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Cyanine Dyes

Trinuclear Cyanines (TNCs) Revisited: A New Class of Electrochromics by Intramolecular π/σ Switching**

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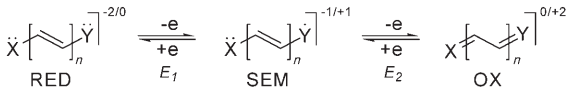
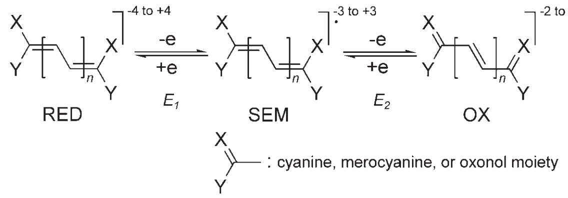
Dedicated to Professor Manfred Christl on the occasion of his 65th birthday

A system is electrochromic when reversible electron transfer reactions are linked to distinctive changes in color. The growing number of monographs and reviews are indicative of the subject's growing importance.[1] Organic systems in particular display rapid changes in color. These systems are derived primarily from violenes (Scheme 1),[2] in which radical ions with long-wavelength absorption are thermodynamically very stable. As, however, sometimes their persistence is limited, research has focused on electrochromic systems that undergo formal two-electron transfer. This can be achieved by coupling two cyanine systems ($1+2n$ methine groups between X and Y), which have thermodynamically unstable radicals.[3] Examples are given in Schemes 2[4] and 3. Redox reactions according to Schemes 1 and 2 change only the number of π electrons. According to Scheme 3, in contrast, σ bonds are also switched.[5]

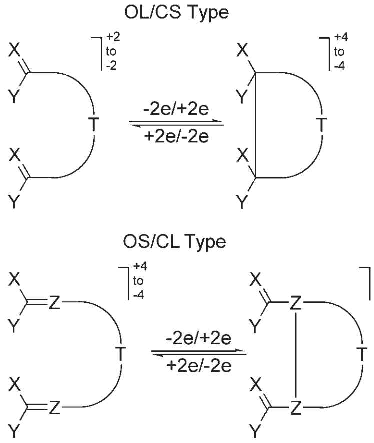


Scheme 1. Structural principle of reversible redox systems of the violene type ($2n$ methine groups between X and Y). The semiquinone formation constant K_{SEM} is very high.

In evaluating (spectro-)electrochemical data, we show that the trinuclear cyanines (TNCs)—established as sensitizers and systematically studied in the meantime[6]—represent a new type of electrochromic compound with intramolecular π/σ switching. For this purpose we propose two complementary types, TNC-A and TNC-B, and provide one example of each. As is already known in some cases, these two TNC types form persistent radicals in a reversible one-electron transfer. Up to now, however, a more significant property has been overlooked: the formal two-electron transfer forming a central methylene cyclopropane unit, which divides the extended Y-shaped π system into three short π systems (probably a mixture of *cis* and *trans* isomers). The result is a strong hypsochromic electrochromic effect. The charge state determined by the terminal X, Y, and Z groups of TNC-A and TNC-B determine which redox processes involving one- and two-electron transfers are, in principle, possible. However, if TNC-A and TNC-B have the same end groups, their redox reactions are mirror images of



Scheme 2. Structural principle of reversible redox systems of the violene/cyanine-hybrid type. K_{SEM} is (very) small.



Scheme 3. Structural principles of reversible redox systems with switching of π/σ bonds. T: saturated or unsaturated spacer; Y−C(=X)−: chromophoric π system of cyanines, merocyanine, and oxonol units which is disconnected in the reaction OL→CS or CL→OS; Z: N or CR; OL: open form, long-wavelength absorption; CS: closed form, short-wavelength absorption; OS: open form, short-wavelength absorption; CL: closed form, long-wavelength absorption.

