Supporting Information for

Construction of Supramolecular Pyrene-Modified Metallocycles via Coordination- Driven Self-Assembly and Their Spectroscopic Behavior

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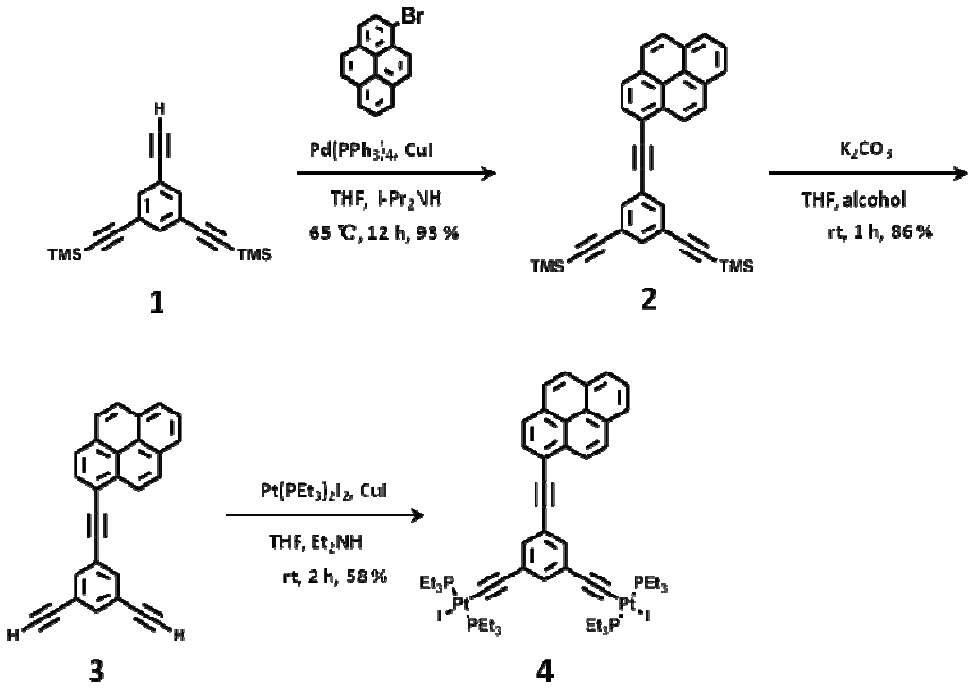
1. Synthesis of compounds 2, 3, and 4



Scheme S1. Synthesis of compounds **2**, **3** and **4**

Synthesis of Compound 2. Under an atmosphere of nitrogen, a mixed solvent of 15 mL THF and 15 mL i-Pr_2NH was added to a mixture of compound **1** (520 mg, 1.76 mmol), 1-bromopyrene (993 mg, 3.52 mmol), $Pd(PPh_3)_4$ (101 mg, 0.088 mmol) and CuI (17 mg, 0.088 mmol) in a 100 mL Schlenk flask. The mixture was stirred at 65 ℃ for 12 hours. After then insoluble materials were filtrated and the solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel with petroleum ether/dichloromethane (v/v, 8/1) as eluent afforded the light yellow powder of **2** with a yield of 93%: R*f* = 0.60 (petroleum ether/dichloromethane, v/v, 8/1). Mp: 187 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (d, *J* = 9.2 Hz, 1H), 8.26-8.03 (m, 8H), 7.75 (s, 2H), 7.59 (s, 1H), 0.28 (s, 18H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.88, 134.54, 131.91, 131.40, 131.12, 130.93, 129.56, 128.42, 128.28, 127.13, 126.21, 125.69, 125.63, 125.29, 124.45, 124.32, 124.15, 124.04, 123.84, 117.03, 103.26, 95.78, 93.28, 89.76, -0.12. MS (EI): m/z (%) = 494 (M^+, 7.50). HRMS calcd for $C_{34}H_{30}Si_2$: 494.1886, found: 494.1881.

Synthesis of Compound 3. Compound **2** (812 mg, 1.64 mmol) was dissolved in a mixture of 45 mL THF and 25 mL methanol. K_2CO_3 (452 mg, 3.24 mmol) was added and the solution was stirred at room temperature for 1 hour. Insoluble materials were filtrated and the solvent was removed by evaporation on a rotary evaporator. Column chromatography with petroleum ether/dichloromethane (v/v, 4/1) as eluent afforded the yellow solid of compound **3** with a yield of 86%: R*f* = 0.56 (petroleum ether/dichloromethane, v/v, 4/1). Mp: 186 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.62 (d, *J* = 9.2 Hz, 1H), 8.26-7.81 (m, 8H), 7.62 (s, 2H), 7.61 (s, 1H), 3.16 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.14, 135.08, 132.02, 131.56, 131.18, 130.98, 129.66, 128.56, 128.41, 127.19, 126.30, 125.79, 125.73, 125.28, 124.51, 124.41, 124.34, 124.22, 122.99, 116.89, 92.97, 90.12, 81.85, 78.62. MS (EI): m/z (%) = 350 (M^+, 9.89). HRMS calcd for $C_{28}H_{14}$: 350.1096, found: 350.1094.

Synthesis of Compound 4. To a solution of CuI (12 mg, 0.063 mmol) and $Pt(PEt_3)_2I_2$ (1.56 g, 2.28 mmol) in a mixed solvent of 20 mL THF and 20 mL Et_2NH was added dropwise a solution of compound **5** (220 mg, 0.628 mmol) in THF (20 mL) under an atmosphere of nitrogen. The mixture was then stirred at room temperature for 2 hours. The solvent was removed in vacuo and the residue was purified via column chromatography with petroleum ether/dichloromethane (v/v, 2/1) as eluent afforded the light yellow solid of **5** with a yield of 58%: R*f* = 0.51 (petroleum ether/dichloromethane, v/v, 1/1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.68-8.65 (d, *J* = 9.2 Hz, 1H), 8.25-8.02 (m, 8H), 7.42 (s, 2H), 7.22 (s, 1H), 2.29-2.23 (m, 24H), 1.24-1.16 (m, 36H). ^{13}C NMR ($CDCl_3$, 100 MHz): 132.86, 131.63, 130.99, 130.94, 130.71, 130.43, 129.30, 128.03, 127.94, 126.96, 126.05, 125.38, 125.14, 124.30, 124.17, 123.98, 123.09, 117.42, 99.17, 94.80, 90.82, 88.18, 16.50, 8.16. ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 8.58 (s, $J_{Pt\text{-}P}$ = 2320.0 Hz) MALDI HRMS: m/z calced for $C_{52}H_{72}I_2P_4Pt_2$, ($[M + H]^+$) 1465.20, found: 1465.27.

2. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra of 2-6

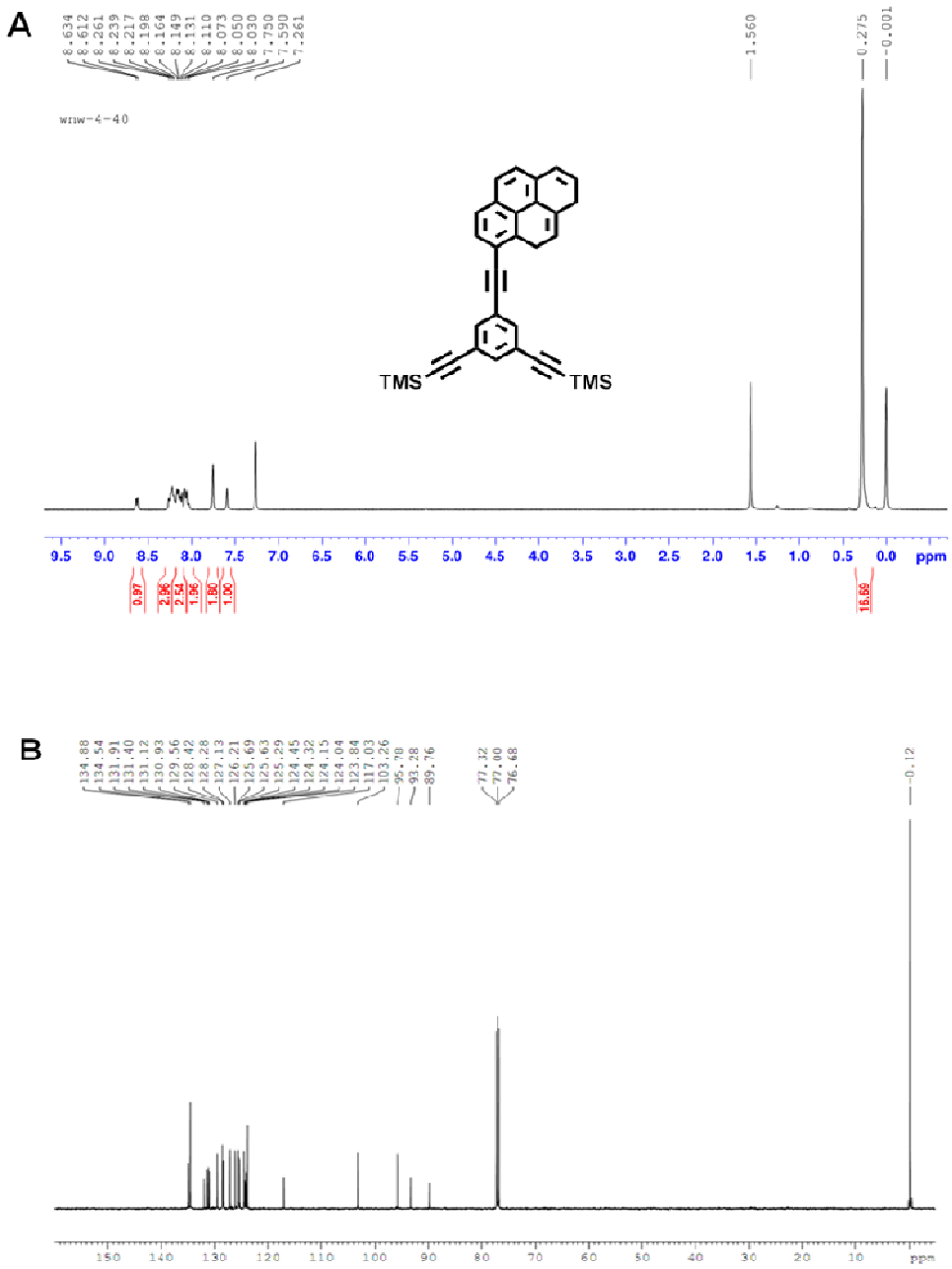


Figure S1. ^{1}H (A) and ^{13}C (B) NMR spectra of **2** in $CDCl_3$

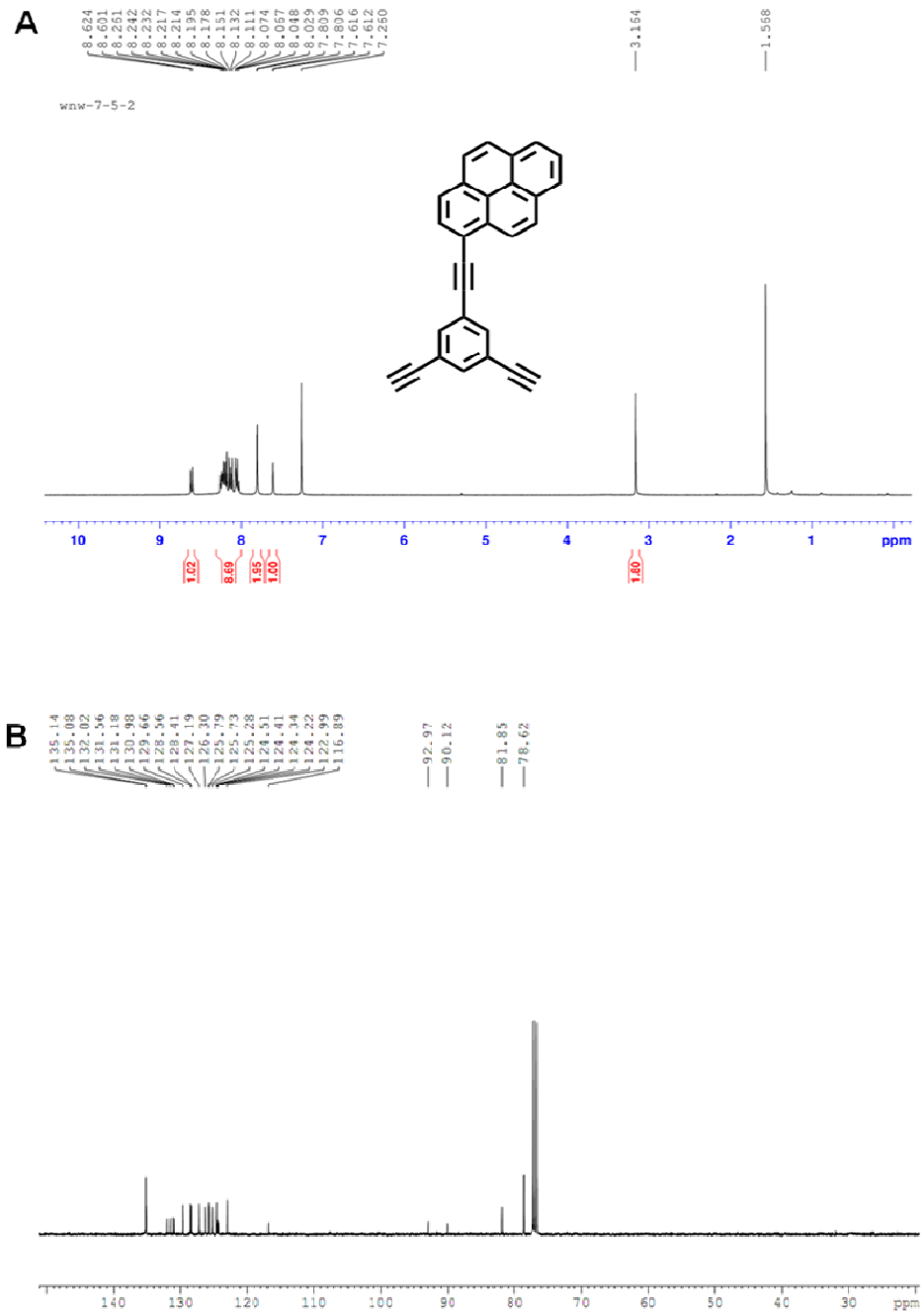
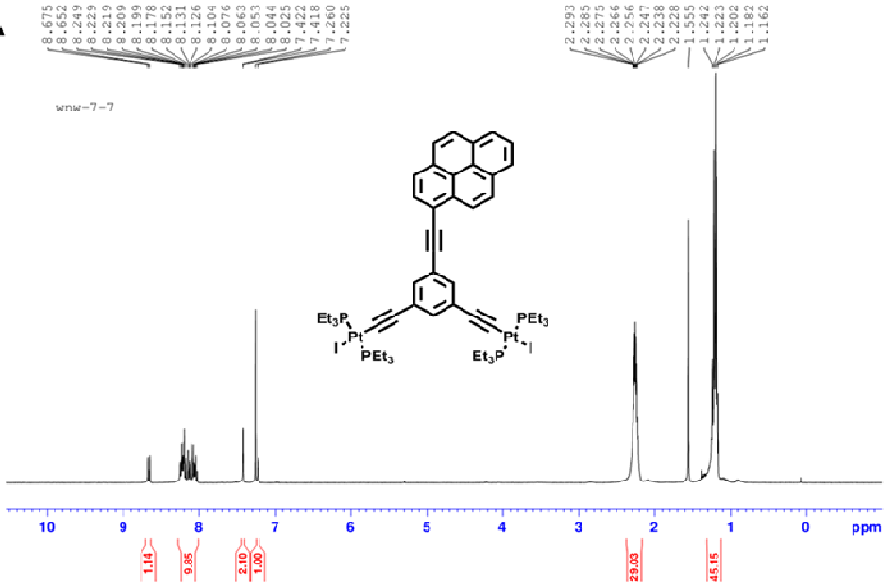


