Doctor Thesis

Construction of Multifunctional Molecular Switches Based on Electrochromic Materials

(エレクトロクロミック物質を利用した多機能型分子スイッチの構築)

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Chapter 0.
General Introduction

0.1. Molecular Switches and Chromic Systems

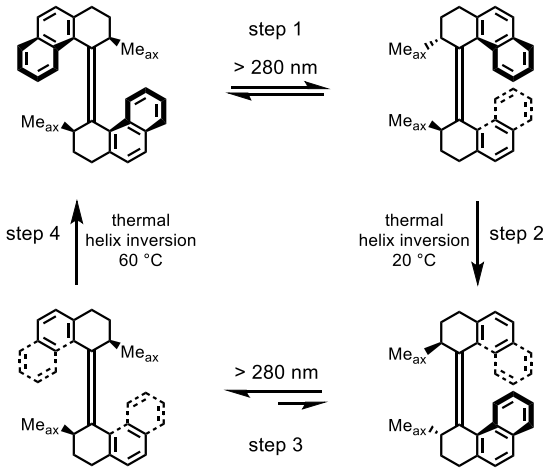
There is a class of molecules or supramolecular assemblies, for which the properties can be modified in response to external stimuli such as electric potential, heat, light, pressure, pH, and solvent polarity. The inter-state transformation of those bistable entities could be also attained by the reversible chemical reaction with metal ions or some reagents.

When the color of the materials changes drastically, the reversibly interconvertible molecular systems are called chromic systems. Depending on the external stimuli that induce the conversion (e.g., heat, light, electron-transfer, mechanical stress), they are either called thermochromic, photochromic, electrochromic, or mechanochromic behavior.

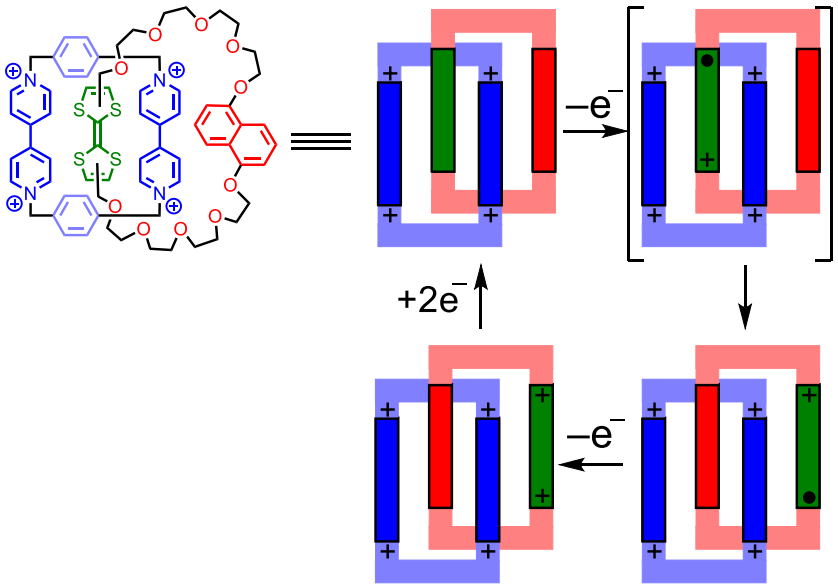
0.2. Molecular Machines

On the other hand, the inter-state transformation is accompanied by a drastic geometrical change, the bistable molecular system can be considered as a molecular machine. When the concept of a machine is extended to the molecular level, an assembly or a discrete number of components in the supramolecular systems is expected to exhibit machine-like movement as a consequence of the external stimuli.

Molecular motors developed by Feringa exhibit conformational changes accompanied by stereoisomerization of the overcrowded olefins, thus realizing one-directional rotation of the molecular half in respective to the rest of molecule (Scheme 0-1). [1] Mechanically interlocked molecules (MIMs) are advantageous in attaining drastic geometrical changes. Stoddart, Sauvage, and Leigh are the representative big stars who developed the molecular machines based on rotaxanes and catenanes (Scheme 0-2). [2]



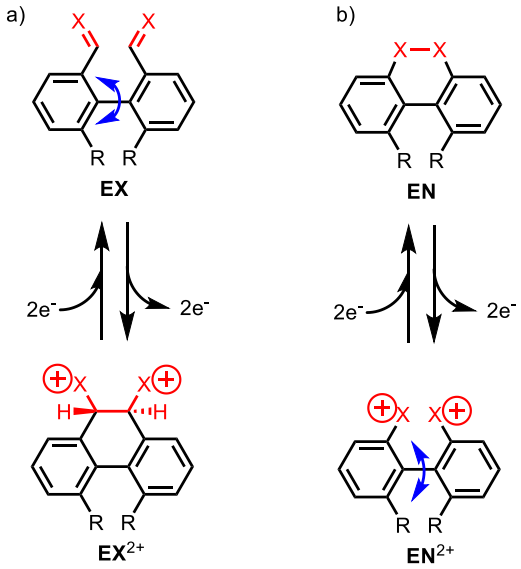
Scheme 0-1. Photochemical and thermal isomerization processes of the molecular motor.



Scheme 0-2. An example of molecular machine based on a catenane.[2c]

0.3. Dynamic Redox Systems

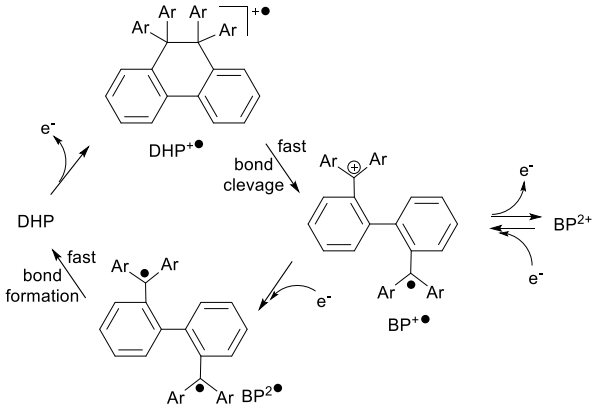
"Dynamic redox (dyrex) systems" is the name given to a certain class of molecules which can be reversibly converted into the corresponding cations/anions upon electron transfer but accompanied by drastic geometrical changes and/or covalent bond formation/cleavage. [3] A series of dyrex systems have been developed in the laboratory the author belongs. The dyrex systems are designed so that bond-formation occurs as an intramolecular process [e.g., biphenyl (BP) - dihydrophenanthrene (DHP) pairs], although the reversible dyrex pairs could also be constructed based on an intermolecular-bonding process.[4] BP-DHP-based dyrex systems can be categorized into two types: an exo-type pair (EX and EX^{2+}) and an endo-type pair (EN and EN^{2+}) (Scheme 0-3).[5] The exo-type system (EX and EX^{2+}) consists of a dication with positive charges located at the exocyclic carbons of the newly formed ring system, whereas the endo-type system (EN and EN^{2+}) consists of a dication with positive charges located at the endocyclic carbons of the starting ring system undergoing bond cleavage.



Scheme 0-3. Two types of dyrex systems.

Redox scheme for DHP-donor and BP-dication is as follows. Fast bond cleavage occurs after 1e oxidation of DHP to $DHP^{\bullet+}$, and the resulting $BP^{\bullet+}$ is a stronger donor than DHP. Thus, the steady-state concentration of the cation radicals is negligible upon oxidation. Although the reduction of BP^{2+} occurs over two steps, disproportionation of $BP^{\bullet+}$ to BP^{2+} and $BP^{2\bullet}$ occurs easily due to fast bond formation of $BP^{2\bullet}$ to DHP. Thus, open-shell species are also short-lived in the reduction process (Scheme 0-4). Due to the mechanism for the interconversion[6], many dyrex systems exhibit electrochemical bistability, and the oxidation potential of the neutral donor and the reduction potential of the corresponding dication are quite different. [7]

As described above, besides MIMs, the dyrex systems are advantageous to construct novel molecular switches in terms of drastic geometrical changes as well as electrochemical bistability.

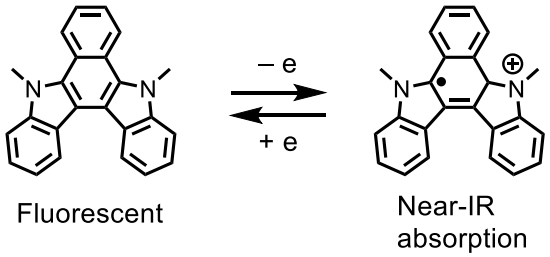


Scheme 0-4. Redox scheme for DHP-donor and BP-dication

0.4. Novel Molecular Switches Studied in This Thesis

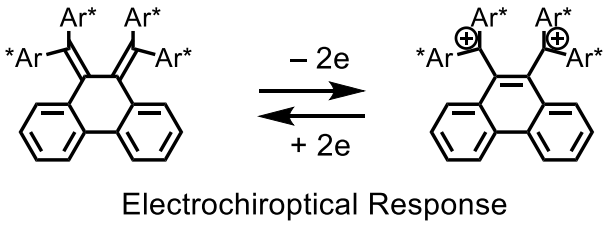
Based on such background, the newly designed molecular switches are reported in this thesis. They all are based on the electrochromic systems, and thus the principal stimulus is the different electric potential that induced redox reaction of the molecules. Actually, all of the designed switches are electron donors, so that, the author has been investigated on the new electrochromic donors that can exhibit multifunctional properties.

In chapter 1, the disk-shaped diamine skeleton (benzindolocarbazole) was newly designed based on the *p*-phenylenediamine core that exhibits colorless-NIR electrochromism accompanied by a fluorescence change (Scheme 0-6).



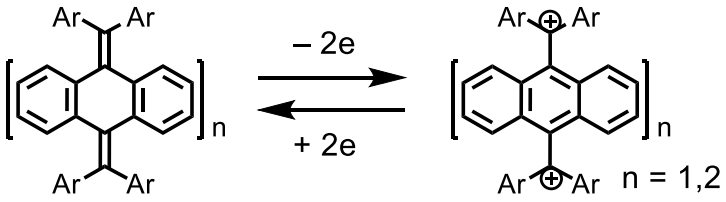
Scheme 0-5

In chapter 2, orthoquinodimethane is used as a redox center, for which the corresponding dicationic states exhibit strong absorption in the long wavelength region due to formation of diarylmethylium dye chromophores. By incorporating point chirality, the chiroptical properties could be endowed (Scheme 0-6).



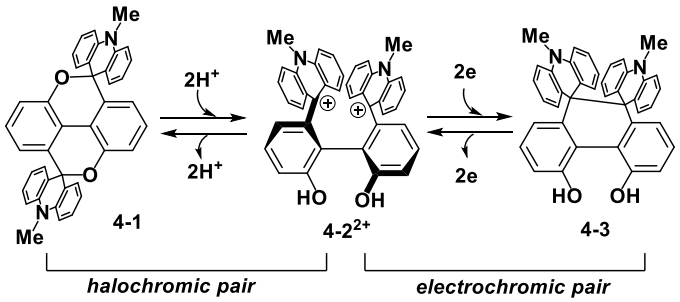
Scheme 0-6

In chapter 3, reversible redox properties of tetraarylanthraquinodimethane was studied, which undergoes drastic structural changes between butterfly-shaped neutral donor and the corresponding dication with nearly perpendicular geometry (Scheme 0-7). The molecules studied in chapters 2 and 3 exhibit electrochemical bistability due to huge geometrical changes upon electron transfer.



Scheme 0-7

In chapter 4, diacridinium-type dye exhibiting dyrex behavior was featured to endow the properties that can also controlled by proton transfer. Thus, the newly designed dye showed two-way chromic systems by redox reaction or by acid-base reaction (Scheme 0-8).



Scheme 0-8

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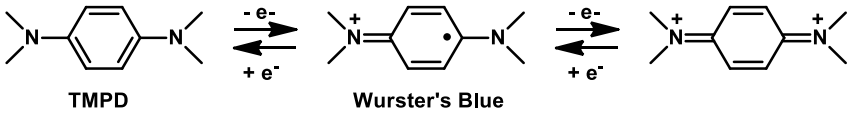
Chapter 1.

5,10-Dihydrobenzo[a]indolo[2,3-c]carbazole: A Highly Fluorescent Disk-shaped Electron Donor Exhibiting Dual UV-Vis-NIR and Fluorescence Spectral Changes Upon Electrolysis

1.1. Introduction

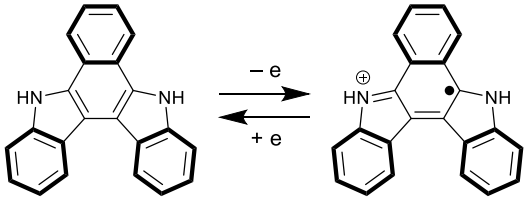
1,4-Phenylenediamines have been known as representative organic redox systems since their radical cation species are stable enough for spectroscopic detection or even for isolation as exemplified by Wurster's Blue (Scheme 1-1).[1] Based on the reversible interconversion with the corresponding oxidized states, they can serve as promising electrochromic materials,[2] by which the electrochemical input is transduced into UV-Vis spectral output.[3] In pursing the advanced chromic materials,[4] the author have got interested in the two-way-output molecular response systems, by which the electrochemical input causes two kinds of spectral changes, e.g. UV-Vis and fluorescence.[5-7] Although emission efficiency of phenylenediamines is not high,[8] some structural modification would make it possible to attain higher fluorescence quantum yield.



Scheme 1-1. Redox states of 1,4-phenylenediamine.

1.2. Molecular Design

By considering that the benzannulated polycyclic amines are highly fluorescent as well demonstrated by some carbazole derivatives,[9] the author designed here 5,10-dihydrobenzo[*a*]indolo[2,3-*c*]carbazole (BIC, **1-1**), in which three benzene nuclei are attached to 1,4-phenylenediamine moiety as shown in Scheme 1-2. The central point of this design is that the newly attached Clar's sextets would remain intact even after one-electron oxidation, and thus loss of resonance energy could be minimized upon oxidation of **1-1**. In this paper, preparation, X-ray structure, and spectral and redox properties are reported along with its electrochromic behavior.

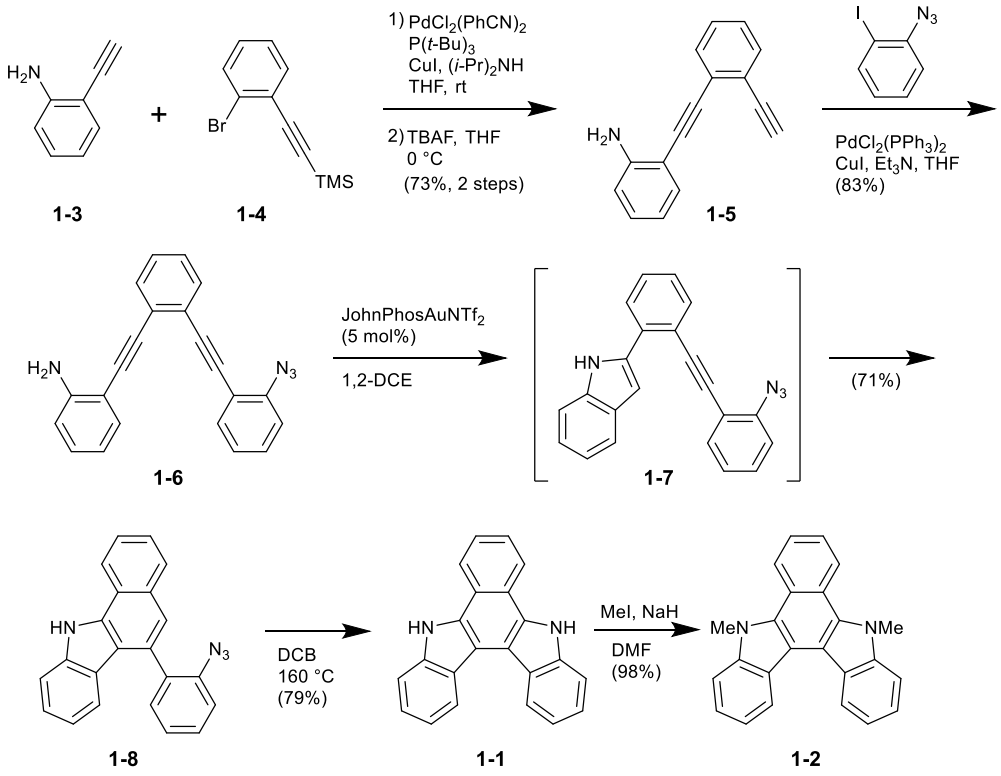


Scheme 1-2. Retention of Clar's sextet of three benzene rings upon oxidation/reduction of **BIC**.

1.3. Synthesis

5,10-Dihydrobenzo[*a*]indolo[2,3-*c*]carbazole (**1-1**) and its N,N'-dimethyl derivative (**1-2**) were chosen as target compounds in this study. Its synthetic scheme is based on a combination of two reliable strategies for carbazole synthesis (Scheme 1-3): (1) reaction integration[10] of gold-catalyzed hydroamination of diynylanilines and subsequent hydroarylation developed by Prof. Ohno at Kyoto University,[11] and (2) intramolecular nitrene insertion by thermal decomposition of 2-azido-1,1'-biphenyls developed by Sapi *et al.*.[12]

The following synthetic scheme was investigated by Yusuke Tokimizu under the guidance of Prof. Ohno at Kyoto University. The known diynylaniline **S3** was prepared by Sonogashira coupling between 2-ethynylaniline (**1-3**) and 1-alkynyl-2-bromobenzene (**1-4**) according to the reported procedure.[11b]



Scheme 1-3. Preparation of **1-1** and **1-2** via tandem cyclization reaction catalyzed by Au(I) catalyst.

Introduction of the azidobenzene moiety to **1-5** was carried out by the second Sonogashira coupling to give the cyclization precursor **1-6**,[13] which was subjected to the gold-catalyzed integrated reaction. As expected, treatment of **1-6** with JohnPhosAuNTf$_2$ (5 mol %) in 1,2-dichloroethane (DCE) gave benzocarbazole **1-8**[13] bearing an azido group in 71% yield. Finally, exposure of **1-8** to the nitrene insertion conditions at 160 °C in dichlorobenzene (DCB) provided the target compound **1-1**[13] in 79% yield. *N*-methylation of **1-1** was accomplished by repeated treatment with NaH and MeI to give **1-2** in 98% yield.

After the synthetic scheme was established, the author visited Prof. Ohno's laboratory and prepared the samples of **1-1** and **1-2**.

1.4. Redox Properties

According to the voltammetric analysis in MeCN,[19] **1-1** undergoes two-stage one-electron oxidation. Comparisons of the peak heights suggested that the second process (E_2^{ox} = + 0.98 V vs SCE) involving the dication is quasi-reversible whereas the first process is completely reversible (E_1^{ox} = + 0.63 V vs SCE) (Fig. 1-1a). Such behaviors can be best accounted for by partial deprotonation from dication **1-1**$^{2+}$ (Scheme 4). In fact, **1-2** without acidic N-H groups undergoes reversible two-stage one-electron oxidation processes (E_1^{ox} = + 0.59 V, E_2^{ox} = + 1.03 V vs SCE) (Fig. 1-1b).

1-1$^{\bullet+}$ seemed to be less stable under the conditions for electrochromic studies due to slow and partial decomposition by deprotonation, and thus **1-2** is more proper for serving as reversible chromic systems by suppressing deprotonation from the oxidized states (e.g. **1-2**$^{\bullet+}$ or **1-2**$^{2+}$).

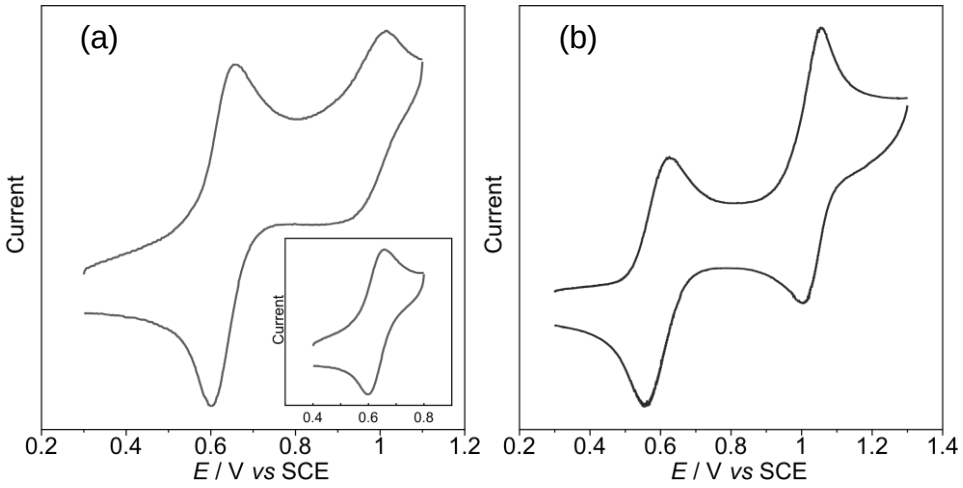
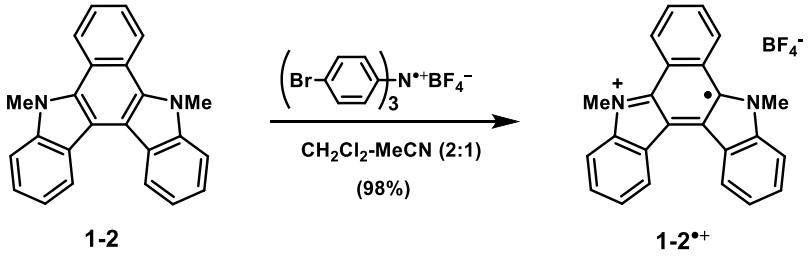


Fig. 1-1. Cyclic voltammogram of (a) **1-1** and (b) **1-2** recorded in MeCN containing Et_4NClO_4 (0.1 mM) as a supporting electrolyte (*E* / V vs SCE, scan rate 100 mV / s, Pt electrode).

1.5. Generation and Isolation of Radical Cation Species

As shown in the previous section, radical cation of **1-2** was suggested to be much more stable than **1-1**$^{\bullet+}$. So that, preparative scale oxidation of **1-2** was conducted to generate **1-2**$^{\bullet+}$. The author successfully isolated a salt of **1-2**$^{\bullet+}$ by oxidizing **1-2** by using one equivalent of tris(*p*-bromophenyl)aminium tetrafluoroborate as one electron oxidizing reagent. The salt was obtained in 98% yield, which exhibits infinite stability under the ambient conditions. On the other hand, several attempts to prepare dication salt of **1-2**$^{2+}$ were unfruitful.



