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DOCTORAL DISSERTATION

Studies on Dynamic Redox Behavior of Hexaphenylethane-type and Diarylethenyl-type Electron Donors Containing the Perfluorobiphenyl Skeleton

(パーフルオロビフェニル骨格を有する
ヘキサフェニルエタン型及びジアリールエテニル型
電子供与体の動的酸化還元挙動に関する研究)

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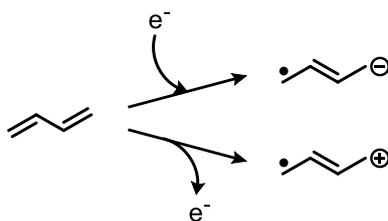
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General Introduction

0-1. Dynamic Redox (*dyrex*) Systems

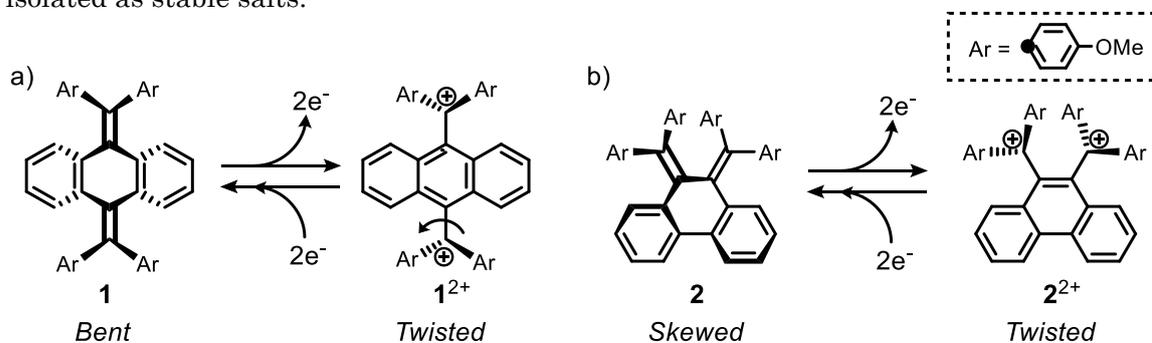
0-1-1. π -Electron Systems Exhibiting Drastic Structural Changes Upon Electron Transfer

Redox reactions^[1] of an organic π -conjugated system induce a change in bond order. Each of conjugated bonds undergoes characteristic change: the bond order of C¹=C² and C³=C⁴ bonds decreases whereas that of C²-C³ bond increases in 1,3-butadiene (Scheme 0-1).



Scheme 0-1. A change in bond order upon one-electron ($1e^-$) oxidation/reduction in 1,3-butadiene system.

In the π -systems suffering steric hindrance (e.g. sterically hindered quinodimethanes^[2,3,4]), the changes in bond order induce characteristic structural changes because the effective mode to release the strain depends on the bond order of the certain bonds (Scheme 0-2). That is, the 9,10-anthraquinodimethane **1**^[5] and 9,10-phenanthraquinodimethane **2**^[6] with electron-donating aryl substituents on the exocyclic bonds (Ar = 4-MeOC₆H₄) drastically changed their geometries since the bond order of the exocyclic C=C bonds were reduced upon two-electron ($2e^-$) oxidation to allow easy transformation of their molecular geometries from the bented/skewed shape in **1** and **2** into the twisted one in **1**²⁺ and **2**²⁺. Such geometrical changes were demonstrated by X-ray analyses on both of the neutral π -systems and their corresponding charged species isolated as stable salts.



Scheme 0-2. The “ π -type” *dyrex* systems exhibiting dynamic structural changes upon electron transfer: (a) 9,10-anthraquinodimethane **1** with a bent geometry giving twisted dication **1**²⁺; (b) 9,10-phenanthraquinodimethane **2** with a skewed geometry giving twisted dication **2**²⁺. All of the geometrical changes were verified by X-ray analyses.

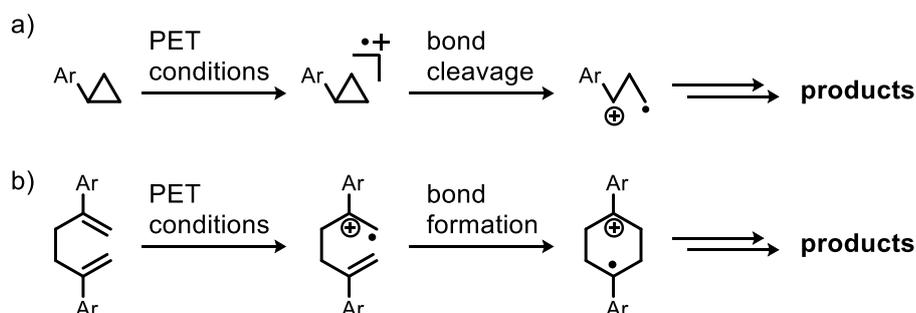
In some cases, the structural changes after the first 1e-oxidation/reduction makes the second redox process proceed facily, resulting in successive 2e-transfer nearly at the same potential. Moreover, there are cases where the electron-transfer of the ion radicals to the corresponding doubly charged diions proceeds more easily than the first oxidation/reduction process, thus minimizing the steady-state concentration of the intermediary ion radicals. By considering that the open-shell species are generally reactive to often cause side-reactions,^[7] such a feature is favored to attain high reversibility of the redox interconversion.

Another characteristic is the separation of redox potentials of the neutral and the charged species since not only the geometrical structure but also the electronic structure are perturbed upon electron-transfer. By adopting the twisted geometry in the doubly charged species, the on-site Coulombic repulsion could be reduced to stabilize the diions electronically. For example, the butterfly-shaped 9,10-anthraquinodimethane derivative **1**^[5] undergoes 2e-oxidation at +0.44 V vs Fc/Fc⁺^[1a] whereas the corresponding dication **1**²⁺ with a twisted geometry exhibits 2e-reduction potential at -0.08 V.^[1a] Similarly, E^{ox} of helically-deformed 9,10-phenanthraquinodimethane derivative **2**^[6a] is +0.40 V^[1b] (2e), which is far different from E^{red} of the twisted dication **2**²⁺ (-0.10 V^[1b] (2e)). The observed separation of redox potentials for the reversibly interconvertible species endows the redox pairs with the electrochemical bistability, which is one of the required features in developing promising functionalized materials such as molecular switches or memories.

The "dynamic redox (*dyrex*) system" is the name given to these systems that experience the dynamic changes in geometrical and electronic structures upon redox reactions as described above. Their characteristic features are facile 2e-transfer nearly at the same potentials and the electrochemical bistability. For the examples shown above, the redox-induced change in the bond order occurs in the π -conjugated systems, thus, they are classified as the " π -type" *dyrex* systems.

0-1-2. Redox Switching of a σ -Bond upon Electron Transfer

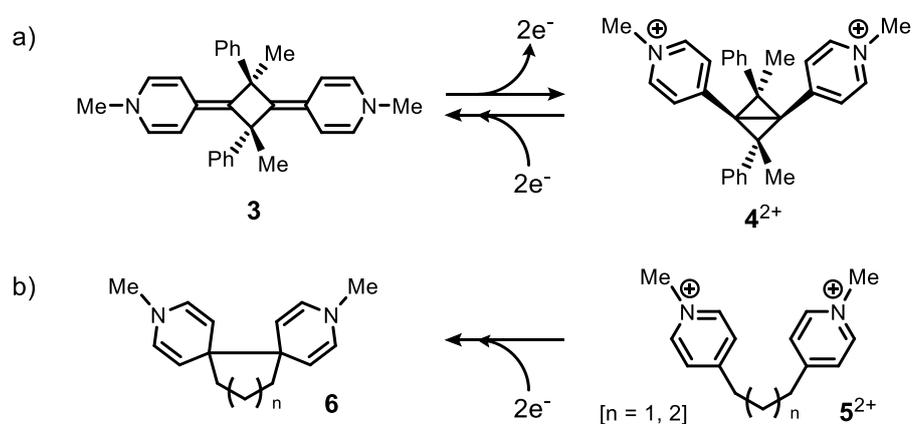
The redox-induced change in the bond order occurs not only in the π -conjugated systems but in the system where the σ -bond formation/cleavage is accompanied by electron transfer (e.g. bond order change of $0 \rightarrow 1$ or $1 \rightarrow 0$). Plethora of research on the photoinduced electron-transfer (PET) reactions afforded many diagnostic examples (Scheme 0-3). Thus, the 1e-oxidation of arylcyclopropanes induced the C-C σ -bond cleavage to give 1,3-propanediyl-type cation radicals,^[8] whereas dimerization of styrenes was also induced under the PET conditions by forming a new C-C σ -bond at their β -positions.^[9] The latter reaction was especially favored when the two styrene units are connected by a spacer so that the bonding process being intramolecular process: e.g. 2,5-diaryl-1,5-hexadienes to cyclohexane-1,4-diyl cation radicals.^[10]



Scheme 0-3. (a) A PET reaction involving C-C bond cleavage in arylcyclopropane; (b) A PET reaction involving C-C bond formation in 2,5-diaryl-1,5-hexadiene.

In these PET reactions, formation/cleavage of the σ -bond was mostly evidenced by time-resolved spectroscopy since the generated ion radicals are highly reactive to undergo various follow-up reactions to give characteristic reaction products. However, by incorporating charge-stabilizing groups, the ion radicals/diions could be, if possibly, isolated as salts. So that, they can be involved in constructing the reversible *dyrex* systems. In terms of drastic structural and electronic changes, the *dyrex* systems involving redox-switching of a σ -bond is more attracting than the “ π -type” *dyrex* systems shown in the previous section.

The historical prototypes of " σ -type" *dyrex* systems include 1,3-dimethylenecyclobutane **3** having two dihydropyridine chromophores on the exocyclic bonds, which underwent oxidative C-C bond formation to give bicyclo[1.1.0]butane-1,3-diyl dication **4**²⁺ (Scheme 0-4a).^[11] The homoconjugation between the two chromophores would facilitate the transformation, which was also the case in their pyran analogues. Although reduction of tethered dipyrindinium derivatives **5**²⁺ was reported to give spiro-type compounds **6** by C-C bond formation (Scheme 0-4b),^[12] dipyrindinium **4**²⁺ generated from **3** was transformed to the starting diene **3** upon 2e⁻ reduction accompanied by cleavage of the newly formed C-C σ -bond.



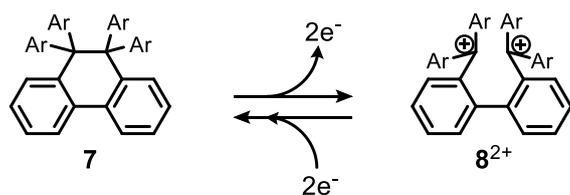
Scheme 0-4. (a) Redox interconversion between 1,3-dimethylenecyclobutane **3** and bicyclo[1.1.0]butane-1,3-diyl dication **4**²⁺ upon electron transfer accompanied by reversible C-C bond formation/cleavage (" σ -type" *dyrex* system). (b) The C-C bond formation of dipyrindinium **5**²⁺ upon 2e⁻ reduction to give spiro-type compound **6**.

0-1-3. Two Types of *Dyrex* Systems Exhibiting Redox Switching of a σ -Bond

The *dyrex* behavior involving redox-switching of a σ -bond was also observed in hexaphenylethane derivatives **7** and biphenyl-based bis(diarylethenyl)-type compound **9** as shown in this sections (Scheme 0-5a,b).

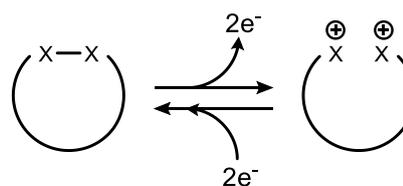
Due to the characteristic elongated C9-C10 bond, 9,9,10,10-tetraaryl-9,10-dihydrophenanthrene (Ar₄DHP) **7** underwent facile C9-C10 bond cleavage to give dication **8**²⁺ upon oxidation. Upon reduction, dication **8**²⁺ having a different reduction peak from oxidation peak of Ar₄DHP **7** reversibly underwent C-C bond formation to regenerate **7**. Thus, the reversible *dyrex* behavior was observed between neutral **7** and dication **8**²⁺. This pair can be classified as the “endo”-type *dyrex* system; the charges in the diion are located at the “endocyclic” carbons of the starting ring system which undergoes the C-C σ -bond cleavage.

(a) The representative “endo”-type *dyrex* compounds

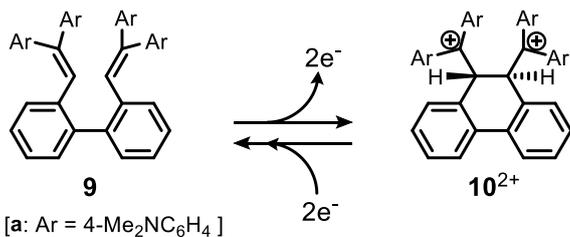


[a: Ar = 4-Me₂NC₆H₄; b: Ar = 4-MeOC₆H₄;
c: Ar = 4-(R)-sec-BuOC₆H₄]

(c) “endo”-type *dyrex* system

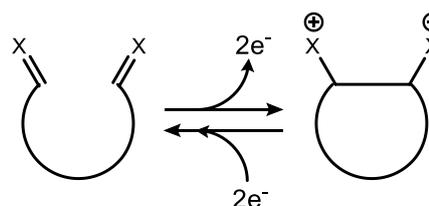


(b) The representative “exo”-type *dyrex* compounds



[a: Ar = 4-Me₂NC₆H₄]

(d) “exo”-type *dyrex* system



Scheme 0-5. Two type of “ σ -type” *dyrex* compounds: (a) The representative “endo”-type compounds of 9,9,10,10-tetraaryl-9,10-dihydrophenanthrene **7**/ biphenyl-2,2'-diylbis(diaryl methylium) **8**²⁺; (b) The representative “exo”-type compounds of 2,2'-diylbis(diarylethenyl) biphenyl **9**/ *trans*-9,10-dihydrophenanthrene-9,10-diylbis(diarylmethylium) **10**²⁺. Two type of “ σ -type” *dyrex* systems: (c) an “endo”-type system consisting of a dication with the positive charges located at the “endocyclic” carbons of the starting ring system undergoing bond cleavage; (d) an “exo”-type system consisting of a dication with the positive charges located at the “exocyclic” carbons of the newly formed ring system.

In contrast, upon oxidation of biphenyl-2,2'-diyl-type compounds **9a** attached with two strong electron-donating 2,2-diarylethenyl groups (e.g. 4-Me₂NC₆H₄), dications **10a**²⁺ with a butane-1,4-diyl dicationic structure^[13] was generated by σ -bond formation and facile ring closure upon electron-transfer, and allowing isolation of *trans*-**10a**²⁺ as a stable salt.^[14,15] In the reversible *dyrex* pair of **9a** ($E^{\text{ox}} = +0.03\text{V}$ vs Fc/Fc⁺)^[1a] and **10a**²⁺ ($E^{\text{red}} = -0.79\text{V}$)^[1a], the charges in the diion are located at the “exocyclic” carbons of the newly formed ring system after the C-C σ bond formation. This pair represents the behavior of the “exo”-type *dyrex* systems.

The two-types of *dyrex* systems (“endo”- and “exo”-systems) can be schematically presented as in Scheme 0-5c,d. By incorporating a ring structure in the molecules, all of the bond formation/cleavage reactions can proceed as unimolecular processes although it is not the essential prerequisite for the *dyrex* behavior.^[14] It is evident that the redox reaction into the corresponding diion is accompanied by the σ -bond cleavage in the “endo”-*dyrex* systems with transforming into the ring-opened diions. In contrast, in the “exo”-*dyrex* systems, the σ -bond formation is the key to leave the charges on the exocyclic groups. When the strong chromophores, such as triarylmethylium dyes,^[16] are incorporated, the *dyrex* pair would exhibit vivid change in color upon interconversion,^[17] thus endowing the systems with the electrochromic function.^[18] Due to the dynamic geometrical changes upon redox reactions, the chromism based on the *dyrex* systems could be accompanied by more advanced features as shown in the following sections.^[19,20]

0-2. Advanced Electrochromic Response of “Endo”- and “Exo”-type *Dyrex* Systems Exhibiting Redox Switching of a σ -bond

0-2-1. Tetraaryldihydrophenanthrenes as Prototypes of “Endo”-*Dyrex* Systems

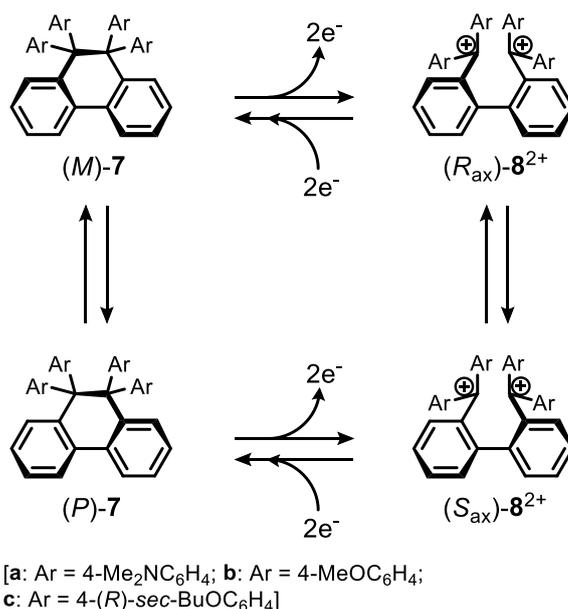
9,9,10,10-Tetraphenyl-9,10-dihydrophenanthrene (Ph₄DHP), already described earlier (Scheme 0-5a), has been known as a stable compound^[21] in spite of the fact that it inherits severe steric repulsion around the C9-C10 bond characteristic to hexaphenylethane.^[22] So that, the C9-C10 bond of Ar₄DHP derivatives would be expanded, and thus the bond length would be much greater than the standard value.^[23,24,25] The elongated bond has a smaller bond-dissociation energy^[25,26] and could be cleaved easily upon redox reactions,^[27] which had prompted the study in detail on a series of Ar₄DHPs as a promising class of compounds to establish the “endo”-type *dyrex* systems.

By attaching the electron-donating aryl groups, such as 4-Me₂NC₆H₄ (**a**) or 4-MeOC₆H₄ (**b**), at the C9 and C10 positions, Ar₄DHPs (**7**) underwent facile 2e-oxidation accompanied by C9-C10 bond cleavage^[28]. At the same time, the resulting biphenyl-2,2'-diyl dications (**8**²⁺) were found to be stable enough for isolation. The electrochemical bistability of these pairs were confirmed by the large difference in redox potentials (+0.21 and -0.95V for **7a/8a**²⁺; +0.91 and -0.32 V for **7b/8b**²⁺, respectively, vs Fc/Fc⁺)^[1a] Upon reduction of dications **8a,b**²⁺, DHPs **7a,b** were effectively regenerated accompanied by formation of a C-C bond.

Another characteristic feature of the *dyrex* pairs of **7/8**²⁺ is drastic difference in their UV-Vis spectra.^[28] Ar₄DHPs **7** exhibit absorptions only in the UV region whereas **8**²⁺ have strong bands in the visible region as in triarylmethyl dyes, whose absorption maxima can be modified by changing the substituents on the aryl groups [**8a**²⁺ (Ar = Ar' = 4-Me₂NC₆H₄): λ_{\max} 661 nm (log ϵ 4.92), 604 (5.05); **8b**²⁺ (Ar = Ar' = 4-MeOC₆H₄): 539sh (4.72), 514 (4.78) in MeCN]. Thus, **7a/8a**²⁺ and **7b/8b**²⁺ pairs could demonstrate electrochromicity with vivid change in color between colorless-deep blue and colorless-deep red, respectively. When the spectral changes were followed by UV-Vis spectroscopy, several isosbestic points were observed because of negligible steady-state concentration of open-shell intermediates.

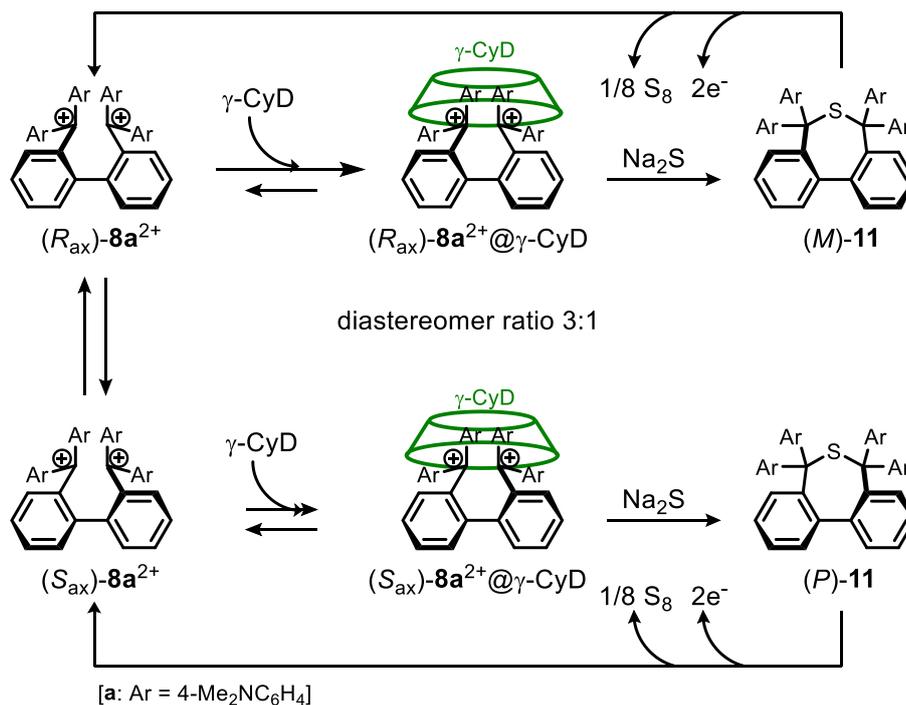
0-2-2. Electrochromism with Chiroptical Output of Chiral "Endo"-*Dyrex* Pair

Each of **7** and **8**²⁺ has a chiral element of helicity and axial chirality, respectively. So that, they exist as a pair of enantiomers (Scheme 0-6). They are configurationally unstable to exist as racemic mixtures due to rapid ring inversion in **7** or facile rotation around the biaryl axis in **8**²⁺. However, when associated with a chiral host, such as cyclodextrin (CyD),^[29] the diastereomeric pairs of the complex (e.g. (*R*_{ax})/(*S*_{ax})-**8**²⁺@CyD) could be configurationally biased to prefer one-handedness.



Scheme 0-6. Configurationally unstable “endo”-type *dyrex* system of (*M*)-**7**/*(R*_{ax})-**8**²⁺ and (*P*)-**7**/*(S*_{ax})-**8**²⁺ undergoing facile inversion of helicity and axial chirality.

This is the case for complexation of **8a**²⁺ with γ -CyD. The UV-Vis and circular dichroism (CD) spectra of **8**²⁺ (10⁵ M⁻¹) changed continuously upon gradual addition of γ -CyD (1-4 equiv.) in water (Figure 0-1). The association constant was proven to be as large as 10⁶ M⁻¹.^[30] Preference of (*R*_{ax})-**8a**²⁺ in 50% de at 25 °C is the reason for giving optically active (*M*)-dihydrothiepin (**11**) upon reaction of **8a**²⁺ salt with Na₂S in the presence of γ -CyD (Scheme 0-7). Since **11** is configurationally more stable than **8a**²⁺, diastereoselective complexation of **8a**²⁺ with γ -CyD followed by chemical transformation into **11** can demonstrate supramolecular chirality transfer^[31] on the *dyrex* component. Upon treatment with iodine, **11** (*E*^{bx} = +0.19 V vs Fc/Fc⁺)^[1b] underwent oxidative desulfurization to regenerate **8a**²⁺ and elemental sulfur,^[32] thus the above transformation can be conducted repeatedly.



Scheme 0-7. Diastereoselective complexation of γ -CyD with $(R_{ax})\text{-}8^{2+}$ and successive transformation into dihydrothiepin $(M)\text{-}11$, demonstrating successful transmission of supramolecular chirality to molecular chirality.

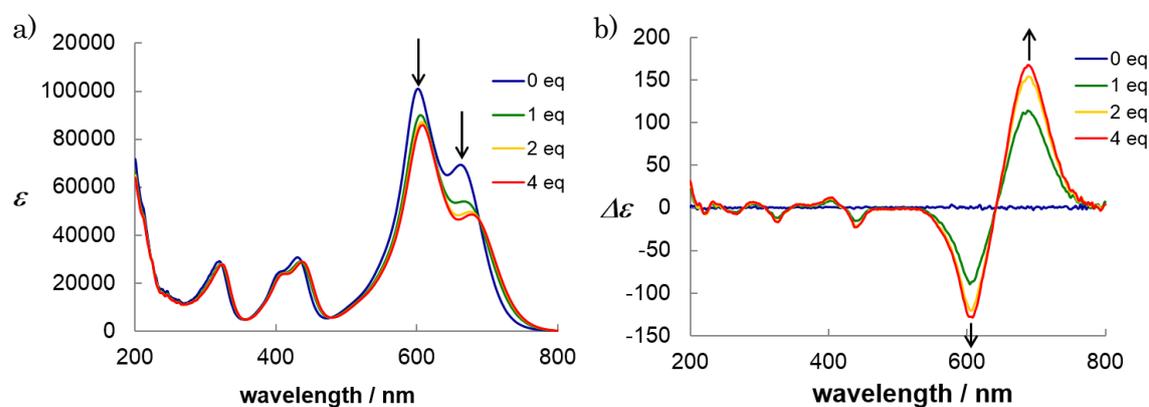


Figure 0-1. Changes in the (a) UV-Vis and (b) CD spectra of $8\mathbf{a}^{2+}(\text{BF}_4^-)_2$ (1.0 x 10⁻⁵ M in H₂O) upon addition of γ -CyD (1-4 equivs) at 25 °C. Diastereomeric complexes of $(R_{ax})\text{-}8\mathbf{a}^{2+}@ \gamma\text{-CyD}$ and $(S_{ax})\text{-}8\mathbf{a}^{2+}@ \gamma\text{-CyD}$ are equilibrated over the minutes, and the CD spectra were measured 30 min after admixing.

Besides the intermolecular chirality transmission in $\mathbf{8a}^{2+}/\gamma$ -CyD system, the sense of axial chirality of the dication was successfully biased to prefer one-handedness by attaching proper chiral auxiliary on the aryl groups.^[33] Thus, a CH_2Cl_2 solution of dication $(R,R,R,R)\text{-}\mathbf{8c}^{2+}$ ($\text{Ar} = \text{Ar}' = (R)\text{-}sec\text{-BuOC}_6\text{H}_4$; $E^{\text{red}} = -0.39$ V vs Fc/Fc^+)^[1a] exhibits bisignated Cotton effects [λ_{ext} 564 nm ($\Delta\epsilon$ +31), 531 (-23)] in the CD spectrum, which is strong enough to be used as an output upon electrolysis of $(R,R,R,R)\text{-}\mathbf{8c}$ ($E^{\text{ox}} = +1.03$ V).^[1a] This is the successful example of electrochiroptical response systems,^[15,34,35] in which the electrochemical input is transduced not only into UV-Vis but also chiroptical outputs.

Since the corresponding monocation with two $(R)\text{-}sec\text{-BuO}$ groups exhibits negligible CD signals [λ_{ext} 506 nm ($\Delta\epsilon$ -1.3) in CH_2Cl_2], the point chiralities in $(R,R,R,R)\text{-}\mathbf{8c}^{2+}$ must be intramolecularly transmitted^[36] to the axial chirality through the π - π overlap of two cationic chromophores. Thus, very strong CD signals are produced in the dication by exciton coupling mechanism.^[37] Comparisons of the X-ray geometries of two diastereomers show that the dication with (S_{ax}) -configuration is less sterically hindered, and thus would be more populated in solution (Figure 0-2). Based on the NMR analyses, the diastereomeric excess of $(R,R,R,R,S_{\text{ax}})\text{-}\mathbf{8c}^{2+}$ over $(R,R,R,R,R_{\text{ax}})\text{-}\mathbf{8c}^{2+}$ was determined to be only 5% in CH_2Cl_2 , however, the de value is 50% in benzene [λ_{ext} 569 nm ($\Delta\epsilon$ +294), 531 (-244)]. Such solvent dependency of de^[38,39] can be accounted for by considering that stabilization by the π - π overlap is more important in the less polar solvent.

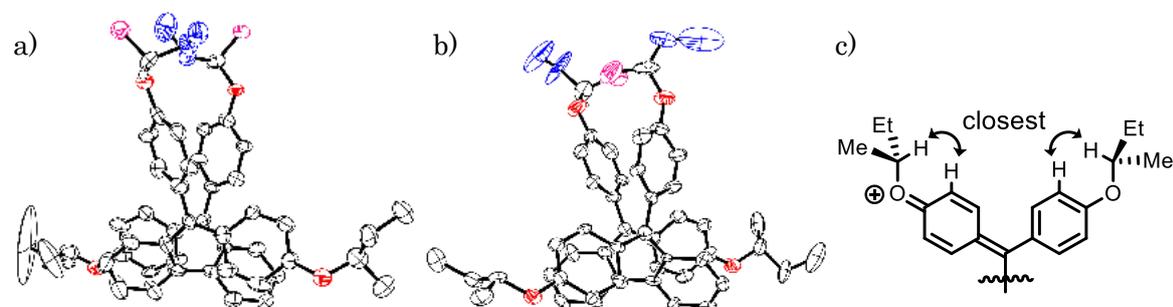


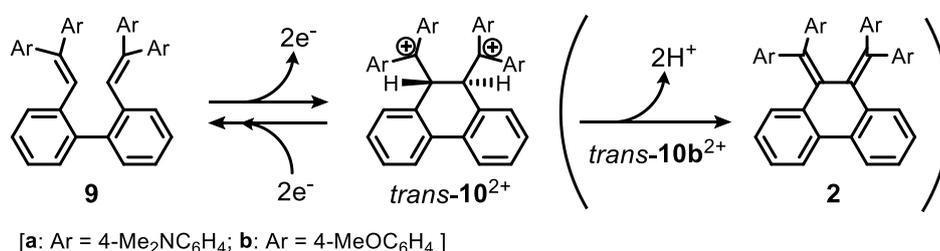
Figure 0-2. ORTEP drawings of (a) $(R,R,R,R,S_{\text{ax}})\text{-}\mathbf{8c}^{2+}$ and (b) $(R,R,R,R,R_{\text{ax}})\text{-}\mathbf{8c}^{2+}$ determined by the low-temperature X-ray analysis of $(R,R,R,R)\text{-}\mathbf{8c}^{2+}(\text{SbCl}_6^-)_2$ salt. Both diastereomers coexist in the same crystal in a 1:1 ratio. The cationic chromophores are stacked in a face-to-face manner, and the steric repulsion between the chiral auxiliaries is smaller in (S_{ax}) -isomer. (c) Schematic drawing of the geometry for $[4\text{-}(R)\text{-}sec\text{-BuOC}_6\text{H}_4]_2\text{C}^+$ unit commonly observed for both diastereomers in $(R,R,R,R)\text{-}\mathbf{8c}^{2+}(\text{SbCl}_6^-)_2$ crystal.

The electrochiroptical systems working under the intramolecular chirality transmission are attracting since the de value (i.e. chiroptical properties) can be modified by external stimuli such as solvent polarity, temperature, or pH. They are promising candidates in developing multi-input molecular response systems.^[40] In developing feature molecular devices, these multi-output response systems have an advantage to the simple electrochromic ones in terms of the error-free detection since the output signals can be verified through the multiple channels.

0-2-3. Bis(diarylethenyl) biphenyls as Prototypes of "Exo"-*Dyrex* Systems

In addition to the dimethylenecycloalkanes such as **3** (Scheme 0-4), α,ω -divinyl compounds can be promising candidates to perform as "exo"-type *dyrex* systems when the two vinylic chromophores are arranged in proximity to undergo facile ring closure by σ -bond formation upon electron transfer. The successful execution of this idea was demonstrated by biphenyl-2,2'-diyl-type compounds **9** attached with two electron-donating 2,2-diarylethenyl groups (Scheme 0-8).

The key issue in this scheme is kinetic stability of dication **10**²⁺ with a butane-1,4-diyl dicationic structure.^[13] The dicationic species of this category have been known to undergo deprotonation easily to generate the corresponding 1,3-dienes. In fact, **10b**²⁺ with four 4-MeOC₆H₄ groups underwent deprotonation under the reaction conditions, resulting in formation of 9,10-phenanthraquinodimethane **2** (scheme 0-2).^[6] On the other hand, the similar butane-1,4-diyl dication could be stabilized when attached with the stronger donating groups (e.g. 4-Me₂NC₆H₄), allowing isolation of *trans*-**10a**²⁺ as a stable salt.^[14,15] Thus, interconversion between **9a** ($E^{\text{ox}} = +0.03\text{V}$ vs Fc/Fc⁺)^[1a] and **10a**²⁺ ($E^{\text{red}} = -0.79\text{V}$)^[1a] proceeded quantitatively with exhibiting electrochromism thanks to strong coloration of **10a**²⁺ [λ_{max} 588 nm (log ϵ 4.98) in MeCN] with two Michler's Hydrol Blue chromophores.

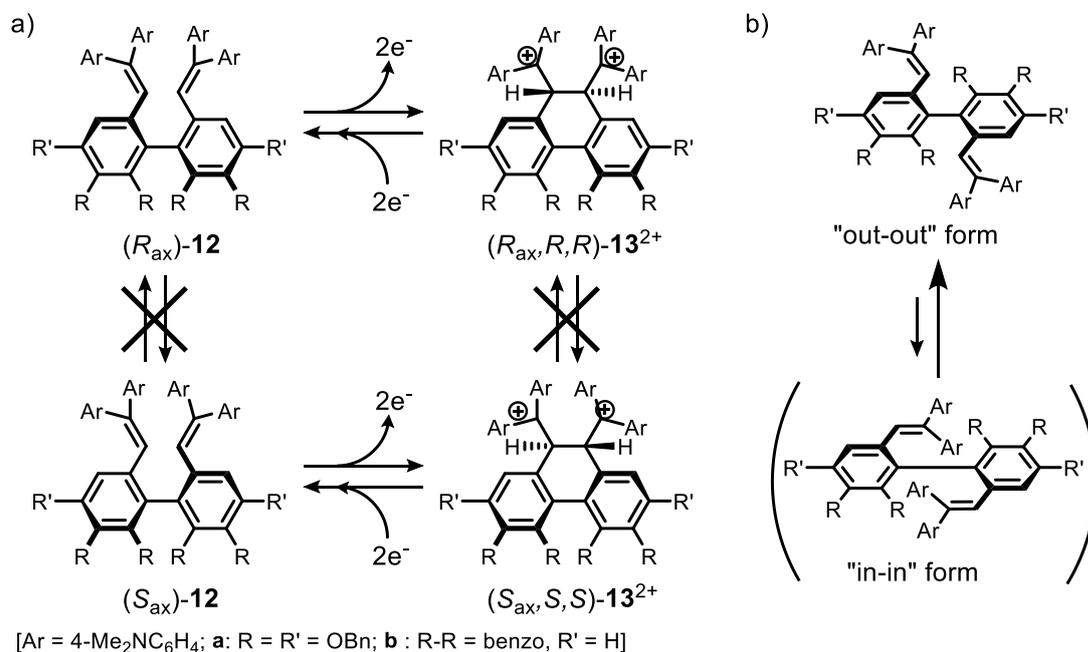


Scheme 0-8. Representative "exo"-*dyrex* system of **9/10**²⁺. The latter species is classified as a butane-1,4-diyl dication, which easily undergoes deprotonation into 1,3-butadiene (e.g. **2**) unless special stabilizing effects are present.

0-2-4. Electrochromism with Chiroptical Output of Chiral "Exo"-*Dyrex* Systems

As in the "endo"-*dyrex* pairs of **7** and **8**²⁺, both components of "exo"-*dyrex* pairs of **9** (axial chirality) and **10**²⁺ (helicity, two point chiralities) have the asymmetric elements. In the *dyrex* pairs having substituents on the biaryl moiety **12/13**²⁺, optically pure samples of (*R*_{ax})- or (*S*_{ax})-**12** ($E^{\text{ox}} = +0.11\text{ V}$ (**a**);^[1a] $+0.06\text{ V}$ (**b**)^[1b] vs Fc/Fc⁺, respectively) were isolated as configurationally stable molecules^[15a,41] which were transformed into dicationic **13**²⁺ ($E^{\text{red}} = -0.76\text{ V}$ (**a**);^[#1a] -0.78 V (**b**)^[1b] respectively) with (*R*_{ax},*R,R*)- or (*S*_{ax},*S,S*)-configuration, respectively (Scheme 0-9a). The 1,4-dicaionic part in **13**²⁺ was again stabilized by 4-Me₂NC₆H₄ groups. The successful transmission of the axial chirality in **12** to the point chiralities in **13**²⁺ could be realized due to conformational preference of the "out-out" form in **12** over the corresponding "in-in" form in terms of the orientation of bulky diarylethenyl groups to avoid steric repulsion (Scheme 0-9b). Due to the stereospecific transformation, not only UV-Vis but also CD spectral changes were observed with several isosbestic points during the electrolyses of optically pure samples, thus demonstrating their electrochiroptical response.^[33,34,35]

The purpose of this work is to develop new *dyrex* systems, especially the arenes having multiple *dyrex* chromophores.



Scheme 0-9. (a) Configurationally stable "exo"-type *dyrex* system of (*R*_{ax})-**12**/ (*R*_{ax},*R,R*)-**13**²⁺ and (*S*_{ax})-**12**/ (*S*_{ax},*S,S*)-**13**²⁺ undergoing no inversion of helicity and axial chirality.

(b) Conformational preference for "out-out" form over the "in-in" form in **12** resulting in the observed stereospecificity upon cyclization into **13**²⁺.

0-3. Perfluoroarenes for Exploitation of Redox Systems

0-3-1. A Unique Properties of Fluoroarenes

Perfluoroarenes (F-arenes)^[42] have a unique properties due to a different quadrupole moment from that in usual arenes,^[43] as exemplified by the formation of stable 1:1 complex between C_6F_6 , a representative F-arene, with C_6H_6 (Figure 0-3).^[44] Although several F-substituted arenes crystallize isomorphously to the corresponding arenes without F atoms,^[45] the packing arrangement often differs to each other especially due to “C-H \cdots F-C”-type hydrogen bonding in F-arenes.^[46] In addition, the face-to-face arrangement is more often adopted in F-arenes in contrast to the herringbone packing favored in usual arenes.^[47] Such a switching of packing preference is advantageous to improve the OFET properties or increase in solubility of oligoacenes by F-substitution (Figure 0-4).^[48] Furthermore, from the synthetic viewpoint, the advantage by incorporating F-arene skeleton is high reactivity toward S_NAr functionalization (Scheme 0-10).^[49]

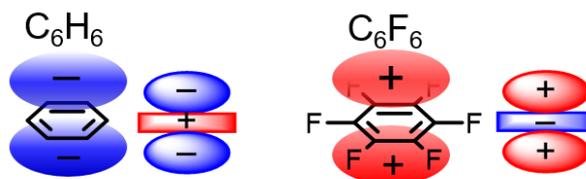


Figure 0-3. The quadrupole moments of benzene and hexafluorobenzene.

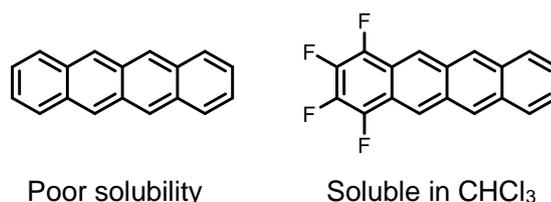
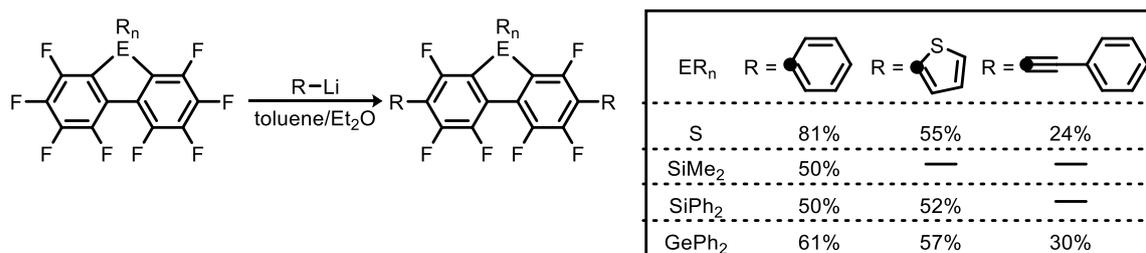


Figure 0-4. The solubility in solution of naphthalene and 1,2,3,4-tetrafluoronaphthalene.



Scheme 0-10. S_NAr functionalization of fluoroarene.

