

## **A Metallo-Amphiphile with Unusual Memory Behaviour: Effect of Temperature and Structure on the Self-Assembly of Triethylene Glycol (TEG)-Pendant Platinum(II) Bzimpy Complexes**

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### **Supporting Information**

#### **Physical Measurements and Instrumentation**

<sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane, (CH<sub>3</sub>)<sub>4</sub>Si. Positive-ion FAB mass spectra were recorded on a Thermo Scientific DFS High Resolution Magnetic Sector mass spectrometer. IR spectra were obtained as KBr disc on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000–400 cm<sup>-1</sup>). Elemental analyses of complexes were performed on a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences. The UV-visible spectra were obtained using a Varian Cary 50 UV-vis spectrophotometer. Steady-state emission spectra at room temperature were recorded on a Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. Variable-temperature UV-vis absorption and emission spectra were obtained using a Varian Cary 50 UV-vis spectrophotometer and a Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector, respectively.

#### **Dynamic Light Scattering (DLS) Studies**

Dynamic light scattering (DLS) experiments were performed on a Malvern (UK) Zetasizer 3000HSA with an internal HeNe laser ( $\lambda = 632.8$  nm).

**Microscopy Studies.** Transmission electron microscopy (TEM) experiments were performed on a Philips Tecnai G2 20 S-TWIN transmission electron microscope with an accelerating voltage of 200 kV. The TEM images were taken by Gatan MultiScan Model 794. The TEM samples were prepared by dropping a few drops of  $10^{-4}$  M solution onto a carbon-coated copper grid and some samples were negatively stained by uranyl acetate for contrast enhancement. Scanning electron microscope (SEM) experiments were performed on a LEO 1530 FEG scanning electron microscope.

#### **Atomic Force Microscopy (AFM) Studies**

Tapping-mode atomic force microscopy (AFM) experiments were performed on a Asylum Research MFP-3D SA with ARC2 SPM Controller under ambient condition. The AFM samples were prepared by loading a few drops of solution of the sample onto a silicon wafer, followed by drying in air overnight.

## Syntheses

### Materials and Reagents

[Pt{bzimpy(C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>}Cl]Cl<sup>S1</sup> and [Pt{bzimpy(TEG)<sub>2</sub>}Cl]Cl<sup>S2</sup> were prepared according to literature procedure. 1-Bromo-3,5-didecyloxybenzene<sup>S3</sup> and 1-bromo-3,5-bis-(triethyleneglycol methyl ether)-benzene<sup>S4</sup> were synthesized according to literature procedures. All other reagents and solvents were of analytical grade and were used as received.

### TMS–C≡CC<sub>6</sub>H<sub>3</sub>–(OC<sub>12</sub>H<sub>25</sub>)<sub>2</sub>-3,5

This was synthesized by a Sonogashira coupling reaction by reacting Br–C<sub>6</sub>H<sub>3</sub>–(OC<sub>12</sub>H<sub>25</sub>)<sub>2</sub>-3,5 (2.4 g, 3.80 mmol) with TMS–C≡CH (0.7 mL, 7.60 mmol). Purification by column chromatography on silica gel using hexane-dichloromethane (15:1, v/v) as the eluent gave the product as a pale yellow. Yield: 1.68 g (82 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 0.24 (s, 9H, –TMS), 0.88 (t, 6H, *J* = 6.8 Hz, –CH<sub>3</sub>), 1.21–1.37 (m, 32H, –CH<sub>2</sub>–), 1.38–1.48 (m, 4H, –CH<sub>2</sub>–), 1.71–1.78 (m, 4H, –CH<sub>2</sub>–), 3.91 (t, 4H, *J* = 6.5 Hz, –CH<sub>2</sub>O), 6.42 (t, 1H, *J* = 2.2 Hz, phenyl), 6.59 ppm (d, 2H, *J* = 2.2 Hz, phenyl). Positive EI MS: *m/z*: 542 [M]<sup>+</sup>.

