Electrochromism

Deutsche Ausgabe: DOI: 10.1002/ange.201510935
Internationale Ausgabe: DOI: 10.1002/anie.201510935

Assembly of an Axially Chiral Dynamic Redox System with a Perfluorobiphenyl Skeleton into Dumbbell- or Tripod-type Electron Donors

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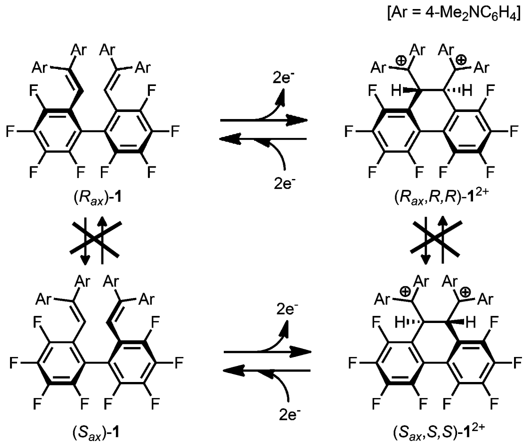
Abstract: *The incorporation of F atoms endows a diethenylbiphenyl-based electron donor with configurational stability and S_NAr reactivity. The former enables the dynamic redox pair of* (R_{ax})*-**1**/*(R_{ax},R,R)*-*$\mathbf{1}^{2+}$ *to exhibit drastic UV/Vis and CD spectral changes upon electrolysis, whereas the latter makes it possible for* (R_{ax})*-**1** to serve as a useful chiral synthon for the production of larger assemblies [*(R_{ax},R_{ax})*-**2 d,p,m** and* (R_{ax},R_{ax},R_{ax})*-**3**] containing two or three dyrex units. These dyads and triad also exhibit a clean electrochiroptical response with isosbestic points owing to one-wave multi-electron transfer.*

Perfluoroarenes (F-arenes)[1] have unique properties owing to the fact that they possess a quadropole moment that is different from that in usual arenes,[2] as exemplified by the formation of a stable 1:1 complex between C_6F_6, a representative F-arene, and C_6H_6.[3] Although several F-substituted arenes crystallize isomorphously to the corresponding arenes without F atoms,[4] they often show different packing arrangements.[5] For example, a face-to-face arrangement is seen more often in F-arenes, in contrast to the herringbone packing favored in non-F arenes.[6] These changes in the packing preference are advantageous for improving OFET properties or increasing the solubility of oligoacenes through F-substitution.[7]

Owing to the Lewis acidity of F-arenes, F-substitution on the molecular skeleton has been commonly used for electron acceptors (for example, F_4-TCNQ) for exploitation in redox chemistry. On the other hand, electron donors containing a F-arene framework are rare,[8] apparently because of destabilization of an oxidized state (for example, dication) by the introduction of highly electronegative F atoms. Thus, the merit of F-arene incorporation has been seldom examined in the development of the electron donors. In this context, dynamic redox (dyrex) systems[9] that undergo reversible C–C bond formation/cleavage upon electron transfer[10] are interesting because such dyrex behavior could minimize the electronic destabilization effects even in the doubly-charged dicationic state by disconnection of the π-conjugation between the cationic chromophore and the F-arene framework upon oxidation. These considerations prompted us to design F-arene-based dyrex systems, such as 2,2′-bis(diarylethenyl)-3,3′,4,4′,5,5′,6,6′-octafluorobiphenyl **1**, as an electron donor to give stable dicationic species ($\mathbf{1}^{2+}$; Scheme 1). The 4-$Me_2NC_6H_4$ group was selected as an aryl group based on a consideration of its high thermodynamic stability[11] and strong coloration in the visible region[12] for Michler's Hydrol Blue chromophore [$(4\text{-}Me_2NC_6H_4)_2CH^+$].



Scheme 1. F-arene based chiral dyrex donor **1** and its stereospecific cyclization to $\mathbf{1}^{2+}$ upon 2e-oxidation.

