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Preparation, Structure, and Unique Redox Properties of Mono-, Bis-, and Tris(diarylmethylene)-1,3,5-trithianes and Related Compounds

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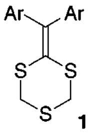
A series of 1,3,5-trithianes **1**−**3** having diarylmethylene units were designed as novel electron donors giving highly colored cationic species upon oxidation. They were prepared along with the dithiane and dithiazine derivatives **4**−**6** by the reactions of lithiated heterocycles with diaryl ketones followed by dehydration. Voltammetric analyses indicate that a large structural change and/or transannular bonding are induced during their electrochemical oxidation. Mono(diarylmethylene) derivative **1a** exhibits electrochromism with vivid change in color from faintly yellow to deep blue with concomitant rotation around the exocyclic bond. Both of the strongly colored salts obtained upon oxidation of 2,4-bis- and 2,4,6-tris(diarylmethylene)-1,3,5-trithianes (**2aa** and **3**) consist of the dications with a 1,2,4-trithiane ring, suggesting the easy skeletal rearrangement of the transannular dications with a trithiabicylo[3.1.0]hexane ring. Upon reduction of these salts were obtained bright yellow **12** and **13**, respectively, with high electron-donating properties due to the tetraarylbutadiene-type conjugation, thus giving another class of electrochromic compounds.

Recently much attention has been focused on the organic redox systems in the field of materials chemistry. Electrochromic systems[1] whose optical properties can be controlled electrochemically are attracting special attention from the viewpoint of molecular devices or switches.[2] One of the essential requirements for such systems is vivid change in color, that could be attained when strongly colored diarylmethylium units such as (p-$Me_2NC_6H_4)_2C^+$ or (p-$MeOC_6H_4)_2C^+$ are formed upon electron transfer (ET). In this connection, 9,9,10,10-tetraaryl-9,10-dihydrophenanthrene derivatives are of interest, which undergo mesolytic C−C bond breaking to give those cationic chromophores upon oxidation.[3] Large structural changes during the interconversion are another characteristic of those chromic compounds, which endow the system with the bistability.[4] On the basis of our recent findings shown above, six-membered sulfur heterocycles **1**−**3** possessing diarylmethylene moieties have been designed as novel chromic systems in the anticipation that geometrical changes other than C−C bond fission would be also effective in attaining the bistability.[5] In these compounds, the diarylmethylium chromophores would be formed upon ET with concomitant transannular bonding and/or twisting around the exo-methylene bonds. We report here the preparation, structures, and unique redox properties of novel trithiane derivatives **1**−**3** along with the related heterocycles **4**−**6**.



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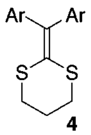

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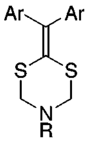
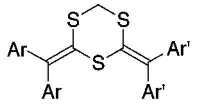
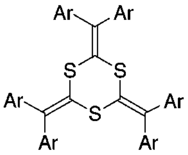


5 (R = Me)
6 (R = *t*-Bu)

(**a**: Ar = p-$Me_2NC_6H_4$ **b**: Ar = p-$MeOC_6H_4$)



2aa: Ar = Ar' = p-$Me_2NC_6H_4$
2ab: Ar = p-$Me_2NC_6H_4$
Ar' = p-$MeOC_6H_4$



3: Ar = p-$Me_2NC_6H_4$

Results and Discussion

Preparation of New Donors. Lithiation of parent 1,3,5-trithiane **7** with *n*-BuLi in THF followed by addition of 4,4′-bis(dimethylamino)benzophenone gave the tertiary alcohol **11a** in nearly quantitative yield, which was converted to olefin **1a** through TsOH-catalyzed dehydration in 86% yield. By the same procedure, 1,3-dithiane **8**, 5-Me-1,3,5-dihydrodithiazine **9**,[6] and 5-*t*-Bu-1,3,5-dihydrodithiazine **10**[7] were transformed into the corresponding bis(4-(dimethylamino)phenyl)methylene derivatives **4a**−**6a** in good yields. By using 4,4′-dimethoxybenzophenone in place of Michler's ketone, new donors having p-$MeOC_6H_4$ groups, **1b** and **4b**−**6b**, were obtained, respectively, from **7**−**10**.

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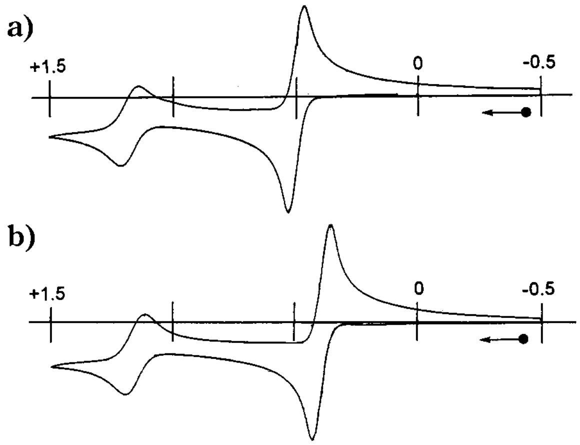


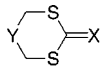
Figure 1. Cyclic voltammograms of **1a** and **4a** measured in MeCN containing 0.1 mol dm^{-3} Et_4NClO_4 (scan rate 100 mV s^{-1}). The narrow peak shape in the first oxidation steps indicates 2e-transfer. The disproportionation constant ($K = [\mathbf{1a}^{+\bullet}]^2/[\mathbf{1a}^0][\mathbf{1a}^{2+}] = 0.4$) was calculated by analyzing the peak shape ($E_p - E_{p/2} = 36$ mV).[8] Exactly the same peak width was observed when n-Bu_4NBF_4 or n-Bu_4NPF_6 (0.1 mol dm^{-3}) was used as a supporting electrolyte, thus showing negligible effects of the counteranions on the disproportionation equilibrium.

2,4-Bis(diarylmethylene)-1,3,5-trithianes **2** could be obtained either by applying the similar three-step sequence (lithiation, reaction with the diaryl ketone, and dehydration) on mono(diarylmethylene) derivatives **1** or by starting from the direct dilithiation of trithiane **7**. Although **2aa** was obtained in 12% yield by the latter procedure after chromatographic separation, the former method giving **2aa** in 85% yield from **1a** seems more promising by considering the higher total yield as well as the facile isolation of the product only by recrystallization. Such a stepwise synthesis is useful in preparing the hybrid compounds **2ab** having two different diarylmethylene units and also applicable in obtaining the tris(diarylmethylene) derivative **3** from **2aa**.

Redox Properties of Mono(diarylmethylene)-trithianes 1 and Dithiane Derivatives 4. The cyclic voltammogram of **1a** shows the two pairs of reversible waves. The former ($E_1^{ox} = +0.50$ V) corresponds to 2e-oxidation since the electric current is nearly twice as large as the latter (Figure 1a). The second oxidation potential ($E_2^{ox} = +1.17$ V) is similar to E^{ox} of $(p\text{-}Me_2NC_6H_4)_2CH^+BF_4^-$ (+1.02 V) but not to that of trithiane **7** (Table 1), indicating that the third electron is removed from the diarylcarbenium moiety of $\mathbf{1a}^{2+}$. The methoxyphenyl derivative **1b** ($E_1^{ox} = +0.89$ V) is a weaker donor and undergoes reversible electrochemical oxidation at higher potential than **1a** (Table 1). Its oxidation process seems also of 2e-transfer as suggested by the narrow peak shape ($E_p - E_{p/2} = 35$ mV),[8] although the direct comparisons of the peak current with the next oxidation process is impossible (E_2^{ox} of **1b** > +1.8 V).

