Electrochromics by Intramolecular Redox Switching of Single Bonds**

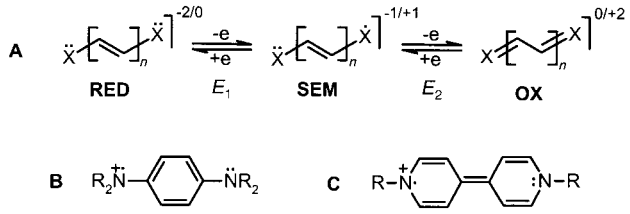
Siegfried Hünig,*[a] Christoph A. Briehn,[a] Peter Bäuerle,[b] and Andreas Emge[b]

Abstract: Two moieties of mono- and trimethincyanines as well as those of styryl dyes were connected by a saturated alkyl tether made from compounds **3a–c**, **5**, **7**, and **9a**,**b**. In most cases, cyclic voltammetry and spectroelectrochemistry for these dyes together with the data for their monomeric models **4**, **6**, **8**, and **10** reveal electrochemically irreversible transfer of two electrons but chemically reversible reaction and discoloration both on reduction and oxidation. Discoloration is interpreted as intramolecular formation of a single bond, which on redox breaking regenerates the starting colored species. Therefore, the investigated dyes exemplify a new general principle for electrochromics.

Keywords: cyanines · cyclic voltammetry · electrochromics · spectroelectrochemistry

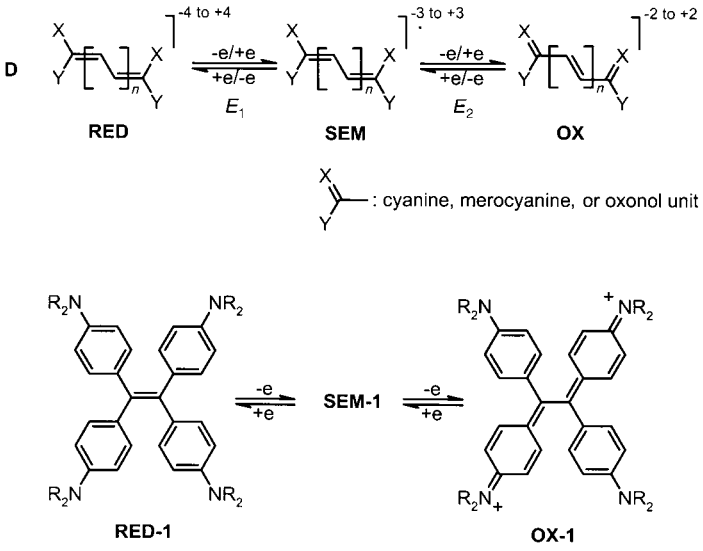
Introduction

The ability of certain compounds to change their color reversibly on transfer of electrons has been intensively studied for their application in electrochromic systems.[1–4] So far, most of the organic electrochromics are based on the general structure **A** of two-step redox systems, in which the open-shell species SEM ("violenes") represents the oxidation state with the longest-wavelength absorption and high thermodynamic stability (cf. Scheme 1 with examples **B** and **C**).[5–8]



Scheme 1. General structure for violene-type electrochromics.

Recently, we have proposed a new type of electrochromics, namely violene/cyanine hybrids with the general structure **D** (Scheme 2).[9–11] In these systems, the ability of violenes to reversibly transfer electrons in a series of steps is principally retained. However, the concentration of SEM is drastically reduced since the formation of two (closed-shell) cyanine-type moieties by transfer of two electrons is preferred. Redox system **1** demonstrates the broad scope of the violene/cyanine hybrids.



Scheme 2. General structure for violene/cyanine hybrid-type electrochromics.

Now, we present another general principle for electrochromics which no longer depends on the violene structure, but capitalizes on the thermodynamic instability of (neutral or ionic) radicals derived from cyanine-type compounds (cyanines, merocyanines, oxonols). Neutral radicals[12] as well as cyanine radical dications[13, 14] derived from tri- and pentamethincyanines have been found to be short lived but able to

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[**] Type OL/CS, Part 1.

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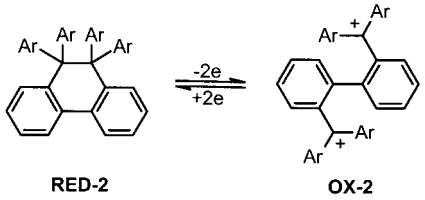
dimerize if sterically not overcrowded. Dimerization of neutral radicals is a generally accepted process. According to recent investigations, dimerization of radical cations even in conducting polymers seems to be much more important than anticipated so far.[15–18] Of course, reversible single-bond formation of appropriate radicals or radical ions should be enhanced and side reactions suppressed if the (formal) intermolecular dimerization is turned into an intramolecular reaction. This approach has already been verified for certain quinone methides (reduction),[19] metal complexes (reduction),[20, 21] octamethoxytetraphenylene (oxidation),[22] and heterocycles connected to ring systems (oxidation[23–25] and reduction[26]). We now extend this structural principle in two versions to electrochromics, which are characterized by strong differences in the light absorption of the reduced and oxidized states.

A structural principle for electrochromics by single-bond redox switching: The two versions of the general principle under discussion are presented in Scheme 3. The **L**ong-wavelength absorption is connected for type OL/CS with the **O**pen state, and the **S**hort-wavelength absorption with the **C**losed state. For type OS/CL, that pattern is reversed. This paper deals only with type OL/CS, whereas discussion of type OS/CL is reserved for Part 2.

Scheme 3 presents only the overall transfer of two electrons since the bond formation may not always follow an EEC[27] mechanism. Bond breaking may occur by an (mesolytic[28, 29]) ECE reaction (chemical transformation after transfer of one electron; in contrast to EEC) or even a concerted[30] reaction depending on the specific system.

The recently published[31, 32] clear cut redox process **RED-2** ⇌ **OX-2** (Scheme 4) was attributed to the weak hexaaryl C–C bond but it can now be envisaged as a good example of the general pattern of type OL/CS in Scheme 3.



Ar = p-$Me_2NC_6H_4$, p-$MeOC_6H_4$

Scheme 4. An example of the general pattern of type OL/CS.

Results and Discussion

New examples of type OL/CS: This type is illustrated by the following examples derived from mono-(**3**) and trimethincyanines (**5** and **7**), and styryl dyes (**9**). Since this project had to be restricted to (spectro)electrochemical investigations, the proposed product structures are based on these methods and analogies from the literature.

By using ESR spectroscopy[33, 34] and MO calculations,[12, 13] the highest spin densities of neutral cyanine radicals have been found to reside mainly at the odd methine carbon atoms, whereas in the corresponding radical dications the highest spin densities rest on the even methine carbon atoms as shown in Figure 1. Alkyl substitution in these positions will stabilize the radical state electronically but also render dimerization more difficult due to steric hindrance.[12, 13] Intramolecular dimerization, however, should counteract the latter steric effect if rings of appropriate size are formed.

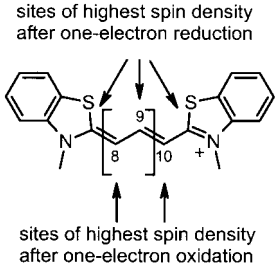
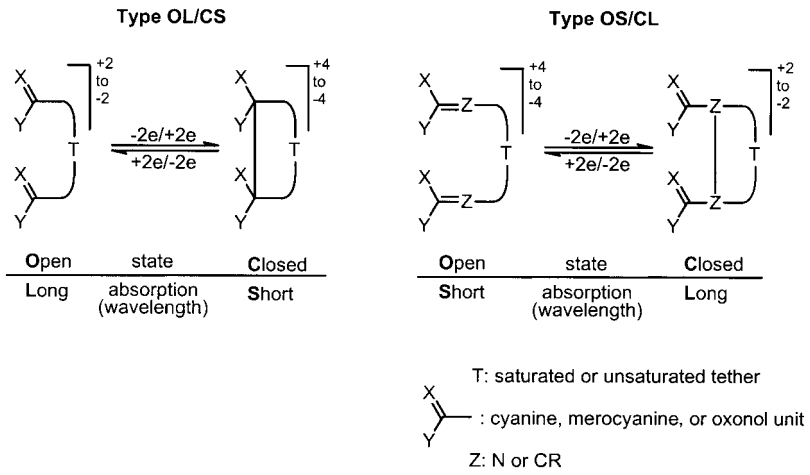


Figure 1. The highest spin densities on the even methine carbon atoms in radical dications.

Cyclovoltammograms (CVs) of 3, 5, 7, and 9: Reduction and oxidation of systems **3**, **5**, **7**, and **9** produce CVs with similar patterns; a typical example for oxidation is given in Figure 2 (exceptions vide infra). The starting alkylbridged bis-dye **A** is oxidized at E_p^1 to product **B** (probably the cyclized form) and at E_p^3 reduced to **A** again. With some systems, however, with increasing scan rate a more positive potential E_p^2 arises (reduction: **3a**, Figure 3; **8**, Figure 4; **9a**, Figure 5; oxidation: **3b**, Figure 3; **3c**, Figure 3). So far, a two-step bond breaking process in similar dimers has not been observed. The observed behavior would agree with an equilibration between two (stereo)isomers (**B** and **B′**), which is slow enough to reduce **B′** at higher scan rates. The very large distances between E_p^1 and E_p^3 (ΔE_p up to 1697 mV) exclude reversible electron transfer but rather point to strong structural changes between **A** and **B**, normally by formation (breaking) of a single bond. The overall chemical process, however, turns out to be reversible since the specific CV patterns are retained on multiscanning. Since the timescale of the CVs ranges from seconds to minutes, intermediate neutral



Scheme 3. General structure for electrochromics by single-bond redox switching.

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cyanine radicals or cation radicals will only show up in special cases. Corresponding models[12–14] have lifetimes of 10^{-4} to 10^{1} seconds. Besides, the pattern of the CVs from systems **3**, **5**, **7**, and **9** is found to be invariant to the concentration of the substrates ($c = 10^{-3}-10^{-5}$ M); the pattern indicates the intramolecular nature of the chemical process (radical–radical coupling) connected to the electron transfer.

Spectroelectrograms (SEs) of 3, 5, 7, and 9: All SEs of **3**, **5**, **7**, and **9** to be discussed below have in common equilibration between two species which can be reversed to the starting position. Since the timescale ranges over hours, radical species can only be seen if exceptionally persistent.

