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pK_a Switching Induced by the Change in the π-Conjugated System Based on Photochromism

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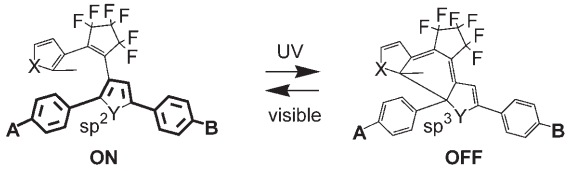
Abstract: Two diarylethene derivatives **1a** and **2a** containing a 2,5-diaryl-3-thienyl group have been designed and synthesized. The pK_a values of these compounds change upon photoirradiation. They have a phenol group as a proton source and a pyridinium group as an acceptor unit at each end of the π-conjugated chain. The cyclization/cycloreversion reactions can be used to control the length of the π-conjugated chain between the proton source and the acceptor. The change in the π-conjugated chain length caused the pK_a-switching.

Keywords: conjugation · diarylethenes · molecular devices · photochromism · pK_a switches

Introduction

Various molecular switching systems have been extensively explored to apply them to molecular devices.[1] Among them, photoswitching systems are advantageous from the viewpoint of fast response and high sensitivity. Most photoswitching systems are composed of a photochromic unit and a functional group. Photochemical as well as photophysical property changes of the photochromic unit control the performance of the functional group. Diarylethene derivatives are widely used as the photochromic unit to control photoswitching systems.[2] Changes in the π-conjugated chain length of diarylethene derivatives upon photoirradiation can be successfully used to control electronic conduction, donor–acceptor interactions, and magnetic interactions.[3–6] Lehn and co-workers reported pK_a-switching systems that use a diarylethene with a phenol group as a proton source and a pyridinium group as an acceptor at each end of the diarylethene π-conjugated chain.[7] The proton dissociation was accelerated in the closed-ring isomer by the enhanced acceptor effect of the pyridinium ion.

The switching of diarylethenes so far reported has been based on the fact that π conjugation between two aryl groups is disconnected in the open-ring isomer and connected in the closed-ring isomer. The switching mode can be reversed by placing two interaction units in the same aryl unit (Scheme 1). The interconversion of the orbital hybridization of the reactive carbon from sp^2 to sp^3 can be used to control the π-conjugated chain length.



Scheme 1. Photoswitching by placing two interaction units (A and B) in the same aryl unit.

In this work, we report on pK_a-switching systems based on the interconversion of the orbital hybridization.

Results and Discussion

Design and synthesis: To control the pK_a, diarylethene derivatives **1a** and **2a** were designed (Scheme 2). These compounds have a phenol group as a proton source and a pyridinium group as an acceptor unit.[8] In compound **1**, both the

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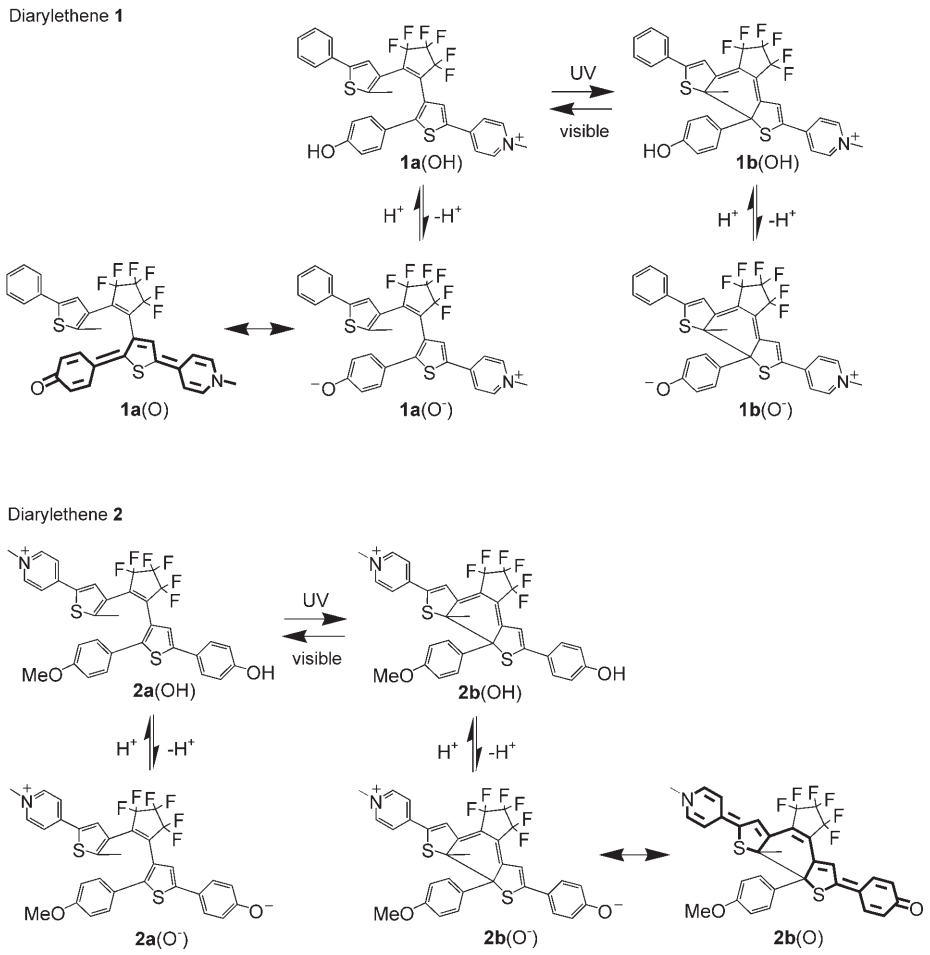