0-3-2. The Electron Donors Containing Fluoroarene Framework

Because of the Lewis acidity of F-arenes, F-substitution on the molecular skeleton has been commonly conducted for electron acceptors (e.g. F₄-TCNQ) for exploitation of redox chemistry. On the other hand, the electron donors containing a F-arene framework are rare,^[50] apparently because of the destabilization of oxidized state (e.g. dication) by introduction of F atoms of strong electronegativity (Figure 0-5). Thus, the merit of F-arene incorporation has been seldom examined in the development of the novel electron donors. In this regard, *dyrex* systems containing F-arene are interesting since they still could exhibit good electron-donating properties. Thus, *dyrex* behavior could minimize the electronic destabilization effects even in the doubly-charged dicationic state by stabilization of electron-donating groups or by disconnection of the π -conjugation between the cationic chromophore and the F-arene framework upon oxidation.

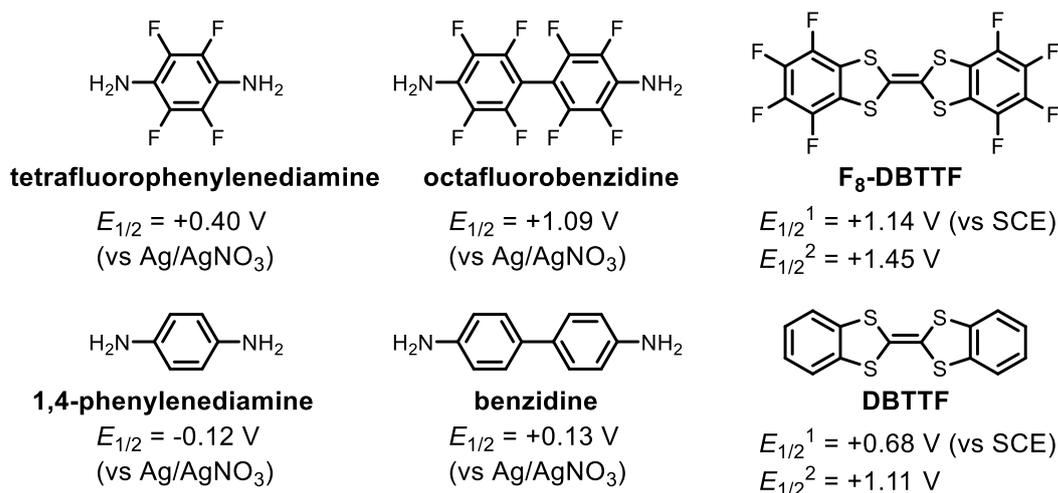
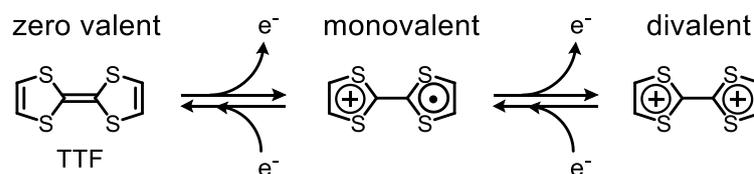


Figure 0-5. Oxidation potentials (V) of fluoroarene-based donors and the corresponding non-fluoro donors. Cyclic voltammograms of tetrafluorophenylenediamine, octafluorobenzidine, 1,4-phenylenediamine and benzidine were measured in MeCN containing 0.1 M Bu₄NClO₄ with Ag/AgNO₃ as the reference electrode and Pt electrode at scan rate 100 mV/s.^[50b] Cyclic voltammograms of F₈-DBTTF^[50a] and DBTTF^[50c] measured in CH₂Cl₂ containing 0.1 M Bu₄NPF₆ with SCE as the reference electrode and Pt electrode.

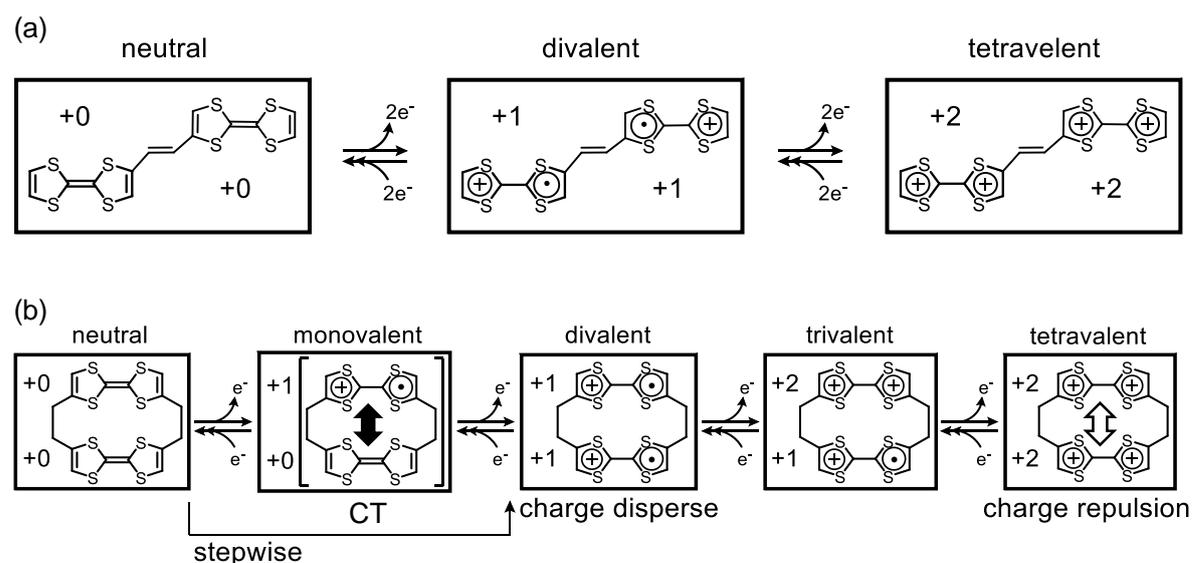
0-4. Multiple Chromophoric Redox Systems

0-4-1. Connection of Two Tetrathiafulvalene as Redox Units

Molecules containing multi redox units, each of which has an ability to undergo reversible oxidation or reduction, are allowed to have several redox states, which is absent in the monomeric framework. The properties of each state can be controlled by the spacer that connects framework units or by connection symmetry. For example, tetrathiafulvalene (TTF) has been long known as a strong electron donor that undergoes two-stage 1e-oxidation steps (Scheme 0-11). The electron donor having two TTF units is allowed to have four redox states with the charge of 0 to +4 (Scheme 0-12).^[51] In particular, charge transfer (CT) interaction works as an attracting force in the monocationic state where one unit of TTF is cation-radical state and the other unit is neutral state. On the other hand, repulsive force will be present that separates the connected units in the tetracationic state since two units are fully oxidized. In this way, many electron donors containing two TTF units have been previously studied by several researchers.



Scheme 0-11. Redox mechanism of TTF.

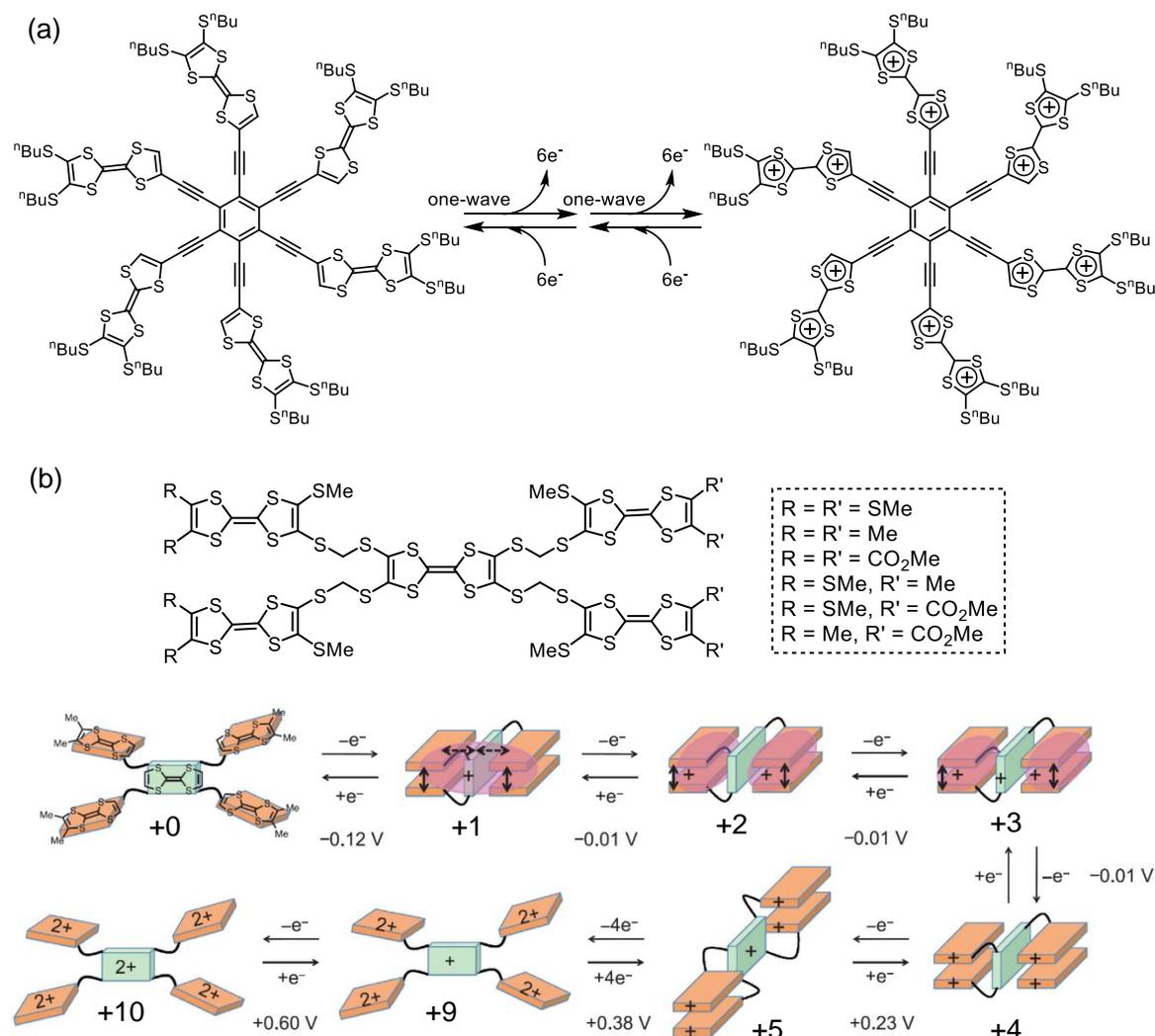


Scheme 0-12. Redox mechanism of the electron donor having two TTFs connected (a) by ethylene spacer and (b) as cyclophane.

0-4-2. Connection of Multi Tetrathiafulvalene as Redox Units

As one of the largest multi redox-site molecular systems, disc-shaped molecule connecting six TTF units was prepared by Iyoda et al., which undergoes one-wave 6e-oxidation, followed by another one-wave 6e-oxidation (Scheme 0-13a).^[52] On the other hand, a TTF pentamer containing uncojugated five TTF units was prepared by Misaki et al. which experienced stepwise oxidation with changing the geometry with folding or unfolding the molecular framework (Scheme 0-13b).^[53] Such a reorientation is caused by the difference in the preferred interaction between the charged moieties.

On the other hand, the corresponding research on the *dyrex* systems having multiple *dyrex* unit have never been conducted, although multi-units *dyrex* systems are attractive alternative in terms of investigating multi-step electron-transfer behavior and generation of polycations.

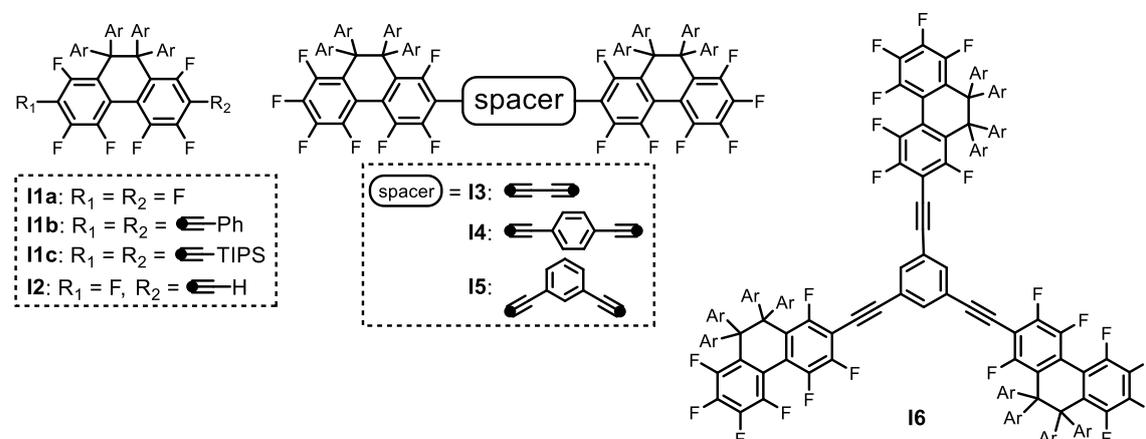


Scheme 0-13. Redox mechanism of (a) disc-type TTFs-hexamer and (b) TTFs-pentamer having flexible spacers.

0-5. Contents of This Thesis

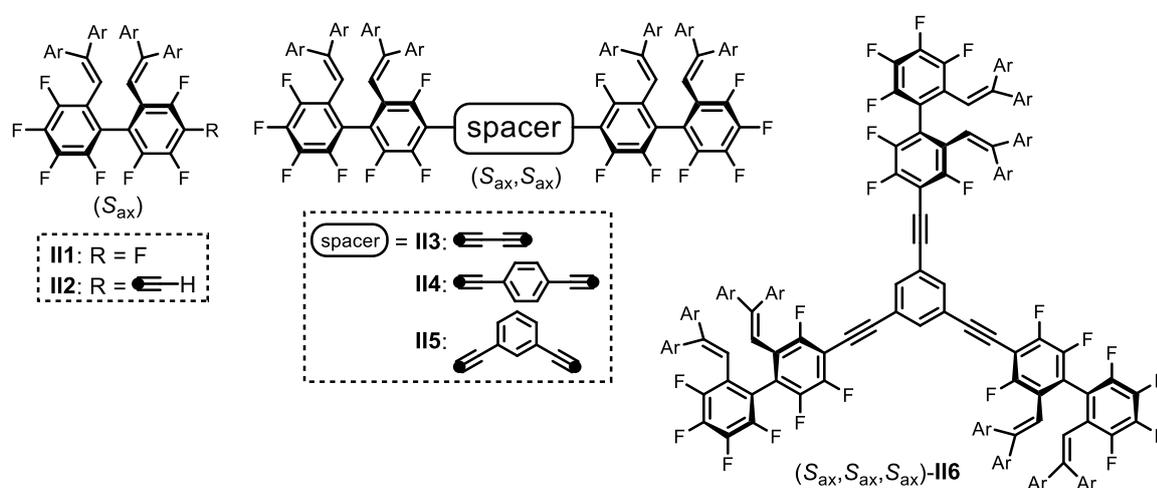
Based on the background shown above, the newly designed *dyrex* systems having perfluoroarene skeleton are studied in this thesis, and it involves both of “endo”- and “exo”-type *dyrex* systems. The newly designed F-arene *dyrex* donors would exhibit similar *dyrex* behavior to the previously studied *dyrex* donors without F atoms since the undesirable effects by the electronegative F atoms on the electron-donating ability or stability of dicationic state would be minimized under the appropriate molecular design. On the other hand, the F-arene *dyrex* donors could work as a versatile synthon to produce larger assemblies containing multiple *dyrex* units, since F-arene skeleton could be modified by S_NAr reaction: in particular selective introduction of substituents by nucleophilic attacks at the 4- or 4,4’-positions of perfluorobiphenyl derivatives. Furthermore, the newly assemblies could exhibit high solubility in common organic solvents despite their large molecular sizes, thanks to the incorporation of the F-arene skeleton that crystallize in a different manner from that of the corresponding non-F-arenes.

In chapter 1, the hexaphenylethane derivatives (“endo”-type) incorporating F-arene skeleton have been investigated (Scheme 0-14). The “endo”-type *dyrex* donor **I1a** could work as a versatile synthon to prepare π -extended analogues and larger assemblies containing multiple *dyrex* units such as dumbbell-type dyads or triad donor. The π -extended analogues could exhibit π -conjugation switching based on torsion angle change accompanied by the change in the central core from dihydrophenanthrene to biphenyl skeleton, thus giving drastic change in the UV-region absorption. The coupling precursor **I2** is attached with an ethynyl pendant that could act as a connecting group under the various metal-catalyzed coupling conditions. All of the newly prepared “exo”-type *dyrex* molecules exhibit electrochromic behavior.



Scheme 0-14. Target compounds of chapter 1.

In chapter 2, the biphenyl-2,2'-diyl-type derivatives (“exo”-type) incorporating F-arene skeleton have been studied (Scheme 0-15). The “exo”-type *dyrex* donor **II1** could work as a versatile synthon to prepare larger assemblies containing multiple *dyrex* units such as dumbbell-type dyads or triad donor. Furthermore, the F atoms at the 6,6'-positions could prevent rotation about the biphenyl axis in **II1** to allow its optical resolution. All “endo”-type *dyrex* molecules exhibit electrochiroptical response, thus not only UV-Vis but also CD spectra since the assemblies are produced in an optically pure form by using resolved synthon. The electrochiroptical response systems that undergo one-wave 4e-/6e-oxidation are unprecedented.



Scheme 0-15. Target compounds of chapter 2.

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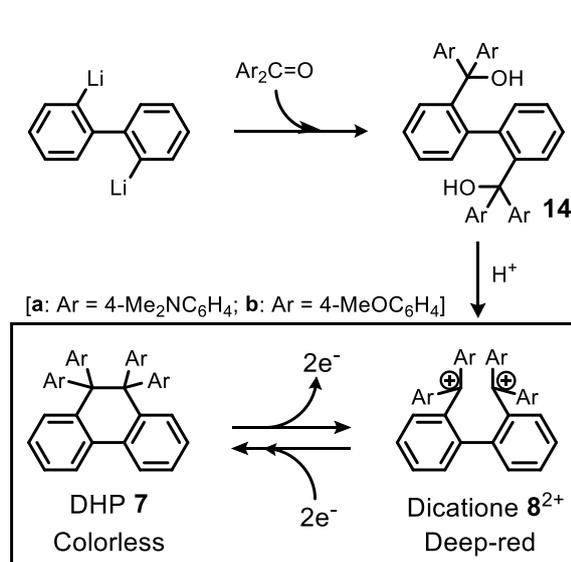
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Chapter 1

1,2,3,4,5,6,7,8-Octafluoro-9,9,10,10-tetrakis(4-methoxyphenyl)-9,10-dihydrophenanthrene Exhibiting Electrochromic Response: Assembly to Dumbbell-type Dyad and Tripod-type Triad that Undergo 4e⁻ and 6e⁻-Transfer

1-1. Introduction

DHPs **7**^[1] are the representative compounds of the “endo”-type *dyrex* system as shown in section 0-1-3. They were prepared by reduction of dication **8**²⁺, which were obtained from the corresponding diols **14** under the acidic dehydrating conditions (Scheme 1-1). Diols **14** were obtained by the reactions of 2,2'-dilithiobiphenyl with the corresponding diarylketone. Figure 1-1 shows a spectroelectrogram of dication **8b**²⁺ having methoxyphenyl groups upon reduction. This dication **8b**²⁺ has a strong absorption at 514 nm and shows deep-red color. It can be transformed into the corresponding colorless DHP **7b** reversibly. Interconversion between DHP **7** and dication **8**²⁺ has been proven to proceed via a two-electron (2e⁻) redox mechanism.



Scheme 1-1. Preparation of DHP **7** and dication **8**²⁺.

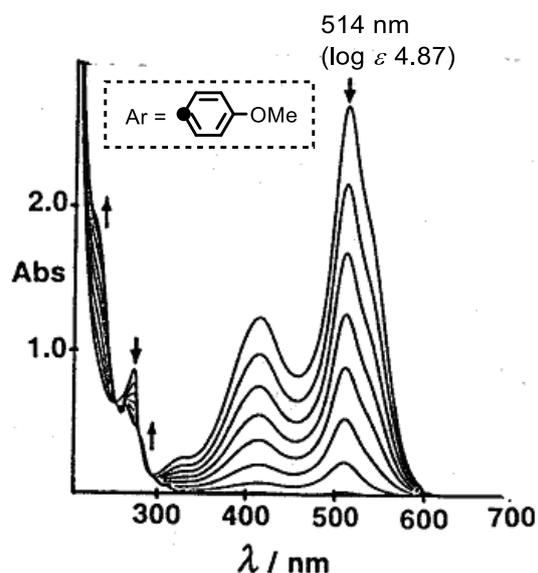
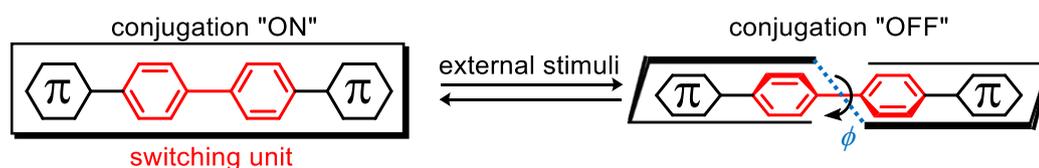


Figure 1-1. UV-Vis spectral changes upon reduction of **8b**²⁺ in MeCN.

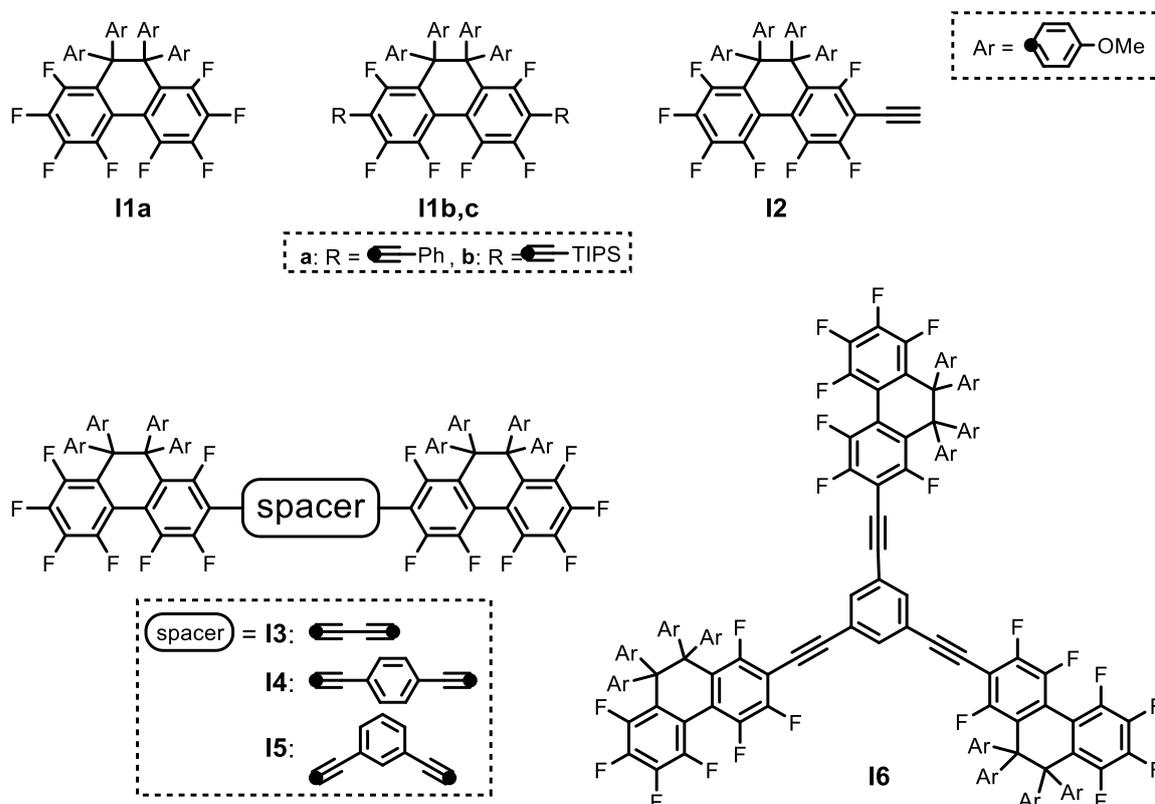
Electron donor **I1** is an octafluoro derivative of **7** and would be interconvertible with bond-dissociated dication **I7**²⁺ upon 2e⁻-transfer. Although the biphenyl skeleton has electron-withdrawing F atoms, electron-donating properties of **I1** would suffer less effect due to disconnection of π-conjugation. On the other hand, the electron-donating groups on each aryl substituent would stabilize positive charges, generated upon 2e⁻-oxidation, to

allow isolation of dication **I7**²⁺. The F atoms at the 6,6'-positions may increase the torsion angle around the biphenyl axis (ϕ) in **I7**²⁺, thereby enhancing geometric contrast of the switching unit in the ON and OFF states (Scheme 1-2). The most important feature of octafluorobiphenyl moiety^[2] is the S_NAr reactivity toward nucleophiles including acetylides. So that, the auxiliary π -unit could be introduced to the skeleton of **I1**.



Scheme 1-2. Conjugation ON and OFF states of the switching unit.

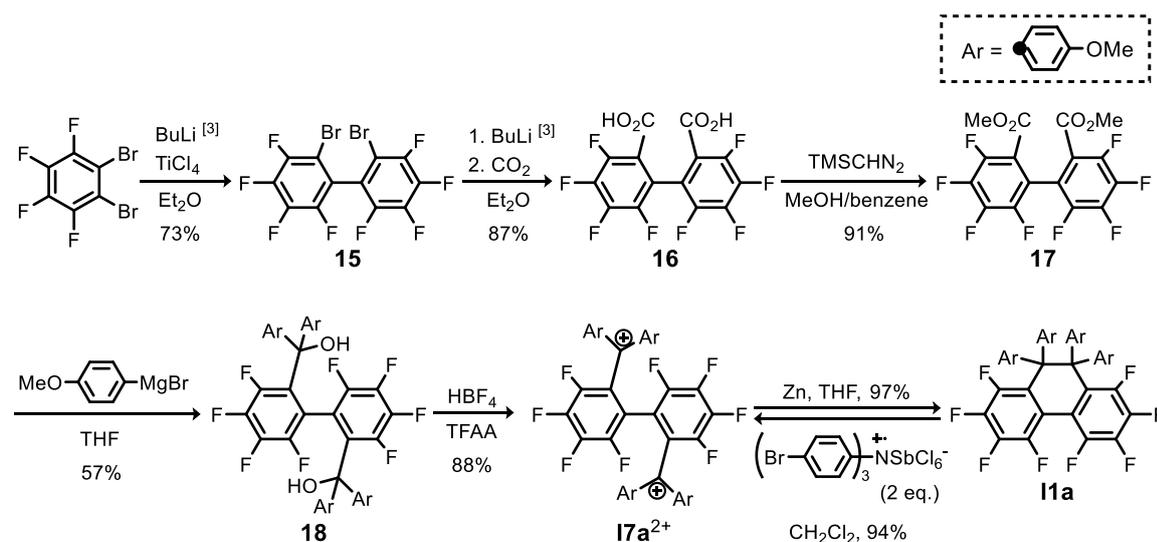
In this chapter, fluoroDHP **I1a** was prepared and used as a synthon to prepare the 2,7-disubstituted derivatives, such as **I1b** and **I1c**, whose switching phenomenon is more discernible due to a linearly π -extended chromophore with strong UV absorptions. Furthermore, connection of 2-substituted units **I2** into large assemblies containing multiple *dyrex* units was performed for the first time. Their redox behavior and spectroscopic properties are also demonstrated.



Scheme 1-3. Target compounds.

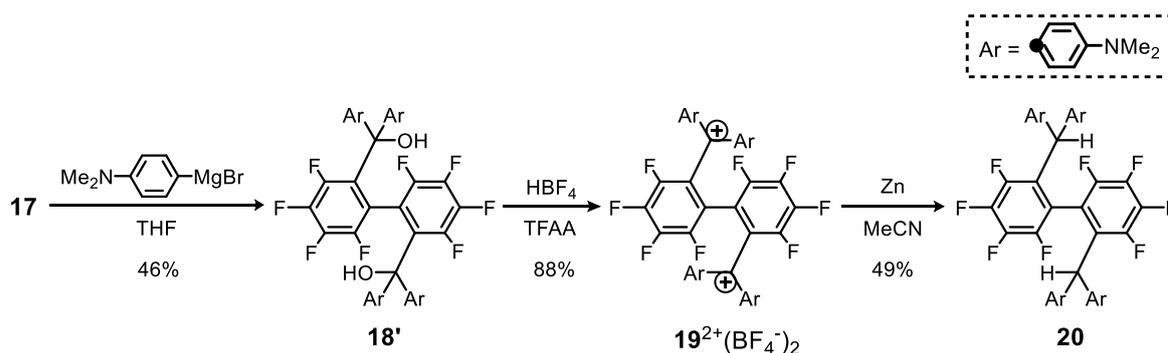
1-2. Preparation

First, fluoroDHP **I1a** having methoxyphenyl groups was prepared in 6 steps as shown in Scheme 1-4. Commercially available 1,2-dibromotetrafluorobenzene **15** was converted to octafluorobiphenyl-2,2'-dicarboxylic acid **16**^[3] by following the reported procedure. Then, **16** was transformed into methyl ester **17** with TMS-diazomethane in 91% yield. Ester **17** was also obtained in 74% yield by using inexpensive methyl iodide (Scheme 1-4). Reaction of **17** with excess Grignard reagent gave diol **18** in 57% yield, which was then transformed, under acidic dehydrating conditions, into stable dication salt **I7a**²⁺(BF₄)₂ in 88% yield. Thus, incorporation of F-arene skeleton did not give fatal destabilization effects on the *dyrex*-type dication. Upon treatment with Zn powder, this salt gave **I1a** in 96% yield. By the reaction of **I1a** with (4-BrC₆H₄)₃N⁺ SbCl₆⁻ (2 equiv), dication **I7a**²⁺ was regenerated and isolated as (SbCl₆)₂ salt in 94% yield. Such a high-yield interconversion indicates that **I1a**/**I7a**²⁺ can be considered as a “reversible” redox pair although electrochemical reversibility is not maintained due to concomitant C-C bond cleavage/formation.^[4]



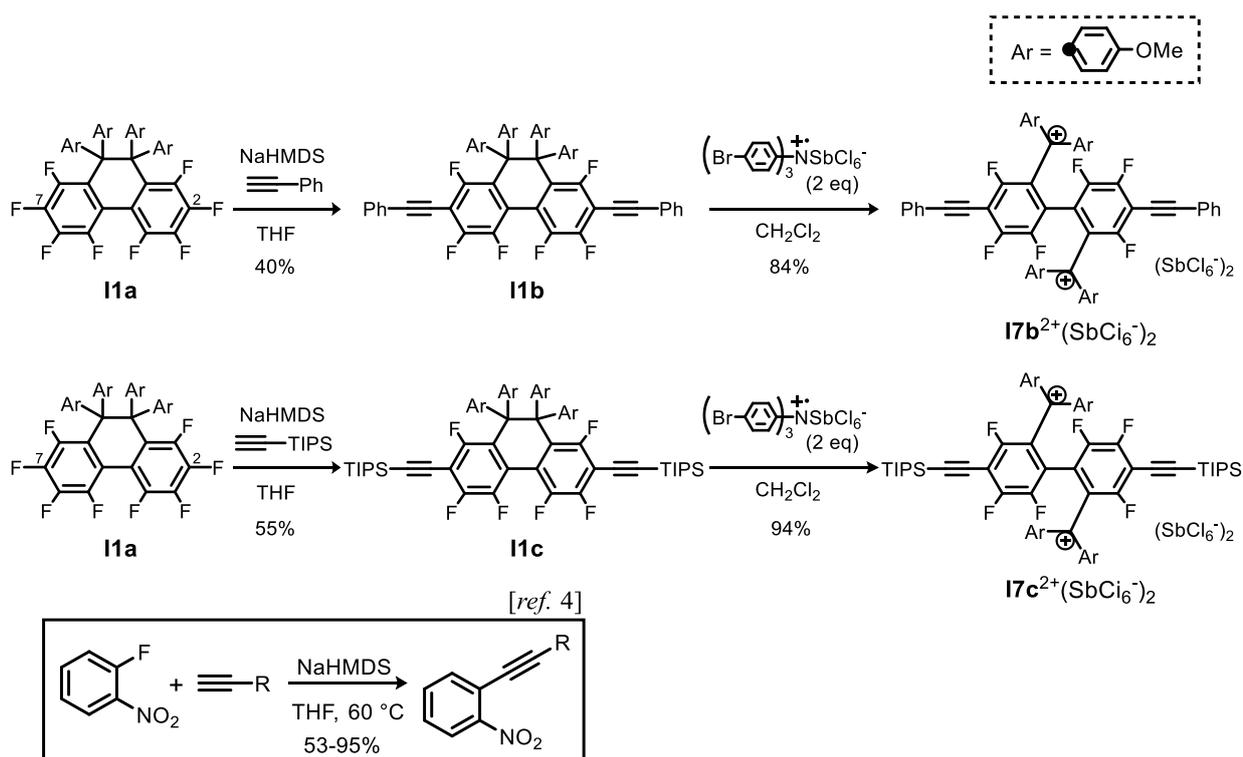
Scheme 1-4. Preparation of fluoroDHP **I1a** and dication **I7a**²⁺.

In contrast, though dication 19^{2+} introduced dimethylaminophenyl groups as aryl groups was prepared, fluoroDHP was not generated upon treatment with Zn powder or with other reducing agent (Scheme 1-5). Instead, hydride adduct **20** [^1H NMR (300 MHz, CDCl_3): δ ppm 6.82 (4H, d, $J = 9.0$ Hz), 6.61 (4H, d, $J = 9.0$ Hz), 6.51 (4H, d, $J = 9.0$ Hz), 6.42 (4H, d, $J = 9.0$ Hz), 4.97 (2H, s), 2.92 (12H, s), 2.85 (12H, s); ν/cm^{-1} ; FD-MS m/z 802 (M^+ , BP), 803 (76), 804 (19)] was formed. The reason of hydride addition would be related to the stability of the resulting diradical upon reduction of 19^{2+} due to capto-dative effects, which may be enhanced by stronger electron-donating dimethylaminophenyl groups. Thus, investigation of fluoroDHP having dimethylaminophenyl groups was given up.

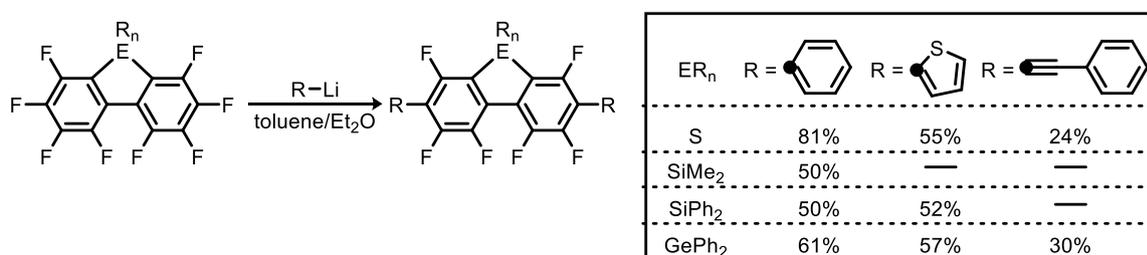


Scheme 1-5. Preparation of dication 19^{2+} and attempted generation of dimethylamino analogue.

Next, **I1a** was used as a synthon to produce extended derivatives having a longer linear conjugation. As shown in Scheme 1-6, the S_NAr reaction of **I1a** with 2.2 equiv. of ethynylbenzene or ethynyltriisopropylsilane in the presence of $NaN(SiMe_3)_2$ proceeded in acceptable yields to give the corresponding 2,7-diethynyl derivatives **I1b** and **I1c**.^[5] Upon treatment with $(4-BrC_6H_4)_3N^+ SbCl_6^-$ (2 equiv), **I1b** and **I1c** were transformed into stable dicationic salts **I7b**²⁺($SbCl_6^-$)₂ (84% yield) and **I7c**²⁺($SbCl_6^-$)₂ (87% yield), respectively. Tilley et al. also reported previously that perfluoroarene skeleton undergo S_NAr reactions at 2,7-positions selectivity (Scheme 1-7).^[2]

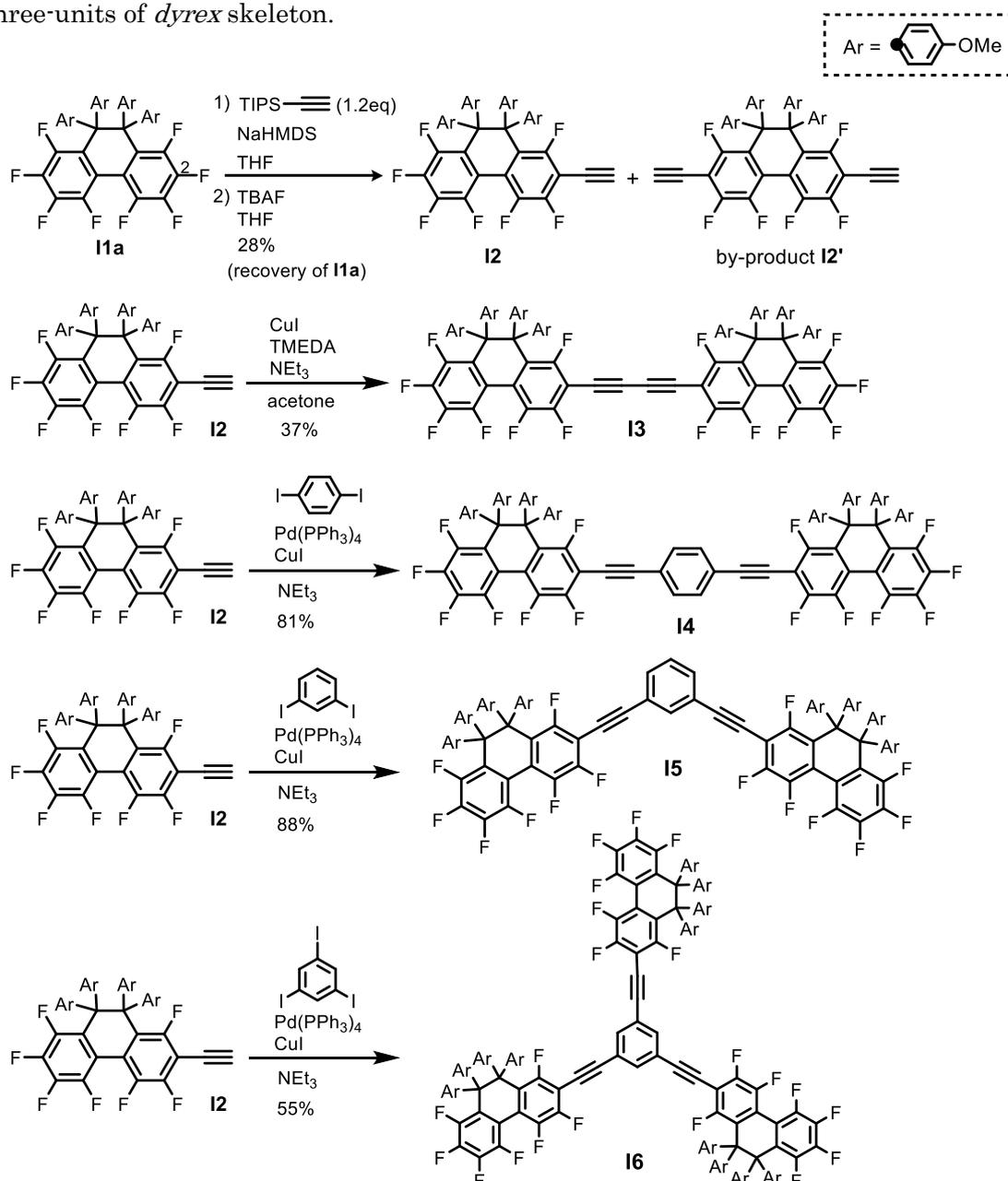


Scheme 1-6. Preparation of disubstituted **I1b,c** and dication **I7b,c**²⁺.



