

**Electronic supplementary information (ESI)**

# Imidazole-based Cu(I)-catalyzed click polymerization of diazides and diynes under mild conditions

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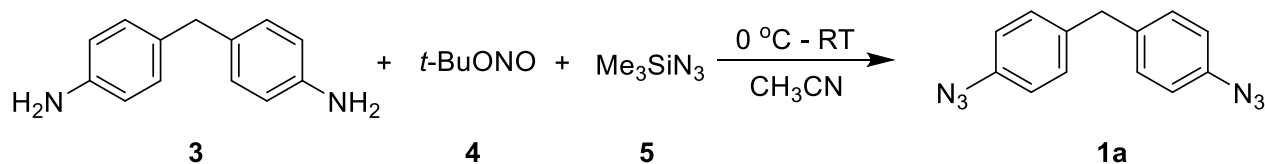
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## Experimental section

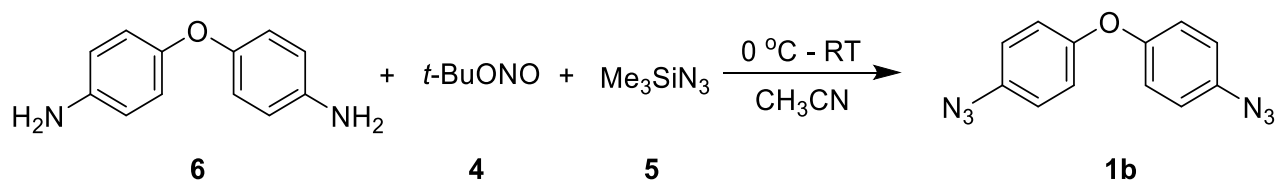
### Synthesis of monomers 1a-1c and 2a-2d

#### Synthesis of bis(4-azidophenyl)methane (1a)



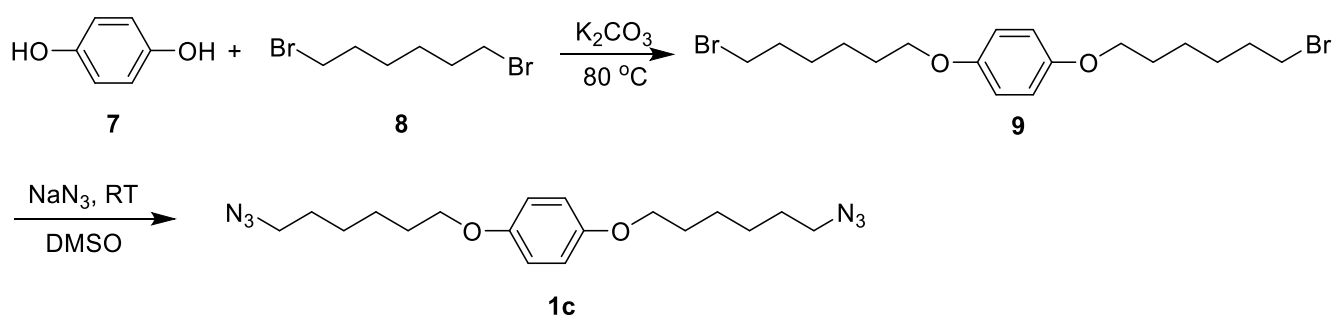
This monomer was prepared according to previously published work.<sup>1</sup>

#### Synthesis of 4,4'-oxybis(azidobenzene) (1b)



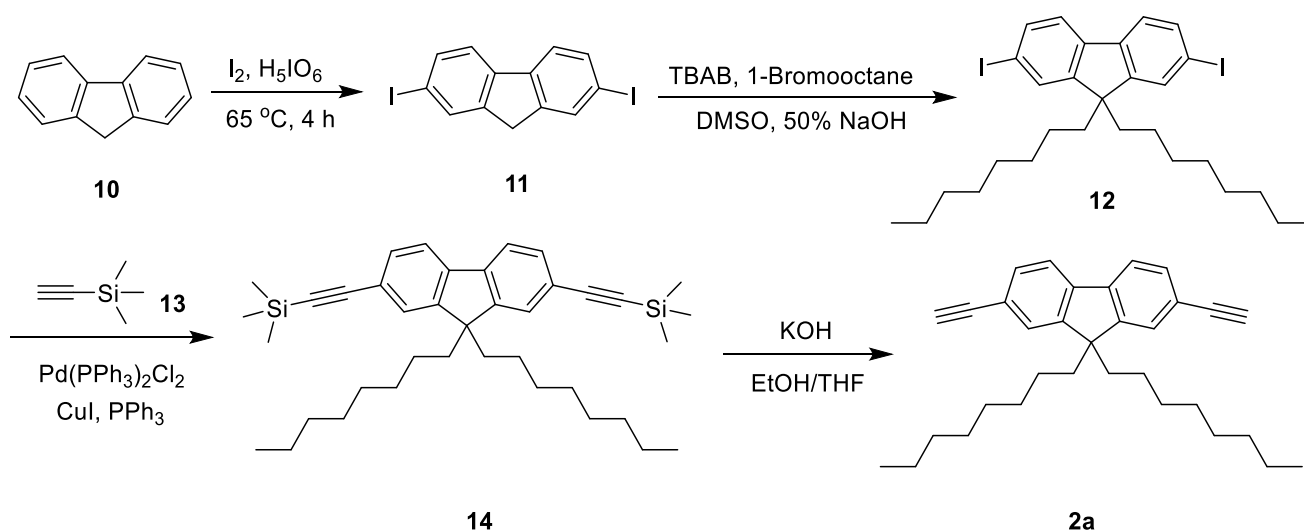
This monomer was prepared according to previously published work.<sup>1</sup>

#### Synthesis of 1,4-bis((6-azidohexyl)oxy)benzene (1c)



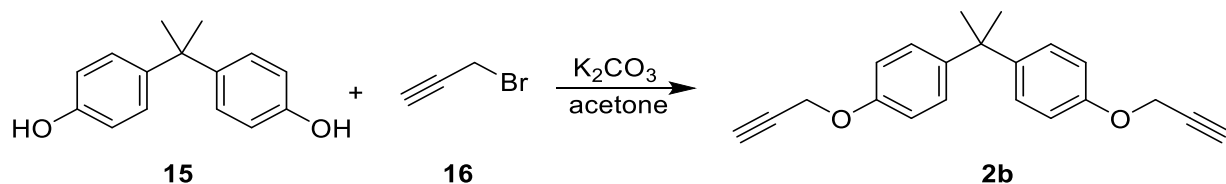
This monomer was prepared according to our previously published procedures.<sup>2</sup>

#### Synthesis of 2,7-diethynyl-9,9-dioctyl-9H-fluorene (2a)



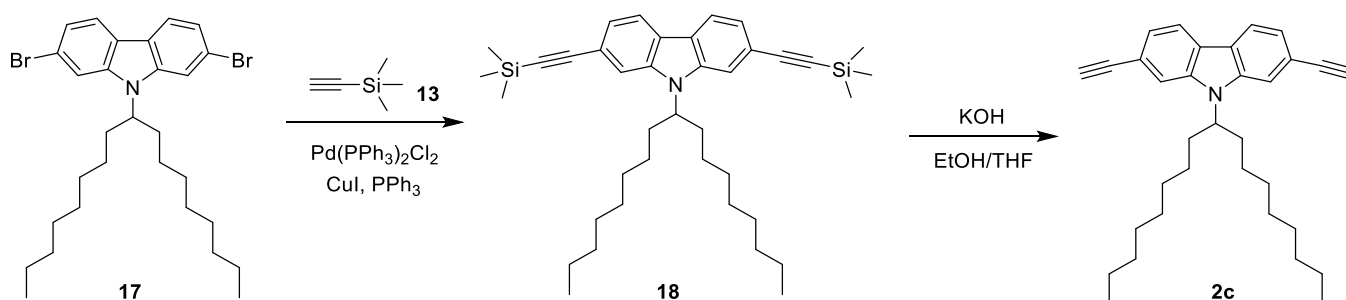
This monomer was prepared according to our previously published procedures.<sup>3</sup>

### Synthesis of 4,4'-(propane-2,2-diyl)bis((prop-2-yn-1-yloxy)benzene) (2b)



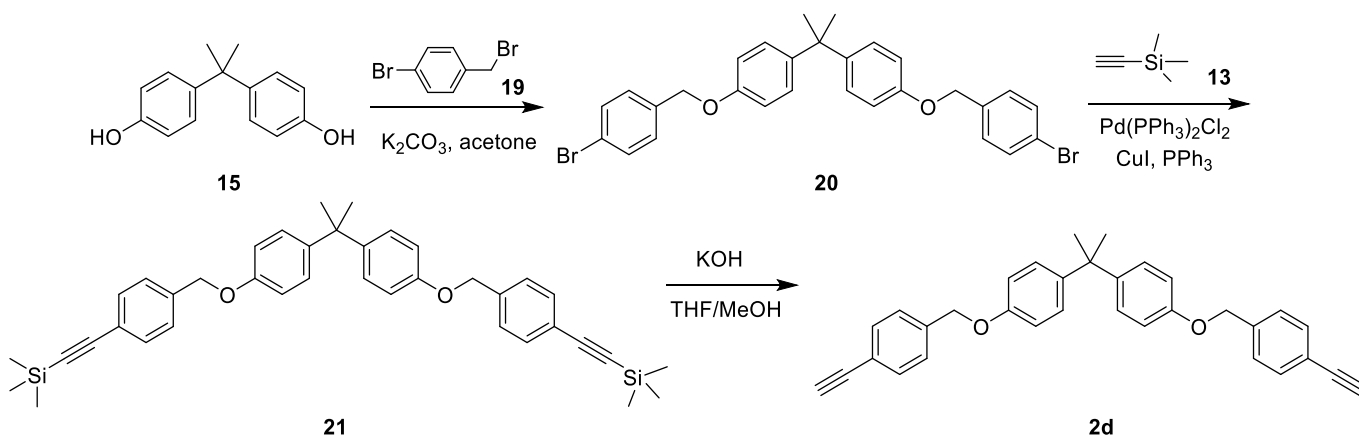
This monomer was prepared according to our previously published procedures.<sup>4</sup>

