DOI: 10.1002/ejoc.200900393

Creation of Stabilized Electrochromic Materials by Taking Advantage of Azulene Skeletons

Shunji Ito*[a] **and Noboru Morita**[b]

Keywords: Cyanines / Cations / Redox chemistry / Electrochemistry / Liquid crystals

The preparative scope of the new structural principle of utilization of azulene skeletons as redox-active chromophores for the production of stabilized electrochromic materials is demonstrated in several examples. The structural principle takes advantage both of the cyanine-type polymethine dyes and of the violene-type redox systems. Appropriate combination of cyanine and/or violene substructures will produce at least one cyanine-type structure in the reduced or oxidized form through an overall two-electron transfer, although some will produce a cross-conjugated cyanine-type structure. Hünig's violene–cyanine hybrid structures, utilizing the bis(enediyne) system, afford electrochromic materials that exhibit strong absorptions in the near-infrared region in the dianionic state. Cyanine–cyanine hybrid structures, consisting of pairs of cyanine units, show two-step color changes based on single electron transfer in each step. Combinations of the cyanine and/or the violene substructures permit the design of novel stabilized electrochromic systems, including polyelectrochromic systems. The flexibility of the structural principle is demonstrated by the violene–violene hybrid, violene–cyanine–cyanine hybrid, violene-cyanine-violene hybrid, and violene-violene-violene hybrid structures. New examples of the violene-like redox system with inverse electron demand are provided by 6-aminoazulene derivatives. The liquid-crystalline properties of the redox-active columnar mesogen are revealed by several azulene-substituted electrochromic materials.

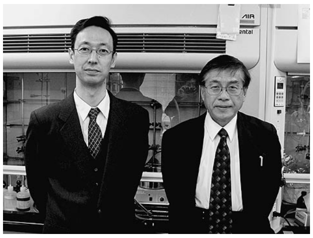
1. Introduction

Electrochromism is observed in reversible redox systems that exhibit significant color changes in their different oxidation states.[1] Stabilization of the redox cycle is very important in the construction of potentially useful electrochromic materials, because the molecules utilized for this application require high redox stabilities. The construction of organic molecules containing multiple redox-active chromophores is important for the preparation of novel polyelectrochromic materials that will respond to different potentials by adopting a variety of colors.[2] The scope of a new structural principle based on azulene skeletons for the preparation of stabilized electrochromic and polyelectrochromic materials is demonstrated in several examples. The aim of this review is to demonstrate the broad applicability of the new structural principle and the efficiency of azulene chromophores as terminal groups for the preparation of

---

[a] Graduate School of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan
Fax: +81-172-39-3541
E-mail: itsnj@cc.hirosaki-u.ac.jp
[b] Department of Chemistry, Graduate School of Science, Tohoku University,
Sendai 980-8578, Japan

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900393.



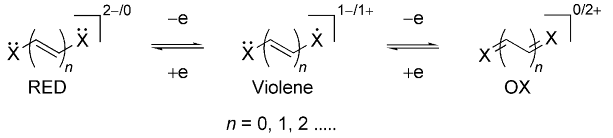
Shunji Ito (left) was born in Tokyo, Japan, in 1962. He was appointed as an assistant at the College of General Education in Tohoku University in 1989 and received his Ph.D. from Tohoku University in 1991 under the supervision of Prof. Toyonobu Asao. He moved to the Faculty of Science in Tohoku University in 1993 and was promoted to an assistant professor in 2003. In 1996–1998 he worked as a postdoctoral fellow with Prof. Klaus Müllen at the Max-Planck-Institut für Polymerforschung, Mainz (Germany). In 2003 he moved to the Faculty of Science and Technology in Hirosaki University as a full professor. The research in his group focuses on the synthetic study of functional materials by employment of novel π-electron systems.

Noboru Morita (right) was born in Kochi, Japan, in 1946. He was appointed as an assistant at the College of General Education in Tohoku University in 1972 and received his Ph.D. from Tohoku University in 1973 under the supervision of Prof. Yoshio Kitahara. He moved to Tokyo Institute of Technology in 1974. From 1976–1977 he worked as a postdoctoral fellow with Prof. Sidney I. Miller at Illinois Institute of Technology, Chicago, Illinois (U.S.A.). He moved to the College of General Education in Tohoku University in 1977 and was promoted to an assistant professor in 1989 and to a full professor in 1992. In 1993 he moved to the Faculty of Science in Tohoku University. The research in his group focuses on the synthetic study on the novel aromatic compounds.

stabilized electrochromic materials including polyelectrochromic materials.[3]

1.1. Violenes and Cyanines

Violenes, the general structure of which is represented in Scheme 1, are typical examples of systems that exhibit electrochromism. A violene consists of a conjugated chain with two redox-active groups and might be classified into two types (see Figure 1). As can be seen from the positions of the end groups, in one type they are separated by an aromatic core, and in the other they are located inside a cyclic π-electron system.[4] In both cases the long-wavelength-absorbing species in violene-type redox systems are radical ionic states. In general, the radical ionic species do not show high redox stabilities, although some of them might have high thermodynamic stabilities, depending on the substituent end groups.



Scheme 1. General structure of violenes.

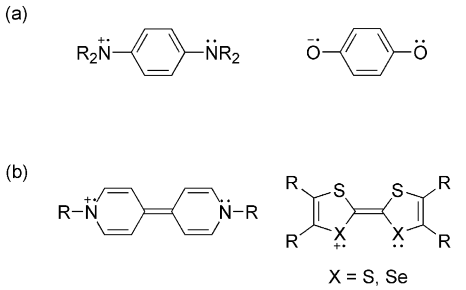


Figure 1. Two types of violene structures: (a) Wurster-type violenes, (b) Weitz-type violenes.

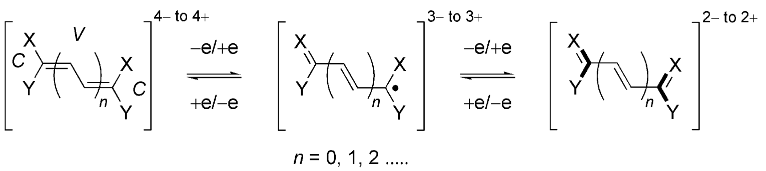
A cyanine, on the other hand, is a polymethine dye consisting of iminium ion and amine units, making up a conjugated π-electron system with an odd number of methine units. The cyanine dye does not in itself possess good electrochemical properties. This is in contrast with the violene system, which is composed of an even number of methine units. In this manuscript, violene (V) and cyanine (C) systems are defined by the numbers of methine units contained in conjugated π-electron systems.

1.2. Violene–Cyanine Hybrids

Hünig et al. have recently proposed a concept of a violene–cyanine hybrid system for the production of stabilized organic electrochromic materials.[5] Such a hybrid is made up of a violene-type redox system containing delocalized closed-shell polymethine (e.g., cyanine) dyes as end groups. Hünig's V–C hybrids are expected to provide colors of cyanine dyes by overall two-electron transfer, as illustrated by the general structure in Scheme 2. The cyanine-type substructure generated by the electron-transfer is represented by the bold line in the general structure. Contrary to the violene-type redox system, both colored and discolored species consist of closed-shell structures. Therefore, persistency of the electrochromic system would be expected in the hybrid structure.

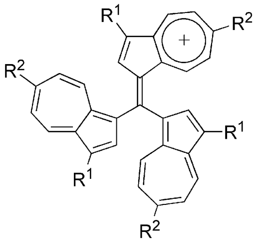
1.3. The Azulene Skeletone as a Redox-Active Chromophore

For the construction of stabilized electrochromic materials it is very important to generate highly colored cyanine-type substructures under electrochemical conditions. Azulene ($C_{10}H_8$) has attracted the interest of many research groups over the years because of its unusual properties arising from its remarkable polarizability, as well as its attractive blue color. The azulene system has a tendency to stabilize cations – as well as anions, depending on the position substituted – through the contributions of its formal tropylium and cyclopentadienide substructures.[6] We found that azulene substitution induces extreme stability in cationic states (Figure 2)[7,8] and also that *tert*-butyl groups on each azulene ring enhance their thermodynamic stabilities. Hydrocarbon-based carbocations, consisting only of carbon and hydrogen atoms, are generally very reactive species. However, the methyl cation **1b**$^+$, stabilized by six *tert*-butyl groups (p$K_R$$^+$ = 14.3), is one of the most stable hydrocarbon-based carbocations ever reported.[7] Introduction of electron-donating substituents such as methoxy or dimethylamino groups stabilized the methyl cation much more efficiently. The tris(dimethylamino)-substituted methyl cation **1c**$^+$ has been shown to have extreme stability for a methyl



Scheme 2. General structure of Hünig's V–C hybrids. One or two of the X=C–Y moieties are cyanines, oxonols, or merocyanines.

cation ($pK_R^+ = 24.3$).[8] Therefore, application of azulene substituents as redox-active end groups in cyanine substructures should offer great advantages for the construction of novel hybrid structures with high thermodynamic stabilities in their ionic states.



