Straightforward access to aryl-substituted tetrathiafulvalenes by palladium-catalyzed direct C–H arylation and their photophysical and electrochemical properties
Yukihiro Mitamura, Hideki Yorimitsu,* Koichiro Oshima* and Atsuhiro Osuka

Table of Contents
Instrumentation and Chemicals 1
Experimental Procedure 2
Characterization Data 3
NMR Spectra 7
X-ray Diffraction Analysis 57
DFT Calculations 60

Instrumentation and Chemicals
All reagents were of commercial reagent grade and were used without further purification unless otherwise noted. $^1$H and $^{13}$C NMR spectra were recorded on a JEOL delta-600 spectrometer, and chemical shifts were reported as the $\delta$ scale in ppm relative to an internal standard CDCl$_3$ ($\delta = 7.26$ ppm for $^1$H, 77.23 ppm for $^{13}$C). Spectroscopic grade solvents were used for all spectroscopic studies without further purification. UV/visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. UV/visible/NIR absorption spectra were recorded on a Shimadzu UV-3150 spectrometer. ESI-TOF-MS spectra were recorded on a Bruker Daltonics micro TOF LC instrument using a positive-ion mode. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Redox potentials were measured by the cyclic voltammetry method on an ALS electrochemical analyzer model 660, and the conditions were the following: 0.1 M Bu$_4$NPF$_6$ in benzonitrile, Ag/Ag$^+$ reference electrode, Pt working electrode, and Pt counter electrode, 50mVs$^{-1}$, Fe/Fe$^+$ (0.16 V referred to Ag/Ag$^+$). Preparative separations were performed by silica gel chromatography (Wako gel C-200) or gel permeation chromatography (GPC) (Bio-Rad Bio-Beads S-X1, packed with CHCl$_3$ in a 6 × 40 cm gravity column). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. Single-crystal diffraction analysis data for compound 1a were collected at –150 °C with a Rigaku RAXIS-RAPID diffraction by using graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by the direct method (SHELXS-97). DFT calculations were performed at the B3LYP/6-31G$^*$[1] level by using Gaussian 09 package.[2]

Experimental Procedure

Typical procedure for palladium-catalyzed monoarylation reactions (1a–c, 1i): Pd(OAc)$_2$ (2.3 mg, 0.01 mmol), PrBu$_3$HBF$_4$ (8.7 mg, 0.03 mmol), and Cs$_2$CO$_3$ (195.5 mg, 0.60 mmol) were placed in a 20-mL reaction flask under nitrogen. THF (0.5 mL) was added and the mixture was stirred for 10 min with heating. A solution of tetrathiafulvalene (102.2 mg, 0.50 mmol) and 4-bromotoluene (34.2 mg, 0.20 mmol) in THF (0.5 mL) was added. The mixture was heated at reflux for 3 h. The organic compounds were extracted with dichloromethane three times. The combined organic part was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by gel permeation chromatography with chloroform as an eluent to afford 2-(4-methylphenyl)tetrathiafulvalene (1a) as a yellow solid (30.0 mg, 0.10 mmol, 50%).

Synthesis of 1d–h, 1j, and 1k: Although the synthetic protocol is the same, purification was performed by silica gel column chromatography with a mixture of hexane/dichloromethane as an eluent, for instance, to yield 2-(4-methoxyphenyl)tetrathiafulvalene (1d) as a yellow solid (29.8 mg, 0.096 mmol, 48%).

Typical procedure for palladium-catalyzed tetraarylation reactions (2a–c, f–m): Pd(OAc)$_2$ (8.4 mg, 0.038 mmol), PrBu$_3$HBF$_4$ (32.6 mg, 0.11 mmol), and Cs$_2$CO$_3$ (244.4 mg, 0.75 mmol) were placed in a 20-mL reaction flask under nitrogen. THF (1.0 mL) was added and the mixture was stirred for 10 min with heating. A solution of tetrathiafulvalene (30.7 mg, 0.15 mmol) and 4-bromotoluene (128.3 mg, 0.75 mmol) in THF (1.0 mL) was added. The mixture was heated at reflux for 15 h. The organic compounds were extracted with chloroform three times. The combined organic part was washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuo. Chromatographic purification on silica gel by using hexane/dichloromethane (or chloroform) as an eluent afforded 2,3,6,7-tetra(4-methylphenyl)tetrathiafulvalene (2a) (84.3 mg, 0.15 mmol, 100%) as a red solid.

