Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Tetraethylene Glycol-Based Polymer Networks for the Efficient Removal of Radioactive Methyl Iodide and Iodine Vapor

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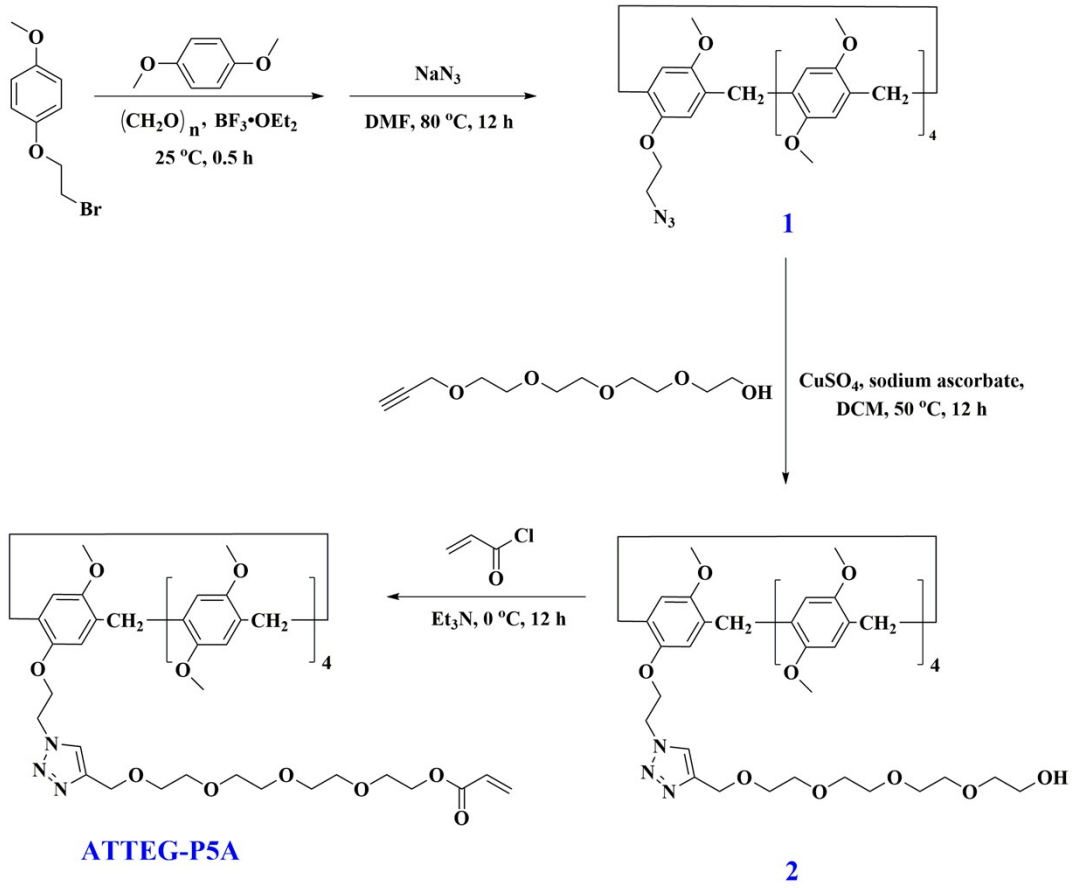
Ⅰ. Experimental Procedures

(1) Synthetic route and characterization of ATTEG-P5A.



Scheme S1 The procedure for the synthesis of **ATTEG-P5A**

Synthesize of compound 1：

1-(2-bromoethoxy)-4-methoxybenzene (1.00 g, 4.4 mmol), 1,4-dimethoxybenzene (9.61g, 69.6 mmol) and paraformaldehyde (18.81 g, 208.8 mmol) were dispersed in dried dichloromethane (200 mL) and the mixture was stirred for 30 min at room temperature under N_2 protection. Then $BF_3{\cdot}O(C_2H_5)_2$ (9.1 mL, 73.95 mmol) was added into the mixture dropwise. The reaction was quenched with addition of 100 mL methyl alcohol. The crude product was filtered and the filtrate was evaporated under reduced pressure. A portion of the residue (0.86g) was dissolved in dimethylformamide (DMF, 10 mL) and then sodium azide (0.26 g,1.4 mmol) was added in portions. The mixture was stirred at 80 ℃ for about 24 hours. After the reaction

was completed, the solvent was evaporated under reduced pressure and then extracted with ethyl acetate and water. The combined organic phase was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:8) to afford compound **1** as a white solid. The NMR and MALDI-TOF-MS spectra of compound **1** are shown in Fig. S1, S2, and S3.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.81-6.69 (m, 10H), 3.86 (t, J = 10.2 Hz, 2H), 3.84- 3.79 (m, 10H), 3.69-3.65 (m, 27H), 3.40 (t, J = 5.4 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$, 298K) δ 151.45, 150.88, 149.39, 128.80, 128.19, 115.53, 114.19, 114.16, 67.44, 55.90, 50.66, 29.85. MALDI-TOF-MS m/z: calcd for $[C_{46}H_{51}N_3O_{10}Na]^+$, 828.9148, found: 828.9486; calcd for $[C_{46}H_{51}N_3O_{10}K]^+$, 844.9233, found: 844.9370.

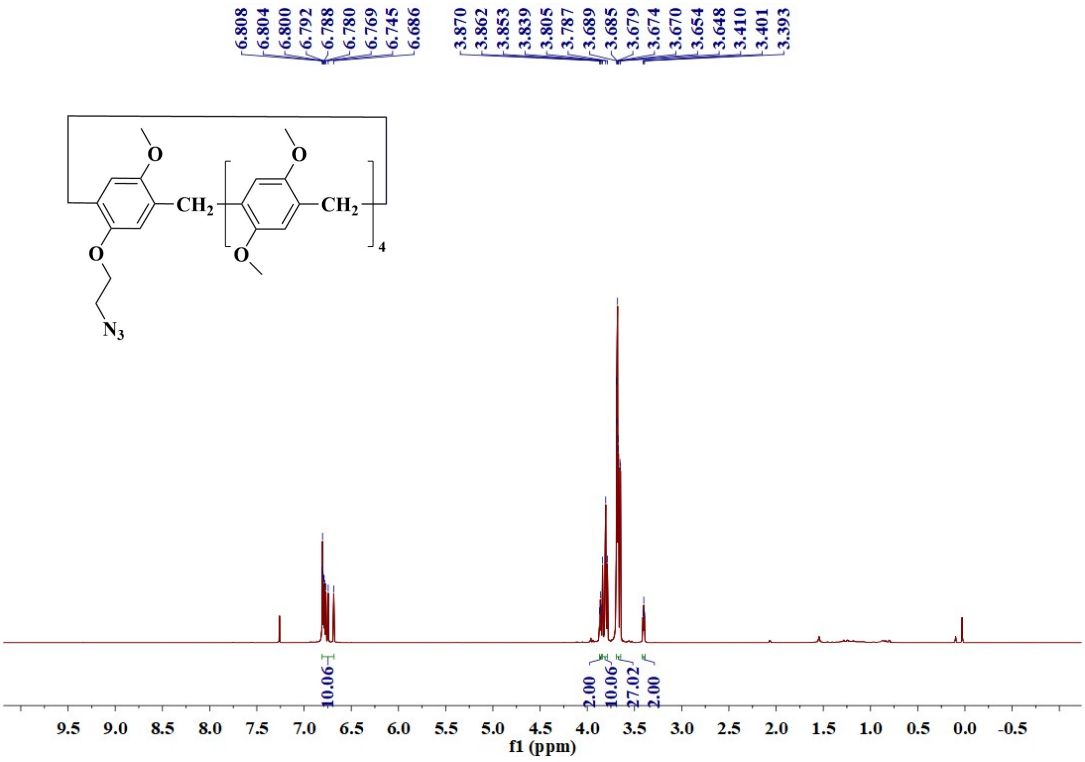


Fig. S1 ^{1}H NMR spectrum of compound **1** (600 MHz, $CDCl_3$, 298K).

