

**Supporting information for**  
**Modification of Polybutadiene with Trifluoromethyl**  
**and Clickable Azide Groups in One-Shot**

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## Experimental section

### Materials

Polybutadiene (PB, predominantly 1,2-addition approx. 90% 1,2-vinyl, Sigma-Aldrich), copper(I) bromide (CuBr, Sigma-Aldrich, 99.99%), trimethylsilyl azide (TMSN<sub>3</sub>, TCI, >95.0%), 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (Togni reagent II, TCI, 98%), 1-pyrenemethanol (Macklin, 98%), tetrakis(acetonitrile)copper (I) hexafluorophosphate (Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub>), Sigma-Aldrich, 97%), 2,2,3,3,4,4,5,5-octafluoropentan-1-ol (Macklin, 98%), poly(ethylene glycol monomethyl ether) (PEG-OH, TCI,  $M_n = 550$  g/mol) and 1,1,4,7,7-Pentamethyldiethylenetriamine (PMDETA, J&K, 98%) were used as received. Dichloromethane (DCM, J&K, 99.9%), acetonitrile (CH<sub>3</sub>CN, J&K, 99.9%) and *N,N*-dimethylformamide (DMF, J&K, 99.9%) were distilled prior to use. Other reagents not specially mentioned were purchased from Aladdin and used as received without further purification.

### Measurements

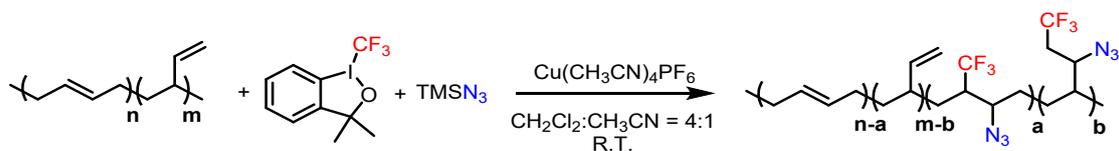
Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500-30,000), HR4 (5,000-600,000), and HR5 (50,000-4,000,000), 7.8×300 mm, particle size: 5 μm). GPC measurements were carried out at 35°C using THF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear polystyrene standards. FT-IR spectra were recorded on a

Nicolet AVATAR-360 FT-IR spectrophotometer with a 4 cm<sup>-1</sup> resolution. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded with a JEOL ECZ400 NMR spectrometer. The contact angle of water on the surface of polymer film was characterized using a JC2000C instrument at room temperature. Differential scanning calorimetry (DSC) was performed on a TA Q200 instrument in N<sub>2</sub> with a heating rate of 10°C/min. Thermogravimetry analysis (TGA) was conducted on a TA TGA 55 thermal analysis system in N<sub>2</sub> with a heating rate of 10°C/min.

### Synthesis of CF<sub>3</sub>/N<sub>3</sub>-modified PB 2a

Polybutadiene (584.8 mg, 10.81 mmol,  $M_n^{\text{GPC}} = 4,400$  g/mol,  $M_w/M_n = 1.41$ ), 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (534.7 mg, 1.62 mmol) and Cu(CH<sub>3</sub>CN)<sub>4</sub>PF<sub>6</sub> (20.1 mg, 0.054 mmol) were added into a flame-dried Schlenk tube. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (16 mL) and CH<sub>3</sub>CN (4 mL) were charged into the flask and the mixture was degassed via three freeze-pump-thaw cycles. After stirring for 30 minutes, TMSN<sub>3</sub> (248.9 mg, 2.16 mmol) was added and then the reaction mixture was stirred for 21 hours at room temperature. The tube was frozen by liquid N<sub>2</sub> and the mixture was diluted by CH<sub>2</sub>Cl<sub>2</sub> and passed through a short Al<sub>2</sub>O<sub>3</sub> column to remove the residual copper catalyst. The solution was concentrated and precipitated into cold CH<sub>3</sub>OH. After repeated purification by dissolving in CH<sub>2</sub>Cl<sub>2</sub> and precipitating in cold CH<sub>3</sub>OH three times, 358.4 mg of brown powder was obtained after drying *in vacuo* overnight. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm): 5.61-5.18 (2H×(n-a), CH<sub>2</sub>CH=CHCH<sub>2</sub>) and 1H×(m-b), CH<sub>2</sub>CHCH=CH<sub>2</sub>), 4.93 (2H×(m-b),

$\text{CH}_2\text{CHCH}=\text{CH}_2$ , 3.73 (1H×a,  $\text{CH}_2\text{CH}(\text{CF}_3)\text{CHN}_3\text{CH}_2$ ), 3.28 (1H×b,  $\text{CH}_2\text{CHCHN}_3\text{CH}_2\text{CF}_3$ ), 2.63 (2H×b,  $\text{CH}_2\text{CHCHN}_3\text{CH}_2\text{CF}_3$ ), 2.49 (1H×a,  $\text{CH}_2\text{CH}(\text{CF}_3)\text{CHN}_3\text{CH}_2$ ), 2.35-0.53 (4H×(n-a),  $\text{CH}_2\text{CH}=\text{CHCH}_2$ ; 3H×(m-b),  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ; 4H×a,  $\text{CH}_2\text{CH}(\text{CF}_3)\text{CHN}_3\text{CH}_2$  and 3H×b,  $\text{CH}_2\text{CHCHN}_3\text{CH}_2\text{CF}_3$ ).  
 $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -64.08~-63.22 (3F×a,  $\text{CHCF}_3$  and 3F×b,  $\text{CH}_2\text{CF}_3$ ). GPC:  $M_n^{\text{GPC}} = 5,400$  g/mol,  $M_w/M_n = 1.43$ .



**Scheme S1.** Synthesis of  $\text{CF}_3/\text{N}_3$ -modified PB **2a**.

### Synthesis of $\text{CF}_3/\text{N}_3$ -modified PB **2b**

Polybutadiene (625.7 mg, 11.57 mmol,  $M_n^{\text{GPC}} = 4,400$  g/mol,  $M_w/M_n = 1.41$ ), 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (1.145 g, 3.47 mmol) and  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (43.1 mg, 0.116 mmol) were added into a flame-dried Schlenk tube. Anhydrous  $\text{CH}_2\text{Cl}_2$  (16 mL) and  $\text{CH}_3\text{CN}$  (4 mL) were charged into the flask and the mixture was degassed via three freeze-pump-thaw cycles. After stirring for 30 minutes,  $\text{TMSN}_3$  (533.4 mg, 4.63 mmol) was added and then the reaction mixture was stirred for 21 hours at room temperature. The tube was frozen by liquid  $\text{N}_2$  and the mixture was diluted by  $\text{CH}_2\text{Cl}_2$  and passed through a short  $\text{Al}_2\text{O}_3$  column to remove the residual copper catalyst. The solution was concentrated and precipitated into cold *n*-hexane/diethyl ether ( $v/v = 2/1$ ). After repeated purification by dissolving in  $\text{CH}_2\text{Cl}_2$  and precipitating in cold *n*-hexane/diethyl ether ( $v/v = 2/1$ ) three times, 467.3 mg of

brown powder was obtained after drying *in vacuo* overnight.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 5.61-5.18 (2H $\times$ (n-a),  $\text{CH}_2\text{CH}=\text{CHCH}_2$  and 1H $\times$ (m-b),  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ), 4.93 (2H $\times$ (m-b),  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ), 3.73 (1H $\times$ a,  $\text{CH}_2\text{CH}(\text{CF}_3)\text{CHN}_3\text{CH}_2$ ), 3.28 (1H $\times$ b,  $\text{CH}_2\text{CHCHN}_3\text{CH}_2\text{CF}_3$ ), 2.63 (2H $\times$ b,  $\text{CH}_2\text{CHCHN}_3\text{CH}_2\text{CF}_3$ ), 2.49 (1H $\times$ a,  $\text{CH}_2\text{CH}(\text{CF}_3)\text{CHN}_3\text{CH}_2$ ), 2.35-0.53 (4H $\times$ (n-a),  $\text{CH}_2\text{CH}=\text{CHCH}_2$ ; 3H $\times$ (m-b),  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ; 4H $\times$ a,  $\text{CH}_2\text{CH}(\text{CF}_3)\text{CHN}_3\text{CH}_2$  and 3H $\times$ b,  $\text{CH}_2\text{CHCHN}_3\text{CH}_2\text{CF}_3$ ).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -64.08~-63.22 (3F $\times$ a,  $\text{CHCF}_3$  and 3F $\times$ b,  $\text{CH}_2\text{CF}_3$ ). GPC:  $M_n^{\text{GPC}} = 6,800$  g/mol,  $M_w/M_n = 1.35$ .

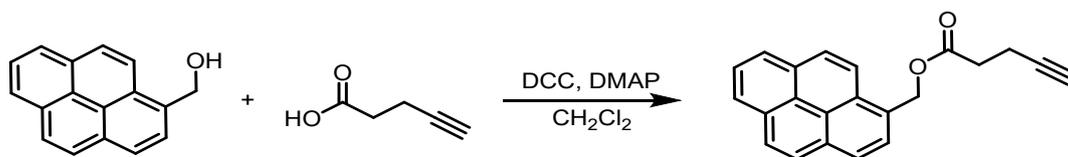
### Synthesis of $\text{CF}_3/\text{N}_3$ -modified PB 2c

Polybutadiene (613.3 mg, 11.34 mmol,  $M_n^{\text{GPC}} = 4,400$  g/mol,  $M_w/M_n = 1.41$ ), 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (1.683 g, 5.10 mmol) and  $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$  (63.3 mg, 0.170 mmol) were added into a flame-dried Schlenk tube. Anhydrous  $\text{CH}_2\text{Cl}_2$  (16 mL) and  $\text{CH}_3\text{CN}$  (4 mL) were charged into the flask and the mixture was degassed via three freeze-pump-thaw cycles. After stirring for 30 minutes,  $\text{TMSN}_3$  (783.4 mg, 6.80 mmol) was added and then the reaction mixture was stirred for 21 hours at room temperature. The tube was frozen by liquid  $\text{N}_2$  and the mixture was diluted by  $\text{CH}_2\text{Cl}_2$  and passed through a short  $\text{Al}_2\text{O}_3$  column to remove the residual copper catalyst. The solution was concentrated and precipitated into cold *n*-hexane/diethyl ether ( $v/v = 2/1$ ). After repeated purification by dissolving in  $\text{CH}_2\text{Cl}_2$  and precipitating in cold *n*-hexane/diethyl ether ( $v/v = 2/1$ ) three times, 688.3 mg of brown powder was obtained after drying *in vacuo* overnight.  $^1\text{H}$  NMR (400 MHz,

CDCl<sub>3</sub>):  $\delta$  (ppm): 5.61-5.18 (2H $\times$ (n-a), CH<sub>2</sub>CH=CHCH<sub>2</sub> and 1H $\times$ (m-b), CH<sub>2</sub>CHCH=CH<sub>2</sub>), 4.93 (2H $\times$ (m-b), CH<sub>2</sub>CHCH=CH<sub>2</sub>), 3.73 (1H $\times$ a, CH<sub>2</sub>CH(CF<sub>3</sub>)CHN<sub>3</sub>CH<sub>2</sub>), 3.28 (1H $\times$ b, CH<sub>2</sub>CHCHN<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub>), 2.63 (2H $\times$ b, CH<sub>2</sub>CHCHN<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub>), 2.49 (1H $\times$ a, CH<sub>2</sub>CH(CF<sub>3</sub>)CHN<sub>3</sub>CH<sub>2</sub>), 2.35-0.53 (4H $\times$ (n-a), CH<sub>2</sub>CH=CHCH<sub>2</sub>; 3H $\times$ (m-b), CH<sub>2</sub>CHCH=CH<sub>2</sub>; 4H $\times$ a, CH<sub>2</sub>CH(CF<sub>3</sub>)CHN<sub>3</sub>CH<sub>2</sub> and 3H $\times$ b, CH<sub>2</sub>CHCHN<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub>). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) -64.08~-63.22 (3F $\times$ a, CHCF<sub>3</sub> and 3F $\times$ b, CH<sub>2</sub>CF<sub>3</sub>). GPC:  $M_n^{GPC}$  = 5,800 g/mol,  $M_w/M_n$  = 1.32.

### Synthesis of pyren-1-ylmethyl pent-4-ynoate (pyrene-alkyne)

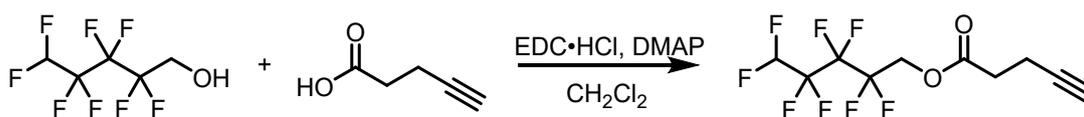
To a DCM solution (15 mL) of 1-pyrenemethanol (1.16 g, 5.0 mmol), 4-pentynoic acid (0.588 g, 6.0 mmol) and DMAP (61.08 mg, 0.50 mmol), DCC (1.03 g, 5.0 mmol) was added at 0°C and the mixture was stirred at 0°C for 1 hour. Next, the mixture was stirred overnight at room temperature. After the filtration of solid residue, the solvent was rotary evaporated. The crude product was purified by silica column chromatography (ethyl acetate:*n*-hexane = 1:20) to afford the product as a yellow solid (1.12 g, 71.7%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm): 8.46-7.93 (m, 9H, ArH), 5.82 (s, 2H, CH≡CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 2.81 (t, 1H, CH≡CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 2.57 (t, 2H, CH≡CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 2.41 (dt, 2H, CH≡CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>).



**Scheme S2.** Synthesis of pyren-1-ylmethyl pent-4-ynoate (pyrene-alkyne).

## Synthesis of perfluoroalkyl-alkyne

4-Pentynoic acid (0.98 g, 10.0 mmol), 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (2.32 g, 10.0 mmol), DMAP (0.122 g, 10.0 mmol), EDC·HCl (1.9 g, 10.0 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL) were added to a 50 mL Schlenk flask, followed by stirring at room temperature for 22 hours. The mixture was washed by NaHCO<sub>3</sub> aqueous solution and brine, and extracted with DCM. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was rotary evaporated. The crude product was purified by silica column chromatography (*n*-hexane:dichloromethane = 5:1) to afford a colorless liquid (1.92 g, 61.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm): 6.03 (t, 1H, CF<sub>2</sub>H), 4.61 (t, 2H, CH≡CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 2.66 (t, 2H, CH≡CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 2.53 (td, 2H, CH≡CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 1.99 (t, 1H, CH≡CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ (ppm): -120.34 (2F, CO<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H), -125.92 (2F, CO<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H), -130.75 (2F, CO<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H), -138.90 (2F, CO<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>H).

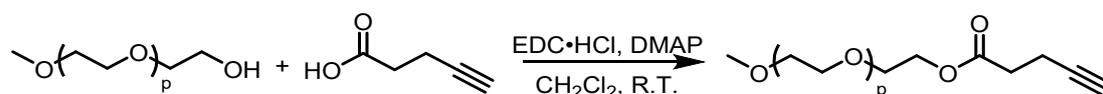


**Scheme S3.** Synthesis of perfluoroalkyl-alkyne.

## Synthesis of PEG-alkyne

PEG-OH (2.2 g, 4.0 mmol), 4-pentynoic acid (0.47 g, 4.8 mmol), DMAP (48.9 mg, 0.4 mmol), EDC·HCl (0.766 g, 4.0 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL) were added to a 100 mL Schlenk flask, followed by stirring at room temperature for 20 hours. The mixture was washed by NaHCO<sub>3</sub> aqueous solution and brine, and extracted with DCM. The

organic phase was dried over  $\text{Na}_2\text{SO}_4$  and the solvent was rotary evaporated. The crude product was purified by silica column chromatography ( $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{OH} = 50:1$ ) to afford a brown liquid (1.42 g, 56.3%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 4.29-4.21 (m, 2H,  $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 3.84-3.43 (m, 44H,  $\text{OCH}_2\text{CH}_2$ ), 3.37 (s, 3H,  $\text{OCH}_3$ ), 2.62-2.53 (m, 2H,  $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 2.49 (ddd, 2H,  $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 1.97 (t, 1H,  $\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ).

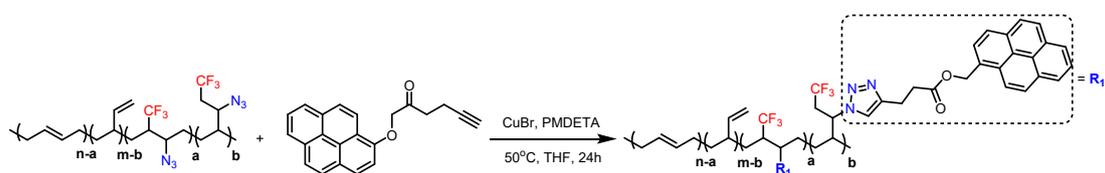


**Scheme S4.** Synthesis of PEG-alkyne.

### Synthesis of pyrene-installed PB

$\text{CF}_3/\text{N}_3$ -modified PB **2b** (100.0 mg, 0.28 mmol,  $M_n^{\text{GPC}} = 6,800$  g/mol,  $M_w/M_n = 1.35$ ), pyren-1-ylmethyl pent-4-ynoate (131.2 mg, 0.42 mmol),  $\text{CuBr}$  (40.2 mg, 0.28 mmol),  $\text{PMDETA}$  (72.8 mg, 0.42 mmol) and THF (20 mL) were added into a flame-dried Schlenk tube. The mixture was degassed via three freeze-pump-thaw cycles and put into an oil bath set at  $50^\circ\text{C}$ . The reaction was allowed to proceed for 24 hours and terminated by liquid  $\text{N}_2$ . The mixture was diluted by THF and passed through a short  $\text{Al}_2\text{O}_3$  column to remove the residual copper catalyst. The solution was concentrated and precipitated into cold diethyl ether. After repeated purification by dissolving in THF and precipitating in cold diethyl ether three times, 50.4 mg of brown powder was obtained after drying *in vacuo* overnight.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 8.36-7.66 (9H $\times$ (a+b), pyrene-H), 6.96 (1H $\times$ (a+b),  $\text{NCH}=\text{CNCH}_2$ ), 5.80 (2H $\times$ (a+b),  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 5.61-5.18 (2H $\times$ (n-a),  $\text{CH}_2\text{CH}=\text{CHCH}_2$  and 1H $\times$ (m-b),

$\text{CH}_2\text{CHCH}=\text{CH}_2$ ), 4.93 ( $2\text{H}\times(\text{m}-\text{b})$ ,  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ), 3.86 ( $1\text{H}\times\text{a}$ ,  $\text{CH}_2\text{CHCF}_3\text{CHNCH}_2$  and  $1\text{H}\times\text{b}$ ,  $\text{CHCHNCH}_2\text{CF}_3$ ), 3.02 ( $2\text{H}\times(\text{a}+\text{b})$ ,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 2.77 ( $2\text{H}\times(\text{a}+\text{b})$ ,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 2.63 ( $2\text{H}\times\text{b}$ ,  $\text{CHNCH}_2\text{CF}_3$ ), 2.49 ( $1\text{H}\times\text{a}$ ,  $\text{CH}_2\text{CHCF}_3\text{CHNCH}_2$ ), 2.35-0.53 ( $4\text{H}\times(\text{n}-\text{a})$ ,  $\text{CH}_2\text{CH}=\text{CHCH}_2$ ;  $2\text{H}\times(\text{m}-\text{b})$ ,  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ;  $1\text{H}\times(\text{m}-\text{b})$ ,  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ;  $2\text{H}\times\text{a}$ ,  $\text{CH}_2\text{CHCF}_3\text{CHNCH}_2$ ;  $2\text{H}\times\text{a}$ ,  $\text{CHCF}_3\text{CHNCH}_2$ ;  $2\text{H}\times\text{b}$ ,  $\text{CH}_2\text{CHCHN}$  and  $1\text{H}\times\text{b}$ ,  $\text{CH}_2\text{CHCHN}$ ).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -64.08~-63.22 ( $3\text{F}\times\text{a}$ ,  $\text{CHCF}_3$  and  $3\text{F}\times\text{b}$ ,  $\text{CH}_2\text{CF}_3$ ).  $M_n^{\text{GPC}} = 8,300$  g/mol,  $M_w/M_n = 1.33$ .

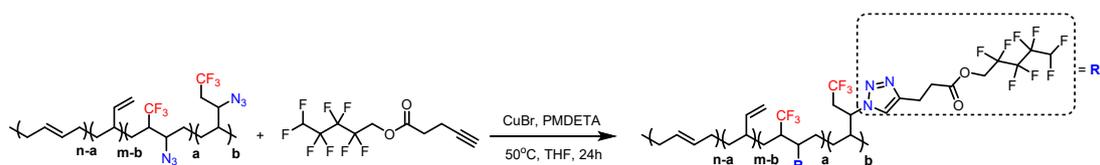


**Scheme S5.** Synthesis of pyrene-installed PB.

### Synthesis of perfluoroalkyl-installed PB

$\text{CF}_3/\text{N}_3$ -modified PB **2b** (100.0 mg, 0.28 mmol,  $M_n^{\text{GPC}} = 6,800$  g/mol,  $M_w/M_n = 1.35$ ), perfluoroalkyl-alkyne (131.1 mg, 0.42 mmol), CuBr (40.2 mg, 0.28 mmol), PMDETA (72.8 mg, 0.42 mmol) and THF (20 mL) were added into a flame-dried Schlenk tube. The mixture was degassed via three freeze-pump-thaw cycles and put into an oil bath set at  $50^\circ\text{C}$ . The reaction was allowed to proceed for 24 hours and terminated by liquid  $\text{N}_2$ . The mixture was diluted by THF and passed through a short  $\text{Al}_2\text{O}_3$  column to remove the residual copper catalyst. The solution was concentrated and precipitated into cold *n*-hexane. After repeated purification by dissolving in THF and precipitating in cold *n*-hexane three times, 50.4 mg of brown powder was

obtained after drying *in vacuo* overnight.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.31 ( $1\text{H}\times(\text{a}+\text{b})$ ,  $\text{NCH}=\text{CNCH}_2$ ), 6.04 ( $1\text{H}\times(\text{a}+\text{b})$ ,  $\text{CF}_2\text{H}$ ), 5.61-5.18 ( $2\text{H}\times(\text{n}-\text{a})$ ,  $\text{CH}_2\text{CH}=\text{CHCH}_2$  and  $1\text{H}\times(\text{m}-\text{b})$ ,  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ), 4.93 ( $2\text{H}\times(\text{m}-\text{b})$ ,  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ), 4.57 ( $2\text{H}\times(\text{a}+\text{b})$ ,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 4.27-4.02 ( $1\text{H}\times\text{a}$ ,  $\text{CH}_2\text{CHCF}_3\text{CHNCH}_2$  and  $1\text{H}\times\text{b}$ ,  $\text{CH}_2\text{CHCHNCH}_2\text{CF}_3$ ), 3.03 ( $2\text{H}\times(\text{a}+\text{b})$ ,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 2.84 ( $2\text{H}\times(\text{a}+\text{b})$ ,  $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2$ ), 2.63 ( $2\text{H}\times\text{b}$ ,  $\text{CHNCH}_2\text{CF}_3$ ), 2.49 ( $1\text{H}\times\text{a}$ ,  $\text{CH}_2\text{CHCF}_3\text{CHNCH}_2$ ), 2.35-0.53 ( $4\text{H}\times(\text{n}-\text{a})$ ,  $\text{CH}_2\text{CH}=\text{CHCH}_2$ ;  $2\text{H}\times(\text{m}-\text{b})$ ,  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ;  $1\text{H}\times(\text{m}-\text{b})$ ,  $\text{CH}_2\text{CHCH}=\text{CH}_2$ ;  $2\text{H}\times\text{a}$ ,  $\text{CH}_2\text{CHCF}_3\text{CHNCH}_2$ ;  $2\text{H}\times\text{a}$ ,  $\text{CHCF}_3\text{CHNCH}_2$ ;  $2\text{H}\times\text{b}$ ,  $\text{CH}_2\text{CHCHN}$  and  $1\text{H}\times\text{b}$ ,  $\text{CH}_2\text{CHCHN}$ ).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -64.08~-63.22 ( $3\text{F}\times\text{a}$ ,  $\text{CHCF}_3$  and  $3\text{F}\times\text{b}$ ,  $\text{CH}_2\text{CF}_3$ ), -120.34 ( $2\text{F}\times(\text{a}+\text{b})$ ,  $\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$ ), -125.92 ( $2\text{F}\times(\text{a}+\text{b})$ ,  $\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$ ), -130.75 ( $2\text{F}\times(\text{a}+\text{b})$ ,  $\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{H}$ ), -138.90 ( $2\text{F}\times(\text{a}+\text{b})$ ,  $\text{CHCF}_2$ ).  $M_n^{\text{GPC}} = 8,900$  g/mol,  $M_w/M_n = 1.33$ .

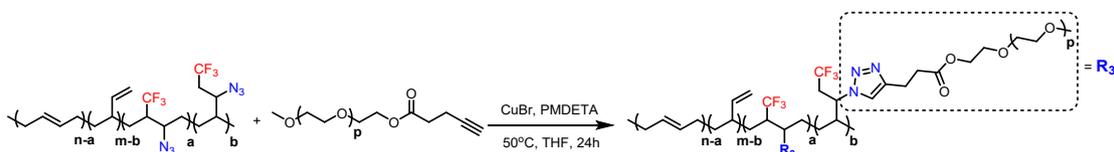


**Scheme S6.** Synthesis of perfluoroalkyl-installed PB.

### Synthesis of PEG-installed PB

$\text{CF}_3/\text{N}_3$ -modified PB **2b** (100.0 mg, 0.28 mmol,  $M_n^{\text{GPC}} = 6,800$  g/mol,  $M_w/M_n = 1.35$ ), PEG-alkyne (352.8 mg, 0.56 mmol,  $M_n = 550$  g/mol), CuBr (80.3 mg, 0.56 mmol), PMDETA (97.0 mg, 0.56 mmol) and THF (20 mL) were added into a flame-dried Schlenk tube. The mixture was degassed via three freeze-pump-thaw cycles and

put into an oil bath set at 50°C. The reaction was allowed to proceed for 24 hours and terminated by liquid N<sub>2</sub>. The mixture was diluted by THF and passed through a short Al<sub>2</sub>O<sub>3</sub> column to remove the residual copper catalyst. The solution was concentrated and precipitated into cold *n*-hexane/diethyl ether (v/v = 2:1). After repeated purification by dissolving in THF and precipitating in cold *n*-hexane/diethyl ether (v/v = 2:1) three times, 46.8 mg of brown viscous polymer was obtained after drying *in vacuo* overnight. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm): 7.31 (1H×(a+b), NCH=CNCH<sub>2</sub>), 5.61-5.18 (2H×(n-a), CH<sub>2</sub>CH=CHCH<sub>2</sub> and 1H×(m-b), CH<sub>2</sub>CHCH=CH<sub>2</sub>), 4.93 (2H×(m-b), CH<sub>2</sub>CHCH=CH<sub>2</sub>), 4.20 (2H×(a+b), CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 3.73-3.57 (1H×a, CH<sub>2</sub>CHCF<sub>3</sub>CHNCH<sub>2</sub>; 1H×b, CHCHNCH<sub>2</sub>CF<sub>3</sub> and 44H×(a+b), OCH<sub>2</sub>CH<sub>2</sub>) 3.36 (3H×(a+b), OCH<sub>3</sub>), 3.00 (2H×(a+b), CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 2.74 (2H×(a+b), CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>2</sub>), 2.63 (2H×b, CHNCH<sub>2</sub>CF<sub>3</sub>), 2.49 (1H×a, CH<sub>2</sub>CHCF<sub>3</sub>CHNCH<sub>2</sub>), 2.35-0.53 (4H×(n-a), CH<sub>2</sub>CH=CHCH<sub>2</sub>; 2H×(m-b), CH<sub>2</sub>CHCH=CH<sub>2</sub>; 1H×(m-b), CH<sub>2</sub>CHCH=CH<sub>2</sub>; 2H×a, CH<sub>2</sub>CHCF<sub>3</sub>CHNCH<sub>2</sub>; 2H×a, CHCF<sub>3</sub>CHNCH<sub>2</sub>; 2H×b, CH<sub>2</sub>CHCHN and 1H×b, CH<sub>2</sub>CHCHN). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ (ppm) -64.08~-63.22 (3F×a, CHCF<sub>3</sub> and 3F×b, CH<sub>2</sub>CF<sub>3</sub>). *M<sub>n</sub>*<sup>GPC</sup> = 12,100 g/mol, *M<sub>w</sub>*/*M<sub>n</sub>* = 1.37.



**Scheme S7.** Synthesis of PEG-installed PB.

## SUPPORTING FIGURES

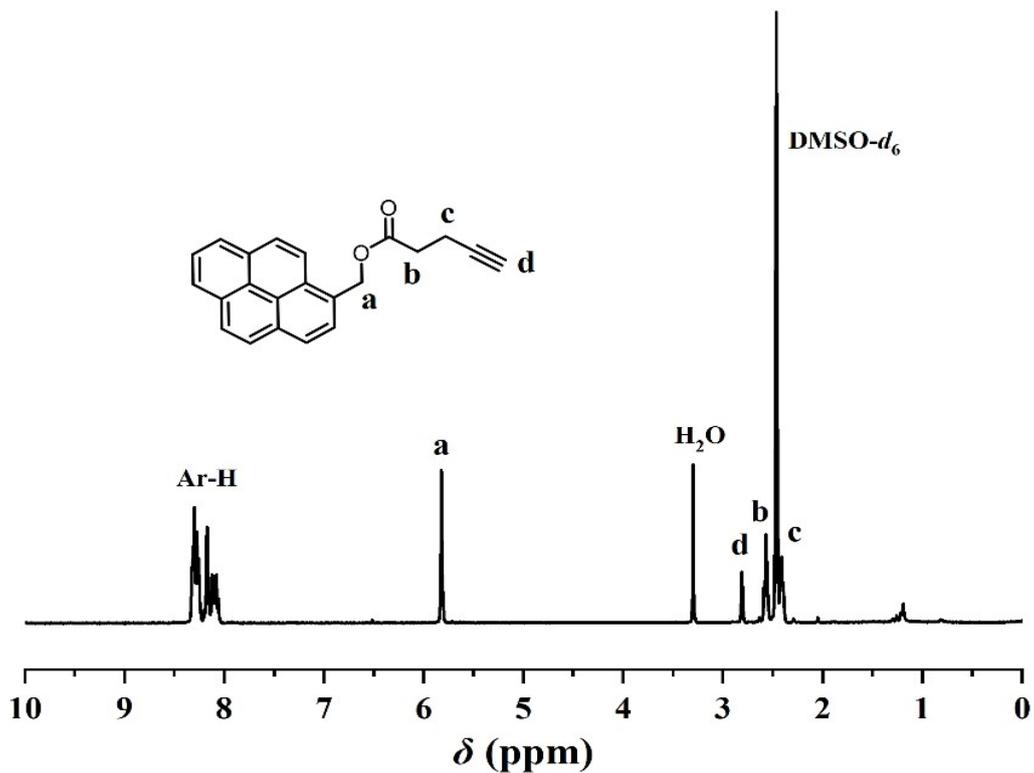


Figure S1. <sup>1</sup>H NMR spectrum of pyren-1-ylmethyl pent-4-ynoate in DMSO-*d*<sub>6</sub>.

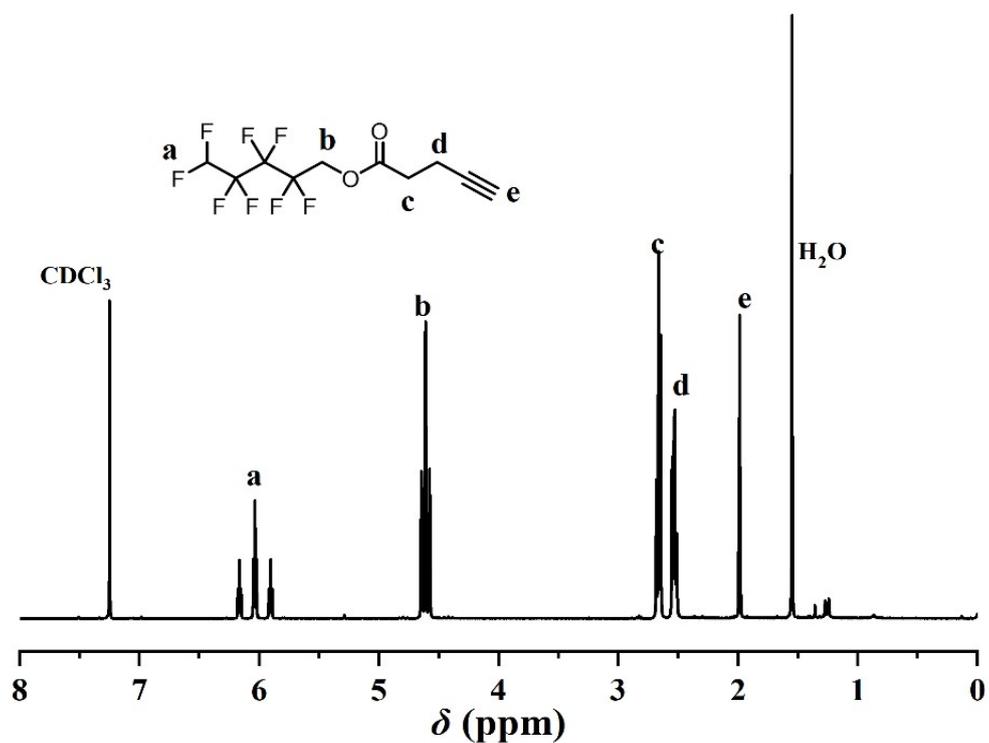


Figure S2. <sup>1</sup>H NMR spectrum of perfluoroalkyl-alkyne in CDCl<sub>3</sub>.

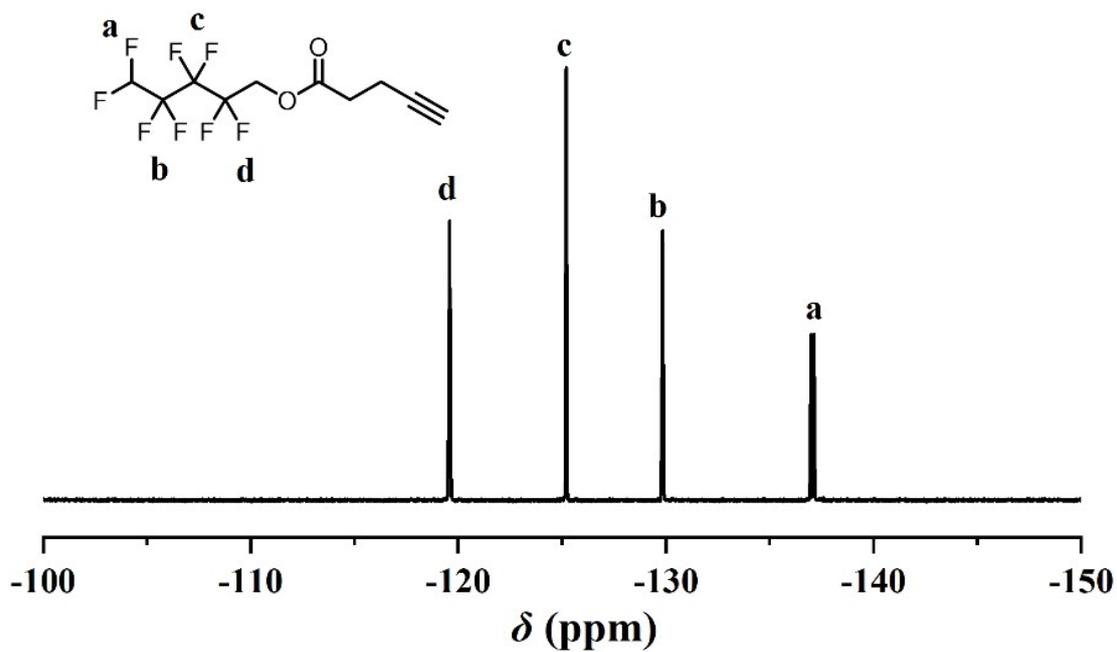


Figure S3.  $^{19}\text{F}$  NMR spectrum of perfluoroalkyl-alkyne in  $\text{CDCl}_3$ .

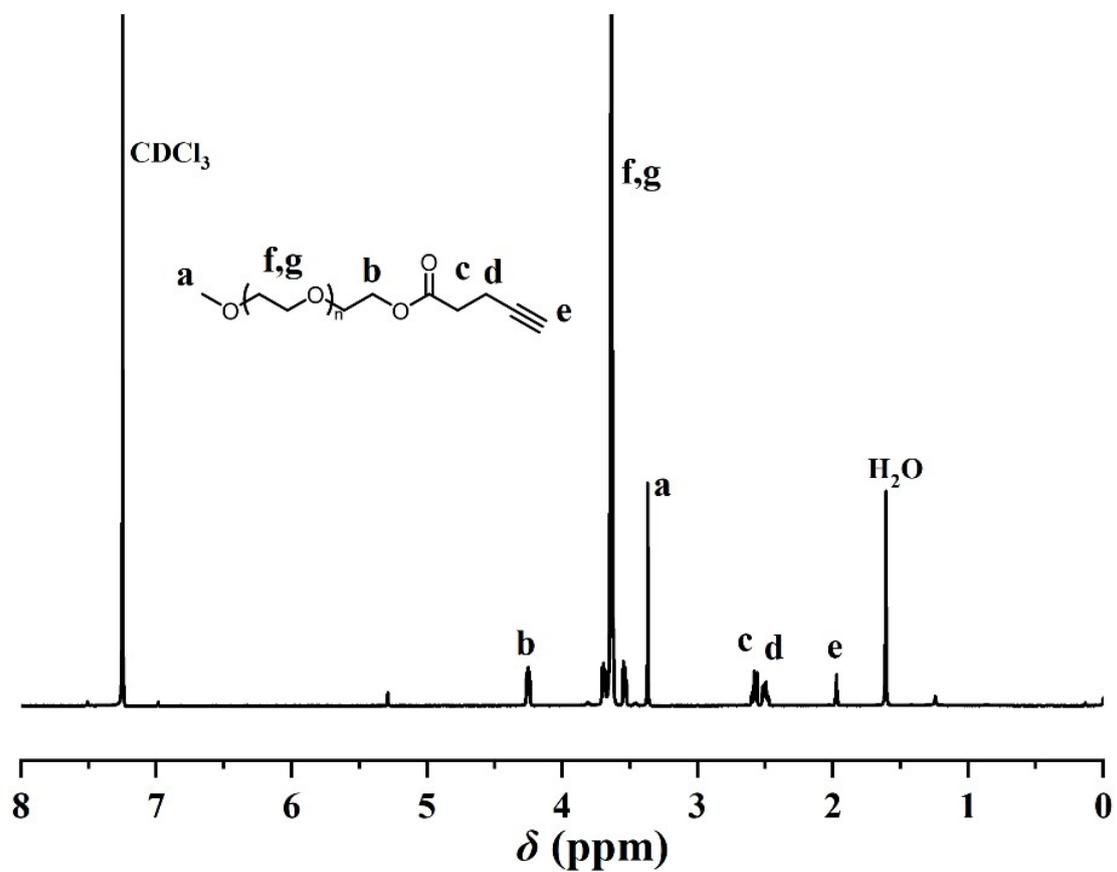
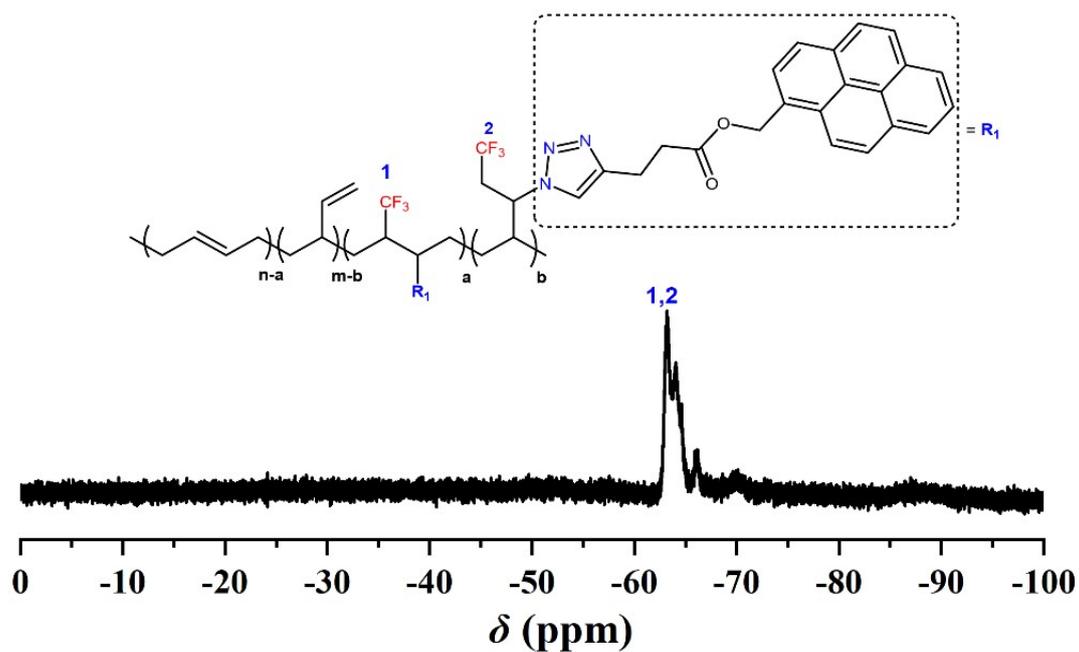
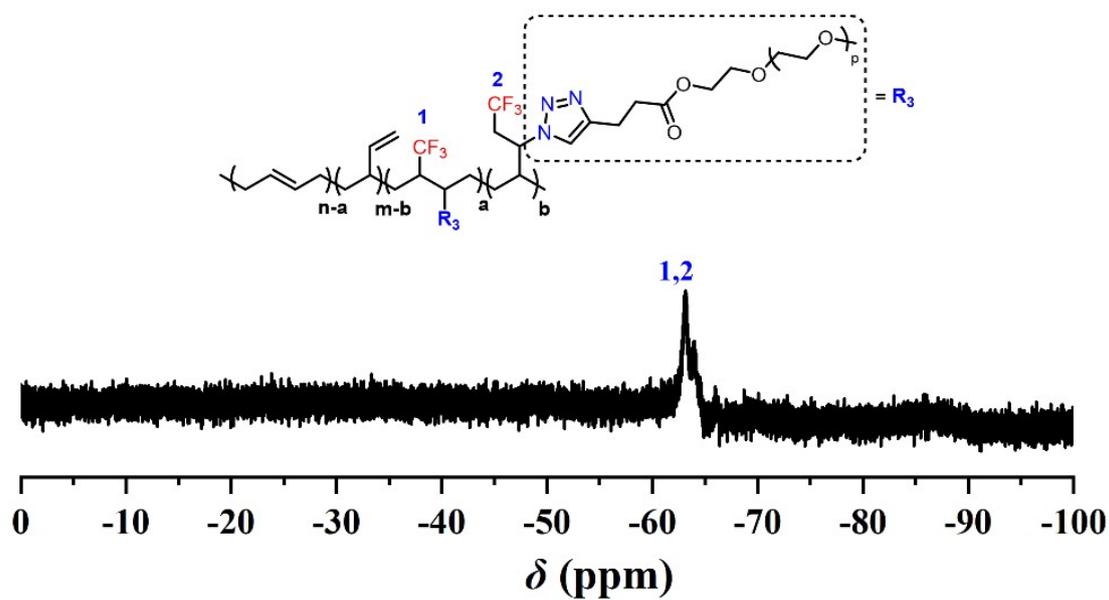


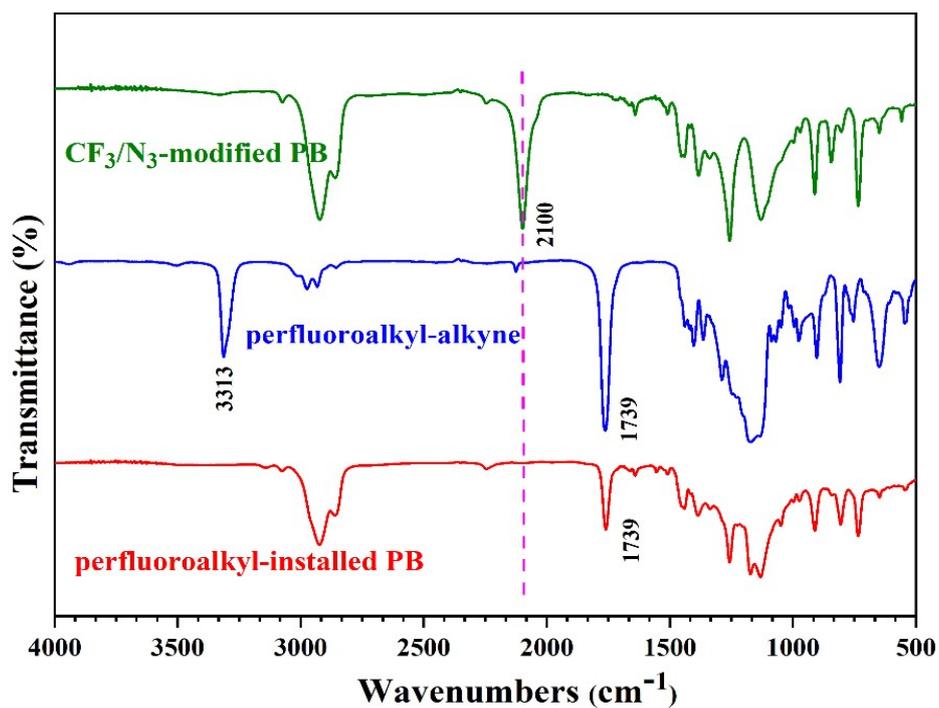
Figure S4.  $^1\text{H}$  NMR spectrum of PEG-alkyne in  $\text{CDCl}_3$ .



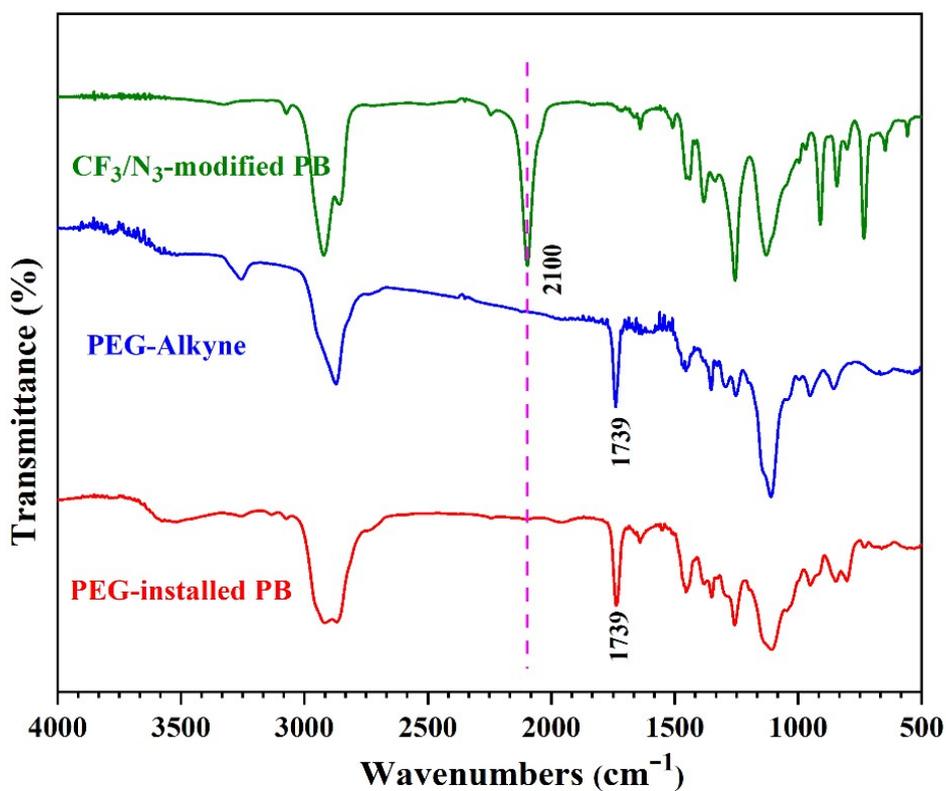
**Figure S5.** <sup>19</sup>F NMR spectrum of pyrene-installed PB in CDCl<sub>3</sub>.



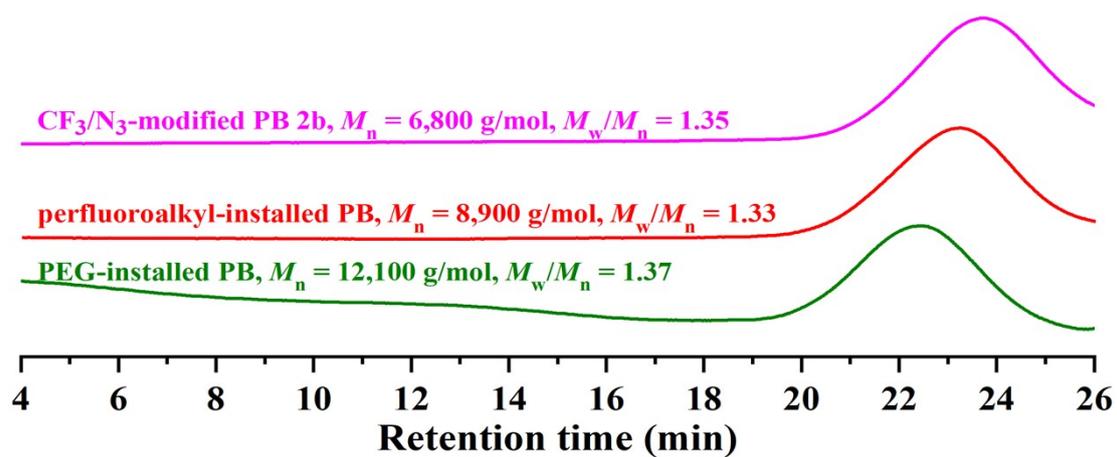
**Figure S6.** <sup>19</sup>F NMR spectrum of PEG-installed PB in CDCl<sub>3</sub>.



**Figure S7.** FT-IR spectra of CF<sub>3</sub>/N<sub>3</sub>-modified PB **2b**, perfluoroalkyl-alkyne and perfluoroalkyl-installed PB.



**Figure S8.** FT-IR spectra of CF<sub>3</sub>/N<sub>3</sub>-modified PB **2b**, PEG-alkyne and PEG-installed PB.



**Figure S9.** GPC curves of CF<sub>3</sub>/N<sub>3</sub>-modified PB **2b**, perfluoroalkyl- and PEG-installed PB in THF.

## References

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