Supplementary Material (ESI) for RSC Advances

Supporting Information for

Branched Platinum-Acetylide Complexes: Synthesis, Properties, and Their Aggregation Behavior

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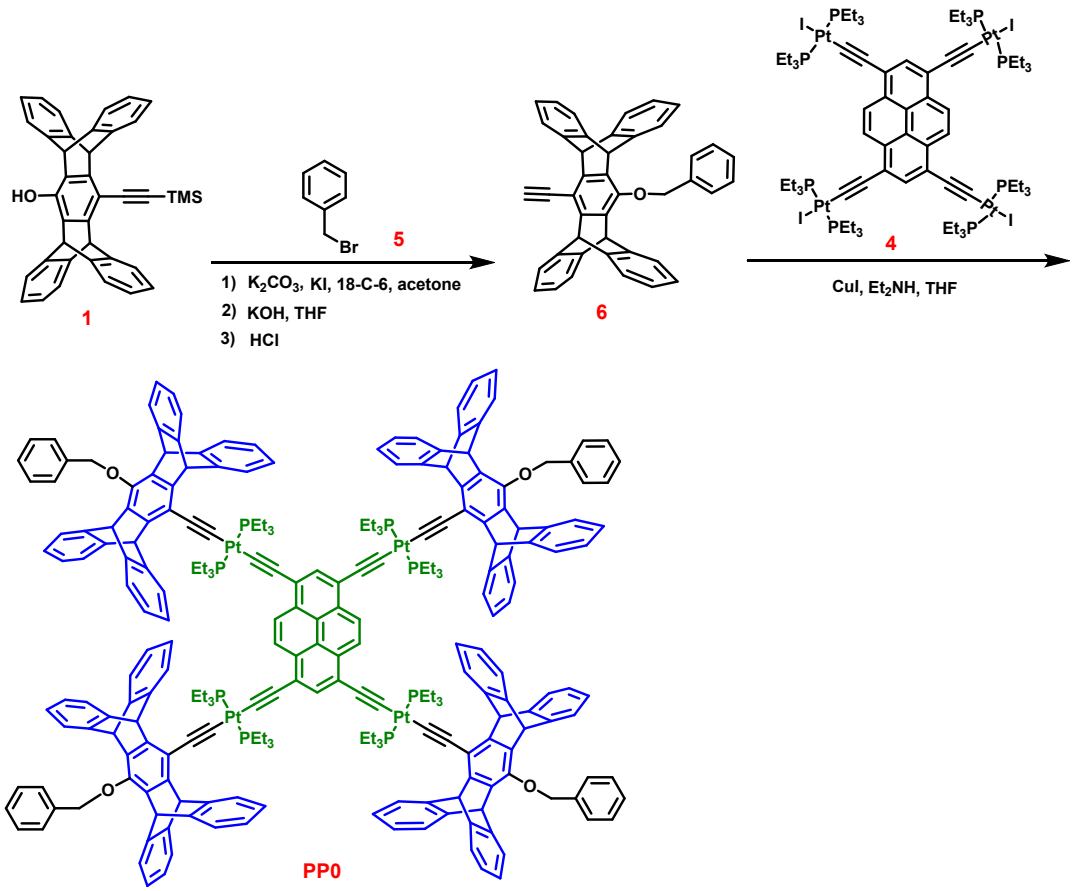
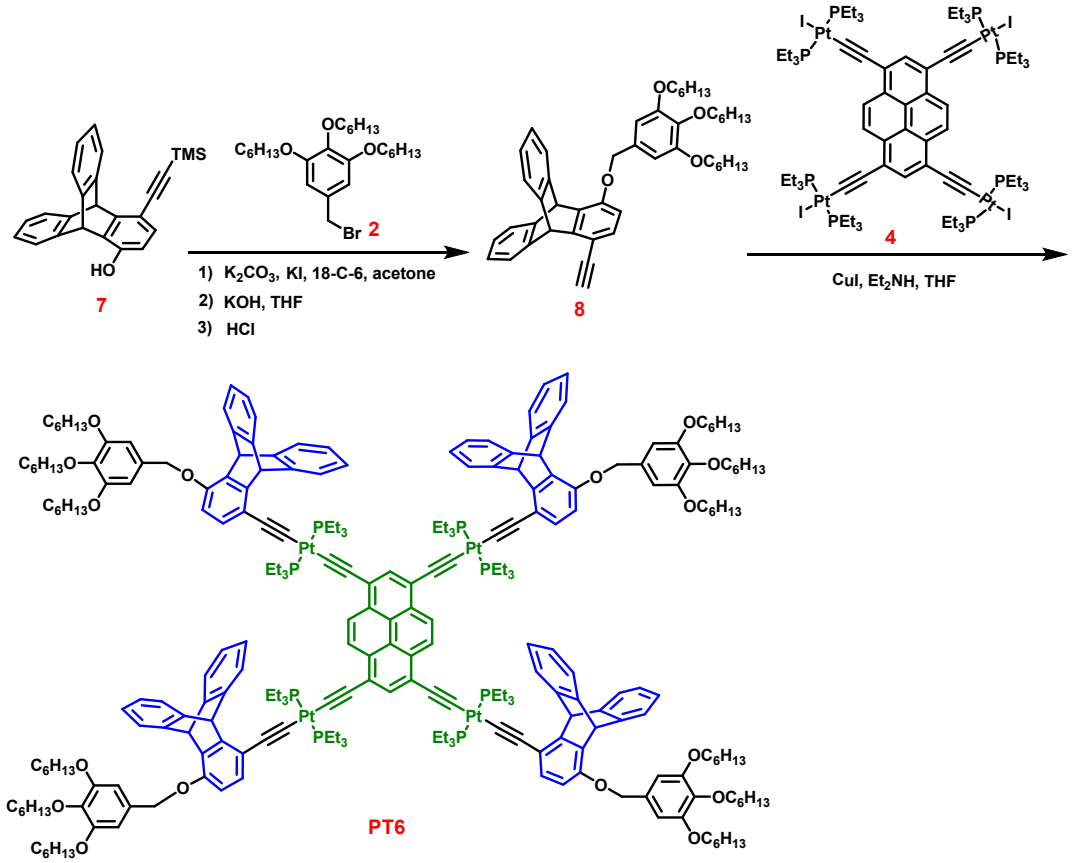
Contents:

1. Synthesis of PP0 and PT6



Scheme S1. Synthesis route of **PP0**.



Scheme S2. Synthesis route of **PT6**.

Compound 3. A mixture of **1** (419 mg, 0.77 mmol), compound **2** (437 mg, 0.93 mmol), K_2CO_3 (245 mg, 1.78 mmol), 18-C-6 (41 mg, 0.15 mmol) and KI (156 mg, 0.94 mmol) in 12 mL of dry acetone was refluxed for 120 h. The solution was cooled and the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with brine. The organic layer was dried over anhydrous $MgSO_4$, Column chromatography with dichloromethane / petroleum (1:1) as eluent afforded the white solid of the precursor with a yield of 76.8%. Then 5 mL of dry THF was added to the precursor, and 0.5 mL solution of KOH (47 mg, 0.83 mmol) in H_2O/CH_3OH(1:1). The mixture was stirred at room temperature for 1 h. the reaction was quenched by 36.5% HCl. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2, and washed with brine. The organic layer was dried over anhydrous $MgSO_4$. Column chromatography with dichloromethane/petroleum (1:1) as eluent afforded the white solid of **3** with a total yield of 72.8%; R*f* = 0.48 (dichloromethane /petroleum ether 1:1). Mp: 69 ℃. ^{1}H NMR ($CDCl_3$, 300 MHz): δ7.37-7.35 (m, 4H), 7.20-7.17 (m, 4H), 6.97-6.88 (m, 8H), 6.72 (s, 2H), 5.83 (s, 2H), 5.63 (s, 2H), 4.93 (s, 2H), 4.07-3.98 (m, 6H), 3.60 (s, 1H), 1.89-1.80 (m, 6H), 1.55-1.51 (m, 6H), 1.40-1.35 (m, 12H), 0.94-0.92 (m, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 153.43, 149.97, 146.67, 145.00, 144.78, 138.19, 135.37, 132.29, 125.16, 123.87, 123.38, 109.97, 106.29, 82.76, 79.20, 77.60, 73.46, 69.18, 52.11, 48.32, 31.77, 31.55, 30.34, 29.34, 25.80, 25.75, 22.68, 22.62, 14.10, 14.03. EI-TOF-MS of **3**, m/z calced for $C_{61}H_{64}O_4$, 860.48 (M^+), found 860.48