Facile 2e-oxidation of the small π-system like **1** suggests the drastic electronic and structural change after 1e-transfer,[9,10] and dications with quite different geometry from the neutral state would be produced as dipicted in Scheme 1 (Y = S). Coulombic repulsion seems reduced enough to account for the 2e-transfer both in the type-A and type-B dications, by rotating the Ar_2C^+ moiety around the exocyclic C−C bond in the former and by the C−S transannular bonding in the latter. Quite similar redox behavior of the dithiane derivatives **4** (Figure 1b) to those of **1** indicates that the bicyclic structure of type-B is inappropriate for $\mathbf{1}^{2+}$, thus suggesting the twisted geometry for $\mathbf{1}^{2+}$ as in the tetraarylethylene dications.[9b]

Table 1. Oxidation Potentials (E^{ox})^a of Mono(diarylmethylene)-type Donors, 1, and 4−6, and Related Heterocycles



Y	X = $C(C_6H_4NMe_2\text{-}p)_2$	X = $C(C_6H_4OMe\text{-}p)_2$	X = H, H
S	**1a** +0.50 (2e), +1.17	**1b** +0.89 (2e)	**7** +1.61^b
CH_2	**4a** +0.40 (2e), +1.16	**4b** +0.80 (2e)	**8** +1.45^b
NMe	**5a** +0.44^{b,c}	**5b** +0.70^{b,c}	**9** +1.25^{b,d}
N^{t}Bu	**6a** +0.32^{b,c}	**6b** +0.72^{b,c}	**10** +1.20^{b,d}

^{a} E/V vs SCE, 0.1 mol dm^{-3} Et_4NClO_4 in MeCN, Pt electrode, scan rate 100 mV s^{-1}. ^{b} Irreversible waves. Values are calculated as $E^{ox} = E^{pa} - 0.03$ V. ^{c} The voltammograms show broad cathodic peaks around −0.5 to −1.0 V in the return cycle. ^{d} Broad anodic waves were observed around +0.5 to +1.0 V before the distinct peaks at +1.2 V.

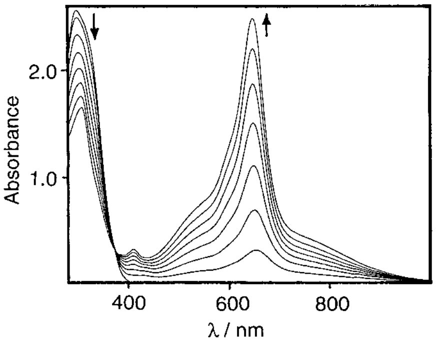
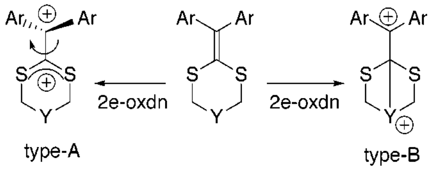


Figure 2. Changes in UV−vis spectra of **1a** (3 mL; 8.28 × 10^{-5} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} n-Bu_4NBF_4) upon constant-current electrochemical oxidation (40 μA) at 2 min intervals.

Scheme 1



Spectrophotometric monitoring of the electrochemical oxidation of **1a** showed an isosbestic point at 370 nm (Figure 2), indicating the clean and quantitative conversion from faintly yellow **1a** [UV−vis (MeCN) λ_{max} 297 nm (log ϵ 4.48)] to deep blue $\mathbf{1a}^{2+}$ ($\lambda_{max} = 646$ nm). It also suggests the negligible steady-state concentration of the intermediary cation radical $\mathbf{1a}^{\bullet+}$, which is consistent with the one-wave 2e-oxidation. Under the experimental conditions, this dication $\mathbf{1a}^{2+}$ is very stable with no

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[10] Such a 2e-process is not surprising when these systems are considered as new examples of the violene/cyanine hybrids (ref 1b).

indication of decomposition, thus representing a new addition to electrochromic systems with a vivid change in color.

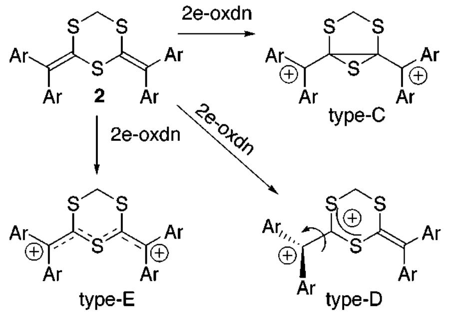
Structure and Redox Properties of Mono(diarylmethylene)dihydrodithiazine Derivatives 5 and 6. Studies on trithianes **1** and dithianes **4** lead to the conclusion that the sulfur atom at the 5-position in **1** does not induce the drastic changes in the redox properties of the diarylketene dithioacetal unit. To investigate the effects of the heteroatom at 5 position, we next studied the dithiazine-type donors **5** which contains N(sp^3) in place of the divalent sulfur.

According to the X-ray analysis, the heterocyclic six-membered ring of **5a** adopts the chair conformation in the solid state (Figure S1 in Supporting Information). One aryl group makes a large dihedral angle with the olefinic plane (73.1°) whereas the other seems to involve π-conjugation at least in part (dihedral angle: 40.3 °). One noteworthy feature is the fact that the N^5-Me group occupies the axial position, which is suitable for the through-bond interaction[11] between the N^5 lone pair and the p-orbital of the exomethylene unit at 2-position (nonbonded C···N distance, 3.20 Å). Such geometry suggests the possible contribution of the type-B dication (Scheme 1, Y = N-Me) upon 2e-oxidation of **5**.

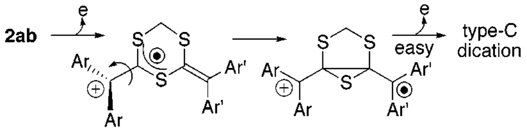
In contrast to the reversible nature observed for the trithiane derivatives **1**, the voltammograms of dithiazine-type donors **5a** and **5b** showed only irreversible waves ($E_p - E_{p/2} = 50$ mV in both cases) although the donating properties are comparable to **1a** and **1b**, respectively (Table 1). The corresponding cathodic peaks are ambiguous but appeared in the far cathodic region, suggesting that a certain chemical process occurs after ET. Many attempts to obtain the dication salt of **5** were unfruitful but giving black or green intractable mixtures. By considering the instability of azetiniums against nucleophilic reagents due to the easy ring-opening polymerization of the four-membered ring,[12] a *t*-Bu group was substituted for the Me group on N^5 in **5**. The redox properties of **6a** and **6b**, however, were quite similar to those of **5a** and **5b**, so that the *t*-Bu group in **6** may not be bulky enough for the kinetic stabilization of the labile dications. Although the N(sp^3) at the 5-position in **5** and **6** was proven to determine the properties and fate of the oxidized species, it is still ambiguous if the dication has the type-B structure with a bicyclo[2.2.0]hexane skeleton. In the following sections, the trithianes having the multiple exo-methylene units such as **2** and **3** were investigated to test the possibility that they undergo transannular C−C bonding upon ET[13,14] to form the cationic species having a thiiran ring.

Structure and Redox Properties of Bis(diarylmethylene) Derivatives 2. The X-ray structural analysis on **2aa** has revealed that the heterocycle adopts the boat conformation (Figure S2). Even when such a conformer is dominant in solution, ring flip of the six-membered ring must be feasible because a sharp singlet was observed at 4.13 ppm for the CH_2 group at 6-position in the ^1H NMR spectrum of **2aa** measured at room temperature. Both diarylmethylene groups are sticking out to the opposite direction to the prow (S^3) and stern (C^6), and the nonbonded distance between two quaternary carbons (C^2 and C^4) is only 2.78 Å. This type of geometry seems suitable for the π-orbital interaction to give the bicyclic dication shown as type-C in Scheme 2.

