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THE ELECTRONIC STRUCTURE OF THIOXANTHYLIUM SCAFFOLDS

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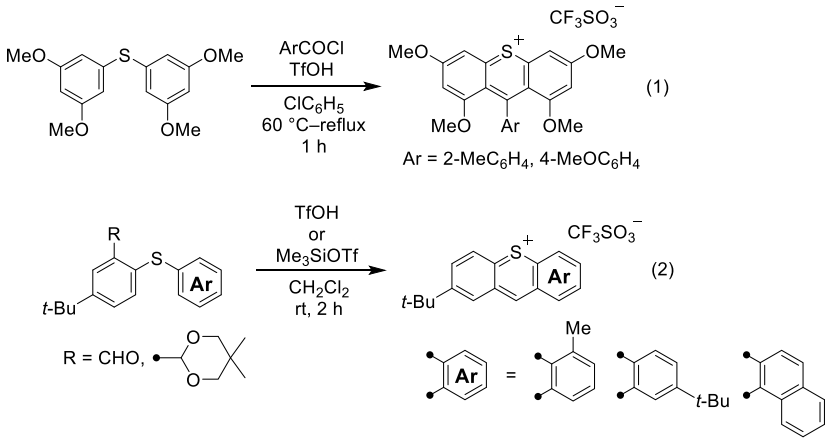
Abstract – A new series of thioxanthylium trifluoromethanesulfonates has been synthesized via a trifluoromethanesulfonic-acid-induced cyclization of thioether precursors. The electronic structure of these thioxanthylium salts were determined by UV−vis absorption spectroscopy, and theoretically investigated by density functional theory calculations.

INTRODUCTION

Thioxanthylium salts represent a new branch of materials that exhibit fascinating structures as well as optoelectronic and physicochemical properties, which may lead to a multitude of potential applications.[1] Moreover, thiopyrylium salts show promising potential as building blocks in nonlinear optical materials and dye-sensitized solar cells.[2] Thus, the development of efficient synthetic methods for the thioxanthylium framework and understanding the electronic structures are challenging issues of particular importance in contemporary organic chemistry. Recently, Hoshino and Honda have demonstrated the synthesis of a series of methoxy-substituted thioxanthylium salts by diarylthioethers with acyl chlorides in the presence of a Brønsted acid (equation 1, Scheme 1).[3] In 2020, we have reported the novel synthetic methods for the formation of thioxanthylium scaffolds promoted by a Brønsted acid (equation 2, Scheme 1).[4] Although these synthetic methods for thioxanthylium compounds have been extensively investigated, fundamental research into their photophysical properties has been limited. Herein, we describe the experimental and theoretical examination of electronic structures of their thioxanthylium scaffolds.

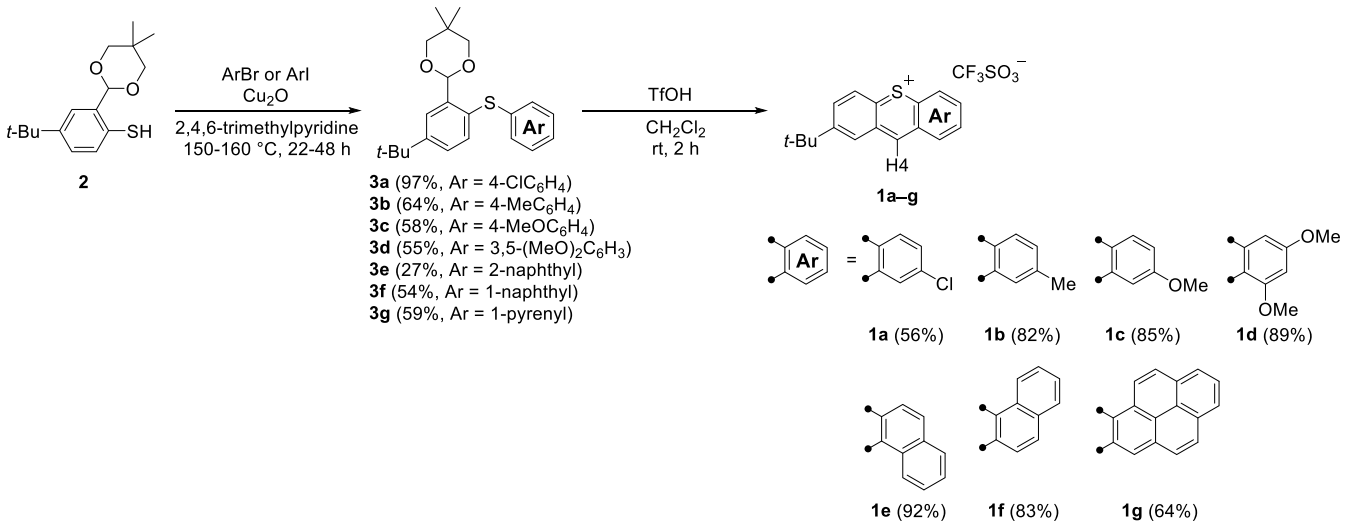


Scheme 1. Recently reported synthetic methods for the formation of thioxanthylium scaffolds

RESULTS AND DISCUSSION

SYNTHESIS OF THIOXANTHYLIUM TRIFLUOROMETHANESULFONATES 1a−1g

Scheme 2 shows the synthetic procedure that we carried out to synthesize a new series of thioxanthylium trifluoromethanesulfonates (**1a−1g**). This methodology involves a Brønsted-acid-induced intramolecular cyclization of thioethers that bear a formyl group, which has been previously developed by us.[4] The treatment of benzenethiol **2** with 4-iodochlorobenzene in the presence of copper(I) oxide afforded thioether **3a** in moderate yield. Thioethers **3b−3g**, which serve as precursors for the desired thioxanthylium salts, were prepared via the similar coupling reaction in good yield. The intramolecular cyclization of **3a−3g** with trifluoromethanesulfonic acid at room temperature proceeded to form thioxanthylium trifluoromethanesulfonates **1a−1g**. The resulting suspension was added dropwise to cold ether, which allowed the isolation of analytically pure crystals of **1a−1g** in moderate yield by centrifugation. The molecular structures of **1a−1g** were determined by spectroscopic methods and elemental analysis.



