

## Supplementary information

### A recyclable and reusable supported Cu(I) catalyzed azide-alkyne click polymerization

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## Experimental Section

**General Information.** Unless otherwise stated, all the chemicals used in this work were purchased from Acros or Alfa. Tetrahydrofuran (THF), toluene, and 1,4-dioxane were distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. *N,N*-Dimethylformamide (DMF) was extra-dry grade. Other solvents were purified by standard methods.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker ADVANCE2B 400 NMR spectrometer in  $\text{CDCl}_3$  using tetramethylsilane (TMS;  $\delta = 0$ ) as the internal reference. IR spectra were taken on a Bruker Vector 22 spectrometer. UV spectra were measured on a Varian VARY 100 Bio UV-visible spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Relative fluorescence quantum yields ( $\Phi_F$ ) were estimated using quinine sulfate in 0.1 N  $\text{H}_2\text{SO}_4$  ( $\Phi_F = 54.6\%$ ) as a standard. The absorbance of the solutions was kept 0.04–0.06 to avoid the internal filter effect. Mass spectra (MS) were carried out on a GCT Premier CAB 048 mass spectrometer operating in a chemical ionization mode (CI). Element analysis was conducted on a Thermo Finnigan Flash EA1112 system. Thermo-gravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer TGA 7 under dry nitrogen at 20  $^\circ\text{C}/\text{min}$ . Average molecular weights ( $M_w$  and  $M_n$ ) and polydispersity indices (PDI) of the polymers were estimated by a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with an interferometric refractometer detector, using a set of monodispersed polystyrenes as calibration standards and THF as the eluent at a flow rate of 1.0 mL/min.

**Purification of Amberlyst A-21 resin:** 20 g commercial wet Amberlyst A-21 resin was suspended in 100 mL methanol for 0.5 h and then filtered. The dried resin was allowed to suspend in 100 mL dichloromethane for 0.5 h and again filtered. The resulting resin was dried in vacuum oven overnight.

### Monomer Preparation

**1a**,<sup>1</sup> **1c**,<sup>2</sup> **2b**<sup>3</sup> and **2c**<sup>4</sup> were prepared according to the published procedures.

**1,1'-Bis(1-propargyl)-4,4'-isopropylidenediphenyl ether (1b).** 3-Bromo-1-propyne (11.2 g, 75 mmol), K<sub>2</sub>CO<sub>3</sub> (10.4 g, 75 mmol) and acetone (100 mL) were added into a 250 mL two-neck round-bottom flask. 4,4'-Isopropylidenediphenol (6.9 g, 30 mmol) in 30 mL of acetone was then added dropwise within 4 h under reflux. The mixture was further refluxed for 12 h and cooled to room temperature. The inorganic salt was filtered and washed with acetone several times. The filtrate was concentrated by a rotary evaporator and purified by a silica gel column using chloroform/petroleum ether (1:5 by volume) as eluent. A white solid was obtained in 89.0% yield (8.1 g). IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3269, 2970, 2117, 1506, 1220, 1018, 696, 555. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 7.12 (d, 4H), 6.90 (d, 4H), 4.68 (d, 4H), 2.53 (t, 2H), 1.67 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm): 155.4, 143.9, 127.7, 114.2, 78.8, 75.5, 55.7, 41.7, 31.0. Elemental analysis (calcd., found for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>): C (82.86, 82.59), H (6.62, 6.55).

**1,1'-Bis(6-bromohexyl)-4,4'-isopropylidenediphenyl ether (4).** Into a 500 mL round-bottom flask were added 1,6-dibromohexane (43.9 g, 180 mmol), K<sub>2</sub>CO<sub>3</sub> (33.2 g, 240 mmol), and 200 mL of acetone. 4,4'-Isopropylidenediphenol (13.7 g, 60

mmol) in 50 mL of acetone was then added dropwise within 4 h under reflux. The mixture was further refluxed for 12 h. After cooled to room temperature, the inorganic salt was filtered and washed with acetone several times. The filtrate was concentrated by a rotary evaporator and the residue was extracted with 200 mL of chloroform. The organic phase was washed with 100 mL of water three times, 100 mL of brine once and then dried over  $\text{MgSO}_4$  overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using chloroform/petroleum ether (1:5 by volume) as eluent. A white solid was obtained in 43.6% yield (14.5 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.13 (d, 4H), 6.78 (d, 4H), 3.93 (t, 4H), 3.28 (t, 4H), 1.78 (q, 4H), 1.62 (s, 10H), 1.47 (q, 8H).

**1,1'-Bis(6-azidohexyl)-4,4'-isopropylidenediphenyl ether (2a).** Into another 500 mL round-bottom flask were added **4** (14.4 g, 26 mmol) and sodium azide (5.1 g, 78 mmol) in 200 mL of DMSO. After stirring at room temperature for 24 h, a small amount of water was added to quench the reaction, during which the solution temperature was increased slightly. After cooled to room temperature, the solution was extracted with 50 mL of diethyl ether five times. The organic layers were combined, washed with water three times and brine once, dried over  $\text{MgSO}_4$  overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using chloroform/petroleum ether (1:5 by volume) as eluent. Monomer **2a** was obtained in 90.3% yield (11.2 g) as colorless viscous oil. IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 2938, 2095, 1510, 1249, 1011, 829, 555.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.15 (d, 4H), 6.81 (d, 4H), 3.95 (t, 4H), 3.30 (t, 4H), 1.80 (q, 4H), 1.66 (s, 10H),

1.52 (q, 8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 156.8, 142.9, 127.6, 113.7, 67.5, 51.3, 41.6, 31.0, 29.2, 28.7, 26.4, 25.9, 25.7. Elemental analysis (calcd., found for  $\text{C}_{27}\text{H}_{38}\text{N}_6\text{O}_2$ ): C (67.75, 68.02), H (8.00, 8.18), N (17.56, 17.27).

**Model reaction.** Phenyl propargyl ether (132.2 mg, 1.0 mmol) and **2a** (239.3 mg, 0.5 mmol) were added into a 25 mL Schlenk tube. After being evacuated and refilled with dry nitrogen three times, THF (5.0 mL) was then injected into the tube. The solution was stirred at 60 °C for 12 h. After evaporation of the solvent, the crude product was purified by a silica gel column using chloroform/ethyl acetate ether (1:2 by volume) as eluent. Model compound **6** was obtained in 96.8% yield (359.6 mg) as colorless viscous oil. IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 2939, 1595, 1502, 1240, 1022, 827.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.56 (s, 2H), 7.25 (q, 4H), 7.15 (d, 4H), 6.96 (q, 6H), 6.76 (d, 4H), 5.16 (s, 4H), 4.29 (d 4H), 3.87 (t, 4H), 1.88 (q, 4H), 1.71 (q, 4H), 1.61 (s, 6H), 1.46 (q, 4H), 1.34 (q, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 158.3, 156.9, 143.1, 129.6, 127.8, 114.9, 113.9, 67.5, 62.0, 50.3, 41.7, 31.1, 30.2, 29.1, 26.2, 25.6.

