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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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## **Contents**

General	S3
Scheme 1. synthesis of 1	S4
Synthetic procedure for all new chemical entities	S5-S6
<sup>1</sup> H and <sup>13</sup> C NMR spectra of all new chemical entities	S7-S8
Figure S3. Expanded UV/vis spectra of 1 shown in Fig. 2a.	
Figure S4. VT UV/vis spectra of 1 in toluene	
Figure S5. AFM images of the cast films of 1	S10
Figure S6. Size of micelles observed in a cryo-TEM image	S11
Figure S7. Size of micelles observed in an AFM image	
Table S1. Summary of quantum yield	
Figure S8, S9. Size comparison of 1 in THF/water with various water volume fractions	S14, S15
Figure S10. Fluorescence spectra of 1 in THF/water	S16
Figure S11. UV/vis spectra of 4 in THF/water	S17
References	S18

General: All reagents and solvents were commercial reagent grade and were used without further purification unless otherwise noted. Dry DMF, dry CH<sub>2</sub>Cl<sub>2</sub> and dry triethylamine (NEt<sub>3</sub>) were obtained by distillation over CaH<sub>2</sub>. <sup>1</sup>H and <sup>13</sup>C 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 <sup>1</sup>H and <sup>13</sup>C, 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 NEt<sub>3</sub> (3.17 mL, 22.7 mmol) in CH<sub>2</sub>Cl<sub>2</sub> 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; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sup>-1</sup>; HRMS (ESI<sup>+</sup>) calcd for C<sub>40</sub>H<sub>44</sub>N<sub>2</sub>O<sub>10</sub>Na m/z 735.28888 [M+Na]<sup>+</sup>, 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 CH<sub>2</sub>Cl<sub>2</sub> (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 CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>, 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; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  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; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  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<sup>-1</sup>; HRMS(ESI<sup>+</sup>) calcd for C<sub>56</sub>H<sub>54</sub>N<sub>4</sub>O<sub>10</sub>NaPt m/z 1160.34119 [M+Na]<sup>+</sup>, found m/z 1160.33799.

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



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

# 



Figure S2. <sup>1</sup>H and <sup>13</sup>C 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  $L^{-1}$ .

![](_page_10_Figure_0.jpeg)

**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".

![](_page_11_Figure_0.jpeg)

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

![](_page_13_Figure_0.jpeg)

**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 %.

![](_page_14_Figure_0.jpeg)

**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 %.

![](_page_15_Figure_0.jpeg)

**Figure S10.** (a) Fluorescence spectra ( $\lambda_{ex} = 444 \text{ nm}$ ) of **1** (0.10 mmol L<sup>-1</sup>) 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<sup>-1</sup>) 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, %).

![](_page_16_Figure_0.jpeg)

**Figure S11.** (a) UV/vis spectra and (b) Fluorescence spectra ( $\lambda_{ex} = 330 \text{ nm}$ ) of **4** (0.30 mmol L<sup>-1</sup>) 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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