Supporting Information

Supramolecular Assembly of Platinum-Containing Polyhedral Oligomeric Silsesquioxanes: An Interplay of Intermolecular Interactions and A Correlation Between Structural Modifications and Morphological Transformations

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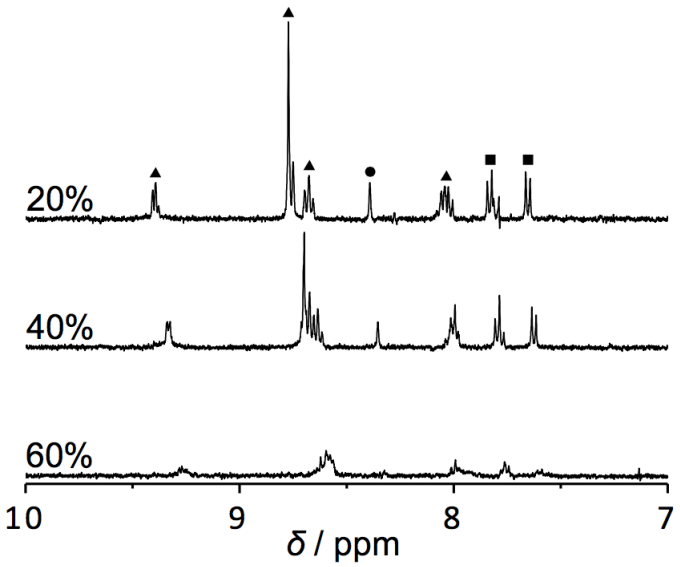


Figure S1. Solvent-dependent ^{1}H NMR spectra of **1** in D_2O–[D_8]THF (v/v). The proton signals correspond to the terpyridine (▲), imine (●) and the alkynyl (■) moieties (1 x 10^{-4} M, 298 K, 400 MHz).

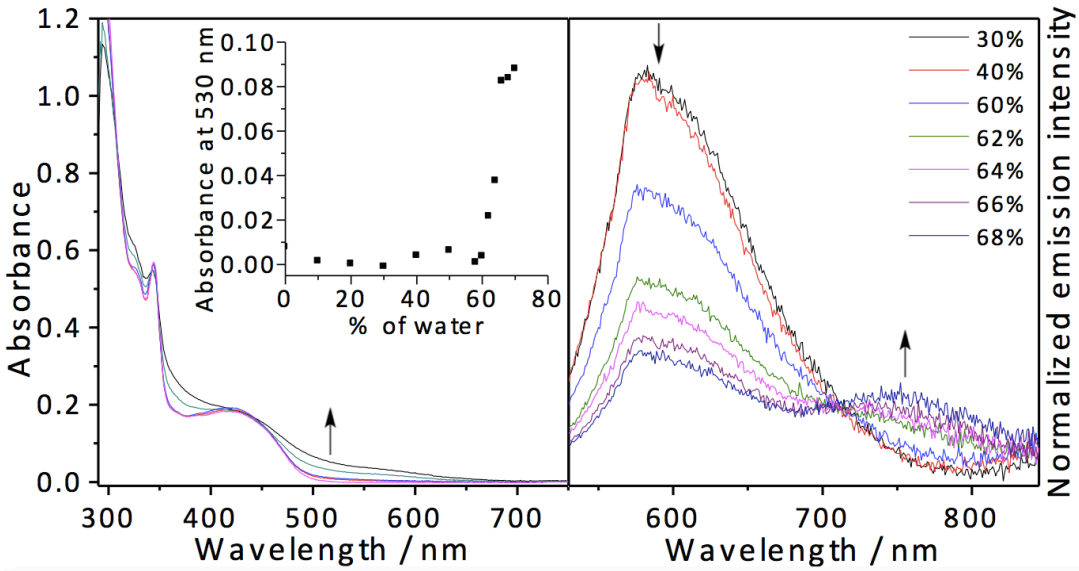


Figure S2. UV-Vis absorption spectra (left) of **2** in THF with increasing water content from 30 to 64 %. The corresponding corrected emission spectral changes (right) upon increasing the water composition from 30 to 68 %.

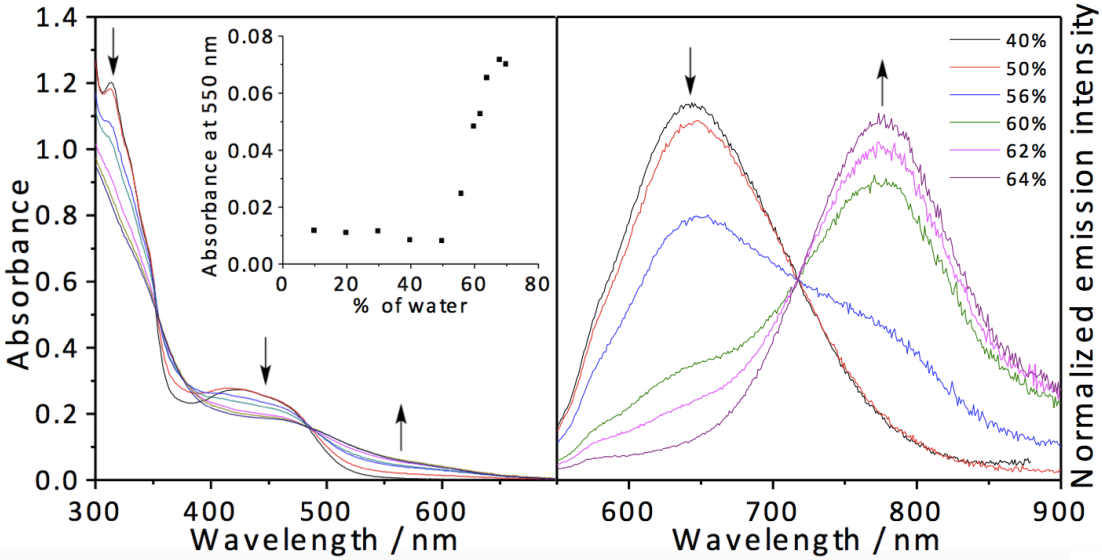


Figure S3. UV-Vis absorption spectra (left) of **3** in THF with increasing water content from 50 to 70 %. The corresponding corrected emission spectral changes (right) normalized at 716 nm upon increasing the water composition from 40 to 64 %.

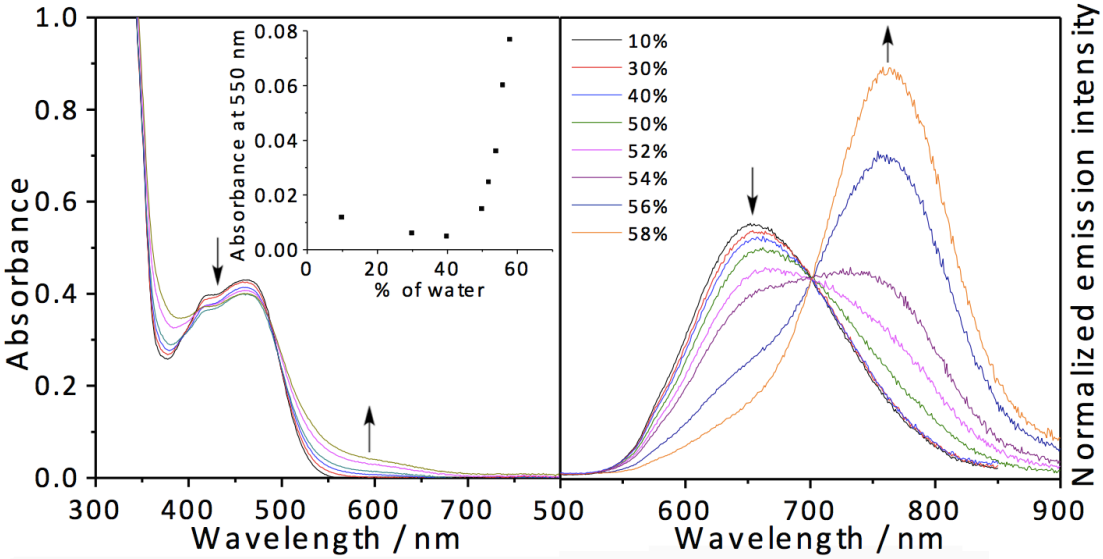


Figure S4. UV-Vis absorption spectra (left) of **4** in THF with increasing water content from 40 to 58 %. The corresponding corrected emission spectral changes (right) normalized at 701 nm upon increasing the water composition from 10 to 58 %.

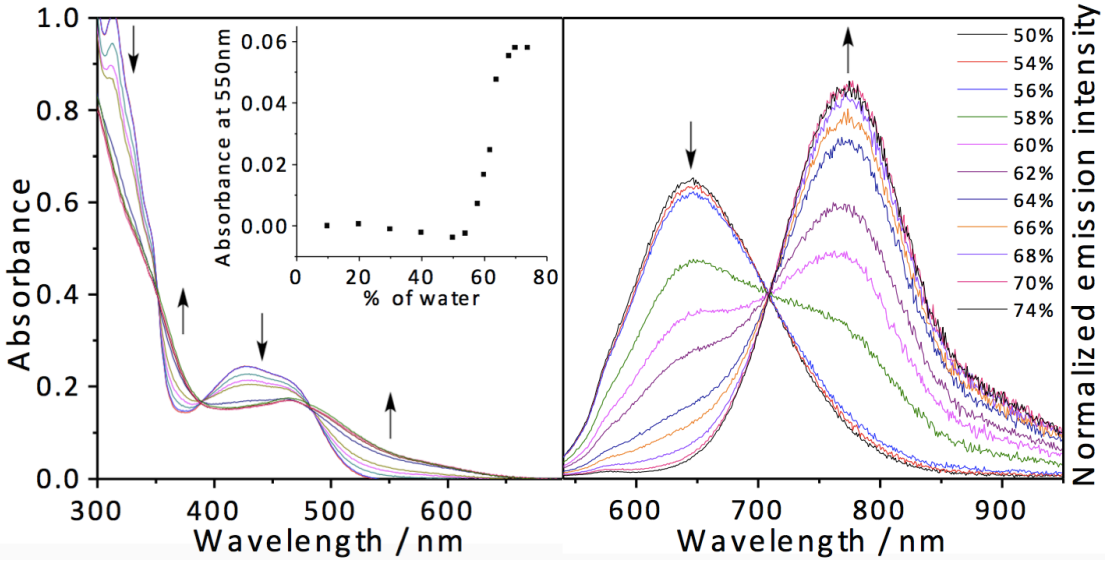


Figure S5. UV-Vis absorption spectra (left) of **5** in THF with increasing water content from 50 to 74 %. The corresponding corrected emission spectral changes (right) normalized at 709 nm upon increasing the water composition from 50 to 74 %.