Figure S2. ^{1}H (A) and ^{13}C (B) NMR spectra of **3** in $CDCl_3$

A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8.063
8.053
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8.025
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7.418
7.260
7.225
2.293
2.285
2.275
2.266
2.256
2.247
2.238
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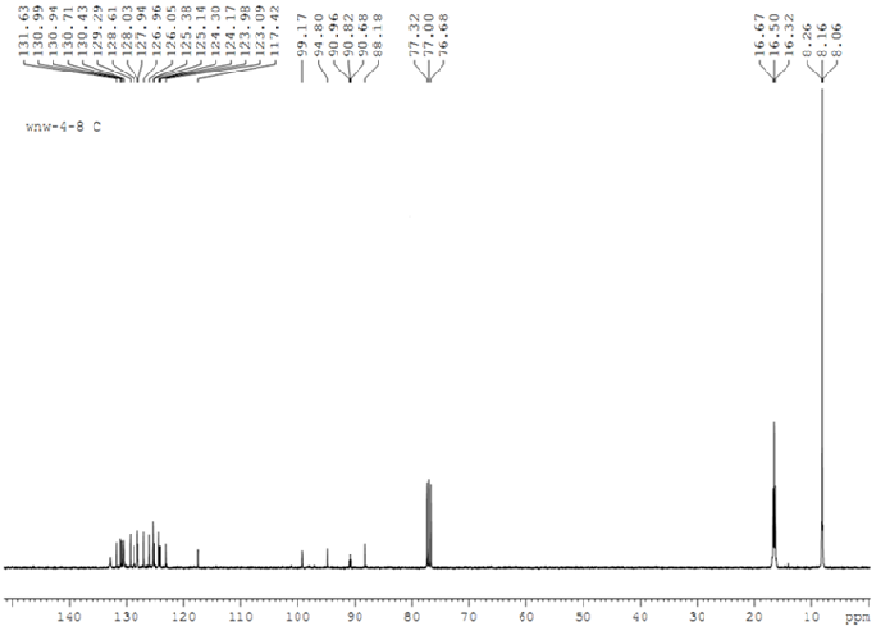
Et3P
PEt3
Pt
I
PEt3
Et3P
10
9
8
7
6
5
4
3
2
1
0
ppm
1.14
9.85
2.10
1.00
29.03
45.15

B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127.94
126.96
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90.96
90.82
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88.18
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77.00
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16.50
16.32
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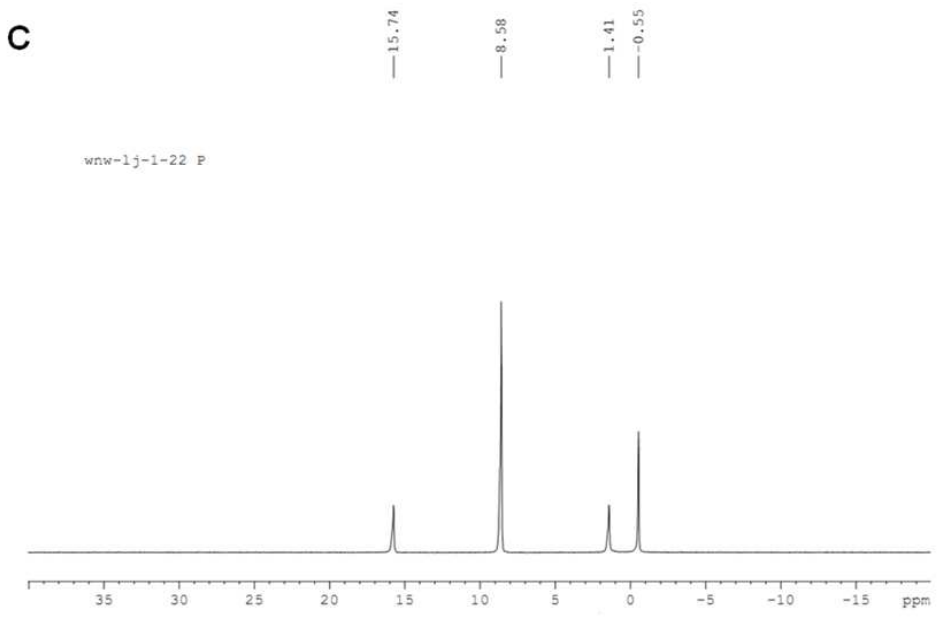