Scheme 2



Scheme 3



(Ar = p-$Me_2NC_6H_4$; Ar' = p-$MeOC_6H_4$)

According to the voltammetric analysis, the first oxidation wave of the symmetric bis(diarylmethylene)trithiane **2aa** [$E_1^{ox} = +0.43$ V (2e; $E_p - E_{p/2} = 35$ mV), $E_2^{ox} = +1.01$ V (1e), $E_3^{ox} = +1.19$ V (1e)] is also 2e-process as in the case of **1a** having only one diarylmethylene unit. By comparing the redox behavior with the unsymmetric derivative **2ab** [$E_1^{ox} = +0.48$ V (2e; $E_p - E_{p/2} = 35$ mV); $E_2^{ox} = +1.15$ V (1e)], however, neither the twisted form (type-D) nor the delocalized one (type-E) is appropriate for the structure of the dication formed upon oxidation of **2**. Thus, **2ab** possessing both p-$Me_2NC_6H_4$ and p-$MeOC_6H_4$ groups shows the 2e-oxidation wave at a similar potential to **2aa** having four p-$Me_2NC_6H_4$ groups. This fact could be accounted for by assuming the involvement of the transannular cation radical having the (p-$MeOC_6H_4)_2C^{\bullet}$ unit that undergoes much easier 1e-oxidation than **2ab** (Scheme 3), thus giving the dication with the type-C structure. This bicyclic dication is expected to undergo further 1e-oxidation at (p-$Me_2NC_6H_4)_2C^+$ unit, and the close similarity of E_2^{ox} (**2ab**) to the oxidation potential of (p-$Me_2NC_6H_4)_2CH^+$ is in good agreement with this hypothesis. Furthermore, separation between E_2^{ox} and E_3^{ox} of **2aa** can be also rationalized by assuming the type-C dication in which two (p-$Me_2NC_6H_4)_2C^+$ units are arranged in a close proximity to allow the through-space π-orbital interaction between them.

Upon electrochemical oxidation of **2ab** [UV−vis (MeCN) λ_{max} 303 (log ϵ 4.50), 255 (4.44) nm] in MeCN, two-stage spectroscopic changes were observed, each of which shows the isosbestic points (Figure 3). The absorption maxima at 524 and 662 nm in the final spectrum in Figure 3b well correspond, respectively, to those of (p-$MeOC_6H_4)_2$-CPh^+ (497 nm) and (p-$Me_2NC_6H_4)_2CPh^+$ (619 nm) measured in MeCN, suggesting the presence of two independent chromophores as in the type-C structure. To our regret, the final spectrum decayed gradually upon standing, suggesting the slow decomposition of the species under the experimental conditions.

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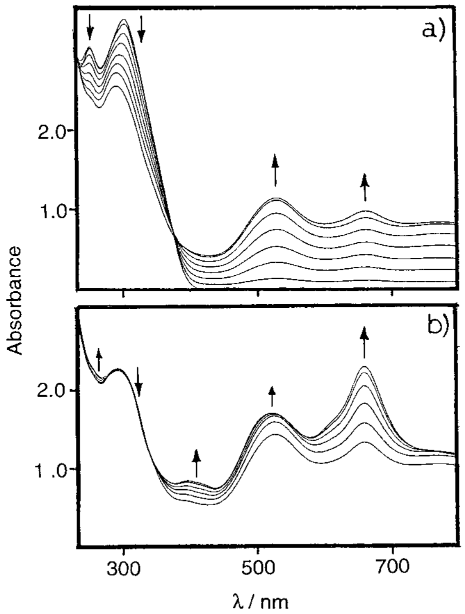
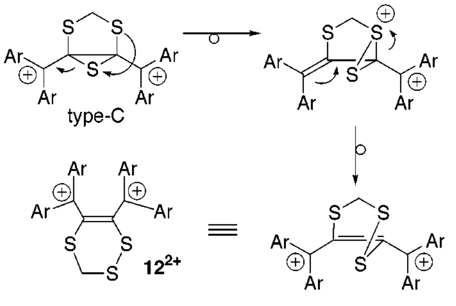


Figure 3. Changes in UV−vis spectra of **2ab** (3 mL; 1.06 × 10^{-4} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} n-Bu$_4$NBF$_4$) upon constant-current electrochemical oxidation (40 μA): (a) first stage, changes at 3 min intervals, isosbestic point at 375 nm; (b) second stage, changes at 6 min intervals, isosbestic points at 344 and 272 nm.

Scheme 4



(Ar = p-Me$_2$NC$_6$H$_4$)

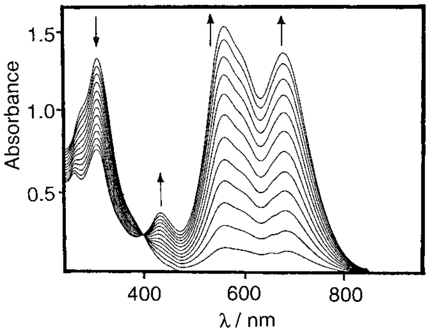
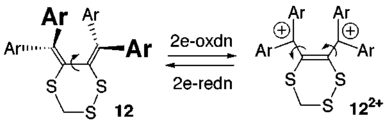


Figure 4. Changes in UV−vis spectra of **12** (3 mL; 3.55 × 10^{-5} mol dm^{-3} in MeCN containing 0.05 mol dm^{-3} n-Bu$_4$NBF$_4$) upon constant-current electrochemical oxidation (20 μA) at 1 min intervals.

Scheme 5



(Ar = p-Me$_2$NC$_6$H$_4$)

Because of such instability, attempts to isolate the type-C dication salt by oxidation of **2aa** did not give the bicyclic one. Instead the monocyclic isomer $\mathbf{12}^{2+}$ having a 1,2,4-trithiane-5-ene skeleton was obtained, whose production is reasonably accounted for by the rearrangement of the type-C dication (Scheme 4).[15] Thus, the black crystalline solid having the experimental formula equivalent to the sum of **2aa** and twice of SbCl$_6^-$ was obtained in 96% yield by the reaction of **2aa** with 2 equiv of (p-BrC$_6$H$_4$)$_3$N$^{+\bullet}$SbCl$_6^-$. In the ^{1}H NMR spectrum of the salt, all the protons are less shielded than those of neutral **2aa** in accord with the presence of two positive charges on the molecule [δ ppm (CD$_3$CN): 6.99 (4H, AA′XX′), 6.92 (4H, AA′XX′), 6.69 (4H, AA′XX′), 6.48 (4H, AA′XX′), 4.16 (2H, s), 2.93 (12H, s), 2.86 (12H, s) for **2aa**; 7.32 (4H, AA′XX′), 7.26 (4H, AA′XX′), 6.81 (4H, AA′XX′), 6.79 (4H, AA′XX′), 4.90 (2H, s), 3.23 (12H, s), 3.21 (12H, s) for the salt $\mathbf{12}^{2+}$(SbCl$_6^-$)$_2$]. The salt $\mathbf{12}^{2+}$(I$_3^-$)$_2$ showing the same NMR was obtained by the reaction of **2aa** with 3 equiv of I$_2$,[16] whose structure was unambiguously determined by X-ray analysis (Figure S3).

Although the conformation of the six-membered heterocycle in $\mathbf{12}^{2+}$ is not so clear due to the disorder at S^2 and C^3, it is evident that the C^5=C^6 moiety is completely planer with the largest deviation of 0.02 Å from the least-squares plane. With this olefinic plane, two diarylmethylium units make the dihedral angles of 62.2 and 62.7°, thus the steric repulsion among the four aryl groups is relieved by rotation around the C$^+$−C$_{\text{olefin}}$ bonds. Upon reduction with Zn, $\mathbf{12}^{2+}$(SbCl$_6^-$)$_2$ salt was transformed to the neutral diene **12** in 78% yield, whose geometry is quite different from the dicationic precursor (Scheme 5). Based on the solid-state structure determined by X-ray analysis (Figure S4), it is evident that neutral **12** suffers from much severe steric hindrance. The torsion angle for the C=C−C=C unit is as large as 51.0°, and the two inner aryl groups are forced to stack in a face-to-face manner (dihedral angle 16.9°; interplanar distance 3.42 Å). Due to such conformational restriction, four aryl groups resonate at different chemical shifts in the ^{1}H NMR spectrum.