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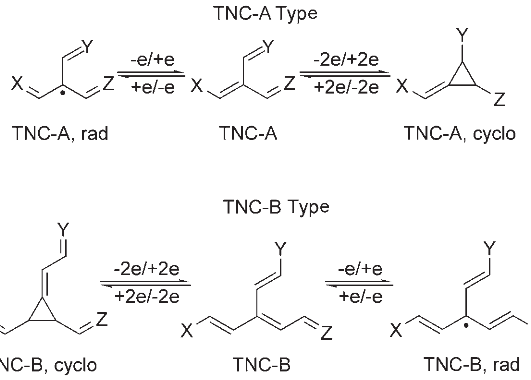
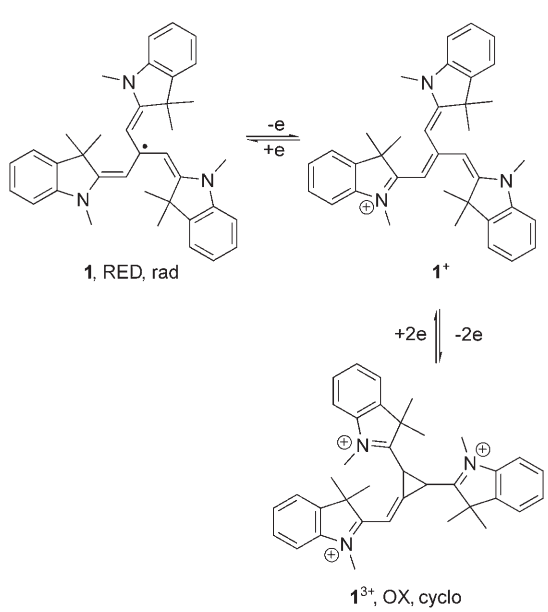
each other (Scheme 4). The newly formed covalent σ bond is probably even weaker than that in the tetramethylmethylenecyclopropane, which has a bond length of 156.3 pm.[7] The new bond is significantly longer than the already long cyclopropane bond (149.9 pm).[8]



Scheme 4. Structural principles of reversible redox systems of the trinuclear cyanine types TNC-A and TNC-B. The charges and, hence, the possibilities of reduction (1 e or 2 e) and oxidation (1 e or 2 e) are determined by the respective end groups; on account of the wide range of variations, they are omitted from the general formulas. X, Y, and Z are end groups typical for cyanines, merocyanines, and oxonols. For clarity only the lowest vinylogues are shown.

The structural principles in Scheme 4 are demonstrated by two known examples with closely related structures: the monocation **1**$^{1+}$ (TNC-A type) and the dication **2**$^{2+}$ (TNC-B type), which, apart from charge, differ only in the number of methine groups (Scheme 5). The dye **1**$^{+}$ is one of the oldest known trinuclear cyanines[9] and has been studied in detail as the **1**-BF$_4$ salt.[10] Owing to the large indolenine end groups, in solution it assumes a twisted conformation with C_3 symmetry.[11,12] Hence, it was questionable whether the oxidation-induced increased compression of the end groups would permit the formation of **1**$^{3+}$,OX,cyclo, especially in view of the Coulombic repulsion of three relatively close positive charges.



Scheme 5.

The cyclic voltammogram (CV) of the reduction of **1**$^{+}$ shows a fully reversible one-electron transfer to **1**,RED,rad.[28] The persistent radical has already been characterized by its absorption maximum at 445 nm[12] and its ESR spectrum,[12,13] whose highly resolved pattern reflects the C_3 symmetry of **1**,RED,rad.[14] In contrast, the cyclic voltammogram for the oxidation of **1**$^{+}$ recorded with a slow scan rate at room temperature shows only one wave at $E_p = 920$ mV. The absence of a peak in the reverse scan close to this potential points to a chemically irreversible redox process. At higher scan rates, the wave splits into two waves (20 °C, 10 V s^{-1}) (Figure 1 a).

