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Syntheses and Photochromic Studies of Dithienylethene-Containing Imidazolium Derivatives and Their Reactivity towards Nucleophiles

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Abstract: A series of dithienylethene-containing imidazolium salts with various substituents on the 2-position of the imidazolium ring has been synthesized. The photochromic properties of these compounds have been studied, and the closed forms are found to be solvatochromic due to the donor–acceptor interaction with the solvent molecules. The closed form of the imidazolium salt shows a much higher affinity towards nucleophiles over the open form of the salt. A reaction pathway has been proposed to account for this reactivity difference based on the structure–property relationship, and the possible structure of the reaction product is discussed.

Keywords: dithienylethene · imidazolium · nucleophilic addition · photochromism · solvatochromism

Introduction

Photochromic dithienylethene compounds have been extensively studied for their potential applications in optical storage and molecular photoswitches, due to their high thermal irreversibility and fatigue resistance.[1] Over the past decades, a large number of dithienylethene compounds with great diversities have been synthesized.[1d–g,2–8] Incorporation of heterocycles into the bridging part of the diarylethene backbone could be dated back to Irie's early work on a maleic anhydride derivative in 1988,[2a] and a closely related maleimide structure was also announced in a later report.[2b] The introduction of a ring system with two or more heteroatoms has opened up new possibilities for both structural and functional modification of this family. Tetrathiafulvalene derivatives were reported in 1999.[3] Krayushkin and co-workers have extensively studied the synthesis and photochromic behavior of a series of azole derivatives since 2001.[4] Photochromic dithienylethene-containing 2-(2-pyridyl)imidazoles and their rhenium(I) complexes were reported by Yam and co-workers in 2007.[5] Diarylethene systems based on cationic imidazolium salt[6] and electron-deficient dioxaborole[7] were both found to be photoregulated electrophiles. At almost the same time, Yam and co-workers reported a series of dithienylethene-containing *N*,*N*′-dialkylimidazolium salts, and their metal *N*-heterocyclic carbene (NHC) complexes; the photochromic properties were also studied.[8] To extend the structural diversity and to study the structure–property relationship in this system, in this report the synthesis of a series of mono- or diarylimidazolium salts that contain the dithienylethene moiety is described. Moreover, various substituents have been introduced at the 2-position of the five-membered ring to investigate their electronic effects on the photochromic properties of the imidazolium salts.

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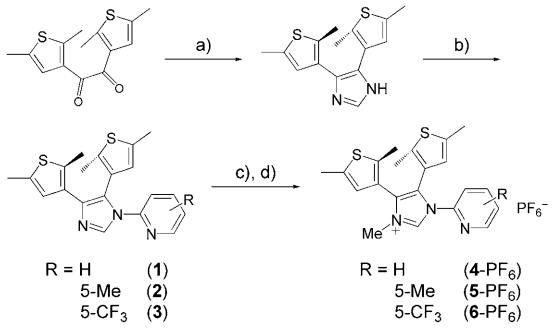
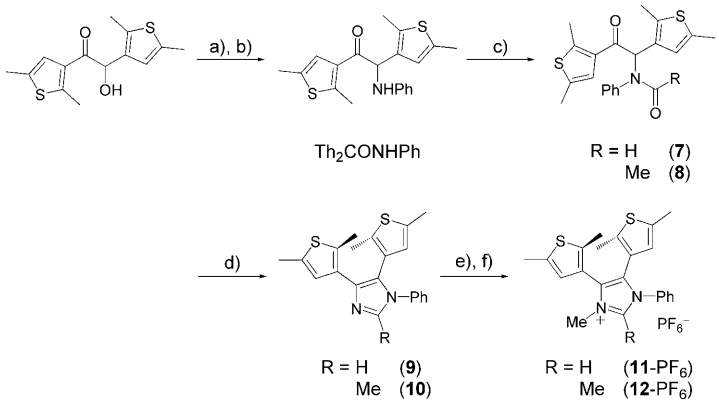
Results and Discussion

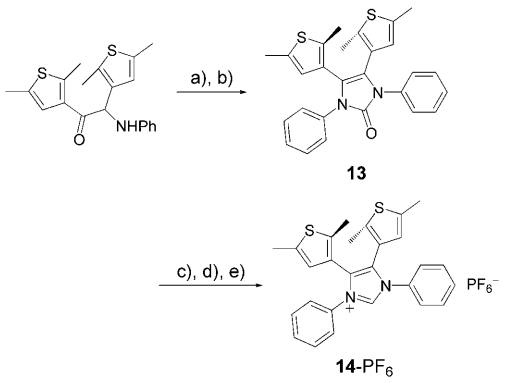
Synthesis and characterization: Schemes 1–5 summarize the synthetic routes to various imidazolium salts in this study. Most of them involve the ring-closing strategy for the imidazole derivatives, followed by methylation with iodomethane. Among them, the α-phenylaminoketone **Th_2CONHPh** is cyclized with thiocyanate anion to form the imidazol-2-thione **15**, which is further converted to the 2-thiomethylimidazole **16** by the preferential methylation at the sulfur atom (Scheme 4).[9] The trifluoromethyl group at the 2-position of the imidazole ring was introduced by condensation reactions with trifluoroacetaldehyde or its hemiacetal (Scheme 5).[10] For the synthesis of the *N*,*N*′-diarylimidazolium salt **14**-PF_6,



Scheme 1. Synthetic routes to *N*-pyridylimidazolium salts. a) Formaldehyde, NH_4OAc, AcOH, reflux; b) 2-bromopyridine (R = H), 2-bromo-5-methylpyridine (R = Me), or 2-chloro-5-trifluoromethylpyridine (R = 5-CF_3), CuI, 1,10-phen, Cs_2CO_3, DMSO; c) MeI, toluene; d) NH_4PF_6.

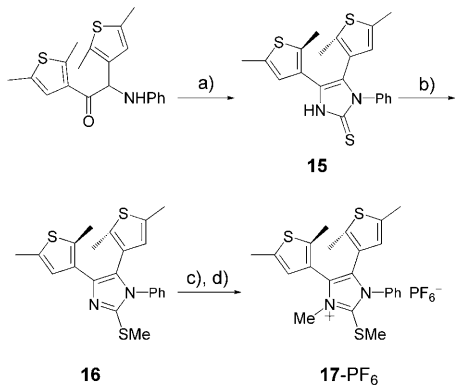


Scheme 2. Synthetic routes to 2-unsubstituted *N*-phenylimidazolium salts. a) $SOCl_2$, cat. DMF; b) $PhNH_2$, NaI, K_2CO_3, MeCN; c) AcOCHO, R = H; AcCl, NEt_3, R = Me; d) NH_4OAc, HOAc, reflux; e) MeI, toluene; f) NH_4PF_6.

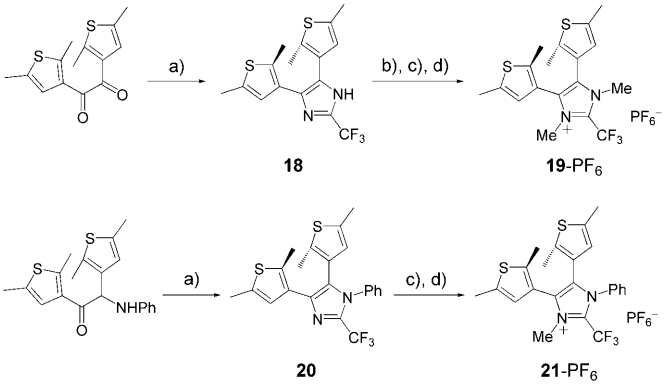


Scheme 3. Synthetic routes to *N*,*N*′-diphenylimidazolium salts. a) PhNCO, 4-DMAP; b) $SOCl_2$, pyridine; c) $LiAlH_4$, R.T.; d) I_2; e) NH_4PF_6.

an alternative strategy was used. The *N*,*N*′-diarylimidazol-2-one **13** was first reduced to the unstable imidazoline[11] and then oxidized to the conjugated imidazolium by iodine (Scheme 3).[12] All imidazolium salts have been characterized by ^{1}H NMR spectroscopy, and the chemical shifts of the protons at the 2-position of the imidazolium ring are



Scheme 4. Synthetic routes to 2-methylthioimidazolium salts. a) NaSCN, HCl, 4-DMAP, acetone–THF, reflux; b) MeI, K_2CO_3, MeOH; c) MeI, toluene; d) NH_4PF_6.



Scheme 5. Synthetic routes to 2-trifluoromethylimidazolium salts. a) $CF_3CH(OH)OEt$, NH_4OAc, HOAc, reflux; b) MeI, K_2CO_3, MeCN; c) MeI, MeCN; d) NH_4PF_6.

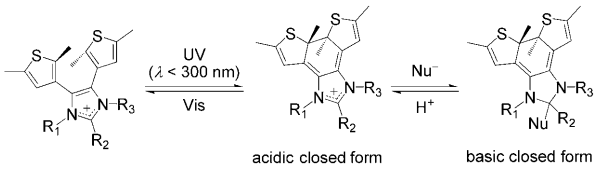
found to show significant dependence on the counteranion (I^- or PF_6^-) and solvent (Table S1 in the Supporting Information), probably due to hydrogen-bonding interactions and ion-pair formation.