#### Polymer characterization:

Characterization Data for **PIab**: This polymer was prepared from the click polymerization of **1a** and **2a**. Light yellow solid; 87.1% yield.  $M_w$  55500; PDI 1.61 (GPC, polystyrene calibration). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 2938, 2094, 1506, 1232, 829, 575.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.66, 7.12, 6.93, 6.78, 5.15, 4.37, 3.91, 1.95, 1.76, 1.63, 1.51, 1.39.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 156.7, 152.7, 143.0, 127.6, 115.7, 113.6, 67.3, 62.6, 50.2, 41.5, 31.0, 30.1, 29.0, 26.1, 25.5.

Characterization Data of **PIab**. This polymer was prepared from the click

polymerization of **1a** and **2b**. White solid; 82.0% yield.  $M_w$  22 100; PDI 1.93 (GPC, polystyrene calibration). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3288, 2937, 2096, 1603, 1506, 1236, 1028, 825, 737, 520.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.61, 7.07, 6.61, 6.79, 5.16, 4.36, 3.86, 1.94, 1.73, 1.49, 1.38.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 158.0, 153.7, 153.5, 152.7, 144.9, 140.3, 137.0, 133.2, 132.1, 128.2, 126.8, 116.5, 114.2, 79.5, 76.1, 68.0, 63.3, 57.2, 51.0, 30.8, 29.7, 26.9, 26.2.

Characterization Data of **PIba**. This polymer was prepared from the click polymerization of **1b** and **2a**. White solid; 83.3% yield.  $M_w$  17 900; PDI 1.86 (GPC, polystyrene calibration). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3280, 2939, 2094, 1608, 1508, 1241, 1014, 831, 735, 567.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.62, 7.15, 6.91, 6.78, 5.18, 4.37, 3.92, 1.95, 1.77, 1.65, 1.51, 1.41.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 157.4, 156.8, 144.3, 143.7, 128.4, 116.5, 114.8, 68.1, 62.8, 51.0, 42.3, 31.7, 30.9, 29.7, 26.9, 26.2.

Characterization Data of **PIbc**. This polymer was prepared from the click polymerization of **1b** and **2c**. Light yellow solid; 65.1% yield.  $M_w$  69 600; PDI 3.25 (GPC, polystyrene calibration). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3284, 2937, 2096, 1606, 1508, 1228, 1012, 829, 735, 567.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.61, 7.15, 6.90, 6.80, 5.17, 4.36, 3.87, 1.94, 1.73, 1.64, 1.51, 1.40.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 156.8, 153.7, 128.4, 116.0, 114.8, 68.8, 62.8, 51.0, 42.3, 31.7, 30.9, 29.8, 26.9, 26.2.

Characterization Data of **PIca**. This polymer was prepared from the click polymerization of **1c** and **2a**. Light yellow solid; 75.2% yield.  $M_w$  27 100; PDI 2.36

(GPC, polystyrene calibration). IR (KBr),  $\nu$  ( $\text{cm}^{-1}$ ): 3288, 2937, 2096, 1608, 1508, 1245, 1045, 829, 701, 575.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 7.68, 7.59, 7.13, 6.81, 4.38, 3.93, 1.96, 1.77, 1.65, 1.53, 1.42.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm): 157.5, 148.2, 144.2, 143.7, 141.5, 132.6, 132.0, 128.5, 125.7, 120.1, 114.4, 68.1, 50.9, 42.3, 31.8, 31.0, 29.8, 26.9, 26.3.

