Electronic Supplementary Information (ESI)

Supramolecular assemblies of dinuclear alkynylplatinum(II) terpyridine complexes with double-decker silsesquioxane nano-cores: the role of isomerism in constructing nano-structures

Ho-Leung Au-Yeung, Sammual Yu-Lut Leung, and Vivian Wing-Wah Yam*

Institute of Molecular Functional Materials (Areas of Excellence Scheme, University Grants Committee (Hong Kong)) and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

Experimental

Materials and Reagents. Potassium tetrachloroplatinate(II) ($K_2[PtCl_4]$) (Chem. Pur.), heptamethylcyclotetrasiloxane (Fluorochem Ltd.), tetrasilanolphenyl POSS (Hybrid Plastic Inc.), phenylacetylene, Karstedt's catalyst, dichloromethylsilane, methyl 3,3-dimethyl-4-pentenoate (Sigma-Aldrich Co. Ltd.), and triethylamine (Apollo Scientific Ltd.) were obtained from the corresponding chemical company. 4-Carboxyphenylacetylene,[1] 3,3-dimethyl-4-penten-1-ol,[2] 1-(bromomethyl)-4-[2-(trimethylsilyl)ethynyl]benzene,[3] 4-ethynylphenol[4] and 3,13-dihydrooctaphenyl double-decker silsesquioxane (2H–DDSQ)[5] were synthesized according to literature methods. [(^{t}Bu$_3$tpy)PtCl](OTf) was prepared according to a modified literature procedure.[6] All other reagents, unless specified otherwise, were of analytical grade and were used as received without further purification.

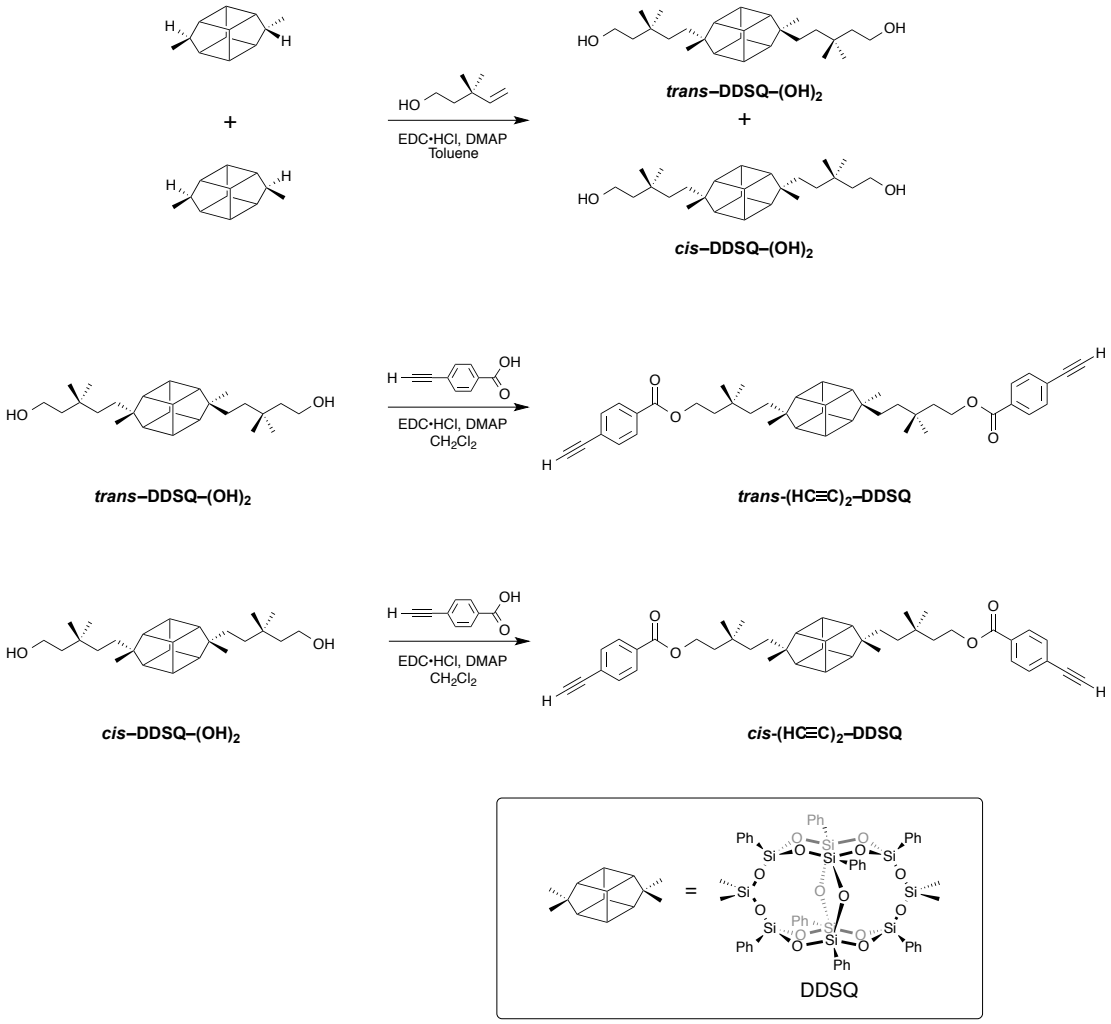
Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AVANCE 300 or 400 (300 and 400 MHz) NMR spectrometer with chemical shifts relative to tetramethylsilane, $Si(CH_3)_4$. Positive-ion FAB mass spectra were recorded on a Thermo Scientific DFS high resolution magnetic sector mass spectrometer. Positive high-resolution ESI mass spectra (HR–ESI–MS) were recorded on a Bruker maXis II mass spectrometer using TuneMix^{TM} (Agilent Technologies) as an external calibration standard. IR spectra were obtained as KBr disk on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000–400 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 a Varian Cary 50 UV-vis spectrophotometer. Emission spectra at room temperature were recorded on a Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with an R2658P PMT detector. Transmission electron microscopy (TEM) experiments were performed on a Philips CM100 Transmission Electron Microscope with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) experiments were performed on a Hitachi S4800 FEG operating at 4.0-6.0 kV. The samples for TEM and SEM were prepared by drop casting dilute solutions onto a carbon coated copper grid and silicon wafer respectively, which were then allowed to undergo slow evaporation of the solvents in air for at least 30 minutes to remove any excess solvent. Powder XRD data were collected by Bruker AXS D8 ADVANCE (Philips PW1830) powder X-ray diffractometer in Bragg-Brentano (θ/2θ) reflection mode with a graphite monochromatized Cu−K_α radiation (λ = 1.540562 Å) and nickel filter.

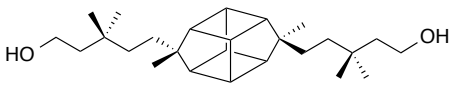
Synthesis and Characterisation

Synthesis

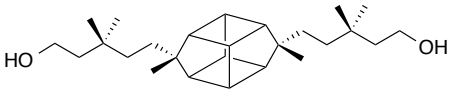
The synthetic schemes for DDSQ-functionalized alkynes were shown in Scheme S1. All reactions, unless specified otherwise, were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques.