Compound **12**-PF_6 has been characterized by X-ray crystallography (Table S2 in the Supporting Information). The imidazolium ring adopts a planar pentagonal structure with an N(1)-C(15)-N(2) angle of 107.8(3)° (Figure S1 in the Supporting Information). The average bond length of N(1)–C(13) and N(2)–C(14) is found to be 1.3885(5) Å, which is considerably shorter than the typical value for a C(sp^2)–N(sp^2) single bond (1.47 Å).[13] On the other hand, the C(13)–C(14) distance (1.367(5) Å) is slightly longer than a typical C=C double bond (1.34 Å). These indicate a certain extent of electron delocalization over the five-membered ring. The phenyl ring is virtually perpendicular to the imidazolium ring with an interplanar angle of 74.4°. The two thiophene rings adopted an antiparallel conformation that features interplanar angles of 66.6 and 75.6°, respectively, with respect to the imidazolium ring. In the crystal, the cations are aligned along the *b* axis of the cell with the imidazolium ring nearly perpendicular to the *b* axis. The PF_6^- anion sits

in between the two imidazolium rings to form an alternating cation–anion array. The distance between one fluorine atom of the PF_6^- anion and the C(15) atom on the adjacent imidazolium ring (3.037 Å) is found to be slightly shorter than the sum of van der Waals radii (3.17 Å),[14] and thus a weak cation–anion ion-pair interaction may be expected. Arrays parallel to each other are connected by weak intermolecular interactions to form the three-dimensional network of the crystal (Figure S2 in the Supporting Information). Acetone molecules are found sitting in the cavity between the arrays.

Photochromic and solvatochromic studies: All imidazolium salts synthesized above show an intense absorption band in the UV region (<260 nm), which is attributed to the $\pi\rightarrow\pi^*$ transitions of the molecules, and probably with some mixing of an $n\rightarrow\pi^*$ character. Upon photoirradiation in the UV region, the colorless solution of the imidazolium salt turns colored due to emergence of new bands in the visible region of the electronic absorption spectra. This reversible photochromic process with a well-defined isosbestic point observed in the electronic absorption spectra indicates the formation of a new species by means of the photoinduced reaction. Based on previous studies,[6,8] it is assigned as the closed form of the imidazolium salt (Scheme 6), in which the more extended π-conjugated structure accounts for the low-energy absorption bands at around 550–650 nm (Figure 1). Electronic absorption data of these imidazolium salts are summarized in Table 1. The appearance of new signals that correspond to the closed form are also observed in the ^{1}H NMR spectra (Tables S3 and S4 in the Supporting Information).

Most imidazolium salts in this study are found to have different electronic absorption



Scheme 6. Photochromic reaction of imidazolium salt and the nucleophilic addition to the closed form.

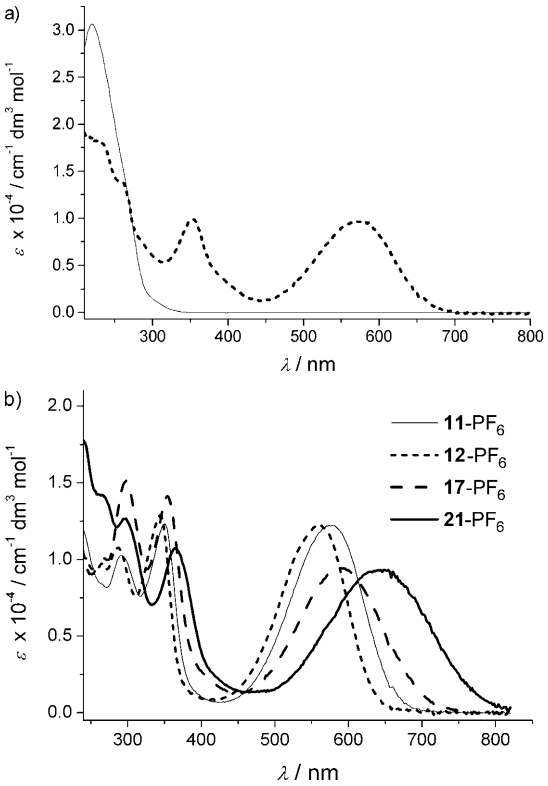


Figure 1. a) Overlaid electronic absorption spectra of the open (——) and closed (-----) forms of **6**-PF_6 in methanol. b) Overlaid electronic absorption spectra of selected imidazolium hexafluorophosphate in MeCN.

Table 1. Electronic absorption data of selected imidazolium salts.

Compound		Absorption λ_{max} [nm] (ε [mol^{-1} dm^3 cm^{-1}])
4-PF_6[a]	(open form)	226 sh (30300), 250 sh (22000)
	(closed form)	226 (21580), 252 sh (15680), 280 sh (8810), 352 (10320), 572 (9350)
5-PF_6[a]	(open form)	226 (31160), 266 sh (13900)
	(closed form)	228 (20440), 258 sh (13570), 286 (8110), 352 (11100), 572 (9780)
6-PF_6[b]	(open form)	258 sh (16650)
	(closed form)	224 (18310), 256 (13940), 354 (9950), 576 (9720)
11-PF_6[c]	(open form)	220 sh (26160)
	(closed form)	230 (13590), 292 (10280), 350 (12320), 578 (12220)
12-PF_6[c]	(open form)	220 sh (23190)
	(closed form)	226 (11920), 288 (10760), 344 (12880), 562 (12230)
14-PF_6[c]	(open form)	228 sh (24380)
	(closed form)	230 (10020), 256 (7660), 308 (10020), 352 (12380), 578 (11040)
17-PF_6[c]	(open form)	230 sh (22980), 278 sh (8380)
	(closed form)	224 (13580), 268 (10090), 298 (15120), 354 (14160), 586 (9450)
19-PF_6[c,d]	(open form)	238 (21300), 292 sh (2520)
	(closed form)	238 (17970), 266 sh (14230), 298 (13660), 364 (10730), 642 (9300)
19-PF_6[e]	(open form)	298 sh (2510)
	(closed form)	274 (10480), 308 (11400), 376 (11280), 670 (9320)
21-PF_6[c,d]	(open form)	234 (22120), 292 sh (2730)
	(closed form)	262 (16310), 302 (15390), 366 (12730), 646 (9230)
21-PF_6[e]	(open form)	304 sh (2790)
	(closed form)	258 (14700), 310 (12170), 376 (11880), 672 (9350)

[a] The extinction coefficient at the lowest energy band maximum of the closed form is measured in $CDCl_3$ and is used for estimating the corresponding value in methanol with an uncertainty of ±15%. [b] Measured in $[D_4]$MeOH with an uncertainty of ±15%. [c] Measured in CD_3CN with an uncertainty of ±15%. [d] Conversion of the closed form was less than 5%. [e] Measured in CH_2Cl_2. The extinction coefficient at the lowest energy band maximum of the closed form was measured in CD_3CN and was used for estimating the corresponding value in CH_2Cl_2 with an uncertainty of ±15%.

spectra in different solvents. On the other hand, the absorption spectra of the closed forms of some neutral imidazoles show quite limited solvent dependence (Table S5 in the Supporting Information), thereby indicating the importance of the presence of the positive charge for solvatochromism. For a quantitative study, the transition energies of the lowest-energy band maxima (in the units of wavenumber, cm^{-1}) are plotted against various scales of solvent polarity, and are found to show poor dependence on the dielectric constant function ($1/n_D^2-1/\varepsilon_r$, in which n_D = refractive index and ε_r = dielectric constant)[15] or the empirical polarity parameter $E_T(30)$[16] of the solvents (Figure S3 in the Supporting Information). However, fairly linear relationships of the transition energies against the donor number (DN) of the solvents[17] are obtained (Figure 2 and Table S6 in the Supporting Information). Generally, molecules with more or stronger electron-withdrawing groups on the imidazolium ring tend to show larger slopes of the linear fit of the plots: 1) with other groups fixed, the slope is found to increase with the substituent at the 2-position of the imidazolium ring in the order of H < SMe[18] ≈ Me[19] ≪ CF_3; 2) with the substituent fixed at the 2-position of the imidazolium ring, the slope is found to increase with the *N*-substituents in the order of alkyl < phenyl < pyridyl. As has been pointed out,[15b] the failure to establish a correlation between the transition energy and the dielectric constant of the solvents generally suggested the existence of specific interactions between the solute and the solvent molecules. Regarding the above trends and the DN as a measurement of the electron-donating ability of the solvent molecule,[20] this interaction may be considered to be a donor–acceptor interaction in nature. The imidazolium ring, especially the C2 atom, on which the positive charge is largely localized,[21] plays an important role as the lone-pair electron acceptor. Similar interaction has been reported in a thiazolium-containing diarylethene system.[22] For some of the 2-unsubstituted imidazolium salts, a moderate correlation between the absorption energy and the Kamlet–Taft β parameter[23] of the solvent is also obtained, which may suggest the possibility of hydrogen-bonding interactions to account for the solvatochromic behavior. It is difficult to differentiate the effect of these two interactions since the Kamlet–Taft β parameter is reported to show a fairly good correlation with the DN of solvent.[23b] However, significant hydrogen bonds can be excluded, at least in the solute–solvent interactions of 2-substituted imidazolium salts.[24]

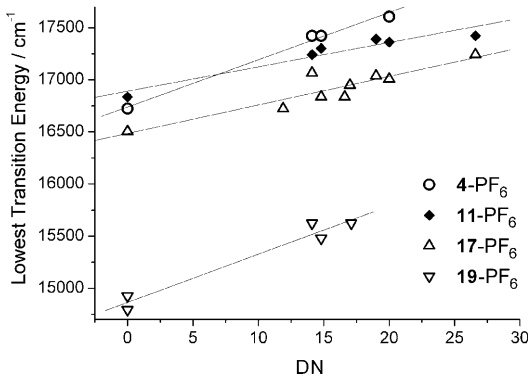


Figure 2. Representative plots of the transition energy of the lowest-energy band of the closed form of selected imidazolium salts against the DN of the solvents.

