Supporting Information for Synthesis and properties of spiro-type heterasumanenes containing group 14 elements as bridging atoms

Shunsuke Furukawa,* Keisuke Hayashi, Ken Yamagishi, Masaichi Saito*

Table of contents

1. General consideration for synthesis and characterization .......................... S2
2. Synthetic procedures for all compounds ........................................... S3
3. X-ray crystallographic analysis ...................................................... S18
4. Electrochemical Study ................................................................. S19
5. Chemical oxidation of spirobistannasumanene 3b ............................... S20
6. Reference ...................................................................................... S20
7. NMR charts .................................................................................. S21
1. General consideration for synthesis and characterization

NMR spectra were recorded on Bruker AVANCE500 spectrometer (\(^1\)H NMR, 500 MHz; \(^{13}\)C NMR, 125 MHz), Bruker AVANCE400 spectrometer (\(^1\)H NMR, 400 MHz; \(^{13}\)C NMR, 100 MHz) and Bruker AVANCE500T spectrometer (\(^{29}\)Si NMR, 99 MHz; \(^{119}\)Sn NMR, 186 Hz). Chemical shifts for \(^1\)H NMR spectra are reported in parts per million (ppm, \(\delta\) scale) downfield from tetramethylsilane, and referenced internally to the residual proton in the solvent (CDCl\(_3\): \(\delta 7.26\)). Chemical shifts for \(^{13}\)C NMR spectra are reported in parts per million (ppm, \(\delta\) scale) downfield from tetramethylsilane, and are referenced to the \(^{13}\)C resonance of the NMR solvent (CDCl\(_3\): \(\delta 77.16\)). Chemical shifts for \(^{29}\)Si NMR spectra are reported in parts per million (ppm, \(\delta\) scale) downfield and are referenced to an external tetramethylsilane as the standard. Chemical shifts for \(^{119}\)Sn NMR spectra are reported in parts per million (ppm, \(\delta\) scale) downfield and are referenced to an external tetramethylstannane as the standard. The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), and integration. Mass spectra were obtained with Bruker AutoflexIII (MALDI-TOF) mass spectrometer. Cyclic voltammetry measurements were performed with Gamry Interface 1000 using a glassy carbon working electrode, a Pt counter electrode and an Ag/AgNO\(_3\) reference electrode at room temperature in CH\(_2\)Cl\(_2\) containing 0.1 M \(n\)-Bu\(_4\)NClO\(_4\) as the supporting electrolyte. Melting points were measured by Yanaco MP-S3 instrument. The intensity data for X-ray crystallographic analyses were collected at –173 °C on Bruker SMART APEX II equipped with a CCD area detector with graphite-monochromated MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å). Column chromatography was performed using Kanto silica gel 60N. Thin layer chromatography was performed using Merck Silica Gel 60 F254, TLC Plates. Medium pressure liquid chromatography was performed with Yamazen Corporation EPCLC AI-580 instrument using Universal columns premium. UV-vis absorption spectra were obtained with JASCO V-770 spectrometer. Electron spin resonance (ESR) spectra were recorded on Bruker EMX6/1 spectrometer.
2. Synthetic procedures for all compounds

Synthesis of 2,3,6,7,10,11-hexabutoxytriphenylene (4a)

Anhydrous iron(III) chloride (39.1 g, 241 mmol) was added to a dichloromethane (400 mL) solution of 1,2-dibutoxybenzene (26.7 g, 120 mmol) for 40 min at room temperature. After stirring for 20 min at the same temperature, ethanol (320 mL) was added to the reaction mixture. The mixture was cooled in an ice-bath and then the resulting solid was corrected by suction filtration. The products were purified by silica gel column chromatography (eluents: hexane : CHCl₃ = 2 : 3, v/v) to give 4a (11.2 g, 16.9 mmol, 42%) as a colorless solid.

Synthesis of 2,3,6,7,10,11-hexaethoxytriphenylene (4b)

A dichloromethane (140 mL) solution of 1,2-diethoxybenzene (36.5 g, 220 mmol) was added to a suspension of anhydrous iron(III) chloride (71.5 g, 441 mmol) in dichloromethane (360 mL) dropwise for 40 min at room temperature. After stirring for 45 min at the same temperature, ethanol (350 mL) was added to the reaction mixture. The mixture was cooled in an ice-bath and then the resulting solid was corrected by suction filtration. The products were purified by silica gel column chromatography (CHCl₃) to give 4b (19.0 g, 38.6 mmol, 52%) as a colorless solid.

Synthesis of 2,3,6,7,10,11-hexabutoxy[4,5-b,c,d]thienotriphenylene[8,9-c’,d’,e’]1’,2’-dithiine (6a)

