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Photo-, Solvent-, and Ion-Controlled Multichromism of Imidazolium-Substituted Diarylethenes

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Abstract: Cationic diarylethenes with an imidazolium ring are synthesized for the first time. The imidazolium cationic moiety is connected directly to the ethene unit as one of the aryl units that take part in the photoinduced pericyclization reaction. The imidazolium-substituted diarylethenes undergo reversible photochromic reactions in a variety of organic media, including ionic liquids, even though they have a delocalized cationic charge in one of the five-membered aromatic rings. The closed-ring isomer shows solvatochromism depending on the solvent donor numbers. Addition of some tetraalkylammonium salts, such as tetrabutyl ammonium nitrate, into the colored organic solution of diarylethene also causes a color change, indicating its ionochromic property. These solvato- and ionochromic properties are considered in connection with the shift of chemical equilibrium between the closed-ring isomers, one with an extended π-conjugation system and one with limited π-conjugation due to the strong interaction with solvent molecules and anions with high donor number.

Keywords: imidazolium compounds · molecular switches · photochromism · solvatochromism

Introduction

In vision, the photoisomerization of visual pigments, such as retinal, triggers the molecular events of the phototransduction cascade.[1] 11-*cis*-Retinal is one of the chromophores of the visual pigments that combines with the apoprotein opsin through a Schiff base linkage to form rhodopsin. The absorbance maximum of 11-*cis*-retinal is about 370 nm in solution, which shifts to longer wavelength when it binds to opsin. The protonation of the Schiff base linkage between 11-*cis*-retinal and opsin is known to be responsible for the bathochromic shift.[2] The environmental effects of the protein on the protonated Schiff base have been considered to give rise to a further absorbance shift (opsin shift). For example, the negatively charged groups of some amino acid residues near the Schiff base could induce a greater degree of delocalization of the π-electron system of retinal through electrostatic interaction, and consequently a red shift in the absorbance maximum occurs.[3] Thus, retinal shows a variety of absorption profiles depending on the geometry, the binding condition with protein, the protonation-deprotonation of the Schiff base, and the interaction with counteranions, giving additional multichromic nature, including halochromism (pH-dependent), solvatochromism, and ionochromism. The presence of Schiff base directly on the conjugated π-backbone of retinal would be predominantly responsible for such multichromic nature. To achieve such a multichromic function in an artificial system, we have designed a series of photochromic molecules based on the structure of diarylethenes.

Photochromic diarylethenes[4–8] have been attracting much interest for their photoswitching capability as well as their photomechanical behavior.[9,10] Photoswitching effects in diarylethenes have been extensively studied for controlling various chemical and physical properties, such as fluorescence intensity and wavelength,[11–14] π-conjugation connection pathways,[15,16] electronic conduction,[17–19] electrochemical response,[20–22] magnetic interactions,[23] chemical reactivity,[24] and self-assembling behavior.[25,26] Most of these photoswitching effects are based, at least partly, on changes in the extent of π-conjugation in diarylethene upon photochromic reactions. On the other hand, the molecular designs have been limited to the addition of functional units to the aryl rings and the substitution of the central ethene group.[4–8,15,22,27–29] Since the heteroaromatic rings of diarylethene undergo reversible deformation into a nonaromatic,

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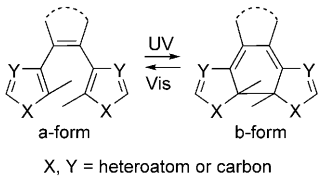
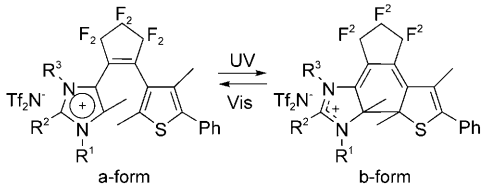
fused heterocycle, as shown in Scheme 1, the direct substitution of the heteroaromatic ring with a functional aryl group would give rise to dramatic changes in the physicochemical



Scheme 1. Photochromism of diarylethene.

properties upon photochromic reactions. In this study, we have replaced an aryl group of diarylethene with a cationic imidazolium ring. The imidazolium ring is one of the N-heteroaromatics, and is also known as the most popular and investigated class of cationic structures of room-temperature ionic liquids.[30] The delocalization or burying of cationic charge and the low reduction potential of the imidazolium cation make ionic liquids chemically stable towards many organic and inorganic substances, which enables a number of organic chemical reactions[31,32] to be carried out in the ionic liquids.

