Fluorescent Metallacycle-Cored Polymers via Covalent Linkage and Their Use as Contrast Agents for Cell Imaging

A Submission to the Proceedings of the National Academy of Science USA

PHYSICAL SCIENCES: Chemistry

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Section A. Materials/General Methods/Instrumentation

1.Gerneral materials and Instrumentation

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). Compounds **5**,[S1] **9**,[S2] **11**[S3] and **12**[S3] were prepared according to the literature procedures. NMR spectra were recorded on a Varian Unity 300 MHz or 400 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}P\{^{1}H\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus. The UV-vis experiments were conducted on a Hitachi U-4100 absorption spectrophotometer. The fluorescent experiments were conducted on a Hitachi F-7000 fluorescence spectrophotometer. Quantum yields were determined using quinine sulfate at 365 nm (Φ_F = 56%). Scanning electron microscopy (SEM) was performed on a FEI Quanta 600 FEG. The size of polymers was measured using a Malvern ZS90 dynamic light scattering instrument with a He-Ne laser (633 nm) and 90° collecting optics. The data were analyzed using the Malvern Dispersion Technology Software 5.10.

2. Cell culture

Cisplatin-resistant non-small cell lung cancer (A549R) cells from American Type Culture Collection was cultured in Roswell Park Memorial Institute medium (RPMI 1640, Invitrogen, Carlsbad, CA) supplied with 10% fetal bovine serum (FBS, ExCell Bio, China), 1% penicillin/streptomycin (Sigma-Aldrich) at 37 °C with 5% CO_2. The cisplatin resistance of A549R cells was maintained by exposure of cells to stepwise increased concentration of cisplatin up to 4 μg/mL. The cisplatin-resistant cells were cultured without cisplatin for 3 weeks before experiments.

3. Confocal laser scanning microscopy observation of intracellular localization of polymers

The A549R cells were seeded at a density of 1×10^4 cells on a round cover slip (diameter 12 mm) in complete RPMI-1640 culture medium. After 24 h, they were treated with polymers at the concentration of 20 μg/mL for 6 h. Cells were then washed twice with cold PBS. The cell nucleus were stained by DAPI, the F-actin was stained by Alexa Fluor 568, and imaged with a Zeiss LSM 710 confocal microscope using a 63× objective. The data was analyzed using ImageJ 1.50b.

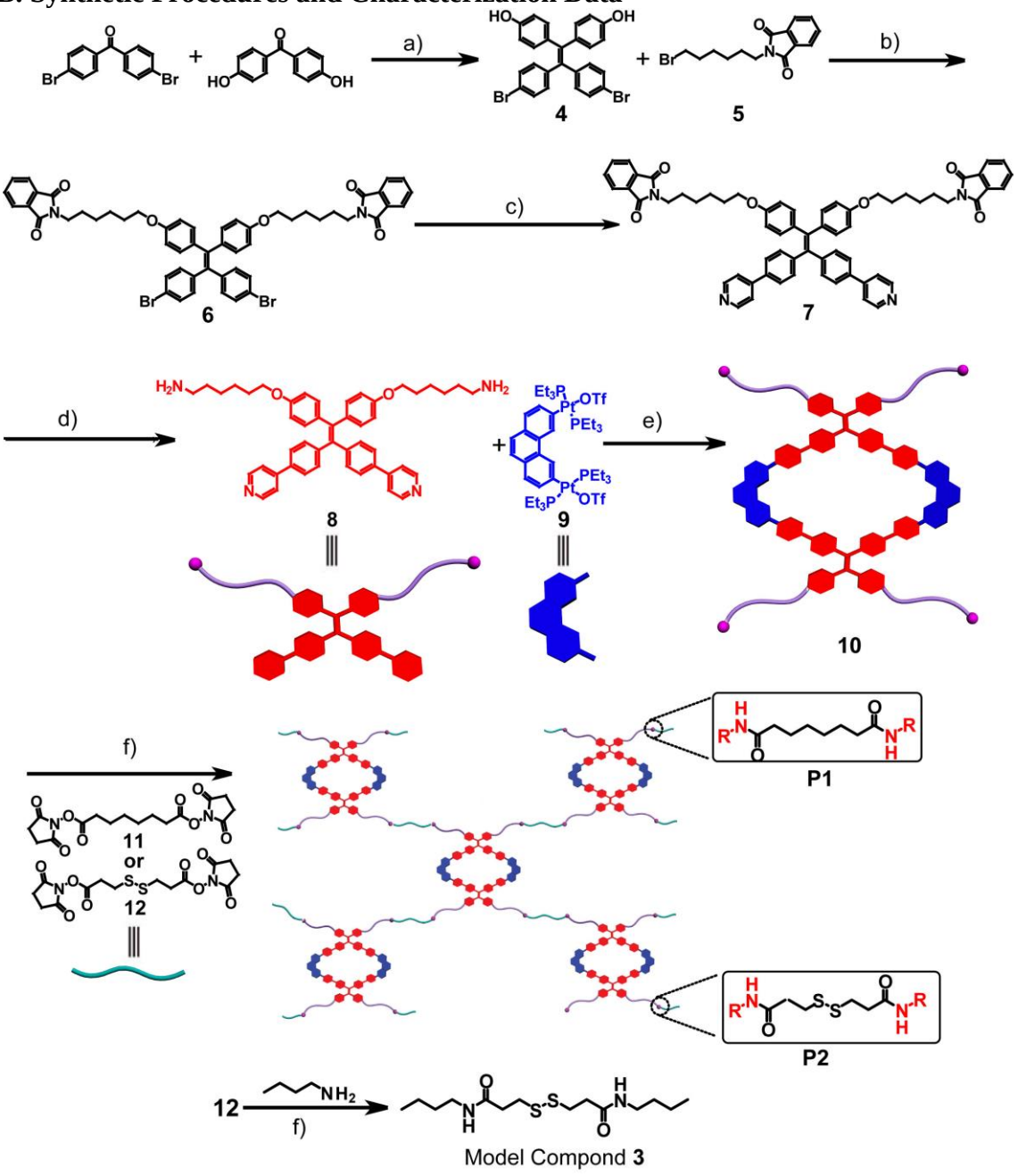
4. Flow cytometry analysis of cellular uptake of polymers

A549R cells were seeded at a density of 1×10^5 cells per well in 24-well tissue culture plates in RPMI 1640 medium. After 24 h, the cells were treated with polymers for 6 h at a concentration of 40 and 200 μg/mL. The cells were washed three times with cold PBS, and then collected by trypsinization. The cells were immediately analyzed *via* Fluorescence Activated Cell Sorter (FACS) Calibur flow cytometer (BD Biosciences, Bedford, MA). The data was analyzed using FlowJo Software 7.6.

5. Animals and tumor model

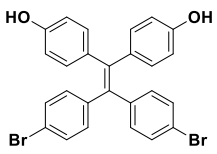
Female balb/c nude mice were obtained from Beijing HFK Bioscience Co., Ltd. All animals received care in compliace with the guidelines outlined in the Guide for the Care and Use of Laboratory Animals. The procedures were approved by the University of Science and Technology of China Animal Care and Use Committee. The MDA-MB-231 tumor model was prepared by inoculating 3×10^6 MDA-MB-231 cells into the subcutaneous fat pad at the second nipple of each Balb/c nude mouse (4 to 6 weeks). The tumors were allowed to grow to about 180 mm^3 before imaging. Animal images were collected on Xenogen IVIS Lumina In Vivo imaging instrument.

Section B. Synthetic Procedures and Characterization Data



Scheme S1. Synthesis of **P1**, **P2** and model compound **3**. Conditions: a) Zn, $TiCl_4$, THF, N_2, reflux, 24 h; 45%; b) K_2CO_3, CH_3CN, N_2, reflux, 12 h; 73%; c) Pydine-4-boronic acid, K_2CO_3, $Pd(PPh_3)_4$, TBAB, toluene/ethanol/water (4:1:1), reflux, 48 h; 45%; d) Hydrazine hydrate, CH_2Cl_2/CH_3OH (1:1), reflux, 2 h; 98%; e) CH_3OH, 50 °C; 100%; f) CH_3OH, room temperature, 24 h; 83-97%.

*1. Synthesis of tetraphenylene derivative **4***



4,4'-Dihydroxybenzophenone (1.06 g, 4.94 mmol), 4,4'-dibromobenzophenone (1.40 g, 4.12 mmol) and zinc dust (2.46 g, 37.5 mmol) were added to a three-neck flask, degassed and purged with nitrogen for three times. Then anhydrous THF (100 mL) was added under nitrogen and the whole system was cooled to 0 °C in an ice bath. $TiCl_4$ (1.5 mL, 13.7 mmol) was added slowly. After addition, the reaction mixture was heated at reflux for another 24 h. The system was cooled down and the mixture was quenched by adding 1 M HCl to adjust the pH into 1. The mixture was extracted by ethyl acetate (100 mL × 3), dried over anhydrous Na_2SO_4 and then the solvent was removed to give a crude product which was purified by flash column chromatography with ethyl acetate : hexane (1:5, v/v) as the eluent to give compound **4** as a light yellow solid (0.97 g, 45%). M. P. 80.7–81.3 °C. ^{1}H NMR (400 MHz, CD_3COCD_3, 295K): 8.34 (s, 2H), 7.30 (d, J = 8.5 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 6.63 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, CD_3COCD_3, 295K): 205.5, 156.4, 143.4, 142.5, 135.8, 134.5, 133.2, 132.5, 130.1, 119.6, 114.7. APCI-HR-MS: m/z 521.9681 [**4**]$^+$, calcd. for $[C_{26}H_{18}{}^{81}Br_2O_2]^+$, 521.9653.

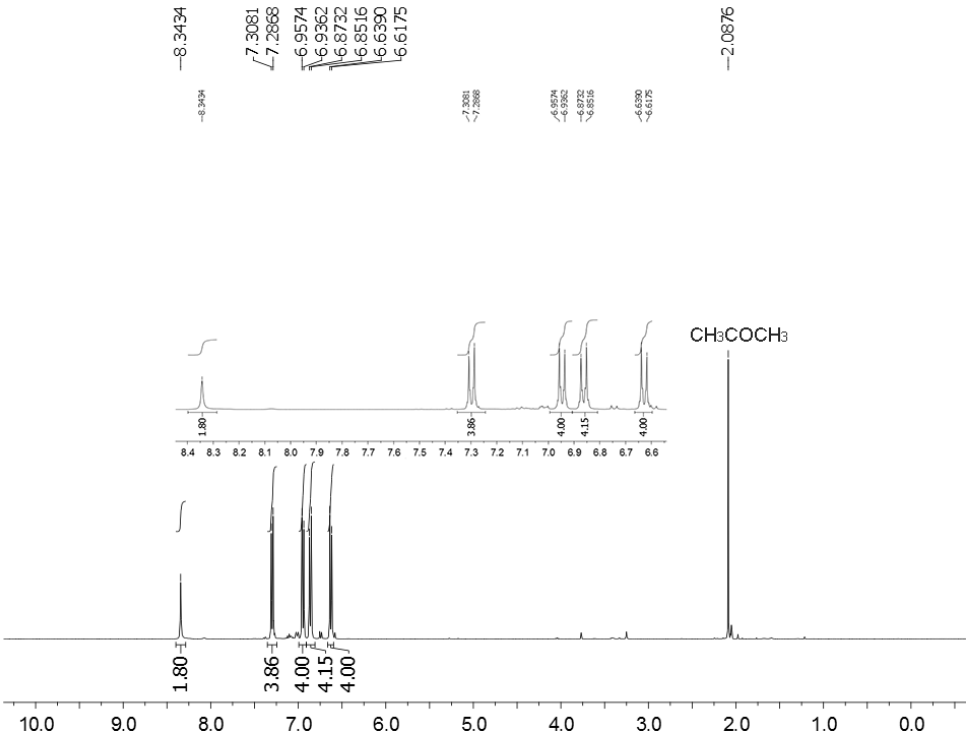


Figure S1. ^{1}H NMR spectrum (400 MHz, CD_3COCD_3, 295 K) recorded for **4**.

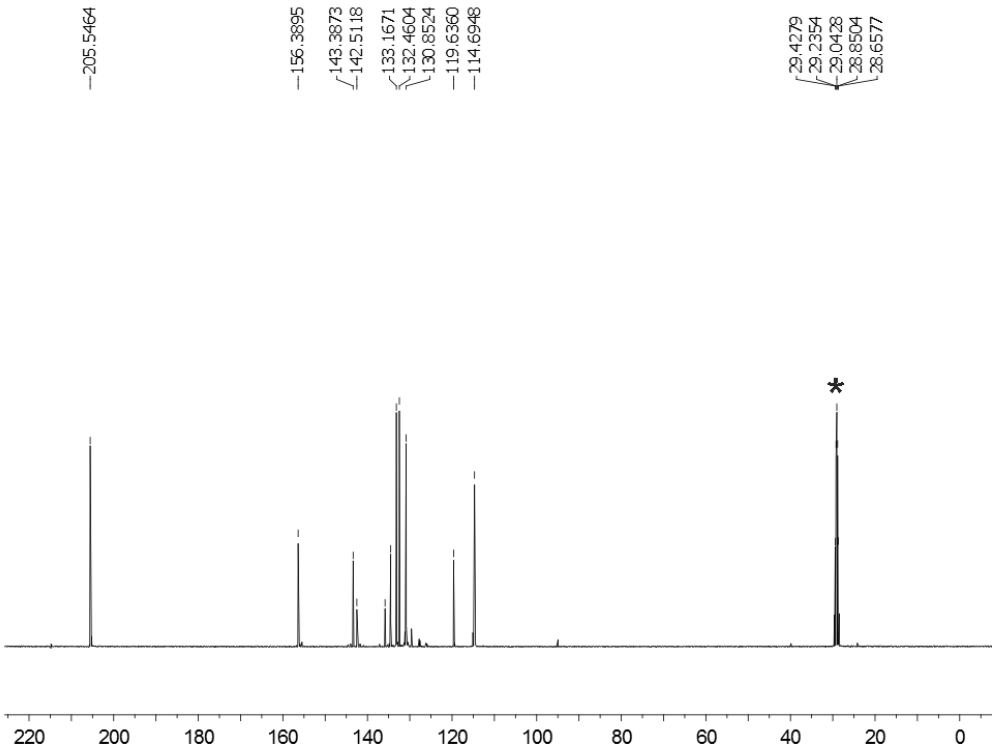


Figure S2. ^{13}C NMR spectrum (100 MHz, CD_3COCD_3, 295 K) recorded for **4** (The acetone peaks were marked with *).

