Electronic Supplementary Information

Telechelic amphiphilic metallopolymers end-functionalized with

platinum(II) complexes: synthesis, luminescence enhancement, and

their self-assembly into flowerlike vesicles and giant flowerlike

vesicles

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EXPERIMENTAL SECTION

General Considerations. ¹H NMR spectra were performed on a *JNM-ESC400* spectrometer. L, PEG-based ligands, and platinum(II)-containing metallopolymers were dissolved in d-chloroform (CDCl₃), in which tetramethylsilane was utilized as an internal standard. Gel permeation chromatography (GPC) plots were recorded on a Shimadzu LC-20AD instrument with a calibration standard of PEG and an eluent solvent of tetrahydrofuran (THF). The flow rate was 1.0 mL min⁻¹ and the column temperature was fixed at 40 °C. Number-average molecular weights (M_n) , weight-average molecular weights (M_w) , and polydispersity indices $(PDI = M_w/M_n)$ were achieved for the PEGs end functionalized with L. Fourier transformation infrared (FT-IR) spectra were recorded on a *Nicolet NEXUS* 670 spectrometer with a resolution of 4 cm^{-1} , where the samples were jammed into thin KBr pellet. C, H, and N elemental analyses were obtained with Elementar Analysensysteme GmbH VarioEL element analyser (Germany). UV-vis absorption and emission spectra was carried out by using a Shimadzu 2550 spectrophotometer and a Hitachi F-7000 spectrofluorimeter, respectively. Dynamic light scattering (DLS) was detected on a Malvern Nano Zetasizer at a fixed detection angle of 173°, during which the solution concentrations of platinum(II)-containing metallopolymers were held at 1.0×10^{-5} mol/L. The viscosity change of the solvent mixtures has been corrected for the DLS experiments. Both bright-field transmission electron microscopy (BF-TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected on an FEI Tecnai F30 operating at 300 kV or a JEM-2100 operating at 200 kV. Scanning electron microscopy (SEM) measurements were performed on a field emission Hitachi S-4800. Before the SEM imaging, a 4-nm thick gold layer was deposited on the specimen by using *Hitachi E-1045* ion sputter. For these microscopic measurements, the sample solutions $(1.0 \times 10^{-5} \text{ mol/L}, 6 \mu\text{L})$ were cast on carbon-coated copper grids and the excess liquid was blotted with a filter paper. Fluorescence microscopy imaging was measured on a *Nikon Eclipse 80i*. Wide-angle X-ray scattering (WAXS) experiments were simultaneously performed on a Nano-inXider ($\lambda = 0.154$ nm, Xenocs, France). All measurements were performed at 20 °C except for GPC under the temperature of 40 °C.

Synthetic Procedures and Characterization Details

The difunctional polymers of EG_n -N₃ (n = 45, 72, 188) were synthesized according to the procedures described previously.^{10c,13} 2-(*N*-dodecylbenzimidazol-2'-yl)-6-(*N*-{[(4-ethynylphenyl)oxy]dodecyl}

benzimidazol-2'-yl)pyridine (L) was prepared on the basis of our previous procedure.¹² N,N-dimethylformamide (DMF) was dried over CaH₂ for 6 h and then used as a reaction medium for click reactions. Other chemicals were commercially used without any further purification. All reaction procedures were operated under an atmosphere of Ar.

EG45-L: CuBr (0.072 g, 0.5 mmol), L (0.4 g, 0.54 mmol), EG45-N3 (0.5 g, 0.25 mmol), and PMDETA (0.115 mL, 0.54 mmol) were dissolved in anhydrous DMF (5 mL) in a round-bottom flask. The resulting mixture was degassed by three freeze-pump-thaw cycles, sealed under vacuum, and placed in an oil bath preheated at 90 °C for 72 h. During this reaction process, the solution changed gradually from brown to deep green. The brown colour should originate from a trace amount of oxidized 1,2-diaminobenzene impurities in the ligand of L. After the click reaction, the solution was changed into a green colour because of the formation of Cu(II)/PMDETA and Cu(II)/L complexes. After cooling the reaction mixture to room temperature, the solvent of DMF was removed under reduced pressure. The crude product was dissolved in CH₂Cl₂ and then passed through a neutral alumina column to remove the copper catalyst. The filtrate was concentrated to 5 mL and precipitated into 50 mL of cold ether. This dissolution-precipitation process was repeated for three times. The resulting white solid was collected via vacuum filtration and then dried under vacuum (Yield: 0.78 g, 87%). ¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, J = 8 Hz, 4H), 8.05 (t, J = 8 Hz, 2H), 7.89 (m, 6H), 7.73 (d, J = 8 Hz, 4H), 7.46 (d, J = 8 Hz, 4H), 7.35 (m, J = 4 Hz, 8H), 6.92 (d, J = 8 Hz, 4H), 4.70 (t, J = 8 Hz, 8H), 4.57 (t, J = 8 Hz, 4H), 3.96 (t, J = 8 Hz, 4H), 3.90 (t,4 Hz, 4H), 3.84-3.35 (polyethylene glycol peak, m, 172H), 1.74 (m, 12H), 1.41 (m, 4H), 1.31-1.00 (m, 64H), 0.87 (t, J = 8 Hz, 6H). GPC: $M_n = 2250$ g mol⁻¹, PDI = 1.04. $M_{n,NMR} = 3562$ g mol⁻¹.