### HC≡CC<sub>6</sub>H<sub>3</sub>–(OC<sub>12</sub>H<sub>25</sub>)<sub>2</sub>-3,5

This was synthesized by reacting TMS–C≡CC<sub>6</sub>H<sub>3</sub>–(OC<sub>12</sub>H<sub>25</sub>)<sub>2</sub>-3,5 (1.40 g, 2.58 mmol) with NaOH (0.20 g, 5.52 mmol). Purification by column chromatography on silica gel using chloroform as the eluent gave the product as a pale yellow solid. Yield: 1.20 g (99 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 0.88 (t, 6H, *J* = 6.5 Hz, –CH<sub>3</sub>), 1.20–1.37 (m, 32H, –CH<sub>2</sub>–), 1.38–1.47 (m, 4H, –CH<sub>2</sub>–), 1.71–1.80 (m, 4H, –CH<sub>2</sub>–), 3.01 (s, 1H, –C≡CH), 3.91 (t, 4H, *J* = 6.5 Hz, –CH<sub>2</sub>O), 6.46 (t, 1H, *J* = 2.0 Hz, phenyl), 6.62 ppm (d, 2H, *J* = 2.0 Hz, phenyl). Positive EI MS: *m/z*: 470 [M]<sup>+</sup>.

### **TMS-C≡CC<sub>6</sub>H<sub>3</sub>-(OTEG)<sub>2-3,5</sub>**

This was synthesized by a Sonogashira coupling reaction by reacting Br-C<sub>6</sub>H<sub>3</sub>-(OTEG)<sub>2-3,5</sub> (1.5 g, 3.80 mmol) with TMS-C≡CH (0.7 mL, 7.60 mmol). Purification by column chromatography on silica gel using ethyl acetate-hexane (3:1, v/v) as the eluent gave the product as a yellow oil. Yield: 1.37 g (72 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 0.24 (s, 9H, -TMS), 3.38 (s, 6H, -OCH<sub>3</sub>), 3.54–3.57 (m, 4H, -CH<sub>2</sub>O), 3.64–3.69 (m, 8H, -CH<sub>2</sub>O), 3.71–3.75 (m, 4H, -CH<sub>2</sub>O), 3.81–3.84 (m, 4H, -CH<sub>2</sub>O), 4.07–4.10 (m, 4H, -CH<sub>2</sub>O), 6.48 (t, 1H, *J* = 2.3 Hz, phenyl), 6.62 ppm (d, 2H, *J* = 2.3 Hz, phenyl). Positive EI MS: *m/z*: 498 [M]<sup>+</sup>.

### **HC≡CC<sub>6</sub>H<sub>3</sub>-(OTEG)<sub>2-3,5</sub>**

This was synthesized by a procedure similar to that described for HC≡CC<sub>6</sub>H<sub>3</sub>-(OC<sub>12</sub>H<sub>25</sub>)<sub>2-3,5</sub> by reacting TMS-C≡CC<sub>6</sub>H<sub>3</sub>-(OTEG)<sub>2-3,5</sub> (1.20 g, 2.41 mmol) with K<sub>2</sub>CO<sub>3</sub> (0.99 g, 7.22 mmol). Purification by column chromatography on silica gel using ethyl acetate as the eluent gave the product as a pale yellow oil. Yield: 1.02 g (99 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K): δ 3.02 (s, 1H, -C≡CH), 3.38 (s, 6H, -OCH<sub>3</sub>), 3.54–3.56 (m, 4H, -CH<sub>2</sub>O), 3.64–3.67 (m, 4H, -CH<sub>2</sub>O), 3.67–3.69 (m, 4H, -CH<sub>2</sub>O), 3.72–3.74 (m, 4H, -CH<sub>2</sub>O), 3.82–3.85 (m, 4H, -CH<sub>2</sub>O), 4.08–4.10 (m, 4H, -CH<sub>2</sub>O), 6.51 (t, 1H, *J* = 2.3 Hz, phenyl), 6.65 ppm (d, 2H, *J* = 2.3 Hz, phenyl). Positive EI MS: *m/z*: 426 [M]<sup>+</sup>.

### **[Pt{bzimpy(TEG)<sub>2</sub>}(C≡CC<sub>6</sub>H<sub>3</sub>-(OC<sub>12</sub>H<sub>25</sub>)<sub>2-3,5</sub>)]Cl (1)**

To a solution of [Pt{bzimpy(TEG)<sub>2</sub>}Cl]Cl (0.17 g, 0.20 mmol) in degassed dichloromethane (30 mL) were added triethylamine (1 mL), HC≡CC<sub>6</sub>H<sub>3</sub>-(OC<sub>12</sub>H<sub>25</sub>)<sub>2-3,5</sub> (0.14 g, 0.30 mmol) and a catalytic amount of CuI. The

