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Supporting Information For:

AIE-active micelles formed by self-assembly of an amphiphilic platinum complex possessing isoxazole moieties

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General: All reagents and solvents were commercial reagent grade and were used without further purification unless otherwise noted. Dry DMF, dry CH₂Cl₂ and dry triethylamine (NEt₃) were obtained by distillation over CaH₂. ¹H and ¹³C NMR spectra were recorded on a Varian mercury-300 spectrometer and chemical shifts were reported on the delta scale in ppm relative to residual chloroform ($\delta = 7.26$ and 77.0 for ¹H and ¹³C, respectively). UV/vis absorption spectra were recorded on a JASCO V-560 spectrometer. Fluorescence spectra were measured using a JASCO FP-6500 spectrometer. The fluorescence quantum yield was recorded on a JASCO FP-6500 with integrating sphere attachment. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL hybrid FTMS by electron splay ionization (ESI) methods. Melting points (M.p.) were measured with a Yanagimoto micro melting point apparatus. Infrared (IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZeSe ATR accessory. Cryogenic transmission electron microscopy (cyro-TEM) was carried out at -178 °C by a JEOL TEM-3100FEF transmission electron microscope operated at 300 kV. Atomic force microscopic (AFM) images were observed using an Agilent 5100 microscope in air at ambient temperature with standard silicon cantilevers (NCH, NanoWorld, NeuchFtel, Switzerland) in the tapping mode. The Pico Image processing program was used for the image analysis. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60 N (spherical, neutral)). Recycling preparative GPC-HPLC separations were carried LC-908s out on JAI using preparative JAIGEL-2H, 2H, 1Hcolumns in series. $4-\{2-[2-(2-Methoxy)ethoxy]ethoxy\}$ benzohydroximinoyl chloride 3^1 , and (6-phenyl-2,2'-bipyridine) platinum chloride 5^2 were synthesized according to reported methods.



Scheme 1. Synthesis of 1.



Synthesis of 5,5'-(5-ethynyl-1,3-phenylene)bis(3-(4-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}phenyl)isoxazole) (4):

To a solution of 1,3,5-triethynylbenzene **2** (490 mg, 3.25 mmol) and dry NEt₃ (3.17 mL, 22.7 mmol) in CH₂Cl₂ was added 4-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}benzohydroximinoyl chloride **3** (2.17 g, 6.82 mmol). After being stirred at room temperature for 24 h under argon atmosphere, the resulting mixture was concentrated under the reduced pressure. The crude product was purified by column chromatography on silica gel (0-80 % ethylacetate in *n*-hexane, eluent) to give the desired product **4** as a white solid (630 mg, 27 %).

Compound data for 4:

M.p.71–73 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.20 (*t*, *J* = 1.8 Hz, 1H), 7.96 (*d*, *J* = 1.8 Hz, 2H), 7.78 (*d*, *J* = 9.0 Hz, 4H), 7.00 (*d*, *J* = 9.0 Hz, 4H), 6.88 (*s*, 2H), 4.18 (*t*, *J* = 5.2 Hz, 4H), 3.88 (*t*, *J* = 5.2 Hz, 4H), 3.72–3.78 (*m*, 4H), 3.64–3.71 (*m*, 8H), 3.52–3.57 (*m*, 4H) 3.37 (*s*, 6H), 3.24 (*s*, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 168.0, 162.7, 160.4, 130.3, 128.6, 128.2, 124.1, 122.9, 121.3, 115.0, 98.6, 81.8, 79.5, 71. 9, 70.9, 70.7, 70.6, 69.6, 67.5, 59.0 ppm; FTIR-ATR (neat): *v* 3221, 2880, 2811, 1610, 1580, 1564, 1527, 1490, 1466, 1434, 1424, 1388, 1303, 1293, 1256, 1246, 1198, 1177, 1117, 1061, 996, 951, 923, 914, 891, 875, 835, 792, 781, 762, 735, 677, 650, 613, 588, 544, 525, 507 cm⁻¹; HRMS (ESI⁺) calcd for C₄₀H₄₄N₂O₁₀Na m/z 735.28888 [M+Na]⁺, found m/z 735.28882.



Synthesis

(6-phenyl-2,2'-bipyridine)

{5,5'-(5-ethynyl-1,3-phenylene)bis(3-(4-{2-[2-(2-Methoxyethoxy)ethoxy]ethoxy}phenyl)isoxazole)}platinum (1):

of

To a solution of the 4 (250 mg, 350 µmol), (6-phenyl-2,2'-bipyridine)platinum chloride 5 (160 mg, 350 µmol) and dry DMF (10 mL) in dry CH₂Cl₂ (60 mL) was added dry triethylamine (0.35 mL, 2.5 mmol). The reaction mixture was deoxygenated by bubbling nitrogen for 30 min, and then CuI (13 mg, 70 µmol) was added. After being stirred for 21 h at room temperature under argon atmosphere in the dark, the resulting mixture was extracted with CH₂Cl₂. The organic layer was washed with water, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (CH₂Cl₂, eluent) and then GPC to give the desired product **1** as an orange solid (160 mg, 40 %).

