## **Electronic Supplementary Information**

## Iodine-doped sumanene and its application for the

## synthesis of chalcogenasumanenes and silasumanenes

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### **1. General Information**

All reagents were obtained from commercial sources without further purification, and solvents were used as received except specifically mentioned. Silica gel plate GF254 were used for thin layer chromatography (TLC) and silica gel 300-400 mesh were used for flash column chromatography. All melting points were taken on a SGW X-4A digital melting point apparatus without correction. Infrared spectra were obtained using an AVATAR 370 FT-IR spectrometer. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded with a Bruker AV-500 spectrometer operating at 500 MHz, 125 MHz and 470 MHz, respectively. Mass spectra and high resolution mass spectra were recorded with an Agilent 5975N using an electron impact (EI) or electrospray ionization (ESI) techniques. MALDI-TOF MS (solid-state analyte in DHB matrix) was carried out on a Thermo Fisher Scientific LTQ FT Ultra spectrometer. Ultraviolet spectra were measured on a PEGeneral spectrometer. Fluorescence spectra were recorded on a LS-55 spectrometer. The lifetimes were measured using a FLSP920 fluorescence spectrophotometer. The crystal structure was recorded on on Bruker APEX-II CCD or Siemens SMART CCD X-ray diffraction spectrometer with a graphite-monochromatized MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise indicated. Cyclic voltammetry (CV) was performed on a CHI660B electrochemical analyzer at room temperature in inert atmosphere with a three-electrode configuration in CH<sub>2</sub>Cl<sub>2</sub> solution (distilled from CaH<sub>2</sub>) containing the substrate (typically ~1.00  $\times$  $10^{-4}$  M) and 0.1 M tetrabutylammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>) as the supporting electrolyte. A glassy carbon disc served as the working electrode, a platinum wire and a commercial Ag/Ag<sup>+</sup> electrode (0.1 M AgNO<sub>3</sub> in CH<sub>3</sub>CN) served as the counter and the reference electrodes, respectively. The scan rate was 0.1 V/s. Theoretical calculations were carried out using the Gaussian 09 program.

### 2. Synthesis and Characterization



### 1,5,9-Triiodotriphenylene (7)

A suspension of the triaminotriphenylene  $6^1$  (4.0 g, 14.6 mmol) in a solution of sulfuric acid (30.0 mL) and water (45 mL) was cooled to 0 °C by an ice bath. A solution of sodium nitrite (4.0 g, 58.5 mmol) in water (40 mL) was added dropwisely with stirring. The resulting brown solution was poured into a vigorously stirred solution of potassium iodide (38.9 g, 234 mmol) in water (60 mL) in a 1.5 L beaker, during which foam generated. After stirring for one hour at room temperature, the reaction was heated at 65 °C by a water bath until the foaming disappeared. The solid was filtered, and washed with water and dilute sodium thiosulfate solution, successively. The solid was extracted with dichloromethane  $(1 \times 500 \text{ mL}, 2 \times 50 \text{ mL})$ , and the insoluble solid was filtered off. The combined dichloromethane solution was washed with sodium thiosulfate solution, dried with anhydrous sodium sulfate and filtered. After removing of the solvent in vacuum, compound 7 was obtained as a black solid (4.7 g, 53%). M.p. 201-203 °C. IR (KBr, cm<sup>-1</sup>): 2921, 1542, 1393, 1095, 750, 649; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  9.19 (d, J = 7.9 Hz, 3H), 8.22 (d, J = 7.7 Hz, 3H), 7.15 (dd, J = 7.9, 7.9 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  143.1, 133.0, 132.7, 127.6, 126.3, 90.8; HRMS (DART, Positive) calcd for C<sub>8</sub>H<sub>9</sub>I<sub>3</sub> [M]<sup>+</sup> 605.7833, found 605.7825.



### Triphenyleno[1,12-bcd: 4,5-b'c'd': 8,9-b''c''d'']triiodonium tris(triflate) (2)

A solution of compound **7** (2.18 g, 3.6 mmol) in 100 mL  $CH_2Cl_2$  in a 500 mL flask was cooled to 5 °C by an ice bath. To the solution was added *m*CPBA (8.0 g, 70% wt%, 32.4 mmol) in  $CH_2Cl_2$  and triflic acid with vigorously stirring, during which a sticky black gum formed on the flask-wall. After stirred for 12 h, the solvent was decanted and the residue was washed with  $CH_2Cl_2$  (3×20 mL). Ether (100 mL) was added to the residue and a well-dispersed brown solid precipitated. After stirring for 10 min, the solid was filtered, washed with ether (3×20 mL), and dried, affording **2** as a brown solid (2.58 g, 68%).

M.p. > 300 °C. IR (KBr, cm<sup>-1</sup>): 3083, 1701, 1642, 1549, 1370, 1241, 1176, 1029, 809, 641; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  8.77 (s, 6H); <sup>19</sup>F NMR (470 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  -77.8 (s, CF<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  138.2, 135.8, 133.2, 126.8, 121.2 (q, <sup>1</sup>*J*<sub>C-F</sub> = 319 Hz); HRMS (MALDI-FT/DHB) m/z calcd for C<sub>21</sub>H<sub>6</sub>F<sub>9</sub>I<sub>3</sub>O<sub>9</sub>S<sub>3</sub> [M-3OTf]<sup>3+</sup> 602.7587, found 602.7598.



