Synthesis and Characterization of Poly (iminofuran-arylene) Containing Bromomethyl Groups Linked at the 5-Position of a Furan Ring via the Multicomponent Polymerizations of Diisocyanides, Dialkylacetylene Dicarboxylates, and Bis(2-bromoacetyl)biphenyl

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1 Experimental

1.1 Materials

Unless otherwise stated, all chemicals were obtained from commercial suppliers and used without further purification. The diisocyanide **1a-c** monomers were prepared by our previous work. Dimethyl acetylenedicarboxylate, diethyl acetylenedicarboxylate, cyclohexyl isocyanide, and 2-Bromoacetophenonewere were purchased from Energy Chemical. 4,4'-Bis(2-bromoacetyl)biphenyl was purchased from Ark. Chloroform-d was purchased from Innochem.

1.2 Equipment

The weight-average molecular weights (M_w) and polydispersity indices (M_w/M_n) of the polymers were obtained using a gel permeation chromatography (GPC) system equipped with a Waters 1515 isocratic HPLC pump and a Waters 2414 refractive index detector. A polystyrene standard was utilized, and THF was used as the eluent at a flow rate of 1.0 mL min^{-1}. The Fourier transform infrared (FT-IR) spectra were measured on a Bruker (ALPHA) spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer. The mass spectra were collected by using a Finnigan BIFLEX III mass spectrometer. The fluorescence spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer. The absolute quantum yields were collected on a FluoroMax-4 (Horiba Jobin Yvon) fluorometer equipped an integrated sphere. The UV-Vis spectra were recorded on a TU-1901 double beam UV-Vis spectrophotometer. The refractive indices were measured on a SENTECH SE 850 DUV Spectroscopic Ellipsometer.

1.3 Polymerization

The multicomponent polymerization (MCP) procedure is described using entry 2 in Table S1 as an example. Diisocyanide **1a** (67.0 mg, 0.5 mmol), DAAD **2b** (170.0 mg, 1.0 mmol), 4,4'-bis(2-bromoacetyl)biphenyl **3** (160.0 mg, 0.4 mmol) and toluene (6 mL) were added to a 30 mL Schlenk tube equipped with a magnetic stir bar. The reaction mixture was heated at 100 °C for 6 h under an air atmosphere. The precipitate was cooled to room temperature and poured into 200 mL of n-hexane under vigorous stirring. Then, the precipitate was filtered, washed with n-hexane, and dried to a constant weight in a vacuum at 60 °C to yield **P1a2b3**. The MCP of the other PIFAs followed the same procedure under various conditions.

Table S1. Effect of the monomer concentration on the MCPs [a]

Entry	[**1a**] (M)	[**3**] (M)	Yield (%)	M_w [b]	$Đ$ [b]	Solubility [c]
1	0.08	0.04	62.6	9200	2.04	○
2	0.08	0.06	80.5	20400	1.92	○
3	0.08	0.08	**73.6**	33900	3.64	○
4	0.16	0.12	76.0	Gel	-	-
5	0.04	0.03	67.1	8400	2.47	○

[a] Carried out in toluene under air at 100 °C for 6 h, **1a** : **2b** = 1 : 2. [b] Determined by GPC in THF on the basis of a linear polystyrene as the calibration standard. M_w = weight-average molecular weight; $Đ = M_w/M_n$, where M_n = number-average molecular weight. [c] ○ = completely soluble in DCM, THF, and DMF.

Table S2. Time course on the MCPs[a]

Entry	Time (h)	Yield (%)	M_w	$Đ$	Solubility
1	3	56.3	13300	2.08	○
2	6	80.5	20400	1.92	○
3	9	82.1	20700	2.59	○

[a] Carried out in toluene under air at 100 °C, [**1a**] = 0.08 M, **1a** : **2b** = 1 : 2 , [**3**] = 0.06 M.

Table S3. Effect of temperature on the MCPs [a]

Entry	Temperature(℃)	Yield (%)	M_w	$Đ$	Solubility
1	60	62.1	4700	1.68	○
2	80	73.9	6200	1.66	○
3	100	80.5	20400	1.92	○

[a] Carried out in toluene under air for 6 h, [**1a**] = 0.08 M, **1a** : **2b** = 1 : 2 , [**3**] = 0.06 M.

1.4 Synthetic route to model compound MC

The synthetic route is shown in Scheme 2. Dimethyl acetylenedicarboxylate **2b** (0.1700 g, 1.0 mmol), 2-Bromoacetophenone **4** (0.4000 g, 1.6 mmol) and 6 mL

toluene were added to a 50 mL Schlenk tube equipped with a magnetic stir bar. Then, **1a** (0.1340 g, 1.0 mmol) dissolved in 6 mL toluene was slowly added. The reaction mixture was heated in an oil bath at 100 °C for 6 h under constant stirring under an air atmosphere and cooled to room temperature. The organic layer was combined and washed with DCM and water, and then dried over $MgSO_4$ for an hour. The **MC** was separated by flash column chromatograph..

1.5 Characterization data of MC

White powder of **MC** was obtained in 76.9% yield. υ (cm^{-1}) = 2981, 2933, 2865, 1721, 1682, 1654, 1283, 1252, 1093,1034; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.44 (d, *J* = 6.8 Hz, 4H), 7.41-7.37 (m, 6H), 4.53-4.51 (d, *J* = 10.8 Hz, 2H), 4.39-4.34 (m, 4H), 4.28-4.18 (m, 4H), 4.13-4.10 (d, *J* = 10.8 Hz, 2H), 3.76 (s, 2H), 2.02-1.92 (m, 4H), 1.62-1.52 (m, 4H), 1.36-1.33 (t, *J* = 6.8 Hz, 6H), 1.26-1.23 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.73, 160.74, 154.80, 142.85, 137.47, 136.96, 129.11, 128.87, 125.85, 90.01, 62.19, 62.09, 56.19, 36.90, 31.83, 31.22, 14.08, 13.80. HRMS (ESI, *m/z*) Calcd for $[M+H]^+$ $C_{40}H_{45}O_{10}N_2Br_2$: 871.1435, Found: 871.1410, error: -2.9 ppm.

1.6 Characterization data of PIFAs

P1a2a3: Light yellow solid; yield 83.2%. M_w: 12 000; $Đ$: 2.50. IR, υ (cm^{-1}) = 2951, 2857, 1726, 1678, 1436, 1352, 1284, 1217, 1093, 1030, 999; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.51 (aromatic protons), 4.58-4.55 (CH_2Br protons), 4.17-4.14 (CH_2Br protons), 3.92-3.80, 2.02-1.56 ; ^{13}C NMR (100 MHz, $CDCl_3$): 162.10, 161.08, 154.68, 142.89, 140.88, 137.61, 136.15, 129.69, 127.59, 126.42, 89.94, 56.33, 53.12-53.01, 36.71, 31.95, 31.25, 29.70.

P1a2b3: Light yellow solid; yield 80.5%. M_w: 20 400; $Đ$: 1.92. IR, υ (cm^{-1}) = 2980, 2934, 2867, 1721, 1680, 1283, 1248, 1093, 1030; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.52 (aromatic protons), 4.55-4.53 (CH_2Br protons), 4.39-4.23, 4.17-4.14 (CH_2Br protons), 3.79 (CH protons), 2.03-1.56, 1.37-1.25 (CH_3 protons); ^{13}C NMR (100 MHz, $CDCl_3$): 161.72, 160.75, 154.72, 142.63, 140.83, 137.61, 136.35, 127.50, 126.48, 89.89, 62.20, 56.23-56.13, 36.79, 31.91, 31.21-31.04, 14.09, 13.82.

P1b2a3: Light yellow solid; yield 76.4%. M_w: 21 800; $Đ$: 2.42. IR, υ (cm^{-1}) = 2925, 2849, 1727, 1680, 1436, 1352, 1285, 1215, 1091, 1029, 999; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.50 (aromatic protons), 4.57-4.54 (CH_2Br protons), 4.15-4.13 (CH_2Br protons), 3.92-3.80, 3.69 (CH protons), 1.95-0.86; ^{13}C NMR (100 MHz, $CDCl_3$): 162.12, 161.09, 154.44, 153.38, 142.79, 142.42, 140.83, 137.93, 137.61,

136.23, 129.68, 127.54, 126.42, 89.78, 57.50, 53.14-52.98, 36.67, 33.79-28.34.

P1b2b3: Light yellow solid; yield 74.8%. M_w: 24 300; $Đ$: 2.09. IR, υ (cm^{-1}) = 2979, 2925, 2851, 1723, 1682, 1372, 1340, 1283, 1211, 1093, 1032; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59-7.51 (aromatic protons), 4.54-4.51 (CH_2Br protons), 4.39-4.20, 4.16-4.13 (CH_2Br protons), 3.69 (CH protons), 1.96-0.98; ^{13}C NMR (100 MHz, $CDCl_3$): 161.72, 160.76, 154.51, 153.35, 142.57, 140.78, 137.57, 136.40, 127.46, 126.49, 89.74, 62.26, 62.10, 57.39, 36.79-28.27, 14.23, 14.08, 13.83.

P1c2a3: Yellow solid; yield 89.7%. M_w: 17 000; $Đ$: 2.50. IR, υ (cm^{-1}) = 2955, 1729, 1689, 1436, 1354, 1281, 1209, 1095, 1038, 995, 977; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.43 (aromatic protons), 6.89-6.84 (aromatic protons), 4.51-4.43 (CH_2Br protons), 3.97-3.64, 2.52, 2.13, 1.14; ^{13}C NMR (100 MHz, $CDCl_3$): 161.83, 160.83, 153.80, 144.23, 141.16, 140.89, 140.60, 137.16, 136.88, 135.62, 133.30, 129.66, 128.27-126.40, 91.29, 53.24, 41.08, 35.84, 25.82, 18.47, 13.97.

P1c2b3: Yellow solid; yield 87.2%. M_w: 12 100; $Đ$: 1.96. IR, υ (cm^{-1}) = 2978, 1723, 1688, 1472, 1395, 1373, 1281, 1207, 1093, 1038; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.45 (aromatic protons), 6.90-6.85 (aromatic protons), 4.51-4.43 (CH_2Br protons), 4.30, 4.02-3.99, 3.83, 2.52, 2.14, 1.39-1.15; ^{13}C NMR (100 MHz, $CDCl_3$): 161.47, 160.46, 153.91, 143.93, 141.27-126.45, 91.26, 62.46, 41.13, 36.00, 25.82, 18.48, 14.19-13.83.

2 Post-functionalization of P1a2b3

P1a2b3 (200.0 mg), 1,4-bis(aminomethyl)benzene (136.0 mg, 1.0 mmol) and K_2CO_3 (138.0 mg, 1.0 mmol) were dissolved in 6 mL of *p-xylene*. The mixture was stirred at 130 ºC for 3 h and cooled to room temperature. The filtrate was added dropwise into hexane to obtain **P1a2b3-1**. Yield: 84%.

