



Supporting Information

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Intramolecular B-N Coordination as a New Scaffold for Design of Electron-Transporting Materials: Synthesis and Properties of Boryl-Substituted Thienylthiazoles

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Experimental Section

General Procedure. Melting points (mp) were measured on a Yanaco MP-S3 instrument. ^1H and ^{13}C NMR spectra were measured with a JEOL A-400 or a GSX-270 spectrometer in CDCl_3 . UV-vis absorption spectra and fluorescence spectra measurements were performed at room temperature with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively, in a degassed spectral grade THF. Cyclic voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an Ag/AgNO_3 reference electrode. The measurements were carried out under argon atmosphere using THF solutions of samples with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The redox potentials were calibrated with ferrocene as an internal standard. Thin layer chromatography (TLC) was performed on plates coated with 0.25 mm thick silica gel 60F-254 (Merck). Column chromatography was performed using Kieselgel 60 (70-230 mesh; Merck). All experiments were carried out under argon atmosphere.

Computational Method. All calculations were conducted using the Gaussian 98 program.¹

2-(3-Bromo-2-thienyl)thiazole. To a solution of 2-(tributylstannyl)thiazole (20.0 g, 53.5 mmol) and 3-bromo-2-iodothiophene (15.4 g, 53.5 mmol) in THF (250 mL), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (0.557 g, 0.538 mmol) and trifurylphosphine (0.501 g, 2.15 mmol) were added and the mixture was refluxed for 72 h. After addition of 10 wt% KF aqueous solution (200 mL), the organic layer was separated and the aqueous layer was extracted with 100 mL of toluene for three times. The combined organic layer was dried over Na_2SO_4 , filtrated, and evaporated under reduced pressure. To the residue,

20 mL of toluene was added and the insoluble solid was removed by filtration. The mixture was purified by a silica gel column chromatography (toluene, $R_f = 0.52$) to give 11.7 g (47.5 mmol) of 2-(3-bromo-2-thienyl)thiazole in 89% yield as colorless solids: mp 47-48 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J_{\text{HH}} = 3.2$ Hz, 1H), 7.38 (d, $J_{\text{HH}} = 3.2$ Hz, 1H), 7.33 (d, $J_{\text{HH}} = 5.2$ Hz, 1H), 7.07 (d, $J_{\text{HH}} = 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 142.4, 133.5, 131.8, 127.3, 118.9, 109.8; EI MS m/z 245 (M^+). Anal. Calcd for $\text{C}_7\text{H}_4\text{BrNS}_2$: C, 34.16; H, 1.64; N, 5.69. Found: C, 34.09; H, 1.68; N, 5.64.

2-(3-Dimesitylboryl-2-thienyl)thiazole (1a). To a solution of 2-(3-bromo-2-thienyl)thiazole (6.61 g, 26.9 mmol) in ether (150 mL) cooled at -78 °C was added n -BuLi (1.60 M in hexane, 16.8 mL, 26.9 mmol) dropwise. After the mixture was stirred at -78 °C for 1.5 h, a solution of dimesitylfluoroborane (7.27 g, 26.9 mmol) in 50 mL of ether was added to the mixture via cannula. The reaction mixture was gradually warmed to room temperature and stirred for 4 h. After the solvent was removed under reduced pressure, the mixture was purified by a silica gel column chromatography (CH_2Cl_2 , $R_f = 0.53$) and the recrystallization from a mixture solvent of CH_2Cl_2 /hexane gave 8.36 g (20.1 mmol) of 1a as pale yellow solids in 75% yield: mp 233-235 °C; ^1H NMR (270 MHz, CDCl_3) δ 7.69 (d, $J_{\text{HH}} = 5.2$ Hz, 1H), 7.46 (d, $J_{\text{HH}} = 6.8$ Hz, 1H), 7.25 (d, $J_{\text{HH}} = 6.8$ Hz, 1H), 6.99 (d, $J_{\text{HH}} = 5.2$ Hz, 1H), 6.67 (s, 4H), 2.21 (s, 6H), 1.88 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.6, 139.9, 137.2, 134.0, 133.3, 130.7, 129.4, 129.1, 116.3, 24.3, 20.8, (two peaks for the carbon atoms bonding to the boron atoms are not observed due to quadrupolar relaxation); ^{11}B NMR (128 MHz, CDCl_3) δ 3.52; EI MS m/z 415 (M^+). Anal. Calcd for $\text{C}_{25}\text{H}_{26}\text{BNS}_2$: C, 72.28; H, 6.31; N, 3.37. Found: C, 72.26; H, 6.25; N, 3.28.