From a synthetic viewpoint, the incorporation of a F-arene skeleton is advantageous because of the high reactivity toward S_NAr functionalization[13] by nucleophiles such as acetylides. Furthermore, the F atoms at the 6,6′-positions could prevent rotation around the biphenyl axis in **1** to allow its optical resolution. Thus, dyrex donor (R_{ax})/(S_{ax})-**1** could serve as a versatile chiral synthon for the production of larger assemblies containing multiple dyrex units, such as dumbbell-type dyads (R_{ax},R_{ax})/(S_{ax},S_{ax})-**2 d,p,m** or a tripod-type triad (R_{ax},R_{ax},R_{ax})/(S_{ax},S_{ax},S_{ax})-**3**, through connection with the acetylene linkers (Scheme 2). With the use of the resolved synthons, assemblies could be synthesized in an optically pure form without being contaminated by their diastereomers. Upon two-electron (2e)-oxidation of each dyrex unit in **1**–**3**, the stereochemistries of the newly formed asymmetric centers were regulated by the transmission of axial chirality of the biphenyl axis. Such stereospecificity endows the present dyrex systems with electrochiroptical properties.[14,15] In fact, drastic changes in the UV/Vis and circular dichroism (CD)

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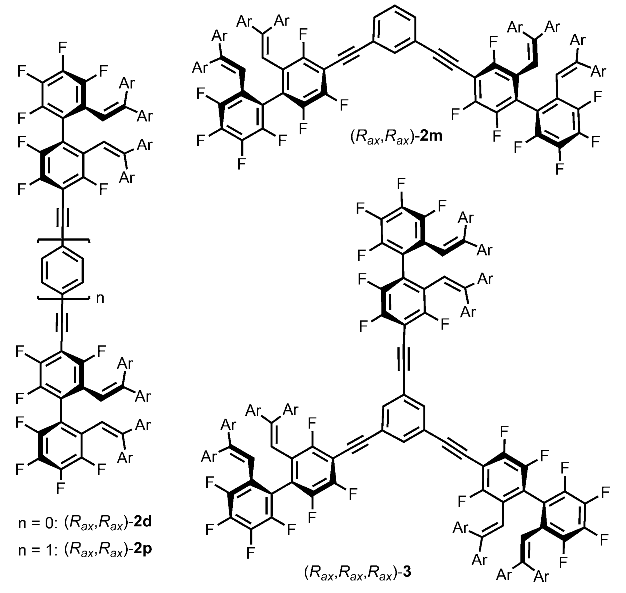
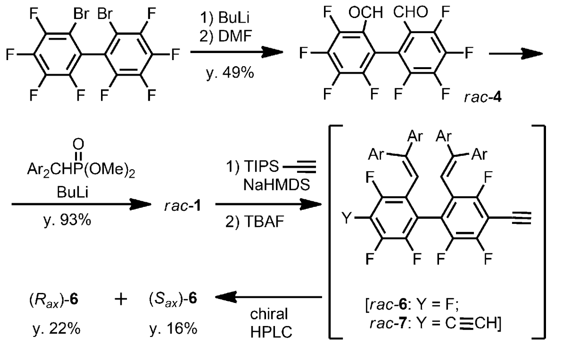
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201510935.



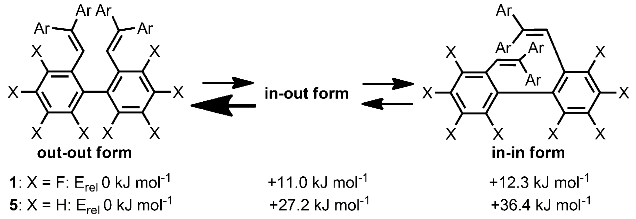
Scheme 2. Structures of chiral assemblies **2** and **3**.

spectra were observed upon electrolysis of optically pure (R_{ax})/(S_{ax})-**1**, (R_{ax},R_{ax})/(S_{ax},S_{ax})-**2 d,p,m**, and (R_{ax},R_{ax},R_{ax})/(S_{ax},S_{ax},S_{ax})-**3** owing to their stereospecific transformation into dication (R_{ax},R,R)/(S_{ax},S,S)-$\mathbf{1}^{2+}$, tetracations (R_{ax},R_{ax},R,R,R,R)/(S_{ax},S_{ax},S,S,S,S)-$\mathbf{2\,d,p,m}^{4+}$, and hexacation (R_{ax},R_{ax},R_{ax},R,R,R,R,R,R)/(S_{ax},S_{ax},S_{ax},S,S,S,S,S,S)-$\mathbf{3}^{6+}$, respectively, as detailed below (Scheme S1).

