



Supporting Information

for

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

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Copies of ^1H and ^{13}C NMR spectra, procedures for the synthesis of diaryl sulfides and thioxanthylum 4, computational data, absorption spectra, and cyclic voltammetry data

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1. Procedure for the synthesis of diaryl sulfide 1

For the synthesis of bis(dimethoxyphenyl) sulfide

Bis(3,5-dimethoxyphenyl) sulfide and bis(3,4-dimethoxyphenyl) sulfide were prepared according to published methods from 3,5-dimethoxyaniline and 3,4-dimethoxyaniline.^{1,2} Bis(3,5-dimethoxyphenyl) sulfide. White solid (0.7748 g, 63% yield). ¹H NMR (300 MHz, CDCl₃): δ 6.85 (d, *J* = 2.3 Hz, 2H), 6.40 (t, *J* = 2.3 Hz, 1H), 3.76 (s, 6H). The spectroscopic data were agreement with literature values.¹

Bis(3,4-dimethoxyphenyl) sulfide. White solid (0.6092 g, 60% yield). ¹H NMR (500 MHz, CDCl₃): δ 6.97-6.86 (m, 4H), 6.86-6.77 (m, 2H), 3.88 (s, 6H), 3.82 (s, 6H). The spectroscopic data were agreement with literature values.³

For the synthesis of bis(3,5-diethoxyphenyl) sulfide

1)^{1,2,4} 1-Iodo-3,5-dimethoxybenzene were prepared according to published methods from 3,5-dimethoxyaniline.² To a solution of 1-iodo-3,5-dimethoxybenzene (0.6824 g, 2.5 mmol) in CH₂Cl₂ (2.5 mL) was placed in a 50 mL recovery flask under N₂. Boron tribromide (10.0 mL, 1.0 M in CH₂Cl₂, 10 mmol) was added slowly at 0 °C. The reaction was warmed to room temperature and stirred overnight. Then, it was cooled to -78 °C, quenched with methanol and concentrated in vacuo. The crude mixture was redissolved in ethyl acetate, washed with H₂O, dried over sodium sulfate, filtered and concentrated in vacuo. The crude product 5-iodobenzene-1,3-diol was used in the subsequent step without further purification.

2)⁴ To an oil of 5-iodobenzene-1,3-diol (2.5 mmol) and potassium carbonate (1.3847 g, 10.0 mmol) in DMF (10 mL) were placed in a 100 mL recovery flask under N₂. Bromoethane (0.746 mL, 10.0 mmol) was then added and the reaction heated to 60 °C for 20 h. The reaction was cooled, diluted in ethyl acetate, washed with H₂O, dried over sodium sulfate, filtered and concentrated in vacuo. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to provide 1,3-diethoxy-5-iodobenzene (0.6014 g, 82 % yield) as a brown oil. ¹H NMR (500 MHz, CDCl₃): δ 6.83 (d, *J* = 2.4 Hz, 2H), 6.39 (t, *J* = 2.0 Hz, 1H), 3.97 (q, *J* = 6.9 Hz, 4H), 1.38 (t, *J* = 7.2 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 160.4, 116.2, 101.4, 94.0, 63.7, 14.7; IR (ATR): 1591, 1434, 1169, 1047, 802, 676 cm⁻¹; LRMS (ESI+) *m/z* calcd for C₁₀H₁₄O₂I ([M+H]⁺): 293.00, found: 293.09.

3)¹ To a mixture of 1,3-diethoxy-5-iodobenzene (0.4857 g, 1.7 mmol), carbon disulfide (0.100 mL, 1.7 mmol), CuI (0.0356 g, 0.17 mmol), and DBU (0.496 mL, 3.3 mmol) in

toluene (3.0 mL) was stirred at reflux under N₂ for 16 h. After H₂O was added, the mixture was extracted with CH₂Cl₂. The organic layer was dried over MgSO₄ and concentrated in vacuo. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 30:1) to provide bis(3,5-diethoxyphenyl)sulfide (0.0727 g, 39% yield) as a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 6.49 (d, *J* = 2.3 Hz, 4H), 6.33 (t, *J* = 2.3 Hz, 2H), 3.96 (q, *J* = 6.9 Hz, 8H), 1.37 (t, *J* = 6.9 Hz, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 160.3, 136.9, 109.3, 100.6, 63.6, 14.7; IR (ATR): 1577, 1430, 1389, 1278, 1166, 1050, 815, 681 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₀H₂₇O₄S ([M+H]⁺): 363.1625, found: 363.1639.

2. Procedure for the synthesis of thioxanthylum salt 4

1)⁵ To a solution of 2-bromotoluene (0.897 mL, 7.5 mmol) in dioxane (17.0 mL) and THF (28.0 mL) was placed in a 100 mL recovery flask under N₂. *n*-BuLi (5.16 mL, 1.6 M in hexane, 8.26 mmol) was added at -78 °C, and the reaction was stirred for 1 h at -78 °C. Thioxanthone (1.0644 g, 5.0 mmol) in dioxane was added, and the reaction was stirred for 24 h at room temperature. The reaction was quenched with sat. diammonium phosphate and extract with CH₂Cl₂. It was concentrated in vacuo. To the organic layer was added hexane, and the mixture was cooled to -30 °C to give white solid. The mixture was filtered and dried in vacuo, affording the desired 9-(2-methylphenyl)-9-thioxanthenol (0.6863 g, 45% yield) as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 7.7 Hz, 1H), 7.43-7.36 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.26-7.23 (m, 2H), 7.12-7.04 (m, 5H), 2.51 (d, *J* = 2.9 Hz, 1H), 1.55 (s, 3H). The spectroscopic data were agreement with literature values.⁵

2)⁵ To a solution of 9-(2-methylphenyl)-9-thioxanthenol (0.3048 g, 1.0 mmol) in Et₂O (5.0 mL) was placed in a 50 mL recovery flask under N₂. Trifluoromethanesulfonic acid (0.177 mL, 2.0 mmol) was slowly added to precipitate a solid. After stirred for 1 h, the mixture was filtered. The solid was washed with Et₂O and dried in vacuo, affording the desired thioxanthylum salt 4 (0.3473 g, 80% yield). Red solid. ¹H NMR (500 MHz, CDCl₃): δ 8.91 (d, *J* = 8.6 Hz, 2H), 8.43 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 2H), 8.16 (d, *J* = 8.6 Hz, 2H), 8.07 (ddd, *J* = 8.5, 7.0, 1.2 Hz, 2H), 7.71-7.66 (m, 1H), 7.61-7.53 (m, 2H), 7.33-7.29 (m, 1H), 1.91 (s, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 171.3, 148.1, 137.9, 135.5, 134.5, 133.7, 131.6, 131.0, 131.0, 129.7, 128.8, 128.3, 126.4, 19.7; ¹⁹F NMR (471 MHz, CDCl₃): δ -81.4; IR (ATR): 1547, 1449, 1373, 1260, 1142, 1029, 736, 634 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₀H₁₅S [M]⁺: 287.0889, found: 287.0879.

3. Characterization data for thioxanthylum salt 3

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

Red solid (0.1109 g, 82% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -81.3; IR (ATR): 1585, 1219, 1143, 1026, 634 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₃H₂₁O₄S ([M]⁺): 393.1155, found: 393.1171; EA calcd. for C₂₄H₂₁F₃O₇S₂: C, 53.13; H, 3.90. found: C, 52.80; H, 4.001.

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

Brown solid (0.1274 g, 92% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -81.3; IR (ATR): 1584, 1220, 1151, 1028, 637 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₄H₂₃O₄S ([M]⁺): 407.1312, found: 407.1324.

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

2-Methoxybenzoyl chloride (0.50 mmol), TfOH (0.50 mmol) were used at 120 °C. Red solid (0.1142 g, 80% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -81.3; IR (ATR): 1585, 1217, 1149, 1026, 636 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₄H₂₃O₅S ([M]⁺): 423.1261, found: 423.1256.

