Centripetal Molecules as Multifunctional Building Blocks for Coordination Networks

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Experimental section

General Procedure. Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich and Fisher Scientific) and used without further purification. Syntheses of ligands L\textsubscript{1} and L\textsubscript{2} are outlined. Solution \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a 300 MHz Varian Mercury spectrometer at room temperature (rt), with tetramethylsilane (TMS) as the internal standard.

Synthesis of 3,5-dibromo-4-iodobenzonitrile (S\textsubscript{2}). 3,5-Dibromo-4-iodobenzonitrile (S\textsubscript{2}) was prepared according to the reported procedure (Eur. Pat. Appl., 1986, 188351). To a stirred mixture of 3,5-dibromo-4-aminobenzonitrile, S\textsubscript{1} (5.53 g, 20 mmol), 98\% H\textsubscript{2}SO\textsubscript{4} (10 mL) and glacial acetic acid (50 mL) was added dropwise a solution of NaNO\textsubscript{2} (1.53 g, 22.17 mmol) in water (24 mL) over 1 h below 5 °C in an ice–salt bath. Then a solution of KI (33.2 g, 200 mmol) in water (30 mL) was added, and the mixture was stirred at rt for an additional 30 min. After neutralization with saturated aqueous NaOH, the organic mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (×3), and the organic phase was washed with Na\textsubscript{2}SO\textsubscript{3} aqueous solution and dried over MgSO\textsubscript{4}. After removal of the solvent on a rotary evaporator, 6.96 g of pure orange solid were obtained (90\% yield based on S\textsubscript{1}). 3,5-Dibromo-4-iodo-benzonitrile (S\textsubscript{2}) thus prepared was used for the next step without further purification. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): δ 7.79 (s, 2H).

Synthesis of 3,5-dibromo-4-trimethylsilyl-ethynylbenzonitrile (3). A Schlenk tube was
Scheme 1. Synthesis of L1

Scheme 2. Synthesis of L2
charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (56.1 mg, 0.08 mmol), triphenylphosphine (104.8 mg, 0.40 mmol), copper(I) iodide (22.8 mg, 0.12 mmol), S2 (1.55 g, 4.0 mmol) and triethylamine (30 mL). The Schlenk tube was then bubbled with nitrogen gas for 5 min. Trimethylsilylacetylene (TMSA, 98%, 0.3 g, 3.0 mmol) in 3 mL triethylamine (pre-flushed with nitrogen) was injected via cannula under nitrogen protection into the mixture. The Schlenk tube was then sealed with the plug and stirred while it was heated to 90 °C overnight (15 h). After it was cooled to rt, the reaction mixture was poured into 100 mL of a 2:1 hexanes/dichloromethane mixture and then filtered through a silica gel plug. The solvents were then removed in vacuo and the brown residue was purified by flash chromatography (silica gel, 1:1 hexanes/dichloromethane) to provide a white solid product (0.82 g, 76% based on TMSA).

### Synthesis of 4-trimethylsilylmethylanisole (5).

4-Trimethylsilylmethylanisole (5) was prepared according to the reported procedure (J. Am. Chem. Soc., 2000, 122, 11380). A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (56.1 mg, 0.08 mmol), copper(I) iodide (7.5 mg, 0.04 mmol), 4-idoanisole (4) (1.87 g, 8.0 mmol) and triethylamine (10 mL). The Schlenk tube was then bubbled with nitrogen gas for 5 min. Trimethylsilylacetylene (TMSA, 98%, 0.96 g, 9.6 mmol) in 3 mL triethylamine (pre-flushed with N2) was injected via cannula under nitrogen protection into the mixture. The Schlenk tube was then sealed with the plug and stirred while it was heated to 70 °C overnight (15 h). After it was cooled to rt, the reaction mixture was poured into 100 mL of a 2:1 hexanes/dichloromethane mixture and then filtered through a silica gel plug. The solvents were then removed in vacuo and the liquid residue was then purified on an alumina column using hexanes as the eluent to provide yellow oily liquid in a yield of 1.33 g, 82% based on 4. 1H NMR (CDCl3, 300 MHz): δ 0.24 (s, 9 H), 3.78 (s, 3H), 6.80 (d, 2H), 7.40 (d, 2H).