Compound 6. A mixture of **1** (297 mg, 0.55 mmol), compound **5** (78 μL, 0.66 mmol), K_2CO_3 (174 mg, 1.26 mmol), 18-C-6 (29 mg, 0.11 mmol) and KI (111 mg, 0.68 mmol) in 9 mL of dry acetone was refluxed for 43 h. The solution was cooled and the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with

brine. The organic layer was dried over anhydrous $MgSO_4$, Column chromatography with dichloromethane / petroleum (1:1) as eluent afforded the white solid of the precursor with a yield of 85.1%. Then 4 mL of dry THF was added to the precursor, and 0.4 mL solution of KOH (261mg, 4.66 mmol) in H_2O/CH_3OH(1:1). The mixture was stirred at room temperature for 3 h. the reaction was quenched by 36.5% HCl. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2, and washed with brine. The organic layer was dried over anhydrous $MgSO_4$. Column chromatography with dichloromethane/petroleum (1:1) as eluent afforded the white solid of **6** with a total yield of 73.3%; R***f*** = 0.49 (dichloromethane /petroleum ether 1:2). Mp: 286 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, *J* =7.6 Hz, 2H), 7.57-7.50 (m, 3H), 7.37-7.36 (m, 4H), 7.24-7.22 (m, 4H), 6.96-6.90 (m, 8H), 5.84 (s, 1H), 5.67 (s, 2H), 4.97 (s, 2H), 3.60 (s, 1H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.87, 146.73, 145.04, 144.81, 137.29, 135.38, 128.92, 128.46, 127.92, 125.23, 123.93, 123.44, 110.09, 82.71, 79.24, 77.50, 52.14, 48.24. EI-TOF-MS of **6**, m/z calced for $C_{43}H_{28}O$, 560.21 (M^+), found 560.21

Compound 8. A mixture of **7** (300 mg, 0.819 mmol), compound **2** (386 mg, 0.819 mmol), K_2CO_3 (260 mg, 1.883 mmol), 18-C-6 (43 mg, 0.164 mmol) and KI (169 mg, 0.999 mmol) in 13 mL of dry acetone was refluxed for 65 h. The solution was cooled and the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 and washed with brine. The organic layer was dried over anhydrous $MgSO_4$, Column chromatography with dichloromethane/ petroleum (1:2) as eluent afforded the white solid of the precursor with a yield of 59.2%. Then 5 mL of dry THF was added to the precursor, and 0.5 mL solution of KOH (272 mg, 4.847 mmol) in H_2O/CH_3OH(1:1). The mixture was stirred at room temperature for 2 h. the reaction was quenched by 36.5% HCl. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2, and washed with brine. The organic layer was dried over anhydrous $MgSO_4$. Column chromatography with dichloromethane/petroleum (1:1) as eluent afforded the white solid of **8** with a total yield of 49.4 %; R***f*** = 0.48 (dichloromethane /petroleum ether 1:1). Mp: 71 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44-7.43 (m, 2H), 7.38-7.36 (m, 2H), 7.08 (d, *J* =9.2 Hz, 1H), 7.00-6.99 (m, 4H), 6.60 (s, 2H), 6.54 (d, *J* =8.0 Hz, 1H), 5.94 (s, 1H), 5.91 (s, 1H), 5.00(s, 2H), 3.99-3.94 (m, 6H), 3.27 (s, 1H), 1.81-1.77 (m, 6H), 1.48-1.33 (m, 18H), 0.92-0.91 (m, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.89, 153.26, 149.86, 145.13, 137.95, 134.02, 131.84, 130.06, 125.16, 124.06, 123.60, 110.39, 109.95, 105.82, 81.53, 78.89, 73.43, 70.64, 69.13, 52.11, 47.09, 31.76, 31.58, 30.28, 29.33, 25.75, 22.67, 22.61, 14.06, 14.01. EI-TOF-MS of **8**, m/z calced for $C_{47}H_{56}O_4$, 684.42 (M^+), found 684.42