Purification of 2d, 2e, and 2n: Purification of 2,3,6,7-tetra(4-methoxyphenyl)tetrathiafulvalene (2d) and 2,3,6,7-tetrais(4-dimethylaminophenyl)tetrathiafulvalene (2e) were performed by reprecipitation from chloroform/methanol to provide orange solids in 78% (79.7 mg, 0.12 mmol) and 60% (56.6 mg, 0.09 mmol) yields, respectively. 2,3,6,7-Tetrakis(4-biphenylyl)tetrathiafulvalene (2n) was obtained from recrystallization from chloroform/methanol as red needles (109.8 mg, 0.14 mmol, 90%).
Characterization Data

2-(4-Methylphenyl)tetrathiafulvalene (1a): ¹H NMR (CDCl₃) δ = 2.35 (s, 3H), 6.33 (s, 2H), 6.43 (s, 1H), 7.16 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H); ¹³C NMR (CDCl₃) δ = 114.41, 112.57, 119.27, 126.36, 129.67, 129.94, 136.33, 138.68; HR-ESI TOF-MS: Observed (m/z) = 293.9659 (Δ = –0.34 ppm). Calcd for C₁₃H₁₀S₄ = 293.9660[M]; CV (in benzonitrile) E₁ = –0.08 V, E₂ = 0.37 V (vs. Fe/Fe⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 277(16100) and 397(3100).

2-(2-Naphthyl)tetrathiafulvalene (1b): ¹H NMR (CDCl₃): δ = 6.35 (s, 2H), 6.62 (s, 1H), 7.47–7.52 (m, 2H), 7.55 (dd, J = 8.5, 1.4 Hz, 1H), 7.77 (s, 1H), 7.80–7.84 (m, 3H); ¹³C NMR (CDCl₃): δ = 109.27, 112.04, 114.29, 119.27, 119.31, 123.62, 126.02, 126.78, 127.02, 127.88, 128.37, 128.69, 129.90, 133.16, 133.53, 136.39; HR-ESI TOF-MS: Observed (m/z) = 329.9662 (Δ = 0.61 ppm). Calcd for C₁₃H₁₀S₄ = 329.9660[M]; CV (in benzonitrile) E₁ = –0.07 V, E₂ = 0.38 V (vs. Fe/Fe⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 297(42500) and 415(7500).

2-(4-Fluorophenyl)tetrathiafulvalene (1c): ¹H NMR (CDCl₃): δ = 2.35 ppm). Calcd for C₁₂H₇FS₄ = 297.9409[M]; CV (in benzonitrile) E₁ = –0.10 V, E₂ = 0.35 V (vs. Fe/Fe⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 283(22900) and 395(1600).

2-(4-Methoxyphenyl)tetrathiafulvalene (1d): ¹H NMR (CDCl₃): δ = 3.82 (s, 3H), 6.33 (s, 2H), 6.35 (s, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H); ¹³C NMR (CDCl₃): δ = 55.59, 109.77, 111.39, 111.41, 111.50, 114.41, 119.26, 125.56, 127.85, 135.98, 159.95; HR-ESI TOF-MS: Observed (m/z) = 309.9606 (Δ = –0.97 ppm). Calcd for C₁₃H₁₀OS₄ = 309.9609[M]; CV (in benzonitrile) E₁ = –0.03 V, E₂ = 0.40 V (vs. Fe/Fe⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 283(22900) and 395(4000).

2-(4-Dimethylaminophenyl)tetrathiafulvalene (1e): ¹H NMR (CDCl₃): δ = 2.98 (s, 6H), 6.25 (s, 1H), 6.32 (s, 2H), 6.66 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H); ¹³C NMR (CDCl₃): δ = 40.52, 109.03, 110.44, 110.45, 110.62, 112.26, 119.26, 120.99, 127.57, 136.76, 150.59; HR-ESI TOF-MS: Observed (m/z) = 322.9922 (Δ = –0.93 ppm). Calcd for C₁₃H₁₂NS₄ = 322.9925[M]; CV (in benzonitrile) E₁ = –0.14 V, E₂ = 0.28 V (vs. Fe/Fe⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 318(28800) and 386(5400).

