

Electronic Supplementary Information (ESI)

A Rational Molecular Design of Triazine-Containing Alkynylplatinum(II) Terpyridine Complexes and its Formation of Helical Ribbons *via* Pt···Pt, π - π Stacking and Hydrophobic-Hydrophobic Interactions

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Experimental section

Materials and reagents

[Pt{tpy-Ph-(OC_nH_{2n+1})₂-3,5}Cl]OTf and [Pt{4',4'',4'''-*tert*-butyl-tpy}Cl]OTf¹ were synthesized according to the previous reported literature. Dimethyl sulfoxide (99+%, for spectroscopy) was purchased from Sigma-Aldrich. All other reagents and solvents were of analytical grade and were used as received.

Syntheses of ligands

Synthesis of 2-*N*-(4-iodophenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine

This was synthesized according to modification of a literature procedure for a related 1,3,5-triazine based compound.² Yield: 1.22 g (51 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.56 (d, *J* = 7.5 Hz, 2H; phenyl protons), 7.31–7.44 (broad, 2H; phenyl protons), 6.62–6.81 (broad, 1H; –NH), 4.76–5.09 (broad, 2H; –NH), 3.31–3.49 (m, 4H; –NHCH₂), 1.48–1.57 (m, 4H; –NHCH₂CH₂), 1.35–1.48 (m, 4H; –NHCH₂CH₂CH₂), 0.95 ppm (t, *J* = 7.2 Hz, 6H; –CH₃); high-resolution positive EI-MS calcd for C₁₇H₂₅IN₆ (found): *m/z*: 440.1185 (440.1187) [M]⁺.

Synthesis of 2-*N*-(4-trimethylsilylphenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine

This was synthesized according to a modified Sonogashira coupling reaction reported previously.³ Yield: 0.89 g (74 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.56 (d, *J* = 6.9 Hz, 2H; phenyl protons), 7.31–7.44 (broad, 2H; phenyl protons), 7.14–7.28 (broad, 1H; –NH), 4.90–5.17 (broad, 2H; –NH), 3.30–3.45 (m, 4H; –NHCH₂), 1.48–1.62 (m, 4H; –NHCH₂CH₂), 1.34–1.48 (m, 4H; –NHCH₂CH₂CH₂), 0.93 (t, *J* = 7.0 Hz, 6H; –CH₃), 0.24 ppm (s, 9H; –Si(CH₃)₃); high-resolution positive EI-MS calcd for C₂₂H₃₄N₆Si (found): *m/z*: 410.2614 (410.2611) [M]⁺.

Synthesis of 2-*N*-(4-ethynylphenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine (L1)

This was synthesized according to a modification of a literature procedure using potassium carbonate

for the deprotection of TMS-protected alkynes.⁴ Yield: 0.40 g (55 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.59 (d, J = 7.9 Hz, 2H; phenyl protons), 7.39–7.33 (broad, 2H; phenyl protons), 7.16–7.58 (broad, 1H; –NH), 4.86–5.22 (broad, 2H; –NH), 3.29–3.47 (m, 4H; –NHCH₂), 3.02 (s, 1H; acetylene proton), 1.48–1.61 (m, 4H; –NHCH₂CH₂), 1.33–1.45 (m, 4H; –NHCH₂CH₂CH₂), 0.94 ppm (t, J = 7.9 Hz, 6H; –CH₃); high-resolution positive EI-MS calcd for C₁₉H₂₆N₆ (found): m/z : 338.2219 (338.2212) [M]⁺.

Synthesis of 2-*N*-(3-bromophenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine

This was synthesized according to modification of a literature procedure for a related 1,3,5-triazine based compound.² Yield: 1.17 g (55 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.68–7.99 (broad, 1H; phenyl proton), 7.51 (d, J = 7.4 Hz, 1H; phenyl proton), 7.22 (t, J = 7.4 Hz, 1H; phenyl proton), 7.13 (d, J = 7.4 Hz, 1H; phenyl proton), 6.62–6.81 (broad, 1H; –NH), 4.76–5.09 (broad, 2H; –NH), 3.31–3.49 (m, 4H; –NHCH₂), 1.48–1.57 (m, 4H; –NHCH₂CH₂), 1.35–1.48 (m, 4H; –NHCH₂CH₂CH₂), 0.94 ppm (t, J = 7.2 Hz, 6H; –CH₃); high-resolution positive EI-MS calcd for C₁₇H₂₅BrN₆ (found): m/z : 392.1324 (392.1315) [M]⁺.

Synthesis of 2-*N*-(3-triisopropylsilylphenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine

This was synthesized according to a modified Sonogashira coupling reaction reported previously.³ Yield: 0.82 g (65 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.64–8.00 (broad, 1H; phenyl proton), 7.51 (d, J = 7.4 Hz, 1H; phenyl proton), 7.22 (t, J = 7.4 Hz, 1H; phenyl proton), 7.14 (d, J = 7.4 Hz, 1H; phenyl proton), 6.53–6.95 (broad, 1H; –NH), 4.76–5.22 (broad, 2H; –NH), 3.28–3.45 (m, 4H; –NHCH₂), 1.48–1.60 (m, 4H; –NHCH₂CH₂), 1.35–1.48 (m, 4H; –NHCH₂CH₂CH₂), 1.05 (s, 21H; –TIPS), 0.94 ppm (t, J = 7.2 Hz, 6H; –CH₃); high-resolution positive EI-MS calcd for C₂₈H₄₆N₆Si (found): m/z : 494.3553 (494.3549) [M]⁺.

Synthesis of 2-*N*-(3-ethynylphenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine (L2)

This was synthesized according to a modification of a literature procedure using tetra-*n*-butylammonium fluoride for the deprotection of TIPS-protected alkynes.⁴ Yield: 0.33 g (54 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 7.71–7.94 (broad, 1H; phenyl proton), 7.51 (d, J = 7.9 Hz, 1H; phenyl proton), 7.22 (t, J = 7.9 Hz, 1H; phenyl proton), 7.13 (d, J = 7.9 Hz, 1H; phenyl proton), 7.16–7.58 (broad, 1H; –NH), 4.86–5.22 (broad, 2H; –NH), 3.29–3.47 (m, 4H; –NHCH₂), 3.02 (s, 1H; acetylene proton), 1.48–1.61 (m, 4H; –NHCH₂CH₂), 1.33–1.45 (m, 4H; –NHCH₂CH₂CH₂), 0.94 ppm (t, J = 7.9 Hz, 6H; –CH₃); high-resolution positive EI-MS calcd for C₁₉H₂₆N₆ (found): m/z : 338.2219 (338.2208) [M]⁺.

