Electronic Supporting Information for:

Phosphorescent Self-Assembled PtII Tetranuclear Metallocycles

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Experimental Procedures

1H NMR spectra were recorded on a Bruker Avance 300 (300 MHz) or a Bruker Avance III 500 (500 MHz) spectrometer. All chemical shifts are referenced to the residual solvent signals previously referenced to TMS and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). 31P NMR spectra were run on a Bruker Avance III 500 spectrometer and chemical shifts were related to external 85% H3PO4. Mass spectra were measured using a Bruker Esquire 3000 Plus spectrometer.

Preparations: 4,4’-di(tert-butyl)-2,2’-bipyridine platinum dichloride [Pt(dbppy)Cl2],1 4-ethynylpyridine,2 4-((4-ethynylphenyl)ethynyl)pyridine,3 1-ethynyl-4-iodobenzene,4 Pt(dppp)(OTf)2,5 were synthesized according to literature procedures and yielded satisfactory mass and 1H NMR spectra.

General Procedure 1 for Chloride to Acetylide Metathesis. To an argon-degassed solution of the platinum dichloride precursor in CH2Cl2 and i-Pr2NH was added the acetylene derivate and CuI. The solution was stirred at room temperature for 12 h, and then the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel and recrystallization in a mixture of CH2Cl2 and n-hexanes.

General Procedure 2 for Polygons Synthesis. To a mixture of platinum bis-acetylide complex and Pt(dppp)(OTf)2 in a Schlenk flask was added CH3CN (5 mL). The mixture was heated at 60°C until complete dissolution of the starting materials and concentrated by rotary
evaporation to 1 mL before precipitation with Et₂O. The residue was purified by recrystallization in a mixture of CH₂Cl₂ and n-hexanes.

**Complex 1.** Prepared using the general procedure 1 from Pt(dbbpy)Cl₂ (72 mg, 0.13 mmol), 4-ethynylpyridine (35 mg, 0.33 mmol), CuI (1 mg, 0.01 mmol), CH₂Cl₂ (10 mL) and i-Pr₂NH (3 mL); chromatography eluting with CH₂Cl₂ to CH₂Cl₂-MeOH (v/v 99/1) to give 70 mg (78%) of 1 as a yellow solid after recrystallization. NMR ¹H (500 MHz, CD₂Cl₂): 9.58 (d, ᵃJ = 6.0 Hz, 2H), 8.42 (s, 4H), 8.03 (s, 2H), 7.63 (dd, ᵃJ = 6.0 Hz, ᵄJ = 2.0 Hz, 2H), 7.29 (d, ᵃJ = 4.0 Hz, 4H), 1.44 (s, 18H); NMR ¹³C (75.5 MHz, CD₂Cl₂): 164.9, 156.6, 151.2, 149.7, 136.1, 126.6, 125.3, 119.8, 100.1, 95.6, 36.2, 30.3; (UV-Vis (CH₃CN) λ, nm (ε, M⁻¹ cm⁻¹): 287 (49 900), 372 (9 200); MS m/z (nature of the peak, relative intensity): 668.2 ([M+H]⁺, 100); Anal. Calcd for C₃₂H₃₂N₄Pt + CH₂Cl₂: C, 52.66; H, 4.55; N, 7.54. Found: C, 52.77; H, 4.71; N, 7.78.

