CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.201203092

7,7,8,8-Tetraaryl-*o*-quinodimethane Stabilized by Dibenzo Annulation: A Helical π-Electron System That Exhibits Electrochromic and Unique Chiroptical Properties

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Dedicated to Prof. James Michael McBride on his retirement

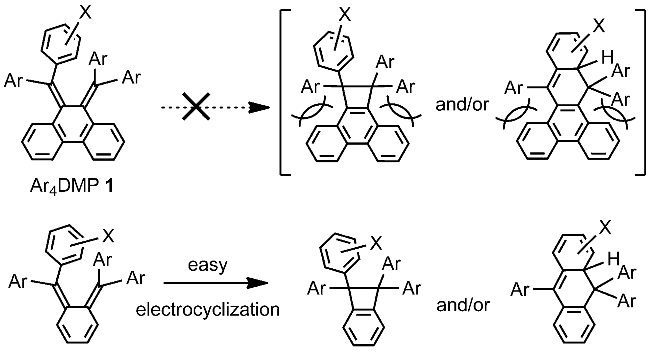
Abstract: When two benzene rings are fused to a tetraaryl-*o*-quinodimethane skeleton, sterically hindered helical molecules **1** acquire a high thermodynamic stability. Because the tetraarylbutadiene subunit contains electron-donating alkoxy groups, **1** undergo reversible two-electron oxidation to $\mathbf{2}^{2+}$, which can be isolated as deeply colored stable salts. Intramolecular transfer of the point chirality (e.g., *sec*-butyl) on the aryl groups to helicity induces a diastereomeric preference in dications $\mathbf{2b}^{2+}$ and $\mathbf{2c}^{2+}$, which represents an efficient method for enhancing circular-dichroism signals. Thus, those redox pairs can serve as new electrochiroptical response systems. X-ray analysis of dication $\mathbf{2}^{2+}$ revealed π–π stacking interaction of the diarylmethylium moieties, which is also present in solution. The stacking geometry is the key contributor to the chirosolvatochromic response.

Keywords: chirality · circular dichroism · electrochromism · helical structures · redox chemistry

Introduction

o-Quinodimethane (*o*QD) is a unique molecule that contains a cross-conjugating π-electron system. This hydrocarbon as well as its derivatives are considered versatile building blocks in synthetic chemistry due to their high reactivity in stereoselective Diels–Alder reactions.[1] In the case of sterically hindered 7,7,8,8-tetraaryl-*o*-quinodimethanes (Ar_4*o*QDs), in which four benzene rings are attached to exocyclic carbons, such intermolecular reactivities are suppressed due to steric congestion, which also causes the unique helical arrangement of π electrons, similar to the cases of helicenes consisting of *ortho*-condensed benzene rings. However, unlike many helicenes, Ar_4*o*QDs are unstable. Spectroscopic characterization can be conducted only at a low temperature due to a facile isomerization to 1,1,2,2-tetraarylbenzocyclobutene (BCB) or 9,9a-dihydro-9,9,10-triarylanthracene (DHA) through electrocyclization (Scheme 1).[2]

If spontaneous transformation into cyclized isomers could be suppressed, Ar_4*o*QDs would become available as thermo-



Scheme 1. Suppression of electrocyclization by dibenzo annulation on Ar_4*o*QD.

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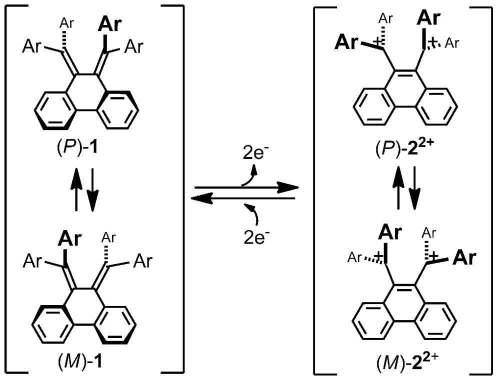
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201203092. CCDC-237042 (**1a**), CCDC-895519 (**1c**), and CCDC-895520 ($\mathbf{2c}^{2+}[SbCl_6^-]_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

dynamically stable species.[3] Keeping this in mind, we designed 9,10-bis(diarylmethylene)phenanthrene (Ar_4DMP, **1**),[4] because dibenzo annulation[5] would destabilize the corresponding BCB and DHA isomers, but not Ar_4DMP itself, by an additional steric repulsion.[6] This idea was supported by the PM3 calculation for Ph_4DMP, which has a much lower heat of formation than BCB- and DHA-type isomers (Figure S1 in the Supporting Information).

