Supporting information of

Digold(I) Thianthrenyl Complexes. Effect of Diphosphine Ligands on Molecular Structures in the Solid State and in Solution

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S1. General

All manipulations were carried out under an argon or nitrogen atmosphere using standard Schlenk techniques. Dehydrated solvents were purchased from Wako Chemical and used as received. Deuterated solvents (CDCl₃) were purchased from ISOTEC and used as received. The $^1$H, $^{13}$C{¹H} and $^{31}$P{¹H} NMR spectra were recorded on a Bruker Avance III HD 500 MHz NMR spectrometers or a Bruker BioSpin AVANCE 400 MHz NMR spectrometers. Chemical shifts in $^1$H and $^{13}$C{¹H} NMR spectra were referenced to the residual peaks of the solvents used. The peak positions of the $^{31}$P{¹H} NMR spectra were referenced to external 85% H₃PO₄ (δ 0) in deuterated solvents. Fluorescence and excitation spectra were measured using a JASCO FP-6300 spectrophotometer. Emission spectra was observed with the excitation wavelength of 300 nm. Excitation spectra was observed at 445 nm. Elemental analysis was performed using a J-science JM10 or a Yanaco HSU-20 autorecorder.

Single crystal X-ray data were collected using a Bruker APEXII ULTRA/CCD D8 VENTURE diffractometer or a Rigaku XtaLAB Synergy-S diffractometer. UV-visible absorption spectra were measured on a JASCO V-530 UV-Vis spectrometer. Electrochemical measurements were performed with ALS/chi Electrochemical Analyzer 660A. A conventional three-electrode configuration was used, with glassy carbon working (BAS PFCE carbon electrode) and platinum wire auxiliary electrode (Nilaco special order) and 0.01 M AgNO₃/Ag reference (BAS RE-5). The commercially available reagents, HAuCl₄·4H₂O (Tanaka), tetrahydrothiophene (TCI), bis(diphenylphosphino)methane (TCI), bis(diphenylphosphino)ethane (TCI), bis(diphenylphosphino)propane (TCI), bis(diphenylphosphino)butane (TCI), thianthrene-1-boronic acid (TCI), 1,8-dibromonaphthalene (TCI), cesium carbonate (Wako), iodobenzene (TCI), were used as received. PhICl₂ was prepared from the oxidation of iodo benzene by Cl₂, which was generated in situ from the reaction of 5% NaClO (commercial household bleach) with conc. HCl.¹
S2. Synthesis and Characterization

\[ \text{[AuCl(tht)] (tht = tetrahydrothiophene), [Au}_{2}\text{Cl}_{2}(\text{dppm}), [Au}_{2}\text{Cl}_{2}(\text{dppe}), [Au}_{2}\text{Cl}_{2}(\text{dppp}), \text{and [Au}_{2}\text{Cl}_{2}(\text{dppp})] were prepared according to the literatures.}^{2-5} \]

Synthesis of Au complex 1.

A mixture of \([\text{AuCl}_{2}(\text{dppm})] \) (340 mg, 0.40 mmol), Cs\(_2\)CO\(_3\) (782 mg, 2.4 mmol), and thianthrene-1-boronic acid (229 mg, 0.88 mmol) in degassed toluene/H\(_2\)O/EtOH (4 mL/1 mL/1mL) was stirred for 46 hours at 80 °C under argon atmosphere. CH\(_2\)Cl\(_2\) (20 mL) was added to the mixture, and the organic phase was washed with water (20 mL×2) then the organic layer was dried over MgSO\(_4\). The crude compound was recrystallized from CH\(_2\)Cl\(_2\) (10 mL)/\(n\)-hexane (20 mL) to give 1 (442 mg, 0.37 mmol, 91%) as a white solid.

\(^1\text{H NMR (500 MHz, CDCl}_3, \text{r.t.}): \delta 7.92-7.89 (m, 8\text{H, C}_6\text{H}_5), 7.41 (m, 14\text{H, C}_6\text{H}_5, \text{C}_6\text{H}_3), 7.20 (d, 2\text{H, J} = 7.4 \text{Hz, C}_6\text{H}_3), 7.13 (t, 2\text{H, J} = 7.5 \text{Hz, C}_6\text{H}_4), 7.06 (m, 4\text{H, C}_6\text{H}_4), 7.00 (d, 2\text{H, J} = 7.7 \text{Hz, C}_6\text{H}_3), 6.74 (t, 2\text{H, J} = 7.4 \text{Hz, C}_6\text{H}_3), 3.72 (t, 2\text{H, J}_{\text{p-H}} = 10.1 \text{Hz, CH}_2).\]