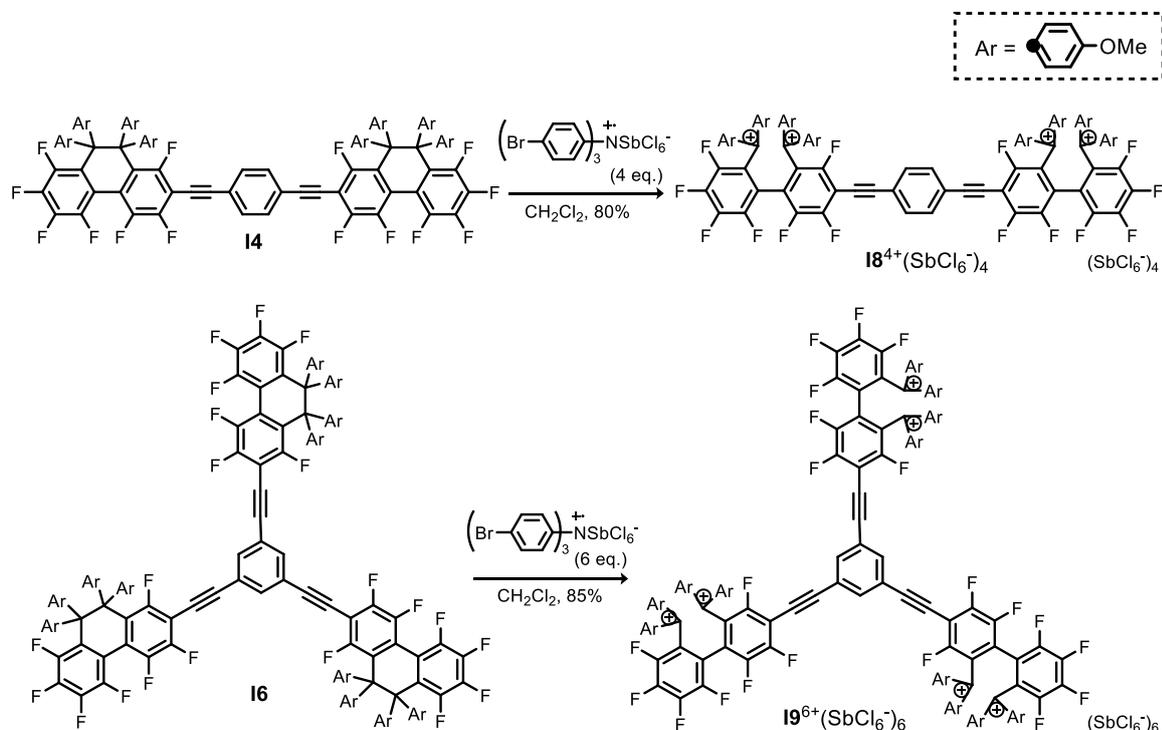
Scheme 1-7. Introduction selectivity of substitutions at biphenyl moieties.^[2]

By using the similar S_NAr protocol, monoethynylated analogue **I2** was prepared by the reaction with reduced amount of ethynyltriisopropylsilane (1.2 equiv.) followed by removal of TIPS group by using TBAF, and isolated from the mixture containing starting material and a small amount of disubstituted **I2'** (Scheme 1-8). Finally, the synthon **I2** was assembled through a variety of coupling reaction to synthesize **I3-I6**. Thus, diyne **I3** was prepared by Hay coupling reaction^[6] of precursor **I2** itself. And, *p*-phenylene-dyad **I4**, *m*-phenylene-dyad **I5**, triad **I6** were obtained by the Sonogashira coupling reaction of **I2** and 1,4-diiodobenzene or 1,3-diiodobenzene or 1,3,5-triiodobenzene (Scheme 1-7). This is the first successful demonstration for the generation of novel molecules containing two or three-units of *dyrex* skeleton.



Scheme 1-8. Preparation of precursor **I2** and dumbbell-type dyads **I3-I5** and tripod-type triad **I6**.

Finally, upon preparative-scale oxidation of dyads **I4** and triad **I6** with oxidation agent, dark red powders were obtained, which can be assigned to the corresponding tetracationic salt **I8⁴⁺(SbCl₆⁻)₄** and hexacationic salt **I9⁶⁺(SbCl₆⁻)₆**, respectively, based on their ¹H NMR spectra (Scheme 1-9).



Scheme 1-9. Oxidation of assemblies **I4** and **I6** with oxidation agent into tetracation and hexacation, respectively.

1-3. X-ray Analysis for Crystal Structure of FluoroDHP **I1a**

According to X-ray crystallography, F-arene based **I1a** adopts a helical geometry as in other DHP derivatives (Figure 1-2). The bond length of ethano bridge shown in red line is 1.632(4) Å, which is much greater than the standard value (1.54 Å). In addition, the torsion angle [$\phi(\text{C}_4\text{-C}_{4a}\text{-C}_{4b}\text{-C}_5)$: 35.1(4) °] is slightly larger than those of the related non-fluoro molecules. This torsion angle is similar to those in the dihydrophenanthrene derivatives with ethynyl- or bromine-groups at bay-region of 4,5-positions.^[7-9] Considering the $\cos^2 \phi$ dependency^[10] of effective π -conjugation in biaryls, ca. 70% of conjugation is still working in this “ON” state (Scheme 1-2). Although the precise geometry of dication **I7a**²⁺ (the “OFF” state) is not available at this moment, as described below, the VT-NMR spectroscopy and the voltammetric analysis suggests that a drastic structural change takes place during the conversion of **I1a** to **I7a**²⁺.

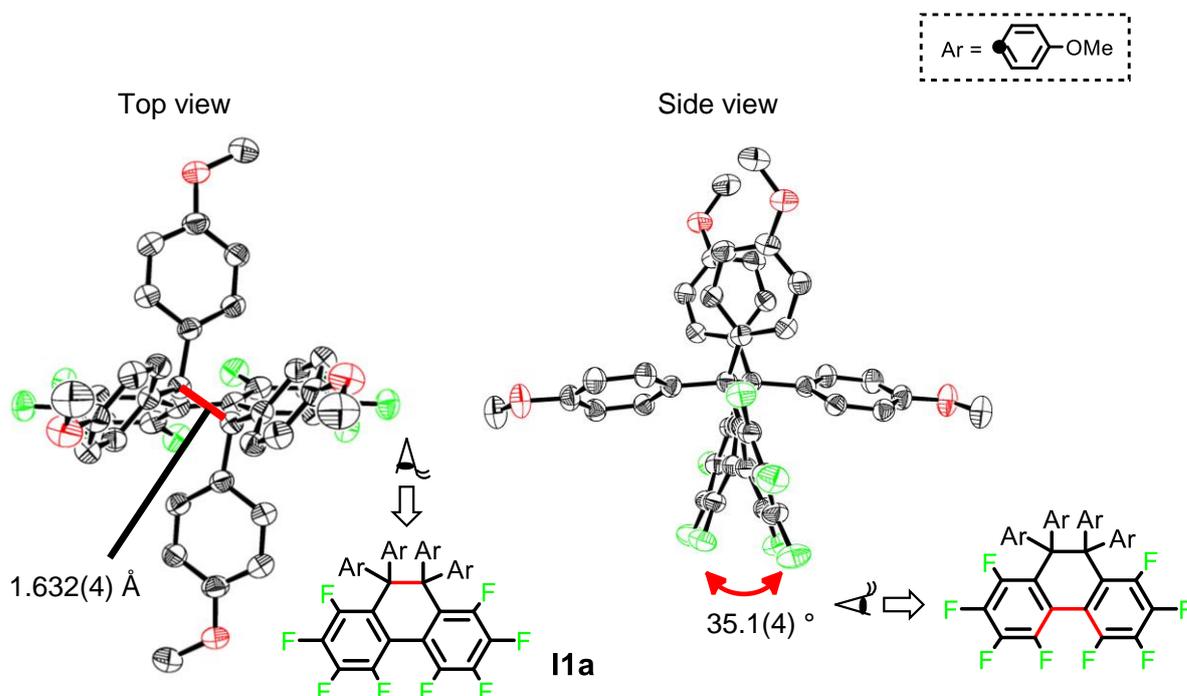
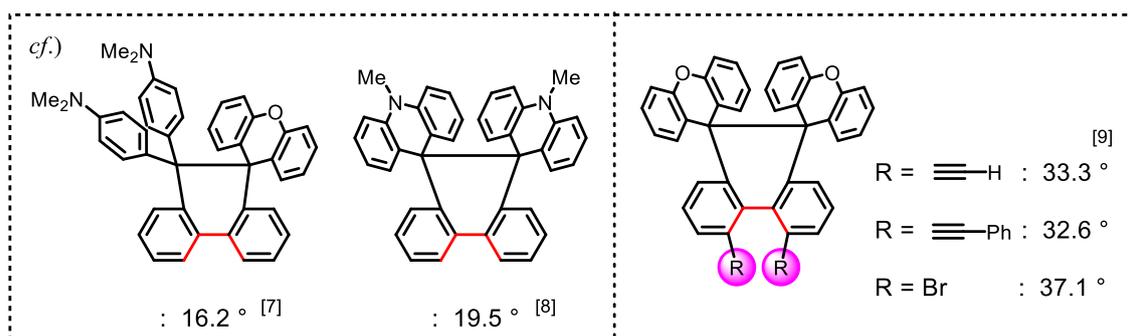


Figure 1-2. Two views of ORTEP drawing of **I1a** · 1/3 hexane solvate crystal (cubic, *Ia*-3, *Z* = 24, *T* = 153 K).



1-4. Estimation of Energy Barrier for Ring Flip in FluoroDHP I1a

Twisted molecular frame is chiral element, thus these compounds are present as pairs of enantiomer. The energy barrier for the ring inversion of the fluoroDHP **I1a** and that for the rotation around the central axis in of the corresponding dication **I7a²⁺** were investigated by VT-NMR spectroscopy (Figure 1-3). Thus, **I1a** undergoes an easy ring-flip at room temperature as in the case of non-fluorinated derivative **7b** (Figure 1-3). In contrast, fluorinated dication **I7a²⁺** has a larger rotational barrier than that of non-fluorinated dication **8b²⁺**. This observation can be explained by the different effects of F atoms as shown in figure 1-4.

In the case of neutral fluorinated donor **I1a**, steric hindrance of fluorine atoms at bay region is working both in the ground and transition states. Thus, not only the transition state but also the ground state are destabilized to the same degree when compared to non-fluorinated analogue **7b**. On the other hand, in the case of dication **I7a²⁺**, its transition state becomes much more destabilized by the larger steric hindrance between methylium carbon and fluorine whereas its ground state is not destabilized due to fully twisted geometry. Therefore, fluorinated dication **I7a²⁺** is more difficult to rotate than non-fluorinated dication **8b²⁺**.

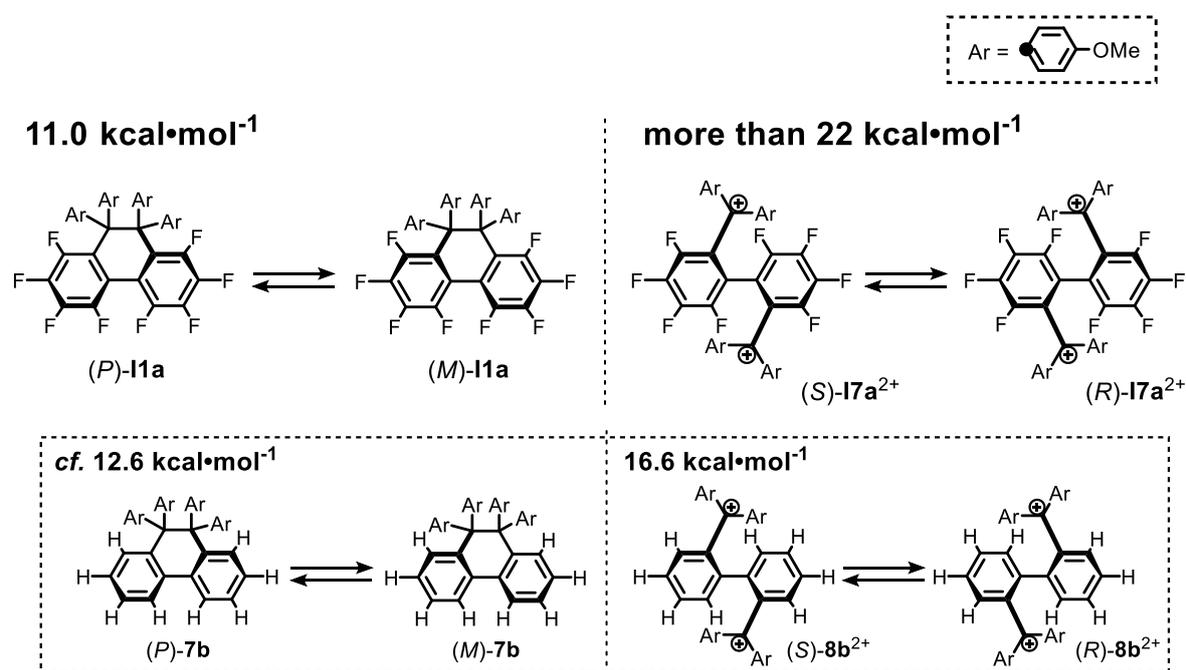


Figure 1-3. Stereoinversion energy barrier of **I1a/I7a²⁺**.

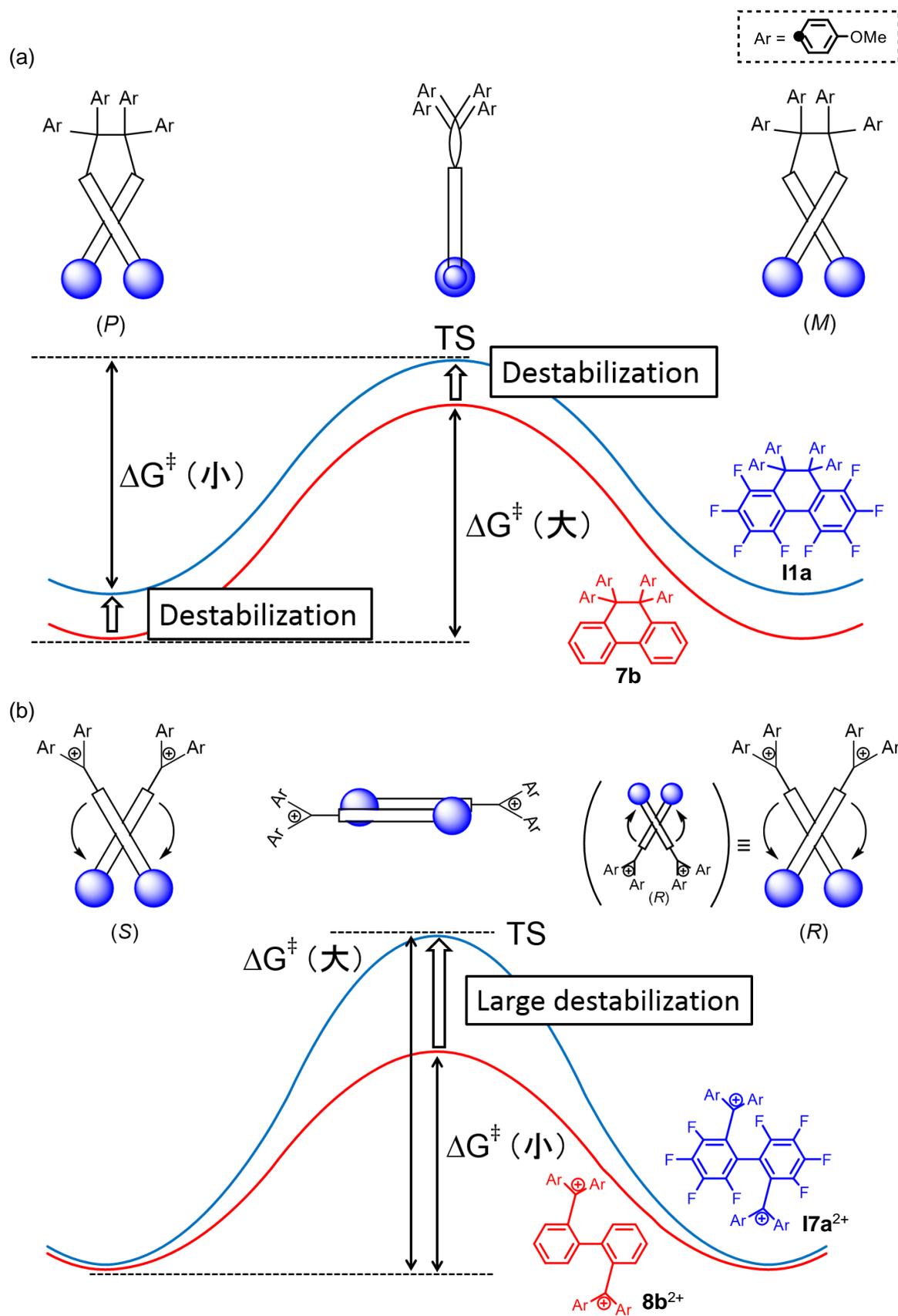


Figure 1-4. Diagram of energy barrier of (a) **I1a/7b** and (b) **I7a²⁺/8b²⁺**.

1-5. Redox Properties of Monomeric *Dyrex* Unit **I1a-c**

By means of cyclic voltammetry, the electron-donating ability of the neutral donor as well as stability of the dicationic state are investigated. The electrochemical oxidation of fluoroDHP **I1a** in MeCN occurs at +1.54 V (vs. SCE), which is an irreversible process as in the case of **7b** (Table 1-1). The corresponding cathodic peak is largely shifted to a negative potential region and assigned as the reduction process of **8b**²⁺ (Figure 1-5). Such a separation of redox peak is characteristic of the *dyrex* pairs.^[3] Negligible steady state concentration of the intermediary cation radical is another feature of the interconversion between **I1a** and **I7a**²⁺. The redox potentials of the substituted redox pairs of **I1b/I7b**²⁺ and **I1c/I7c**²⁺ were virtually identical to that of **I1a/I7a**²⁺ (Table 1-1), since π -extension along the longer axis of the biphenyl skeleton hardly affects the frontier orbitals of **I1a/I7a**²⁺.

Besides, fluorinated donor **I1** is easier reduced than non-fluorinated donor **3**, since the electron-withdrawing nature of F lowers the LUMO of the dication, as shown by the less negative E^{red} of **I7a**²⁺ by 0.2 V than that of **8b**²⁺. These observations clearly demonstrate that fluoroDHP **I1** inherits attractive features of **7b** or other DHPs as a reversible electrochromic system with bistability.

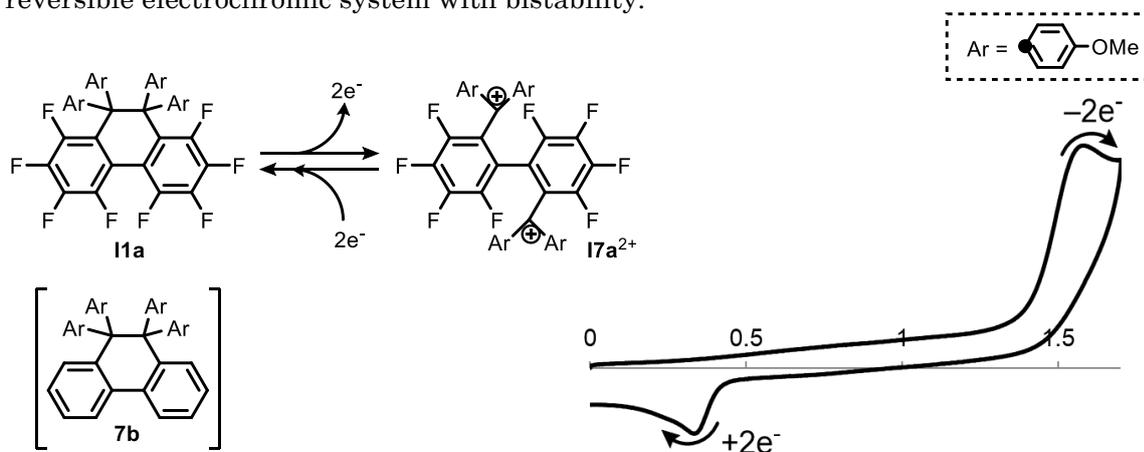


Figure 1-5. Cyclic voltammogram of **I1a** measured in MeCN (0.1 M Et₄NClO₄, Pt electrode, scan rate 500 mV/s).

Table 1-1. Oxidation and reduction potentials measured in MeCN (500 mV s⁻¹).

	E^{ox}	E^{red}
I1a/I7a ²⁺	+1.54	+0.37
I1b/I7b ²⁺	+1.53	+0.37
I1c/I7c ²⁺	+1.55	+0.38
<i>cf.</i> ^[1] 7b/8b ²⁺	+1.47	+0.18

(V vs SCE)

1-6. Electrochromic Behavior of Monomeric *Dyrex* Unit **I1a-c**

A continuous change of UV-Vis spectrum with several isosbestic points was observed upon constant-current oxidation of **I1a** in MeCN (Figure 1-6a). The strongest absorption in the visible region is identical to that of the isolated salt of **I7a**²⁺ [λ_{\max} 534 nm (log ϵ 4.79) in MeCN (Figure 1-9b, dot-line)], which is red-shifted compared with that of **8b**²⁺ [λ_{\max} 514 nm (log ϵ 4.87)], which is consistent with the lower LUMO of **I7a**²⁺ estimated by CV.

Meanwhile, the UV absorption profiles were significantly different among **I1a-I1c** (Figure 1-6). Thus, the π -extended compound **I1b** has a strong band at 345 nm (log ϵ 4.58 in MeCN), which is absent in **I1a** [271 nm (4.15)] and assignable as the absorption band due to 4,4'-bis(phenylethynyl)perfluorobiphenyl chromophore (the "ON" state). Upon electrochemical oxidation of **I1b** to **I7b**²⁺, this band gradually disappeared with concomitant appearance of the blue-shifted band at 318 nm (4.79) (Figure 1-6b). The observed behavior is best described as the successful ON/OFF switching of π -conjugation shown in Scheme 1-2 based on the external control of the torsion angle. It is noteworthy that interconversion between **I1b** and **I7b**²⁺ is accompanied by a drastic change also in the visible region by reversible appearance/disappearance of triarylmethyl cation dye units. The redox pair of **I1c/I7c**²⁺ likewise exhibited electrochromism, while the UV-region absorption bands were slightly blue-shifted in both states [**I1c**: 330 nm (4.47); **I7c**²⁺ 275 nm (4.75) in MeCN]^[11] (Figure 1-6c). For further assistance of the rationale, UV spectrum of hydride adduct **21** (291, 309 nm), obtained by dication **I7b**²⁺ with NaBH₄ in CH₂Cl₂/EtOH, was compared to that of the dication. It only shows the characteristic band of diphenylacetylene derivatives^[12] (Table 1-2), which is distinctly different from that of **I1b** (345 nm, Figure 1-7). Thus, this switching phenomenon depending on the π -conjugation length was successfully demonstrated thanks to the ethynyl groups introduced at the 2,7-positions of phenanthrene skeleton.

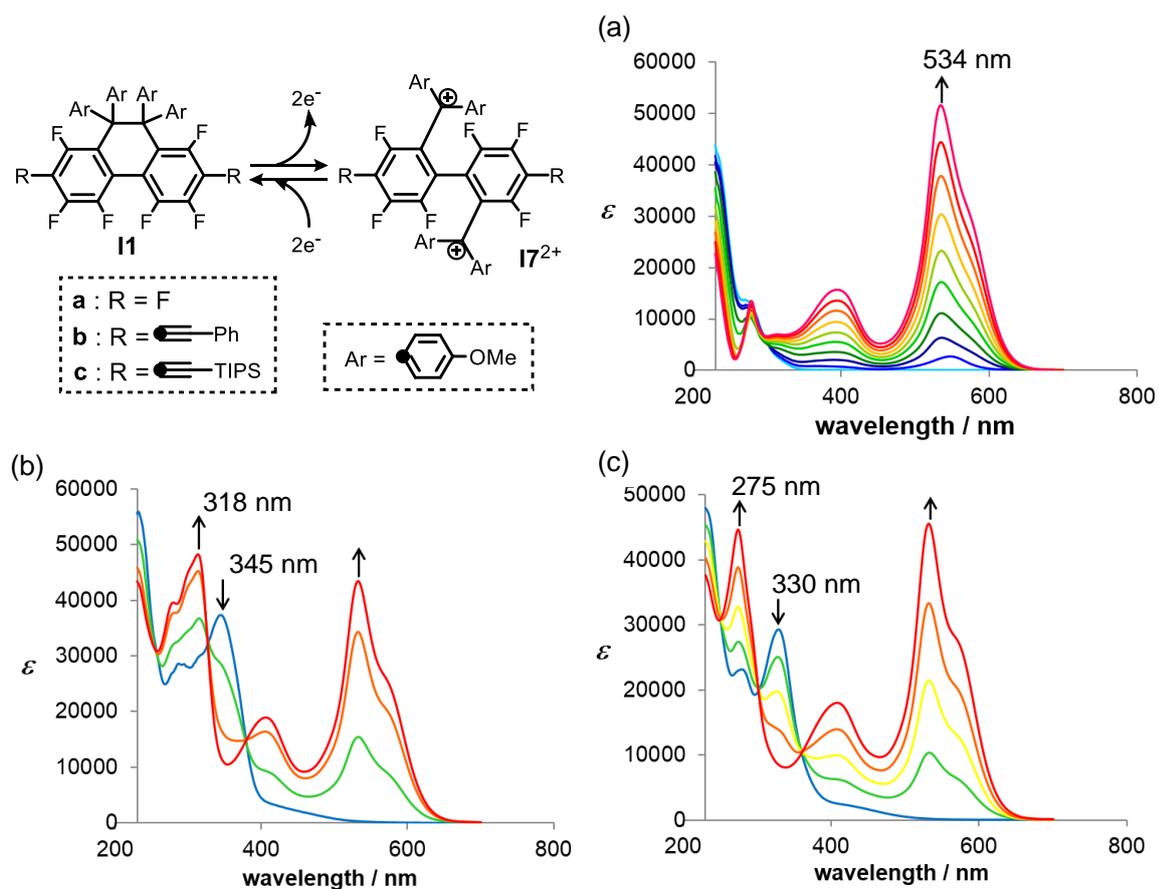


Figure 1-6. UV-Vis spectral changes upon electrochemical oxidation (60 μ A) of (a) **I1a** (24 μ M, every 2 min), (b) **I1b** (17 μ M, every 5 min), (c) **I1c** (22 μ M, every 5 min) in MeCN containing 0.05 M Et_4NClO_4 .

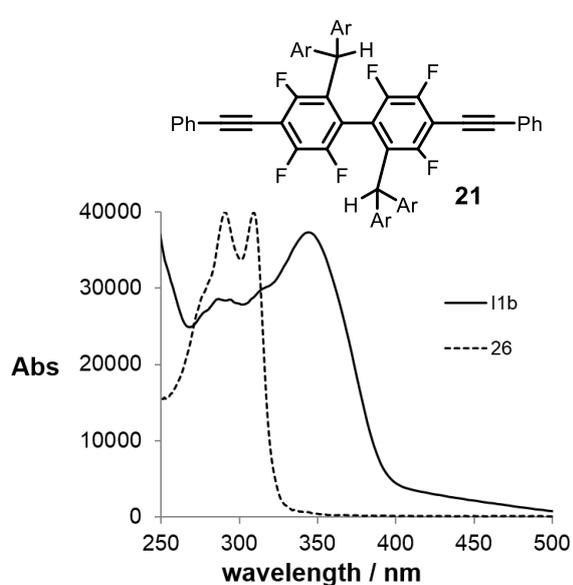


Figure 1-7. UV-Vis spectra of **I1a** (solid line) and **21** (dotted line)

Table 1-2. UV absorption maximum of diphenylacetylene derivatives. ^[11]

	λ_{max} : 279 nm (in MeCN) ^[11a]
	λ_{max} : 278, 296 nm (in MeCN) ^[11b]
	λ_{max} : 308 nm (in dioxane) ^[11c]

1-7. *Dyrex* Behavior and Electrochromic Behavior of Dumbbell-type Dyads and Tripod-type Triad I3-I6

A continuous change of UV-Vis spectrum with several isosbestic points was also observed upon constant-current oxidation of precursor **I2** and assemblies **I3-I6** in MeCN (Figure 1-8, 1-9a) as in the case of fluoroDHP **I1a**. During the conversion, the presence of several isosbestic points was observed in all cases although an absorbance in the long-wavelength region assignable to the cationic moieties was larger in **I3-6** than in the case of monomeric donors **I1,2** (Figure 1-9b), which is indicative of transformation of **I3-6** into the corresponding polycations. These observations can be accounted for by assuming the multi-electron (e.g., four- or six-electron) oxidation occur nearly simultaneously, although the transformation process might involve the "halfway-cationic species", in which neutral *dyrex* unit still remains in the same molecule (Scheme 1-9).

In fact, the cyclic voltammograms of dyads **I3,4,5** and triad **I6** showed a broad oxidation wave [E^{ox} (**I3,4,5,6**) = +1.56 - +1.60 V vs SCE in CH₂Cl₂] at the similar potential to that of **I1** [E^{ox} = +1.60 V] (Figure 1-10), indicating that one-wave-four-electron or one-wave-six-electron oxidation occurs in dyads **I3,4,5** and triad **I6**, respectively. On the other hand, a reduction wave was not broad, and small peak current was accounted for by diffusion of the as-generated cationic species.

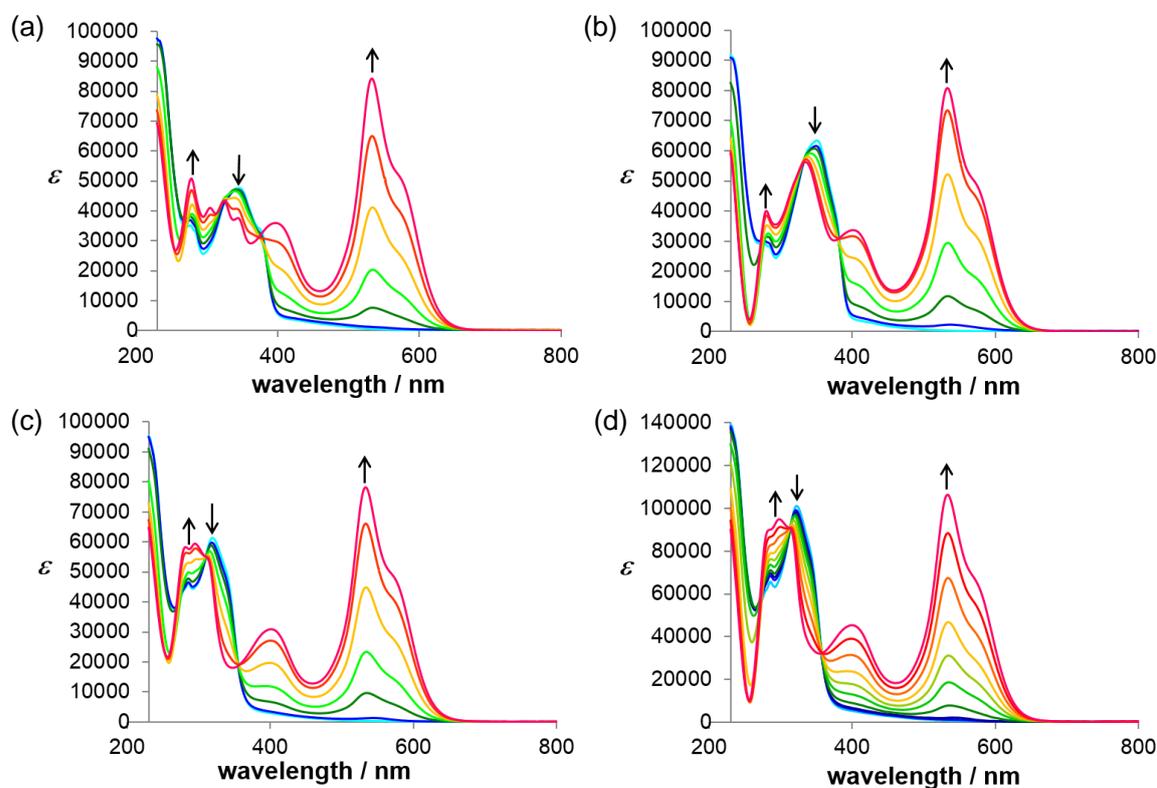
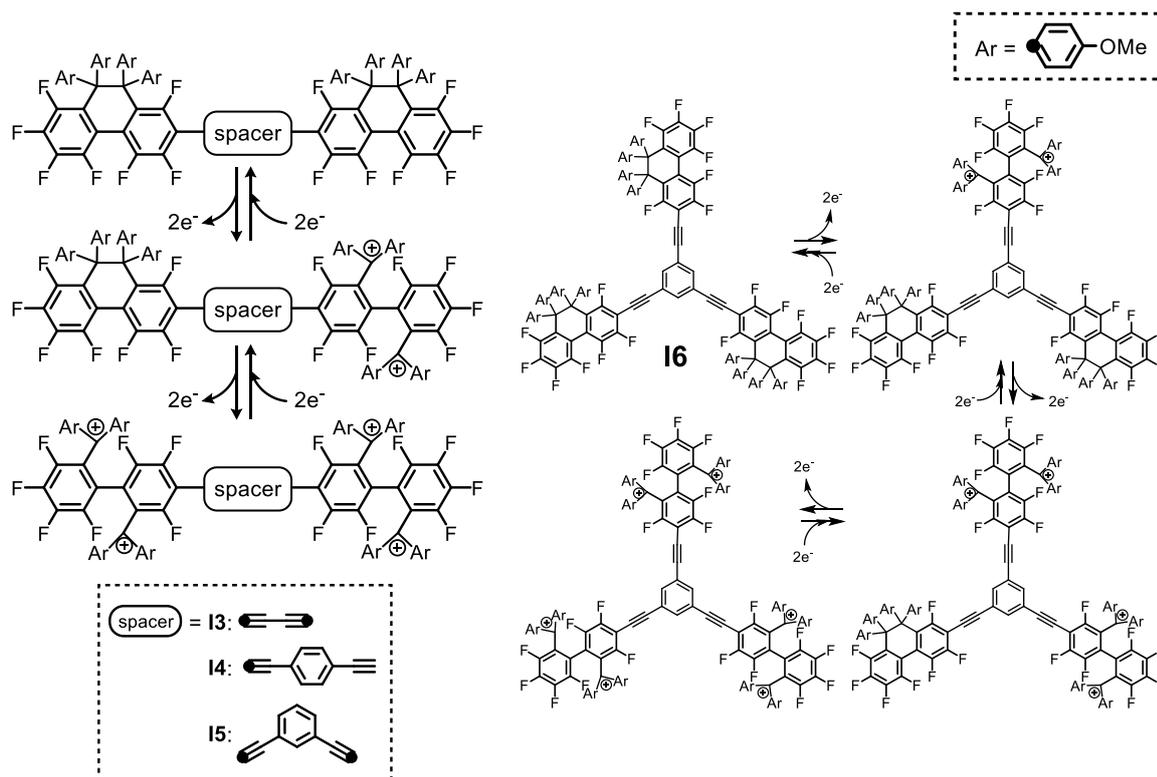


Figure 1-8. UV-Vis spectral changes upon electrochemical oxidation (60 μ A) of (a) **I3** (15 μ M, every 4 min), (b) **I4** (12 μ M, every 4 min), (c) **I5** (17 μ M, every 4 min), (d) **I6** (7.0 μ M, every 2 min) in MeCN containing 0.05 M Et₄NClO₄.



Scheme 1-10. The transformation process into polycation of assemblies **I3-6** upon electrochemical oxidation.

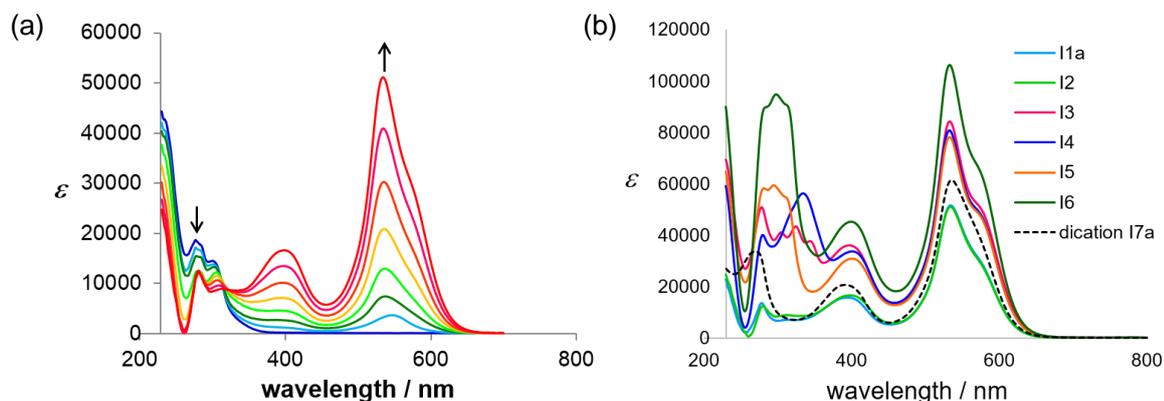


Figure 1-9. (a) UV-Vis spectral changes upon electrochemical oxidation ($60 \mu\text{A}$) of **I2** ($15 \mu\text{M}$) every 2 min in MeCN containing $0.05 \text{ M Et}_4\text{NClO}_4$. (b) UV-Vis spectra of corresponding cation species upon oxidation of **I1a, I2-6** and UV-Vis spectrum of **I7a²⁺** in MeCN.

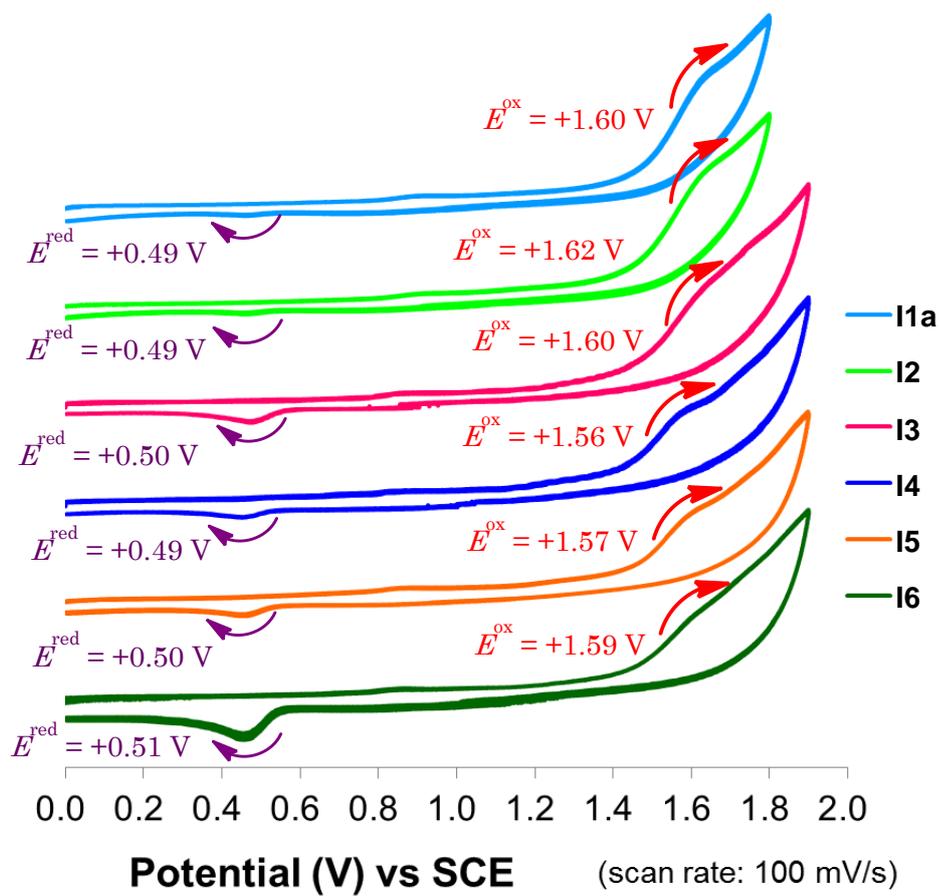


Figure 1-10. Cyclic voltammograms of I1-6 in CH_2Cl_2 (0.1 M Bu_4NBF_4 , Pt electrode, scan rate 100 mV/s).

1-8. Conclusion

The present work demonstrates that, despite the incorporation of F-arene skeleton, fluoroDHP donors exhibits enough electron-donating properties and the corresponding dications still have enough stability for isolation, thus the present *dyrex* pair exhibited electrochromism behavior as in the case of non-fluoro analogue. Attachment of F atoms enables facile S_NAr reaction with acetylides, so that the π -extended derivatives **I1b,c** can be generated. Those new analogues are endowed with a switching behavior of UV absorption due to the change in conjugation length caused by drastic geometrical change of the *dyrex* unit upon electron-transfer.

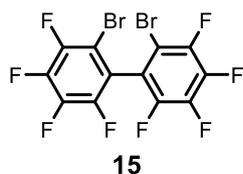
It is delighted that the ethynylated analogue works nicely as a key synthon to produce larger molecular assemblies containing two or three *dyrex* units through a variety of transition-metal catalyzed coupling reactions. This is the first demonstration for the production of compounds containing multiple units of *dyrex* skeleton. Further interesting point is that the assemblies **I3-I6** exhibit electrochromic behavior with undergoing multiple electron-transfers. Even though the assemblies consist of multiple *dyrex* units, they are spatially separated by the spacer to reduce repulsion among them. Thus, fluoroDHP provides desirable prototype for developing one-dimensional rod-like oligomer molecules^[12] with multiple numbers of the switching units.