On the other hand, the lowest-energy absorption band maxima of the closed form also vary among solvents of negligible donor ability. For example, the λ_{max} of **14**-PF_6 was blueshifted from approximately 604 nm in dichloromethane to approximately 593 nm in chloroform, with an energy difference ΔE of around 300 cm^{-1} (Table S7 in the Supporting Information). A general observation appears to be that the solute tends to absorb lower transition energy in solvents with a larger dielectric constant (ε_r), and the energy difference is found to be related to the structure of the imidazolium cation. Compound **21**-PF_6, which bears a trifluoromethyl group at the 2-position of the imidazolium ring, shows the largest ΔE value of around 480 cm^{-1}, whereas the 2-methyl counterpart **12**-PF_6 shows less than one-third of the value (150 cm^{-1}). As the dielectric constant is considered to reflect the solvation ability of a solvent, these observations imply the formation of compact ion pair in solvents with poor solvation ability, in which the cation–anion interaction will considerably affect the absorption spectra of the solute. According to its similarity with the solvatochromism described above, the nature of the interaction might be considered to be a donor–acceptor interaction[6,22] since PF_6^- anion is also reported to be a weak Lewis base (DN = 2.50),[25] although the possibility of hydrogen bonding cannot be completely excluded for the 2-unsubstituted imidazolium salts. A similar trend is not observed in the solvents with low dielectric constant and high donor number, for example, 1,4-dioxane, in which the cation–solvent interaction dominates. All of the 2-substituted imidazolium salts show essentially the same λ_{max} in chloroform and benzene, whereas the 2-unsubstituted compounds show further blueshift of the absorption energy in benzene than that in chloroform, probably due to the C2−H···π(benzene) interaction.[26]

It is also interesting to note the dependence of the absorption energy on the structure of the imidazolium cation. For this purpose, the values in dichloromethane or 1,2-dichloroethane are used, since these solvents may be considered as inert and represent mostly the intrinsic property of the solute. The experimental data show an increase of the wavelength of the lowest-energy transition band with the electron-withdrawing effect of the substituent at the 2-position, that is, Me < H < SMe < CF_3. 2-Methylimidazolium salt (**12**-PF_6) absorbs at around 580 nm, whereas the 2-trifluoromethyl analogues (**19**-PF_6 and **21**-PF_6) absorb at around 670 nm (Table S6 in the Supporting Information). Although the low absorption energy in these ring-closed systems is generally considered to be a consequence of large π conjugation,[1a] in this series none of these substituents is expected to significantly extend the conjugation of the imidazolium ring. Sub-

stituents on the nitrogen atoms are also found to affect the λ_{max} value, however, in a rather limited manner.

Exploration of an acid–base equilibrium: Upon photoirradiation, the open form of **4**-PF_6 in methanol is partially converted to the closed form. The resulting purple solution is found to turn yellow upon addition of NaOH, and is recovered by neutralization with sulfuric acid. Electronic absorption spectral studies show gradual disappearance of the absorption bands of the closed form at 350 and 570 nm during this process, whereas two new bands at 320 and 460 nm are formed. Well-resolved isosbestic points are observed in the visible region where the open form does not absorb (Figure 3). This suggests the interconversion between a new

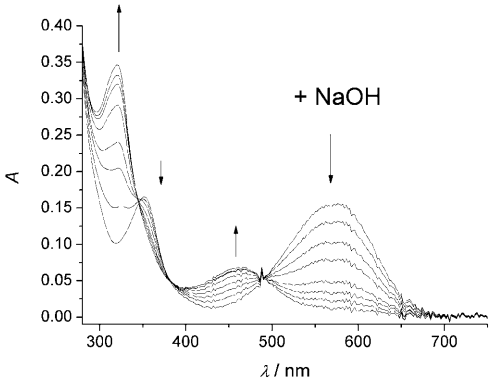


Figure 3. Spectral changes in the closed form of **4**-PF_6 in methanol upon addition of NaOH.

species, referred to as the basic closed form, and the original photogenerated closed form, referred to as the acidic closed form. The process is found to be almost totally reversible upon alternate addition of bases and acids, thereby indicating that both forms are sufficiently thermally stable under experimental conditions to maintain a virtually constant total concentration of the two forms. On the other hand, addition of NaOH to the methanolic solution of the open form of **4**-PF_6 did not result in any observable change in the UV/Vis spectra. However, the possibility of a reaction that involved the open form could not be completely excluded. A similar reaction has also been observed in other imidazolium salts with a phenyl group in place of the pyridine moiety, such as in **11**-PF_6 and **14**-PF_6, thereby indicating that the reaction responsible for the observation probably does not involve the protonation of the pyridine unit.

Titration studies were performed to give a quantitative understanding of the reactivity of both the open and closed forms. The electronic absorption titration plot of the closed form can be fitted using a 1:1 equilibrium model, and the equilibrium constants K_c are summarized in Table 2. However, the ^{1}H NMR spectroscopic titration result shows that the open form of **5**-PF_6, if not unreactive, has a reactivity at least four orders of magnitude lower towards OH^- in comparison to the closed form. In other words, in systems that

Table 2. Equilibrium constants of the reaction between selected imidazolium salts and OH^-/N_3^- in MeOH at 293 K

Compound	$\log_{10}K_o$[a] (with OH^-)	$\log_{10}K_c$[b] (with OH^-)	$\log_{10}K_c$[b] (with N_3^-)
4-PF_6	–[c]	5.52 ± 0.02	4.66 ± 0.01
5-PF_6	<1.0	5.23 ± 0.03	4.19 ± 0.01
6-PF_6	–[c]	6.06 ± 0.07	–[c]
11-PF_6	–[c]	4.04 ± 0.06	–[c]
12-PF_6	–[c]	3.31 ± 0.01	–[c]
14-PF_6	–[c]	6.00 ± 0.03	–[c]

[a] K_o refers to the equilibrium constant of the reaction with the open form. Estimated using ^{1}H NMR spectroscopic titration. [b] K_c refers to the equilibrium constant of the reaction with the closed form. Determined using UV/Vis absorption titration, whereas the open form is assumed to be inert. [c] Not measured.

contain both the open and closed forms of **5**-PF_6 in methanol, the hydroxide ion will have a high reaction selectivity between the open and closed form species, and essentially only reactions with the closed form will take place. This also makes the determination of K_c more reliable. It would be reasonable to extend this conclusion to other structurally related imidazolium salts in this study. It was also found that other anions with much lower basicity, such as azide and acetate, undergo similar reactions with the equilibrium constant not much smaller than that of the hydroxide, thereby suggesting that the interconversion is not a simple acid–base equilibrium.

Several trends have been observed for the substituent effect on the reaction equilibrium constant: 1) with one *N*-methyl group fixed, the equilibrium constant is found to increase from *N*-phenyl (**11**-PF_6, $\log_{10}K_c=4.04$) to *N*-pyridyl (**4**-PF_6, $\log_{10}K_c=5.52$); 2) with one *N*-phenyl group fixed, the equilibrium constant is found to increase from *N*-methyl (**11**-PF_6, $\log_{10}K_c=4.04$) to *N*-phenyl (**14**-PF_6, $\log_{10}K_c=6.00$); 3) with an increase in the electron-withdrawing effect of the substituent on the pyridine ring, the equilibrium constant is found to increase (i.e., Me (**5**-PF_6, $\log_{10}K_c=5.23$) < H (**4**-PF_6, $\log_{10}K_c=5.52$) < CF_3 (**6**-PF_6, $\log_{10}K_c=6.06$)); and 4) among all imidazolium salts studied, **12**-PF_6 with a methyl group at the 2-position of the imidazolium ring shows the least reactivity ($\log_{10}K_c=3.31$). In short, the reactivities of the imidazolium cations are found to be strongly enhanced by electron-withdrawing substituents at the imidazolium ring, thus suggesting the imidazolium ring as the reaction center. As a result, a reaction pathway that involves the nucleophilic attack at the positively charged 2-carbon atom is proposed (Scheme 6), similar to that suggested in a closely related 2-phenylimidazolium system reported very recently.[6] In its open form, the bond formation enthalpy of the nucleophilic attack at the 2-position of an imidazolium ring has to compensate for the loss of aromaticity upon destruction of the conjugated ring for the reaction to take place. However, after ring closing, the aromaticity of the imidazolium ring has already been largely destroyed, thus leaving the N-C-N part more or less as an isolated iminium cation.[6] It is well known that iminium cations readily undergo nucleophilic additions,[27a] and imidazolinium cations react with alkoxide

to form 2-alkoxyimidazoline.[27b] Similarly, a study on the pseudobase equilibrium of thiazolium cations shows that the saturated thiazolinium ring is about eight orders of magnitude more reactive towards the nucleophilic addition of methoxide than the unsaturated thiazolium ring.[27c] Based on these reports, the nucleophilic-addition pathway could satisfactorily rationalize the much higher reactivity of the closed form over the open form. Furthermore, the nucleophilic pathway is in accordance with the substituent effect described previously (i.e., a more electron-withdrawing group will destabilize the cationic imidazolium ring and favor the addition product more). In fact, compounds such as trifluoromethyl that bear a strong electron-withdrawing group at the 2-position of the imidazolium ring will readily form the basic closed form in solvents with high DN (such as THF, DMF, and DMSO), even without addition of an external nucleophile.