Synthesis of 2-*N*-(2-bromophenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine

This was synthesized according to modification of a literature procedure for a related 1,3,5-triazine based compound.² Yield: 1.11 g (52 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.39–8.63 (broad, 1H; phenyl proton), 7.51 (d, J = 7.5 Hz, 1H; phenyl proton), 7.27 (t, J = 7.5 Hz, 1H; phenyl proton), 6.90–7.17 (broad, 1H; –NH), 6.86 (t, J = 7.5 Hz, 1H; phenyl proton), 4.69–5.07 (broad, 2H; –NH), 3.26–3.52 (m, 4H; –NHCH₂), 1.52–1.62 (m, 4H; –NHCH₂CH₂), 1.35–1.46 (m, 4H; –NHCH₂CH₂CH₂), 0.94 ppm (t, J = 7.3 Hz, 6H; –CH₃); high-resolution positive EI-MS calcd for C₁₇H₂₅BrN₆ (found): m/z : 392.1324 (392.1315) [M]⁺.

Synthesis of 2-*N*-(2-triisopropylsilylphenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine

This was synthesized according to a modified Sonogashira coupling reaction reported previously.³ Yield: 0.54 g (43 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.44–8.70 (broad, 1H; phenyl proton), 7.41 (d, J = 7.3 Hz, 1H; phenyl proton), 7.28 (t, 1H; J = 7.3 Hz; phenyl proton), 6.90 (t, 1H, J = 7.3 Hz; phenyl proton), 6.93–7.20 (broad, 1H; –NH), 4.74–4.96 (broad, 2H; –NH), 3.29–3.51 (m, 4H; –NHCH₂), 1.52–1.61 (m, 4H; –NHCH₂CH₂), 1.34–1.49 (m, 4H; –NHCH₂CH₂CH₂), 1.05 (s, 21H; –TIPS), 0.94 ppm (t, J = 7.2 Hz, 6H; –CH₃); high-resolution positive EI-MS calcd for C₂₈H₄₆N₆Si

(found): m/z : 494.3548 (494.3549) [M]⁺.

Synthesis of 2-*N*-(2-ethynylphenyl)amino-4,6-*N*-dibutylamino-1,3,5-triazine (L3)

This was synthesized according to a modification of a literature procedure using tetra-*n*-butylammonium fluoride for the deprotection of TIPS-protected alkynes.⁴ Yield: 0.40 g (65 %). ¹H NMR (400 MHz, CDCl₃, 298 K): δ = 8.46–8.72 (broad, 1H; phenyl proton), 7.43 (d, J = 7.3 Hz, 1H; phenyl proton), 7.32 (t, J = 7.3 Hz; 2H; phenyl proton), 6.91 (t, J = 7.3 Hz; 1H; phenyl proton), 6.93–7.20 (broad, 1H; –NH), 4.69–5.07 (broad, 2H; –NH), 3.51 (s, 1H; acetylene proton), 3.27–3.50 (m, 4H; –NHCH₂), 1.51–1.65 (m, 4H; –NHCH₂CH₂), 1.34–1.47 (m, 4H; –NHCH₂CH₂CH₂), 0.95 ppm (t, J = 7.2 Hz, 6H; –CH₃); high-resolution positive EI-MS calcd for C₁₉H₂₆N₆ (found): m/z : 338.2213 (338.2208) [M]⁺.

Syntheses of triazine-containing alkynylplatinum(II) terpyridine complexes

Complexes **1–5** were synthesized by treating the corresponding chloroplatinum(II) terpyridine complexes with the triazine-modified alkynyl ligands through copper(I)-catalyzed dehydrohalogenation reactions in dichloromethane solutions. All complexes were purified by column chromatography followed by recrystallization through a slow diffusion of diethyl ether into a dichloromethane solution of the complexes. All complexes were isolated as triflate (OTf⁻) salts and have been characterized with ¹H NMR spectroscopy, FAB mass spectrometry, IR spectroscopy and gave satisfactory elemental analysis.

Synthesis of 1: This was synthesized according to modification of a literature procedure for [Pt(tpy)(C≡CR)]X.⁵ **L1** (0.06 g, 0.18 mmol) and [Pt{tpy-Ph-(OC₄H₉)_{2-3,5}}Cl]OTf (0.07 g, 0.09 mmol) were dissolved in degassed dichloromethane (10 mL). Triethylamine (1 mL) and a catalytic amount of CuI were added to the reaction mixture. After stirring for one day, the resulting mixture was evaporated to dryness and purified by column chromatography on silica gel using dichloromethane-acetone (10:1 v/v) as the eluent. Recrystallization through a slow evaporation of **1** in dichloromethane-acetone solution afforded a black solid. Yield: 51 mg (51 %). ¹H NMR (400 MHz, CDCl₃, 318 K): δ = 9.11 (d, *J* = 5.5 Hz, 2H; tpy), 8.71 (d, *J* = 7.80, 2H; tpy), 8.40 (s, 2H; tpy), 8.22–8.31 (m, 2H; tpy), 7.48–7.58 (m, 4H; tpy and phenyl), 7.35 (d, *J* = 8.5 Hz, 2H; phenyl), 6.87 (d, *J* = 2.3 Hz, 2H; tpy-Ph), 6.60–6.77 (broad, 1H; -NH), 6.39 (t, *J* = 2.3 Hz, 1H; tpy-Ph), 4.80–5.00 (broad, 2H; -NH), 3.98 (t, *J* = 6.2 Hz, 4H; -OCH₂), 3.34–3.49 (m, 4H; -NHCH₂), 1.56–1.69 (m, 4H; -NHCH₂CH₂), 1.39–1.48 (m, 4H; -NHCH₂CH₂CH₂), 1.25–1.38 (m, 8H; C₄-alkyl), 0.91–1.04 ppm (m, 12H; -CH₃); IR (KBr): ν = 2130 cm⁻¹ (C≡C); positive FAB-MS: *m/z*: 986 [M]⁺; elemental analysis calcd (%) for C₄₉H₅₆F₃N₉O₅PtS·3CH₂Cl₂: C, 44.93; H, 4.50; N, 9.07; found: C, 45.21; H, 4.48; N, 9.22.

