Electronic Supplementary Information (ESI) For

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

Xing-Dong Xu,[a] Jing Zhang,[a] Li-Jun Chen,[a] Rong Guo,[a] De-Xian Wang,[b] and Hai-Bo Yang*[a]

[a] *Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 N. Zhongshan Road, Shanghai 200062, P.R. China.*

[b] *Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China.*

hbyang@chem.ecnu.edu.cn

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_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 × 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.

(a) K. Tashiro and T. Aida, *Chem. Soc. Rev.*, 2007, **36**, 189; (b) R. Charvet, Y. Yamamoto, T. Sasaki, J. Kim, K. Kato, M. Takata, A. Saeki, S. Seki, and T. Aida, *J. Am. Chem. Soc.*, 2012, **134**, 2524; (c) T. Yamaguchi, T. Kimura, H. Matsuda, and T. Aida *Angew. Chem., Int. Ed.*, 2004, **43**, 6350; (d) D.-L. Jiang and T. Aida, *J. Am. Chem. Soc*., 1998, **120**, 10895; (e) S. Sengupta, D. Ebeling, S. Patwardhan, X. Zhang, H. v. Berlepsch, C. Böttcher, V. Stepanenko, S. Uemura, C. Hentschel, H. Fuchs, F. C. Grozema, L. D. A. Siebbeles, A. R. Holzwarth, L. Chi, and F. Würthner, *Angew. Chem. Int. Ed.*, 2012, **51**, 6378; (f) S. Sengupta, S. Uemura, S. Patwardhan, V. Huber, F. C. Grozema, L. D. A. Siebbeles, U. Baumeister, and F. Würthner, *Chem. Eur. J.* 2011, **17**, 5300; (g) V. Huber, S. Sengupta, and F. Würthner, *Chem. Eur. J.*, 2008, **14**, 7791; (h) F. A. Helmich, M. M. J. Smulders, C. C. Lee, A. P. H. J. Schenning, and E.W. Meijer, *J. Am. Chem. Soc.*, 2011,**133**, 12238; (i) F. A. Helmich, C. C. M. Lee, M. M. L. Nieuwenhuizen, J. C. Gielen, P. C. M. Christianen, A. Larsen, G. Fytas, P. E. L. G. Leclère, A. P. H. J. Schenning, and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2010, **49**, 3939; (j) F. A. Helmich, C. C. M. Lee, A. P. H. J. Schenning, and E.W. Meijer, *J. Am. Chem. Soc.*, 2010, **132**, 16753; (k) F. J. M. Hoeben, M. Wolffs, J. Zhang, S. D. Feyter, P. Leclère, A. P. H. J. Schenning, and E. W. Meijer, *J. Am. Chem. Soc.*, 2007, **129**, 9819; (l) F. J. M. Hoeben, M. J. Pouderoijen, A. P. H. J. Schenning, and E. W. Meijer, *Org. Biomol. Chem.*, 2006, **4**, 4460; (m) S. V. Bhosale, M. A. Bissett, C. Forsyth, S. J. Langford, S. M. Neville, J. G. Shapter, L. Weeks, and C. P. Woodward, *Org. Lett.*, 2008, **10**, 2943; (n) L. Wu, Q. Wang, J. Lu, Y. Bian, J. Jiang and X. Zhang, *Langmuir*, 2010, **26**, 7489; (o) X. Zhang, Q. Wang, L. Wu, W. Lv, J. Lu, Y. Bian and J. Jiang, *J. Phys. Chem. B*, 2010, **114**, 1233; (p) G. Lu, Y. Chen, Y. Zhang, M. Bao, Y. Bian, X. Li and J. Jiang, *J. Am. Chem. Soc.*, 2008, **130**, 11623; (q) G. Lu, X. Zhang, X. Cai, and J. Jiang, *J. Mater. Chem.*, 2009, **19**, 2417; (r) K. E. Martin, Z. Wang, T. Busani, R. M. Garcia, Z. Chen, Y. Jiang, Y. Song, J. L. Jacobsen, T. T. Vu, N. E. Schore, B. S. Swartzentruber, C. J. Medforth and J. A. Shelnutt, *J. Am. Chem. Soc.*, 2010, **132**, 8194; (s) H. Wang, Y. Song, Z. Wang,

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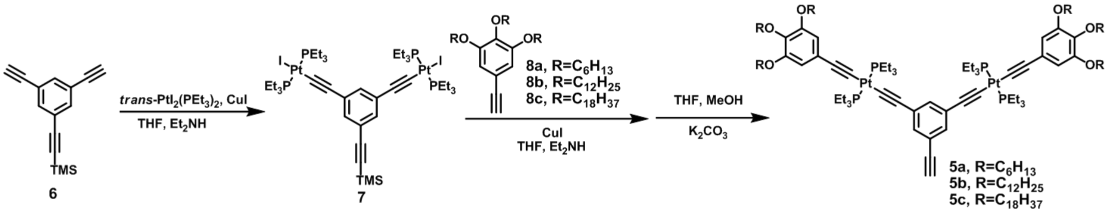
3. Synthetic Procedures and Characterizations of New Compounds

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. Compounds **2**[1], **6**[2], and **8a–8c**[3] were prepared as previous report.

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



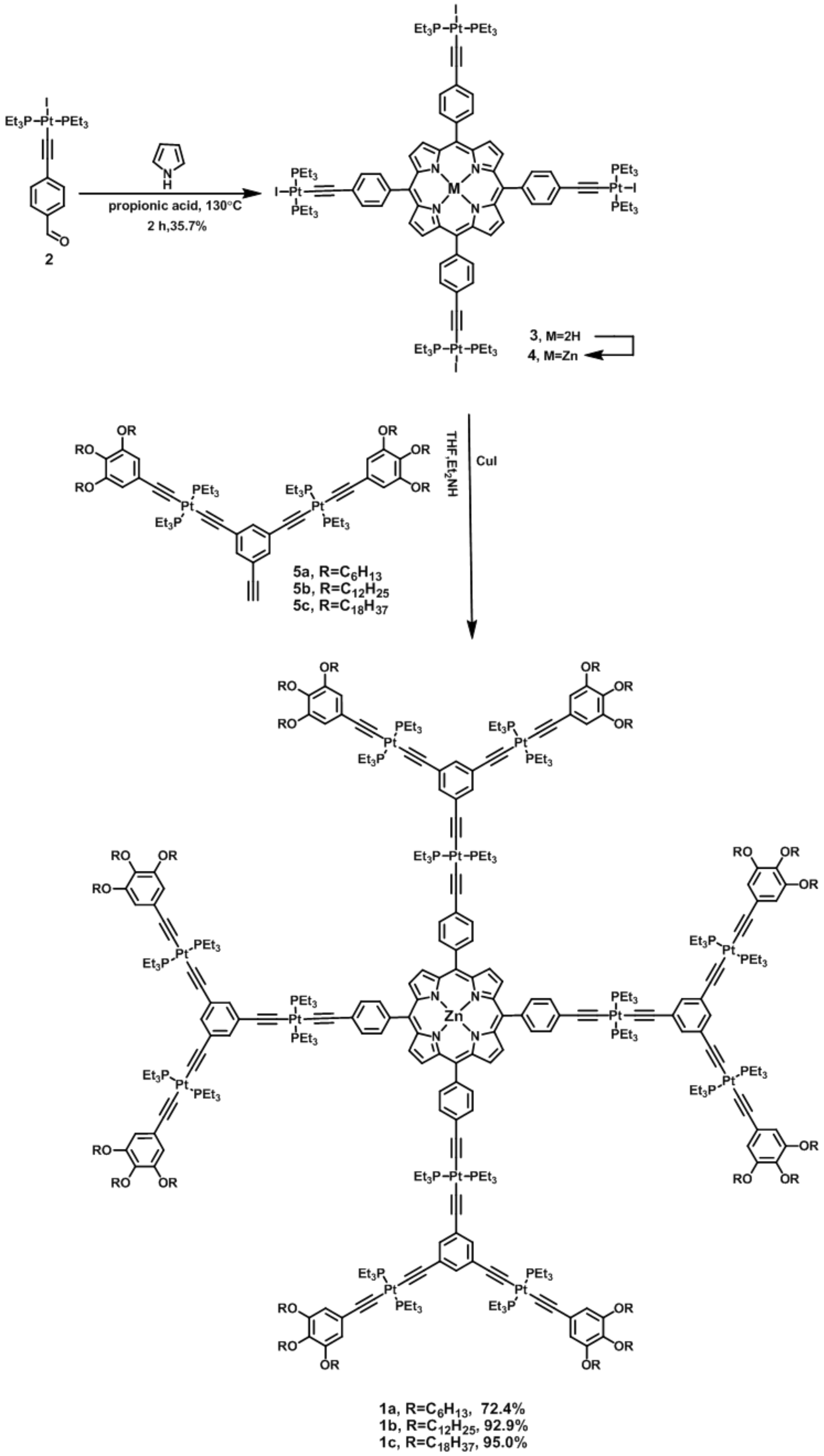
Synthesis of compound 7. A solution of *trans*-diiodobis (triethyl phosphine) platinum (1.16 g, 1.34 mmol), cuprous iodide (6.4 mg, 5 mol%) and **6** (150 mg, 0.68 mmol) in a mixture solvent of THF/Et$_2$NH (20 mL/12 mL) was stirred at room temperature. After 2.5 h a small amount of diethylammonium iodide 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%. R***f*** = 0.69 (dichloromethane/petroleum ether 1:1). M.p. 185 ℃. ^{1}H NMR (CDCl$_3$, 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); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 133.2, 131.0, 128.4, 122.7, 105.0, 99.3, 93.7, 90.5, 16.6, 8.3; ^{31}P NMR (CDCl$_3$, 121.4 MHz): δ 8.79 (s, $J_{\text{Pt-P}}$=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 N$_2$. 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%. R***f*** = 0.41 (dichloromethane/ petroleum ether 2:1) Mp:106 ℃. ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.18 (s, $J_{Pt\text{-}P}$=2368.60 Hz). Anal. Calcd for $C_{88}H_{146}O_6P_4Pt_2$: 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 Et_2NH (10 mL). Yield: 494.6 mg. 88.0%. R***f*** = 0.64 (dichloromethane/ petroleum ether 2:1); Mp: 78 ℃. ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 11.73 (s, $J_{Pt\text{-}P}$=2372.16 Hz). Ionspec HiResMALDI MS of **5b**: m/z calcd for $C_{124}H_{219}O_6P_4Pt_2$ ($[M+H]^+$) 2318.51, found 2318.390. Anal. Calcd for $C_{124}H_{218}O_6P_4Pt_2$: 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 Et_2NH (8 mL). Yield: 506.2 mg. 94.0%. R***f*** = 0.73 (dichloromethane/ petroleum ether 2:1); Mp: 84 ℃. ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 11.69 (s, $J_{Pt\text{-}P}$=2370.94 Hz). Ionspec HiResMALDI MS of **5c**: m/z calcd for $C_{160}H_{291}O_6P_4Pt_2$ ($[M+H]^+$) 2823.07, found 2823.069. Anal. Calcd for $C_{160}H_{290}O_6P_4Pt_2$: C, 68.05; H, 10.35. Found: C, 68.15; H, 10.19.

Scheme S2. Synthesis route of target moleculars **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 $CHCl_3$. 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/ 98% $CHCl_3$ to give product **3** as a purple solid. Yield: 260.0 mg, 35.7%. Mp: >300 ℃. ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 8.84 (s, $J_{Pt\text{-}P}$=2321.6 Hz).

Synthesis of compound 4. The free-base porphyrin **3** (613 mg, 0.21 mmol) was dissolved in CH_2Cl_2/CH_3OH (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 CH_2Cl_2/CH_3OH (99:1). The product was obtained as a purple powder. Yield: 604.4 mg, 96.5%. Mp: >300 ℃. ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 8.82 (s, $J_{Pt\text{-}P}$=2323.3 Hz). Anal. Calcd for $C_{100}H_{144}I_4N_4P_8Pt_4Zn$: 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 N_2. 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%. R*f* = 0.72 (dichloromethane/methanol 400:1); Mp: 150 ℃. ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 11.21 (s, $J_{Pt\text{-}P}$=2365.4 Hz), 11.05 (s, $J_{Pt\text{-}P}$=2368.6 Hz). MALDI-TOF MS of **1a**: m/z calcd for $C_{452}H_{725}N_4O_{24}P_{24}Pt_{12}Zn$ ([M+H]$^+$) 9741.43, found 9741.45.

1b: Yield: 394.9 mg. 92.9%. R*f* = 0.40 (petroleum ether/methanol 10:1); Mp: 97 ℃. ^{1}H NMR ($CDCl_3$, 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, 648H), 0.90 (br, 72H); ^{13}C NMR ($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 11.64(s, $J_{Pt\text{-}P}$=2374.58 Hz), 11.49(s, $J_{Pt\text{-}P}$=2379.44 Hz). MALDI-TOF MS of **1b**: m/z calcd for $C_{596}H_{1013}N_4O_{24}P_{24}Pt_{12}Zn$ ([M+H]$^+$) 11759.69, found 11759.65.

