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Synthesis, X-ray crystallographic analysis, and theoretical structure analysis of tetrathienylethenes designed for photo- and electrochromism

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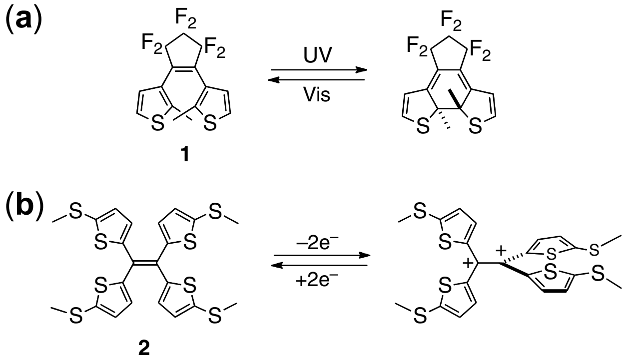
Dedicated to the memory of Professor Yoshihiro Matsumura (Nagasaki University)

Abstract—As part of an effort to develop a new chromic system that responds to both photoexcitation and electron transfer, tetrakis(2-methylthien-3-yl)ethene (**3a**) and its tetrakismethylthio derivative (**3b**) were synthesized. The results of X-ray crystallographic and theoretical analyses of these substances suggest that (1) conformers of **3** with an *antiparallel* arrangement of two vicinal thienyl groups will undergo photocyclization, and (2) the most stable conformer of **3** having an *anti-double parallel* conformation will not. These predictions were preliminarily confirmed by the results of photochemical and cyclic voltammetry studies.

1. Introduction

The reversible reaction interconverting *cis*-stilbene (*cis*-1,2-diphenylethene) and dihydrophenanthrene is a fundamental process in organic photochemistry. By replacing the phenyl groups of stilbene by thienyl groups and introducing a perfluoropropano-bridge, Irie et al. were able to develop so-called diarylethene photochromic systems (Scheme 1a, **1**).[1] Another consequence associated with incorporating thienyl groups is an enhancement of the oxidation ability of diarylethenes. In fact, Suzuki and Miyashi reported that tetrakis[5-(methylthio)thien-2-yl]ethene (**2**) displays electrochromic behavior associated with a dynamic change in its molecular geometry on two-electron transfer oxidation and reduction (Scheme 1b) and proposed a concept of ‘dynamic redox systems’.[2]

Based on these earlier findings and as part of an effort to develop a new chromic system that responds to both photoexcitation[3] and electron transfer,[5] we have designed tetrakis(2-methylthien-3-yl)ethene (Scheme 2, **3a**) and its tetrakismethylthio derivative (**3b**), of which expected photo- and electrochromism as shown in Scheme 2. In this Letter, we report the preparation of **3** and the results of X-ray crystallographic and theoretical analyses. This investigation has provided important information about their photo- and electrochromic properties, which are also reported preliminarily.



Scheme 1. (a) Photochromism of **1** and (b) electrochromism of **2**.

2. Synthesis

Tetrathienylethenes **3a**–**b** were synthesized starting with commercially available 3-bromothiophene (**5**) by the

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Keywords: Photochromism; Electrochromism; Electron transfer; Reaction mechanism.

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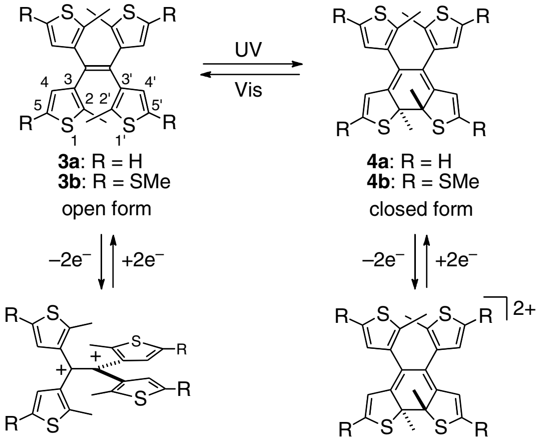
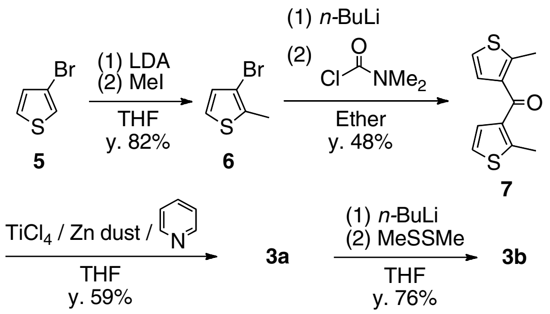


Scheme 2. Expected photo- and electrochromic behavior of **3** and **4**.