Scheme 2. Design of pK_a switching systems.

pyridinium and phenol units are located on the same thiophene ring. The donor and acceptor groups of the open-ring isomer **1a** can interact through the π-conjugated chain, however, the closed-ring isomer **1b** does not have this ability because the π-conjugated system between the pyridinium and phenol units has been disconnected by the formation of a sp^3-hybridized carbon atom at the 2-position of the thiophene ring.[9,10] In compound **2**, the phenol unit interacts with the electron-donating methoxy group in the open-ring isomer, however, in the closed-ring isomer the electron-accepting pyridinium group interacts with the phenol group. This switch from the methoxyphenyl to the pyridinium group is anticipated to affect the pK_a of the phenol group.

Diarylethenes **1** and **2** were synthesized according to the routes shown in Scheme 3. We were unable to synthesize **3** from route B, therefore, we employed route A. The deprotection of the methoxymethyl (MOM) group and the *N*-alkylation were carried out with $CF_3SO_3CH_3$.[11,1]

Photochromic reactions

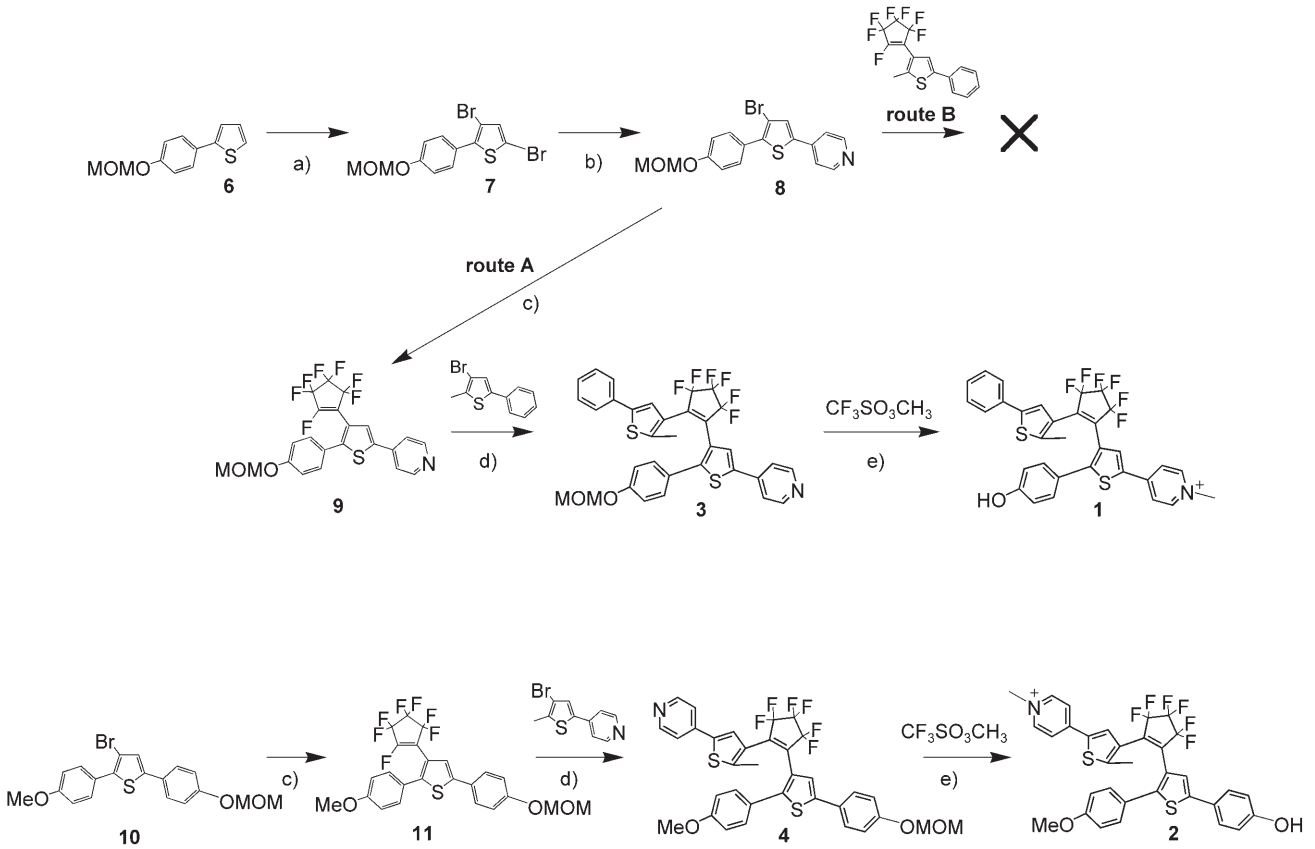
*Compounds **1** and **3***: Diarylethenes **1** and **3** underwent reversible photochromic reactions by means of alternative irradiation with $\lambda = 365$ and > 600 nm light (see the Supporting Information). Upon irradiation with UV light, a solution of **3** in methanol changed from colorless to blue and a new absorption maximum was observed at $\lambda = 600$ nm. On the other hand, the solution of *N*-methylated compound **1** changed from light yellow to green. The absorption maximum of the photogenerated isomer showed a redshift to $\lambda =$ 662 nm.