1c: Yield: 390.6 mg. 95.0%. R*f* = 0.29 (petroleum ether/methanol 10:1); Mp: 177 ℃. ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, 121.4 MHz): δ 11.34 (s, $J_{Pt\text{-}P}$=2374.58 Hz), 11.18 (s, $J_{Pt\text{-}P}$=2378.23 Hz). MALDI-TOF MS of **1c**: m/z calcd for $C_{740}H_{1301}N_4O_{24}P_{24}Pt_{12}Zn$ ([M+H]$^+$) 13777.94, found 13777.99.

4. Additional SEM Images at Different Scale.

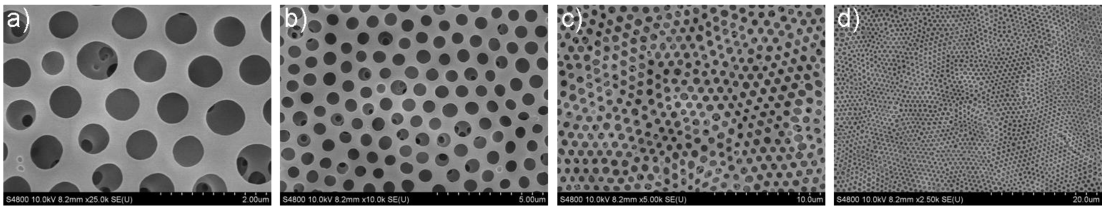


Fig. S1. SEM of **1a** prepared in CH_2Cl_2/hexane at different scale.

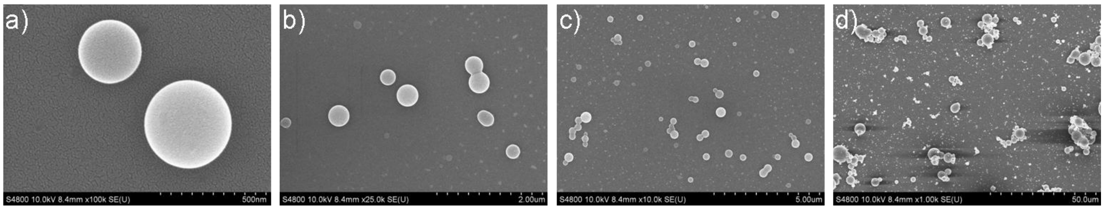


Fig. S2. SEM of **1a** prepared in CH_2Cl_2/MeOH at different scale.

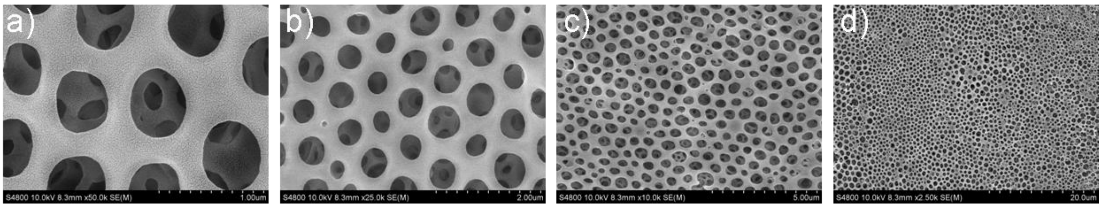


Fig. S3. SEM of **1b** prepared in CH_2Cl_2/hexane at different scale.

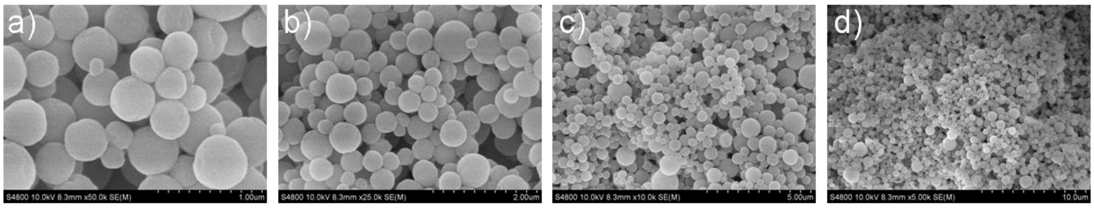


Fig. S4. SEM of **1b** prepared in CH_2Cl_2/MeOH at different scale.

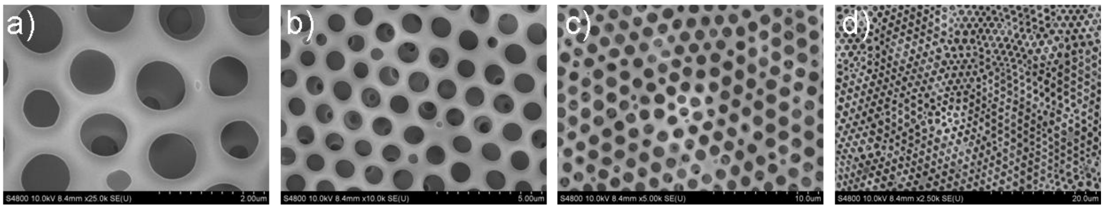


Fig. S5. SEM of **1c** prepared in CH_2Cl_2/hexane at different scale.

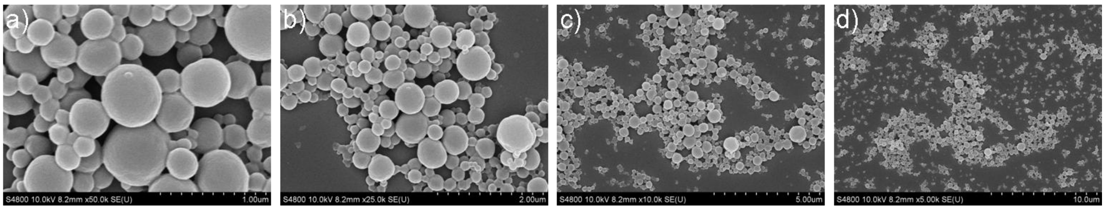


Fig. S6. SEM of **1c** prepared in CH_2Cl_2/MeOH at different scale.

5. Additional Photophysical Data for 1a–1c

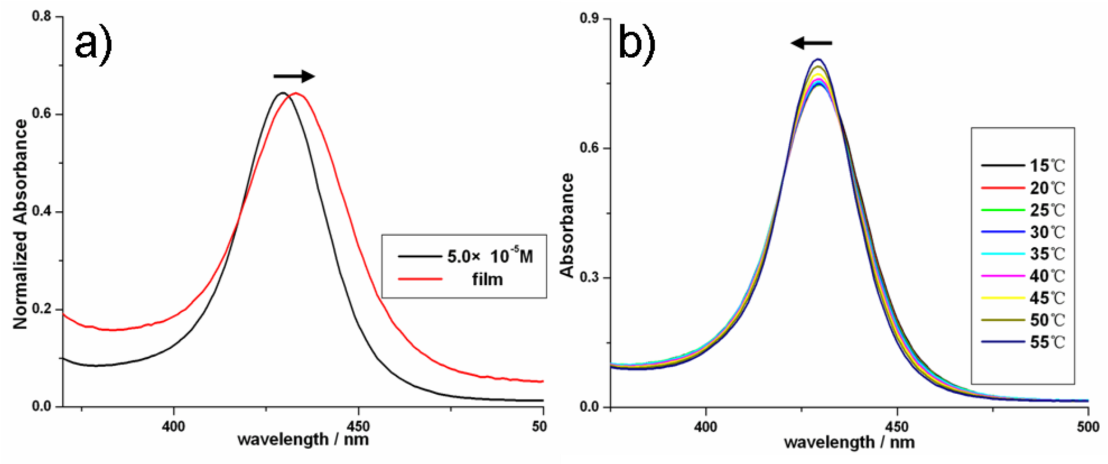


Fig. S7. Normalized UV/Vis spectra of **1a** in hexane (5.0×10^{-5} M) and in film state (a); Temperature dependent UV/Vis spectra in 5.0×10^{-5} M of **1a** in hexane (b).

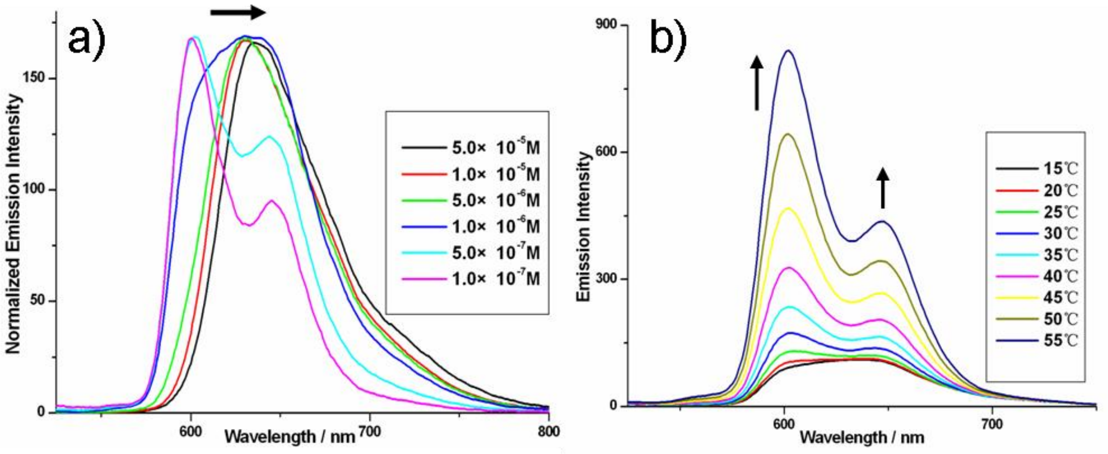


Fig. S8. Concentration (a) and temperature (b) dependent (1.0×10^{-6} M) emission spectra of **1a** in hexane.

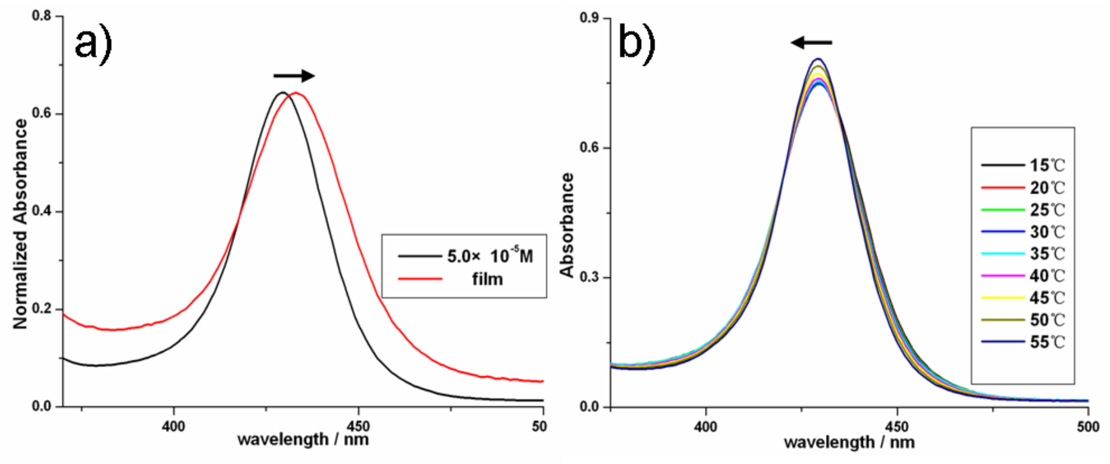


Fig. S9. Normalized UV/Vis spectra of **1c** in hexane (5.0×10^{-5} M) and in film state (a); Temperature dependent UV/Vis spectra in 5.0×10^{-5} M of **1c** in hexane (b).

