Cooperative Self-Assembly and Gelation of Organogold(I) Complexes via Hydrogen Bonding and Aurophilic Au---Au Interactions

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1. Materials and Methods

4-Iodoaniline, 4-iodoanisole, trimethylsily acetylene, 2,2'-dicarboxydiphenylamine, $Pd(PPh_3)_2Cl_2$, 4-dimethylamino pyridine (DMAP), CuI, *N*-(3-dimethylaminopropyl)-*N*'- ethylcarbodiimide (EDC) are reagent grade and used as received. All other reagents were employed as purchased. 4-Ethynylbenzoic acid^[S1], *N*-(2-aminoethyl)-3,4,5-tris(((*S*)-3,7-dimethyloctyl)oxy)benzamide **4**,^[S2] and chloro(tetrahydrothiophene) gold [Au(tht)Cl]^[S3] were synthesized according to the previously reported procedures.

¹H NMR spectra were collected on a Varian Unity INOVA-300 spectrometer with TMS as the internal standard. ¹³C NMR spectra were recorded on a Varian Unity INOVA-300 spectrometer at 75 MHz. Electrospray ionization mass spectra (ESI-MS) were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Breman, Germany) equipped with an ESI interface and ion trap analyzer. UV/Vis spectra were recorded on UV-1800 Shimadzu spectrometer. Circular dichroism (CD) measurements were performed on a Jasco J-1500 circular dichroism spectrometer, equipped with a PFD-425S/15 Peltier-type temperature controller. Steady-state emission spectra were recorded on a FluoroMax-4 spectrofluorometer (Horiba Scientific), and analyzed with an Origin (*v*8.1) integrated software FluoroEssence (*v*2.2). Transmission electron microscope (TEM) images were performed on a Tecnai G2 Spirit BioTWIN electron microscope (acceleration voltage: 120 kV).

2. Synthetic routes to monomer 1



Scheme S1. Synthetic route to the designed monomer 1.

2.1. Synthesis of 2



Compound **4** (500 mg, 0.79 mmol), 4-ethynylbenzoic acid (126 mg, 0.87 mmol), EDC (227 mg, 1.18 mmol) and DMAP (135 mg, 1.10 mmol) were dissolved in CH₂Cl₂ (40 mL) and stirred at room temperature for 24 hours. The mixture was extracted with H₂O/CH₂Cl₂ for three times. The organic extracts were combined and concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography (silica, CH₂Cl₂ as the eluent) to provide **2** as a pale yellow solid (493 mg, 82%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.78 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.33 (m, 1H), 7.09 (m, 1H), 7.00 (m, 2H), 4.02 (m, 6H), 3.70 (s, 4H), 3.19 (s, 1H), 1.85 (m, 3H), 1.61 (m, 3H), 1.52 (m, 6H), 1.40–1.08 (m, 18H), 0.94–0.90 (m, 9H) 0.86 (d, *J* = 6.6 Hz, 18H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 168.9, 167.8, 153.1, 141.1, 133.8, 132.4, 128.7, 127.0, 125.6, 105.5, 82.7, 79.6, 71.7, 67.50, 41.2, 39.3, 37.4, 36.4, 29.8, 28.0, 24.7, 22.6, 19.5. ESI–MS *m*/*z*: [M + Na]⁺ C₄₈H₇₆N₂NaO₅, 783.52.

(7777) (7777) (7777) (7555) (7556) (7566)



Figure S1. ¹H NMR spectrum (300 MHz, CDCl₃, room temperature) of 2.



Figure S2. ¹³C NMR spectrum (75 MHz, CDCl₃, room temperature) of 2.



Figure S3. Electrospray ionization spectrum of 2.

