

Redox Switching of Conjugation Length Using 9,9,10,10-Tetraaryl-9,10-dihydrophenanthrene as an ON/OFF Unit: Preparation, X-ray Structure, and Redox Properties of Perfluorobiphenyl Derivative and Its S_NAr Reactions to π -Extended Analogues

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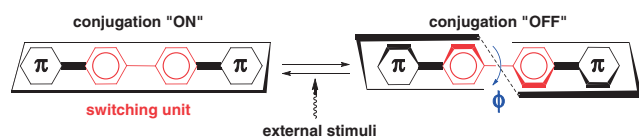
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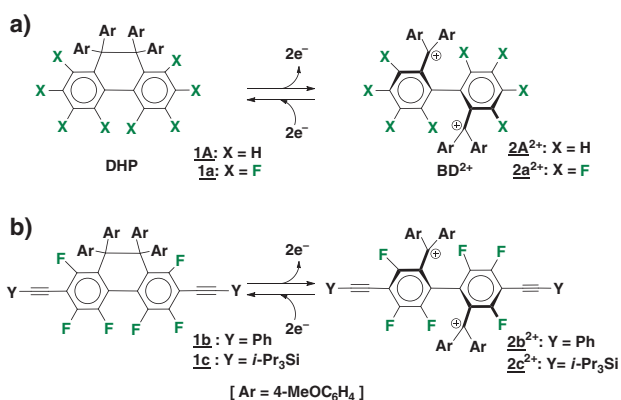
(Received March 5, 2013; CL-130190; E-mail: tak@mail.sci.hokudai.ac.jp)

Octafluorobiphenyl-2,2'-diylbis(diarylmethylium) dye $2a^{2+}$ prepared from 1,2-dibromotetrafluorobenzene is interconvertible with colorless dihydrophenanthrene donor $1a$. By the S_NAr reactions of $1a$ with acetylides, π -extended analogues $1b$ and $1c$ were obtained. Their electrochromic behavior is accompanied by a drastic absorption change not only in the visible but also UV region, because the torsion angle of the biaryl unit is modified upon redox reactions.

Biaryls can adopt various conformation in terms of the torsion angle (ϕ) about the central C–C bond.¹ Thus, the control of ϕ by external stimuli is a reliable protocol to modify π -conjugation between the two aryl groups in the biaryl unit² (Scheme 1). During the course of our studies on organic electrochromic systems with bistability (e.g., $1A/2A^{2+}$),³ we found that the biaryl geometry in the redox pairs of 9,9,10,10-tetraaryl-9,10-dihydrophenanthrenes (DHP) and biphenyl-2,2'-diyl-type dication (BD^{2+}) is drastically changed since their redox interconversion is accompanied by C–C bond formation/cleavage (Scheme 2):⁴ the biaryl unit in DHP is more or less coplanar (ϕ : ca. 20°) due to the C₉–C₁₀ ethano bridge whereas BD^{2+} adopts a twisted conformation (ϕ : ca. 70°). This finding



Scheme 1.



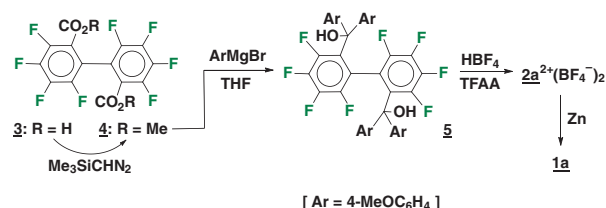
Scheme 2.

prompted us to design a novel biaryl-based switching unit to modify conjugation length using DHP/ BD^{2+} pairs.

Electron donor $1a$ is an octafluoro derivative of $1A$ and would be interconvertible with bond-dissociated dication $2a^{2+}$ upon two-electron transfer. Although the biphenyl skeleton has electron-withdrawing F atoms, the methoxy group on each aryl substituent would stabilize positive charges, generated upon two-electron oxidation, to allow isolation of dication $2a^{2+}$. The F atoms at the 6,6'-positions may increase the ϕ value in $2a^{2+}$, thereby enhancing geometric contrast of the switching unit in the ON and OFF states. The most important feature of octafluorobiphenyl moiety⁵ is the S_NAr reactivity toward nucleophiles including acetylides. Hence, $1a$ could be used as a synthon to prepare the 2,7-disubstituted derivatives, such as $1b$ and $1c$, whose switching phenomenon is more discernible due to a linearly π -extended chromophore with strong UV absorptions. Here we report preparation, redox behavior, and spectroscopic properties of $1/2^{2+}$ with the fluorobiphenyl skeleton.