There are some reports on cationic diarylethenes containing pyridinium cation units as the side group connected to the photoreactive thienyl moieties.[20,21,33] For example, Lehn and co-workers have demonstrated π-conjugation switching in some pyridinium-substituted diarylethenes.[20a] Some of them exhibit characteristic photon-mode switching in their electrochemical properties upon photochromic ring-cyclization and cycloreversion reactions. Matsuda et al. have reported that the ionic-repulsive interaction in the dithienylethene with two pyridinium side groups results in its improved photochromic properties in methanol.[33] As shown in Scheme 2, the present molecules, imidazolium-substituted diarylethenes **1**–**4**, are very different from these previous molecules based on dithienylethenes.[20,21,33] A cationic imidazolium group is connected directly to the central ethene unit as an aryl group and participates in the photochromic hexatriene–cyclohexadiene reaction. The delocalized nature



Scheme 2. Photochromic reaction of imidazolium-substituted diarylethenes **1**–**4**.

of its positive charge would be modulated significantly and reversibly upon the photochromic reactions, since the five-membered ring is no longer the aromatic unit in the closed-ring form isomer (b-form, Scheme 2). Various chemical and electrical properties of molecules **1**–**4** are hence expected to be modulated with the photochromic reactions. Furthermore, the presence of cationic quaternized nitrogen directly on the π-conjugation backbone of the closed-ring isomers of diarylethenes is expected to affect significantly the absorption spectra in a similar manner to the Schiff base on retinal through interaction with counteranions and bases.

Results and Discussion

Photochromism in organic solvents: Imidazolium-substituted diarylethene **1** showed reversible photochromic reactions in a wide range of organic solvents, including chloroform, toluene, 2-methyltetrahydrofuran (MeTHF), dimethyl sulfoxide, pyridine, and even in ionic liquids. As shown in Figure 1, the

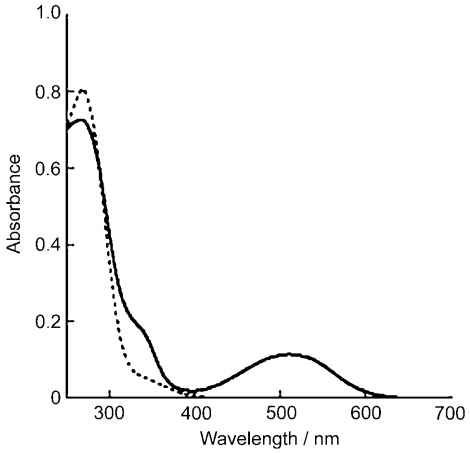


Figure 1. Absorption spectral change of **1** in MeTHF solution ([**1**] = 3.3×10^{-5} M): open-form **1a** (dotted line) and photostationary state under irradiation with 313 nm light (solid line).

absorption band at 270 nm with a molar absorbance coefficient of $2.4\times10^{4}\,M^{-1}\,cm^{-1}$ observed in the original state was suppressed, and a new absorption band appeared at around 510 nm after UV-light irradiation in MeTHF. The absorption spectral change upon photoirradiation was accompanied by an isosbestic point at 290 nm, which clearly indicates a two-component photochromic reaction, the composition ratio of which changes with light irradiation. It should also be noted that the colored state can be stored under dark conditions without remarkable spontaneous bleaching at room temperature, whereas it can be completely bleached upon irradiation with visible light to give an absorption spectrum identical to that of the initial solution of **1a**. The coloration and decoloration cycles can be repeated at least twenty times with no marked photodegradation. Thus, compound **1** basically shows a similar photochromic nature to that of previ-

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ously reported diarylethenes,[4] reversible photochromic reactivity in solution, and thermal stability in both bleached and colored states, despite having a cationic moiety in the reactive unit.

The closed-ring isomer **1b** was difficult to isolate from the colored solution of **1** by normal- and reverse-phase HPLC due to its ionic nature and the low conversion ratio, even though the colored state is thermally stable. To confirm the photoisomerization reaction product, the ^{1}H NMR spectral change was studied carefully.[34] Briefly, characteristic signals of methyl protons of the open-ring form isomer **1a** were observed at 2.12, 2.37, 2.42, 3.44, and 3.71 ppm in $CDCl_3$. After UV irradiation, five additional peaks were observed at 1.87, 2.07, 2.14, 3.14, and 3.47 ppm, and were attributed to the five methyl groups in the closed-ring isomer **1b** shown in Scheme 2. The conversion ratio between **1a** and **1b** at the photostationary state achieved by irradiation with UV light ($\lambda = 313$ nm) was estimated to be 25% from the integrated peak intensity of the ^{1}H NMR spectrum. The molar absorbance coefficient of the ring-closed isomer **1b** was estimated to be 1.2×10^4 M^{-1}cm^{-1} at the peak maximum, 510 nm from the conversion of the photochromic reaction. Upon visible irradiation the colored solution turned colorless and the five methyl peaks disappeared in the ^{1}H NMR spectrum. The photochromic reaction quantum yields were also evaluated by the standard procedure with bis(1-benzothiophene-3-yl)-hexafluorocyclopentene in hexane as the reference.[35] Relatively high quantum yields were found for both photocyclization and photocycloreversion reactions: 0.3 (313 nm) and 0.4 (546 nm), respectively. The relatively large cycloreversion quantum yield is responsible for the low conversion ratio at the photostationary state. Since imidaozlium-substituted diarylethenes **2**–**4** have structures analogous with **1**, they also showed similar photochromic behavior to **1**. The substitutents on the imidazolium ring hardly affected their photochromic performance except for the absorption maxima.[34]

