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Electronic Supplementary Information

Indium-catalyzed Polycyclotrimerization of Diynes: A Facile Route to Prepare Regioregular Hyperbranced Polyarylenes

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Materials. 4-Iodophenol (**5**), 1,6-dibromohexane (**6**), bisphenol A (**10**) were purchased from Sigma-Aldrich or Alfa and used as received without further purification. Toluene, o-xylene were distilled under nitrogen at normal pressure from sodium benzophenone ketyl immediately prior to use. Triethylamine (Et_3N) was distilled and dried over potassium hydroxide. *N*,*N*-dimethylformamide (DMF) was extra-dry grade.

Instruments. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer as thin films on KBr pellets. ^1H and ^{13}C NMR spectra were measured on a Bruker AV 500, Bruker AV 400 or Varian NMR 300 spectrometer in dichloromethane-d_2 using tetramethylsilane (TMS; δ = 0) as internal reference. Elemental analysis was performed on a ThermoFinnigan Flash EA 1112. Relative molecular weights (M_w and M_n) and polydispersity indices (PDI, M_w/M_n) of the polymers were estimated by a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with refractive index (RI) detector, using a set of monodisperse polystyrenes as calibration standards and THF as the eluent at a flow rate of 1.0 mL/min. Thermal stabilities were evaluated by measuring thermogravimetric analysis (TGA) thermograms on a Perkin-Elmer TGA 7 under dry nitrogen at a heating rate of 10 °C/min

Synthesis procedure of monomer 1a

The synthetic route of model monomer **1a** is shown in Scheme S2. The other monomers were prepared according to previously published procedures. Detailed experimental procedures for the synthesis of **1a** are given below as an example.

*1,6-Bis(4-iodophenoxy)hexane (***7***).* To a solution of 1,6-dibromohexane (2.44 g, 10 mmol) in acetone (60 mL) was added 3.45 g of potassium carbonate (25 mmol). After the mixture was refluxed for 30min, a solution of 4-iodophenol (4.40 g, 20 mmol) in 20 ml of acetone was added dropwise. The resulting suspension was refluxed overnight and then cooled down to room temperature. After filtration and solvent evaporation, the crude product was recrystallization in acetone. A white solid was obtained in 90% yield (4.70g). ^1H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.53 (m, 4H, Ar-*H*), 6.66 (m,4H, Ar-*H*), 3.92 (t, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.41(m, 2H, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (ppm): 158.9, 138.2, 116.9, 82.5, 67.9, 29.1, 25.8.

*1,6-Bis(4-((trimethylsilyl)ethynyl)phenoxy)hexane (**9**).* Into a 250 mL round-bottom flask were added $PdCl_2(PPh_3)_2$ (316 mg, 0.45 mmol), CuI (85 mg, 0.45 mmol), PPh_3 (118 mg, 0.45 mmol), **7** (4.69 g, 9 mmol) in glove box. A mixture of THF/TEA (2:1 v/v) (100 mL) was injected and stirred for 30min. After the catalysts were completely dissolved, the solution was heated to 50 ^{o}C under stirring. Trimethylsilylacetylene (**8**, 3.0 mL, 21 mmol) was injected and the resulting mixture was stirred overnight. Afterward, the mixture was cooled down to room temperature, filtered and washed with DCM. The filtrate was concentrated by a rotary evaporator under reduced pressure and the crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate (50:1 v/v) as eluent. White powder of **9** was obtained in 85% yield (3.167 g). ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.39 (m, 4H, Ar-H), 6.79 (m,4H, Ar-H), 3.94 (t, 2H, CH_2), 1.80 (m, 2H, CH_2), 1.52(m, 2H, CH_2), 0.26 [s, 18H, $Si(CH_3)_3$]. ^{13}C NMR (75 MHz, CD_2Cl_2), δ (ppm): 159.2, 133.4, 115.0, 114.2, 105.2, 92.2, 67.7, 29.0, 25.7, 0.015.

*1,6-Bis(4-ethynylphenoxy)hexane (**1a**).* Into a 250 mL round-bottom flask was added **9** (2.07 g, 5mmol) and THF (40 mL). Then KOH (1.68 g, 30 mmol) dissolved in methanol (40 mL) was added. The mixture was stirred at room temperature overnight. After most of the solvent was evaporated, 1 M HCl solution (40 mL) was added. The aqueous solution was extracted with DCM for three times. The organic phases were combined and washed with water and brine, and then dried over $MgSO_4$ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether/ethyl acetate (100:1 v/v) as eluent. White powder of **1a** was obtained in 85% yield (1.36g). IR (thin film), ν (cm^{-1}): 3275 (≡C-H stretching), 2108 (weak C≡C stretching). ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 7.28 (m, 4H, Ar-H), 6.72 (m,4H, Ar-H), 3.85 (t, 2H, CH_2), 2.92 (s, 2H, ≡CH), 1.69 (m, 2H, CH_2), 1.41(m, 2H, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (ppm): 159.8, 133.5, 114.5, 113.8, 83.6, 75.5, 68.0, 29.1, 25.8. Anal. Calcd for $C_{22}H_{22}O_2$: C, 86.81; H, 6.18. Found: C, 82.63; H, 7.05.