Upon treatment of **12** with 2 equiv of (p-BrC$_6$H$_4$)$_3$N$^{+\bullet}$-SbCl$_6^-$, the dication salt $\mathbf{12}^{2+}$(SbCl$_6^-$)$_2$ was isolated in 85% yield. The novel redox pair of **12** [UV−vis (MeCN) $\lambda_{\max}$ 394 sh (log ϵ 3.95), 310 (4.62), 276 sh (4.49) nm] and $\mathbf{12}^{2+}$ [677 (4.64), 593 sh (4.63), 561 (4.68), 434 (4.09), 303 (4.38), 265 (4.46) nm] can be also interconverted electrochemically with the drastic spectral change as shown in Figure 4, and the presence of an isosbestic point at 400 nm is in accord with the one-wave 2e-oxidation of **12** [E_1^{ox} = +0.18 V (2e), E_2^{ox} = +1.11 V (2e)]. This is another new entry into the electrochromic system exhibiting large structural change upon ET.

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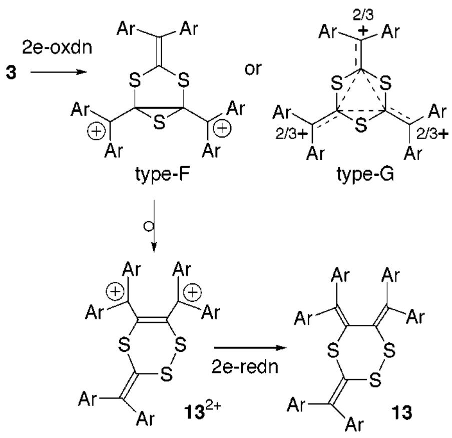
[15] Under the EI-MS conditions, 2,4,6-triphenyl-1,3,5-trithiane was reported to undergo skeletal rearrangement by S···S bonding: Chattopadhyaya, J. B.; Rao, A. V. R. *Org. Mass Spectrom.* **1974**, *9*, 649.

[16] Oxidation of **2aa** with iodine formed a small amount (10−20%) of another kind of cationic species [δ ppm (CD$_3$CN): ca. 7.32 (8H, br AA′XX′), 6.78 (8H, AA′XX′), 5.04 (2H, s), 3.22 (24H, s)] which is difficult to isolate. Its proportion against $\mathbf{12}^{2+}$ varied during the dissolution and crystallization process. Because the combustion analysis of the mixture gave satisfactory values for C$_{37}$H$_{42}$N$_4$S$_3$I$_6$, it seems that this compound is the interconvertible isomer of $\mathbf{12}^{2+}$(I$_3^-$)$_2$ although its structure is still ambiguous.

Scheme 6



(Ar = *p*-$Me_2NC_6H_4$)

Redox Properties of Tris(diarylmethylene)trithiane 3. Electron donors having 3-fold symmetry[17] like **3** have attracted considerable attention in the field of molecular magnetism due to the possibility of triplet dication formation. In the present case, however, oxidation of **3** will not result in such an open-shell species because transannular bonding is expected as in the case of **2** (type-F, Scheme 6). X-ray analysis on **3** has revealed that the nonbonded distances between quaternary carbons of the trithiane ring are 2.70, 2.73, and 2.75 Å, which are slightly shorter than that in **2**. Although crystalline **3** does not adopt C_3-symmetric geometry but rather a twist conformation with pseudo-C_2 symmetry (Figure S5), all of the aryl groups are equivalent in the ^{1}H NMR spectrum. On the basis of the conformational flexibility of **3**, there is a possibility of rapid equilibrium between three degenerated dicationic species, so that the two positive charges could be equally distributed over the three diarylmethylene moieties (type-G).

According to the voltammetric analysis, **3** undergoes two-stage electrochemical oxidation [$E_1^{ox} = +0.35$ V (2e; $E_p - E_{p/2} = 30$ mV), $E_2^{ox} = +0.72$ (1e, irrev) V].[18] The first 2e-oxidation process is closely related to that of **2**, indicating transannular bonding in the dication. To investigate the possibile contribution from the type-G structure for the dication, **3** was subjected to oxidation with (*p*-$BrC_6H_4)_3N^{+\bullet}SbCl_6^-$. In the ^{1}H NMR spectrum of the salt, peaks in the aromatic region are broadened probably due to the restricted conformational behavior, thus being noninformative about the structure. Resonances for 12 Me groups appear around 3.2 and 3.0 ppm in a 2:1 ratio, which are assigned to Ar_2C^+ moieties and neutral Ar groups, respectively. The latter is split into two singlets, suggesting the lower symmetry of the species than expected for the type-F or type-G dication, and the rearranged sturucture **13**$^{2+}$ seems most suitable for the isolated salt. Thus, the stabilization by charge delocalization in the type-G structure may not be enough, if any, to prevent the skeletal rearrangement from trithiabicyclo[3.1.0]hexane to 1,2,4-trithian-5-ene. Upon reduction of the deeply colored salt was obtained the new triene **13** ($E_1^{ox} = +0.11$ V), which exhibits very strong electron-donating properties such as **12**.

Conclusion

In this work, we have investigated the redox properties of cyclic dithioacetal-type compounds substituted with the electron-donating aryl groups. It is evident that sulfur atoms at the vinyl positions play an important role in stabilizing oxidized species by delocalization.[19] At the same time, however, they induce deterioration of the charged species by skeletal rearrangement, thus preventing reversible interconversion between the neutral donors and the transannular dications in the cases of **2** and **3**. Yet, we have successfully constructed the reversible redox pairs (**1** and **1**$^{2+}$; **12** and **12**$^{2+}$) that exhibit electrochromicity with a vivid change in color (faintly or bright yellow to deep blue). According to their electrochemical and crystallographic studies, large structural changes by twisting around exocyclic bond(s) occur upon ET in these systems. Introduction of proper substituents as well as application of the modern technology of surface manipulation to the presented motif would lead to the production of novel materials for electrochemical sensing. Studies in this vein are now under way.

Experimental Section

Preparation of Mono(diarylmethylene)-type Donors (1, 4, 5, and 6). To a colorless suspension of trithiane **7** (690 mg, 5.0 mmol) in dry THF (23 mL) was added dropwise *n*-BuLi (1.59 mol dm^{-3} in *n*-hexane, 3.14 mL, 5.0 mmol) at −78 °C under Ar. After being stirred for 2.5 h at −78 °C, the mixture was allowed to warm to −20 °C and kept at this temperature for 2 h. Then, to the resultant solution of 2-lithio-1,3,5-trithiane was added a suspension of 4,4′-bis(dimethylamino)benzophenone (1.34 g, 5.0 mmol) in 20 mL of dry THF at −78 °C and. The whole mixture was allowed to warm to the ambient temperature. After addition of 0.1 mL of water and evaporation of solvent, the remaining solid was suspended in water and extracted with $CHCl_3$. The organic layer was washed with brine and dried over Na_2SO_4. Pale tan solid of crude alcohol **11a** (2.22 g) was obtained by evaporation of the solvent, which can be directly used for the further transformation.

