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Friedel-Crafts approach to the one-pot synthesis of methoxy substituted thioxanthylium salts

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Abstract

An efficient synthesis of methoxy substituted thioxanthylium salts has been developed. The reaction of diaryl sulfides with benzoyl chlorides in the presence of TfOH smoothly proceeded to give the desired thioxanthylium salts in good yields. In their UV-vis spectra, the maximum absorption wavelengths of methoxy functionalized thioxanthylium salts were observed at around 460 nm, which show a drastic red shift compared to the parent thioxanthylium salts. The present reaction provides a versatile access to functionalized thioxanthylium salts, and therefore it constitutes a promising tool for the synthesis of biologically and photochemically active molecules.

Keywords

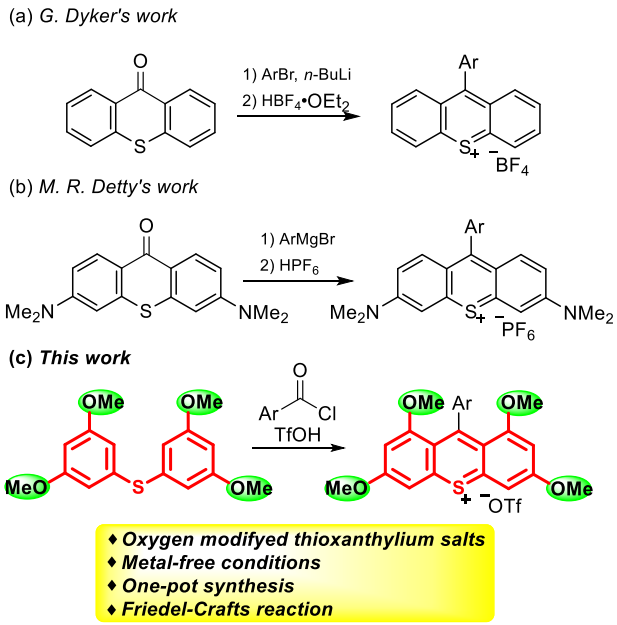
thioxanthylium salt; metal-free conditions; one-pot synthesis; photoredox catalyst; Friedel-Crafts reaction

Introduction

Thioxanthylium salt is one of the important structural motifs found in biologically active compounds and photochemical materials [1–8]. Owing to these useful properties, several research groups have developed methodologies to synthesize them. The typical synthetic methods for thioxanthylium salts include the reaction of thioxanthone with aryl bromide in the presence of *n*-butyllithium or Grignard reagents followed by dehydration by acids such as hexafluorophosphoric acid (Scheme 1a and 1b) [3–4,9–10], oxidation of thioxanthene in the presence of PbO_2 followed by dehydration by tetrafluoroboric acid [1], the reaction of 4,4'-bis(dimethylamino)diphenylmethane with sulfur in the presence of $ZnCl_2$ [11], and ring-closure reaction of diaryl sulfide in the presence of Lewis acid such as $SnCl_4$ and $AlCl_3$ [12-14]. While these reactions were proven to be useful, they require the use of stoichiometric metals and/or toxic metal reagents. Moreover, there are only a few methods for the synthesis of thioxanthylium salts despite their useful active properties. Thus, developing efficient synthetic routes and more economic approaches is highly desirable. In addition, only amino groups were introduced to the thioxanthylium core except 9-position of thioxanthylium salt (Scheme 1b), and the physical properties of these substituted compounds have not been examined.

We have developed the synthesis of multi-substituted condensed heterocyclic compounds in the presence of acid catalyst [15–23]. More recently, we have reported the design and synthesis of thioxanthylium organophotoredox catalysts, which can work under green light irradiation [24]. In the course of this study, we found that these

thioxanthylium photocatalysts efficiently oxidized styrene derivatives such as *trans*-anethole, and promoted radical cation Diels-Alder reaction. Based on the background mentioned above, in order to expand the utility of the synthesis of thioxanthylium salts and investigate their physical properties, we report the Friedel-Crafts approach as an efficient synthetic method of methoxy substituted thioxanthylium salts (Scheme 1c).