2. ^{1}H, ^{31}P, ^{13}C NMR of 3, 6, 8, PT6, PP0, and PP6 in $CDCl_3$

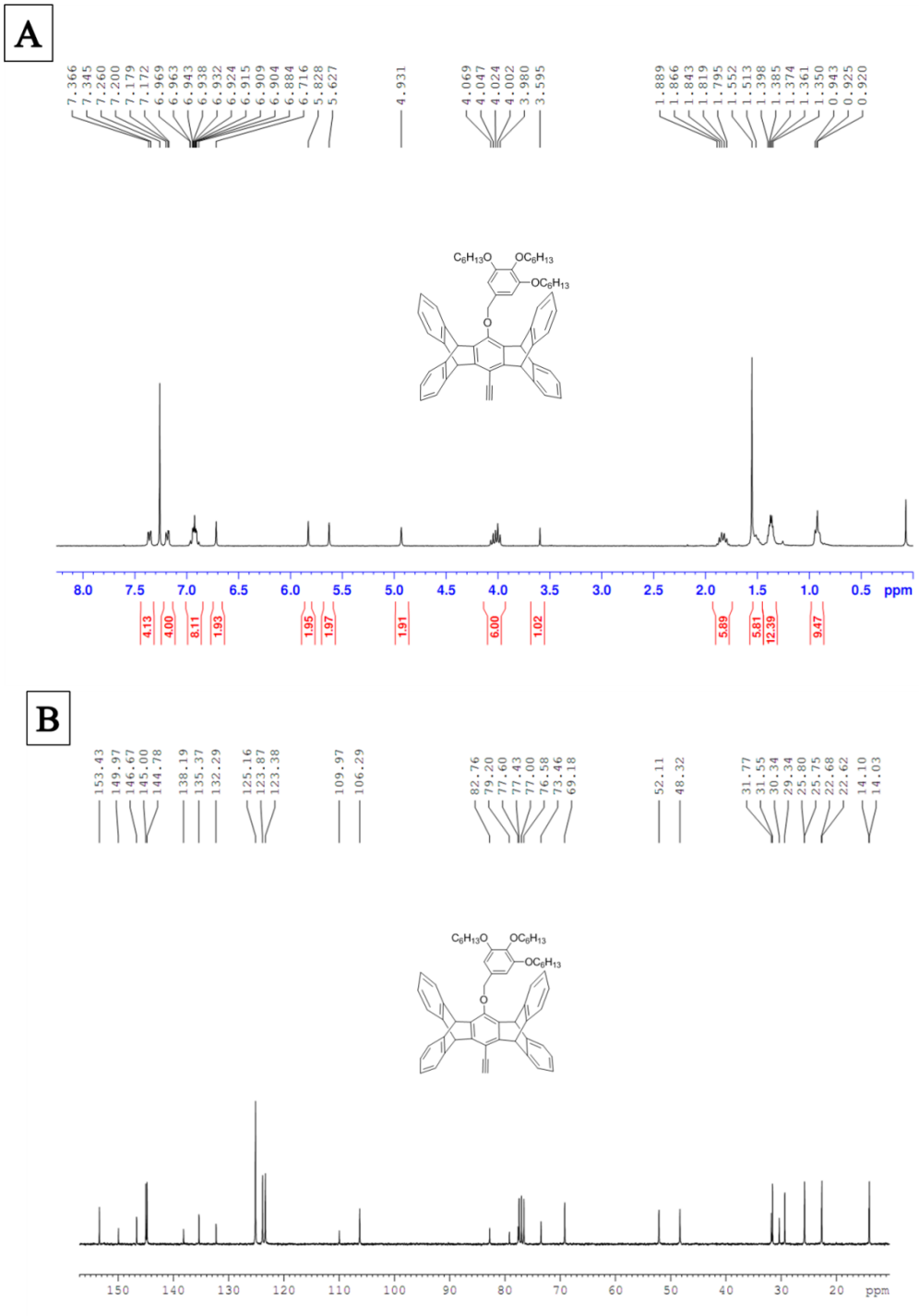


Figure S1. ^{1}H (A), ^{13}C (B) NMR of compound **3** in $CDCl_3$.

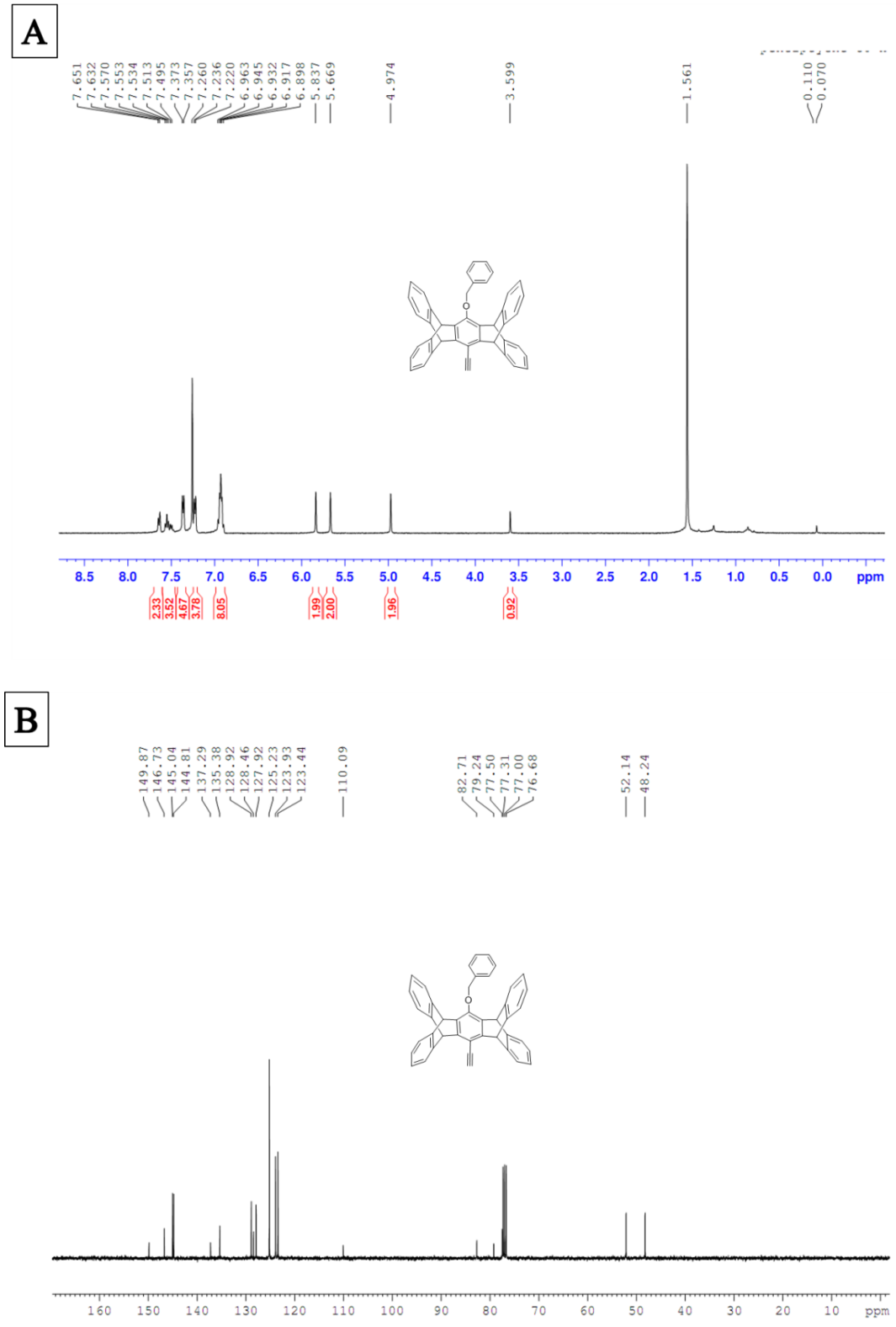


Figure S2. ^{1}H (A), ^{13}C (B) NMR of compound **6** in $CDCl_3$.

