

Tuning of Spectroscopic Properties Via Variation of the Alkyl Chain Length: A Systematic Study of Molecular Structural Changes on Self-Assembly of Amphiphilic Sulfonate-Pendant Platinum(II) Bzimpy Complexes in Aqueous Medium†

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Supporting Information

Materials and Reagents

[Pt{bzimpy}(PrSO₃)₂]Cl]PPN,¹ 1-(dodecyloxy)-4-ethynylbenzene,² and 1-ethynyl-4-(hexadecyloxy)benzene² were synthesized according to literature procedures. 4-Iodophenol (ABCR, 98+ %), 1-bromododecane (Alfa Aesar, 98 %), 1-bromodocosane (C₂₂H₄₅Br) (Lancaster, 97 %), phenylacetylene (Aldrich 98 %), *p*-tolylacetylene (GFS Chemicals Inc., 98 %), 1-ethynyl-4-methoxybenzene (Maybridge Chemical Co., Ltd.), and 1-ethynyl-4-(heptyloxy)benzene (Maybridge Chemical Co., Ltd.) were purchased from the corresponding chemical suppliers. All other reagents and solvents were of analytical grade and were used as received.

Synthesis

I-C₆H₄-OC₂₂H₄₅-4

It was synthesized by a modified literature procedure for alkylation of phenol derivatives.³ A mixture of 4-iodophenol (5.00 g, 22.7 mmol) and K₂CO₃ (6.29 g, 45.5 mmol) in degassed DMF was stirred under N₂ atmosphere for 30 min. After addition of C₂₂H₄₅Br, the mixture was heated in N₂ overnight. DMF was removed by distillation under reduced pressure and the product was extracted with chloroform and purified by column chromatography on silica gel using hexane as eluent to give a white solid. Yield: 10.4 g (87 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 0.87 (t, 3H, *J* = 6.8 Hz, -CH₃), 1.20–1.33 (m, 34H, -CH₂-), 1.33–1.44 (m, 2H, -CH₂-), 1.40–1.47 (m, 2H, -CH₂-), 1.71–1.78 (m, 2H, -CH₂-), 3.89 (t, 2H, *J* = 6.6 Hz, -CH₂O), 6.66 (t, 2H, *J* = 9.0 Hz, phenyl), 7.52 ppm (d, 2H, *J* = 9.0 Hz, phenyl). Positive EI HRMS: *m/z* found: (calcd) for C₂₈H₄₉OI: 528.2818 (528.2823).

(CH₃)₃Si-C≡CC₆H₄-OC₂₂H₄₅-4

This was synthesized by a Sonogashira coupling reaction.² I-C₆H₄-OC₂₂H₄₅-4 (5.03 g,

9.52 mmol) was dissolved in degassed triethylamine (60 mL) and $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{CH}$ (1.7 mL, 3.00 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.33 g, 0.48 mmol) and CuI (0.09g, 0.48 mmol) were added to the solution. The mixture was heated under reflux in N_2 atmosphere overnight. After removal of amine under reduced pressure, diethyl ether was added and any insoluble salt was filtered off. The crude product was purified by column chromatography on silica gel using hexane as the eluent to give the pure product as a white solid. Yield: 4.38 g (92 %). ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.23 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 0.88 (t, 3H, $J = 6.8$ Hz, $-\text{CH}_3$), 1.20–1.37 (m, 36H, $-\text{CH}_2-$), 1.40–1.47 (m, 2H, $-\text{CH}_2-$), 1.73–1.80 (m, 2H, $-\text{CH}_2-$), 3.94 (t, 2H, $J = 6.6$ Hz, $-\text{CH}_2\text{O}$), 6.90 (t, 2H, $J = 8.8$ Hz, phenyl), 7.38 ppm (d, 2H, $J = 8.8$ Hz, phenyl). Positive EI HRMS: m/z found: (calcd) for $\text{C}_{33}\text{H}_{58}\text{OSi}$: 498.4262 (498.4251).