### Synthesis of 4-ethynylanisole (6).

Under nitrogen protection, a reaction mixture of 4-trimethylsilylmethylanisole, (5, 1.02 g, 5.0 mmol) and potassium carbonate (99%, 2.76 g, 20.0
mmol) in methanol (40 mL, pre-purged with N₂) was stirred at rt overnight. The solvent was then removed on a rotary evaporator. The white residue was then dissolved in dichloromethane, and the dichloromethane solution was then filtered through a silica gel plug. The solvents were then removed in vacuo to yield a yellow oily liquid (0.48 g, 72% based on 5). 4-Ethynylanisole (6) thus prepared was used for the next step without further purification. $^1$H NMR (CDCl₃, 300 MHz): δ 3.04 (s, 1H), 3.84 (s, 3H), 6.86 (d, 2H), 7.45 (d, 2H).

**Synthesis of 3, 5-bis(4-methoxyphenylethylnyl)-4-trimethylsilylethynyl-benzonitrile (7).** A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (45.1 mg, 0.06 mmol), triphenylphosphine (90 mg, 0.34 mmol), copper(I) iodide (18.0 mg, 0.09 mmol), 6 (0.32 g, 2.4 mmol), 3 (0.35 g, 1.0 mmol), triethylamine (15 mL) and THF (15 mL). The Schlenk tube was then bubbled with nitrogen gas for 5 min. The Schlenk tube was then sealed with the plug and stirred while it was heated to 90 °C overnight (15 h). After it was cooled to rt, the reaction mixture was poured into 100 mL of a 1:1 hexanes/dichloromethane mixture and then filtered through a silica gel plug. The solvents were then removed in vacuo and the brown residue was purified by flash chromatography (silica gel, 1:1 hexanes/dichloromethane) to provide a yellow crystalline solid product (0.40 g, 67% based on 3). $^1$H NMR (CDCl₃, 300 MHz): δ 0.31 (s, 9 H), 3.85 (s, 6H), 6.89-6.92 (m, 4H), 7.49-7.52 (m, 4H), 7.66 (s, 2H). $^{13}$C NMR (CDCl₃, 75 MHz): δ 0.21, 55.60, 82.56, 84.57, 83.89, 94.05, 95.01, 105.02, 120.56, 125.49, 129.63, 129.75, 137.31, 139.25, 160.21.

**Synthesis of 3, 5-bis(4-methoxyphenylethylnyl)-4-ethynyl-benzonitrile (8).** Compound 7 (0.35 g, 0.76 mmol) was placed in a round-bottom flask and dissolved in CH₂Cl₂ (20 mL). The flask was cooled to 0 °C, and tetrabutylammonium fluoride (0.76 mL of a 1 M solution in THF, 0.76 mmol) was added via syringe. The reaction mixture was stirred for 2 h at 0 °C and then filtered through a silica gel plug. The solvents were then removed in vacuo to provide a yellow crystalline solid product (0.25 g, 85% based on 7). $^1$H NMR (CDCl₃, 300 MHz): δ 3.61 (s, 6H), 4.20 (s, 1H), 6.62-6.70 (m, 4H), 7.26-7.27 (m, 4H), 7.43 (s, 2H). $^{13}$C NMR (CDCl₃, 75 MHz): δ 55.59, 85.05, 85.53, 89.02, 96.71, 112.46, 114.41, 125.83, 128.81, 128.86, 133.56, 133.77,
Compound 8 thus prepared was used for the next step without further purification.