Scheme 1-4. Generation of radical cation **1-2**$^{\bullet+}$ using one electron oxidizing reagent.

1.6. X-ray Crystal Structure

Single crystals of **1-1** and **1-2** suitable for X-ray crystal structural analyses were obtained by recrystallization, which enabled to investigate the structural feature of benzo[*a*]indolo[2,3-*c*]carbazole skeleton. **1-1** crystallizes in the orthorhombic space group of *F*dd2 (Z = 16).[15,16] As shown in Fig.1-2, it adopts a planar geometry, despite a closer contact between the two hydrogen atoms at C1 and C14 (1.96 Å) than the sum of vdW radii for H -- H (2.4 Å).[17] This planar disk-shaped molecule has an approximate atom-to-atom diameter of 10.5 Å.[14] **1-2** crystallizes in the monoclinic space group of *C*2/*c* (Z = 8), adopting a similar planner geometry. The detailed geometrical data could be determined with high accuracy for **1-2**.

Single crystals of radical cation salt **1-2**$^{\bullet+}BF_4^-$ was obtained after many trials, and benzene solvate crystal was grown from DMSO-benzene, that enabled to reveal its planar geometry by X-ray structural analysis (triclinic, *P*1bar, Z = 2). Comparing the structures of **1-2** and **1-2**$^{\bullet+}$ indicated that drastic change in bond lengths occur at the phenylenediamine unit upon redox reaction. Thus, the hexagon in **1-2**$^{\bullet+}$ is close to that of *p*-quinodimethane with two exocyclic C-N bonds being closer to the iminium structure. On the other hand, the difference in the bond lengths at the three benzene rings annulated to the phenylenediamine unit is very small, indicating the reduction of aromaticity upon oxidation is minimized.

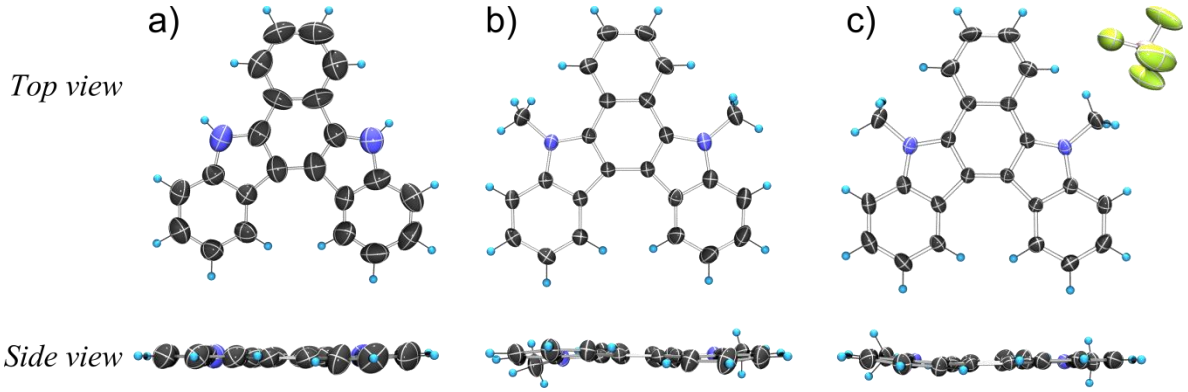


Fig. 1-2. Top view and side view of molecular structures of (a) **1-1**, (b) **1-2** and (c) **1-2**$^{\bullet+}$$BF_4^-$ determined by X-ray crystal structural analyses. Thermal ellipsoids are shown at the 50% probability level.

1.7. UV-Vis-NIR absorption and fluorescence spectra

The absorption and fluorescence spectra of **1-1** and **1-2** were measured in MeCN (Fig. 1-3a). Rigidity of BIC skeleton was suggested by their absorption spectra exhibiting vibrational structures.[14] The first absorption bands of **1-2** [λ_{max} (log ε) = 408 (3.98), 387 (3.90), 368 (3.75) nm] was red-shifted than those of **1-1** [λ_{max} (log ε) = 393 (3.99), 373 (3.89), 357 (3.69) nm], indicating that the HOMO level of **1-2** is higher than that of **1-1** resulting from substitution of electron-donating methyl groups on nitrogen atoms as confirmed electrochemical study (*vide infra*).

The fluorescence spectrum resembles the mirror image of the first absorption band (Fig. 1-3b), indicating that the vibrational energy level spacing is similar for the ground and excited states, so that emission maxima of **1-2** [λ_{pl} = 441, 420 nm] again appeared in the longer-wavelength regeion than those of **1-1** [λ_{pl} = 423, 393 nm]. The fluorescence quantum yields of **1-1** and **1-2** were measured in MeCN by using 9,10-diphenylanthracene as an external standard.[16] The high values [Φ_{pl} (**1-1**) = 0.73, Φ_{pl} (**1-2**) = 0.71] indicate the validity of my molecular design on BIC molecules.

Radical cation **1-2**$^{\bullet+}$ is non-emissive, so the redox reaction can be used for ON/OFF switching of fluorescence of **1-2**. As shown in Fig. 1-5c, the first absorption band of **1-2**$^{\bullet+}$ was observed in the near IR region that extends up to 1200 nm, which can be accounted for by a small SOMO-LUMO gap. At any event, drastic changes in spectroscopic properties of **1-2** and **1-2**$^{\bullet+}$ are favored for their use in electrochromic materials.

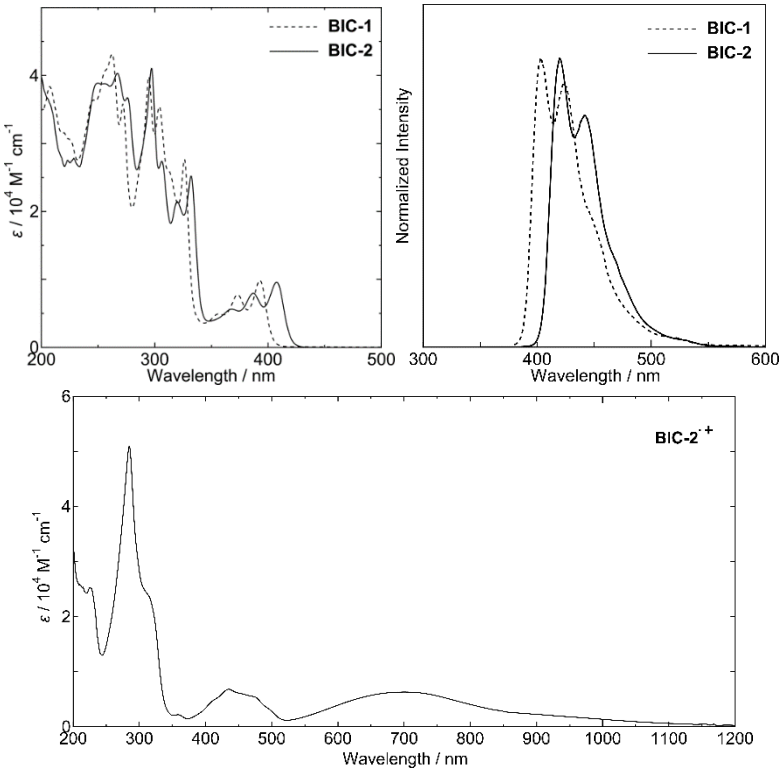


Fig. 1-3. (a) Absorption spectra of **1--1** (3.33×10^{-5} M) and **1-2** (3.02×10^{-5} M). (b) Fluorescence spectra of **1-1** (3.33×10^{-6} M) and **1-2** (3.02×10^{-6} M). (c) An absorption Spectrum of **1-2**$^{\bullet+}$ (3.72×10^{-5} M). Each spectrum was measured in MeCN solution.

1.8. Electrospectroscopy

Changes of UV-Vis-NIR and fluorescence spectra at regular time intervals were observed upon constant-current electrochemical oxidation of **1-2** in MeCN. A clean conversion was observed with exhibiting isosbestic points (Fig. 1-4). Thus, the intensity of the UV bands decreased with a concomitant appearance of a new broad absorption in the longer-wavelength region (λ_{max} = ca. 700 nm) with an absorption tail extended to 1200 nm. The final spectrum is identical to that of isolated **1-2**$^{\bullet+}$. When the same electrolysis was followed by fluorescence spectrum, a continuous decrease in emission intensity was observed (Fig. 1-4a). Applying reverse current to the measuring solution gave almost recovery of UV-region absorption and fluorescence though not completely (Fig. 1-4b).

Upon constant-current electrochemical oxidation of **1-1**, a similar change of UV-Vis-NIR spectrum was observed exhibiting several isosbestic points (Fig. 1-4c). The spectrum observed after oxidation should be assigned to **1-1**$^{\bullet+}$ by considering similarity in the spectral shape of the newly appeared species to that of **1-2**$^{\bullet+}$. However, the spectrum of oxidized species showed notable decay upon standing, suggesting slow decomposition of of **1-1**$^{\bullet+}$ by deprotonation.

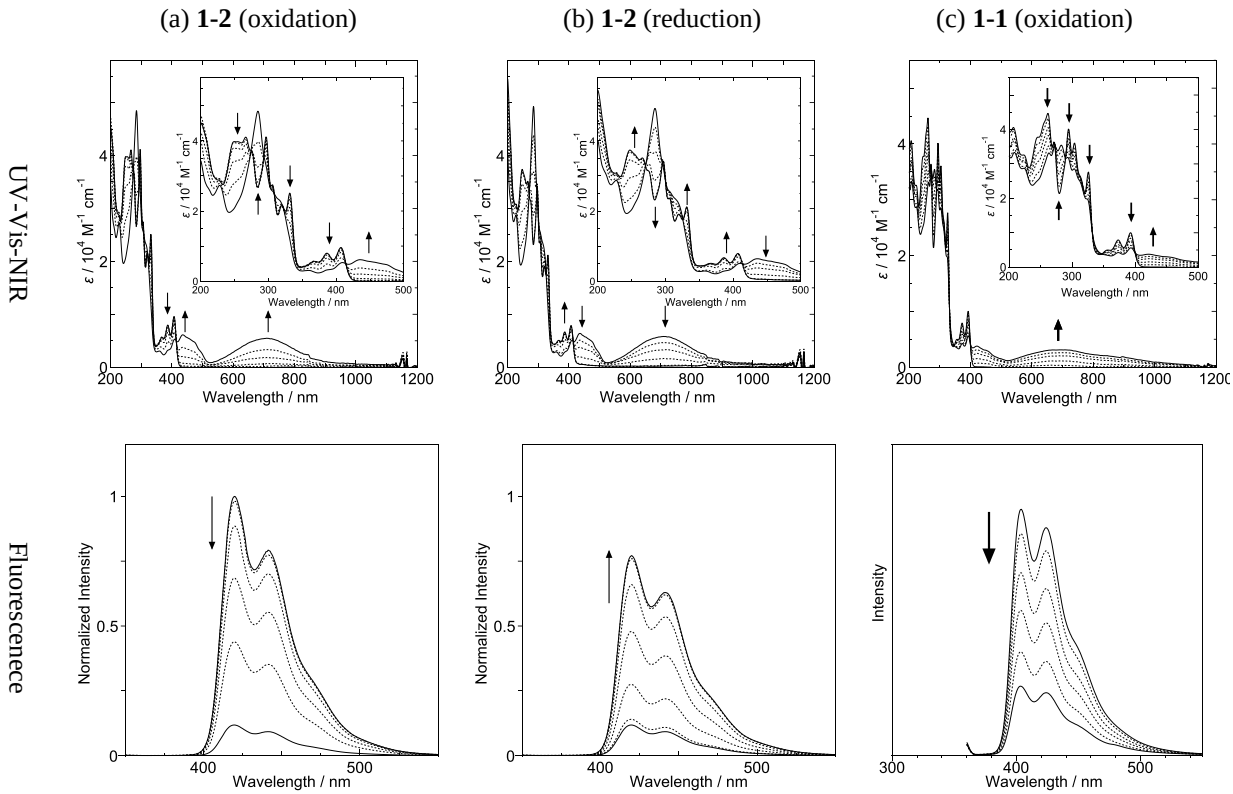


Fig. 1-4. Continuous changes in UV-Vis-NIR and fluorescence spectra upon constant current electrochemical (a) oxidation and (b) continuous reduction of **1-2** (5.3×10^{-6} M) in MeCN containing 0.05 M Et_4NClO_4 (20 μA, every 2 min (oxi.), 1 min (red.)) on Pt electrode. (c) Continuous changes in UV-Vis-NIR and fluorescence spectra upon constant current electrochemical oxidation of **1-1** (1.1×10^{-5} M) in MeCN containing 0.05 M Et_4NClO_4 (20 μA, every 2 min) on Pt electrode.

1.9. Summary

The title electron diamine donors (**1-1**) prepared through gold(I)-catalyzed cascade cyclization as a key step undergo a reversible one-electron oxidation process. *N*,*N*'-dimethyl derivative (**1-2**) is superior than the parent molecule (**1-1**) in terms of high stability in the cationic states. Isolation and high-quality X-ray analyses of **1-2**$^{\bullet+}$ salt enabled detailed comparisons of geometry before and after the oxidation. Upon electrolysis, **1-1** and **1-2** exhibited electrochromic response in the UV-Vis-NIR region, which was accompanied by a drastic change in fluorescence spectrum since only the neutral donor is highly fluorescent.

1.10. Experimental

General Methods.

General Methods. IR spectra were determined on a JASCO FT/IR-4100 spectrometer. Exact mass (HRMS) spectra were recorded on JMS-HX/HX 110A mass spectrometer. 1 H NMR spectra were recorded using a JEOL AL-500 spectrometer at 500 MHz frequency. Chemical shifts are reported in δ (ppm) relative to Me4Si (in CDCl3) as internal standard. 13C NMR spectra were recorded using a JEOL AL-500 and referenced to the residual solvent signal. Melting points were measured by a hot stage melting points apparatus (uncorrected).

Preparation of radical cation salt **1-2**$^{\bullet+}BF_4^-$.

To a solution of **1-2** (12.0 mg, 35.9 μmol) in dry CH_2Cl_2 (4 mL) was added a solution of tris(4-bromophenyl)aminium tetrafluoroborate (17.0 mg, 29.9 μmol) in MeCN at ambient temperature under Ar, and the mixture was stirred for 4 h. The dark blue powder was precipitated by adding of dry benzene then the precipitation was isolated by filtration under reduced pressure and rinsed with 20 mL of dry benzene then 10 mL of dry Et_2O to give **1-2**$^{\bullet+}BF_4^-$ (12.0 mg, yield 95%).

Data for 5,10-Dihydrobenzo[*a*]indolo[2,3-*c*]carbazole **(1-1)**

^{1}H NMR (500 MHz, DMSO-d_6) δ: 7.41 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.49 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.73-7.76 (m, 2H), 7.78 (d, *J* = 7.4 Hz, 2H), 8.72-8.75 (m, 2H), 8.83 (d, *J* = 7.4 Hz, 2H), 12.28 (br s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 111.5 (2C), 112.2 (2C), 118.9 (2C), 120.6 (2C), 122.2 (2C), 122.5 (2C), 122.8 (2C), 123.7 (2C), 125.2 (2C), 130.8 (2C), 138.6 (2C). HRMS (ESI) calcd for $C_{22}H_{14}N_2$ (M^+): 306.1157; found: 306.1158. Absorbance (MeCN): λ_{abs} / nm (log ε) 393 (3.99), 373 (3.89), 357 (3.69), 326 (4.44), 313sh (4.41), 304 (4.55), 295 (4.60), 272 (4.55), 263 (4.63), 256sh (4.61), 246 (4.56), 207 (4.58)

Data for 5,10-dimethylbenzo[*a*]indolo[2,3-*c*]carbazole **(1-2)**

^{1}H NMR (500 MHz, DMSO-d_6) δ: 4.46 (s, 6H), 7.41 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.54 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.70-7.74 (m, 2H), 7.82 (d, *J* = 7.7 Hz, 2H), 8.86 (d, *J* = 7.7 Hz, 2H), 8.98-9.00 (m, 2H), ^{13}C NMR (125 MHz, DMSO-d_6) δ: 34.6 (2C), 109.7 (2C), 113.1 (2C), 118.8 (2C), 121.5 (2C), 121.8 (2C), 121.9 (2C), 123.2 (2C), 123.8 (2C), 124.2 (2C), 131.5 (2C), 140.9 (2C); IR (KBr): *v* / cm^{-1} 3047, 2932, 1608, 1480, 1470, 1464, 1434, 1423, 1390, 1362, 1339, 1331, 1259, 1230, 1211, 1158, 1144, 1103, 1032, 1016, 921, 734, 579, 473; HRMS (ESI) calcd for $C_{24}H_{18}N_2$ (M^+): 334.1470; found: 334.1467. Absorbance (MeCN): λ_{abs} / nm (log ε) 408 (3.98), 387 (3.90), 368 (3.75), 332 (4.40), 320 (4.33), 306 (4.44), 297 (4.61), 276 (4.56), 267 (4.61)

Data for **1-2**$^{\bullet+}BF_4^-$:

m.p. 203-204 °C (DMSO-benzene); IR (KBr): ν / cm^{-1}: 3078, 1565, 1546, 1468, 1443, 1384, 1367, 1326, 1312, 1394, 1229, 1197, 1100, 1084, 1060, 1036, 788, 744; Absorbance (MeCN): λ_{abs} / nm (log ε): 702 (3.80), 435 (3.83), 285 (4.71).

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[14] Relatively a large thermal ellipsoid was observed for many atoms, suggesting that the disk-like shape of the molecule allows an in-plane dislocation or a rotational motion in the crystal lattice.

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Chapter 2.

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

2.1. Introduction

The electrochiroptical response systems are novel class of molecular response systems which give chiroptical output, for example, changes of circular dichroism (CD) or optical rotatory dispersion (ORD) spectrum when electric potential is applied. Such materials may be candidate for applications such as optical displays, telecommunications, or molecular electronics. For example, Canary group reported Cu(II) complex coordinated with tris(quinoline) compound and thiocyanate ion. This complex shows an intense split CD spectrum, whereas Cu(I) complex formed by reductive electron transfer affords further weaker CD signals.

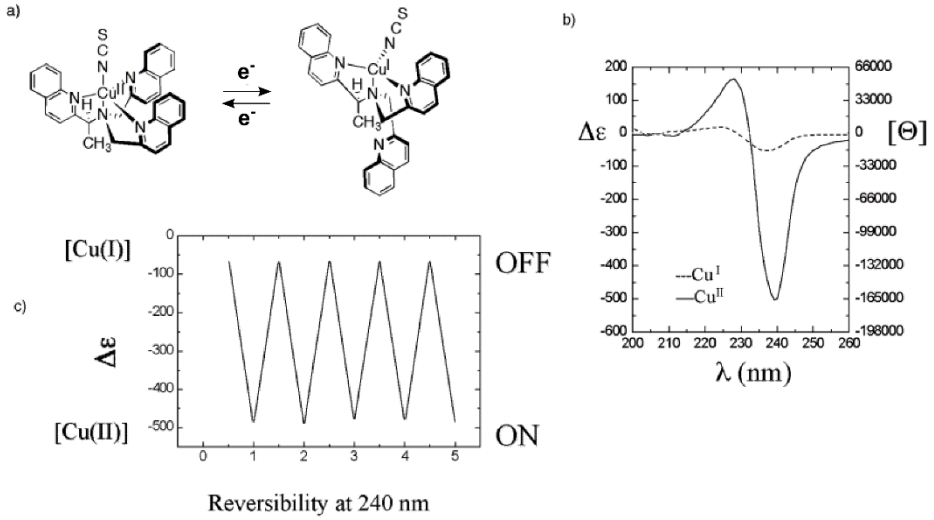
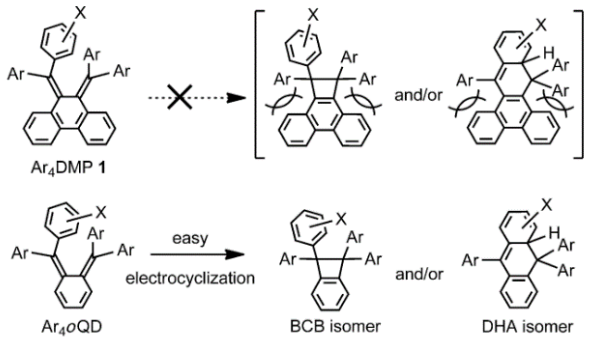


Fig. 2-1. On/off chiroptical molecular switch. (a) One-electron reduction results in dissociation of an arm of the tripodal ligand; (b) CD spectra of Cu^{+} and Cu^{2+} complexes; (c) oxidation and reduction cycles with ascorbate and persulfate.

2.1.1. 7,7,8,8-tetraaryl-*o*-quinodimethane

o-Quinodimethane (*o*QD) is a unique molecule with a cross-conjugating π-electron system. This hydrocarbon as well as its derivatives have been known as versatile building blocks in synthetic chemistry due to their high reactivity for stereoselective Diels-Alder reactions.[1] In the case of sterically hindered 7,7,8,8-tetraaryl-*o*-quinodimethanes (Ar_4*o*QDs) attached with four benzene rings on the exocyclic carbons, such intermolecular reactivities are suppressed due to steric conjestion, which also causes the unique helical arrangement of π-electrons as in the cases of helicenes consisting of *ortho*-fused benzene rings. Unlike

many helicenes, however, Ar$_4$*o*QDs are unstable. Spectroscopic characterization can be conducted only at low temperature due to facile isomerization to 1,1,2,2-tetraarylbenzocyclobutene (BCB) or 9,9a-dihydro-9,9,10-triarylanthracene (DHA) through electrocyclization (Scheme 2-1).[2]



Scheme 2-1. Suppression of electrocyclization by dibenzo annulation on Ar$_4$*o*QD.

2.1.2. 9,10-bis(diarylmethylene)phenanthrene

Previously, in this laboratory, Iwashita have envisaged that Ar$_4$oQDs would become available as thermodynamically stable species by suppressing spontaneous transformation into the cyclized isomers. And thus, he designed 9,10-bis(diarylmethylene)phenanthrene (Ar$_4$DMP, **2-1**)[3] in anticipation that the dibenzo-annulation causes destabilization of the corresponding BCB and DHA isomers by additional steric repulsion but not in Ar$_4$DMP itself. That idea was supported by the PM3 calculation on Ph$_4$DMP, whose heat of formation is smaller than those of BCB- and DHA-type isomers (Fig. 2-2).