Scheme 3. Synthesis of **3**.

sequence shown in Scheme 3. 3-Bromo-2-methylthiophene (**6**) was produced from **5** by regioselective methylation[6] and then converted to bis(2-methylthien-3-yl)-ketone (**7**) by reaction with *N*,*N*-dimethylcarbamoyl chloride.[7] McMurry coupling reaction of **7** using $TiCl_4$ and Zn gave **3a**,[8] which was converted to **3b** by sequential lithiation and treatment with dimethyl disulfide.[2]

3. X-ray crystallographic analysis

It is important to gain information about the structures of **3a–b** because it is known that the *antiparallel* orientation of vicinal thienyl groups in **1** is essential for facile photocyclization to take place, especially in the crystalline state.[1] The X-ray crystallographic structures of **3a** and **3b** are shown in Figure 1.[9–11] In the case of **3a**, two pairs of vicinal thienyl groups are oriented in a *parallel* arrangement, while the pairs of geminal thienyl groups exist in a *syn* orientation (Fig. 1, top). Likewise, in **3b** two pairs of vicinal thienyl groups are arranged in a *parallel* orientation (Fig. 1, bottom). In contrast, two pairs of the geminal thienyl groups in **3b** exist in an *anti* arrangement. Therefore, in the crystalline state, **3a** and **3b** have *syn-double parallel* and *anti-double parallel* conformations, respectively.

To gain more insight into the differences of **3a** (*syn-double parallel*) and **3b** (*anti-double parallel*) in the molecular structures, we analyzed the crystal structures and searched for a possible S···S contact that often induces geometric changes in the crystalline state. Although no significant S···S contact was found, we conclude that the crystal structures of **3a** and **3b** may be a result of crystal packing forces because the calculation result described below indicated that the energy gap between the most stable *anti-double parallel* conformer and the most unstable *syn-double parallel* conformer is only ca. 1.4 kcal/mol for **3a** and ca. 1.9 kcal/mol for **3b**.

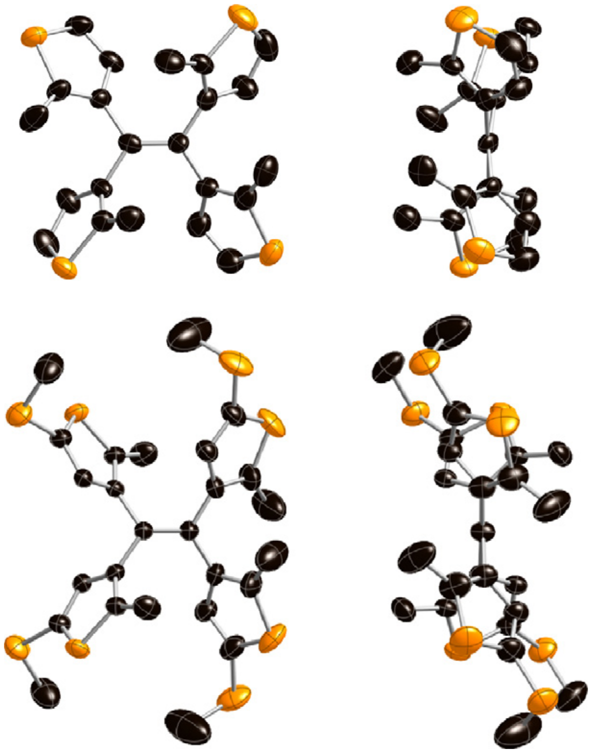


Figure 1. ORTEP drawings of **3a** (top, *syn-double parallel*) and **3b** (bottom, *anti-double parallel*), derived from X-ray crystallographic data displayed with 50% probability thermal ellipsoids. Hydrogen atoms are not shown for clarity.

4. Semiempirical theoretical analysis

The existence of two pairs of vicinal thienyl groups with *parallel* orientations in the structures of **3a** and **3b** indicates that these substances will only reluctantly undergo photocyclization reactions to form **4** in the crystalline state. However, if the *antiparallel* conformers can be populated even to a small extent in solution, **3a** and **3b** might be capable of undergoing photocyclization reactions. Therefore, knowledge about the structures of **3a–b** in solution and the gas phase is important to understand the potential chromic properties of these substances. For this purpose, the structures and conformer energies of **3b** were determined by using PM3 based calculations.[12]

In Figure 2 is shown the five, theoretically derived, major conformations of **3b**, which include in order of their decreasing stability (i) *anti-double parallel* ($E^{\text{rel}} =$ 0 kcal/mol), (ii) *antiparallel* and *parallel* (ca. 0.9 kcal/mol),

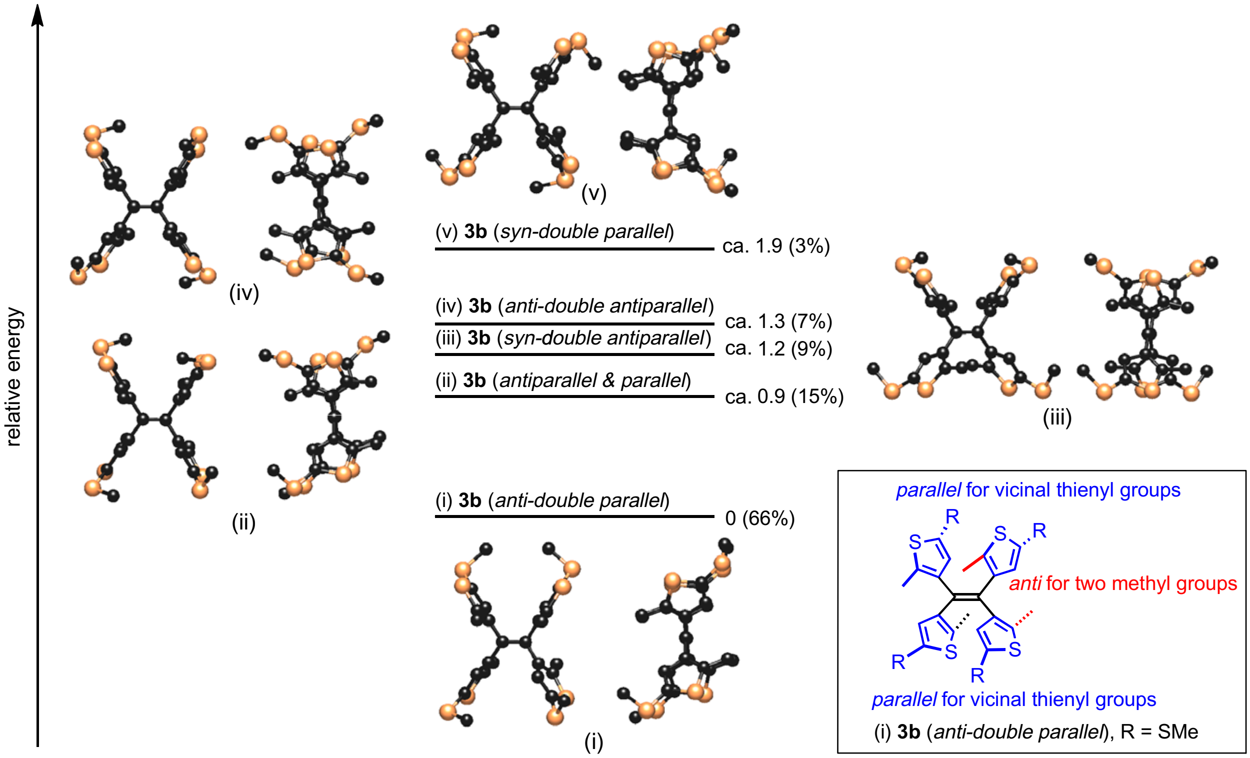


Figure 2. Conformers of **3b**, their relative energies (kcal/mol) calculated by using the PM3 method,[15] and the existence ratios at 298 K. Left: front view, right: side view.

(iii) *syn-double antiparallel* (ca. 1.2 kcal/mol), (iv) *anti-double antiparallel* (ca. 1.3 kcal/mol), and (v) *syn-double parallel* (ca. 1.9 kcal/mol).[15] The conformers are predicted to exist in an approximate ratio of 66:15:9:7:3 at $T = 298$ K. The most stable *anti-double parallel* conformer of **3b** is the one that exists in the crystalline state of this substance. Although photocyclization reaction of this conformer is predicted to be difficult,[1] the metastable *antiparallel* and *parallel*, *syn-double antiparallel,* and *anti-double antiparallel* conformers, calculated to comprise 31% of **3b**, should undergo this photocyclization. This prediction is supported by the relatively short C···C contacts (4.23 Å for the *antiparallel* and *parallel* conformer, 3.93 and 4.36 Å for the *syn-double antiparallel* conformer, and 4.33 and 4.51 Å for the *anti-double antiparallel* conformer) seen between C2 and C2′ of the vicinal thienyl groups of **3b**. This observation suggests that photoreaction of **3b** to **4b** should be facile.[16]

5. Preliminary studies of the photo- and electrochromic properties

The crystal state photochemistry of **3a–b** was investigated first. Single crystals of **3a** or **3b**, prepared by crystallization from EtOH and CH_2Cl_2–MeOH, respectively, were irradiated with 335 nm UV light.[17] No obvious changes were observed in the color of the crystals or the UV–vis absorption spectra of CH_2Cl_2 solutions of the crystals even after 1-h irradiation. The lack of photoreactivity of **3a–b** is likely due to the fact that the thienyl groups are arranged in a *parallel* orientation of the vicinal thienyl groups in the single crystalline state (Fig. 1).

In contrast, photochromism of **3** was observed in solution. Upon irradiation with UV light (350 nm) for 1 min, a CH_2Cl_2 solution of **3a** (5×10^{-5} M) underwent a change from colorless to pale yellow associated with growth of absorption bands at $\lambda_{ab} = 314$ and ca. 463 nm ($A =$ ca. 0.03).[18] The 463-nm band disappeared almost completely, when the resulting solution was irradiated with Vis light (450 nm)[17] for 30 min.[18] Similar but even more facile photochromism was observed with **3b**. A colorless solution of **3b** in CH_2Cl_2 quickly turned to orange when irradiated with UV light (350 nm) for 0.5 min. The new absorption bands at $\lambda_{ab} = 327$ and 489 nm ($A =$ ca. 0.08) along with the orange color slowly disappeared when the solution was exposed to Vis light (490 nm) for 5 min (Fig. 3). The similar absorption band at 490 nm, which arose by irradiating **3b** in cyclohexane, also disappeared when the solution was heated at 60 °C. The photochromic processes were repeated several times, suggesting that the colored products formed in the photoreactions are cyclic isomers **4**.[18] The results demonstrate that **3a–b** are photochromic in the solution phase.

Cyclic voltammetry (CV)[19] studies have been used to establish the electrochromic properties of **3b**. Initial information came from inspection of the cyclic voltammogram of **3b** in CH_3CN containing 0.1 M Et_4NClO_4. The cyclic voltammogram of **3b** showed at first a wave

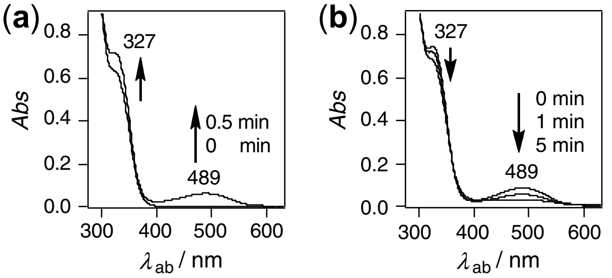


Figure 3. UV–vis spectral changes of **3b** (5.0×10^{-5} M) (a) on UV (350 nm) irradiation for 0.5 min and (b) on the succeeding Vis (490 nm) irradiation for 5 min in CH_2Cl_2.

at E_{ap} (anodic peak potential) = ca. +0.76 V vs Ag/Ag^+ for single electron transfer (SET) oxidation (Fig. 4). This wave was not completely reversible, the reduction wave being observed at E_{cp} (cathodic peak potential) = ca. +0.14 V. A successive scanning of the solution gave a new wave at E_{ap} = ca. +0.21 V, which was shown to correspond to the SET oxidation potential of **4b** by the observation that the CV of **4b**, generated on UV irradiation of **3b** in CH_3CN containing 0.1 M Et_4NClO_4, has an E_{ap} = ca. +0.23 V and an E_{cp} = ca. +0.17 V. Thus, the occurrence of an ECE mechanism strongly suggests that **3b** is irreversibly transformed to **4b** via **3b**$^{\cdot+}$ and **4b**$^{\cdot+}$ upon SET promoted oxidation. Considering that cycloreversion of **4b** to **3b** occurs thermally, the observations conclude that **3b** displays electrochromic behavior (Scheme 4), which is quite different form the first expectation shown in Scheme 2. The cyclization of **3b**$^{\cdot+}$ is assumed to proceed also from its *antiparallel* conformers.

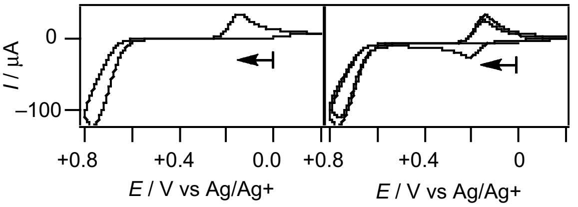
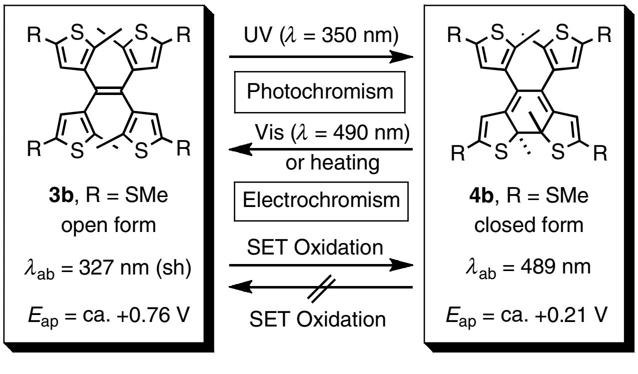


Figure 4. Cyclic voltammograms (scan rate, 10 mV/s) of **3b** on one- (left) and two-cycle scans (right) in CH_3CN containing 0.1 M Et_4NClO_4.



Scheme 4. A plausible photo- and electrochromism of **3b** and **4b**.

6. Conclusion

The results described above show that the new tetrathienylethenes **3** are dual chromic compounds in photo- and electrochromism: they undergo color changes in response to both photoexcitation (**3a–b**) and SET oxidation (**3b**). X-ray crystallographic analysis and semiempirical calculations suggest that the *antiparallel* conformations of **3** allow them to cyclize to form **4**, while the most stable *anti-double parallel* conformer will be reluctant to cyclize. The predictions gain support from the observation that irradiation of these substances in the crystalline state does not result in formation of **4**. In contrast, upon irradiation or electrochemical oxidation **3** are transformed to **4**. Detailed studies of the photo- and electrochromic properties[20,21] of **3** and **4** are now in progress.

Acknowledgements

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Supplementary data

The PM3 calculation result for **3b** [(i) *anti-double parallel*], and **4b** [(vi) *anti-antiparallel* and *trans*], and energy diagram for the conformers of **3a**/**4a** and **3b**/**4b**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.09.100.

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8. *Physical data of key and new compounds* **6**: Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ_{ppm} 2.40 (s, 3H), 6.89 (d, $J = 5.4$ Hz, 1H), 7.06 (d, $J = 5.4$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ_{ppm} 14.44, 109.39, 122.79, 129.96, 134.21; IR (neat) 590, 766, 785, 853, 1003, 1084, 1155, 1340, 1439, 1528, 2856, 2920 cm^{-1}; EIMS *m/z* 177 (35, M^+), 176 (66), 175 (33), 97 (100). Compound **7**: Colorless solid (*n*-hexane), mp 99–100 °C; ^{1}H NMR ($CDCl_3$) δ_{ppm} 2.66 (s, 6H), 7.01 (d, $J = 5.4$ Hz, 2H), 7.12 (d, $J = 5.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ_{ppm} 14.95 (2C), 121.08 (2C), 129.63 (2C), 137.80 (2C), 147.66 (2C), 187.46; IR (KBr) 716, 739, 849, 1265, 1366, 1435, 1520, 1638 cm^{-1}; EIMS *m/z* 222 (63, M^+), 221 (24), 209 (10), 208 (15), 207 (100), 189 (36), 174 (13), 161 (13), 125 (46), 97 (19), 96 (12), 53 (22); Anal. Calcd for $C_{11}H_{10}S_2O$: C, 59.43; H, 4.53; S, 28.84. Found: C, 59.73; H, 4.62; S, 29.08. Compound **3a**: Colorless solid (CH_2Cl_2–MeOH); mp 203–204 °C; ^{1}H NMR ($CDCl_3$) δ_{ppm} 1.92 (s, 12H), 6.49 (d, $J = 5.4$ Hz, 4H), 6.84 (d, $J = 5.4$ Hz, 4H); ^{13}C NMR ($CDCl_3$) δ_{ppm} 13.72 (4C), 120.49 (4C), 130.23 (4C), 131.65 (2C), 136.18 (4C), 139.18 (4C); IR (KBr) 646, 660, 708, 725, 835, 1256, 1429 cm^{-1}; UV (CH_2Cl_2) $\lambda = 314$ nm (max, $\log\varepsilon = 4.17$); EIMS *m/z* 412 (100, M^+), 397 (15), 207 (12), 414 (20); Anal. Calcd for $C_{22}H_{20}S_4$: C, 64.04; H, 4.89; S, 31.08. Found: C, 3.84; H, 4.98; S, 31.78. Compound **3b**: Colorless solid (CH_2Cl_2–*n*-hexane): mp 119–120 °C; ^{1}H NMR ($CDCl_3$) δ_{ppm} 1.90 (s, 12H), 2.34 (s, 12H), 6.50 (s, 4H); ^{13}C NMR ($CDCl_3$) δ_{ppm} 14.02 (4C), 22.47 (4C), 131.21 (2C), 131.82 (4C), 134.63 (4C), 138.83 (4C), 139.60 (4C); IR (KBr) 507, 860, 966, 1151, 1188, 1204, 1312, 1418, 1431 cm^{-1}; UV (CH_2Cl_2) $\lambda = 327$ nm (sh, $\log\varepsilon = 4.10$); HRMS (ESI) Calcd for $C_{26}H_{28}S_8$+Na, 618.9849; found, 618.9846. Anal. Calcd for $C_{26}H_{28}S_8$: C, 52.31; H, 4.73; S, 45.05. Found: C, 52.40; H, 4.94; S, 43.94.
9. Crystallographic data of **3a** and **3b** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC 654282 and 654283, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
10. Figure 1 was depicted with CrystalMaker for Mac OS X Ver. 7.2.3 2006.[11]
11. CrystalMaker Software Limited. Website: http://www.crystalmaker.com.
12. PM3 calculations were performed using the program GAUSSIAN 98.[13] The Cartesian coordinates for the optimized structures of **3b** [(i) *anti-double parallel*] and **4b** [(vi) *anti-antiparallel* and *trans*] are given in the Supplementary data. Molecular geometries in Figure 2 were drawn using the WinMOPAC 3.9 software.[14]
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15. The energies obtained by using the PM3 method were assumed to contain considerable errors as compared with those arising from DFT calculations, which are now in progress.
16. Calculations indicate that photoproduct **4b** can exist in three conformationally isomeric forms, including (vi) *anti-antiparallel* and *trans*{ca. 20.1 kcal/mol relative to **3b** [(i) *anti-double parallel*]}, (vii) *parallel* and *trans* (ca. 20.7 kcal/mol), and (viii) *syn-antiparallel* and *trans* (ca. 21.2 kcal/mol),[15] in a ratio of 66:24:10 at 298 K. A similar energy diagram was obtained for **3a** and **4a**. For the detail, see the Supplementary data.
17. A single crystal or solution of **3** was irradiated with a 150 W Xe lamp [$\lambda = 335$ or 350 nm for UV, 450 or 490 nm for Vis, band pass 20 nm] through a spectrometer equipped to a JASCO FP-6300 spectrofluorometer.
18. A prolonged UV irradiation of **3** resulted in the formation of an unidentified product (**8**). The photocycloreversion of **4** to **3** may be concurrent with the formation of **8**. Isolation of **4** and **8** and identification of **8** are now in progress and will be published elsewhere.
19. E_{ap} and E_{cp} were measured on the ALS model 600C electrochemical analyzer by CV (Pt electrode, scan rate 10 mV/s) in CH_3CN containing Et_4NClO_4 (0.1 M) as a supporting electrolyte.
20. An attempt of electron-transfer reactions using one-electron oxidant was also investigated preliminarily. For example, the oxidation of **3b** with tris(*p*-bromophenyl)-aminium hexachloroantimonate (2 equiv $\lambda_{max} = 728$ nm) in CH_2Cl_2 resulted in the coloration of the solution ($\lambda_{max} = 582$ nm), suggesting a formation of $\mathbf{4b}^{2+}$ The detail will be given elsewhere.
21. As one of the reviewers pointed out, the stereochemistry of the products of photochemical and electrochemical reactions is a quite important issue. In our case, it is strongly suggested that the product **4b** of photochemical reaction is identical with that of electrochemical reaction, because their oxidation potentials are almost the same (See the text). The detail will be given elsewhere.