Because 1,1,4,4-tetraarylbutadienes[7] are important members of violene/cyanine-hybrid-type[7,8] electrochromic systems,[9] stabilized Ar_4DMPs **1** may also serve as new chromic materials. If a suitable electron-donating group, such as an alkoxy group, is attached to each of the aryl rings of **1**, the corresponding dications $\mathbf{2}^{2+}$ should become stable enough for isolation of their salts that exhibit strong absorption in the visible region, which is characteristic of triarylmethylium dyes.[10]

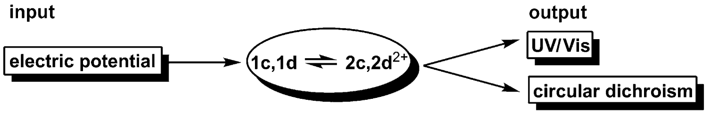
Because the redox-active chromophore is framed in the helically deformed skeleton of Ar_4DMPs **1**, a drastic change in geometry is expected upon electron transfer. Two of the four aryl rings in **1** are forced to overlap in proximity to cause a large steric repulsion,[11] whereas two-electron oxidation would induce twisting of the diarylmethylium units around the exocyclic bonds [$C^{9(10)}$–C^+] against the planarized phenanthrene core in $\mathbf{2}^{2+}$ so as to reduce the steric repulsion. Such a structural change is favorable for the construction of molecular response systems in terms of reversibility and bistability, which has been demonstrated in studies on “dynamic redox systems”.[12] Another interesting feature of the redox pair of $\mathbf{1}/\mathbf{2}^{2+}$ is the chiral element[13] of the helicity of their skeletal frameworks, although the stereoisomers of the dications cannot be separated due to a rapid inversion of their helical sense by rotation around $C^{9(10)}$–C^+ bonds [(P)-$\mathbf{2}^{2+} <=> (M)$-$\mathbf{2}^{2+}$]. It was found here that configuration of the helical sense in Ar_4DMPs **1** is also unstable [(P)-$\mathbf{1} <=> (M)$-$\mathbf{1}$] (Scheme 2), similar to other DMP compounds.[14]



Ar = 4-ROC_6H_4
a: RO = CH_3O
b: RO = $C_8H_{17}O$
c: RO = (R)-$C_2H_5CH(CH_3)O$
d: RO = (R)-$C_6H_{13}CH(CH_3)O$

Scheme 2. Helicity inversion in Ar_4DMP **1** and dicationic dye $\mathbf{2}^{2+}$.

Herein, the successful generation and isolation of a series of $(4\text{-}ROC_6H_4)_4DMPs$ **1a**–**1d** [RO = CH_3O, $C_8H_{17}O$, (R)-$C_2H_5CH(CH_3)O$, (R)-$C_6H_{13}CH(CH_3)O$] as new isolable examples of Ar_4*o*QD is reported.[4] The helically deformed structure in **1** as well as the twisted geometry in the dication $\mathbf{2}^{2+}$ were demonstrated by low-temperature X-ray analyses. As was designed, quinodimethane donors **1** and phenanthrene-9,10-diyl dications $\mathbf{2}^{2+}$ constitute reversible electrochromic pairs that exhibit a vivid color change from yellow to violet. Notably, the point chirality of the chiral alkoxy group attached on the aryl rings is transmitted to a helicity preference[15] to bias the diastereomeric ratio of $\mathbf{2c}^{2+}$ and $\mathbf{2d}^{2+}$, which enables us to newly construct electrochiroptical systems that give two kinds of spectral output [UV/Vis and circular dichroism (CD)] in response to electrochemical input (Scheme 3).[16]

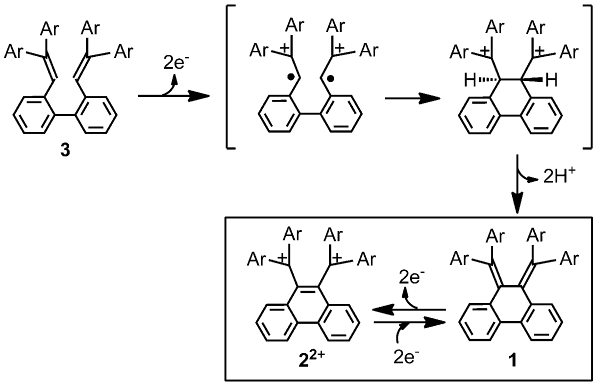


Scheme 3. Electrochiropitical response system with two kinds of spectroscopic output.

