Syntheses and properties of new photochromic diarylethene derivatives having a pyrazole unit

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Abstract—New photochromic diarylethenes **1a, 2a** and **3a** bearing a pyrazole unit have been synthesized. Their properties, including photochromic reactivity, fluorescence and electrochemical properties were investigated. These compounds showed good photochromic properties, high cycloreversion quantum yield and relatively strong fluorescence. The cycloreversion quantum yields of **1a, 2a** and **3a** are 0.46, 0.53 and 0.57, respectively, which are larger than those of their cyclization quantum yields (0.43, 0.45 and 0.47, respectively). The oxidations of diarylethenes **1a, 2a** and **3a** were initiated at 0.73, 1.11 and 0.79 V, respectively. Moreover, the position of the methoxyl substituent had remarkable impacts on the above optical and electrochemical properties.
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The design and synthesis of photochromic compounds is an area of intense research because of their widespread potential application in photonic devices such as high-density optical recording materials and photoswitches.[1–6] Among various types of photochromic compounds, photochromic diarylethene derivatives with heterocyclic aryl rings are the most promising organic photochromic compounds for photoelectronic applications because of the excellent thermal stability of both of the two isomers, fatigue resistant character, rapid response and high reactivity in solid state.[7–10]
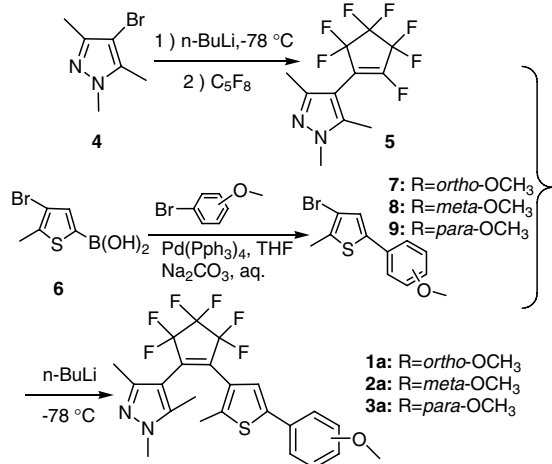
To date, a large number of publications concerning synthesis and investigation of their photochromic properties of diarylethenes with heterocyclic aryl rings have been reported. Among diarylethene derivatives so far synthesized, most of the hetero-aryl moieties have been thiophene or benzothiophene rings,[10–19] and other hetero-aryl moieties, such as thiazole,[20,21] indole,[22,23] benzofuran,[24] crysothiophene,[25] pyrrole[26] and indene,[27] have also been reported partially. The photochromic performance of each kind of diarylethene is strongly dependent on the aryl moieties. Diarylethenes with thiophene or benzothiophene moieties, for instance, exhibit excellent thermal stability and remarkable fatigue resistance;[10] diarylethenes with indole rings exhibit strong fluorescence;[22] whereas diarylethenes with pyrrole rings

are thermally unstable and return to the open-ring isomers even in the dark.[24] When the aryl groups have low aromatic stabilization energy, the derivatives undergo thermally irreversible photochromic reactions.[27] Pyrazole is an attractive aryl unit because of its low aromatic stabilization energy and the structure is similar to isothiazole, expecting to undergo thermally irreversible photochromic reactions. Until now, photochromic hybrid diarylethene derivatives with pyrazole and thiophene moieties have not yet been reported.

In the present work, we have synthesized three new diarylethenes having a pyrazole unit, 1-(1,3,5-trimethyl-1-pyrazol-4-yl)-2-[2-methyl-5-(2-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (**1a**), 1-(1,3,5-trimethyl-1-pyrazol-4-yl)-2-[2-methyl-5-(3-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (**2a**) and 1-(1,3,5-trimethyl-1-pyrazol-4-yl)-2-[2-methyl-5-(4-methoxylphenyl)-1-thien-3-yl]perfluorocyclopentene (**3a**). The effect of electron-donating methoxyl substituent position on the properties of photochromic diarylethenes was investigated based on the absorption spectra, fluorescence and electrochemical properties. The photochromism of diarylethenes **1a**–**3a** which are discussed in this letter, is shown in Scheme 1.