$\text{HC}\equiv\text{CC}_6\text{H}_4-\text{OC}_{22}\text{H}_{45}-4$

A mixture of $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{CC}_6\text{H}_4-\text{OC}_{22}\text{H}_{45}-4$ (2.00 g, 4.02 mmol) and NaOH (2.18 g, 54.5 mmol) in a solvent mixture of dichloromethane (60 mL)-methanol (15 mL) was stirred under N_2 atmosphere for 2 hr at room temperature. After quenching with water, it was extracted with dichloromethane and dried over anhydrous MgSO_4 . Further purification by column chromatography on silica gel using hexane as eluent gave the pure product as a white solid. Yield: 1.40 g (82 %). ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.88 (t, 3H, $J = 6.8$ Hz, $-\text{CH}_3$), 1.21–1.37 (m, 36H, $-\text{CH}_2-$), 1.39–1.49 (m, 2H, alkyl), 1.73–1.81 (m, 2H, $-\text{CH}_2-$), 2.99 (s, 1H, $-\text{C}\equiv\text{CH}$), 3.95 (t, 2H, $J = 6.6$ Hz, $-\text{CH}_2\text{O}$), 6.82 (d, 2H, $J = 8.9$ Hz, phenyl), 7.41 ppm (d, 2H, $J = 8.9$ Hz, phenyl). Positive EI MS: m/z : 426 $[\text{M}]^+$. Positive EI HRMS: m/z found: (calcd) for $\text{C}_{30}\text{H}_{50}\text{O}$: 426.3857 (426.3856).

[Pt{bzimpy(PrSO₃)₂}(C≡CPh)]K ([1]K)

To a solution of [Pt{bzimpy(PrSO₃)₂}Cl]PPN (0.30 g, 0.22 mmol) in degassed dichloromethane (60 mL) were added phenylacetylene (0.08 mL, 0.76 mmol), tri-*n*-octylamine (1 mL) and a catalytic amount of CuI. The reaction mixture was allowed to heat under reflux overnight in N₂ atmosphere. After removal of solvents, the solid was washed with diethyl ether and dichloromethane was then added to dissolve the solid. After filtration, an acetonitrile solution of KPF₆ was added to the solution for the metathesis reaction to yield a red solid of the product. The product was further purified by converting to its PPN⁻ salt, followed by recrystallization via diffusion of diethyl ether into a dichloromethane solution of the complex and subsequent conversion back to its potassium salt. Yield: 0.04 g (65 %). ¹H NMR (400 MHz, DMSO-*d*⁶, 298 K): δ 2.16–2.26 (m, 4H, –CH₂–), 2.68 (t, 4H, *J* = 5.3 Hz, –CH₂SO₃), 5.00 (t, 4H, *J* = 7.3 Hz, –CH₂N), 7.30–7.35 (m, 1H, phenyl), 7.44–7.51 (m, 4H, phenyl), 7.59–7.61 (m, 4H, benzimidazolyl), 8.00–8.03 (m, 2H, benzimidazolyl), 8.34 (t, 1H, *J* = 8.2 Hz, pyridyl), 8.53–8.55 (m, 2H, benzimidazolyl), 8.86 ppm (d, 2H, *J* = 8.2 Hz, pyridyl). IR (KBr): ν = 2116 cm⁻¹ (w; ν(C≡C)). Negative FAB MS: *m/z*: 850 [M–K]⁻. Elemental analysis calcd (%) for C₃₃H₂₈KN₅O₆PtS₂•H₂O•0.5CH₂Cl₂: C, 42.38; H, 3.29; N, 7.38; found: C, 42.33; H, 3.20; N, 7.24.

[Pt{bzimpy(PrSO₃)₂}(C≡CC₆H₄–CH₃-4)]K ([2]K)

This was synthesized by a procedure similar to that described for **1** by reacting [Pt{bzimpy(PrSO₃)₂}Cl]PPN (0.15 g, 0.11 mmol) with *p*-tolylacetylene (0.02 mL, 0.14 mmol) to yield a red solid. Yield: 0.06 g (60 %). ¹H NMR (400 MHz, DMSO-*d*⁶, 298 K): δ 2.19–2.28 (m, 4H, –CH₂–), 2.38 (s, 3H, –CH₃), 2.66–2.68 (m, 4H, –CH₂SO₃), 5.03–5.07 (m, 4H, –CH₂N), 7.26 (d, 2H, *J* = 7.9 Hz, phenyl), 7.41 (d,

