

Electronic Supplementary Information (ESI)

Photostable and biocompatible AIE-active conjugated polyelectrolytes for efficient heparin detection and specific lysosome labelling

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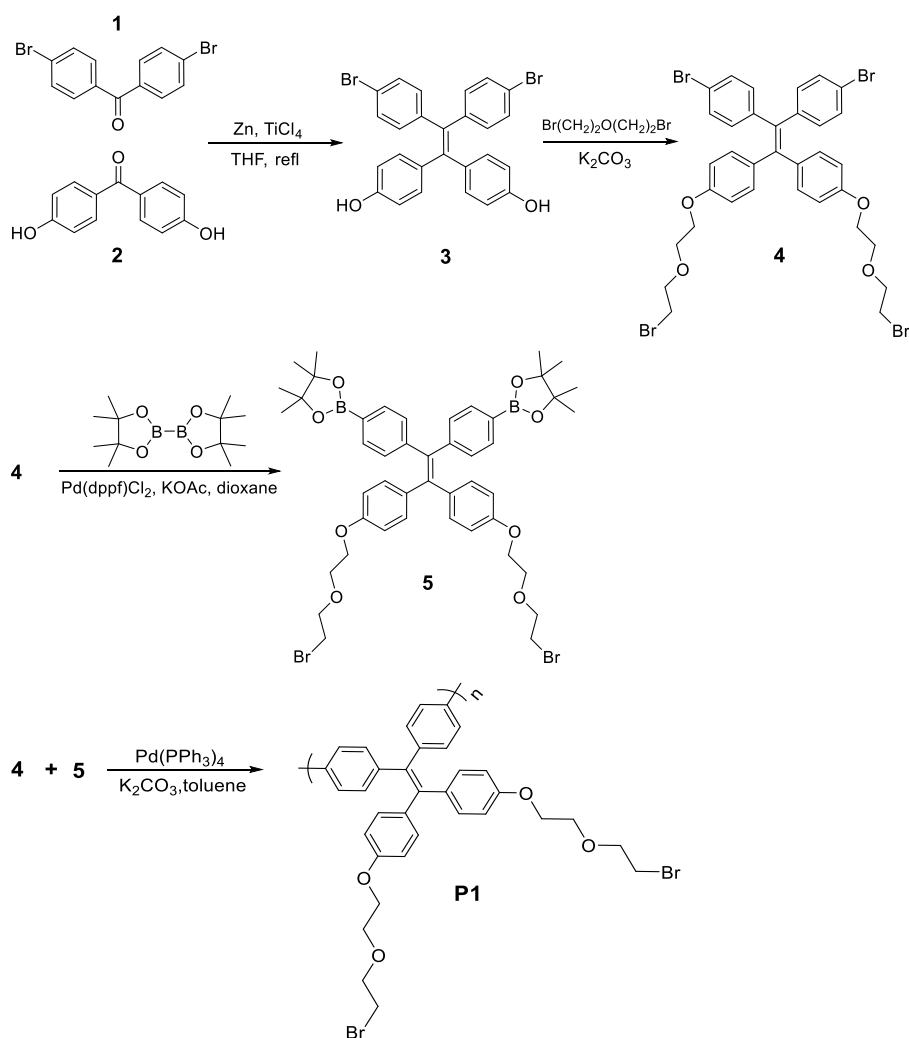
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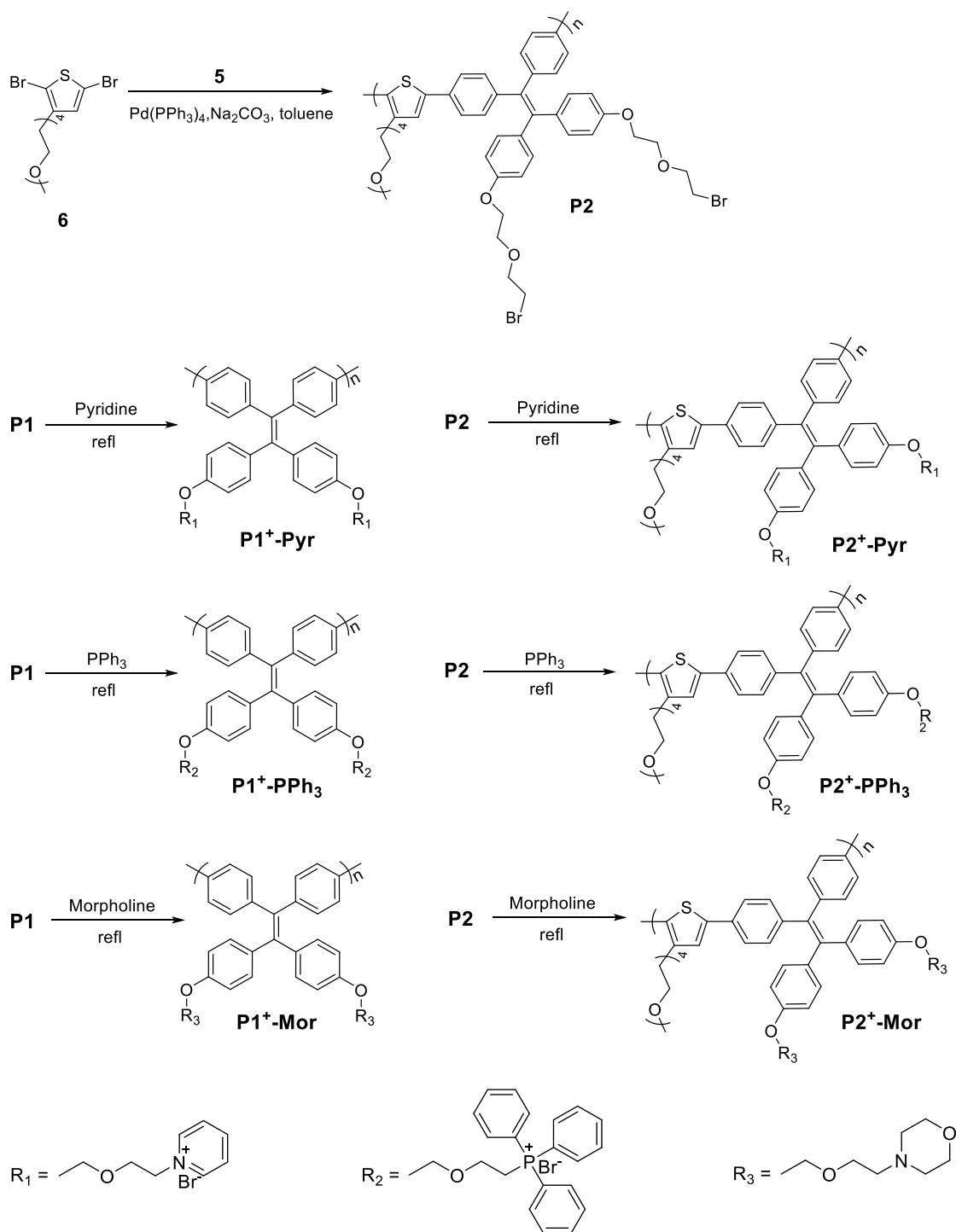
Materials and Instrumentation

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. and reagents were purchased from Aldrich and J&K Scientific Ltd., and used as received without further purification. HeLa cells were obtained from the American Type Culture Collection. ¹H and ¹³C NMR spectra of small molecules were measured on a Bruker AV 500 spectrometer in deuterated solvents (chloroform, DMSO, CD₃OD or dichloromethane) using tetramethylsilane (TMS; δ = 0) as the internal reference. ¹H spectra of polymers P1-P2 were measured on an Agilent MR 400 spectrometer in deuterated chloroform using TMS as the internal reference. ¹³C NMR of polymers P1-P2 spectra were measured on an Agilent 500 spectrometer in deuterated chloroform using TMS as the internal reference. ¹H NMR spectra of polyelectrolytes P1⁺-Pyr, P1⁺-PPh₃, P1⁺-Mor, P2⁺-Pyr, P2⁺-PPh₃ and P2⁺-Mor spectra were measured on an Agilent MR 400 spectrometer in deuterated DMSO using TMS as the internal reference. ¹³C NMR spectra of polyelectrolytes P1⁺-Pyr, P1⁺-PPh₃, P1⁺-Mor, P2⁺-Pyr, P2⁺-PPh₃ and P2⁺-Mor were measured on an Agilent 500 spectrometer in deuterated DMSO using TMS as the internal reference. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Photoluminescence was recorded on a Perkin-Elmer LS 55 spectrofluorometer. Fluorescent decay data were acquired using a Hamamatsu time-resolved spectrometer C11367-11 Quantaaurus-Tau. Mass spectra were recorded on a Thermo Scientific™ Dionex UltiMate 3000 LC/Exactive™ Plus Orbitrap MS. The number average (M_n) and weight average (M_w) molecular weights and polydispersity indices (PDI) of the polymers were estimated by a

Waters Associates gel permeation chromatography (GPC 2414) system equipped with RI and UV detectors. Aggregated particle morphologies of all the polymers were measured by a Hitachi HT-7700 transmission electron microscope (TEM) operated at 80 kV. The preparation of TEM samples was as follows: distribution of a polymer in solvent mixture was sonicated using a microtip probe sonicator (XL2000, Misonix Incorporated, NY) at 12 W output for 60 s; a drop of the mixture solution was dropped on a 300-mesh Formvar-coated copper grid and dried under vacuum at room temperature. Z-average particle sizes and polydispersities (PDIs) of particles were measured by DLS (Zetasizer Nanoseries) at 25 °C under a scattering angle of 90°. Particle sizes were given as the average of three measurements. Confocal Laser Scanning Microscopy (CLSM) images were obtained on a confocal microscope (Leica SP5, Germany) using the LAS AF imaging software.

Synthesis





Scheme S1. Molecular structures and synthetic routes to conjugated polyelectrolytes (P1⁺-Pyr, P1⁺-PPh₃, P1⁺-Mor, P2⁺-Pyr, P2⁺-PPh₃, P2⁺-Mor) based on TPE.

4,4'-(2,2-Bis(4-bromophenyl)ethene-1,1-diyl)diphenol (3): To a mixture of 4,4'-dibromobenzophenone (3.4 g, 10 mmol), 4,4'-dihydroxybenzophenone (2.14 g, 10 mmol), zinc dust (15.69 g, 0.24 mol) in 80 mL dry THF was added dropwise titanium (IV) chloride (4.55 g, 24 mmol) under N₂ at -78 °C. After stirring for 20 min, the reaction mixture was warmed to room temperature and then heated to reflux for 3.5 h. The mixture was cooled to room temperature and poured into water, and extracted with dichloromethane by three times. The combined organic layers were washed with saturated brine solution and water, and dried over anhydrous MgSO₄. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane (2:1) as eluent. White solid of **3** was obtained in 59% yield. ¹H NMR (500 MHz, DMSO), δ (TMS, ppm): 9.38 (s, 2H), 7.31 (d, *J* = 8.4 Hz, 4H), 6.84 (d, *J* = 8.4 Hz, 4H), 6.72 (d, *J* = 8.5 Hz, 4H), 6.51 (d, *J* = 8.5 Hz, 4H). ¹³C NMR (126 MHz, DMSO), δ (TMS, ppm): 156.74, 143.48, 142.57, 135.57, 133.98, 133.41, 132.54, 131.31, 119.78, 115.24. HRMS: *m/z* 522.9729 ([M+H]⁺, calcd for C₂₆H₁₉Br₂O₂ 522.9731).

4,4'-(2,2-Bis(4-(2-(2-bromoethoxy)ethoxy)phenyl)ethene-1,1-diyl)bis(bromobenzene) (4): To a mixture of **3** (2.09 g, 4 mmol), Br(CH₂)₂O(CH₂)₂Br (4.70 g, 20 mmol), K₂CO₃ (2.76 g, 20 mmol) and KI (33.2 mg, 0.2 mmol) in 30 mL acetone. The reaction mixture was heated to reflux for 15 h. The mixture was cooled to room temperature and poured into water, and extracted with dichloromethane by three times. The combined organic layers were washed with saturated brine solution and water, and dried over anhydrous MgSO₄. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane (1:3) as eluent. White solid of **4** was obtained in 51% yield. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.22 (d, *J* = 8.5 Hz, 4H), 6.87 (dd, *J* = 19.4, 8.6 Hz, 8H), 6.67 (d, *J* = 8.8 Hz, 4H), 4.10-4.07 (m, 4H), 3.89-3.83 (m, 8H), 3.49 (t, *J* = 6.3 HZ, 4H). ¹³C NMR (126 MHz, CDCl₃), δ (TMS, ppm): 157.52, 142.71, 141.38, 136.76, 135.88, 133.00, 132.51, 131.03, 120.34, 113.93, 71.40, 69.66, 67.26, 30.24. HRMS: *m/z* 824.9036 ([M+H]⁺, calcd for C₃₄H₃₂Br₄O₄ 824.9071).

2,2'-((2,2-Bis(4-(2-(2-bromoethoxy)ethoxy)phenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(4,4,5,5-tetra methyl-1,3,2-dioxaborolane) (5): **4** (2.48 g, 3 mmol), bis-(pinacolato)diborane (3.81 g, 15 mmol), KOAc

(3.93 g, 40 mmol), and dioxane (100 mL) were mixed together in a 250 mL flask. After degassing, [Pd(dppf)Cl₂] (0.75 g, dppf = 1,1'-bis(diphenylphosphanyl)ferrocene) was added. The reaction mixture was kept at 100 °C for 24 h, and then cooled to room temperature. The organic solvent was distilled out, and the residual solid was dissolved in dichloromethane and washed with saturated brine solution. After drying with anhydrous MgSO₄, the solvent was distilled out. The crude product was purified by flash chromatography using dichloromethane as the eluent and then recrystallized in isopropanol to give **5** as white crystals (1.67 g, 63%). ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.52 (d, *J* = 7.9 Hz, 4H), 6.99 (d, *J* = 7.9 Hz, 4H), 6.90 (d, *J* = 8.6 Hz, 4H), 6.63 (d, *J* = 8.6 Hz, 4H), 3.88 (t, *J* = 6.4 Hz, 4H), 4.08-4.04 (m, 4H), 3.89-3.92 (m, 8H), 3.48 (t, *J* = 6.3 Hz, 4H), 1.32 (s, 24H). ¹³C NMR (126 MHz, CDCl₃), δ (TMS, ppm): 157.27, 147.13, 141.01, 139.21, 136.43, 134.13, 132.62, 130.80, 113.74, 83.69, 71.39, 69.68, 67.17, 30.23, 24.92. HRMS: *m/z* 919.2558 ([M+H]⁺, calcd for C₄₆H₅₇B₂Br₂O₈ 919.2586).

P1: To a mixture of **4** (206 mg, 0.25 mmol), **5** (230 mg, 0.25 mmol), Pd(PPh₃)₄ (12 mg, 0.01 mmol) and K₂CO₃ (276 mg, 2 mmol) in a 10 mL round-bottomed flask. A mixture of toluene (1 mL) and water (1 mL) was added to the flask, and the reaction vessel was degassed. The mixture was vigorously stirred at 90 °C for 24 h and then cooled to room temperature. After extraction with dichloromethane, the combined organic layers were washed successively with water and then dried over anhydrous MgSO₄. The polymer was filtered and precipitated into methanol, and then dried under vacuum for 24 h to afford the neutral polymer P1 as a green solid in 71% yield. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.33 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 8.1 Hz, 4H), 6.96 (d, *J* = 8.0 Hz, 4H), 6.66 (d, *J* = 6.7 Hz, 4H), 4.06 (d, *J* = 6.7 Hz, 4H), 4.06 (br, 4H), 3.89-3.77 (m, 4H). ¹³C NMR (126 MHz, CDCl₃), δ (TMS, ppm): 157.17, 143.15, 140.15, 138.52, 137.95, 136.69, 132.60, 131.83, 125.89, 113.75, 71.35, 69.64, 67.19, 30.22. *M_n* = 5.929 × 10³; PDI (*M_w*/*M_n*) = 2.04.

P2: The procedure was analogous to that described for P1. Green solid, yield 80%. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.27 (br, 2H), 7.17-7.03 (m, 2H), 7.03-6.83 (m, 8H), 6.60 (d, *J* = 6.5 Hz, 5H), 4.06 (br, 4H), 3.83-3.70 (m, 8H), 3.61-3.35 (m, 18H), 3.26 (s, 3H), 2.86 (br, 2H). ¹³C NMR (126 MHz, CDCl₃), δ

(TMS, ppm): 157.17, 143.15, 140.15, 138.52, 137.95, 136.69, 132.60, 131.83, 125.89, 113.75, 71.35, 69.64, 67.19, 30.22. $M_n = 3.482 \times 10^4$; PDI (M_w/M_n) = 1.47.

P1⁺-Pyr: The polymer P1 (30 mg) was dissolved in pyridine (5 mL), and the mixture was stirred at 60 °C under nitrogen for 48 h. The solvent was then removed by evaporation under pressure, and the residue was precipitated with acetone to give dark green P1⁺-Pyr with a yield of 85%. ¹H NMR (500 MHz, CD₃OD), δ (TMS, ppm): 8.94 (s, 2H), 7.96 (s, 4H), 7.38 (s, 4H), 7.06-6.84 (m, 8H), 6.61 (br, 4H), 4.45-3.80 (m, 12H), 3.77 (br, 4H). ¹³C NMR (126 MHz, CD₃OD), δ (TMS, ppm): 157.40, 145.63, 145.12, 143.34, 136.50, 132.32, 131.68, 127.63, 125.67, 113.54, 69.35, 68.87, 67.00, 61.30.

P1⁺-PPh₃: The polymer P1 (30 mg, 0.05 mmol) and triphenylphosphine (100 mg, 0.38 mmol) were dissolved in acetonitrile (5 mL), and the mixture was stirred at 100 °C for 48 h. The solvent was then removed by evaporation under pressure, and the residue was precipitated with toluene to give dark green P1⁺-PPh₃ with a yield of 80%. ¹H NMR (500 MHz, DMSO), δ (TMS, ppm): 7.80-7.53 (m, 22H), 7.46-7.40 (m, 4H), 7.34-6.35 (m, 16H), 3.97 (br, 4H), 3.71 (br, 8H), 3.59-3.41 (m, 4H). ¹³C NMR (126 MHz, DMSO), δ (TMS, ppm): 162.63, 135.02, 134.16, 134.08, 132.53, 131.91, 130.62, 130.53, 130.33, 130.23, 129.37, 129.28, 128.68, 126.12, 119.73, 119.04, 114.22, 72.90, 69.78, 69.29, 68.73, 60.68, 59.99.

P1⁺-Mor: The polymer P1 (30 mg) was dissolved in morpholine (5 mL), and the mixture was stirred at 60 °C under nitrogen for 48 h. The solvent was then removed by evaporation under pressure, and the residue was precipitated with n-hexane to give dark green P1⁺-Mor with a yield of 87%. ¹H NMR (500 MHz, DMSO), δ (TMS, ppm): 7.56-7.24 (m, 4H), 7.23-6.75 (m, 4H), 6.69 (br, 4H), 3.98 (br, 4H), 3.69-3.41 (m, 12H), 3.31 (br, 4H), 2.41 (br, 12H). ¹³C NMR (126 MHz, DMSO), δ (TMS, ppm): 161.45, 157.52, 154.55, 154.19, 138.28, 132.54, 131.91, 126.09, 114.14, 68.70, 67.20, 66.62, 66.22, 65.62, 58.04, 54.12, 45.56, 44.80.

P2⁺-Pyr: The procedure was analogous to that described for P1⁺-Pyr. Green solid, yield 81%. ¹H NMR (500 MHz, CD₃OD), δ (TMS, ppm): 8.95 (s, 4H), 8.45 (s, 2H), 7.97 (s, 4H), 7.43-7.18 (m, 4H), 7.16-6.73 (m, 8H), 6.61 (s, 4H), 4.19-3.84 (m, 8H), 3.83-3.63 (m, 6H), 3.61-3.34 (m, 14H), 3.22-3.01 (m, 5H), 2.77 (br, 2H).

P2⁺-PPh₃: The procedure was analogous to that described for P2⁺-PPh₃. Green solid, yield 80%. ¹H NMR (500 MHz, DMSO), δ (TMS, ppm): 7.92-7.48 (m, 28H), 7.42-6.82 (m, 14H), 6.57 (br, 5H), 3.95 (br, 6H), 3.81-3.33 (m, 21H), 3.15 (br, 6H). ¹³C NMR (126 MHz, DMSO), δ (TMS, ppm): 157.73, 135.23, 134.17, 134.08, 132.61, 132.06, 131.92, 130.63, 130.53, 130.33, 129.37, 128.68, 118.97, 114.25, 72.90, 71.70, 70.26, 70.02, 60.00, 58.47, 53.17.

P2⁺-Mor: The procedure was analogous to that described for P2⁺-Mor. Green solid, yield 87%. ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm): 7.28 (m, 2H), 7.16-6.15 (m, 3H), 7.01-6.85 (m, 8H), 6.59 (br, 4H), 3.99 (br, 4H), 3.91 (br, 2H), 3.85-3.72 (m, 10H), 3.71-3.45 (m, 19H), 3.43 (br, 2H), 3.26 (br, 4H), 3.13 (br, 2H), 2.84 (br, 8H).

Cell Imaging: HeLa cells were grown in a 35 mm Petri dish with a coverslip at 37 °C. The living cells were stained with the polyelectrolytes (1 μg mL⁻¹ or 5 μg mL⁻¹) for 48 h and LysoTracker red (100 μM) for 20 min. The cells were washed for three times with phosphate-buffered saline (PBS) buffer and imaged under CLSM. The six polyelectrolytes were excited at 405 nm and the fluorescence were collected at 450–550 nm. The LysoTracker red was excited at 543 nm and the fluorescence was collected at 580–680 nm.

Cell Viability Evaluated by MTT Assay: Viability of the cells was assayed by using cell proliferation Kit I with the absorbance of 595 nm being detected using a Perkin-Elmer Victor plate reader. Five thousand cells were seeded per well in a 96-well plate. After overnight culture, various concentrations of CPEs were added into the 96-well plate. After 48 h treatment, 10 μL of 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyltetrazolium bromide (MTT) solution (5 mg/mL in phosphate

buffer solution) was added into the each well. After 4 h incubation at 37 °C, 100 μ L of solubilization solution containing 10% SDS and 0.01 M HCl was added to dissolve the purple crystals. After 12 h incubation, the optical density readings at 595 nm were taken using a plate reader. Each of the experiments was performed at least 3 times.

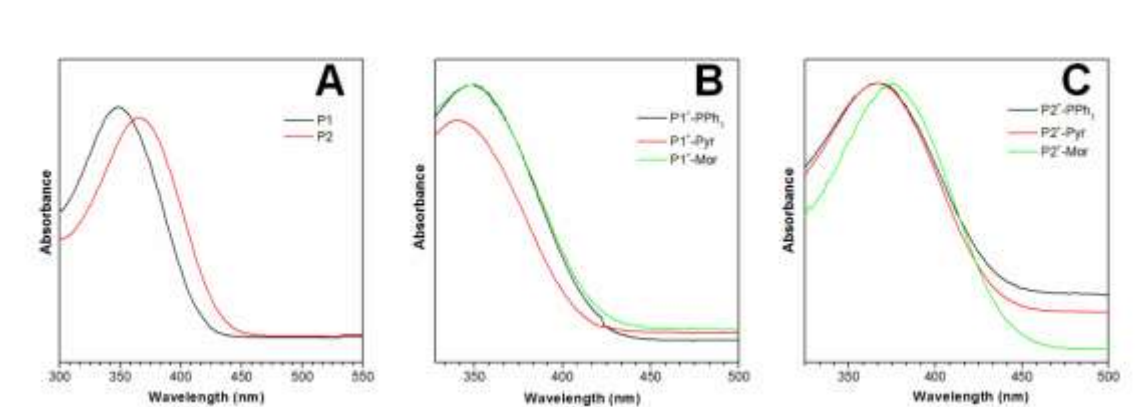


Fig. S1 (A) Absorption spectra of polymers P1 and P2 in THF solution; (B) Absorption spectra of polymers P1⁺-Pyr in methanol solution, and P1⁺-PPh₃ and P1⁺-Mor in DMSO solution; (C) Absorption spectra of polymers P2⁺-Pyr in methanol solution, and P2⁺-PPh₃ and P2⁺-Mor in DMSO solution.

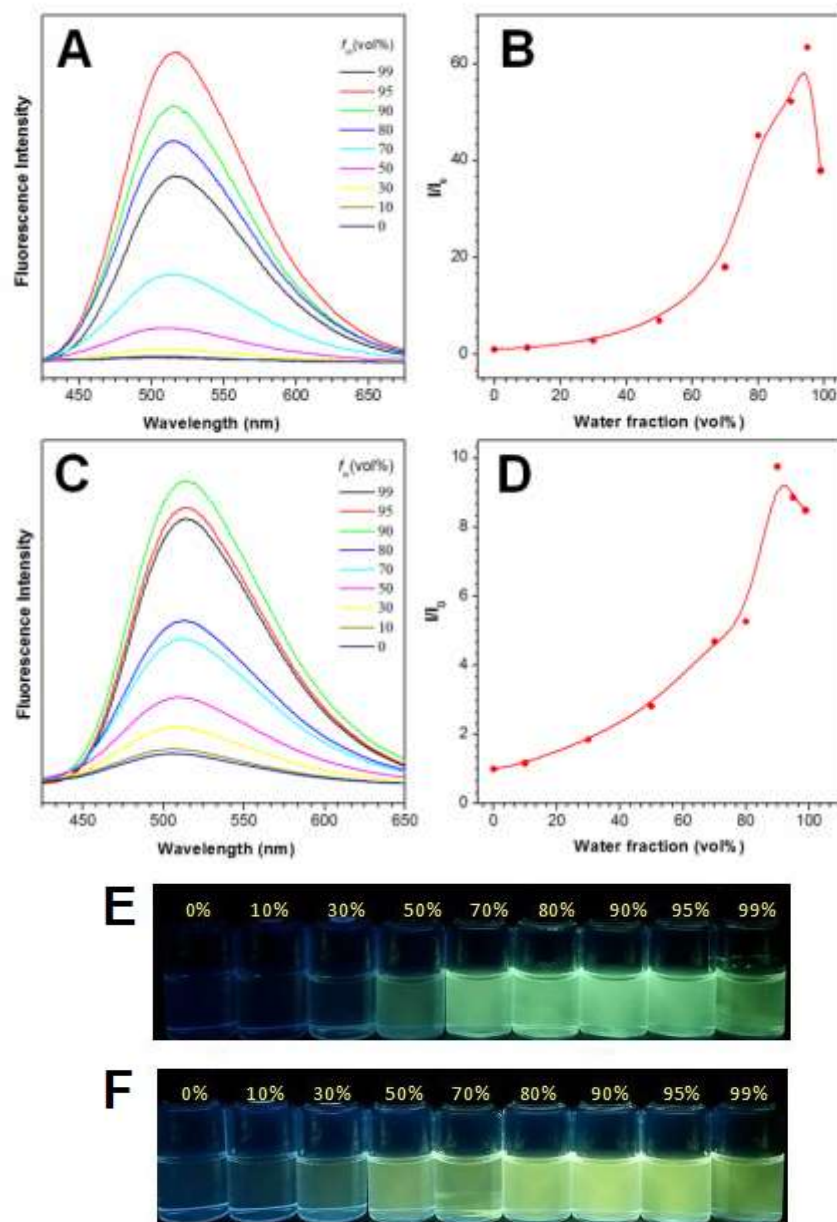


Fig. S2 (A, C) PL spectra of P1 (A) and P2 (C) in THF/H₂O mixtures with different water fraction (f_w); (B, D) Plots of I/I_0 of P1 (B) and P2 (D) versus the compositions of the aqueous mixtures; Fluorescent photographs of P1 (E) and P2 (F) in THF/H₂O mixtures with different f_w . I_0 = PL intensity in pure THF solution. Concentration: 10 μ M; excitation wavelength: 350 nm (A, B); 370nm (C, D).

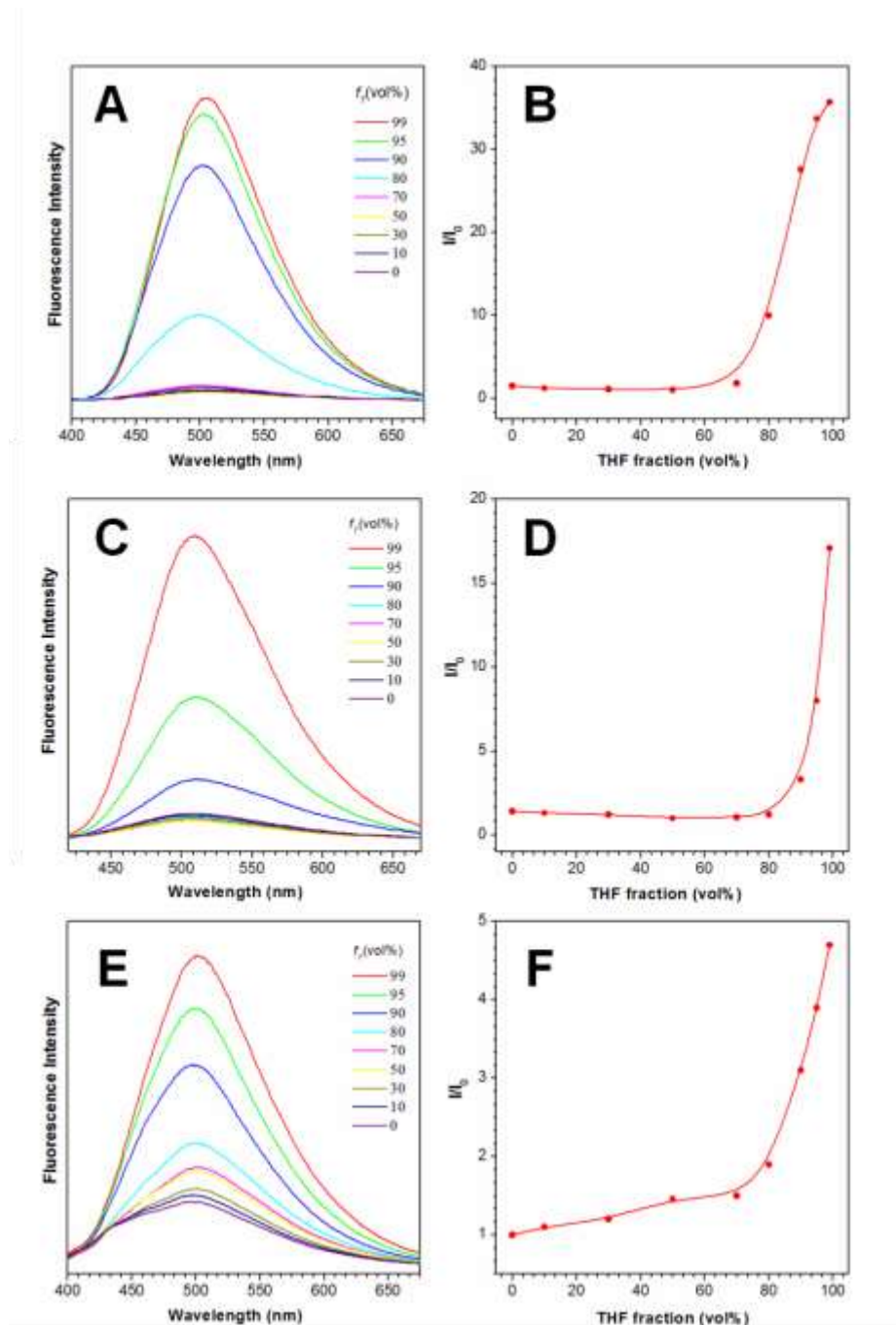


Fig. S3 (A, C, E) PL spectra of P1⁺-Mor (A) and P1⁺-PPh₃ (C) in DMSO/THF and P1⁺-Pyr (E) in methanol/THF mixtures with different THF fraction (f_T); (B, D, F) Plots of I/I_0 of P1⁺-Mor (B), P1⁺-PPh₃ (D) and P1⁺-Pyr (F) versus the compositions of the solution mixtures. I_0 = PL intensity in pure DMSO or methanol solution. Concentration: 10 μ M; excitation wavelength: 350 nm.

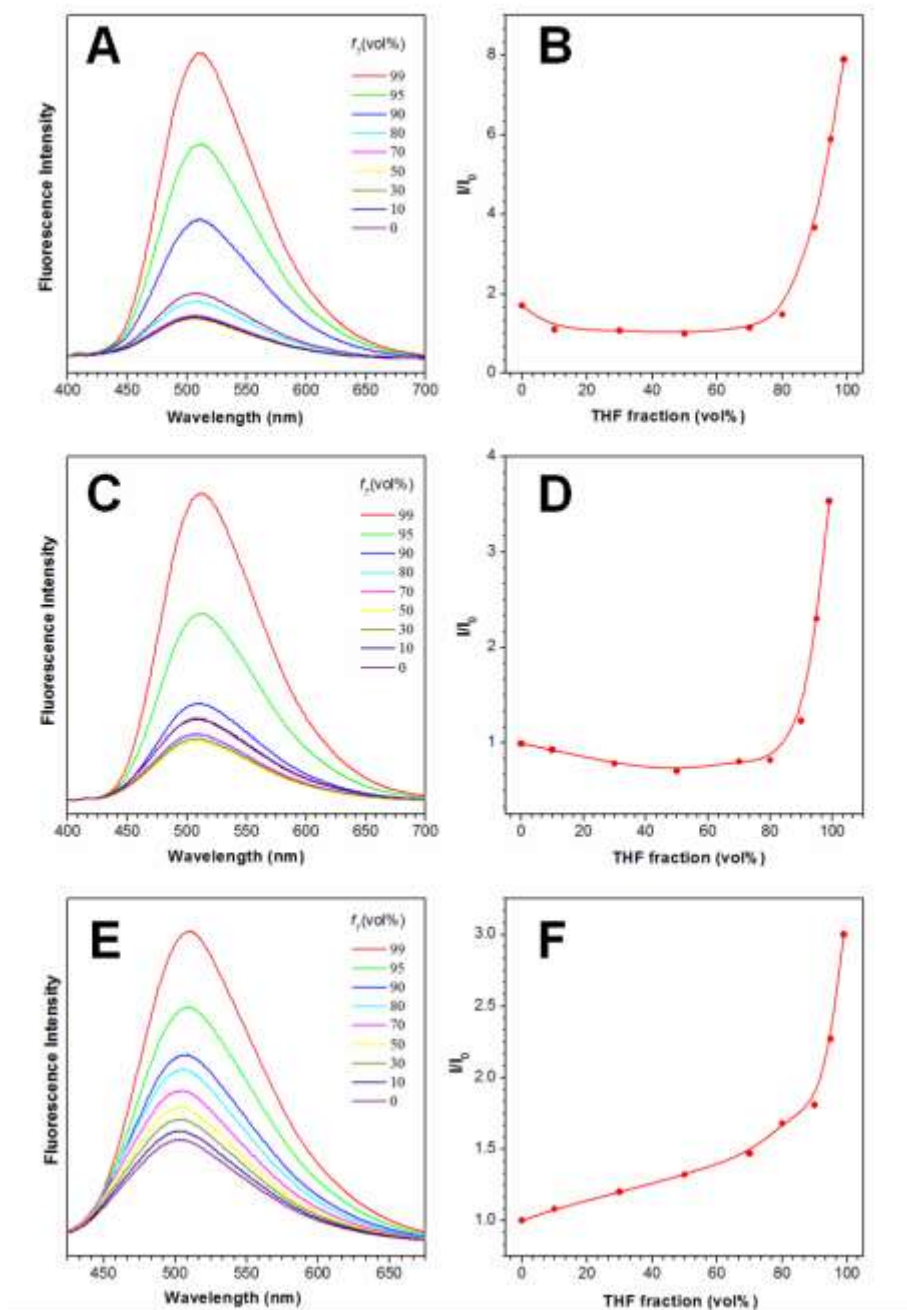


Fig. S4 (A, C, E) PL spectra of P2⁺-Mor (A) and P2⁺-PPh₃ (C) in DMSO/THF, P2⁺-Pyr (E) in methanol/THF mixtures with different THF fraction (f_T); (B, D, F) Plots of I/I_0 of P2⁺-Mor (B), P2⁺-PPh₃ (D) and P2⁺-Pyr (F) versus the compositions of the solution mixtures. I_0 = PL intensity in pure DMSO or methanol solution. Concentration: 10 μ M; excitation wavelength: 370 nm.

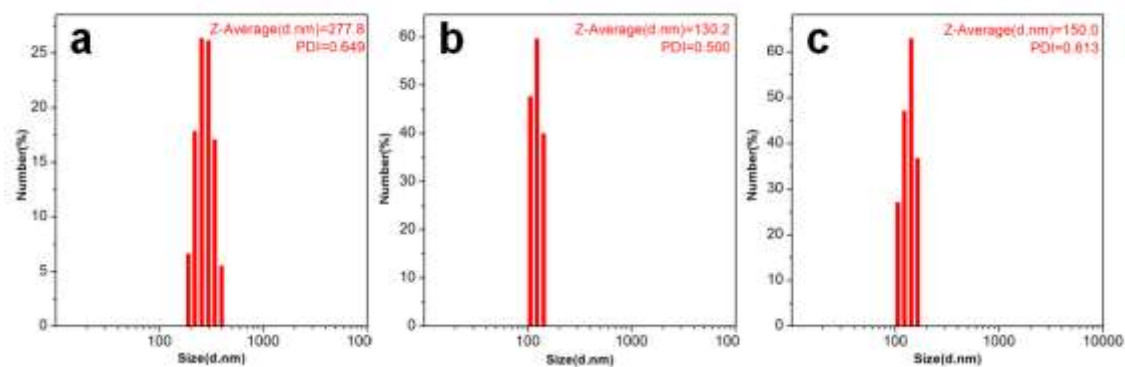


Fig. S5 Particle size distributions of all the polymers P1⁺-Mor (a), P1⁺-PPH₃ (b) and P1⁺-Pyr (c). P1⁺ was measured in DMSO/H₂O mixed solutions (2:98 v/v).

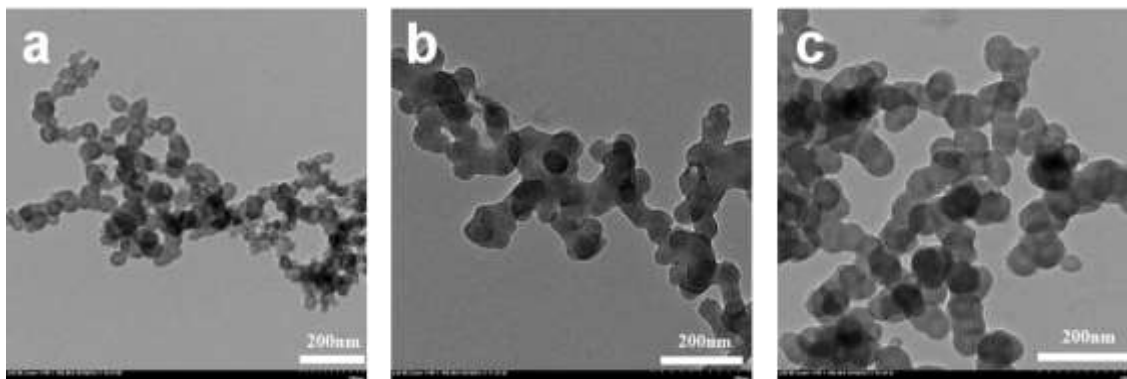


Fig. S6 TEM images of all the polymers P1⁺-Mor (a), P1⁺-PPH₃ (b) and P1⁺-Pyr (c). P1⁺ was measured in DMSO/H₂O mixed solutions (2:98 v/v).

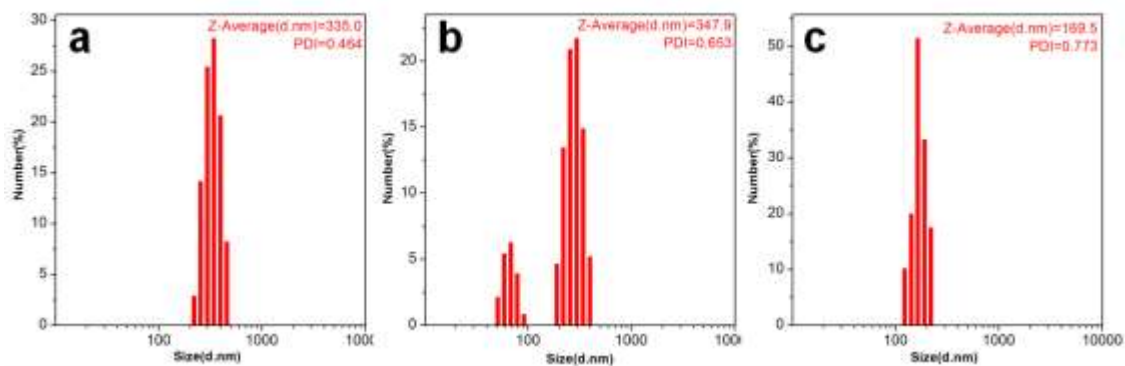


Fig. S7 Particle size distributions of all the polymers P2⁺-Mor (a), P2⁺-PPH₃ (b) and P2⁺-Pyr (c). P2⁺ was measured in DMSO/H₂O mixed solutions (2:98 v/v).

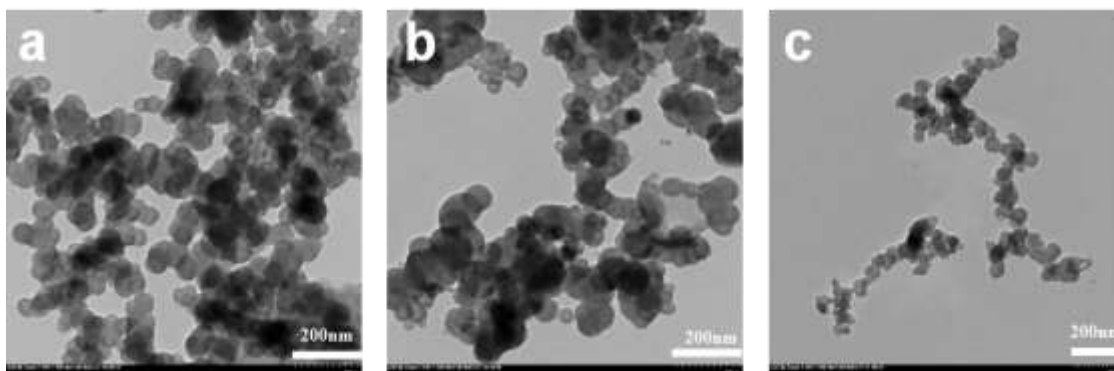
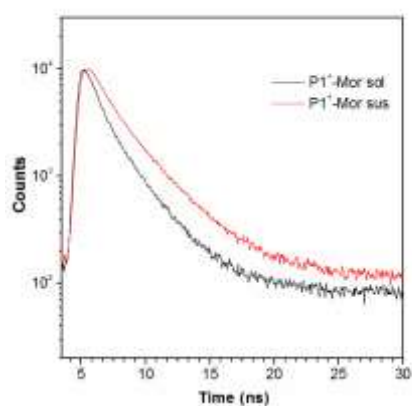
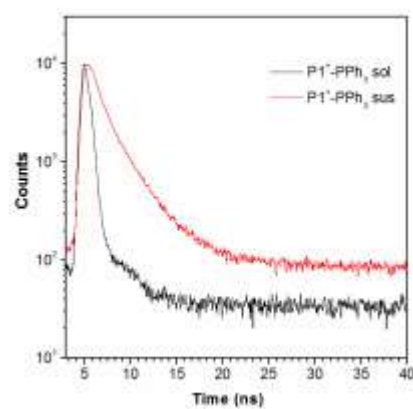


Fig. S8 TEM images of all the polymers P2⁺-Mor (a), P2⁺-PPH₃ (b) and P2⁺-Pyr (c). P2⁺ was measured in DMSO/H₂O mixed solutions (2:98 v/v).



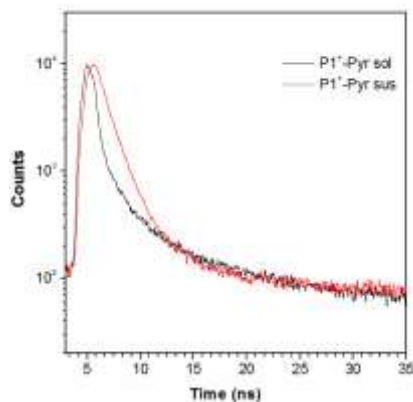
$$\text{P1-Mor}^+ \text{ sol: } \tau_{\text{AVE}} = 0.5 \times 38\% + 2.43 \times 62\% = 1.70 \text{ ns}$$

$$\text{P1-Mor}^+ \text{ sus: } \tau_{\text{AVE}} = 0.92 \times 30\% + 3.1 \times 70\% = 2.45 \text{ ns}$$



$$\text{P1-PPH}_3^+ \text{ sol: } \tau_{\text{AVE}} = 0.16 \times 97\% + 3.50 \times 3.0\% = 0.26 \text{ ns}$$

$$\text{P1-PPH}_3^+ \text{ sus: } \tau_{\text{AVE}} = 0.69 \times 41\% + 2.73 \times 59\% = 1.89 \text{ ns}$$



$$\text{P1-Pyr}^+ \text{ sol: } \tau_{\text{AVE}} = 0.3 \times 74\% + 3.43 \times 26\% = 1.11 \text{ ns}$$

$$\text{P1-Pyr}^+ \text{ sus: } \tau_{\text{AVE}} = 0.79 \times 75\% + 3.31 \times 25\% = 1.42 \text{ ns}$$

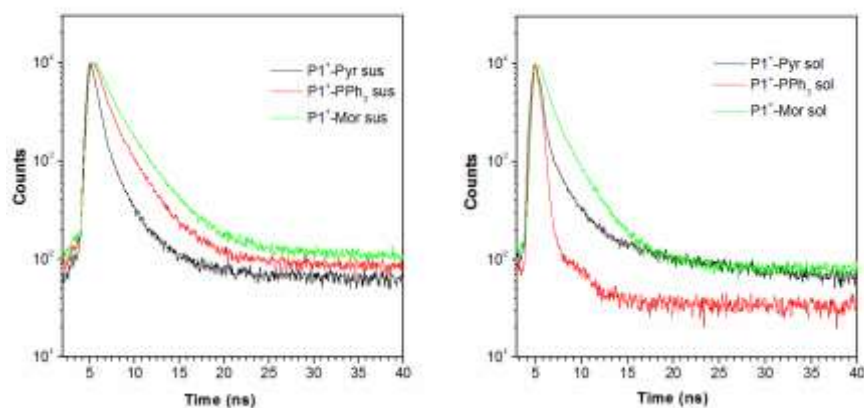
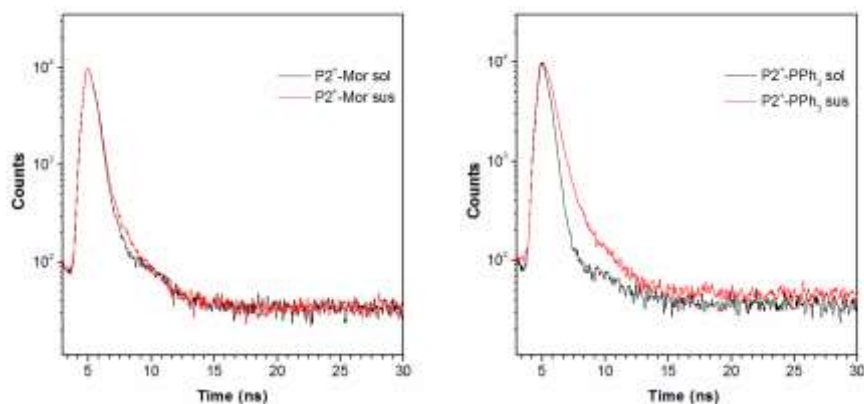
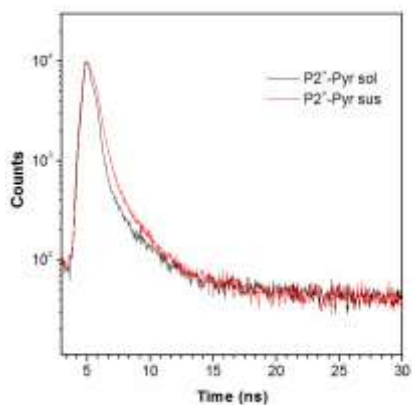


Fig. S9 Fluorescence decay curves of P1⁺-PPh₃ and P1⁺-Mor in DMSO solution, P1⁺-Pyr in methanol solution and all in THF suspension.



P2⁺-Mor sol: $\tau_{AVE}=0.19 \times 94\% + 2.14 \times 6\% = 0.31$ ns P2⁺-PPh₃ sol: $\tau_{AVE}=0.16 \times 97\% + 3.50 \times 3.0\% = 0.26$ ns
P2⁺-Mor sus: $\tau_{AVE}=0.23 \times 90\% + 1.69 \times 10\% = 0.38$ ns P2⁺-PPh₃ sus: $\tau_{AVE}=0.34 \times 81\% + 1.51 \times 19\% = 0.56$ ns



P2⁺-Pyr sol: $\tau_{AVE}=0.19 \times 88\% + 2.90 \times 12\% = 0.31$ ns
P2⁺-Pyr sus: $\tau_{AVE}=0.30 \times 82\% + 2.17 \times 18\% = 0.64$ ns

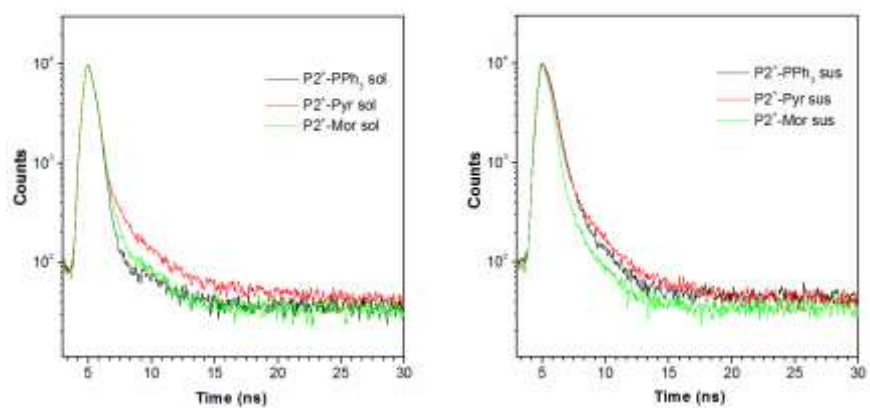


Fig. S10 Fluorescence decay curves of P2⁺-PPh₃ and P2⁺-Mor in DMSO solution, P2⁺-Pyr in methanol solution and all in THF suspension.

