Supporting Information For

Novel platinum-acetylide metallocycles constructed via a stepwise fragment coupling approach and their aggregation behaviour

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1. General Information.

All solvents were dried according to standard procedures and all of them were degassed under N$_2$ for 30 minutes before use. Reagents were used as purchased. All air-sensitive reactions were carried out under N$_2$ atmosphere.

$^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectra were recorded on Bruker 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$_4$ (δ 0.0). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. IR spectra were recorded on a Bruker Tensor 27 infrared spectrophotometer.

UV-Vis spectra were recorded on a Cary 50Bio UV-Visible spectrophotometer. Fluorescence spectra were measured on a cary eclipse fluorescence spectrophotometer. Samples for UV-Vis absorption measurements were contained in 1.0 cm × 1.0 cm or 0.4 cm × 0.1 cm quartz cuvettes and fluorescence emission measurements were contained in 1.0 cm × 1.0 cm quartz cuvettes. SEM images of the sample morphologies were obtained using an S-4800 (Hitachi Ltd.) with an accelerating voltage of 10.0 kV. Samples were prepared by dropping solution onto a silicon wafer.
2. Synthetic Procedures and Characterizations of New Compounds

Scheme S1. Synthesis route of compound 5a.

Materials and Reagents. THF was distilled from sodium. Et$_2$NH was dried from potassium hydroxide. Both of them were degassed under N$_2$ for 30 minutes before use. All reactions were performed in standard glassware under an inert N$_2$ atmosphere. Compound 1 and 2a were prepared as the reported procedure$^{S1-S2}$.

Synthesis of compound 3a. A 250 mL Schlenk flask was charged with 1 (1.16 g, 0.85 mmol), 2a (371 mg, 1.87 mmol) and CuI (23 mg, 14 mol%), degassed, and back-filled three times with N$_2$. Dried THF (90 mL) and Diethylamine (60 mL) were introduced into the reaction flask by syringe. The reaction was stirred under an inert atmosphere at room temperature for 2 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel to give 3a as a yellow solid. Yield: 1.113 g, 87.2%. R$_f$ = 0.42 (dichloromethane/petroleum ether = 1:1). Mp: 241-242 ºC. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.69 (s, 2 H), 7.91-7.96 (dd, 4 H, $J = 12.8$ Hz, 8.0 Hz), 7.88 (s, 2 H), 7.38 (s, 2 H), 7.23-7.26 (m, 4 H), 7.13-7.17 (m, 2 H), 2.25 (br, 24 H), 1.24-1.32 (m, 36 H), 0.26 (s, 18 H); $^{31}$P NMR (CDCl$_3$, 161.9 MHz): $\delta$ 11.81 (s, $J_{P,P}$ = 2370.2 Hz). IR (neat): 2966, 2936, 2903, 2880, 2153, 2089, 1588, 1562,
1473, 1455, 1413, 1377 cm$^{-1}$. IonSpec HiResMALDI MS of 3a: m/z calcd for C$_{70}$H$_{92}$P$_8$Pt$_2$Si$_2$ ([M+H]$^+$) 1505.51, found 1505.5.

**Synthesis of compound 4a.** Compound 3a (360 mg, 0.24 mmol) was dissolved in THF/MeOH (46 mL/23 mL). After the 3a was dissolved, potassium carbonate (330 mg, 2.4 mmol) was added. Then the reaction mixture was stirred at room temperature for 1.8 h. The solution was filtered and the solvent was removed by evaporation on a rotary evaporator. The crude product was purified by column chromatography on silica gel to give 4a as a yellow solid. Yield: 297 mg, 91.4%. Rf = 0.26 (dichloromethane/petroleum ether = 1:1). Mp: > 300 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.69 (s, 2 H), 7.91-7.96 (dd, 4 H, $J = 14.0$ Hz, 8.4 Hz), 7.88 (s, 2 H), 7.42 (s, 2 H), 7.26-7.30 (m, 4 H), 7.16-7.20 (m, 2 H), 3.05 (s, 2 H), 2.25 (br, 24 H), 1.24-1.32 (m, 36 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 134.36, 131.42, 131.38, 129.24, 129.06, 128.94, 128.67, 128.01, 126.39, 126.03, 124.90, 124.14, 123.73, 121.73, 115.23, 109.12, 108.91, 108.64, 83.82, 16.50, 8.40; $^{31}$P NMR (CDCl$_3$, 161.9 MHz): $\delta$ 12.22 (s, $J_{P,P} = 2368.6$ Hz). IR (neat): 3307, 3232, 3037, 2965, 2928, 2879, 2854, 2093, 1589, 1563, 1474, 1455, 1413, 1377 cm$^{-1}$. IonSpec HiResMALDI MS of 4a: m/z calcd for C$_{66}$H$_{78}$P$_8$Pt$_2$ ([M+H]$^+$) 1360.43, found 1360.4. Anal. Calcd for C$_{66}$H$_{78}$P$_8$Pt$_2$: C, 56.46; H, 5.78. Found: C, 56.82; H, 6.031.

