Electronic Supplementary Information (ESI) For

Design and Preparation of Ethynyl-Pyrene Modified Platinum-Acetylide Gelators and Their Application in Dispersion of Graphene

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1. General Information

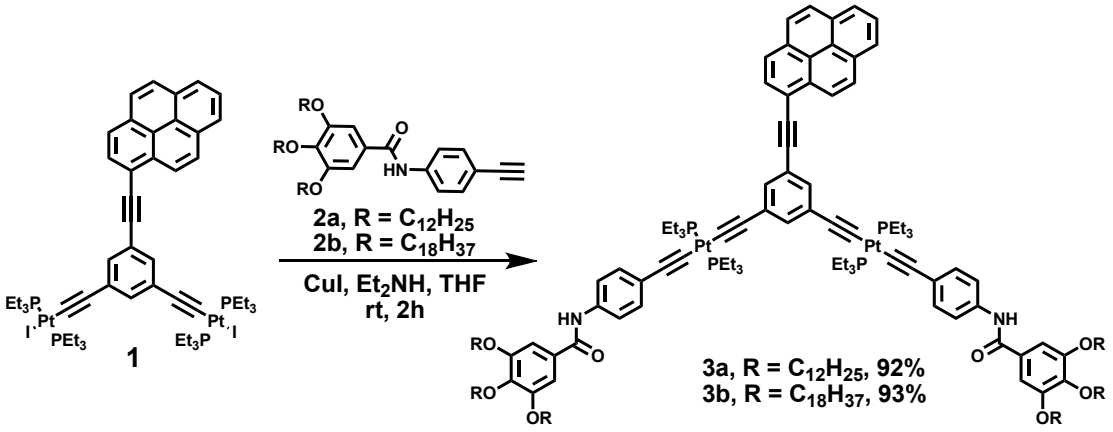
All solvents were dried according to the standard procedures and all of them were degassed under N_2 for 30 minutes before use. Reagents were used as purchased. All air-sensitive reactions were carried out under nitrogen atmosphere. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on Bruker 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 the residual solvent signals, and ^{31}P NMR resonances are referenced to an internal standard sample of 85% H_3PO_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.

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 × 0.2 cm quartz cuvettes. SEM images of the xerogels were obtained using a S-4800 (Hitachi Ltd.) with an accelerating voltage of 1.0-3.0 kV. Samples were prepared by dropping dilute gels onto a silicon wafer. TEM images were recorded on a Tecnai G^2 F30 (FEI Ltd.). The sample for TEM measurements was prepared by dropping the dilute gels onto a carbon-coated copper grid.

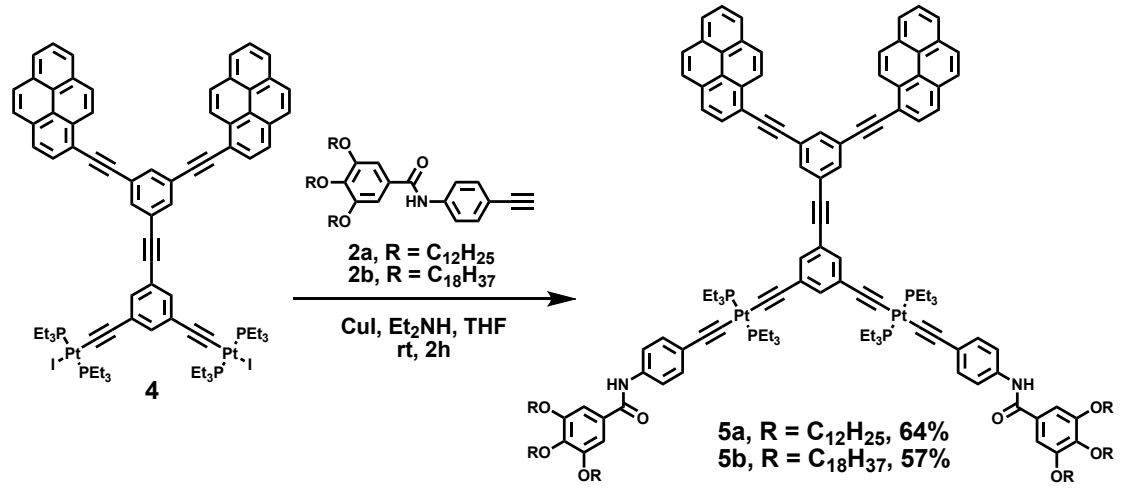
2. Synthetic Procedures and Characterizations

The precursors **1**[1], **4**[2], and **2a**–**b**[3] were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.

Scheme S1. Synthetic procedure of target molecules **3a**–**b**.



Scheme S2. Synthetic procedure of target molecules **5a**–**b**.



Synthesis of compound 3a. A 50ml of Schlenk flask was charged with the precursor **1** (100 mg, 0.068 mmol), **2a** (116 mg, 0.15 mmol) and CuI (1.3 mg, 0.0068 mmol), degassed, and back-filled there times with N_2. A mixed solvent of dried THF (10 mL) and Et_2NH (10 ml) was added into the reaction flask by syringe. The reaction was stirred at room temperature for 2 hours. The solvent was removed by evaporation on a rotary evaporator and the residue was purified via column chromatography on silica gel (petroleum ether/acetone 5/1) to afford product **3a** (173 mg, 92%) as pale yellow solid. R*f* = 0.54 (petroleum ether/acetone 3/1). Mp: 96 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.69 (d, *J* = 9.2 Hz, 1H), 8.25–8.02 (m, 8H), 7.70 (s, 2H), 7.50 (d, *J* = 8.0 Hz, 4H), 7.39 (s, 2H),

7.30–7.26 (m, 5H), 7.03 (s, 4H), 4.04–3.99 (m, 12H), 2.22 (br, 24H), 1.85–1.71 (m, 12H), 1.47 (br, 12H), 1.30–1.22 (br, 132H), 0.92–0.89 (t, J = 5.6 Hz, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.49, 153.26, 141.40, 135.18, 133.64, 131.99, 131.55, 131.33, 131.21, 131.16, 130.76, 130.09, 129.64, 128.86, 128.28, 128.15, 127.34, 126.29, 125.74, 125.63, 125.16, 124.59, 124.41, 122.84, 119.85, 118.09, 109.24, 108.81, 108.52, 107.37, 105.78, 95.56, 87.90, 73.61, 69.47, 32.00, 30.38, 29.81, 29.78, 29.72, 29.66, 29.48, 29.45, 29.41, 26.15, 22.77, 16.43, 14.20, 8.48; ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ = 11.69 ppm (s, $J_{Pt\text{-}P}$ = 2357.2 Hz); MALDI-TOF-MS: m/z calcd for $C_{154}H_{236}N_2O_8P_4Pt_2$: 2757.64 [$M$ + H]$^+$; found: 2757.65. Anal. Calcd for $C_{154}H_{236}N_2O_8P_4Pt_2$: C, 67.08; H, 8.63; N, 1.02. Found: C, 66.92; H, 8.90; N, 1.05.

Synthesis of compound 3b. Following the procedure for the preparation of **3a**: the precursor **1** (100 mg, 0.068 mmol), **2b** (154 mg, 0.15 mmol) and CuI (1.3 mg, 0.0068 mmol), THF (10 mL), Et_2NH (10 mL). The product **3b** was obtained as a pale yellow solid (206 mg, 93%). Rf = 0.43 (petroleum ether/acetone 4/1). Mp: 125 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.69 (d, J = 9.6 Hz, 1H), 8.25–8.02 (m, 8H), 7.63 (s, 2H), 7.48 (d, J = 8.0 Hz, 4H), 7.38 (s, 2H), 7.29–7.26 (m, 5H), 7.03 (s, 4H), 4.05–3.99 (m, 12H), 2.21 (br, 24H), 1.84–1.73 (m, 12H), 1.47 (br, 12H), 1.30–1.22 (m, 204H), 0.92–0.89 (t, J = 5.6 Hz, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.45, 153.07, 141.19, 135.21, 133.56, 131.85, 131.36, 131.19, 131.08, 131.01, 130.63, 129.95, 129.49, 128.72, 128.14, 128.01, 127.18, 126.15, 125.57, 125.49, 124.90, 124.43, 124.26, 122.76, 119.79, 117.93, 109.18, 108.69, 108.27, 106.97, 105.68, 95.38, 87.82, 73.45, 69.29, 67.87, 31.87, 29.67, 29.61, 29.36, 29.31, 26.02, 25.52, 22.63, 16.30, 14.06, 8.34; ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ = 11.49 ppm (s, $J_{Pt\text{-}P}$ = 2365.4 Hz); MALDI-TOF-MS: m/z calcd for $C_{190}H_{308}N_2O_8P_4Pt_2$: 3262.20 [$M$ + H]$^+$; found: 3262.21. Anal. Calcd for $C_{190}H_{308}N_2O_8P_4Pt_2$: C, 69.95; H, 9.52; N, 0.86. Found: C, 69.85; H, 9.63; N, 0.90.

Synthesis of compound 5a. Following the procedure for the preparation of **3a** or **3b**: the precursor **4** (174 mg, 0.097 mmol), **2a** (165 mg, 0.21 mmol) and CuI (1.8 mg, 0.0097 mmol), THF (10 mL), Et_2NH (10 mL). The product **5a** was obtained as a yellow solid (191 mg, 64%). Rf = 0.45 (petroleum ether/acetone 3/1). Mp: 103 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.73 (d, J = 8.8 Hz, 2H), 8.26–8.02 (m, 16H), 7.91 (s, 2H), 7.64 (s, 2H), 7.48 (d, J = 8.0 Hz, 4H), 7.29–7.24 (m, 5H), 7.03 (s, 4H), 4.03–4.01 (m, 12H), 2.21 (br, 24H), 1.84–1.74 (m, 12H), 1.48 (br, 12H), 1.26 (br, 132H), 0.91 (br, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.39, 153.14, 141.30, 135.11, 134.15,

132.02, 131.48, 131.43, 131.18, 131.00, 130.73, 129.97, 129.66, 128.81, 128.51, 128.34, 127.19, 126.26, 125.73, 125.67, 125.39, 125.04, 124.52, 124.42, 124.33, 122.08, 119.75, 117.14, 108.56, 107.23, 105.69, 93.55, 91.12, 89.89, 87.11, 73.49, 69.36, 31.89, 31.28, 29.70, 29.67, 29.61, 29.55, 29.37, 29.34, 29.31, 26.04, 22.66, 16.33, 14.09, 8.37; ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ = 11.62 ppm (s, $J_{Pt\text{-}P}$ = 2366.98 Hz); MALDI-TOF-MS: m/z calcd for $C_{180}H_{248}N_2O_8P_4Pt_2$: 3082.74 [$M$ + H]$^+$; found: 3082.74. Anal. Calcd for $C_{180}H_{248}N_2O_8P_4Pt_2$: C, 70.15; H, 8.11; N, 0.91. Found: C, 69.87; H, 8.18; N, 0.91.

Synthesis of compound 5b. Following the same procedure for the preparation of **3a** or **3b**: the precursor **4** (128 mg, 0.071 mmol), **2b** (160 mg, 0.16 mmol) and CuI (1.4 mg, 0.0071 mmol), THF (10 mL), Et_2NH (10 mL). The product **5b** was obtained as a yellow solid (145 mg, 57%). Rf = 0.54 (petroleum ether/acetone 3/1). Mp: 132 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.73 (d, J = 8.8 Hz, 2H), 8.26-8.02 (m, 16H), 7.91 (s, 2H), 7.64 (s, 2H), 7.48 (d, J = 7.6 Hz, 4H), 7.29-7.24 (m, 5H), 7.03 (s, 4H), 4.53-4.00 (m, 12H), 2.22 (br, 24H), 1.84-1.74 (m, 12H), 1.48 (br, 12H), 1.26 (br, 204H), 0.89 (t, J = 5.2 Hz, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): 165.33, 153.22, 141.50, 135.09, 134.20, 133.91, 132.09, 131.54, 131.46, 131.24, 131.07, 130.71, 130.03, 129.71, 128.86, 128.56, 128.37, 127.23, 126.29, 125.77, 125.70, 125.45, 125.14, 124.55, 124.49, 124.39, 124.30, 122.10, 119.76, 117.21, 114.04, 109.18, 108.59, 107.28, 105.58, 93.60, 91.18, 89.92, 87.10, 73.53, 69.48, 31.91, 29.70, 29.65, 29.58, 29.40, 29.35. 26.07, 22.67, 16.41, 14.09, 8.39; ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ = 11.62 ppm (s, $J_{Pt\text{-}P}$ = 2366.98 Hz); MALDI-TOF-MS: m/z calcd for $C_{216}H_{320}N_2O_8P_4Pt_2$: 3587.30 [$M$ + H]$^+$; found: 3587.31. Anal. Calcd for $C_{216}H_{320}N_2O_8P_4Pt_2$: C, 72.33; H, 8.99; N, 0.78. Found: C, 72.03; H, 9.13; N, 0.86.