Solvent-controlled chromism: The imidazolium-substituted diarylethenes showed characteristic solvent-dependent absorption spectra in their closed-ring states. Table 1 summarizes λ_{max} of open- and closed-ring isomers of **1** in various solvents together with their donor numbers (DN) and dielectric constants (ε).[36] Whereas the peak positions are almost identical independently of solvents for open-ring isomer **1a**, the absorption profiles for closed-ring isomer **1b** were significantly dependent on the medium. The λ_{max} of **1b** shows a good correlation with the solvent DNs rather than the solvent polarity. With the increase of DN, the absorption peak shifts to shorter wavelength. The spectral shift of **1b** upon the addition of a solvent with high DN, for example, pyridine, to the solution of **1b** in toluene was studied in order to investigate the origin of the observed solvatochromism. As shown in Figure 2, the absorption peak of **1** at the photostationary state in toluene shifted to shorter wavelength, accompanied by a decrease of the absorbance at 520 nm, and with the successive peak progression at 460 nm by the addition of a small amount of pyridine. The presence of an isosbestic point at 495 nm clearly demonstrates that the mechanism of the solvatochromism should be attributed to the shift of the two-component chemical equilibrium at the ground state of the closed-ring isomer **1b**, like that observed for some merocyanine dyes, the photoisomers of spiroheterocyclic compounds.[37] For clarity, the components with absorption peak positions at around 520 nm and 460 nm are hereinafter referred to as "red" and "yellow components", respectively. The ratio of red and yellow components should be dominated by the DN of the solvent, which determines the apparent absorption peak position of the closed-ring isomer. Since the yellow component is likely to appear in solvents with high DN, the closed-ring isomer **1b** is regarded to interact strongly with donor solvents.

Table 1. Absorption maxima of the open- and closed-ring isomers of **1**, together with the donor numbers (DN) and dielectric constants (ε) of solvents.

solvents	λ_{max} (**1a**) [nm]	λ_{max}[a] (**1b**) [nm]	DN[b] [kcal mol^{-1}]	ε[b]
chloroform	270	521	0	4.8
toluene	–[c]	520	0.1	2.4
acetonitrile	270	515	14.1	38.0
acetone	–[c]	509	17.0	20.7
tetrahydrofuran	270	470	20.0	7.6
dimethyl sulfoxide	271	463	29.8	45.0
pyridine	–[c]	461	33.1	12.3
emimTf_2N	273	521	–	–
emim$EtSO_4$	–[c]	462	–	–

[a] Absorption maximum in the visible region. [b] Ref. [36]. [c] n.d. = not detected due to the absoption of solvent.

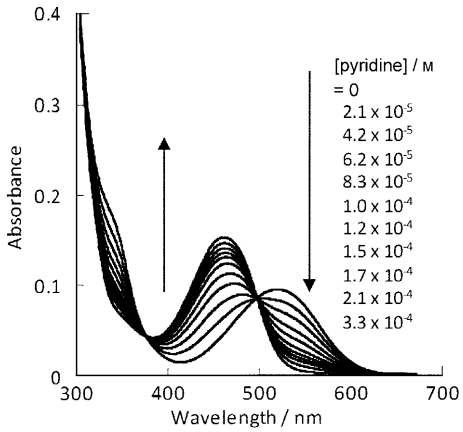

Figure 2. Absorption spectral change of **1** at the photostationary state (achieved by irradiation with 313 nm light) by the addition of pyridine to the solution of **1** in toluene ([**1**] = 4.0×10^{-5} M).

Ion-controlled chromism: The solvatochromic behavior was also observed in ionic liquids. As shown in Table 1, the closed-ring isomer **1b** exhibits different absorption spectra depending on the anion species of the ionic liquid. The red component dominates in 1-ethyl-3-methylimidazolium bis-

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(trifluoromethanesulfonyl)imide (emimTf_2N), whereas the yellow one is the major component in 1-ethyl-3-methylimidazolium ethylsulfate (emim$EtSO_4$). Although the electrostatic interaction in ionic liquids should be substantially lower than in conventional organic solvents, the observed difference in absorption profile may be attributable to the difference in ionic interactions between closed-ring isomer **1b**, possessing localized cationic charge, and the anionic components of the ionic liquids, Tf_2N^- and $EtSO_4^-$. Such ionochromic behavior of **1b** was demonstrated clearly by the titration of nucleophilic anions in the MeTHF and also reproduces the spectral shift observed for solvatochromims described above. As shown in Figure 3, the visible absorption band of **1b** dramatically changed with the addition of tetrabutylammonium nitrate ($TBANO_3$) in a similar fashion to that observed in Figure 2. The isosbestic point also appeared at 495 nm, identical to that observed for the toluene–pyridine system. The components in equilibrium giving the absorption peaks at longer and shorter wavelength should have substantially similar π-conjugation structures to the red and yellow components, respectively. The present ionochromism could also be explained by the DNs of the anions. The DN for the hard base NO_3^- was estimated to be around 20,[38] which is substantially larger than that of Tf_2N^- (DN ≈ 5.4),[39] the original bulky counteranion of **1**, even though these values are dependent on the medium. The addition of 0.8 equivalents (against the concentration of **1**) of $TBANO_3$ to the solution of **1b** in MeTHF was enough to reach saturation. The binding constant between closed-ring isomer **1b** and NO_3^- could be estimated to be roughly of the order of $10^7\,M^{-1}$. The addition of an equimolar amount of other anions with strong basicity, such as Br^- and HSO_4^-, also gave rise to the spectral shift at shorter wavelength, whereas the equimolar addition of bulky anions with small DNs, such as ClO_4^- and PF_6^-, had almost no effect on the absorption profile of **1b**.[34]

