Electronic Supporting Information (ESI)

Benzyne-Azide Polycycloaddition: A Facile Route toward Functional Polybenzotriazoles

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Materials and Instruments

Cesium fluoride was purchased from TCI and dried in vacuum at 130 ℃ for 1 h and then stored in a glovebox. The rest of chemicals were purchased from the Energy Chemical, Bide Pharmatech Ltd., J&K, Meryer, Aladdin, and TCI, and used as received. All the solvents were purified by standard techniques.

The weight-average molecular weights (M_w) and polydispersities (M_w/M_n) were measured by a Waters Advanced Polymer Chromatography (APC) system equipped with photo-diode array (PDA) detector. A set of monodispersed polystyrene covering the molecular weight range from 10^3 to 10^7 g/mol were utilized as standards and THF was used as the eluent in a flow rate of 0.5 mL/min. The polymers were dissolved in tetrahydrofuran (THF) (~1 mg/mL) and filtered through 0.22 μm PTFE syringe-type filters before testing. Using deuterated chloroform ($CDCl_3$), deuterated dichloromethane (CD_2Cl_2) or deuterateddimethyl sulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS, $\delta = 0$ ppm) as internal reference, ^{1}H and ^{13}C NMR spectra were collected on Bruker Avance 500 MHz NMR spectrometer or Brucker Advance 400 MHz NMR spectrometer. Fourier transform infrared (FT-IR) spectra were measured on a Bruker Vector 33 FT-IR spectrometer (KBr disk). High resolution mass spectrometry (HRMS) measurements were performed on a Bruker maxis impact mass spectrometer. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449 F3 at a heating rate of 20 ^{o}C/min in a nitrogen flow. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer with bandwidth of 1 nm, medium scanning rate, and quartz cuvettes of 1 cm path length.

Photoluminescence (PL) spectra were measured on a Horiba Fluoromax-4 spectrofluorometer. The melting point was obtained using a WRS-1B melting point apparatus. Refractive indices (*n*) of the polymer films on silicon wafers were measured on a J. A. Woolam V-VASE spectroscopic ellipsometer in a wavelength region of 400-1700 nm.

Monomer Preparation

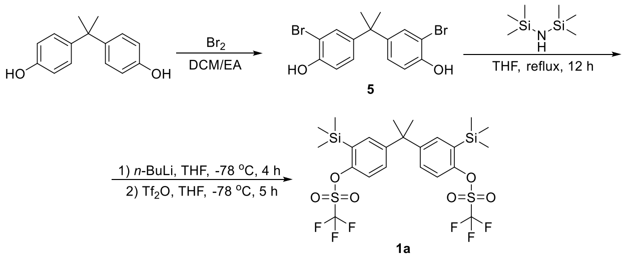
Synthesis of benzyne precursors

The synthesis of benzyne precursors were according to a modified literature procedures.[1] The synthetic routes of **1a**, **1b** and **1c** are show in Schemes S1, S2 and S3, respectively.

Synthesis of propane-2,2-diylbis(2-(trimethylsilyl)-4,1-phenylene) bis(trifluoromethanesulfonate) (1a)

To a stirred solution of bisphenol A (6.85 g, 30.0 mmol) in a dichloromethane (DCM)/ethyl acetate (EA) (100 mL) mixture (1:1 v/v) was added a solution of bromine (3.0 mL, 60.0 mmol) in DCM (40 mL) dropwise at room temperature and the reaction mixture was stirred for 6 h. This mixture was poured into saturated sodium sulfite aqueous solution and the mixture was extracted with DCM, washed with water, dried over anhydrous $MgSO_4$, filtered and evaporated in vacuum. Then the crude product was purified by a silica gel column using petroleum ether (PE)/DCM (2:1 v/v, R_f = 0.2) mixture as eluent. Colorless oil **5** was obtained in 72% yield (8.31 g). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.31 (d, *J* = 2.3 Hz, 2H), 7.02 (dd, *J* = 8.5, 2.3 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.49 (s, 2H), 1.59 (s, 6H).

To a solution of **5** (3.86 g, 10.0 mmol) in THF (35 mL) was added hexamethyldisilazane (HMDS) (6.96 g, 40.0 mmol) under nitrogen. The reaction mixture was refluxed for 12 h. After cooling to room temperature, the solvent was removed in vacuum. The residue was dissolved in THF (40 mL) under nitrogen and cooled to –78 ℃. To the solution was added *n*-butyllithium (10.0 mL, 24.0 mmol, 2.4 M solution in hexane) dropwise. After stirring at –78 ℃ for 4 h, Tf$_2$O (4.0 mL, 24.0 mmol) was added to reaction mixture dropwise at –78 ℃. After stirring at –78 ℃ for 5 h, the reaction mixture was quenched with saturated NaHCO$_3$ aqueous solution at –78 ℃ and this mixture was warmed to room temperature. The layers were separated, and then the aqueous layer was extracted with PE three times. The combined organic layers were dried over anhydrous MgSO$_4$. The solvent was removed in vacuum, and the residue was purified by a silica gel column with PE (R$_f$ = 0.2) as eluent. **1a** as a white solid was obtained in 45.0% yield (2.87 g). m.p.: 47.3-47.9 ^{o}C. FT-IR (KBr disk), ν (cm^{-1}): 2980, 1589, 1470, 1414, 1251, 1210, 1134, 1047, 911, 840, 754, 698, 613, 569, 517, 442, 424. ^{1}H NMR (500 MHz, CDCl$_3$), δ (TMS, ppm): 7.33-7.30 (m, 2H), 7.25-7.23 (m, 4H), 1.70 (s, 6H), 0.31 (s, 18H). ^{13}C NMR (125 MHz, CDCl$_3$), *δ* (TMS, ppm): 153.19, 148.89, 134.18, 132.05, 129.77, 119.21, 118.64 (q,), 42.75, 30.74, -0.86. HRMS: *m/z* 636.0948 (calcd 636.0927).



Scheme S1. Synthetic routes to **1a**.

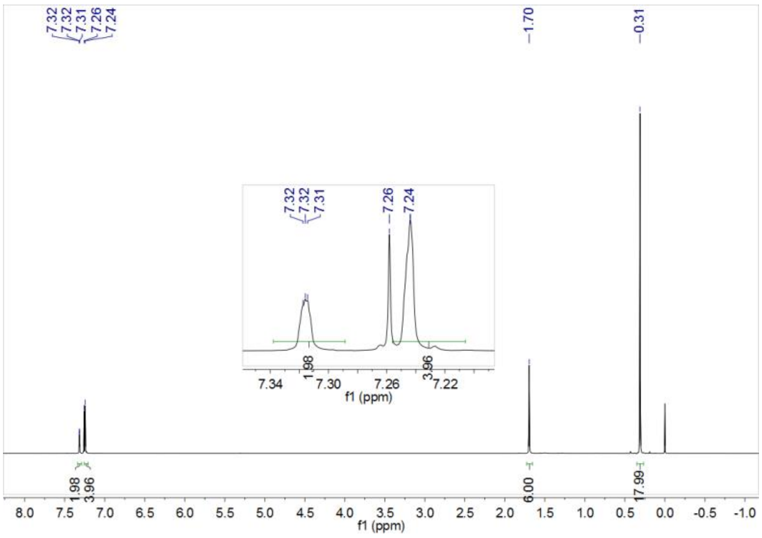


Figure S1. ^{1}H NMR spectrum of **1a** in $CDCl_3$.

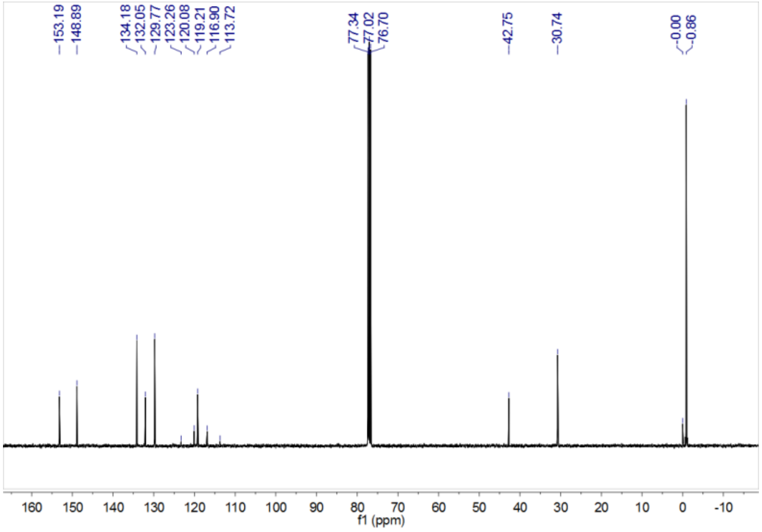


Figure S2. ^{13}C NMR spectrum of **1a** in $CDCl_3$.