Scheme S1. Synthetic routes for DDSQ–functionalized alkynes



***trans*–DDSQ–(OH)$_2$**

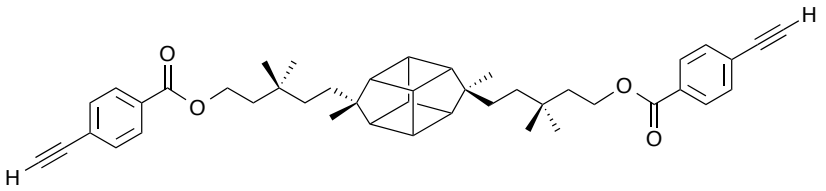


***cis*–DDSQ–(OH)$_2$**

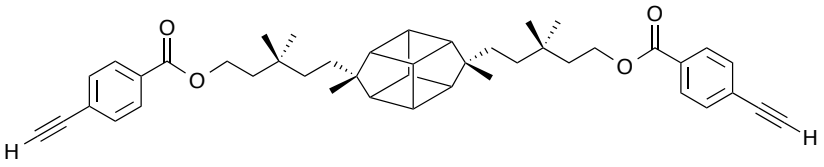
***Trans*–DDSQ–(OH)$_2$** and ***cis*–DDSQ–(OH)$_2$:** The titled ligands were prepared according to a modified literature procedure.[7] To a solution of 3,13-dihydrooctaphenyl double-decker silsesquioxane (2H–DDSQ, 1000 mg, 0.87 mmol), 3,3-dimethyl-4-penten-1-ol (235 mg, 2.19 mmol) and toluene (50 ml) was added a few drops of Karstedt's catalyst. The resultant mixture was stirred at ambient temperature for 1 h, followed by refluxing for 48 h. The crude product was evaporated to dryness and the residue was further purified by column chromatography using dichloromethane–EA (11:1 v/v) as eluent to afford pure *trans*–DDSQ–(OH)$_2$ and *cis*–DDSQ–(OH)$_2$ as a white crystalline solid from the mixture of isomers.

***Trans*–DDSQ–(OH)$_2$.** Yield: 360 mg, 0.26 mmol, 30 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.29 (s, 6H, Si–CH_3), 0.61–0.65 (m, 4H, –CH_2–), 0.70 (s, 12H, –CH_3), 1.22–1.32 (m, 8H, –CH_2–), 3.42 (m, 4H, –CH_2–), 7.20–7.56 (m, 40H, –Ph). Positive FAB-MS: *m*/*z*: 1381 $[M + H]^+$. IR (KBr) : v = 1134 cm^{-1} ν(Si–O). Anal. Found (%): C, 54.41; H, 5.58; N, <0.3. Calcd for $C_{64}H_{76}O_{16}Si_{10}$•1.5$H_2O$: C, 54.55; H, 5.64; N, 0.

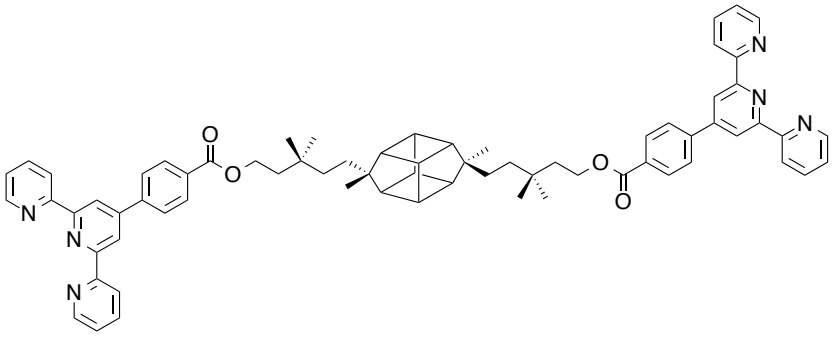
***Cis*–DDSQ–(OH)$_2$.** Yield: 240 mg, 0.174 mmol, 20 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.29 (s, 6H, Si–CH_3), 0.60–0.64 (m, 4H, –CH_2–), 0.71 (s, 12H, –CH_3), 1.22–1.32 (m, 8H, –CH_2–), 3.42 (m, 4H, –CH_2–), 7.21–7.56 (m, 40H, –Ph). Positive FAB-MS: *m*/*z*: 1381 $[M + H]^+$. IR (KBr) : v = 1134 cm^{-1} ν(Si–O). Anal. Found (%): C, 55.40; H, 5.77; N, <0.3. Calcd for $C_{64}H_{76}O_{16}Si_{10}$: C, 55.62; H, 5.54; N, 0.



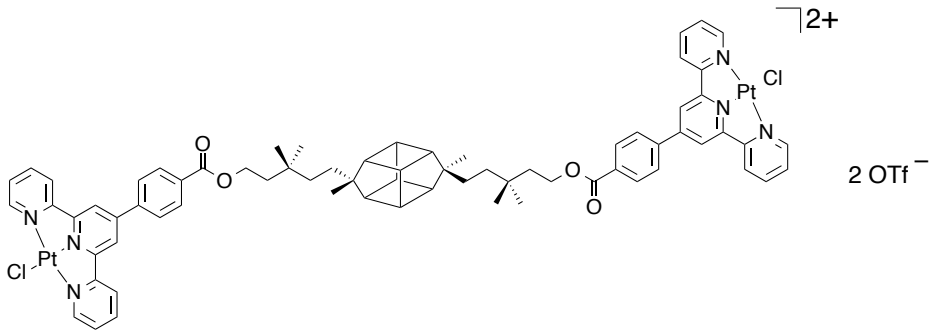
***Trans*-(HC≡C)$_2$–DDSQ:** The titled ligand was prepared according to a modified literature procedure.[8] *Trans*–DDSQ–(OH)$_2$ (100 mg, 0.07 mmol), 4-carboxyphenylacetylene (40 mg, 0.27 mmol), EDC•HCl (100 mg, 0.51 mmol) and 4-dimethylaminopyridine (4-DMAP) (10 mg, 0.08 mmol) were dissolved in dichloromethane (150 ml). The resultant mixture was stirred at ambient temperature for 24 h, after which the residue was purified by column chromatography using dichloromethane–hexane (2:1 v/v) as eluent, followed by recrystallisation from hexane to afford pure *trans*-(HC≡C)$_2$–DDSQ as a white solid. Yield: 48 mg, 0.029 mmol, 40 %. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.28 (s, 6H, Si–CH_3), 0.63–0.69 (m, 4H, –CH_2–), 0.74 (s, 12H, –CH_3), 1.27–1.33 (m, 4H, –CH_2–), 1.45–1.57 (m, 4H, –CH_2–), 3.22 (s, 2H, C≡C–H), 4.18 (t, 4H, J = 7.6 Hz, –CH_2–), 7.15–7.55 (m, 44H, –Ph and –C_6H_4–), 7.92 (d, 4H, J = 8.4 Hz, –C_6H_4–). Positive FAB-MS: *m*/*z*: 1637 $[M + H]^+$. IR (KBr) : v = 1134 cm^{-1} ν(Si–O). Anal. Found (%): C, 57.50; H, 5.1; N, <0.30. Calcd for $C_{82}H_{84}O_{18}Si_{10}$•$CH_2Cl_2$: C, 57.85; H, 5.03; N, 0.