\(^{31}\text{P\{^1\text{H}\} NMR (202 MHz, CDCl}_3, \text{r.t.}): \delta 31.3 (s).}\)

\(^{13}\text{C\{^1\text{H}\} NMR (100 MHz, CDCl}_3, \text{r.t.): \delta 144.3, 138.7, 137.9, 136.0, 133.7 (t, J} = 7.1 \text{Hz), 131.6, 131.0 (d, J} = 27.2 \text{Hz), 129.2 (t, J} = 5.6 \text{Hz), 128.2, 128.1, 126.7, 126.6, 126.3, 125.6. The }^{13}\text{C signal of C}_{ipso} \text{ and P-C were not observed because of low solubility.}\]

Anal. Calcd for C\(_{49}\)H\(_{36}\)Au\(_2\)P\(_2\)S\(_4\): C, 48.68; H, 3.00. Found: C, 48.51; H, 3.45.
Figure S1. $^1$H NMR spectrum of Au complex 1 (500 MHz, CDCl$_3$, r.t.).

Figure S2. $^{31}$P$^{(1)}$H NMR spectrum of Au complex 1 (202 MHz, CDCl$_3$, r.t.).
Figure S3. $^{13}$C{$_1^1$H} NMR spectrum of Au complex 1 (100 MHz, CDCl$_3$, r.t.).

Synthesis of Au complex 2.

A mixture of [AuCl$_2$(dppe)] (165 mg, 0.19 mmol), Cs$_2$CO$_3$ (391 mg, 1.2 mmol), and thianthrene-1-boronic acid (114 mg, 0.44 mmol) in degassed toluene/H$_2$O/EtOH (4 mL/1 mL/1 mL) was stirred for 38 hours at 80 °C under argon atmosphere, CH$_2$Cl$_2$ (20 mL) was added to the mixture, and the organic phase was washed with water (20 mL×2) then the organic layer was dried over MgSO$_4$. The crude compound was recrystallized from CH$_2$Cl$_2$ (10 mL)/n-hexane (20 mL) to give 2 (145 mg, 0.11 mmol, 60%) as a white
solid.

$^1$H NMR (500 MHz, CDCl$_3$, r.t.): $\delta$ 7.90-7.85 (m, 8H, C$_6$H$_5$) 7.52-7.43 (m, 16H, C$_6$H$_5$, C$_6$H$_4$), 7.26-7.14 (m, 4H, C$_6$H$_4$, C$_6$H$_3$), 7.18-7.09 (m, 4H, C$_6$H$_4$, C$_6$H$_3$), 7.05 (t, 2H, $J$ = 7.3 Hz, C$_6$H$_3$), 2.99 (s, 4H, CH$_2$).

$^{31}$P{$^1$H} NMR (202 MHz, CDCl$_3$, r.t.): $\delta$ 40.9 (s).

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, r.t.): $\delta$ 173.0 (dd, $J$ = 39.0 Hz), 145.1, 138.1, 137.3, 135.8, 133.6 (t, $J$ = 6.8 Hz), 132.8 (t, $J$ = 3.3 Hz), 131.7, 130.4 (t, $J$ = 16.2 Hz), 129.4 (t, $J$ = 5.4 Hz), 128.34, 128.31, 126.98, 126.93, 126.8 (t, $J$ = 2.9 Hz), 126.2, 24.2 (t, $J$ = 17.9 Hz).

Anal. Calcd for C$_{50}$H$_{38}$Au$_2$P$_2$S$_4$: C, 49.11; H, 3.13. Found: C, 48.81; H, 3.28.

Figure S4. $^1$H NMR spectrum of Au complex 2 (500 MHz, CDCl$_3$, r.t.).
Figure S5. $^{31}$P{$^1$H} NMR spectrum of Au complex 2 (202 MHz, CDCl$_3$, r.t.).

Figure S6. $^{13}$C{$^1$H} NMR spectrum of Au complex 2 (100 MHz, CDCl$_3$, r.t.).
Synthesis of Au complex 3.