Anhydrous hexane (28 mL) and TMEDA (6.4 mL, 43.0 mmol) were added to 4a (7.06 g, 10.7
mmol) in a dried three-necked-flask under argon atmosphere. \(n\)-BuLi in hexane (2.66 M, 16.1 mL, 42.8 mmol) was added dropwise to the suspension for 20 min. The suspension was stirred at room temperature for 3 hours. Volatiles were removed under reduced pressure. THF (210 mL) was added to the resulting solid and then cooled to under \(-70^\circ\text{C}\). Sulfur powder (5.50 g, 21.4 mmol) was added to the suspension. After stirring for 30 min at \(-70^\circ\text{C}\), the mixture was allowed to warm to room temperature and stirred for 12 hours. After stirring, aqueous NH\(_4\)Cl was added to the mixture, and insoluble materials were removed by suction filtration. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown viscous solid (9.54 g). Carbon tetrachloride (180 mL) and iodine (19.0 g, 75.0 mmol) were added to the viscous solid under argon atmosphere, and the mixture was stirred at room temperature for 50 min. After heating under reflux conditions for 14 hours, the mixture was cooled to room temperature, then aqueous sodium sulfite was added. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a dark yellow solid. The products were purified by silica gel column chromatography (eluent, hexane: CHCl\(_3\), 2:3, v/v) to give 6a (6.16 g, 8.18 mmol, 76%) as a yellow solid. mp. 105-107\(^\circ\text{C}\); \(\text{\text{\text{\text{H}}} NMR (500 MHz, CDCl}_3) \delta 1.01-1.08 (m, 18H), 1.58-1.67 (m, 12H), 1.83-1.90 (m, 8H), 1.91–1.97 (m, 4H), 4.20–4.28 (m, 8H), 4.34-4.39 (m, 4H), 7.74 (s, 1H), 7.76 (s, 1H); \(\text{\text{\text{\text{C}}} NMR (125 MHz, CDCl}_3) \delta 14.07-14.14 (m, CH}_3\), 19.42 (CH\(_2\)), 19.46 (CH\(_2\)), 19.51 (CH\(_2\)), 19.59 (CH\(_2\)), 31.57 (CH\(_2\)), 31.85 (CH\(_2\)), 32.57, 32.59 (CH\(_2\)), 32.60 (CH\(_2\)), 32.62 (CH\(_2\)), 68.84 (CH\(_2\)), 70.32 (CH\(_2\)), 73.22 (CH\(_2\)), 73.29 (CH\(_2\)), 73.86 (CH\(_2\)), 74.74 (CH\(_2\)), 105.08 (CH), 105.83 (CH), 120.53 (C), 121.30 (C), 122.56 (C), 123.43 (C), 123.91 (C), 126.49 (C), 127.11 (C), 128.30 (C), 128.34 (C), 130.71 (C), 143.29 (C), 145.01 (C), 146.28 (C), 146.47 (C), 152.36 (C), 152.82 (C); MS (MALDI) \(m/z\) calcld for C\(_{42}\)H\(_{56}\)O\(_6\)S\(_3\) ([M]\(^+\)) 752.3, found: 752.2; elemental analysis calcld for C\(_{42}\)H\(_{56}\)O\(_6\)S\(_3\): C, 66.98; H, 7.50, found: C, 66.99; H, 7.55.

**Synthesis of 2,3,6,7,10,11-hexaethoxy[4,5-b,c,d]thienotriphenylene[8,9-c’,d’,e’]1’,2’-dithiine (6b)**

Anhydrous hexane (250 mL) was added to 4b (5.01 g, 10.2 mmol) in a dried three-necked-flask under argon atmosphere. \(n\)-BuLi in hexane (2.66 M, 24.0 mL, 63.8 mmol) was added dropwise to the suspension. The suspension was refluxed for 3 hours. Volatiles were removed under reduced pressure. THF (200 mL) was added to the resulting solid and then the mixture was cooled to under
−70 °C. Sulfur powder (5.32 g, 20.7 mmol) was added to the suspension, and stirred for 30 min at −70 °C. The mixture was allowed to warm to room temperature and stirred for 12 hours. After stirring, aqueous NH$_4$Cl was added to the mixture, and insoluble materials were removed by suction filtration. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH$_2$Cl$_2$ = 2 : 3, v/v) to give 6b (3.04 g, 5.20 mmol, 51%) as a yellow solid. mp. 169-170 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.48-1.53 (m, 12H), 1.57 (t, J = 7.0 Hz, 6H), 4.27–4.34 (m, 8H), 4.43 (q, J = 7.0 Hz, 4H), 4.47 (q, J = 7.0 Hz, 4H), 7.71 (s, 1H), 7.72 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 15.02 (CH$_3$), 15.27 (CH$_3$), 15.92 (CH$_3$), 15.96 (CH$_3$), 16.12 (CH$_3$), 64.72 (CH$_2$), 66.07 (CH$_2$), 68.94 (CH$_2$), 68.98 (CH$_2$), 69.76 (CH$_2$), 70.49 (CH$_2$), 105.03 (CH), 105.83 (CH), 120.43 (C), 121.18 (C), 122.39 (C), 123.31 (C), 123.77 (C), 126.30 (C), 127.01 (C), 128.24 (C), 128.26 (C), 130.65 (C), 142.87 (C), 144.75 (C), 145.98 (C), 146.13 (C), 152.01 (C), 152.53 (C); MS (MALDI) m/z calcd for C$_{30}$H$_{32}$O$_6$S$_3$ ([M]+) 584.1, found: 584.4; elemental analysis calcd for C$_{30}$H$_{32}$O$_6$S$_3$: C, 61.62; H, 5.52, found: C, 61.29; H, 5.44.

Synthesis of 2,3,6,7,10,11-hexabutoxy[4,5-b,c,d:8,9-b',c',d']dithiophene (7a)

![Synthesis of 2,3,6,7,10,11-hexabutoxy[4,5-b,c,d:8,9-b',c',d']dithiophene (7a)](image)

Compound 6a (4.18 g, 5.55 mmol) and copper powder (3.70 g, 58.3 mmol) were mixed in a flask, and the mixture was heated at 230 °C for 2 days under argon atmosphere. After cooled to room temperature, dichloromethane was added to the reaction mixture, and the resulting insoluble solid was removed by suction filtration. The filtrate was concentrated and further purified by column chromatography on silica (eluent, hexane : CH$_2$Cl$_2$ = 3 : 2, v/v) to give 7a as a yellow solid (3.00 g, 4.16 mmol, 75%), mp. 111-112 °C; $^1$H NMR (500 MHz, CDCl$_3$) δ 1.02-1.08 (m, 18H), 1.61-1.69 (m, 12H), 1.85-1.98 (m, 12H), 4.28 (t, J = 6.5 Hz, 4H), 4.41 (t, J = 6.5 Hz, 4H), 4.45 (t, J = 6.5 Hz, 4H), 7.84 (s, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 14.09 (CH$_3$), 14.11 (CH$_3$), 19.43 (CH$_2$), 19.46 (CH$_2$), 19.60 (CH$_2$), 31.93 (CH$_2$), 32.50 (CH$_2$), 32.59 (CH$_2$), 70.58 (CH$_2$), 72.89 (CH$_2$), 73.08 (CH$_2$), 106.68 (CH), 123.11 (C), 123.56 (C), 125.09 (C), 127.52 (C), 132.49 (C), 143.70 (C), 145.99 (C), 152.24 (C); MS (MALDI) m/z calcd for C$_{42}$H$_{56}$O$_{6}$S$_{2}$ ([M]+) 720.4, found: 720.2; elemental analysis calcd for C$_{42}$H$_{56}$O$_{6}$S$_{2}$: C, 69.96; H, 7.83, found: C, 69.82; H, 7.88.
Synthesis of 2,3,6,7,10,11-hexaethoxy[4,5-b,c,d:8,9-b',c',d']dithiophene (7b)