2-(3-Dimesitylboryl-2-thienyl)-5-tributylstannylthiazole (1c). To a solution of **1a** (1.48 g, 3.56 mmol) in THF (35 mL) cooled at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (1.47 M in hexane, 2.42 mL, 3.56 mmol) dropwise. After the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, tributylstannyl chloride (0.966 mL, 3.56 mmol) was added to the mixture at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was gradually warmed to room temperature and stirred for 2 h. After the solvent was removed under reduced pressure, 50 mL of toluene was added to the residue and the solution was passed through a florisil column. The mixture was purified by a silica gel column chromatography (1:1 hexane/toluene, $R_f = 0.53$) to give 2.06 g (2.92 mmol) of **1b** in 82% yield as pale yellow solids: mp $230\text{--}231\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (s, 1H), 7.41 (d, $J_{\text{HH}} = 4.6\text{ Hz}$, 1H), 7.22 (d, $J_{\text{HH}} = 4.6\text{ Hz}$, 1H), 6.64 (s, 4H), 2.18 (s, 6H), 1.85 (s, 12H), 1.54–1.48 (m, 6H), 1.34–1.28 (m, 6H), 1.13 (t, $J_{\text{HH}} = 8.0\text{ Hz}$, 9H), 0.88 (t, $J_{\text{HH}} = 7.2\text{ Hz}$, 9H); ^{13}C NMR (67.5 MHz, CDCl_3) δ 170.9, 143.6 (br), 142.5 (t, $J_{\text{CF}} = 12.8\text{ Hz}$), 140.0, 133.7, 132.5, 130.7, 129.3, 129.2, 126.6 (t, $J_{\text{CF}} = 95.7\text{ Hz}$), 28.9, 27.2, 24.2, 20.8, 13.7, 11.4 (one peak for the carbon atom bonding to the boron atoms is not observed due to quadrupolar relaxation); ^{11}B NMR (128 MHz, CDCl_3) δ 2.50. HRMS (EI) Calcd for $\text{C}_{37}\text{H}_{52}\text{BNS}_2\text{Sn}$; 705.2656. Found; 705.2667.

2-(3-Dimesitylboryl-5-iodo-2-thienyl)-5-iodothiazole (1d). To a solution of **1a** (8.35 g, 20.1 mmol) in THF (250 mL) cooled at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (1.60 M in hexane, 25.2 mL, 40.2 mmol) dropwise. After the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1.5 h, a solution of iodine (20.4 g, 80.4 mmol) in THF (50 mL) was added to the mixture at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was gradually warmed to room temperature and stirred for 2 h. After addition of 10 wt% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution, the organic layer was separated and the aqueous layer was extracted with toluene three times. The combined organic layer was dried over MgSO_4 , filtered, and evaporated under reduced pressure. The mixture was purified by recrystallization from a mixed solvent of

CH₂Cl₂ and hexane to give 11.7 g (17.5 mmol) of **1c** in 87% yield as pale yellow solids: mp 198-200 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (s, 1H), 7.36 (s, 1H), 6.67 (s, 4H), 2.20 (s, 6H), 1.85 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 143.9, 140.7, 140.1, 135.1, 135.0, 129.6, 85.2, 65.1, 24.2, 20.8 (two peaks for the carbon atoms bonding to the boron atoms are not observed due to quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃) δ 8.06. HRMS (EI) Calcd for C₂₅H₂₄BI₂NS₂; 666.9533. Found; 666.9537.