2H, $J = 7.9$ Hz, phenyl), 7.59–7.64 (m, 4H, benzimidazolyl), 8.04–8.08 (m, 2H, benzimidazolyl), 8.40 (t, 1H, $J = 8.3$ Hz, pyridyl), 8.60–8.62 (m, 2H, benzimidazolyl), 8.87 ppm (d, 2H, $J = 8.3$ Hz, pyridyl). IR (KBr): $\nu = 2112$ cm^{-1} (w; $\nu(\text{C}\equiv\text{C})$). Negative FAB MS: m/z : 864 $[\text{M}-\text{K}]^-$. Elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{30}\text{KN}_5\text{O}_6\text{PtS}_2 \cdot 2\text{H}_2\text{O} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 42.22; H, 3.59; N, 7.14; found: C, 42.21; H, 3.47; N, 7.22.

[Pt{bzimpy(PrSO₃)₂}(C≡C₆H₄-OCH₃-4)]K ([3]K)

This was synthesized by a procedure similar to that described for **1** by reacting [Pt{bzimpy(PrSO₃)₂}Cl]PPN (0.18 g, 0.14 mmol) with 1-ethynyl-4-methoxybenzene (0.04 g, 0.27 mmol) to yield a red solid. Yield: 0.10 g (85 %). ¹H NMR (400 MHz, DMSO-*d*⁶, 298 K): δ 2.18–2.25 (m, 4H, -CH₂-), 2.67–2.70 (m, 4H, -CH₂SO₃), 3.83 (s, 3H, -OCH₃), 5.00–5.05 (m, 4H, -CH₂N), 7.04 (d, 2H, $J = 8.6$ Hz, phenyl), 7.43 (d, 2H, $J = 8.6$ Hz, phenyl), 7.58–7.60 (m, 4H, benzimidazolyl), 8.01–8.03 (m, 2H, benzimidazolyl), 8.34 (t, 1H, $J = 8.3$ Hz, pyridyl), 8.55–8.58 (m, 2H, benzimidazolyl), 8.85 ppm (d, 2H, $J = 8.3$ Hz, pyridyl). IR (KBr): $\nu = 2106$ cm^{-1} (w; $\nu(\text{C}\equiv\text{C})$). Negative FAB MS: m/z : 880 $[\text{M}-\text{K}]^-$. Elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{30}\text{KN}_5\text{O}_7\text{PtS}_2 \cdot 3.5\text{H}_2\text{O}$: C, 41.59; H, 3.80; N, 7.13; found: C, 41.58; H, 3.54; N, 7.30.

[Pt{bzimpy(PrSO₃)₂}(C≡CC₆H₄-OC₇H₁₅-4)]K ([4]K)

This was synthesized by a procedure similar to that described for **1** by reacting [Pt{bzimpy(PrSO₃)₂}Cl]PPN (0.10 g, 0.08 mmol) with 1-ethynyl-4-heptyloxybenzene (0.03 g, 0.15 mmol) to yield a red solid. Yield: 0.04 g (55 %). ¹H NMR (400 MHz, DMSO-*d*⁶, 298 K): δ 0.89 (t, 3H, $J = 6.7$ Hz, -CH₃), 1.26–1.40 (m, 6H, -CH₂-), 1.40–1.49 (m, 2H, -CH₂-), 1.73–1.80 (m, 2H, -CH₂-), 2.12–2.24 (m, 4H, -CH₂-),

2.64–2.67 (m, 4H, $-\text{CH}_2\text{SO}_3$), 4.04 (t, 2H, $J = 6.4$ Hz, $-\text{CH}_2\text{O}$), 4.90–4.94 (m, 4H, $-\text{CH}_2\text{N}$), 7.02 (d, 2H, $J = 8.6$ Hz, phenyl), 7.37 (d, 2H, $J = 8.6$ Hz, phenyl), 7.52–7.57 (m, 4H, benzimidazolyl), 7.90–7.92 (m, 2H, benzimidazolyl), 8.25 (t, 1H, $J = 8.2$ Hz, pyridyl), 8.44–8.46 (m, 2H, benzimidazolyl), 8.79 ppm (d, 2H, $J = 8.2$ Hz, pyridyl). IR (KBr): $\nu = 2120 \text{ cm}^{-1}$ (w; $\nu(\text{C}\equiv\text{C})$). Negative FAB MS: m/z : 963 $[\text{M}-\text{K}]^-$. Elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{42}\text{KN}_5\text{O}_7\text{PtS}_2\cdot 5\text{H}_2\text{O}$: C, 43.94; H, 4.79; N, 6.41; found: C, 44.00; H, 4.35; N, 6.61.

