Supporting Materials for:

Stimuli-Sensitive Aggregation-Induced Emission of Organogelators Containing Mesogenic Au(I) Complexes

*Supattra Panthai, Ryota Fukuhara, Kyohei Hisano, Osamu Tsutsumi**

Department of Applied Chemistry, Ritsumeikan University
1-1-1 Nojihigashi, Kusatsu 525-8577, Japan.
Email: tsutsumi@sk.ritsumei.ac.jp

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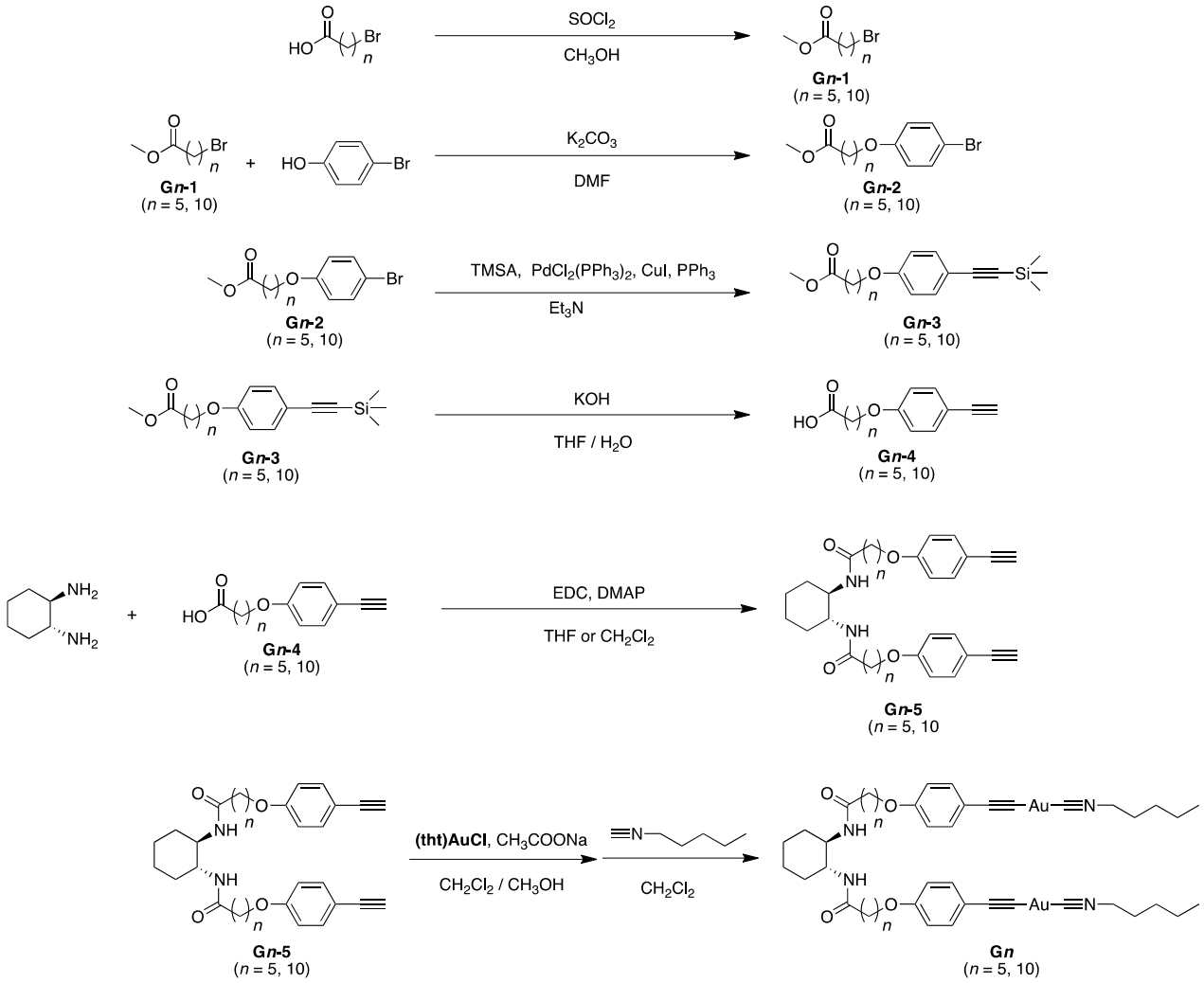
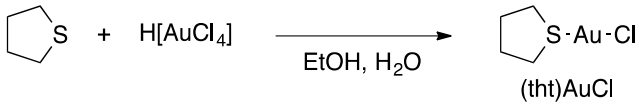
1. Preparation of materials

Au complexes, **G*n*** were newly synthesized according to Scheme S1. The structure of Au complexes was fully characterized by ^{1}H NMR were recorded in $CDCl_3$, using ECS-400 spectrometer (JEOL, Tokyo, Japan) at 400 MHz, Chemical shifts were appeared in part per million (ppm), using the residual proton in NMR solvent as an internal reference. Infrared (IR) spectra were obtained using KBr disk method with FT/IR-4100 spectrometer (JASCO, Tokyo, Japan), all spectra were reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were taken with a micrOTOF-Q Ⅱ mass spectrometer (Bruker, Daltonics, MA, USA).