### Dithieno[2',3',4',5':4,5;2'',3'',4'',5'':8,9]triphenyleno[1,12-cde][1,2]dithiine (8)

To a 500 mL flask was added compound **2** (5.0 g, 4.76 mmol), CuCl<sub>2</sub> (76 mg, 0.57 mmol) and AcSK (8.2 g, 71.43 mmol). After evacuated and backfilled with N<sub>2</sub>, DMSO (100 mL) wad added. After degassed and backfilled with N<sub>2</sub>, the reaction mixture was stirred at 110 °C for 48 h. After the reaction, water (200 mL), DCM (400 mL) and CS<sub>2</sub> (80 mL) were added, followed by vigorously stirring for 30 min. The organic layer was separated and washed with saturated brines once. After dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by evaporator. Then ethyl alcohol (50 mL) was added to the residue and stirred for 15 min. The solid was filtered and washed with EtOH (2×2 mL). The desired product **8** was obtained as a brown solid (707.1 mg, 42%). M.p. >300 °C. IR (KBr, cm<sup>-1</sup>): 3047, 2922, 2856, 1638, 1546, 1448, 1392, 1348, 1147, 1106, 794, 589, 525; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> = 3 : 1):  $\delta$  8.12 (s, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> = 3 : 1):  $\delta$  141.9, 134.1, 131.6, 128.9, 126.6, 125.5, 125.1, 122.7, 121.2; LC-MS (ESI): m/z 350.9 [M+H]<sup>+</sup>; HRMS (DART Positive) calcd for C<sub>18</sub>H<sub>6</sub>S<sub>4</sub> [M+H]<sup>+</sup> 350.9425, found 350.9422.



### **General Procedure:**

An oven-dried Schlenk tube was charged with compound 2 (147 mg, 0.14 mmol), Cs<sub>2</sub>CO<sub>3</sub> (684 mg, 2.1 mmol) and sulfur powder (54 mg, 0.21 mmol). The Schlenk tube was evacuated and backfilled with N<sub>2</sub>, followed by the addition of DMSO (5 mL). After degassed and backfilled with N<sub>2</sub>, the reaction mixture was stirred at the temperature of **80 °C**, **100 °C**, **120 °C**, and **140 °C**, respectively, and for the time of **12** h or **24** h. After the reaction, water (10 mL), DCM (30 mL) and CS<sub>2</sub> (6 mL) were

added, followed by vigorously stirring for 30 min. The organic layer was separated and washed with saturated brines once. After dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by evaporator. Then EtOH (10 mL) was added to the residue and stirred for 15 min. The solid was filtered and washed with ethyl alcohol ( $2\times 2$  mL). The desired products were obtained as a brown solid. The distribution of the products is shown in **Table S1**.

Entry	Temp. (°C)	Time (h)	Product ( <b>8</b> / <b>9</b> ) (molar ratio) <sup>b</sup>	Weight	Yield of <b>8</b> or <b>9</b>
1	140	12	1:0.07	22.9 mg	47% <sup>c</sup>
2	120	12	1:0.86	32.4 mg	-
3	120	24	1:0.34	25.5 mg	-
4	100	12	1:2.55	27.6 mg	-
5	80	12	1:5.38	24.9 mg	40% <sup>d</sup>

Table S1. The effect of temperature and time on the transformation of 2 to 8 and  $9^{a}$ .

<sup>*a*</sup>Reaction conditions: **2** (147 mg, 0.14 mmol), sulfur powder (54 mg, 0.21 mmol),  $Cs_2CO_3$  (684 mg, 2.1 mmol), DMSO (5 mL), N<sub>2</sub>. <sup>*b*</sup>Determined by <sup>1</sup>H NMR. <sup>*c*</sup>Yield of **8**. <sup>*d*</sup>Yield of **9**.

### **Characterization of** $(9)^2$

Compound **9** contaminated with ~ 15% of **8**, which can not be separated, but they are distinguishable from the <sup>1</sup>H NMR spectrum. M.p. > 300 °C. IR (KBr, cm<sup>-1</sup>): 3056, 2919, 2852, 1620, 1546, 1406, 1331, 1135, 1117, 804, 612, 532. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> = 3 : 1):  $\delta$  7.99 (d, *J* =8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.61 (s, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> = 3 : 1):  $\delta$  138.9, 130.9, 130.8, 129.6, 127.9, 126.5, 126.2, 125.9, 122.1; LC-MS (ESI): m/z 382.9 [M+H]<sup>+</sup>; HRMS (DART, Positive) for **9**: calcd for C<sub>18</sub>H<sub>6</sub>S<sub>5</sub> [M+H]<sup>+</sup> 382.9146, found 382.9141.



### Trithiasumanene $(3)^3$

To a 100 mL flask was added compound **8** (385 mg, 1.1 mmol), copper powder (7.04 g, 0.11 mol) and tetralin (15 mL). After evacuated and backfilled with N<sub>2</sub>, the mixture was heated to 200 °C by an oil bath for 2 h. After cooled down, DCM (100 mL) was added and the mixture was stirred for 10 min. The mixture was filtered through a pad of silica gel and washed with DCM ( $2 \times 10$  mL). A clear brown solution was obtained. DCM was removed by evaporator, followed by removal of the tetralin by distillation.

To the residue, hexane (15 mL) was added. The solid was filtered and washed with hexane (2×2 mL) to give the crude product, which was contaminated with some amount of triphenyleno[1,12-bcd:4,5-b'c'd']dithiophene. Pure trithiasumanene **3** was obtained by recrystallization from hot tetralin (1.5 mL) as light brown needles (86.6 mg, 25%). M.p. > 300 °C. IR (KBr, cm<sup>-1</sup>): 2921, 2855, 1512, 1387, 1146, 868, 785, 674, 617, 533; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.01 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> = 5 : 1):  $\delta$  141.2, 135.7, 122.7; LC-MS (ESI): m/z 319.0 [M+H]<sup>+</sup>; HRMS (DART, Positive) for **3**: calcd for C<sub>18</sub>H<sub>6</sub>S<sub>3</sub> [M+H]<sup>+</sup> 318.9704, found 318.9699.