To a solution of **11a** in benzene (80 mL) was added a catalytic amount of TsOH (10 mg). After refluxing for 1 h, the mixture was washed with water and brine and dried over Na_2SO_4. Evaporation of the solvent gave 1.99 g of yellow solid which was purified by recrystallization from benzene−EtOH. Pure 2-[bis(4-dimethylaminophenyl)methylene]trithiane **1a** (1.68 g) was obtained as yellow crystals in 86% yield over two steps from **7**. Data of **1a**: mp 198.5−199.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.03 (4H, AA′XX′), 6.65 (4H, AA′XX′), 4.09 (4H, s), 2.96 (12H, s); IR (KBr) 1606, 1520, 1444 cm^{-1}; EI-MS *m*/*z* (relative intensity) 388 (M$^+$, 67), 296 (100), 126 (16); UV−vis (see text). Anal. Calcd for $C_{20}H_{24}N_2S_3$: C, 61.81; H, 6.22; N, 7.21; S, 24.75. Found: C, 61.78; H, 6.25; N, 7.05; S, 24.54. **11a**: colorless crystals ($CHCl_3$); mp 184.0−184.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.35 (4H, AA′XX′), 6.66 (4H, AA′XX′), 5.08 (1H, s), 4.26 (2H, d, $J = 14.4$ Hz), 4.00 (2H, d, $J = 14.4$ Hz), 3.10 (1H, s), 2.93 (12H, s); IR (KBr) 3456, 1614, 1522 cm^{-1};

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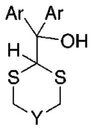
[17] Schumaker, R. R.; Rajeswari, S.; Joshi, M. V.; Cava, M. P.; Takassi, M. A.; Metzgar, R. M. J. *Am. Chem. Soc.* **1989**, *111*, 308. Fourmigué, M.; Johannsen, I.; Boubekeur, K.; Nelson, C.; Batail, P. J. *Am. Chem. Soc.* **1993**, *115*, 3752.

[18] The numbers of electron involved in each process are tentative. Although the current ratio of E_1^{ox} and E_2^{ox} is nearly 2:1, there is a possibility that four and two electrons are concerned in each process. However, such a possibility was rejected by the measurement conducted under the presence of 1 equiv of anthraquinone [$E_1^{red} = -0.93$ V (1e), $E_2^{red} = -1.53$ V (1e)] as an internal standard. The current ratio for E_1^{ox}(**3**) and E_1^{red}(AQ) is 1.74, indicating that the 4e-oxidation of **3** in the first process is unlikely.

[19] Oxidation of 4-(diarylmethylene)-2,3,5,6-tetrahydrothiopyran gave the diarylcarbenium derivative substituted with 4-thiacyclohexene ring, whose formation is reasonably accounted for by decomposition of the resulted dication by deprotonation at C^3: (the late) Tatsuo Nakamura, Graduate Thesis at the Department of Chemistry, Faculty of Science, Tohoku University, 1995.

FD-MS *m/z* 406 (M^+). Anal. Calcd for $C_{20}H_{26}ON_2S_3$: C, 59.07; H, 6.46; N, 6.89; S, 23.66. Found: C, 58.82; H, 6.41; N, 6.87; S, 23.59.



11 (Y = S)
14 (Y = CH_2)
15 (Y = NMe)
16 (Y = N*t*-Bu)

(**a**: Ar = *p*-$Me_2NC_6H_4$; **b**: Ar = *p*-$MeOC_6H_4$)

Other 2-[bis(4-dimethylaminophenyl)methylene] derivatives (**4a**, **5a,** and **6a**) were prepared similarly by the two-step procedure starting from 1,3-dithiane **8**, 5-methyldihydro-1,3,5-dithiazine **9**, and 5-(2,2-dimethylpropyl)dihydro-1,3,5-dithiazine **10**, respectively, in place of trithiane **7**. Intermediary alcohols (**14a**, **15a**, and **16a**) were purified by recrystallization. Data of **4a**: yield 97%; yellow crystals (benzene); mp 215.5−217.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.08 (4H, AA′XX′), 6.65 (4H, AA′XX′), 2.95 (12H, s), 2.93 (4H, t, $J = 6.3$ Hz), 2.12 (2H, quint, $J = 6.3$ Hz); IR (KBr) 1608, 1520, 1446 cm^{-1}; FD-MS *m/z* 370 (M^+). Anal. Calcd for $C_{21}H_{26}N_2S_2$: C, 68.06; H, 7.07; N, 7.56; S, 17.30. Found: C, 68.16; H, 7.13; N, 7.46; S, 17.46; **5a**: yield 87%; pale yellow crystals (benzene); mp 201.0−202.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.11 (4H, AA′XX′), 6.64 (4H, AA′XX′), 4.35 (4H, s), 2.95 (12H, s), 2.74 (3H, s); IR (KBr) 1608, 1520, 1352 cm^{-1}; EI-MS *m/z* (relative intensity) 385 (M^+, 21), 353 (21), 296 (100), 126 (10). Anal. Calcd for $C_{21}H_{27}N_3S_2$: C, 65.41; H, 7.06; N, 10.90; S, 16.63. Found: C, 65.42; H, 7.15; N, 10.72; S, 16.61; **6a**: yield 91%; yellow crystals (acetone); mp 183.3−184.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.09 (4H, AA′XX′), 6.65 (4H, AA′XX′), 4.46 (4H, s), 2.94 (12H, s), 1.29 (9H, s); IR (KBr) 1608, 1522, 1350 cm^{-1}; EI-MS *m/z* (relative intensity) 427 (M^+, 12), 395 (18), 296 (100), 126 (7). Anal. Calcd for $C_{24}H_{33}N_3S_2$: C, 67.40; H, 7.78; N, 9.83; S, 14.99. Found: C, 67.29; H, 7.75; N, 9.77; S, 15.04; **14a**: yield 77%; pale greenish crystals ($CHCl_3$); mp 216.0−217.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.40 (4H, AA′XX′), 6.66 (4H, AA′XX′), 5.03 (1H, s), 3.09 (1H, s), 2.92 (12H, s), 2.82−2.89 (4H, m), 2.04−2.09 (1H, m), 1.81−1.88 (1H, m); IR (KBr) 3504, 1616, 1524, 1448 cm^{-1}; FD-MS *m/z* 388 (M^+). Anal. Calcd for $C_{21}H_{28}ON_2S_2$: C, 64.91; H, 7.26; N, 7.21; S, 16.50. Found: C, 64.80; H, 7.27; N, 7.05; S, 16.61; **15a**: yield 81%; faintly brown crystals ($CHCl_3$); mp 183.2−184.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.40 (4H, AA′XX′), 6.67 (4H, AA′XX′), 5.19 (1H, s), 4.68 (2H, d, $J = 12.9$ Hz), 4.09 (2H, d, $J = 12.9$ Hz), 3.06 (1H, s), 2.92 (12H, s), 2.56 (3H, s); IR (KBr) 3504, 1614, 1520, 1350 cm^{-1}; FD-MS *m/z* 403 (M^+). Anal. Calcd for $C_{21}H_{29}ON_3S_2$: C, 62.49; H, 7.24; N, 10.41; S, 15.89. Found: C, 62.30; H, 7.24; N, 10.22; S, 15.83. **16a**: yield 78%; colorless crystals ($CHCl_3$); mp 174.8−175.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.40 (4H, AA′XX′), 6.65 (4H, AA′XX′), 5.32 (1H, s), 4.61 (2H, d, $J = 13.2$ Hz), 4.49 (2H, d, $J = 13.2$ Hz), 3.10 (1H, s), 2.91 (12H, s), 1.30 (9H, s); IR (KBr) 3432, 1614, 1522, 1350 cm^{-1}; FD-MS *m/z* 445 (M^+). Anal. Calcd for $C_{24}H_{35}ON_3S_2$: C, 64.68; H, 7.92; N, 9.43; S, 14.41. Found: C, 64.55; H, 7.87; N, 9.43; S, 14.55.