**Synthesis of compound 5a.** A solution of CuI (4 mg, 14 mol%) in a mixture solvent of THF/E$_2$NH (20 mL/50 mL) was stirred under nitrogen atmosphere at room temperature, then 4a (200 mg, 0.147 mmol) and 1 (201 mg, 0.147 mmol) dissolved in THF (40 mL) respectively were added dropwise for 1 hour in the same speed rate and some yellow solid started precipitating out of solution. The reaction mixture was stirred under nitrogen atmosphere at room temperature for another 3.5 h. The crude product was purified by column chromatography on silica gel to give 5a as a yellow solid. Yield: 202 mg, 55.6%. Rf = 0.33 (dichloromethane). Mp: > 300 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.74 (s, 4 H), 7.91-7.96 (dd, 8 H, $J = 14.8$ Hz, 8.0 Hz), 7.88 (s, 4 H), 7.33 (s, 2 H), 7.10 (br, 6 H), 2.27-2.29 (m, 48 H), 1.26-1.33 (m, 72 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ 133.73, 131.56, 129.22, 128.58, 128.42, 127.63, 126.37, 126.09, 124.90, 124.11, 123.79, 109.78, 82.15, 16.51, 8.44; $^{31}$P NMR (CDCl$_3$, 161.9 MHz): $\delta$ 11.97 (s, $J_{P,P} = 2371.8$ Hz). IR (neat): 2961, 2924, 2853, 2091, 1583, 1558, 1487, 1456, 1413, 1377 cm$^{-1}$. MALDI-TOF MS of 5a: m/z calcd for C$_{108}$H$_{144}$P$_8$Pt$_4$ ([M+H]$^+$) 2469.78, found 2469.75. Anal. Calcd for C$_{108}$H$_{144}$P$_8$Pt$_4$H$_2$O: C, 52.13; H, 5.91. Found: C, 52.09; H, 5.816.
Scheme S2. Synthesis route of compound 2b.

**Materials and Reagents.** THF was distilled from sodium. \(i\)-Pr\(_2\)NH was dried from potassium hydroxide. Both of them were degassed under \(N_2\) for 30 minutes before use. All reactions were performed in standard glassware under an inert \(N_2\) atmosphere. Compound 6 and 8 were prepared as the reported procedure\(^{S3-S4}\).

**Synthesis of compound 7.** A 200 mL Schlenk flask was charged with 6 (1.3 g, 3.91 mmol), Pd(PPh\(_3\))\(_4\) (227 mg, 5 mol%) and CuI (38 mg, 5 mol%), degassed, and back-filled three times with \(N_2\). Then 2-Methyl-3-butyldiol (0.38 mL, 3.91 mmol), dried THF (40 mL) and \(i\)-Pr\(_2\)NH (25 mL) were introduced into the reaction flask by syringe. The reaction mixture was heated at 65 °C under nitrogen atmosphere for 23 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel to give 7 as a colorless oil. Yield: 668 mg, 51%. \(R_f = 0.41\) (petroleum ether/acetone = 12:1). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.53 (s, 1 H), 7.49 (s, 1 H), 7.44 (s, 1 H), 1.97 (s, 1 H), 1.59 (s, 6 H), 0.23 (s, 9 H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 134.25, 134.18, 133.58, 125.05, 124.62, 121.65, 102.39, 96.61, 95.61, 79.94, 65.50, 31.30, -0.25. IR (neat): 3339, 2981, 2899, 2159, 1585, 1553, 1456, 1424, 1364, 1290 cm\(^{-1}\). MS (EI): 334 (M\(^+\), 20), 336 [(M+2\(^+\)], 21), 321 (100), 319 (98), 43 (52), 225 (29), 320 (22), 322