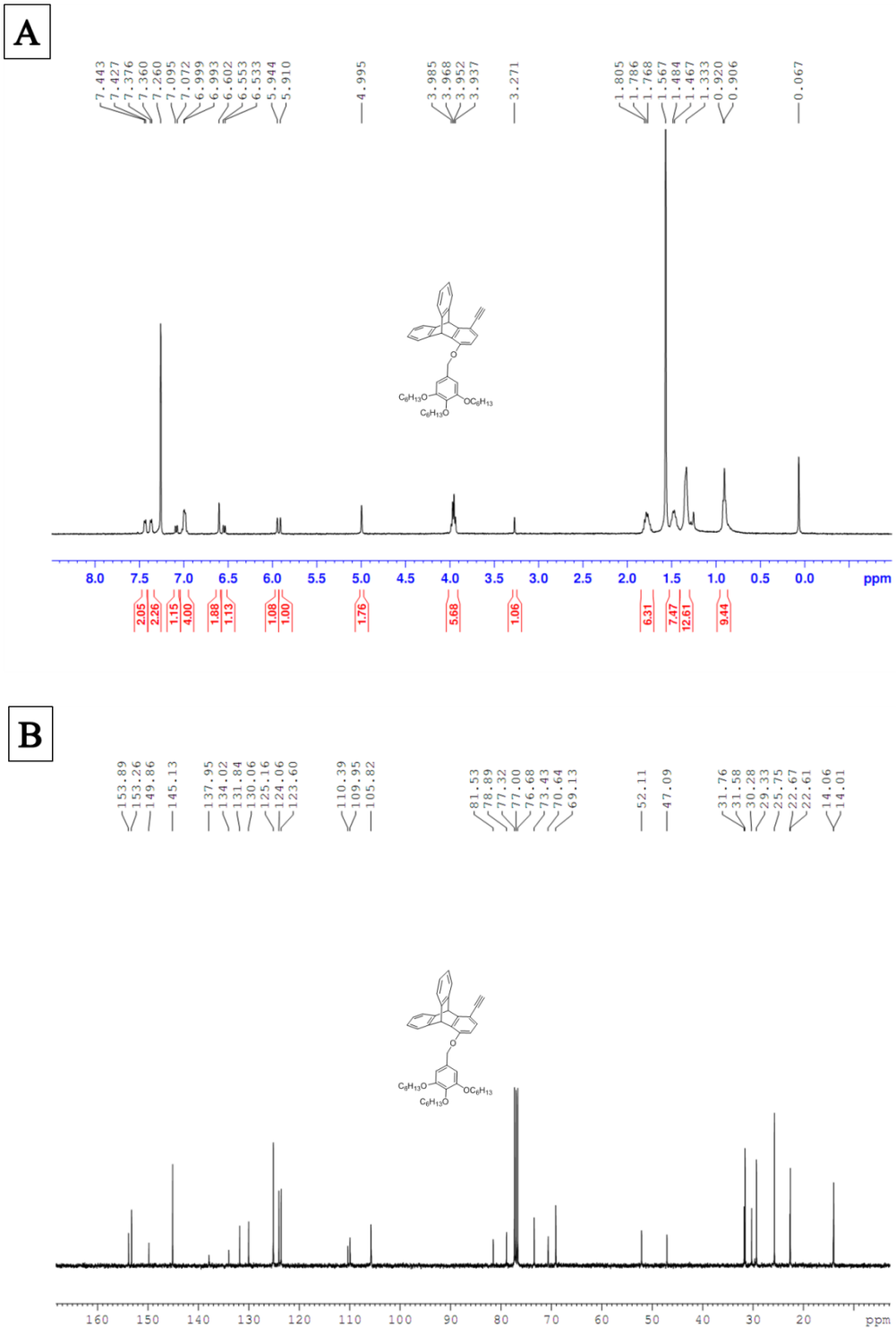
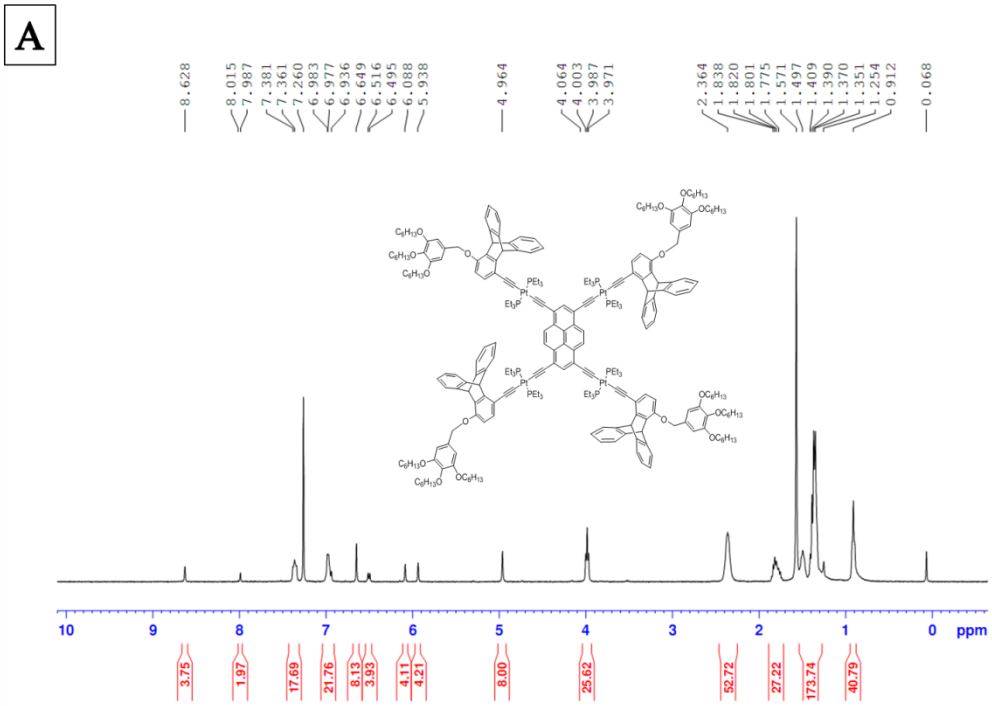
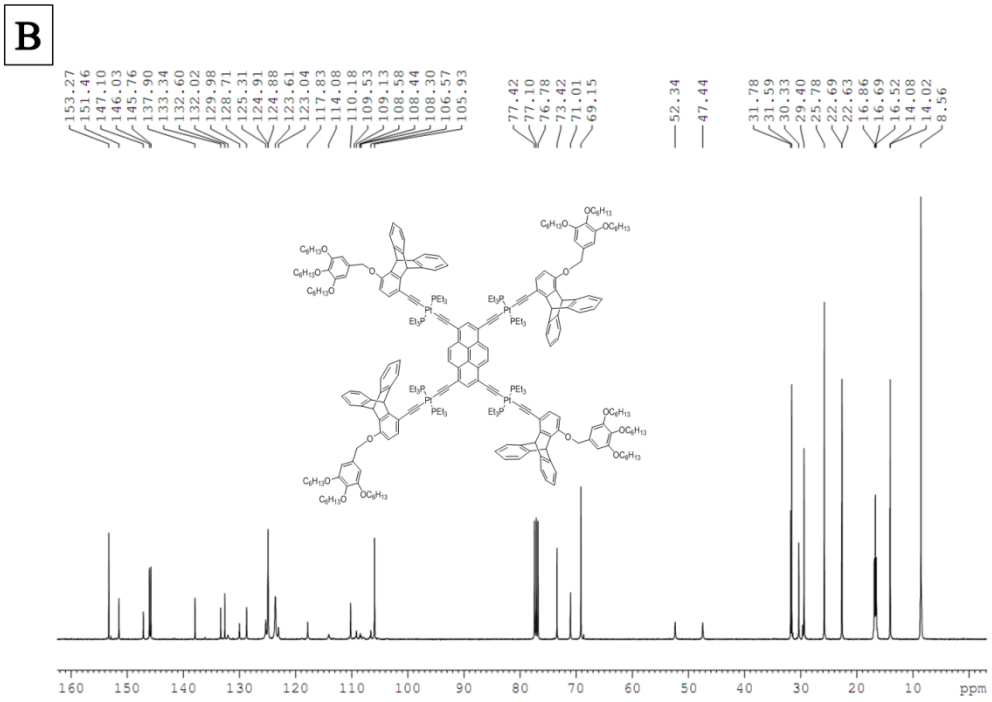


Figure S3. ^{1}H (A), ^{13}C (B) NMR of compound **8** in $CDCl_3$.