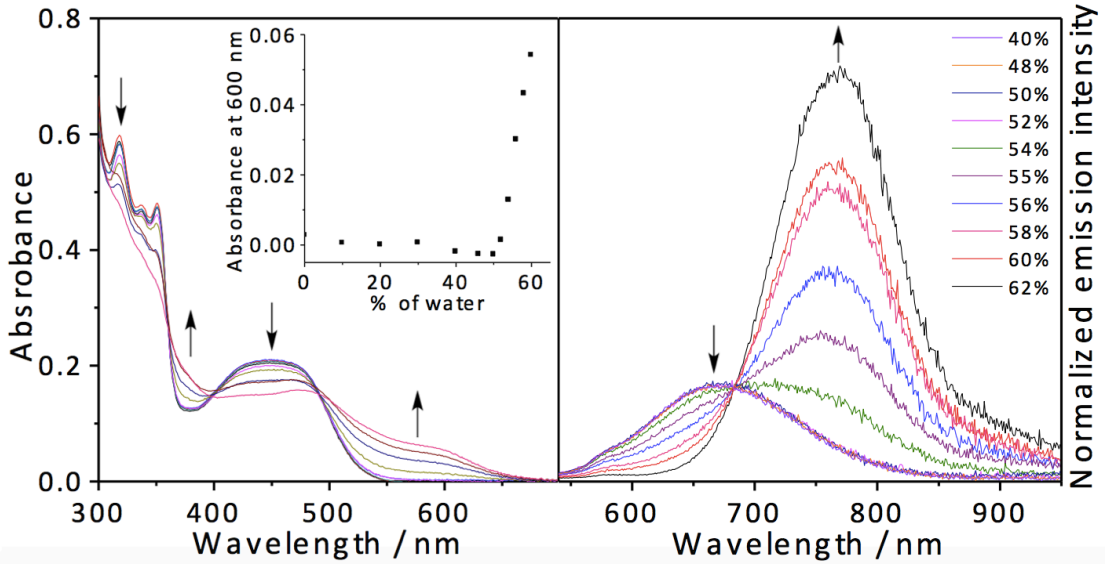


Figure S6. UV-Vis absorption spectra (left) of **6** in THF with increasing water content from 40 to 60 %. The corresponding corrected emission spectral changes (right) normalized at 684 nm upon increasing the water composition from 40 to 62 %.

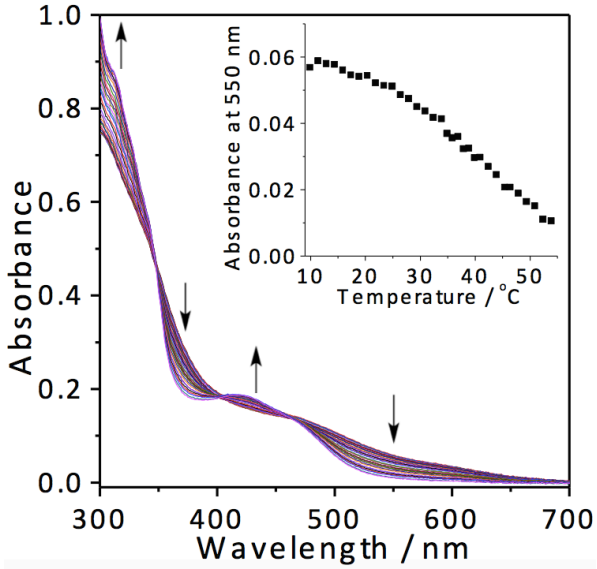


Figure S7. Temperature-dependent UV-vis absorption spectra of **3** in 65 % water–THF mixture, with increasing temperature from 10 to 54 °C. The inset shows the corresponding absorbance at 550 nm as a function of temperature.

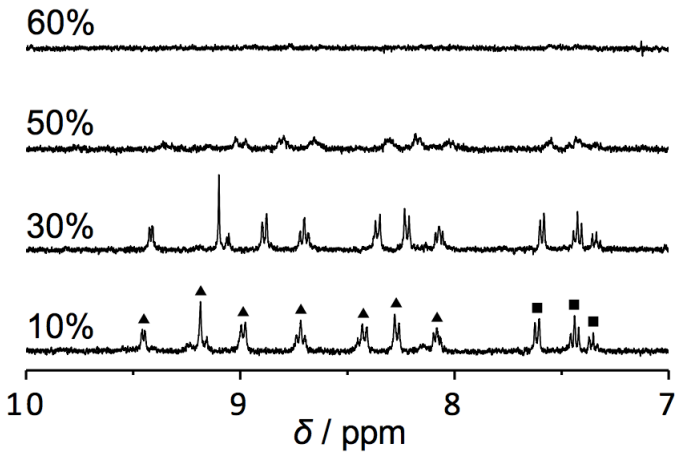


Figure S8. Solvent-dependent ^{1}H NMR spectra of **3** in D_2O–[D_8]THF (v/v). The proton signals correspond to the terpyridine (▲) and the alkynyl (■) protons (1 x 10^{-4} M, 298 K, 400 MHz).

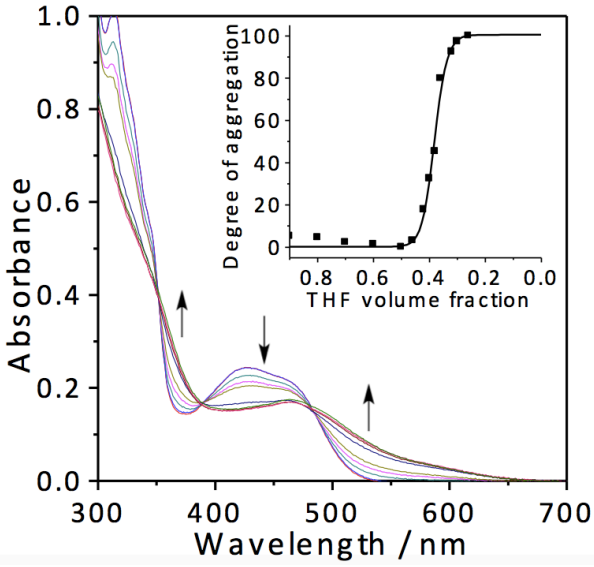


Figure S9. Solvent-dependent UV-vis absorption spectra of **5** in water–THF mixture, with increasing water composition. The insets show the plot of normalized degree of aggregation against THF volume fraction with curve fitting to the nucleation–elongation model.

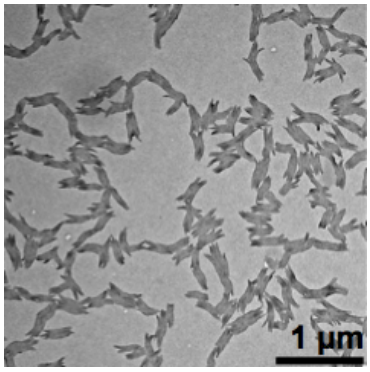


Figure S10. TEM images of the superstructures prepared from **5** (2×10^{-4} M) in 30 % water–THF mixture.

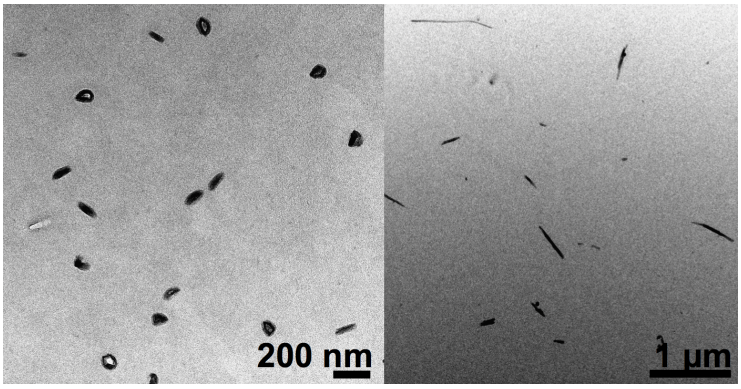


Figure S11. TEM images of the superstructures prepared from **1** (2×10^{-4} M) incubated for 48 hrs under ambient temperature in (left) 30 % and (right) 70 % water–THF mixture.

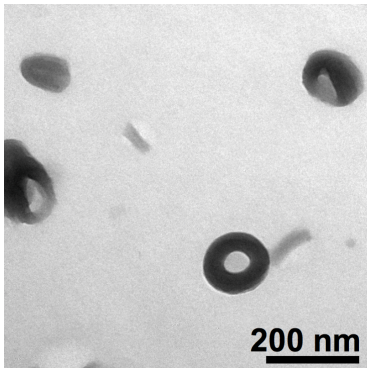


Figure S12. TEM images of the superstructures prepared from **2** (2×10^{-4} M) in 30 % water–THF mixture.

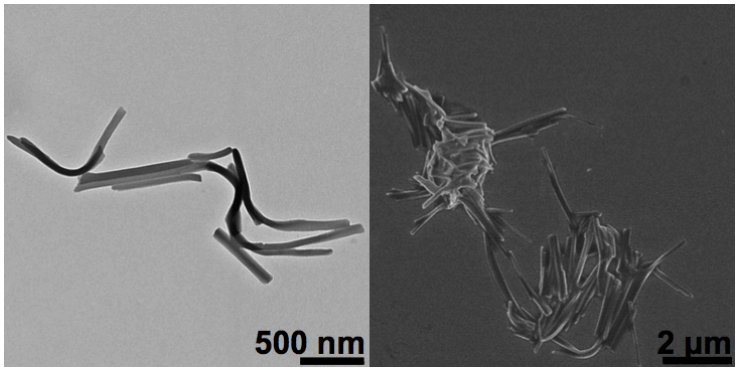


Figure S13. TEM (left) and SEM (right) images of the superstructures prepared from **8** (2×10^{-4} M) in 20 % water−THF mixture.

Table S1 Photophysical data of **1**–**8**

Complex	Medium (T / K)	Absorption λ_{max} / nm (ε / $dm^3mol^{-1}cm^{-1}$)	Emission λ_{max} / nm (τ_0 / μs)	Φ_{em}[a]
1	THF (298)	314 (33800), 346 (13500), 442 (4540), 547 sh (460)	626 (0.20)	2.3×10^{-3}
2	THF (298)	347 (16000), 370 (8240), 451 (4000), 518 sh (440)	598 (0.32)	3.9×10^{-3}
3	THF (298)	315 (28200), 417 (7770), 471 (5650), 536 sh (640)	629 (0.14)	1.3×10^{-3}
4	THF (298)	422 (9900), 477 (10500)	648 (0.23)	1.8×10^{-3}
5	THF (298)	314 (27300), 430 (7520), 472 (6560)	625 (0.14)	1.2×10^{-3}
6	THF (298)	318 (17400), 339 (13100), 352 (13300), 422 (5610), 476 (4890)	641 (0.14)	1.2×10^{-3}
7	THF (298)	332 sh (17200), 415 (3800), 505 (4240)	745 (0.13)	4.5×10^{-3}
8	THF (298)	295 (31600), 321 (22600), 425 (6700), 500 (1980)	–[b]	–[b]

[a]The luminescence quantum yield, measured at room temperature using $[Ru(bpy)_3]Cl_2$ as reference for **1–6**, **8** and oxazine 1 as reference for **7**. [b]Non-emissive.