Experimental Section

General

^1H , ^{19}F and ^{13}C NMR spectra were recorded on BRUKER Ascend TM400 ($^1\text{H}/400$ MHz), AMX500 ($^{19}\text{F}/470$ MHz, GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University) and JEOL AL300 ($^1\text{H}/300$ MHz), α 400 ($^{13}\text{C}/100$ MHz), ECA600 ($^1\text{H}/600$ MHz, High-Resolution NMR Laboratory, Graduate School of Science, Hokkaido University) spectrometers, respectively. IR spectra were obtained on a JEOL JIR-WINSPEC100 FT/IR spectrophotometer. Mass spectra were recorded on a JMS-T100GCV spectrometer in FD mode (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Column chromatography was performed on a silica gel I-6-40 (YMC) with a particle size of 40-63 μm . Melting points were measured on a Yamato MELTING POINT APPARATUS MODEL MP-21. Element analyses were performed on a J-SCIENCE LAB MICRO CORDER JM10 at the Center for Instrumental Analysis of Hokkaido University. UV/Vis spectra were recorded on a HITACHI U-3500 spectrophotometer. All commercially available compounds were used without further purification. Solvents were dehydrated prior to use as appropriate.

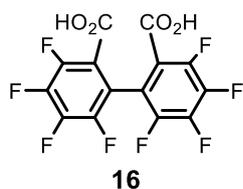
• Preparation of 2,2'-dibromooctafluorobiphenyl **15**^[3]



To a solution of 13.4 g (43.6 mol) of 1,2-dibromotetrafluorobenzene in 200 mL of dry ether cooled at -78 °C was added *n*BuLi (1.63 M solution in hexane, 32 mL, 52.3 mmol) dropwise over 40 min under Ar. After the solution was stirred for 30 min, 7.2 mL (12.4 g, 65.4 mol) of TiCl₄ was added to the orange solution. The reaction mixture was stirred at this temperature for an additional 3 h before the flask was left to warm up overnight. The reaction mixture was hydrolyzed with water. The whole mixture was extracted with ether three times. The combined organic layers were washed with water and brine, and dried over anhydrous MgSO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) and recrystallization from hexane at -78 °C to give dibromooctafluorobiphenyl **15** (7.10 g) as a colorless solid in 73% yield.

The melting point and IR are identical to those in the literature.

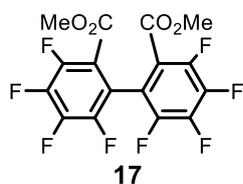
• Preparation of 2,2'-octafluorodiphenic acid **16**^[3]



To a solution of 14.1 g (30.9 mmol) of dibromooctafluorobiphenyl **15** in dry ether (500 mL) cooled at -78 °C was added 48 mL of *n*BuLi (1.62 M solution in hexane, 77.3 mmol) dropwise over 40 min under Ar. The reaction mixture was allowed to stir at this temperature for 80 min, and then dry ice was added before the flask was left to warm up overnight. To the mixture was added dry ice, and then it was diluted with saturated Na₂CO₃ aq. The whole mixture was extracted with saturated Na₂CO₃ aq three times. The combined water layers were acidified with 4N HCl aq. The solution was extracted with ether three times. The combined organic layers were washed with water and brine, and dried over anhydrous MgSO₄. After filtration, the solvent was concentrated under reduced pressure to give octafluorodiphenic acid **16** (10.4 g) as a colorless solid in 87% yield.

The melting point and IR are identical to those in the literature.

• Preparation of dimethyl 2,2'-octafluorobiphenate **17**



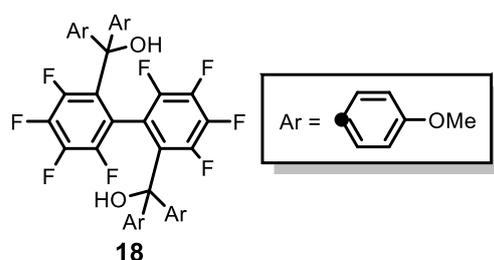
2,2'-Octafluorodiphenic acid **16** (1.26 g, 3.26 mmol) and K₂CO₃ (4.71 g, 32.6 mmol) were dissolved in dry acetone (10 mL) at room temperature under Ar. To the solution was added iodomethane (2.0 mL, 32.6 mmol) and the reaction mixture was refluxed for 4.5 h. The solution was concentrated under reduced pressure. After the

addition of water and ether, the whole mixture was extracted with ether three times. The combined organic layers were washed with water and brine, and dried over anhydrous MgSO_4 . After filtration, the solvent was concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (hexane/ $\text{CH}_2\text{Cl}_2 = 6$) to afford **17** (1.35 g, y. 74%) as a colorless solid.

As another procedure, to a solution of 2,2'-octafluorodiphenic acid (1.53 g, 3.96 mmol) in 10 mL of benzene and 10 mL of methanol was added trimethylsilyldiazomethane (2.0 M in hexane, 7.9 mL, 15.8 mmol) at room temperature. The mixture was stirred for a few minutes. The solution was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2 = 6$) to give **17** (1.50 g) as a colorless solid in 91% yield.

17: m.p. 58.0-61.0 °C; ^1H NMR (300 MHz, CDCl_3): δ /ppm 7.26 (6H, s); ^{13}C NMR (MHz, CDCl_3): δ /ppm ; 162.02, 146.74 (C, dd, $J_{\text{C-F}} = 260, 10$ Hz), 145.07 (C, dd, $J_{\text{C-F}} = 260, 10$ Hz), 142.28 (C, ddd, $J_{\text{C-F}} = 260, 15, 10$ Hz), 141.32 (C, ddd, $J_{\text{C-F}} = 260, 15, 10$ Hz), 116.93 (C, d, $J_{\text{C-F}} = 18$ Hz), 115.83 (C, dt, $J_{\text{C-F}} = 16$ Hz), 53.12; IR (neat): ν/cm^{-1} 3011, 2961, 2850, 1741, 1636, 1616, 1514, 1479, 1438, 1365, 1334, 1294, 1237, 1188, 1114, 1096, 1051, 991, 892, 833, 765, 756, 717, 709, 665, 443; FD-MS m/z 414 (M^+ , BP), 415 (18), 416 (2); HR-MS (FD) Calcd. for $\text{C}_{16}\text{H}_6\text{F}_8\text{O}_4$: 414.0138. Found: 414.0147; Anal. Calcd. for $\text{C}_{16}\text{H}_6\text{F}_8\text{O}_4 \cdot 1/10\text{hexane}$: C, 47.15; H, 1.76. Found: C, 47.15; H, 1.74%.

• Preparation of 2,2'-bis[bis(4-methoxyphenyl)hydroxymethyl]octafluorobiphenyl **18**



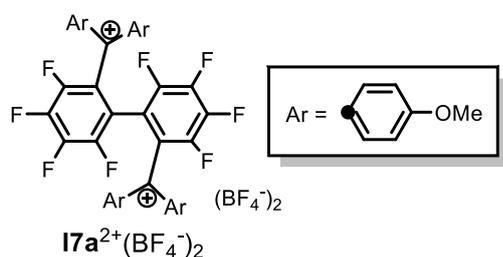
To a suspension of Mg (566 mg, 22.9 mmol) in 240 mL of dry THF was added 4-bromoanisole (2.77 mL, 21.8 mmol). The mixture was refluxed for 1 h, and then cooled to room temperature under Ar. To the Grignard reagent was added diester **17** (100 mg) in 2 mL of

dry THF, and the mixture was refluxed for 3 h. After the addition of saturated NH_4Cl aq., the whole mixture was extracted with EtOAc three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc: CH_2Cl_2 :hexane = 1:2:8) to give **18** (1.62 g) as a yellow solid in 57% yield.

18: m.p. 185.0-188.0 °C; ^1H NMR (300 MHz, CDCl_3): δ /ppm 7.17 (4H, d, $J = 9.0$ Hz), 7.00 (4H, d, $J = 9.0$ Hz), 6.85 (4H, d, $J = 9.0$ Hz), 6.74 (4H, d, $J = 9.0$ Hz), 3.82 (6H, s), 3.76 (6H, s), 3.23 (2H, s); ^{13}C NMR (MHz, CDCl_3): δ /ppm 159.06, 159.06, 144.64 (C, dd, $J_{\text{C-F}} = 240, 10$ Hz), 144.12 (C, dd, $J_{\text{C-F}} = 240, 10$ Hz), 140.42 (C, ddd, $J_{\text{C-F}} = 240, 10$ Hz), 139.25 (C,

ddd, $J_{C-F} = 240, 10$ Hz), 138.33, 135.35, 129.07 (C, d, $J_{C-F} = 10$ Hz), 128.09, 127.86, 117.63 (C, dt, $J_{C-F} = 10$ Hz), 113.59, 113.28, 81.08, 55.26, 55.18; IR (KBr): $\nu_{cm^{-1}}$ 3424, 2934, 2359, 1610, 1510, 1454, 1297, 1252, 1177, 1110, 1034, 1005, 833, 808, 768, 714, 611; FD-MS m/z 782 (M^+ , BP), 783 (48), 784 (12), 785 (2); HR-MS (FD) Calcd. for $C_{42}H_{30}F_8O_6$: 782.1914. Found: 782.1923; Anal. Calcd. for $C_{42}H_{30}F_8O_6 \cdot 1/6$ hexane: C, 64.80; H, 4.09. Found: C, 64.93; H, 4.10%.

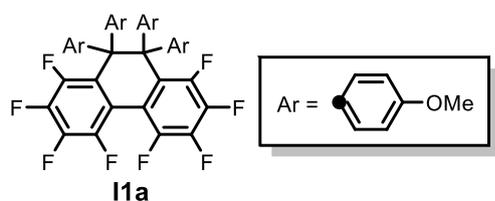
• Preparation of octafluorobiphenyl-2,2'-diylbis[bis(4-methoxyphenyl)methylium] bis(tetrafluoroborate) salt **I7a**²⁺(BF₄)₂



To a solution of diol **24** (645 mg, 824 μ mol) in TFAA 5 mL was added HBF₄ (42% aq, 350 μ L, 2.14 mmol) at room temperature under Ar, and the mixture was stirred at room temperature for 1 h. The addition of dry ether led to precipitation of the dication salt. The

precipitates were collected, washed with dry ether five times, and dried under reduced pressure to give **I7a**²⁺(BF₄)₂ (672 mg) as a dark red powder in 88% yield.

• Preparation of 9,9,10,10-tetrakis(4-methoxyphenyl)octafluoro-9,10-dihydrophenanthrene **I1a**



A mixture of dication salt **I7a**²⁺(BF₄)₂ (1.89 g, 2.06 mmol) and Zn (4.01 g, 61.8 mmol) in 10 mL of dry MeCN was stirred at room temperature for 3 h under Ar. The resulting suspension was diluted with water. The whole

mixture was extracted with CH₂Cl₂ three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The resulting solid was triturated with a small amount of MeOH to give **I1a** (1.10 mg) as a yellow solid in 71% yield.

I1a: m.p. 162.0-166.0 °C; ¹H NMR (400 MHz, CDCl₃): δ ppm 6.7-7.0 (8H, br), 6.53 (8H, d, $J = 9.0$ Hz), 3.74 (12H, s); ¹⁹F NMR (470 MHz, CDCl₃): δ ppm -127.54 (2F, d, $J_{C-F} = 20$ Hz), -133.49 (2F, s), -152.00 (2F, t, $J = 20$ Hz), -156.58 (2F, d, $J = 6$ Hz); ¹³C NMR (100 MHz, CD₂Cl₂): δ ppm ; 158.86, 144.88 (C, dd, $J_{C-F} = 250, 10$ Hz), 144.70 (C, ddd, $J_{C-F} = 250, 12, 3$ Hz), 142.01 (C, ddd, $J_{C-F} = 250, 12, 3$ Hz), 140.02 (C, ddd, $J_{C-F} = 250, 10, 3$ Hz), 134.12, 132.77, 128.86 (C, d, $J_{C-F} = 5$ Hz), 114.77, 111.68, 63.17 (C, d, $J_{C-F} = 3$ Hz), 55.46; IR (KBr): $\nu_{cm^{-1}}$ 3003, 2949, 2835, 1607, 1581, 1510, 1472, 1297, 1258, 1190, 1104, 1059, 1033, 960,

822, 740, 670; LR-MS (FD) m/z 748 (M^+ , BP), 749 (47), 750 (12), 751 (2); HR-MS (FD) Calcd. for $C_{42}H_{28}F_8O_4$: 748.1859. Found: 748.1855; Anal. Calcd. for $C_{42}H_{28}F_8O_6 \cdot 1/3CH_2Cl_2$: C, 65.44; H, 3.72. Found: C, 65.35; H, 3.86%; UV-Vis (CH_2Cl_2): λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) sh 270 (14700); (MeCN): 271 (14100), 230 (44800).

• Preparation of octafluorobiphenyl-2,2'-diylbis[bis(4-methoxyphenyl)methylum] bis(hexachloroantimonite) salt **I7a**²⁺(SbCl₆)₂

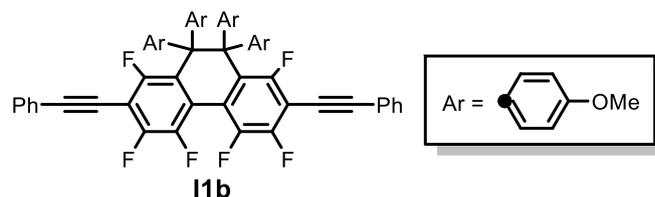
A mixture of **I1a** (24.5 mg, 32.7 μ mol) and tris(4-bromophenyl)aminium hexachloroantimonate (50.6 mg, 62.1 μ mol) in 3 mL of dry CH_2Cl_2 was stirred at room temperature for 2 h under Ar. The addition of dry ether led to precipitation of the dication salt. The precipitates were collected, washed with dry ether five times, and dried under reduced pressure to give **I7a**²⁺(SbCl₆)₂ (43.5 mg) as a dark red powder in 93% yield.

I7a²⁺(SbCl₆)₂: m.p. 217.5-218.5 °C; ¹H NMR (400 MHz, CD₃CN): δ /ppm 7.7-8.0 (2H, br), 7.55 (4H, d, J = 8.8 Hz), 7.2-7.5 (2H, br), 7.30 (4H, d, J = 8.8 Hz), 7.0-7.2 (2H, br), 6.8-7.0 (2H, br), 4.18 (6H, s), 4.15 (6H, s); ¹⁹F NMR (470 MHz, CD₃CN): δ /ppm -127.54 (2F, t, J_{C-F} = 11 Hz), -130.43 (2F, t, J_{C-F} = 11 Hz), -147.35 (2F, td, J = 20, 9 Hz), -148.79 (2F, td, J = 20, 7 Hz); IR (KBr): ν/cm^{-1} 3078, 2937, 2850, 1612, 1578, 1547, 1511, 1455, 1399, 1376, 1312, 1282, 1257, 1190, 1160, 1126, 1072, 1064, 1000, 909, 851, 816, 807, 549; LR-MS (FD) m/z 748 (M^+ , BP), 749 (50), 750 (36), 751 (15), 752 (5); HR-MS (FD) Calcd. for $C_{42}H_{28}F_8O_4$: 748.18598. Found: 748.18519; UV-Vis (CH_2Cl_2): λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) sh 580 (62800), 545 (90900), 402 (27600), 277 (39600); (MeCN): 536 (61500), 392 (20700), 270 (33700).

• Preparation of **I1a** from dication salt **I7a**²⁺(SbCl₆)₂

A mixture of dication salt **I7a**²⁺(SbCl₆)₂ (53.1 mg, 37.7 μ mol) and Zn (80.8 mg, 1.13 mmol) in 3 mL of dry THF was stirred at room temperature for 19 h under Ar. The resulting suspension was diluted with water. The whole mixture was extracted with CH_2Cl_2 three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure to give **I1a** (27.0 mg) as a yellow solid in 96% yield.

• Preparation of 2,7-bis(phenylethynyl)-9,9,10,10-tetrakis(4-methoxyphenyl)hexafluoro-9,10-dihydrophenanthrene **I1b**

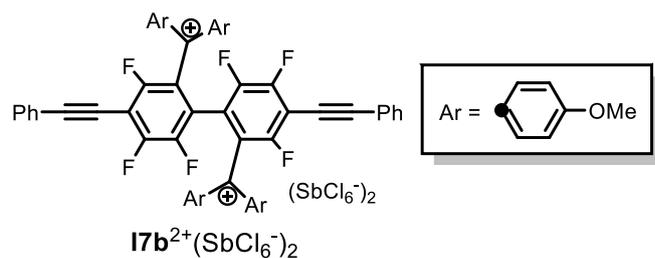


To a solution of **I1a** (140 mg, 187 μmol) in dry THF (10 mL) were added phenylacetylene (45 μL , 411 μmol) and NaHMDS (1.09 M solution in THF, 515 μL , 561 μmol)

at room temperature under Ar, and the mixture was refluxed for 19 h. After being diluted with water, the whole mixture was extracted with AcOEt three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 10, 1% Et_3N) to give **I1b** (69 mg) as an orange solid in 40% yield.

I1b: m.p. 180.5-182.0 $^\circ\text{C}$; ^1H NMR (300 MHz, CDCl_3): δ ppm 7.56-7.53 (4H, m), 7.38-7.32 (6H, m), 6.90 (8H, br), 6.53 (8H, d, $J = 9.0$ Hz), 3.74 (12H, s); ^{19}F NMR (470 MHz, CDCl_3): δ ppm 27.2 (2F, s), 30.9 (2F, dd, $J = 10, 10$ Hz), 64.0 (2F, s); IR (KBr): ν/cm^{-1} 2931, 2835, 2217, 1607, 1580, 1510, 1460, 1442, 1383, 1294, 1255, 1189, 1109, 1087, 1036, 827, 808, 755, 689, 588, 540; LR-MS (FD) m/z 912 (M^+ , BP), 913 (62), 914 (18); HR-MS (FD) Calcd. for $\text{C}_{58}\text{H}_{38}\text{F}_6\text{O}_4$: 912.2674. Found: 912.2656; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 347 (45500); (MeCN): 345 (37800), 287 (28400).

• Preparation of hexafluorobiphenyl-4,4'-bis(phenylethynyl)-2,2'-diylbis[bis(4-methoxyphenyl)methyl] bis(hexachloroantimonate) salt **I7b** $^{2+}(\text{SbCl}_6^-)_2$

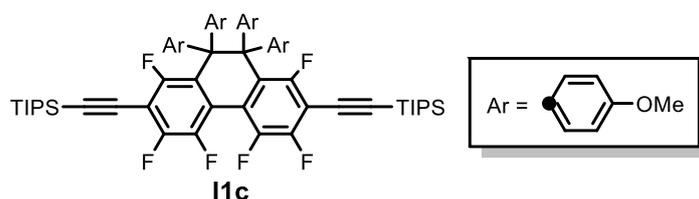


A mixture of **I1b** (31 mg, 41.1 μmol) and tris(4-bromophenyl)aminium hexachloroantimonate (65 mg, 82.2 μmol) in 3 mL of dry CH_2Cl_2 was stirred for 2 h under Ar at room temperature. The addition of dry

ether led to precipitation of the dication salt. The precipitates were collected, washed with dry ether five times, and dried under reduced pressure to give **I7b** $^{2+}(\text{SbCl}_6^-)_2$ (55 mg) as a dark red powder in 84% yield.

I7b $^{2+}(\text{SbCl}_6^-)_2$: m.p. 218.0 $^\circ\text{C}$; ^1H NMR (300 MHz, CD_3CN): δ ppm 7.60-7.40 (18H, m), 7.29 (8H, d, $J = 9.0$ Hz), 4.17 (6H, s), 4.13 (6H, s); IR (KBr): ν/cm^{-1} 1608, 1576, 1456, 1387, 1312, 1285, 1185, 1157, 1125, 995, 906, 853; LR-MS (FD) m/z 912 (M^+ , 23), 913 (14); HR-MS (FD) Calcd. for $\text{C}_{58}\text{H}_{38}\text{F}_6\text{O}_4$: 912.2674. Found: 912.2655.

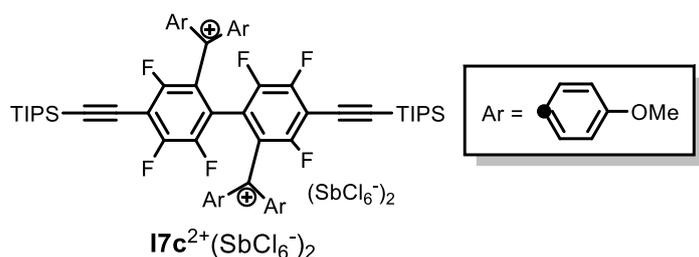
• Preparation of 2,7-bis(triisopropylsilylethynyl)-9,9,10,10-tetrakis(4-methoxyphenyl)hexafluoro-9,10-dihydrophenanthrene **I1c**



To a solution of **I1a** (143 mg, 190 μmol) in dry THF (10 mL) were added ethynyltriisopropylsilane (TIPS-acetylene, 93 μL , 419 μmol) and NaHMDS (1.09 M solution in THF, 437 μL , 476 μmol) at room temperature under Ar, and the mixture was refluxed for 20 h. After being diluted with water, the whole mixture was extracted with AcOEt three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 30, 1% Et_3N) to give **I1c** (112 mg) as an orange solid in 55% yield.

I1c: $^1\text{H NMR}$ (300 MHz, CDCl_3): δ ppm 6.83 (8H, br), 6.52 (8H, d, $J = 9.0$ Hz), 3.74 (12H, s), 1.20-1.00 (42H, s); IR (KBr): ν/cm^{-1} 2943, 2865, 1607, 1510, 146, 1293, 1254, 1181, 1036, 997, 883, 829, 723, 679, 668; LR-MS (FD) m/z 1073 (M^+ , BP), 1074 (81), 1075 (36), 1076 (18); HR-MS (FD) Calcd. for $\text{C}_{64}\text{H}_{70}\text{F}_6\text{O}_4\text{Si}_2$: 1072.4716. Found: 1072.4699; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 331 (31000), 286 (22300); (MeCN): 330 (29300), 285 (22700), 277 (22800).

• Preparation of hexafluorobiphenyl-4,4'-bis(triisopropylsilylethynyl)-2,2'-diylbis[bis(4-methoxyphenyl)methylammonium] bis(hexachloroantimonate) salt **I7c²⁺(SbCl₆⁻)₂**

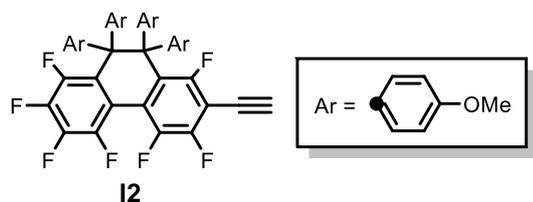


A mixture of **I1c** (11 mg, 10.4 μmol) and tris(4-bromophenyl)ammonium hexachloroantimonate (17 mg, 20.2 μmol) in 1 mL of dry CH_2Cl_2 was stirred at room temperature for 2 h under Ar. The mixture was concentrated under reduced pressure. The residue was dissolved in dry MeCN. The solution was washed with dry hexane five times, and dried under reduced pressure to give **I7c²⁺(SbCl₆⁻)₂** (19 mg) as a dark red powder in 100% yield.

I7c²⁺(SbCl₆⁻)₂: m.p. 133.0-134.0 $^\circ\text{C}$; $^1\text{H NMR}$ (300 MHz, CD_3CN): δ ppm 7.57 (8H, d, $J = 9.0$ Hz), 7.27 (8H, d, $J = 9.0$ Hz), 4.17 (6H, s), 4.12 (6H, s), 1.10-1.00 (42H, m); IR (KBr): ν/cm^{-1} 2943, 2864, 2359, 2342, 1606, 1577, 1510, 1462, 1381, 1313, 1283, 1159, 997,

912, 854, 816, 680, 550; LR-MS (FD) m/z 1073 (M^+ , 58), 1074 (52), 1075 (34), 1076 (17); HR-MS (FD) Calcd. for $C_{64}H_{70}F_6O_4Si_2$: 1072.4716. Found: 1072.4692.

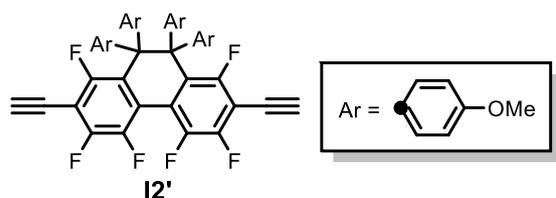
• Preparation of 2-ethynyl-9,9,10,10-tetrakis(4-methoxyphenyl)heptafluoro-9,10-dihydrophenanthrene **I2**



To a solution of **I1a** (354 mg, 473 μmol) in dry THF (10 mL) were added TIPS-acetylene (126 μL , 567 μmol) and NaHMDS (1.1 M solution in THF, 515 μL , 567 μmol) at 0 °C under Ar, and the mixture was stirred at

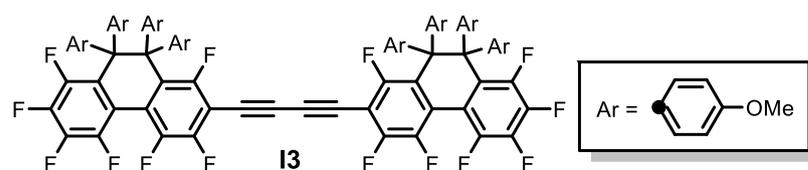
0 °C for 1.5 h. After being diluted with water, the whole mixture was extracted with AcOEt three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was concentrated under reduced pressure. To a solution of the residue in dry THF (10 mL) was added TBAF (1M solution in THF, 560 μL , 560 μmol) at 0 °C under Ar, and the mixture was stirred for 10 min. After being diluted with saturated NH_4Cl aq., the whole mixture was extracted with AcOEt three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 10) to give **I2** (100 mg, y. 28%) as a yellow solid along with recovery of the starting material **I1a** and containing by-product **I2'**.

I2: m.p. 127.0-130.0 °C; ^1H NMR (400 MHz, CDCl_3): δ ppm 6.7-7.0 (8H, br), 6.52 (8H, d, $J = 9.6$ Hz), 3.74 (12H, s), 3.57 (1H, s); ^{19}F NMR (470 MHz, CDCl_3): δ ppm -98.55 (1F, d, $J = 13$ Hz), -127.59 (1F, s), -127.61 (1F, t, $J = 10$ Hz), -131.57 (1F, d, $J = 22$ Hz), -132.45 (1F, ddd, $J = 93, 12, 6$ Hz), -151.12 (1F, t, $J = 19$ Hz), -156.47 (1F, t, $J = 20$ Hz); ^{13}C NMR (100 MHz, CD_2Cl_2): δ ppm ; 158.90, 158.86, 154.93 (C, d, $J_{\text{C-F}} = 250$ Hz), 151.05 (C, dd, $J_{\text{C-F}} = 250, 15$ Hz), 150.98 (C, dd, $J_{\text{C-F}} = 250, 15$ Hz), 144.99 (C, d, $J_{\text{C-F}} = 250$ Hz), 144.88 (C, d, $J_{\text{C-F}} = 250$ Hz), 144.23 (C, dd, $J_{\text{C-F}} = 250, 12$ Hz), 140.07 (C, dt, $J_{\text{C-F}} = 250, 15$ Hz), 134.12, 134.06, 132.89, 129.23, 128.46 (C, d, $J_{\text{C-F}} = 10$ Hz), 128.41 (C, d, $J_{\text{C-F}} = 10$ Hz), 121.04, 121.14, 115.20, 115.09, 113.89, 111.71, 63.18, 63.15, 55.47; IR (KBr): ν/cm^{-1} 3297, 2955, 2933, 2837, 1608, 1580, 1510, 1463, 1292, 1256, 1190, 1101, 1034, 954, 826; LR-MS (FD) m/z 754 (M^+ , BP), 755 (49), 756 (13); HR-MS (FD) Calcd. for $C_{44}H_{29}F_7O_4$: 754.1954. Found: 754.1960; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 327 (44000), sh 267 (44200), 242 (52300); (MeCN): 328 (41800), 265 (44600), 241 (48800).



12': m.p. 137.0-140.0 °C; ^1H NMR (400 MHz, CDCl_3): δ ppm 6.7-7.0 (8H, br), 6.52 (8H, d, $J = 9.6$ Hz), 3.74 (12H, s), 3.59 (2H, s); ^{19}F NMR (470 MHz, CDCl_3): δ ppm -98.68 (2F, s), -131.53 (2F, t, $J = 10$ Hz), -135.36 (2F, s); ^{13}C NMR (100 MHz, CD_2Cl_2): δ ppm ; 158.84, 154.95 (C, d, $J_{\text{C-F}} = 250$ Hz), 151.01 (C, ddd, $J_{\text{C-F}} = 250, 15, 7$ Hz), 144.38 (C, ddd, $J_{\text{C-F}} = 250, 35, 15$ Hz), 134.01, 132.91, 128.80, 128.76, 128.71, 128.66, 121.34, 111.70, 63.13 (C, d, $J_{\text{C-F}} = 35$ Hz), 55.46; IR (KBr): $\nu_{\text{cm}^{-1}}$ 3293, 3000, 2933, 2836, 1607, 1579, 1510, 1482, 1460, 1292, 1255, 1189, 1093, 1036, 944, 825; LR-MS (FD) m/z 760 (M^+ , BP), 761 (53), 762 (15); HR-MS (FD) Calcd. for $\text{C}_{46}\text{H}_{30}\text{F}_6\text{O}_4$: 760.2048. Found: 760.2037.

• Preparation of 1,3-butadiyne-1,4-diylbis[9,9,10,10-tetrakis(4-methoxyphenyl)heptafluoro-9,10-dihydrophenanthrene] **13**

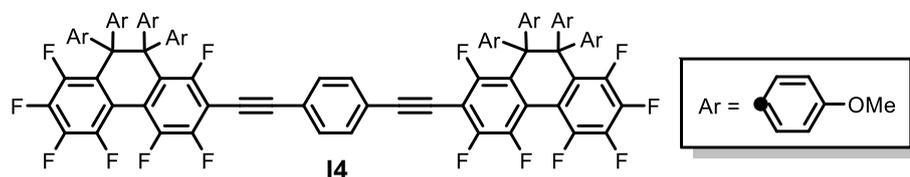


13 (71.2 mg, 94.3 μmol), TMEDA (90 μL , 566 μmol), CuI (18.0 mg, 94.3 μmol) and Et_3N (400 μL , 2.83 mmol) were suspended in dry acetone (10 mL) at room temperature under air. The reaction mixture was stirred at this temperature for 4 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel (hexane/AcOEt = 5) to give **13** (26.5 mg) as an orange solid in 37% yield.

13: m.p. 176.0-177.5 °C; ^1H NMR (400 MHz, CDCl_3): δ ppm 6.7-7.0 (16H, br), 6.52 (16H, d, $J = 8.0$ Hz), 3.74 (12H, s), 3.74 (12H, s); ^{19}F NMR (470 MHz, CDCl_3): δ ppm -96.99 (2F, d, $J_{\text{C-F}} = 12$ Hz), -127.54 (2F, s), -130.14 (2F, d, $J = 22$ Hz), -132.12 (2F, dd, $J = 95, 12$ Hz), -135.83 (2F, ddd, $J = 95, 22, 12$ Hz), -150.65 (2F, t, $J = 20$ Hz), -156.31 (2F, t, $J = 20$ Hz); ^{13}C NMR (100 MHz, CD_2Cl_2): δ ppm ; 158.87, 158.84, 155.31 (C, d, $J_{\text{C-F}} = 250$ Hz), 151.23 (C, dd, $J_{\text{C-F}} = 250, 10$ Hz), 148.27 (C, d, $J_{\text{C-F}} = 250$ Hz), 145.05 (C, d, $J_{\text{C-F}} = 250$ Hz), 144.89 (C, d, $J_{\text{C-F}} = 250$ Hz), 144.15 (C, dd, $J_{\text{C-F}} = 250, 10$ Hz), 140.14 (C, dd, $J_{\text{C-F}} = 250, 10$ Hz), 134.05, 133.97, 132.76, 132.63, 129.24, 128.46 (C, d, $J_{\text{C-F}} = 10$ Hz), 128.50 (C, d, $J_{\text{C-F}} = 10$ Hz), 122.12 (C, d, $J_{\text{C-F}} = 10$ Hz), 116.98 (C, d, $J_{\text{C-F}} = 12$ Hz), 115.04, 114.95, 111.71, 63.16, 63.08, 55.45; IR (KBr): $\nu_{\text{cm}^{-1}}$ 2997, 2954, 2933, 2836, 1607, 1580, 1510, 1463, 1442, 1292, 1256, 1189, 1101, 1036, 957, 788, 719, 588; LR-MS (FD) m/z 1582 (M^+ , 94), 1583 (BP), 1584 (53), 1585 (21), 1586 (7); LR-MS (FD) m/z 1506 (M^+ , BP), 1507 (97), 1508 (50), 1509 (18), 1510 (7); HR-MS (FD) Calcd. for $\text{C}_{88}\text{H}_{56}\text{F}_{14}\text{O}_8$: 1506.3751. Found: 1506.3743; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) sh 350 (80100), 325 (90400), sh 269 (72000), 240 (75700);

(MeCN): sh 346 (98700), 324 (119000), 263 (92600), 242 (92000).

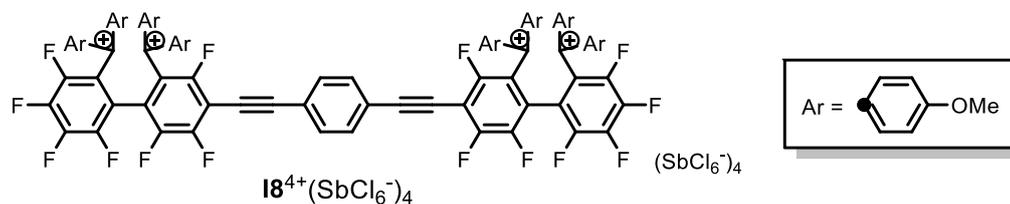
• Preparation of 1,4-phenylenediethyne-2,2'-diylbis[9,9,10,10-tetrakis(4-methoxyphenyl)heptafluoro-9,10-dihydrophenanthrene] **I4**



A mixture of **I2** (200 mg, 264 μmol), *p*-diiodobenzene (26.1 mg, 79.2 μmol), Pd(PPh₃)₄ (61.0 mg, 52.8 μmol) and CuI (10.0 mg, 52.8 μmol) in degassed Et₃N (10 mL) was heated at 50 °C for 2 h under Ar. After being diluted with water, the whole mixture was extracted with EtOAc twice. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 5→3) to give **I4** (100.0 mg) as an orange solid in 81% yield.

I4: m.p. 185.0-188.0 °C; ¹H NMR (400 MHz, CDCl₃): δ ppm 7.50 (4H, s), 6.7-7.0 (16H, br), 6.53 (16H, t, *J* = 7.2 Hz), 3.74 (12H, s), 3.73 (12H, s); ¹⁹F NMR (470 MHz, CDCl₃): δ ppm -98.35 (2F, d, *J*_{C-F} = 12 Hz), -127.69 (2F, s), -131.59 (2F, d, *J* = 22 Hz), -132.44 (2F, dd, *J* = 95, 12 Hz), -136.38 (2F, ddd, *J* = 95, 22, 12 Hz), -151.32 (2F, t, *J* = 20 Hz), -156.56 (2F, t, *J* = 20 Hz); ¹³C NMR (100 MHz, CD₂Cl₂): δ ppm ; 158.84, 158.79, 154.12 (C, d, *J*_{C-F} = 250 Hz), 150.21 (C, dd, *J*_{C-F} = 250, 15 Hz), 150.07 (C, dd, *J*_{C-F} = 250, 15 Hz), 144.95 (C, d, *J*_{C-F} = 250 Hz), 144.82 (C, d, *J*_{C-F} = 250 Hz), 144.33 (C, ddd, *J*_{C-F} = 250, 15, 5 Hz), 139.98 (C, d, *J*_{C-F} = 250 Hz), 135.30 (C, d, *J*_{C-F} = 15 Hz), 134.06, 134.02, 132.95, 132.86, 132.25, 129.18, 128.42 (C, d, *J*_{C-F} = 5 Hz), 128.30 (C, d, *J*_{C-F} = 5 Hz), 123.15, 120.47 (C, d, *J*_{C-F} = 12 Hz), 115.26, 115.15, 111.68, 63.16, 63.12, 55.45; IR (KBr): ν cm⁻¹ 3042, 2999, 2954, 2933, 2907, 2836, 1607, 1579, 1510, 1481, 1463, 1293, 1256, 1189, 1125, 1099, 1036, 955, 826, 807, 789, 588; LR-MS (FD) *m/z* 1582 (M⁺, 94), 1583 (BP), 1584 (53), 1585 (21), 1586 (7); HR-MS (FD) Calcd. for C₉₄H₆₀F₁₄O₈: 1582.4064. Found: 1582.4083; UV-Vis (CH₂Cl₂): λ_{max} /nm (ϵ /M⁻¹cm⁻¹) 328 (129000), 271 (74900), 234 (86600); (MeCN): 326 (127000), 268 (75000), 231 (79800).

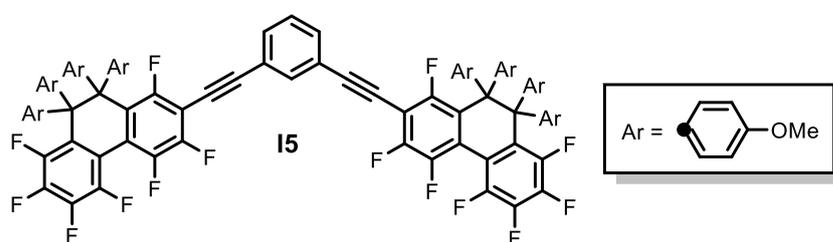
• Preparation of 1,4-phenylenediethyne-2,2'-diylbis{3,3',4',5,5',6,6'-heptafluorobiphenyl-2,2'-diylbis[bis(4-methoxyphenyl)methylium] tetrakis(hexachloroantimonite) salt **I8**⁴⁺(SbCl₆⁻)₄



To a solution of **I4** (10.3 mg, 6.60 μ mol) in 2 mL of dry CH₂Cl₂ was added tris(4-bromophenyl)aminium hexachloroantimonate (21.4 mg, 26.3 μ mol) at 0 °C under Ar, and the mixture was stirred at room temperature for 1 h. The addition of dry ether led to precipitation of the dication salt. The precipitates were filtrated and washed with dry ether same times to give **I8**⁴⁺(SbCl₆⁻)₄ (14.9 mg) as a dark red powder in 77% yield.

I8⁴⁺(SbCl₆⁻)₄: m.p. 213.5-217.0 °C; ¹H NMR (400 MHz, CD₃CN): δ ppm 7.7-8.0 (4H, br), 7.61 (4H, s), 7.57 (8H, dd, J = 8.8, 3.6 Hz), 7.3-7.5 (4H, br), 7.30 (4H, dd, J = 8.8, 3.6 Hz), 7.1-7.3 (4H, br), 6.9-7.1 (4H, br), 4.18 (6H, s), 4.17 (6H, s), 4.15 (6H, s), 4.14 (6H, s); ¹⁹F NMR (470 MHz, CD₃CN): δ ppm -103.26 (2F, d, J_{C-F} = 12 Hz), -121.90 (2F, d, J_{C-F} = 20 Hz), -127.12 (2F, d, J = 20 Hz), -129.51 (2F, s), -130.31 (2F, s), -147.16 (2F, s), -148.58 (2F, t, J = 20 Hz); IR (KBr): ν /cm⁻¹ 1610, 1577, 1510, 1453, 1382, 1313, 1285, 1186, 1159, 1038, 996, 911, 854, 809, 551; LR-MS (ESI) m/z 2586 (C₉₄H₆₀Cl₁₈F₁₄O₈Sb₃⁺), 1125 (C₉₄H₆₀Cl₁₂F₁₄O₈Sb₂²⁺), 639 (C₉₄H₆₀Cl₆F₁₄O₈Sb₃⁺), 395 (C₉₄H₆₀F₁₄O₈⁴⁺); HR-MS (ESI) Calcd. for C₉₄H₆₀Cl₁₂F₁₄O₈Sb₂²⁺: 1125.9177. Found: 1125.9210, 1125.9215, 1125.9288; UV-Vis (CH₂Cl₂): λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) sh 580 (101000), 545 (1616000), 410 (61600), 343 (70000), 276 (85800); (MeCN): 536 (121000), 400 (48300), 336 (80000), 272 (78100).

• Preparation of 1,3-phenylenediethyne-2,2'-diylbis[9,9,10,10-tetrakis(4-methoxyphenyl)heptafluoro-9,10-dihydrophenanthrene] **I5**



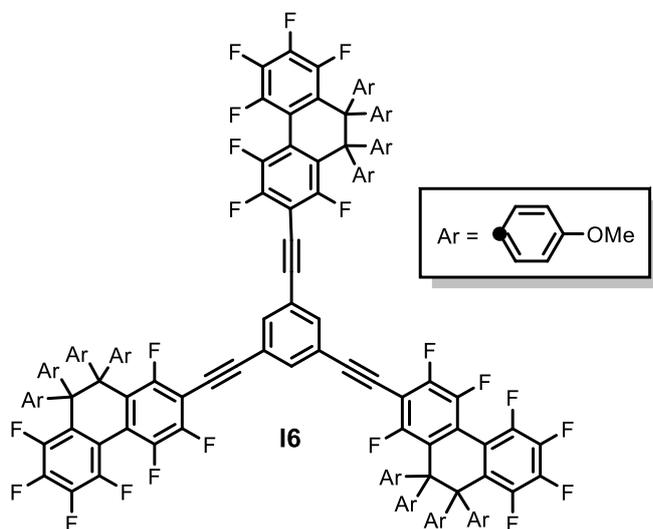
A mixture of **I2** (39.2 mg, 51.9 μ mol), *m*-diiodobenzene (4.6 mg, 14 μ mol), Pd(PPh₃)₄ (11.9 mg, 10.3 μ mol) and CuI

(1.9 mg, 10 μ mol) in degassed Et₃N (2 mL) was heated at 50 °C for 2 h under Ar. After being diluted with water, the whole mixture was extracted with EtOAc twice. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The

residue was purified by column chromatography on silica gel (hexane/EtOAc = 5→3) to give **I5** (19.3 mg) as an orange solid in 88% yield.