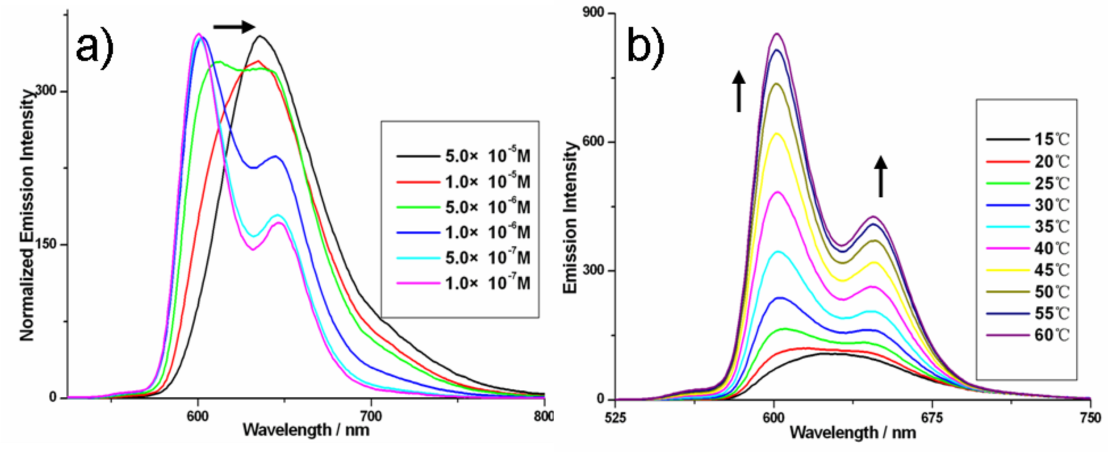
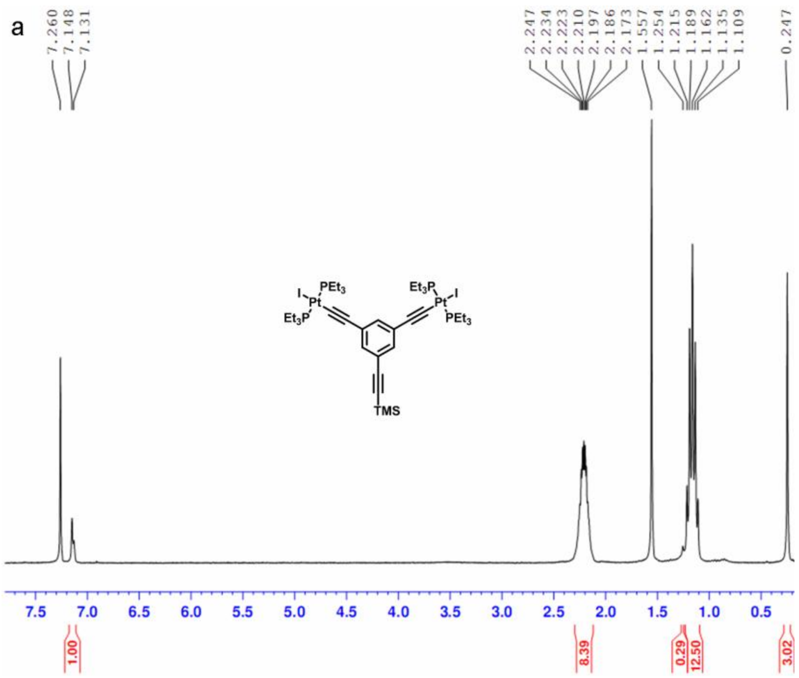
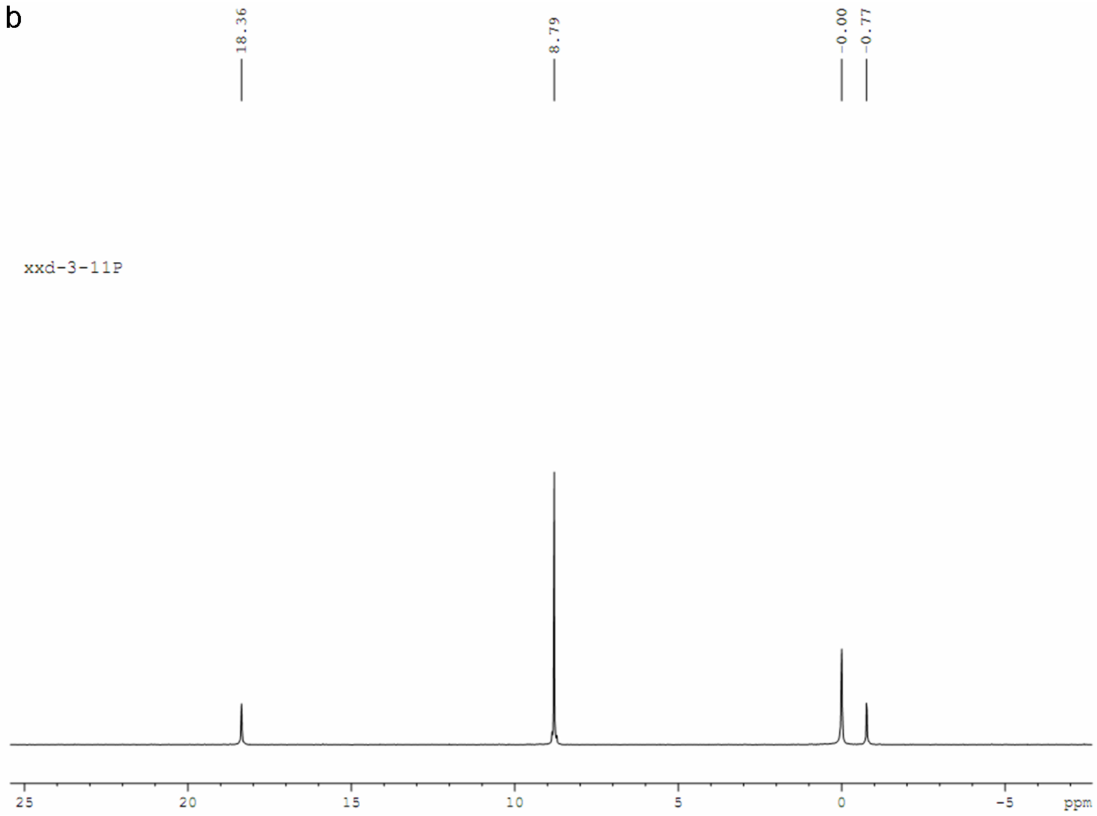


Fig. S10. Concentration (a) and temperature (b) dependent (5.0×10^{-6} M) emission spectra of **1c** in hexane.

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 $CDCl_3$





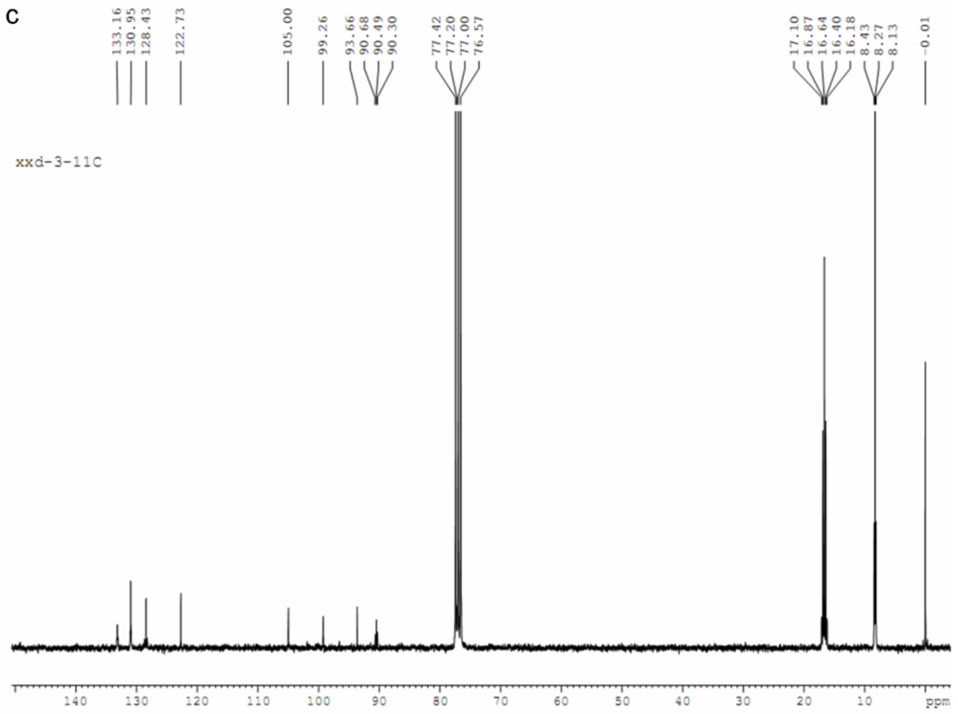
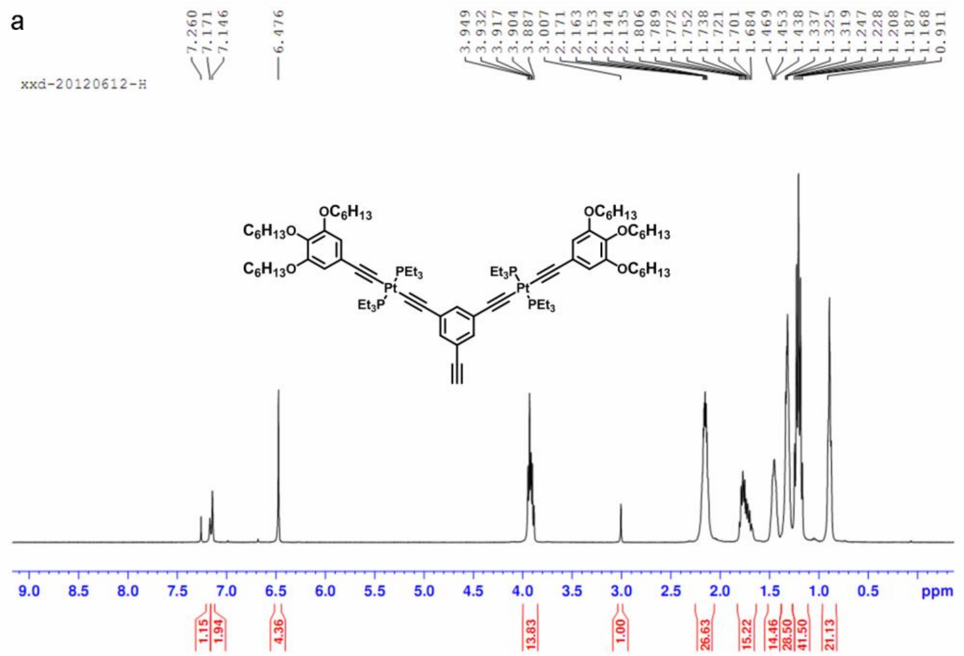
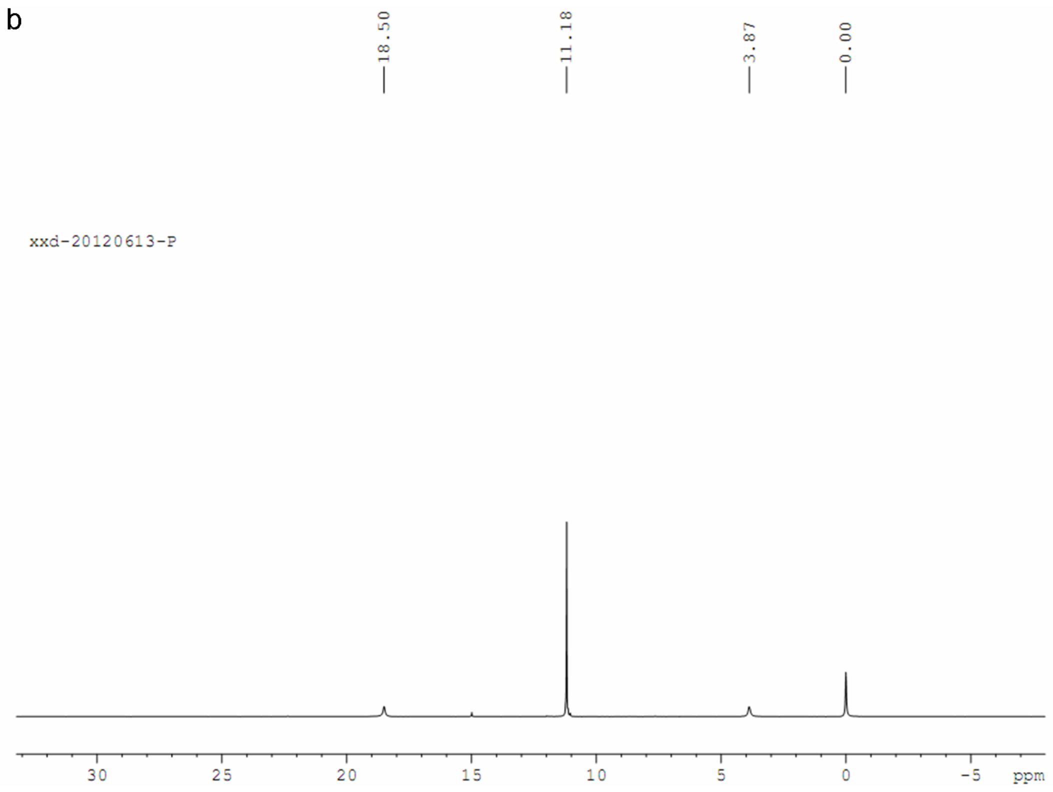

C
133.16
130.95
128.43
122.73
105.00
99.26
93.66
90.68
90.49
90.30
77.42
77.20
77.00
76.57
17.10
16.87
16.64
16.40
16.18
8.43
8.27
8.13
-0.01
xxd-3-11C
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