2-(4-Ethoxycarbonylphenyl)tetrathiafulvalene (1f): ¹H NMR (CDCl₃): δ = 1.40 (t, J = 6.8 Hz, 3H), 4.38 (q, J = 6.8 Hz, 2H), 6.35 (s, 2H), 6.67 (s, 1H), 7.45 (dt J = 8.7, 1.8 Hz, 2H), 8.02 (dt, J = 8.7, 1.8 Hz, 2H); ¹³C NMR (CDCl₃): δ = 14.53, 61.33, 108.40, 112.74, 116.40, 119.24, 119.30, 126.12, 130.18, 130.30, 135.34, 136.52, 166.11; HR-ESI TOF-MS: Observed (m/z) = 351.9706 (Δ = –2.56 ppm). Calcd for C₁₄H₁₂O₂S₄ = 351.9720[M]; CV (in benzonitrile) E₁ = –0.04 V, E₂ = 0.40 V (vs. Fe/Fe⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 296(23700) and 443(3460).

2-(4-Nitrophenyl)tetrathiafulvalene (1g): ¹H NMR (CDCl₃) δ = 6.36 (s, 2H), 6.79 (s, 1H), 7.53 (d, J = 8.7 Hz, 2H), 8.22 (d, J = 8.7 Hz, 2H); ¹³C NMR (CDCl₃): δ = 107.24, 114.21, 118.99, 119.29, 119.33, 124.51, 126.84, 134.14, 138.40, 147.23; HR-ESI TOF-MS: Observed (m/z) = 324.9361 (Δ = 2.20 ppm). Calcd for C₁₃H₁₂NO₂S₄ = 324.9354[M]; CV (in benzonitrile) E₁ = –0.01 V, E₂ = 0.42 V (vs. Fe/Fe⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 324(31400) and 522(4700).

2-(3-Methoxyphenyl)tetrathiafulvalene (1h): ¹H NMR (CDCl₃): δ = 4.83 (s, 3H), 6.34 (s, 2H),
Electronic Supplementary Material (ESI) for Chemical Science

1H NMR (CDCl3): δ = 6.35 (s, 2H), 6.62 (s, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 2H), 7.65 (s, 1H); 13C NMR (CDCl3) δ = 108.31, 113.07, 115.87, 119.25, 119.31, 123.13 (q, J_{C-F} = 2.9 Hz), 124.00 (q, J_{C-F} = 2.9 Hz), 125.14 (d, J_{C-F} = 2.9 Hz), 129.63 (two signals merge), 133.50, 134.75; HR-ESI TOF-MS: Observed (m/z) = 347.9375 (Δ = –0.57 ppm). Calcd for C_{13}H_{7}F_{3}S_{4} = 347.9377[M]; CV (in benzonitrile) E_{1} = –0.04 V, E_{2} = 0.40 V (vs Fc/Fc'); UV-Vis (in CHCl3) λ[nm] (ε [M^{-1} cm^{-1}]) 283(20000) and 414(3200).

2-(4-Cyanophenyl)tetraethiafulvalene (1k): 1H NMR (CDCl3): δ = 2.60 (s, 3H), 6.35 (s, 2H), 6.70 (s, 1H), 7.48 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.3 Hz, 2H); 13C NMR (CDCl3): δ = 108.46, 111.78, 113.85, 118.00, 118.63, 119.29, 119.31, 123.66, 123.77, 131.47, 139.46, 136.63; HR-ESI TOF-MS: Observed (m/z) = 304.9460 (Δ = –1.31 ppm). Calcd for C_{13}H_{7}CF_{4}S_{4} = 304.9456[M]; CV (in benzonitrile) E_{1} = –0.02 V, E_{2} = 0.42 V (vs Fc/Fc'); UV-Vis (in CHCl3) λ[nm] (ε [M^{-1} cm^{-1}]) 297(18500) and 455(3000).

2,3,6,7-Tetra(4-methylphenyl)tetraethiafulvalene (2a): 1H NMR (CDCl3): δ = 2.30 (s, 12H), 7.03 (d, J = 7.8 Hz, 8H), 7.11 (d, J = 7.8 Hz, 8H); 13C NMR (CDCl3): δ = 21.50, 108.33, 128.70, 129.19, 129.46, 130.15, 138.38; HR-ESI TOF-MS: Observed (m/z) = 564.1053 (Δ = –2.66 ppm). Calcd for C_{36}H_{28}S_{4} = 564.1068[M]; CV (in benzonitrile) E_{1} = –0.08 V, E_{2} = 0.37 V (vs Fc/Fc'); UV-Vis (in CHCl3) λ[nm] (ε [M^{-1} cm^{-1}]) 277(26300) and 399(4700).