2,2′-Dibromo-3,3′,4,4′,5,5′,6,6′-octafluorobiphenyl[16] was selected as a F-arene skeleton, and was first converted to the corresponding 2,2′-dialdehyde *rac*-**4**[17] via its dilithio derivative in 49 % yield. The Horner–Emmons reaction with the use of (4-$Me_2NC_6H_4$)$_2$CHPO(OMe)$_2$[18] proceeded smoothly to give *rac*-**1**[17] in 93 % yield (Scheme 3). A conformational search for **1** predicted three energy-minimized structures,[19] the geometries of which differed at the diarylethenyl groups (Scheme 4). The out–out conformer is most stable due to reduced steric congestion because the two diarylethenyl groups are extended outward (Supporting Information, Figure S1). These conformers undergo interconversion very rapidly in solution at room temperature, so that the NMR spectrum of **1** in CD_2Cl_2 shows a set of sharp resonances assignable to a single species with strong time-averaged C_{2h} symmetry (Figure S2). We could isolate the least stable in–in conformer upon crystallization (*rac*-**1**·$CHCl_3$; Figure S3),[20] which clearly showed partial but nearly parallel π-stacking of C_6F_4 and 4-$Me_2NC_6H_4$ groups with a shortest C–C contact of 3.22(1) Å. Based on DFT calculations (B3LYP/6–31G*; Figure S4), the HOMO and HOMO-1 energy levels are nearly the same for the out–out and in–in forms. Thus, the redox properties of **1** reflect those of the more stable out–out conformer, which is dominantly present in solution. According to a voltammetric analysis (Figure 1), **1** exhibits strong electron-donating properties ($E^{ox}=+0.86$ V vs. SCE in CH_2Cl_2).[21] The oxidation process is irreversible in the sense that the return peak appeared in the far cathodic region, which corresponds to the reduction of dication $\mathbf{1}^{2+}$ ($E^{red}=-0.09$ V) with a newly formed C–C bond between the two methine carbons. Such a large separation of redox peaks[22] as well as nearly simultaneous 2e-transfer are characteristic of dyrex systems undergoing reversible C–C bond formation/cleavage upon electron transfer,[9] and were also found in the analogous redox pair of $\mathbf{5}/\mathbf{5}^{2+}$[15] without F atoms. Upon treatment of *rac*-**1** with iodine (3 equiv), the dication salt $\mathbf{1}^{2+}(I_3^-)_2$[17] was obtained as a deep blue powder in 95 % yield, which regenerated neutral donor *rac*-**1** upon Zn-reduction in 92 % yield. A sharp singlet at 5.41 ppm for the methine protons in the NMR spectrum ($CDCl_3$) of $\mathbf{1}^{2+}(I_3^-)_2$ is consistent with the formation of a new C_{sp3}–C_{sp3} bond. In addition to axial chirality, dication $\mathbf{1}^{2+}$ has two asymmetric centers. Their configurations are R,R (or S,S) when the axial chirality is R_{ax} (or S_{ax}),[23] demonstrating that oxidative ring-closure selectively occurs from the major out–out conformer of (R_{ax})- and (S_{ax})-**1** with the perfect transmission of axial



Scheme 3. Preparation of *rac*-**1** and chiral synthon (R_{ax})-and (S_{ax})-**6**.



Scheme 4. Facile conformational change in **1** and non-F derivative **5**.

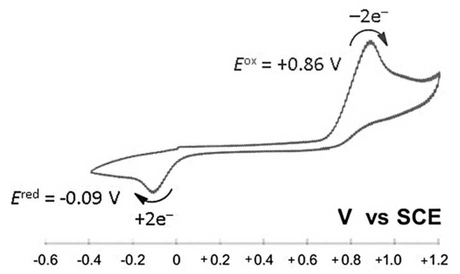


Figure 1. Cyclic voltammogram of **1** measured in CH_2Cl_2 (E/V vs. SCE, Pt electrode, scan rate 500 mV s^{-1}).

chirality to give dications with (R_{ax},R,R) and (S_{ax},S,S) configurations, respectively.