Upon addition of base, the absorption spectra of **1a** and the photostationary-state solution changed as shown in Figure 1. The absorption band of **1a** at $\lambda = 380$ nm decreased and a new band appeared at $\lambda = 465$ nm. The absorption maximum showed a redshift of as much as $\lambda = 80$ nm, which suggests the presence of a strong intramolecular donor–acceptor interaction between the phenoxide and pyridinium units.[13,14] In the photostationary state, the bands at $\lambda = 380$ and 660 nm decreased and the band at $\lambda = 470$ nm increased. The band at $\lambda = 660$ nm was slightly redshifted.

*Compounds **2** and **4***: Upon irradiation with UV light, the solution of **4** in methanol changed from colorless to blue and a new absorption maximum was observed at $\lambda = 600$ nm. On the other hand, the solution of *N*-methylated compound **2** changed from light yellow to green. As a result of the *N*-methylation, the absorption maximum of the photoirradiated solution shifted to a longer wavelength by as much as $\lambda =$ 66 nm (see the Supporting Information).

Although diarylethene **4** underwent reversible, photochromic reactions in methanol, the closed-ring isomer **2b** decomposed on irradiation with $\lambda = 365$ nm UV light even under neutral conditions. The decomposition was strongly suppressed by the addition of acid. It is inferred from this acid effect that the deprotonated closed-ring isomer **2b**(O^-) is not stable on being irradiated with UV light. A similar phenomenon has also been reported for a diarylethene with phenol groups.[5]

Upon addition of base, the absorption spectra of **2a** and the photostationary-state solution changed as shown in Figure 2. The absorption band of **2a** at $\lambda = 300$ nm decreased. In the photostationary state, the bands at $\lambda = 300$ and 666 nm decreased and the band at $\lambda = 732$ nm increased.