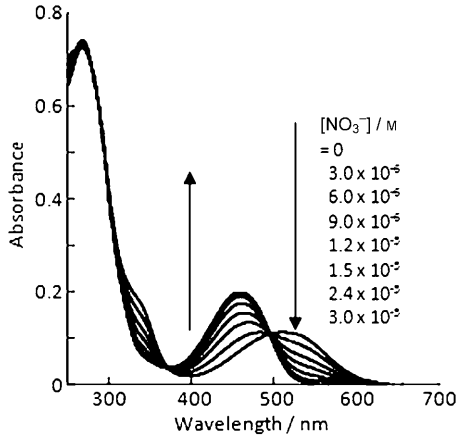

Figure 3. Absorption spectral change of **1** at the photostationary state (achieved by irradiation with 313 nm light) by the addition of $TBANO_3$ to the solution of **1** in MeTHF ($[\mathbf{1}] = 3.7 \times 10^{-5}$ M).

These solvent- and ion-controlled chromisms were also observed for other imidazolium-substituted diarylethenes, including **3** with an ethyl group as the R^2 group, which clearly indicates that the source of these chromisms should not be attributed to the conformational twisting between the R^2 phenyl ring and the fused heterocycles, but rather to the difference in electronic structure of the π-conjugation system.

^{1}H NMR study for the yellow and red components: To explore the electronic structures of the red and yellow components, we conducted a ^{1}H NMR study for **2–4** in $CDCl_3$ and [D_5]pyridine, giving the red and yellow components as closed-ring photoisomers, respectively. In contrast to diarylethene **1**, the N1 and N3 nitrogen atoms of which were both methylated, diarylethenes **2–4** possess an ethyl group as the R^1–R^3 substituents, respectively, on the imidazolium ring, which enables us to take advantage of homonuclear proton-proton correlation spectroscopy (COSY). Because the ethyl group is only detectable for these molecules by ^{1}H–^{1}H COSY (methyl–methylene correlation), the change of electronic structure around the imidazolium ring upon the photochromic reaction could be evaluated by following the chemical shift of the methylene (−CH_2−) of the ethyl group for **2–4** in each medium. Table 2 and Figure 4 summarize the chemical shifts of the methylene of the ethyl group for **2–4** before and after UV irradiation in $CDCl_3$ and [D_5]pyridine.[34] These chemical shifts directly reflect the electron density of adjacent atoms (N1 and N3 nitrogen

Table 2. Chemical shifts of the methylene protons of the ethyl group for **2–4** and their change upon photocyclization reaction in $CDCl_3$ and [D_5]pyridine.

	in $CDCl_3$			in [D_5]pyridine		
	δ [ppm] before irrad.	δ [ppm] after irrad.	Δδ [ppm]	δ [ppm] before irrad.	δ [ppm] after irrad.	Δδ [ppm]
2	4.16	3.40	−0.76	4.15	3.20	−0.95
3	3.12	3.11	−0.01	3.15	2.12	−1.03
4	3.73	3.85	0.12	4.10	3.55	−0.55

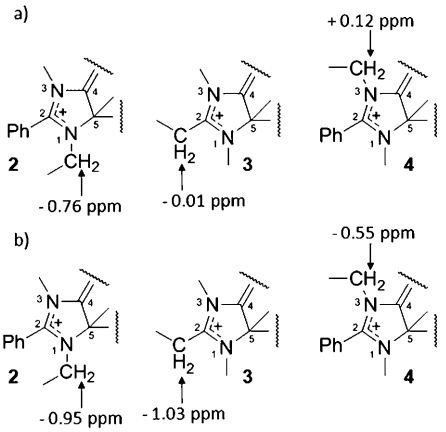

Figure 4. Change of the chemical shifts of the methylene protons for **2–4** upon photocyclization reaction in $CDCl_3$ (a) and in [D_5]pyridine (b). For clarity, only parts of the structures are depicted.