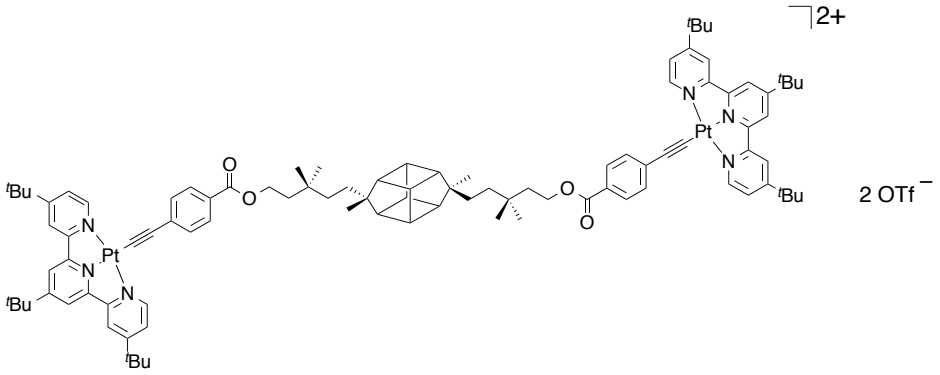
***Cis*-(HC≡C)$_2$–DDSQ:** The titled ligand was prepared according to the procedure similar to that described for the preparation of *trans*-(HC≡C)$_2$–DDSQ, except *cis*–DDSQ–(OH)$_2$ (100 mg, 0.07 mmol) was used to afford the pure ligand as a colourless oil. Yield: 36 mg, 0.021 mmol, 30 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.30 (s, 6H, Si–CH_3), 0.64–0.71 (m, 4H, –CH_2–), 0.76 (s, 12H, –CH_3), 1.27–1.33 (m, 4H, –CH_2–), 1.51 (m, 4H, –CH_2–), 3.24 (s, 2H, C≡C–H), 4.19 (t, 4H, *J* = 7.5 Hz, –CH_2–), 7.16–7.56 (m, 44H, –Ph and –C_6H_4–), 7.93 (d, 4H, *J* = 8.5 Hz, –C_6H_4–). Positive ESI-MS: *m*/*z*: 1637 $[M + H]^+$. HRMS (Positive ESI) calcd for $C_{82}H_{85}O_{18}Si_{10}$: *m/z*: 1637.3423; found: 1637.3388 $[M + H]^+$.



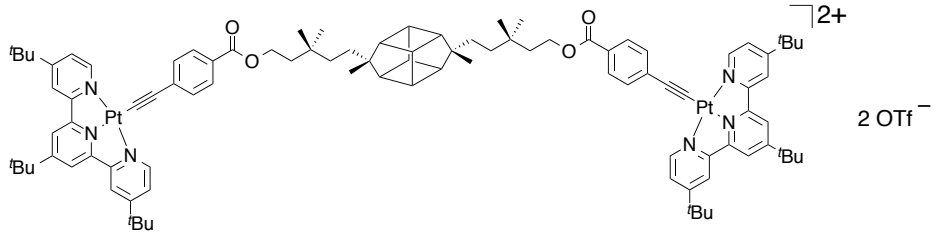
***Trans*-(tpy)$_2$DDSQ:** The compound was prepared according to the similar procedure described for *trans*-(HC≡C)$_2$–DDSQ, excepted that carboxyphenyl-2,2':6',2''-terpyridine (100 mg, 0.28 mmol) was used in place of 4-carboxyphenylacetylene. The crude product was purified by alumina column chromatography using dichloromethane–ethylacetate (1:1 v/v) as eluent, followed by recrystallisation from methanol to afford the pure ligand as a white solid. Yield: 30 mg, 0.015 mmol, 20 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.30 (s, 6H, Si–CH_3), 0.66–0.71 (m, 4H, –CH_2–), 0.77 (s, 12H, –CH_3), 1.32–1.37 (m, 4H, –CH_2–), 1.51–1.54 (m, 4H, –CH_2–), 4.22 (t, 4H, *J* = 7.5 Hz, –CH_2–), 7.16–7.56 (m, 44H, –Ph and –C_6H_4–), 7.88–7.94 (m, 4H, tpy and –C_6H_4–), 8.11 (d, 4H, *J* = 8.4 Hz, –C_6H_4–), 8.68 (d, 4H, *J* = 7.9 Hz, tpy), 8.73–8.76 (m, 8H, tpy). Positive ESI-MS: *m*/*z*: 2051 $[M + H]^+$. HRMS (Positive ESI) calcd for $C_{108}H_{102}N_6O_{18}Si_{10}$: *m/z*: 2051.4943; found: 2051.4999 $[M + H]^+$.



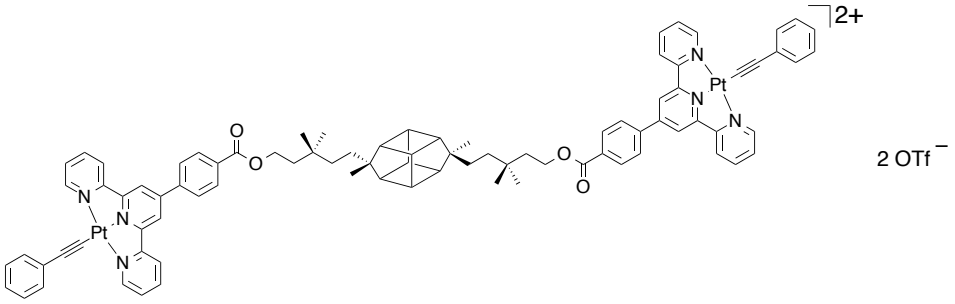
***Trans*–[{Pt(tpy)Cl}$_2$–DDSQ](OTf)$_2$:** The chloroplatinum(II) precursor complex was prepared according to a modified literature method for the synthesis of chloroplatinum(II) terpyridine complexes,[6,9] except that *trans*-(tpy)$_2$DDSQ (150 mg, 0.024 mmol) and [Pt(PhCN)$_2$Cl$_2$] (20 mg, 0.05 mmol) were used. The crude product was recrystallized from DMF and hexane to give the precursor complex as a golden yellow solid. Yield: 100 mg, 0.036 mmol, 50 %. ^{1}H NMR (400 MHz, [D^6]DMSO, 298 K, relative to Me$_4$Si, δ / ppm): δ 0.33 (s, 6H, Si–CH$_3$), 0.73 (s, 12H, –CH$_3$), 1.32–1.36 (m, 4H, –CH$_2$–), 1.50 (t, 4H, *J* = 7.1 Hz, –CH$_2$–), 4.20 (t, 4H, *J* = 7.1 Hz, –CH$_2$–), 7.22–7.54 (m, 40H, –Ph), 8.00 (t, 4 H, *J* = 6.5 Hz, tpy), 8.15 (d, 4H, *J* = 8.4 Hz, –C$_6$H$_4$–), 8.31 (d, 4H, *J* = 8.4 Hz, –C$_6$H$_4$–), 8.57 (t, 4H, *J* = 7.9 Hz, tpy), 8.86 (d, 4H, *J* = 7.9 Hz, tpy), 8.98 (d, 4H, *J* = 6.5 Hz, tpy), 9.05 (s, 4H, tpy). Positive ESI-MS: *m*/*z*: 1255 [M – 2OTf]$^{2+}$. HRMS (Positive ESI) calcd for $C_{108}H_{102}Cl_2N_6O_{18}Pt_2Si_{10}$: *m/z*: 1255.1797; found: 1255.1759 [M – 2OTf]$^{2+}$.