2-(3-Dimesitylboryl-5-iodo-2-thienyl)thiazole (1e). To a solution of **1d** (80 mg, 0.12 mmol) in THF (2 mL) cooled at -78 °C was added *n*-BuLi (1.60 M in hexane, 0.075 mL, 0.12 mmol) dropwise. After the mixture was stirred at -78 °C for 1 h, the mixture was gradually warmed to room temperature. After addition of water (1 mL), the organic layer was separated and the aqueous layer was extracted with toluene three times. The combined organic layer was dried over MgSO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (2:1 hexane/toluene, *R*_f = 0.31) to give 476 mg (0.086 mmol) of **1d** in 72% yield as pale yellow solids: mp 210-212 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J*_{HH} = 3.6 Hz, 1H), 7.39 (s, 1H), 7.06 (d, *J*_{HH} = 3.6 Hz, 1H), 6.66 (s, 4H), 2.19 (s, 6H), 1.84 (s, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 140.5, 140.0, 137.2, 134.3, 134.1, 129.6, 116.8, 84.8, 24.2, 20.7 (two peaks for the carbon atoms bonding to the boron atoms is not observed due to quadrupolar relaxation); ¹¹B NMR (128 MHz, CDCl₃) δ 2.50; EI MS *m/z* 541 (M⁺). Anal. Calcd for C₂₅H₂₅BINS₂: C, 55.47; H, 4.66; N, 2.59. Found: C, 55.30; H, 4.61; N, 2.56.

Head-to-Head Dimer (2). To a solution of **1e** (200 mg, 0.37 mmol) in THF (2 mL) were added Ni₂Br₂(PPh₃)₂ (82.4 mg, 0.11 mmol), Zn (36.7 mg, 0.55 mmol), and triethylammonium iodide (95.5 mg, 0.37 mmol). The mixture was stirred at 50 °C for

24 h. The solvent was removed under reduced pressure and the mixture was purified by a silica gel column chromatography (1:1, hexane/CH₂Cl₂, R_f = 0.54) to give 38.1 mg (0.046 mmol) of **2** in 25% yield as yellow solids: mp >300 °C; ¹H NMR (270 MHz, CDCl₃) δ 7.68 (d, J_{HH} = 3.6 Hz, 2H), 7.31 (s, 2H), 7.03 (d, J_{HH} = 3.6 Hz, 2H), 6.65 (s, 8H), 2.18 (s, 12H), 1.85 (s, 24 H); ¹³C NMR spectrum could not be observed due to the poor solubility. Anal. Calcd for C₅₀H₅₀B₂N₂S₄: C, 72.46; H, 6.08; N, 3.38. Found: C, 72.20; H, 6.22; N, 3.26.

