Supporting Information

Cyclometalated Platinum(II) Complexes of 1,3-Bis(1-*n*-butylpyrazol-3-yl)benzenes: Synthesis, Characterization, Electrochemical, Photophysical, and Gelation Behavior Studies

Yeye Ai,[a,b] Yongguang Li,*[a] Huiqing Ma,[a] Cheng-Yong Su,[a] Vivian Wing-Wah Yam*[a,b]

[a] Lehn Institute of Functional Materials, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, (P. R. China)

[b] 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)

Fax: (+)(852) 2857-1586; E-mail: liyongguang@mail.sysu.edu.cn; wwyam@hku.hk

Experimental section

General. All starting materials were obtained from commercial suppliers and were used as received. 1,3-Diacetytlbenzene, 4-iodoaniline, 2-propynylamine, 1-bromobutane, and trimethylsilylacetylene were purchased from Aladdin Industrial Co. *N*,*N*-Dimethylformamide dimethyl acetal, K_2PtCl_4, and 4-methoxyphenylacetylene were obtained from Energy Chemical. 4-Nitrophenylacetylene was supplied by Bide Pharmatech Ltd. Hydrazine hydrate was provided from J&K Scientic Ltd. 1-Bromohexadecane was supplied by Beijing HWRK Chen Co. Cholesteryl chloroformate (99%) was purchased from Alfa Aesar. Cholesteryl 4-ethynylphenyl carbamate and cholesteryl 2-propyn-1-yl carbamate were synthesized according to literature-reported procedures.[1] 1,3-Di(1*H*-pyrazol-3-yl)benzene, 1,3-bis(1-*n*-butyl-1*H*-pyrazol-3-yl)benzene, 1,3-bis(1-*n*-hexadecanyl-1*H*-pyrazol-3-yl)benzene, cholesterol acid amide phenylacetylene, and complexes **1** and **2** were synthesized according to modifications of the methods described in the literature.[2]

Physical measurements and instrumentation

^{1}H NMR spectra were recorded on a Bruker DPX 400 FT–NMR spectrometer (400 MHz) at 298 K. Electrospray ionization mass spectra were performed on a Bruker Maxis 4G ESI–Q–TOF using electrospray ionization (positive ion mode: ESI) in acetonitrile or methanol solution. Elemental analyses of the complexes were performed on a Vario EL elemental analyzer at the instrumental analysis & research center, Sun Yat–Sen University, Guangzhou, China.

Electronic absorption spectra were recorded using a Shimadzu UV–3600 spectrophotometer. The photoluminescence spectra were measured on Edinburgh FS 5 or FLS 980 fluorescence

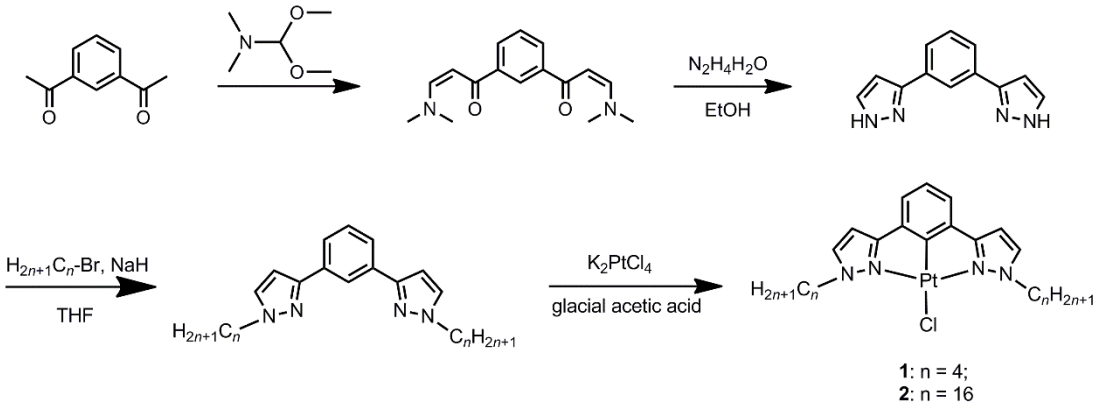
spectrophotometer. All solutions for photophysical studies were prepared under high vacuum in a 10 cm^3 round-bottomed flask equipped with a sidearm 1 cm fluorescence cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were rigorously degassed on a high-vacuum line in a two-compartment cell with no less than five successive freeze-pump-thaw cycles. Solid-state photophysical measurements were carried out with the solid sample loaded on a quartz glass slide. Liquid nitrogen was placed into the Dewar flask for low temperature (77 K) photophysical measurements. CD measurements were recorded using a Jasco (Tokyo, Japan) J–810 CD spectropolarimeter with the metallogel sealed in a 10×1 mm quartz cell. Scanning electron microscope experiments were performed by using Thermal Field Emission Enviromental Sem Eds EBSD on quanta 400F or Sigma 300/VP. The SEM sample was prepared by dropping dilute gels onto a silicon wafer. Slow evaporation of solvents in air for at least two days led to xerogels. The digital photographs of metallogels were taken by Sony ILCE-7. Cyclic voltammetric measurements ware performed by using a CH Instruments, Inc. model CHI 760 E electrochemical analyzer using a three-electrode single-cell compartment in a dichloromethane solution with 0.1 M $^{n}Bu_4PF_6$ as supporting electrolyte at room temperature. The reference electrode was an $Ag/AgNO_3$ (0.1 $moldm^{-3}$ in acetonitrile) electrode and the working electrode was a glassy carbon electrode (Gaossunion, Inc.) with a platinum wire as the counter electrode. The working electrode surface was first polished with a 1 μm alumina slurry (Gaossunion, Inc.) on a microcloth (Gaossunion, Inc.) and then with a 0.3μm alumina slurry (Gaossunion, Inc.). It was then rinsed with ultra-pure deionized water and sonicated in a beaker containing ultra-pure water for 3 times. The working electrode was finally rinsed under a stream of ultra-pure deionized water. The ferrocenium / ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference.[3] All solutions for electrochemical

