Electronic Supplementary Material (ESI) for Chemical Communications

Supramolecular graft copolymers in moderately polar media based on hydrogen-bonded aromatic oligoamide units

Xusong Pan,[a] Chao Chen,[a] Jiang Peng,[a] Yongan Yang,[a] Yinghan Wang,[a] Wen Feng,*[a] Pengchi Deng*[b] and Lihua Yuan*[a]

[a] College of Chemistry, Key Laboratory for Radiation Physics and Technology of Ministry of Education, Institute of Nuclear Science and Technology, State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610064, China.

[b] Analytical & Testing Center of Sichuan University, Sichuan University, Chengdu 610064, China.

Supporting Information

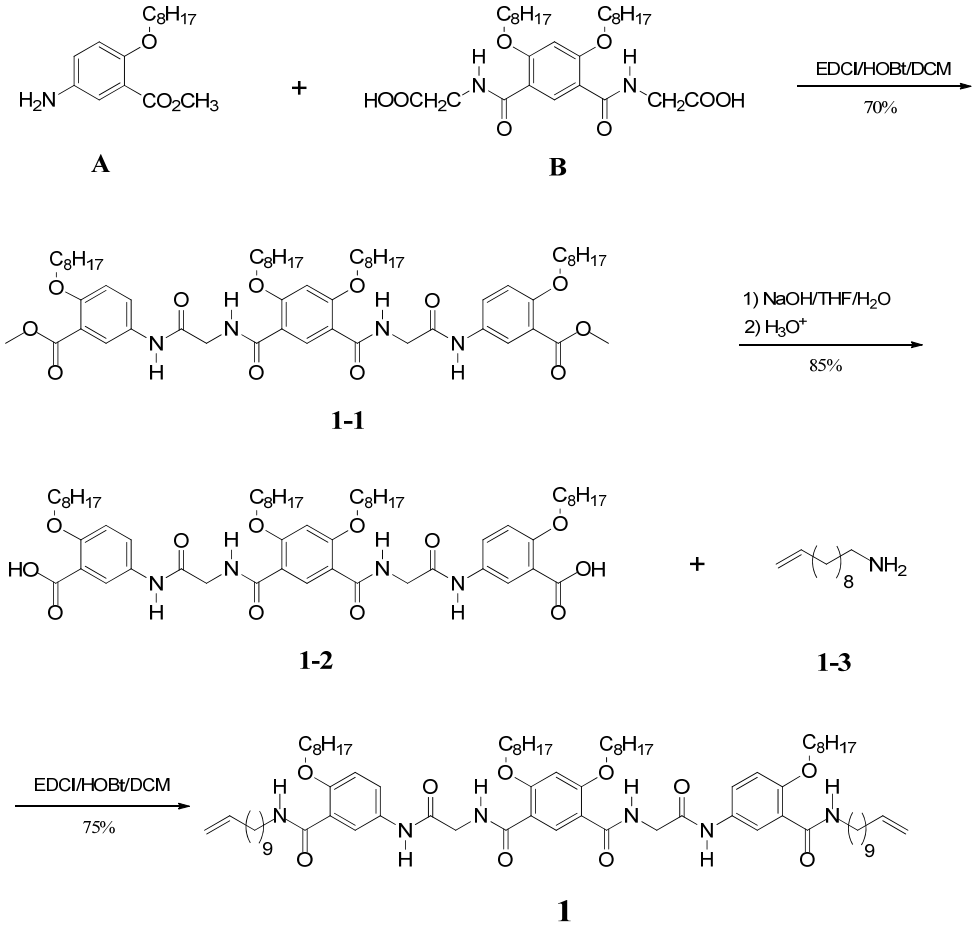
1. General Experimental Methods

All reactions were conducted with oven-dried glassware under atmosphere or nitrogen. Chemical grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Column chromatography was carried out using silica gel (300-400 mesh). The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz) and Bruker Avance AVANCE AV II-600 MHz (^{1}H: 600 MHz; ^{13}C: 150 MHz). Chemical shifts were expressed in parts per million (δ) using tetramethylsilane (TMS) or residual solvent protons as internal standards (^{1}H: chloroform: δ 7.26 ppm; DMSO: δ 2.49 ppm; DMF: δ 8.01 ppm; ^{13}C: $CDCl_3$: 77.23 ppm.). Coupling constants in ^{1}H NMR were expressed in Hertz. Multiplicities were denoted as follows: s = singlet, d = doublet, t = triplet and m = multiplet. Gel permeation chromatography (GPC) was used to determine the molecular weights and polydispersity indices of the polymers on the basis of a polystyrene calibration curve. The GPC instrument was performed on Waters 150-c ALC/GPC and was equipped with two consecutive Waters Styragel columns (2 × 30 cm) including a RI detector. UV-vis spectra were measured by UV-2350.

2. Synthesis of Compounds for Supramolecular Graft Copolymer

2.1 Synthesis of Monomer 1

Scheme S1 Synthetic route of monomer **1**



General procedure for the synthesis of compounds A and B.

Compounds **A** and **B** were prepared according to previously reported literature procedure,[S1] and compound **A** was used for the next step without isolation and further purification after catalytic hydrogenation.

Compound B

White solid (90% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.76 (br, 2H), 8.53 (s, 1H), 8.29 (t, J = 5.2 Hz, 2H), 6.79 (s, 1H), 4.25 (t, J = 6.4 Hz, 4H), 4.02 (d, J = 5.2 Hz, 4H), 1.85 (m, 4H), 1.43-1.20 (m, 20H), 0.85 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.88, 163.52, 160.14, 134.87, 113.87, 97.88, 69.44, 41.39, 31.02, 28.49, 28.41, 28.11, 25.33, 21.88, 13.73.

Compound 1-1[S1]

A mixture of acid **B** (3.90 g, 7.30 mmol), EDCI (1.70 g, 8.80 mmol) and HOBt (1.20 g, 8.80 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and stirred for 1 h. Then the solution of amide A (4.30 g, 14.5 mmol) in dry CH_2Cl_2 (10 mL) was dropped into the mixture under N_2 atmosphere. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The crude product was further purified by column chromatography (silica, 5% methanol/chloroform) to give **1-1** as a white solid (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.12 (s, 2H), 9.06 (s, 1H), 8.46 (t, J = 4.9 Hz, 2H), 7.91 (d, J = 2.6 Hz, 2H), 7.85 (dd, J = 9.0, 2.6 Hz, 1H), 6.93 (d, J = 9.0 Hz, 2H), 6.52 (s, 1H), 4.37 (d, J = 4.9 Hz, 4H), 4.09 (d, J = 5.5 Hz, 4H), 3.87 (dd, J = 5.5, 2.0 Hz, 4H), 3.85 (s, 6H), 1.98 (dt, J = 12.0, 6.0 Hz, 2H), 1.73 (dt, J = 12.2, 6.0 Hz, 2H), 1.62 – 1.23 (m, 32H), 0.97 (t, J = 7.4 Hz, 6H), 0.93 – 0.85 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.83, 165.01, 164.52, 160.54, 153.22, 136.44, 132.89, 124.95, 123.51, 121.85, 115.33, 112.97, 96.51, 69.91, 69.58, 44.69, 40.13, 31.92, 31.81, 31.62, 29.52, 29.47, 29.41, 29.38, 29.24, 26.86, 26.30, 22.65, 22.61, 14.07, 13.97. m/z calcd for $[C_{60}H_{90}N_4O_{12}+H]^+$ 1059.6555; found: 1059.6587.

Compound 1-2

Compound **1-1** (0.58 g, 0.55 mmol) was dissolved in THF (20 mL), to which a solution of NaOH (0.066 g, 20 mL) in H_2O (20 mL) was added. The mixture was heated under reflux for 30-40 minutes, and water (100 mL) was added. The aqueous layer was neutralized by addition of concentrated HCl to pH 3.0. The precipitated crude product was collected, and recrystallized from MeOH to give **1-2** as a white solid (93% yield).

Compound 1-3

Compound **1-3** was prepared according to previously reported literature procedure.[S2] White solid (69.5% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (m, 1H), 4.96 (m, 2H), 2.67 (t, 2H), 2.02 (dd, 2H), 1.32 (m, 16H).

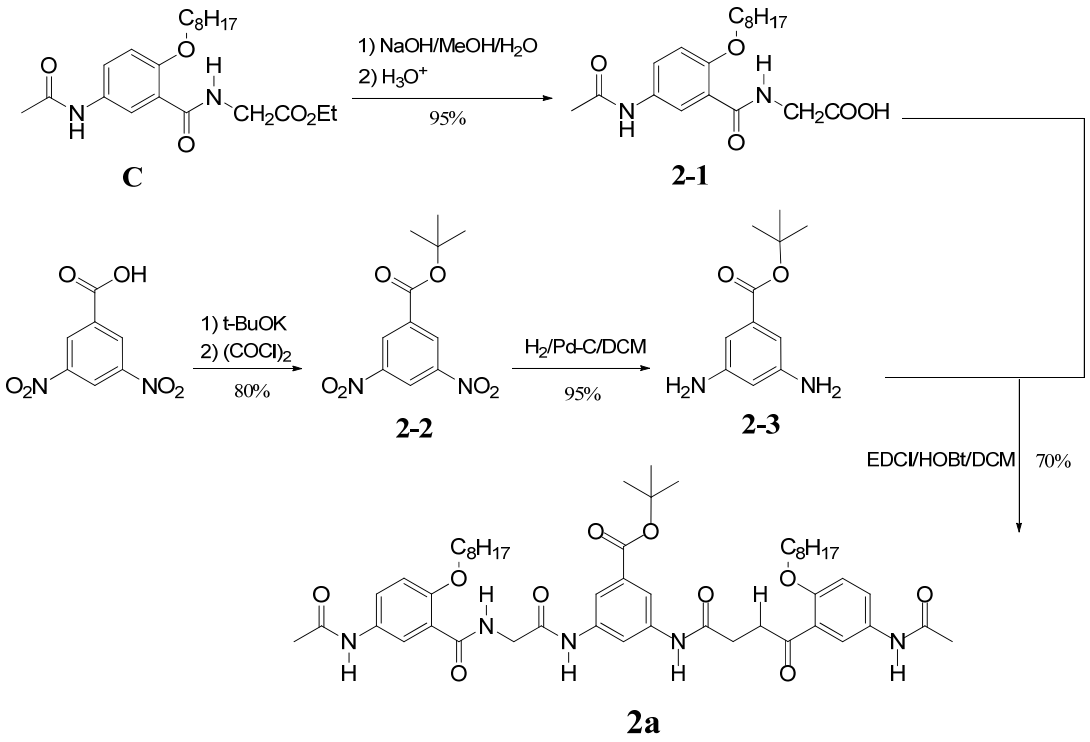
Monomer 1

A mixture of acid **1-2** (0.21 g, 0.21 mmol), EDCI (0.10 g, 0.57 mmol) and HOBt (0.077 g, 0.57 mmol) was dissolved in dry CH_2Cl_2 (5 mL) and stirred for 1 h. Then the solution of **1-3** (0.11 g, 0.51 mmol) in dry CH_2Cl_2 (5 mL) was added into the mixture under N_2 atmosphere. After stirring overnight at room temperature, the solvent was

removed under reduced pressure. The crude product was further purified by column chromatography (silica, 3% methanol/chloroform) to give **1** as a white solid (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s, 2H), 8.92 (s, 1H), 8.36 (s, 2H), 8.20 (dd, J = 8.8, 2.0 Hz, 2H), 8.08 (d, J = 2.5 Hz, 2H), 8.06 – 8.01 (m, 2H), 6.89 (d, J = 9.1 Hz, 2H), 6.44 (s, 1H), 5.73 (ddt, J = 17.0, 10.2, 6.7 Hz, 2H), 4.88 (dd, J = 23.3, 13.7 Hz, 4H), 4.53 (d, J = 3.9 Hz, 4H), 4.03 – 3.90 (m, 8H), 3.42 (dd, *J* = 12.9, 6.6 Hz, 4H), 1.97 (dt, J = 14.3, 7.1 Hz, 6H), 1.71 (dd, J = 12.0, 5.9 Hz, 2H), 1.61-0.85 (m, 84H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.76, 165.01, 164.65, 163.01, 153.36, 149.20, 139.16, 136.80, 131.92, 124.97, 123.65, 123.51, 121.52, 114.51, 112.64, 72.44, 71.58, 40.16, 39.62, 38.97, 33.81, 30.77, 29.61 29.55, 29.48, 29.43, 29.14, 29.09, 29.02, 28.94, 27.17, 24.10, 23.06, 14.10, 14.06. ESI-MS, m/z calcd for $[C_{80}H_{128}N_6O_{10}+H]^+$ 1333.9792; found: 1333.9747.