Experimental

Materials and Reagents. Potassium tetrachloroplatinate(II) ($K_2[PtCl_4]$) (Chem. Pur.), 3-aminopropylisobutyl POSS, tirsilanolphenyl POSS (Hybrid Plastic Inc.), phenylacetylene, tetrabutylammonium hydroxide (TBAOH) 30-hydrate (Sigma-Aldrich Co. Ltd.), and triethylamine (Apollo Scientific Ltd.) were obtained from the corresponding chemical company. 3-Aminopropyl-functionalized heptaphenyl POSS (PhPOSS−NH_2),[1] 2-(4-ethynylphenoxy)-N, N-dimethyl-ethanamine,[2] 4-ethynylbenzaldehyde,[3] 4-ethynylphenol,[4] 4'-carboxyphenyl-2,2':6',2''-terpyridine,[5] 2,2':6',2''-terpyridine-4'-carboxylic acid,[6] 1-ethynyl-4-(2-phenylethynyl)-benzene[7] and 4-ethynylbenzoic acid[8] were synthesized according to literature methods. Tetrahydrofuran (Acros Organics Co. Ltd., spectroscopic grade) were used for spectroscopic studies without further purification. All other reagents, unless otherwise specified, were of analytical grade and were used as received without further purification.

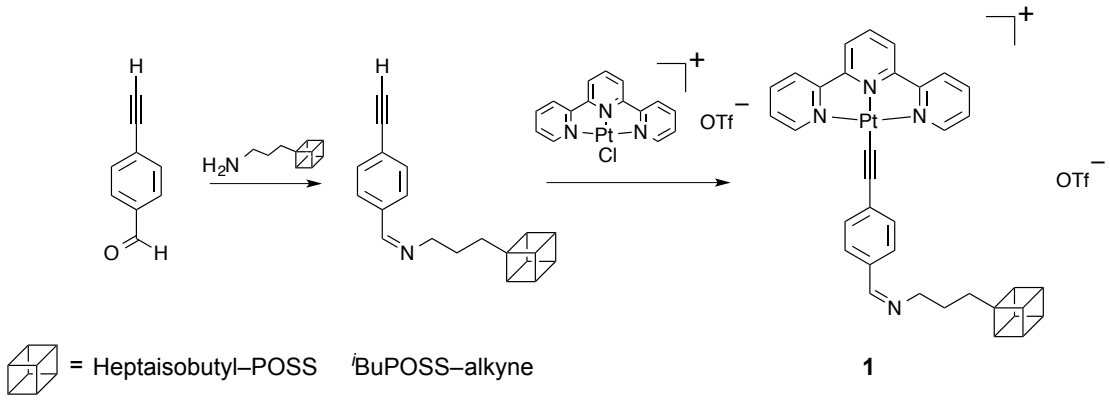
Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AVANCE 300 or 400 (300 and 400 MHz) NMR spectrometer. Positive-ion FAB mass spectra were recorded on a Thermo Scientific DFS high resolution magnetic sector mass spectrometer. IR spectra were obtained as KBr disk on 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 Hewlett-Packard 8452A diode array 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. Topographical images and phase images of atomic force micrographs (AFM) were collected on an Asylem MFP3D atomic force microscope with ARC2 SPM Controller under constant temperature and atmospheric pressure. Samples were prepared by drop casting dilute solutions onto a silicon wafer.

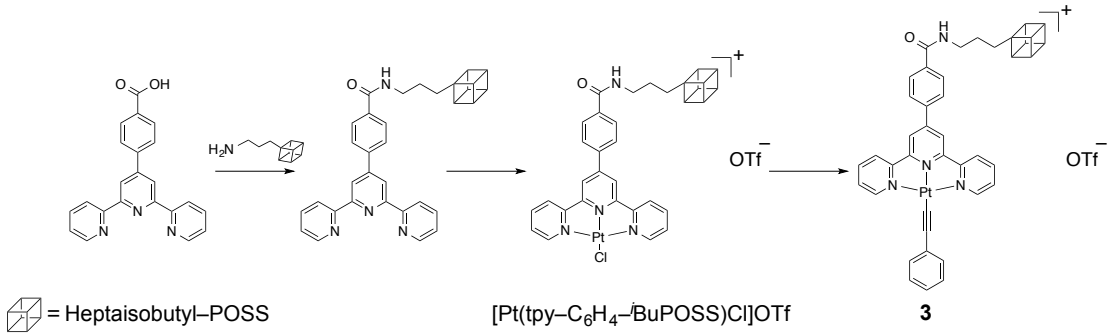
Synthesis and characterization

Synthesis

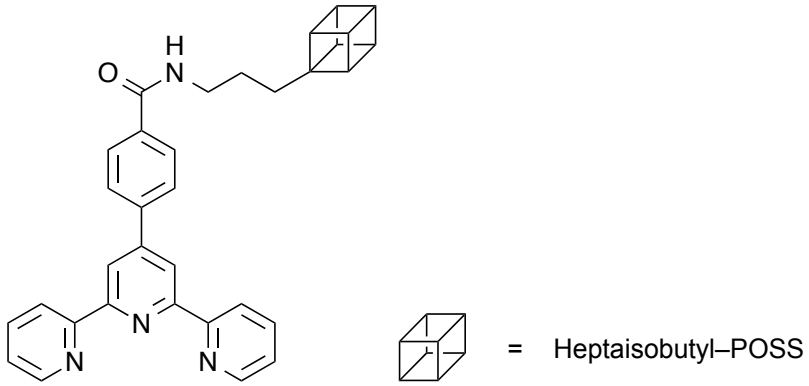
The synthetic routes for complex **1** and **2** are shown in Scheme S1 and S2 respectively. All reactions, unless otherwise specified, were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques.



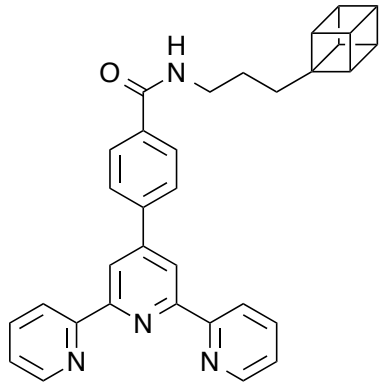
Scheme S1. Synthetic route for complex **1**.



Scheme S2. Synthetic route for complex **3**.

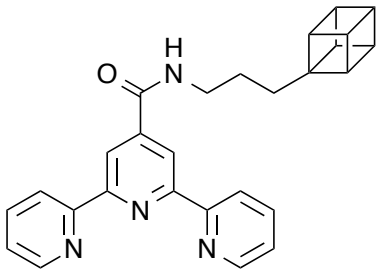


^{i}BuPOSS–phenyl–terpyridine (tpy–C_6H_4–^{i}BuPOSS): The titled ligand was prepared according to a modified literature method for the synthesis of VPOSS–phenyl–terpyridine[9] using 3-aminopropylisobutyl POSS (^{i}BuPOSS−NH_2, 260 mg, 0.30 mmol) instead of monohydroxyl-functionalized heptavinyl POSS. The crude product was purified by column chromatography using dichloromethane followed by dichloromethane–acetone (10:1 v/v) as eluent to afford pure tpy–C_6H_4–^{i}BuPOSS as a white solid. Yield: 80 mg, 0.067 mmol, 20 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 0.62 (t, 14H, *J* = 8.1 Hz, –CH_2–Si), 0.72 (t, 2H, *J* = 8.2 Hz, –CH_2–), 0.96–0.98 (m, 42H, –CH_3), 1.74–1.78 (m, 2H, –CH_2–), 1.82–1.90 (m, 7H, –CH–), 3.51 (q, 2H, *J* = 6.0 Hz, –CH_2–N), 6.20 (t, 1H, *J* = 4.4 Hz, –NH–), 7.38 (t, 2H, *J* = 6.3 Hz, tpy), 7.88–7.92 (m, 4H, tpy and –C_6H_4–), 7.98 (d, 2H, *J* = 7.9 Hz, –C_6H_4–), 8.69 (d, 2H, *J* = 7.9 Hz, tpy), 8.74–8.76 (m, 4H, tpy). Positive FAB-MS: *m*/*z*: 1209 $[M + H]^+$. IR (KBr) : 1111 cm^{-1} ν(Si–O). Anal. Found (%): C, 52.31; H, 7.06; N, 4.42. Calcd for tpy–C_6H_4–^{i}BuPOSS: C, 52.61; H, 7.00; N, 4.63.



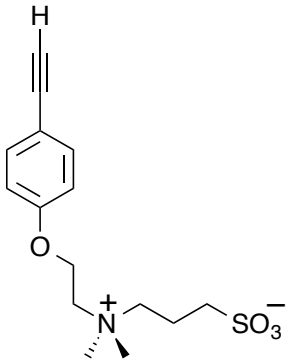

= Heptaphenyl–POSS

PhPOSS–phenyl–terpyridine (tpy–C_6H_4–PhPOSS): The titled ligand was prepared according to the procedure similar to that described for the preparation of tpy–C_6H_4–^{i}BuPOSS, except 3-aminopropylheptaphenyl POSS (PhPOSS−NH_2, 400 mg, 0.39 mmol) was used in place of ^{i}BuPOSS−NH_2. The product was further recrystallizing in ethanol to afford pure tpy–C_6H_4–PhPOSS as a white solid. Yield: 90 mg, 0.07 mmol, 20 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 0.95 (t, 2H, J = 8.1 Hz, –CH_2–Si), 1.86 (m, 2H, –CH_2–), 3.50 (q, 2H, J = 6.8 Hz, –CH_2–N), 6.07 (t, 1H, J = 5.0 Hz, –NH–), 7.31–7.46, 7.73–7.78 (m, 41H, Si–C_6H_5, –C_6H_4– and tpy), 7.89 (d, 2H, J = 8.3 Hz, –C_6H_4–), 8.68 (d, 2H, J = 8.0 Hz, tpy), 8.73–8.75 (m, 4H, tpy). Positive FAB-MS: *m/z*: 1349 $[M + H]^+$. IR (KBr) : 1134 cm^{-1} ν(Si–O). Anal. Found (%): C, 59.65; H, 4.62; N, 3.86. Calcd for tpy–C_6H_4–PhPOSS•EtOH: C, 59.37; H, 4.48; N, 4.01.