Scheme 2. Synthesis of thioxanthylium trifluoromethanesulfonates **1a−1g**

NMR SPECTROSCOPIC ANALYSIS OF THIOXANTHYLIUM TRIFLUOROMETHANESULFONATES 1a−1g

The molecular structures of **1a**−**1g** in CD_3CN were investigated by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of **1a**−**1g** showed deshielded resonances for all aromatic protons, which suggest the presence of a significant diatropic ring current in the π-scaffold of **1a**−**1g**. The resonances for **1a**−**1g** shifted to lowest field can be assigned to the H4 protons (Scheme 1) at 10.15 (**1a**), 10.08 (**1b**), 9.98 (**1c**), 9.92 (**1d**), 10.87 (**1e**), 10.02 (**1f**), and 9.56 (**1g**) ppm. The results can be regarded as a combination of deshielding effects by the ring current and the electron-deficient nature of the thiopyrylium cation subunit. In the ^{13}C NMR spectra, all signals for the six-membered thiopyrylium ring were observed in a range of 129−182 ppm, which is comparable to the ^{13}C NMR data of previously reported thiopyrylium salts.[3,4] Moreover, the observed ^{13}C NMR chemical shifts are different from those of carbocations such as Ph_2HC^+ (δ = 201) and Ph_3C^+ (δ = 212),[5] suggesting that **1a**−**1g** do not exhibit the characteristics of a localized carbocation (**B** in Figure 1), but major resonance contributions from a thioxanthylium cation in solution (**A** in Figure 1).

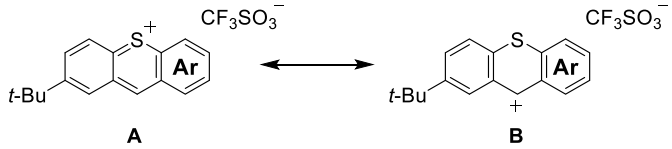


Figure 1. Plausible resonance structures **A** and **B** of thioxanthylium salts

ELECTRONIC STRUCTURES OF THIOXANTHYLIUM TRIFLUOROMETHANESULFONATES 1a−1g

UV−vis absorption spectra of **1a**−**1g** were measured in CH_2Cl_2 to examine their electronic structures (Figure 2). The photophysical parameters of the UV−vis absorption spectra are summarized in Table 1. The red-edge absorption bands were observed at 499 (**1a**), 530 (**1b**), 535 (**1c**), 543 (**1d**), 516 (**1e**), 521 (**1f**), 686 (**1g**) nm, which can be assigned to the π−π* electron transitions of the thioxanthylium chromophore in **1a**−**1g**. Chloro-substituted **1a** exhibits the most blue-shifted absorption among them. Introduction of methyl/methoxy groups to the thioxanthylium unit in **1b**/**1c** and **1d** cause a bathochromic shift of the absorption relative to the absorption of **1a**, which indicates perturbation of the electronic structure of the thioxanthylium framework. Naphthalene-fused thioxanthylium salts **1e** and **1f** show similar wavelengths of the red-edge absorption bonds. In the case of **1g**, a broad absorption was observed around 686 nm, which is the lowest energy transition. An expansion of the π-electron system with the pyrene subunit has a profound effect on the electronic structure. Thus, we confirmed that **1a**−**1g** contain a thioxanthylium chromophore with tunable electronic properties by introducing an electron-donating substituent and/or by expansion of the π-electron system.

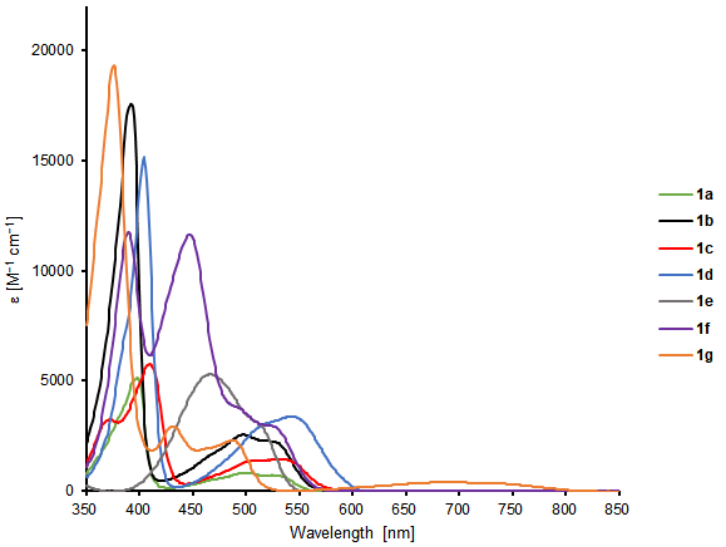


Figure 2. UV−vis absorption spectra of **1a**−**1g** in CH_2Cl_2 solution (concentration: 1.20−6.15 × 10^{-5} mol/L) at room temperature

Table 1. Photophysical data of thioxanthylium trifluoromethanesulfonates **1a**−**1g**

Compound	Absorption	
	λ_{max} [nm]	ε [M^{-1} cm^{-1}]
1a	499	1020
1b	498, 530(sh)	2560, 2180
1c	535	1400
1d	543	3380
1e	466, 516(sh)	5300, 2870
1f	521	2990
1g	686	1300

THEORETICAL INVESTIGATIONS INTO THIOXANTHYLIUM CATIONS 1a´−1g´

In order to obtain insight into the electronic structures of **1a**−**1g**, theoretical investigations were carried out on model thioxanthylium cations (**1a´**−**1g´**), where the counter anions were omitted. These molecules were optimized using density functional theory (DFT) methods implemented using the Gaussian 16 program.[6] Figure 3 shows the frontier molecular orbitals and their associated energy levels for **1a´**−**1g´**. The theoretically derived highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for **1a´**−**1f´** are delocalized exclusively over the π- and π*-orbitals of the entire molecular framework, respectively. Meanwhile, the HOMO and LUMO of **1g´** are somewhat localized over the pyrene and the thiopyrylium subunits, respectively. Regarding their energy levels, the introduction of methoxy groups into the thioxanthylium framework elevates both the HOMOs and LUMOs. Upon incorporation of the pyrene subunit in the thioxanthylium cation, the HOMO is dramatically destabilized.