Head-to-Tail Dimer (3). To a solution of **1c** (1.06 g, 1.50 mmol) and **1e** (0.813 g, 1.50 mmol) in toluene (15 mL) were added Pd₂(dba)₃•CHCl₃ (0.0311 g, 0.03 mmol) and trifurylphosphine (0.0281 g, 0.12 mmol). The mixture was refluxed for 15 h. After addition of water (10 mL), the organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ three times. The combined organic layer was dried over MgSO₄, filtered, and evaporated under reduced pressure. The mixture was purified by a silica gel column chromatography (CH₂Cl₂, R_f = 0.95) and recrystallized from CH₂Cl₂ to give 0.845 g (1.02 mmol) of **3** in 68% yield as yellow solids: mp 250 °C (dec); ¹H NMR (270 MHz, CDCl₃) δ 7.71 (d, J_{HH} = 3.6 Hz, 1H), 7.70 (s, 1H), 6.66 (s, 8H), 7.48 (d, J_{HH} = 4.4 Hz, 1H), 7.21 (d, J_{HH} = 4.4 Hz, 1H), 7.21 (s, 1H), 7.10 (d, J_{HH} = 3.6 Hz, 1H), 2.18 (s, 12H), 1.88 (s, 12H), 1.84 (s, 12H); ¹³C NMR (270 MHz, 5:1, CS₂/CDCl₃) δ 139.7, 139.5, 139.4, 137.4, 134.1, 134.0, 133.4, 133.1, 130.9, 129.6, 129.4, 128.9, 128.8, 128.0, 125.1, 116.5, 24.4, 24.3, 20.8, 20.8 (two peaks for the carbon atoms bonding to the boron atoms is not observed due to quadrupolar relaxation). Anal. Calcd for C₅₀H₅₀B₂N₂S₄: C, 72.46; H, 6.08; N, 3.38. Found: C, 72.27; H, 6.28; N, 3.55.

Tail-to-Tail Dimer (4). To a solution of **1a** (3.99 g, 9.62 mmol) in THF (100 mL) cooled at –78 °C was added *n*-BuLi (1.60 M in hexane, 6.01 mL, 9.62 mmol) dropwise.

After the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1.5 h, CuCl_2 (2.72 g, 20.2 mmol) was added. The reaction mixture was gradually warmed to room temperature and stirred for 12 h. The solvent was removed under reduced pressure and the mixture was purified by a silica gel column chromatography (toluene, $R_f = 0.72$), followed by the recrystallization from CH_2Cl_2 to give 1.25 g (1.51 mmol) of **4** in 31% yield as yellow solids: mp $187\text{--}189\text{ }^{\circ}\text{C}$; ^1H NMR (270 MHz, CDCl_3) δ 7.59 (s, 2H), 7.50 (d, $J_{\text{HH}} = 4.8\text{ Hz}$, 2H), 7.19 (d, $J_{\text{HH}} = 4.8\text{ Hz}$, 2H), 6.66 (s, 8H), 2.18 (s, 12H), 1.89 (s, 24H); ^{13}C NMR (CDCl_3) δ 141.4, 139.6, 134.9, 134.7, 133.1, 131.5, 130.9, 129.4, 124.5, 31.7, 24.1, 23.0, 20.8, 14.3 (two peaks for the carbon atoms bonding to the boron atoms is not observed due to quadrupolar relaxation). Anal. Calcd for $\text{C}_{50}\text{H}_{50}\text{B}_2\text{N}_2\text{S}_4$: C, 72.46; H, 6.08; N, 3.38. Found: C, 72.24; H, 6.34; N, 3.35.

X-Ray Crystal Structure Analysis of Compound 1a. Single crystals of **1a** suitable for X-ray crystal analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **1a**. Intensity data were collected at 173 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) and graphite monochromator. A total of 7314 reflections were measured at a maximum 2θ angle of 50.0° , of which 3775 were independent reflections ($R_{\text{int}} = 0.0199$). The structure was solved by direct methods (SHELXS-97²) and refined by the full-matrix least-squares on F^2 (SHELEXL-97²). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $\text{C}_{25}\text{H}_{26}\text{B}_1\text{N}_1\text{S}_2$; FW = 415.40, crystal size $0.20 \times 0.20 \times 0.20\text{ mm}^3$, Triclinic, $P\bar{1}$, $a = 8.1921(18)\text{ \AA}$, $b = 10.118(2)\text{ \AA}$, $c = 13.205(3)\text{ \AA}$, $\alpha = 90.093(5)^{\circ}$, $\beta = 91.356(5)^{\circ}$, $\gamma = 90.159(5)^{\circ}$, $V = 1094.3(4)\text{ \AA}^3$, $Z = 2$, $D_c = 1.261\text{ g cm}^{-3}$. The refinement converged to $R_1 = 0.0406$, $wR_2 = 0.1026$ ($I > 2\sigma(I)$), GOF = 1.043.