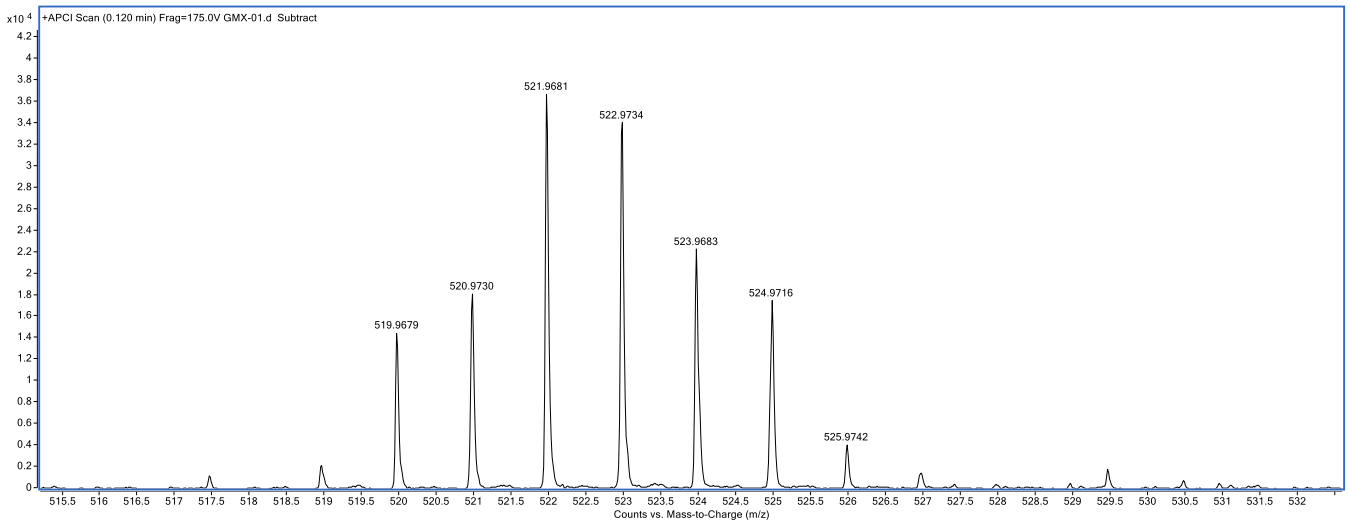
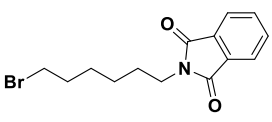


Figure S3. APCI-HR-MS spectrum of **4**.

*2. Synthesis of compound **5***



Compound **5** was synthesized according to literature procedure.[S1] The ^1H NMR of **5** matches well with the reported data. ^1H NMR (400 MHz, $CDCl_3$, 295K): 7.82–7.87 (m, 2H), 7.68–7.74 (m, 2H), 3.69 (t, *J* = 7.2 Hz, 2H), 3.39 (t, *J* = 7.2 Hz, 2H), 1.86 (p, *J* = 7.2 Hz, 2H), 1.70 (p, *J* = 7.2 Hz, 2H), 1.49 (p, *J* = 7.2 Hz, 2H), 1.37 (p, *J* = 7.2 Hz, 2H).

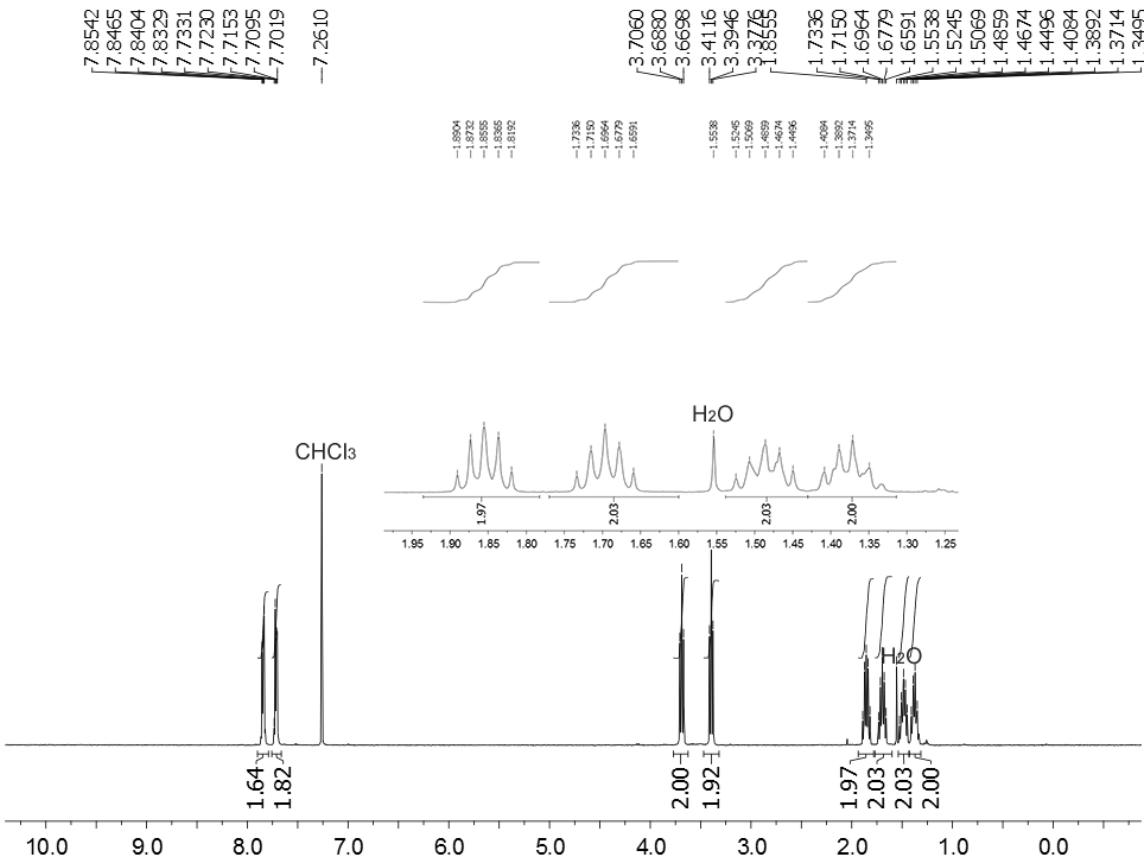
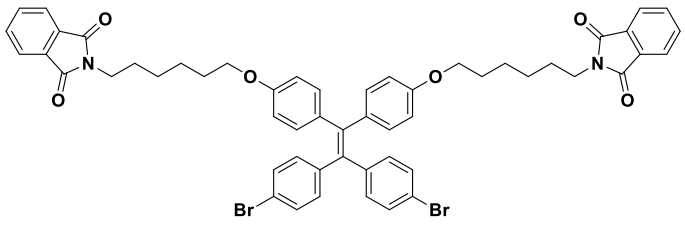


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 295 K) recorded for **5**.

*3. Synthesis of compound **6***



Compound **4** (0.82 g, 1.57 mmol), **5** (1.46 g, 4.71 mmol) and K_2CO_3 (1.38 g, 10 mmol) were added in CH_3CN (100 mL) and the whole system was heated at reflux for 12 h under nitrogen. After cooling, the mixture was filtered and the solvent was removed to give a crude product which was purified by flash column chromatography with ethyl acetate : hexane (1:5, *v*/*v*) as the eluent to give compound **6** as a light yellow solid (1.13 g, 73%). M. P. 49.3–49.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 295K): 7.82–7.85 (m, 4H), 7.69–7.72 (m, 4H), 7.08 (d, J = 8.0 Hz, 4H), 7.01(d, J = 8.0 Hz, 4H), 6.89 (d, J = 8.8 Hz, 4H), 6.59 (d, J = 8.8 Hz, 4H), 3.85 (t, J = 6.2 Hz, 4H), 3.69 (t, J = 7.1 Hz, 4H), 1.66–1.78 (m, 8H), 1.36–1.53 (m, 8H). ^{13}C NMR (75 MHz, CDCl3, 295K): 168.7, 158.1, 143.1, 141.8, 136.5, 135.6, 134.1, 133.2, 132.7, 132.4, 131.2, 123.4, 120.4, 114.9, 113.9, 67.8, 38.2, 29.4, 28.8, 26.9, 25.9. LRESI-MS: *m*/*z* 1003.9 [**6** + Na]$^{+}$, HR-MS: *m*/*z* 1001.1793 ([**6** + Na]$^{+}$, calcd. for $[C_{54}H_{48}{}^{79}Br_2N_2O_6Na]^{+}$, 1001.1777.

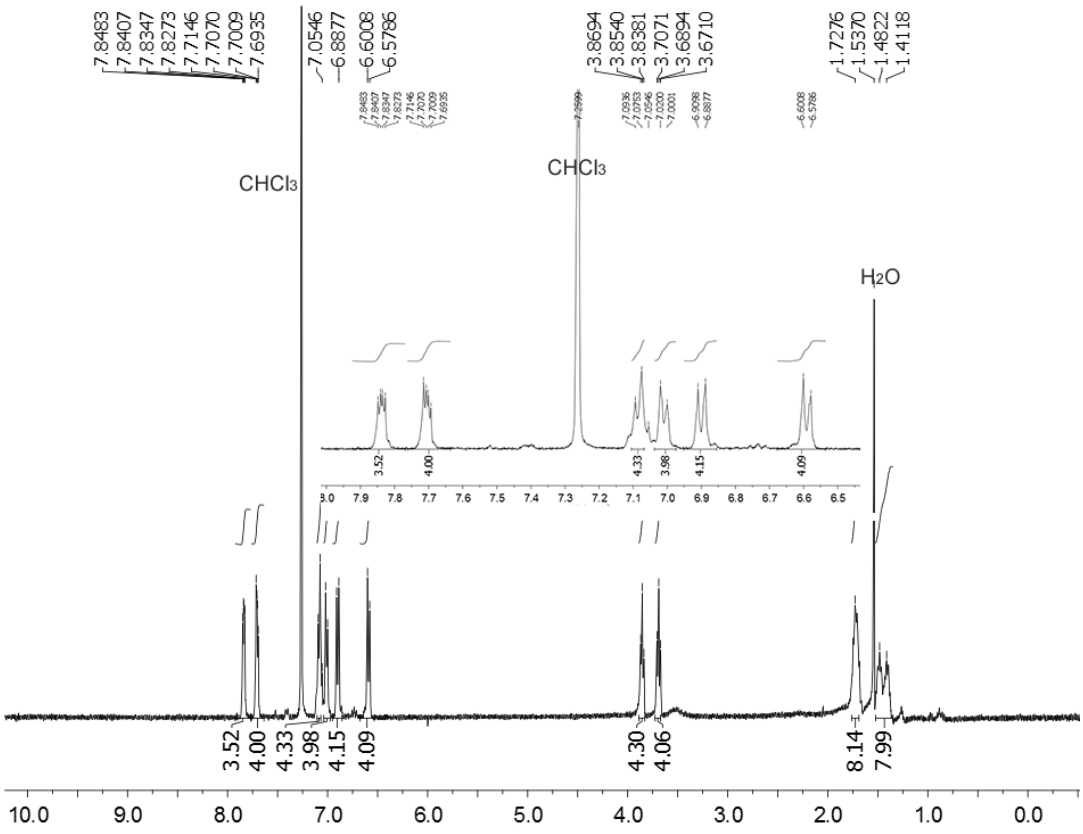


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 295 K) recorded for **6**.

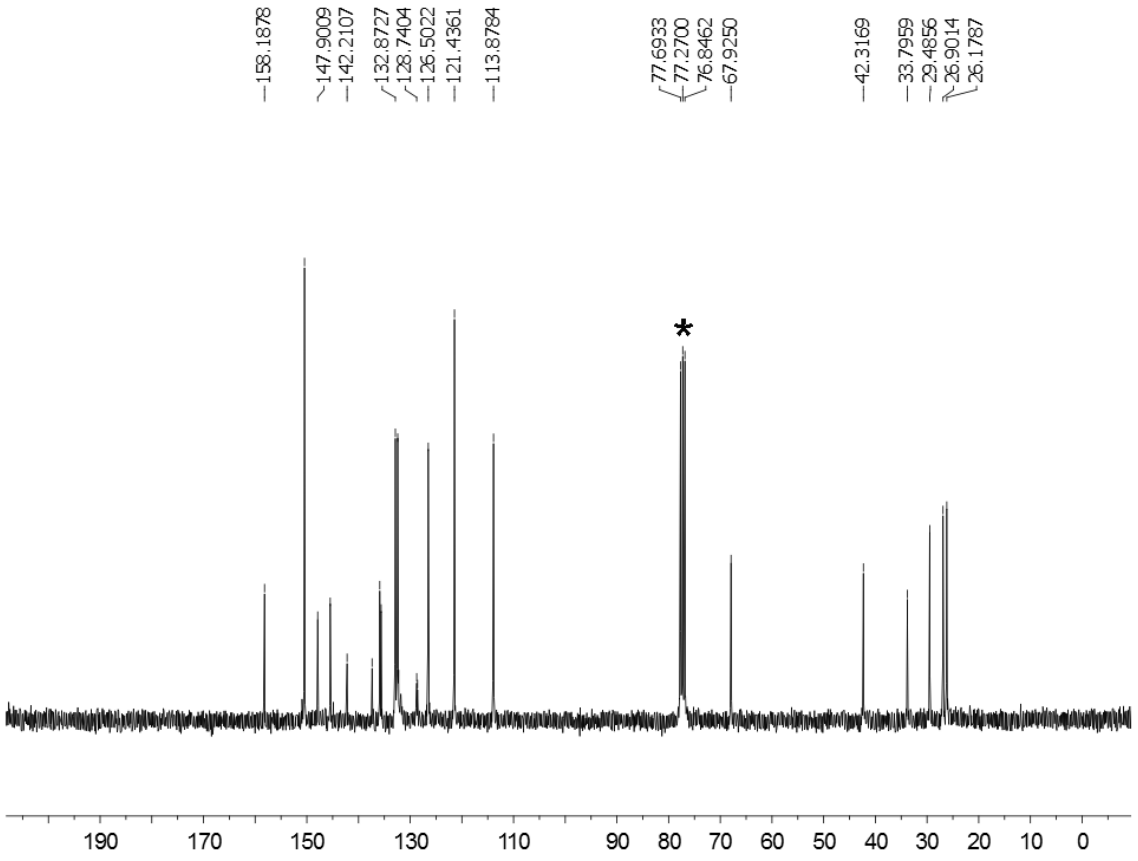


Figure S6. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 295 K) recorded for **6** (The chloroform peaks were marked with *).