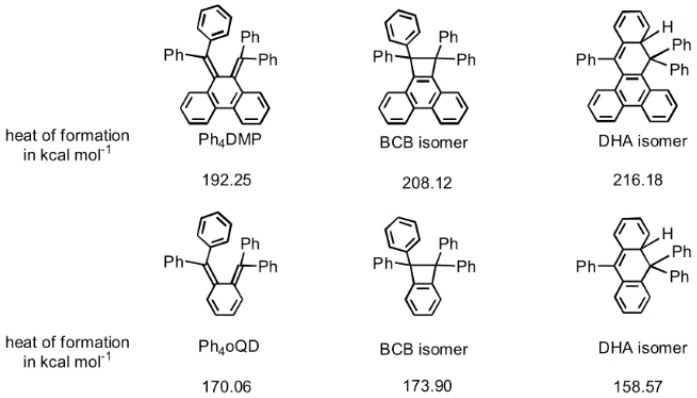
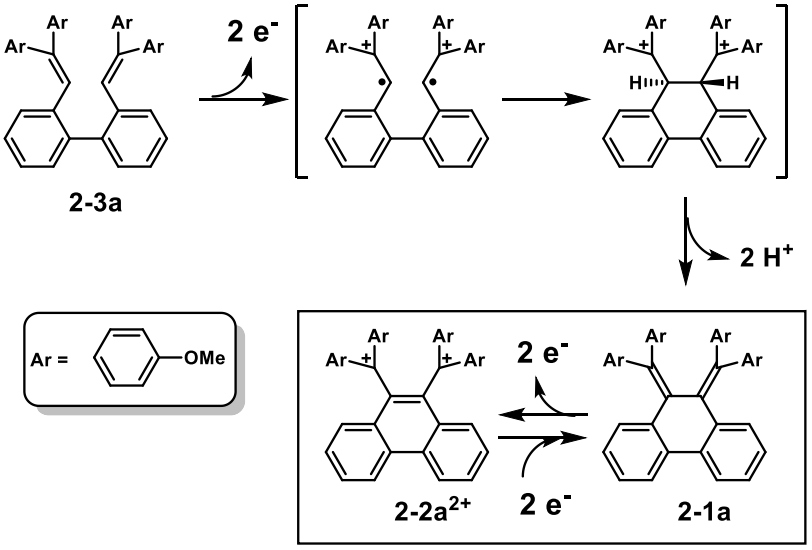


Fig. 2-2. Heat of formation calculated by PM3 for Ph$_4$DMP and Ph$_4$*o*QD and their isomers.

By considering that 1,1,4,4-tetraarylbutadienes[4] are the important members of violene/cyanine-hybrid-type[4,5] electrochromic systems,[6] he proposed the stabilized Ar$_4$DMPs **2-1** can also serve as novel chromic

material. By attaching the proper electron-donating group such as alkoxy on each of the aryl rings of **2-1**, the corresponding dications **2-2**$^{2+}$ would become stable enough to be isolated as salts that exhibit strong absorption in the visible region characteristic to triarylmethylium dyes.[7]

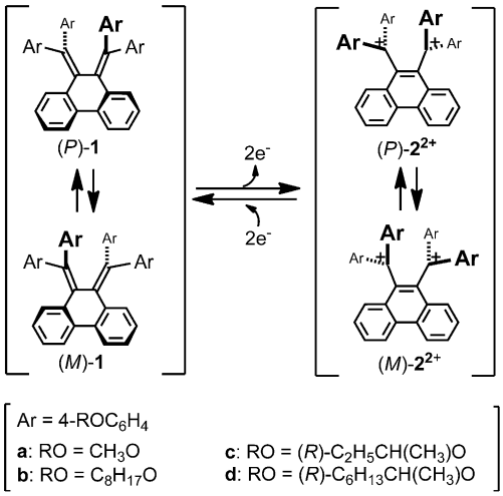
He pursued formation of tetramethoxy-substituted Ar$_4$DMPs **2-1a** from the less hindered dications **2-2a**$^{2+}$, which in turn would be obtained from 2,2'-bis(diarylethenyl)biphenyls **3a** (Scheme 2-2). The oxidative cyclization of **2-3a** to **2-2a**$^{2+}$ consists of several steps: i) C-C bond formation between the benzylidene carbons upon two-electron oxidation of **2-3**, ii) double deprotonation from the resulting butane-1,4-diyl dication[14] to give **2-1**, iii) further two-electron oxidation of **2-1a** to furnish **2-2a**$^{2+}$. He demonstrated that **2-1a** adopts helical geometry by X-ray analysis, and he also succeeded in observing electrochromic behavior by following the electrochemical oxidation of **2-1a** to **2-2a**$^{2+}$.



Scheme 2-2. Preparation of Ar$_4$DMP **2-1a** and interconversion with dicationic dye **2-2a**$^{2+}$.

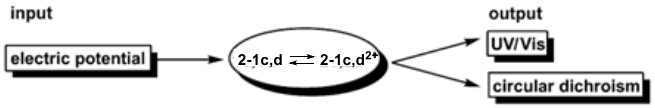
2.1.3. Design of Electrochiroptical Systems Based on Helical geometry of Ar$_4$DMPs and Dication

Because tetraarylbutadiene chromophore is framed in the helically deformed skeleton of Ar$_4$DMPs **2-1**, drastic geometric change is expected upon redox reactions. As Iwashita revealed for **2-1a**, two of the four aryl rings in Ar$_4$DMPs are forced to overlap in a proximity to cause large steric repulsion,[8] whereas two-electron oxidation would induce twisting of the diarylmethylium units around the exocyclic bond against the planarized phenanthrene core in **2-2**$^{2+}$ so as to reduce the steric repulsion. Such a structural feature endows the redox pair of **2-1**/**2-2**$^{2+}$ with the chiral element[10] of helicity of their skeletal frameworks. As the author found (*vide infra*), separation of stereoisomers cannot be conducted due to rapid inversion of their helical sense [(*P*)- **2-1**/**2-2**$^{2+}$ <=> (*M*)- **2-1**/**2-2**$^{2+}$] (Scheme 2-3).



Scheme 2-3. Helicity inversion in Ar_4DMP **2-1** and dicationic dye **2-2**$^{2+}$.

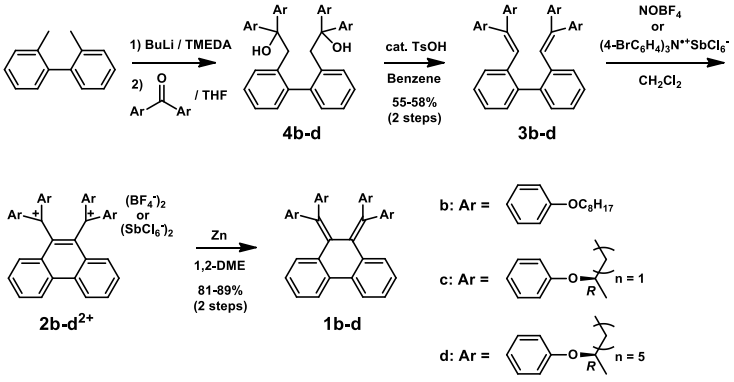
In this chapter, the author report successful generation and isolation of a series of $(4\text{-}ROC_6H_4)_4$DMPs **2-1b-d** [RO = $C_8H_{17}O$, (*R*)-$C_2H_5CH(CH_3)O$, (*R*)-$C_6H_{13}CH(CH_3)O$] as the new members of Ar_4oQD.[3] A noteworthy feature is that the point chirality attached on the aryl rings is transmitted to helicity preference to bias the diastereomeric ratio in **2-1c**,**d**/**2-2c**,**d**$^{2+}$,[11] thus enabled me to newly construct the electrochiroptical systems with giving two kinds of spectral outputs [UV/Vis and circular dichroism (CD)] in response to the electrochemical input[12] (Scheme 2-4).



Scheme 2-4. Electrochiropitical response system with two kinds of spectroscopic output.

2.2. Synthesis of Ar4DMP

As in the case of tetramethoxy derivative 1a, newly designed derivatives were prepared as shown in Scheme 2-5. Thus, the reaction of 2,2′-bitolyl with BuLi in the presence of TMEDA gave 2,2′-bis(lithiomethyl)biphenyl,[15] which was then treated with 4,4′-dialkoxybenzophenone 5b-d in THF to give diol **2-4b-d**. Treatment with a catalytic amount of TsOH in refluxing benzene gave **2-3b-d** in 56%, 58%, and 55% over two steps. Then, the oxidative cyclization [11] was conducted by treatment with 4 equivalents of one-electron oxidant such $NO^+BF_4^-$ or $(4\text{-}BrC_6H_4)_3N^{\bullet+}SbCl_6^-$. Without purification, the resulting deep purple dication salts of **2b-d**$^{2+}$ were subjected to reduction with Zn to give Ar_4DMPs as yellow crystals (**2-1c**, y. 89%) or yellow amorphous (**2-1b**, y. 81%; **2-1d**, 83%). As in the case of **2-1a**, no signs of electrocyclization to their isomers were observed, thus further confirming thermodynamic stability of Ar_4DMP.



Scheme 2-5. Preparation of Ar_4DHP **2-1b-d**.

2.3. Determination of inversion barrier by VT-NMR measurement

To get some clue of the configurational stability of **2-1**, The author have conducted a VT-NMR experiment on **2-1a**. In the ^{1}H NMR spectrum (300 MHz), methoxy protons on the *p*-methoxyphenyl groups appeared as two sharp singlets (3.50 and 3.30 ppm in bromobenzene-d_5) at 25 °C. The former resonance is assigned as that for the CH_3O in the inner aryl groups, which is downfield-shifted due to deshielding effects. Upon raising the temperature, the two peaks gradually became coalesced (T_c = 100 °C) and then sharp single resonance was observed at higher temperature (Fig. 2-3), showing that the inner and outer *p*-methoxylphenyl groups are exchanged with the energy barrier of 18.4 kcal mol^{-1}. This value also corresponds to the inversion of helicity [(*P*)- **2-1a** <=> (*M*)- **2-1a**], and the such a small barrier makes it impossible to conduct optical resolution of (*P*) and (*M*)- **2-1a**.

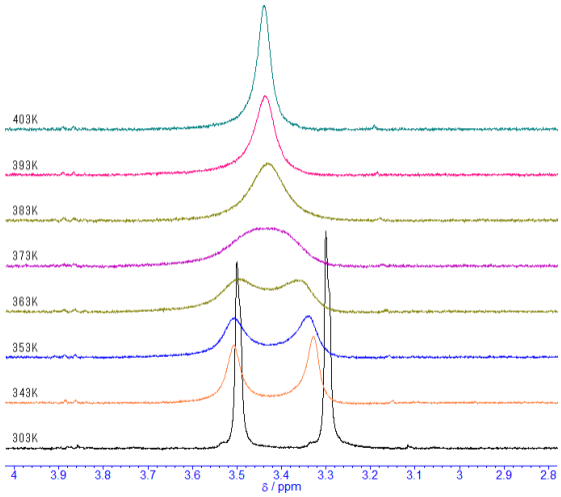


Fig. 2-3. ^{1}H-NMR (300 MHz) spectra of **2-1a** (methoxy protons) in bromobenzene-d_5 at various temperatures.

This would be also the case for other Ar$_4$DMPs **2-1b-d**. Although **2-1c,d** 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 consisting of diastereomers with the opposite sense of helicity, they were treated as single entities due to facile interconversion. In the ^{1}H NMR spectrum of **2-1c**, the only one set of resonances correesponding to a single *C*2-symmetric species were observed, showing that the two diasteromers [(*P*)- and (*M*)- **2-1c**] exhibit indistinguishable chemical shifts. Although the slightly different steric interactions for the diastereomeric pair may bias the equilibrium ratio in favor of (*P*)-helicity the value cannot be determined experimentally in **2-1c** nor in **2-1d** by the same reason.

2.4. Structural features by X-ray crystal structural analyses

To determine the detailed structural features of the isolable derivative of Ar$_4$oQD, the low-temperature X-ray analysis of **2-1a** was conducted by Iwashita ($CHCl_3$ solvate, *I*4bar, *Z* = 8). The most striking feature is the large torsion angle of 63.4(6)° for the Ar$_2$*C*=*C*–*C*=*C*Ar$_2$ unit although the twisting angle of the biphenyl skeleton is only 19.6(7)° as 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)°]. Such deformation is surely induced to avoid anomalous proximity of the two inner 4-methoxyphenyl groups, which are still close enough for π–π interaction (Fig. 2-4). They are overlapped nearly in parallel in a face-to-face manner with the closest contact between the facing aromatic carbons of 3.19(1) Å, which is much shorter than the sum of the van der Waals radii (3.40 Å).

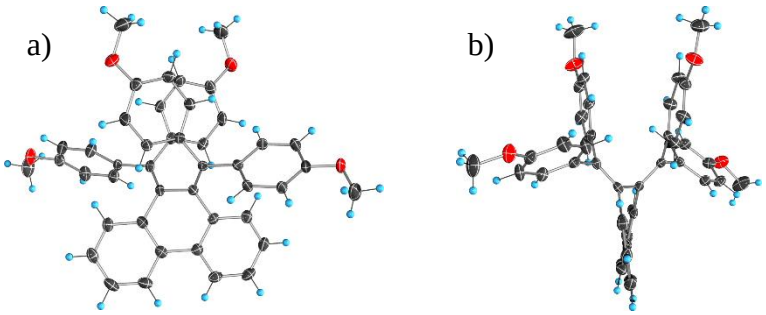


Fig. 2-4. Top view and side view of X-ray structures of (*P*)-**2-1a** in the racemic crystal [**2-1a**·$(CHCl_3)_2$] determined at 123 K. Thermal ellipsoids are shown at the 50% probability level.

Upon recrystallization, the author have succeeded in obtaining single crystalline specimen of **2-1c** (*P*212121, *Z* = 8, two independent molecules). Interestingly, the crystal is composed of an equal amount of diastereomers [(*P*)-**2-1c** for molecule-1, (*M*)-**2-1c** for molecule-2], which is less common crystallizing phenomenon.[11a,b] Thus, its X-ray analysis provided the structural information on both diastereomers with the same point chiralities on the aryl rings but with the different helical sence (Fig. 2-8b). Dispite the similar helical geometries of (*P*)- and (*M*)-isomers**,** their structural parameters marginally differ to indicate larger deformation in (*M*)-isomer. The torsion angle for the $Ar_2C{=}C{-}C{=}CAr_2$ unit, twisting angle of the biphenyl skeleton, twisting angles of the two exocyclic bonds are 23.1(9), 59.7(8), 4(1) and 2(1)° in (*P*)-isomer whereas those values in (*M*)-isomer are 25.2(8), 69.4(6), 10(1), and 8(1)°, respectively.

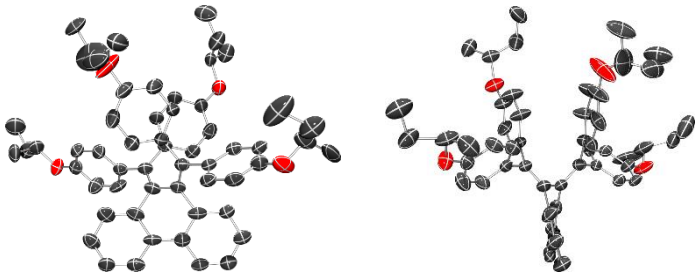


Fig. 2-5. Top view and side view of X-ray structures of (*P*)-**2-1c** in the crystal of **2-1c** containing both diastereomers [(*P*)- and (*M*)-**2-1c**] determined by X-ray analysis at 123 K. Thermal ellipsoids are shown at the 30% probability level.

2.5. Cyclic volutammetry

Not only by the electron-donating alkoxy groups but also by the observed skeletal deformation and intramolecular π–π interaction, Ar_4DMP **2-1a** has a raised HOMO level, so that it undergoes facile electrochemical oxidation (E^{ox} +0.61 V *vs*. Ag/Ag^+ in CH_2Cl_2; 2e process). Variation of the alkyl group seldom affects the donating properties (E^{ox} +0.66, +0.61, and +0.67 V Ag/Ag^+, for **2-1b-d**, respectively) (Fig. 2-6). Upon treatment of **2-1a-d** with two equivalents of $(4\text{-}BrC_6H_4)_3N^{+\cdot}SbCl_6^-$, the corresponding dication salts **2-2a-d**$^{2+}$$(SbCl_6^-)_2$ were isolated as deep purple crystals or amorphous in high yields (87, 95, 98, and 97%, respectively). Not only the salt of **2-2a**$^{2+}$ (*vide supra*) but also those of **2-2b-d**$^{2+}$ reproduced Ar_4DMP **2-1a-d** upon reduction with Zn dust in high yields (92, 95, 100, and 97%, respectively), thus confirming the reversible nature of the present redox pairs.

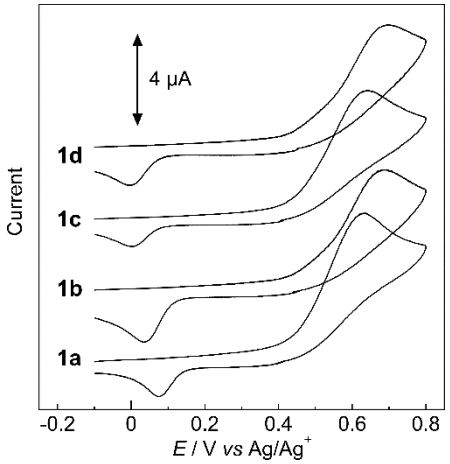


Fig. 2-6. Cyclic voltammograms of **2-1a-d** recorded in CH_2Cl_2 (c = 0.5 mM) containing Bu_4NBF_4 (0.1 mM) as a supporting electrolyte (E/V vs Ag/Ag^+, scan rate 100 mV/s, Pt electrode).

It is interesting to note that the reduction potentials of **2a-d**$^{2+}$ were observed in the far cathodic region (E^{red} +0.11, +0.07, +0.03 and +0.03 V *vs*. Ag/Ag^+ for **2a-d**$^{2+}$, respectively; 2e process). Such a large shift of redox peaks as well as one-wave 2e oxidation process have been commonly observed in the dynamic redox pairs[9] undergoing drastic structural changes and/or reversible C-C bond making/breaking upon electron transfer.[4],[5],[16] The separation by ca. 0.6 V corresponds to high electrochemical bistability of the redox couples of **2-1**/**2-2**$^{2+}$, which is favorable to realize switching phenomena of redox molecules.

2.6. Chiroptical Properties of 1c,d/2c,d^{2+} and Multi-input-multi-output Response

Upon recrystallization of **2-2c**$^{2+}$($SbCl_6^-$)$_2$ from CH_2Cl_2 - ether, a single crystalline specimen with high quality was obtained, whose X-ray analysis (*P*21, *Z* = 2) revealed that the phenanthrene core in **2-2c**$^{2+}$ is nealy planar, as expected (Fig. 2-7). The two diarylmethylium units are attached at 9,10-positions with large twisting angles [68(1) and 63(1)°] to furnish helical arrangement of π-system, whose helical sense is similar to that in (*P*)- **2-1c**. Although the helical inversion of (*P*)- **2-2c**$^{2+}$ can readily occur in solution through the rotation about C^9-C^+ and C^{10}-C^+ bonds, there are no diastereomeric dications of (*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 the shortest C -- C contact of 3.05(1) Å. Such an asymmetric geometry is suitable to realize exciton coupling[17] of the two chromophores, and the CD spectrum of **2-2c**$^{2+}$($SbCl_6^-$)$_2$ salt taken as the KBr tablet shows the negative bisignated Cotton effects in the 500-600 nm region (Fig. 2-7b).

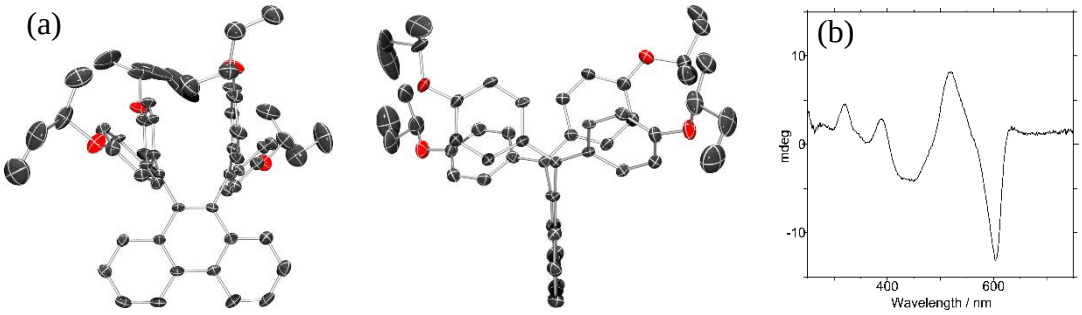


Fig. 2-7. (a) Molecular structure of dication **2-2c**$^{2+}$ in the $SbCl_6^-$ salt determined by X-ray analysis at 153 K. All of the molecules in the crystal have the same configuration of (*P*)-helicity in terms of the twisting around $C^{9(10)}$--C^+ bonds. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. (b) CD spectrum of **2-2b**$^{2+}$($SbCl_6^-$)$_2$ in KBr disk.

The large negative couplet was also observed in the CD spectrum of **2-2c**$^{2+}$($SbCl_6^-$)$_2$ salt measured in CH_2Cl_2 [λ_{ext} = 591 (Δε −23), 520 (+17) nm], showing that transmission of point chirality to helicity[11] also occurs in solution to induce preference of (*P*)-helicity in **2-2c**$^{2+}$. In the ^{1}H NMR spectrum of **2-2c**$^{2+}$($SbCl_6^-$)$_2$ in CD_3CN, the only one set of resonances correesponding to a single $C2_v$-symmetric species were observed, showing that two diasteromers [(*P*) and (*M*)- **2-2c**$^{2+}$] are interconverting so rapidly, thus preventing us from determination of diasteromeric excess in terms of the helicity preference. The observed ellipticity in **2-2c**$^{2+}$ is much larger than the reference monocation [4-(*R*)-$C_2H_5CH(CH_3)O$-C_6H_4]$_2CPh^+BF_4^-$ [λ_{ext} 508 (Δε −1.3), 411 (−0.83), 270 (−1.4) nm],[11a] which can be rationalized by effective amplification of CD signals through exciton coupling of the two

cationic chromophores in the preferred (*P*)-diastereomer. This is also the case for **2-2d**$^{2+}$ attached with (*R*)-$C_6H_{13}CH(CH_3)O$ chiral auxiliaries on the aryl group [λ_{max} 589 ($\Delta\varepsilon$ –18), 519 (+14) nm in CH_2Cl_2].