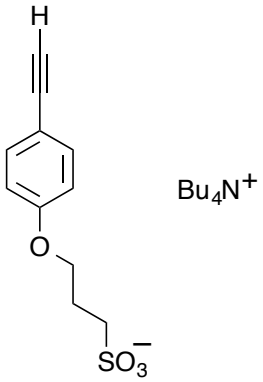


 = Heptaisobutyl–POSS

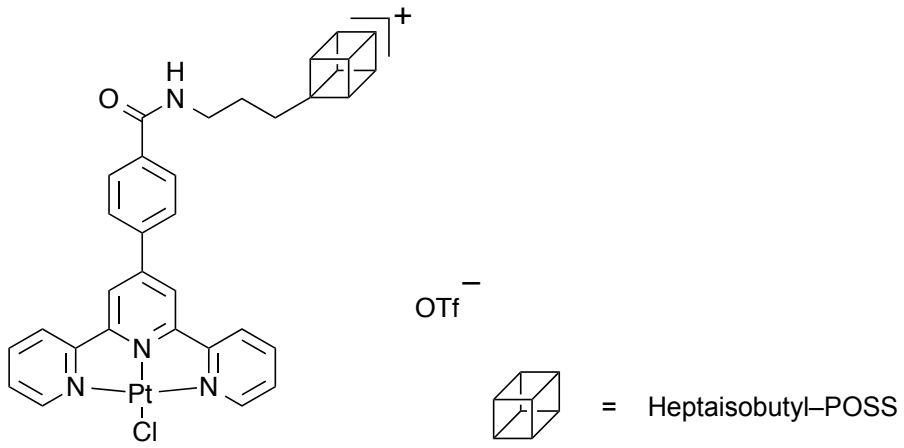
***i*BuPOSS–terpyridine (tpy–*i*BuPOSS):** The titled ligand was prepared according to the procedure similar to that described for the preparation of tpy–C_6H_4–*i*BuPOSS, except 2,2':6',2''-terpyridine-4'-carboxylic acid was used in place of 4'-carboxyphenyl-2,2':6',2''-terpyridine to afford pure tpy–*i*BuPOSS as a white solid. Yield: 140 mg, 0.12 mmol, 30 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 0.61 (t, 14H, *J* = 8.1 Hz, –CH_2–Si), 0.70 (t, 2H, *J* = 8.1 Hz, –CH_2–), 0.95–0.97 (m, 42H, –CH_3), 1.70–1.78 (m, 2H, –CH_2–), 1.81–1.89 (m, 7H, –CH–), 3.51 (q, 2H, *J* = 6.2 Hz, –CH_2–N), 6.45 (m, 1H, –NH–), 7.37 (t, 2H, *J* = 6.7 Hz, tpy), 7.88 (t, 2H, *J* = 6.7 Hz, tpy), 8.62 (d, 2H, *J* = 6.7 Hz, tpy), 8.73 (d, 2H, *J* = 6.7 Hz, tpy), 8.77 (s, 2H, tpy). Positive FAB-MS: *m*/*z*: 1133 $[M + H]^+$. IR (KBr) : 1107 cm^{-1} ν(Si–O). Anal. Found (%): C, 49.06; H, 7.11; N, 4.94. Calcd for tpy–*i*BuPOSS•H_2O: C, 49.01; H, 7.18; N, 4.86.



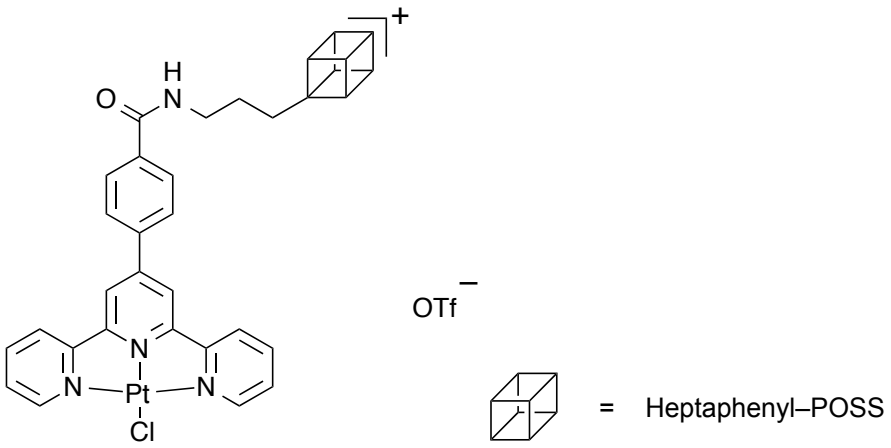
HC≡C–C_6H_4–sulfobetaine (sulfobetaine–alkyne). The titled ligand was prepared according to a modified literature method[10] using 2-(4-ethynylphenoxy)-N,N-dimethyl-ethanamine (800 mg, 4.23 mmol) instead of dimethylethylamine. The product was collected by filtration and was further recrystallized in methanol and diethyl ether to give sulfobetaine–alkyne as a white solid. Yield: 800 mg, 2.5 mmol, 60 %. ^{1}H NMR (300 MHz, [D_4]MeOD, 297 K, relative to Me_4Si): δ 2.25–2.33 (m, 2H, –CH_2–), 2.89 (t, 2H, J = 6.8 Hz, –CH_2–), 3.24 (s, 6H, –CH_3), 3.38 (s, 1H, –C≡C–H), 3.62–3.68 (m, 2H, –CH_2–), 3.86 (t, 2H, J = 4.6 Hz, –CH_2–), 4.50 (m, 2H, –CH_2–), 7.02 (d, 2H, J = 8.8 Hz, –C_6H_4–), 7.44 (d, 2H, J = 8.8 Hz, –C_6H_4–). Positive FAB-MS: *m/z*: 312 [M + H]$^+$. Anal. Found (%): C, 56.88; H, 6.86; N, 4.45. Calcd for sulfobetaine–alkyne•0.5MeOH: C, 56.86; H, 7.08; N, 4.28.



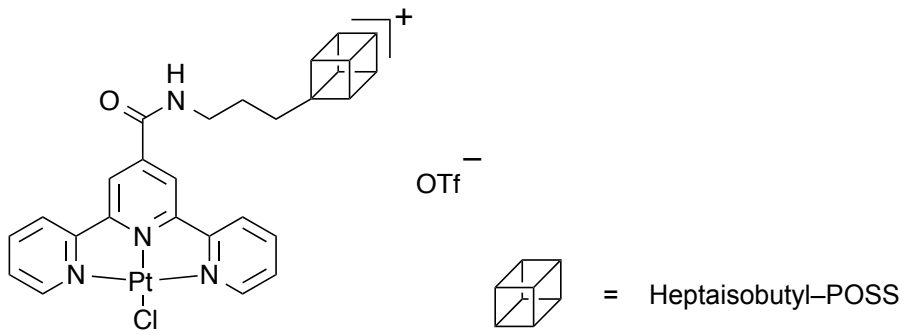
HC≡C–C_6H_4–sulfonate (sulfonate–alkyne). The titled ligand was prepared according to a modified literature method[11] using 4-ethynylphenol (800 mg, 6.78 mmol) and TBAOH•30H_2O (4.6 g, 5.75 mmol) instead of 4-bromophenol and K_2CO_3 respectively to yield pure sulfonate–alkyne as brown oil. Yield: 550 mg, 1.2 mmol, 20%. ^{1}H NMR (300 MHz, $CDCl_3$, 297 K, relative to Me_4Si): δ 0.98–1.03 (m, 12H, TBA), 1.41–1.48 (m, 8H, TBA), 1.59–1.68 (m, 8H, TBA), 2.29–2.32 (m, 2H, –CH_2–), 2.96–2.99 (m, 3H, –CH_2– and –C≡C–H), 3.26–3.32 (m, 8H, TBA), 4.13 (m, 2H, –CH_2–), 6.82 (d, 2H, *J* = 8.8 Hz, –C_6H_4–), 7.38 (d, 2H, *J* = 8.8 Hz, –C_6H_4–). Negative ESI-MS: *m/z*: 239 $[M]^-$. HRMS (Negative ESI) calcd for $C_{11}H_{11}O_4S$: *m/z*: 239.0378; found: 239.0353 $[M]^-$.



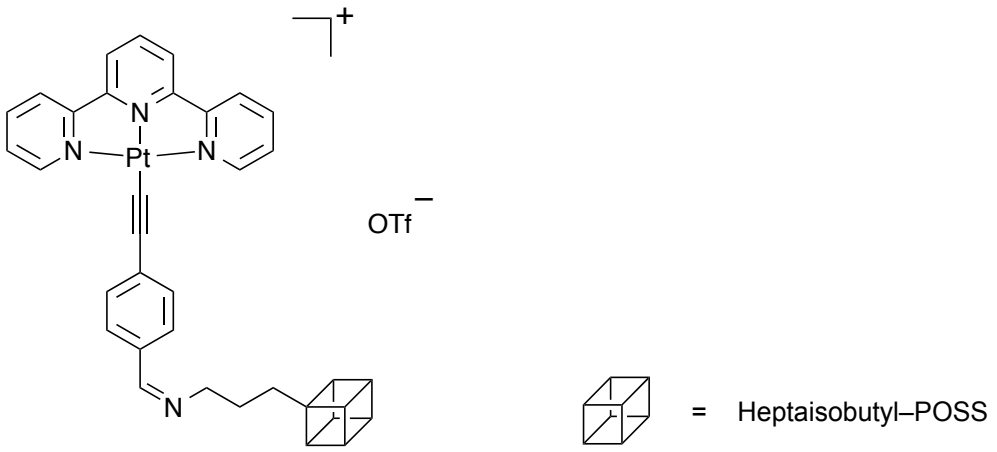
[Pt(tpy–C_6H_4–^{i}BuPOSS)Cl]OTf: The chloroplatinum(II) precursor complex was prepared according to a modified literature method for the synthesis of chloroplatinum(II) terpyridine complexes[12] using tpy–C_6H_4–^{i}BuPOSS instead of terpyridine. The crude product was recrystallized in ethyl acetate and hexane (3:1 v/v) mixture to give the precursor complex as an orange solid. Yield: 270 mg, 0.17 mmol, 65 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 0.61 (t, 14H, *J* = 7.7 Hz, –CH_2–Si), 0.69 (t, 2H, *J* = 8.4 Hz, –CH_2–), 0.95–0.96 (m, 42H, –CH_3), 1.70–1.76 (m, 2H, –CH_2–), 1.81–1.91 (m, 7H, –CH–), 3.47 (q, 2H, *J* = 5.5 Hz, –CH_2–N), 6.66 (t, 1H, *J* = 6.0 Hz, –NH–), 7.60 (d, 2H, *J* = 8.3 Hz, –C_6H_4–), 7.72 (t, 2H, *J* = 6.6 Hz, tpy), 7.91 (d, 2H, *J* = 8.3 Hz, –C_6H_4–), 8.26 (t, 2H, *J* = 7.6 Hz, tpy), 8.54 (s, 2H, tpy), 8.73 (d, 2H, *J* = 7.6 Hz, tpy), 9.01 (d, 2H, *J* = 7.6 Hz, tpy). Positive FAB-MS: *m*/*z*: 1440 [M − OTf]$^+$. IR (KBr) : 1111 cm^{-1} ν(Si–O). Anal. Found (%): C, 39.97; H, 5.21; N, 3.49. Calcd for [Pt(tpy–C_6H_4–^{i}BuPOSS)Cl]OTf •2H_2O: C, 39.90; H, 5.46; N, 3.45.