studies was degassed with pre-purified argon prior measurements.

Crystal structure determination. Single-crystal diffraction data of complex **1** and **5** were collected on an Agilent SuperNova X-ray diffractometer using micro-focus dual with X-ray Source of Cu–Kα radiation (λ = 1.54178 Å) at 293 K and 150 K respectively. Using Olex2[4] the structure was solved with the ShelXS[5] structure solution program using direct methods and refined with the XL[5] refinement package using least squares minimization.

Gelation test: The gelator and the solvent were placed in a screw-capped sample vial and the mixture was heated until the solid dissolved. The sample vial was cooled in atmospheric air, and was then left for 1 min at room temperature. The state of the materials was evaluated by the "stable-to-inversion of a test tube" method.

Synthetic methods and characterization:



Scheme S1. Synthetic routes of bpzb ligands and complexes **1**–**2.**

Synthesis of 1,3-di(1*H*-pyrazol-3-yl)benzene: A mixture of 1,1'-(1,3-phenylene)bis(3-(dimethylamino)prop-2-en-1-one) (150 mg, 0.55 mmol), $N_2H_4 \cdot H_2O$ (0.39 mL, 8.25 mmol) and ethanol (3 mL) was heated at 70℃ overnight. After cooling to room temperature, acetone was added to quench the excess $N_2H_4 \cdot H_2O$. Removal of the solvent under reduced pressure afforded the crude product. The pure product was obtained after washing with acetone / water (1:1 v / v; 50 mL). Yield: 115 mg, 85 %; ^{1}H NMR (400 MHz, [D_6]DMSO, 298 K): δ = 6.78 (d, J = 2.0 Hz, 2H; pyrazolyl proton), 7.45 (t, J = 7.7 Hz, 1H; phenyl proton), 7.73–7.75 (m, 4H; phenyl and pyrazolyl proton), 8.23 (s, 1H; phenyl proton), 12.93 ppm (br s, 2H; pyrazolyl proton); MS (ESI$^+$): m/z: 211.11 $[M+H]^+$.

Synthesis of 1,3-bis(1-*n*-butylpyrazilyl-3-yl)benzene: NaH (1.67 g, 41.1 mmol) and 1-bromobutane (7 mL, 51.4 mmol) were added to the solution of 1,3-di(1*H*-pyrazol-3-yl)benzene (2.16 g, 10.3 mmol) in THF (100 mL), and the mixture was heated at 70℃ for 2 days under N_2. After removal of the solvents, the organic phase was washed with deionized water (3 times) and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure afforded the crude

product, which was purified by column chromatography on silica gel using dichloromethane-ethyl acetate (1:1 v / v) as the eluent to give the desired product as a yellow oil. Yield: 2.24 g, 68 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.96 (t, J = 4 Hz, 6H; –*CH*$_3$), 1.33–1.42 (m, 4H; –*CH*$_2$–CH_3), 1.86–1.94 (m, 4H; –*CH*$_2$–CH_2CH_3), 4.17 (t, J = 7.2 Hz, 4H; N–*CH*$_2$–), 6.60 (d, J = 2.3 Hz, 2H; pyrazolyl proton), 7.39–7.42 (m, 3H; phenyl and pyrazolyl proton), 7.73–7.75 (m, 2H; phenyl proton), 8.17 ppm (t, J = 1.6 Hz, 1H; phenyl proton); MS (ESI$^+$): m/z: 322.24 [M+H]$^+$.