Scheme S1. Synthesis route of **G*n*** (*n* = 5, 10)



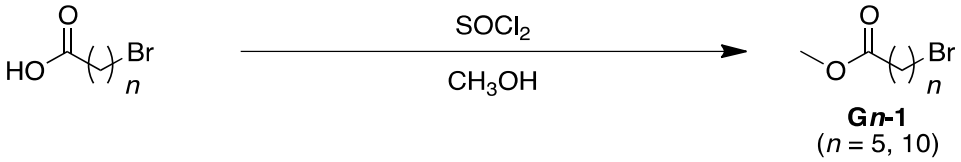
Synthesis of (tht)AuCl



A solution of tetrachloroauric (III) acid (1.0 g, 2.4 mmol) in water (2 mL) was added to ethanol (8 mL) and stirred at room temperature. To the resultant solution, 0.44 mL (4.9 mmol) of tetrahydrothiophene was added slowly, stirred at room temperature for 1 h, and then white precipitate was appeared. The precipitate was collected by filtration, washed with amount of ethanol and dried in ambient temperature to give 0.75 g (2.3 mmol) of white solid (**(tht)AuCl**) in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.52-3.31 (br, 4H; S-CH_2), 2.29-2.09 (br, 4H; S-CH_2CH_2).

Synthesis of gold(I) complexes

G*n*-1 (n = 5, 10)

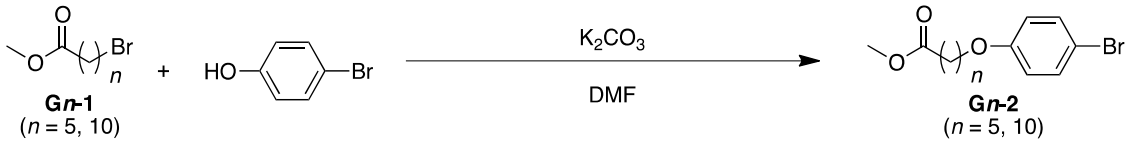


Methyl 2-bromoacetate (**G5-1**). 6-bromoacetic acid (2.0 g, 10 mmol), Thionyl chloride (1.4 g, 12 mmol), were added to 20 mL of methanol, and the solution was stirred at room temperature for 2 h. A solid suspended in the reaction mixture was filtered off. After the filtrate was concentrated under reduced pressure. The solvent was removed to give 2.0 g (9.4 mmol) of colorless oil **(G5-1**) in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.67 (s, 3H; OCH_3), 3.40 (t, J = 6.7 Hz; 2H; BrCH_2), 2.40 (t, J = 7.5 Hz; 2H; COCH_2), 1.88 (quin, J = 7.3 Hz; 2H; $BrCH_2CH_2$), 1.67 (quin, J = 7.3 Hz; 2H; $COCH_2CH_2$), 1.48 (quin, J = 7.1 Hz; 2H; Br $CH_2CH_2CH_2$).

Methyl 11-bromoundecanoate (G10-1). According to above procedure, compound **G10-1** was obtained.

G10-1: Yield = 95 %. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.66 (s, 3H; OCH_3), 3.40 (t, J = 6.7 Hz; 2H; BrCH_2), 2.30 (t, J = 7.5 Hz; 2H; COCH_2), 1.84 (quin, J = 7.3 Hz; 2H; $BrCH_2CH_2$), 1.61 (quin, J = 7.3 Hz; 2H; $COCH_2CH_2$), 1.41 (quin, J = 7.1 Hz; 2H; $BrCH_2CH_2CH_2$), 1.28 (br, 10H; $BrCH_2CH_2CH_2(CH_2)_5$).

G*n*-2 (*n* = 5, 10)



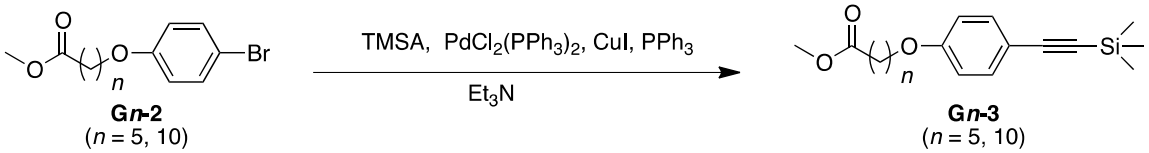
G*n*-1 (*n* = 5, 10) **G*n*-2** (*n* = 5, 10)