#### **Trithiasumanene (3)**

To an oven-dried Schlenk tube was added compound **9** (10 mg, 0.026 mmol), copper powder (133 mg, 2.08 mmol) and tetralin (0.5 mL). After evacuated and backfilled with N<sub>2</sub>, the mixture was heated to 200 °C by an oil bath for 1 h. After cooled down, DCM (10 mL) was added and the mixture was stirred for 10 min. The mixture was filtered through a pad of silica gel and washed with DCM ( $2\times5$  mL). A clear yellow solution was obtained. DCM was removed by evaporator, followed by removal of the tetralin by distillation. To the residue, hexane (3 mL) was added. The solid was filtered and washed with hexane ( $2\times2$  mL). The desired product was obtained as a light yellow solid (4.8 mg, 58%).



Diselenopheno[2',3',4',5':4,5;2'',3'',4'',5'':8,9]triphenyleno[1,12-*cde*][1,2]diselenin e (11) and triphenyleno[1,12-*bcd*:4,5-*b'c'd'*:8,9-*b''c''d''*]tris(selenophene) (4) An oven-dried Schlenk tube was charged with compound 2 (315 mg, 0.3 mmol), KO<sup>t</sup>Bu (505 mg, 4.5 mmol) and selenium powder (213.3 mg, 2.7 mmol). The Schlenk

tube was evacuated and backfilled with N<sub>2</sub>, followed by the addition of DMSO (8 mL). After degassed and backfilled with N<sub>2</sub>, the reaction mixture was stirred at 70 °C for 24 h. After the reaction, water (15 mL), DCM (60 mL) and CS<sub>2</sub> (10 mL) were added, followed by vigorously stirring for 30 min. The organic layer was separated and washed with saturated brines once. After dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by evaporator. Then ethanol (20 mL) was added to the residue and stirred for 15 min. The solid was filtered and washed with ethanol ( $2\times 2$  mL). Then the crude product was afforded as a reddish brown solid (67.5 mg). <sup>1</sup>H NMR analysis indicated the crude product contained a mixture of **4** and **10**, which are difficult to separate. Thus, the mixture was heated with copper powder to convert compound **10** to **4** as followed.

The solid (67.5 mg), copper powder (173 mg, 2.7 mmol) and tetralin (4 mL) were added to an oven-dried Schlenk tube. After evacuated and backfilled with N<sub>2</sub>, the mixture was heated to 200 °C in an oil bath for 1 h. After cooled, DCM (20 mL) was added and the mixture was filtered through a pad of silica gel and washed with DCM (2×20 mL). After removal of the DCM, most of tetralin was distilled by an oil pump. To the residue, hexane (5 mL) was added. The solid was filtered and washed with hexane (2×2 mL) to remove remained tetralin. The desired product **4** was obtained a light yellow solid (30.6 mg, 22% yield of two steps). The solid was fundamentally pure by proton NMR analysis. Simple washing of the solid by a small amount of DCM could give the product **4** in high purity.

Characterization of compound **10**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.17 (s, 2H), 8.03 (d, J = 7.9 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H). <sup>13</sup>C NMR of **10** could not be assigned due to its minor amount in an inseparable mixture. LC-MS (ESI): m/z 542.7[M(4Se<sup>80</sup>)+H]<sup>+</sup>, 540.7 [M(3Se<sup>80</sup>+1Se<sup>78</sup>)+H]<sup>+</sup>, 538.7 [M(2Se<sup>80</sup>+2Se<sup>78</sup>)+H]<sup>+</sup>. HRMS (DART, Positive): calcd for C<sub>18</sub>H<sub>6</sub>Se<sub>4</sub> [M(4Se<sup>80</sup>)+H]<sup>+</sup> 542.7203, found 542.7202.

Characterization of compound **4**: M.p. > 300 °C. IR (KBr, cm<sup>-1</sup>): 3054, 1640, 1550, 1384, 1139, 790, 676, 507. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> = 5 : 1):  $\delta$  8.22 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub> = 5 : 1):  $\delta$  137.1, 134.7, 124.5; LC-MS (ESI): m/z 462.8 [M(3Se<sup>80</sup>)+H]<sup>+</sup>, 460.8 [M(2Se<sup>80</sup>+1Se<sup>78</sup>)+H]<sup>+</sup>, 458.8 [M(1Se<sup>80</sup>+2Se<sup>78</sup>)+H]<sup>+</sup>; HRMS (DART, Positive): calcd for C<sub>18</sub>H<sub>6</sub>Se<sub>3</sub> [M(3Se<sup>80</sup>)+H]<sup>+</sup> 462.8038, found 462.8036.



**1,4,5,8,9,12-Hexaiodotriphenylene** (11)<sup>4</sup>

To a 250 mL flask was added compound **2** (3.45 g, 3.29 mmol), KI (4.93 g, 29.7 mmol), CuI (0.75 g, 3.94 mmol) and *trans-N',N''*-dimethylcyclohexane-1,2-diamine (1.13 g, 7.94 mmol). DMSO (65 mL) was added, and the mixture was evacuated and backfilled with N<sub>2</sub>. Then, the mixture was heated to 70 °C under a nitrogen atmosphere for 20 h. After cooled down, the mixture was poured into a diluted ammonia solution (400 mL, containing 25 mL concentrated ammonia) with stirring. The precipitation was filtered and washed with water (3×30 mL), ethanol (2×20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL), successively. The solid was dried in vacuum to afford the desired 1,4,5,8,9,12-hexaiodotriphenylene **11** (2.35 g, 73%) as a mixture of  $C_2$  and  $D_3$  isomers which show poor solubility in most common solvents except only sparingly soluble in DMSO. The poor solubility precluded <sup>13</sup>C NMR and MS characterization. M.p. > 300 °C. IR (KBr, cm<sup>-1</sup>): 3042, 2930, 2856, 1570, 1414, 1357, 1108, 1026, 807, 673; <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ , 80 °C) for major isomer ( $C_2$ -**11**):  $\delta$  8.78 (s, 2H), 8.59 (d, J = 8.1 Hz, 2H), 8.34 (d, J = 8.6 Hz, 2H); for minor isomer ( $D_3$ -**11**):  $\delta$  8.05 (s, 6H).