1a$^+$: $R^1 = H$, $R^2 = H$
1b$^+$: $R^1 = tBu$, $R^2 = tBu$
1c$^+$: $R^1 = H$, $R^2 = NMe_2$

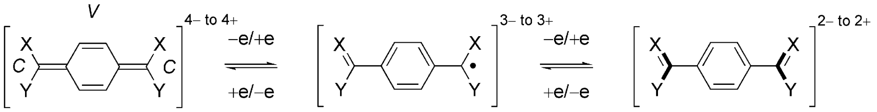
Figure 2. Azulene-substituted methyl cations with extremely high stabilities.

2. Wurster-Type V–C Hybrid Systems

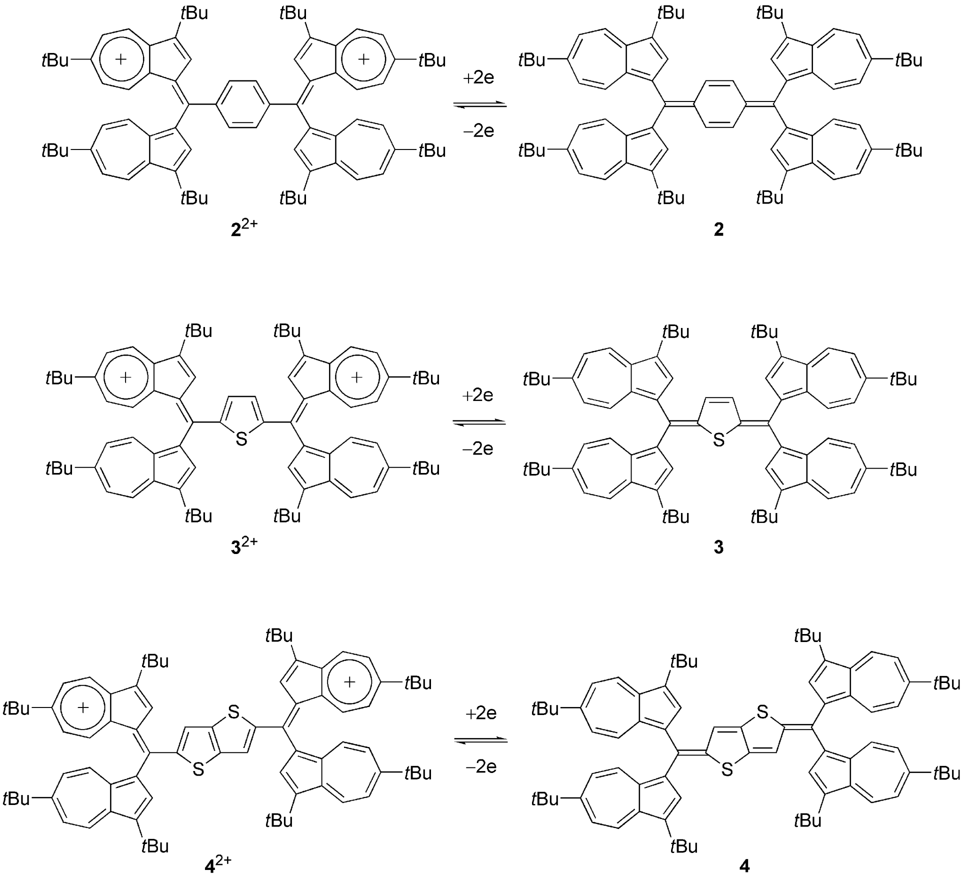
2.1. Inverse Wurster-Type V–C Hybrid Systems

Because of the polyolefinic structure in the violene core, the general structure proposed by Hünig et al. should be based on open-chain vinylogous redox systems.[4] We found the V–C hybrid structure with the inverse Wurster-type violene core in our reported compounds, which exhibit two-color changes between quinoid colors and cyanine colors (Scheme 3).[9]

Dication $\mathbf{2}^{2+}$ ($\lambda_{max} = 703$ nm), composed of two bis(1-azulenyl)methylium units connected through a *p*-phenylene spacer, exemplifies a V–C hybrid structure with an inverse Wurster-type violene core exhibiting aromatic character in its oxidized form (Scheme 4). In general, a dicationic structure would be expected to show destabilization, but the V–C hybrid dication exhibits high thermodynamic stability. Dication $\mathbf{2}^{2+}$ exhibits the presumed one-step, two-electron reduction upon CV, but transformation of the dication $\mathbf{2}^{2+}$



Scheme 3. General structure of V–C hybrids containing inverse Wurster-type violene cores.

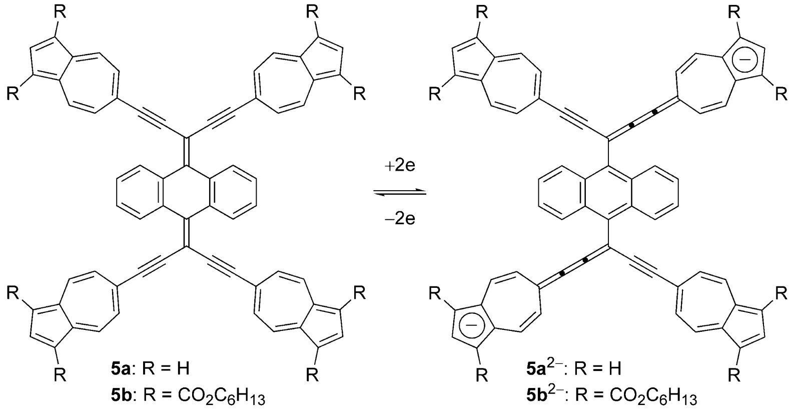


Scheme 4. V–C hybrids with inverse Wurster-type violene cores.

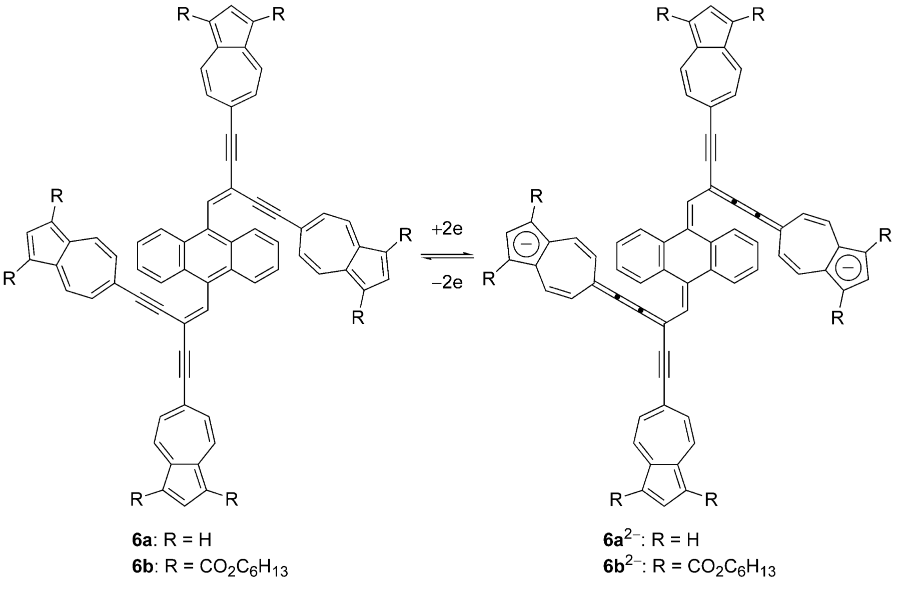
into the quinoid structure **2** is hampered by the instability of the reduced species. The presumed two color changes are accomplished through the preparation of two types of new dications: $\mathbf{3}^{2+}$ ($\lambda_{\max}$ = 729 nm) and $\mathbf{4}^{2+}$ ($\lambda_{\max}$ = 718 nm), with thiophenediyl and thienothiophenediyl spacers incorporated as the violene cores (Scheme 4). The thienoquinoid substructures in **3** ($\lambda_{\max}$ = 556 nm) and **4** ($\lambda_{\max}$ = 601 nm) are responsible for the stabilization of the reduced species instead of the generation of quinoidal forms as in the case of dication $\mathbf{2}^{2+}$. These dications $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$ behave as V–C hybrids with inverse Wurster-type violene cores, in which the four end groups in the general structure are azulenes.