Methyl 6-(4-bromophenoxy)hexanoate (G5-2). **G5-1** (1.7 g, 8.1 mmol), 4-bromophenol (2.0 g, 8.9 mmol), potassium carbonate (1.7 g, 12.1 mmol) were added in 20 mL of dimethylformamide, stirred and refluxed for 21 h at 90 °C. The product was extracted with diethyl ether, washed with water (100 mL) and a saturated aqueous sodium chloride (50 mL). After that the organic layer was dried with anhydrous sodium sulfate. The product was concentrated by evaporation. The crude product was purified on a silica gel column chromatography (eluent: CH_2Cl_2) and then solvent was completely removed by evaporation, to give 1.7 g (5.0 mmol) of white solid in 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.54 (dd, J = 6.7, 2.4 Hz; 2H; 3,5-H in phenyl), 6.66 (dd, J = 6.7, 2.0 Hz; 2H; 2,6-H in phenyl), 3.91 (t, J = 6.5 Hz; 2H; OCH_2), 3.67 (s, 3H; OCH_3), 2.35 (t, J = 7.7 Hz; 2H; COCH_2), 1.79 (quin, J = 6.9 Hz; 2H; OCH_2CH_2), 1.70 (quin, J = 7.5 Hz; 2H; $COCH_2CH_2$), 1.49 (quin, J = 7.3 Hz; 2H; $OCH_2CH_2CH_2$).

Methyl 11-(4-bromophenoxy)undecanoate (G10-2). According to above procedure, compound **G10-2** was obtained.

G10-2. Yield = 62%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.53 (dd, J = 6.7, 2.4 Hz; 2H; 3,5-H in phenyl), 6.67 (dd, J = 6.7, 2.0 Hz; 2H; 2,6-H in phenyl), 3.90 (t, J = 6.5 Hz; 2H; OCH_2), 3.66 (s, 3H; OCH_3), 2.30 (t, J = 7.7 Hz; 2H; COCH_2), 1.75 (quin, J = 6.9 Hz; 2H; OCH_2CH_2), 1.61 (quin, J = 7.5 Hz; 2H; $COCH_2CH_2$), 1.43 (quin, J = 7.3 Hz; 2H; $OCH_2CH_2CH_2$), 1.29 (br, 10H; $OCH_2CH_2CH_2(CH_2)_5$).

G*n*-3 (*n* = 5, 10)



G*n*-2 (*n* = 5, 10) **G*n*-3** (*n* = 5, 10)

Methyl 6-[4-((trimethylsilyl)ethynyl)phenoxy]hexanoate (**G5-3**). **G5-2** (1.7 g, 4.9 mmol), bis(triphenylphosphine) palladium dichloride (0.15 g, 0.1mmol), copper iodide (39 mg, 0.2 mmol) and triphenylphosphine (55 mg, 0.2 mmol) were added to 20 mL of triethylamine. The suspended solution was stirred under argon atmosphere at room temperature. TMSA (0.72 g, 7.4 mmol) were added into the solution mixture, stirred and refluxed for 22 h at 90℃. The solid suspended in the reaction mixture was filtered off. After filtrate was concentrated by evaporation. The product was extracted with dichloromethane and washed with saturated aqueous ammonium chloride (50 mL), water (50 mL) and

saturated aqueous sodium chloride (50 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated by evaporation. The crude product was purified on a silica gel column chromatography (eluent: CH_2Cl_2/Hexane = 4/1). The solvent was completely removed to give 1.1 g (3.5 mmol) of pale yellow in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 (dd, J = 8.3, 1.6 Hz; 2H; 3,5-H in phenyl), 6.80 (dd, J = 8.3, 1.6 Hz; 2H; 2,6-H in phenyl), 3.93 (t, J = 6.5 Hz; 2H; OCH_2), 3.66 (s, 3H; OCH_3), 2.30 (t, J = 7.3 Hz; 2H; COCH_2), 1.76 (quin, J = 7.0 Hz; 2H; OCH_2CH_2),1.61 (quin, J = 7.1 Hz; 2H; $COCH_2CH_2$), 1.43 (quin, J = 7.1 Hz; 2H; $OCH_2CH_2CH_2$), 1.29 (br, 10H; $OCH_2CH_2CH_2(CH_2)_5$), 0.22 (s, 9H, -Si(CH_3)).

Methyl 11-[4-((trimethylsilyl)ethynyl)phenoxy]undecanoate (**G10-3)**. According to above procedure, compound **G10-3** was obtained.

G10-3. Yield = 62%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 (dd, J = 8.3, 1.6 Hz; 2H; 3,5-H in phenyl), 6.80 (dd, J = 8.3, 1.6 Hz; 2H; 2,6-H in phenyl), 3.93 (t, J = 6.5 Hz; 2H; OCH_2), 3.66 (s, 3H; OCH_3), 2.30 (t, J = 7.3 Hz; 2H; COCH_2), 1.76 (quin, J = 7.0 Hz; 2H; OCH_2CH_2),1.61 (quin, J = 7.1 Hz; 2H; $COCH_2CH_2$), 1.43 (quin, J = 7.1 Hz; 2H; $OCH_2CH_2CH_2$), 1.29 (br, 10H; $OCH_2CH_2CH_2(CH_2)_5$), 0.22 (s, 9H, -Si(CH_3)).