Results and Discussion

Preparation and helical geometry of 9,10-bis(diarylmethylene)phenanthrenes (Ar_4DMPs, 1):

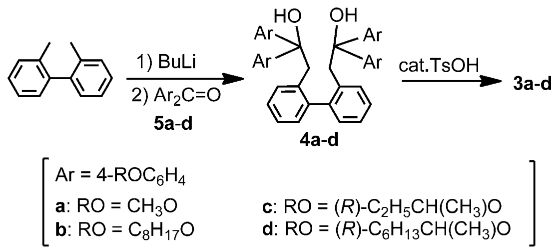
*Synthetic strategy for **1***: Sterically hindered molecules are generally difficult to obtain, and successful syntheses often adopt a common approach, in which they are generated from a less-hindered precursor by intramolecular reactions to minimize the disadvantage associated with entropy.[17] Against this background, we pursued the formation of Ar_4DMPs **1** from less-hindered dications $\mathbf{2}^{2+}$, which in turn would be obtained from 2,2′-bis(diarylethenyl)biphenyls **3** (Scheme 4). The oxidative cyclization of **3** to $\mathbf{2}^{2+}$ consists of several steps: 1) formation of a C–C bond between the benzylidene carbons upon the two-electron oxidation of **3**; 2)



Scheme 4. Preparation of Ar_4DMP **1** and interconversion with dicationic dye $\mathbf{2}^{2+}$.

double deprotonation from the resulting butane-1,4-diyl dication[18] to give **1**; and 3) the further two-electron oxidation of **1** to furnish **2**$^{2+}$.

As shown in Scheme 5, the reaction of 2,2′-dimethylbiphenyl with BuLi in the presence of TMEDA gave 2,2′-bis(lithiomethyl)biphenyl,[19] which was then treated with 4,4′-dimethoxybenzophenone **5a** in THF to give bis[bis(4-methoxyphenyl)ethanol] derivative **4a**. Treatment with a catalytic amount of TsOH in benzene at reflux gave bis[bis(4-methoxyphenyl)ethenyl]biphenyl **3a** in 50 % yield over two steps. Next, oxidative cyclization[11a] was performed by the treatment of **3a** with four equivalents of $NOBF_4$ in CH_2Cl_2. The dark purple powder of dicationic salt **2a**$^{2+}[BF_4^-]_2$ was obtained in 94 % yield. When a smaller amount of oxidant was used, the same salt was obtained, and the starting material **3a** was recovered, because **1a** generated in situ is more easily oxidized than the starting material **3a** (Scheme 4).



Scheme 5. Preparation of 2,2′-bis[2,2-bis(4-alkoxyphenyl)ethenyl]biphenyl **3**.

The dication exhibits a characteristic strong absorption band in the visible region [$\lambda_{max} = 502$ nm ($\log\varepsilon = 4.76$) in MeCN]. When **2a**$^{2+}[BF_4^-]_2$ was treated with excess Zn powder in dry DME, the deep purple color disappeared rapidly, and Ar_4DMPs **1a** [$\lambda_{max} = 325$ nm (sh; $\log\varepsilon = 4.04$) in MeCN] was isolated as stable yellow cubes in 92 % yield after recrystallization. Its thermodynamic stability was demonstrated by quantitative recovery after heating at reflux for 24 h in toluene with no signs of electrocyclization to its isomers.

When other 4,4′-dialkoxybenzophenones **5b–d** were used in the reactions of 2,2′-bis(lithiomethyl)biphenyl, bis(diarylethenyl)biphenyls **3b–d** with different alkoxy groups were similarly obtained via diols **4b–d** in respective yields of 56, 58, and 55 % over two steps. The oxidative cyclization of **3b–d** was conducted by using four equivalents of $(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$. Without purification, the resulting dication salts of **2b**$^{2+}$–**d**$^{2+}$ were subjected to reduction with Zn to give Ar_4DMPs as yellow crystals (**1c**, 89 % yield) or yellow oils (**1b**, 81 %; **1d**, 83 %). Again, they are thermodynamically stable and can be kept at room temperature under air, which validates our design concept for stabilizing Ar_4*o*QD by dibenzo annulation.

*Structural features of **1***: To investigate the detailed structural features of the isolable derivative of Ar_4*o*QD, **1a** was subjected to a low-temperature X-ray analysis ($CHCl_3$ solvate, $I\bar{4}$ bar, $Z = 8$). The most striking feature is the large torsion angle of 63.4(6)° for the $Ar_2C{=}C{-}C{=}CAr_2$ unit, although the twisting angle of the biphenyl skeleton is only 19.6(7)°, as was determined by the torsion angle for the bay-region carbons. The two exocyclic double bonds also deviate from planarity [twisting angles: 7(1) and 3(1)°]. This deformation is surely induced to avoid the anomalous proximity of the two inner aryl groups, which are still close enough for π–π interaction (Figure 1 a and b). They overlap nearly in parallel in a face-to-face manner and the closest contact between the facing aromatic carbons is 3.19(1) Å, which is much shorter than the sum of the van der Waals radii (3.40 Å).