3. PM6 Semi-empirical Simulated Molecular Models of 3a–b and 5a–b.

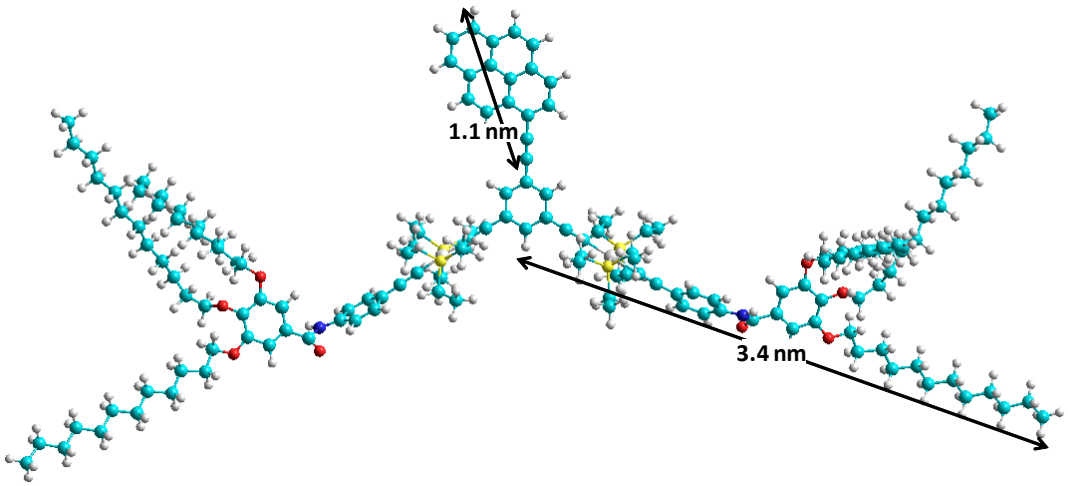


Figure S1. PM6 semi-empirical simulated molecular model of **3a.**

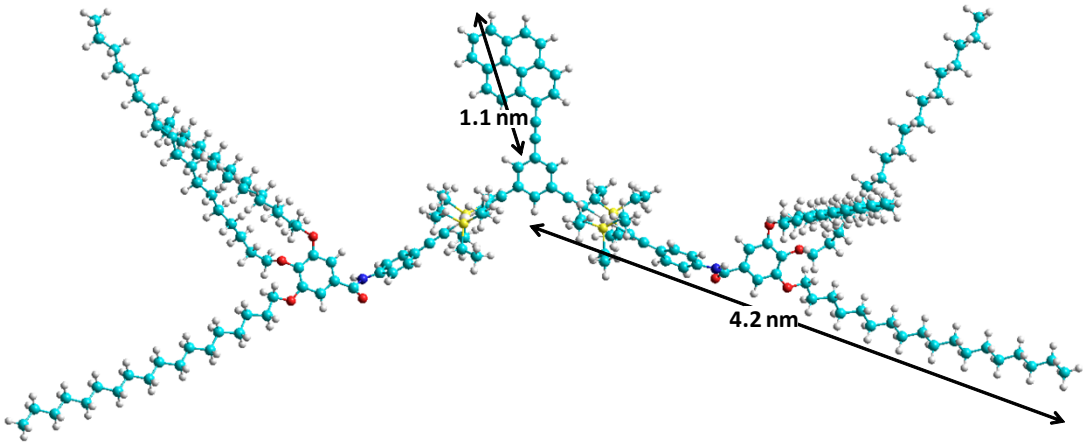


Figure S2. PM6 semi-empirical simulated molecular model of **3b.**

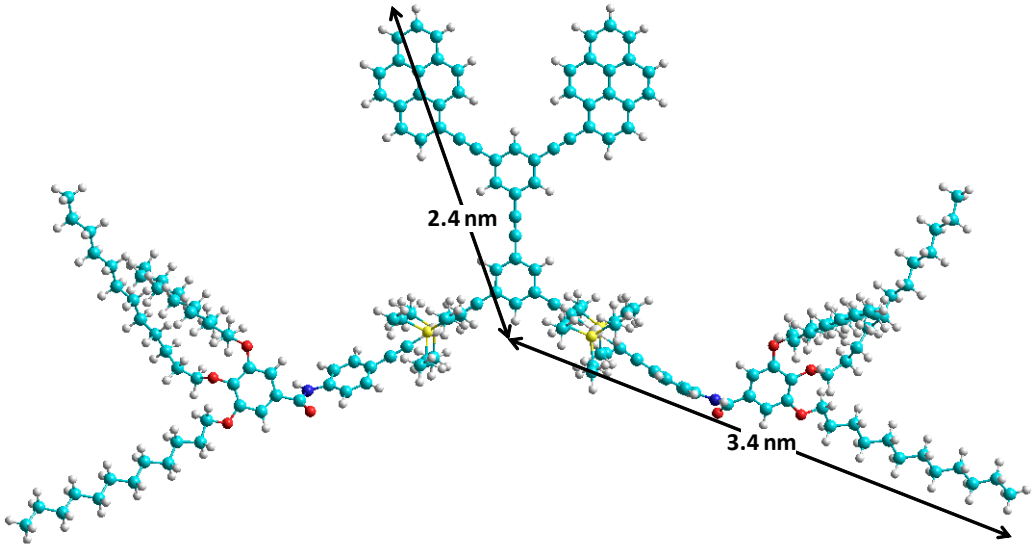


Figure S3. PM6 semi-empirical simulated molecular model of **5a.**

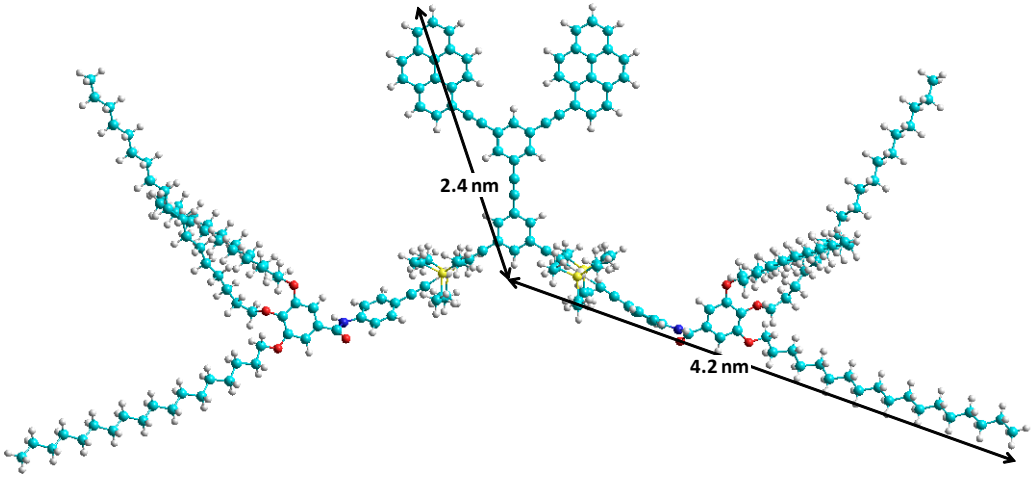


Figure S4. PM6 semi-empirical simulated molecular model of **5b.**

4. Additional Gelation Tests.

Table S1. Solvents tested for gelation with complexes **3a–b** and **5a–b.**[a]

solvent	**3a**	**3b**	**5a**	**5b**
cyclohexane	P	G (36.0)	I	I
n-hexane	P	I	I	I
n-decane	PG	I	I	I
dodecane	PG	I	I	I
benzene	S	S	S	S
toluene	S	S	S	S
xylenes	S	S	S	S
ethyl acetate	P	P	P	P
tetrahydrofuran	S	S	S	S
dioxane	S	P	S	S
acetone	G (20.8)	I	I	I
n-propanol	I	I	I	I
2-propanol	I	I	I	I
cyclohexane/benzene (5/1, v/v)	G (7.8)	G (8.1)	P	P
cyclohexane/benzene (5/2, v/v)	G (11.2)	G (12.3)	G (19.6)	G (26.5)
n-hexane/benzene (5/1, v/v)	G (7.9)	G (15.0)	P	P
n-hexane/benzene (5/2, v/v)	G (19.8)	G (16.5)	G (18.5)	G (29.4)
n-decane/benzene (5/2 v/v)	G (16.0)	G (17.2)	G (19.3)	G (22.7)
dodecane/benzene (5/2 v/v)	G (16.0)	G (17.6)	G (25.4)	G (30.0)

[a] G = pale-yellow gel; PG = part gel; S = soluble; I = insoluble; P = precipitation. The values in parentheses are the critical gelation concentrations (CGCs) in mg/mL.

5. Additional UV-vis and Emission Spectra.

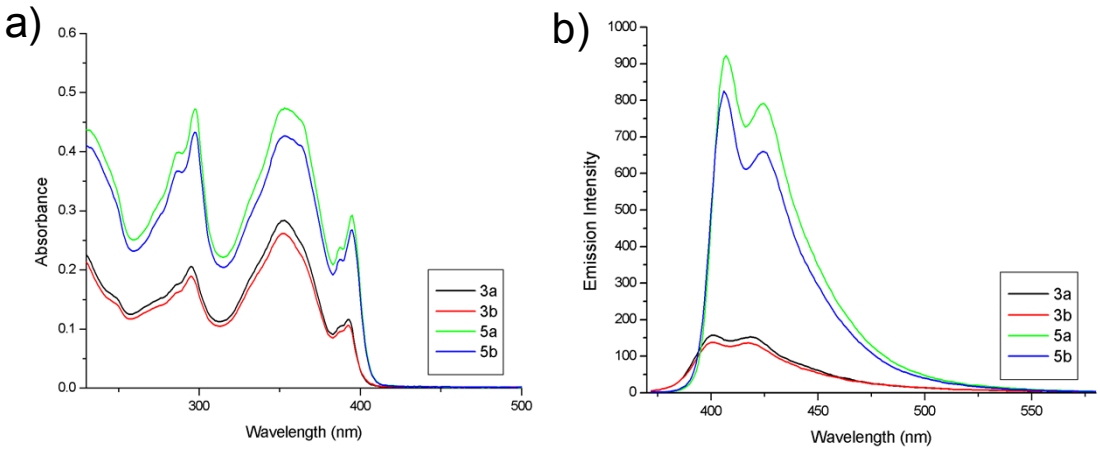


Figure S5. a) UV–vis absorption spectra and b) emission spectra of **3a**–**b** and **5a**–**b** at 298 K in CH_2Cl_2 (1.0×10^{-5} M).

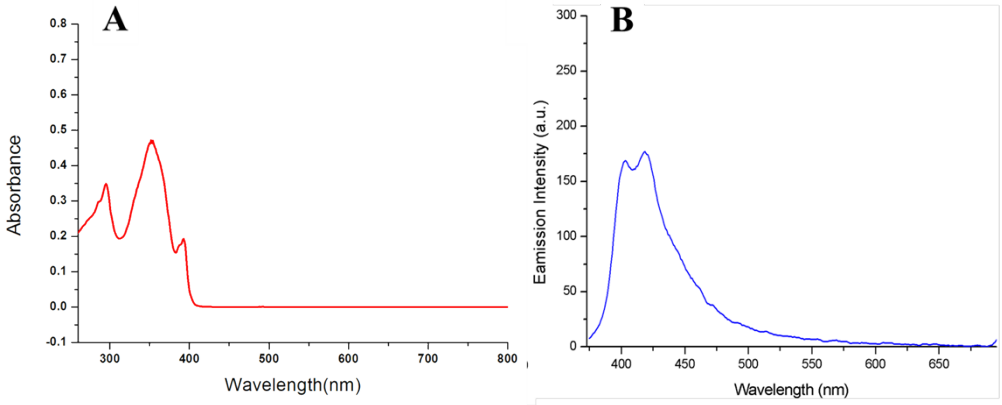


Figure S6. Absorption (A) and emission (B) spectrum of **3a** in the degassed dichloromethane solution at 1.0×10^{-5} M. The fluorescence lifetimes of **3a** in the solution were determined to be 4.15 ns and 13.97 ns, respectively.