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

Brown solid (0.0906 g, 59% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -63.0, -81.3; IR (ATR): 1585, 1237, 1222, 1029, 637 cm⁻¹; HRMS (ESI+) m/z calcd for C₂₄H₂₀O₄F₃S ([M]⁺): 461.1029, found: 461.1037; EA calcd. for C₂₅H₂₀F₆O₇S₂: 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-tetramethoxythioxanthylum trifluoromethanesulfonate (**3e**)¹

4-Methoxybenzoyl chloride (0.50 mmol), TfOH (0.50 mmol) were used. Brown solid (0.1158 g, 81% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -81.3; IR (ATR): 1587, 1219, 1146, 1027, 635 cm⁻¹; HRMS (ESI+) m/z calcd for C₂₄H₂₃O₅S ([M]⁺): 423.1261, found: 423.1253. EA calcd. for C₂₄H₂₁F₃O₇S₂: C, 52.44; H, 4.05. found: C, 51.75; H, 4.285.

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

4-(Trifluoromethyl)benzoyl chloride (0.50 mmol), TfOH (0.50 mmol) were used. Brown solid (0.0990 g, 65% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -65.6, -81.3; IR (ATR): 1592, 1403, 1219, 1027, 840, 636 cm⁻¹; HRMS (ESI+) m/z calcd for C₂₄H₂₀O₄F₃S ([M]⁺): 461.1029, found: 461.1041.

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

The reaction was carried out for 20 h. Black solid (0.1261 g, 86% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -81.4; IR (ATR): 1584, 1219, 1150, 1027, 837, 634 cm⁻¹; HRMS (ESI+) m/z calcd for C₂₃H₂₀NO₆S ([M]⁺): 438.1006, found: 438.0991.

9-(4-Cyanophenyl)-1,3,6,8-tetramethoxythioxanthylum trifluoromethanesulfonate (**3h**)
Black solid (0.1359 g, 96% yield). ^1H 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 $\text{C}_{24}\text{H}_{20}\text{NO}_4\text{S}$ ($[\text{M}]^+$): 418.1108, found: 418.1098.

9-(4-Fluorophenyl)-1,3,6,8-tetramethoxythioxanthylum trifluoromethanesulfonate (**3i**)
Brown solid (0.0970 g, 69% yield). ^1H 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 $\text{C}_{23}\text{H}_{20}\text{O}_4\text{FS}$ ($[\text{M}]^+$): 411.1061, found: 411.1064.

9-(4-Chlorophenyl)-1,3,6,8-tetramethoxythioxanthylum trifluoromethanesulfonate (**3j**)
Brown solid (0.0951 g, 66% yield). ^1H 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 $\text{C}_{23}\text{H}_{20}\text{O}_4\text{SCl}$ ($[\text{M}]^+$): 427.0765, found: 427.0767.

9-(2,6-Difluorophenyl)-1,3,6,8-tetramethoxythioxanthylum trifluoromethanesulfonate (**3k**)
Brown solid (0.1177 g, 81% yield). ^1H 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 $\text{C}_{23}\text{H}_{19}\text{O}_4\text{F}_2\text{S}$ ($[\text{M}]^+$): 429.0967, found: 429.0966.

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

The reaction was carried out for 2 h. Black Solid (0.0793 g, 55% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -81.3, -113.9; IR (ATR): 1586, 1404, 1218, 1141, 1027, 850, 635 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₃H₁₉O₄F₂S ([M]⁺): 429.0967, found: 429.0968.

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

2,4,6-Trichlorobenzoyl chloride (0.50 mmol), TfOH (0.50 mmol) were used at 120 °C. Brown solid (0.0417 g, 33% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -81.3; IR (ATR): 1586, 1222, 1154, 1029, 636 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₃H₁₈O₄SCl₃ ([M]⁺): 494.9986, found: 464.9999; EA calcd. for C₂₄H₁₈Cl₃F₃O₇S₂: C, 44.63; H, 2.81. found: C, 44.58; H, 2.975.

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

Brown solid (0.1259 g, 74% yield). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; ¹⁹F NMR (376 MHz, CDCl₃): δ -81.3; IR (ATR): 1594, 1248, 1231, 1161, 1024, 638 cm⁻¹; HRMS (ESI+) *m/z* calcd for C₂₃H₁₇O₄SCl₄ ([M]⁺): 528.9596, found: 528.9614.

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

Brown solid (0.0975 g, 51% yield). ¹H NMR (500 MHz, CDCl₃): 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); ¹³C NMR (126 MHz, CDCl₃): 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 $\text{C}_{28}\text{H}_{31}\text{O}_4\text{S}$ ($[\text{M}]^+$): 463.1938, found: 463.1937.

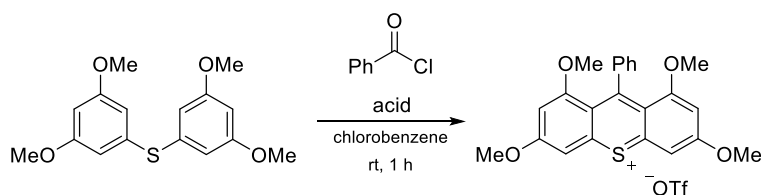
9-(2-Methylphenyl)-2,3,6,7-tetramethoxythioxanthylum trifluoromethanesulfonate (3q)

Brown solid (0.0937 g, 67% yield). ^1H 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 $\text{C}_{24}\text{H}_{23}\text{O}_4\text{S}$ ($[\text{M}]^+$): 407.1312, found: 407.1315.

9-(naphthalene-1-yl)-1,3,6,8-tetramethoxythioxanthylum trifluoromethanesulfonate (3o)

Red solid (0.1420 g, 73% yield). ^1H 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 $\text{C}_{27}\text{H}_{23}\text{O}_4\text{S}$ ($[\text{M}]^+$): 443.1312, found: 443.1316.

4. Investigation of the Lewis acids



Entry	acid	Yield (%)
1	AlCl_3	0
2	$\text{BF}_3 \cdot \text{OEt}_2$	0
3	$\text{Sc}(\text{OTf})_3$	0

When we investigated the Lewis acids such as AlCl_3 , $\text{BF}_3 \cdot \text{OEt}_2$ and $\text{Sc}(\text{OTf})_3$ the reaction did not proceed, suggesting that TfOH is the best acid in the reaction system.

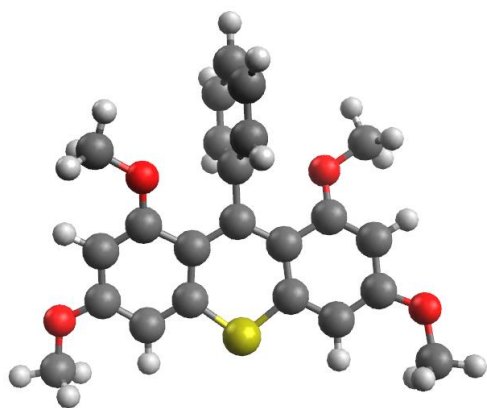
5. Computational data

Structure optimizations and frequency analyses of cations **3a** and **4a** were carried out at the B3LYP level of density functional theory (DFT) with the 6-31G(d,p) basis set on the ORCA program package.⁷

9-Phenyl-1,3,6,8-tetramethoxythioxanthylum cation

atom type	x	y	z
C	0.098289	0.212300	-1.259567
C	-0.048430	1.637149	-1.378192
C	-0.186286	2.306630	-2.592329
C	-0.119796	1.574514	-3.781309
C	0.151294	0.193490	-3.741241
C	0.302373	-0.475146	-2.540210
C	-0.000172	-0.460670	0.000080
C	-0.098675	0.211989	1.259956
C	0.048120	1.636846	1.378826
S	-0.000139	2.693604	0.000423
C	-0.302955	-0.475562	2.540575
C	-0.151790	0.192919	3.741679
C	0.119541	1.573877	3.781928
C	0.186088	2.306135	2.593051
C	0.000200	-1.961032	-0.000366
C	1.156660	-2.662899	0.361318
C	1.156940	-4.057529	0.352482
C	0.001028	-4.759099	-0.001674
C	-1.155263	-4.057882	-0.355283
C	-1.155778	-2.663242	-0.362910
O	-0.667038	-1.760043	2.494520
O	0.665809	-1.759825	-2.494120
O	-0.258582	2.093560	-5.004712
O	0.258367	2.092753	5.005398
C	-0.865079	-2.501778	3.702304
C	0.863396	-2.501759	-3.701854
C	0.512693	3.495491	5.160825