[Pt(tpy–C_6H_4–PhPOSS)Cl]OTf: The chloroplatinum(II) precursor complex was prepared according to a modified literature method for the synthesis of chloroplatinum(II) terpyridine complexes[12] using tpy–C_6H_4–PhPOSS instead of terpyridine. The crude product was recrystallized with chloroform and diethyl ether to give the pure precursor complex as a yellow solid. Yield: 310 mg, 0.18 mmol, 70 %. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 0.90 (t, 2H, *J* = 8.0 Hz, –CH_2–Si–), 1.81–1.82 (m, 2H, –CH_2–), 3.41–3.43 (m, 2H, –CH_2–N), 6.53 (m, 1H, –NH–), 7.34–7.45, 7.72 –7.79 (m, 39H, Si–C_6H_5, tpy and –C_6H_4–), 7.87 (d, 2H, *J* = 8.0 Hz, –C_6H_4–), 8.17 (t, 2H, *J* = 7.3 Hz, tpy), 8.47 (s, 2H, tpy), 8.66 (d, 2H, *J* = 7.3 Hz, tpy), 8.90 (d, 2H, *J* = 7.3 Hz, tpy). Positive ESI-MS: *m/z*: 1580 [M − OTf]$^+$. IR (KBr) : 1134 cm^{-1} ν(Si–O). Anal. Found (%): C, 43.72; H, 3.10; N, 2.77. Calcd for [Pt(tpy–C_6H_4–PhPOSS)Cl]OTf •1.5$CHCl_3$: C, 43.74; H, 3.04; N, 2.99.

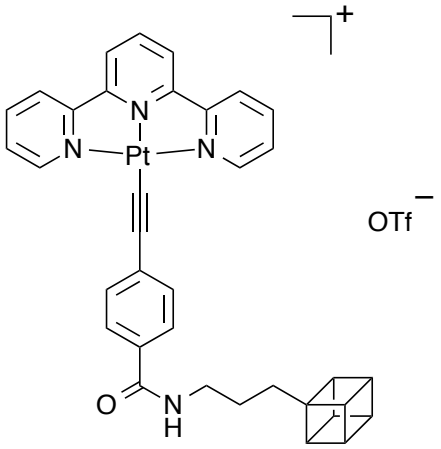


[Pt(tpy–^{i}BuPOSS)Cl]OTf: The chloroplatinum(II) precursor complex was prepared according to a modified literature method for the synthesis of chloroplatinum(II) terpyridine complexes[12] using tpy–^{i}BuPOSS (340 mg, 0.30 mmol) instead of terpyridine. The crude product was purified by column chromatography using dichloromethane-acetonitrile (2:1 v/v) mixture as eluent followed by recrystallization in methanol to give the pure precursor complex as a golden yellow solid. Yield: 240 mg, 0.16 mmol, 60 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ 0.57–0.63 (m, 14H, –CH_2–Si), 0.70 (t, 2H, J = 8.5 Hz, –CH_2–), 0.94–0.96 (m, 42H, –CH_3), 1.80–1.88 (m, 9H, –CH_2– and –CH–), 3.50 (q, 2H, J = 6.7 Hz, –CH_2–N), 7.83 (t, 2H, J = 6.6 Hz, tpy), 8.40 (t, 2H, J = 6.6 Hz, tpy), 8.60 (d, 2H, J = 6.6 Hz, tpy), 8.89 (t, 2H, J = 5.4 Hz, –NH–), 8.98 (s, 2H, tpy), 9.18 (d, 2H, J = 6.6 Hz, tpy). Positive FAB-MS: *m/z*: 1363 $[M - OTf]^+$. IR (KBr) : 1107 cm^{-1} ν(Si–O). Anal. Found (%): C, 37.72; H, 5.40; N, 3.67. Calcd for [Pt(tpy–^{i}BuPOSS)Cl]OTf•H_2O: C, 37.65; H, 5.40; N, 3.66.



[Pt(tpy)(C≡C–C_6H_4–CH=N–^{i}BuPOSS)]OTf (1): Complex **1** was prepared according to a modified literature method for the synthesis of alkynylplatinum(II) terpyridine complexes.[13] Alkyne ligand (HC≡C–C_6H_4–CH=N–^{i}BuPOSS, 135 mg, 0.09 mmol), which was prepared according to a modified literature method[14] using 3-aminopropylisobutyl POSS instead of benzyl amine, was added to a solution of chloroplatinum(II) precursor complex (135 mg, 0.10 mmol) in degassed dichloromethane with triethylamine and a catalytic amount of CuI. The resultant solution was stirred overnight at ambient temperature, followed by recrystallization in dichloromethane and diethyl ether to afford **1** as a dark solid. Yield: 30 mg, 0.020 mmol, 20 %. ^{1}H NMR (400 MHz, [D_6]DMSO, 330 K, relative to Me_4Si): δ 0.60–0.63 (m, 14H, –CH_2–Si), 0.69 (t, 2H, *J* = 8.0 Hz, –CH_2–), 0.94–0.96 (m, 42H, –CH_3), 1.72–1.76 (m, 2H, –CH_2–), 1.81–1.88 (m, 7H, –CH–), 3.58 (t, 2H, *J* = 6.0 Hz, –CH_2–N), 7.57 (d, 2H, *J* = 7.9 Hz, –C_6H_4–), 7.71 (d, 2H, *J* = 7.9 Hz, –C_6H_4–), 7.95 (t, 2H, *J* = 6.1 Hz, tpy), 8.32 (s, 1H, –CH=N), 8.51 (t, 2H, *J* = 6.1 Hz, tpy), 8.54–8.68 (m, 5H, tpy), 9.22 (d, 2H, *J* = 6.1 Hz, tpy). Positive FAB-MS: *m/z*: 1414 [M − OTf]$^+$. IR (KBr) : 1111 cm^{-1} ν(Si–O), 2120 cm^{-1} ν(C≡C). Anal.

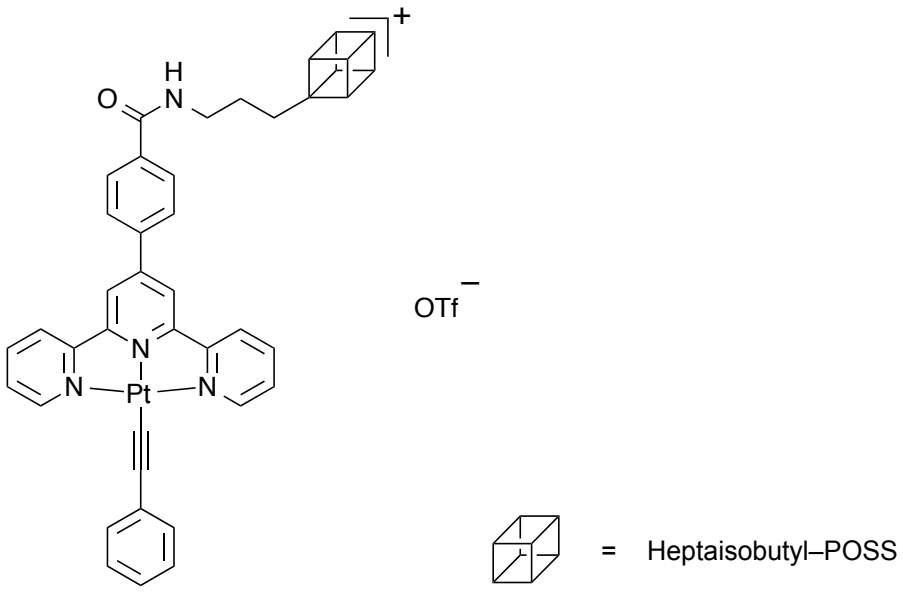
Found (%): C, 41.62; H, 5.36; N, 3.61. Calcd for **1**•CH_2Cl_2: C, 41.54; H, 5.32; N, 3.46.