**Fig. S1** Variant temperature <sup>1</sup>H NMR of 1,4,5,8,9,12-hexaiodotriphenylene **11**.



# Thieno[2',3',4',5':8,9]triphenyleno[1,12-cde:4,5-c'd'e']bis([1,2]dithiine)(9),dithieno[2',3',4',5':4,5;2'',3'',4'',5'':8,9]triphenyleno[1,12-cde][1,2]dithiine(8),andTrithiasumanene (3)

An oven-dried Schlenk tube was charged with compound **11** (885 mg, 0.9 mmol), CuI (154 mg, 0.81 mmol),  $K_2CO_3$  (1.5 g, 10.8 mmol), and sulfur powder (346 mg, 10.8 mmol). The Schlenk tube was evacuated and backfilled with N<sub>2</sub>, followed by the addition of DMF (20 mL). After degassed and backfilled with N<sub>2</sub>, the reaction mixture was stirred at 120 °C for 7 h. After the reaction, most of DMF was evaporated. To the residue, diluted ammonia (30 mL) and DCM (200 mL) were added, followed by vigorously stirring for 15 min. The insoluble solid was filtered off. The organic layer was separated and washed with dilute ammonia once. After dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed to afford the crude product as a reddish brown solid (294 mg). The crude product was purified by washing with DCM (10 mL) to give a yellow solid (150 mg), which includes a mixture of **8** and **9**. The ratio did not change after purification. The two compounds are inseparable, but they are distinguishable from the <sup>1</sup>H NMR spectrum. The spectra of the products are consistent with the methods from the iodium salt **2**.

To an oven-dried Schlenk tube was added a mixture of **8** and **9** (50 mg, purified by washing with DCM), copper powder (800 mg, 12.5 mmol) and tetralin (3 mL). After evacuated and backfilled with N<sub>2</sub>, the mixture was heated to 210 °C by an oil bath for 3 h. After cooled down, DCM (20 mL) was added and the mixture was stirred for 10 min. The mixture was filtered through a pad of silica gel and washed with DCM (2×10 mL). A clear yellow solution was obtained. DCM was removed by evaporator, followed by removal of the tetralin by distillation. To the residue, hexane (2 mL) was added. The solid was filtered and washed with hexane (2×2 mL). The desired product **3** was obtained as a light yellow solid (24 mg, 25% yield of two steps). <sup>1</sup>H NMR shows it is essentially pure. A light yellow needle could be obtained by slow evaporation of the solution of **3** in CS<sub>2</sub>-hexane (2/1).



Diselenopheno[2',3',4',5':4,5;2'',3'',4'',5'':8,9]triphenyleno[1,12-cde][1,2]diselenin e (11) and triphenyleno[1,12-bcd:4,5-b'c'd':8,9-b"c"d"]tris(selenophene) (4) An oven-dried Schlenk tube was charged with compound 11 (295 mg, 0.3 mmol), CuI (11.5 mg, 0.06 mmol), K<sub>2</sub>CO<sub>3</sub> (248 mg, 1.8 mmol), and selenium powder (142.2 mg, 1.8 mmol). The Schlenk tube was evacuated and backfilled with N<sub>2</sub>, followed by the addition of DMF (10 mL). After degassed and backfilled with N2, the reaction mixture was stirred at 120 °C for 27 h. After the reaction, most of DMF was evaporated by distillation. To the residue, DCM (90 mL) was added, followed by vigorously stirring for 15 min. The insoluble solid was filtered off through a pad of diatomite. The organic layer was separated and washed with dilute ammonia once. After dried over Na<sub>2</sub>SO<sub>4</sub> and filtrated through a pad of silica gel, the solvent was removed to afford the crude product as a reddish brown solid (76 mg). Proton NMR analysis indicated the crude product contained inseparable compound 4 and 10. Thus, the mixture was heated with copper powder to remove compound 10 as followed. The solid (76 mg), copper powder (190 mg, 2.97 mmol) and tetralin (6 mL) were added to a oven-dried Schlenk tube. After evacuated and backfilled with N<sub>2</sub>, the mixture was heated to 210 <sup>o</sup>C in an oil bath for 2 h. After cooled, DCM (50 mL) was added and the mixture was filtered through a pad of silica gel and washed with DCM ( $3 \times 25$  mL). After removal of the DCM, most of tetralin was distilled by an oil pump. The residue was washed with hexane to remove remained tetralin. The desired product 4 was obtained a light yellow solid (48 mg, 35% yield of two steps).



**3,3,6,6,9,9-Hexamethyltriphenyleno-[1,12**-*bcd*:**4,5**-*b'c'd'*:**8,9**-*b''c''d''*]trisilole (5): An oven-dried Schlenk tube was charged with compound **11** (98.4 mg, 0.1 mmol).

The Schlenk tube was evacuated and backfilled with N<sub>2</sub>, followed by the addition of THF (1 mL) and toluene (1 mL). After cooled down to -78 °C, *n*-BuLi (2.5 M in hexane; 0.53 mL, 1.32 mmol) was added to the mixture. After stirred for 2 h from -78 °C to -50 °C, dichlorodimethylsilane (0.15 mL, 1.5 mmol) was added dropwise at -78 °C to the solution and the mixture was then warmed to room temperature slowly. After stirred overnight, water (2 mL) was added and the mixture was extracted with dichloromethane (2×10 mL). The organic layer was separated and washed with saturated brines once. After dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed by evaporator. Then the residue was purified by preparative TLC (100% petroleum ether) to afford **5** (3.2 mg, 8%) as a white solid. M.p. 226-228 °C. IR (KBr, cm<sup>-1</sup>): 3026, 2956, 2898, 1455, 1357, 849, 773, 667; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.87 (s, 6H), 0.60 (s, 18H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  138.5, 138.4, 130.9, -2.3; HRMS (DART, Positive) m/z calcd for C<sub>24</sub>H<sub>24</sub>Si<sub>3</sub> [M]<sup>+</sup> 396.1186, found 396.1180.

### 3. X-ray Crystallography of 3 and 5

Suitable single crystals for X-ray crystallography of **3** were obtained as colorless cuboid by crystallization from hot tetralin, and the single crystals for X-ray crystallography of **5** were obtained by slow evaporation of a solution in hexane. The crystal structure was recorded on Bruker APEX-II CCD or Siemens SMART CCD X-ray diffraction spectrometer with a graphite-monochromatized MoK $\alpha$  ( $\lambda = 0.71073$  Å) radiation at 296(2) K. The structure was solved and refined by SHELXL-97. The crystallographic details are given in the attached CIF file. The crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (no. 1544157 for **3**, and no. 1519866 of compound **5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif.

Compound	3	5
Formula	C <sub>18</sub> H <sub>6</sub> S <sub>3</sub>	$C_{24}H_{24}Si_3$
CCDC No.	1544157	1519866
Solvent	tetralin	hexane
Crystal dimensions	0.22×0.06×0.05 mm	0.23×0.20×0.05 mm
Crystal color	colorless	colorless
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space	Monoclinic, P2(1)	Monoclinic, P2(1)/c
group		
a	9.785(3) Å	12.0400(14) Å
b	7.3055(19)Å	20.685(2) Å
С	9.929(3) Å	18.893(2) Å
α	90.00°	90.00°
β	118.840(2)°	93.345(2)°
γ	90.00°	90.00°
Volume	$621.7(3)\text{\AA}^3$	4697.4(10) Å <sup>3</sup>
Ζ	2	8
Absorption coefficient	$0.581 \text{ mm}^{-1}$	0.208 mm <sup>-1</sup>
F(000)	324	1680
Theta range for data	2.34-26.43°	2.19-21.32°
collection		
Goodness-of-fit on $F^2$	1.045	0.806
Final R indices $[I >$	R1 = 0.0317	R1 = 0.0557,
2sigma(I)]	wR2 = 0.0700	wR2 = 0.1687
R indices (all data)	R1 = 0.0361	R1 = 0.1372,
	wR2 = 0.0732	wR2 = 0.2445
Flack parameter	-0.11(9)	-

Table S2 X-ray crystallographic structure and data for 3 and 5



**Fig. S2** X-ray crystallographic structure of trithiasumanene **3**. Thermal ellipsoids are drawn at the 50% probability level.



**Fig. S3** X-ray crystallographic structure of trisilasumanene **5**. Thermal ellipsoids are drawn at the 50% probability level.

## 4. Photophysical Properties



Fig. S4 UV-Vis absorption (solid curves) and emission spectra (dotted curves) of trithiasumanene 3 (red) and triselenasumanene 4 (black) in  $CH_2Cl_2$ .



Fig. S5 UV-Vis absorption (solid curves) and emission spectra (dotted curves) of 8 in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. S6 UV-Vis absorption (solid curves) and emission spectra (dotted curves) of trisilasumanene 5 in  $CH_2Cl_2$ .



Fig. S7 Time-resolved emission decay of compound 3 and 5 in dichloromethane solution.

## **5. Electrochemical Properties**



**Fig. S8** Cyclic voltammograms (red curves) of trithiasumanene **3**, triselenasumanene **4** and compound **8** in  $CH_2Cl_2$  containing 0.10 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>. Scan rate: 100 mV/s. The potentials were calibrated using the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (0.12 V *vs.* Ag/Ag<sup>+</sup>) as an external standard which was measured under the same condition before and after measurement of the samples.

### 6. Theoretic Calculations

All calculations were carried out with the GAUSSIAN 09 program package.<sup>5</sup> All the minima and transition states were calculated using the density functional theory (DFT) in the gas phase a 6-31G(d) basis set<sup>6</sup> for all atoms except iodine atoms, which have been described by the LANL2DZ basis set.<sup>7</sup> Optimized minima and transition states are verified by vibrational analysis at the same level to have no and one imaginary frequency, respectively. Zero point energy (ZPE) was obtained from harmonic vibrational frequency calculations. The intrinsic reaction coordinate (IRC) analysis was performed to confirm that the stationary points are smoothly connected.

### **6.1 Predicted Geometries**



Fig. S9 Geometry predicted by DFT.

### 6.2 Theoretic Investigation for the Interconversion of C<sub>2</sub>-11 and D<sub>3</sub>-11

The geometry of  $C_2$ -11,  $D_3$ -11, TS-11 was optimized by DFT calculation at the B3LYP level of theory using 6-311+G(d,p) basis set in gas phase for all the atoms except iodine atoms, which has been described by the LANL2DZ basis set. Harmonic frequency calculations were performed at the same level for every structure to confirm it as a local minimum or transition state and to derive the thermochemical corrections (ZPE) for enthalpies and free energies. The intrinsic reaction coordinate (IRC) analysis was carried out to confirm that the stationary points are smoothly connected to each other.



**Fig. S10** DFT calculated geometry of  $C_2$ -11,  $D_3$ -11 and the transition state **TS-11** and the energy profile. The interconversion rate  $k = 1.16 \times 10^{-4} \text{ s}^{-1}$  at 473 K, according to Erying equation:  $\Delta G = \text{RT} \ln(k_{\text{B}}\text{T/hk})$ , where  $\Delta G$  is the activation energy (J • mol<sup>-1</sup>), R is the gas constant 8.314 J • mol<sup>-1</sup> • K<sup>-1</sup>, T is the absolute temperature (K), K<sub>B</sub> is the Boltzmann constant (1.38×10<sup>-23</sup> J • K<sup>-1</sup>), h is the Planck constant (6.626×10<sup>-34</sup> J • S). The high energy barrier indicates that the interconversion of  $C_2$ -11 and  $D_3$ -11 is only possible at high temperature (200 °C,  $t_{1/2} = (\ln 2)/2k = 0.8$  h).