The ^{1}H NMR spectroscopic characterization revealed two sets of signals that belonging to the basic closed form of **5**-PF_6, in a ratio of 2:3 (Figure S4, S5, and Table S8 in the Supporting Information), due to the third chiral center generated by the nucleophilic addition.[28] Both diastereomers are found to show large upfield shift of the protons in comparison to the acidic closed form, especially for the *N*-methyl signal ($\Delta\delta \approx -0.75$ ppm). These observations strongly support the neutralization of the positive charge on the ring after the reaction and provide solid pieces of evidence for the structure of the basic closed form proposed in Scheme 6.

Adopting the structure of the basic closed form, the large hypsochromic shift of the absorption energy compared to the acidic closed form may be attributed to the loss of conjugation over the imidazolium ring. Interestingly, the electronic absorption maximum of the closed form of **13** is found to be 474 nm; whereas that of other related imidazol-2-one analogues have been observed at around 450-464 nm,[4c] for which quite limited π conjugation over the five-membered ring has been suggested.[29] The absorption wavelengths of the basic closed forms fall in the same range (454–468 nm; Table 3), which is in agreement with their structural similarity.

Table 3. A summary of the electronic absorption λ_{max} of the basic closed forms of imidazolium salts and imidazol-2-one.

Compound		λ_{max} [nm]
imidazolium salt[a]	**4**-PF_6	320, 462
	5-PF_6	320, 460
	6-PF_6	324, 466
	11-PF_6	320, 454
	12-PF_6	318, 458
	14-PF_6	328, 468
imidazol-2-one[b]	**13**	474

[a] Measured in methanol. [b] Measured in MeCN.

On the other hand, upon photoirradiation at 460 nm of the basic closed form, cycloreversion of the dithienylethene moiety takes place and only the recovery of the original imidazolium salt is observed, as revealed by the ^{1}H NMR spectroscopic experiments. Thus it is believed that the nucleophilic adduct of the open form is unstable and readily undergoes the elimination to release the nucleophile during this process.

Photochemical quantum yield: The photocyclization and photocycloreversion quantum yields of these imidazolium salts have been recorded in various solvents (Table 4). With the exception of **19**-PF_6 and **21**-PF_6, which bear a trifluoromethyl group at the 2-position of the imidazolium ring, the photocyclization quantum yields for all compounds fall in the range of 0.25–0.36 without the correction for the percentage of the active antiparallel conformation. Compounds **19**-PF_6 and **21**-PF_6 show very low photocyclization quantum yields in acetonitrile, whereas the values are substantially larger in dichloromethane. This might be attributed to the preferential formation of an inactive twisted intramolecular charge transfer (TICT) excited state in a more polar solvent, as has been suggested in the dithienylmaleic anhydride systems.[30] All quantum yields of photocycloreversion are found to be smaller than 0.15, which is remarkably smaller than those for the photocyclization. This is in line with that generally observed in diarylethene systems.[1a]

Table 4. Photochemical quantum yields of selected imidazolium hexafluorophosphates in various solvents at 293 K.

Compound	Photochemical quantum yields (Φ)[a]		
	Photocyclization	Photocycloreversion	
	Φ_{280}	Φ_{350}	Φ_{500}
4-PF_6	0.36[b]	0.105[b,c]	0.066[b]
5-PF_6	0.33 (0.35[b])	0.095[c] (0.090[b,c])	0.060[b]
6-PF_6	0.36[b]	0.087[b,c]	0.053[b]
11-PF_6	0.28	0.085	0.059
12-PF_6	0.28	0.11	0.081
14-PF_6	0.25	0.078	0.053
17-PF_6	0.30	0.042	0.020
19-PF_6	0.026[d] (0.21[d,e])	0.015[f] (0.012[e,f])	–[h]
21-PF_6	0.015[d] (0.13[d,e])	0.0072[f] (0.004[e,g])	–[h]

[a] All photocyclization quantum yields are not corrected for the ratio of the antiparallel conformation with ±20% uncertainty. All data are measured in acetonitrile unless otherwise specified. [b] Measured in methanol. [c] Excited at 360 nm. [d] Excited at 290 nm. [e] Measured in dichloromethane. [f] Excited at 370 nm. [g] Excited at 390 nm. [h] Not measured.

Conclusion

In conclusion, a series of dithienylethene-containing imidazolium salts has been synthesized by using ring-closing or C–N cross-coupling reactions. These imidazolium salts and the related imidazoles undergo a photocyclization reaction upon photoirradiation in the UV region, and the reverse reaction takes place upon excitation at the visible region. The closed form of the imidazolium salt undergoes nucleophilic addition reactions with anionic nucleophiles at the 2-position of the five-membered ring to generate the neutral prod-

uct, whereas the open form is found to be essentially inert towards nucleophiles. This significant difference between the open and closed forms has been attributed to their differences in aromaticity. As a result, a reversible photogated switch in reactivity can be obtained in these systems. Donor–acceptor interaction between the closed form of the imidazolium cation and electron-donating solvent molecules in a manner similar to that of the nucleophilic attack has been observed. This interaction is thought to account for the dependence of the electronic absorption energy of the closed form on the solvent.

Experimental Section

Materials: 4-Dimethylaminopyridine (4-DMAP, 99%) and 2-bromo-5-methylpyridine (98%) were obtained from Lancaster Synthesis Ltd. Phenyl isothiocyanate (98%, Fluka) and cesium carbonate (99%) were obtained from Aldrich Chemical Company. Lithium aluminum hydride (95%) was obtained from Acros Organics. 1,10-Phenanthroline (anhydrous, 99%), 2-bromopyridine (99%), and 2-chloro-5-trifluoromethylpyridine (97%) were obtained from Alfa Aesar. All other reagents and solvents were of analytical grade and used as received unless specifically mentioned. Dry tetrahydrofuran, dry diethyl ether, and dry toluene were distilled over sodium. Methanol for photophysical measurement was distilled over magnesium. Acetonitrile for measurement was distilled over CaH_2. 4,5-Bis(2,5-dimethylthiophen-3-yl)-1*H*-imidazole (**Th_2im**) was synthesized from 1,2-bis(2,5-dimethylthiophen-3-yl)ethane-1,2-dione[31] according to a modification methods reported in the literature.[4a,32] 1,2-Bis(2,5-dimethylthiophen-3-yl)-2-hydroxyl-ethanone was synthesized according to literature methods with minor modifications.[3,4b] A solution of 1-ethoxy-2,2,2-trifluoroethanol in acetic acid (around 35% wt) was prepared by modification of a patent method.[33]

Compound 1: The reaction was performed under nitrogen using Schlenk techniques. A mixture of **Th_2im** (0.81 g, 2.8 mmol), cesium carbonate (1.5 g, 4.6 mmol), copper(I) iodide (0.11 g, 0.58 mmol), and 1,10-phenanthroline (0.11 g, 0.59 mmol) was placed in a two-necked round-bottom flask charged with a reflux condenser. Degassed DMSO (30 mL) was added to the flask, followed by 2-bromopyridine (0.55 g, 3.5 mmol). The resulting mixture was heated to 130–140 °C under nitrogen, and the reaction was monitored by TLC. After cooling to room temperature, ethyl acetate (30 mL), Na_2EDTA, water (30 mL), and aqueous NH_4Cl solution (saturated, 5 mL) were added to the reaction mixture. The mixture was allowed to stir in open air for about 30 min. The resulting mixture was extracted with ethyl acetate (20 mL × 3), and the combined organic extracts were washed with water (20 mL × 4) and brine. After solvent removal, the residue was purified by flash column chromatography on silica gel (pretreated with 1% triethylamine in hexane) by using ethyl acetate/petroleum ether (1:2 v/v) as eluent. The desired product was obtained as an off-white solid. Yield: 0.83 g, 2.3 mmol; 65%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89 (s, 3H; 2-Me), 2.22 (s, 3H; 2-Me), 2.35 (s, 6H; two 5-Me), 6.31 (s, 1H; thienyl), 6.49 (s, 1H; thienyl), 6.75 (d, J = 8.2 Hz, 1H; pyridyl 3-H), 7.23 (dd, J = 7.4, 5.0 Hz, 1H; pyridyl 5-H), 7.61 (td, J = 7.8, 1.9 Hz, 1H; pyridyl 4-H), 8.27 (s, 1H; imidazolyl 2-H), 8.53–8.51 ppm (m, 1H; pyridyl 6-H); MS (EI)$^+$: m/z: 365 $[M]^+$, 350 $[M-Me]^+$, 273 $[M-Me-C_5H_3N]^+$; elemental analysis calcd (%) for $C_{20}H_{19}N_3S_2 \cdot {}^1/_3H_2O$: C 64.66, H 5.34, N 11.31; found: C 64.55, H 5.20, N 11.00.

