Chiral Organic Radical Cation and Dication. A Reversible Chiroptical Redox Switch Based on Stepwise Transformation of Optically Active Tetrakis(*p*-alkoxyphenyl)ethylenes to Radical Cations and Dications

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Optically active tetrakis(*p*-alkoxyphenyl)ethylenes were found to function as reversible chiroptical switches upon redox transformations. Successive one-electron oxidations of chirally modified tetraarylethylene to the corresponding radical cation and then to the dication led to dramatic changes in the electronic absorption and circular dichroism (CD) spectra. The neutral species showed no color or CD in the visible region, while the radical ion was blue in color and exhibited a weak Cotton effect, with the dication green and giving an intense Cotton effect and a sign opposite that observed for the radical cation, at a longer wavelength. Molecular orbital calculations and X-ray crystallographic studies clearly indicate that the olefinic C═C bond is significantly twisted in the dication to minimize the electrostatic and steric repulsions. By lowering the temperature of the dication, the twist around the double bond is more firmly fixed in either *P* or *M* chirality to give a stronger Cotton effect and a larger anisotropy (*g*) factor. Since the spectral changes are completely reversible and reproducible for multiple redox cycles, this chiral redox system can be used in novel redox-driven chiroptical applications, such as molecular switches and memory devices, in which the information is written/read chiroptically in the ternary mode, giving zero CD signal in the neutral form, positive CD for the radical cation, and negative CD for the dication at a given wavelength.

Introduction

Chiroptical molecular devices for molecular switches and data storage systems have recently attracted much attention.[1−3] For these purposes, a variety of photochromic[1,4,5] and electochromic[6−8] molecules, which show significant spectral changes upon photo- and electrochemical transformations, have been proposed. Chiroptical molecular redox switches require thermal stability and photo/electrochemical sensitivity and reversibility. Apart from the chiroptical property switching upon redox reaction of binaphthyl boron dipyrromethane,[6] cyclohexanediol bispyrene ester,[7] and dihydro[5]helicene[8] reported recently, practically no systematic study has hitherto been done to directly relate the stereochemical and electronic structural changes with the resulting chiroptical properties. Hence, it is highly desirable to elucidate the relationship between structure and its chiroptical consequences to develop a new strategy for systematically modulating the chiroptical properties of molecular switches. In the present study, we have chosen a series of chirally modified tetraarylethylenes as redox-sensitive substrates for systematically elucidating the structure−chiroptical property relationship, and also as candidates for redox-driven chiroptical switches.

It is likely that the through-space interaction between a pair of vicinal aromatic rings in di- and tetraarylethylenes is responsible for the lowered oxidation potentials and the enhanced electron-transfer reactivity.[9] Consequently, the ionization potentials of (*Z*)-stilbene derivatives are much lower than those of the corresponding (*E*)-stilbenes.[10] Similarly, 2,3-diarylbicyclo[2.2.2]oct-2-enes, possessing a fixed (*Z*)-stilbene skeleton, consistently afford relatively low oxidation potentials of 0.98−1.45 V (vs SCE) and are readily oxidized to radical cations in quantitative yield.[11] Tetraarylethylenes are of particular interest, possessing mutually interacting aromatic and olefinic moieties as electron reservoirs in a single molecule. As a consequence of the low oxidation potentials, most tetraarylethylenes undergo a variety of chemical transformations such as reduction, oxidation, photocyclization, halogenation, and oxygenation,[12,13] precise control of which is, in general, fairly difficult. In contrast, tetraanisylethylene exhibits a more controllable oxidation behavior, which allows us to successively oxidize it to the radical cation and then to the dication by choosing the appropriate oxidant. As a result, one can isolate two oxidized species, i.e., the radical cation and dication, which are reasonably stable and suited for conventional analysis by X-ray crystallography.[14] By replacing all or some of the methoxy groups of tetraanisylethylene with chiral alkoxyl groups, a reversible chiral redox molecular system is obtained without seriously altering the original spectral and redox properties as well as the reactivity and stability.

The exciton chirality method is a versatile spectroscopic tool for elucidating the absolute configuration and conformation of chiral organic compounds.[15] It is well documented that most chirally modified benzenes exhibit only week Cotton effect peaks of low molar circular dichroism (CD) intensities ($\Delta\epsilon$) on the order of 10^{-2}.[16] This is also the case with aromatic radical cations; we have recently shown that the radical cations of simple chiral benzene derivatives give only very weak CD intensities.[17] As the amplitude of the exciton couplet (*A*) is proportional to the extinction coefficient (ϵ) and inversely proportional to the square of the distance between the coupling chromophores, the use of chiral stilbene and tetraarylethylene

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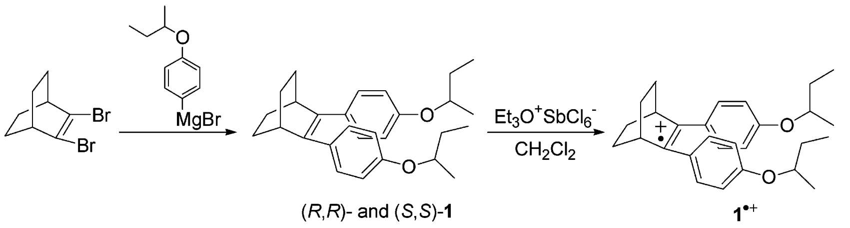
SCHEME 1: Syntheses of Chiral 2,3-Diarylbicyclo[2.2.2]oct-2-ene 1 and Radical Cation $1^{\bullet+}$



derivatives, possessing two or more chromophores in a single molecule, is advantageous for sensitive detection of the chiroptical signals of radical cationic and dicationic species.

Taking into account all the foregoing observations and discussion, we have employed a series of chirally modified tetraarylethylenes (**2**−**4**) and stilbene **1** (as a reference) as sources of chiral radical cations and dications and examined their chiroptical properties for the first time. These tetraarylethylenes are readily oxidized successively to the corresponding radical cations and dications in a controlled fashion by choosing appropriate oxidants or applying a controlled electrostatic potential. Since the chiral radical cations and dications produced are stable and the redox processes reversible if these chiral species display completely different UV−vis and particularly CD spectra, this system is expected to function as a redox-driven chiroelectrochemical ternary switch.

Results and Discussion

Redox and Chiroptical Properties of Stilbenoid Donor 1. We first examined the redox and chiroptical behavior of chiral stilbenoid donor **1**, since the methoxy analogue 2,3-di-*p*-anisylbicyclo[2.2.2]oct-2-ene is known to give a stable radical cation upon mild oxidation. Chiral stilbene **1** was synthesized by the Grignard coupling of chiral (*R*)- or (*S*)-4-(2-methylpropyloxy)phenylmagnesium bromide with 2,3-dibromobicyclooctene (Scheme 1).

The UV−vis and CD spectra of the neutral donor were recorded at 25 °C for a 10^{-5} M dichloromethane solution. As can be seen from Figure 1, the antipodal (*R*,*R*)- and (*S*,*S*)-**1** afforded almost mirror-imaged CD spectra, exhibiting first negative/positive and second positive/negative Cotton effects, which coincide in wavelength with the ^1L_b and ^1L_a bands, respectively. A weak molar CD ($\Delta\epsilon = \pm 0.05$) for the ^1L_b transition is typical of chiral benzene derivatives[15,16] (Table 1), with no excitation couplets observed for either the ^1L_b or ^1L_a bands of donor **1**, most likely due to the parallel orientation of the two transition moments of the aromatic rings.

Stilbenoid **1** was readily oxidized by using a variety of oxidants. Electrochemical oxidation of donor **1** in anhydrous dichloromethane occurred reversibly at a potential of $E^0_{OX} =$

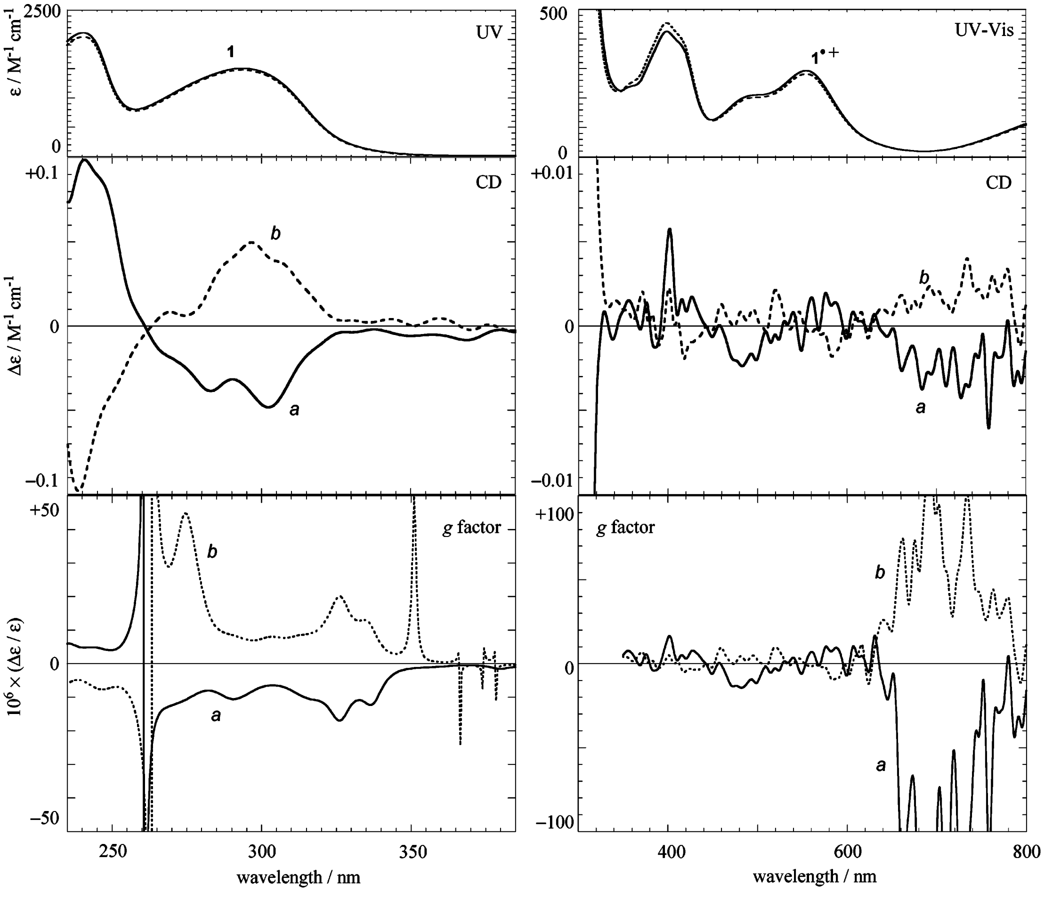


Figure 1. (Left) UV and CD spectra and anisotropy (*g*) factors of neutral (a) (*R*,*R*)-**1** and (b) (*S*,*S*)-**1** in dichloromethane at 25 °C. (Right) UV−vis and CD spectra and *g* factors of radical cations (a) (*R*,*R*)-$1^{\bullet+}$ and (b) (*S*,*S*)-$1^{\bullet+}$ in dichloromethane at 25 °C, obtained by treating **1** (10^{-4} M) with 1.5 equiv of $Et_3O^+SbCl_6^-$.