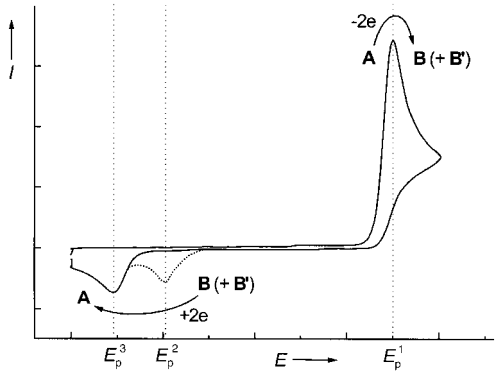
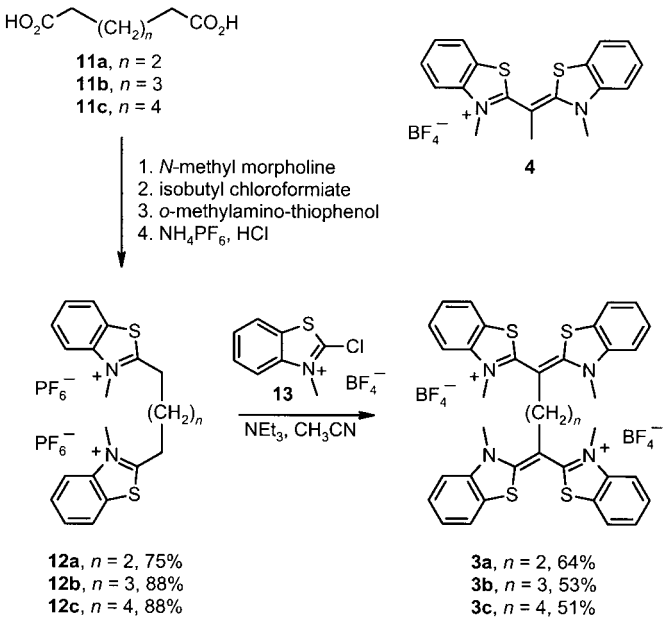


Figure 2. General pattern of the CVs of systems **3**, **5**, **7**, and **9**.

Bis-monomethincyanines

Synthesis of ***3a–c*** *and model* ***4***: Bis-monomethincyanines **3a–c** were easily obtained in two steps as shown in Scheme 5. First, according to well-developed procedures in peptide synthesis, appropriate dicarboxylic acids **11a–c** were activated through their mixed carboanhydrides and transformed with *o*-methylaminothiophenol into the bis-benzothiazolium salts **12a–c**.[35]



Scheme 5. Synthesis of bis-monomethincyanines **3a–c**.

Condensation of **12a–c** with 2-chloro-3-methylbenzothiazolium salt **13**[36] afforded the expected bis-monomethincyanines **3a–c** in good yield (51–64%).[37] Similarly, the model compound **4** was prepared from 2-ethyl-3-methylbenzothiazolium toluene-4-sulfonate[38] and **13** in 68% yield.

Cyclic voltammetry and spectroelectrochemistry of 3a–c and model 4: Except for the oxidation of **3a**, the cyanine band of monomethincyanines **3a–c** at approximately $\lambda = 460$ nm is lost both by reduction and oxidation in acetonitrile; new weak and broad bands are formed at $\lambda = 300-350$ nm (Figure 3).

These SE data in conjunction with the CV measurements are interpreted as intramolecular dimerization of (neutral or cationic) radicals of **3a–c** both by reduction and oxidation as shown in Scheme 6. We ascribe the structure of **RED-3** to a cycloalkane moiety, to which two of the heterocyclic units are attached as spiro rings, whereas the two others are connected by a double bond. These latter units should cause an absorption at approximately 300–310 nm, which compares well with the dimeric methylene base **17** ($\lambda_{max} = 308$ nm, ethanol).[39] The very similar CV and SE for the reduction of the model monomethincyanine **4** signalize smooth intermolecular reductive dimerization under the applied conditions. Interestingly, **RED-4** and **RED-3c** are re-oxidized at much lower potentials than **RED-3a** and **RED-3b** (Table 1). The dimers are expected to be stabilized much more for the two latter ones (six- and seven-membered rings) than for the former.

Table 1. Peak potentials E_{pa} and E_{pc} [mV vs Fc/Fc^+] and their differences ΔE_p for oxidation and reduction of **3a** ($c = 1.74$ mM), **3b** ($c = 1.59$ mM), **3c** ($c = 1.65$ mM), and **4** ($c = 3.03$ mM) as determined by cyclic voltammetry in CH_3CN/n-BuN_4PF_6 at a scan rate $\nu = 100$ mV s^{-1}.

	Reduction			Oxidation		
	E_{pc}^{Red}	E_{pa}^{Red}	ΔE_p^{Red}	E_{pa}^{Ox}	E_{pc}^{Ox}	ΔE_p^{Ox}
3a	−1602	−470; −311	1132; 1291	+745	−771	1516
3b	−1746	−280	1466	+614	−832; −1047	1446; 1661
3c	−1735	−958	777	+775	−610; −922	1385; 1697
4	−1763	−1122	641	+709[a]	–[a]	–[a]

[a] $E_{1/2}$; oxidation reversible.

On oxidation of **3**, ring closure at the *meso*-position is expected, and the reaction yields the more strained cycloalkane derivative **OX-3** with four benzothiazolium moieties; the observed absorption of the oxidation product at approximately 300 nm matches that ($\lambda_{max} = 295$ nm, $EtOH/H_2O$) of the corresponding protonated *meso*-methyl monomethincyanine.[40]

A puzzling effect is observed on the oxidation of **3a**. Whilst the CV displays "normal behavior", namely a totally irreversible oxidation process ($\nu = 100$, 500, and 1000 mV s^{-1}), not more than 30% of **3a** could be oxidized in the SE. We have no

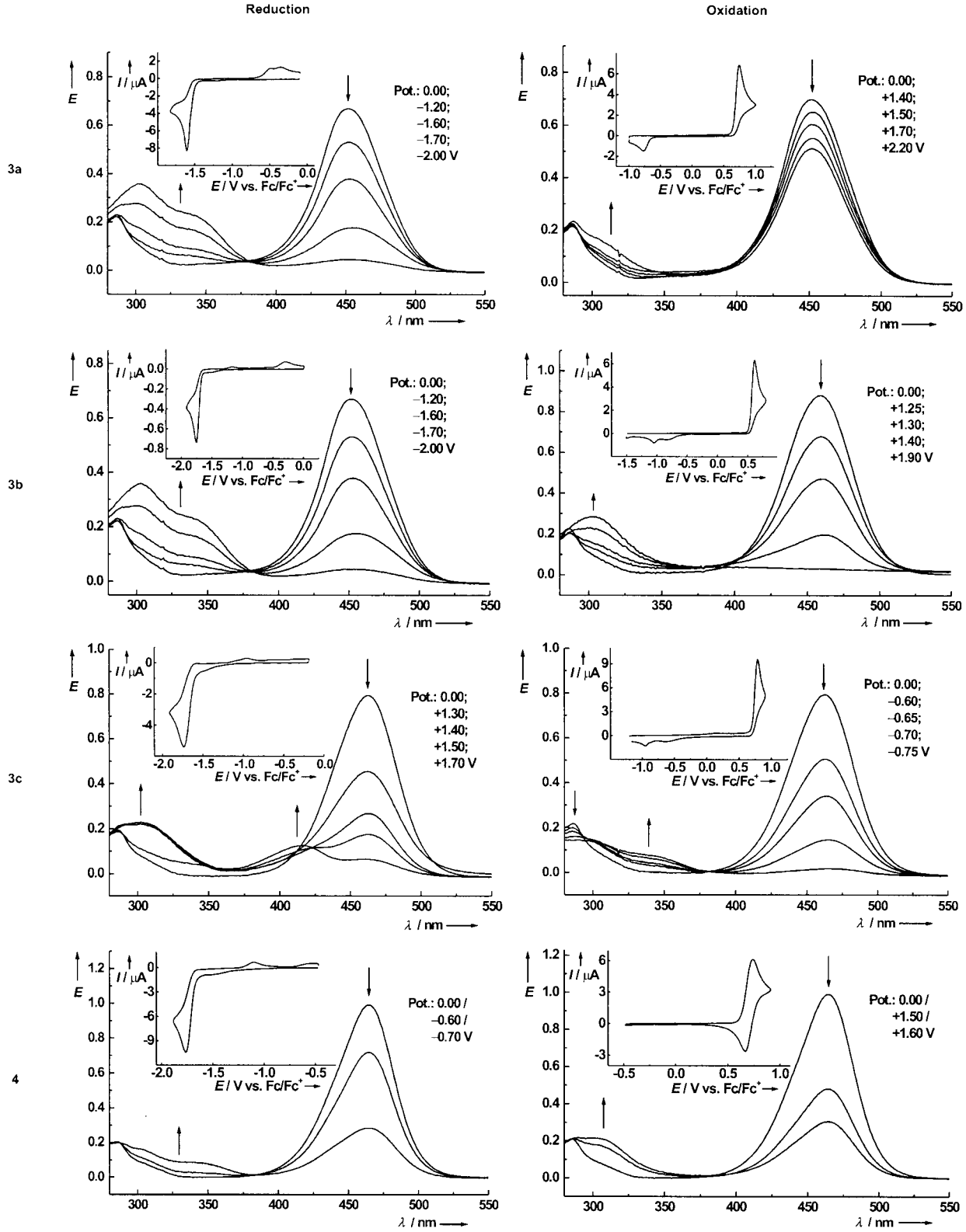


Figure 3. CVs (vs Fc/Fc^+, $\nu = 100\ mV\,s^{-1}$) and SEs (vs Ag/AgCl) for reduction and oxidation of bis-monomethincyanines **3a**–**c** compared with those of **4** in acetonitrile; concentrations for CV measurements: **3a**: $c = 1.74$ mM; **3b**: $c = 1.59$ mM; **3c**: $c = 1.65$ mM; **4**: $c = 3.03$ mM.

convincing explanation for this discrepancy between the CV and SE, which however represent different timescales. Since this anomaly is not observed with homologues **3b**, **3c**, and monomer **4**, both ring strain and crowding in **OX-3a** may be involved.

The CV for oxidation of **4** is unique since it represents a quasireversible one electron transfer, which indicates the formation of the persistent radical dication **SEM-4**. This is in sharp contrast to the irreversible CVs of **3a**–**c** at the same scan rates, which indicate a faster intramolecular ring closure.

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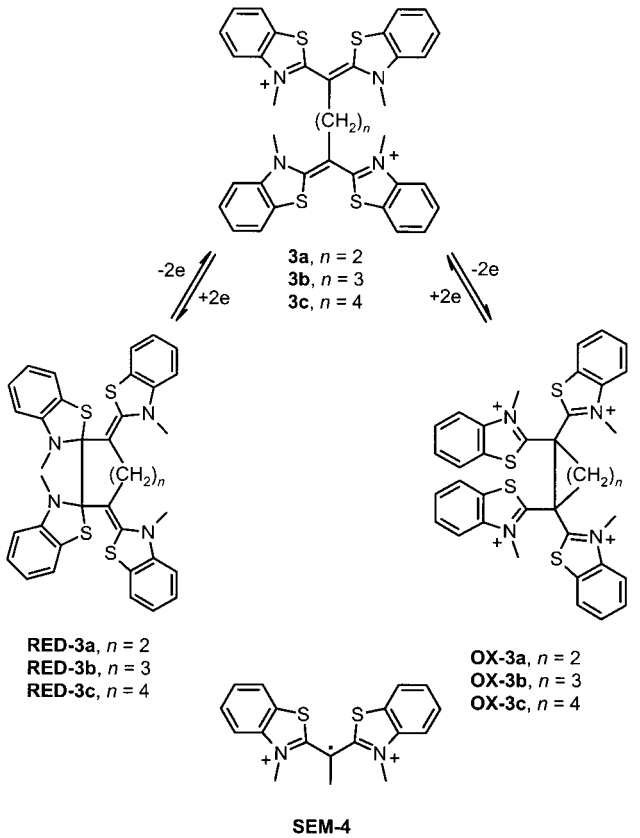
Similar to some mono- and trimethincyanines,[12–14] the structure of **SEM-4** seems to be too crowded to allow fast dimerization at the central carbon atom. Although this radical dication is persistent on the cyclic voltammetric timescale the species obviously dimerizes on that of the corresponding SE, which is much longer (vide supra). The SE does not show the presence of the persistent radical species with an expected absorption between 400 and 450 nm but supports a possible dimer formation.