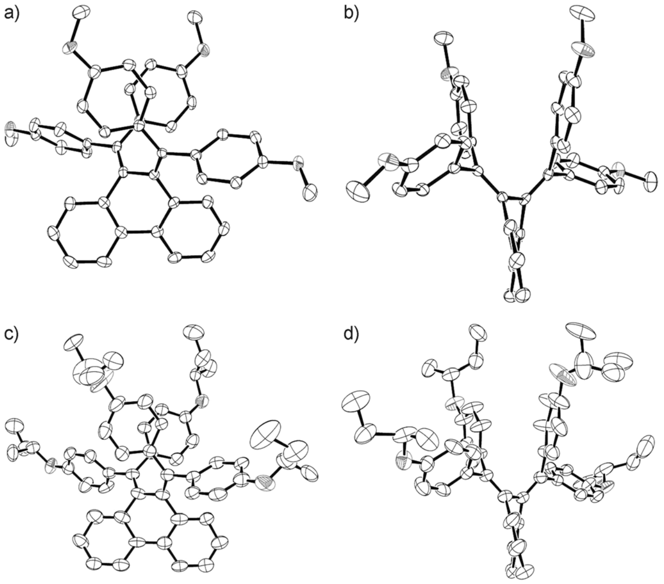


Figure 1. a) Top view and b) side view of X-ray structures of (*P*)-**1a** in the racemic crystal [**1a**•$(CHCl_3)_2$] determined at 123 K. Thermal ellipsoids are shown at the 50 % probability level. c) Top view and d) side view of X-ray structures of (*P*)-**1c** in the crystal of **1c** containing both diastereomers [(*P*)- and (*M*)-**1c**] determined by X-ray analysis at 123 K. Thermal ellipsoids are shown at the 30 % probability level.

In the ^{1}H NMR spectrum of **1a** (300 MHz), methoxy protons on the aryl groups appeared as two sharp singlets ($\delta =$ 3.50 and 3.30 ppm in [D$_5$]bromobenzene) at 25 °C. The former resonance is assigned as that for the CH_3O in the inner aryl groups, which is shifted downfield due to deshielding effects. When the temperature increases, the two peaks gradually coalesce ($T_c = 100$ °C), and a sharp single resonance was then observed at higher temperature (Figure S2 in the Supporting Information), which shows that the inner and outer aryl groups are exchanged with an energy barrier of 18.4 kcal mol^{-1}. This value also corresponds to the inversion of helicity [(*P*)-**1a**< = >(*M*)-**1a**]. Such a small barrier makes it impossible to perform the optical resolution of (*P*)- and (*M*)-**1a**. This should also be the case for other Ar_4DMPs **1b–d**. Although **1c** and **1d** with four chiral alkoxy groups [(*R*)-$C_2H_5CH(CH_3)O$ or (*R*)-$C_6H_{13}CH(CH_3)O$, respectively] exist as mixtures of diastereomers with an opposite sense of helicity, they were treated as single entities due to facile interconversion.

Upon recrystallization, a single-crystal specimen of **1c** ($P2_12_12_1$, $Z=8$, two independent molecules) was obtained. Interestingly, the crystal is composed of an equal amount of diastereomers [(*P*)-**1c** for molecule-1, (*M*)-**1c** for molecule-2], which is not a common crystallization phenomenon.[15a,b] X-ray analysis provided structural information on both diastereomers with the same point chiralities on the aryl rings, but with a different helical sense (Figures 1 c, d, and S3 in the Supporting Information). Despite the similar helical geometries of the (*P*)- and (*M*)-isomers, their structural parameters differ slightly and indicate larger deformation in the (*M*)-isomer. The torsion angle for the $Ar_2C{=}C{-}C{=}CAr_2$ unit, the twisting angle of the biphenyl skeleton, and the twisting angles of the two exocyclic bonds are 59.7(8), 23.1(9), 4(1), and 2(1)° in the (*P*)-isomer and 69.4(6), 25.2(8), 10(1), and 8(1)° in the (*M*)-isomer, respectively.

In the ^{1}H NMR spectrum of **1c** at room temperature, the only one set of resonances that correspond to a single C_2-symmetric species was observed, which shows that the two diastereomers [(*P*)- and (*M*)-**1c**] exhibit indistinguishable chemical shifts. The slightly different steric interactions for the diastereomeric pair may or may not bias the equilibrium ratio in favor of one of the two diastereomers,[20] however, this issue cannot be detailed experimentally in either **1c** or **1d** for the same reason.