The synthetic route for diarylethenes **1a, 2a** and **3a** is shown in Scheme 2. At first, 1-(1,3,5-trimethyl-1-pyrazol-4-yl)perfluorocyclopentene (**5**) was synthesized according to the similar procedure of Peters et al.[28] A solution of 4-bromo-1,3,5-trimethylpyrazole (**4**)

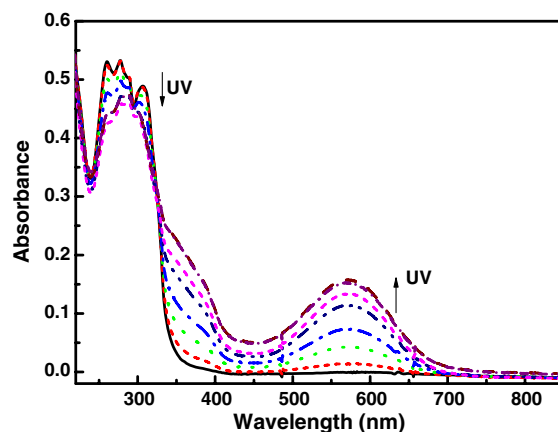* Corresponding author. Tel.: +86 791 3805183; fax: +86 791 3805212; e-mail: pushouzhi@tsinghua.org.cn
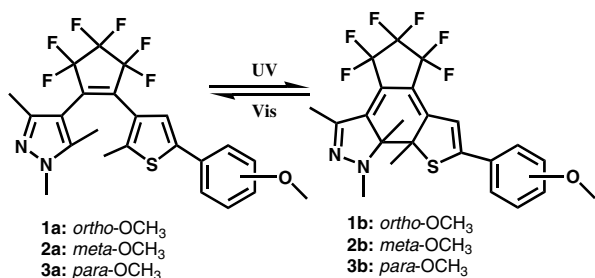
Scheme 1. Photochromism of diarylethenes **1a**–**3a**.

Scheme 2. Synthetic route for the target compounds.

Figure 1. Absorption spectra of diarylethenes **1a** in hexane solution ($C = 2.0 \times 10^{-5}$ mol/L).

Table 1. Absorption spectral properties of diarylethenes **1**–**3** in hexane at 2.0×10^{-5} mol/L

| Compound	$\lambda_{o,max}$ (nm)[a] (ε/L mol^{-1} cm^{-1})	$\lambda_{c,\,max}$ (nm)[b] (ε/L mol^{-1} cm^{-1})	Φ^{c}	
			Φ_{o-c}	Φ_{c-o}
1	278 (2.7×10^4)	573 (1.1×10^4)	0.43	0.46
2	284 (2.5×10^4)	573 (7.9×10^3)	0.45	0.53
3	291 (2.9×10^4)	573 (1.0×10^4)	0.47	0.57

[a] Absorption maxima of open-ring forms.
[b] Absorption maxima of closed-ring forms.
[c] Quantum yields of cyclization reaction (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.

(2.0 g, 10.6 mmol) in an anhydrous THF (30 mL) cooled to −78 °C was treated with *n*-BuLi/hexane solution (6.6 mL, 1.6 M) dropwise under an argon atmosphere. After 30 min, perfluorocyclopentene (1.45 mL, 10.7 mmol) was slowly added to the reaction mixture. The reaction mixture was stirred at this low temperature for 3 h, then was extracted with diethyl ether and evaporated in vacuo, and purified by column chromatography (chloroform) to give compound (**5**) in 65.8% yield. Then, Suzuki coupling of three isomeric bromobenzenes with thiophene boronic acid (**6**)[29] gave methoxylphenyl-thiophene derivatives (**7**–**9**). Finally, they were lithiated and then coupled with compound **5** to give methoxyl-substituted diarylethene derivatives (**1a**–**3a**). The structures of compounds **1a**–**3a**[30] were confirmed by ^{1}H NMR and ^{19}F NMR spectroscopy, mass spectrometry, IR and UV–vis spectroscopy.

Figure 1 shows the absorption spectral change of diarylethene **1a** by photoirradiation in hexane ($C = 2.0 \times 10^{-5}$ mol/L). In hexane solution, the absorption maximum of **1a** was observed at 278 nm ($\varepsilon = 2.7 \times 10^4$ L mol^{-1} cm^{-1}). Upon irradiation with 313 nm light, the color of the hexane solution turned blue, in which the absorption maximum was observed at 573 nm ($\varepsilon = 7.6 \times 10^3$ L mol^{-1} cm^{-1}). The blue solution turned colorless, upon irradiation with visible light ($\lambda > 500$ nm).

The spectral changes of diarylethenes **2a** and **3a** were similar to that of diarylethene **1a**. Their absorption spec-

tral properties are summarized in Table 1. The quantum yields for diarylethenes **1**–**3** were measured in hexane using 1,2-bis(2-methyl-5-phenyl-thien-3-yl)perfluoro-cyclopentene as a reference,[31] and the results are also shown in Table 1. From these data, we can see that the maxima wavelengths of closed-ring forms and the molar absorption coefficients, both open-ring and closed-ring forms, of the three diarylethene compounds are not evidently different. However, the maxima wavelengths of open-ring forms and their quantum yields of cyclization reactions and cycloreversion reactions are relatively remarkable. Among diarylethenes **1**–**3**, the maxima wavelength of the open-ring form and its quantum yields of cyclization and cycloreversion reactions of the *ortho*-substituted derivative are the smallest ($\lambda_{O,max} = 278$ nm, $\Phi_{O-C} = 0.43$, $\Phi_{C-O} = 0.46$); while those of the *para*-substituted derivative are the biggest ($\lambda_{O,max} = 291$ nm, $\Phi_{O-C} = 0.47$, $\Phi_{C-O} = 0.57$). The values of the *meta*-substituted derivative are in between those of the *ortho*- and *para*-substituted derivatives ($\lambda_{O,max} = 284$ nm, $\Phi_{O-C} = 0.45$, $\Phi_{C-O} = 0.53$). In addition, for diarylethenes **1**–**3**, all of the cycloreversion quantum yields are higher than their cyclization quantum yields (Table 1). This is a unique characteristic of diarylethene derivatives having a pyrazole unit, and it is a significant difference between diarylethenes reported herein and all other diarylethenes reported so far.
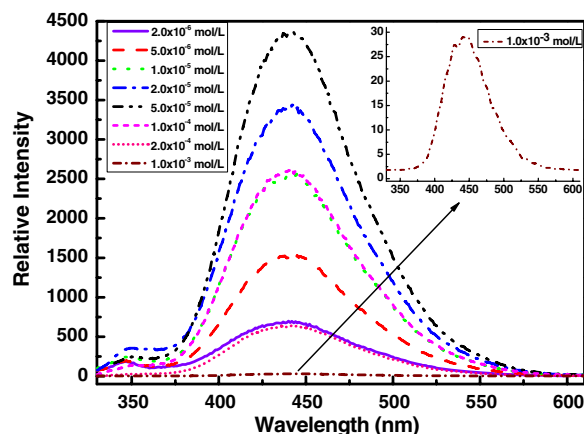
The fluorescence spectra of diarylethenes **1a**–**3a** ($C = 2.0 \times 10^{-5}$ mol/L) in hexane at room temperature are illustrated in Figure 2. All of them showed good
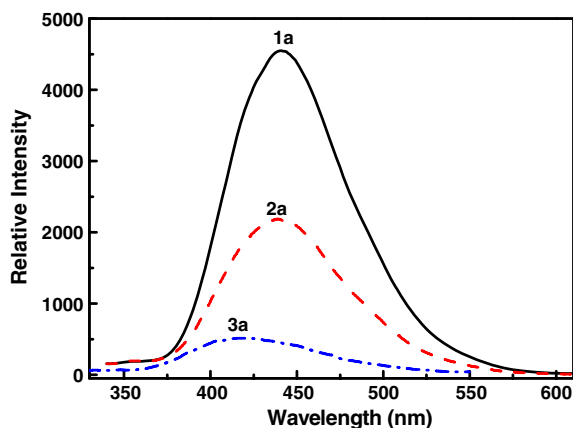
Figure 2. Fluorescence spectra of diarylethenes **1a**–**3a** in hexane solution ($C = 5.0 \times 10^{-5}$ mol/L) at room temperature, excited at 315, 317 and 280 nm, respectively.