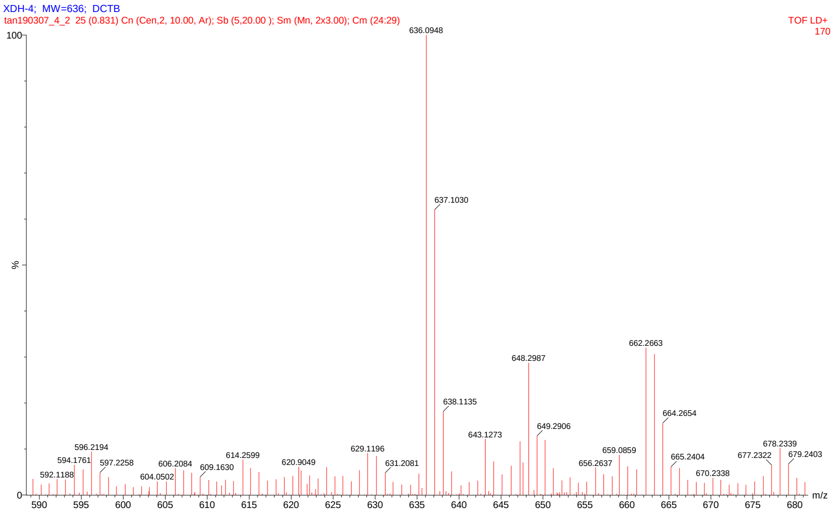
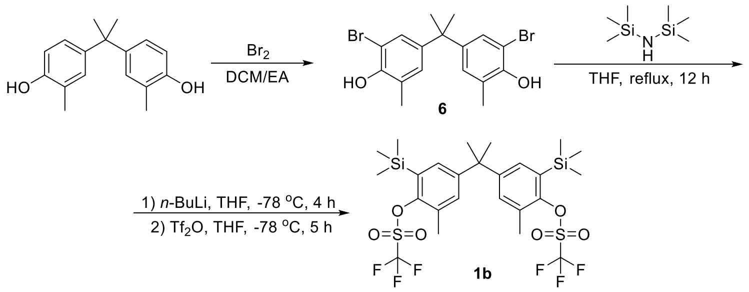


Figure S3. HRMS spectrum of **1a**.

Synthesis of propane-2,2-diylbis(2-methyl-6-(trimethylsilyl)-4,1-phenylene) bis(trifluoromethanesulfonate) (1b)

The synthesis of **6** was similar to the above procedures. Bisphenol A was replaced with bisphenol C. The crude product was purified by a silica gel column using PE/DCM (3:1 v/v, R_f = 0.2) mixture as eluent. White solid **6** was obtained in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.14 (s, 2H), 6.86 (s, 2H), 5.43 (s, 2H), 2.24 (s, 6H), 1.57 (s, 6H).

Synthesis of **1b** was similar to the step of **1a**. The crude product was purified by a silica gel column using PE (R_f = 0.15) as eluent. White solid of **1b** was obtained in 50% yield. m.p.: 109.2-110.9 ^{o}C. FT-IR (KBr disk), ν (cm^{-1}): 2971, 1584, 1474, 1399, 1257, 1216, 1143, 1063, 881, 845, 760, 703, 662, 618, 513, 434. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.13 (m, 4H), 2.35 (s, 6H), 1.67 (s, 6H), 0.30 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 149.27, 149.21, 134.12, 132.93, 132.00, 130.80, 118.63, 42.50, 30.69, 17.51, 0.03.



Scheme S2. Synthetic routes to **1b**.

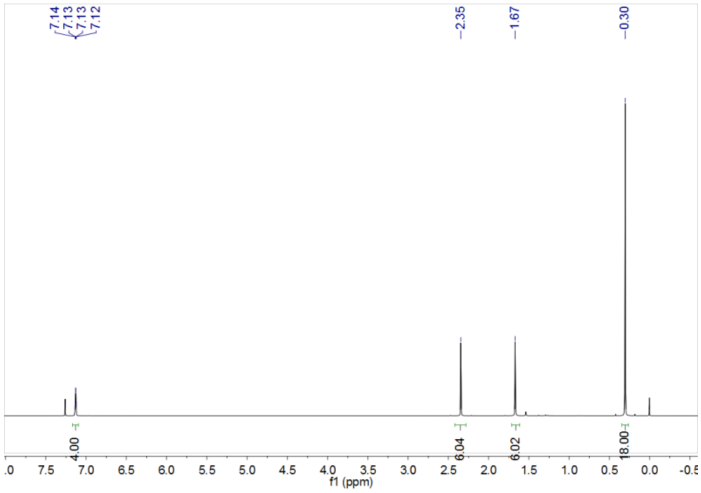


Figure S4. ^{1}H NMR spectrum of **1b** in CDCl$_3$.

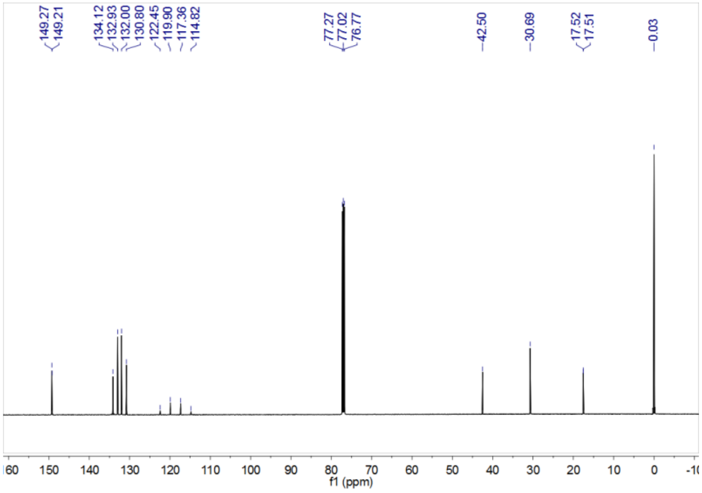


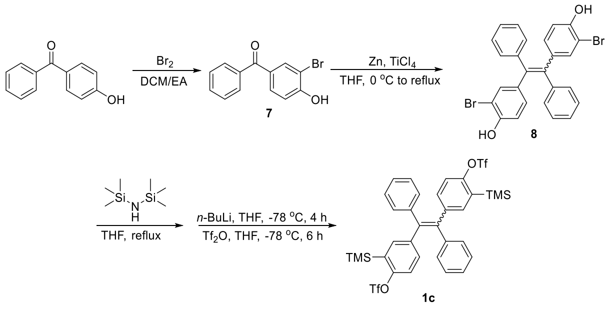
Figure S5. ^{13}C NMR spectrum of **1b** in CDCl$_3$.

Synthesis of (1,2-diphenylethene-1,2-diyl)bis(2-(trimethylsilyl)-4,1-phenylene) bis(trifluoromethanesulfonate) (1c)

To a stirred solution of (4-hydroxyphenyl)(phenyl)methanone (7.93 g, 40.0 mmol) in a DCM/EA (100 mL) mixture (1:1 v/v) was added a solution of bromine (2.0 mL, 40.0 mmol) in DCM (40 mL) dropwise at room temperature and the reaction mixture was stirred for 6 h. This mixture was poured into saturated sodium sulfite aqueous solution and the mixture was extracted with DCM, washed with water, dried over anhydrous MgSO$_4$, filtered and evaporated in vacuum. Then the crude product was washed three times with EA. White powder **7** was obtained in 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 8.03 (d, J = 2.0 Hz, 1H), 7.77-7.70 (m, 3H), 7.62-7.57 (m, 1H), 7.52-7.47 (m, 2H), 7.10 (dd, J = 8.49 Hz, 1H), 6.06 (s, 1H).

Into a 250 mL two-necked round bottom flask equipped with a condenser was placed **7** (5.54g, 20.0 mmol), zinc powder (3.92 g, 60.0 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times and then 100 mL THF was added. The mixture was cooled to 0 ℃ and $TiCl_4$ (3.30 mL, 30.0 mmol) was injected dropwise. The mixture was slowly heated to reflux and then stirred for 12 h. The mixture was quenched with 10 % aqueous Na_2CO_3 solution and filtered. The filtrate was extracted with EA three times. The organic layer was washed with water and dried over anhydrous $MgSO_4$. After solvent evaporation, the crude product was purified by a silica gel column using PE/EA (3:1 v/v, R_f = 0.2) mixture as eluent. White powder **8** was obtained in 48% yield. ^{1}H NMR (500 MHz, DMSO-d_6), δ (TMS, ppm): 10.18 (s, 2H), 7.23-7.12 (m, 6H), 7.02-6.99 (m, 4H), 6.95 (d, J = 2.0 Hz, 2H), 6.71 (dd, J = 8.4, 2.0 Hz, 2H), 6.67 (d, J = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 150.73, 142.93, 139.29, 137.44, 134.44, 132.24, 131.19, 128.01, 127.80, 126.87, 115.15, 109.55.

Synthesis of **1c** was similar to the precedures of **1a**. The crude product was purified by a silica gel column using PE/DCM (20:1 v/v, R_f = 0.15) mixture as eluent. White solid was obtained in 50% yield. m.p.: 112.3-117.2 ^{o}C. FT-IR (KBr disk), v (cm^{-1}): 2960, 1597, 1584, 1465, 1422, 1252, 1211, 1143, 1052, 911, 887, 842, 755, 701, 611, 512. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.18-7.10 (m, 10H), 7.02 (m, 6H), 0.13 (d, 18H). ^{13}C NMR (125 MHz, CDCl$_3$), δ (TMS, ppm): 153.43, 153.35, 142.64, 142.55, 142.47, 142.13, 140.56, 140.52, 139.58, 139.49, 133.77, 133.66, 131.89, 131.26, 131.24, 131.20, 128.23, 127.94, 127.17, 127.11, 119.08, 118.83, 118.44(q, J = 320.3 Hz), -1.09, -1.11. HRMS: m/z 772.1214 (calcd 772.1240).



Scheme S3. Synthetic routes to **1c**.