Synthesis of 2: **2** was prepared according to procedures similarly to that described for **1** except that

[Pt{tpy-Ph-(OC₈H₁₇)_{2-3,5}}Cl]OTf (0.08 g, 0.09 mmol) was used instead of [Pt{tpy-Ph-(OC₄H₉)_{2-3,5}}Cl]OTf. The complex was purified by column chromatography on silica gel using dichloromethane/acetone (20:1 v/v) as the eluent. Recrystallization through a slow evaporation of **2** in dichloromethane/acetone solution afforded a black solid. Yield: 48 mg (43 %). ¹H NMR (400 MHz, CDCl₃, 318 K): δ = 9.11 (d, *J* = 5.5 Hz, 2H; tpy), 8.72 (d, *J* = 7.80, 2H; tpy), 8.40 (s, 2H; tpy), 8.26–8.29 (m, 2H; tpy), 7.49–7.58 (m, 4H; tpy and phenyl), 7.33 (d, *J* = 8.5 Hz, 2H; phenyl), 6.86 (d, *J* = 2.3 Hz, 2H; tpy-Ph), 6.69–6.81 (broad, 1H; -NH), 6.38 (t, *J* = 2.3 Hz, 1H; tpy-Ph), 4.72–5.15 (broad, 2H; -NH), 3.98 (t, *J* = 6.2 Hz, 4H; -OCH₂), 3.35–3.52 (m, 4H; -NHCH₂), 1.56–1.69 (m, 4H; -NHCH₂CH₂), 1.39–1.48 (m, 4H; -NHCH₂CH₂CH₂), 1.25–1.38 (m, 24H; C₈-alkyl), 0.98 (t, *J* = 7.2 Hz, 6H; -CH₃), 0.90 ppm (t, *J* = 6.2 Hz, 6H; -CH₃); IR (KBr): ν = 2120 cm⁻¹ (C≡C); positive FAB-MS: *m/z*: 1097 [M]⁺; elemental analysis calcd (%) for C₅₇H₇₂F₃N₉O₅PtS·2CH₃COCH₃: C, 55.49; H, 6.21; N, 9.25; found: C, 54.62; H, 5.96; N, 9.09.

Synthesis of 3: **3** was prepared according to procedures similarly to that described for **1** except that [Pt{tpy-Ph-(OC₁₂H₂₅)_{2-3,5}}Cl]OTf (0.10 g, 0.09 mmol) was used instead of [Pt{tpy-Ph-(OC₄H₉)_{2-3,5}}Cl]OTf. The complex was purified by column chromatography on silica gel using dichloromethane/acetone (20:1 v/v) as the eluent. Recrystallization through a slow evaporation of **3** in dichloromethane/acetone solution afforded a black solid. Yield: 58 mg (45 %). ¹H NMR (400 MHz, CDCl₃, 318 K): δ = 9.12 (d, *J* = 5.5 Hz, 2H; tpy), 8.71 (d, *J* = 7.80, 2H; tpy), 8.41 (s, 2H; tpy), 8.26–8.29 (m, 2H; tpy), 7.53–7.55 (m, 4H; tpy and phenyl), 7.32 (d, *J* = 8.5 Hz, 2H; phenyl), 7.21 (d, *J* = 2.3 Hz, 2H; tpy-Ph), 6.89–6.91 (broad, 1H; -NH), 6.36 (t, *J* = 2.3 Hz, 1H; tpy-Ph), 4.93–5.01 (broad, 2H; -NH), 3.99 (t, *J* = 6.2 Hz, 4H; -OCH₂), 3.40–3.45 (m, 4H; -NHCH₂), 1.54–1.65 (m, 4H; -NHCH₂CH₂), 1.36–1.48 (m, 4H; -NHCH₂CH₂CH₂), 1.23–1.38 (m, 40H; C₁₂-alkyl), 0.92–1.02 ppm (m, 12H; -CH₃); IR (KBr): ν = 2120 cm⁻¹ (C≡C); positive FAB-MS: *m/z*: 1209 [M]⁺; elemental analysis calcd (%) for C₆₄H₈₈F₃N₉O₅PtS·CH₃COCH₃: C, 57.61; H, 6.68; N, 8.89; found: C, 57.78; H, 6.82; N, 8.68.

Synthesis of 4: This was synthesized according to procedures similar to that of **3** except that **L2** (0.08 g, 0.23 mmol) was used in replace of **L1**. The complex was purified by column chromatography on silica gel using dichloromethane/acetone (20:1 v/v) as the eluent. Recrystallization through a slow evaporation of **4** in dichloromethane/acetone solution afforded a red solid. Yield: 95 mg (57 %). ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): 9.16 (d, *J* = 5.6 Hz, 2H; tpy), 8.94 (s, 2H; tpy), 8.89 (d, *J* = 7.7 Hz, 2H; tpy), 8.52 (t, *J* = 5.6 Hz, 2H; tpy), 7.92 (t, *J* = 5.6 Hz, 2H; tpy), 7.57–7.83 (broad, 1H; phenyl proton), 7.26 (s, 2H; tpy–Ph), 7.12–7.20 (m, 2H; phenyl protons), 7.02 (d, *J* = 7.1 Hz, 1H; phenyl proton), 6.74 (s, 1H; tpy–Ph), 4.10 (t, *J* = 4.1 Hz, 4H; –OCH₂), 3.40–3.49 (m, 4H; –NHCH₂), 1.71–1.81 (m, 4H; –NHCH₂CH₂), 1.15–1.59 (m, 44H; –NHCH₂CH₂CH₂ and C12-alkyl), 0.74–0.93 ppm (m, 12H; –CH₃); IR (KBr): $\nu = 2120\text{ cm}^{-1}$ (C≡C); positive FAB-MS: *m/z*: 1209 [M]⁺; elemental analysis calcd (%) for C₆₄H₈₈F₃N₉O₅PtS·0.5CH₂Cl₂: C, 56.11; H, 6.40; N, 8.99; found: C, 56.07; H, 6.43; N, 9.05.

Synthesis of 5: This was synthesized according to procedures similar to that of **3** except that **L3** (0.08 g, 0.23 mmol) was used in replace of **L1**. The complex was purified by column chromatography on silica gel using dichloromethane/acetone (20:1 v/v) as the eluent. Recrystallization through a slow evaporation of **5** in dichloromethane/acetone solution afforded a dark red solid. ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): 9.17 (d, *J* = 5.6 Hz, 2H; tpy), 8.97 (s, 2H; tpy), 8.91 (d, *J* = 7.7 Hz, 2H; tpy), 8.54 (t, *J* = 5.6 Hz, 2H; tpy), 7.89 (t, *J* = 5.6 Hz, 2H; tpy), 7.45 (d, *J* = 7.1 Hz, 1H; phenyl proton), 7.29 (s, 2H; tpy–Ph), 7.21 (t, *J* = 8.0 Hz, 1H; phenyl proton), 6.93 (m, 2H; phenyl protons), 6.77 (s, 1H; tpy–Ph), 4.10 (t, *J* = 4.2 Hz, 4H; –OCH₂–), 3.40–3.49 (m, 4H; –NHCH₂), 1.71–1.81 (m, 4H; –NHCH₂CH₂–), 1.15–1.59 (m, 44H; C12-alkyl), 0.74–0.93 ppm (m, 12H; –CH₃); IR (KBr): $\nu = 2120\text{ cm}^{-1}$ (C≡C); positive FAB-MS: *m/z*: 1209 [M]⁺; elemental analysis calcd (%) for C₆₄H₈₈F₃N₉O₅PtS·2CH₃COCH₃: C, 57.79; H, 6.83; N, 8.54; found: C, 58.01; H, 6.88; N, 8.53.