### Synthesis of 2,7-diethynyl-9-(heptadecan-9-yl)-9H-carbazole (2c)



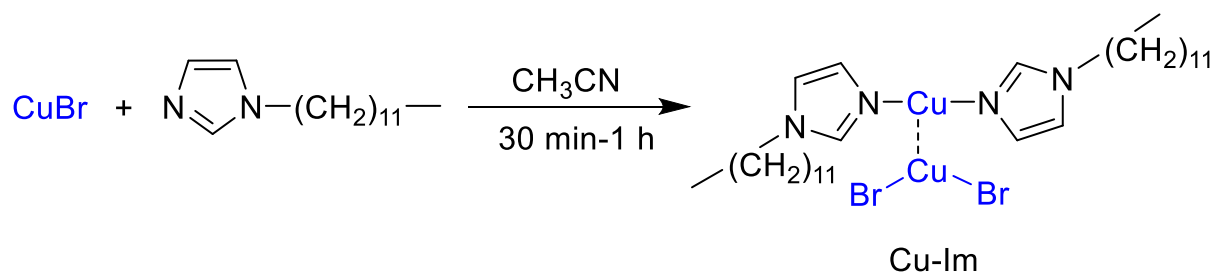
This monomer was prepared according to our previously published procedures.<sup>3</sup>

### Synthesis of 4,4'-(isopropylidenediphenyl)-bis(4-ethynylbenzyl) ether (2d)

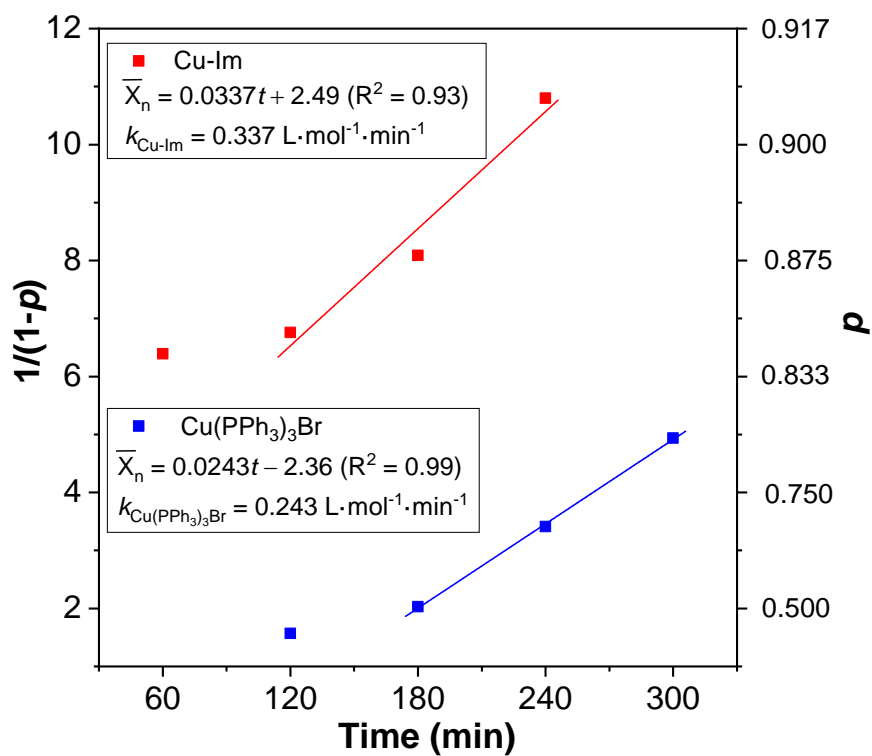


This monomer was prepared according to our previously published procedures.<sup>5,6</sup>

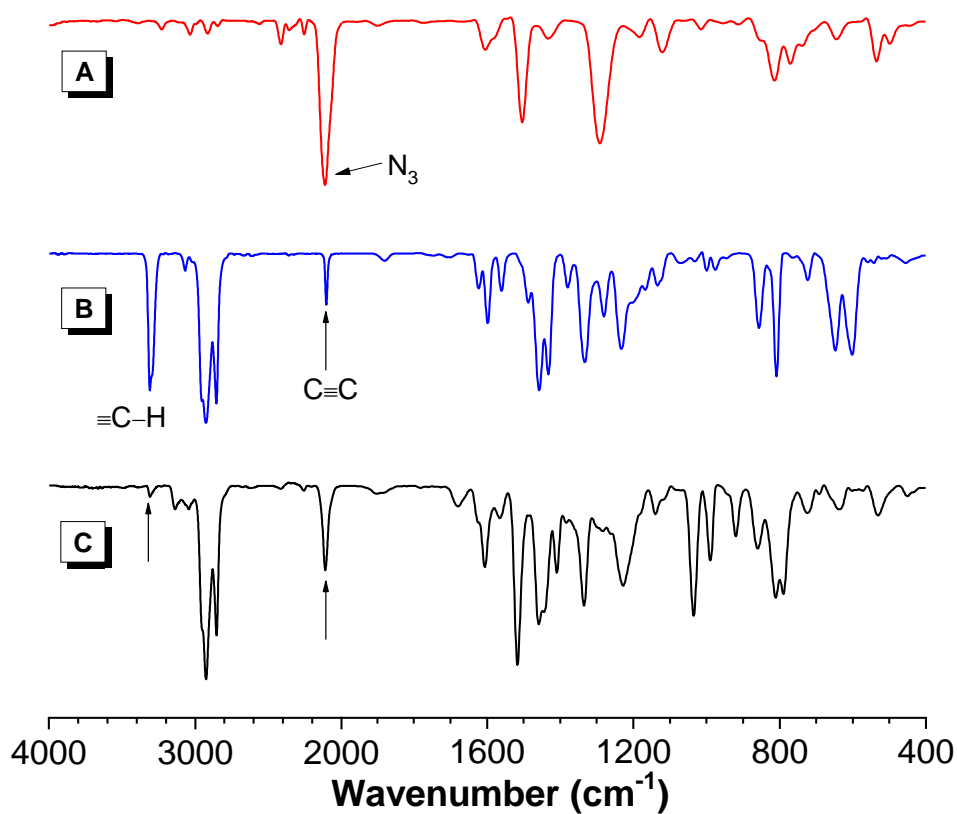
### Synthesis of Cu-Im catalyst



This catalyst was prepared according to previously published papers.<sup>7,8</sup>



**Fig. S1** Kinetics curves of different copper catalysts on the click polymerization.



**Fig. S2** FT-IR spectra of **1a** (A), **2c** (B) and **P1a2c** (C).

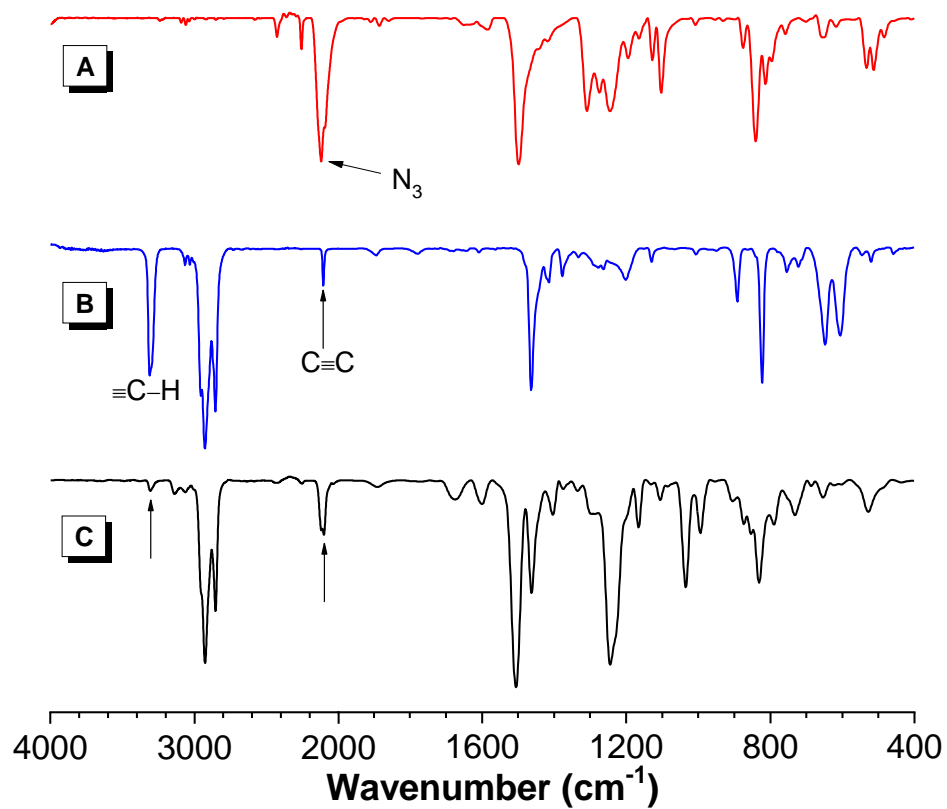


Fig. S3 FT-IR spectra of **1b** (A), **2a** (B) and **P1b2a** (C).