C	-0.512713	3.496352	-5.159959
H	-0.324325	3.381135	-2.600956
H	0.266673	-0.315514	-4.688717
H	-0.267378	-0.316162	4.689094
H	0.324224	3.380627	2.601827
H	2.056687	-2.120362	0.638908
H	2.060648	-4.596207	0.624789
H	0.001345	-5.845936	-0.002171
H	-2.058632	-4.596838	-0.628159
H	-2.056077	-2.120977	-0.640150
H	-1.149078	-3.501501	3.375429
H	-1.669374	-2.062156	4.302908
H	0.059428	-2.550035	4.288427
H	1.146890	-3.501606	-3.374917
H	1.667892	-2.062607	-4.302532
H	-0.061165	-2.549581	-4.287927
H	0.604156	3.655430	6.234780
H	-0.321808	4.088171	4.769363
H	1.446889	3.779068	4.663824
H	-0.604154	3.656443	-6.233893
H	0.321868	4.088869	-4.768422
H	-1.446870	3.779995	-4.662921



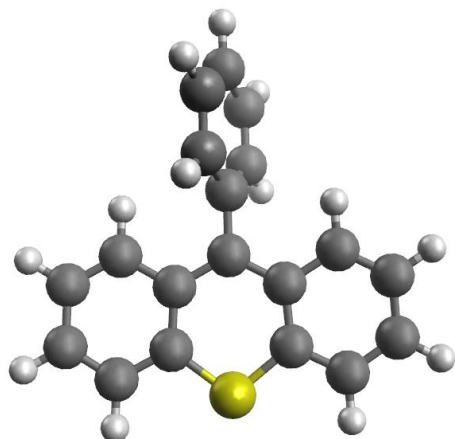
Total Energy: -1587.13327102 hartree

Imaginary Frequencies: 0

9-Phenylthioxanthylum cation

atom type	x	y	z
C	0.012766	-1.262464	0.390821
C	-0.013433	-1.376506	1.819830
C	-0.027469	-2.637633	2.445485
C	0.004556	-3.788733	1.680883
C	0.070917	-3.710651	0.273252
C	0.081039	-2.485682	-0.351445
C	0.002161	-0.001927	-0.283219
C	-0.007121	1.253571	0.400184
C	0.021920	1.356969	1.829933
S	0.005312	-0.013698	2.885260
C	-0.076875	2.482279	-0.332817
C	-0.065479	3.702563	0.300969
C	0.003715	3.770176	1.709005
C	0.037236	2.613398	2.464933
C	0.000773	0.003640	-1.772225
C	1.117101	0.483200	-2.481241
C	1.116962	0.473661	-3.875672
C	-0.001963	0.014655	-4.575388
C	-1.119498	-0.449897	-3.877117
C	-1.116914	-0.470398	-2.482804
H	-0.149117	2.437877	-1.411587
H	0.151000	-2.433155	-1.429995
H	-0.004855	-4.757405	2.171275
H	0.014137	4.735158	2.206593
H	-0.056602	-2.700380	3.529520
H	0.124918	-4.619712	-0.316437
H	-0.120675	4.615985	-0.281847
H	0.068557	2.668066	3.549349
H	1.988954	0.841032	-1.941344
H	1.990884	0.827526	-4.414024
H	-0.003056	0.019015	-5.661318
H	-1.994473	-0.799519	-4.416525

H -1.987748 -0.832423 -1.944042



Total Energy: -1129.58253481 hartree

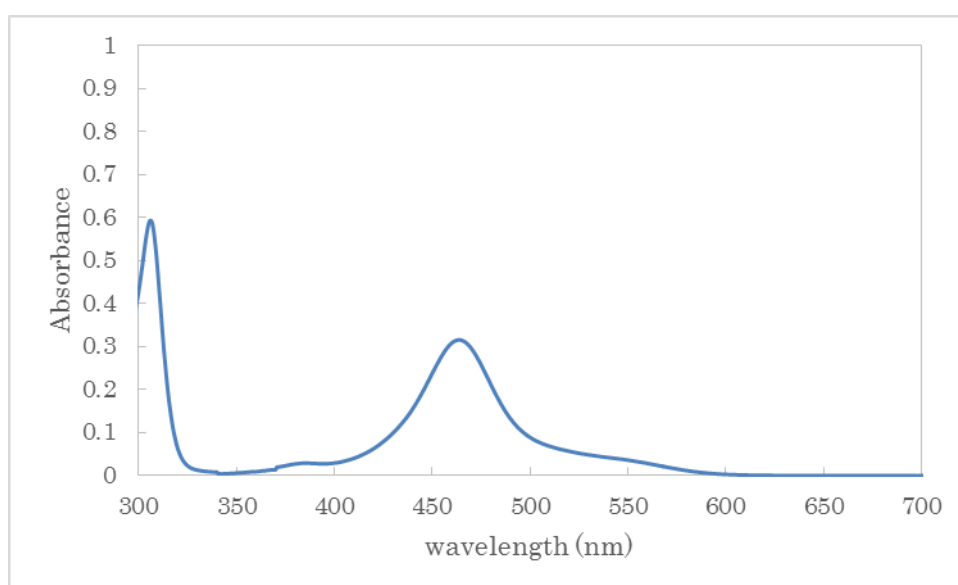
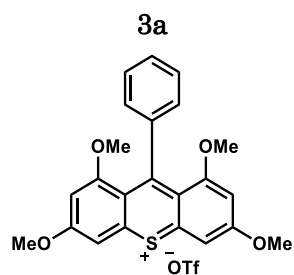
Imaginary Frequencies: 0

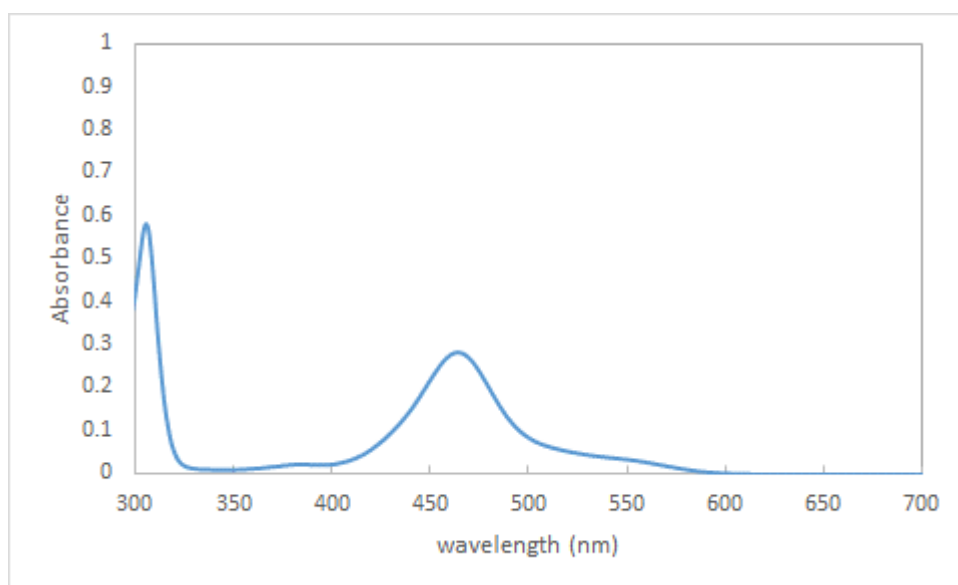
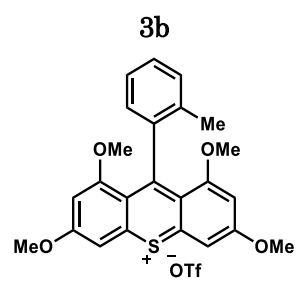
6. Reference