X-Ray Crystal Structure Analysis of Compound 2. Single crystals of **2** suitable for X-ray crystal analysis were obtained by sublimation at 260-275 °C under reduced pressure (10^{-4} Pa). Intensity data were collected at 100 K on a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo K α radiation ($\lambda = 0.71073$ Å) and graphite monochromator. A total of 14103 reflections were measured at a maximum 2θ angle of 50.0° , of which 3715 were independent reflections ($R_{\text{int}} = 0.0333$). The structure was solved by direct methods (SHELXS-97²) and refined by the full-matrix least-squares on F^2 (SHELEXL-97²). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: C₅₀H₅₀B₂N₂S₄; FW = 828.78, crystal size $0.20 \times 0.10 \times 0.10$ mm³, Monoclinic, $P21/c$, $a = 7.8642(15)$ Å, $b = 15.824(3)$ Å, $c = 17.361(3)$ Å, $\beta = 100.0793(9)^\circ$, $V = 2127.2(7)$ Å³, $Z = 2$, $D_c = 1.294$ g cm⁻³. The refinement converged to $R_1 = 0.0412$, $wR_2 = 0.0956$ ($I > 2\sigma(I)$), GOF = 1.073.

X-Ray Crystal Structure Analysis of Compound 4. Single crystals of **4** suitable for X-ray crystal analysis were obtained by slow diffusion of hexane into a CH₂Cl₂ solution of **4**. Intensity data were collected at 173 K on a Rigaku Singlecrystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with Mo K α radiation ($\lambda = 0.71073$ Å) and graphite monochromator. A total of 10268 reflections were measured at a maximum 2θ angle of 50.0° , of which 5264 were independent reflections ($R_{\text{int}} = 0.0326$). The structure was solved by direct methods (SHELXS-97²) and refined by the full-matrix least-squares on F^2 (SHELEXL-97²). The disordered solvent molecules of CH₂Cl₂ and hexane were included in a lattice. The chlorides of the former disordered CH₂Cl₂ (Cl1andCl2) were restrained by DFIX instrument during refinement with fixed C-Cl bond distances. Except for the disordered solvent molecule of CH₂Cl₂, all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were

placed using AFIX instructions. The crystal data are as follows: $C_{58}H_{68}B_2Cl_4N_2S_4$; FW = 1084.80, crystal size $0.20 \times 0.20 \times 0.20 \text{ mm}^3$, Triclinic, $P-1$, $a = 8.532(4) \text{ \AA}$, $b = 14.323(6) \text{ \AA}$, $c = 14.644(6) \text{ \AA}$, $\alpha = 116.479(5)^\circ$, $\beta = 105.988(5)^\circ$, $\gamma = 90.376(4)^\circ$, $V = 1522.2(11) \text{ \AA}^3$, $Z = 1$, $D_c = 1.183 \text{ g cm}^{-3}$. The refinement converged to $R_1 = 0.0804$, $wR_2 = 0.2360$ ($I > 2\sigma(I)$), GOF = 1.102.

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- (2) G. M. Sheldrick, *SHELX-97, Program for the Refinement of Crystal Structures*; University of Gottingen: Gottingen, Germany, 1997.

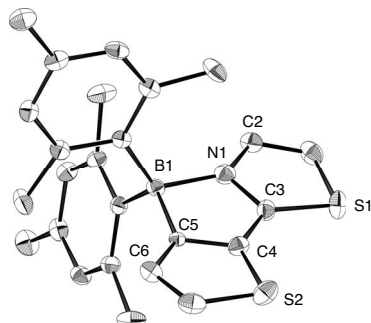


Figure S1. ORTEP drawing of **1a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selective bond length (Å) and angles (deg) are as follows: N1–B1, 1.667(3); C5–B1, 1.658(3); C3–N1–C2, 110.94(17); C3–N1–B1, 110.38(16); C2–N1–B1, 137.93(16); C4–C5–C6, 111.28(17); C4–C5–B1, 110.00(16); C6–C5–B1, 137.95(17).