Figure S3. ^{1}H (A) ^{13}C (B) and ^{31}P (C) NMR of **4** in $CDCl_3$

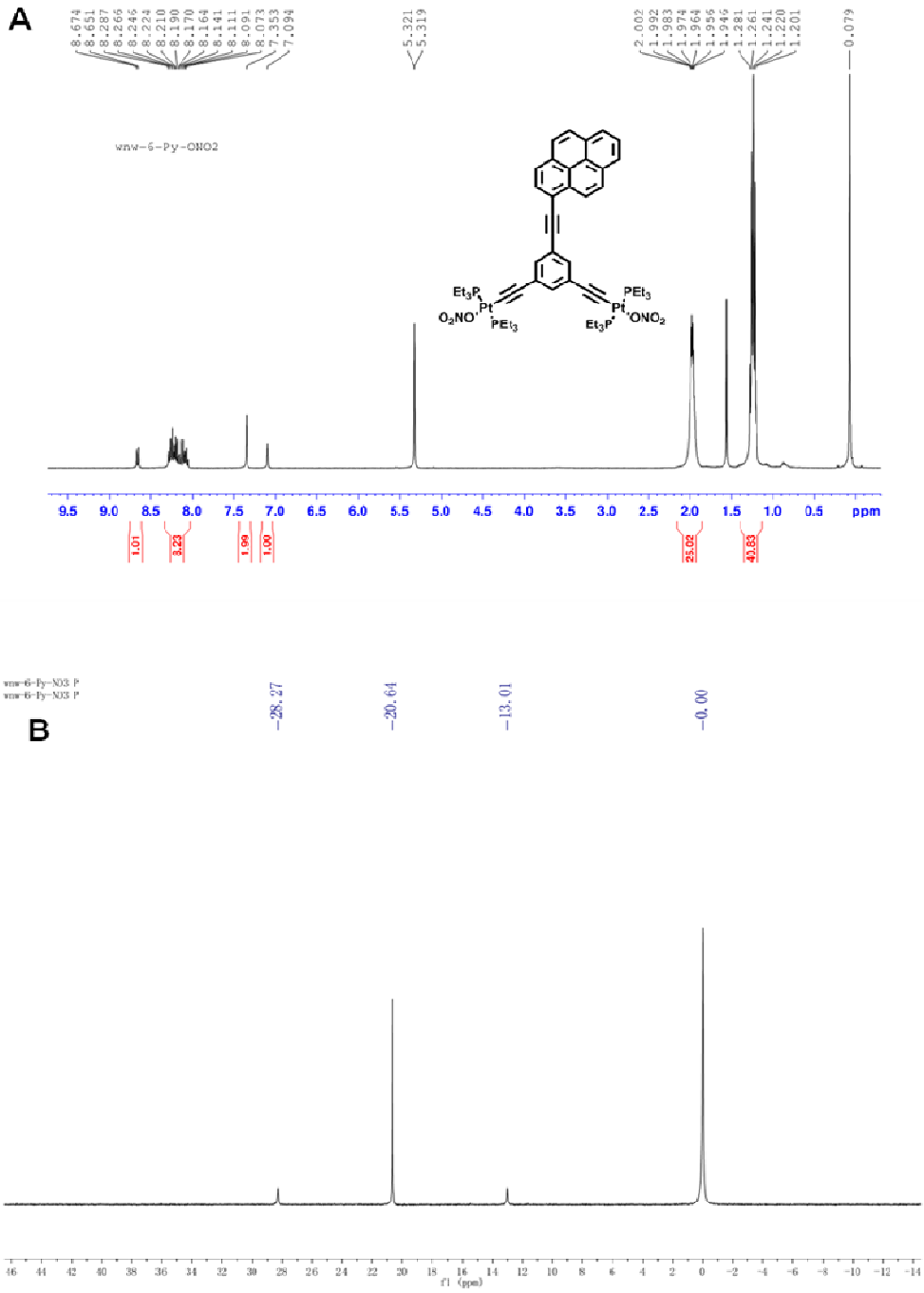

Figure S4. ^{1}H (A) and ^{31}P (B) NMR of **5** in CD_2Cl_2

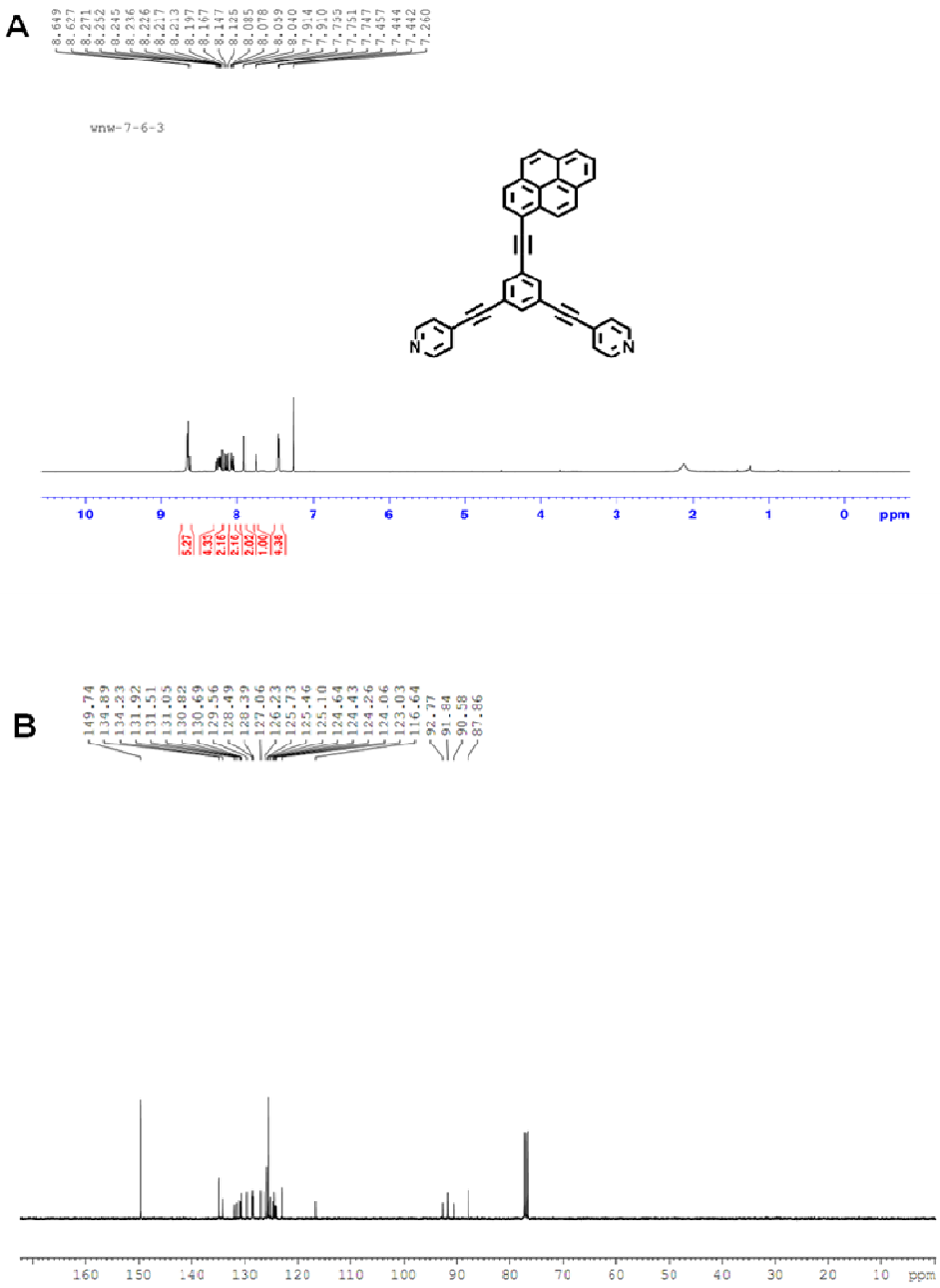