***Trans*-[(^{t}Bu$_3$tpy)Pt(C≡C–DDSQ–C≡C)Pt(tpy^{t}Bu$_3$)](OTf)$_2$ (1$_{(trans)}$):** Complex **1**$_{(trans)}$ was prepared according to a modified literature method for the synthesis of alkynylplatinum(II) terpyridine complexes.[10,11] To a solution of [(^{t}Bu$_3$tpy)PtCl](OTf) (200 mg, 0.26 mmol) and *trans*-(HC≡C)$_2$–DDSQ (170 mg, 0.10 mmol) in degassed dichloromethane and triethylamine was added a catalytic amount of CuI. The resultant solution was stirred overnight at ambient temperature. The crude product was then purified by column chromatography using dichloromethane-acetone (3:1 v/v) mixture as eluent, followed by recrystallisation from dichloromethane–methanol to give **1**$_{(trans)}$ as a yellow solid. Yield: 80 mg, 0.025 mmol, 25 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.30 (s, 6H, Si–CH_3), 0.65–0.70 (m, 4H, –CH_2–), 0.76 (s, 12H, –CH_3), 1.33 (m, 4H, –CH_2–), 1.50–1.53 (m, 40H, –CH_2– and –^{t}Bu), 1.62 (s, 18H, –^{t}Bu), 4.20 (t, 4H, J = 7.6 Hz, –CH_2–), 7.16–7.63 (m, 48H, tpy, –Ph and –C_6H_4–), 7.95 (d, 4H, J = 8.3 Hz, –C_6H_4–), 8.39 (s, 4H, tpy), 8.47 (s, 4H, tpy), 9.12 (d, 4H, J = 6.1 Hz, tpy). Positive FAB-MS: m/z: 1414 [M – 2OTf]$^{2+}$. IR (KBr): v = 1134 cm^{-1} ν(Si–O), 2114 cm^{-1} ν(C≡C). Anal. Found (%): C, 52.11; H, 5.04; N, 2.79. Calcd for $C_{138}H_{152}F_6N_6O_{24}Pt_2S_2Si_{10}$•$2H_2O$: C, 52.39; H, 4.97; N, 2.66.



***Cis*-[(^t^Bu$_3$tpy)Pt(C≡C–DDSQ–C≡C)Pt(tpy^t^Bu$_3$)](OTf)$_2$ (1$_{(cis)}$):** Complex **1**$_{(cis)}$ was prepared according to the procedure similar to that described for the preparation of **1**$_{(trans)}$, except that *cis*-(HC≡C)$_2$–DDSQ (170 mg, 0.10 mmol) was used in place of *trans*-(HC≡C)$_2$–DDSQ. The product was recrystallized from dichloromethane–methanol to give **1**$_{(cis)}$ as a golden yellow solid. Yield: 100 mg, 0.032 mmol, 30 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si, δ / ppm): δ 0.31 (s, 6H, Si–CH_3), 0.70 (m, 4H, –CH_2–), 0.78 (s, 12H, –CH_3), 1.32 (m, 4H, –CH_2–), 1.50–1.53 (m, 40H, –CH_2– and –^{t}Bu), 1.62 (s, 18H, –^{t}Bu), 4.21 (t, 4H, J = 7.6 Hz, –CH_2–), 7.17–7.63 (m, 48H, tpy, –Ph and –C_6H_4–), 7.95 (d, 4H, J = 8.3 Hz, –C_6H_4–), 8.39 (s, 4H, tpy), 8.46 (s, 4H, tpy), 9.12 (d, 4H, J = 6.1 Hz, tpy). Positive FAB-MS: m/z: 1414 $[M–2OTf]^{2+}$. IR (KBr) : v = 1126 cm^{-1} ν(Si–O), 2114 cm^{-1} ν(C≡C). Anal. Found (%): C, 52.44; H, 5.28; N, 2.56. Calcd for $C_{138}H_{152}F_6N_6O_{24}Pt_2S_2Si_{10}$•$H_2O$: C, 52.69; H, 4.93; N, 2.67.



***Trans*-[(C_6H_5–C≡C)Pt(tpy–DDSQ–tpy)Pt(C≡C–C_6H_5)](OTf)$_2$ (2$_{(trans)}$):**

Complex **2**$_{(trans)}$ was prepared according to the procedure similar to that described for the preparation of **1**$_{(trans)}$, except that *trans*–[{Pt(tpy)Cl}$_2$–DDSQ](OTf)$_2$ (100 mg, 0.036 mmol) in degassed dimethylformamide (50 ml) and phenylacetylene (18 mg, 0.18 mmol) were used in place of [(^{t}Bu$_3$tpy)PtCl](OTf) and *trans*-(HC≡C)$_2$–DDSQ respectively. The crude product was then recrystallizated from dimethylformamide–diethyl ether to give **2**$_{(trans)}$ as a dark brown solid. Yield: 20 mg, 0.007 mmol, 20 %. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 330 K, relative to Me$_4$Si, δ / ppm): δ 0.33 (s, 6H, Si–CH$_3$), 0.72–0.76 (m, 16H, –CH$_2$– and –CH$_3$), 1.35–1.39 (m, 4H, –CH$_2$–), 1.53 (t, 4H, *J* = 7.1 Hz, –CH$_2$–), 4.26 (t, 4H, *J* = 7.3 Hz, –CH$_2$–), 7.17–7.59 (m, 50H, tpy and –Ph), 7.98 (t, 4H, *J* = 7.4 Hz, tpy), 8.15 (d, 4H, *J* = 8.3 Hz, –C$_6$H$_4$–), 8.27 (d, 4H, *J* = 8.3 Hz, –C$_6$H$_4$–), 8.54 (t, 4H, *J* = 7.7 Hz, tpy), 8.84 (d, 4H, *J* = 7.7 Hz, tpy), 9.04 (s, 4H, tpy), 9.25 (d, 4H, *J* = 5.0 Hz, tpy). Positive ESI-MS: *m*/*z*: 1321 [M – 2OTf]$^{2+}$. IR (KBr): *v* = 1134 cm^{-1} ν(Si–O), 2114 cm^{-1} ν(C≡C). HRMS (Positive ESI) calcd for $C_{124}H_{112}N_6O_{18}Pt_2Si_{10}$: *m/z*: 1321.2503; found: 1321.2450 [M – 2OTf]$^{2+}$.