Synthesis of compound 9. A 200 mL Schlenk flask was charged with 7 (803 mg, 2.40 mmol), 8 (2.04 g, 2.64 mmol), Pd(PPh3)$_4$ (139 mg, 5 mol%), and CuI (23 mg, 5 mol%), degassed, and back-filled three times with N$_2$. Dried THF (50 mL) and i-Pr$_2$NH (30 mL) were introduced into the reaction flask by syringe. The reaction mixture was heated at 65 ºC under nitrogen atmosphere for 29 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel to give 9 as a faint yellow oil. Yield: 1.81 g, 73.6%. R$_f$ = 0.38 (petroleum ether/ethyl acetate = 6:1). $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.77 (s, 1 H), 7.64 (d, 2 H, $J$ = 8.0 Hz), 7.55 (s, 1 H), 7.50-7.51 (m, 3 H), 7.47 (s, 1 H), 7.04 (s, 2 H), 4.02-4.05 (m, 6 H), 2.00 (s, 1 H), 1.74-1.84 (m, 6 H), 1.61 (s, 6 H), 1.48 (br, 6 H), 1.27 (br, 48 H), 0.87-0.90 (m, 9 H), 0.25 (s, 9 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 165.74, 153.20, 141.66, 138.40, 134.35, 134.31, 134.18, 132.48, 129.55, 123.90, 123.78, 123.36, 119.82, 118.47, 105.87, 103.24, 94.90, 90.283, 87.50, 80.60, 73.56, 69.45, 65.50, 31.90, 31.37, 30.31, 29.71, 29.68, 29.63, 29.56, 29.40, 29.34, 26.06, 22.66, 14.07, -0.19. IR (neat): 3305, 2923, 2853, 2211, 2158, 1649, 1580, 1512, 1495, 1467, 1427, 1405, 1336, 1294 cm$^{-1}$. IonSpec HiResMALDI MS of 9: m/z calcd for C$_{67}$H$_{102}$NO$_3$Si ([M+H]+) 1028.74, found 1028.8.

Synthesis of compound 2b. A solution of 9 (778 mg, 0.756 mmol) and NaOH (122 mg, 3.03 mmol) in freshly distilled toluene (50 mL) was heated at reflux for 2.5 h. This solution was filtered while hot. The solvent was removed by evaporation on a rotary evaporator. The crude product was purified by column chromatography on silica gel to give 2b as a faint yellow solid. Yield: 487 mg, 66.3%. R$_f$ = 0.48 (petroleum ether/ethyl acetate = 18:1). Mp: 51 ºC. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.78 (s, 1 H), 7.65 (d, 2 H, $J$ = 7.6 Hz), 7.60 (s, 1 H), 7.57 (s, 1 H), 7.50-7.52 (m, 3 H), 7.03 (s, 2 H), 4.02-4.04 (m, 6 H), 3.09 (s, 1 H), 1.72-1.84 (m, 6 H), 1.48 (br, 6 H), 1.27 (br, 48 H), 0.87-0.90 (m, 9 H), 0.25 (s, 9 H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 165.75, 153.21, 141.64, 138.46, 134.90, 134.73, 134.60, 132.51, 129.55, 124.01, 123.90, 122.75, 119.81, 118.39, 105.84, 103.07, 95.87, 90.44, 87.35, 81.94, 78.24, 73.55, 69.44, 31.91, 30.32, 29.71, 29.69, 29.64, 29.57, 29.41, 29.35, 26.06, 22.66, 14.07, -0.20. IR (neat): 3310, 2923, 2853, 2214, 2160, 1648, 1579, 1512, 1496, 1467, 1427, 1405, 1337, 1294 cm$^{-1}$. IonSpec HiResMALDI MS of 2b: m/z calcd for C$_{64}$H$_{93}$NO$_3$Si ([M+H]+) 970.70, found 970.7. HRMS (ESI): Exact mass calcd for C$_{64}$H$_{93}$NNaO$_3$Si [M+Na]+: 992.6923, Found: 992.6873.
**Scheme S3.** Synthesis route of compound 5b.