2.2. Synthesis of 3



Compound **2** (200 mg, 0.26 mmol), 4-iodoanisole (110 mg, 0.47 mmol), Pd(PPh₃)₂Cl₂ (9.10 mg, 0.013 mmol) and CuI (4.9 mg, 0.026 mmol) in 20 mL of NEt₃ were mixed together under nitrogen atmosphere. After stirring at 70 °C for 12 hours, the reaction mixture was evaporated, and the residue was extracted with H₂O/CH₂Cl₂. After the combined organic extracts were dried over anhydrous Na₂SO₄ and evaporated with a rotary evaporator, the residue was purified by flash column chromatography (silica, CH₂Cl₂/CH₃OH, 150 : 1 *v/v* as the eluent) to afford **3** as a gray solid (150 mg, 67%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.79 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.24 (s, 1H), 7.13 (s, 1H), 7.01 (s, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.03 (m, 6H), 3.84 (s, 3H), 3.71 (s, 4H), 1.85 (m, 3H), 1.70 (m, 3H), 1.52 (m, 6H), 1.38–1.09 (m, 18H), 0.98–0.90 (m,9H) 0.86 (d, *J* = 6.6 Hz, 18H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 168.7, 168.1, 159.9, 153.1, 141.0 133.2, 132.7, 131.5, 128.7, 127.2, 127.1, 114.8, 114.1, 105.5, 92.1, 87.4, 75.0, 71.7, 69.3, 67.5, 59.1, 55.3, 41.1, 40.9, 39.3, 39.3, 37.5, 37.4, 36.4, 31.9, 29.8, 29.7, 29.3, 28.0, 27.2, 25.5, 24.7, 22.6, 21.3, 19.5, 16.5, 14.1. ESI–MS *m/z*: [M + H]⁺ C₅₅H₈₃N₂O₆, 867.55.



Figure S4. ¹H NMR spectrum (300 MHz, CDCl₃, room temperature) of **3**.



Figure S5. ¹³C NMR spectrum (75 MHz, CDCl₃, room temperature) of **3**.



Figure S6. Electrospray ionization spectrum of 3.

2.3. Synthesis of monomer 1



Au(tht)Cl (172 mg, 0.54 mmol) was added to a solution of compound 2 (400 mg, 0.53 mmol) and NaOAc (220 mg, 2.68 mmol) in MeOH/THF (9:1 v/v; 60 mL). The mixture was stirred for 1 h. The yellow precipitate was filtered, washed with water and methanol, and dried under vacuum. The crude sample was directly submitted to the next step without further purification.

To a solution of 1-isocyano-4-methoxybenzene (44 mg, 0.33 mmol) in dichloromethane was added to the above crude sample (300 mg, 0.31 mmol). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to give a white solid, which was subjected to flash column chromatography (aluminum oxide, neutral, CH₂Cl₂/CH₃OH, 200 : 1 *v/v* as the eluent) to provide **1** as an off-white solid (270 mg, 79%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.70 (d, *J* = 8.1 Hz, 2H), 7.48 (t, *J* = 8.1 Hz, 4H), 7.35 (s, 1H), 7.14 (s, 1H), 7.04 (s, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 4.03 (m, 6H), 3.86 (s, 3H), 3.66 (s, 4H), 1.85 (m, 3H), 1.70 (m, 3H), 1.52 (m, 6H), 1.38–1.09 (m, 18H), 0.98–0.90 (m, 9H) 0.86 (d, *J* = 6.6 Hz, 18H). ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 168.4, 161.7, 153.1, 140.9, 132.5, 131.7, 128.6, 126.8, 115.2, 105.4, 103.0, 71.7, 67.4, 55.8, 41.5, 40.8, 39.3, 37.4, 36.4, 29.8, 28.0, 24.8, 22.7, 19.6. ESI–MS *m/z*: [M + H]⁺ C₅₆H₈₃N₃O₆Au, calculated, 1090.5947, found, 1090.5953, error, 0.6 ppm.



Figure S7. ¹H NMR spectrum (300 MHz, CDCl₃, room temperature) of 1.



Figure S8. ¹³C NMR spectrum (75 MHz, CDCl₃, room temperature) of 1.



Figure S9. Electrospray ionization spectrum of 1.



Figure S10. FT–IR spectrum of 1. Two IR bands were observed at 2123 cm⁻¹ and 2215 cm⁻¹, which can be assigned to the vibration peaks of $C \equiv C$ and $N \equiv C$ units, respectively.

3. Gelation test for 1-2



Figure S11. a) Compound 2 in MCH/CHCl₃ (95 : 5, v/v; 20.0 mM). b) Monomer 1 in MCH/CHCl₃ (95 : 5, v/v; 10.0 mM) upon sonication for 1 hour. No gelation can be visualized for 2. In comparison, the designed monomer 1 displays strong gelation tendency, which is unaffected by sonication.