X–Ray Crystal Structure Determination

Single crystals of the ligand *cis*–DDSQ–$(OH)_2$ and complex **1**$_{(trans)}$ suitable for X-ray crystallographic studies were obtained by the layering of hexane and diethyl ether into a concentrated dichloromethane solution of the compound respectively. Both crystals were mounted on loops, and the intensity data were collected on a Bruker D8 Venture Diffractometer using compact optics monochromated microfocus Mo–Kα radiation (λ = 1.54178 Å) and Photon100 CMOS detector. Raw frame data were integrated using the APEX program.[12] Semi-empirical absorption corrections with SADABS were applied. The structures were solved by direct methods employing the XT program[13] and refined by full-matrix least-squares on F^2 using the SHELXL2014/7 program.[14] In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated by the program SHELXL2014/7.[14] The positions of hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final R indices.

Crystal data for *cis*–DDSQ–$(OH)_2$: A colourless block crystal of $C_{64}H_{76}O_{16}Si_{10}$, having approximate dimensions of 0.146 mm x 0.342 mm x 0.611 mm was mounted on loop. All measurements were made on a Bruker *D8 Venture Diffractometer* equipped with compact optics monochromated microfocus Mo–Kα radiation and Photon100 CMOS detector. Cell constants and orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions: *a* = 14.0299 (19) Å, *b* = 14.3439 (20) Å, *c* = 18.6928 (26) Å, *V* = 3461.7 (8) $Å^3$, α = 78.286 (4)°, β = 82.614 (4)°, γ = 70.360 (4)°. For Z = 2 and F.W. = 1382.14, the calculated density was 1.326 g/cm^3. Based on a statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be: $P\bar{1}$ (No. 2). The data were collected at a temperature of 100 K to a maximum 2θ value of 50.05°. The crystal-to-detector distance was 50.00 mm. The exposure time was 10 sec/0.5°. Of the 80374 reflections that were collected, 12226 reflections were unique. (R_{int} = 0.1373); equivalent reflections were merged. The crystal and structure determination data for the ligand were given in Table S1.

Table S1 Crystal and structure determination data for *cis*–DDSQ–$(OH)_2$

formula	$C_{64}H_{76}O_{16}Si_{10}$
fw	1382.14
a / Å	14.0299(19)
b / Å	14.3439(20)
c / Å	18.6928(26)
α / °	72.286(4)
β / °	82.614(4)
γ / °	70.360(4)
V / Å^3	3461.7(8)
Z	2
crystal system	Triclinic
colour/habit	Colourless block crystal
space group	$P\bar{1}$ (No. 2)
D_c / g cm^{-3}	1.326
T / K	100
μ / mm^{-1}	0.25
F(000)	1456
no. of reflections	80374
no. of independent reflections	12226
R_{int}	0.1373
R_1[a], wR_2[b] ($I > 2(I)$)	0.041, 0.113
GoF[c]	1.04

[a] $R_1 = \Sigma ||F_o|-|F_c|| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma w(|F_o^2|-|F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$.
[c] $\text{GoF} = [\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

Crystal data for **1**$_{(trans)}$: A yellow prism crystal of $[C_{136}H_{150}N_6O_{18}Pt_2Si_{10}]^{2+}2[CF_3SO_3]^-$, having approximate dimensions of 0.098 mm x 0.138 mm x 0.497 mm was mounted on loop. All measurements were made on a Bruker *D8 Venture* X-ray Diffractometer equipped with compact optics monochromated microfocus Mo–Kα radiation and Photon100 CMOS detector. Cell constants and an orientation matrix for data collection corresponded to a primitive triclinic cell with dimensions: a = 10.1326 (7) Å, b = 34.949 (2) Å, c = 21.8804 (16) Å, V = 7561.4 (9) Å^3, β = 102.609 (2)°. For Z = 2 and F.W. = 3125.83, the calculated density was 1.373 g/cm^3. Based on a statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be: *P2$_1$/c* (No. 14). The data were collected at a temperature of 120 K to a maximum 2θ value of 50.05°. The crystal-to-detector distance was 50.00 mm. The exposure time was 55 sec/0.5°. Of the 89079 reflections that were collected, 13326 reflections were unique. (R_{int} = 0.0547); equivalent reflections were merged. The crystal and structure determination data for **1**$_{(trans)}$ were given in Table S2. Selected bond lengths and bond angles of the complex were collected in Table S3.

Table S2 Crystal and structure determination data for **1**$_{(trans)}$

formula	$C_{136}H_{150}N_6O_{18}Pt_2Si_{10}$•2($CF_3O_3S$)
fw	3125.83
a / Å	10.1326(7)
b / Å	34.949(2)
c / Å	21.8804(16)
β / °	102.609(2)
V / Å^3	7561.4(9)
Z	2
crystal system	Monoclinic
colour/habit	Yellow prism crystal
space group	$P\,2_1/c$ (No. 14)
D_c / g cm^{-3}	1.373
T / K	120
μ / mm^{-1}	2.03
F(000)	3188
no. of reflections	89079
no. of independent reflections	13326
R_{int}	0.055
R_1[a], wR_2[b] ($I > 2(I)$)	0.064, 0.152
GoF[c]	1.12

[a] $R_1 = \Sigma\,||F_o|-|F_c||\,/\,\Sigma\,|F_o|$. [b] $wR_2 = [\,\Sigma\,w(|F_o^2|-|F_c^2|)^2\,/\,\Sigma\,w|F_o^2|^2]^{1/2}$.
[c] GoF = $[\,\Sigma\,w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{1/2}$.

Table S3 Selected bond distances and angles with estimated standard deviations in parentheses for **1**$_{(trans)}$

Bond Distances / Å			
Pt(1)−N(1)	2.007(6)	Pt(1)−N(2)	1.936(6)
Pt(1)−N(3)	2.022(6)	Pt(1)−C(28)	1.977(7)
C(28)−C(29)	1.170(1)		
Bond Angles / deg			
N(1)−Pt(1)−N(2)	80.5(2)	N(1)−Pt(1)−C(28)	98.8(3)
N(2)−Pt(1)−N(3)	80.7(2)	N(2)−Pt(1)−C(28)	177.4(3)
N(1)−Pt(1)−N(3)	161.0(2)	N(3)−Pt(1)−C(28)	100.0(3)
Pt(1)−C(28)−C(29)	176.3(7)		

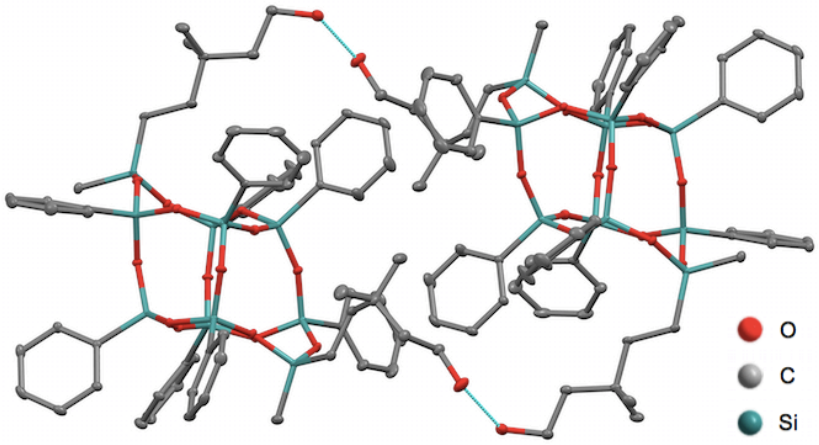


Figure S1. Crystal packing diagrams of the ligand molecule, *cis*-DDSQ–$(OH)_2$, showing a dimeric structure with hydrogen bonds