EG₇₂-L: EG₇₂-L was synthesized by following the reaction procedure depicted for EG₄₅-L except that EG₇₂-N₃ (0.8 g, 0.25 mmol) was utilized instead of EG₄₅-N₃ (Yield: 1.03 g, 86%). ¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, J = 8 Hz, 4H), 8.05 (t, J = 8 Hz, 2H), 7.89 (s, 2H), 7.86 (d, J = 8 Hz, 2H), 7.73 (d, J = 8 Hz, 4H), 7.46 (d, J = 8 Hz, 4H), 7.35 (m, J = 4 Hz, 8H), 6.92 (d, J = 8 Hz, 4H), 4.70 (t, J = 8 Hz, 8H), 4.57 (t, J = 8 Hz, 4H), 3.96 (t, J = 8 Hz, 4H), 3.90 (t, J = 4 Hz, 4H), 3.84-3.35 (polyethylene glycol peak, m, 280H), 1.74 (m, 12H), 1.41 (m, 4H), 1.31-1.00 (m, 64H), 0.87 (t, J = 8 Hz, 6H). GPC: M_n = 3450 g mol⁻¹, PDI = 1.03. $M_{n,NMR}$ = 4752 g mol⁻¹.

EG₁₈₈-L: EG₁₈₈-L was synthesized by following the reaction procedure depicted for EG₄₅-L except that EG₁₈₈-N₃ (2.25 g, 0.25 mmol) was utilized instead of EG₄₅-N₃ (Yield: 2.12 g, 80%). ¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, J = 8 Hz, 4H), 8.05 (t, J = 8 Hz, 2H), 7.89 (s, 2H), 7.86 (d, J = 8 Hz, 2H), 7.73 (d, J = 8 Hz, 4H), 7.46 (d, J = 8 Hz, 4H), 7.35 (m, J = 4 Hz, 8H), 6.92 (d, J = 8

Hz, 4H), 4.70 (t, J = 8 Hz, 8H), 4.57 (t, J = 8 Hz, 4H), 3.96 (t, J = 8 Hz, 4H), 3.90 (t, J = 4 Hz, 4H), 3.84-3.35 (polyethylene glycol peak, m, 744H), 1.74 (m, 12H), 1.41 (m, 4H), 1.31-1.00 (m, 64H), 0.87 (t, J = 8 Hz, 6H). GPC: $M_n = 8940$ g mol⁻¹, PDI = 1.06. $M_{n,NMR} = 9862$ g mol⁻¹.