Moreover, the assignment of the UV−vis absorption spectra was based on the results of time-dependent (TD) DFT calculations at the B3LYP/6-31G(d) level of theory (Table 2). The experimentally observed red-edge absorption bands of **1a**−**1g** were assigned to the HOMO−LUMO transitions, which are symmetry-allowed π−π* transitions. In the case of **1g´**, the HOMO−LUMO transitions exhibit a lower oscillator strength and intramolecular charge-transfer character, which is in good agreement with the experimentally observed results for **1g**. It can therefore be concluded that the electronic structures of these new thioxanthylium salts and the characteristic bathochromic shift of the absorption of the π-extended **1g** arise from intramolecular charge-transfer transitions.

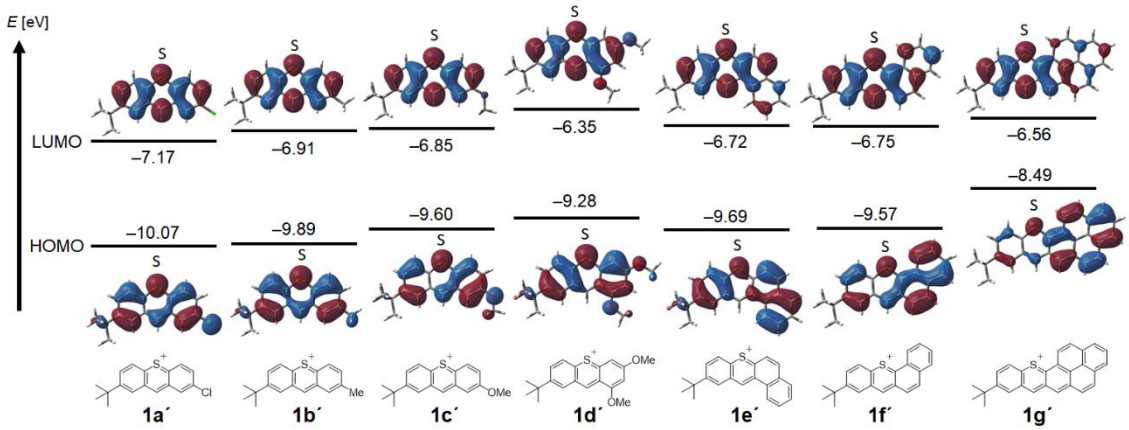


Figure 3. HOMOs and LUMOs (isovalue: 0.02) of thioxanthylium cations **1a´**−**1g´** calculated at the B3LYP/6-31G(d) level of theory

Table 2. Summary of the results obtained from the TD-DFT calculations on **1a´**−**1g´**[a]

Molecule	*E* [eV][b]	λ [nm][c]	*f*[d]	Transition
1a´	2.850	486.5	0.0479	HOMO → LUMO
1b´	2.533	489.5	0.0488	HOMO → LUMO
1c´	2.373	522.6	0.0552	HOMO → LUMO
1d´	2.481	499.8	0.1535	HOMO → LUMO
1e´	2.579	456.8	0.2177	HOMO → LUMO
1f´	2.393	518.2	0.0577	HOMO → LUMO
1g´	1.619	765.6	0.0233	HOMO → LUMO

[a]Calculations were carried out at the TD-PCM(CH_2Cl_2)-B3LYP/6-31G(d)//B3LYP/6-31G(d) level of theory.

[b]Excitation energy.

[c]Excitation wavelength.

[d]Oscillator strength.

CONCLUSIONS

Herein, we have described a new synthetic method for the transformation of thioether precursors into thioxanthylium salts via a Brønsted-acid-induced intramolecular cyclization. The electronic structures of the resulting thioxanthylium salts were examined by UV-vis absorption spectroscopy and theoretical investigations. The results of this survey can be expected to provide insight into the electronic character of cationic sulfur-heterocycles such as thiopyrylium compounds. The methodology described here can be used to extend the structural diversity and the availability of sulfur-containing building blocks with a thiopyrylium moiety.

EXPERIMENTAL

GENERAL.

All solvents were purified by standard methods. Preparative thin-layer chromatography (PTLC) was performed on Merck silica gel 60 PF254. Column chromatography was performed on silica gel 60N (Kanto Chemical) under an ambient atmosphere. ^{1}H (400 MHz) and ^{13}C NMR (101 Hz) spectra were recorded in $CDCl_3$ on a Bruker Avance spectrometer using the residual resonances of $CHCl_3$ (δ_H = 7.26) and $CDCl_3$ (δ_C = 77.0) as well as of CD_3CN (δ_H = 1.94; δ_C = 1.32) as the internal standards to reference the ^{1}H and ^{13}C NMR spectra. ^{19}F NMR spectra (376 MHz) were recorded on a Bruker Avance spectrometer using $CFCl_3$ (δ_F = 0.00) as an external standard. The assignment of the signals was typically accomplished on the basis of 1D (homodecoupling and DEPT) and 2D (COSY, HMQC, and HMBC) NMR techniques. Unless otherwise stated, all ^{13}C and ^{19}F NMR experiments were performed using broad-band ^{1}H decoupling. EI and ESI-TOF mass spectral data were obtained on a JEOL JMS-GCmateII and a JEOL JMS-T100CS spectrometer, respectively. Absorption spectra were recorded on a JASCO V-550 UV/Vis spectrometer. Elemental analyses were carried out on a JM11 CHN analyzer by J-Science Lab. All melting points were determined on a Yanaco micro-melting point apparatus or a Mettler Toledo MP90 melting point system, and are uncorrected.