Figure 3. Fluorescence spectra of diarylethene **1a** in various concentrations in hexane at room temperature, monitored at 315 nm.

fluorescence at their respective excitation wavelengths, and their fluorescence intensity decreased dramatically along with the photochromism from open-ring isomer to closed-ring isomer upon irradiation with 313 nm light.[32,33] As shown in Figure 2, we can clearly see that the hexane solutions of diarylethenes **1a**–**3a** showed strong fluorescence at 441, 438 and 416 nm when excited at 315, 317 and 280 nm, respectively. When irradiated by light of 313 nm, the photocyclization reactions were carried out and the non-fluorescent closed-ring forms of these three compounds were produced. The back irradiation by appropriate wavelength visible light regenerated the open-ring forms of diarylethenes **1a**–**3a** and recovered the original emission spectra. The phenomena are useful for application as the fluorescence switches.[34,35] The fluorescence maxima of diarylethenes **1a**–**3a** were observed at 416 and 441 nm, indicating that the electron-donating methoxyl substituent position effect on the fluorescence peak is significant. On the other hand, the fluorescence intensities changed dramatically along with the substituent position. The values decreased rapidly from *ortho*-substituted to *para*-substituted diarylethene derivative. Among the three compounds, the relative fluorescence intensity of *ortho*-substituted derivative is the strongest, and that of *para*-substituted derivative is the weakest. The values of the *meta*-substituted derivative are located in between those of the *ortho*- and *para*-substituted derivatives. The result is exactly contrary to that reported in our previous letter.[36] In that letter, the electron-withdrawing fluorine substituent position does not affect significantly on the fluorescence peak of dithienylethene, but can affect remarkably on the fluorescence intensity, with the fluorescence intensity of *ortho*-substituted derivative being the weakest, and that of *para*-substituted derivative the strongest. The possible reason is ascribed to the electron-donating nature of methoxyl substituent of the terminal phenyl group, and the pyrazole ring can also possibly affect the fluorescence properties of the three diarylethenes.

The concentration dependence on the fluorescence spectrum of diarylethene **1a** was measured in hexane at room temperature, as shown in Figure 3. When the concentration of diarylethene **1a** in hexane was increased from 2.0×10^{-6} to 5.0×10^{-5} mol/L, the maximum emission almost arose at 441 nm when excited at 315 nm, and the relative fluorescence intensity increased dramatically. However, when the concentration increased from 5.0×10^{-5} to 1.0×10^{-3} mol/L, the maximum emission appeared in a minor red shift from 441 to 446 nm, and the relative fluorescence intensity decreased remarkably. The hexane solution showed very weak fluorescence when the concentration was increased to 1.0×10^{-3} mol/L. Just as for **1a**, compounds **2a** and **3a** showed similar fluorescent properties depending on the concentration employed. The results are summarized in Table 2. These data show that all fluorescences of the three compounds are remarkably concentration dependent. The fluorescence peaks showed a minor red shift upon increasing the concentration. However, the relative fluorescence intensity showed relatively complex change. They showed a remarkable initial increase with subsequent dramatic decrease with increasing concentration. The biggest and the smallest values were obtained at 5.0×10^{-5} and 1.0×10^{-3} mol/L, respectively. The results also demonstrated that molecular aggregation and the fluorescence quenching may occur when the concentration increases.[37]

The solvent effect on the fluorescence spectra of diarylethenes **1a**–**3a** was also investigated. Fluorescence

Table 2. The concentration effect on the fluorescence spectra of diarylethenes **1a**–**3a** at room temperature in hexane, monitored at 290 nm

