Electronic Supplementary Information

Solvent induced helical aggregation in the self-assembly of cholesterol tailed platinum complexes

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1. Synthesis and characterizations of complexes 1a-1c

Scheme S1: Synthesis route of 1a-1c



 $K_2PtCl_4 \longrightarrow cis-PtCl_2(DMSO)_2$





The synthesis routes of **1a-1c** are shown in Scheme S1. The details of the synthesis are as follows.

(3R, 10S, 13S, 17S) -10, 13-Dimethyl-17-((S)-6-methylheptan-2-yl)-2, 3, 6, 7, 8, 9, 10, 11. 12. 15, 16, 17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 13. 14. (6-aminohexyl) carbamate (2). 2 was prepared according to the reference.¹ A CHCl₃ solution (100 mL) of cholesteryl chloroformate (1.2 g, 2.69 mmol, 1 eq) was added into a CHCl₃ (100 mL) solution containing hexamethylenediamine (2.5 g, 21.55 mmol, 8 eq) and Et₃N. The mixture was stirred at room temperature overnight. The solvent was removed, and the solid was purified with a silica gel column (dichloromethane: methanol = 10: 1) to give 2 as a white solid (0.85 g, 1.61 mmol), yield: 60%. ¹H NMR (CDCl₃, 400 MHz, CDCl₃): δ 0.68 (s, 3H), 0.86-2.45 (m, 45H), 2.72 (t, 2H), 3.16 (d, 2H), 4.55 (m, 2H), 5.38 (t, 1H). ¹³C NMR: 11.86, 18.71, 19.35, 21.04, 22.56, 22.83, 23.86, 24.28, 26.33, 26.60, 28.00, 28.23, 29.84, 29.97, 31.87, 35.81, 36.19, 36.54, 37.00, 38.62, 39.51, 39.74, 40.69, 40.96, 42.30, 49.98, 56.16, 56.68, 74.11, 122.45, 139.85, 156.27. ESI-MS: m/z calculated for C₃₄H₆₁O₂N₂⁺ [M+H⁺]: 529.4733 (100%), 530.4767. Found: 529.4759 (100%), 530.4783.

Bis((3R,10S,13S,17S)-10,13-dimethyl-17-((S)-6-methylheptan-2-yl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)

((([2,2'-bipyridine]-4,4'-dicarbonyl)bis(azanediyl))bis(hexane-6,1-diyl))dicarbamate (3). **3** was prepared according to the reference.¹ 2, 2'-Bipyridine-4, 4'-dicarboxylic acid (1.01 g, 4.14 mmol, 1 eq) was added to an excess of thionyl chloride (SOCl₂). The mixture was heated to reflux at 60 °C for 3 hours, and the unreacted SOCl₂ was distilled until removed. The residual was dissolved in CH₂Cl₂ and added to a CH₂Cl₂ (200 mL) solution of **2** (6.56 g, 12.42 mmol, 1.5 eq), and the mixture was stirred at room temperature overnight. The solvent was removed, and the solid was purified with a silica gel column (dichloromethane: methanol = 250: 1 - 50: 1) to give 3 as a white solid (3.92 g, 3.1 mmol), yield: 74.9%. ¹H NMR (CDCl₃, 400 MHz, CDCl₃): δ 0.67 (s, 6H), 0.86-2.34 (m, 92H), 3.18 (t, 4H), 3.51 (m, 4H), 4.47(m, 4H), 4.71 (s, 4H), 5.33 (t, 2H), 7.93 (s, 2H), 8.81 (d, 2H), 8.95 (d, 2H). ESI-MS: m/z calculated for C₈₀H₁₂₅O₆N₆⁺ [M+H⁺]: 1265.9661 (100%), 1266.9694. Found: 1265.9653 (100%), 1266.9663.