MATERIALS.

All materials were purchased from common commercial chemical suppliers and used without further purification unless stated otherwise. All reactions were carried out under an inert atmosphere of argon or nitrogen. 4-*tert*-Butyl-2-(5,5-dimethyl-1,3-dioxan-2-yl)benzenethiol (**2**) was prepared according to the reported procedure.[4]

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(4-CHLOROPHENYLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3a.

Benzenethiol **2** (1.445 g, 5.15 mmol), 1-chloro-4-iodobenzene (1.490 g, 6.25 mmol), and copper(I) oxide (1.570 g, 11.0 mmol) were dissolved in 2,4,6-trimethylpyridine (15 mL). After being stirred at 150 °C for 24 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: CH_2Cl_2/hexane = 1/2, v/v) afforded 2-[(5-*tert*-butyl)-2-(4-chlorophenylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3a** (1.947 g, 4.98 mmol, 97%) as pale yellow oil. **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 2.4 Hz, 1H, ArH), 7.32 (dd, J = 2.4, 8.0 Hz, 1H, ArH), 7.26 (d, J = 8.0 Hz, 1H, ArH), 7.21 (d, J = 8.8 Hz, 2H, ArH), 7.14 (d, J = 8.8 Hz, 2H, ArH), 5.82 (s, 1H, CH), 3.72 (d, J = 10.4 Hz, 2H, CH_2), 3.62 (d, J = 10.4 Hz, 2H, CH_2), 1.33 (s, 9H, CH_3), 1.32 (s, 3H, CH_3), 0.77 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.0 (C), 139.4 (C), 136.1 (C), 133.7 (CH), 132.1 (C), 130.7 (CH), 129.1 (CH), 129.0 (C), 127.1 (CH), 123.8 (CH), 99.8 (CH), 77.8 (CH_2), 34.8 (C), 31.2 (CH_3), 30.2 (C), 23.2 (CH_3), 21.8 (CH_3); MS (EI, positive mode): *m/z* 390 ([M]$^+$); Anal. Calcd for $C_{22}H_{27}ClO_2S$: C, 67.59; H, 6.96%; found: C, 67.64; H, 6.86%.

REACTION OF 3a WITH TfOH.

Trifluoromethanesulfonic acid (0.278 g, 1.85 mmol) was added to a solution of compound **3a** (0.325 g, 0.831 mmol) in CH_2Cl_2 (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et_2O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-*tert*-butyl-7-chlorothioxanthylium trifluoromethanesulfonate **1a** (0.261 g, 0.598 mmol, 72%) as red waxy solids. ^{1}H NMR (400 MHz, CD_3CN) δ 10.15 (s, 1H, ArH), 8.88 (d, J = 2.0 Hz, 1H, ArH), 8.81 (d, J = 2.0 Hz, 1H, ArH), 8.76 (d, J = 9.2 Hz, 1H, ArH), 8.75 (d, J = 9.2 Hz, 1H, ArH), 8.62 (dd, J = 2.0, 9.2 Hz, 1H, ArH), 8.34 (dd, J = 2.0, 9.2 Hz, 1H, ArH), 1.52 (s, 9H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 160.3 (CH), 156.7 (C), 148.7 (C), 147.7 (C), 140.0 (CH), 139.1 (CH), 137.8 (C), 135.7 (CH), 133.2 (CH), 132.2 (C), 131.9 (C), 130.2 (CH), 128.5 (CH), 121.4 (q, J_{CF} = 320 Hz, CF_3), 36.6 (C), 30.8 (CH_3); ^{19}F NMR (376 MHz, CD_3CN) δ –79.4 (s); MS (ESI-TOF, positive mode): *m/z* 287 ([M−OTf]$^+$); HRMS (ESI-TOF, positive mode): *m/z* found 287.0655 ([M−TfO]$^+$), calcd for $C_{17}H_{16}{}^{35}ClS$: 287.0661.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(4-METHYLPHENYLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3b.

Benzenethiol **2** (1.517 g, 5.41 mmol), 1-iodo-4-methylbenzene (0.840 g, 4.91 mmol), and copper(I) oxide (1.164 g, 8.13 mmol) were dissolved in 2,4,6-trimethylpyridine (30 mL). After being stirred at 160 °C for

22 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 1/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(4-methylphenylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3b** (1.288 g, 3.48 mmol, 64%) as colorless oil. **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 2.4 Hz, 1H, ArH), 7.25 (dd, J = 2.4, 8.4 Hz, 1H, ArH), 7.20 (d, J = 8.0 Hz, 2H, ArH), 7.15 (d, J = 8.4 Hz, 1H, ArH), 7.08 (d, J = 8.0 Hz, 2H, ArH), 5.84 (s, 1H, CH), 3.74 (d, J = 11.2 Hz, 2H, CH_2), 3.66 (d, J = 11.2 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.32 (s, 9H, CH_3), 0.78 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.7 (C), 138.2 (C), 136.7 (C), 132.9 (C), 132.2 (CH), 131.00 (CH), 130.96 (C), 129.8 (CH), 126.8 (CH), 123.3 (CH), 99.8 (CH), 77.7 (CH_2), 34.7 (C), 31.2 (CH_3), 30.2 (C), 23.2 (CH_3), 21.8 (CH_3), 21.0 (CH_3); MS (EI, positive mode): *m/z* 370 ([M]$^+$); Anal. Calcd for $C_{23}H_{30}O_2S$: C, 74.55; H, 8.16%; found: C, 74.21; H, 7.99%.

REACTION OF 3b WITH TfOH.