Strong CD signaling in **2-2c,d**$^{2+}$ is favored for their use as the electrochiroptical material, by which the electrochemical input is transduced into two kinds of outputs: UV/Vis and CD. Thus, upon electrochemical oxidation of **2-1c** to **2-2c**$^{2+}$, not only UV/Vis but also CD spectra changed drastically as shown in Fig. 2-8a. Presence of several isosbestic points indicates clean conversion between **2-1c** and **2-2c**$^{2+}$ as well as negligible steady-state concentration of the intermediary radical cation species. Also in the case of **2-1d**/**2-2d**$^{2+}$, the two-way-output response was similarly observed (Fig. 2-8b), thus confirming validity of our molecular design concept in constructing novel electrochiroptical systems[12] based on Ar_4DMPs by attaching chiral auxiliaries on the aryl groups.

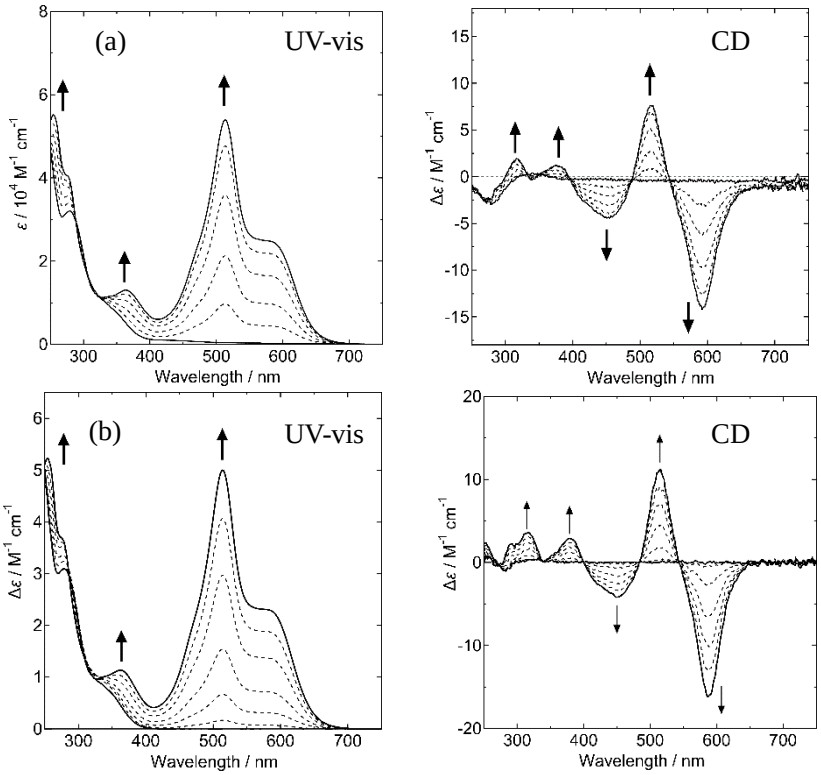


Fig. 2-8. Changes in UV/Vis and CD spectra upon constant current oxidative electrolysis of (a) **2-1c** (27 μA, every 5 min) and (b) **2-1d** (50 μA, every 5 min) in CH_2Cl_2 containing Bu_4NBF_4 (0.05 M) as a electrolyte.

2.7. Solvato- and Chirosolvatochromic Behavior of 2-2c,d^{2+}

Through the overlapping of the two cationic chromophores, electrostatic destabilization of **2-2**$^{2+}$ can be reduced by π-π interaction,[18] which is more important when the salt is dissolved in a less-polar solvent without enough stabilization by solvation.[19] Thus, the UV/Vis and/or CD spectra of some helical dicationic dyes often exhibit interesting solvent-dependency of spectra,[11a],[12i] which is also the case of the present dications **2-2**$^{2+}$. The solvatochromic behavior can be demonstrated more easily

by using **2-2b,d**$^{2+}$ with long alkyl chains thanks to their higher solubility in less-polar solvents such as benzene. As shown in Table 2-1 and Fig. 2-9, the strongest absorption band of **2-2b**$^{2+}$ appeared at 504 nm, whereas it is at 523 nm when measured in benzene. The red-shift is not so spectacular, but the continuous changes were observed in THF, CH_2Cl_2, and $CHCl_3$ with the intermediate solvent polarity. This is also the case for **2-2d**$^{2+}$ with chiral auxiliaries (Tables 2-1, 2-2, and Fig. 2-9), in which not only UV/Vis but also CD spectra change by solvent polarity. Thus, the present molecules can serve as multi-input-multi-output response systems.

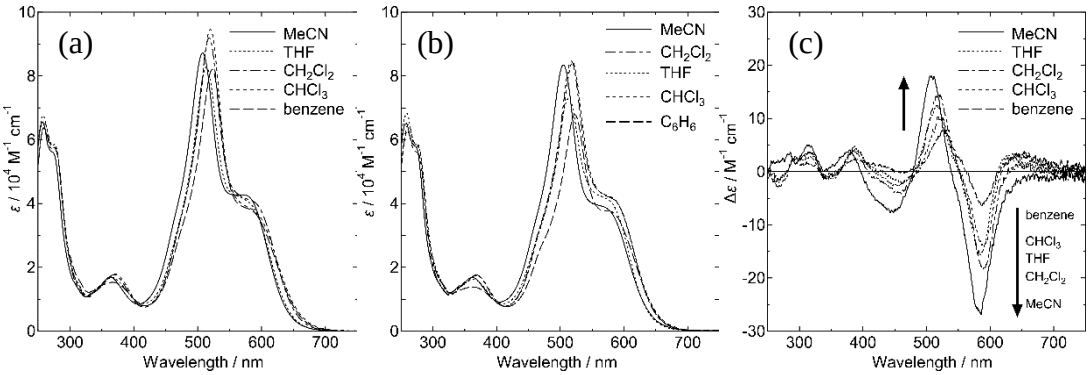


Fig. 2-9., UV-Vis spectra of (a) **2-2b**$^{2+}$$SbCl_6^-$ and (b) **2-2d**$^{2+}$$SbCl_6^-$ in a various solvents. (c) CD spectra of **2-2d**$^{2+}$$SbCl_6^-$ in a various solvents.

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

Solvent	Dielectric constant	λ [nm] (logε)	
		2b^{2+}	**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 logε) and shoulders for the first band.

Table 2-2. Solvent-dependent CD spectra[a] of $[SbCl_6^-]_2$ salts of **2-2d**$^{2+}$.

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.

2.8. Summary

The present work demonstrates that the molecular framework of Ar_4DMP **2-1** could be used as a unique platform to construct a new series of molecular response systems. The effective interconversion between the stabilized quinodimethanes **2-1** and the dicationic dyes **2-2**$^{2+}$ upon electron transfer is the key feature for establishing the novel electrochromic systems, to which the helical molecular framework in both redox states adds chiroptical properties. The mobile helicity can be biased to prefer one-handedness by the transmission of point chirality on the aryl groups especially in the dications **2-2**$^{2+}$ with a π-π stacking geometry. Due to the solvent dependency in association of the triarylmethylium units, the present

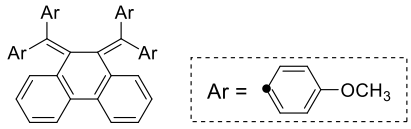
dications exhibit solvatochromic behavior, which can be detected not only in UV/Vis but also in CD spectroscopy, thus presenting the new members of the multi-input-multi-output response system.

2.9. Experimental

General method

^{1}H NMR spectra were recorded on a JEOL AL300 (300 MHz) spectrometer. IR spectra were taken on a JEOL JIR-WINSPEC100 FT/IR spectrophotometer. Mass spectra were recorded on JMS-AX500 or JMS-SX102A spectrometers in FD and FAB mode (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Column chromatography was performed on silica gel I-6-40 (YMC) of particle size 40-63 μm and alumina 90 standardized (Merck 63-200 μm). Melting points were measured on a Yamato MP-21 or a Yanagimoto micro melting point apparatus and reported uncorrected. Elemental analyses were taken on a J-Science micro corder JM10 or a Yanaco CHN corder MT-6 at the Center for Instrumental Analysis of Hokkaido University. UV/Vis spectra were recorded on a Hitachi U-3500 spectrophotometer. CD spectra were measured on a JASCO J-820 spectropolarimeter. Specific optical rotations were recorded on a JASCO P-1020 polarimeter. All commercially available compounds were used without further purification. Solvents were purified prior to use.

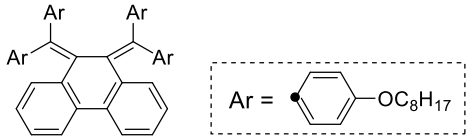
Preparation of **2-1a** from **2-2a**$^{2+}$(BF_4^-)$_2$ by reduction



To a solution of **2-2a**$^{2+}$(BF_4^-)$_2$ (50.0 mg, 62.3 μmol) in dry DME (5 mL) was added Zn powder (40.7 mg, 623 μmol) at 20 °C under Ar. After stirring for 12 h, water was added to the reaction mixture and extracted with benzene. The organic layer was washed with water and brine, and dried over Na_2SO_4. Then, the solvent was removed and the crude product was purified by column chromatography on silica gel (benzene) and recrystallization from $CHCl_3$/hexane to give **2-1a** (36.0 mg) as yellow cubes in 92% yield.

Data for **2-1a**: m.p. 97–98 °C, ^{1}H NMR (acetone-d_6) δ/ppm 7.89 (2H, d, J = 7.5 Hz),7.29 (2H, dd, J = 7.5, 7.5 Hz), 7.14 (2H, d, J = 7.5 Hz), 6.75–6.83 (16H, m), 3.84 (6H, s), 3.72 (6H, s); IR (KBr): ν/cm^{-1} 2954, 2926, 2832, 1603, 1509, 1462, 1441, 1284, 1244, 1172, 1105, 1034, 8314, 747, 732, 559; UV/Vis (MeCN): λ_{max}/nm (log ε) 325sh (4.04), 276 (4.67), 239 (4.75); LR-FDMS: *m/z* (%) 628 (M^+, BP); Anal. Calcd. (%) for $C_{44}H_{36}O_4$: C 84.05, H 5.77; Found: C 83.99, H 5.97.

Preparation of **2-1b** from **2-3b** via **2-2b**$^{2+}$



To a solution of **2-3b** (416 mg, 406 μmol) in dry CH_2Cl_2 (2 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (1.33 g, 1.63 mmol) at 24 °C under Ar, and the mixture was stirred for 7 h. The solvent was removed to give a mixture of dication salt **2-2b**$^{2+}$($SbCl_6^-$)$_2$ and tris(4-bromophenyl)ammonium hexachloroantimonate. To a solution of the residue in dry DME (4 mL) was added Zn powder (797 mg, 12.2 mmol) at 24 °C under Ar. After stirring for 22 h, the reaction mixture was diluted with AcOEt and filtrated through Celite. The

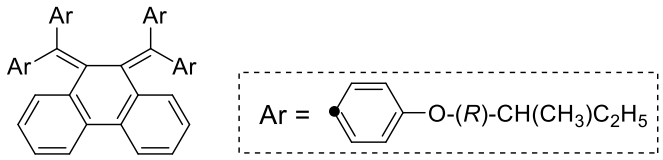
filtrate was washed with water and brine, and dried over Na_2SO_4. Then, the solvent was removed and the crude product was purified by column chromatography on alumina (hexane/CH_2Cl_2 = 5) to give **2-1b** (337 mg) as a yellow viscous oil in 81% yield.

Data for **2-1b**: ^{1}H NMR (300 MHz, acetone-d_6): δ/ppm 7.88 (2H, d, J = 7.7 Hz), 7.28 (2H, dd, J = 7.5, 7.5 Hz), 7.14 (2H, d, J = 7.7 Hz), 7.05 (2H, dd, J = 7.5, 7.5 Hz), 6.71-6.85 (16H, m), 4.05 (4H, t, 6.4 Hz), 3.89 (4H, t, J = 6.4 Hz), 1.66-1.87 (8H, m), 1.23-1.55 (40H, m), 0.84-0.93 (12H, m); IR (neat): ν/cm^{-1} 3058, 3031, 2954, 2926, 2855, 1886, 1605, 1566, 1506, 1467, 1445, 1379, 1280, 1241, 1176, 1121, 1060, 1038, 944, 829, 746, 729; LR-FDMS: m/z (%) 1021 (M^+, bp); UV/Vis (CH_2Cl_2): λ_{max}/nm (log ε) 333sh (4.01), 281 (4.51), 240 (4.73); Anal. Calcd. (%) for $C_{72}H_{92}O_4$: C 84.66, H 9.08; Found: C 84.72, H 9.19.

Preparation of **2-1b** from **2-2b**$^{2+}$($SbCl_6^-$)$_2$ by reduction

To a solution of **2-2b**$^{2+}$($SbCl_6^-$)$_2$ (49.7 mg, 29.4 μmol) in dry DME (2 mL) was added Zn powder (57.7 mg, 882 μmol) at 20 °C under Ar. After stirring for 14 h, the reaction mixture was diluted with AcOEt and washed with water and brine, and dried over Na_2SO_4. Then, the solvent was removed and the crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 6 → 3) to give **2-1b** (28.6 mg) as a yellow viscous oil in 95% yield.

Preparation of **2-1c** from **2-3c** via **2-2c**$^{2+}$



To a solution of **2-3c** (178 mg, 222 μmol) in dry CH_2Cl_2 (2 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (726 mg, 890 μmol) at 20 °C under Ar, and the mixture was stirred for 24 h. The solvent was removed to give a mixture of dication salt **2-2c**$^{2+}$($SbCl_6^-$)$_2$ and tris(4-bromophenyl)ammonium hexachloroantimonate. To a solution of the residue in dry DME (4 mL) was added Zn powder (582 mg, 8.90 mmol) at 22 °C under Ar. After stirring for 18 h, the reaction mixture was diluted with AcOEt and filtrated through Celite. The filtrate was washed with water and brine, and dried over Na_2SO_4. Then, the solvent was removed and the crude product was purified by column chromatography on alumina (hexane/CH_2Cl_2 = 5) to give **2-1c** (158 mg) as a yellow solid in 89% yield. Recrystallization from hexane/EtOH gave yellow crystals of **2-1c** that contain equal amount of diastereomers (*P*)/(*M*)- **2-1c**.

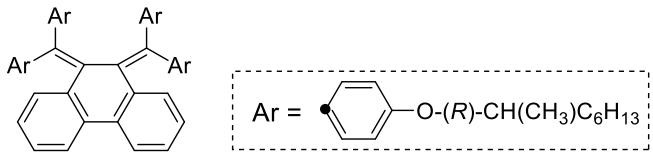
Data for **2-1c:** mp 142-143 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (2H, d, J = 7.9 Hz), 7.25 (2H, m), 6.97–7.04 (4H, m), 6.65–6.82 (16H, m), 4.31 (2H, sextet, J = 6.0 Hz), 4.18 (2H, sextet, J = 6.0 Hz), 1.49–1.88 (8H, m), 1.35 (6H, t, J = 6.6 Hz), 1.22 (6H, d, J = 5.8 Hz), 1.02 (6H, m, J = 7.4 Hz), 0.93 (6H, t, J = 7.4 Hz); IR (KBr): ν/cm^{-1} 3057, 3029, 2970, 2933, 2877, 2360, 1891, 1603, 1571, 1504, 1478, 1463, 1444, 1376, 1279, 1240, 1179, 1127, 1097, 1028, 989, 922, 830, 748, 733, 639, 618, 611, 566; LR-FDMS: m/z (%) 796 (M^+, bp), 398 (M^{2+}, 6); $[\alpha]^{25}_D$ = –26 (c = 0.98 in $CHCl_3$); UV/Vis (CH_2Cl_2): λ_{max}/nm (log ε)

317sh (4.09), 280 (4.51); CD (CH_2Cl_2, 23 °C): λ_{ext}/nm ($\Delta\varepsilon$) 282 (−2.4); Anal. Calcd. (%) for $C_{56}H_{60}O_4$: C 84.38, H 7.59; Found: C 84.28, H 7.67.

Preparation of **2-1c** from **2-2c**$^{2+}$($SbCl_6^-$)$_2$

To a solution of **2-2b**$^{2+}$($SbCl_6^-$)$_2$ (37.6 mg, 25.6 μmol) in dry DME (2 mL) was added Zn powder (57.7 mg, 882 μmol) at 20 °C under Ar. After stirring for 18 h, the reaction mixture was diluted with AcOEt and washed with water and brine, and dried over Na_2SO_4. Then, the solvent was removed and the crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 6 → 3) to give **2-1c** (20.7 mg) as a yellow solid in quantitative yield.

Preparation of **2-1d** from **2-3d** via **2-2d**$^{2+}$



To a solution of **2-3d** (659 mg, 644 μmol) in dry CH_2Cl_2 (10 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (2.10 g, 2.57 mmol) at 22 °C under Ar, and the mixture was stirred for 15 h. The solvent was removed under give a mixture of dication salt **2-2d**$^{2+}$($SbCl_6^-$)$_2$ and tris(4-bromophenyl)ammonium hexachloroantimonate. To a solution of the residue in dry DME (10 mL) was added Zn powder (1.26 g, 19.3 mmol) at 22 °C under Ar. After stirring for 22 h, the reaction mixture was diluted with AcOEt and filtrated through Celite. The filtrate was washed with water and brine, and dried over Na_2SO_4. Then, the solvent was removed and the crude product was purified by column chromatography on alumina (hexane/CH_2Cl_2 = 5) to give a diastereomer mixture of (*P*)/(*M*)- **2-1d** (545 mg) as a yellow viscous oil in 83% yield.

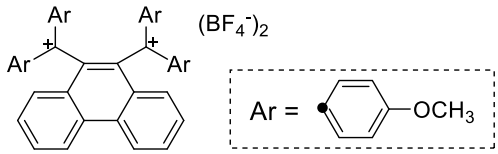
Data for **2-1d**: ^{1}H NMR (300 MHz, acetone-d_6): δ/ppm 7.89 (2H, d, J = 7.7 Hz), 7.29 (2H, dd, J = 7.5, 7.5 Hz), 7.15 (2H, d, J = 7.7 Hz), 7.05 (2H, dd, J = 7.5, 7.5 Hz), 6.72-6.85 (16H, m), 4.46-4.60 (2H, m), 4.37 (2H, sextet, J = 6.1 Hz), 1.15-1.86 (52H, m), 0.82-0.92 (12H, m); IR (neat): ν/cm^{-1} 3058, 3031, 2954, 2926, 2855, 1886, 1605, 1566, 1506, 1467, 1445, 1379, 1280, 1241, 1176, 1121, 1060, 1038, 944, 829, 746, 729; LR-FDMS: m/z (%) 1021 (M^+, bp); $[\alpha]^{23}_D$ = +1.2 (c = 1.0 in $CHCl_3$); UV/Vis (CH_2Cl_2): λ_{max}/nm (log ε) 334sh (3.99), 282 (4.50), 240 (4.73); CD (CH_2Cl_2, 20 °C): λ_{ext}/nm ($\Delta\varepsilon$) 283 (−0.8); Anal. Calcd. (%) for $C_{72}H_{92}O_4$: C 84.66, H 9.08; Found: C 84.72, H 9.19.

Preparation of 1d from **2-2d**$^{2+}$($SbCl_6^-$)$_2$

To a solution of **2-2d**$^{2+}$($SbCl_6^-$)$_2$ (50.9 mg, 30.1 μmol) in dry DME (2 mL) was added Zn powder (59.1 mg, 903 μmol) at 20 °C under Ar. After stirring for 14 h, the reaction mixture was diluted with AcOEt and filtrated through Celite. The filtrate was washed with water and brine, and dried over Na_2SO_4. Then, the solvent was removed and the crude product was purified by column chromatography on silica gel

(hexane/CH_2Cl_2 = 6 → 3) to give **2-1d** (29.7 mg) as a yellow viscous oil in 97% yield.

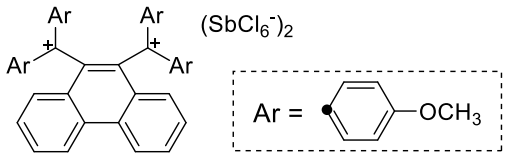
Preparation of **2-2a**$^{2+}$(BF_4^-)$_2$ from **2-3a**



To a solution of **2-3a** (417 mg, 0.659 mmol) in dry CH_2Cl_2 (6 mL) was added $NOBF_4$ (312 mg, 2.67 mmol) under Ar, and the mixture was stirred for 14 h at 20 °C. After addition of dry ether (50 mL), the resultant precipitates were filtered to give **2-2a**$^{2+}$(BF_4^-)$_2$ (498 mg) as a dark purple solid in 94% yield.

Data for **2-2a**$^{2+}$(BF_4^-)$_2$: m.p. 172-174 °C; ^{1}H NMR (CD_3CN): δ/ppm 9.07 (2H, d, J = 8.4Hz), 7.94 (2H, dd, J = 8.4, 8.4 Hz), 7.54–7.60 (10H, m), 7.41 (2H, d, J = 8.4 Hz), 7.06 (8H, AA'XX'), 4.03 (12H, s); UV/Vis (MeCN): λ_{max}/nm (log ε) 550sh (4.50), 502 (4.76), 366 (4.11), 272 (4.48), 254 (4.65); Anal. Calcd. (%) for $C_{44}H_{36}O_4B_2F_8 \cdot 2.5H_2O$: C 62.36, H 4.88; Found: C 62.32, H 4.46.

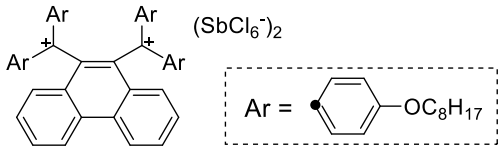
Preparation of **2-2a**$^{2+}$($SbCl_6^-$)$_2$ from **2-1a**



To a solution of **2-1a** (30.2 mg, 48.0 μmol) in dry CH_2Cl_2 (3 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (78.4 mg, 96.0 μmol) under Ar, and the mixture was stirred for 20 h at 22 °C. After addition of dry ether (50 mL), the resultant precipitates were filtered to give **2-2a**$^{2+}$($SbCl_6^-$)$_2$ (57.5 mg) as a dark purple solid in 93% yield.