Concentration (mol/L)	$\lambda_{em,\,max}$ (Relative intensity)		
	1a	**2a**	**3a**
2.0×10^{-6}	440 (699)	438 (219)	414 (102)
5.0×10^{-6}	441 (1529)	438 (484)	418 (193)
1.0×10^{-5}	441 (2573)	436 (816)	412 (320)
2.0×10^{-5}	441 (3394)	440 (1323)	420 (396)
5.0×10^{-5}	441 (4366)	438 (2180)	416 (514)
1.0×10^{-4}	442 (2637)	439 (2005)	421 (228)
2.0×10^{-4}	442 (641)	443 (1084)	421 (48)
1.0×10^{-3}	446 (29)	445 (24)	441 (7)
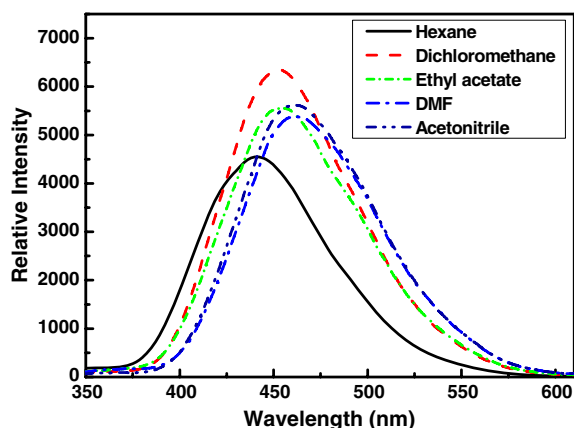
Figure 4. Fluorescence spectra of diarylethene **1a** in various solvents in 5.0×10^{-5} mol/L at room temperature, monitored at 333 nm.

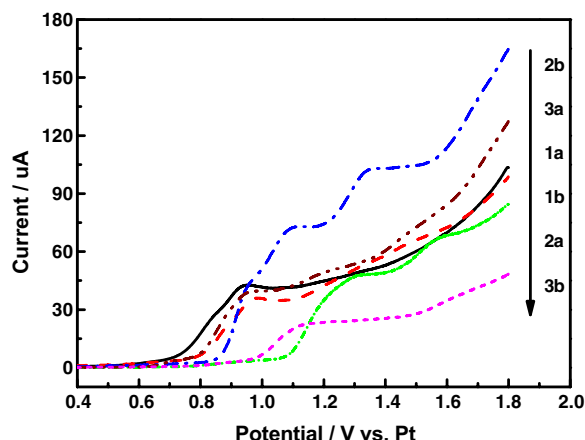**Figure 5.** The anodic polarization curves of diarylethene **1**–**3**.

spectra of **1a** in different solvents at room temperature are shown as in Figure 4, and the fluorescent properties of these three compounds in various solvents at room temperature are summarized in Table 3. From these data, we can see that the fluorescence spectra depended on the polarity of the solvent. It gave a systematic red shift when the polarity of the solvent increased. However, the relative fluorescence intensity is irregular upon increasing the polarity of the solvent.

The electrochemical properties of diarylethene are being used for molecular switching and can also be potentially applied to molecular-scale electronic switches.[36] In order to investigate the electrochemical properties of diarylethenes having a pyrazole unit, we performed electrochemical examinations by linear sweep method under the same experimental conditions using diarylethenes **1a**, **2a** and **3a**, respectively. Experimental method and condition were the same as that described in our previous letter.[36] The typical electrolyte was acetonitrile (5 mL) containing 0.15 mol/L LiClO$_4$ and 4.0×10^{-3} mol/L dithienylethene. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments. Figure 5 showed the anodic polarization curves of **1a**, **1b**, **2a**, **2b**, **3a** and **3b** on Platinum electrode. It can be clearly seen from Figure 5 that the oxidation of **1a**, **1b**, **2a**, **2b**, **3a** and **3b** was initiated at 0.73, 0.78, 1.11, 0.87, 0.79 and 1.00 V, respectively. From these data together with those shown in Figure 5, a conclusion can be reasonably drawn that the substitution of electron-donating methoxyl group has great effect on the

title compounds. For *ortho*-position substitution of methoxyl group of **1a** and **1b**, the electron-donating effect together with its steric effect plays a main role, which made the oxidation potential onset of **1a** and **1b** almost similar to each other. On the other hand, when substituted at *para*-position, the oxidation potential onset of closed-ring form (**3b**) is higher than that of open-ring form (**3a**). This indicates that the electron-donating effect of methoxyl group is more significant in open-ring form. However, when substituted at *meta*-position, opposite results can be easily observed. The oxidation potential onset of closed-ring form (**2b**) is lower than that of open-ring form (**2a**). This implies that the electron-donating effect of methoxyl group is more significant in closed-ring form of compound **2**. In addition, three oxidation processes can be easily observed during anodic oxidation of **2a** and **2b**, while only two oxidation processes can be observed during anodic oxidation of the other two compounds. The three oxidation processes may involve the oxidation of pyrazole ring, thiophene ring, together with the benzene ring of compound **2**. However, the substitution of methoxyl group at *para*-and *ortho*-position made the oxidation process of benzene not very clear for **1a**, **1b**, **3a** and **3b**. All these electrochemical results indicated that the substitution of methoxyl group on benzene and the pyrazole unit had great effect on both the open-ring and closed-ring forms of the three diarylethene derivatives. The detailed explanation requires further investigation.