**Complex 2.** Prepared using the general procedure 1 from Pt(dbbpy)Cl₂ (200 mg, 0.37 mmol), 4-[(4-ethynylphenyl)ethynyl]pyridine (167 mg, 0.82 mmol), CuI (4 mg, 0.02 mmol), CH₂Cl₂ (40 mL) and i-Pr₂NH (8 mL); chromatography eluting with AcOEt to give 290 mg (89%) of 2 as a yellow solid after recrystallization. NMR ¹H (500 MHz, CD₂Cl₂): 9.56 (d, ᵃJ = 6.0 Hz, 2H), 8.56 (d, ᵃJ = 5.5 Hz, 4H), 8.02 (d, ᵄJ = 1.5 Hz, 2H), 7.63 (dd, ᵃJ = 6.0 Hz, ᵄJ = 1.5 Hz, 2H), 7.48 (s, 8H), 7.40 (d, ᵃJ = 5.5 Hz, 4H), 1.44 (s, 18H); NMR ¹³C (75.5 MHz, CD₂Cl₂): 164.2, 156.3, 150.8, 149.8, 131.9, 131.5, 131.4, 129.4, 125.3, 124.9, 119.3, 118.7, 101.6, 94.2, 92.0, 87.3, 35.8, 30.0; UV-Vis (CH₃CN) λ, nm (ε, M⁻¹ cm⁻¹): 322 (81 000), 343 (81 000), 385 (21 500); MS m/z (nature of the peak, relative intensity): 868.3 ([M+H]⁺, 100); Anal. Calcd for C₄₈H₄₀N₄Pt + CH₂Cl₂: C, 61.76; H, 4.44; N, 5.88. Found: C, 62.12; H, 4.54; N, 5.74.

**Complex 3a.** Prepared using the general procedure 1 from Pt(dbbpy)Cl₂ (670 mg, 1.25 mmol), 4-ethynylpyridine (136 mg, 1.32 mmol), 1-ethynyl-4-iodobenzene (300 mg, 1.32 mmol), CuI (12 mg, 0.06 mmol), CH₂Cl₂ (70 mL) and i-Pr₂NH (15 mL); chromatography eluting with CH₂Cl₂ to give 237 mg (24%) of 3 as a yellow solid after recrystallization. NMR ¹H (500 MHz, CD₂Cl₂): 9.54 (d, ᵃJ = 6.0 Hz, 1H), 9.49 (d, ᵃJ = 6.0 Hz, 1H), 8.48-8.45 (m, 2H), 8.02 (s, 2H), 7.62-7.57 (m, 4H), 7.48 (s, 8H), 7.30 (s, 2H), 7.21 (d, ᵃJ = 8.5 Hz, 2H), 1.44 (s, 18H); MS m/z (nature of the peak, relative intensity): 793.1 ([M+H]⁺, 100); Anal. Calcd for C₃₃H₃₂IN₄Pt + CH₂Cl₂: C, 46.53; H, 3.91; N, 4.79. Found: C, 46.19; H, 4.01; N, 4.70.
Complex 3. To a 30 min argon degassed solution of 3a (100 mg, 0.13 mmol), 4-ethynylpyridine (34 mg, 0.33 mmol) in CH$_3$CN (35 mL) and i-Pr$_2$NH (2 mL) was added tetrakis(triphenylphosphine)palladium(0) (8 mg, 6.50 x 10$^{-3}$ mmol). The solution was stirred at room temperature for 4 h, and then the solvent was evaporated under vacuum. The residue was purified by column chromatography on silica gel eluting with CH$_2$Cl$_2$ to CH$_2$Cl$_2$-MeOH (v/v 97.5 / 2.5) to give 62 mg (64 %) of 4 as a yellow solid after recrystallization in a mixture of CH$_2$Cl$_2$ and n-hexanes. NMR $^1$H (500 MHz, CD$_2$Cl$_2$): 9.56 (d, $^3$J = 6.0 Hz, 1H), 9.46 (d, $^3$J = 6.0 Hz, 1H), 8.57 (d, $^3$J = 4.5 Hz, 2H), 8.44 (s, 2H), 8.03 (d, $^4$J = 2.0 Hz, 2H), 7.65 (m, 2H), 7.46 (s, 4H), 7.40 (m, 4H), 1.44 (s, 18H); UV-Vis (CH$_3$CN) $\lambda$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 287 (43 200), 321 (4 5 300), 3 39 (4 2 400), 379  (1 4 800); MS m/z (nature of the peak, relative intensity): 768.3 ([M+H$^+$], 100); Anal. Calcd for C$_{40}$H$_{36}$N$_4$Pt + CH$_2$Cl$_2$: C, 57.75; H, 4.49; N, 6.57. Found: C, 57.91; H, 4.39; N, 6.71.