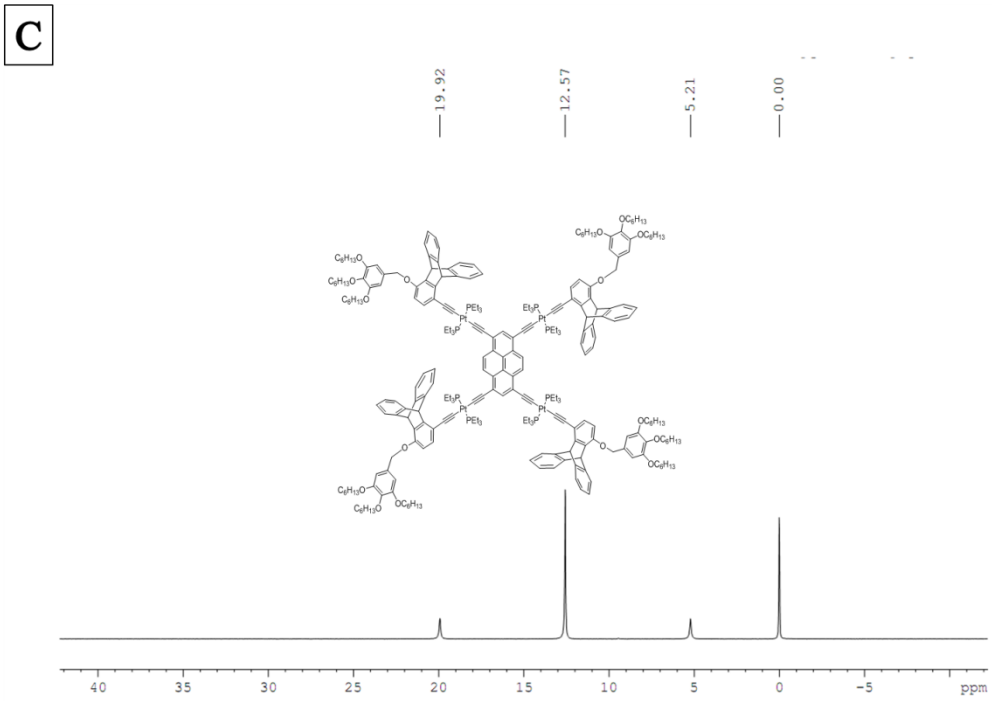
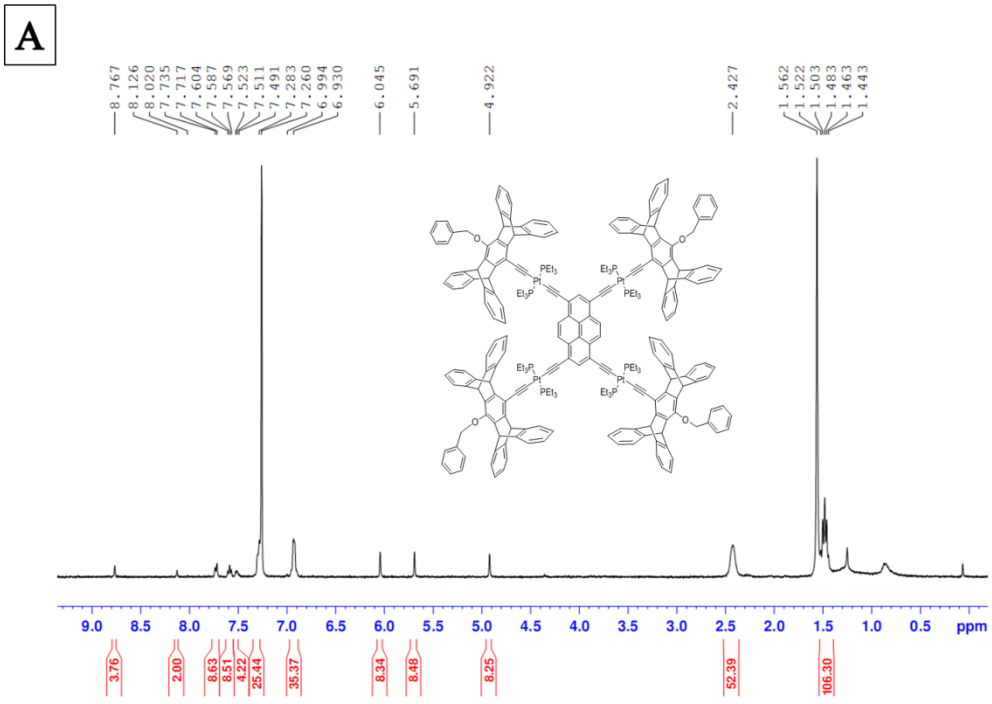


Figure S4. ^{1}H (A), ^{13}C (B) and ^{31}P(C) NMR of compound **PT6** in $CDCl_3$.



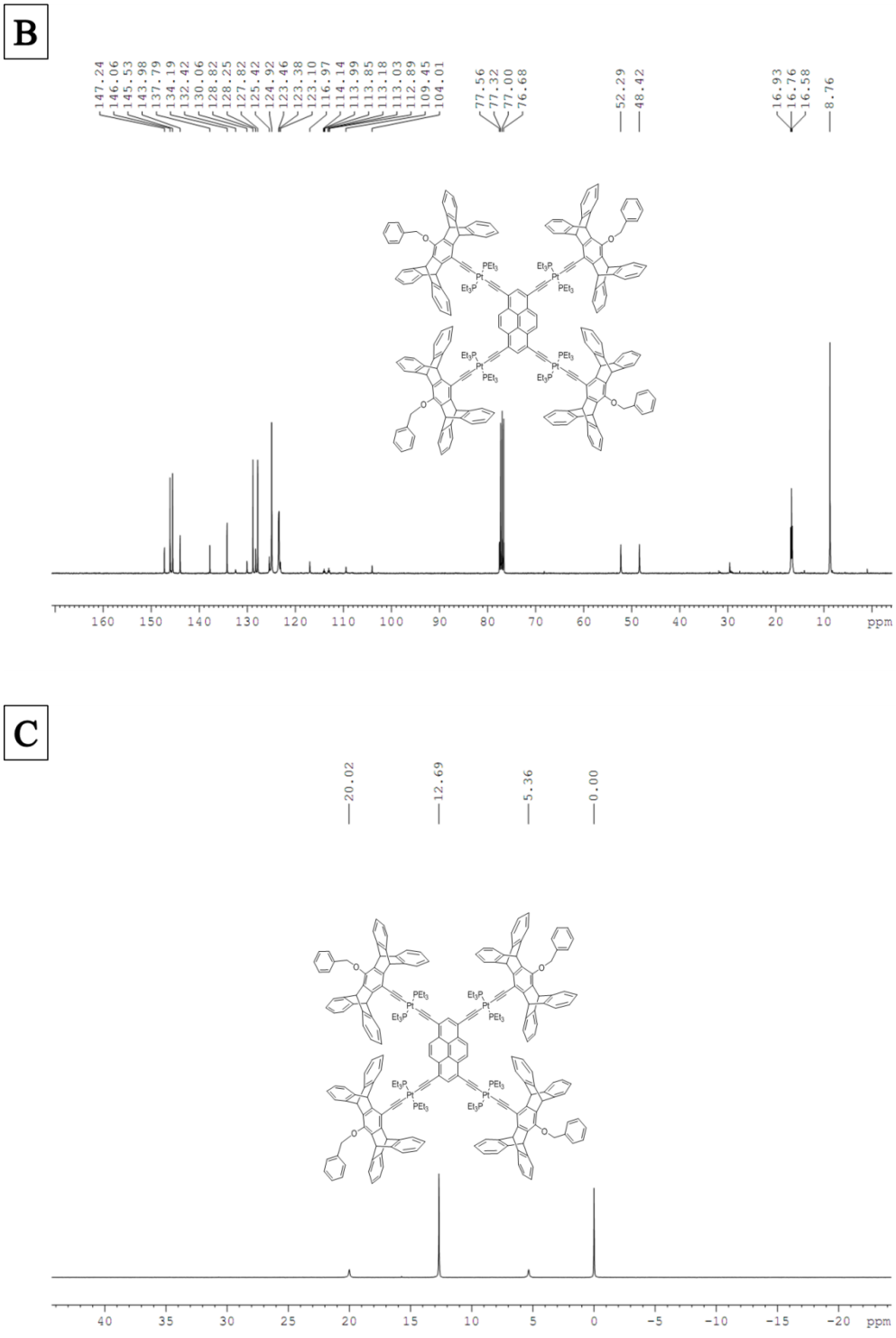
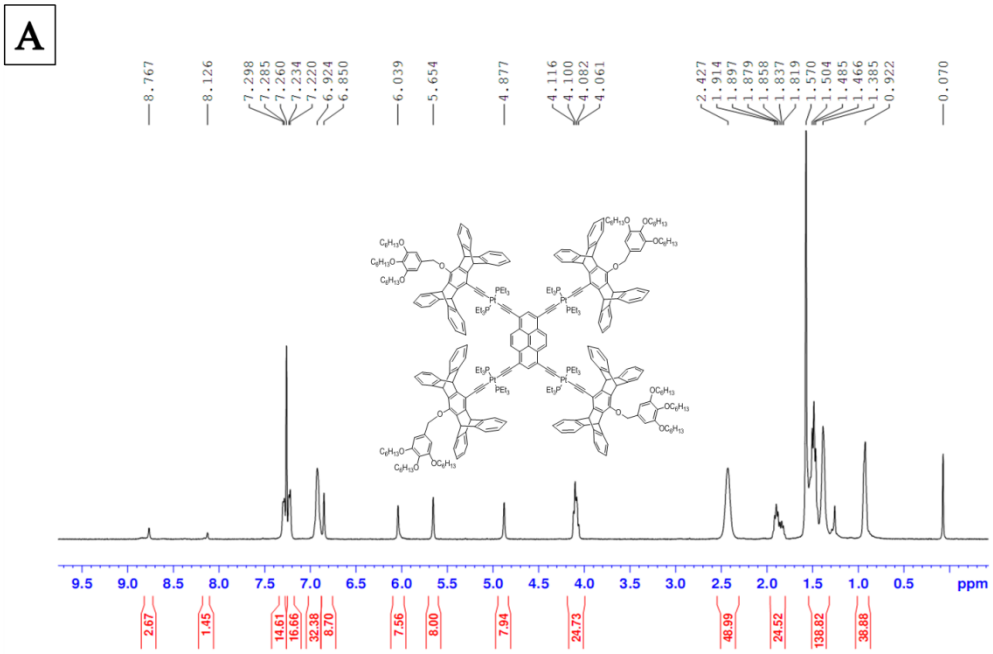
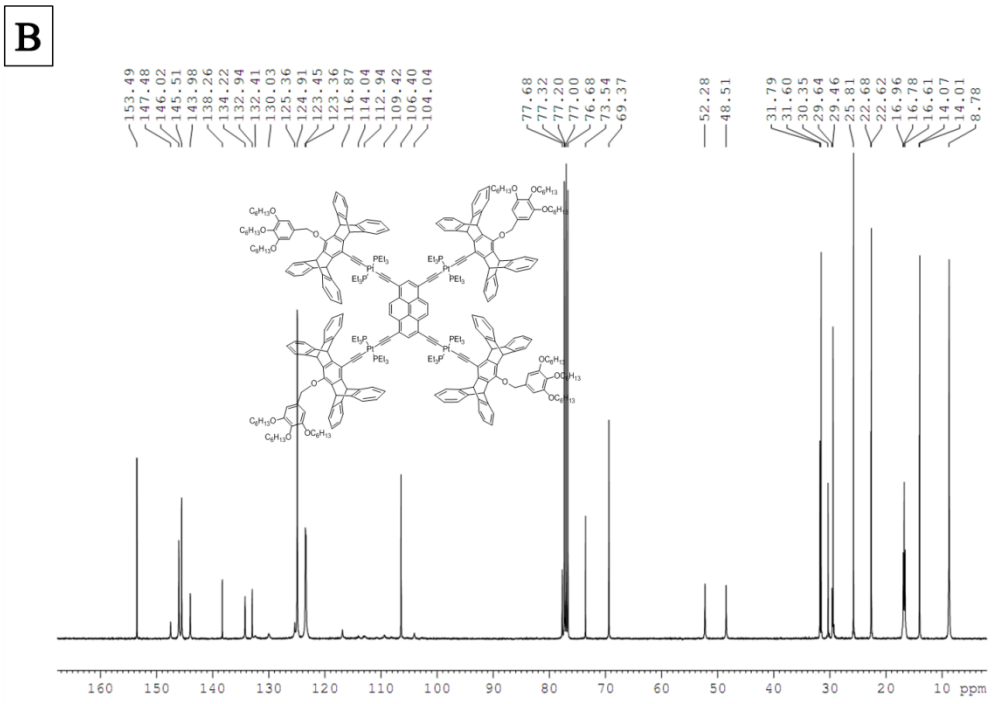