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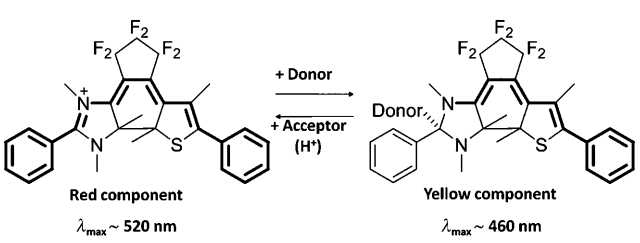
atoms and C2 carbon of imidazolium). In $CDCl_3$, which predominantly gives the red component as a photoproduct, the chemical shift of the methylene of compounds **2**–**4** showed upfield shift, almost no shift, and downfield shift, respectively. The photochromic reaction induces the loss in aromatic character of aryl units, leading to slight upfield shifts (less than 0.1 ppm) for protons that were lying within the deshielding region of the aromatic ring in general. Despite this, the methyl signal for R^2-ethyl-substituted **3** showed almost no peak shift and that for **4** even exhibited a downfield shift of 0.12 ppm. The photocyclization reaction changes the localization state of cationic charge of the imidazolium ring. In the open-ring isomer, the cationic charge delocalized around the five-membered imidazolium ring, which is responsible for the weak interaction with nucleophilic species. Upon photocyclization, the cationic charge preferentially localized on the N3 nitrogen rather than the N1 nitrogen atom, leading to the enhancement of the electron-withdrawing nature of the N3 nitrogen and C2 carbon atoms. On the other hand, in [D_5]pyridine, all methylene signals around the imidazolium ring showed significantly large upfield shifts, which is beyond the estimation taking the loss of aromaticity of the imidazolium ring into account. One plausible explanation for this would include the strong interaction between the cationic charge of the closed-ring isomer and the nucleophilic pyridines, which may neutralize the cationic charge on the imidazolium ring to reduce the electron-withdrawing character of the heterocycle. The resulting enhancement of electron density of each methylene carbon by the photocyclization reaction in pyridine should cause considerable upfield shifts of the methylene proton signals. Since the degree of upfield shift was most significant for the R^2-ethyl group, the nucleophilic species should predominantly interact with the carbon atom between two nitrogen atoms.

Taking the explanations described above into account, the canonical structures for the red and yellow components are depicted in Scheme 3. The red component has a cationic nitrogen directly on the π-conjugation system, stabilizing the cationic charge. The extended π-conjugated structure is in good agreement with the absorbance peak appearing at longer wavelength. In fact, the red component of **3b**, which does not have a phenyl group at the C2 position of the imidazolium ring, has shorter effective π-conjugation length, resulting in the absorbance peak, at 490 nm, considerably shorter than those of **1**, **2**, and **4**.[34] The yellow components



Scheme 3. Equilibrium between the red and yellow components of closed-ring isomer **1b**.

of **1b**–**4b** seem to have a limited π-conjugation structure due to the strong interaction with donors at the C2 position,[40] which leads to the absorption peak wavelength shorter than those of the red components. Interestingly, the yellow component of **3b** also showed a similar peak wavelength, of about 460 nm, to those of **1b**, **2b**, and **4b**.[34] Thus, the presence of a phenyl substitutent at the C2 position of the imidazolium ring has almost no effect on the absorbance peak position, which also supports the limited π-conjugation system in the yellow component disconnected at the C2 position of the imidazolium ring. Because these two components are in equilibrium, the addition of a strong acceptor, such as trifluoroacetic acid (acceptor number = 105), reversibly converts the yellow component to the red one by interacting with donor species. Scheme 4 shows the synthetic pathways for imidazolium substituted diarylethenes **1**–**4**.

Conclusion

We have designed novel diarylethenes that possess an imidazolium ring as an aryl unit. These imidazolium-substituted diarylethenes undergo reversible photochromic reactions in a wide range of solvents, including ionic liquids, even though they contain a cationic aryl unit. The presence of positively charged nitrogen directly on the conjugated π-system provides characteristic solvent- and anion-dependent absorption profiles in a similar manner to 11-*cis*-retinal. The spectral shift of the closed-ring isomer controlled by solvents and coexisting anions was attributed to the shift of the two-component chemical equilibrium at the ground state. The red and yellow components were studied by solvent-dependent ^{1}H NMR and ^{1}H–^{1}H COSY measurements to be characterized by the extent of the effective π-conjugation length. The red component has an extended π-conjugation system from one side to the other, whereas the yellow one possesses limited π-conjugation due to the strong binding of donors such as nucleophilic solvent molecules and anions. The precise control of the position of interaction of the nucleophilic species would enable us to design a multicolor dye system by using a single artificial chromophore.

Experimental Section

General: ^{1}H NMR spectra were recorded on a JEOL AL-300 spectrometer (300 MHz). Separative HPLC was performed on a JASCO LC-2000 Plus Series. Mass spectra were measured with a mass spectrometer JEOL JMS-T100 LC AccuTOF. Absorption spectra in solution were studied with a JASCO V-550 spectrophotometer. Photoirradiation was carried out using a USHIO 500 W Ultra-High-Pressure Mercury Lamp or a 500 W Xenon Short-Arc Lamp as the exciting light sources. Monochromic light was obtained by passing the light through a monochromator (Shimazu SPG-120S, 120 mm, $f = 3.5$).