Bis-trimethincyanines

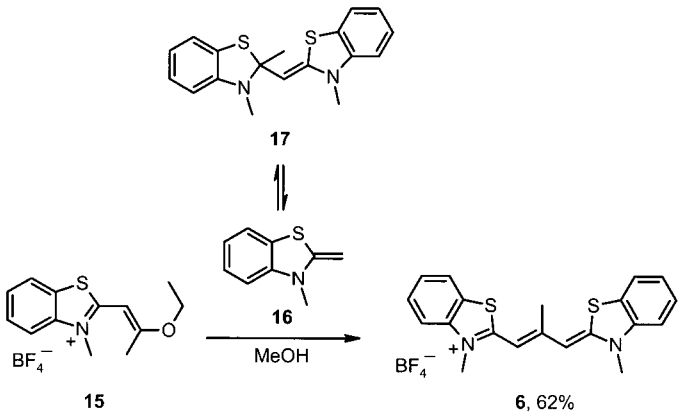
Synthesis of ***5***, ***7***, *and models* ***6*** *and* ***8***: Especially for the synthesis of trimethincyanines, various effective routes have been developed.[37] We tested the following one for the well-known **6**, since this route should be applicable to bis-trimethincyanines that lead directly to the preferred tetrafluoroborate salts.

2,3-Dimethyl-benzothiazolium methosulfate (**14**)[41] was acetylated by acetylchloride/pyridine, and the resulting ketone[42–45] (71 % yield) *O*-alkylated by triethyloxonium tetrafluoroborate to yield the enol ether **15**[46] (91 %). Reaction of **15** with the methylene base **16**[47] in situ developed from its dimer **17** finally afforded **6** in 62 % yield (Scheme 7).

When this approach was adapted for the dimeric cyanine **5**, some difficulties arose (Scheme 8). Acylation of two equivalents of **14** with glutaric acid dichloride (**18a**) afforded only the cyclized product **19**, an example of an enamine diketone. Reaction of **14** with adipic acid dichloride (**18b**), however,



Scheme 6. Proposed structures of redox products of **3a–c**.



Scheme 7. Synthesis of trimethincyanine **6**.

yielded the expected bis-acylenamine **20a**; the reaction illustrates the larger entropic factor for the closure of seven-membered rings.

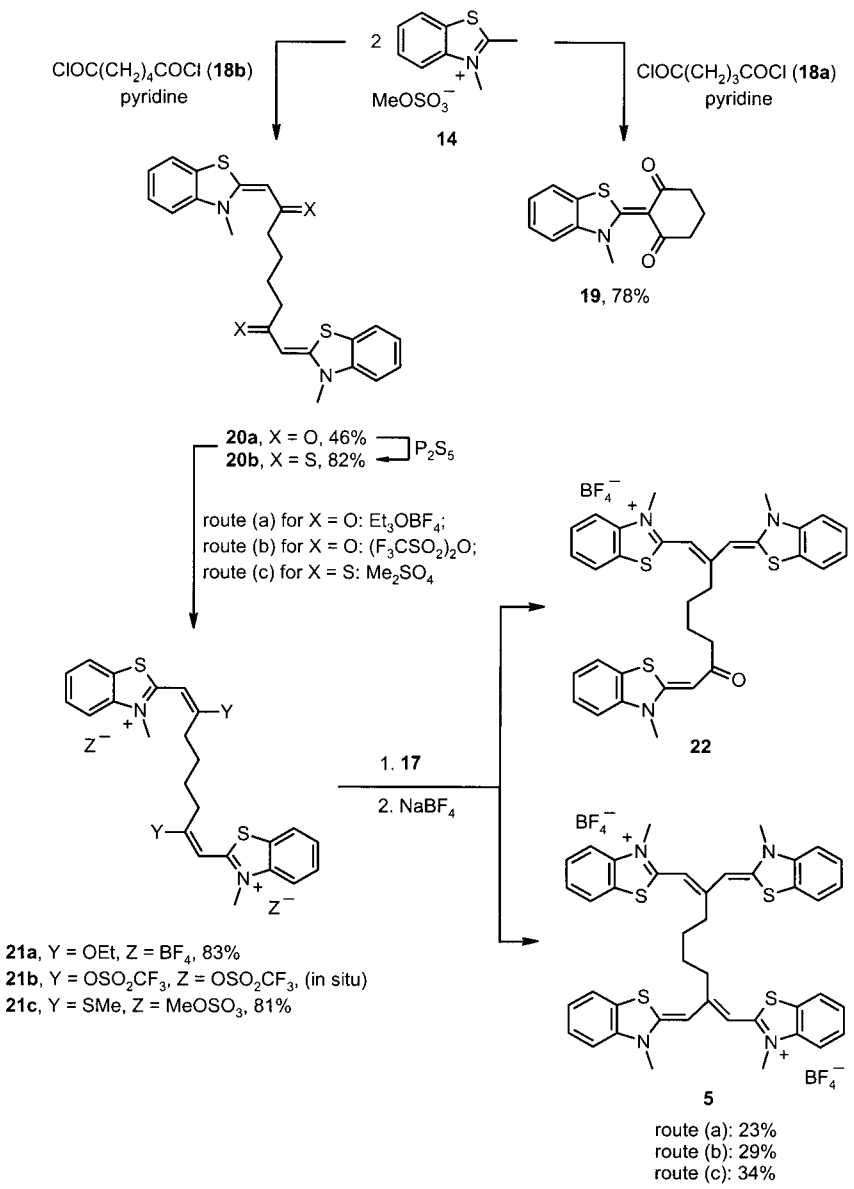
Bis-*O*-alkylation of **20a** with triethyloxonium tetrafluoroborate went smoothly to **21a** (route (a)). Unfortunately, all attempts to react **21a** with **17** to form exclusively bis-cyanine **5** failed. The main product always turned out to be trimethincyanine **22**, probably due to a low solubility in connection with its tetrafluoroborate anion. Gratifyingly, trimethincyanine **22** could be quantitatively removed by extraction with propan-2-ol. To circumvent the problem of solubility, **20a** was bis-*O*-activated in situ with triflate anhydride (route (b)); the reaction furnished **21b**, which was transformed with **17** to **5** in moderate yield (29 %).

In cyanine synthesis a thioalkyl group is known to be a much better leaving group than an alkoxy group.[37] We tried to capitalize on this effect and transformed **20a** with diphosphorous pentasulfide into dithioketone **20b** (82 %).[44, 48] Its bis-*S*-methylation with dimethylsulfate produced the expected bis-salt **21c** (81 %), which on reaction with **17**, however, yielded **5** in not more than 34 % yield (route (c)).

Bis-trimethincyanine **7** with a C_4-bridge in the α-position of the methine chain was much more convenient to prepare by adaption of the method in ref. [49]. Reaction of **12c** with thiovinylether **23** and pyridine afforded **7** in 46 % yield (Scheme 9).

Cyclic voltammetry and spectroelectrochemistry of 5, 7, and models 6 and 8: Systems **5** and **7** duplicate the general behavior of **3** both on reduction and oxidation (Figure 4 and Table 2). All trimethincyanines can be completely decolorized by reduction or oxidation, and this creates new low-intensity absorption bands at approximately 350 nm. This behavior is in full accord with the proposed reductive and oxidative dimerization processes as depicted in Scheme 10.

According to the spin density pattern of neutral cyanine radicals and dication radicals (vide supra), reductive dimerization of trimethincyanines always occurs at the *meso*-position (carbon 9), whereas oxidative dimerization takes place at the α-positions (carbon 8 and 10) of the methine chain. As these positions are substituted with the alkyl tether



Scheme 8. Synthesis of bis-trimethincyanine **5**.

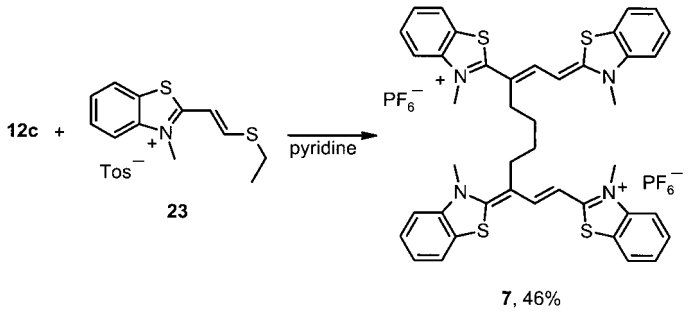
tetrasubstituted carbon atoms have to be created with **5** (and **6**) on reduction and with **7** (and **8**) on oxidation.

For **RED-5**, the formation of a cyclohexane ring has to be assumed to which four methylene-benzothiazoline units are attached. Model dye **6** displays similar behavior on reduction. Therefore, the redox product **RED-6** corresponds to **RED-5** and carries a methyl group in place of the tether.

The oxidation process for trimethincyanine **5** is unique since a new electrochemically reversible wave appears at $E_{1/2} = -18$ mV in addition to the irreversible wave at $E_{pa}^{Ox} = +447$ mV. This new reversible wave whose intensity increases to a certain extent upon multiscanning can be attributed to the generation of a new redox system. However, besides the decrease in the size of the cyanine band at $\lambda_{max} = 539$ nm, no significant change in absorption can be observed, which indicates the development of a new redox system.

Parton et al. reported for similar nontethered trimethincyanines (and pentamethincyanines) after oxidation the deprotonation of the initially formed dimer that results in a species, in which the two trimethincyanine moieties create the reduced form of a new reversible redox system of the violene-type.[14] Further oxidation of this bis-dye afforded the oxidized violene-type form as a tetracationic cross-conjugated species. This reported process may offer a possible explanation for the newly formed reversible redox system on oxidation of **5**. It should include deprotonation of **OX-5** to **RED-5a**, which is reversibly oxidized at $E_{1/2} = -18$ mV to **OX-5a**.

In contrast to **OX-5**, the oxidative dimer of model dye **6** seems to be stable towards deprotonation in the timeframe of CV, as no new redox wave appears.



Scheme 9. Synthesis of bis-trimethincyanine **7**.

Table 2. Peak potentials E_{pa} and E_{pc} [mV vs Fc/Fc^+] and their differences ΔE_p for oxidation and reduction of **5** (low solubility, saturated solution in benzonitrile), **6** ($c = 2.54$ mM in acetonitrile), **7** (low solubility, saturated solution in benzonitrile), and **8** ($c = 2.89$ mM in acetonitrile) as determined by cyclic voltammetry using nBuN$_4$PF$_6$ at a scan rate $\nu = 100$ mV s^{-1}.