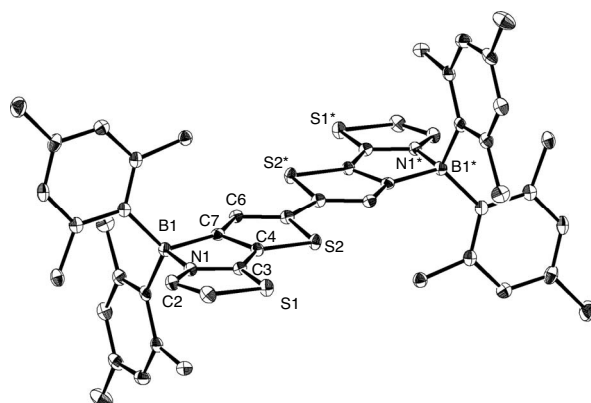


Figure S2. ORTEP drawing of **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selective bond length (Å) and angles (deg) are as follows: N1-B1, 1.633(3); C7-B1, 1.638(3); C3-N1-C2, 112.64(16); C3-N1-B1, 112.91(15); C2-N1-B1, 134.19(16); C4-C7-C6, 109.62(17); C4-C7-B1, 110.30(16); C6-C7-B1, 139.40(17).

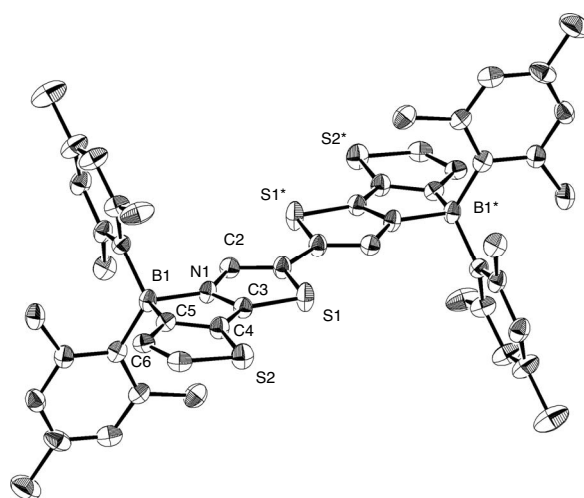


Figure S3. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules and Hydrogen atoms are omitted for clarity. Selective bond length (Å) and angles (deg) are as follows: N1-B1, 1.653(5); C5-B1, 1.632(5); C3-N1-C2, 112.4(3); C3-N1-B1, 111.9(3); C2-N1-B1, 135.2(3); C4-C5-C6, 109.1(3); C4-C5-B1, 110.6(3); C6-C5-B1, 139.6(3).