As in other 2,2′,6,6′-substituted biphenyls, rotation around the central axis in **1** is prohibited to allow its optical resolution by HPLC with a chiral stationary phase (CHIRALPAK-IA, hexane/$CH_2Cl_2 = 5$). The CD spectrum of the 1st fraction exhibits a large positive couplet around 360 nm [λ_{ext} 388 nm ($\Delta\varepsilon$ +20), 338 (−27) in MeCN at 293 K], which originates from the exciton coupling[24] of the two diarylethenyl chromophores in the out–out conformer with an S_{ax}-configuration.[25] No racemization occurred under the experimental conditions.[26] The CD spectrum of (S_{ax})-**1** exhibits reversible temperature-dependence (273–344 K in MeCN) and solvent dependence (Figures 2 and S5), thus the multi-input/multi-output properties are endowed by the F-arene incorporation.

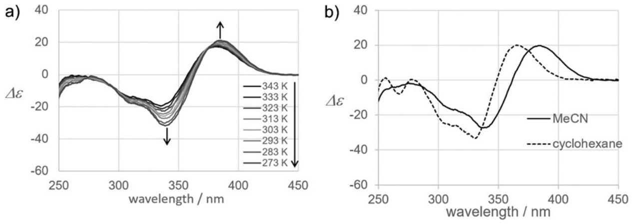


Figure 2. a) A reversible change in CD spectrum of (S_{ax})-**1** in MeCN by temperature (273–343 K). b) CD spectra of (S_{ax})-**1** measured in MeCN and cyclohexane at 293 K.

Very clean changes in the UV/Vis and CD spectra were observed upon the electrochemical oxidation of (S_{ax})-**1** to (S_{ax},S,S)-$\mathbf{1}^{2+}$ in MeCN (Figure 3). The presence of several isosbestic points is consistent with nearly simultaneous 2e-transfer and indicative of a negligible steady-state concentration of the intermediary cation radical species during interconversion (Scheme S2). Based on a consideration of the high reactivity of open-shell species in general, a very short life-time of the cation radical intermediates is favored in the construction of highly reversible chromic systems. In this way, the optically pure dyrex pair of **1**/$\mathbf{1}^{2+}$ was demonstrated to act as a new electrochiroptical system, and an outstanding feature is the large amplitude ($A = 47$ at 293 K in MeCN) of the CD couplet in the neutral donor **1**. Next, larger assemblies (**2** and **3**) containing multiple units of **1** were constructed in optically pure form.

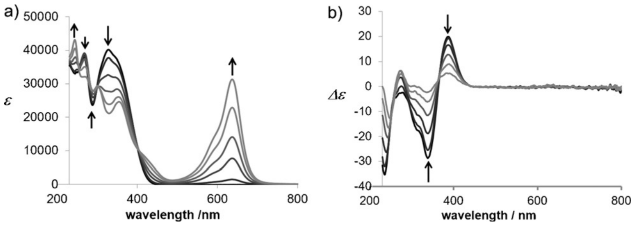


Figure 3. Changes in a) UV/Vis and b) CD spectra of (S_{ax})-**1** (2.0×10^{-5} M) upon constant-current electrochemical oxidation in MeCN containing 0.05 M Et_4NClO_4 (10 μA, every 5 min).

The S_NAr reactions of perfluorobiphenyl derivatives with nucleophiles proceed selectively at the 4- or 4,4′-positions.[13] Thus, we designed (R_{ax})- or (S_{ax})-**6** with an ethynyl group at the 4-position as a versatile synthon to prepare the optically pure dyad- and triad-assemblies, since the ethynyl group could act as a connecting group under the various metal-catalyzed coupling conditions. The reaction of *rac*-**1** with ethynyltriisopropylsilane in the presence of NaHMDS followed by removal of the TIPS group by using TBAF gave *rac*-**6** along with the disubstituted derivative (*rac*-**7**; Scheme 3). Selective substitution at the 4- or 4,4′-positions was confirmed by the X-ray analysis[20] of 4,4′-diethynyl derivative *rac*-**7** (Figure S3). After separation of the mixture by chiral HPLC (CHIRALPAK-IA, hexane/$CH_2Cl_2 = 5$), (R_{ax})- and (S_{ax})-**6**[17] were isolated in respective yields of 22 % and 16 % over two steps. The configuration of the 1st fraction of ethynyl derivative **6** was assigned to be S_{ax} based on a comparison of its CD spectrum [λ_{ext} 390 nm ($\Delta\varepsilon$ + 18), 340 (−29) in MeCN at 293 K] with that of (S_{ax})-**1**. The redox behavior of the dyrex unit of **1** was scarcely affected by attachment of ethynyl group [E^{ox} (**6**) = + 0.86 V and E^{red} ($\mathbf{6}^{2+}$) = −0.13 V vs. SCE in CH_2Cl_2][21] (Figure S5).