G*n*-4 (n = 5, 10)

G*n*-3
(n = 5, 10)

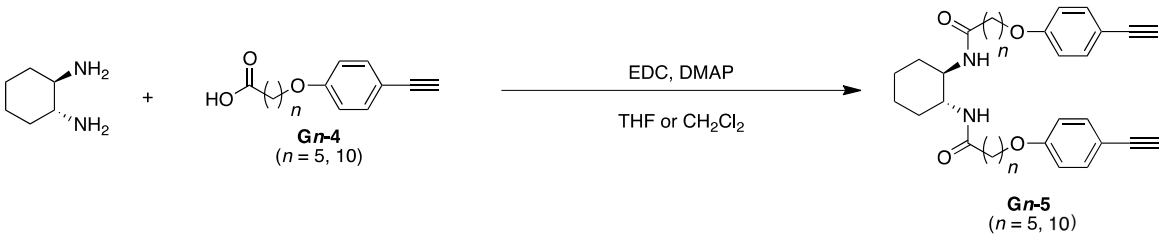
G*n*-4
(n = 5, 10)

6-(4-ethynylphenoxy)hexanoic acid (G5-4). **G5-3** (1.3 g, 4.1 mmol) and potassium hydroxide (0.68 g, 12 mmol) were added to 15 mL of tetrahydrofuran, stirred and refluxed for 4 h at 80 °C. A suspended of the reaction mixture was acidified (pH = 2) with hydrochloric acid (1 mol L^{-1}). The product was extracted with dichloromethane, and washed with water (50 mL) and saturated aqueous sodium chloride (50 mL). The organic layer was dried with anhydrous sodium sulfate and the solvent was removed to give 0.89 g (3.8 mmol) of brown solid in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.67(br, 1H; COOH), 7.41 (dd, J = 9.4, 2.5 Hz; 2H; 3,5-H in phenyl), 6.84 (dd, J = 9.2, 2.3 Hz; 2H; 2,6-H in phenyl), 3.96 (t, J = 6.3 Hz; 2H; OCH_2), 3.00 (s, 1H; -≡CH), 2.41 (t, J = 7.2 Hz; 2H; COCH_2), 1.82 (quin, J = 6.3 Hz; 2H; OCH_2CH_2),1.72 (quin, J = 7.1 Hz; 2H; $COCH_2CH_2$), 1.50 (quin, J = 6.3 Hz; 2H; $OCH_2CH_2CH_2$).

11-(4-ethylnylphenoxy)undecanoic acid (G10-4). According to above procedure, compound **G10-4** was obtained.

G10-4. Yield = 93%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.41 (dd, J = 8.3, 1.6 Hz; 2H; 3,5-H in phenyl), 6.83 (dd, J = 8.3, 1.6 Hz; 2H; 2,6-H in phenyl), 3.95 (t, J = 7.3 Hz; 2H; OCH_2), 2.99 (s, 1H; -≡CH), 2.35 (t, J = 7.7 Hz; 2H; COCH_2), 1.77 (quin, J = 6.9 Hz; 2H; OCH_2CH_2), 1.63 (quin, J = 6.7 Hz; 2H; $COCH_2CH_2$), 1.44 (quin, J = 6.7 Hz; 2H; $OCH_2CH_2CH_2$), 1.30 (br, 10H; $OCH_2CH_2CH_2(CH_2)_5$).

G*n*-5 (*n* = 5, 10)