I5: m.p. 175.5-177.0 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ /ppm 7.69 (1H, s), 7.52 (2H, dd, $J = 8.0, 1.2$ Hz), 7.34 (1H, d, $J = 7.2$ Hz), 6.7-7.0 (16H, br), 6.53 (16H, dd, $J = 9.2, 5.2$ Hz), 3.74 (12H, s), 3.74 (12H, s); $^{19}\text{F NMR}$ (470 MHz, CDCl_3): δ /ppm -98.33 (2F, d, $J_{\text{C-F}} = 12$ Hz), -127.72 (2F, s), -131.61 (2F, d, $J = 22$ Hz), -132.43 (2F, dd, $J = 90, 12$ Hz), -136.39 (2F, ddd, $J = 95, 22, 12$ Hz), -151.35 (2F, t, $J = 20$ Hz), -156.58 (2F, t, $J = 20$ Hz); $^{13}\text{C NMR}$ (100 MHz, CD_2Cl_2): δ /ppm ; 158.89, 158.84, 154.21 (C, d, $J_{\text{C-F}} = 250$ Hz), 150.34 (C, dd, $J_{\text{C-F}} = 250, 15$ Hz), 150.27 (C, dd, $J_{\text{C-F}} = 250, 15$ Hz), 144.99 (C, d, $J_{\text{C-F}} = 250$ Hz), 144.89 (C, d, $J_{\text{C-F}} = 250$ Hz), 141.90 (C, dd, $J_{\text{C-F}} = 250, 20$ Hz), 140.15 (C, dd, $J_{\text{C-F}} = 250, 20$ Hz), 134.16, 134.07, 132.97, 132.87, 130.91, 130.84, 129.36, 129.23, 128.47, 128.36, 120.60, 120.45, 115.34, 115.22, 111.73, 63.18, 55.48; IR (KBr): ν/cm^{-1} 3059, 2998, 2953, 2907, 2836, 1607, 1579, 1509, 1463, 1293, 1256, 1189, 1099, 1037, 956, 826, 788, 588; LR-MS (FD) m/z 1582 (M^+ , 96), 1583 (BP), 1584 (55), 1585 (21), 1586 (7); HR-MS (FD) Calcd. for $\text{C}_{94}\text{H}_{60}\text{F}_{14}\text{O}_8$: 1582.4064. Found: 1582.4048; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 312 (122000); (MeCN): 309 (106000), 270 (95000).

• Preparation of 1,3,5-benzenetriyltriethyne-2,2',2''-triyl[9,9,10,10-tetrakis(4-methoxyphenyl)heptafluoro-9,10-dihydrophenanthrene] **I6**



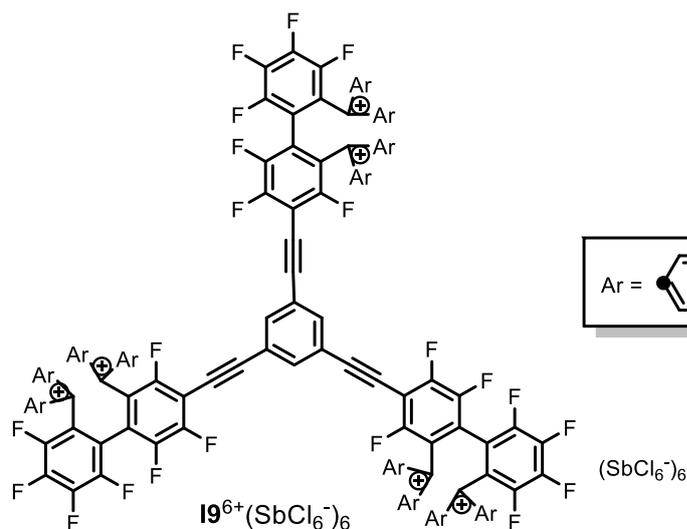
A mixture of **I2** (67.3 mg, 89.1 μmol), 1,3,5-triiodobenzene (8.8 mg, 19 μmol), $\text{Pd}(\text{PPh}_3)_4$ (10.3 mg, 8.91 μmol) and CuI (1.7 mg, 8.9 μmol) in degassed Et_3N (4 mL) was heated at 50 °C for 3 h under Ar. After being diluted with water, the whole mixture was extracted with EtOAc twice. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was

concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 5→3→2) to give **I6** (25.0 mg) as an orange solid in 55% yield.

I6: m.p. 204.0-209.0 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ /ppm 7.65 (3H, s), 6.7-7.0 (24H, br), 6.53 (24H, dd, $J = 8.8, 5.2$ Hz), 3.74 (18H, s), 3.74 (18H, s); $^{19}\text{F NMR}$ (470 MHz, CDCl_3): δ /ppm -98.08 (3F, d, $J_{\text{C-F}} = 12$ Hz), -127.70 (3F, s), -131.35 (3F, d, $J = 22$ Hz), -

132.35 (3F, d, $J = 90$ Hz), -136.24 (3F, ddd, $J = 95, 22, 12$ Hz), -151.17 (3F, t, $J = 20$ Hz), -156.51 (3F, t, $J = 20$ Hz); ^{13}C NMR (100 MHz, CD_2Cl_2): δ /ppm ; 158.89, 158.84, 154.24 (C, d, $J_{\text{C-F}} = 250$ Hz), 150.24 (C, dd, $J_{\text{C-F}} = 250, 15$ Hz), 150.20 (C, dd, $J_{\text{C-F}} = 250, 15$ Hz), 144.99 (C, d, $J_{\text{C-F}} = 250$ Hz), 144.90 (C, d, $J_{\text{C-F}} = 250$ Hz), 144.33 (C, dd, $J_{\text{C-F}} = 250, 10$ Hz), 140.13 (C, dd, $J_{\text{C-F}} = 250, 10$ Hz), 135.57, 134.10, 134.06, 132.91, 129.23, 128.51, 120.87 (C, d, $J_{\text{C-F}} = 15$ Hz), 120.86 (C, d, $J_{\text{C-F}} = 15$ Hz), 115.28, 115.18, 111.73, 63.21, 63.17, 55.47; IR (KBr): ν/cm^{-1} 3042, 2998, 2953, 2933, 2836, 1607, 1580, 1510, 1463, 1293, 1256, 1189, 1100, 1037, 959, 825, 787, 589; LR-MS (FD) m/z 2334 (M^+ , 66), 2335 (BP), 2336 (83), 2337 (43), 2338 (22), 2339 (9); HR-MS (FD) Calcd. for $\text{C}_{138}\text{H}_{87}\text{F}_{21}\text{O}_{12}$: 2334.5862. Found: 2334.5834; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 312 (194000), 275 (135000); (MeCN): 309 (181000), 272 (142000), 240 (119000).

• Preparation of 1,3,5-benzenetriyltriethyne-2,2',2''-triyl{3,3',4',5,5',6,6'-heptafluorobiphenyl-2,2'-diylbis[bis(4-methoxyphenyl)methylium] hexakis(hexachloroantimonite) salt **I** $\mathbf{9}^{6+}(\text{SbCl}_6^-)_6$



To a solution of **I6** (14.8 mg, 6.3 μmol) in 2 mL of dry CH_2Cl_2 was added tris(4-bromophenyl)aminium hexachloroantimonate (31.0 mg, 38.0 μmol) at 0 $^\circ\text{C}$ under Ar, and the mixture was stirred at room temperature for 1 h. The addition of dry ether led to precipitation of the dication salt. The precipitates were filtrated and washed with dry ether same times to give $\mathbf{I9}^{6+}(\text{SbCl}_6^-)_6$ (23.5 mg) as a dark red powder in 85% yield.

$\mathbf{I9}^{6+}(\text{SbCl}_6^-)_6$: m.p. 214-220.0 $^\circ\text{C}$; ^1H NMR (400 MHz, CD_3CN): δ /ppm 7.85 (3H, s), 7.7-8.0 (6H, br), 7.57 (12H, d, $J = 7.6$ Hz), 7.5-7.7 (6H, br), 7.35 (6H, d, $J = 8.8$ Hz), 7.29 (6H, d, $J = 8.8$ Hz), 7.1-7.4 (6H, br), 6.8-7.1 (6H, br), 4.19 (9H, s), 4.19 (9H, s), 4.15 (9H, s), 4.12 (9H, s); ^{19}F NMR (470 MHz, CD_3CN): δ /ppm -104.13 (3F, s), -122.45 (3F, d, $J_{\text{C-F}} = 22$ Hz), -127.31 (3F, s), -129.91 (3F, dd, $J = 20, 12$ Hz), -130.37 (3F, t, $J = 10$ Hz), -147.24 (3F,

dd, $J = 20, 10$ Hz), -148.70 (3F, t, $J = 20$ Hz); IR (KBr): ν/cm^{-1} 3100, 2939, 2850, 1610, 1577, 1510, 1453, 1381, 1313, 1285, 1186, 1159, 1125, 1063, 997, 912, 854, 815, 552; LR-MS (FD) m/z 4008 ($\text{C}_{138}\text{H}_{87}\text{Cl}_{30}\text{F}_{21}\text{O}_{12}\text{Sb}_5^+$), 1836 ($\text{C}_{138}\text{H}_{87}\text{Cl}_{24}\text{F}_{21}\text{O}_{12}\text{Sb}_4^{2+}$), 1112 ($\text{C}_{138}\text{H}_{87}\text{Cl}_{18}\text{F}_{21}\text{O}_{12}\text{Sb}_3^{3+}$); HR-MS (ESI) Calcd. for $\text{C}_{138}\text{H}_{87}\text{Cl}_{24}\text{F}_{21}\text{O}_{12}\text{Sb}_4^{2+}$: 1836.7213. Found: 1836.7192, 1836.7200, 1836.7194; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) sh 586 (137000), 544 (222000), 410 (85400), 276 (161000).

Redox Potential Measurements

Redox potentials (E^{ox} and E^{red}) were measured by cyclic voltammetry in dry CH_2Cl_2 or dry MeCN containing 0.1 mol dm^{-3} Bu_4NBF_4 or Et_4NClO_4 as a supporting electrolyte, respectively. All of the values shown in the text are in E/V versus SCE measured at the scan of 100 mV s^{-1} . A Pt disk electrodes were used as the working and counter electrodes, respectively. The working electrode was polished using a water suspension of Al_2O_3 ($0.05 \mu\text{m}$) before use. The irreversible half-wave potentials were estimated from the anodic peak potentials (E^{pa}) as $E^{\text{ox}} = E^{\text{pa}} - 0.03$ or the cathodic peak potentials (E^{pc}) as $E^{\text{red}} = E^{\text{pc}} + 0.03$.

X-ray analyses

Crystal data of **I1a** · 1/3hexane

Crystals were obtained by recrystallizing from EtOAc/hexane. $\text{C}_{44}\text{H}_{32.67}\text{F}_8\text{O}_4$, $M_r = 777.40$, pale yellow prism, $0.10 \times 0.10 \times 0.10 \text{ mm}^3$, cubic $Ia\bar{3}$ (#206), $a = 27.6408(9) \text{ \AA}$, $V = 21118.0(12) \text{ \AA}^3$, ρ ($Z = 24$) = 1.467 g cm^{-3} , $T = 153 \text{ K}$, $\mu = 1.212 \text{ cm}^{-1}$. The final $R1$ and $wR2$ values are 0.076 ($I > 2\sigma I$) and 0.215 (all data) for 4045 reflections and 252 parameters. Esds for **I1a** are $0.004\text{--}0.005 \text{ \AA}$ for bond lengths and $0.2\text{--}0.3^\circ$ for bond angles, respectively. CCDC 923999.

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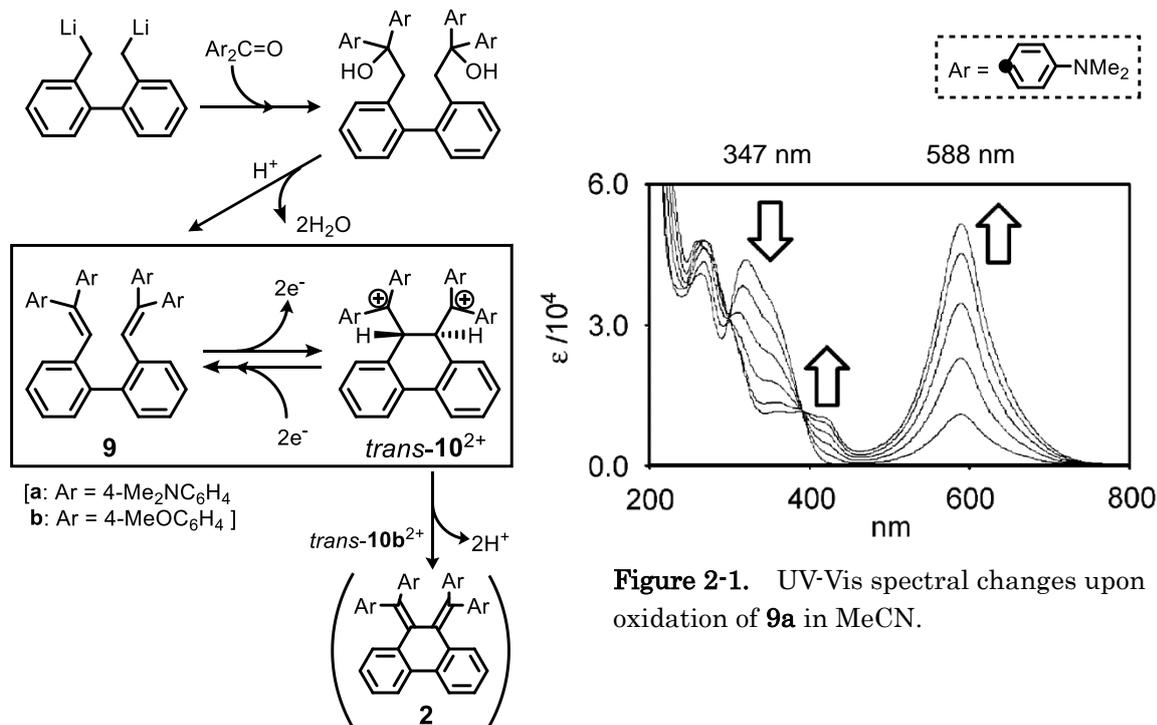
Chapter 2

3,3',4,4',5,5',6,6'-Octafluoro-2,2'-bis[2,2-bis(4-dimethylaminophenyl)-ethenyl]biphenyl Exhibiting Electrochiroptical Response: Assembly to Optically Pure Dumbbell-type Dyad and Tripod-type Triad That Undergo 4e⁻ and 6e⁻-Transfer

2-1. Introduction

Biphenyl-2,2'-diyl-type donors **9**^[1] are the representative compounds of the “exo”-type *dyrex* system as shown in section 0-1-3. They were prepared from the corresponding diol **30** under acidic dehydrating conditions (Scheme 2-1). Diol **30** was obtained from 2,2'-bis(lithiomethyl)biphenyl with the corresponding diarylketone. Figure 2-1 shows a spectroelectrogram obtained upon electric oxidation of neutral **9a** having dimethylaminophenyl groups. Donor **9a** was transformed into the corresponding dication **10a**²⁺ with an absorption at 588 nm and shows deep-blue color. Interconversion between neutral **9a** and dication **10a**²⁺ is reversible upon 2e⁻-transfer.

Another example is a binaphthyl-based **12b**^[1] with configurational stability in terms of axial chirality (Figure 2-2), thus not only UV-Vis but also CD spectral changes were observed upon oxidation of optically resolved **12b**. This behavior is called “electrochiroptical” response.



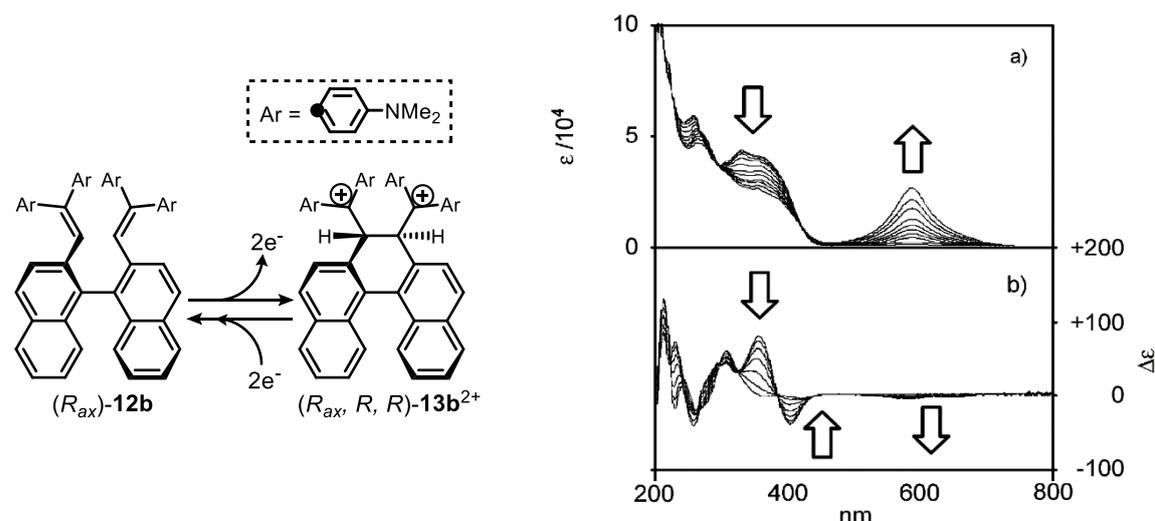
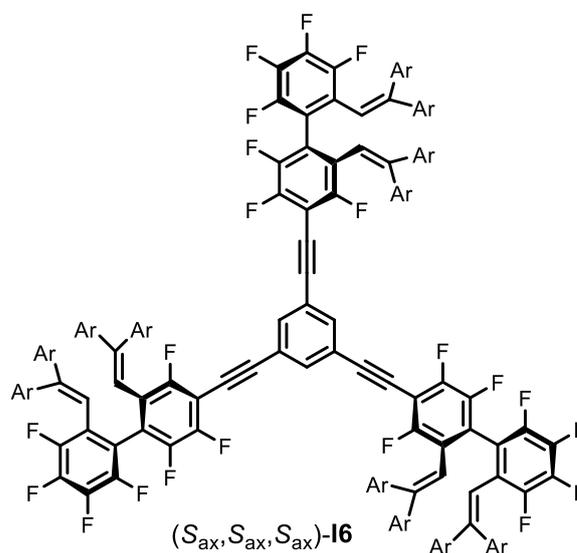
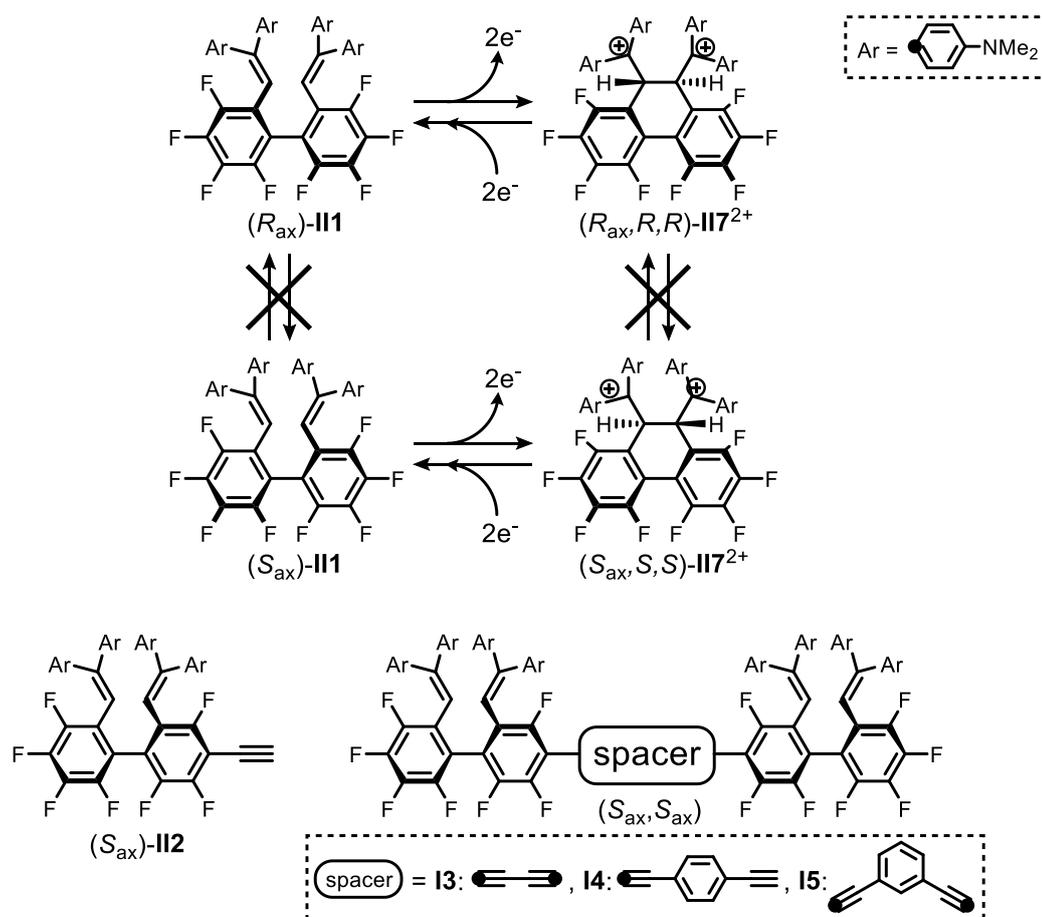


Figure 2-2. (a) A change in UV-Vis spectrum of *rac*-**12b** (39 μ M) and (b) a change in CD spectrum of (R_{ax}) -**12b** (21 μ M) upon constant-current oxidation (30 μ A) every 4 min in MeCN.

Electron donor **II1** which is an octafluoro derivative of **12b** is interesting because it 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 (Scheme 2-2). Moreover, the F atoms at the 6,6'-positions could prevent rotation around the biphenyl axis in **II1** to allow its optical resolution. Thus, dyrex donor $(R_{ax})/(S_{ax})$ -**II1** could serve as a versatile chiral synthon for the production of larger assemblies containing multiple *dyrex* units such as dumbbell-type dyads $(R_{ax}, R_{ax})/(S_{ax}, S_{ax})$ -**II3-5** or a tripod-type triad $(R_{ax}, R_{ax}, R_{ax})/(S_{ax}, S_{ax}, S_{ax})$ -**II6** through connection with the acetylene linkers. With the use of the resolved synthons, assemblies could be synthesized in an optically pure form without being contaminated by their diastereomers. Upon 2e-oxidation of each *dyrex* unit in **II1-6**, 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.^[1,2]

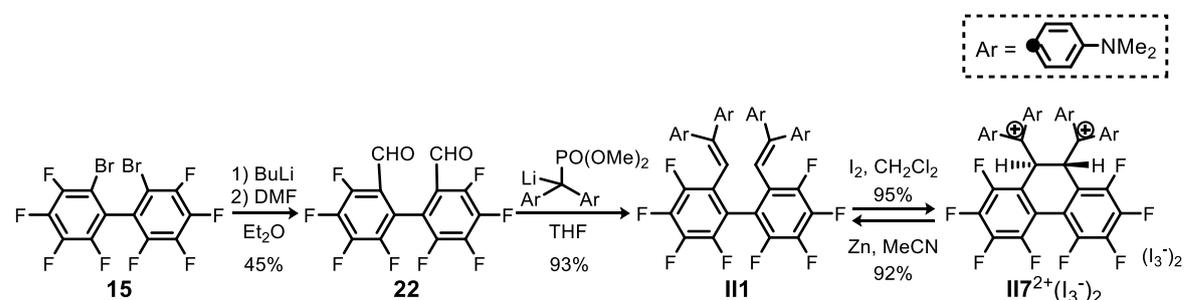
In this chapter, F-arene **II1** was prepared and its properties were studied in terms of the effects by incorporation of F-arene skeleton. In addition, coupling precursor **II2** and assemblies **II3-II6** were successfully produced. Their *dyrex* behavior and spectroscopic properties were also demonstrated.



Scheme 2-2. Target compounds.

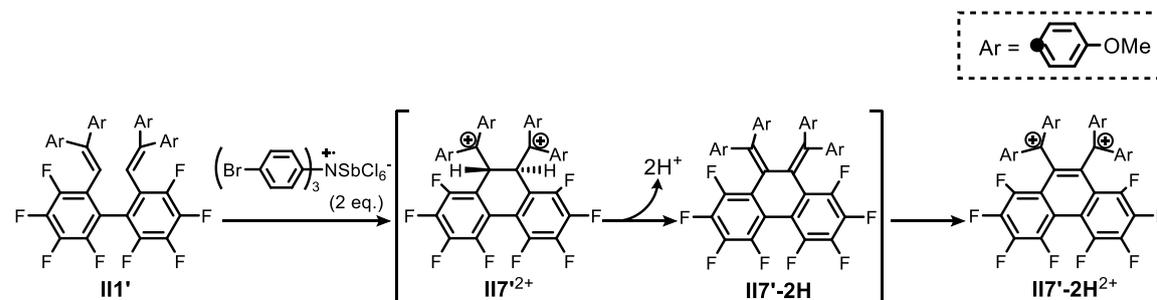
2-2. Preparation

"Exo"-type F-arene based **II1** was prepared in 2 steps as shown in Scheme 2-2 from 2,2'-dibromo-3,3',4,4',5,5',6,6'-octafluorobiphenyl **15**.^[3] Thus, **15** was first converted to the corresponding 2,2'-dialdehyde *rac*-**22** via its dilithio derivative in 49% yield. The Horner-Emmons reaction with the use of (4-Me₂NC₆H₄)₂CHPO(OMe)₂^[4] proceeded smoothly to give *rac*-**II1** in 93% yield, which was then transformed, under oxidative conditions, into stable dication salt **II7**²⁺(I₃)₂ in 95% yield. Upon treatment with Zn powder, this salt gave **II1** in 92% yield, thus confirming that **II1** has an enough electron-donating properties and that **II7**²⁺ is stable enough for isolation despite the F-arene incorporation. Due to configurational stability, *rac*-**II1** was resolved into (*S*_{ax})- and (*R*_{ax})-**II1** by chiral HPLC.



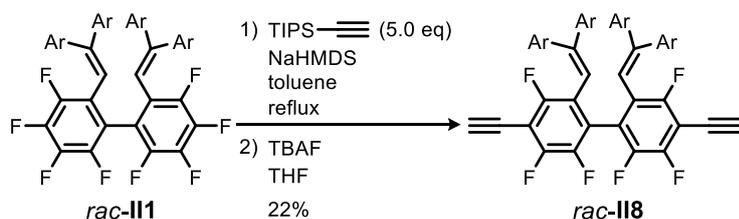
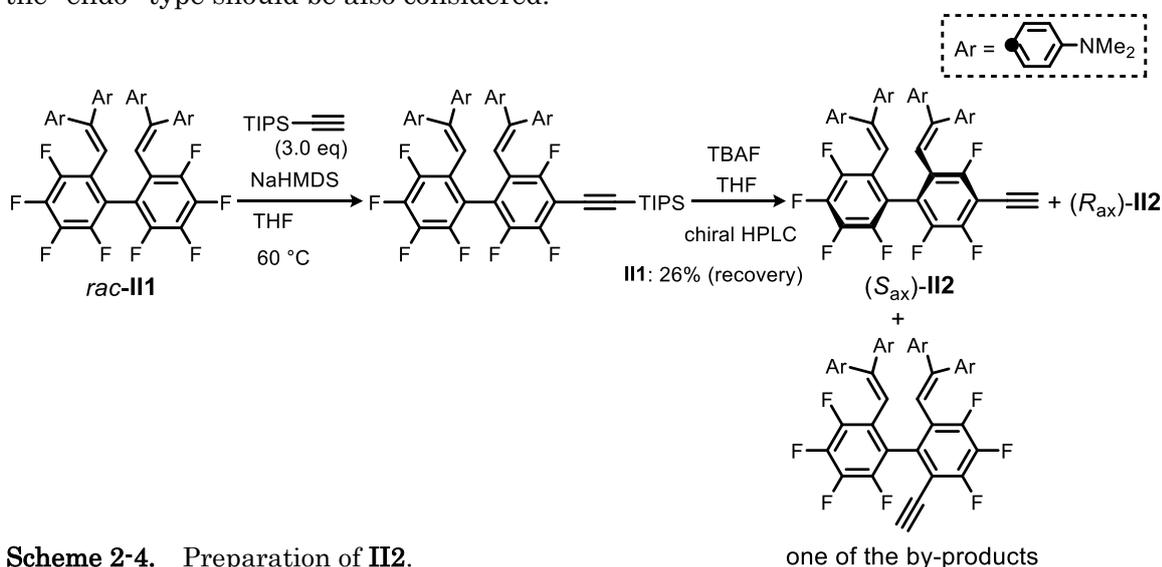
Scheme 2-2. Preparation of F-arene **II1** and dication **II7**²⁺.

In contrast, when *rac*-**II1'** having methoxyphenyl groups instead of dimethylaminophenyl groups was oxidized, dication salt **II7'-2H**²⁺(SbCl₆)₂ was obtained instead of **II7**²⁺ under oxidative conditions (Scheme 2-3). Thus, the 4-Me₂NC₆H₄ group was essential as an aryl group based on a consideration of its high thermodynamic stability^[5] and strong coloration in the visible region^[6] for Michler's Hydrol Blue chromophore [(4-Me₂NC₆H₄)₂CH⁺]



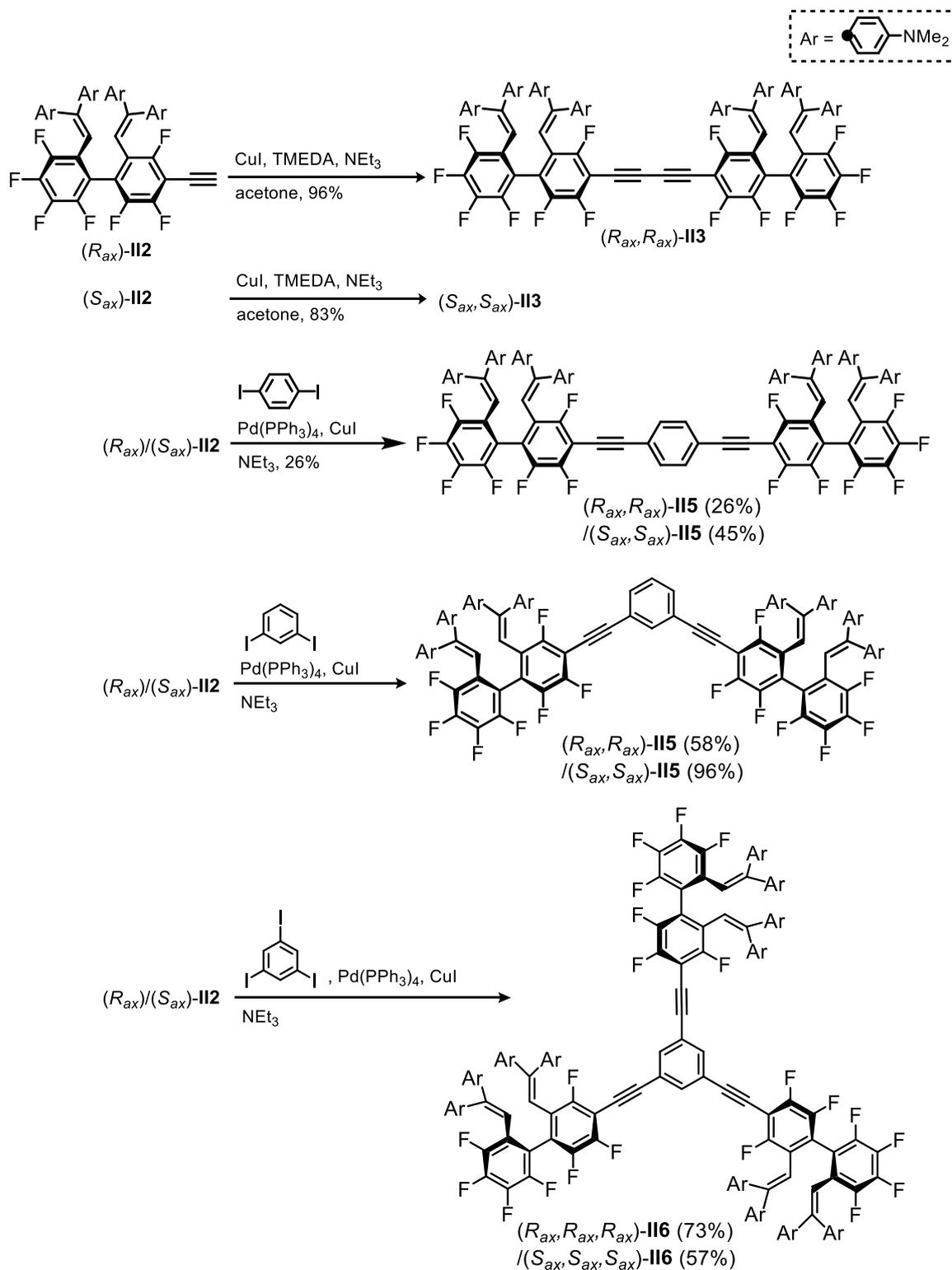
Scheme 2-3. Spontaneous deprotonation to **II7'-2H**²⁺ under the reaction conditions.

By adopting the similar strategy to those in the π -extended “endo”-type molecules **I1b,c**, and **I2**, the S_NAr reaction of **II1** with 3.0 equiv. of ethynyltriisopropylsilane (TIPS-acetylene) in the presence of $NaN-(SiMe_3)_2$ followed by removal of TIPS group by using TBAF gave *rac*-**II2** along with the starting material and other by-products (Scheme 2-4). After separation of the mixture by chiral HPLC, (*R*_{ax})- and (*S*_{ax})-**II2** were isolated in respective yields of 22% and 16% over two steps. Disubstituted derivative **II8** were also produced under the modified conditions (Scheme 2-5). In contrast to the easy double S_NAr reaction of **I1a** to give diethynylated derivatives, mono-substitution was preferred for **II1**. This could be rationalized by considering that the dimethylaminophenyl groups have higher electron-donating properties than the methoxyphenyl groups. The fact that the aryl groups are conjugated better with the biphenyl moiety in the “exo”-type than in the “endo”-type should be also considered.



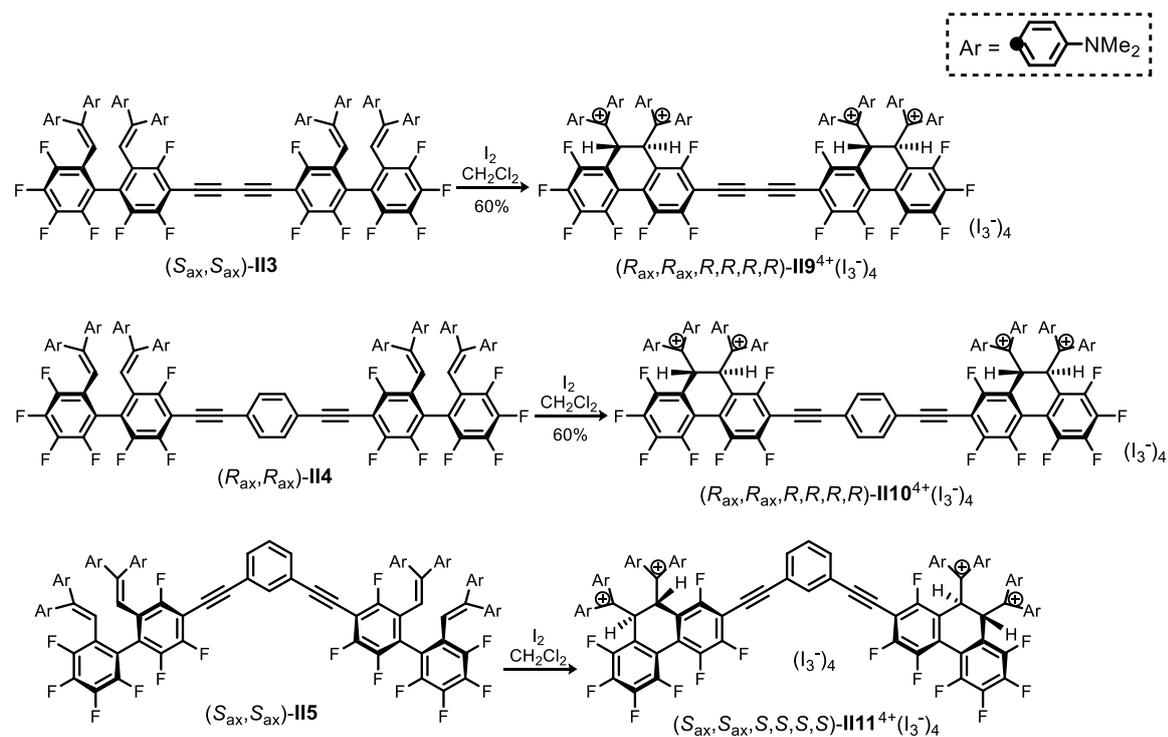
Optically pure assemblies **II3-6** were obtained by a variety of coupling reaction using optically active (*S*_{ax})/(*R*_{ax})-**II2** as in the case of “endo”-type. Amazingly, despite the strong electron-donating properties, the oxidative alkyne coupling of **II2** under Hey conditions (Cu/air) proceeded smoothly. Thus, a dumbbell-shaped *dyrex* dyad (*R*_{ax},*R*_{ax})-**II3** was obtained from (*R*_{ax})-**II2** in 96% yield, whereas (*S*_{ax},*S*_{ax})-**II3** was obtained from (*S*_{ax})-

II2. Under Sonogashira conditions, (R_{ax})- and (S_{ax})-**II2** 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})-**II4** (y. 60%) and **II5** (y. 96%), respectively. A tripod-type triad (R_{ax}, R_{ax}, R_{ax})- or (S_{ax}, S_{ax}, S_{ax})-**II6** was successfully synthesized with the use of 1,3,5-triiodobenzene (y. 73%).



Scheme 2-6. Preparation of assemblies **II3-6**.

Finally, upon preparative-scale oxidation of dyads (R_{ax}, R_{ax})- or (S_{ax}, S_{ax})-**II3,4,5** with iodine, dark green powders were obtained, which can be assigned to the corresponding tetracationic salts **II9,10,11**⁴⁺(I₃⁻)₄, respectively, based on their ¹H NMR spectra (Scheme 2-7). Upon treatment of triad **II6** with iodine, the dark green powder was obtained whose NMR analysis was hampered due to its low solubility in common solvents.



Scheme 2-7. Oxidation of assemblies **II3-5** with iodine into tetracations.

2-3. X-ray Analysis for Crystal Structure of Fluorinated **II1**/**II7**²⁺(BF₄)₂ and **II2**

According to X-ray crystallography (Figure 2-3), F-arene **II1** adopts an unique “in-in” geometry, which is different from those in other biphenyl-2,2'-diyl-type derivatives (Chapter 2-1), although the torsion angle [$\phi(\text{C}_6\text{-C}_1\text{-C}_1\text{-C}_6)$]: 59.8(2)° is almost same as that in the corresponding non-fluoro derivative (57.6°).^[1a] Thus, the two diarylethenyl groups are folded inward. A characteristic geometry of F-arene **II1** is partially caused by a stacking interaction between C₆F₄ and 4-Me₂NC₆H₄. This kind of “in-in” geometry in biphenyl-2,2'-diyl-type derivatives was found for the first time. Similar “in-in” conformation was also found in the 4,4'-diethynyl derivative *rac*-**II8** (Figure 2-4). From its structure, selective substitution at the 4,4'-positions was also confirmed.