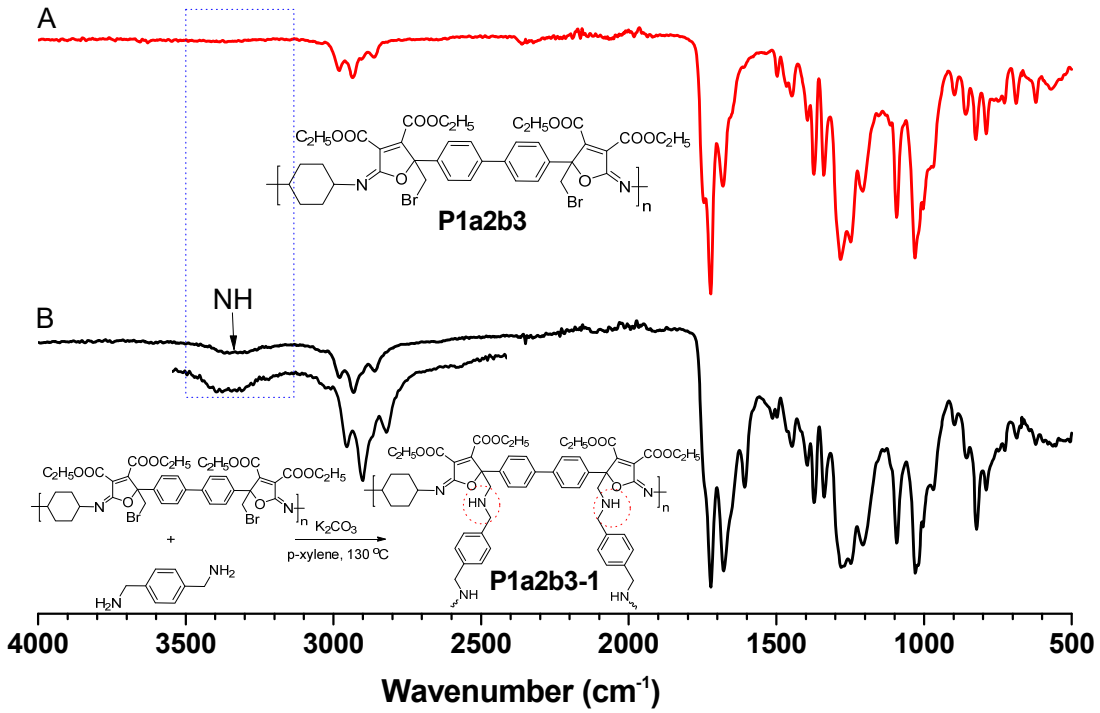


Figure S1. FT-IR spectra of (A) **P1a2b3**, and (B) **P1a2a3-1**.

P1a2b3 (200.0 mg), 1-benzylimidazole (158.0 mg, 1.0 mmol) and KI (16.6 mg, 0.1 mmol) were dissolved in 6 mL of *toluene*. The mixture was stirred at 100 ºC for 24 h and cooled to room temperature. The filtrate was added dropwise into hexane to obtain **P1a2b3-2**. Yield: 85%. Transformation degree: 41.6%.

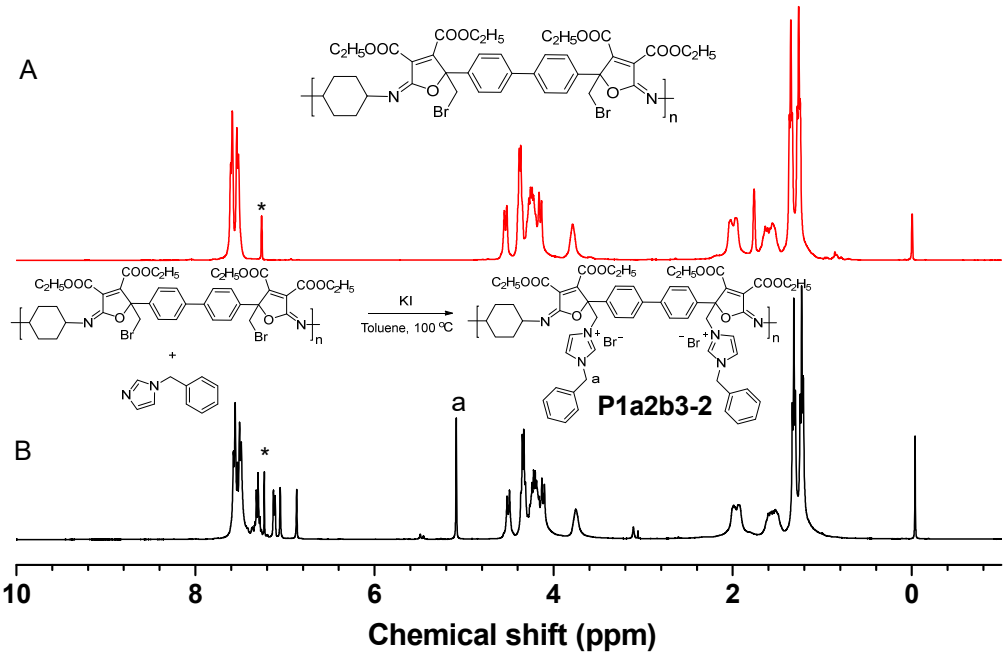


Figure S2. ^{1}H NMR spectra of (A) **P1a2b3**, and (B) **P1a2a3-4** in $CDCl_3$.

P1a2b3 (200.0 mg), NaN_3 (65.0 mg, 1.0 mmol) and KI (16.6 mg, 0.1 mmol) were dissolved in 6 mL of *DMF*. The mixture was stirred at 80 ºC for 12 h and cooled to room temperature. The mixture was extracted with DCM and water for three times. The organic layers were combined, and then dried over $MgSO_4$. The filtrate was added dropwise into hexane to obtain **P1a2b3-3**. Yield: 71%.

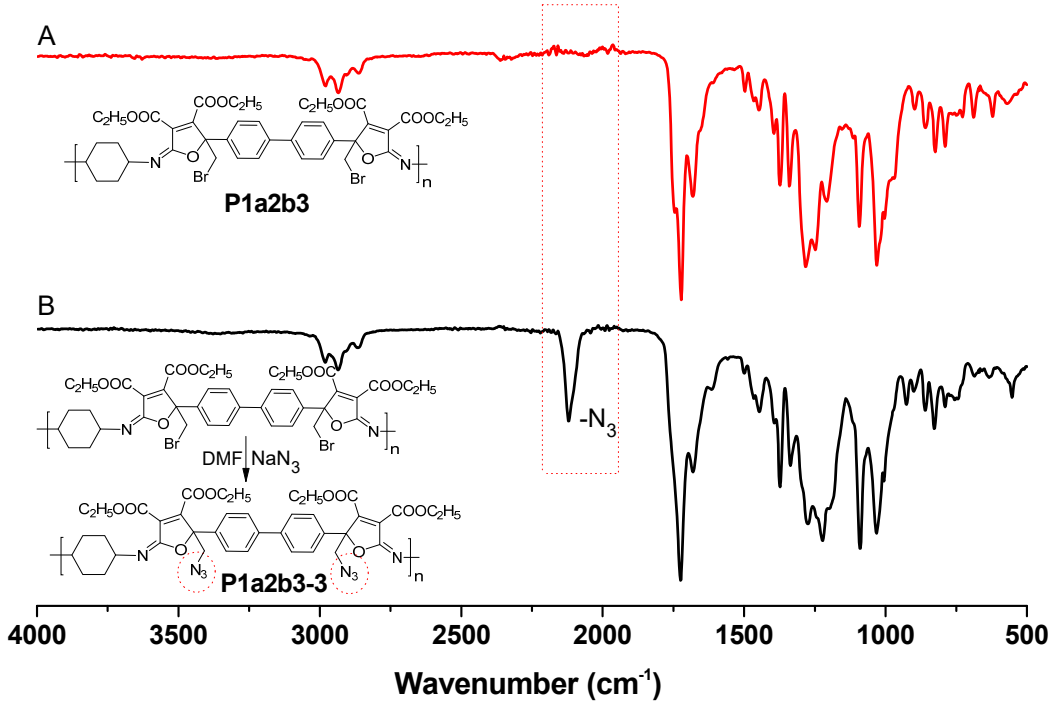


Figure S3. FT-IR spectra of (A) **P1a2b3**, and (B) **P1a2a3-3**.

P1a2b3-3 (100.0 mg) and 1-hexyne (41.0 mg, 0.5 mmol) were dissolved in 6 mL THF. An aqueous solution of sodium ascorbate (8.0 mg, 0.05 mmol) and copper (II) sulphate (4.0 mg, 0.025 mmol) was then added. The mixture was stirred 8 h at 60 ºC and cooled to room temperature. The reaction mixture was washed with water and extracted with DCM. The organic phase was separated, dried over $MgSO_4$, and concentrated to ~3 mL before the residue was added dropwise into hexane. The precipitate was filtered and dried in vacuum to give **P1a2b3-4**. Yield:74%. Transformation degree: 98.0%.

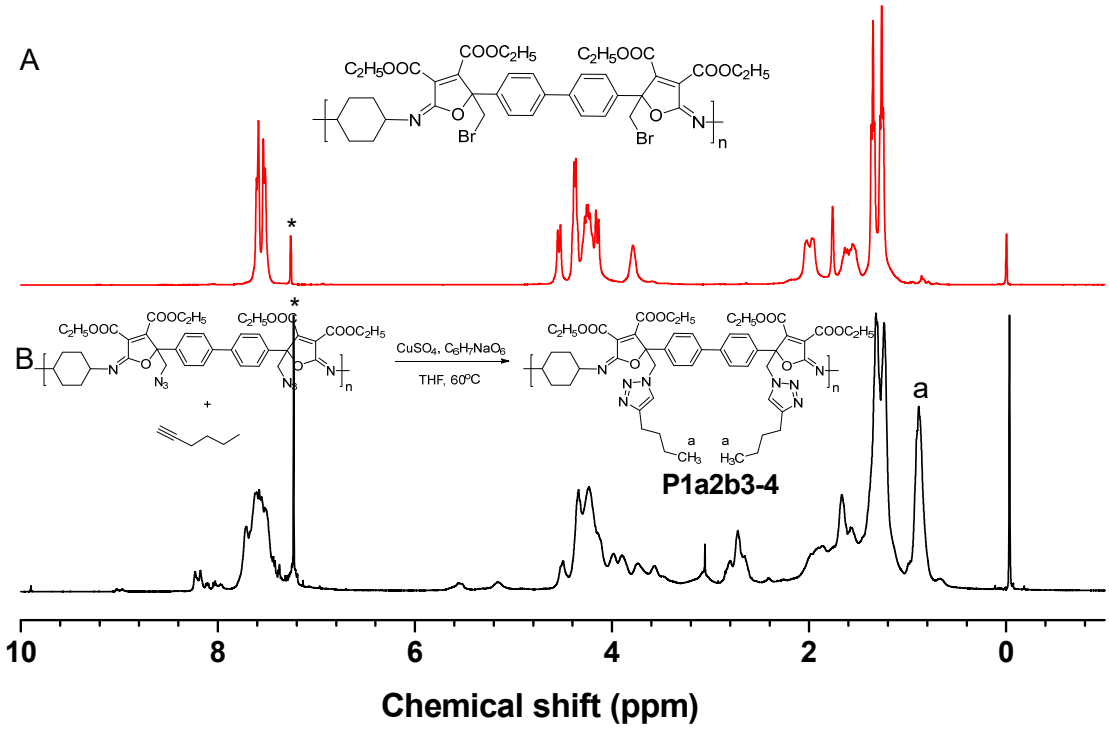


Figure S4. ^{1}H NMR spectra of (A) **P1a2b3**, and (B) **P1a2a3-4** in $CDCl_3$.