4. Solvent-state spectroscopic measurements of 1



Figure S12. Solvent-dependent UV-Vis spectra of **1** in MCH/CHCl₃ (0.10 mM, 2 mm cuvette). An isosbestic point appears at 326 nm upon varying the solvent composition of MCH/CHCl₃, illustrating the reversible transition of **1** between the molecularly dissolved and aggregated states.



Figure S13. Temperature-dependent fluorescent spectra of 1 in MCH/1,2-C₂H₄Cl₂ (95 : 5, v/v; 0.1 mM, $\lambda_{ex} = 345$ nm). The emission band deriving from Au(I)–Au(I) interacting signals of 1 gradually decreases upon heating.



Figure S14. Solvent-dependent fluorescent spectra of 1 (0.10 mM, $\lambda_{ex} = 345$ nm). The emission band deriving from Au(I)–Au(I) interacting signals of 1 disappears upon addition 20% (ν/ν) CHCl₃ in MCH.



Figure S15. Fluorescent lifetime measurement for **1** in MCH/CHCl₃ (95 : 5, v/v; 0.10 mM). The lifetime is determined to be 2.96 µs, reflecting its triplet emission character.



Figure S16. Fluorescence (*left*) and its lifetime (*right*) measurements for monomer **1** in the gel state (MCH/CHCl₃ (95 : 5, v/v; 10.0 mM, $\lambda_{ex} = 345$ nm, $\tau_0=2.78$ µs). Comparable lifetime values are obtained for apolar solvent (Fig. S15) and gel systems, proving the presence of self-assembled states for both cases.



Figure S17. CD spectra of monomer 1 in CHCl₃ (black line), MCH/1,2-C₂H₄Cl₂ (95 : 5, v/v;
0.20 mM) at 25 °C (red line) and 80°C (blue line). Cotton effect between 240 and 320 nm can be observed in MCH/1,2-C₂H₄Cl₂ (95 : 5, v/v) solution at 25 °C. Nevertheless, no Cotton effect can be observed in the low-energy LLCT absorption region of 1. The failure to induce the helical bias at the supramolecular level could be potentially ascribed to the remote distance between the chiral periphery and the alkynyl–gold(I)–isocyanide unit on 1.



Figure S18. Concentration-dependent ¹H NMR spectra (300 MHz, CDCl₃, 298 K) of monomer **1**: a) 0.63 mM, b) 0.83 mM, c) 1.25 mM, d) 2.50 mM, e) 5.00 mM, f) 6.67 mM, g) 10.0 mM, h) 20.0 mM. The arrows show the shifting of N*H* protons. Upon increasing the monomer concentration from 0.63 to 20.0 mM in *d*-chloroform, the two amide protons display significant downfield shifts (from 7.17 and 6.96 ppm to 7.35 and 7.14 ppm, respectively), suggesting the presence of intermolecular hydrogen bonds.



Figure S19. Solvent-dependent UV-Vis spectra of 1 in MCH/CHCl₃ (95 : 5, v/v, 0.10 mM, 5 mm cuvette). When adding trace amount of polar solvent MeOH [~0.5% (v/v)] to the MCH/CHCl₃ (95 : 5, v/v) solution of 1, the absorption signal originating from Au(I)-Au(I) interactions can be completely destroyed. Such phenomena highlight the significance of hydrogen bonds for self-assembly of 1.

5. Acquirement of thermodynamic parameters for the self-assembly process

To acquire the detailed thermodynamic parameters for the supramolecular polymerization process, normalized UV heating curve of **1** is fitted with the Meijer–Schenning–van der Schoot mathematical model.^[S4] Specifically, the supramolecular polymerization can be divided into two separated steps: the nucleation and elongation regimes. In the elongation regime, the fraction of aggregated molecules φ_n is described by Eq. S1:

$$\varphi_n = \varphi_{SAT}\{1 - exp[(-h_e) \times (T - T_e)/(R \times T_e^2)]\}$$
(Eq. S1)

In this equation, h_e denotes the molecular enthalpy release due to the non-covalent supramolecular polymerization, T and T_e stand for the absolute temperature and elongation temperature, respectively. R represents the universal gas constant. φ_{SAT} is a parameter that is introduced to prevent the relation φ_n/φ_{SAT} surpassing the value of 1.

In the nucleation regime, it means that at temperatures below the elongation temperature T_e . φ_n is described by Eq. S2:

$$\varphi_{n=\sqrt[3]{K_a}} \times exp\left[\left(\frac{2}{3}K_a^{-1/3} - 1\right) \times h_e \times (T - T_e)/(R \times T_e^2)\right]$$
(Eq. S2)

where K_a is the dimensionless equilibrium constant for the nucleation step at T_e .

The average length of the stack, $\langle N_n(T_e) \rangle$, averaged over the nucleated species, at the elongation temperature is given by Eq. S3:

$$\langle N_n(T_e) \rangle = \frac{1}{\kappa_a^{1/3}}$$
 (Eq. S3)

Hence, a higher degree of cooperativity, expressed in a smaller K_a value, will lead to a larger nucleus before elongation.

For variable-temperature experiments, α_{agg} at each temperature was determined by the following equation:^[5]

$$\mathcal{O}_{agg}(T) \approx \frac{A(T) - Amon}{Aagg - Amon}$$
(Eq. S4)



Figure S20. Temperature-dependent aggregation of monomer **1** in MCH/1,2-C₂H₄Cl₂ (95 : 5, *v*/*v*, 10 mm cuvette) at the monomer concentration of a) 0.125 mM, b) 0.100 mM, c) 0.075 mM, d) 0.050 mM. The red lines denote the Meijer–Schenning–van der Schoot mathematical model fitting of the curves. Inset: variable-temperature UV-Vis spectra at different monomer concentration.

 Table S1. Self-assembly thermodynamic parameters of monomer 1 from the Meijer–Schenning–van der Schoot mathematical model.

5	U		
Concentration[M]	T _e	h _e (kJ mol⁻¹)	K _a
1.25 x 10 ⁻⁴	348.1	-61.6	2.38x 10 ⁻⁶
1.00 x 10 ⁻⁴	343.9	-60.9	8.51 x 10 ⁻⁶
7.50 x 10 ⁻⁵	340.5	-60.5	1.22x 10⁻⁵
5.00 x 10 ⁻⁵	335.7	-62.5	1.26x 10 ⁻⁵



Figure S21. a) Temperature-dependent UV-Vis spectra of monomer 1, b) absorbance at 345 nm upon heating and cooling. It shows the overlapping of heating and cooling curves, suggesting the thermodynamic equilibrium between the monomeric and aggregated states.



Figure S22. Meijer–Schenning–van der Schoot mathematical model fitting of the melting curve of monomer **1** in MCH/1,2-C₂H₄Cl₂ (95 : 5, v/v, 0.05 mM), by monitoring the UV–Vis absorbance at 310 nm versus temperature. T_e (critical elongation temperature) and h_e (enthalpy release upon elongation) values are determined to be 335.8 K and –83.2 kJ mol⁻¹, which are similar to those acquired from 345 nm (see main text, $T_e = 335.7$ K, and $h_e = -62.5$ kJ mol⁻¹).

6. Microscopic measurements of 1



Figure S23. TEM of monomer **1** in MCH/CHCl₃ (95 : 5, *v*/*v*, 0.40 mM).

7. Stimuli-responsiveness of 1



Figure S24. Fluorescent spectra of monomer 1 (black line, $\lambda_{ex} = 345$ nm), with the successive addition of AgOTf (red line, $\lambda_{ex} = 410$ nm) and Bu₄NI (blue line, $\lambda_{ex} = 345$ nm).



Figure S25. a) FT–IR spectra for monomer 1 (red line), together with the mixture of 1 and AgOTf (black line). Inset: shifting of $v(C \equiv C)$ frequency from 2122 cm⁻¹ to 2055 cm⁻¹. b) FT–IR spectra for monomer 1 in 1,2-C₂H₄Cl₂ (black line, 1.50 mM) and in MCH/1,2-C₂H₄Cl₂ (95 : 5, v/v, 1.50 mM) (red line). Inset: shifting of v(N-H) frequency from 3297 cm⁻¹ to 3263 cm⁻¹.

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