Trifluoromethanesulfonic acid (0.157 g, 1.05 mmol) was added to a solution of compound **3b** (0.185 g, 0.500 mmol) in CH_2Cl_2 (8 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et_2O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-*tert*-butyl-7-methylthioxanthylium trifluoromethanesulfonate **1b** (0.171 g, 0.410 mmol, 82%) as red solids. **1b**: mp 162–164 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 10.08 (s, 1H, ArH), 8.77 (d, J = 2.0 Hz, 1H, ArH), 8.70 (d, J = 9.0 Hz, 1H, ArH), 8.66 (d, J = 8.8 Hz, 1H, ArH), 8.62–8.61 (m, 1H, ArH), 8.55 (dd, J = 2.0, 9.0 Hz, 1H, ArH), 8.27 (dd, J = 2.0, 8.8 Hz, 1H, ArH), 2.75 (s, 3H, CH_3), 1.52 (s, 9H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 160.4 (CH), 155.9 (C), 147.6 (C), 147.4 (C), 143.6 (C), 141.7 (CH), 138.9 (CH), 136.3 (CH), 132.9 (CH), 131.61 (C), 131.59 (C), 128.2 (CH), 128.1 (CH), 122.1 (quart, J_{CF} = 322 Hz, CF_3), 36.5 (C), 30.9 (CH_3), 21.7 (CH_3); ^{19}F NMR (376 MHz, CD_3CN) δ –79.5 (s); MS (ESI-TOF, positive mode): *m/z* 267 ([M–OTf]$^+$); Anal. Calcd for $C_{19}H_{19}F_3O_3S_2$: C, 54.80; H, 4.60%; found: C, 54.59; H, 4.53%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(4-METHOXYPHENYLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3c.

Benzenethiol **2** (1.301 g, 4.64 mmol), 1-bromo-4-methoxybenzene (0.955 g, 5.58 mmol), and copper(I) oxide (1.294 g, 9.04 mmol) were dissolved in 2,4,6-trimethylpyridine (20 mL). After being stirred at 150 °C for 24 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane CH_2Cl_2 = 3/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(4-methoxyphenylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3c** (1.006 g, 2.60 mmol, 58%) as colorless crystals. **3c**: mp 138.0–138.7 °C; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 2.4 Hz, 1H, ArH), 7.32 (d, J = 8.8 Hz, 2H, ArH), 7.22 (dd, J = 2.4, 8.0 Hz, 1H, ArH), 7.01 (d, J = 8.0 Hz, 1H, ArH), 6.85 (d, J = 8.8 Hz, 2H, ArH), 5.83 (s, 1H, CH), 3.79 (s, 3H, OCH_3), 3.76 (d, J = 10.8 Hz, 2H, CH_2), 3.68 (d, J = 10.8 Hz, 2H, CH_2), 1.33 (s, 3H, CH_3), 1.30 (s, 9H, CH_3), 0.80 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.3 (C), 149.9 (C), 136.9 (C), 134.1 (C), 132.6 (C), 130.5 (CH), 126.7 (CH), 126.0 (C), 123.1 (CH), 114.8 (CH), 99.6 (CH), 77.7 (CH_2), 55.3 (CH_3), 34.6 (C), 31.2 (CH_3), 30.3 (C), 23.2 (CH_3), 21.9 (CH_3); MS (EI, positive mode): *m/z* 386 ($[M]^+$); Anal. Calcd for $C_{23}H_{30}O_3S$: C, 71.47; H, 7.82%; found: C, 71.55; H, 7.98%.

REACTION OF 3c WITH TfOH.

Trifluoromethanesulfonic acid (0.157 g, 1.05 mmol) was added to a solution of compound **3c** (0.193 g, 0.500 mmol) in CH_2Cl_2 (10 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et_2O (40 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-*tert*-butyl-7-methoxythioxanthylium trifluoromethanesulfonate **1c** (0.184 g, 0.425 mmol, 85%) as red waxy solids. **1c**: ^1H NMR (400 MHz, CD_3CN) δ 9.98 (s, 1H, ArH), 8.69 (d, J = 2.0 Hz, 1H, ArH), 8.66 (d, J = 9.0 Hz, 1H, ArH), 8.64 (d, J = 9.2 Hz, 1H, ArH), 8.49 (dd, J = 2.0, 9.0 Hz, 1H, ArH), 8.11 (d, J = 2.7 Hz, 1H, ArH), 8.02 (dd, J = 2.7, 9.2 Hz, 1H, ArH), 4.10 (s, 3H, OCH_3), 1.51 (s, 9H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN) δ 162.1 (C), 158.2 (CH), 155.9 (C), 146.7 (C), 144.2 (C), 138.1 (CH), 133.7 (C), 132.5 (CH), 132.1 (CH), 131.7 (C), 129.7 (CH), 128.1 (CH), 121.5 (quart, $^1J_{CF}$ = 319 Hz, CF_3), 114.0 (CH), 57.5 (CH), 36.5 (C), 30.8 (CH); ^{19}F NMR (376 MHz, CD_3CN) δ –79.4 (s); MS (ESI-TOF, positive mode): *m/z* 283 ($[M–OTf]^+$); Anal. Calcd for $C_{19}H_{19}F_3O_4S_2$: C, 52.77; H, 4.43%; found: C, 52.99; H, 4.67%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(3,5-DIMETHOXYPHENYLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3d.

Benzenethiol **2** (0.648 g, 2.31 mmol), 1-bromo-3,5-dimethoxybenzene (0.609 g, 2.81 mmol), and copper(I) oxide (0.678 g, 4.74 mmol) were dissolved in 2,4,6-trimethylpyridine (10 mL). After being stirred at 150 ^oC for 48 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 1/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(3,5-dimethoxyphenylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3d** (0.526 g, 1.26 mmol, 55%) as colorless oil. **3d**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 2.0 Hz, 1H, ArH), 7.32-7.27 (m, 2H, ArH), 6.41 (d, J = 2.0 Hz, 2H, ArH), 6.28 (t, J = 2.4 Hz, 1H, ArH), 5.81 (s, 1H, ArH), 3.74 (d, J = 11.2 Hz, 2H, CH_2), 3.71 (s, 6H, OCH_3), 1.33 (s, 9H, CH_3), 1.32 (s, 3H, CH_3), 0.78 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 161.0 (C × 2), 151.5 (C), 139.1 (C), 133.4 (CH), 129.2 (C), 126.9 (CH), 123.6 (CH), 107.6 (CH), 99.8 (CH), 99.0

(CH), 77.8 (CH_2), 55.4 (OCH_3), 34.8 (C), 31.2 (CH_3), 30.3 (C), 23.3 (CH_3), 21.9 (CH_3); MS (EI, positive mode): *m/z* 416 ($[M]^+$); Anal. Calcd for $C_{24}H_{32}O_4S$: C, 69.20; H, 7.74%; found: C, 68.98; H, 7.50%.