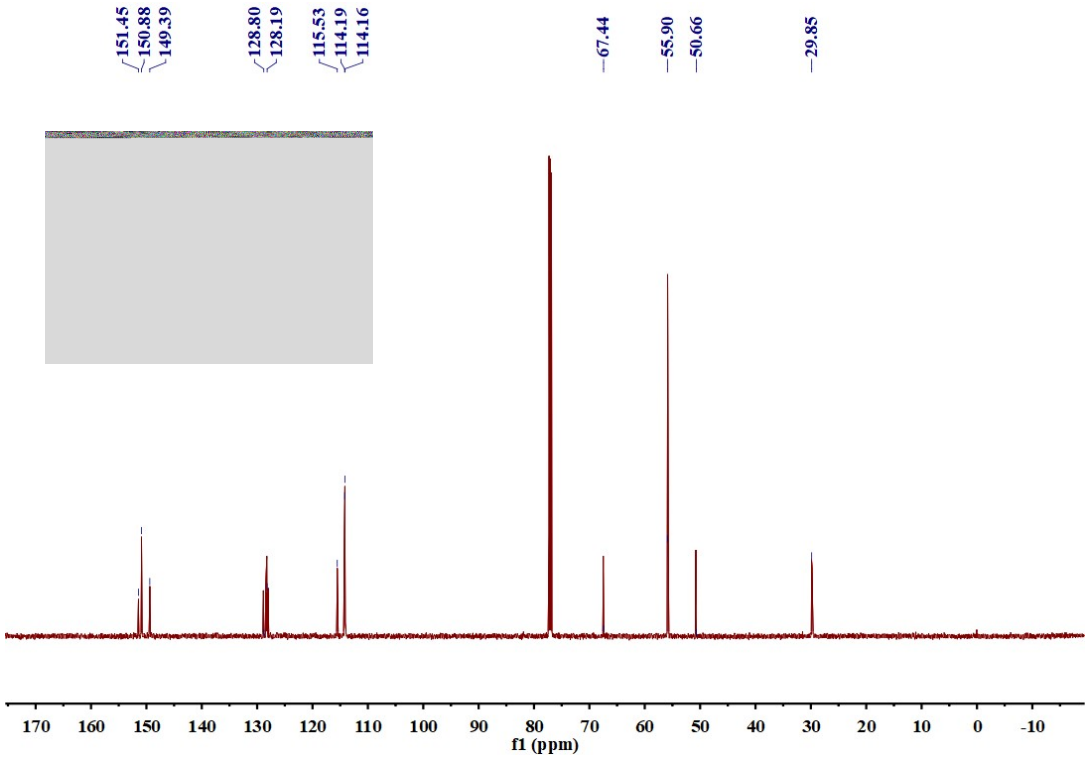


Fig. S2 ^{13}C NMR spectrum of compound **1** (151 MHz, $CDCl_3$, 298K).

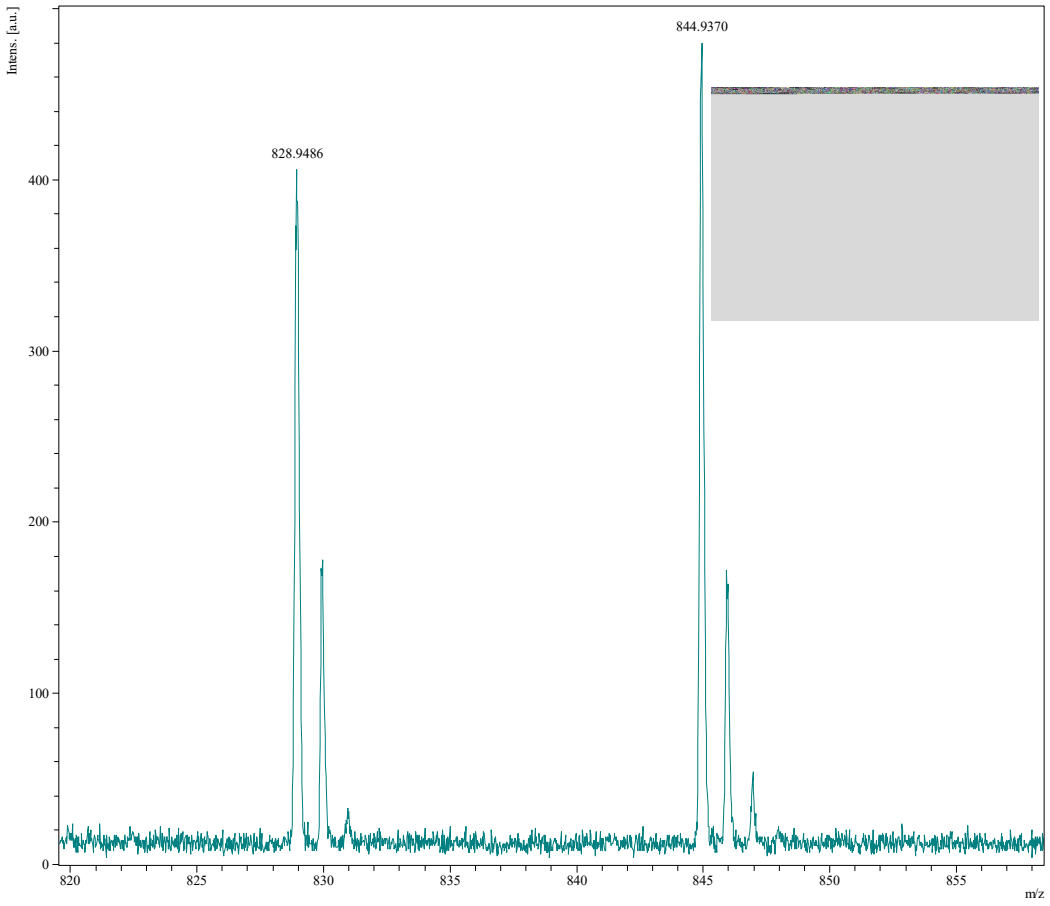


Fig. S3 MALDI-TOF-MS spectrum of compound **1**.

Synthesize of compound 2：

Compound **1** (0.50 g, 0.6 mmol), 3, 6, 9, 12-tetraoxapentadec-14-yn-1-ol (0.15 g, 0.6 mmol), copper sulfate (24.6 mg, 0.12 mmol) and sodium ascorbate (12.3 mg, 0.06 mmol) were dispersed in 10 mL anhydrous dichloromethane and the mixture was refluxed for 12 h. After the reaction was finished, the mixture was extracted with water and dichloromethane. The combined organic phase was washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by chromatography on silica gel (methanol/ dichloromethane = 1:20). Product **2** was obtained as white solid (0.48 g, 75 %). The NMR and MALDI-TOF-MS spectra of compound **2** are shown in Fig. S4, S5, and S6.

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 7.18 (s, 1H), 6.72 (d, J = 3.6 Hz, 2H), 6.68-6.64 (m, 6H), 6.45 (s, 1H), 6.39 (s, 1H), 4.60 (s, 2H), 4.36 (t, J = 4.8 Hz, 2H), 3.86 (t, J = 4.8 Hz, 2H), 3.71-3.64 (m, 10H), 3.60 (s, 8H), 3.57-3.52 (m, 27H), 3.49-3.43 (m, 8H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 154.42, 152.22, 116.11, 114.75, 68.83, 55.73, 29.38. MALDI-TOF-MS m/z: calcd for $[C_{57}H_{71}N_3O_{15}]^{+}$ 1037.4898, found 1037.4890; calcd for $[C_{57}H_{71}N_3O_{15}Na]^{+}$, 1060.4777, found: 1060.4771.

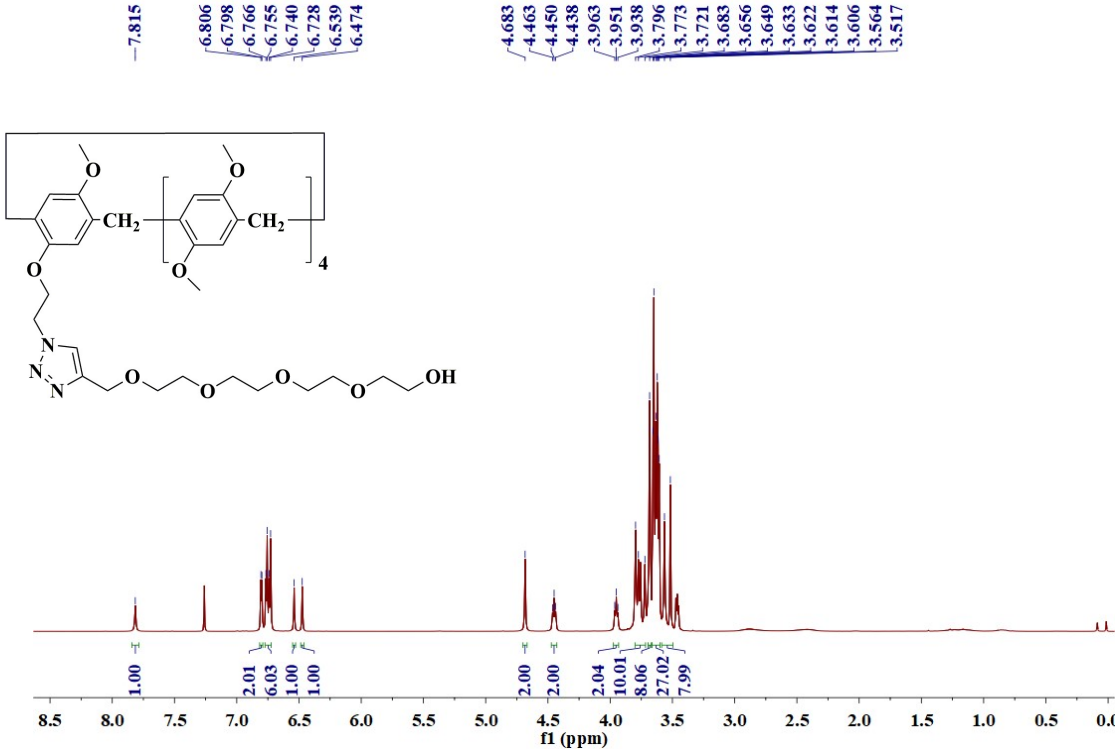


Fig. S4 ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$, 298K).

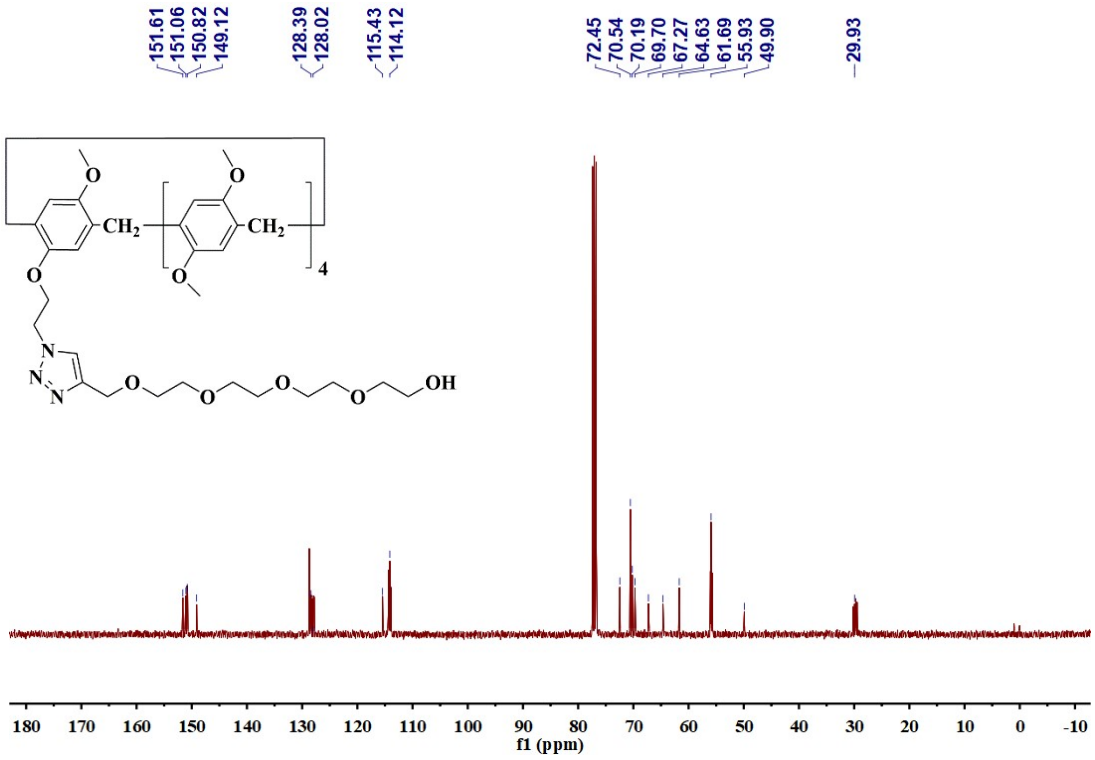


Fig. S5 ^{13}C NMR spectrum of compound **2** (101 MHz, $CDCl_3$, 298K).

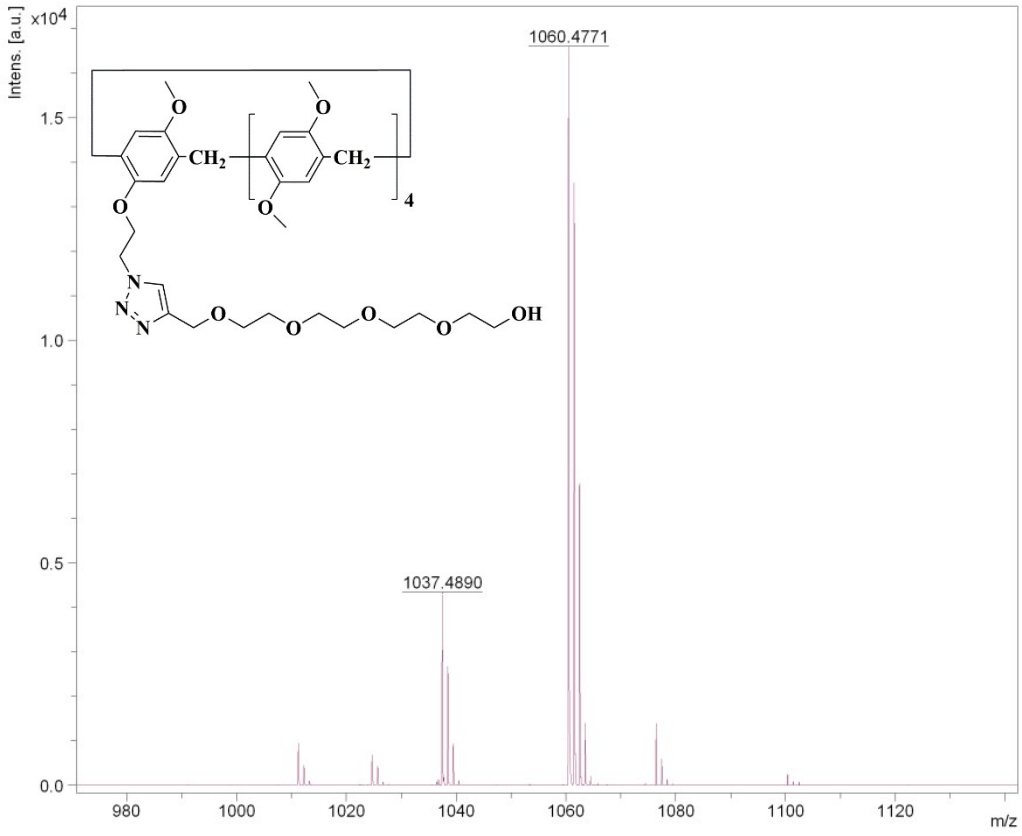


Fig. S6 MALDI-TOF-MS spectrum of compound **2**.

The synthesis of ATTEG-P5A

Under nitrogen protection, compound **2** (1.14 g, 1.1 mmol) was added to 20 mL anhydrous dichloromethane, and the solution was stirred for 30 min at 0 °C. Then acryloyl chloride (0.20 g, 2.2 mmol) was added to the above solution slowly. The mixture was stirred for about 10 h at room temperature. After the reaction finished, the mixture was extracted with dichloromethane and water. The organic phase was combined and washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane /methanol = 50:1) to afford **ATTEG-P5A** as a light yellow solid (1.02 g, 85%). The NMR and HR-ESI-MS spectra of **ATTEG-P5A** are shown in Fig. S7, S8, and S9.

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 7.77 (s, 1H), 6.79 (d, *J* = 4.8 Hz, 2H), 6.75-6.71 (m, 6H), 6.50 (s, 1H), 6.44 (s, 1H), 6.41 (dd, *J* = 17.2, 1.2 Hz, 1H), 6.13 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.66 (s, 2H), 4.40 (t, *J* = 4.8 Hz, 2H), 4.29 (t, *J* = 4.4 Hz, 2H), 3.90 (t, *J* = 4.8 Hz, 2H), 3.78-3.72 (m, 10H), 3.71 (s, 3H), 3.67 (s, 8H), 3.64-3.59 (m, 27H), 3.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, 298K) δ 166.17, 151.62, 150.86, 149.12, 145.23, 131.02, 128.30, 127.79, 123.69, 115.38, 114.13, 70.60, 69.69, 69.11, 67.25, 64.61, 63.71, 55.93, 49.85, 29.72. MALDI-TOF-MS m/z: calcd for $[C_{60}H_{74}N_3O_{16}Na]^+$, 1115.4967, found: 1115.4802; calcd for $[C_{60}H_{74}N_3O_{16}K]^+$, 1131.4706, found: 1131.4740.

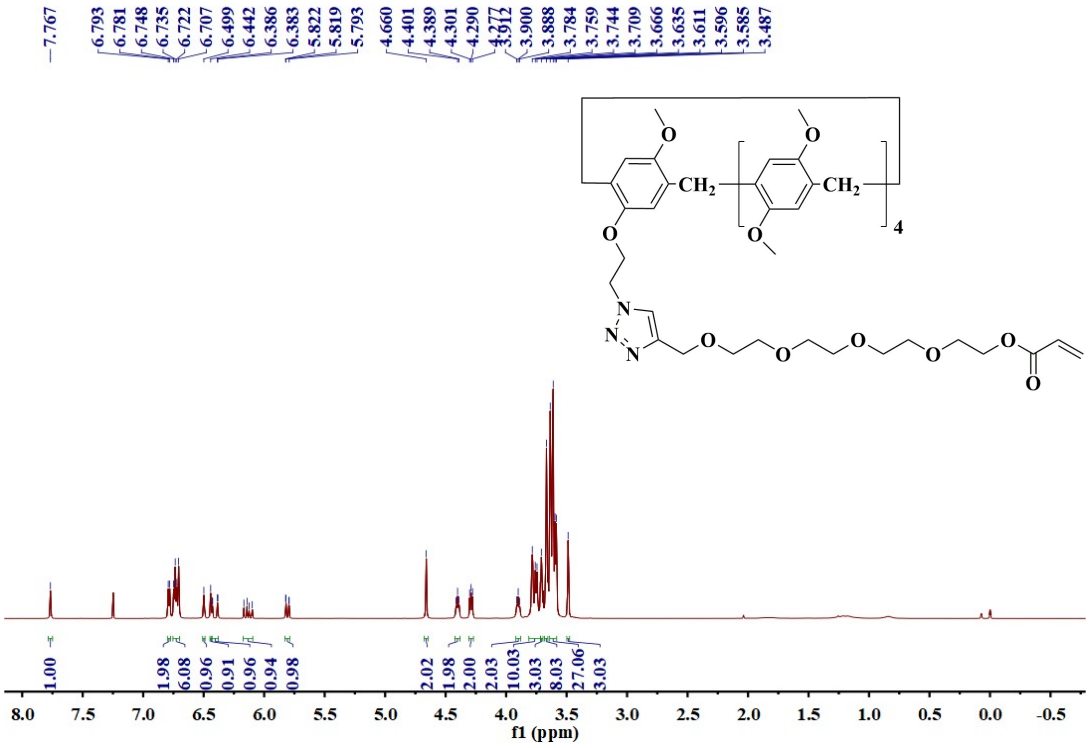


Fig. S7 ^{1}H NMR of **ATTEG-P5A** (400 MHz, $CDCl_3$, 298K).

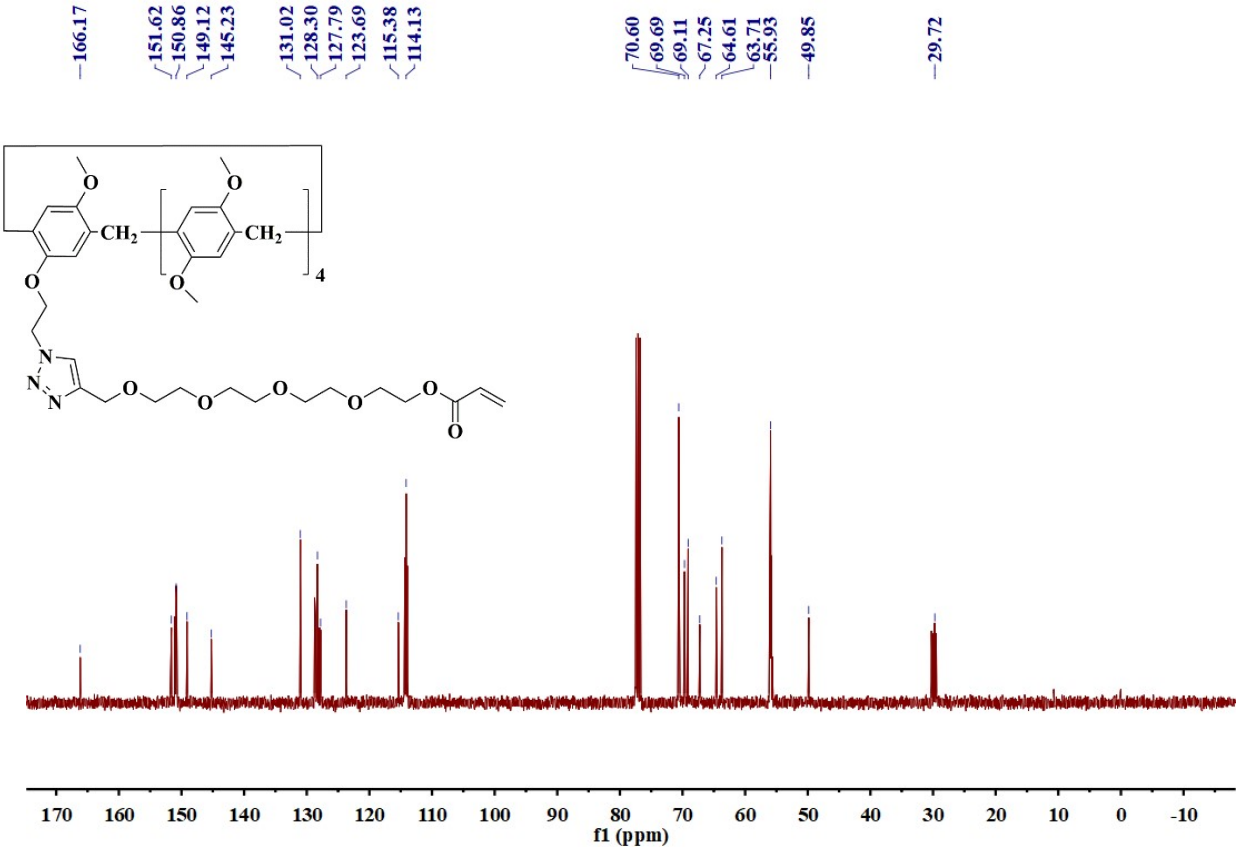


Fig. S8 ^{13}C NMR of **ATTEG-P5A** (101 MHz, $CDCl_3$, 298K).

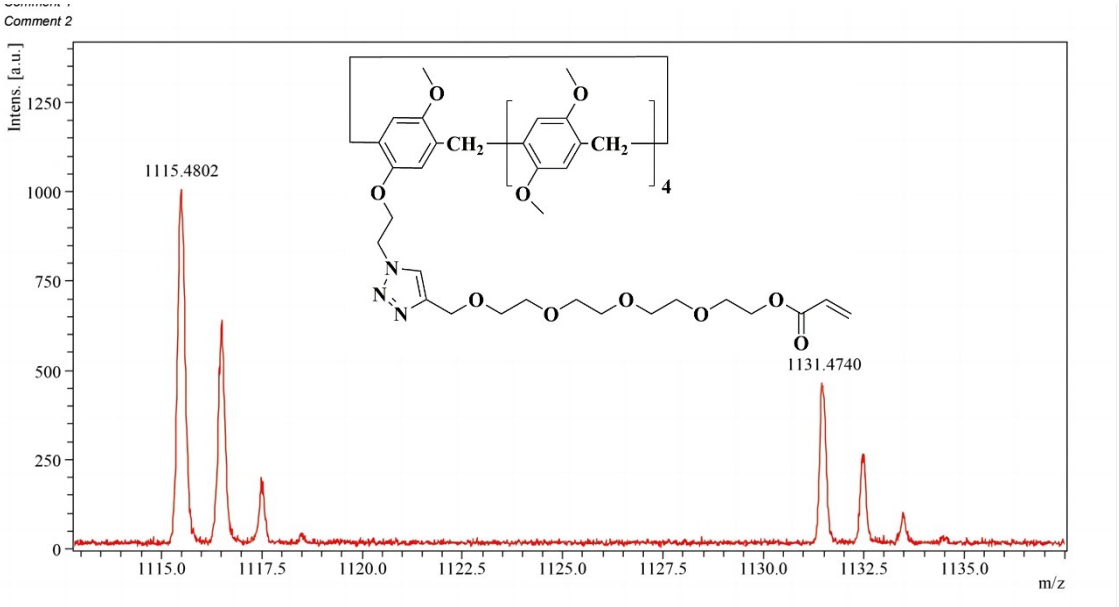
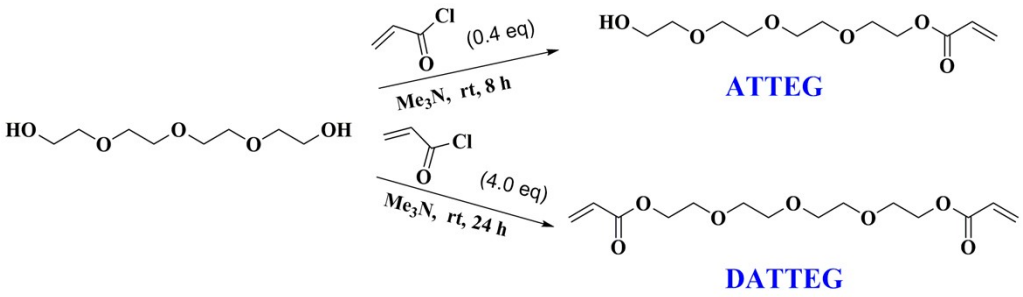


Fig. S9 MALDI-TOF-MS of **ATTEG-P5A**.

(2) Synthetic route and characterization of ATTEG and DATTEG.



Scheme S2 The procedure for the synthesis of **ATTEG** and **DATTEG**.

The synthesis of ATTEG.

Under nitrogen protection, tetraethylene glycol (4.00 g, 20.6 mmol) and trimethylamine (0.55 g, 10.3 mmol) were added into 20 mL anhydrous dichloromethane and the solution was stirred for 30 min at 0 °C. Then acryloyl chloride solution (8.3 mmol acryloyl chloride in 30 mL anhydrous dichloromethane) was added into the above solution drop by drop. The mixture was stirred at room temperature and monitored by thin-layer chromatography. After the reaction finished, the mixture was extracted with dichloromethane and water. The organic phase was combined and washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether /ethyl

acetate = 1:1) to afford **ATTEG** as a colorless liquid (4.35 g, 85%). The NMR and HR-ESI-MS spectra of **ATTEG** are shown in Fig. S10, S11, and S12.

^{1}H NMR (400 MHz, $CDCl_3$, 298K) δ 6.44 (dd, *J* = 17.2, 1.6 Hz, 1H), 6.16 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.85 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.33 (t, *J* = 4.8 Hz, 2H), 3.76-3.74 (m, 4H), 3.67 (s, 8H), 3.61 (t, *J* = 4.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, 298K) δ 166.11, 130.99, 128.23, 72.52, 70.54, 70.29, 69.07, 63.62, 61.62. HR-ESI-MS m/z: calcd for $[C_{11}H_{20}O_6Na]^+$, 271.1152, found: 271.1156.

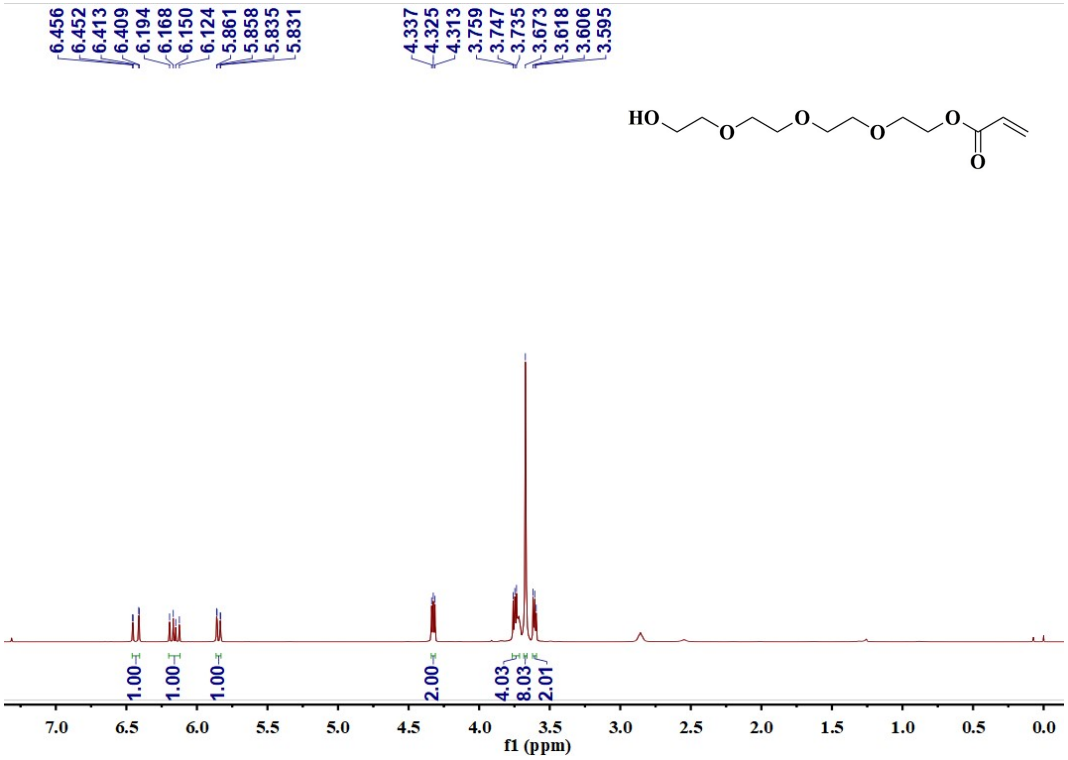


Fig. S10 ^{1}H NMR of **ATTEG** (400 MHz, $CDCl_3$, 298K).

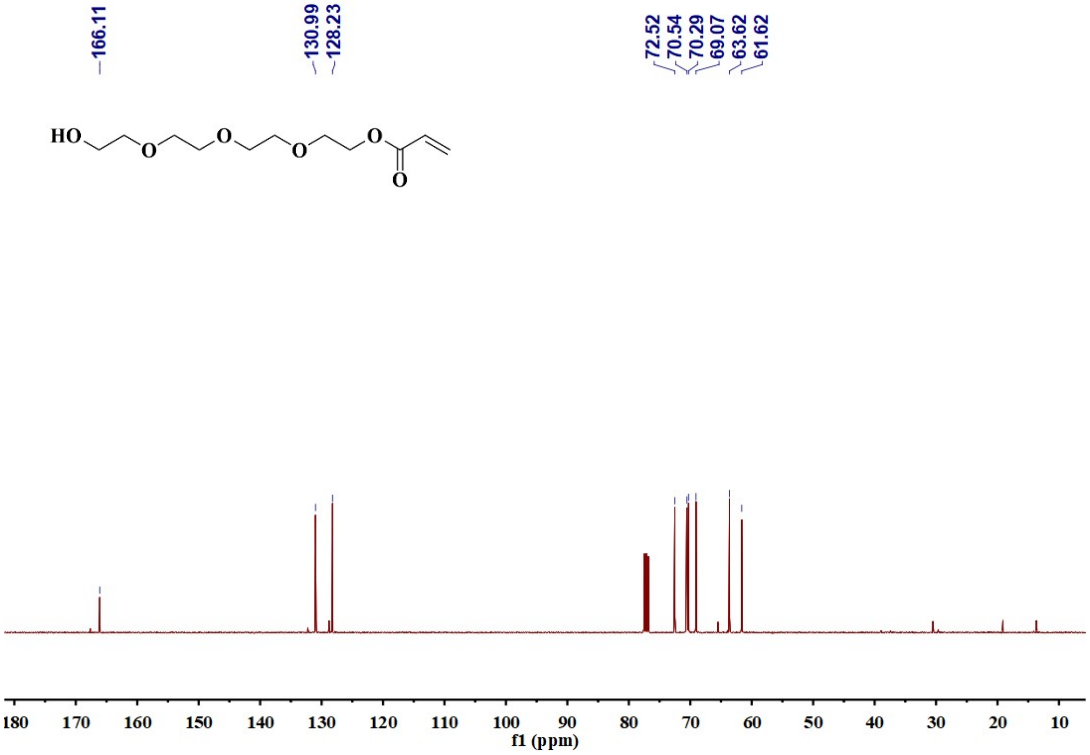


Fig. S11 ^{13}C NMR of **ATTEG** (101 MHz, $CDCl_3$, 298K).

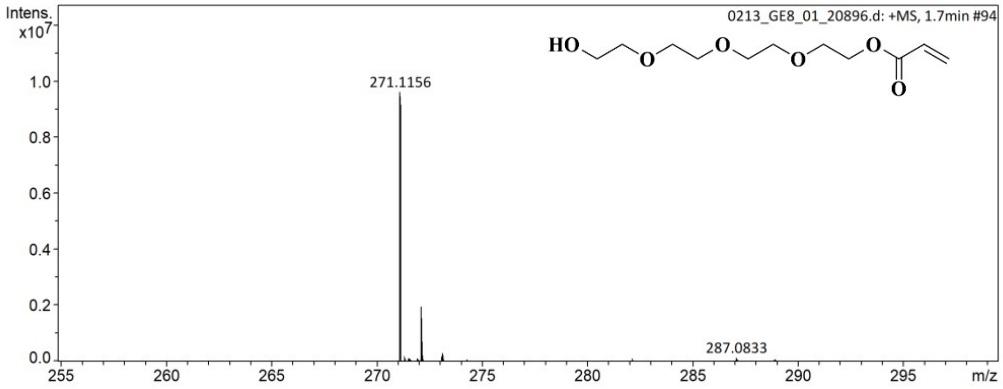


Fig. S12 HR-ESI-MS of **ATTEG**.

Synthesis of DATTEG.

Under nitrogen protection, tetraethylene glycol (2.00 g, 10.3 mmol) and trimethylamine (4.17 g, 41.20 mmol) were added into 15 mL anhydrous dichloromethane and the solution was stirred for 30 min at 0 °C. Then acryloyl chloride (3.71 g, 41.20 mmol) was added into the above solution drop by drop. The mixture was stirred for about 24 h at room temperature. After the reaction finished, the mixture was extracted with

dichloromethane and water. The organic phase was combined and washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether /ethyl acetate = 6:1) to afford **DATTEG** as a colorless liquid (2.65 g, 85 %). The NMR and HR-ESI-MS spectra of **DATTEG** are shown in Fig. S13, S14 and S15.

^{1}H NMR (600 MHz, $CDCl_3$, 298K) δ 6.35 (dd, J = 17.4, 1.2 Hz, 2H), 6.08 (dd, *J* = 17.4, 10.2 Hz, 2H), 5.77 (dd, *J* = 10.8, 1.2 Hz, 2H), 4.24 (t, *J* = 4.8 Hz, 4H), 3.67 (t, *J* = 4.8 Hz, 4H), 3.59 (s, 8H). ^{13}C NMR (151 MHz, $CDCl_3$, 298K) δ 166.10, 130.97, 128.27, 70.61, 69.09, 63.65. HR-ESI-MS m/z: calcd for $[C_{14}H_{22}O_7Na]^+$, 325.1258, found: 325.1253.

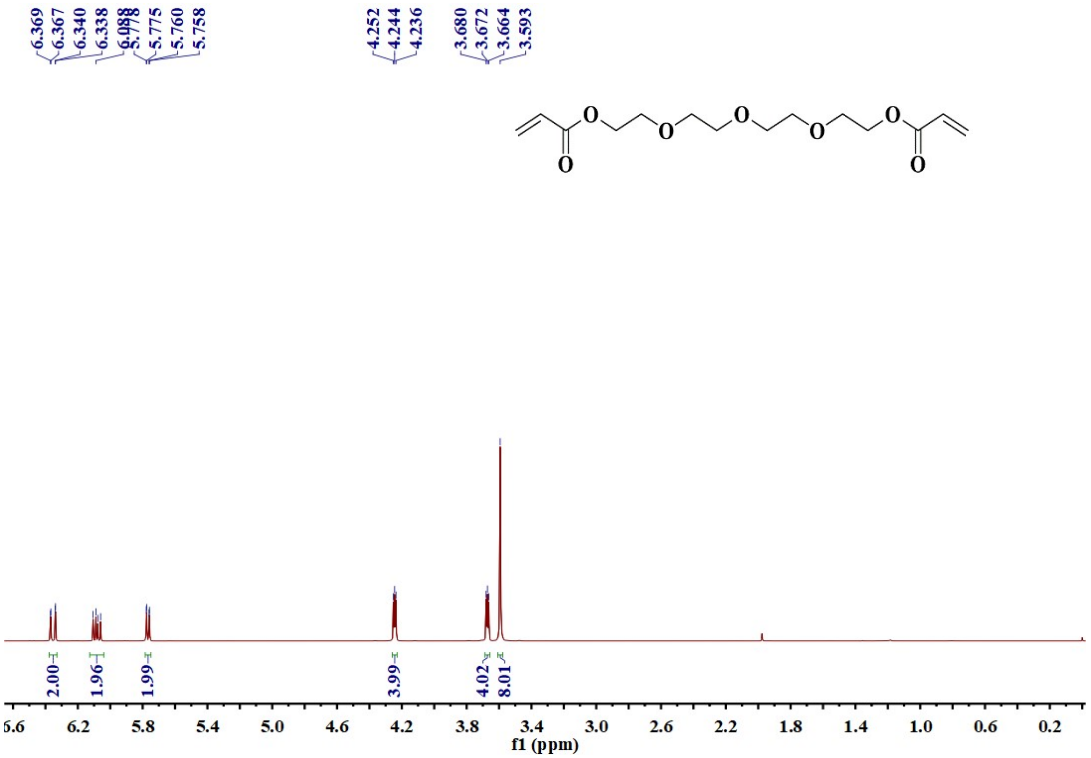


Fig. S13 ^{1}H NMR of monomer **DATTEG** (600 MHz, $CDCl_3$, 298K)

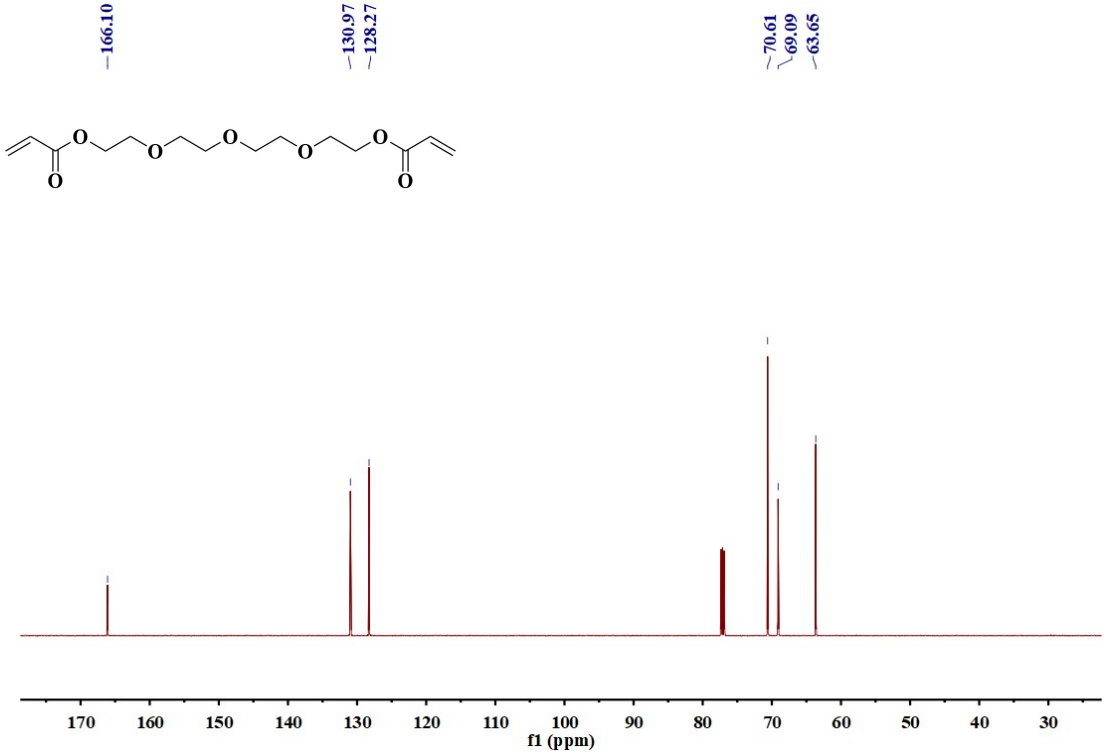


Fig. S14 ^{13}C NMR of monomer **DATTEG** (151 MHz, $CDCl_3$, 298K)

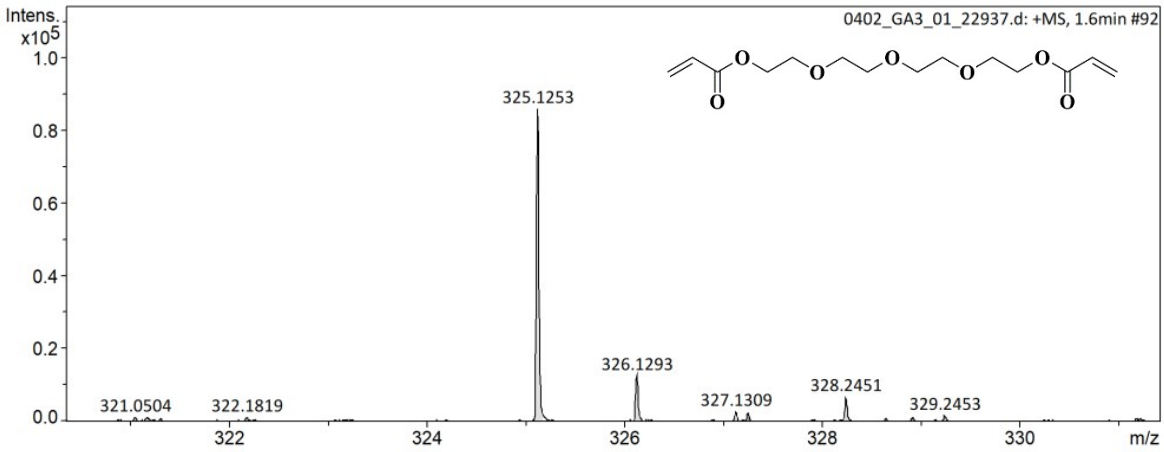


Fig. S15 HR-ESI-MS of monomer **DATTEG**

(3) Copolymeraization and characterization of P1-P3.

ATTEG-P5A (88.0 mg, 0.08 mmol), **ATTEG** (1000.0 mg, 4.0 mmol), **DATTEG** (244.0 mg, 0.8 mmol), 2, 2-azobisisobutyronitrile (**AIBN**, 2.2 mg, 13.4 mmol) were dissolved in dry dimethylformamide (1.2 mL) in Schlenk tube. The solution was degassed by three freeze-pump-thaw cycles, and heated at 80 °C for 10 h to give a jelly-like solid. The solid was soaked with DMF repeatedly to remove unreacted monomers and oligomers, then soaked with water repeatedly to replace the DMF molecules, and then dried under vacuum to afford the copolymer **P1** as a colorless transparent viscous solid (992.0 mg). Copolymer **P2** and **P3** were prepared through a similar method. The solid ^{13}C NMR, FT-IR, and TGA spectra for polymers are shown in Fig. S16, S17, and S18. **P2** and **P3** are too sticky to perform the ^{13}C NMR experiments.

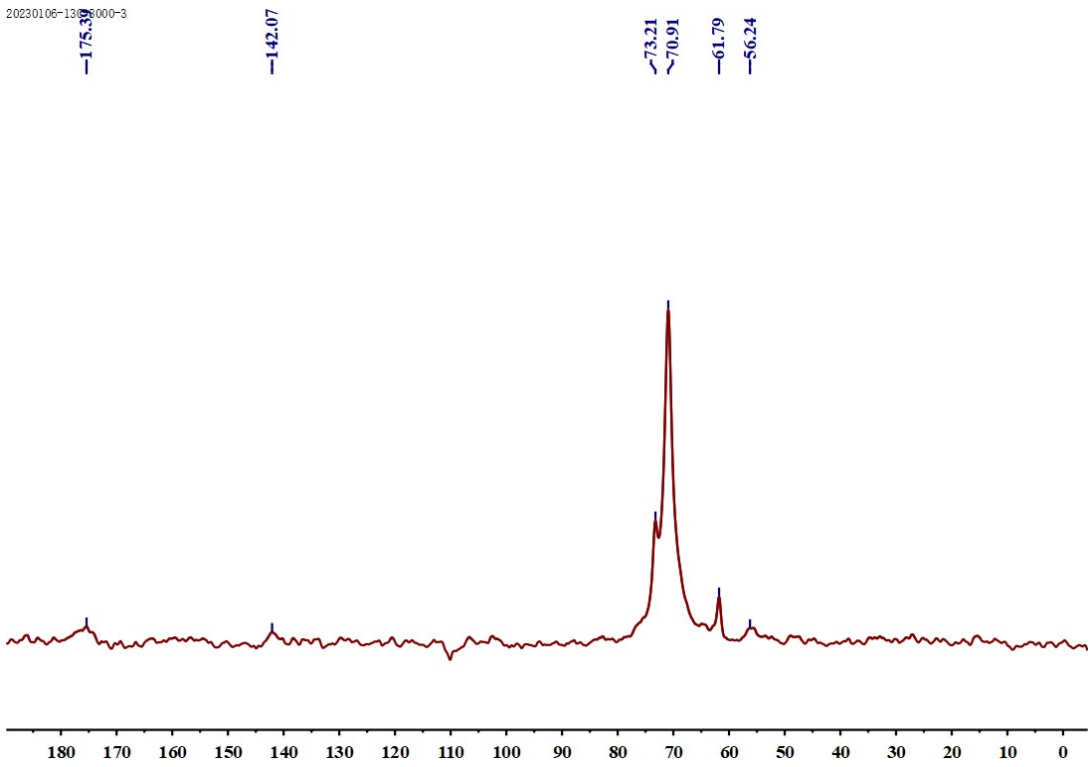


Fig. S16 Solid-state ^{13}C NMR spectrum of **P1** (400 MHz, 298K).

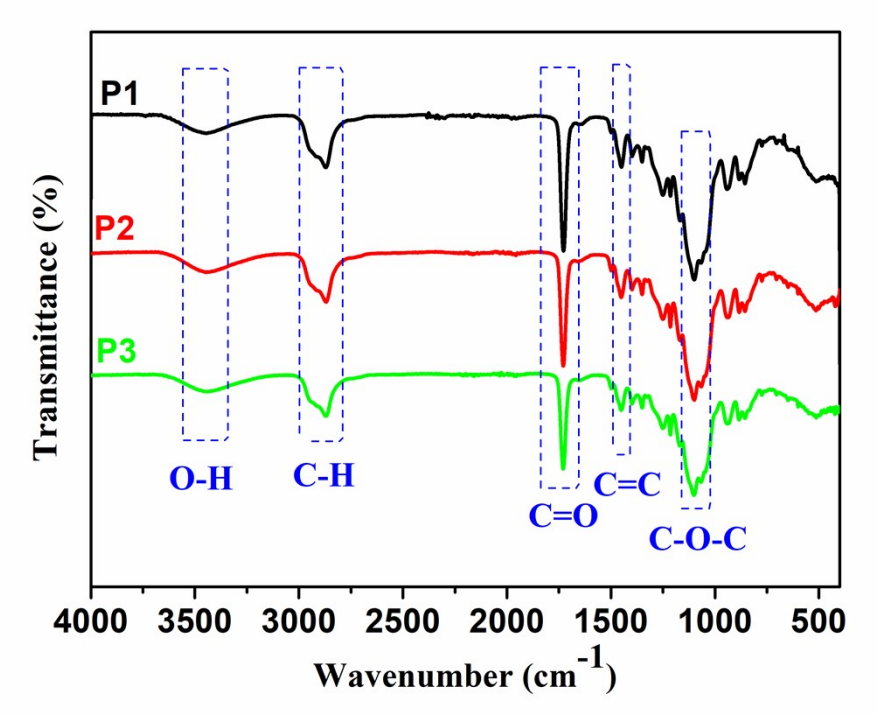


Fig. S17 FT-IR spectra of **P1**, **P2**, and **P3**.

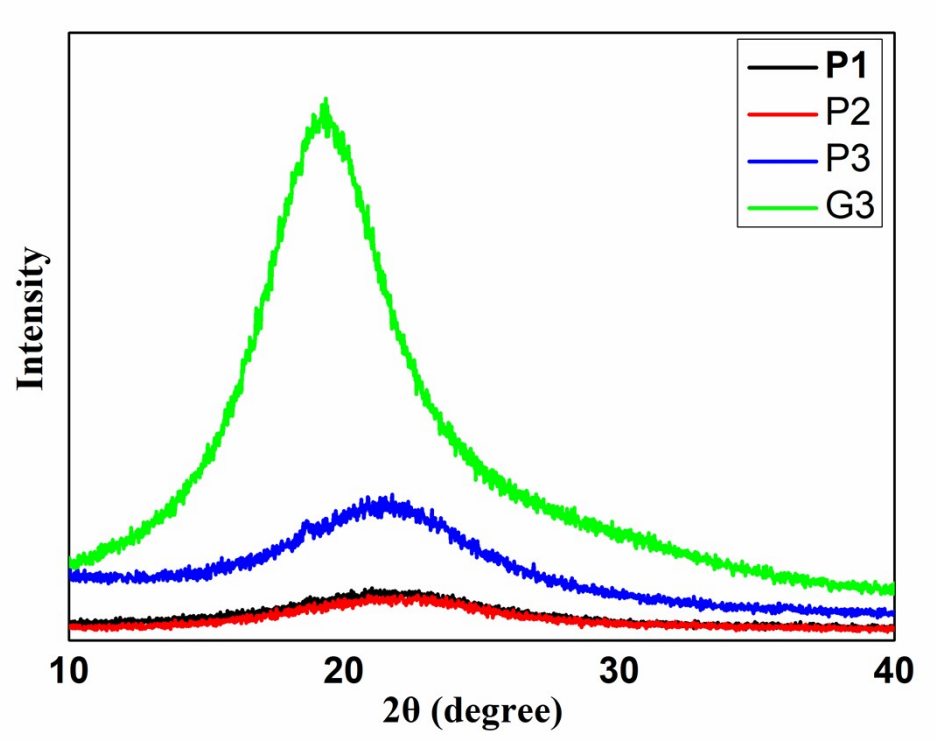


Fig. S18 PXRD spectra of **P1**, **P2**, **P3** and **G3.**

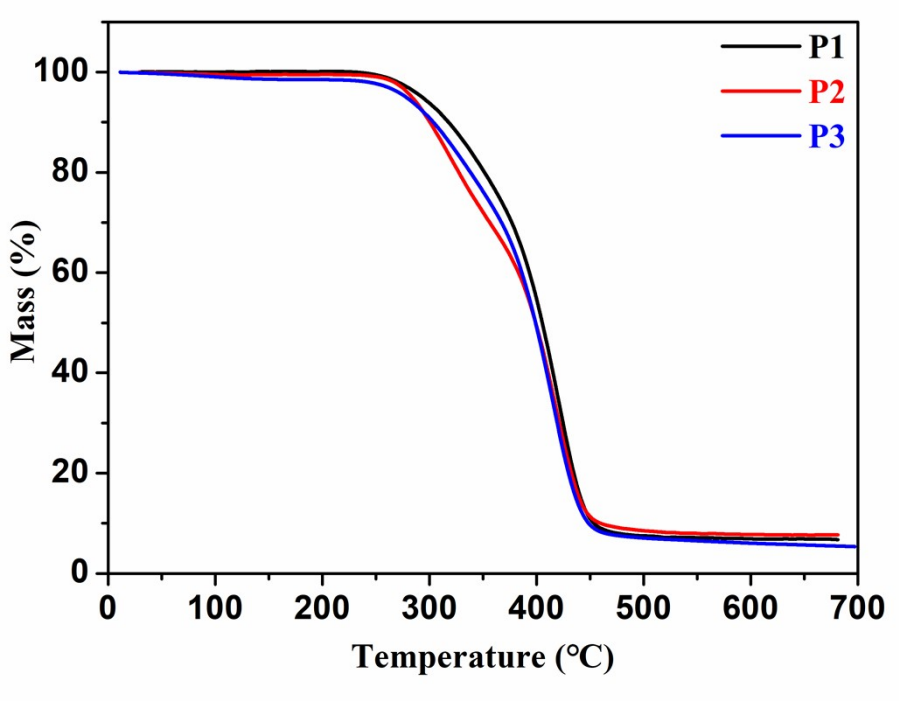


Fig. S19 TGA spectra of **P1**, **P2**, and **P3**.

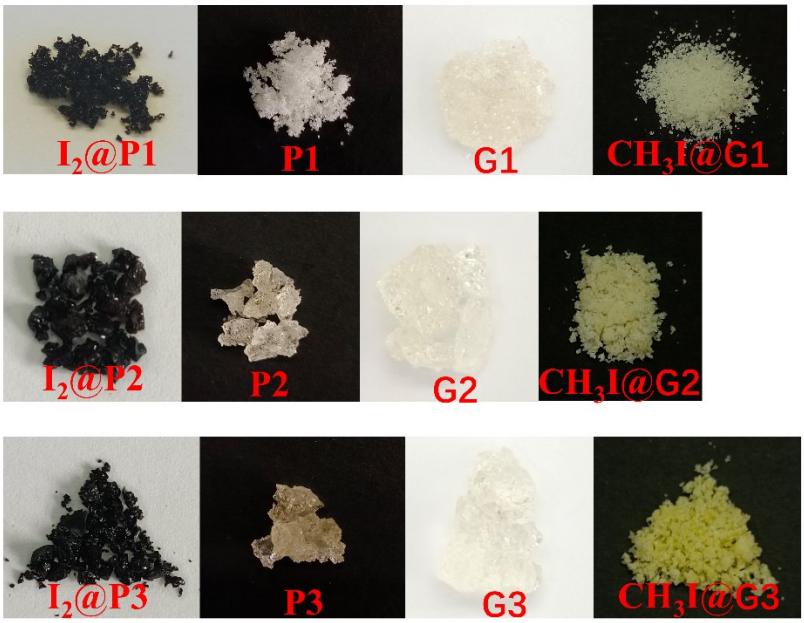


Fig. S20 Photographs showing the state and color changes before and after CH_3I/I_2 capture.

Table S1 Static CH_3I adsorption performances of various adsorbents.

Type	Adsorbent	Temperature (°C)	CH_3I uptake ($g \cdot g^{-1}$)	Ref.
MOFs	MIL-101-Cr-TED	150	0.71	Nat. Commun., 2017, 8, 485.
COFs	SCU-COF-2	75	1.45	Chem, 2021, 7, 699.
	COF-TAPT	25	1.53	Nat. Commun., 2022, 13, 2878.
Polymers	MHP-P5Q	25	0.803	Nat. Commun., 2020, 11, 1086.
	Polysulfate	25	1.573	*Angew. Chem. Int. Ed.,* 2022, *61*, e202208577.
	Tetraethylene Glycol-Based Polymer	25	1.685	This work

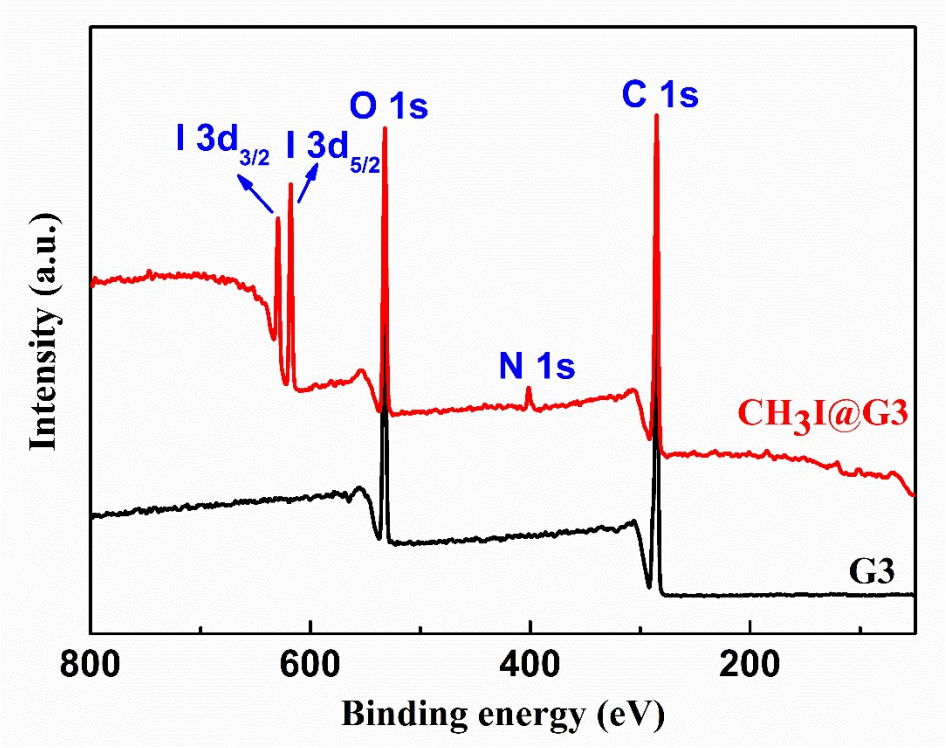


Fig. S21 Full survey XPS spectra of **G3** and **CH_3I@G3**, related to Fig. 2b and 2c. When preparing the sample, pyridine in **G3** evaporated completely due to reduced pressure. So, no peak corresponding to N 1s appeared.

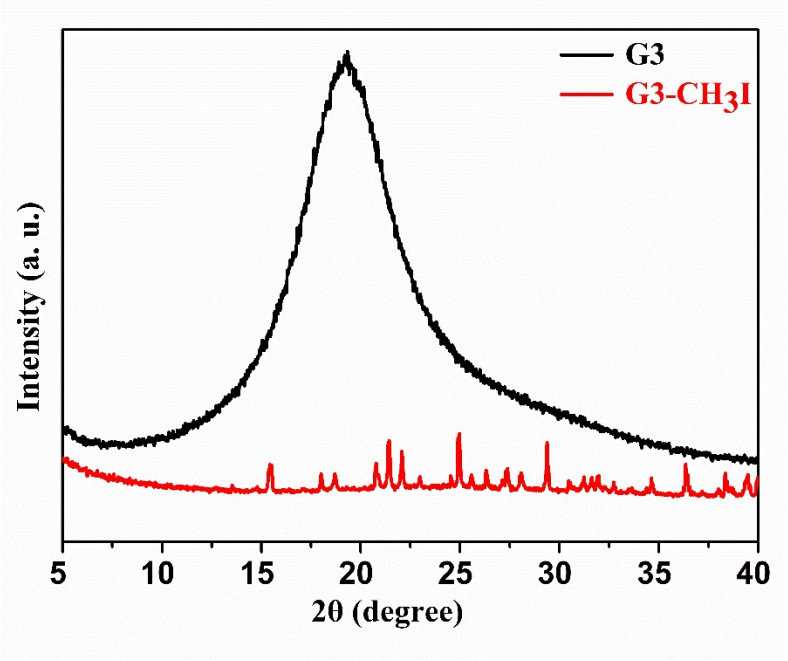


Fig. S22 PXRD spectra of **G3** and **CH_3I@G3**.

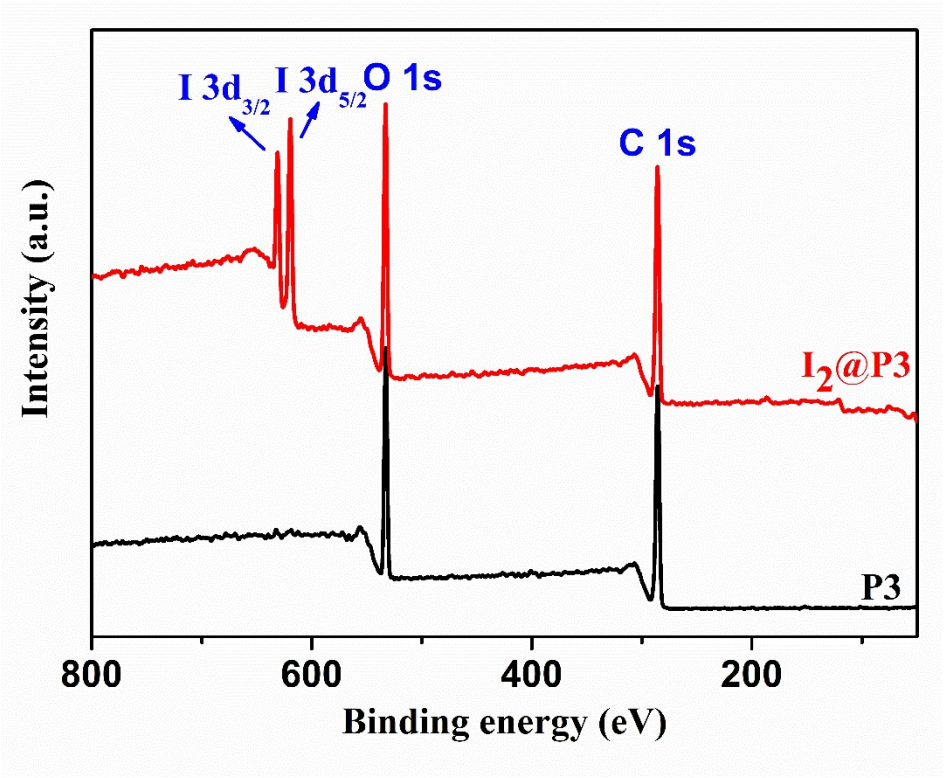


Fig. S23 Full survey XPS spectra of **P3** and **I_2@P3**, related to Fig. 4d.

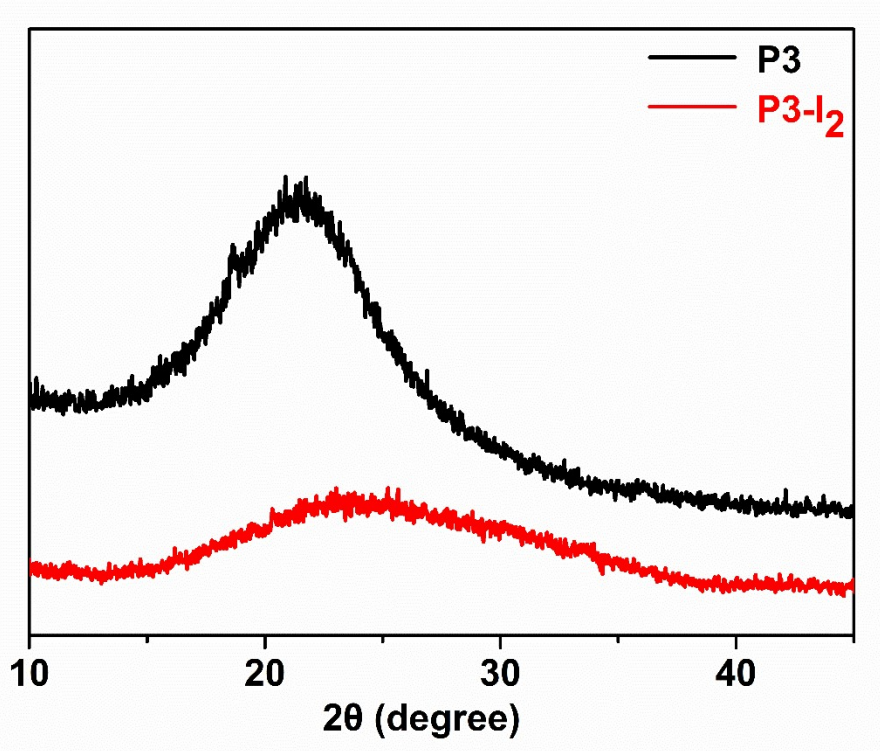


Fig. S24 PXRD spectra of **P3** and **I_2@G3**.