2,3,6,7-Tetra(2-naphthyl)tetraethiafulvalene (2b): 1H NMR (CDCl3): δ = 7.23 (d, J = 1.9 Hz, 2H), 7.24 (d, J = 1.9 Hz, 2H), 7.44–7.49 (m, 8H), 7.61 (d, J = 8.7 Hz, 4H), 7.71–7.76 (m, 8H), 7.89 (s, 4H); 13C NMR (CDCl3): δ = 108.77, 126.73, 126.82, 126.92, 127.90, 128.37, 128.42, 128.88, 129.62, 130.48, 133.18, 133.44; HR-ESI TOF-MS: Observed (m/z) = 708.1050 (Δ = –2.54 ppm). Calcd for C_{36}H_{28}S_{4} = 708.1068[M]; CV (in benzonitrile) E_{1} = –0.02 V, E_{2} = 0.40 V (vs Fc/Fc'). It was impossible to determine λ and ε because the maximum absorption were not observed within the range of 250 to 900 nm.

2,3,6,7-Tetra(4-fluorophenyl)tetraethiafulvalene (2c): 1H NMR (CDCl3): δ = 6.94 (t, J = 8.2, 2.6 Hz, 8H), 7.16–7.19 (m, 8H); 13C NMR (CDCl3): δ = 108.47, 116.09 (d, J_{C-F} = 21.6 Hz), 128.36, 128.62 (d, J_{C-F} = 2.9 Hz), 131.20 (d, J_{C-F} = 8.6 Hz), 162.71 (d, J_{C-F} = 247.0 Hz); HR-ESI TOF-MS: Observed (m/z) = 580.0050 (Δ = –2.59 ppm). Calcd for C_{30}H_{16}F_{4}S_{4} = 580.0065[M]; CV (in benzonitrile) E_{1} = 0.01 V, E_{2} = 0.43 V (vs Fc/Fc'); UV-Vis (in CHCl3) λ[nm] (ε [M^{-1} cm^{-1}]) 303(30100) and 402(4000).

2,3,6,7-Tetra(4-methoxyphenyl)tetraethiafulvalene (2d): 1H NMR (CDCl3): δ = 3.77 (s, 12H), 6.75 (dt, J = 8.7, 2.3 Hz, 8H), 7.15 (dt, J = 8.7, 2.3 Hz, 8H); 13C NMR (CDCl3): δ = 55.45, 108.19, 114.19, 125.45, 127.85, 130.63, 159.57; HR-ESI TOF-MS: Observed (m/z) = 628.0851 (Δ = –2.23
ppm). Calcd for C_{38}H_{40}N_{4}S_{4} = 680.2130; UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 262(37500) and 390(5500).

2,3,6,7-Tetakis(4-dimethylaminophenyl)tetrathiafulvalene (2e): ^1^H NMR (CDCl₃): δ = 2.93 (s, 24H), 6.55 (d, J = 8.3 Hz, 8H), 7.11 (d, J = 8.3 Hz, 8H); ^1^C NMR (CDCl₃): δ = 40.49, 112.12, 112.30, 114.33, 127.01, 130.19, 149.98; HR-ESI TOF-MS: Observed (m/z) = 680.2109 (Δ = −3.09 ppm). Calcd for C_{38}H_{40}N_{4}S_{4} = 680.2130[M]; CV (in benzonitrile) E₁ = −0.24 V, E₂ = 0.15 V (vs Fc/Fc⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 314(80100).

2,3,6,7-Tetra(4-ethoxycarbonylphenyl)tetrathiafulvalene (2f): ^1^H NMR (CDCl₃): δ = 1.37 (t, J = 7.1 Hz, 12H), 4.36 (q, J = 7.1 Hz, 8H), 7.25–7.27 (m, 8H), 7.91 (dt, J = 8.7, 1.8 Hz, 8H); ^1^C NMR (CDCl₃): δ = 14.51, 61.42, 108.92, 129.27, 130.06, 130.19, 130.80, 136.82, 166.02; Elemental Analysis: Found: C, 62.99; H, 4.38%. Calcd for C_{34}H_{28}O_{4}S_{4}: C, 52.31; H, 2.07% ; CV (in benzonitrile) E₁ = 0.07 V, E₂ = 0.48 V (vs Fc/Fc⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 307(51600) and 443(4400).