Physical measurements and instrumentation: ^1H and ^1H - ^1H NOESY NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) and 500 (500 MHz) Fourier-transform NMR spectrometers with chemical shifts reported relative to tetramethylsilane, $(\text{CH}_3)_4\text{Si}$. The UV-visible spectra were obtained by using a Varian Cary 50 UV/Vis spectrophotometer. Steady-state excitation and emission spectra at room temperature were recorded on a Spex-Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector, respectively. Positive-FAB mass spectra were recorded on a Thermo Scientific DFS High Resolution Magnetic Sector mass spectrometer. Elemental analyses of complexes were performed on a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences. IR spectra were obtained as KBr disc on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer ($4000\text{--}400\text{ cm}^{-1}$).

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. Scanning electron microscopy (SEM) experiments were performed on a LEO 1530 FEG scanning electron microscope.

Circular dichroism (CD) measurements: CD measurements were recorded using a Jasco (Tokyo, Japan) J-815 CD spectropolarimeter.

Determination of proton distances from ^1H - ^1H NOESY NMR experiment: The integrals of the cross peaks in ^1H - ^1H NOESY NMR were extracted. The distance between adjacent protons on the terpyridine unit is assumed to be 2.47 \AA and used as a standard. The distances between protons in close proximities were determined using the relation:⁶

$$\frac{A_1}{A_2} = \frac{r_2^6}{r_1^6}$$

Curve-fitting for the solvent-dependent self-assembly:

The nucleation-elongation model for solvent-dependent self-assembly was reported by Meijer and co-workers.⁷ In this model, the Gibbs free energy gain upon monomer addition $\Delta G^{\circ'}$ is linearly correlated with the good solvent volume fraction f :

$$\Delta G^{\circ'} = \Delta G^{\circ} + m \cdot f$$

where ΔG° is the Gibbs free energy gain upon monomer addition in poor solvent and m is the parameter showing the dependence of $\Delta G^{\circ'}$ on f . The normalized degree of aggregation was deduced from the changes in UV-vis absorption band maxima,

$$\text{normalized degree of aggregation } (f) = \frac{Abs(f) - Abs(f=0)}{Abs(f=1) - Abs(f=0)}$$

The simulations and the curve-fittings with the equilibrium model were performed using Matlab R2013a under an isodesmic system.⁷



Fig. S1 Solutions of **3**, **4** and **5** (from left to right) in DMSO solutions.

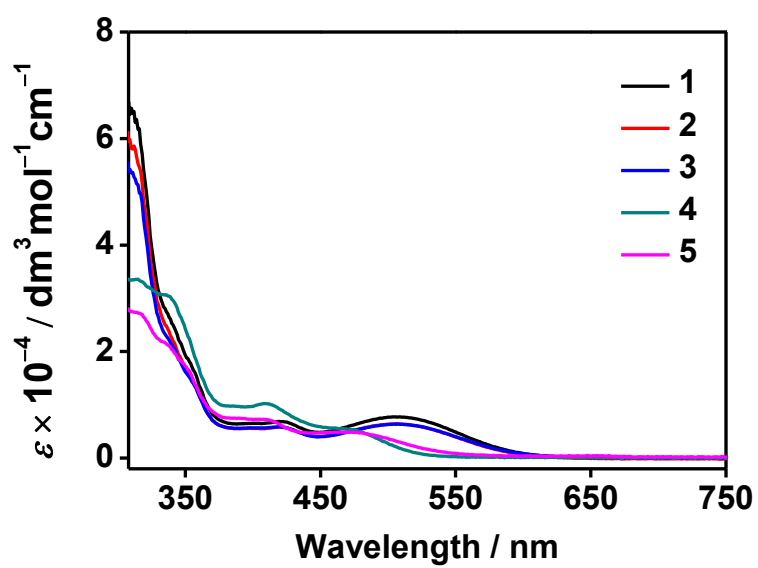


Fig. S2 UV-Vis absorption spectra of **1–5** in DMSO solution.

Table S1. Photophysical data of **1–5** in DMSO solution at 298 K

Complex	$\lambda_{\text{abs}} / \text{nm} (\epsilon / \text{dm}^3\text{mol}^{-1}\text{cm}^{-1})$	$\lambda_{\text{em}} / \text{nm} (\tau_0 / \mu\text{s})$
1	298 (58900), 315 (51300), 357 (13500), 421 (5830), 509 (6370)	— ^[a]
2	298 (62400), 315 (53600), 357 (16200), 421 (3790), 509 (5110)	— ^[a]
3	298 (72700), 315 (61700), 357 (16200), 421 (6840), 509 (7750)	— ^[a]
4	298 (62400), 315 (53600), 341 (16200), 411 (4250), 493 (6000)	— ^[a]
5	317 (27090), 336 (23530), 410 (7260), 490 (4270)	— ^[a]

[a] non-emissive.



Fig. S3 Solutions of **3** in DMSO (left) and 30 % DMSO-H₂O solution (right).

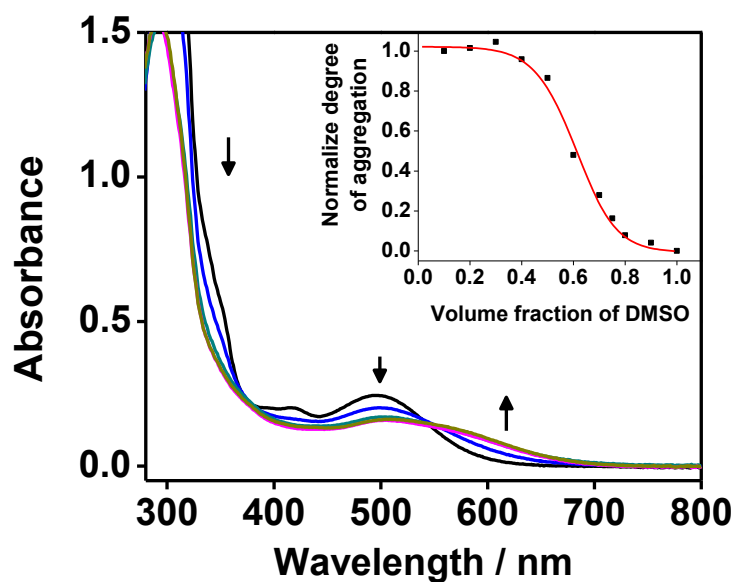


Fig. S4 UV-Vis absorption spectra of **2** in DMSO upon increasing H₂O content. Inset: a plot of normalized degree of aggregation against volume fraction of DMSO.