Synthesis of 4. K₂PtCl₄ (0.104 g, 0.25 mmol) was dissolved in DMSO (6 mL) and stirred for several hours at room temperature to give *cis*-PtCl₂(DMSO)₂. The DMSO solution of *cis*-PtCl₂(DMSO)₂ was added into a turbid CHCl₃ solution (50 mL) of **3** (0.3019 g, 0.24 mmol), and the mixture was stirred at room temperature overnight for 2 days until the turbid solution became clear. The solvent was removed, and the solid was purified with a silica gel column (dichloromethane: methanol = 98: 2) to give **4** as a yellow solid (0.33 g, 0.216 mmol), yield: 90.31%. ¹H NMR (CDCl₃, 400 MHz, CDCl₃): δ 0.66 (s, 6H), 0.85-1.99 (m, 88H), 2.29 (m, 4H), 3.23 (s, 4H), 3.49 (m, 4H), 4.42 (s, 4H), 4.88 (s, 4H), 5.27 (s, 2H), 7.69 (d, 2H), 7.89 (s, 2H), 8.31 (s, 2H), 9.13 (s, 2H). ¹³C NMR: 11.85, 18.72, 19.33, 21.04, 22.56, 22.82, 23.88, 24.28, 26.03, 26.36, 28.01, 28.22, 28.97, 29.91, 31.86, 35.81, 36.19, 36.55, 37.00, 38.63, 39.52, 39.70, 40.40, 41.03, 42.31, 49.99, 56.14, 56.63, 74.41, 122.50, 125.95, 139.79, 146.30, 148.76, 156.23, 156.62, 164.26. ESI-MS: *m/z* calculated for C₈₀H₁₂₄O₆N₆PtCl₂Na⁺ [M+Na⁺]: 1552.8505 (100%), 1551.8484 (82.5%). Found: 1551.8473 (40%), 1552.8486 (68%), 1553.8500 (100%).

4-((Trimethylsilyl) ethynyl) phenol (5). Trimethylsilyl acetylene (5 mL, 36.1 mmol, 1.5 eq) was added to a degassed solution (THF/ triethylamine = 3: 1, 80 mL) containing *p*-iodophenol (5.3 g, 24.5 mmol), Pd (PPh₃)₂Cl₂ (510 mg, 0.73 mmol) and CuI (140 mg, 0.73 mmol). The solution was stirred for 3 h at 80 °C under a nitrogen atmosphere. The reaction product was filtrated, and the filtrate was evaporated. The solid was purified with a silica gel column (petroleum ether: ethyl acetate = 1:1) to give **5** as a brown oil (4.7 g, 24.7 mmol), yield: 82.71%. ¹H NMR (CDCl₃, TMS, 400 MHz): δ 0.24 (s, 9 H), 5.34 (s, 1 H,), 6.75 (d, *J* = 8 Hz, 2 H, Ar), 7.36 (d, *J* = 9 Hz, 2 H, Ar).²

Synthesis of 6b and 6c. The synthesis processes of 6b and 6c were similar.

2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy) ethyl 4-methylbenzenesulfonate (6c). A total of 10 g tetraethylene glycol (0.05 mol) and 5.06 g triethylamine (0.05 mol) were dissolved in acetonitrile (150 mL), and 9.5 g toluene-p-sulfonyl chloride (0.05 mol) was added dropwise over 3 h. The reaction mixture was stirred for 14 hours at room temperature. The white precipitate of triethylamine hydrochloride was filtered off. The solvent of the filtrate was evaporated, and the solid was purified with a silica gel column (dichloromethane: acetone = 10: 1 as the eluent) to give **6c** as a colorless oil (5.2 g, 14.94 mmol), yield: 29.88%. ¹H NMR: 2.42 (s, 3H, -CH₃), 2.58 (s, 1H, -CH₂OH), 3,51–4.18 (m, 16 H, -OCH₂), 7.32 (d, 2H), 7.77 (d, 2H).³

2-(2-hydroxyethoxy) ethyl 4-methylbenzenesulfonate (6b): ¹H NMR (400 MHz, CDCl₃) δ 2.45 (s, 3H), 3.52 (t, 2H), 3.67 (m, 4H), 4.19 (t, 2H), 7.36 (d, 2H), 7.79 (d, 2H). ¹³CNMR (400 MHz, CDCl₃) δ 21.61, 61.51, 68.49, 69.32, 72.50, 127.90, 129.99, 132.81, 145.02.

Synthesis of 7b and 7c. The synthesis processes of 7b and 7c were similar. The synthesis details of 7c are shown as an example.

2-(2-(2-(4-Ethynylphenoxy) ethoxy)ethoxy)ethoxy)ethanol (7c). 6c (0.348 g, 1 mmol, 1 eq), **5** (0.19 g, 1 mmol, 1 eq), K_2CO_3 (1.38 g, 10 mmol, 10 eq) and DMF (15

mL) were added to a three-necked flask, and the mixture was reacted with the protection of N₂ at 80 °C. The solvent DMF was removed with the rotary evaporator. Next, the appropriate amount of CH₂Cl₂ was added into the flask and the insoluble solid was removed by filtration. Then, the filtrate was evaporated and purified with a silica gel column (hexane: ethyl acetate = 10: 1) to give **7c** as a brown oil (0.204 g, 0.694 mmol), yield: 69.38%. ¹H NMR (400 MHz, CDCl₃) δ 2.36 (bs, 1H), 3.00 (s, 1H), 3.55-3.80 (m, 12H), 3.86 (t, 2H), 4.14 (t, 2H), 6.86 (d, 2H), 7.41 (d, 2H).

2-(2-(4-ethynylphenoxy) ethoxy) ethanol (7b). 7b was given as a brown oil (1.549 g, 7.52 mmol), yield: 42.78%. ¹HNMR (400 MHz, CDCl₃) δ 3.06 (s, 1H), 3.60-4.20 (m, 8H), 6.88 (d, 2H), 7.42 (d, 2H).

Synthesis of 1a, 1b and 1c. The synthesis processes of 1a-1c were similar. The synthesis details of 1c are shown as an example.

Synthesis of the platinum complex 1c. Compounds 4 (1.26 g, 0.8264 mmol, 1 eq), 7c (0.7296 g, 2.48 mmol, 1.5 eq) and CuI (35 mg) were added to a three-necked flask, and the flask was degassed and protected by N₂. The dry solvent (dichloromethane: diisopropylamine = 80: 26, 106 mL) was added to the flask with an injection syringe. The mixture was reacted at room temperature for 12 hours. Then, the mixture was evaporated and purified with a silica gel column (dichloromethane: acetone = 5: 1) to give 1c as a red solid (0.92 g, 0.449 mmol), yield: 54.38%. Mp: 280 °C. ¹H NMR (CDCl₃, 400 MHz, CDCl₃): δ 0.67 (s, 6H), 0.80-2.10 (m, 88H), 2.24 (m, 6H), 3.29 (s, 4H), 2.94 (s, 4H), 3.55-3.80 (m, 24H), 3.86 (m, 4H), 4.14 (s, 4H), 4.44 (s, 2H), 5.06 (s, 2H), 5.30 (s, 8H), 6.85 (s, 4H), 7.11 (s, 4H), 7.75 (s, 2H), 8.44 (s, 2H), 9.23 (s, 2H). ¹³C NMR: 11.86, 18.71, 19.34, 21.04, 22,47, 22.71, 23.89, 24.28, 26.30, 26.66, 28.13, 28.29, 29.25, 29.88, 31.96, 35.82, 36.36, 36.57, 36.98, 38.63, 39.52, 39.70, 40.65, 41.34, 42.31, 49.96, 56.14, 56.62, 61.63, 67.47, 69.70, 70.25, 70.56, 70.64, 70.73, 72.64, 74.16, 77.26, 114.44, 122.44, 126.38, 132.62, 139.84, 145.10, 150.26, 156.22, 157.47. ESI-MS: m/z calculated for C₁₁₂H₁₆₇O₁₆N₆Pt⁺ [M+H⁺]: 2047.2099 (79.6%), 2048.2120 (100%); Found: 2047.2051 (80%), 2048.2132 (100%).

The characterization of **1a**: **1a** was given as a red solid (0.320 g, 0.192 mmol), yield: 72.4%. Mp: 176°C. ¹HNMR (CDCl₃, 400 MHz, CDCl₃): δ 0.67 (s, 6H), 0.80-2.10 (m, 118H), 2.24 (s, 4H), 2.61 (s, 6H), 3.10 (m, 5H), 3.33 (s, 4H), 4.44 (s, 2H), 4.72 (s, 2H), 5.30 (s, 3H), 7.27 (s, 4H), 7.37 (s, 4H), 7.62 (s, 2H), 8.24 (s,4H), 9.09 (s, 2H). ¹³C NMR: 11.86, 18.71, 19.34, 21.05, 22,57, 22.84, 23.90, 24.28, 26.21, 26.59, 27.99, 28.24, 29.12,29.84, 31.86, 35.82, 36.20, 36.53, 36.99, 38.65, 39.51,39.71, 40.67, 40.93, 42.31, 49.96, 56.17, 56.62, 74.16, 86.09, 102.91, 122.11, 122.45, 126.22, 126.60, 128.32, 131.58, 136.99, 139.80, 145.91, 149.75, 155.17, 155.35, 156.33, 162.49, 165.27. ESI-MS: m/z calculated for C₉₆H₁₃₄O₆N₆PtNa⁺ [M+ Na⁺]: 1684.9923 (90.4%), 1685.9944 (100%); Found: 1684.9914 (85%), 1685.9943 (100%).

The characterization of **1b**: **1b** was given as a red solid (0.43 g, 0.230 mmol), yield: 69.5%. Mp. 269°C. ¹H NMR (CDCl₃, 400 MHz, CDCl₃): δ 0.66 (s, 6H), 0.80-2.05 (m, 98H), 2.28 (m, 6H), 3.05 (s, 4H), 3.37 (s, 4H), 3.69 (s, 2H), 3.78 (s, 2H), 3.88 (m, 4H), 4.13 (s, 4H), 4.45 (s, 2H), 4.95 (s, 2H), 5.31 (s, 2H), 6.80 (s, 4H), 7.42 (s, 4H), 7.61 (s, 2H), 8.66 (s, 2H), 9.16 (s, 2H). ¹³C NMR: 11.86, 18.72, 19.34, 21.05, 22,57, 22.84, 23.88, 24.29, 24.94, 26.32, 26.69, 28.02, 28.24, 29.32, 29.92, 31.87, 35.82, 36.20, 36.55, 36.99, 38.63, 39.52, 39.71, 40.70, 41.56, 42.32, 43.55, 49.98, 51.70, 52.76, 56.15, 56.65, 58.67, 61.69, 66.98, 67.54, 67.86, 69.62, 72.11, 72.79, 73.44, 74.27, 75.61, 77.24, 114.58, 122.50, 126.35, 132.75, 139.82, 150.08, 155.37, 156.39. ESI-MS: m/z calculated for

 $C_{104}H_{150}O_{12}N_6PtNa^+ \ [M+Na^+]: 1893.0970 \ (82.32\%), \ 1894.0891 \ (100\%); \ Found: 1893.0853 \ (85\%), 1894.0890 \ (100\%).$

2. Additional images and spectra



Fig. S1 The TEM images of organogel of **1a** in DMSO: (a) The copper grid was in the normal direction; (b) The copper grid was put in reverse. The experiment shows that the image gives reversed handedness when the copper grid is put in reverse.



Fig. S2 Molecular size of (a) 1a and (b) 1c.



Fig. S3 CD spectra of **1a** gel (37.5 mg·mL⁻¹, 2.25×10^{-2} mol L⁻¹) diluted to 15, 30, 60 and 120 times (1 cm cell)



Fig. S4 The CD spectra of 1b in water/ethanol with different percentage of water.



Fig. S5 SEM images of 1b in water/ethanol with the ratio of water being 0% (a), 2% (b) and 33% (c). The scale bar is 2 μ m.



Fig. S6 DLS of **1c** aqueous ethanol solution with different r_{aq} . Size distribution is by number; the data (unit, nm) beside the peak shows the average size of the distribution.



Fig. S7 The CD spectra of **1a** (a), **1b** (b), and **1c** (c) in water/THF with various ratio of water. The concentration of solutions is 10^{-4} mol·L⁻¹.



Fig. S8 SEM images of **1a** (a, b), **1b** (c, d) and **1c** (e, f) in water/THF with the ratio of water being 0% (a, c, e) and 50% (b, d, f). The concentration of solution is $10^{-4} \text{ mol} \cdot \text{L}^{-1}$. The scale bar is 2 µm.



Fig. S9 The XRD of the precipitation of 1c in ethanol

References

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