**Synthesis of 1,4-bis(4-cyano-2,6-bis(4-methoxyphenylethynyl)phenyl)butadiyne** (L1). A mixture of 8 (0.25 g, 0.65 mmol) and Cu(OAc)$_2$ · H$_2$O (0.52 g, 2.6 mmol) in acetonitrile (5 mL) was stirred for 2 h at 60 °C. After cooling, the solvent was removed on a rotary evaporator. The residue was dispersed in CH$_2$Cl$_2$ (50 mL), and the insoluble matter was removed by filtration. The filtrate was washed with water (×2) and dried over anhydrous MgSO$_4$. The solvent was removed by evaporation, and purification of the residue by silica gel column chromatography (hexane:dichloromethane = 1:4) 0.20 g of L1 was obtained (80% yield based on 8). $^1$H NMR (CDCl$_3$, 300 MHz): δ 3.71 (s, 12H), 6.67-6.69 (m, 8H), 7.42-7.45 (m, 8H) 7.69 (M, 4H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 55.47, 82.61, 84.74, 84.99, 98.05, 112.91, 113.93, 114.32, 117.45, 129.54, 129.79, 132.76, 133.85, 160.63.

**Synthesis of 4-trimethylsilylethynyl-1-methylthiobenzene** (10). 4-Trimethylsilylethynyl-1-methylthiobenzene, (10) was prepared according to the reported procedure (*CrystEngComm*, 2004, 6, 184). A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (42.0 mg, 0.06 mmol), triphenylphosphine (78.6 mg, 0.30 mmol), copper(I) iodide (15 mg, 0.09 mmol), 1-methylthio-4-bromobenzene (9) (0.60 g, 3.0 mmol) and triethylamine (15 mL). The Schlenk tube was then bubbled with nitrogen gas for 5 min. Trimethylsilylacetylene (TMSA, 98%, 0.35 g, 3.6 mmol) in 3 mL triethylamine (pre-flushed with nitrogen) was injected via cannula under nitrogen protection into the mixture. The Schlenk tube was then sealed with the plug and stirred while it was heated to 110 °C for 8 h. After it was cooled to rt, the reaction mixture was poured into 100 mL of a 2:1 hexanes/dichloromethane mixture and then filtered through a silica gel plug. The solvents were then removed in vacuo and the liquid residue was then purified on an alumina column using hexanes as the eluent to provide a yellow oily liquid as the product (0.50 g, 77% based on 9). $^1$H NMR (CDCl$_3$, 300 MHz): δ 0.24 (s, 9 H), 2.47 (s, 3 H), 7.12-7.15 (m, 2 H), 7.35-7.38 (m, 2 H). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ 0.10, 15.21, 94.10, 104.91, 119.43, 125.74, 132.22, 139.62.
Synthesis of 4-ethynyl-1-methylthiobenzene (11). 4-Ethynyl-1-methylthiobenzene (11) was prepared according to the reported procedure (CrystEngComm, 2004, 6, 184). Under nitrogen protection, a reaction mixture of 4-trimethylsilylethynyl-methylthiobenzene (10, 0.50 g, 2.2 mmol) and potassium carbonate (99%, 1.25 g, 9.0 mmol) in methanol (20 mL, pre-purged with nitrogen) was stirred at rt overnight. The solvent was then removed on a rotary evaporator. The white residue was then dissolved in dichloromethane, and the dichloromethane solution was then filtered through a silica gel plug. The solvents were then removed in vacuo to yield a yellow oily liquid (0.35 g, 94% based on 10). $^1$H NMR (CDCl₃, 300 MHz): $\delta$ 2.47 (s, 3H), 3.08 (s, 1H) 7.15-7.18 (m, 2H), 7.38-7.41 (m, 2H). $^{13}$C NMR (CDCl₃, 75 MHz): 15.31, 76.80, 83.51, 118.32, 125.81, 132.42, 140.12. Compound 11 thus prepared was used for the next step without further purification.