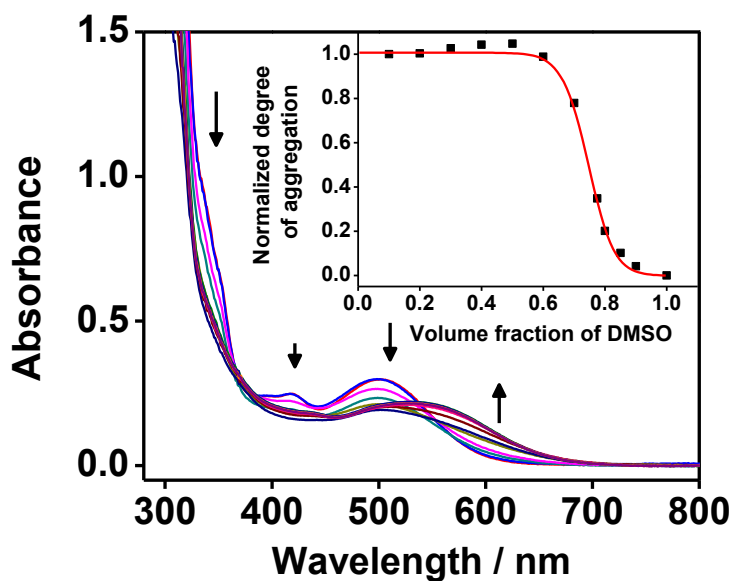


Fig. S5 UV-Vis absorption spectra of **3** in DMSO upon increasing H₂O content. Inset: a plot of normalized degree of aggregation against volume fraction of DMSO.

Table S2. Thermodynamic parameters of the self-assembly process of **1–3** in DMSO upon the addition of H₂O.

Complex	$\Delta G^\circ / \text{kJ mol}^{-1}$	$m / \text{kJ mol}^{-1}$	σ
1	-44.8 ± 2.0	36.8 ± 3.4	1
2	-44.6 ± 1.9	33.7 ± 3.0	1
3	-71.3 ± 2.8	65.0 ± 3.6	1

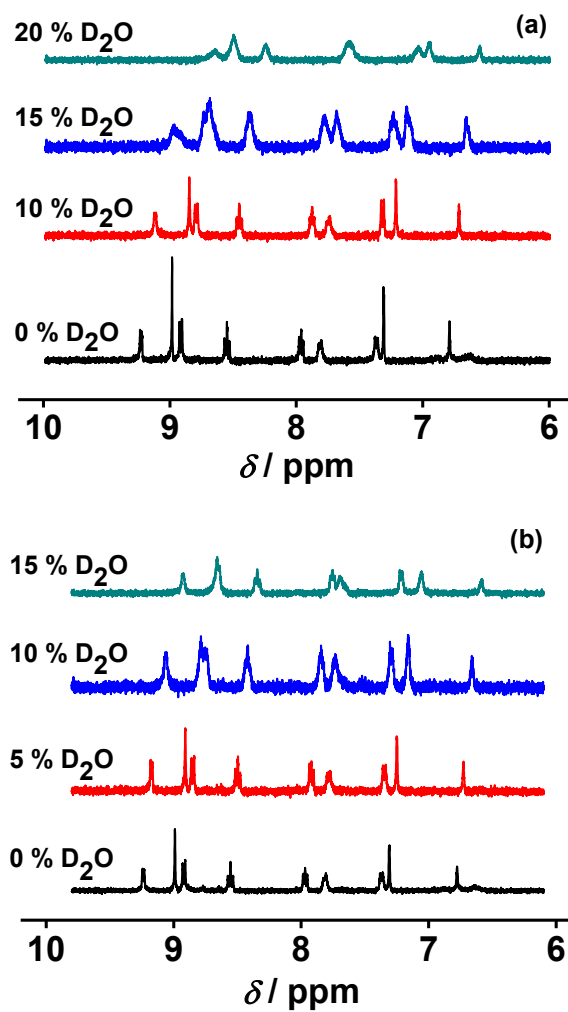


Fig. S6 Partial ^1H NMR spectra of (a) **2** and (b) **3** in $\text{DMSO-}d_6$ upon increasing D_2O content.

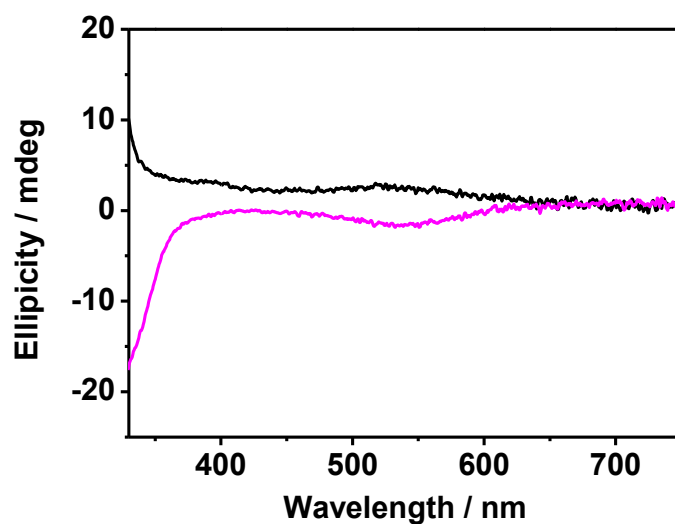


Fig. S7 Circular dichroic (CD) spectra of two independent samples prepared from **3** in DMSO upon the addition of 90 % H₂O. The CD signals are the results of the random supramolecular chirality arising from the self-assembly of achiral alkynylplatinum(II) terpyridine complexes which would occasionally give a slight excess of either left- or right-handed nanoribbons.

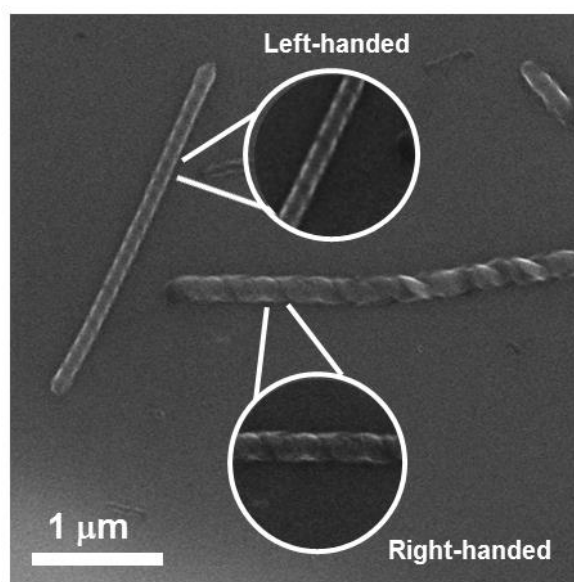


Fig. S8 SEM image of **3** prepared from 30 % H₂O in DMSO solution showing the co-existence of both left- and right-handed helical ribbons.