Polymer Synthesis. All the polymerization reactions were carried out under nitrogen atmosphere using a standard Schlenk technique. A typical procedure for the polymerization of **1a** is given below as an example.

Into a 10 mL Schlenk tube was placed **1a** (47.8mg, 0.15 mmol), after evacuated and refilled with nitrogen for three times, Indium chloride tetrahydrate (3.3mg, 0.011mmol) and 2-iodophenol (22.0mg, 0.10mmol) were added in glovebox. PhCl (1.0 mL) was then injected into the tube and stirred for 5min. The solution was then stirred at 130 ºC for 5 h. Afterward, the resulting solution was diluted with THF (5.0 mL) and added dropwise into 200 mL of hexane via a cotton filter under rigidly stirring. The precipitate was allowed to stand overnight and then collected by filtration. The polymer was washed with hexane for several times and dried under vacuum at room temperature to a constant weight.

Characterization Data of PIa. Grey powder; yield: 94.1%. M_w 13200; M_w/M_n 2.47. IR (thin film), ν (cm^{-1}): 2991, 2856, 1677, 1596, 1503, 1459, 1361, 1252, 1175, 1116, 1012, 958, 832, 745, 582. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (TMS, ppm): 7.80, 7.44, 7.20, 6.83, 6.73, 3.91, 3.83, 1.72, 1.43. ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 163.1, 130.5, 129.8, 128.2, 126.8, 122.5, 114.1, 85.5, 79.8, 68.0, 29.1, 25.8.

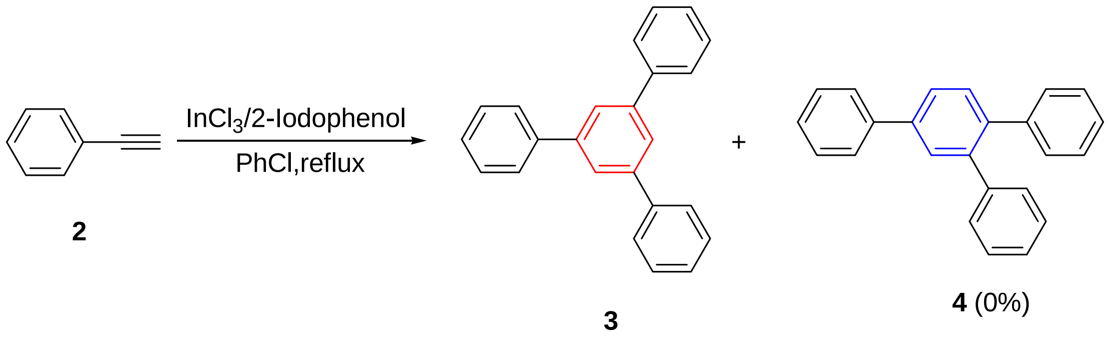
Characterization Data of PIb. The reaction time is 2 h. Brown powder; yield: 82.8%. M_w 12200; M_w/M_n 1.54. IR (thin film), v (cm^{-1}): 2966, 1758, 1637, 1495, 1442, 1405, 1385, 1358, 1238, 1179, 1121, 1095, 1043, 990, 938, 880, 822, 759, 680, 637, 579, 542, 495. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (TMS, ppm): 7.16, 6.88, 6.65, 4.96, 3.63, 1.52. Due to relatively poor solubility in CD_2Cl_2 and DMSO-d_6, we cannot obtain satisfactory ^{13}C NMR spectrum.

Characterization Data of PIc. The reaction time is 2 h. Yellow powder; yield: 87.8%. M_w 10000; M_w/M_n 1.56. IR (thin film), v (cm^{-1}): 3414, 3053, 2870, 1731, 1683, 1595, 1497, 1442, 1399, 1344, 1262, 1105, 1023, 952, 821, 739, 701, 631. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (TMS, ppm): 7.43-7.16, 3.13. ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 131.3, 129.9, 128.5, 127.8, 126.6, 31.5.

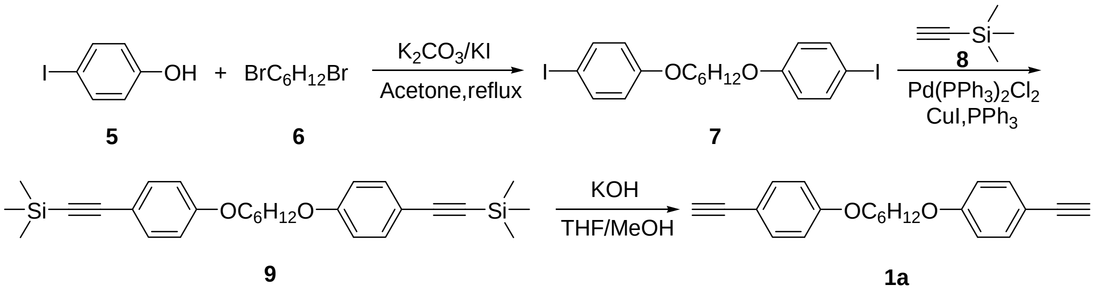
Characterization Data of PId. The reaction time is 1 h. Yellow powder; yield: 50%. M_w 5400; M_w/M_n 1.64. IR (thin film), v (cm^{-1}): 3058, 2923, 2856, 1662, 1583, 1484, 1436, 1389, 1258, 1204, 1120, 1015, 873, 784, 737, 679, 579. ^{1}H NMR (400 MHz,