### Appendix I: Calculated Energies and Geometrical Coordinates of 11



 $C_2$ -11: E(B3LYP) = -757.892943 hartree; Zero-point correction= 0.17409 Hartree; Sum of electronic and zero-point Energies = -757.718851 Hatree. Coordinates at B3LYP/6-311+G(d,p)/ LANL2DZ level:

Tag	Symbol	Х	Y	Z	Tag	Symbol	Х	Y	Z
1	С	-0.3746920	0.6080970	-1.1052840	16	С	-0.3746920	-3.5010200	1.2484920
2	С	0.3746920	-0.6080970	-1.1052840	17	С	-0.7441600	-2.8044780	2.3893190
3	С	0.2160060	-1.4270080	0.1136400	18	С	-0.6933590	-1.4177520	2.3885990
4	С	-0.1021790	-0.7269070	1.3215230	19	I	-2.8621360	2.0099910	-2.3096320
5	С	0.1021790	0.7269070	1.3215230	20	I	2.8621360	-2.0099910	-2.3096320
6	С	-0.2160060	1.4270080	0.1136400	21	I	-0.2492130	-4.0349050	-1.6629860
7	С	0.6933590	1.4177520	2.3885990	22	L	-1.8654640	-0.4605400	3.9022480
8	С	0.7441600	2.8044780	2.3893190	23	L	1.8654640	0.4605400	3.9022480
9	С	0.3746920	3.5010200	1.2484920	24	I	0.2492130	4.0349050	-1.6629860
10	С	0.0040870	2.8222720	0.0904580	25	н	1.1514090	3.3434650	3.2340130
11	С	-1.0065140	0.9560080	-2.3135750	26	н	0.4931720	4.5760940	1.2302340
12	С	-0.5583650	0.4198460	-3.5142170	27	н	-1.0323730	0.6909730	-4.4483220
13	С	0.5583650	-0.4198460	-3.5142170	28	н	1.0323730	-0.6909730	-4.4483220
14	С	1.0065140	-0.9560080	-2.3135750	29	н	-0.4931720	-4.5760940	1.2302340
15	С	-0.0040870	-2.8222720	0.0904580	30	н	-1.1514090	-3.3434650	3.2340130



 $D_3$ -11: E(B3LYP) = -757.886157 hartree; Zero-point correction= 0.173552 Hartree; Sum of electronic and zero-point Energies = -757.712606 Hatree. Coordinates at B3LYP/6-311+G(d,p)/ LANL2DZ level:

Tag	Symbol	Х	Y	Z	Tag	Symbol	Х	Y	Z
1	С	-0.7057650	1.2455460	0.0883980	16	С	3.4886850	-1.2928440	0.3144320
2	С	0.7057650	1.2455460	-0.0883980	17	С	2.8639780	-2.3748680	-0.3144320
3	С	1.4315570	-0.0115620	0.0883980	18	С	1.4939420	-2.3596430	-0.4907660
4	С	0.7257910	-1.2339830	-0.0883980	19	I	-3.7289390	1.3371570	-1.7560830
5	С	-0.7257910	-1.2339830	0.0883980	20	I	-3.0224810	2.5607770	1.7560830
6	С	-1.4315570	-0.0115620	-0.0883980	21	I	3.0224810	2.5607770	-1.7560830
7	С	-1.4939420	-2.3596430	0.4907660	22	I	3.7289390	1.3371570	1.7560830
8	С	-2.8639780	-2.3748680	0.3144320	23	I	0.7064570	-3.8979340	-1.7560830
9	С	-3.4886850	-1.2928440	-0.3144320	24	I	-0.7064570	-3.8979340	1.7560830
10	С	-2.7904820	-0.1139700	-0.4907660	25	н	-3.4512970	-3.2274000	0.6281160
11	С	-1.2965400	2.4736130	0.4907660	26	н	-4.5206590	-1.3752110	-0.6281160
12	С	-0.6247070	3.6677120	0.3144320	27	н	-1.0693620	4.6026110	0.6281160
13	С	0.6247070	3.6677120	-0.3144320	28	н	1.0693620	4.6026110	-0.6281160
14	С	1.2965400	2.4736130	-0.4907660	29	н	4.5206590	-1.3752110	0.6281160
15	С	2.7904820	-0.1139700	0.4907660	30	Н	3.4512970	-3.2274000	-0.6281160



**TS-11:** E(B3LYP) = -757.833517 Hartree; Zero-point correction= 0.172918 Hartree; Sum of electronic and zero-point Energies = -757.660599 Hatree. Coordinates at B3LYP/6-311+G(d,p)/ LANL2DZ level:

Tag	Symbol	Х	Y	Z	Tag	Symbol	Х	Y	Z
1	С	0.9922200	0.8267590	0.4251790	16	С	-0.3619020	-3.7409870	-0.4230500
2	С	1.3465830	-0.4661930	0.0117780	17	С	-1.6586830	-3.3408900	-0.6818580
3	С	0.2429630	-1.4118550	-0.1485470	18	С	-2.0845390	-2.0407960	-0.4047830
4	С	-1.1517380	-0.9702980	-0.2547420	19	I	1.8064470	3.4794350	-1.4598100
5	С	-1.3814750	0.5241830	-0.3715770	20	I	1.1976730	3.1933930	2.4143810
6	С	-0.2052660	1.3394830	-0.2442960	21	I	3.5211210	-1.9471840	-1.6894290
7	С	-2.5300020	1.2790150	-0.8096890	22	I	2.0374850	-3.5962990	1.3238360
8	С	-2.3748650	2.4828550	-1.4837460	23	I	-4.1620250	-2.2606050	0.1538570
9	С	-1.1351190	3.0738290	-1.6652900	24	I	-4.6178010	1.2086660	-0.2317600
10	С	-0.0662360	2.5437100	-0.9808020	25	н	-3.2472460	2.9936400	-1.8654040
11	С	1.8772220	1.5541310	1.2358850	26	н	-1.0338960	3.9516070	-2.2880480
12	С	3.1916630	1.1340720	1.3623560	27	н	3.8849830	1.6600030	2.0049980
13	С	3.6444090	0.0865440	0.5514000	28	н	4.7058870	-0.1092860	0.4746390
14	С	2.7363320	-0.7026070	-0.1367070	29	н	-0.1124820	-4.7935320	-0.4313930
15	С	0.5344270	-2.7885310	0.0097180	30	Н	-2.3868470	-4.0994340	-0.9291340