A mixture of [AuCl₂(dppp)] (219 mg, 0.25 mmol), Cs₂CO₃ (391 mg, 1.2 mmol), and thianthrene-1-boronic acid (130 mg, 0.50 mmol) in degassed toluene/H₂O/EtOH (4 mL/1 mL/1mL) was stirred for 38 hours at 80 °C under argon atmosphere, CH₂Cl₂ (20 mL) was added to the mixture, and the organic phase was washed with water (20 mL×2) then the organic layer was dried over MgSO₄. The crude compound was recrystallized from CH₂Cl₂ (10 mL)/n-hexane (20 mL) to give 3 (279 mg, 0.22 mmol, 87%) as a white solid.

¹H NMR (500 MHz, CDCl₃, r.t.): δ 7.83-7.80 (m, 8H, C₆H₅) 7.45 (d, 2H, J = 7.6 Hz, C₆H₄), 7.41-7.36 (m, 4H, C₆H₄,C₆H₃), 7.32-7.29 (m, 12H, C₆H₅), 7.18-7.14 (m, 6H, C₆H₃), 7.02 (t, 2H, J = 7.3 Hz, C₆H₃), 3.18-3.14 (m, 4H, CH₂), 2.12-2.02 (m, 2H, CH₂).

³¹P {¹H} NMR (202 MHz, CDCl₃, r.t.): δ 31.9 (s).

¹³C {¹H} NMR (100 MHz, CDCl₃, r.t.): δ 172.8, 171.6, 144.9, 138.7, 137.7, 135.8, 133.6 (d, J = 13.2 Hz), 132.1 (d, J = 6.7 Hz), 131.2 (d, J = 2.2 Hz), 131.0, 130.5, 129.0 (d, J = 10.5 Hz), 128.2 (d, J = 9.7 Hz), 126.9 (d, J = 4.7 Hz), 126.7 (d, J = 6.3 Hz), 125.8, 28.4 (d, J = 9.1 Hz), 28.1 (d, J = 9.1 Hz), 19.3,

Anal. Calcd for C₅₁H₄₀Au₂P₂S₄: C, 49.52; H, 3.26. Found: C, 49.66; H, 3.38.
**Figure S7.** $^1$H NMR spectrum of Au complex 3 (500 MHz, CDCl$_3$, r.t.).

**Figure S8.** $^{31}$P{$^1$H} NMR spectrum of Au complex 3 (202 MHz, CDCl$_3$, r.t.).
Figure S9. $^{13}$C-$^1$H NMR spectrum of Au complex 3 (100 MHz, CDCl$_3$, r.t.).

**Synthesis of Au complex 4.**

A mixture of [AuCl$_2$(dppb)] (446 mg, 0.50 mmol), Cs$_2$CO$_3$ (977 mg, 3.0 mmol), and thianthrene-1-boronic acid (286 mg, 1.1 mmol) in degassed toluene/H$_2$O/EtOH (4 mL/1 mL/1 mL) was stirred for 38 hours at 80 °C under argon atmosphere, CH$_2$Cl$_2$ (20 mL) was added to the mixture, and the organic phase was washed with water (20 mL×2) then the organic layer was dried over MgSO$_4$. The crude compound was recrystallized from CH$_2$Cl$_2$ (10 mL)/n-hexane (20 mL) to give 4 (462 mg, 0.36 mmol, 71%) as a white
solid.

$^1$H NMR (500 MHz, CDCl$_3$, r.t.): $\delta$ 7.78-7.74 (m, 8H, C$_6$H$_5$), 7.47-7.37 (m, 18H, C$_6$H$_5$, C$_6$H$_4$, C$_6$H$_4$), 7.23 (d, 2H, $J$ = 8.0 Hz, C$_6$H$_5$), 7.18-7.14 (m, 4H, C$_6$H$_4$), 7.11 (t, 2H, $J$ = 8.0 Hz C$_6$H$_3$), 2.51 (s, 4H, CH$_2$), 2.00 (s, 4H, CH$_2$).

$^{31}$P{$^1$H} NMR (202 MHz, CDCl$_3$, r.t.): $\delta$ 37.9.

$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, r.t.): $\delta$ 173.2, 145.1, 138.1, 137.6, 135.8, 133.4 (d, $J$ = 13.4 Hz), 131.1, 130.7 (d, $J$ = 9.5 Hz), 129.1 (d, $J$ = 10.3 Hz), 128.6, 128.3, 127.7, 126.9, 126.7, 126.1, 28.0 (d, $J$ = 28.4 Hz), 27.0 (d, $J$ = 10.5 Hz)

Anal. Calcd for C$_{52}$H$_{42}$Au$_2$P$_2$S$_4$+1/2(C$_7$H$_8$): C, 51.37; H, 3.61. Found: C, 51.43; H, 3.55.