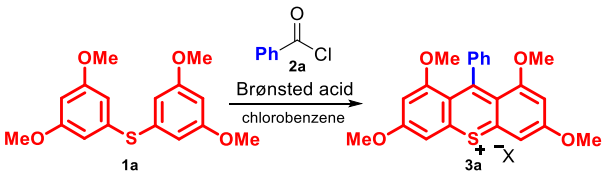
Scheme 1: The representative synthesis of thioxanthylium salts

Results and Discussion

Initially, we screened the reaction of bis[3,5-dimethoxyphenyl]sulfide (**1a**) with benzoyl chloride (**2a**) in the presence of Brønsted acids in chlorobenzene at several temperatures (Table 1). When we used a strong Brønsted acid such as trifluoromethanesulfonic acid (TfOH) at room temperature, the desired thioxanthylium salt was obtained with 21% yield while other typical Brønsted acids did not work efficiently (entries 1-8) [2,9-10]. At 60 °C, the yield effectively improved to 60% (entry 9). Moreover, when the reaction temperature was increased to 90 °C, 120 °C, and reflux, higher yields were observed, especially under reflux condition providing the

product in 82% yield (entries 10-12). Decreasing the amount of TfOH did not improve the yield (entry 13). It is suggested that the cyclization and dehydration were efficiently promoted at high temperature. Fortunately, when the reaction carried out to use benzoic acid, which is more easily available substrate comparison with benzyl chloride, the desired product was obtained in good yield. It was found that the reaction can be applied to not only benzoyl chloride but also benzoic acid.

Table 1: Optimization of the reaction conditions[a]

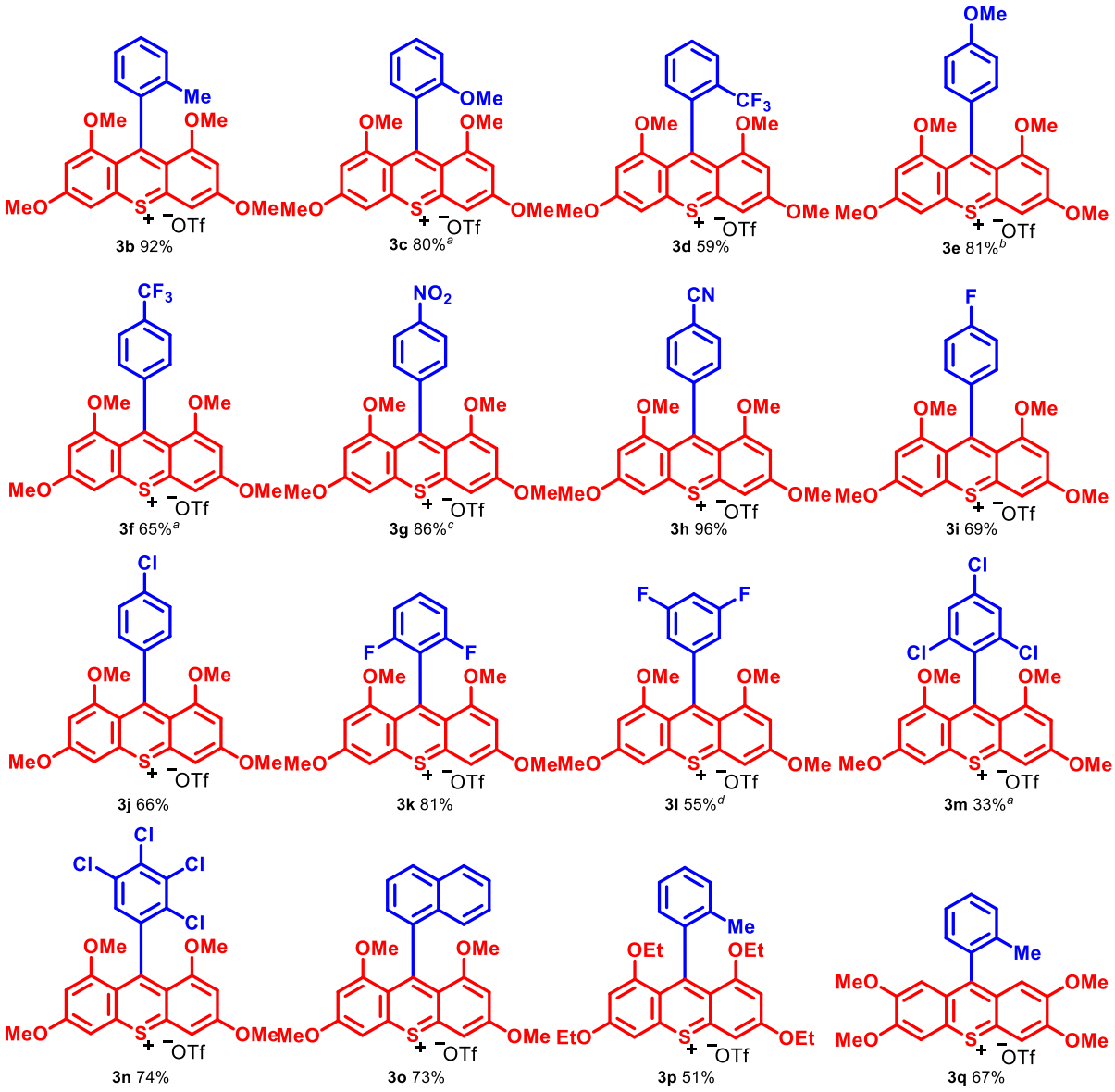


Entry	Brønsted acid	Temperature (°C)	Yield (%)
1	H_3PO_4	rt	0
2	HCl	rt	0
3	TsOH	rt	0
4	MsOH	rt	0
5	HBF_4	rt	0
6	HPF_6	rt	0
7	$HClO_4$	rt	trace
8	TfOH	rt	21
9	TfOH	60	60
10	TfOH	90	72
11	TfOH	120	75
12	TfOH	reflux	82
13[b]	TfOH	reflux	78
14[c]	TfOH	reflux	72

[a]All reactions were carried out with **1a** (0.25 mmol), **2a** (0.75 mmol), TfOH (3.0 equiv.) in chlorobenzene (5.0 mL) for 1 h under N_2. [b]TfOH (2.0 equiv.) was used. [c]benzoic acid (0.75 mmol) was used instead of benzoyl chloride **2a**.

With the optimized conditions in hand, we investigated the generality of diaryl sulfide **1** and benzoyl chloride **2** (Table 2). *o*-Toluoyl chloride smoothly afforded the desired product with an excellent yield (**3b**). In addition, 2-methoxy and 2-trifluoromethyl functionalized benzoyl chloride can be applied to the reaction (**3d**). 4-Methoxy group was also tolerated in the reaction (**3e**). Substrates with strong electron-withdrawing groups such as 4-trifluoromethyl, 4-nitro and 4-cyano groups reacted with moderate to excellent yields (**3f**-**3h**). The benzoyl chlorides bearing a variety of halogeno groups were suitable for this reaction (**3i**-**3n**). While naphthalene is a sterically hinder functionality, the reaction smoothly proceeded (**3o**). The diaryl sulfide with ethoxy substituents furnished the corresponding product in moderate yield (**3p**). Interestingly, when bis(3,4-dimethoxyphenyl)sulfide was used as a substrate, the reaction proceeded to afford the desired 2,3,6,7-tetra methoxy substituted thioxanthylium salt (**3q**). It was found out that the present reaction can be applied to various benzoyl chloride bearing either electron-donating or electron-withdrawing groups.

Table 2: The generality of diaryl sulfide **1** and benzoyl chloride **2**.



[a]**2** (2.0 equiv.) and TfOH (2.0 equiv.) were used at 120 °C. [b]**2** (2.0 equiv.) and TfOH (2.0 equiv.) were used. [c]20 h. [d]2 h.

Subsequently, we measured the UV-vis spectra of thioxanthylium salts. As shown in Figure 1, almost all of the same UV-vis spectra were observed in spite of different substituents on benzene ring at the 9-position. Moreover, when the solvent effects were examined using MeCN, CH_3NO_2, DMSO and MeOH, no substantial shifts of the main peak at around 460 nm in UV-vis absorption spectra were observed,[4] indicating

that the main absorption of these catalysts would be due to π-π* transition, and it is supported by DFT calculation (TD-DFT B3LYP method) (Figure 2 (a) - (b)). Based on these calculations, it was found that tetra methoxy substituents of thioxanthylium core up-shifted the both HOMO/LUMO energy levels compared to thioxanthylium salt without methoxy groups (Figure 2 (c) - (d)). The maximum absorption wavelength of thioxanthylium salt **3b** (λ_{max} = 464 nm) showed a drastic red shift compared to thioxanthylium salt **4b** (λ_{max} = 383 nm), which has no methoxy groups (Figure 3 and 4).