Figure S5. ^{1}H (A) and ^{13}C (B) NMR of **6** in $CDCl_3$

3. ^{1}H, ^{31}P NMR and Mass Spectra of Metallocycles 8a-b and 10a-b

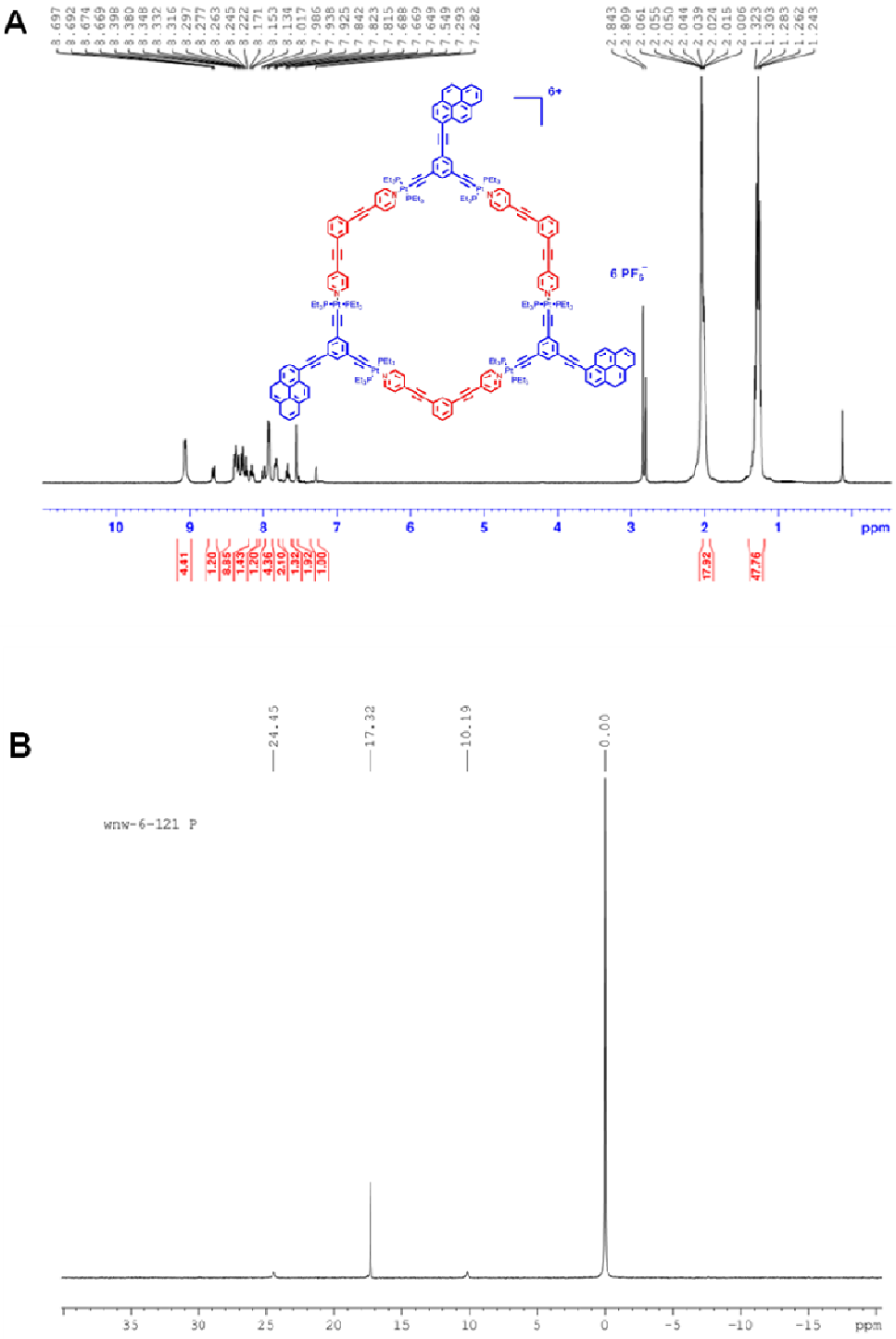

Figure S6. ^{1}H (A) and ^{31}P (B) NMR of **8a** in acetone-d_6