3 FT-IR spectra of PIFAs

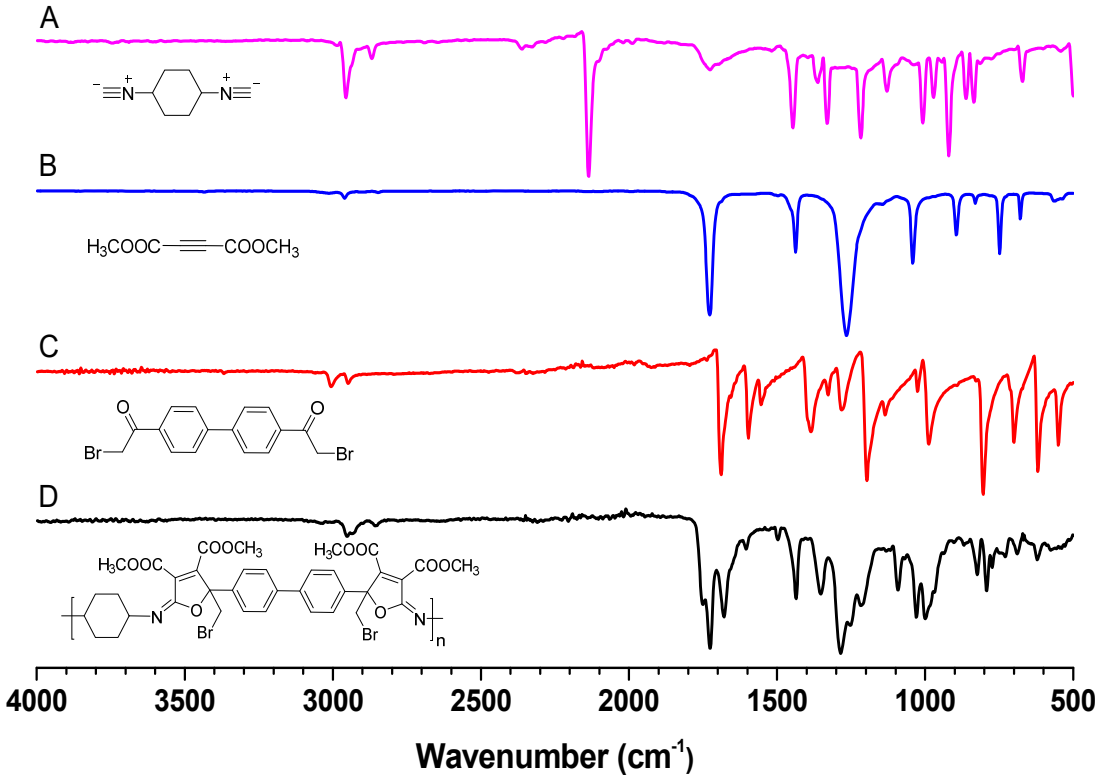


Figure S5. FT-IR spectra of (A) **1a**, (B) **2a**, (C) **3**, and (D) **P1a2a3**.

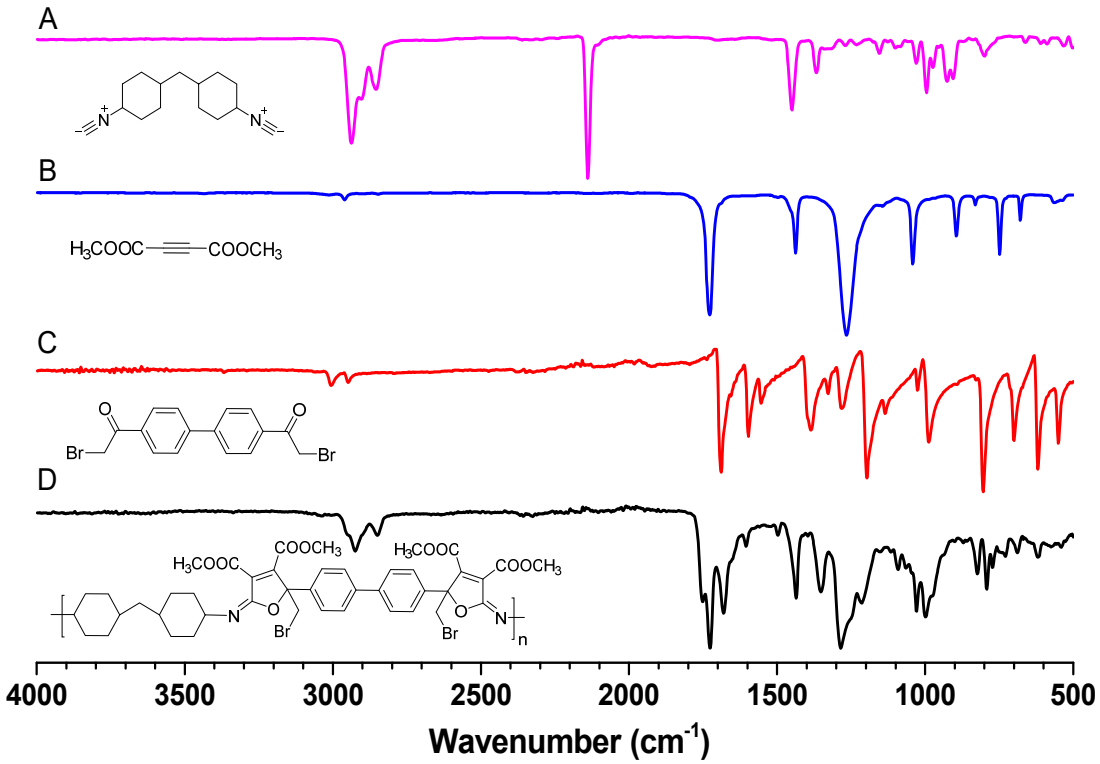


Figure S6. FT-IR spectra of (A) **1b**, (B) **2a**, (C) **3**, and (D) **P1b2a3**.

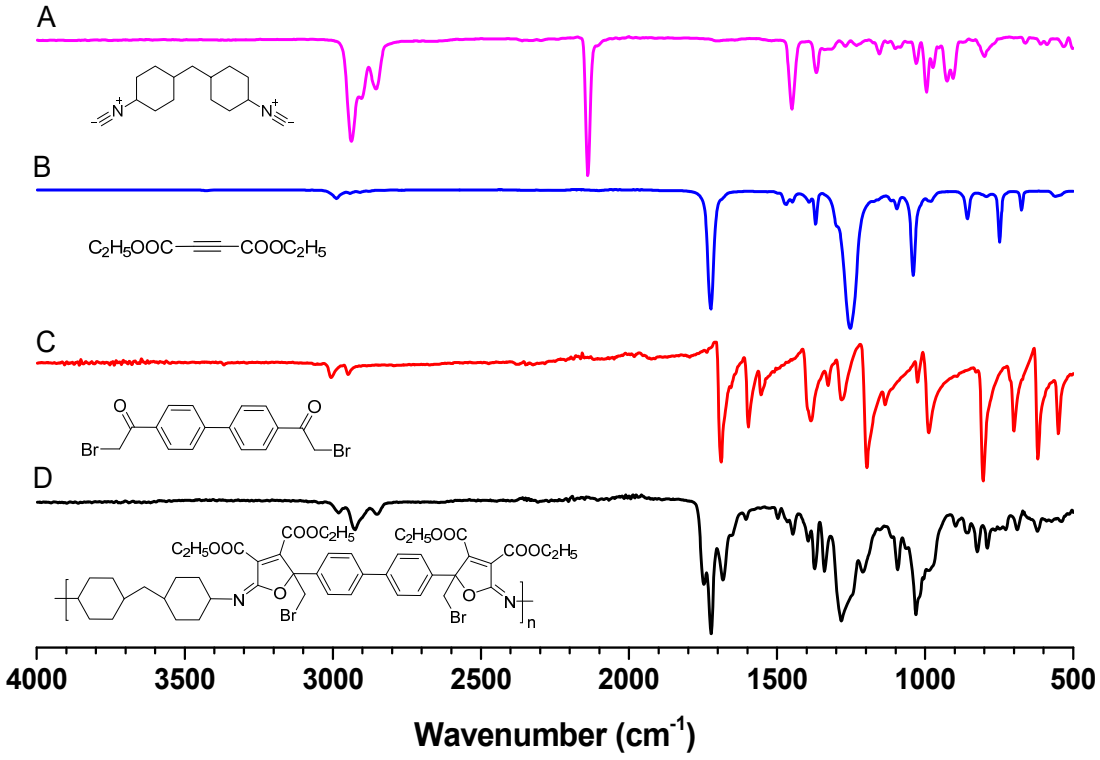


Figure S7. FT-IR spectra of (A) **1b**, (B) **2b**, (C) **3**, and (D) **P1b2b3**.

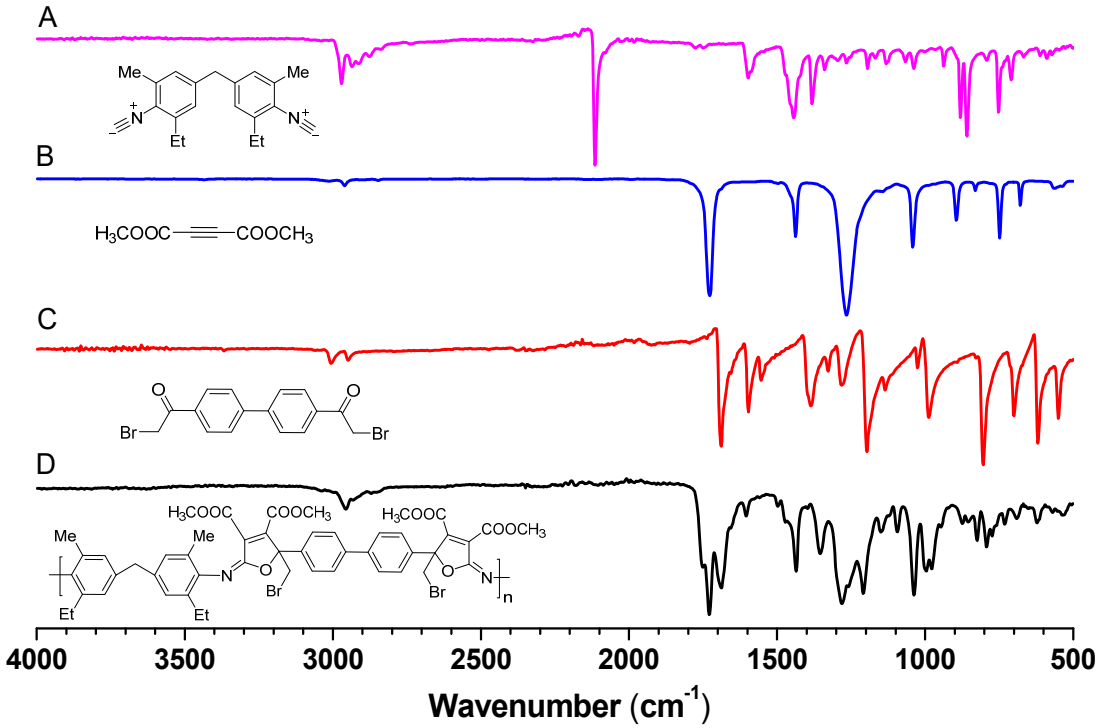


Figure S8. FT-IR spectra of (A) **1c**, (B) **2a**, (C) **3**, and (D) **P1c2a3**.