2,3,6,7-Tetra(4-nitrophenyl)tetrathiafulvalene (2g): ^1^H NMR (CDCl₃): δ = 7.38 (d, J = 7.8 Hz, 8H), 8.15 (d, J = 7.8 Hz, 8H); ^1^C NMR (CDCl₃): δ = 109.18, 124.58, 130.22, 130.29, 138.19, 148.06; HR-ESI TOF-MS: Observed (m/z) = 687.9829 (Δ = −2.33 ppm). Calcd for C_{38}H_{16}N_{4}O_{8}S_{4} = 687.9845[M]; CV (in benzonitrile) E₁ = 0.17 V, E₂ = 0.54 V (vs Fc/Fc⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 318(53000) and 499(5800).

2,3,6,7-Tetakis(4-trifluoromethylphenyl)tetrathiafulvalene (2h): ^1^H NMR (CDCl₃): δ = 7.32 (d, J = 8.2 Hz, 8H), 7.53 (d, J = 8.2 Hz, 8H); ^1^C NMR (CDCl₃): δ = 108.91, 123.86 (q, J_C,F = 270.0 Hz), 126.13 (d, J_C,F = 2.9 Hz), 129.67, 131.07 (q, J_C,F = 31.6 Hz), 135.81; Elemental Analysis: Found: C, 52.04; H, 2.11%. Calcd for C_{38}H_{16}F_{12}S_{4}: C, 52.31; H, 2.07%; CV (in benzonitrile) E₁ = 0.10 V, E₂ = 0.50 V (vs Fc/Fc⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 297(25200) and 429(2600).

2,3,6,7-Tetakis(3-trifluoromethylphenyl)tetrathiafulvalene (2i): ^1^H NMR (CDCl₃): δ = 7.36–7.41 (m, 8H), 7.45 (s, 4H), 7.54 (d, J = 7.4 Hz, 4H); ^1^C NMR (CDCl₃): δ = 108.88, 123.71 (q, J_C,F = 271.4 Hz), 125.79 (q, J_C,F = 4.3 Hz), 126.16 (q, J_C,F = 4.3 Hz), 129.42, 129.69, 131.64 (q, J_C,F = 31.6 Hz), 132.53, 133.00; Elemental Analysis: Found: C, 52.32; H, 2.32%. Calcd for C_{38}H_{16}F_{12}S_{4}: C, 52.31; H, 2.07%; CV (in benzonitrile) E₁ = 0.11 V, E₂ = 0.50 V (vs Fc/Fc⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 288(17000) and 420(2800).

2,3,6,7-Tetra(3-methoxyphenyl)tetrathiafulvalene (2j): ^1^H NMR (CDCl₃): δ = 3.65 (s, 12H), 6.75–6.77 (m, 4H), 6.79 (dm, J = 8.7 Hz, 4H), 6.83 (dm, J = 6.8 Hz, 4H), 7.14 (t, J = 7.8 Hz, 4H); ^1^C NMR (CDCl₃): δ = 55.39, 108.55, 114.35, 114.88, 121.80, 129.25, 129.84, 134.10, 159.74; HR-ESI TOF-MS: Observed (m/z) = 628.0854 (Δ = −1.75 ppm). Calcd for C_{38}H_{20}O_{8}S_{4} = 628.0865[M]; CV (in benzonitrile) E₁ = −0.03 V, E₂ = 0.40 V (vs Fc/Fc⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 296(24300) and 409(3600).

2,3,6,7-Tetra(3,5-dimethoxyphenyl)tetrathiafulvalene (2k): ^1^H NMR (CDCl₃): δ = 3.65 (s, 24H), 6.34 (t, J = 2.3 Hz, 4H), 6.41 (d, J = 2.3 Hz, 8H); ^1^C NMR (CDCl₃): δ = 55.57, 101.33, 107.27, 108.57, 129.31, 134.53, 160.90; HR-ESI TOF-MS: Observed (m/z) = 748.1271 (Δ = −2.27 ppm). Calcd for C_{38}H_{36}O_{8}S_{4} = 748.1288[M]; CV (in benzonitrile) E₁ = −0.04 V, E₂ = 0.39 V (vs Fc/Fc⁺); UV-Vis (in CHCl₃) λ[nm] (ε [M⁻¹ cm⁻¹]) 294(26600) and 404(3800).