Scheme 3. Synthetic routes to compounds **1** (above) and **2** (below). Reagents and conditions: a) *N*-bromosuccinimide (NBS) and THF; b) *n*BuLi, $B(OBu)_3$, and then $[Pd(PPh_3)_4]$, 4-bromopyridine hydrochloride, 20 wt% Na_2CO_3 (aq), and THF; c) *n*BuLi, and then octafluorocyclopentene and THF; d) *n*BuLi and THF; e) dichloromethane.

On the addition of base, the absorption maximum at $\lambda =$ 666 nm showed a redshift of as much as $\lambda = 66$ nm.

Photochemical switching of the pK_a: pK_a values of the open- and closed-ring isomers were determined spectroscopically for compounds **1** and **2** in a mixed solvent of methanol/water (5:2). The colored isomers were very stable. Thermal cycloreversion was not observed during the acid–base titrations at room temperature. Figures 3 and 4 illustrate the acid–base titration curves for **1** and **2**, respectively. The curves were obtained by measuring the absorption changes at $\lambda = 475$ nm for **1a** and at $\lambda = 350$ nm for **2a**. The absorption changes at $\lambda = 660$ and 770 nm were followed for **1b** and **2b**, respectively. The pK_a value of **1a** was determined to be 9.8, whereas it increased to 10.2 for **1b**. The pK_a value of **1** increased upon photoirradiation. The difference in the pK_a values between **1a** and **1b** is very small. To increase the change in pK_a upon photoirradiation, we designed compound **2** and measured the photoirradiation effect. The switch from the donor methoxyphenyl group to the acceptor pyridinium group is anticipated to strongly perturb the proton dissociation of phenol in **2**. The pK_a values of **2a** and **2b** were determined to be 10.2 and 9.0, respectively. In compound **2**, a reversible pK_a change upon irradiation with UV and visible light was observed.

To reveal the difference in behavior between **1** and **2**, theoretical calculations were carried out by using the B3LYP/6-31G(d)[15] method in Gaussian 03.[16] The results are summarized in Table 1 and Figure 5. E(OH) and $E(O^-)$ are the total energies of the OH and O^- forms, respectively, and ΔE(prot) is the difference between E(OH) and $E(O^-)$. When ΔE(prot) is small, a proton readily dissociates even at low pH.[17] This result indicates that the pK_a of **1a** is smaller than that of **1b**. On the other hand, the pK_a of **2b** is much smaller than that of **2a**. Moreover, the difference in ΔE(prot) between the open- and closed-ring isomers for **2** is larger than that for **1**. The calculated results agree well with the experimental results.

Although both **1** and **2** showed pK_a changes upon photoisomerization between the two isomers, the effect observed for **1** was much smaller than expected. The pK_a of **1a**(OH) was larger than that of **2b**(OH). To reveal the reason for this, theoretical calculations of the most stable conformations of **1a**(O^-) and **2b**(O^-) were carried out. Figure 5 shows the conformations of **1a**(O^-) and **2b**(O^-). The molecular planarity of the π-conjugated chains, that is, pyridinium–thiophene–phenoxide rings, is of interest here. The planarity is strongly perturbed in the case of **1a**(O^-), whereas in **2b**(O^-), the pyridinium and phenoxide groups are almost coplanar. The phenoxide group rotates due to the steric hin-

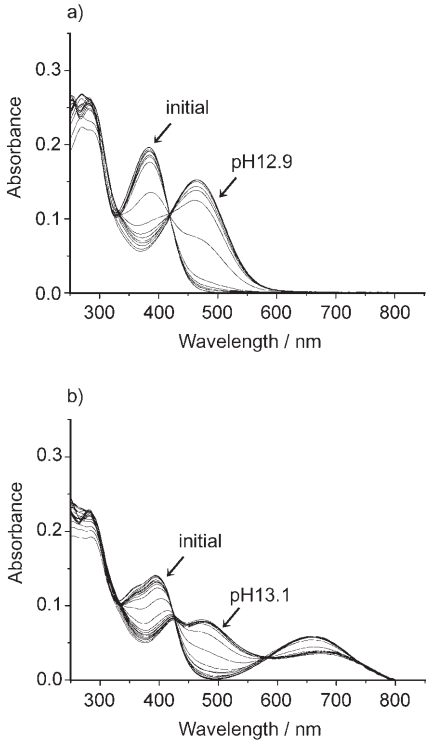


Figure 1. a) Absorption spectral change of **1a** in a mixed solvent (CH_3OH/water 5:2) following the addition of aqueous KOH. b) Absorption spectral change of the photostationary-state solution under irradiation with $\lambda = 365$ nm light in a mixed solvent (CH_3OH/water 5:2) following the addition of aqueous KOH.