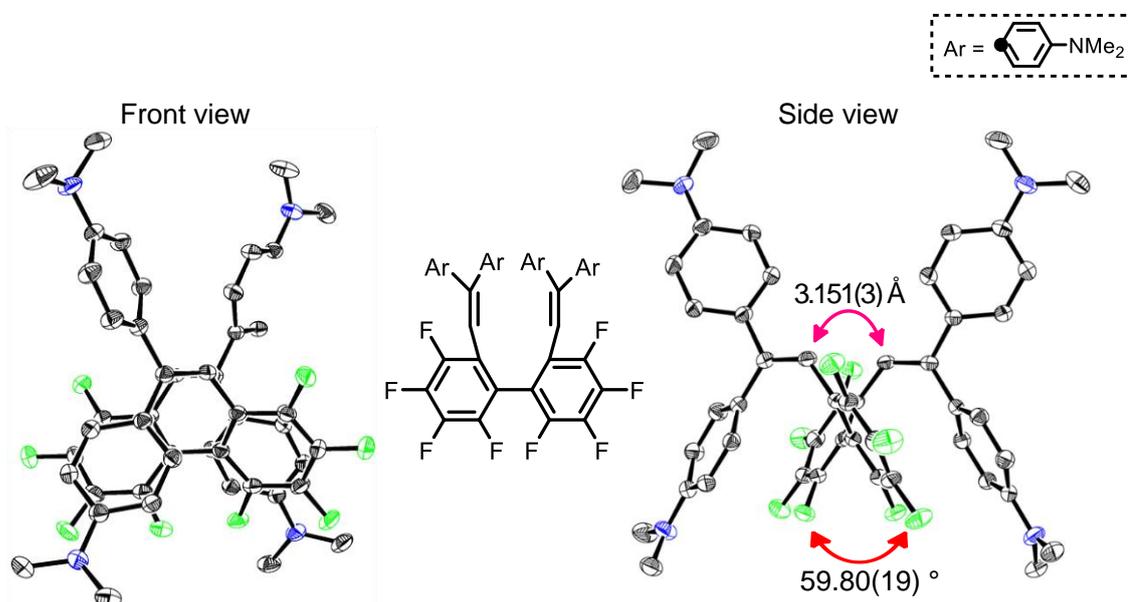


Figure 2-3. Two views of ORTEP drawing of **II1**·CHCl₃ solvate crystal (triclinic, P-1, Z = 2, T = 150 K).

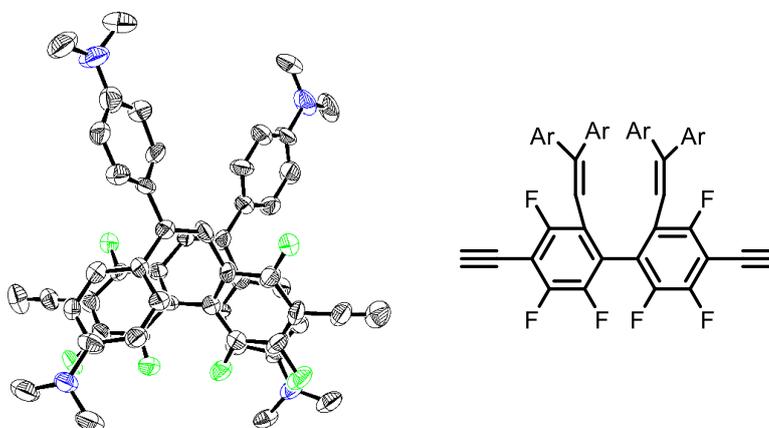
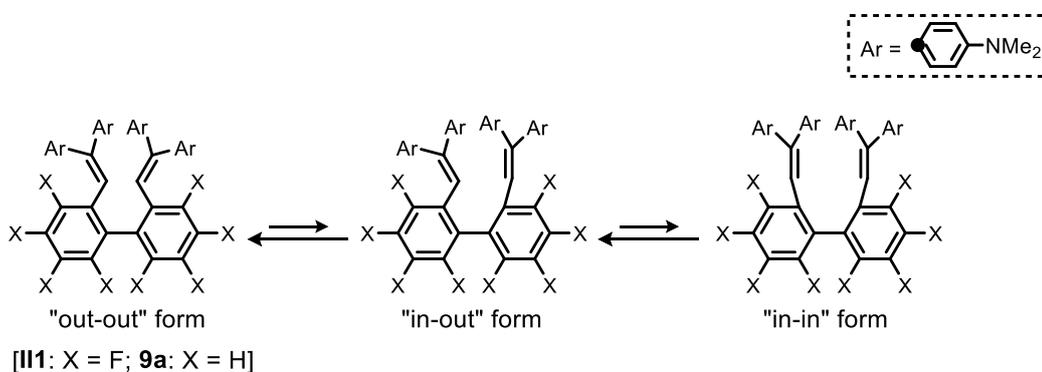


Figure 2-4. A view of ORTEP drawing of **II8**·CHCl₃ solvate crystal (orthorhombic, Pca21, Z = 4, T = 150 K).

2-4. Conformational Search of **II1**

A conformational search for **II1** predicted three energy-minimized structures (MacroModel, OPLS force field), the geometries of which differed at the diarylethenyl groups (Scheme 2-8). The "out-out" conformer is more stable due to reduced steric congestion because the two diarylethenyl groups are extended outward, whereas in the "in-in" conformer ($E_{\text{rel}} = 2.94 \text{ kcal mol}^{-1}$), two ethenyl groups are folded inward to enable the face-to-face arrangement between C_6F_4 and $4\text{-Me}_2\text{NC}_6\text{H}_4$ groups (Figure 2-5). The less spatial geometry as well as the intramolecular π -stacking effects can account for the presence of less stable "in"-conformer in *rac*-**II1**• CHCl_3 crystal (section 2-3). The other conformer adopts the intermediary conformation ("in-out", $E_{\text{rel}} = 2.63 \text{ kcal mol}^{-1}$), whose energy is close to that in the "in-in" conformer.

The similar calculation on non-F derivative **9a**^[1] showed that the "out-out" form is again the most stable conformer (Scheme 2-8). The energy of the corresponding "in-in" form is higher by $8.70 \text{ kcal mol}^{-1}$, and the "in-out" conformer was also found at the energy of $+6.50 \text{ kcal mol}^{-1}$. The conformational study indicates that the "out-out" form is the sole predominant conformer of **9a** at ambient temperature whereas other metastable conformers of **II1** should be present in solution.



Scheme 2-8. Three conformations in **II1** and non-F derivative **9a**.

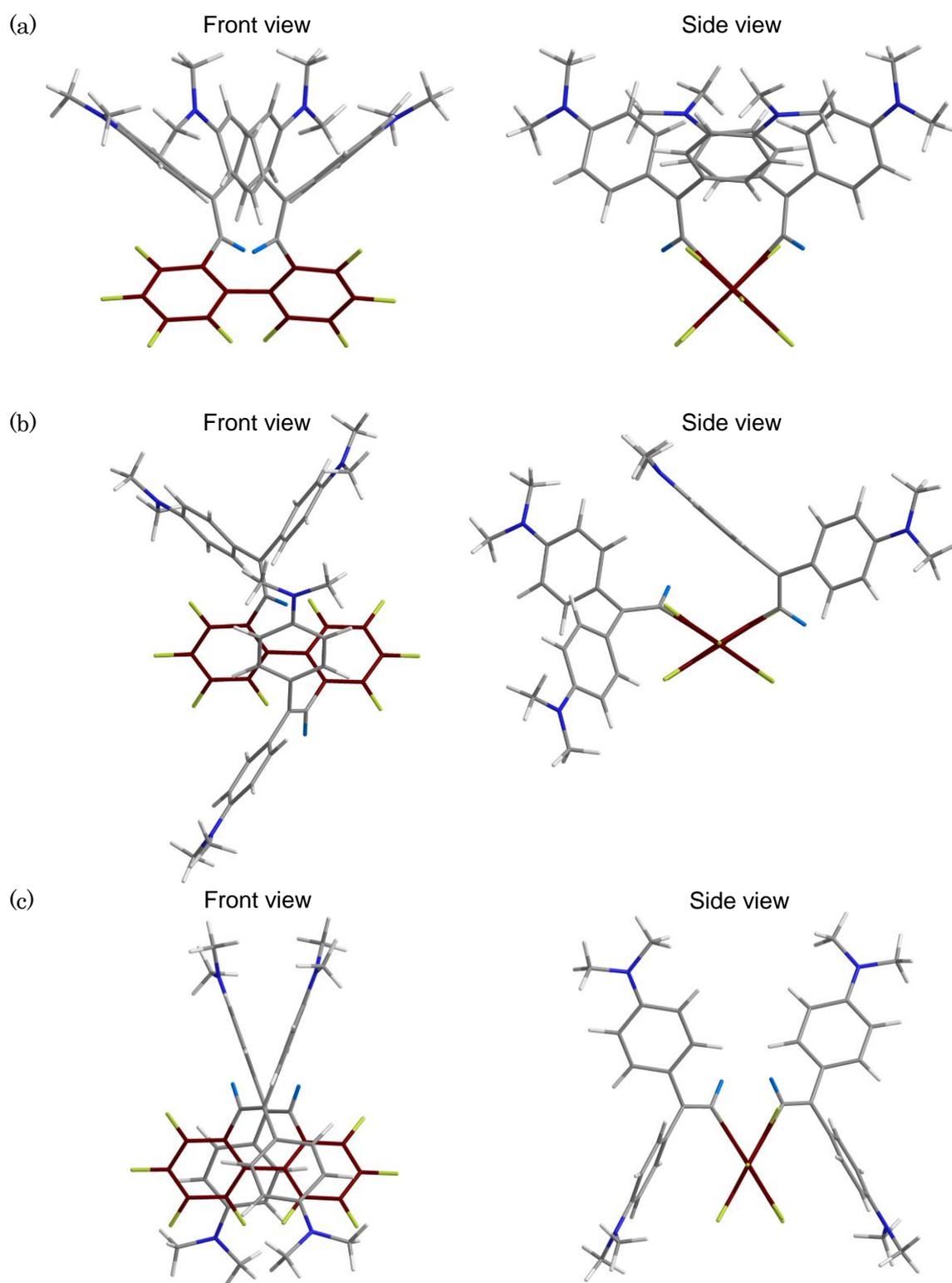


Figure 2-5. Energy-minimized structures for **III**: (a) "out-out" conformer (rel. 0 kcal mol⁻¹), (b) "in-out" conformer (+2.63 kcal mol⁻¹), and (c) "in-in" conformer (+2.94 kcal mol⁻¹) obtained by a conformational search with Macro Model software (v9.9 OPLS_2005, Monte Carlo Multiple Minimum method, non-solvated, 50000 steps).

2-5. Determination of the Energy Barrier for the Conformational Change of **II1** by VT-NMR

The conformers undergo interconversion very rapidly in solution at room temperature, so that the NMR spectrum of **II1** in CD_2Cl_2 shows a set of sharp resonances assignable to a single species with strong time-averaged C_{2h} symmetry with two sets of methyl protons. When the temperature is lowered, two pairs of resonances for two sets of methyl gradually appear at an approximate ratio of 3:1 at 213 K (Figure 2-6). The stronger resonance can be assigned to those of "out-out" (double) and "in-out" whereas the weaker resonance can be assigned to those of "in-out" and "in-in" conformers (Scheme 2-8). By considering the similarity in the relative energy for "in-out" and "in-in" conformers, the ratio would be close to 4:1:1 for "out-out":"in-out":"in-in" conformers. From the coalescence temperature of one of the *N*-methyl resonances ($T_c = 213$ K, $\Delta\nu = 8.0$ Hz), the energy barrier for the conformational change between "out-out" and "in-out" was determined to be 11.1 kcal mol⁻¹. Assignment of protons were deduced based on the NOE measurement between methine and aromatic protons meta to the amino group.

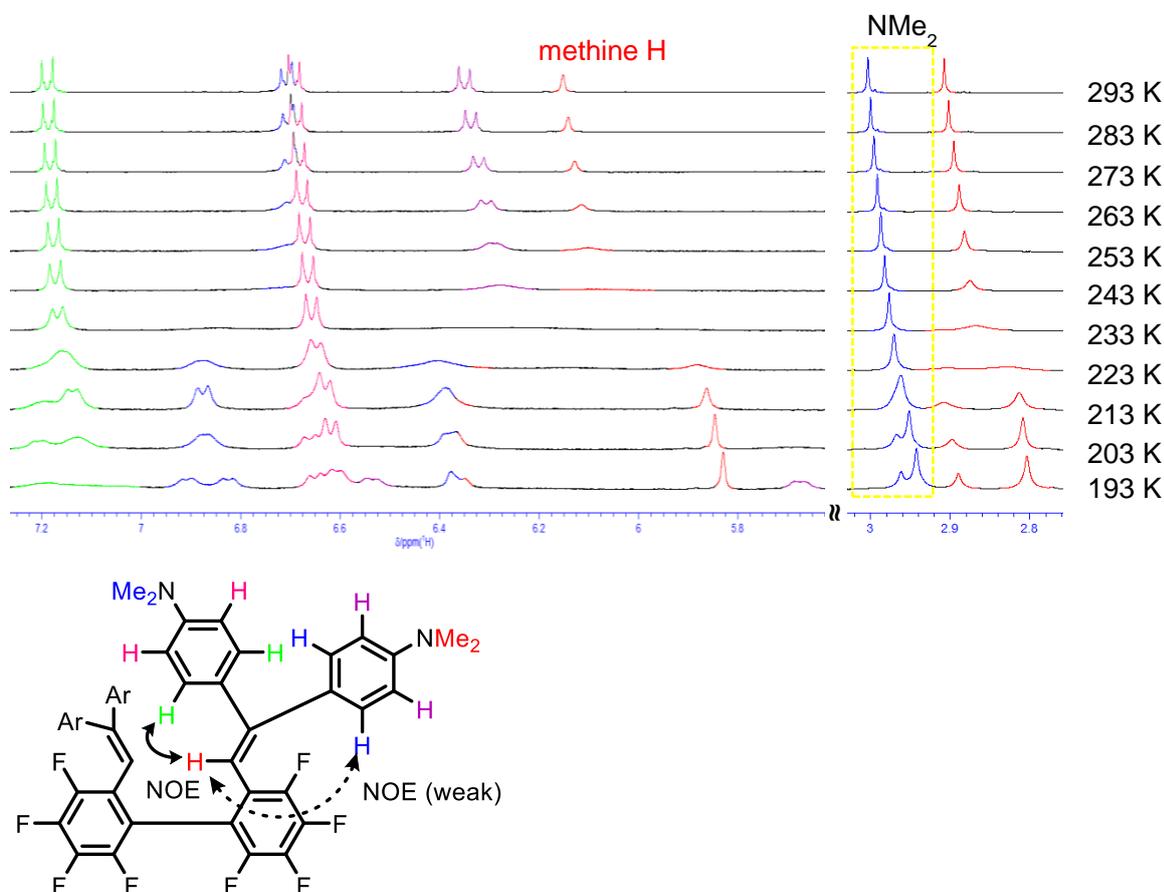


Figure 2-6. VT-NMR analysis of the conformational change of **II1** in CD_2Cl_2 . The color of proton in the formula is used to indicate the corresponding resonances in the spectrum.

2-6. Optical Resolutions of **II1** and **II2** by Chiral HPLC

Configurational stability in terms of axial chirality in **II1** is stable to allow its optical resolution by using chiral HPLC (CHIRALPAK-IA, hexane/CH₂Cl₂ = 5/1, Figure 2-7a). The configuration of the 1st fraction was deduced to be (*S*_{ax}) by comparing its CD spectrum with that of (*S*_{ax})-2,2'-bis[2,2-bis(4-dimethylaminophenyl) ethynyl]binaphthyl [(*S*_{ax})-**12b**]^[1] prepared from (*S*_{ax})-2,2'-dimethylbinaphthyl (Figure 2-8b). Thus, both of the 1st fraction of **II1** [λ_{ext} 383 nm ($\Delta\epsilon$ +20), 338 (-27)] and (*S*_{ax})-**12b** exhibit a large positive couplet around 380 nm (Figure 2-8), which originates from the exciton coupling of two diarylethenyl chromophores in their “out-out” conformers.

Diethynyl derivative (*S*_{ax})/(*R*_{ax})-**II2** was also resolved by using chiral HPLC (CHIRALPAK-IA, hexane/CH₂Cl₂ = 5/1, Figure 2-8b). The configuration of the 1st fraction was again deduced to be (*S*_{ax}) by comparing its CD spectrum [λ_{ext} 390 nm ($\Delta\epsilon$ +18), 340 (-29)] with that of (*S*_{ax})-**II1** (Figure 2-8a).

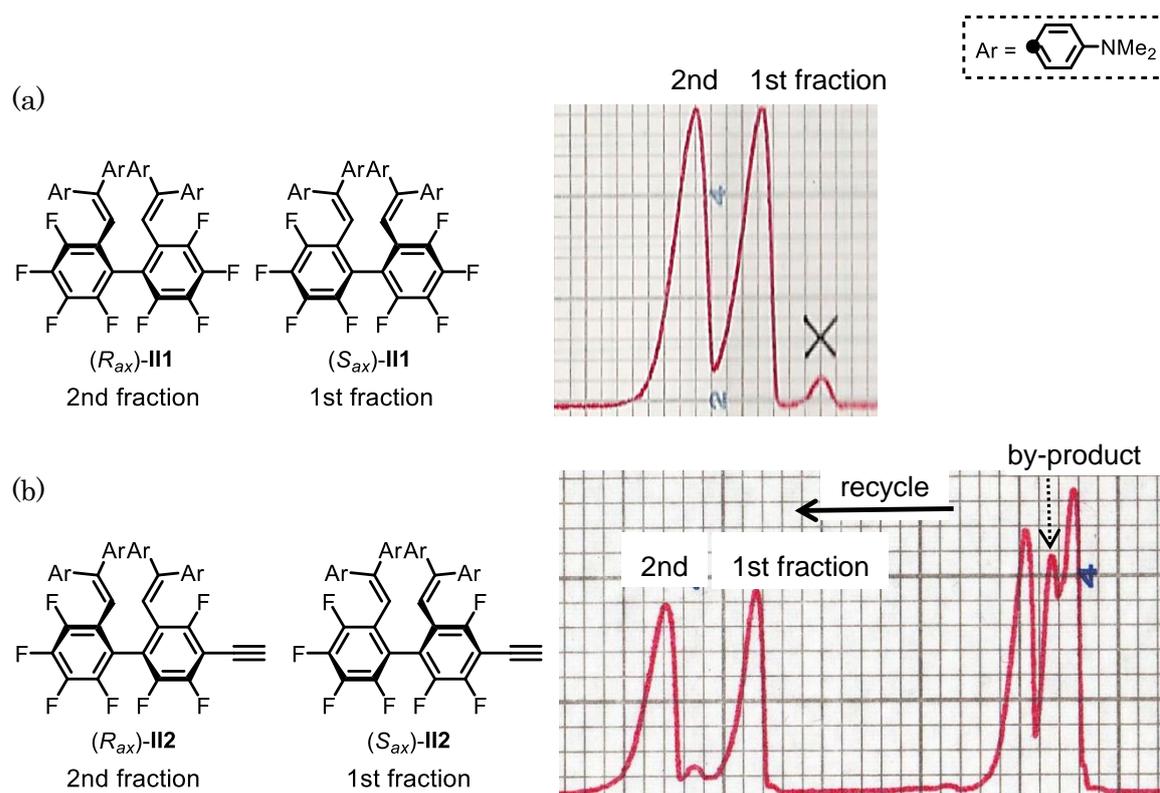


Figure 2-7. Chromatograms of (a) *rac*-**III1** and (b) *rac*-**II2** [Chiralpak IA, solv. Hexane / CH₂Cl₂ = 5/1].

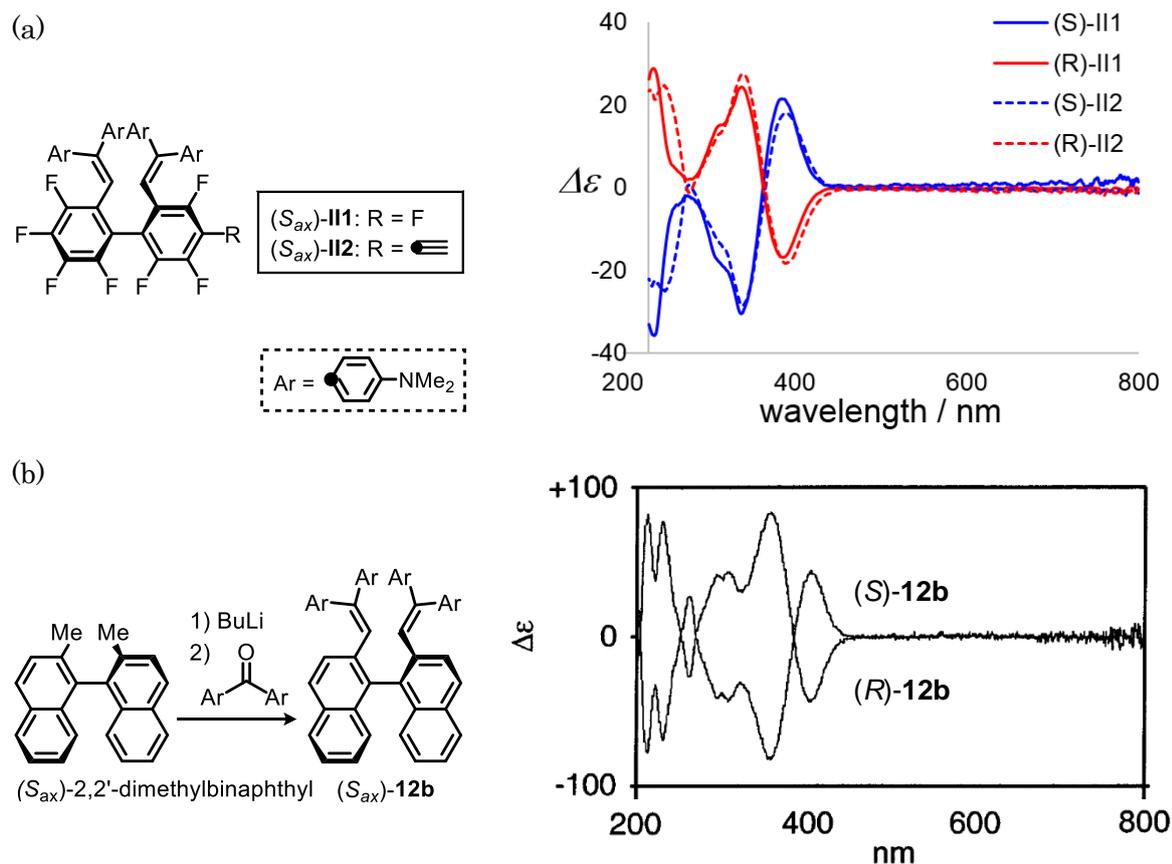


Figure 2-8. CD spectra of (a) $(S_{ax})/(R_{ax})$ -**II1** and **II2** and (b) $(S_{ax})/(R_{ax})$ -**12b** in MeCN.

No racemization occurs under the experimental conditions, as conformed by negligible change in the CD spectra of optically pure **5a** after heating at 343 K for 5 h or iodine-oxidation to the dicationic salt followed by Zn-reduction of the as-prepared dication salt (Figure 2-9).

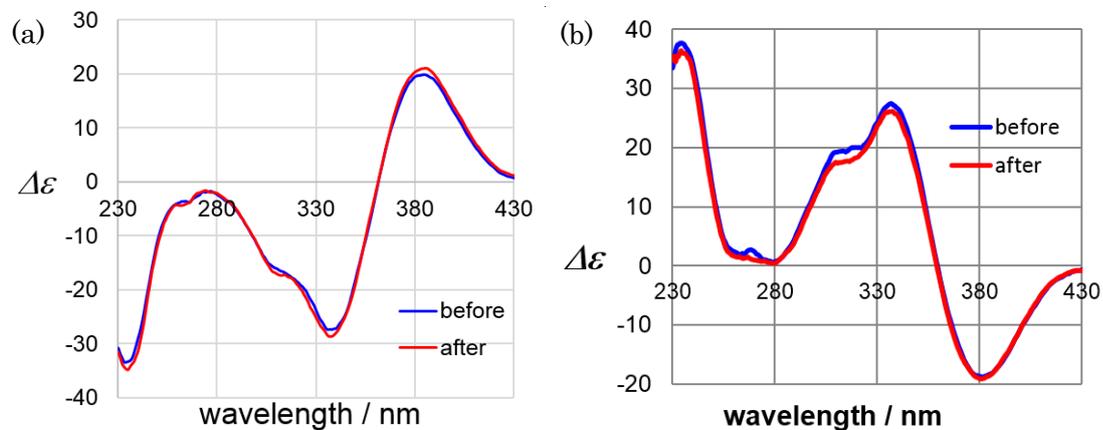


Figure 2-9. (a) CD spectra of (S_{ax}) -**II1** before (blue) and after (red) heating at 343 K for 5 h. (b) CD spectra of (R_{ax}) -**II1** before (blue) and after (red) iodine-oxidation followed by Zn-reduction.

2-7. Chiroptical Change by Heat and Solvent-polarity

The CD spectrum of (S_{ax})-**III1** exhibits reversible temperature-dependence (273 K - 344 K in MeCN) (Figure 2-10c), and the greater ellipticity with the red-shifted λ_{ext} was observed at the lower temperature (Scheme 2-7). At this moment, the precise rational is still unclear but increased population of the most stable "out-out" conformer at lower temperature could be a reason for chiroptical change by heat. Another explanation might be the reduced torsion angle in the "out-out" conformer at the lower temperature.

Solvent dependency of the UV-Vis and CD spectra was also observed, which can be rationalized by the preferred π -stacking arrangement between C_6F_4 and 4-Me₂NC₆H₄ groups in less polar solvents to increase the population of the "in-in" conformer in cyclohexane and methylcyclohexane (Figure 2-10a,b). In the case of VT-CD of (S_{ax})-**III1** in cyclohexane, the negative couplet was greater without wavelength shift at the lower temperature (Figure 2-10d). Despite the undetermined mechanism of the chiroptical changes, F-arene based chiral donor **III1** is interesting as the less well-explored multi-input-multi-output response system.

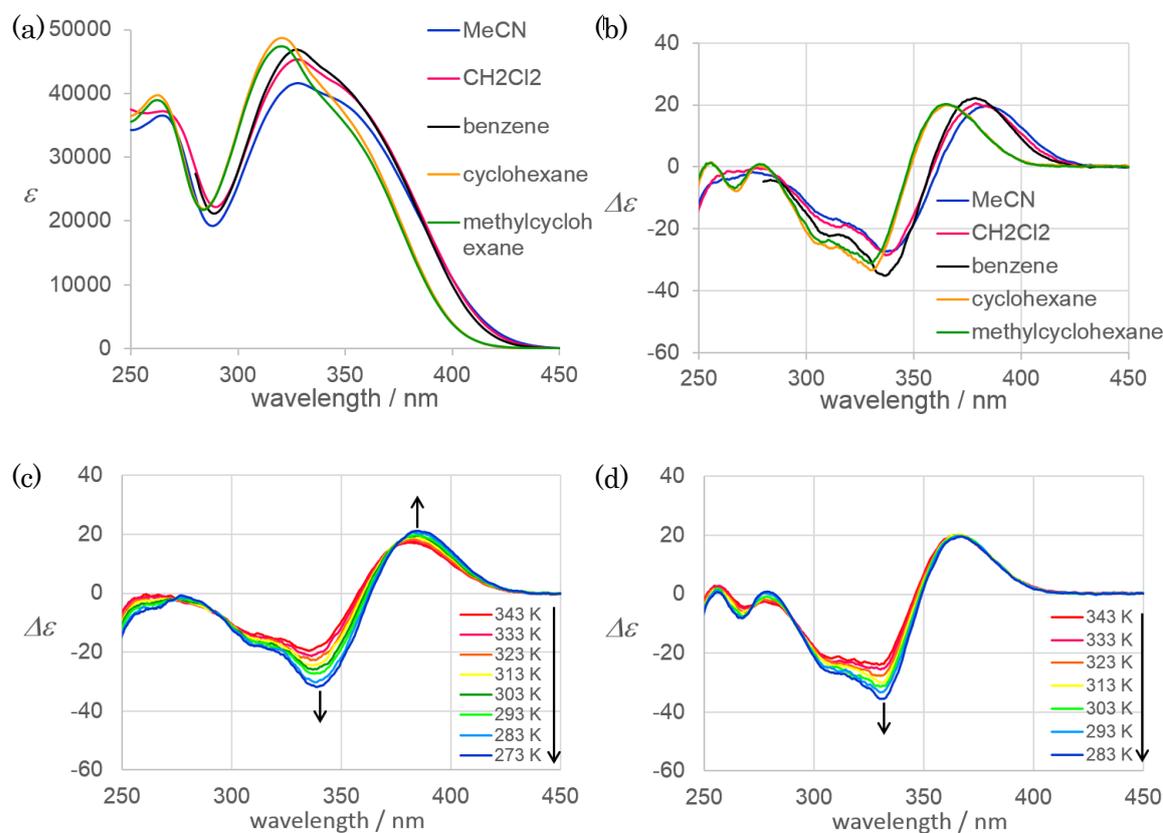


Figure 2-10. Solvent dependency of (a) UV-Vis and (b) CD spectra of (S_{ax})-**III1**. CD spectral changes of (S_{ax})-**III1** at 273-343 K in (c) MeCN and (d) cyclohexane.

2-8. DFT Calculations of **II1**

The DFT calculations (B3LYP/6-31G*) were conducted for the two symmetric conformers to figure out if the electron-donating properties differ among the conformers (Figure 2-11). It was shown that the HOMO and HOMO-1 energy level are nearly the same for the "out-out" and "in-in" forms. Thus, the redox properties of **II1** in solution reflect those of the more stable "out-out" conformer ($\Delta E = 1.91$ kcal mol⁻¹), which is dominantly present in solution.

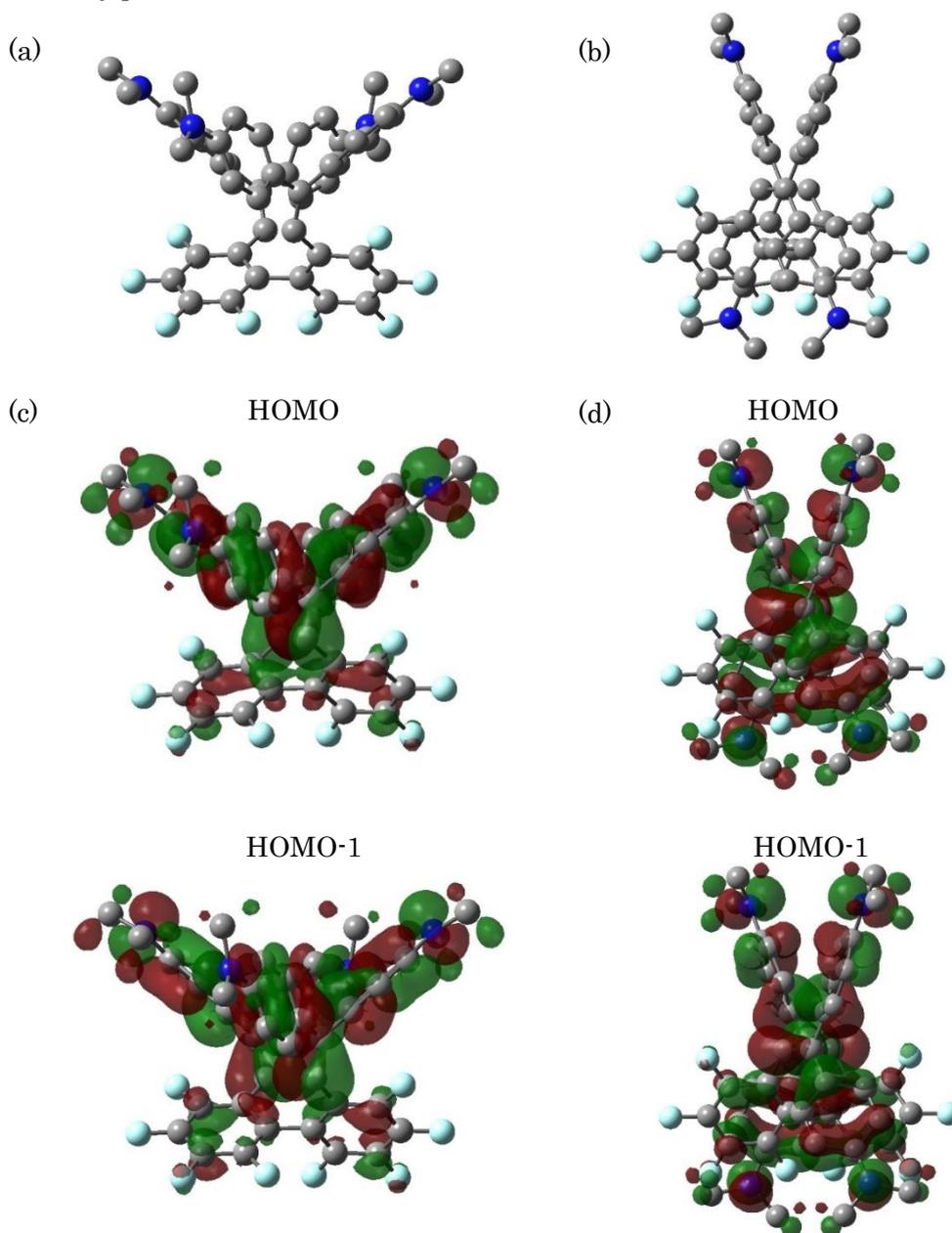


Figure 2-11. Optimized structures of (a) "out-out" form of **II1** (rel. 0 kcal mol⁻¹) and (b) "in-in" form of **II1** (+1.91 kcal mol⁻¹) determined by DFT calculations. HOMOs and HOMO-1s of (c) "out-out" form of **II1** (-4.77 eV, -4.79 eV) and (d) "in-in" form of **II1** (-4.70 eV, -4.81 eV) determined by DFT calculations.

As mentioned in section 2-2, upon treatment of *rac*-**II1** with iodine, the dication salt **II7**²⁺(I₃⁻)₂ was obtained. A sharp singlet at 5.41 ppm for the methine protons in the NMR spectrum (CD₃CN₃) of **II7**²⁺(I₃⁻)₂ is consistent with the formation of a new C_{sp3}-C_{sp3} bond. In addition to axial chirality, dication **II7**²⁺ has two asymmetric centers. Their configurations are *R,R* (or *S,S*) when the axial chirality is *R*_{ax} (or *S*_{ax}) by X-ray structure (Figure 2-12), demonstrating that oxidative ring-closure selectively occurs from the major “out-out” conformer of (*R*_{ax})- and (*S*_{ax})-**II1** with the perfect transmission of axial chirality to give dications with (*R*_{ax},*R,R*) and (*S*_{ax},*S,S*) configurations, respectively.

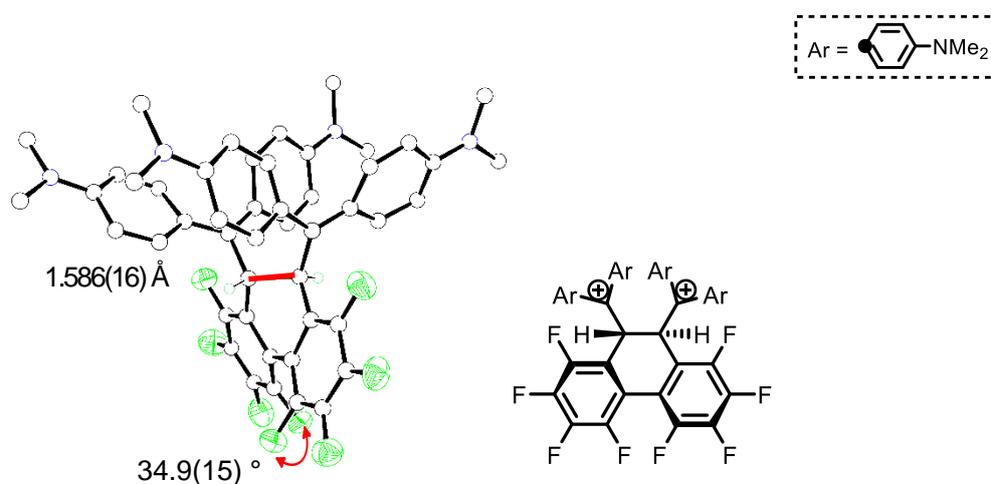


Figure 2-12. A view of ORTEP drawing of **II7**²⁺(BF₄⁻)₂·CH₂Cl₂ solvate crystal (monoclinic, P1 21/c 1, *Z* = 4, *T* = 150 K).

2-9. Redox Properties of **II1**

According to the voltammetric analysis (Figure 2-13), F-arene-based donor **II1** exhibits strong electron-donating properties ($E^{bx} = +0.55$ V vs SCE in MeCN). The oxidation process is irreversible in the sense that the return peak being appeared in the far cathodic region, which corresponds to the reduction process of dication **II7**²⁺ ($E^{red} = -0.47$ V) with a newly formed C-C bond between two methine carbons. Such a large separation of redox peaks as well as nearly simultaneous 2e-transfer are characteristic of *dyrex* systems, and were also found in the analogous redox pair of **9a/10a**²⁺ ($E^{bx} +0.41$ V, $E^{red} -0.41$ V)^[1] without F atoms. Besides, fluorinated donor **II1** is easier oxidized than non-F donor **9a**, since the electron-withdrawing nature of F lowers the HOMO, as shown by the more positive E^{bx} of **II1** by 0.14 V than that of **9a**. In the voltammogram of **II1** measured in CH₂Cl₂ ($E^{bx} = +0.86$ V, $E^{red} = -0.09$ V), a large separation of redox peaks was again observed as that in MeCN (Figure 2-13).

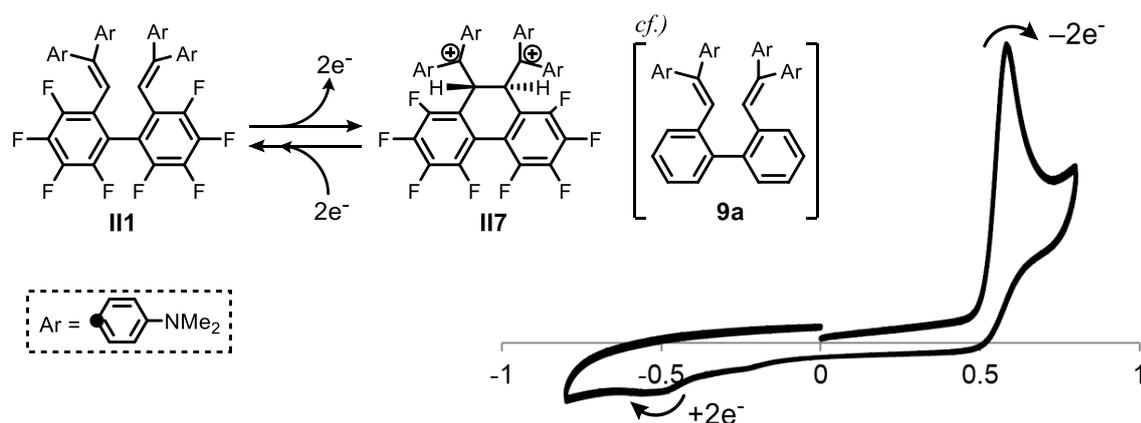


Figure 2-13. Cyclic voltammogram of **II1** measured in MeCN (0.1 M Et₄NClO₄, Pt electrode, scan rate 500 mV/s).

2-10. Electrochiroptical Properties of **II1**

Very clean changes in UV-Vis and CD spectra were observed upon the electrochemical oxidation of (S_{ax}) -**II1** to (S_{ax},S,S) -**II7**²⁺ in MeCN (Figure 2-14). 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, which is favored in constructing reversible electrochromic systems. In this way, the optically pure *dyrex* pair of **II1**/**II7**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 **II1**. In contrast, an exciton coupling in long-wavelength region for the cation moieties was not observed. Similar behavior was observed in the structurally related binaphthyl donor **12b**/**13b**²⁺[1] having 4-Me₂NC₆H₄ because transition moments of pigment framework were almost parallel.

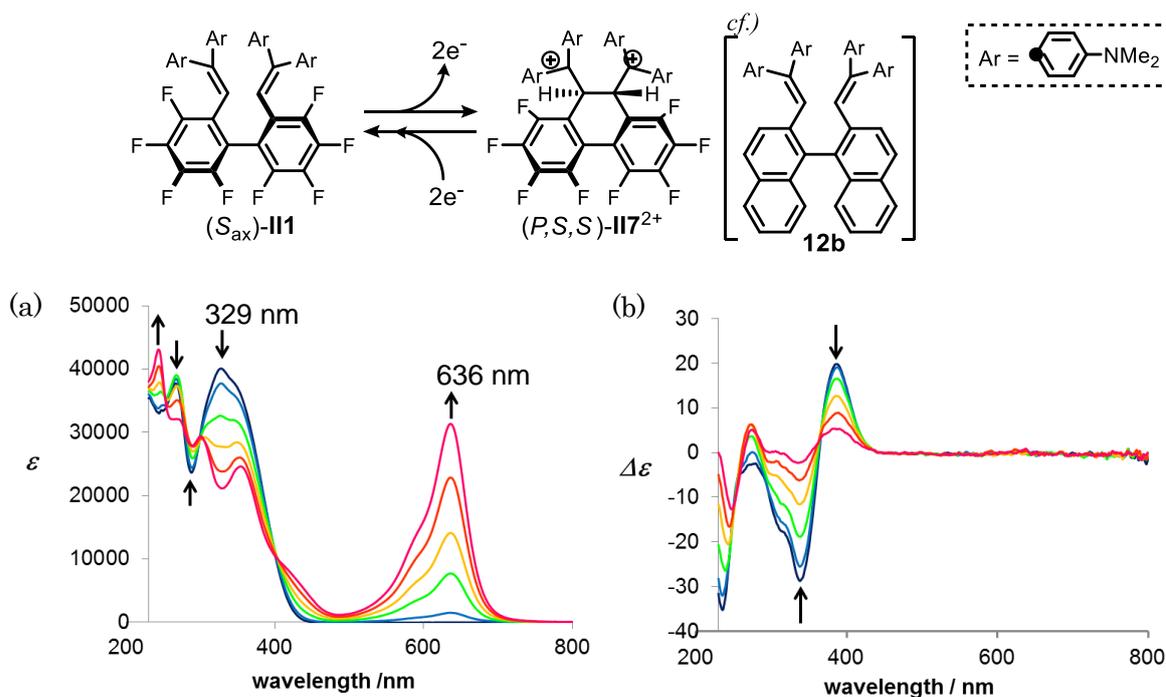


Figure 2-14. (a) UV-Vis and (b) CD spectral changes upon electrochemical oxidation (10 μ A) of (S_{ax}) -**II1** (20 μ M) every 5 min in MeCN containing 0.05 M Et₄NClO₄.