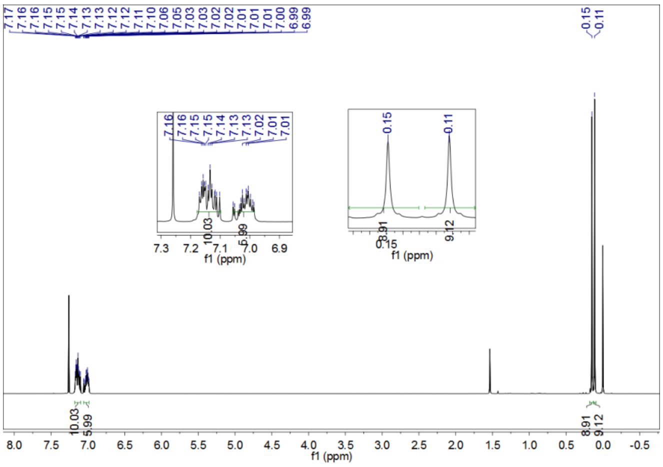


Figure S6. ^{1}H NMR spectrum of **1c** in CDCl$_3$.

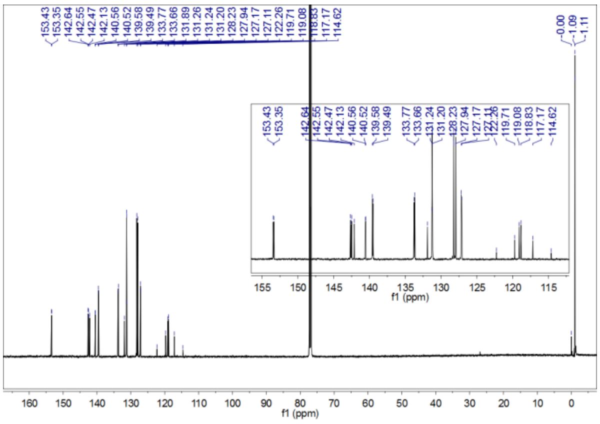


Figure S7. ^{13}C NMR spectrum of **1c** in CDCl$_3$.

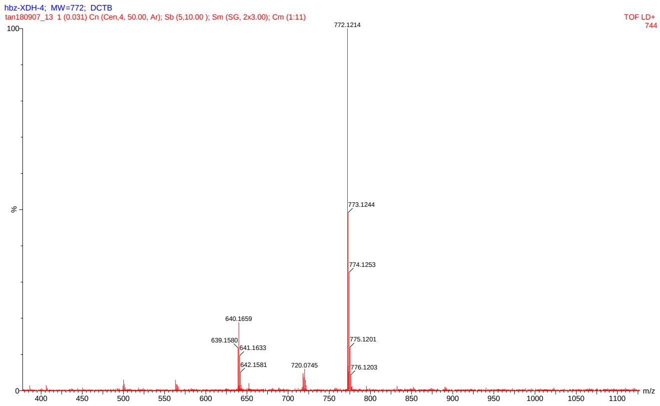


Figure S8. HRMS spectrum of **1c**.

Table S1. Crystal Data and Structure Refinement for Compound **1c**

Empirical formula	$C_{34}H_{34}F_6O_6$ S_2 Si_2	
Formula weight	772.91g mol^{-1}	
Temperature	149.99(10)	
Wavelength	1.54184 Å	
Crystal system,space group	monoclinic, P 1 21/c 1	
	a = 18.6890(2) Å	α = 90
Unit cell dimensions	b = 9.29070(10) Å	β = 93.7450(10)
	c = 20.9995(2) Å	γ = 90
Volume	3638.44(7) Å^3	
Z	4	
Density (calculated)	1.411g cm^{-3}	
Absorption coefficient	2.613 mm^{-1}	
F(000)	1600	
Crystal size	0.08 × 0.07 × 0.06 mm^3	
Theta range for data collection	2.369°to 67.080°	
Index ranges	-13<=h<=22, -10<= k <= 11, -25<= l <=24	
Reflections collected	17802	
Independent reflections	6479[R(int) =0.0230]	
Completeness to theta = 67.04°	99.90%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.95979	
Refinement method	Full-matrix least-squares on F^2	
Data /restraints /parameters	6479/ 0 / 451	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.0967	
R indices (all data)	R1= 0.0645, wR2 = 0.0990	
Largest diff. peak and hole	0.908 and -0.353e.Å^{-3}	

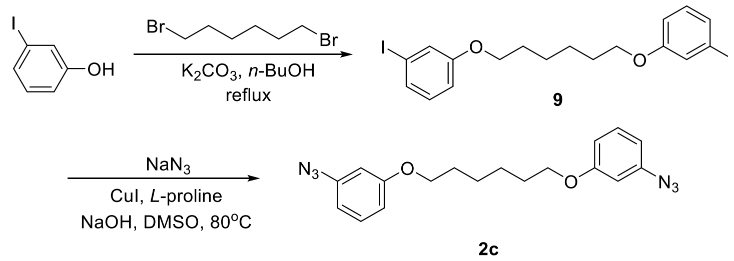
Synthesis of Azide Monomers.

2c was synthesized according to the routes shown in Scheme S4.

Synthesis of 1,6-bis(3-azidophenoxy)hexane (2c)

Into a 250 mL round-bottom flask were added 3-iodophenol (6.60 g, 30.0 mmol), K_2CO_3 (11.0 g, 80.0 mmol), and *n*-BuOH (120 mL). 1,6-Dibromohexane (2.44 g, 10 mmol) was added dropwise under nitrogen by reflux. The mixture was stirred for 24 h. After cooling to room temperature and the solvent was evaporated, the residue was dissolved with DCM and washed with water for three times and dried over anhydrous $MgSO_4$. After filtration and removal of solvent in vacuum, the residue was purified by a silica gel column using PE/DCM (10:1 v/v) as eluent. White solid **9** was obtained in 65% yield (3.41 g).

Then **9** (2.61 g, 5.0 mmol), CuI (190 mg, 1.0 mmol), *L*-proline (230 mg, 2.0 mmol), NaN_3 (1.3 g, 20.0 mmol), and NaOH (80 mg, 2.0 mmol) in dry DMSO (20 mL) were stirred at 80 ^{o}C for 24 h under nitrogen. Afterward, the mixture was cooled to room temperature, diluted with 100 mL DCM and washed with water. The organic phase was dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column using PE/DCM (10:1 v/v) as eluent. A white powder **2c** was obtained in 47% yield (0.827 g). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.24 (t, 2H), 6.68 (m, 2H), 6.63 (m, 2H), 6.55 (t, 2H), 3.96 (t, 4H), 1.85-1.78 (m, 4H), 1.56-1.52 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 160.29, 141.21, 130.41, 111.18, 111.17, 105.46, 67.93, 29.11, 25.82.



Scheme S4. Synthetic routes to **2c**.

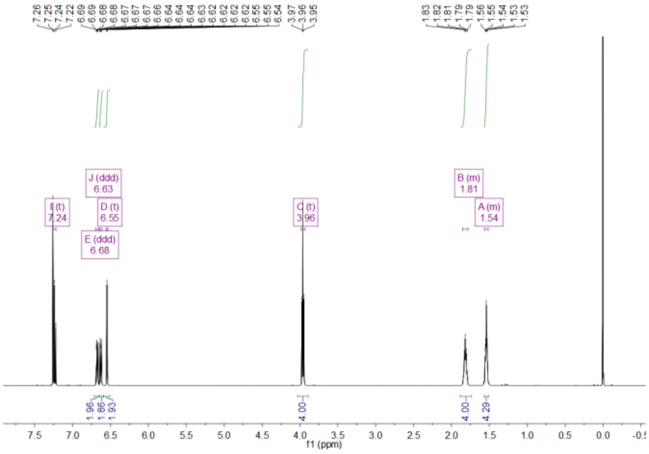


Figure S9. ^{1}H NMR spectrum of **2c** in $CDCl_3$.

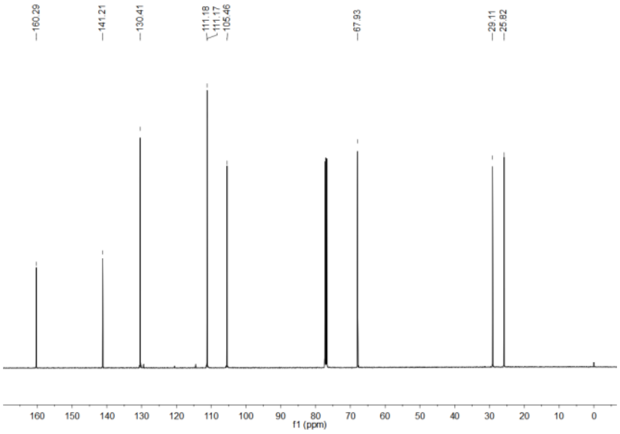


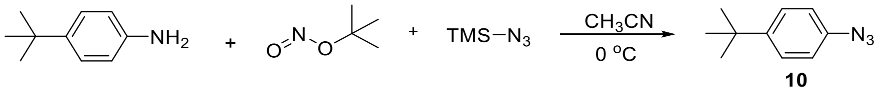
Figure S10. ^{13}C NMR spectrum of **2c** in $CDCl_3$.

Synthesis of model compound 4

The synthetic routes of 1-azido-4-(*tert*-butyl)benzene was illustrated in Scheme S5.