Measurements at −35 °C clearly indicate two one-electron transfer processes. The first forms an intermediate radical dication[12] and is in principle reversible; in contrast, the second is followed by an irreversible chemical reaction (Figure 1 b).[15] At slow scan rates only one 2 e^{-} wave is observed as a result of a disproportionation that constantly regenerates the starting **1**$^{+}$ species, enabling the entire heterogeneous electron transfer to proceed exclusively through the transformation **1**$^{+}$→**1**$^{2+}$.[28] All experimental findings show unequivocally that the oxidation of **1**-BF$_4$ proceeds by means of an EEC/Disp mechanism.[15,16] As spectroelectrochemical measurements attest (Figure 1 c), the

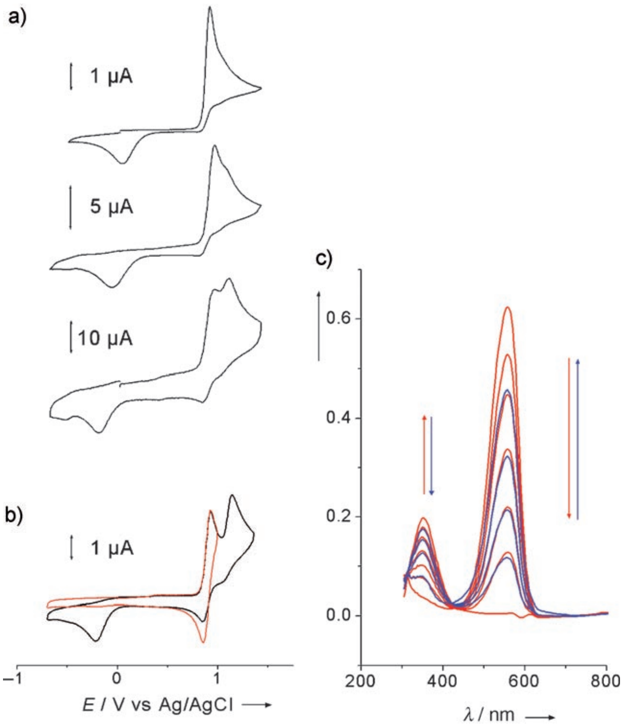


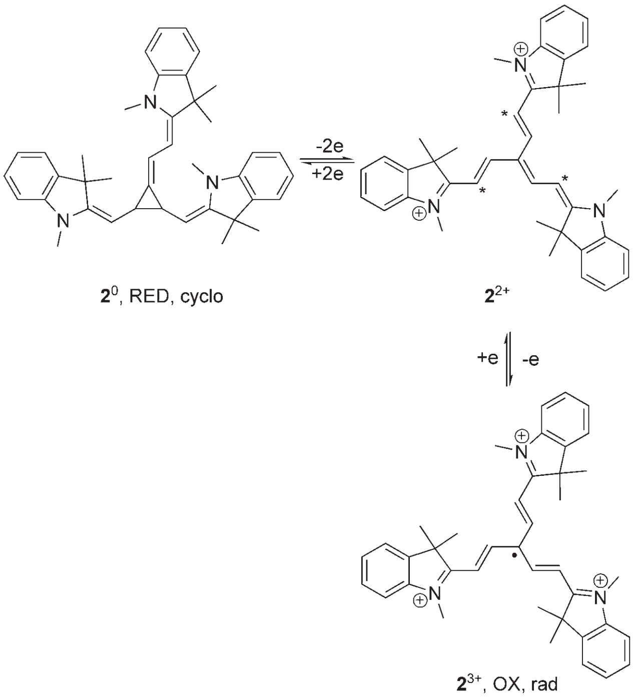
Figure 1. a) Cyclic voltammograms of the oxidation of **1**-BF$_4$ ($c = 1$ mM) in CH$_3$CN/0.1 M (C$_4$H$_9$)$_4$NPF$_6$, $\nu = 0.1$, 1 and 10 V s^{-1} at room temperature, b) $\nu = 1$ V s^{-1} at −35 °C. c) UV/Vis spectra recorded during the oxidation of **1**-BF$_4$ ($c = 1$ mM) in CH$_2$Cl$_2$/0.1 M (C$_4$H$_9$)$_4$NPF$_6$ (red) and during the rereduction of the follow-up product (blue). The cyclic voltammetric measurement[28] of the electrochemically induced oxidation and reduction took place at 0.1 V s^{-1} in a spectroelectrochemical thin-layer cell with a thickness of 20 μm.