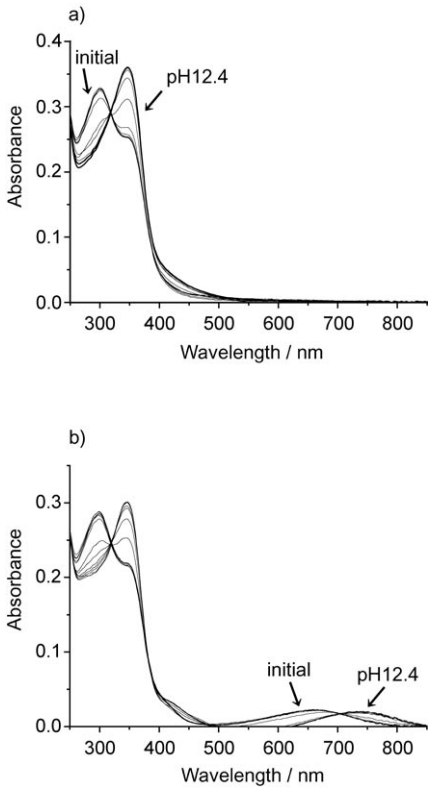


Figure 2. a) Absorption spectral change of **2a** in a mixed solvent (CH_3OH/water 5:2) following the addition of aqueous HCl and aqueous KOH. b) Absorption spectral change of the photostationary-state solution under irradiation with $\lambda = 365$ nm light in mixed solvent (CH_3OH/water 5:2) following the addition of aqueous KOH.

drance between the phenylthiophene group and the phenoxide group. This is the reason why **1a** cannot have a low pK_a. On the other hand, the planar conformation is attained in form **2b**(O^-), which results in the formation of quinoid structure **2b**(O). The steric hindrance prevents a large pK_a change in compound **1**.

The photochromic reaction was also affected by the addition of base. Under high-pH conditions, that is, pH values greater than the pK_a of **1a**(OH), the photocyclization reaction of **1a**(O^-) was strongly prohibited. This is ascribed to the formation of the quinoid-type resonance structure **1a**(O).[18]

Conclusion

Diarylethene derivatives **1** and **2** showed reversible, photoinduced changes in pK_a based on photoisomerization between open- and closed-ring isomers. A change in the π-conjugated system in one of the aryl groups caused the pK_a to change. The pK_a change of compound **1** from 9.8 to 10.2 upon UV irradiation was smaller than that observed for compound **2**, in which the pK_a value decreased from 10.2 to 9.0. To explain the small effect observed for **1**, theoretical calculations were carried out. The small difference in pK_a for **1** is attributed to the nonplanar conformation of the pyridinium–thiophene–phenoxide rings in the open-ring isomer. The conformation of the molecules also plays an important role in controlling the pK_a in addition to the configurational change between the open- and closed-ring isomers. The concept of changing the π-conjugated system in one of the aryl groups by means of the photocyclization reaction is useful for controlling molecular properties, such as, magnetic interactions, electric conduction, and energy transfer, among others.

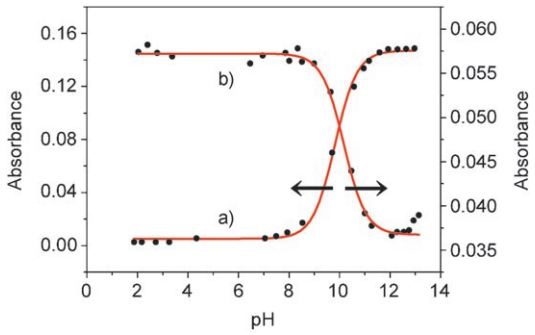


Figure 3. a) Titration curve of **1a**. The absorption change at $\lambda = 475$ nm was monitored in the pH range from 12.94 to 1.88 in a mixed solvent (CH_3OH/water 5:2). b) Titration curve of **1b**. The absorption change at $\lambda = 660$ nm was monitored in the pH range from 13.11 to 2.05 in a mixed solvent (CH_3OH/water 5:2).