Into a 100 mL round-bottom flask equipped with a stir bar were added 4-*tert*-butylaniline (2.99g, 20.0 mmol) and acetonitrile (CH_3CN) (50 mL). After stirring at 0 °C for 0.5 h, *tert*-butyl nitrite (3.09g, 30.0 mmol) and azidotrimethylsilane

(3.45 g, 30.0 mmol) were added dropwise into the reaction system by syringe. 12 h later, the reaction mixture was concentrated by a rotary evaporator. The crude product was purified by a silica gel column using petroleum ether as eluent. A yellow oil **10** was obtained in 90% yield (3.15 g). ^{1}H NMR (500 MHz, $CDCl_3$), *δ* (TMS, ppm): 7.38-7.34 (m, 2H), 6.98-6.94 (m, 2H), 1.31 (s, 9H).



Scheme S5. Synthetic route to 1-azido-4-(tert-butyl)benzene **10**.

Into a 25 mL Schlenk tube equipped with a stir bar were added **1b** (332 mg, 0.5 mmol) and CsF (303 mg, 2.0 mmol). After evacuated and refilled with nitrogen for three times, **10** (262.8 mg, 1.5 mmol), CH_3CN (2.5 mL) and THF (2.5 mL) was added into the reaction system by syringes. The resulting mixture was stirred at 75 ^{o}C under a nitrogen atmosphere. After reacting for 5 h, the system was cooled to room temperature, quenched with water, diluted with DCM (20 mL), and extracted with 50 mL of saturated brines for 3 times. The organic layer was collected and the solvent was removed by a rotary evaporator. The crude product was purified by a silica gel column using PE/EA (8:1 v/v, R_f = 0.19, 0.20, 0.21) mixture as eluent. The white isomeric products 4**a**, 4**b**, and 4**c** were obtained.

Compound **4a**. ^{1}H NMR (500 MHz, CD_2Cl_2), δ (TMS, ppm): 7.63-7.59 (m, 4H), 7.58-7.54 (m, 4H), 7.51 (d, *J* = 0.7 Hz, 2H), 6.79 (s, 2H), 2.57 (s, 6H), 1.70 (s, 6H), 1.31 (s, 18H). ^{13}C NMR (125 MHz, CD_2Cl_2), δ (TMS, ppm): 152.28, 151.30, 145.36, 135.15, 132.90, 130.66, 127.22, 125.45, 122.94, 104.73, 44.42, 35.15, 31.46, 31.04, 16.96. HRMS: *m/z* 571.3557 ($M+H^+$, calcd 571.3544).

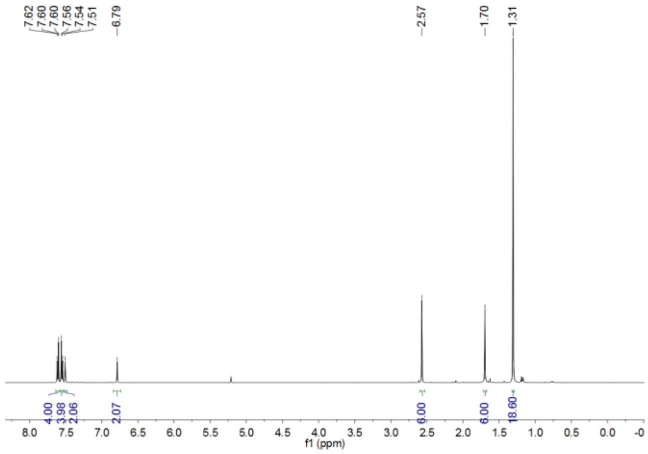


Figure S11. ^{1}H NMR spectrum of **4a** in CDCl$_3$.

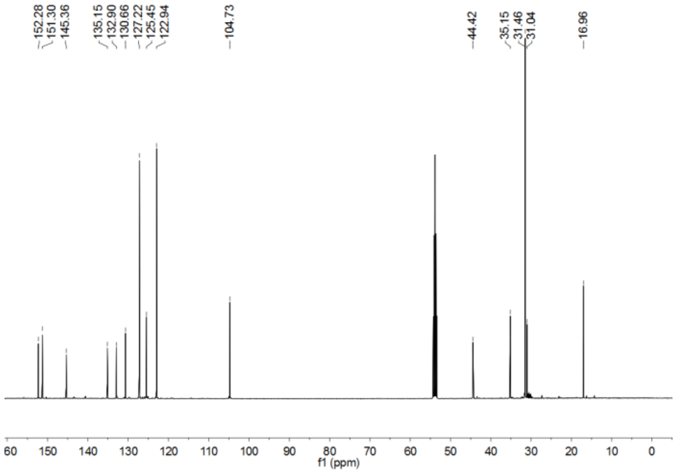


Figure S12. ^{13}C NMR spectrum of **4a** in CDCl$_3$.

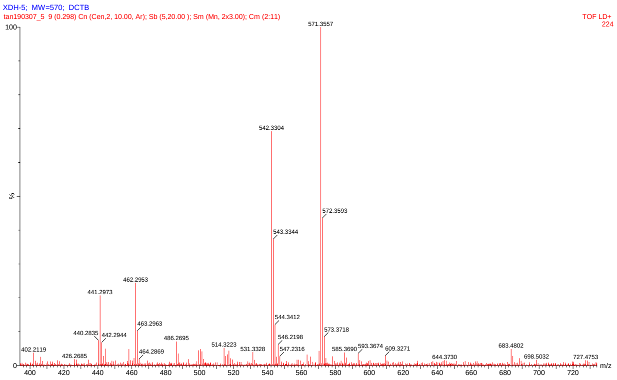


Figure S13. HRMS spectrum of **4a**.

Compound **4b**. FT-IR (KBr disk), *v* (cm^{-1}): 2962, 1595, 1518, 1462, 1364, 1242, 1206, 1111, 1045, 845, 564. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$), δ (TMS, ppm): 7.89 (d, *J* = 0.8 Hz, 1H), 7.63-7.59 (m, 2H), 7.58-7.53 (m, 2H), 7.49-7.45 (m, 2H), 7.34-7.30 (m, 2H), 6.88 (s, 1H), 6.84 (s, 1H), 2.60 (s, 3H), 1.96 (s, 3H), 1.74 (s, 6H), 1.31 (s, 9H), 1.29 (s, 9H). ^{1}H NMR (500 MHz, $CDCl_3$) δ (TMS, ppm): 8.03 (s, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.60-7.52 (m, 3H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.92 (s, 1H), 6.85 (s, 1H), 2.06 (s, 3H), 1.82 (s, 6H), 1.41 (s, 9H), 1.39 (s, 9H).^{13}CNMR (125 MHz, $CDCl_3$) δ (TMS, ppm):153.37, 151.96, 151.12, 146.79, 146.54, 145.13, 135.00, 134.87, 132.63, 131.90, 130.56, 130.04, 126.94, 126.86, 126.08, 125.29, 122.79, 121.29, 113.89, 104.40, 43.64, 35.07, 35.01, 31.47, 31.04, 18.85, 17.12.^{13}C NMR (125 MHz, CD_2Cl_2), *δ* (TMS, ppm):153.66, 152.21, 151.50, 147.08, 146.77, 145.36, 135.39, 135.19, 132.90, 132.18, 130.58, 130.21, 127.21, 127.11, 126.38, 125.49, 122.92, 121.65, 114.08, 104.84, 43.88, 35.21, 35.14, 31.48, 31.04, 18.80, 17.02. HRMS: *m/z* 571.3514 (M+H$^+$, calcd 571.3544).

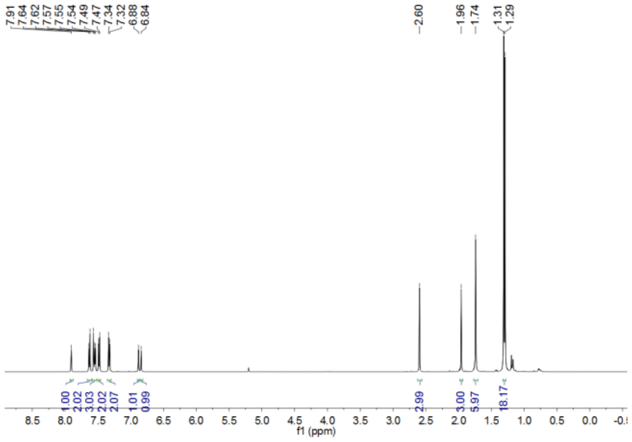


Figure S14. ^{1}H NMR spectrum of **4b** in CD_2Cl_2.

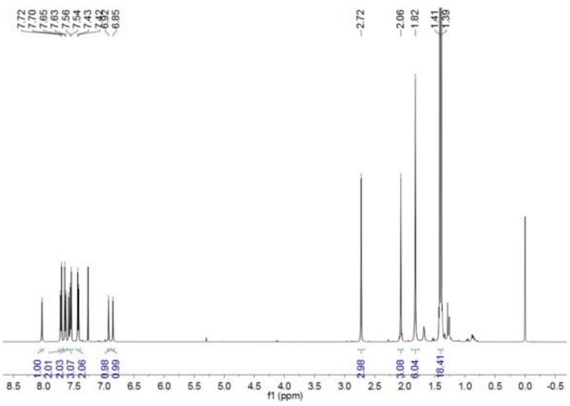


Figure S15. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

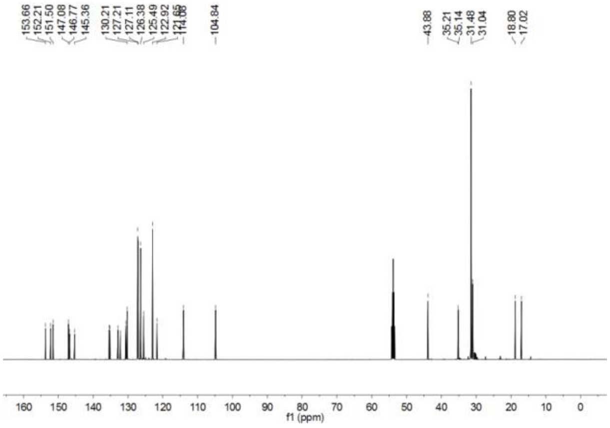


Figure S16. ^{13}C NMR spectrum of **4b** in CD_2Cl_2.