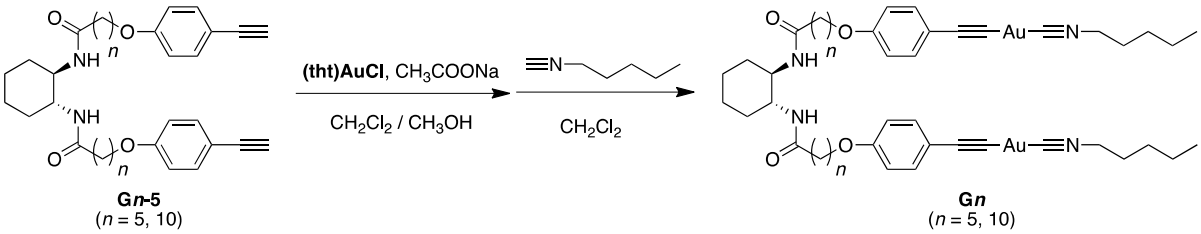


***N,N'-((1R,2R)*-cyclohexane-1,2-diyl)bis[6-(4-ethynylphenoxy)hexanamide] (G5-5)**. **G5-4** (0.48 g, 2.1 mmol), *trans*-1,2-Cyclohexanediamine (0.12 g, 1.0 mmol), EDC (0.48 g, 2.5 mmol), DMAP (64 mg, 0.52 mmol) were added to 10 mL of dichloromethane and stir for 11 h at room temperature under argon atmosphere with precipitate was appeared. The precipitated was collected by filtration. The crude product obtained was purified on a silica gel column chromatography (eluent: $CHCl_3$/MeOH = 9/1), the solvent was removed to give 0.36 g (0.67 mmol) of white solid in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.40 (dd, J = 6.7, 2.0 Hz; 4H; 3,5-H in phenyl), 6.80 (dd, J = 6.7, 2.0 Hz; 4H; 2,6-H in phenyl), 5.90 (s, 2H; CONH)), 3.91 (t, J = 6.3 Hz; 4H; OCH_2), 3.64 (m, 2H; NHCH), 2.99 (s, 2H; -≡CH), 2.13 (t, J = 7.5 Hz; 4H; $OCH_2CH_2CH_2CH_2CH_2$), 2.01(d, 2H; equatorial 2,5-H in cyclohexane), 1.76 (quin, J = 6.8 Hz; 6H; OCH_2CH_2, equatorial 3,4-H in cyclohexane), 1.64 (m, 4H; $OCH_2CH_2CH_2CH_2$), 1.44 (quin, J = 7.7 Hz; 4H; $OCH_2CH_2CH_2$), 1.26 (m, 2H; axial 2,5-H in cyclohexane, 2H; axial 3,4-H in cyclohexane).

***N,N'-((1R,2R)*-cyclohexane-1,2-diyl)bis[11-(4-ethynylphenoxy)undecanamide] (G10-5)**. **G10-4** (0.85 g, 2.8 mmol), *trans*-1,2-cyclohexanediamine (0.16 g, 1.4 mmol), EDC (0.53 g, 2.8 mmol) were added to 15 mL of dichloromethane and stirred at 0 °C for 10 min. DMAP in 5 mL of dichloromethane were added into the solution and stirred for 23 h at room temperature. The product was washed with aqueous hydrochloric acid (1 mol L^{-1}), water (50 mL) and saturated aqueous sodium chloride (50 mL). The organic layer was dried with anhydrous sodium sulfate and concentrated by evaporation. The crude product obtained was purified on a silica gel column chromatography (eluent: $CHCl_3$/EtOAc = 4/1). After solvent was removed to give 0.10 g (0.15 mmol) of white solid in 10% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.41 (dd, J = 6.7, 2.0 Hz; 4H; 3,5-H in phenyl), 6.82 (dd, J = 6.7, 2.0 Hz; 4H; 2,6-H in phenyl), 5.87 (s, 2H; CONH), 3.93 (t, J = 6.6 Hz; 4H; OCH_2), 3.64 (m, 2H; NHCH), 2.99 (s, 2H; -≡CH), 2.10 (dd, J = 6.7, 2.0 Hz; 4H; COCH_2), 2.02 (d, J = 13.6 Hz; 2H; equatorial 2,5-H in cyclohexane), 1.76 (m, 4H; OCH_2CH_2, 2H; equatorial 3,4-H in cyclohexane), 1.60-

1.50 (m, 4H; $COCH_2CH_2$), 1.43 (q, J = 7.7 Hz; 4H; $OCH_2CH_2CH_2$), 1.34-1.20 (m, 20H; $OCH_2CH_2CH_2(CH_2)_5$, 2H; axial 2,5-H in cyclohexane, 2H; axial 3,4-H in cyclohexane).

G*n* (n = 5, 10)



G*n*-5 (n = 5, 10) **G*n*** (n = 5, 10)

***N,N'-((*1*R*,2*R*)-cyclohexane-1,2-diyl)bis{6-[4-pentylisocyano-(phenoxyethynylgold(I))] hexanamide} (G5)**. **G5-5** (81 mg, 0.19 mmol), a solution of CH_3COONa (78 mg, 5.0 mmol) in 5 mL of methanol, and **(tht)AuCl** (62 mg, 0.19 mmol) were added to 10 mL of dichloromethane. Then the solution was stirred for 1 h at room temperature. The precipitate solid was appeared in the reaction mixture and then collected by filtration. The product was washed with methanol and water and dichloromethane. The obtained yellow solid was suspended to 10 mL of dichloromethane and 1-pentyl isocyanide (45 μL, 0.19 mmol) was added to the resultant suspension. The mixture was stirred for 2 h at room temperature, and then passed through Celite, followed by removal solvent with evaporation. The crude product was purified on a silica gel column chromatography (eluent: CH_2Cl_2/EtOAc = 1/1), and then solvent was completely removed to give 0.16 g (0.14 mmol) of white solid in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39 (dd, J = 6.7, 2.0 Hz; 4H; 3,5-H in phenyl), 6.75 (dd, J = 6.7, 2.0 Hz; 4H; 2,6-H in phenyl), 5.90 (s, 2H; CON*H*)), 3.90 (t, J = 6.3 Hz; 4H; OCH_2), 3.62 (m, 6H; NHC*H*, NCH_2), 2.10 (t, J = 7.3 Hz; 4H; $OCH_2CH_2CH_2CH_2CH_2$), 2.02 (d, J = 12 Hz; 2H; equatorial 2,5-H in cyclohexane) 1.83 (m, 4H; NCH_2CH_2), 1.73 (quin, J = 7.0 Hz; 6H; OCH_2CH_2, equatorial 3,4-H in cyclohexane), 1.65-1.57 (m, 4H; $OCH_2CH_2CH_2CH_2$), 1.47-1.20 (m, 16H; $OCH_2CH_2CH_2$, 2H; axial 2,5-H in cyclohexane, 2H; axial 3,4-H in cyclohexane, $NCH_2CH_2(CH_2)_2$), 0.95 (t, J =7.1 ; 6H; $N(CH_2)_4CH_3$). FTIR (KBr, ν): 3286, 2932, 2859, 2245, 1639, 1504, 1243 cm^{-1}. TOF-MS (ESI, m/z): calcd for $C_{46}H_{63}Au_2N_4O_4$ $[M+H]^+$, 1129.4175; found, 1129.3689.