Redox properties and interconversion between Ar$_4$DMPs (1) and phenanthrene-9,10-diylbis(diarylmethylium)s (2): Due to not only by the electron-donating alkoxy groups, but also the observed skeletal deformation and intramolecular π–π interaction, Ar$_4$DMP **1a** has an increased HOMO level, so that it undergoes a facile electrochemical oxidation ($E^{ox}=+0.61$ V vs. Ag/Ag$^+$ in CH_2Cl_2; two-electron process). Variation of the alkyl group seldom affects the donating properties ($E^{ox}=+0.66$, $+0.61$, and $+0.67$ V, for **1b–d**, respectively; Figure 2). Upon treatment of **1a–d** with two equivalents of $(4\text{-}BrC_6H_4)_3N^{+\bullet}SbCl_6^-$, the corresponding dication salts $\mathbf{2a}^{2+}$–$\mathbf{d}^{2+}[SbCl_6^-]_2$ were isolated as deep purple crystals or amorphous compounds in high yields (93, 95, 98, and 97 %, respectively).[21] The salt of $\mathbf{2a}^{2+}$ (see above) and those of $\mathbf{2b}^{2+}$–$\mathbf{d}^{2+}$ reproduced Ar$_4$DMP **1a–d** upon reduction with Zn dust in high yields (92, 95, 100, and 97 %, respectively), as was confirmed by the reversible nature of the present redox pairs.

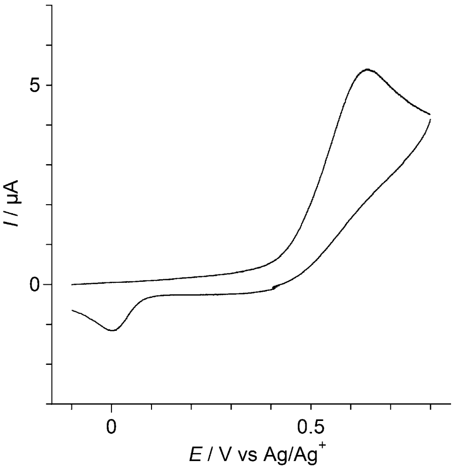


Figure 2. Cyclic voltammogram of **1c** recorded in CH_2Cl_2 (0.5 mM) containing Bu_4NBF_4 (0.1 M) as a supporting electrolyte (*E*/V vs Ag/Ag$^+$, scan rate 100 mV s^{-1}, Pt electrode).

Interestingly, the reduction potentials of $\mathbf{2a}^{2+}$–$\mathbf{d}^{2+}$ were observed in the far cathodic region ($E^{red}=+0.11$, $+0.07$, $+0.03$ and $+0.03$ V for $\mathbf{2a}^{2+}$–$\mathbf{d}^{2+}$, respectively; two-electron process). Such a large shift of redox peaks as well as a one-wave two-electron oxidation process are commonly observed in dynamic redox pairs[12] undergoing drastic structural changes and/or reversible formation/breaking of C–C bonds upon electron transfer.[7,8,14,22] The separation by approximately 0.6 V indicates a high electrochemical bistability of the redox couples of $\mathbf{1}/\mathbf{2}^{2+}$, which is favorable for realizing switching phenomena of redox active molecules.

Upon crystallization of $\mathbf{2c}^{2+}[SbCl_6^-]_2$ from CH_2Cl_2/ether, a high-quality, single-crystal specimen was obtained, X-ray analysis of which ($P2_1$, $Z=2$) revealed that the phenanthrene core in $\mathbf{2c}^{2+}$ is nearly planar (Figure 3). The two diarylmethylium units are attached at the 9,10-positions with large twisting angles [68(1) and 63(1)°] to give a helical arrangement of the π system, the helical sense of which is similar to that in (*P*)-**1c**. Although the helical inversion of (*P*)-$\mathbf{2c}^{2+}$ can readily occur in solution through rotation about the $C^{9(10)}$–C^+ bonds, there are no diastereomeric dications with (*M*)-helicity in the crystal. Thus, the point chirality of the alkoxy group [(*R*)-$C_2H_5CH(CH_3)O$] is transmitted to the (*P*)-helicity preference of the dication, in which the two chromophores are stacked nearly in parallel with a shortest C–C contact of 3.05(1) Å. Such an asymmetric geometry is suitable for realizing exciton coupling of the two chromophores.[23] Accordingly, the CD spectrum of $\mathbf{2c}^{2+}[SbCl_6^-]_2$ salt, taken as a KBr tablet, showed the negative bisignated Cotton effects in the $\lambda=500$–600 nm region (Figure S4 in the Supporting Information).