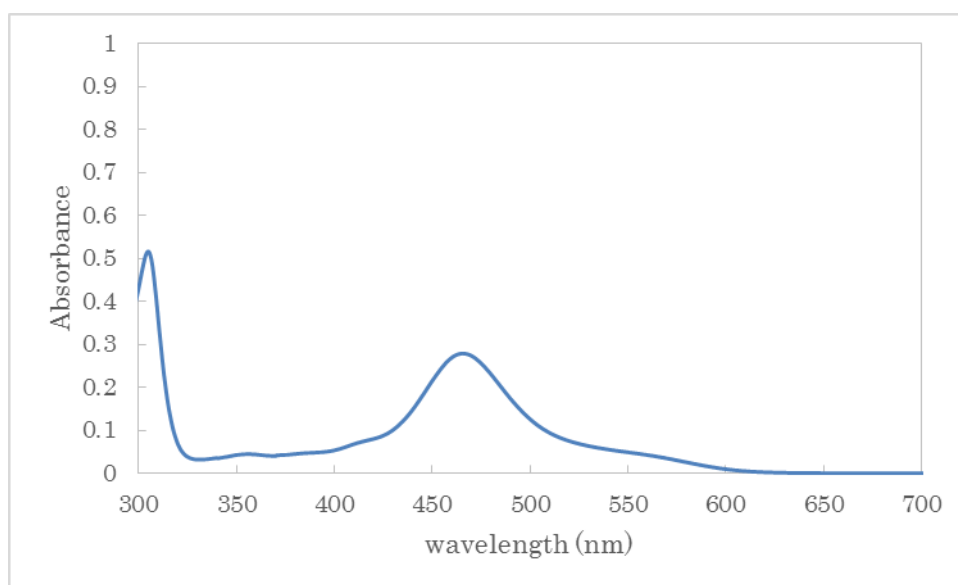
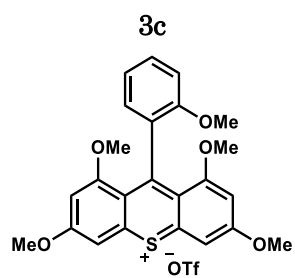
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7. For the ORCA program system; a) Neese, F.; *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, *2*, 73-78. b) Neese, F. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2017**, *8*, e1327.

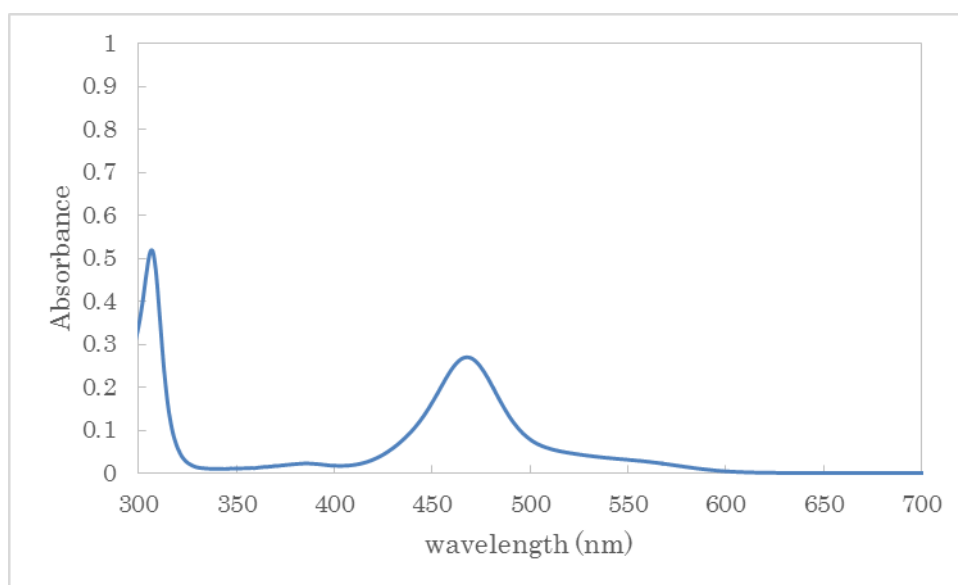
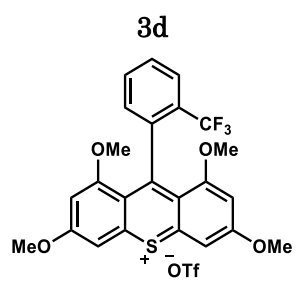
7. UV-vis spectrum of **3** and **4**

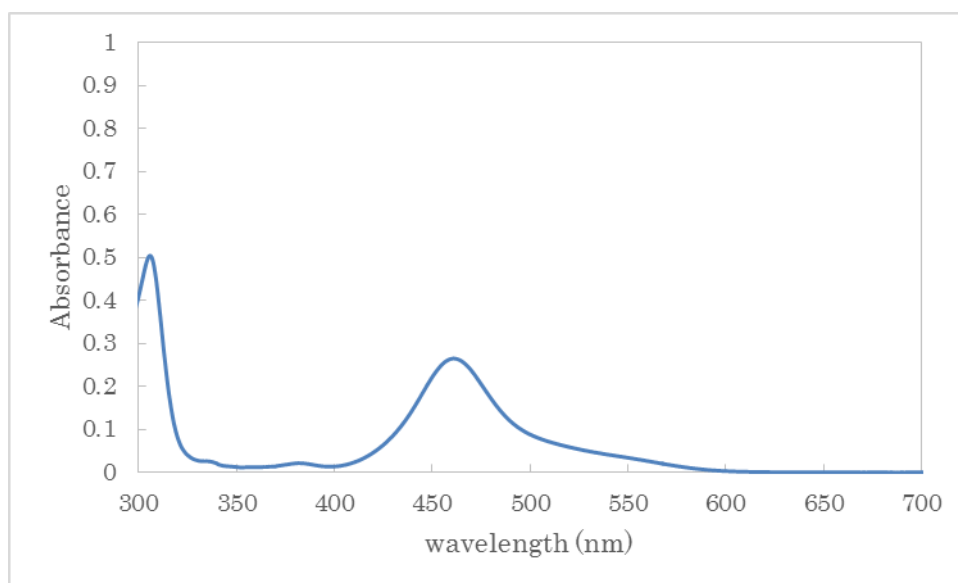
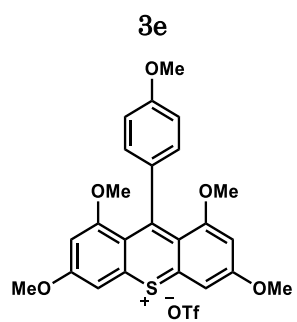
UV-vis spectra of **3** and **4** (0.1 mM) in CH₃CN.