Compound data for 1:

M.p. 177–180 °C; ¹H NMR (300 MHz, CDCl₃): δ 9.23 (*d*, *J* = 5.0 Hz, 1H), 8.03–8.10 (*m*, 4H), 7.98 (*d*, *J* = 7.6 Hz, 1H), 7.90 (*d*, *J* = 7.6 Hz, 1H), 7.85 (overlapped, 1H), 7.82 (*d*, *J* = 9.3 Hz, 4H), 7.53–7.64 (*m*, 3H), 7.37 (*d*, *J* = 7.6 Hz, 1H), 7.22 (*d*, *J* = 7.6 Hz, 1H), 7.08 (*t*, *J* = 7.6 Hz, 1H), 7.02 (*d*, *J* = 9.3 Hz, 4H), 6.89 (*s*, 2H), 4.20 (*t*, *J* = 5.2 Hz, 4H), 3.90 (*t*, *J* = 5.2 Hz, 4H), 3.74–3.79 (*m*, 4H), 3.65–3.73 (*m*, 8H), 3.53–3.59 (*m*, 4H), 3.38 (*s*, 6H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 169.2, 165.1, 162.6, 160.2, 157.8, 154.3, 151.4, 146.8, 142.1, 138.7, 138.6, 138.1, 131.4, 130.6, 130.2, 128.2, 128.0, 127.5, 124.5, 123.7, 122.7, 121.5, 119.2, 118.3, 117.9, 114.9, 110.6, 104.4, 98.1, 71.9, 70.8, 70.6, 70.6, 69.6, 67.5, 59.0 ppm; FTIR-ATR (neat): *v* 3047, 2926, 2869, 2093, 1610, 1581, 1559, 1524, 1487, 1459, 1434, 1385, 1295, 1249, 1197, 1177, 1101, 1059, 992, 947, 916, 874, 835, 787, 759, 732, 684, 648, 632, 611, 586, 569, 543, 527, 513 cm⁻¹; HRMS(ESI⁺) calcd for C₅₆H₅₄N₄O₁₀NaPt m/z 1160.34119 [M+Na]⁺, found m/z 1160.33799.

8 6 7 7 8 8 7 7 9 9 10 <th10</th> <th10</th> <th10</th>



Figure S1. ¹H and ¹³C NMR spectra of 4 in chloroform-*d*.



Figure S2. ¹H and ¹³C NMR spectra of 1 in chloroform-*d*.



Figure S3. Expanded UV/vis spectra of 1 shown in Fig. 2a.



Figure S4. Changes in fluorescence spectra of **1** in toluene at concentrations of (a) 0.20 mmol L^{-1} , (b) 0.30 mmol L^{-1} , and (c) 0.40 mmol L^{-1} upon cooling the solution. The temperatures are 80, 70, 60, 50, 40, 30, 20, 10, and 0 °C. Red and blue lines in the graphs denote the spectra observed at 80 °C and 0 °C, respectively.



Figure S5. AFM images of the cast films of 1 in toluene at the concentrations of (a) 0.10 mmol L^{-1} and (b) 0.50 mmol L^{-1} .



Figure S6. Size of micelles observed in the cryo-TEM image. Lengths described in the figure represent diameters of spheres or the longer axis of "ellipsoids".



Figure S7. Size distribution of micelles observed in the AFM image. *d* denotes diameter of the micelles.

Table S1. Summary of fluorescence quantum yield of 1 in THF/water mixed solvent described in Fig 4d.

water content in THF (v/v, %)	0	10	20	30	40	50	60	70	80	90
Quantum Yield (%)	0.206	0.298	0.458	0.468	0.637	0.685	0.839	16.2	1.41	0.836



Figure S8. Hydrodynamic diameter (*d*) of existing species in THF/water mixed solvent of **1** at a concentration of 0.30 mmol L^{-1} , as inferred from DLS experiments. The water contents in THF (v/v, %) are (a) 0 %, (b) 10 %, (c) 20 %, (d) 30 %, (e) 40 %, (f) 50 %, (g) 60 %, (h) 80 %, and (i) 90 %.



Figure S9. Hydrodynamic diameter (*d*) of existing species in THF/water mixed solvent of **1** at concentrations of (a–c) 0.10 mmol L^{-1} and (d–f) 0.50 mmol L^{-1} , as inferred from DLS experiments. The water contents in THF (v/v, %) are (a) 50 %, (b) 80 %, (c) 90 %, (d) 50 %, (e) 60 %, and (f) 80 %.



Figure S10. (a) Fluorescence spectra ($\lambda_{ex} = 444 \text{ nm}$) of **1** (0.10 mmol L⁻¹) in THF/water mixed solvent. The inset denotes the expanded graph. The water contents in THF (v/v, %) are 0 % (black line), 50 % (red line), 80 % (brown line), and 90 % (blue line). (b) plot of the fluorescence emission intensity shown in (a) at 572 nm against water content in THF (v/v, %). (c) Fluorescence spectra ($\lambda_{ex} = 444 \text{ nm}$) of **1** (0.50 mmol L⁻¹) in THF/water mixed solvent. The inset denotes the expanded graph. The water contents in THF (v/v, %) are 0 % (black line), 50 % (red line), 60 % (brown line), 80 % (green line) and 90 % (blue line). (d) plot of the fluorescence emission intensity shown in (c) at 572 nm against water content in THF (v/v, %).



Figure S11. (a) UV/vis spectra and (b) Fluorescence spectra ($\lambda_{ex} = 330 \text{ nm}$) of **4** (0.30 mmol L⁻¹) in THF/water mixed solvent. The water contents in THF (v/v, %) are 0 % (black line), 10 % (purple line), 50% (red line), 70% (brown line), 80 % (green line), and 90% (blue line).

References

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