	Reduction			Oxidation		
	E_{pc}^{Red}	E_{pa}^{Red}	ΔE_p^{Red}	E_{pa}^{Ox}	E_{pc}^{Ox}	ΔE_p^{Ox}
5	−1529	−305	1224	+447	−906	1353
6	−1539	−427	1112	+433	−875	1308
7	−1614	−369	1245	+245	−832	1077
8	−1564	−420; −212	1144; 1352	+251	−1039	1290

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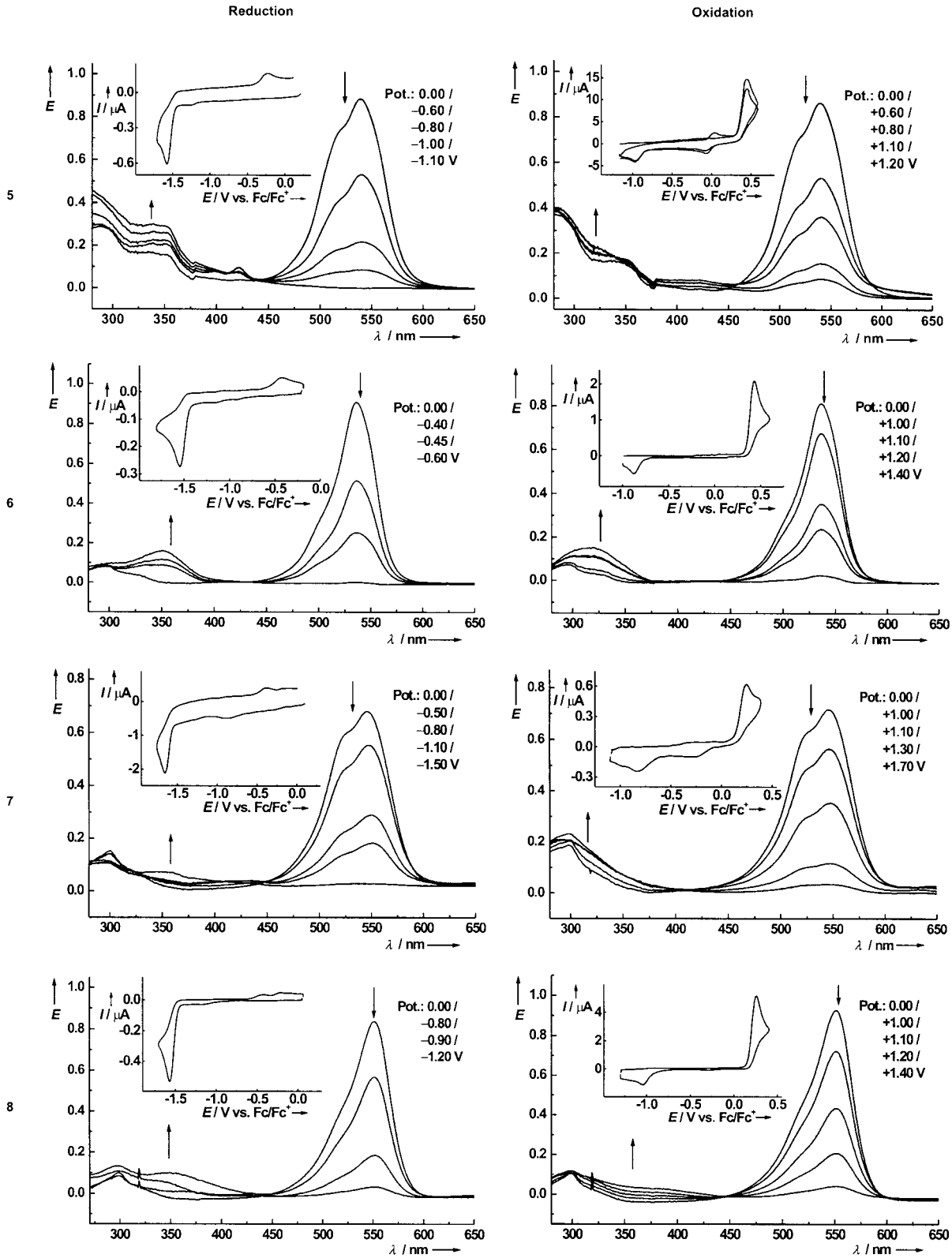
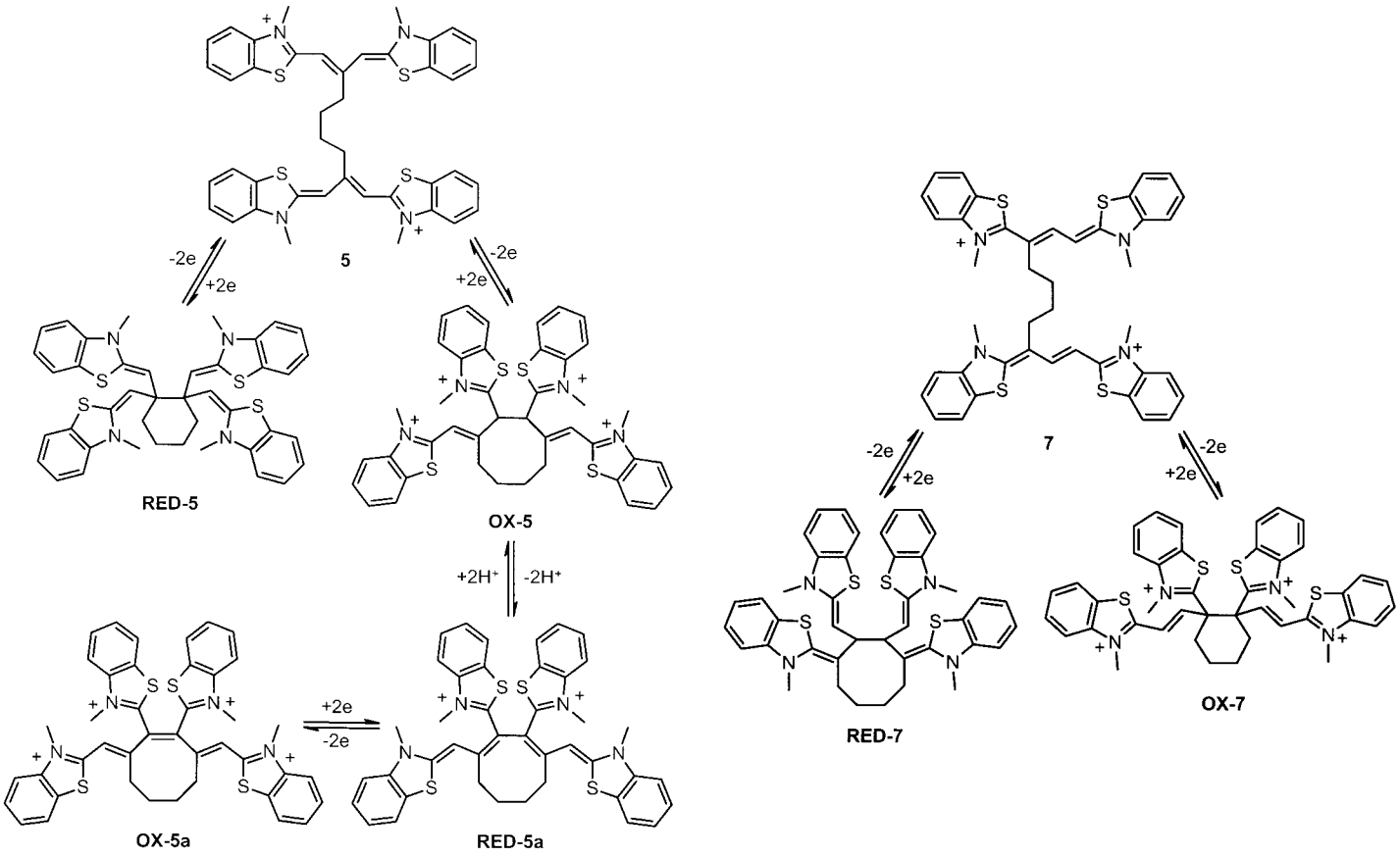


Figure 4. CVs (vs Fc/Fc^+, $\nu = 100\,mV\,s^{-1}$) and SEs (vs Ag/AgCl) for reduction and oxidation of bis-trimethincyanines **5** and **7** (in benzonitrile) compared with those of **6** and **8** (in acetonitrile); concentrations for CV measurements: **5**, **7**: saturated solutions; **6**: $c = 2.54\,mM$; **8**: $c = 2.89\,mM$.

As can be judged from Figure 4, **7** and **8** behave very similarly in terms of their CVs and SEs. For the oxidation of **7**, out of the three possible dimerization products (8,8′; 8,10′; and 10,10′ dimers) the formation of a six-membered ring **OX-7** seems to be most likely. Model **8** may behave in the same way or dimerize on the unsubstituted α-methine (carbon 10) group.

In the compounds under discussion, electrochemical scission of the single bonds should afford more energy if a ring has to be opened compared with the formation of two independ-



Scheme 10. Proposed structures of redox products of **5** and **7**.

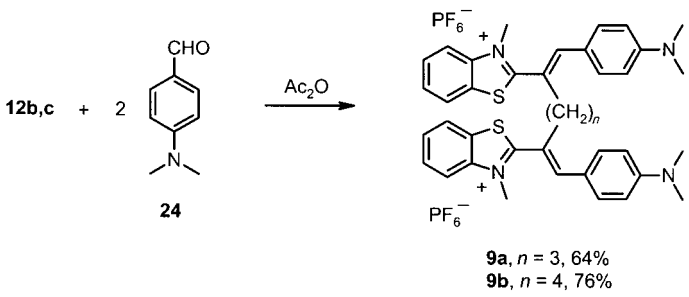
ent molecules. A qualitative comparison of the peak potentials may be allowed although simulation of the CVs would be needed to substantiate the following speculations. Reversion to the starting dyes by reduction and oxidation is expected to be more difficult for the ring-closed products **RED-5**, **OX-5**, **RED-7**, and **OX-7** than for the dimers derived from **6** and **8** (cf. Table 2). Indeed, oxidative reversion of **RED-5** (six-membered ring) to the parent dye needs a potential of 122 mV more positive than that of the reductive dimer of **6**. For the reductive dimer **RED-7**, the difference between it and its model **RED-8** drops to 51 mV, probably due to the less stable eight-membered ring. For the oxidative dimers from **7** and **8**, the situation has reverted back, probably dictated by the conformation-dependent distances of the four positive charges. Here, the oxidative dimer of **5** (eight-membered ring) is reduced at a potential 31 mV more negative than that derived from **6**. In contrast, the oxidative dimer of **7** (six-membered ring) needs a potential 207 mV more positive than that of oxidative dimer of **8**.

Bis-styryl dyes

*Synthesis of **9a**,**b** and model **10***: The monomeric model **10** was readily obtained from 2-ethyl-3-methyl benzothiazolium salts and 4-dimethylaminobenzaldehyde (**24**) by reacting them with acetic acid anhydride.[50] Accordingly, the tethered benzothiazolium salts **12b** and **12c** on condensation with **24** afforded **9a** and **9b**, respectively, in reasonable yields (Scheme 11).

Cyclic voltammetry and spectroelectrochemistry of 9a,b and model 10: On reduction, the behavior of styryl dyes **9a**,**b** together with that of model **10** fits completely into the general pattern observed for **3**, **5**, and **7** as illustrated in Figure 5. Electrochemically irreversible CVs correspond to the reversible SEs characterized by complete discoloration of the dye cation, a well-defined isosbestic point, and a new absorption band at $\lambda = 310$ nm (**RED-9a**,**b**) and $\lambda = 330$ nm (**RED-10**). In all three cases, a dimeric reduction product is to be expected as shown in Scheme 12.

However, our data do not allow us to discriminate definitely between a dimerization at the benzothiazole ring forming spiro compounds **RED-9** or the isomeric ring systems **RED-9′** (or a mixed system). The absorption of the redox product points more to the pictured structures of **RED-9**, since the incorporated moiety of 4-dimethylaminostyrene



Scheme 11. Synthesis of bis-styryl dyes **9a**,**b**.