EG45-Pt: Red solid K₂PtCl₄ (0.1 g, 0.24 mmol) was first added to a DMSO solution of EG₄₅-L (0.3 g, 0.1 mmol, 20 mL). The resulting mixture was heated and stirred at 90 °C for 3 days, where an orange red solution formed. After removing the solvent of DMSO under reduced pressure, the crude product was dissolved in CH₂Cl₂, and stirred vigorously with an aqueous solution of NH₄PF₆ (0.24g, 1.48 mmol, 20 mL) over night. The organic phase was collected and washed with cold water for five times (20×5 mL). After evaporating the solvent of CH₂Cl₂, a dark red solid was isolated with a yield of 96% (0.38 g) based on EG₄₅-L. ¹H NMR (400 MHz, CDCl₃): δ 8.61 (broad, 4H), 7.96 (broad, 2H), 7.89 (s, 2H), 7.69 (broad, 4H), 7.50 (broad, 4H), 7.24~6.96 (m, broad, 12H), 6.88 (broad, 4H), 4.56 (broad, 4H), 4.24 (broad, 8H), 3.91 (broad, 8H), 3.80-3.44 (polyethylene glycol peak, m, 172H), 1.78 (broad, 12H), 1.40 (broad, 4H), 1.31-1.00 (m, 64H), 0.86 (t, J = 8 Hz, 6H). IR (KBr): 3443, 2921, 2856, 1653, 1467, 1343, 1280, 1248, 1113, 842, 748, 557 cm^{-1} . Elemental analysis 1036, 951, calcd. for EG₄₅-Pt (C₁₉₂H₃₁₀Cl₂F₁₂N₁₆O₄₅P₂Pt₂(H₂O)₄, 4385.66 g mol⁻¹): C 52.58, H 7.31, N 5.11. Found: C 52.59, H 7.30, N 5.25.

EG₇₂-**Pt**: Similarly, **EG**₇₂-**Pt** was prepared as a dark red solid, but using **EG**₇₂-**L** (0.3 g, 0.06 mol) and K₂PtCl₄ (0.06 g, 0.14 mmol) as reactants. The yield was 94% (0.34 g) based on **EG**₇₂-**L**. ¹H NMR (400 MHz, CDCl₃): δ 8.60 (weak, broad), 8.37 (weak, broad), 8.15 (d, J = 8 Hz, weak), 7.99 (weak, broad), 7.89 (s, weak), 7.69 (weak, broad), 7.49 (weak, broad), 7.20 (weak, broad), 7.01 (weak, broad), 6.90 (d, J = 8 Hz, weak), 4.66 (weak, broad), 4.56 (weak, broad), 4.28 (weak, broad), 3.92 (m, weak, broad), 3.80-3.44 (polyethylene glycol peak, m), 1.77 (broad), 1.40 (broad), 1.31-1.00 (m, broad), 0.84 (m, broad). FT-IR (KBr): 3441, 2885, 2741, 2697, 1610, 1468, 1346, 1282, 1244, 1147, 1110, 1050, 958, 842, 749, 556, 529 cm⁻¹. Elemental analysis calcd. for **EG**₇₂-**Pt** (C₂₄₆H₄₁₈Cl₂F₁₂N₁₆O₇₂P₂Pt₂(H₂O)₃, 5557.06 g mol⁻¹): C 53.17, H 7.69, N 4.03. Found: C 53.13, H 7.84, N 3.33.

EG₁₈₈-Pt: Similarly, EG₁₈₈-Pt was prepared as a dark red solid, but using EG₁₈₈-L (0.3 g, 0.03 mol) and K₂PtCl₄ (0.025 g, 0.06 mmol) as reactants. The yield was 95% (0.31 g) based on EG₁₈₈-L. ¹H NMR (400 MHz, CDCl₃): δ 8.68 (very weak, broad), 8.09 (very weak, broad), 7.90 (s, very weak), 7.72 (very weak, broad), 7.18 (very weak, broad), 6.91 (very weak), 4.57 (very weak), 4.32 (very weak, broad), 3.92 (very weak, broad), 3.80-3.44 (polyethylene glycol peak, m), 1.78 (broad), 1.39 (broad), 1.31-1.00 (m, broad), 0.84 (m, broad). FT-IR (KBr): 3448, 2887, 2741, 2697, 1629, 1469, 1347, 1283, 1244, 1147, 1109, 1032, 958, 841, 748, 556, 532 cm⁻¹. Elemental analysis calcd. for EG₁₈₈-Pt (C₄₇₈H₈₈₂Cl₂F₁₂N₁₆O₁₈₈P₂Pt₂, 10613.11 g mol⁻¹): C 54.09, H 8.38, N 2.11. Found: C 54.99, H 8.38, N 1.86.



Fig. S2¹ H NMR spectra of EG₇₂-L (top) and EG₇₂-Pt (bottom).



Fig. S3 1 H NMR spectra of EG₁₈₈-L (top) and EG₁₈₈-Pt (bottom).



Fig. S4 IR spectra of (left, EG₄₅-N₃, EG₄₅-L, and EG₄₅-Pt), (central, EG₇₂-N₃, EG₇₂-L, and EG₇₂-Pt), and (right, EG₁₈₈-N₃, EG₁₈₈-L, and EG₁₈₈-Pt).