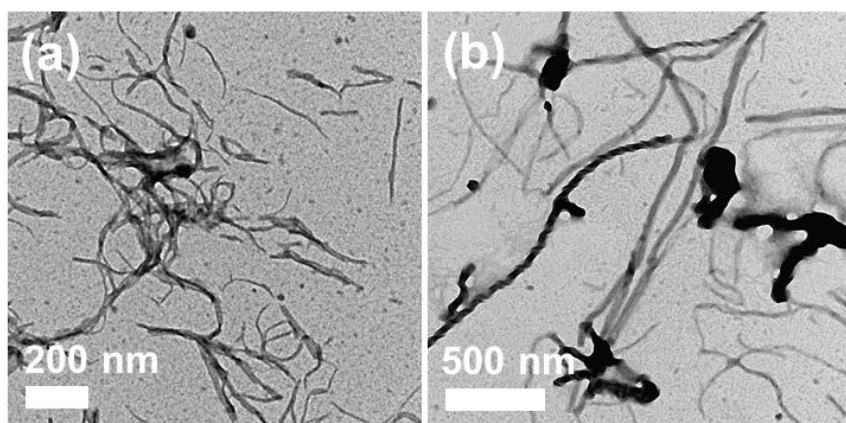


Fig. S9 TEM images of **2** prepared from 30 % H₂O in DMSO solution at (a) lower and (b) higher magnification.

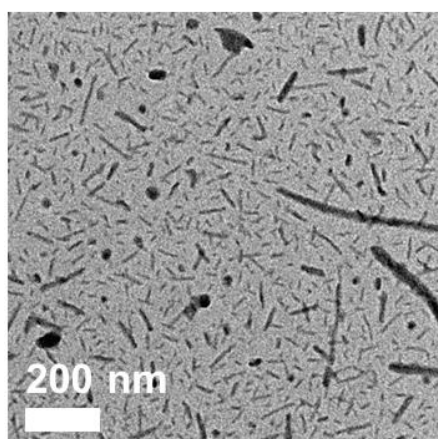


Fig. S10 TEM images of **1** prepared from 30 % H₂O in DMSO solution.

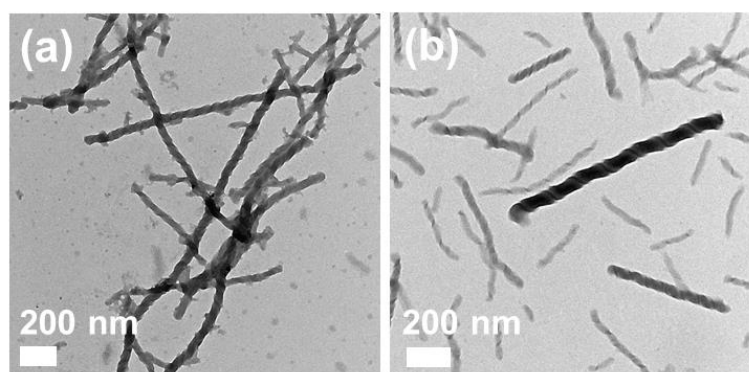


Fig. S11 TEM images of (a) **4** and (b) **5** prepared from 30 % H₂O in DMSO solution.

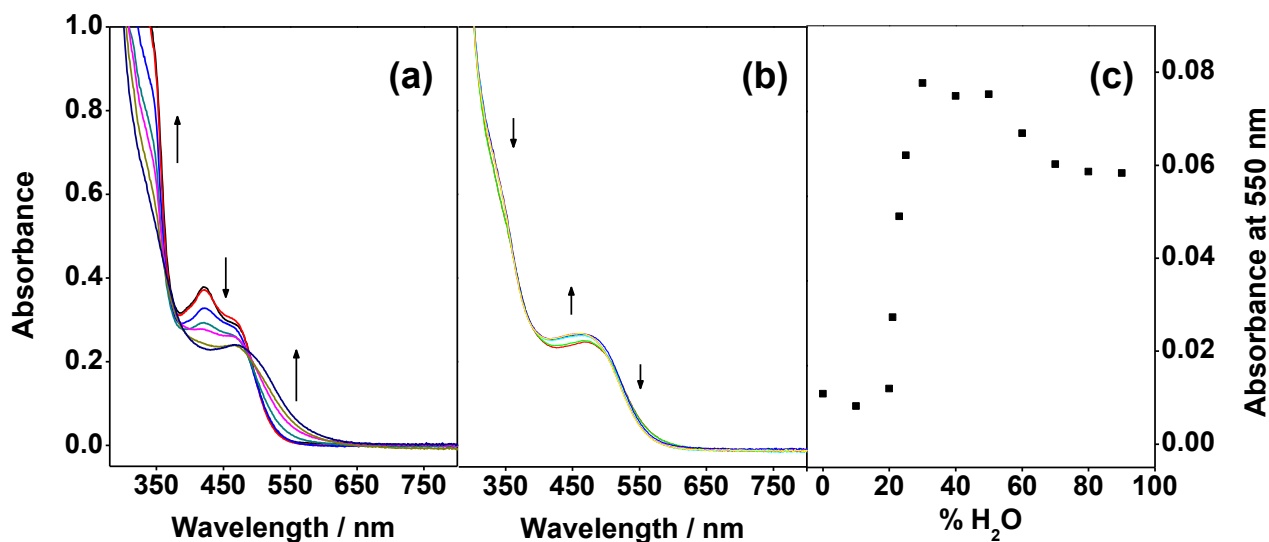


Fig. S12 (a) UV-Vis absorption spectra of **4** upon increasing H₂O content from 0 % to 30 %, and (b) 40 % to 90 %. (c) A plot of absorbance at 550 nm against % H₂O content.

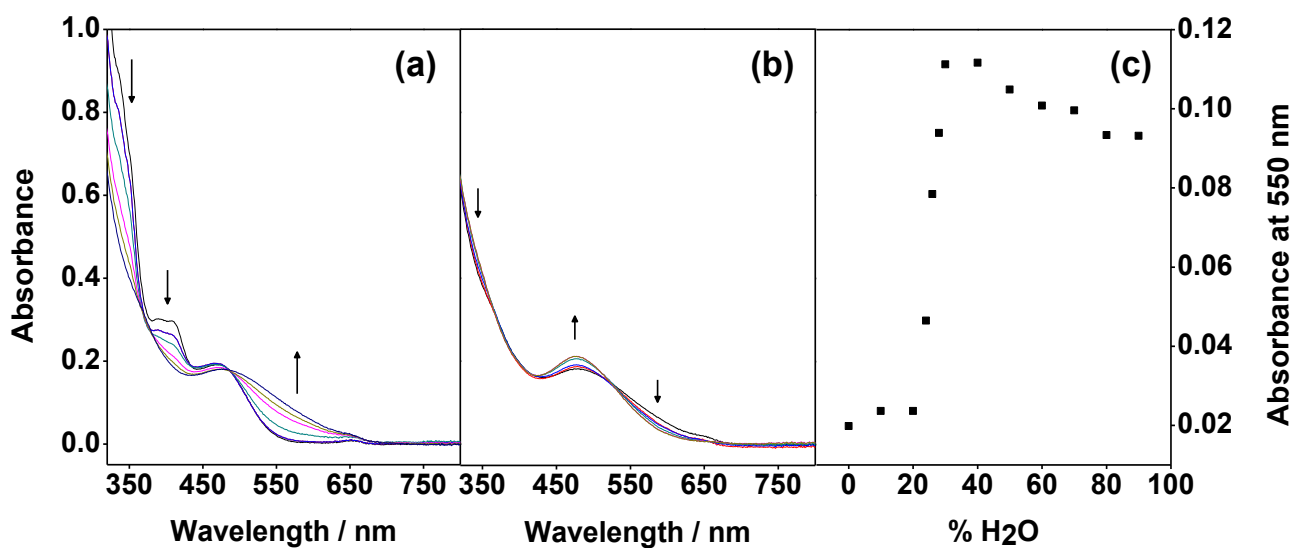


Fig. S13 (a) UV-Vis absorption spectra of **5** upon increasing H₂O content from 0 % to 30 %, and (b) 40 % to 90 %. (c) A plot of absorbance at 550 nm against % H₂O content.