Data for **2-2a**$^{2+}$($SbCl_6^-$)$_2$: m.p. 179-183 °C; ^{1}H NMR (300 MHz, CD_3CN): δ/ppm 9.07 (2H, d, J = 8.4 Hz), 7.94 (2H, dd, J = 8.4, 8.4 Hz), 7.54–7.61 (10H, m), 7.41 (2H, d, J = 8.4 Hz), 7.06 (8H, AA'XX'), 4.04 (12H, s); IR (KBr) ν/cm^{-1} 2938, 2849, 2365, 1605, 1578, 1445, 1376, 1372, 1284, 1160, 999, 895, 845, 520; UV/Vis (MeCN): λ_{max}/nm (log ε) 550sh (4.50), 502 (4.76), 366 (4.11), 272 (4.48), 254 (4.65); HR-FABMS: m/z Calcd. for $C_{44}H_{36}O_4$ [M−2$SbCl_6$]$^+$: 628.2614, found: 628.2618.

Preparation of **2-2b**$^{2+}$($SbCl_6^-$)$_2$ from **2-1b**

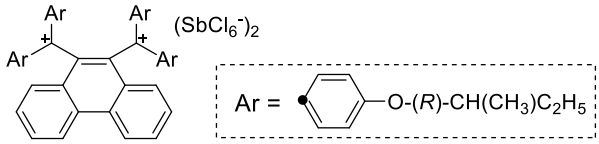


To a solution of **2-1b** (99.2 mg, 97.1 μmol) in dry CH_2Cl_2 (2 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (158.6 mg, 194.2 μmol) at 23 °C under Ar, and the mixture was stirred for 2 h. The solvent was removed under reduced pressure. The residue was dissolved in dry CH_3CN (2 mL), and the solution was washed with dry hexane (20 mL × 5). Then, the solvent was removed and the residue was dried *in vacuo* to give **2-2b**$^{2+}$($SbCl_6^-$)$_2$ (156 mg) as a dark purple solid in 95% yield.

Data for **2-2b**$^{2+}$($SbCl_6^-$)$_2$: m.p. 66-67 °C; ^{1}H NMR (300 MHz, CD_3CN): δ/ppm 9.06 (2H, d, J = 8.3 Hz), 7.93 (2H, ddd, J = 7.2, 7.1, 1.2 Hz), 7.39-7.61 (12H, m), 7.02 (8H, brm), 4.30-4.16 (8H, m), 1.67-1.81 (8H,

brm), 1.18-1.42 (40H, m), 0.85-0.91 (12H, m); ^{13}C NMR (75 MHz, CD_3CN): δ/ppm 188.79, 174.20, 145.55, 140.63, 133.61, 133.03, 132.55, 131.36, 129.86, 129.64, 124.47, 119.17, 72.34, 32.49, 29.87, 29.82, 29.30, 26.28, 23.32, 14.36; IR (KBr): ν/cm^{-1} 2925, 2854, 1610, 1578, 1447, 1377, 1318, 1284, 1184, 1161, 968, 895, 845, 801, 758, 723; UV/Vis (CH_2Cl_2): λ_{max}/nm (log ε) 575sh (4.62), 517 (4.93), 369 (4.25), 271sh (4.75), 260 (4.80); HR-FDMS: *m*/*z* Calcd. for $C_{72}H_{92}Cl_6O_4Sb$ [M−$SbCl_6$]$^+$: 1351.4187, found: 1351.4165.

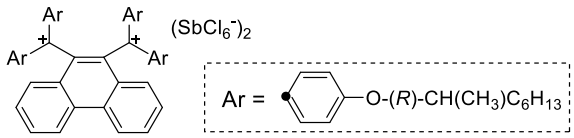
Preparation of **2-2c**$^{2+}$($SbCl_6^-$)$_2$ from **2-1c**



To a solution of **2-1c** (45.1 mg, 56.4 μmol) in dry CH_2Cl_2 (1 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (91.4 mg, 112 μmol) at 22 °C under Ar, and the mixture was stirred for 24 h. The solvent was removed under reduced pressure. The residue was dissolved in dry CH_3CN (2 mL), and the solution was washed with dry hexane (15 mL × 5). Then, the solvent was removed and the residue was dried in vacuo to give **2-2c**$^{2+}$($SbCl_6^-$)$_2$ (81.0 mg) as a dark purple solid in 98% yield.

Date for **2-2c**$^{2+}$ ($SbCl_6^-$)$_2$: m.p. 196–197 °C (decomp.); ^{1}H NMR (300 MHz, CD_3CN): δ/ppm 9.06 (2H, d, *J* = 8.4 Hz), 7.93 (2H, dt, *J* = 7.7, 1.0 Hz), 7.44–7.62 (12H, m), 7.00 (8H, br), 4.71 (4H, m), 1.68 (8H, m), 1.29 (6H, d, *J* = 6.0 Hz), 1.25 (6H, d, *J* = 6.0 Hz), 0.91 (6H, t, *J* = 7.4 Hz), 0.90 (6H, t, *J* = 7.4 Hz); IR (KBr) 2976, 2359, 1611, 1578, 1450, 1376, 1287, 1160, 1101, 1080, 1024, 993, 969, 935, 913, 895, 848, 801, 766, 726, 628, 558, 529 cm^{-1}; LR-FABMS: *m*/*z* = 796 ([M−2$SbCl_6$]$^+$, 12%); UV/Vis (CH_2Cl_2): λ_{max}/nm (log ε) 579sh (4.62), 517 (4.98), 369 (4.29), 274sh (4.77), 259 (4.83); CD (CH_2Cl_2, 23 °C): λ_{ext}/nm ($\Delta\varepsilon$) 594 (–20), 519 (+15), 453 (–6.2), 377 (+1.8), 339 (–0.4), 315 (+3.2), 278 (–1.4), 259 (+1.2); Anal. Calcd. (%) for $C_{56}H_{60}Cl_{12}Sb_2O_4$: C 45.88, H 4.13; Found: C 45.59, H 4.02.

Preparation of **2-2d**$^{2+}$($SbCl_6^-$)$_2$ from **2-1d**

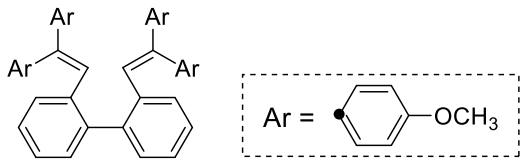


To a solution of **1d** (109.7 mg, 107.4 μmol) in dry CH_2Cl_2 (1 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (175.4 mg, 214.8 μmol) at 22 °C under Ar, and the mixture was stirred for 5 h. The solvent was removed under reduced pressure. The residue was dissolved in dry CH_3CN (2 mL), and the solution was washed with dry hexane (10 mL × 9). Then, the solvent was removed and the residue was dried in vacuo to give **2-2d**$^{2+}$($SbCl_6^-$)$_2$ (177 mg) as a dark purple solid in 97% yield.

Data for **2-2d**$^{2+}$($SbCl_6^-$)$_2$: m.p. 96–98 °C; ^{1}H NMR (300 MHz, CD_3CN): δ/ppm 9.06 (2H, d, *J* = 8.3 Hz), 7.93 (2H, ddd, *J* = 7.2, 7.1, 1.2 Hz), 7.41-7.63 (12H, m), 6.98 (8H, brm), 4.67-4.81 (4H, m), 1.66 (8H, brm), 1.18-1.38 (44H, m), 0.85-0.91 ppm (12H, m); ^{13}C NMR (75 MHz, CD_3CN): δ/ppm 188.03, 173.62,

173.34, 145.69, 145.26, 140.67, 133.21, 132.96, 132.50, 131.31, 129.85, 129.59, 124.47, 119.55, 118.2, 79.39, 79.07, 36.56, 36.52, 32.38, 29.75, 29.71, 25.78, 23.23, 19.95, 19.84, 14.32; IR (KBr): ν/cm^{-1} 2929, 2856, 2357, 2342, 1610, 1577, 1448, 1378, 1285, 1185, 1163, 1110, 1066, 1030, 1008, 969, 936, 896, 846, 802, 757, 723, 668, 615, 587, 562, 524; UV/Vis (CH_2Cl_2): λ_{max}/nm (log ε) 579sh (4.62), 518 (4.96), 369 (4.25), 276 (4.76), 260 (4.80); CD (CH_2Cl_2, 20 °C): λ_{ext}/nm ($\Delta\varepsilon$) 589 (−18), 521 (+14), 460 (−4.2), 383 (+4.2), 341 (−1.3), 317 (+3.8), 267 (−1.7); HR-FDMS: *m*/*z* Calcd. for $C_{72}H_{92}O_4$ [M−2$SbCl_6$]$^+$: 1020.6996, found: 1020.6992.

Preparation of **2-3a**

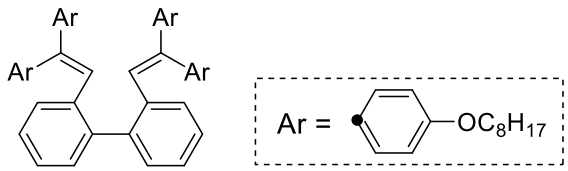


To a solution of 2,2'-dimethylbiphenyl (1.11 mL, 6.0 mmol) in dry TMEDA (1.82 mL, 12.1 mmol) was added dropwise *n*BuLi in hexane (1.58 M, 7.82 mL, 12.05 mmol) at 20 °C under Ar, and the mixture was stirred for 3 h at 65 °C. Then, to the resultant suspension of 2,2'-bis(lithiomethyl)biphenyl was added a suspension of 4,4'-dimethoxybenzophenone (**2-5a)** (2.96 g, 12.2 mmol) in 30 mL of dry THF at -20 °C, and the mixture was kept at this temperature for 2 h. Then, the whole mixture was allowed to warm and stirred for 3 h at 20 °C. After addition of water and evaporation of solvent, the remaining solid was suspended in water and mixture was extracted with 1,2-dichloroethane. The organic layer was washed with brine and dried over Na_2SO_4. The yellow solid of the intermediary diol **2-4a** (4.73 g) was obtained by evaporation of the solvent, which was directly used for the next transformation.

To a solution of crude **2-4a** in benzene (70 mL) was added a catalytic amount of TsOH·H_2O (37 mg, 0.19 mmol). After refluxing for 2 h, further TsOH·H_2O (120 mg, 0.63 mmol) was added and reflux was continued for 60 h under dehydrating conditions (Dean-Stark). Water was added to the suspension and extracted with benzene. The organic layer was washed with water and brine, and dried over Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography on silica gel (CH_2Cl_2/hexane = 1/1) and recrystallization (hexane-CH_2Cl_2) to give **2-3a** (1.91 g) as colorless prisms in 50% yield.

Data for **2-3a**: m.p. 191-192 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.23 (2H, d, J = 7.5 Hz), 7.15 (2H, dd, J = 7.5, 7.5 Hz), 7.06 (4H, AA'XX'), 6.95 (2H, dd, J = 7.5, 7.5 Hz), 6.83-6.88 (6H, m), 6.77 (4H, AA'XX'), 6.43 (2H, s), 6.43 (4H, AA'XX'), 3.79 (6H, s), 3.70 (6H, s); IR (KBr): ν/cm^{-1} 2945, 2832, 1604, 1571, 1510, 1462, 1439, 1366, 1291, 1246, 1172, 1146, 1110, 1034, 1004, 835, 756, 619, 584, 537, 522, 511; LR-FDMS: *m*/*z* (%) 630 (M$^+$, bp); Anal. Calcd. (%) for $C_{44}H_{38}O_4$: C 83.78, H 6.07; Found: C 83.69, H 6.19.

Preparation of **2-3b**

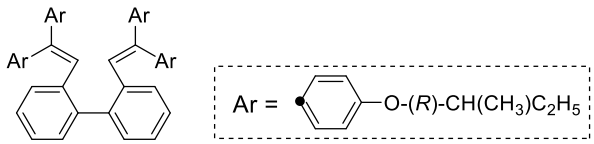


To a solution of 2,2-dimethylbiphenyl (543 mg, 3.0 mmol) in dry TMEDA (0.91 mL, 6.0 mmol) was added dropwise *n*BuLi in hexane (1.63 M, 3.70 mL, 6.0 mmol) at 21 °C under Ar, and the mixture was stirred for 3 h at 65 °C. After the resultant suspension of 2,2'-bis(lithiomethyl)biphenyl was diluted with dry THF (40 mL) at -20 °C, 4,4'-dioctyloxybenzophenone (**2-5b**) (2.68 g, 2.0 mmol) was added to the mixture, and the mixture was kept at this temperature for 10 min. Then, the whole mixture was allowed to warm and stirred for 16 h at 21 °C. After addition of water (3 mL) and evaporation of solvent, the remaining solid was suspended in water and extracted with CH_2Cl_2. The organic layer was washed with 1M HCl aq., water, and brine, and dried over Na_2SO_4. The yellow solid of the intermediary diol **2-4b** was obtained by evaporation of the solvent, which was directly used for the next transformation.

To a solution of crude diol **2-4b** in benzene (30 mL) was added a catalytic amount of $TsOH \cdot H_2O$ (50 mg, 0.26 mmol). After refluxing for 20 h under the dehydration conditions (Dean-Stark), the reaction mixture was washed with water and brine, and dried over Mg_2SO_4. The solvent was removed and the crude product was purified by column chromatography on silica gel (hexane/$CHCl_3$ = 5) to give **2-3b** (1.71 g) as a pale yellow oil in 56% yield.

Data for **2-3b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.22 (2H, d, J = 7.5 Hz), 7.14 (2H, dd, J = 7.5, 7.2 Hz), 7.04 (4H, d, J = 8.6 Hz), 6.94 (2H, dd, J = 7.8, 7.2 Hz), 6.85 (6H, m), 6.75 (4H, d, J = 8.6 Hz), 6.38-6.45 (6H, m), 3.91 (4H, t, J = 6.6 Hz), 3.81 (4H, t, J = 6.6 Hz), 1.67-1.81 (4 H, m), 1.22-1.49 (40H, m), 0.84-0.92 (12H, m); IR (neat): ν/cm^{-1} 3058, 3036, 2926, 2856, 1891, 1606, 1571, 1510, 1468, 1377, 1290, 1244, 1172, 1110, 1030, 952, 831, 755; LR-FDMS: m/z (%) 1023 (M^+, bp); Anal. Calcd. (%) for $C_{72}H_{94}O_4$: C 84.49, H 9.26; Found: C 84.49, H 9.50.

Preparation of **2-3c**

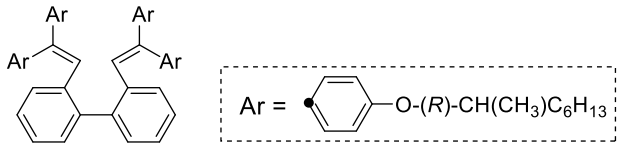


To a solution of 2,2'-dimethylbiphenyl (200.5 mg, 1.1 mmol) in dry TMEDA (350 μL, 2.3 mmol) was added *n*BuLi in hexane (1.62 M, 1.42 mL, 2.31 mmol) at 22 °C under Ar, and the mixture was stirred for 3 h at 65 °C. Then, to the resultant suspension of 2,2'-bis(lithiomethyl)biphenyl was add a solution of 4,4'-bis[(*R*)-*sec*-butyloxy]benzophenone (**2-5c**) (755 mg, 2.31 mmol) in dry THF (5.5 mL) at -20 °C, and the mixture was kept at this temperature for 10 min. Then, the whole mixture was allowed to warm and stirred for 18 h at 22 °C. After addition of water (1 mL) and evaporation of solvent, the remaining solid was suspended in water and extracted with CH_2Cl_2. The organic layer was washed with 1M HCl aq. and water, and dried over Na_2SO_4. The yellow oil of the intermediary diol **2-4c** (1.01 g) was obtained by evaporation of the solvent, which was directly used for the next transformation.

To a solution of crude diol **2-4c** in benzene (10 mL) was added a catalytic amount of $TsOH \cdot H_2O$ (3.0 mg, 16 μmol). After refluxing for 30 min under the dehydration conditions (Dean-Stark), the reaction mixture was washed with water and dried over Na_2SO_4. After filtration, the solvent was removed and the crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 2) and recrystallization from hexane to give **2-3c** (514 mg) as colorless prisms in 58% yield.

Data for **2-3c**: m.p. 133-134 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.21 (2H, d, J = 7.3 Hz), 7.13 (2H, t, J = 7.3 Hz), 7.06 (4H, d, J = 8.6 Hz), 6.94 (2H, t, J = 7.3 Hz), 6.87 (6H, d, J = 8.8 Hz), 6.74 (4H, d, J = 8.6 Hz), 6.38-6.46 (6H, m), 4.26 (2H, sextet, J = 6.0 Hz), 4.14 (2H, sextet, J = 5.5 Hz), 1.51-1.89 (8H, m), 1.19-1.32 (12H, m), 0.95-1.04 (12H, m); IR (KBr) ν/cm^{-1} 3056, 3032, 2970, 2933, 2877, 1604, 1570, 1508, 1465, 1415, 1375, 1288, 1242, 1178, 1146, 1127, 1113, 1098, 1028, 989, 952, 923, 833, 755, 593, 561, 519; LR-FDMS: m/z (%) 798 (M^+, bp); $[\alpha]^{24}_D$ = +21 (c = 0.89 in $CHCl_3$); Anal. Calcd. (%) for $C_{56}H_{62}O_4$: C 84.17, H 7.82; Found: C 84.23, H 7.94.

Preparation of **2-3d**



To a solution of 2,2'-dimethylbiphenyl (273 mg, 1.5 mmol) in dry TMEDA (500 μL, 3.1 mmol) was added *n*BuLi in hexane (1.62 M, 1.91 mL, 2.31 mmol) at 25 °C under Ar, and the mixture was stirred for 3 h at 50 °C. Then, to the resultant suspension of 2,2'-bis(lithiomethyl)biphenyl was add a solution of 4,4'-bis[(*R*)-2-octyloxy]benzophenone (**2-5d**) (1.36 g, 2.1 mmol) in dry THF (2 mL) at -20 °C, and the mixture was kept at this temperature for 10 min. Then, the whole mixture was allowed to warm and stirred for 13 h at 25 °C. After addition of water (1 mL) and evaporation of solvent, the remaining solid was suspended in water and extracted with EtOAc. The organic layer was washed with 1M HCl aq., water and brine, and dried over Na_2SO_4. The yellow oil of the intermediary diol **2-4d** (1.62 g) was obtained by evaporation of the solvent, which was directly used for the next transformation.

To a solution of crude diol **2-4d** in benzene (10 mL) was added a catalytic amount of $TsOH \cdot H_2O$ (5.2 mg, 28 μmol). After refluxing for 30 min under the dehydration conditions (Dean-Stark), the reaction mixture was washed with water and dried over Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography on silica gel (hexane/CH_2Cl_2 = 5) to give **2-3d** (843 mg) as a pale yellow oil in 55% yield.

Data for **2-3d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.21 (2H, d, J = 7.5 Hz), 7.13 (2H, dd, J = 7.5, 7.2 Hz), 7.06 (4H, d, J = 8.6 Hz), 6.94 (2H, dd, J = 7.8, 7.2 Hz), 6.88 (6H, m), 6.73 (4H, d, J = 8.6 Hz), 6.38-6.46 (6H, m), 4.31 (2H, sextet, J = 5.7 Hz), 4.20 (2H, sextet, J = 5.7 Hz), 1.60-1.80 (4 H, m), 1.10-1.80 (48H, m), 0.84-0.92 (12H, m); IR (neat): ν/cm^{-1} 3058, 3031, 2926, 2855, 1891, 1605, 1572, 1506, 1467, 1379, 1286, 1241, 1176, 1121, 1066, 1038, 944, 835, 757; LR-FDMS: m/z (%) 1023 (M^+, bp); $[\alpha]^{24}_D$ = +53 (c = 1.0 in $CHCl_3$); Anal. Calcd. (%) for $C_{72}H_{94}O_4$: C 84.49, H 9.26; Found: C 84.51, H 9.40.

<<X-ray Crystallography>>

・Crystal data of **2-1a**·$(CHCl_3)_2$

$C_{46}H_{38}Cl_4O_4$, M 867.52, tetragonal $I\bar{4}$, a = 27.728(4), c = 11.005(2) Å, V = 8461.0(1) Å^3, D_c (Z = 8) = 1.362 g cm^{-3}, T = 123 K, μ = 4.49 cm^{-1}. The final R value is 0.052 for 3232 independent reflections (2σ cut) and 509 parameters.

The crystal is racemic and contains both enantiomers with a difference sense of helicity [(*P*)- and (*M*)-**1a**]. There are positional disorders of chlorine atoms in one of the two solvent molecules.

・Crystal data of **2-1c**

$C_{56}H_{60}O_4$, M 797.09, orthorhombic $P2_12_12_1$, a = 14.922(2), b = 19.136(2), c = 31.779(4) Å, V = 9074(2) Å^3, D_c (Z = 8) = 1.164 g cm^{-3}, T = 143 K, μ = 0.71 cm^{-1}. The final R value is 0.1638 for 12506 independent reflections (2σ cut) and 1081 parameters.

The absolute configuration [(*R*)-configuration for the point chirality of the *sec*-butyl group] was determined by chemical correlation. The crystal contains two independent molecules: they are the diastereomers with a difference sense of helicity [(*P*)- and (*M*)-**1c**], which can be easily interconverted in solution. The final R value is relatively high due to some positional disorder for the terminal alkyl groups in (*M*)-**1c** (for ORTEP drawings: See Figure S3).

・Crystal data of **2-2c**$^{2+}$$(SbCl_6^-)_2$

$C_{56}H_{60}Cl_{12}O_4Sb_2$, M 1466.02, monoclinic $P2_1$, a = 12.920(2), b = 19.372(2), c = 12.822(1) Å, β = 103.254(2)°, V = 3123.6(6) Å^3, D_c (Z = 2) = 1.559 g cm^{-3}, T = 153 K, μ = 14.19 cm^{-1}. The final R value is 0.038 for 6230 independent reflections (2σ cut) and 668 parameters.

The absolute configuration [(*R*)-configuration for the point chirality of the *sec*-butyl group] was determined by chemical correlation. All the molecules in this crystal have a *P*-helicity.

Reference for chapter 2

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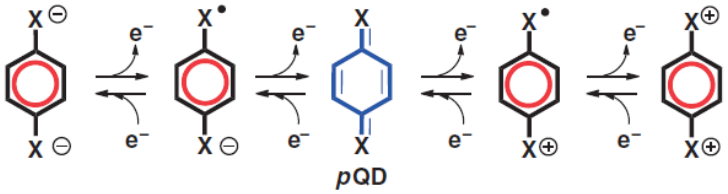
Chapter 3.