Synthesis of 1,3-bis(1-*n*-hexadecylpyrazilyl-3-yl)benzene: The procedure was similar to that for 1,3-bis(1-*n*-butylpyrazilyl-3-yl)benzene, except 1-bromohexadecane (5.00 g, 16.34 mmol) was used in place of 1-bromobutane. The crude product was purified by column chromatography on silica gel using dichloromethane-ethyl acetate (50:1 v / v) as the eluent to give the desired product as a white solid. Yield: 2.00 g, 77 %; ^{1}H NMR (400 MHz, [D_6]DMSO, 298 K, relative to Me_4Si): δ = 0.84 (t, J = 6.8 Hz, 6H; –*CH*$_3$), 1.15–1.41 (m, 52H; –*(CH*$_2$*)*$_{13}$–CH_3), 1.78–1.83 (m, 4H; N–CH_2–*CH*$_2$–), 4.13 (t, J = 7.0 Hz, 4H; N–*CH*$_2$–), 6.70 (d, J = 2.2 Hz, 2H; pyrazolyl proton), 7.38 (t, J = 7.7 Hz, 1H; phenyl proton), 7.65–7.67 (m, 2H; phenyl proton), 7.76 (d, J = 2.2 Hz, 2H; pyrazolyl proton), 8.21 ppm (s, 1H; phenyl proton); MS (ESI$^+$): m/z: 659.62 [M].

Synthesis of complex 1: 1,3-Bis(1-*n*-butyl-1*H*-pyrazol-3-yl)benzene (1 g, 2.40 mmol) and K_2PtCl_4 (1 g, 2.40 mmol) were added into glacial acetic acid (15 mL). The mixture was heated to 108 ℃ for 5 days. Dark green solid was obtained after filtration and was washed with diethyl ether. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in DMSO gave **1** as light green crystals. Yield: 1.33 g, 63 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.95 (t, J = 7.4 Hz, 6H; –*CH*$_3$), 1.34–1.43 (m, 4H; –*CH*$_2$–CH_3), 1.89–1.96 (m, 4H; –*CH*$_2$–CH_2CH_3), 4.89 (t, J = 7.1 Hz, 4H; N–*CH*$_2$-), 6.46 (d, J = 2.7 Hz, 2H; pyrazolyl proton),

7.10–7.18 (m, 3H; phenyl and pyrazolyl proton), 7.41 ppm (d, J = 2.7 Hz, 2H; phenyl proton); MS (ESI^+): m/z : 516.15 $[M–Cl]^+$; elemental analysis calcd (%) for $C_{20}H_{25}ClN_4Pt$ (**1**): C 43.52, H 4.57, N 10.15; found: C 43.41, H 4.43, N 10.12.

Synthesis of complex 2: The procedure was similar to that for **1**, except 1,3-bis(1-*n*-hexadecylpyrazilyl-3-yl)benzene (1.03 g, 1.57 mmol) was used in place of 1,3-bis(1-*n*-butylpyrazilyl-3-yl)benzene to give the product as a green solid. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **2** as a pale green solid. Yield: 447 mg, 42 %; ^1H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.87 (t, J = 6.8 Hz, 6H; $–CH_3$), 1.23–1.32 (m, 52H; $–(CH_2)_{13}–CH_3$), 1.90–1.97 (m, 4H; $N–CH_2–CH_2–$), 4.87 (t, J = 7.2 Hz, 4H; $N–CH_2–$), 6.46 (d, J = 2.7 Hz, 2H; pyrazolyl proton), 7.10–7.18 (m, 3H; phenyl and pyrazolyl proton), 7.39–7.44 ppm (d, J = 2.7 Hz, 2H; phenyl proton); MS (ESI^+): *m/z* : 852.76 $[M–Cl]^+$; elemental analysis calcd (%) for $C_{44}H_{73}ClN_4Pt$ (**2**): C 59.52, H 8.23, N 6.31; found: C 59.48, H 8.30, N 6.10.

Synthesis of complex 3: Sodium hydroxide (14 mg, 0.36 mmol) was added into a well-stirred solution of phenylacetylene (0.036 mL, 0.36 mmol) in methanol (15 mL). After stirring for 30 min, complex **1** was added to the above reaction mixture. The mixture was stirred for 24 h at RT. The light yellow solid was obtained after filtration and washed with deionized water, methanol and *n*-hexane in succession. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **3** as a light yellow solid. Yield: 73 mg, 62 %. ^1H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.87 (t, J = 7.4 Hz, 6H; $–CH_3$), 1.24–1.34 (m, 4H; $–CH_2–CH_3$), 1.92–1.99 (m, 4H; $–CH_2–CH_2CH_3$), 4.96 (t, J = 7.0 Hz, 4H; $N–CH_2–$), 6.46 (d, J = 2.7 Hz, 2H; pyrazolyl proton), 7.09–7.14 (m, 2H; phenyl and pyrazolyl proton), 7.23–7.25 (m,

3H; phenyl proton), 7.38–7.40 ppm (m, 5H; phenyl and pyrazolyl proton) ; MS (ESI^+): *m/z* : 617.21 $[M]^+$; 516.18 [*M*–alkynyl]$^+$; elemental analysis calcd (%) for $C_{28}H_{30}N_4Pt$ (**3**): C 54.45, 4.90, 9.07; found: C 54.14, H 4.79, N 9.06.