Commercially available 1,2-dibromotetrafluorobenzene was converted to octafluorobiphenyl-2,2'-dicarboxylic acid 3 ,⁶ which was transformed into methyl ester 4 ⁷ in 91% yield (Scheme 3). Reaction of 4 with excess $ArMgBr$ gave diol 5 ⁷ in 54% yield, which was then transformed, under acidic dehydrating conditions, into stable dication salt $2a^{2+}(BF_4^-)_2$ ⁷ in 88% yield. Upon treatment with Zn powder, this salt gave $1a$,⁷ the switching unit with the fluorobiphenyl skeleton, in 97% yield. By the reaction of $1a$ with $(4-BrC_6H_4)_3N^+ SbCl_6^-$ (2 equiv), dication $2a^{2+}$ was regenerated and isolated as $(SbCl_6^-)_2$ salt⁷ in 87% yield. Such a high-yield interconversion indicates that $1a/2a^{2+}$ can be considered as a “reversible” redox pair although electrochemical reversibility is not maintained due to concomitant C–C bond formation/breaking (“dynamic redox pair”).³

According to X-ray crystallography,⁹ $1a$ adopts a helical geometry as in other DHP derivatives (Figures 1 and S1⁸). The torsion angle [$\phi(C_4-C_{4a}-C_{4b}-C_5)$: 35.1(4)°] is slightly larger than those of the related molecules.^{4b,4c} Nevertheless, as observed by VT-NMR spectroscopy, $1a$ undergoes an easy



Scheme 3.

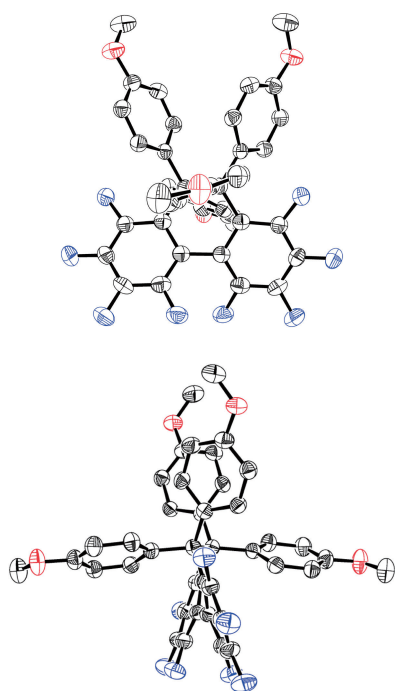


Figure 1. Two views of ORTEP drawing of **1a** in **1a**·1/3hexane solvate crystal (cubic, $Ia\bar{3}$, $Z = 24$, $T = 153$ K). The elongated C₉–C₁₀ bond [1.632(4) Å] is characteristic of the sterically congested DHP derivatives.³

Table 1. Redox potentials measured in MeCN^a

| Compd | | E^{ox} (1 → 2 ²⁺) | E^{red} (2 ²⁺ → 1) |
|--|------------------------------------|---|--|
| 1a / 2a ²⁺ | (X = F) | +1.56 | +0.37 |
| 1b / 2b ²⁺ | (Y = Ph) | +1.56 | +0.37 |
| 1c / 2c ²⁺ | (Y = <i>i</i> -Pr ₃ Si) | +1.61 | +0.38 |
| 1A / 2A ²⁺ ^b | (X = H) | +1.47 | +0.18 |

^a E /V vs. SCE, 0.1 M Et₄NClO₄, Pt electrode, scan rate 500 mV s⁻¹. All of the waves are irreversible, and the oxidation potentials (E^{ox}) and reduction potentials (E^{red}) were estimated as $E^{\text{anodic peak}} - 0.03$ and $E^{\text{cathodic peak}} + 0.03$ V, respectively. Ferrocene undergoes one-electron oxidation at +0.38 V under similar conditions. ^bRef. 4a.

ring-flip at room temperature¹⁰ suggesting that the steric repulsion caused by the bay-region substituents is not severe. Considering the $\cos^2 \phi$ -dependency¹¹ of effective π -conjugation in biaryls, ca. 70% of conjugation is still working in this “ON” state (Scheme 1). Although the precise geometry of dication **2a**²⁺ (the “OFF” state) is not available at this moment, as described below, the voltammetric analysis suggests that a drastic structural change takes place during the conversion of **1a** to **2a**²⁺.

The electrochemical oxidation of **1a** in MeCN occurs at +1.56 V (vs. SCE), which is an irreversible process as in the case of **1A** (Table 1). The corresponding cathodic peak is largely shifted to a negative potential region and assigned as the reduction process of **2a**²⁺ (Figure 2).⁸ Such a separation of redox peak is characteristic of the redox pairs with dynamic structural changes.³ Negligible steady-state concentration of the intermediary cation radical is another feature of the intercon-

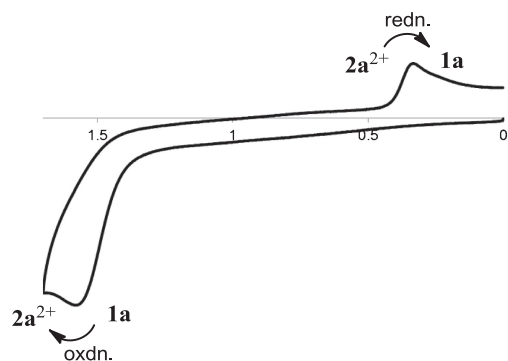


Figure 2. Cyclic voltammogram of **1a** measured in MeCN (E /V vs. SCE, 0.1 M Et₄NClO₄, Pt electrode, scan rate 500 mV s⁻¹).

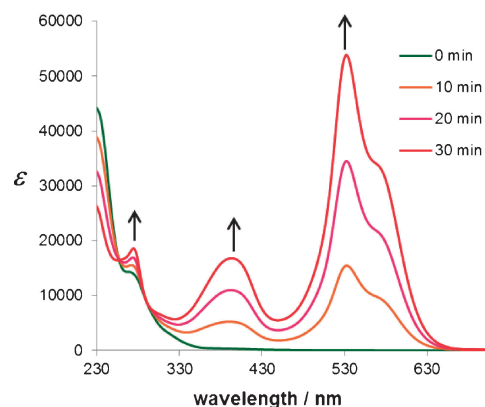
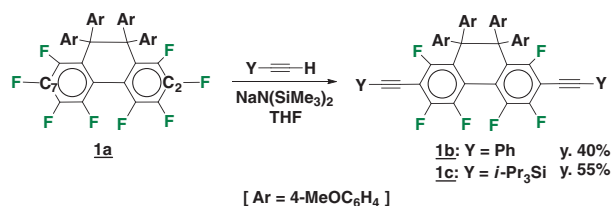


Figure 3. A continuous change in UV–vis spectrum upon constant current electrochemical oxidation of **1a** [4.2×10^{-5} M] in MeCN containing 0.05 M Et₄NClO₄ (60 μ A, every 10 min).

version between **1a** and **2a**²⁺, and thus a continuous change of UV–vis spectrum with several isosbestic points was observed upon electrolysis of **1a** (Figure 3). The strongest absorption in the visible region of **2a**²⁺ [λ_{max} 533 nm ($\log \epsilon$ 4.80) in MeCN]¹² is red-shifted compared with that of **2A**²⁺ [514 nm ($\log \epsilon$ 4.87)], since the electron-withdrawing nature of F lowers the LUMO of the dication, as shown by the less negative E^{red} of **2a**²⁺ by 0.2 V than that of **2A**²⁺. These observations clearly demonstrate that octafluoro derivative **1a** inherits attractive features of **1A** or other DHPs as a reversible electrochromic system with bistability.

We next turn our attention to use **1a** as a synthon to produce π -extended derivatives having a longer linear conjugation. As shown in Scheme 4, the S_NAr reaction of **1a** with ethynylbenzene or ethynyltriisopropylsilane under the presence of NaN(SiMe₃)₂ proceeded in an acceptable yield to give the corresponding 2,7-diethynyl derivative **1b** or **1c**. Upon treatment with (4-BrC₆H₄)₃N⁺ SbCl₆⁻ (2 equiv), **1b** and **1c** were transformed into stable dicationic salts **2b**²⁺(SbCl₆⁻)₂ (84% yield) and **2c**²⁺(SbCl₆⁻)₂ (87% yield), respectively. The redox potentials of the newly prepared redox pairs of **1b**/**2b**²⁺ and **1c**/**2c**²⁺ were virtually identical to that of **1a**/**2a**²⁺ (Table 1), since π -extension along the longer axis of the biphenyl skeleton hardly affects the frontier orbitals of **1a**/**2a**²⁺.



Scheme 4.

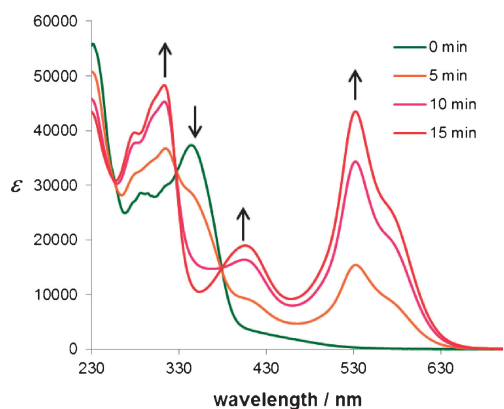


Figure 4. A continuous change in UV-vis spectrum upon constant current electrochemical oxidation of **1b** [1.7×10^{-5} M] in MeCN containing 0.05 M Et₄NClO₄ (60 μA, every 5 min).

Meanwhile, the UV absorption profiles¹² were significantly different among **1a–1c** (Figure S2).¹³ Thus, the π -extended compound **1b** has a strong band at 345 nm ($\log \epsilon$ 4.58 in MeCN), which is absent in **1a** [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 **1b** to **2b²⁺**, this band gradually disappeared with concomitant appearance of the blue-shifted band at 318 nm (4.79) (Figure 4). The observed behavior is best described as the successful ON/OFF switching of π -conjugation shown in Scheme 1 based on the external control of the torsion angle. It is noteworthy that interconversion between **1b** and **2b²⁺** is accompanied by a drastic change also in the visible region by reversible appearance/disappearance of triarylmethyl cation dye units. The redox pair of **1c/2c²⁺** likewise exhibited electrochromism, while the UV-region absorption bands were slightly blue-shifted in both states [**1c**: 330 nm (4.47); **2c²⁺** 275 nm (4.75) in MeCN]¹² (Figure S3).⁸

We are currently developing one-dimensional rod-like molecules¹⁴ with multiple numbers of the switching units, using bis(triisopropylsilylethynyl) derivative **1c** as a key intermediate.

This work was performed under the Cooperative Research Program of “Network Joint Research Center for Materials and Devices.” This work was supported by Grant-in-Aid for Scientific Research on Innovative Areas: “Organic Synthesis Based on Reaction Integration” (No. 2105) from MEXT, Japan.

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- 7 Experimental details and physical data for new compounds are given in Supporting Information (Ref. 8).
- 8 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- 9 Crystal data of **1a**·1/3hexane is as follows: C₄₄H_{32.67}F₈O₂, $M_r = 544.69$, pale yellow prism, $0.10 \times 0.10 \times 0.10$ mm³, cubic $Ia\bar{3}$ (#206), $a = 27.6408(9)$ Å, $V = 21118.0(12)$ Å³, $\rho(Z = 24) = 1.467$ g cm⁻³, $T = 123$ K, $\mu = 1.212$ 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 **1a** are 0.005–0.005 Å for bond lengths and 0.2–0.3° for bond angles, respectively. CCDC 923999.
- 10 Two of the four aryl groups are located at the quasi equatorial positions whereas other two at the quasi axial positions on the central 6-membered ring. According to the VT-NMR analysis, the two MeO resonances at 3.68 and 3.64 ppm are coalesced at 213 K (300 MHz). Thus, (*P*)- and (*M*)-**1a** are interconverting easily with the ring-flip energy-barrier of 11.0 kcal mol⁻¹, which is similar to that of DHP (12.6 kcal mol⁻¹) (Ref. 4).
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- 12 UV-vis spectral data [λ_{\max}/nm ($\log \epsilon$)] in MeCN are as follows. **1a**: 271 (4.15); **1b**: 345 (4.58); **1c**: 330 (4.47); **2a²⁺**(SbCl₆⁻)₂: 564sh (4.62), 533 (4.80), 380 (4.41), 275 (4.55); **2b²⁺**(SbCl₆⁻)₂: 570sh (4.62), 533 (4.87), 411 (4.45), 318 (4.79), 279 (4.79); **2c²⁺**(SbCl₆⁻)₂: 566sh (4.50), 534 (4.70), 409 (4.30), 274 (4.75). Close similarity in the wavelength of the first-band among **2a²⁺**–**2c²⁺** can be accounted for by assuming that the orbital coefficients in their frontier orbitals are localized on the bis(4-methoxyphenyl)(polyfluorophenyl)carbenium unit.
- 13 The “OFF”-state absorption was estimated by measuring the spectrum of 4,4'-bis(phenylethynyl)-2,2'-bis[bis(4-methoxyphenyl)methyl]-3,3',5,5',6,6'-hexafluorobiphenyl **H₂2b** [λ_{\max}/nm ($\log \epsilon$): 313 (4.76), 293 (4.78)] in CH₂Cl₂, which was obtained by hydride addition on **2b²⁺**(SbCl₆⁻)₂ using NaBH₄.
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