2,3,6,7-Tetra(4-cyanophenyl)tetrathiafulvalene (2l): ^1^H NMR (CDCl₃): δ = 7.29 (d, J = 8.3 Hz, 8H), 7.57 (d, J = 8.3 Hz, 8H); ^1^C NMR (CDCl₃): δ = 108.99, 113.12, 118.08, 129.90, 130.10,
132.96, 136.44; HR-ESI TOF-MS: Observed \((m/z) = 608.0254\) (\(\Delta = 0.33\) ppm). Calcd for \(C_{34}H_{16}N_4S_4 = 608.0252M\); CV (in benzonitrile) \(E_1 = 0.15\ V, E_2 = 0.52\ V\) (vs \(Fc/Fc^+\)); UV-Vis (in \(CHCl_3\) \(\lambda[\text{nm}] \) (\(\varepsilon [M^{-1} \text{ cm}^{-1}]\)) 257(49500) and 429(2600).

2,3,6,7-Tetra(3-pyridyl)tetrathiafulvalene (2m): \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.22\) (dd, \(J = 7.8, 5.0\) Hz, 4H), 7.54 (dt, \(J = 7.8, 2.3\) Hz, 4H), 8.46 (dm, \(J = 2.3\) Hz, 4H), 8.52 (broad d, \(J = 5.0\) Hz, 4H); \(^1^3\)C NMR (CDCl\(_3\)): \(\delta = 109.18, 123.78, 127.97, 128.48, 136.59, 149.97, 150.09\); HR-ESI TOF-MS: Observed \((m/z) = 512.0240\) (\(\Delta = 2.34\) ppm). Calcd for \(C_{26}H_{16}N_4S_4 = 512.0252M\); CV (in benzonitrile) \(E_1 = 0.11\ V, E_2 = 0.50\ V\) (vs \(Fc/Fc^+\)); UV-Vis (in \(CHCl_3\) \(\lambda[\text{nm}] \) (\(\varepsilon [M^{-1} \text{ cm}^{-1}]\)) 265(28900) and 415(4200).

2,3,6,7-Tetrakis(4-biphenylyl)tetrathiafulvalene (2n): \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.33–7.36\) (m, 12H), 7.41–7.44 (m, 8H), 7.49–7.51 (m, 8H), 7.56–7.59 (m, 8H); \(^1^3\)C NMR (CDCl\(_3\)): \(\delta = 108.62, 127.19, 127.48, 127.85, 129.06, 129.15, 129.79, 131.91, 140.39, 141.32\); HR-ESI TOF-MS: Observed \((m/z) = 812.1685\) (\(\Delta = 1.11\) ppm). Calcd for \(C_{54}H_{36}S_4 = 812.1694M\); CV (in benzonitrile) \(E_1 = -0.03\ V, E_2 = 0.40\ V\) (vs \(Fc/Fc^+\)); UV-Vis (in \(CHCl_3\) \(\lambda[\text{nm}] \) (\(\varepsilon [M^{-1} \text{ cm}^{-1}]\)) 276(70400) and 402(5900).
NMR Spectra

Figure S1-1. $^1$H NMR Spectrum of 1a
Figure S1-2. $^{13}$C NMR Spectrum of 1a
Figure S2-1. $^1$H NMR Spectrum of 1b
Figure S2-2. $^{13}$C NMR Spectrum of 1b
Figure S3-1. $^1$H NMR Spectrum of 1c
Figure S3-2. $^{13}$C NMR Spectrum of 1c
Figure S4-1. $^1$H NMR Spectrum of 1d
Figure S4-2. $^{13}$C NMR Spectrum of 1d
Figure S5-1. $^1$H NMR Spectrum of 1e