2-[Bis(4-methoxyphenyl)methylene] derivatives (**1b**, **4b**, **5b**, and **6b**) were also prepared by the reactions of heterocycles **7**−**10** with 4,4′-dimethoxybenzophenone via alcohols **11b**, **14b**, **15b**, and **16b**. Data of **1b**: yield 85%; colorless crystals (benzene); mp 154.2−155.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.08 (4H, AA′XX′), 6.86 (4H, AA′XX′), 4.09 (4H, s), 3.81 (6H, s); IR (KBr) 1604, 1510, 1250 cm^{-1}; EI-MS *m/z* (relative intensity) 362 (M^+, 68), 270 (100), 255 (19), 113 (15); UV−vis (MeCN) λ_{max} 300 (log ϵ 4.04), 255 (4.15) nm. Anal. Calcd for $C_{18}H_{18}O_2S_3$: C, 59.63; H, 5.00; S, 26.53. Found: C, 59.43; H, 4.99; S, 26.58; **4b**: yield 91%; colorless crystals (benzene); mp 132.5−133.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.12 (4H, AA′XX′), 6.85 (4H, AA′XX′), 3.80 (6H, s), 2.95 (4H, t, $J = 6.3$ Hz), 2.13 (2H, quint, $J = 6.3$ Hz); IR (KBr) 1606, 1508, 1248 cm^{-1}; FD-MS *m/z* 344 (M^+). Anal. Calcd for $C_{19}H_{20}O_2S_2$: C, 66.24; H, 5.85; S, 18.61. Found: C, 66.17; H, 5.95; S, 18.83; **5b**: yield 86%; colorless crystals (benzene); mp 159.0−160.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.15 (4H, AA′XX′), 6.84 (4H, AA′XX′), 4.35 (4H, s), 3.80 (6H, s), 2.73 (3H, s); IR (KBr) 1606, 1510, 1244 cm^{-1}; EI-MS *m/z* (relative intensity) 359 (M^+, 11), 270 (100), 255 (33), 113 (7). Anal. Calcd for $C_{19}H_{21}O_2NS_2$: C, 63.48; H, 5.89; N, 3.90; S, 17.84. Found: C, 63.54; H, 6.03; N, 3.80; S, 18.00. **6b**: yield 56%; pale brown crystals (acetone); mp 138.8−142.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.14 (4H, AA′XX′), 6.84 (4H, AA′XX′), 4.47 (4H, s), 3.80 (6H, s), 1.29 (9H, s); IR (KBr) 1606, 1510, 1248 cm^{-1}; EI-MS *m/z* (relative intensity) 401 (M^+, 16), 270 (100), 255 (18). Anal. Calcd for $C_{22}H_{27}O_2NS_2$: C, 65.79; H, 6.78; N, 3.49; S, 15.97. Found: C, 65.83; H, 6.84; N, 3.26; S, 15.98. **11b**: yield 31%; colorless crystals ($CHCl_3$); mp 145.5−147.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.42 (4H, AA′XX′), 6.85 (4H, AA′XX′), 5.10 (1H, s), 4.26 (2H, d, $J = 14.7$ Hz), 4.01 (2H, d, $J = 14.7$ Hz), 3.78 (6H, s), 3.24 (1H, s); IR (KBr) 3460, 1608, 1512, 1252 cm^{-1}; FD-MS *m/z* 380 (M^+). Anal. Calcd for $C_{18}H_{20}O_3S_3$: C, 56.81; H, 5.30; S, 25.28. Found: C, 56.94; H, 5.29; S, 25.14. **14b**: yield 77%; colorless crystals ($CHCl_3$); mp 169.2−171.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.46 (4H, AA′XX′), 6.84 (4H, AA′XX′), 5.05 (1H, s), 3.78 (6H, s), 3.22 (1H, s), 2.86−2.90 (4H, m), 2.05−2.10 (1H, m), 1.78−1.90 (1H, m); IR (KBr) 3484, 1608, 1512, 1250 cm^{-1}; FD-MS *m/z* 362 (M^+). Anal. Calcd for $C_{19}H_{22}O_3S$: C, 62.95; H, 6.12; S, 17.69. Found: C, 63.15; H, 6.20; S, 17.73. **15b**: yield 87%; colorless crystals ($CHCl_3$); mp 142.0−142.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.46 (4H, AA′XX′), 6.85 (4H, AA′XX′), 5.21 (1H, s), 4.69 (2H, d, $J = 13.2$ Hz), 4.10 (2H, d, $J = 13.2$ Hz), 3.77 (6H, s), 3.18 (1H, s), 2.55 (3H, s); IR (KBr) 3500, 1610, 1512, 1250 cm^{-1}; FD-MS *m/z* 377 (M^+). Anal. Calcd for $C_{19}H_{23}O_3NS_2$: C, 60.45; H, 6.14; N, 3.71; S, 16.99. Found: C, 60.48; H, 6.18; N, 3.60; S, 17.16. **16b**: yield 81%; colorless crystals ($CHCl_3$); mp 159.7−160.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.47 (4H, AA′XX′), 6.84 (4H, AA′XX′), 5.35 (1H, s), 4.63 (2H, d, $J = 13.2$ Hz), 4.51 (2H, d, $J = 13.2$ Hz), 3.77 (6H, s), 3.21 (1H, s), 1.31 (9H, s); IR (KBr) 3432, 1614, 1510, 1250 cm^{-1}; FD-MS *m/z* 419 (M^+). Anal. Calcd for $C_{22}H_{29}O_3NS_2$: C, 62.97; H, 6.97; N, 3.34; S, 15.28. Found: C, 62.84; H, 6.94; N, 3.23; S,15.35.

Preparation of Bis- and Tris(diarylmethylene)-type Donors (2 and 3). To a solution of **1a** (776 mg, 2.0 mmol) in dry THF (25 mL) was added dropwise *n*-BuLi (1.53 mol dm^{-3} in *n*-hexane, 1.31 mL, 2.0 mmol) at −78 °C under Ar. Then, the mixture was allowed to warm to −20 °C and kept at this temperature for 2 h. To the resultant pale yellow suspension was added a suspension of 4,4′-bis(dimethylamino)benzophenone (536 mg, 2.0 mmol) in 15 mL of dry THF at −20 °C. The whole mixture was gradually warmed to the ambient temperature during 4 h. After addition of 0.1 mL of water and evaporation of solvent, the remaining solid was suspended in water and extracted with $CHCl_3$. The organic layer was washed with brine and dried over Na_2SO_4. Yellow solid of the alcohol (1.58 g) was directly used for the further transformation.

To a solution of the crude alcohol in benzene (60 mL) was added a catalytic amount of TsOH (5 mg). After refluxing for 1 h, the mixture was washed with water and brine and dried over Na_2SO_4. Evaporation of the solvent gave 1.54 g of yellow solid which was purified by recrystallization from acetone to give yellow crystals of pure **2aa** (1.08 g) in 85% yield over two steps. Data of **2aa**: mp 230.0−233.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.13 (4H, AA′XX′), 7.02 (4H, AA′XX′), 6.67 (4H, AA′XX′), 6.42 (4H, AA′XX′), 4.13 (2H, s), 2.96 (12H, s), 2.87 (12H, s); IR (KBr) 1608, 1520, 1356 cm^{-1}; EI-MS *m/z* (relative intensity) 638 (M^+, 10), 388 (29), 296 (100), 126 (18); UV−vis (MeCN) λ_{max} 358 sh (log ϵ 4.38), 309 (4.69) nm. Anal. Calcd for $C_{37}H_{42}N_4S_3$: C, 69.55; H, 6.63; N, 8,77; S, 15.05. Found: C, 69.29; H, 6.65; N, 8.51; S, 15.12.