***N,N'-((*1*R*,2*R*)-cyclohexane-1,2-diyl)bis{11-[4-pentylisocyano-(phenoxyethynylgold(I))]undecanamide} (G10)**. According to above procedure, compound **G10** was obtained.

G10. Yield = 85 %: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.38 (dd, J = 6.7, 2.0 Hz; 4H; 3,5-H in phenyl), 6.76 (dd, J = 6.7, 2.0 Hz; 4H; 2,6-H in phenyl), 5.91 (s, 2H; CON*H*), 3.91 (t, J = 6.5 Hz; 4H; OCH_2), 3.61 (m, 6H; NHC*H*, NCH_2), 2.10 (t, J = 7.3 Hz; 4H; $COCH_2$), 2.02 (d, J = 12.2 Hz; 2H; equatorial 2,5-H in cyclohexane) 1.82 (m, 4H; NCH_2CH_2), 1.73 (quin, J = 7.2 Hz; 6H; OCH_2CH_2, equatorial 3,4-

H in cyclohexane), 1.65-1.57 (m, 4H; $COCH_2CH_2$), 1.41 (m, 12H; $OCH_2CH_2CH_2$, $NCH_2CH_2(CH_2)_2$), 1.34-1.20 (m, 20H; $OCH_2CH_2CH_2(CH_2)_5$, 2H; axial 2,5-H in cyclohexane, 2H; axial 3,4-H in cyclohexane), 0.94 (t, J = 7.0 ; 6H; $N(CH_2)_4CH_3$). FTIR (KBr, ν): 3285, 2925, 2853, 2247, 1637, 1504, 1243 cm^{-1}. TOF-MS (ESI, m/z): calcd for $C_{56}H_{83}Au_2N_4O_4$ $[M+H]^+$, 1269.5740; found, 1269.6100.

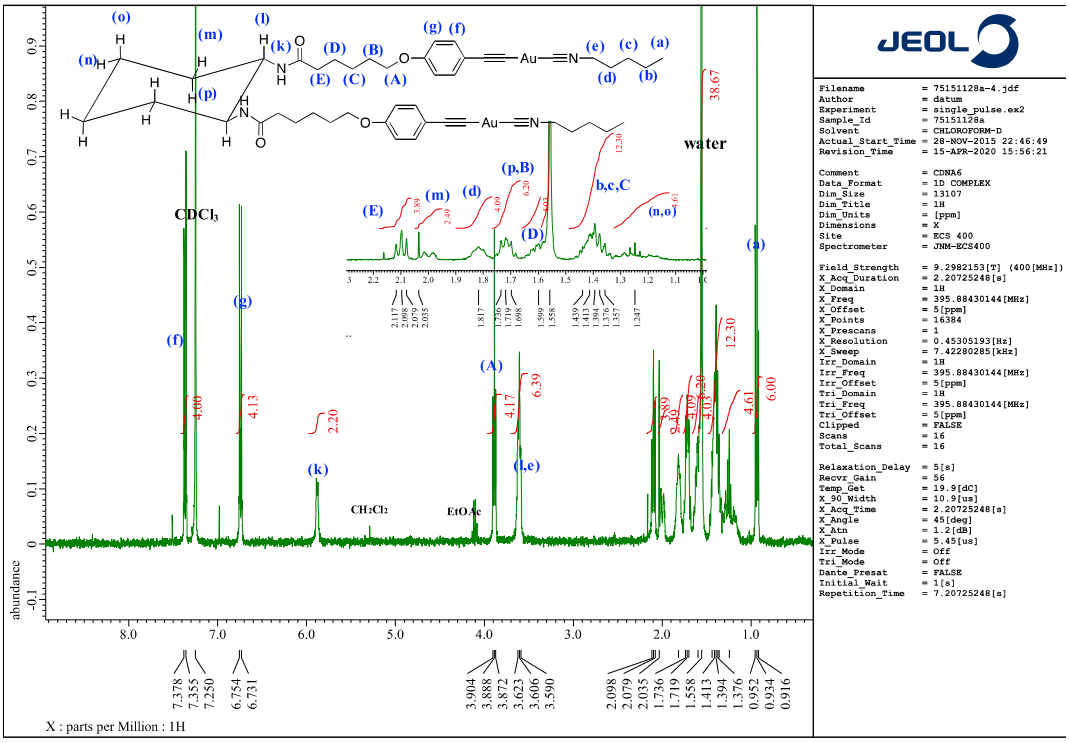


Figure S1. ^{1}H NMR spectrum of **G5** in $CDCl_3$.