2.2 Synthesis of Oligoamide-terminated PEG Chains

Scheme S2 Synthetic route of monomer **2a**



Compound C

Compound **C** was prepared according to previously reported literature procedure.[S1] White solid (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.13 (q, J = 2.4 Hz, 8.8, 1H), 7.83 (d, J = 2.4 Hz, 1H), 7.38 (s, 1H), 6.96 (d, J = 8.8 Hz, 1H), 4.25 (q, J = 8.8, 14.0 Hz, 4H), 4.13 (t, J = 6.6 Hz, 2H), 2.17 (s, 3H), 1.93 (m, 2H), 1.48 (m, 2H), 1.37-1.29 (m, 12H), 0.88 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.76,

168.49, 164.96, 153.89, 131.80, 125.59, 123.24, 120.64, 113.06, 69.74, 61.41, 42.16, 31.78, 29.27, 29.20, 29.07, 26.14, 24.35, 22.63, 14.19, 14.06. ESI-MS, m/z calcd for $[C_{21}H_{32}N_2O_5+H]^+$ 393.2389; found: 393.2314.

Compound 2-1

Compound **2-1** was prepared according to previously reported literature procedure.[S1] White solid (95% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.80 (br, 1H), 9.95 (s, 1H), 8.52 (t, J = 5.0 Hz, 1H), 8.0 (s, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 8.4 Hz, 1H), 4.08 (t, J = 6.2 Hz, 2H), 4.01 (d, J = 3.6 Hz, 2H), 2.0 (s, 3H), 1.80 (m, 2H), 1.40-1.24 (m, 10H), 0.843 (t, J = 6.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.07, 167.99, 164.23, 152.49, 132.64, 123.59, 121.71, 121.19, 113.57, 69.16, 41.55, 31.20, 28.70, 28.62, 28.43, 25.53, 23.78, 22.07, 13.96.

Compound 2-2

3,5-Dinitobenzenecarboxylic acid (20.0 g, 94.3 mmol) and $(COCl)_2$ (18.0 g, 141 mmol) were dissolved in dry CH_2Cl_2 (50 mL), and then a drop of dry DMF as the initiator was added. The mixture was stirred under N_2 atmosphere for 2 h, and then the solvent was removed in vacuo. The crude acid chloride was directly used for the next step without further purification. To a solution of acid chloride in THF (100 mL) was added a solution of t-BuOK in THF (13.8 g, 123 mmol). The reaction mixture was allowed to stir at room temperature. After 5 h, the solvent was evaporated, the residue was dissolved in ether (100 mL), and the solution was washed with $NaHCO_3$ (3 × 30 mL). After drying over Na_2SO_4 and filtering, the solution was evaporated to give **2-2** as a yellow solid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 9.03 (s, 2H), 1.59 (s, 9H).

Compound 2-3

Compound **2-2** was reduced by catalytic hydrogenation in methanol at room temperature using Pd-C (10%) as the catalyst. Removal of catalyst and solvent gave the crude product **2-3**, which was used for the next step without further purification (95% yield).

Monomer 2a

A mixture of acid **2a** (0.99 g, 2.70 mmol), EDCI (0.78 g, 4.10 mmol) and HOBt (0.55 g, 4.10 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and stirred for 1 h. Then the

solution of **2c** (0.23 g, 1.10 mmol) in dry CH_2Cl_2 (10 mL) was added into the mixture under N_2 atmosphere. After stirring overnight at room temperature, the solvent was removed under reduced pressure. The crude product was further purified by column chromatography (silica, 3% methanol/chloroform) to give **2a** as a white solid (70% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.37 (s, 2H), 9.97 (s, 2H), 8.56 (s, 2H), 8.05 (s, H), 8.04 (s, 2H), 7.97 (s, 2H), 7.79 (d, J = 4 Hz, 2H), 7.16 (d, J = 4 Hz, 2H), 4.20 (2, J = 2 Hz, 4H), 4.01 (d, J = 4 Hz, 4H), 2.02 (s, 6H), 1.86 (t, J = 8 Hz, 2H), 1.54 (s, 9H), 1.53-1.23 (m, 16H), 0.89 (t, J =4 Hz, 6H), 0.80 (t, J = 4 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.03, 167.40, 164.59, 164.43, 152.67, 139.23, 132.58, 132.26, 123.61, 121.75, 121.29, 114.83, 113.71, 113.40, 80.71, 79.09, 71.72, 29.95, 28.37, 27.66, 23.72, 23.23, 22.46, 13.80, 10.76. ESI-MS, m/z calcd for $[C_{49}H_{68}N_6O_{10}+H]^+$ 901.5075; found: 901.5061

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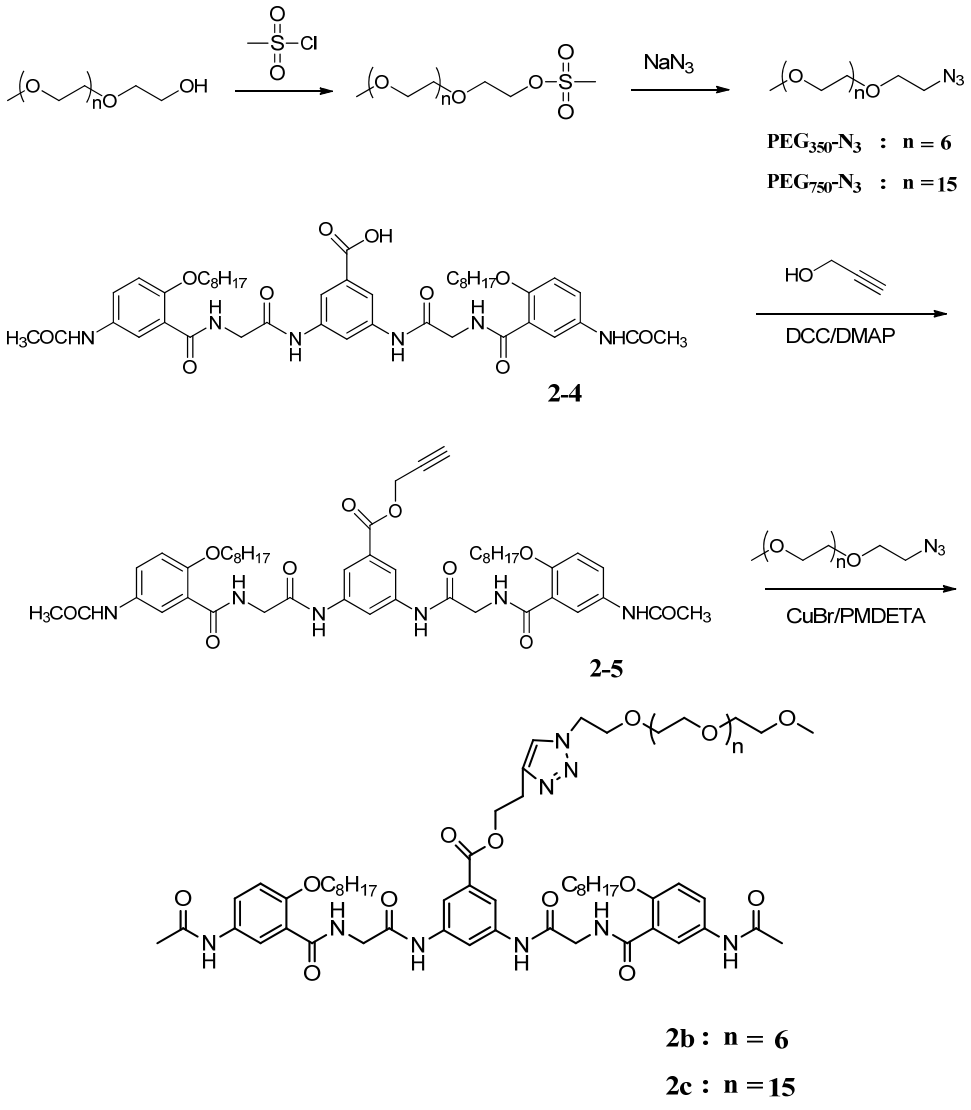
Scheme S3 Synthetic route of **2a** and **2c**



PEG_{750}-N_3 [S3]

Methoxypolyethylene glycols (Mn ~ 750 g/mol, 1.80 g, 2.60 mmol) and Methanesulfonyl chloride (0.6 mL, 7.70 mmol) were dissolved in THF (40 mL) at 0 ℃ under N_2 atmosphere, and then a drop of triethylamine (1.1 mL, 8.00 mmol) in THF (10 mL) was added. The mixture was stirred under N_2 atmosphere for 24 h, then a solution of $NaHCO_3$ (210 mg, 2.50 mmol) and NaN_3 (0.55 g, 8.50 mmol) in H_2O (50 mL) was added, and the resulting mixture was concentrated under heating to half of its original volume. After heating under reflux for 24 h and cooling down to ambient temperature, the mixture was diluted with H_2O (50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The organic phase was dried over Na_2SO_4, and the solvent was distilled under reduced presure to afford **PEG_{750}-N_3** as a yellow oil (87% yield). ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.8, 70.5, 69.9, 58.8, 50.3.

PEG_{350}-N_3

Following a similar procedure for **PEG_{750}-N_3**, **PEG_{350}-N_3** was obtained as a yellow oil (83% yield). ^{13}C NMR (100 MHz, $CDCl_3$): δ71.7, 70.5, 69.7, 59.0, 50.9.

Compound 2-4

Compound **2a** (50 mg，0.056 mmol) was dissolved in CH_2Cl_2 (20 mL) in 0 ℃ under N_2 atmosphere, and then a drop of trifluoroacetic acid (2 mL) in CH_2Cl_2 (10 mL) was added. The mixture was stirred under N_2 atmosphere for 0.5 h, then a saturated solution of $NaHCO_3$ (20 mL) was added and a white soild precipitated out, which was allowed to settle. The soild was then dried under reduced pressure to afford **2-4** as a white soild (97% yield). ^1H NMR (400 MHz, DMSO-d_6): δ 10.37 (s, 2H), 9.97 (s, 2H), 8.56 (s, 2H), 8.05 (s, H), 8.04 (s, 2H), 7.97 (s, 2H), 7.79 (d, J = 4 Hz, 2H), 7.16 (d, J = 4 Hz, 2H), 4.20 (d, J = 2 Hz, 4H), 4.01 (d, J = 4 Hz, 4H), 2.02 (s, 6H), 1.86 (t, J = 8 Hz, 2H), 1.53-1.23 (m, 16H), 0.89 (t, J =4 Hz, 6H), 0.80 (t, J = 4 Hz, 6H).

Compound 2-5

Compound **2-4** (50 mg，0.06 mmol), DCC (18.0 mg，0.09 mmol), DMAP (2.30 mg，0.02 mmol) and propiolic alcohol (8.50 mg，0.12 mmol) was dissolved in CH_2Cl_2 (20 mL), The mixture was stirred under N_2 atmosphere for 24 h. The crude product was further purified by column chromatography (silica, 5% methanol/chloroform) to give **2-5** as a white solid (70% yield). ^1H NMR (400 MHz, DMSO-d_6): δ 10.37 (s, 2H), 9.97 (s, 2H), 8.56 (s, 2H), 8.05 (s, H), 8.04 (s, 2H), 7.97 (s, 2H), 7.79 (d, J = 4 Hz,

2H), 7.16 (d, J = 4 Hz, 2H), 4.33(t, J = 2 Hz, 2H), 4.20 (d, J = 2 Hz, 4H), 4.01 (d, J = 4 Hz, 4H), 2.82(s, 1H), 2.63(s, 2H), 2.02 (s, 6H), 1.86 (t, J = 8 Hz, 2H), 1.53-1.23 (m, 16H), 0.89 (t, J =4 Hz, 6H), 0.80 (t, J = 4 Hz, 6H).