Chiroptical properties and a multi-input/multi-output response of 1c/2c^{2+} and 1d/2d^{2+}: A large negative couplet was observed in the CD spectrum of $\mathbf{2c}^{2+}[SbCl_6^-]_2$ salt recorded in CH_2Cl_2 [$\lambda_{ext}=591$ nm ($\Delta\varepsilon=-23$), 520 (+17)], showing that the transmission of point chirality to helicity[15] also occurs in solution to induce a preference for (*P*)-helicity in $\mathbf{2c}^{2+}$. In the ^{1}H NMR spectrum of $\mathbf{2c}^{2+}[SbCl_6^-]_2$, only one set of resonances that corresponded to a single C_2-symmetric species was observed, indicating that the two diastereomers [(*P*)- and (*M*)-$\mathbf{2c}^{2+}$] interconvert so rapidly that we cannot determine the diastereomeric excess in terms of the helicity preference. The observed ellipticity in $\mathbf{2c}^{2+}$ is much larger than that in the reference monocation [4-(*R*)-$C_2H_5CH(CH_3)O\text{-}C_6H_4]_2CPh^+BF_4^-$ [$\lambda_{ext}=508$ ($\Delta\varepsilon=-1.3$), 411 (-0.83), 270 nm (-1.4)],[15a] which can be explained by the effective amplification of CD signals through exciton coupling of the two cationic chromophores in the preferred

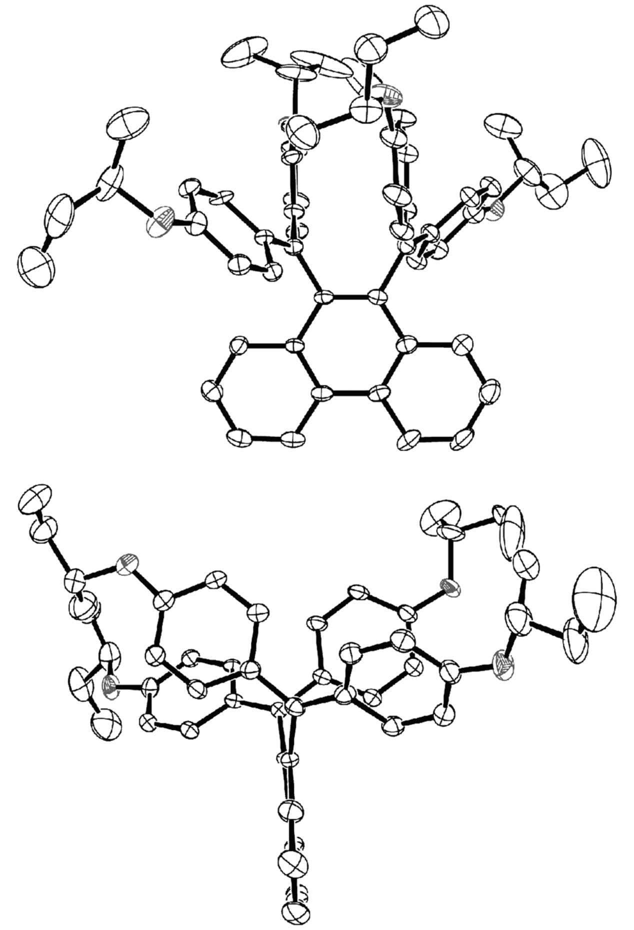


Figure 3. Molecular structure of dication $\mathbf{2c}^{2+}$ in the $SbCl_6^-$ salt determined by X-ray analysis at 153 K. All of the molecules in the crystal have the same configuration of (*P*)-helicity in terms of the twisting around $C^{9(10)}$–C^{+} bonds. Thermal ellipsoids are shown at the 50% probability level.

(*P*)-diastereomer. This is also the case for $\mathbf{2d}^{2+}$ having (*R*)-$C_6H_{13}CH(CH_3)O$ chiral auxiliaries on the aryl group [$\lambda_{ext}=589$ ($\Delta\varepsilon=-18$), 519 nm (+15) in CH_2Cl_2].

Strong CD signaling in $\mathbf{2c}^{2+}$ and $\mathbf{2d}^{2+}$ is advantageous for their use as an electrochiroptical material, because an electrochemical input can be transduced into two kinds of outputs, namely, UV/Vis and CD spectral changes. Thus, upon electrochemical oxidation of **1c** to $\mathbf{2c}^{2+}$, both UV/Vis and CD spectra changed drastically, as shown in Figure 4. The presence of several isosbestic points indicates a clean conversion between **1c** and $\mathbf{2c}^{2+}$ as well as a negligible steady-state concentration of the intermediary cation radical species. A two-way-output response was similarly observed in the case of $\mathbf{1d}/\mathbf{2d}^{2+}$ (Figure S5 in the Supporting Information). The observation validates our molecular design concept for constructing novel electrochiroptical systems[16] based on Ar_4DMPs by attaching chiral auxiliaries on the aryl groups.