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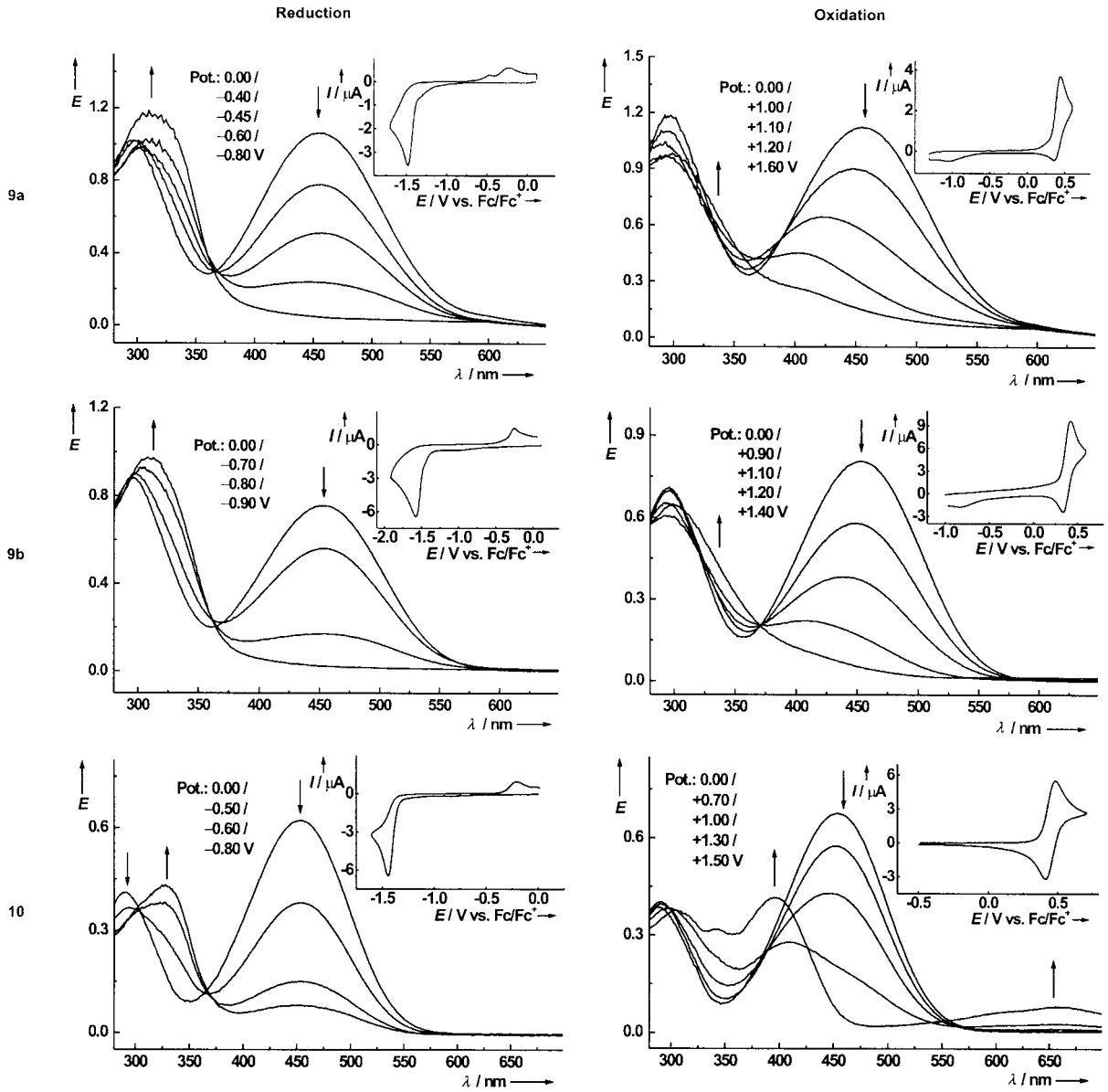


Figure 5. CVs (vs Fc/Fc^+, $\nu = 100\ mV\,s^{-1}$) and SEs (vs Ag/AgCl) for reduction and oxidation of bis-styryl dyes **9a**,**b** compared with those of **10** in acetonitrile; concentrations for CV measurements: **9a**: $c = 1.45$ mM; **9b**: $c = 1.42$ mM; **10**: $c = 2.93$ mM.

absorbs at $\lambda_{max} = 294$ nm (ethanol).[51] The band at $\lambda = 330$ nm for the reduced model **RED-10**, however, could arise from the unsaturated benzothiazoline moiety in a dimer corresponding to **RED-9′** with absorption bands similar to those found for **RED-3**, **RED-5**, and **RED-7** with λ_{max} near 350 nm.

By contrast, **9a**,**b** and **10** reveal different behavior on oxidation. From the CV of **10**, one can observe reversible one electron transfer even at scan rates as low as $20\ mV\,s^{-1}$ (Table 3). The lifetime of this radical dication **SEM-10** must be in the range of hours, since the SE indicates the formation of a new colored species with $\lambda_{max} = 395$ nm together with a very broad absorption at approximately 660 nm. On discoloration of the starting **10**, the absorption maximum is shifted to shorter wavelengths, probably due to increasing amounts of **SEM-10**. This observed resistance to dimerization may be due both to coulomb repulsion and better delocalization of the single electron in the oxidized form of **10**.

Table 3. Peak potentials E_{pa} and E_{pc} [mV vs Fc/Fc^+] and their differences ΔE_p for oxidation and reduction of **9a** ($c = 1.45$ mM), **9b** ($c = 1.42$ mM), and **10** ($c = 2.93$ mM) as determined by cyclic voltammetry using $CH_3CN/n-Bu_4NPF_6$ at a scan rate $\nu = 100\ mV\,s^{-1}$.

	Reduction			Oxidation		
	E_{pc}^{Red}	E_{pa}^{Red}	ΔE_p^{Red}	E_{pa}^{Ox}	E_{pc}^{Ox}	ΔE_p^{Ox}
9a	−1480	−469; −234	1011; 1246	+441[a]	−1049	1490
9b	−1540	−292	1248	+408[a]	−843	1251
10	−1442	−212	1230	+448[b]	–[b]	–[b]

[a] Oxidation partially reversible. [b] $E_{1/2}$; oxidation reversible.

Even in bis-dyes **9a**,**b**, the CVs clearly show on a scan rate of $\nu = 100\ mV\,s^{-1}$ not complete electrochemically irreversible but partially reversible oxidation, which increases at $\nu =$

500 mV s^{-1}. Obviously, the oxidized species remains partly in a non-ring-closed diradical tetracation structure. Nevertheless, the intramolecular enhancement of dimerization on oxidation of **9a**,**b** compared with that for the nontethered dye **10** is clearly seen. On the much longer timescale of the SEs, **9a**,**b** produce no extra diradical tetracation bands as observed for **SEM-10**. But in both cases the weakening absorption maxima are shifted to much shorter wavelengths with increasing oxidation potential, probably due to small amounts of the intermediate radical species.

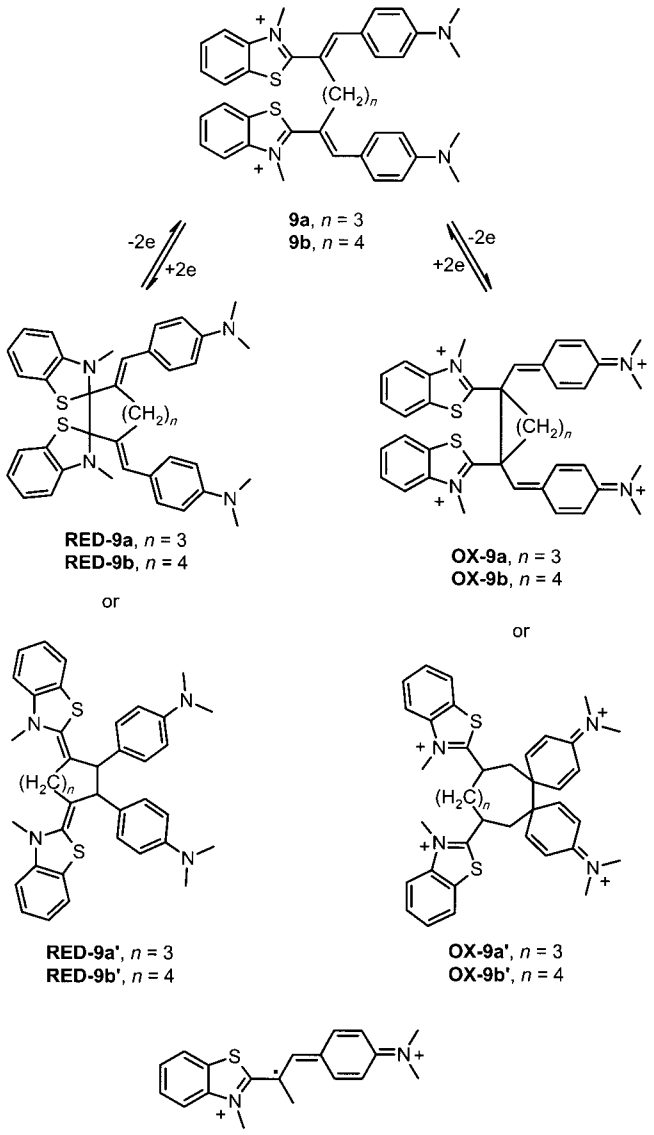
From these styryl dyes, one can observe the general tendency for the dimerization of cyanine-type radicals: mainly as a result of coulomb repulsion, radical dications are more persistent than the corresponding neutral radicals.

Conclusion

The newly synthesized systems **3**, **5**, **7**, and **9** with two cyanine-type moieties are linked by saturated C_2-C_4 tethers. All bis-dyes could be oxidized and reduced in a chemically reversible process (CV multisweep) under discoloration.

With a few exceptions, the CVs signalize electron transfers that are connected to strong structural changes of the substrate. In analogy to similar trimethincyanines, these changes are interpreted as intramolecular dimerizations. Normally, a tether connected to five- or six-membered carbocycles will enhance ring closure compared with the corresponding monomer (e.g. **OX-3c** vs **OX-4**), but this tendency is reversed if the ring-closed product becomes too crowded or the ring size would be too large (**OX-3a** vs **4**). In the case of the models **4** and **10**, radical dications are formed (CV), which in the former case cannot be seen in its SE as a result of the much longer timescale. This behavior applies also to **OX-9b**.

These examples clearly demonstrate that the new type of electrochromics OL/CS will be valid within a broad range of compounds covered by the general structure of Scheme 3.



Scheme 12. Proposed structures of redox products of **9a**,**b** and **10**.

Experimental Section

General: Melting points were determined on a hot-stage microscope (Fa. Reichert) and were corrected. IR: Perkin Elmer 1420 spectrophotometer; ^{1}H (RT) and ^{13}C (RT) NMR spectroscopy: Bruker AC 250 (250 MHz) and Bruker (600 MHz) spectrometers, standardized by solvent signals; MS: Varian MT CH7 and Finnigan MAT 8200 spectrometers.

Electrochemical measurements: Cyclic voltammetry (CV) was performed in a three-electrode single-compartment cell (5 mL) using a computer-controlled EG&G PAR 273 potentiostat. CV data were obtained at a glassy carbon disk electrode with a surface of $A = 0.785$ mm^2. The counter-electrode consisted of a platinum wire, and the reference electrode was a Ag/AgCl secondary electrode. Acetonitrile (Licrosolv, Merck) was filtered over aluminum oxide directly into the electrochemical cell. Benzonitrile was distilled prior to use. Tetrabutylammonium hexafluorophosphate puriss. (Bu_4NPF_6) and tetrafluoroborate (Bu_4NBF_4) were obtained from Fluka and dried in vacuo at 200 °C. All potentials were measured at 21 °C and internally referenced to a ferrocene–ferricenium couple.