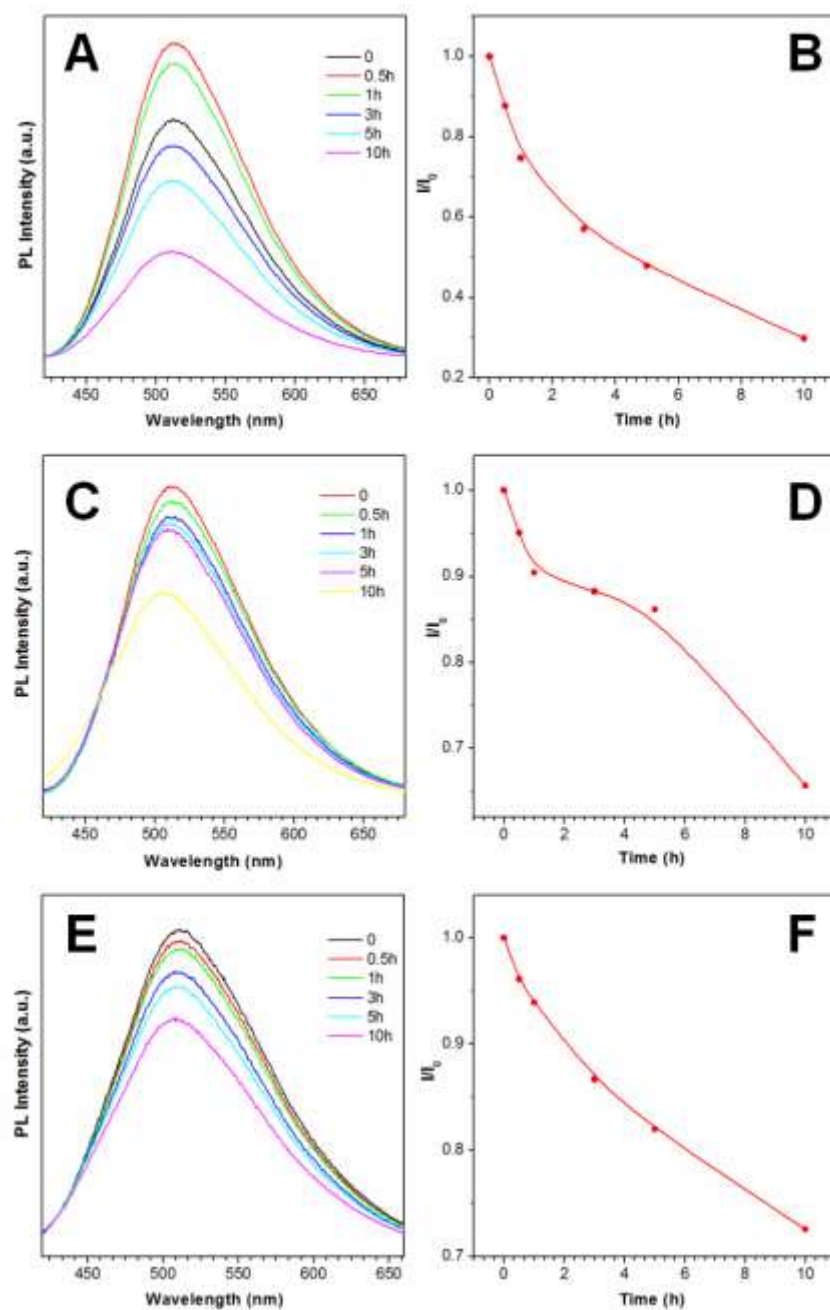


Fig. S11 (A, C, E) PL spectra of P1⁺-Mor (A), P1⁺-PPH₃ (C) and P1⁺-Pyr (E) in THF solution under UV light with different exposure times; (B, D, F) Plots of I/I_0 of P1⁺-Mor (B), P1⁺-PPH₃ (D) and P1⁺-Pyr (F) versus the different exposure times. I_0 = PL intensity with 10 h exposure time. Concentration: 10 μ M; excitation wavelength: 370 nm.

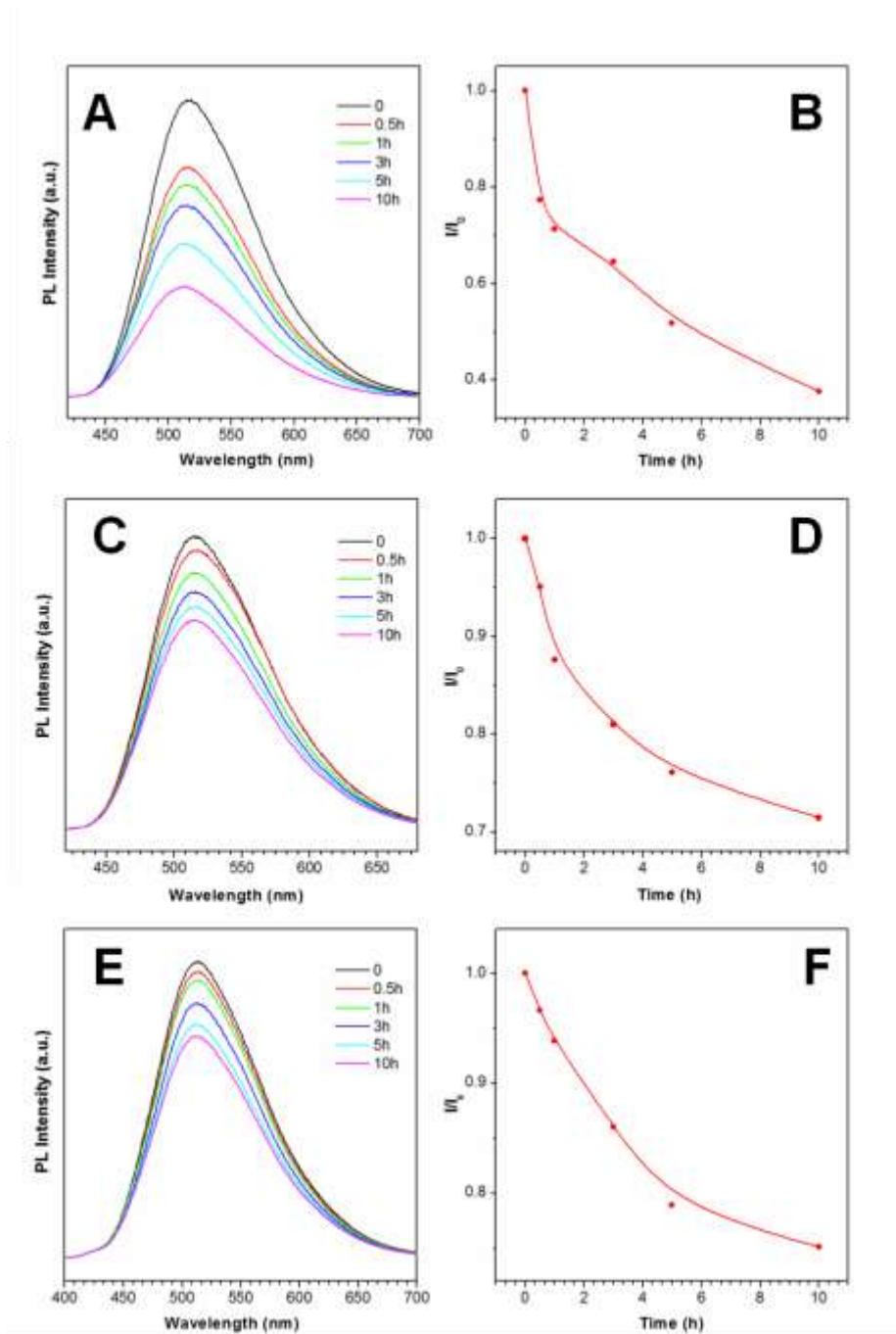


Fig. S12 (A, C, E) PL spectra of P2⁺-Mor (A), P2⁺-PPh₃ (C), and P2⁺-Pyr (E) in THF solution under UV light with different exposure times, respectively; (B, D, F) Plots of I/I₀ of P2⁺-Mor (B), P2⁺-PPh₃ (D) and P2⁺-Pyr (F) versus the different exposure times. I₀ = PL intensity with 10 h exposure time. Concentration: 10 μM; excitation wavelength: 370 nm.

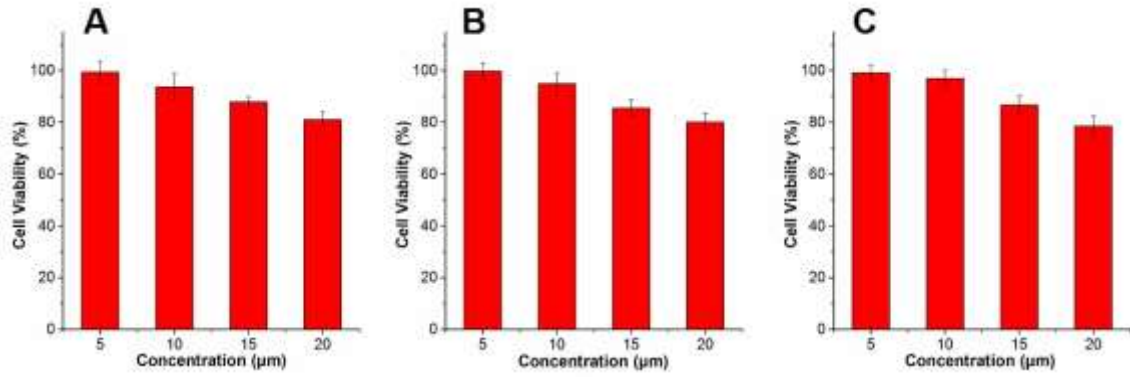


Fig. S13 Cytotoxicity of P1⁺-Mor (A), P1⁺-PPh₃ (B) and P1⁺-Pyr (C) on HeLa cells determined by MTT assay.

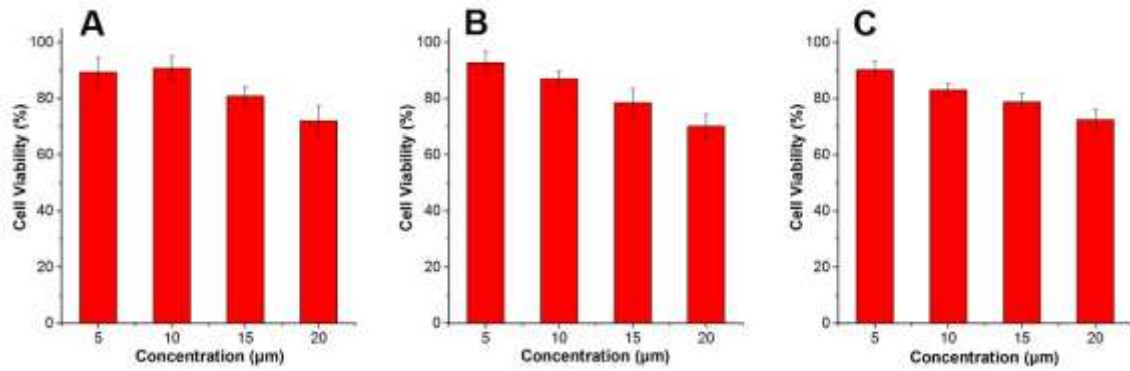


Fig. S14 Cytotoxicity of P2⁺-Mor (A), P2⁺-PPh₃ (B) and P2⁺-Pyr (C) on HeLa cells determined by MTT assay.

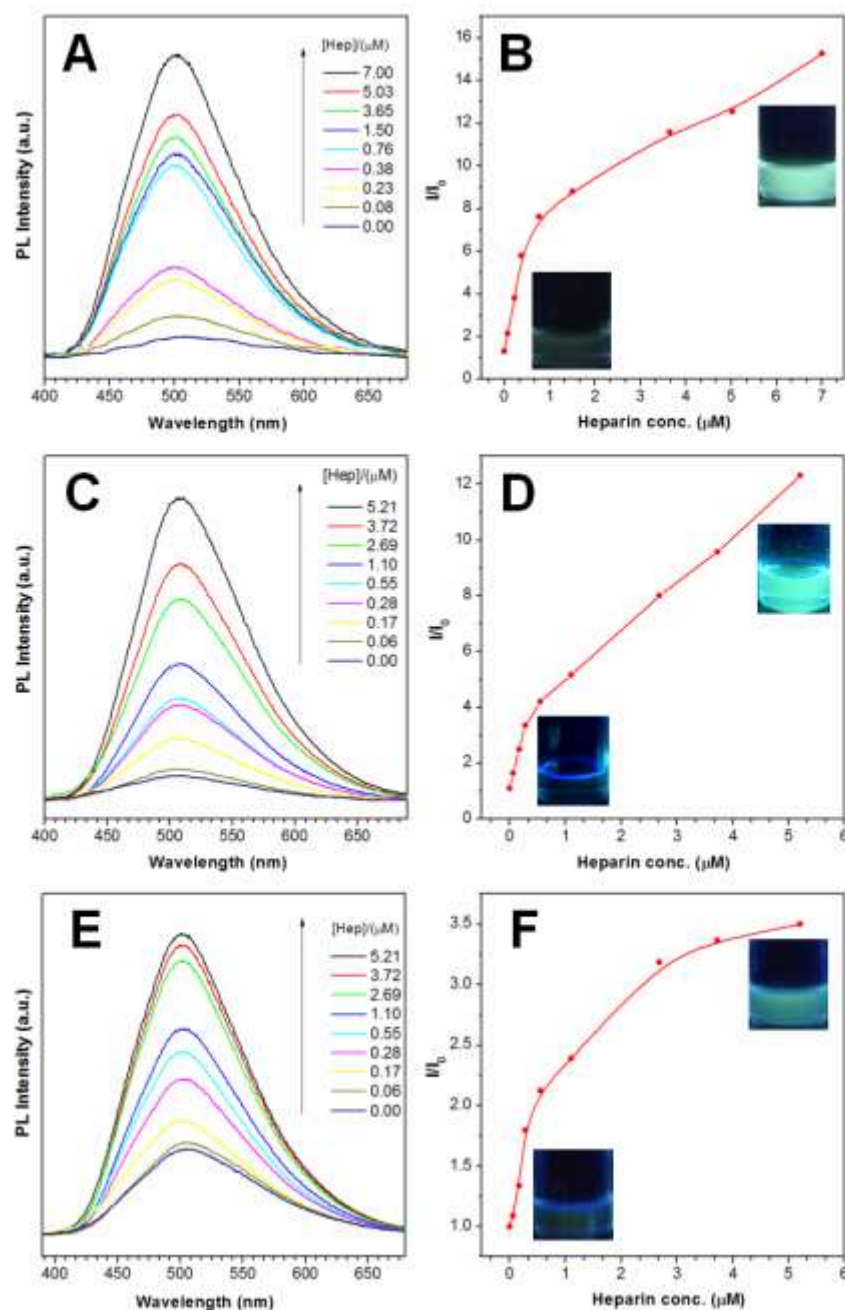


Fig. S15 (A, C, E) Fluorescence spectra of P1⁺-Mor (0.052 g/L) in THF/DMSO/PBS mixed solutions (v/v/v = 3: 10: 10), P1⁺-PPh₃ (0.04 g/L) in THF/DMSO/PBS mixed solutions (v/v/v = 1: 1: 1), P1⁺-Pyr (0.04g/L) in THF/DMSO/PBS mixed solutions (v/v/v = 1: 1: 1) with different amounts of heparin (Hep); (B, D, F) Plots of the relative PL intensity (I/I₀) of P1⁺-Mor, P1⁺-PPh₃ and P1⁺-Pyr at 510 nm versus the Hep concentrations in mixed solutions. Inset: (B) Photographs of P1⁺-Mor in mixed solutions without Hep and with 7.00 μM Hep taken under illumination of a UV lamp;

(D, F) Photographs of P1⁺-PPh₃ and P1⁺-Pyr in mixed solutions without Hep and with 5.21 μM Hep taken under illumination of a UV lamp, respectively; excitation wavelength: 350 nm.

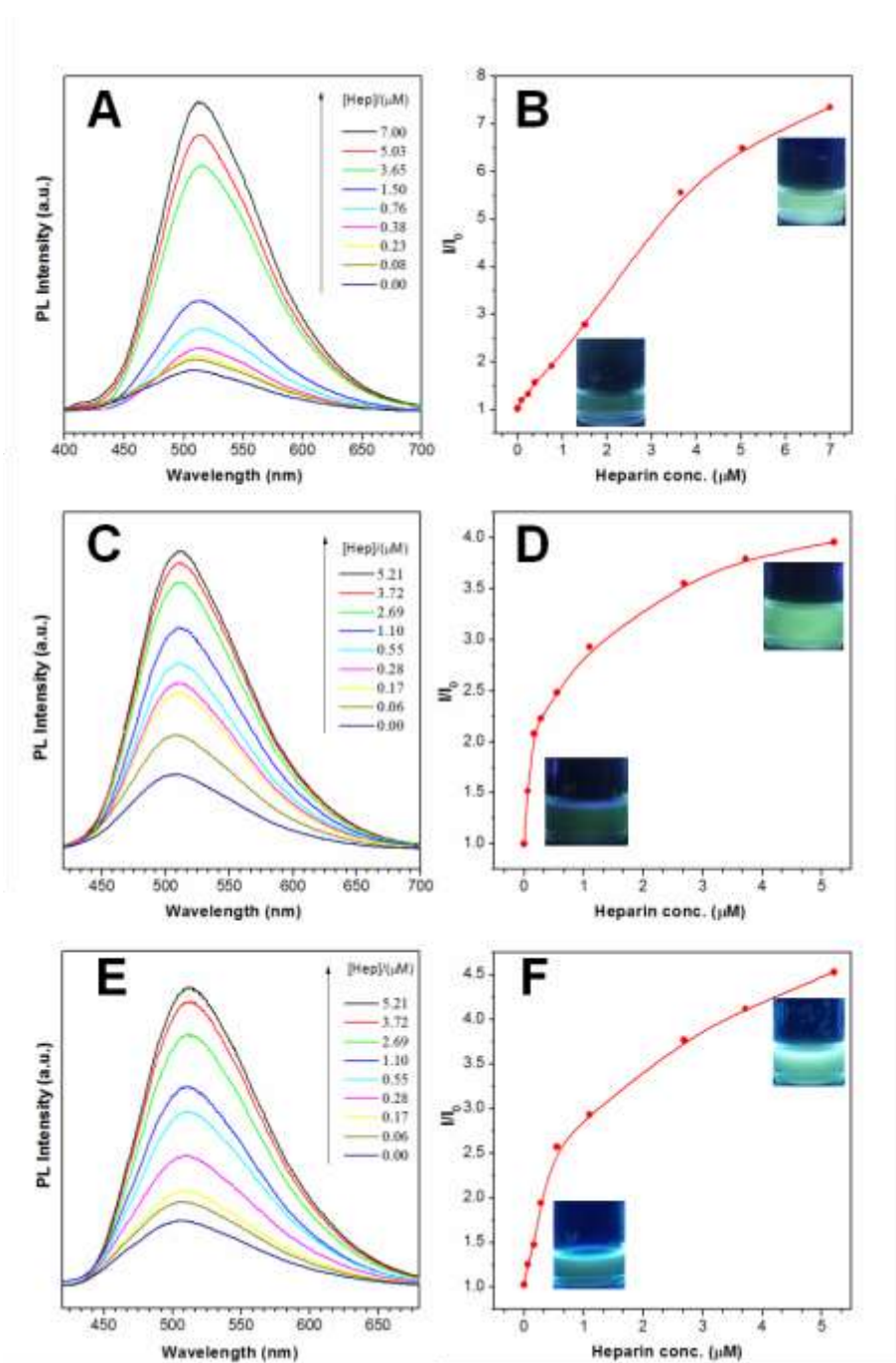


Fig. S16 (A, C, E) Fluorescence spectra of P2⁺-Mor (0.052 g/L) in THF/DMSO/PBS mixed solutions (v/v/v = 3: 10: 10) , P2⁺-PPh₃ (0.04 g/L) in THF/DMSO/PBS mixed solutions (v/v/v = 1: 1: 1), P2⁺-Pyr (0.04 g/L) in THF/DMSO/PBS mixed solutions (v/v/v = 1: 1: 1) with different amounts of heparin (Hep); (B, D, F) Plots of the

relative PL intensity (I/I_0) of P2⁺-Mor, P2⁺-PPh₃ and P2⁺-Pyr at 510 nm versus the Hep concentrations in mixed solutions. Inset: (B) Photographs of P2⁺-Mor in mixed solutions without Hep and with 7.00 μM Hep taken under illumination of a UV lamp; (D, F) Photographs of P2⁺-PPh₃ and P2⁺-Pyr in mixed solutions without Hep and with 5.21 μM Hep taken under illumination of a UV lamp; excitation wavelength: 370 nm.

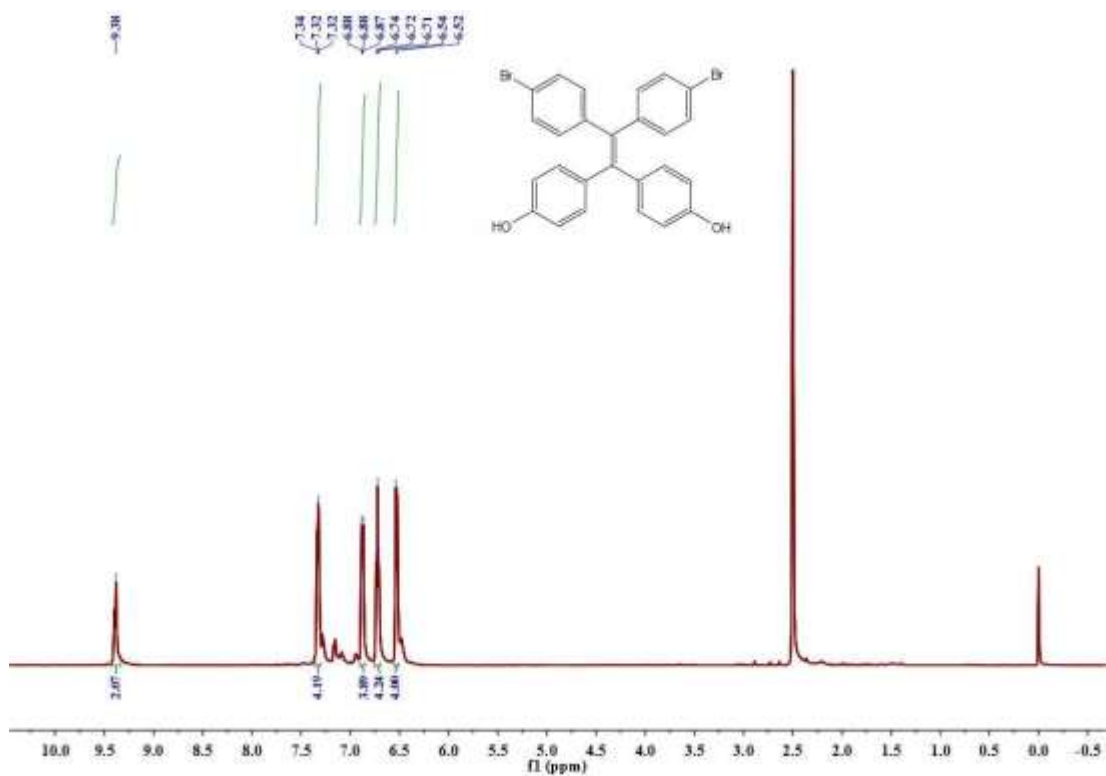


Fig. S17 ¹H NMR spectrum of compound 3.

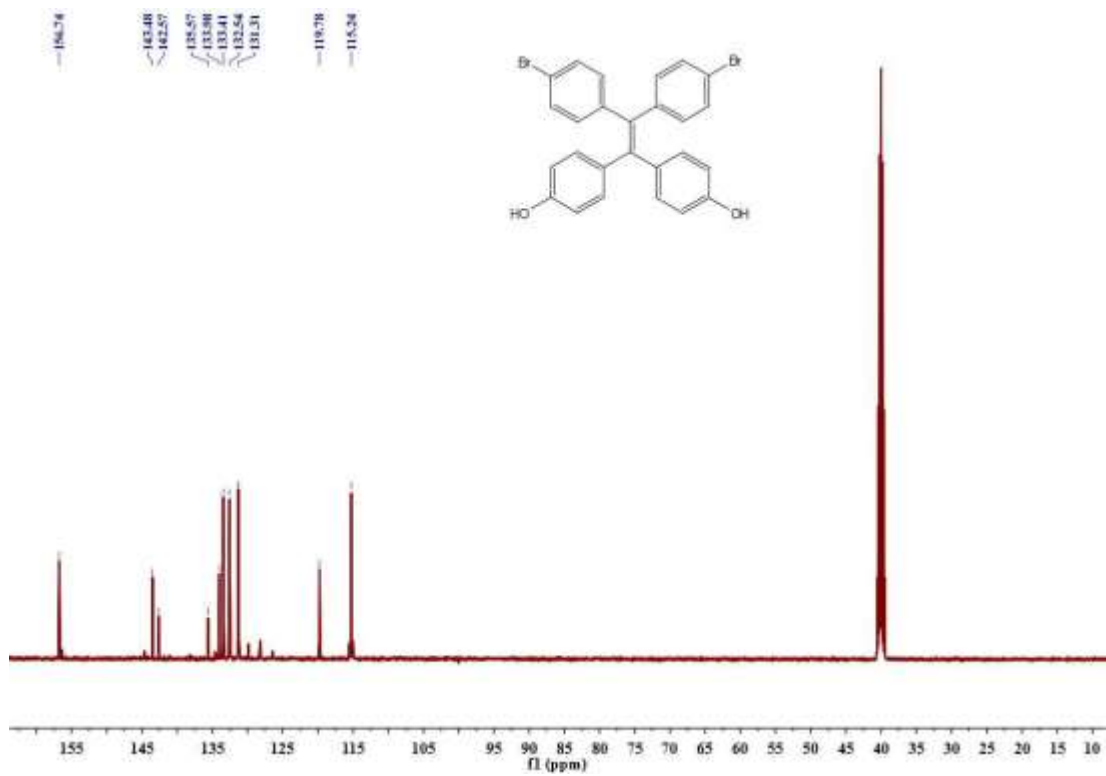


Fig. S18 ^{13}C NMR spectrum of compound 3.

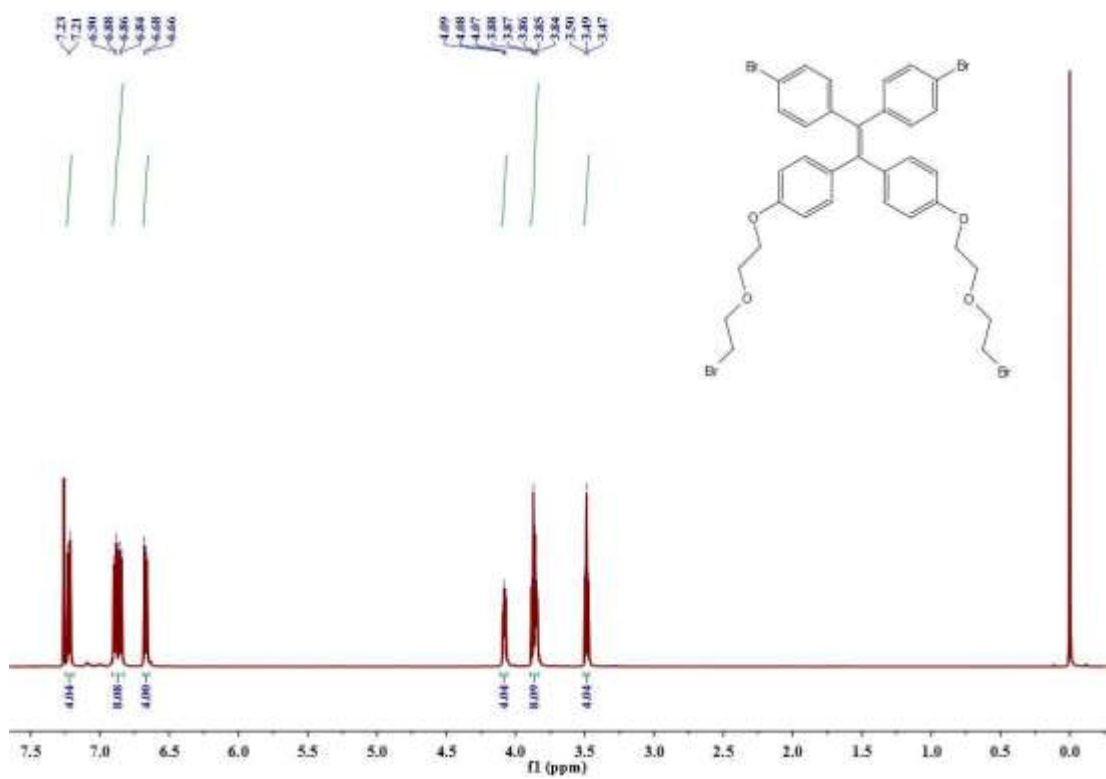


Fig. S19 ^1H NMR spectrum of compound 4.

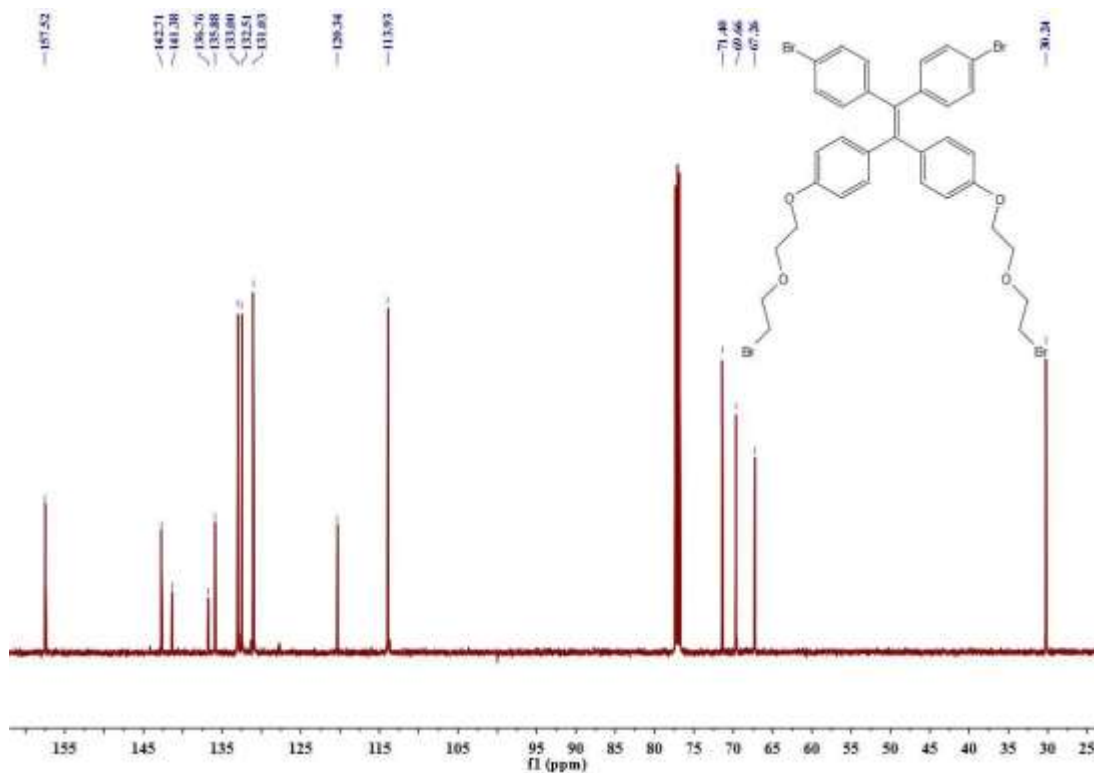


Fig. S20 ^{13}C NMR spectrum of compound 4.

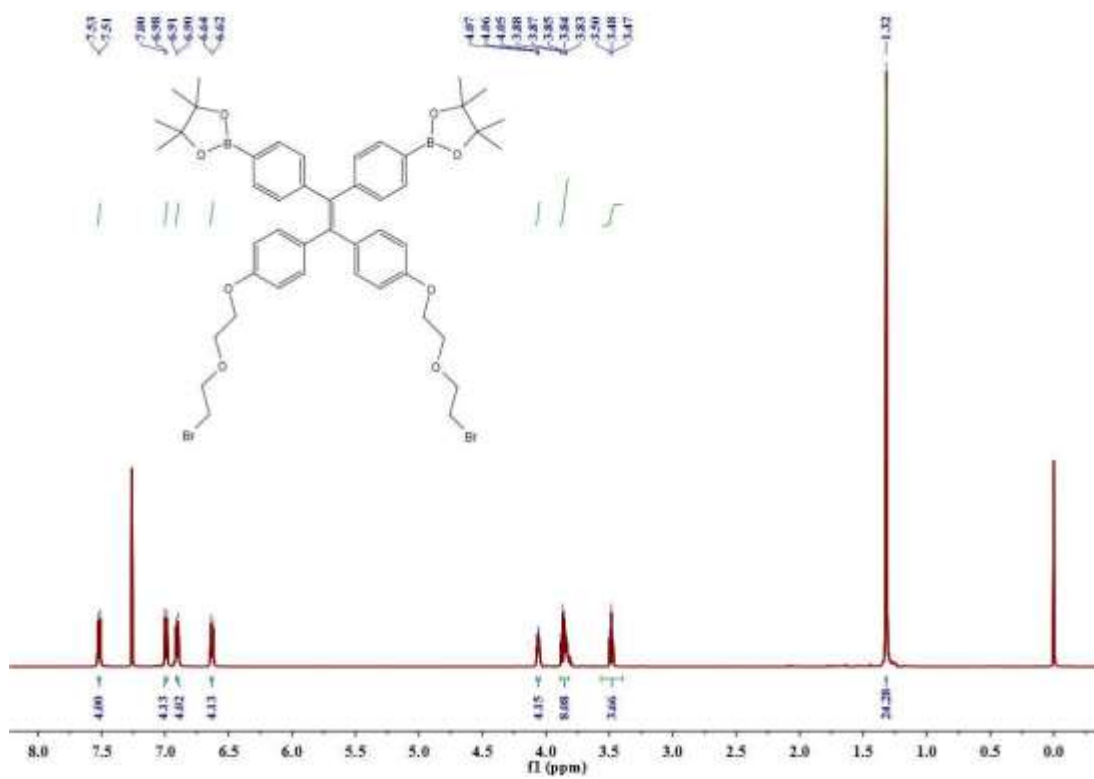


Fig. S21 ^1H NMR spectrum of compound 5.

