THE ELECTRONIC STRUCTURE OF THIOXANTHONYLUM SCAFFOLDS

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

INTRODUCTION

Thioxanthylum 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 thioxanthylum 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 thioxanthylum 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 thioxanthylum scaffolds promoted by a Brønsted acid (equation 2, Scheme 1).4 Although these synthetic methods for thioxanthylum 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 thioxanthylum scaffolds.
RESULTS AND DISCUSSION

SYNTHESIS OF THIOXANTHYLUM TRIFLUOROMETHANESULFONATES 1a−1g

Scheme 2 shows the synthetic procedure that we carried out to synthesize a new series of thioxanthylum 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. 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 thioxanthylum 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 thioxanthylum 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 thioxanthylum trifluoromethanesulfonates 1a−1g
The molecular structures of 1a–1g in CD$_3$CN were investigated by $^1$H and $^{13}$C NMR spectroscopy. The $^1$H 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. Moreover, the observed $^{13}$C NMR chemical shifts are different from those of carbocations such as Ph$_2$HC$^+$ ($\delta = 201$) and Ph$_3$C$^+$ ($\delta = 212$), 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 thioxanthylum salts](image)

**Electronic Structures of Thioxanthylum Trifluoromethanesulfonates 1a–1g**

UV–vis absorption spectra of 1a–1g were measured in CH$_2$Cl$_2$ 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 thioxanthylum 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 CH2Cl2 solution (concentration: 1.20−6.15 × 10−5 mol/L) at room temperature

Table 1. Photophysical data of thioxanthylum trifluoromethanesulfonates 1a−1g

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption λmax [nm]</th>
<th>ε [M−1 cm−1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>499</td>
<td>1020</td>
</tr>
<tr>
<td>1b</td>
<td>498, 530 (sh)</td>
<td>2560, 2180</td>
</tr>
<tr>
<td>1c</td>
<td>535</td>
<td>1400</td>
</tr>
<tr>
<td>1d</td>
<td>543</td>
<td>3380</td>
</tr>
<tr>
<td>1e</td>
<td>466, 516 (sh)</td>
<td>5300, 2870</td>
</tr>
<tr>
<td>1f</td>
<td>521</td>
<td>2990</td>
</tr>
<tr>
<td>1g</td>
<td>686</td>
<td>1300</td>
</tr>
</tbody>
</table>

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

In order to obtain insight into the electronic structures of 1a−1g, theoretical investigations were carried out on model thioxanthylum 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 thiopyrylium subunits, respectively. Regarding their energy levels, the introduction of methoxy groups into the thioxanthylum framework elevates both the HOMOs and LUMOs. Upon incorporation of the pyrene subunit in the thioxanthylum 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 thioxanthylum 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 thioxanthylum cations 1a'−1g' calculated at the B3LYP/6-31G(d) level of theory](image)

Table 2. Summary of the results obtained from the TD-DFT calculations on 1a'−1g'

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E$ [eV]</th>
<th>$\lambda$ [nm]</th>
<th>$f$</th>
<th>Transition</th>
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<tr>
<td>1a'</td>
<td>2.850</td>
<td>486.5</td>
<td>0.0479</td>
<td>HOMO → LUMO</td>
</tr>
<tr>
<td>1b'</td>
<td>2.533</td>
<td>489.5</td>
<td>0.0488</td>
<td>HOMO → LUMO</td>
</tr>
<tr>
<td>1c'</td>
<td>2.373</td>
<td>522.6</td>
<td>0.0552</td>
<td>HOMO → LUMO</td>
</tr>
<tr>
<td>1d'</td>
<td>2.481</td>
<td>499.8</td>
<td>0.1535</td>
<td>HOMO → LUMO</td>
</tr>
<tr>
<td>1e'</td>
<td>2.579</td>
<td>456.8</td>
<td>0.2177</td>
<td>HOMO → LUMO</td>
</tr>
<tr>
<td>1f'</td>
<td>2.393</td>
<td>518.2</td>
<td>0.0577</td>
<td>HOMO → LUMO</td>
</tr>
<tr>
<td>1g'</td>
<td>1.619</td>
<td>765.6</td>
<td>0.0233</td>
<td>HOMO → LUMO</td>
</tr>
</tbody>
</table>