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





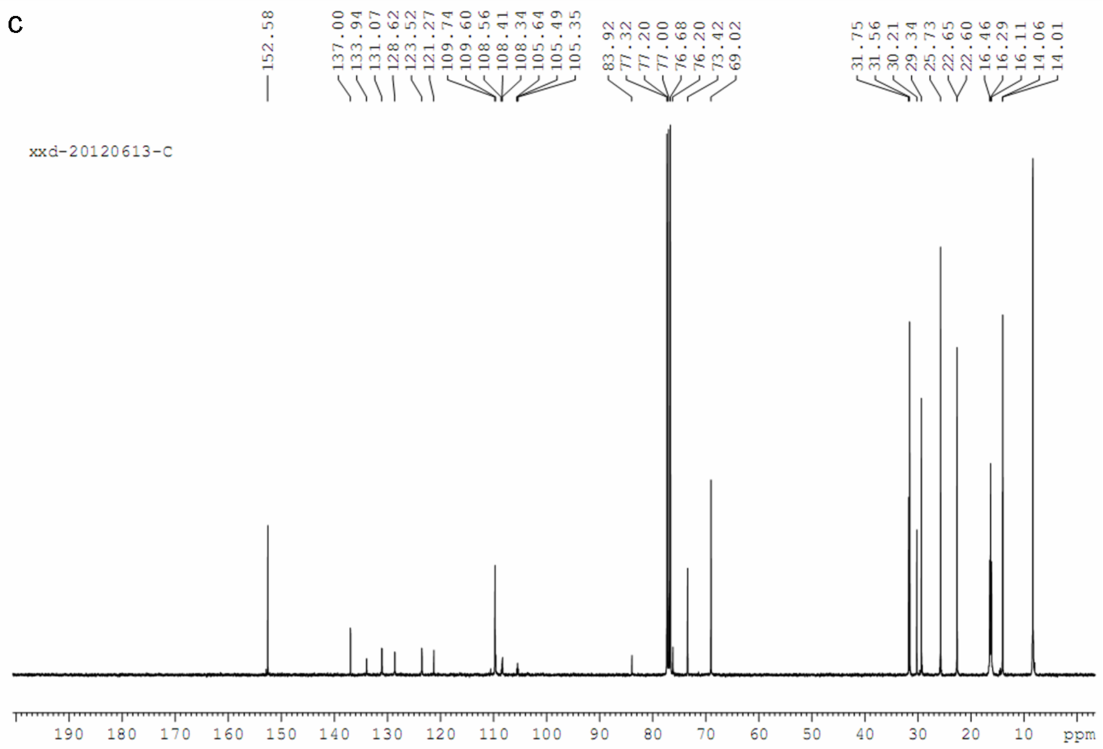
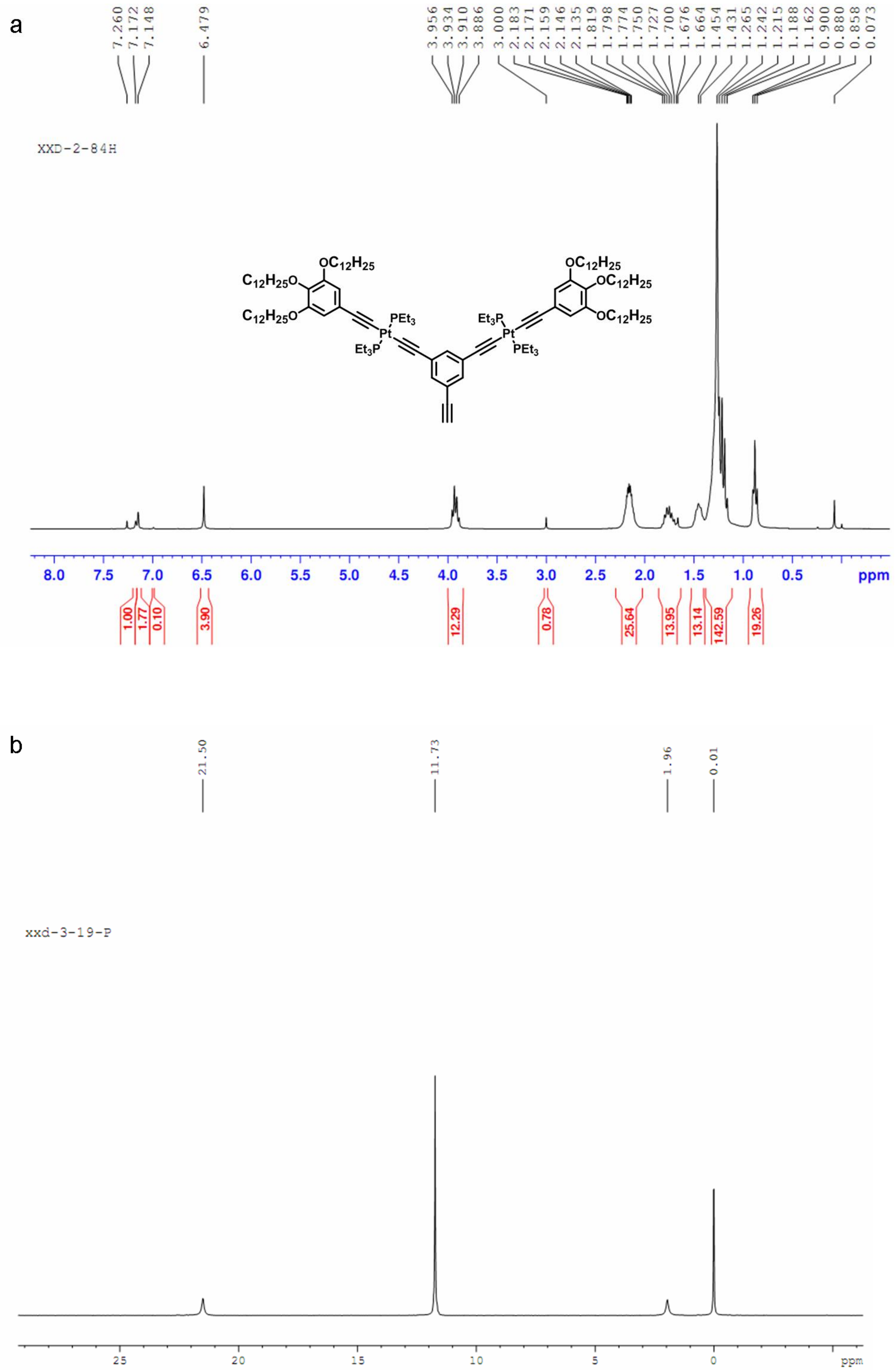

c
152.58
137.00
133.94
131.07
128.62
123.52
121.27
109.74
109.60
108.56
108.41
108.34
105.64
105.49
105.35
83.92
77.32
77.20
77.00
76.68
76.20
73.42
69.02
31.75
31.56
30.21
29.34
25.73
22.65
22.60
16.46
16.29
16.11
14.06
14.01
xxd-20120613-C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Fig. S13. **a**) ^{1}H, **b**)^{31}P and **c**) ^{13}C NMR spectra of **5b** in $CDCl_3$



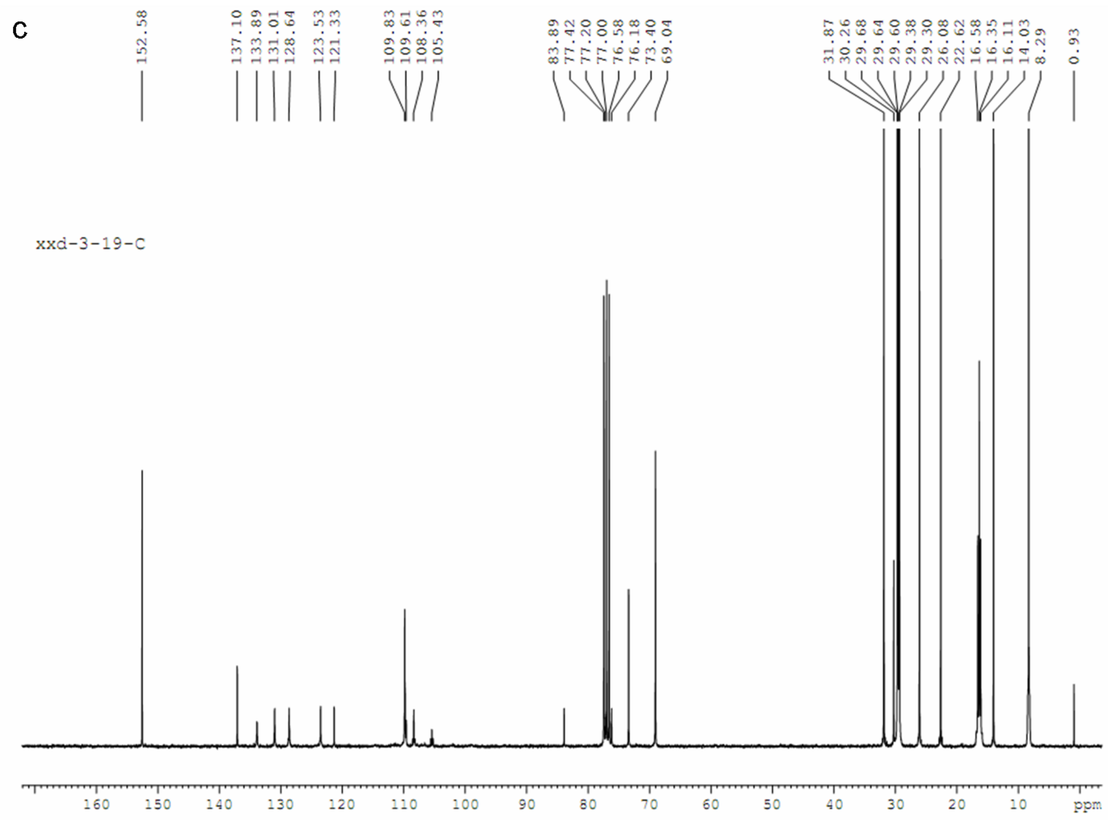
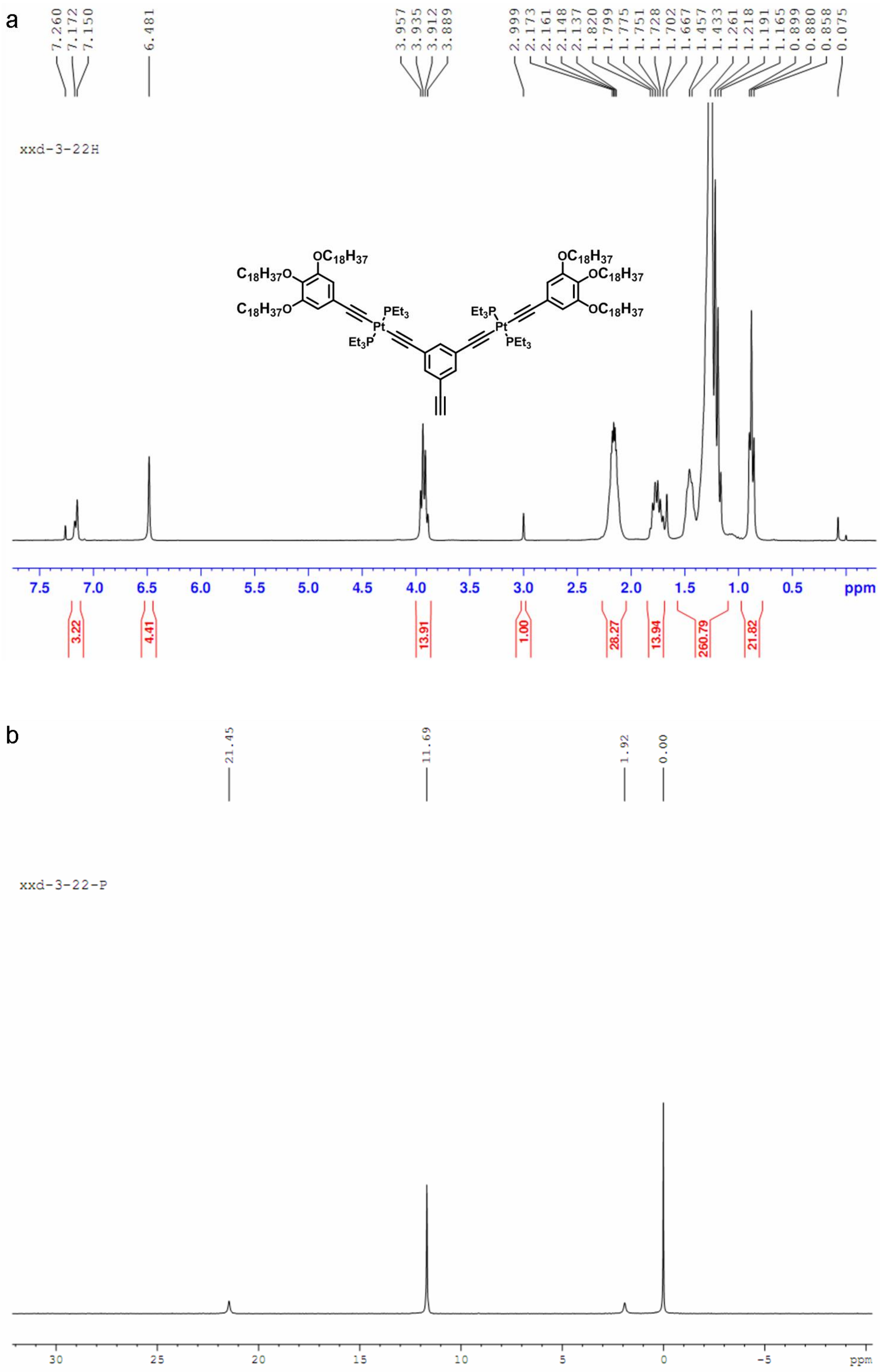

c
xxd-3-19-C
152.58
137.10
133.89
131.01
128.64
123.53
121.33
109.83
109.61
108.36
105.43
83.89
77.42
77.20
77.00
76.58
76.18
73.40
69.04
31.87
30.26
29.68
29.64
29.60
29.38
29.30
26.08
22.62
16.58
16.35
16.11
14.03
8.29
0.93
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Fig. S14. **a**) ^{1}H, **b**)^{31}P and **c**) ^{13}C NMR spectra of **5c** in $CDCl_3$



c

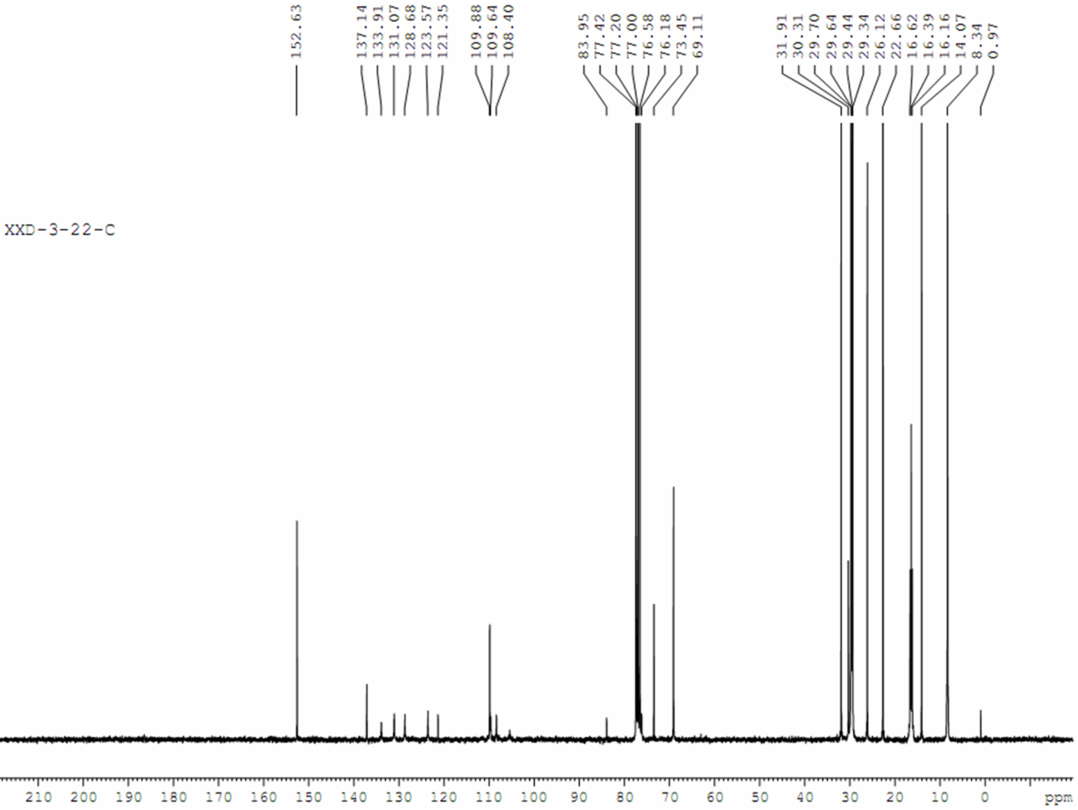
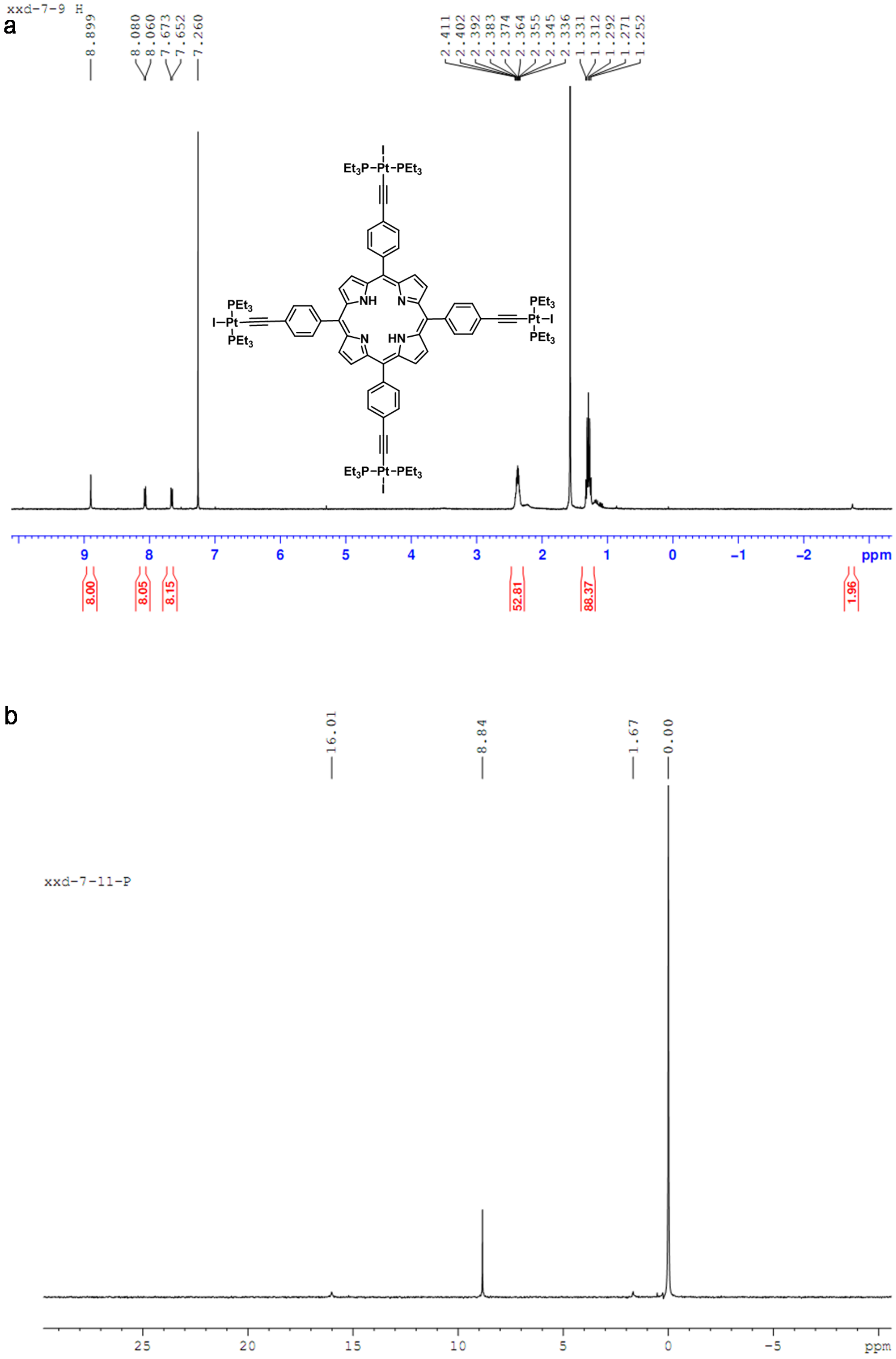

152.63
137.14
133.91
131.07
128.68
123.57
121.35
109.88
109.64
108.40
83.95
77.42
77.20
77.00
76.58
76.18
73.45
69.11
31.91
30.31
29.70
29.64
29.44
29.34
26.12
22.66
16.62
16.39
16.16
14.07
8.34
0.97
XXD-3-22-C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Fig. S15. **a**) ^{1}H, **b**)^{31}P and **c**) ^{13}C NMR spectra of **3** in $CDCl_3$



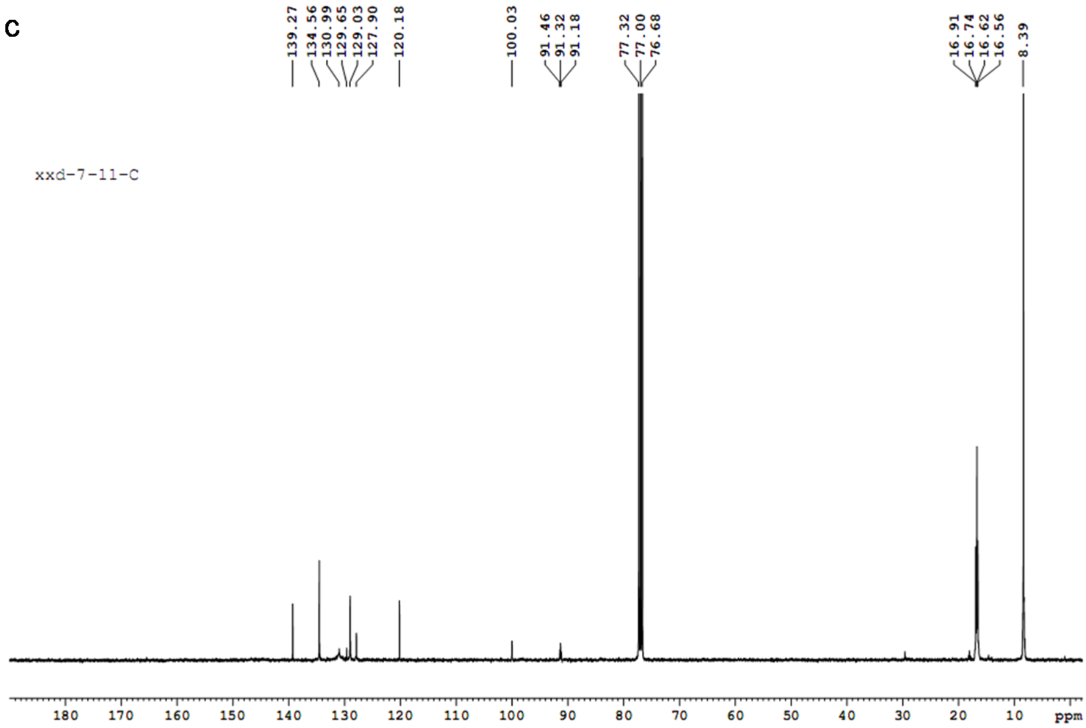
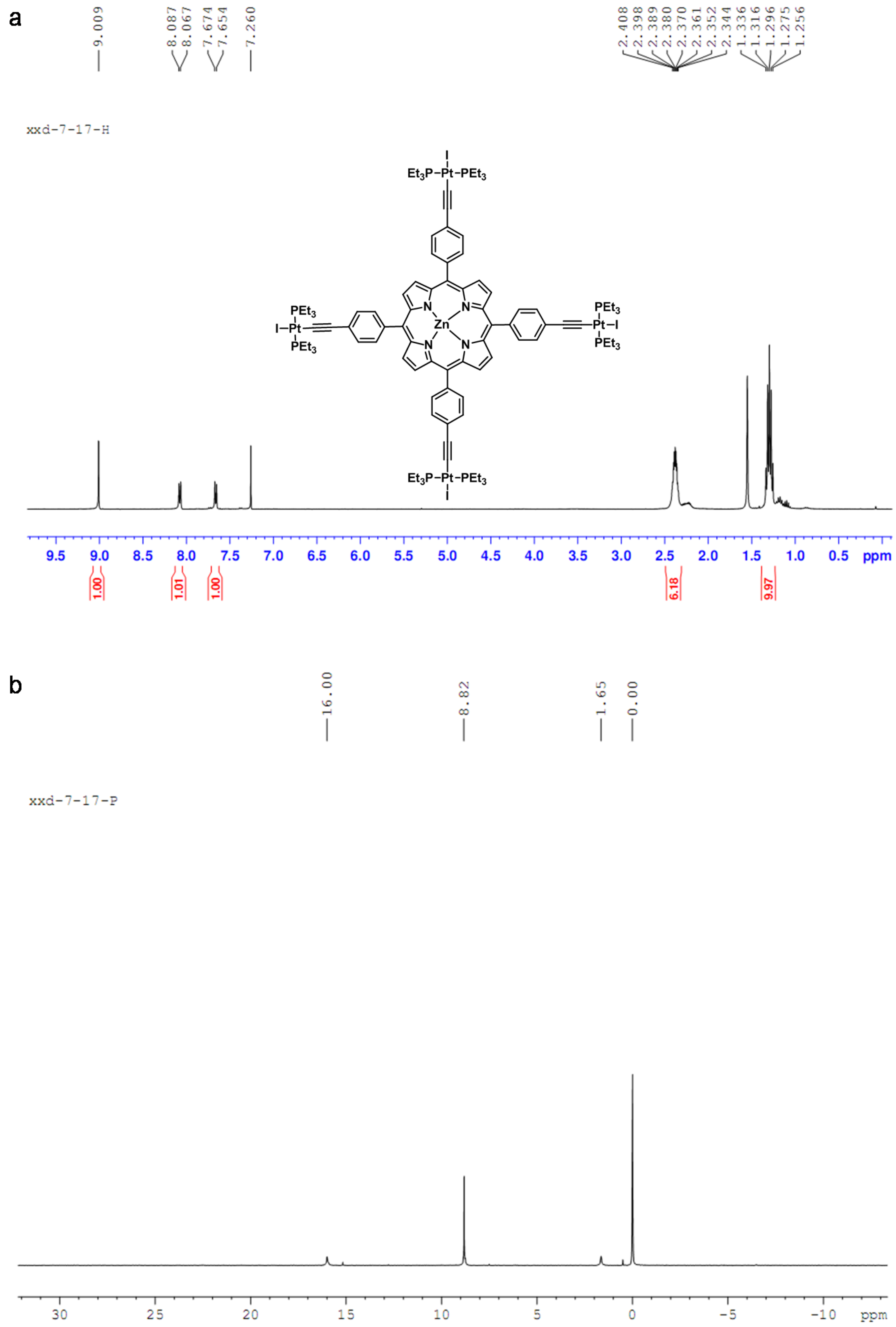