Preparation, Redox Properties, and X-ray Structures of Electrochromic 11,11,12,12-Tetraarylanthraquinodimethane and Its Bianthraquinodimethane Analogue: Drastic Geometrical Changes upon Interconversion with Dicationic Dyes

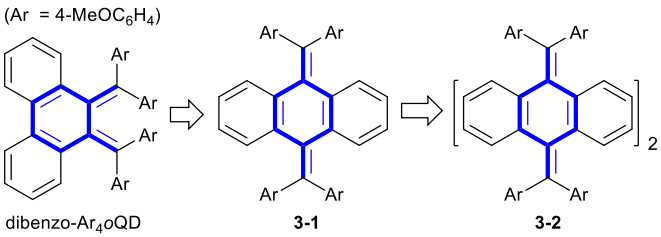
3.1. Introduction

o- and *p*-Quinodimethanes (oQD, pQD) are representative cross-conjugated π-electron systems. Attachment of charge stabilizing end groups on the exocyclic carbons provides a useful protocol to construct reversible redox systems[1-3] since generation of the Clar's sextet facilitates their redox reactions (Scheme 3-1).



Scheme 3-1. Redox scheme of a pQD-based system.

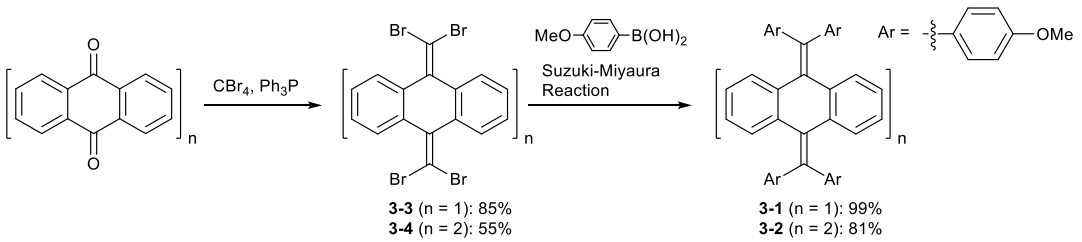
As a successful example, we previously reported tetraaryl substituted oQDs fused with two benzene rings (dibenzo-Ar$_4$*o*QDs), which undergo facile 2e-oxidation to give the corresponding dications.[4] In the course of our continuing studies[5] on novel electrochromic systems[6] based on organic cationic dyes, the author planned further exploitation of dibenzo-Ar$_4$oQD, including the study on the *p*QD-type isomer **3-1** (Scheme 3-2). Unlike the *o*QD counterpart, π-extension of the system could be attained easily in **3-1** by inserting an anthrylidene unit, as in bianthraquinodimethane **3-2**. Here the author report preparation and redox properties of **3-1** and **3-2**, along with their electrochromic behavior based on the reversible interconversion with the corresponding dications **3-1**$^{2+}$ and **3-2**$^{2+}$. The author successfully isolated the dicationic salts, whose X-ray analyses demonstrated outstanding difference in geometry between the bent form in *p*QDs (**3-1**, **3-2**) and the twisted form in the dications (**3-1**$^{2+}$, **3-2**$^{2+}$).



Scheme 3-2. Molecular design based on the QD skeletons.

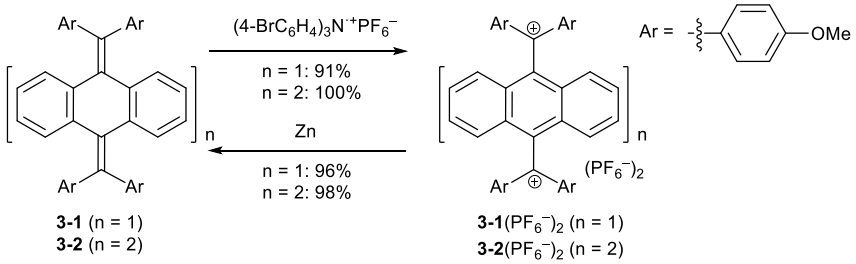
3.2. Preparation

As in the case of dibenzo-Ar$_4$oQD, 4-methoxyphenyl group was chosen as an aryl group on the exocyclic carbons to attain enough stability in the dicationic state. By the Suzuki-Miyaura coupling[7] of 11,11,12,12-tetrabromo-9,10-anthraquinodimethane **3-3**[8] and 11,11,11',11'-tetrabromo-10,10'-bianthraquinodimethane **3-4**[9] with 4-methoxyphenylboronic acid, **3-1** and **3-2** was obtained in 99% and 81% yields, respectively. (Scheme 3-3).



Scheme 3-3. Preparation of **3-1** and **3-2**.

Upon oxidation of **3-1** and **3-2** with 2 equiv. of (4-BrC$_6$H$_4$)$_3$N$^{\bullet+}$PF$_6^-$, dicationic salts **3-1**$^{2+}$(PF$_6^-$)$_2$ and **3-2**$^{2+}$(PF$_6^-$)$_2$ were obtained as green lustrous crystals in 91% and 100% yields, respectively. Upon treatment of **3-1**$^{2+}$(PF$_6^-$)$_2$ and **3-2**$^{2+}$(PF$_6^-$)$_2$ with Zn dust under argon, **3-1** and **3-2** was regenerated in 93% and 98% yields, respectively.



Scheme 3-4. Redox interconversion with oxidative and reductive agent.

3.3. Spectroscopy

The dication dye exhibits a strong absorption in visible region, characteristic to the diarylmethylium unit, along with the NIR absorption assignable to the intermolecular CT absorption from the anthracene moiety to the diarylmethylium units. [λ_{max}/nm (log ε): **3-1:** 531 (5.20), 710 (3.96); **3-2**: 530 (5.22), 728 (4.16) in CH_2Cl_2]. (Fig. 3-1)

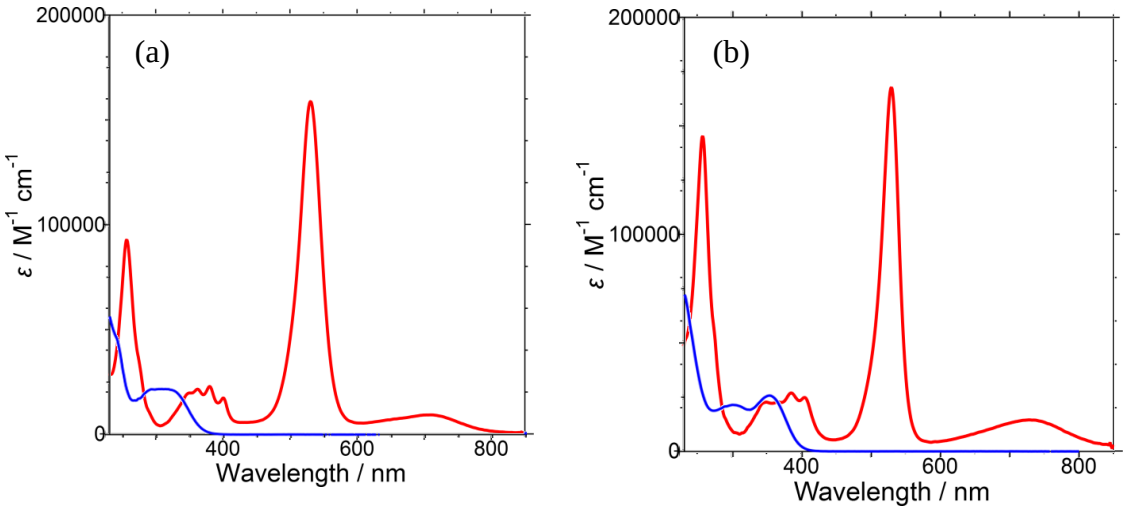


Fig. 3-1. (a) UV-Vis spectrum of **3-1** (blue) and **3-1**$^{2+}$(PF_6^-)$_2$ (red) in CH_2Cl_2. (b) UV-Vis spectrum of **3-2** (blue) and **3-2**$^{2+}$(PF_6^-)$_2$ (red) in CH_2Cl_2.

3.4. X-ray analyses

Due to steric repulsion between bulky aryl groups and the *peri*-hydrogens on the anthracene unit, both neutral and dicationic states would adopt severely deformed geometries: e.g. a butterfly shape in **3-1** and **3-2** and a largely twisted structure around the exocyclic bonds in **3-1**$^{2+}$ and **3-2**$^{2+}$. Previously, the X-ray analyses on the molecules structurally related to **3-1** had revealed the bent geometry for the 9,10-anthraquinodimethane skeleton,[10,11] and we confirmed here that **3-1** actually suffers from a similar deformation by conducting its X-ray analysis[12] [bent angle:[13] 33.2(2) and 34.1(2)º] (Fig. 3-2a), which is similar to the result of X-ray structural analyses of molecules structurally related to **3-1**. On the other hand, the anthracene core in **3-1**$^{2+}$ is nearly planar [the atomic deviation from the average plane is 0.02 Å at the maximum][16], to which the two diarylmethylium units are attached with a large torsion angle of 76.7(3)°[12]. The twisted geometry similar to **3-1**$^{2+}$ was reported for the 9,10-anthrylidenebis(1,3-dithiolium)s. Such a geometrical change is related to the decrease in the π-bond order of the exocyclic C=C bonds upon two electron redox. The bond lengths in **3-1** [1.354(6) and 1.352(6) Å] and **3-1**$^{2+}$ [1.444(14) Å] clearly show that the bonds in **3-1** are typical double bonds whereas those in **3-1**$^{2+}$ are single bonds, thus switching the way to reduce steric repulsion.

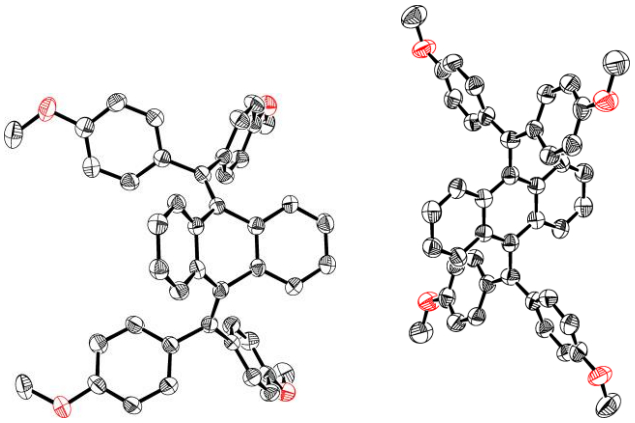


Fig. 3-2. ORTEP drawings of (a) **3-1** in benzene solvate and (b) **3-1**$^{2+}$ in **3-1**$^{2+}$(PF_6^-)$_2$ salt determined by X-ray analyses measured at 150 K.

As with **3-1**/**3-1**$^{2+}$, a dramatic geometrical change occurred between **3-2** and **3-2**$^{2+}$ (Fig. 3-3). In the doubly bent bianthraquinodimethane **3-2**,[9a] the central [1.354(4) Å] and two terminal exocyclic bonds [1.349(3) and 1.351(4) Å] are almost planar and typical lengths for C=C bond. The bent angles in the two 9,10-dihydroanthracene units are 35.9(1)-38.9(1)º, which are close to those in **3-1**. The twisted deformation observed in **3-2**$^{2+}$ is outstanding since the central [1.500(4) Å] and exocyclic [1.489(4) Å] bonds reduced their bond order as can be seen the bond lengths. The two anthracene units are arranged nearly perpendicularly[19] [dihederal angle: 86.5(2)]. The diarylmethylium units are attached on both ends of the bianthrylidene core with a large torsion angle of 63.4(2)º in **3-2**$^{2+}$.

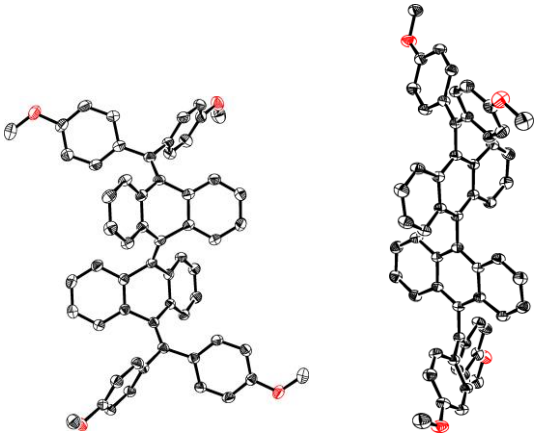


Fig. 3-3. ORTEP drawings of (a) **3-2** in ether solvate and (b) **3-2**$^{2+}$ in **3-2**$^{2+}$(PF_6^-)$_2$ salt MeCN solvate determined by X-ray analyses measured at 150 K.

3.5. Electrochemistry

Because of the drastic structural change upon redox interconversion, the cyclic voltammogram[17] of **3-1** exhibited a two-electron oxidation peak at +1.00 V vs. SCE in CH_2Cl_2, whereas the return peak appeared

in the far cathodic region (+0.42 V) that corresponds to the 2e-reduction process of **3-1**$^{2+}$ (Fig. 3-4a). Such a separation of redox peaks is characteristic of the "dynamic redox systems,"[18] in which the steady-state concentration of the intermediary radical cation **3-1**$^{\bullet+}$ is negligible. In fact, upon electrochemical oxidation of **3-1** in CH_2Cl_2, a continuous change was observed as shown in Fig. 3-5 exhibiting several isosbestic points, and the final spectrum is identical to that of isolated **3-1**$^{2+}$ salt. Reversibility of the chromic behavior was confirmed by the electrochemical reduction of as-prepared **3-1**$^{2+}$ by switching the polarity of the electrodes. By considering that the open-shell species in general exhibit high reactivity to undergo side reactions, the low concentration of **3-1**$^{\bullet+}$ in the interconversion is favored to attain reversibility of this electrochromism. In this way, the redox cycle of **3-1**/**3-1**$^{2+}$, including the geometrical change, is shown in Scheme 3-5a [(b): bent vs. (t): twisted], and only the two species **3-1**(b) and **3-1**(t)$^{2+}$ are apparently involved in the chromic behavior.

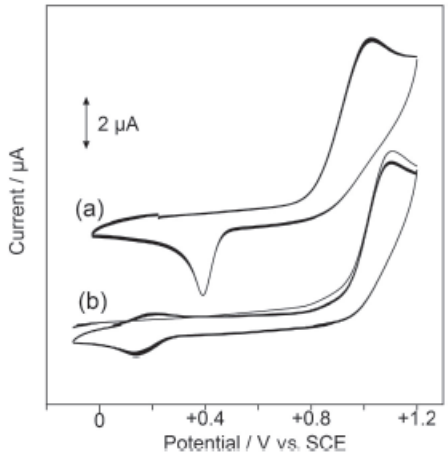


Fig. 3-4. Cyclic voltammograms of (a) **3-1**/**3-1**$^{2+}$ and (b) **3-2**/**3-2**$^{2+}$ measured in CH_2Cl_2 (0.1 M Bu_4NBF_4, *E*/V vs. SCE, Pt electrode, 100 mV s^{-1}).

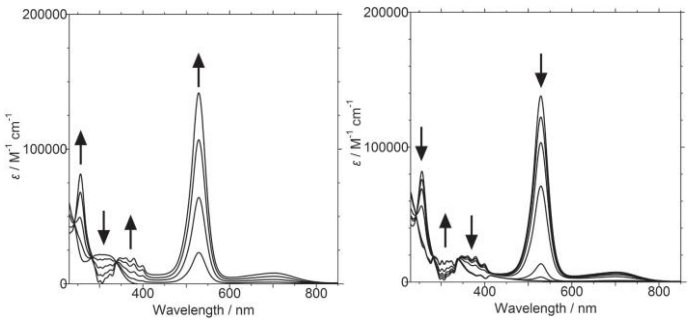
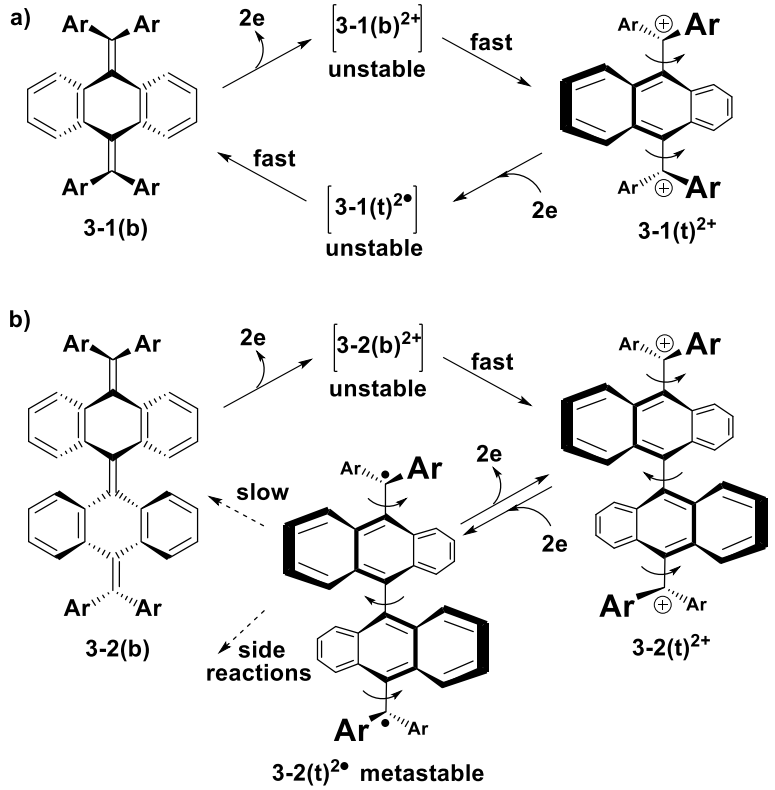


Fig. 3-5. A continuous change in UVvis spectrum a) upon constant current electrochemical oxidation of **3-1** (8.1×10^{-6} M) (50 μA, every 4 min) and b) upon constant current electrochemical reduction (50 μA, every 4 min) of as-prepared **3-1**$^{2+}$ generated from in situ oxidation of **3-1** in CH_2Cl_2 containing 0.05 M Bu_4NBF_4.



Scheme 3-5a. Redox scheme for a) **3-1**/**3-1**$^{2+}$ and b) **3-2**/**3-2**$^{2+}$ accompanied by geometrical changes. [b: bent form, t: twist form]

The voltammogram of **3-2**/**3-2**$^{2+}$ pair exhibited a significant difference from that of **3-1**/**3-1**$^{2+}$. Oxidation of **3-2** proceeded at +1.08 V vs. SCE in CH_2Cl_2 to transform into **3-2**$^{2+}$. However, in the return cycle, a pair of quasi-reversible redox peaks was observed at +0.17 V, which was observed in the voltammogram of isolated **3-2**$^{2+}$(PF_6^-)$_2$ as well. Thus, the electrochemically generated twisted diradical **3-2**(t)$^{2\bullet}$ is a long-lived metastable species because of slow relaxation[9,20] into the doubly bent structure in bianthraquinodimethane **3-2**(b). Although **3-2**(b) was recovered in 98% yield upon reduction of **3-2**(t)$^{2+}$(PF_6^-)$_2$ with Zn dust, reversibility in transformation under electrochemical conditions could not be attained easily (Fig. 3-6). Thus, upon electrochemical oxidation of **3-2**(b) in CH_2Cl_2, a continuous change in UV-vis-NIR spectrum to that of **3-2**(t)$^{2+}$ was observed with several isosbestic points. However, upon reduction of **3-2**(t)$^{2+}$, clean conversion to **3-2**(b) was not observed because the open-shell intermediate **3-2**(t)$^{2\bullet}$ underwent some side reaction(s)[21] before regenerating **3-2**(b). Thus, **3-1**/**3-1**$^{2+}$ system was proven to be more promising than **3-2**/**3-2**$^{2+}$ in constructing reversible electrochromic systems because of very small steady-state concentration of open-shell species.

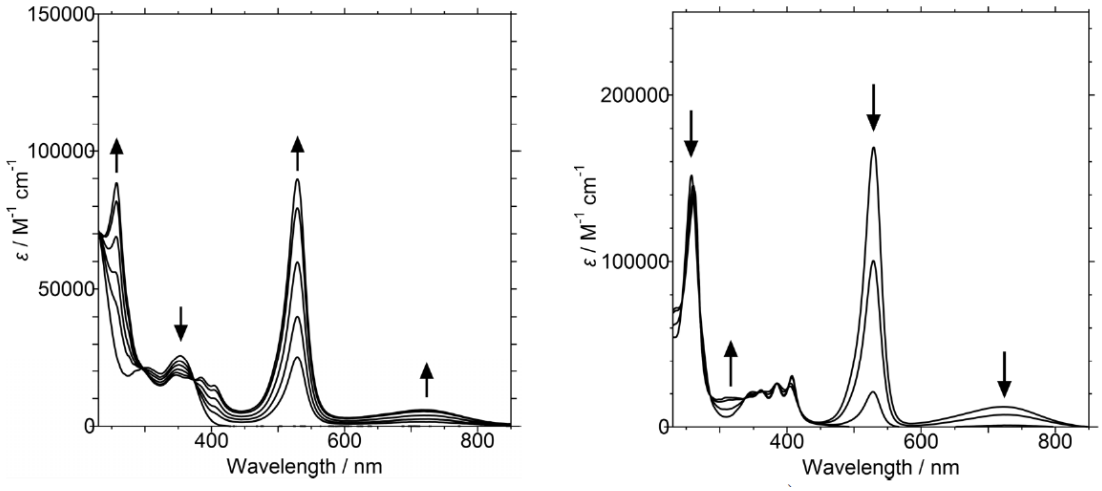


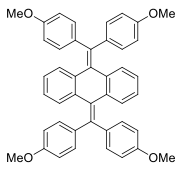
Fig. 3-6. Continuous changes in UV-Vis spectrum a) upon constant current electrochemical oxidation of **3-2** (9.6×10^{-6} M) (35 μA, every 16 min) and b) upon constant current electrochemical reduction (40 μA, every 4 min) of **3-2**$^{2+}$(PF_6^-)$_2$ (1.0×10^{-5} M) in containing 0.05 M Bu_4NPF_6 at 298 K.

3.6. Summary

The author synthesized electron-donating anthraquinodimethane and biantraquinodimethane in which 4-methoxyphenyl group was substituted for methylene terminal. It was possible to isolate tetraaryl-type anthraquinodimethane and biantraquinodimethane dication and succeeded in their X-ray structural analyses, which showed the neutral form have a bent structure and the dications have a twisted structure, and the dramatic structural change due to redox can be confirmed. Electrochemical measurements showed that the rate of conversion from diradical species to closed shells caused by reduction of dications is important for the reversibility of the electrochromic system.