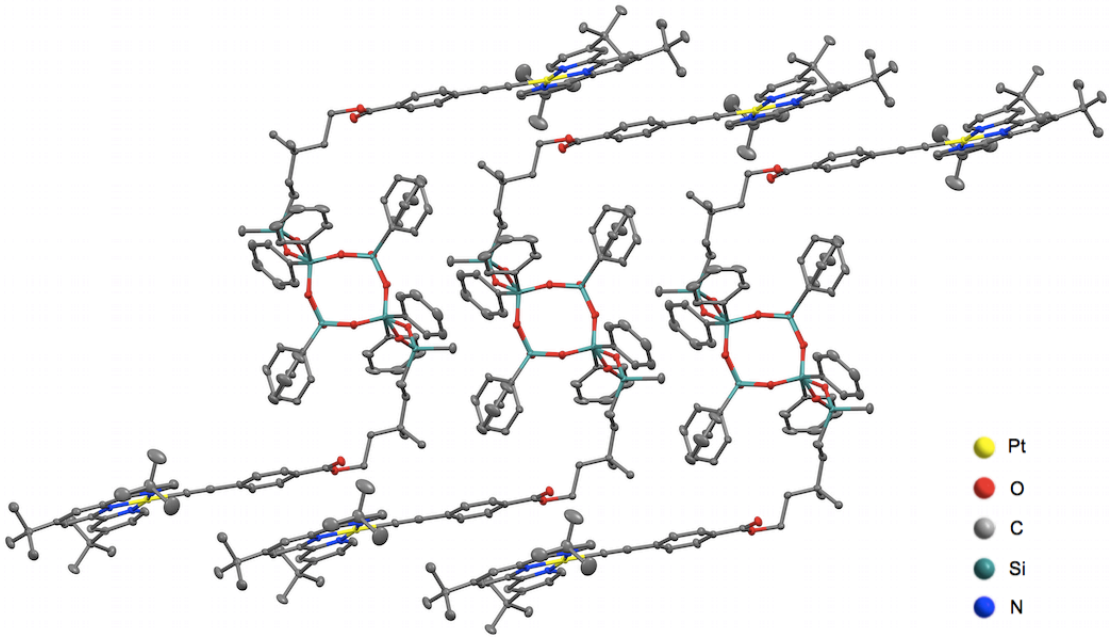


Figure S2. Crystal packing diagrams of the complex cations of **1**$_{(trans)}$ showing a linear stacking configuration

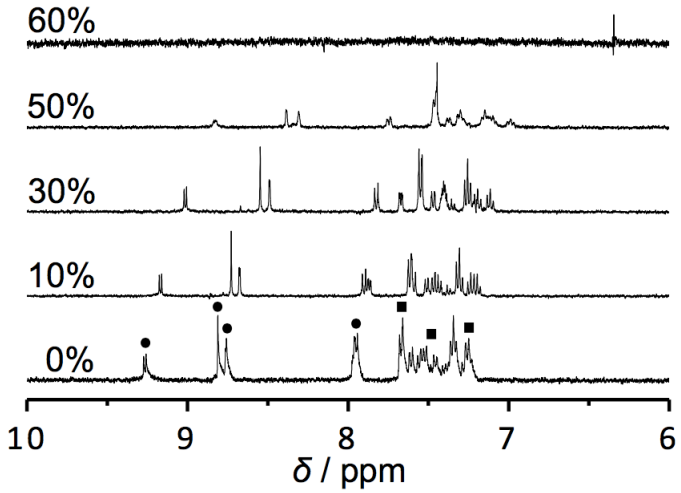


Figure S3. Solvent–dependent ^{1}H NMR spectra of **1**$_{(trans)}$ in D_2O–[D_6]acetone (v/v). The signals correspond to the proton resonances of terpyridine (●) and the phenyl groups on the DDSQ (■) moieties (1 x 10^{-4} M, 298 K, 400 MHz)

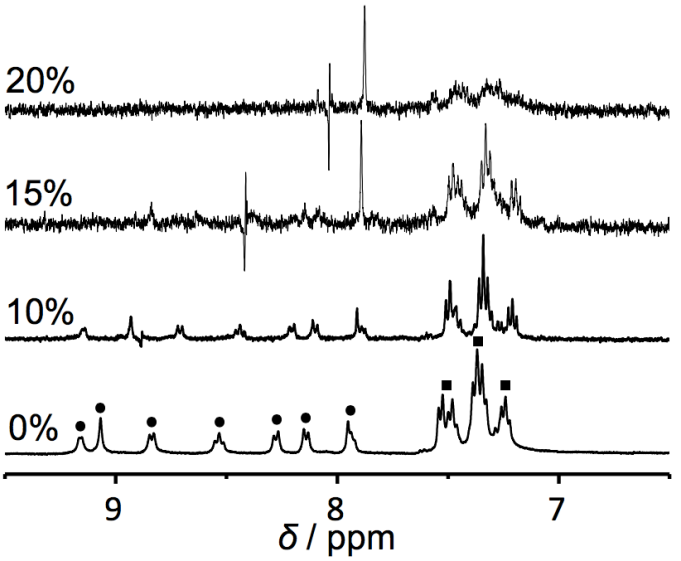


Figure S4. Solvent–dependent ^{1}H NMR spectra of **2**$_{(trans)}$ in D_2O–[D_6]DMSO (v/v). The proton signals correspond to the terpyridine (●) and the phenyl groups on the DDSQ moieties (■) (1 x 10^{-4} M, 298 K, 400 MHz)

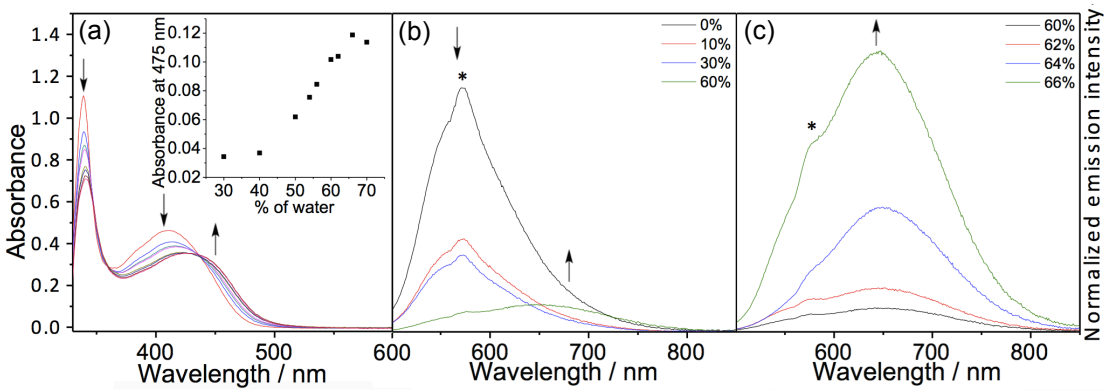


Figure S5. (a) UV-Vis absorption spectral changes of **1**$_{(trans)}$ (3.2 x 10^{-5} M) in acetone with increasing water content from 40 to 78 %. The corresponding emission spectral changes in acetone with increasing water composition from (b) 0 to 60 %; (c) 60 to 66 %. The asterisk denotes an instrumental artifact