2.2. Wurster-Type V–C Hybrids with Strong Absorption in the Near-Infrared Region

Enediyne structures are molecular scaffolds designed for molecular architectures that contain one- and two-dimensional carbon networks.[10] Electrochemical studies of the enediyne system have so far revealed its strongly electron-accepting properties and an ability to undergo multi-electron reduction under cyclic voltammetric conditions.[11] The 6-azulenyl group has a strong ability to stabilize anionic species, owing to the remarkable polarizability of the azulene ring. 6-Azulenyl groups can thus be combined with the enediyne units of the V–C hybrid structure as redox-active end groups to provide stabilized electrochromic materials exhibiting strong absorptions in the near-infrared region. We have prepared the 9,10-bis[3-(6-azulenyl)-1-(6-azulenylethynyl)-2-propynylidene]-9,10-dihydroanthracenes **5a** and **5b** (Scheme 5) as new V–C hybrids with Wurster-type violene cores exhibiting strong absorption in the near-infrared region.[12] The anthraquinodimethane unit in **5a** and **5b** is introduced in order to decrease the redox interaction in the anion units through aromatization in their two-electron-reduced states $\mathbf{5a}^{2-}$ and $\mathbf{5b}^{2-}$. As would be expected from their V–C hybrid structures with Wurster-type violene cores, **5a** and **5b** each exhibit two one-step, two-electron



Scheme 5. V–C hybrid systems based on enediyne structures and Wurster-type violene cores.



Scheme 6. V–C hybrids prepared with enediyne structures and inverse Wurster-type violene cores.

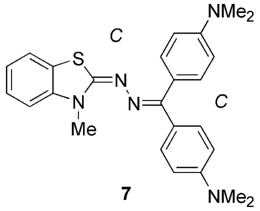
reductions upon CV and also afford strong absorption in the longer-wavelength region in their two-electron-reduced states **5a**$^{2-}$ ($\lambda_{\max}$ = 844 nm) and **5b**$^{2-}$ ($\lambda_{\max}$ = 885 nm).

When the two endiyne units are located outside the aromatic core, the redox system should behave as a V–C hybrid with an inverse Wurster-type violene core. We demonstrate this hybrid structure with the 9,10-bis[4-(6-azulenyl)-2-(6-azulenylethynyl)but-1-en-3-ynyl]anthracenes **6a** and **6b**, in which electrochemical reduction should produce anthraquinodimethane substructures, in addition to the formation of cyanine-type substructures in their two-electron-reduced states **6a**$^{2-}$ and **6b**$^{2-}$ (Scheme 6).[13] The dianionic structures were expected to produce bathochromic shifts of the strong absorptions in the near-infrared region. As anticipated, the V–C hybrids with the inverse Wurster-type violene core exhibited significant bathochromic shifts in the strong absorptions in the near-infrared region, especially in the case of the two-electron reduced state **6b**$^{2-}$ (**6a**$^{2-}$: $\lambda_{\max}$ = 837 nm; **6b**$^{2-}$: $\lambda_{\max}$ = 967 nm).

3. Cyanine–Cyanine Hybrids

These results indicate that the two-colored states could be established with V–C hybrids based on Wurster-type violene cores. These systems, however, would not exhibit multiple color changes, which are important for the construction of polyelectrochromic materials. To achieve multiple color changes, we proposed a molecular design derived from cyanine-based polymethine dyes.[3] Cyanine dyes do not in themselves possess good electrochemical properties. However, if either one or two end groups are replaced by other cyanine substructures, two-step redox activities with three color changes should be inducible in the hybrid structures.

The general structure of a C–C hybrid with a cyanine substructure at one terminus is represented in Scheme 7. Typical electric charges in the hybrid structure are represented. The central radical ionic state in Scheme 7 may be stabilized by the capto-dative substituents effect,[14] so the C–C hybrid should possess two-step redox properties associated with significant color changes. The C–C hybrid would be exemplified by the structure **7** reported by Hünig et al. together with the V–C hybrid,[5] although they do not designate their structure as a C–C hybrid (Figure 3). Compound **7** is reported to exhibit stepwise oxidation with significant color changes.



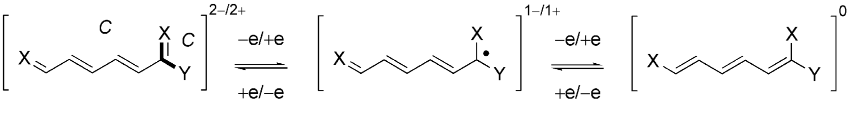
7

Figure 3. C–C hybrid consisting of two cyanine substructures.

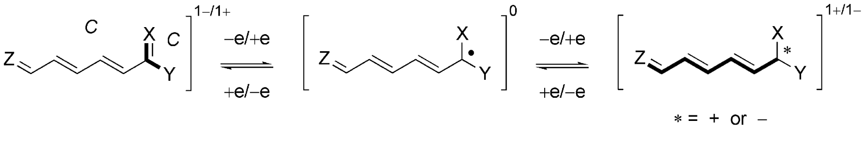
3.1. C–C Hybrid Consisting of Two Cyanine Substructures

The electronic natures of the end groups should be very important for the design of the C–C hybrid structures. The general structure of a C–C hybrid consisting of two cyanine substructures with different electronic demand is represented in Scheme 8. The moieties Z and X/Y (X=C–Y) in the general structure represent combinations of donor and acceptor groups, so the system should also exhibit two-step redox properties as illustrated in Scheme 8. In this case the cyanine substructure in the C–C hybrid is transformed into a different cyanine substructure by two-electron transfer, via the neutral radical state. The neutral radical state should be stabilized by the capto-dative substituents effect, because the radical is substituted by the donor and acceptor groups, so the radical state should also exhibit an absorption in the visible region. Stabilized three-colored states should therefore be achieved by this C–C hybrid structure.

The bis(1-azulenyl)methyl cations **8**$^+$, **9**$^+$, and **10**$^+$ with electron-withdrawing π-electron systems represented in Figure 4 exemplify this type of C–C hybrid.[15,16] Reduction of these systems should afford the neutral radicals, stabilized by the capto-dative substituents effect, because the neutral radicals can interact with both donor and acceptor substituents. The anionic states are also stabilized by the contributions of the electron-withdrawing π-electron systems, which should give rise to the third color in this system. The new cations **8**$^+$, **9**$^+$, and **10**$^+$ are obtained as stable, intensely colored crystals that can be stored in the crystalline state, despite the fact that the cations are substituted with elec-



Scheme 7. General structure of a C–C hybrid based on two cyanine substructures.



Scheme 8. General structure of a C–C hybrid made up of two cyanine substructures with different electronic demand. The moieties Z and X/Y (X=C–Y) represent combinations of donor and acceptor groups.