CD_2Cl_2), δ (TMS, ppm): 7.66, 7.52, 7.33, 7.09, 3.94, 3.41, 1.74, 1.47. ^{13}C NMR (100 MHz, CD_2Cl_2), δ (ppm): 137.6, 129.8, 122.5, 121.6, 80.5, 80.0, 68.3, 28.9, 25.6.

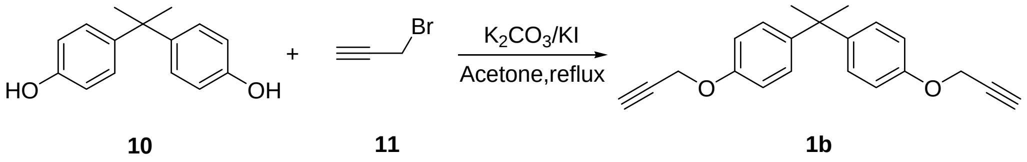
Scheme S1. Indium-catalyzed cyclotrimerization of phenylacetylene.



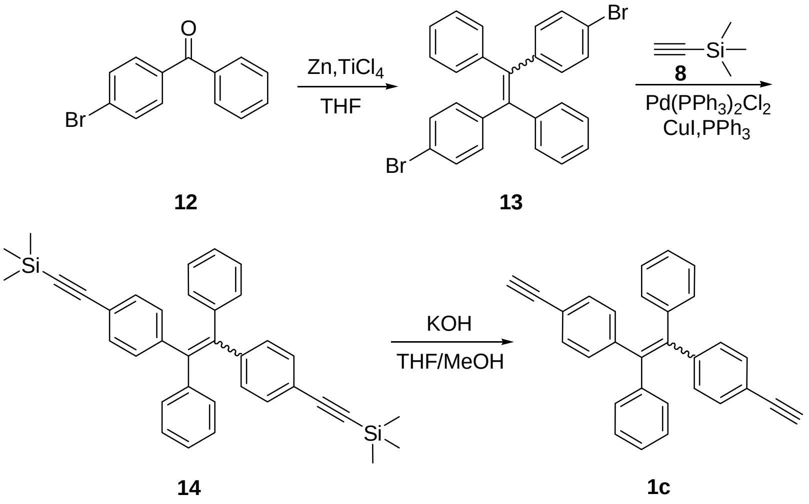
Scheme S2. Synthetic route to monomer **1a**.



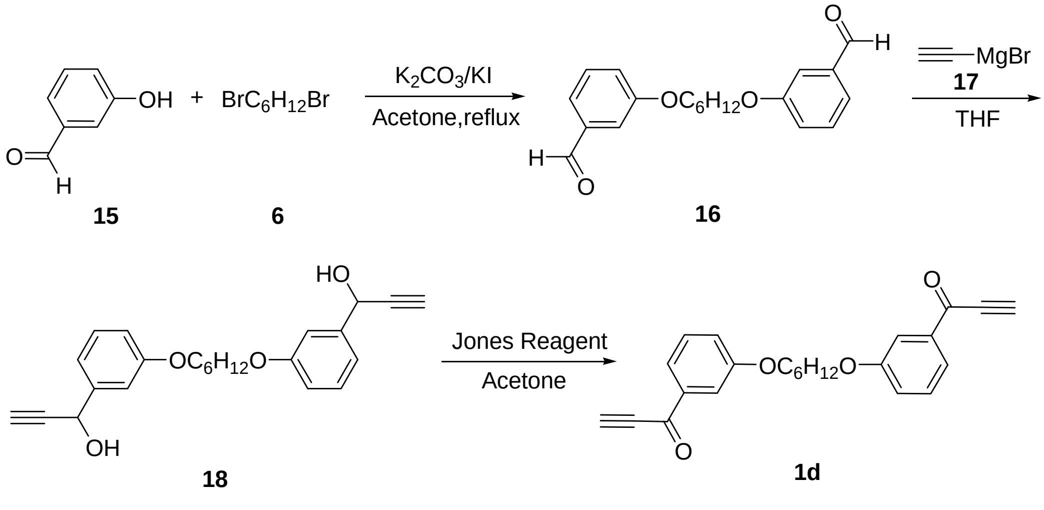
Scheme S3. Synthetic route to monomer **1b**