2,4-Dimethyl-3-(perfluorocyclopent-1-enyl)-5-phenylthiophene (5): *n*-Butyllithium (*n*BuLi, 1.6 M in hexane, 12 mL, 16 mmol) was added slowly at −78 °C under Ar to a solution of 3-bromo-2,4-dimethyl-5-phenylthiophene (4.0 g, 15 mmol) in dry THF (100 mL), and the mixture was stirred for 2 h at that temperature. Perfluorocyclopentene (3.8 mL, 28 mmol)

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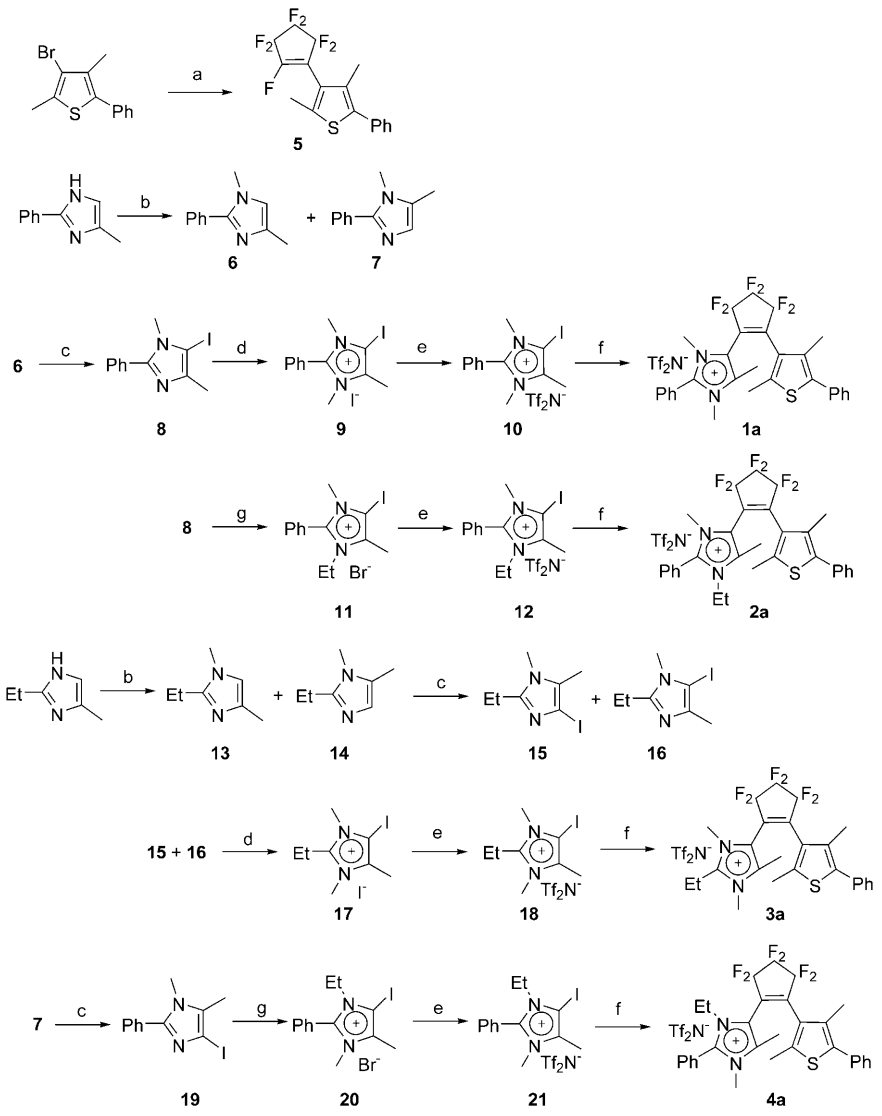

Scheme 4. Synthesis of imidazolium-substituted diarylethenes **1**–**4**. Reagents: a) 1. *n*BuLi, 2. perfluorocyclopentene; b) CH_3I, *t*BuOK, [18]crown-6; c) I_2, H_5IO_6; d) CH_3I; e) $LiTf_2N$, f) *n*BuLi; g) CH_3CH_2Br.

was then quickly added and the mixture stirred for another 2 h at −78 °C. The reaction mixture was allowed to warm up to room temperature. Methanol was added to the reaction mixture and extracted with ethyl acetate. The combined organic fraction was washed with water, dried with anhydrous magnesium sulfate, and concentrated. The residue was subjected to silica gel column chromatography (hexane) to give product **5** (2.1 g) as a colorless powder in 37 % yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS,): $\delta = 2.11$ (s, 3H), 2.38 (s, 3H), 7.28–7.40 ppm (m, 5H).

1,4-Dimethyl-2-phenyl-1*H*-imidazole (6) and 1,5-dimethyl-2-phenyl-1*H*-imidazole (7): Iodomethane (4.0 mL, 65 mmol) was added to a solution of 4-methyl-2-phenyl-1*H*-imidazole (10 g, 64 mmol), [18]crown-6 (1.5 g, 6.4 mmol) and potassium-*tert*-butoxide (7.6 g, 64 mmol) in dry THF (110 mL) under N_2. After stirring for 12 h at ambient temperature, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by alumina gel column chromatography (hexane/ethylacetate = 2:1) to give 5.1 g of **6** ($R_f = 0.3$) in 47 % yield as a yellowish oil and 2.8 g of **7** ($R_f = 0.1$) in 25 % yield as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) **6**: $\delta = 2.26$ (s, 3H), 3.63 (s, 3H), 6.62 (s, 1H), 7.31–7.59 ppm (m, 5H); **7**: $\delta = 2.27$ (s, 3H), 3.59 (s, 3H), 6.88 (s, 1H), 7.29–7.60 ppm (m, 5H).