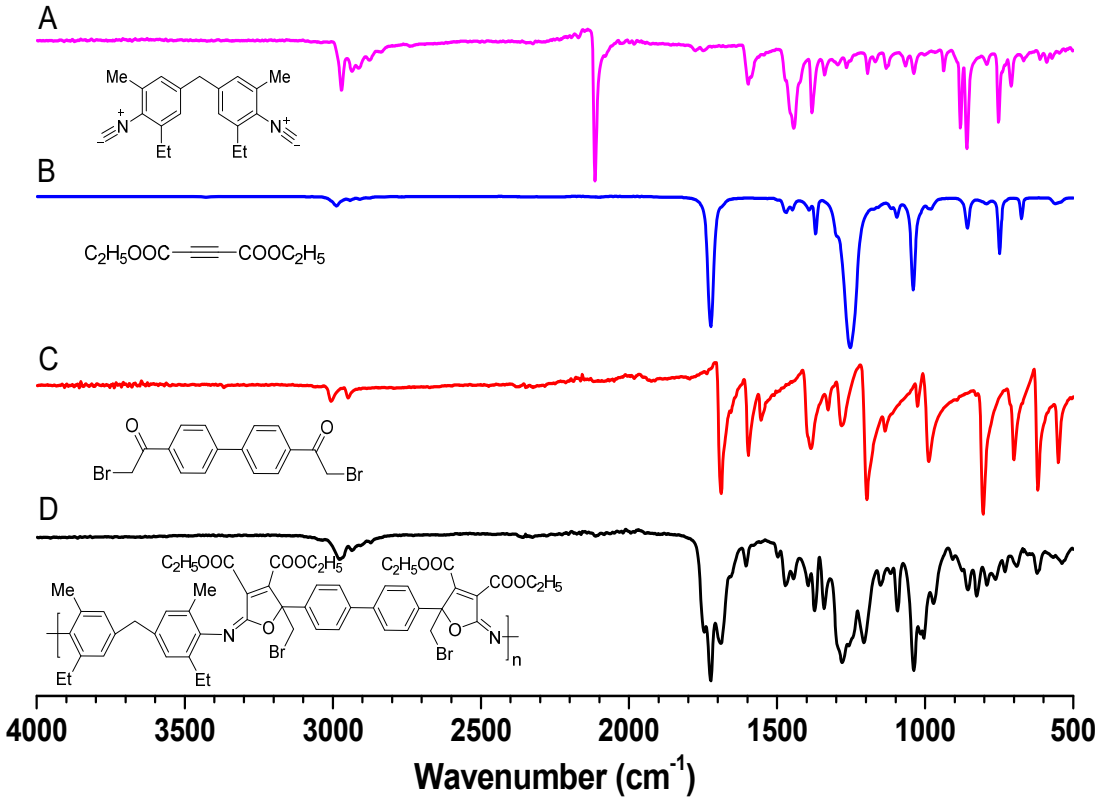


Figure S9. FT-IR spectra of (A) **1c**, (B) **2b**, (C) **3**, and (D) **P1c2b3**.

4 ^{1}H NMR spectra of PIFAs

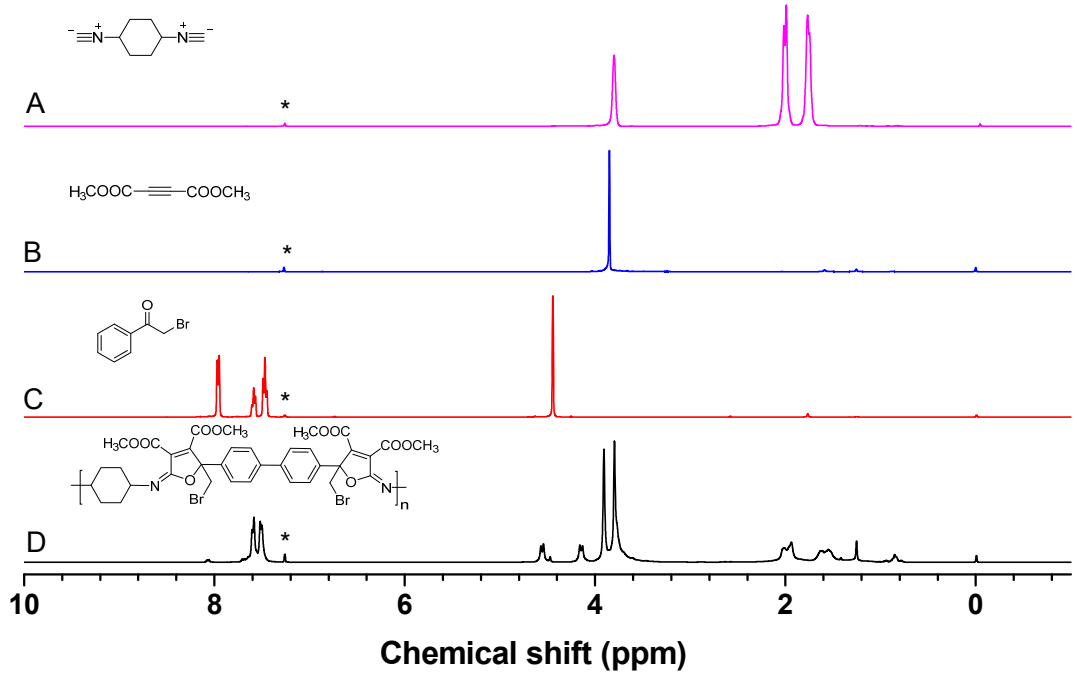


Figure S10. ^{1}H NMR spectra of (A) **1a**, (B) **2a**, (C) **4**, and (D) **P1a2a3** in $CDCl_3$. The solvent peaks are marked with asterisks.

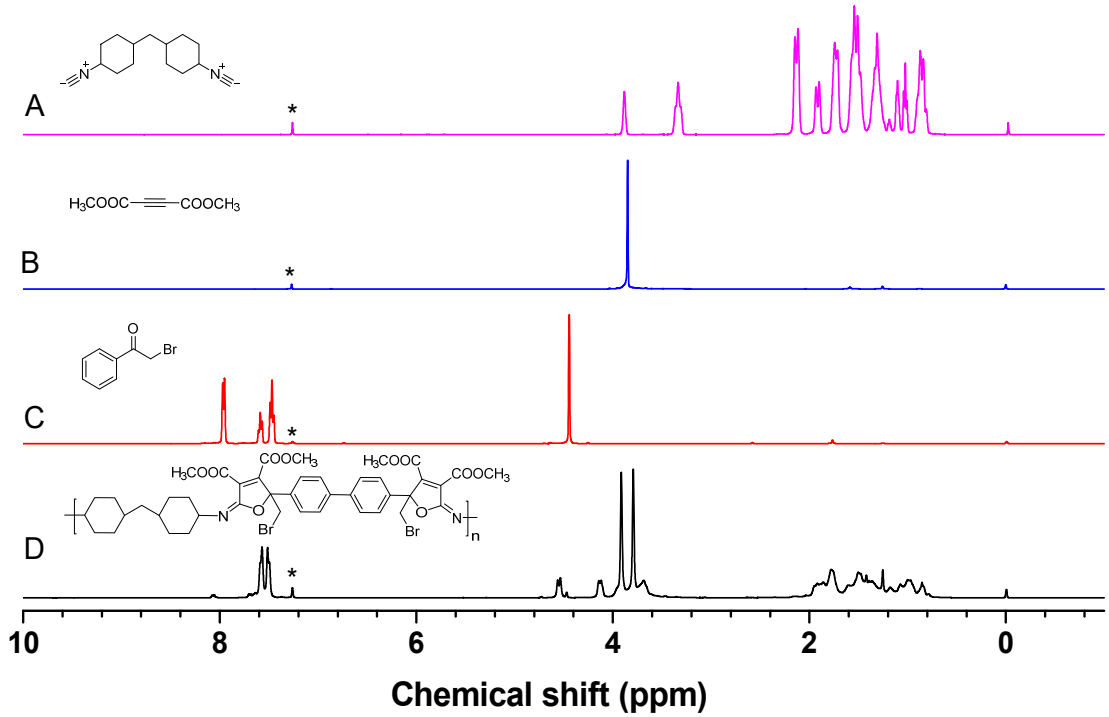


Figure S11. ^{1}H NMR spectra of (A) **1b**, (B) **2a**, (C) **4**, and (D) **P1b2a3** in $CDCl_3$.

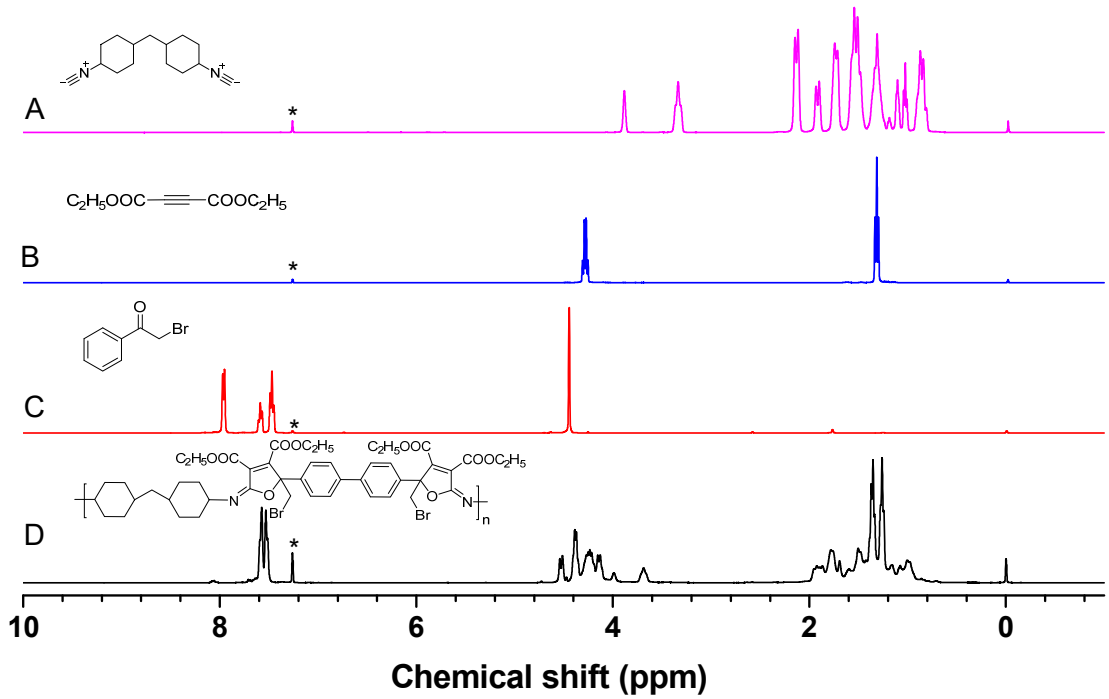


Figure S12. ^{1}H NMR spectra of (A) **1b**, (B) **2b**, (C) **4**, and (D) **P1b2b3** in $CDCl_3$.