TABLE 1: Chiroptical Properties of the Chiral Radical Cations and Dications of 1−4[a]

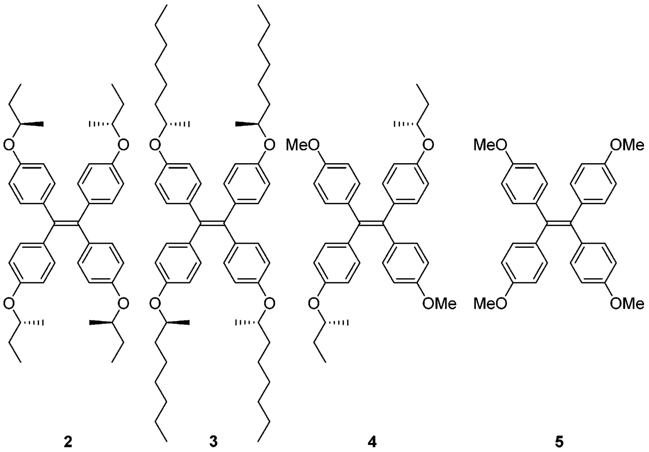
compd	config	oxidant	species[b]	λ_{max}/nm ($\log \epsilon$)[c]	λ_{ext}/nm ($\Delta\epsilon$)[d]	10^{-6} g[e]
1	*R*,*R*		N	294 (4.15)	302 (−0.048)	−9.7
				241 (4.31)	241 (+0.099)	+4.8
		$Et_3O^+SbCl_6^-$	RC	>900[f]	700 (−0.002)[f]	−100[f]
				554 (3.46)	560 (+0.002)	+7.0
				485 (3.30)[g]	483 (−0.002)	−1.4
				398 (3.56)	402 (+0.006)	+1.6
	S,*S*		N	293 (4.14)	297 (+0.050)	+6.9
				241 (4.28)	239 (−0.098)	+4.9
		$Et_3O^+SbCl_6^-$	RC	>900[f]	700 (+0.002)[f]	+90[f]
				554 (3.45)	583 (−0.002)	−0.9
				485 (3.29)[g]	482 (+0.001)	+4.3
				398 (3.66)	418 (−0.002)	−5.1
2	*R*,*R*,*R*,*R*		N	327 (4.29)	337 (+0.315)	+15
					297 (−0.612)	−64
				261 (4.55)	263 (+0.852)	+25
		$Et_3O^+SbCl_6^-$	RC	>900[f]	700 (+0.092)[f]	+5.5[f]
				582 (4.17)	582 (+0.183)	+12
				360 (4.35)	371 (+0.290)	+14
				271 (4.52)		
		$SbCl_5$	DC	660 (4.50)[g]	646 (−1.872)	+64
				577 (4.65)	592 (−0.923)	−22
				471 (4.40)	470 (+0.735)	+29
				422 (4.43)	412 (−0.619)	−25
3	*S*,*S*,*S*,*S*		N	326 (4.19)	333 (−0.506)	−51
				300 (4.16)[g]	300 (+1.706)	+118
				262 (4.51)	265 (−1.541)	−75
		$Et_3O^+SbCl_6^-$	RC	>900[f]	700 (−0.245)[f]	−26[f]
				586 (3.77)	~580 (−0.047)	−7.4
				329 (4.35)	373 (−0.578)	−27
					305 (+0.683)	+56
		$SbCl_5$	DC	670 (4.01)[g]	661 (+1.341)	+112
				579 (4.24)	579 (−1.109)	−64
				475 (3.96)	471 (−1.925)	−193
				423 (3.98)	404 (+0.475)	+60
4	*R*,*R*		N	326 (4.21)	335 (+0.255)	+18
				260 (4.47)	256 (+0.547)	+20
		$Et_3O^+SbCl_6^-$	RC	>900[f]	700 (−0.013)	−2.1
				576 (4.00)	576 (+0.052)	+5.2
				352 (4.27)	349 (+0.245)	+12
				264 (4.60)		
		$SbCl_5$	DC	650[g] (4.51)	659 (−1.173)	−42
					594 (−0.305)	−9.4
				572 (4.66)	572 (+0.123)	+2.7
				465 (4.46)	460 (+0.686)	+24
				417 (4.51)	403 (−0.094)	−8.7

[a] All spectra obtained in dichloromethane at 25 °C under an Ar atmosphere. [b] Oxidation state: N, neutral; RC, radical cation; DC, dication. [c] Electronic absorption maxima λ_{max} and molar extinction coefficient ϵ in M^{-1} cm^{-1}. [d] Circular dichroism extrema λ_{ext} and molar circular dichroism $\Delta\epsilon$ in M^{-1} cm^{-1}. [e] Anisotropy factor g ($=\Delta\epsilon/\epsilon$) at λ_{ext}, unless noted otherwise. [f] Peak observed at >900 nm, and therefore, the $\Delta\epsilon$ and g values at 700 nm are reported. [g] Shoulder.

1.02 V (vs SCE). A stable magenta solution of radical cation was obtained on a preparative scale by anodic oxidation of **1** in anhydrous dichloromethane containing 0.2 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte, using a 1×1 cm^2 platinum working electrode. Alternatively, the radical cation was produced upon treatment with a mixture of chloranil and methanesulfonic acid in dichloromethane.[18] More conveniently, the dark red radical cation was obtained by mixing **1** (0.1 mM) with triethyloxonium hexachloroantimonate (1.5 equiv) in anhydrous dichloromethane at 0 °C.[19] A UV−vis analysis of the resulting solution revealed the quantitative formation of the radical cation (Figure 1). Major new bands attributable to $\mathbf{1}^{\bullet+}$ appeared at 398, 485 (sh), 554, and >900 nm. The last two bands are slightly red-shifted from those of the dianisyl analogue ($\lambda = 547$ and 880 nm) reported earlier,[11] but the general profile is consistent with the absorption characteristics of (*Z*)-stilbene radical cations.[20]

As can be seen from Figure 1, the CD spectrum of the dichloromethane solution of the dark-red radical cation $\mathbf{1}^{\bullet+}$ is very weak in intensity, yet shows appreciable mirror-imaged deviations from the baseline to the negative/positive direction for (*R*,*R*)- and (*S*,*S*)-$\mathbf{1}^{\bullet+}$ at a wavelength >700 nm with $|\Delta\epsilon| < 0.005$. The anisotropy factors ($g = \Delta\epsilon/\epsilon$), shown in Figure 1, also exhibit mirror-imaged behavior although the data are moderately scattered. The g factors for neutral donor **1** and the corresponding radical cation $\mathbf{1}^{\bullet+}$ were on the order of 10^{-5}, which is almost similar to or slightly smaller than the ordinary values obtained for the allowed transitions of simple chirally substituted arenes.[15,16] It is interesting to note that the g factor of the radical cation was twice as large as that of the corresponding neutral donor. For the radical cations, the g factor was only detectable for the d_0−d_1 band, and was almost negligible at other transition wavelengths. Although we cannot elucidate the exact reason(s) for this very weak CD intensity of radical cation $\mathbf{1}^{\bullet+}$ at present, the twist angle around the original olefinic bond would seem to be responsible at least in part. Recent studies of radical cationic bicyclo[2.2.2]oct-2-ene by EPR spectroscopy as well as by DFT calculations revealed that

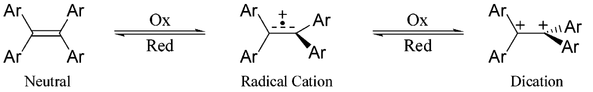
CHART 1: Chiral Tetraarylethylene Donors 2−4 and the Parent Tetraanisylethylene 5



the original double bond is twisted by 11−12°, while dimethylation at the 2,3-positions of bicyclo[2.2.2]oct-2-ene reduces the twist angle of the radical cation significantly to 6°.[21] 2,3-Diarylation of **1** may similarly reduce the twist angle, since it has been demonstrated that the amplitude of exciton coupling (A) is maximized at a projection angle of ~70°, but is reduced to almost zero if the angle is 0° or 180°.[22,23]

Oxidation of Tetraarylethylene Donors 2−4. Recently, tetraarylethylenes, such as tetraanisylethylene and tetratolylethylene, were successfully isolated as crystalline salts in neutral, radical cation, and dication forms.[14] In this study, to explore redox-active chiroptical switches, we prepared a series of chirally modified tetraarylethylenes (**2**−**4**). By the Mitsunobu coupling[24] of (S)-(+)-2-butanol or (R)-(−)-2-octanol with dihydroxybenzophenone, we synthesized the corresponding enantiopure dialkoxybenzophenones, which were subjected in turn to the McMurry coupling using a conventional low-valent titanium reagent[25] (Chart 1). This allows us, by simple modifications of the peripheral substituents, to directly compare the steric effects on the chiroptical properties in different redox states. These tetraarylethylenes **2**−**4** are expected to be readily oxidized or reduced in a stepwise manner by conventional chemical oxidants or reductants, as is the case with tetraanisyl derivative **5**.[14] Hence, we first examined the electrochemical behavior of **2**−**4** by means of cyclic voltammetry (CV) to gain quantitative information for these redox systems.

Electrochemical Oxidation of Chiral Tetraarylethylenes. Chirally modified tetraarylethylenes **2**−**4** (1 mM) were oxidized electrochemically in anhydrous dichloromethane containing 0.2 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte by using a platinum electrode. For each of **2**−**4**, a reversible cyclic voltammogram with two closely coupled one-electron oxidation waves was consistently obtained at a scan rate of 0.2 V s^{-1} with an accompanying theoretical anodic/cathodic peak current ratio (i_a/i_c) of unity, as shown in Figure 2. By calibration with ferrocene on Osteryoung square-wave voltammograms (OSWV measurements), the reversible two-step oxidation potentials (E^0_{OX}), shown in Table 2, were determined for the production of radical cations via the one-electron redox couple and of dications via the two-electron redox couples (eq 1).