Table S2. Photophysical properties of **3a**–**b** and **5a**–**b** at 298 K in CH_2Cl_2 (1.0×10^{-5} M).

Compound	λ_{abs} (nm)	ε ($M^{-1}cm^{-1}$)	λ_F (nm)	ΦF (%)
3a	393	58500	401	4.2
	353	142000		
	295	103000		
3b	393	53000	400	3.7
	353	131000		
	295	94500		
5a	395	146500	407	15
	353	237000	424	
	297	235500		
5b	395	132500	406	15
	353	213500	424	
	297	215000		

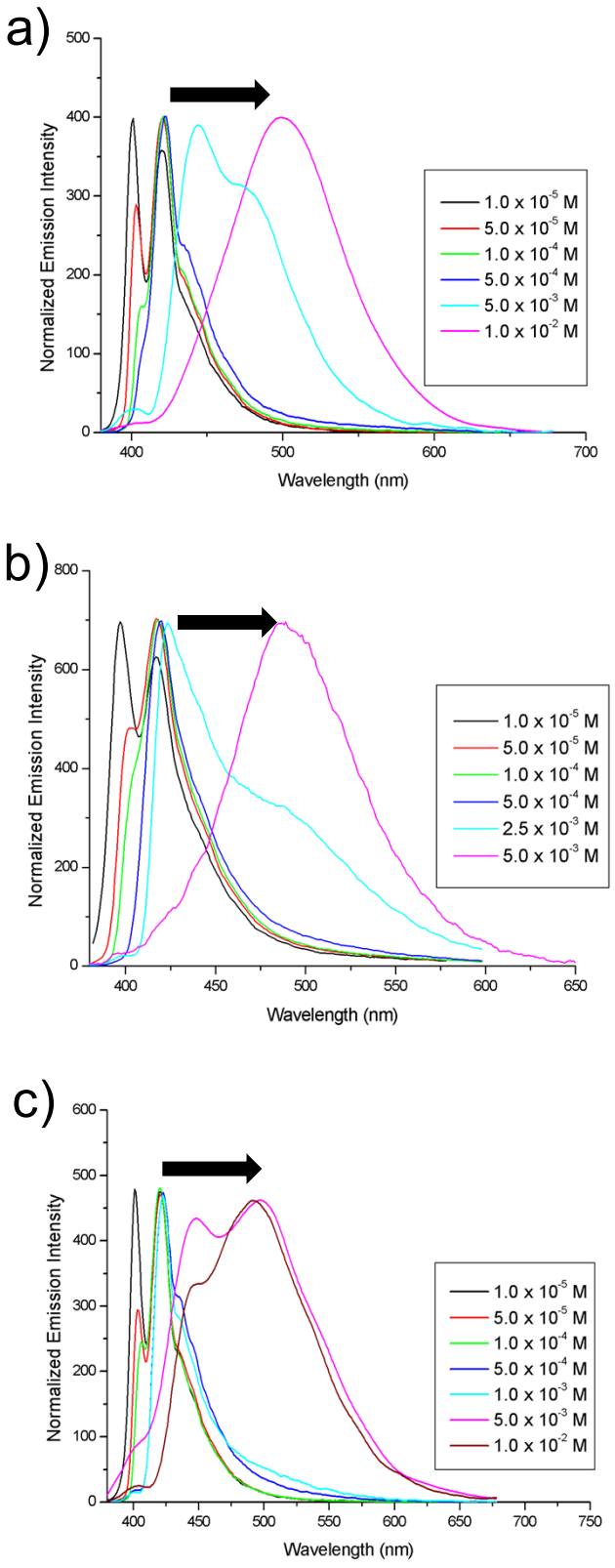


Figure S7. Emission spectra of a) **3b** in cyclohexane/benzene (5/1 v/v), b) **5a,** and c) **5b** in cyclohexane/benzene (5/2 v/v) at different concentrations.

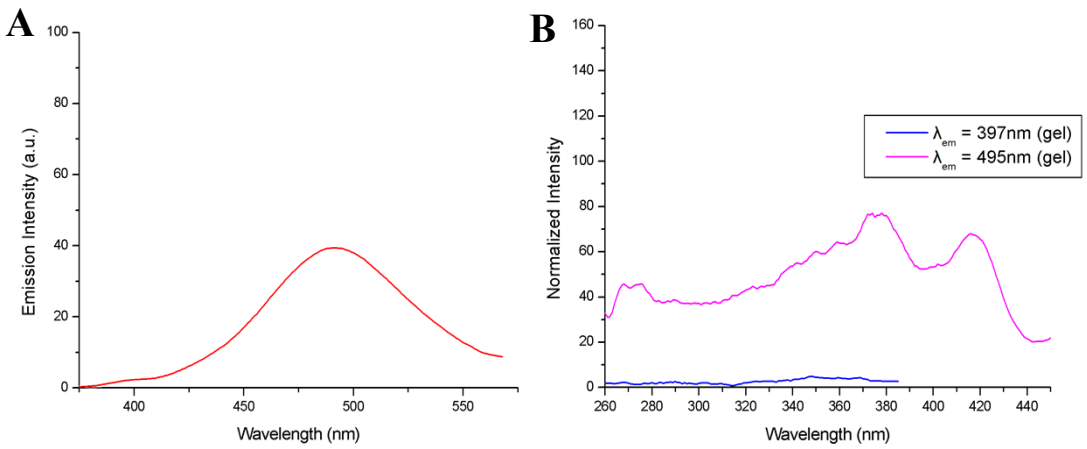


Figure S8. Emission spectrum (A) and excitation spectra (normalized) (B) monitored at different wavelength of **3a** in the mixed solvent of cyclehexane and benzene (5/1 v/v) at 5.0×10^{-3} M (***gel***).

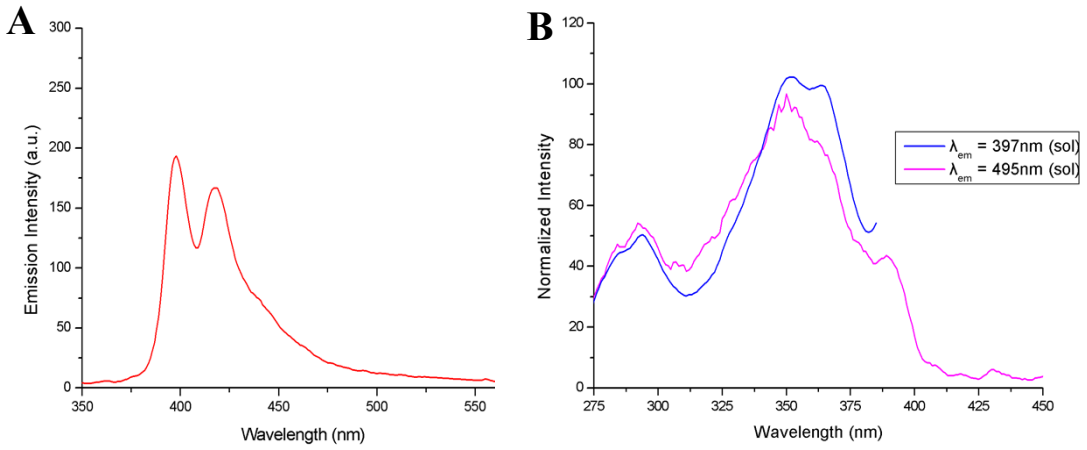


Figure S9. Emission spectrum (A) and excitation spectra (normalized) (B) monitored at different wavelength of **3a** in the mixed solvent of cyclehexane and benzene (5/1 v/v) at 1.0×10^{-5} M (***sol***).

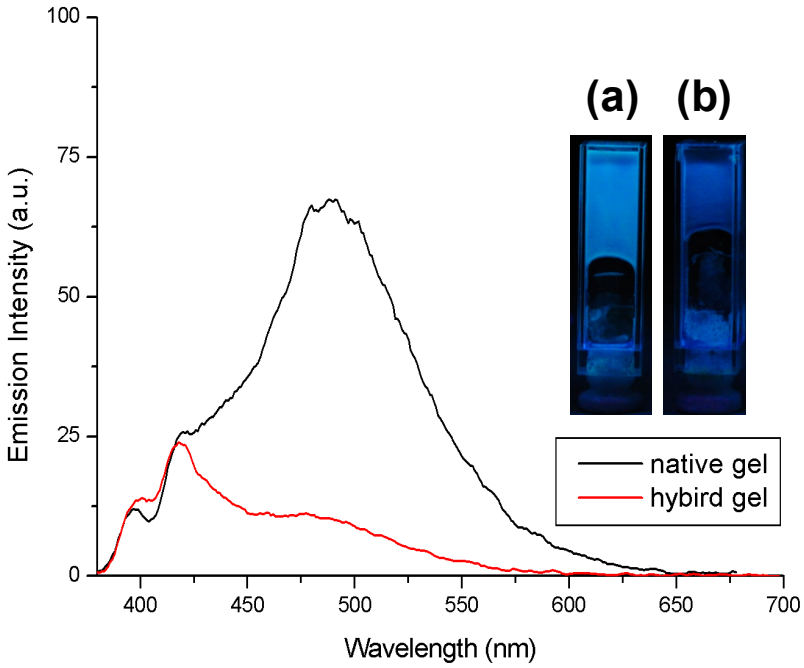


Figure S10. Comparison of emission spectra of **3a** between native gel (black line) and graphene-containing hybrid gel (red line). The inset shows the photographs of 3a in native gel (a) and hybrid gel (b) under UV light (365 nm), respectively.

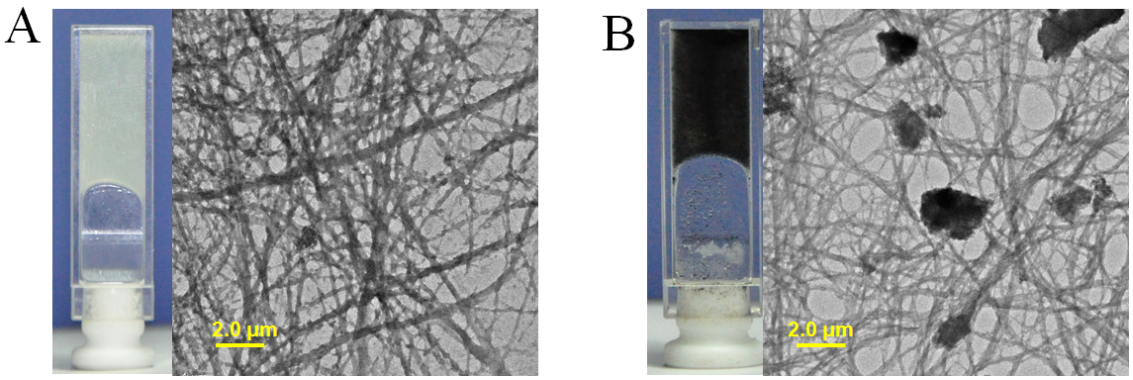


Figure S11. Photograph and TEM images of **3a** from the native gel (A) and the hybrid gel with graphene (B) in cyclohexane/benzene (5/1 v/v) under day light.