2-11. Absence of Steric and Electrostatic Repulsion in Dyad and Triad

In the NMR spectra of **II3,4,5** and **II6** (CDCl_3), the resonances of the F-arene-based dyrex units have nearly the same chemical shifts as those of ethynyl derivative **II2**, 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 (**III12**⁶⁺), three of the dicationic moieties are placed in a *C*₃-symmetric fashion with adequate separation among them (Figure 2-15). Thus, electrostatic interaction would also be minimized even in hexacation **3**⁶⁺, and this could also hold true for the dumbbell-shaped tetracations **II9,10,11**⁴⁺. Based on the above consideration, the present large assemblies **II3,4,5** and **II6** could serve as the pseudo two-state (neutral - polycation) switching systems, as in the monomeric F-arene system **III1**, with a higher sensitivity due to the multiple chromophores.

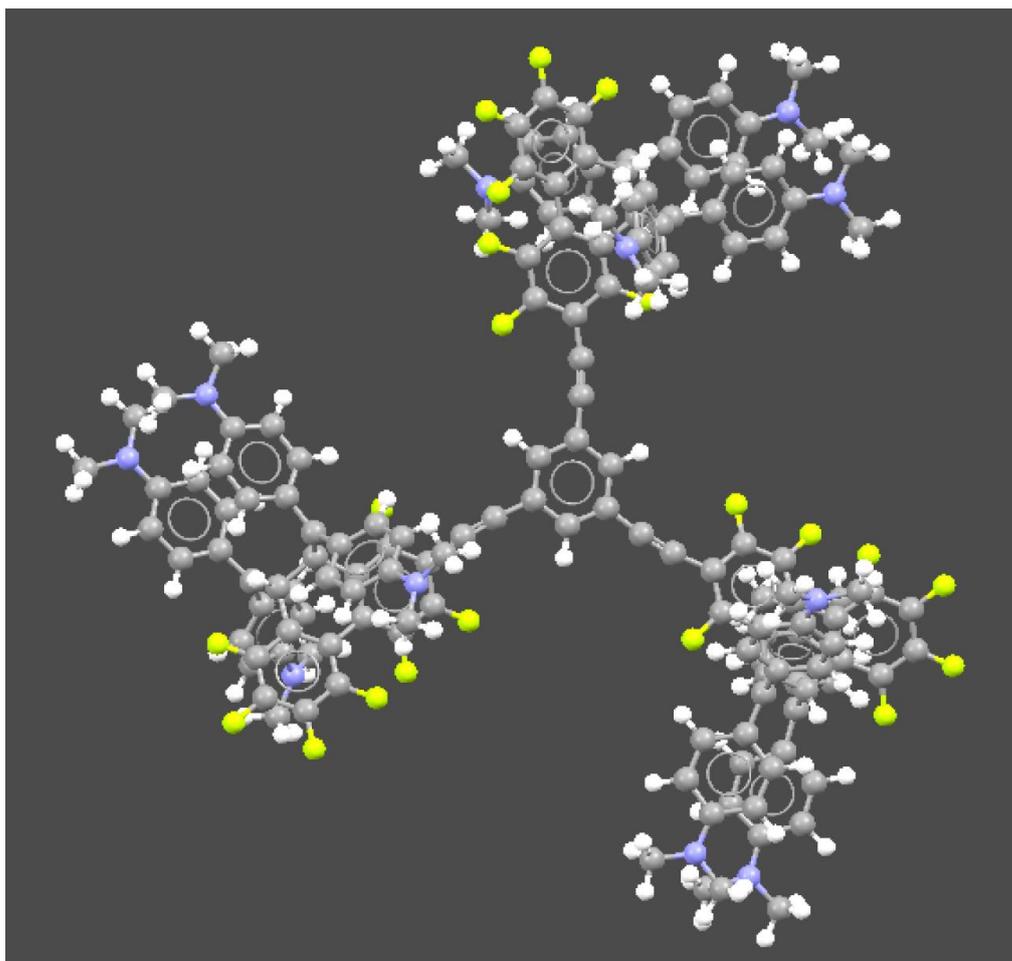


Figure 2-15. Energy-minimized structure for hexacation **III12**⁶⁺ obtained by a conformational search with MacroModel software (v9.9 OPLS_2005, Monte Carlo Multiple Minimum method, non-solvated).

2-12. Redox Properties of Assemblies II3-II6

The cyclic voltammograms (CH₂Cl₂) of dyads **II3,4,5** and triad **II6** show a pair of redox waves at potentials [E^{ox} (**II3,4,5,6**) = +0.88 - +0.93 V and E^{red} (**II9,10,11** 4+, **II12** 6+) = -0.12 - -0.17 V vs SCE in CH₂Cl₂] similar to those of **II1** (E^{ox} = +0.86 V, E^{red} = -0.09 V, Figure 2-16). No other peaks current assignable to the redox process of the species were observed. Further voltammetric experiment was performed to gain the information for concentration dependence of peak current in **II1-6** in CH₂Cl₂ (Figure 2-17). Linear correlation between the anodic peak current and the concentration of the substrate was conformed, and the slope is the function of the number of transferred electron and the diffusion constant (Figure 2-18) since the voltammograms were obtained by using the same electrode with the same sweep rate. The relative values of the slope are 2 (standard), 2.00, 3.12, 3.00, 2.66 and 4.22 for **II1-6**, respectively. The peak currents in the voltammograms of **II3,4,5** are much larger than that seen for **II1**. An even larger current was observed in **II6**, suggesting that **II3,4,5** and **II6** undergo one-wave four- and six-electron transfer, respectively, at the peak potentials.

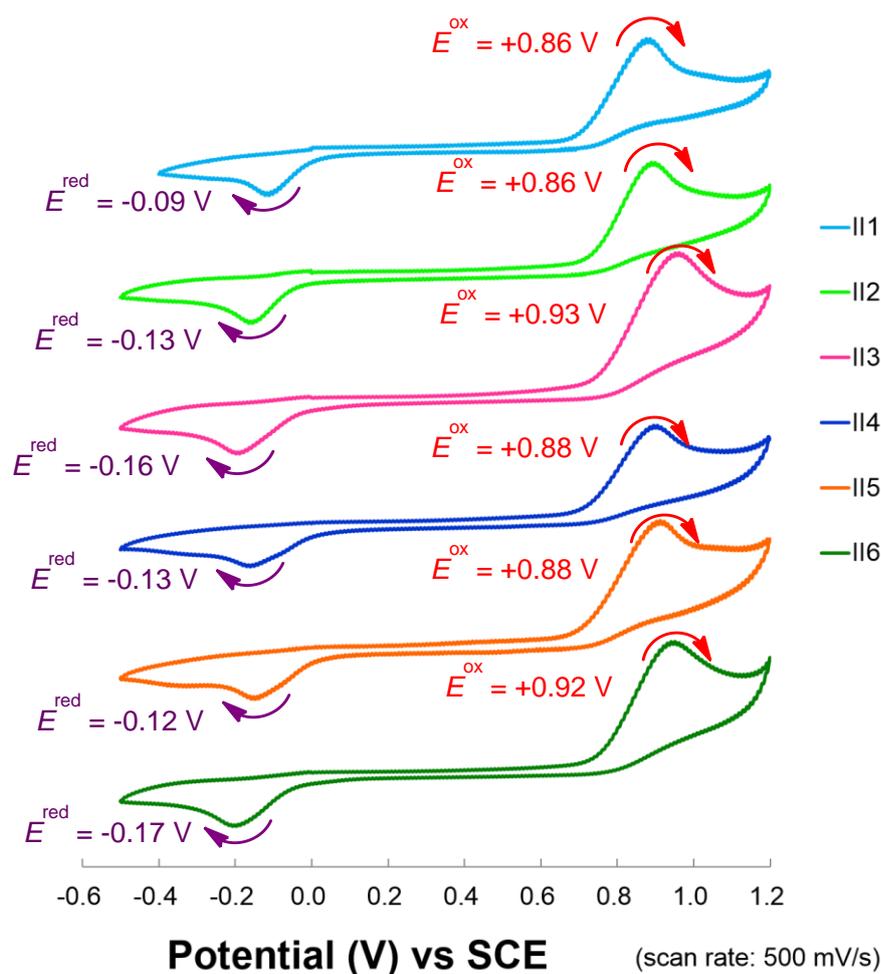


Figure 2-16. Cyclic voltammograms of **II1-6** in CH₂Cl₂ (0.1 M Bu₄NBF₄, Pt electrode, scan rate 500 mV/s).

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 **II3,4,5** and **II6** than the doubled or tripled value of **II1** can be accounted for, at least in part, by the smaller D for **II3,4,5** and **II6** due to the larger molecular-size. In fact, the smaller D values of **II3** ($6 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ in CD_2Cl_2 at 298 K) and **II5** ($6 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) were determined compared to that of **II1** ($8 \times 10^{-10} \text{ m}^2\text{s}^{-1}$).

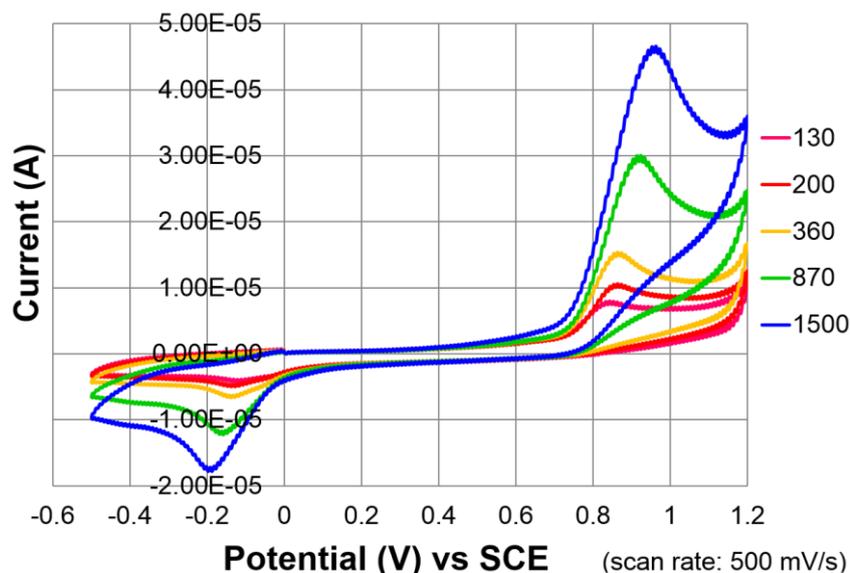


Figure 2-17. Cyclic voltammograms of **II3** (130, 200, 360, 870, 1500 μM , respectively) in CH_2Cl_2 (0.1 M Bu_4NBF_4 , Pt electrode, scan rate 500 mV/s).

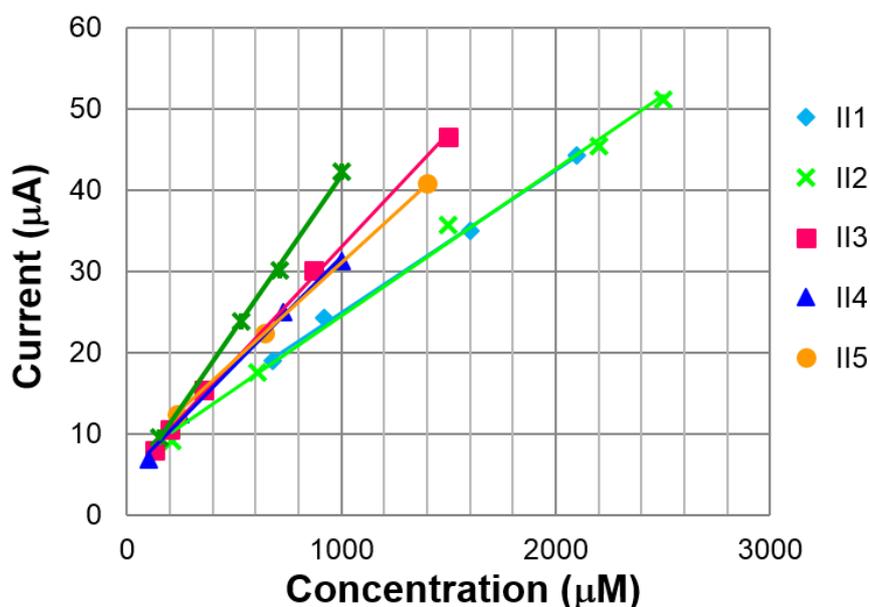
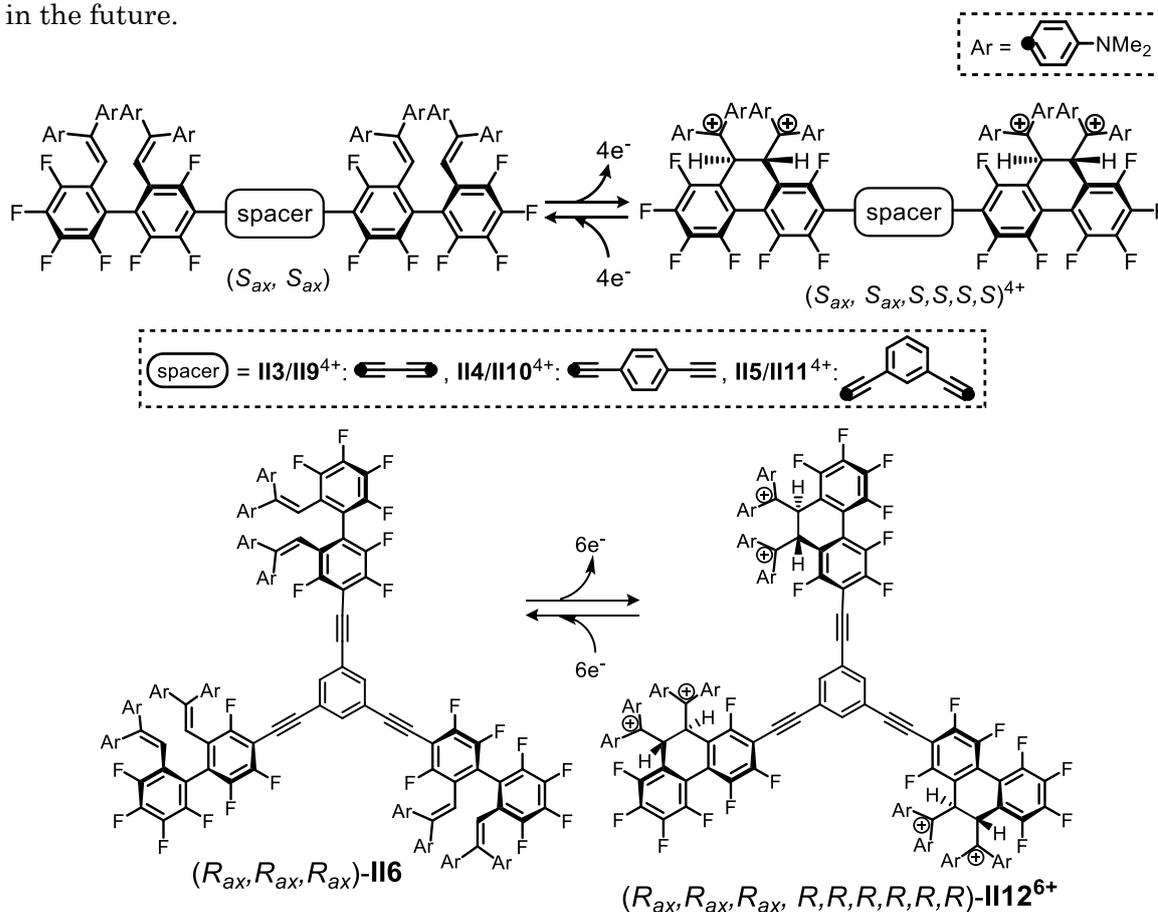


Figure 2-18. Linear correlation between the anodic peak current and the concentration of the substrate in the voltammograms of **II1-6** in CH_2Cl_2 (0.1 M Bu_4NBF_4 , Pt electrode, scan rate 500 mV/s).

2-13. Electrochiroptical Properties of Assemblies II3-II6

When constant-current electrolysis was conducted on the optically pure dyads $(R_{ax}, R_{ax})/(S_{ax}, S_{ax})$ -II3,4,5 and triad $(R_{ax}, R_{ax}, R_{ax})/(S_{ax}, S_{ax}, S_{ax})$ -II6, very clean changes in UV-Vis and CD spectra were again observed (Figure 2-19) as in the case of coupling precursor $(R_{ax})/(S_{ax})$ -II2 (Figure 2-20). 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 (Scheme 2-9). All of the large assemblies of II3-6 exhibit the larger amplitude of the CD couplet ($A = 58, 56, 62,$ and 103 for II3-6, respectively, in MeCN at 293 K) than II1,2, thus they can serve as more sensitive electrochiroptical systems.

At the final stage of electrochemical oxidation of II3-6, the absorption in long-wavelength region assignable to the cation moieties was larger than those in monomeric donors II1,2: the relative intensities are 2 (standard), 2.06, 3.32, 3.01, 2.09 and 3.15 for II1-6, respectively. In the case of II5 and II6 with a *m*-phenylene unit, current efficiencies to generate II11⁴⁺ or II12⁶⁺ from II5 or II6 were smaller, which needs further examination in the future.



Scheme 2-9. Transformation into polycations of assemblies II3-6 upon electrochemical oxidation.

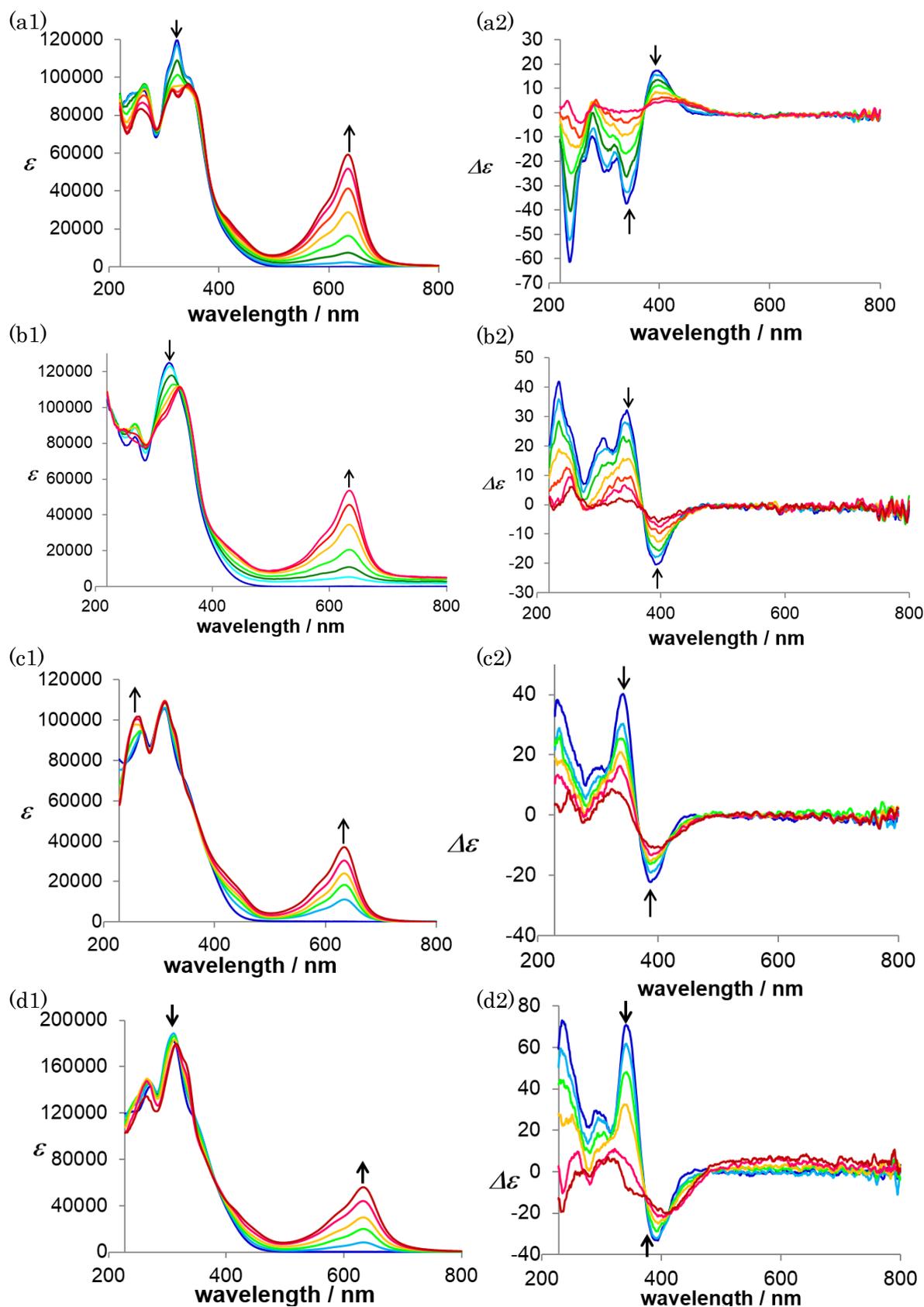


Figure 2-19. (1) UV-Vis and (2) CD spectral changes upon electrochemical oxidation ($10 \mu\text{A}$) of (a) $(S_{ax}, S_{ax})\text{-II3}$ ($13 \mu\text{M}$, every 5 min), (b) $(R_{ax}, R_{ax})\text{-II4}$ ($7.7 \mu\text{M}$, every 4 min), (c) $(R_{ax}, R_{ax})\text{-II5}$ ($11 \mu\text{M}$, every 16 min), (d) $(R_{ax}, R_{ax}, R_{ax})\text{-II6}$ ($6.8 \mu\text{M}$, every 15 min) in MeCN containing $0.05 \text{ M Et}_4\text{NClO}_4$.

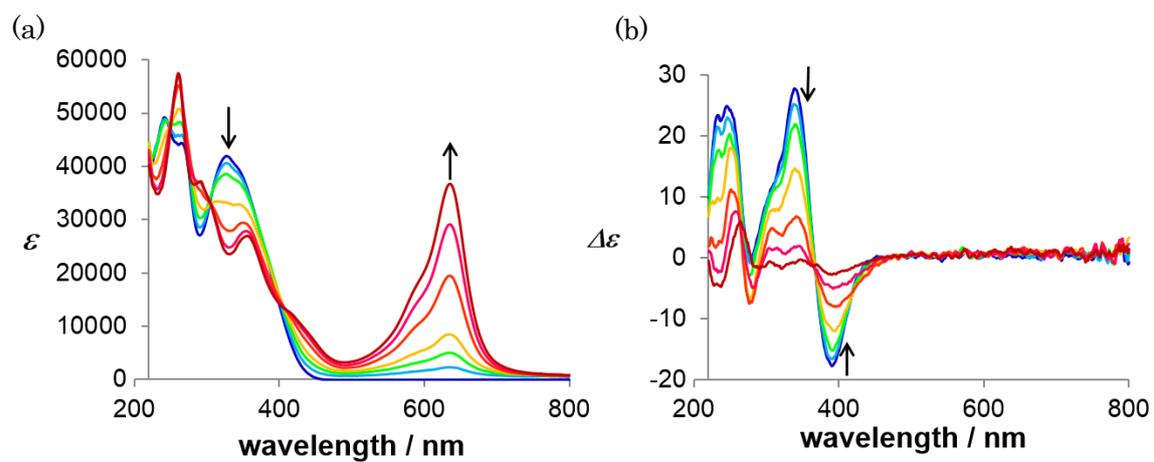


Figure 2-20. (1) UV-Vis and (2) CD spectral changes upon electrochemical oxidation ($10 \mu\text{A}$) of $(R_{\text{ax}})\text{-II2}$ ($16 \mu\text{M}$) every 5 min in MeCN containing 0.05 M Et_4NClO_4 .

2-14. Conclusion

The present work demonstrates that, despite the incorporation of F-arene skeleton, diarylethynyl donors exhibit enough electron-donating properties and the corresponding dications still have enough stability for isolation. The F atoms at 6,6'-positions in the biphenyl skeleton allowed optical resolution, thus the present *dyrex* pair exhibited electrochiroptical response, which cannot be attained in the corresponding non-fluoro analogue. Attachment of F atoms also enables facile S_NAr reaction with acetylide to prepare ethynylated analogue that works nicely as a key synthon to produce larger molecular assemblies containing two or three *dyrex* units through a variety of transition-metal catalyzed coupling reactions. By using optically pure synthon, chiral assemblies were obtained in an optically pure form. This is the first demonstration for the production of compounds containing multiple units of optically pure *dyrex* skeleton.

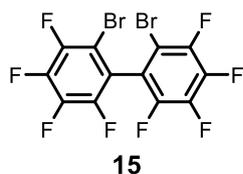
In addition to their advanced electrochromic behavior shown above, these *dyrex* systems are interesting in terms of molecular electronics, since the electrochemical bistability of the *dyrex* unit is the key to realizing "unimolecular memory", where one *dyrex* unit acts as a 1-bit.^[7] The present molecules containing multiple *dyrex* units can pave the way toward "unimolecular n-bit memory", where one molecule can act as an n-bit.

Experimental Section

General

^1H , ^{19}F and ^{13}C NMR spectra were recorded on BRUKER Ascend TM400 ($^1\text{H}/400$ MHz), AMX500 ($^{19}\text{F}/470$ MHz, GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University) and JEOL α 400 ($^{13}\text{C}/100$ MHz), ECA600 ($^1\text{H}/600$ MHz, High-Resolution NMR Laboratory, Graduate School of Science, Hokkaido University) spectrometers, respectively. IR spectra were obtained on a JEOL JIR-WINSPEC100 FT/IR spectrophotometer. Mass spectra were recorded on a JMS-T100GCV spectrometer in FD mode (GC-MS & NMR Laboratory, Graduate School of Agriculture, Hokkaido University). Column chromatography was performed on a silica gel I-6-40 (YMC) with a particle size of 40-63 μm . Melting points were measured on a Yamato MELTING POINT APPARATUS MODEL MP-21. Element analyses were performed on a J-SCIENCE LAB MICRO CORDER JM10 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. Optical resolutions were performed by chiral HPLC on a DAICEL CHIRALPAK IA. All commercially available compounds were used without further purification. Solvents were dehydrated prior to use as appropriate.

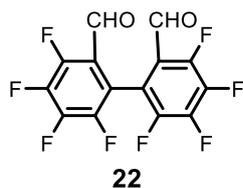
• Preparation of 2,2'-dibromooctafluorobiphenyl **15**^[3]



To a solution of 13.4 g (43.6 mol) of 1,2-dibromotetrafluorobenzene in 200 mL of dry ether cooled at -78 °C was added *n*BuLi (1.63 M solution in hexane, 32 mL, 52.3 mmol) dropwise over 40 min under Ar. After the solution was stirred for 30 min, 7.2 mL (12.4 g, 65.4 mol) of TiCl₄ was added to the orange solution. The reaction mixture was stirred at this temperature for an additional 3 h before the flask was left to warm up overnight. The reaction mixture was hydrolyzed with water. The whole mixture was extracted with ether three times. The combined organic layers were washed with water and brine, and dried over anhydrous MgSO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) and recrystallization from hexane at -78 °C to give dibromooctafluorobiphenyl **15** (7.10 g) as a colorless solid in 73% yield.

The melting point and IR are identical to those in the literature.

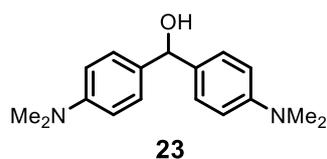
• Preparation of 3,3',4,4',5,5',6,6'-octafluoro-biphenyl-2,2'-dialdehyde **22**



To a solution of 4.89 g (10.7 mmol) of dibromooctafluorobiphenyl **15** in dry ether (170 mL) cooled at -78 °C was added *n*BuLi (1.60 M solution in hexane, 16 mL, 25.7 mmol) dropwise over 30 min under Ar. The reaction mixture was stirred for 1 h, and then 8.3 mL of DMF was added at -78 °C and stirred for 40 min at the same temperature. The mixture was hydrolyzed with saturated NH₄Cl aq. and allowed to warm up to room temperature. The whole mixture was extracted with ether three times. The combined organic layers were washed with water and brine, and dried over anhydrous MgSO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ = 5→3). After evaporation of the solvent, the resulting solid was triturated with a small amount of hexane to give **22** (707 mg) as a colorless solid in 45% yield.

22: m.p. 82.0-85.0 °C; ¹H NMR (400 MHz, CDCl₃): δ/ppm 10.21 (2H, s); ¹³C NMR (MHz, CDCl₃): δ/ppm ; 184.17, 151.45 (C, dd, *J*_{C-F} = 260, 13 Hz), 145.42 (C, dd, *J*_{C-F} = 260, 13 Hz), 144.50 (C, dt, *J*_{C-F} = 260, 13 Hz), 141.02 (C, dt, *J*_{C-F} = 260, 13 Hz), 118.36, 114.67 (C, d, *J*_{C-F} = 16 Hz); IR (neat): ν/cm⁻¹ 1704, 1621, 1514, 1475, 1414, 1354, 1312, 1287, 1267, 1128, 1046, 811, 720, 666, 630, 605, 506; FD-MS *m/z* 354 (M⁺, BP), 355 (18); Anal. Calcd. for C₁₄H₂F₈O₂: C, 47.48; H, 0.57. Found: C, 47.61; H, 0.84%.

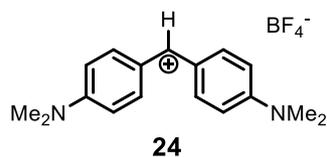
• Preparation of 4,4'-bis(dimethylamino)benzhydrol **23**^[4]



To a solution of 4,4'-bis(dimethylamino)benzophenone (11.3 g, 42.2 mmol) in dry THF 600 mL was added LiAlH₄ (3.48 g, 46.4 mmol) at room temperature under Ar, and the mixture was stirred for 1.5 h. The resulting suspension was cooled to 0 °C and saturated Rochelle salt aq. was added to decompose the aluminum complex. The whole mixture was extracted with CH₂Cl₂ three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure to give 4,4'-bis(dimethylamino)benzhydrol **23** (11.4 g) as a colorless solid in 100% yield.

¹H NMR data were identical to those in literature.

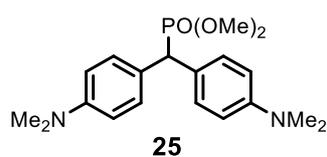
• Preparation of bis(4-dimethylaminophenyl)methylium tetrafluoroborate **24**^[4]



4,4'-Bis(dimethylamino)benzhydrol **23** (11.4 g, 42.2 mmol) was dissolved in THF (160 mL). Addition of 42% HBF₄ aq. (7.6 mL, 50.6 mmol) resulted in a deep blue solution. The solution was stirred at room temperature for 2.5 h and then cooled to 0 °C for 30 min. The precipitates were washed with cold THF three times and filtered to give **24** (14.5 g) as a dark purple powder in 100% yield.

¹H NMR data were identical to those in literature.

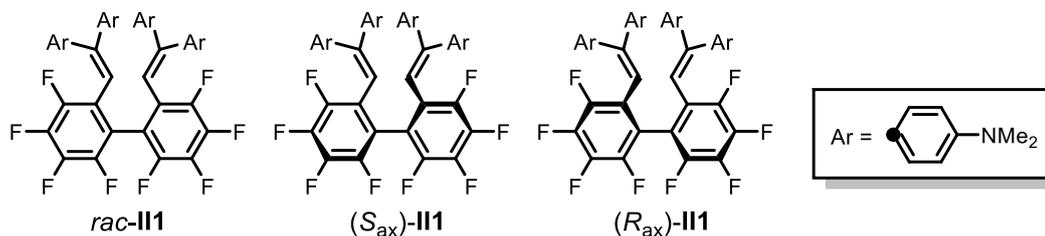
• Preparation of dimethyl bis(4-dimethylaminophenyl)methyl phosphonate **25**^[4]



Dye salt **24** (14.5 g, 42.2 mmol) and NaI (6.33 g, 42.2 mmol) were dissolved in MeCN (400 mL) at room temperature. To the solution was added trimethyl phosphite (5.22 mL, 44.3 mmol), and the reaction mixture was stirred at room temperature for 1 h. After the addition of saturated NaHCO₃ aq., the whole mixture was extracted with CH₂Cl₂ three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (AcOEt) to afford **25** (11.7 g, y. 76%) as a colorless solid.

¹H NMR data were identical to those in literature.

• Preparation of 3,3',4,4',5,5',6,6'-octafluoro-2,2'-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]biphenyl **III1**



To a solution of dimethyl bis(4-dimethylaminophenyl)methyl phosphonate **25** (1.35 g, 3.72 mmol) in 45 mL of dry THF was added *n*BuLi (1.55 M solution in hexane, 2.93 mL, 4.54 mmol) dropwise over 30 min at -78 °C under Ar, and the mixture was stirred for 2 h. To the suspension was added dialdehyde **22** (487 mg, 1.38 mmol) at -78 °C, and the mixture was stirred for 3 h at -78 °C. The mixture was gradually warmed to room temperature and stirred overnight. After being diluted with water, the whole mixture was extracted with CH₂Cl₂ three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/EtOAc = 10) to give *rac*-III1 (1.06 g) as a greenish-yellow solid in 93% yield. With the use of a chiral column (CHIRALPAK IA, hexane/CH₂Cl₂ = 5), optically pure samples of (*S*_{ax})/(*R*_{ax})-**5a** were obtained from *rac*-III1.

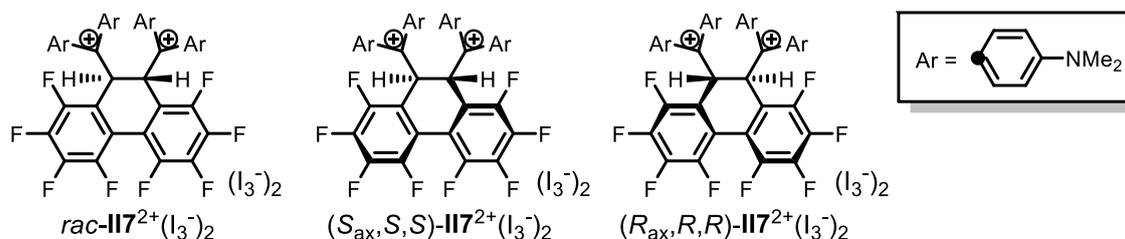
rac-III1: m.p. 138.0-139.5 °C; ¹H NMR (400 MHz, CDCl₃): δ_{ppm} 7.20 (4H, d, *J* = 9.0 Hz), 6.66 (8H, d, *J* = 8.8 Hz), 6.34 (4H, d, *J* = 9.0 Hz), 6.15 (2H, s), 2.98 (12H, s), 2.88 (12H, s); ¹⁹F NMR (470 MHz, CDCl₃): δ_{ppm} -137.91 (4F, br), -156.53 (2F, s), -158.81 (2F, t, *J* = 21.6 Hz); ¹³C NMR (100 MHz, CDCl₃): δ_{ppm} 150.49, 150.10, 149.47, 145.11 (C, dd, *J*_{C-F} = 250, 10 Hz), 145.01 (C, dd, *J*_{C-F} = 250, 10 Hz), 140.58 (C, d, *J*_{C-F} = 250 Hz), 138.91 (C, d, *J*_{C-F} = 250 Hz), 131.01, 130.63, 129.71, 127.13, 124.04 (C, d, *J*_{C-F} = 10 Hz), 115.42 (C, d, *J*_{C-F} = 10 Hz), 111.64, 111.61, 110.77, 40.38, 40.30; IR (KBr): ν_{cm⁻¹} 2887, 2802, 1608, 1522, 1496, 1466, 1357, 1226, 1192, 1166, 1126, 1063, 984, 972, 948, 817, 722, 569; LR-MS (FD) *m/z* 826 (M⁺, BP), 827 (55), 828 (15), 829 (3); HR-MS (FD) Calcd. for C₄₈H₄₂F₈N₄: 826.3281. Found: 826.3299; UV-Vis (CH₂Cl₂): λ_{max}/nm (ε/M⁻¹cm⁻¹) 328 (45400), 266 (37200); (MeCN): 328 (41800), 265 (36300); (benzene): 328 (46900); (cyclohexane): 321 (49500), 262 (39000); (methylcyclohexane): 321 (48400), 262 (38000)

(*S*_{ax})-III1: [α]_D²⁴ (CHCl₃, *c* = 0.11): -135; CD (20 °C, CH₂Cl₂): λ_{ext}/nm (Δε/M⁻¹cm⁻¹) 379 (+21), 337 (-28), 236 (-40); (MeCN): 383 (+20), 338 (-27), 235 (-33); (benzene): 378 (+22), 337 (-35); (cyclohexane): 367 (+20), 330 (-33), 233 (-54); (methylcyclohexane): 365 (+20), 330 (-31), 233 (-51).

(*R*_{ax})-III1: [α]_D²⁴ (CHCl₃, *c* = 0.11): +80; CD (20 °C, CH₂Cl₂): λ_{ext}/nm (Δε/M⁻¹cm⁻¹) 379 (-16), 337 (+24), 237 (+32); (MeCN): 383 (-16), 338 (+23), 235 (+28); (benzene): 378 (-17),

337 (+29); (cyclohexane): 365 (-15), 330 (+29), 234 (+45); (methylcyclohexane): 365 (-16), 330 (+27), 233 (+43).

• Preparation of 1,2,3,4,5,6,7,8-octafluoro-9,10-dihydrophenanthrene-9,10-diylbis[bis(4-methoxyphenyl)methylium] bis(triiodide) salt **II7²⁺(I₃⁻)₂**



To a solution of *rac*-**II1** (50.9 mg, 61.5 μ mol) in 5 mL of dry CH_2Cl_2 was added a solution of iodine (62.4 mg, 246 μ mol) in 5 mL of dry CH_2Cl_2 at 0 $^\circ\text{C}$ under Ar, and the mixture was stirred at room temperature for 1 h. The addition of dry ether led to precipitation of the dication salt. The precipitates were collected, washed with dry ether three times, and dried *in vacuo* to give *rac*-**II7²⁺(I₃⁻)₂** (93.1 mg) as a dark green powder in 95% yield. By a similar procedure, optically pure antipode (*S*_{ax},*S,S*)/(*R*_{ax},*R,R*)-**II7²⁺(I₃⁻)₂** (11.4 mg) was obtained from (*S*_{ax})/(*R*_{ax})-**II1**, respectively.

rac-**II7²⁺(I₃⁻)₂**: ¹H NMR (400 MHz, CD_3CN): δ ppm 7.19 (8H, d, $J = 8.8$ Hz), 6.78 (8H, d, $J = 8.8$ Hz), 5.41 (2H, s), 3.26 (24H, s); IR (KBr): ν cm^{-1} 2359, 2336, 1584, 1478, 1403, 1377, 1165, 1123, 943, 825, 724, 668; LR-MS (FD) m/z 824 (BP), 825 (63), 826 (M⁺, 73), 827 (32), 828 (7); HR-MS (FD) Calcd. for $\text{C}_{48}\text{H}_{40}\text{F}_8\text{N}_4$: 824.3113. Found: 824.3125.

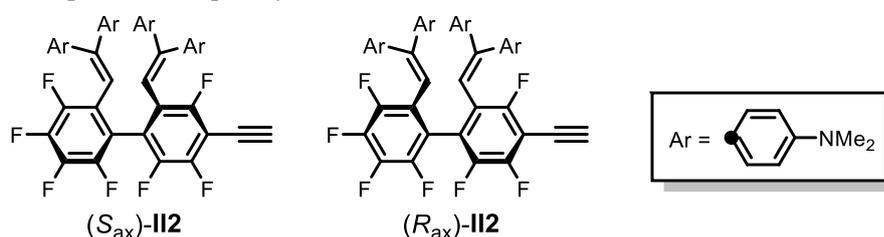
• Preparation of 1,2,3,4,5,6,7,8-octafluoro-9,10-dihydrophenanthrene-9,10-diylbis[bis(4-methoxyphenyl)methylium] bis(triiodide) salt **II7²⁺(BF₄⁻)₂**

To a solution of AgBF_4 (17.3 mg, 88.9 μ mol) in 5 mL of dry acetone was added *rac*-**II1** (38.7 mg, 46.8 μ mol) at room temperature under Ar, and the mixture was stirred for 30 min. After filtration, the residue was washed with dry CH_2Cl_2 and dry ether. The organic solvent was then concentrated under reduced pressure to give *rac*-**II7²⁺(BF₄⁻)₂** (30.8 mg) as a dark blue powder. While pure *rac*-**II7²⁺(BF₄⁻)₂** was not useful, crystalline *rac*-**II7²⁺(BF₄⁻)₂** made it possible to analyze its X-ray structure.