Synthesis of 3,5-bis[4-(methylthiophenyl)ethynyl]-4-trimethylsilylethynyl-benzonitrile (12). A Schlenk tube was charged with a magnetic stirring bar, bis(triphenylphosphine)palladium(II) chloride (45.1 mg, 0.06 mmol), triphenylphosphine (90 mg, 0.34 mmol), copper(I) iodide (18.0 mg, 0.09 mmol), 11 (0.35 g, 2.2 mmol), 3 (0.35 g, 1 mmol), triethylamine (15 mL) and THF (15 mL). The Schlenk tube was then bubbled with nitrogen gas for 5 min. The Schlenk tube was then sealed with the plug and stirred while it was heated to 90 °C overnight (15 h). After it was cooled to rt, the reaction mixture was poured into 100 mL of a 1:1 hexanes/dichloromethane mixture and then filtered through a silica gel plug. The solvents were then removed in vacuo and the brown residue was purified by flash chromatography (silica gel, 1:1 hexanes/dichloromethane) to provide a yellow crystalline solid product (0.30 g, 61% based on 11). $^1$H NMR (CDCl₃, 300 MHz): $\delta$ 0.30 (s, 9 H), 2.52 (s, 6H), 7.21-7.24 (m, 4H), 7.45-7.48 (m, 4H), 7.68 (s, 2H). $^{13}$C NMR (CDCl₃, 75 MHz): $\delta$ 0.16, 15.43, 86.43, 96.16, 101.10, 108.46, 112.01, 117.48, 118.60, 125.93, 128.17, 131.53, 132.33, 133.59, 141.07.

Synthesis of 3,5-bis[4-(methylthiophenyl)ethynyl]-4-ethynyl-benzonitrile (13). Compound 11 (0.14 g, 0.28 mmol) was placed in a round-bottom flask and dissolved in CH₂Cl₂ (10 mL). The
flask was cooled to 0 °C, and tetrabutylammonium fluoride (0.30 mL of a 1 M solution in THF, 0.30 mmol) was added via syringe. The reaction mixture was stirred for 2 h at 0 °C and then filtered through a silica gel plug. The solvents were then removed in vacuo to provide a yellow crystalline solid product (0.10 g, 83% based on 10). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 2.52 (s, 6H), 3.86 (s, 1H), 7.21-7.24 (m, 4H), 7.46-7.49 (m, 4H), 7.70 (s, 2H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 15.45, 80.18, 86.12, 89.28, 96.42, 112.56, 117.34, 118.39, 125.93, 128.58, 130.53, 132.40, 133.59, 141.23. Compound 13 thus prepared was used for the next step without further purification.

**Synthesis of 1,4-bis{4-cyano-2,6-bis[4-(methylthiophenyl)ethynyl]}butadiyne (L2).** A mixture of 13 (0.14 g, 0.33 mmol) and Cu(OAc)$_2$ · H$_2$O (0.26 g, 1.2 mmol) in acetonitrile (5 mL) was stirred for 2 h at 60 °C. After cooling, the solvent was removed on a rotary evaporator. The residue was dispersed in CH$_2$Cl$_2$ (50 mL), and the insoluble matter was removed by filtration. The filtrate was washed with water (×2) and dried over anhydrous MgSO$_4$. The solvent was removed by evaporation, and purification of the residue by silica gel column chromatography (hexane:dichloromethane = 1:4) 0.12 g of L2 was obtained (85% yield based on 13). $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 2.39 (s, 12H), 6.95-6.98 (m, 8H), 7.35-7.38 (m, 8H), 7.71 (s, 4H). $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 15.26, 82.54, 84.79, 85.98, 97.76, 113.07, 117.29, 117.73, 125.75, 129.29, 130.01, 132.36, 133.17, 141.35.