(eq 1)

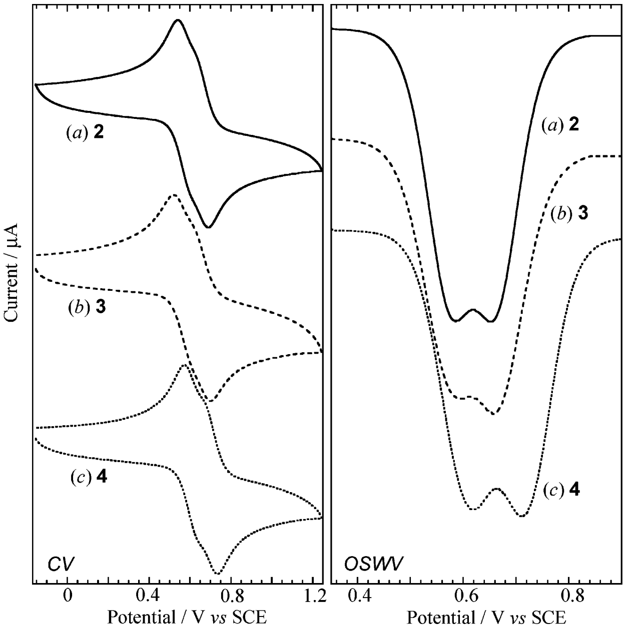


Figure 2. Cyclic voltammograms (left, scanning rate 0.2 V s^{-1}, Pt electrode) and Osteryoung square-wave voltammograms (right) of 1 mM chiral tetraarylethylenes (a) **2**, (b) **3**, and (c) **4** in dichloromethane containing 0.2 M tetrabutylammonium hexafluorophosphate as an electrolyte at 25 °C.

TABLE 2: Disproportionation Constants for Tetraarylethylene Cation Radicals (K_{disp}) Determined by Electrochemical Analysis of the Cyclic Voltammetric Data

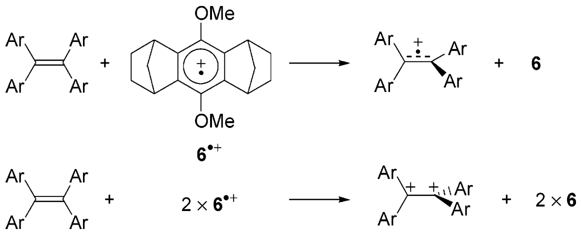
compd	solvent	E^0_{OX}(I)[a]	E^0_{OX}(II)[a]	ΔE[b]/mV	K_{disp}[c]/M^{-1}
2	CH_2Cl_2	0.83	0.90	66	7.6×10^{-2}
3	CH_2Cl_2	0.84	0.90	62	8.9×10^{-2}
4	CH_2Cl_2	0.86	0.96	96	2.4×10^{-2}
5	CH_2Cl_2	0.79	0.91	120	9.3×10^{-3} (2×10^{-3} [d])
	MeCN[e]	0.90	0.90	0	8.4×10^{-1}

[a] The first and second oxidation potentials shown in volts versus SCE, obtained by Osteryoung square-wave voltammetry. See ref 28. [b] $\Delta E = E^0_{OX}(II) - E^0_{OX}(I)$. [c] Calculated from the cyclic voltammetric data using the Nernstian expression $K_{disp} = \exp(-0.039\Delta E)$ at 25 °C. [d] Value determined by the spectroscopic method; for details, see ref 14. [e] Reference 29.

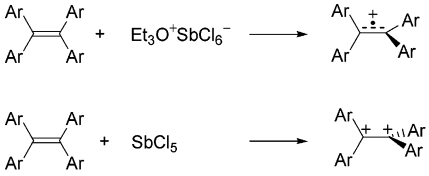
The first and second oxidation potentials of **2**−**4** were separated by only 62−96 mV (Table 2). A qualitative treatment of these two oxidation potentials gave disproportionation constants of the relevant radical cations, $K_{disp} = [\mathbf{R}^{2+}][\mathbf{R}]/[\mathbf{R}^{\bullet+}]^2$ (**R** = **2**, **3**, or **4**), shown in Table 2. The small K_{disp} values of 0.02−0.09 M^{-1} clearly indicate that the radical cation $\mathbf{R}^{\bullet+}$ is the dominant species in dichloromethane solutions of $\mathbf{R}^{\bullet+}$. The difference between the two oxidation potentials (ΔE^0_{OX}) decreases as the size of the (chiral) alkyl substituents becomes larger: from methyl (**5**, $\Delta E = 0.12$ V) to methyl/1-methylpropyl (**4**, $\Delta E = 0.10$ V) to 1-methylpropyl (**2**, $\Delta E = 0.07$ V), and then to 1-methylheptyl (**3**, $\Delta E = 0.06$V). This may be attributed to the increased hydrophobicity caused by elongating the alkyl chains, which disturbs in particular the first oxidation step, while the E^0_{OX}(II) values are comparable for most tetraarylethylenes except the unsymmetrically substituted **4**.

Chemical Oxidation of 2−4 to Radical Cations and Dications. Possessing a reduction potential of 1.11 V, the robust radical cation salt of methanoanthracene derivative $\mathbf{6}^{\bullet+}$ (Scheme 2) functions as a selective organic oxidant.[26] The treatment of tetraarylethylene **2** with $\mathbf{6}^{\bullet+}$ under an argon atmosphere in anhydrous dichloromethane at 25 °C immediately yielded a bright blue solution; the UV−vis spectral profile is very close

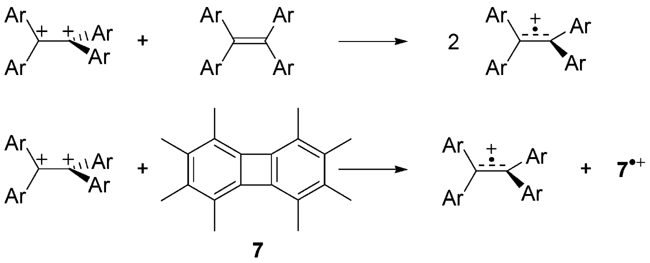
SCHEME 2: Chemical Oxidation of Tetraarylethylenes to Radical Cations and Dications by Electron Exchange with Methanoanthrancene Radical Cation



SCHEME 3: Oxidation of Chiral Tetraarylethylenes with Antimony Oxidants



SCHEME 4: Electron Transfer from Tetraarylethylene Dications to Neutral Tetraarylethylene and Biphenylene Donors



to that of tetraanisylethylene radical cation ($\mathbf{5}^{\bullet+}$), showing the characteristic absorption at 580 nm. A careful spectral analysis of the blue solution indicates the essentially quantitative formation of radical cation $\mathbf{2}^{\bullet+}$. Treatment of **2** with 2 equiv of $\mathbf{6}^{\bullet+}$ at 25 °C immediately gave a dark green solution of dication $\mathbf{2}^{2+}$ in a quantitative yield. Thus, the radical cation $\mathbf{2}^{\bullet+}$ and dication $\mathbf{2}^{2+}$ could be generated cleanly in discrete one- and two-electron oxidations by simply adjusting the amount of the oxidant.

Antimony pentachloride is a strong electron-transfer oxidant,[27] which was used in the preparation and isolation of pure tetraarylethylene dications. Thus, the treatment of **2** (1.0 mmol) with excess $SbCl_5$ (5.0 mmol) in anhydrous dichloromethane at −78 °C immediately gave a dark green solution, from which the crystalline dication salt readily precipitated in a quantitative yield upon slow addition of anhydrous ether or hexane (Scheme 3). The microcrystalline precipitate was filtered under an argon atmosphere and dried in vacuo.

Triethyloxonium hexachloroantimonate was also used as a selective oxidant to produce $\mathbf{2}^{\bullet+}$. A suspension of $Et_3O^+SbCl_6^-$ (3.0 mmol) and **2** (2.0 mmol) in dichloromethane was stirred at −10 °C for 3 h to give a dark blue solution. The UV−vis spectral analysis of the highly colored solution indicated the formation of the radical cation, showing the characteristic spectrum at 580 nm, in an essentially quantitative yield.

When a dark green solution of $\mathbf{2}^{2+}$ was mixed with an equimolar amount of neutral **2**, the color immediately changed to bright blue. UV−vis spectral analysis established the concurrent oxidation of neutral **2** and reduction of $\mathbf{2}^{2+}$, giving the radical cation $\mathbf{2}^{\bullet+}$ (Scheme 4). In the absorption spectra, a pair of isosbestic points were observed upon stepwise addition of $\mathbf{2}^{2+}$ to a solution of **2**. If dication $\mathbf{2}^{2+}$ was treated with an equimolar amount of electron-rich octamethylbiphenylene (**7**) ($E^0_{OX} = 0.80$ V),[30] the solution again turned dark blue, displaying a pair of major absorption maxima at 600 and >800 nm. Subtraction of the spectrum of $\mathbf{2}^{\bullet+}$ from the resulting spectra afforded well-resolved absorption bands at 602 and 550(sh) nm, indicating the quantitative formation of octamethylbiphenylene radical cation ($\mathbf{7}^{\bullet+}$). When a solution of dication $\mathbf{2}^{2+}$ was treated with an excess amount of zinc dust, the solution immediately turned colorless, and neutral donor **2** was recovered as indicated by the UV−vis analysis.

X-ray Crystallography and Molecular Orbital Studies on Conformational Changes upon Stepwise Oxidation. Tetraanisylethylenes are known to undergo considerable conformational changes around the ethylenic double bond upon successive oxidations from the neutral state to radical cation and then to the dication. AM1 calculations nicely simulated the conformational differences of neutral, radical cationic, and dicationic **2**. The calculated central C−C bond length is elongated upon stepwise oxidations by more than 10% (overall) from 1.354 Å for **2** to 1.430 Å for $\mathbf{2}^{\bullet+}$ and then to 1.493 Å for $\mathbf{2}^{2+}$, and the dihedral, or twist, angle around the original ethylenic bond is increased from 4° to 35° and then to 79° for **2**, $\mathbf{2}^{\bullet+}$, and $\mathbf{2}^{2+}$, respectively. DFT calculations at the B3LYP/6-31G(d) level for AM1-optimized structures also afforded similarly optimized structures, which are illustrated in Figure 3. The central C−C bond length and the twist angle shifted in a similar manner, from 1.370 Å and 13.7° for **2** to 1.421 Å and 27.9° for $\mathbf{2}^{\bullet+}$ and then to 1.503 Å and 57.5° for $\mathbf{2}^{2+}$, as summarized in Table 3. The calculated twist angles are in good agreement with those determined by X-ray crystallography, i.e., 5°, 31°, and 62° for **5**, $\mathbf{5}^{\bullet+}$, and $\mathbf{5}^{2+}$, respectively.[14] A more dramatic twisting of the ethylenic double bond has been proposed to occur in the unsubstituted ethylene dication[31] and radical cation.[32] Thus, the theoretical calculations predict a bisected structure for the ethylene dication with a twist angle of up to 90° and a C−C bond length of up to 1.46 Å. The sudden conformational change from the planar neural form to the bisected radical cation and dication forms may be interpreted in terms of the decreased bond order and Coulombic repulsion, particularly in dications, both of which are directly reflected in their structure in the absence of conjugating (aromatic) chromophore(s). Such a twist has also been observed with some push−pull substituted ethylenes, and is attributed to their highly polar zwitterionic natures.[33]

Crystals of the neutral donor **2** and of its dication salt $\mathbf{2}^{2+}(SbCl_6^-)_2$were obtained, but no single crystal suitable for X-ray crystallography was obtained for the radical cation $\mathbf{2}^{\bullet+}$, despite extensive efforts. The dication crystals were prepared by the slow diffusion of anhydrous hexane into a dichloromethane solution of the dication salt at −20 °C. The X-ray structures are shown in Figure 4 (also see the Supporting Information for details). The neutral donor **2** shows the average dihedral angle of 9° with a central C−C bond length of 1.35 Å. These values are in good agreement with those reported for the corresponding anisyl derivative **5**, i.e., 5° and 1.35 Å.[14] The dihedral angle and C−C bond length are dramatically increased in dication $\mathbf{2}^{2+}$ up to 83° and 1.53 Å.