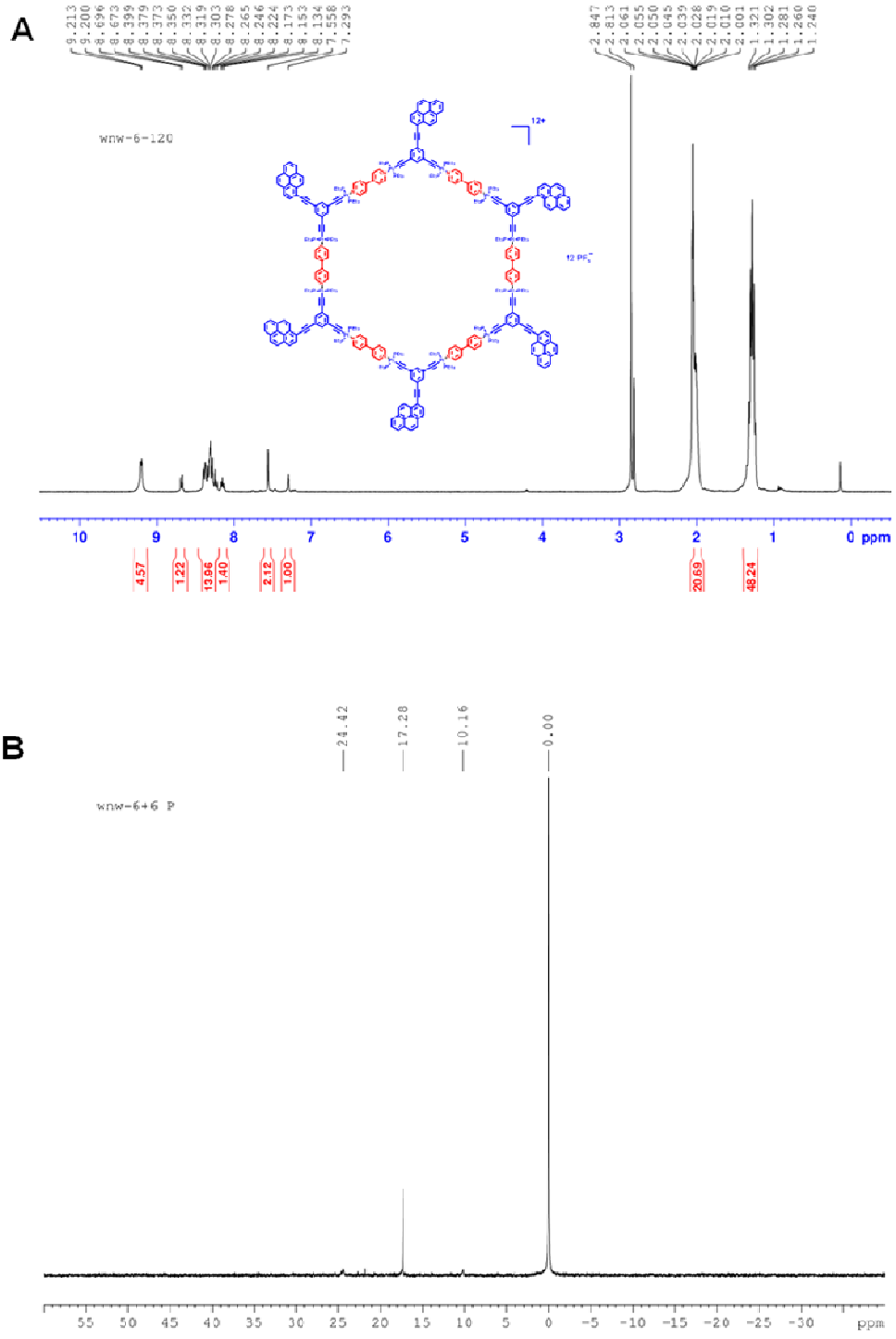

Figure S7. ^{1}H (A) and ^{31}P (B) NMR of **8b** in CD_2Cl_2

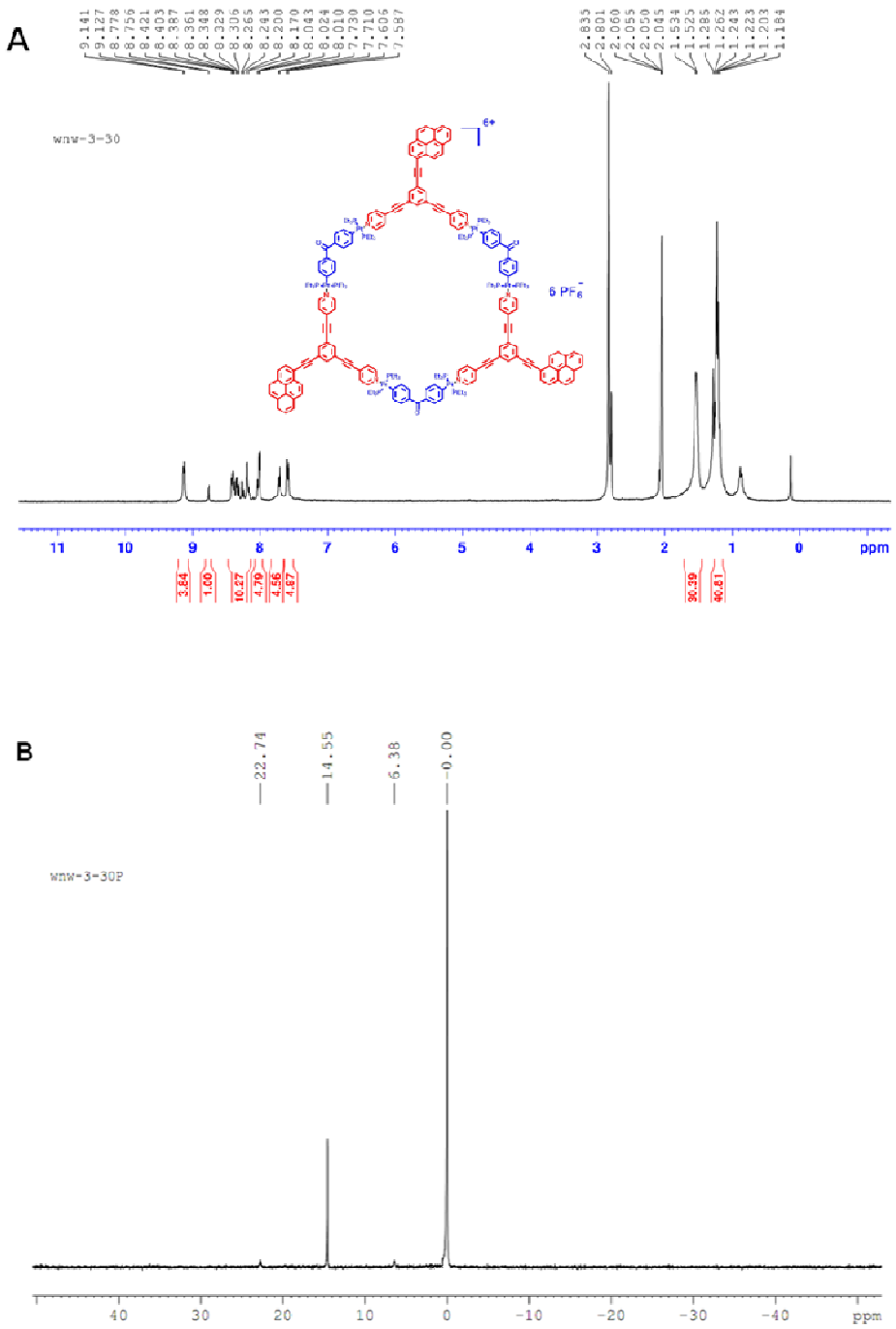

Figure S8. ^{1}H (A) and ^{31}P (B) NMR of hexagon **10a** in acetone-d_6

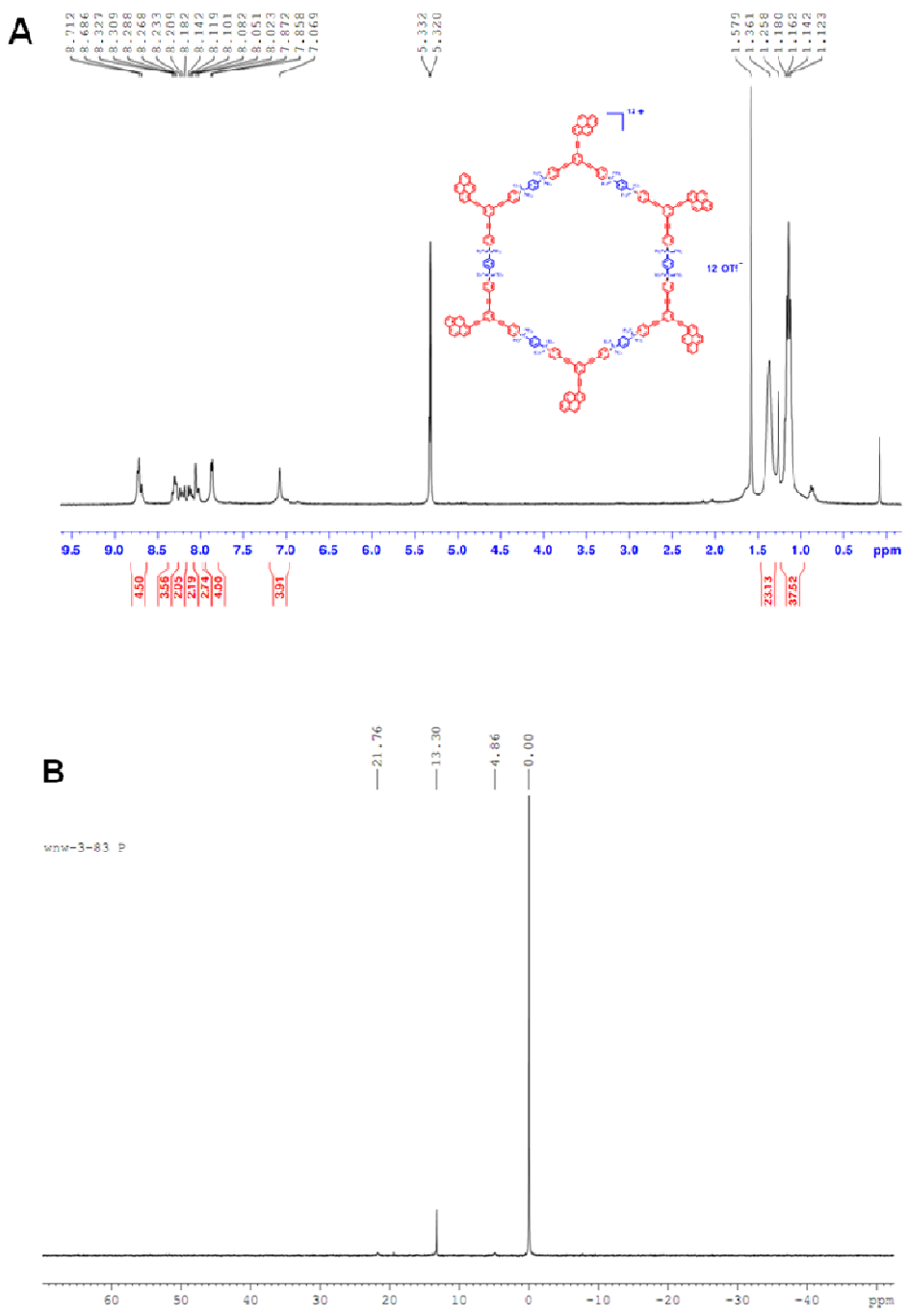