In conclusion, new types of photochromic diarylethenes having a pyrazole unit were synthesized and their optical and electrochemical properties were investigated. The results showed that the photochromic reactivity, fluorescence and electrochemical properties were remarkably dependent on the substituent position effect of methoxyl group and the pyrazole unit. The reason may be attributed to the different electron-donating effects when the methoxyl group was substituted on the different positions of the terminal benzene ring and the different aromatic stabilization energies of pyrazole unit from that of thiophene unit. The results of this study are useful for the design of efficient photoactive and excellent characteristic diarylethene compounds.

Table 3. Fluorescent properties of diarylethenes **1a**–**3a** in various solutions at 5.0×10^{-5} mol/L

Solvent	λ,max (nm)[a]		
	1a	**2a**	**3a**
Hexane	441 (4366)	438 (2180)	416 (514)
Dichloromethane	452 (6354)	450 (2739)	440 (549)
Ethyl acetate	452 (5560)	452 (2196)	443 (433)
DMF	460 (5376)	460 (2225)	456 (376)
Acetonitrile	463 (5629)	460 (2130)	470 (330)

[a] Fluorescence maxima, excited at 333, 330 and 320 nm for **1a**, **2a** and **3a**, respectively.

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30. Selected data for **1a**–**3a**: Compound **1a**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.96 (s, 3H, –CH$_3$), 1.97 (s, 3H, –CH$_3$), 2.04 (s, 3H, –CH$_3$), 3.69 (s, 3H, –OCH$_3$), 3.92 (s, 3H, –NCH$_3$), 6.98 (dd, 2H, $J = 8.0$ Hz, benzene–H), δ 7.28 (d, 1H, $J = 8.0$ Hz, benzene–H), δ 7.42 (s, 1H, thiophene–H), δ 7.58 (dd, 1H, $J = 7.6$ Hz, benzene–H); ^{19}F NMR (100 MHz, CDCl$_3$) δ −109.46 (2F), −110.51 (2F), −132.57 (2F); MS *m/z* (M$^+$) 487.2; IR (KBr, cm^{-1}) 751, 1127, 1274, 1341,1438, 1635, 2839, 2942; Compound **2a**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.96 (s, 3H, –CH$_3$), 1.97 (s, 3H, –CH$_3$), 2.03 (s, 3H, –CH$_3$), 3.70 (s, 3H, –OCH$_3$), 3.86 (s, 3H, –NCH$_3$), 6.85 (d, 1H, $J = 8.0$ Hz, benzene–H), 7.05 (s, 1H, thiophene–H), 7.12 (d, 1H, $J = 7.6$ Hz, benzene–H), 7.24 (s, 1H, benzene–H), 7.30 (t, 1H, $J = 8.0$ Hz, benzene–H); ^{19}F NMR (100 MHz, CDCl$_3$) δ −109.45 (2F), −110.51 (2F), −132.58 (2F); MS *m/z* (M$^+$) 487.2; IR (KBr, cm^{-1}) 687, 770, 799, 882, 1121, 1271, 1336,1434, 1602, 2841, 2948, 2966; Compound **3a**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.94 (s, 3H, –CH$_3$), 1.97 (s, 3H, –CH$_3$), 2.03 (s, 3H, –CH$_3$), 3.70 (s, 3H, –OCH$_3$), 3.84 (s, 3H, –NCH$_3$), 6.91 (d, 2H, $J = 8.4$ Hz, benzene–H), 7.13 (s, 1H, thiophene–H), 7.45 (d, 2H, $J = 8.4$ Hz, benzene–H); ^{19}F NMR (100 MHz, CDCl$_3$) δ −109.43 (2F), −110.52 (2F), −132.58 (2F); MS *m/z* (M$^+$) 487.2; IR (KBr, cm^{-1}) 800, 821, 1124, 1255, 1341,1477, 1550, 1611, 2841, 2927, 2960.
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