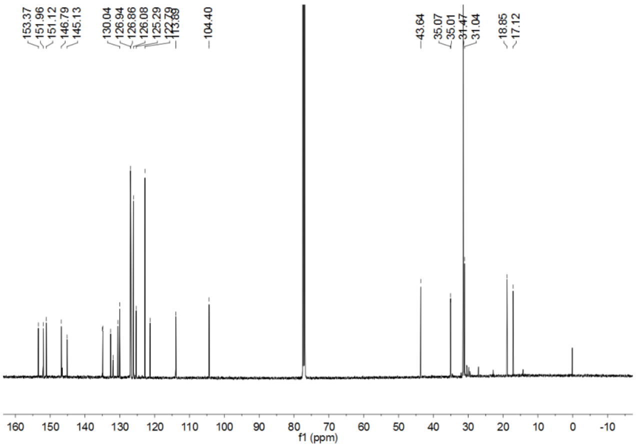


Figure S17. ^{13}C NMR spectrum of **4b** in $CDCl_3$.

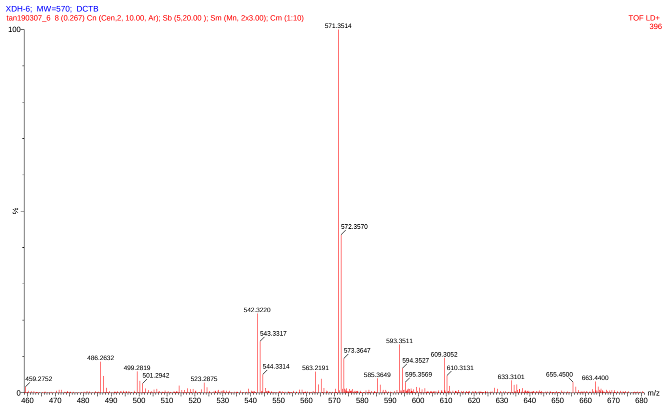


Figure S18. HRMS spectrum of **4b**.

Compound **4c**. ^{1}H NMR (500 MHz, CD_2Cl_2), δ (TMS, ppm): 7.89 (d, *J* = 0.8 Hz, 2H), 7.53-7.47 (m, 4H), 7.37-7.31 (m, 4H), 6.91 (s, 2H), 1.98 (s, 6H), 1.77 (s, 6H), 1.31 (s, 18H). ^{13}C NMR (125 MHz, CD_2Cl_2), δ (TMS, ppm): 153.68, 147.26, 146.76, 135.40, 132.16, 130.28, 127.11, 126.38, 121.59, 114.15, 43.35, 35.22, 31.46, 30.99, 18.81. HRMS: *m/z* 571.3579 ($M+H^+$, calcd 571.3544).

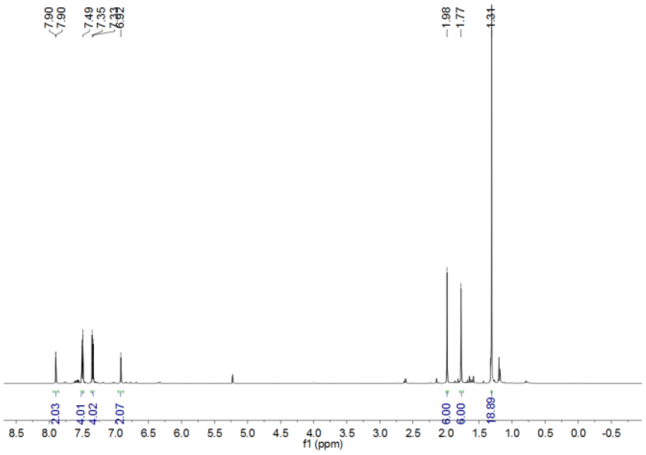


Figure S19. ^{1}H NMR spectrum of **4c** in CD_2Cl_2.

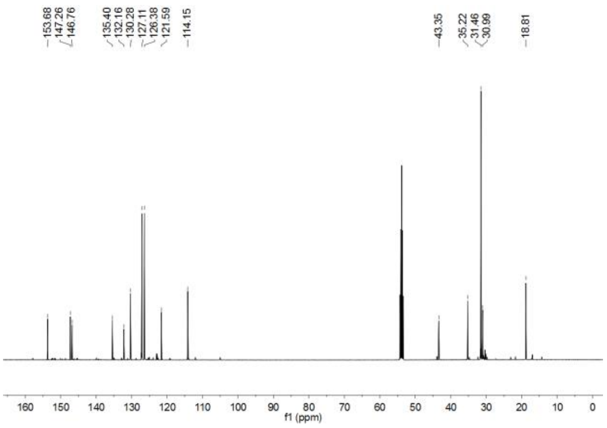


Figure S20. ^{13}C NMR spectrum of **4c** in CD_2Cl_2.

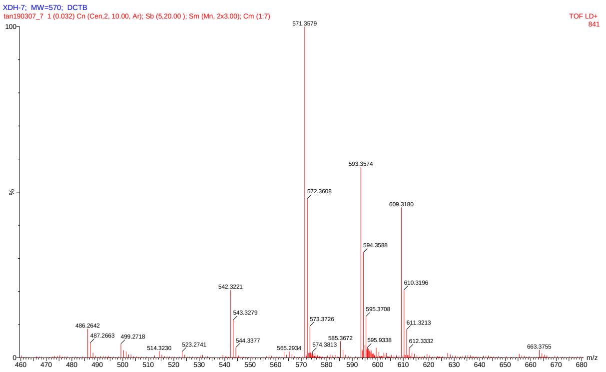


Figure S21. HRMS spectrum of **4c**.

Polymer Synthesis

Unless otherwise stated, all the polymerizations were performed under nitrogen using a standard Schlenk technique with freshly distilled solvents. Typical experimental procedures for the benzyne-azide polymerization of **1a** and **2a** are described below.

Into a 10 mL Schlenk tube equipped with a magnet stirrer were added **1a** (95.4 mg, 0.15 mmol) and **2a** (66.4 mg, 0.15 mmol) and CsF (91.0 mg, 0.6 mmol). After evacuated and refilled with nitrogen for three times, CH_3CN (500 μL) and THF (500 μL) was added into the reaction system by syringes. The resultant mixture was stirred at 75 ^{o}C under a nitrogen atmosphere for 10 h. Then, the mixture was diluted with 2 mL chloroform, and precipitated in 60 mL of CH_3OH via a cotton filter under stirring.

The precipitate was allowed to stand overnight and collected by filtration. The product was washed with CH_3OH for several times and dried under vacuum at 40 ^oC to a constant weight.

*Characterization data for P****1a2a***. A yellow solid was obtained in 75% yield (Table 2, entry 1). M_w: 12100, *Đ*: 1.78. FT-IR (KBr disk), v (cm^{-1}): 3059, 2954, 2101, 1617, 1491, 1438, 1276, 1226, 1073, 960, 816, 754, 695. ^1H NMR ($CDCl_3$, 500 MHz), δ (TMS, ppm): 8.11-7.99 (m), 7.89-7.72 (m), 7.19-6.65 (m), 5.78-5.50 (m), 4.22 (s), 1.88-1.48 (m). ^{13}C NMR ($CDCl_3$, 125 MHz), δ (TMS, ppm): 150.16, 149.71, 146.50, 145.99, 144.70, 143.71, 143.08, 142.91, 140.67, 132.95, 132.71, 131.76, 131.63, 131.35, 131.12, 128.23, 128.09, 127.81, 127.74, 127.62, 127.10, 127.04, 126.71, 124.95, 124.80, 119.60, 116.19, 109.63, 106.14, 54.58, 52.24,51.81, 43.57, 30.81.

*Characterization data for P****1a2d***. A white solid was obtained in 66% yield (Table 2, entry 2). M_w: 8300, *Đ*: 1.52. FT-IR (KBr disk), v (cm^{-1}): 3053, 2935, 2861, 1726, 1603, 1508, 1464, 1443, 1242, 1173, 1031, 830, 729, 699, 637. ^1H NMR ($CDCl_3$, 500 MHz), δ (TMS, ppm): 8.13-8.07 (m), 7.90-7.81 (m), 7.47, 7.36-7.29 (m), 7.14-6.96 (m), 6.94-6.84, 6.69-6.51 (m), 6.64-6.51 (m), 4.67-4.53 (m), 3.90-3.76 (m), 3.29-3.24 (m), 2.10-1.33 (m). ^{13}C NMR ($CDCl_3$, 125 MHz), δ (TMS, ppm): 157.42, 157.36, 150.12, 149.78, 146.36, 146.26, 146.10, 144.53, 144.29, 144.23, 139.60, 136.28, 133.07, 132.50, 131.47, 131.37, 128.21, 128.09, 127.64, 127.53, 126.14, 124.73, 119.64, 116.22, 113.57, 113.47, 109.14, 105.75, 67.41, 53.43, 51.38, 48.16, 47.92, 44.11, 43.70, 31.03, 30.96, 30.86, 29.61, 29.12, 28.78, 26.59, 26.51, 25.65, 25.62.

