Electronic supplementary information (ESI)

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

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

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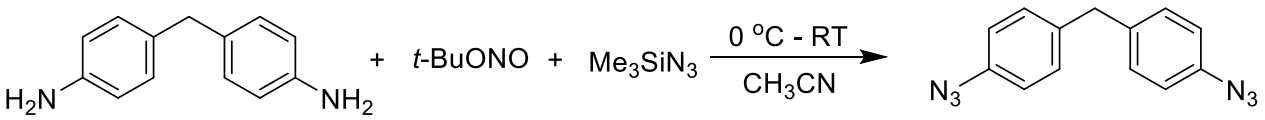
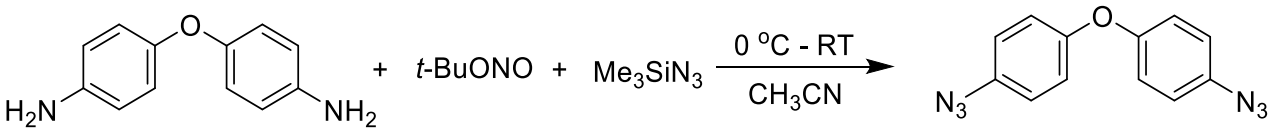


3 **4** **5** **1a**

This monomer was prepared according to previously published work.[1]

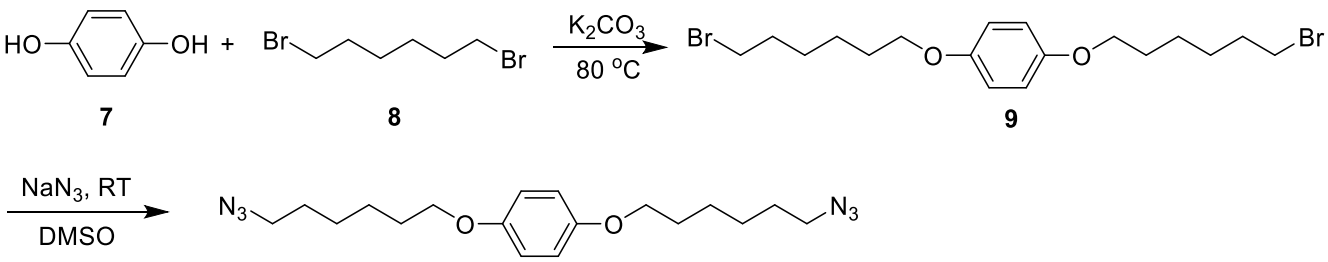
Synthesis of 4,4'-oxybis(azidobenzene) (1b)



6 **4** **5** **1b**

This monomer was prepared according to previously published work.[1]

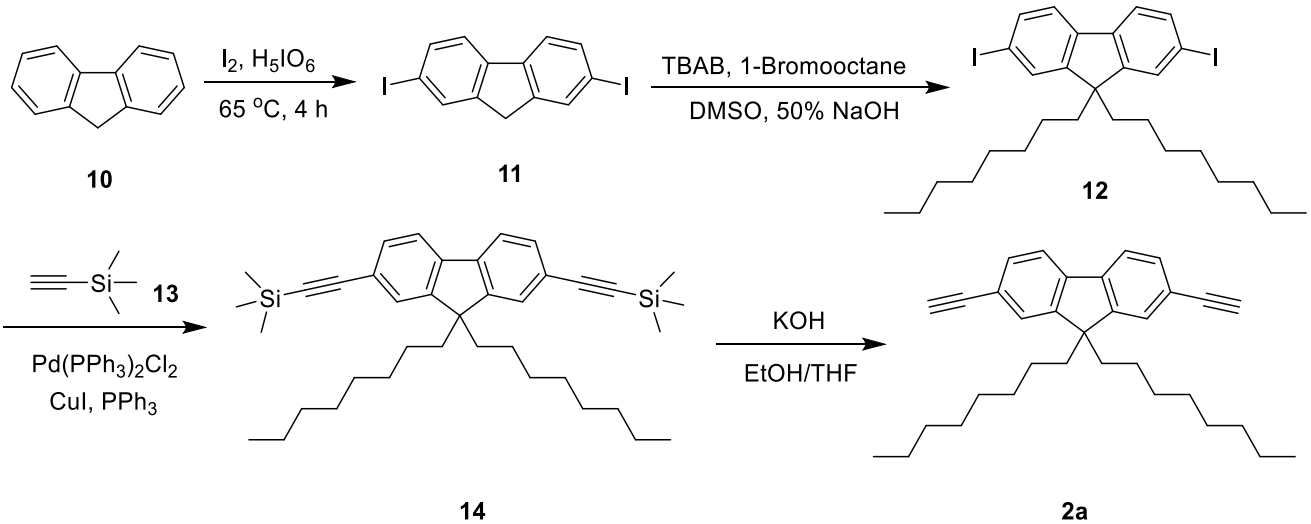
Synthesis of 1,4-bis((6-azidohexyl)oxy)benzene (1c)



7 **8** **9** **1c**

This monomer was prepared according to our previously published procedures.[2]

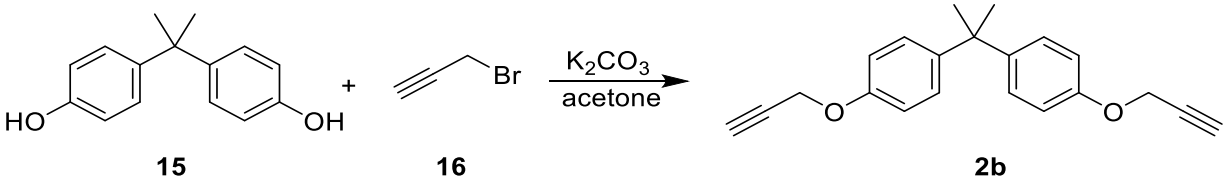
Synthesis of 2,7-diethynyl-9,9-dioctyl-9H-fluorene (2a)



10 **11** **12** **14** **2a**

This monomer was prepared according to our previously published procedures.[3]

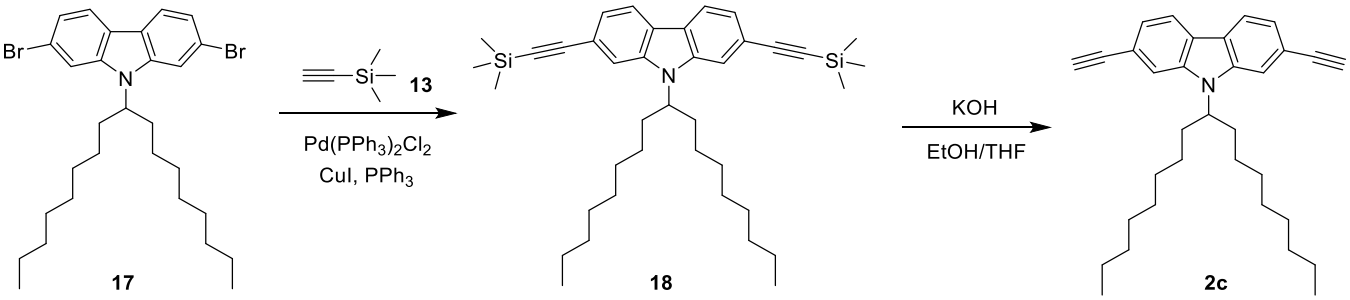
Synthesis of 4,4'-(propane-2,2-diyl)bis((prop-2-yn-1-yloxy)benzene) (2b)



15 16 2b

This monomer was prepared according to our previously published procedures.[4]

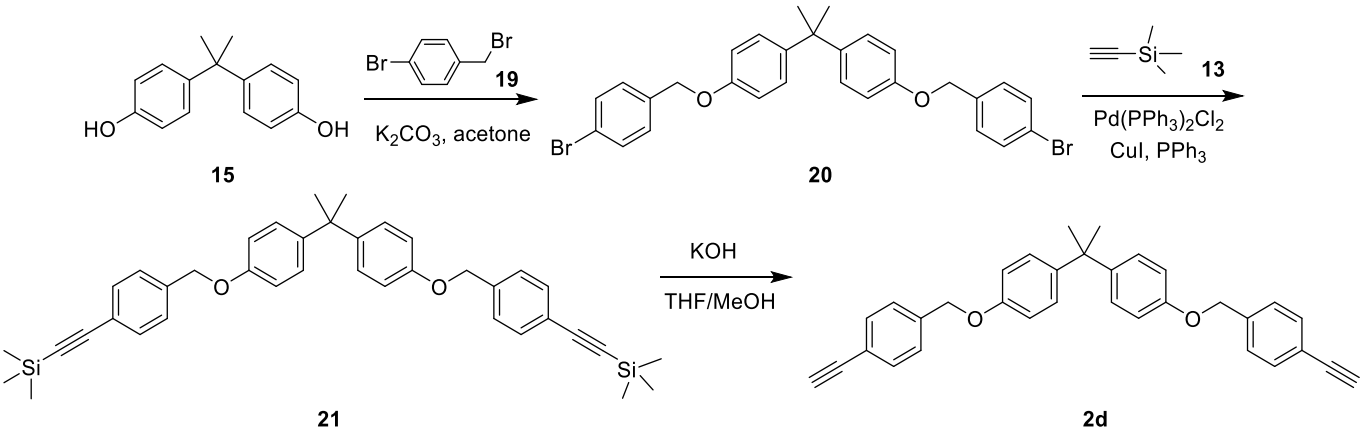
Synthesis of 2,7-diethynyl-9-(heptadecan-9-yl)-9H-carbazole (2c)