General procedure for CV measurements: A solution (0.1 M) of Bu_4NPF_6 or Bu_4NBF_4 in acetonitrile or benzonitrile was deoxygenated with dry argon for 15 min. The corresponding compounds were characterized at a concentration of approximately 1 mM using a scan rate of $\nu = 100$ mV s^{-1}.

Spectroelectrochemical measurements (SEs): SEs were recorded on a Perkin-Elmer Spectrophotometer Lambda 19 in conjunction with an EG&G PAR potentiostat (model 363). All optical measurements were carried out at 21 °C in a thin-layer electrochemical cell (distance working electrode/light conductor: 60 μm) according to Salbeck[52] incorporating a polished platinum disk electrode (ϕ6 mm) as a working electrode, an Ag/AgCl wire as a reference electrode, and a platinum sheet as a counter-electrode. Spectra were recorded in a reflection modus at the platinum electrode with the aid of a *y*-type optical fiber bundle.

General procedure for SE measurements: The potentials given in the figures were applied to a solution of the substrate (ca. 0.1 mM) in acetonitrile or benzonitrile containing Bu_4NPF_6 or Bu_4NBF_4 (0.1 mol L^{-1}), and the spectra were recorded after equilibration was observed. The potentials did not match those from CV measurements. Differences up to 300 mV occurred due to the actual geometry of the electrochemical cell used in the specific experiment.

Model dyes **8**[49] and **10**[50] were readily available by adopting literature procedures.

General procedure A for bis-benzothiazolium salts 12a–c: According to ref. [35], isobutyl chloroformiate (8.88 g, 65.0 mmol) and, after 15 min, 2-methylaminothiophenol (9.04 g, 65.0 mmol) were added into a solution of alkane dicarboxylic acid **11a–c** (30.0 mmol) and *N*-methyl morpholine (6.27 g, 62.0 mmol) in THF (45 mL) at −20 °C. After stirring the

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suspension for 45 min at ambient temperature, a solution of ammonium hexafluorophosphate (25 g) in concentrated hydrochloric acid (50 mL) was slowly added. The white precipitate was isolated and washed with ice water and diethyl ether. White crystals were obtained from acetonitrile.

*Compound **12a***: General procedure A with **11a** (4.38 g, 30.0 mmol). Compound **12a** (14.5 g, 75%) was obtained as white needles; m.p. 253–256 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 2.10$ (m, 4H; CH_2), 3.62 (m, 4H; CH_2), 4.26 (s, 6H; NCH_3), 7.78–8.47 (m, 8H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 26.6$ (CH_2), 29.5 (CH_2), 36.3 (NCH_3), 116.9, 124.5, 128.1, 129.4 ($C_{arom}H$), 128.5, 141.9 (C_{arom}), 180.5 (CNS); IR (KBr): $\tilde{\nu} = 1580$, 1510, 1470, 1420, 1340, 1050, 790 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 352 (20), 203 (57), 189 (10), 176 (100), 163 (6), 150 (9); elemental analysis calcd (%) for $C_{20}H_{22}N_2S_2P_2F_{12}$ (644.5): C 37.27, H 3.44, N 4.35, S 9.95; found[53] C 36.70, H 3.33, N 4.12, S 8.23.

*Compound **12b***: General procedure A with **11b** (4.80 g, 30.0 mmol). Compound **12b** (17.4 g, 88%) was obtained as white crystals; m.p. 224–226 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.76$ (m, 2H; CH_2), 1.98 (m, 4H; CH_2), 3.53 (m, 4H; CH_2), 4.25 (s, 6H; NCH_3), 7.78–8.46 (m, 8H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 26.7$ (CH_2), 27.7 (CH_2), 29.8 (CH_2), 36.2 (NCH_3), 116.8, 124.4, 128.1, 129.4 ($C_{arom}H$), 128.5, 141.8 (C_{arom}), 180.9 (CNS); IR (KBr): $\tilde{\nu} = 1580$, 1520, 1460, 1330, 830, 760 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 366 (11), 353 (26), 229 (7), 202 (16), 189 (28), 176 (100), 163 (50), 150 (45); elemental analysis calcd (%) for $C_{21}H_{24}N_2S_2P_2F_{12}$ (658.5): C 38.30, H 3.67, N 4.25, S 9.74; found[53] C 36.59, H 3.46, N 4.08, S 9.61.

*Compound **12c***: General procedure A with **11c** (5.22 g, 30.0 mmol). Compound **12c** (17.7 g, 88%) was obtained as white needles; m.p. 252–256 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.59$ (m, 4H; CH_2), 1.88 (m, 4H; CH_2), 3.52 (m, 4H; CH_2), 4.24 (s, 6H; NCH_3), 7.76–8.49 (m, 8H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 27.1$ (CH_2), 27.9 (CH_2), 30.1 (CH_2), 36.3 (NCH_3), 116.9, 124.5, 128.2, 129.5 ($C_{arom}H$), 128.5, 141.9 (C_{arom}), 181.2 (CNS); IR (KBr): $\tilde{\nu} = 1620$, 1580, 1510, 1340, 1200, 840, 780 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 380 (6), 365 (100), 347 (7), 215 (18), 190 (13), 176 (50), 163 (39), 150 (25); elemental analysis calcd (%) for $C_{22}H_{26}N_2S_2P_2F_{12}$ (672.5): C 39.29, H 3.90, N 4.17, S 9.53; found[53] C 38.42, H 3.79, N 4.11, S 8.03.

General procedure B for bis-monomethincyanines 3a–c: Triethylamine (4 mL) was slowly added to a solution of **12a–c** (2.00 mmol) and 2-chloro-3-methylbenzothiazolium tetrafluoroborate (**13**)[36] (1.63 g, 6.00 mmol) in acetonitrile (60 mL). On cooling of the refluxed mixture (30 min), the product **3a–c** was deposited as orange crystals, which were recrystallized from acetonitrile/diethylether.

*Bis-monomethincyanine **3a***: General procedure B with **12a** (1.29 g, 2.00 mmol). Compound **3a** (1.05 g, 64%); m.p. 297–299 °C.

^{1}H NMR (250 MHz, CD_3CN): $\delta = 3.22$ (s, 4H; CH_2), 3.29 (s, 12H; NCH_3), 7.51–7.95 (m, 16H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 37.9$ (NCH_3), 38.0 (CH_2), 86.1 (C_q), 114.8, 123.1, 125.8, 128.3 ($C_{arom}H$), 125.9, 142.0 (C_{arom}), 167.0 (CNS); IR (KBr): $\tilde{\nu} = 1580$, 1485, 1410, 1310, 1165, 1050, 850, 760 cm^{-1}; elemental analysis calcd (%) for $C_{36}H_{32}N_4S_4B_2F_8$ (822.5): C 52.57, H 3.92, N 6.81, S 15.59; found[53] C 51.86, H 4.03, N 6.89, S 15.37.

*Bis-monomethincyanine **3b***: General procedure B with **12b** (1.32 g, 2.00 mmol). Compound **3b** (0.88 g, 53%) was obtained; m.p. 298–300 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 2.21$ (m, 2H; CH_2), 2.97 (m, 4H; CH_2), 3.43 (s, 12H; NCH_3), 7.47–8.02 (m, 16H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 38.0$ (NCH_3), 38.6 (CH_2), 45.4 (CH_2), 87.4 (C_q), 114.8, 122.9, 125.7, 128.2 ($C_{arom}H$), 125.9, 142.2 (C_{arom}), 166.8 (CNS); IR (KBr): $\tilde{\nu} = 1500$, 1405, 1270, 1050, 840, 760 cm^{-1}; elemental analysis calcd (%) for $C_{37}H_{34}N_4S_4B_2F_8$ (836.6): C 53.12, H 4.10, N 6.70, S 15.33; found[53] C 52.69, H 4.30, N 6.79, S 14.21.

*Bis-monomethincyanine **3c***: General procedure B with **12c** (1.35 g, 2.00 mmol). Compound **3c** (0.86 g, 51%) was obtained; m.p. 330 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.85$ (m, 4H; CH_2), 2.90 (m, 4H; CH_2), 3.37 (s, 12H; NCH_3), 7.46–8.06 (m, 16H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 37.9$ (NCH_3), 38.7 (CH_2), 45.3 (CH_2), 88.0 (C_q), 114.7, 123.0, 125.7, 128.2 ($C_{arom}H$), 125.9, 142.1 (C_{arom}), 166.7 (CNS); IR (KBr): $\tilde{\nu} = 1500$, 1410, 1310, 1060, 840, 750 cm^{-1}; elemental analysis calcd (%) for $C_{38}H_{36}N_4S_4B_2F_8$ (850.6): C 53.66, H 4.27, N 6.59, S 15.08; found[53] C 52.46, H 4.37, N 6.85, S 14.19.

Monomethincyanine 4: Triethylamine (1.5 mL) was added to a solution of 2-ethyl-3-methylbenzothiazolium toluene-4-sulfonate[38] (1.61 g, 4.61 mmol) and **13**[36] (1.25 g, 4.61 mmol) in ethanol (20 mL). After refluxing for 30 min, **4** (1.29 g, 68%) was deposited as orange prisms; m.p. 287–289 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 2.44$ (s, 3H; CH_3), 3.50 (s, 6H; NCH_3), 7.45–8.08 (m, 8H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 23.5$ (CH_3), 38.6 (NCH_3), 82.9 (C_q), 114.6, 122.9, 125.5, 128.2 ($C_{arom}H$), 126.0, 142.4 (C_{arom}), 166.6 (CNS).

Compound 15: According to ref. [46], 1-(3-methyl-3-H-benzothiazolo-2-ylidene)[43–45] (225 mg, 1.10 mmol) in dichloromethane (6 mL) was treated at 0 °C with triethyloxonium tetrafluoroborate (230 mg, 1.21 mmol). After stirring for 30 min at 0 °C and 30 min at room temperature, **15** was deposited as a white solid. Recrystallization from methanol yielded **15** (321 mg, 91%) in white prisms; m.p. 191–193 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.53$ (t, $J = 7.0$ Hz, 3H; CH_3), 2.50 (s, 3H; CH_3), 4.08 (s, 3H; NCH_3), 4.57 (q, $J = 7.0$ Hz, 2H; CH_2), 6.71 (s, 1H; CH), 7.60–8.29 (m, 4H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 14.8$ (CH_3), 19.6 (CH_3), 35.1 (NCH_3), 67.8 (CH_2), 93.6 (CH), 115.4, 123.6, 126.7, 128.7 ($C_{arom}H$), 127.6, 139.9 (C_{arom}), 165.8 (CNS), 177.0 (C_q); IR (KBr): $\tilde{\nu} =$ 1600, 1580, 1500, 1050, 760 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 233 (15), 205 (45), 190 (100), 174 (25), 162 (21); elemental analysis calcd (%) for $C_{13}H_{16}NOSBF_4$ (321.1): C 48.62, H 5.02, N 4.36, S 9.98; found[53] C 47.32, H 5.01, N 4.46, S 10.12.