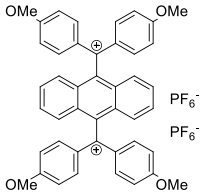
3.7. Experimental

Preparation of **3-1**



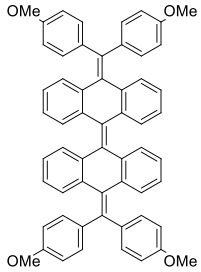
The mixture of 9,10-bis(dibromomethylene)-9,10-dihydroanthracene (200 mg, 0.385 mmol), 4-methoxyphenylboronic acid (351 mg, 2.31 mmol), K_2CO_3 (426 mg, 3.08 mmol) and $(Ph_3P)_4Pd$ (22 mg, 0.019 mmol) in a mixture of PhMe (4.0 mL), EtOH (0.4 mL) and H_2O (0.4 mL) was stirred at 80 °C for 22 h. After cooling to ambient temperature, the reaction mixture was diluted with EtOAc, washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica-gel, hexane-EtOAc (10:1)) to give **1** as a white solid (241 mg, 99%). M. p. 230-232 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 7.26 (8H, d, J = 8.8 Hz), 7.01 (4H, dd, J = 5.7, 3.3 Hz), 6.81 (8H, d, J = 8.8 Hz), 6.74 (4H, dd, J = 5.8, 3.3 Hz), 3.78 (12H, s); ^{13}C NMR (400 MHz, $CDCl_3$): δ/ppm 158.2, 138.8, 138.2, 135.3, 135.2, 130.9, 127.9, 125.0, 113.6, 55.2; IR (KBr): ν/cm^{-1} 3057, 3029, 2995, 2960, 2832, 2050, 2020, 1951, 1911, 1879, 1604, 1570, 1508, 1449, 1440, 1286, 1241, 1170, 1106, 1031, 847, 835, 807, 761, 747, 646, 587, 556; LR-MS (FD): m/z (%) 628 (M^+, bp), 314 (M^{2+}, 16); HR-MS (FD): calcd for $C_{44}H_{36}O_4$ (M^+) 628.2614, found: 628.2596;

Preparation of **3-1**$^{2+}(PF_6^-)_2$



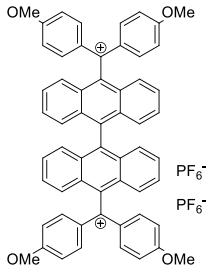
To a solution of **1** (20.0 mg, 31.8 μmol) in dry CH_2Cl_2 (0.5 mL) as added (4-$BrC_6H_4)_3N^{\bullet+}PF_6^-$ (39.9 mg, 63.6 μmol) and the mixture was stirred at ambient temperature for 30 min. After addition of dry Et_2O (10 mL) to the dark purple reaction mixture, the green lustrous crystals were produced, then the pale purple supernatant was carefully removed. The residue was repeatedly washed with dry Et_2O (10 mL) twice and the solvent was removed under reduced pressure to give **1**$^{2+}(PF_6^-)_2$ as green lustrous crystals (26.7 mg, 91%). M. p. 188-189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 7.96 (8H, d, J = 8.8 Hz), 7.56 (4H, dd, J = 7.2, 3.3 Hz), 7.49 (4H, dd, J = 7.2, 3.2 Hz), 7.35 (8H, d, J = 9.0 Hz), 4.18 (12H, s); ^{13}C NMR (400 MHz, $CDCl_3$): δ/ppm 191.2, 175.0, 145.0, 138.1, 135.0, 131.4, 129.1, 126.9, 118.9, 58.6; IR (KBr) ν/cm^{-1} 3108, 2946, 2852, 1983, 1607, 1578, 1509, 1449, 1377, 1280, 1188, 1161, 1135, 1124, 1002, 917, 838, 806, 758, 597, 558, 534; LR-MS (FD): m/z (%) 628 ([M–2PF_6]$^+$, 81), 314 ([M–2PF_6]$^{2+}$, 90); HR-MS (FD): calcd for $C_{44}H_{36}O_4$ ([M–2PF_6]$^{2+}$) 314.1307, found 314.1315; UV-Vis (CH_2Cl_2): λ/ nm (log ε) 710 (3.96), 531 (5.20), 401 (4.23), 380 (4.36), 362 (4.33), 257 (4.97).

Preparation of **3-2**



The mixture of 11,11,11',11'-tetrabromo-10,10'-bianthraquinodimethane **4** (200 mg, 0.287 mmol), 4-methoxyphenylboronic acid (262 mg, 1.72 mmol), K_2CO_3 (238 mg, 1.72 mmol), Cs_2CO3 (225 mg, 0.689 mmol) and $(Ph_3P)_4Pd$ (16 mg, 0.014 mmol) in a mixture of PhMe (40 mL), EtOH (0.4 mL) and H_2O (1.5 mL) was stirred at 80 °C for 48 h. After cooling to ambient temperature, the reaction mixture was diluted with EtOAc, washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography (alumina, hexane-EtOAc (10:1) → CH_2Cl_2) to give **2** as yellow crystals (186 mg, 81%). M. p. 185 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm; 7.37 (8H, d, J = 8.7 Hz), 7.17-7.07 (8H, m), 6.92-6.81 (16H, m), 3.81 (12H, s); ^{13}C NMR (400 MHz, $CDCl_3$): δ/ppm 158.3, 139.4, 139.0, 137.5, 135.3, 135.2, 132.1, 130.8, 128.6, 128.3, 125.7, 124.8, 113.7, 55.2; IR (KBr) ν/cm^{-1} 3058, 3019, 2952, 2926, 2833, 2130, 2109, 2091, 1604, 1573, 1508, 1461, 1449, 1290, 1243, 1172, 1032, 839, 808, 758, 599, 584; LR-MS (FD): m/z (%) 804 (M^+, bp), 402 (M^{2+}, 1); HR-MS (FD): calcd for $C_{58}H_{44}O_4$ (M^+) 804.3240, found 804.3241;

Preparation of **3-2**$^{2+}$(PF_6^-)$_2$



To a solution of **2** (36.8 mg, 45.7 μmol) in dry CH_2Cl_2 (1.5 mL) as added (4-$BrC_6H_4)_3N^{\bullet+}PF_6^-$ (57.3 mg, 91.4 μmol) and the mixture was stirred at ambient temperature for 3 h. The reaction mixture was concentrated to ca. 0.5 mL by flowing argon gas. After addition of dry Et_2O (10 mL) to the dark purple residual mixture, the green lustrous crystals were produced, then the pale purple supernatant was carefully removed. The residue was repeatedly washed with dry Et_2O (10 mL) twice and the solvent was removed under reduced pressure to give **2**$^{2+}$(PF_6^-)$_2$ as green lustrous crystals (50.2 mg, quant.). M. p. 194 °C (decomp); ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm; 8.03 (8H, d, J = 7.6 Hz), 7.62 (4H, d, J = 8.8 Hz), 7.49 (4H, ddd, J = 7.7, 6.2, 1.5 Hz), 7.44-7.32 (16H, m), 4.19 (12H, s); ^{13}C NMR (400 MHz, $CDCl_3$): δ/ppm 193.0, 174.5, 144.8, 134.0, 135.8, 135.1, 132.8, 131.3, 129.2, 127.7, 127.6, 127.0, 118.7, 58.4; IR (KBr) ν/cm^{-1} 3108, 3077, 2951, 2850, 1982, 1606, 1578, 1444, 1374, 1279, 1186, 1160, 1133, 1004, 839, 558, 539; LR-MS (FD): m/z (%) 804 ([M–2PF_6]$^+$, 89), 402 ([M–2PF_6]$^{2+}$, 74); HR-MS (FD): calcd for $C_{58}H_{44}O_4$ ([M–2PF_6]$^{2+}$) 402.1620, found 402.1605; UV-Vis (CH_2Cl_2): λ/ nm (log ε) 728 (4.16), 530 (5.22), 405 (4.39), 385 (4.43), 366 (4.35), 258 (5.16).

Reduction of dications **3-1**/**3-2**$^{2+}$ to **3-1**/**3-2** with Zn dust

A solution of **3-1**$^{2+}$(PF_6^-)$_2$ (15.9 mg, 17.3 μmol) in dry MeCN (1.0 mL) was deoxygenated by argon bubbling for 20 min. Then, Zn dust (113 mg, 1.73 mmol) was added to the solution. The dark purple color was immediately disappeared. After stirring for 2 h, 1 M NaOH aq. (3 mL) was added. The mixture was

extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give **1** (10.5 mg, 96%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$) showed no signs of by-product.

A suspension of **3-2**$^{2+}$(PF_6^-)$_2$ (39.3 mg, 35.9 μmol) in a mixture of dry MeCN (2.0 mL) and dry CH_2Cl_2 (2.0 mL) was deoxygenated by argon bubbling for 20 min. Then, Zn dust (235 mg, 3.59 mmol) was added to the solution. The dark purple color was slowly disappeared. After stirring for 25 h, 1 M NaOH aq. (6 mL) was added. The mixture was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to give **3-2** (28.2 mg, 98%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$) showed no signs of by-product.

Electrochemical reduction of **3-2**$^{2+}$

Into a glass cell divided by glass filter equipped with Pt anode and cathode was placed **3-2**$^{2+}$(PF_6^-)$_2$ (10.6 mg, 9.7 μmol) in the cathodic chamber. The whole apparatus was purged with argon. A solution of E*t*$_4$NClO$_4$ (223 mg, 1.00 mmol) in MeCN (10 mL) was added to both chambers. The resulting mixture was electrolyzed under constant current conditions (50 μA, 27 h). The catholyte was poured into H_2O and extracted with CH_2Cl_2. The combined organic layer was washed with H2O and brine, dried over NaSO4, and concentrated under reduced pressure. The crude product was purified by column chromatography (alumina, hexane-EtOAc (5:1)) to give an inseparable mixture of **3-2** (2.1 mg, 27%) and 4,4'-methoxybenzophenone (0.4 mg, 18%). The ratio was determined by ^{1}H-NMR.

Reference for chapter 3

[1] The representative Wurster-type electron acceptors, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) (ref. 2a) and *N*,*N*'-dicyano-*p*-quinodiimine (DCNQI) (ref. 2b) are the most successful examples of this molecular design. The oQD-pQD hybrid-type electron acceptor was also reported (ref. 3).

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[12] (a) CCDC deposition numbers are as follows: **3-1**●$(PhH)_2$ [*P*21/c, *Z* = 4] 991887; **3-1**$^{2+}(PF_6^-)_2$ [*P*4/m, *Z* = 2] 996246; **1**$^{2+}(SbCl_6^-)_2$ [*P*1bar, *Z* = 1] 991885; **3-2**●$(ether)_2$ [*P*21/c, *Z* = 4] 991888; **3-2**$^{2+}(PF_6^-)_2$●$(MeCN)_2$ [*C*2/c, *Z* = 4] 991886. (b) Due to only a small single crystal of **3-1**$^{2+}(SbCl_6^-)_2$ was available, quality of the X-analysis is not high. However, the geometrical features of **3-1**$^{2+}$ in $(SbCl_6^-)_2$ salt is similar to that in $(PF_6^-)_2$ salt, showing that the twisted geometry is not caused by crystal packing but by intramolecular factors.

[13] The bent angle of *p*QD is defined as the dihedral angle between the two planes defined by C1-C2-(C6/C7) and C2-C3-C5-C6 [or C3-C4-(C5/C8) and C2-C3-C5-C6].

[14] Tetraarylanthraquinodimethanes, tetraarylbianthraquinodimethanes, oligoanthrylidenes, and their higher analogues have been studied as the precursors to generate polycondensed hydrocarbons (e.g. tetrabenzocoronene, octabenzocircumbiphenyl, or polyperiacenes) via cyclization through oxidative dehydrogenation and/or photoirradiation (ref. [17]). In contrast, oxidation of **3-1** or **3-2** afforded no cyclized products in this study.

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[16] For the 9,10-anthrylidenebis(1,3-dithiolium)s, the twisted geometry similar to **3-1**$^{2+}$ was reported (ref. [11]).

[17] Cyclic voltammetry was conducted in CH_2Cl_2 containing 0.1 M Bu_4NBF_4 as a supporting electrolyte (*E* / V vs SCE, Pt electrode, scan rate 100 mV s^{-1}). For the irreversible waves, the oxidation potentials (E^{ox}) and reduction potentials (E^{red}) were estimated as $E^{ox} = E^{peak} - 0.03$ V and $E^{red} = E^{peak} + 0.03$ V, respectively. Ferrocene undergoes one-electron oxidation at + 0.53 V under the similar conditions.

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[19] The largest twisting angle of two π-units in the dications is 90.0: T. Suzuki, H. Shiohara, M. Monobe, T. Sakimura, S. Tanaka, Y. Yamashita, T. Miyashi, *Angew. Chem. Int. Ed.* **1992**, *31*, 455.

[20] Very slow conversion ($\tau_{1/2}$ = 495 min at 298 K) was reported for the structurally related diradical,

10,10'-(9,9'-bianthrylidene)bis[bis(4-tert-butylphenyl)methyl], to convert into the corresponding bianthraquinodimethane (ref [9a]).

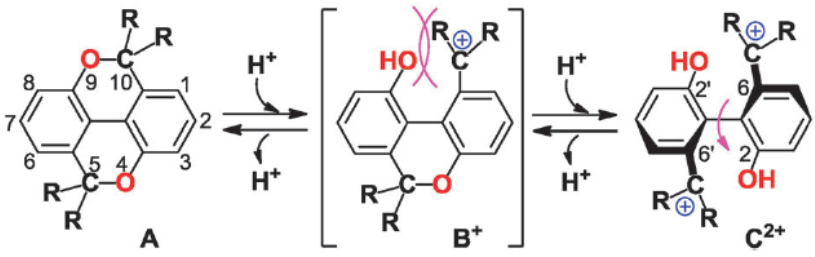
[21] In the electrochemical reduction of **3-2**(t)$^{2+}$(PF_6^-)$_2$ in MeCN, 4,4'-dimethoxybenzophenone (18%) was obtained in addition to **3-2**(b), suggesting that the reaction with O_2 is one of the major side reactions of **3-2**(t)$^{2\bullet}$.

Chapter 4.

Two-way chromic interconversion of the 2,2'-biphenol-6,6'-diyl dication with 5H,10H-dioxapyrene or 9H,10H-4,5-dihydroxyphenanthrene

4.1. Introduction

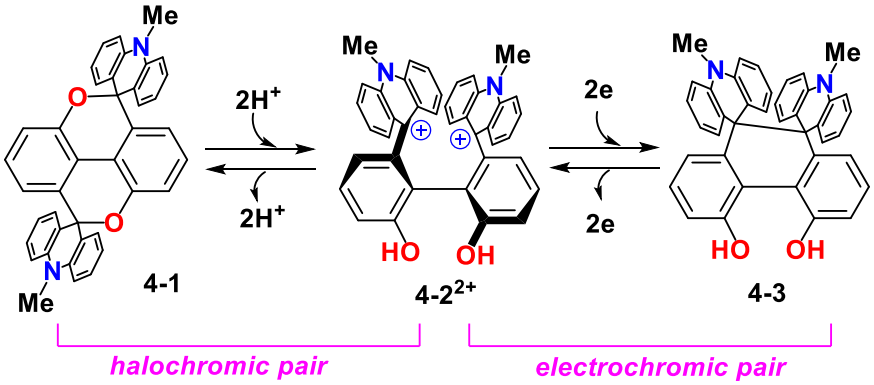
Research on oxidation-reduction systems involving cleavage and formation of C-C bonds by electron transfer based on hexaphenylethane derivatives has been conducted in the laboratory to which the author belongs. Among them, in addition to the response by oxidation and reduction, there is a system showing another response by addition of an acid/base. The authors realized the introduction of hydroxyl groups in the bay region of the biphenyl moiety of this hexaphenylethane derivative, which results in the conversion of the dicationic and neutral states accompanying the cleavage and formation of the C-O bond by addition of acid and base. 5*H*,10*H*-Dioxapyrene (diopy; 5*H*,10*H*-[1]benzopyrano[5,4,3-*cde*][1]benzopyran) of the neutral state is a less-studied heterocyclic skeleton[1] in contrast to its 5,10-dione analogue. Upon acid treatment of diopy (**A**) with cation-stabilizing substituents at 5,10-positions, the biphenolic dication ($\mathbf{C}^{2+}$) would be generated via the monocationic intermediate ($\mathbf{B}^{+}$). When B^{+} suffers from severe steric repulsion at the bay-region, this amphiprotic species easily undergoes acid–base disproportionation to **A** and $\mathbf{C}^{2+}$, so that double protonation/deprotonation between **A** and $\mathbf{C}^{2+}$ would occur nearly simultaneously. Such a simplified pseudo-two-state switching is favored for the construction of promising molecular response systems.[2] When the cationic part in $\mathbf{C}^{2+}$ is endowed with a strong absorption in the visible region, interconversion between **A** and $\mathbf{C}^{2+}$ is accompanied by halochromism,[3] since diopy **A** shows absorptions only in the UV region.



Scheme 4-1. Interconversion of diopy **A** and biphenolic dication C^{2+} upon double protonation/deprotonation via intermediate $\mathbf{B}^{+}$.

To generate and isolate the dicationic state as a stable entity despite the presence of hydroxy groups within the molecule, the cationic subunit should have a large pK_{R+} value, which prompted us to select the 10-methylacridinium chromophore[4,5] (Scheme 4-2). Due to the bulkiness of the chromophore, the biphenol skeleton in $\mathbf{4\text{-}2}^{2+}$ would have a large torsion angle, whereas the diopy skeleton in **4-1** would be nearly planar, since the spiro(10-methylacridan) units do not induce any steric hindrance. Such a drastic structural change would realize the two-state halochromic interconversion between **4-1** and $\mathbf{4\text{-}2}^{2+}$. Another interesting point

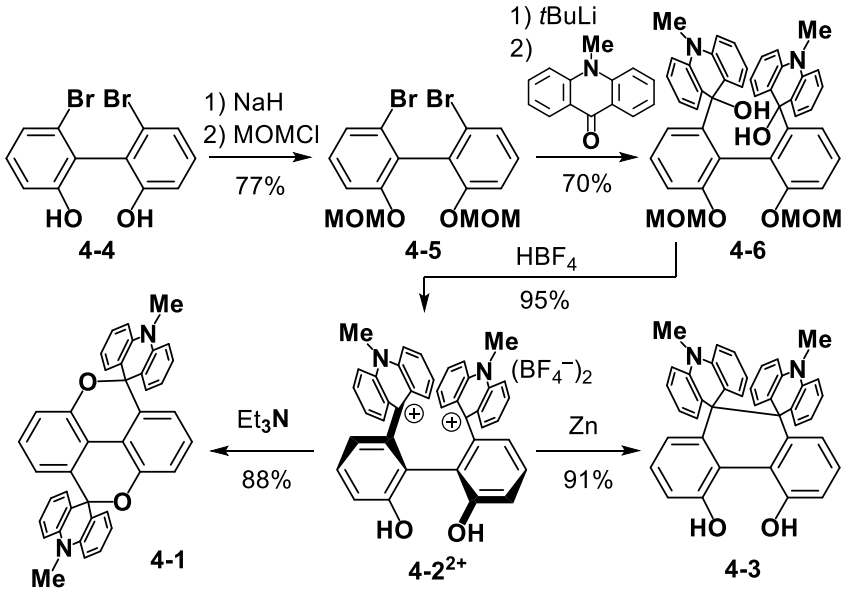
is that, upon reduction, dication **4-2**$^{2+}$ would be transformed into a dihydrophenanthrene (DHP) derivative **4-3** accompanied by C(sp3)–C(sp3) bonding through "dynamic redox (dyrex)" behavior,[6] and the interconversion between **4-2**$^{2+}$ and **4-3** would also exhibit electrochromism[7] and structural changes. Thus, **4-1**, **4-2**$^{2+}$ and **4-3** can serve as a novel motif for multi-input molecular response systems. [8]



Scheme 4-2. Two-way chromic interconversion of dication **4-2**$^{2+}$ with diopy **4-1** by protonation/deprotonation and with DHP **4-3** by oxidation/reduction.

4.2. Preparation

6,6'-Dibromo-2,2'-biphenol **4-4**[9] was first reacted with methoxymethyl (MOM) chloride/NaH in DMF to give MOM-protected biphenol **4-5** in 77% yield. The dilithio derivative derived from **4-5** and 4 equiv. of *t*BuLi in THF was then reacted with 10-methyl-9(10*H*)-acridone to give bis(hydroxy)base **4-6** in 70% yield. Upon treatment of **4-6** with HBF_4 in MeOH–$CHCl_3$ at reflux afforded the desired **4-2**$^{2+}$(BF_4^-)$_2$ as yellow-orange crystals in 95% yield. The reaction of **4-2**$^{2+}$(BF_4^-)$_2$ with Et_3N in MeCN gave colorless crystals of diopy **4-1** in 88% yield (Scheme 4-3).



Scheme 4-3. Preparation of **4-2**$^{2+}$(BF_4^-)$_2$ and its transformation into **4-1** and **4-3**.

4.3. X-ray analyses

Based on the results of an X-ray analysis[10] at 150 K, the diopy core in **4-1** is nearly planar (largest deviation of an atom from the mean plane: 0.23 Å), although the pyran rings adopt a very shallow twist-chair form (Fig. 4-1a). The two benzene rings are coplanar (dihedral angle: 0 °). To this core are attached the spiro(10-methylacridan) units, which are slightly deformed into a butterfly-shape [dihedral angle between two benzene nuclei of acridan: 21.3(2)°], as found in other structurally-related molecules.[11] In contrast, the two molecular halves in dication **4-2**$^{2+}$ are largely twisted in the crystal of (BF_4^-)$_2$ salt (Fig. 4-1b). The dihedral angle of the biphenyl unit is 68.8(1)° (*syn*-form), and there are no signs to indicate coordination of the hydroxy groups to the acridinium chromophores. If we consider that the two oxygen atoms at the 2,2'-positions are separated by a distance of 3.050(2) Å, intermolecular H-bonding is not effective in **4-2**$^{2+}$ (typical distance for the H-bonded O-O: 2.75 ± 0.2 Å). The π–π interaction between two acridinium units must be the major directing force to give the observed *syn*-form (Fig. 4-1), and thus the chromophores are stacked nearly in parallel [dihedral angle: 3.92(3)1] with the shortest C–C contact of 3.284(3) Å (sum of van der 3.40 Å).

