Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for

Nonstoichiometric Hydroarylation Polyaddition for Synthesis of Pyrrole-based Poly(arylenevinylene)s

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Experimental section

Materials

All reagents from commercial sources were used without further purification, unless otherwise noted. Anhydrous solvents were purchased from Kanto Chemical. 4-Ethynyltoluene was purchased from Tokyo Chemical Industry. Neodecanoic acid (NDA) was purchased from Wako Pure Chemical Industries. 1-(2-Pyrimidinyl)pyrrole (**1a**) was prepared referring to a procedure in the literature.[1] 2,7-Bis(4-ethynylphenyl)-9,9-bis(2-ethylhexyl)fluorene (**2a**) was prepared referring to procedures in the literature[2–4] and the ^{1}H NMR spectrum essentially agrees with that in the previous report.[2] 1-(2-Pyridyl)pyrrole (**1b**), 2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene (**2b**), and $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ were prepared by the same method as our previous report.[2] 1-(*N*,*N*-dimethylcarbamoyl)pyrrole (**1c**) was prepared referring to a procedure in the literature.[5] The other regents were also purchased from Kanto Chemical, Tokyo Chemical Industry, and Sigma Aldrich.

General methods

^{1}H NMR spectra were recorded on Bruker AVANCE-400 or AVANCE-600 NMR spectrometers. ^{1}H NMR spectra were measured with TMS (0.00 ppm for ^{1}H NMR) and $C_2HD_3Cl_2$ (3.72 ppm for ^{1}H NMR) as an internal reference. Gel permeation chromatography (GPC) measurements were carried out on a SHIMADZU prominence GPC system equipped with polystyrene gel columns, using THF as an eluent after calibration with polystyrene standards. MALDI-TOF-MS were recorded on an AB SCIEX MALDI TOF/TOF 5800 using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. GC-MS were recorded on a SHIMADZU GC-2010 Plus and a GCMS-QP2010 Ultra.

Procedure for time course model reaction

To a stirred solution of a pyrrole substrate (0.10 mmol), 4-ethynyltoluene (12.7 µL, 0.10 mmol), and 1,3,5-trimethoxybenzene (11.2 mg, 0.067 mmol) in anhydrous 1,2-dichloroethane-d_4 (1.5 mL) was added $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (1.58 mg, 0.0020 mmol) at 0 ˚C. A portion of 500 µL was transfer from the mixture to the NMR tube under a nitrogen atmosphere. After adding neodecanoic acid (1.89 µL, 0.010 mmol) to the reaction mixture, ^{1}H NMR data were measured at 0, 5, 10, 20, 30, 40, 50, 60, 90, 130, and 180 min at 10 ˚C.

General procedure for equimolar model reactions

To a stirred solution of a pyrrole substrate (0.10 mmol), 4-ethynyltoluene (12.7 µL, 0.10 mmol), and 1,3,5-trimethoxybenzene (11.2 mg, 0.067 mmol) in anhydrous 1,2-dichloroethane (DCE, 1.5 mL) was added $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (1.58 mg, 0.0020 mmol) and neodecanoic acid (NDA, 5.68 µL, 0.030 mmol) at 0 ˚C. The reaction mixture was stirred for 3 h at 10 ˚C under nitrogen atmosphere. A portion of the reaction mixture was sampled at 0, 1, 2, and 3 h. The NMR yield at each reaction time was obtained from the integral value of the signal for the product on the basis of the internal standard (1,3,5-trimethoxybenzene).

General procedure for nonstoichiometric hydroarylation polyaddition

To a stirred solution of a pyrrole monomer and an alkyne monomer with the prescribed feed ratio at 0.10 mmol scale in anhydrous DCE (1.5 mL) was added $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (1.58 mg, 0.0020 mmol) and NDA (5.68 μL, 0.030 mmol) at 0 ˚C. The reaction mixture was stirred for a prescribed time at 10 ˚C under nitrogen atmosphere in the dark. Then the reaction mixture was diluted with DCE (50 mL) and poured into NH_3 solution (28% in water, 50 mL). The organic layer was washed with NH_3 solution and distilled water (100 mL x 2). The organic layer was dried over sodium sulfate and filtered through a Celite®□ plug. The solution of DCE was concentrated and reprecipitated into methanol. The precipitate was washed with hexane and a polymeric product was obtained.

Hydroarylation of Paa with 1-(*N*,*N*-dimethylcarbamoyl)pyrrole (1c)

To a stirred solution of **Paa** (20 mg, $M_{n(NMR)}$ = 4,500, 0.0044 mmol, $M_{n(GPC)}$ = 7,100, PDI = 2.3) and 1-(*N*,*N*-dimethylcarbamoyl)pyrrole (**1c**) (13.8 mg, 0.10 mmol) in anhydrous DCE (1.5 mL) was added $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (1.58 mg, 0.0020 mmol) and NDA (5.68 μL, 0.030 mmol). The reaction mixture was stirred for 24 h at 30 ˚C under nitrogen atmosphere in the dark. The reaction mixture was diluted with DCE (10 mL) and poured into NH_3 solution (28% in water, 10 mL). The organic layer was washed with NH_3 solution and distilled water (10 mL x 3). The organic layer was dried over sodium sulfate and filtered through a Celite®□ plug. The solution of DCE was concentrated and reprecipitated into methanol. The precipitate was collected as a yellow solid in 63% yield (13.3 mg, $M_{n(NMR)}$ = 5,200, $M_{n(GPC)}$ = 7,400, PDI = 2.6).