Although the quality of the crystals of the dication $\mathbf{2}^{2+}(SbCl_6^-)_2$[34] was not accurate enough to discuss the detailed structural changes, the X-ray analysis clearly revealed that the (*R*,*R*,*R*,*R*)-substituents in $\mathbf{2}^{2+}$ induce *S* (*M*) chirality around the central C−C bond. This assignment is consistent with that elucidated by the CD exciton chirality method applied to the

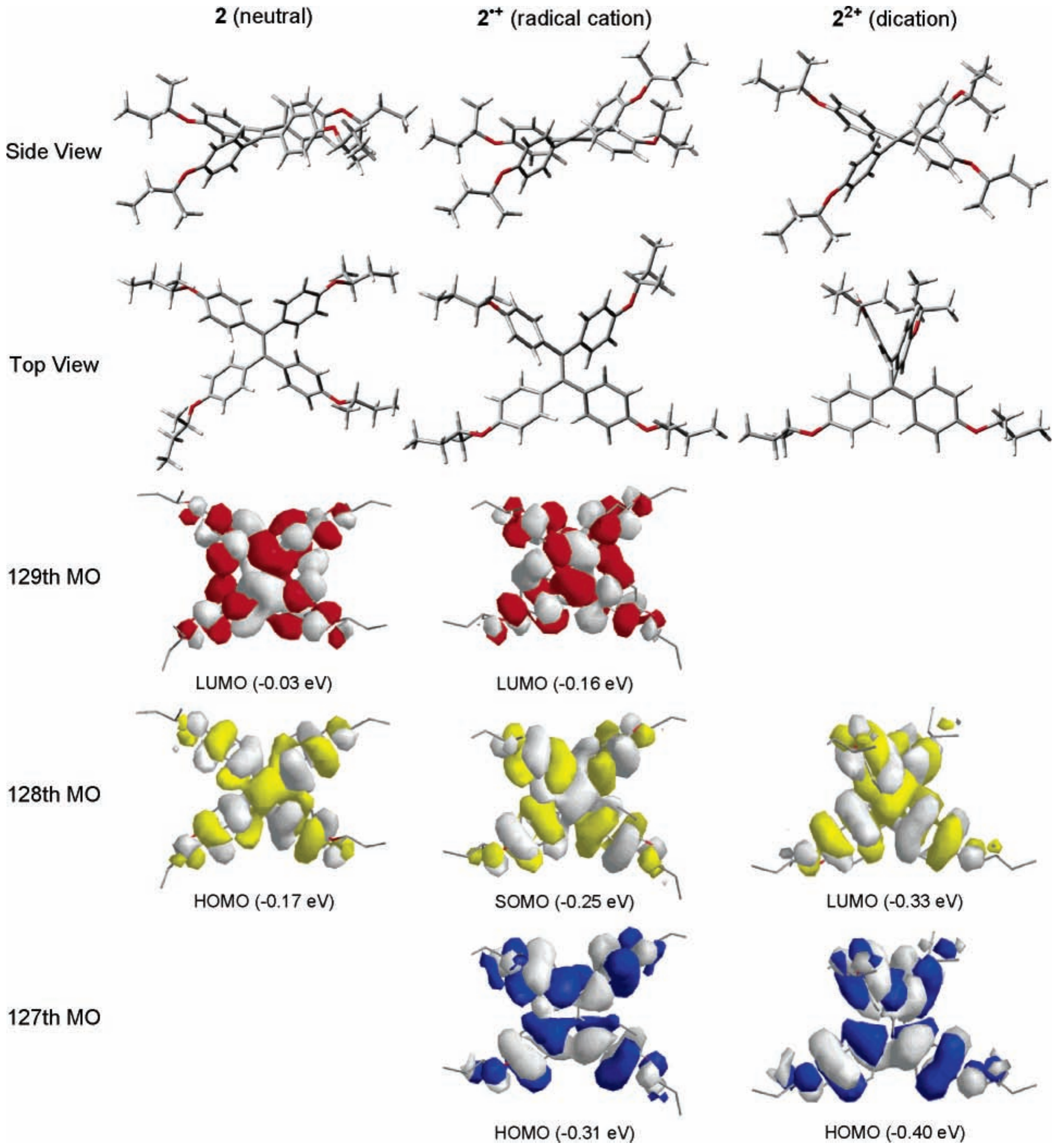


Figure 3. B3LYP/6-31G(d)-optimized structures of neutral, radical cationic, and dicationic forms of tetraarylethylenes **2** and relevant molecular orbitals.

TABLE 3: Structural Features, Chiroptical Responses and Color of Neutral, Radical Cationic and Dicationic Tetraarylethylenes 2 and 3

oxidation state	dihedral angle[a]/deg	C−C bond length[a]/Å	sign of the Cotton effect[b]		color (λ_{max}/nm)
			2	3	
neutral	9 (14, 4)	1.35 (1.37, 1.35)	0	0	colorless (∼330)
radical cation	− (28, 35)	− (1.42, 1.43)	+	−	blue (∼580)
dication	83 (58, 79)	1.53 (1.50, 1.49)	−	+	green (∼660)

[a] Values obtained by X-ray crystallography; B3LYP/6-31G(d)- and AM1-calculated values in parentheses. [b] At 640 nm.

absorption around 700 nm for dication $\mathbf{2}^{2+}$, as discussed in the following section.

CD Spectra of Neutral, Radical Cationic, and Dicationic Tetraarylethylenes with Chiral Auxiliaries. Neutral **2**, possessing (*S*)-(+)-2-methylpropyl auxiliaries, showed the first positive, second negative, and third positive Cotton effect peaks, as shown in Figure 5 and Table 1. By using Lorenzian deconvolution, the observed CD spectrum of **2** was analyzed as a sum of two coupled signals of $A_1 = +0.65$ at 312 nm and $A_2 = -1.80$ at 264 nm, assignable to the ^1L_b and ^1L_a transitions. As can been seen from Figure 3, the four aromatic rings of **2** are positioned like propeller blades attached to the central C=

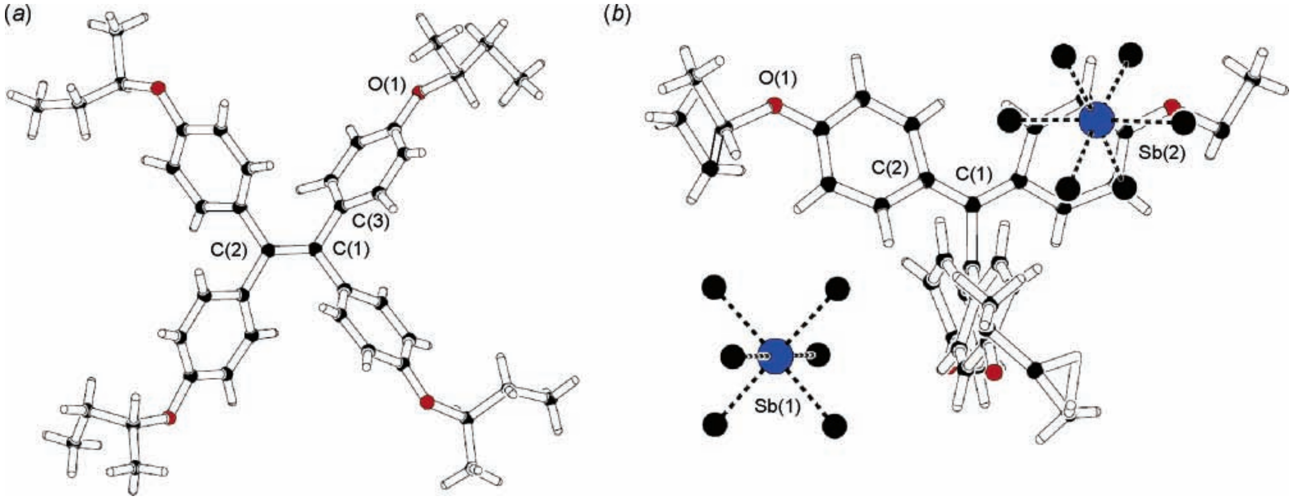


Figure 4. PLUTO drawings of (a) the neutral donor **2** and (b) the corresponding dication $\mathbf{2}^{2+}(SbCl_6^-)_2$. Some atoms are omitted for clarity.