Figure S10. $^1$H NMR spectrum of Au complex 4 (500 MHz, CDCl$_3$, r.t.).
Figure S11. $^{31}$P{$^{1}$H} NMR spectrum of Au complex 4 (202 MHz, CDCl$_3$, r.t.).

Figure S12. $^{13}$C{$^{1}$H} NMR spectrum of Au complex 4 (100 MHz, CDCl$_3$, r.t.).
Synthesis of compound 5.

A mixture of 1,8-dibromonaphthalene (143 mg, 0.50 mmol), Pd(PPh$_3$)$_4$ (29 mg, 25 mmol), Cs$_2$CO$_3$ (652 mg, 2.0 mmol), and thianthrene-1-boronic acid (260 mg, 2 mmol) in degassed toluene/H$_2$O/EtOH (8 mL/2 mL/2 mL) was stirred for 13 hours at 100 °C under argon atmosphere. The precipitate was collected by suction filtration and washed with EtOH (10 mL) to give 5 (201 mg, 0.36 mmol, 72 %) as a white solid.

$^1$H NMR (400 MHz, CDCl$_3$, r.t.): $\delta$ 8.09 (d, 2H, $J = 8.4$ Hz, C$_{10}$H$_6$) 7.60 (t, 2H, $J = 7.2$ Hz, C$_{10}$H$_6$), 7.50 (d, 2H, $J = 7.4$ Hz, C$_{10}$H$_6$), 7.37 (d, 2H, $J = 7.6$ Hz, C$_6$H$_4$), 7.32 (t, 2H, $J = 7.6$ Hz, C$_6$H$_4$), 7.25 (t, 2H, $J = 7.6$ Hz, C$_6$H$_4$), 7.20 (t, 2H, $J = 7.2$ Hz, C$_6$H$_4$), 6.78-6.73 (m, 4H, C$_6$H$_3$), 5.44 (t, 2H, $J = 7.6$ Hz).

Figure S13. $^1$H NMR spectrum of compound 5 (500 MHz, CDCl$_3$, r.t.).
Figure S14. NMR spectra of 1 with different concentration (upper) and temperature (lower). The spectra were obtained at 500 MHz in CDCl₃.
Figure S15. 2D-Roesy NMR spectrum of complex 1

Figure S16. Fluorescence (a) and excitation (b) spectra of complex 1 (CHCl₃ solvent).
S3 Crystallographic Results

**Table S1.** Selected bond parameters (Å or deg) of 1-3

|                  | Complex 1 (dppm) | Complex 2 (dppe) | Complex 3 (dppp) |
|------------------|-------------------|------------------|------------------|
| Au1−Au2          | 3.2171(3)         | 2.2963(9)        | 3.0735(2)        |
| Au1−P1           | 2.2880(8)         | 2.2818(9)        | 2.298(1)         |
| Au2−P2           | 2.2963(9)         | 2.2777(9)        | 2.300(1)         |
| Au1−C_thia1      | 2.052(3)          | 2.048(3)         | 2.063(4)         |
| Au2−C_thia2      | 2.063(3)          | 2.047(3)         | 2.054(4)         |
| P1-C_inner       | 1.840(3)          | 1.828(3)         | 1.831(4)         |
| P2-C_inner       | 16.767(1)         | 1.830(3)         | 1.833(4)         |
| Au1−Au2−P2       | 85.79(2)          | 86.46(3)         |                  |
| Au2−Au1−P1       | 88.24(2)          | 82.20(3)         |                  |
| Au1−P1−C_inner   | 117.3(1)          | 117.7(1)         | 116.1(1)         |
| Au2−P2−C_inner   | 112.8(1)          | 112.1(1)         | 114.4(1)         |

P1 and P2 are reversed for complex 3.
Table S2  Selected bond parameters (Å or deg) of 4.