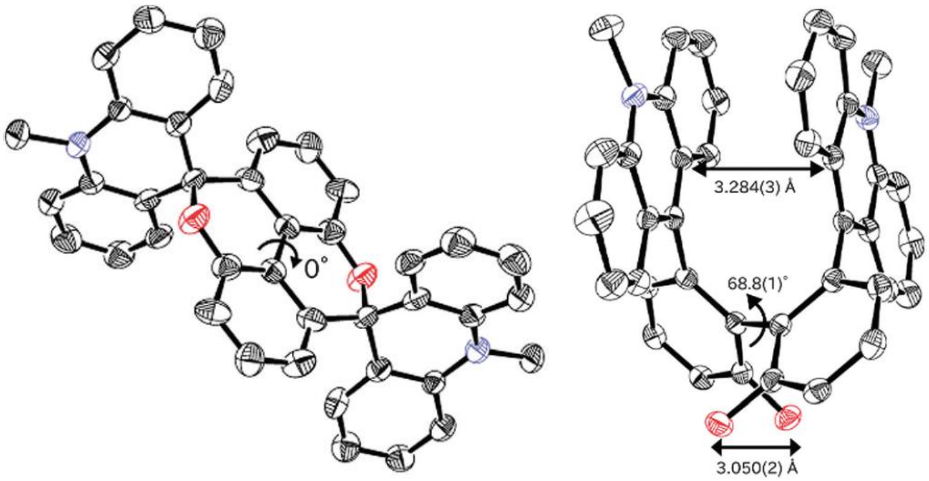


Fig. 4-1. ORTEP drawings of **4-1** and **4-2**$^{2+}$ in $(BF_4^-)_2$ salt determined by X-ray analysis at 150 K.

4.4. Halochromic Response

Diopy **4-1** is colorless, with absorptions only in the UV region [λ_{max}/nm (log ε): 339 (4.30) in CH_2Cl_2], whereas **4-2**$^{2+}$ exhibits a yellow-orange color [358(3.92) in MeCN] due to the characteristic absorptions of acridinium (Fig. 4-2). Although 10-methylacridinium itself is highly fluorescent, **4-2**$^{2+}$ is non-fluorescent due to the charge shift type quenching of the excited state by the electron-donating biphenol unit. Upon the aliquot addition of TfOH to a DMSO-d_6 solution of **4-1**, a clean conversion to **4-2**$^{2+}$ was observed (Fig. 4-3).

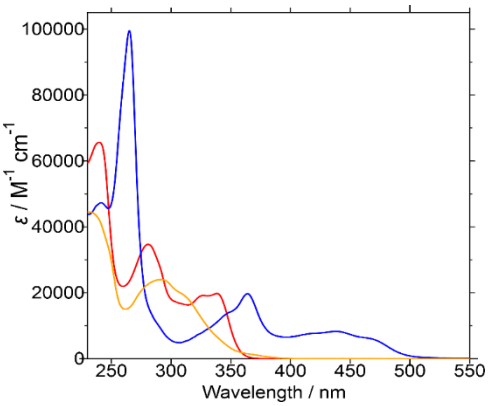


Fig 4-2. UV-vis spectra of **4-2**$^{2+}(BF_4^-)_2$ in MeCN (blue), **4-1** in CH_2Cl_2 (red) and **4-3** in CH_2Cl_2-MeCN (4:1) (yellow).

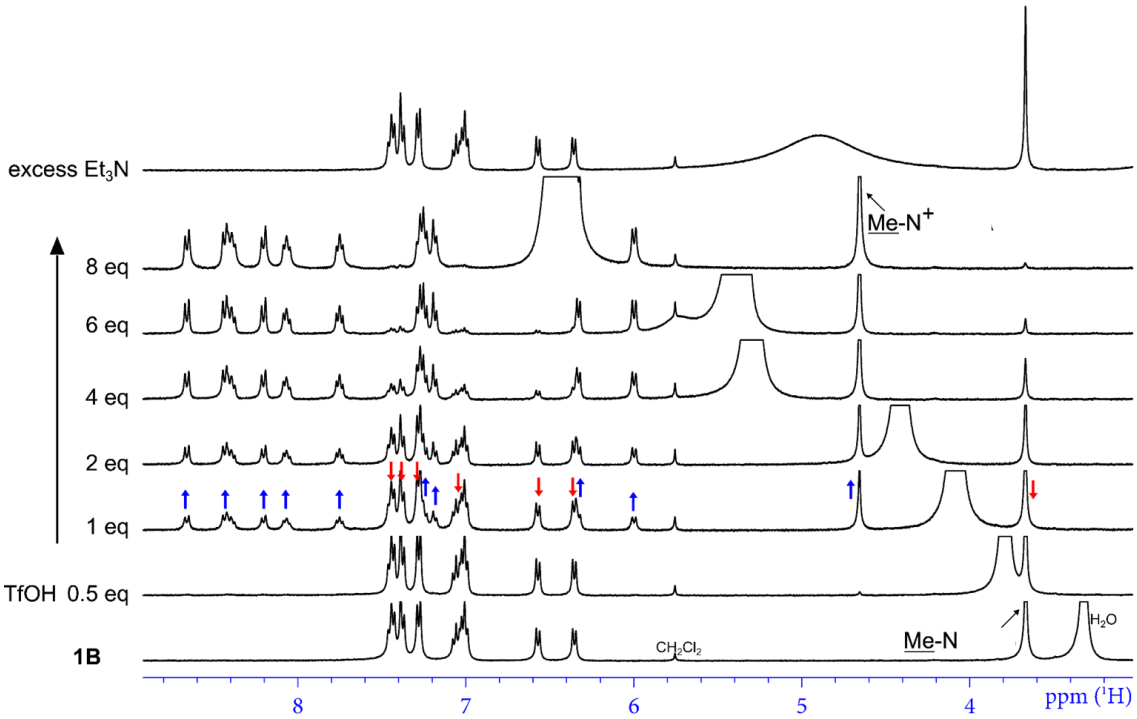


Fig. 4-3. Changes of partial ^{1}H NMR spectra of **4-1** (8 mM) to **4-2**$^{2+}$ in DMSO-d_6 upon addition of TfOH. As-prepared **4-2**$^{2+}$ was converted to **4-1** by addition of excess Et_3N.

The resulting spectra showed the presence of only two species (**4-1** and **4-2**$^{2+}$), which demonstrated that the steady-state concentration of the intermediary monocationic derivatives is negligible. The reversibility of this conversion was confirmed by the regeneration of **4-1** from as-prepared **4-2**$^{2+}$ by addition of excess Et_3N.

4.5. Electrochemistry

According to the results of a voltammetric analysis,[12] **4-3** undergoes irreversible two-electron oxidation at an anodic peak potential (E_{pa}) of +0.32 V in CH_2Cl_2/MeCN (4:1) vs SCE (Fig. 4-4a). The return peak was observed in the far cathodic region (E_{pc} = –0.23 V), which corresponds to the reduction process of dication **4-2**$^{2+}$ (Fig. 4-4b). In fact, Zn-reduction of **4-2**$^{2+}$(BF_4^-)$_2$ induced C(sp3)–C(sp3) bonding at the C6 and C6' positions to give DHP **4-3**. Colorless crystals of **4-3** [λ_{max}/nm: 285 (4.37) in CH_2Cl_2] were isolated in 91% yield, and regenerated **4-2**$^{2+}$(BF_4^-)$_2$ in 87% yield upon treatment with 2 equiv. of ferrocenium tetrafluoroborate in CH_2Cl_2/MeCN. In this way, reversible redox interconversion between **4-2**$^{2+}$ and **4-3** accompanied by C–C bond formation/cleavage ("dyrex" behavior) was confirmed. Due to the dynamic geometrical changes[13], two-electron transfer occurs nearly simultaneously, which was confirmed by the negligible steady-state concentration of intermediary cation radical upon the electrochemical interconversion of **4-2**$^{2+}$ and **4-3** (Fig. 4-5).

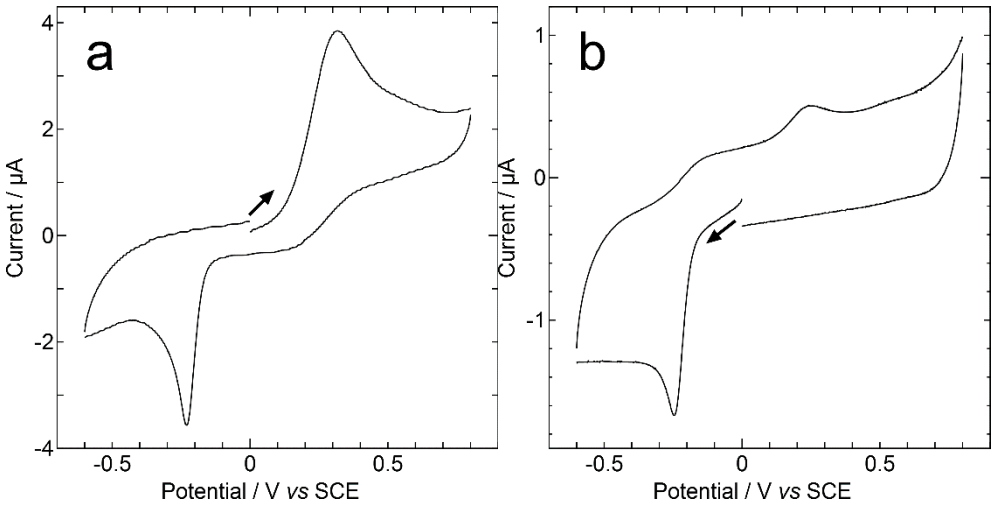


Fig. 4-4 Cyclic voltammograms of (a) DHP **4-3** and (b) dication **4-2**$^{2+}$$(BF_4^-)_2$ in CH_2Cl_2/MeCN (4:1) (*c* = 0.5 mM) containing 0.1M Bu_4NBF_4. (*E*/V vs. SCE, Pt electrode, 100 mVs^{-1}).

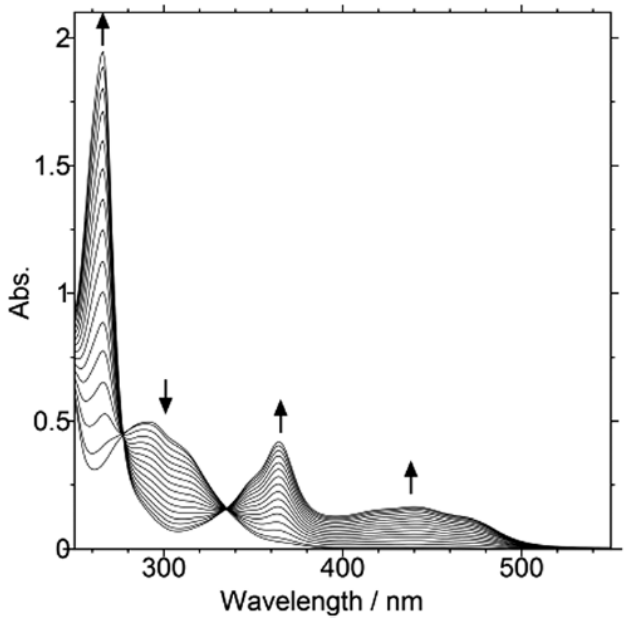


Fig. 4-5 A continuous change in the UV-vis spectra of **4-3** [2.1× 10^{-5} M; 3 mL] to **4-2**$^{2+}$ in CH_2Cl_2/MeCN (4:1) containing 0.05 M Bu_4NBF_4 upon constantcurrent electrochemical oxidation on a Pt electrode (30 microA, every 1 min).

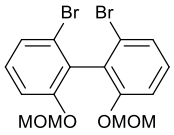
4.6. Summary

In this work, we have demonstrated the reversible halochromic and electrochromic interconversion of 2,2'-biphenyl-6,6'-diyl dication with two kinds of neutral molecules (diopy and DHP). This is the first

example of concomitant but independent two-proton or two-electron transfer with a negligible concentration of the intermediates. A drastic structural change is the key to this novel feature, which may represent a new molecular design concept for multi-input response systems with advanced features.

4.7. Experimental

Preparation of bis(methoxymethyl) ether **4-5**



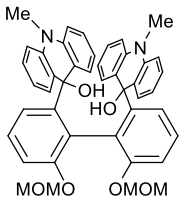
To a suspension of NaH (60% in oil, 1.27 g, 31.7 mmol) in dry DMF (20 mL) under argon was added a solution of 6,6'-dibromo-2,2'-biphenol **4-4** (2.73 g, 7.94 mmol) in dry DMF (20 mL) at 0 °C. After stirring for 10 min at ambient temperature, MOMCl (2.4 mL, 31.7 mmol) was added to the mixture. After stirring for 80 min at ambient temperature, water was added at 0 °C and the whole mixture was extracted with CH_2Cl_2 twice. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/CH_2Cl_2 = 2:3) to afford partially purified **4-5** (2.99 g). Further purification was conducted by recrystallization from EtOH to afford **4-5** (2.66 g, 77%) as a pale yellow solid;

mp: 156-157 °C. ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.32 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.20 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.15 (dd, *J* = 8.0, 1.3 Hz, 2H), 5.05 (d, *J* = 6.8 Hz, 2H), 5.03 (d, *J* = 6.8 Hz, 2H), 3.34 (s, 6H). ^{13}C-NMR (101 MHz; $CDCl_3$): δ 155.7, 129.9, 129.2, 125.7, 125.1, 113.6, 94.7, 56.0

IR (KBr): 2996, 2957, 2941, 2908, 2849, 2830, 2797, 1584, 1569, 1485, 1451, 1442, 1409, 1402, 1306, 1261, 1248, 1206, 1184, 1163, 1157, 1142, 1092, 1084, 984, 921, 828, 772, 731, 669, 641, 564, 531, 426.

FD-HRMS: *m/z* calcd for $C_{16}H_{16}Br_2O_4$ $[M]^+$: 429.9415; found: 429.9415

Preparation of bis(hydroxy)base **4-6**

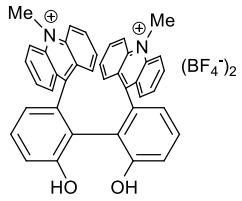


To a solution of **4-5** (800 mg, 1.85 mmol) in dry THF (25 mL) under argon was added *t*-BuLi (1.60 M in pentane, 4.6 mL, 7.41 mmol) at -78 °C. After stirring for 1 h at -78 °C, a suspension of *N*-methylacridone (774 mg, 3.70 mmol) in dry THF (25 mL) was added with a dropping funnel. After addition, the reaction mixture was warmed up to ambient temperature and stirred for 21 h. Water was added and the organic solvents were removed in vacuo. The residue was extracted with EtOAc three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/EtOAc = 4:1 + 5% Et_3N) to afford **4-6** (904 mg, 70%) as a pale yellow solid.

mp: > 300 °C, ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.78 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.34 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 2H), 7.22 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 2H), 7.14 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.09 (dd, *J* = 8.2, 1.0 Hz, 2H),

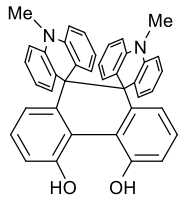
7.05 (dd, *J* = 8.2, 8.2 Hz, 2H), 7.01-6.97 (m, 4H), 6.94 (dd, *J* = 8.2, 1.0 Hz, 2H), 6.80-6.76 (m, 2H), 6.50 (dd, *J* = 8.0, 1.2 Hz, 2H), 4.75 (d, *J* = 6.5 Hz, 2H), 4.56 (d, *J* = 6.5 Hz, 2H), 3.85 (s, 2H), 3.51 (s, 6H), 3.19 (s, 6H). ^{13}C-NMR (101 MHz; $CDCl_3$): δ 155.5, 142.5, 141.8, 141.1, 130.1, 129.2, 128.15, 128.10, 127.91, 127.88, 127.5, 126.8, 124.4, 120.4, 119.7, 112.7, 111.78, 111.71, 94.7, 55.7, 33.5. IR (KBr): 3373, 3060, 2883, 2821, 1735, 1593, 1572, 1499, 1468, 1402, 1347, 1308, 1270, 1246, 1199, 1151, 1131, 1076, 1030, 994, 956, 930, 920, 863, 820, 863, 820, 796, 750, 707, 647, 642. FD-HRMS: *m/z* calcd for $C_{44}H_{40}N_2O_6$ $[M]^+$: 692.2886; found: 692.2880.

Preparation of dication salt **4-2**$^{2+}$$(BF_4^-)_2$



A mixture of diol **4-6** (216 mg, 0.311 mmol) and 42% HBF_4 aq. (1.0 mL, 6.3 mmol) in $CHCl_3$ (2.0 mL) and MeOH (2.0 mL) was heated at reflux for 1.5 h with stirring. After cooling, organic solvents were removed in vacuo. The remaining yellow precipitates were suspended in Et_2O and filtered to afford **4-2**$^{2+}$$(BF_4^-)_2$ (229 mg, 95%) as a yellow solid.
mp > 300 °C. ^{1}H-NMR (400 MHz; CD_3CN): δ 8.50 (d, *J* = 9.2 Hz, 2H), 8.45 (dd, *J* = 8.6, 0.8 Hz, 2H), 8.35 (ddd, *J* = 9.2, 6.7, 1.2 Hz, 2H), 8.14 (s, 2H), 8.08-8.02 (m, 4H), 7.82 (ddd, *J* = 8.6, 6.7, 0.8 Hz, 2H), 7.31 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.23 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.18-7.13 (m, 2H), 6.44 (dd, *J* = 7.6, 1.2 Hz, 2H), 6.27 (d, *J* = 8.6 Hz, 2H), 4.60 (s, 6H). ^{13}C NMR (101 MHz; CD_3CN): δ 159.8, 156.3, 140.66, 140.64, 139.0, 138.0, 133.4, 130.8, 129.5, 127.8, 127.4, 126.5, 125.9, 125.5, 125.0, 123.6, 118.5, 117.6, 38.5. IR (KBr): 3439, 3098, 1609, 1578, 1549, 1461, 1439, 1373, 1286, 1084, 1054, 851, 805, 767, 661, 602, 521. FD-LRMS: *m/z* 568 $[M-2H]^+$. Anal. Calc. for $C_{40}H_{30}B_2F_8N_2O_2$: C, 64.55; H, 4.06; N, 3.76. Found: C, 64.28; H, 4.17; N, 3.99%.

Preparation of dihydrophenanthrene **4-3**

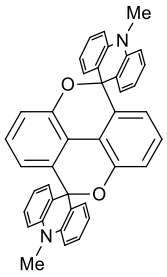


To a solution of dication **4-2**$^{2+}$$(BF_4^-)_2$ (150 mg, 0.194 mmol) in a mixture of 1 M HBF_4 aq. (0.5 mL) and MeCN (5.0 mL) under argon was added zinc dust (1.27 g, 19.4 mmol). After stirring for 2 h at ambient

temperature, the reaction mixture was poured into a saturated $NaHCO_3$ aq. (40 mL) and extracted with EtOAc twice. The combined organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo to afford **4-3** (105 mg, 95%) as a pale yellow solid.

mp > 300 °C. ^{1}H-NMR (400 MHz; $CDCl_3$; 240 K): δ 7.15-7.09 (m, 4H), 7.03-6.99 (m, 6H), 6.79 (dd, *J* = 6.8, 2.2 Hz, 2H), 6.59-6.55 (m, 4H), 6.45 (d, *J* = 8.0 Hz, 2H), 6.25-6.21 (m, 2H), 5.85 (d, *J* = 7.6 Hz, 2H), 2.70 (s, 6H). ^{13}C NMR (101 MHz; $CDCl_3$; 240 K): δ 150.1, 144.9, 144.0, 142.6, 133.0, 131.3, 128.5, 127.4, 126.5, 125.3, 124.7, 123.5, 119.4, 116.6, 116.4, 112.2, 110.1, 58.2, 34.2. IR (KBr): 2972, 2893, 1591, 1473, 1436, 1363, 1271, 1166, 1133, 1090, 1057, 1035, 863, 836, 788, 755, 728, 697, 658. FD-HRMS: *m/z* calcd for $C_{44}H_{30}N_2O_2$ $[M]^+$: 570.2307; found: 570.2308.

Preparation of dioxopyran **4-1**



To a solution of dication **4-2**$^{2+}$$(BF_4^-)_2$ (136 mg, 0.176 mmol) in MeCN (10 mL) was added Et_3N (0.5 mL, 3.6 mmol). The precipitates were formed immediately. This solid was filtered and washed with MeCN to afford **4-1** (92 mg, 88%).

mp > 300 °C. ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.47-7.40 (m, 8H), 7.25-7.21 (m, 4H), 7.02-6.98 (m, 6H), 6.61 (dd, *J* = 8.0, 0.9 Hz, 2H), 6.49 (dd, *J* = 8.0, 0.9 Hz, 2H), 3.72 (s, 6H). ^{13}C NMR (101 MHz; $CDCl_3$): δ 148.7, 139.9, 133.8, 130.0, 129.23, 129.15, 124.5, 121.0, 120.0, 115.5, 114.6, 112.8, 80.2, 33.7. IR (KBr): 3069, 3034, 3008, 2960, 2895, 2828, 1595, 1575, 1472, 1438, 1360, 1263, 1182, 1168, 1131, 1105, 1051, 1012, 997, 903, 757, 747. FD-HRMS: *m/z* calcd for $C_{40}H_{28}N_2O_2$ $[M]^+$: 568.2151; found: 568.2150.

Oxidation of DHP **4-3** to **4-2**$^{2+}$ with an oxidative reagent.

To a solution of **4-3** (104 mg, 0.182 mmol) in CH_2Cl_2 (5 mL) was added ferrocenium tetrafluoroborate (99 mg, 0.363 mmol) then MeCN (5 mL). After stirred at ambient temperature for 20 min, the solvent was removed in vacuo. The residue was dissolved in MeCN (1.5 mL) and poured into Et_2O (50 mL). The precipitations were filtered to afford **4-2**$^{2+}$$(BF_4^-)_2$ (122 mg, 87%) as a yellow solid.

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[10] CCDC deposition numbers are as follows: **4-1** [*P*21/*c*, *Z* = 2] 1061368; **4-2**$^{2+}$(BF_4^-)$_2$ [*Pbca*, *Z* = 8] 1061367.

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[12] Cyclic voltammetry was conducted in CH_2Cl_2/MeCN (4:1) containing 0.1 M Bu_4NBF_4 as a supporting electrolyte (*E*/V vs. SCE, Pt electrode, scan rate 100 mV s^{-1}). Ferrocene undergoes 1e-oxidation at +0.53 V under similar conditions.

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