

## Supporting Information

# Transition-Metal-free Polymerization of Bromoalkynes and Phenols

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**Materials and Instruments.** *N*-Bromosuccinimide (NBS) and diphenols were recrystallized before use. Bis(bromoalkyne)s were synthesized by using literature methods. All other chemicals and reagents were purchased from Sigma-Aldrich or Alfa and used as received without further purification. Tetrahydrofuran (THF) and toluene were distilled under nitrogen at normal pressure from sodium benzophenone ketyl immediately prior to use. DMF, DMSO and DMA were extra-dry grade.

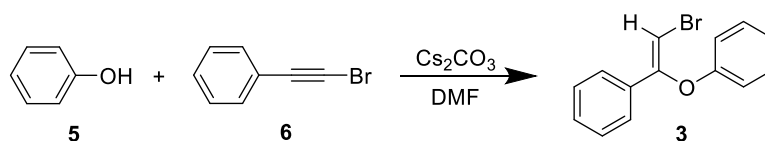
FT-IR spectra were recorded on a Bruker Vector 22 spectrometer as thin films on KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AV 500, Bruker AV 400 spectrometer in  $\text{CDCl}_3$  using tetramethylsilane (TMS;  $\delta = 0$ ) as internal reference. The Relative weight-average and number-average molecular weights ( $M_w$  and  $M_n$ ) and polydispersity indices ( $D$ ,  $M_w/M_n$ ) of the polymers were measured by a Waters Advanced Polymer Chromatography (APC) system equipped with photo-diode array (PDA) detectors, using a set of monodisperse polymethyl methacrylate as calibration standards and THF as the eluent in a flow rate of 0.5 mL/min. Thermal stabilities were evaluated by measuring thermogravimetric analysis (TGA) thermograms on a PerkinElmer TGA 7 under dry nitrogen at a heating rate of 10 °C/min. UV-vis spectra were measured on a Varian VARY 100 Bio UV-vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. For the AIE measurement, a stock solution of **P4** in THF ( $1 \times 10^{-4}$  M) was first prepared. Aliquots of this stock solution were transferred into volumetric flasks (10 mL), into which appropriate volumes of THF and water were added dropwise under vigorous stirring to furnish  $1 \times 10^{-5}$  M

solutions with different water contents (0 – 90 vol%). UV and PL spectra were measured immediately after the solutions were prepared.

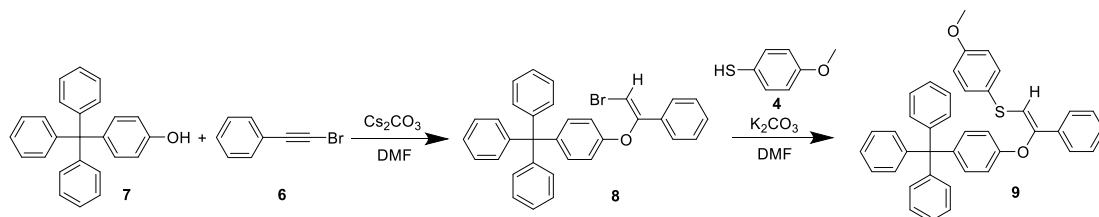
**Monomer Preparation.** Into a round-bottom flask was dissolved 1,4-diethynylbenzene (1.790 g, 14.2 mmol) in acetone (60 mL), and NBS (7.590 g, 42.6 mmol) and AgNO<sub>3</sub> (531 mg, 3.1 mmol) was added. The reaction mixture was stirred at room temperature under exclusion of light overnight. Upon completion the reaction mixture was concentrated under reduced pressure and the crude product was purified by a silica gel column chromatography using hexane as eluent. Light yellow powder of monomer **2a** was obtained in 85.0% yield (3.427 g). FT-IR (KBr),  $\nu$  (cm<sup>-1</sup>): 2189, 1904, 1657, 1497, 1396, 1258, 1096, 1012, 828, 533. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (TMS, ppm): 7.38 (s, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 131.98, 123.01, 79.60, 52.21.

Monomer **2b** was prepared by the same procedures using compound **11** as a starting material. Here are its characterization data. FT-IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3053, 3025, 2194, 1596, 1497, 1441, 1404, 1107, 1074, 1022, 974, 914, 838, 808, 746, 698, 619, 574. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  (TMS, ppm): 7.21-7.07 (m, 10H), 7.01-6.91 (m, 8H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 144.06, 143.97, 142.90, 142.83, 140.94, 131.49, 131.36, 131.29, 127.97, 127.81, 126.96, 126.85, 120.86, 120.69, 80.12, 49.91.