Scheme S4. Synthetic route to monomer **1c**



Scheme S5. Synthetic route to monomer **1d**



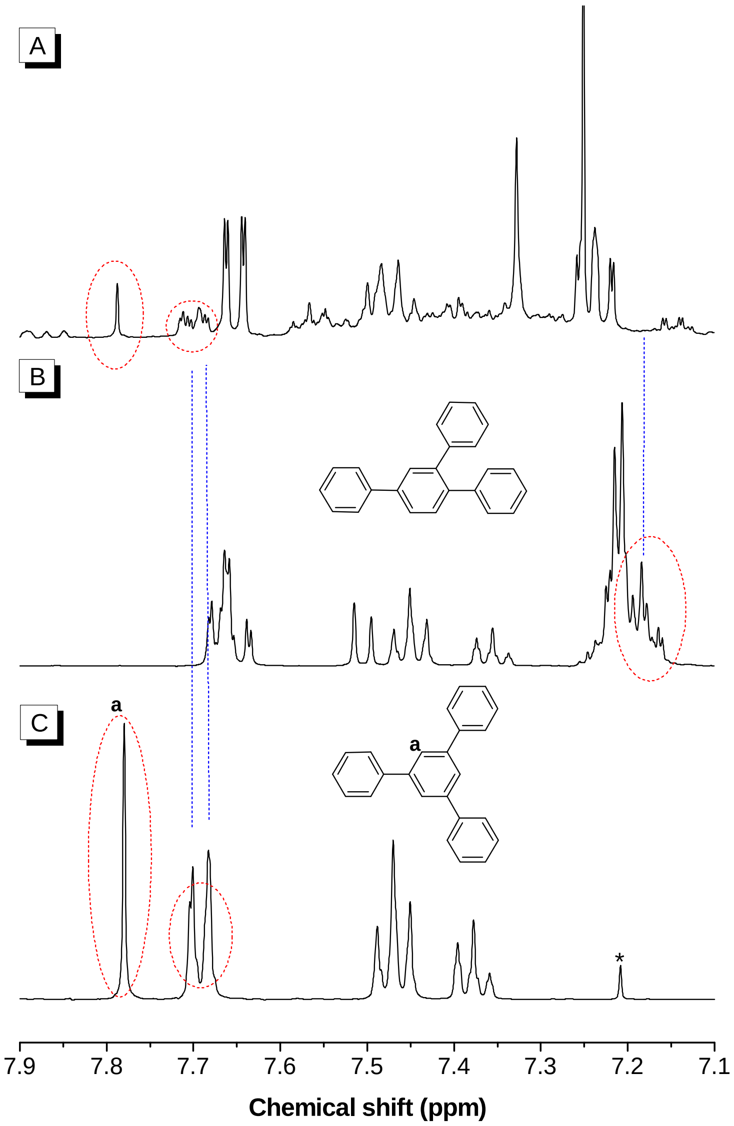


Figure S1. ^{1}H NMR spectra of (A) crude product, (B) 1,2,4-triphenylbenzene and (C) 1,3,4-triphenylbenzene in $CDCl_3$. The solvent peaks are marked with asterisks.

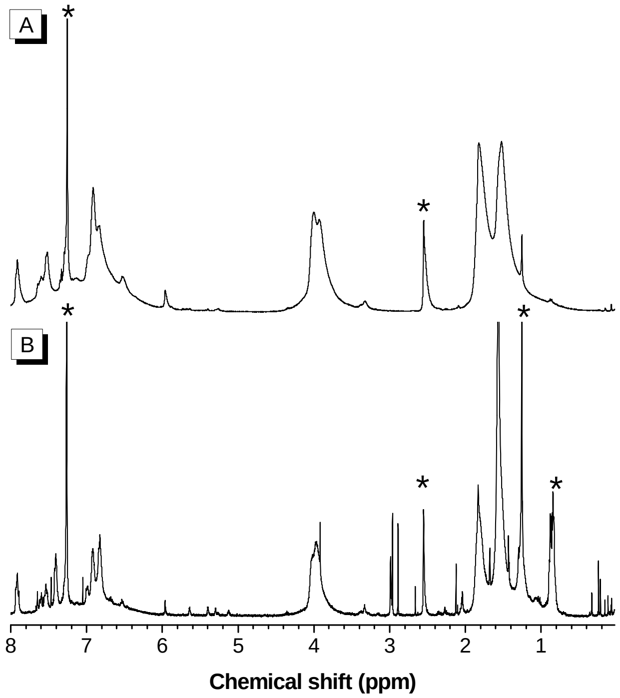


Figure S2. ^{1}H NMR spectra of (A) polymer **1a** catalyzed by Indium chloride tetrahydrate and (B) by Indium chloride in $CDCl_3$. The solvent peaks are marked with asterisks.

