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

$^1$H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane, (CH$_3$)$_4$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$^{-1}$). Elemental analyses of complexes were preformed 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).

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**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

\([\text{Pt\{bzimpy(C_{12}H_{25})_{2}\}Cl}]\text{Cl}^{S1}\) and \([\text{Pt\{bzimpy(TEG)_{2}\}Cl}]\text{Cl}^{S2}\) were prepared according to literature procedure. 1-Bromo-3,5-didecyloxybenzene\(^{S3}\) and 1-bromo-3,5-bis-(triethylene glycol methyl ether)-benzene\(^{S4}\) were synthesized according to literature procedures. All other reagents and solvents were of analytical grade and were used as received.

**TMS–C≡CC_{6}H_{3}–(OC_{12}H_{25})_{2}-3,5**

This was synthesized by a Sonogashira coupling reaction by reacting Br–C_{6}H_{3}–(OC_{12}H_{25})_{2}-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 %). \(^1\)H NMR (400 MHz, CDCl\(_3\), 298 K): \(\delta\) 0.24 (s, 9H, –TMS), 0.88 (t, 6H, \(J = 6.8\) Hz, –CH\(_3\)), 1.21–1.37 (m, 32H, –CH\(_2\)), 1.38–1.48 (m, 4H, –CH\(_2\)), 1.71–1.78 (m, 4H, –CH\(_2\)), 3.91 (t, 4H, \(J = 6.5\) Hz, –CH\(_2\)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]\(^+\).

**HC≡CC_{6}H_{3}–(OC_{12}H_{25})_{2}-3,5**

This was synthesized by reacting TMS–C≡CC_{6}H_{3}–(OC_{12}H_{25})_{2}-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 %). \(^1\)H NMR (400 MHz, CDCl\(_3\), 298 K): \(\delta\) 0.88 (t, 6H, \(J = 6.5\) Hz, –CH\(_3\)), 1.20–1.37 (m, 32H, –CH\(_2\)), 1.38–1.47 (m, 4H, –CH\(_2\)), 1.71–1.80 (m, 4H, –CH\(_2\)), 3.01 (s, 1H, –C≡CH), 3.91 (t, 4H, \(J = 6.5\) Hz, –CH\(_2\)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]\(^+\).
TMS–C≡CC₆H₃–(OTE₉)₂-3,5

This was synthesized by a Sonogashira coupling reaction by reacting Br–C₆H₃–(OTE₉)₂-3,5 (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 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 0.24 (s, 9H, –TMS), 3.38 (s, 6H, –OCH₃), 3.54–3.57 (m, 4H, –CH₂O), 3.64–3.69 (m, 8H, –CH₂O), 3.71–3.75 (m, 4H, –CH₂O), 3.81–3.84 (m, 4H, –CH₂O), 4.07–4.10 (m, 4H, –CH₂O), 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]+.

HC≡CC₆H₃–(OTE₉)₂-3,5

This was synthesized by a procedure similar to that described for HC≡CC₆H₃–(OC₁₂H₂₅)₂-3,5 by reacting TMS–C≡CC₆H₃–(OTE₉)₂-3,5 (1.20 g, 2.41 mmol) with K₂CO₃ (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 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 3.02 (s, 1H, –C≡CH), 3.38 (s, 6H, –OCH₃), 3.54–3.56 (m, 4H, –CH₂O), 3.64–3.67 (m, 4H, –CH₂O), 3.67–3.69 (m, 4H, –CH₂O), 3.72–3.74 (m, 4H, –CH₂O), 3.82–3.85 (m, 4H, –CH₂O), 4.08–4.10 (m, 4H, –CH₂O), 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]+.

[Pt{bzimpy(TEG)}₂(C≡CC₆H₃–(OC₁₂H₂₅)₂-3,5)]Cl (1)

To a solution of [Pt{bzimpy(TEG)}₂Cl]Cl (0.17 g, 0.20 mmol) in degassed dichloromethane (30 mL) were added triethylamine (1 mL), HC≡CC₆H₃–(OC₁₂H₂₅)₂-3,5 (0.14 g, 0.30 mmol) and a catalytic amount of CuI. The
reaction mixture was allowed to stir in N₂ 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 %). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 0.88 (t, 6H, J = 7.0 Hz, –CH₃), 1.27–1.42 (m, 32H, –CH₂–), 1.46–1.54 (m, 4H, –CH₂–), 1.81–1.88 (m, 4H, –CH₂–), 3.25 (s, 6H, –OCH₃), 3.30–3.36 (m, 12H, –CH₂O), 3.48–3.50 (m, 4H, –CH₂O), 4.00–4.03 (m, 8H, –CH₂O), 5.06–5.08 (m, 4H, –CH₂N), 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): v = 2120 cm⁻¹ (w; ν(C≡C)). Positive FAB MS: m/z: 1267 [M–Cl]⁺. Elemental analysis calcd (%) for C₆₅H₉₄ClN₅O₈Pt₂•2CH₃OH: C, 58.82; H, 7.51; N, 5.12; found: C, 58.65; H, 7.41; N, 4.85.

[Pt{bzimpy(C₁₂H₂₅)₂}{C≡CC₆H₃–(OTEG)₂-3,5}]Cl (2)

To a solution of [Pt{bzimpy(C₁₂H₂₅)₂}Cl]Cl (0.20 g, 0.22 mmol) in degassed dichloromethane (30 mL) were added triethylamine (1 mL), HC≡CC₆H₃–(OTEG)₂-3,5 (0.13 g, 0.33 mmol) and a catalytic amount of CuI. The reaction mixture was allowed to heat under reflux in N₂ 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 %). ¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ 0.85 (t, 6H, J = 7.0 Hz, –CH₃), 1.19–1.30 (m, 32H, –CH₂–), 1.33–1.39 (m, 4H, –CH₂–), 1.87–14.9 (m, 4H, –CH₂–), 3.38 (s, 6H, –OCH₃), 3.56–3.58 (m, 4H, –CH₂O), 3.68–3.70 (m, 4H, –CH₂O), 3.73–3.76 (m, 4H, –CH₂O), 3.80–3.82 (m, 4H, –CH₂O), 3.94–3.97 (m, 4H, –CH₂O), 4.22–4.24 (m, 4H, –CH₂O), 4.79–4.82 (m, 4H, –CH₂N), 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): ν = 21146 cm⁻¹ (w; ν(C≡C)). Positive FAB MS: m/z: 1267 [M–Cl]⁺. Elemental analysis calcd (%) for C₆₅H₉₄ClN₅O₈Pt•2H₂O: C, 58.26; H, 7.37; N, 5.23; found: C, 58.47; H, 7.41; N, 5.20.

References
S1 I. Mathew and W. Sun, Dalton Trans., 2010, 39, 5885–5898.