Appendix II: Calculated geometrical coordinates and HOMO/LUMO orbitals of iodine-doped sumanene [2-3OTf]<sup>3+</sup> and 2, chalcogenasumanenes 3 and 4, and silasumanene 5



[2-30Tf]<sup>3+</sup>

Tag	Symbol	Х	Y	Z	Tag	Symbol	Х	Y	Z
1	С	0.0074120	1.4170910	-0.0000420	15	С	2.4133320	-1.4413330	0.0000660
2	С	1.2235380	0.7149340	-0.0001800	16	С	2.4532870	-2.8252930	0.0001520
3	С	1.2235310	-0.7149650	-0.0000420	17	С	1.2201240	-3.5372610	0.0001010
4	С	0.0073820	-1.4170820	-0.0001800	18	С	0.0415650	-2.8106640	-0.0000580
5	С	-1.2309430	-0.7021260	-0.0000420	19	I	-2.0304470	3.5167970	-0.0000130
6	С	-1.2309200	0.7021480	-0.0001800	20	I	4.0608580	0.0000200	-0.0000130
7	С	-2.4548970	-1.3693400	0.0000660	21	I	-2.0304120	-3.5168170	-0.0000130
8	С	-3.6734190	-0.7119620	0.0001520	22	н	-4.6282180	-1.2287260	0.0002820
9	с	-3.6734190	0.7119720	0.0001010	23	н	-4.6282580	1.2287330	0.0001950

10	С	-2.4548890	1.3693360	-0.0000580	24	н	1.2500010	4.6225170	0.0002820
11	С	0.0415650	2.8106730	0.0000660	25	н	3.3782430	3.3938230	0.0001950
12	С	1.2201320	3.5372560	0.0001520	26	н	3.3782170	-3.3937910	0.0002820
13	С	2.4532960	2.8252880	0.0001010	27	н	1.2500150	-4.6225560	0.0001950
14	с	2.4133240	1.4413280	-0.0000580					



Iodine-doped sumanene 2

Tag	Symbol	Х	Y	Z	Tag	Symbol	Х	Y	Z
1	С	-1.014796	1.010529	-0.028791	27	S	3.685014	-6.029482	-0.522659
2	С	0.32712	1.381147	-0.200685	28	0	4.642161	-6.452544	-1.538543
3	С	1.34608	0.381644	-0.308754	29	0	2.371991	-6.699069	-0.436211
4	С	0.996222	-0.975114	-0.242341	30	0	-5.637852	-0.781036	0.580276
5	С	-0.370624	-1.362481	-0.066838	31	С	-7.822247	-0.634534	-0.876854
6	С	-1.362636	-0.376376	0.039208	32	F	-9.058836	-0.139421	-0.942819
7	С	-0.707554	-2.712131	-0.00201	33	F	-7.870994	-1.961945	-1.026179
8	С	-2.032834	-3.094565	0.171493	34	F	-7.092694	-0.116234	-1.878653
9	С	-3.048947	-2.109975	0.282599	35	S	-7.048184	-0.194896	0.754329
10	С	-2.681857	-0.775826	0.211133	36	0	-7.833837	-0.884369	1.771439
11	С	-2.007078	1.981886	0.076618	37	0	-6.978031	1.279601	0.764223
12	С	-1.675445	3.330441	0.011661	38	0	2.113379	5.317387	-0.46679
13	С	-0.322688	3.723048	-0.162114	39	С	3.453862	6.879753	1.165799
14	С	0.641244	2.732826	-0.262428	40	F	4.501633	7.69582	1.286438
15	С	2.675266	0.759946	-0.480315	41	F	3.60923	5.845145	2.009402
16	С	3.669046	-0.206109	-0.588961	42	F	2.340843	7.539812	1.50124
17	С	3.332717	-1.583387	-0.523802	43	S	3.331496	6.248087	-0.577399
18	С	2.001805	-1.927334	-0.350128	44	0	4.55422	5.446867	-0.783785
19	I	-3.944783	0.983364	0.341237	45	0	3.086363	7.416651	-1.414543
20	I	2.782916	2.95222	-0.529864	46	н	-2.324392	-4.138685	0.22725
21	I	1.123203	-3.906107	-0.212673	47	н	-4.085089	-2.394518	0.421204
22	0	3.494173	-4.505342	-0.468512	48	н	-2.42773	4.109013	0.09037
23	С	4.503097	-6.345455	1.115824	49	н	-0.050846	4.770518	-0.214952
24	F	3.714759	-5.901781	2.108702	50	н	4.712622	0.059625	-0.725313
25	F	5.674557	-5.705282	1.181559	51	н	4.097194	-2.346386	-0.608811
26	F	4.707627	-7.653213	1.279033					



### Trithiasumanene 3

Tag	Symbol	Х	Y	Z	Tag	Symbol	Х	Y	Z
1	С	-1.388827	0.193596	0.433816	15	С	1.616563	2.216993	0.073214
2	С	-0.538873	1.294495	0.433544	16	С	2.980822	1.991794	-0.205309
3	С	0.862114	1.105998	0.433569	17	С	3.520072	0.678787	-0.205508
4	С	1.390626	-0.180507	0.433701	18	С	2.70814	-0.440325	0.073191
5	С	0.526797	-1.299494	0.433893	19	н	0.613904	-4.553807	-0.490458
6	С	-0.851577	-1.113972	0.433995	20	н	-1.796395	-4.229319	-0.4904
7	С	1.111649	-2.508427	0.073592	21	н	-4.250822	1.745332	-0.490138
8	С	0.234513	-3.577296	-0.204877	22	н	-2.764647	3.670389	-0.490346
9	С	-1.172197	-3.387942	-0.204823	23	н	3.636876	2.808609	-0.490749
10	С	-1.735357	-2.12519	0.073801	24	н	4.560871	0.55889	-0.490952
11	С	-2.72823	0.291484	0.07358	25	S	-3.373246	-1.385814	-0.164807
12	С	-3.215361	1.58556	-0.204838	26	S	2.886747	-2.228384	-0.165171
13	С	-2.347999	2.709146	-0.204884	27	S	0.486448	3.614143	-0.165892
14	С	-0.972707	2.565427	0.073169					







Tris	elenasun	nanene 4							
Tag	Symbol	Х	Y	Z	Tag	Symbol	Х	Y	Z
1	С	0.04025	1.402124	0.000218	15	С	2.40696	-1.417421	-0.000159
2	С	1.227827	0.678162	0.000092	16	С	2.348483	-2.820812	-0.000234
3	С	1.194085	-0.7359	-0.000009	17	С	1.102757	-3.500968	-0.000181
4	С	-0.02665	-1.402424	0.000026	18	С	-0.109266	-2.791218	-0.000087
5	С	-1.234309	-0.666165	0.000149	19	н	-4.589407	-1.106948	0.00026
6	С	-1.201155	0.724308	0.000241	20	н	-4.531437	1.324544	0.000429
7	С	-2.430866	-1.375837	0.000148	21	н	1.336049	4.528174	0.000333
8	С	-3.617017	-0.623549	0.00029	22	н	3.41275	3.262306	0.000096
9	С	-3.583191	0.795344	0.000394	23	н	3.25326	-3.421353	-0.000398
10	С	-2.362534	1.490206	0.000338	24	н	1.118597	-4.586758	-0.000313
11	С	0.023969	2.793247	0.000301	25	Se	3.824959	-0.091252	-0.000386
12	С	1.268474	3.444378	0.000319	26	Se	-1.833455	3.357855	0.000212
13	С	2.480359	2.705606	0.000177	27	Se	-1.991499	-3.266623	-0.000202
14	С	2.471824	1.301042	0.000042					







### Trisilasumanene 5

Tag	Symbol	Х	Y	Z	Tag	Symbol	Х	Y	Z
1	С	1.298699	0.578806	-0.000009	27	С	-2.900206	-3.90887	1.551565
2	С	0.177775	1.410763	-0.000009	28	н	1.755678	4.411138	-0.000012
3	С	0.291982	2.81739	-0.000009	29	н	3.713412	2.958031	-0.000012
4	С	1.5911	3.335071	-0.000011	30	н	2.942002	-3.725836	-0.00001
5	С	2.731127	2.488904	-0.00001	31	н	0.70524	-4.694815	-0.00001
6	С	2.611827	1.095542	-0.000009	32	н	-4.69776	-0.684939	-0.00001
7	С	1.132721	-0.859052	-0.000009	33	н	-4.417948	1.73679	-0.000009
8	С	-0.148154	-1.413904	-0.000009	34	н	5.57941	0.248745	-1.580137
9	С	-1.310349	-0.551468	-0.000009	35	н	5.377596	-1.510274	-1.581121
10	С	-1.150174	0.835261	-0.000009	36	н	4.227642	-0.486793	-2.459123
11	С	2.293765	-1.661246	-0.000009	37	н	4.227562	-0.486615	2.459136
12	С	2.092473	-3.045158	-0.00008	38	н	5.377376	-1.510372	1.581276
13	С	0.789752	-3.609494	-0.000009	39	Н	5.579482	0.248613	1.580123
14	С	-0.357364	-2.809582	-0.000009	40	Н	-1.381498	5.411626	-1.582525
15	С	-2.585584	-1.155997	-0.000009	41	Н	-3.005461	4.706392	-1.581524
16	С	-3.683446	-0.289724	-0.000009	42	Н	-1.69219	3.902935	-2.459006
17	С	-3.520541	1.120593	-0.00008	43	Н	-1.692085	3.902874	2.459021
18	С	-2.254285	1.714019	-0.00008	44	Н	-1.38155	5.41161	1.582561
19	Si	-2.256717	-3.040976	-0.00003	45	Н	-3.005463	4.706256	1.581631
20	Si	3.761467	-0.433941	0.000000	46	н	-3.996573	-3.900822	-1.581889
21	Si	-1.505192	3.474834	0.000001	47	Н	-2.574474	-4.95573	-1.581872
22	С	4.835934	-0.557058	-1.55106	48	Н	-2.534796	-3.416358	-2.458966
23	С	4.835874	-0.55707	1.551102	49	Н	-2.534829	-3.416237	2.458971
24	С	-1.935824	4.465742	-1.551585	50	Н	-3.996536	-3.900902	1.581889
25	С	-1.93581	4.465686	1.551628	51	н	-2.574331	-4.955666	1.581972
26	С	-2.900244	-3.908899	-1.551539					

### 7. Reference

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## 8. Copies of NMR Spectra for New Compounds









S28



 $^{1}$ H NMR spectra of the reaction of Triiodosumanene 2 with sulfur powder, Cs<sub>2</sub>CO<sub>3</sub> in DMSO at different temperature and time.





The crude <sup>1</sup>H NMR spectra of the reaction of Triiodosumanene 2 with Se, KOt-Bu in DMSO at 70  $^{\circ}$ C





18 04 02 02 02 02 05 63 63	29
888877777	~
	1



~ 1.48 ~ 1.29 - 0.05

The crude <sup>1</sup>H NMR spectra of the reaction of 11 with sulfur powder and cat. Cul in DMF at 120  $^{\circ}$ C.



The crude  $^1\!H$  NMR spectra of the reaction of 11 with Se and cat. Cul in DMF at 120 °C.