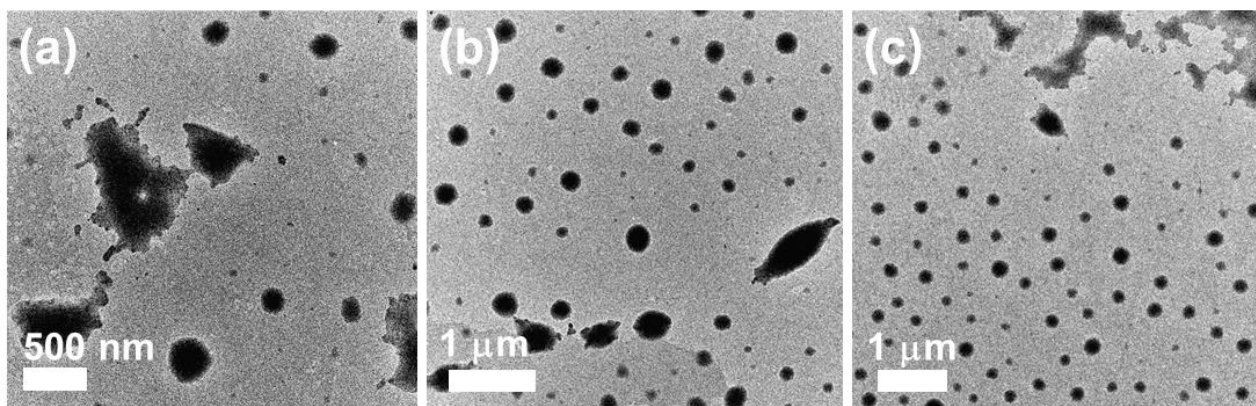


Fig. S14 TEM images of triazine-modified alkynyl ligand (a) **L1**, (b) **L2** and (c) **L3** prepared from 30 % H₂O in DMSO solution.

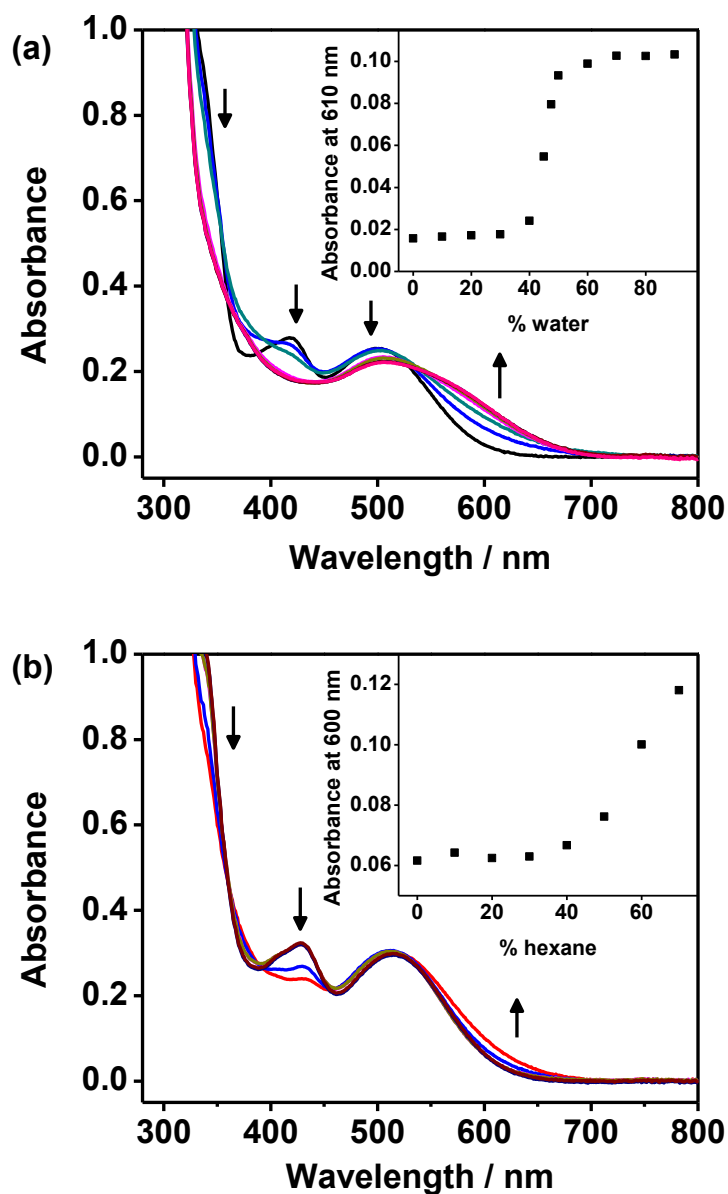


Fig. S15 UV-Vis absorption spectra of **3** in (a) 1,4-dioxane upon the addition of H₂O and (b) dichloromethane upon the addition of hexane. Inset of (a): A plot of absorbance at 610 nm against % water. Inset of (b): A plot of absorbance at 600 nm against the % hexane.

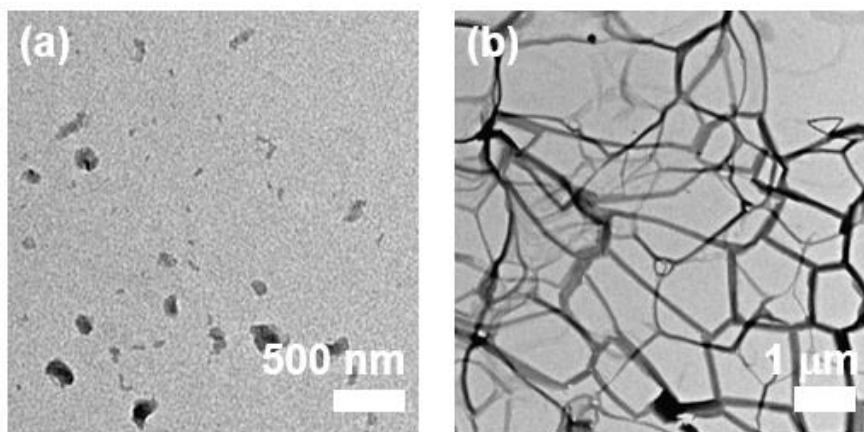


Fig. S16 TEM images of **3** prepared from (a) 90 % 1,4-dioxane in H₂O and (b) 90 % hexane in dichloromethane.