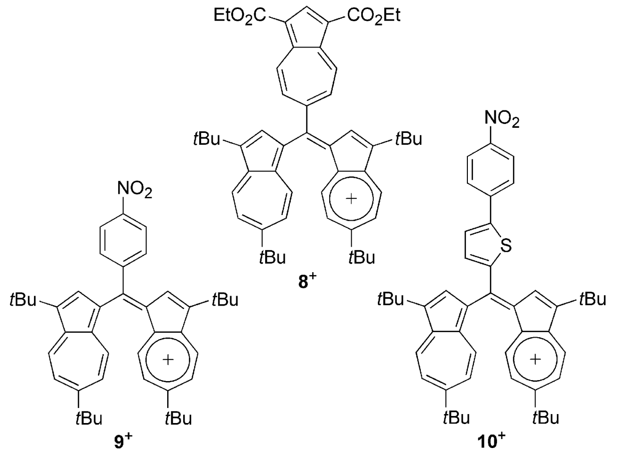
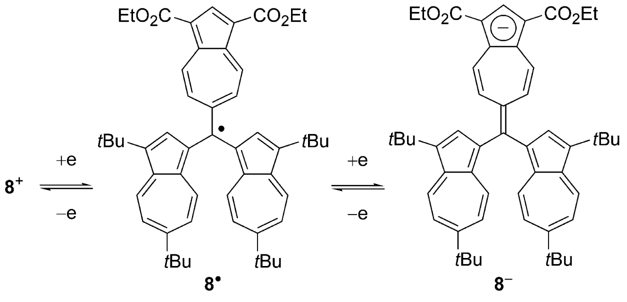


Figure 4. C–C hybrids based on two cyanine substructures with different electronic demands.



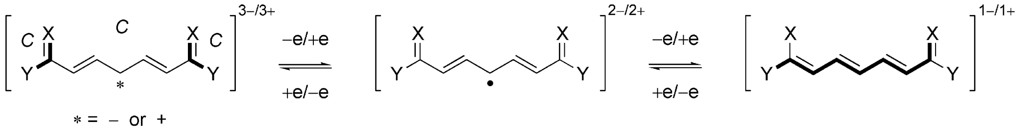
Scheme 9. Redox properties of the push-pull-substituted methyl cation $\mathbf{8}^+$.

tron-withdrawing substituents. They each possess three-stage reduction properties with a small numerical sum of the first and the second reduction potentials. It is noteworthy that cation $\mathbf{8}^+$ exhibits three primary colors, depending on the charged state: deep green for monocation $\mathbf{8}^+$, deep blue for neutral radical $\mathbf{8}^{\cdot}$, and red for anion $\mathbf{8}^-$ (Scheme 9).[15]

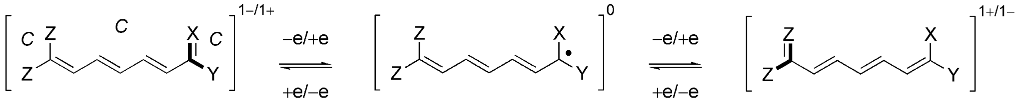
3.2. C–C Hybrids Containing Cyanine Substructures in the Two Termini

The general structure of a C–C hybrid with cyanine substructures at both of its termini is represented in Scheme 10. These systems should also present two-step redox properties with three color changes. However, defects in the conjugation will be induced in the core cyanine units during the redox reaction. Such defects should decrease the redox stabilities.

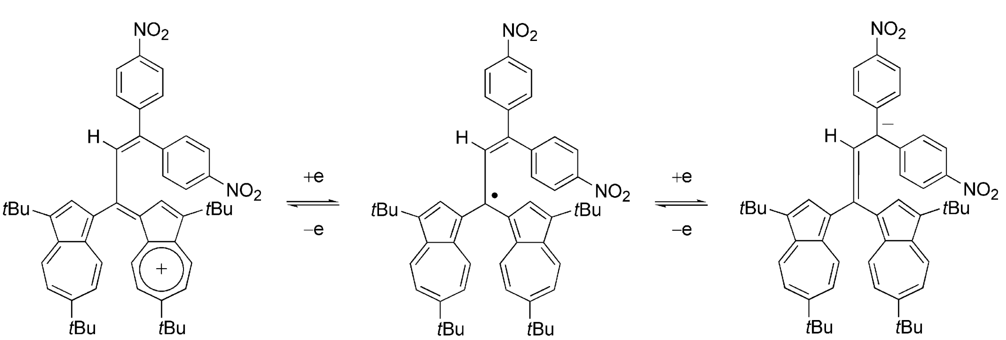
When the two end groups in such a C–C hybrid are two cyanine substructures with different electronic demands, the system should avoid such a disadvantage in the conjugation. The general structure of a C–C hybrid bearing cyanine substructures with different electronic demands at its two termini is represented in Scheme 11. The moieties Z in Z=C–Z and X and Y in X=C–Y in the general structure represent combinations of donor and acceptor groups. Similarly to the situation in Scheme 8, the neutral radical state should also be stabilized by the capto-dative substituents effect, because the radical is substituted by the donor and acceptor groups. The radical state should also exhibit an absorption in the visible region, so three stabilized col-



Scheme 10. General structure of C–C hybrid containing cyanine substructures at both of its termini.



Scheme 11. General structure of a C–C hybrid bearing cyanine substructures with different electronic demands at its two termini.



Scheme 12. C–C hybrid based on cyanine substructures with different electronic demand at its two termini.

ored states should also be expected for this C–C hybrid structure.

The 3,3-bis(3,6-di-*tert*-butyl-1-azulenyl)-1,1-bis(4-nitrophenyl)propenylium ion ($\mathbf{11}^+$) is a representative C–C hybrid based on cyanine substructures with different electronic demands at its two termini (Scheme 12).[17] The cation $\mathbf{11}^+$ possesses three-stage reduction properties with a small numerical sum of the first and the second reduction potentials. Depending on the charge, the system **11** exhibits three colored states: the monocation $\mathbf{11}^+$, the neutral radical $\mathbf{11}^{\cdot}$, and the anion $\mathbf{11}^-$. However, the color changes do not exhibit good reversibility (ca. 48% recovery), although good reversibility was observed by CV with this example.

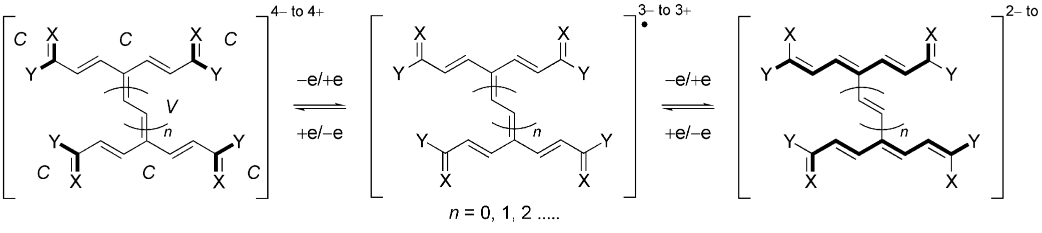
3.3. Tetracations as V–C–C Hybrids

The unfavorable defect in the conjugation in the C–C hybrid illustrated in Scheme 10 could also be avoided by interconnection of two C–C hybrid structures through a violene chain. The general structure for the next hybrid system is therefore as illustrated in Scheme 13 and should be called a V–C–C hybrid. The colored cyanine substructure would be converted into another cyanine substructure by an overall two-electron transfer. Both colored species should be closed-shell systems, thanks to which higher stability should be expected in this hybrid structure.

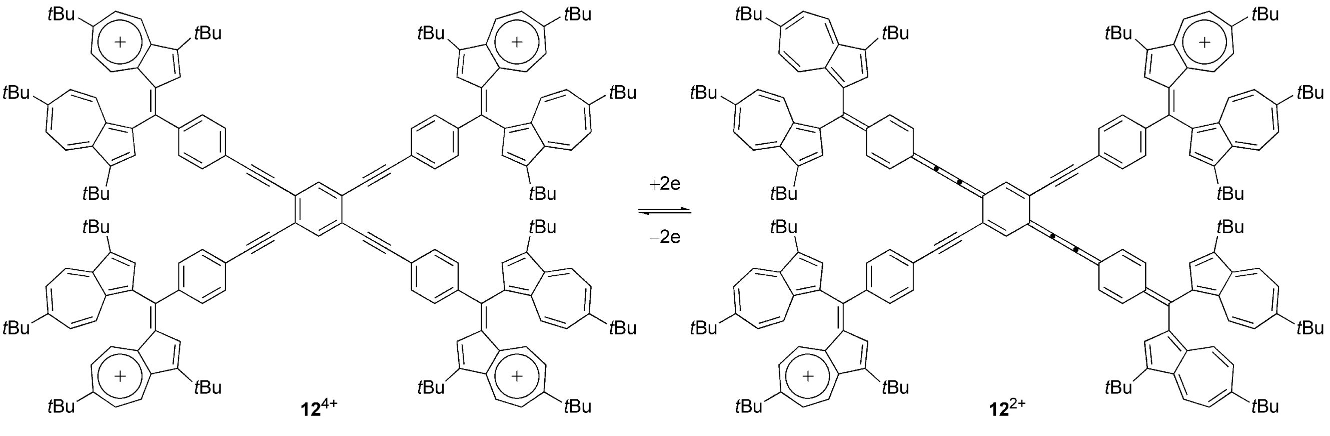
Tetracation $\mathbf{12}^{4+}$ represents an early example of the V–C–C hybrid (Scheme 14).[18] For the central violene π-system we chose a benzene ring with four acetylene spacers to decrease steric hindrance between the large cationic centers. As illustrated in Scheme 14, the cyanine substructure in tetracation $\mathbf{12}^{4+}$ could be transformed into another cyanine substructure as in dication $\mathbf{12}^{2+}$ by two-electron transfer. Carbocations of this kind with more than four cationic centers are rare species, and very few have been obtained as isolable salts.[19] Use of the azulene system, however, enabled us to prepare the multiply charged methylium compounds with very high stability. We were therefore able to prepare the highly stable tetracation $\mathbf{12}^{4+}$ despite the presence of four positive charges in the structure.