transfer of two electrons in the subsequent reduction of the oxidation product regenerates the starting system **1**$^+$ (peak at $E_p = -40$ mV). As the potential increases during the oxidation of **1**$^+$, the long-wavelength maximum at 558 nm in the spectrovoltammogram disappears completely. The simultaneous appearance of weak bands at short wavelengths indicates the formation of shorter conjugated molecular units. In keeping with the diminished extinction, about 75% of **1**$^+$ is regained from the rereduction of the oxidation products and about 25% is lost in unknown side reactions. In the cyclic voltammogram of several repetitions of the redox cycle these appear as weak peaks in the range of −100 mV to 325 mV.[28] The fact that side reactions occur during the generation of trications is not surprising, as such highly charged particles easily undergo nucleophilic reactions.

Our experimental findings do not support the potential inversion associated with an EE mechanism that is repeatedly observed in formal two-electron processes[17] and in which the second electron transfer is energetically favored on account of marked structural changes in the system.

What evidence can be found for the formation of the methylene cyclopropane unit at the trication level? Measurements at different scan rates and concentrations and in different solvents show that the follow-up reaction is a pure first-order reaction.[28] This excludes intermolecular reactions and is evidence of an intramolecular coupling reaction of the trication **1**$^{3+}$ to give **1**$^{3+}$,OX,cyclo. The driving force behind this is the spin coupling between the two "radical" indolenium groups, which results in the formation of the cyclopropane ring and simultaneous rehybridization ($sp^2 \rightarrow sp^3$) of the coupled C atoms. This type of σ dimerization of charged radical species in intermolecular reactions has been reported several times recently.[18] Those examples are unequivocal; however, many other literature reports postulate not a σ dimerization, but a π dimerization.[19] In the present case, though, π dimerization after the oxidation of **1**$^+$ to **1**$^{3+}$ can be completely excluded on account of geometric factors, as direct intramolecular overlapping of π-conjugated units in the molecule is impossible. Moreover, the experiments prove that despite the existence of ions with the same charge, in suitable (polar) solvents σ bonds between ionic radical centers are possible. This refutes the frequent assertion that the Coulombic repulsion between particles with the same charge prevents charged radical ions from reacting to form σ bonds.[19] The results are in excellent agreement with Debye's classic theory, which predicts "high" kinetic rates for such ionic reactions.[20]

In solution the dye **2**-$(BF_4)_2$, known since 1972, was assigned the preferred conformation of a *meso*-substituted pentamethine cyanine.[21] As expected, the redox behavior of **2**$^{2+}$ is the mirror-image of that of **1**$^{1+}$ (Scheme 6). Once again, at slow scan rates the cyclic voltammogram of the reduction of **2**$^{2+}$ exhibits a single irreversible wave at $E_p = -780$ mV, which indicates a chemical follow-up reaction (Figure 2a). Analogous to system **1**, at higher scan rates this wave splits into two waves that can be attributed to one-electron-transfer processes, the first of which is evidently chemically reversible and the second is coupled to a chemical follow-up reaction. In other words, once again a total of two electrons is transferred.



Scheme 6.

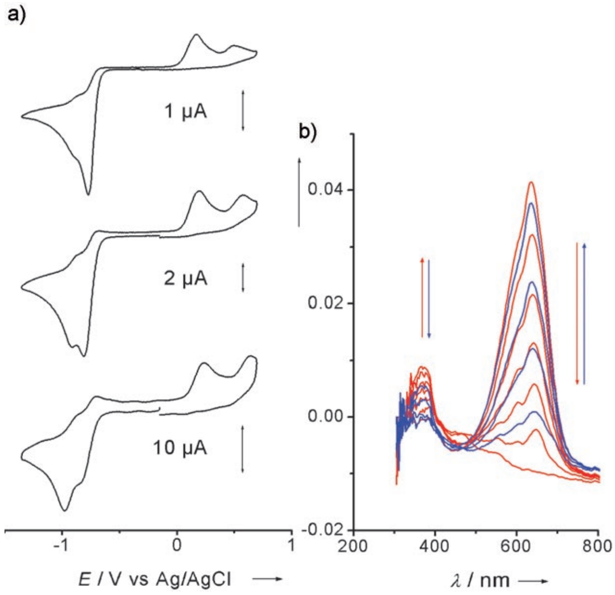
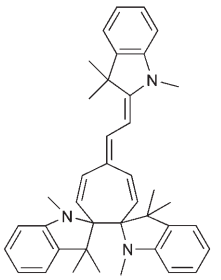