Despite the strong electron-donating properties, the oxidative alkyne coupling of **6** under Hey conditions (Cu/air) proceeded smoothly. Thus, a dumbbell-shaped dyrex dyad (R_{ax},R_{ax})-**2d** was obtained from (R_{ax})-**6**[17] in 96 % yield, whereas (S_{ax},S_{ax})-**2d** was obtained from (S_{ax})-**6**. Under Sonogashira conditions, (R_{ax})- and (S_{ax})-**6** were reacted with 1,4-diiodobenzene or 1,3-diiodobenzene to give another series of dyads (R_{ax},R_{ax})- or (S_{ax},S_{ax})-**2p**[17] (y. 60 %) and -**2m**[17] (y. 96 %), respectively. A tripod-type triad (R_{ax},R_{ax},R_{ax})- or (S_{ax},S_{ax},S_{ax})-**3**[17] was successfully synthesized with the use of 1,3,5-triiodobenzene (y. 73 %). All of the large assemblies of **2d,p,m** and **3** are stable greenish-yellow solids with the larger amplitude of the CD couplet ($A = 58$, 56, 62, and 103 for **2d,p,m**, and **3**, respectively, in MeCN at 293 K). They exhibit high solubility in common organic solvents despite their large molecular sizes (MF and MW of **3**: $C_{156}H_{129}F_{21}N_{12}$ and 2570.80), owing to the incorporation of the F-arene skeleton.[7] In the NMR spectra of **2d,p,m**, and **3** ($CDCl_3$), the resonances of the F-arene-based dyrex units have nearly the same chemical shifts as those of ethynyl derivative **6**, indicating that the inter-unit interaction is minimal, and thus, the 1,3- and 1,4-diethynylbenene units, as well as the buta-1,3-diyne unit, are large enough for spatial isolation of the multiple dyrex units in the present dyads and triad. As suggested by the energy-minimized structure of the tripod-type hexacationic species ($\mathbf{3}^{6+}$), three of the dicationic moieties are placed in a C_3-symmetric fashion with adequate separation among them[19a] (Figure S1). Thus, electrostatic interaction would also be minimized even in hexacation $\mathbf{3}^{6+}$, and this could also hold true for the dumbbell-shaped tetracations $\mathbf{2d,p,m}^{4+}$. Based on the above consideration, the present large assemblies **2d,p,m**, and **3** could serve as the pseudo two-state (neutral–polycation) switching systems, as in the monomeric F-arene system **1**, with a higher sensitivity owing to the multiple chromophores.

The cyclic voltammograms (CH_2Cl_2) of dyads **2d,p,m** and triad **3** show a pair of redox waves at potentials [E^{ox}

(**2 d,p,m**,**3**) = +0.88 to +0.93 V and E^{red} (**2 d,p,m**$^{4+}$,**3**$^{6+}$) = −0.12 to −0.17 V vs. SCE in CH_2Cl_2] similar to those of **1** (Figure S6). The peak currents in the voltammograms of **2 d,p,m** are much larger than that seen for **1** (Figure S6). An even larger current was observed in **3**, suggesting that **2 d,p,m**, and **3** undergo one-wave four- and six-electron transfer, respectively, at the peak potentials.[27] Upon preparative-scale oxidation of dyads (R_{ax},R_{ax})- or (S_{ax},S_{ax})-**2 d,p,m** with iodine, dark green powders were obtained, which can be assigned to the corresponding tetracationic salts **2 d,p,m**$^{4+}(I_3^-)_4$, respectively, based on their ^{1}H NMR spectra.[28] When constant-current electrolysis was conducted on the optically pure dyads (R_{ax},R_{ax})/(S_{ax},S_{ax})-**2 d,p,m** and triad (R_{ax},R_{ax},R_{ax})/(S_{ax},S_{ax},S_{ax})-**3**, very clean changes in the UV/Vis and CD spectra were again observed (Figure S7). The presence of several isosbestic points is consistent with nearly simultaneous multiple electron-transfer, and indicative of stereospecific transformation into polycations, where each component of a dyrex unit with an (R_{ax}) or (S_{ax}) configuration was converted into a dicationic moiety with an (R_{ax},R,R) or (S_{ax},S,S) configuration, respectively.