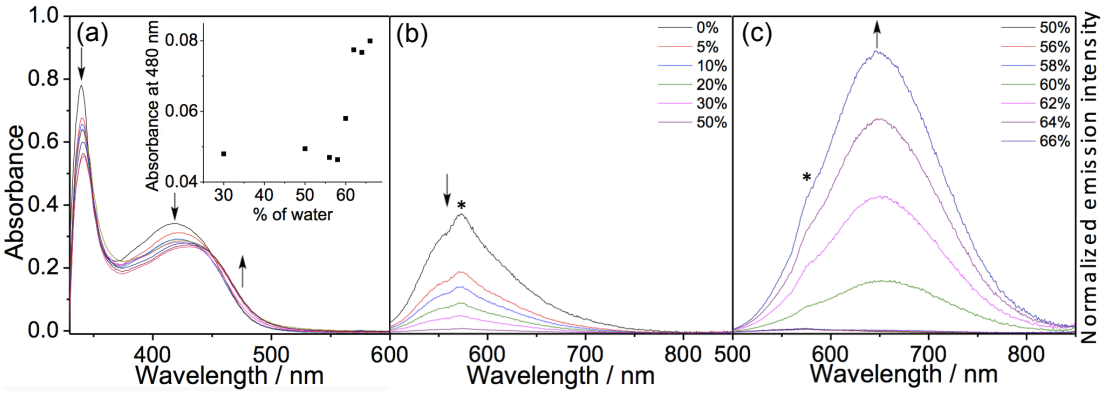


Figure S6. (a) UV-Vis absorption spectral changes of **1**$_{(cis)}$ (2.6 x 10^{-5} M) in acetone with increasing water content from 30 to 70 %. The corresponding emission spectra changes in acetone with increasing water composition from (b) 0 to 50 %; (c) 50 to 66 %. The asterisk denotes an instrumental artefact

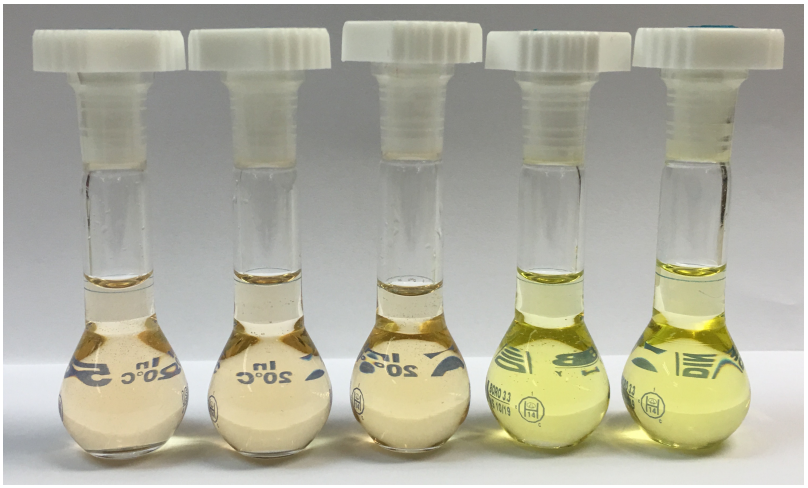


Figure S7. Solutions of **2**$_{(trans)}$ in water−DMSO mixture (1.8 x 10^{-5} M, percentage of water in DMSO from left to right: 70, 50, 30, 10 and 0 %)

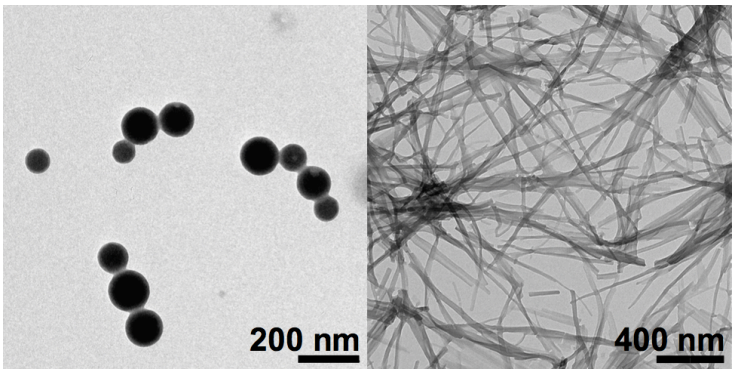


Figure S8. TEM images of the superstructures prepared from (left) **1**$_{(cis)}$ (1 x 10^{-4} M) and (right) **1**$_{(trans)}$ (1 x 10^{-4} M) in 60 % water−acetone mixture