By the reaction with 4,4′-dimethoxybenzophenone, the similar procedure gave the unsymmetrically substituted bis(diarylmethylene) derivative **2ab** in 65% yield from **1a**. Tris(diarylmethylene) derivative **3** was obtained in the similar way from **2aa** and 4,4′-bis(dimethylamino)benzophenone in 54% yield, and *t*-BuLi was proven more effective than *n*-BuLi in the lithiation of **2aa**. Data of **2ab**: mp 109.2−113.5 °C (acetone); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 7.19 (2H, AA′XX′),

7.13 (2H, AA′XX′), 7.04 (2H, AA′XX′), 6.97 (2H, AA′XX′), 6.87 (2H, AA′XX′), 6.66 (2H, AA′XX′), 6.63 (2H, AA′XX′), 6.39 (2H, AA′XX′), 4.14 (2H, s), 3.81 (3H, s), 3.72 (3H, s), 2.96 (6H, s), 2,88 (6H, s); IR (KBr) 1606, 1510, 1356, 1246 cm^{-1}; EI-MS *m/z* (relative intensity) 612 (M^+, 93), 296 (100), 252 (16); UV−vis (see text). Anal. Calcd for $C_{35}H_{36}N_2O_2S_3$: C, 68.59; H, 5.92; N, 4.57; S, 15.70. Found: C, 68.75; H, 5.87; N, 4.52; S, 15.76; **3**: mp 295.2−298.5 °C (acetone−CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 7.09 (12H, AA′XX′), 6.53 (12H, AA′XX′), 2.92 (36H, s); IR (KBr) 1608, 1520, 1354 cm^{-1}; FD-MS *m/z* 888 (M^+); UV−vis (MeCN) λ_{max} 390 (log ϵ 4.53), 314 (4.83), 282 sh (4.78) nm. Anal. Calcd for $C_{54}H_{60}N_6S_3$: C, 72.93; H, 6.80; N, 9.45; S, 10.82. Found: C, 72.88; H, 6.90; N, 9.33; S, 10.75.

Oxidation of Bis(diarylmethylene)trithiane 2aa. To a suspension of (p-$BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ (571 mg, 0.700 mmol) in dry CH_2Cl_2 (18 mL) was added a yellow solution of **2aa** (223 mg, 0.350 mmol) in dry CH_2Cl_2 (10 mL) under Ar. After the deep purple mixture containing black tarry material was stirred for 2 d, the resulting crystalline solid of $\mathbf{12}^{2+}(SbCl_6^-)_2$ (437 mg) was filtered (yield 96%): mp > 300 °C; ^1H NMR (see text); IR (KBr) 1580, 1372,1170 cm^{-1}; FAB-MS *m/z* (relative intensity) 638 (M^+, 62), 560 (51), 528 (100), 264 (35), 136 (71); UV−vis (see text). Anal. Calcd for $C_{37}H_{42}N_4S_3Sb_2Cl_{12}\cdot H_2O$: C, 33.51; H, 3.35; N, 4.23; S, 7.25; Cl, 32.09. Found: C, 33.30; H, 3.24; N, 4.24; S, 7.43; Cl, 32.04.

Similar oxidation by using iodine (3 equiv) in place of the aminium salt gave black crystalline solid of $\mathbf{12}^{2+}(I_3^-)_2$ salt[16] in 82% yield: mp > 300 °C; ^1H NMR (400 MHz, CD_3CN) δ/ppm 7.32 (4H, AA′XX′), 7.27 (4H, AA′XX′), 6.81 (4H, AA′XX′), 6.80 (4H, AA′XX′), 4.91 (2H, s), 3.23 (12H, s), 3.21 (12H, s); IR (KBr) 1580, 1368, 1166 cm^{-1}; FAB-MS *m/z* (relative intensity) 638 (M^+, 1), 358 (18), 307 (13). Anal. Calcd for $C_{37}H_{42}N_4S_3I_6$: C, 31.73; H, 3.02; N, 4.00; S, 6.87; I, 54.37. Found: C, 31.95; H, 3.10; N, 3.93; S, 6.71; I, 54.18.

Interconversion between Dication Salt $\mathbf{12^{2+}(SbCl_6^-)_2}$ and Neutral Diene 12. To a suspension of $\mathbf{12}^{2+}(SbCl_6^-)_2$ (300 mg, 0.230 mmol) in CH_3CN (40 mL) was added large excess of activated Zn powder (625 mg, 9.56 mmol) and stirred vigorously for 12 h. The mixture was added water and extracted with benzene. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of solvent and recrystallization from acetone−CH_2Cl_2 gave red crystals of **12** (115 mg) in 78% yield: mp 163.5−167.0 °C; ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 6.97 (2H, AA′XX′), 6.94 (2H, AA′XX′), 6.81 (2H, AA′XX′), 6.79 (2H, AA′XX′), 6.60 (4H, AA′XX′), 6.51 (2H, AA′XX′), 6.47 (2H, AA′XX′), 4.30 (1H, d, J = 11.7 Hz), 4.16 (1H, d, J = 11.7 Hz), 2.94 (6H, s), 2.93 (6H, s), 2.91 (6H, s), 2.87 (6H, s); IR (KBr) 1606, 1520, 1354 cm^{-1}; FD-MS *m/z* 638 (M^+); UV−vis (see text). Anal. Calcd for $C_{37}H_{42}N_4S_3$: C, 69.55; H, 6.63; N, 8.77; S, 15.05. Found: C, 69.30; H, 6.64; N, 8.58; S, 15.30.

To a suspension of (p-$BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ (77 mg, 0.094 mmol) in dry CH_2Cl_2 (3 mL) was added a degassed solution of **12** (30 mg, 0.047 mmol) in dry CH_2Cl_2 (5 mL). After stirring overnight under Ar, the deeply colored solution was concentrated, and the black precipitates formed upon addition of ether were collected by suction to give $\mathbf{12}^{2+}(SbCl_6^-)_2$ (52 mg, yield 85%).

Oxidation of Tris(diarylmethylene)trithiane 3. To a degassed yellow solution of **3** (20 mg, 0.023 mmol) in dry CH_2Cl_2 (7 mL) was added (p-$BrC_6H_4)_3N^{+\bullet}SbCl_6^-$ (37 mg, 0.045 mmol). After stirring for 2 d under Ar, an insoluble black solid was removed, and the mother liquor was concentrated into a half of the volume. Black precipitates were formed upon addition of ether, which was collected by suction and dried in vacuo to give $\mathbf{13}^{2+}(SbCl_6^-)_2$ (20 mg, yield 57%): mp 230−250 °C (dec); ^1H NMR (300 MHz, CD_3CN) 7.22−7.63 (ca. 14H, m), 6.75−6.82 (ca. 10H, m), 3.24 (12H, s), 3.22 (12H, s), 3.09 (6H, s), 3.04 (6H, s); IR (KBr) 1580, 1374, 1170 cm^{-1}; MS spectrum could not be obtained under the FAB technique. Anal. Calcd for $C_{54}H_{60}N_6S_3Sb_2Cl_{12}\cdot C_4H_{10}O$: C, 42.67; H, 4.32; N, 5.15; S, 5.89. Found: C, 42.92; H, 4.04; N, 5.62; S, 6.35. Analytically pure sample could not be obtained due to the difficulty in its purification. The initially formed insoluble solid (11 mg) seems also to be the salt of $\mathbf{13}^{2+}$, as suggested by the formation of **13** upon reduction with Zn (vide infra), yet it showed a slightly different ^1H NMR spectrum: (300 MHz, CD_3CN) 7.48−7.22 (ca. 14H, m), 6.81−6.79 (ca. 10H, m), 3.23 (12H, s), 3.22 (12H, s), 3.12 (6H, s), 3.06 (6H, s).