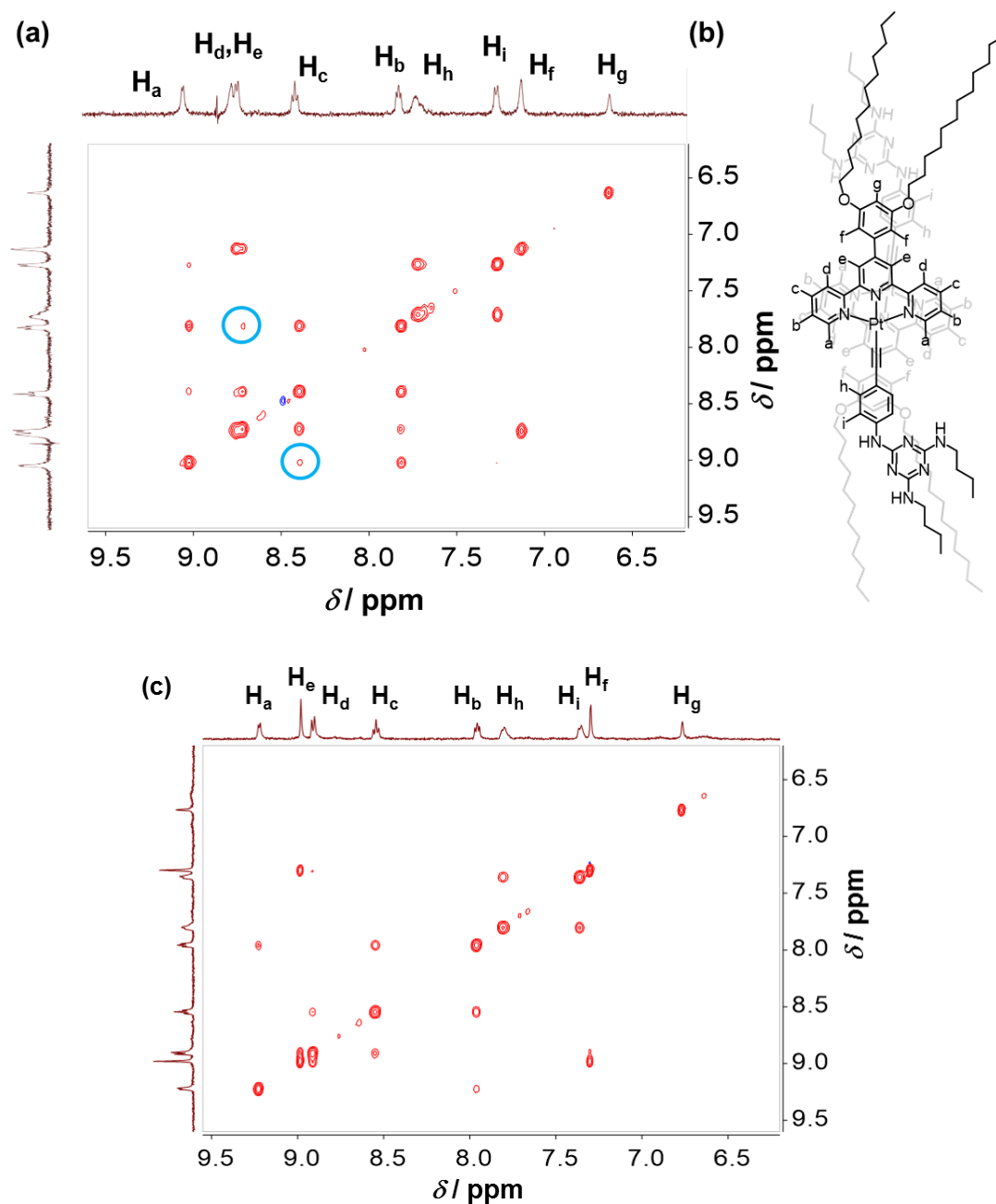


Fig. S17 (a) Partial ^1H - ^1H NOESY NMR spectrum of **3** in $\text{DMSO-}d_6$ upon the addition of 10 % D_2O . (b) Plausible head-to-tail stacking arrangement of **3** in DMSO upon increasing H_2O content. (c) Partial ^1H - ^1H NOESY NMR spectrum of **3** in $\text{DMSO-}d_6$ for comparison. The absence of cross peaks between H_a and H_c , H_b and H_d indicates the signals are intermolecular in nature.

Table S3. Summary of intermolecular distances determined from ^1H - ^1H NOESY NMR experiment.

Proton	Relative integral intensity	Distance between the protons / Å
H _a -H _c	0.271	3.07
H _b -H _d	0.268	3.07

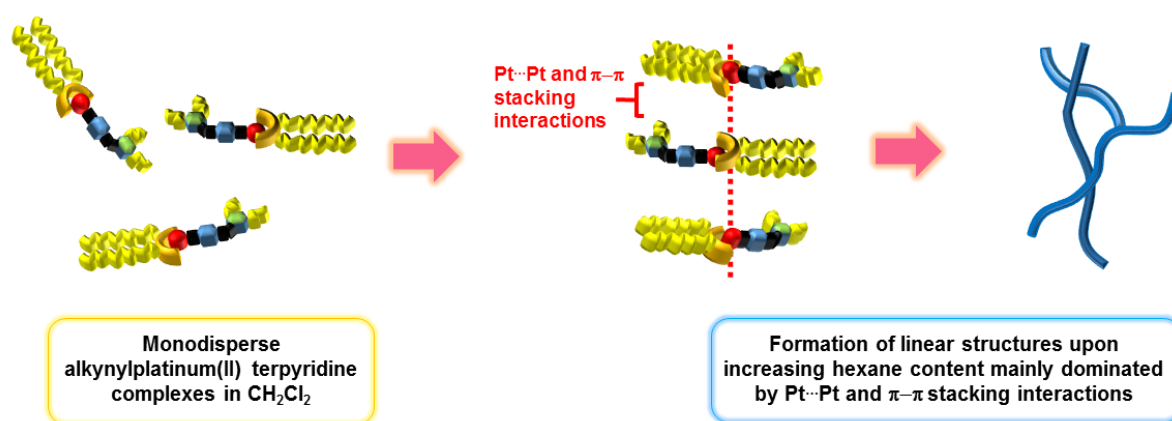


Fig. S18 Schematic drawing showing the proposed mechanism for the formation of linear aggregates from **3** in dichloromethane-hexane mixtures.

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