[Pt{bzimpy(PrSO₃)₂}(C≡CC₆H₄-OC₁₂H₂₅-4)]K ([5]K)

This was synthesized by a procedure similar to that described for **1** by reacting [Pt{bzimpy(PrSO₃)₂}Cl]PPN (0.10 g, 0.08 mmol) with 1-dodecyloxy-4-ethynylbenzene (0.08 g, 0.30 mmol) in methanol by using triethylamine (1 mL) as the base to yield a red solid. Yield: 0.07 g (83 %). ¹H NMR (400 MHz, DMSO-*d*⁶, 298 K): δ 0.86 (t, 3H, $J = 6.6$ Hz, $-\text{CH}_3$), 1.18–1.38 (m, 16H, $-\text{CH}_2-$), 1.38–1.49 (m, 2H, $-\text{CH}_2-$), 1.70–1.79 (m, 2H, $-\text{CH}_2-$), 2.16–2.25 (m, 4H, $-\text{CH}_2-$), 2.65–2.71 (m, 4H, $-\text{CH}_2\text{SO}_3$), 4.03 (t, 2H, $J = 5.9$ Hz, $-\text{CH}_2\text{O}$), 4.91–5.00 (m, 4H, $-\text{CH}_2\text{N}$), 7.01 (d, 2H, $J = 8.3$ Hz, phenyl), 7.38 (d, 2H, $J = 8.3$ Hz, phenyl), 7.53–7.62 (m, 4H, benzimidazolyl), 7.91–7.99 (m, 2H, benzimidazolyl), 8.30 (t, 1H, $J = 8.0$ Hz, pyridyl), 8.45–8.51 (m, 2H, benzimidazolyl), 8.80 ppm (d, 2H, $J = 8.0$ Hz, pyridyl). IR (KBr): $\nu = 2120 \text{ cm}^{-1}$ (w; $\nu(\text{C}\equiv\text{C})$). Negative ESI MS: m/z : 1034 $[\text{M}-\text{K}]^-$. Elemental analysis calcd (%) for $\text{C}_{45}\text{H}_{52}\text{KN}_5\text{O}_7\text{PtS}_2\cdot \text{CHCl}_3$: C, 46.32; H, 4.47; N, 5.87; found: C, 46.09; H, 4.61; N, 5.96.

[Pt{bzimpy(PrSO₃)₂}(C≡CC₆H₄-OC₁₆H₃₃-4)]K ([6]K)

This was synthesized by a procedure similar to that described for **1** by reacting [Pt{bzimpy(PrSO₃)₂}Cl]PPN (0.20 g, 0.15 mmol) with

1-ethynyl-4-hexadecyloxybenzene (0.26 g, 0.76 mmol) in DMF to yield a red solid. Yield: 0.14 g (80 %). ^1H NMR (400 MHz, DMSO- d_6 , 298 K): δ 0.84 (t, 3H, J = 6.6 Hz, $-\text{CH}_3$), 1.18–1.38 (m, 24H, $-\text{CH}_2-$), 1.40–1.49 (m, 2H, $-\text{CH}_2-$), 1.70–1.79 (m, 2H, $-\text{CH}_2-$), 2.16–2.26 (m, 4H, $-\text{CH}_2-$), 2.64–2.71 (m, 4H, $-\text{CH}_2\text{SO}_3$), 4.02 (t, 2H, J = 6.3 Hz, $-\text{CH}_2\text{O}$), 4.95–5.04 (m, 4H, CH_2N), 7.00 (d, 2H, J = 8.4 Hz, phenyl), 7.40 (d, 2H, J = 8.4 Hz, phenyl), 7.56–7.62 (m, 4H, benzimidazolyl), 7.98–8.04 (m, 2H, benzimidazolyl), 8.33 (t, 1H, J = 7.7 Hz, pyridyl), 8.53–8.58 (m, 2H, benzimidazolyl), 8.84 ppm (d, 2H, J = 7.7 Hz, pyridyl). IR (KBr): ν = 2120 cm^{-1} (w; $\nu(\text{C}\equiv\text{C})$). Negative FAB MS: m/z : 1089 $[\text{M}-\text{K}]^-$. Elemental analysis calcd (%) for $\text{C}_{49}\text{H}_{60}\text{KN}_5\text{O}_7\text{PtS}_2\cdot 3\text{H}_2\text{O}$: C, 49.73; H, 5.62; N, 5.92; found: C, 49.80; H, 5.45; N, 5.90.