*Calculations were carried out at the TD-PCM(CH$_2$Cl$_2$)-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 thioxanthylum salts via a Brønsted-acid-induced intramolecular cyclization. The electronic structures of the resulting thioxanthylum 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$_3$ ($\delta_H = 7.26$) and CDCl$_3$ ($\delta_C = 77.0$) as well as of CD$_3$CN ($\delta_H = 1.94$; $\delta_C = 1.32$) 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$_3$ ($\delta_F = 0.00$) 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."
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: CH2Cl2/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: 1H NMR (400 MHz, CDCl3) 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, CH2), 3.62 (d, J = 10.4 Hz, 2H, CH2), 1.33 (s, 9H, CH3), 1.32 (s, 3H, CH3), 0.77 (s, 3H, CH3); 13C{1H} NMR (101 MHz, CDCl3) 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 (CH2), 34.8 (C), 31.2 (CH3), 30.2 (C), 23.2 (CH3), 21.8 (CH3); MS (EI, positive mode): m/z 390 ([M]+); Anal. Calcd for C22H27ClO2S: 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 CH2Cl2 (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et2O (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. 1H NMR (400 MHz, CD3CN) 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, CH3); 13C{1H} NMR (101 MHz, CD3CN) 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 (CH2), 34.8 (C), 31.2 (CH3), 30.2 (C), 23.2 (CH3), 21.8 (CH3); MS (EI, positive mode): m/z 287 ([M–OTf]+); HRMS (ESI-TOF, positive mode): m/z found 287.0655 ([M–TfO]+), calcd for C17H1635ClS: 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/CH₂Cl₂ = 1/1, v/v) afforded 2-[(5-tert-butyl)-2-(4-methoxyphenylthio)phenyl]-5,5-dimethyl-1,3-dioxane 3b (1.288 g, 3.48 mmol, 64%) as colorless oil. 3b: ¹H NMR (400 MHz, CDCl₃) 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, CH₂), 3.66 (d, J = 11.2 Hz, 2H, CH₂), 2.31 (s, 3H, CH₃), 1.32 (s, 3H, CH₃), 1.32 (s, 9H, CH₃), 0.78 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) 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 (CH₂), 34.7 (C), 31.2 (CH₃), 30.2 (C), 23.2 (CH₃), 21.8 (CH₃), 21.0 (CH₃); MS (EI, positive mode): m/z 370 ([M]+); Anal. Calcd for C₂₃H₂₃O₂S: 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 CH₂Cl₂ (8 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (30 mL). Purification of the resulting suspension using a centrifugal separator afforded 2-tert-butyl-7-methylthioxanthanylum trifluoromethanesulphonate 1b (0.171 g, 0.410 mmol, 82%) as red solids. 1b: mp 162–164 °C; ¹H NMR (400 MHz, CD₂CN) 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, CH₃), 1.52 (s, 9H, CH₃); ¹³C{¹H} NMR (101 MHz, CD₂CN) 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, J₉F = 322 Hz, CF₃), 36.5 (C), 30.9 (CH₃), 21.7 (CH₃); ¹⁹F NMR (376 MHz, CD₂CN) δ −79.5 (s); MS (ESI-TOF, positive mode): m/z 267 ([M–OTf]+); Anal. Calcd for C₁₉H₁₉F₃O₃S₂: 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-trimethylpyrididine (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 CH₂Cl₂ = 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; ¹H
NMR (400 MHz, CDCl₃) 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, OCH₃), 3.76 (d, J = 10.8 Hz, 2H, CH₂), 3.68 (d, J = 10.8 Hz, 2H, CH₂), 1.33 (s, 3H, CH₃), 1.30 (s, 9H, CH₃), 0.80 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) 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 (CH₂), 55.3 (CH), 34.6 (C), 31.2 (CH₃), 30.3 (C), 23.2 (CH₃), 21.9 (CH₃); MS (EI, positive mode): m/z 386 ([M]+); Anal. Calcd for C₂₃H₃₀O₃S: 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 CH₂Cl₂ (10 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (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, CDCl₃) 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, OCH₃), 1.51 (s, 9H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) 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, J_CF = 319 Hz, CF₃), 114.0 (CH), 57.5 (CH), 36.5 (C), 30.8 (CH); ¹⁹F NMR (376 MHz, CDCl₃) δ −79.4 (s); MS (ESI-TOF, positive mode): m/z 283 ([M–OTf]+); Anal. Calcd for C₁₉H₁₉F₃O₄S₂: 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 °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/CH₂Cl₂ = 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, CDCl₃) 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, CH₂), 3.71 (s, 6H, OCH₃), 1.33 (s, 9H, CH₃), 1.32 (s, 3H, CH₃), 0.78 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) 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 (CH2), 55.4 (OCH3), 34.8 (C), 31.2 (CH3), 30.3 (C), 23.3 (CH3), 21.9 (CH3); MS (EI, positive mode): m/z 416 ([M]+); Anal. Calcd for C24H32O4S: 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 CH2Cl2 (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et2O (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.); 1H NMR (400 MHz, CD3CN) 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, OCH3), 4.19 (s, 3H, OCH3), 1.47 (s, 9H, CH3); 13C{1H} NMR (101 MHz, CD3CN) 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, CF3), 121.0 (C), 103.4 (CH), 101.7 (CH), 59.2 (OCH3), 58.9 (OCH3), 36.2 (C), 31.1 (CH3); 19F NMR (376 MHz, CD3CN) δ –79.3 (s); MS (ESI-TOF, positive mode): m/z 313 ([M–OTf]+); Anal. Calcd for C20H21F3O5S2: 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/CH2Cl2 = 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; 1H NMR (400 MHz, CDCl3) 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, CH2), 3.64 (dd, J =10.8 Hz, 2H, CH2), 1.34 (s, 9H, CH3), 1.32 (s, 3H, CH3), 0.76 (s, 3H, CH3); 13C{1H} NMR (101 MHz, CDCl3) 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 (CH2), 34.8 (C), 31.2 (CH3), 30.2 (C), 23.2 (CH3), 21.8 (CH3); MS (EI, positive mode): m/z 406 ([M]+); Anal. Calcd for C26H30O2S: 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 CH₂Cl₂ (5 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (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 ℃; ¹H NMR (400 MHz, CD₃CN) 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, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃CN) 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, JCF = 318 Hz, CF₃SO³⁻), 36.7 (C), 31.1 (CH); ¹⁹F NMR (376 MHz, CD₃CN) δ -76.4 (s, CF₃SO³⁻); MS (ESI-TOF, positive mode): m/z 303 ([M–OTf]⁺); Anal. Calcd for C₂₂H₁₉F₃O₃S₂: 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 ℃ 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/CH₂Cl₂ = 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 ℃; ¹H NMR (400 MHz, CDCl₃) δ 8.37–8.35 (m, 1H, ArH), 7.86–7.84 (m, 1H, ArH), 7.80 (d, J = 2.4 Hz, 1H, ArH), 7.80 (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, CH₂), 3.65 (d, J = 10.8 Hz, 2H, CH₂), 1.34 (s, 3H, CH₃), 1.30 (s, 9H, CH₃), 0.76 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) 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 (CH₂), 34.7 (C), 31.2 (CH₃), 30.3 (C), 23.3 (CH₃), 21.8 (CH₃); MS (EI, positive mode): m/z 406 ([M⁺]); Anal. Calcd for C₂₆H₃₀O₂S: 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 CH₂Cl₂ (6 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (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.); ¹H NMR (400 MHz, CD₃CN) 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, CH₃); ¹³C{¹H} NMR (101 MHz, CD₃CN) 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, CF₃), 36.6 (C), 30.9 (CH₃); ¹⁹F NMR (376 MHz, CD₃CN) δ –79.3 (s); MS (ESI-TOF, positive mode): m/z 303 ([M–OTf]⁺); Anal. Calcd for C₂₂H₁₉F₃O₃S₂: 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, 2.12 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/CH₂Cl₂ = 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; ¹H NMR (400 MHz, CDCl₃) 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, CH₂), 3.68 (d, J = 10.4 Hz, CH₂), 1.35 (s, 3H, CH₃), 1.29 (s, 9H, CH₃), 0.76 (s, 3H, CH₃); ¹³C{¹H} NMR (101 MHz, CDCl₃) 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 (CH₂), 34.7 (C), 31.2 (CH₃), 30.3 (C), 23.3 (CH₃), 21.8 (CH₃); MS (EI, positive mode): m/z 480 ([M⁺]); Anal. Calcd for C₃₂H₃₂O₂S: 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 CH₂Cl₂ (7 mL) at room temperature. After the solution was stirred at room temperature for 2 h, the reaction mixture was added dropwise to cold Et₂O (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 ºC (decomp.);

1H NMR (400 MHz, CD₃CN) 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, CH₃); 19F NMR (376 MHz, CD₃CN) δ −79.3 (s); MS (ESI-TOF, positive mode): m/z 377 ([M–OTf]+); Anal. Calcd for C₂₈H₂₁F₃O₃S₂: C, 63.87; H, 4.02%; found: C, 63.51; H, 3.90%. Satisfactory ¹³C NMR data of 1g could not be obtained due to its low solubility in common organic solvents such as CD₃CN, DMSO-d₆, DMF-d₇, and CD₂Cl₂.

COMPUTATIONAL DETAILS.

All density functional theory (DFT) calculations were performed utilizing the Gaussian 16 package. The Becke’s three-parameter hybrid functional with Lee-Yang-Parr correlation functional (B3LYP) 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), denoted as “PCM(CH₂Cl₂)-”.

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