In addition to their advanced electrochromic behavior shown above, these dyrex systems are interesting in terms of molecular electronics, since the electrochemical bistability of the dyrex unit is the key to realizing unimolecular memory, where one dyrex unit acts as a 1-bit.[9a] The present molecules containing multiple dyrex units can pave the way toward unimolecular n-bit memory, where one molecule can act as an n-bit. Studies in this vein are now in progress.

Acknowledgements

H.T. is grateful for a Research Fellowship for Young Scientists from JSPS (No. 2125). T.S. thanks Prof. Takanori Fukushima at TITECH and the Cooperative Research Program of "Network Joint Research Center for Materials and Devices".

Keywords: cationic dye · chirality · electrochromism · fluoroarenes · multielectron transfer

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 2582–2586
Angew. Chem. **2016**, *128*, 2628–2632

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[19] The conformational search was conducted by using the MacroModel software (v9.9 OPLS_2005, Monte Carlo Multiple Minimum method, non-solvated, 50000 steps).

[20] CCDC 1436781 (*rac*-**1**·$CHCl_3$ triclinic, $P\bar{1}$, $Z = 2$) and 1436782 (*rac*-**7**·$CHCl_3$, orthorhombic, $Pca2_1$, $Z = 4$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[21] The redox potentials (E^{ox} and E^{red}) were measured by cyclic voltammetry (Pt electrode, scan rate 500 $mV s^{-1}$) in CH_2Cl_2 containing 0.1 M Bu_4NBF_4. The oxidation potential of ferrocene measured under the similar conditions is +0.53 V vs. SCE. E^{ox} and E^{red} were calculated as $E^{ox} = E^{anodic\ peak} - 0.03$ and $E^{red} = E^{cathodic\ peak} + 0.03$, respectively.

[22] Similar separation of redox peaks was also observed in MeCN containing 0.1 M Et_4NClO_4 (E^{ox} of ferrocene = +0.38 V). The redox potentials of **1**/$\mathbf{1}^{2+}$ are +0.55 and −0.47 V, respectively, whereas those for non-F derivative **5**/$\mathbf{5}^{2+}$ are +0.41 and −0.41 V (Ref. [15]), respectively. Weaker donating properties of **1** than **5** are caused by F-substitution. The potential of $\mathbf{1}^{2+}$ is closer to that of $\mathbf{5}^{2+}$, and the smaller effect than in the neutral donor can be accounted for by disconnected conjugation between the Ar_2C^+ units from the F-arene skeleton of $\mathbf{1}^{2+}$.

[23] Upon oxidation of *rac*-**1** with $AgBF_4$, $\mathbf{1}^{2+}(BF_4^-)_2$ was obtained as tiny needle-like single-crystals. The salt only contains the pair of (R_{ax},*R*,*R*)- and (S_{ax},*S*,*S*)-stereoisomers as confirmed by its X-ray analysis. CCDC 1436783 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[24] *Circular Dichroism: Principles and Applications*. 2nd ed. (Ed.: N. Berova, K. Nakanishi, R. W. Woody), Wiley-VCH, New York, **2000**.

[25] The absolute configuration was deduced by the similarity in the bisignated CD signal to that of (S_{ax})-2,2′-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]binaphthyl [λ_{ext} 404 nm ($\Delta\varepsilon$ +44), 357 (−83) in MeCN] (Ref. [15]).

[26] No racemization was confirmed by negligible changes in the CD spectrum of optically pure **1** after heat treatment at 343 K for 5 h or after the preparative-scale redox cycle (iodine-oxidation/ Zn-reduction).

[27] Although the peak current in the voltammogram is proportional to the numbers of transferred electrons, it is also the function of the diffusion constant (D) of the substrate. Thus, the smaller peak current in **2** and **3** than the doubled or tripled value of **1** can be accounted for, at least in part, by the smaller D for **2** and **3** owing to the larger molecular-size. In fact, the smaller D values of **2d** ($6 \times 10^{-10}\ m^2 s^{-1}$ in CD_2Cl_2 at 298 K) and **2m** ($6 \times 10^{-10}\ m^2 s^{-1}$) were determined compared to that of **1** ($8 \times 10^{-10}\ m^2 s^{-1}$).

[28] Upon treatment of triad **3** with iodine, the dark green powder was obtained whose NMR analysis was hampered owing to its low solubility in common solvents.

Received: November 25, 2015
Revised: December 10, 2015