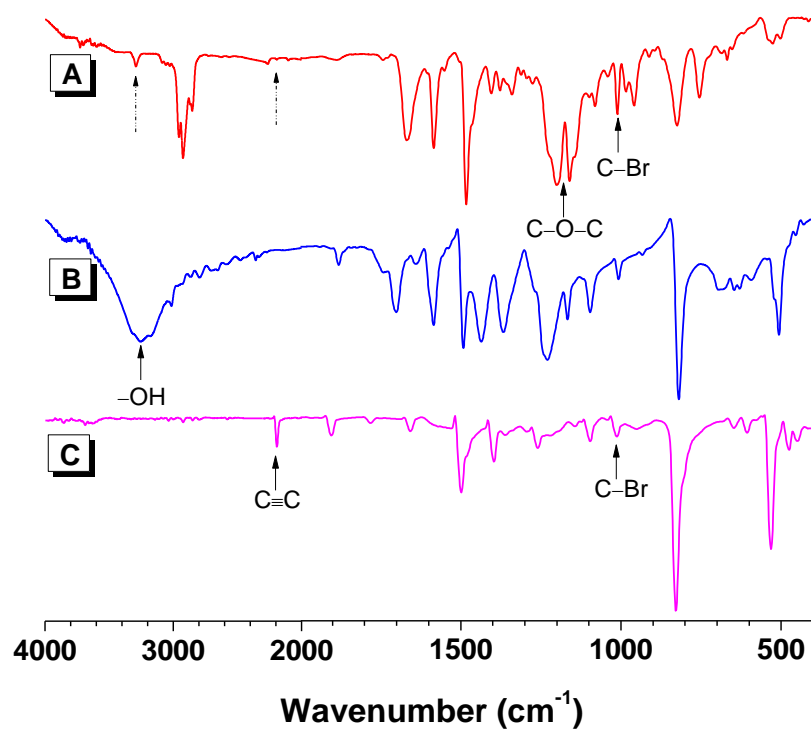
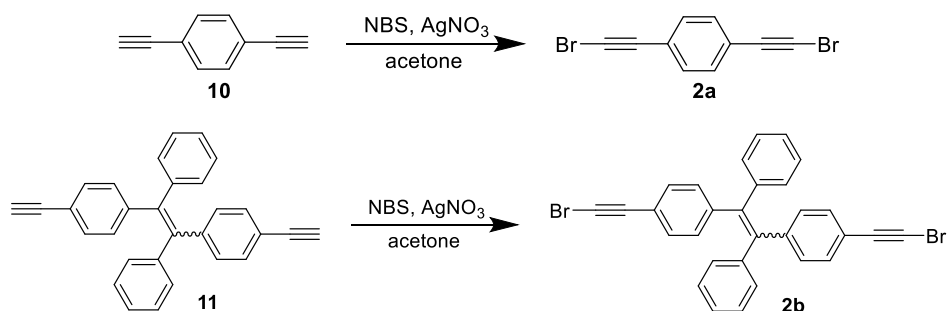
**Scheme S1.** Synthetic Route to Model Compound **3**.



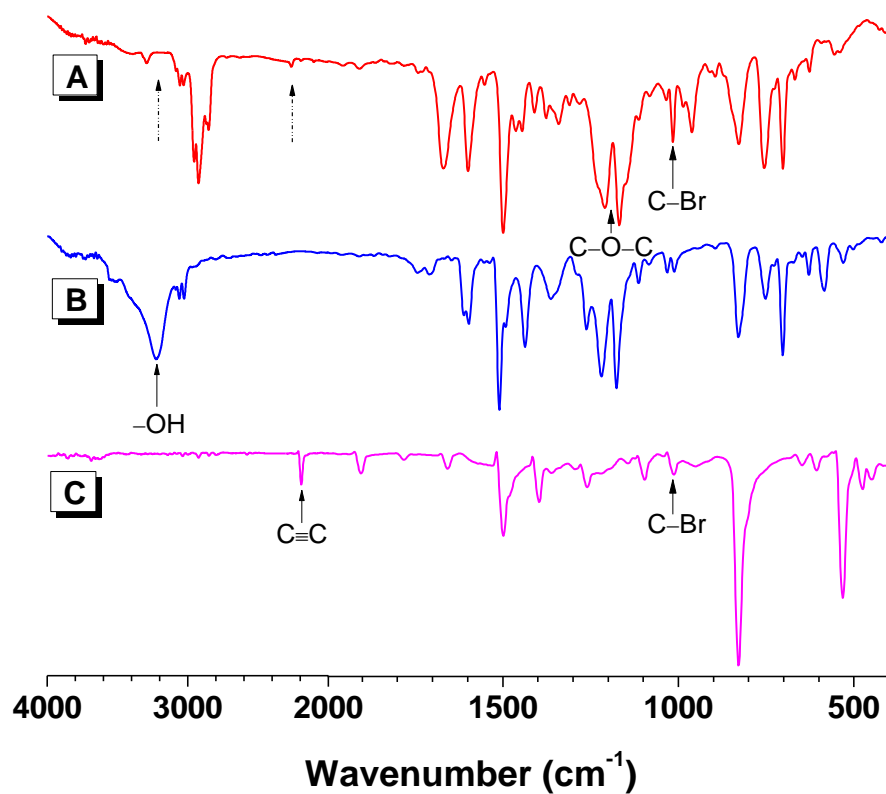
**Scheme S2.** Synthetic Route to model compound **9**.