Compound 6b (2.30 g, 3.94 mmol) and copper powder (2.49 g, 3.92 mmol) were mixed in a flask, and the mixture was heated at 240 °C for 2 days under argon atmosphere. After cooled to room temperature, dichloromethane was added to the reaction mixture, and the resulting insoluble solid was removed by suction filtration. The filtrate was concentrated and further purified by column chromatography on silica (eluent, hexane : CH₂Cl₂ = 2 : 5, v/v) to give 7b as a pale yellow solid (1.676 g, 3.03 mmol, 75%). mp. 174 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.52 (t, J = 8.5 Hz, 6H), 1.54 (t, J = 8.5 Hz, 6H), 1.58 (t, J = 8.5 Hz, 6H), 4.35 (q, J = 8.5 Hz, 4H), 4.49 (q, J = 8.5 Hz, 4H), 4.52 (q, J = 8.5 Hz, 4H), 7.85 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 30.21 (CH₂), 66.47 (CH₂), 68.68 (CH₂), 68.85 (CH₂), 106.92 (CH), 123.19 (C), 123.58 (C), 125.11 (C), 127.57 (C), 132.52 (C), 143.48 (C), 145.70 (C), 151.97 (C); MS (MALDI) m/z calcd for C₃₀H₂₂O₈S₂ ([M⁺]) 552.2, found: 552.2; elemental analysis calcd for C₃₀H₂₂O₈S₂: C, 65.19; H, 5.84, found: C, 64.97; H, 5.75.

Synthesis of 2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2',3',4',5',1',1'-diphenyl-1H-silolo[8,9-b,c,d:12,1-b',c',d']dithiophene (9a)

Anhydrous hexane (4.4 mL) and TMEDA (0.40 mL, 2.68 mmol) were added to 7a (948 mg, 1.32 mmol) in a dried three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 1.00 mL, 2.66 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (26 mL) was added to the resulting solid and then the mixture was cooled to under −70 °C. Dichlorodiphenylsilane (0.28 mL, 1.33 mmol) was added slowly to the solution and stirred for 30 min at −70 °C. The mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with
chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 1:1, v/v) to give 9a (681 mg, 0.755 mmol, 57%) as a yellow solid. mp. 128-129 °C; ¹H NMR (400 MHz, CDCl₃) δ 0.74 (t, J = 9.0 Hz, 6 H), 1.02 (t, J = 9.5 Hz, 6H), 1.04 (t, J = 9.0 Hz, 6H), 1.19 (sext, J = 9.5 Hz, 4H), 1.51-1.68 (m, 12H), 1.85-1.93 (m, 8H), 3.92 (t, J = 9.0 Hz, 4H), 4.40 (t, J = 8.0 Hz, 4H), 4.43 (t, J = 8.0 Hz, 4H), 7.32-7.43 (m, 6H), 7.81-7.83 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 13.84 (CH₃), 14.02 (CH₃), 19.03 (CH₃), 19.41 (CH₂), 32.03 (CH₂), 32.39 (CH₂), 32.43 (CH₂), 72.43 (CH₂), 72.93 (CH₂), 73.53 (CH₂), 120.07 (C), 125.78 (C), 126.05 (C), 126.97 (C), 128.28 (CH), 130.42 (CH), 133.09 (C), 133.36 (C), 135.05 (C) 135.82 (CH), 146.40 (C), 146.49 (C), 156.25 (C); ²⁹Si NMR (99 MHz, CDCl₃) δ −0.04; MS (MALDI) m/z calcd for C₅₃H₆₇O₈Si ([M⁺]) 900.4, found: 900.5; elemental analysis calcd for C₅₃H₆₇O₈Si: C, 71.97; H, 7.16, found: C, 71.88; H, 7.21.

Synthesis of 2,3,6,7,10,11-hexaethoxytriphenylene[4,5-2',3',4',5']1',1'-diphenyl-1H-silolo[8,9-b,c,d:12,1-b',c',d']dithiophene (9b)

Anhydrous hexane (15 mL) and TMEDA (0.30 mL, 2.01 mmol) were added to 7b (510 mg, 0.92 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 0.72 mL, 1.91 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (15 mL) was added to the resulting solid and then cooled to under −70 °C. A THF (5 mL) solution of dichlorodiphenylsilane (0.20 mL, 0.96 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 2 : 3, v/v) to give 9b (53 mg, 0.073 mmol, 8%) as a yellow solid. mp. 216-217 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.16 (t, J = 7.0 Hz, 6 H), 1.52 (t, J = 7.0 Hz, 6H), 1.54 (t, J = 7.0 Hz, 6H), 4.02 (q, J = 7.0 Hz, 4H), 4.48 (q, J = 7.0 Hz, 4H), 4.51 (q, J = 7.0 Hz, 4H), 7.34-7.37 (m, 4H), 7.40-7.44 (m, 2H), 7.82-7.84
Synthesis of 2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2ʹ,3ʹ,4ʹ,5ʹ]1ʹ,1ʹ-diphenyl-1H-germolo[8,9-b,c,d:12,1-bʹ,cʹ,dʹ]dithiophene (10a)