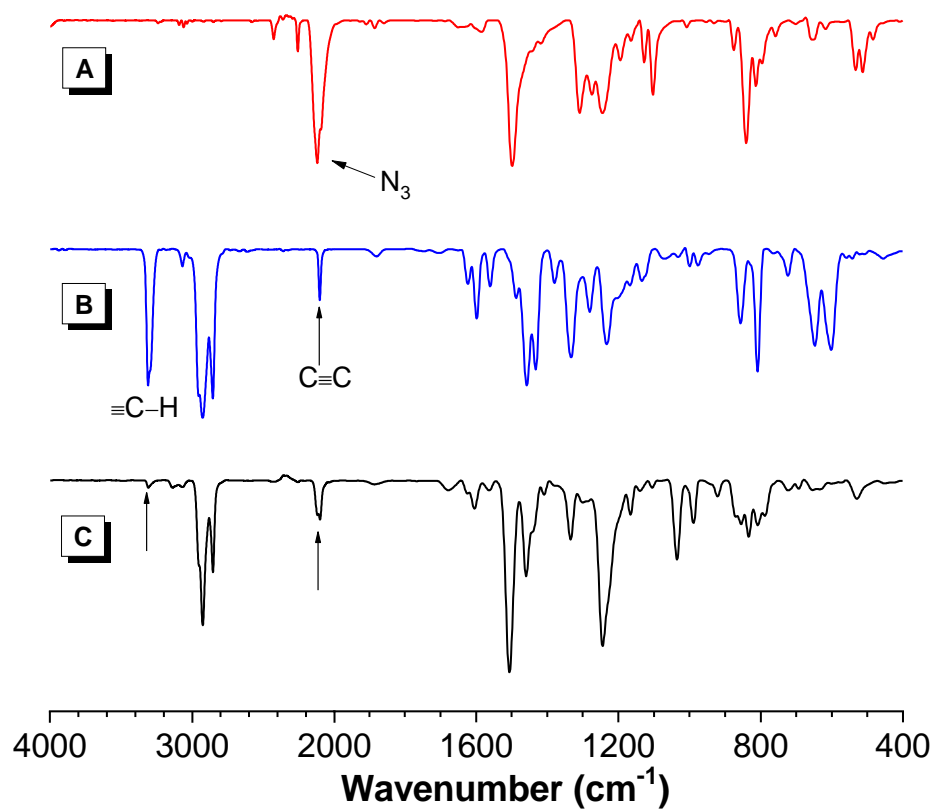
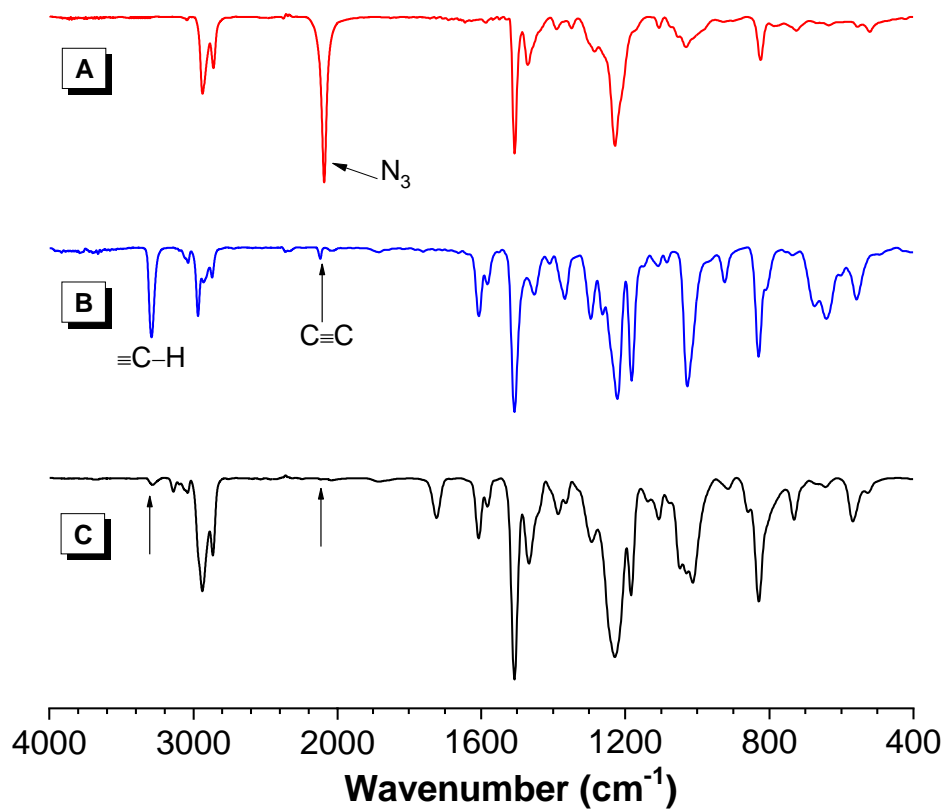
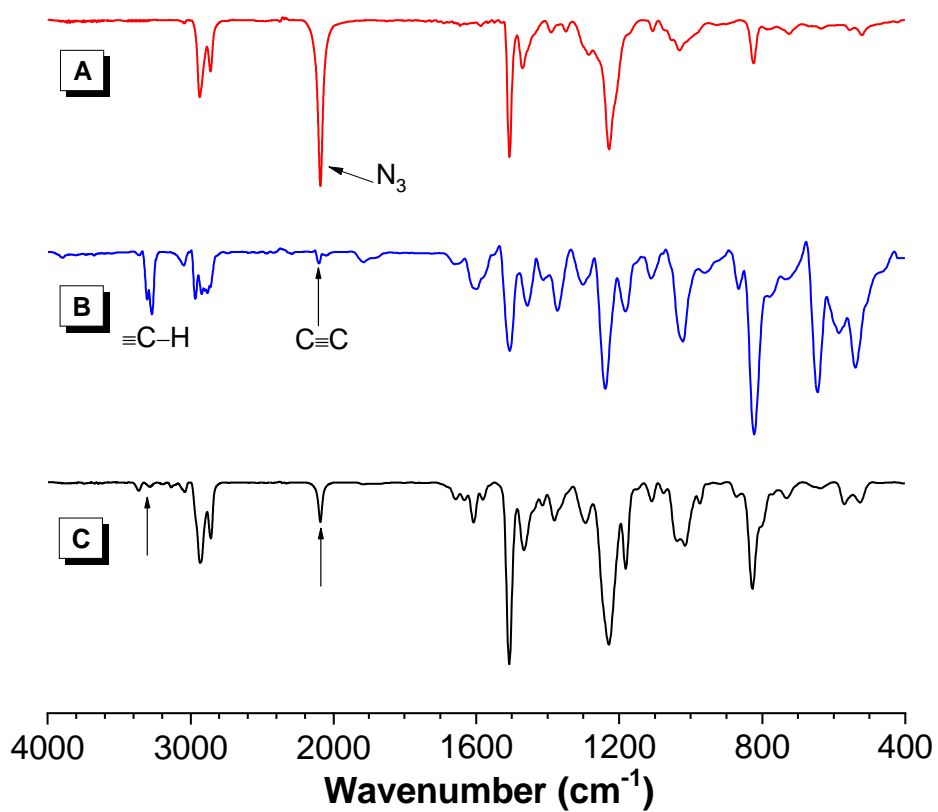


Fig. S4 FT-IR spectra of **1b** (A), **2c** (B) and **P1b2c** (C).