Figure S5. ^{1}H (A), ^{13}C (B) and ^{31}P(C) NMR of compound **PP0** in $CDCl_3$.





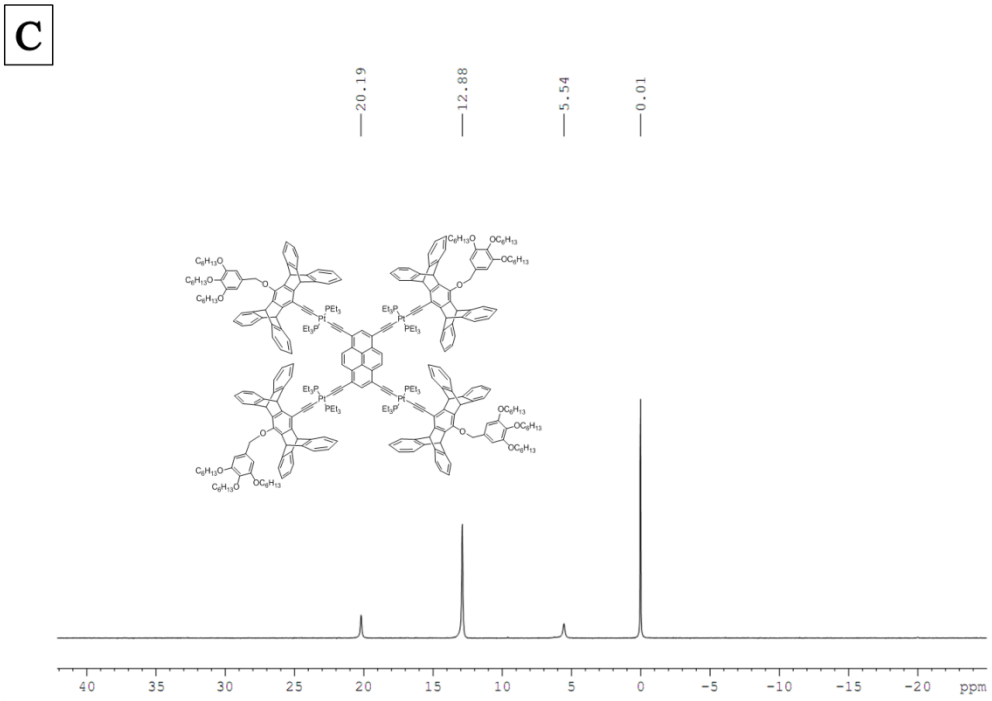


Figure S6. ^{1}H (A), ^{13}C (B) and ^{31}P(C) NMR of compound **PP6** in $CDCl_3$.