Synthesis of complex 4: The procedure was similar to that for complex **3**, except 4-methoxyphenylacetylene (48 mg, 0.36 mmol) was used in place of phenylacetylene to give the product as a yellow solid. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **4** as yellow crystals. Yield: 107 mg, 91 %; ^{1}H NMR (400 MHz, [D_6]DMSO, 298 K): δ = 0.83 (t, *J* = 7.3 Hz, 6H; –*CH*$_3$), 1.20–1.25 (m, 4H; –*CH*$_2$–CH_3), 1.80–1.88 (m, 4H; –*CH*$_2$–CH_2CH_3), 3.74 (s, 3H; –O*CH*$_3$), 4.96 (t, *J* = 6.8 Hz, 4H; N–*CH*$_2$–), 6.67 (d, *J* = 1.6 Hz, 2H; pyrazolyl proton), 6.85 (d, *J* = 8.2 Hz, 2H; phenyl proton), 7.10 (t, *J* = 7.5 Hz, 1H; phenyl proton), 7.18 (d, *J* = 8.2 Hz, 2H; phenyl proton), 7.34 (d, *J* = 7.5 Hz, 2H; phenyl proton), 8.01 ppm (d, *J* = 1.6 Hz, 2H; pyrazolyl proton); MS (ESI^+): *m/z* : 647.23 $[M]^+$; 516.78 [*M*–alkynyl]$^+$; elemental analysis calcd (%) for $C_{29}H_{32}N_4OPt$ (**4**): C 53.78, H 4.98, N 8.65; found: C 54.14, H 4.79, N 9.06.

Synthesis of complex 5: The procedure was similar to that for complex **3**, except 4-nitrophenylacetylene (79 mg, 0.36 mmol) was used in place of phenylacetylene to give the product as an orange solid. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **5** as orange crystals. Yield: 112 mg, 93 %; ^{1}H NMR (400 MHz, [D_6]DMSO, 298 K): δ = 0.83 (t, *J* = 7.2 Hz, 6H; –*CH*$_3$), 1.14–1.23 (m, 4H; –*CH*$_2$–CH_3), 1.79–1.87 (m, 4H; –*CH*$_2$–CH_2CH_3), 4.96 (t, *J* = 6.9 Hz, 4H; N–*CH*$_2$–), 6.67 (d, *J* = 0.8 Hz, 2H; pyrazolyl proton),7.12 (t, *J* = 7.5 Hz, 1H; phenyl proton), 7.36 (d, *J* = 7.5 Hz, 2H; phenyl proton), 7.45 (d, *J* = 8.3 Hz, 2H; phenyl proton), 8.05 (d, *J* = 1.6 Hz, 2H; pyrazolyl proton), 8.16

ppm (d, J = 8.3 Hz, 2H; phenyl proton); MS (ESI^+): *m/z* : 663.19 $[M]^+$, 516.16 [*M*–alkynyl]$^+$; elemental analysis calcd (%) for $C_{28}H_{29}N_5O_2Pt$ (**5**·H_2O·0.5C_6H_{14}): C 51.45, H 5.26, N 9.68; found: C 51.69, H 4.91, N 9.49.

Synthesis of complex 6: The procedure was similar to that for complex **3**, except 4-ethynylaniline (35 mg, 0.36 mmol) was used in place of phenylacetylene to give the product as a pale yellow solid. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **6** as a brown solid. Yield: 100 mg, 87 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.88 (t, J = 7.4 Hz, 6H; –*CH*$_3$), 1.26–1.35 (m, 4H; –*CH*$_2$–CH_3), 1.91–1.99 (m, 4H; –*CH*$_2$–CH_2CH_3), 3.61 (s, 2H; –*NH*$_2$), 5.00 (t, J = 7.0 Hz, 4H; N–*CH*$_2$–), 6.45 (d, J = 2.7 Hz, 2H; pyrazolyl proton), 6.60 (d, J = 8.5 Hz, 2H; phenyl proton), 7.10 (t, J = 7.5 Hz, 1H; phenyl proton), 7.20–7.26 (m, 4H; phenyl proton), 7.38 ppm (d, J = 2.7 Hz, 2H; pyrazolyl proton); MS (ESI^+): *m/z* : 632.24 $[M]^+$, 516.18 [*M*–alkynyl]$^+$; elemental analysis calcd (%) for $C_{28}H_{31}N_5Pt$ (**6**·0.5H_2O): C 52.41, H 5.03, N 10.91; found: C 52.42, H 4.82, N 10.83.

Synthesis of complex 7: The procedure was similar to that for complex **3**, except cholesteryl 4-ethynylphenyl carbamate (192 mg, 0.36 mmol) was used in place of phenylacetylene to give the product as a pale yellow solid. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **7** as a pale yellow solid. Yield: 174 mg, 92 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.68 (s, 3H; cholesteryl proton), 0.86–1.54 (m, 43 H; cholesteryl proton, –*CH*$_2$–*CH*$_3$ and –(*CH*$_3$)$_2$), 1.78–2.03 (m, 9 H; cholesteryl proton and –*CH*$_2$–CH_2*CH*$_3$), 2.31–2.46 (m, 2H; cholesteryl proton), 4.56–4.64 (m, 1H, –O*CH*– on cholesteryl proton), 4.96 (t, J = 7.0 Hz, 4H; N–*CH*$_2$–), 5.40 (s, 1H, –*CH*=C– on cholesteryl), 6.45–6.48 (m, 3H; pyrazolyl proton and –*NH*–), 7.11 (t, J = 7.5 Hz, 1H; phenyl proton), 7.24–7.45 ppm (m, 8H; phenyl

and pyrazolyl proton); MS (ESI^+): *m/z* : 516.18 [*M*–alkynyl]$^+$; elemental analysis calcd (%) for $C_{56}H_{75}N_5O_2Pt$ (**7**): C 64.34, H 7.23, N 6.70; found: C 64.55, H 7.30, N 6.46.

Synthesis of complex 8: The procedure was similar to that for complex **3**, except cholesteryl 2-propyn-1-yl carbamate (197 mg, 0.36 mmol) was used in place of phenylacetylene to give the product as a pale yellow solid. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **8** as a light yellow solid. Yield: 113 mg, 63 %; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.68 (s, 3H; cholesteryl proton), 0.86–1.60 (m, 43 H; cholesteryl proton, –*CH*$_2$–*CH*$_3$ and –(*CH*$_3$)$_2$), 1.78–2.02 (m, 9 H; cholesteryl proton and –*CH*$_2$–CH_2CH_3), 2.25–2.39 (m, 2H; cholesteryl proton), 4.26 (d, *J* = 4.5 Hz, 2H; –NH–*CH*$_2$–), 4.45–4.51 (m, 1H, –O*CH*– on cholesteryl proton), 4.75 (s, 1H; –*NH*–), 4.92 (t, *J* = 7.1 Hz, 4H; –N–*CH*$_2$–), 5.38 (s, 1H, –*CH*=C– on cholesteryl), 6.44 (d, *J* = 2.7 Hz, 2H; pyrazolyl proton), 7.10 (t, *J* = 7.5 Hz, 1H; phenyl proton), 7.22–7.25 (d, *J* = 7.5 Hz, 2H; phenyl proton), 7.38 ppm (d, *J* = 2.7 Hz, 2H; pyrazolyl proton); MS (ESI^+): *m/z* : 516.34 [*M*–alkynyl]$^+$; elemental analysis calcd (%) for $C_{51}H_{73}N_5O_2Pt$ (**8**): C 62.30, H 7.48, N 7.12; found: C 61.93, H 7.54, N 6.96.

Synthesis of complex 9: The procedure was similar to that for complex **3**, except cholesteryl 4-ethynylphenyl carbamate (119 mg, 0.22 mmol) and complex **2** were used in place of phenylacetylene and complex **1** respectively in methanol and CH_2Cl_2 mixed solvent (1:1 v / v; 30 mL) under N_2 atmosphere. The mixture was stirred for 24 h at RT. After evaporation of most solvent and filtration, the crude product was washed with deionized water, methanol and *n*-hexane in succession. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **9** as a light yellow solid. Yield: 131 mg, 84 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.68 (s, 3H; cholesteryl proton), 0.86–1.52 (m, 91 H;

cholesteryl proton, –*(CH₂)₁₃*–*CH₃* and –*(CH₃)₂*), 1.79–2.03 (m, 9 H; cholesteryl proton and –*CH₂*–CH_2CH_3), 2.30–2.45 (m, 2H; cholesteryl proton), 4.46–4.64 (m, 1H, –O*CH*– on cholesteryl proton), 4.93 (t, *J* = 7.1 Hz, 4H; –N–*CH₂*–), 5.41 (s, 1H, –*CH*=C– on cholesteryl), 6.45–6.47 (m, 3H; pyrazolyl proton and –*NH*–), 7.11 (t, *J* = 7.5 Hz, 1H; phenyl proton), 7.24–7.38 ppm (m, 8H; phenyl and pyrazolyl proton); MS (ESI^+): *m/z* : 852.76 [*M*–alkynyl]$^+$; elemental analysis calcd (%) for $C_{80}H_{123}N_5O_2Pt$ (**9**): C 69.53, H 8.97, N 5.07; found: C 69.45, H 9.02, N 4.77.

Synthesis of complex 10: The procedure was similar to that for complex **9**, except cholesteryl 2-propyn-1-yl carbamate (119 mg, 0.22 mmol) and complex **2** were used in place of cholesteryl 4-ethynylphenyl carbamate and complex **1** respectively to give the product as a light yellow solid. Subsequent recrystallization by vapor diffusion of diethyl ether into a solution of the product in dichloromethane gave **10** as a pale yellow solid. Yield: 119 mg, 80 %. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 0.67 (s, 3H; cholesteryl proton), 0.85–1.53(m, 91H; cholesteryl proton, –*(CH₂)₁₃*–*CH₃* and –*(CH₃)₂*), 1.82–2.02 (m, 9 H; cholesteryl proton and –*CH₂*–CH_2CH_3), 2.24–2.38 (m, 2H; cholesteryl proton), 4.25 (d, *J* = 2.6 Hz, 2H; –*CH₂*C≡C–), 4.46–4.53 (m, 1H, –O*CH*– on cholesteryl proton), 4.75 (s, 1H; –*NH*–), 4.89 (t, *J* = 6.7 Hz, 4H; –N–*CH₂*–), 5.37 (s, 1H, –*CH*=C– on cholesteryl), 6.43 (d, *J* = 2.7 Hz, 2H; pyrazolyl proton), 7.09 (t, *J* = 7.5 Hz, 1H; phenyl proton), 7.21–7.25 (d, *J* = 7.5 Hz, 2H; phenyl proton), 7.38 ppm (d, *J* = 2.7 Hz, 2H; pyrazolyl proton); MS (ESI^+): *m/z* : 852.76 [*M*–alkynyl]$^+$; elemental analysis calcd (%) for $C_{75}H_{121}N_5O_2Pt$ (**10**): C 68.25, H 9.24, N 5.31; found: C 68.16, H 9.34, N 5.01.

Table S1. Selected bond distances (Å) and bond angles (deg) for complexes **1** and **5** with estimated standard deviations (e.s.d.s.) in parentheses.

1		**5**	
Bond Length [Å]			
Pt(1)–N(2)	2.059(5)	Pt(1)–N(2)	2.044(3)
Pt(1)–N(3)	2.050(5)	Pt(1)–N(3)	2.045(3)
Pt(1)–Cl(1)	2.4162(15)	Pt(1)–C(21)	2.058(4)
Pt(1)–C(9)	1.948(6)	Pt(1)–C(9)	1.978(4)
		C(21)–C(22)	1.208(6)
Bond angles [°]			
N(2)–Pt–C(9)	78.7(2)	N(2)–Pt–C(9)	77.54(15)
N(3)–Pt–C(9)	78.6(2)	N(3)–Pt–C(9)	78.33(15)
N(2)–Pt–N(3)	157.28(19)	N(2)–Pt–N(3)	155.85(13)
C(9)–Pt–Cl(1)	179.70(19)	C(9)–Pt–C(21)	177.40(15)
		Pt(1)–C(21)–C(22)	175.3(3)

Table S2. Electrochemical data of complexes **1**–**10** and *p*-nitrophenylacetylene.

	Oxidation	Reduction
	E_{pa} /V vs SCE[a]	$E_{1/2}$ /V vs SCE[a]
1	+1.15[b]	–[c]
2	+1.14[b]	–[c]
3	+0.87[b]	–[c]
4	+0.84[b]	–[c]
5	+1.07[b]	–1.16[d]
6	+1.03[b]	–[c]
7	+0.86[b]	–[c]
8	+0.96[b]	–[c]
9	+1.05[b]	–[c]
10	+0.93[b]	–[c]
p–nitrophenylacetylene	–[e]	–0.97 [d]

[a] In dichloromethane solution with 0.1 $_{M}$ $^{n}Bu_4NPF_6$ as supporting electrolyte at room temperature; scan rate 100 mV s^{-1}.; $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are anodic peak and cathodic peak potentials. [b] Irreversible oxidation waves. [c] No reduction waves were recorded within the solvent window. [d] Quasi-reversible reduction waves. [e] No oxidation waves were recorded within the solvent window.

Table S3. Summary of gelation properties of complexes **7–10**.

Solvents	**7**	**8**	**9**	**10**
Methanol	P	P	P	P
Ethanol	P	P	P	P
Cyclohexane	P	P	CG[a] (2.6)	S
Toluene	S	S	S	S
THF	S	S	S	S
Acetone	S	S	P	P
i-propanol	P	P	P	P
n-butanol	P	P	OG[a] (7.5)	P
DMSO	S	S	OG[a] (3.9)	P

[a] The values in parentheses are the critical gelation concentrations in mg mL^{-1} at 25 ℃. G = Gel; OG = Opaque gel; P = Precipitation; S = Solution; CG = Clear gel.

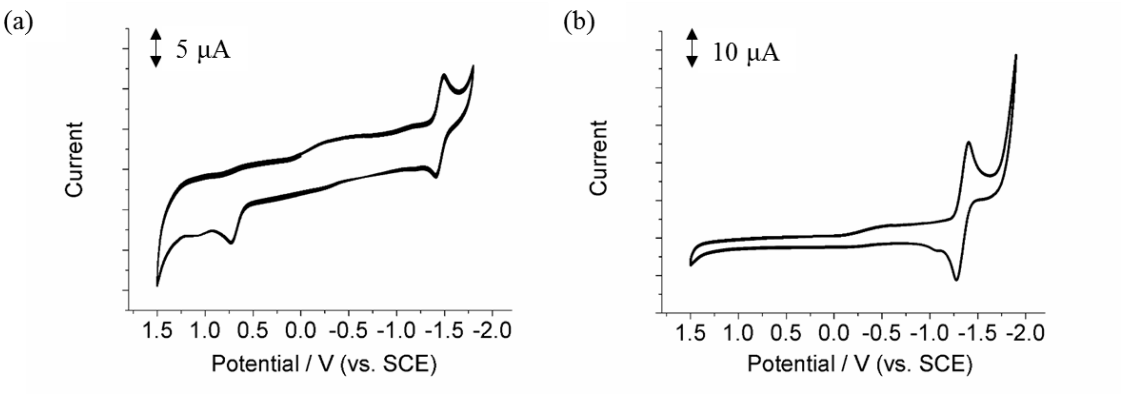


Figure S1. Cyclic voltammograms of (a) **5** and (b) *p*-nitrophenylacetylene ligand in CH_2Cl_2 (0.1 mol dm^{-3} $^nBu_4NPF_6$).

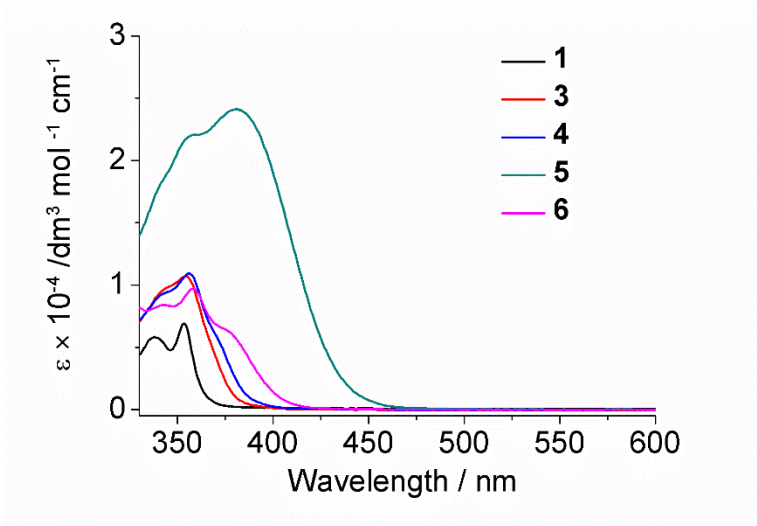


Figure S2. Electronic absorption spectra of complexes **1** and **3**–**6** in acetone at room temperature.

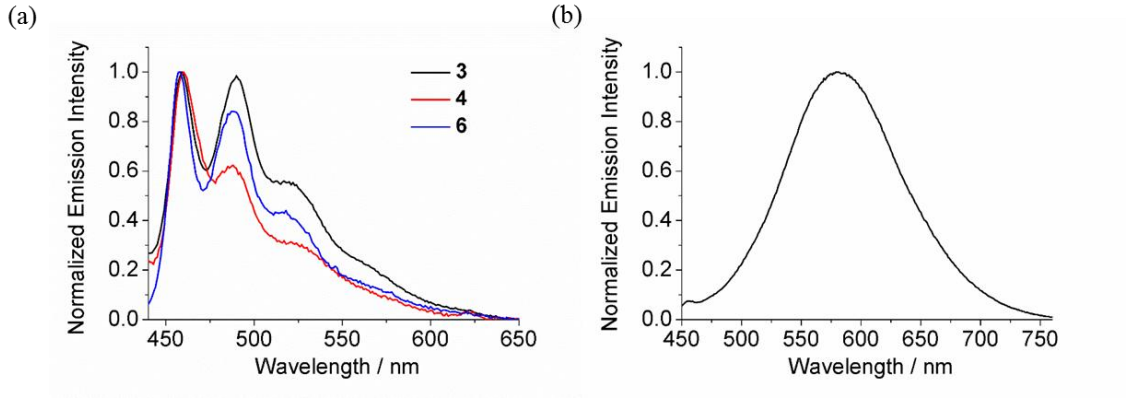


Figure S3. (a) Normalized emission spectra of complexes **3**, **4** and **6** in degassed dichloromethane solution at room temperature; (b) Normalized emission spectrum of complex **5** in degassed dichloromethane solution at room temperature.

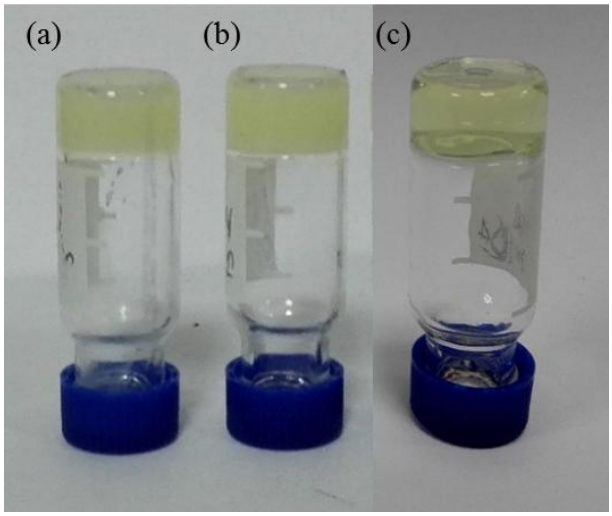


Figure S4. Photographs of metallogels of complex **9** in (a) *n*-butanol, (b) DMSO, and (c) cyclohexane.