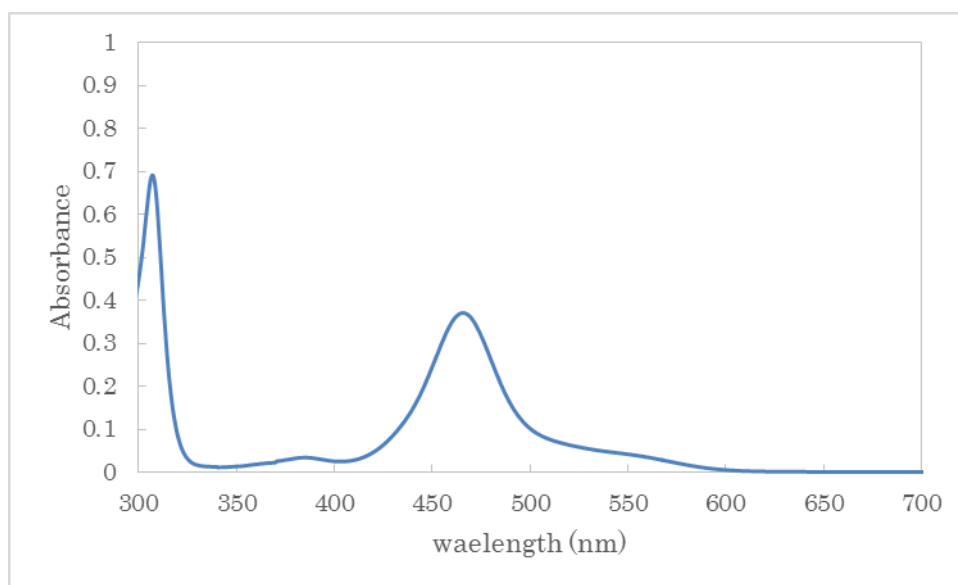
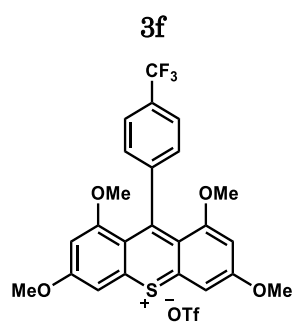


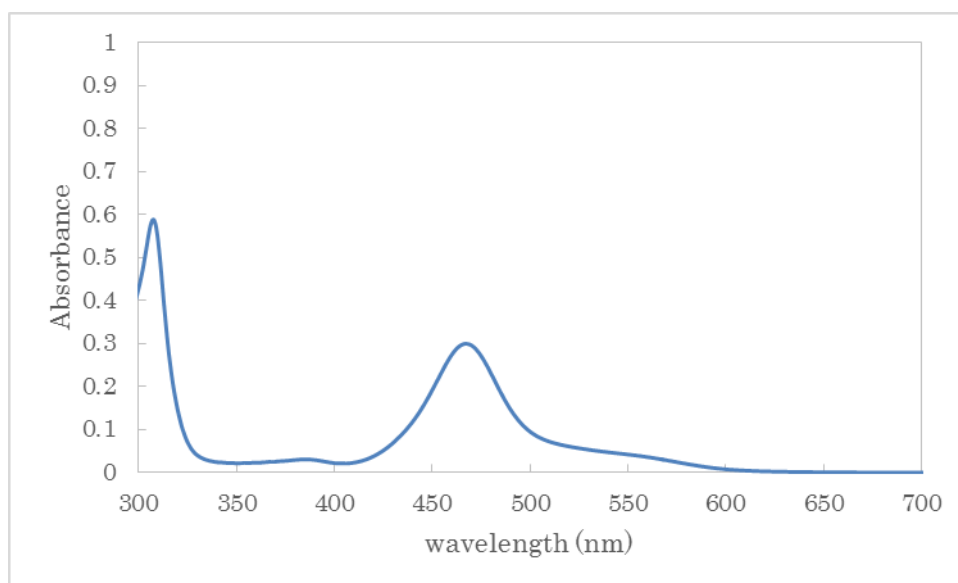
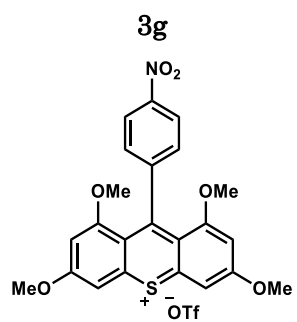


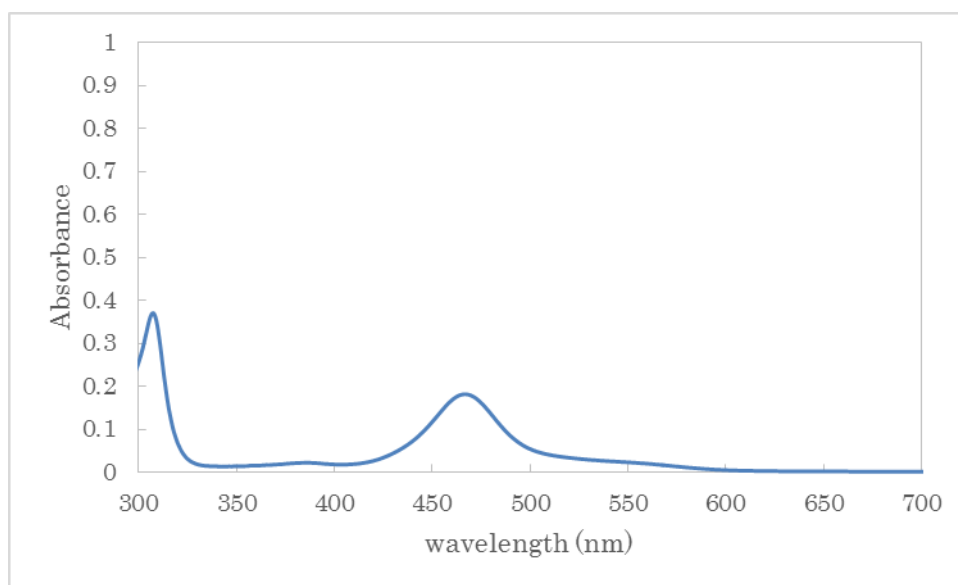
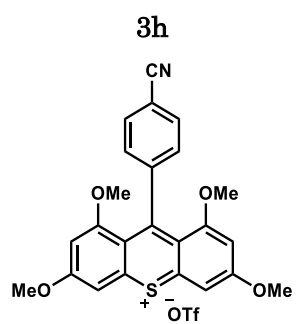


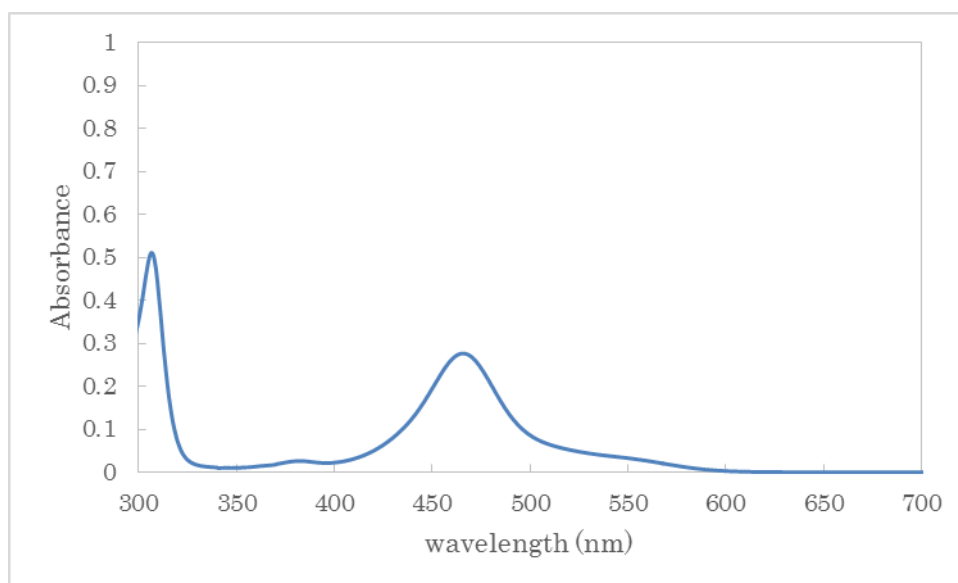
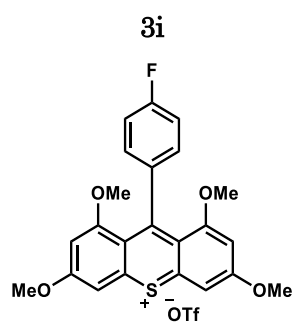