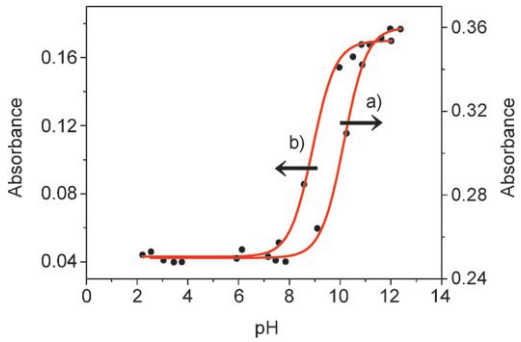


Figure 4. a) Titration curve of **2a**. The absorption change at $\lambda = 350$ nm was monitored in the pH range from 12.37 to 2.91 in a mixed solvent (CH_3OH/water 5:2). b) Titration curve of **2b**. The absorption change at $\lambda = 770$ nm was monitored in the pH range from 12.40 to 2.59 in a mixed solvent (CH_3OH/water 5:2).

Table 1. Relative energies calculated at the B3LYP/6-31G(d) level of theory and the experimental pK_a values for **1** and **2**.

	E(OH) [a.u.][a]	E(O$^-$) [a.u.][a]	ΔE(prot) [kJ mol^{-1}]	pK_a
1a	−2757.8168	−2757.3767	66.01	9.8
1b	−2757.7816	−2757.3057	71.37	10.2
2a	−2872.3421	−2871.8701	70.79	10.2
2b	−2872.3149	−2871.8866	64.24	9.0

[a] a.u. = atomic units.

Experimental Section

General: ^{1}H NMR spectra were recorded on a Bruker AVANCE-400 spectrometer operating at 400 MHz. UV/Vis spectra were recorded on a Hitachi U-3500 absorption spectrophotometer. Fast-atom bombardment (FAB) high-resolution mass spectrometry (HRMS) data were obtained on an JEOL JMS mate II instrument. Photoirradiation was carried out by using a 500 W super-high-pressure mercury lamp as the light source.

Determination of pK_a: Measurements of the pH values were carried out by using a HORIBA pH meter F-51. The pK_a values were calculated by using the Henderson–Hasselbach equation derived from the absorbance spectral data.

In this work, all acid–base titrations were carried out from pH ≈ 13 to 2 by using aqueous HCl and aqueous KOH. The pK_a values of the closed-ring isomers were determined from the absorbance in the photostationary state under irradiation with $\lambda = 365$ nm light.

Syntheses

*4-[4-(2,3,3,4,4,5,5-heptafluorocyclopent-1-enyl)-5-(4-methoxymethoxyphenyl)thiophen-2-yl]pyridine (**9**)*: Under an argon atmosphere, a solution of 15% *n*-butyllithium in hexane (7.6 mL, 1.2 mmol) was added to a stirred solution of 3-bromo-2-(4-methoxymethoxyphenyl)-5-(4-pyridyl)thiophene **8** (4.00 g, 10.6 mmol) in dry THF (250 mL) at −78 °C. After 30 min, octafluorocyclopentene (5.7 mL, 42.4 mmol) was added to the reaction mixture at −78 °C. The mixture was left to reach room temperature. After 1.5 h, the reaction was stopped by the addition of water. The product was extracted with diethyl ether and washed with brine three times. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by using silica gel column chromatography with hexane/ethyl acetate (1:2) as the eluent. Compound **9** was obtained as a yellow wax (1.45 g, 28%).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 3.51$ (s, 3H), 5.23 (s, 2H), 7.10 (d, J = 8.8 Hz, 2H), 7.31 (d, $J = 8.8$ Hz, 2H), 7.48 (d, $J = 6$ Hz, 2H), 7.52 (s, 1H), 8.65 ppm (d, $J = 6$ Hz, 2H); FAB HRMS: m/z calcd for $C_{22}H_{15}F_7NO_2S$ $[M+H]^+$: 490.0712; found: 490.0698.