**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.

**Synthesis of compound 3b.** A 250 mL Schlenk flask was charged with 1 (295 mg, 0.216 mmol), 2b (419 mg, 0.432 mmol) and CuI (6 mg, 14 mol%), degassed, and back-filled three times with N₂.
Dried THF (53 mL) and Et₂NH (35 mL) were introduced into the reaction flask by syringe. The reaction was stirred under an inert atmosphere at room temperature for 2.5 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel to give 3b as a yellow solid. Yield: 491 mg, 74.5%. Rf = 0.36 (dichloromethane/ethyl acetate = 500:1). Mp: 133-135 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.70 (s, 2 H), 7.86-7.95 (m, 8 H), 7.66 (d, 4 H, J = 7.6 Hz), 7.53 (d, 4 H, J = 7.2 Hz), 7.42 (s, 2 H), 7.39 (s, 2 H), 7.33 (s, 2 H), 7.03 (s, 4 H), 4.00-4.03 (m, 12 H), 2.26 (br, 24 H), 1.73-1.83 (m, 12 H), 1.47 (br, 12 H), 1.27-1.31 (m, 132 H), 0.87-0.90 (m, 18 H), 0.26 (s, 18 H); ³¹P NMR (CDCl₃, 161.9 MHz): δ 12.35 (s, Jₑₚ= 2365.4 Hz). IR (neat): 3295, 2923, 2852, 2214, 2159, 2092, 1649, 1574, 1511, 1493, 1459, 1426, 1405, 1378, 1336, 1293 cm⁻¹. MALDI-TOF MS of 3b: m/z calcd for C₁₇₂H₂₅₀N₂O₈P₄Pt₂Si₂ ([M⁺]⁺) 3047.75, found 3047.69.

**Synthesis of compound 4b.** Compound 3b (434 mg, 0.142 mmol) was dissolved in THF/MeOH (41 mL/21 mL). After the 3b was dissolved, potassium carbonate (197 mg, 1.42 mmol) was added. Then the reaction mixture was stirred at room temperature for 2.4 h. The solution was filtered and the solvent was removed by evaporation on a rotary evaporator. The crude product was purified by column chromatography on silica gel to give 4b as a yellow solid. Yield: 331 mg, 80.1%. Rf = 0.29 (dichloromethane/ethyl acetate = 500:1). Mp: 193-195 °C. ¹H NMR (CDCl₃, 400 MHz): δ 8.70 (s, 2 H), 7.91-7.97 (dd, 4 H, J = 13.6 Hz, 8.0 Hz), 7.87-7.88 (m, 4 H), 7.66 (d, 4 H, J = 8.0 Hz), 7.54 (d, 4 H, J = 8.0 Hz), 7.42 (br, 4 H), 7.37 (s, 2 H), 7.03 (s, 4 H), 4.00-4.03 (m, 12 H), 3.07 (s, 2 H), 2.26 (br, 24 H), 1.74-1.83 (m, 12 H), 1.47 (br, 12 H), 1.27-1.31 (m, 132 H), 0.87-0.90 (m, 18 H); ¹³C NMR (CDCl₃, 100 MHz): δ 165.69, 153.22, 141.59, 138.21, 134.09, 132.50, 131.44, 131.38, 129.57, 129.35, 129.25, 128.89, 126.40, 126.03, 124.88, 124.14, 123.68, 123.36, 122.15, 119.72, 118.77, 115.07, 110.53, 109.23, 107.95, 105.75, 105.75, 89.39, 88.35, 82.97, 73.54, 69.42, 31.91, 30.31, 29.72, 29.69, 29.63, 29.57, 29.40, 29.35, 26.06, 22.67, 16.50, 14.09, 8.41; ³¹P NMR (CDCl₃, 161.9 MHz): δ 12.32 (s, Jₑₚ= 2363.7 Hz). IR (neat): 3302, 3238, 2957, 2922, 2852, 2093, 1646, 1574, 1512, 1494, 1465, 1425, 1405, 1378, 1335, 1293 cm⁻¹. MALDI-TOF MS of 4b: m/z calcd for C₁₆₆H₂₃₅N₂O₈P₄Pt₂ ([M⁺]⁺) 2903.67, found 2903.57. Anal. Calcd for C₁₆₆H₂₃₅N₂O₈P₄Pt₂: C, 68.62; H, 8.33; N, 0.96. Found: C, 68.89; H, 8.527; N, 0.554.