6. Concentration-Dependent and Temperature-Dependent ^{1}H NMR Spectra.

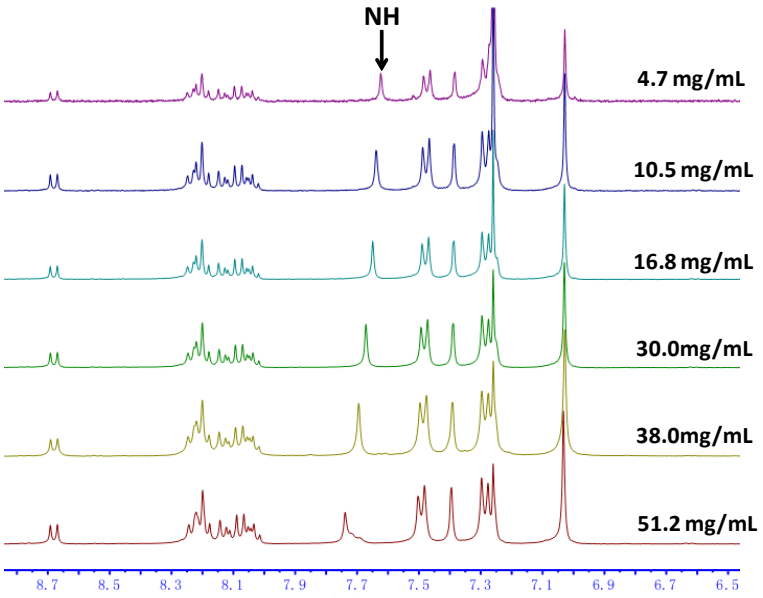


Figure S12. Region of the ^{1}H NMR spectrum (400MHz, $CDCl_3$, 298 K) of compound **3a** at different concentrations.

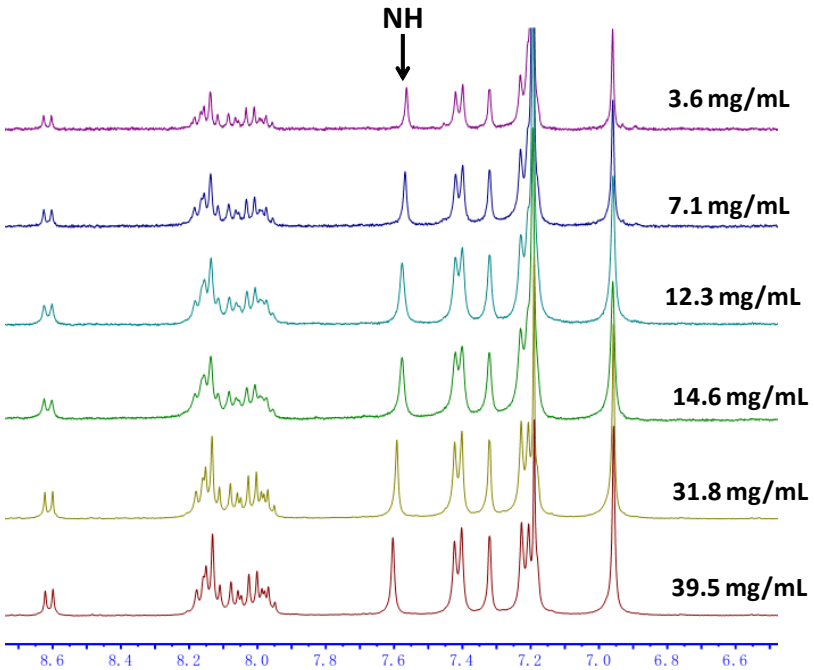


Figure S13. Region of the ^{1}H NMR spectrum (400MHz, $CDCl_3$, 298 K) of compound **3b** at different concentrations.

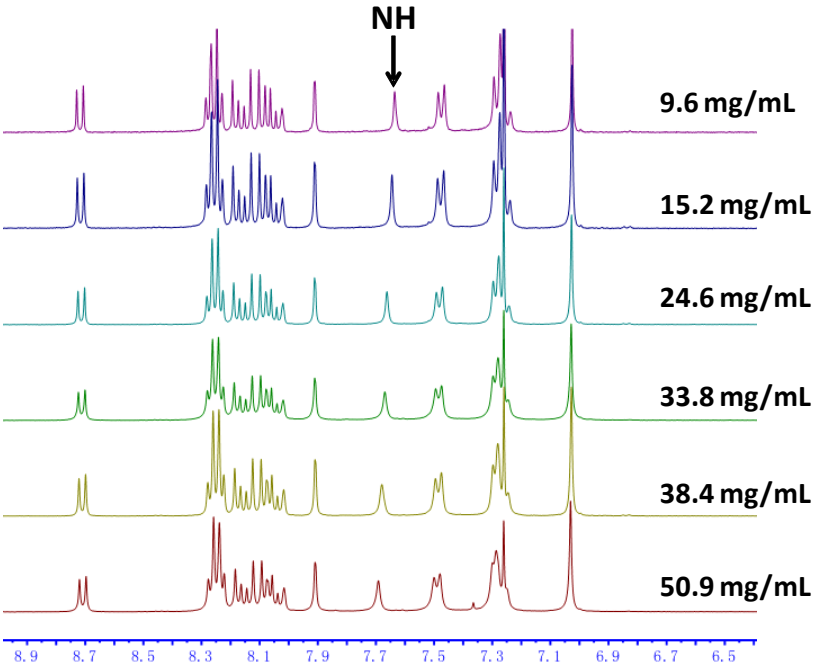


Figure S14. Region of the ^{1}H NMR spectrum (400MHz, $CDCl_3$, 298 K) of compound **5a** at different concentrations.

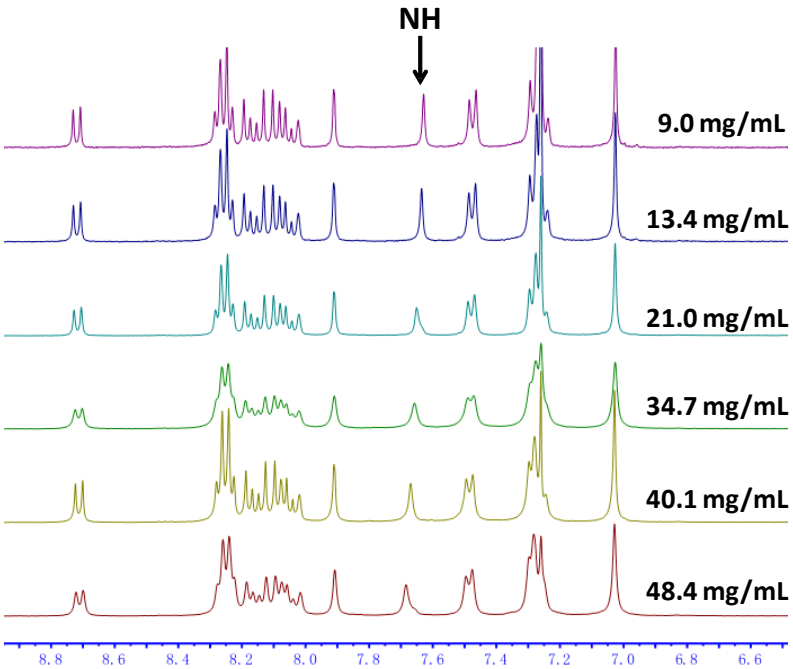


Figure S15. Region of the ^{1}H NMR spectrum (400MHz, $CDCl_3$, 298 K) of compound **5b** at different concentrations.

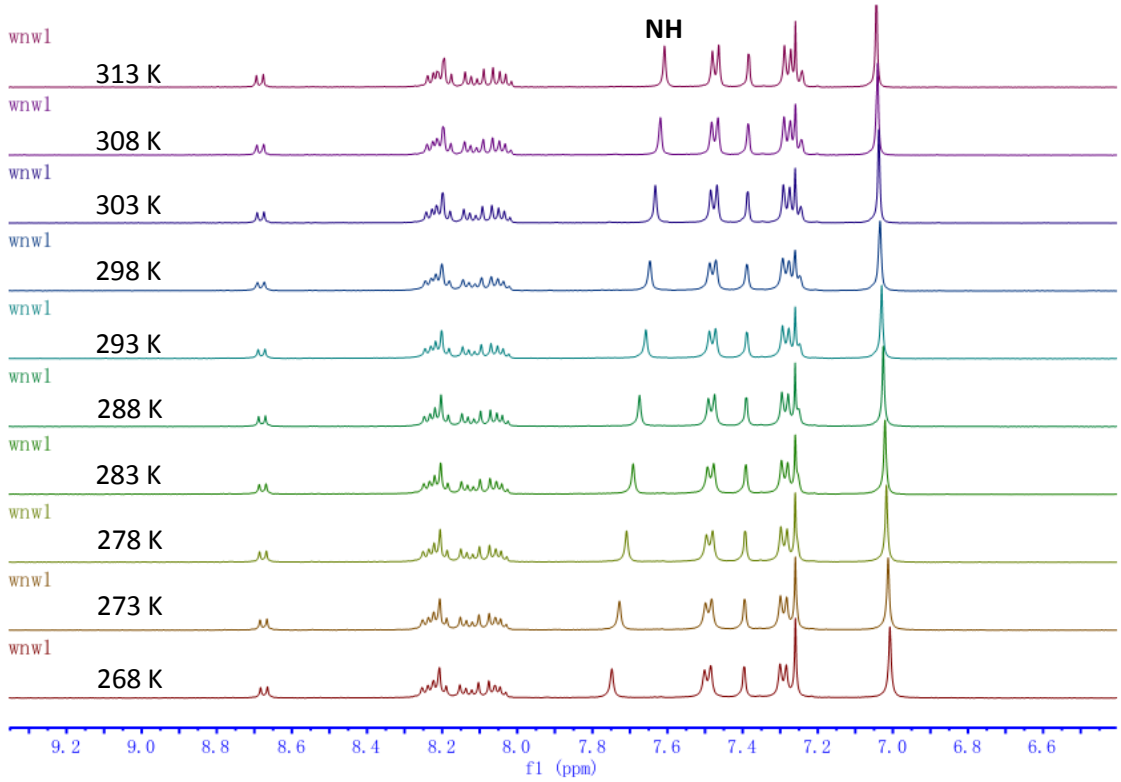


Figure S16. Partial ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 mg/mL) of **3a** at variable temperature.

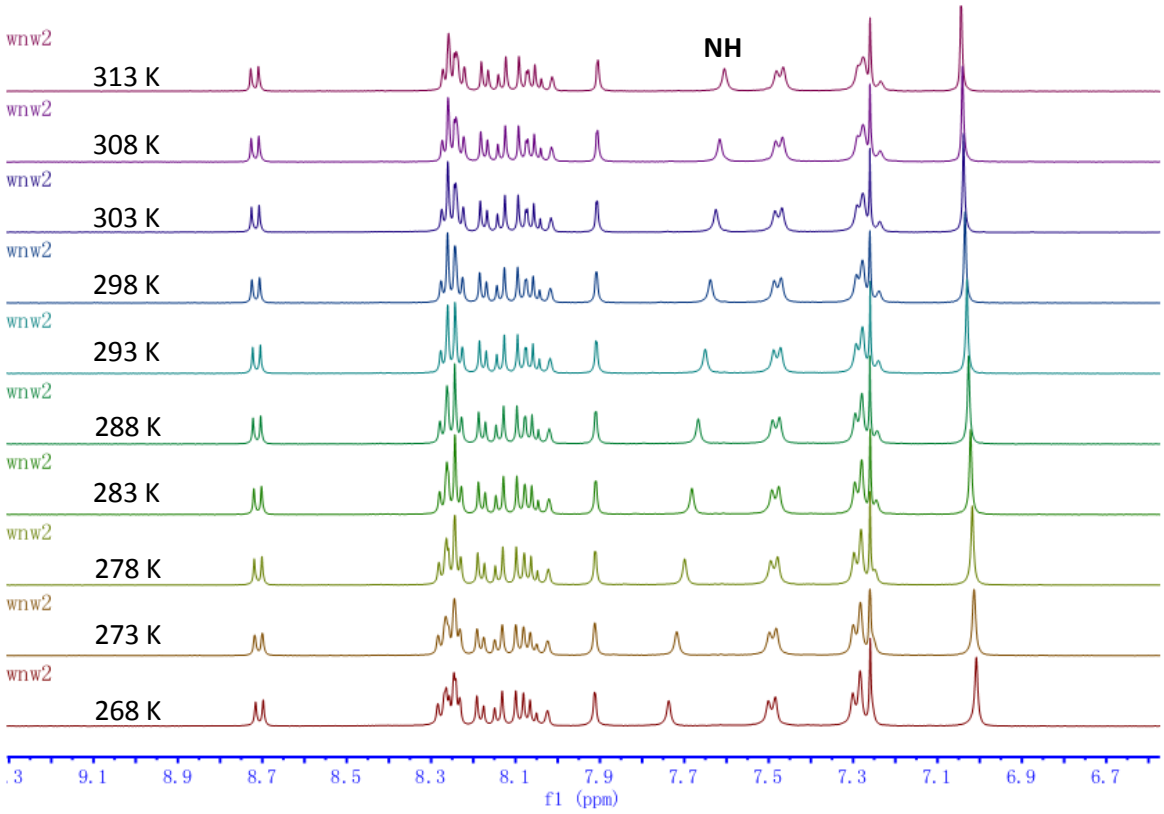


Figure S17. Partial ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 mg/mL) of **5a** at variable temperature.