Contrary to expectations, tetracation $\mathbf{12}^{4+}$ was found to exhibit one four-electron transfer in one step to generate a neutral species with a color change during the electrochemical reduction, probably due to less effective electrochemical interaction among the four positive charges. The absence of an isosbestic point during the color change under electrochemical conditions suggests instability of the reduced species in this case. Reverse oxidation of the pale-colored solution obtained on electrochemical reduction did not regenerate the spectrum of $\mathbf{12}^{4+}$ (ca. 35% recovery), although good reversibility was observed by CV. However, the tetracation represents multiple-electron transfer as a function of the substituted bis(1-azulenyl)phenylmethylium units and also exhibits a color change during electrochemical reduction, although it remains a problem in terms of the reversibility of the redox reaction.

Thiophene units should offer opportunities to improve the reversibility of the redox reaction through the formation of thienoquinoid structures. The tetracation $\mathbf{13}^{4+}$, incorporating bis(1-azulenyl)thienylmethylium units as the terminal cyanine units, was also prepared (Figure 5).[18] However,



Scheme 13. General structure of a V–C–C hybrid.



Scheme 14. Tetracation $\mathbf{12}^{4+}$ as a V–C–C hybrid.

this molecular design does not improve the redox interaction among the four cation units and the reversibility of the color changes. This might be attributable to the disadvantage of the conjugation of the positively charged units through the central benzene ring.

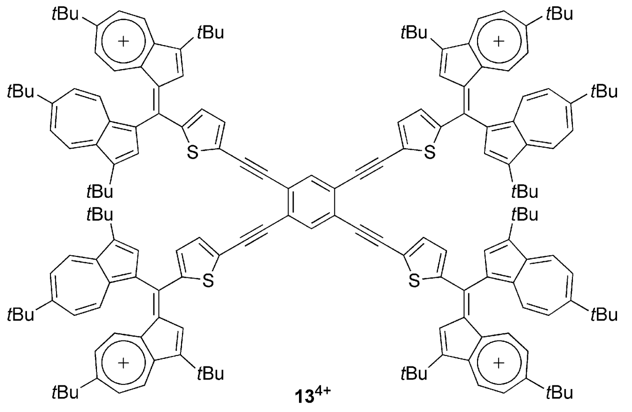


Figure 5. Tetracation **13^{4+}** as another example of a V–C–C hybrid.

4. Structural Principle for the Construction of Multiple-Electron Redox Systems

We proposed a new general structure for stabilized electrochromic systems in which cyanine units were combined as in Schemes 8, 11, and 13 in order to develop stabilized novel electrochromic materials including polyelectrochromic materials. Despite less effective electrochemical activities of the cyanine structures, the hybrid structures enable multiple electron transfer to be induced. Like the V–C hybrid system, our C–C hybrid system should also produce closed-shell cyanine-type structures in their reduced or oxidized forms with each two-electron transfer. The C–C hybrid structural principle, identifiable in already known compounds, should allow us to design stabilized novel electrochromic materials.

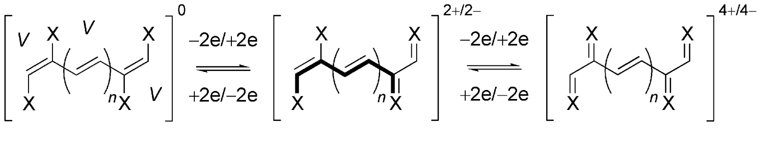
A number of variants of these hybrid structures could be designed through the combination of both cyanine- and violene-type π-electron systems. One of the simplest extensions would be a V–V hybrid, composed of two or three even-numbered conjugated π-electron systems with branched structures. In this molecular design, the hybrid structures possess either one or two violene substructures as end groups on a violene core. The general structure of a V–V hybrid possessing two violene substructures with equal electronic natures at its two termini is shown in Scheme 15. Typical electric charges in the hybrid structure are shown in the general structures. In either the oxidized or the reduced form the cross-conjugated cyanine-type structure will be generated by two-electron transfer.

There are a wide variety of possibilities for combinations of violenes and cyanines. One of these would be the V–C–C hybrid demonstrated by the azulene-substituted tetracations in Scheme 14. In each combination, either one or two termini could be replaced by one or two conjugated π-electron systems. The electronic natures of the terminal groups would also be one of the important variables for the design of the hybrid structures. In most of the hybrid structures closed-shell cyanine-type structures should appear in their reduced or oxidized forms upon each two-electron transfer during the electrochemical reaction, although some of them would produce cross-conjugated cyanine-type structures. In addition to the hybrid structures described above, some of the general structures for the other combinations of the two or three substructures are summarized in the Supporting Information. Here we describe some of the examples of novel hybrid structures that we have encountered.

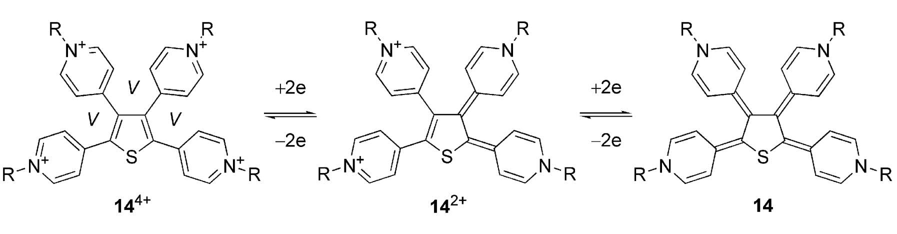
4.1. V–V and V–C–V Hybrid Derivatives

Hünig et al. presented a general V–V hybrid structure, although they do not designate their structure as such.[20] The 2,3,4,5-thiophenetetrayltetrakis(1-ethyl-4-pyridinium) ion (**14^{4+}**) exemplifies the hybrid structure, which will produce a cross-conjugated cyanine-type structure in the two-electron reduced form **14^{2+}** (Scheme 16).

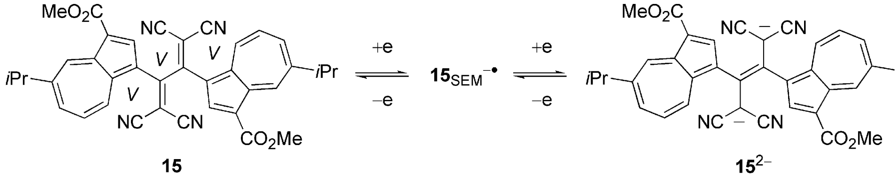
Diederich et al. extensively studied 4-(*N*,*N*-dialkylanilino)-substituted (DAA-substituted) derivatives of 1,1,4,4-tetracyano-1,3-butadienes (TCBDs).[21] Recently, we have also reported several 1-azulene-substituted novel TCBD de-



Scheme 15. General structure of a V–V hybrid bearing violene substructures at both termini.