Reduction of Dication Salt $\mathbf{13^{2+}(SbCl_6^-)_2}$. To a suspension of $\mathbf{13}^{2+}(SbCl_6^-)_2$ (59 mg, 0.038 mmol) in CH_3CN (15 mL) was added large excess of activated Zn powder (222 mg, 3.39 mmol) and stirred vigorously for 3 h. The mixture was added water and extracted with benzene. The organic layer was washed with brine and dried over Na_2SO_4. Evaporation of solvent gave orange crystals of **13** (32 mg) in 96% yield: mp 165−200 °C (dec); ^1H NMR (400 MHz, $CDCl_3$) δ/ppm 7.06 (2H, AA′XX′), 7.04 (2H, AA′XX′), 6.97 (2H, AA′XX′), 6.95 (2H, AA′XX′), 6.86 (2H, AA′XX′), 6.67 (2H, AA′XX′), 6.61 (2H, AA′XX′), 6.59 (2H, AA′XX′), 6.56 (2H, AA′XX′), 6.52 (4H, AA′XX′), 6.42 (2H, AA′XX′), 2.97 (6H, s), 2.95 (6H, s), 2.92 (6H, s), 2.92 (6H, s), 2.91, (6H, s), 2.84 (6H, s); IR (KBr) 1608, 1520, 1354 cm^{-1}; FD-MS *m/z* 888 (M^+). Anal. Calcd for $C_{54}H_{60}N_6S_3$: C, 72.93; H, 6.80; N, 9.45; S, 10.82. Found: C, 72.65; H, 6.92; N, 9.23; S, 10.63.

Redox Potentials and Spectroelectrochemical Measurements. Oxidation potentials (E^{ox}) were measured by cyclic voltammetry in dry MeCN containing 0.1 mol dm^{-3} Et_4NClO_4 as a supporting electrolyte unless otherwise noted. Ferrocene undergoes 1e-oxidation at +0.38 V under the same conditions. All of the values shown in the text are in *E*/V vs SCE. A Pt disk electrode (diameter, 1.6 mm) and a Pt wire electrode were used as working and counter electrodes, respectively. The working electrode was polished using a water suspension of Al_2O_3 (0.05 μm) before use. In the case of irreversible waves, half-wave potentials were estimated from the anodic peak potentials (E^{pa}) as $E^{ox} = E_{pa} - 0.03$ V.

Spectroelectrochemical measurements were carried out in a quartz cell (10 × 10 × 40 mm) equipped with a Pt mesh as a working electrode and a salt bridge. A Pt wire was placed in the latter as a counter electrode. Electrical current was monitored by a microampere meter.

X-ray Analyses. Crystal data for **2aa**: $C_{37}H_{42}N_4S_3$, *M* 638.95, yellow prism, 0.35 × 0.35 × 0.20 mm, monoclinic $P2_1/a$, $a = 12.919(2)$, $b = 16.659(2)$, $c = 16.376(2)$ Å, $\beta = 99.17(1)°$, $V = 3479.4(7)$ Å^3, ρ ($Z = 4$) = 1.220 g cm^{-1}. A total of 8279 unique data ($2\theta_{max} = 55°$) was measured at $T = 296$ K by a four-circle diffractometer with $\omega-2\theta$ scan mode (Mo−Kα radiation, $\lambda = 0.71069$ Å). No absorption correction was applied ($\mu = 2.44$ cm^{-1}). The structure was solved by the Patterson method (DIRDIF92 PATTY) and refined by the full-matrix least-squares method on *F* with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. Their isotropic temperature factors were included in the refinement. The final *R* and *Rw* values are 0.044 and 0.036 for 5007 reflections with $I > 3\sigma I$ and 397 parameters.

Crystal data for $\mathbf{3}\cdot(CH_2Cl_2)_2$: $C_{56}H_{64}N_6S_3Cl_4$, *M* 1059.15, very fluorescent yellow cube, 0.30 × 0.30 × 0.15 mm, triclinic *P*1 bar, $a = 11.7697(6)$, $b = 15.766(3)$, $c = 16.000(1)$ Å, $\alpha = 87.257(4)°$, $\beta = 77.318(5)°$, $\gamma = 73.061(5)°$, $V = 2770.5(5)$ Å^3, ρ (Z = 2) = 1.270 g cm^{-1}. A total of 11784 unique data ($2\theta_{max} = 55°$) was measured at $T = 203$ K by a CCD camera apparatus (Mo−Kα radiation, $\lambda = 0.71069$ Å). Numerical absorption correction was applied ($\mu = 3.68$ cm^{-1}). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on *F* with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms except those of solvents were located at the calculated positions. The final *R* and *Rw* values are 0.106 and 0.129 for 7775 reflections with $I > 3\sigma I$ and 632 parameters. Relatively high *R* values are due to the rapid deterioration of the crystal due to the solvent loss as well as the disorder of the solvent position in the crystal.

Crystal data for **5a**: $C_{21}H_{27}N_3S_2$, *M* 385.58, colorless rod, 0.40 × 0.20 × 0.20 mm, orthorhombic $P2_12_12_1$, $a = 17.952(4)$, $b = 19.219(3)$, $c = 6.026(4)$ Å, $V = 2079(1)$ Å^3, ρ ($Z = 4$) = 1.232 g cm^{-1}. A total of 2770 unique data ($2\theta_{max} = 55°$) was measured at $T = 296$ K by a four-circle diffractometer with $\omega-2\theta$ scan mode (Mo−Kα radiation, $\lambda = 0.71069$ Å). No absorption correction was applied (μ = 2.66 cm^{-1}). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. Their isotropic temperature factors were included in the refinement. The final R and Rw values are 0.042 and 0.025 for 2095 reflections with $I > 3\sigma I$ and 235 parameters.

Crystal data for **12**: $C_{37}H_{42}N_4S_3$, M 638.95, red prism, 0.45 × 0.25 × 0.25 mm, monoclinic $P2/c$, a = 10.821(2), b = 11.311(2), c = 15.349(1) Å, β = 94.640(8)°, V = 1872.5(4) Å^3, ρ (Z = 2) = 1.134 g cm^{-1}. A total of 4539 unique data ($2\theta_{max}$ = 55°) was measured at T = 296 K by a four-circle diffractometer with $\omega - 2\theta$ scan mode (Mo−Kα radiation, λ = 0.71069 Å). No absorption correction was applied (μ = 2.28 cm^{-1}). The structure was solved by the direct method (SAPI91) and refined by the full-matrix least-squares method on F with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. Their isotropic temperature factors were included in the refinement. The final R and Rw values are 0.059 and 0.053 for 2829 reflections with $I > 3\sigma I$ and 208 parameters. Refinement by supposing a lower symmetric space group (Pc) did not give more fruitful results. Even in this case, S_2 and C_3 atoms still suffer from positional disorder.

Crystal data for **12**$^{2+}(I_3^-)_2$: $C_{37}H_{42}I_6N_4S_3$, M 1400.37, black plate, 0.20 × 0.30 × 0.10 mm, triclinic P1 bar, a = 14.266(1), b = 15.722(1), c = 12.0915(9) Å, α = 97.424(3)°, β = 110.926(3)°, γ = 108.438(2)°, V = 2311.6(3) Å^3, ρ (Z = 2) = 2.012 g cm^{-1}. A total of 10114 unique data ($2\theta_{max}$ = 55°) was measured at T = 296 K by an imaging plate apparatus (Mo−Kα radiation, λ = 0.71069 Å). Numerical absorption correction was applied (μ = 41.98 cm^{-1}). The structure was solved by the direct method (SIR92) and refined by the full-matrix least-squares method on F with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were not included in the refinement. The final R and Rw values are 0.057 and 0.054 for 8000 reflections with $I > 3\sigma I$ and 437 parameters.

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Supporting Information Available: Ortep drawings (Figure S1−S5) and structural data for the X-ray analyses (positional and thermal parameters; bond distances and angles) of **2aa**, **3**, **5a**, **12**, and **12**$^{2+}(I_3^-)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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