Compound 2b [S3]

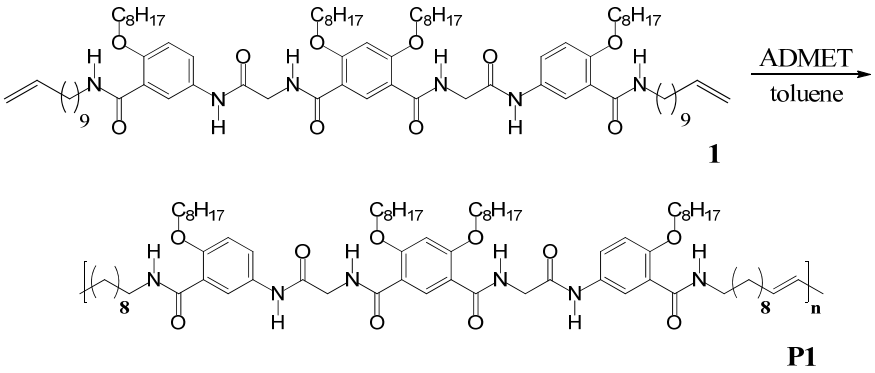
A typical procedure for synthesis of oligoamide-terminated PEG chains **2b** and **2c** involved the use of reagents [PEG-N3]/[2-5]/[CuBr]/[PMDETA] in a molar ratio of 1.70/1/0.33/0.33. The click coupling reaction between **PEG_{350}-N_3** (30 mg，6.0 μmol) and **2-5** (5.0 mg，5.7 μmol) was conducted in a 5 mL Schlenk flask with THF (1 mL) as solvent and CuBr (0.2 mg，1.6 μmol)/PMDETA (0.5 μL，1.6 μmol) as catalyst. The tube was then placed into a liquid nitrogen bath and connected to the vacuum line for a while, and then was allowed to warm to room temperature (25 ℃). The mixture was stirred for 48 h. The crude product was collected after removing solvent, and reprecipitated from MeOH. The crude product was further purified by column chromatography (silica, 5%methanol/chloroform) to give **2b** as a yellow solid (90% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 4H), 9.97 (s, 4H), 8.56 (s, 4H), 8.07 (s, H), 8.04 (s, 4H), 7.99 (s, 4H), 7.93 (s, 1H), 7.69 (d, J = 4 Hz, 4H), 7.17 (d, J = 4 Hz, 4H), 4.47-4.49(m, 4H), 4.33(t, J = 2 Hz, 4H), 4.20 (d, J = 2 Hz, 4H), 4.01 (d, J = 4 Hz, 4H), 3.57(s, 2H), 3.31-3.41(m, 50H), 3.07(t, 2H), 3.19(s, 3H), 2.02 (s, 6H), 1.86 (t, J = 8 Hz, 2H), 1.53-1.23 (m, 16H), 0.89 (t, J =4 Hz, 6H), 0.80 (t, J = 4 Hz, 6H). Mn = 1638, PDI=1.09 (determined by DMF GPC with linear PS standards).

Compound 2c

Following a similar procedure of **2b**, **2c** was obtained as a yellow oil (87% yield). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.47 (s, 4H), 9.97 (s, 4H), 8.56 (s, 4H), 8.07 (s, H), 8.04 (s, 4H), 7.99 (s, 4H), 7.93 (s, 1H), 7.69 (d, J = 4 Hz, 4H), 7.17 (d, J = 4 Hz, 4H), 4.47-4.49(m, 4H), 4.33(t, J = 2 Hz, 4H), 4.20 (d, J = 2 Hz, 4H), 4.01 (d, J = 4 Hz, 4H), 3.57(s, 2H), 3.31-3.41(m, 24H), 3.07(t, 2H), 3.19(s, 3H), 2.02 (s, 6H), 1.86 (t, J = 8 Hz, 2H), 1.53-1.23 (m, 16H), 0.89 (t, J =4 Hz, 6H), 0.80 (t, J = 4 Hz, 6H). Mn = 1258，PDI=1.16 (determined by DMF GPC with linear PS standards).

2.3 Synthesis of Polymer P1

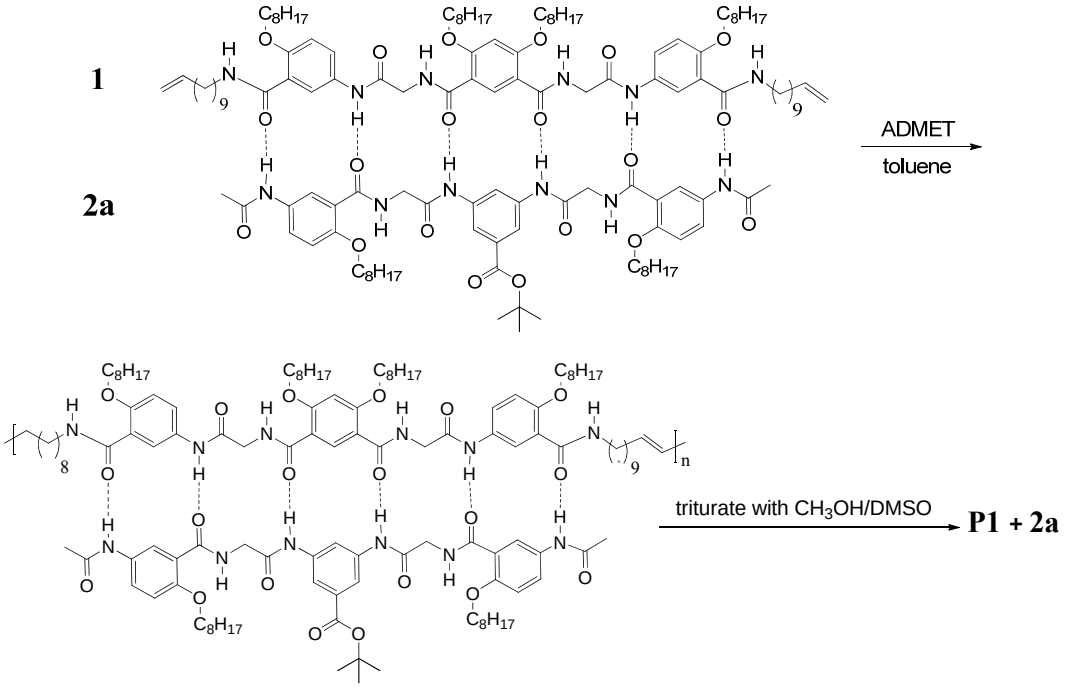
Scheme S4 General procedure of ADMET polymerization of monomer **1**



Polymer P1 (protecting-free)

Toluene (0.2 mL), monomer **1** (50 mg, 0.036 mmol), and Grubbs' ruthenium catalyst (2nd generation, 3 mg) were charged into a sealed Schlenk-type tube equipped with Kontes high-vacuum valves in the dry-box. The tube was then placed into a liquid nitrogen bath and was then connected to the vacuum line for a while. The tube was then placed into an oil bath preheated at the prescribed temperature (55 ℃) and the mixture was stirred for prescribed time (24 h). During the reaction, the mixture was put in a liquid nitrogen bath followed by opening the valve connected to the vacuum line to remove ethylene from the reaction medium twice. Then it was put in the oil bath to continue the reaction at 55 ℃. An additional 1.7 mg of Grubbs' ruthenium catalyst in toluene (0.1 mL) was added 24 h later. The reaction lasted for a total of 48 h. The polymerization was quenched by adding ethyl vinyl ether in excess amount. The reaction mixture was then stirred for 1 h for completion. The solvent was removed by evaporation; the residue was dissolved in a minimum amount of chloroform and precipitated in hot ethanol. The hoariness precipitate was collected by filtration. Separation by PTLC (chloroform/methanol, 15:1) provided polymer **P1**.

Scheme S5 General procedure of ADMET polymerization in protecting strategy



Polymer P1 (supramolecular protecting strategy)

Toluene (0.1 mL), monomer **1** (48 mg, 0.036 mmol), and the protecting monomer **2a** (32 mg, 0.036 mmol) were charged into a sealed Schlenk-type tube equipped with Kontes high-vacuum valves in the dry-box. The resulting dispersion was stirred at 50 ℃ until the monomers were completely dissolved. Grubbs' ruthenium catalyst (2nd generation, 3 mg) in 0.1 mL toluene was added to this solution. The tube was placed into a liquid nitrogen bath and deoxygenated. After connected to the vacuum line for a while, the solution was placed into an oil bath preheated at the prescribed temperature (55 ℃) and the mixture was stirred for prescribed time (24 h). During the reaction, the mixture was put in a liquid nitrogen bath followed by opening the valve connected to the vacuum line to remove ethylene from the reaction medium twice. Then it was put in the oil bath to continue the reaction at 55 ℃. An additional 1.7 mg of Grubbs' ruthenium catalyst in toluene (0.1 mL) was added 24 h later. The reaction lasted for a total of 48 h. The polymerization was quenched by adding ethyl vinyl ether in excess amount. The reaction mixture was then stirred for 1 h for completion. The solvent was removed by evaporation. The residue was dissolved in a minimum amount of chloroform and precipitated in hot ethanol. The hoariness precipitate was collected by filtration. The residual precipitate was dispersed in the mixed solvent of CH_3OH/DMSO (1:1, v/v) and stirred for 1 h, followed by filtration. Polymer P1 with > 95% removal of monomer **2a** was taken.

Table S1. **ADMET polymerization of monomer 1**[a]

Run	cat.(equiv) [b]	Additive	DP [c]	PDI (GPC)	Conv. (%)
1	1st (10)	No	4	1.75	75
2	1st (15)[d]	No	14	2.05	n.c[e]
3	1st (10)	No	12	2.27	80
4	2nd (10)	No	17	1.97	n.c[e]
5	1st (10)	**2a** (1 eq)	24	2.33	80
6	2nd (10)	**2a** (1 eq)	24	2.00	n.c[e]
7	2nd (10)	**2a** (0.5 eq)	35	1.91	n.c[e]
8	2nd (10)	**2a** (0.25 eq)	25	2.03	n.c[e]
9	2nd (10)	**2a** (0.125 eq)	20	1.94	n.c[e]

a. Condition: initial monomer concentration: 180 mM; time:48 h; temperature:55 ℃;

b. Molar ratio based on monomer/Ru;

c. Determined by GPC in DMF versus polystyrene standards;

d. Postpolymerization using oligomer (DP = 4) as reactant;

e. Near-quantitative conversion of monomer to polymer.