![1H NMR Spectrum of 1e](image)
Figure S5-2. $^{13}$C NMR Spectrum of 1e
Figure S6-1. $^1$H NMR Spectrum of 1f
Figure S6-2. $^{13}$C NMR Spectrum of 1f
Figure S7-1. $^1$H NMR Spectrum of 1g
Figure S7-2. $^{13}$C NMR Spectrum of 1g
Figure S8-1. $^1$H NMR Spectrum of 1h
Figure S8-2. $^{13}$C NMR Spectrum of 1h
Figure S9-1. $^{1}$H NMR Spectrum of 1i
Figure S9-2. $^{13}$C NMR Spectrum of 1i
Figure S10-1. $^1$H NMR Spectrum of 1j
Figure S10-2. $^{13}$C NMR Spectrum of 1j
Figure S11-1. $^1$H NMR Spectrum of 1k
Figure S11-2. $^{13}$C NMR Spectrum of 1k
Figure S12-1. $^1$H NMR Spectrum of 2a
Figure S12-2. $^{13}$C NMR Spectrum of 2a
Figure S13-1. $^1$H NMR Spectrum of 2b
Figure S13-2. $^{13}$C NMR Spectrum of 2b
Figure S14-1. $^1$H NMR Spectrum of 2c
Figure S14-2. $^{13}$C NMR Spectrum of 2c
Figure S15-1. $^1$H NMR Spectrum of 2d
Figure S15-2. $^{13}$C NMR Spectrum of 2d
Figure S16-1. $^1$H NMR Spectrum of 2e
Figure S16-2. $^{13}$C NMR Spectrum of 2e
Figure S17-1. $^1$H NMR Spectrum of 2f
Figure S17-2. $^{13}$C NMR Spectrum of $2f$

![NMR Spectrum Image]
Figure S18-1. $^1$H NMR Spectrum of 2g
Figure S18.1. $^{13}$C NMR Spectrum of 2g
Figure S19-1. $^1$H NMR Spectrum of 2h
Figure S19-2. $^{13}$C NMR Spectrum of 2h
Figure S20-1. $^1$H NMR Spectrum of 2i
Figure S20-2. $^{13}$C NMR Spectrum of 2i
Figure S21-1. $^1$H NMR Spectrum of 2j
Figure S21-2. $^{13}$C NMR Spectrum of 2j
Figure S22-1. $^1$H NMR Spectrum of 2k
Figure S22-2. $^{13}$C NMR Spectrum of 2k
Figure S23-1. $^1$H NMR Spectrum of 2I
Figure S23-2. $^{13}$C NMR Spectrum of 2l
Figure S24-1. $^1$H NMR Spectrum of 2m
Figure S24-2. $^{13}$C NMR Spectrum of 2m
Figure S25-1. $^1$H NMR Spectrum of 2n
**Figure S25-2.** $^{13}$C NMR Spectrum of 2n
**X-ray Diffraction Analysis**

**Crystallographic Data for 2a:** $C_{34}H_{28}S_4$, $M_w = 564.85$, triclinic, $P-1$, $a = 9.217(5)$ Å, $b = 11.524(4)$ Å, $c = 15.597(6)$ Å, $\alpha = 100.750(14)$°, $\beta = 105.128(17)$°, $\gamma = 110.659(17)$°, $V = 1423.6(10)$ Å$^3$, $T = 123$ K, $Z = 2$, $R_1 = 0.0342$, $wR_2 = 0.0948$, GOF = 1.007. CCDC No.: 818657.

**Figure S26.** Selected Bond Lengths of 2a

![Selected Bond Lengths of 2a](image)

**Figure S27.** Selected Bond Angles of 2a

![Selected Bond Angles of 2a](image)
**Figure S28.** Dihedral Angles between TTF Moiety with Aryl Ring (Angles $\alpha_i (i = 1, 2, 3, 4)$ are defined by the dihedral angle between the plane of $S_jC_kC_m$ and the mean plane of 4-methylphenyl ring)

<table>
<thead>
<tr>
<th>$j$</th>
<th>$k$</th>
<th>$m$</th>
<th>$\alpha_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>4</td>
<td>38.8</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>3</td>
<td>42.8</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>6</td>
<td>36.3</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>5</td>
<td>49.7</td>
</tr>
</tbody>
</table>

**Figure S29.** Packing Structure of 2a (a) Distances between two planes and space filling model. (b) S-S distances. (c) Side view and top view.
DFT Calculations

**Figure S30.** Energy Diagram of Kohn-Sham Orbitals of Monoaryl TTFs

(Gaussian 09, B3LYP/6-31G(d))
Figure S31. Energy Diagram of Kohn-Sham Orbitals of Radical Cations of Monoaryl TTFs

(Gaussian 09, UB3LYP/6-31G(d))
Figure S32. Energy Diagram of Kohn-Sham Orbitals of Tetraaryl TTF

(Gaussian 09, B3LYP/6-31G(d))
Figure S33. Energy Diagram of Kohn-Sham Orbitals of Radical Cations of Tetraaryl TTFs
(Gaussian 09, UB3LYP/6-31G(d))