REACTION OF 3d WITH TfOH.

Trifluoromethanesulfonic acid (0.106 g, 0.706 mmol) was added to a solution of compound **3d** (0.116 g, 0.278 mmol) in CH_2Cl_2 (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et_2O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-*tert*-butyl-7-methoxythioxanthylium trifluoromethanesulfonate **1d** (0.116 g, 0.250 mmol, 89%) as red solids. **1d**: mp 246 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 9.92 (s, 1H, ArH), 8.60 (d, *J* = 2.0 Hz, 1H, ArH), 8.33 (d, *J* = 8.8 Hz, 1H, ArH), 8.33 (dd, *J* = 8.8, 2.0 Hz, 1H, ArH), 7.65 (d, *J* = 2.0 Hz, 1H, ArH), 6.94 (d, *J* = 2.0 Hz, 1H, ArH), 4.21 (s, 3H, OCH_3), 4.19 (s, 3H, OCH_3), 1.47 (s, 9H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 173.0 (C), 165.4 (C), 154.6 (C), 152.8 (CH), 152.7 (C), 141.9 (C), 136.9 (CH), 133.8 (CH), 129.1 (C), 127.2 (CH), 122.2 (q, *J* = 321 Hz, CF_3), 121.0 (C), 103.4 (CH), 101.7 (CH), 59.2 (OCH_3), 58.9 (OCH_3), 36.2 (C), 31.1 (CH_3); ^{19}F NMR (376 MHz, CD_3CN) δ –79.3 (s); MS (ESI-TOF, positive mode): *m/z* 313 ($[M–OTf]^+$); Anal. Calcd for $C_{20}H_{21}F_3O_5S_2$: C, 51.94; H, 4.58%; found: C, 51.99; H, 4.66%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(NAPHTH-2-YLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3e.

Benzenethiol **2** (3.001 g, 10.7 mmol), 2-bromonaphthalene (2.668 g, 12.8 mmol), and copper(I) oxide (3.070 g, 21.4 mmol) were dissolved in 2,4,6-trimethylpyridine (20 mL). After being stirred at 145 °C for 24 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 4/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(naphth-2-ylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3e** (1.154 g, 2.84 mmol, 27%) as pale yellow crystals. **3e**: mp 96.8–98.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.4 Hz, 1H, ArH), 7.77–7.73 (m, 2H, ArH), 7.46–7.38 (m, 2H, ArH), 7.33–7.27 (m, 1H, ArH), 7.28 (d, *J* = 2.0 Hz, 1H, ArH), 7.24 (d, *J* = 5.6 Hz, 1H, ArH), 5.89 (s, 1H, CH), 3.73 (dd, *J* =10.8 Hz, 2H, CH_2), 3.64 (dd, *J* =10.8 Hz, 2H, CH_2), 1.34 (s, 9H, CH_3), 1.32 (s, 3H, CH_3), 0.76 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 151.4 (C), 138.9 (C), 134.4 (C), 133.7 (C), 133.2 (CH), 132.0 (C), 129.8 (C), 128.6 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 126.4 (CH), 125.8 (CH), 123.5 (CH), 99.8 (CH), 77.7 (CH_2), 34.8 (C), 31.2 (CH_3), 30.2 (C), 23.2 (CH_3), 21.8 (CH_3); MS (EI, positive mode): *m/z* 406 ($[M]^+$); Anal. Calcd for $C_{26}H_{30}O_2S$: C, 76.81; H, 7.44%; found: C, 76.95. H, 7.58%.

REACTION OF 3e WITH TfOH.

Trifluoromethanesulfonic acid (0.090 g, 0.60 mmol) was added to a solution of compound **3e** (0.142 g, 0.350 mmol) in CH_2Cl_2 (5 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et_2O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 10-*tert*-butylbenzo[*a*]thioxanthen-7-ium trifluoromethanesulfonate **3e** (0.146 g, 0.332 mmol, 92%) as red powder. **3e**: mp 253.1–254.5 ℃; ^{1}H NMR (400 MHz, CD_3CN) δ 10.87 (s, 1H, ArH), 9.21 (d, J = 8.4 Hz, 1H, ArH), 8.97 (d, J = 2.0 Hz, 1H, ArH), 8.74 (d, J = 8.4 Hz, 1H, ArH), 8.71 (d, J = 8.0 Hz, 1H, ArH), 8.57 (dd, J = 2.4, 9.2 Hz, 1H, ArH), 8.53 (d, J = 6.9 Hz, 1H, ArH), 8.35 (d, J =1.3 Hz, 1H, ArH), 8.33 (d, J = 1.3 Hz, 1H, ArH), 8.17 (dd, J = 7.2, 1.4 Hz, 1H, ArH), 8.05 (dd, J = 7.2, 1.4 Hz, 1H, ArH), 1.56 (s, 9H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 181.5 (C), 156.8 (C), 155.2 (C), 152.6 (CH), 143.6 (C), 142.4 (CH), 137.5 (CH), 133.1 (C), 132.8 (C), 132.5 (CH), 132.0 (CH), 131.79 (CH), 131.77 (CH), 130.1 (C), 127.9 (CH), 125.0 (CH), 124.8 (CH), 122.0 (quart, J_{CF} = 318 Hz, $CF_3SO_3^-$), 36.7 (C), 31.1 (CH); ^{19}F NMR (376 MHz, CD_3CN) δ –76.4 (s, $CF_3SO_3^-$); MS (ESI-TOF, positive mode): *m/z* 303 ([M–OTf]$^+$); Anal. Calcd for $C_{22}H_{19}F_3O_3S_2$: C, 58.40; H, 4.23%; found: C, 58.20. H, 4.15%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(NAPHTH-1-YLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3f.