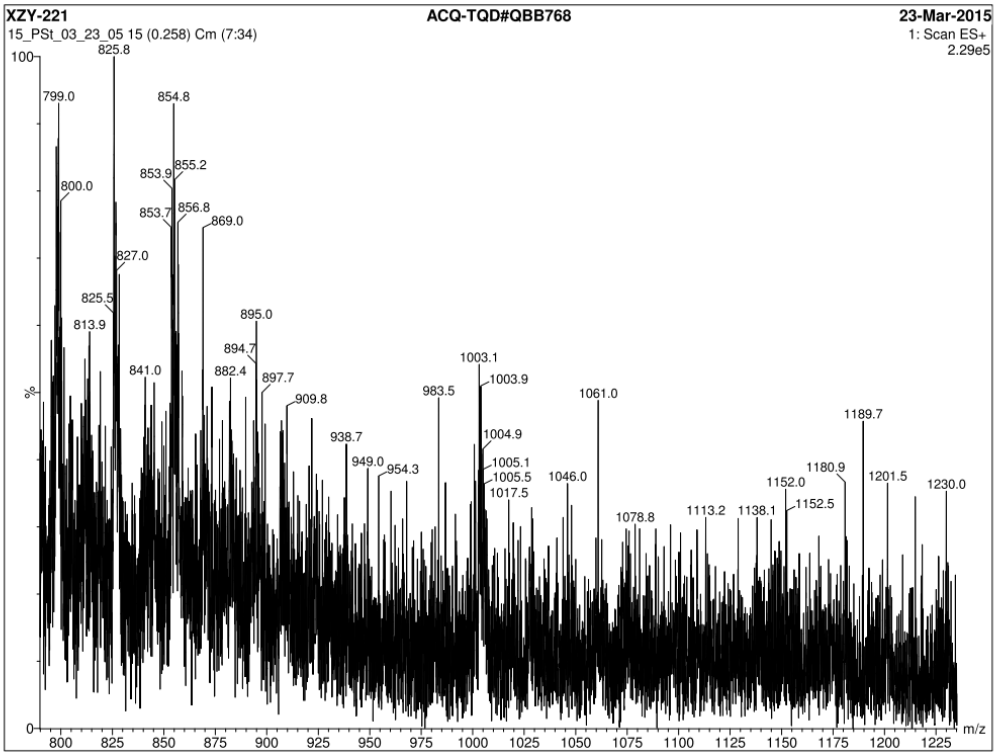
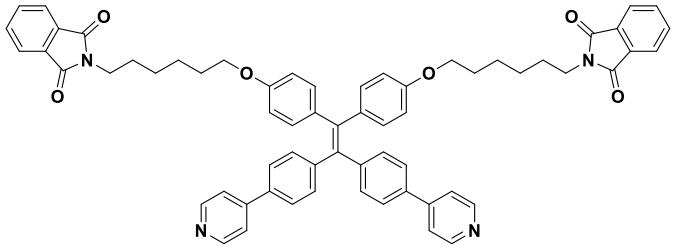


Figure S7. Electrospray ionization mass spectrum of **6**.

*4. Synthesis of compound **7***



To **6** (1.13 g, 1.15 mmol), 4-pyridylboronic acid (0.85 g, 6.90 mmol) and tetrabutylammonium bromide (TBAB) (38 mg, 0.12 mmol) in toluene (60 mL), aqueous K_2CO_3 (1.90 g, 13.8 mmol) solution (15 mL) and ethanol (15 mL) were added. Then $Pd(PPh_3)_4$ (138 mg, 0.12 mmol) was added and the reaction mixture was stirred at 80 °C for 48 h under nitrogen atmosphere. After cooling to room temperature, the product was concentrated and purified by flash column chromatography with CH_2Cl_2:CH_3OH (50:1, v/v) as the eluent to afford compound **7** (0.51 g, 45%) as pale yellow powder. M. P. 75.5–76.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 295K): 8.77 (d, *J* = 4.2 Hz, 4H), 8.09 (d, *J* = 4.2 Hz, 4H), 7.83 (d, *J* = 4.0 Hz, 4H), 7.72(d, *J* = 4.0 Hz, 4H), 7.55–7.63 (m, 8H), 7.19 (d, *J* = 8.8 Hz, 4H), 6.65 (d, *J* = 8.8 Hz, 4H), 3.93 (t, *J* = 6.6 Hz, 4H), 3.69 (t, *J* = 5.8 Hz, 4H), 1.65–1.83 (m, 12H), 1.35–1.46 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, 295K): 168.7, 158.2, 148.3, 142.4, 132.9, 132.3, 126.6, 121.5, 113.9, 67.8, 38.1, 29.3, 28.7, 26.8, 25.9. LRESI-MS: *m*/*z* 977.3 [**7** + H]$^+$, 999.5 [**7** + Na]$^+$. HR-MS: *m*/*z* 999.4104 ([**7** + Na]$^+$, calcd. for $[C_{64}H_{56}N_4O_6Na]^+$, 999.4098.

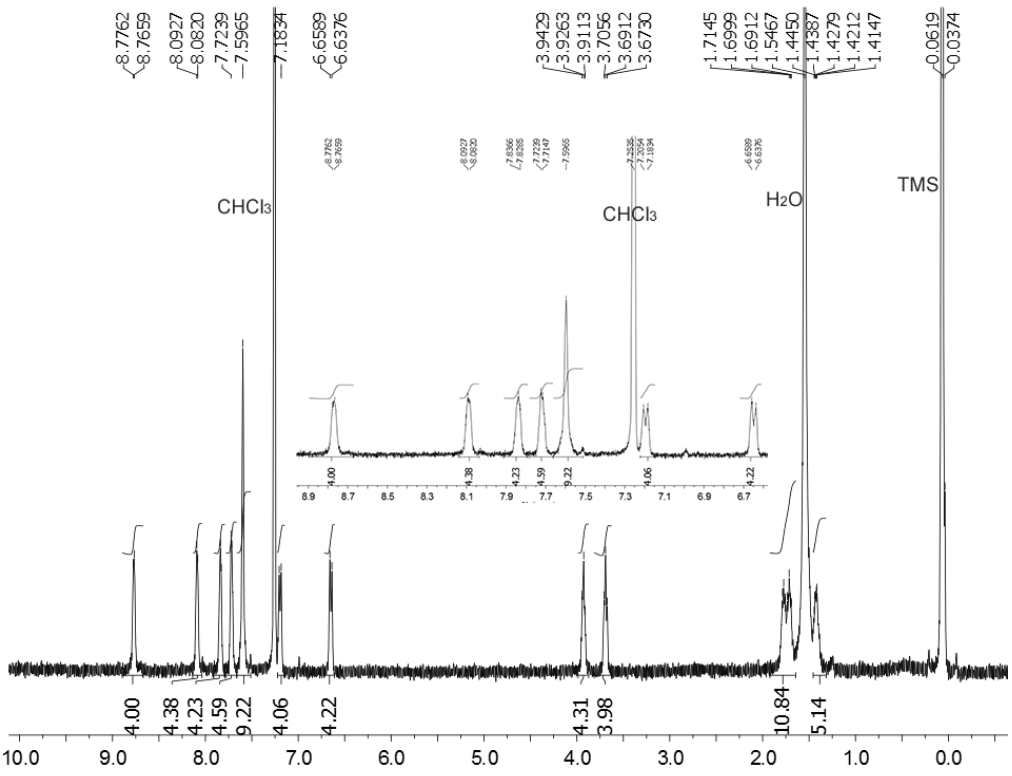


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 295 K) recorded for **7**.

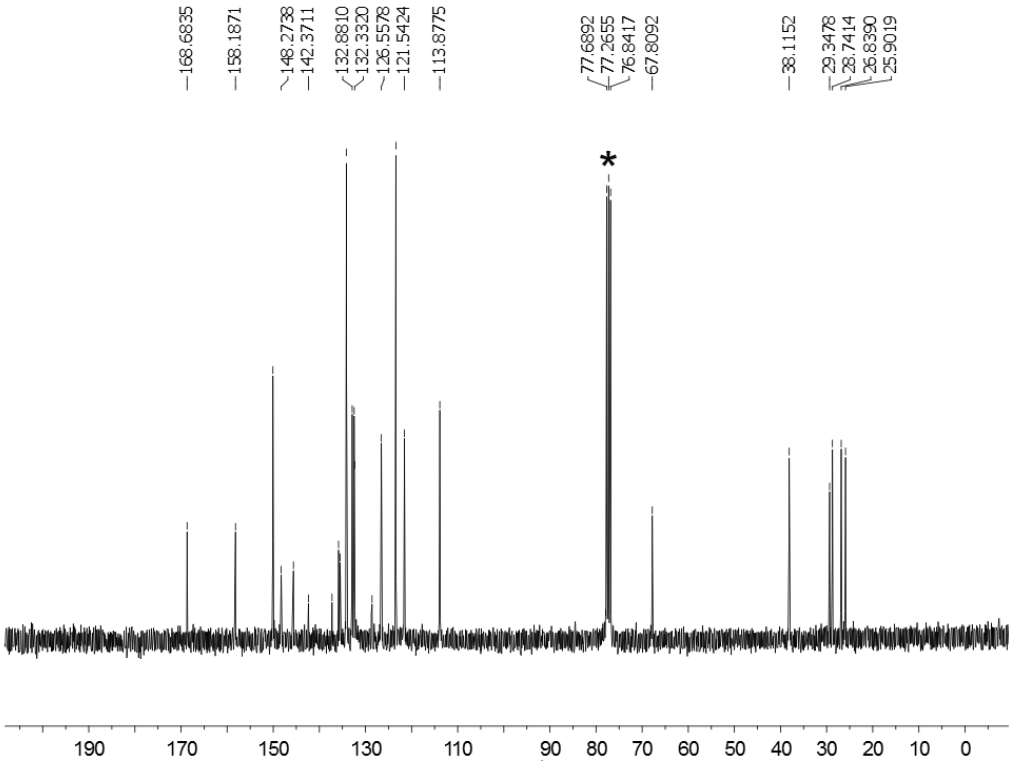


Figure S9. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 295 K) recorded for **7** (The chloroform peaks were marked with *).

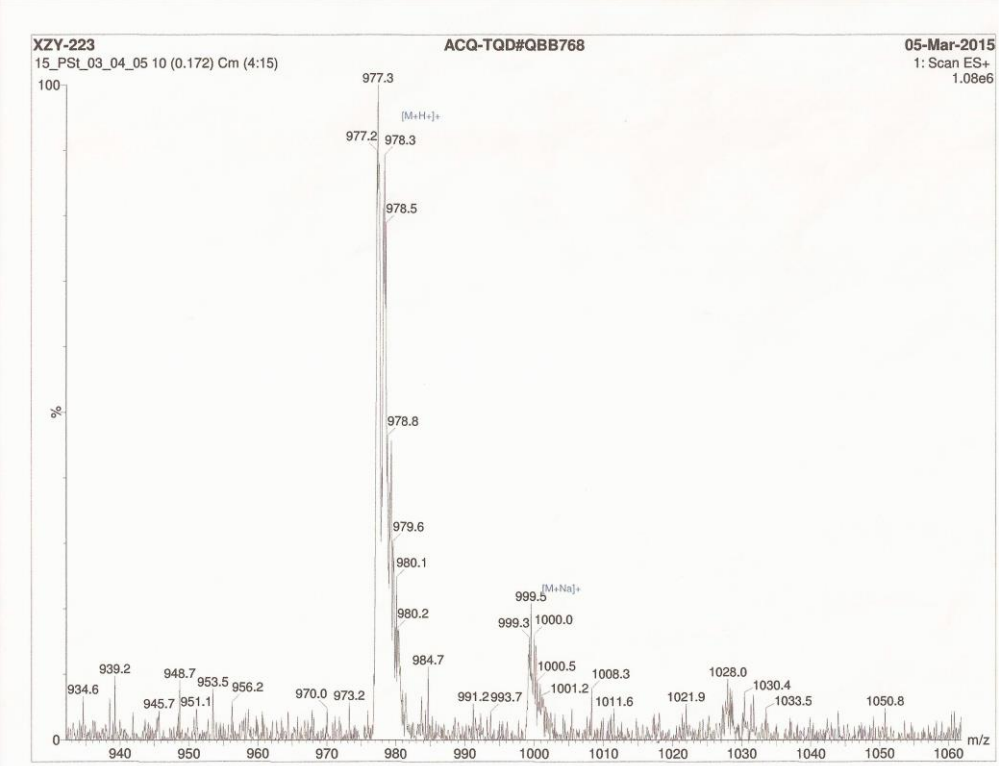
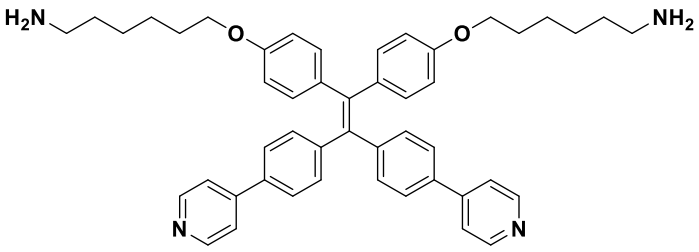


Figure S10. Electrospray ionization mass spectrum of **7**.

*5. Synthesis of compound **8***



Compound **7** (480 mg, 0.49 mmol) was dissolved in CH_2Cl_2/CH_3OH (40 mL, 1:1, *v*/*v*) and then 80% hydrazine hydrate aquous solution was added. The whole system was stirred at reflux for 2 h. After cooling, the solvent was removed and the residue was dissolved in CH_2Cl_2 (10 mL). Hexane (100 mL) was added into the solution to give a precipitate which was filtered and dried to give compound **4** as a yellow solid (345 mg, 98%). M. P. 59.8–60.9 °C. ^{1}H NMR (400 MHz, CD_3OD, 295 K): 8.53 (d, *J* = 4.6 Hz, 4H), 7.67 (d, *J* = 4.6 Hz, 4H), 7.57 (d, *J* = 8.2 Hz, 4H), 7.18 (d, *J* = 8.2 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 4H), 6.68 (d, *J* = 8.8 Hz, 4H), 3.90 (t, *J* = 5.6 Hz, 4H), 2.65 (t, *J* = 7.0 Hz, 4H), 1.68–1.80 (m, 4H), 1.32–1.56 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, 295K): 158.2, 147.9, 142.2, 132.9, 128.7, 126.5, 121.4, 113.9, 67.9, 42.3, 33.8, 29.5, 26.9, 26.2. LRESI-MS: *m*/*z* 717.4 [**8** + H]$^+$. HR-MS: *m*/*z* 717.4166 ([**8** + H]$^+$, calcd. for $[C_{48}H_{53}N_4O_2]^+$, 717.4169.