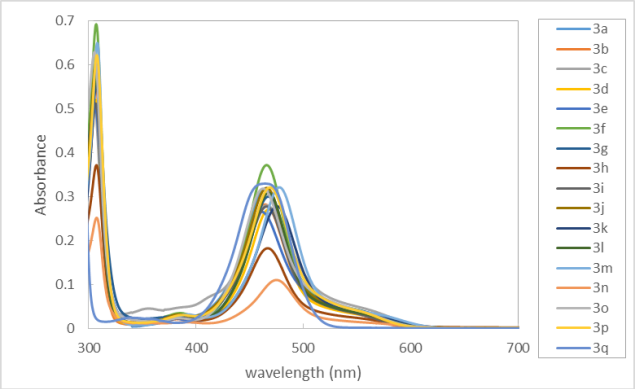
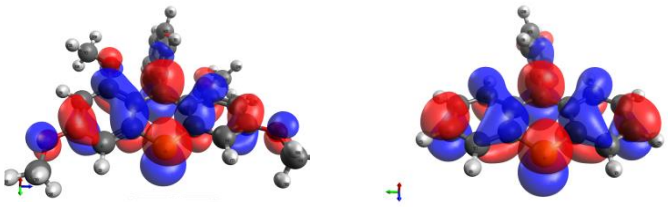
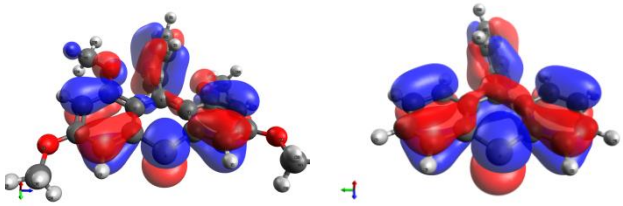


Figure 1: The UV-vis spectra of thioxanthylium salt (0.1 mM) in CH_3CN.



(a) (c)



(b) (d)

Figure 2: Frontier orbitals of thioxanthylium salts, calculated by DFT at the B3LYP/6-31G(d,p) level of Orca. (a) LUMO localization of **3a** (energy level: -5.745 eV), (b) HOMO localization of **3a** (energy level: -8.842 eV), (c) HOMO localization of **4a** (energy level: -6.812 eV), (d) HOMO localization of **4a** (energy level: -9.788 eV).

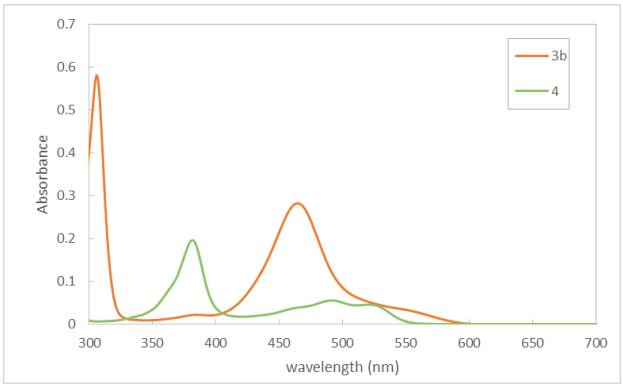
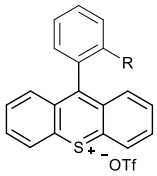


Figure 3: UV-vis spectra of thioxanthylium salts **3b** and **4b** (0.1 mM) in CH_3CN.



4a R = H
4b R = Me

Figure 4: The structure of thioxanthylium salt **4**.

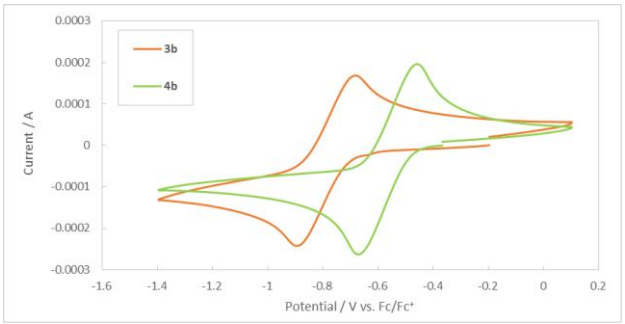


Figure 5: The cyclic voltammograms of thioxanthylium salts **3b** and **4b**.

Finally, we measured the cyclic voltammograms (CV) of thioxanthylium salts **3b** and **4b** (Figure 5). The CV data analysis implies that the reduction potential of **3b** (E_0' = -

0.79 V vs Fc/Fc^+) afforded negative shift compared to **4b** (E_0' = -0.56 V vs Fc/Fc^+). It is obviously indicated that methoxy groups lower the reduction potential by the strong electron donating effect.

In conclusion, we have developed the Friedel-Crafts approach as an efficient method to synthesize oxygen modified thioxanthylium salts. When the reaction of diaryl sulfide with benzoyl chloride in the presence of TfOH was carried out under reflux condition in chlorobenzene, the desired thioxanthylium salt was obtained in good yield. A variety of benzoyl chlorides bearing both electron-donating and electron-withdrawing groups can be applied to the reaction. It was found out that the main absorption of thioxanthylium salts around 460 nm in UV-vis spectra would be due to π-π* transition, which was supported by DFT calculations. The present reaction provides a versatile access to functionalized thioxanthylium salts, and therefore constitutes a promising tool for the synthesis of biologically and photochemically active molecules.