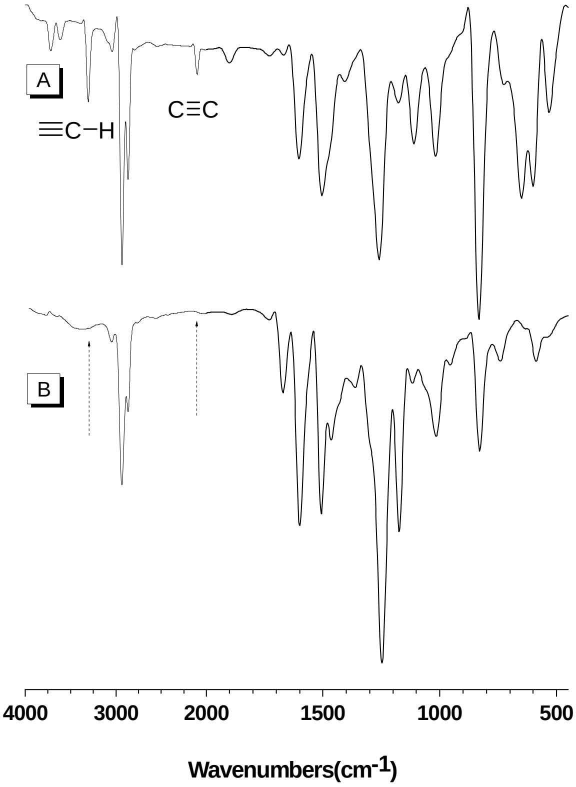


Figure S3. IR spectra of monomers (A) **1a** and (B) polymer P**1a**

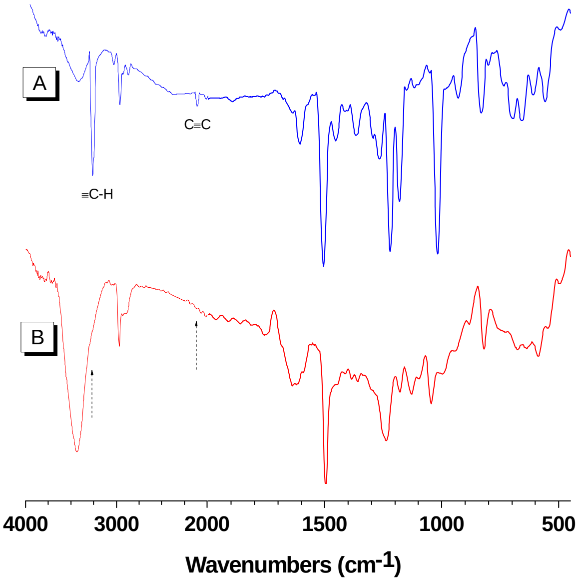


Figure S4. IR spectra of monomers (A) **1b** and (B) polymer P**1b.**

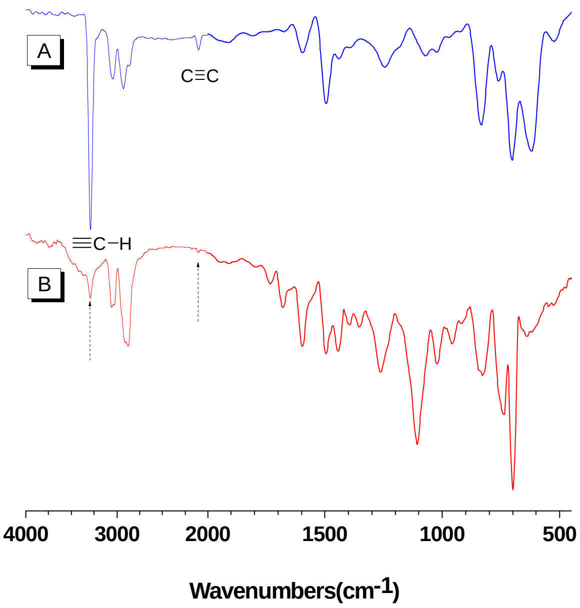


Figure S5. IR spectra of monomers (A) **1c** and (B) polymer P**1c**.