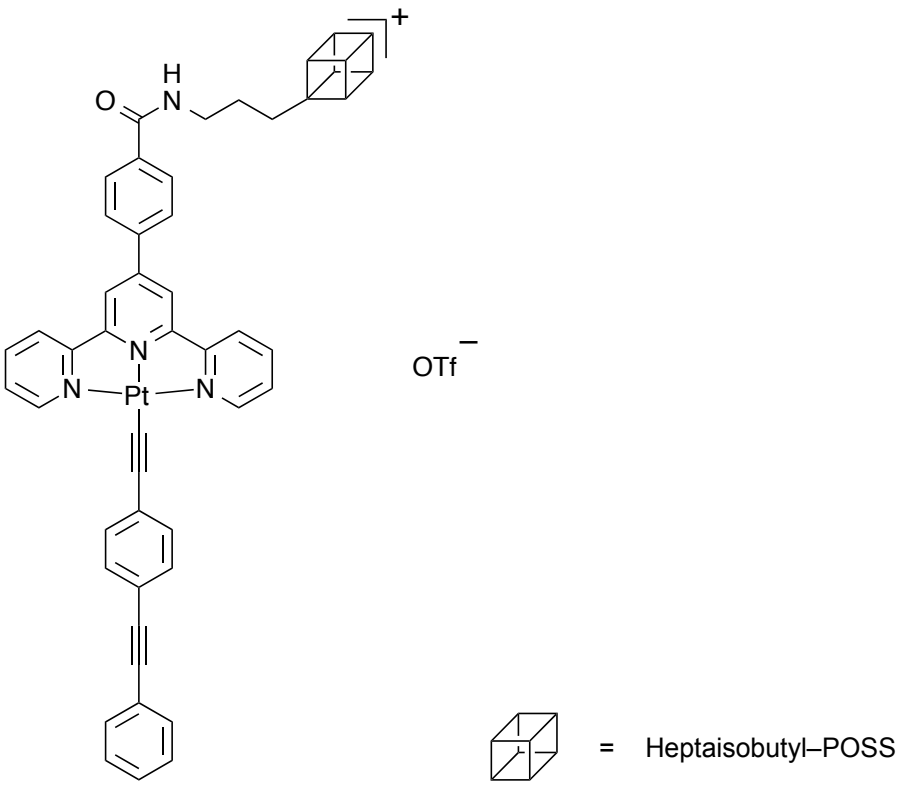
 = Heptaisobutyl–POSS

[Pt(tpy)(C≡C–C_6H_4–C=ONH–^{i}BuPOSS)]OTf (2): Complex **2** was prepared according to a modified literature method for the synthesis of alkynylplatinum(II) terpyridine complexes.[13] Alkyne ligand (HC≡C–C_6H_4–C=ONH–^{i}BuPOSS, 135 mg, 0.09 mmol), which was prepared according to the procedure similar to that described for the preparation of tpy–C_6H_4–^{i}BuPOSS, except 4-ethynylbenzoic acid was used in place of 4'-carboxyphenyl-2,2':6',2''-terpyridine, was added to a solution of chloroplatinum(II) precursor complex (135 mg, 0.10 mmol) in degassed dichloromethane with triethylamine and a catalytic amount of CuI. The resultant solution was stirred overnight at ambient temperature, followed by recrystallization in dimethylformamide and methanol to give **2** as a reddish brown solid. Yield: 43 mg, 0.030 mmol, 30 %. ^{1}H NMR (600 MHz, [D_6]DMSO, 350 K, relative to Me_4Si): δ 0.59–0.61 (m, 14H, –CH_2–Si), 0.65 (t, 2H, J = 8.3 Hz, –CH_2–), 0.93–0.94 (m, 42H, –CH_3), 1.61–1.64 (m, 2H, –CH_2–), 1.81–1.85 (m, 7H, –CH–), 3.25 (t, 2H, J = 6.5 Hz, –CH_2–N), 7.56 (d, 2H, J = 8.1 Hz, –C_6H_4–), 7.82 (d, 2H, J = 8.1 Hz, –C_6H_4–), 7.95 (t, 2H, J = 6.4 Hz, tpy), 8.25 (m, 1H, –NH–), 8.51 (t, 2H, J = 6.4 Hz, tpy), 8.57–8.66 (m, 5H, tpy), 9.23 (d, 2H, J = 6.4 Hz, tpy). Positive ESI-MS: *m/z*: 1429 $[M - OTf]^+$. HRMS (Positive ESI) calcd for $C_{55}H_{85}O_{13}N_4PtSi_8$: *m/z*: 1429.3921; found: 1429.4033 $[M - OTf]^+$. IR (KBr) : 1111 cm^{-1} ν(Si–O), 2122

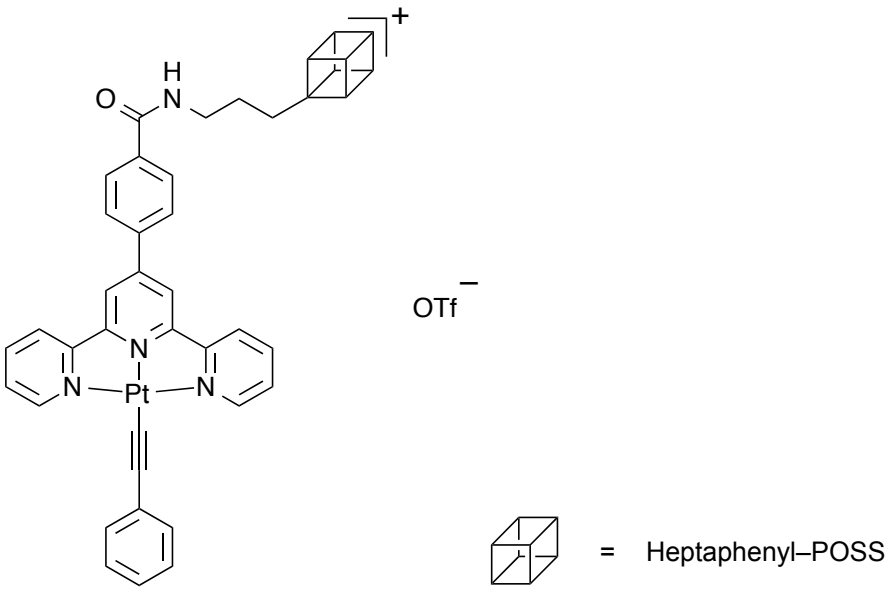
cm^{-1} ν(C≡C). Anal. Found (%): C, 40.71; H, 5.50; N, 3.25. Calcd for **2**•1.5CH_2Cl_2: C, 40.47; H, 5.20; N, 3.28.



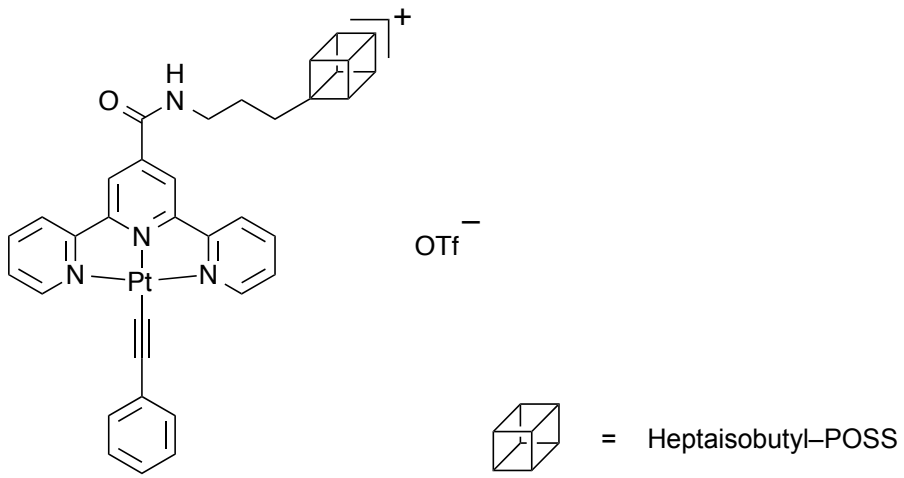
[Pt(^{i}BuPOSS–Ph–tpy)(C≡C–C_6H_5)]OTf (3). Complex **3** was prepared according to a modified literature method for the synthesis of alkynylplatinum(II) terpyridine complexes,[13] except that chloroplatinum(II) precursor complex [Pt(tpy–C_6H_4–^{i}BuPOSS)Cl]OTf (135 mg, 0.09 mmol) was used. The crude product was purified by column chromatography using dichloromethane-acetone (3:1 v/v) mixture as eluent to give **3** as a dark red solid. Yield: 70 mg, 0.043 mmol, 50 %. ^{1}H NMR (400 MHz, [D_6]DMSO, 330 K, relative to Me_4Si): δ 0.62 (t, 14H, *J* = 7.3 Hz, –CH_2–Si), 0.69 (t, 2H, *J* = 8.1 Hz, –CH_2–), 0.94–0.96 (m, 42H, –CH_3), 1.66–1.70 (m, 2H, –CH_2–), 1.81–1.88 (m, 7H, –CH–), 3.32 (q, 2H, *J* = 6.0 Hz, –CH_2–N), 7.27 (t, 1H, *J* = 7.4 Hz, –C_6H_5), 7.36 (t, 2H, *J* = 7.4 Hz, –C_6H_5), 7.51 (d, 2H, *J* = 7.4 Hz, –C_6H_5), 7.98 (t, 2H, *J* = 6.5 Hz, tpy), 8.11 (d, 2H, *J* = 8.4 Hz, –C_6H_4–), 8.28 (d, 2H, *J* = 8.4 Hz, –C_6H_4–), 8.54–8.57 (m, 3H, tpy and –NH–), 8.87 (d, 2H, *J* = 6.5 Hz, tpy), 9.12 (s, 2H, tpy), 9.25 (d, 2H, *J* = 6.5 Hz, tpy). Positive FAB-MS: *m/z*: 1505 [M − OTf]$^+$. IR (KBr) : 1111 cm^{-1} ν(Si–O), 2122 cm^{-1} ν(C≡C). Anal. Found (%): C, 42.71; H, 4.95; N, 3.40. Calcd for **3**•$CHCl_3$: C, 42.64; H, 5.11; N, 3.16.



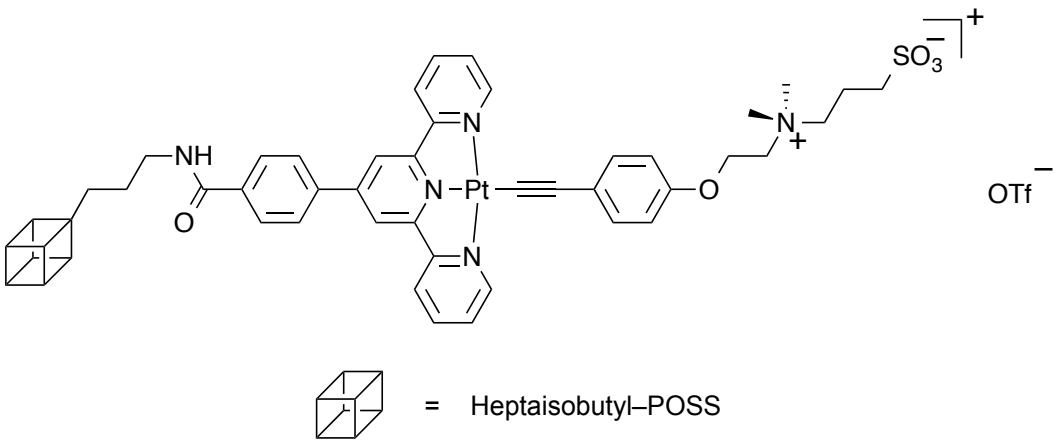
[Pt(*i*BuPOSS–Ph–tpy)(C≡C–C_6H_4–C≡C–C_6H_5)]OTf (4). Complex **4** was prepared according to the procedure similar to that described for the preparation of **3**, except 4–(phenylethynyl)phenylacetylene (70 mg, 0.35 mmol) was used in place of phenylacetylene to give **4** as a dark red solid. Yield: 70 mg, 0.040 mmol, 40 %. ^{1}H NMR (400 MHz, [D_6]DMSO, 340 K, relative to Me_4Si): δ 0.60–0.64 (m, 14H, –CH_2–Si), 0.70 (t, 2H, *J* = 8.2 Hz, –CH_2–), 0.95–0.97 (m, 42H, –CH_3), 1.67–1.71 (m, 2H, –CH_2–), 1.81–1.89 (m, 7H, –CH–), 3.33 (q, 2H, *J* = 6.8 Hz, –CH_2–N), 7.43–7.45 (m, 3H, –C_6H_4–C≡C–C_6H_5), 7.52–7.58 (m, 6H, –C_6H_4–C≡C–C_6H_5), 7.99 (t, 2H, *J* = 6.4 Hz, tpy), 8.11 (d, 2H, *J* = 8.4 Hz, –C_6H_4–), 8.28 (d, 2H, *J* = 8.4 Hz, –C_6H_4–), 8.49 (t, 1H, *J* = 5.4 Hz, –NH–), 8.56 (t, 2H, *J* = 6.4 Hz, tpy), 8.89 (d, 2H, *J* = 6.4 Hz, tpy), 9.06 (s, 2H, tpy), 9.27 (d, 2H, *J* = 6.4 Hz, tpy). Positive FAB-MS: *m/z*: 1606 [M − OTf]$^+$. IR (KBr) : 1111 cm^{-1} ν(Si–O), 2116 cm^{-1} ν(C≡C). Anal. Found (%): C, 48.15; H, 5.54; N, 3.32. Calcd for **4**: C, 47.90; H, 5.34; N, 3.19.