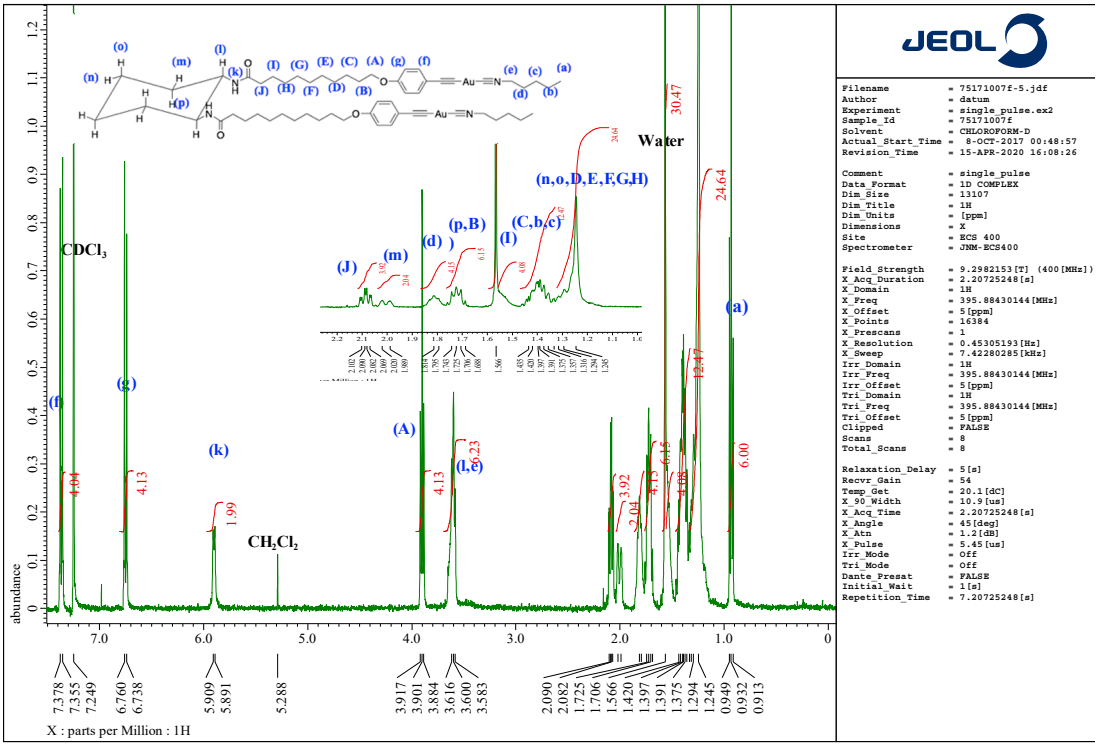


Figure S2. ^{1}H NMR spectrum of **G10** in $CDCl_3$.

Preparation of gel and xerogel

To examine the gelation ability of gold(I) complexes in various solvent, 10 mg of complex, **G*n*** was dissolved in 1.0 mL of solvents upon heating, and then the gelators were performed at room temperature. The xerogel was prepared by casting the obtained gel on a glass substrate, air-drying in ambient temperature for removal of the solvent.

2. Photophysical properties of G*n*

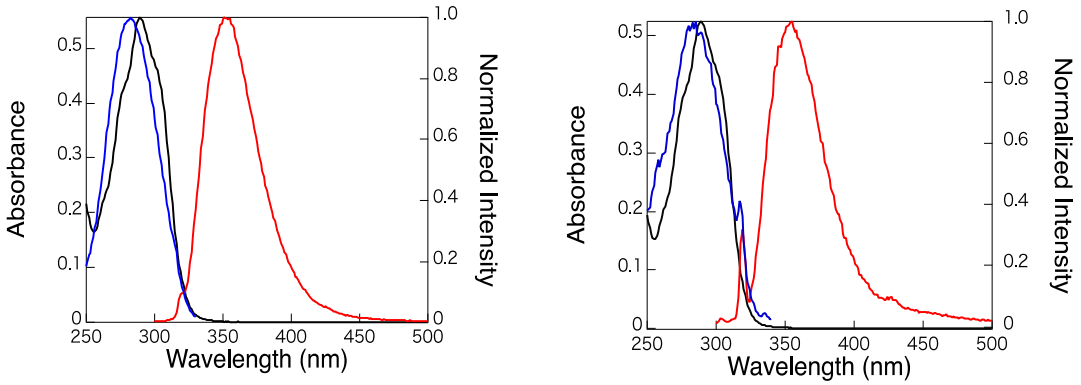


Figure S3 Photophysical properties of gold complexes (a) **G5** and (b) **G10** in solution. Blue: absorption spectrum in CH_2Cl_2 (1.0×10^{-5} mol L^{-1}), black: normalized excitation spectrum (1.0×10^{-6} mol L^{-1}, λ_{em} = 360 nm), and red: normalized emission spectrum (1.0×10^{-6} mol L^{-1}, λ_{ex} = 288 nm).