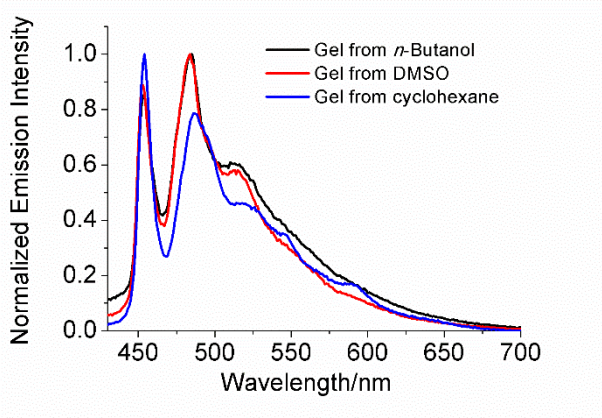


Figure S5. Normalized emission spectra of complex **9** in wet gel prepared from *n*-butanol, DMSO, cyclohexane.

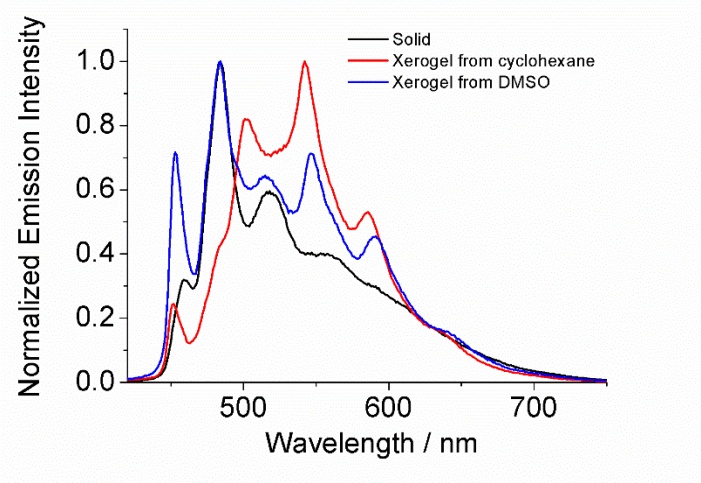


Figure S6. Normalized emission spectra of complex **9** in solid state and xerogel prepared from cyclohexane and DMSO.

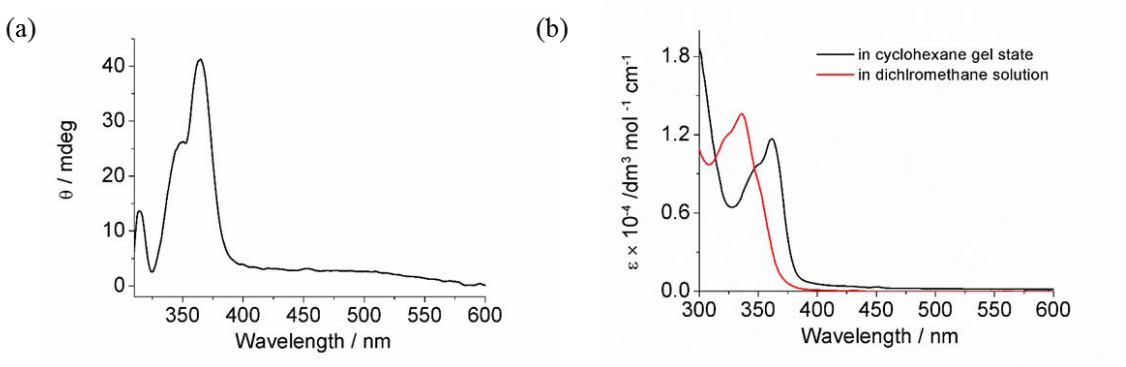


Figure S7. (a) CD spectra of the gel of complex **9** in cyclohexane at room temperature. (b) The electronic absorption spectra of complex **9** in cyclohexane gel state and dichloromethane solution at room temperature.

References:

(1) Li, Y. G.; Zhao, L.; Tam, A. Y.-Y.; K. Wong, M.-C.; Wu, L. X.; Yam, V. W.-W. Luminescent Amphiphilic 2,6-Bis(1,2,3-triazol-4-yl)pyridine Platinum(II) Complexes: Synthesis, Characterization, Electrochemical, Photophysical, and Langmuir–Blodgett Film-Formation Studies. *Chem. Eur. J.* **2013**, *19*, 14496–14505.

(2) Baik, C.; Han, W. S.; Kang, Y. J.; Kang, S. O.; Ko, J. J. Synthesis and Photophysical Properties of Luminescent Platinum(II) Complexes with Terdentate Polypyridine Ligands: [Pt(bpqb)X] and [Pt(tbbpqpy)X](PF_6) (Bpqb-H = 1,3-Bis(4'-phenyl-2'-quinolinyl) Benzene; Tbbpqpy = 4-*tert*-butyl-1,3-Bis(4'-phenyl-2'-quinolinyl)pyridine; X = Cl, C≡CC_6H_5, C≡C$C_6H_4NMe_2$, C≡C$C_6H_4NO_2$). *J. Organomet. Chem*. **2006**, *691*, 5900–5910.

(3) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. *Chem. Rev.* **1996**, *96*, 877–910.

(4) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339.

(5) Sheldrick, G. M. A Short History of *SHELX*. *Acta Cryst*. **2008**. *A64*, 112.