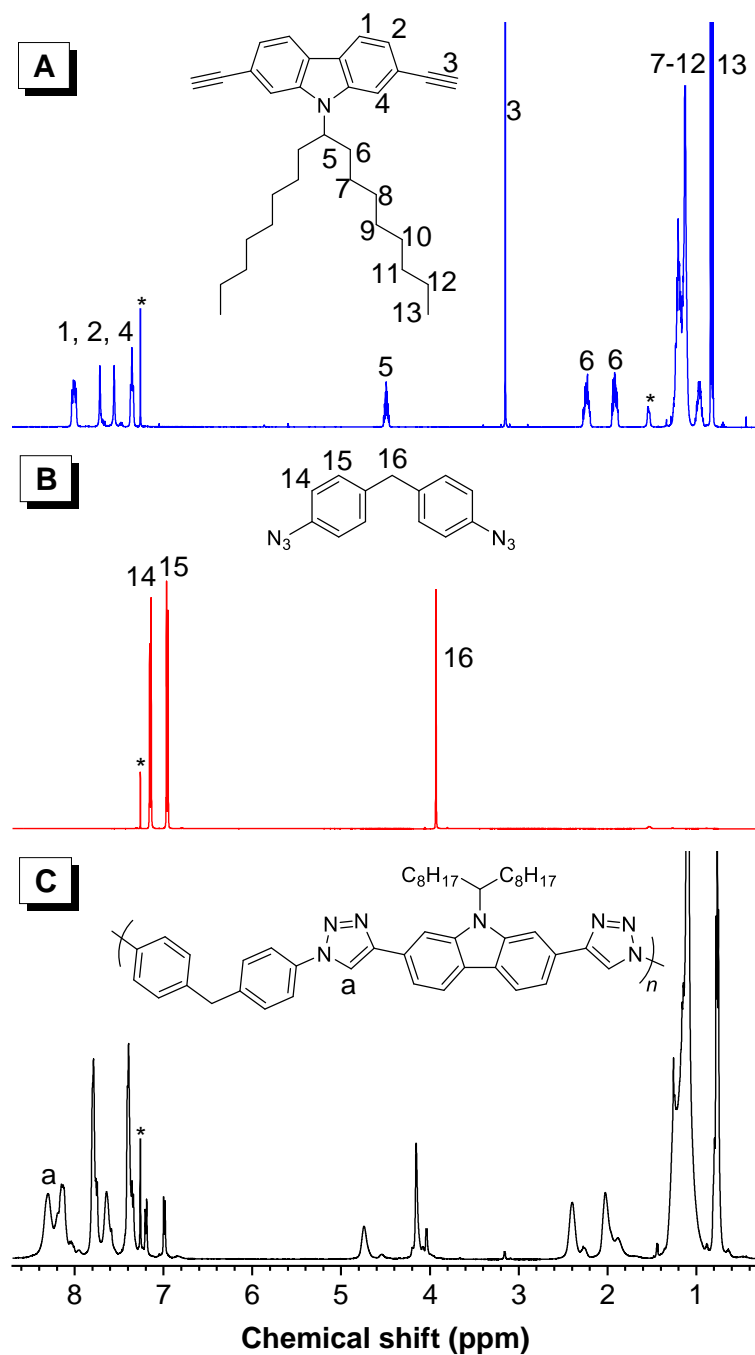


**Fig. S5** FT-IR spectra of **1c** (A), **2b** (B) and **P1c2b** (C).

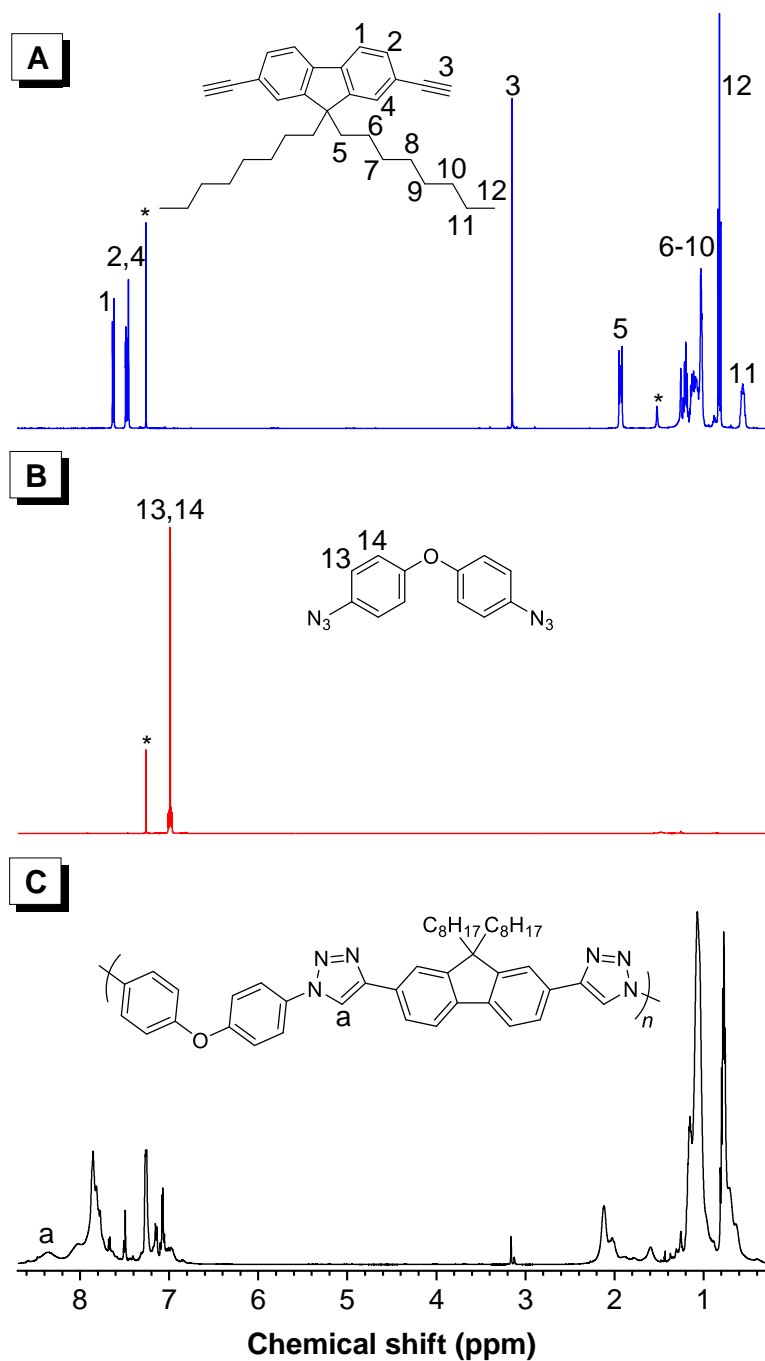


**Fig. S6** FT-IR spectra of **1c** (A), **2d** (B) and **P1c2d** (C).

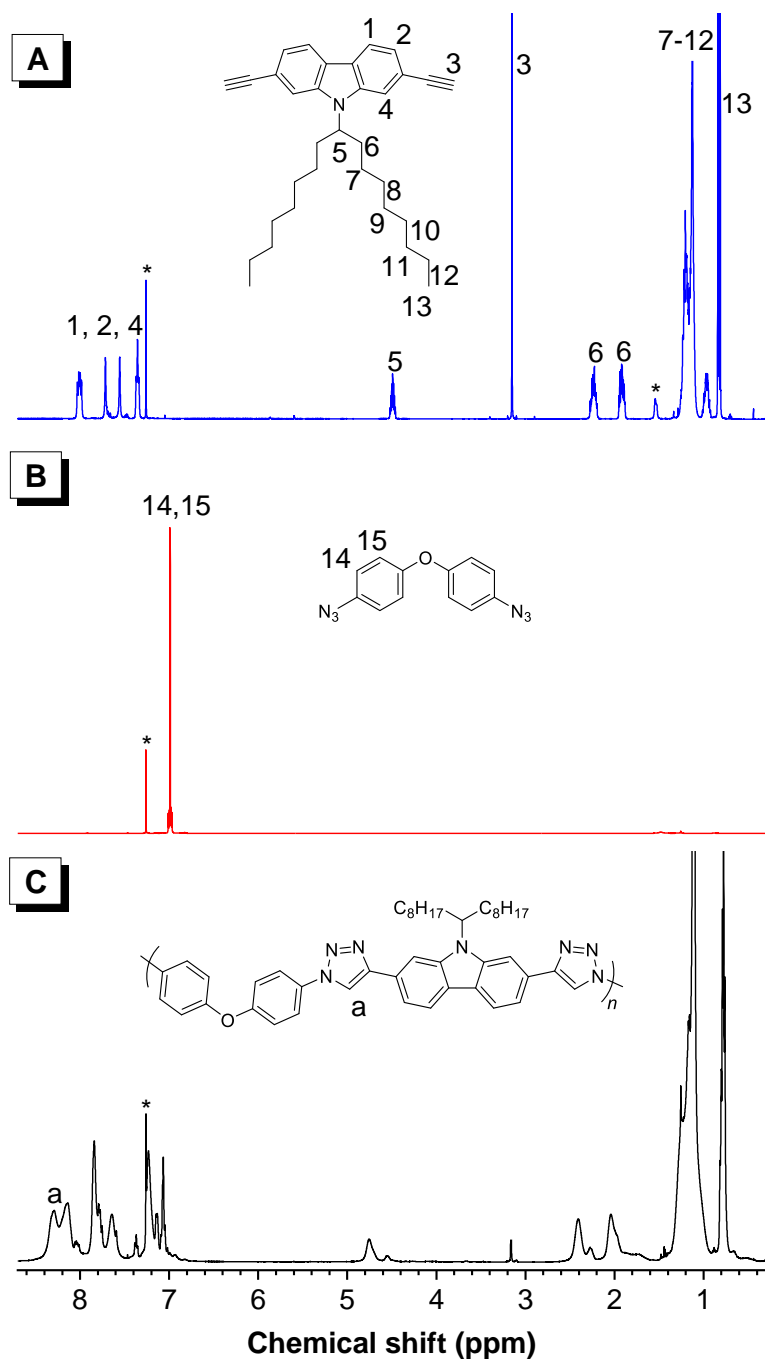




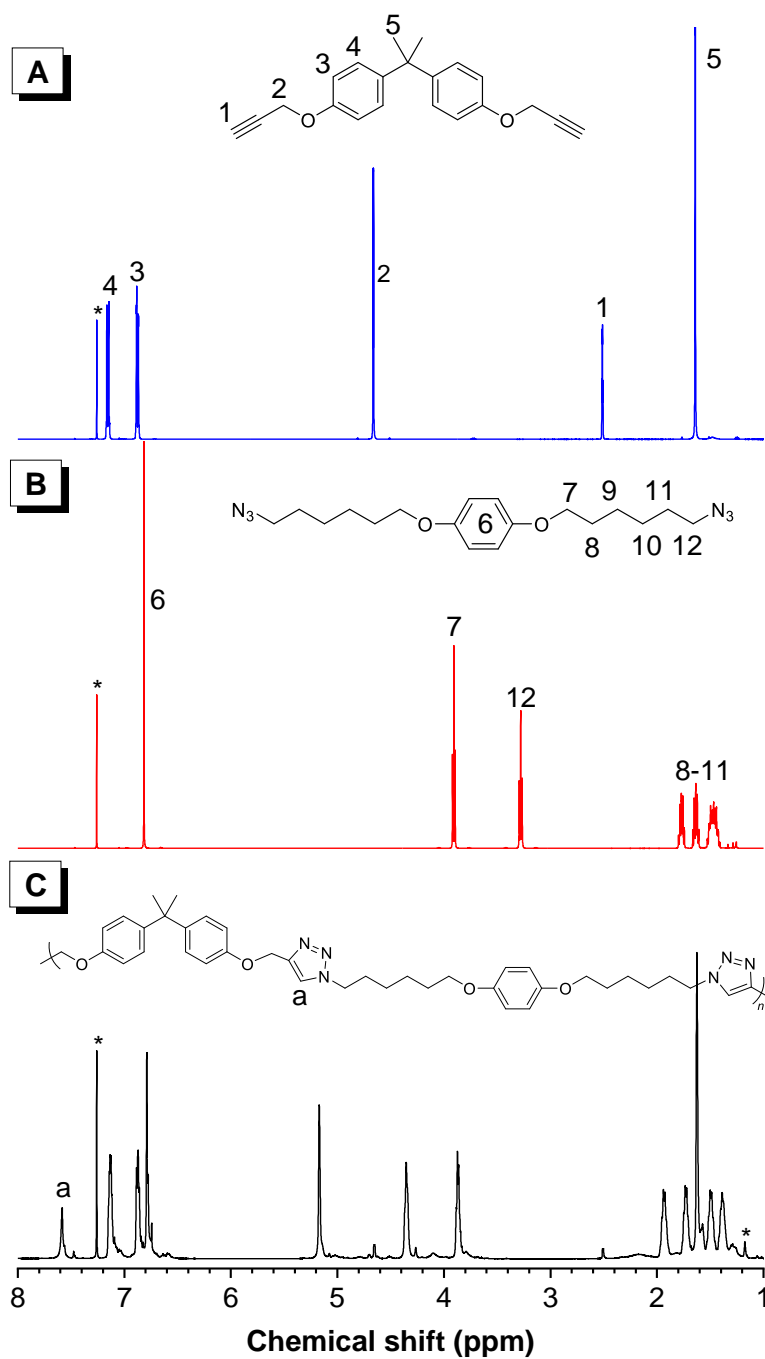
**Fig. S7**  $^1\text{H}$  NMR spectra of **2c** (A), **1a** (B) and **P1a2c** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



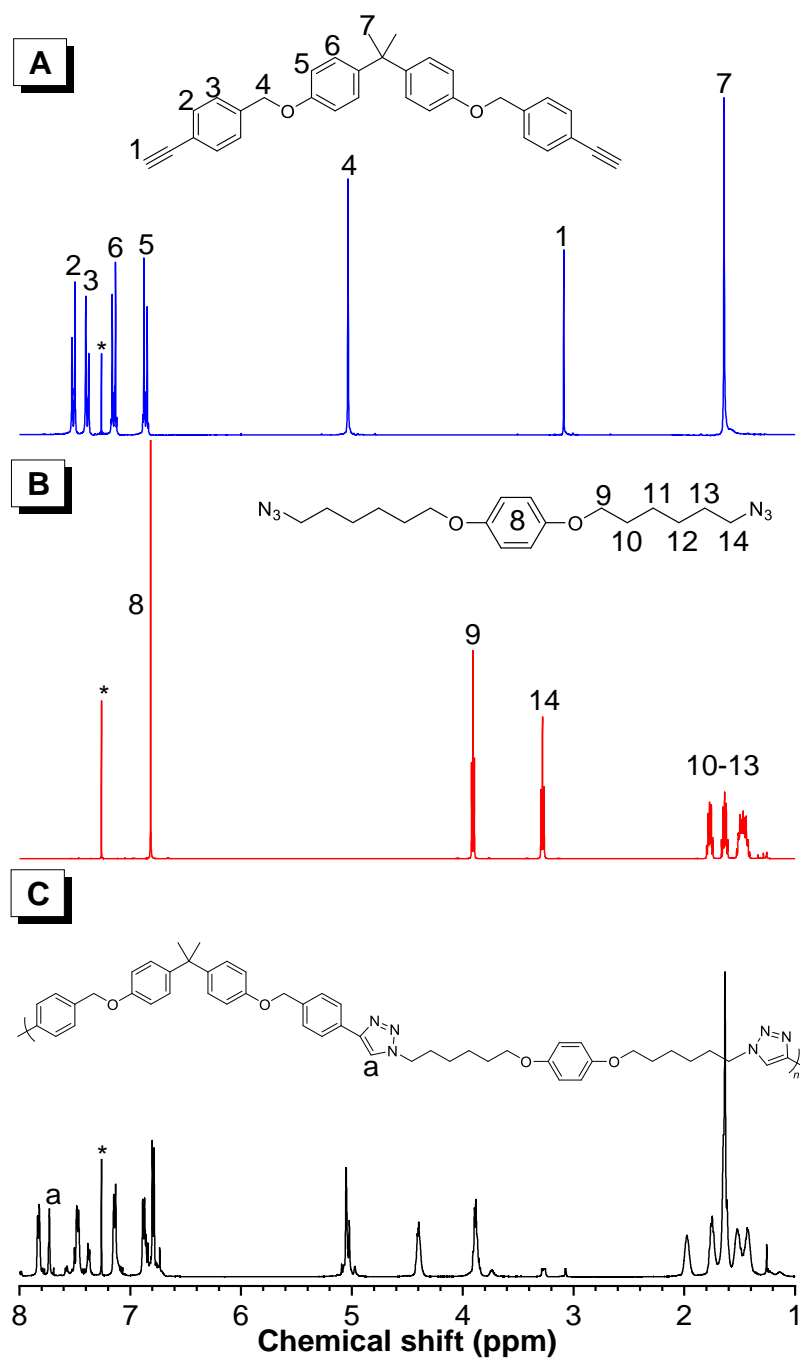
**Fig. S8** <sup>1</sup>H NMR spectra of **2a** (A), **1b** (B) and **P1b2a** (C) in CDCl<sub>3</sub>. The solvent peaks are marked with asterisks.



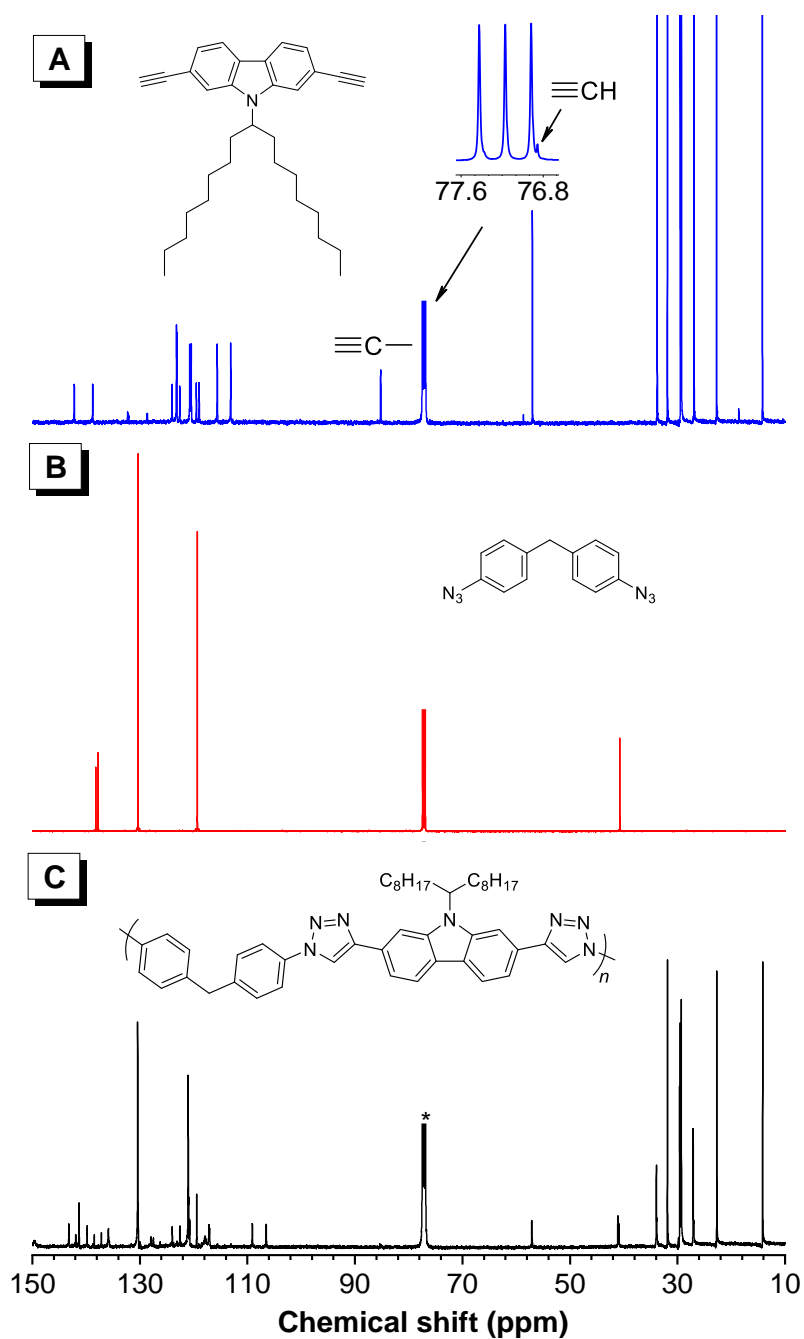
**Fig. S9**  $^1\text{H}$  NMR spectra of **2c** (A), **1b** (B) and **P1b2c** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



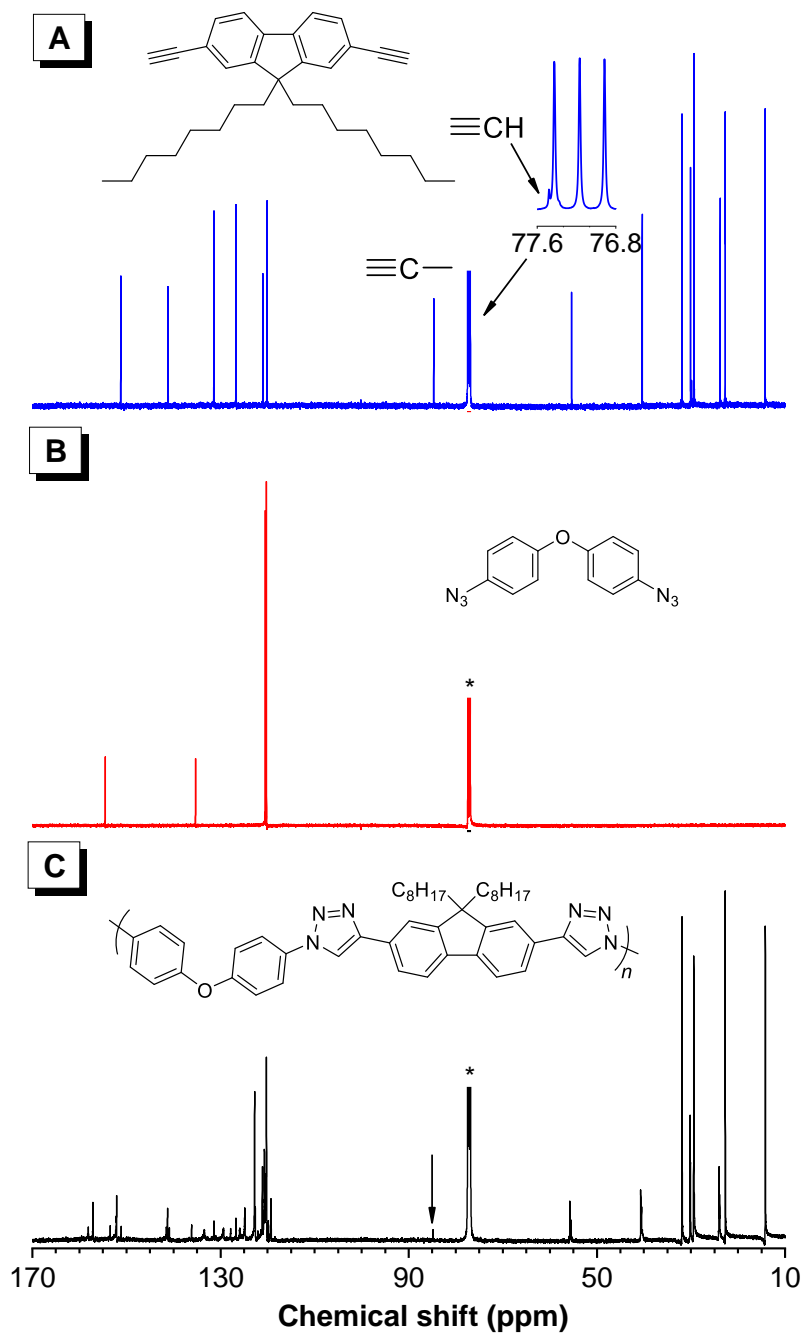
**Fig. S10**  $^1\text{H}$  NMR spectra of **2b** (A), **1c** (B) and **P1c2b** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



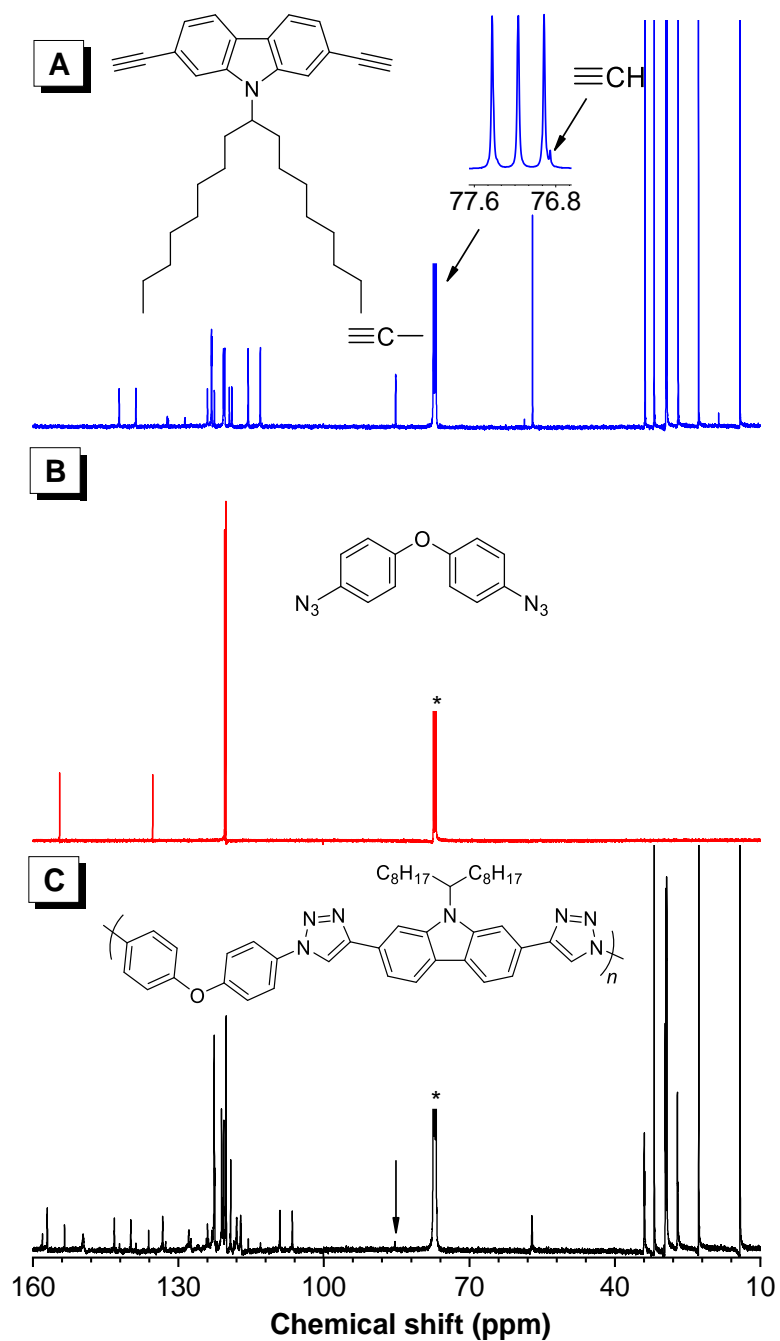
**Fig. S11**  $^1\text{H}$  NMR spectra of **2d** (A), **1c** (B) and **P1c2d** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



**Fig. S12**  $^{13}\text{C}$  NMR spectra of **2c** (A), **1a** (B) and **P1a2c** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.

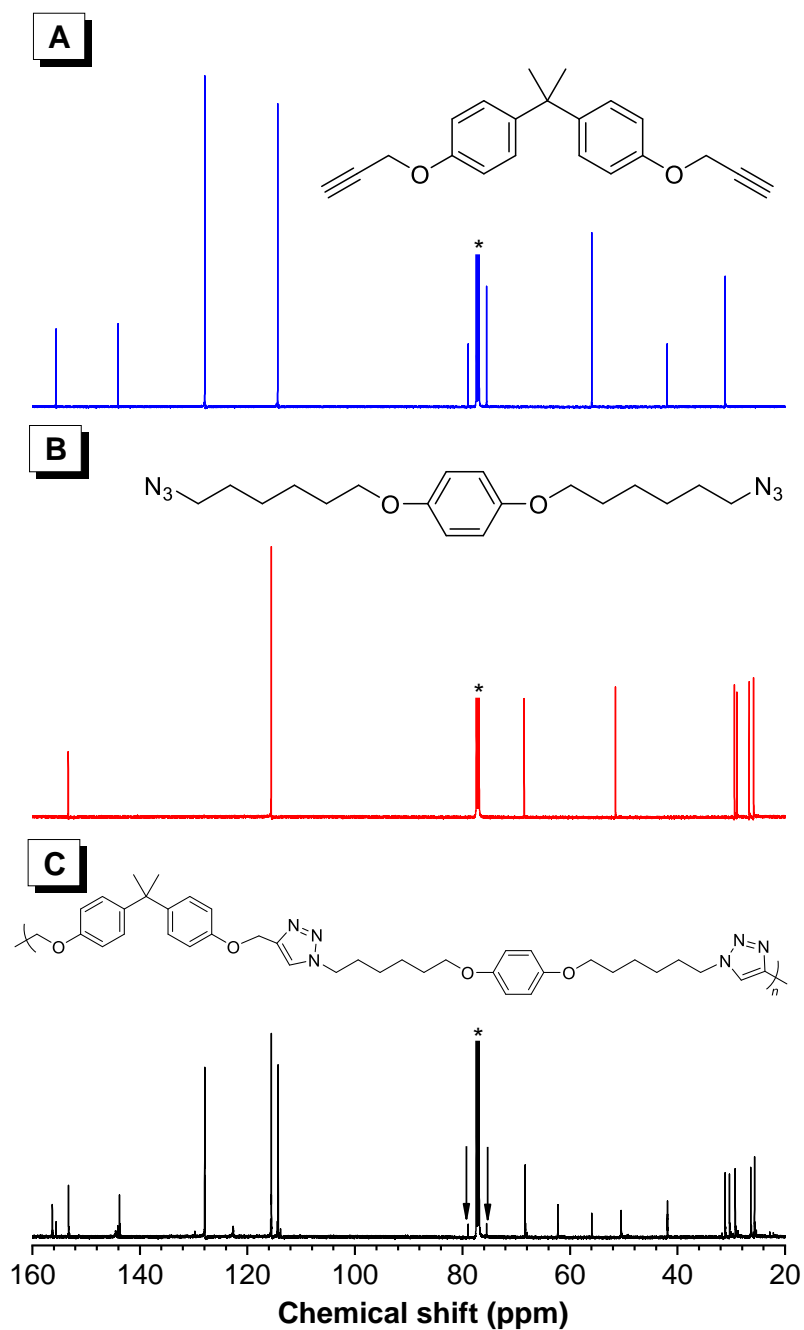


**Fig. S13**  $^{13}\text{C}$  NMR spectra of **2a** (A), **1b** (B) and **P1b2a** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.

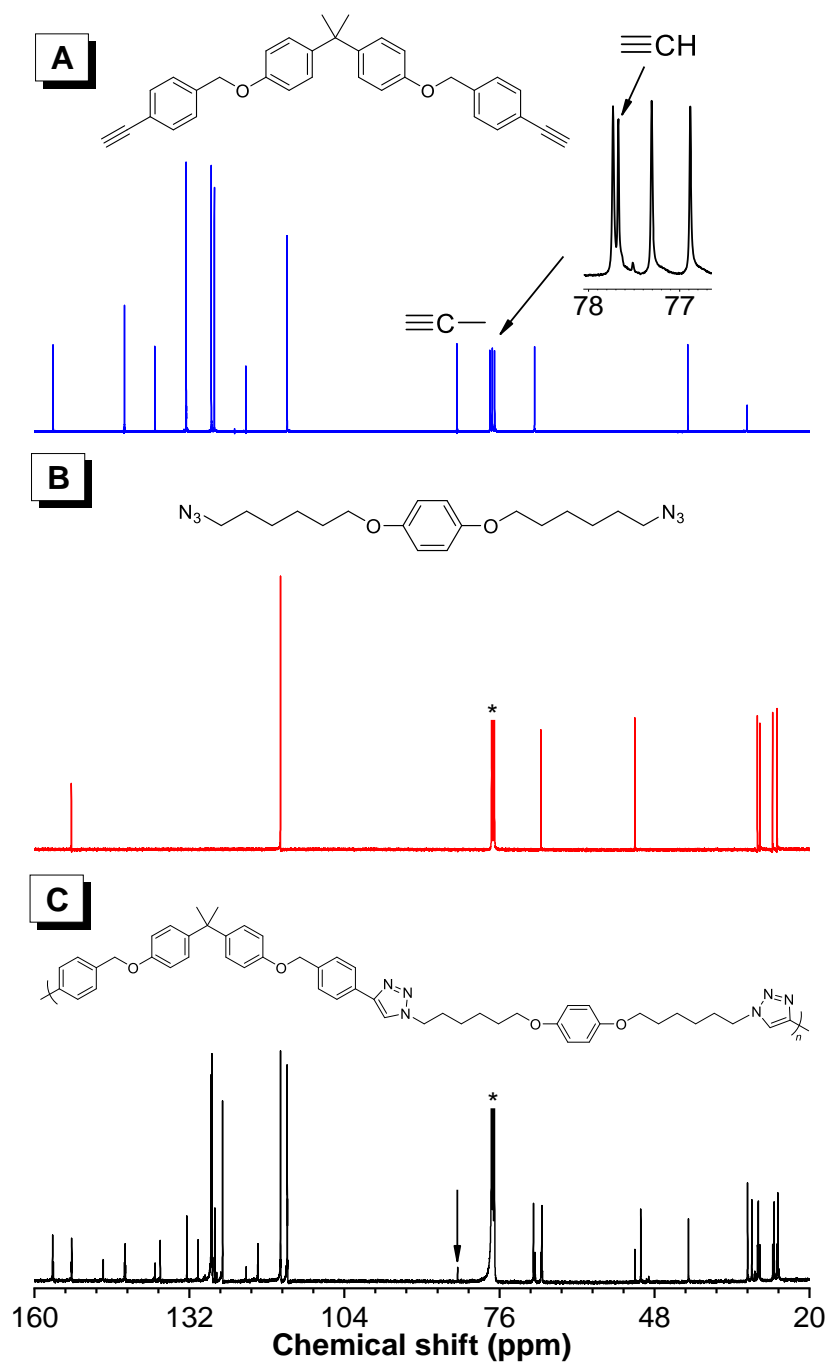


**Fig. S14**  $^{13}\text{C}$  NMR spectra of **2c** (A), **1b** (B) and **P1b2c** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.

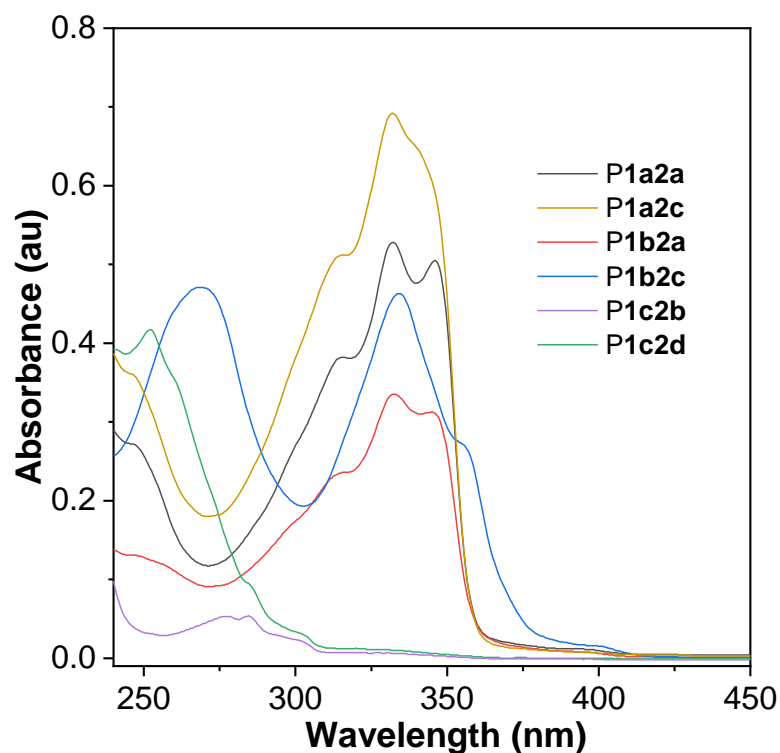




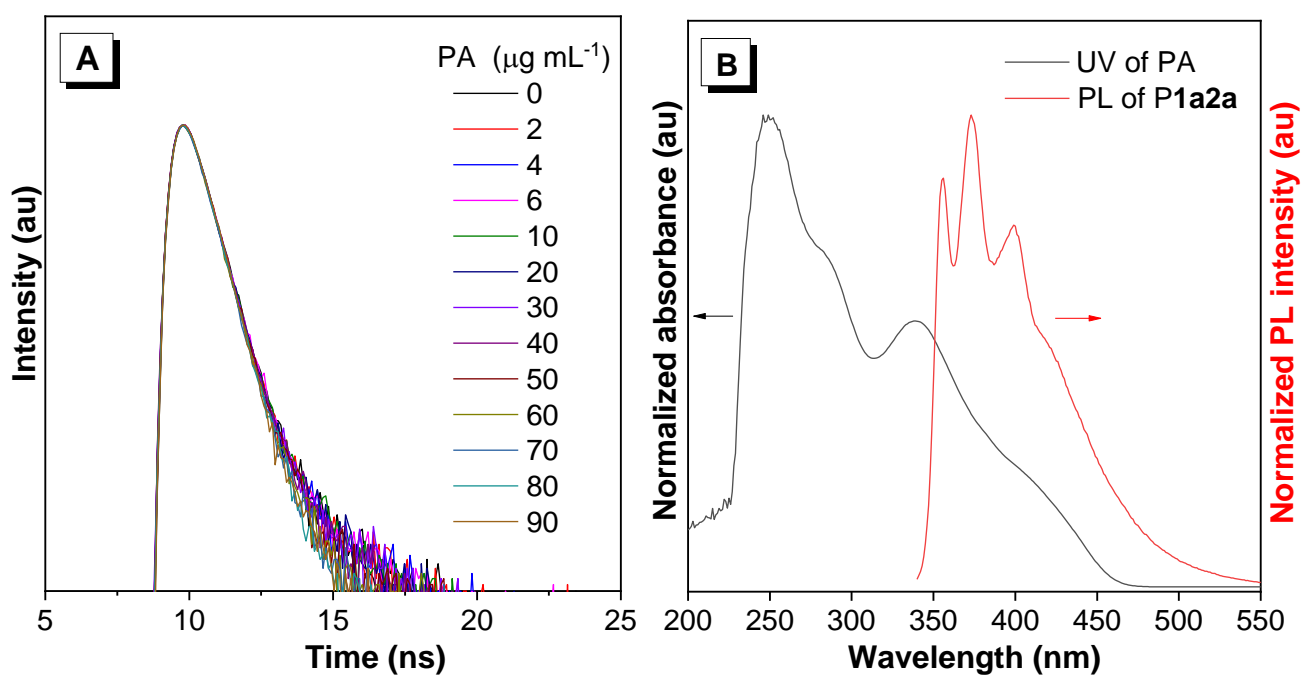
**Fig. S15**  $^{13}\text{C}$  NMR spectra of **2b** (A), **1c** (B) and **P1c2b** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



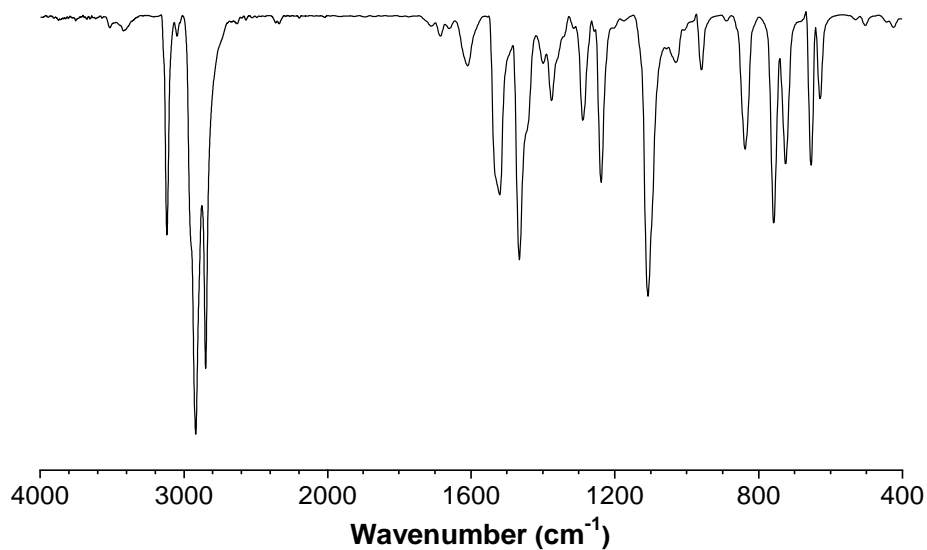
**Fig. S16**  $^{13}\text{C}$  NMR spectra of **2d** (A), **1c** (B) and **P1c2d** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



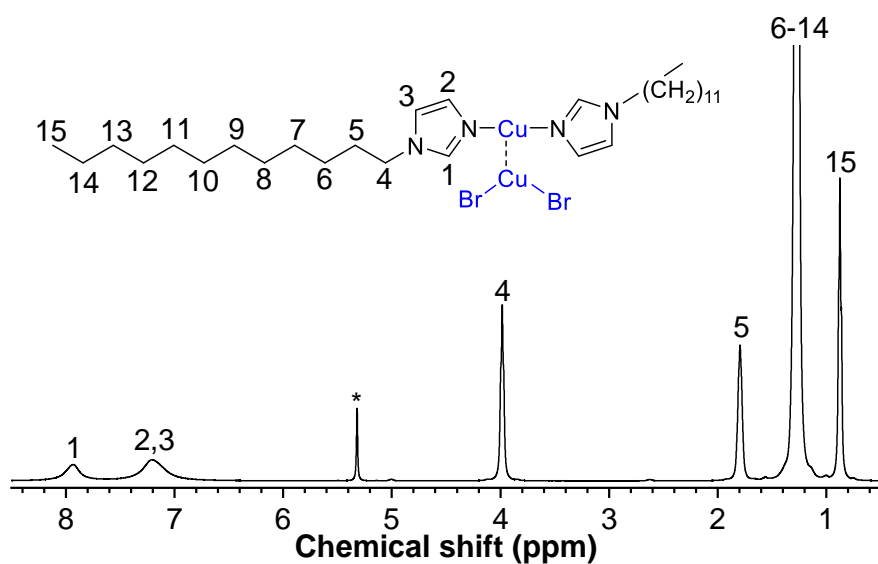
**Fig. S17** UV-vis absorption spectra of P1a2a-P1c2d in THF solutions, polymer concentration:  $10^{-5}$  M.



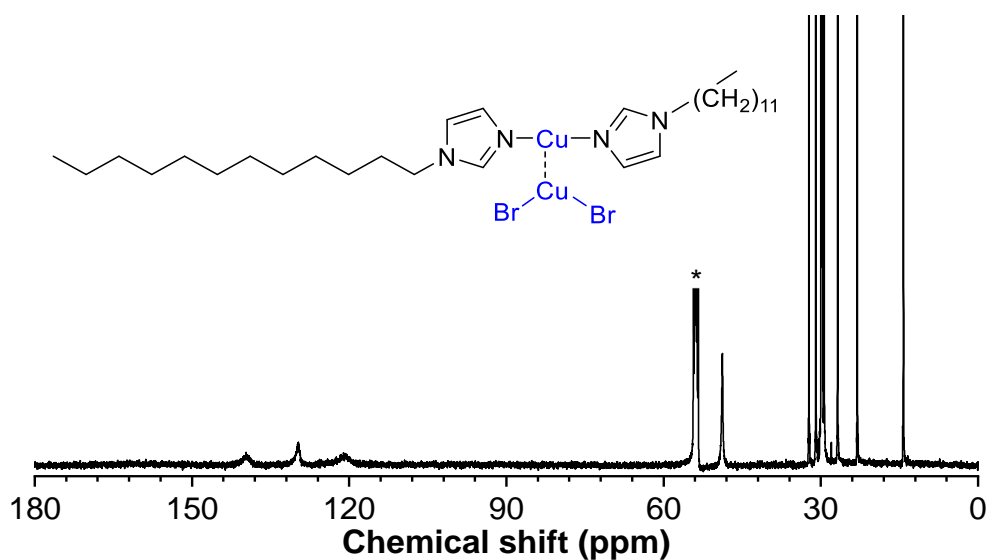
**Fig. S18** (A) PL decay curves of P1a2a at 374 nm in THF solution in the presence of different amounts of PA. Polymer concentration: 10  $\mu\text{M}$ ;  $\lambda_{\text{ex}}$ : 320 nm. (B) Normalized absorption spectrum of PA and PL spectrum of P1a2a in THF solutions.



**Fig. S19** FT-IR spectrum of Cu-Im.



**Fig. S20**  $^1\text{H}$  NMR spectrum of Cu-Im in  $\text{CD}_2\text{Cl}_2$ . The solvent peak is marked with asterisk.



**Fig. S21**  $^{13}\text{C}$  NMR spectrum of Cu-Im in  $\text{CD}_2\text{Cl}_2$ . The solvent peak is marked with asterisk.

**Table S1** Effect of different copper catalysts on the click polymerization<sup>a</sup>

| <b>Cu-Im</b>                             | <i>t</i> (h) | Yield (%) | <i>M<sub>w</sub></i> <sup>b</sup> | PDI <sup>b</sup> | <i>M<sub>n</sub></i> <sup>b</sup> | $\bar{X}_n$ <sup>c</sup> | <i>p</i> <sup>d</sup> |
|--|--------------|-----------|-----------------------------------|------------------|-----------------------------------|--------------------------|-----------------------|
|  | 1            | 13        | 6600                              | 1.50             | 4400                              | 6.39                     | 0.84                  |
|  | 2            | 30        | 7500                              | 1.61             | 4658                              | 6.76                     | 0.85                  |
|  | 3            | 62        | 11 200                            | 2.01             | 5572                              | 8.09                     | 0.88                  |
|  | 4            | 92        | 16 000                            | 2.15             | 7442                              | 10.80                    | 0.91                  |
| <b>Cu(PPh<sub>3</sub>)<sub>3</sub>Br</b> | <i>t</i> (h) | Yield (%) | <i>M<sub>w</sub></i> <sup>b</sup> | PDI <sup>b</sup> | <i>M<sub>n</sub></i> <sup>b</sup> | $\bar{X}_n$ <sup>c</sup> | <i>p</i> <sup>d</sup> |
|  | 2            | trace     | 1105                              | 1.02             | 1083                              | 1.57                     | 0.36                  |
|  | 3            | trace     | 1790                              | 1.28             | 1398                              | 2.03                     | 0.51                  |
|  | 4            | trace     | 3600                              | 1.53             | 2352                              | 3.41                     | 0.71                  |
|  | 5            | trace     | 3640                              | 1.07             | 3401                              | 4.94                     | 0.80                  |

<sup>a</sup> Carried out in THF at 30 °C under nitrogen, [1a] = [2a] = 0.05 M, [Cu]/[1a] = 0.1. <sup>b</sup> Estimated by APC using THF as the eluent on the basis of a PS calibration, *M<sub>w</sub>* = weight-average molecular weight, PDI = *M<sub>w</sub>*/*M<sub>n</sub>*, *M<sub>n</sub>* = number-average molecular weight. <sup>c</sup> Degree of polymerization. <sup>d</sup> Extent of reaction.

**Table S2** Refractive indices (*n*), Abbé numbers (*v*), modified Abbé numbers (*v'*), optical dispersions (*D* and *D'*) and thickness of thin films of polymers **P1a2a-P1c2d**, *n* values of commercial polymers

| Polymer      | <i>n</i> <sup>a</sup> | <i>v</i> <sup>b</sup> | <i>D</i> <sup>c</sup> | <i>v'</i> <sup>d</sup> | <i>D'</i> <sup>e</sup> | Thickness (nm) | Commercial polymer        | <i>n</i> <sup>f</sup> |
|--------------|-----------------------|-----------------------|-----------------------|------------------------|------------------------|----------------|---------------------------|-----------------------|
| <b>P1a2a</b> | 1.611                 | 55.7                  | 0.0179                | 214.1                  | 0.0047                 | 45.34          | poly(methyl methacrylate) | 1.489                 |
| <b>P1a2c</b> | 1.566                 | 35.8                  | 0.0279                | 137.4                  | 0.0073                 | 51.89          | poly(dimethylsiloxane)    | 1.428                 |
| <b>P1b2a</b> | 1.644                 | 12.5                  | 0.0797                | 74.6                   | 0.0134                 | 110.87         | poly(vinyl chloride)      | 1.540                 |
| <b>P1b2c</b> | 1.634                 | 15.7                  | 0.0636                | 56.9                   | 0.0176                 | 62.98          | poly(vinyl alcohol)       | 1.477                 |
| <b>P1c2b</b> | 1.583                 | 32.2                  | 0.0310                | 141.5                  | 0.0071                 | 99.08          | poly(lactic acid)         | 1.451                 |
| <b>P1c2d</b> | 1.591                 | 30.3                  | 0.0329                | 179.7                  | 0.0056                 | 50.06          | cellulose                 | 1.468                 |

<sup>a</sup> Data of polymers at 632.8 nm. <sup>b</sup>  $v = (n_{589.3} - 1)/(n_{486.1} - n_{656.3})$ . <sup>c</sup>  $D = 1/v$ . <sup>d</sup>  $v' = (n_{1319} - 1)/(n_{1060} - n_{1550})$ . <sup>e</sup>  $D' = 1/v'$ .

<sup>f</sup> Data of commercial polymers at 632.8 nm taken from refractive index database.

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