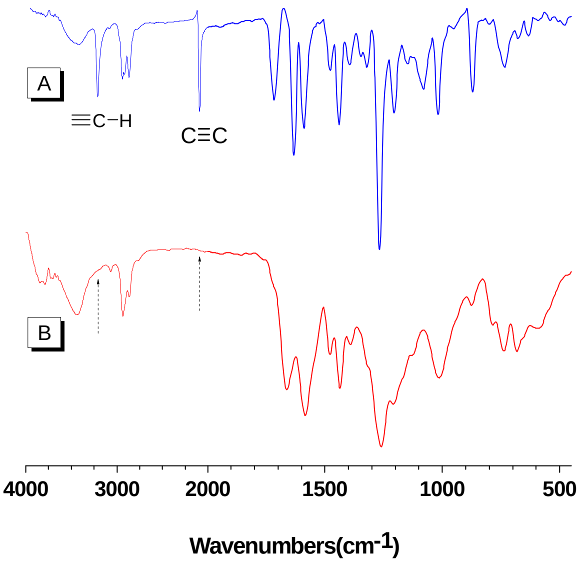


Figure S6. IR spectra of monomers (A) **1d** and (B) polymer P**1d**

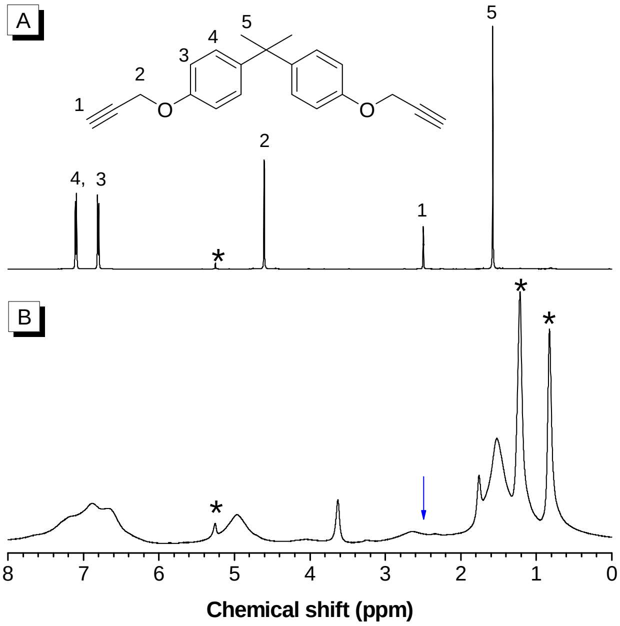


Figure S7 ^{1}H NMR spectra of (A) monomer **1b** and (B) polymer P**1b** in CD_2Cl_2. The solvent peaks are marked with asterisks.

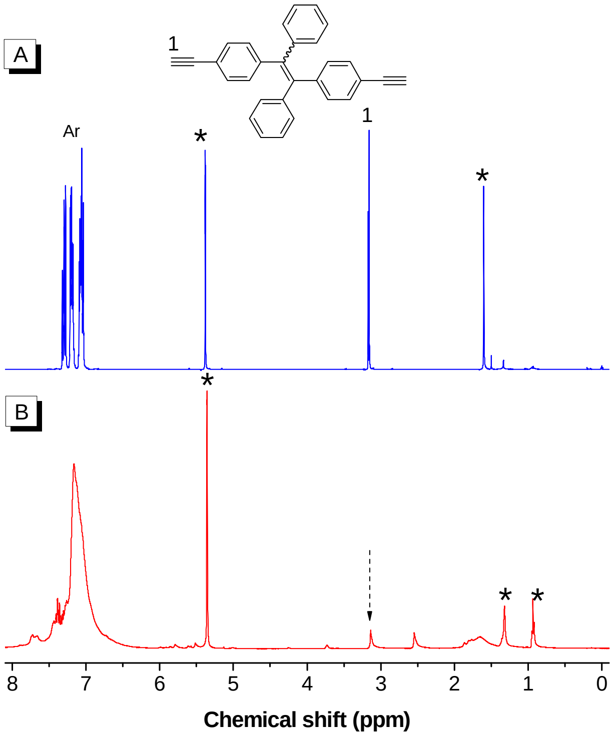


Figure S8. ^{1}H NMR spectra of (A) monomer **1c** and (B) polymer P**1c** in CD_2Cl_2. The solvent peaks are marked with asterisks.

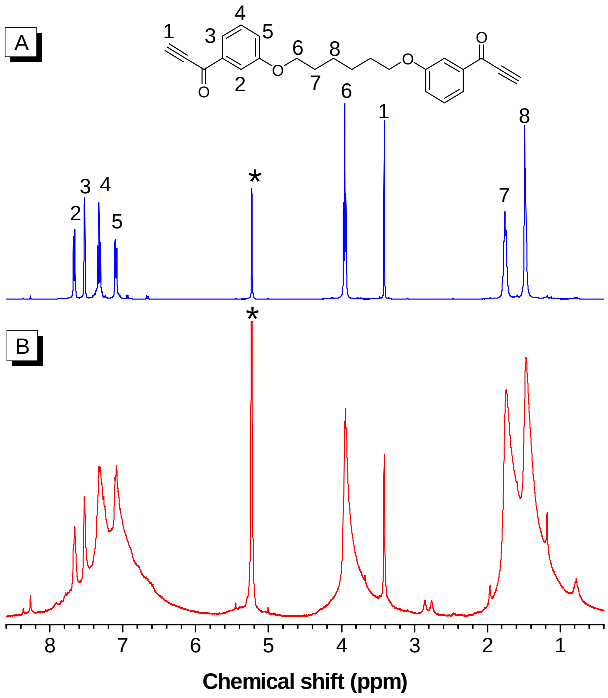


Figure S9. ^{1}H NMR spectra of (A) monomers **1d** and (B) polymer P**1d** in CD_2Cl_2. The solvent peaks are marked with asterisks.