$[\text{Pt}\{\text{bzimpy}(\text{PrSO}_3)_2\}(\text{C}\equiv\text{CC}_6\text{H}_4-\text{OC}_{22}\text{H}_{45}-4)]\text{K}$ ([7]K)

This was synthesized by a procedure similar to that described for **1** by reacting $[\text{Pt}\{\text{bzimpy}(\text{PrSO}_3)_2\}\text{Cl}]\text{PPN}$ (0.14 g, 0.11 mmol) with 1-ethynyl-4-docosyloxybenzene (0.15 g, 0.35 mmol) in DMF to yield a red solid. Yield: 0.11 g (80 %). ^1H NMR (400 MHz, DMSO- d_6 , 343 K): δ 0.85 (t, 3H, J = 6.8 Hz, $-\text{CH}_3$), 1.15–1.40 (m, 36H, $-\text{CH}_2-$), 1.40–1.50 (m, 2H, $-\text{CH}_2-$), 1.73–1.79 (m, 2H, $-\text{CH}_2-$), 2.27–2.34 (m, 4H, $-\text{CH}_2-$), 2.71–2.74 (m, 4H, $-\text{CH}_2\text{SO}_3$), 4.04 (t, 2H, J = 6.3 Hz, $-\text{CH}_2\text{O}$), 5.10–5.14 (m, 4H, $-\text{CH}_2\text{N}$), 7.00 (d, 2H, J = 8.7 Hz, phenyl), 7.45 (d, 2H, J = 8.7 Hz, phenyl), 7.60–7.66 (m, 4H, benzimidazolyl), 8.10–8.12 (m, 2H, benzimidazolyl), 8.43 (t, 1H, J = 8.3 Hz, pyridyl), 8.70–8.72 (m, 2H, benzimidazolyl), 8.93 ppm (d, 2H, J = 8.3 Hz, pyridyl). IR (KBr): ν = 2116 cm^{-1} (w; $\nu(\text{C}\equiv\text{C})$). Negative FAB MS: m/z : 1174 $[\text{M}-\text{K}]^-$. Elemental analysis calcd (%) for $\text{C}_{55}\text{H}_{72}\text{KN}_5\text{O}_7\text{PtS}_2\cdot 3.5\text{CH}_3\text{OH}$: C, 53.00; H, 6.53; N, 5.28; found: C, 52.96; H, 6.28; N, 5.05.

Physical Measurements and Instrumentation. ^1H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane, $(\text{CH}_3)_4\text{Si}$. Negative-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 ($4000\text{-}400\text{ cm}^{-1}$). Elemental analyses of the 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 Varian Cary 50 UV-vis spectrophotometer. Steady-state excitation and emission spectra at room temperature and at 77 K 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. Solid-state photophysical studies were carried out with solid samples contained in a quartz tube inside a quartz-walled Dewar flask. Measurements of glass samples and solid samples at 77 K were similarly conducted with liquid nitrogen filled into the optical Dewar flask. Emission lifetime measurements were performed using a conventional laser system. The excitation source used was the 355-nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser. Luminescence decay signals were detected by a Hamamatsu R928 PMT, recorded on a Tektronix model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope, and analyzed using a program for exponential fits. Photoluminescence quantum yields were measured at room temperature by the optical dilute method reported by Demas and Crosby^{4a} using a degassed aqueous solution of $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$

(excitation wavelength = 436 nm, $\Phi = 0.042$) as reference.^{4b} All solutions for emission lifetime and luminescence quantum yield studies were degassed on a high-vacuum line in a two compartment cell consisting of a 10-mL Pyrex bulb and a 1-cm path length quartz cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were rigorously degassed with at least four successive freeze-pump-thaw cycles.

Electron 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 all samples were negatively stained by uranyl acetate for contrast enhancement.

References

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