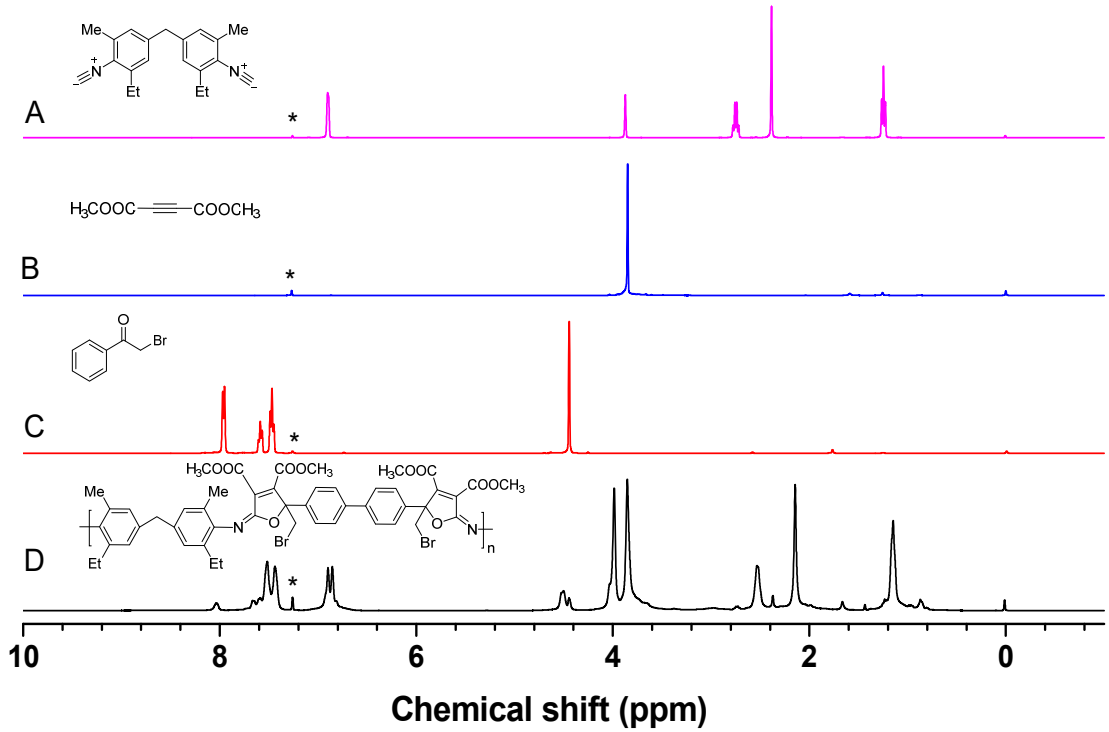


Figure S13. ^{1}H NMR spectra of (A) **1c**, (B) **2a**, (C) **4**, and (D) **P1c2a3** in $CDCl_3$.

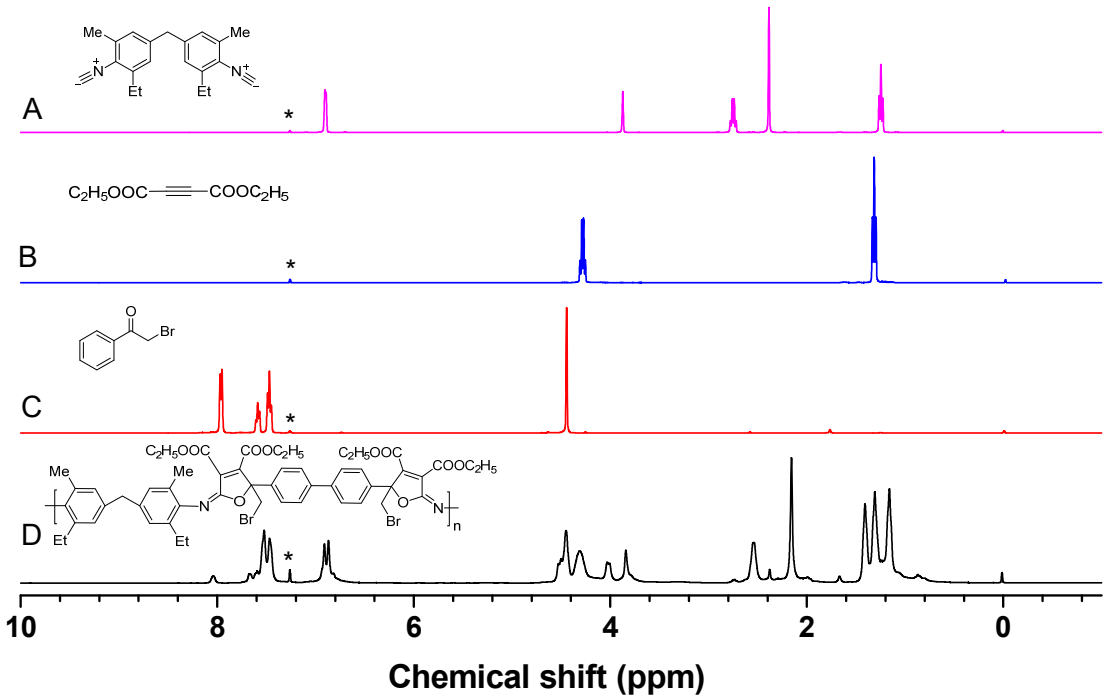


Figure S14. ^{1}H NMR spectra of (A) **1c**, (B) **2b**, (C) **4**, and (D) **P1c2b3** in $CDCl_3$.

5 ^{13}C NMR spectra of PIFAs

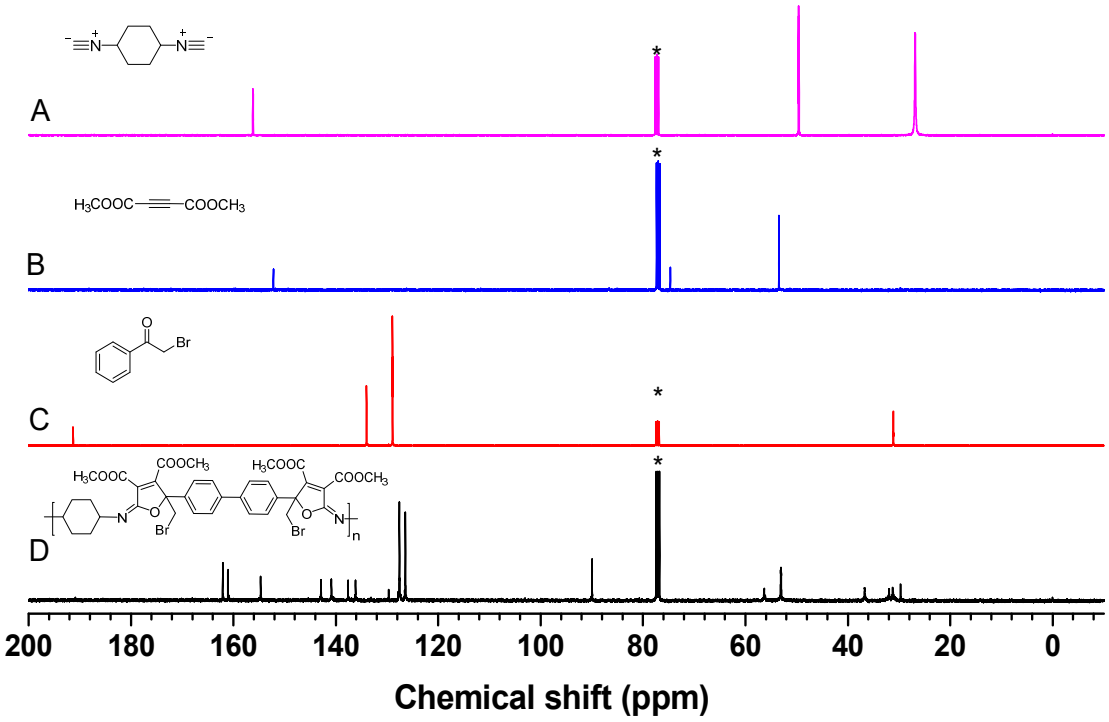


Figure S15. ^{13}C NMR spectra of (A) **1a**, (B) **2a**, (C) **4**, and (D) **P1a2a3** in $CDCl_3$.

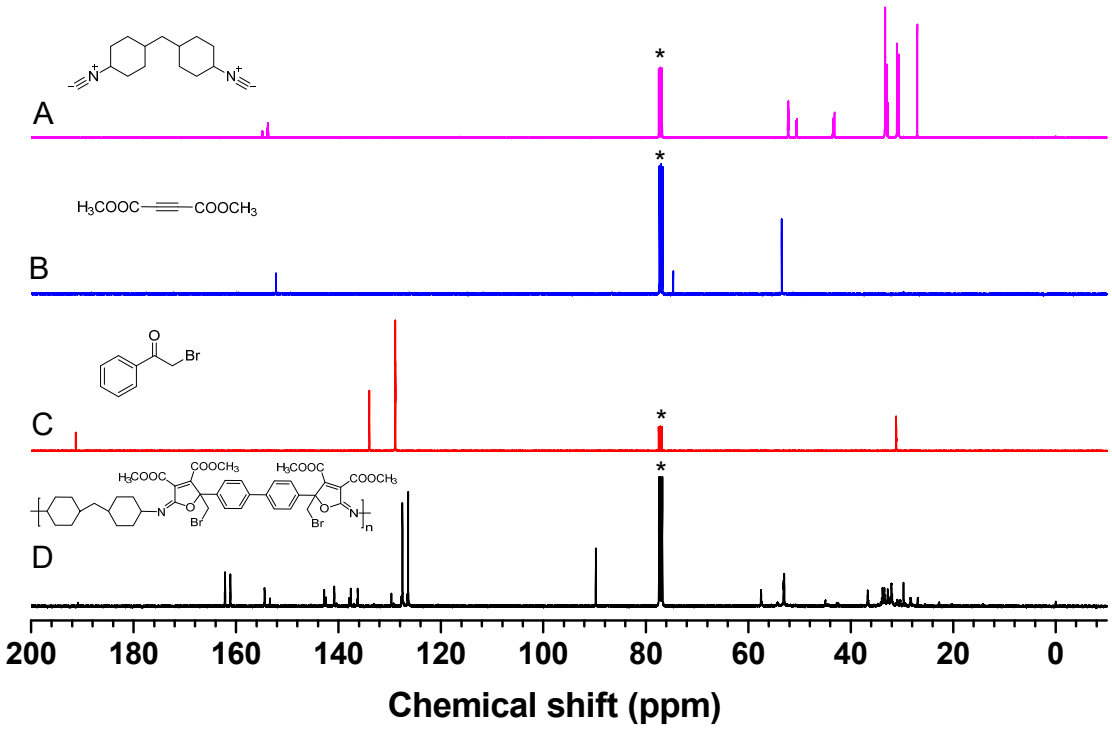


Figure S16. ^{13}C NMR spectra of (A) **1b**, (B) **2a**, (C) **4**, and (D) **P1b2a3** in $CDCl_3$.