C
139.27
134.56
130.99
129.65
129.03
127.90
120.18
100.03
91.46
91.32
91.18
77.32
77.00
76.68
16.91
16.74
16.62
16.56
8.39
xxd-7-11-C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Fig. S16. **a**) ^{1}H, **b**)^{31}P and **c**) ^{13}C NMR spectra of **4** in $CDCl_3$



C

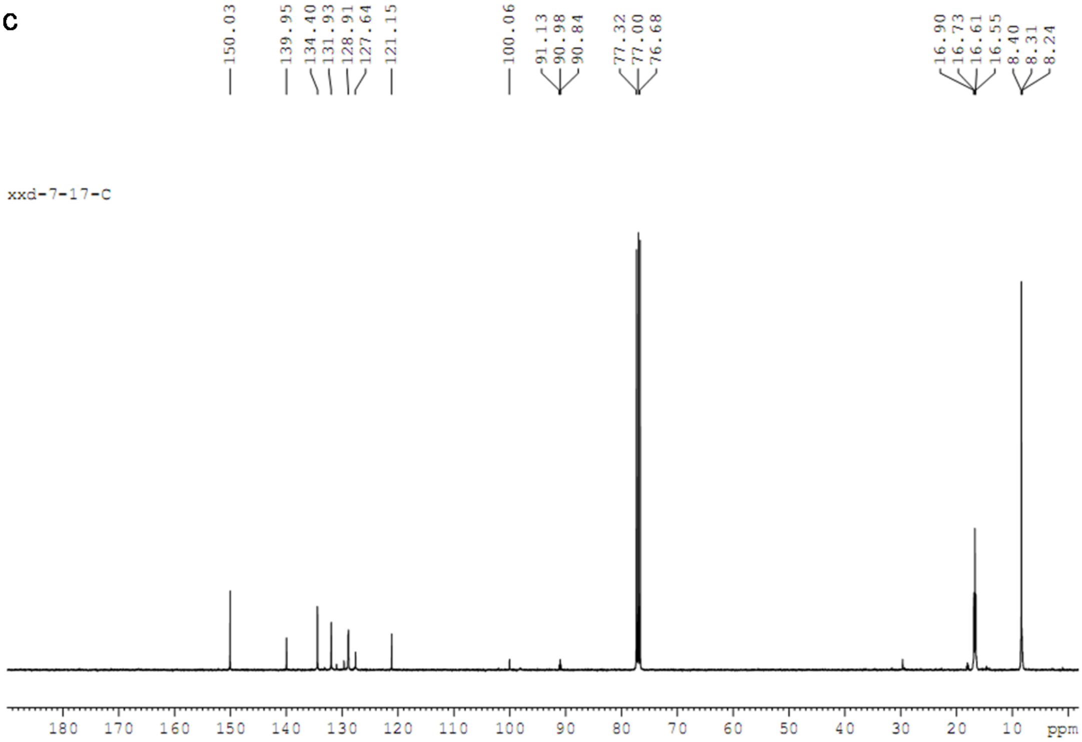
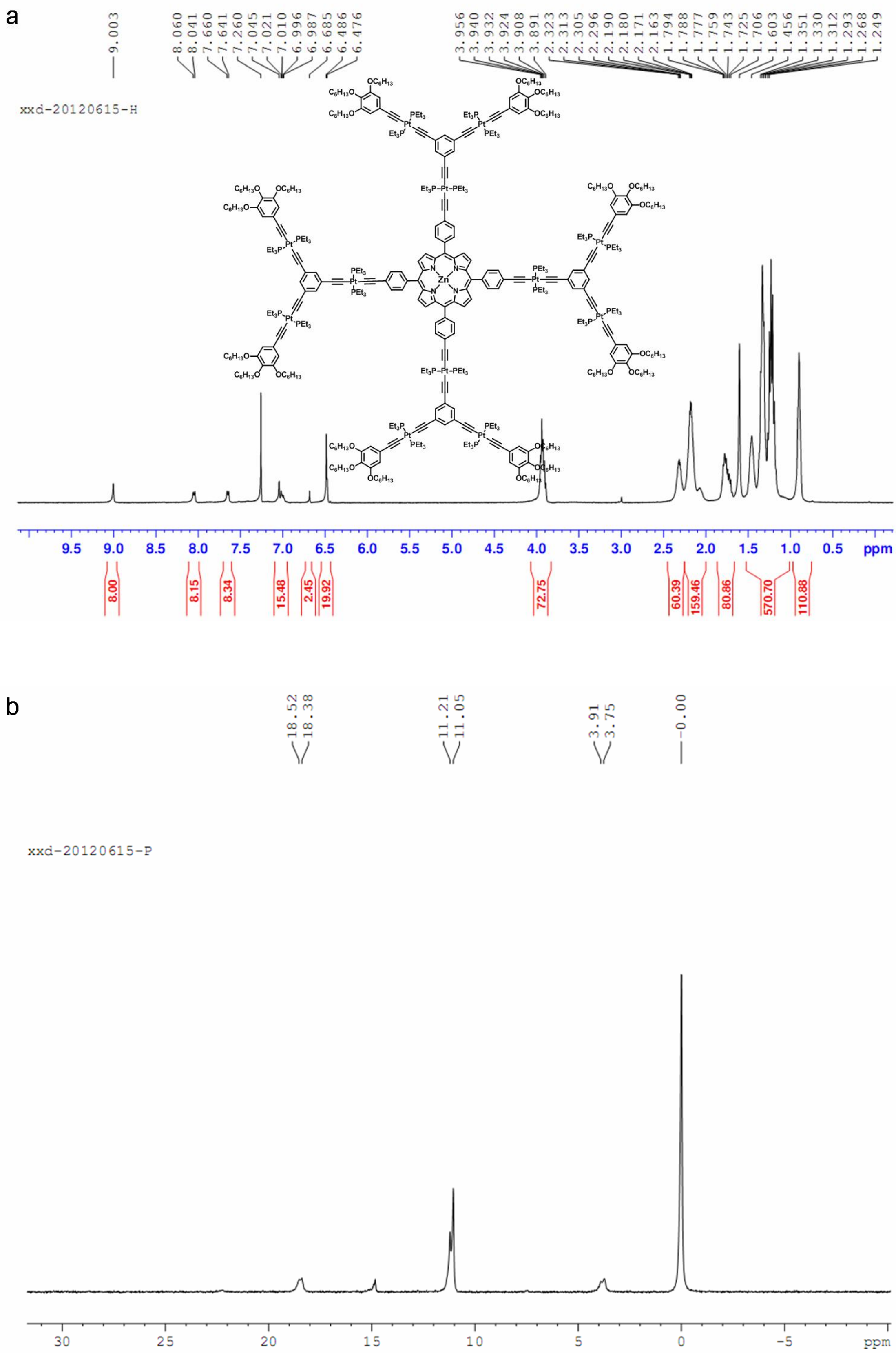

150.03
139.95
134.40
131.93
128.91
127.64
121.15
100.06
91.13
90.98
90.84
77.32
77.00
76.68
16.90
16.73
16.61
16.55
8.40
8.31
8.24
xxd-7-17-C
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Fig. S17. **a**) ^{1}H, **b**)^{31}P and **c**) ^{13}C NMR spectra of **1a** in $CDCl_3$



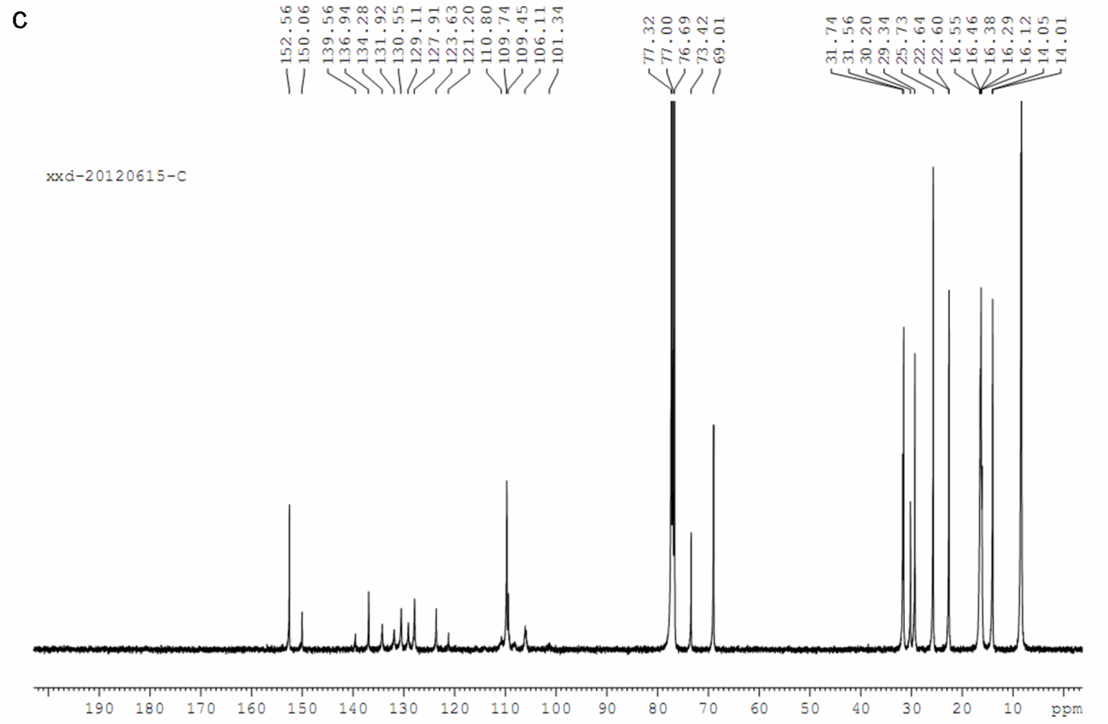
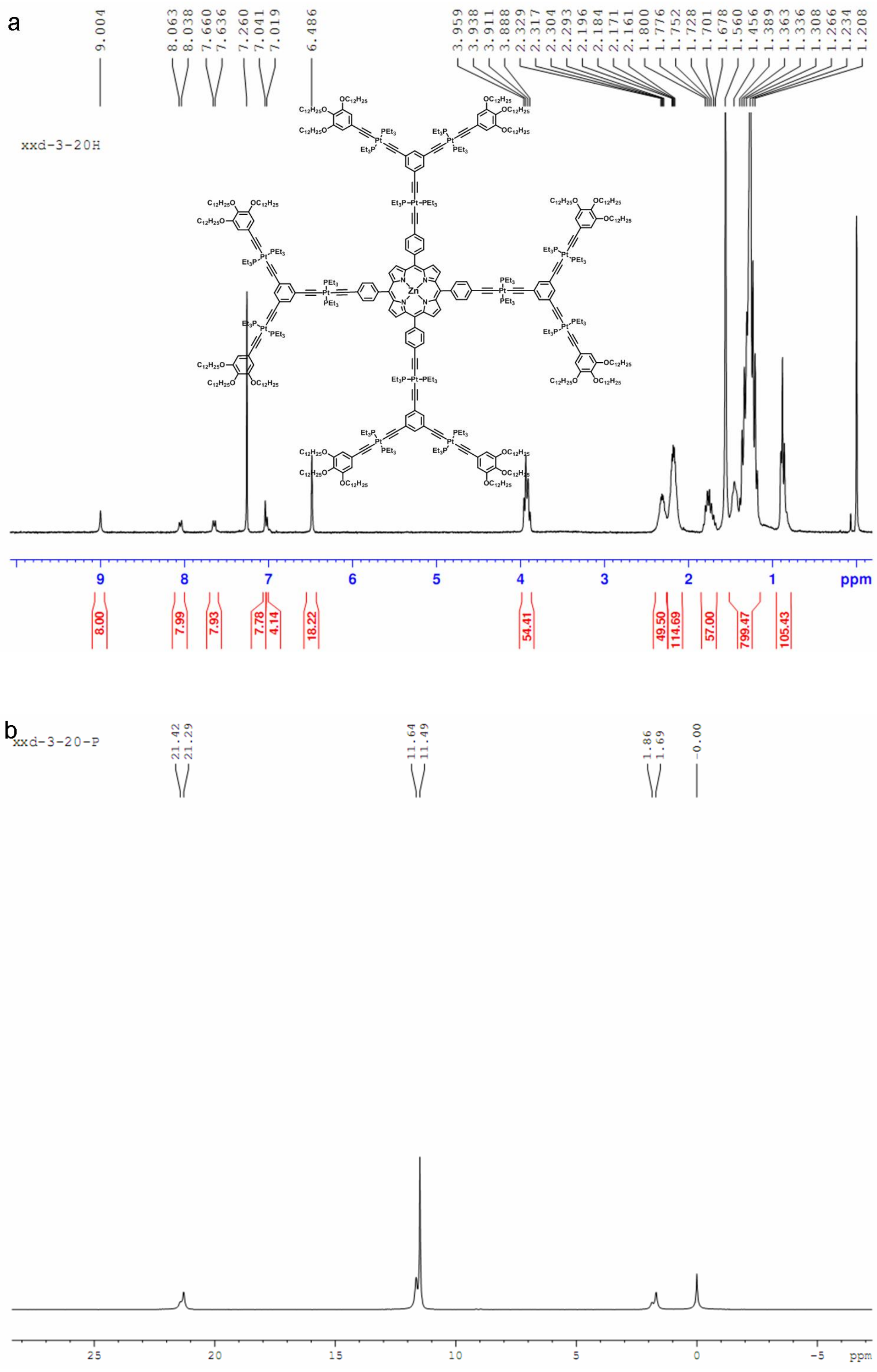

C
152.56
150.06
139.56
136.94
134.28
131.92
130.55
129.11
127.91
123.63
121.20
110.80
109.74
109.45
106.11
101.34
77.32
77.00
76.69
73.42
69.01
31.74
31.56
30.20
29.34
25.73
22.64
22.60
16.55
16.46
16.38
16.29
16.12
14.05
14.01
xxd-20120615-C
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Fig. S18. **a**) ^{1}H, **b**)^{31}P and **c**) ^{13}C NMR spectra of **1b** in $CDCl_3$



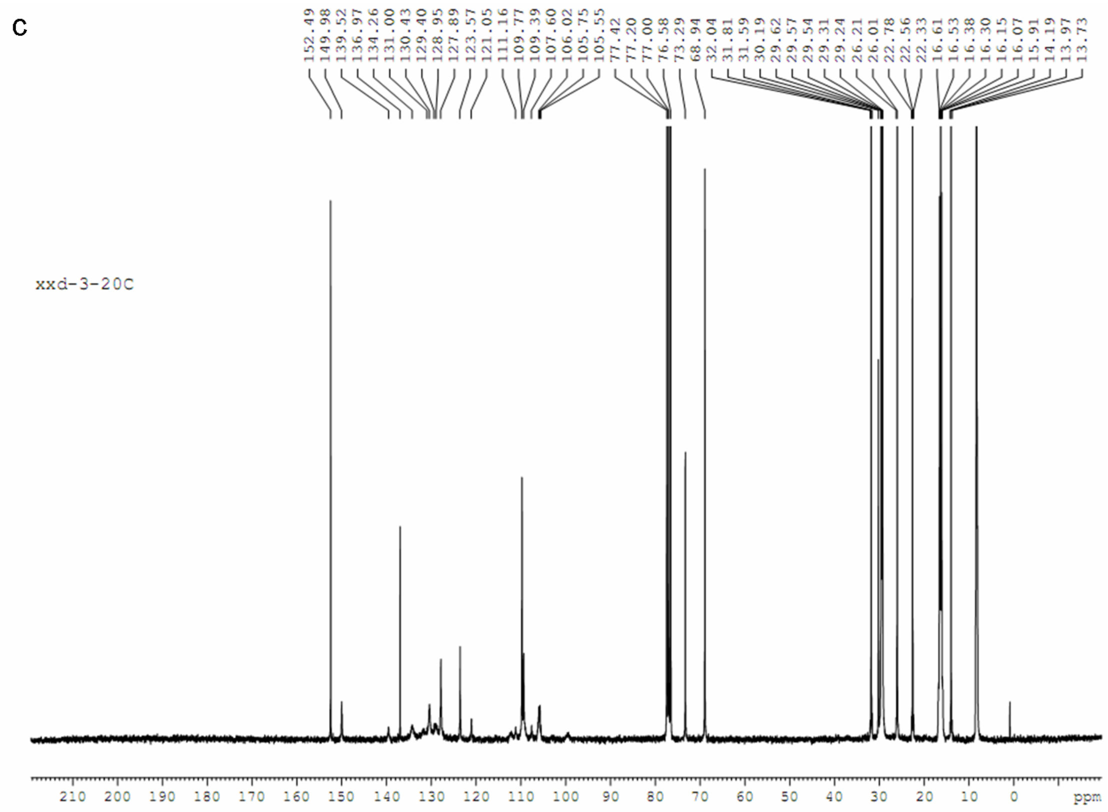
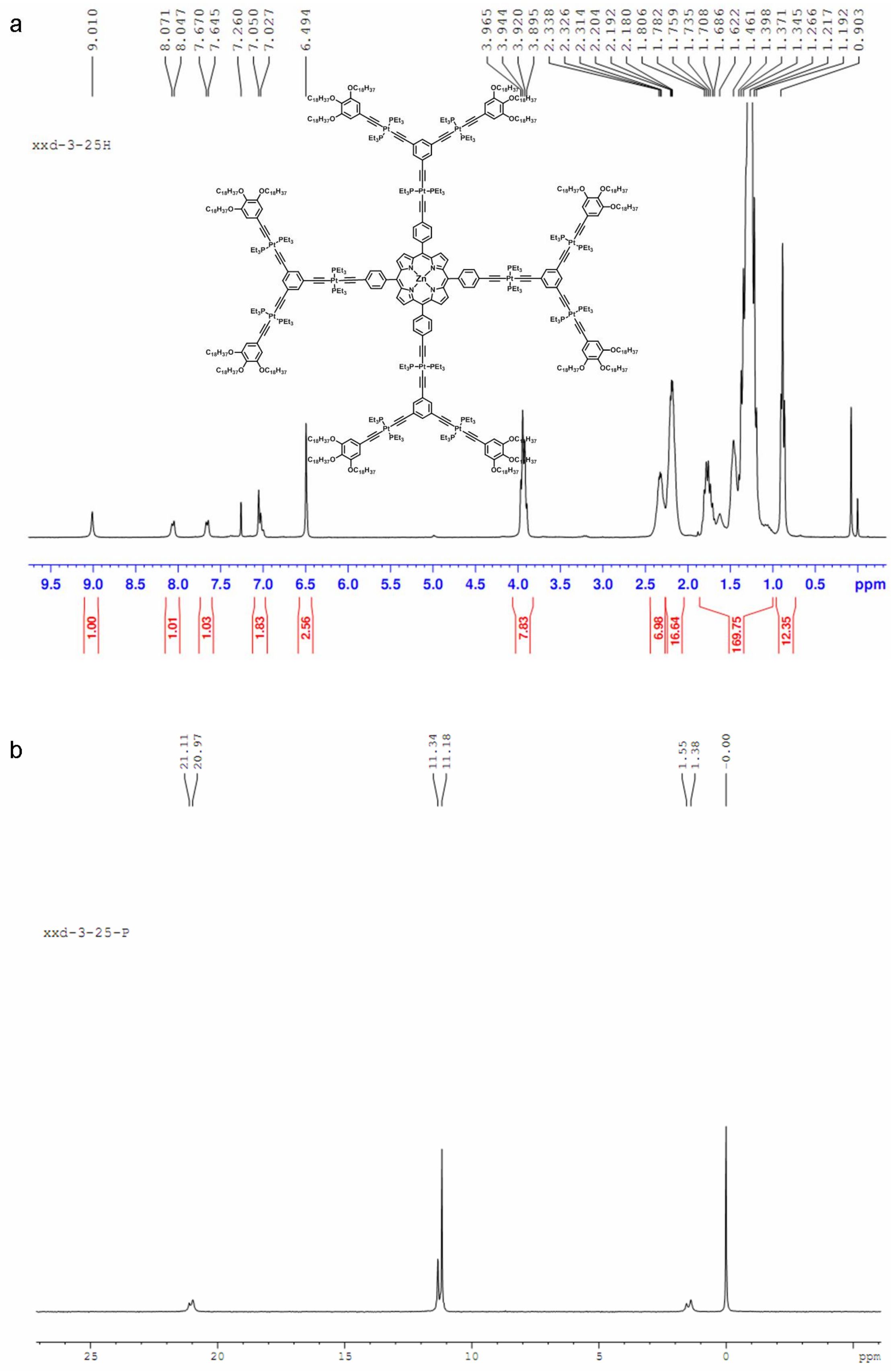
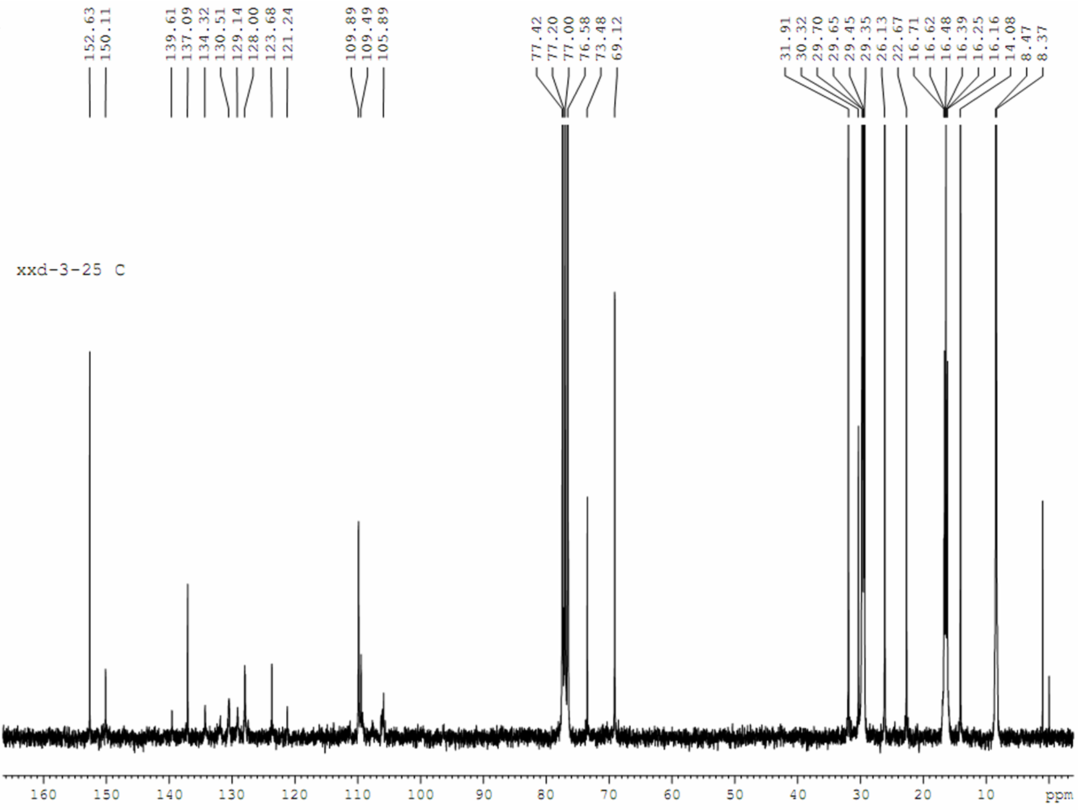

c
152.49
149.98
139.52
136.97
134.26
131.00
130.43
129.40
128.95
127.89
123.57
121.05
111.16
109.77
109.39
107.60
106.02
105.75
105.55
77.42
77.20
77.00
76.58
73.29
68.94
32.04
31.81
31.59
30.19
29.62
29.57
29.54
29.31
29.24
26.21
26.01
22.78
22.56
22.33
16.61
16.53
16.38
16.30
16.15
16.07
15.91
14.19
13.97
13.73
xxd-3-20C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Fig. S19. **a**) ^{1}H, **b**)^{31}P and **c**) ^{13}C NMR spectra of **1c** in CDCl$_3$

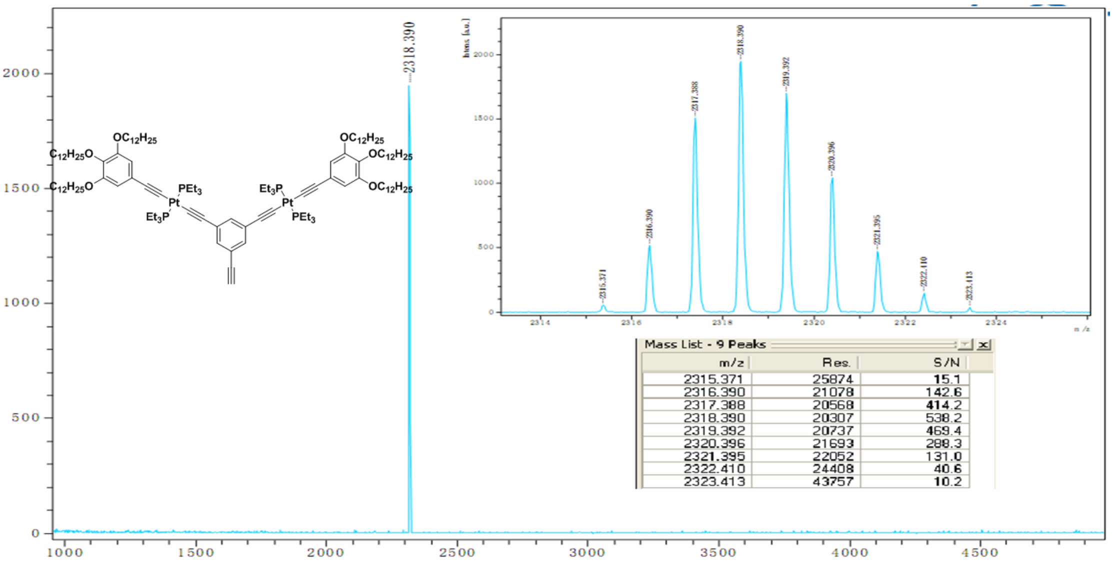


C


152.63
150.11
139.61
137.09
134.32
130.51
129.14
128.00
123.68
121.24
109.89
109.49
105.89
77.42
77.20
77.00
76.58
73.48
69.12
31.91
30.32
29.70
29.65
29.45
29.35
26.13
22.67
16.71
16.62
16.48
16.39
16.25
16.16
14.08
8.47
8.37
xxd-3-25 C
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

7. MALDI-TOF MS of New Compounds

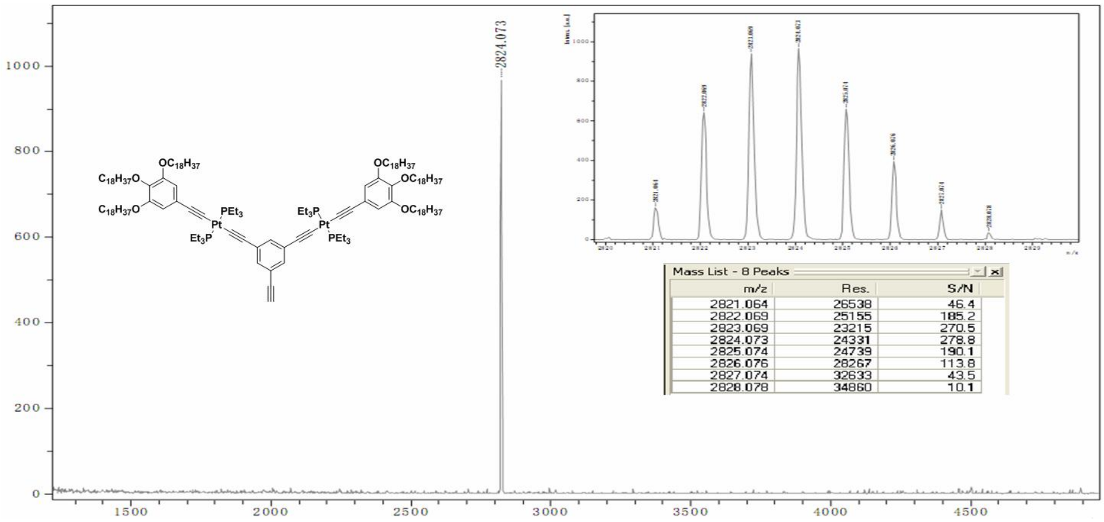
Fig. S20. MALDI-TOF mass spectra of **5b** and the isotope peaks (insert).



Mass List - 9 Peaks

m/z	Res.	S/N
2315.371	25874	15.1
2316.390	21078	142.6
2317.388	20568	414.2
2318.390	20307	538.2
2319.392	20737	469.4
2320.396	21693	288.3
2321.395	22052	131.0
2322.410	24408	40.6
2323.413	43757	10.2

Fig. S21. MALDI-TOF mass spectra of **5c** and the isotope peaks (insert).



Mass List - 8 Peaks

m/z	Res.	S/N
2821.064	26538	46.4
2822.069	25155	185.2
2823.069	23215	270.5
2824.073	24331	278.8
2825.074	24739	190.1
2826.076	28267	113.8
2827.074	32633	43.5
2828.078	34860	10.1

Fig. S22. MALDI-TOF mass spectra of **1a** (a) and the isotope peaks (b).

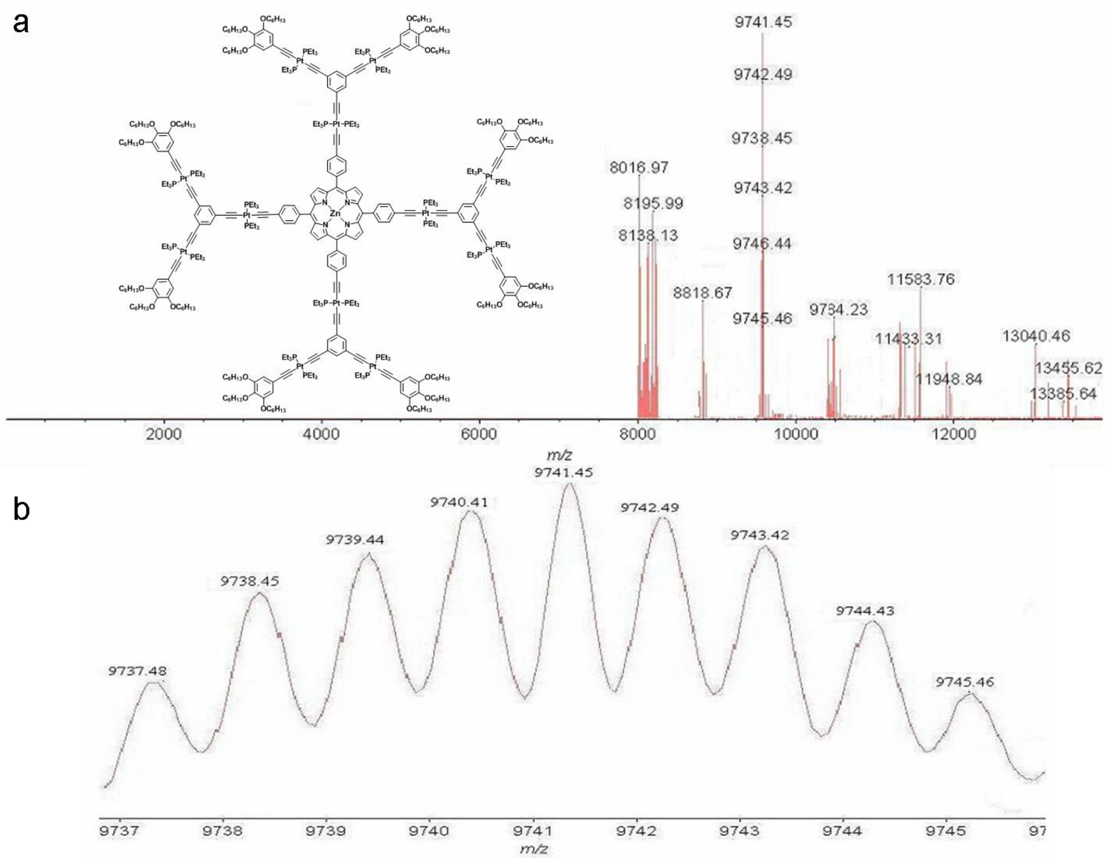
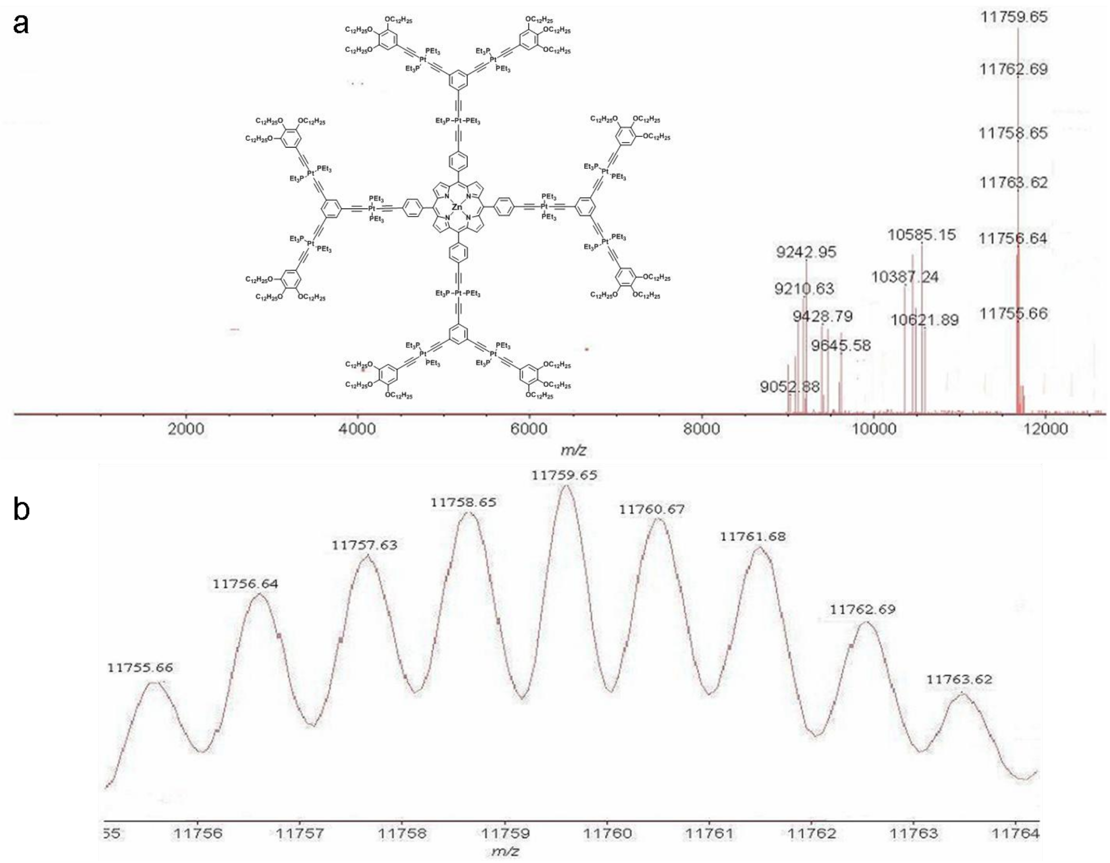


Fig. S23. MALDI-TOF mass spectra of **1b** (a) and the isotope peaks (b).



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1. W. Wu, X. Xu, H. Yang, J. Hua, X. Zhang, L. Zhang, Y. Long and H. Tian, *J. Mater. Chem.*, 2011, **21**, 10666.

2. (a) J. G. Rodríguez and J. Esquivias, *Tetrahedron Lett.*, 2003, **44**, 4831; (b) K. L. Chandra, S. Zhang and C. B. Gorman, *Tetrahedron*, 2007, **63**, 7120.

3. (a) X.-D. Xu, J. Zhang, L.-J. Chen, X.-L. Zhao, D.-X. Wang and H.-B. Yang, *Chem. Eur. J.*, 2012, **18**, 1659; (b) J. Zhang, X.-D. Xu, L.-J. Chen, Q. Luo, N.-W. Wu, D.-X. Wang, X.-L. Zhao and H.-B. Yang, *Organometallics*, 2011, **30**, 4032; (c) L.-J. Chen, J. Zhang, J. He, X.-D. Xu, N.-W. Wu, D.-X. Wang, Z. Abliz and H.-B. Yang, *Organometallics*, 2011, **30**, 5590.