**Synthesis of compound 5b.** A solution of Cul (1 mg, 14 mol%) in a mixture solvent of THF/Et₂NH (30 mL/40 mL) was stirred under nitrogen atmosphere at room temperature, then 4b
(100 mg, 0.034 mmol) and 1 (47 mg, 0.034 mmol) dissolved in THF (35 mL) respectively were added dropwise for 1 hour in the same speed rate. The reaction mixture was stirred under nitrogen atmosphere at room temperature for another 2.5 h. The crude product was purified by column chromatography on silica gel to give 5b as a yellow solid. Yield: 88 mg, 63.8%. Rf = 0.49 (dichloromethane/ethyl acetate = 150:1). Mp: > 250 °C, decomposed. 1H NMR (CD2Cl2, 400 MHz): 8.74 (s, 4 H), 7.88-8.00 (m, 14 H), 7.69 (d, 4 H, J = 7.6 Hz), 7.57 (d, 4 H, J = 8.0 Hz), 7.24 (br, 6 H), 7.06 (s, 4 H), 3.98-4.06 (m, 12 H), 2.29 (br, 48 H), 1.71-1.85 (m, 12 H), 1.48-1.49 (m, 12 H), 1.28-1.33 (m, 168 H), 0.87-0.88 (m, 18 H); 13C NMR (CDCl3, 100 MHz): δ 165.53, 153.28, 141.67, 137.86, 132.50, 131.52, 130.46, 129.66, 129.23, 128.69, 126.39, 126.06, 124.87, 124.13, 123.72, 122.62, 119.27, 115.35, 109.08, 105.78, 89.52, 88.35, 73.58, 69.49, 31.92, 30.31, 29.73, 29.69, 29.65, 29.63, 29.57, 29.39, 29.36, 26.07, 22.69, 16.48, 14.12, 8.45; 31P NMR (CD2Cl2, 161.9 MHz): δ 12.53 (s, Jp,P = 2358.9 Hz). IR (neat): 3323, 3287, 3046, 2962, 2923, 2852, 2092, 1675, 1642, 1569, 1512, 1494, 1457, 1425, 1406, 1378, 1336, 1261 cm⁻¹. MALDI-TOF MS of 5b: m/z calcd for C210H307N2O8P8Pt4 ([M+H]+) 4013.01, found 4013.09.

Reference:

More pertinent reference for reactions such as the coupling reaction with CuI/base system, the conversion TMS-alkyne derivatives into terminal alkynes with K2CO3/MeOH and so on are presented as follows:
3. UV-Vis and Fluorescence Spectra of Compounds 5a, 4b and 5b

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*The excitation wavelength of compounds 5a, 4b and 5b is 358 nm.

![Figure S1](image_url)  

**Figure S1.** UV-vis absorption spectra of compounds 5a, 4b and 5b in dichloromethane at 298 K (concentration: 5a = 5.79 × 10^{-6} M; 4b = 5.06 × 10^{-6} M; 5b = 5.16 × 10^{-6} M)
Figure S2. Emission spectra of compounds 5a, 4b and 5b in dichloromethane at 298 K (concentration: 5a = 5.79 × 10^{-6} M; 4b = 5.06 × 10^{-6} M; 5b = 5.16 × 10^{-6} M)
4. Concentration-dependent and Variable-temperature UV-Vis Spectroscopy of 5a, 4b and 5b

**Figure S3.** Normalized UV-Vis absorption spectra of the metallocycle 5a in dichloromethane at different concentrations at 298 K.

**Figure S4.** UV-Vis absorption spectra of the metallocycle 5a in dichloromethane at different temperatures at concentration $5 \times 10^{-5}$ M.
**Figure S5.** Normalized UV-Vis absorption spectra of the oligomer 4b in dichloromethane at different concentrations at 298 K.

**Figure S6.** UV-Vis absorption spectra of the oligomer 4b in dichloromethane at different temperatures at concentration $1 \times 10^{-4}$ M.

**Figure S7.** Normalized UV-Vis absorption spectra of the metallocycle 5b in dichloromethane at different concentrations at 298 K.