| Compound          | Complex 4 (dppb) C$_2$H$_4$Cl$_2$ | Complex 4 (dppb) aetone |
|-------------------|-----------------------------------|-------------------------|
| Au1–Au4           | 3.070(4)                          | Au3–Au4                 |
| Au1–P1            | 2.287(1)                          | Au3–P3                  |
| Au4–P4            | 2.293(2)                          | Au3–P3                  |
| Au1–C$_{thia1}$   | 2.067(9)                          | Au2–C$_{thia1}$         |
| Au4–C$_{thia2}$   | 2.075(8)                          | Au3–C$_{thia2}$         |
| P1–C$_{inner}$    | 1.832(8)                          | P2–C$_{inner}$          |
| P4–C$_{inner}$    | 1.825(8)                          | P3–C$_{inner}$          |
| Au1–Au4–P4        | 85.79(2)                          | Au2–Au3–P3              |
| Au4–Au1–P1        | 88.24(2)                          | Au3–Au2–P2              |
| Au1–P1–C$_{inner}$| 118.1(3)                          | Au2–P2–C$_{inner}$      |
| Au4–P4–C$_{inner}$| 112.5(3)                          | Au3–P3–C$_{inner}$      |

| Compound          | Complex 4 (dppb) aetone |
|-------------------|-------------------------|
| Au1–Au2           | Au3–Au4                 |
| Au1–P1            | Au3–P3                  |
| Au2–P2            | Au4–P4                  |
| Au1–C$_{thia1}$   | Au3–C$_{thia1}$         |
| Au2–C$_{thia2}$   | Au4–C$_{thia2}$         |
| P1–C$_{inner}$    | P3–C$_{inner}$          |
| P2–C$_{inner}$    | P4–C$_{inner}$          |
| Au1–Au2–P2        | Au3–Au4–P4              |
| Au2–Au1–P1        | Au4–Au3–P3              |
| Au1–P1–C$_{inner}$| Au3–P3–C$_{inner}$      |
| Au4–P2–C$_{inner}$| Au4–P3–C$_{inner}$      |
Figure S17. ORTEP drawing of Au complex 1 (50% level of probability): (a) molecular structure, (b) structure of unit cell.

Figure S18. ORTEP drawing of Au complex 2 (50% level of probability): (a) molecular structure, (b) structure of unit cell.
Figure S19. ORTEP drawing of Au complex 3 (50% level of probability): (a) molecular structure, (b) structure of unit cell.

Figure S20. ORTEP drawing of Au complex 4 (from C₂H₄Cl₂-hexane, 20% level of probability): (a) molecular structure, (b) structure of unit cell.
Figure S21. ORTEP drawing of Au complex 4 (from acetone, 20% level of probability): (a) molecular structure, (b) structure of unit cell.

Figure S22. ORTEP drawing of compound 5 (50% level of probability): (a) molecular structure, (b) structure of unit cell.
| Table S3. Crystal data and structure refinement for Au complex 1 |
|---------------------------------------------------------------|
| CCDC No. | 2116852 |
| Solvent system | C_{2}H_{2}Cl_{4}/n-Hexane |
| Color | Colorless |
| Formula | C_{49}H_{36}Au_{2}P_{2}S_{4} |
| F_{w} | 1208.90 |
| Crystal system | Monoclinic |
| Space group | Pn (No. 6) |
| a /Å | 14.3012 (12) |
| b /Å | 8.9089 (8) |
| c /Å | 16.7670 (14) |
| α /° | 90 |
| β /° | 96.005 (1) |
| γ /° | 90 |
| V /Å³ | 2124.5 (3) |
| Z | 2 |
| D_{c} /g cm⁻³ | 1.890 |

| No. of reflections measured | 11346 |
| No. of unique reflections | 6950 |
| No. observations | 6767 (I > 2σ(I)) |
| R | 0.0125 |
| R_w | 0.0273 |
| GOF | 0.735 |
| Table S4. Crystal data and structure refinement for Au complex 2 |
|---------------------------------------------------------------|
| **CCDC No.** | 2116853 |
| **Solvent system** | C₂H₂Cl₄/n-Hexane |
| **Color** | Colorless |
| **Formula** | C₅₀H₃₈Au₂P₂S₄ |
| **F_w** | 1222.93 |
| **Crystal system** | Monoclinic |
| **Space group** | P2₁/n (No. 14) |
| **a /Å** | 12.3768 (1) |
| **b /Å** | 16.5846 (2) |
| **c /Å** | 21.3999 (2) |
| **α /°** | 90 |
| **β /°** | 101.368 (1) |
| **γ /°** | 90 |
| **V /Å³** | 4306.46 (8) |
| **Z** | 4 |
| **Dc /g cm⁻³** | 1.886 |
| **No. of reflections measured** | 8323 |
| **No. of unique reflections** | 8175 |
| **No. observations** | 7467 (I > 2σ(I)) |
| **R** | 0.0255 |
| **R_w** | 0.0633 |
| **GOF** | 1.038 |
Table S5. Crystal data and structure refinement for Au complex 3