Table S1. Molecular Characteristics of EG_m-L and EG_n-Pt.

Sample	$M_{\rm n}{}^a$ / g mol ⁻¹	PDI ^a	$M_{n,NMR}$ ^b /g mol ⁻¹	Sample	$M_{\rm n}$ ^c / g mol ⁻¹
EG ₄₅ -L	2250	1.04	3562	EG ₄₅ -Pt	4314
EG ₇₂ -L	3450	1.03	4752	EG ₇₂ -Pt	5503
EG188-L	8940	1.06	9862	EG ₁₈₈ -Pt	10613

^{*a*}The values of M_n , M_w , and M_w/M_n (PDI) were determined by GPC. ^{*b*}The values of $M_{n,NMR}$ were determined by ¹H NMR spectroscopy. ^{*c*}The M_n values of platinum(II)-containing metallopolymers were obtained by adding the molecular weight of PtClPF₆ with those of the corresponding polymer ligands, respectively.



Fig. S5 (a and b) UV-vis absorption and (c and d) emission spectral changes of EG_{72} -Pt upon increasing the water composition from 0 to 91 vol %.



Fig. S6 (a and b) UV-vis absorption and (c and d) emission spectral changes of EG_{45} -Pt upon increasing the water composition from 0 to 91 vol %.



Fig. S7 DLS plots of EG_{45} -Pt (a) and EG_{72} -Pt (b) in the methanol/water mixture solvents with water volume ratios from 0 to 91%.



Fig. S8 TEM images of EG_{188} -Pt dispersed in the methanol/water mixture solvents with water volume ratios of 66 (a and b) and 91% (c and d).



Fig. S9 TEM images of EG_{45} -Pt (a and b) and EG_{72} -Pt (c) dispersed in the methanol/water mixture solvent with a water volume ratio of 91%.



Fig. S10 Microscopic observations of giant flowerlike vesicles formed by annealing the aqueous solution of **EG₁₈₈-Pt**: (a and b) SEM and (c) TEM images.

Additional results and discussion.

In this study, the metallopolymer of **EG**₁₈₈-**Pt** could be directly dissolved in water. We also prepared the aqueous solution of **EG**₁₈₈-**Pt** by dialyzing its MeOH solution in water (91 vol % water). The resulting UV-vis absorption spectrum showed a tail band ranging from 500 to 700 nm, which was assigned to a MMLCT transition (Fig. S11). In the emission spectrum, a ³MMLCT emission band was observed at 629 nm, consistent with that obtained from the solution of **EG**₁₈₈-**Pt**, where the metallopolymer was directly dissolved in water (Fig. S11). But, both the absorption and emission bands showed a significant decrease in intensity, due to the dilution effect during the dialyzing process. Flowerlike vesicles formed in both the aqueous solutions (Fig. S12). The total diameter was estimated to be 350 ± 50 nm, which was much larger than that of the vesicles directly obtained in water (42 ± 8.0 nm). The wall thickness was 5.5 nm, similar to that of the vesicles directly obtained in water (6.0 ± 0.2 nm). Here, the sample preparation did not show any significant influence on the self-assembly morphology. This was presumably due to the much smaller volume of the hydrophobic platinum(II) complex block than those of hydrophobic macromolecular blocks in block copolymers. Moreover, Pt…Pt and π - π stacking interactions are rather strong and play a key role for the construction of the flowerlike vesicles.

On the other hand, both EG_{45} -Pt and EG_{72} -Pt can be not directly dissolved in water. Similarly, they were also insoluble even by dialyzing their MeOH solutions in water.



Fig. S11 (a) UV-vis absorption and (b) emission spectra of EG_{188} -Pt were obtained from the aqueous solution by dialyzing its MeOH solution in water (91 vol % water).



Fig. S12 TEM images of EG_{188} -Pt were obtained from the aqueous solution by dialyzing its MeOH solution in water (91 vol % water).



Fig. S13 Excitation spectra of EG_{45} -Pt (a), EG_{72} -Pt (b), and EG_{188} -Pt (c). Two broad shoulders were clearly observed at 534 and 570 nm, which were at energies similar to the MMLCT absorption bands observed in the aforementioned UV-vis absorption spectra (Fig. 2c, d, S5a, b, S6a, b). This consistency agreed well with the above assignment of the ³MMLCT excited state.