Figure 2. a) Cyclic voltammograms of the reduction of **2**-$(BF_4)_2$ ($c = 1$ mM) in CH_2Cl_2/0.1 M $(C_4H_9)_4NPF_6$ at $\nu = 0.1, 1, 10$ V s^{-1} and room temperature. b) UV/Vis spectra taken during the reduction of **2**-$(BF_4)_2$ ($c = 1$ mM) in CH_2Cl_2/0.1 M $(C_4H_9)_4NPF_6$ (red) and during the reoxidation of the follow-up products (blue). The cyclic voltammetric measurement of the electrochemical reduction and oxidation[28] took place at 0.1 V s^{-1} in a spectroelectrochemical thin-layer cell with a thickness of 20 µm.

The rate dependency of the voltammetric data proves conclusively that we are dealing with an EEC/Disp mechanism. Furthermore, kinetic investigations prove that the formation of the follow-up product of **2** involves a first-order reaction; the most likely step, once again, is an intramolecular reaction resulting in the formation of the central methylenecyclopropane ring in **2**^{0},RED,cyclo. The spectroscopic data support this interpretation (Figure 2b). In contrast to system **1**$^{+}$, in **2**$^{2+}$ the ring is formed at the level of a neutral species and involves the coupling of two indolinyl radical units and the formation of a σ bond, accompanied by spin saturation and rehybridization. Since there are no charged species, this is apparently a purely radical coupling step with a very low activation barrier. The spectroelectrochemical measurements (Figure 2b) are proof of these processes. The strong absorption band of **2**$^{2+}$ at 635 nm disappears almost completely during the reduction and is accompanied by the formation of an isosbestic point, whereby only a weak band appears at about 375 nm. This dramatic hypsochromic effect over the entire visible spectrum is in perfect agreement with the formation of a methylenecyclopropane ring. In analogy to **1**$^{3+}$, the Y-shaped π system of **2**$^{2+}$ is divided intramolecularly into three short π subunits. On the reoxidation of **2**^{0},RED,cyclo, the starting spectrum of **2**$^{2+}$ reappears almost quantitatively (92%), which is conclusive proof of the regeneration of **2**$^{2+}$ from the follow-up product. That said, the cyclic voltammogram for the reoxidation of **2**^{0},RED highlights a complication. Besides the oxidation peak at $E_p = 175$ mV, a second wave appears at $E_p = 500$ mV, which, as spectroscopically verified, also regenerates the starting system **2**$^{2+}$. Thus, a follow-up or competitive reaction occurs during the reduction of **2**$^{2+}$ to the neutral **2**^{0},RED,cyclo. All available data prove a supplementary reaction of this nature that, depending on the temperature, accounts for between 5 and 20%. One conceivable explanation is an intramolecular coupling of a biradical preliminary stage of **2**^{0} to form a seven-membered-ring compound corresponding to structure **3**.[28]



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It is also possible that **3** is formed from the *cis* form of **2**^{0},RED,cyclo through electrocyclical rearrangement, which in the case of *cis*-1,2-divinylcyclopropane takes place spontaneously already at −50°C.[22] As, however, the oxidation of all of these follow-up products leads back to the starting system, their structure is irrelevant for the electrochromic effect. Structure **3** would be in agreement with the observed weak short-wave bands as well as with the fact that its oxidation to **2**$^{2+}$ occurs at a more positive potential than the reoxidation of **2**^{0},RED,cyclo.