|                          |               |
|--------------------------|---------------|
| CCDC No.                 | 2116855       |
| Solvent system           | Acetone       |
| Color                    | Colorless     |
| Formula                  | C_{51}H_{40}Au_{2}P_{2}S_{4} |
| F_w                      | 1238.01       |
| Crystal system           | Orthorhombic  |
| Space group              | Pbcn (No. 60) |
| a /Å                     | 18.4800 (4)   |
| b /Å                     | 16.1182 (16)  |
| c /Å                     | 33.0678 (4)   |
| α /°                     | 90            |
| β /°                     | 90            |
| γ /°                     | 90            |
| V/Å³                     | 9849.7 (3)    |
| Z                        | 4             |
| D_c /g cm⁻³              | 1.786         |
| No. of reflections measured | 10293       |
| No. of unique reflections | 9762          |
| No. observations         | 8672 (I > 2σ(I)) |
| R                        | 0.0302        |
| R_w                      | 0.0779        |
| GOF                      | 1.060         |
Table S6. Crystal data and structure refinement for Au complex 4

| Property                      | Value                                      |
|-------------------------------|--------------------------------------------|
| CCDC No.                      | 2116851                                    |
| Solvent system                | C$_2$H$_2$Cl$_4$/n-Hexane                  |
| Color                         | Colorless                                  |
| Formula                       | C$_{52}$H$_{42}$Au$_2$P$_2$S$_4$           |
| $F_w$                         | 1252.90                                    |
| Crystal system                | Triclinic                                  |
| Space group                   | P-1 (No. 2)                                |
| $a$ /Å                        | 16.0501 (2)                                |
| $b$ /Å                        | 17.0934 (2)                                |
| $c$ /Å                        | 20.7010 (3)                                |
| $\alpha$ /°                   | 91.582 (1)                                 |
| $\beta$ /°                    | 108.552 (1)                                |
| $\gamma$ /°                   | 96.765 (1)                                 |
| $V$ /Å$^3$                    | 5333.93 (12)                               |
| $Z$                           | 2                                          |
| $D_c$ /g cm$^{-3}$            | 1.767                                      |
| No. of reflections measured   | 20640                                      |
| No. of unique reflections     | 20234                                      |
| No. observations              | 17882 ($I > 2\sigma(I)$)                   |
| $R$                           | 0.0664                                     |
| $R_w$                         | 0.1939                                     |
| GOF                           | 1.045                                      |
Table S7. Crystal data and structure refinement for Au complex 4

| Property                        | Value           |
|---------------------------------|-----------------|
| CCDC No.                        | 2116854         |
| Solvent system                  | Acetone/n-Hexane|
| Color                           | Colorless       |
| Formula                         | C_{32}H_{42}Au_{2}P_{2}S_{4} |
| $F_w$                           | 1252.90         |
| Crystal system                  | Triclinic       |
| Space group                     | P-1 (No. 2)     |
| $a$ /Å                          | 12.3914 (2)     |
| $b$ /Å                          | 18.5659 (4)     |
| $c$ /Å                          | 22.6960 (4)     |
| $\alpha$ /°                     | 87.752 (2)      |
| $\beta$ /°                      | 79.865 (2)      |
| $\gamma$ /°                     | 77.404 (2)      |
| $V$ /Å$^3$                      | 5016.20 (17)    |
| $Z$                             | 2               |
| $D_c$ /g cm$^{-3}$              | 1.695           |
| No. of reflections measured     | 21120           |
| No. of unique reflections       | 20257           |
| No. observations                | 16646 ($I > 2\sigma(I)$) |
| $R$                             | 0.0464          |
| $R_w$                           | 0.1260          |
| GOF                             | 1.046           |
Table S8. Crystal data and structure refinement for compound 5