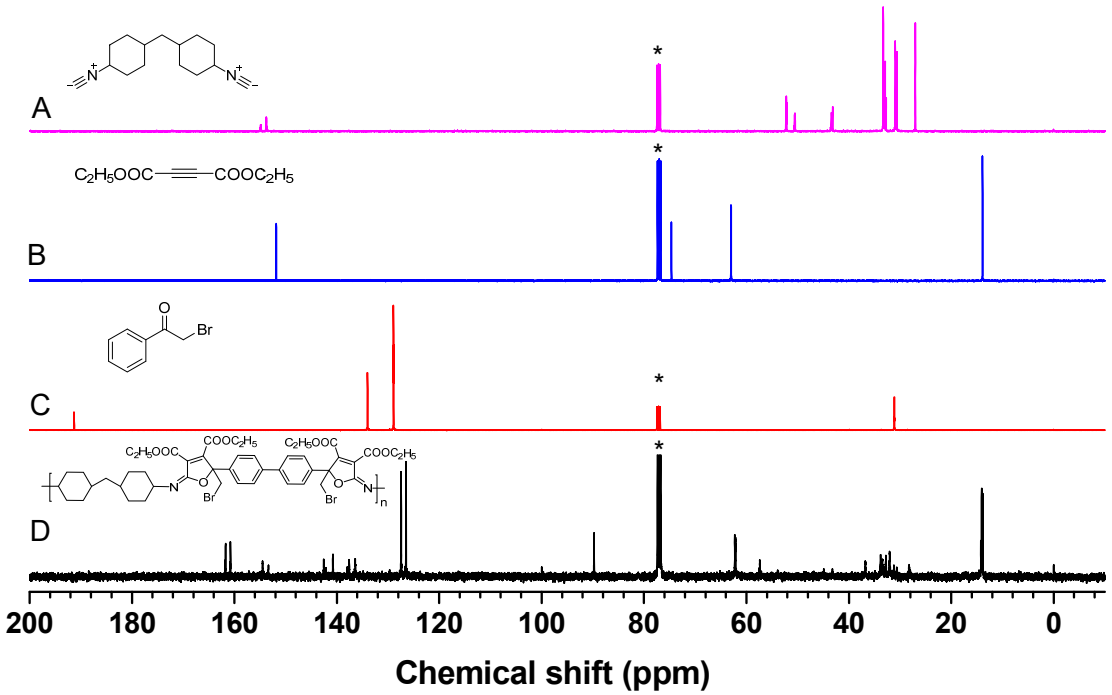


Figure S17. ^{13}C NMR spectra of (A) **1b**, (B) **2b**, (C) **4**, and (D) **P1b2b3** in $CDCl_3$.

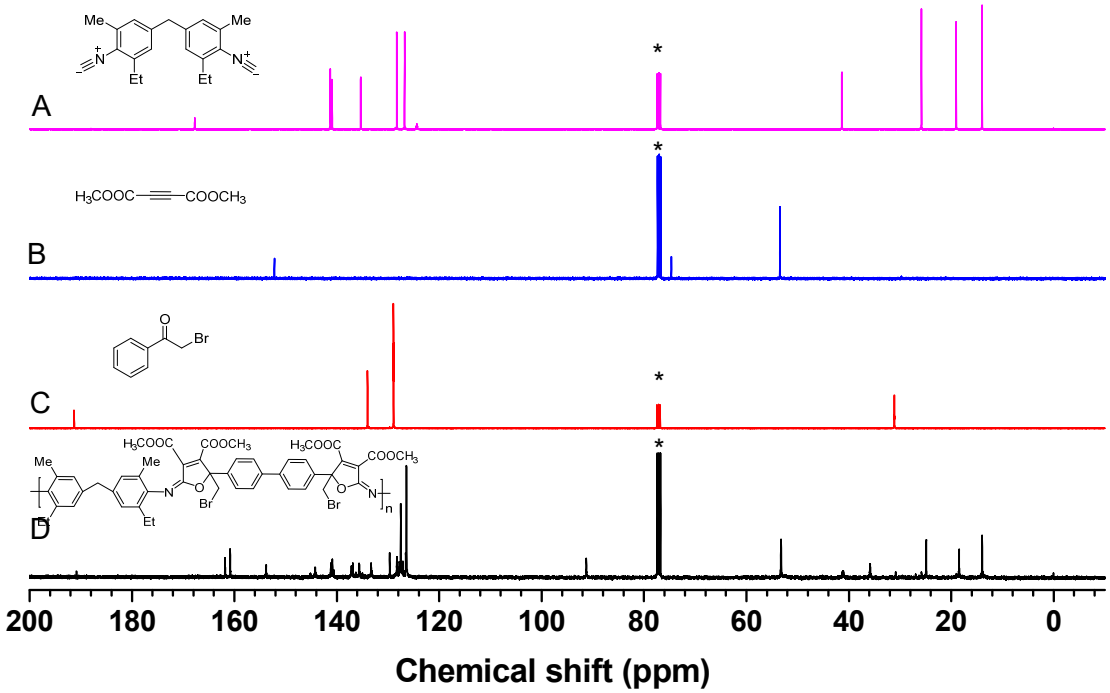


Figure S18. ^{13}C NMR spectra of (A) **1c**, (B) **2a**, (C) **4**, and (D) **P1c2a3** in $CDCl_3$.

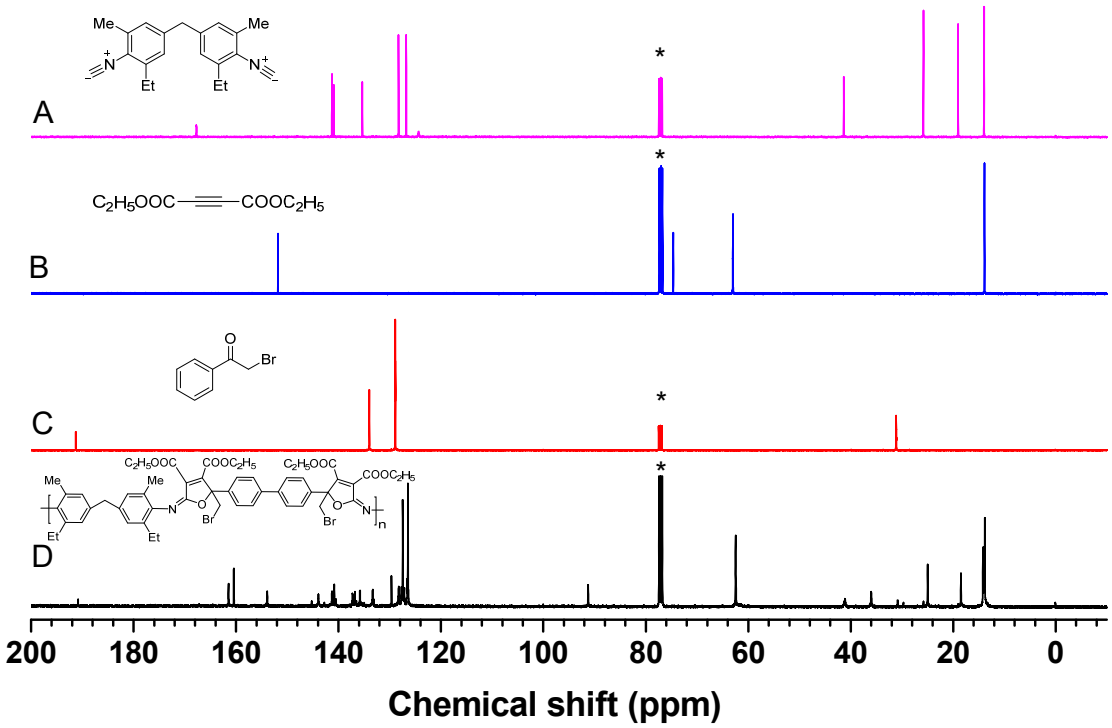


Figure S19. ^{13}C NMR spectra of (A) **1c**, (B) **2b**, (C) **4**, and (D) **P1c2b3** in $CDCl_3$.

6 Refractive indices of PIFAs

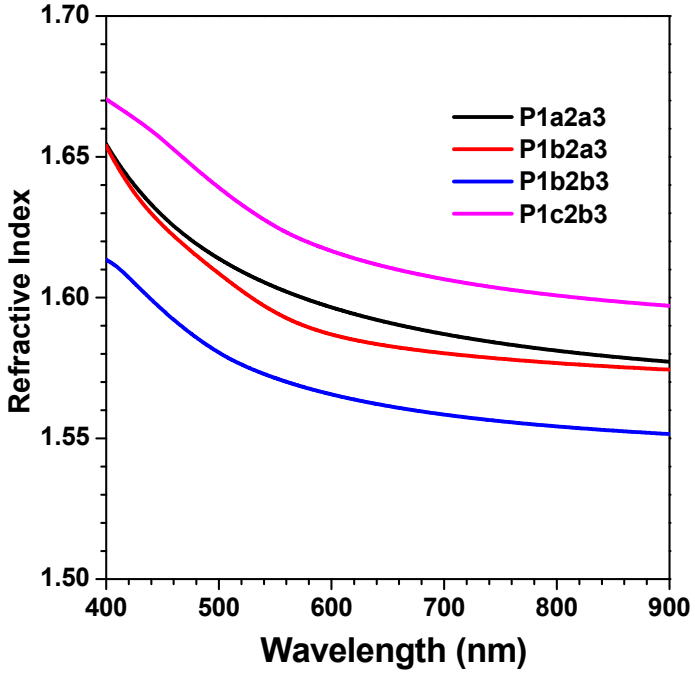


Figure S20. Refractive indices of thin solid films of **P1a2a3**, **P1b2a3**, **P1b2b3**, and **P1c2b3**.