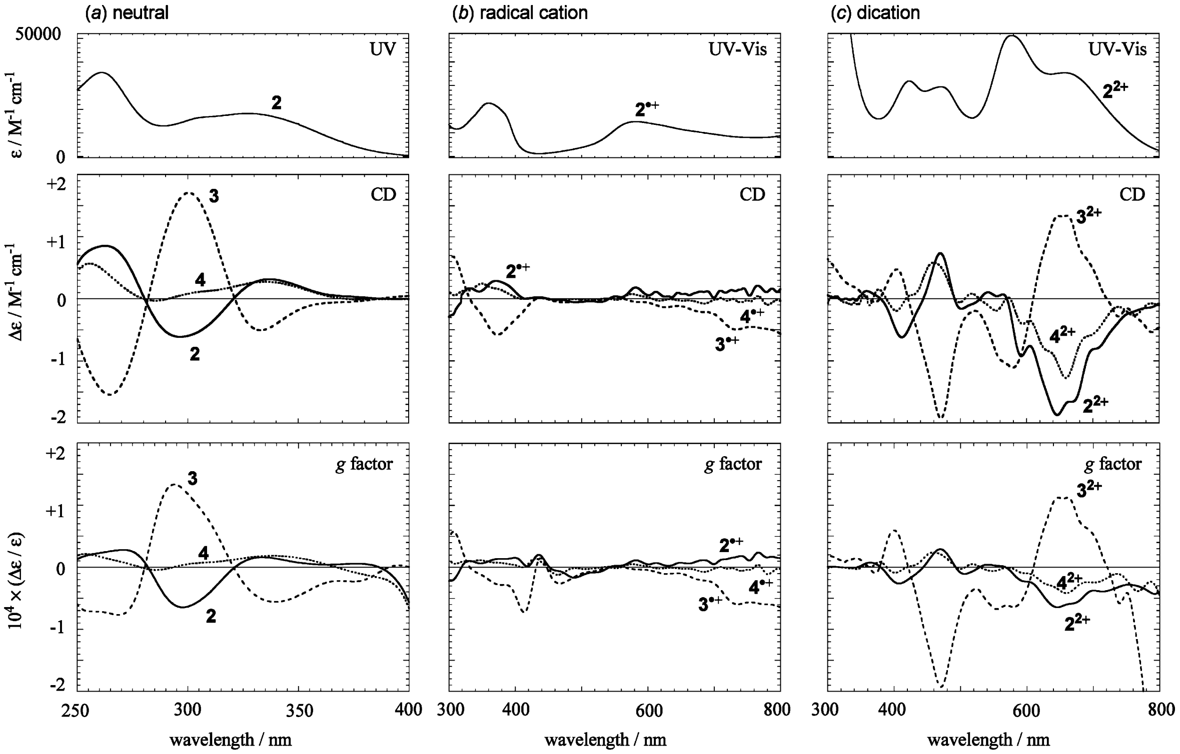


Figure 5. UV−vis and CD spectra and anisotropy (*g*) factors of (a) neutral, (b) radical cation, and (c) dication forms of tetraarylethylenes **2**, **3**, and **4** (10^{-5} M) in dichloromethane at 25 °C. Note that the UV−vis spectra of **2**−**4** gave essentially the same shape; only those of **2** are presented here for clarity.

C bond with a twist around the vinylic bond. In such a conformation, each transition of the aromatic chromophores is likely to couple with each other;[15,22] this is also the case with **3**. Possessing larger antipodal auxiliaries, neutral **3** displayed stronger signals of opposite signs ($A_1 = -1.44$ at 291 nm, $A_2 = +3.70$ at 267 nm). Interestingly, when two chiral groups of **2** in the *trans* positions are replaced by achiral methyls, the resulting hemichiral **4** never shows exciton coupling,[35] although the UV−vis spectra of **2**−**5** are quite similar to each other. This may indicate that the geminal aryls are mostly responsible for the exciton coupling. This tentative conclusion is also compatible with the fact that stilbenoid **1** does not show any exciton coupling.

The spectral presentation of the anisotropy (*g*) factor at each wavelength, shown in Figure 5 (bottom), resembles in shape the related CD spectrum. The observed *g* factors of neutral donors **2**−**4** are in the range of 10^{-5}−10^{-4}, which are comparable to that of stilbenoid **1**. These small *g* factors are typical of the allowed π−π* transitions.[15,16] It is noted however that the longer chiral substituents in **3** give larger $\Delta\epsilon$ and *g* factor values, while the *trans*-disubstitution in **4** greatly reduces these values, presumably due to the lack of exciton coupling.

Chiroptical Properties of Radical Cations $\mathbf{2}^{\bullet+}$−$\mathbf{4}^{\bullet+}$. Oxidations of **2**−**4** were performed by using triethyloxonium hexachloroantimonate.[19] The UV−vis spectra of the resulting radical cations $\mathbf{2}^{\bullet+}$−$\mathbf{4}^{\bullet+}$ were essentially superimposable, though with slight differences in absorption coefficient, as exemplified in Figure 5, for compound **2**. The spectral changes upon successive oxidations to radical cation and then to the dication were in excellent agreement with those reported for tetraanisylethylene (**5**).[14] Although the radical cations $\mathbf{2}^{\bullet+}$−$\mathbf{4}^{\bullet+}$ could be isolated as crystalline salts, we were unable to obtain good single crystals suitable for X-ray crystallographic analysis (vide supra). CD spectra of the radical cations were then measured by redissolving the isolated salts into freshly prepared anhydrous dichloromethane under argon at 25 °C. Essentially no disproportionation was observed under the conditions employed (vide supra). Only weak, but appreciable, CD spectra were obtained for radical cations of **2**−**4**, the CD intensities of which were much smaller than those of the neutral species (Figure 5). However, antipodal $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ gave the opposite CD signs at ca. 350 and >700 nm, indicating that these faint signals are not artificial or noise. Although radical cations $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$ appear to show a weak exciton-coupled pattern at ca. 250 nm, an overlap with the absorption of the counteranion prevents further analysis.

The neutral and oxidized species are considered to give the same sign in the CD spectrum, since the sign of the Cotton effect of the ^1L_b band of the neutral species always coincides with that of the d_0−d_1 transition. For instance, both of the first absorption bands of neutral **2** (∼330 nm) and radical cation $\mathbf{2}^{\bullet+}$ (>900 nm) gave a positive Cotton effect, and this may indicate that the transition moment of the arene ring(s) is essentially oriented in the same direction, as indicated by molecular orbital calculations shown in Figure 3. Thus, the shapes of frontier molecular orbitals (127th−129th) are essentially unchanged between the neutral and radical cationic species.

As can be seen from Figure 5 and Table 1, the anisotropy (*g*) factors observed for tetraarylethylene radical cations $\mathbf{2}^{\bullet+}$−$\mathbf{4}^{\bullet+}$ are significantly smaller than those exhibited by the corresponding neutral dicationic species. The largest *g* factors are obtained mostly for the lowest energy transition of $\mathbf{2}^{\bullet+}$−$\mathbf{4}^{\bullet+}$, as is the case with the stilbenoid $\mathbf{1}^{\bullet+}$. Interestingly, the *g* factor is almost negligible for the other d−d transitions, probably due to the random orientation of the relevant transition moments.

Chiroptical Properties of Dications $\mathbf{2}^{2+}$−$\mathbf{4}^{2+}$. Further oxidation of radical cations $\mathbf{2}^{\bullet+}$−$\mathbf{4}^{\bullet+}$ or direct two-electron oxidation of neutral **2**−**4** with an excess amount of (stronger) oxidant affords dicationic species $\mathbf{2}^{2+}$−$\mathbf{4}^{2+}$. Such dications were isolated as hexachloroantimonate salts by simply filtering the precipitates formed upon addition of dry hexane or ether to the solution under an argon atmosphere. The obtained salts of dications $\mathbf{2}^{2+}$−$\mathbf{4}^{2+}$ were sufficiently pure (>95%), as determined by iodometry.[14] Dichloromethane solutions of the isolated salts exhibited essentially the same CD spectra as those of the dications generated in situ in dichloromethane using a slight excess of antimony pentachloride. In sharp contrast to the relevant neutral and in particular radical cationic species, dications $\mathbf{2}^{2+}$−$\mathbf{4}^{2+}$ show much stronger Cotton effects. In all cases, the first Cotton effect, observed at ∼650 nm, gives a fairly strong CD signal with a sign opposite that observed for the first Cotton effect peak (^1L_b band) of the corresponding neutral species. The CD spectra of $\mathbf{2}^{2+}$−$\mathbf{4}^{2+}$ show an inverted sign at wavelengths around 500−600 nm to give opposite Cotton effect peaks at ∼480 nm. The opposite first Cotton effect signs observed for neutral versus dicationic species can be attributed simply to the twisted structure of the dications, in which the first transition moment is perpendicular to that of the neutral species. However, it is more reasonable to attribute the observed CD to the exciton coupling between the two diarylcarbenium chromophores in the bisected dication, where each moiety consists of one quinoidal and one coplanar benzene ring (see the DFT-calculated structure in Figure 3). Such an assumption is further supported by molecular orbital calculations (Figure 3), in which the dication $\mathbf{2}^{2+}$ shows an axisymmetric HOMO. The pattern of the MOs of the dication differ completely from those of the neutral and radical cationic species **2** and $\mathbf{2}^{\bullet+}$, whose HOMO or SOMO clearly shows central symmetry. The structural feature is unique to the dicationic tetraarylethylenes, differing from those of the neutral and radical cationic species, where the twist around the central double bond is much smaller and the four alkoxyphenyl groups have essentially the same degree of quinoidal character. Thus, the negative first Cotton effect of (*R*,*R*,*R*,*R*)-$\mathbf{2}^{2+}$ can be related to the left-handed twist, which is consistent with the X-ray crystallographic structure.

As was the case with the neutral and radical cationic species, the $\Delta\epsilon$ value of the dication increases with increasing bulkiness and the number of the appended chiral auxiliaries; i.e., $\Delta\epsilon(\mathbf{2}^{2+}) < \Delta\epsilon(\mathbf{3}^{2+})$ and $\Delta\epsilon(\mathbf{4}^{2+}) < \Delta\epsilon(\mathbf{2}^{2+})$. The X-ray crystallographic structure and the sign of the CD couplet of $\mathbf{2}^{2+}$ consistently indicate that (*S*,*S*,*S*,*S*)-$\mathbf{3}^{2+}$ possesses *P* chirality, while (*R*,*R*)-$\mathbf{4}^{2+}$ has *M* chirality. It is interesting to compare the CD spectrum of "hemichiral" $\mathbf{4}^{2+}$ with that of "fully" chiral $\mathbf{2}^{2+}$. Thus, the half number of chiral auxiliaries in $\mathbf{4}^{2+}$ does not immediately lead to half-reduced CD intensities but causes only slight decreases in intensity compared to that for $\mathbf{2}^{2+}$. This seems reasonable, as the four aromatic rings in $\mathbf{2}^{2+}/\mathbf{4}^{2+}$ no longer behave as independent chromophores but rather form two diarylcarbenium chromophores, the twist angle of which is governed by the chiral group introduced at the *para* position(s). Intriguingly, the CD intensity, as a measure of chiral induction, is not proportional to the number of chiral auxiliaries at the *para* position, but is more sensitive to the presence/absence (and the bulkiness) of the chiral auxiliary. In other words, the first chiral auxiliary introduced to the diarylcarbenium chromophore is more effective than the second one in inducing the chiral twist in tetraarylethylene dication.