Anhydrous hexane (4.5 mL) and TMEDA (0.35 mL, 2.35 mmol) were added to 7a (827 mg, 1.15 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 0.87 mL, 2.31 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (22 mL) was added to the resulting solid and then cooled to under −70 °C. Dichlorodiphenylgermane (0.25 mL, 1.20 mmol) was added slowly to the solution. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour. Then the mixture was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 2 : 3, v/v) to give 10a (813 mg, 0.859 mmol, 75%) as a pale yellow solid, mp. 126 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.74 (t, J = 7.5 Hz, 6 H), 1.02 (t, J = 7.5 Hz, 6 H), 1.04 (t, J = 7.5 Hz, 6 H), 1.21 (sext, J = 7.5 Hz, 4 H), 1.56-1.68 (m, 12 H), 1.85-1.93 (m, 8 H), 3.97 (t, J = 7.5 Hz, 4 H), 4.40 (t, J = 7.5 Hz, 4 H), 4.44 (t, J = 7.5 Hz, 4 H), 7.35-7.42 (m, 6 H), 7.72-7.73 (m, 4 H); ¹³C NMR (100 MHz, CDCl₃) δ 13.84 (CH₃), 14.08 (CH₃), 19.07 (CH₂), 19.44 (CH₂), 32.04 (CH₂), 32.43 (CH₂), 32.48 (CH₂), 72.54 (CH₂), 73.00 (CH₂), 73.07 (CH₂), 121.13 (C), 125.40 (C), 125.81 (C), 126.92 (C), 128.78 (CH), 129.97 (CH), 132.44 (C), 134.10 (C), 134.95 (CH), 136.16 (C), 146.05 (C), 146.48 (C), 155.95 (C); MS (MALDI) m/z calcd for C₅₂H₇₁O₆S₂Ge (M⁺) 946.3; found: 992.3; elemental analysis calcd for C₅₂H₇₁O₆S₂Ge: C, 68.57; H, 6.82; found: C, 68.47; H, 6.82.

Synthesis of 2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2ʹ,3ʹ,4ʹ,5ʹ]1ʹ,1ʹ-diphenyl-1H-germolo[8,9-b,c,d:12,1-bʹ,cʹ,dʹ]dithiophene (10b)

Synthesis of 2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2ʹ,3ʹ,4ʹ,5ʹ]1ʹ,1ʹ-diphenyl-1H-germolo[8,9-b,c,d:12,1-bʹ,cʹ,dʹ]dithiophene (10b)
Anhydrous hexane (15 mL) and TMEDA (0.40 mL, 2.60 mmol) were added to 7b (678 mg, 1.23 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.65 M, 0.87 mL, 2.31 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (15 mL) was added to the resulting solid and the mixture was cooled to under −78 °C. Dichlorodiphenylgermane (0.26 mL, 1.25 mmol) was added slowly to the solution at −78 °C and stirred for 30 min at the same temperature. The mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 1 : 1, v/v) to give 10b (198 mg, 0.255 mmol, 21%) as a pale yellow solid. mp. 224-225 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.20 (t, J = 7.0 Hz, 6 H), 1.53 (t, J = 7.0 Hz, 6H), 1.55 (t, J = 7.0 Hz, 6H), 4.07 (q, J = 7.0 Hz, 4H), 4.49 (q, J = 7.0 Hz, 4H), 4.53 (q, J = 7.0 Hz, 4H), 7.35-7.42 (m, 6H), 7.73-7.75 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 15.41 (CH₃), 15.96 (CH₃), 16.00 (CH₃), 68.38 (CH₂), 68.82 (CH₂), 69.02 (CH₂), 122.04 (C), 125.61 (C), 125.94 (C), 127.18 (C), 128.78 (CH), 130.00 (CH), 132.48 (C), 134.17 (C), 134.90 (CH) 135.95 (C), 146.25 (C), 146.27 (C), 155.62 (C); MS (MALDI) m/z calcd for C₄₂H₄₀O₆S₂Ge ([M]+) 778.1, found: 778.2; elemental analysis calcd for C₄₂H₄₀O₆S₂Ge: C, 64.88; H, 5.19, found: C, 65.04; H, 5.12.
Anhydrous hexane (4.0 mL) and TMEDA (0.32 mL, 2.15 mmol) were added to 7a (764 mg, 1.32 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 0.80 mL, 2.13 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (16 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A THF (7 mL) solution of dichlorodiphenylstannane (384 mg, 1.12 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour. The solution was refluxed for 12 hours. After cooling to room temperature, aqueous NH$_4$Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH$_2$Cl$_2$ = 2 : 3, v/v) to give 11a (782 mg, 0.788 mmol, 74%) as a pale yellow solid. mp. 125-126 °C (dec.); $^1$H NMR (500 MHz, CDCl$_3$) δ 0.75 (t, $J = 7.5$ Hz, 6 H), 1.02 (t, $J = 7.5$ Hz, 6H), 1.04 (t, $J = 7.0$ Hz, 6H), 1.27 (sext, $J = 7.5$ Hz, 4H), 1.58-1.70 (m, 12H), 1.85-1.93 (m, 8H), 4.08 (t, $J = 7.0$ Hz, 4H), 4.40 (t, $J = 6.5$ Hz, 4H), 4.46 (t, $J = 6.5$ Hz, 4H), 7.37-7.42 (m, 6H), 7.67-7.69 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 13.78 (CH$_3$), 14.09 (CH$_3$), 19.19 (CH$_2$), 19.45 (CH$_2$), 30.06 (CH$_2$), 32.03 (CH$_2$), 32.45 (CH$_2$), 32.56 (CH$_2$), 71.56 (CH$_2$), 72.65 (CH$_2$), 72.97 (CH$_2$), 118.71 (C), 124.22 (C), 125.23 (C), 127.05 (C), 129.25 (CH), 129.98 (CH), 133.07 (C), 134.94 (C), 137.05 (CH), 138.87 (C), 145.37 (C), 146.35 (C), 157.46 (C); $^{119}$Sn NMR (186 MHz, CDCl$_3$) δ −62.96; MS (MALDI) m/z calcd for C$_{54}$H$_{64}$O$_6$S$_2$Sn ([M]+) 992.3, found: 992.3; elemental analysis calcd for C$_{54}$H$_{64}$O$_6$S$_2$Sn: C, 65.39; H, 6.50, found: C, 65.25; H, 6.53.
Synthesis of 2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2',3',4',5']1',1'-diphenyl-1H-stannolo[8,9-b,c,d:12,1-b',c',d']dithiophene (11b)