Conclusion

We have developed the Friedel-Crafts approach as an efficient method to synthesize oxygen modified thioxanthylium salts. When the reaction of diaryl sulfide with benzoyl chloride in the presence of TfOH was carried out under reflux condition in chlorobenzene, the desired thioxanthylium salt was obtained in good yield. A variety of benzoyl chlorides bearing both electron-donating and electron-withdrawing groups can be applied to the reaction. It was found out that the main absorption of thioxanthylium salts around 460 nm in UV-vis spectra would be due to π-π* transition, which was supported by DFT calculations. The present reaction provides a

versatile access to functionalized thioxanthylium salts, and therefore constitutes a promising tool for the synthesis of biologically and photochemically active molecules.

Experimental

General

Infrared (IR) spectra were recorded on a JASCO FT/IR-4100. ^{1}H NMR spectra were recorded on a Bruker DRX-300 (300 MHz) spectrometer, a Bruker DRX-500 (500 MHz) spectrometer or a JEOL JNM ECA-500 (500 MHz) with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm from TMS. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants, integration. ^{13}C NMR spectra were recorded on a Bruker DRX-500 (126 MHz) or a JEOL JNM ECA-500 (126 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard ($CDCl_3$: δ 77.0). ^{19}F NMR spectra were recorded on a JEOL JNM AL-400 (376 MHz) or a JEOL JNM ECA-500 (471 MHz) spectrometer with hexafluorobenzene (C_6F_6: δ -164.9) as internal standard. High-resolution mass spectra (HRMS) were obtained with Hitachi Nanofrontier LD Spectrometer (ESI/TOF). Elemental analyses of carbon, hydrogen, nitrogen, and sulfur were performed with a CHNOS Elemental Analyzer Vario ELIII Elemental (Elementar Co.). Column chromatography was carried out with Cicareagent silica gel 60 N (spherical, particle size 63-210 mm). Thinlayer chromatography (TLC) was carried out with Merck TLC plates with silica gel 60 F254. Unless otherwise noted, reagents were commercially available and were used without purification. Single-crystal X-ray diffraction analysis was performed at 223 K using a Rigaku XtaLAB P200 diffractometer with a graphitemonochromatic Cu Ka

radiation source (l ¼ 1.54187 Å). The UV absorption spectra were measured with a JASCO V-630 spectrometer. Cyclic voltammetry measurements were carried out with a computer-controlled potentiostat Model 660C (ALS Co., Ltd.).

General procedure for the synthesis of thioxanthylium salt 3

To a solution of diaryl sulfide **1** (0.25 mmol) and benzoyl chloride **2** (0.75 mmol) in chlorobenzene (5.0 mL) was placed in a 50 mL recovery flask under N_2. Trifluoromethanesulfonic acid (0.75 mmol) was slowly added to the solution, which was heated to reflux for 1 h. It was cooled to room temperature and excess Et_2O was added to precipitate a solid. After stirred for 1 h, the mixture was filtered. The solid was washed with Et_2O and dried in vacuo, affording the desired thioxanthylium salt **3**.

9-Phenyl-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3a**)

Red solid (0.1109 g, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, *J* = 2.2 Hz, 2H), 7.44-7.38 (m, 3H), 7.14-7.10 (m, 2H), 6.51 (d, *J* = 2.5 Hz, 2H), 4.15 (s, 6H), 3.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3. 165.5. 165.2. 147.8. 142.2. 127.2. 127.0. 125.6. 116.9. 101.8. 101.4. 57.7. 56.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1585, 1219, 1143, 1026, 634 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{23}H_{21}O_4S$ ($[M]^+$): 393.1155, found: 393.1171; EA calcd. for $C_{24}H_{21}F_3O_7S_2$: C, 53.13; H, 3.90. found: C, 52.80; H, 4.001.

9-(2-Methylphenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3b**)

Brown solid (0.1274 g, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 2.2 Hz, 2H), 7.28 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.26-7.23 (m, 1H), 7.23-7.17 (m, 1H), 6.73 (d, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 2.2 Hz, 2H), 4.15 (s, 6H), 3.40 (s, 6H), 2.03 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3, 166.0, 165.5, 147.7, 142.1, 134.2, 128.0, 127.5,

125.1, 124.0, 116.7, 102.0, 101.3, 57.7, 56.9, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1584, 1220, 1151, 1028, 637 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{23}O_4S$ ($[M]^+$) : 407.1312, found: 407.1324.