3. 2D-NOESY Spectroscopy of Graft Copolymer P1•2a

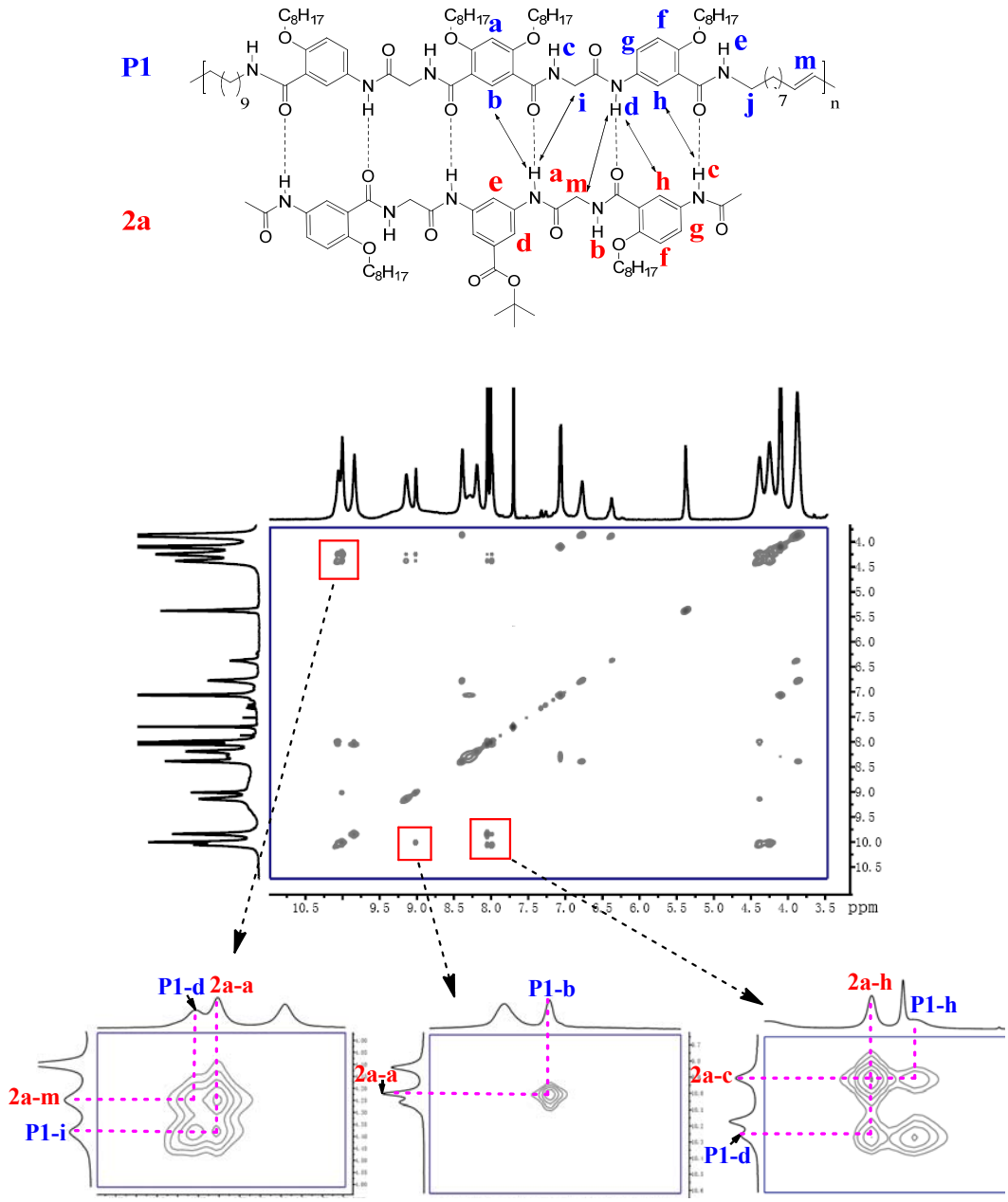


Figure S1 Partial 2D-NOESY spectra of graft copolymer **P1•2a** (10 g/L, **P1**:**2a** = 1:2 based on recognition units) in $CDCl_3$/DMF-d_7 (3:2, v/v) (600 MHz, mixing time: 0.3 s) at 298 K.

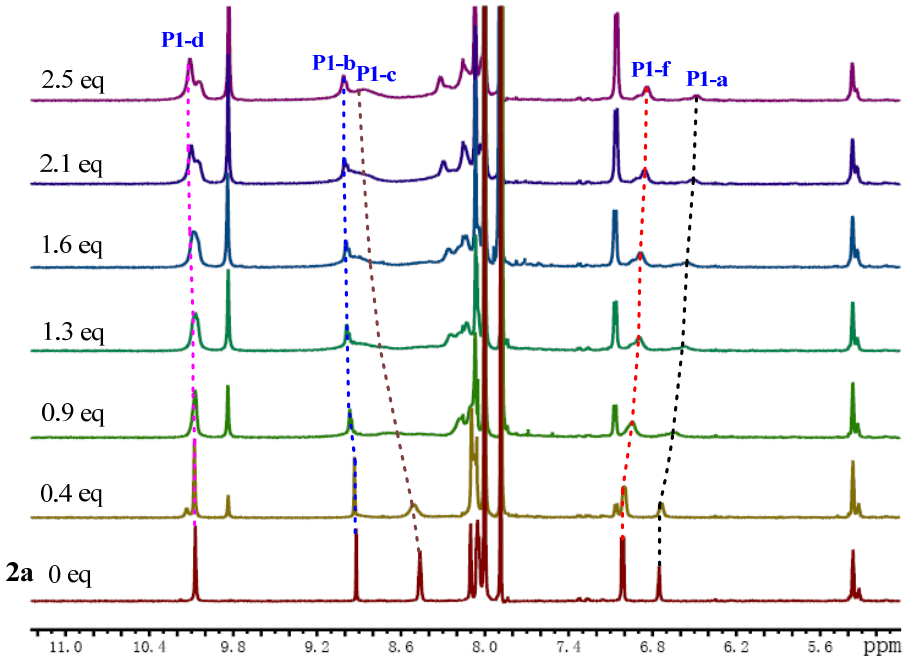


Figure S2 Stacked partial ^{1}H NMR spectra of polymer **P1** (1.2 g/L) when titrated with monomer **2a**, from 0 to 2.5 equivalents in $CDCl_3$/DMF-d_7 (3:2, v/v) (600 Hz) at 298 K.

4. GPC Measurement

The GPC measurement was carried out with chloroform/DMF (1:1, v/v) as the eluent at a flow rate of 1.0 mL/min. The column temperature was set at 30, 40 or 50 °C. The polymer solution concentration was approximately 1.0 g/L and the solution was filtered through a Teflon membrane with a pore size of 450 nm to eliminate the dust before measurement.

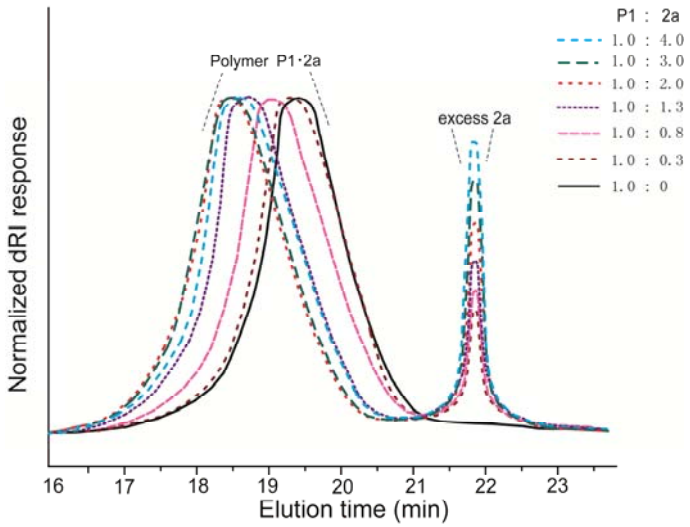


Figure S3 GPC traces of graft copolymer **P1•2a** in $CHCl_3$/DMF (1:1, v/v) at 30℃ at different molar ratios of **P1** and **2a** (based on recognition units).

Table S2 GPC data of graft copolymer **P1•2a** at different molar ratios of **P1** and **2a**

Samples	Mn	PDI
P1 : **2a** = 1.0 : 0	29990	1.94
P1 : **2a** = 1.0 : 0.3	31761	2.04
	871	1.05
P1 : **2a** = 1.0 : 0.8	38680	2.12
	827	1.13
P1 : **2a** = 1.0 : 1.3	44972	2.12
	909	1.03
P1 : **2a** = 1.0 : 2.0	48088	2.10
	847	1.12
P1 : **2a** = 1.0 : 3.0	47869	2.16
	815	1.12
P1 : **2a** = 1.0 : 4.0	48300	2.12
	885	1.07

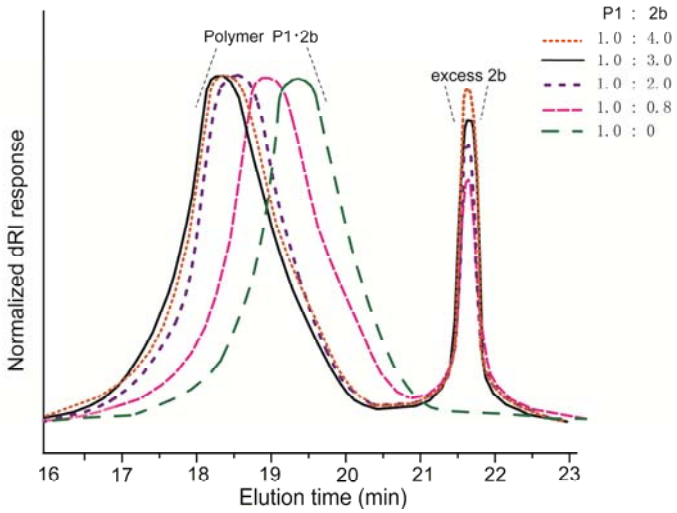


Figure S4 GPC traces of graft copolymer **P1•2b** in $CHCl_3$/DMF (1:1, v/v) at 30℃ at different molar ratios of **P1** and **2b** (based on recognition units).

Table S3 GPC data of graft copolymer **P1•2b** at different molar ratios of **P1** and **2b**

Samples	Mn	PDI
P1 : **2b** = 1.0 : 0	29990	1.94
P1 : **2b** = 1.0 : 0.8	38533	2.04
	1141	1.05
P1 : **2b** = 1.0 : 2.0	47443	2.12
	1152	1.13
P1 : **2b** = 1.0 : 3.0	51105	2.08
	1171	1.03
P1 : **2b** = 1.0 : 4.0	50773	2.10
	1155	1.12

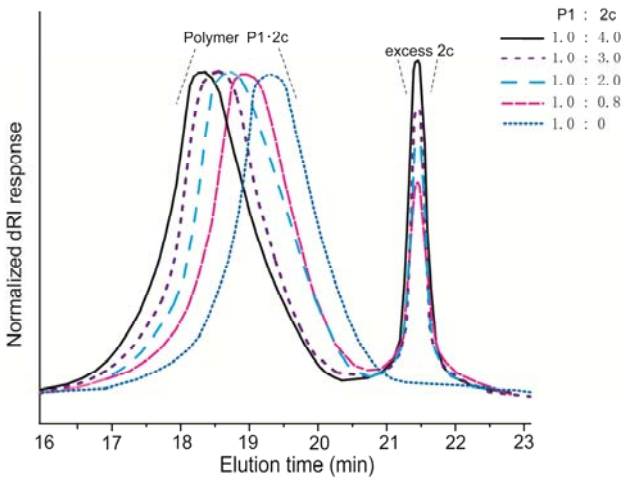


Figure S5 GPC traces of graft copolymer **P1•2c** in $CHCl_3$/DMF (1:1, v/v) at 30℃ at different molar ratios of **P1** and **2c** (based on recognition units).

Table S4 GPC data of graft copolymer **P1•2c** at different molar ratios of **P1** and **2c**

Samples	Mn	PDI
P1 : **2c** = 1.0 : 0	29990	1.94
P1 : **2c** = 1.0 : 0.8	38224	2.24
	1620	1.10
P1 : **2c** = 1.0 : 2.0	45525	2.23
	1622	1.11
P1 : **2c** = 1.0 : 3.0	49093	2.18
	1654	1.09
P1 : **2c** = 1.0 : 4.0	52793	2.22
	1655	1.12

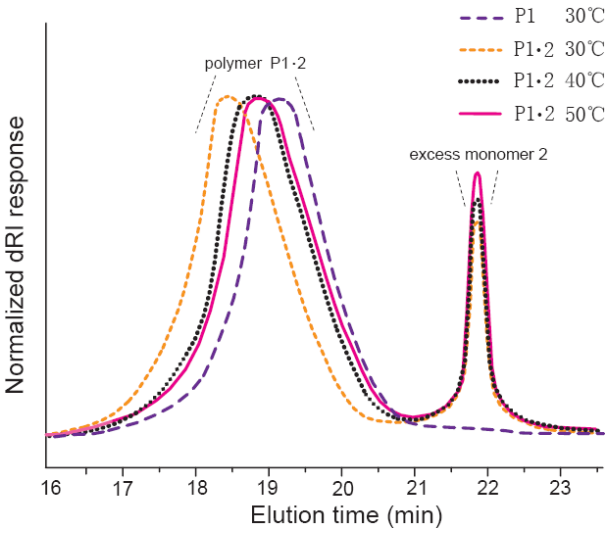


Figure S6 GPC traces of graft copolymer **P1•2a** (**P1**:**2a** = 1:2, based on recognition units) at various column temperatures in DMF/$CHCl_3$ (1:1, v/v).

Table S5 GPC data of graft copolymer **P1•2a** at various column temperature

Temperature	Mn	PDI
30 ℃	48088	2.10
	847	1.04
40 ℃	41267	2.14
	861	1.09
50 ℃	39670	2.07
	869	1.11

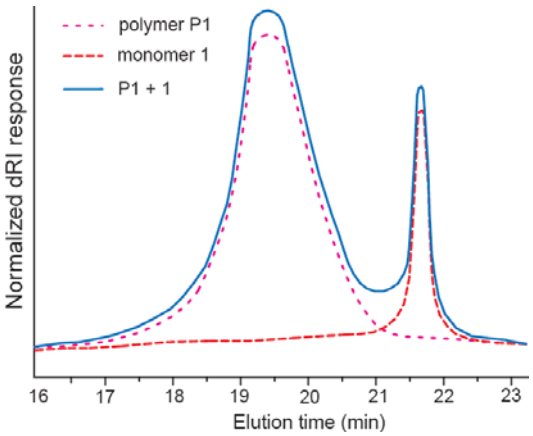


Figure S7 GPC traces of a mixture of polymer **P1** and monomer **1** (**P1**:**1** = 1:1 based on recognition units) in $CHCl_3$/DMF (1:1, v/v) at 30 ℃.

5. 2D-DOSY Spectroscopy

2D-DOSY experiments on sample concentration of 2 mM in DMF-d_7/$CDCl_3$ (2:3, v/v) were performed on a Bruker Avance II-600 MHz equipped with a 5mm TXI probe equipped with gradient capabilities at 298 K. The NMR tubes (5 mm) and samples were dried over P_2O_5 under dynamic vacuum for 24 hours to remove any trace amounts of water. The DOSY bipolar pulse pair longitudinal-eddy-current delay (BPPLED) sequence was used for the determination of the diffusion coefficients of the different components. Temperature calibration was achieved by observing the temperature dependent chemical-shift separation between the OH and CH_3 resonance in mixed solvent MeOD/MeOH (96:4, v/v). In all experiments the 90° pulse widths were determined. Firstly, the strength of the B0 field gradient was calibrated by measuring the self-diffusion coefficient of the residual HDO signal in a 1% D_2O sample, at 298 K ($D(H_2O) = 19 \times 10^{-10}$ m^2/s). The experimental diffusion data can be fitted into the following equation:

$$I = I_0 \exp\left(- D\,(\gamma\delta G)^2\,(\Delta - \delta/3 - \tau/2)\right)$$

In which I represents the experimental signal intensity, I_0 the initial signal intensity, γ is the magnetogyric ratio for ^{1}H, τ the time interval between the bipolar pulse pair, δ the length of the pulsed field gradient, G the strength of the pulsed field gradient and Δ the diffusion period. Using this equation we can determine D from a plot of $\ln(I/I_0)$ *vs* G^2. Using the calibrated field gradients we first measured the diffusion constant of $CHCl_3$ in DMF-d_7/$CDCl_3$ (2:3, v/v) resulting in a value of 24.5×10^{-10} m^2/s at 298 K. 2D DOSY measurements on samples in DMF-d_7/$CDCl_3$ (2:3, v/v) (2 mM, based on recognition units) were performed using a diffusion period (Δ) of 60 ms and a pulsed field gradient length of 4 ms (δ). A total of 64k transients were collected for each of the 32 steps while the gradient strength was changed from 0.2675 G/cm to 5.0825 G/cm. In all experiments the D values are the average values determined through the analysis of at least three proton signals. The ratios between the diffusion coefficients of $CHCl_3$ in CDCl3/DMF-d7 (v/v, 3:2) ($D_{sol,pure}$) and the experimental diffusion coefficients ($D_{sol,m}$) were used to correct the experimental value (D_m) in the following equation to give the viscosity corrected value (D_c):

$$D_c = D_m \times \frac{D_{sol,pure}}{D_{sol,m}}$$

For spheres diffusing in a medium of viscosity η, the relation between the diffusion coefficient D and the effective hydrodynamic radius of the sphere R_h is given by the Stokes–Einstein equation:

$$R_h = k_bT/6\pi\eta D$$

where k_b is the Boltzmann constant and T is the absolute temperature. The viscosity of DMF-d_7/$CDCl_3$ (2:3, v/v), η (298 K) = 0.645 cp was used.

Table S6 Diffusion constants of supramolecular Graft copolymers

Sample	$D_{sol,\ m}$ ($10^{-10}m^2/s$)	D_m ($10^{-10}m^2/s$)	D_c ($10^{-10}m^2/s$)	R_h (Å)
2a	26.9	7.08	6.45	5.2
2b	27.5	6.17	5.41	6.3
2c	27.9	5.75	5.04	6.7
P1	28.8	1.48	1.27	26.6
P1●2a	29.5	1.26	1.05	32.2
P1●2b	30.2	1.17	0.95	34.9
P1●2c	30.2	1.07	0.87	38.9

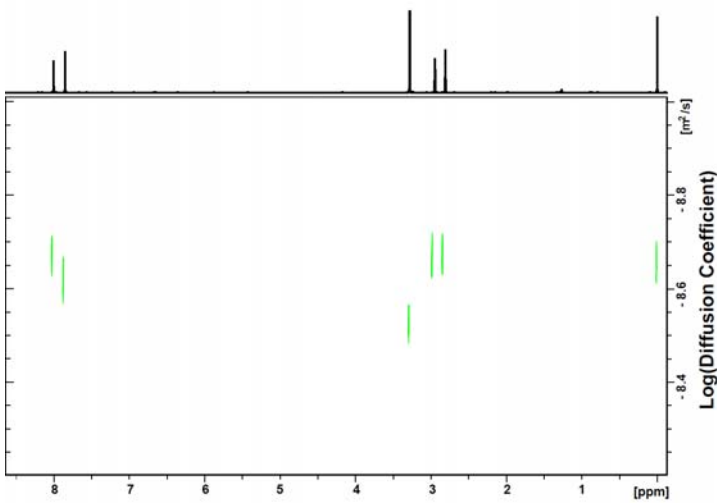


Figure S8 Proton 2D-DOSY spectrum of $CHCl_3$ in DMF-d_7/$CDCl_3$ (v/v, 2:3).

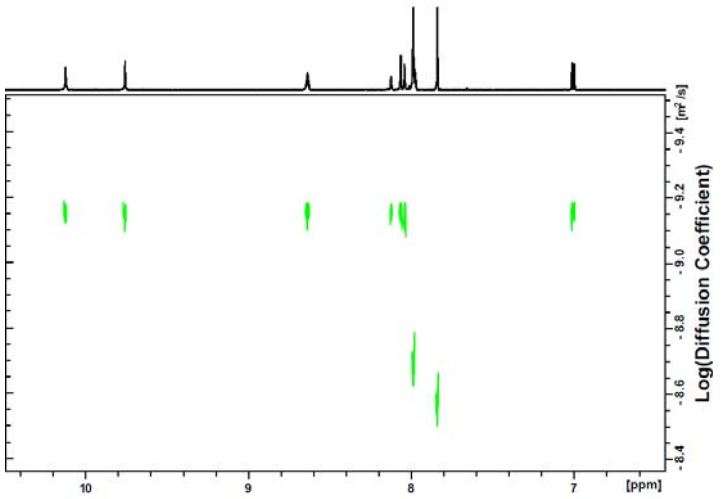


Figure S9 Partial proton 2D-DOSY spectrum of **2a** (2 mM) in DMF-d_7/$CDCl_3$ (v/v, 2:3).

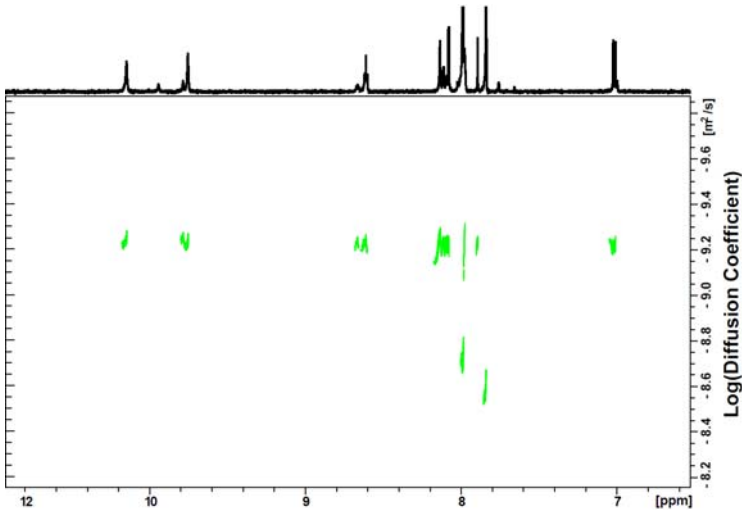


Figure S10 Partial proton 2D-DOSY spectrum of **2b** (2 mM) in DMF-d_7/$CDCl_3$ (v/v, 2:3).

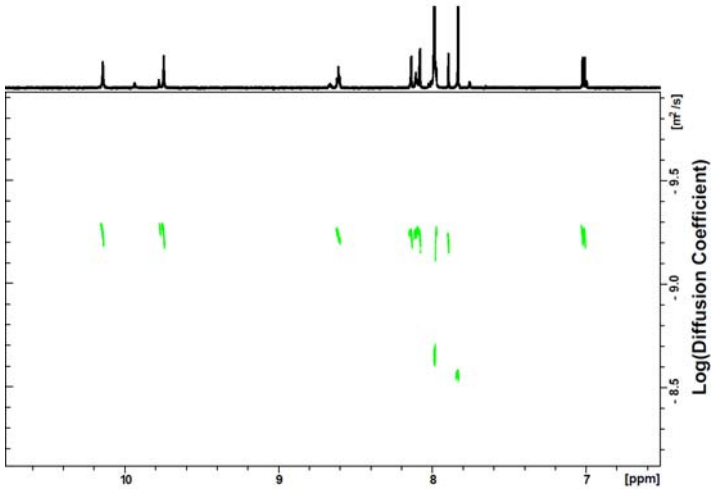


Figure S11 Partial proton 2D-DOSY spectrum of **2c** (2 mM) in DMF-d_7/$CDCl_3$ (v/v, 2:3).

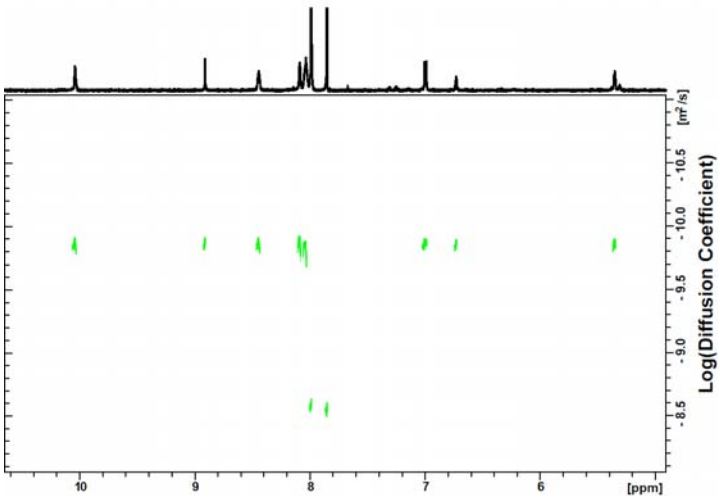


Figure S12 Partial proton 2D-DOSY spectrum of polymer **P1** (2 mM based on recognition units) in DMF-d_7/$CDCl_3$ (v/v, 2:3).

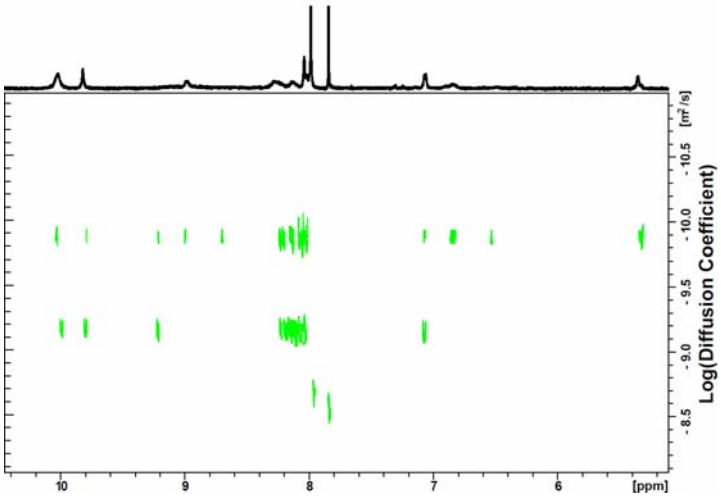


Figure S13 Partial proton 2D-DOSY spectrum of **P1●2a** (**P1**:**2a**=1:2, based on recognition units) in DMF-d_7/$CDCl_3$ (v/v, 2:3).

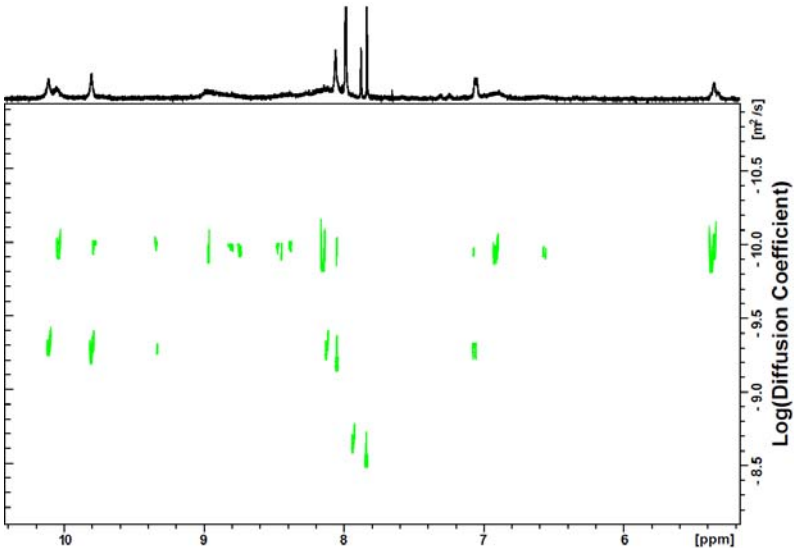


Figure S14 Partial proton 2D-DOSY spectrum of **P1●2b** (**P1**:**2b**=1:2, based on recognition units) in DMF-d_7/$CDCl_3$ (v/v, 2:3).

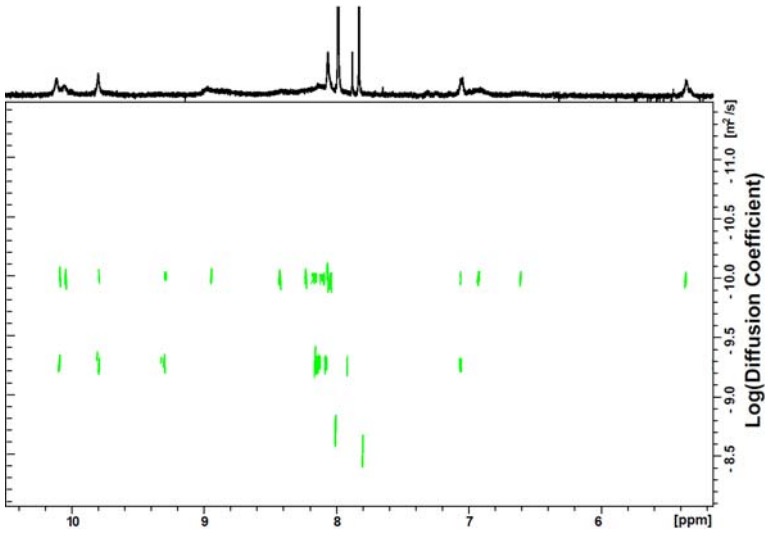


Figure S15 Partial proton 2D-DOSY spectrum of **P1●2c** (**P1**:**2c**=1:2, based on recognition units) in DMF-d_7/$CDCl_3$ (v/v, 2:3).

6. Variable-polarity ^{1}H NMR of Dimer1•2a

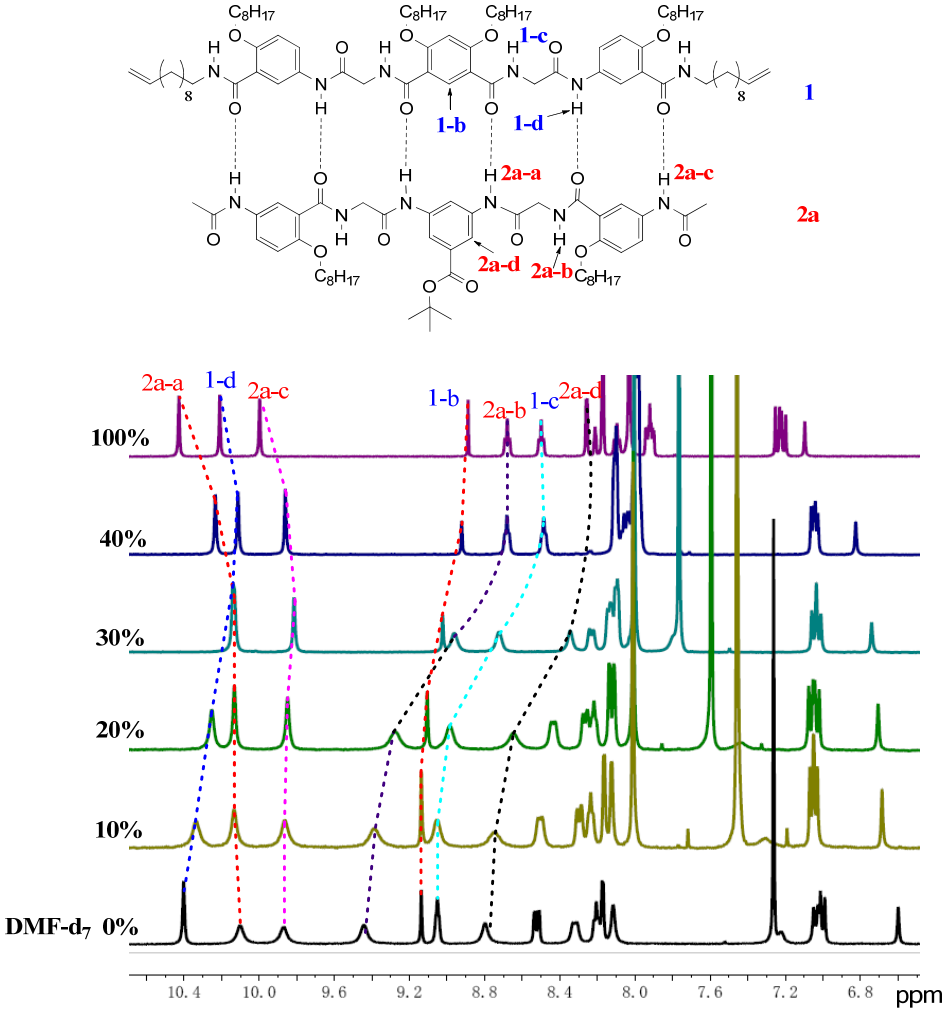


Figure S16 Stacked partial ^{1}H NMR spectra of dimer **1•2a** (10 mM, **1**:**2a** = 1:1) in a series of $CDCl_3$/DMF-d_7 binary solvents containing 0%, 10%, 20%, 30%, 40%, 100% DMF-d_7 (600 MHz) at 298 K.

7. Association Constants of 1•2, P1•2a, P1•2b and P1•2c

Association Constants of Dimer **1•2a**

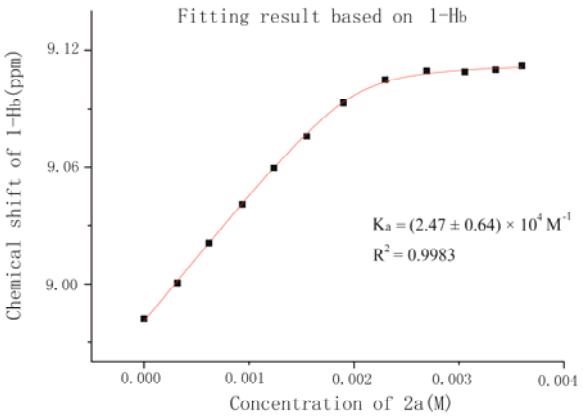


Figure S17 Determination of the association constant of dimer **1•2a** in $CDCl_3$/DMF-d_7 (4:1, v/v) at 298 K. Fitting result based on 1-H_b.

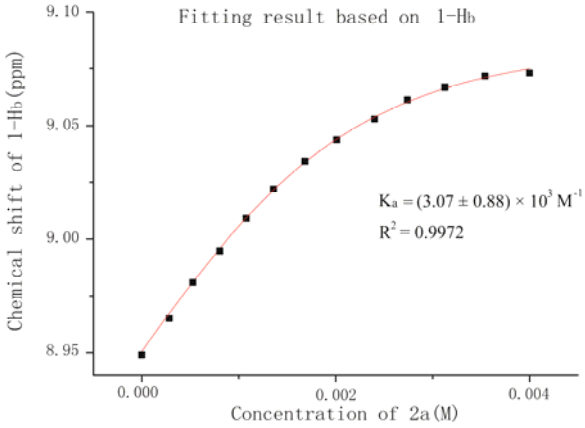


Figure S18 Determination of the association constant of dimer **1•2a** in $CDCl_3$/DMF-d_7 (7:3, v/v) at 298 K. Fitting result based on 1-H_d.

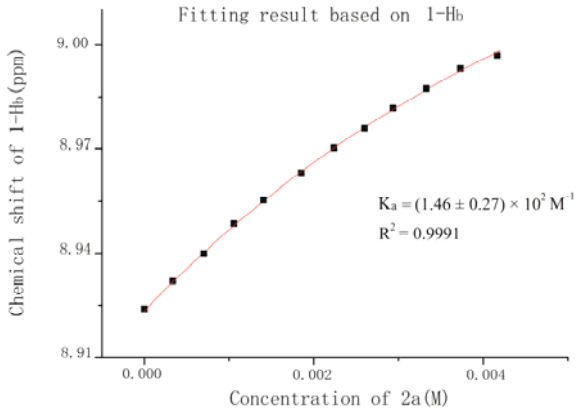


Figure S19 Determination of the association constant of dimer **1•2a** in $CDCl_3$/DMF-d_7 (3:2, v/v) at 298 K. Fitting result based on 1-H_d.

Association Constants of Graft Copolymer **P1•2a**

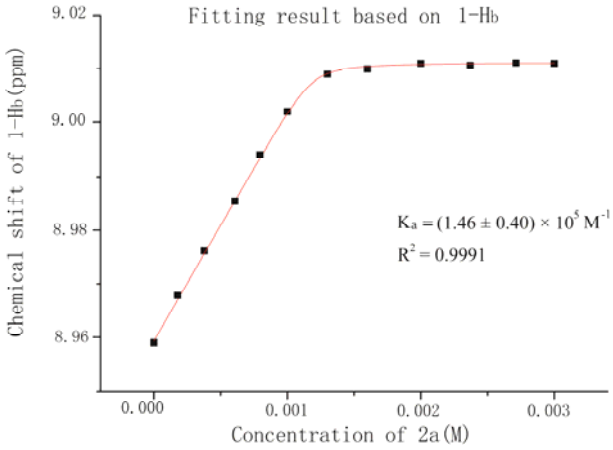


Figure S20 Determination of the association constant of polymer **P1•2a** in $CDCl_3$/DMF-d_7 (4:1, v/v) at 298 K. Fitting result based on P1-H_b.

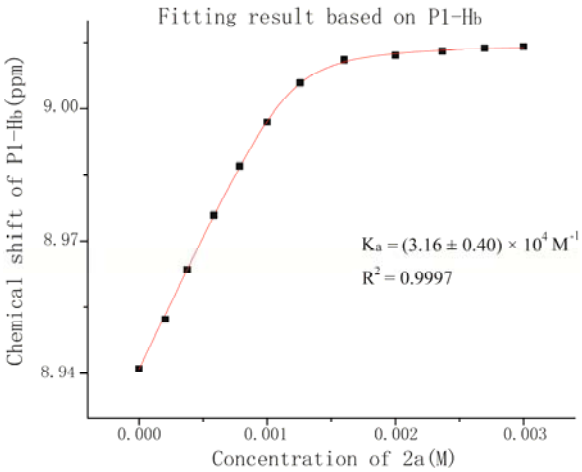


Figure S21 Determination of the association constant of graft copolymer **P1•2a** in $CDCl_3$/DMF-d_7 (7:3, v/v) at 298 K. Fitting result based on P1-H_b.

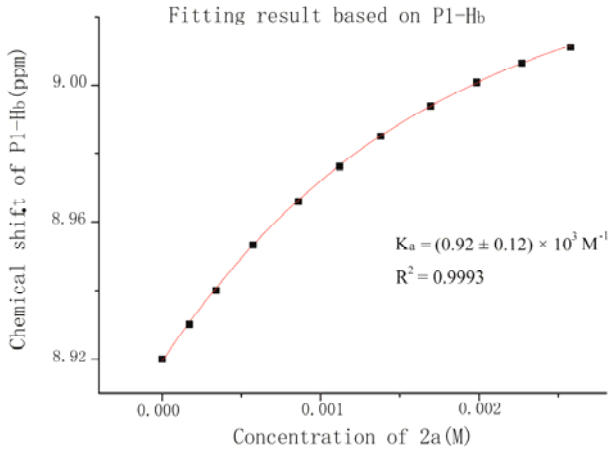


Figure S22 Determination of the association constant of graft copolymer **P1•2a** in $CDCl_3$/DMF-d_7 (3:2, v/v) at 298 K. Fitting result based on P1-H_b.

Association Constants of Graft Copolymer **P1•2b**

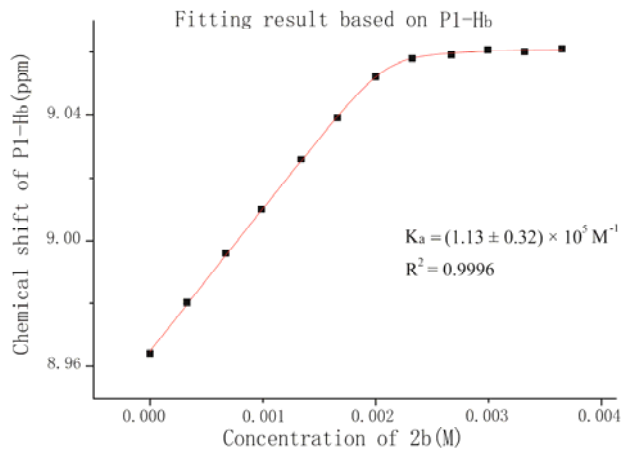


Figure S23 Determination of the association constant of graft copolymer **P1•2b** in $CDCl_3$/DMF-d_7 (4:1, v/v) at 298 K. Fitting result based on P1-H_b.

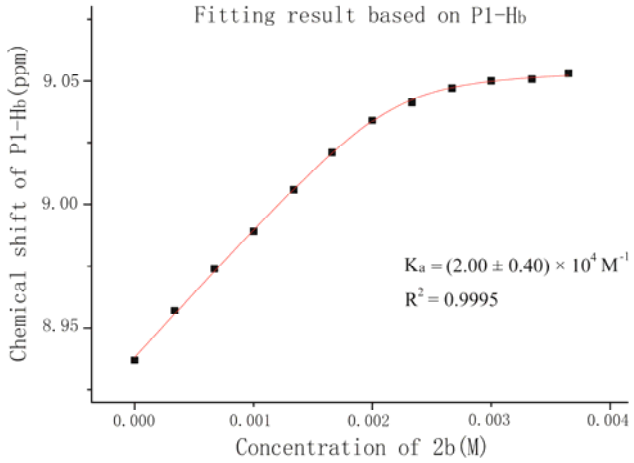


Figure S24 Determination of the association constant of graft copolymer **P1•2b** in $CDCl_3$/DMF-d_7 (7:3, v/v) at 298 K. Fitting result based on P1-H_b.

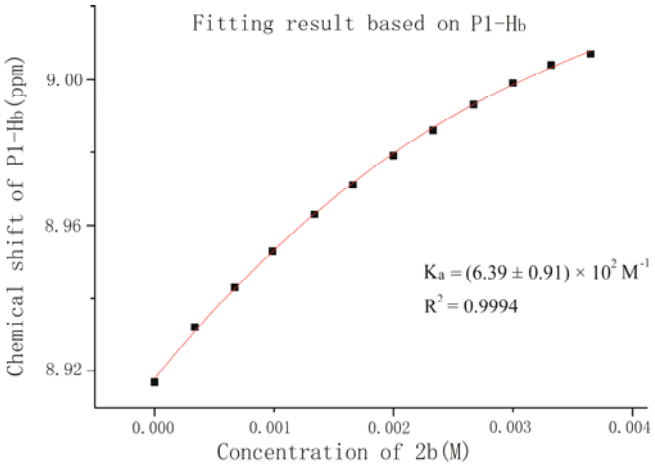


Figure S25 Determination of the association constant of graft copolymer **P1•2b** in $CDCl_3$/DMF-d_7 (3:2, v/v) at 298 K. Fitting result based on P1-H_b.

Association Constants of Graft Copolymer **P1•2c**

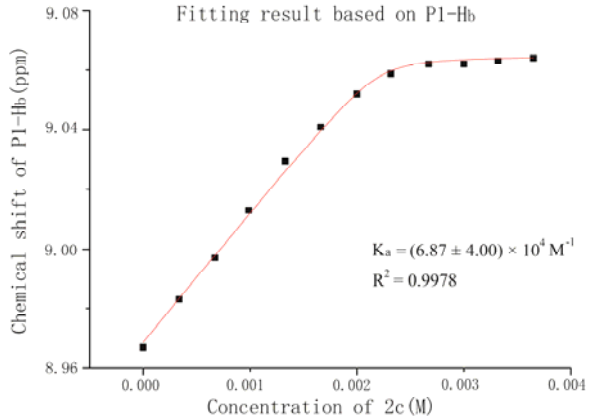


Figure S26 Determination of the association constant of graft copolymer **P1•2c** in $CDCl_3$/DMF-d_7 (4:1, v/v) at 298 K. Fitting result based on P1-H_b.

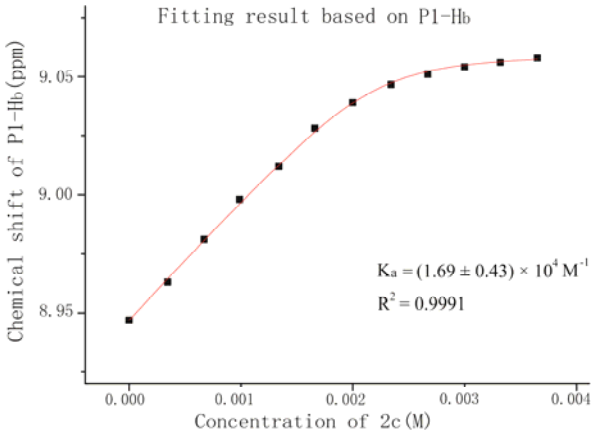


Figure S27 Determination of the association constant of graft copolymer **P1•2c** in $CDCl_3$/DMF-d_7 (7:3, v/v) at 298 K. Fitting result based on P1-H_b.

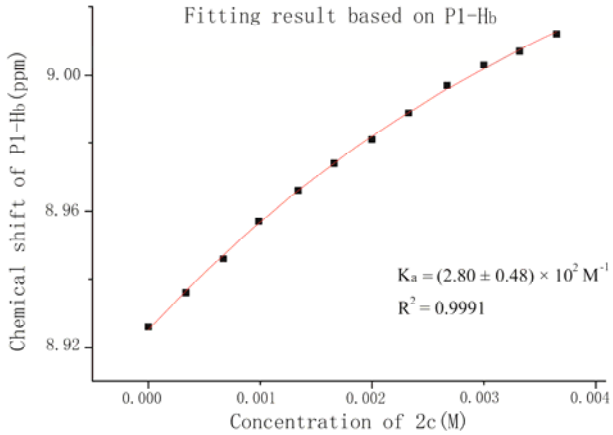


Figure S28 Determination of the association constant of graft copolymer **P1•2c** in $CDCl_3$/DMF-d_7 (3:2, v/v) at 298 K. Fitting result based on P1-H_b.

The method for determination of K_a is according to the reference.[S4]

8. UV-vis Experiment

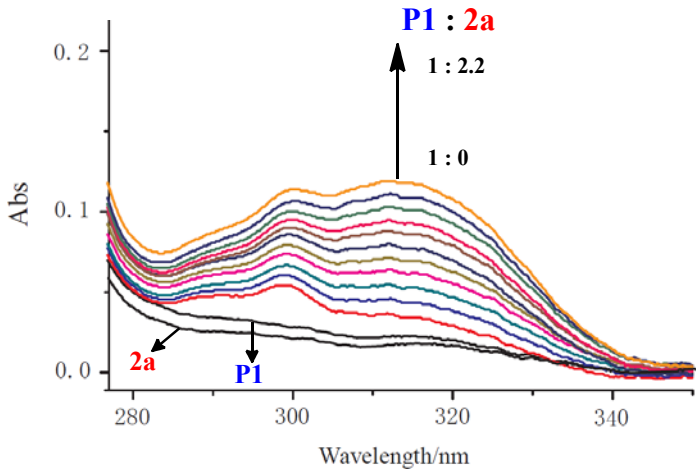


Figure S29 Variation of the UV-vis spectrum of polymer **P1** (5×10^{-2} mM) as a function of increasing amounts of **2a** (based on recognition units) in $CHCl_3$/DMF (3:2, v/v) at 30 ℃.

9. NMR and ESI-MS Spectra

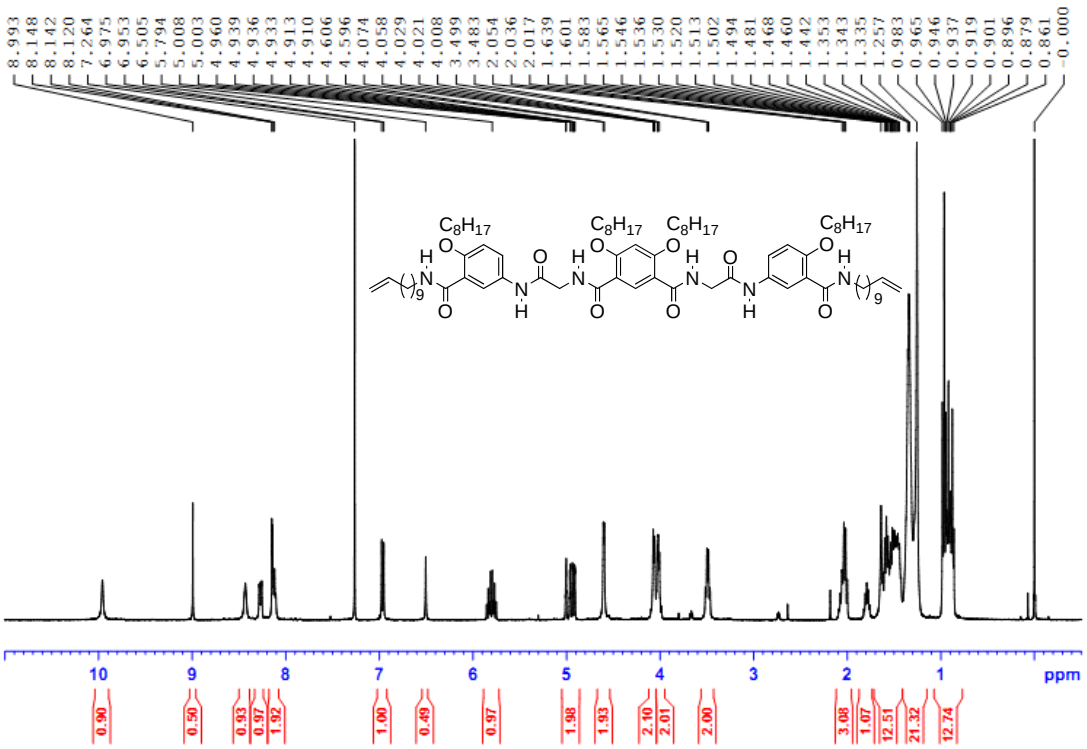


Figure S30 ^1H NMR spectrum of monomer **1** in $CDCl_3$ (400 MHz) at 298 K.

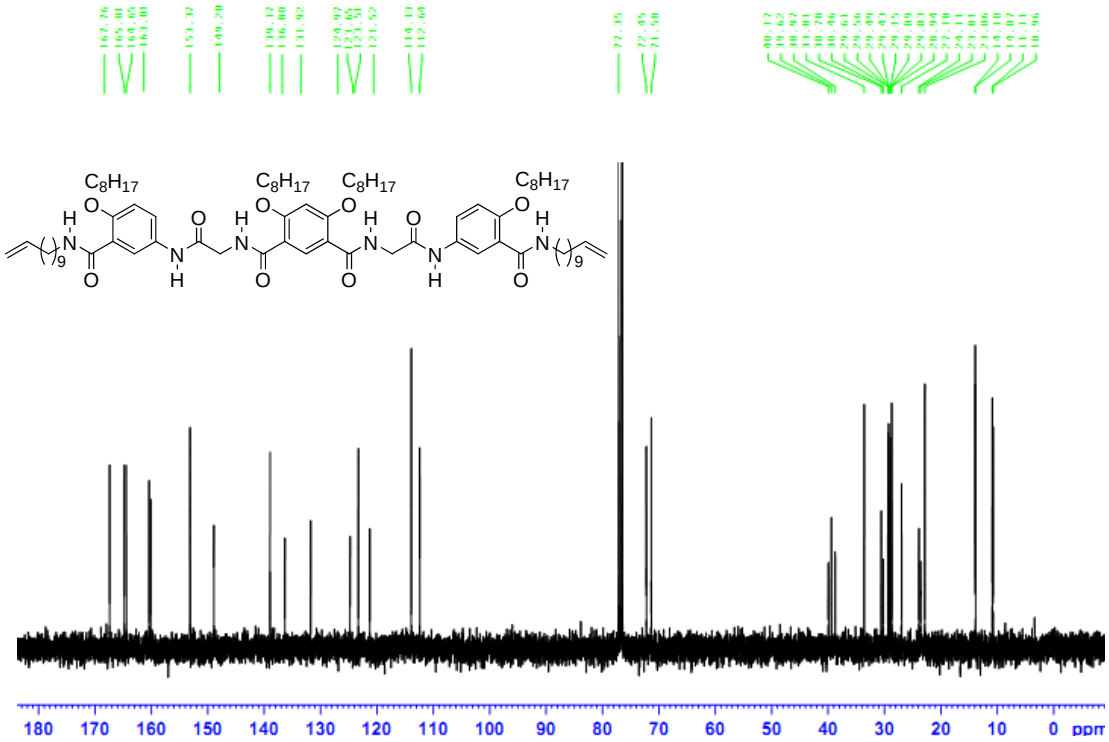


Figure S31 ^{13}C NMR spectrum of monomer **1** in $CDCl_3$ (100 MHz) at 298 K.

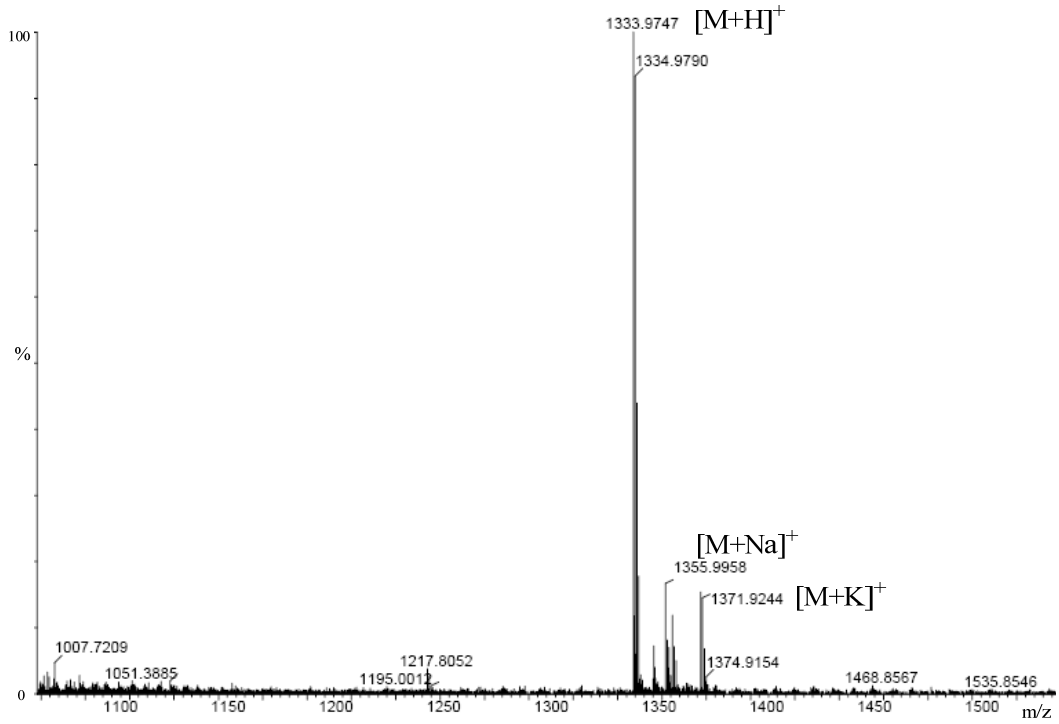


Figure S32 ESI-MS spectrum of monomer **1**.

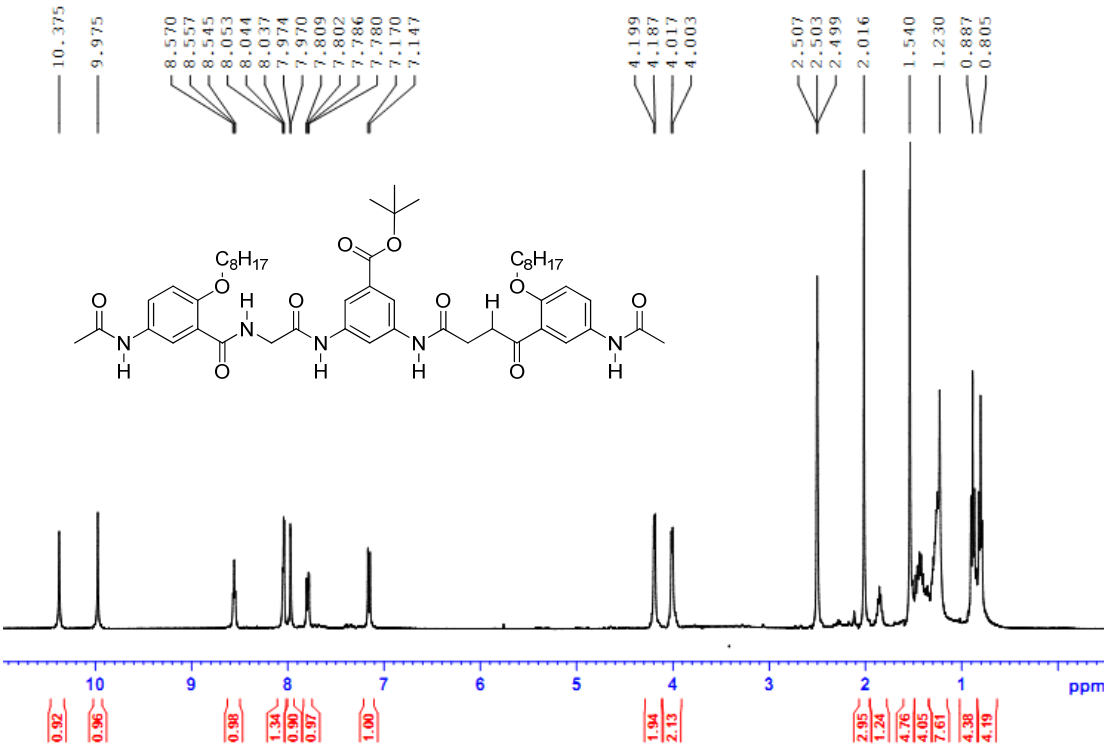


Figure S33 ^{1}H NMR spectrum of monomer **2a** in DMSO-d_6 (400 MHz) at 298 K.

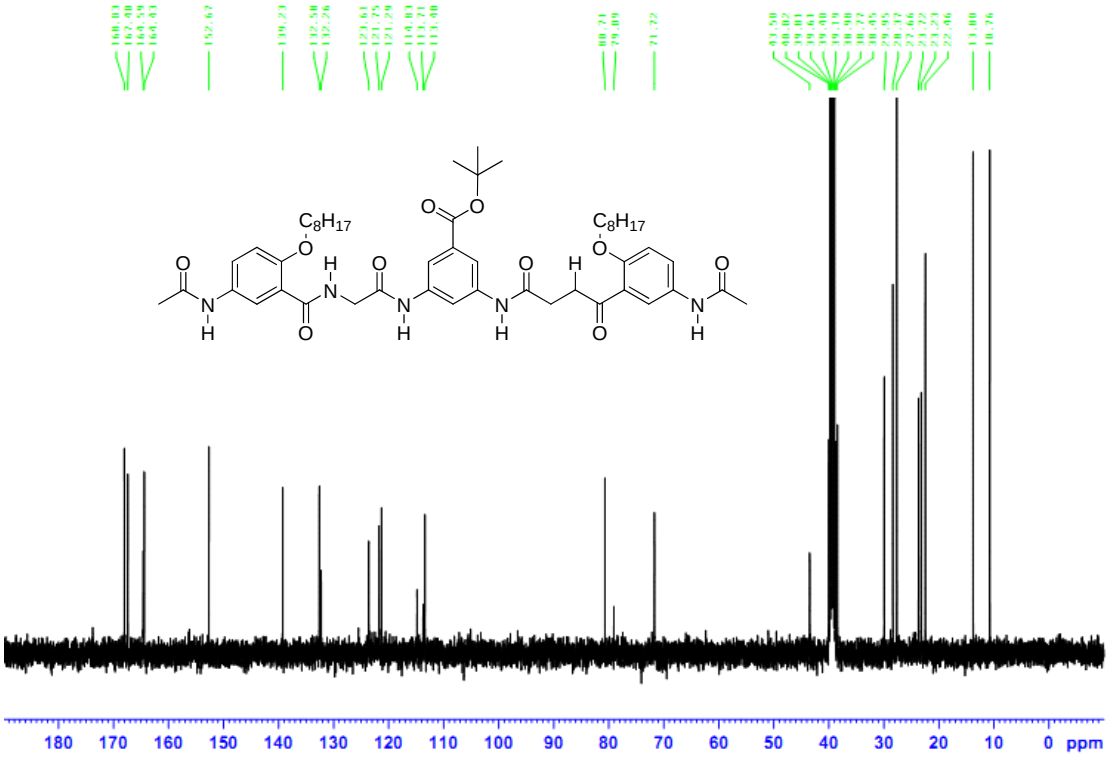


Figure S34 ^{13}C NMR spectrum of monomer **2a** in DMSO-d_6 (100 MHz) at 298 K.

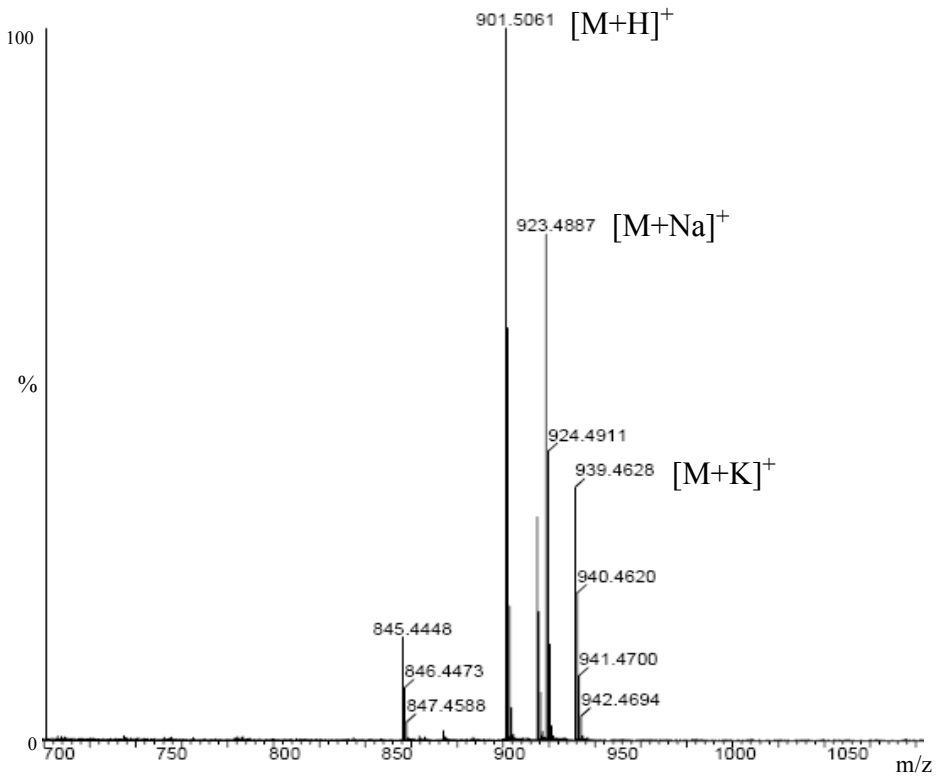


Figure S35 ESI-MS spectrum of monomer **2a**.

Reference:

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