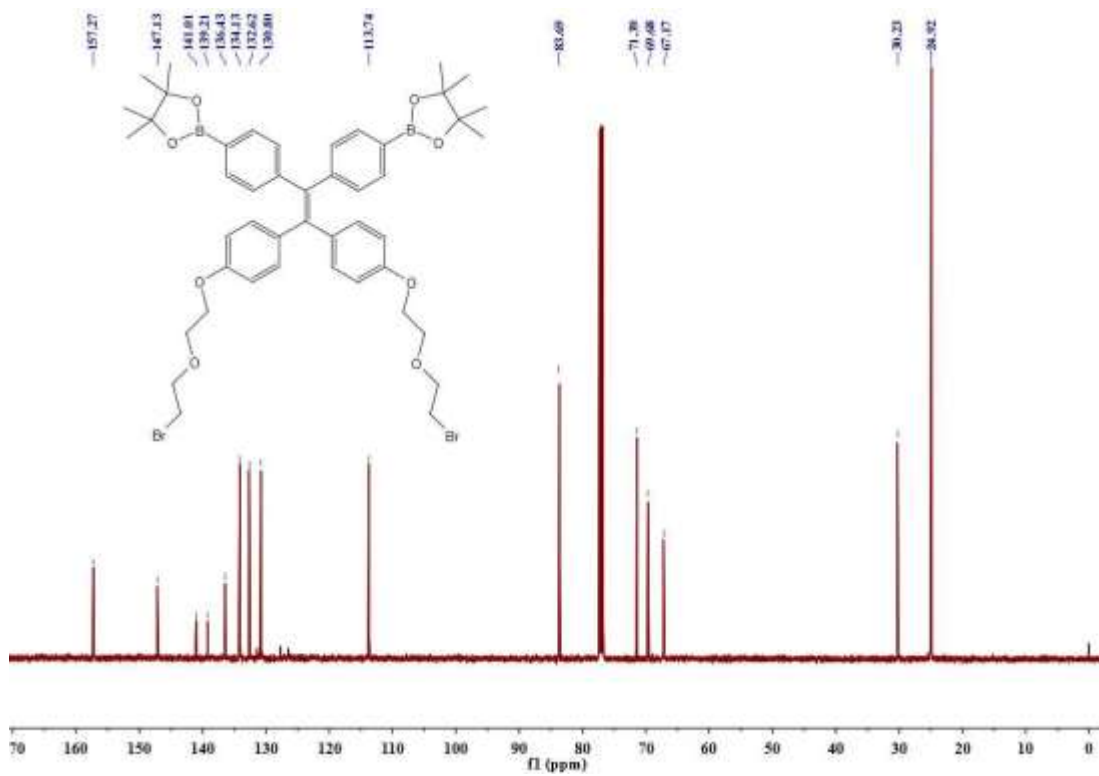


Fig. S22 ¹³C NMR spectrum of compound 5.

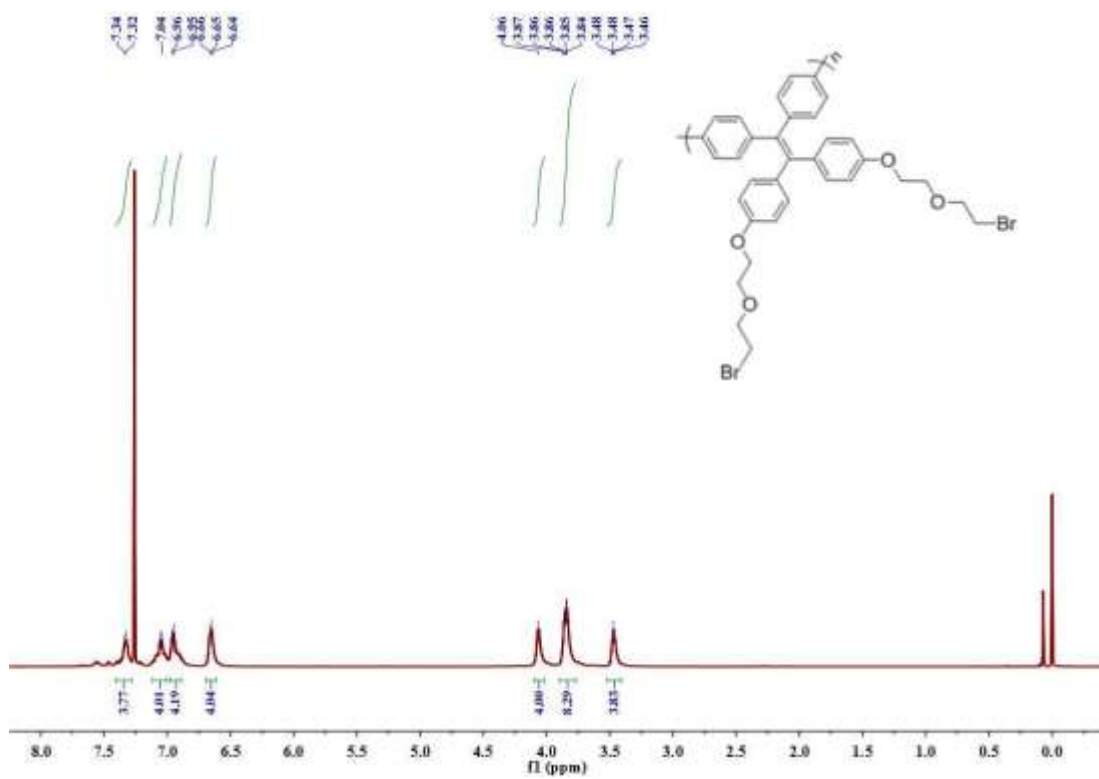


Fig. S23 ¹H NMR spectrum of polymer P1.

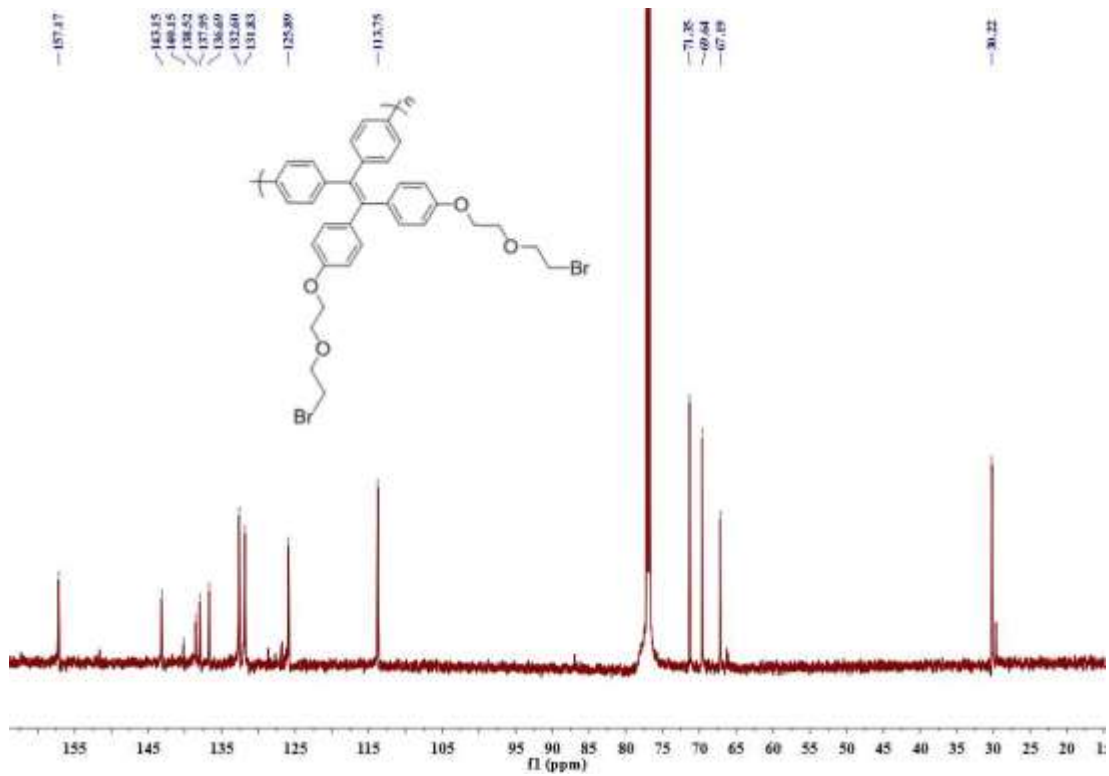


Fig. S24 ¹³C NMR spectrum of polymer P1.

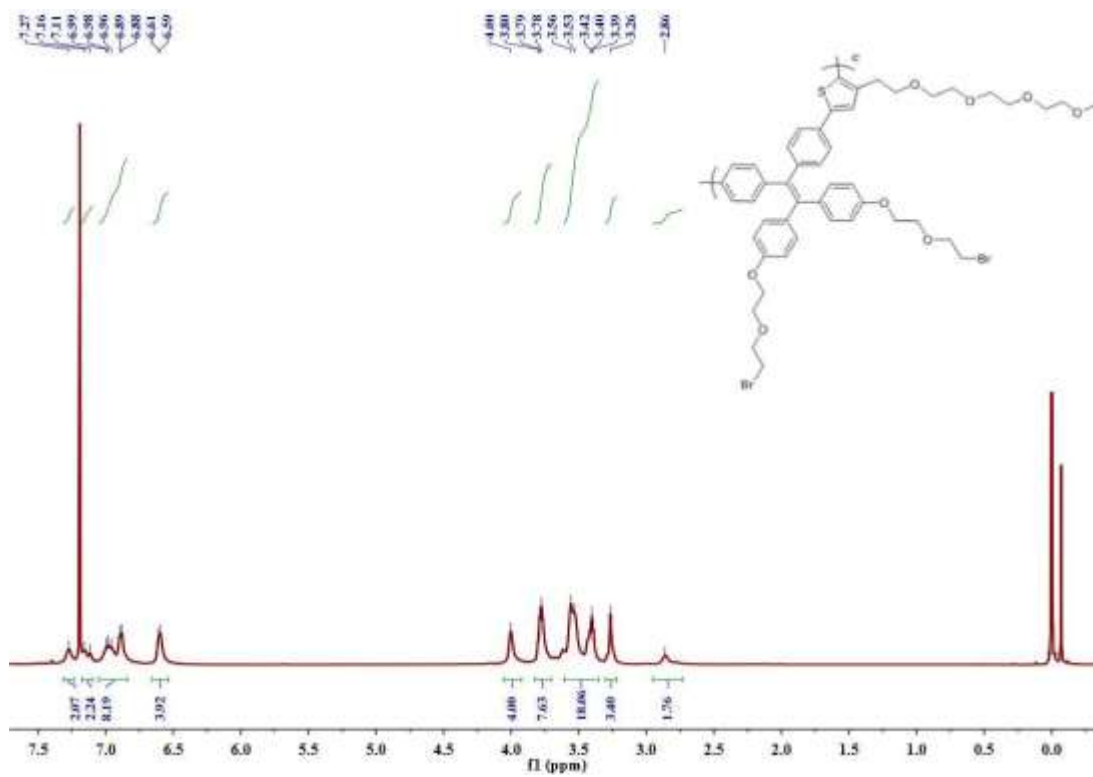


Fig. S25 ¹H NMR spectrum of copolymer P2.

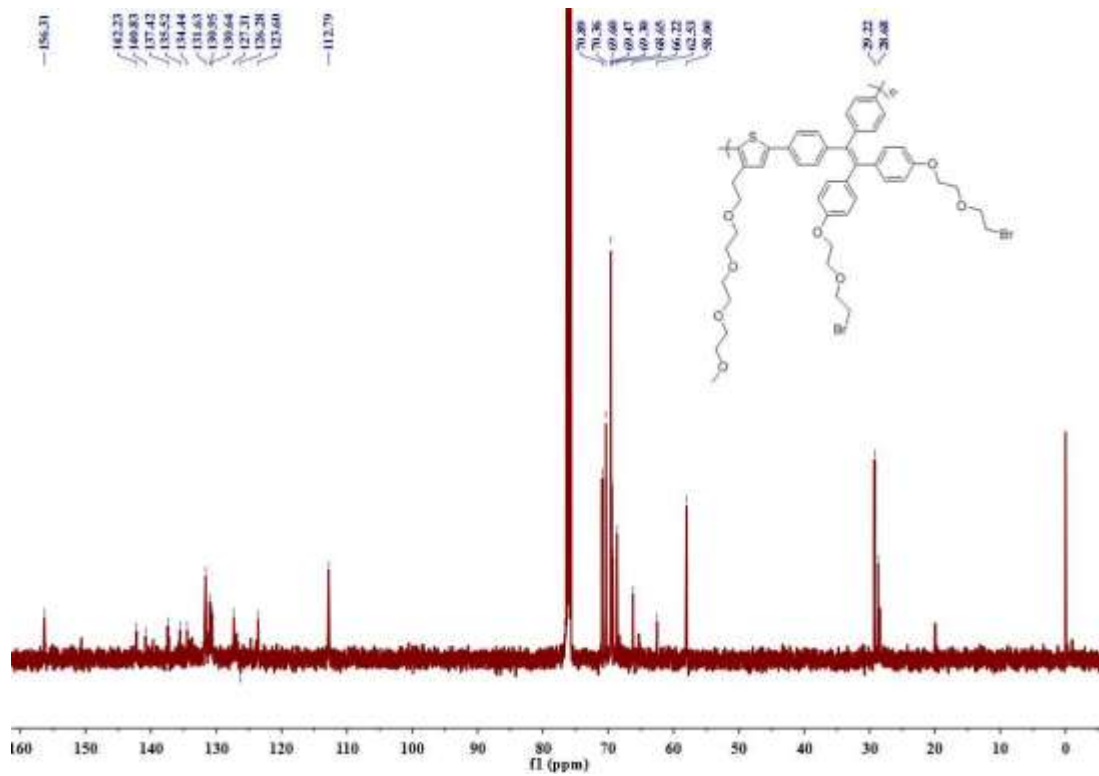


Fig. S26 ^{13}C NMR spectrum of copolymer P2.

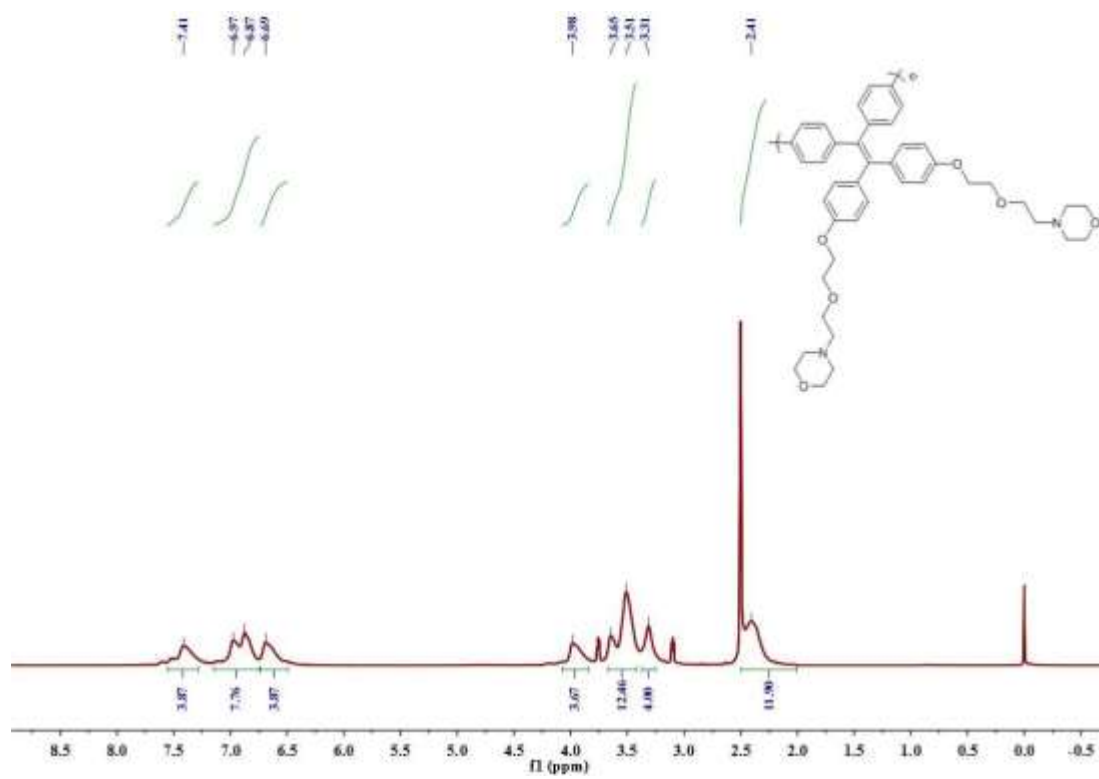


Fig.

Fig. S27 ^1H NMR spectrum of polymer P1⁺-Mor.

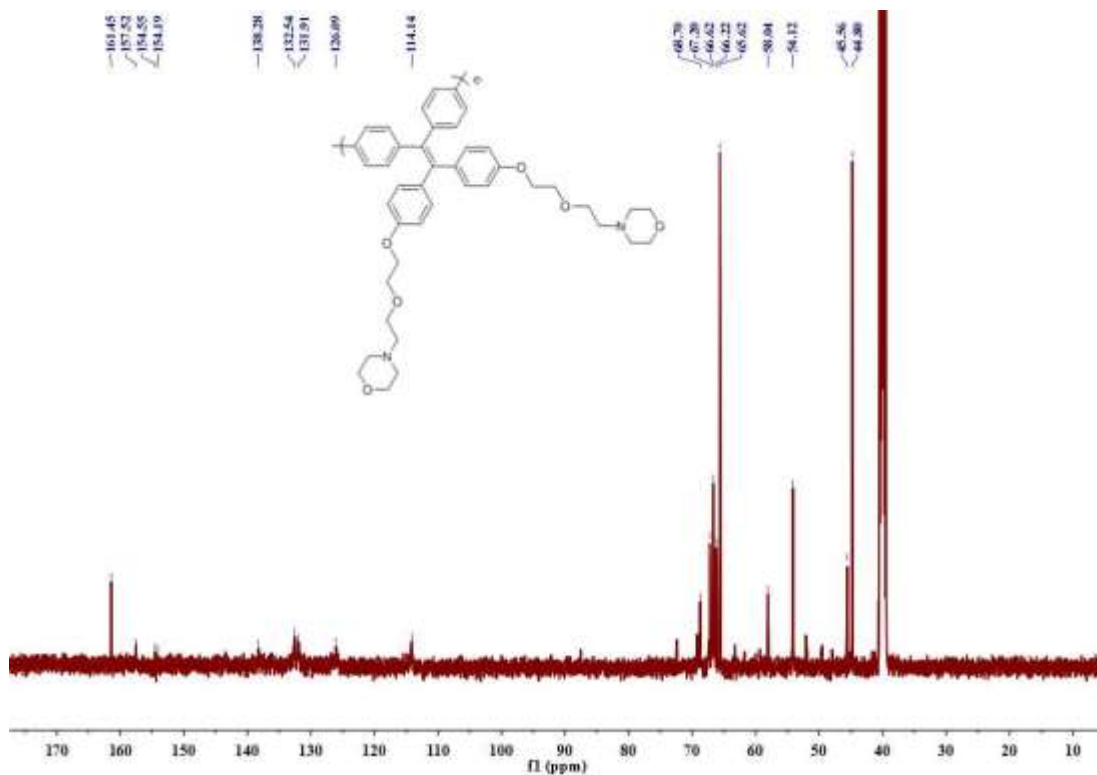


Fig. S28 ^{13}C NMR spectrum of polymer **P1⁺-Mor**.

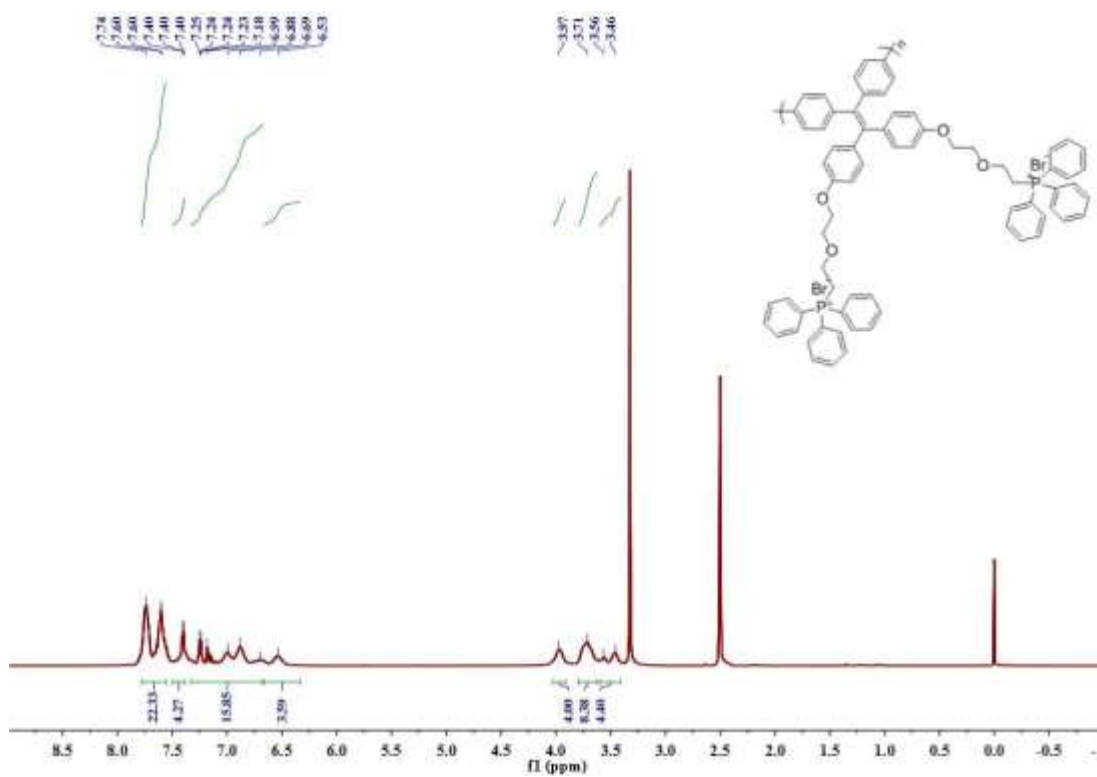


Fig.

Fig. S29 ^1H NMR spectrum of polymer **P1⁺-PPh₃**.

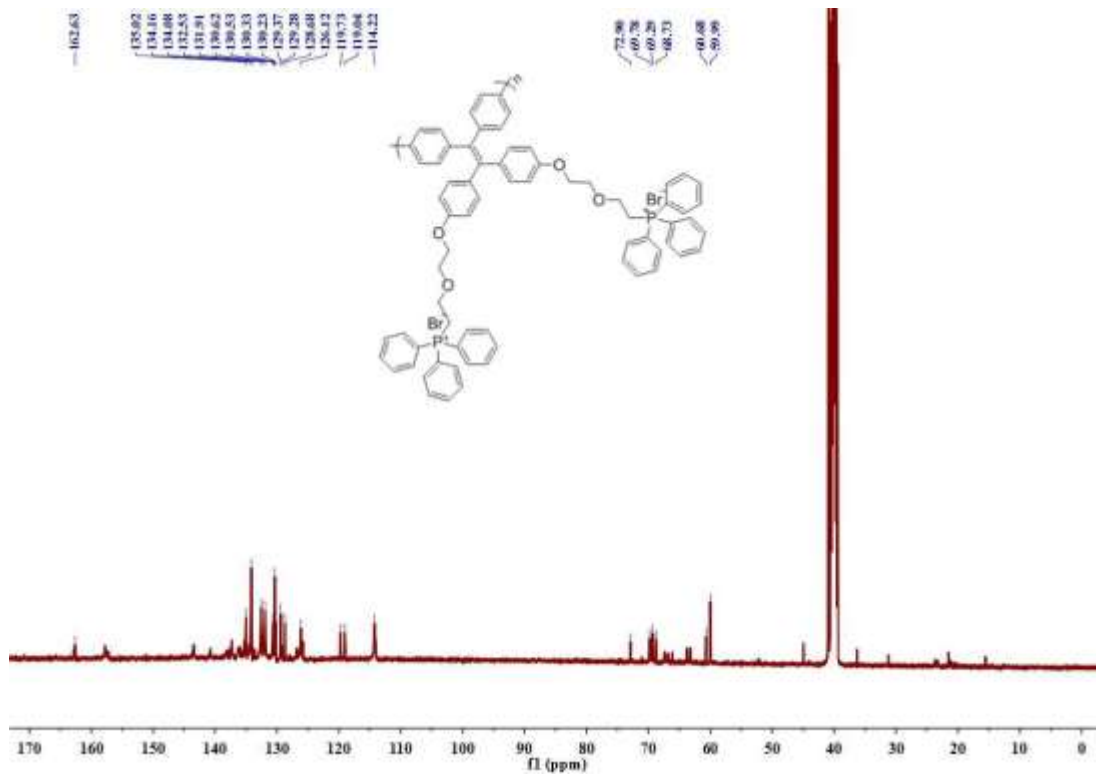


Fig. S30 ¹³C NMR spectrum of polymer **P1⁺-PPh₃**.

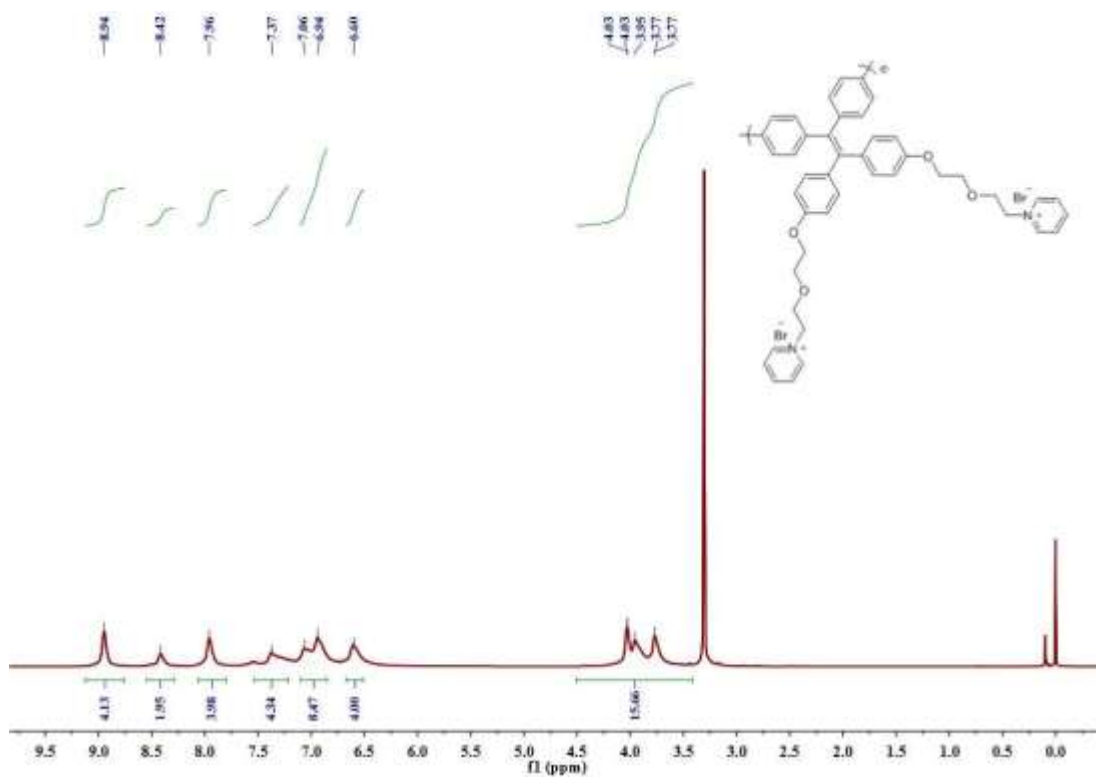


Fig. S31 ¹H NMR spectrum of polymer **P1⁺-Pyr**.

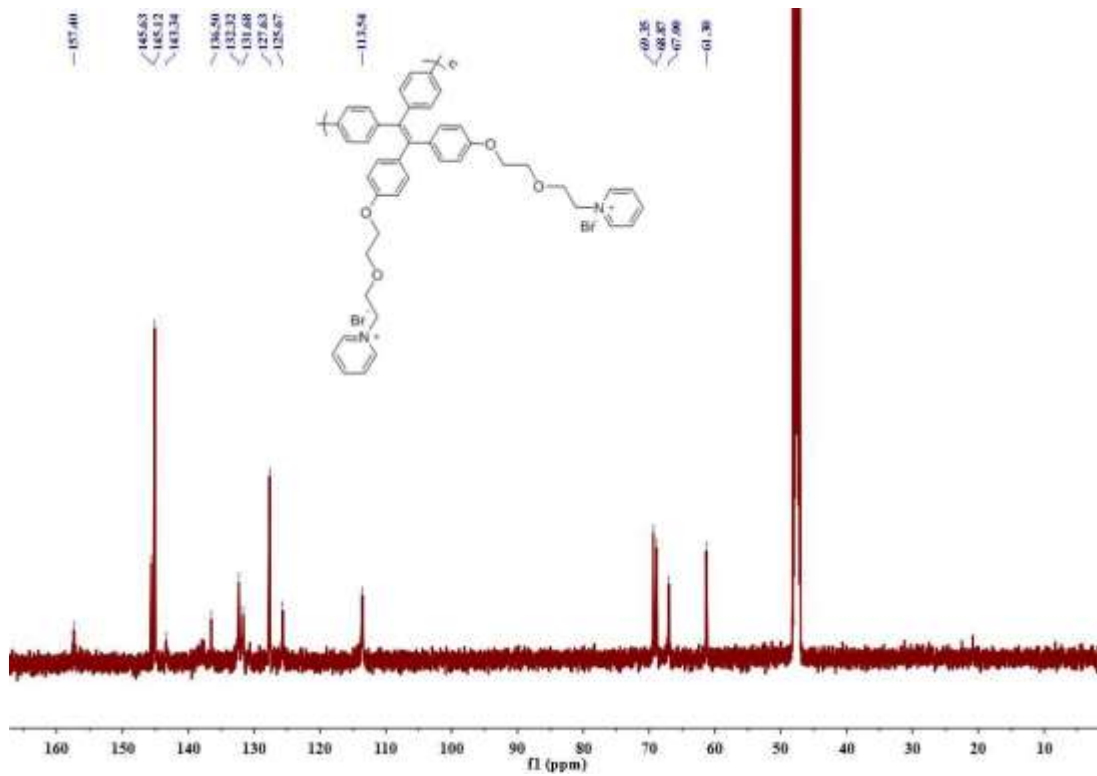


Fig. S32 ^{13}C NMR spectrum of polymer $P1^+-Pyr$.

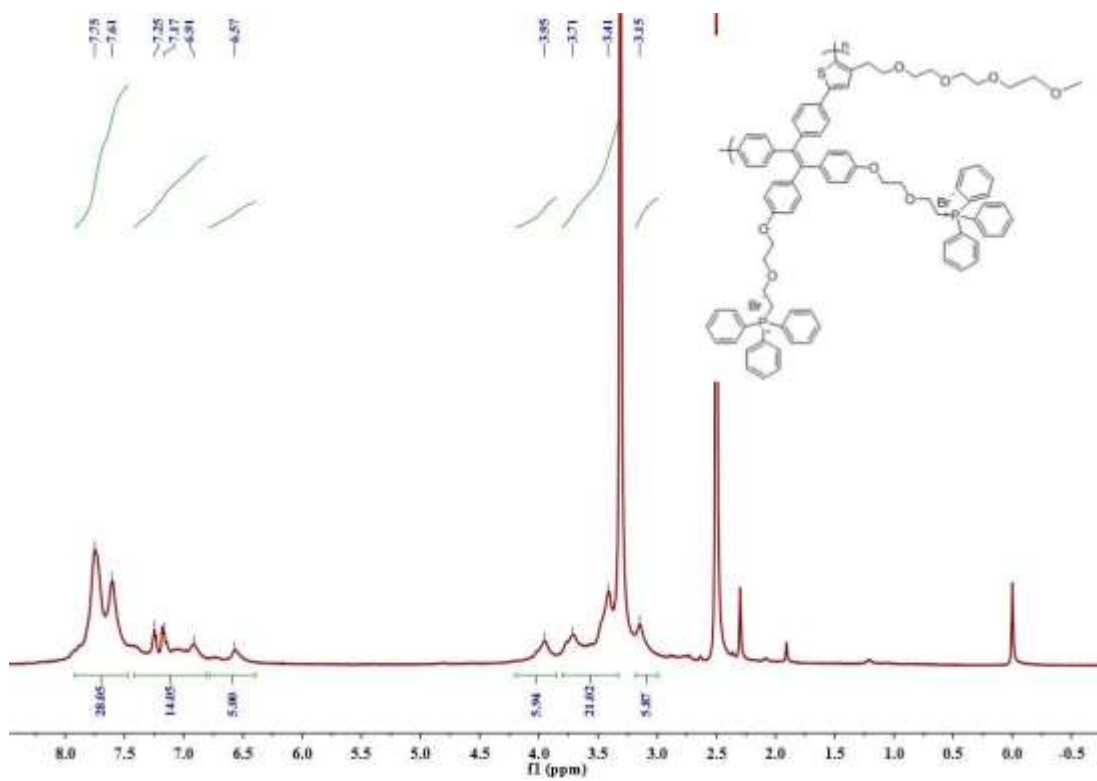


Fig. S33 1H NMR spectrum of copolymer $P2^+-PPh_3$.

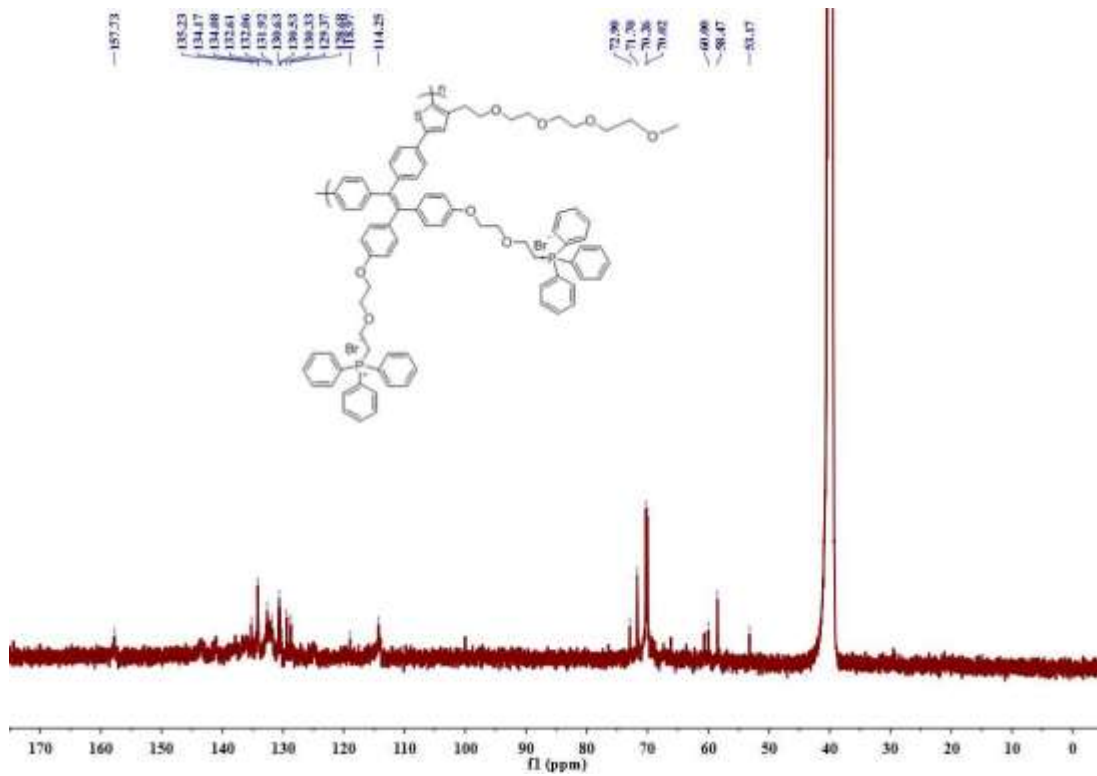


Fig. S34 ^{13}C NMR spectrum of copolymer $P2^+-PPh_3$.

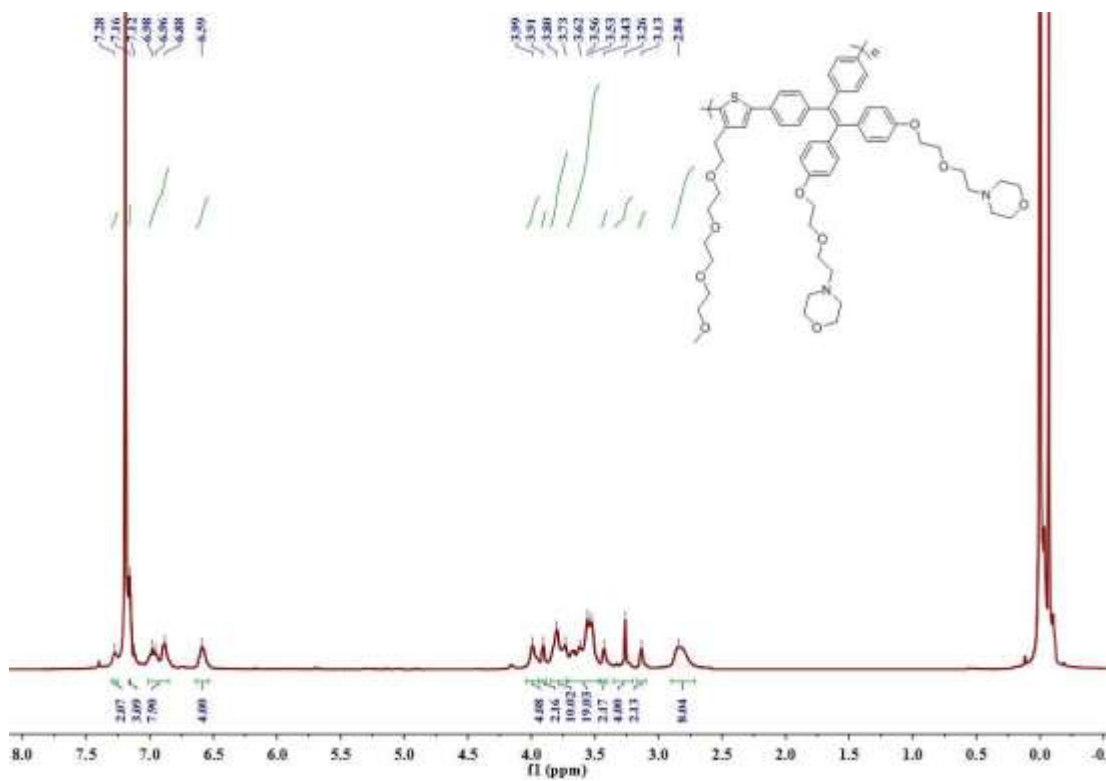


Fig. S35 1H NMR spectrum of copolymer $P2^+-Mor$.

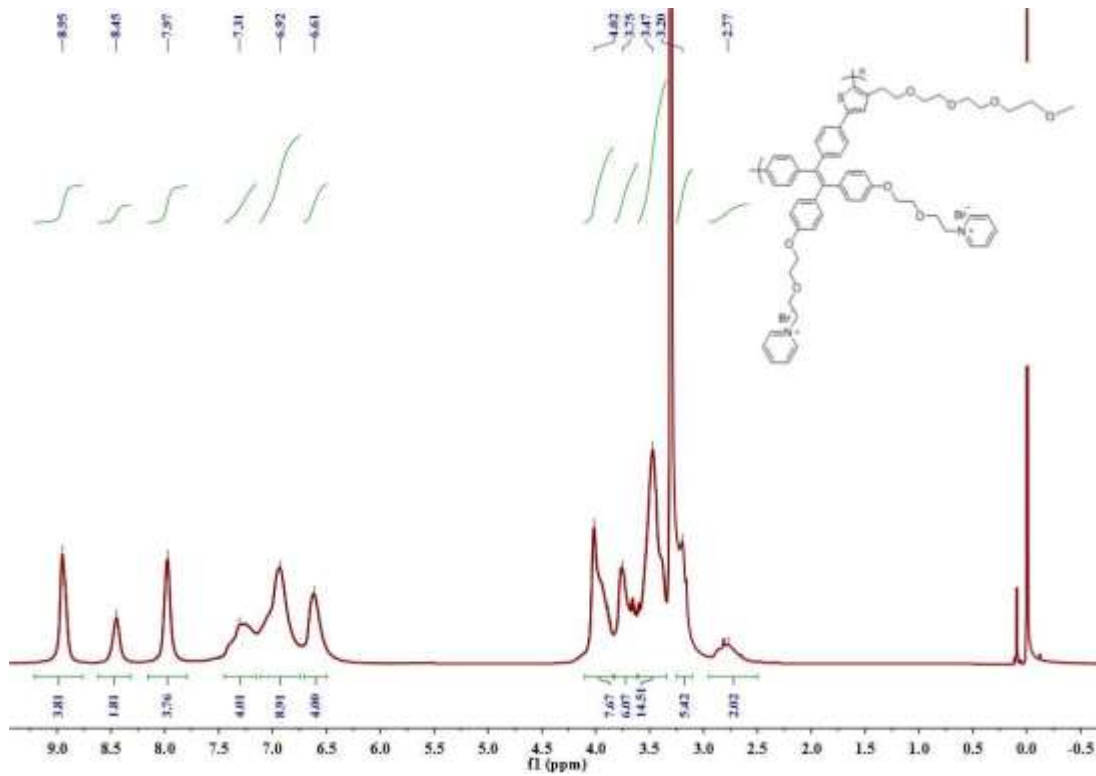


Fig. S36 ¹H NMR spectrum of copolymer P2⁺-Pyr.

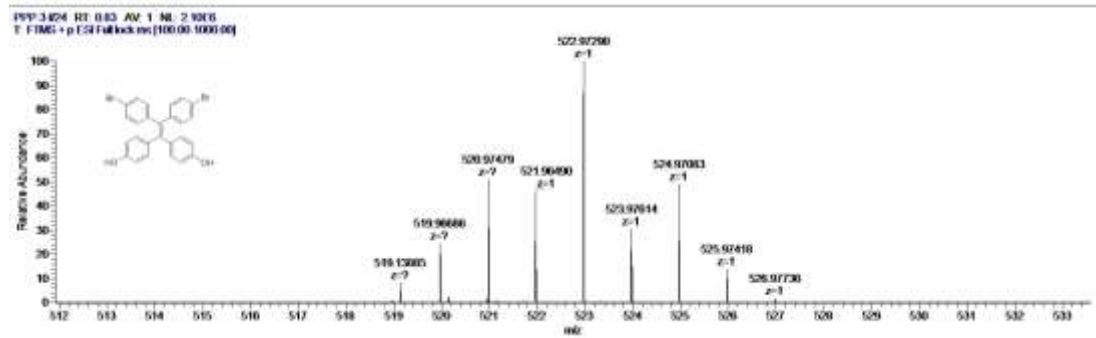


Fig. S37 Mass spectrum of compound 3.

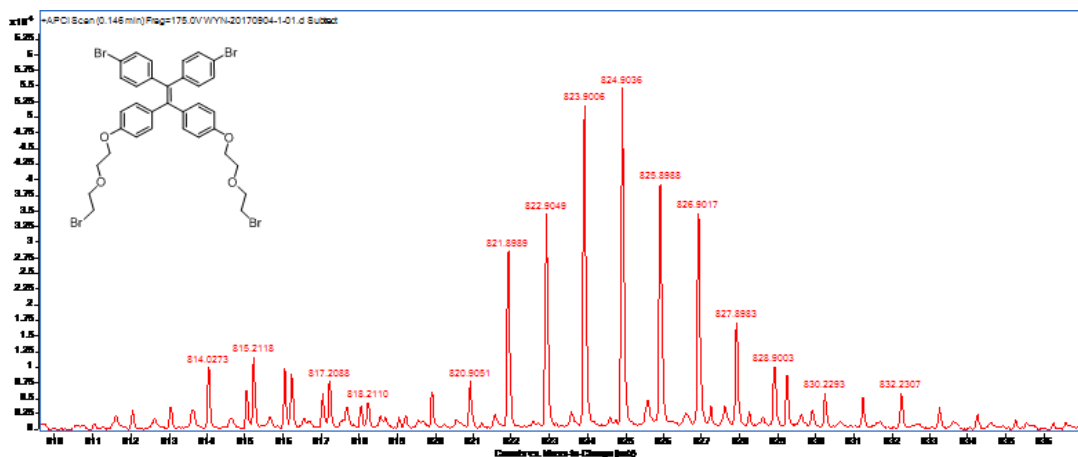


Fig. S38 Mass spectrum of compound 4.

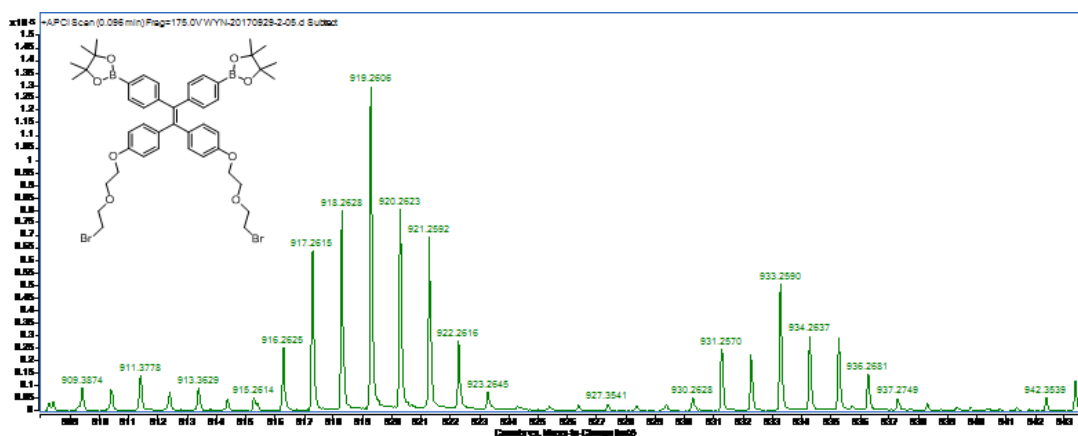


Fig. S39 Mass spectrum of compound 5.

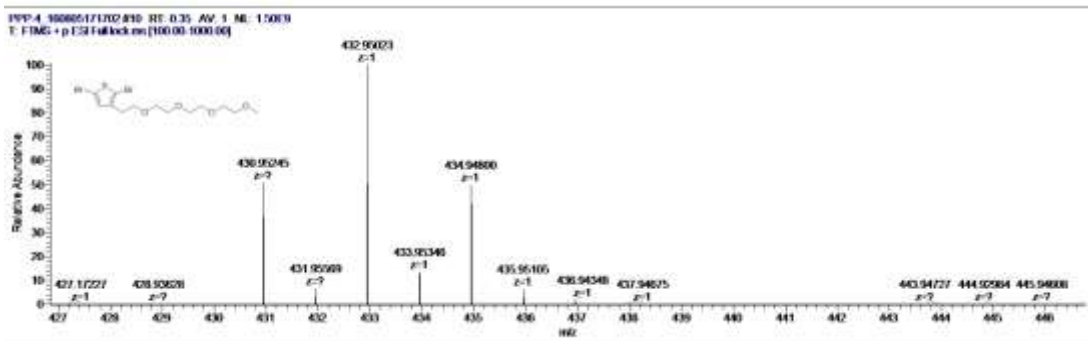


Fig. S40 Mass spectrum of compound 6.

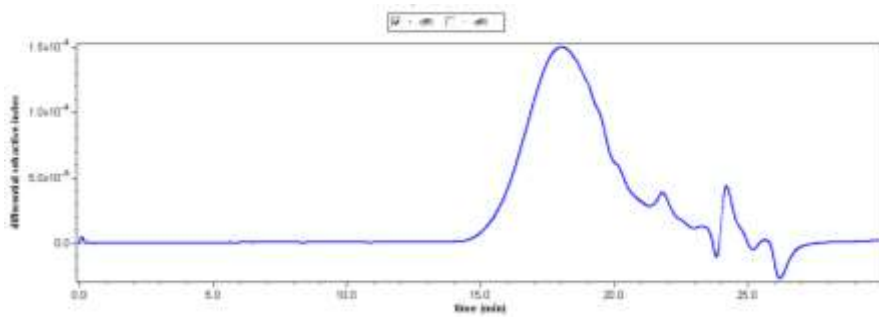


Fig. S41 GPC of polymer P1.

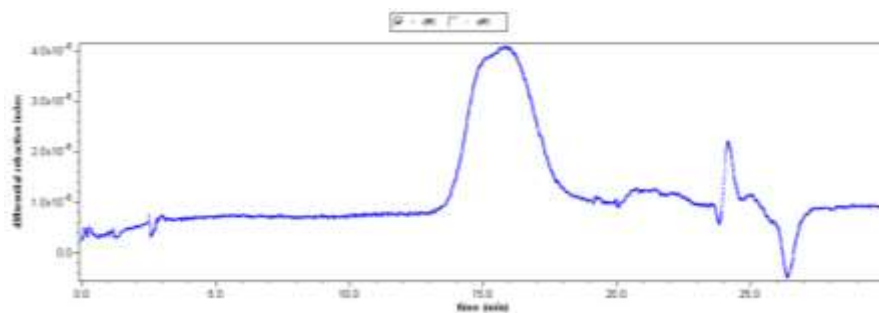


Fig. S42 GPC of copolymer P2.