*Characterization data for P****1b2a***. A yellow solid was obtained in 70% yield (Table 2, entry 3). M_w: 13000, *Đ*: 1.80. FT-IR (KBr disk), *ν* (cm^{-1}): 3050, 2969, 2095, 1594, 1487, 1440, 1240, 1067, 912, 841, 743, 701. ^1H NMR ($CDCl_3$, 500 MHz), δ (TMS, ppm): 7.86, 7.26, 7.02, 6.94, 6.76, 6.69, 5.86, 5.67, 2.63, 2.60, 2.29, 2.28, 1.78, 1.71, 1.65. ^{13}C NMR ($CDCl_3$, 125 MHz), δ (TMS, ppm): 149.91, 148.33, 147.03, 146.06, 144.77, 144.17, 143.59, 143.13, 142.98, 141.48, 140.62, 137.80, 134.92, 134.60, 133.04, 132.90, 131.73, 131.12, 130.24, 129.95, 129.39, 127.81, 127.73, 127.18, 126.98, 126.68, 126.01, 125.59, 124.96, 124.68, 124.53, 123.31, 120.49, 113.98, 103.54, 54.48, 52.83, 51.78, 43.70, 43.27, 42.86, 30.80, 18.54, 16.89.

*Characterization data for P****1b2b***. A grey powder was obtained in 59% yield (Table 2, entry 4). M_w: 12300, *Đ*: 1.98. FT-IR (KBr disk), *ν* (cm^{-1}): 3078, 2998, 2135, 1599, 1514, 1447, 1271, 1041, 838, 763, 699. ^1H NMR ($CDCl_3$, 500 MHz), δ (TMS, ppm): 8.02-7.87 (m), 7.67-7.44 (m), 7.41-6.97 (m), 6.94-6.45 (m), 2.75-2.28 (m), 2.10-1.88 (m), 1.85-1.50 (m). ^{13}C NMR ($CDCl_3$, 125 MHz), δ (TMS, ppm): 150.85, 146.75, 146.33, 145.03, 143.60, 143.05, 142.80, 142.39, 140.94, 135.76, 132.85, 132.72, 132.23, 131.99, 131.87, 131.74, 131.42, 131.35, 131.27, 130.61, 128.23, 128.07, 128.01, 127.21, 127.00, 126.90, 126.76, 125.38, 122.01, 120.91, 118.63, 118.42, 113.92, 104.12, 44.06, 43.50, 42.99, 30.83, 18.62, 16.94.

*Characterization data for P****1b2c***. A grey powder was obtained in 69% yield (Table 2, entry 5). M_w: 9700, *Đ*: 1.59. FT-IR (KBr disk), *ν* (cm^{-1}): 2929, 2867, 2109, 1602, 1493, 1448, 1282, 1236, 1048, 844, 767, 686. ^1H NMR ($CDCl_3$, 500 MHz), δ (TMS, ppm): 8.03-7.97 (m), 7.60, 7.56, 7.52-7.37 (m), 7.35-7.28 (m), 7.11-7.05(m), 6.91, 6.87, 6.69-6.51 (m), 4.15-3.89 (m), 2.82-2.66 (m), 2.13-2.06 (m), 1.90-1.63 (m), 1.56. ^{13}C NMR ($CDCl_3$, 125 MHz), δ (TMS, ppm): 160.35, 159.58, 151.24, 151.07, 146.99, 146.81, 146.49, 145.16, 141.29, 138.52, 138.35, 138.30, 132.54, 132.51, 131.75, 130.65, 130.52, 130.18, 130.09, 129.77, 125.40, 125.25, 121.24, 121.15, 119.45, 116.45, 116.41, 115.10, 114.74, 114.13, 113.99, 113.48, 111.27, 109.56, 109.52, 105.57, 104.46, 104.39, 68.38, 68.35, 68.05, 44.23, 43.64, 43.12, 31.08, 30.99, 29.19, 25.98, 25.96, 25.94, 18.85, 18.83, 17.10, 17.06.

Characterization data for ***P1b2d***. A white powder was obtained in 69% yield (Table 2, entry 6). M_w: 10200, *Đ*: 1.71. FT-IR (KBr disk), v (cm^{-1}): 3056, 2932, 2864, 2090, 1599, 1505, 1438, 1240, 1172, 1037, 829, 766, 699.609. ^{1}H NMR ($CDCl_3$, 500 MHz), δ (TMS, ppm): 7.91, 7.407.20 (m), 7.15-6.97 (m), 6.90, 6.59, 4.74, 4.59, 3.83, 2.61, 2.48-2.37 (m), 2.31-2.14 (m), 2.00, 1.75, 1.46. ^{13}C NMR ($CDCl_3$, 125 MHz), δ (TMS, ppm): 157.37, 150.09, 149.93, 146.81, 146.35, 144.61, 144.57, 144.30, 144.24, 139.60, 136.33, 136.28, 132.95, 132.50, 131.39, 131.36, 130.88, 130.83, 130.23, 129.47, 129.36, 127.63, 127.52, 126.13, 124.48, 120.13, 113.97, 113.57, 113.47, 103.16, 67.43, 58.43, 49.63, 47.93, 43.91, 43.79, 43.36, 42.84, 31.61, 31.07, 30.90, 30.72, 29.64, 29.13, 26.59, 26.43, 25.67, 21.81, 18.60, 18.44, 16.91.

Characterization data for ***P1c2c***. A grey powder was obtained in 55% yield (Table 2, entry 7). M_w: 9000, *Đ*: 1.57. FT-IR (KBr disk), v (cm^{-1}): 2932, 2853, 2112, 1596, 1491, 1456, 1382, 1242, 1059, 696. ^{1}H NMR ($CDCl_3$, 500 MHz), δ(TMS, ppm): 7.99-7.74 (m), 7.52-7.36 (m), 7.27, 7.21-6.87 (m), 6.77-6.44 (m), 4.08-3.86 (m), 1.90-1.71 (m), 1.56. ^{13}C NMR ($CDCl_3$, 125 MHz), δ(TMS, ppm): 160.15, 146.68, 145.25, 143.86, 143.36, 143.05, 142.78, 142.48, 141.99, 141.83, 141.64, 141.17, 140.90, 140.30, 139.97, 137.69, 131.91, 131.34, 131.28, 131.22, 131.16, 131.08, 130.49, 130.41, 130.33, 128.32, 128.20, 128.00, 127.23, 127.08, 122.69, 114.86, 114.31, 113.81, 111.15, 108.98, 105.45, 68.24, 68.17, 29.09, 25.82.

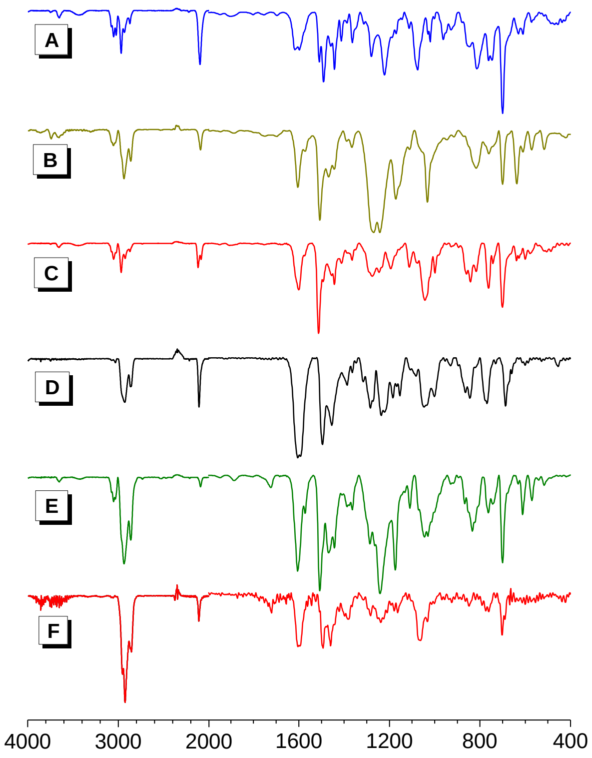


Figure S22. FT-IR spectra of P**1a2a** (A), P**1a2d** (B), P**1b2b** (C), P**1b2c** (D), P**1b2d** (E), P**1c2c** (F).

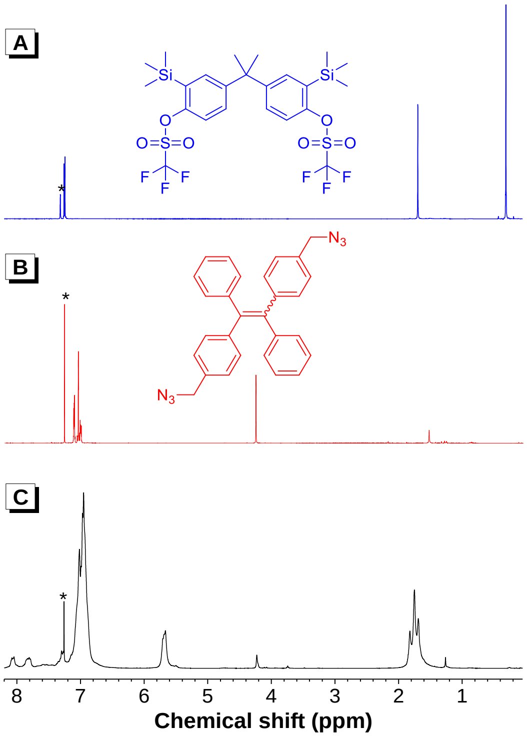


Figure S23. ^{1}H NMR spectra of **1a** (A), **2a** (B) and P**1a2a** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

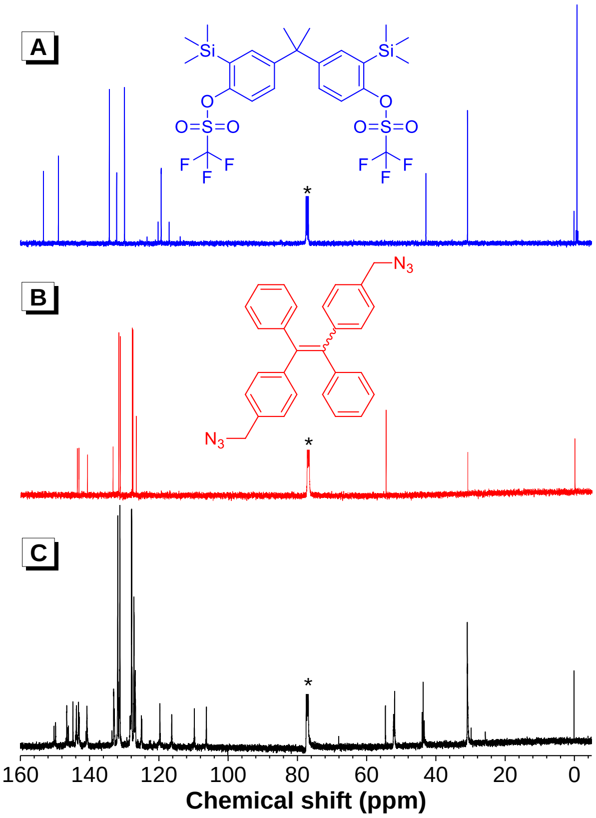


Figure S24. ^{13}C NMR spectra of **1a** (A), **2a** (B) and P**1a2a** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

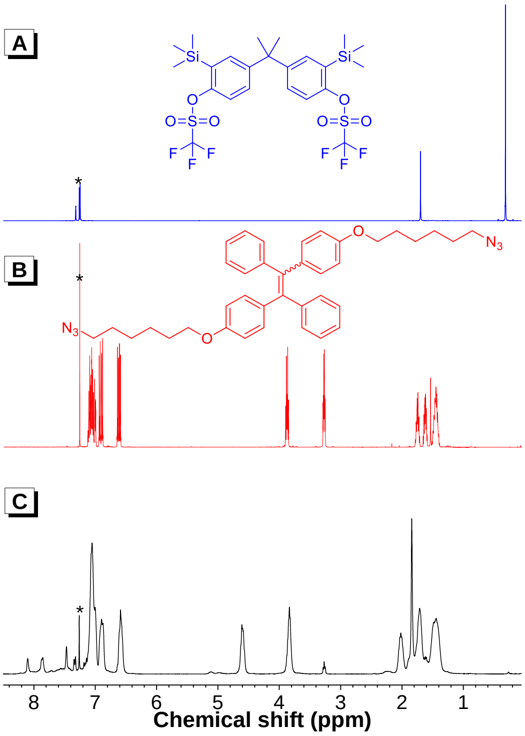


Figure S25. ^{1}H NMR spectra of **1a** (A), **2d** (B) and P**1a2d** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

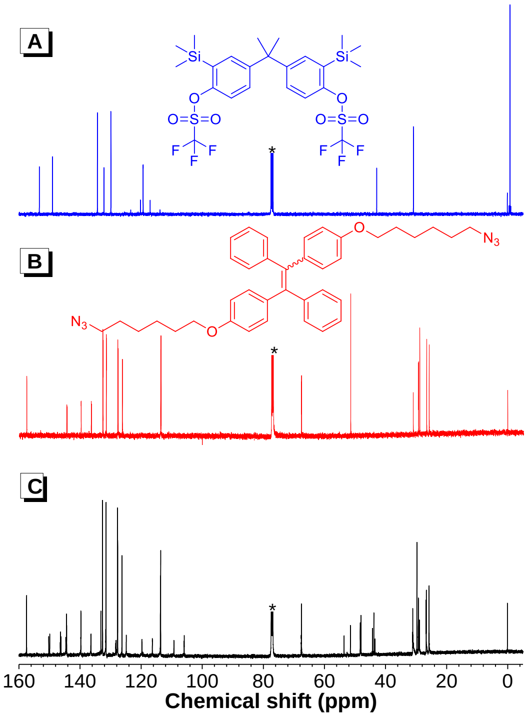


Figure S26. ^{13}C NMR spectra of **1a** (A), **2d** (B) and P**1a2d** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

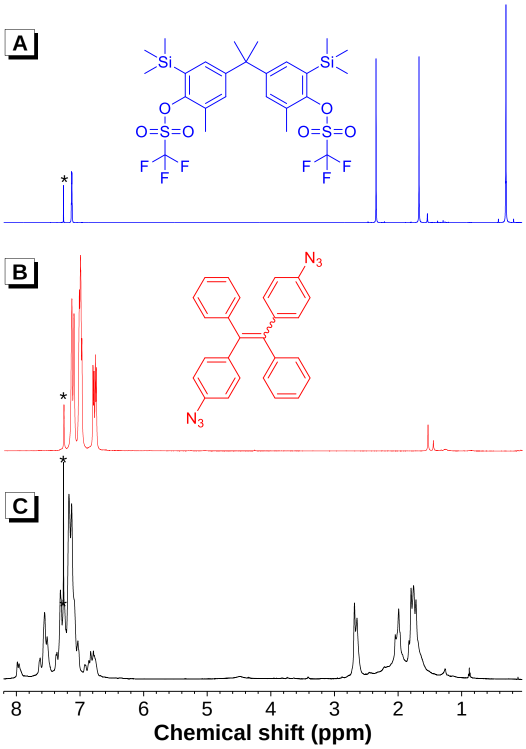


Figure S27. ^{1}H NMR spectra of **1b** (A), **2b** (B) and P**1b2b** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

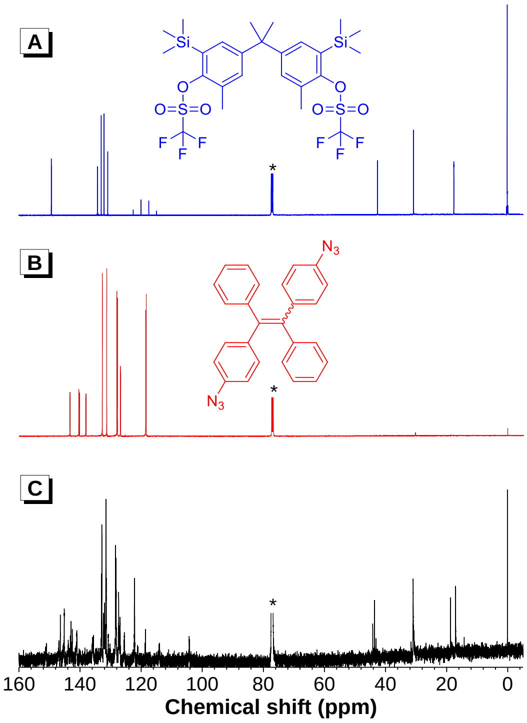


Figure S28. ^{13}C NMR spectra of **1b** (A), **2b** (B) and P**1b2b** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

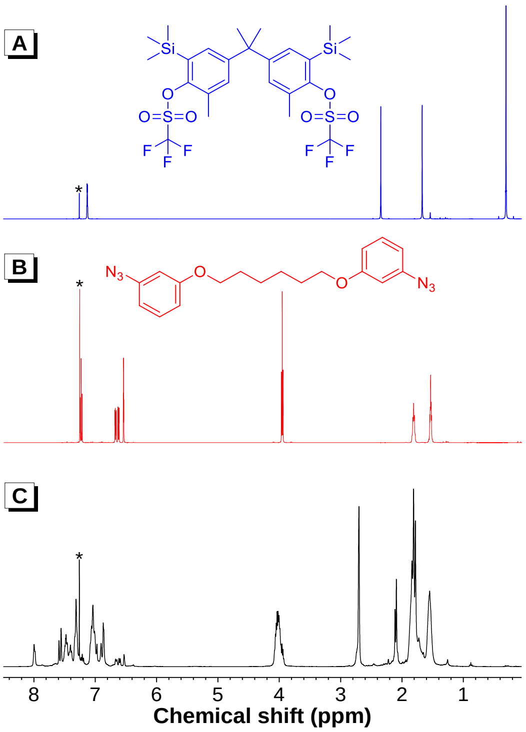


Figure S29. ^{1}H NMR spectra of **1b** (A), **2c** (B) and P**1b2c** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

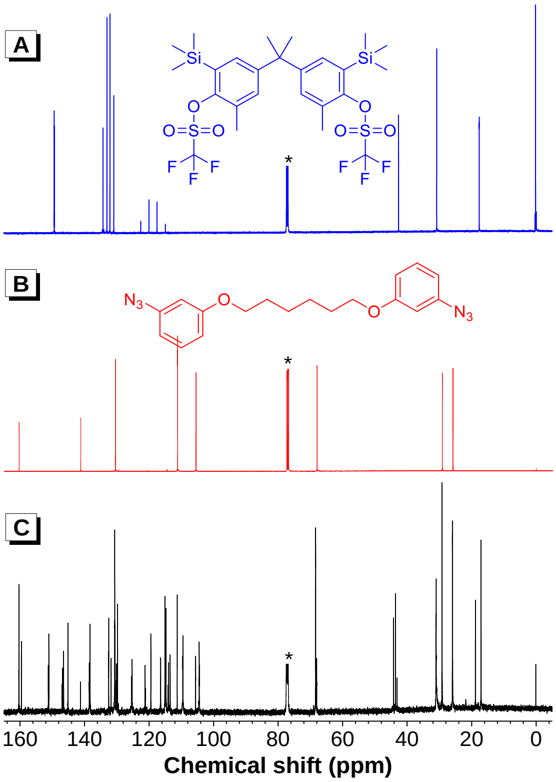


Figure S30. ^{13}C NMR spectra of **1b** (A), **2c** (B) and P**1b2c** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

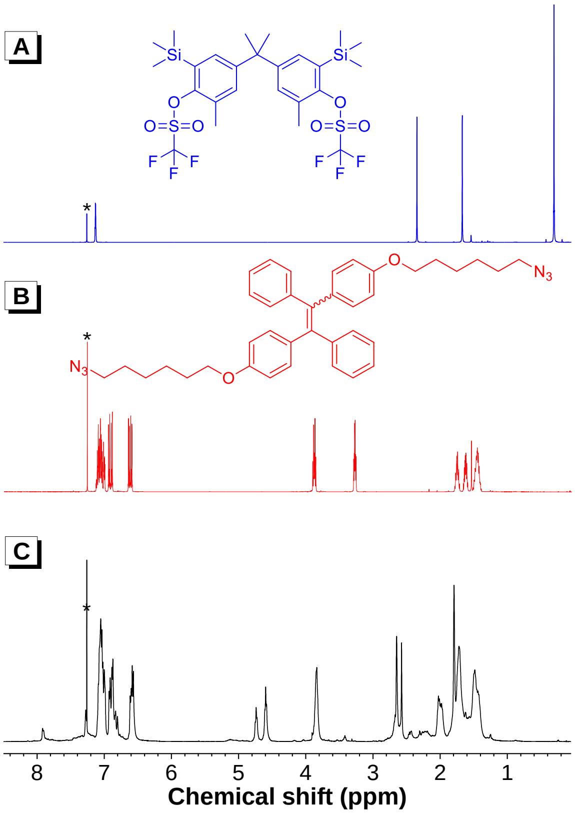


Figure S31. ^{1}H NMR spectra of **1b** (A), **2d** (B) and P**1b2d** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

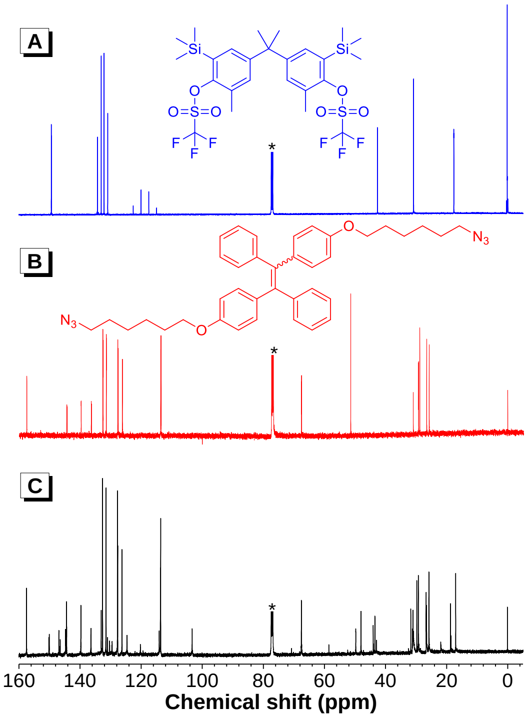


Figure S32. ^{13}C NMR spectra of **1b** (A), **2d** (B) and P**1b2d** (C) in $CDCl_3$. The solvent peaks are marked with asterisks.

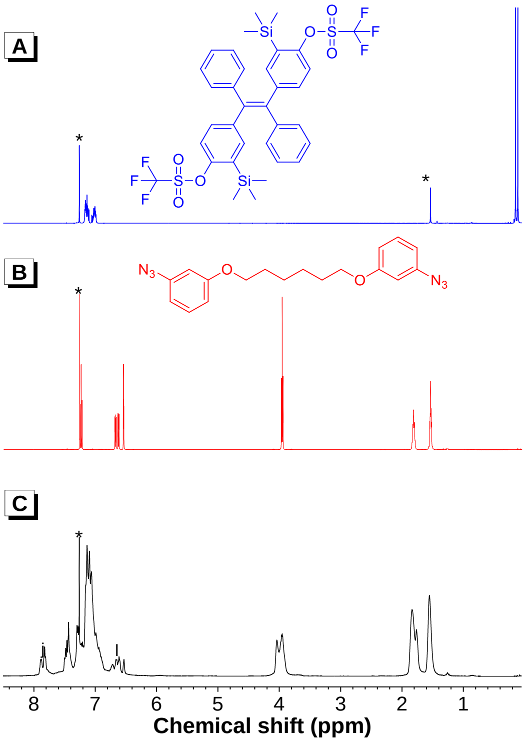


Figure S33. ^{1}H NMR spectra of **1c** (A), **2c** (B) and P**1c2c** (C) in CDCl$_3$. The solvent peaks are marked with asterisks.

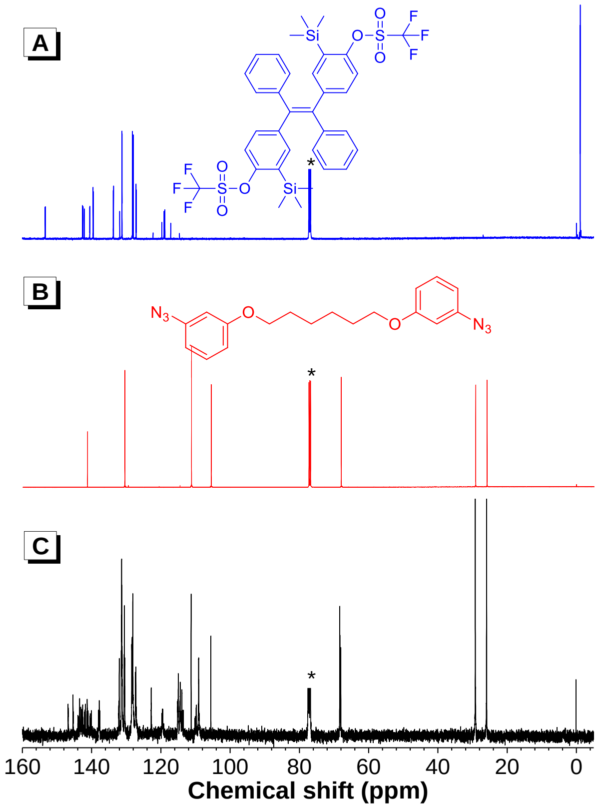


Figure **S34**. ^{13}C NMR spectra of **1c** (A), **2c** (B) and P**1c2c** (C) in CDCl$_3$. The solvent peaks are marked with asterisks.

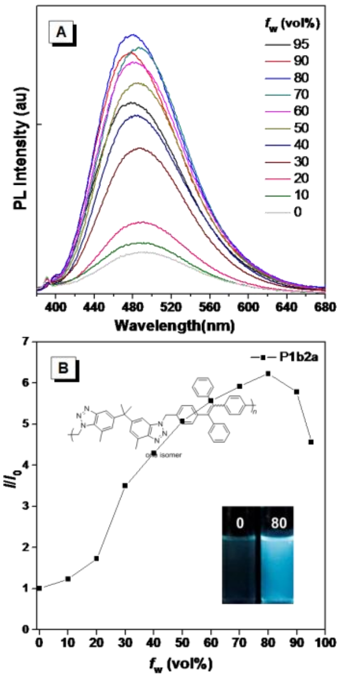


Figure S35. (A) PL spectra of P**1b2a** in THF and THF/water mixtures with different water fractions (f_w). (B) Plots of I/I_0 of P**1b2a** versus water fraction, where I = peak intensity and I_0 = peak intensity at $f_w = 0$. Inset: photograph taken under illumination of hand-held UV lamp. Concentrations: 10 μM; excitation wavelength: 350 nm.

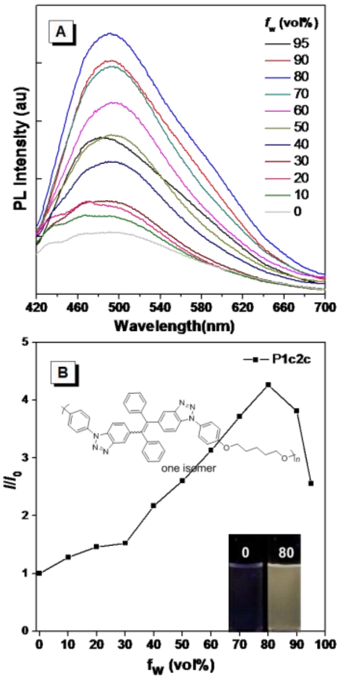


Figure S36. (A) PL spectra of P**1c2c** in THF and THF/water mixtures with different water fractions (f_w). (B) Plots of I/I_0 of P**1c2c** versus water fraction, where I = peak intensity and I_0 = peak intensity at $f_w = 0$. Inset: photograph taken under illumination of hand-held UV lamp. Concentrations: 20 μM; excitation wavelength: 360 nm.

Reference:

1. D. Peña, A. Cobas, D. Pérez and E. Guitián, *Synthesis*, 2002, **10**, 1454-1458.