7 PL spectra of P1b2b3 in THF/H_2O mixtures and in solid

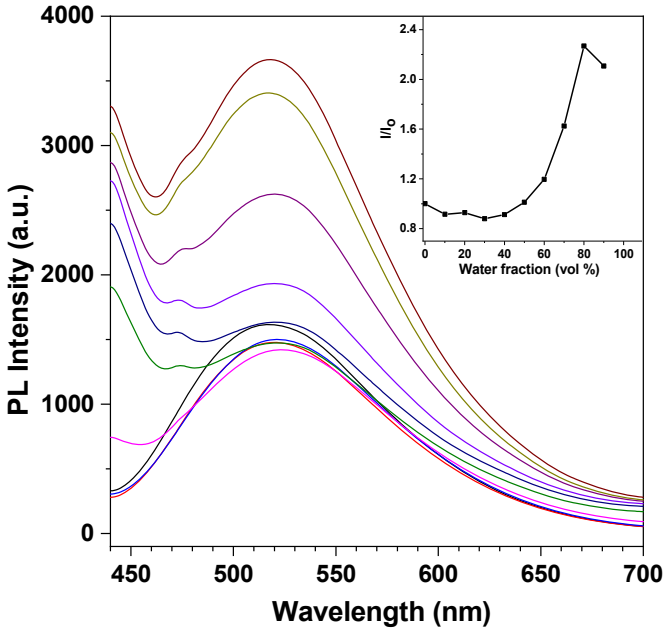


Figure S21. PL spectra of **P1b2b3** in different water fraction of THF/H_2O mixtures (1.0 mM) at excitation wavelength of 420 nm. Insert: Variation of maximum PL intensity of **P1a2b3** with the water fraction in THF/H_2O.

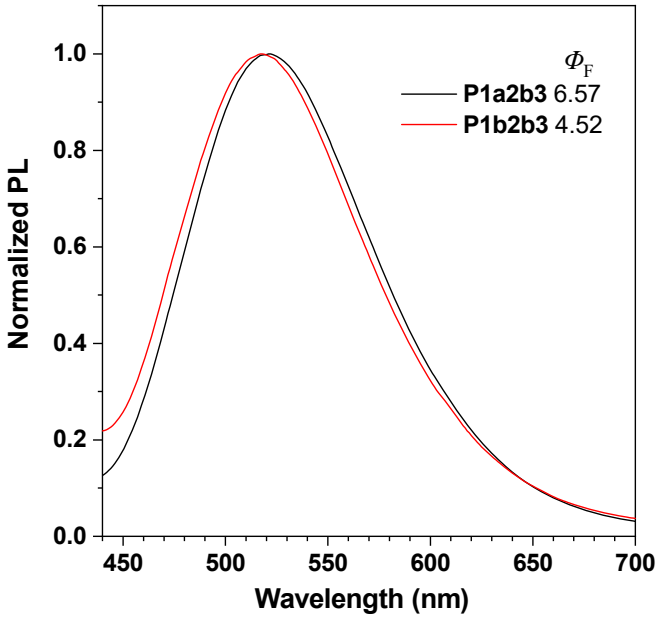
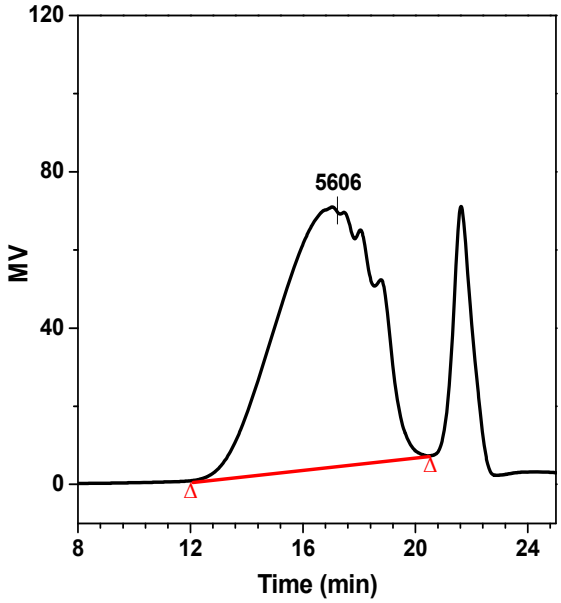


Figure S22. PL spectra of **P1a2b3** and **P1b2b3** in solid at excitation wavelength of 420 nm. Insert: The absolute quantum yields (Φ_F).

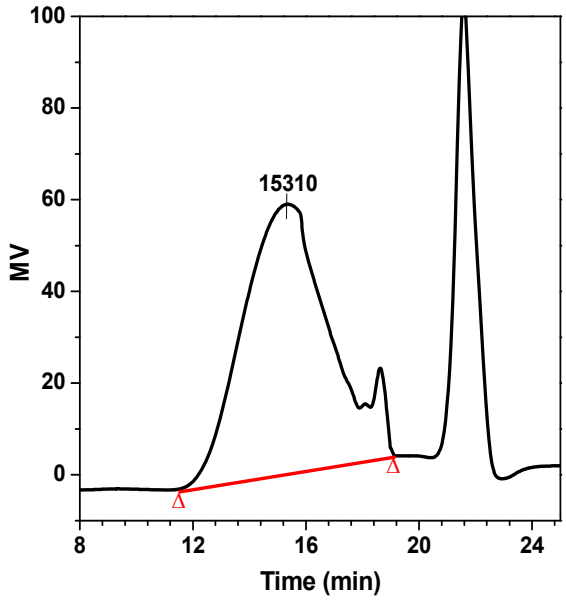
8 GPC data of PIFAs



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.045	17.045	17.045	4489	9246	5606	17707	28029	1.915029	3.031413

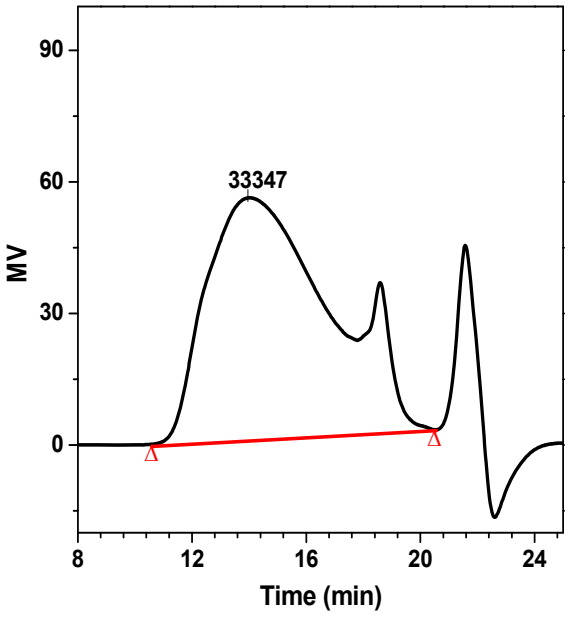
Figure S23. The GPC result of entry 1 in Table S1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.283	15.283	15.283	10614	20475	15310	34593	51958	1.689509	2.537624

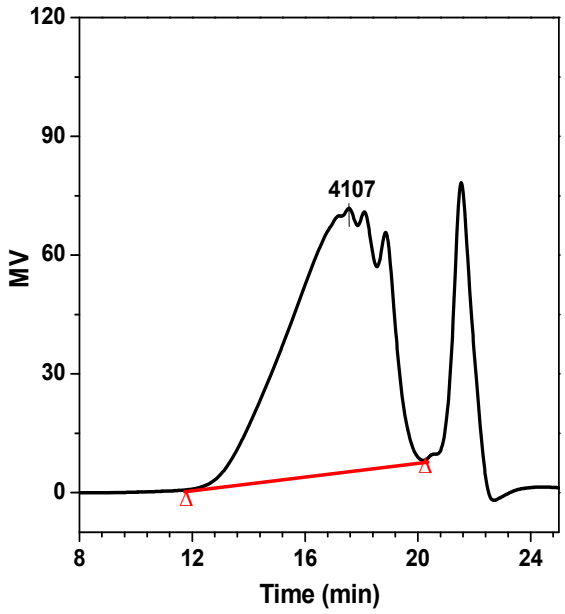
Figure S24. The GPC result of entry 2 in Table S1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		13.967	13.967	13.967	9291	33948	33347	74264	112491	2.187569	3.313598

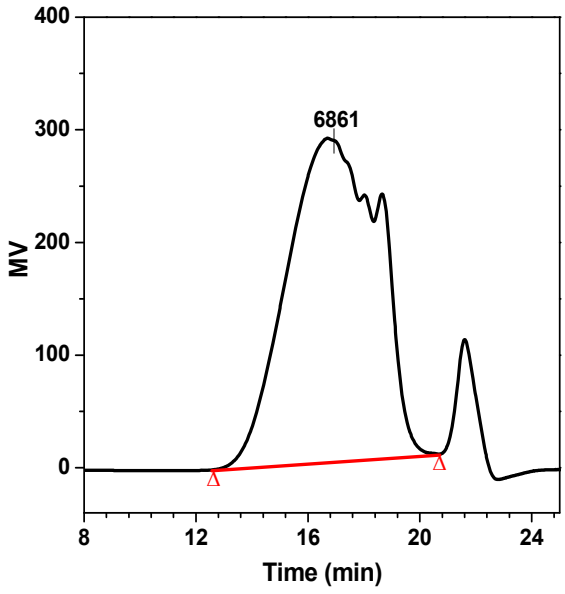
Figure S25. The GPC result of entry 3 in Table S1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.555	17.555	17.555	3846	8394	4107	17712	29357	2.110039	3.497380

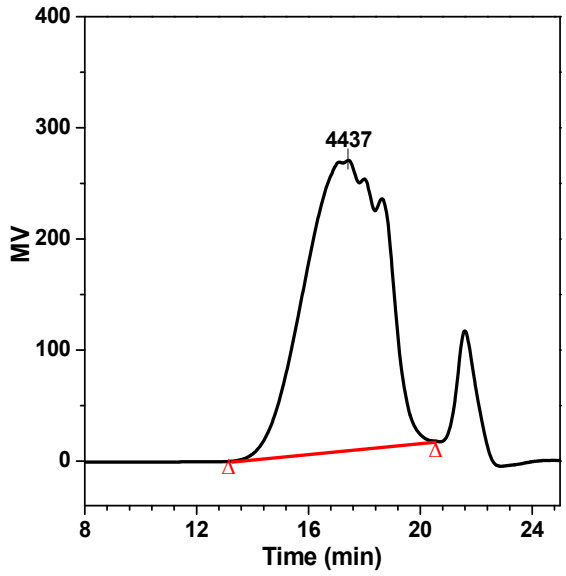
Figure S26. The GPC result of entry 5 in Table S1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.701	16.701	16.701	4243	7968	6861	13413	19213	1.683256	2.411126

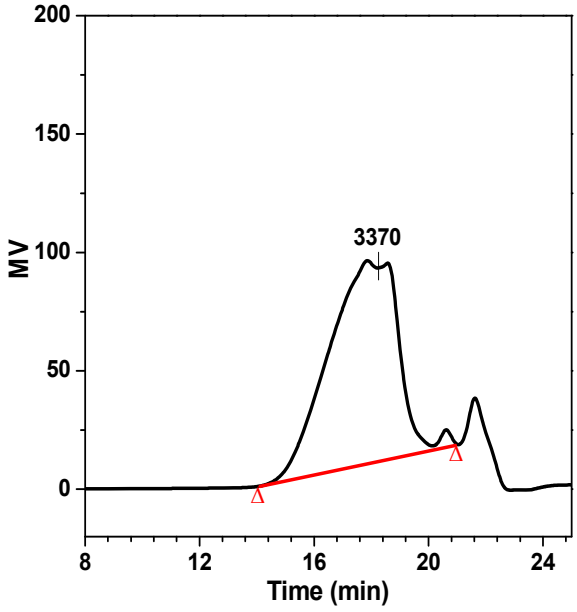
Figure S27. The GPC result of entry 2 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.431	17.431	17.431	3663	6071	4437	9510	13361	1.566399	2.200671