Anhydrous hexane (50 mL) and TMEDA (0.60 mL, 4.03 mmol) were added to 7b (1.00 g, 1.82 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 1.40 mL, 3.72 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (50 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A THF (10 mL) solution of dichlorodiphenylstannane (635 mg, 1.85 mmol) was transferred to the reaction mixture via a PTFE tube over 5 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 1 : 1, v/v) to give 11b (386 mg, 0.47 mmol, 26%) as a pale yellow solid. mp. 237-238 °C; ¹H NMR (500 MHz, CDCl₃) δ 1.16 (t, J = 7.0 Hz, 6 H), 1.52 (t, J = 7.0 Hz, 6H), 1.54 (t, J = 7.0 Hz, 6H), 4.02 (q, J = 7.0 Hz, 4H), 4.48 (q, J = 7.0 Hz, 4H), 4.51 (q, J = 7.0 Hz, 4H), 7.34-7.37 (m, 4H), 7.40-7.43 (m, 2H), 7.82-7.84 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 15.52 (CH₃), 15.98 (CH₃), 16.07 (CH₃), 67.64 (CH₂), 68.48 (CH₂), 68.77 (CH₂), 119.70 (C), 124.38 (C), 125.31 (C), 127.26 (C), 129.28 (CH), 130.02 (CH), 133.07 (C), 134.99 (C), 137.02 (CH) 138.67 (C), 145.38 (C), 146.09 (C), 157.17 (C); ¹¹⁹Sn NMR (186 MHz, CDCl₃) δ −62.13; MS (MALDI) m/z calcd for C₄₂H₄₀O₆S₂Sn ([M]+) 824.1, found: 824.1; elemental analysis calcd for C₄₂H₄₀O₆S₂Sn: C, 61.25; H, 4.90, found: C, 61.25; H, 4.73.
Synthesis of spirobi[2,3,6,7,10,11-hexabutoxytriphenylene][4,5-2',3',4',5',1',1'-diphenyl -1H-silolo[8,9-b,c,d;12,1-b',c',d']dithiophene] (1a)

Anhydrous hexane (4.0 mL) and TMEDA (0.32 mL, 2.15 mmol) were added to 7a (764 mg, 1.32 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 0.80 mL, 2.13 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (16 mL) was added to the resulting solid and the mixture was cooled to under ~70 °C. A THF (7 mL) solution of dichlorodiphenylstannane (384 mg, 1.12 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at ~70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 2 : 3, v/v) to give 1a (782 mg, 0.788 mmol, 74%) as a pale yellow solid. mp. 84-85 °C (dec.); ¹H NMR (500 MHz, CDCl₃) δ −0.06 (t, J = 7.5 Hz, 12H), −0.01-0.05 (m, 8H), 0.97 (t, J = 7.5 Hz, 12H), 1.03-1.11 (m, 8H), 1.06 (t, J = 7.5 Hz, 12H), 1.51-1.59 (m, 8H), 1.66 (sext, J = 7.5 Hz, 8H), 1.79 (quin, J = 7.5 Hz, 8H), 1.92 (quint, J = 7.5 Hz, 8H), 3.60 (t, J = 7.5 Hz, 8H), 4.29 (t, J = 6.5 Hz, 12H), 4.47 (t, J = 6.5 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 12.88 (CH₃), 14.02 (CH₃), 14.07 (CH₃), 17.71 (CH₃), 19.35 (CH₂), 19.45 (CH₂), 30.96 (CH₂), 32.38 (CH₂), 32.40 (CH₂), 70.21 (CH₂), 72.76 (CH₂), 73.09 (CH₂), 114.81 (C), 125.31 (C), 125.68 (C), 126.27 (C), 134.57 (C), 134.95 (C), 144.68 (C), 146.69 (C), 156.94 (C); ²⁹Si NMR (99 MHz, CDCl₃) δ 3.39; MS (MALDI) m/z calcd for C₈₄H₁₀₂O₁₃S₄Si ([M+H⁺]⁺) 1465.6, found: 1465.3; elemental analysis calcd for C₈₄H₁₀₂O₁₃S₄Si: C,68.82; H, 7.42, found: C,68.79; H, 7.46.
Synthesis of spirobi[2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2',3',4',5']1',1'-diphenyl-1H-silolo[8,9-b,c,d]:12,1-b',c',d'[dithiophene] (1b)

Anhydrous hexane (34 mL) and TMEDA (0.58 mL, 3.89 mmol) were added to 7b (1.03 g, 1.87 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 1.40 mL, 3.72 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (34 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A toluene (21 mL) solution of tetrachlorosilane (0.12 mL, 1.05 mmol) was transferred to the reaction mixture via a PTFE tube over 15 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluient, hexane : CH₂Cl₂ = 1 : 4, v/v) to give 1b (158 mg, 0.140 mmol, 15%) as a yellow solid. mp. 226 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.61 (t, J = 7.0 Hz, 12 H), 1.44 (t, J = 7.0 Hz, 12H), 1.59 (t, J = 7.0 Hz, 12H), 3.71 (q, J = 7.0 Hz, 8H), 4.40 (q, J = 7.0 Hz, 8H), 4.57 (q, J = 7.0 Hz, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 14.92 (CH₃), 15.89 (CH₃), 15.99 (CH₂), 66.41 (CH₂), 68.48 (CH₂), 68.89 (CH₂), 114.64 (C), 125.05 (C), 125.14 (C), 125.78 (C), 134.00 (C), 134.47 (C), 144.91 (C), 146.54 (C), 156.72 (C); ²⁹Si NMR (99 MHz, CDCl₃) δ 2.72; MS (MALDI) m/z calced for C₆₀H₄₁O₁₂S₄Si ([M+H]+) 1129.3, found: 1129.1; elemental analysis calced for C₆₀H₄₁O₁₂S₄Si: C, 63.80; H, 5.35, found: C, 63.44; H, 5.29.