Compound 2: Compound **2** was synthesized using a method similar to that for **1**, except 2-bromo-5-methylpyridine (0.62 g, 3.6 mmol) was used in place of 2-bromopyridine. Purification by flash column chromatography on silica gel (pretreated with 1% triethylamine in hexane) by using an ethyl acetate/petroleum ether mixture (1:1 v/v) as eluent gave the desired product as a pale yellow solid after solvent removal. Yield: 0.59 g, 2.0 mmol; 55%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (s, 3H; 2-Me), 2.21 (s, 3H; 2-Me), 2.35 (s, 9H; two 5-Me and pyridyl 5-methyl), 6.30 (s, 1H; thienyl), 6.50 (s, 1H; thienyl), 6.64 (d, J = 8.6 Hz, 1H; pyridyl 3-H), 7.40 (dd, J = 8.6, 2.3 Hz, 1H; pyridyl 4-H), 8.20 (s, 1H; imidazolyl 2-H), 8.32–8.33 ppm (m, 1H; pyridyl 6-H); MS (EI)$^+$: m/z: 379 $[M]^+$, 364 $[M-Me]^+$, 273 $[M-Me-C_6H_5N]^+$; elemental analysis calcd (%) for $C_{21}H_{21}N_3S_2$: C 66.47, H 5.58, N 11.07; found: C 66.20, H 5.70, N 10.67.

Compound 3: Compound **3** was synthesized using a method similar to that for **1**, except 2-chloro-5-trifluoromethylpyridine (0.64 g, 3.5 mmol) was used in place of 2-bromopyridine. Purification by flash column chromatography on silica gel (pretreated with 1% triethylamine in hexane) by using an ethyl acetate/petroleum ether mixture (1:9 to 1:4 v/v) as eluent gave the desired product as a very pale yellow solid after solvent removal. Yield: 1.2 g, 2.8 mmol; 80%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (s, 3H; 2-Me), 2.27 (s, 3H; 2-Me), 2.34 (s, 3H; 5-Me), 2.39 (s, 3H; 5-Me), 6.35 (s, 1H; thienyl), 6.44 (s, 1H; thienyl), 6.82 (d, J = 8.6 Hz, 1H; pyridyl 3-H), 7.82 (dd, J = 8.6, 1.9 Hz, 1H; pyridyl 4-H), 8.40 (s, 1H; imidazolyl 2-H), 8.77 ppm (s, 1H; pyridyl 6-H); MS (EI)$^+$: m/z: 433 $[M]^+$, 418 $[M-Me]^+$, 273 $[M-Me-C_6H_2NF_3]^+$; elemental analysis calcd (%) for $C_{21}H_{18}N_3S_2F_3 \cdot {}^1/_4H_2O$: C 57.58, H 4.26, N 9.59; found: C 57.68, H 4.29, N 9.29.

Compound 4-PF_6: Iodomethane (0.2 mL, 3 mmol) was added to a solution of **1** (190 mg, 0.50 mmol) in toluene (8 mL), and the mixture was stirred at 50–60 °C. White precipitate was formed in several hours. After 24 h, more iodomethane (0.2 mL, 3 mmol) was added, and the mixture was further stirred for one day. The imidazolium iodide was collected by filtration and washed with toluene and diethyl ether. Metathesis of the iodide with NH_4PF_6 in a MeOH/water mixture gave the analytically pure **4**-PF_6 as white crystals. Yield: 140 mg, 0.26 mmol; 53%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3H; 2-Me), 2.02 (br s, 3H; 2-Me), 2.29 (s, 3H; 5-Me), 2.45 (s, 3H; 5-Me), 3.86 (s, 3H; NMe), 6.23 (s, 1H; thienyl), 6.71 (s, 1H; thienyl), 7.20 (d, J = 8.1 Hz, 1H; pyridyl 3-H), 7.46 (ddd, J = 7.5, 4.9, 0.8 Hz, 1H; pyridyl 5-H), 7.81 (td, J = 7.8, 1.8 Hz, 1H; pyridyl 4-H), 8.55 (ddd, J = 4.9, 1.8, 0.8 Hz, 1H; pyridyl 6-H), 8.94 ppm (s, 1H; imidazolyl 2-H); MS (FAB)$^+$: m/z: 380 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{21}H_{22}N_3S_2PF_6 \cdot {}^1/_4H_2O$: C 47.59, H 4.28, N 7.93; found: C 47.63, H 4.25, N 7.91.

Compound 5-PF_6: Compound **5**-PF_6 was obtained as white crystals using a method similar to that for **4**-PF_6, except **2** (217 mg, 0.50 mmol) was used in place of **1**. Yield: 104 mg, 0.20 mmol; 40%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3H; 2-Me), 2.01 (br s, 3H; 2-Me), 2.29 (s, 3H; 5-Me), 2.41 (s, 3H; pyridyl 5-Me), 2.45 (s, 3H; 5-Me), 3.84 (s, 3H; NMe), 6.23 (s, 1H; thienyl), 6.70 (s, 1H; thienyl), 7.08 (d, J = 8.2 Hz, 1H; pyridyl 3-H), 7.59 (dd, J = 8.2, 2.2 Hz, 1H; pyridyl 4-H), 8.34 (d, J = 2.2 Hz, 1H; pyridyl 6-H), 8.88 ppm (s, 1H; imidaolyl 2-H); MS (FAB)$^+$: m/z: 394 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{22}H_{24}N_3S_2PF_6 \cdot {}^1/_3C_4H_{10}O$: C 49.67, H 4.88, N 7.45; found: C 49.44, H 4.90, N 7.48.

Compound 6-PF_6: Compound **6**-PF_6 was obtained as white crystals using a method similar to that for **4**-PF_6, except **3** (217 mg, 0.50 mmol) was used in place of **1**. Yield: 144 mg, 0.24 mmol; 48%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (br s, 3H; 2-Me), 2.05 (br s, 3H; 2-Me), 2.32 (s, 3H; 5-Me), 2.46 (s, 3H; 5-Me), 3.86 (s, 3H; NMe), 6.25 (s, 1H; thienyl), 6.71 (s, 1H; thienyl), 7.31 (d, J = 8.5 Hz, 1H; pyridyl 3-H), 8.04 (dd, J = 8.5, 2.3 Hz, 1H; pyridyl 4-H), 8.81–8.83 (m, 1H; pyridyl 6-H), 9.02 ppm (s, 1H; imidazolyl 2-H); MS (FAB)$^+$: m/z: 448 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{22}H_{21}N_3S_2PF_9$: C 44.52, H 3.57, N 7.08; found: C 44.46, H 3.63, N 7.06.

Compound Th_2CONHPh: 1,2-Bis(2,5-dimethyl-3-thienyl)-2-hydroxyethanone (1.30 g, 4.64 mmol) was dissolved in thionyl chloride (8 mL) with several drops of DMF added as catalyst, and the mixture was stirred at room temperature for 2–3 h. The reaction was monitored by TLC. After completion, the reaction mixture was poured into an ice-water mixture carefully with stirring to destroy the excess amount of thionyl chloride. The mixture was then extracted with ethyl acetate/hexane mixture (1:1 v/v, 20 mL × 2). The combined organic extracts were washed with water, neutralized with solid $NaHCO_3$, and then washed with brine. Removal of the solvent gave a brown to red residue. Aniline (0.50 mL, 5.5 mmol) was added to a mixture of the residue, K_2CO_3 (1.02 g, 7.4 mmol), and NaI (0.10 g, 0.69 mmol) in degassed dry MeCN (10 mL) under an N_2 atmos-

phere. The mixture was stirred at 60–70 °C for 6–8 h. After solvent removal under reduced pressure, the residue was mixed with water and extracted with ethyl acetate (20 mL × 2). The combined extracts were washed with water and brine successively, and then evaporated to dryness. Flash column chromatography on silica gel using an ethyl acetate/petroleum ether mixture (1:50 to 1:40, v/v) as eluent gave **Th_2CONHPh** as a very pale yellow oil or an off-white solid after removal of the solvent. Yield: 1.27 g, 3.57 mmol; 77 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H; 5-Me), 2.38 (s, 3H; 5-Me), 2.50 (s, 3H; 2-Me), 2.62 (s, 3H; 2-Me), 4.97 (br s, 1H; NH), 5.57 (d, J = 5.5 Hz, 1H; −COCH−), 6.50 (s, 1H; thienyl), 6.60 (d, J = 7.7 Hz, 2H; phenyl 2,6-H), 6.69 (t, J = 7.3 Hz, 1H; phenyl 4-H), 6.93 (s, 1H; thienyl), 7.13 ppm (t, J = 7.5 Hz, 2H; phenyl 3,5-H); MS (EI)$^+$: m/z: 216 $[M-C_6H_7SCO]^+$.

Compound 7: Formic acid (98 %, 1.5 mL) and acetic anhydride (3 mL) were added slowly to a flask charged with condenser and drying tube at 0 °C. The mixture was stirred at 50 °C for 1.5 h and then cooled in an ice-water bath. **Th_2CONHPh** (0.23 g, 0.65 mmol) was dissolved in the mixture and stirred at 50–60 °C for 3 h. The reaction mixture was cooled in an ice-water bath, quenched with water, and carefully neutralized with aqueous NaOH solution. The mixture was extracted with ethyl acetate (20 mL × 2). The combined extracts were washed with water and brine and then evaporated to dryness to obtain the crude product as a pale yellow to pale brown oil. No further purification was performed. Yield: 0.26 g, 0.65 mmol; > 95 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3H; 5-Me), 2.30 (s, 3H; 2-Me), 2.32 (s, 3H; 5-Me), 2.70 (s, 3H; 2-Me), 6.05 (s, 1H; thienyl), 6.68 (s, 1H; −COCH−), 6.78 (s, 1H; thienyl), 7.10–7.15 (m, 2H; phenyl), 7.21–7.23 (m, 3H; phenyl), 8.37 ppm (s, 1H; CHO).

Compound 8: Acetyl chloride (1.0 mL, 14 mmol) and triethylamine (0.35 mL, 2.5 mmol) were added to a solution of **Th_2CONHPh** (0.48 g, 1.3 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was stirred at ambient temperature for two hours. The reaction as monitored by TLC. After completion, cold water was added to the reaction mixture, and the mixture was neutralized with aqueous Na_2CO_3 solution. Extraction of the mixture with ethyl acetate (20 mL × 2) of the mixture gave the crude product as a brown oil after removal of the solvent. The product was used directly in the next step. Alternatively, further purification by flash column chromatography on silica gel using am ethyl acetate/petroleum ether mixture (1:9 to 1:4 v/v) as eluent gave **8** as a yellow oil after solvent removal. Yield: 0.43 g, 1.1 mmol; 80 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 3H; 5-Me), 2.31 (s, 3H; 5-Me), 2.33 (s, 3H; 2-Me), 2.69 (s, 3H; 2-Me), 5.87 (s, 1H; −COCH−), 6.72 (s, 1H; thienyl), 6.80 (s, 1H; thienyl), 7.1–8.2 ppm (m, 5H; phenyl).

Compound 9: A mixture of NH_4OAc (0.36 g, 4.7 mmol) and crude **7** (around 0.6 mmol) in glacial HOAc (8 mL) was heated to gentle boiling for 16–20 h. After cooling, most glacial acetic acid was removed under reduced pressure. The residue was neutralized with aqueous NaOH solution and extracted with ethyl acetate (20 mL × 2). The combined extracts were washed with water and brine and then evaporated to dryness. Flash column chromatography on silica gel (pretreated with approximately 1 % triethylamine solution in petroleum ether) using an ethyl acetate/petroleum ether mixture (1:5 to 1:4 v/v) as eluent gave **9** as a pale yellow oil or an off-white solid after removal of the solvent. Yield: 0.17 g, 0.47 mmol; 70 % for two steps; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (s, 3H; 2-Me), 2.18 (s, 3H; 2-Me), 2.28 (s, 3H; 5-Me), 2.35 (s, 3H; 5-Me), 6.17 (s, 1H; thienyl), 6.55, (s, 1H; thienyl), 7.10–7.14 (m, 2H; phenyl), 7.28–7.36 (m, 3H; phenyl), 7.78 ppm (s, 1H; imidazolyl 2-H); MS (EI)$^+$: m/z: 364 $[M]^+$, 349 $[M-Me]^+$, 273 $[M-Me-C_6H_4]^+$; elemental analysis calcd (%) for $C_{21}H_{20}N_2S_2$: C 69.19, H 5.53, N 7.68; found: C 69.01, H 5.57, N 7.26.

Compound 10: A mixture of NH_4OAc (0.64 g, 8.3 mmol) and crude **8** (0.43 g, 1.1 mmol) in glacial HOAc (5 mL) was heated to reflux. After all the starting material **8** had been consumed as shown by TLC, most glacial acetic acid was removed under reduced pressure. The residue was neutralized with aqueous Na_2CO_3 solution and extracted with ethyl acetate (20 mL × 2). The combined extracts were washed with water and brine and then evaporated to dryness. Flash column chromatography on silica gel (pretreated with approximately 1 % triethylamine solution in petroleum ether) using an ethyl acetate/petroleum ether mixture (1:6 to 1:3 v/v) gave the desired compound. Analytically pure **10** was obtained as an off-white solid by washing with diethyl ether/*n*-hexane mixture (1:1 v/v). Yield: 0.16 g, 0.42 mmol; 39 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (s, 3H; 2-Me), 2.06 (s, 3H; 2-Me), 2.22 (s, 3H; 5-Me), 2.35 (s, 3H; imidazolyl 2-Me), 2.36 (s, 3H; 5-Me), 6.05 (s, 1H; thienyl), 6.65, (s, 1H; thienyl), 7.09–7.11 (m, 2H; phenyl), 7.33–7.40 ppm (m, 3H; phenyl); MS (EI)$^+$: m/z: 378 $[M]^+$, 363 $[M-Me]^+$, 287 $[M-Me-C_6H_4]^+$; elemental analysis calcd (%) for $C_{22}H_{22}N_2S_2$: C 69.80, H 5.86, N 7.40; found: C 69.55, H 5.88, N 6.96.

Compound 11-PF_6: Compound **11**-PF_6 was obtained as tiny white crystals by using a method similar to that for **4**-PF_6, except **9** (175 mg, 0.47 mmol) was used in place of **1**. Yield: 149 mg, 0.28 mmol; 61 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.86 (s, 3H; 2-Me), 2.01 (br s, 3H; 2-Me), 2.26 (s, 3H; 5-Me), 2.46 (s, 3H; 5-Me), 3.82 (s, 3H; NMe), 6.13 (s, 1H; thienyl), 6.64 (s, 1H; thienyl), 7.31–7.34 (m, 2H; phenyl), 7.38–7.46 (m, 3H; phenyl), 8.82 ppm (s, 1H; imidazolyl 2-H); MS (FAB)$^+$: m/z: 379 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{22}H_{23}N_2S_2PF_6$: C 50.38, H 4.42, N 5.34; found: C 50.06, H 4.52, N 5.23.

Compound 12-PF_6: Compound **12**-PF_6 was obtained as pale yellow needlelike crystals by using a method similar to that for **4**-PF_6, except **10** (156 mg, 0.42 mmol) was used in place of **1**. Yield: 180 mg, 0.34 mmol; 80 %; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 3H; 2-Me), 2.04 (br s, 3H; 2-Me), 2.19 (s, 3H; 5-Me), 2.44 (s, 3H; 5-Me), 2.59 (s, 3H; imidazolyl 2-Me), 3.70 (s, 3H; NMe), 6.12 (s, 1H; thienyl), 6.79 (br s, 1H; thienyl), 7.14 (br s, 1H; phenyl), 7.33–7.66 ppm (m, 4H; phenyl); MS (FAB)$^+$: m/z: 393 $[M-PF_6]^+$; elemental analysis calcd (%) for $C_{23}H_{25}N_2S_2PF_6 \cdot {}^1/_4C_3H_6O \cdot {}^1/_2H_2O$: C 50.75, H 4.93, N 4.98; found: C 50.53, H 4.66, N 4.98.

Compound 13: Phenyl isocyanate (0.20 mL, 1.8 mmol) and a catalytic amount of 4-DMAP (10 mg) were added to a solution of **Th_2CONHPh** (489 mg, 1.38 mmol) in dry CH_2Cl_2 (10 mL). The solution was stirred at room temperature under nitrogen for 24 h, during which white precipitate appeared gradually. Pyridine (0.8 mL, 10 mmol) and thionyl chloride (0.3 mL, 4 mmol) were added to the mixture, and the mixture was stirred at room temperature for two hours, during which all solid dissolved. The reaction solution was washed with aqueous $NaHCO_3$ solution, dilute hydrochloric acid, water, and brine successively. After removal of the solvent, the residue was purified by flash column chromatography on silica gel by using an ethyl acetate/petroleum ether mixture (1:6 to 1:4 v/v) as eluent. The major band was collected and evaporated to give an off-white solid. The solid was taken up with diethyl ether (30 mL), and the solution was left to stand in the refrigerator overnight. The mixture was filtered and washed with diethyl ether. The combined filtrates were evaporated to give **13** as an off-white solid. Yield: 592 mg, 1.30 mmol; 94 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83 (s, 6H; 2-Me), 2.24 (s, 6H; 5-Me), 6.08 (s, 2H; thienyl), 7.20–7.30 ppm (m, 10H; phenyl).

Compound 14-PF_6: The reaction was performed under nitrogen using Schlenk techniques. Compound **13** (96 mg, 0.21 mmol) was added to a suspension of lithium aluminum hydride (79 mg, 2.1 mmol) in degassed dry diethyl ether (10 mL) under nitrogen at 0 °C. The mixture was allowed to warm to room temperature and stirred for 4 h. The solution turned pale yellow, and TLC showed the complete consumption of the starting material. The reaction was quenched by successive addition of water (0.8 mL), aqueous NaOH solution (15 %, 0.8 mL), and water (1.0 mL) at 0 °C. Diethyl ether (5 mL) was added to the mixture. Concentrated hydrochloric acid (around 0.8 mL, 9 mmol) was then added carefully to neutralize the base released during the quenching process, followed by some solid $NaHCO_3$. A solution of iodine (63 mg, 0.25 mmol) in chloroform (6 mL) was added to the resulted mixture dropwise, and the mixture was stirred at room temperature for 10 min. The organic layer was separated, washed with aqueous $Na_2S_2O_3$ solution, and then dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was treated with diethyl ether to give the imidazolium iodide as a white solid. Metathesis of the iodide with NH_4PF_6 in MeOH gave the analytically pure **14**-PF_6 as white crystals. Yield: 56 mg, 0.10 mmol; 46 %; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (s, 6H; 2-Me), 2.27 (br s, 6H; 5-Me), 6.25 (s, 2H; thienyl), 7.40–7.60 (m, 10H; phenyl), 8.71 ppm (s, 1H; imidazolyl 2-H); MS (FAB)$^+$: m/z: 441 $[M-PF_6]^+$; elemental analysis

calcd (%) for $C_{27}H_{25}N_2S_2PF_6 \cdot {}^1/_2H_2O$: C 54.44, H 4.40, N 4.70; found: C 54.33, H 4.50, N 4.63.

Compound 15: Concentrated hydrochloric acid (0.33 mL, 4.0 mmol) was added dropwise to a solution of sodium thiocyanate (335 mg, 4.1 mmol) in acetone (5 mL). White precipitate formed immediately. The mixture was further stirred for 15 min at room temperature, and a solution of **Th_2CONHPh** (143 mg, 0.40 mmol) in THF (1 mL) was added, followed by a catalytic amount of 4-DMAP. The resulted mixture was heated to reflux for 3 h. After removal of the solvent under reduced pressure, the residue was dissolved in chloroform, and washed with water and brine. Removal of chloroform led to the isolation of **15** as an off-white solid. No further purification was performed. Yield: 152 mg, 0.38 mmol; 96%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.85$ (s, 3H; 2-Me), 2.02 (s, 3H; 2-Me), 2.20 (s, 3H; 5-Me), 2.37 (s, 3H; 5-Me), 6.02 (s, 1H; thienyl), 6.48 (s, 1H; thienyl), 7.20–7.30 (m, 2H; phenyl), 7.34–7.39 (m, 3H; phenyl), 9.80 ppm (brs, 1H; NH); MS (EI)$^+$: *m/z*: 396 [*M*]$^+$, 381 [*M*−Me]$^+$, 364 [*M*−S]$^+$, 349 [*M*−S−Me]$^+$.

Compound 16: A mixture of **15** (95 mg, 0.24 mmol) and NaOH (15 mg, 0.38 mmol) in MeOH (6 mL) was stirred at room temperature for 30 min to form a dark red solution. Iodomethane (24 μL, 0.38 mmol) was added to the solution, and the reaction was completed in about 10 min. The solvent was removed under reduced pressure. The residue was taken up in ethyl acetate and washed with water and brine. Removal of chloroform led to isolation of the crude product as an off-white solid. Flash column chromatography on silica gel by using an ethyl acetate/petroleum ether mixture (1:9 v/v) as eluent gave **16** as a white solid after removal of the solvent. Yield: 90 mg, 0.22 mmol; 91%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 1.87 (s, 3H; 2-Me), 2.21 (s, 3H; 2-Me), 2.22 (s, 3H; 5-Me), 2.33 (s, 3H; 5-Me), 2.63 (s, 3H; SMe), 6.10 (s, 1H; thienyl), 6.55 (s, 1H; thienyl), 7.13–7.16 (m, 2H; phenyl), 7.33–7.36 ppm (m, 3H; phenyl); MS (EI)$^+$: *m/z*: 410 [*M*]$^+$, 395 [*M*−Me]$^+$; elemental analysis calcd (%) for $C_{22}H_{22}N_2S_3 \cdot {}^1/_2C_3H_6O$: C 64.20, H 5.73, N 6.37; found: C 63.84, H 5.55, N 6.33.

Compound 17-PF_6: Compound **17**-PF_6 was obtained as a white crystalline solid using a method similar to that for **4**-PF_6, except **16** (156 mg, 0.42 mmol) was used in place of **1**. Yield: 144 mg, 0.25 mmol; 60%. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.94$ (s, 3H; 2-Me), 1.99 (brs, 3H; 2-Me), 2.19 (s, 3H; 5-Me), 2.36 (s, 3H; SMe), 2.44 (s, 3H; 5-Me), 3.89 (s, 3H; NMe), 6.16 (brs, 1H; thienyl), 6.92 (brs, 1H; thienyl), 7.26 (brs, 1H; phenyl), 7.35–7.70 ppm (m, 5H; phenyl); MS (FAB)$^+$: *m/z*: 425 [*M*−PF_6]$^+$; elemental analysis calcd (%) for $C_{23}H_{25}N_2S_3PF_6 \cdot {}^1/_4C_3H_6O$: C 48.75, H 4.56, N 4.79; found: C 48.94, H 4.33, N 5.10.

Compound 18: A solution of the prepared 1-ethoxy-2,2,2-trifluoroethanol (approximately 35% wt, 1.2 g, 2.8 mmol) in acetic acid was added to a mixture of 1,2-bis(2,5-dimethyl-3-thienyl)ethane-1,2-dione (0.32 g, 1.2 mmol) and ammonium acetate (0.65 g, 8.4 mmol) in glacial acetic acid (3 mL). The mixture was heated to reflux for 20 h. After removal of acetic acid, the residue was taken up with chloroform, washed with aqueous $NaHCO_3$ solution, and dried over anhydrous $MgSO_4$. Flash column chromatography on silica gel by using a chloroform/petroleum ether mixture (1:4 v/v) that contained 0.1% (v/v) of triethylamine as eluent gave a trace amount of 2-trifluoromethyloxazole as byproduct. Further elution with an ethyl acetate/petroleum ether mixture (1:6 to 1:4 v/v) gave the desired **18** as a white solid after solvent removal. Yield: 0.19 g, 0.54 mmol; 47%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.03$ (s, 3H; 2-Me), 2.11 (s, 3H; 2-Me), 2.36 (s, 3H; 5-Me), 2.42 (s, 3H; 5-Me), 6.59 (s, 1H; thienyl), 6.62 (s, 1H; thienyl), 9.37 ppm (brs, 1H; NH); MS (EI)$^+$: *m/z*: 356 [*M*]$^+$, 341 [*M*−Me]$^+$; elemental analysis calcd (%) for $C_{16}H_{15}N_2S_2F_3 \cdot {}^1/_3CH_4O$: C 53.44, H 4.48, N 7.63; found: C 53.24, H 4.20, N 7.30.

Compound 19-PF_6: Iodomethane (25 μL, 0.40 mmol) was added to a mixture of **18** (100 mg, 0.28 mmol) and K_2CO_3 (50 mg, 0.36 mmol) in acetonitrile (10 mL), and the mixture was heated to 50°C under nitrogen for two hours. The solvent was removed under reduced pressure. The residue was taken up in ethyl acetate and washed with water and brine. Removal of the solvent led to the isolation of an off-white solid. The solid was dissolved in acetonitrile (3 mL), and iodomethane (3 mL) was added to this solution. The mixture was heated to reflux for two days. The solvent was removed under reduced pressure. Toluene (1 mL) and diethyl ether (5 mL) were added to the resulting solid. The pale yellow imidazolium iodide precipitate was collected by filtration and washed with diethyl ether. Metathesis of the iodide with NH_4PF_6 in MeOH gave the analytically pure **19**-PF_6 as white crystals. Yield: 81 mg, 0.15 mmol; 55%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.97$ (s, 3.9H; 2-Me, antiparallel), 2.20 (s, 2.1H; 2-Me, parallel), 2.38 (s, 2.1H; 5-Me, parallel), 2.43 (s, 3.9H; 5-Me, antiparallel), 3.85 (s, 1.04H; NMe, parallel), 3.87 (brs, 1.96H; NMe, antiparallel), 6.52 (brs, 0.69H; thienyl, parallel), 6.97 ppm (brs, 1.31H; thienyl, antiparallel); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -58.1$ (s, 1.9F; CF_3, antiparallel), −58.2 (s, 1.1F; CF_3, parallel), −74.8 ppm (d, ^2J(P,F) = 710 Hz, 6F; PF_6); MS (FAB)$^+$: *m/z*: 385 [*M*−PF_6]$^+$; elemental analysis calcd (%) for $C_{18}H_{20}N_2S_2PF_9$: C 40.76, H 3.80, N 5.28; found: C 40.57, H 3.76, N 5.30.

Compound 20: A solution of 1-ethoxy-2,2,2-trifluoroethanol (approximately 35 wt%, 1.2 g, 2.8 mmol) in acetic acid was added to a mixture of **Th_2CONHPh** (328 mg, 0.92 mmol) and ammonium acetate (268 mg, 3.5 mmol) in acetic acid (5 mL). The mixture was heated to reflux for 24 h in open air. After removal of acetic acid, the residue was taken up with chloroform, washed with aqueous $NaHCO_3$ solution, and dried over anhydrous $MgSO_4$. Flash column chromatography on silica gel by using an ethyl acetate/petroleum ether mixture (1:40 v/v) as eluent gave the desired product as a pale yellow solid after removal of the solvent. Yield: 262 mg, 0.60 mmol; 66%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.91$ (s, 3H; 2-Me), 2.19 (s, 3H; 5-Me), 2.23 (s, 3H; 2-Me), 2.31 (s, 3H; 5-Me), 6.12 (s, 1H; thienyl), 6.54 (s, 1H; thienyl), 7.1–7.3 (m, 2H; phenyl), 7.3–7.4 ppm (m, 3H; phenyl); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -59.6$ ppm (s, 3F; CF_3); MS (EI)$^+$: *m/z*: 432 [*M*]$^+$, 417 [*M*−Me]$^+$; elemental analysis calcd (%) for $C_{22}H_{19}N_2S_2F_3 \cdot {}^1/_2C_3H_6O$: C 61.15, H 4.80, N 6.07; found: C 61.02, H 4.61, N 5.89.

Compound 21-PF_6: Compound **21**-PF_6 was obtained as colorless needle-like crystals using a method similar to that for **19**-PF_6, except **20** (100 mg, 0.231 mmol) was used in place of **18**. Yield: 67 mg, 0.11 mmol; 50%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.95$ (s, 3H; 2-Me), 2.05 (brs, 3H; 2-Me), 2.18 (s, 3H; 5-Me), 2.44 (s, 3H; 5-Me), 3.98 (brs, 3H; NMe), 6.16 (brs, 1H; thienyl), 6.81 (brs, 1H; thienyl), 7.26 (brs, 1H; phenyl 2′-H), 7.41 (brs, 1H; phenyl 4-H), 7.52 (brs, 2H; phenyl 3-H), 7.62 ppm (brs, 1H; phenyl 2-H); ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -56.3$ (s, 3F; CF_3), −74.1 ppm (d, ^2J(P,F) = 711 Hz, 6F; PF_6); MS (FAB)$^+$: *m/z*: 447 [*M*−PF_6]$^+$; elemental analysis calcd (%) for $C_{23}H_{22}N_2S_2PF_9$: C 46.62, H 3.74, N 4.73; found: C 46.47, H 3.72, N 4.64.

Physical measurements and instrumentation: NMR spectra were recorded using either a Bruker DPX 300 (300 MHz) or a Bruker AVANCE 400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ) were reported in ppm relative to tetramethylsilane (Me_4Si). Electron impact (EI) and fast-atom bombardment (FAB) mass spectra were recorded using a Finnigan MAT 95 mass spectrometer. Negative-ion electrospray ionization (ESI) mass spectra were recorded using a Finnigan LCQ spectrometer. Elemental analyses of ligands and metal complexes were performed using a Flash EA 1112 elemental analyzer by the Institute of Chemistry at the Chinese Academy of Sciences in Beijing. UV/Vis absorption spectra were recorded using a Hewlett–Packard 8452A diode-array spectrophotometer. Steady-state emission and excitation spectra were recorded using a Spex Fluorolog-2 Model F111 fluorescence spectrometer with or without corning filters.

The extinction coefficient of the closed form was determined in the following way. Photoirradiation of a solution with a known concentration of the open form of the molecule gave rise to a solution mixture of the open and closed forms. The ratio between the open and closed forms was determined by ^{1}H NMR spectroscopy, and the extinction coefficient of the closed form was calculated from the ratio and the electronic absorption spectra of this mixture. Based on literature reports[34a] and experiments,[34b] the extinction coefficients of the closed form of one specific compound in various solvents were assumed to be identical within experimental uncertainty at the respective lowest-energy band maxima.

Determination of equilibrium constant with nucleophiles: The reaction equilibrium constants K_c between the closed form of the imidazolium cations and nucleophiles (OH^- and so on) were determined by electronic

absorption titrations at 293 K. A certain volume (approximately 2.0 mL) of the solution of imidazolium hexafluorophosphate in methanol with a known concentration (approximately 5×10^{-5} mol dm^{-3}) was irradiated with UV light for a period of time, thereby leading to the generation of a substantial concentration of the acidic closed form (usually in the range of 1–2$\times10^{-5}$ mol dm^{-3}, determined by the absorbance at the lowest-energy band maximum of the acidic closed form). The resulting solution was then titrated using small volumes of methanolic solution of NaOH or other nucleophiles with a known concentration while keeping the volume change to be within 5%. The absorbance at a selected wavelength was recorded and plotted against the amount of the nucleophile added. The equilibrium constant was obtained from a nonlinear least-squares fitting of the experimental data using a 1:1 model.

The reaction equilibrium constant K_o between the open form of the imidazolium cation of **5**-PF_6 and OH^- was estimated by an ^{1}H NMR spectroscopic titration study at 293 K. nBu$_4$NBF$_4$ (ca. 0.2 mg) as internal standard was added to a solution of **5**-PF_6 in [D$_4$]MeOH (1.0 mL, approximately 1.8×10^{-3} mol dm^{-3}), and the ^{1}H NMR spectrum of this solution was recorded. Small volumes of 0.012 mol dm^{-3} NaOH solution in methanol were successively added to this solution, thus keeping the total volume change to be within 10%. The ^{1}H NMR spectra were recorded upon the titration. Since neither appearance of new signal nor intensity decrease of the original signals was observed until the concentration of NaOH had reached 7.2×10^{-3} mol dm^{-3}, the upper limit of the equilibrium constant K_o was estimated to be 10 by assuming that the concentration of the equilibrium product, if any, would be lower than 1×10^{-4} mol dm^{-3}.

X-ray crystallography: Single crystals of the imidazolium salt **12**-PF_6 suitable for X-ray diffraction structure determination were obtained by slow diffusion of diethyl ether vapor into an acetone solution of **12**-PF_6. Pale yellow needlelike crystals were formed. [$C_{23}H_{25}F_6N_2PS_2\cdot0.5\,C_3H_6O$]: M_r = 568.59; monoclinic, $P2_1/c$; a = 18.228(4), b = 8.006(2), c = 19.649(5) Å; β = 100.26(4)°; V = 2821.4(12) Å^3; Z = 4; ρ_{cald} = 1.339 g cm^{-3}; μ(Mo$_{K\alpha}$) = 0.303 mm^{-1}; $F(000)$ = 1180; T = 301 K. A crystal of dimensions 0.56 × 0.14mm × 0.08 mm mounted in a glass capillary was used for data collection at 28°C using a Bruker Smart CCD 1000 using graphite-monochromatized Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). Raw frame data were integrated with the SAINT program.[35a] Semiempirical absorption correction with SADABS[35b] was applied.

The structure was solved by direct methods by employing the SHELXS-97 program[35c] on a PC. Sulfur and many non-hydrogen atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares procedures using the program SHELXL-97[35c] on a PC. There was one formula unit in the asymmetric unit. One PF_6 anion was located. Half of an acetone solvent molecule was located near the special position; restraints were applied to the C–C bond length (assumed to be around 1.50(2) Å). According to the SHELXL-97 program,[35c] all 5338 independent reflections ($R_{int}=\Sigma|F_o^2-F_o^2(\text{mean})|/\Sigma[F_o^2]=0.0452$, 3000 reflections larger than $4\sigma(F_o)$) from a total 15930 reflections were participated in the full-matrix least-squares refinement against F^2. These reflections were in the range $-21\le h\le22$, $-9\le k\le9$, $-23\le l\le23$ with $2\theta_{max}$ equal to 51.36°. One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, non-hydrogen atoms of acetone were refined isotropically; other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated by the program SHELXL-97.[35c] The positions of hydrogen atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R indices. Since the structure refinements are against F^2, R indices based on F^2 are larger than (more than double) those based on F. For comparison with older refinements based on F and an OMIT threshold, a conventional index R_1 based on observed F values larger than $4\sigma(F_o)$ is also given (corresponding to intensity $\ge2\sigma(I)$). $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, The goodness-of-fit is always based on F^2: GOF = $S=\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$, in which n is the number of reflections and p is the total number of parameters refined. The weighting scheme is: $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$, in which P is $[2F_c^2+\max(F_o^2,0)]/3$. Convergence ($(\Delta/\sigma)_{max}$ = 0.001, avg. 0.001) for 325 variable parameters by full-matrix least-squares refinement on F^2 reaches to R_1 = 0.0740 and wR_2 = 0.2089 with a goodness-of-fit of 1.044, the parameters a and b for weighting scheme are 0.1347 and 0.6687. The final difference Fourier map shows maximum rest peaks and holes of 0.588 and −0.290 e Å^{-3}, respectively.

CCDC-777029 (**12**-PF_6) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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