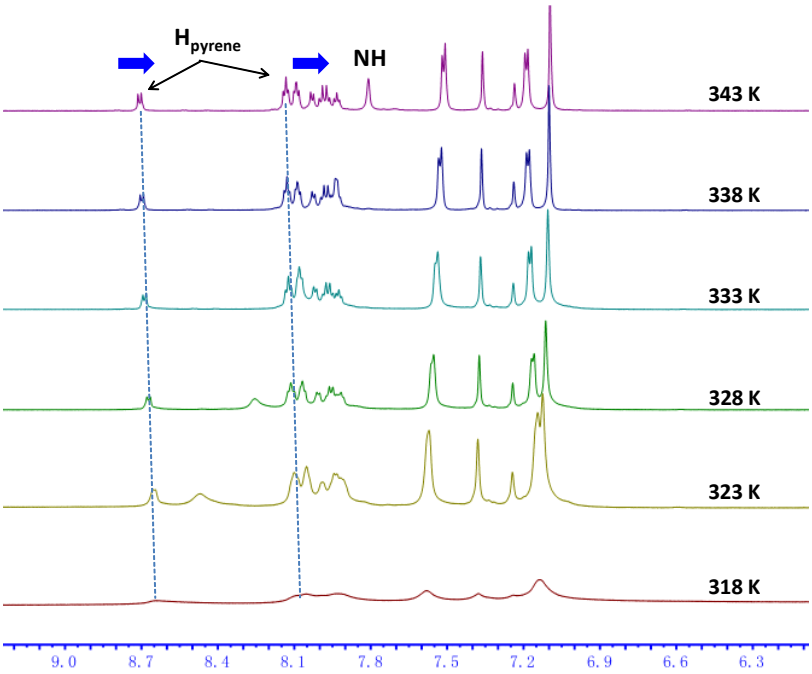


Figure S18. Partial ^{1}H NMR spectrum (500 MHz, cyclehexane-d_{12}, 36 mg/mL) of **3b** at the variable temperature (343K–318 K).

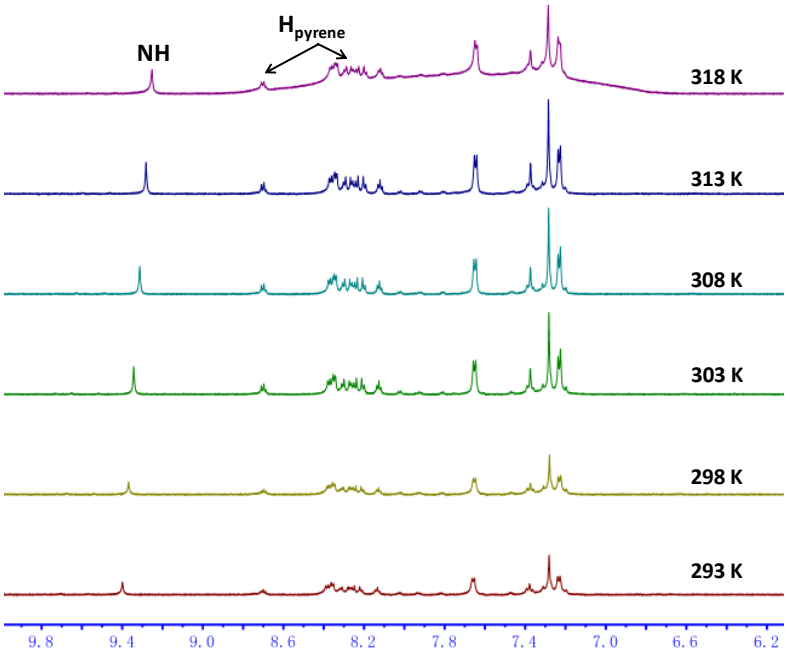


Figure S19. Partial ^{1}H NMR spectrum (500 MHz, acetone-d_6, 21 mg/mL) of **3a** at the variable temperature (343K–318 K).

7. Rheological Investigation of Native Gel 3a and Graphene-containing Hybrid Gel

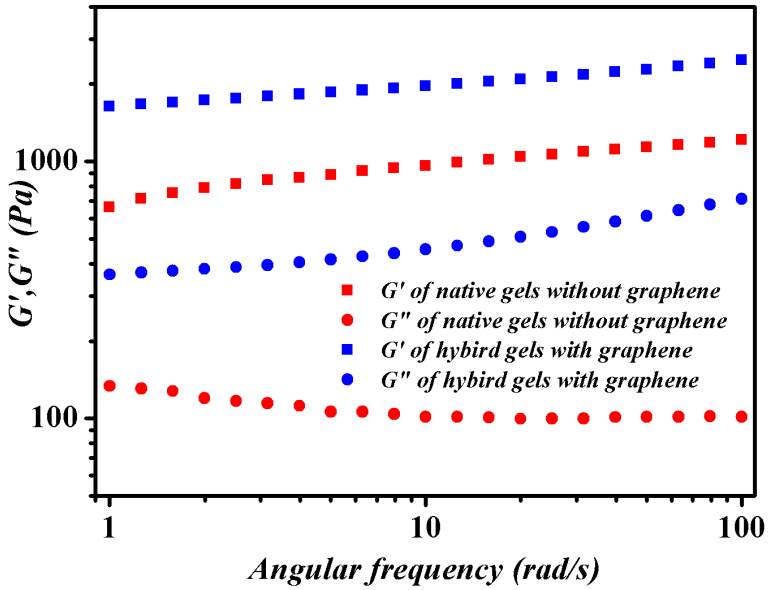


Figure S20. Frequency dependence of the dynamic storage moduli (G') and the loss moduli (G'') of native gel **3a** (red lines) and graphene-containing hybrid gel (blue lines) in cyclehexane/benzene (5/1 v/v).

8. Raman Spectrum of Graphene-containing Hybrid Gel

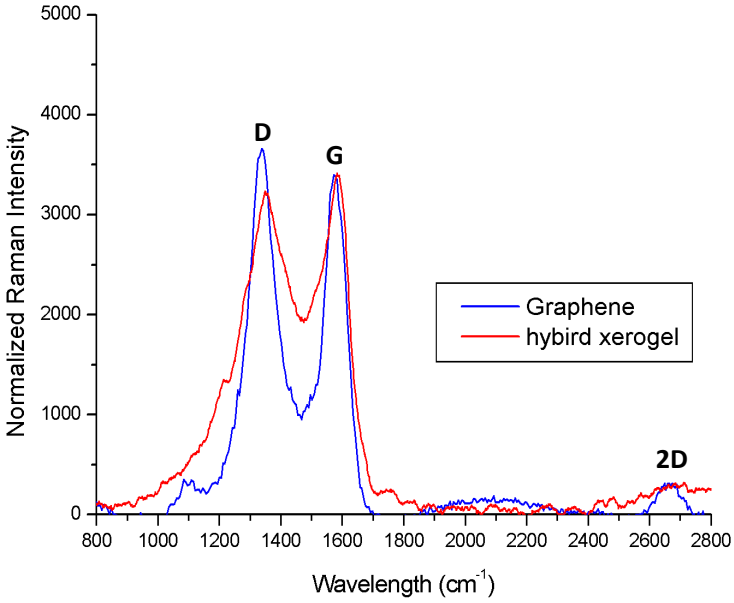
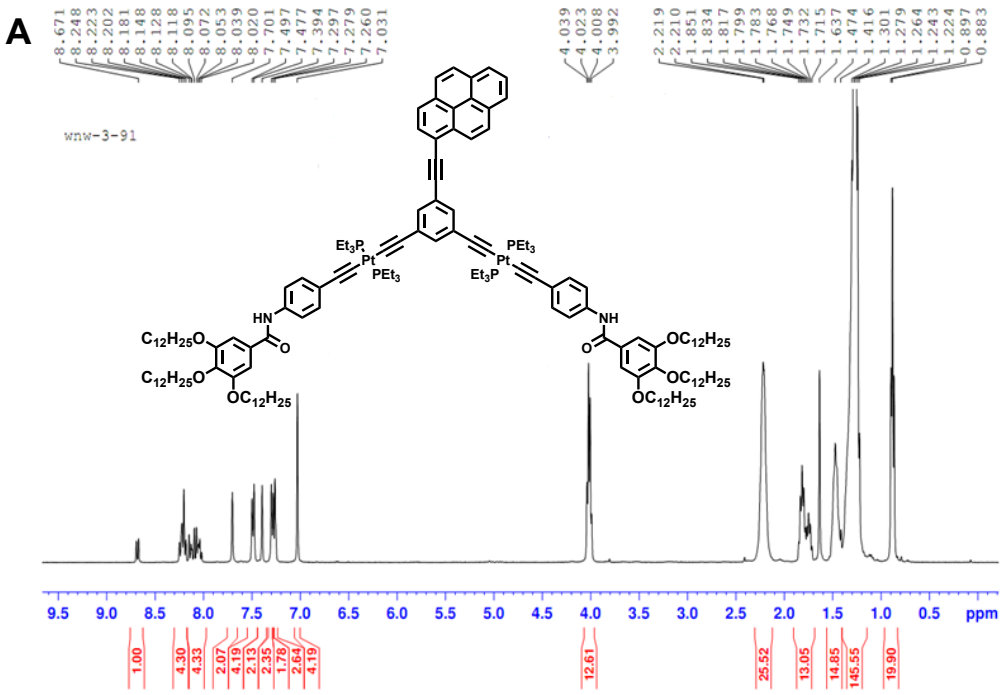
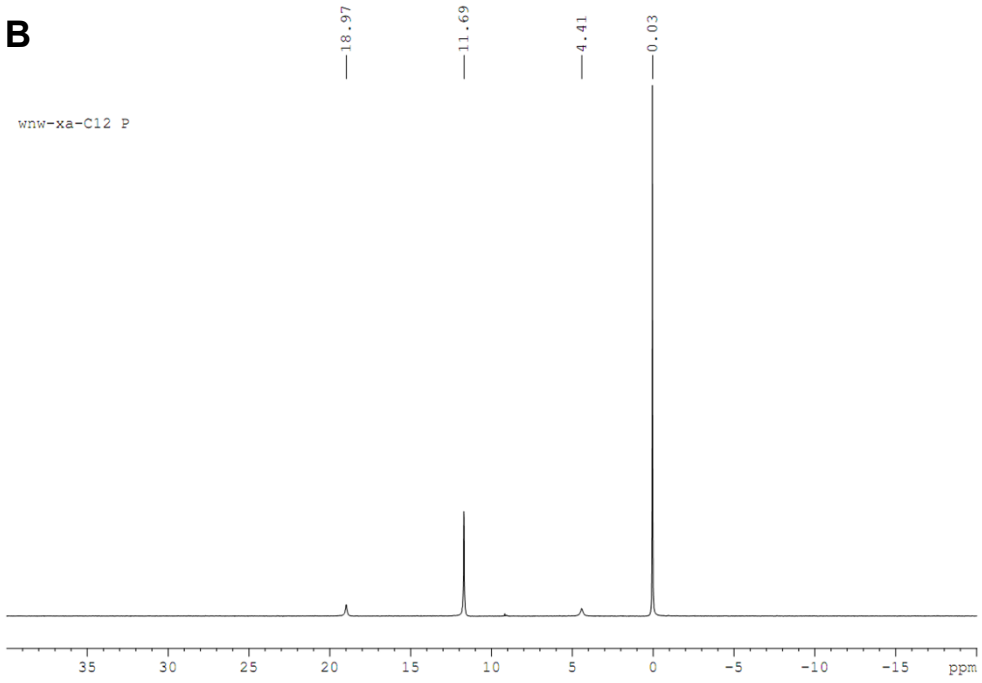


Figure S21. Raman spectrum of graphene (blue line) and graphene-containing hybrid xerogel (red line).