• Preparation of **II1** (Reduction of dication salt *rac*-**II7**²⁺(I₃⁻)₂)

A mixture of dication salt *rac*-**II7**²⁺(I₃⁻)₂ (53.5 mg, 33.7 μmol) and Zn (66.1 mg, 1.01 mmol) in 4 mL of dry MeCN was stirred at room temperature for 1 h under Ar. The resulting suspension was diluted with water. The whole mixture was extracted with CH₂Cl₂ three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure to give **II1** (25.6 mg) as a yellow-green solid in 92% yield.

• Preparation of 2,2'-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]-4-ethynyl-3,3',4',5,5',6,6'-heptafluorobiphenyl **II2**



To a solution of *rac*-**II1** (592 mg, 716 μmol) in dry THF (100 mL) were added ethynyltriisopropylsilane (TIPS-acetylene, 476 μL, 2.14 mmol) and NaHMDS (1.1 M solution in THF, 2.15 mL, 2.36 mmol) at room temperature under Ar, and the mixture was heated at 60 °C for 16 h. After being diluted with water, the whole mixture was extracted with AcOEt three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/AcOEt = 10) to give a mixture containing TIPS-ethynylated derivative. To a solution of the mixture in dry THF (10 mL) was added TBAF (1M solution in THF, 1.5 mL, 1.5 mmol) at 0 °C under Ar, and the mixture was stirred for 20 min. After being diluted with saturated NH₄Cl aq., the whole mixture was extracted with AcOEt three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 10) to give *rac*-**II2** containing some by-products, which was separated by chiral HPLC (chiralpak IA, hexane/CH₂Cl₂ = 5) to give (S_{ax})-**II2** (49 mg, y. 16%) and (R_{ax})-**II2** (68 mg, y. 22%) as a greenish-yellow solid along with recovery of the starting material *rac*-**II1** (153 mg).

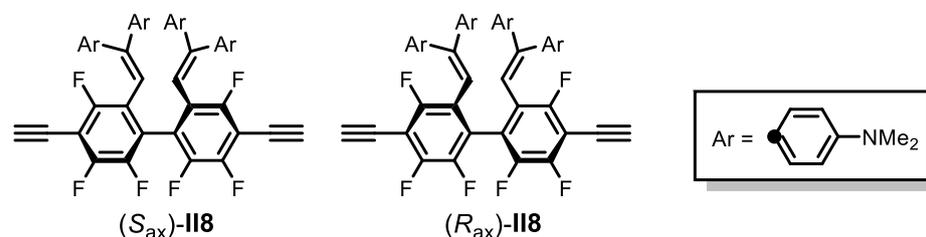
(S_{ax})/(R_{ax})-**II2**: m.p. 144-146 °C; ¹H NMR (400 MHz, CDCl₃): δ/ppm 7.21 (4H, d, *J* = 8.8 Hz), 6.67 (4H, dd, *J* = 9.2, 2.0 Hz), 6.58 (2H, d, *J* = 8.8 Hz), 6.57 (2H, d, *J* = 8.8 Hz), 6.36 (4H, d, *J* = 8.8 Hz), 6.35 (1H, s), 6.30 (1H, s), 3.49 (1H, s), 2.98 (6H, s), 2.98 (6H, s), 2.89 (6H, s), 2.89 (6H, s); ¹⁹F NMR (470 MHz, CDCl₃): δ/ppm -111.53 (1F, s), -133.79 (1F, d,

$J = 23.5$ Hz), -137.07 (1F, s), -138.70 (1F, s), -139.16 (1F, s), -156.81 (1F, s), -158.8 (1F, t, $J = 23.5$ Hz); ^{13}C NMR (MHz, CDCl_3): δ_{ppm} 156.57 (C, d, $J_{\text{C-F}} = 250$ Hz), 150.44, 150.40, 150.17, 150.17, 149.65 (C, ddd, $J_{\text{C-F}} = 250$, 15, 2 Hz), 149.15, 148.49, 145.31 (C, dd, $J_{\text{C-F}} = 245$, 10 Hz), 145.01 (C, dd, $J_{\text{C-F}} = 245$, 10 Hz), 144.69 (C, ddd, $J_{\text{C-F}} = 250$, 15, 2 Hz), 140.50 (C, dddd, $J_{\text{C-F}} = 250$, 25, 15, 2 Hz), 138.90 (C, dddd, $J_{\text{C-F}} = 250$, 25, 15, 2 Hz), 131.118, 131.07, 130.56, 130.56, 129.57, 129.54, 126.96, 126.89, 123.53 (C, t, $J_{\text{C-F}} = 15$ Hz), 122.04 (C, d, $J_{\text{C-F}} = 15$ Hz), 115.51 (C, d, $J_{\text{C-F}} = 15$ Hz), 111.72, 111.67, 111.67, 111.67, 111.67, 111.41, 110.75, 102.92 (C, dd, $J_{\text{C-F}} = 25$, 20 Hz), 88.17, 70.35 (C, d, $J_{\text{C-F}} = 2$ Hz), 40.39, 40.39, 40.38, 40.32; IR (KBr): $\nu_{\text{cm}^{-1}}$ 3303, 2920, 2888, 2855, 2801, 1608, 1523, 1480, 1462, 1455, 1356, 1269, 1226, 1191, 1166, 984, 818; LR-MS (FD) m/z 832 (M^+ , BP), 833 (59), 834 (18); HR-MS (FD) Calcd. for $\text{C}_{50}\text{H}_{43}\text{F}_7\text{N}_4$: 832.3376. Found: 832.3351; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 327 (44000), sh 267 (44200), 242 (52300); (MeCN): 328 (41800), 265 (44600), 241 (48800).

(S_{ax})-**II2**: $[\alpha]_{\text{D}}^{24}$ (CHCl_3 , $c = 0.19$): -201 ; CD (25 °C, MeCN): $\lambda_{\text{ext}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 390 (+18), 340 (-29) 250 (-25).

(R_{ax})-**II2**: $[\alpha]_{\text{D}}^{24}$ (CHCl_3 , $c = 0.25$): $+201$; CD (25 °C, CH_2Cl_2): $\lambda_{\text{ext}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 383 (-16), 339 (+29); (MeCN): 390 (-18), 340 (+27), 250 (+25).

• Preparation of 2,2'-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]-4,4'-diethynyl-3,3',5,5',6,6'-hexafluorobiphenyl

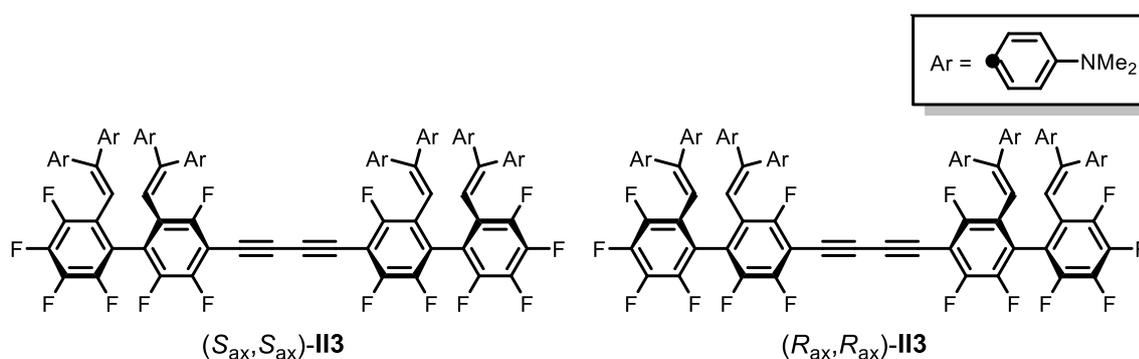


To a solution of *rac*-**II1** (96.0 mg, 116 μmol) in dry toluene (10 mL) were added ethynyltriisopropylsilane (TIPS-acetylene, 129 μL , 581 μmol) and KHMDS (0.5 M solution in toluene, 1.16 mL, 581 μmol) at room temperature under Ar, and the mixture was refluxed overnight. After being diluted with water, the whole mixture was extracted with AcOEt three times. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (Hexane/AcOEt = 10) to give a mixture containing TIPS-ethynylated derivative. To a solution of the mixture in dry THF (10 mL) was added TBAF (1M solution in THF, 230 μL , 230 μmol) at 0 °C under Ar, and the mixture was stirred for 20 min. After being diluted with saturated NH_4Cl aq., the whole mixture was extracted with AcOEt three times.

The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt = 10) to give *rac*-**II8** (21.5 mg, y. 22%), which can be separated by chiral HPLC (chiralpak IA, hexane/ CH_2Cl_2 = 5), as a greenish-yellow solid.

rac-**II8**: ^1H NMR (400 MHz, CDCl_3): δ ppm 7.23 (4H, d, J = 8.8 Hz), 6.68 (4H, d, J = 8.8 Hz), 6.49 (2H, d, J = 8.8 Hz), 6.37 (4H, d, J = 8.8 Hz), 6.35 (2H, s), 3.51 (2H, s), 2.99 (12H, s), 2.90 (12H, s); ^{19}F NMR (470 MHz, CDCl_3): δ ppm -112.32 (2F, s), -133.76 (2F, d, J = 23.5 Hz), -138.42 (2F, s); LR-MS (FD) m/z 838 (M^+ , BP), 839 (59), 840 (17).

• Preparation of 1,3-butadiyne-1,4-diylbis{2,2'-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]-3,3',4',5,5',6,6'-heptafluorobiphenyl} **II3**



(R_{ax}, R_{ax}) -**II2** (49.1 mg, 59 μmol), TMEDA (2 μL , 20 mol%), CuI (1 mg, 10 mol%) and Et_3N (25 μL , 177 μmol) were suspended in dry acetone (1 mL) at room temperature. The reaction mixture was stirred at this temperature overnight until (R_{ax}, R_{ax}) -**II2** was totally consumed. The solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel (hexane/AcOEt = 5 \rightarrow 2) to give (R_{ax}, R_{ax}) -**II3** (47 mg) as a green solid in 96% yield. By a similar procedure, optically pure antipode (S_{ax}, S_{ax}) -**II3** (11.4 mg) was obtained from (S_{ax}) -**5c** in 83% yield.

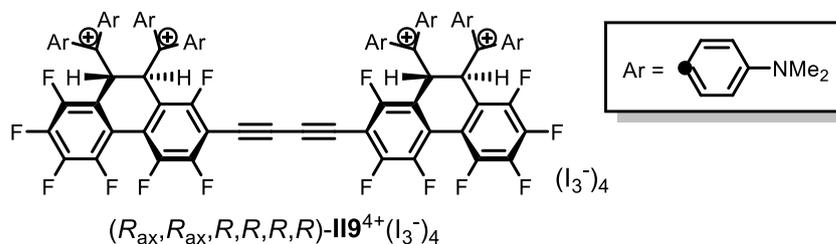
$(S_{ax}, S_{ax})/(R_{ax}, R_{ax})$ -**II3**: m.p. 177-180 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ ppm 7.21 (4H, d, J = 8.8 Hz), 7.21 (4H, d, J = 8.8 Hz), 6.67 (4H, d, J = 8.8 Hz), 6.67 (4H, d, J = 8.8 Hz), 6.55 (4H, d, J = 8.8 Hz), 6.55 (4H, d, J = 8.8 Hz), 6.37 (4H, d, J = 8.8 Hz), 6.36 (4H, d, J = 8.8 Hz), 6.26 (4H, s), 2.98 (24H, s), 2.90 (12H, s), 2.89 (12H, s); ^{19}F NMR (470 MHz, CDCl_3): δ ppm -109.47 (2F, s), -131.78 (2F, d, J = 24.5 Hz), -136.34 (2F, s), -137.99 (2F, s), -138.20 (2F, s), -156.13 (2F, s), -158.19 (2F, t, J = 23.5 Hz); ^{13}C NMR (MHz, CDCl_3): δ ppm 157.00 (C, d, $J_{\text{C-F}}$ = 250 Hz), 150.48, 150.41, 150.22, 150.22, 149.18, 148.65, 145.46 (C, dd, $J_{\text{C-F}}$ = 250, 15 Hz), 145.01 (C, dd, $J_{\text{C-F}}$ = 250, 15 Hz), 144.61 (C, dd, $J_{\text{C-F}}$ = 250, 15 Hz), 140.45 (C, d, $J_{\text{C-F}}$ = 250 Hz), 139.78 (C, d, $J_{\text{C-F}}$ = 250 Hz), 139.75 (C, dd, $J_{\text{C-F}}$ = 250 Hz), 132.19, 131.13, 131.00, 130.75, 130.57, 129.73, 129.53, 126.79, 126.75, 123.64 (C, t, $J_{\text{C-F}}$

= 15 Hz), 123.02 (C, m), 115.27 (C, d, J_{C-F} = 15 Hz), 111.70, 111.70, 111.70, 111.70, 111.17, 110.63, 83.23, 70.63, 40.40, 40.40, 40.39, 40.37; IR (KBr): $\nu_{cm^{-1}}$ 2922, 2893, 2854, 2802, 1608, 1522, 1444, 1356, 1192, 1166, 984, 817; LR-MS (FD) m/z 1663 (M^+ , BP), 1662 (86), 1664 (57), 1665 (20); HR-MS (FD) Calcd. for $C_{100}H_{84}F_{14}N_8$: 1662.6595. Found: 1662.6613; UV-Vis (CH_2Cl_2): λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) sh 350 (80100), 325 (90400), sh 269 (72000), 240 (75700); (MeCN): sh 346 (98700), 324 (119000), 263 (92600), 242 (92000).

(S_{ax}, S_{ax})-**II3**: CD (25 °C, CH_2Cl_2): λ_{ext}/nm ($\Delta\epsilon/M^{-1}cm^{-1}$) 390 (+14), 339 (-29), 302 (-22), 240 (-50); (MeCN): 396(+18), 340 (-40), 300 (-26), 238 (-65).

(R_{ax}, R_{ax})-**II3**: $[\alpha]_D^{24}$ ($CHCl_3$, c = 0.25): +321

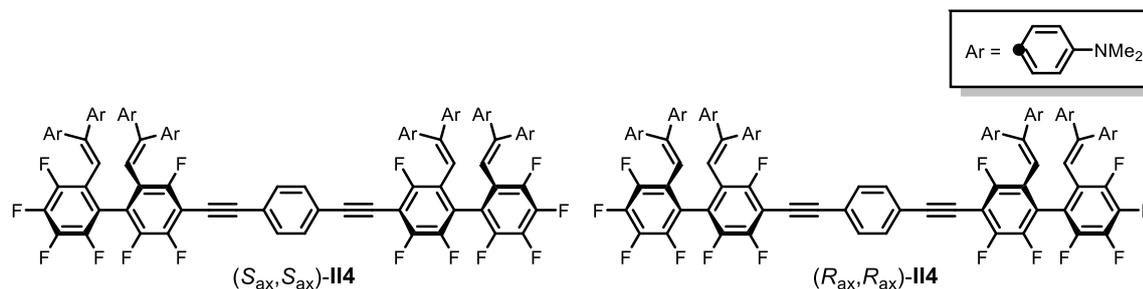
• Preparation of 1,3-butadiyne-1,4-diylbis{1,3,4,5,6,7,8-heptafluoro-9,10-dihydrophenanthrene-9,10-diylbis[bis(4-methoxyphenyl)methyl]methyl}tetrakis(triiodide) salt **II9**⁴⁺(I₃⁻)₄



To a solution of (R_{ax}, R_{ax})-**II9** (9.0 mg, 5.4 μ mol) in 1 mL of dry CH_2Cl_2 was added a solution of iodine (8.2 mg, 32 μ mol) in 1 mL of dry CH_2Cl_2 at 0 °C under Ar, and the mixture was stirred at room temperature for 1 h. The addition of dry ether led to precipitation of the dication salt. The precipitates were collected, washed with dry ether three times, and dried *in vacuo* to give ($R_{ax}, R_{ax}, R, R, R, R$)-**II9**⁴⁺(I₃⁻)₄ (10 mg) as a dark green powder in 60% yield.

($R_{ax}, R_{ax}, R, R, R, R$)-**II9**⁴⁺(I₃⁻)₄: ¹H NMR (400 MHz, CD_3CN): δ ppm 7.20 (16H, d, J = 8.0 Hz), 6.79 (16H, d, J = 8.0 Hz), 5.42 (2H, s), 5.39 (2H, s), 3.27 (48H, s).

• Preparation of 1,4-phenylenediethyne-2,2'-diylbis{2,2'-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]-3,3',4',5,5',6,6'-heptafluorobiphenyl} **II4**

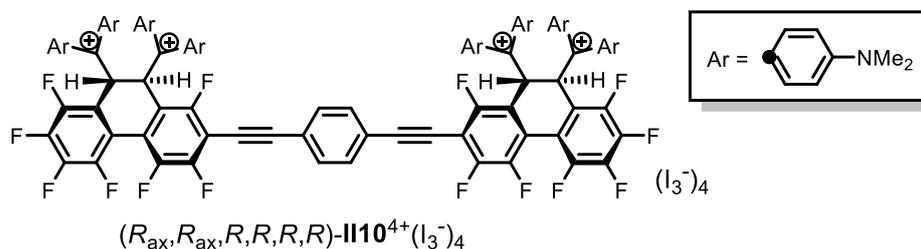


A mixture of (R_{ax})-**II2** (31.5 mg, 38 μ mol), *p*-diiodobenzene (5.6 mg, 17 μ mol), Pd(PPh₃)₄ (4.4 mg, 10 mol%) and CuI (0.7 mg, 10 mol%) in degassed Et₃N (3 mL) was heated at 50 °C for 15 h under Ar. After being diluted with water, the whole mixture was extracted with EtOAc twice. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 5→2) to give (R_{ax},R_{ax})-**II4** (20 mg) as a green solid in 60% yield. By a similar procedure, optically pure antipode (S_{ax},S_{ax})-**II4** was obtained from (S_{ax})-**II2** in 45% yield.

(S_{ax},S_{ax})/(R_{ax},R_{ax})-**II4**: m.p. 222-225 °C; ¹H NMR (400 MHz, CDCl₃): δ ppm 7.53 (4H, s), 7.22 (8H, d, J = 8.8 Hz), 6.68 (4H, d, J = 8.8 Hz), 6.67 (4H, d, J = 8.8 Hz), 6.58 (4H, d, J = 8.8 Hz), 6.57 (4H, d, J = 8.8 Hz), 6.38 (4H, d, J = 8.8 Hz), 6.37 (4H, d, J = 8.8 Hz), 6.31 (2H, s), 6.26 (2H, s), 2.98 (12H, s), 2.97 (12H, s), 2.90 (12H, s), 2.89 (12H, s); ¹⁹F NMR (470 MHz, CDCl₃): δ ppm -111.51 (2F, s), -133.63 (2F, d, J = 28 Hz), -136.94 (2F, s), -138.95 (2F, s), -139.26 (2F, s), -157.00 (2F, s), -158.86 (2F, t, J = 23.5 Hz); ¹³C NMR (MHz, CDCl₃): δ ppm 155.91 (C, d, J_{C-F} = 250 Hz), 150.43, 150.38, 150.20, 150.20, 149.07, 148.31, 148.58 (C, dd, J_{C-F} = 200, 15 Hz), 145.28 (C, dd, J_{C-F} = 250, 15 Hz), 144.91 (C, dd, J_{C-F} = 250, 15 Hz), 140.88 (C, d, J_{C-F} = 250 Hz), 139.99 (C, d, J_{C-F} = 250 Hz), 138.65 (C, dd, J_{C-F} = 250 Hz), 131.76, 131.30, 131.12, 130.61, 130.60, 129.54, 129.53, 126.99, 126.90, 123.49 (C, d, J_{C-F} = 50 Hz), 123.24 (C, d, J_{C-F} = 50 Hz), 122.92, 121.45, 115.60 (C, d, J_{C-F} = 15 Hz), 114.51 (C, m), 112.04 (C, d, J_{C-F} = 50 Hz), 111.68, 111.68, 111.68, 111.68, 110.84, 110.84, 99.47, 40.40, 40.40, 40.40, 40.40; IR (KBr): ν cm⁻¹ 2886, 2885, 2802, 1608, 1522, 1445, 1356, 1225, 1192, 1166, 948, 818; LR-MS (FD) m/z 1739 (M⁺, BP), 1738 (82), 1740 (66), 1741 (30), 1742 (11); HR-MS (FD) Calcd. for C₁₀₆H₈₈F₁₄N₈: 1738.6908. Found: 1738.6890; UV-Vis (CH₂Cl₂): λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) 328 (129000), 271 (74900), 234 (86600); (MeCN): 326 (127000), 268 (75000), 231 (79800).

(R_{ax},R_{ax})-**II4**: [α]_D²⁴ (CHCl₃, c = 0.05): +259; CD (25 °C, CH₂Cl₂): λ_{ext}/nm ($\Delta\epsilon/M^{-1}cm^{-1}$) 388 (-21), 343 (+35), 236 (+56); (MeCN): 390 (-20), 340 (+36), 230 (+45).

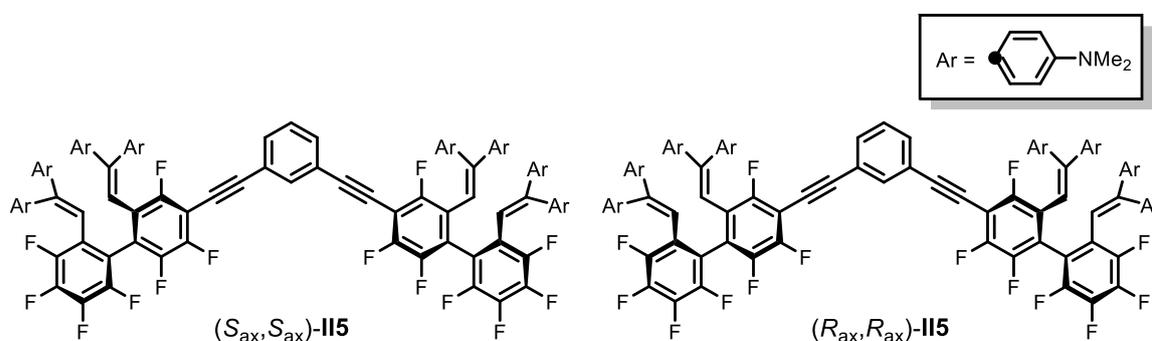
- Preparation of 1,4-phenylenediethyne-2,2'-diylbis{1,3,4,5,6,7,8-heptafluoro-9,10-dihydrophenanthrene-9,10-diylbis[bis(4-methoxyphenyl)methylium]tetrakis(triiodide) salt **II1** $0^{4+}(\text{I}_3^-)_4$



To a solution of $(R_{ax}, R_{ax})\text{-II4}$ (7.5 mg, 4.3 μmol) in 1 mL of dry CH_2Cl_2 was added a solution of iodine (8.8 mg, 35 μmol) in 1 mL of dry CH_2Cl_2 at 0 $^\circ\text{C}$ under Ar, and the mixture was stirred at room temperature for 1 h. The addition of dry ether led to precipitation of the dication salt. The precipitates were collected, washed with dry ether three times, and dried *in vacuo* to give $(R_{ax}, R_{ax}, R, R, R, R)\text{-II10}^{4+}(\text{I}_3^-)_4$ (8.5 mg) as a dark green powder in 60% yield.

$(R_{ax}, R_{ax}, R, R, R, R)\text{-II10}^{4+}(\text{I}_3^-)_4$: $^1\text{H NMR}$ (400 MHz, CD_3CN): δ ppm 7.64 (4H, s), 7.22 (16H, d, $J = 8.0$ Hz), 6.79 (16H, d, $J = 8.0$ Hz), 5.42 (4H, s), 3.27 (48H, s).

- Preparation of 1,3-phenylenediethyne-2,2'-diylbis{2,2'-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]-3,3',4',5,5',6,6'-heptafluorobiphenyl} **II5**



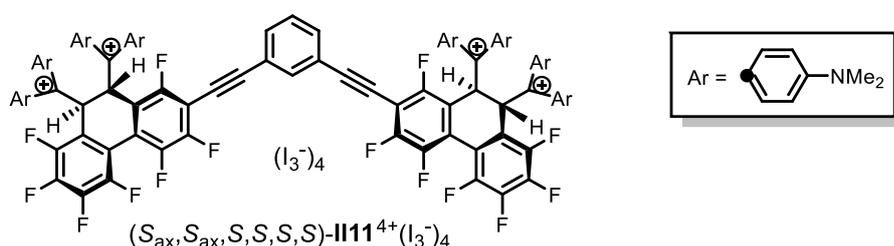
A mixture of $(S_{ax})\text{-II2}$ (44.9 mg, 54 μmol), *m*-diiodobenzene (7.1 mg, 22 μmol), $\text{Pd}(\text{PPh}_3)_4$ (6.2 mg, 10 mol%) and CuI (1.0 mg, 10 mol%) in degassed Et_3N (3 mL) was heated at 50 $^\circ\text{C}$ for 15 h under Ar. After being diluted with water, the whole mixture was extracted with EtOAc twice. The combined organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4 . After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ $\text{EtOAc} = 5 \rightarrow 2$) to give $(S_{ax}, S_{ax})\text{-II5}$ (36 mg) as a green solid in 96% yield. By a similar procedure, optically pure antipode $(R_{ax}, R_{ax})\text{-II5}$ was obtained from $(R_{ax})\text{-II2}$ in 58% yield.

(S_{ax}, S_{ax})/(R_{ax}, R_{ax})-**II5**: m.p. 214-217 °C; ^1H NMR (400 MHz, CDCl_3): δ /ppm 7.72 (1H, s), 7.54 (2H, dd, $J = 10, 1.6$ Hz), 7.35 (1H, t, $J = 7.6$ Hz), 7.23 (4H, d, $J = 8.8$ Hz), 7.22 (4H, d, $J = 8.8$ Hz), 6.68 (4H, d, $J = 8.8$ Hz), 6.67 (4H, d, $J = 8.8$ Hz), 6.59 (4H, d, $J = 8.8$ Hz), 6.58 (4H, d, $J = 8.8$ Hz), 6.38 (4H, d, $J = 8.8$ Hz), 6.37 (4H, d, $J = 8.8$ Hz), 6.31 (2H, s), 6.26 (2H, s), 2.98 (12H, s), 2.97 (12H), 2.90 (12H, s), 2.89 (12H, s); ^{19}F NMR (470 MHz, CDCl_3): δ /ppm -110.84 (2F, s), -133.80 (2F, d, $J = 24$ Hz), -136.43 (2F, s), -138.40 (2F, br), -138.79 (2F, s), -156.50 (2F, s), -158.34 (2F, t, $J = 22$ Hz); ^{13}C NMR (MHz, CDCl_3): δ /ppm 155.96 (C, d, $J_{\text{C-F}} = 250$ Hz), 150.43, 150.37, 150.19, 150.19, 149.09, 148.87 (C, ddd, $J_{\text{C-F}} = 250, 15, 8$ Hz), 148.31, 145.33 (C, dd, $J_{\text{C-F}} = 250, 15$ Hz), 144.95 (C, ddd, $J_{\text{C-F}} = 250, 15, 8$ Hz), 144.82 (C, dd, $J_{\text{C-F}} = 250, 15$ Hz), 140.40 (C, dt, $J_{\text{C-F}} = 250, 15$ Hz), 138.93 (C, dt, $J_{\text{C-F}} = 250, 15$ Hz), 134.82, 132.27, 131.30, 131.10, 130.61, 130.61, 129.54, 129.54, 128.55, 126.97, 126.61, 123.64 (C, d, $J_{\text{C-F}} = 20$ Hz), 123.37 (C, d, $J_{\text{C-F}} = 20$ Hz), 122.81, 121.48 (C, dd, $J_{\text{C-F}} = 15, 5$ Hz), 115.68 (C, d, $J_{\text{C-F}} = 15$ Hz), 112.06 (C, d, $J_{\text{C-F}} = 15$ Hz), 112.04 (C, d, $J_{\text{C-F}} = 50$ Hz), 111.69, 111.69, 111.69, 111.69, 110.85, 110.85, 102.95 (C, dd, $J_{\text{C-F}} = 20, 15$ Hz), 98.51, 40.39, 40.39, 40.39, 40.39; IR (KBr): ν/cm^{-1} 2926, 2893, 2849, 2799, 1609, 1522, 1479, 1445, 1355, 1227, 1192, 1166, 969, 818; LR-MS (FD) m/z 1739 (M^+ , BP), 1738 (84), 1740 (63), 1741 (27), 1742 (9); HR-MS (FD) Calcd. for $\text{C}_{106}\text{H}_{88}\text{F}_{14}\text{N}_8$: 1738.6908. Found: 1738.6899; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 312 (122000); (MeCN): 309 (106000), 270 (95000).

(S_{ax}, S_{ax})-**II5**: $[\alpha]_{\text{D}}^{24}$ ($\text{CHCl}_3, c = 0.20$): -235;

(R_{ax}, R_{ax})-**II5**: CD (25 °C, CH_2Cl_2): $\lambda_{\text{ext}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 386 (-23), 339 (+47), 234 (+46); (MeCN): 388 (-22), 341 (+40), 233 (+38).

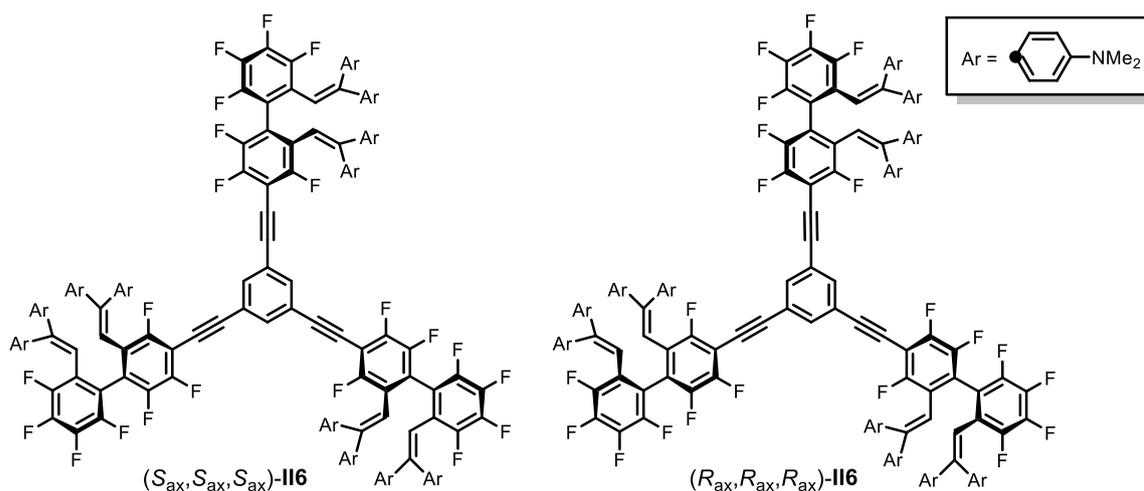
• Preparation of 1,3-phenylenediethyne-2,2'-diylbis[1,3,4,5,6,7,8-heptafluoro-9,10-dihydrophenanthrene-9,10-diylbis[bis(4-methoxyphenyl)methylium]tetrakis(triiodide) salt **II11** $4^+(\text{I}_3^-)_4$



To a solution of (S_{ax}, S_{ax})-**II5** (7.0 mg, 4.0 μmol) in 1 mL of dry CH_2Cl_2 was added a solution of iodine (8.2 mg, 32 μmol) in 1 mL of dry CH_2Cl_2 at 0 °C under Ar, and the mixture was stirred at room temperature for 1 h. The addition of dry ether led to precipitation of the dication salt. The precipitates were collected, washed with dry ether three times, and dried *in vacuo* to give ($S_{ax}, S_{ax}, S, S, S, S$)-**II11** $4^+(\text{I}_3^-)_4$ (7.9 mg) containing some materials as a dark green powder.

(*S*_{ax},*S*_{ax},*S*,*S*,*S*,*S*)-**II11**⁴⁺ (I₃)₄: ¹H NMR (400 MHz, CD₃CN): δ/ppm 7.79 (1H, s), 7.67 (2H, d, *J* = 8.0 Hz), 7.53 (1H, t, *J* = 8.0 Hz), 7.22 (16H, d, *J* = 8.0 Hz), 6.80 (16H, d, *J* = 8.0 Hz), 5.42 (4H, s), 3.28 (48H, s).

• Preparation of 1,3,5-Benzenetriyltriethyne-2,2',2''-triyl{2,2'-bis[2,2-bis(4-dimethylaminophenyl)ethenyl]-3,3',4',5,5',6,6'-heptafluorobiphenyl} **II6**



A mixture of (*R*_{ax})-**II2** (13.4 mg, 16.1 μmol), 1,3,5-triiodobenzene (2.2 mg, 4.8 μmol), Pd(PPh₃)₄ (1.9 mg, 10 mol%) and CuI (0.3 mg, 10 mol%) in degassed Et₃N (1 mL) was heated at 50 °C for 16 h under Ar. After being diluted with water, the whole mixture was extracted with EtOAc twice. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, the solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 4→1) to give (*R*_{ax},*R*_{ax},*R*_{ax})-**II6** (9.1 mg) as a green solid in 73% yield. By a similar procedure, optically pure antipode (*S*_{ax},*S*_{ax},*S*_{ax})-**II6** was obtained from (*S*_{ax})-**II2**.

(*S*_{ax},*S*_{ax},*S*_{ax})/(*R*_{ax},*R*_{ax},*R*_{ax})-**II6**: m.p. 220-222 °C; ¹H NMR (400 MHz, CDCl₃): δ/ppm 7.69 (3H, s), 7.23 (6H, d, *J* = 8.8 Hz), 7.22 (6H, d, *J* = 8.8 Hz), 6.68 (6H, d, *J* = 8.8 Hz), 6.66 (6H, d, *J* = 8.8 Hz), 6.58 (6H, d, *J* = 8.8 Hz), 6.57 (6H, d, *J* = 8.8 Hz), 6.38 (6H, d, *J* = 8.8 Hz), 6.37 (6H, d, *J* = 8.8 Hz), 6.30 (3H, s), 6.26 (3H, s), 2.99 (18H, s), 2.96 (18H), 2.90 (18H, s), 2.88 (18H, s); ¹⁹F NMR (470 MHz, CDCl₃): δ/ppm -111.04 (3F, s), -133.40 (3F, d, *J* = 24 Hz), -136.97 (3F, s), -139.17 (6F, s), -156.95 (3F, s), -158.85 (3F, t, *J* = 22 Hz); ¹³C NMR (MHz, CDCl₃): δ/ppm 156.13 (C, d, *J*_{C-F} = 250 Hz), 150.46, 150.39, 150.23, 150.22, 149.16, 148.87 (C, d, *J*_{C-F} = 250 Hz), 148.42, 145.33 (C, d, *J*_{C-F} = 250 Hz), 144.95 (C, d, *J*_{C-F} = 250 Hz), 144.82 (C, d, *J*_{C-F} = 250 Hz), 140.40 (C, d, *J*_{C-F} = 250 Hz), 138.93 (C, d, *J*_{C-F} = 250 Hz), 135.01, 131.29, 131.12, 130.63, 130.63, 129.56, 129.56, 126.98, 126.91, 123.77 (C, d, *J*_{C-F} = 20 Hz), 123.52 (C, d, *J*_{C-F} = 20 Hz), 123.36, 121.25 (C, d, *J*_{C-F} = 15 Hz), 115.34 (C, d, *J*_{C-F} =

15 Hz), 111.71, 111.71, 111.71, 111.71, 111.61, 110.82, 99.76, 97.82, 97.79, 40.44, 40.41, 40.41, 40.41; IR (KBr): ν/cm^{-1} 2883, 2855, 2805, 1608, 1522, 1477, 1445, 1355, 1225, 1192, 1166, 1060, 948, 818; LR-MS (FD) m/z 2570 (M^+ , BP), 2571 (93), 2572 (54), 2569 (49), 2573 (25), 2574 (10); HR-MS (FD) Calcd. for $C_{156}H_{129}F_{21}N_{12}$: 2569.0128. Found: 2569.0145; UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 312 (194000), 275 (135000); (MeCN): 309 (181000), 272 (142000), 240 (119000).

($S_{\text{ax}}, S_{\text{ax}}, S_{\text{ax}}$)-**II6**: $[\alpha]_{\text{D}}^{24}$ (CHCl_3 , $c = 0.10$): -260

($R_{\text{ax}}, R_{\text{ax}}, R_{\text{ax}}$)-**II6**: CD (25 °C, CH_2Cl_2): $\lambda_{\text{ext}}/\text{nm}$ ($\Delta\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 386 (-32), 342 (+67), 234 (+72); (MeCN): 392 (-33), 342 (+70), 235 (+67).

Redox Potential Measurements

Redox potentials (E^{ox} and E^{red}) were measured by cyclic voltammetry in dry CH_2Cl_2 or dry MeCN containing 0.1 mol dm^{-3} Bu_4NBF_4 or Et_4NClO_4 as a supporting electrolyte, respectively. All of the values shown in the text are in E/V versus SCE measured at the scan of 100 mV s^{-1} . A Pt disk electrodes were used as the working and counter electrodes, respectively. The working electrode was polished using a water suspension of Al_2O_3 (0.05 μm) before use. The irreversible half-wave potentials were estimated from the anodic peak potentials (E^{pa}) as $E^{\text{ox}} = E^{\text{pa}} - 0.03$ or the cathodic peak potentials (E^{pc}) as $E^{\text{red}} = E^{\text{pc}} + 0.03$.

X-ray analyses

Crystal data of **II1** · CHCl_3

Crystals were obtained by recrystallizing from $\text{CHCl}_3/\text{hexane}$. $C_{49}H_{43}Cl_3F_8N_4$, $M_r = 946.25$, yellow prism, 0.40 x 0.40 x 0.20 mm^3 , triclinic $P\bar{1}$ (#2), $a = 11.360(6)$ Å, $b = 11.798(7)$ Å, $c = 16.916(9)$ Å, $\alpha = 97.162(11)^\circ$, $\beta = 90.868(5)^\circ$, $\gamma = 100.646(13)^\circ$, $V = 2209(3)$ Å³, ρ ($Z = 2$) = 1.422 g cm^{-3} , $T = 150$ K. The final $R1$ and $wR2$ values are 0.045 ($I > 2\sigma I$) and 0.123 (all data) for 9466 reflections and 577 parameters. Esds for **II1** are 0.003 Å for bond lengths and 0.14·0.2 ° for bond angles, respectively. CCDC 1436781.

Crystal data of II7²⁺(BF₄⁻)₂•CH₂Cl₂

Crystals were obtained by recrystallizing from CH₂Cl₂/Et₂O. C₄₉H₄₄B₂Cl₂F₁₆N₄, $M_r = 1085.41$, green needle, 0.50 x 0.01 x 0.01 mm³, monoclinic P21/c (#14), $a = 11.894(6)$ Å, $b = 16.430(8)$ Å, $c = 24.321(12)$ Å, $\beta = 91.298(11)^\circ$, $V = 4752(4)$ Å³, $\rho (Z = 4) = 1.517$ g cm⁻³, $T = 150$ K. The final $R1$ and $wR2$ values are 0.156 ($I > 2\sigma$) and 0.185 (all data) for 6943 reflections and 383 parameters. Esds for II7²⁺ are 0.014-0.03 Å for bond lengths and 1.0-1.4 ° for bond angles, respectively. CCDC 1436783.

Crystal data of II8•CHCl₃

Crystals were obtained by recrystallizing from CHCl₃/hexane. C₅₃H₄₅Cl₃F₆N₄, $M_r = 958.31$, yellow platelet, 0.40 x 0.05 x 0.05 mm³, orthorhombic $Pca2_1$ (#29), $a = 12.248(7)$ Å, $b = 20.989(12)$ Å, $c = 18.133(11)$ Å, $V = 4662(5)$ Å³, $\rho (Z = 4) = 1.365$ g cm⁻³, $T = 150$ K. The final $R1$ and $wR2$ values are 0.137 ($I > 2\sigma$) and 0.378 (all data) for 10378 reflections and 595 parameters. Esds for II8 are 0.009-0.015 Å for bond lengths and 0.7-1.1 ° for bond angles, respectively. CCDC 1436782.

Computational Methods**DFT calculations of II1**

DFT calculations were performed with the Gaussian 09 program package.^[S2] The geometries of the compounds were optimized using the B3LYP method with the 6-31G* basis set. The natures of the stationary points were assessed by means of vibration frequency analysis. (a) SCF Done: E(RB3LYP) = -2872.00748435 A.U. after 16 cycles. (b) SCF Done: E(RB3LPY) = -2872.00445863 A.U. after 16 cycles.

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