Through overlap of the two cationic chromophores, the electrostatic destabilization of $\mathbf{2}^{2+}$ can be reduced by π–π interaction,[24] which is more important when the salt is dissolved in a less-polar solvent without enough stabilization by solvation.[25] Thus, the UV/Vis and/or CD spectra for some helical dicationic dyes often exhibit spectra with interesting solvent-dependent feature.[15a,16i] This falls true for the case of the present dications $\mathbf{2}^{2+}$. The solvatochromic behavior can be demonstrated more easily by using $\mathbf{2b}^{2+}$ with long alkyl chains due to their higher solubility in a variety of solvents including less-polar ones, such as benzene. As shown in Table 1 and Figure S5 in the Supporting Information, the strongest absorption band of $\mathbf{2b}^{2+}$ in MeCN appeared at λ = 504 nm, whereas when recorded in benzene, it is at 523 nm. Although the shift is not so spectacular, continuous changes were observed in THF, CH_2Cl_2, and $CHCl_3$ with intermediate polarity. Such solvent dependency is likely originated from the stacking geometry allowing π–π

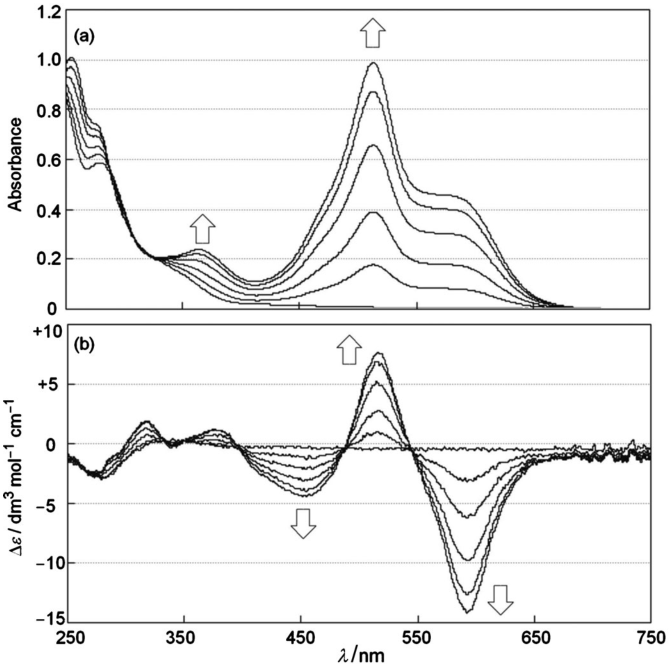


Figure 4. Changes in a) UV/Vis and b) CD spectra upon constant current (27 μA) electrolysis of **1c** (3.5 mL, 1.8×10^{-5} M) in CH_2Cl_2 containing Bu_4NBF_4 (0.05 M) as a supporting electrolyte (every 5 min).

Table 1. Solvent-dependent UV/Vis spectra[a] of $[SbCl_6^-]_2$ salts of $\mathbf{2b}^{2+}$ and $\mathbf{2d}^{2+}$.

Solvent	Dielectric constant	λ [nm] (log ε) $\mathbf{2b}^{2+}$	$\mathbf{2d}^{2+}$
MeCN	37.5	504 (4.92)	508 (4.94)
		560 (sh; 4.60)	565 (sh; 4.62)
CH_2Cl_2	9.1	517 (4.93)	518 (4.96)
		575 (sh; 4.62)	580 (sh; 4.62)
THF	7.6	513 (4.86)	514 (4.92)
		567 (sh; 4.62)	565 (sh; 4.62)
$CHCl_3$	4.9	519 (4.93)	520 (4.98)
		573 (sh; 4.63)	580 (sh; 4.59)
benzene	2.3	523 (4.83)	523 (4.91)
		572 (sh; 4.58)	576 (sh; 4.59)

[a] Data of absorption maxima (λ_{max} and log ε) and shoulders for the first band.

interaction between two cationic chromophores, because the Davydov splitting of the band is evident in all cases. Similar solvatochromism was observed for **2d**$^{2+}$ with chiral auxiliaries, in which not only UV/Vis, but also CD spectra change according to the solvent polarity (Tables 1, 2, and Figure 5).

Table 2. Solvent-dependent CD spectra[a] of **2d**$^{2+}$[SbCl$_6^-$]$_2$ in various solvents.

Solvent	Dielectric constant	λ_{ext} [nm] ($\Delta\varepsilon$)
MeCN	37.5	581 (−27), 508 (+18)
CH_2Cl_2	9.1	589 (−18), 519 (+15)
THF	7.6	586 (−16), 514 (+13)
$CHCl_3$	4.9	589 (−14), 520 (+11)
benzene	2.3	587 (−6), 527 (+8)

[a] Data of extrema (λ_{ext} and $\Delta\varepsilon$) for the first couplet.