**Crystallization of 2L1·4AgSbF$_6$·8benzene (1).** A benzene solution of L1 (2.3 mg, 3.0 mM, 0.5 mL) was loaded into a glass tube and on top of that was layered a toluene solution of AgSbF$_6$ (2.4 mg, 7.0 mM, 0.5 mL) carefully without disturbing the interface. The tube was then sealed and kept in the dark. Needle-like, yellow crystals suitable for X-ray studies formed after one week. The pure phase bulk sample was prepared as follows. A benzene solution of L1 (9.2 mg, 12.0 mM, 2 mL) was mixed with a benzene solution of AgSbF$_6$ (8.23 mg, 24.0 mM, 2 mL) in a vial. The vial was then sealed and kept in the dark for 24 h. The yellow needle-like crystals were collected by suction filtration and rinsed with benzene (e.g., 1 mL x 3) and hexanes (e.g., 2 mL x 3) to provide the final product (18.2 mg, 83.0% yield based on L1). An X-ray powder diffraction
study indicated a single phase consistent with the single-crystal structure of 2L1·4AgSbF₆·8benzene. Chemical analysis of the product C₁₅₆H₁₁₂Ag₄F₂₄N₄O₈Sb₄ yields the following: Anal. Calcd [C (52.80%), H (3.16%), N (1.58%)]. Found [C (52.01%), H (3.04%), N (1.76%)]. In a preliminary effort to assess the phase purity of the crystalline product, a quick powder X-ray scan (about 30 min, done in air) of the as-synthesized sample provided a diffraction pattern consistent with the single crystal structure (see Fig. S1). However, the instability of the sample in open air requires a more advanced setup (e.g., sealed in a capillary tube with the mother liquor) for the collection of higher-quality powder patterns.

![Fig. S1 X-ray diffraction patterns (Cu Kα, λ = 1.5418 Å) of 2L1·4AgSbF₆·8benzene (I): (a) observed for a powder solid sample; and (b) calculated from the single-crystal structure with random orientation of crystallites. The strong noise in spectrum a is due to the short acquisition time (the sample decays significantly in air).](image-url)
Fig. S2 X-ray diffraction patterns (Cu Kα, λ = 1.5418 Å) of L2·AgSbF6 (2): (a) observed for a powder solid sample; and (b) calculated from the single-crystal structure with the refined unit cell constants from pattern a and with random orientation of crystallites (see below for details of the refinement). The asterisked peak is not indexed, and may be from a minor unknown phase.


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yqlb4.lst

Initial values : (Refinement keys on 2nd line)

Zero Lambda a b c alpha beta gamma volume
0.000 1.54180 21.3769 21.3769 21.9480 90.00 90.00 90.00 10029.62

H K L 2Th(obs) 2Th_obs-shift 2Th(Calc) diff.

1 1 2 10.0000 10.0000 9.9601 0.0399
1 3 0 13.0800 13.0800 13.064 0.0164
1 3 2 15.4200 15.4200 15.3945 0.0255
0 4 0 16.6400 16.6400 16.5876 0.0524
2 0 4 18.2000 18.2000 18.1732 0.0268
3 3 2 19.3600 19.3600 19.3844 -0.0244
2 2 4 20.0400 20.0400 19.9964 0.0436
1 3 4 20.8800 20.8800 20.8505 0.0295
4 2 4 24.6800 24.6800 24.7008 -0.0208
1 1 6 25.0600 25.0600 25.0454 0.0146
0 2 6 25.7400 25.7400 25.7405 -0.0005
4 6 0 30.1600 30.1600 30.1459 0.0141
3 3 6 30.1600 30.1600 30.1907 -0.0307
2 2 8 34.7600 34.7600 34.7869 -0.0269
0 4 8 36.8000 36.8000 36.8248 -0.0248
\[
\sqrt{\text{Sum}(2\,\text{Th} - \text{O-C})^2}/(\text{Nref} - \text{Npar}) \]: 0.0310  \\
\sqrt{\text{Sum}(2\,\text{Th} - \text{O-C})^2}/\text{Nref} \): 0.0288  \\
\text{Final values} : (\text{Standard errors on 2nd line}) \\
\text{------------} \\
\text{Zero}  \quad \text{Lambda}  \quad a  \quad b  \quad c  \quad \text{alpha}  \quad \text{beta}  \quad \text{gamma}  \quad \text{volume}  \\
0.000 1.54180 21.3769 21.3769 21.9492 90.00 90.00 90.00 10030.20  \\
0.0000 0.00000 0.0382 0.0000 0.0010 0.000 0.000 0.000 17.919 \\
\]

\[
\begin{array}{cccccccccc}
H & K & L & 2\text{Th(obs)} & 2\text{Th}_{\text{obs-shift}} & 2\text{Th(Calc)} & \text{diff.} \\
1 & 1 & 2 & 10.0000 & 10.0000 & 9.9597 & 0.0403 \\
1 & 3 & 0 & 13.0800 & 13.0800 & 13.0964 & -0.0164 \\
1 & 3 & 2 & 15.4200 & 15.4200 & 15.3943 & 0.0257 \\
0 & 4 & 0 & 16.6400 & 16.6400 & 16.5876 & 0.0524 \\
2 & 0 & 4 & 18.2000 & 18.2000 & 18.1724 & 0.0276 \\
3 & 3 & 2 & 19.3600 & 19.3600 & 19.3842 & -0.0242 \\
2 & 2 & 4 & 20.0400 & 20.0400 & 19.9957 & 0.0443 \\
1 & 3 & 4 & 20.8800 & 20.8800 & 20.8498 & 0.0302 \\
1 & 1 & 6 & 25.0600 & 25.0600 & 25.0441 & 0.0159 \\
0 & 2 & 6 & 25.7400 & 25.7400 & 25.7392 & 0.0008 \\
4 & 6 & 0 & 30.1600 & 30.1600 & 30.1459 & 0.0141 \\
3 & 3 & 6 & 30.1600 & 30.1600 & 30.1896 & -0.0296 \\
2 & 2 & 8 & 34.7600 & 34.7600 & 34.7852 & -0.0252 \\
0 & 4 & 8 & 36.8000 & 36.8000 & 36.8232 & -0.0232 \\
\end{array}
\]

\[
\sqrt{\text{Sum}(2\,\text{Th} - \text{O-C})^2}/(\text{Nref} - \text{Npar}) \]: 0.0309  \\
\sqrt{\text{Sum}(2\,\text{Th} - \text{O-C})^2}/\text{Nref} \): 0.0288  \\

**Crystallization of L2·AgSbF6 (2).** A THF solution of L2 (2.6mg, 3.0 mM, 0.5 mL) were loaded into a glass tube and on top of that was layered a toluene solution of AgSbF6 (2.4mg, 7.0 mM, 0.5 mL) carefully without disturbing the interface, respectively. The tube was then sealed and kept in the dark. Orange diamond crystals of 2 suitable for X-ray studies were obtained after one week. Yield: 34% for 2 (based on L2). Anal. Calcd. for C54H32AgF6N2S4Sb: C, 54.93; H, 2.73; N, 2.37%. Found: C, 54.00; H, 3.26; N, 2.88%. An X-ray powder diffraction study indicated a dominant phase consistent with the single-crystal structure of L2·4AgSbF6 (see Figure S2 for more details).

**Thermogravimetric Analysis**

The solid sample of 1 is unstable in air, and quickly loses the benzene guests and decomposes into an amorphous black solid. TG analysis of an as-synthesized solid sample of 1 was able to capture part of the initial step of weight loss of 4.46% at around 100 ºC (Fig. S3),
which corresponds to the removal of two benzene molecules per formula unit (calcd. 4.41%).

**Fig. S3** TGA plot of 2L1·4AgSbF₆·8benzene (1) (heating rate: 5 °C/min; in dry He atmosphere from 30 to 600 °C).

**Fig. S4** The conformations of L1 and L2 and the associated Ag⁺ ions in the structures of 1 and 2, Color code: Ag, red; O, orange; C, grey; N, blue. Disorder is omitted for clarity.
**Fig. S5** The coordination environment around Ag1 atom in the crystal structure of 2L1·4AgSbF6·8benzene (1). Color code: red sphere, Ag(I); blue sphere, N; grey sphere, C; orange sphere, O [Bond length: Ag1-N1, 2.077(1) Å; Ag1-N2, 2.108(9) Å; Ag1-C66, 2.722(5) Å]. Disorder is omitted for clarity.

**Fig. S6** The coordination environments around Ag2 and Ag4 atoms in the crystal structure of 2L1·4AgSbF6·8benzene (1). Color code: red sphere, Ag(I); blue sphere, N; grey sphere, C; orange sphere, O [Bond length: Ag2-N3, 2.109(1) Å; Ag2-N4, 2.090(1) Å; Ag2-C83A, 2.826(2) Å; Ag2-C84A, 2.682(2) Å; Ag4-C71A, 2.441(2) Å; Ag4-C76A, 2.634(2) Å; Ag4-C85A, 2.429(1) Å; Ag4-C86A, 2.626(1) Å; Ag4-C77, 2.532(1) Å; Ag4-C78, 2.816(1) Å]. Disorder is omitted for clarity.
**Fig. S7** View of the overall structure of $2\text{L}_1 \cdot 4\text{AgSbF}_6 \cdot 8\text{benzene (1)}$ along the $c$ axis. Color code: Ag, red; O, orange; C, grey; N, blue.

**Fig. S8** The construction of the first type of helical tube (along $b$ axis) with the same chirality in $\text{L}_2 \cdot \text{AgSbF}_6$ (2), showing two helical chains being weaved by each other through sharing Ag vertices and butadiyne bonds. Hydrogen atoms are omitted for clarity.
Fig. S9 The construction of the second type of helical tube (along $a$ axis) with the same chirality in 2-L·AgSbF$_6$ (2), showing two helical chains being weaved by each other through sharing Ag vertices and butadiyne bonds. Hydrogen atoms are omitted for clarity.

Fig. S10 Emission spectra of 1 ($\lambda_{ex} = 370\text{nm}$) in solid state at room temperature in the air, indicating the steady decay of the sample over time.
Fig. S11 Emission spectra of (a) L1 in THF (5×10⁻⁵ M, λex = 352 nm), (b) L1 in solid state (λex = 370 nm), (c) 1 in solid state (λex = 370 nm).

Fig. S12 Emission spectra of (a) L2 in THF (5×10⁻⁵ M, λex = 352 nm), (b) L2 in solid state (λex = 370 nm), (c) 2 in solid state (λex = 370 nm).
M1

M2
Further Crystallographic Data from X-ray Single Crystal Diffraction Studies

Fig. S13 A thermal ellipsoid (50% probability) presentation of the crystal structure of 1.
**Table S1.** Crystal data and structure refinement for complex 1

Identification code: 07mz056m

Empirical formula: C156 H112 Ag4 F24 N4 O8 Sb4

Moiety formula: C90 H68 Ag3 F12 N2 O4 Sb2, C66 H44 Ag N2 O4, 2(F6 Sb)

Formula weight: 3545.02

Temperature: 100(2) K

Wavelength: 0.71073 Å

Crystal system: Trigonal

Space group: P3121

Unit cell dimensions:

- \(a = 21.3675(10) \, \text{Å}, \alpha = 90^\circ\)
- \(b = 21.3675(10) \, \text{Å}, \beta = 90^\circ\)
- \(c = 27.279(3) \, \text{Å}, \gamma = 120^\circ\)

Volume, \(Z\): 10786.1(13) \, Å\(^3\), 3

Density (calculated): 1.637 Mg/m\(^3\)

Absorption coefficient: 1.362 mm\(^{-1}\)

\(F(000)\): 5244

Crystal size: 0.47 \(\times\) 0.20 \(\times\) 0.17 mm

Crystal shape, colour: block, yellow

\(\theta\) range for data collection: 1.10 to 26.37\(^\circ\)

Limiting indices: \(-26 \leq h \leq 26, -26 \leq k \leq 26, -34 \leq l \leq 34\)

Reflections collected: 92898

Independent reflections: 14532 \((R\text{int}) = 0.0395\)

Completeness to \(\theta = 26.37^\circ\): 100.0%

Absorption correction: multi-scan

Max. and min. transmission: 0.793 and 0.632

Refinement method: Full-matrix least-squares on \(F^2\)

Data / restraints / parameters: 14532 / 436 / 1071

Goodness-of-fit on \(F^2\): 1.233

Final \(R\) indices \([I>2\sigma(I)]\): \(R1 = 0.0654, \, wR2 = 0.1626\)

\(R\) indices (all data): \(R1 = 0.0685, \, wR2 = 0.1662\)

Largest diff. peak and hole: 1.832 and -0.861 e \(\times\) Å\(^{-3}\)

Refinement of \(F^2\) against ALL reflections. The weighted \(R\)-factor \(wR\) and goodness of fit are based on \(F^2\), conventional \(R\)-factors \(R\) are based on \(F\), with \(F\) set to zero for negative \(F^2\). The threshold expression of \(F^2 > 2\sigma(F^2)\) is used only for calculating \(R\)-factors.
Comments:
The silver ions and several sections of the adjoining ligands are disordered around two fold axes of symmetry. The bond distances in these sections were restrained using similarity restraints (SADI) with other not disordered sections with a standard deviation of 0.02, disordered aromatic rings were restrained to resemble ideal hexagons with C-C = 1.39 Å, and overlapping atoms were set to have identical ADPs. The disordered atoms were restrained to be isotropic within standard deviations ranging from 0.01 to 0.04.

Treatment of hydrogen atoms:
All hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of the adjacent carbon atom.

**Fig. S14** A thermal ellipsoid (50% probability) presentation of the crystal structure of 2.

**Table S2.** Crystal data and structure refinement for complex 2:
Identification code: 07mz004m
Empirical formula: C54 H32 Ag F6 N2 S4 Sb
Moiety formula: C54 H32 Ag N2 S4, F6 Sb
Formula weight: 1180.68
Temperature: 100(2) K
Wavelength: 0.71073 Å
Crystal system: Tetragonal
Space group: I-42d
Unit cell dimensions:
a = 21.4042(8) Å, α = 90°
b = 21.4042(8) Å, β = 90°
c = 21.4080(16) Å, γ = 90°
Volume, Z: 9807.9(9) Å³, 8
Density (calculated): 1.599 Mg/m³
Absorption coefficient: 1.182 mm⁻¹
F(000): 4688
Crystal size: 0.19 × 0.18 × 0.06 mm
Crystal shape, colour: platelet, red
θ range for data collection: 1.35 to 28.27°
Limiting indices: −28 ≤ h ≤ 28, −28 ≤ k ≤ 28, −23 ≤ l ≤ 28
Reflections collected: 36308
Independent reflections: 6110 (R(int) = 0.0605)
Completeness to θ = 28.28°: 100%
Absorption correction: multi-scan
Max. and min. transmission: 0.932 and 0.575
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 6110 / 55 / 330
Goodness-of-fit on F²: 1.065
Final R indices [I>2σ(I)]: R1 = 0.0497, wR2 = 0.1116
R indices (all data): R1 = 0.0700, wR2 = 0.1193
Largest diff. peak and hole: 1.694 and -0.398 e x Å⁻³

Refinement of F² against ALL reflections. The weighted R-factor wR and
goodness of fit are based on F², conventional R-factors R are based
on F, with F set to zero for negative F². The threshold expression of
F² > 2σ(F²) is used only for calculating R-factors
Comments:
The silver atom is disordered over two positions with an occupancy ratio of 0.929(1)
to 0.079(1). The minor silver atom was restrained to have the same anisotropic
displacement parameter as the major one. Four of the six fluorine atoms of the
SbF₆ anion are disordered over two equally occupied positions. The disordered F
atoms were restrained to have the same Sb-F and F-F distances and all F atoms were
restrained to be isotropic within a standard deviation of 0.01.
Ignoring the disorder of the SbF6 anion and assuming a 1:1 disorder of the silver
anion the structure could also be represented in a smaller orthorhombic cell in
F222 with the parameters 10.704, 21.404, 21.404.

Treatment of hydrogen atoms:
All hydrogen atoms were placed in calculated positions and were refined with an
isotropic displacement parameter 1.5 (methyl) or 1.2 times (all others) that of
the adjacent carbon atom.