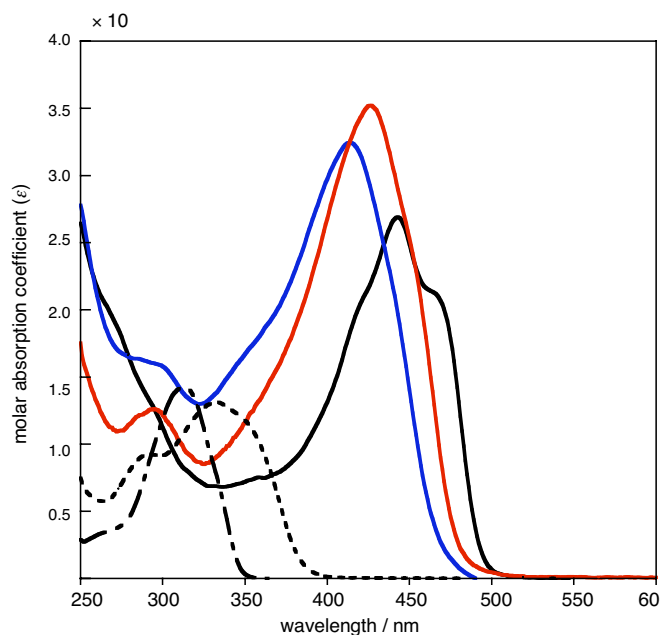


Figure S4. UV-vis spectra of thienylthiazole derivatives, **1a**, **2**, **3**, and **4** in THF: dashed line, thienylthiazole; dotted line, **1a**; black line, **2**; red line, **3**; blue line, **4**.

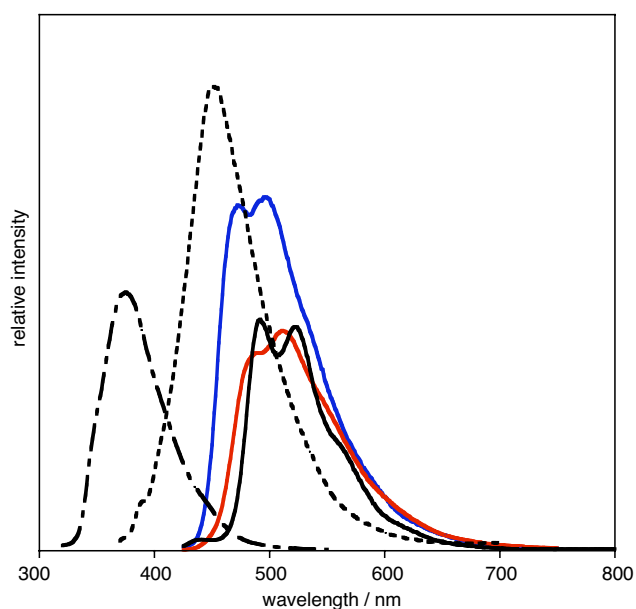


Figure S5. Fluorescence spectra of thienylthiazole derivatives, **1a**, **2**, **3**, and **4** in THF: dashed line, thienylthiazole; dotted line, **1a**; black line, **2**; red line, **3**; blue line, **4**.

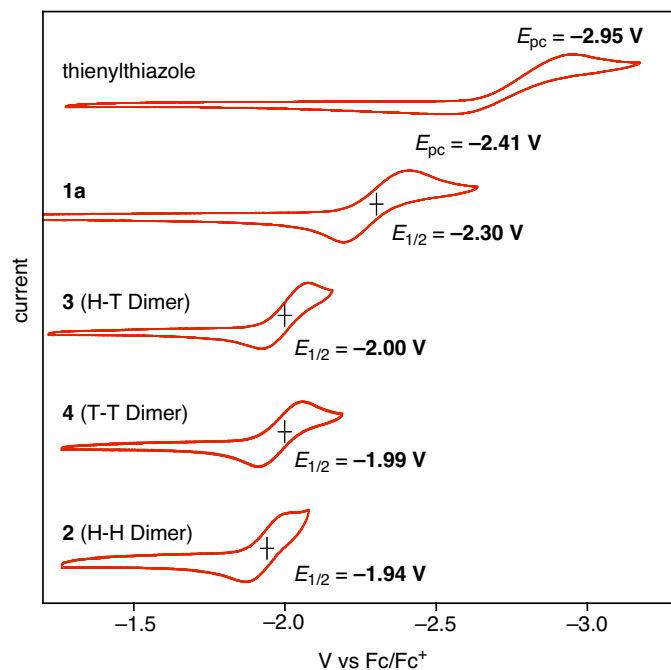


Figure S6. Cyclic voltammograms of thienylthiazole derivatives, **1a**, **2**, **3**, and **4** in THF, measured with $\text{Bu}_4\text{N}^+\text{PF}_6^-$ (0.1 M) as a supporting electrolyte at a scan rate of 100 mVs^{-1} .