Trimethincyanine 6: Compound **15** (300 mg, 0.93 mmol) was suspended in methanol (50 mL). After adding **17** (455 mg, 1.40 mmol), the mixture was heated to reflux for 1 h. On cooling **6** (256 mg, 62%) was deposited as purple prisms; m.p. 281 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 2.56$ (s, 3H; CH_3), 3.88 (s, 6H; NCH_3), 6.44 (s, 2H; CH), 7.35–8.04 (m, 8H; ArH).

General procedure C for acylation of 2,3-dimethyl-benzothiazolium methosulfate (14) with dicarboxylic acid dichlorides (18a,b): According to ref. [43–45], dicarboxylic acid dichloride (**18a**,**b**, 50.0 mmol) was slowly added at 0 °C to **14**[41] (27.5 g, 100 mmol) in pyridine (150 mL). After stirring at 0 °C (30 min), the mixture was heated to 80 °C (15 min) before methanol (150 mL) was added. The resulting precipitate was crystallized from pyridine/methanol.

Compound 19: General procedure C with glutaric acid dichloride (**18a**, 8.45 g, 50.0 mmol). Compound **19** (10.1 g, 78%) was obtained as white needles; m.p. 266–268 °C.

^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.01$ (quint, $J = 6.3$ Hz, 2H; CH_2), 2.56 (t, $J = 6.3$ Hz, 4H; CH_2), 3.73 (s, 3H; NCH_3), 7.35–7.79 (m, 4H; ArH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 19.3$ (CH_2), 37.5 (CH_2), 40.4 (NCH_3), 107.2 (C_q), 113.3, 122.3, 125.2, 127.2 ($C_{arom}H$), 129.0, 140.7 (C_{arom}), 169.1 (CNS), 193.0 (C=O); IR (KBr): $\tilde{\nu} = 1620$, 1570, 1480, 1390, 1360, 840, 770 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 259 (100), 242 (71), 216 (40), 189 (90), 161 (49); elemental analysis calcd (%) for $C_{14}H_{13}NO_2S$ (259.3): C 64.84, H 5.05, N 5.40, S 12.36; found C 64.59, H 5.32, N 5.63, S 12.24.

Compound 20a: General procedure C with adipic acid dichloride (**18b**, 9.15 g, 50.0 mmol). Compound **20a** (10.0 g, 46%) as white needles; m.p. 218 °C.

^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.77$ (m, 4H; CH_2), 2.52 (m, 4H; CH_2), 3.52 (s, 6H; NCH_3), 5.86 (s, 2H; CH), 7.05–7.57 (m, 8H; ArH); ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 25.9$ (CH_2), 32.3 (NCH_3), 41.8 (CH_2), 90.0 (CH), 109.5, 122.3, 122.5, 126.3 ($C_{arom}H$), 127.1, 139.9 (C_{arom}), 160.5 (CNS), 194.1 (C=O); IR (KBr): $\tilde{\nu} = 1610$, 1590, 1480, 1122, 938, 745 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 436 (10), 246 (10), 218 (19), 190 (71), 150 (100); elemental analysis calcd (%) for $C_{24}H_{24}N_2O_2S_2$ (436.6): C 66.03, H 5.54, N 6.42, S 14.69; found C 65.81, H 5.38, N 6.39, S 14.97.

Compound 20b: According to ref. [44, 48], **20a** (1.74 g, 4.00 mmol) was treated with diphosphorous pentasulfide (0.89 g, 4.00 mmol) in pyridine (15 mL). After heating the mixture to reflux for 1 h, the precipitate was isolated, washed with water, and recrystallized from pyridine to afford **20b** (1.54 g, 82%) as yellow prisms; m.p. 259–261 °C.

^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.78$ (m, 4H; CH_2), 2.86 (m, 4H; CH_2), 3.85 (s, 6H; NCH_3), 7.30 (s, 2H; CH), 7.36–7.96 (m, 8H; ArH); IR (KBr): $\tilde{\nu} = 1610$, 1500, 1340, 1300, 1270, 830, 740 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{24}N_2S_4$ (468.7): C 61.50, H 5.16, N 5.98, S 27.36; found C 61.60, H 5.03, N 5.97, S 27.47.

Compound 21a: Compound **20a** (4.36 g, 10.0 mmol) was treated with triethyloxonium tetrafluoroborate (5.69 g, 30.0 mmol) in dichloromethane (60 mL). To remove any traces of acid, ethyldiisopropylamine (0.39 g, 3 mmol) was added. On stirring (60 min) at room temperature, **21a** (5.55 g, 83%) was deposited as white prisms; m.p. 255 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.57$ (t, $J = 7.0$ Hz, 6H; CH_3), 1.71, 1.82 (m, 4H; CH_2), 2.85, 2.87 (m, 4H; CH_2), 4.13, 4.16 (s, 6H; NCH_3), 4.61 (q, $J = 7.0$ Hz, 4H; CH_2), 6.60, 6.66 (s, 2H; CH), 7.62 – 8.30 (m, 8H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 15.0$ (CH_3), 25.9, 31.5 (CH_2), 35.3 (NCH_3), 67.4 (OCH_2), 93.5 (CH), 115.5, 123.7, 126.8, 128.8 ($C_{arom}H$), 127.7, 140.0 (C_{arom}), 165.9 (CNS), 179.0 (C_q); IR (KBr): $\tilde{\nu} = 1600$, 1575, 1400, 1100, 770 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{34}N_2O_2S_2B_2F_8$ (668.3): C 50.32, H 5.13, N 4.19, S 9.59; found[53] C 49.16, H 5.06, N 4.15, S 9.67.

Compound 21c: A suspension of **20b** (0.93 g, 2.00 mmol) in chlorobenzene (25 mL) was treated with dimethyl sulfate (0.76 g, 6.00 mmol) and heated to reflux for 3 h. On cooling, **21c** was deposited as a yellow solid, that was isolated, washed with diethyl ether and acetone, and dried in vacuo. The product was used in the next step without further purification.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.83$ (m, 4H; CH_2), 2.88 (s, 6H; CH_3), 3.03 (m, 4H; CH_2), 4.23 (s, 6H; NCH_3), 7.49 (s, 2H; CH), 7.72 – 8.42 (m, 8H; ArH).

Bis-trimethincyanine 5

Route (*a*): Compound **17**[50] (980 mg, 3.00 mmol) was added to a suspension of **21a** (668 mg, 1.00 mmol) in methanol (60 mL) at 40 °C. After refluxing the mixture (3 h) and cooling, the precipitate was isolated and extracted with propan-2-ol. The residue solid with a greenish metallic luster consisted of **5** (208 mg, 23%); m.p. 295 – 296 °C. From the extract, **22** was obtained as red needles; m.p. 241 – 243 °C.

Compound ***5***: ^{1}H NMR (600 MHz, [D$_6$]DMSO): $\delta = 2.00$ (m, 4H; CH_2), 3.03 (m, 4H; CH_2), 3.92 (s, 12H; NCH_3), 6.47 (s, 4H; CH), 7.34 – 7.90 (m, 16H; ArH); ^{13}C NMR (151 MHz, [D$_6$]DMSO): $\delta = 33.8$ (NCH_3), 100.1 (C_q), 113.2, 122.7, 124.1, 128.1 ($C_{arom}H$), 125.3, 140.1 (C_{arom}), 159.8 (CNS); IR (KBr): $\tilde{\nu} = 1510$, 1470, 1320, 1300, 1230, 1050 cm^{-1}; elemental analysis calcd (%) for $C_{42}H_{40}N_4S_4B_2F_8$ (902.7): C 55.89, H 4.47, N 6.21, S 14.21; found[53] C 55.08, H 4.51, N 6.31, S 13.53.

Compound ***22***: ^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.67$ (m, 2H; CH_2), 1.89 (m, 2H; CH_2), 2.52 (m, 2H; CH_2), 2.84 (m, 2H; CH_2), 3.55 (s, 3H; NCH_3), 3.86 (s, 6H; NCH_3), 6.08 (s, 1H; CH), 6.35 (s, 2H; CH), 7.10 – 7.97 (m, 12H; ArH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 25.5$ (CH_2), 32.3, 33.9 (NCH_3), 40.9 (CH_2), 89.8 (CH), 100.1 (C_q), 122.2, 122.4, 122.8, 126.5, 128.2 ($C_{arom}H$, CH), 125.3, 125.6, 139.7, 140.3 (C_{arom}), 159.0, 160.0 (CNS), 192.4 (C=O).

Route (*b*): Following refs. [54, 55], triflate anhydride (1.16 g, 4.10 mmol) was added at 0 °C to a solution of **20a** (0.87 g, 2.00 mmol) in dichloromethane (6 mL). After 60 min, **17**[50] (1.63 g, 5.00 mmol) was added. On stirring (2 h) at room temperature, purple crystals of **5** as bis-triflate (596 mg, 29%) separated. To convert the bis-triflate salt into the corresponding bis-tetrafluoroborate salt, a solution of the bis-triflate in acetonitrile was added dropwise to a saturated aqueous solution of $NaBF_4$. The resulting precipitate was isolated and dried in vacuo. Spectroscopic data for **5** were in accord with data given in route (a).

Route (*c*): Compound **17**[50] (980 mg, 3.00 mmol) was added to a suspension of **21c** (721 mg, 1.00 mmol) in methanol (60 mL). After refluxing (4 h), the mixture was cooled to room temperature and added dropwise to a saturated aqueous solution of $NaBF_4$. The purple precipitate was isolated and extracted with propan-2-ol. The residue solid with a greenish metallic luster consisted of **5** (307 mg, 34%). Spectroscopic data for **5** were in accord with data given in route (a).

Bis-trimethincyanine 7: Following ref. [49], a solution of 2-(ethyl-sulfanyl-vinyl)-3-methylbenzothiazolium toluene-4-sulfonate (**23**) (0.50 g, 1.20 mmol) and **12c** (0.32 g, 0.49 mmol) in pyridine (20 mL) was refluxed for 30 min. On cooling, **7** was deposited and was isolated and recrystallized from acetonitrile. Blue crystals with metallic luster were obtained (240 mg, 46%); m.p. 284 – 285 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.77$ (m, 4H; CH_2), 2.79 (m, 4H; CH_2), 3.74 (s, 6H; NCH_3), 4.09 (s, 6H; NCH_3), 6.17 (d, $J = 13.1$ Hz, 2H; CH), 7.07 – 8.06 (m, 18H; ArH, including CH); ^{13}C NMR (63 MHz, [D$_6$]DMSO): $\delta = 32.8$ (NCH_3), 39.0 (NCH_3), 93.0 (CH), 110.4 (C_q), 112.3, 114.6, 122.3, 122.7, 124.1, 125.2, 127.4, 128.2 ($C_{arom}H$), 124.08, 125.73, 142.0, 145.8 (C_{arom}), 143.3 (CH), 163.6, 169.4 (CNS); IR (KBr): $\tilde{\nu} = 1540$, 1470, 1440, 1230, 1110, 830 cm^{-1}; elemental analysis calcd (%) for $C_{42}H_{40}N_4S_4P_2F_{12}$ (1019.0): C 49.51, H 3.96, N 5.50, S 12.59; found[53] C 49.19, H 3.89, N 5.72, S 11.62.