**Figure S8.** UV-Vis absorption spectra of the metallocycle 5b in dichloromethane at different temperatures at concentration $5 \times 10^{-5}$ M.
5. Concentration-dependent and Variable-temperature Fluorescence Spectroscopy of 5a, 4b and 5b

Figure S9. Emission spectra of the metallocycle 5a in dichloromethane at different concentrations at 298 K ($\lambda_{ex} = 358$ nm).

Figure S10. Emission spectra of the metallocycle 5a in dichloromethane at different temperatures at concentration $5 \times 10^{-5}$ M ($\lambda_{ex} = 358$ nm).
**Figure S11.** Emission spectra of the oligomer 4b in dichloromethane at different concentrations at 298 K ($\lambda_{\text{ex}} = 358$ nm).

**Figure S12.** Emission spectra of the oligomer 4b in dichloromethane at different temperatures at concentration $1 \times 10^{-4}$ M ($\lambda_{\text{ex}} = 358$ nm).

**Figure S13.** Emission spectra of the metallocycle 5b in dichloromethane at different concentrations at 298 K ($\lambda_{\text{ex}} = 358$ nm).

**Figure S14.** Emission spectra of the metallocycle 5b in dichloromethane at different temperatures at concentration $5 \times 10^{-5}$ M ($\lambda_{\text{ex}} = 358$ nm).
6. Concentration-dependent $^1$H NMR of 4b and 5b

**Figure S15.** $^1$H NMR (CDCl$_3$, 400 MHz) spectra of the oligomer 4b at different concentrations at 298 K (a. 3.95 mg/mL; b. 7.35 mg/mL; c. 11.92 mg/mL; d. 15.95 mg/mL; e. 20.28 mg/mL; f. 28.47 mg/mL; g. 31.63 mg/mL).

**Figure S16.** Partial $^1$H NMR (CDCl$_3$, 400 MHz) spectra of the oligomer 4b at different concentrations at 298 K (a. 3.95 mg/mL; b. 7.35 mg/mL; c. 11.92 mg/mL; d. 15.95 mg/mL; e. 20.28 mg/mL; f. 28.47 mg/mL; g. 31.63 mg/mL).
Figure S17. $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) spectra of the metallocycle 5b at different concentrations at 298 K (a. 1.45 mg/mL; b. 2.96 mg/mL; c. 5.34 mg/mL; d. 8.86 mg/mL; e. 13.54 mg/mL; f. 17.22 mg/mL; g. 20.82 mg/mL, h. 25.02 mg/mL).

Figure S18. Partial $^1$H NMR (CD$_2$Cl$_2$, 400 MHz) spectra of the metallocycle 5b at different concentrations at 298 K (a. 1.45 mg/mL; b. 2.96 mg/mL; c. 5.34 mg/mL; d. 8.86 mg/mL; e. 13.54 mg/mL; f. 17.22 mg/mL; g. 20.82 mg/mL, h. 25.02 mg/mL).
7. SEM Images at of the Oligomer 4b and the Metallocycles 5a-b

Figure S19. SEM images of the oligomer 4b in dichloromethane : methanol = 1:1 at different scales.

Figure S20. SEM images of the oligomer 4b in chloroform : methanol = 1:1 at different scales.

Figure S21. SEM images of the oligomer 4b in chloroform : ethyl acetate = 1:1 at different scales.

Figure S22. SEM images of the metallocycle 5b in dichloromethane : methanol = 1:1 at different scales.
Figure S23. SEM images of the metallocycle 5b in chloroform : methanol = 1:1 at different scales.

Figure S24. SEM images of the metallocycle 5b in chloroform : ethyl acetate = 1:1 at different scales.

Figure S25. SEM images of the metallocycle 5a in dichloromethane : methanol = 1:1 at different scales.

Figure S26. SEM images of the metallocycle 5a in chloroform : methanol = 1:1 at different scales.
**Figure S27.** SEM images of the metallocycle 5a in chloroform : ethyl acetate = 1:1 at different scales.
8. X-ray Crystal Data of Metallocycle 5a

![Figure S28. Ball-and-stick model of the X-ray crystal structure of metallocycle 5a.](image)