9-(2-Methoxyphenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3c**)

2-Methoxybenzoyl chloride (0.50 mmol), TfOH (0.50 mmol) were used at 120 °C. Red solid (0.1142 g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (d, *J* = 2.2 Hz, 2H), 7.38 (td, *J* = 8.0, 1.7 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.72 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 2H), 4.15 (s, 6H), 3.73 (s, 3H), 3.43 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.1, 165.4, 163.6, 156.4, 147.8, 132.2, 129.0, 125.2, 120.3, 117.4, 108.5, 101.7, 101.4, 57.7, 56.8, 55.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1585, 1217, 1149, 1026, 636 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{23}O_5S$ ($[M]^+$): 423.1261, found: 423.1256.

9-(2-Trifluoromethylphenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3d**)

Brown solid (0.0906 g, 59% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.0 Hz, 1H), 7.61-7.54 (m, 2H), 7.53 (d, *J* = 2.5 Hz, 2H), 6.98 (dd, *J* = 8.2, 3.5 Hz, 1H), 6.53 (d, *J* = 2.5 Hz, 2H), 4.15 (s, 6H), 3.39 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.5, 164.9, 162.4, 147.4, 140.1 (q, *J* = 2.8 Hz), 131.1, 127.7, 127.5 (q, *J* = 30.9 Hz), 126.0, 125.0 (q, *J* = 4.6 Hz), 124.3 (q, *J* = 274.0 Hz), 120.9 (q, *J* = 320.5 Hz, OTf^-), 116.4, 102.1, 101.2, 57.7, 56.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.0, -81.3; IR (ATR): 1585, 1237, 1222, 1029, 637 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{20}O_4F_3S$ ($[M]^+$): 461.1029, found: 461.1037; EA calcd. for $C_{25}H_{20}F_6O_7S_2$: C, 49.18; H, 3.30; S, 10.50. found: C, 48.97; H, 3.280; S, 10.30.

9-(4-Methoxyphenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3e**)

4-Methoxybenzoyl chloride (0.50 mmol), TfOH (0.50 mmol) were used. Brown solid (0.1158 g, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, *J* = 2.2 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.54 (d, *J* = 2.2 Hz, 2H), 4.14 (s, 6H), 3.91 (s, 3H), 3.45 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3, 165.9, 165.8, 159.2, 147.3, 134.4, 127.2, 117.3, 112.5, 101.7, 101.2, 57.6, 56.8, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1587, 1219, 1146, 1027, 635 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{23}O_5S$ ($[M]^+$): 423.1261, found: 423.1253. EA calcd. for $C_{24}H_{21}F_3O_7S_2$: C, 52.44; H, 4.05. found: C, 51.75; H, 4.285.

9-(4-Trifluoromethylphenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3f**)

4-(Trifluoromethyl)benzoyl chloride (0.50 mmol), TfOH (0.50 mmol) were used. Brown solid (0.0420 g, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 2.0 Hz, 2H), 7.60-7.59 (m, 2H), 7.32 (d, *J* = 2.0 Hz, 2H), 6.51 (d, *J* = 0.6 Hz, 2H), 4.17 (s, 6H), 3.35 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.5, 165.0, 162.7, 147.8, 146.1, 129.3 (q, *J* = 32.5 Hz), 126.2, 124.1 (q, *J* = 272.8 Hz), 123.8 (q, *J* = 3.5 Hz), 120.8 (q, *J* = 320.9 Hz, OTf^-), 116.3, 102.1, 101.5, 57.8, 56.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -65.6, -81.3; IR (ATR): 1592, 1403, 1219, 1027, 840, 636 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{20}O_4F_3S$ ($[M]^+$): 461.1029, found: 461.1041.

9-(4-Nitrophenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3g**)

The reaction was carried out for 20 h. Black solid (0.1261 g, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 2.5 Hz, 2H), 7.42-7.40 (m,

2H), 6.53 (d, *J* = 2.2 Hz, 2H), 4.15 (s, 6H), 3.38 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.7,164.6, 161.3, 149.4, 148.0, 146.8, 127.1, 122.2, 116.1, 102.3, 101.7, 57.8, 56.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.4; IR (ATR): 1584, 1219, 1150, 1027, 837, 634 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{23}H_{20}NO_6S$ ($[M]^+$): 438.1006, found: 438.0991.

9-(4-Cyanophenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3h**)

Black solid (0.1359 g, 96% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, *J* = 2.0 Hz, 2H), 7.58 (d, *J* = 0.5 Hz, 2H), 7.34 (d, *J* = 2.3 Hz, 2H), 6.53-6.51 (m, 2H), 4.17 (s, 6H), 3.39 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 164.9, 161.8, 147.5, 147.3, 130.7, 126.7, 120.6 (q, *J* = 320.9 Hz, OTf^-), 118.7, 115.9, 110.6, 102.2, 101.4, 57.7, 56.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.4; IR (ATR): 1584, 1402, 1213, 1154, 1028, 823, 636 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{20}NO_4S$ ($[M]^+$): 418.1108, found: 418.1098.

9-(4-Fluorophenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3i**)

Brown solid (0.0970 g, 69% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 2.3 Hz, 2H), 7.18-7.09 (m, 4H), 6.52 (d, *J*=2.3 Hz, 2H), 4.16 (s, 6H), 3.43 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.4, 165.3, 164.1, 162.0 (d, *J* = 247.6 Hz), 147.7, 138.0, 127.5 (d, *J* = 7.2 Hz), 116.9, 114.1 (d, *J* = 21.7 Hz), 101.8, 101.4, 57.7, 56.7; ^{19}F NMR (471 MHz, $CDCl_3$): δ -81.3, -117.4; IR (ATR): 1585, 1415, 1220, 1153, 1027, 836, 636, 573 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{23}H_{20}O_4FS$ ($[M]^+$): 411.1061, found: 411.1064.

9-(4-Chlorophenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3j**)

Brown solid (0.0951 g, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, *J* = 2.3 Hz, 2H), 7.46-7.40 (m, 2H), 7.13-7.06 (m, 2H), 6.52 (d, *J* = 2.9 Hz, 2H), 4.16 (s, 6H), 3.43

(s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.5, 165.3, 163.6, 147.5, 140.6, 133.1, 127.2, 127.1, 116.6, 102.0, 101.3, 57.7, 56.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1588, 1424, 1219, 1027, 850, 635, 571 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{23}H_{20}O_4SCl$ ($[M]^+$): 427.0765, found: 427.0767.

9-(2,6-Difluorophenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3k**)

Brown solid (0.1177 g, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 2.2 Hz, 2H), 7.45-7.40 (m, 1H), 7.02-6.98 (m, 2H), 6.60 (d, *J* = 2.5 Hz, 2H), 4.18 (s, 6H), 3.54 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.5, 164.9, 158.5 (dd, *J* = 252.0, 11.0 Hz), 151.7, 147.9, 129.9 (t, *J* = 9.6 Hz), 120.9 (q, *J* = 320.8 Hz, OTf^-), 118.9 (t, *J* = 20.2 Hz), 116.9, 110.3 (dd, *J* = 19.3, 5.5 Hz), 102.2, 101.5, 57.9, 57.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3, -116.6; IR (ATR): 1593,1245, 1148, 1026, 634 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{23}H_{19}O_4F_2S$ ($[M]^+$): 429.0967, found: 429.0966.

9-(3,5-Difluorophenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3l**)

The reaction was carried out for 2 h. Black Solid (0.0793 g, 55% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.53 (m, 2H), 6.91 (t, *J* = 8.6 Hz, 1H), 6.75 (d, *J* = 6.7 Hz, 2H), 6.56 (s, 2H), 4.17 (s, 6H), 3.51 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.6, 165.0, 162.3 (dd, *J* = 250.0, 13.2 Hz), 160.8, 147.7, 145.1 (t, *J* = 10.8 Hz), 116.0, 109.3 (dd, *J* = 21.7, 6.0 Hz), 102.5 (t, *J* = 25.3 Hz), 102.2, 101.4, 57.8, 57.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3, -113.9; IR (ATR): 1586, 1404, 1218, 1141, 1027, 850, 635 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{23}H_{19}O_4F_2S$ ($[M]^+$): 429.0967, found: 429.0968.

9-(2,4,6-Trichlorophenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3m**)

2,4,6-Trichlorobenzoyl chloride (0.50 mmol), TfOH (0.50 mmol) were used at 120 °C. Brown solid (0.0417 g, 33% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 2.2 Hz, 2H), 7.45 (s, 2H), 6.60 (d, *J* = 2.2 Hz, 2H), 4.19 (s, 6H), 3.58 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.5, 164.5, 156.9, 148.3, 139.0, 134.1, 132.0, 126.8, 115.8, 102.6, 101.5, 58.0, 57.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1586, 1222, 1154, 1029, 636 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{23}H_{18}O_4SCl_3$ ($[M]^+$): 494.9986, found: 464.9999; EA calcd. for $C_{24}H_{18}Cl_3F_3O_7S_2$: C, 44.63; H, 2.81. found: C, 44.58; H, 2.975.