9. Multiple Nuclear NMR (^{1}H, ^{31}P and ^{13}C) Spectra and MALDI-TOF MS of new compounds





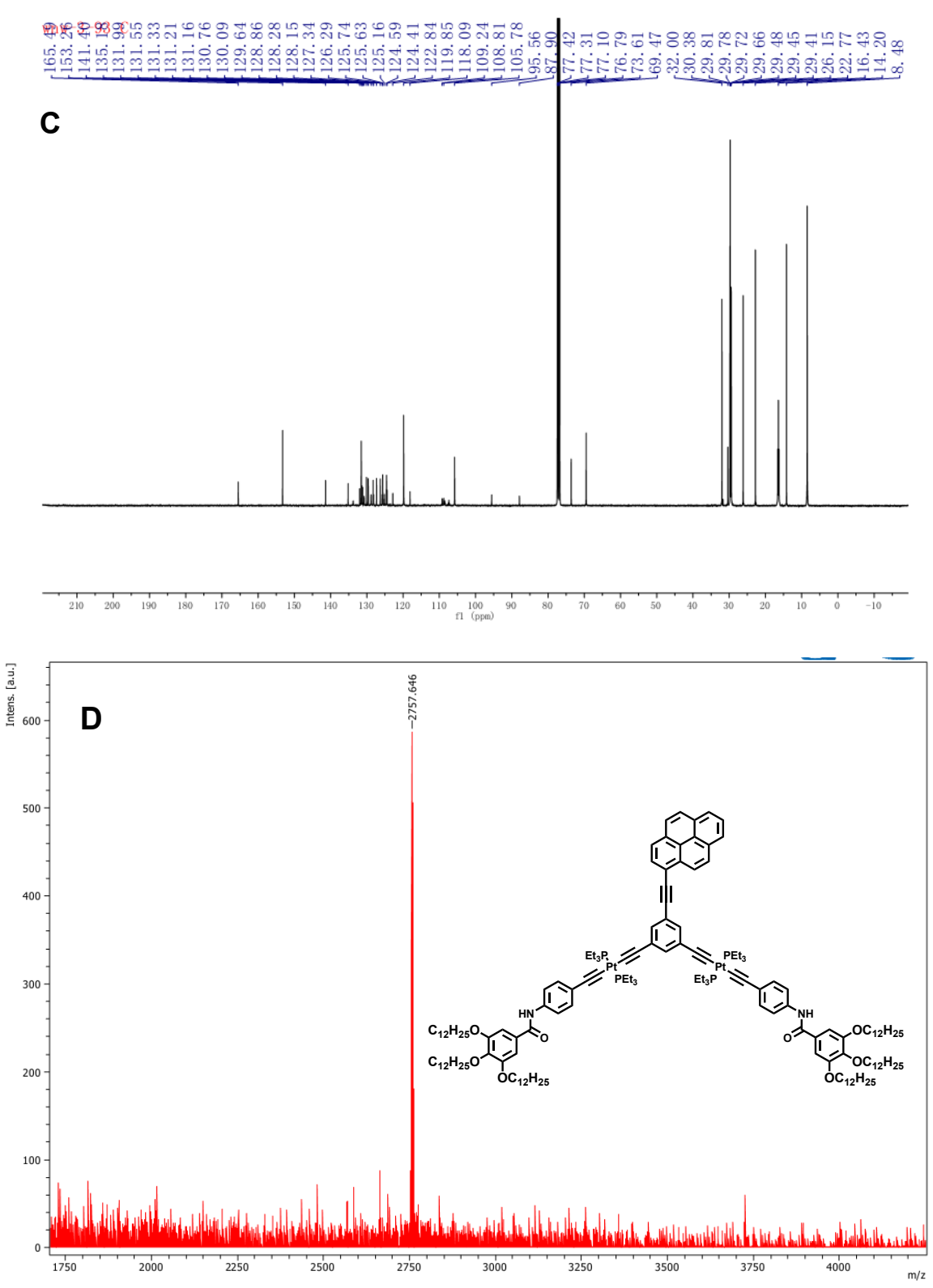
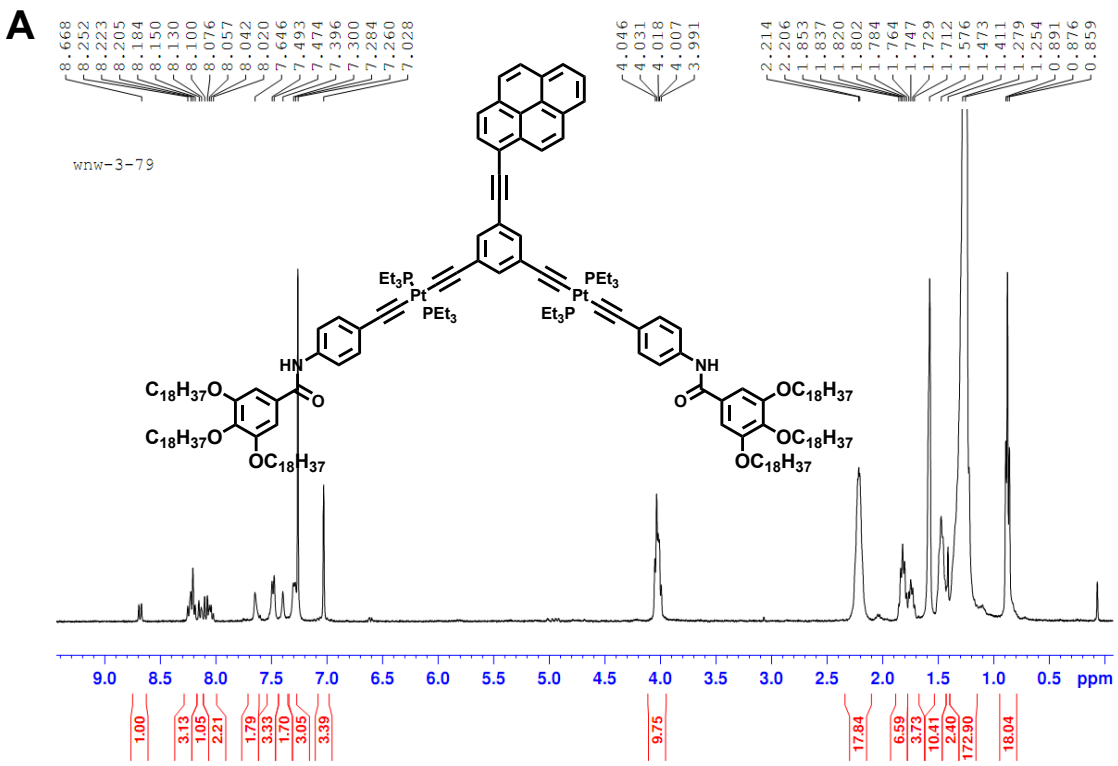
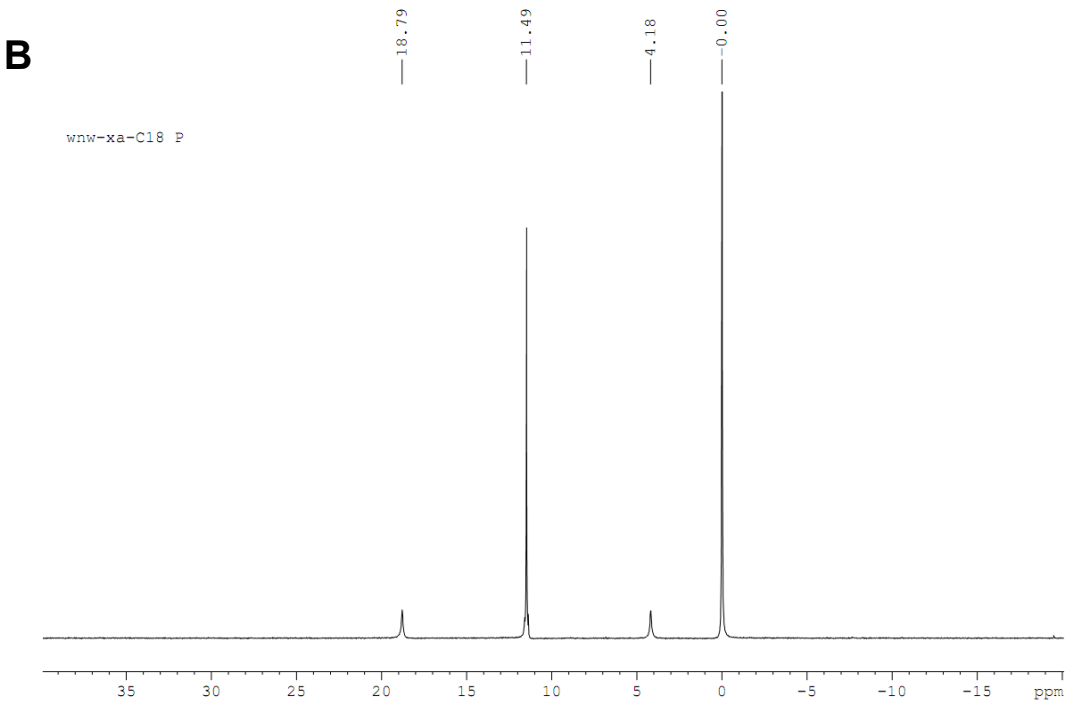
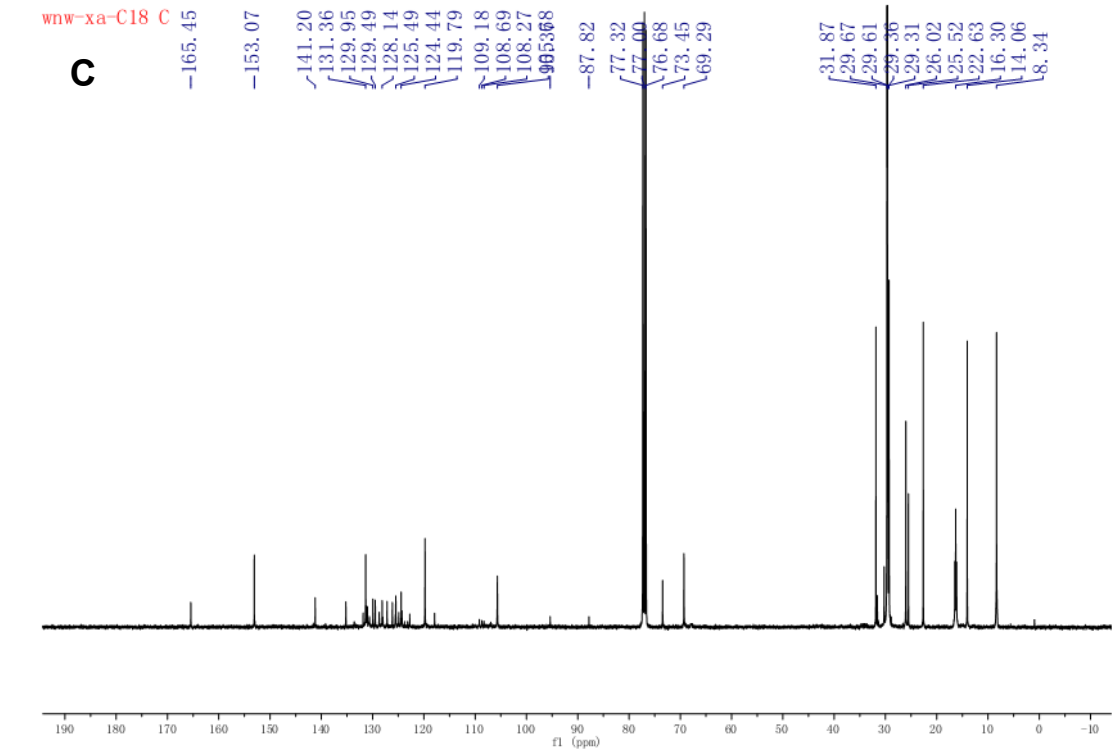


Figure S22. ^{1}H (A), ^{31}P (B) ^{13}C (C) NMR spectra and MALDI-TOF-MS (D) of **3a** in $CDCl_3$.