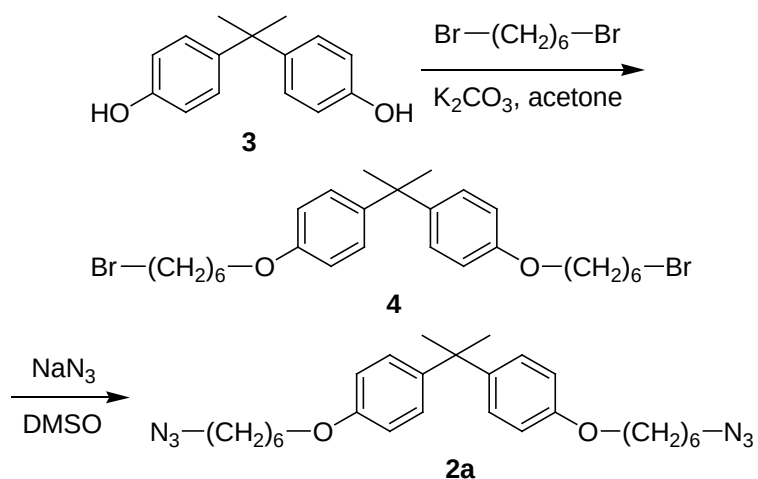


**Figure S1** | Synthetic route to monomer **2a**.

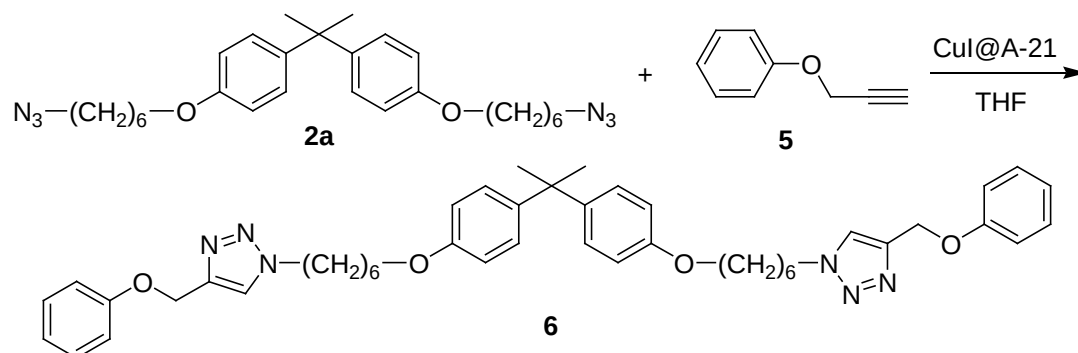


**Figure S2** | Synthetic route to model compound **6**

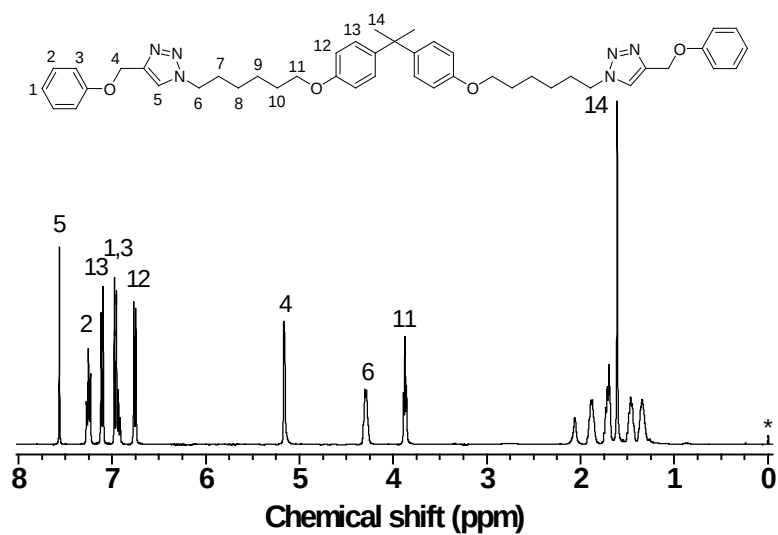


**Figure S3** |  $^1\text{H}$  NMR spectra of model compound **6** in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.

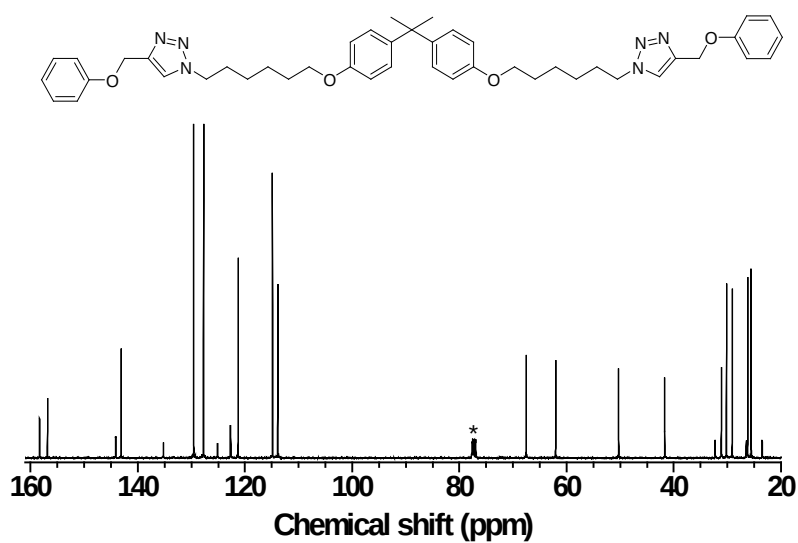


**Figure S4** |  $^{13}\text{C}$  NMR spectra of model compound **6** in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

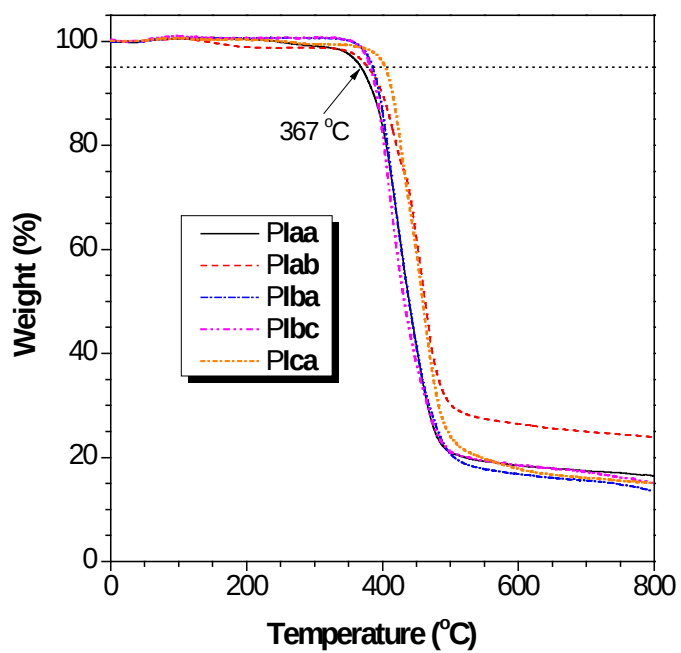


**Figure S5** | TGA thermograms of the polymers recorded under nitrogen at a heating rate of  $20\text{ }^{\circ}\text{C}/\text{min}$ .

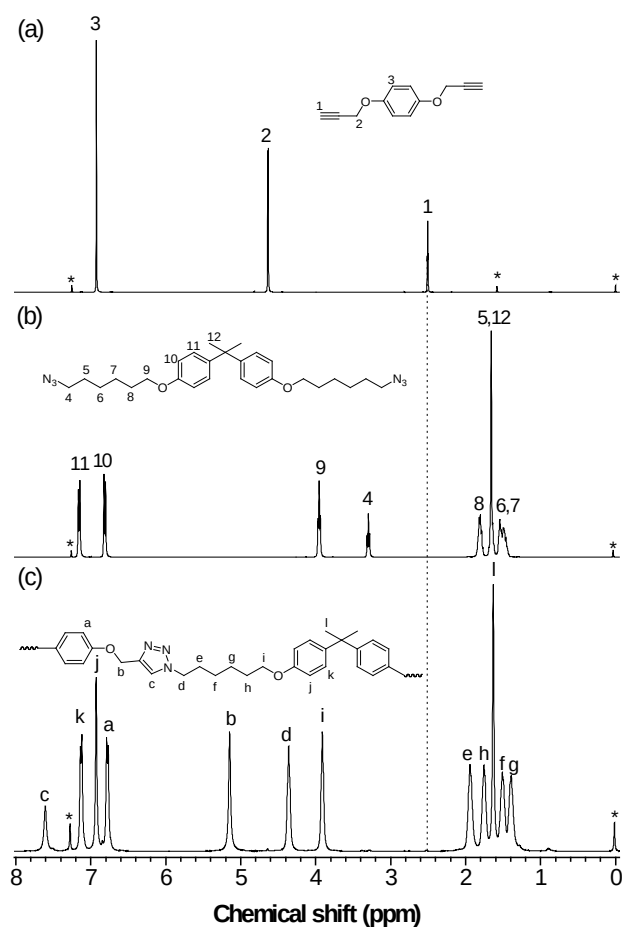


**Figure S6** |  $^1\text{H}$  NMR spectra of monomers **1a** (a), **2a** (b), and their polymer **PIaa** (c) in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