*4-[4-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl]-5-(4-methoxymethoxyphenyl)thiophen-2-yl]pyridine (**3a**)*: Under an argon atmosphere, a solution of 15% *n*-butyllithium in hexane (1.1 mL, 1.84 mmol) was added to a stirred solution of 2-methyl-3-bromo-5-phenylthiophene (0.41 g, 1.6 mmol) in dry THF (50 mL) at −78 °C. After 30 min, a solution of **9** (1.19 g, 2.4 mmol) in dry THF (20 mL) was added to the reaction mixture at −78 °C. The mixture was left to reach room temperature. After 3 h, the reaction was stopped by the addition of water. The product was extracted with diethyl ether and washed with brine three times. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by using silica gel column chromatography with hexane/ethyl acetate (1:1) as the eluent and reversed-phase HPLC with methanol/acetonitrile (1:1). Compound **3a** was obtained as a colorless solid (80 mg, 8%).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.83$ (s, 3H), 3.33 (s, 3H), 4.70 (s, 2H), 6.26 (s, 1H), 6.77 (d, $J = 8.4$ Hz, 2H), 6.91 (d, $J = 8.4$ Hz, 2H), 7.34 (m, 5H), 7.49 (d, $J = 6.8$ Hz, 2H), 7.52 (s, 1H), 8.65 ppm (d, $J = 6$ Hz, 2H); FAB HRMS: m/z calcd for $C_{33}H_{24}F_6NO_2S_2$ $[M+H]^+$: 644.1153; found: 644.1146.

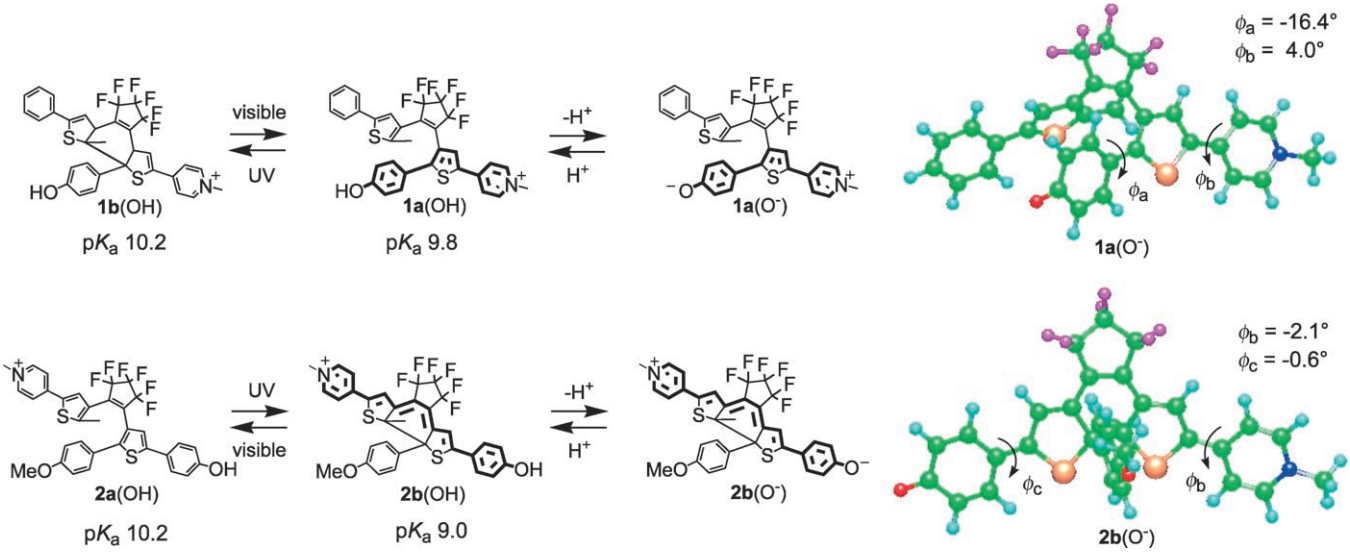


Figure 5. Conformational structures of **1a**(O$^-$) and **2b**(O$^-$) calculated at the B3LYP/6-31G(d) level of theory.