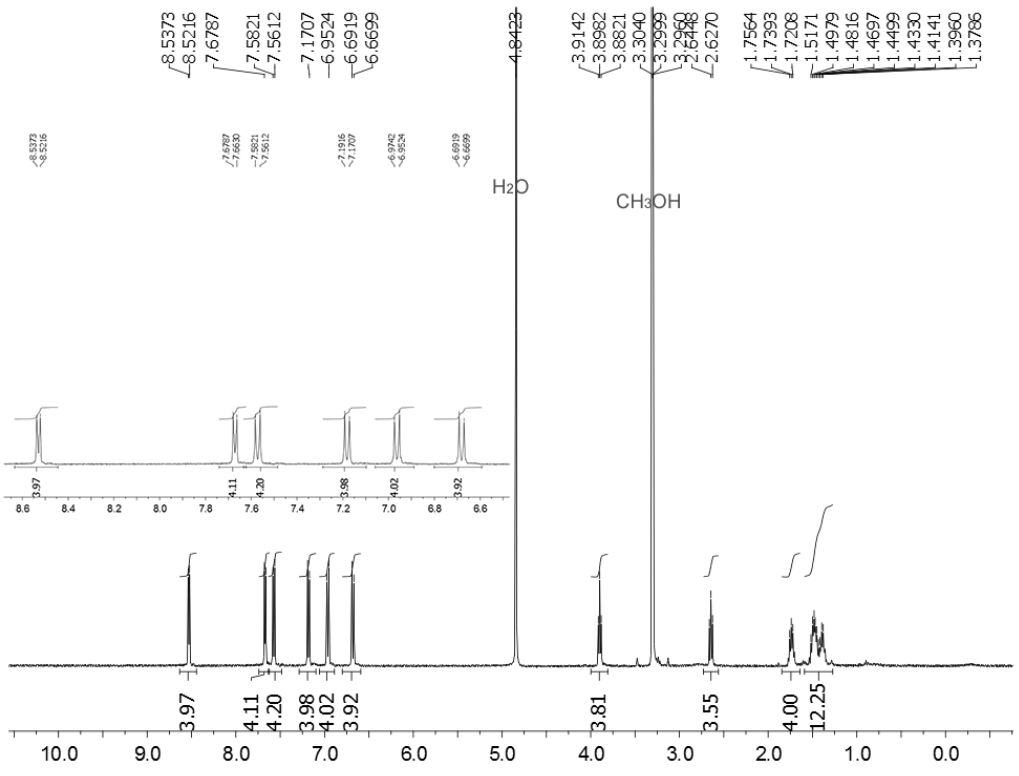


Figure S11. ^{1}H NMR spectrum (400 MHz, CD_3OD, 295 K) recorded for **8**.

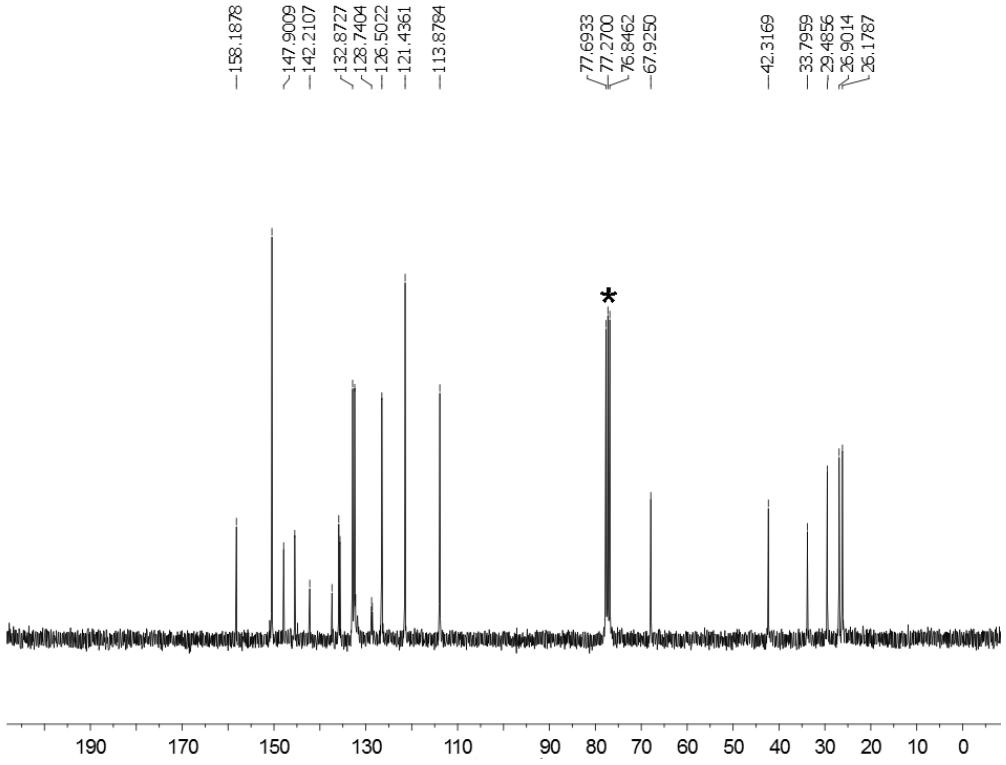


Figure S12. ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 295 K) recorded for **8** (The chloroform peaks were marked with *).

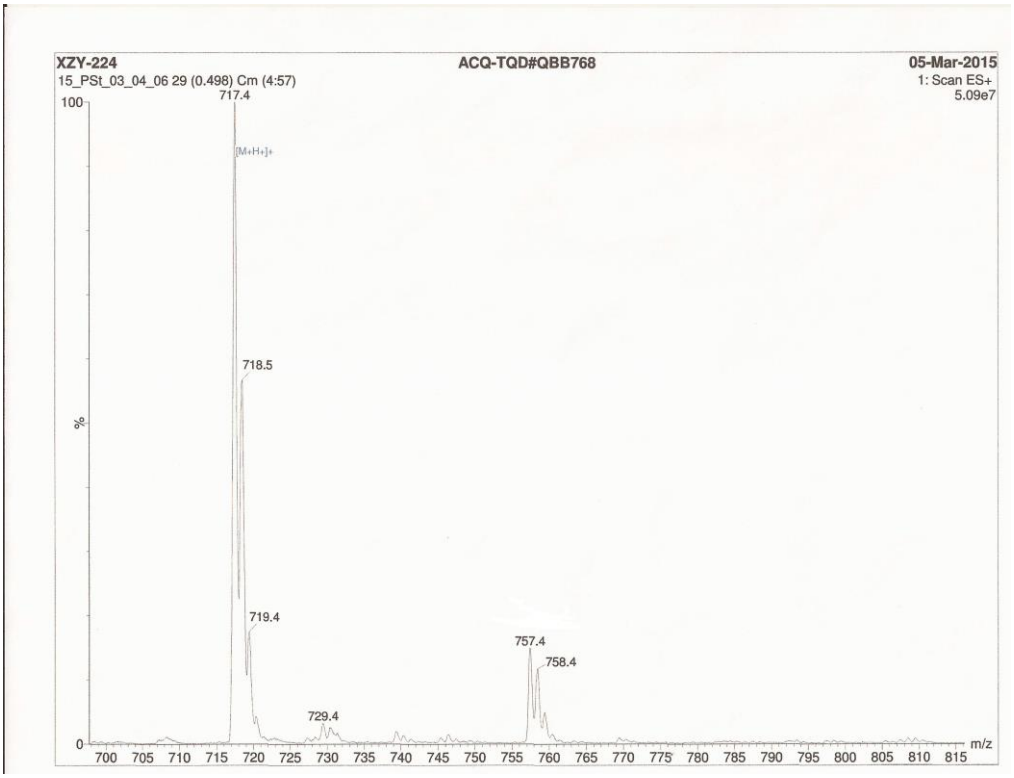
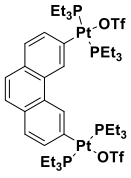


Figure S13. Electrospray ionization mass spectrum of **8**.

*6. Synthesis of compound **9***



Compound **9** was synthesized according to literature procedure.[S2] The ^{1}H NMR and ^{31}P NMR of **9** matches well with the reported data.

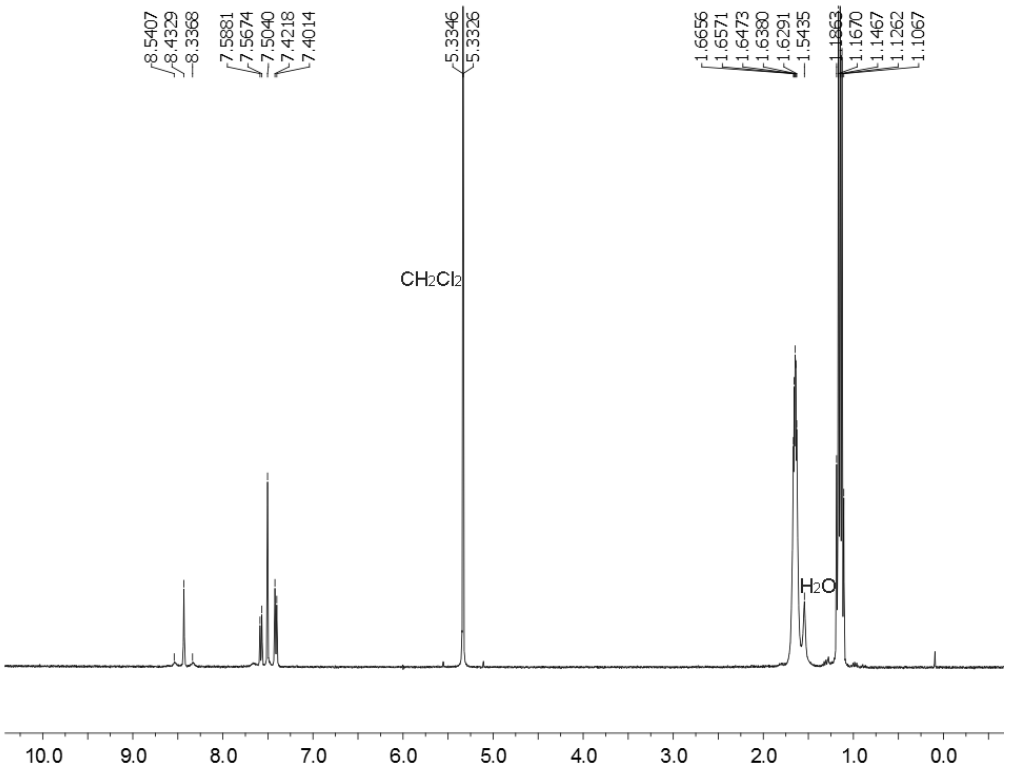


Figure S14. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 295 K) recorded for **9**.

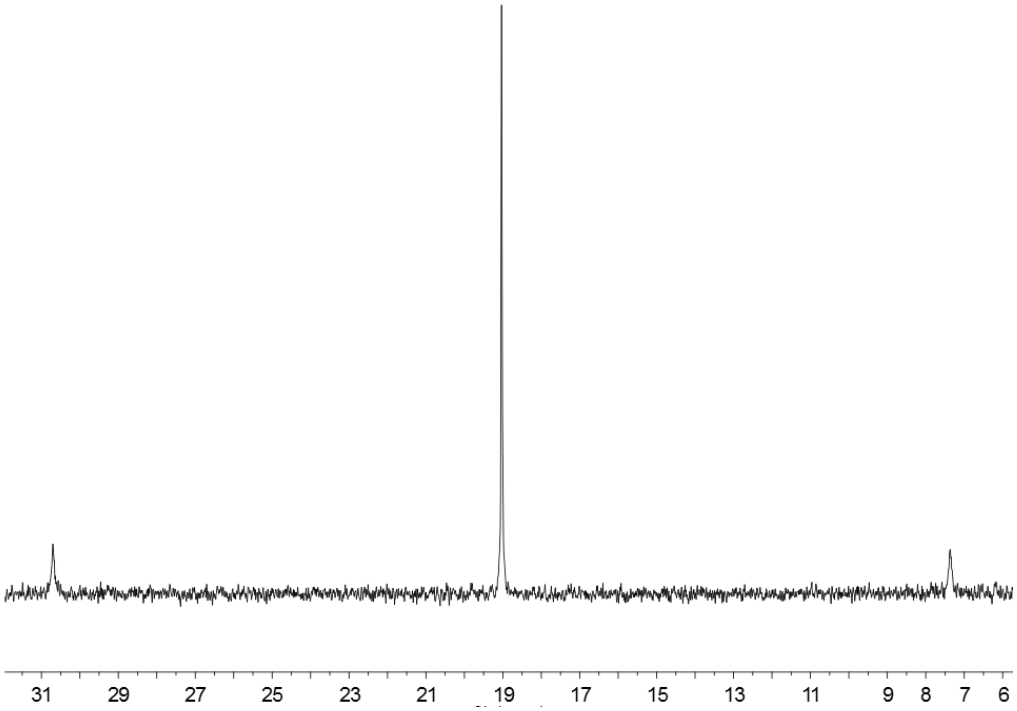
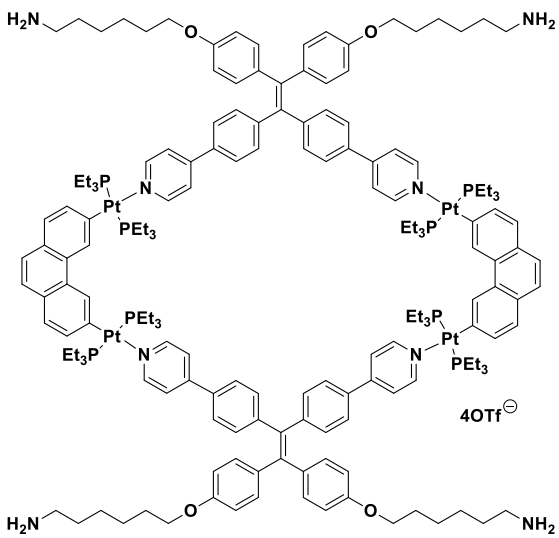


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2, room temperature, 121.4 MHz) recorded for **9**.

*7. Synthesis of rhomboidal metallacycle **10***



Compounds **8** (7.16 mg, 0.01 mmol) and **9** (13.37 mg, 0.01 mmol) were added in methanol (5 mL) and heated at 50 °C for 24 h. After cooling, the solvent was removed to give compound **10** as a yellow solid (20.5 mg, 100%). ^{1}H NMR (400 MHz, CD_3OD, 295K): 8.87 (m, 8H), 8.46–8.75 (m, 4H), 7.99 (m, 8H), 7.45–7.85 (m, 20H), 7.28 (d, J = 8.2 Hz, 8H), 7.02 (d, J = 8.8 Hz, 8H), 6.74 (d, J = 8.8 Hz, 8H), 3.95 (t, J = 5.6 Hz, 8H), 2.75 (t, J = 7.0 Hz, 4H), 0.90–1.90 (m, 152H). $^{31}P\{^{1}H\}$ NMR (CD_3OD, room temperature, 121.4 MHz) δ (ppm): 13.92 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt-P}$ = 2661.8 Hz). ESI-TOF-MS: m/z 877.3635 ([**10** – 4OTf]$^{4+}$, 1220.1737 ([**10** – 3OTf]$^{3+}$, 1904.7172 ([**10** – 2OTf]$^{2+}$.