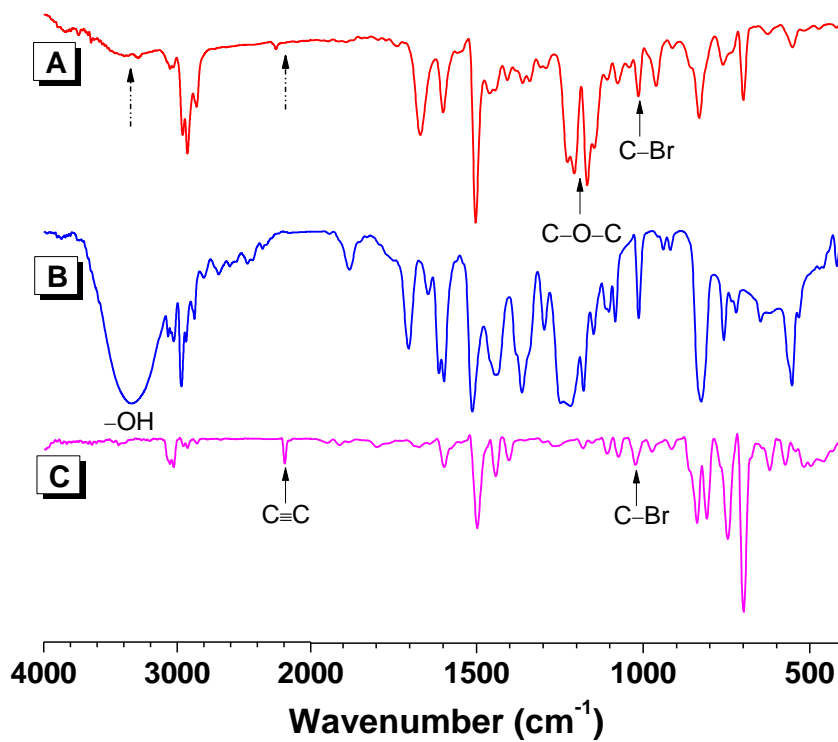
**Scheme S3.** Synthetic routes to monomers **2a** and **2b**.



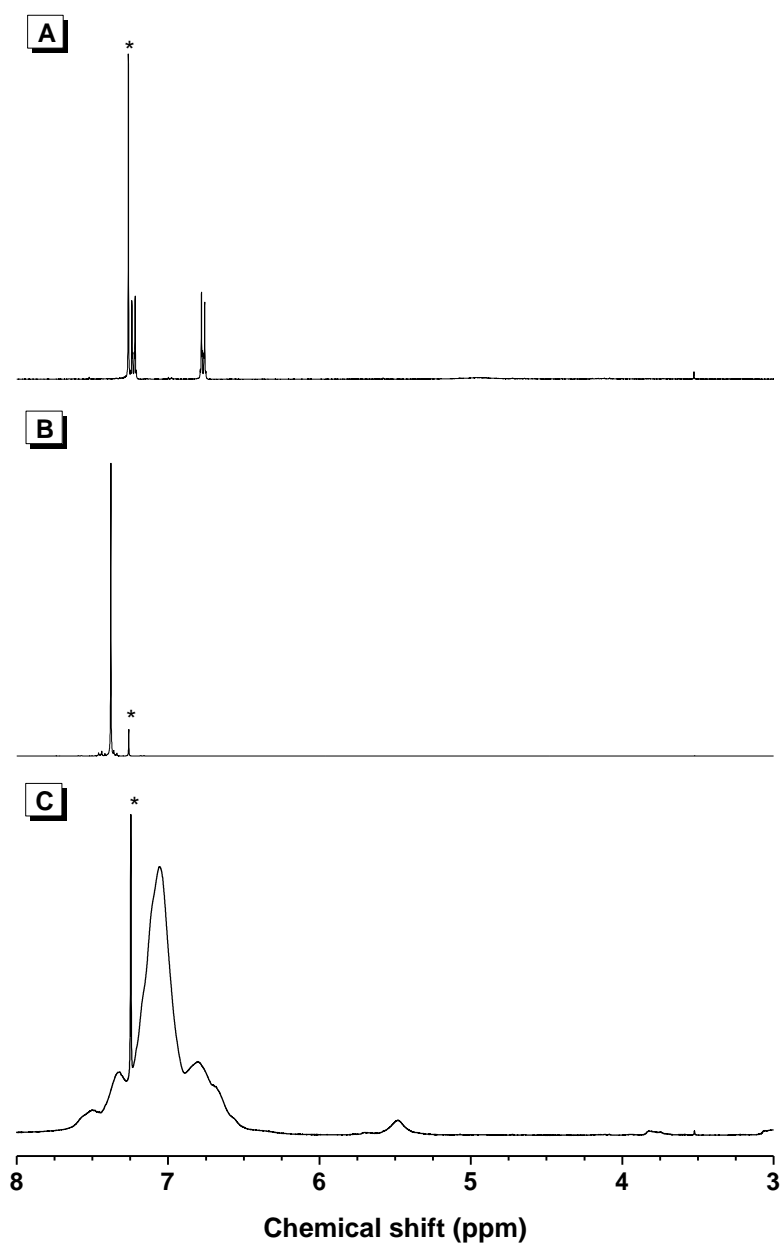
**Figure S1.** FT-IR spectra of PII (A), **1b** (B) and **2a** (C).



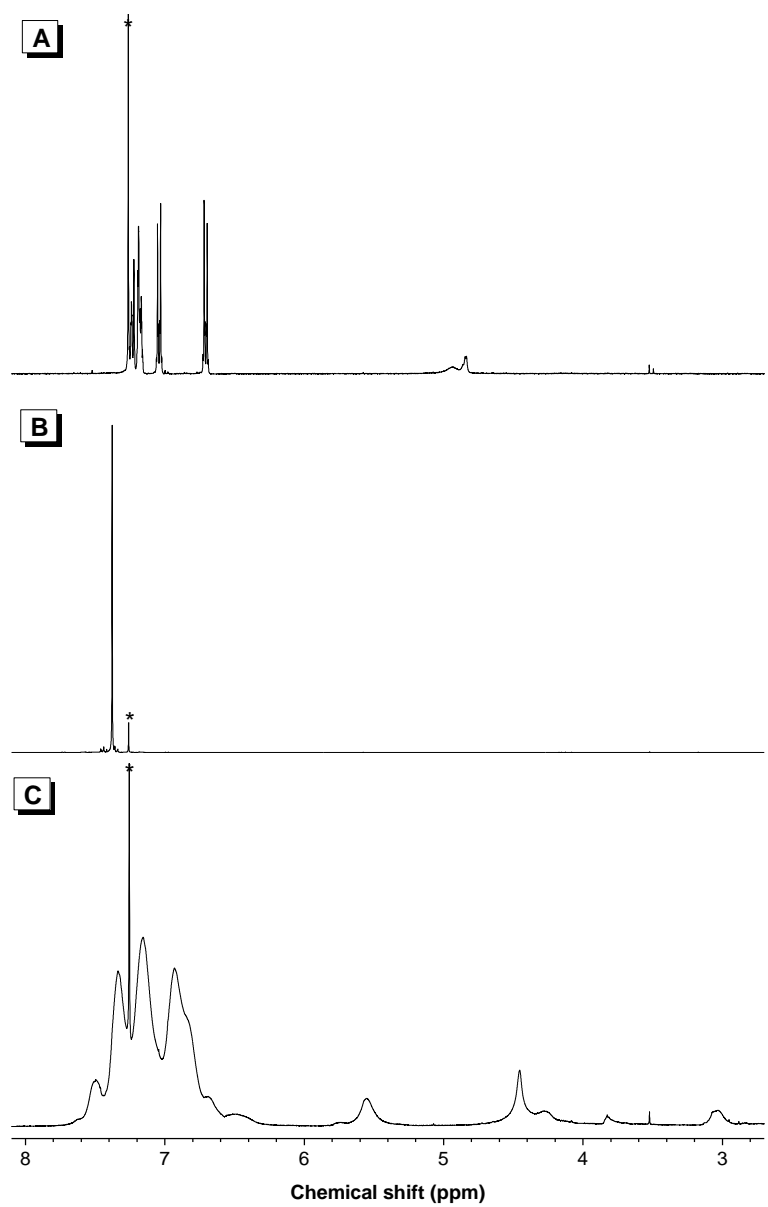
**Figure S2.** FT-IR spectra of **PIII** (A), **1c** (B) and **2a** (C).



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

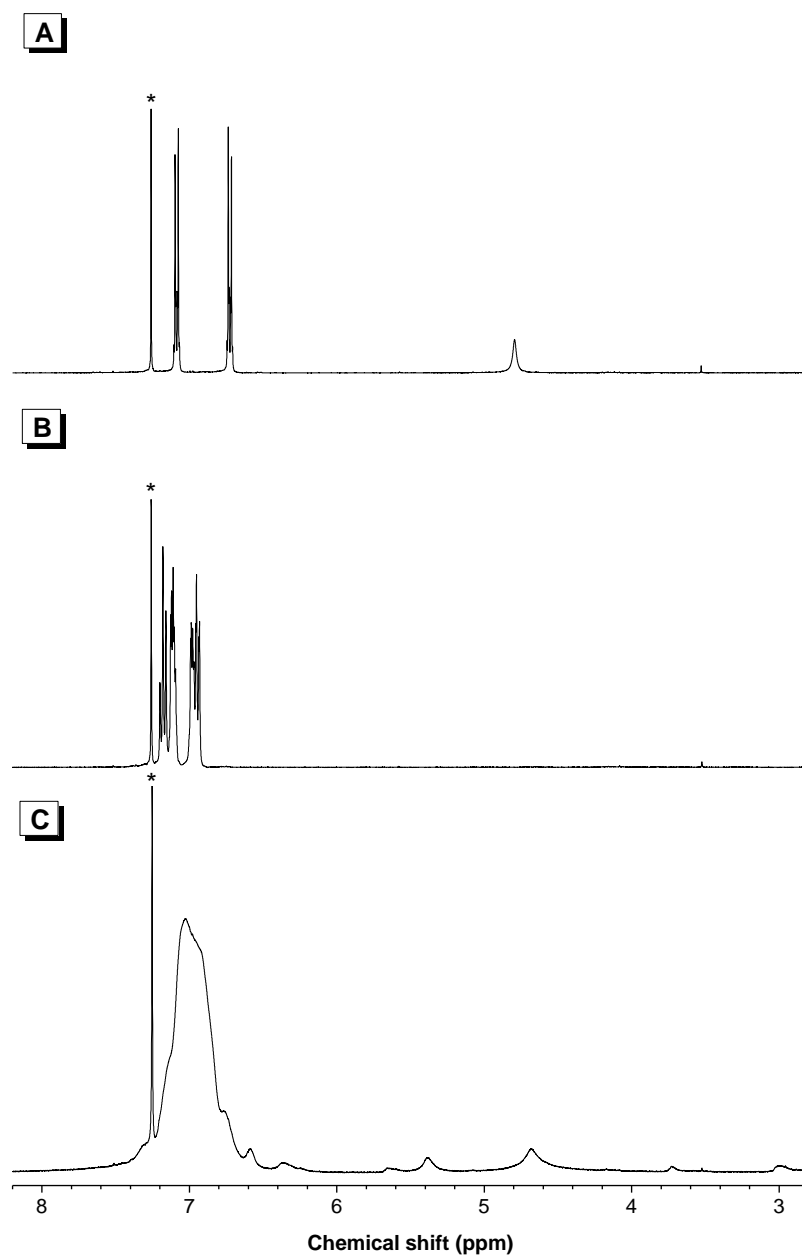


**Figure S4.**  $^1\text{H}$  NMR spectra of **1b** (A), **2a** (B) and **P11** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.

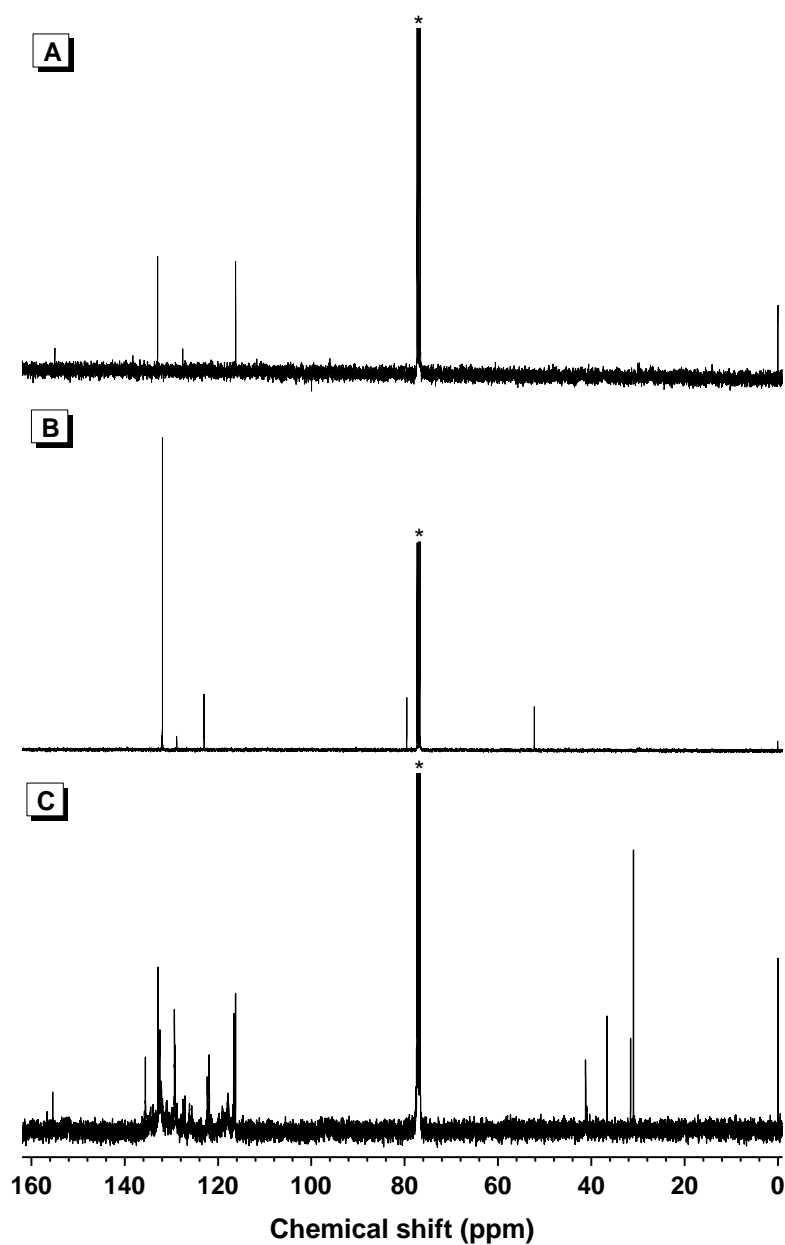


**Figure S5.**  $^1\text{H}$  NMR spectra of **1c** (A), **2a** (B), model compound(C) and **P111** in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.

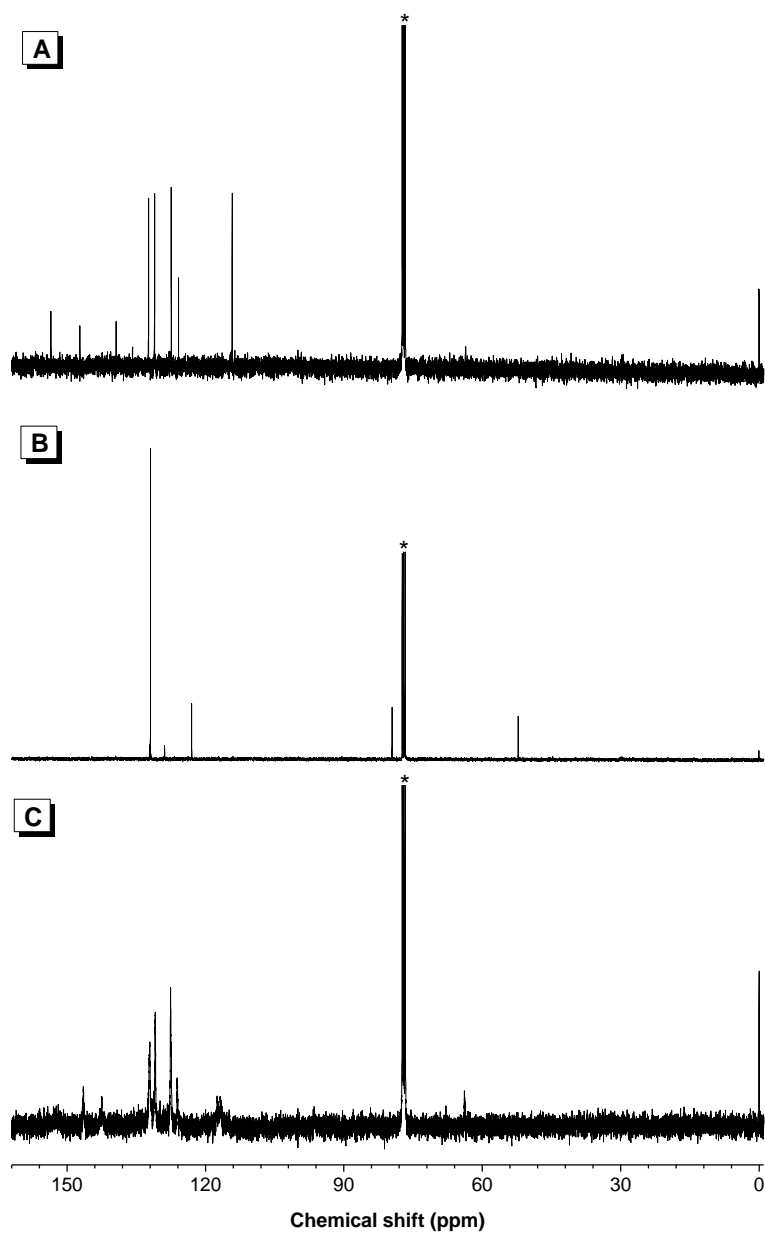




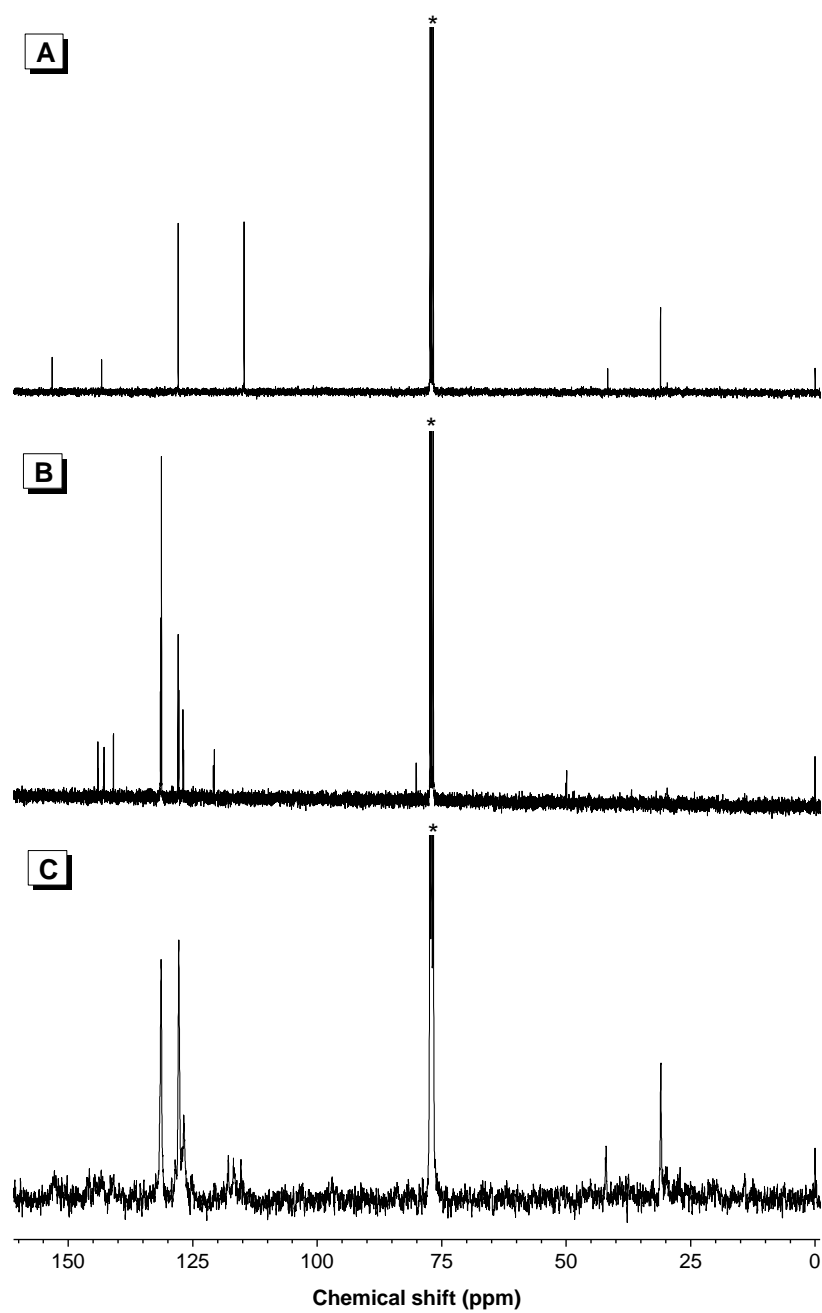
**Figure S6.**  $^1\text{H}$  NMR spectra of **1a** (A), **2b** (B), model compound **3** (C) and **PIV** in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



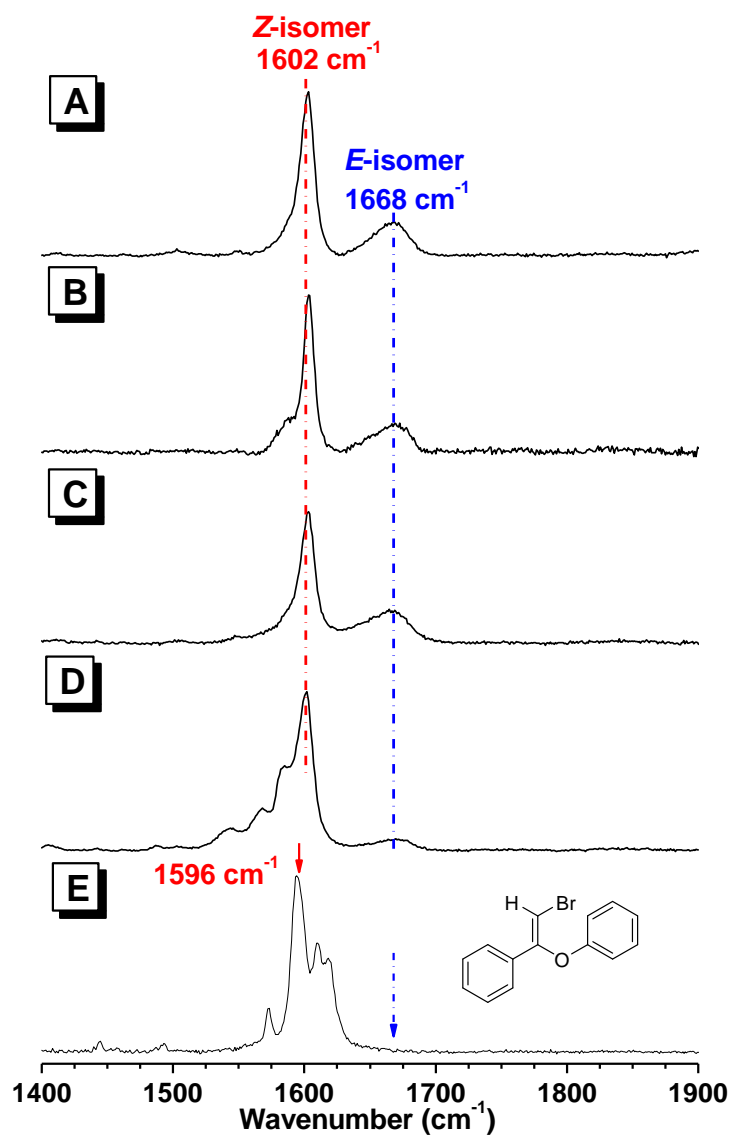
**Figure S7.**  $^{13}\text{C}$  NMR spectra of **1b** (A), **2a** (B) and **PII** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



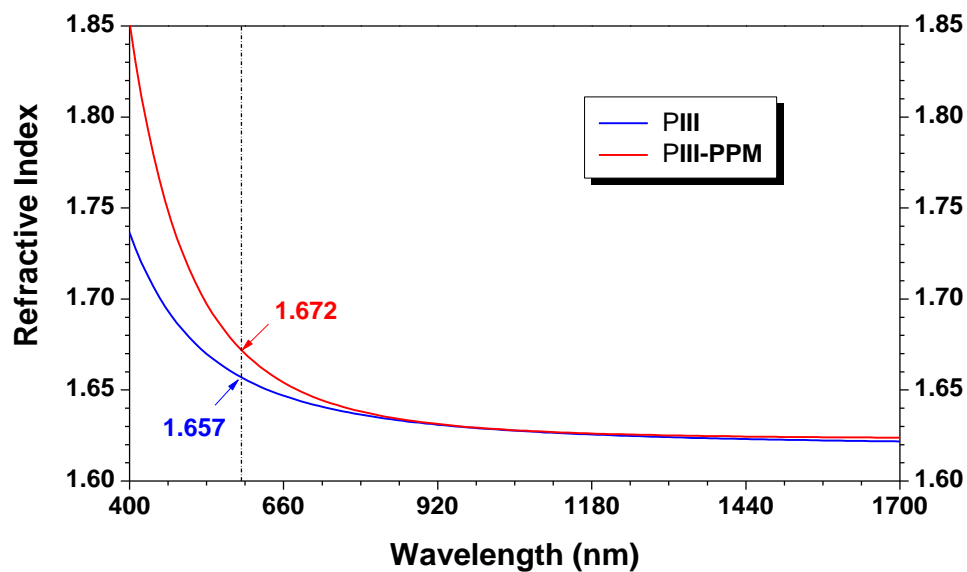
**Figure S8.**  $^{13}\text{C}$  NMR spectra of **1c** (A), **2a** (B) and **PIII** (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



**Figure S9.**  $^{13}\text{C}$  NMR spectra of **1a** (A), **2b** (B) and PIV (C) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



**Figure S10.** Raman spectra of PI(A), PII(B), PIII(C), PIV (D) and compound 3(E).



**Figure S11.** Light refraction spectra of thin solid films of **PIII** and **PIII-PPM**.

**Table S1.** Preliminary Experiments of the Polymerization of **1a** and **2a**<sup>a</sup>

entry	additive	<i>t</i> (h)	<i>M</i> <sub>w</sub>	<i>Đ</i> <sup>b</sup>	yield (%)
1	K <sub>2</sub> CO <sub>3</sub>	15	6100	1.42	95.7
2	K <sub>2</sub> CO <sub>3</sub>	10	6900	1.37	84.0
3	K <sub>2</sub> CO <sub>3</sub>	5	9100	1.39	87.9
4	K <sub>2</sub> CO <sub>3</sub>	4	9000	1.35	N.D.
5	K <sub>2</sub> CO <sub>3</sub>	3	9600	1.39	N.D.
6	K <sub>2</sub> CO <sub>3</sub>	2	8400	1.48	N.D.
7	K <sub>2</sub> CO <sub>3</sub>	1	7400	1.43	N.D.
8	Cs <sub>2</sub> CO <sub>3</sub>	3	10300	1.40	92.1
9	CsF	3	-	-	trace

<sup>a</sup> Carried out in DMF at 110 °C under air condition ([**1a**]/[**2a**] = 1, [additive]/[**2a**] = 2, [**2a**] = 0.1 M). <sup>b</sup> Weight-average molecular weight (*M*<sub>w</sub>) and polydispersity index (*Đ*, *M*<sub>w</sub>/*M*<sub>n</sub>) of polymers were estimated by GPC in THF on the basis of a polymethyl methacrylate calibration.

**Table S2.** Post-modification of **PIII** by thiophenol derivative **4**.

entry	polymer	$M_w^b$	$M_n$	$\bar{D}^b$	yield (%)
1	<b>PIII</b>	42300	11900	3.55	
2	<b>PIII-PM</b>	40800	15200	2.69	96

The grafting degree of **PIII-PM** is given as  $x$ , then unreacted part accounts for  $1-x$

$$\frac{6x}{32x + 24(1-x)} = \frac{6}{59.8}$$

$$x = 0.4$$