A
wnw-3-79
8.668
8.252
8.223
8.205
8.184
8.150
8.130
8.100
8.076
8.057
8.042
8.020
7.646
7.493
7.474
7.396
7.300
7.284
7.260
7.028
4.046
4.031
4.018
4.007
3.991
2.214
2.206
1.853
1.837
1.820
1.802
1.784
1.764
1.747
1.729
1.712
1.576
1.473
1.411
1.279
1.254
0.891
0.876
0.859
Et3P
Pt
PEt3
HN
O
C18H37O
OC18H37
NH
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
3.13
1.05
2.21
1.79
3.33
1.70
3.05
3.39
9.75
17.84
6.59
3.73
10.41
2.40
172.90
18.04


B
wnw-xa-C18 P
18.79
11.49
4.18
0.00
35
30
25
20
15
10
5
0
-5
-10
-15
ppm



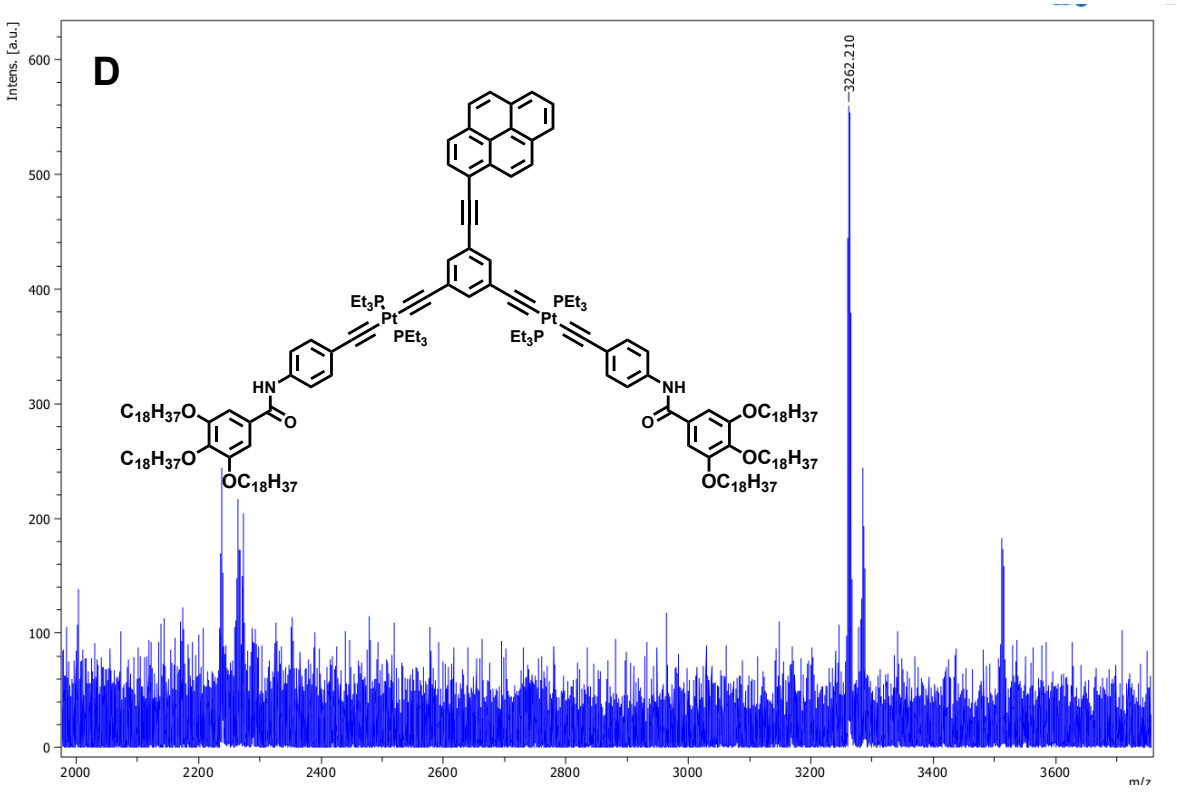
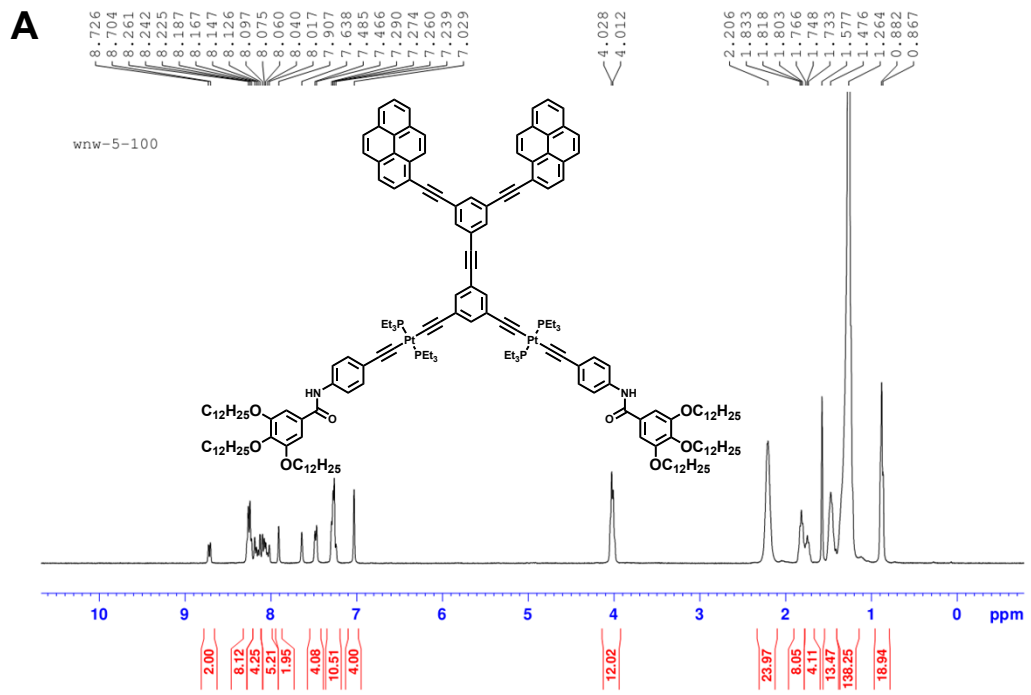
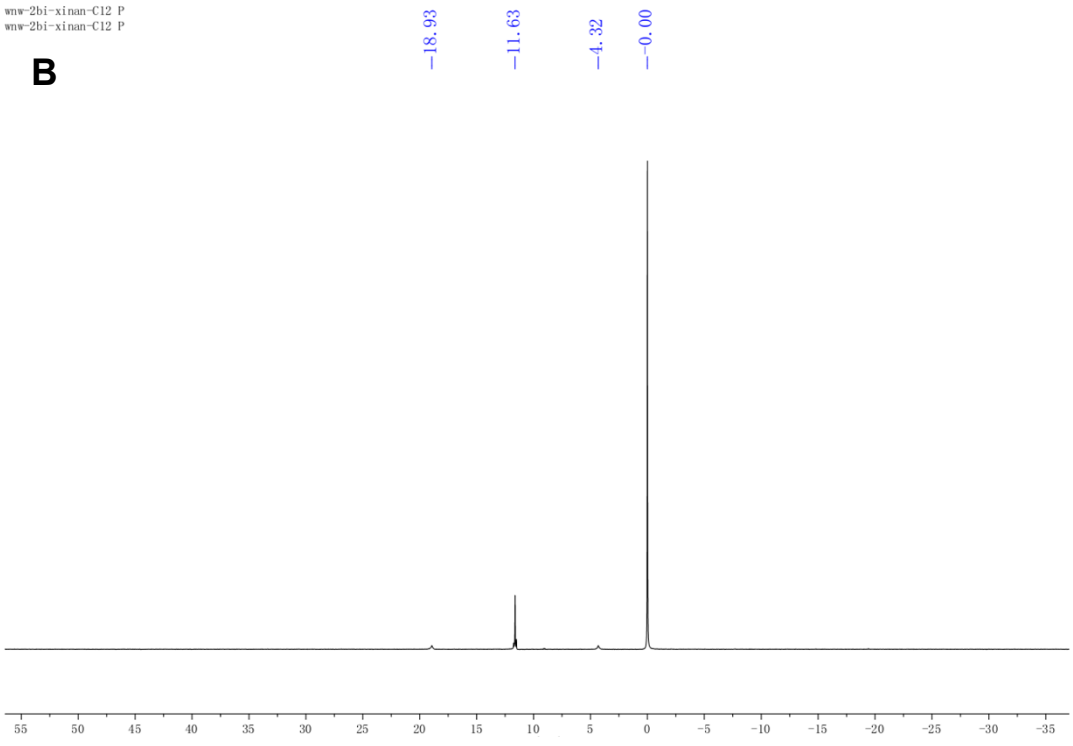


Figure S23. ^{1}H (A), ^{31}P (B) and ^{13}C (C) NMR spectra and MALDI-TOF-MS (D) of **3b** in $CDCl_3$.


A
8.726
8.704
8.261
8.242
8.225
8.187
8.167
8.147
8.126
8.097
8.075
8.060
8.040
8.017
7.907
7.638
7.485
7.466
7.290
7.274
7.260
7.239
7.029
4.028
4.012
2.206
1.833
1.818
1.803
1.766
1.748
1.733
1.577
1.476
1.264
0.882
0.867
wnw-5-100
Et3P
Pt
PEt3
HN
NH
O
C12H25O
OC12H25
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
8.12
4.25
5.21
1.95
4.08
10.51
4.00
12.02
23.97
8.05
4.11
13.47
138.25
18.94


wnw-2bi-xinan-C12 P
wnw-2bi-xinan-C12 P
B
-18.93
-11.63
-4.32
-0.00
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35