The *g* factors of dications $\mathbf{2}^{2+}$−$\mathbf{4}^{2+}$ are roughly comparable to those observed for the corresponding neutral species, being on the order of 10^{-4}−10^{-5}, which are slightly larger than the values reported for the allowed transitions of monosubstituted benzenes.[15,16] In sharp contrast to the mutually resembling profile and intensity of $\Delta\epsilon$ and *g* for **2**−**4** (cf. the middle and bottom traces in Figure 5a,b), the relative intensity of the *g* factors of dications $\mathbf{2}^{2+}$−$\mathbf{4}^{2+}$ is very different from that of the $\Delta\epsilon$ values, being strongly dependent upon the size (and number) of the introduced chiral substituents. Thus, the *g* factor of $\mathbf{3}^{2+}$ is much larger than those of the lower homologues $\mathbf{2}^{2+}$ and $\mathbf{4}^{2+}$ over all the wavelengths examined. Indeed, the UV spectra of the neutral and radical cationic species are almost superimposable for **2**−**4**, while the dications show small substituent-dependent UV spectra, giving smaller ϵ values in particular for $\mathbf{3}^{2+}$ (although radical cation $\mathbf{3}^{\bullet+}$ also gives slightly smaller values compared with $\mathbf{2}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ which are reflected in its appreciably enhanced *g* values). It is noted that the size of the alkyl substituent that is introduced at a distal position and is seemingly irrelevant to the electronic transition does affect the UV and CD spectra (and hence *g* factor) of dicationic and, to a lesser extent, radical cationic species, probably through the conformational changes of the ethylenic moiety due to the steric bulk of the introduced substituent.

Temperature Effects on the Chiroptical Properties of Neutral 2 and Dication $\mathbf{2}^{2+}$. In the above discussion, the fairly strong Cotton effect observed for dication $\mathbf{2}^{2+}$ was tentatively assigned not to a simple CD induced by the chiral *para*-auxiliary but to the exciton coupling of the two diarylcarbenium chromophores. To further examine this hypothesis, the CD spectra of neutral **2**, radical cation $\mathbf{2}^{\bullet+}$, and dication $\mathbf{2}^{2+}$ were recorded in 1,2-dichloroethane at temperatures ranging from −10 to +70 °C. As shown in Figure 6, the CD spectrum of neutral **2**

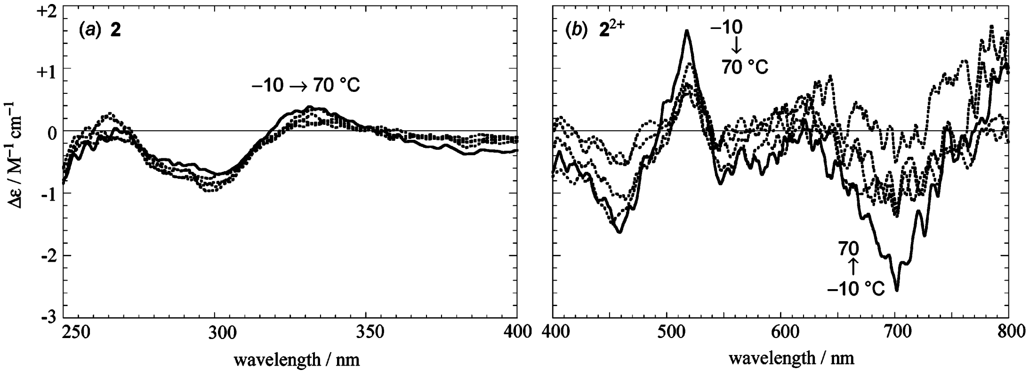


Figure 6. Variable-temperature CD spectra of (a) chiral tetraarylethylene **2** and (b) dication $\mathbf{2}^{2+}$ in 1,2-dichloroethane at −10, 10, 30, 50, and 70 °C.

exhibited only small bathochromic shifts with very small accompanying intensity changes over the temperature range employed. Similarly, the radical cation $\mathbf{2}^{\bullet+}$ showed only negligible CD changes in the same temperature range (see the Supporting Information). These results clearly indicate that simple conformational changes in the chiral auxiliary are not sufficient to cause any appreciable changes in the CD spectrum within the temperature range examined, at least in the present system. In contrast, the CD spectrum of dication $\mathbf{2}^{2+}$ turned out to be more sensitive to temperature, as shown in Figure 6. Although the spectra obtained are somewhat noisy due to the instrumental limitations of the cryostat and the CD spectrometer, the CD intensity dramatically decreases with increasing temperature from −10 to +70 °C, without accompanying a peak shift. In contrast, the UV−vis spectra of neutral, radical cationic, and dicationic species (**2**, $\mathbf{2}^{\bullet+}$, $\mathbf{2}^{2+}$) showed no significant changes over the same temperature range. Hence, the observed temperature dependence of the g factor is most probably attributable to the gradual conformational fixation of distal chiral groups at decreased temperatures, which affects the overall CD signal to a different degree that depends on the oxidation state.

Recent theoretical calculations have shown that chiral 2-butanol can adopt nine conformations with different dihedral angles.[36,37] DFT calculations at the B3LYP/6-31G* level indicate that 68% of 2-butanol molecules are populated to the three most stable conformers at room temperature.[38] Although the energy of each conformer and the population ratio would be different in the case of the 1-methylpropoxy group used in the present study, the temperature-insensitive CD spectrum of neutral **2** experimentally reveals that no serious conformational changes that affect the CD spectrum take place in chiral 1-methylpropoxy auxiliaries over the temperature range employed. The temperature-dependent CD spectrum of dication $\mathbf{2}^{2+}$ can be rationalized by the conformational fixation of the chiral group, which enhances the exciton coupling between the two diarylcarbenium chromophores. This finding indicates that the chiroptical properties of chiral tetraarylethylenes can be modulated not only by temperature but also by other entropy-related factors such as pressure and solvent polarity, the fundamental idea of which has recently been recognized in asymmetric photoreactions.[39] Temperature-driven chiroptical inversion of flexible linear polysilylenes[40] and helical switching of polystyrene modified with β-cyclodextrin[41] have also been reported recently.

Redox-Driven Chiroptical Switching. Since the present redox system is completely reversible, we examined the chiroptical properties of chiral tetraarylethylene species in different oxidation states produced upon successive oxidation−reduction cycles. First investigated was the CD spectral behavior of tetraarylethylene **2** upon complete redox cycles. Thus, neutral **2** was oxidized with 4 equiv of antimony pentachloride in dichloromethane to afford a dark green solution, the CD spectrum of which indicated the complete formation of dication $\mathbf{2}^{2+}$. After the solution was left for 10 min at room temperature, the dication formed was reduced by adding Zn powder to the solution, quantitatively regenerating neutral **2**. A clear solution of **2**, retrieved by removing the excess zinc dust by filtration under Ar, was subjected to the same oxidation−reduction−filtration cycle. This protocol was repeated several times without any accompanying loss of CD intensity at 640 nm, as shown in Figure 7, which indicates the completely reversible nature of the process.

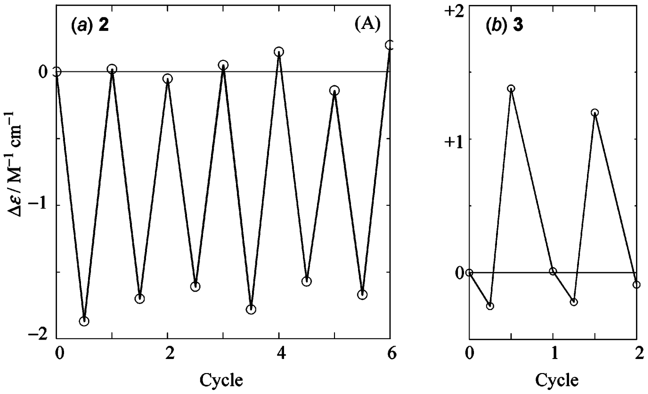


Figure 7. (a) On/off, or 0/−, switching of the CD signal of **2** at 640 nm upon repeated oxidation−reduction cycles and (b) ternary 0/−/+ switching of the CD signal of **3** at 640 nm upon successive oxidation−reduction cycles; see the text for the detailed conditions.

A stepwise oxidation−reduction cycle is also possible, consisting of the first two successive one-electron oxidations with subsequent two-electron reduction. For instance, neutral donor **3** was selectively oxidized to radical cation $\mathbf{3}^{\bullet+}$ by using 1.5 equiv of triethyloxonium hexachloroantimonate, which was further oxidized to dication $\mathbf{3}^{2+}$ with antimony pentachloride. The resulting solution was treated with zinc powder to regenerate neutral **3** in quantitative yield; thus, the colorless solution of **3** obtained after filtration of excess zinc power afforded a CD spectrum essentially identical to the original one in shape and intensity. This oxidation−reduction−filtration cycle was repeated to give the CD spectral changes at 640 nm shown in Figure 7. It is noteworthy that this reversible three-stage redox cycle may function as a ternary switching device that uses the negative/null/positive chiroptical output and/or the color change among colorless/blue/green. Table 3 summarizes the chiroptical property changes of these tetraarylethylenes induced by the multistep redox cycle. Thus, the alterations in dihedral angle and C−C bond length are systematically converted to the welldistinguishable chiroptical/colorimetric ternary digit information, assigning the absence of a CD signal or color of the neutral donor to "0", the positive CD signal or blue color of the radical cation to "+1", and the negative CD or green color of the dication to "−1". Although we have not examined other donor molecules or redox methods, this ternary chiroptical switch involving neutral/radical cationic/dicationic states of a chiral donor is potentially applicable to a wide variety of optically active electron-rich molecules by using the appropriate chemical and electrochemical redox processes.

Conclusions

We have investigated the chiroptical properties of chirally modified tetraarylethylenes in different oxidation states. Stepwise electrochemical or chemical oxidations of these tetraarylethylenes in anhydrous dichloromethane afford the corresponding stable radical cations and dications in quantitative yields. Judging from the disproportionation constant (K_{disp}) determined by the electrochemical analysis, the generated radical cation does not disproportionate to neutral and dicationic species and exists as the predominant species in dichloromethane solution, which allowed us to determine their chiroptical properties and also to use the radical cationic species as an element of the sequential redox switch. Neutral, radical cationic, and dicationic tetraarylethylenes with chiral auxiliaries display distinctly different chiroptical properties and visible color changes, reflecting the alteration in twist angle and bond length of the bisected chromophores. In the tetraarylethylene system, (*R*)-1-methylalkyl groups introduced to the *para* positions induce a left-handed twist, or *M* helicity, to the bisected chromophore of $\mathbf{2}^{2+}$. Taking into account the durability upon repeated redox cycles, this system may be used in novel chiroptical devices, such as switches and memory devices working on ternary logic.

Experimental Section

General Procedures. All starting materials, reagents, and solvents were commercially available and used without further purification, unless stated otherwise. Chiral alcohols (*S*)-(+)- and (*R*)-(−)-2-butanol and (*R*)-(−)-2-octanol were used as obtained from Aldrich. Dichloromethane (Nacalai) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (∼10% v/v), until the acid layer remained clear. After separation, it was washed with water, aqueous sodium bicarbonate, brine, and water and then dried over calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk tube equipped with a Teflon valve fitted with Viton O-rings. Tetrahydrofuran (THF; Wako) was freshly distilled from sodium/benzophenone. Anhydrous toluene (Wako) and dry hexane (Wako) were distilled from calcium hydride under Ar and stored in Schlenk flasks. Chemical and electrochemical oxidations were performed by following the literature procedure.[14]

Column chromatography was performed on silica gel (70−230 mesh, Merck) and GPC on Jaigel 1-H and 2-H columns (Japan Analytical Industry Co.) with chloroform as an eluent. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with a JEOL GSX-400. All chemical shifts are reported in parts per million relative to the peak for Me_4Si (0 ppm) or residual solvent ($CDCl_3$ as 77.16 ppm for ^{13}C) as a reference, with coupling constants (*J*) reported in hertz. IR and UV spectra were obtained on a JASCO FT/IR-230 and JASCO V-550 equipped with a temperature controller. Gas chromatographic analyses were performed on a Shimadzu GC-14B instrument fitted with a C-R6A integrator using a capillary column (SUPELCO, SPB5, 30 m × 0.25 mm i.d.). Melting points were measured with a Yanaco MP-21 apparatus and are uncorrected. Mass spectra were obtained with a JEOL JMS-DX-303 instrument. Elemental analysis was performed at the Center for Chemical Analyses, Osaka University. CD spectra were measured in a conventional quartz cell (light path 1 cm) on a JASCO J-720WI spectropolarimeter equipped with a PTC-348WI temperature controller. An aqueous solution of (+)-ammonium camphorsulfonate-d_{10} (0.06%) was used for calibration of the spectrometer sensitivity and wavelength ($\theta = 190.4$ mdeg at 290.5 nm). Δ-Tris(ethylenediamine)cobalt(III) was further employed for calibration in the visible region ($\Delta\epsilon = +1.89$ M^{-1} cm^{-1} at 490 nm).[42] The optical rotations were measured in a thermostated conventional 10 cm cell with a JASCO DIP-1000 digital polarimeter at the sodium D-line (589.3 nm). Cyclic voltammetry was performed on a BAS CV-100B electrochemical analyzer. Stilbenoid donor **1** and tetraarylethylene **2**−**4** (1 mM) and tetra-*n*-butylammonium hexafluorophosphate (0.2 M) as an electrolyte were placed in a gastight Schlenk-type separated cell under Ar. Anodic and cathodic peak potentials were measured with a Pt electrode in anhydrous dichloromethane at a sweep rate of 0.2 V s^{-1}. A $Ag^+/AgNO_3$ reference electrode was used and calibrated with ferrocene ($E_{1/2} = 0.02$ V), with the measured potential converted to the voltage vs SCE by using the relationship $E(\mathrm{SCE}) = E(\mathrm{Ag^+/AgNO_3}) + 0.25$ V. All DFT calculations were performed using the GAUSSIAN 98 software package[43] running on 16-CPU parallel Pentium IV processors at the Handai FRC Computer Center. The optimizations were performed at the B3LYP/6-31G(d) level for an AM1-optimized structure, with the molecular orbital calculation followed by the POP=Full keyword. Semiempirical calculations were performed with the MOPAC (version 6) program using the PM3 and AM1 Hamiltonians implemented on a Sony Tektronix CAChe system (version 3.5). Unrestricted Hartree−Fock wave functions were employed, and the calculations were fully optimized using an extra keyword, PRECISE.

Synthesis of (*R*,*R*)-2,3-Bis(*p*-(1-methylpropyloxy)phenyl)-bicyclo[2.2.2]oct-2-ene (1). *p*-Bromophenol (5.19 g, 30 mmol), triphenylphosphine (7.87 g, 30.0 mmol) and (*S*)-(−)-2-butanol (2.76 mL, 30.1 mmol) were dissolved in THF (100 mL), to which diisopropyl azodicarboxylate (DIAD; 6.50 mL, 33.0 mmol) was added dropwise under Ar at ambient temperature. The solution was stirred for 2 days, and the solvent was evaporated to give a residue which was chromatographed on silica gel with a hexane eluent to afford 4.36 g (63%) of the corresponding chiral (*R*)-ether; the (*S*)-isomer was obtained in the corresponding manner. The (*R*,*R*)-isomer of **1** was obtained according to the literature procedure.[44,45] Thus, magnesium turnings (0.48 g, 20 mmol) and the corresponding chiral aryl bromide (2.86 g, 13 mmol) were dissolved in THF (25 mL), and the solution was refluxed for 5 h. In a separate flask, 2,3-dibromobicyclo[2.2.2]oct-2-ene[44] was dissolved in THF (20 mL), the Grignard reagent added via a cannula, and the mixture refluxed for 20 h under Ar. The resulting solution was quenched with aqueous ammonium chloride, and the organic components were extracted with ether. The ether extract was washed with water and brine, and dried over anhydrous $MgSO_4$. The mixture was filtered and evaporated in vacuo to afford a residue, which was purified by silica gel column chromatography with hexane/ether (1:1) eluent to afford 4.58 g (91%) of the corresponding chiral stilbenoids.

Data for (*S*)-*p*-bromo-1-methylpropyloxybenzene: colorless oil; ^{1}H NMR δ 0.88 (3H, t, $J = 7.2$), 1.19 (3H, d, $J = 6.2$), 1.53 (1H, sym m, $J = 6.2$), 1.63 (1H, sym m, $J = 7.3$), 4.15

(1H, m, *J* = 6.2), 6.68 (2H, d, *J* = 9.1), 7.26 (2H, d, *J* = 9.1); ^{13}C NMR δ 9.85, 19.25, 29.20, 75.56, 112.58, 117.83, 132.37, 157.49; HRMS *m*/*z* found 228.0157, calcd for $C_{10}H_{13}BrO$ 228.0150.

Data for (*R*,*R*)-2,3-bis(*p*-(1-methylpropyloxy)phenyl)-bicyclo[2.2.2]oct-2-ene (1): mp 74−75 °C; ^{1}H NMR δ 0.96 (6H, t, *J* = 7.3), 1.26 (6H, d, *J* = 5.9), 1.50−1.78 (12H, m), 2.87 (2H, s), 4.22 (2H, sym m, *J* = 5.9), 6.69 (4H, d, *J* = 8.4), 7.00 (4H, d, *J* = 8.4); ^{13}C NMR δ 9.94, 19.44, 26.45, 29.35, 37.61, 75.06, 115.45, 129.63, 133.72, 138.77, 156.44; IR (CaF_2, ν/cm^{-1}) 1240, 1502, 1604, 2860, 2937, 2969; HRMS *m*/*z* found 404.2713, calcd 404.2715; $[\alpha]^{25}_D$(*c* 0.10, $CHCl_3$) = −22.0°. Anal. Calcd for $C_{28}H_{36}O_2$: C, 83.12; H, 8.97. Found: C, 82.98; H, 8.93. The corresponding (*S*,*S*)-isomer was similarly obtained in 86% yield, and the spectroscopic characteristics are essentially the same. Anal. Found: C, 82.83; H, 9.00.

Synthesis of Tetrakis(*p*-(1-methylpropyloxy)phenyl)ethylene (2). 4,4′-Dihydroxybenzophenone (10.28 g, 48 mmol), (*S*)-(+)-2-butanol (7.94 g, 107 mmol), and triphenylphosphine (28.09 g, 107 mmol) were dissolved in THF (175 mL), to which DIAD (23.0 mL, 117 mmol) in THF (25 mL) was added dropwise over 1 h under an Ar atmosphere at 0 °C. The resulting solution was warmed to room temperature and stirred for an additional 20 h. After evaporation of the solvent, the crude product was chromatographed on silica gel with hexanes−ethyl acetate (50:1) as an eluent to afford 15.0 g (96%) of the corresponding ketone as the second fraction. The ketone (11.34 g, 35 mmol) and zinc dust (6.88 g, 105 mmol) were vigorously stirred in THF (200 mL) under Ar, to which titanium tetrachloride (5.8 mL, 105 mmol) was added dropwise, with the resulting black chalky mixture refluxed for 20 h. The resulting mixture was poured into an aqueous sodium carbonate solution and the organic material extracted with ether (3 × 500 mL). The combined ether extract was washed with brine and water, and then dried over sodium sulfate. After filtration, the solution was evaporated to dryness and the residue purified by silica gel column chromatography with hexanes−ethyl acetate (50:1) eluent. The crude product obtained was further purified by recrystallization from an ethanol/dichloromethane mixture to give a colorless solid, yield 8.42 g (78%).

Data for (*R*,*R*)-bis(*p*-1-methylpropyloxy)benzophenone: colorless oil; ^{1}H NMR δ 0.99 (6H, t, *J* = 7.3, 6.2), 1.33 (6H, d, *J* = 5.9), 1.66 (2H, m, *J* = 7.3, 6.2), 1.78 (2H, m, *J* = 7.3, 6.2), 4.41 (2H, m, *J* = 5.9), 6.93 (4H, d, *J* = 8.8), 7.77 (4H, d, *J* = 8.8); ^{13}C NMR δ 9.84, 19.28, 29.23, 75.27, 115.00, 130.49, 132.24, 161.76, 194.49; IR (As_2Se_3, ν/cm^{-1}) 2973, 2935, 1647, 1601, 1508, 1303, 1252, 925, 769, 618; HRMS *m*/*z* found 326.1879, calcd 326.1882. Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 76.98; H, 7.97.

Data for (*R*,*R*,*R*,*R*)-tetrakis(*p*-(1-methylpropyloxy)phenyl)-ethylene (2): mp 174−175 °C; ^{1}H NMR δ 0.87 (12H, t, *J* = 7.4), 1.17 (12H, d, *J* = 5.8), 1.50 (4H, m, *J* = 7.4, 6.3), 1.64 (4H, m, *J* = 7.4, 6.2), 4.13 (4H, sym m, *J* = 6.2, 5.8), 6.53 (8H, d, *J* = 8.3), 6.83 (8H, d, *J* = 8.3); ^{13}C NMR δ 9.94, 19.38, 29.33, 75.03, 115.13, 132.72, 136.91, 138.59, 156.53; IR (KBr, ν/cm^{-1}) 2971, 2935, 1605, 1284, 1240, 1175, 1128, 1115, 989, 925, 834; HRMS *m*/*z* found 620.3862, calcd 620.3866; $[\alpha]^{25}_D$-(*c* 0.10, $CHCl_3$) = −53.2°. Anal. Calcd for $C_{42}H_{52}O_4$: C, 81.25; H, 8.44. Found: C, 81.01; H, 8.38.

Data for (*S*,*S*,*S*,*S*)-tetrakis(*p*-(1-methylheptyloxy)phenyl)-ethylene (3): pale yellow oil; ^{1}H NMR δ 0.80 (12H, t, *J* = 7.3), 1.15 (12H, d, *J* = 6.2), 1.16−1.36 (36H, m), 1.35−1.49 (4H, m), 1.52−1.67 (4H, m), 4.17 (4H, sym m, *J* = 6.2), 6.51 (8H, d, *J* = 8.4), 6.82 (8H, d, *J* = 8.4); ^{13}C NMR δ 14.20, 19.84, 22.72, 25.63, 29.42, 31.93, 36.64, 73.84, 115.08, 132.69, 136.87, 138.52, 156.51; HRMS *m*/*z* found 844.6368, calcd for $C_{58}H_{84}O_4$ 844.6370.

Synthesis of (*R*,*R*)-(*E*)-Bis(*p*-(1-methylpropyloxy)phenyl)-bis(*p*-methoxyphenyl)ethylene (4). 4,4′-Dihydroxybenzophenone (51.3 g, 0.24 mol) and potassium carbonate (35.4 g, 0.26 mol) were dissolved in acetone (1 L), to which iodomethane (20.0 mL, 0.32 mol) was added all at once. The mixture was refluxed for 12 h, and then the organic solvent was evaporated. The crude mixture was chromatographed on silica gel with a hexanes−ethyl acetate (2:1) eluent. The first fraction was the dimethylated product (4.7 g, 8%), and the second fraction was the desired monomethylated benzophenone 4-hydroxy-4′-methoxybenzophenone,[46] yield 13.6 g (25%), mp 150−151 °C. The ketone (4.56 g, 20 mmol), (*S*)-(+)-2-butanol (1.92 g, 26 mmol), and triphenylphosphine (5.24 g, 20 mmol) were dissolved in THF (100 mL), to which DIAD (5.0 mL, 23 mmol) in THF (30 mL) was added dropwise over 3 h under an Ar atmosphere. The solution was warmed to room temperature and stirred for an additional 30 h. After evaporation of the solvent the crude product was chromatographed on silica gel with a hexane−dichloromethane (5:1) eluent to afford 5.80 g (99%) of the corresponding chiral alkylated ketone. The chiral monomethoxybenzophenone (5.82 g, 20 mmol) and zinc dust (5.69 g, 60 mmol) were vigorously stirred in THF (200 mL) under Ar, to which titanium tetrachloride (3.3 mL, 30 mmol) was added dropwise at 0 °C, with the resulting mixture refluxed for 10 h. The obtained crude mixture was poured onto an aqueous sodium carbonate solution, and the organic material was extracted with ether (2 × 200 mL). The organic phase was washed with brine and water and dried over sodium sulfate. The filtrate was evaporated to give a residue, which was purified by silica gel column chromatography with a hexanes−ethyl acetate (25:1) eluent. The material obtained (4.12 g, 77%) was further purified by recrystallization from ethanol to give 3.51 g (66%, *E*/*Z* > 98) of the gas chromatographically pure (*E*)-isomer.

Data for (*R*)-4-methoxy-4′-(1-methylpropyloxy)benzophenone: colorless oil; ^{1}H NMR δ 0.99 (3H, t, *J* = 7.3), 1.34 (3H, d, *J* = 5.9), 1.67 (1H, m, *J* = 6.2), 1.78 (1H, m, *J* = 7.7), 3.88 (3H, s), 4.41 (1H, m, *J* = 5.9), 6.93 (2H, d, *J* = 8.8), 6.96 (2H, d, *J* = 8.8), 7.77 (2H, d, *J* = 9.2), 7.79 (2H, d, *J* = 9.5); ^{13}C NMR δ 9.87, 19.31, 29.25, 55.59, 75.30, 113.56, 115.03, 130.41, 130.99, 132.33, 132.43, 161.85, 162.90, 194.57; HRMS *m*/*z* found 284.1414, calcd 284.1412. Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.83; H, 7.06.

Data for (*R*,*R*)-(*E*)-bis(*p*-(1-methylpropyloxy)phenyl)bis-(*p*-methoxyphenyl)ethylene (4): mp 167−168 °C; ^{1}H NMR δ 0.95 (3H, t, *J* = 7.5), 1.24 (3H, d, *J* = 6.2), 1.57 (1H, m, *J* = 7.0), 1.72 (1H, m, *J* = 6.2), 3.74 (3H, s), 4.21 (1H, m, *J* = 5.9), 6.60 (2H, d, *J* = 8.8), 6.63 (2H, d, *J* = 8.8), 6.89 (2H, d, *J* = 8.1), 6.94 (2H, d, *J* = 8.4); ^{13}C NMR δ 9.93, 19.39, 29.32, 55.22, 75.01, 113.10, 115.14, 132.66, 132.72, 136.81, 137.13, 138.51, 156.55, 157.87; IR (KBr, ν/cm^{-1}) 2971, 2934, 1606, 1506, 1463, 1173, 1127, 1107,1034, 989, 924, 836; HRMS *m*/*z* found 536.2922, calcd 536.2927; $[\alpha]^{25}_D$(*c* 0.10, $CHCl_3$) = −25.4°. Anal. Calcd for $C_{36}H_{40}O_4$: C, 80.56; H, 7.51. Found: C, 80.34; H, 7.45.

Preparative Oxidation of Tetraarylethylenes with Antimony Pentachloride. General Procedure. A solution of antimony pentachloride in dichloromethane (0.01 M, 5 mL) was cooled at −78 °C under an argon atmosphere while tetraarylethylene **2** (62 mg, 0.1 mmol) in anhydrous dichloromethane (10 mL) was slowly added. The reaction mixture immediately took a green coloration, and the mixture was stirred for 10 min.

Addition of prechilled anhydrous hexane (50 mL) led to the precipitation of the dication salt. The dark microcrystalline precipitate [$\mathbf{2}^{2+}(SbCl_6^-)_2$] ($\lambda_{max} = 422, 471, 577, 660$; $\log \epsilon_{577} = 4.65$ M^{-1} cm^{-1}) was filtered under an argon atmosphere, washed with dry diethyl ether (3 × 10 mL), and dried in vacuo to give dark microcrystals (71 mg, 55%). The purity of the dication was determined by iodometric titration[14] and found to be 96%.

X-ray Crystallography of Neutral Tetraarylethylene 2. A colorless prismatic crystal was cut into a cubic shape with approximate dimensions of 0.30 × 0.30 × 0.30 mm. This was mounted on a glass fiber. All X-ray crystallographic measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 16.3$ cm^{-1}) with a rotating anode generator at 23 ± 1 °C (Brutto formula $C_{45}H_{52}O_4$, MW = 620.87, monoclinic $P2_1$, $a = 9.481(5)$ Å, $b = 14.163(5)$ Å, $c = 13.946(4)$ Å, $\beta = 98.51(3)°$, $V = 1852(1)$ Å^3, $D_c = 1.11$ g cm^{-3}, $Z = 2$). The total number of reflections measured was 4700, 4436 of which were symmetrically nonequivalent. The structure was solved by direct methods,[47] expanded using Fourier techniques,[48] and refined by the full-matrix least-squares procedure with the teXsan[49] crystallographic software package of Molecular Structure Co. The final residuals were R1 = 0.065 and wR2 = 0.165 for 1893 observed reflections with $I > 2\sigma(I)$ and 495 variable parameters. CCDC 258915 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Rd., Cambridge CB2 1EZ, U.K., fax +44 1223 336033.

X-ray Crystallography of Tetraarylethylene Dication $\mathbf{2}^{2+}$. Tetraarylethylene **2** (62 mg, 0.10 mmol) and triethyloxonium hexachloroantimonate (66 mg, 0.15 mmol) were dissolved in dichloromethane (10 mL) under Ar at 0 °C, and the solution was stirred for 1 h to complete the oxidation. To the resulting blue-purple solution was added anhydrous ether to form a precipitate, which was then filtered under an argon atmosphere. The filtrate was washed with prechilled dry hexane (2 × 10 mL), and then redissolved in anhydrous dichloromethane (20 mL). The organic phase was carefully layered with anhydrous toluene (30 mL) and stored in a freezer at −20 °C for 5 days; slow diffusion of toluene afforded the dication salt produced through the disproportionation of the radical cationic species. Note that crystals of the same dication salt (of lower quality) were obtained by the reaction of **2** and antimony pentachloride at −78 °C and the subsequent crystallization procedures using the slow diffusion of toluene as mentioned above. A red prism crystal with approximate dimensions of 0.30 × 0.30 × 0.10 mm was mounted on a glass fiber. All X-ray crystallographic measurements were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 16.3$ cm^{-1}) at 23 ± 1 °C (Brutto formula $C_{45}H_{52}O_4Sb_2Cl_{12}$, MW = 1289.81, tetragonal $I4_1$, $a = 11.3809(3)$ Å, $c = 41.655(1)$ Å, $V = 5395.3(3)$ Å^3, $D_c = 1.59$ g cm^{-3}, $Z = 4$). The total number of reflections measured was 24868, 3092 of which were symmetrically nonequivalent. The structure was solved by direct methods,[47] expanded using Fourier techniques,[48] and refined by the full-matrix least-squares procedure with teXsan.[49] The final residuals were R1 = 0.043 and wR2 = 0.078 for 1603 observed reflections with $I > 2\sigma(I)$ and 272 variable parameters. CCDC 258916 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, U.K., fax +44 1223 336033.

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Supporting Information Available: Lorenzian deconvoluted curve fittings for the CD spectra of the neutral donors **2**−**4**, CD spectra of the radical cation $\mathbf{2}^{\bullet+}$ at different temperatures, calculated conformations of neutral donor **2**, radical cation $\mathbf{2}^{\bullet+}$, and dication $\mathbf{2}^{2+}$, and ORTEP drawings of **2** and $\mathbf{2}^{2+}$ obtained by X-ray crystallographic analyses (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) See the Supporting Information for details. Spectral deconvolution was performed for the unsymmetrical donor **4** to give a good fit, tentatively postulating a single exciton couplet at 256 nm ($A_2 = -1.19$) and noncoupled peaks at other wavelengths.

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