As expected, the oxidation of **2**$^{2+}$ to the trication **2**$^{3+}$,OX,rad is a fully reversible one-electron transfer[12] (Scheme 6 and reference [28]). At the expense of the absorption of the band of **2**$^{2+}$ at 635 nm, a new band with lower intensity (ca. 60%) forms at 513 nm; it must be attributed to the trication radical **2**$^{3+}$,OX, rad.

As representative of the TNC-A and TNC-B types, the TNC examples **1**$^{+}$ and **2**$^{2+}$ exhibit the expected mirror-image redox behavior. Hence, we can conclude that when the molecule closes to form a central methylene cyclopropane unit, a long Y-shaped π system is converted intramolecularly into three short π systems, and vice versa: when the unit is opened, the short π systems transform into a long system. In principle, if systems with favorable potentials are chosen, the two molecule types are capable of reversible redox switching. One consequence of this rearrangement is a substantial electrochromic effect.

Similar behavior may be expected of other derivatives with the general TNC-A and TNC-B structures (Scheme 4). Certain end groups could probably even make the methylenecyclopropane form the thermodynamically more stable one, which would generate bathochromic electrochromism. We expect that other groups will also work on potential applications as on scope and limitations of the electrochemical principle presented here.

Experimental Section

All electrochemical experiments were conducted under argon atmosphere in specially constructed cells with an internal dry column of activated aluminum oxide.[23] The spectroelectrochemical experiments were conducted under argon atmosphere in a special thin-layer cell in reflection mode. A combined working and counterelectrode was used for the measurements. The working electrode (disk electrode) was made of a platinum wire (∅ = 1 mm) sealed in glass; the counterelectrode was a platinum wire wound around the vitreous body. A silver wire served as the reference electrode. The potentials were calibrated with the ferrocinium/ferrocene system vs Ag/AgCl.

The cyclic voltammograms were performed with a computer-supported transient recorder system based on a Keithley DAS-1700 series A/D converter card. This experiment setup was driven by a Jaissle potentiostat-galvanostat IMP 88 PC; an EG&G PARC model 175 scan generator was used to control the potential scan rate.

A Zeiss spectrometer MCS 500—a modular spectrometer system consisting of an NMC 105 power supply, CLH 500 lamp module, and MCS 521 Vis spectrometer module with Y light guide—was used to measure the UV/Vis spectra.

The TNC **1**-BF_4 was synthesized as described in the literature;[10] for **2**-$(BF_4)_2$ the synthesis and purification were simplified as follows: 1,3,3-Trimethyl-2-methyleneindolenine (0.37 mL, 1.00 mmol) was added to a solution of 2-dimethylaminomethylene-1,3-bis(dimethylimmonium)propanebis(tetrafluoroborate)[24] 100 mg (0.28 mmol) in 5 mL of Ac_2O and KOAc (98.1 mg, 1.00 mmol) and stirred for 4 h at room temperature. The formation of the blue dye was monitored by thin-layer chromatography (CH_2Cl_2/MeOH 8:1); the silica gel sheets were treated before use with NaBr in MeOH according to reference [25]. After the reaction was complete, the solvent was distilled off and the residue was treated with at least 4 × 25 mL of methanol and the filtered solution was evaporated.[10] The residue was chromatographed with CH_2Cl_2/MeOH 10:1 on silica gel treated before use with NaBr in MeOH according to reference [25]. The dye fraction was concentrated just before solid material precipitated. Then the concentrated solution was added dropwise 100 mL of a highly concentrated solution of $NaBF_4$ in water with constant stirring. After a few hours a solid matter precipitated (cf. references [26] and [27]), which was filtered and recrystallized from MeOH/H_2O (1:4). The solid appears as shining green crystals. Yield: 82.0 mg (0.11 mmol, 39%) **2**-$(BF_4)_2$. Melting point, UV/Vis, and ^{1}H NMR data are in accord with those in reference [26].

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[28] See the Supporting Information.