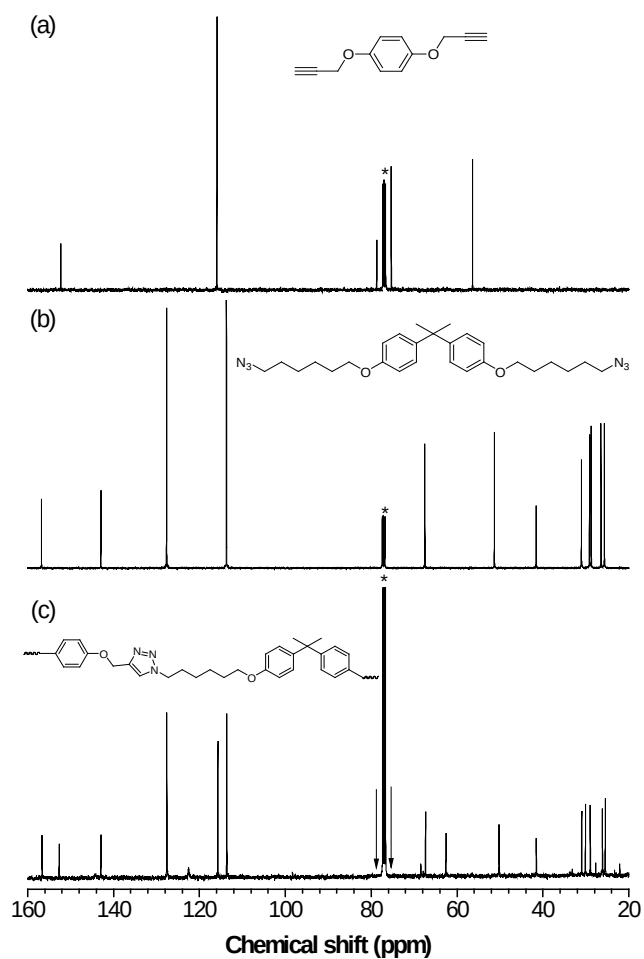


**Figure S7** |  $^{13}\text{C}$  NMR spectra of monomers **1a** (a), **2a** (b), and their polymer **PIaa** (c) of  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

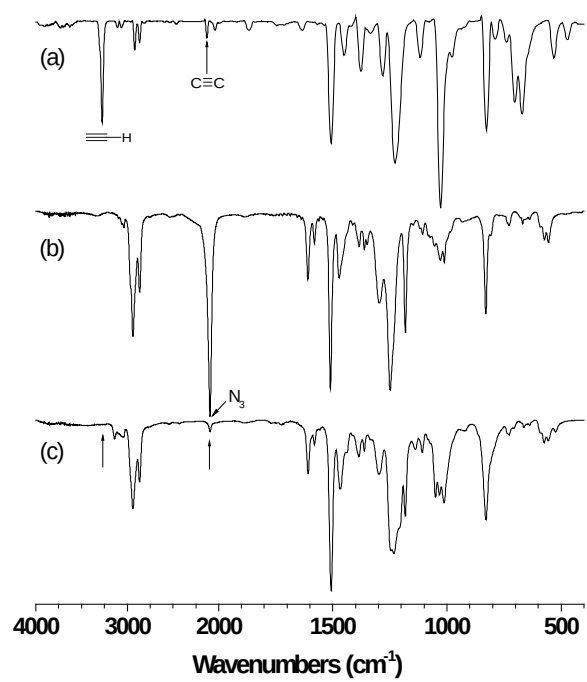


**Figure S8** | IR spectrum of monomers **1a** (a), **2a** (b), and their polymer **PIaa** (c).

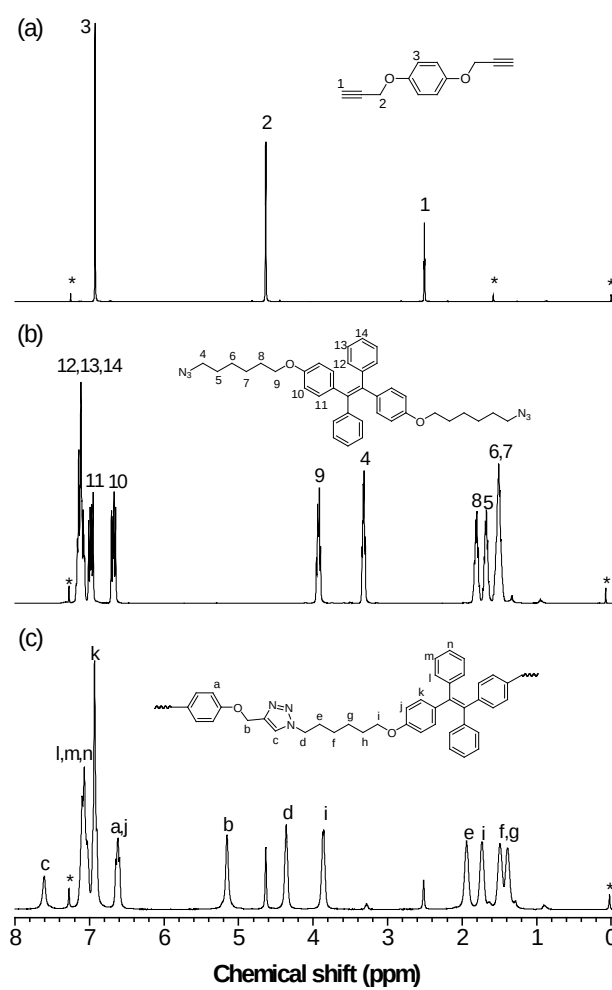


**Figure S9** |  $^1\text{H}$  NMR spectra of monomers **1a** (a), **2b** (b), and their polymer **PIab** (c) in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

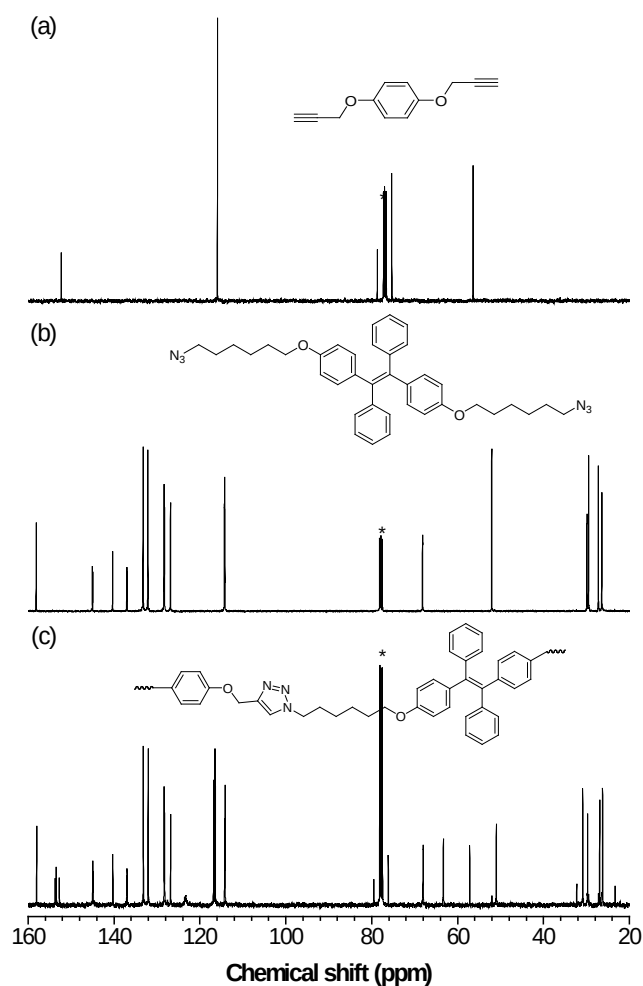


**Figure S10** |  $^{13}\text{C}$  NMR spectra of monomers **1a** (a), **2b** (b), and their polymer **PIab** (c) in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

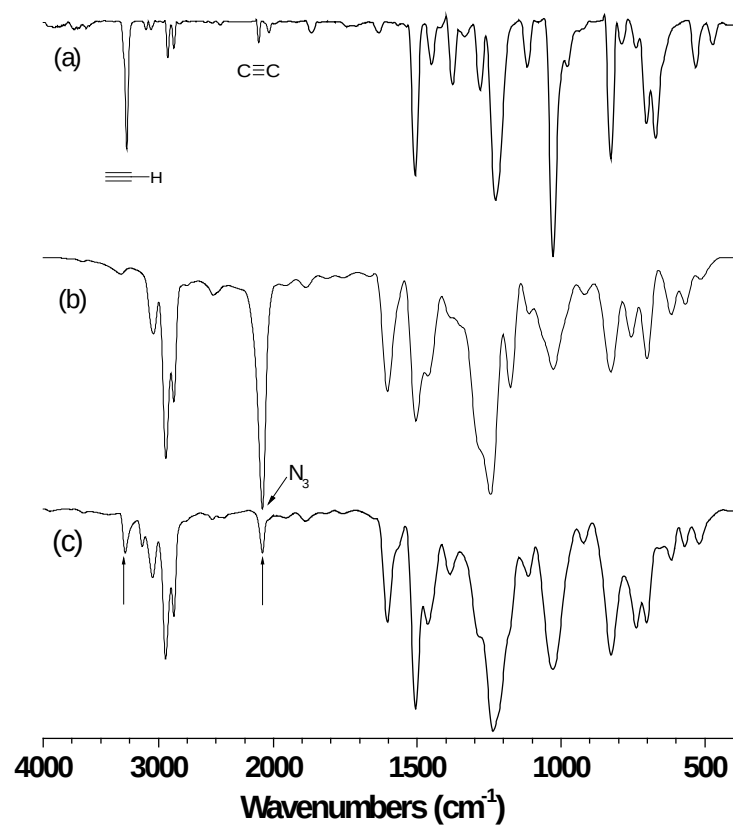


**Figure S11** | IR spectrum of monomers **1a** (a), **2b** (b), and their polymer **PIab** (c).

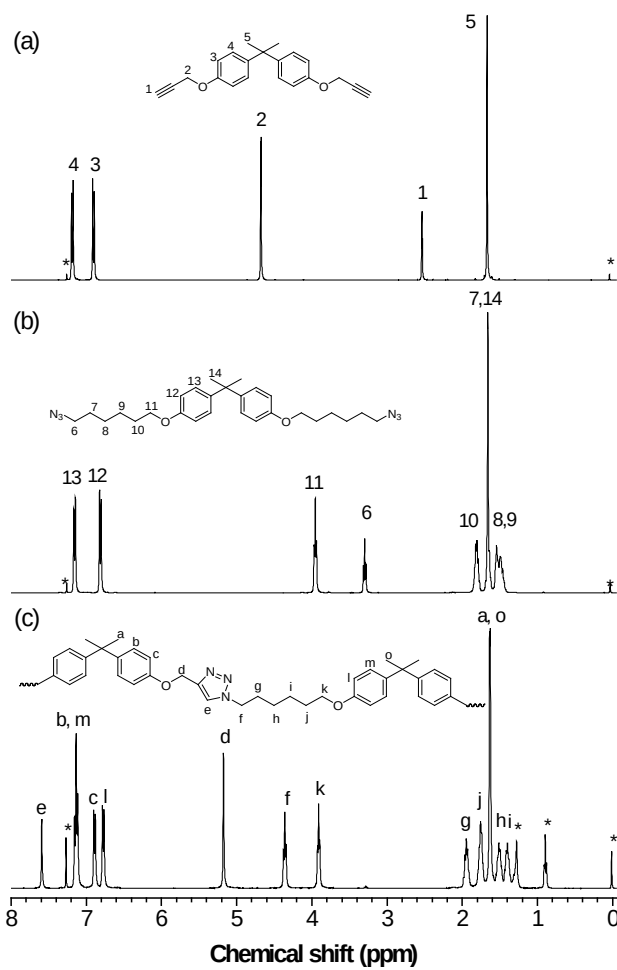


**Figure S12** |  $^1\text{H}$  NMR spectra of monomers **1b** (a), **2a** (b), and their polymer **PIba** (c) in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

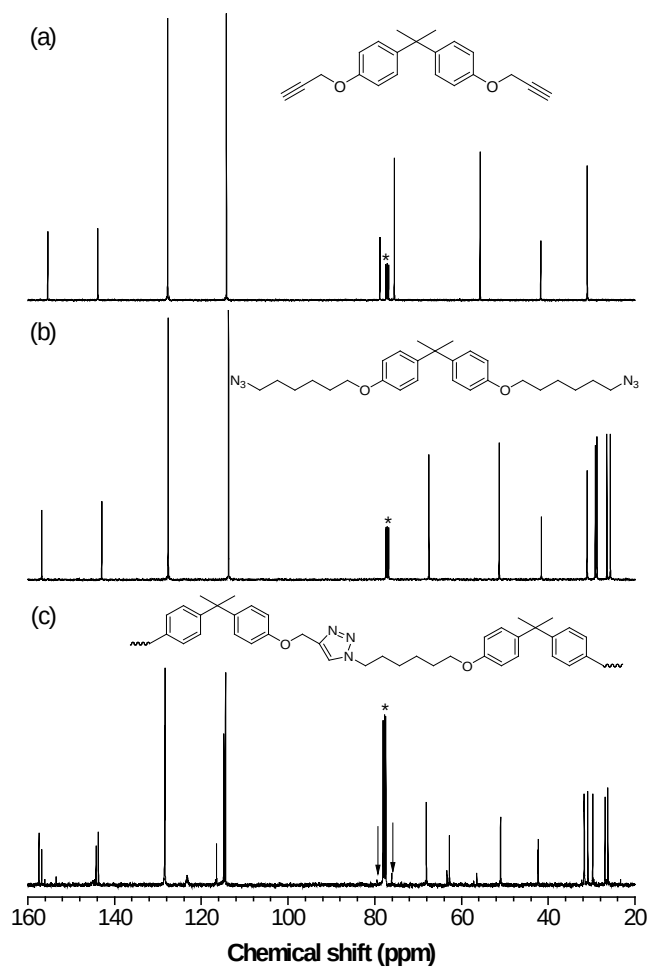


**Figure S13** |  $^{13}\text{C}$  NMR spectra of monomers **1b** (a), **2a** (b), and their polymer **PIba** (c) in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

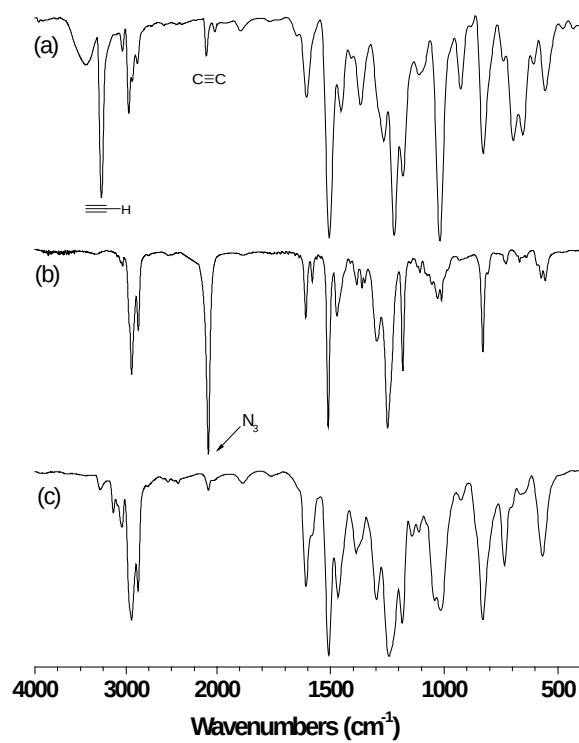


**Figure S14** | IR spectrum of monomers **1b** (a), **2a** (b), and their polymer **PIba** (c).

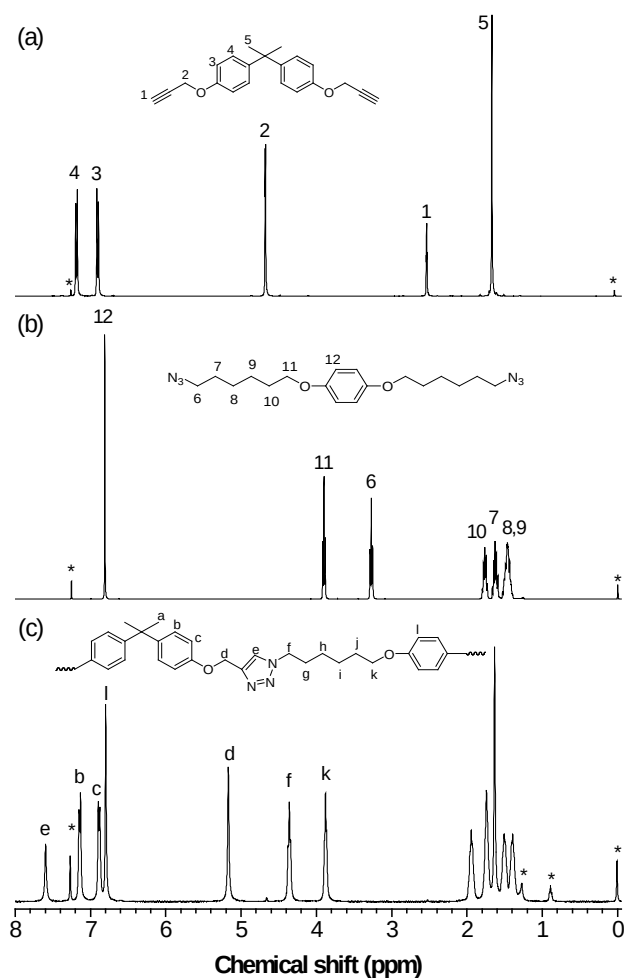


**Figure S15** | <sup>1</sup>H NMR spectra of monomers **1b** (a), **2c** (b), and their polymer **PIbc** (c) in CDCl<sub>3</sub>. The solvent and water peaks are marked with asterisks.

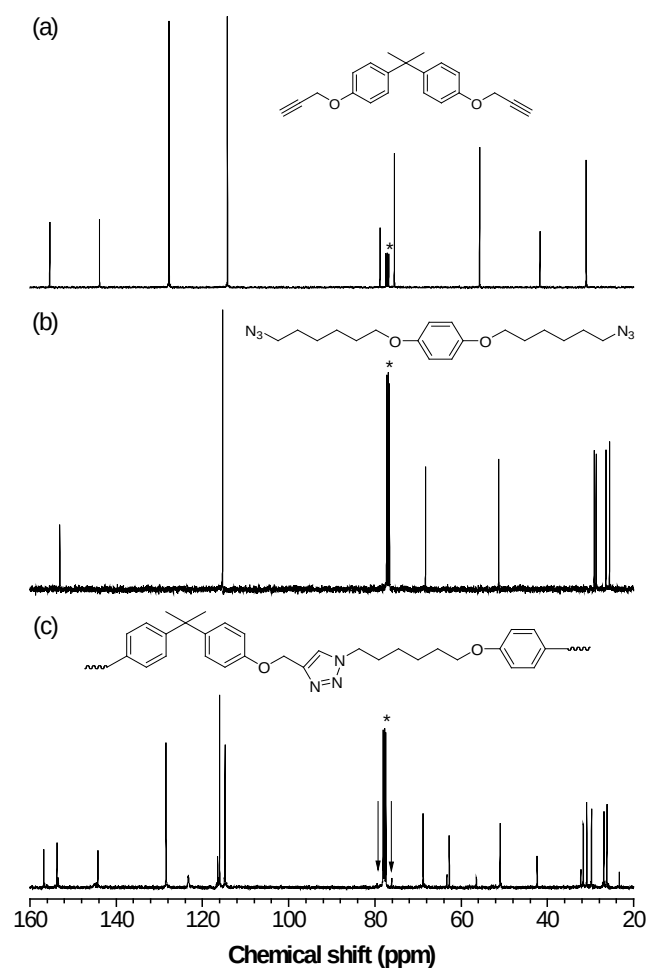


**Figure S16** |  $^{13}\text{C}$  NMR spectra of monomers **1b** (a), **2c** (b), and their polymer **PIbc** (c) in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

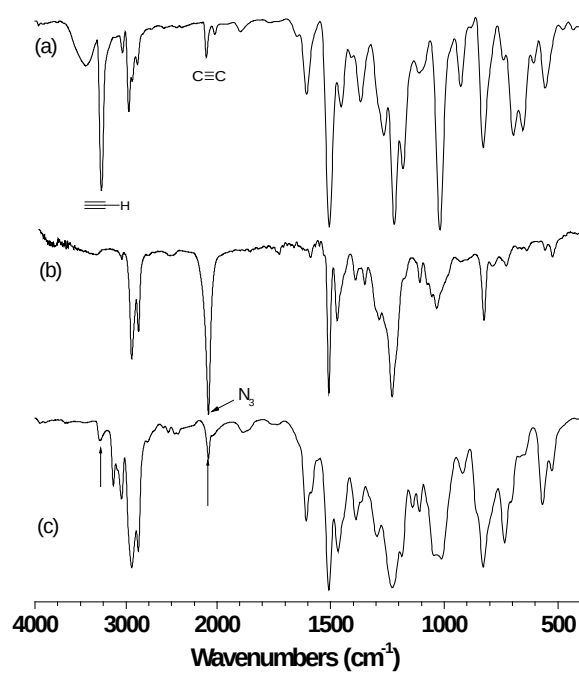


**Figure S17** | IR spectrum of monomers **1b** (a), **2c** (b), and their polymer **PIbc** (c).

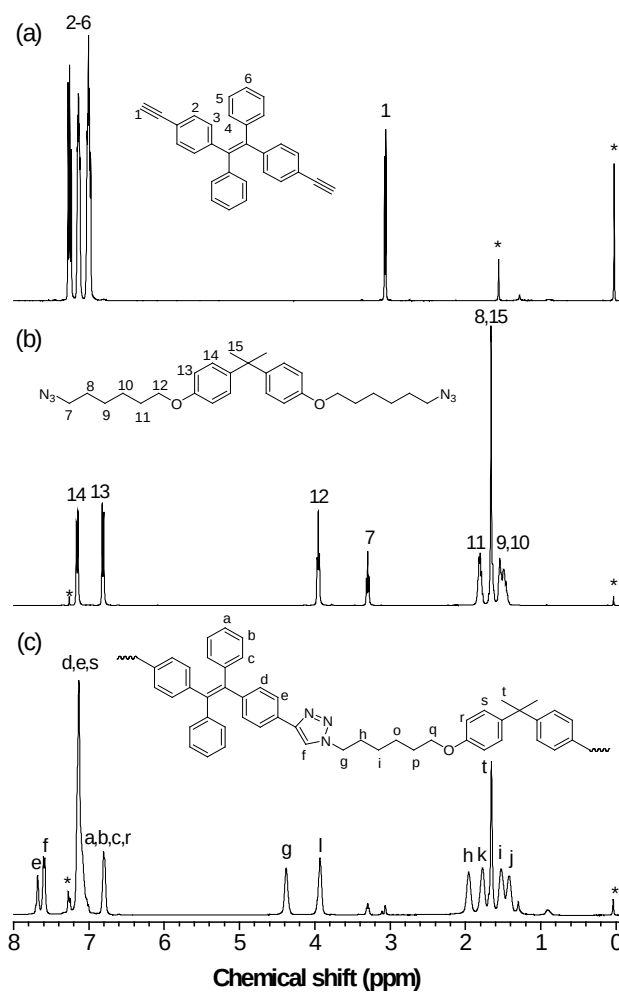


**Figure S18** |  $^1\text{H}$  NMR spectra of monomers **1c** (a), **2a** (b), and their polymer **PIca** (c) in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

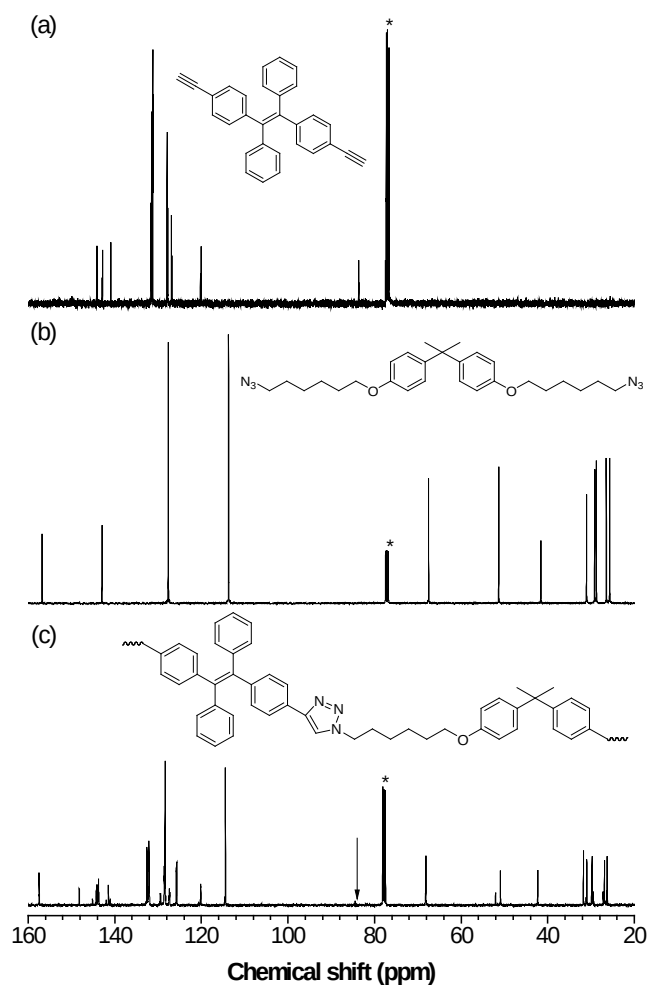


**Figure S19** |  $^{13}\text{C}$  NMR spectra of monomers **1c** (a), **2a** (b), and their polymer **PIca** (c) in  $\text{CDCl}_3$ . The solvent and water peaks are marked with asterisks.

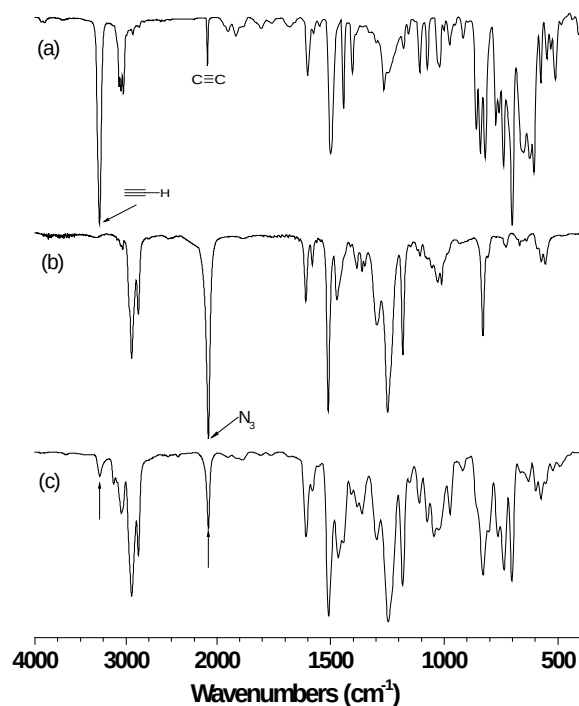


**Figure S20** | IR spectra of monomers **1c** (a), **2a** (b), and their polymer **PIca** (c).

**Table S1** | Time courses on the CuI@A-21 catalyzed click polymerization of **1a** and **2a**<sup>a</sup>

| no. | <i>t</i> (h) | yield (%) | <i>M<sub>w</sub></i> <sup>b</sup> | PDI <sup>b</sup> | <i>S</i> <sup>c</sup> |
|-----|--------------|-----------|-----------------------------------|------------------|-----------------------|
| 1   | 6            | 51.9      | 7900                              | 2.75             | √                     |
| 2   | 9            | 72.8      | 42700                             | 1.72             | √                     |
| 3   | 12           | 86.1      | 55500                             | 1.61             | √                     |
| 4   | 16           | 85.1      | 91600                             | 1.74             | Δ                     |
| 5   | 20           | 87.8      | 82700                             | 1.73             | Δ                     |
| 6   | 24           | 91.2      | 57500                             | 1.61             | Δ                     |

<sup>a</sup> Carried out in THF at 60 °C under nitrogen at a monomer concentration of 0.1 M. <sup>b</sup> *M<sub>w</sub>* and PDI of polymer were estimated by GPC in THF on the basis of a PS calibration. <sup>c</sup> Solubility in THF, √ = completely soluble, Δ = partially soluble.

**Table S2 | Solvent effect on the CuI@A-21 catalyzed click polymerization of 1a and 2a<sup>a</sup>**

| no. | solvent | yield (%) | $M_w^b$ | PDI <sup>b</sup> | S <sup>c</sup> | [Cu] (ppm) <sup>d</sup> |
|-----|---------|-----------|---------|------------------|----------------|-------------------------|
| 1   | THF     | 86.1      | 55500   | 1.61             | √              | 197                     |
| 2   | DMF     | 96.0      | 73500   | 2.24             | Δ              | 1709                    |
| 3   | toluene | 61.8      | 132000  | 1.90             | Δ              | 117                     |
| 4   | dioxane | 79.3      | 47700   | 1.96             | √              | 142                     |

<sup>a</sup> Carried out at 60 °C for 12 h under nitrogen at a monomer concentration of 0.1 M. <sup>b</sup>  $M_w$  and PDI of polymer were estimated by GPC in THF on the basis of a PS calibration. <sup>c</sup> Solubility in THF, √ = completely soluble, Δ = partially soluble. <sup>d</sup> Copper residue in the polymer, estimated by AAS.

**Table S3 | Recyclability of the CuI@A-21 for the click polymerization of 1a and 2b<sup>a</sup>**

| cycle | yield (%) | $M_w^b$ | PDI <sup>b</sup> | [Cu] (ppm) <sup>c</sup> |
|-------|-----------|---------|------------------|-------------------------|
| 1     | 82.0      | 22100   | 1.93             | 102                     |
| 2     | 79.4      | 10500   | 2.13             | 182                     |
| 3     | 85.8      | 15700   | 2.35             | 132                     |
| 4     | 82.3      | 3600    | 2.22             | 112                     |

<sup>a</sup> Carried out at 60 °C for 12 h under nitrogen at a monomer concentration of 0.1 M. <sup>b</sup>  $M_w$  and PDI of polymer were estimated by GPC in THF on the basis of a PS calibration. <sup>c</sup> Copper residue estimated by AAS.

**Table S4 | Recyclability of the CuI@A-21 for the click polymerization of 1b and 2a<sup>a</sup>**

| cycle | yield (%) | $M_w^b$ | PDI <sup>b</sup> | [Cu] (ppm) <sup>c</sup> |
|-------|-----------|---------|------------------|-------------------------|
| 1     | 83.3      | 17900   | 1.86             | 102                     |
| 2     | 87.0      | 22700   | 2.24             | 132                     |
| 3     | 83.8      | 21300   | 2.18             | 142                     |
| 4     | 83.9      | 5900    | 1.93             | 122                     |

<sup>a</sup> Carried out at 60 °C for 12 h under nitrogen at a monomer concentration of 0.1 M. <sup>b</sup>  $M_w$  and PDI of polymer were estimated by GPC in THF on the basis of a PS calibration. <sup>c</sup> Copper residue estimated by AAS.

**Table S5 | Effect of post-purification on the copper residues in polymers<sup>a</sup>**

| no. | catalyst                              | yield (%) | $M_w^b$ | PDI <sup>b</sup> | S <sup>c</sup> | [Cu] (ppm) <sup>d</sup> |
|-----|---------------------------------------|-----------|---------|------------------|----------------|-------------------------|
| 1   | CuI@A-21                              | 74.9      | 77 400  | 1.85             | √              | 17                      |
| 2   | Cu(PPh <sub>3</sub> ) <sub>3</sub> Br | 81.8      | 19 900  | 1.75             | Δ              | 85                      |

<sup>a</sup> The polymers were obtained by Cu<sup>I</sup>-catalyzed click polymerization of **1a** and **2a** at 60 °C for 12 h under nitrogen at a monomer concentration of 0.1 M. After reaction, the mixture was diluted with THF, and added dropwise into a 5% EDTA solution through a cotton filter under stirring. <sup>b</sup>  $M_w$  and PDI of polymer were estimated by GPC in THF on the basis of a PS calibration. <sup>c</sup> Solubility in THF, √ = completely soluble, Δ = partially soluble. <sup>d</sup> Copper residue estimated by AAS.

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