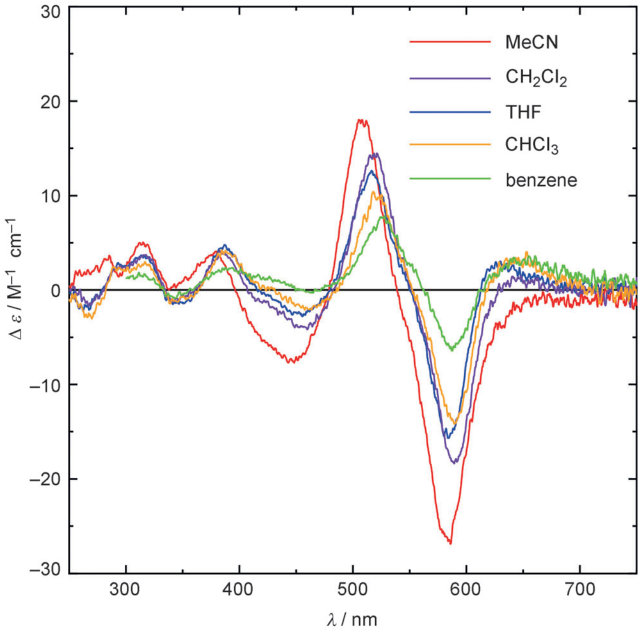


Figure 5. CD spectra of **2d**$^{2+}$[SbCl$_6^-$]$_2$ salt recorded in various solvents.

The shift of λ_{ext} in CD spectra simply corresponds to the different absorption maximum in each solvent. The dependence of CD amplitude, as was verified by the *A* value for the first couplet, is more interesting, because the value in MeCN (−45) is three times as large as that in benzene (−14), which suggests higher diastereomeric excess[26] in polar solvents with keeping preference for the (*P*)-helicity. The longer alkyl group in the chiral auxiliary in **2d**$^{2+}$ may play an important role to realize chirosolvatochromism by solvophobic effects, because *sec*-butyl derivative **2c**$^{2+}$ does not exhibit such drastic and polarity-dependent change in the *A* value.[27]

Conclusion

The present work demonstrates that the molecular framework of Ar$_4$DMP **1** could be used as a unique platform for constructing a new series of molecular-response systems. The effective interconversion between the stabilized quinodimethanes **1** and dicationic dyes **2**$^{2+}$ upon electron transfer is the key feature for establishing these new electrochromic systems to which the helical molecular framework in both redox states adds chiroptical properties. The mobile helicity in dications **2**$^{2+}$ with a π–π stacking geometry can be biased to prefer one handedness by the transmission of point chirality on the aryl groups. Due to the solvent dependency of the association of triarylmethylium units, as well as solvophobic effects, dication **2d**$^{2+}$ exhibits solvato- and chirosolvatochromic behavior, latter of which can be detected by both UV/Vis and CD spectroscopy, and thus **1d**/**2d**$^{2+}$ may present a new multi-input/multi-output response system.

Acknowledgements

This work was performed under the Cooperative Research Program of "Network Joint Research Center for Materials and Devices". The Grant-in-Aid for Scientific Research on Innovative Areas "Organic Synthesis based on Reaction Integration. Development of New Methods and Creation of New Substances" (No. 2105) is gratefully acknowledged. We thank Prof. Tamotsu Inabe (Department of Chemistry, Faculty of Science, Hokkaido University) for the use of facilities to analyze the X-ray structures. Elemental analyses were done at the Center for Instrumental Analysis of Hokkaido University. Mass spectra were measured by Dr. Eri Fukushi at the GC-MS & NMR Laboratory (Faculty of Agriculture, Hokkaido University).

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[21] Diastereomers of **2c**$^{2+}$ and **2d**$^{2+}$cannot be separated due to a rapid inversion of their helical sense by rotation around $C^{9(10)}-C^+$ bonds, showing that configuration of **2a**$^{2+}$ and **2b**$^{2+}$ is also unstable.

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[26] Additional factor for rationalizing the change in *A* values would be the solvent-dependent alternation in geometry, because the efficiency of exciton coupling is angle dependent.

[27] The *A* values of **2c**$^{2+}$[$SbCl_6^-$]$_2$ measured in several solvents are as follows: -22 in MeCN, -35 in CH_2Cl_2, and -29 in $CHCl_3$. The value in benzene cannot be determined due to low solubility of the salt.

Received: August 31, 2012

Please note: Minor changes have been made to this manuscript since its publication in *Chemistry—A European Journal* Early View. The Editor.