3. MALDI-TOF-MS spectrometry of PT6 and PP0

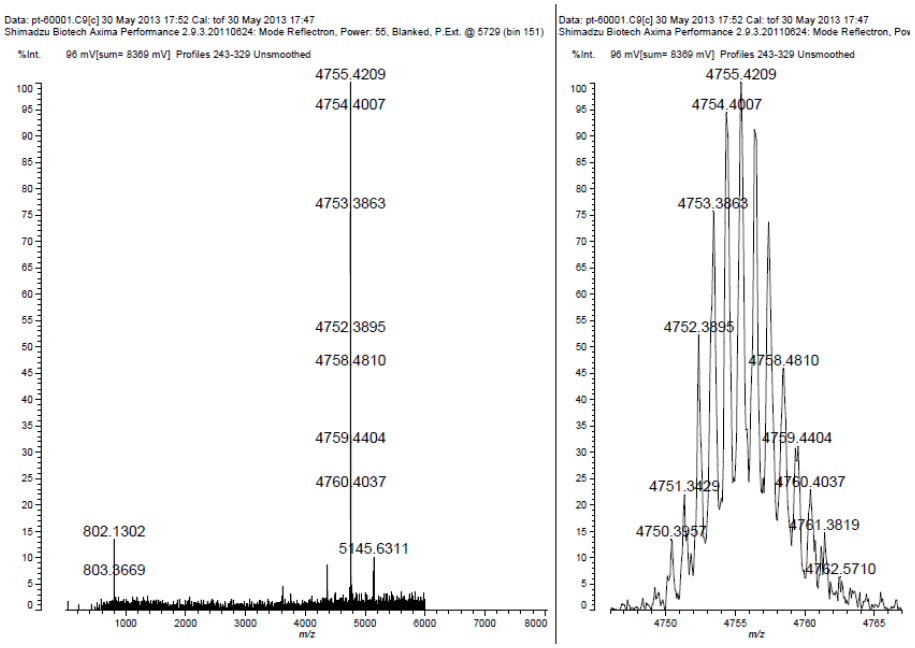


Figure S7. MALDI-TOF-MS spectrometry of **PT6**, m/z calced for $C_{260}H_{346}O_{16}P_8Pt_4$, 4755.28 ($M^+$), found 4755.42.

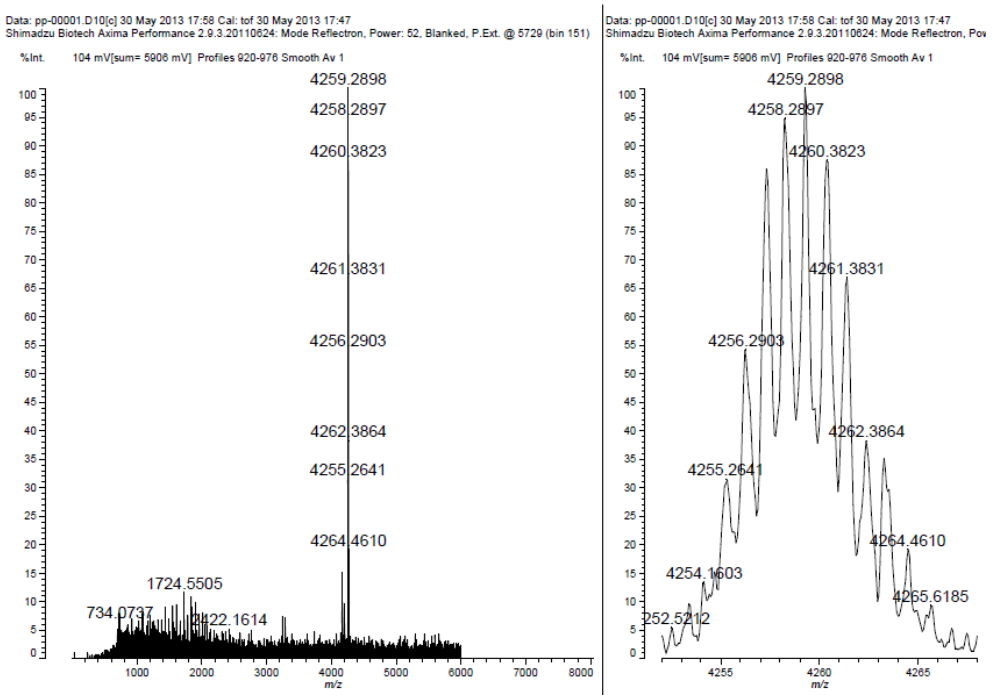


Figure S8. MALDI-TOF-MS spectrometry of **PP0**, m/z calced for $C_{244}H_{234}O_4P_8Pt_4$, 4258.47 (M^+), found 4258.29

4. Solvent-variation absorption and emission spectra

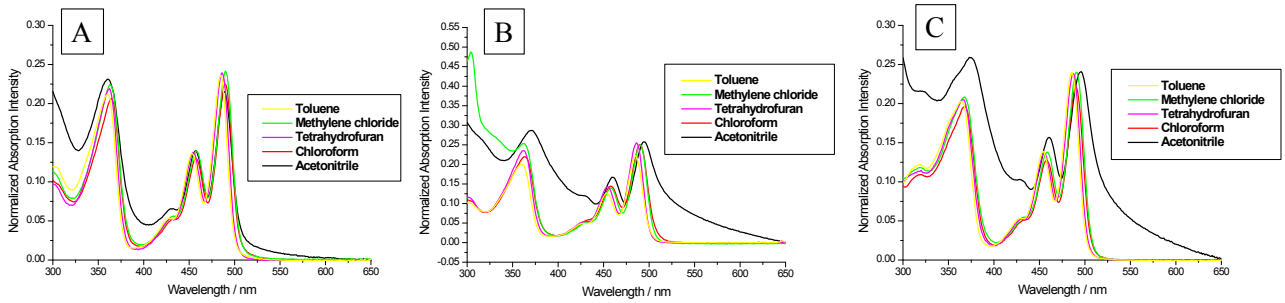


Figure S9. Solvent-variation absorption spectra of **PP0** (A), **PP6** (B), and **PT6**(C).

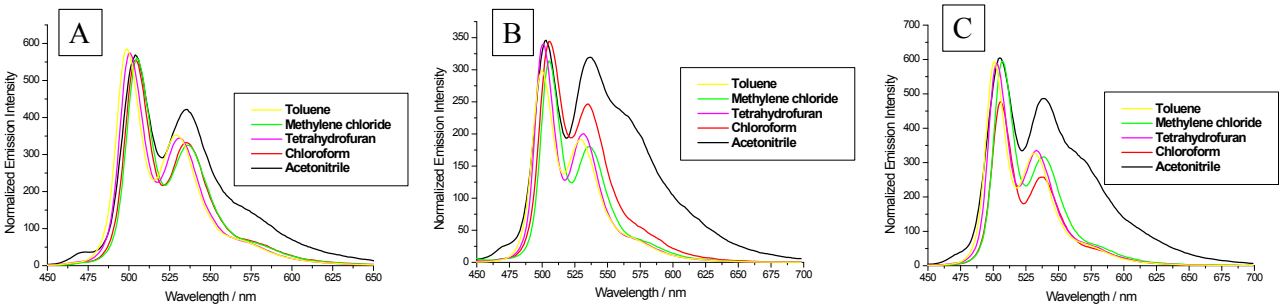


Figure S10. Solvent-variation emission spectra of **PP0** (A), **PP6** (B), and **PT6**(C).

5. Concentraction-variation absorption and emission spectra

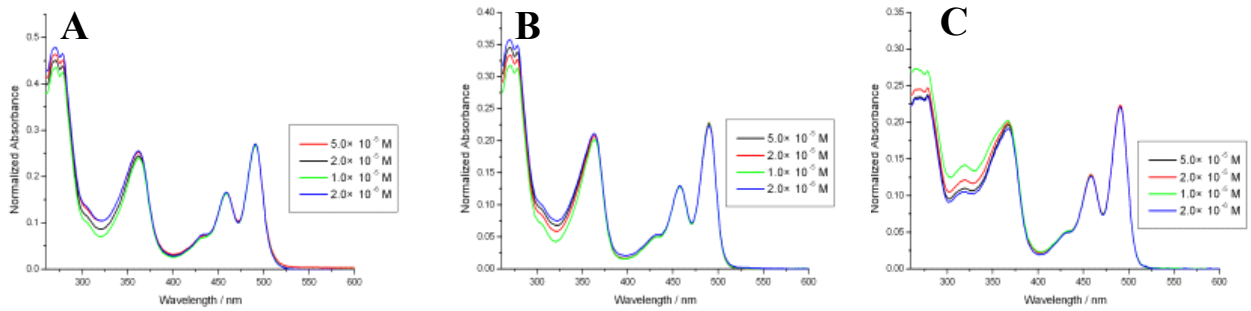


Figure S11. Absorption spectra of (A) **PP6**, (B) **PP0**, (C) **PT6** in dichloromethane at different concentrations.