17 18 2c

This monomer was prepared according to our previously published procedures.[3]

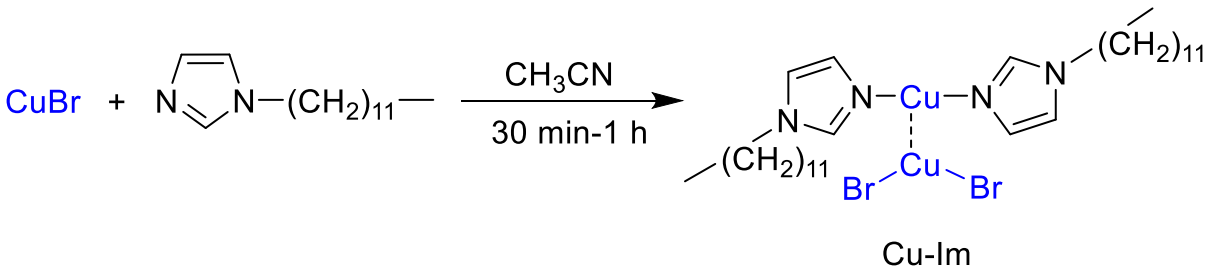
Synthesis of 4,4′-(isopropylidenediphenyl)-bis(4-ethynylbenzyl) ether (2d)



15 20 21 2d

This monomer was prepared according to our previously published procedures.[5,6]

Synthesis of Cu-Im catalyst



Cu-Im

This catalyst was prepared according to previously published papers.[7,8]

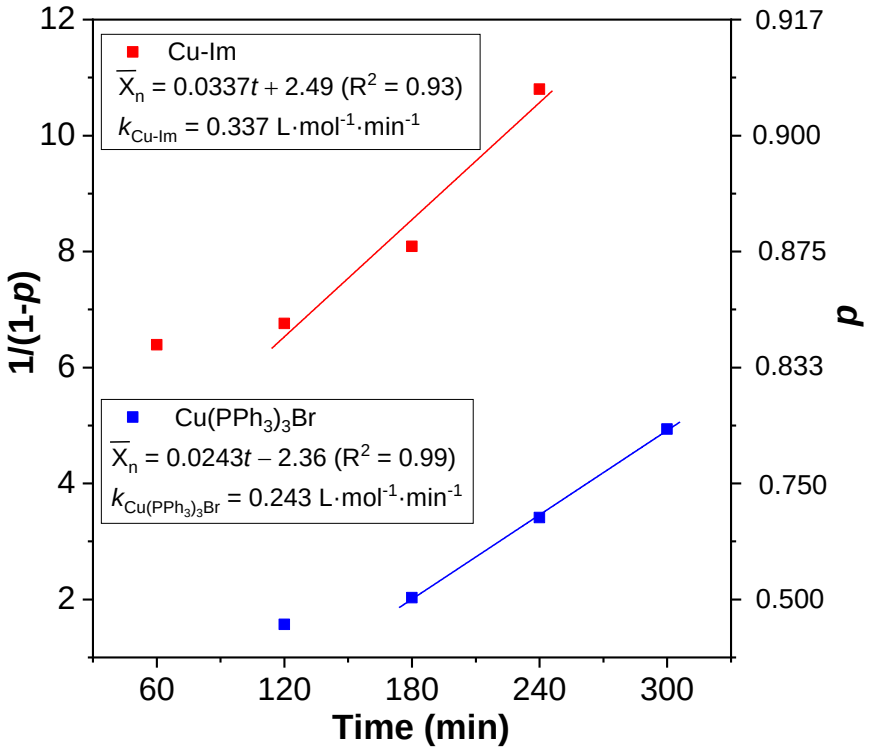


Fig. S1 Kinetics curves of different copper catalysts on the click polymerization.

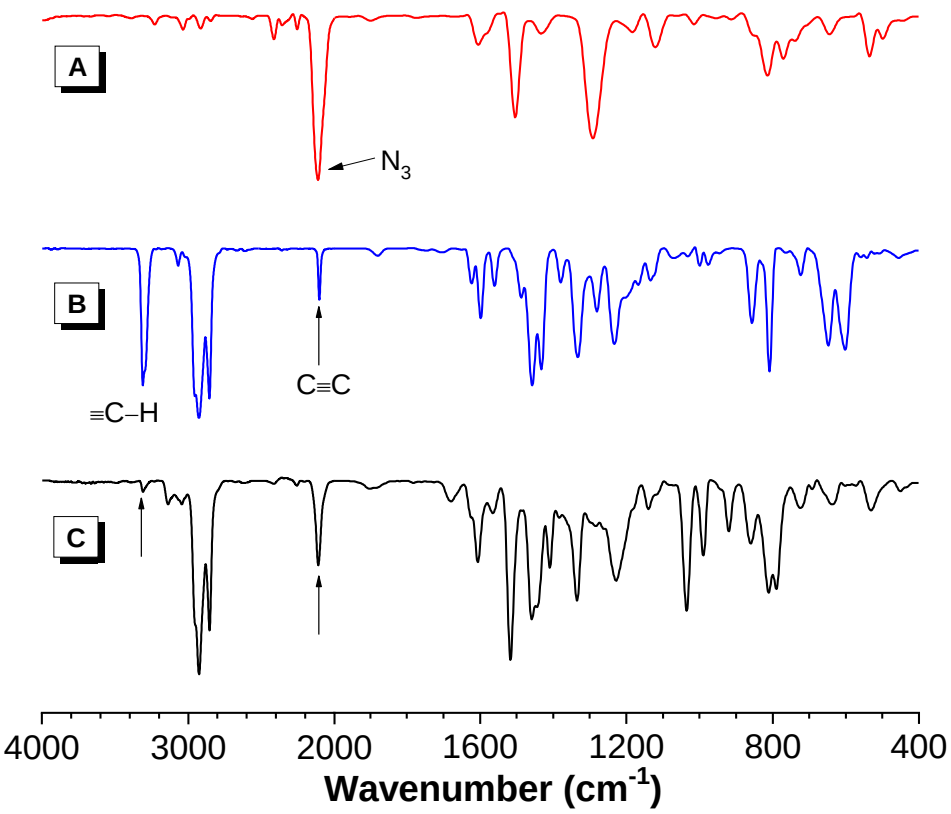


Fig. S2 FT-IR spectra of **1a** (A), **2c** (B) and P**1a2c** (C).

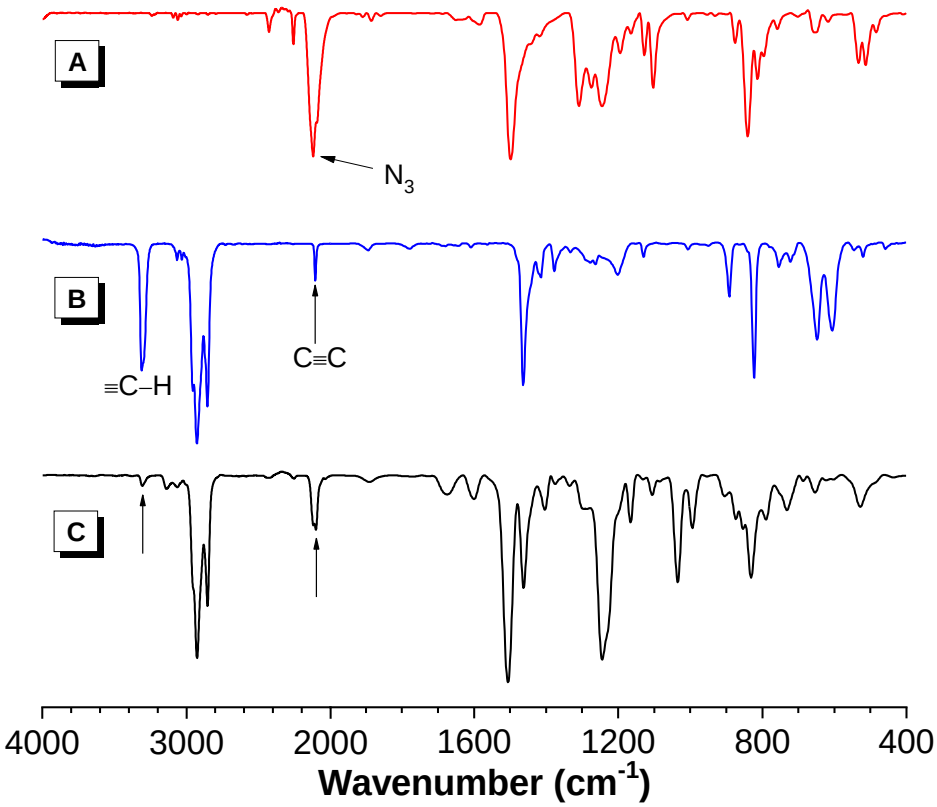


Fig. S3 FT-IR spectra of **1b** (A), **2a** (B) and P**1b2a** (C).

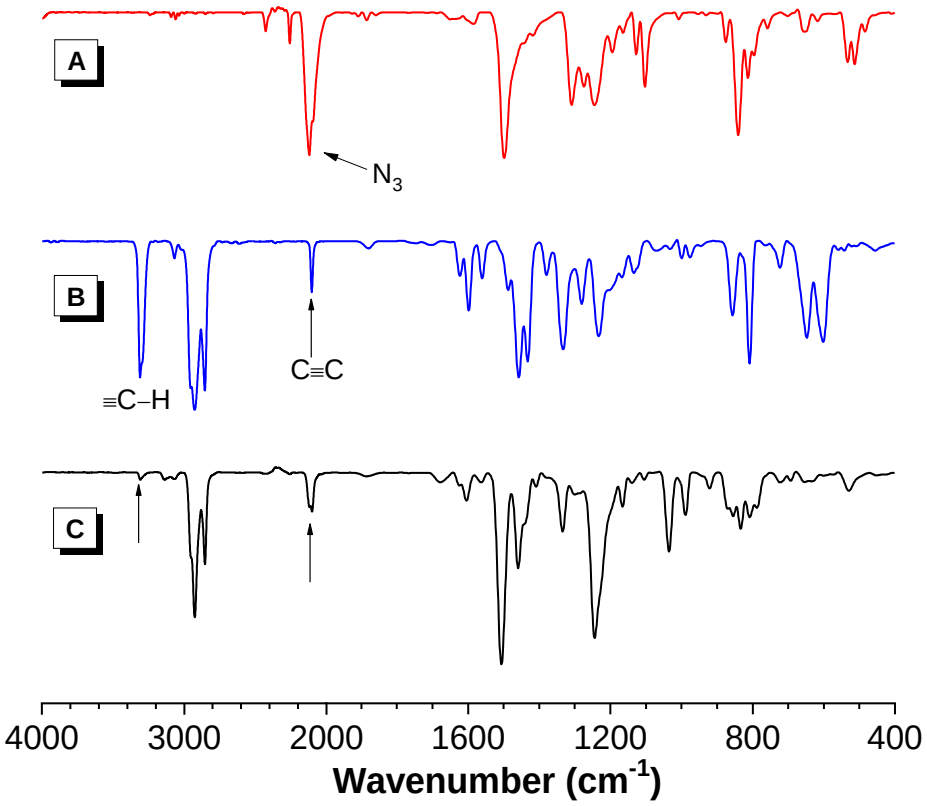


Fig. S4 FT-IR spectra of **1b** (A), **2c** (B) and P**1b2c** (C).

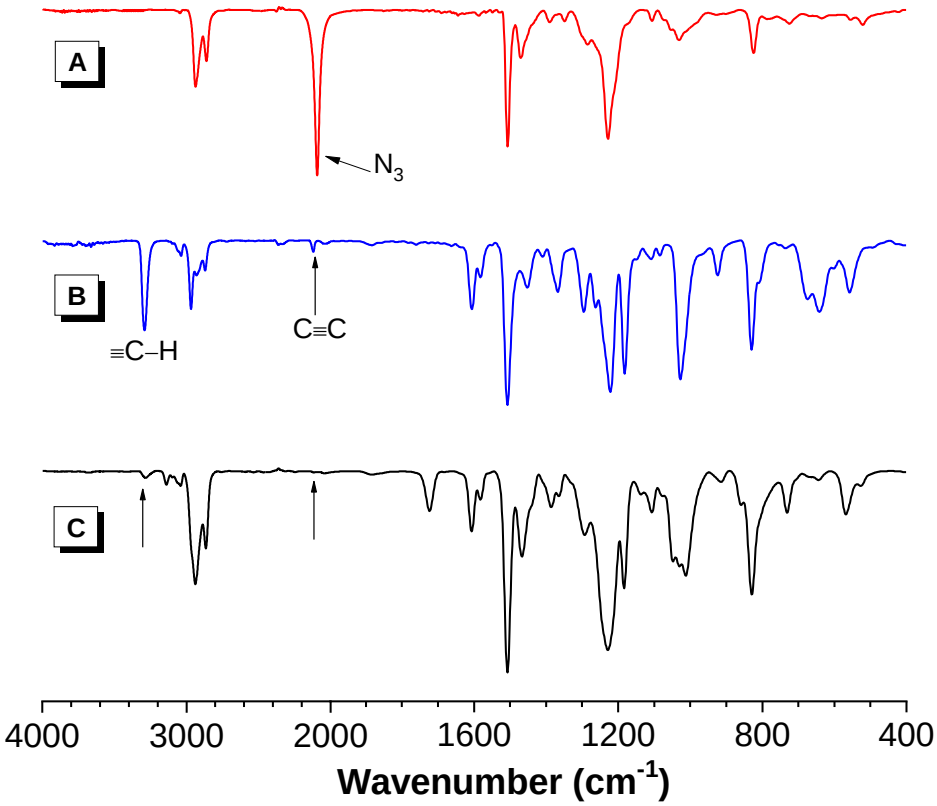
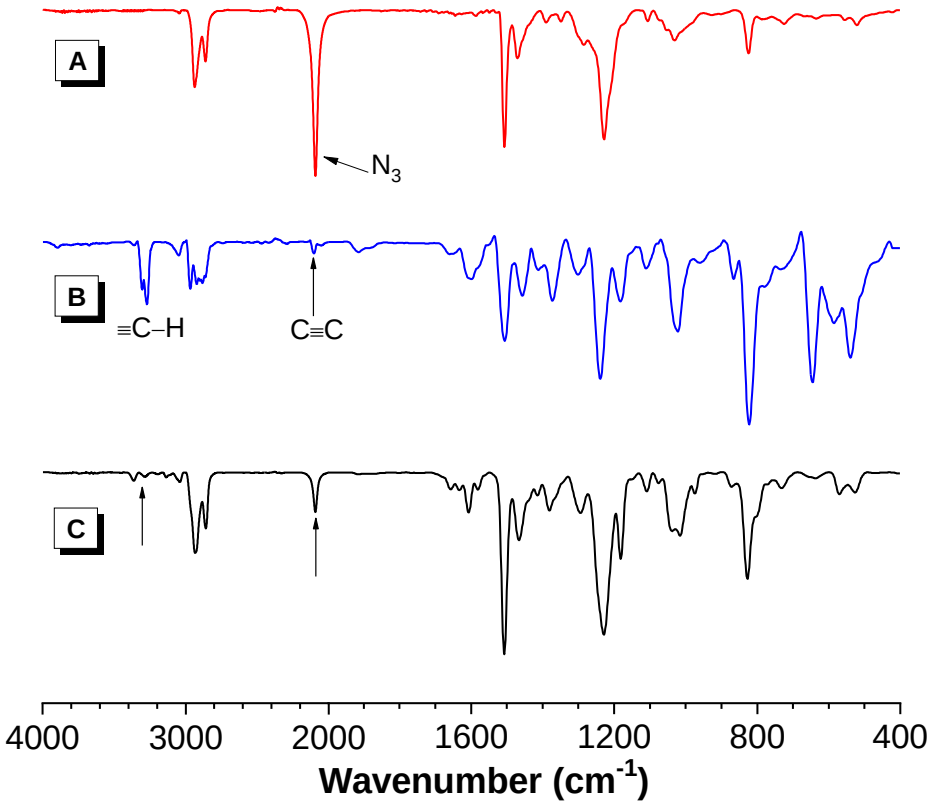


Fig. S5 FT-IR spectra of **1c** (A), **2b** (B) and P**1c2b** (C).



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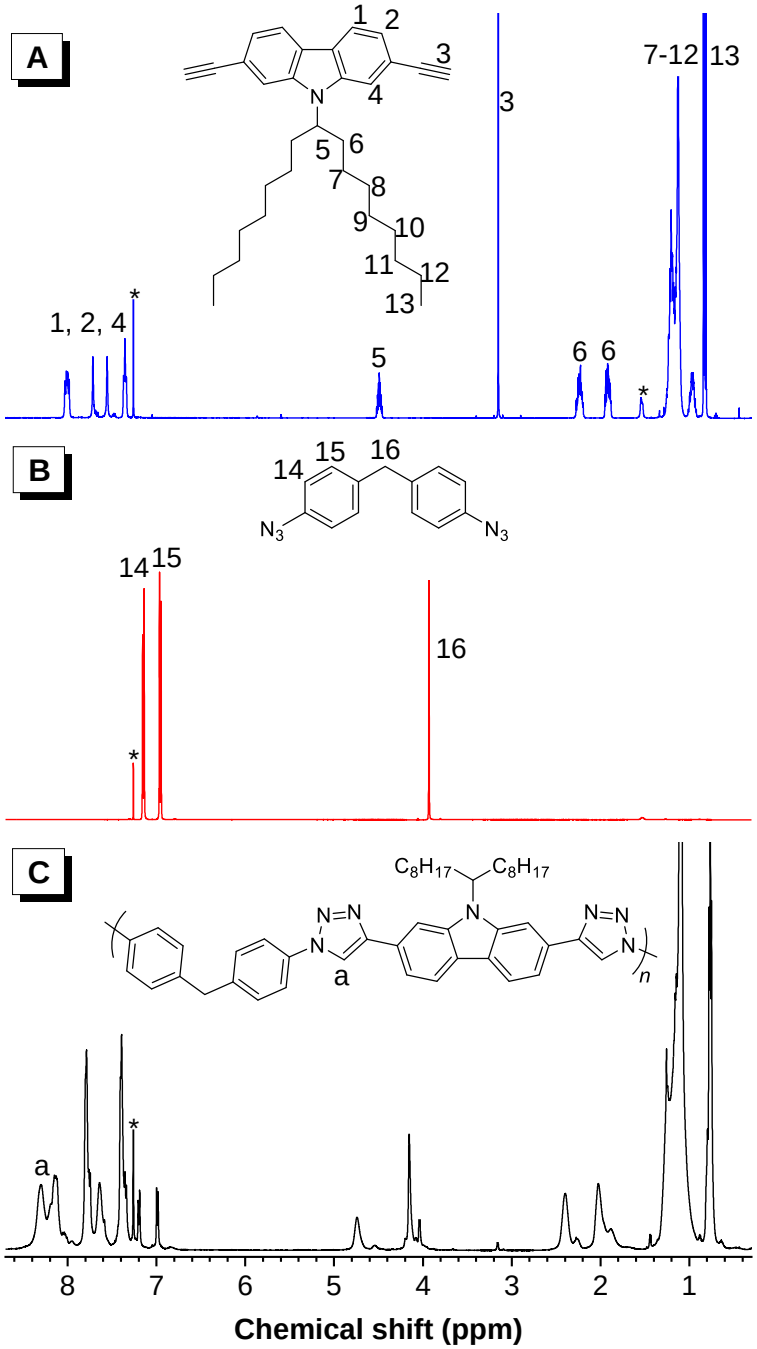

Fig. S7 ^{1}H NMR spectra of **2c** (A), **1a** (B) and P**1a2c** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

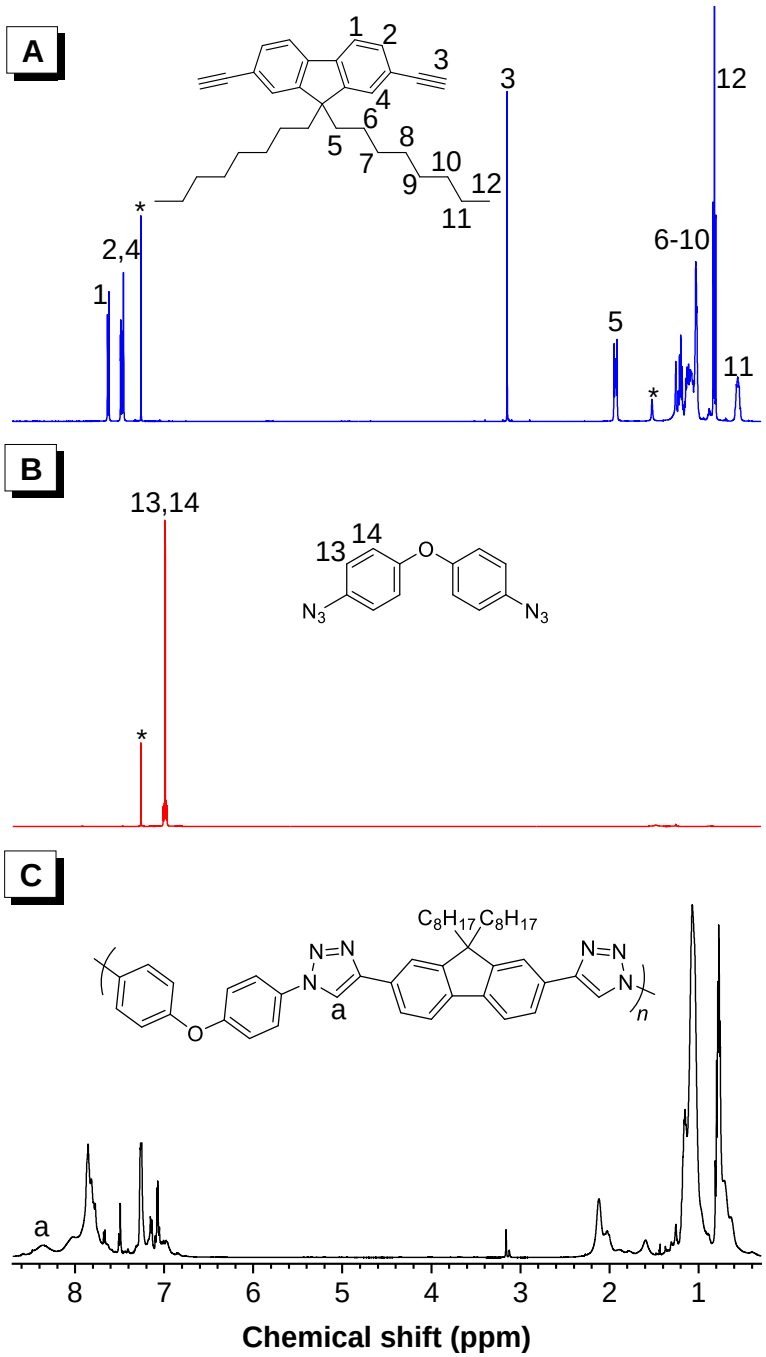

Fig. S8 ^{1}H NMR spectra of **2a** (A), **1b** (B) and P**1b2a** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

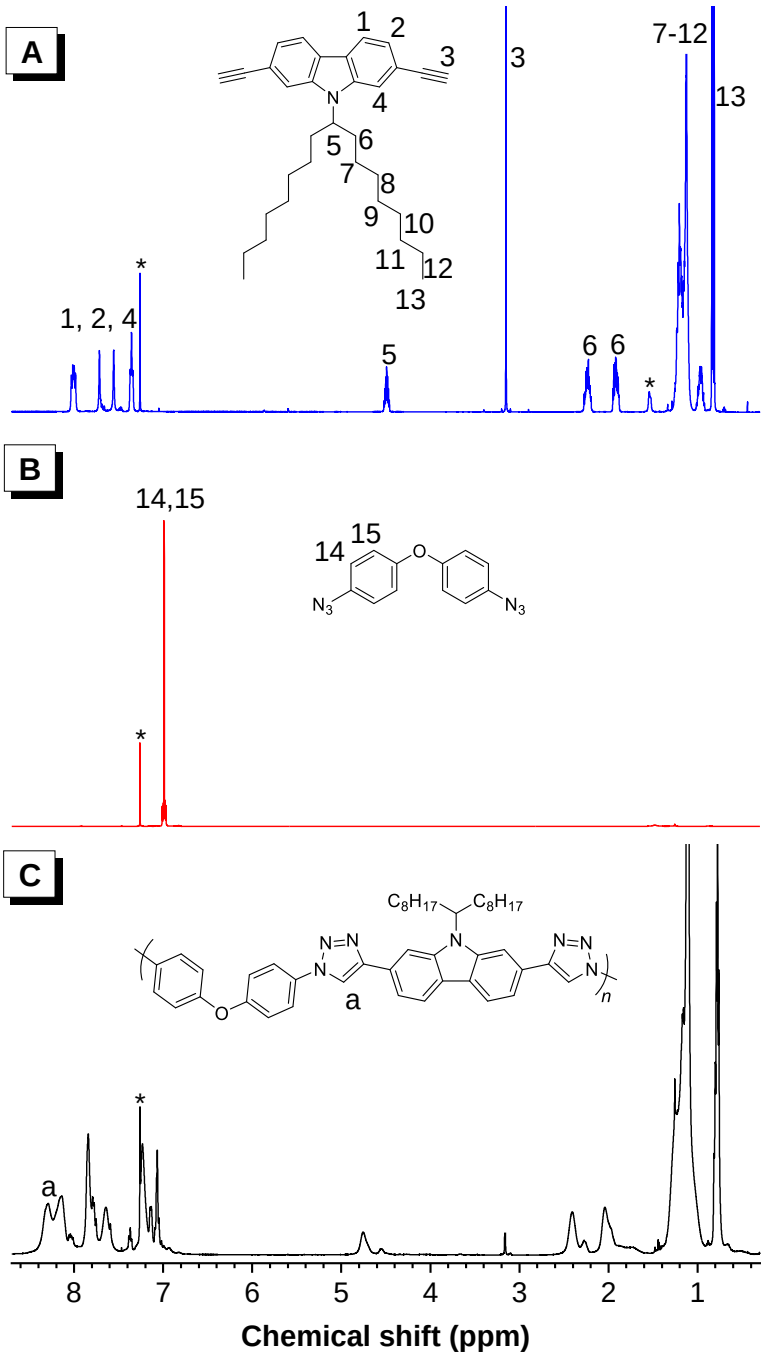

Fig. S9 ^{1}H NMR spectra of **2c** (A), **1b** (B) and P**1b2c** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

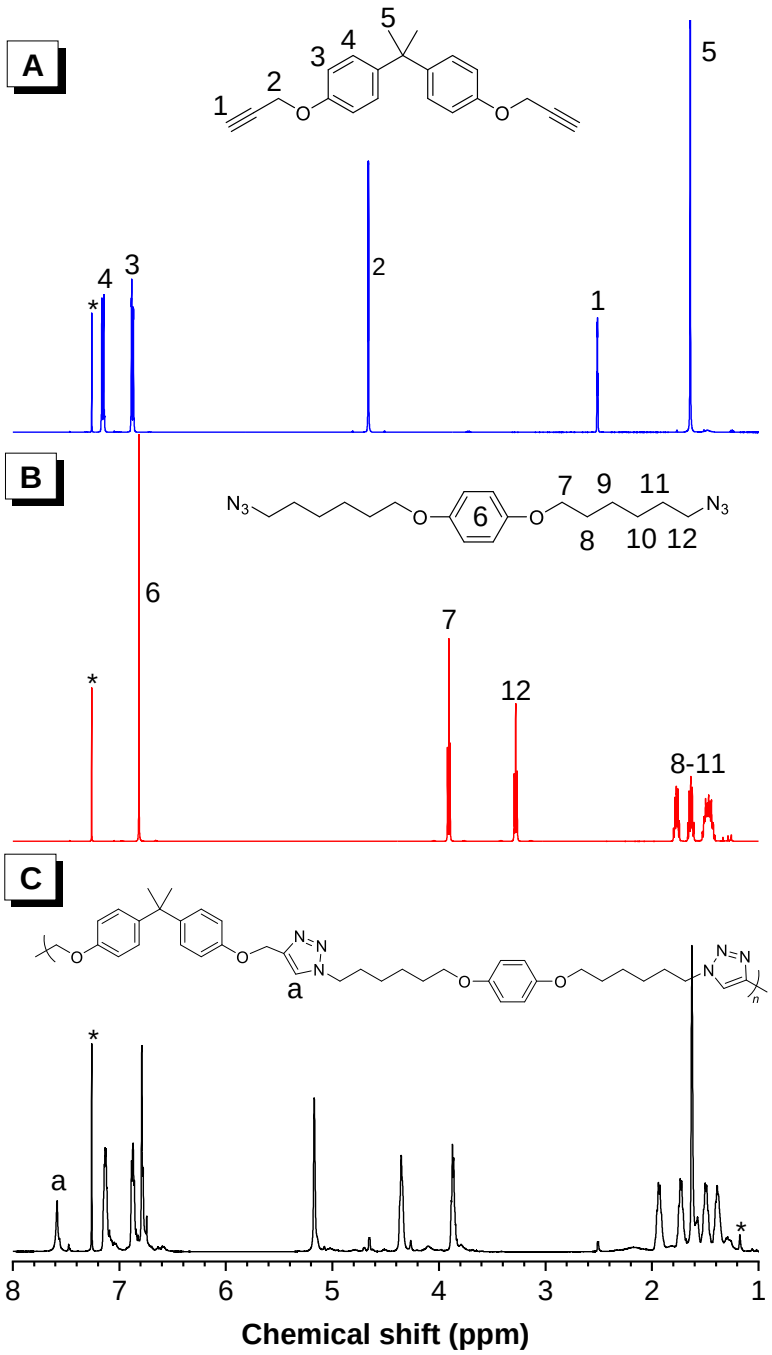

Fig. S10 ^{1}H NMR spectra of **2b** (A), **1c** (B) and P**1c2b** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

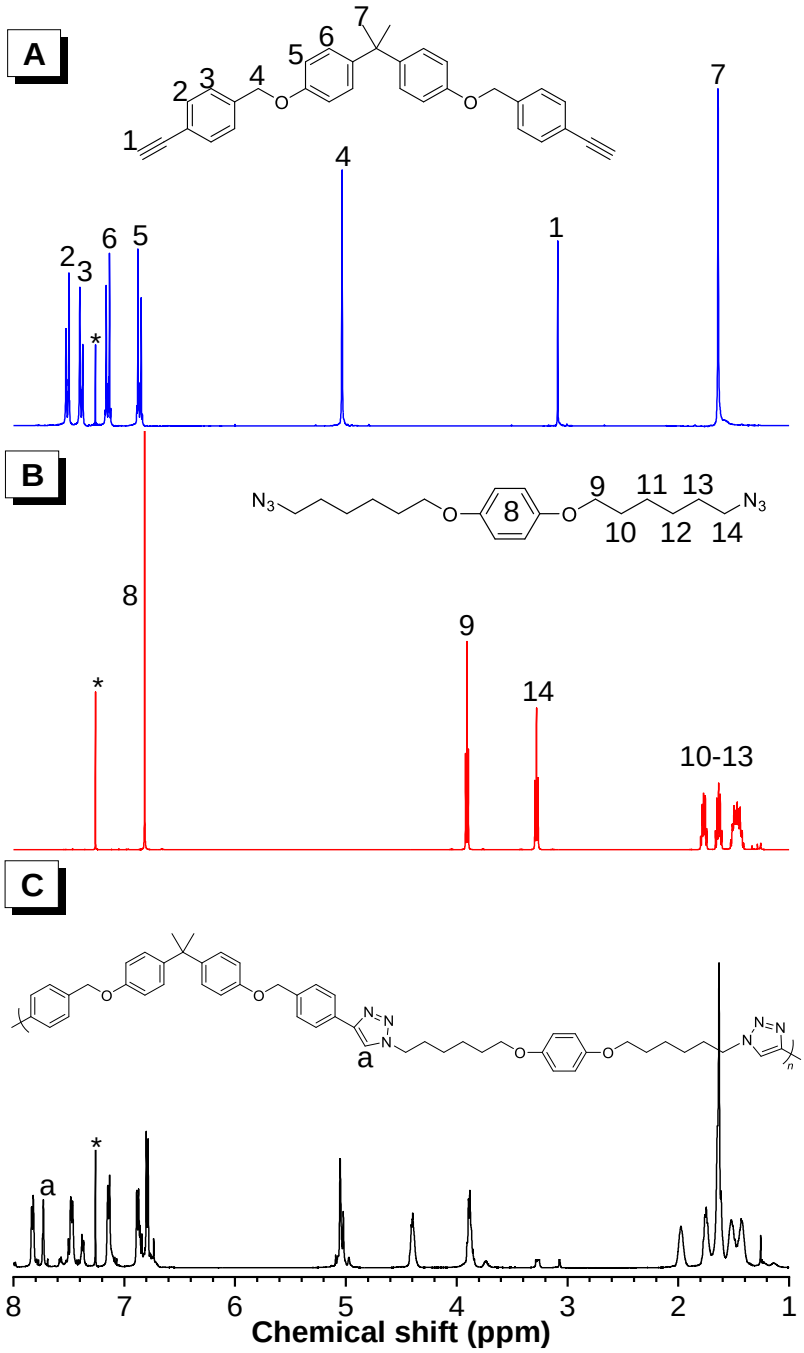

Fig. S11 ^{1}H NMR spectra of **2d** (A), **1c** (B) and P**1c2d** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

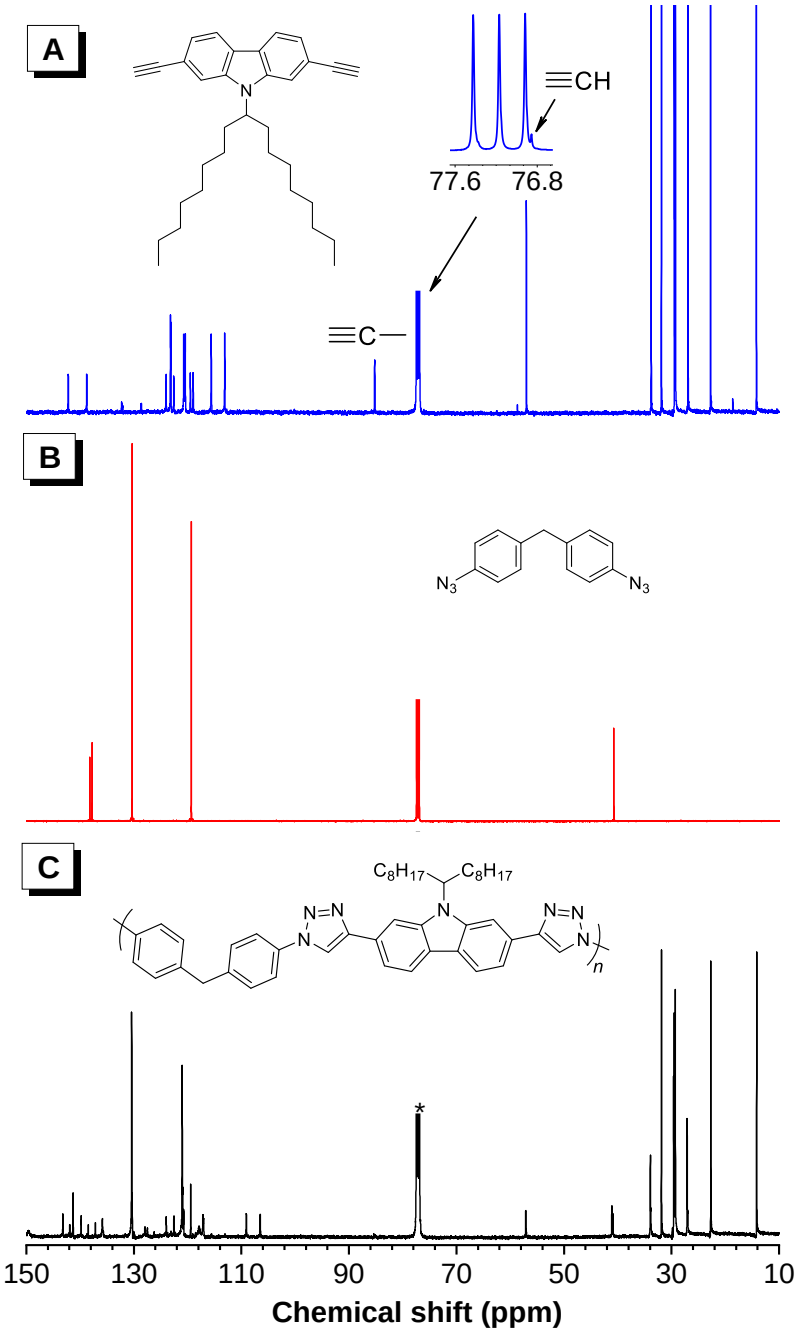

Fig. S12 ^{13}C NMR spectra of **2c** (A), **1a** (B) and P**1a2c** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

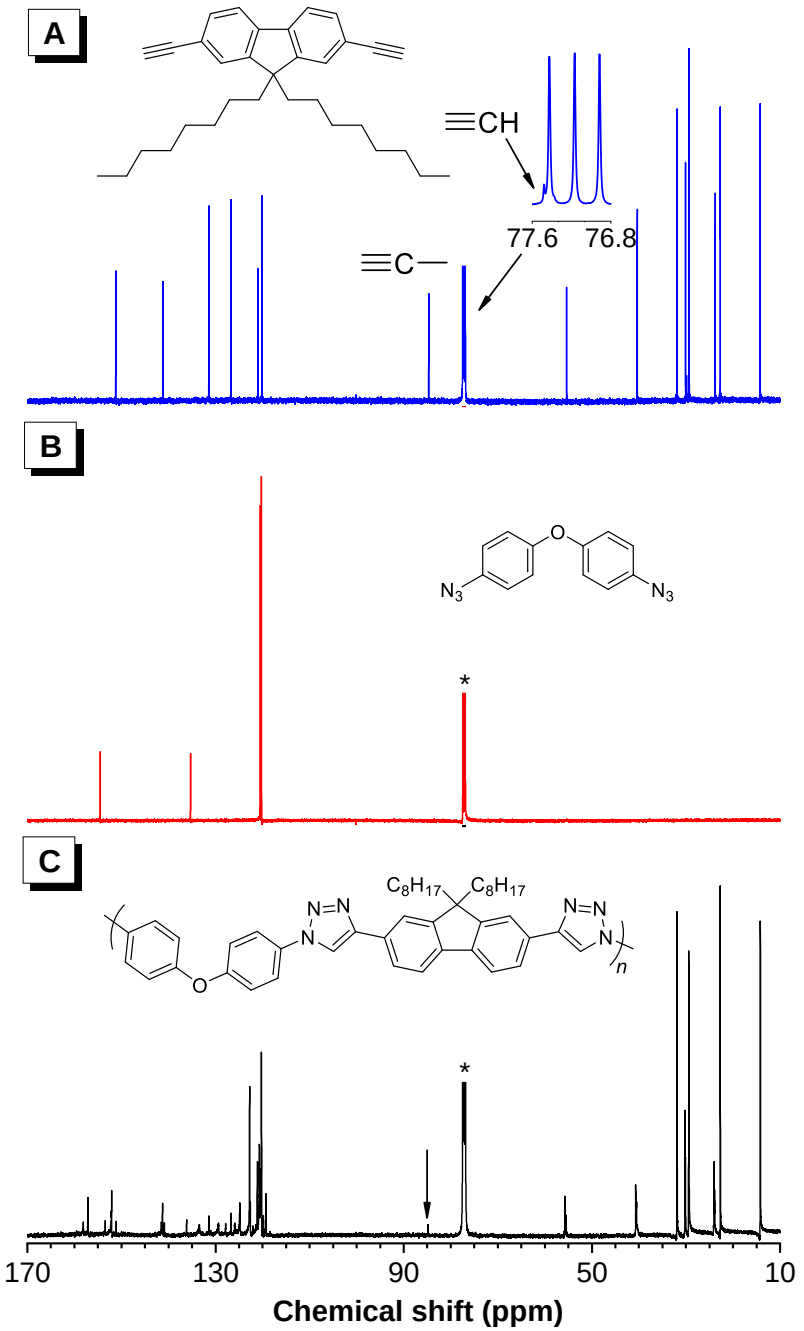

Fig. S13 ^{13}C NMR spectra of **2a** (A), **1b** (B) and P**1b2a** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

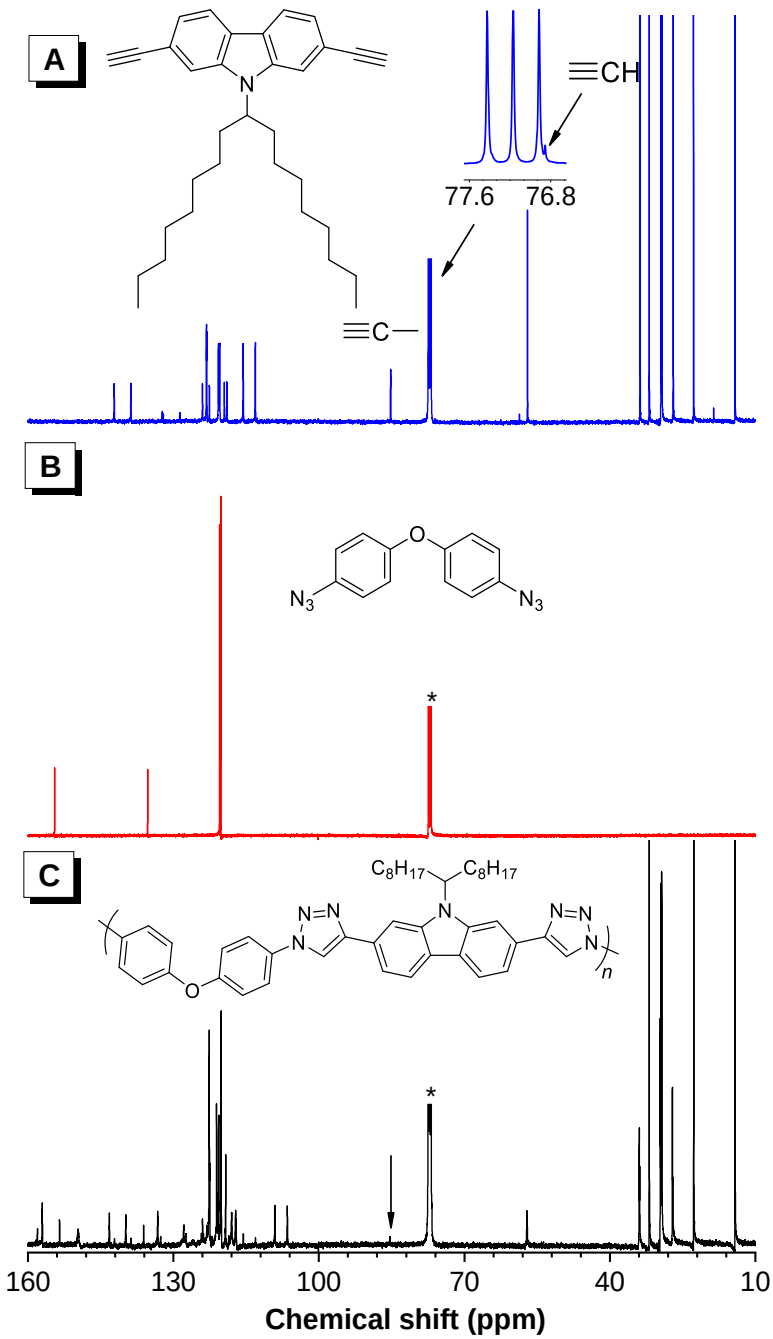

Fig. S14 ^{13}C NMR spectra of **2c** (A), **1b** (B) and P**1b2c** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

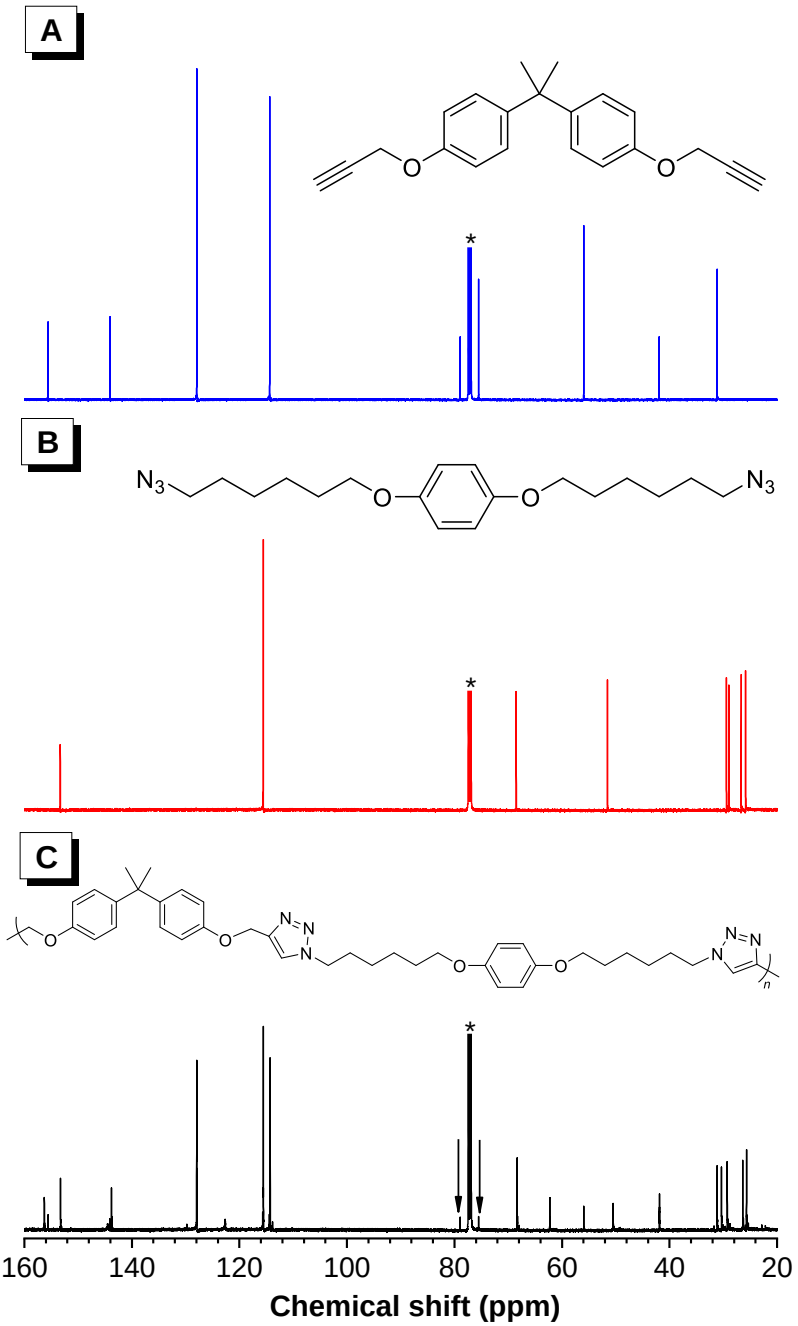

Fig. S15 ^{13}C NMR spectra of **2b** (A), **1c** (B) and P**1c2b** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

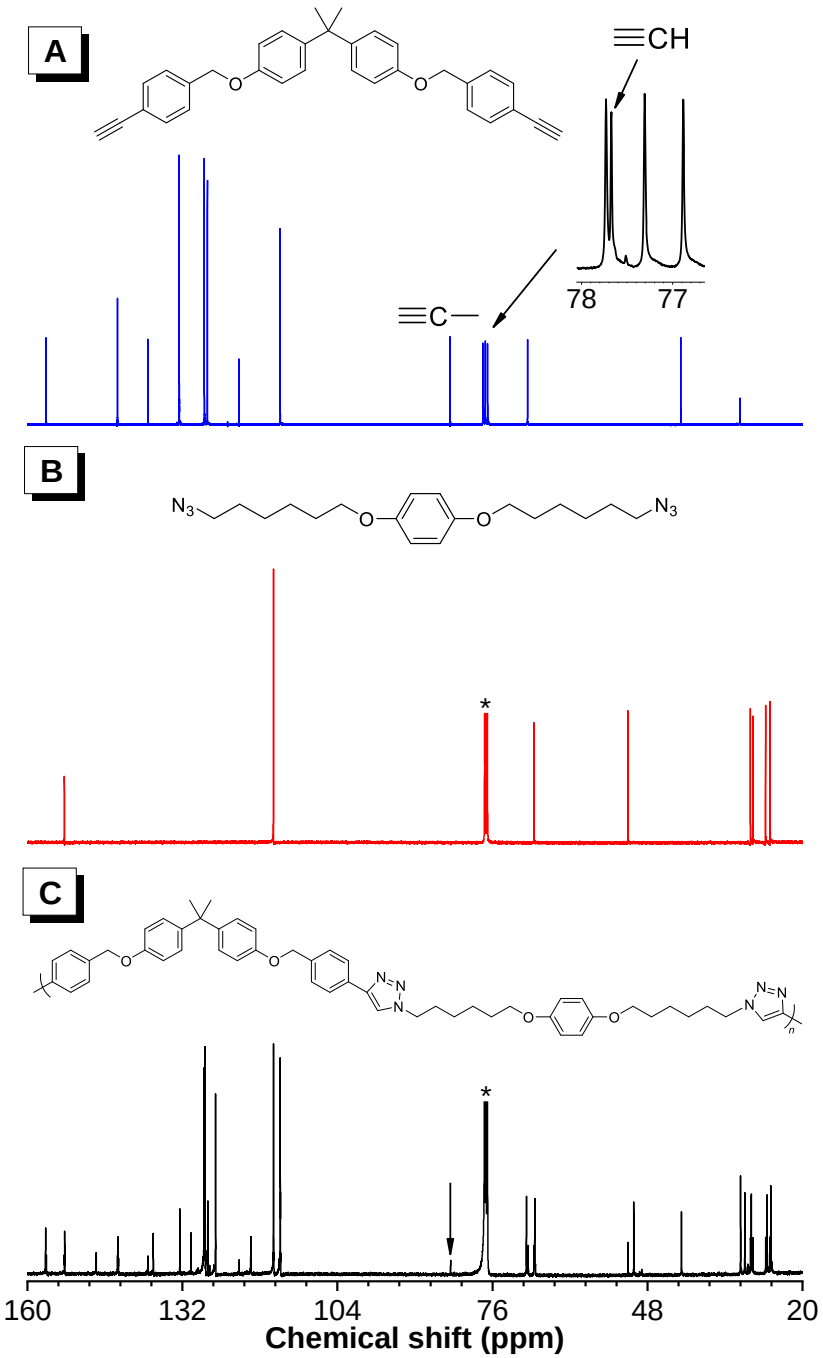

Fig. S16 ^{13}C NMR spectra of **2d** (A), **1c** (B) and P**1c2d** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

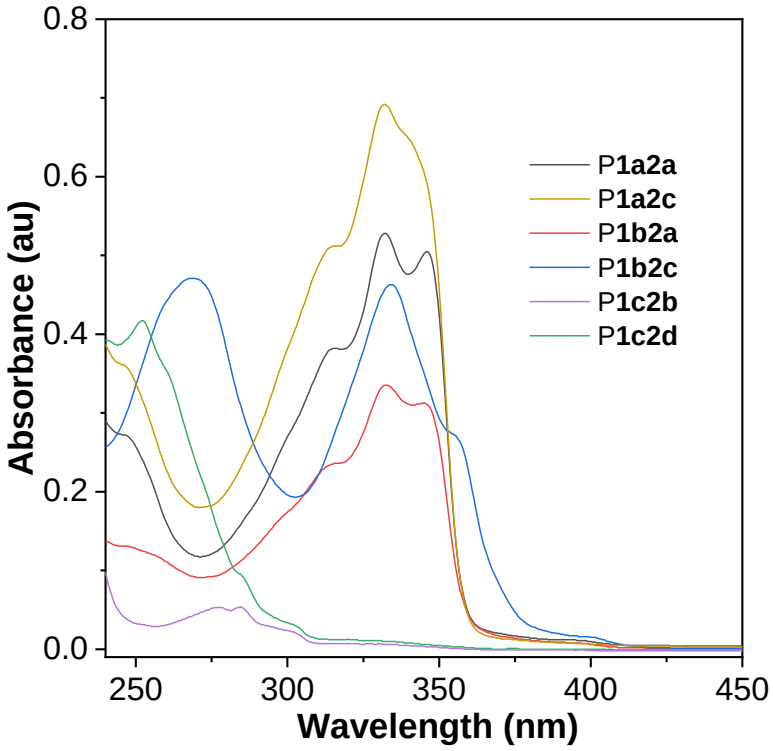

Fig. S17 UV-vis absorption spectra of P**1a2a**-P**1c2d** in THF solutions, polymer concentration: 10^{-5} M.

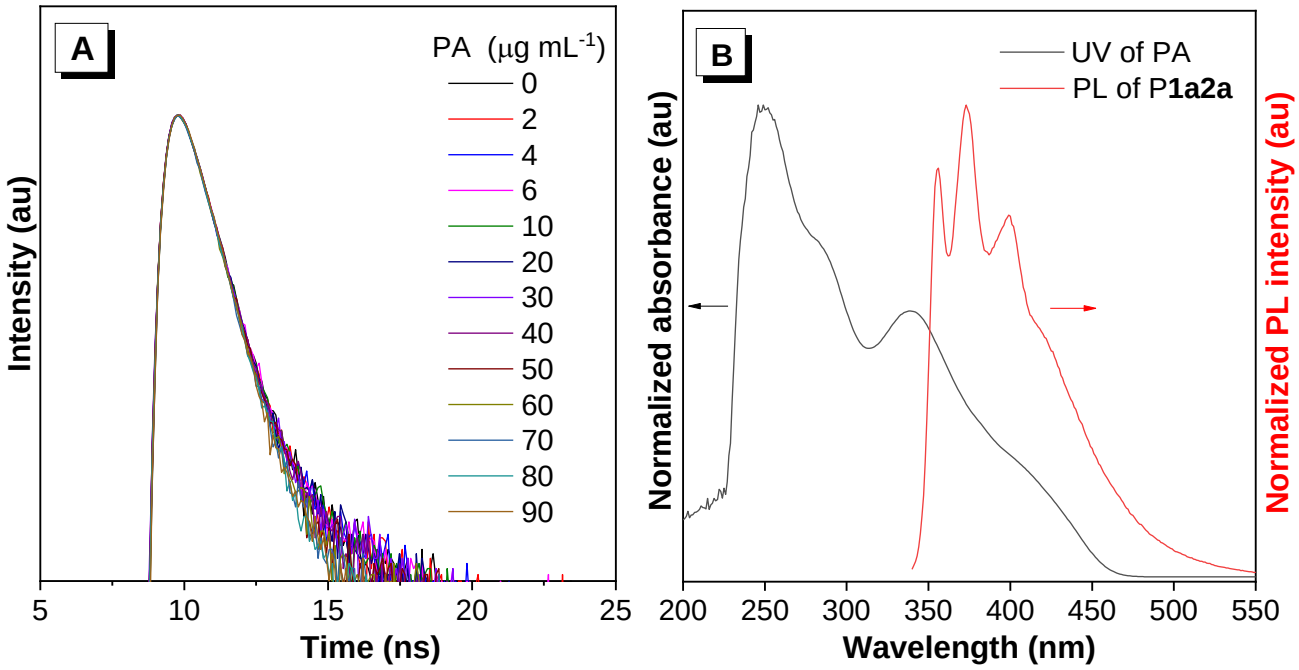

Fig. S18 (A) PL decay curves of P**1a2a** at 374 nm in THF solution in the presence of different amounts of PA. Polymer concentration: 10 μM; λ_{ex}: 320 nm. (B) Normalized absorption spectrum of PA and PL spectrum of P**1a2a** in THF solutions.

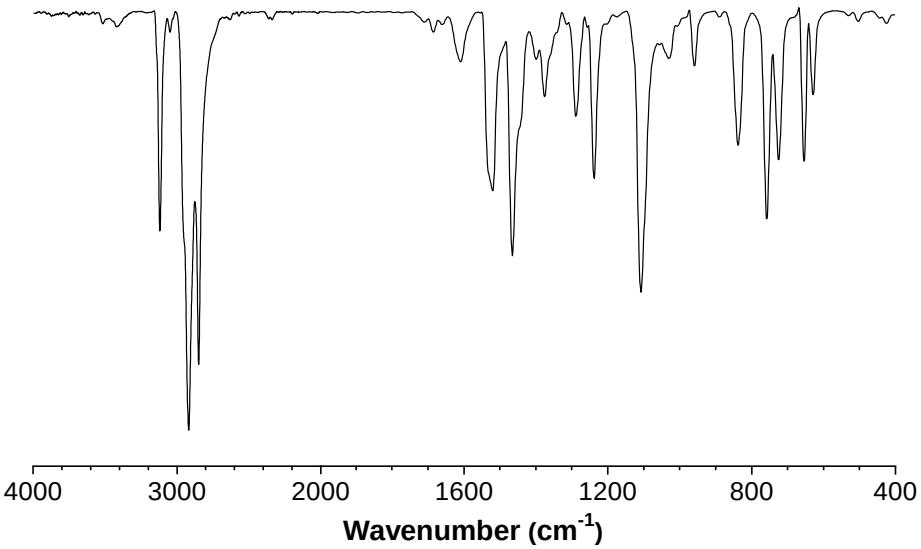

Fig. S19 FT-IR spectrum of Cu-Im.

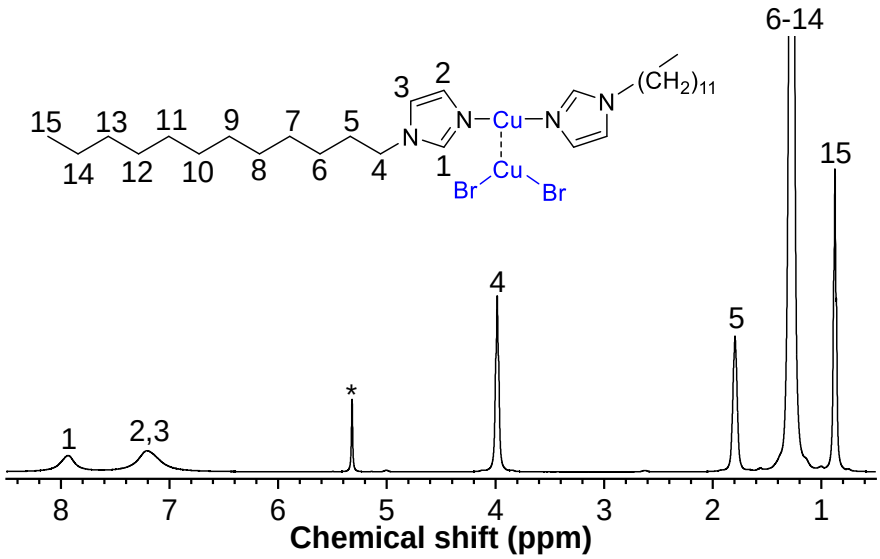

Fig. S20 ^{1}H NMR spectrum of Cu-Im in CD_2Cl_2. The solvent peak is marked with asterisk.

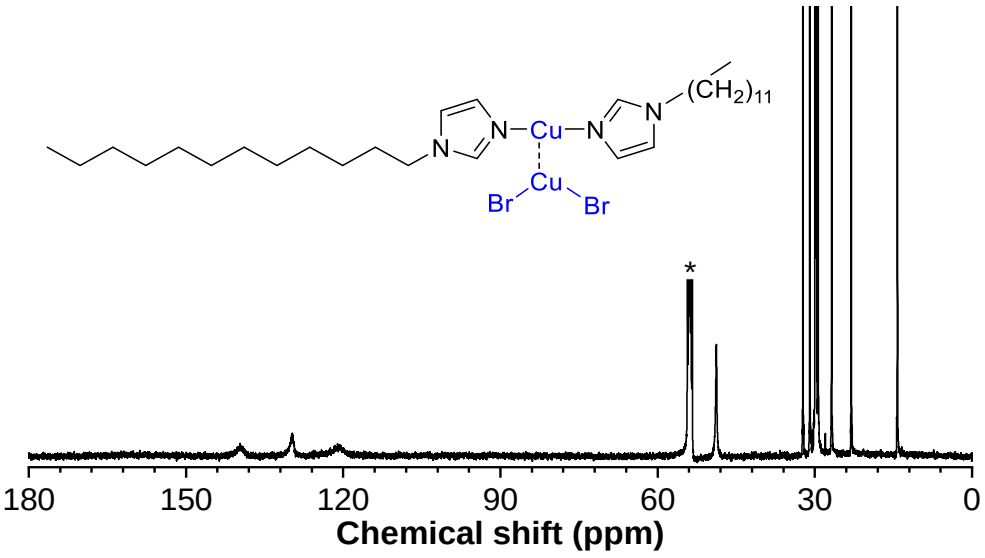

Fig. S21 ^{13}C NMR spectrum of Cu-Im in CD_2Cl_2. The solvent peak is marked with asterisk.

Table S1 Effect of different copper catalysts on the click polymerization[a]

Cu-Im	*t* (h)	Yield (%)	M_w[b]	PDI[b]	M_n[b]	$\bar{X}_n$[c]	*p*[d]
	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
Cu(PPh$_3$)$_3$Br	*t* (h)	Yield (%)	M_w[b]	PDI[b]	M_n[b]	$\bar{X}_n$[c]	*p*[d]
	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

[a] Carried out in THF at 30 °C under nitrogen, [**1a**] = [**2a**] = 0.05 M, [Cu]/[**1a**] = 0.1. [b] Estimated by APC using THF as the eluent on the basis of a PS calibration, M_w = weight-average molecular weight, PDI = M_w/M_n, M_n = number-average molecular weight. [c] Degree of polymerization. [d] 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 P**1a2a**-P**1c2d**, *n* values of commercial polymers

Polymer	n^a	v^b	D^c	v'^d	D'^e	Thickness (nm)	Commercial polymer	n^f
P**1a2a**	1.611	55.7	0.0179	214.1	0.0047	45.34	poly(methyl methacrylate)	1.489
P**1a2c**	1.566	35.8	0.0279	137.4	0.0073	51.89	poly(dimethylsiloxane)	1.428
P**1b2a**	1.644	12.5	0.0797	74.6	0.0134	110.87	poly(vinyl chloride)	1.540
P**1b2c**	1.634	15.7	0.0636	56.9	0.0176	62.98	poly(vinyl alcohol)	1.477
P**1c2b**	1.583	32.2	0.0310	141.5	0.0071	99.08	poly(lactic acid)	1.451
P**1c2d**	1.591	30.3	0.0329	179.7	0.0056	50.06	cellulose	1.468

[a] Data of polymers at 632.8 nm. [b] $v = (n_{589.3}-1)/(n_{486.1}-n_{656.3})$. [c] $D = 1/v$. [d] $v' = (n_{1319}-1)/(n_{1060}-n_{1550})$. [e] $D' = 1/v'$. [f] Data of commercial polymers at 632.8 nm taken from refractive index database.

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