Figure S9. ^{1}H (A) and ^{31}P (B) NMR of hexagon **10b** in CD_2Cl_2.

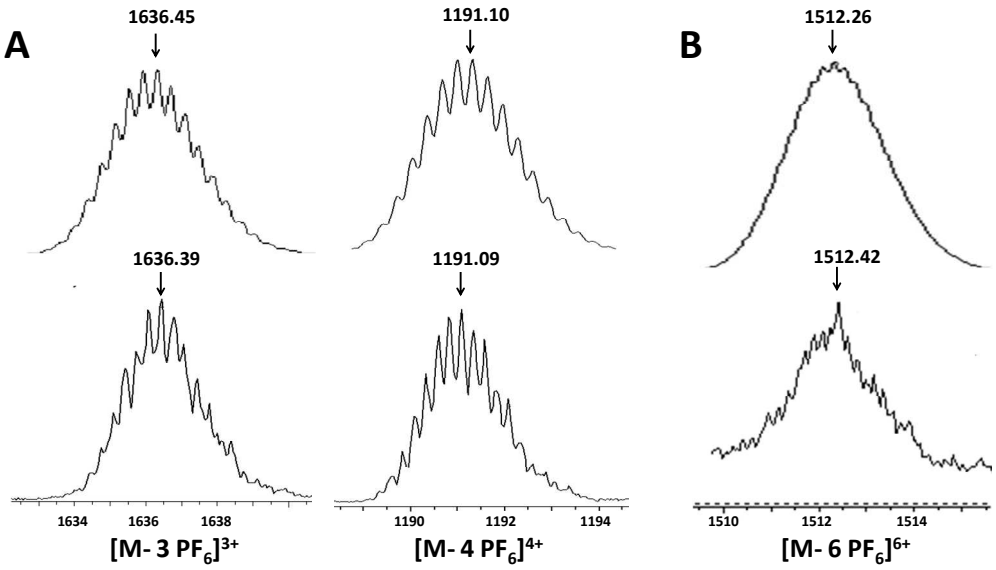

Figure S10. Theoretical (top) and experimental (bottom) CSI-TOF-MS results of **8a** (A) and **8b** (B).