9-(2,3,4,5-Tetrachlorophenyl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3n**)

Brown solid (0.1259 g, 74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.5 Hz, 2H), 7.10 (s, 1H), 6.61 (d, *J* = 2.2 Hz, 2H), 4.18 (s, 6H), 3.57 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 164.2, 156.9, 148.5, 141.9, 132.1, 131.9, 131.3, 130.2, 125.0, 115.9, 102.5, 102.0, 58.0, 57.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1594, 1248, 1231, 1161, 1024, 638 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{23}H_{17}O_4SCl_4$ ($[M]^+$): 528.9596, found: 528.9614.

9-(2-Methylphenyl)-1,3,6,8-tetraethoxythioxanthylium trifluoromethanesulfonate (**3p**)

Brown solid (0.0975 g, 51% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, *J* = 2.3 Hz, 2H), 7.40-7.31 (m, 1H), 7.21-7.16 (m, 2H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 2.3 Hz, 2H), 4.42 (q, *J* = 7.3 Hz, 4H), 3.80-3.69 (m, 2H), 3.69-3.59 (m, 2H), 2.04 (s, 3H), 1.52 (t, *J* = 6.9 Hz, 6H), 0.79 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.5, 165.3, 164.9, 147.5, 142.2, 134.7, 128.9, 127.9, 125.4, 124.7, 116.5, 101.9, 101.6,

66.5, 65.4, 20.2, 14.3, 13.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1586, 1442, 1214, 1028, 824, 635 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{28}H_{31}O_4S$ ($[M]^+$): 463.1938, found: 463.1937.

9-(2-Methylphenyl)-2,3,6,7-tetramethoxythioxanthylium trifluoromethanesulfonate (**3q**)

Brown solid (0.0937 g, 67% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (s, 2H), 7.69-7.61 (m, 1H), 7.58-7.52 (m, 2H), 7.23 (d, *J* = 6.9 Hz, 1H), 6.94 (s, 2H), 4.29 (s, 6H), 3.74 (s, 6H), 1.93 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.8, 157.5, 152.1, 143.3, 135.3, 134.9, 131.2, 130.6, 128.2, 126.9, 124.8, 109.7, 107.8, 58.2, 56.1, 19.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1608, 1506, 1426, 1222, 1029, 748, 636, 571 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{24}H_{23}O_4S$ ($[M]^+$): 407.1312, found: 407.1315.

*For the synthesis of 9-(naphthalene-1-yl)-1,3,6,8-tetramethoxythioxanthylium trifluoromethanesulfonate (**3o**)*

To a solution of 1-naphtoic acid (0.1746 g, 1.0 mmol) in dry CH_2Cl_2 (2.5 mL) at 0 °C under N_2 was added dropwise $(COCl)_2$ (0.100 mL, 1.2 mmol). After a catalytic amount of dry DMF (2 drops) was added, the solution was allowed to warm to room temperature, and stirred at that temperature for 2 h. The reaction mixture was concentrated in vacuo to afford the corresponding crude acid chloride. After the residue was dissolved in chlorobenzene, bis[3,5-dimethoxyphenyl]sulfide **1a** (0.1005 g, 0.33 mmol) and trifluoromethanesulfonic acid (0.087 mL, 0.99 mmol) were added. The reaction temperature was increased to reflux and the solution was stirred for 1 h. It was cooled to room temperature and excess Et_2O was added. After it was stirred for 1 h, filtered, and the solid was washed with Et_2O and dried in vacuo to afford the desired thioxanthylium **3o** (0.1420 g, 73% yield). Red solid. ^{1}H NMR (500 MHz,

$CDCl_3$): δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 2.2 Hz, 2H), 7.53-7.45 (m, 2H), 7.36-7.32 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 7.1, 1.1 Hz, 1H), 6.43 (d, *J* = 2.2 Hz, 2H), 4.15 (s, 6H), 2.96 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.4, 165.2, 164.7, 147.6, 140.7, 132.1, 132.0, 128.2, 127.5, 126.4, 125.9, 125.0, 124.4, 121.3, 117.6, 102.0, 101.5, 57.7, 56.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.3; IR (ATR): 1593, 1245, 1148, 1026, 634 cm^{-1}; HRMS (ESI+) m/z calcd for $C_{27}H_{23}O_4S$ $[M]^+$: 443.1312, found: 443.1316.

Supporting Information

Supporting Information File 1

Copies of ^{1}H and ^{13}C NMR spectra, Procedure for the synthesis of diaryl sulfides and thioxanthylium **4**. Computational data, absorption spectra, cyclic voltammetry data.

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