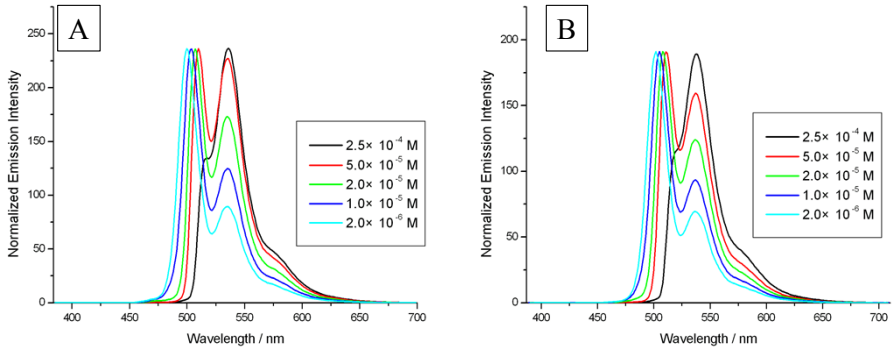


Figure S12. Emission spectra of (A) **PP0** and (B) **PT6** in dichloromethane at different concentrations.

6. LCSM images of the aggregates formed by PP0 and PT6

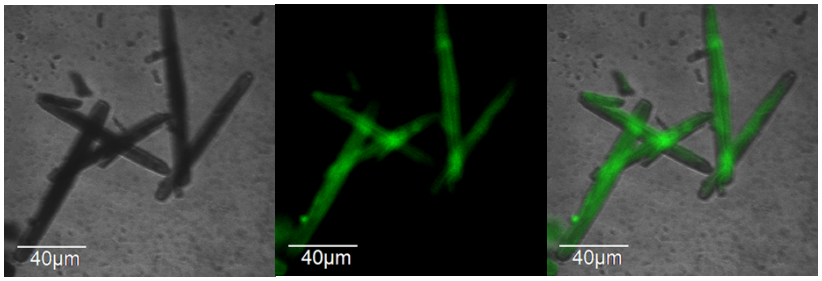


Figure S13. LCSM images of **PP0** in toluene/*n*-propanol = 1/1 (lex=362 nm, emission was collected at 450–690 nm).

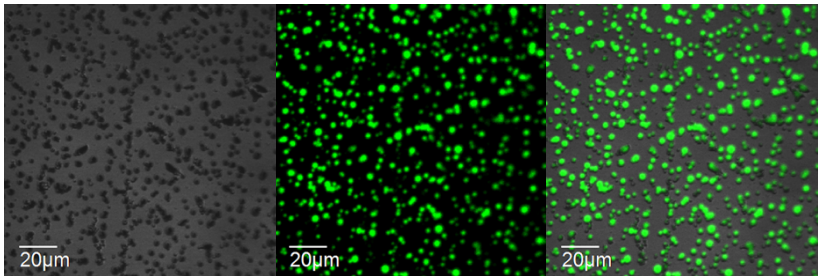


Figure S14. LCSM images of **PT6** in toluene/*n*-propanol = 1/1 (lex=362 nm, emission was collected at 450–690 nm).

7. Emission profiles of the aggregates

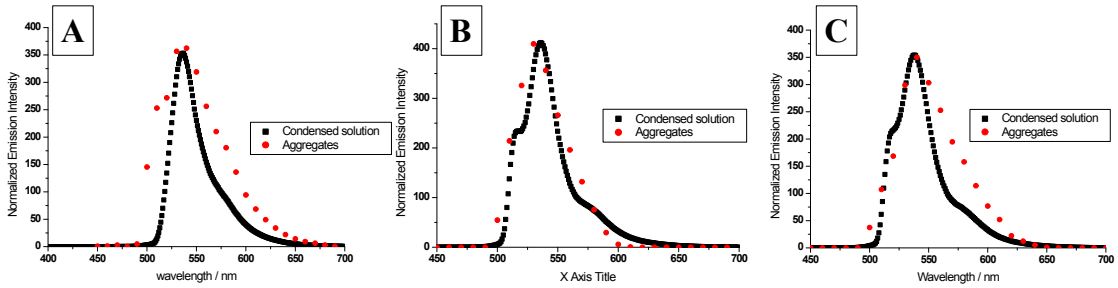


Figure S15. The emission spectra of the microstructures formed by **PP6**(A), **PP0**(B), **PT6**(C) and their emission spectra in condensed solution (c = 0.25 mM in dichloromethane). λex = 362 nm.

8. EDX results of PP0 and PT6

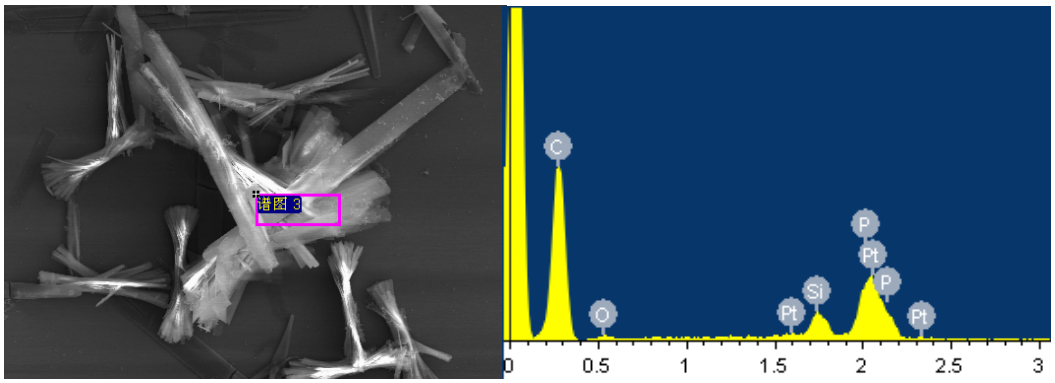


Figure S16. The EDX results of **PP0** were collected from the area marked by the pink boxes shown at the right side of the image.

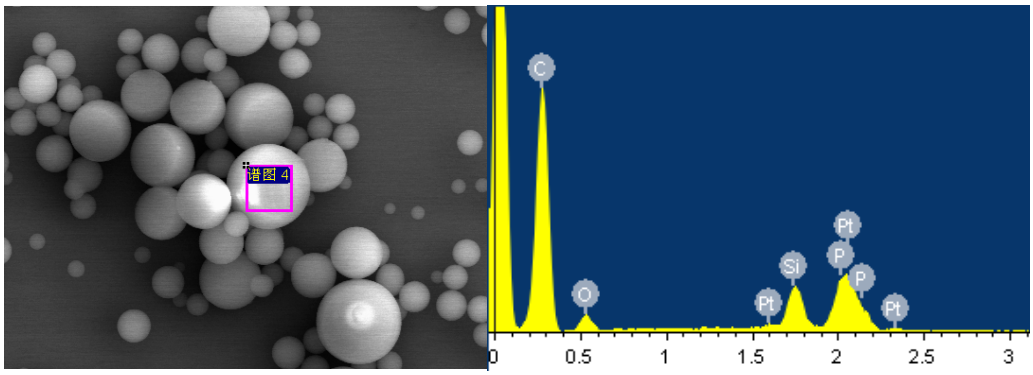


Figure S17. The EDX results of **PT6** were collected from the area marked by the pink boxes shown at the right side of the image.