reaction mixture was allowed to stir in N<sub>2</sub> atmosphere at room temperature overnight. The product was purified by column chromatography on silica gel using chloroform-methanol (6:1, v/v) as the eluent and was dried under vacuum to give a red solid. Yield: 0.20 g (77 %). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>Cl, 298 K): δ 0.88 (t, 6H, *J* = 7.0 Hz, -CH<sub>3</sub>), 1.27–1.42 (m, 32H, -CH<sub>2</sub>-), 1.46–1.54 (m, 4H, -CH<sub>2</sub>-), 1.81–1.88 (m, 4H, -CH<sub>2</sub>-), 3.25 (s, 6H, -OCH<sub>3</sub>), 3.30–3.36 (m, 12H, -CH<sub>2</sub>O), 3.48–3.50 (m, 4H, -CH<sub>2</sub>O), 4.00–4.03 (m, 8H, -CH<sub>2</sub>O), 5.06–5.08 (m, 4H, -CH<sub>2</sub>N), 6.45 (t, 1H, *J* = 2.1 Hz, phenyl), 6.63 (d, 2H, *J* = 2.1 Hz, phenyl), 7.45–7.49 (m, 2H, benzimidazolyl), 7.53–7.60 (m, 4H, benzimidazolyl), 8.48 (t, 1H, *J* = 8.3 Hz, pyridyl), 8.55 (d, 2H, *J* = 8.3 Hz, benzimidazolyl), 8.79 ppm (d, 2H, *J* = 8.3 Hz, pyridyl). IR (KBr): ν = 2120 cm<sup>-1</sup> (w; ν(C≡C)). Positive FAB MS: *m/z*: 1267 [M-Cl]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>65</sub>H<sub>94</sub>ClN<sub>5</sub>O<sub>8</sub>Pt<sub>2</sub>•2CH<sub>3</sub>OH: C, 58.82; H, 7.51; N, 5.12; found: C, 58.65; H, 7.41; N, 4.85.

**[Pt{bzimpy(C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>}{C≡CC<sub>6</sub>H<sub>3</sub>-(OTEG)<sub>2</sub>-3,5}]Cl (2)**

To a solution of [Pt{bzimpy(C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>}Cl]Cl (0.20 g, 0.22 mmol) in degassed dichloromethane (30 mL) were added triethylamine (1 mL), HC≡CC<sub>6</sub>H<sub>3</sub>-(OTEG)<sub>2</sub>-3,5 (0.13 g, 0.33 mmol) and a catalytic amount of CuI. The reaction mixture was allowed to heat under reflux in N<sub>2</sub> atmosphere overnight. The product was purified by column chromatography on silica gel using chloroform-methanol (8:1, v/v) as the eluent and was dried under vacuum to give a red solid. Yield: 0.19 g (66 %). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>Cl, 298 K): δ 0.85 (t, 6H, *J* = 7.0 Hz, -CH<sub>3</sub>), 1.19–1.30 (m, 32H, -CH<sub>2</sub>-), 1.33–1.39 (m, 4H, -CH<sub>2</sub>-), 1.87–14.9 (m, 4H, -CH<sub>2</sub>-), 3.38 (s, 6H, -OCH<sub>3</sub>), 3.56–3.58 (m, 4H, -CH<sub>2</sub>O), 3.68–3.70 (m, 4H, -CH<sub>2</sub>O), 3.73–3.76 (m, 4H, -CH<sub>2</sub>O), 3.80–3.82 (m, 4H, -CH<sub>2</sub>O), 3.94–3.97 (m, 4H, -CH<sub>2</sub>O), 4.22–4.24 (m, 4H, -CH<sub>2</sub>O), 4.79–4.82 (m, 4H, -CH<sub>2</sub>N), 6.52 (t, 1H, *J* =

2.2 Hz, phenyl), 6.61 (d, 2H,  $J = 2.2$  Hz, phenyl), 7.36–7.38 (m, 2H, benzimidazolyl), 7.52–7.59 (m, 4H, benzimidazolyl), 8.44–8.46 (m, 2H, benzimidazolyl), 8.62 (d, 2H,  $J = 8.1$  Hz, pyridyl), 8.72 ppm (t, 1H,  $J = 8.1$  Hz, pyridyl). IR (KBr):  $\nu = 21146 \text{ cm}^{-1}$  (w;  $\nu(\text{C}\equiv\text{C})$ ). Positive FAB MS:  $m/z$ : 1267  $[\text{M}-\text{Cl}]^+$ . Elemental analysis calcd (%) for  $\text{C}_{65}\text{H}_{94}\text{ClN}_5\text{O}_8\text{Pt}\cdot 2\text{H}_2\text{O}$ : C, 58.26; H, 7.37; N, 5.23; found: C, 58.47; H, 7.41; N, 5.20.

### References

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