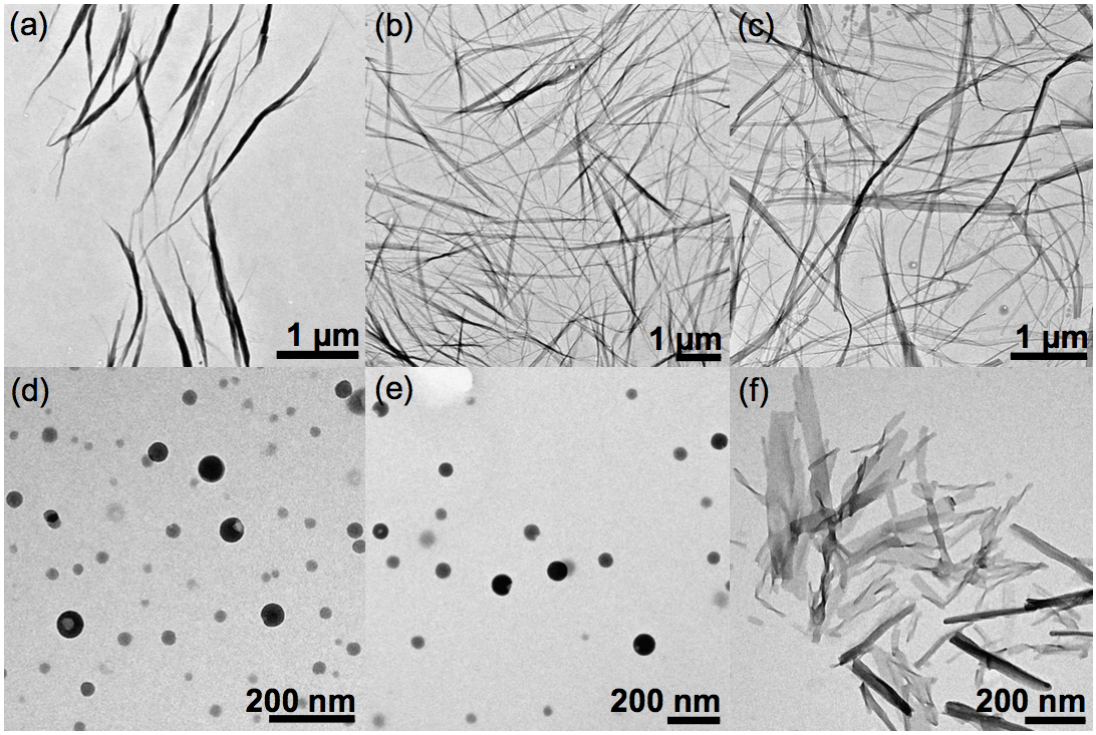


Figure S9. Electron micrographs of the superstructures prepared from mixtures of $\mathbf{1}_{(cis)}$ and $\mathbf{1}_{(trans)}$ ([Pt] = 2 x 10^{-4} M) in (a–c) 50 % and (d–e) 60 % water−acetone compositions. TEM images obtained from isomeric ratios ($\mathbf{1}_{(cis)}$/$\mathbf{1}_{(trans)}$) of (a,d) 1:3, (b,e) 1:1 and (c,f) 3:1 respectively

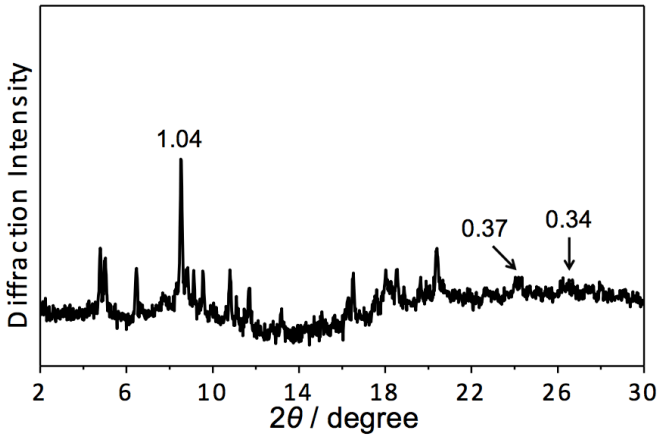


Figure S10. XRD patterns obtained from powder sample of **1**$_{(trans)}$. Numerical values represent *d*-spacing (nm)

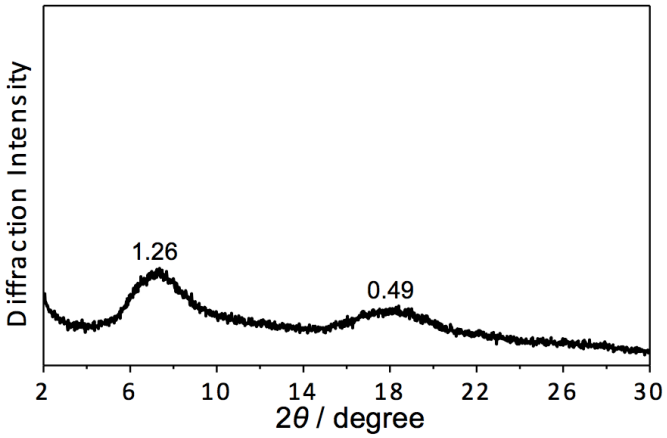


Figure S11. XRD patterns obtained from powder sample of **1**$_{(cis)}$. Numerical values represent *d*-spacing (nm)

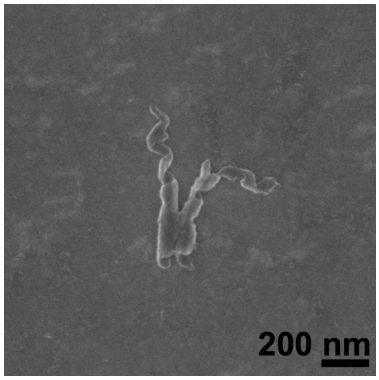


Figure S12. SEM image of the superstructures prepared from **2**$_{(trans)}$ (1 x 10^{-4} M) in 70 % water–DMSO mixture, revealing the derivation of nanotubes through helical ribbons

Table S4 Photophysical data for **1** and **2** at 298 K

Complex	Medium	Absorption	Emission	
		λ_{max} / nm (ε / dm^{3}mol^{-1}cm^{-1})	λ_{max} / nm (τ_0 / μs)	Φ_{em}[a]
1$_{(trans)}$	Acetone	339 (38100), 418 (14500)	571 (0.10)	4.2 x 10^{-3}
1$_{(cis)}$	Acetone	339 (39200), 415 (15200)	571 (0.20)	2.1 x 10^{-3}
2	DMSO	293 (89100), 350 (25800), 435 (12400), 466 (11700)	600 (---)[b]	---[b]

[a]The relative luminescence quantum yield, measured at room temperature using $[Ru(bpy)_3]Cl_2$ as reference. [b]Weak in intensity, not measurable.

References

1. T. Suzuki; Y. Ota; M. Ri; M. Bando; A. Gotoh; Y. Itoh; H. Tsumoto; P. R. Tatum; T. Mizukami; H. Nakagawa; S. Iida; R. Ueda; K. Shirahige; N. Miyata, *J. Med. Chem.* **2012**, *55*, 9562.
2. Y. Zhu; X. Yang; X. Fang; X. Yang; L. Ye; W. Cai; Y. Zhang; F. Wu, *Tetrahedron* **2011**, *67*, 1251.
3. N. Leventis; A.-M. M. Rawashdeh; I. A. Elder; J. Yang; A. Dass; C. Sotiriou-Leventis, *Chem. Mater.* **2004**, *16*, 1493.
4. K. Arunrungvichian; V. V. Fokin; O. Vajragupta; P. Taylor, *ACS Chem. Neurosci.* **2015**, *6*, 1317.
5. H. Chi; S. L. Lim; F. Wang; C. He; W. S. Chin, *Macromol. Rapid Commun.* **2014**, *35*, 801.
6. H. K. Yip; L. K. Cheng; K. K. Cheung; C. M. Che, *J. Chem. Soc., Dalton Trans.* **1993**, 2933.
7. K. Wei; L. Wang; S. Zheng, *Polym. Chem.* **2013**, *4*, 1491.
8. H. Tsuji; H. Yamamoto, *J. Am. Chem. Soc.* **2016**, *138*, 1428.
9. J. A. Bailey; M. G. Hill; R. E. Marsh; V. M. Miskowski; W. P. Schaefer; H. B. Gray, *Inorg. Chem.* **1995,** *34*, 4591.
10. A. Y.-Y. Tam; K. M.-C. Wong; G. Wang; V. W.-W. Yam, *Chem. Commun.* **2007**, 2028.
11. W. Lu; Y. C. Law; J. Han; S. S. Y. Chui; D. L. Ma; N. Zhu; C. M. Che, *Chem. Asian J.* **2008**, *3*, 59.
12. Bruker AXS Inc. APEX3 v2015.5-2, Madison, Wisconsin, USA, **2015**.
13. G. M. Sheldrick, *Acta Crystallogr. Sect A* **2015**, *71*, 3-8.
14. G. M. Sheldrick, *Acta Crystallogr. Sect C* **2015**, *71*, 3-8.