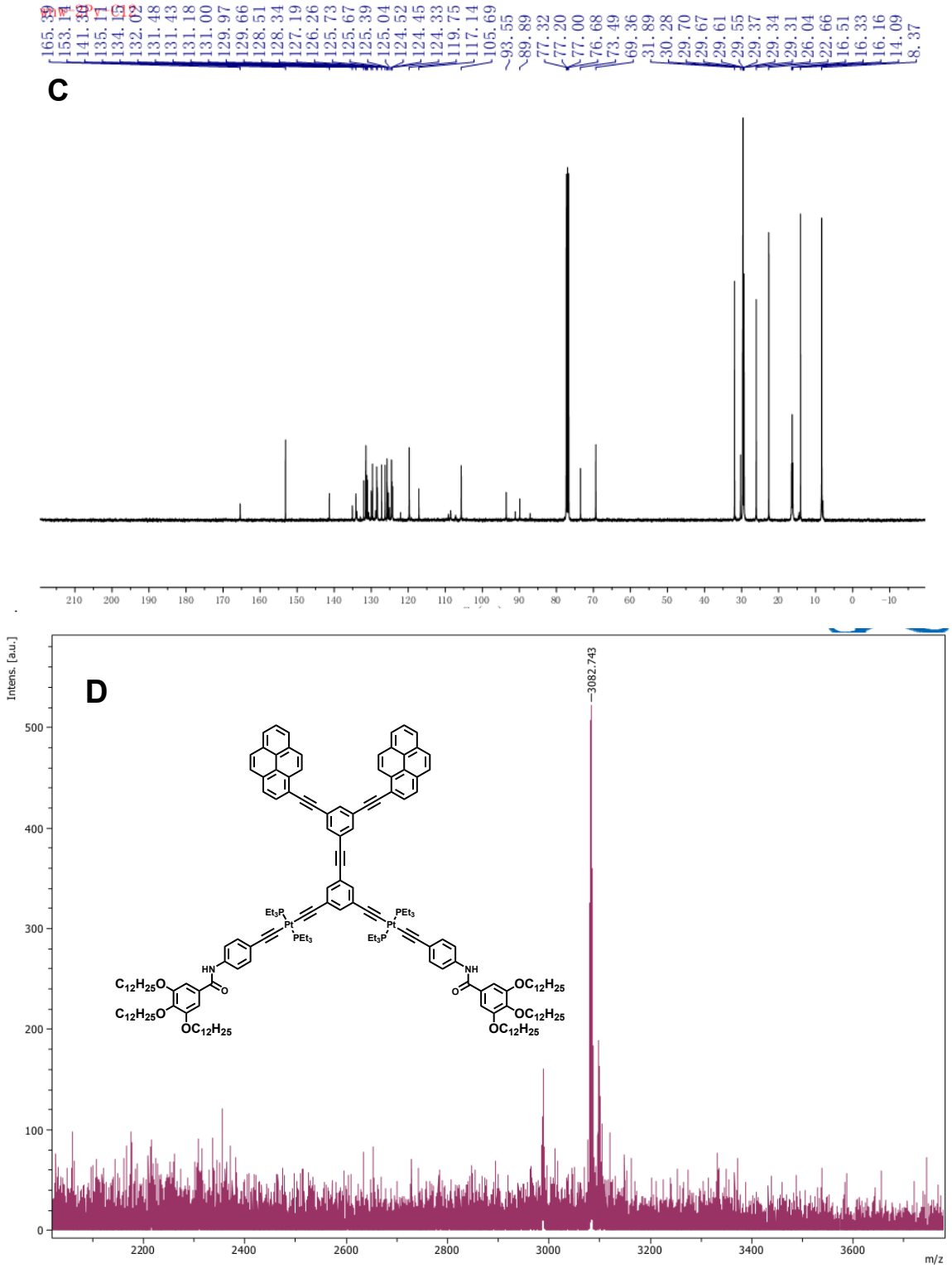
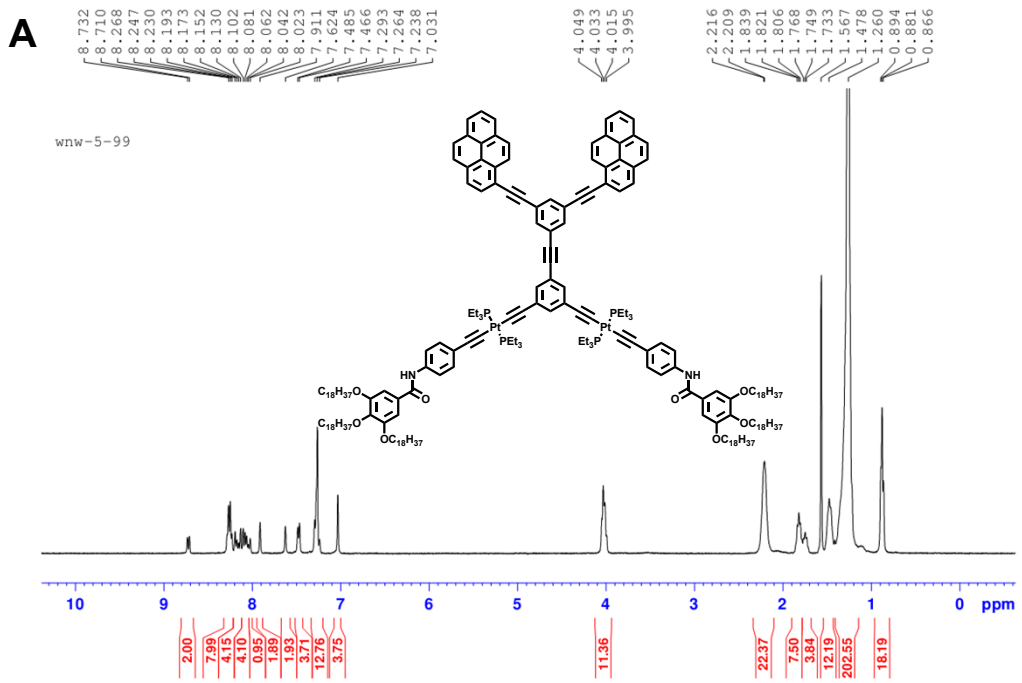
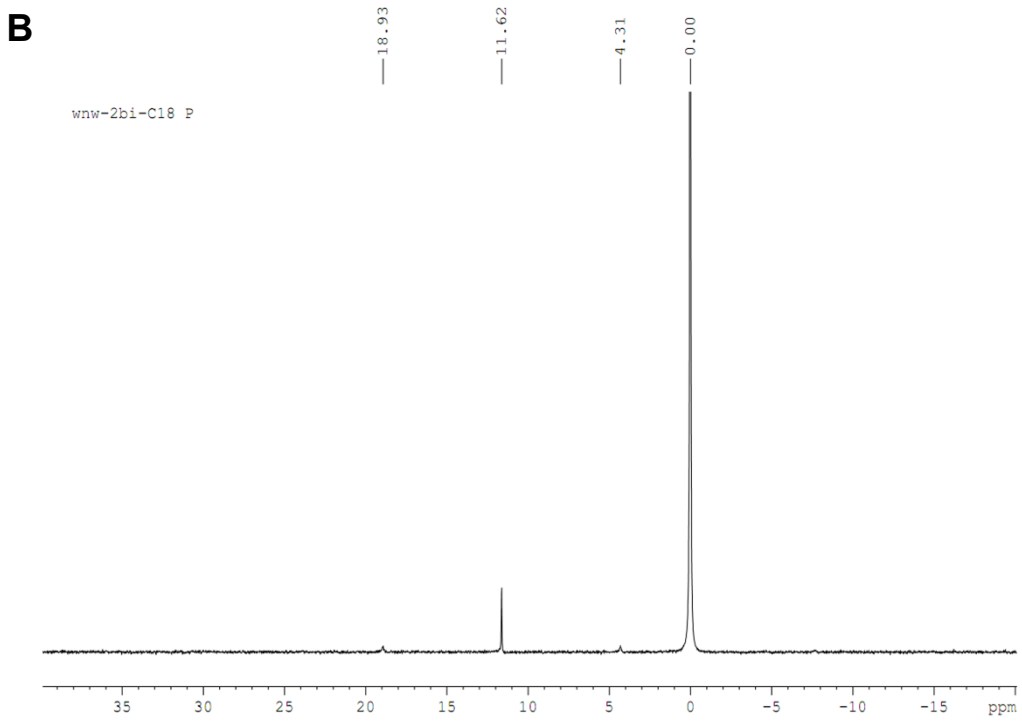


Figure S24. ^{1}H (A), ^{31}P (B) ^{13}C (C) NMR spectra and MALDI-TOF-MS (D) of **5a** in $CDCl_3$


A
8.732
8.710
8.268
8.247
8.230
8.193
8.173
8.152
8.130
8.102
8.081
8.062
8.042
8.023
7.911
7.624
7.485
7.466
7.293
7.264
7.238
7.031
4.049
4.033
4.015
3.995
2.216
2.209
1.839
1.821
1.806
1.768
1.749
1.733
1.567
1.478
1.260
0.894
0.881
0.866
wnw-5-99
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
7.99
4.15
4.10
0.95
1.89
1.93
3.71
12.76
3.75
11.36
22.37
7.50
3.84
12.19
202.55
18.19


B
18.93
11.62
4.31
0.00
wnw-2bi-C18 P
35
30
25
20
15
10
5
0
-5
-10
-15
ppm

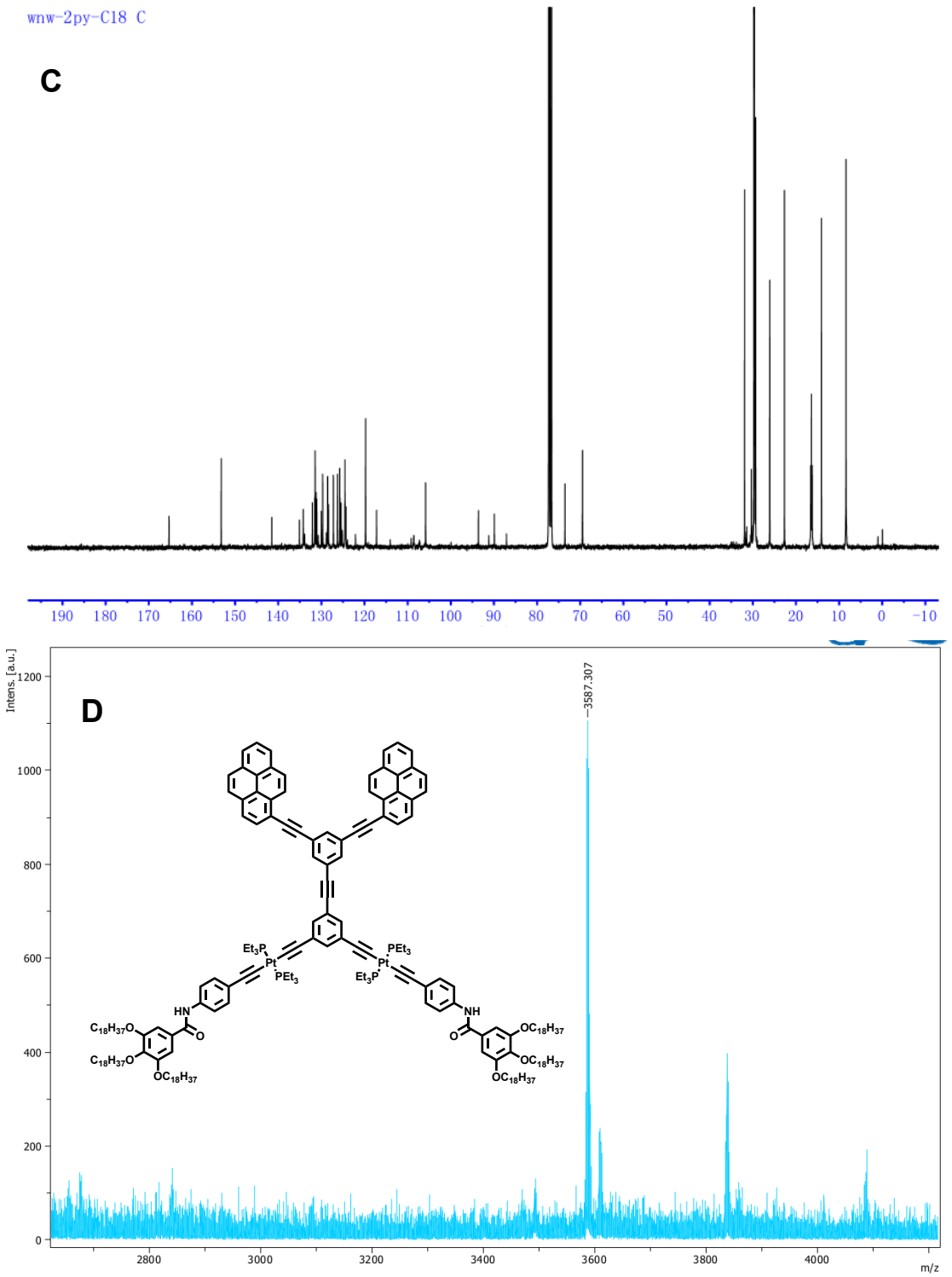


Figure S25. ^{1}H (A), ^{31}P (B) ^{13}C (C) NMR spectra and MALDI-TOF-MS (D) of **5b** in $CDCl_3$

10. References

1. N.-W. Wu, J. Zhang, D. Ciren, Q. Han, L.-J. Chen, L. Xu, H.-B, Yang. *Organometallics*, 2013, **32**, 2536.

2. M. He, Q. Han, J. He, Q. Li, Z. Abliz, H. Tan, L. Xu, H. Yang, *Chin. J. Chem.* 2013, **31***,* 663.

3. X.-D. Xu, J. Zhang, L.-J. Chen, X.-L. Zhao, D-X. Wang, H.-B. Yang, *Chem. Eur. J*. 2012, 18, 1659.