Benzenethiol **2** (1.678 g, 5.98 mmol), 1-bromonaphthalene (1.489 g, 7.19 mmol), and copper(I) oxide (1.717 g, 12.0 mmol) were dissolved in 2,4,6-trimethylpyridine (12 mL). After being stirred at 150 ^{o}C for 48 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 1/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(naphth-1-ylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3f** (1.321 g, 3.24 mmol, 54%) as colorless crystals. **3f**: mp 159–161 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37–8.35 (m, 1H, ArH), 7.86–7.84 (m, 1H, ArH), 7.80 (d, J = 2.4 Hz, 1H, ArH), 7.76 (d, J = 8.0 Hz, 1H, ArH), 7.53–7.49 (m, 2H, ArH), 7.43 (dd, J = 7.6, 1.2 Hz, 1H, ArH), 7.36 (dd, J = 8.0, 8.0 Hz, 1H, ArH), 7.17 (dd, J = 8.4, 2.4 Hz, 1H, ArH), 6.95 (d, J = 8.4 Hz, 1H, ArH), 5.91 (s, 1H, CH), 3.75 (d, J = 10.8 Hz, 2H, CH_2), 3.65 (d, J = 10.8 Hz, 2H, CH_2), 1.34 (s, 3H, CH_3), 1.30 (s, 9H, CH_3), 0.76 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.5 (C), 137.7 (C), 134.0 (C), 132.94 (C), 132.85 (C), 131.4 (CH), 130.7 (CH), 130.6 (C), 128.5 (CH), 128.0 (CH), 126.9 (CH), 126.6 (CH), 126.3 (CH), 125.8 (CH), 125.3 (CH), 123.4 (CH), 99.7 (CH), 77.8 (CH_2), 34.7 (C), 31.2 (CH_3), 30.3 (C), 23.3 (CH_3), 21.8 (CH_3); MS (EI, positive mode): *m/z* 406 ([M]$^+$); Anal. Calcd for $C_{26}H_{30}O_2S$: C, 76.81; H, 7.44%; found: C, 76.48; H, 7.59%.

REACTION OF 3f WITH TfOH.

Trifluoromethanesulfonic acid (0.090 g, 0.60 mmol) was added to a solution of compound **3f** (0.126 g, 0.310 mmol) in CH_2Cl_2 (6 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et_2O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 9-*tert*-butylbenzo[*c*]thioxanthen-12-ium trifluoromethanesulfonate **1f** (0.112 g, 0.248 mmol, 83%) as red powder. **1f**: mp 170 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 10.02 (s, 1H, ArH), 8.98 (d, J = 8.4 Hz, 1H, ArH), 8.76 (d, J = 2.0 Hz, 1H, ArH), 8.74 (d, J = 8.8 Hz, 1H, ArH), 8.56 (dd, J = 2.0, 8.8 Hz, 1H, ArH), 8.36 (d, J = 8.8 Hz, 1H, ArH), 8.30 (d, J = 8.8 Hz, 1H, ArH), 8.20 (d, J = 8.0 Hz, 1H, ArH), 8.08–8.12 (m, 1H, ArH), 7.98 (dd, J = 8.0, 7.2 Hz, 1H, ArH), 1.55 (s, 9H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 158.8 (CH), 156.9 (C), 154.6 (C), 143.5 (C), 138.1 (CH), 136.3 (CH), 135.7 (C), 133.0 (CH), 132.1 (CH), 131.6 (C), 131.3 (C), 131.1 (CH), 130.9 (CH), 130.4 (CH), 128.8 (C), 128.4 (CH), 126.1 (CH), 122.1 (q, J = 321 Hz, CF_3), 36.6 (C), 30.9 (CH_3); ^{19}F NMR (376 MHz, CD_3CN) δ –79.3 (s); MS (ESI-TOF, positive mode): *m/z* 303 ([M–OTf]$^+$); Anal. Calcd for $C_{22}H_{19}F_3O_3S_2$: C, 58.40; H, 4.23%; found: C, 58.61; H, 4.50%.

SYNTHESIS OF 2-[(5-*tert*-BUTYL)-2-(PYREN-1-YLTHIO)PHENYL]-5,5-DIMETHYL-1,3-DIOXANE 3g.

Benzenethiol **2** (2.987 g, 10.6 mmol), 1-bromopyrene (4.124 g, 12.8 mmol), and copper(I) oxide (3.033 g, 21.2 mmol) were dissolved in 2,4,6-trimethylpyridine (20 mL). After being stirred at 150 °C for 48 h using an oil bath, the reaction mixture was allowed to cool to room temperature. After the solvent was removed under reduced pressure, purification of the crude product by column chromatography on silica gel (eluent: hexane/CH_2Cl_2 = 1/1, v/v) afforded 2-[(5-*tert*-butyl)-2-(pyren-1-ylthio)phenyl]-5,5-dimethyl-1,3-dioxane **3g** (2.987 g, 6.21 mmol, 59%) as pale yellow crystals. **3g**: mp 180–181 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 9.2 Hz, 1H, ArH), 8.19–8.17 (m, 2H, ArH), 8.11 (d, J = 9.2 Hz, 1H, ArH), 8.07–7.95 (m, 5H, ArH), 7.83 (d, J = 2.4 Hz, 1H, ArH), 7.12 (dd, J = 2.4, 8.4 Hz, 1H, ArH), 6.89 (d, J = 8.4 Hz, 1H, ArH), 3.78 (d, J = 11.5 Hz, CH_2), 3.68 (d, J = 10.4 Hz, CH_2), 1.35 (s, 3H, CH_3), 1.29 (s, 9H, CH_3), 0.76 (s, 3H, CH_3); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.2 (C), 137.4 (C), 131.7 (C), 131.4 (C), 131.3 (C), 131.2 (C), 131.1 (CH), 131.0 (C), 130.9 (C), 130.0 (C), 128.2 (CH), 127.7 (CH), 127.3 (CH), 126.9 (CH), 126.2 (CH), 125.4 (CH × 2), 125.3 (C), 125.2 (CH), 124.7 (CH), 124.5 (CH), 123.4 (CH), 99.8 (CH), 77.8 (CH_2), 34.7 (C), 31.2 (CH_3), 30.3 (C), 23.3 (CH_3), 21.8 (CH_3); MS (EI, positive mode): *m/z* 480 ([M]$^+$); Anal. Calcd for $C_{32}H_{32}O_2S$: C, 79.96; H, 6.71%; found: C, 79.78; H, 6.88%.

REACTION OF 3g WITH TfOH.

Trifluoromethanesulfonic acid (0.106 g, 0.706 mmol) was added to a solution of compound **3e** (0.148 g, 0.307 mmol) in CH_2Cl_2 (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et_2O (50 mL). Purification of the resulting suspension using a centrifugal separator afforded 9-*tert*-butylphenaleno[1,9-*bc*]thioxanthen-12-ium trifluoromethanesulfonate **1g** (0.107 g, 0.203 mmol, 64%) as dark green powder. **1g**: mp 256 °C (decomp.); ^{1}H NMR (400 MHz, CD_3CN) δ 9.56 (s, 1H, ArH), 8.52–8.49 (m, 2H, ArH), 8.44–8.41 (m, 2H, ArH), 8.34 (d, J = 8.8 Hz, 1H, ArH), 8.22 (d, J = 8.8 Hz, 1H, ArH), 7.97 (d, J = 7.6 Hz, 1H, ArH), 7.88–7.82 (m, 2H, ArH), 7.77 (d, J = 7.6 Hz, 1H, ArH), 7.69 (dd, J = 7.6, 7.6 Hz, 1H, ArH), 1.62 (s, 9H, CH_3); ^{19}F NMR (376 MHz, CD_3CN) δ –79.3 (s); MS (ESI-TOF, positive mode): *m/z* 377 ($[M–OTf]^+$); Anal. Calcd for $C_{28}H_{21}F_3O_3S_2$: C, 63.87; H, 4.02%; found: C, 63.51; H, 3.90%. Satisfactory ^{13}C NMR data of **1g** could not be obtained due to its low solubility in common organic solvents such as CD_3CN, DMSO-d_6, DMF-d_7, and CD_2Cl_2.

COMPUTATIONAL DETAILS.

All density functional theory (DFT) calculations were performed utilizing the Gaussian 16 package.[6] The Becke´s three-parameter hybrid functional with Lee-Yang-Parr correlation functional (B3LYP)[7] which was recently reported to demonstrate broader accuracy, were employed with a standard split valence-type basis sets. The geometries of **1a´**−**1e´**, where the counter anions were omitted, were optimized by the 6-31G(d) basis sets. Molecular orbitals and TD-DFT calculations were carried out at the 6-31G(d) levels using the B3LYP density functional models. The bulk solvent effects of dichloromethane might be adequately evaluated by using polarizable continuum model (PCM),[8] denoted as "PCM(CH_2Cl_2)-".

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REFERENCES

1. (a) 'Six-Membered Hetarenes with One Chalcogen,' ed. by W.-D. Rudorf, Science of Synthesis, Vol. 14, pp. 649−770, Thieme, 2006; (b) A. T. Balaban, 'Aromaticity of Six-Membered Rings with One Heteroatom,' Aromaticity in Heterocyclic Compounds (*Top. Heterocycl. Chem.*), 2009, 19, pp.

204−246.

2. (a) A. Scarpaci, A. Nantalaksakul, J. M. Hales, J. D. Matichak, S. Barlow, M. Rumi, J. W. Perry, and S. R. Marder, *Chem. Mater.*, 2012, **24**, 1606; (b) T. Maeda, S. Nitta, H. Nakao, S. Yagi, and H. Nakazumi, *J. Phys. Chem. C*, 2014, **118**, 16618; (c) S. Barlow, J.-L. Brédas, Y. A. Getmanenko, R. L. Gieseking, J. M. Hales, H. Kim, S. R. Marder, J. W. Perry, C. Risko, and Y. Zhang, *Mater. Horiz.*, 2014, **1**, 577; (d) R. L. Gieseking, S. Mukhopadhyay, C. Risko, S. R. Marder, and J.-L. Brédas, *Chem. Mater.*, 2014, **26**, 6439; (e) H. Kearns, S. Sengupta, I. R. Sasselli, L. Bromley III, K. Faulds, T. Tuttle, M. A. Bedics, M. R. Detty, L. Velarde, D. Graham, and W. E. Smith, *Chem. Sci.*, 2016, **7**, 5160; (f) B. Ding, Y. Xiao, H. Zhou, X. Zhang, C. Qu, F. Xu, Z. Deng, Z. Cheng, and X. Hong, *J. Med. Chem.*, 2019, **62**, 2049.
3. K. Tanaka, Y. Tanaka, M. Kishimoto, Y. Hoshino, and K. Honda, *Beilstein J. Org. Chem.*, 2019, **15**, 2105.
4. N. Nagahora, R. Tanaka, T. Tada, A. Yasuda, Y. Yamada, K. Shioji, and K. Okuma, *Org. Lett.*, 2020, **22**, 6192.
5. H.-O. Kalinowski, S. Berger, and S. Braun, Carbon 13 NMR Spectroscopy, John Wiley and Sons, 1988, pp. 409−415.
6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.
7. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
8. J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999.