Polygon P1. Prepared using the general procedure 2 from complex 1 (25 mg, 0.04 mmol) and Pt(dppp)(OTf)$_2$ (34 mg, 0.04 mmol); precipitation gave 46 mg (78 %) of P1 as a pale yellow solid. NMR $^1$H (300 MHz, CD$_3$CN): 8.93 (d, $^3$J = 6.0 Hz, 4H), 8.30 (d, $^4$J = 1.7 Hz, 4H), 8.23 (d, $^3$J = 5.9 Hz, 8H), 7.64-7.40 (m, 44H), 6.87 (d, $^3$J = 6.4 Hz, 8H), 3.19 (b, 8H), 2.22 (b, overlapping with water), 1.33 (s, 36H); NMR $^{31}$P{$_1$H} (121.6 MHz, CD$_3$CN): $\delta$ -14.27 (s), -14.91 (d, $^1$J = 3098 Hz); UV-Vis (CH$_3$CN) $\lambda$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 287 (62 400), 371 (15 500); MS m/z (nature of the peak, relative intensity): 637.4 ([M-4OTf]$^{4+}$, 90), 899.5 ([M-3OTf]$^{3+}$, 100), 1424.2 ([M-2OTf]$^{2+}$, 40); Anal. Calcd for C$_{122}$H$_{116}$F$_{12}$N$_8$O$_{12}$P$_4$Pt$_4$S$_4$ + 2 CH$_2$Cl$_2$: C, 44.91; H, 3.65; N, 3.38. Found: C, 44.11; H, 3.78; N, 3.46.

Polygon P2. Prepared using the general procedure 2 from complex 2 (25 mg, 0.03 mmol) and Pt(dppp)(OTf)$_2$ (26 mg, 0.03 mmol); precipitation to give 43 mg (84 %) of P2 as a yellow solid. NMR $^1$H (300 MHz, CD$_3$CN): 9.38 (d, $^3$J = 6.0 Hz, 4H), 8.49 (d, $^3$J = 6.0 Hz, 8H), 8.31 (d, $^4$J = 1.7 Hz, 4H), 7.71 (dd, $^3$J = 6.1 Hz, $^4$J = 1.9 Hz, 4H), 7.63-7.37 (m, 56H), 7.18 (d, $^3$J = 6.5 Hz, 8H), 3.18 (b, 8H), 2.17 (b, overlapping with water), 1.43 (s, 36H); NMR $^{31}$P{$_1$H} (121.6 MHz, CD$_3$CN): $\delta$ -14.90 (s), -14.90 (d, $^1$J = 3025 Hz); UV-Vis (CH$_3$CN) $\lambda$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$): 320 (121 000), 341 (115 800), 380 (37 600); MS m/z (nature of the peak, relative intensity): 737.3 ([M-4OTf]$^{4+}$, 100), 1033.17 ([M-3OTf]$^{3+}$, 10), 1624.2 ([M-2OTf]$^{2+}$, 5); Anal. Calcd for C$_{154}$H$_{132}$F$_{12}$N$_8$O$_{12}$P$_4$Pt$_4$S$_4$ + 2 CH$_2$Cl$_2$: C, 50.41; H, 3.69; N, 3.01. Found: C, 50.05; H, 3.78; N, 2.97.
**Polygon P3.** Prepared using the general procedure 2 from complex 4 (25 mg, 0.03 mmol) and Pt(dppp)(OTf)$_2$ (29 mg, 0.03 mmol); precipitation to give 48 mg (90 %) of P3 as a yellow solid. NMR $^1$H (300 MHz, CD$_3$CN): 9.33 (d, $^3J = 6.0$ Hz, 2H), 9.05 (d, $^3J = 6.0$ Hz, 2H), 8.40 (d, $^3J = 5.2$ Hz, 4H), 8.32 (m, 4H), 8.23 (d, $^3J = 5.2$ Hz, 4H), 7.70 (m, 4H), 7.60-7.40 (m, 40), 7.31 (AB, $^{4B}J = 5.9$ Hz, νδ$_{AB}$, 8H), 7.14 (d, $^3J = 6.3$ Hz, 4H), 6.97 (d, $^3J = 6.6$ Hz, 4H), 3.16 (b, 8H), 2.13 (b, overlapping with water), 1.45 (s, 18H), 1.43 (s, 18H); NMR $^{31}$P{$^1$H} (121.6 MHz, CD$_3$CN): δ -14.57 (s), -14.57 (d, $^1J = 3022$ Hz); UV-Vis (CH$_3$CN) λ, nm (ε, M$^{-1}$ cm$^{-1}$): 286 (65 200), 319 (67 800), 338 (63 100), 376 (22 600); MS m/z (nature of the peak, relative intensity): 687.5 ([M-4OTf]$^{4+}$, 100), 966.2 ([M-3OTf]$^{3+}$, 15), 1523.8 ([M-2OTf]$^{2+}$, 5); Anal. Caled for C$_{138}$H$_{124}$F$_{12}$N$_{8}$O$_{12}$P$_4$Pt$_4$S$_4$ + 2 CH$_2$Cl$_2$: C, 47.81; H, 3.67; N, 3.19. Found: C, 48.12; H, 3.56; N, 3.09.