[Pt(PhPOSS–Ph–tpy)(C≡C–C_6H_5)]OTf (5). Complex **5** was prepared according to the procedure similar to that described for the preparation of **3**, except [Pt(tpy–C_6H_4–PhPOSS)Cl]OTf (100 mg, 0.06 mmol) was used to give **5** as an orange solid. Yield: 60 mg, 0.032 mmol, 60 %. ^{1}H NMR (400 MHz, [D_6]DMSO, 330 K, relative to Me_4Si): δ 1.01 (t, 2H, *J* = 7.7 Hz, –CH_2–Si–), 1.79–1.84 (m, 2H, –CH_2–), 3.36 (m, 2H, –CH_2–N), 7.21–7.53, 7.68 –7.76 (m, 40H, –C_6H_5), 7.98 (d, 2H, *J* = 7.5 Hz, tpy), 8.09 (d, 2H, *J* = 8.4 Hz, –C_6H_4–), 8.25 (d, 2H, *J* = 8.4 Hz, –C_6H_4–), 8.53–8.57 (m, 3H, tpy and –NH–), 8.86 (d, 2H, *J* = 7.5 Hz, tpy), 9.04 (s, 2H, tpy), 9.26 (d, 2H, *J* = 7.5 Hz, tpy). Positive FAB-MS: *m/z*: 1647 [M − OTf]$^+$. IR (KBr) : 1134 cm^{-1} ν(Si–O), 2122 cm^{-1} ν(C≡C). Anal. Found (%): C, 47.72; H, 3.52; N, 3.10. Calcd for **5**•2CH_2Cl_2: C, 47.68; H, 3.33; N, 2.85.

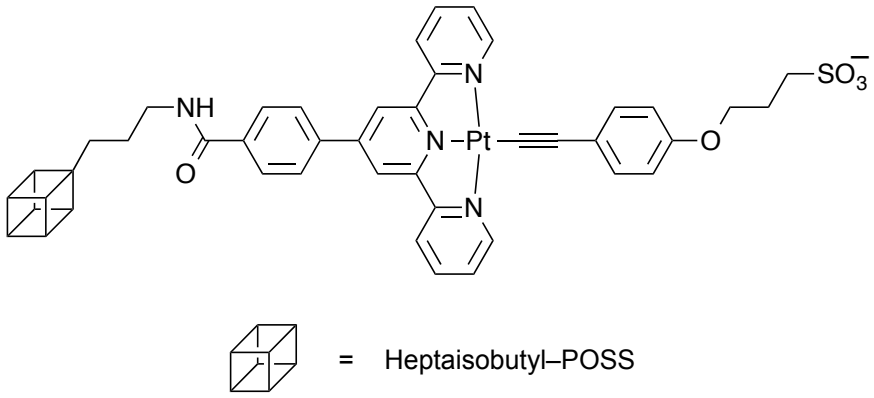


[Pt(^{i}BuPOSS–tpy)(C≡C–C_6H_5)]OTf (6). Complex **6** was prepared according to the procedure similar to that described for the preparation of **3**, except [Pt(tpy–^{i}BuPOSS)Cl]OTf (100 mg, 0.07 mmol) was used. The resulting product was further recrystallized in chloroform and methanol to give pure **6** as a reddish-brown solid. Yield: 40 mg, 0.026 mmol, 40 %. ^{1}H NMR (400 MHz, [D_6]DMSO, 330 K, relative to Me_4Si): δ 0.62 (t, 14H, *J* = 7.1 Hz, –CH_2–Si), 0.74 (t, 2H, *J* = 8.1 Hz, –CH_2–), 0.94–0.98 (m, 42H, –CH_3), 1.69–1.74 (m, 2H, –CH_2–), 1.80–1.88 (m, 7H, –CH–), 3.40 (q, 2H, *J* = 6.0 Hz, –CH_2–N), 7.28 (t, 1H, *J* = 7.3 Hz, –C_6H_5), 7.37 (t, 2H, *J* = 7.3 Hz, –C_6H_5), 7.52 (d, 2H, *J* = 7.3 Hz, –C_6H_5), 8.00 (t, 2H, *J* = 6.0 Hz, tpy), 8.55 (t, 2H, *J* = 7.1 Hz, tpy), 8.68 (d, 2H, *J* = 7.1 Hz, tpy), 8.90–8.93 (m, 3H, tpy and –NH–), 9.26 (d, 2H, *J* = 7.1 Hz, tpy). Positive FAB-MS: *m/z*: 1428 [M − OTf]$^+$. IR (KBr) : 1109 cm^{-1} ν(Si–O), 2120 cm^{-1} ν(C≡C). Anal. Found (%): C, 39.39; H, 5.17; N, 3.24. Calcd for **6**•1.5$CHCl_3$: C, 39.28; H, 4.96; N, 3.19.



 = Heptaisobutyl–POSS

[Pt(*i*BuPOSS–Ph–tpy)(C≡C–C_6H_4–sulfobetaine)]OTf (7). Complex **7** was prepared according to the procedure similar to that described for the preparation of **3**, except sulfobetaine–alkyne (100 mg, 0.32 mmol) was used in place of phenylacetylene. The solid was further recrystallized in dichloromethane and hexane to give **7** as a dark red solid. Yield: 60 mg, 0.032 mmol, 35 %. ^{1}H NMR (400 MHz, [D_6]DMSO, 330 K, relative to Me_4Si): δ 0.62 (t, 14H, *J* = 7.4 Hz, –CH_2–Si), 0.69 (t, 2H, *J* = 7.2 Hz, –CH_2–), 0.94–0.96 (m, 42H, –CH_3), 1.10 (m, 2H, –CH–), 1.65–1.68 (m, 4H, –CH_2–), 1.80–1.87 (m, 7H, –CH–), 2.09–2.11 (m, 2H, –CH–), 3.32 (q, 2H, *J* = 6.5 Hz, –CH_2–), 3.58–3.62 (m, 2H, –CH_2–), 3.80 (t, 2H, *J* = 5.0 Hz, –CH_2–), 4.50 (m, 2H, –CH_2–), 7.04 (d, 2H, *J* = 8.6 Hz, –C_6H_4–O), 7.49 (d, 2H, *J* = 8.6 Hz, –C_6H_4–O), 7.99 (t, 2H, *J* = 7.0 Hz, tpy), 8.11 (d, 2H, *J* = 8.4 Hz, –C_6H_4–), 8.28 (d, 2H, *J* = 8.4 Hz, –C_6H_4–), 8.54–8.58 (m, 3H, tpy and –NH–), 8.88 (d, 2H, *J* = 7.0 Hz, tpy), 9.07 (s, 2H, tpy), 9.26 (d, 2H, *J* = 7.0 Hz, tpy). Positive FAB-MS: *m/z*: 1713 [M − OTf]$^+$. IR (KBr) : 1109 cm^{-1} ν(Si–O), 2154 cm^{-1} ν(C≡C). Anal. Found (%): C, 43.63; H, 5.74; N, 3.84. Calcd for **7**•2H_2O: C, 43.61; H, 5.73; N, 3.69.



 = Heptaisobutyl–POSS

[Pt(*i*BuPOSS–Ph–tpy)(C≡C–C_6H_4–sulfonate)] (8). Complex **8** was prepared according to the procedure similar to that described for the preparation of **3**, except sulfonate–alkyne (90 mg, 0.38 mmol) was used in place of phenylacetylene. The solid was further recrystallized in chloroform and hexane to give **8** as a dark solid. Yield: 30 mg, 0.020 mmol, 20 %. ^{1}H NMR (500 MHz, [D_6]DMSO, 353 K, relative to Me_4Si): δ 0.62 (m, 14H, –CH_2–Si), 0.69 (t, 2H, J = 7.5 Hz, –CH_2–), 0.94–0.96 (m, 42H, –CH_3), 1.70 (m, 2H, –CH_2–), 1.85 (m, 7H, –CH–), 3.33 (m, 2H, –CH_2–), 4.14 (m, 2H,–CH_2–), 6.90 (d, 2H, J = 7.8 Hz, –C_6H_4–), 7.40 (d, 2H, J = 7.8 Hz, –C_6H_4–), 7.97 (br, 2H, tpy), 8.08 (d, 2H, J = 7.1 Hz, –C_6H_4–), 8.22 (d, 2H, J = 7.1 Hz, –C_6H_4–), 8.31 (br, 1H, –NH–), 8.50 (br, 3H, tpy), 8.81 (br, 2H, tpy), 8.97 (s, 2H, tpy), 9.27 (br, 2H, tpy). Positive FAB-MS: *m/z*: 1642 [M – OTf]$^+$. IR (KBr) : 1111 cm^{-1} ν(Si–O), 2137 cm^{-1} ν(C≡C). Anal. Found (%): C, 44.07; H, 5.58; N, 3.15. Calcd for **8**•$CHCl_3$: C, 44.29; H, 5.43; N, 3.18.

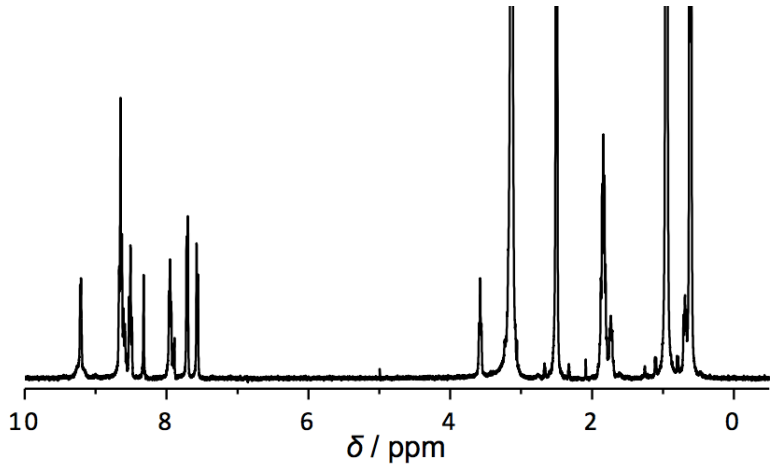


Figure S14. ^{1}H NMR spectrum of **1** in [D_6]DMSO at 330 K.