Synthesis of spirobi[2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2',3',4',5']1',1'-diphenyl-1H-germolo[8,9-b,c,d]:12,1-b',c',d'[dithiophene] (2a)

Anhydrous hexane (7.0 mL) and TMEDA (0.57 mL, 3.83 mmol) were added to 7a (1.37 g, 1.90 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 1.45 mL,
3.86 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (25 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A THF (10 mL) solution of tetrachlorogermane (0.11 mL, 0.964 mmol) was transferred to the reaction mixture via a PTFE tube over 15 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour then was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 2 : 3, v/v) to give 2a (209 mg, 0.138 mmol, 14%) as a yellow solid. mp. 113-115 °C (dec.)°C; ¹H NMR (500 MHz, CDCl₃) δ −0.07 (t, J = 7.5 Hz, 12H), 0.09 (sext, J = 7.5 Hz, 8H), 0.97 (t, J = 7.5 Hz, 12H), 1.06 (t, J = 7.5 Hz, 12H), 1.13 (quint, J = 7.5 Hz, 8H), 1.55-1.60 (m, 8H), 1.66 (sext, J = 7.5 Hz, 12H), 1.80 (quint, J = 8.0 Hz, 8H), 1.93 (quint, J = 7.0 Hz, 8H), 3.67 (t, J = 7.5 Hz, 12H), 4.31 (t, J = 6.5 Hz, 12H), 4.48 (t, J = 6.5 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 12.82 (CH₃), 14.03 (CH₃), 14.09 (CH₃), 17.79 (CH₂), 19.37 (CH₂), 19.46 (CH₂), 30.97 (CH₂), 32.41 (CH₂), 70.15 (CH₂), 72.81 (CH₂), 73.06 (CH₂), 117.06 (C), 124.95 (C), 125.36 (C), 126.22 (C), 132.75 (C), 134.23 (C), 144.85 (C), 146.68 (C), 156.14 (C); MS (MALDI) m/z calcd for Cₘ₄H₁₀₀O₁₂S₂Ge ([M+H]+) 1511.6, found: 1511.7; elemental analysis calcd for Cₘ₄H₁₀₀O₁₂S₂Ge: C, 66.79; H, 7.21, found: C, 66.60; H, 7.26.

**Synthesis of spirobi[2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2',3',4',5'1',1'-diphenyl-1H-germolo[8,9-b,c,d:12,1-b',c',d']dithiophene] (2b)**

Anhydrous hexane (14 mL) and TMEDA (0.27 mL, 1.81 mmol) were added to 7b (482 mg, 0.872 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 0.66 mL, 1.76 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (14 mL) was added to the resulting solid and the mixture was cooled to under −70 °C. A toluene (10 mL) solution of tetrachlorogermane (60 μL, 0.52 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at −70 °C, the mixture was allowed to warm to room temperature and stirred for an hour
then was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 1 : 3, v/v) to give 2b (80 mg, 69.8 µmol, 16%) as a pale yellow solid. mp. 236 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.68 (t, J = 7.0 Hz, 12H), 1.45 (t, J = 7.0 Hz, 12H), 1.59 (t, J = 7.0 Hz, 12H), 3.78 (q, J = 7.0 Hz, 8H), 4.42 (q, J = 7.0 Hz, 8H), 4.58 (q, J = 7.0 Hz, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 15.01 (CH₃), 15.91 (CH₃), 16.01 (CH₃), 66.29 (CH₂), 68.53 (CH₂), 68.87 (CH₂), 116.99 (C), 124.77 (C), 124.96 (C), 125.78 (C), 132.21 (C), 133.79 (C), 145.02 (C), 146.55 (C), 155.92 (C); MS (MALDI) m/z calcd for C₁₀H₁₀O₂S₂Ge [(M⁺)] 1174.2, found: 1174.6; elemental analysis calcd for C₁₀H₁₀O₂S₂Ge: C, 61.38; H, 5.15, found: C, 61.40; H, 5.00.

Synthesis of spirobi[2,3,6,7,10,11-hexabutoxytriphenyleno[4,5-2ʹ,3ʹ,4ʹ,5ʹ]1ʹ,1ʹ-diphenyl-1H-stannolo[8,9-b,c,d:12,1-bʹ,cʹ,dʹ]dithiophene (3a)

Anhydrous hexane (4.0 mL) and TMEDA (0.37 mL, 2.48 mmol) were added to 7a (873 mg, 1.21 mmol) in dried a three-necked-flask under argon atmosphere. n-BuLi in hexane (2.66 M, 0.92 mL, 2.45 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (18 mL) was added to the resulting solid and the mixture was cooled to under -70 °C. A toluene (8 mL) solution of tetrachlorostannane (76 µL, 0.650 mmol) was transferred to the reaction mixture via a PTFE tube over 15 min. After stirring for 30 min at -70 °C, the mixture was allowed to warm to room temperature and stirred for an hour. The solution was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give an orange solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 1 : 1, v/v) to give 3a (480 mg, 0.308 mmol, 51%) as a yellow solid. mp. 126 °C (dec.); ¹H NMR (500 MHz, CDCl₃) δ 0.04 (t, J = 7.5 Hz, 12H), 0.38 (sext, J = 7.5 Hz, 8H), 0.98 (t, J = 7.5 Hz, 12H), 1.06 (t, J = 7.5 Hz, 12H), 1.28 (quint, J = 7.5 Hz, 8H), 1.58 (sext, J = 7.5 Hz, 8H), 1.67 (sext, J = 7.5 Hz, 8H), 1.82 (quint, J = 7.5 Hz, 8H), 1.93 (quint, J = 7.5 Hz, 8H), 3.84 (t, J = 7.5 Hz, 12H), 4.34 (t, J = 6.5 Hz, 12H), 4.50 (t, J = 6.5 Hz, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 12.88 (CH₃), 13
14.03 (CH₃), 14.09 (CH₃), 18.19 (CH₂), 19.38 (CH₂), 19.47 (CH₂), 30.08 (CH₂), 32.45 (CH₂), 32.47 (CH₂), 70.13 (CH₂), 72.81 (CH₂), 73.01 (CH₂), 116.65 (C), 124.05 (C), 124.86 (C), 126.71 (C), 133.05 (C), 134.30 (C), 145.04 (C), 146.57 (C), 157.12 (C); \(^{119}\)Sn NMR (186 MHz, CDCl₃) \(\delta\) -25.86; MS (MALDI) \(m/z\) calcd for C₈₄H₁₀₈O₁₂S₄Sn ([M+H]⁺) 1557.6, found: 1557.4; elemental analysis calcd for C₈₄H₁₀₈O₁₂S₄Sn: C, 64.81; H, 6.99, found: C, 64.82; H, 6.99.