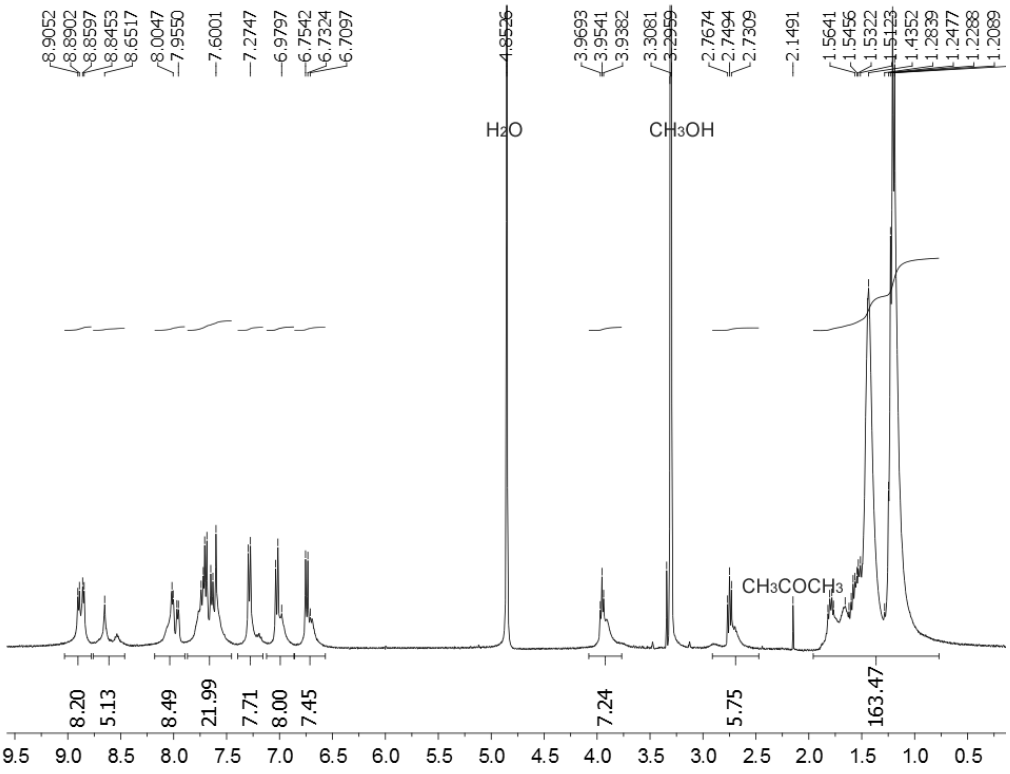


Figure S16. ^{1}H NMR spectrum (400 MHz, CD_3OD, 295 K) recorded for **10**.

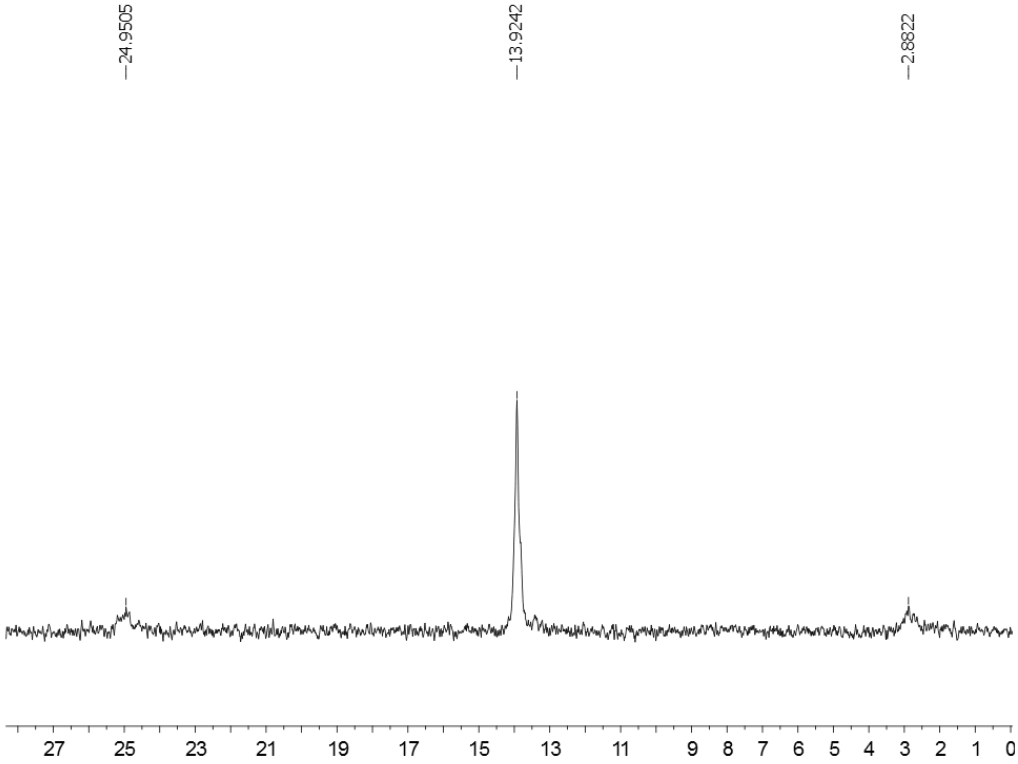


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum (CD_3OD, room temperature, 121.4 MHz) recorded for **10**.

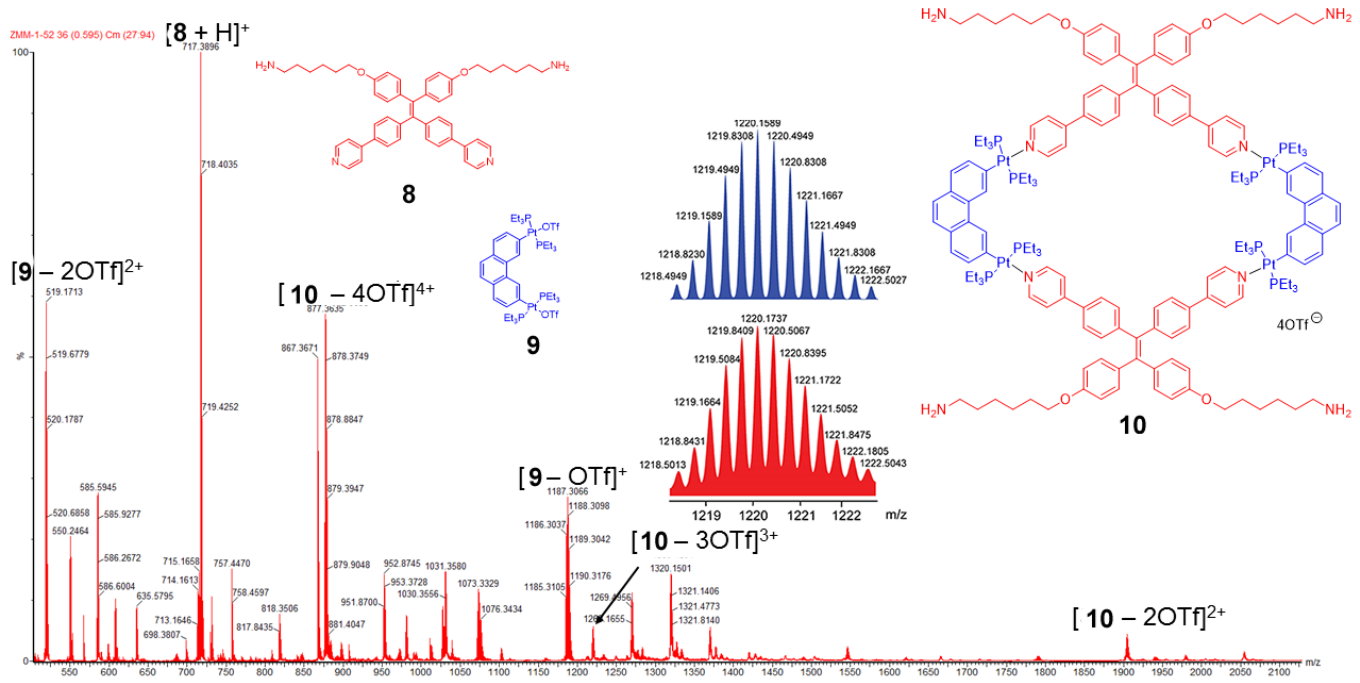
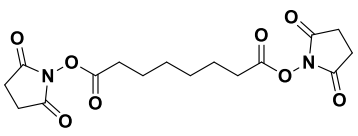


Figure S18. ESI-TOF-MS of **10** and experimental (red) and calculated (blue) spectra of [**10** – 3OTf]$^{3+}$.

*8. Synthesis of Compound **11***



Compound **11** was synthesized according to literature procedure.[S3] The ^{1}H NMR of **11** matches well with the reported data.

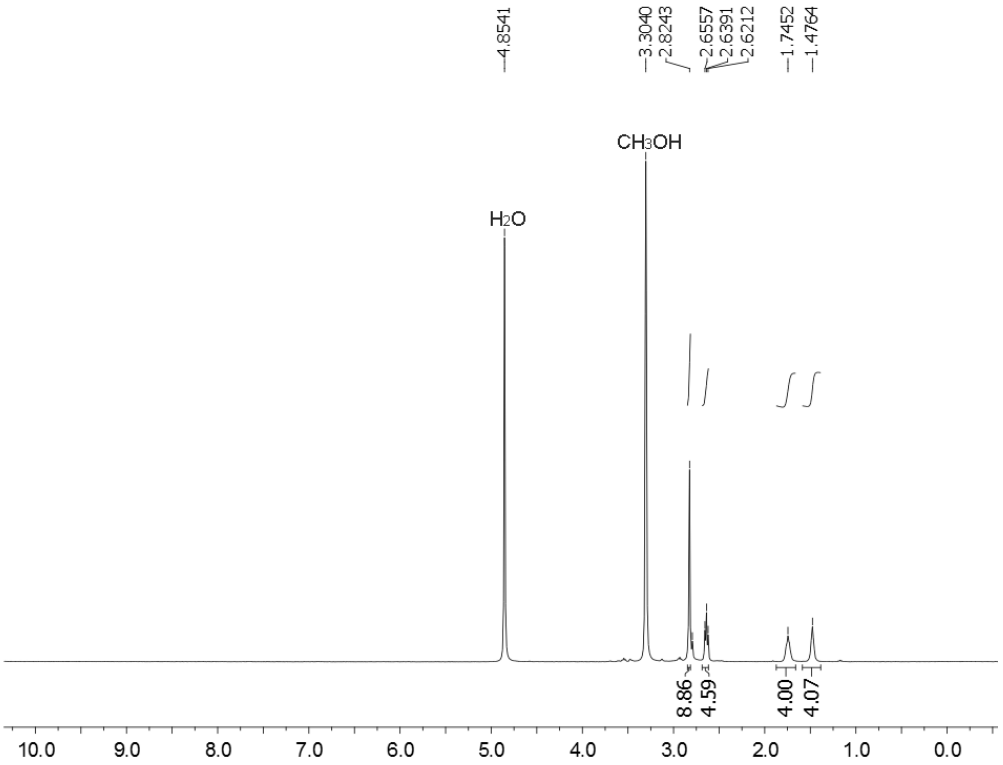
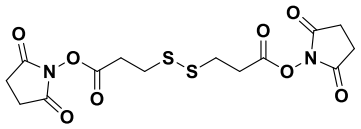


Figure S19. ^{1}H NMR spectrum (400 MHz, CD_3OD, 295 K) recorded for **11**.

*9. Synthesis of Compound **12***



Compound **12** was synthesized according to literature procedure.[S3] The ^{1}H NMR of **12** matches well with the reported data.

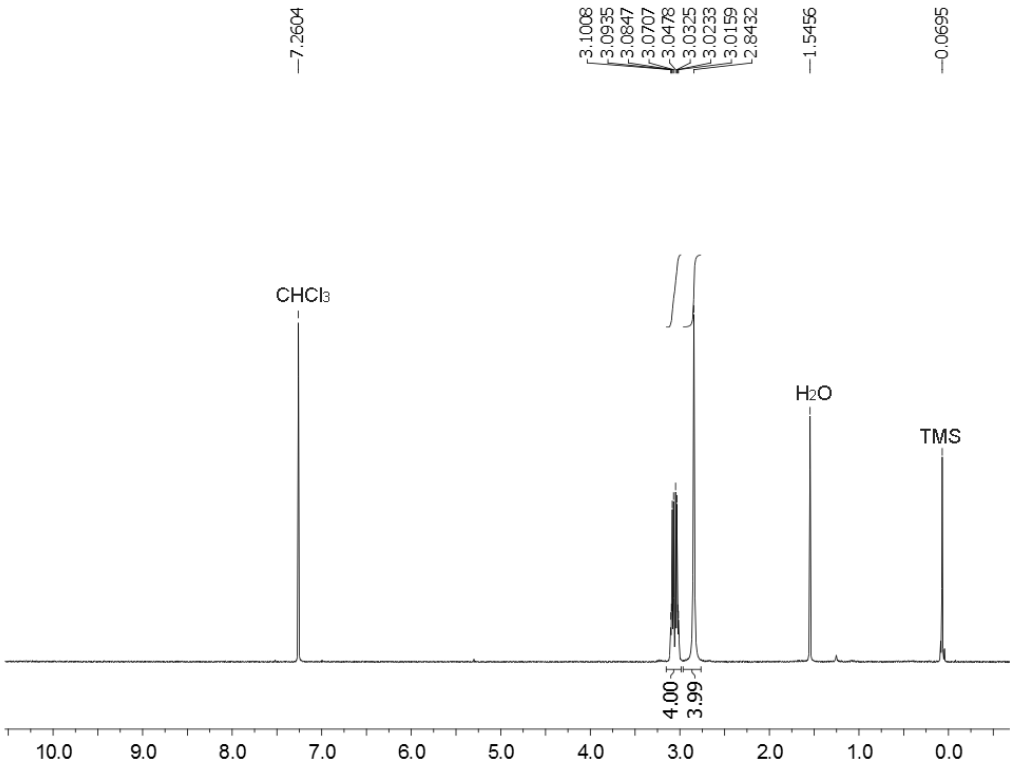
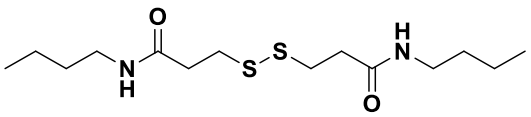


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$, 295 K) spectrum recorded for **12**.

*10. Synthesis of Model Compound **3***



Compound **12** (40.4 mg, 0.1 mmol) and butylamine (14.6 mg, 0.2 mmol) were added in methanol (20 mL) and the whole mixture was stirred at room temperature overnight. After that, the solvent was removed to give a crude product which was purified by flash colum chromatography with CH_2Cl_2:CH_3OH (10:1, v/v) as the eluent to afford compound **3** (31 mg, 97%) as a white solid. M. P.: 40.7–41.3 °C. ^{1}H NMR (400 MHz, CD_3OD, 295K): 3.15 (t, J = 7.2 Hz, 4H), 2.46 (t, J = 7.2 Hz, 4H), 2.35 (t, J = 7.2 Hz, 4H), 1.42–1.52 (m, 4H), 1.28–1.40 (m, 4H), 0.93 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CD_3OD, 295K): 174.1, 171.2, 40.2, 32.5, 32.0, 29.3, 26.3, 21.1, 14.1. HR-MS: *m/z* 343.1490 ([**12** + Na]$^+$, calcd. for $[C_{14}H_{28}N_2NaO_2S_2]^+$, 343.1512.

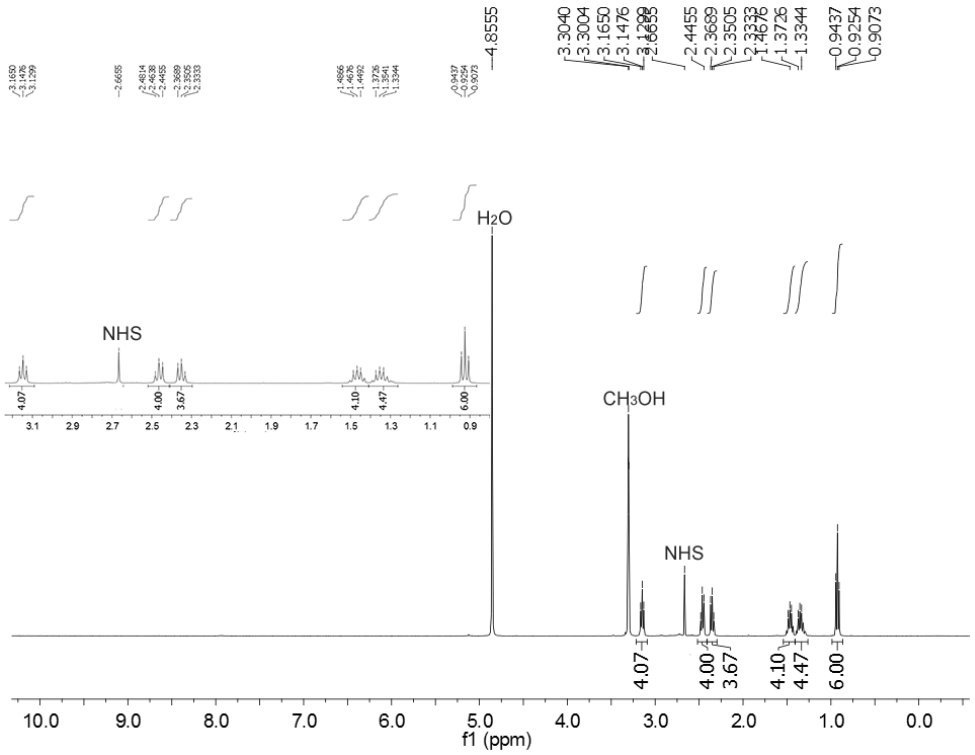


Figure S21. ^{1}H NMR spectrum (400 MHz, CD_3OD, 295 K) recorded for **3**.

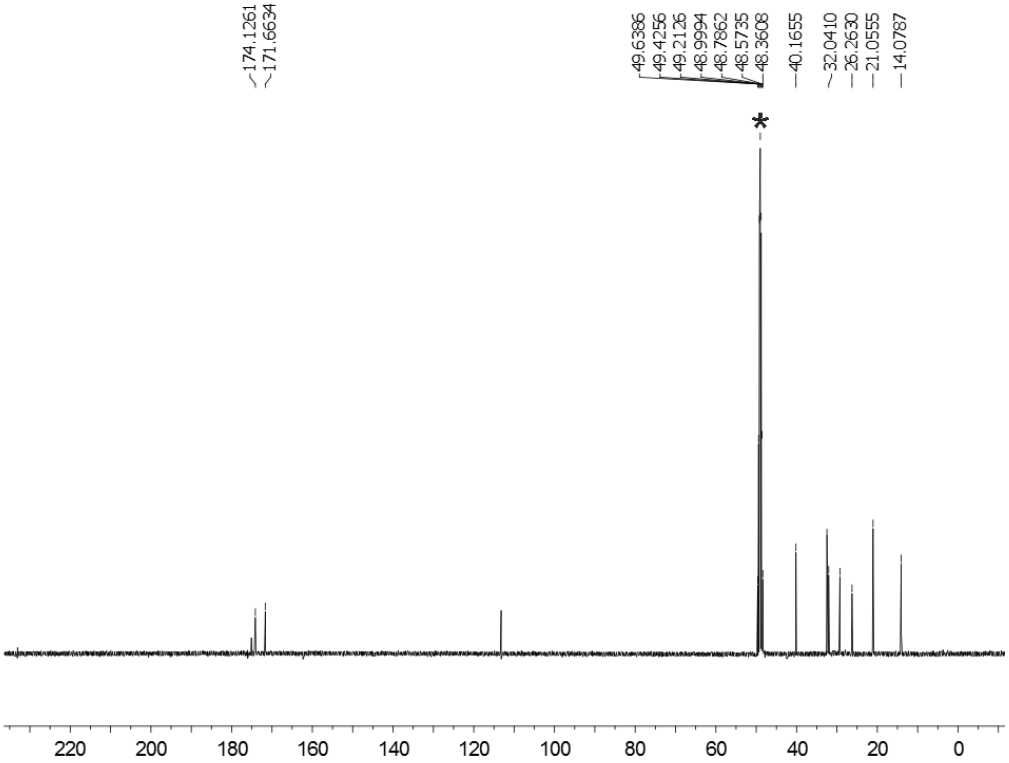


Figure S22. ^{13}C NMR spectrum (100 MHz, CD_3OD, 295 K) recorded for **3** (The methanol peaks were marked with *).

*11. Synthesis of **P1***

Compound **10** (39.6 mg, 0.01 mmol) and **11** (7.37 mg, 0.02 mmol) were added in methanol (40 mL) and the whole mixture was stirred at room temperature for 24 h. After that, the solvent was removed to give a crude product which was dialysised against methanol for another 24 h to give **P1** (35.2 mg, 83%) as a yellow powder. ^{1}H NMR (400 MHz, CD_3OD, 295K): 8.87 (m, 8H), 8.46–8.75 (m, 4H), 7.99 (m, 8H), 7.45–7.85 (m, 20H), 7.28 (d, J = 8.2 Hz, 8H), 7.02 (d, J = 8.8 Hz, 8H), 6.74 (d, J = 8.8 Hz, 8H), 4.00 (t, J = 5.6 Hz, 8H), 3.18 (t, J = 7.0 Hz, 8H), 2.13 (t, J = 7.0 Hz, 8H), 0.90–1.90 (m, 168H). ^{31}P{^{1}H} NMR (CD_3OD, room temperature, 121.4 MHz) δ (ppm): 13.27 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt-P}$ = 2693.9 Hz).

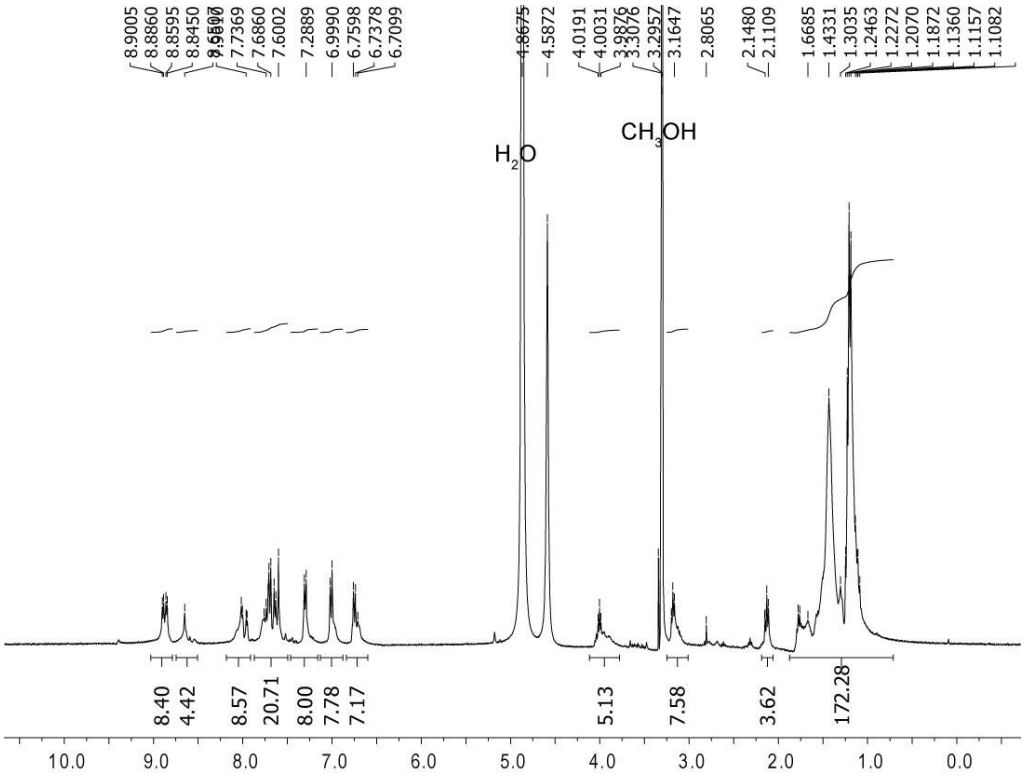


Figure S23. ^{1}H NMR spectrum (400 MHz, CD_3OD, 295 K) recorded for **P1**.

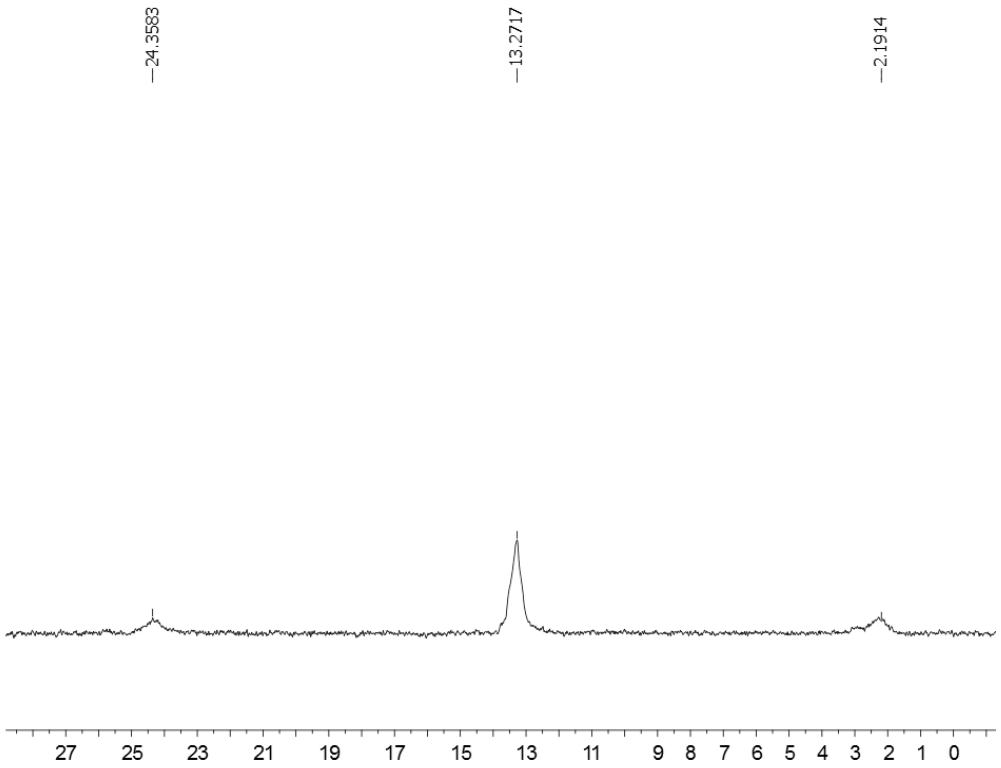


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum (CD_3OD, room temperature, 121.4 MHz) recorded for **P1**.

*12. Synthesis of **P2***

Compound **10** (39.6 mg, 0.01 mmol) and **12** (8.1 mg, 0.02 mmol) were added in methanol (40 mL) and the whole mixture was stirred at room temperature for 24 h. After that, the solvent was removed to give a crude product which was dialysised against methanol for another 24 h to give **P2** (37.1 mg, 86%) as a yellow powder. ^{1}H NMR (400 MHz, CD_3OD, 295K): 8.87 (m, 8H), 8.46–8.75 (m, 4H), 7.99 (m, 8H), 7.45–7.85 (m, 20H), 7.28 (d, J = 8.2 Hz, 8H), 7.02 (d, J = 8.8 Hz, 8H), 6.74 (d, J = 8.8 Hz, 8H), 4.01 (t, J = 5.6 Hz, 8H), 3.21 (t, J = 7.0 Hz, 8H), 2.91 (t, J = 7.2 Hz, 8H), 2.55 (t, J = 7.2 Hz, 8H), 1.78 (t, J = 6.6 Hz, 8H), 0.90–1.60 (m, 152H). $^{31}P\{^{1}H\}$ NMR (CD_3OD, room temperature, 121.4 MHz) δ (ppm): 13.33 ppm (s, ^{195}Pt satellites, $^{1}J_{Pt-P}$ = 2698.1 Hz).

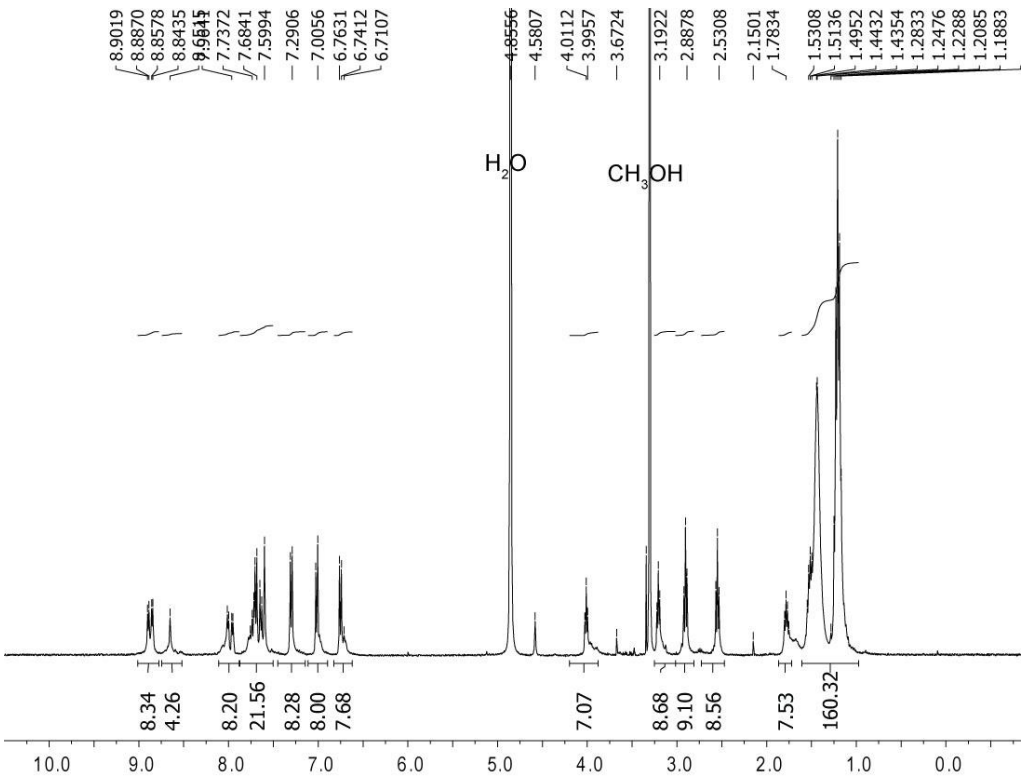


Figure S25. ^{1}H NMR spectrum (400 MHz, CD_3OD, 295 K) recorded for **P2**.

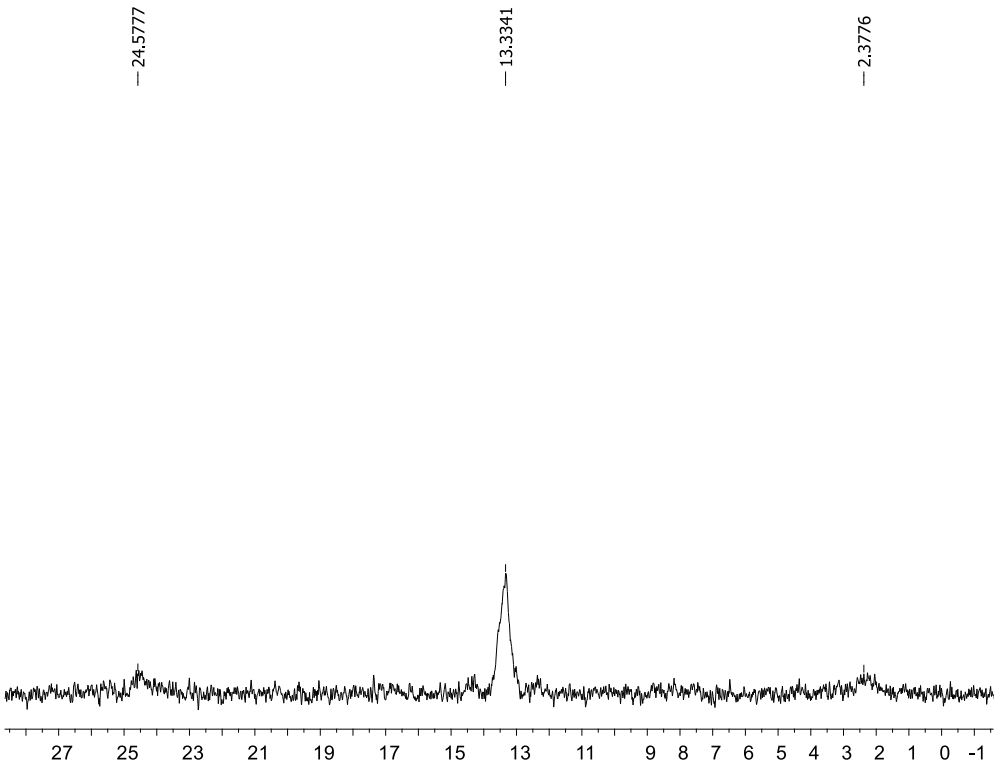


Figure S26. ^{31}P{^{1}H} NMR spectrum (CD_3OD, room temperature, 121.4 MHz) recorded for **P2**.

Section C. Absorption and emission data and SEM images

1. Absorption and emission data

Table S1. Absorption and emission data of compounds **8**, **10**, **P1** and **P2** in different solvents.

Compounds	λ_{max}, nm ($\varepsilon \times 10^4$, $M^{-1}\cdot cm^{-1}$), CH_3OH	λ_{em}, nm CH_3OH	Φ_F (%), CH_3OH	λ_{max}, nm ($\varepsilon \times 10^4$, $M^{-1}\cdot cm^{-1}$), CH_3OH/H_2O (1/9)	λ_{em}, nm CH_3OH/H_2O (1/9)	Φ_F (%), CH_3OH/H_2O (1/9)
8	262 (3.30), 336 (2.03)	500	0.046	262 (2.80), 336 (1.44)	501	1.22
10	257 (14.6), 266 (14.8), 290 (10.6), 362 (5.78)	522	0.237	257 (12.8), 266 (12.8), 290 (8.79), 362 (4.55)	522	2.13
P1	257 (14.6), 266 (14.8), 290 (10.4), 362 (5.62)	520	0.329	257 (13.3), 266 (13.1), 290 (8.21), 362 (4.04)	519	2.77
P2	257 (15.8), 266 (15.9), 290 (11.1), 362 (5.93)	521	0.337	257 (15.5), 266 (15.3), 290 (9.39), 362 (4.62)	520	2.89

*2. SEM images of **P1** at different concentrations*

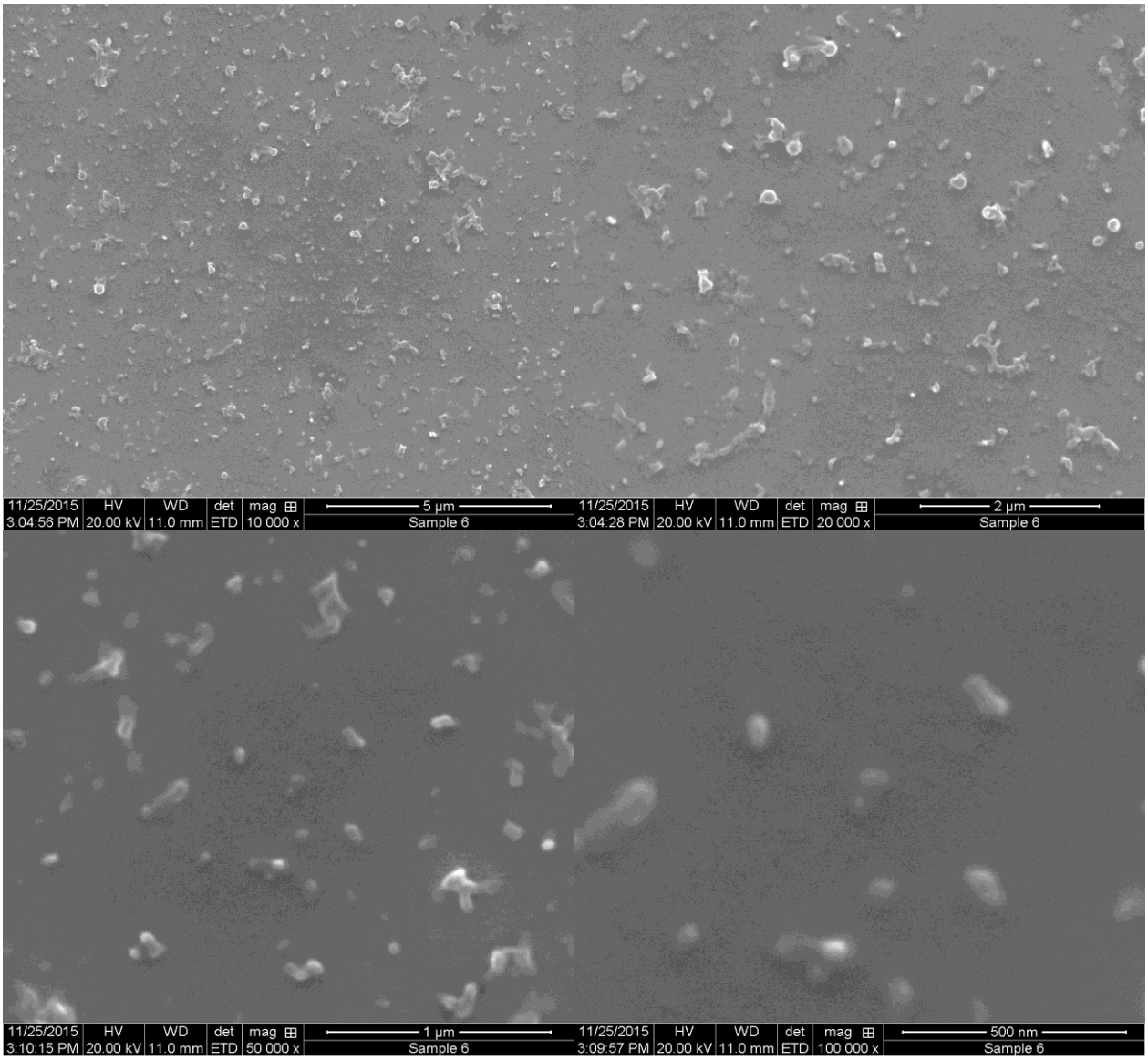


Figure S27. SEM images of **P1** in methanol at the concentration of 0.1 mg/mL.

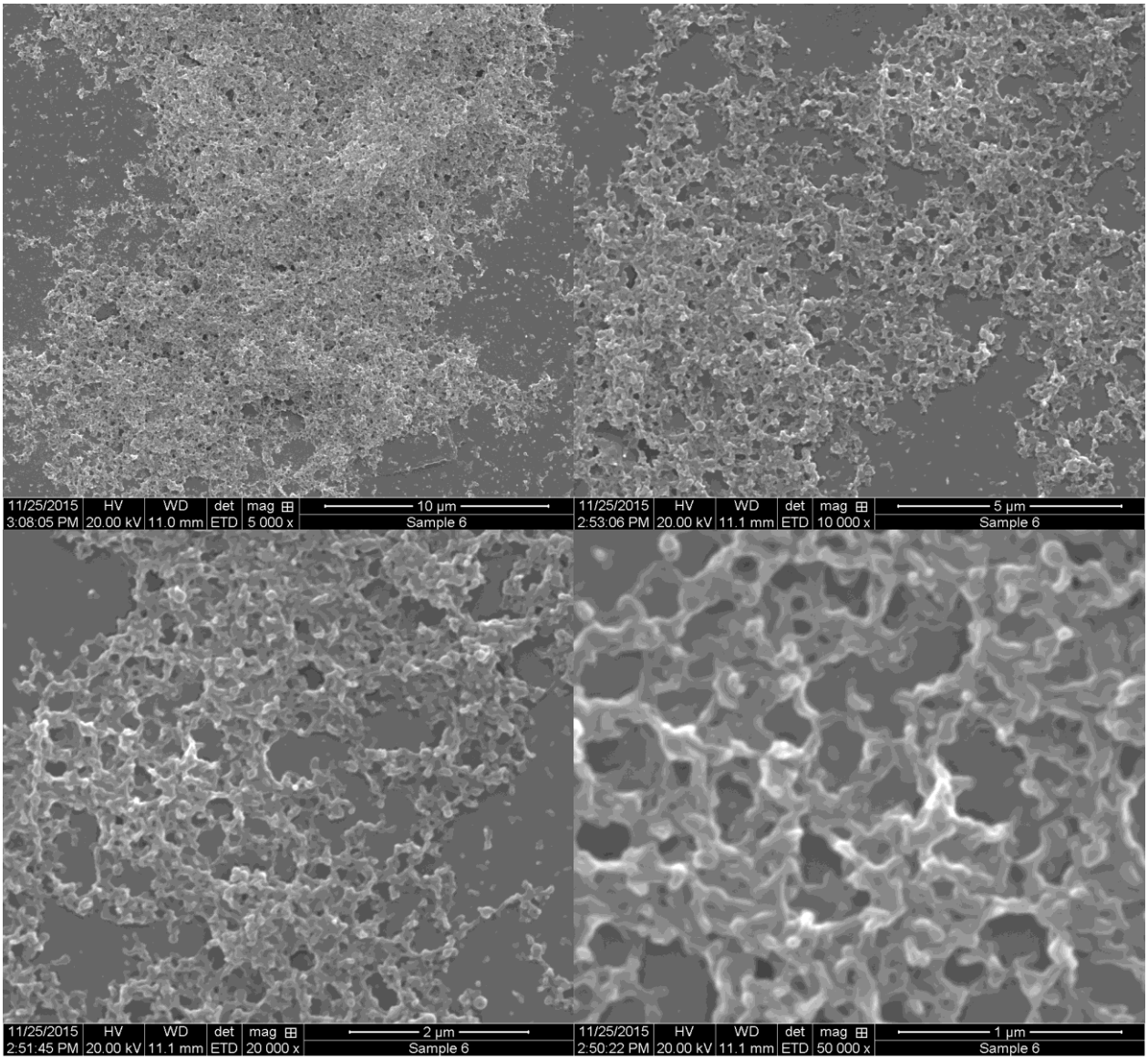


Figure S28. SEM images of **P1** in methanol at the concentration of 1.0 mg/mL.

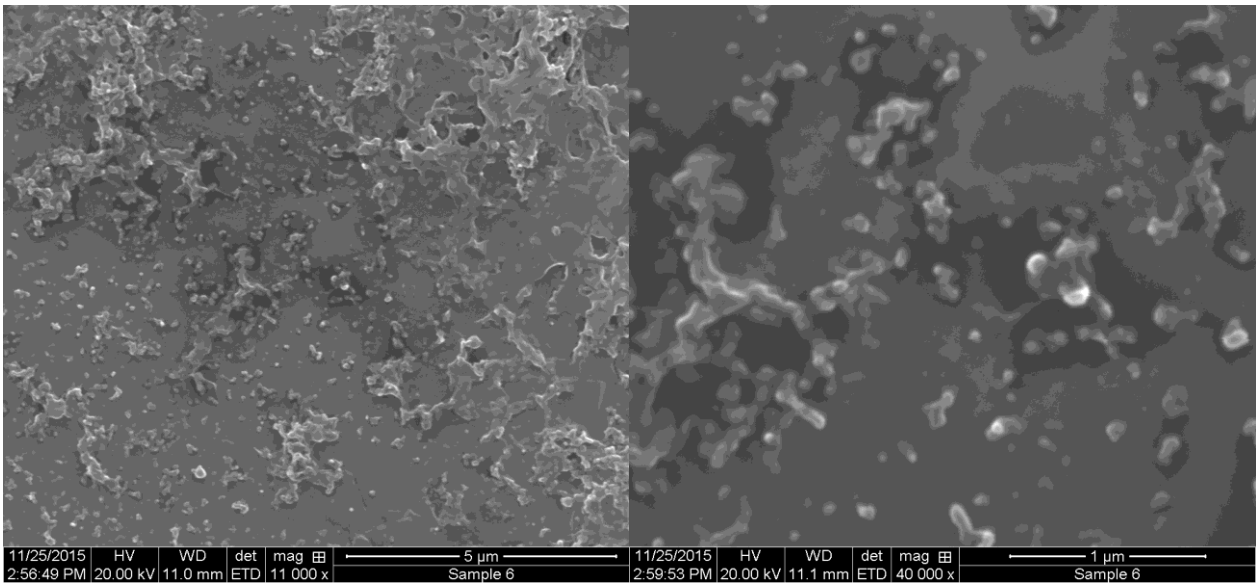


Figure S29. SEM images of **P1** in methanol at the concentration of 0.1 mg/mL observe at the edge of the silica wafer, indicating the coexistence of both well-dispersed nanoparticles and network structures.

*3. SEM images of **P2** at different concentrations*

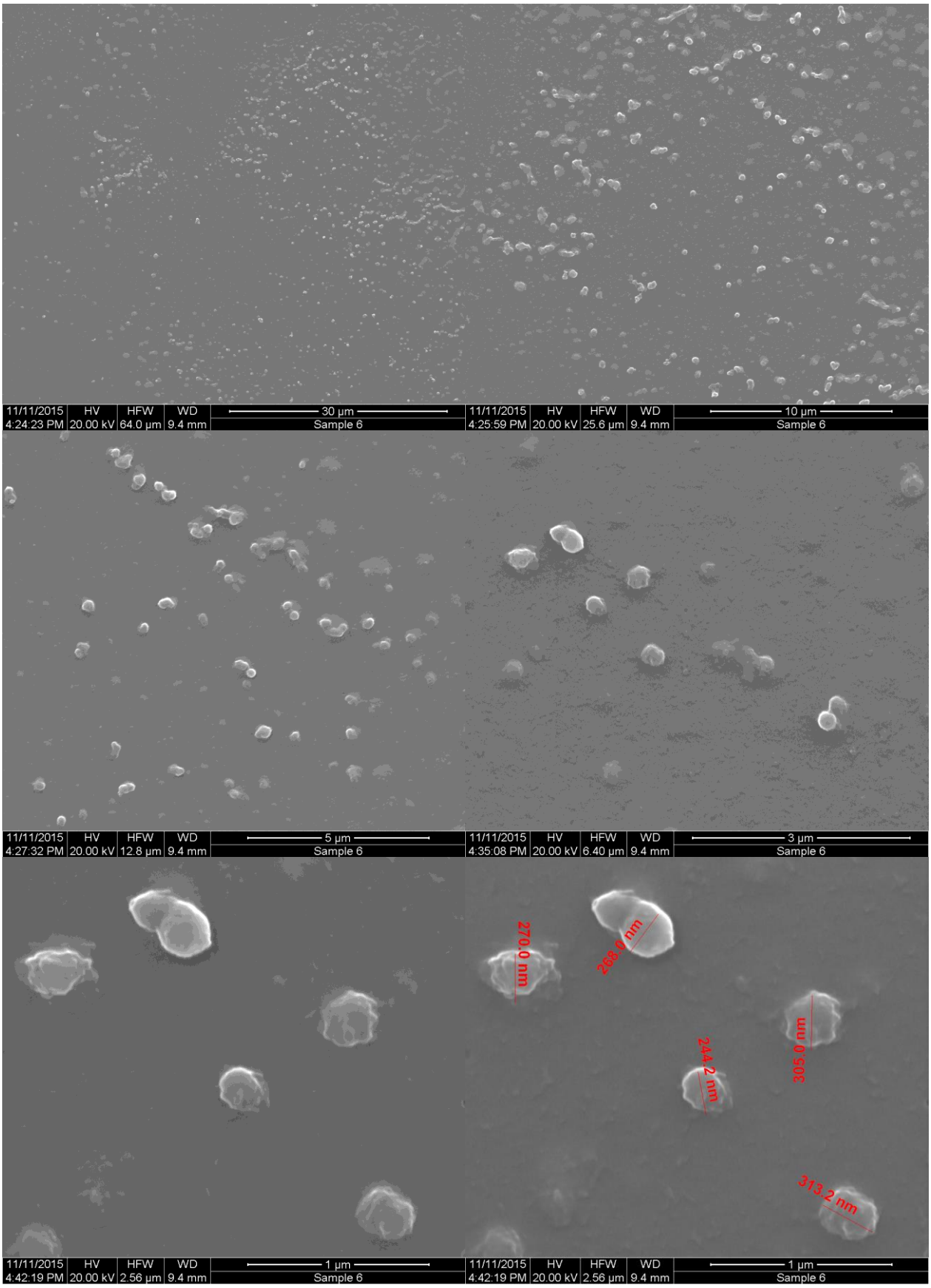


Figure S30. SEM images of **P2** in methanol at the concentration of 0.1 mg/mL.

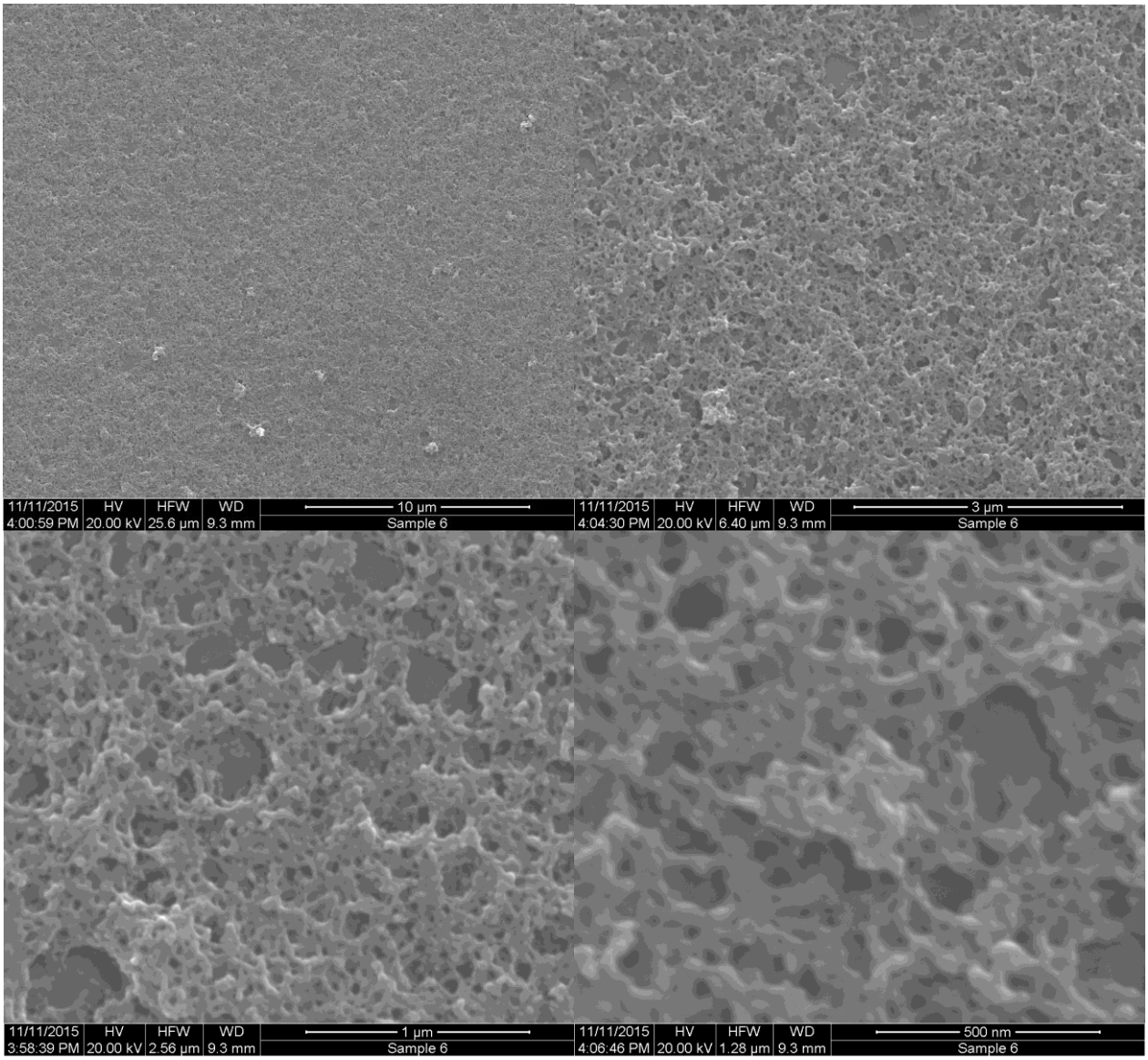


Figure S31. SEM images of **P2** in methanol at the concentration of 0.1 mg/mL.

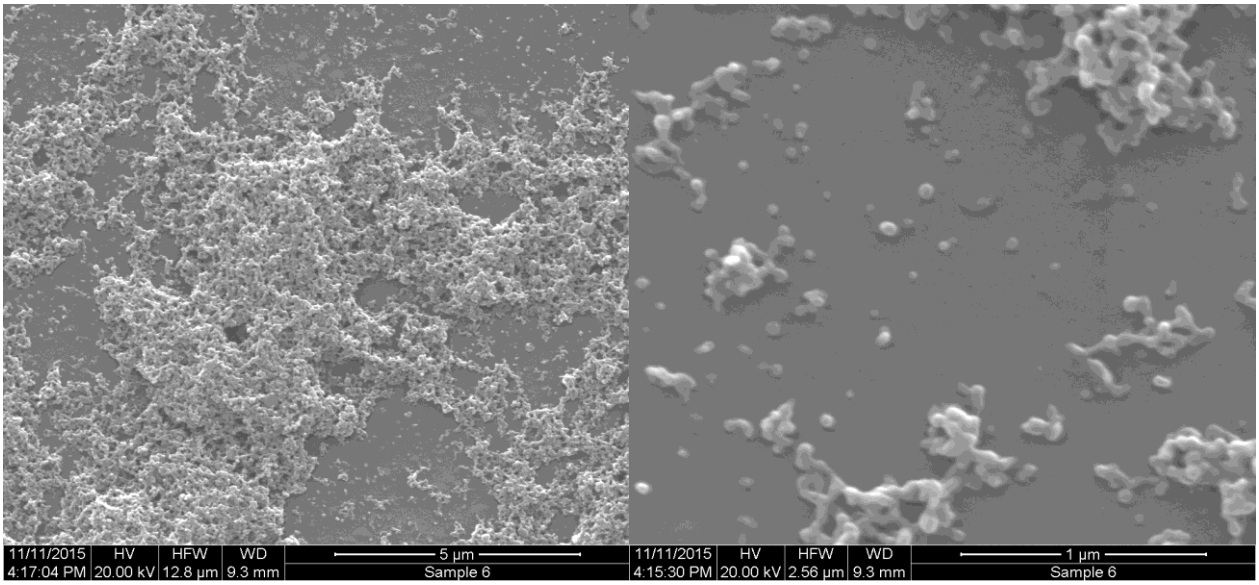


Figure S32. SEM images of **P2** in methanol at the concentration of 0.1 mg/mL observe at the edge of the silica wafer, indicating the coexistence of both well-dispersed nanoparticles and network structures.

Section D. Confocal laser scanning microscopy images

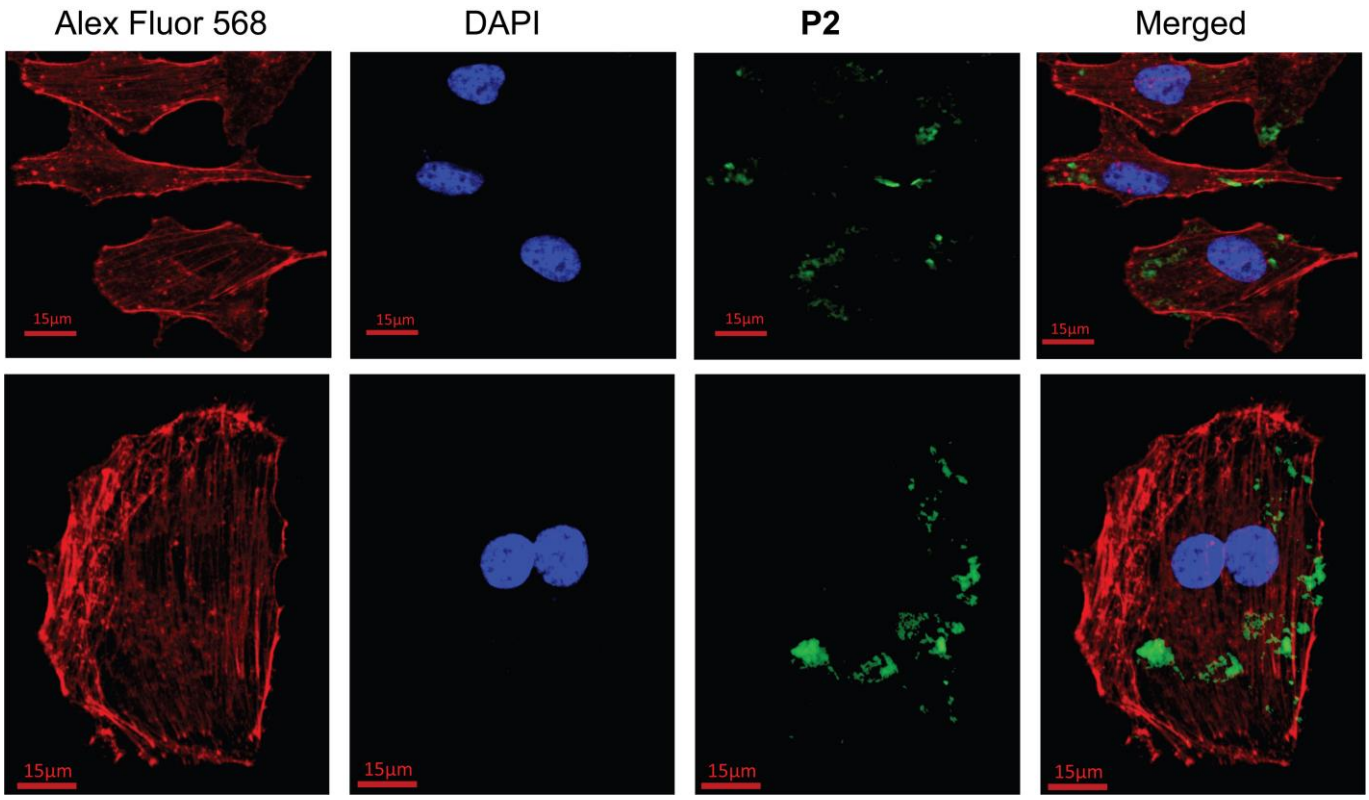


Figure S33. CLSM images of A549R cells after incubation with 20 μg/mL **P2**.

Section E. References

S1. Kong X, et al. (2011) A mesogenic triphenylene-perylene-triphenylene triad. *Org Lett* 13(4):764–767.

S2. Kryschenko YK, Seidel SR, Arif AM, Stang PJ (2003) Coordination-driven self-assembly of predesigned supramolecular triangles. *J Am Chem Soc* 125(17):5193–5198.

S3. Kim E, et al. (2010) Facile, template-free synthesis of stimuli-responsive polymer nanocapsules for targeted drug delivery. *Angew Chem Int Ed Engl* 49(26):4405–4408.