**Table S2. Crystal data and structure refinement for 5a**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>z</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C55 H12 Cl3 P4 Pt2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1293.06</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 9.7909(7) Å, alpha = 109.142(2)°</td>
</tr>
<tr>
<td></td>
<td>b = 17.1119(12) Å, beta = 94.876(2)°</td>
</tr>
<tr>
<td></td>
<td>c = 19.0280(14) Å, gamma = 101.713(2)°</td>
</tr>
<tr>
<td>Volume</td>
<td>2909.1(4) Å³</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>2, 1.476 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>5.082 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>1218</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.35 x 0.21 x 0.17 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.15 to 25.01°</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-11&lt;=h&lt;=11, -20&lt;=k&lt;=20, -22&lt;=l&lt;=22</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>33947 / 10204 [R(int) = 0.0479]</td>
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<tr>
<td>Completeness to theta = 25.01°</td>
<td>99.5 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>10204 / 41 / 522</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.113</td>
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<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R₁ = 0.0822, wR₂ = 0.2414</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.1118, wR₂ = 0.2626</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>5.619 and -3.548 e.Å³</td>
</tr>
</tbody>
</table>
9. Multiple Nuclear NMR (\(^1\)H, \(^{31}\)P, and \(^{13}\)C NMR) Spectra of New Compounds

Figure S29. a) \(^1\)H and b) \(^{31}\)P NMR spectra of 3a in CDCl\(_3\)
Figure S30. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 4a in CDCl$_3$.
Figure S31. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 5a in CDCl$_3$. 

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Figure S32. a) $^1$H and b) $^{13}$C NMR spectra of 7 in CDCl$_3$.
Figure S33. a) $^1$H and b) $^{13}$C NMR spectra of 9 in CDCl$_3$
Figure S34. a) $^1$H and b) $^{13}$C NMR spectra of 2b in CDCl$_3$
Figure S35. a) $^1$H and b) $^{31}$P NMR spectra of 3b in CDCl$_3$
Figure S36. a) $^1$H, b) $^{31}$P and c) $^{13}$C NMR spectra of 4b in CDCl$_3$
Figure S37. a) $^1$H, b) $^{31}$P NMR spectra of 5b in CD$_2$Cl$_2$ and c) $^{13}$C NMR spectra in CDCl$_3$.
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10. MS Spectra of New Compounds.

Figure S38. IonSpec HiResMALDI MS of 3a: m/z calcd for C70H95P4Pt2Si2 ([M+H]+) 1505.51, found 1505.5.

Figure S39. IonSpec HiResMALDI MS of 4a: m/z calcd for C64H78P4Pt2 ([M]+) 1360.43, found 1360.4.
**Figure S40.** MALDI-TOF MS of 5a: m/z calcd for $\text{C}_{108}\text{H}_{145}\text{Pt}_4 ([M+H]^+)$ 2469.78, found 2469.75.

![Image of MALDI-TOF MS spectrum for 5a]

**Figure S41.** MS (EI) of 7: 334 (M$^+$, 20), 336 [(M+2)$^+$, 21], 321 (100), 319 (98), 43 (52), 225 (29), 320 (22), 322 (21); HRMS (EI) of 7: Exact mass calcd for $\text{C}_{16}\text{H}_{19}\text{BrO}_5 \text{Si}[M]^+$: 334.0389, Found: 334.0388.

![Image of MS (EI) spectrum for 7]
**Figure S42.** IonSpec HiResMALDI MS of 9: m/z calcd for C_{67}H_{102}NO_{5}Si ([M+H]^+) 1028.74, found 1028.8.
Figure S43. IonSpec HiResMALDI MS of 2b: m/z calcd for C_{64}H_{96}NO_{2}Si ([M+H]^+) 970.70, found 970.7.

Figure S44. HRMS (ESI) of 2b: Exact mass calcd for C_{64}H_{95}NNaO_{4}Si [M+Na]^+: 992.6923, Found: 992.6873.
**Figure S45.** MALDI-TOF MS of 3b: m/z calcd for C_{172}H_{256}N_{2}O_{8}P_{4}Pt_{2}Si_{2} ([M]+) 3047.75, found 3047.69.

**Figure S46.** MALDI-TOF MS of 4b: m/z calcd for C_{166}H_{240}N_{2}O_{8}P_{4}Pt_{2} ([M]+) 2903.67, found 2903.57.
Figure S47. MALDI-TOF MS of 5b: m/z calcd for C$_{210}$H$_{307}$N$_{2}$O$_{8}$P$_{4}$Pt$_{4}$ ([M+H$^+$]) 4013.01, found 4013.09.