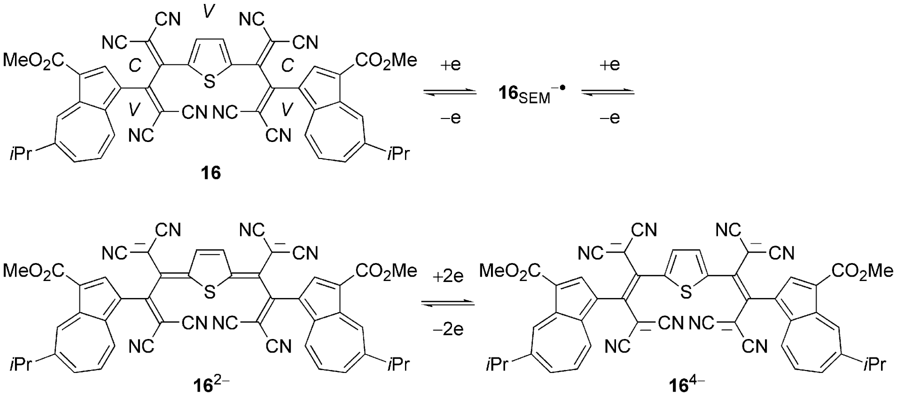


Scheme 16. Redox properties of 2,3,4,5-thiophenetetrayltetrakis(1-ethyl-4-pyridinium) ion (**14^{4+}**).



15 **15**$^{2-}$

Scheme 17. Redox properties of the bis(1-azulene)-substituted TCBD **15**.



16 **16**$^{2-}$ **16**$^{4-}$

Scheme 18. Redox properties of the bis(1-azulene)-substituted TCBD **16** with a thiophene core.

rivatives, in which we identified some novel hybrid structures with the presumed redox activities.[22] The bis(1-azulene)-substituted TCBD **15** (Scheme 17) is an example of a V–V hybrid. The central single bond in the TCBD unit would act as a violene core in compound **15**. The two 1-azulene-substituted dicyanoethylene units would be treated as substituted violene terminal groups, although the units consist of donor and acceptor groups. The hybrid compound **15** exhibits a reversible two-step, two-electron reduction wave upon CV, together with a color change.

The bis(1-azulene-substituted) TCBD **16** with a thiophene core (Scheme 18) is an example of a V–C–V hybrid. Counting the number of methine units making up the substructures from the center of the molecule up to the terminal groups allows them to be assigned to the violene or cyanine classes. The central thiophene core in compound **16** would thus be regarded as a violene substructure. The next two dicyanopropenediyl groups should be treated as a cyanine substructure, because the conjugated π-electron system consists of an odd number of carbon units. As described in the analysis of structure **15**, the two terminal 1-azulene-substituted dicyanoethylene units would be regarded as violene end groups substituted on the central V–C core. Upon CV this hybrid compound **16** exhibits a presumed reversible four-electron reduction wave, featuring a two-electron transfer in one step in its third reduction wave. Compound **16** also exhibits multiple color changes during the electrochemical reduction.

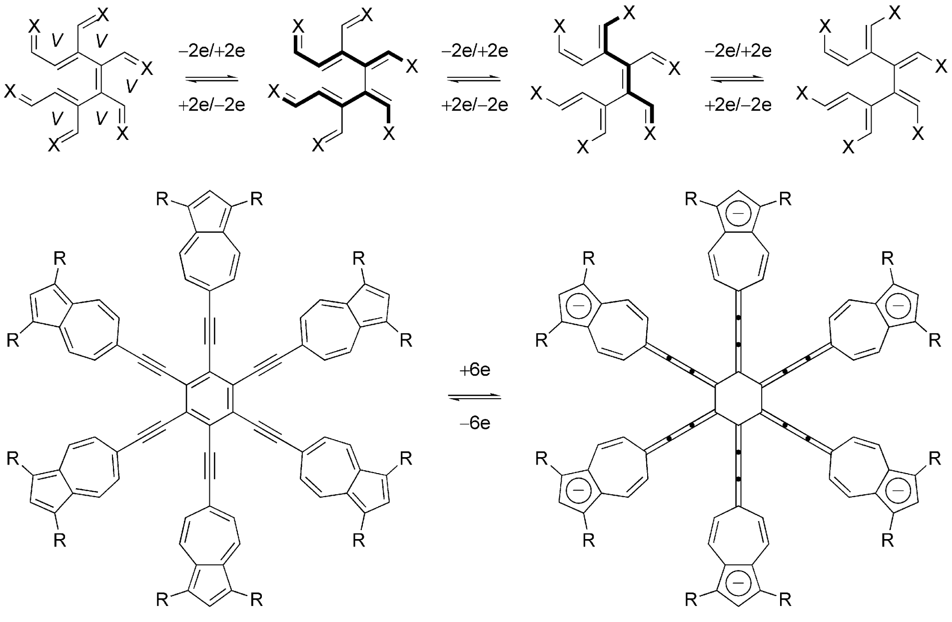
4.2. 6-Azulene-Substituted Benzene Derivatives as V–V–V Hybrids

A new example of a V–V–V hybrid structure is to be found in benzene derivatives multiply substituted by azulenes.[23,24] The hexakis(6-azulenylethynyl)benzene **17** (Scheme 19) is a typical example prepared with the cyclic structure as a core unit. Structural analysis revealed the V–V–V hybrid structure as illustrated, although the core C_6 unit is in this case part of a ring. The hexakis(6-azulenylethynyl)benzene **17** exhibits presumed six-electron transfer, but in one step, probably due to the formation of formal cyclopentadienide substructures by the electrochemical reduction of each azulene ring. Compound **17** also exhibits a color change during electrochemical reduction, although no reversibility of the color change is observed in this case.

The tetrakis(6-azulenyl)benzene **18**[23] and the tetrakis(6-azulenylethynyl)benzene **19**,[24] which would be classified as V–C hybrids, are illustrated in Scheme 20. These compounds each exhibit presumed two-step reduction properties, with two-electron transfer in each step. Therefore, the one-step reduction of the hexakis(6-azulenylethynyl)benzene **17** should be attributable to the less effective redox interaction between the six terminal 6-azulenyl groups.

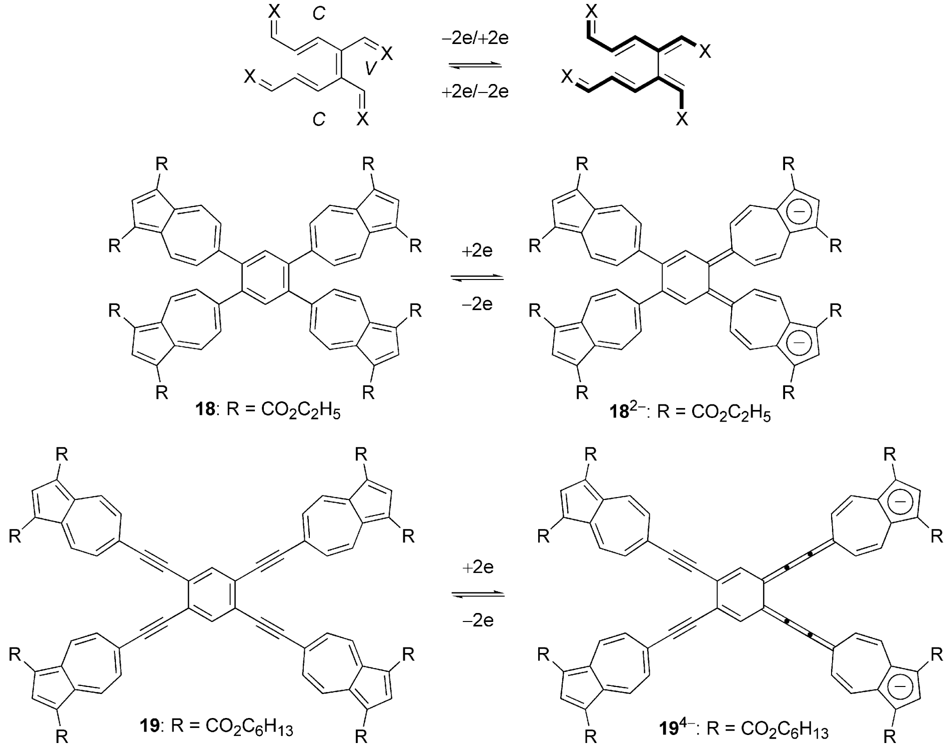
4.3. Utility of 2-Azulene-Substituted Derivatives as Electrochromic Materials

Poly(6-azulenyl)- and -(6-azulenylethynyl)benzenes exhibit multiple-electron transfer because of the formation of formal cyclopentadienide substructures through the electrochemical reduction of each azulene ring. Although 2-azulenyl substituents do not form formal cyclopentadienide substructures in their electrochemically reduced forms, poly(2-azulenyl)- and -(2-azulenylethynyl)benzenes also exhibited multiple-electron reduction depending on the number of azulene rings substituted.[25,26] In the case of the



17: R = $CO_2C_6H_{13}$ **17**$^{6-}$: R = $CO_2C_6H_{13}$

Scheme 19. Hexakis(6-azulenylethynyl)benzene **17** as a V–V–V hybrid.

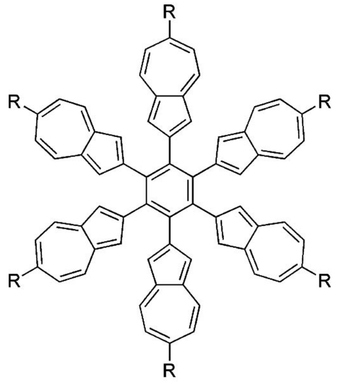


18: R = $CO_2C_2H_5$ **18**$^{2-}$: R = $CO_2C_2H_5$

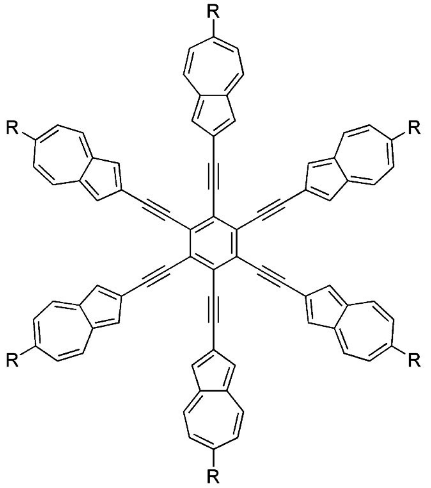
19: R = $CO_2C_6H_{13}$ **19**$^{4-}$: R = $CO_2C_6H_{13}$

Scheme 20. The tetrakis(6-azulenyl)benzene **18** and the tetrakis(6-azulenylethynyl)benzene **19** as examples of V–C hybrids.

reduction of hexakis(6-octyl-2-azulenyl)benzene (**20**, Figure 6) the compound exhibited six-electron reduction in one step upon CV, whereas hexakis(6-hexadecyl-2-azulenylethynyl)benzene (**21**) exhibited a stepwise six-electron reduction wave, showing a two-electron transfer in one step in its fifth reduction wave. These results are indicative that the 2-azulenyl group might be also utilizable as a redox-active end group, similarly to the 6-azulenyl substituent.



20: R = C_8H_{17}

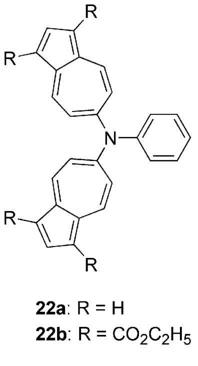


21: R = $C_{16}H_{33}$

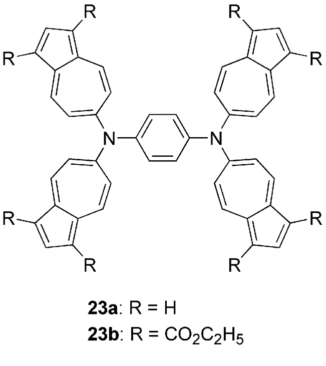
Figure 6. Hexakis(6-octyl-2-azulenyl)benzene (**20**) and hexakis(6-hexadecyl-2-azulenylethynyl)benzene (**21**) as examples of V–V–V hybrids.

5. 6-Aminoazulene Derivatives as a New Class of Electrochromic Materials

Substitution of azulenes at the 6-position induces facile electrochemical reduction to provide stabilized anionic species. In addition to the property of aromatic amines of exhibiting facile oxidation, the electronic properties of azulene provided an opportunity to construct aromatic amines with highly amphoteric redox properties. The azulene-substituted aromatic amines and diamines **22a**, **22b**, **23a**, and **23b** (Figure 7) each exhibited a reversible reduction wave along with an irreversible oxidation wave upon CV.[27] The colors of solutions of the azulene-substituted aromatic amines and diamines **22a**, **22b**, **23a**, and **23b** changed reversibly from red to green on electrochemical reduction, except in the case of diamine **23a**. These derivatives **22a**, **22b**, **23a**, and **23b** provide a new example of a violene-type redox system with inverse electron demand.



22a: R = H
22b: R = $CO_2C_2H_5$



23a: R = H
23b: R = $CO_2C_2H_5$

Figure 7. 6-Azulene-substituted aromatic amines and diamines **22** and **23**.

6. Liquid-Crystalline Properties in Electrochromic Materials

Disk-like compounds with long alkyl chains have attracted interest because of their ability to self-assemble to form columnar mesophases.[28] The stacking behavior of discotic liquid crystals (LCs) provides opportunities in fields involving materials with one-dimensional transport processes, such as energy migration, electronic conductivity, and photoconductivity.[29] The hexakis(6-azulenylethynyl)benzene **17**, substituted with 12 hexyloxycarbonyl groups, forms stable columnar mesophases over a wide temperature range from 77.3 to ca. 270 °C (the decomposition temperature).[24] The 2-azulene derivative **20**, possessing an octyl chain at the 6-position on each azulenyl group, also showed a large temperature range of hexagonal columnar mesophases ($\mathrm{Col_{ho}}$), from 115.5 to 199.9 °C.[25] Because of the long alkyl chain on each azulenyl group, these azulene-substituted electrochromic materials should possess good solubility, fusibility, and the ability to self-organize as columnar LCs. LCs should exhibit a variety of functional properties. Redox-active columnar mesogens might have great advantages for device production involving electrochromic materials.[30]

7. Conclusions

By taking advantage of the ability of azulene systems to stabilize ionic states, novel structural motifs for the preparation of stabilized electrochromic materials have been demonstrated in several examples, although some still have problems in the reversibilities of their redox reactions. Through application of V–C hybrid structures with Wurster-type violene cores, two-colored states between quinoid colors and cyanine colors with strong absorptions in the near-infrared region can be established. The bis(1-azulenyl)(6-azulenyl)methyl cation **8**$^+$, which would be a candidate as a C–C hybrid system with a cyanine unit at one terminus, exhibits the presumed three-stage reduction properties, with three colored states. The tetracation **12**$^{4+}$, of the V–C–C hybrid structure, has been found to exhibit a presumed four-electron transfer, but in one step to generate a neutral species with a color change during the electrochemical reduction, although there is a problem in the reversibility of the redox reaction. 1-Azulene-substituted TCBDs represent V–V and V–C–V hybrids. The V–V–V hybrid structure is found in benzene derivatives multiply substituted with azulenes. It has been revealed that the 2-azulenyl group can be utilized as a redox-active end group in a manner similar to the 6-azulenyl group, which forms a formal cyclopentadienide substructure in the reduced form. Some of the electrochromic materials prepared from azulene components form stable columnar mesophases over wide temperature ranges.

The structural principles presented above demonstrate that a large variety of hybrid structures could be designed through the combination of violene- and cyanine-type substructures. As the results of this new structural principle it should be possible to design a great variety of novel polyelectrochromic materials that would respond to different potentials with a variety of colors. Some of them might be found in already known compounds. However, the novel structural principle should contribute new designs for stabilized electrochromic materials including polyelectrochromic materials. Utilization of azulene systems as redox-active end groups could be very effective for the construction of stabilized electrochromic materials because of these systems' high redox activities and abilities to stabilize the ionic states, as well as the strong absorptions in the visible region provided by their cyanine forms. LC properties in electrochromic materials may provide great advantages for device production. Syntheses of novel electrochromic materials incorporating these new structural motifs through the utilization of azulene skeletons are now in progress in our laboratory.

Supporting Information (see footnote on the first page of this article): Some general structures not dealt with above representing these new structural motifs in the employment of two or three violene and/or cyanine substructures.

Acknowledgments

This work was partially supported by a Grant-in-Aid for Scientific Research (Grant 18550026 to S. I.) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

---

[1] P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, *Electrochromism: Fundamentals and Applications*, VCH, Weinheim, Germany, **1995**.

[2] a) K. Komatsu, K. Ohta, T. Fujimoto, I. Yamamoto, *J. Mater. Chem.* **1994**, *4*, 533–536; b) D. R. Rosseinsky, D. M. S. Monk, *J. Appl. Electrochem.* **1994**, *24*, 1213–1221.

[3] a) S. Ito, N. Morita, T. Kubo, *J. Synth. Org. Chem.* **2004**, *62*, 766–777; b) S. Ito, K. Akimoto, N. Morita, "Stabilized Carbocations as Redox Active Chromophores: Preparation of Electrochromic Materials Using Stabilized Carbocations", in *ACS symposium series 965 – Recent Developments in Carbocation and Onium Ion Chemistry* (Ed.: K. K. Laali), ACS, USA, **2007**, pp. 160–183.

[4] K. Deuchert, S. Hünig, *Angew. Chem.* **1978**, *90*, 927–938; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 875–886.

[5] a) S. Hünig, M. Kemmer, H. Wenner, I. F. Perepichka, P. Bäuerle, A. Emge, G. Gescheidt, *Chem. Eur. J.* **1999**, *5*, 1969–1973; b) 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; c) S. Hünig, I. F. Perepichka, M. Kemmer, H. Wenner, P. Bäuerle, A. Emge, *Tetrahedron* **2000**, *56*, 4203–4211.

[6] K.-P. Zeller, "Azulene", in *Houben–Weyl*, *Methoden der Organischen Chemie*, 4th ed. (Ed.: H. Kropf), Georg Tieme, Stuttgart, Germany, **1985**, vol. V, part 2c, pp. 127–418.

[7] S. Ito, N. Morita, T. Asao, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1409–1436.

[8] a) S. Ito, S. Kikuchi, N. Morita, T. Asao, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 839–849; b) S. Ito, S. Kikuchi, N. Morita, T. Asao, *J. Org. Chem.* **1999**, *64*, 5815–5821.

[9] a) S. Ito, N. Morita, T. Asao, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1865–1874; b) S. Ito, S. Kikuchi, T. Okujima, N. Morita, T. Asao, *J. Org. Chem.* **2001**, *66*, 2470–2479.

[10] a) F. Diederich, *Pure Appl. Chem.* **1999**, *71*, 265–273; b) M. B. Nielsen, F. Diederich, *Synlett* **2002**, 544–552; c) F. Diederich, *Chem. Commun.* **2001**, 219–227; d) H. Hopf, J. Kämpen, P. Bubenitschek, P. G. Jones, *Eur. J. Org. Chem.* **2002**, 1708–1721.

[11] J. Anthony, A. M. Boldi, C. Boudon, J.-P. Gisselbrecht, M. Gross, P. Seiler, C. B. Knobler, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 797–817.

[12] S. Ito, H. Inabe, N. Morita, A. Tajiri, *Eur. J. Org. Chem.* **2004**, 1774–1780.

[13] S. Ito, T. Iida, J. Kawakami, N. Morita, to be published.

[14] a) L. Stella, Z. Janousek, R. Merényi, H. G. Viehe, *Angew. Chem.* **1978**, *90*, 741–742; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 691–692; b) H. G. Viehe, R. Merényi, L. Stella, Z. Janousek, *Angew. Chem.* **1979**, *91*, 982–997; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 917–932; c) H. G. Viehe, Z. Janousek, R. Merényi, *Acc. Chem. Res.* **1985**, *18*, 148–154.

[15] S. Ito, T. Kubo, N. Morita, T. Ikoma, S. Tero-Kubota, A. Tajiri, *J. Org. Chem.* **2003**, *68*, 9753–9762.

[16] S. Ito, A. Mizushima, J. Kawakami, S. Kikuchi, N. Morita, to be published.

[17] S. Ito, A. Mizushima, J. Kawakami, N. Morita, to be published.

[18] S. Ito, K. Akimoto, J. Kawakami, A. Tajiri, T. Shoji, H. Satake, N. Morita, *J. Org. Chem.* **2007**, *72*, 162–172.

[19] a) N. J. Head, G. K. S. Prakash, A. Bashir-Hashemi, G. A. Olah, *J. Am. Chem. Soc.* **1995**, *117*, 12005–12006; b) M. D. Heagy, Q. Wang, G. A. Olah, G. K. S. Prakash, *J. Org. Chem.* **1995**, *60*, 7351–7354; c) R. Rathore, C. L. Burns, I. A. Guzei, *J. Org. Chem.* **2004**, *69*, 1524–1530.

[20] S. Hünig, A. Langels, M. Schmittel, H. Wenner, I. F. Perepichka, K. Peters, *Eur. J. Org. Chem.* **2001**, 1393–1399.

[21] a) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* **2005**, 737–739; b) T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889–1905; c) M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Angew. Chem.* **2007**, *119*, 6473–6477; *Angew. Chem. Int. Ed.* **2007**, *46*, 6357–6360; d) P. Reutenauer, M. Kivala, P. D. Jarowski, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, *Chem. Commun.* **2007**, 4898–4900; e) M. Kivala, T. Stanoeva, T. Michinobu, B. Frank, G. Gescheidt, F. Diederich, *Chem. Eur. J.* **2008**, *14*, 7638–7647.

[22] T. Shoji, S. Ito, K. Toyota, M. Yasunami, N. Morita, *Chem. Eur. J.* **2008**, *14*, 8398–8408.

[23] a) S. Ito, H. Inabe, T. Okujima, N. Morita, M. Watanabe, H. Harada, K. Imafuku, *J. Org. Chem.* **2001**, *66*, 7090–7101; b) S. Ito, T. Okujima, N. Morita, *J. Chem. Soc. Perkin Trans. 1* **2002**, 1896–1905.

[24] S. Ito, H. Inabe, N. Morita, K. Ohta, T. Kitamura, K. Imafuku, *J. Am. Chem. Soc.* **2003**, *125*, 1669–1680.

[25] a) S. Ito, T. Terazono, T. Kubo, T. Okujima, N. Morita, T. Murafuji, Y. Sugihara, K. Fujimori, J. Kawakami, A. Tajiri, *Tetrahedron* **2004**, *60*, 5357–5366; b) S. Ito, M. Ando, A. Nomura, N. Morita, C. Kabuto, H. Mukai, K. Ohta, J. Kawak-

ami, A. Yoshizawa, A. Tajiri, *J. Org. Chem.* **2005**, *70*, 3939–3949.

[26] S. Ito, S. Tahata, J. Kawakami, N. Morita, to be published.

[27] S. Ito, T. Kubo, N. Morita, T. Ikoma, S. Tero-Kubota, J. Kawakami, A. Tajiri, *J. Org. Chem.* **2005**, *70*, 2285–2293.

[28] See, e.g a) T. Komatsu, K. Ohta, T. Fujimoto, I. Yamamoto, *J. Mater. Chem.* **1994**, *4*, 533–536; b) S. Ito, M. Wehmeier, J. D. Brand, C. Kübel, R. Epsch, J. P. Rabe, K. Müllen, *Chem. Eur. J.* **2000**, *6*, 4327–4342; c) K. Hatsusaka, K. Ohta, I. Yamamoto, H. Shirai, *J. Mater. Chem.* **2001**, *11*, 423–433.

[29] a) D. Adam, P. Schuhmacher, J. Simmerer, L. Häussking, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer, *Nature* **1994**, *371*, 141–143; b) A. M. van de Craats, M. P. de Haas, J. M. Warman, *Synth. Met.* **1997**, *86*, 2125–2126; c) A. M. van de Craats, J. M. Warman, H. Hasebe, R. Naito, K. Ohta, *J. Phys. Chem. B* **1997**, *101*, 9224–9232; d) A. M. van de Craats, J. M. Warman, K. Müllen, Y. Geerts, J. D. Brand, *Adv. Mater.* **1998**, *10*, 36–38.

[30] H.-C. Chang, T. Shiozaki, A. Kamata, K. Kishida, T. Ohmori, D. Kiriya, T. Yamauchi, H. Furukawa, S. Kitagawa, *J. Mater. Chem.* **2007**, *17*, 4136–4138.

Received: April 9, 2009