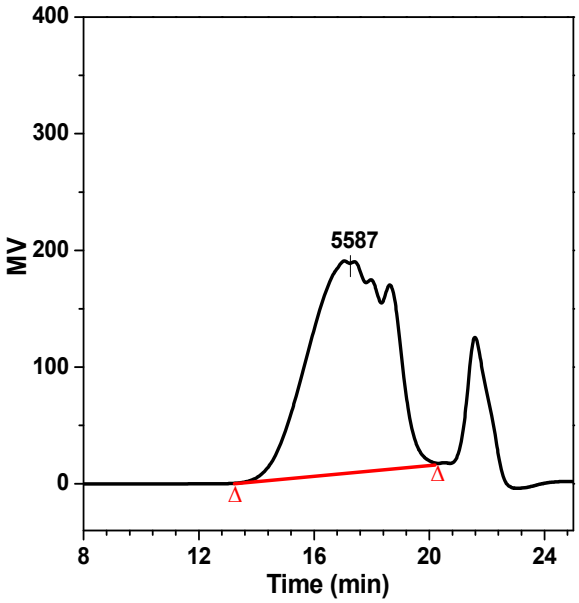
Figure S28. The GPC result of entry 3 in Table 1.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.864	17.864	17.864	2824	4673	3370	6949	9381	1.486972	2.007414

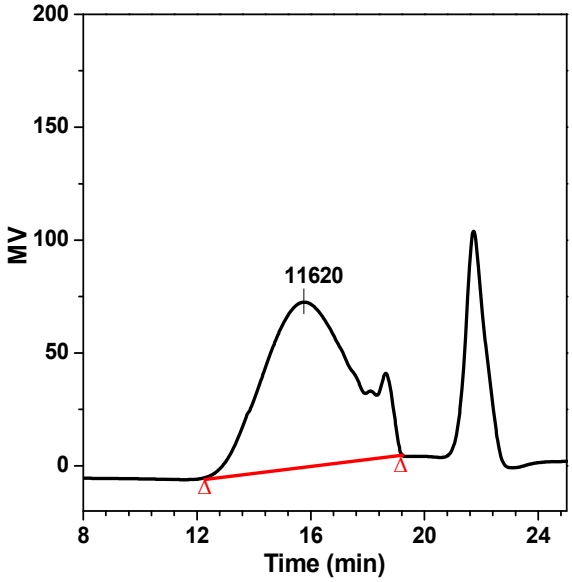
Figure S29. The GPC result of entry 1 in Table S2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		17.050	17.050	17.050	3746	6172	5587	9498	13016	1.538724	2.108717

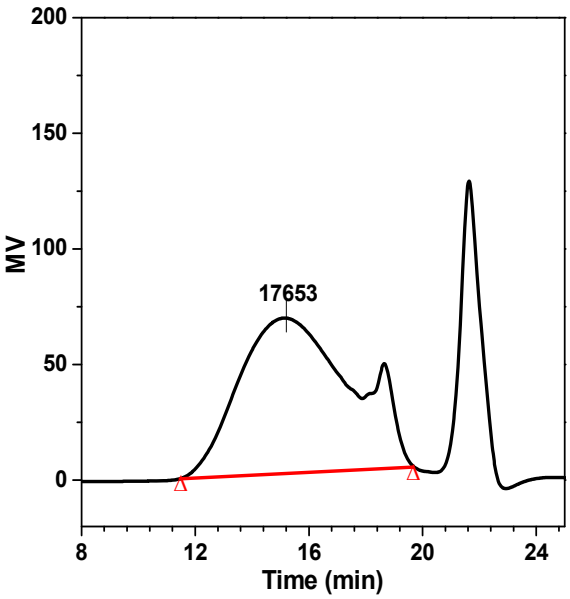
Figure S30. The GPC result of entry 2 in Table S2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.773	15.773	15.773	6370	13295	11620	23524	34849	1.769440	2.621285

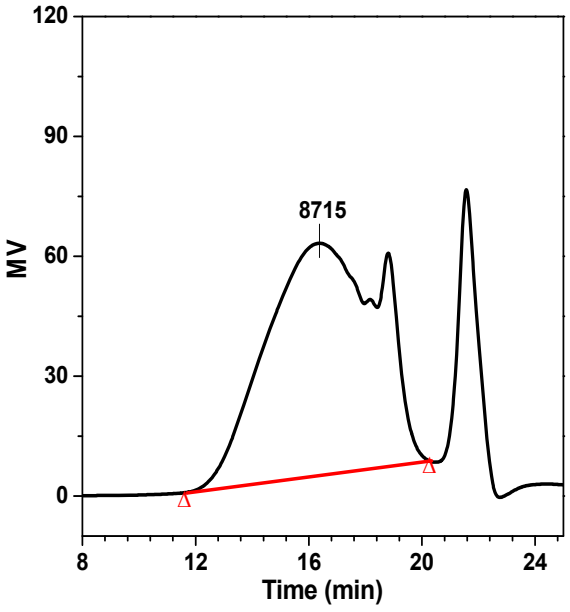
Figure S31. The GPC result of entry 1 in Table S3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.033	15.033	15.033	7985	20681	17653	41693	67226	2.015997	3.250600

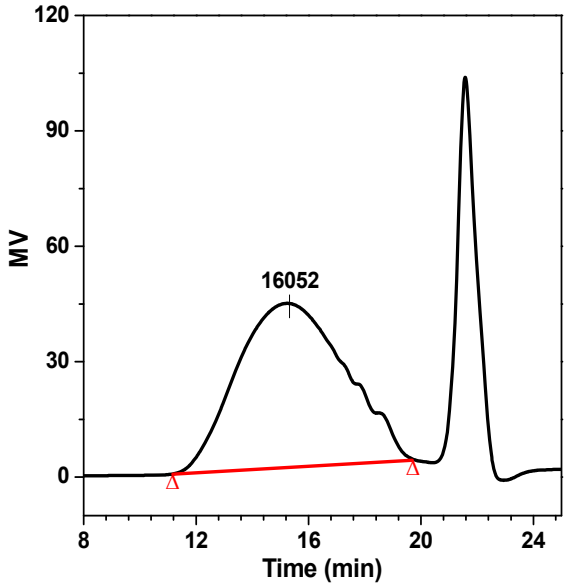
Figure S32. The GPC result of entry 3 in Table S3.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.283	16.283	16.283	4811	12011	8715	25531	41960	2.125594	3.493440

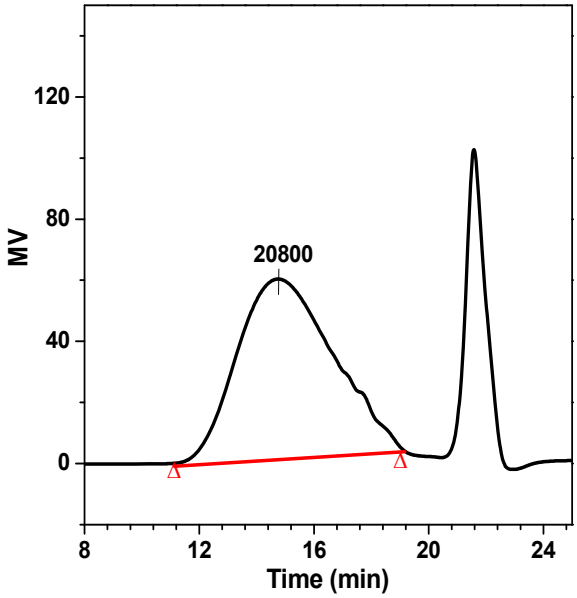
Figure S33. The GPC result of entry 1 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.200	15.200	15.200	8606	21835	16052	46193	76098	2.115571	3.485143

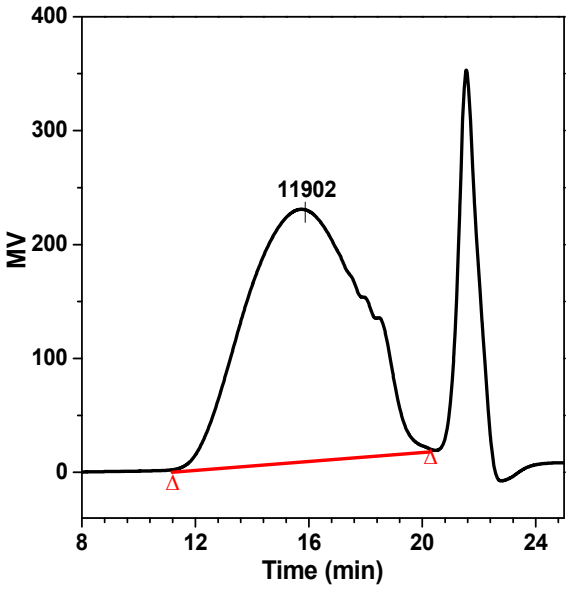
Figure S34. The GPC result of entry 3 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		14.749	14.749	14.749	11205	24271	20800	45507	72045	1.874994	2.968401

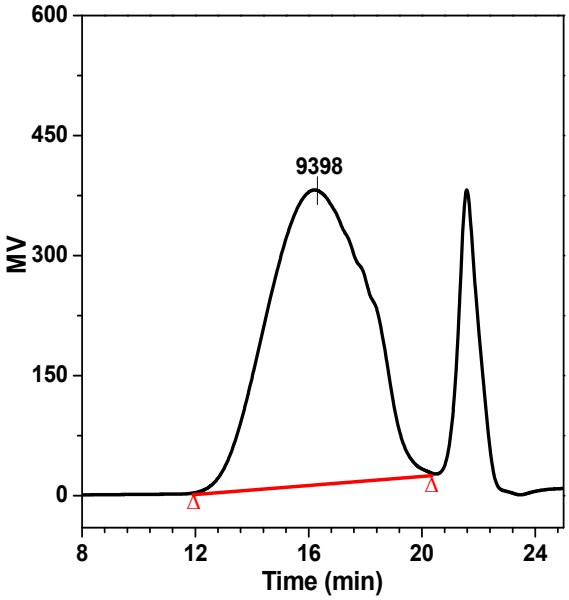
Figure S35. The GPC result of entry 4 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		15.730	15.730	15.730	6685	17647	11902	38557	63557	2.184894	3.601536

Figure S36. The GPC result of entry 5 in Table 2.



GPC Results

	Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1		16.150	16.150	16.150	6096	1211€	9398	22151	34783	1.828231	2.870772

Figure S37. The GPC result of entry 6 in Table 2.