5-Iodo-1,4-dimethyl-2-phenyl-1*H*-imidazole (8): Iodine (3.8 g, 15 mmol) and H_5IO_6 (1.7 g, 7.5 mmol) were added sequentially to a solution of **6** (5.1 g, 30 mmol) in AcOH (30 mL), water (30 mL), and conc. H_2SO_4 (5.2 mL). After stirring for 7 h at 70 °C, the reaction mixture was neutralized with aqueous NaOH, followed by extraction with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (ethyl acetate) afforded 6.9 g of **8** in 63 % yield as a yellowish powder. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.32$ (s, 3H), 3.65 (s, 3H), 7.40–7.48 (m, 3H), 7.55 ppm (d, $J = 9.0$ Hz, 2H).

5-Iodo-1,3,4-trimethyl-2-phenyl-1*H*-imidazolium bis(trifluoromethanesulfonyl)imide (10): Compound **8** (8.7 g, 29 mmol) was dissolved in acetonitrile (45 mL). Iodomethane (8.8 mL, 150 mmol) was added to the solution at room temperature under N_2. After stirring for two days, the reaction mixture was filtered off from insoluble substances, and then evaporated under reduced pressure. The residue was re-precipitated from ethyl acetate to give the product 5-iodo-1,3,4-trimethylimidazolium iodide (**9**) as a colorless powder. This powder was re-dissolved in chloroform and an aqueous solution of lithium bis(trifluoromethanesulfonyl)imide ($LiTf_2N$, 9.0 g, 32 mmol) was added, followed by vigorous stirring for 12 h. The organic layer was dried over anhydrous magnesium sulfate, and then evaporated in vacuo to leave a yellowish powder (**10**, 11 g) in 94 % yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.48$ (s, 3H), 3.65 (s, 3H), 3.66 (s, 3H) 7.61–7.75 ppm (m, 5H).

4-(2-(2,4-Dimethyl-5-phenylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-1,3,5-trimethyl-2-phenyl-1*H*-imidazolium Tf_2N (1a): *n*BuLi (1.6 M in hexane, 4.0 mL, 6.8 mmol) was added in a dropwise manner to a solution of **10** (2.1 g, 3.5 mmol) in dry THF (20 mL) at −78 °C under Ar and stirred for 0.5 h at that temperature. Then compound **5** (1.1 g, 2.9 mmol) in dry THF (5 mL) was added slowly and the mixture was stirred for another 1 h. The reaction mixture was allowed to warm up to room temperature, and then methanol was added, followed by extraction with ethyl acetate. The combined extract was washed with brine, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give an oily residue, which was purified with alumina gel column chromatography (hexane/acetone). The resulting oily product was further purified with reversed phase HPLC (methanol) to give 1.0 g of **1a** in 49 % yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 2.13$ (s, 3H), 2.37 (s, 3H), 2.42 (s, 3H), 3.45 (s, 3H), 3.72 (s, 3H), 7.26–7.72 ppm (m, 10H); ESI HRMS: *m*/*z* calcd for $C_{29}H_{25}F_6N_2S^+$ $[M-Tf_2N]^+$: 547.1637; found: 547.1643; elemental analysis calcd (%) for $C_{31}H_{28}F_{12}N_3O_4S_3$: C 44.98, H 3.04, N 5.08; found: C 45.03, H 2.89, N 4.98.

1-Ethyl-4-iodo-3,5-dimethyl-2-phenyl-1*H*-imidazolium Tf_2N (12): Bromoethane (1.9 mL, 25 mmol) was added to a solution of **8** (3.0 g, 10 mmol) in acetonitrile (25 mL) and the mixture was stirred for 24 h at 80 °C. The reaction mixture was evaporated and the residue was re-precipitated

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from ethyl acetate to give the product, 1-ethyl-4-iodo-3,5-dimethyl-2-phenyl-1*H*-imidazolium bromide (**11**), as a colorless powder. This powder was re-dissolved in chloroform and an aqueous solution of $LiTf_2N$ (4.6 g, 16 mmol) was added, followed by vigorous stirring for 12 h. The organic layer was dried over anhydrous magnesium sulfate, and then evaporated in vacuo to leave a yellowish powder (**12**, 3.8 g) in 78% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.28$ (t, $J = 7$ Hz, 3H), 2.48 (s, 3H), 3.59 (s, 3H), 4.04 (q, $J = 7$ Hz, 2H), 7.58–7.73 ppm (m, 5H).

4-(2-(2,4-Dimethyl-5-phenylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-1-ethyl-3,5-dimethyl-2-phenyl-1*H*-imidazolium Tf_2N (2a): This compound was prepared by the same procedure as used as for **1a**, except that **10** was replaced by **12**. From **12** (2.0 g, 3.2 mmol), **5** (1.2 g, 3.2 mmol), and *n*BuLi (2.1 mL, 3.4 mmol), **2a** (1.2 g, 44%) was obtained as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.26$ (t, $J = 7$ Hz, 3H), 2.13 (s, 3H), 2.36 (s, 3H), 2.44 (s, 3H), 3.39 (s, 3H), 4.15 (q, $J = 8$ Hz, 2H), 7.32–7.76 ppm (m, 10H); ESI HRMS: *m*/*z* calcd for $C_{62}H_{54}F_{18}N_5O_4S_4^+$ $[2M-Tf_2N]^+$: 1402.2766; found: 1402.2778.

2-Ethyl-4-iodo-1,3,5-trimethyl-1*H*-imidazolium Tf_2N (18): Iodomethane (3.0 mL, 47 mmol) was added to a solution of 2-ethyl-4-Methyl-1*H*- imidazole (5.0 g, 46 mmol), [18]crown-6 (1.2 g, 4.5 mmol) and potassium-*tert*-butoxide (5.1 g, 45 mmol) in dry THF (50 mL) under N_2. After stirring for 12 h at ambient temperature, the reaction mixture was extracted with ethyl acetate and washed with water. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated to give a mixture of structural isomers, **13** and **14**. This mixture (2.7 g) was dissolved in acetic acid (22 mL) and water (20 mL). Iodine (2.8 g, 11 mmol), conc. H_2SO_4 (3.8 mL) and H_5IO_6 (1.3 g, 5.5 mmol) were added to the solution. After heating under reflux for 5 h, the reaction mixture was neutralized with aqueous NaOH, followed by extraction with ethyl acetate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (ethyl acetate) afforded 3.8 g of the mixture of **15** and **16** as the product in 33% yield, and was used for further reaction as a mixture.

The mixture of **15** and **16** (2.5 g, 10 mmol) was dissolved in acetonitrile (15 mL). Iodomethane (1.6 mL, 25 mmol) was added to the solution and the mixture was stirred for two days at room temperature. The reaction mixture was then filtered off from insoluble substances, and evaporated under reduced pressure. The residue was re-precipitated from ethyl acetate to give the product, 2-ethyl-4-iodo-1,3,5-trimethyl-1*H*-imidazolium iodide (**17**), as a colorless powder. This powder was re-dissolved in chloroform and an aqueous solution of $LiTf_2N$ (6.9 g, 24 mmol) was added, followed by vigorous stirring for 12 h. The organic layer was dried over anhydrous magnesium sulfate, and then evaporated in vacuo to leave a colorless powder (**18**, 4.2 g) in 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.29$ (t, $J = 8$ Hz, 3H), 2.37 (s, 3H), 3.11 (q, $J = 8$ Hz, 2H), 3.45 ppm (m, 6H).

4-(2-(2,4-Dimethyl-5-phenylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-2-ethyl-1,3,5-trimethyl-1*H*-imidazolium Tf_2N (3a): This compound was prepared by the same procedure as used for **1a**, except that **10** was replaced with **18**. From **18** (1.7 g, 3.1 mmol), **5** (1.0 g, 2.6 mmol), and *n*BuLi (2.1 mL, 3.3 mmol), **3a** (0.50 g, 27%) was obtained as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.25$ (t, $J = 8$ Hz, 3H), 2.08 (s, 3H), 2.27 (s, 3H), 2.37 (s, 3H), 3.13 (q, $J = 8$ Hz, 2H), 3.57 (s, 3H), 3.77 (s, 3H), 7.31–7.43 ppm (m, 5H); ESI HRMS: *m*/*z* calcd for $C_{52}H_{50}F_{18}N_5O_4S_4^+$ $[M-Tf_2N]^+$: 1278.2453; found: 1278.2443.

1-Ethyl-5-iodo-3,4-dimethyl-2-phenyl-1*H*-imidazolium Tf_2N (21): This compound is the structural isomer of **12** and was prepared from **7**, the structural isomer of **6**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.30$ (t, 3H), 2.45 (s, 3H), 3.59 (s, 3H), 4.00 (q, 2H), 7.43–7.53 ppm (m, 5H).

5-(2-(2,4-Dimethyl-5-phenylthiophene-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-enyl)-1-ethyl-3,4-dimethyl-2-phenyl-1*H*-imidazolium Tf_2N (4a): This compound was prepared by the same procedure as used for **1a**, except that **10** was replaced with **21**. From **21** (1.0 g, 1.6 mmol), **5** (0.68 g, 1.8 mmol), and *n*BuLi (1.2 mL, 1.9 mmol), **4a** (0.34 g, 25%) was obtained as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): $\delta = 1.06$ (br s, 3H), 2.17 (s, 3H), 2.36 (s, 3H), 2.51 (s, 3H), 3.73 (m, 5H), 7.32–7.76 ppm (m, 10H); ESI HRMS: *m*/*z*: calcd for $C_{62}H_{54}F_{18}N_5O_4S_4^+$ $[2M-Tf_2N]^+$: 1402.2766; found: 1402.2775.

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