General procedure D for bis-styryl dyes 9a,b: Following ref. [50], a solution of **12b,c** (1.00 mmol) and 4-dimethylaminobenzaldehyde (**24**, 330 mg, 2.20 mmol) in acetic anhydride (10 mL) was heated to reflux for 30 min. The hot reaction mixture was added dropwise to an aqueous solution (30 mL) of ammonium hexafluorophosphate (650 mg, 4.00 mmol). The resulting precipitate was isolated and washed with water. For purification of the crude dyes, the well-established anion-exchange procedure was applied.[56] Et_3NHCl was added in excess to a solution of the precipitate in acetonitrile. After stirring for 12 h, the precipitate was isolated, washed with diethyl ether, and dried in vacuo. Saturated aqueous solution of NH_4PF_6 was added dropwise to a solution of the dried precipitate in H_2O. Compound **9a,b** was deposited as a red solid, which was isolated, washed with water, and dried in vacuo.

Bis-styryl dye ***9a***: General procedure D with **12b** (660 mg, 1.00 mmol). Compound **9a** (590 mg, 64%) was obtained as red crystals; m.p. 154 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 3.01$ (s, 12H; NCH_3), 4.23 (s, 6H; NCH_3), 7.25 (s, 2H; CH), 6.75 – 8.42 (m, 8H; ArH); ^{13}C NMR (63 MHz, [D$_6$]acetone): $\delta = 37.6$ (CH_2), 38.9 (CH_2), 39.4 (NCH_3), 39.6 (NCH_3), 112.1, 112.4, 117.4, 117.8, 121.2, 121.3, 121.4, 121.5, 124.2, 124.7, 128.9, 129.5, 130.2, 130.5, 130.6, 130.7, 132.8, 132.9, 143.2, 145.0, 145.2, 152.3, 178.9 ($C_{arom}H$, C_{arom}, CH, C_q, CNS); IR (KBr): $\tilde{\nu} = 1600$, 1560, 1410, 1170, 840 cm^{-1}; elemental analysis calcd (%) for $C_{39}H_{42}N_4S_2P_2F_{12}$ (920.8): C 50.87, H 4.60, N 6.08, S 6.96; found[53] C 49.85, H 4.89, N 5.84, S 5.79.

Bis-styryl dye ***9b***: General procedure D with **12c** (670 mg, 1.00 mmol). Compound **9b** (710 mg, 76%) was obtained as red crystals; m.p. 158 °C.

^{1}H NMR (250 MHz, [D$_6$]DMSO): $\delta = 1.72$ (m, 4H; CH_2), 2.95 (m, 4H; CH_2), 3.00 (s, 12H; NCH_3), 4.23 (s, 6H; NCH_3), 7.24 (s, 2H; CH), 6.75 – 8.41 (m, 8H; ArH); ^{13}C NMR (63 MHz, [D$_6$]acetone): $\delta = 34.1$ (CH_2), 38.7 (NCH_3), 39.6 (NCH_3), 41.4 (CH_2), 114.5, 118.6, 119.1, 124.1, 125.5, 125.9, 130.3, 130.4, 130.8, 131.5, 131.8, 133.9, 143.2, 144.3, 145.5, 179.9 ($C_{arom}H$, C_{arom}, CH, C_q, CNS); IR (KBr): $\tilde{\nu} = 1610$, 1565, 1360, 1180, 830 cm^{-1}; elemental analysis calcd (%) for $C_{40}H_{44}N_4S_2P_2F_{12}$ (934.9): C 51.39, H 4.74, N 5.99, S 6.86; found[53] C 49.89, H 4.89, N 5.72, S 5.62.

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[1] P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, *Electrochromism*, VCH, Weinheim, **1995**.
[2] R. J. Mortimer, *Chem. Soc. Rev.* **1997**, *26*, 147 – 156.
[3] T. Yamase, *Chem. Rev.* **1998**, *98*, 307 – 325.
[4] M. Nanasawa in *Organic Photochromic and Thermochromic Compounds*, *Vol. 1* (Eds.: J. C. Crano, R. J. Guglielmetti), Kluwer/Plenum, New York, **1998**, pp. 354 – 370.
[5] For a review, see: S. Hünig, *Chimia* **1978**, *32*, 91 – 93.
[6] For a review, see: K. Deuchert, S. Hünig, *Angew. Chem.* **1978**, *90*, 927 – 938; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 875 – 886.
[7] For a review, see: S. Hünig, H. Berneth, *Top. Curr. Chem.* **1980**, *92*, 1 – 44.
[8] For a theoretical comparison of violenes and cyanines, see: F. Nelson, H. Q. Tran, M. A. Nagy, *J. Am. Chem. Soc.* **1998**, *120*, 298 – 304.
[9] Part I: S. Hünig, M. Kemmer, H. Wenner, I. F. Perepichka, P. Bäuerle, A. Emge, G. Gescheidt, *Chem. Eur. J.* **1999**, *5*, 1969 – 1973.
[10] Part II: S. Hünig, M. Kemmer, H. Wenner, F. Barbosa, G. Gescheidt, I. F. Perepichka, P. Bäuerle, A. Emge, K. Peters, *Chem. Eur. J.* **2000**, *6*, 2618 – 2632.
[11] Part III: S. Hünig, I. F. Perepichka, M. Kemmer, H. Wenner, P. Bäuerle, A. Emge, *Tetrahedron* **2000**, *56*, 4203 – 4211.
[12] J. R. Lenhard, A. D. Cameron, *J. Phys. Chem.* **1993**, *97*, 4916 – 4925.
[13] J. R. Lenhard, R. L. Parton, *J. Am. Chem. Soc.* **1987**, *109*, 5808 – 5813.
[14] R. L. Parton, J. R. Lenhard, *J. Org. Chem.* **1990**, *55*, 49 – 57.

  0947-6539/01/0713-2756 $ 17.50+.50/0

[15] A. Smie, J. Heinze, *Angew. Chem.* **1997**, *109*, 375–379; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 363–367; and references therein.
[16] J. Heinze, P. Tschuncky in *Electronic Materials* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**, Chapter 9.
[17] P. Hübler, J. Heinze, *Ber. Bunsenges. Phys. Chem.* **1998**, *102*, 1506–1509.
[18] P. Tschuncky, J. Heinze, A. Smie, G. Engelmann, G. Koßmehl, *J. Electroanal. Chem.* **1997**, *433*, 223–226.
[19] W. Freund, S. Hünig, *J. Org. Chem.* **1987**, *52*, 2154–2161.
[20] M. Rosi, A. Sgamellotti, F. Franceschi, C. Floriani, *Chem. Eur. J.* **1999**, *5*, 2914–2920.
[21] F. Franceschi, E. Solari, R. Scopelliti, C. Floriani, *Angew. Chem.* **2000**, *112*, 1751–1753; *Angew. Chem. Int. Ed.* **2000**, *39*, 1685–1687.
[22] R. Rathore, P. Le Magueres, S. V. Lindeman, J. K. Kochi, *Angew. Chem.* **2000**, *112*, 818–821; *Angew. Chem. Int. Ed.* **2000**, *39*, 809–812.
[23] S. Hünig, M. Horner, *J. Am. Chem. Soc.* **1977**, *99*, 6120–6122.
[24] K. Hesse, S. Hünig, *Liebigs Ann. Chem.* **1985**, 740–750.
[25] T. Suzuki, M. Kondo, T. Nakamura, T. Fukushima, T. Miyashi, *Chem. Commun.* **1997**, 2325–2326.
[26] T. Muramatsu, A. Toyota, M. Kudou, Y. Ikegami, M. Watanabe, *J. Org. Chem.* **1999**, *64*, 7249–7253.
[27] EEC means chemical transformation after stepwise transfer of two electrons.
[28] P. Maslak, T. M. Vallombroso, W. H. Chapman, J. N. Narvaez, *Angew. Chem.* **1994**, *106*, 110–113; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 73–76.
[29] R. Akaba, Y. Niimura, T. Fukushima, Y. Kawai, T. Tajima, T. Kuragami, A. Negishi, M. Kamata, H. Sakuragi, K. Tokumaru, *J. Am. Chem. Soc.* **1992**, *114*, 4460–4464.
[30] C. P. Andrieux, J. M. Saveant, C. Tardy, *J. Am. Chem. Soc.* **1997**, *119*, 11546–11547.
[31] T. Suzuki, J. Nishida, T. Tsuji, *Angew. Chem.* **1997**, *109*, 1387–1389; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1329–1331.
[32] T. Suzuki, J. Nishida, T. Tsuji, *Chem. Commun.* **1998**, 2193–2194.
[33] F. Baer, H. Oehling, *Org. Magn. Reson.* **1974**, *6*, 421–429.
[34] H. Oehling, F. Baer, *Org. Magn. Reson.* **1977**, *9*, 465–466.
[35] H. Quast, E. Schmitt, *Chem. Ber.* **1969**, *102*, 568–574.
[36] S. Hünig, *Justus Liebigs Ann. Chem.* **1966**, *697*, 116–139.
[37] General procedures for cyanines: L. Berlin, O. Riester in *Methoden Org. Chem.* (Houben-Weyl), **1972**, *Vol. 51/d*, pp. 226–299.
[38] G. Arnold, G. Paal, *Tetrahedron* **1969**, *25*, 5995–6000.
[39] J. J. Vorsanger, *Bull. Soc. Chim. Fr.* **1964**, 863–864.
[40] H. C. A. van Beek, C. F. Hendriks, G. J. van der Net, L. Schaper, *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 31–34.
[41] A. F. Vompe, L. M. Meshki, *Zh. Org. Khim.* **1981**, *17*, 1735–1739.
[42] R. A. O'Ferrall, B. A. Murray, *J. Chem. Soc. Perkin Trans. 2* **1994**, *12*, 2461–2470.
[43] J. A. van Allan, J. D. Mee, C. A. Maggiulli, R. S. Henion, *J. Heterocycl. Chem.* **1975**, *12*, 1005–1007.
[44] L. G. S. Brooker, G. H. Keyes, F. L. White, *J. Am. Chem. Soc.* **1951**, *73*, 5326–5332.
[45] A. Carpmael (IG Farben), BP 498012, **1938**.
[46] H. Yamaguchi, *Yakugaku Zasshi* **1966**, *86*, 918–922.
[47] H. Quast, M. Ach, M. Kindermann, P. Rademacher, M. Schindler, *Chem. Ber.* **1993**, *126*, 503–516.
[48] K. Hartke, H.-D. Gerber, *J. Prakt. Chem.* **1996**, *338*, 763–765.
[49] J. D. Kendall, J. R. Majer, *J. Chem. Soc.* **1948**, 687–690.
[50] F. M. Hamer, *J. Chem. Soc.* **1956**, 1480–1496.
[51] X.-K. Jiang, G.-Z. Ji, D. Z.-R. Wang, *J. Phys. Org. Chem.* **1995**, *8*, 143–148.
[52] J. Salbeck, *J. Electroanal. Chem.* **1992**, *340*, 169.
[53] In accordance with earlier experience in heterocyclic BF_4 and PF_6 salts, 1–2% less carbon and sulfur is found than calculated. We assume a systematic error in the intensity of the V.p.c. signals in the combustion machine.
[54] S. Sforza, A. Dossena, R. Corradini, *Tetrahedron Lett.* **1998**, *39*, 711–714.
[55] A. G. Martinez, R. M. Alvarez, J. O. Barcina, M. Hanack, L. R. Subramanian, *J. Chem. Soc. Chem. Commun.* **1990**, 1571–1572.
[56] W.-K. Gries, E. Günther, S. Hünig, *Liebigs Ann. Chem.* **1991**, 1021–1028.

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