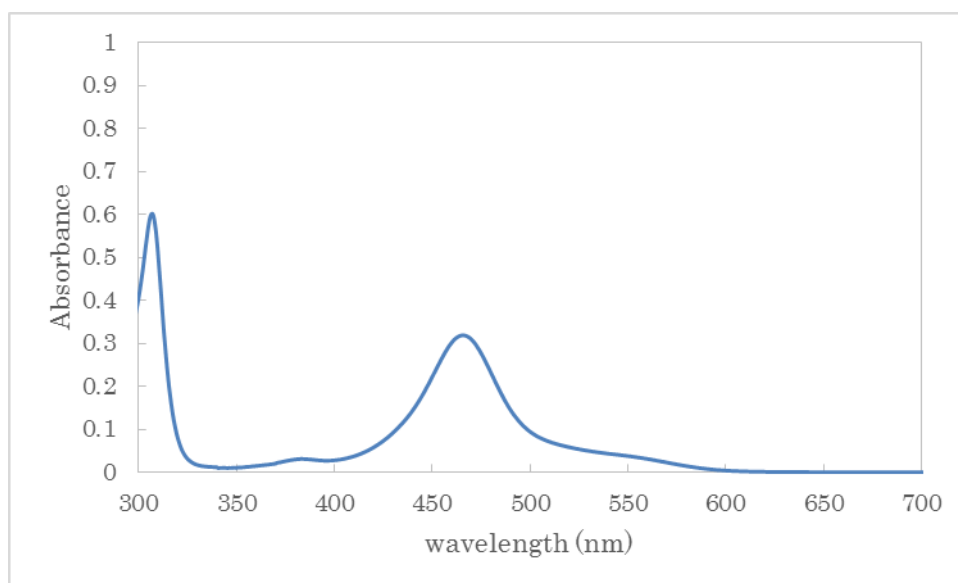
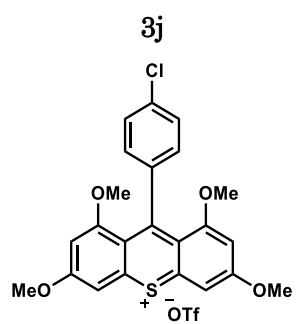


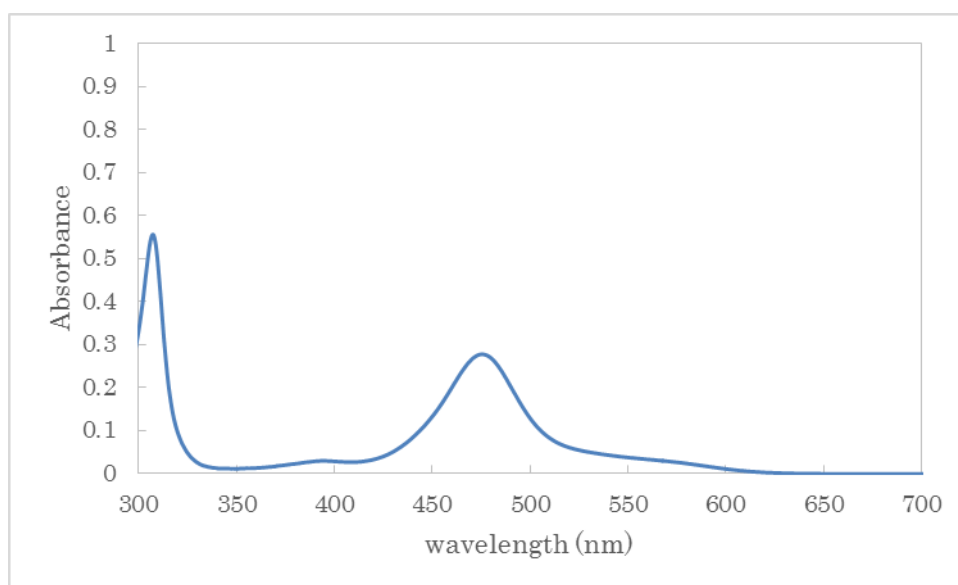
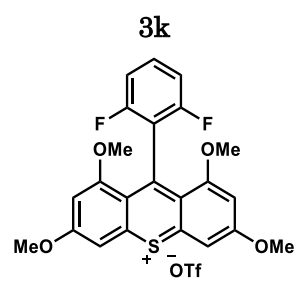


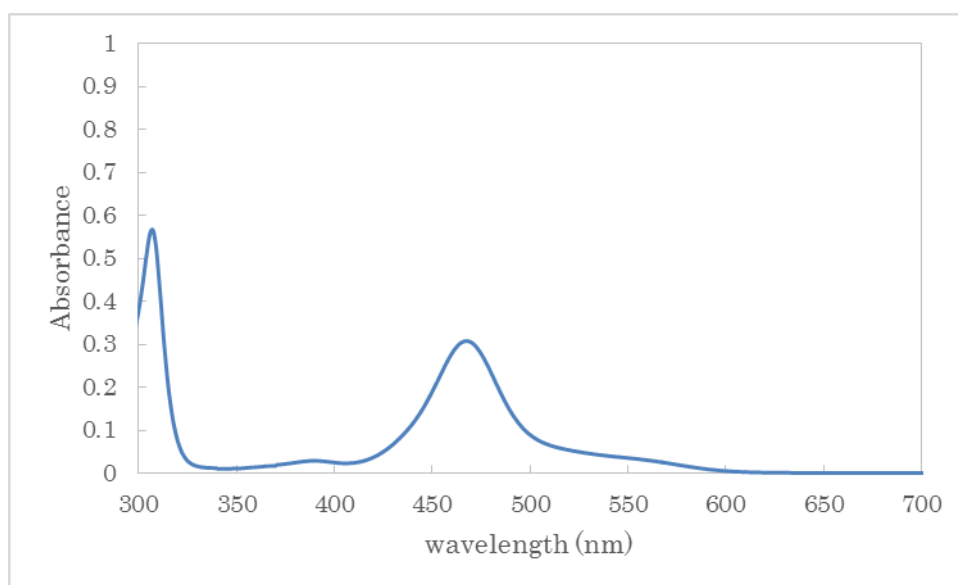
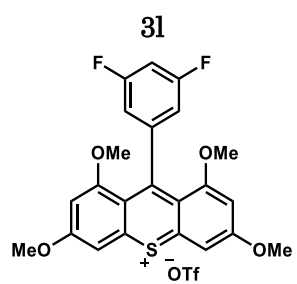


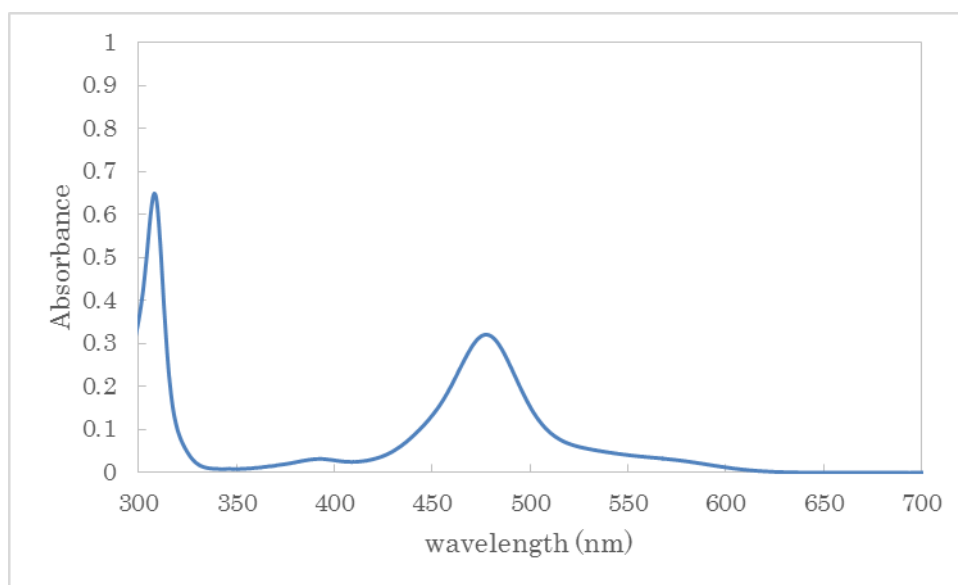
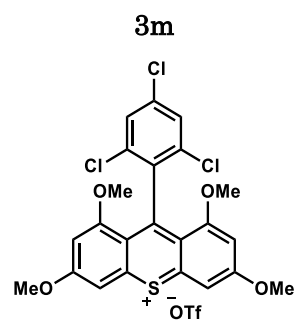


