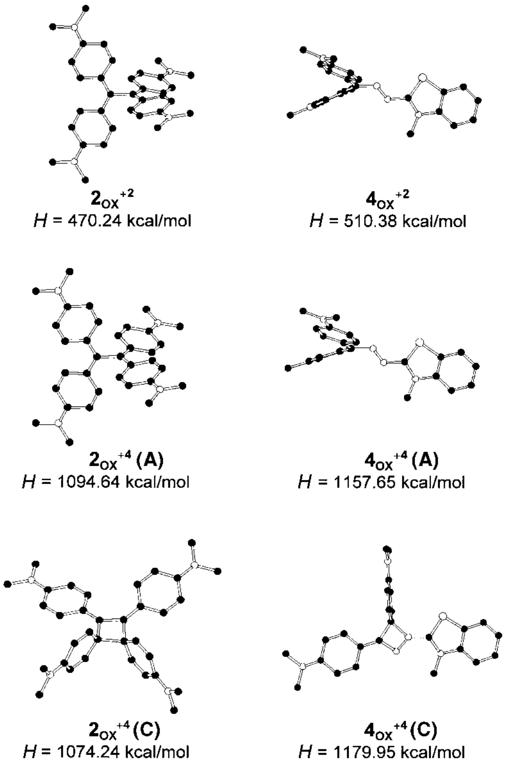


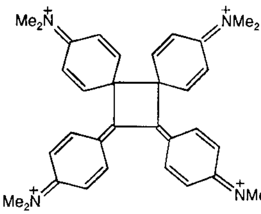
Figure 9. PM3 optimized structures with heats of formation (ΔH). A and C mark the acyclic and cyclic msinima energy structures of the same oxidation level OX^{+4}.

The expected higher energies of OX^{+4} compared to OX^{+2} are clearly indicated. However, in the case of the acyclic **2_{OX}^{+4}(A)** an optimized cyclic structure **2_{OX}^{+4}(C)** with a central cyclobutane ring is evidently the preferred structure owing to its lower energy, as much as 20 kcal mol^{-1}, in comparison with **2_{OX}^{+4} (A)**. We assume that such a cyclic structure is also involved in the redox couple of **1** for **1_{OX}** at positive potentials (Figure 1). By contrast, cyclization of **4_{OX}^{+4}(A)** to the 1,2-diazetine **4_{OX}^{+4}(C)** is unlikely because of its higher energy (by 22 kcal mol^{-1}).

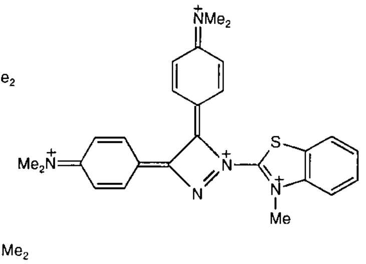
As verification of the general structure **F** for violene/cyanine hybrids examples, **1–3** clearly demonstrate that in these systems the thermodynamic stability typical for violene systems[2] can be dramatically reduced. Both reduced and oxidized forms of these electrochromics consist of closed-shell systems separated by a remarkable large difference in absorption maxima. The colored forms also exhibit very high extinction coefficients. Although closed-shell systems are produced the current efficiency of the violene/cyanine hybrids **F** is the same as violenes **A**: one moiety is colored or discolored by the transfer of one electron.

Conclusions

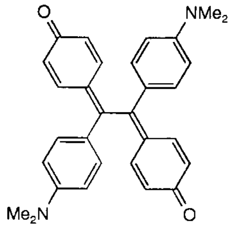
The examples presented above clearly demonstrate that a nearly unlimited number of violene/cyanine hybrids can be designed based on the well-developed chemistry of violenes and polymethines of the cyanine, oxonol, and merocyanine type. Obvious additional examples in connection with systems **1** and **2** are the oxonol/cyanine **5_{OX}** and the bis-merocyanine **6_{OX}**.



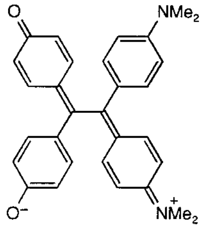
1_{OX}^{+4}(C)



4_{OX}^{+4}(C)



5_{OX}



6_{OX}

As a result of this great variability it should be possible to devise electrochromic systems with properly adjusted change in color and range of potentials based on the general structure **F** outlined in this paper.

Acknowledgments

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[14] Details will be given in Part II of this series.

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