**Figure S1.** DOSY NMR spectra of polygons P1, P2, and P3 recorded in CD$_3$CN at 298 K.
**Photophysical Measurements.** Steady-state absorption spectra were measured using a Cary 50 Bio UV-Vis Spectrophotometer (Varian), accurate to ± 2 nm. Uncorrected steady-state photoluminescence spectra were measured with single photon counting PTI spectrofluorimeter with a 75 W Xe lamp as the excitation source. Photoluminescence quantum yields were determined as described previously. The resulting values represent the average of three independent measurements. For the preparation of the photoluminescence samples spectroscopic grade solvents were used in all instances. Absorption measurements were performed in 1 cm² quartz cell (Starna Cells) using optically dilute (OD = 0.09-0.11) solutions. Samples for emission spectra and lifetime intensity decay measurements were degassed using the freeze-pump-thaw method (at least 3 cycles). Emission lifetimes of complexes 2, 3, P2, and P3 were measured using a nitrogen-pumped broadband dye (2-3 nm fwhm) from PTI (GL-3300 N₂ laser, GL- 301 dye laser) with the BPDB dye in order to tune excitation wavelength. An average of 64 transients were collected and processed via Origin 8.0. The reliability of each single exponential fit was established by visual inspection of
residuals. The short lifetimes (less than 15 ns) exhibited by 1 and P1 were impossible to determine using this technique due to the limited time resolution of the system. Low-temperature emission spectra were measured in frozen glasses (4:1 EtOH:MeOH) at 77 K using 5.5 mm inner diameter NMR tubes containing $10^{-5}$ M solution of the appropriate compound. Samples were contained in a quartz-tipped LN$_2$-filled Dewar placed inside the fluorimeter.

**Figure S3.** Photoluminescence intensity decay and single exponential fit of 2 in degassed CH$_3$CN.

**Figure S4.** Photoluminescence intensity decay and single exponential fit of 3 in degassed CH$_3$CN.
**Figure S5.** Photoluminescence intensity decay and single exponential fit of P2 in degassed CH₃CN.

**Figure S6.** Photoluminescence intensity decay and single exponential fit of P3 in degassed CH₃CN.
**Figure S7.** Static photoluminescence spectrum of 1 in 4:1 EtOH:MeOH at 77 and 298 K. Emission maxima are ± 2 nm.

**Figure S8.** Static photoluminescence spectrum of 2 in 4:1 EtOH:MeOH at 77 and 298 K. Emission maxima are ± 2 nm.
**Figure S9.** Static photoluminescence spectrum of 3 in 4:1 EtOH:MeOH at 77 and 298 K. Emission maxima are ± 2 nm.

**Figure S10.** Static photoluminescence spectrum of P1 in 4:1 EtOH:MeOH at 77 and 298 K. Emission maxima are ± 2 nm.
Figure S11. Static photoluminescence spectrum of P2 in 4:1 EtOH:MeOH at 77 and 298 K. Emission maxima are ± 2 nm.

Figure S12. Static photoluminescence spectrum of P3 in 4:1 EtOH:MeOH at 77 and 298 K. Emission maxima are ± 2 nm.

ESI References