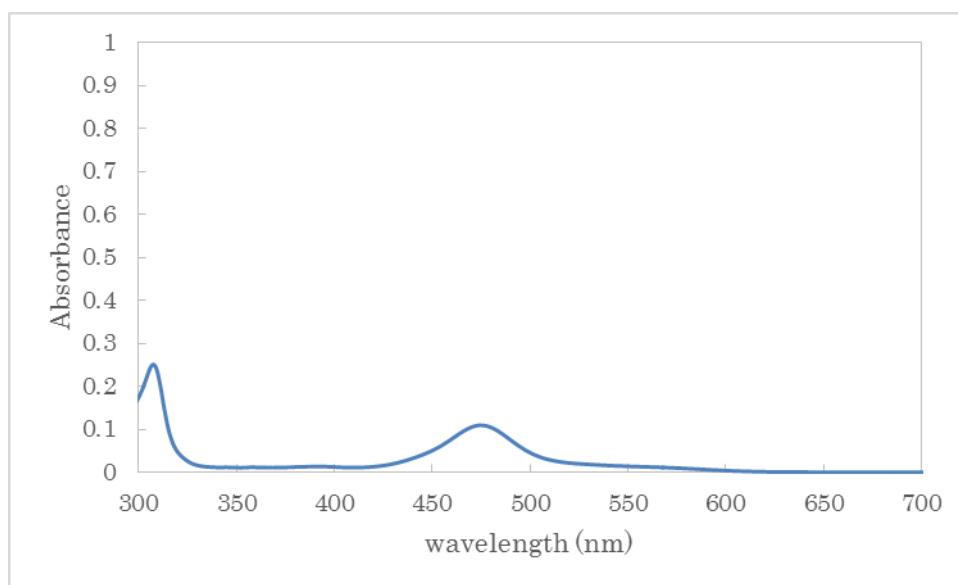
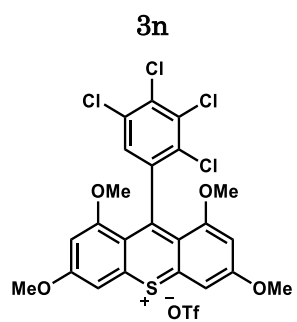


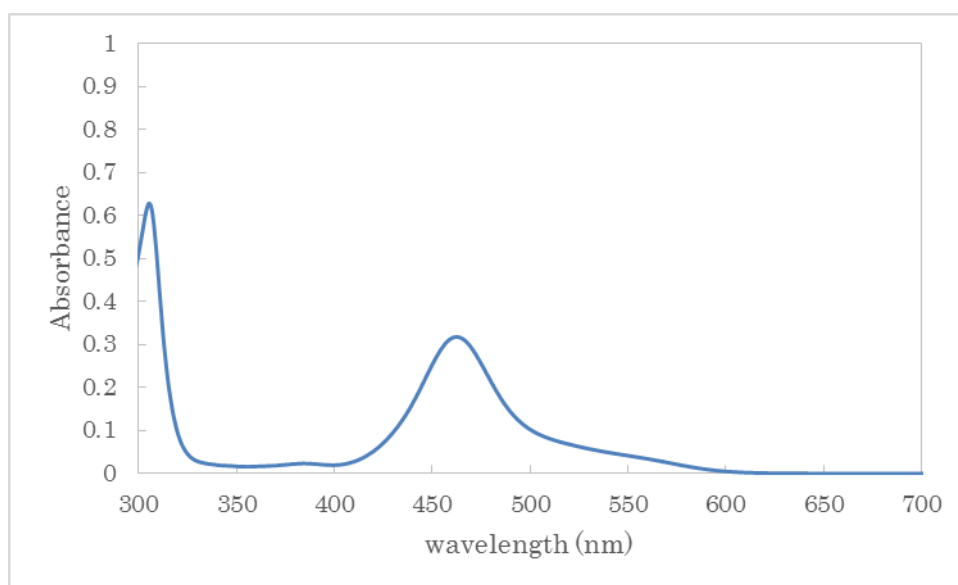
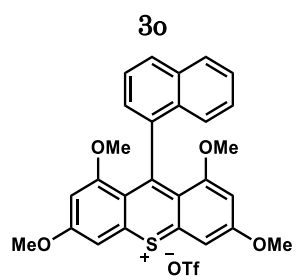


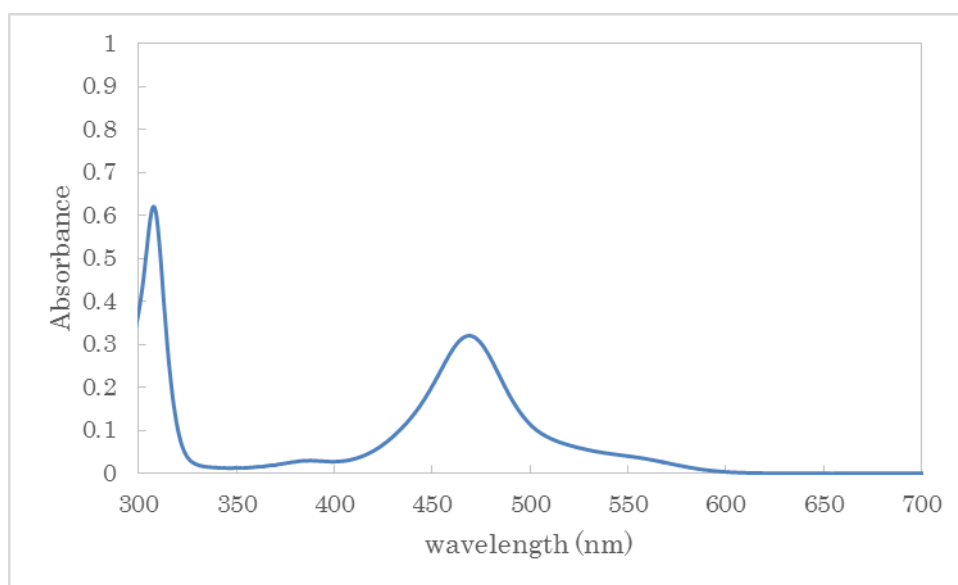
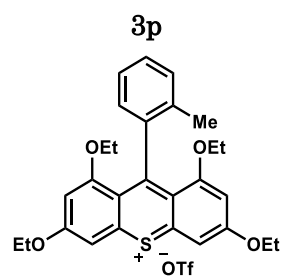


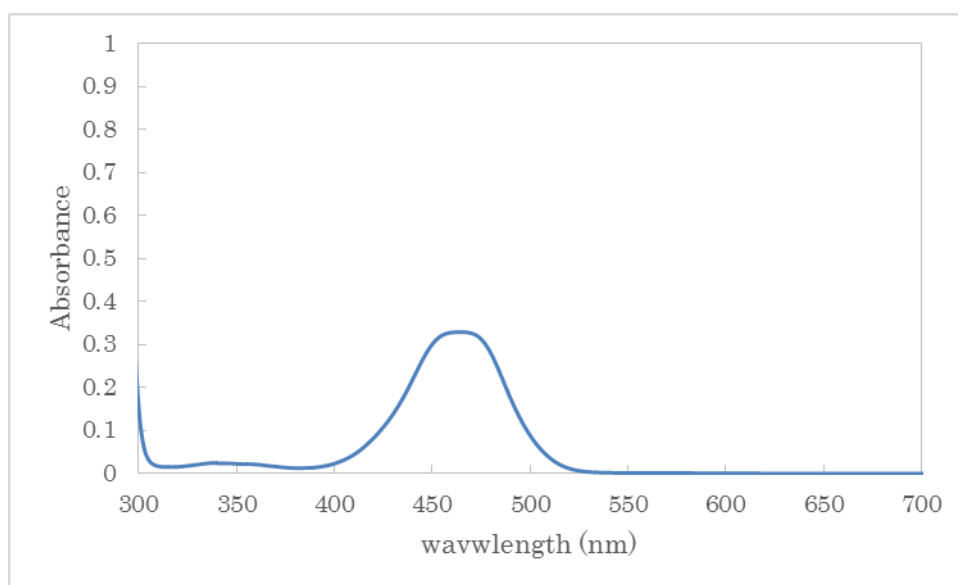
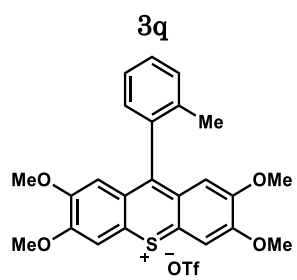