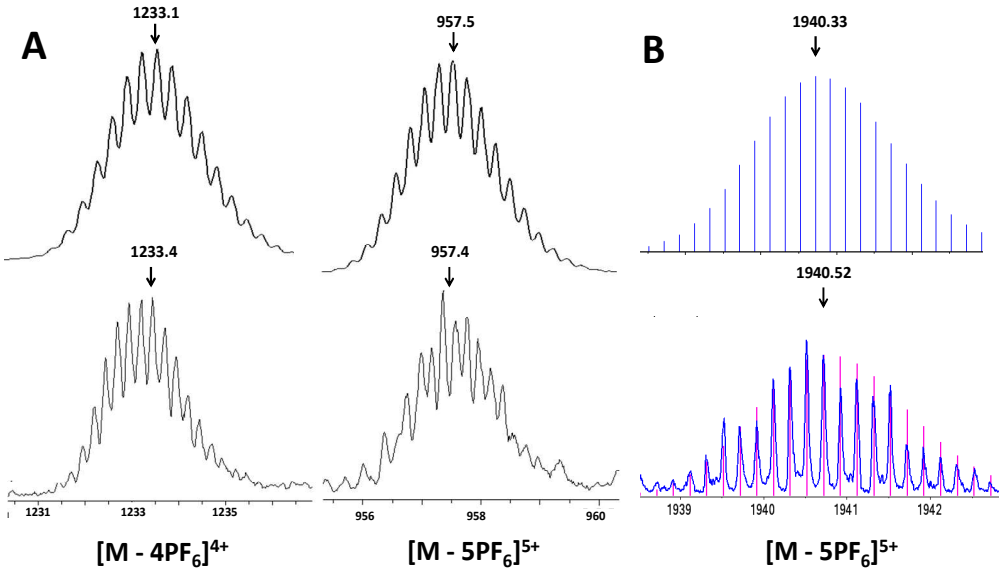

Figure S11. Theoretical (top) and experimental (bottom) CSI-TOF-MS results of **10a** (A), and ESI-TOF-MS result of **10b** (B).

4. Spectroscopic Behavior of 5, 6, 8a-b and 10a-b

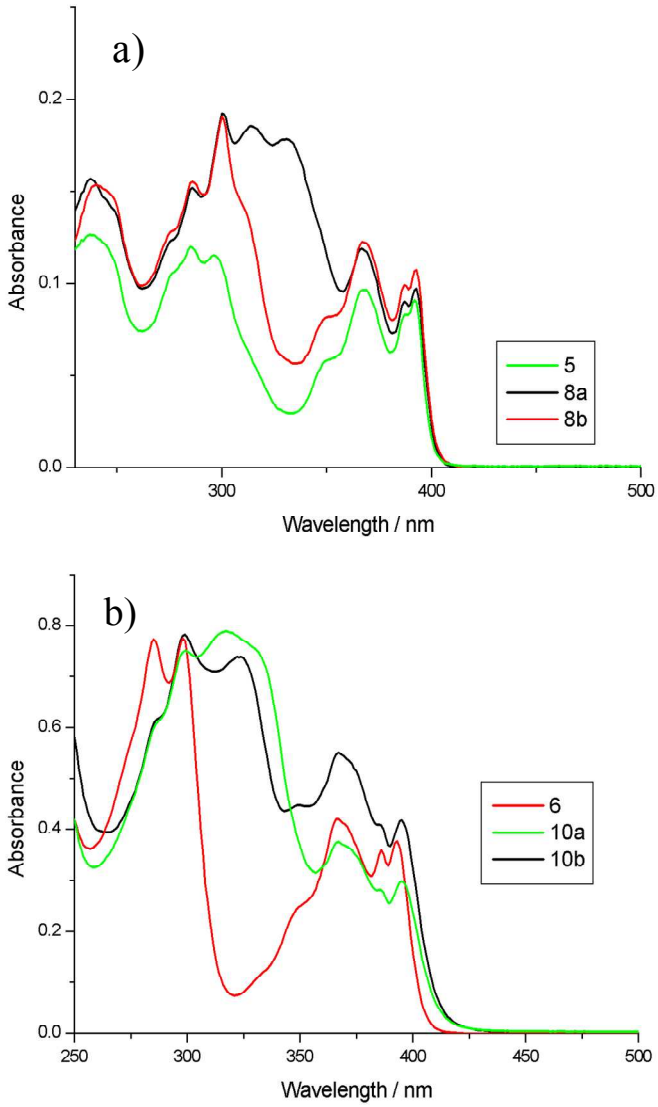

Figure S12. Absorption spectra of **5** (10^{-5} M), **6** (10^{-5} M), **8a** (0.33×10^{-5} M), **8b** (0.17×10^{-5} M), **10a** (0.33×10^{-5} M) and **10b** (0.17×10^{-5} M) in CH_2Cl_2.

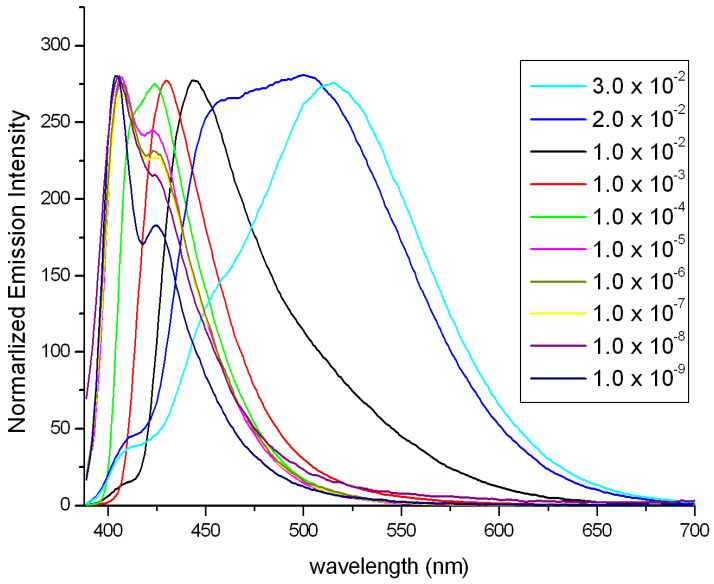

Figure S13. Normalized emission titration spectra of **6** in CH_2Cl_2.

Table S1. Photophysical Data for **5**, **8a**, **8b**, **6**, **10a**, and **10b**

Compound (concentration)/M^{-1}	Solvent (298K)	λ_{abs}(nm)	ε ($M^{-1}cm^{-1}$)	λ_F(nm)	ΦF
5 (1.0×10^{-5})	CH_2Cl_2	392	91000	398	0.87
		367	97000	420	
		285	120000		
8a (0.33×10^{-5})	CH_2Cl_2	393	291000	420	0.030
		367	357000		
		300	576000		
8b (0.17×10^{-5})	CH_2Cl_2	393	642000	424	0.013
		367	738000		
		300	1140000		
6 (1.0×10^{-5})	CH_2Cl_2	392	210160	407	0.12
		367	231956		
		285	310714		
10a (0.33×10^{-5})	CH_2Cl_2	392	879078	551	0.0097
		367	1078986		
		331	1638720		
		300	1787040		
10b (0.17×10^{-5})	CH_2Cl_2	392	3490002	548	0.0032
		367	4031046		
		299	6416826		

Table S2. Charge Density Data for **5**, **8a**, **8b**, **6**, **10a** and **10b**

	5	8a	8b	6	10a	10b
Charge Density ($C\cdot m^{-2}$)	0.086166	0.133250	0.148520	0.101246	0.150779	0.150779