| Property                    | Value                     |
|-----------------------------|---------------------------|
| CCDC No.                    | 2117727                   |
| Solvent system              | CH$_2$Cl$_2$/Et$_2$O      |
| Color                       | Colorless                 |
| Formula                     | C$_{34}$H$_{20}$S$_4$     |
| $F_w$                       | 556.8                     |
| Crystal system              | Monoclinic                |
| Space group                 | $P2_1/n$ (No. 14)         |
| $a$ /Å                       | 21.0190 (18)              |
| $b$ /Å                       | 7.8788 (7)                |
| $c$ /Å                       | 46.469 (4)                |
| $\alpha$ /°                 | 90                        |
| $\beta$ /°                  | 97.2750 (10)              |
| $\gamma$ /°                 | 90                        |
| $V$ /Å$^3$                   | 7633.5 (11)               |
| $Z$                          | 12                        |
| $D_c$ /g cm$^{-3}$           | 1.453                     |
| No. of reflections measured | 19292                     |
| No. of unique reflections   | 18528                     |
| No. observations            | 13024 ($I > 2\sigma(I)$) |
| $R$                         | 0.0473                    |
| $R_w$                       | 0.1048                    |
| GOF                         | 1.010                      |
S4. Oxidation of Complexes

Oxidation of Au complex 1 by NOBF₄.

In a NMR tube, to a acetone- $_d$₆ (500 µL) solution of 1 (3.0 mg, 2.5 µmol) was added NOBF₄ (0.25 mol/L in Acetone-$_d$₆, 20 µL, 2.5 µmol) and the mixture was shook for a few seconds. The obtained product was analyzed by NMR measurement and single-crystal X-ray structure analysis.

Date for thianthrene; $^1$H NMR (400 MHz, CDCl₃, r.t.) $\delta$ 7.51-7.46 (m, 4H, C₆H₄), 7.25-7.22 (m, 4H, C₆H₄).

Figure S23. Changes in $^1$H NMR during oxidation of Au complex 1 caused by addition of NOBF₄ (400 MHz, CDCl₃, r.t.).
Oxidation of Au complex 1 by PhICl₂.

To a degassed DMF solution (4 mL) of Au complex 1 (6.1 mg, 5.0 μmol) was added PhICl₂ (2.5 mmol/L in DMF, 2 mL, 5.0 μmol) dropwise with stirring at –60 ºC for 5 min. The reaction mixture was stirred at the same temperature for 30 min, then it was warmed to 25 ºC and stirred overnight. The color of the mixture was changed from yellow to colorless. Solvent and iodobenzene (by-product) were removed under vacuum. The crude product was purified by silica gel PTLC (eluent: n-hexane/CHCl₃ = 5:1) to give thianthrene (0.56 mg, 2.5 μmol, 26%), and its dimer as a white solid (0.74 mg, 1.7 μmol, 34%). Date for thianthrene; ¹H NMR (400 MHz, CDCl₃, r.t.) δ 7.51-7.46 (m, 4H, C₆H₄), 7.25-7.22 (m, 4H, C₆H₄). Date for thianthrene dimer; ¹H NMR (400 MHz, CDCl₃, r.t.) δ 7.59 (d, 2H, C₆H₃, J = 7.6 Hz), 7.52-7.50 (m, 2H, C₆H₃), 7.33 (t, J = 7.6 Hz, C₆H₃) 7.26-7.22 (m, 4H, C₆H₄), 7.17-7.13 (m, 4H, C₆H₄).

Oxidation of Au complex 4 by PhICl₂.

To a degassed DMF solution (4 mL) of Au complex 1 (6.1 mg, 5.0 μmol) was added PhICl₂ (6.3 mmol/L in DMF, 4 mL, 25 μmol) dropwise with stirring at –60 ºC for
5 min. The reaction mixture was stirred at the same temperature for 30 min, then it was warmed to 25 °C and stirred overnight. The color of the mixture was changed from yellow to colorless. Solvent and iodobenzene (by-product) were removed under vacuum. The crude product was purified by silica gel PTLC (eluent: n-hexane/CHCl₃ = 5:1) to give thianthrene (3.1 mg, 14 μmol, 28%), and its dimer as a white solid (2.9 mg, 6.7 μmol, 26%).
**S5. Computational Details**

All theoretical calculations were carried out using ORCA 5.0.1. Geometry optimization was conducted at the r^2SCAN-3c level of theory. The optimized structures were verified as minima by frequency calculations. The single point calculation was performed to obtain accurate energies and frontier orbitals at the ωB97M-V/def2-TZVP level of theory. The solvent effects of CHCl₃ or CH₂CH₂ were evaluated by the SMD solvation model. The RIJCOSX approximation was applied with the def2/J auxiliary basis set. The Gibbs free energies were included in the Gibbs energy correction of unscaled vibrational analysis at the r^2SCAN-3c level of theory. TD-DFT calculation was carried out at the mPW1PW/def2-TZVP level of theory with Tamm–Dancoff approximation (TDA). The solvation effect of CHCl₃ was considered through the CPCM solvation model. All calculation was used larger DefGrid3 due to Au–Au weak interaction. The geometries, frontier orbitals (isosurface 0.02) and density differences (isosurface 0.001) were drawn with PyMOL 2.3.0. The absorption spectra, including the first 24 states, were drawn by ChemCraft version 1.8. The spectra broadened by Gaussian function with band width at 1/2 height was set to 18.
**Detailed results of TD-DFT calculations**

**Table S9.** The first three states of calculated transition properties of 1 with Au–Au interaction (mPW1PW/def2-TZVP).

| state | wavelength/nm | $f_{osc}$ | assignment |
|-------|----------------|-----------|------------|
| 1     | 338            | 0.00427   | HOMO→LUMO, 85% |
| 2     | 330            | 0.0397    | HOMO–1→LUMO, 79% |
| 3     | 310            | 0.0299    | HOMO→LUMO+1, 50%  
            |               |           | HOMO–2→LUMO, 20% |

**Table S10.** The first three states of calculated transition properties of 1 without Au–Au interaction (mPW1PW/def2-TZVP).

| state | wavelength/nm | $f_{osc}$ | assignment |
|-------|----------------|-----------|------------|
| 1     | 303            | 0.00133   | HOMO→LUMO, 85% |
| 2     | 302            | 0.00503   | HOMO–1→LUMO, 83% |
| 3     | 298            | 0.00251   | HOMO→LUMO+6, 60%  
            |               |           | HOMO→LUMO+3, 12% |
Frontier Orbitals and Density Difference Related to Excitation

**Figure S24.** Frontier orbitals of 1 with Au–Au interaction at the CPCM(CHCl₃)-mPW1PW/def2-TZVP level of theory. (a) HOMO−1 (−5.91 eV), (b) HOMO (−5.75 eV), (c) LUMO (−1.42 eV). An isosurface is 0.02.

**Figure S25.** Density difference of 1 with Au–Au interaction at the CPCM(CHCl₃)-mPW1PW/def2-TZVP level of theory. (a) First excited state, (b) second excited state. An isosurface is 0.001. The yellow surface indicated an increase in electron density, and the blue surface showed a decrease in electron density.

**Figure S26** Frontier orbitals of 1 without Au–Au interaction at the CPCM(CHCl₃)-mPW1PW/def2-TZVP level of theory. (a) HOMO−1 (−6.06 eV), (b) HOMO (−6.05 eV), (c) LUMO (−1.37 eV). An isosurface is 0.02.
Figure S27  Density difference of 1 without Au–Au interaction at the CPCM(CHCl$_3$)-mPW1PW/def2-TZVP level of theory. (a) First excited state, (b) second excited state. An isosurface is 0.001. The yellow surface indicated an increase in electron density, and the blue surface showed a decrease in electron density.
Relative Gibbs Energies of Natural and Cationic Species

Figure S28. Geometries and relative Gibbs energies of natural species of 1 in CHCl₃.
Figure S29. Geometries and relative Gibbs energies of natural species of 1 in CH₂Cl₂.

Figure S30. Geometries and relative Gibbs energies of monocationic species of 1 in CH₂Cl₂.
Figure S31. Geometries and relative Gibbs energies of dicationic species of 1 in CH₂Cl₂.

Figure S32. Geometries and relative Gibbs energies of tricationic species of 1 in CH₂Cl₂.
Figure S33. Frontier orbitals of most stable species at the SMD(CH$_2$Cl$_2$)-ωB97M-V/def2-TZVP level of theory. (a) HOMO (−7.75 eV) of natural species of I, (b) LUMO (0.376 eV) of natural species of I, (c) SOMO (−6.48 eV) of monocationic species of I, (d) SUMO (−1.07 eV) of monocationic species of I, (e) HOMO (−8.72 eV) of dicationic species of I, (f) LUMO (−0.805 eV) of dicationic species of I, (g) SOMO (−9.42 eV) of tricationic species of I, (h) SUMO (−4.09 eV) of tricationic species of I. An isosurface is 0.02.
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