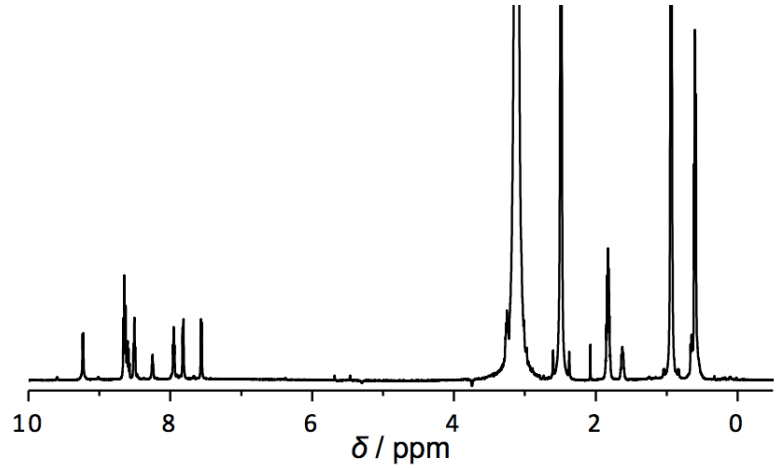


Figure S15. ^{1}H NMR spectrum of **2** in [D_6]DMSO at 330 K.

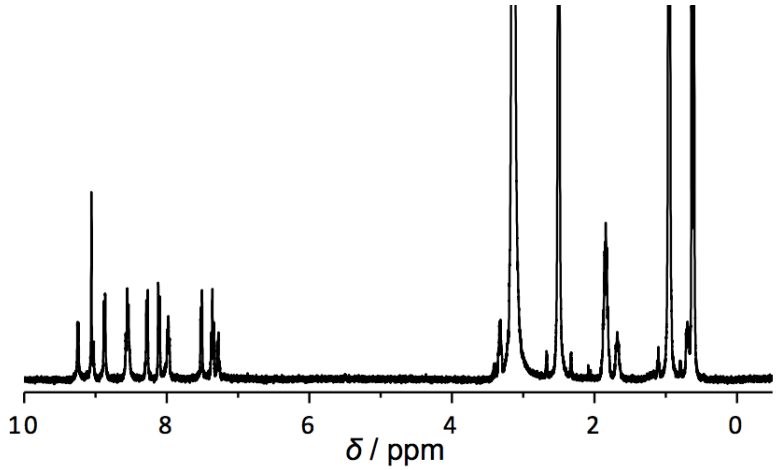


Figure S16. ^{1}H NMR spectrum of **3** in [D_6]DMSO at 330 K.

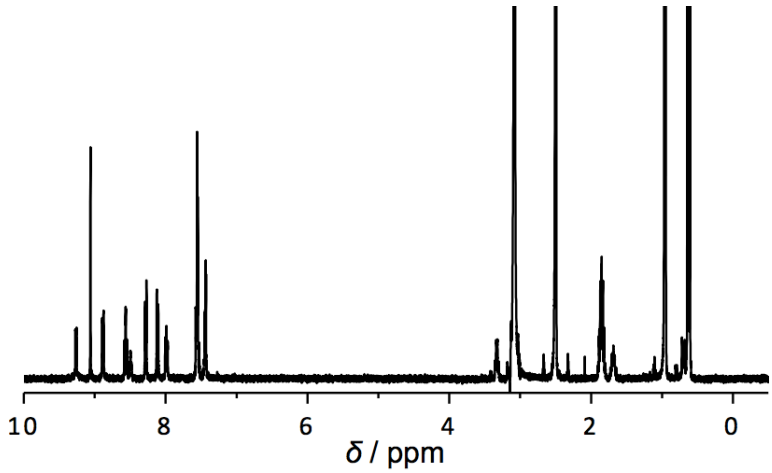


Figure S17. ^{1}H NMR spectrum of **4** in [D_6]DMSO at 330 K.

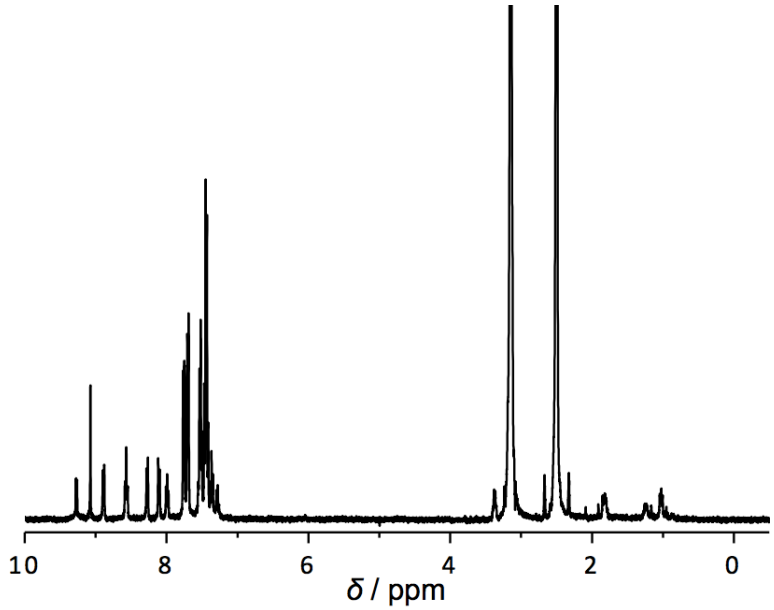


Figure S18. ^{1}H NMR spectrum of **5** in [D_6]DMSO at 340 K.

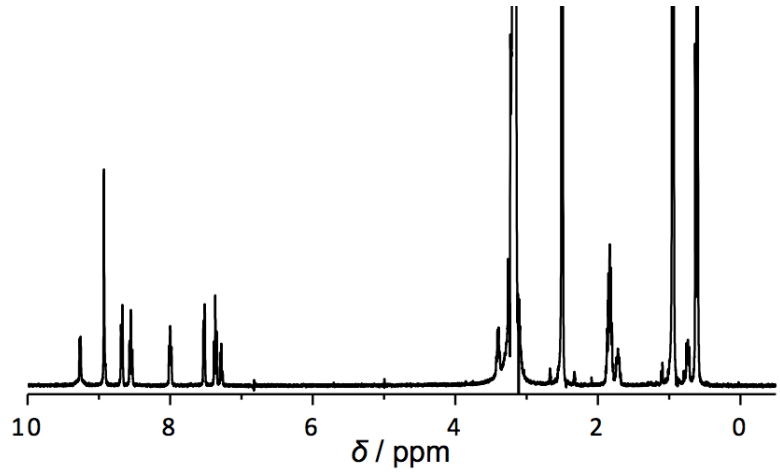


Figure S19. ^{1}H NMR spectrum of **6** in [D_6]DMSO at 330 K.

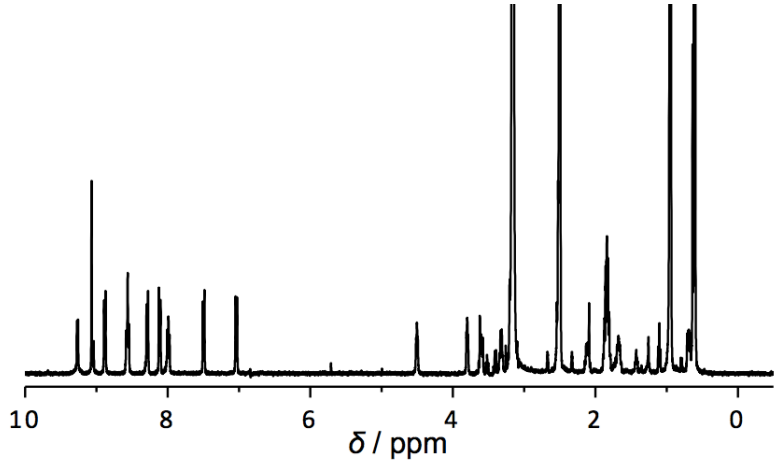


Figure S20. ^{1}H NMR spectrum of **7** in [D_6]DMSO at 330 K.

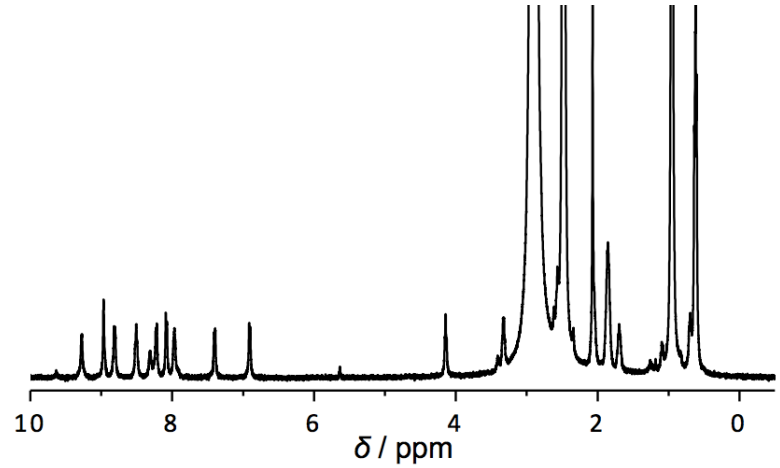


Figure S21. ^{1}H NMR spectrum of **8** in [D_6]DMSO at 353 K.

Curve-fitting with the nucleation-elongation equilibrium model. The nucleation-elongation model for solvent-dependent self-assembly was reported by Meijer and coworkers.[15] In this model, the Gibbs free energy gain upon monomer addition $\Delta G^{0,}$ is linearly correlated with the good solvent volume fraction f:

$$\Delta G^{0,} = \Delta G^{0} + m \cdot f$$

where ΔG^{0} is the Gibbs free energy gain upon monomer addition in poor solvent and m is the parameter showing the dependence of $\Delta G^{0,}$ on f.

The normalized degree of aggregation was deduced from the changes in UV-vis absorption band maxima (**5**, *ca*. 530 nm),

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

where f is the THF volume fraction.

The simulations and the curve-fittings with the equilibrium model were performed using Matlab R2013a under an isodesmic system.[15,16]

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