**Synthesis of spirobi[2,3,6,7,10,11-hexaethoxytriphenyleno[4,5-2ʹ,3ʹ,4ʹ,5ʹ]1ʹ,1ʹ-diphenyl-1H-stannolo[8,9-b,c,d:12,1-bʹ,cʹ,dʹ]dithiophene (3b)**

Anhydrous hexane (44 mL) and TMEDA (0.76 mL, 5.10 mmol) were added to 7b (1.36 g, 2.49 mmol) in dried a three-necked-flask under argon atmosphere. \(n\)-BuLi in hexane (2.66 M, 1.87 mL, 4.97 mmol) was added dropwise to the suspension. After the suspension was refluxed for 3 hours, volatiles were removed under reduced pressure. THF (44 mL) was added to the resulting solid and the mixture was cooled to under -70 °C. A toluene (15 mL) solution of tetrachlorostannane (0.15 mL, 1.28 mmol) was transferred to the reaction mixture via a PTFE tube over 10 min. After stirring for 30 min at -70 °C, the mixture was allowed to warm to room temperature and stirred for an hour. The solution was refluxed for 12 hours. After cooling to room temperature, aqueous NH₄Cl was added to the mixture. The reaction mixture was extracted with chloroform and the extract was dried over anhydrous magnesium sulfate. The extract was concentrated under reduced pressure to give a brown solid. The products were purified by silica gel column chromatography (eluent, hexane : CH₂Cl₂ = 1 : 3, v/v) to give 3b (364 mg, 0.299 mmol, 24%) as a pale yellow solid. mp. 236 °C; \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 0.87 (t, \(J = 7.0\) Hz, 12H), 1.48 (t, \(J = 7.0\) Hz, 12H), 1.59 (t, \(J = 7.0\) Hz, 12H), 3.94 (q, \(J = 7.0\) Hz, 8H), 4.46 (q, \(J = 7.0\) Hz, 8H), 4.58 (q, \(J = 7.0\) Hz, 8H); \(^{13}\)C NMR (125 MHz, CDCl₃) \(\delta\) 15.21 (CH₃), 15.98 (CH₃), 16.02 (CH₃), 66.14 (CH₂), 68.59 (CH₂), 68.89 (CH₂), 117.04 (C), 124.19 (C), 124.88 (C), 126.60 (C), 132.92 (C), 134.12 (C), 145.11 (C), 146.41 (C), 156.86 (C); \(^{119}\)Sn NMR (186 MHz, CDCl₃) \(\delta\) -28.72; MS (MALDI) \(m/z\) calcd for C₆₀H₆₀O₁₂S₄Sn ([M+]⁺) 1174.2, found: 1174.6; elemental analysis calcd for C₆₀H₆₀O₁₂S₄Sn: C, 61.38; H, 5.15, found: C, 61.40; H, 5.00.
3. X-ray crystallographic analysis

Table S1. Crystal data for 1b, 2b and 3c.

<table>
<thead>
<tr>
<th></th>
<th>1b</th>
<th>2b</th>
<th>3c</th>
</tr>
</thead>
<tbody>
<tr>
<td>crystal system</td>
<td>triclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P2₁ / n</td>
</tr>
<tr>
<td>a/Å</td>
<td>9.7198(13)</td>
<td>9.7680(7)</td>
<td>9.2728(7)</td>
</tr>
<tr>
<td>b/Å</td>
<td>13.5510(18)</td>
<td>11.2196(8)</td>
<td>21.8232(16)</td>
</tr>
<tr>
<td>c/Å</td>
<td>21.616(3)</td>
<td>25.3543(18)</td>
<td>27.505(2)</td>
</tr>
<tr>
<td>α/deg</td>
<td>104.724(2)</td>
<td>88.261(1)</td>
<td>–</td>
</tr>
<tr>
<td>β/deg</td>
<td>100.877(1)</td>
<td>82.947(1)</td>
<td>88.261(1)</td>
</tr>
<tr>
<td>γ/deg</td>
<td>95.266(2)</td>
<td>86.248(1)</td>
<td>–</td>
</tr>
<tr>
<td>V/Å³</td>
<td>2674.7(6)</td>
<td>2751.0(3)</td>
<td>5523.1(7)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>D_{calc}/g cm(^{-3})</td>
<td>1.402</td>
<td>1.502</td>
<td>1.569</td>
</tr>
<tr>
<td>R₁ (I&gt;2σ(I))</td>
<td>0.0395</td>
<td>0.0352</td>
<td>0.0295</td>
</tr>
<tr>
<td>R₂ (all data)</td>
<td>0.1104</td>
<td>0.0888</td>
<td>0.0723</td>
</tr>
<tr>
<td>goodness of fit</td>
<td>1.023</td>
<td>1.032</td>
<td>1.016</td>
</tr>
<tr>
<td>T/K</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
4. Electrochemical study

**Table S2.** Electrochemical properties of 9b–11b and 1b–3b.

<table>
<thead>
<tr>
<th></th>
<th>$E_{pa}^{1}$ [V]</th>
<th>$E_{pc}^{1}$ [V]</th>
<th>$E_{1/2}^{1}$ [V]</th>
<th>$E_{pa}^{2}$ [V]</th>
<th>$E_{pc}^{2}$ [V]</th>
<th>$E_{1/2}^{2}$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9b</td>
<td>0.45</td>
<td>0.36</td>
<td>0.40</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>10b</td>
<td>0.44</td>
<td>0.35</td>
<td>0.40</td>
<td>0.74</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>11b</td>
<td>0.47</td>
<td>0.34</td>
<td>0.41</td>
<td>0.72</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1b</td>
<td>0.44</td>
<td>0.37</td>
<td>0.40</td>
<td>0.57</td>
<td>0.50</td>
<td>0.54</td>
</tr>
<tr>
<td>2b</td>
<td>0.45</td>
<td>0.38</td>
<td>0.41</td>
<td>0.59</td>
<td>0.51</td>
<td>0.55</td>
</tr>
<tr>
<td>3b</td>
<td>0.44</td>
<td>0.38</td>
<td>0.41</td>
<td>0.58</td>
<td>0.50</td>
<td>0.54</td>
</tr>
</tbody>
</table>

**Fig. S1** Cyclic voltammograms of 10b (0.62 mM) and 11b (0.67 mM) in CH$_2$Cl$_2$ containing 0.1 M $n$-Bu$_4$NClO$_4$ at scan rate of 100 mV s$^{-1}$. 
5. Chemical oxidation of spirobistannasumanene 3b

**Scheme S1** Chemical oxidation of 3b using AgSbF$_6$ as an oxidant.

An anhydrous THF (1 mL) solution of silver hexafluoroantimonate(V) (8.1 mg, 23.6 µmol) was added dropwise to a THF (3 mL) solution of 9b (26 mg, 21.3 µmol) at −78 °C. After stirring for 30 min at the same temperature, the mixture was allowed to warm to room temperature and stirred for an hour. The reaction mixture was concentrated under reduced pressure to give a blue solid. The solid was extracted with dichloromethane and the extract was concentrated under reduced pressure to give a green solid (30.9 mg). An ESR spectrum of the product in CH$_2$Cl$_2$ showed a signal at $g$ value of 2.0061 (Fig. S2).

![ESR spectrum](image)

*Fig. S2* ESR spectrum of the product of the oxidation reaction of 3b using 1 equiv. of AgSbF$_6$, measured in CH$_2$Cl$_2$ at room temperature.

6. Reference

7. NMR charts

$^1$H NMR spectrum of 6a in CDCl$_3$
$^{13}$C NMR spectrum of 6a in CDCl$_3$
$^1$H NMR spectrum of 6b in CDCl$_3$
$^{13}$C NMR spectrum of 6b in CDCl$_3$
$^1$H NMR spectrum of 7a in CDCl$_3$
13C NMR spectrum of 7a in CDCl₃
H NMR spectrum of 7b in CDCl₃
$^{13}$C NMR spectrum of $7b$ in CDCl$_3$
$^1$H NMR spectrum of 9a in CDCl$_3$
$^{29}\text{Si} \text{NMR spectrum of 9a in CDCl}_3$
H NMR spectrum of 9b in CDCl₃

**S36**

**NAME**
S166777

**PROTON**
1

**Date**
2037-01-01

**Time**
23.00

**INSTRUM**
specto

**PROBID**
5 mm PABAO BB-

**PRMSRC**
as50

**SOLVENT**
CDCl₃

**NS**
8

**JMN**
10300.576 Hz

**FIFURES**
0.197623 Hz

**AQ**
3.4173922 sec

**RD**
164

**DE**
48.400 usec

**TE**
381.3 MHz

**TL**
1.00000000 sec

**CHANNEL**
1

**H2C1**
16

**FI**
12.00 usec

**FJ**
3.400 usec

**FW**
15.32224562 W

**F0U1**
500.133091 MHz

**F1**
32748

**F2**
500.1330126 MHz

**NWI**
8N

**FIP**
8N

**FJR**
0.730 Hz

**FPG**
1.000

**9b**
$^{29}$Si NMR spectrum of 9b in CDCl$_3$
$^1$H NMR spectrum of 10a in CDCl$_3$
$^{1}H$ NMR spectrum of 11a in CDCl$_3$
$^{13}$C NMR spectrum of 11a in CDCl$_3$
DEPT-135 of 11a in CDCl₃
$^{119}\text{Sn}$ NMR spectrum of 11a in CDCl$_3$
$^1$H NMR spectrum of $11b$ in CDCl$_3$
$^{13}$C NMR spectrum of 11b in CDCl$_3$
$^{119}$Sn NMR spectrum of 11b in CDCl$_3$
H NMR spectrum of 1a in CDCl₃
$^{13}$C NMR spectrum of 1a in CDCl$_3$
$^{29}$Si NMR spectrum of 1a in CDCl$_3$
$^1$H NMR spectrum of 1b in CDCl$_3$
$^{29}$Si NMR spectrum of 1b in CDCl$_3$
$^{13}$C NMR spectrum of 2a in CDCl$_3$
$^1$H NMR spectrum of 2b in CDCl$_3$
$^{13}$C NMR spectrum of 2b in CDCl$_3$
DEPT-135 of 2b in CDCl$_3$
$^1$H NMR spectrum of 3a in CDCl$_3$
$\text{C NMR spectrum of 3a in CDCl}_3$
$^{119}$Sn NMR spectrum of 3a in CDCl$_3$
$^1$H NMR spectrum of 3b in CDCl$_3$. 

Bruker
$^{13}$C NMR spectrum of 3b in CDCl$_3$
$^{119}\text{Sn} \text{ NMR spectrum of 3b in CDCl}_3$