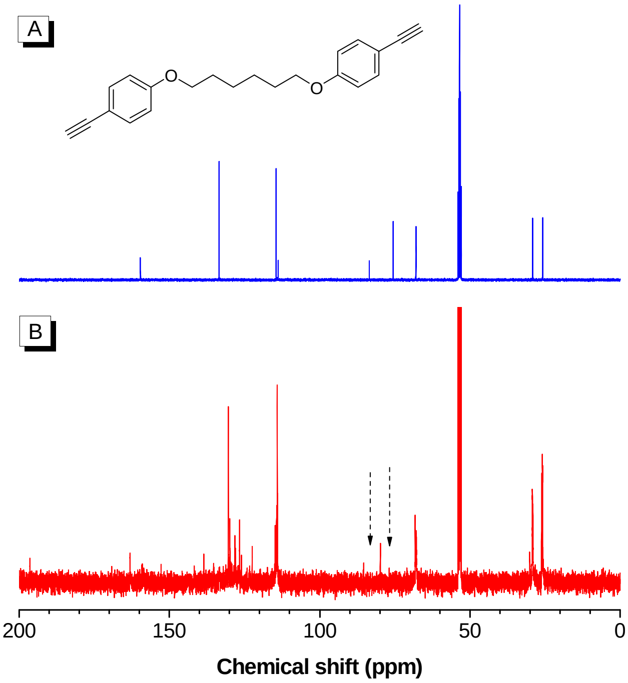


Figure S10. ^{13}C NMR spectra of (A) monomer **1a** and (B) polymer P**1a** in CD_2Cl_2.

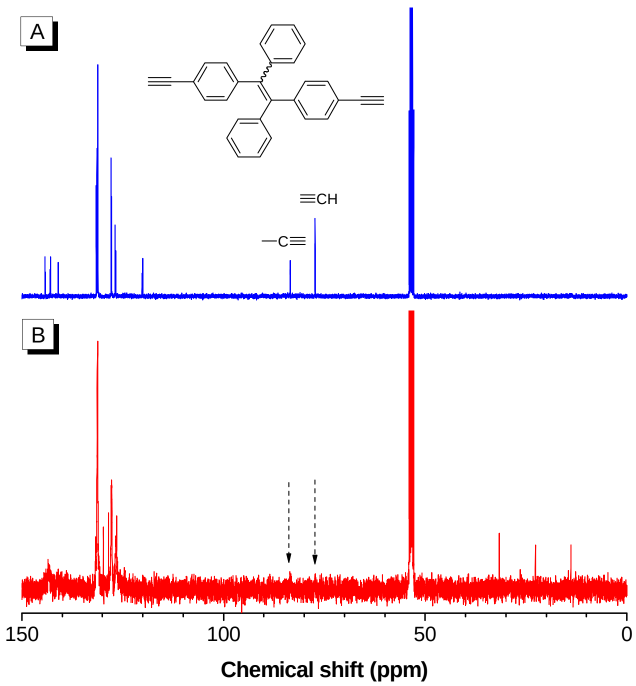


Figure S11. ^{13}C NMR spectra of (A) monomer **1c** and (B) polymer P**1c** in CD_2Cl_2.

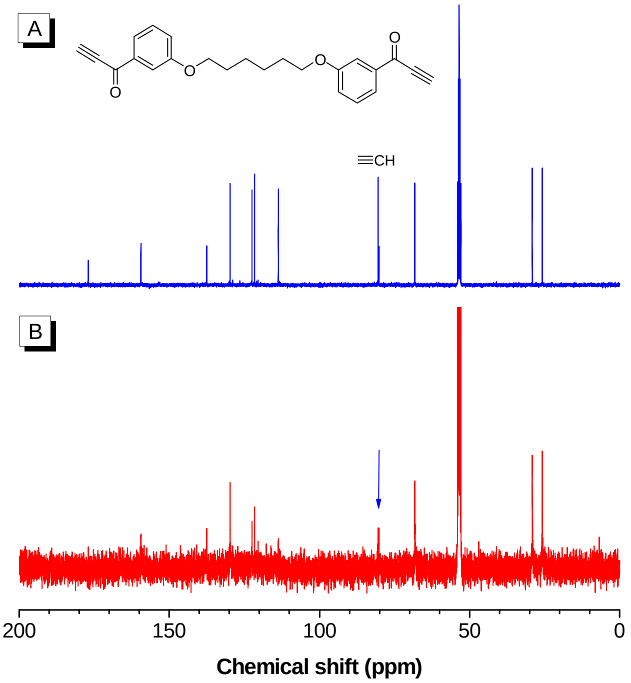


Figure S12. ^{13}C NMR spectra of (A) monomers **1d** and (B) polymer P**1d** in CD_2Cl_2.

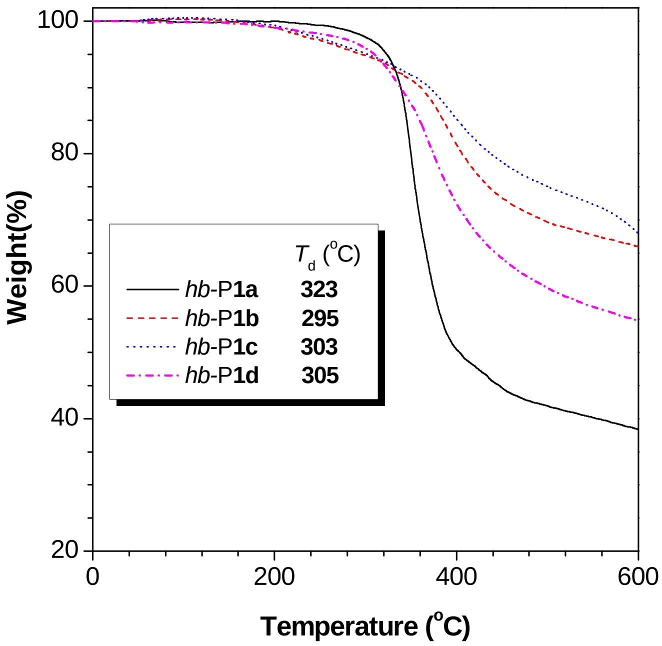


Figure S13. TGA thermograms of P**1a**-P**1d** under nitrogen at a heating rate of 10°C/min

Table S1. Time Effect on Polycyclomerizations of Diyne 1a[a]

entry	*t* (h)	yield (%)	M_w[b]	PDI[b]
1	1	20.0	6700	2.20
2	3	76.8	11500	2.78
3	4	85.6	12200	4.21
4	5	94.1	13200	2.47
5	6	91.1	11800	2.06
6	7	86.9	12100	2.73

[a] Carried out in chlorobenzene under nitrogen at 130 °C for 5h. [**1a**]= 0.15 M; [In] = 0.011 M; [2-iodophenol] = 0.10 M. [b] Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; PDI = polydispersity index.

Table S2. Solvent Effect on Polycyclotrimerizations of Diyne 1a[a]

entry	solvent	yield (%)	M_w[b]	PDI[b]
1	PhCl	94.0	14600	2.37
2	toluene[d]	trace		
3	*o*-DCB	83.5	10000	2.67
4	*o*-xylene	40.0	8700[c]	1.98
5	DMF	trace		

[a] Carried out in chlorobenzene under nitrogen at 130 °C for 5h. [**1a**] = 0.15 M; [In] = 0.011 M; [2-iodophenol] = 0.10 M. Abbreviation: PhCl = chlorobenzene; *o*-DCB = 1,2-dichlorobenzene. [b] Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration. [c] Soluble part. [d] Reacted at 110 °C.

Table S3. Temperature Effect on Polycyclotrimerizations of Diyne 1a[a]

entry	T (°C)	yield (%)	M_w[b]	PDI[b]
1	110	64.0	9400	2.47
2	120	85.0	12000	2.65
3	130	94.1	13100	2.94

[a] Carried out in chlorobenzene under nitrogen for 5h. [**1a**] = 0.15 M; [In] = 0.011 M; [2-iodophenol] = 0.10 M. [b] Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration.

Table S4. Effect of Monomer Concentration on Polycyclotrimerization of 1a[a]

entry	[**1a**] (M)	yield (%)	M_w[b]	PDI[b]
1	0.10	62.3	7000	2.04
2	0.12	84.9	10600	2.90
3	0.15	94.1	13200	2.91
4	0.18	90.0	12800	3.12

[a] Carried out in chlorobenzene under nitrogen at 130 °C for 5h. [In] = 0.011 M; [2-iodophenol] = 0.10 M. [b] Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration.

Table S5. Effect of Catalyst Concentrations on Polycyclotrimerizations of 1a[a]

entry	[In] (M)	yield (%)	M_w[b]	PDI[b]
1	0.004	77.6	10700	3.08
2	0.008	82.9	11700	2.73
3	0.011	94.1	12300	2.68
4	0.015	91.0	12800	3.12

[a] Carried out in chlorobenzene under nitrogen at 130 °C for 5h. [**1a**] = 0.15 M; [2-iodophenol] = 0.10 M. [b] Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration.

Table S6. Effect of Additive Concentrations on Polycyclotrimerizations of 1a[a]

entry	[additive] (M)	yield (%)	M_w[b]	PDI[b]
1	0.05	67.4	10000	3.41
2	0.08	71.6	12300	2.87
3	0.10	94.1	12600	2.68
4	0.13	100.0	12700[c]	3.07

[a] Carried out in chlorobenzene under nitrogen at 130 °C for 5h. [**1a**] = 0.15M; [In] = 0.011 M. [b] Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration.

Table S7. $InCl_3$ catalyzed polycyclotrimerization of 1a with or without additives

additive	M_w	M_w/M_n
2-iodophenol	17200	3.36
iodobenzene	6130	1.53
phenol	1440	1.15
none	6800	1.78

[a] Carried out in chlorobenzene under nitrogen at 130 °C for 5h. [**1a**] = 0.15M; [In] = 0.011 M. [b] Estimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration.