Electronic Supplementary Information (ESI) For

Design and synthesis of branched platinum-acetylide complexes possessing a porphyrin core and their self-assembly behaviour

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1. General Information.

$^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectra were recorded on 300 MHz Spectrometer ($^1$H: 300 MHz; $^{13}$C: 75 MHz; $^{31}$P: 121.4 MHz) or 400 MHz Spectrometer ($^1$H: 400 MHz; $^{13}$C: 100 MHz; $^{31}$P: 161.9 MHz) at 298 K. The $^1$H and $^{13}$C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}$P NMR resonances are referenced to a internal standard sample of 85% H$_3$PO$_4$ ($\delta$ 0.0). Coupling constants ($J$) are denoted in Hz and chemical shifts ($\delta$) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. UV-Vis spectra were recorded on a Cary 50Bio UV-Visible spectrophotometer. Fluorescence spectra were measured on a Cary Eclipse fluorescence spectrophotometer. Samples for absorption and emission measurements were contained in 1 cm × 1 cm or 1 cm × 0.2 cm quartz cuvettes. SEM images were obtained using an S-4800 (Hitachi Ltd.) with an accelerating voltage of 10.0 kV. Samples were prepared by evaporating a solution of molecules 1a–1c onto a SiO$_2$/Si substrate (1×1 cm$^2$).
2. Additional References of Porphyrin Aggregates.

Due to space limitation, a number of important papers on porphyrin aggregates are not cited in the main text. Although the list reported here is far from complete, it does give the reader a broader view on the subject.

3. Synthetic Procedures and Characterizations of New Compounds

**Materials and Reagents.** THF was distilled from sodium. Et₂NH was dried from potassium hydroxide. Both of them were degassed under N₂ for 30 minutes before use. All reactions were performed in standard glassware under an inert N₂ atmosphere. Compounds 2¹, 6², and 8a-8c³ were prepared as previous report.

**Scheme S1.** Synthesis route of the precursors 5a–c.

**Synthesis of compound 7.** A solution of *trans*-diodobis (triethyl phosphine) platinum (1.16 g, 1.34 mmol), cuprous iodide (6.4 mg, 5 mol%) and 6 (150 mg, 0.68 mmol) in a mixture solvent of THF/Et₂NH (20 mL/12 mL) was stirred at room temperature. After 2.5 h a small amount of diethylammonium iodide started precipitating out of solution. After removal of the solvent, the product was further purified by column chromatography on silica gel to give product 7 as a pale solid. Yield: 536.0 mg, 68.6%. Rf = 0.69 (dichloromethane/petroleum ether 1:1). M.p. 185 °C. H NMR (CDCl₃, 300 MHz): δ 7.15 (s, 2H), 7.13 (s, 1H), 2.25-2.17 (m, 24H), 1.25-1.11 (m, 36H), 0.25 (s, 9H); C NMR (CDCl₃, 75 MHz): δ 133.2, 131.0, 128.4, 122.7, 105.0, 99.3, 93.7, 90.5, 16.6, 8.3; P NMR (CDCl₃, 121.4 MHz): δ 8.79 (s, J Pt-P=2322.38 Hz).

**Synthesis of compound 5a.** A 100 mL Schlenk flask was charged with 7 (140.6 mg, 0.105 mmol), 8a (169.4 mg, 0.421 mmol), and cuprous iodide (2.8 mg, 7 mol%), degassed, and back-filled three times with N₂. Ethylamine (7 mL) and dried THF (7 mL) were introduced into the reaction flask by syringe. The reaction was stirred under an inert atmosphere at room temperature for 12 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel to give the trimethylsilyl-protected precursor as a pale solid. Yield: 182.9 mg, 92.2%. The compound without further characterization was deprotected in THF and
methanol with potassium carbonate in room temperature for 1 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by a short plug to give 5a as a pale solid. Yield: 133.0 mg, 94.3%. Rf = 0.41 (dichloromethane/ petroleum ether 2:1) Mp: 106 °C. 1H NMR (CDCl3, 400 MHz): δ 7.17 (s, 1H), 7.15 (s, 2H), 6.48 (s, 4H), 3.95-3.89 (m, 12H), 3.01 (s, 1H), 2.17-2.14 (m, 24H), 1.81-1.68 (m, 12H), 1.47-1.44 (m, 12H), 1.34-1.32 (m, 24H), 1.25-1.17 (m, 36H), 0.91 (br, 18H); 13C NMR (CDCl3, 100 MHz): δ 152.6, 137.0, 133.9, 131.1, 128.6, 123.5, 121.3, 109.7, 109.6, 108.4, 105.5, 83.9, 76.2, 73.4, 69.0, 31.8, 31.6, 30.2, 29.3, 25.7, 22.7, 22.6, 16.3, 14.1, 8.3; 31P NMR (CDCl3, 161.9 MHz): δ 11.18 (s, J_pH=2368.60 Hz). Anal. Calcd for C88H146O6P2Pt2: C, 58.26; H, 8.11. Found: C, 58.58; H, 8.12.

**Synthesis of compound 5b.** Following the procedure for the preparation of 5a, 7 (335.0 mg, 0.25 mmol), 8b (361.0 mg, 0.55 mmol), and CuI (8.0 mg, 8 mol%) were used in THF (10 mL) and Et3NH (10 mL). Yield: 494.6 mg, 88.0%. Rf = 0.64 (dichloromethane/ petroleum ether 2:1) Mp: 78 °C. 1H NMR (CDCl3, 300 MHz): δ 7.17 (s, 1H), 7.15 (s, 2H), 6.48 (s, 4H), 3.96-3.89 (m, 12H), 3.00 (s, 1H), 2.18-2.14 (m, 24H), 1.82-1.66 (m, 12H), 1.45-1.16 (m, 144H), 0.88 (t, J = 6.6 Hz, 18H); 13C NMR (CDCl3, 75 MHz): δ 152.6, 137.1, 134.0, 131.0, 128.6, 123.5, 121.3, 109.8, 109.6, 108.4, 105.4, 83.9, 76.2, 73.4, 69.0, 31.9, 30.3, 29.68, 29.64, 29.60, 29.4, 29.3, 26.1, 22.6, 16.4, 14.0, 8.3; 31P NMR (CDCl3, 121.4 MHz): δ 11.73 (s, J_pH=2372.16 Hz). Ionspec HiResMALDI MS of 5b: m/z calcd for C123H131O6P2Pt2 ([M+H]+) 2318.51, found 2318.390. Anal. Calcd for C123H131O6P2Pt2: C, 64.22; H, 9.47. Found: C, 64.31; H, 9.277.

**Synthesis of compound 5c.** Following the procedure for the preparation of 5a, 7 (250.0 mg, 0.19 mmol), 8c (373.4 mg, 0.41 mmol), and CuI (5.7 mg, 8 mol%) were used in THF (10 mL) and Et3NH (8 mL). Yield: 506.2 mg, 94.0%. Rf = 0.73 (dichloromethane/ petroleum ether 2:1) Mp: 84 °C. 1H NMR (CDCl3, 300 MHz): δ 7.17 (s, 1H), 7.15 (s, 2H), 6.48 (s, 4H), 3.96-3.89 (m, 12H), 3.00 (s, 1H), 2.17-2.14 (m, 24H), 1.82-1.67 (m, 12H), 1.46-1.17 (m, 216H), 0.88 (t, J = 6.6 Hz, 18H); 13C NMR(CDCl3, 75 MHz): δ 152.6, 137.1, 133.9, 131.1, 128.7, 123.6, 121.4, 109.9, 109.6, 108.4, 84.0, 76.2, 73.5, 69.1, 31.9, 30.3, 29.7, 29.6, 29.4, 29.3, 26.1, 22.6, 16.4, 14.0, 8.3; 31P NMR (CDCl3, 121.4 MHz): δ 11.69 (s, J_pH=2370.94 Hz). Ionspec HiResMALDI MS of 5c: m/z calcd for C160H290O6P2Pt2 ([M+H]+) 2823.07, found 2823.069. Anal. Calcd for C160H290O6P2Pt2: C, 68.05; H, 10.35. Found: C, 68.15; H, 10.19.
Scheme S2. Synthesis route of target molecules 1a–1c.
**Synthesis of compound 3.** Pyrrole (64.0 μL, 0.99 mmol) was added dropwise to a refluxing solution of 2 (680.0 mg, 0.99 mmol) in propionic acid (4 mL). The solution quickly changed color from yellow to black. The solution was stirred at reflux for 1.5 h. The reaction flask was cooled in an ice/water bath. The solution was refrigerated overnight. The purple precipitate that formed was isolated by vacuum filtration. The solid was washed with MeOH. The crude product mixture (1.25 g) was loaded on a silica gel column and eluted with CHCl₃. Porphyrins 3 was isolated by loading the mixture of the crude product from the first column onto a second silica gel column. The column was eluted with 2% MeOH/CHCl₃ to give product 3 as a purple solid. Yield: 260.0 mg, 35.7%. Mp: >300°C. ¹H NMR (CDCl₃, 400 MHz): δ 8.90 (s, 8H), 8.07 (d, J=8.0 Hz, 8H), 7.66 (d, J=8.0 Hz, 8H), 2.41-2.34 (m, 48H), 1.33-1.25 (m, 72H), -2.74 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 139.3, 134.6, 131.0, 129.7, 129.0, 127.9, 120.2, 100.0, 91.3, 16.6, 8.4; ³¹P NMR (CDCl₃, 161.9 MHz): δ 8.84 (s, J_P-P=2321.6 Hz).

**Synthesis of compound 4.** The free-base porphyrin 3 (613 mg, 0.21 mmol) was dissolved in CH₂Cl₂/CH₃OH (5:1, 180 mL) and zinc acetate (459.0 mg, 2.10 mmol) was added. The reaction mixture was protected from light and stirred at room temperature for 4 h. After removal of the solvents under reduced pressure, the product was purified by column chromatography on alumina eluting with CH₂Cl₂/CH₃OH (99:1). The product was obtained as a purple powder. Yield: 604.4 mg, 96.5%. Mp: >300°C. ¹H NMR (CDCl₃, 400 MHz): δ 9.01 (s, 8H), 8.08 (d, J=8.0 Hz, 8H), 7.66 (d, J=8.0 Hz, 8H), 2.41-2.34 (m, 48H), 1.34-1.26 (m, 72H); ¹³C NMR (CDCl₃, 100 MHz): δ 150.0, 140.0, 134.4, 131.9, 128.9, 127.6, 121.2, 100.1, 91.0, 16.6, 8.3; ³¹P NMR (CDCl₃, 161.9 MHz): δ 8.82 (s, J_P-P=2323.3 Hz). Anal. Calcd for C₁₀₀H₁₄₄I₄N₄P₄Pt₂Zn: C, 39.99; H, 4.83; N, 1.87. Found: C, 40.40; H, 5.026; N, 1.681.

**General Procedure for the Preparation of 1a–1c.**

A 100 mL Schlenk flask was charged with 4 (66.0 mg, 0.022 mmol), 5a (240.0 mg, 6 eq), and cuprous iodide (0.6 mg, 7 mol%), degassed, and back-filled three times with N₂. Ethylamine and dried THF were introduced into the reaction flask by syringe. The reaction was stirred under an inert atmosphere at room temperature for about 3 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (dichloromethane/ methanol ~ 99/1) to give 1a as an purple solid. The similar procedure was followed to prepare compounds 1b and 1c.
**1a**: Yield: 155.3 mg, 72.4%. *Rf* = 0.72 (dichloromethane/methanol 400:1); Mp: 150 °C. ¹H NMR (CDCl₃, 400 MHz): δ 9.00 (s, 8H), 8.05 (d, *J* = 7.6 Hz, 8H), 7.65 (d, *J* = 7.6 Hz, 8H), 7.05 (s, 8H), 7.02 (s, 4H), 6.48 (s, 16H), 3.96-3.89 (m, 48H), 2.32-2.30 (m, 48H), 2.19-2.16 (m, 96H), 1.79-1.71 (m, 48H), 1.47-1.25 (m, 216H), 0.90 (br, 72H); ¹³C NMR (CDCl₃, 100 MHz): δ 152.6, 150.1, 139.6, 136.9, 134.3, 131.9, 130.6, 129.1, 127.9, 123.6, 121.2, 110.8, 109.7, 109.5, 106.1, 101.3, 73.4, 69.0, 31.7, 31.6, 30.2, 29.3, 25.7, 22.64, 22.60, 16.6, 16.5, 16.4, 16.3, 16.1, 14.1, 14.0, 8.5; ³¹P NMR (CDCl₃, 161.9 MHz): δ 11.21 (s, *J*ₚ₋ₓ=2365.4 Hz), 11.05 (s, *J*ₚ₋ₓ=2368.6 Hz). MALDI-TOF MS of 1a: *m/z* calcd for C₄₅₂H₇₂₆N₄O₂₈P₂₃Pt₁₂Zn ([M+H]⁺) 9741.43, found 9741.45.

**1b**: Yield: 394.9 mg, 92.9%. *Rf* = 0.40 (petroleum ether/methanol 10:1); Mp: 97 °C. ¹H NMR (CDCl₃, 300 MHz): δ 9.00 (s, 8H), 8.05 (d, *J* = 7.5 Hz, 8H), 7.65 (d, *J* = 7.5 Hz, 8H), 7.04 (s, 8H), 7.02 (s, 4H), 6.49 (s, 16H), 3.96-3.89 (m, 48H), 2.34-2.29 (m, 48H), 2.21-2.16 (m, 96H), 1.82-1.68 (m, 48H), 1.45-1.27 (m, 64H), 0.90 (br, 72H); ¹³C NMR (CDCl₃, 75 MHz): δ 152.5, 150.0, 139.5, 137.0, 134.3, 131.0, 130.4, 129.4, 129.0, 127.9, 123.6, 121.1, 111.2, 109.8, 107.6, 106.0, 105.8, 105.6, 73.3, 68.9, 32.0, 31.8, 31.6, 30.2, 29.62, 29.57, 29.54, 29.3, 29.2, 26.2, 26.0, 22.8, 22.6, 22.3, 16.6, 16.5, 16.4, 16.3, 16.2, 16.1, 15.9, 14.2, 14.0, 13.7, 8.5; ³¹P NMR (CDCl₃, 121.4 MHz): δ 11.64 (s, *J*ₚ₋ₓ=2374.58 Hz), 11.49 (s, *J*ₚ₋ₓ=2379.44 Hz). MALDI-TOF MS of 1b: *m/z* calcd for C₉₉₆H₁₀₁₃N₄O₂₈P₂₃Pt₁₂Zn ([M+H]⁺) 11759.69, found 11759.65.

**1c**: Yield: 390.6 mg, 95.0%. *Rf* = 0.29 (petroleum ether/methanol 10:1); Mp: 177 °C. ¹H NMR (CDCl₃, 300 MHz): δ 9.01 (s, 8H), 8.06 (d, *J* = 7.2 Hz, 8H), 7.66 (d, *J* = 7.5 Hz, 8H), 7.05 (s, 8H), 7.03 (s, 4H), 6.49 (s, 16H), 3.97-3.90 (m, 48H), 2.34-2.31 (m, 48H), 2.20-2.18 (m, 96H), 1.81-1.69 (m, 48H), 1.46-1.19 (m, 936H), 0.90 (br, 72H); ¹³C NMR (CDCl₃, 75 MHz): δ 152.6, 150.1, 139.6, 137.1, 134.3, 130.5, 129.1, 128.0, 123.7, 121.2, 109.9, 109.5, 105.9, 73.5, 69.1, 31.9, 30.3, 29.70, 29.65, 29.5, 29.4, 26.1, 22.7, 16.6, 16.5, 14.1, 8.4; ³¹P NMR (CDCl₃, 121.4 MHz): δ 11.34 (s, *J*ₚ₋ₓ=2374.58 Hz), 11.18 (s, *J*ₚ₋ₓ=2378.23 Hz). MALDI-TOF MS of 1c: *m/z* calcd for C₇₄₆H₁₃₈₀N₄O₂₈P₂₃Pt₁₂Zn ([M+H]⁺) 13777.94, found 13777.99.
4. Additional SEM Images at Different Scale.

Fig. S1. SEM of 1a prepared in CH$_2$Cl$_2$/hexane at different scale.

Fig. S2. SEM of 1a prepared in CH$_2$Cl$_2$/MeOH at different scale.

Fig. S3. SEM of 1b prepared in CH$_2$Cl$_2$/hexane at different scale.

Fig. S4. SEM of 1b prepared in CH$_2$Cl$_2$/MeOH at different scale.
Fig. S5. SEM of 1c prepared in CH$_2$Cl$_2$/hexane at different scale.

Fig. S6. SEM of 1c prepared in CH$_2$Cl$_2$/MeOH at different scale.
5. Additional Photophysical Data for 1a–1c

Fig. S7. Normalized UV/Vis spectra of 1a in hexane (5.0×10⁻⁵ M) and in film state (a); Temperature dependent UV/Vis spectra in 5.0×10⁻⁵ M of 1a in hexane (b).

Fig. S8. Concentration (a) and temperature (b) dependent (1.0×10⁻⁶ M) emission spectra of 1a in hexane.
Fig. S9. Normalized UV/Vis spectra of 1c in hexane (5.0×10⁻⁵ M) and in film state (a); Temperature dependent UV/Vis spectra in 5.0×10⁻⁵ M of 1c in hexane (b).

Fig. S10. Concentration (a) and temperature (b) dependent (5.0×10⁻⁶ M) emission spectra of 1c in hexane.
6. Multiple Nuclear NMR ($^{1}$H, $^{31}$P, and $^{13}$C NMR) Spectra of New Compounds

Figure S11. a) $^{1}$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 7 in CDCl$_3$
Fig. S12. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 5a in CDCl$_3$
Fig. S13. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of $5b$ in CDCl$_3$
Fig. S14. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 5c in CDCl$_3$. 

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Fig. S15. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 3 in CDCl$_3$.
Fig. S16. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 4 in CDCl$_3$. 

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Fig. S17. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 1a in CDCl$_3$.
Fig. S18. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 1b in CDCl$_3$
Fig. S19. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 1c in CDCl$_3$
7. MALDI-TOF MS of New Compounds

Fig. S20. MALDI-TOF mass spectra of 5b and the isotope peaks (insert).

Fig. S21. MALDI-TOF mass spectra of 5c and the isotope peaks (insert).
Fig. S22. MALDI-TOF mass spectra of 1a (a) and the isotope peaks (b).
Fig. S23. MALDI-TOF mass spectra of 1b (a) and the isotope peaks (b).

References: