

Supporting Information

# **Synthesis of Functional Poly(propargyl imine)s by Multicomponent Polymerization of Bromoarenes, Isonitriles and Alkynes**

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## Experimental Section

**Materials.** The organic solvents such as tetrahydrofuran (THF), toluene and 1,4-dioxane were distilled prior to use. Dimethyl sulfoxide (DMSO), dimethylformamide (DMF), palladium(II) acetate, bis[(2-diphenylphosphino)phenyl] ether (DPEPhos), cesium carbonate, dibromoarene **1a** and isocyanides **2a–b** were purchased from Aldrich or J&K used as received without further purification. Dibromoarenes **2–4a** and diynes **3a–b** were prepared according to the reported procedures.<sup>1</sup>

**Characterization.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub>, unless otherwise noted, on a Bruker ARX 400 NMR spectrometer using residual chloroform ( $\delta = 7.26$  for <sup>1</sup>H and  $\delta = 77.16$  for <sup>13</sup>C) as internal standard. High resolution mass spectra (HRMS) were performed on a GCT Premier CAB 048 mass spectrometer operated in MALDI–TOF mode. IR spectra were recorded on a Perkin Elmer 16 PC FT-IR spectrophotometer. Gel permeation chromatography (GPC) was performed in THF at 40 °C at an elution rate of 1.0 mL min<sup>-1</sup> on a Waters GPC system equipped with a Waters 515 HPLC pump, a Waters 486 UV–vis detector, a column temperature controller and a set of Styragel columns (HT3, HT4 and HT6; molecular weight range: 10<sup>2</sup>–10<sup>7</sup>). The polymers were dissolved in THF (about 2 mg mL<sup>-1</sup>) and filtered through a 0.45  $\mu$ m PTFE filter before being injected into the GPC system. UV spectra were measured on a Milton Ray Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS 55 spectrophotometer. Thermogravimetric analysis (TGA) was carried out under nitrogen on a TA TGA Q5000 at a heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) analysis was performed on a TA Instruments DSC Q1000 at a heating rate of 10 °C min<sup>-1</sup>. RI values were estimated on a J. A. Woollam M-2000 V multiwavelength ellipsometer in a wavelength region of 400–900 nm. Photopatterning of the films of **P1a/2a/3** and **P1c/2a/3a** were conducted on a Spectroline ENF-280C/F UV lamp at a distance of 5 cm as light source. The incident light intensity was  $\sim 18.5$  mW cm<sup>-2</sup>. The films were prepared by spin-coating the polymer solutions (10 mg of **P1a/2/3** in 1 mL of 1,2-dichloroethane) at 1000 rpm for 1 min on silicon wafers. The polymer films were dried in a vacuum oven at room temperature overnight. The patterns were generated by UV irradiation of the polymer films in air through copper photomasks for 20 min. The exposed parts (lines) undergo photo-oxidation in the presence of UV irradiation, which quenches their light emission. However, the unexposed areas (squares) remained intact and emit light when irradiated. The photos were taken on an optical microscope (Olympus BX 41) under a UV light source.

**Polymer Synthesis.** All the polymerization reactions were performed under nitrogen atmosphere using a standard Schlenk technique. A typical procedure for the preparation of **P1a/2a/3a** was given below as an example. Into a 10 mL Schlenk tube with a magnetic stirrer were placed **1a** (0.2 mmol, 1.0 equiv.), **3a** (0.2 mmol, 1.0 equiv.), Pd(OAc)<sub>2</sub> (0.01 mmol, 0.05 equiv.), DPEPhos (0.02 mmol, 0.1 equiv.), and Cs<sub>2</sub>CO<sub>3</sub> (0.42 mmol, 2.1 equiv.). The tube was purged with argon and isocyanide **2a** (55  $\mu$ L, 0.48 mmol, 2.4 equiv.) and THF (2 mL) were then injected. The resulting solution was stirred at 100 °C for 18 h. After cooling to room temperature, the reaction mixture was added dropwise into 100 mL methanol via a cotton filter under stirring. The precipitate was washed with methanol and dried under vacuum at room temperature to a constant weight. A yellow powder of polymer **P1a/2a/3a** was obtained in 85% yield.  $M_w = 38\,200$ ;  $M_w/M_n = 2.23$ . IR (neat),  $\nu$  (cm<sup>-1</sup>): 3058, 2965, 2872, 2199, 1664, 1584, 1495, 1442, 1356, 1291, 1202, 1019. <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.12 (4H, aromatic protons), 7.63 (4H, aromatic protons), 7.43–7.30 (4H, aromatic protons), 7.22–7.00 (14H, aromatic protons), 1.54 (18H, CH<sub>3</sub> protons). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 146.6, 145.2, 142.9, 142.3, 141.3, 138.9, 131.7, 131.5, 131.2, 128.3, 128.0, 127.8, 127.3, 127.0, 120.1, 99.1, 84.5, 57.2, 29.7.

**P1a/2b/3a.** Yellow powder; yield 81% (Table 2, entry 2).  $M_w = 18\,800$ ;  $M_w/M_n = 1.85$ . IR (neat),  $\nu$  (cm<sup>-1</sup>): 3058, 2953, 2901, 2197, 1653, 1586, 1492, 1477, 1363, 1291, 1208, 1020. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.14 (4H, aromatic protons), 7.65 (4H, aromatic protons), 7.44–7.30 (4H, aromatic protons), 7.43–7.30 (4H, aromatic protons), 7.23–6.99 (14H, aromatic protons), 2.00 (4H, CH<sub>2</sub> protons), 1.60 (12H, CH<sub>3</sub> protons), 1.04 (18H, CH<sub>3</sub> protons). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 145.2, 142.9, 142.1, 141.3, 139.2, 131.7, 131.5, 131.1, 128.3, 128.0, 127.8, 127.3, 127.0, 120.3, 98.6, 84.9, 61.2, 55.6, 32.2, 32.2, 30.0.

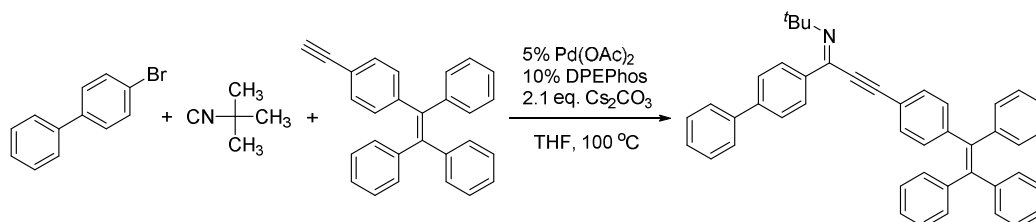
**P1b/2a/3a.** Yellow powder; yield 93% (Table 2, entry 3).  $M_w = 13\,200$ ;  $M_w/M_n = 1.59$ . IR (neat),  $\nu$  (cm<sup>-1</sup>): 3058, 2967, 2198, 2250, 1669, 1582, 1553, 1494, 1402, 1360, 1291, 1202, 1173. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.84 (4H, aromatic protons), 7.36–7.26 (4H, aromatic protons), 7.22–6.96 (28H, aromatic protons), 1.51 (18H, CH<sub>3</sub> protons). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 146.9, 145.7, 145.1, 143.6, 142.8, 141.2, 137.5, 131.6, 131.5, 131.4, 131.1, 128.2, 128.0, 127.8, 127.3, 126.9, 126.7, 120.1, 99.1, 84.5, 57.0, 29.7.

**P1c/2a/3a.** Yellow powder; yield 86% (Table 2, entry 4).  $M_w = 30\,500$ ;  $M_w/M_n = 1.99$ . IR (neat),  $\nu$  (cm<sup>-1</sup>): 3057, 2961, 2928, 2859, 2199, 1668, 1587, 1567, 1505, 1462, 1360, 1295, 1199, 1209. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.09–7.97 (4H, aromatic protons), 7.70 (2H, aromatic protons), 7.44–7.30 (4H, aromatic protons), 7.44–7.30 (4H, aromatic protons), 7.23–6.97 (14H, aromatic protons), 2.00 (4H, CH<sub>2</sub> protons), 1.57 (18H, CH<sub>3</sub> protons), 1.13–0.92 (16H, CH<sub>2</sub> protons), 0.72 (6H, CH<sub>3</sub> protons). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 151.5, 147.4, 145.2, 142.9, 142.5, 141.3, 139.1, 131.7, 131.5, 131.2, 128.3, 127.3, 126.5, 122.0, 120.5, 119.8, 98.9, 85.2, 57.1, 55.2, 40.3, 31.6, 29.8, 23.9, 22.7, 14.2.

**P1d/2a/3a.** Yellow powder; yield 82% (Table 2, entry 5).  $M_w = 14\,300$ ;  $M_w/M_n = 1.76$ . IR (neat),  $\nu$  (cm<sup>-1</sup>): 3055, 2961, 2927, 2867, 2198, 1665, 1595, 1493, 1470, 1385, 1266, 1207. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.24–6.79 (20H, aromatic protons), 3.95 (4H, CH<sub>2</sub> protons), 1.90–0.67 (40H, CH<sub>2</sub> protons and CH<sub>3</sub> protons). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 150.9, 147.6, 144.8, 142.9, 141.2, 131.4, 131.0, 128.1, 127.2, 114.5, 98.7, 86.1, 69.5, 57.5, 31.7, 29.7, 29.5, 25.8, 22.6, 14.2.

**P1d/2a/3b.** Yellow powder; yield 78% (Table 2, entry 6).  $M_w = 20\,800$ ;  $M_w/M_n = 1.95$ . IR (neat),  $\nu$  (cm<sup>-1</sup>): 3034, 2959, 2928, 2868, 2198, 1662, 1590, 1493, 1467, 1410, 1386, 1269, 1210. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.71–7.39 (8H, aromatic protons), 7.09–6.88 (2H, aromatic protons), 4.18–3.80 (4H, CH<sub>2</sub> protons), 2.02–0.62 (40H, CH<sub>2</sub> protons and CH<sub>3</sub> protons). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 151.1, 147.6, 141.0, 132.2, 127.2, 127.0, 114.5, 98.1, 86.7, 69.6, 57.6, 31.7, 29.7, 29.6, 25.9, 22.6, 14.1.

**Scheme S1.** Preparation of model compound **4**.

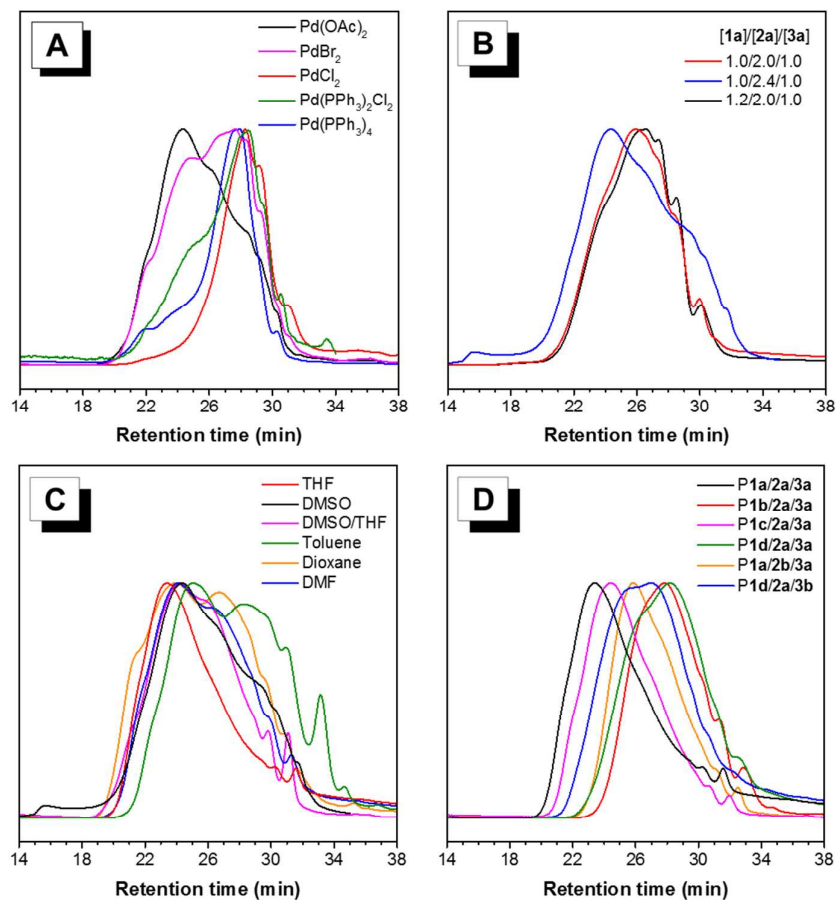


**Model Reaction.** The experimental procedure was similar to that for preparing **P1a/2a/3a**. Yellow solid was obtained in yield 83% after purification by column chromatography.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.13 (d,  $J = 8.3$  Hz, 2H), 7.63 (d,  $J = 8.1$  Hz, 4H), 7.46 (t,  $J = 7.6$  Hz, 2H), 7.41–7.30 (m, 3H), 7.22–6.95 (m, 17H), 1.55 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 146.8, 145.7, 143.5, 143.4, 143.3, 142.8, 142.3, 140.8, 140.1, 138.7, 131.7, 131.5, 131.5, 131.4, 131.2, 128.9, 128.1, 128.0, 127.8, 127.7, 127.3, 127.0, 126.9, 126.8, 119.8, 99.4, 84.4, 77.5, 57.1, 29.7. HRMS (MALDI–TOF):  $m/z$   $[\text{M}+\text{H}^+]$ : calcd for  $\text{C}_{45}\text{H}_{38}\text{N}$ , 592.2999; found 592.3021.

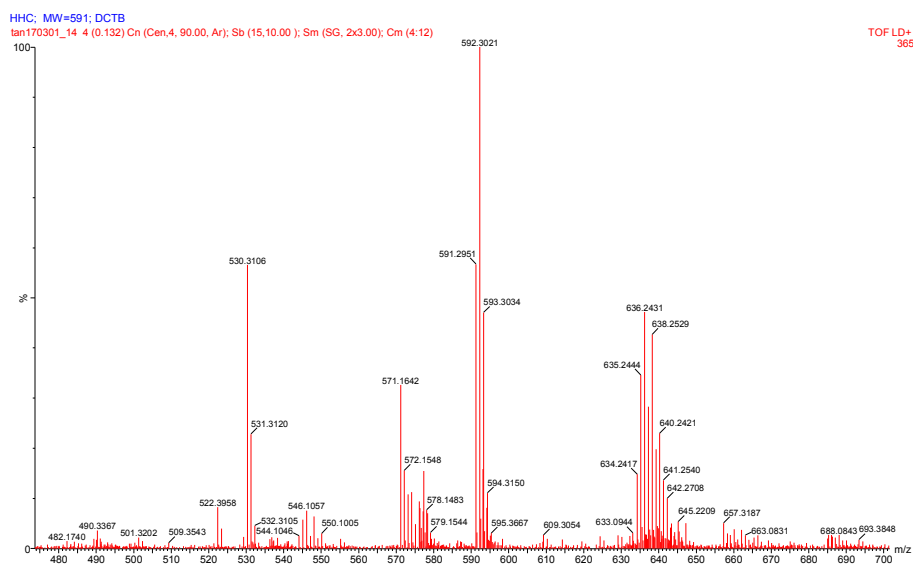
**Table S1.** Effects of different catalysts on the polymerization.<sup>a</sup>

entry	catalyst	yield (%)	$M_w^b$	$M_w/M_n^b$	$DP_n^c$
1	$\text{Pd}(\text{PPh}_3)_4$	70	7900	1.4	8
2	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	68	15600	2.4	9
3	$\text{PdCl}_2$	66	5300	1.3	6
4	$\text{PdBr}_2$	74	25400	3.4	11
5 <sup>c</sup>	$\text{Pd}(\text{OAc})_2$	71	33000	3.0	16

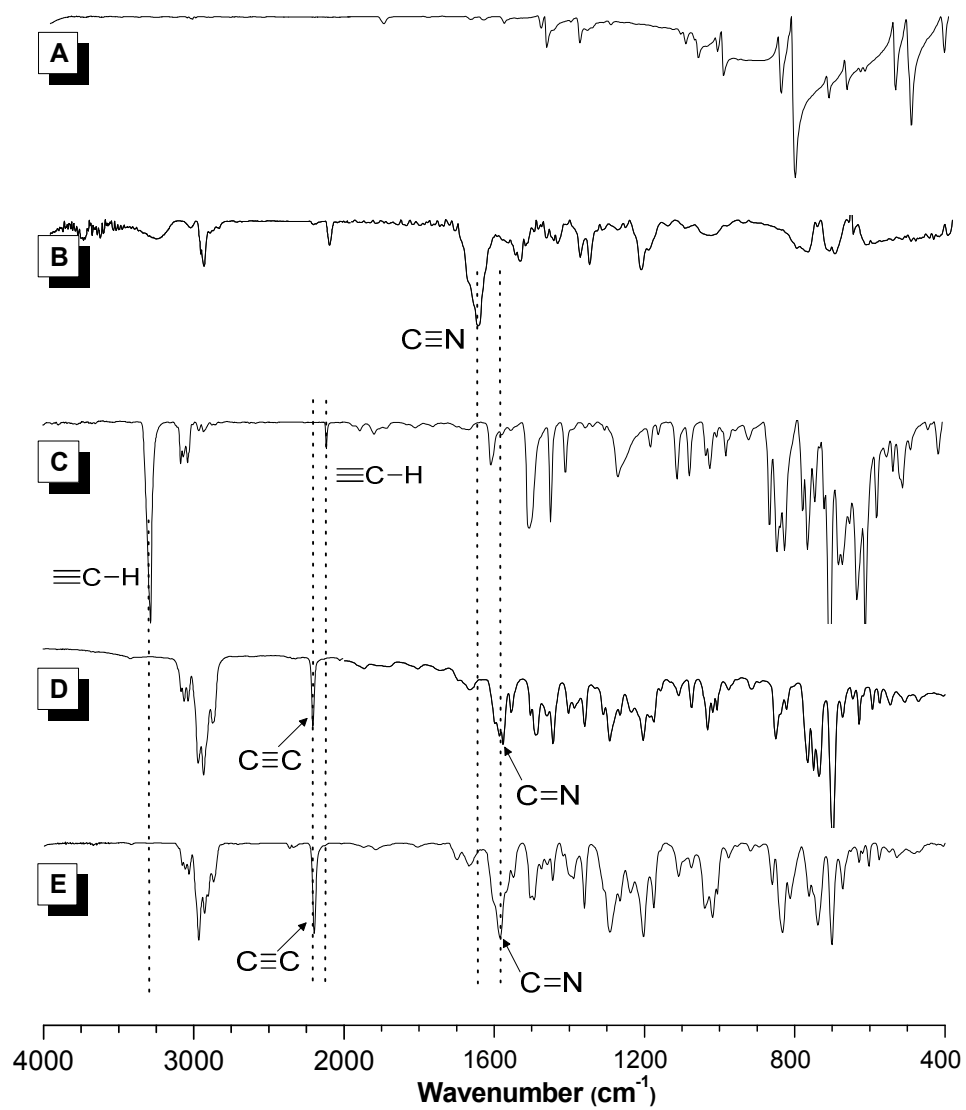
<sup>a</sup>Carried out in DMSO under nitrogen in the presence of [Pd], DPEPhos and  $\text{Cs}_2\text{CO}_3$  at 100 °C for 18 h.  $[\mathbf{3a}] = 0.1$  M,  $[\text{Pd}] = 5$  mol %,  $[\text{DPEPhos}] = 10$  mol %,  $\text{Cs}_2\text{CO}_3 = 2.1$  equiv. <sup>b</sup>Determined by GPC on the basis of a polystyrene calibration. <sup>c</sup>Data taken from Table 1, entry 2. <sup>c</sup> $DP_n = M_n/M_0$ .  $M_0$  is the molecular weight of repeating unit.



**Figure S1.** GPC traces for (A) different catalysts, (B) different feed ratio of [1a]/[2a]/[3a], (C) different solvents, and (D) different monomers.

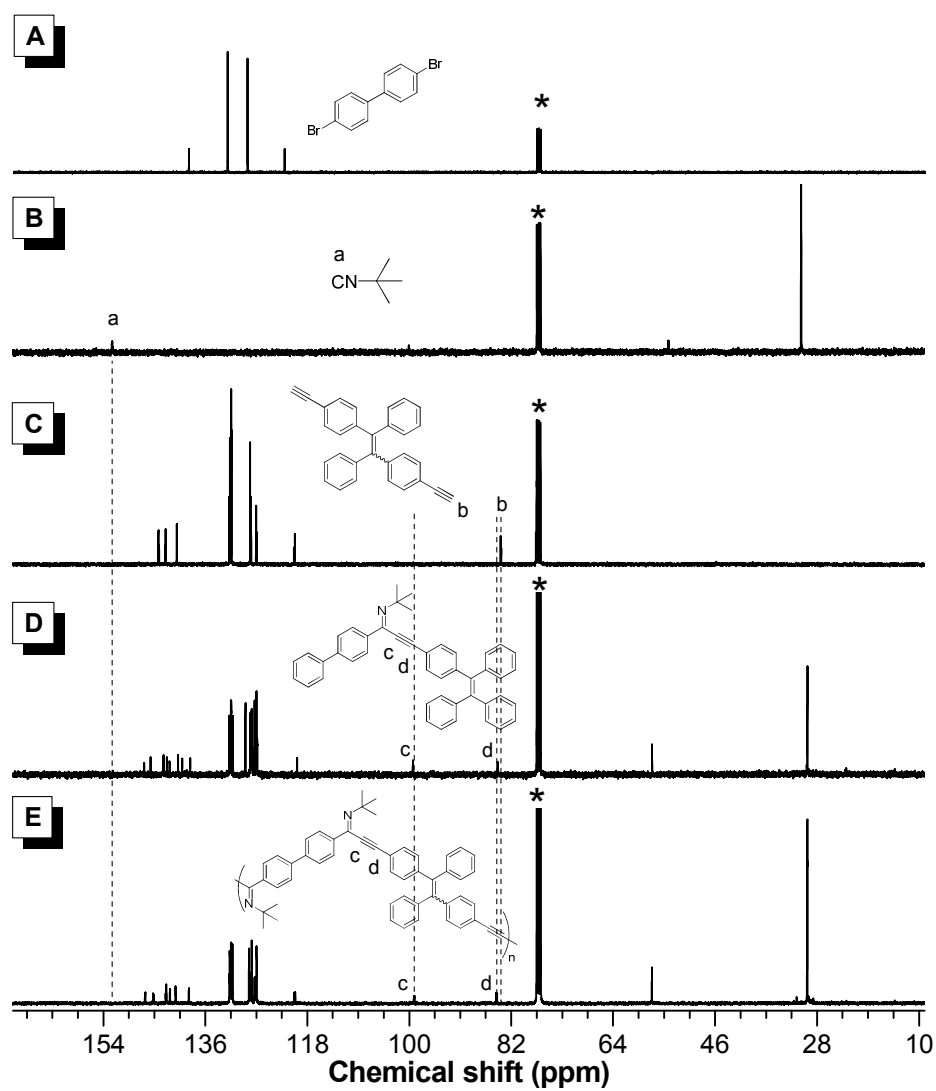


**Figure S2.** High resolution mass spectrum of model compound 4.

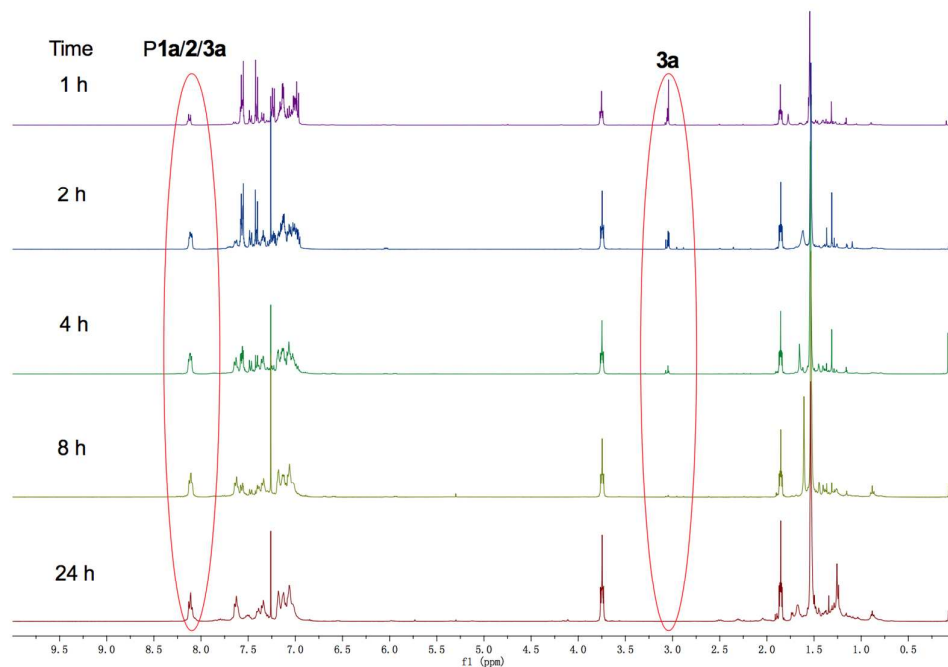


**Figure S3.** IR spectra of (A) **1a**, (B) **2a**, (C) **3a**, (D) **4**, and (E) **P1a/2a/3a**.

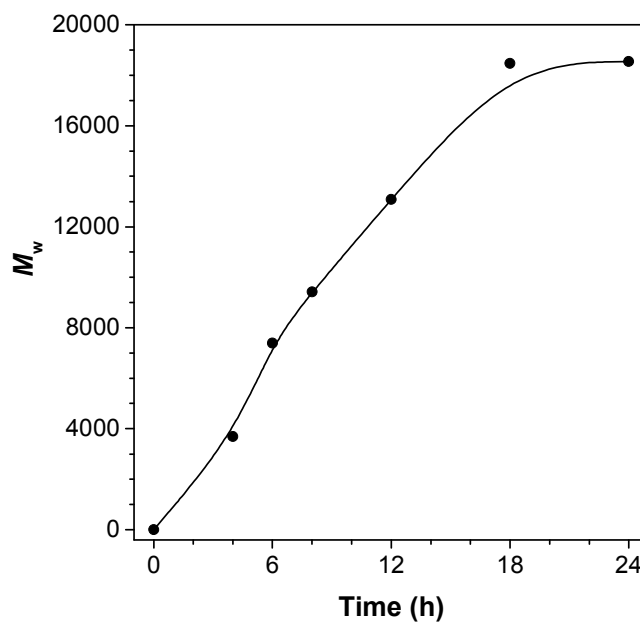




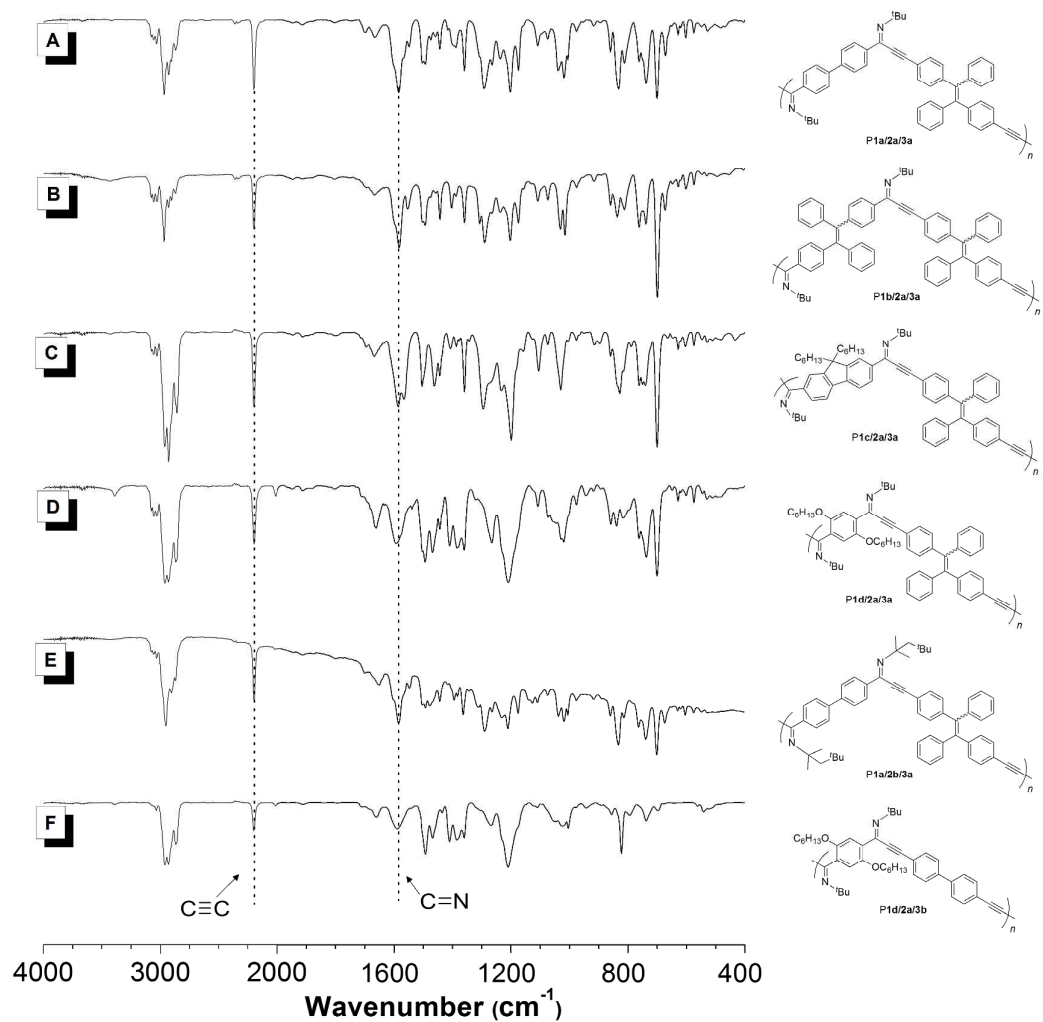
**Figure S4.**  $^{13}\text{C}$  NMR spectra of (A) 1a, (B) 2a, (C) 3a, (D) 4, and (E) P1a/2a/3a in  $\text{CDCl}_3$ . The solvent peaks were marked with asterisks.



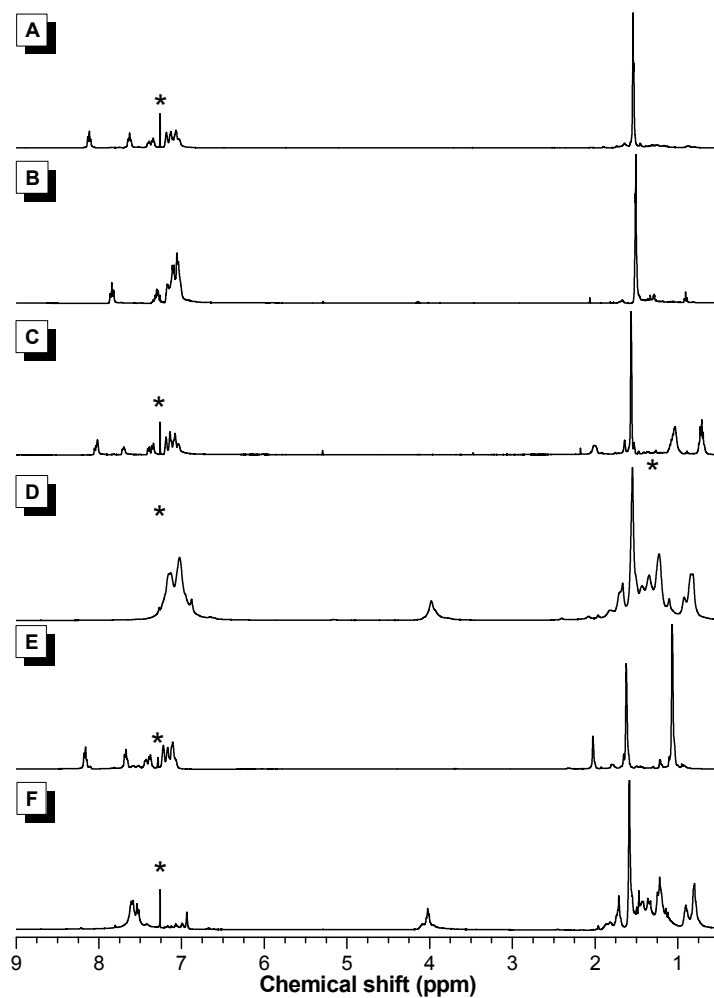
**Figure S5.**  $^1\text{H}$  NMR spectra of the polymerization mixtures at different times in  $\text{CDCl}_3$ .



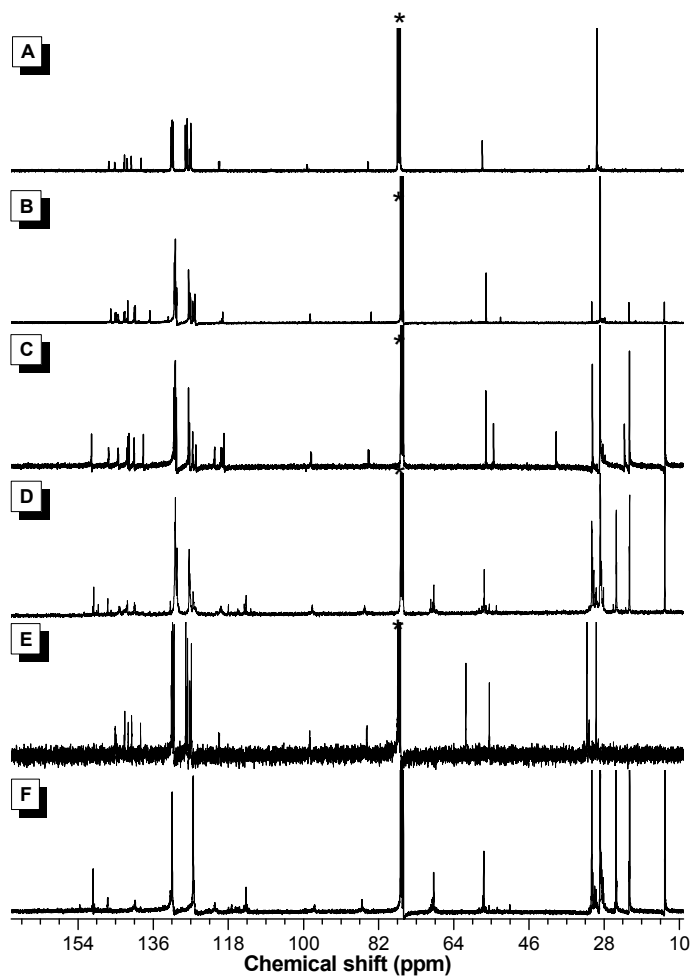
**Figure S6.**  $M_w$  against polymerization time.



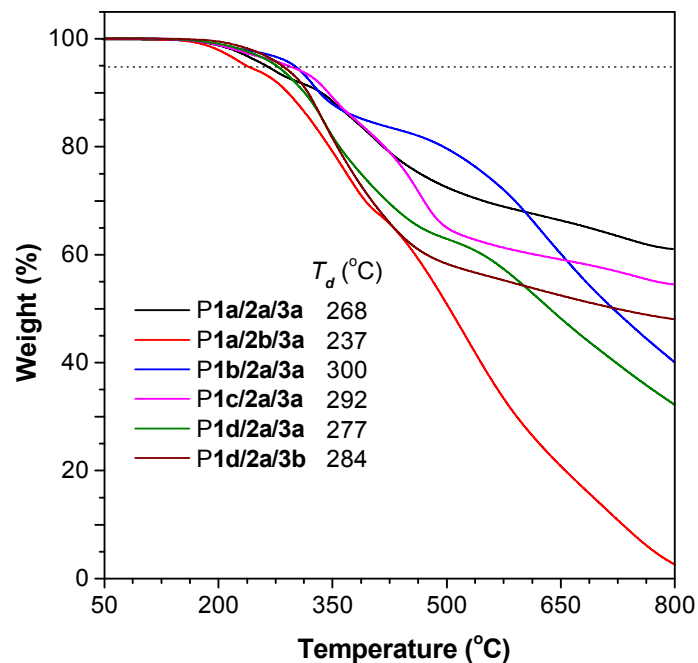
**Figure S7.** IR spectra of (A) P1a/2a/3a, (B) P1b/2a/3a, (C) P1c/2a/3a, (D) P1d/2a/3a (E) P1a/2b/3a, and (F) P1d/2a/3b.



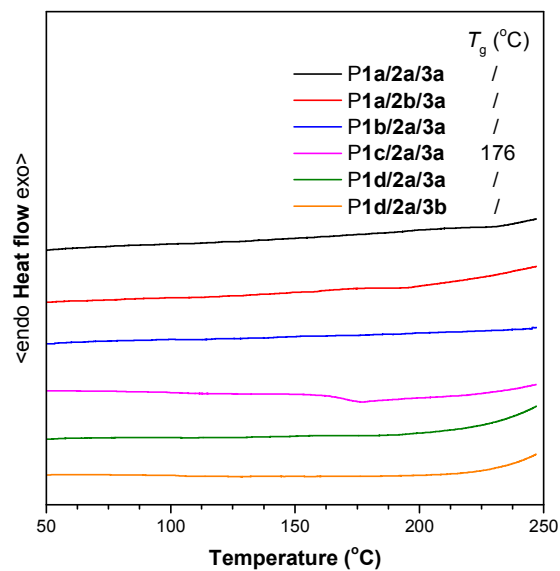
**Figure S8.**  $^1\text{H}$  NMR spectra of (A) P1a/2a/3a, (B) P1b/2a/3a, (C) P1c/2a/3a, (D) P1d/2a/3a (E) P1a/2b/3a, and (F) P1d/2a/3b in  $\text{CDCl}_3$ . The solvent peaks were marked with asterisks.



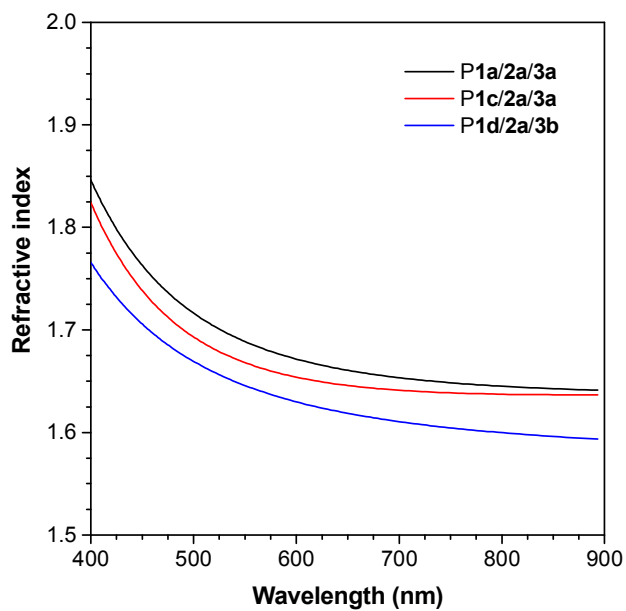
**Figure S9.**  $^{13}\text{C}$  NMR spectra of (A) P1a/2a/3a, (B) P1b/2a/3a, (C) P1c/2a/3a, (D) P1d/2a/3a (E) P1a/2b/3a, and (F) P1d/2a/3b in  $\text{CDCl}_3$ . The solvent peaks were marked with asterisks.



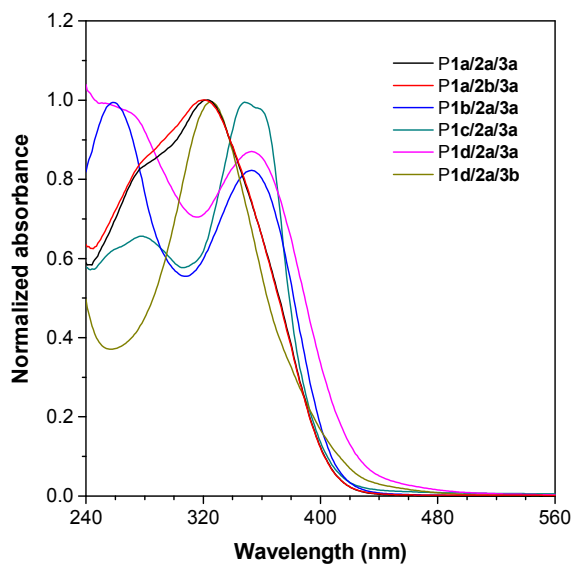
**Figure S10.** TGA thermograms of P1/2/3 recorded under nitrogen at a heating rate of 10 °C/min.



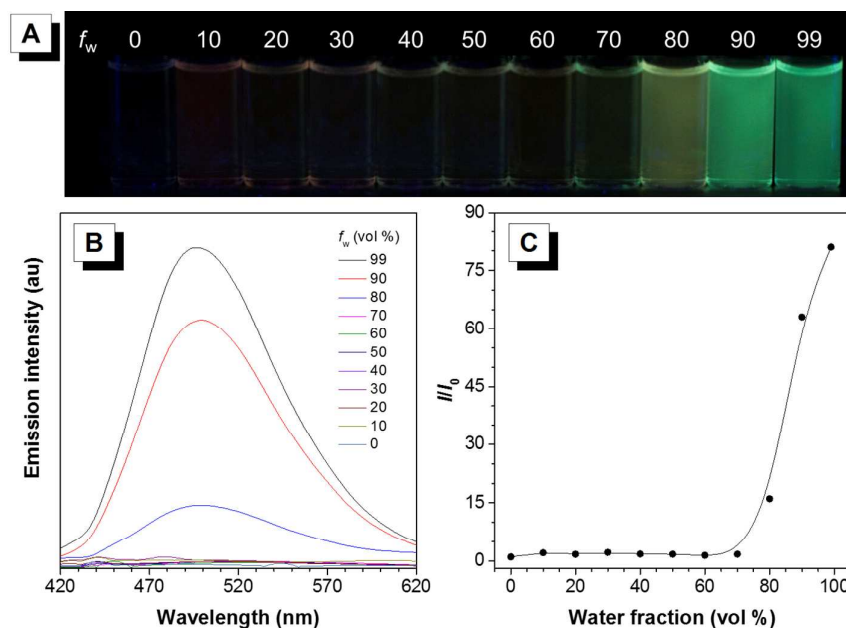
**Figure S11.** DSC thermograms of P1/2/3 recorded under nitrogen during the second heating cycle at a heating rate of 10 °C/min.



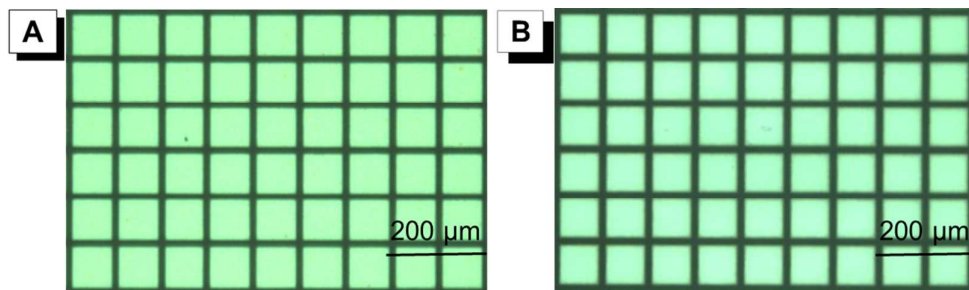
**Figure S12.** Wavelength-dependent refractive indices of thin films of P1/2/3.



**Figure S13.** Absorption spectra of P1/2/3 in THF solutions. Concentration: 10  $\mu$ M.

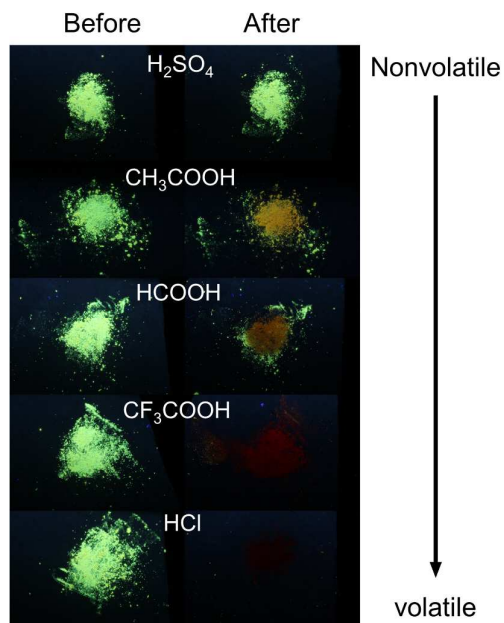


**Figure S14.** (A) Photographs of model compound **4** in THF/water mixtures with different water fractions ( $f_w$ ) taken under 365 nm UV irradiation from a hand-held UV lamp. (B) PL spectra of **4** in THF/water mixtures with different water fractions. Solution concentration: 10  $\mu$ M; excitation wavelength: 390 nm. (C) Plot of relative emission intensity ( $I/I_0$ ) versus the composition of the THF/water mixture of **4**, where  $I_0$  = peak intensity in pure THF.

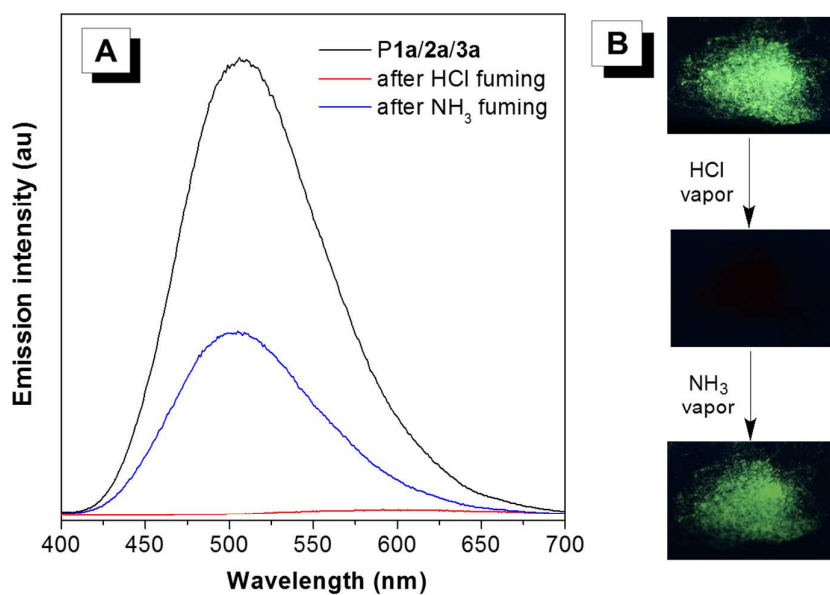


**Figure S15.** Two-dimensional fluorescent photopatterns generated by photolithography of films of (A) P1a/2a/3a and (B) P1c/2a/3a through copper masks taken under UV irradiation. Excitation wavelength: 330–385 nm.



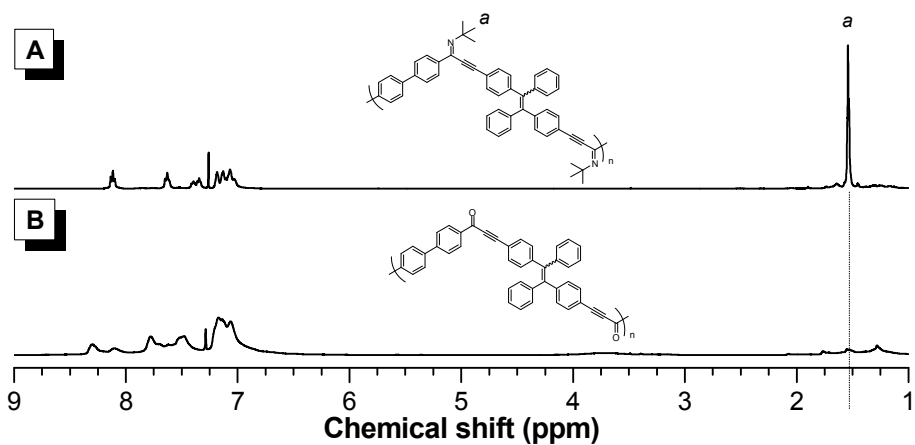
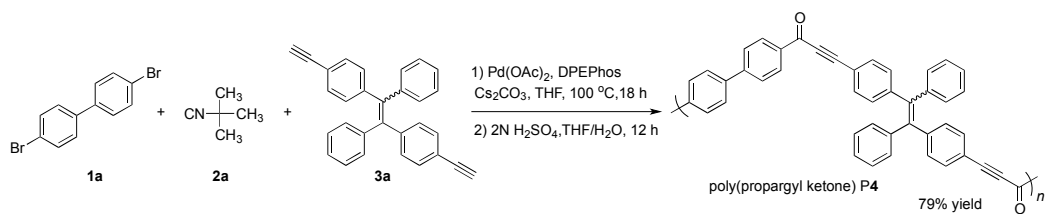


**Figure S16.** Photographs of different acids fuming of **P1a/2a/3a** under 365 nm hand-held UV lamp.

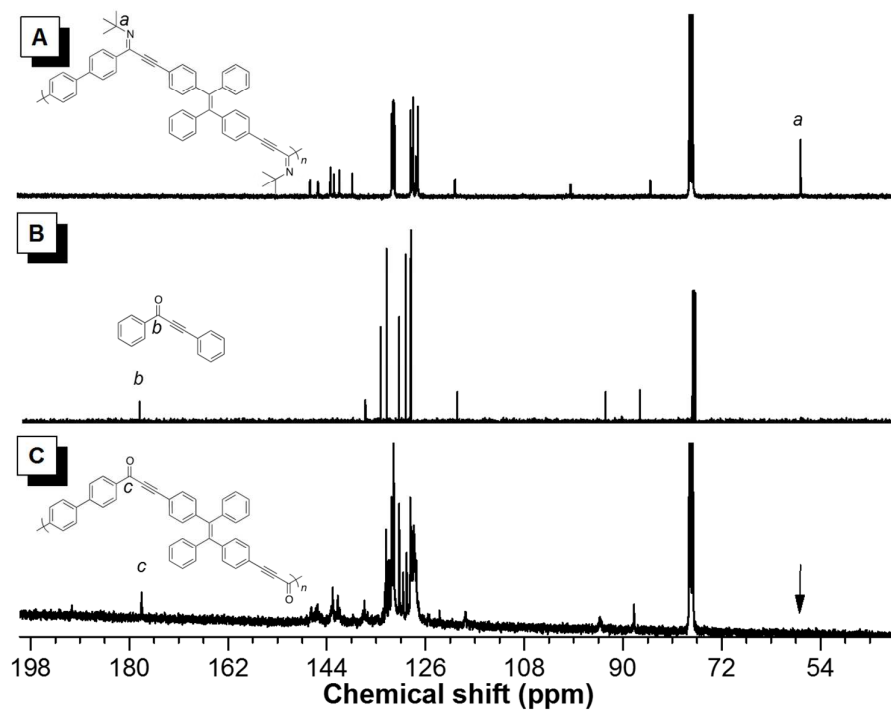


**Figure S17.** HCl and  $\text{NH}_3$  fuming of **P1a/2a/3a**. (A) PL spectra and (B) photographs taken under 365 nm UV hand-held UV lamp.

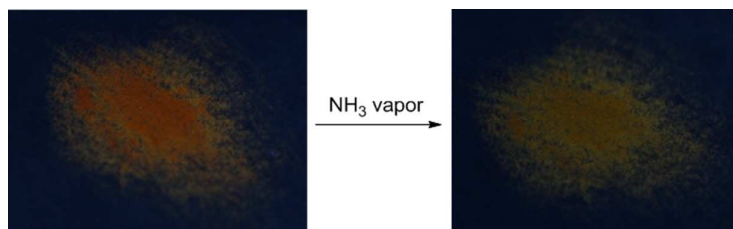
**Scheme S2.** Post transformation of P1a/2a/3a by strong acid.



**Figure S18.**  $^1\text{H}$  NMR spectra for post transformation of P1a/2a/3a in  $\text{CDCl}_3$ .



**Figure S19.**  $^{13}\text{C}$  NMR spectra for post transformation of P1a/2a/3a in  $\text{CDCl}_3$ .



**Figure S20.** Photographs of  $\text{NH}_3$  fuming of poly(propargyl ketone) P4 under 365 nm hand-held UV lamp.

## References

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