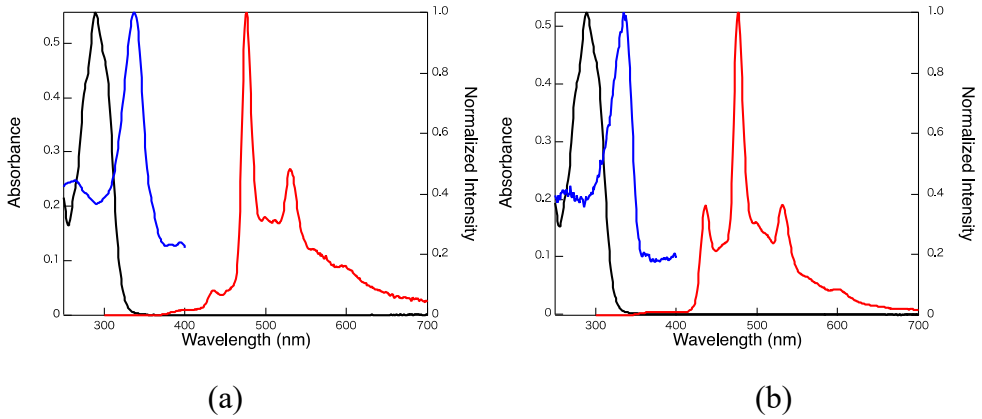
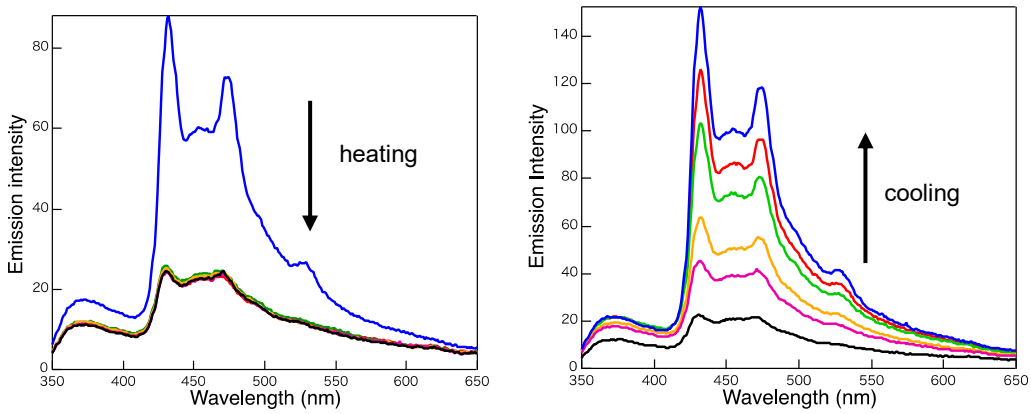


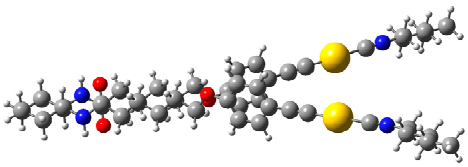
Figure S4. Photophysical properties of gold complexes (a) **G5** and (b) **G10** in crystals: black; absorption spectrum in CH_2Cl_2 solution (1.0×10^{-5} mol L^{-1}), red; photoluminescence in crystals (λ_{ex} = 288 nm), blue; excitation spectrum in crystals (λ_{em} = 475 nm).



(a) (b)

Figure S5. Temperature dependence of the luminescence spectra of the **G5** in hexane/$CHCl_3$ (1/2, v/v) upon (a) 2nd heating and (b) 2nd cooling. The spectra were recorded every 5 °C between 30 °C and 55 °C: blue, 30 °C; red, 35 °C; green, 40 °C; orange, 45 °C; purple, 50 °C; black, 55 °C.

Side view



Top view

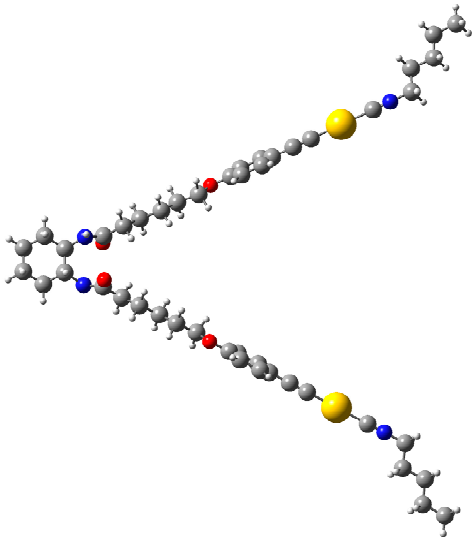


Figure S6. Plausible 3D model of **G5** Molecule optimized by a semiempirical calculation using PM6.