*4-{4-[3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl]-5-(4-hydroxyphenyl)thiophen-2-yl}-1-methylpyridinium (**1**)*: Methyl trifluoromethanesulfonate (1.0 mL, 6.1 mmol) was added to a stirred solution of **3** (80 mg, 0.12 mmol) in dry dichloromethane (80 mL). The reaction was stirred at ambient temperature in the dark under a nitrogen atmosphere. After 36 h, the resulting suspension was filtered. The reaction solution was concentrated. The residue was purified by using reverse-phase silica gel column chromatography with acetonitrile/methanol (1:1) as the eluent and reversed-phase HPLC with methanol/acetonitrile (1:1). Compound **1a** was obtained as a yellow solid (50 mg, 68%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.77 (s, 3H), 4.25 (s, 3H), 6.21 (s, 1H), 6.54 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 7.20 (m, 5H), 7.25 (s, 1H), 8.23 (d, J = 6 Hz, 2H), 8.69 ppm (d, J = 6.4 Hz, 2H); UV/Vis (CH_3OH/water 5:2): λ_{max} (ε) = 287 (19870), 380 nm (13419 $mol^{-1}dm^3cm^{-1}$); FAB HRMS: m/z calcd for $C_{32}H_{22}F_6NOS_2$ $[M]^+$: 614.1041; found: 614.1013.

*3-(2,3,3,4,4,5,5-heptafluorocyclopent-1-enyl)-5-(4-methoxymethoxyphenyl)-2-(4-methoxyphenyl)thiophene (**11**)*: This compound was prepared from 2.73 g (6.73 mmol) of compound **10** by using a similar procedure to that used to prepare **9**. The product was purified by using silica gel column chromatography with dichloromethane/hexane (1:1) as the eluent. Compound **11** was obtained as a yellow wax (2.62 g, 75%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.50 (s, 3H), 3.85 (s, 3H), 5.21 (s, 2H), 6.94 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 7.22 (s, 1H), 7.30 (d, J = 8.8 Hz, 2H), 7.53 ppm (d, J = 8.8 Hz, 2H); FAB HRMS: m/z calcd for $C_{24}H_{17}F_7O_3S$ $[M]^+$: 518.0787; found: 518.0780.

*4-(4-{3,3,4,4,5,5-hexafluoro-2-[5-(4-methoxymethoxyphenyl)-2-(4-methoxyphenyl)thiophen-3-yl]cyclopent-1-enyl}-5-methylthiophen-2-yl)pyridine (**4**)*: This compound was prepared from 1.22 g (2.35 mmol) of compound **11** by using a similar procedure to that used to prepare **3**.

The product was purified by silica gel column chromatography with hexane/ethyl acetate (1:1) as the eluent and reversed-phase HPLC with methanol. Compound **4** was obtained as a white solid (50 mg, 4%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.86 (s, 3H), 3.42 (s, 3H), 3.50 (s, 3H), 5.23 (s, 2H), 6.59 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 6.4 Hz, 2H), 7.37 (s, 1H), 7.55 (d, J = 8.8 Hz, 2H), 8.56 ppm (d, J = 6 Hz, 2H); FAB HRMS: m/z calcd for $C_{34}H_{25}F_6NO_3S_2$ $[M]^+$: 673.1180; found: 673.1184.

*4-(4-{3,3,4,4,5,5-hexafluoro-2-[5-(4-hydroxyphenyl)-2-(4-methoxyphenyl)thiophen-3-yl]cyclopent-1-enyl}-5-methylthiophen-2-yl)-1-methylpyridinium (**2**)*: This compound was prepared from 50 mg (0.07 mmol) of compound **4** by using a similar procedure to that used to prepare **1**. The product was purified by using silica gel column chromatography with acetonitrile/methanol (1:1) as the eluent and reversed-phase HPLC with methanol/water (20:1). Compound **2** was obtained as a yellow solid (10 mg, 22%).

^{1}H NMR (CD_3OD, 400 MHz): δ = 1.98 (s, 3H), 2.91 (s, 3H), 4.33 (s, 3H), 6.67 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.99 (s, 1H), 7.42 (s, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 7.2 Hz, 2H), 8.74 ppm (d, J = 6.8 Hz, 2H); UV/Vis (CH_3OH/water 5:2): λ_{max} (ε) = 350 nm (21987 $mol^{-1}dm^3cm^{-1}$); FAB HRMS: m/z calcd for $C_{33}H_{24}F_6NO_2S_2$ $[M]^+$: 644.1147; found: 644.1115.

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