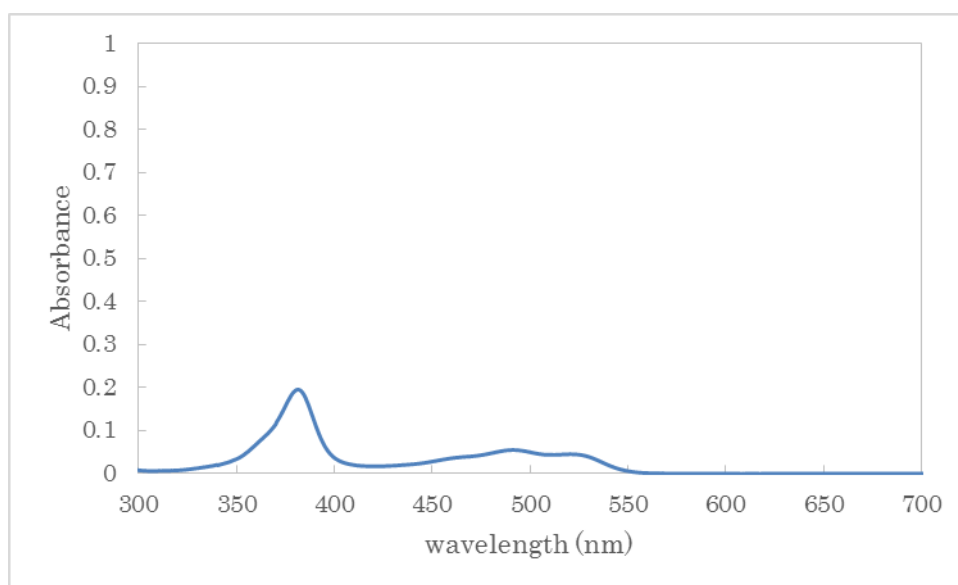
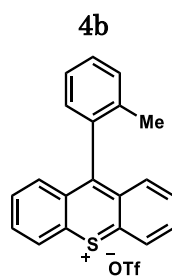






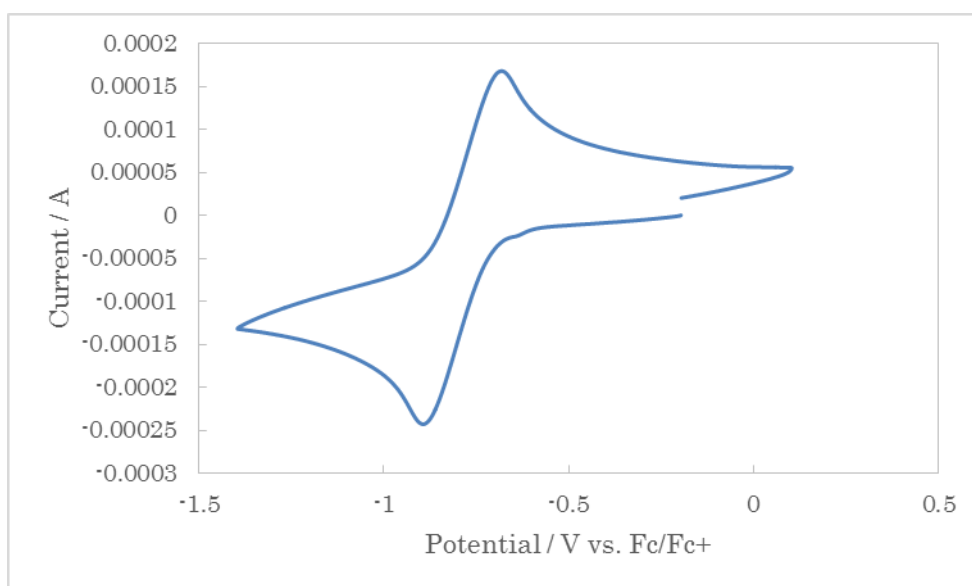
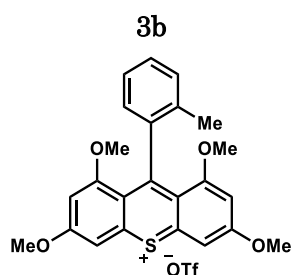




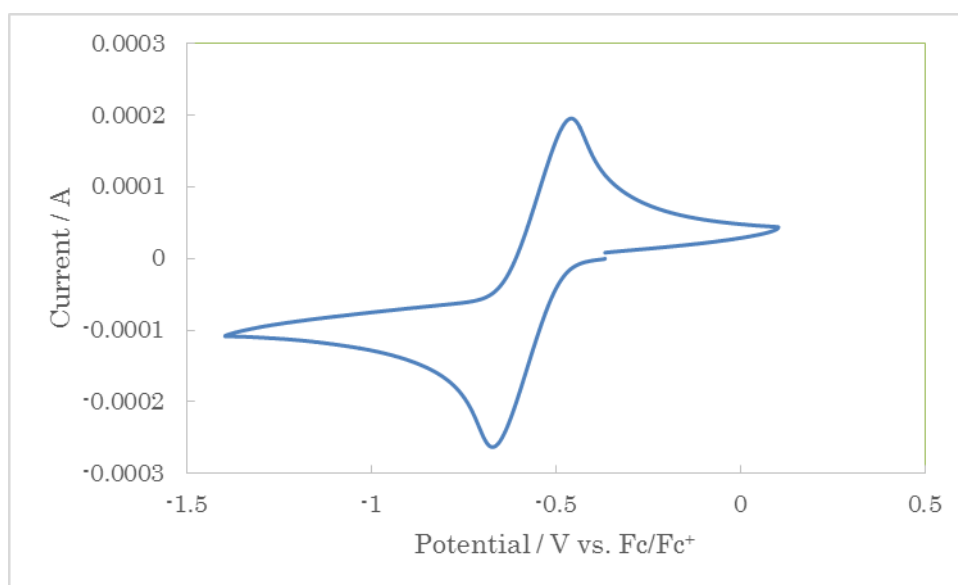
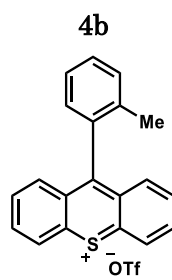


8. Cyclic voltammograms of 3 and 4

Samples for electrochemical measurements were prepared with 10 mL of a 0.01 M tetra-*n*-butylammonium tetrafluoroborate solution in dry CH₃CN and 0.01 mmol of thioxanthylum salt. Cyclic voltammetry measurements were carried out with a computer-controlled potentiostat Model 660C (ALS Co., Ltd.). Cyclic Voltammetry was recorded using an undivided cell equipped with a working electrode (Pt disk electrode, ϕ 3 mm), a counter electrode (Pt wire), and a reference electrode (Ag wire). The ferrocene / ferrocenium couple (Fc/Fc⁺) was also measured in the same electrochemical system, and the electrode potential was reported as values referred to the apparent standard potential of the system. A scan rate was used 1.0 V/s.



$$E'_0 = -0.79 \text{ V vs. Fc/Fc}^+$$



$$E_0' = -0.56 \text{ V vs. Fc/Fc}^+$$

9. ^1H NMR and ^{13}C NMR spectrum data