Synthesis of Paa (Table 1, Entry 4)

1-(2-Pyrimidinyl)pyrrole (**1a**) (29.0 mg, 0.20 mmol) and 2,7-bis(4-ethynylphenyl)-9,9-bis(2-ethylhexyl)fluorene (**2a**) (59.1 mg, 0.10 mmol) were used as the monomers. The reaction was carried out at 10 ˚C for 90 min, giving **Paa** as a yellow solid in 81% yield (59.8 mg, M_n = 5.2 x 10^4, PDI = 4.3). ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 8.97 (d, *J* = 4.8 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.65-7.62 (br m, 8H), 7.46 (d, *J* = 7.0 Hz, 4H), 7.40 (t, *J* = 4.8 Hz, 1H), 7.21 (d, *J* = 15.6 Hz, 2H), 6.98 (d, *J* = 15.8 Hz, 2H), 6.79 (s, 2H), 2.04 (br s, 4H), 0.86-0.52 (m, 30H). Minor signals corresponding for the 1,1-vinylidene unit: δ 8.57 (d, *J* = 4.6 Hz), 7.37 (d, *J* = 7.7 Hz), 6.92 (s), 6.58 (s), 5.47 (br s), 5.41 (br s). The ^{1}H NMR spectrum essentially agrees with that in the previous report.[2]

Synthesis of Pab (Scheme 4a)

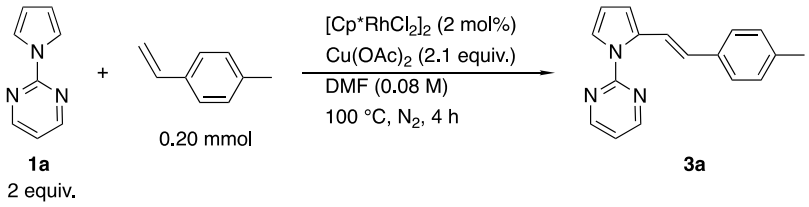
1-(2-Pyrimidinyl)pyrrole (**1a**) (29.0 mg, 0.20 mmol) and 2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene (**2b**) (43.9 mg, 0.10 mmol) were used as the monomers. The reaction was carried out at 10 ˚C for 90 min, giving **Pab** as an orange solid in 83% yield (48.4 mg, M_n = 2.8 x 10^4, PDI = 2.7). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 8.93 (d, *J* = 3.7 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.38-7.30 (m, 5H), 7.17 (d, *J* = 16.3 Hz, 2H), 6.98 (d, *J* = 15.0 Hz, 2H), 6.76 (s, 2H), 1.93 (s, 4H), 1.06-0.57 (m, 30H). Minor signals corresponding for the 1,1-vinylidene unit: δ 8.61 (s), (br m), 7.05 (s), 6.41 (s), 5.34-5.13 (br m). The ^{1}H NMR spectrum essentially agrees with that in the previous report.[2]

Synthesis of Pba (Scheme 4b)

1-(2-Pyridyl)pyrrole (**1b**) (25.9 μL, 0.20 mmol) and 2,7-bis(4-ethynylphenyl)-9,9-bis(2-ethylhexyl)fluorene (**2a**) (59.1 mg, 0.10 mmol) were used as the monomers. The reaction was carried out at 10 ˚C for 25 min, giving **Pba**

as a yellow solid in 67% yield (48.9 mg, M_n = 2.4 x 10^4, PDI = 2.4). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 8.79 (d, *J* = 4.2 Hz, 1H), 7.94 (t, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.57-7.53 (m, 9H), 7.47 (t, *J* = 6.1 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 4H), 6.90 (d, *J* = 15.9 Hz, 2H), 6.82-6.74 (m, 4H), 2.04 (br s, 4H), 0.84-0.51 (m, 30H). Minor signals corresponding for the 1,1-vinylidene unit: δ 8.47 (s), 7.17 (d, *J* = 7.3 Hz), 7.10 (t, *J* = 5.9 Hz), 6.48 (s), 5.39 (br s), 5.24 (br s). The ^{1}H NMR spectrum essentially agrees with that in the previous report.[2]

Synthesis of monoalkenylated compound (3a) by Rh-catalyzed direct alkenylation[6]

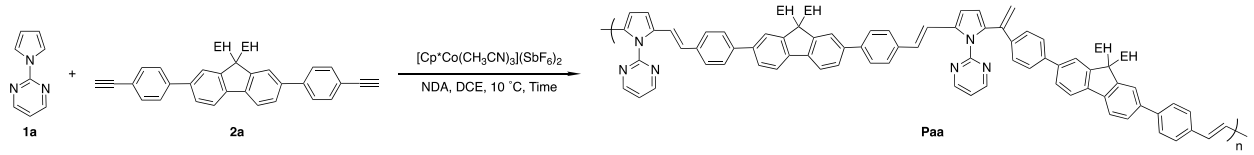


Scheme S1. Synthesis of monoalkenylated compound (3a)

A mixture of $Cu(OAc)_2 \cdot H_2O$ (168 mg, 0.84 mmol), $[Cp^*RhCl_2]_2$ (4.94 mg, 8.0 µmol), 1-(2-pyrimidinyl)pyrrole (29.0 mg, 0.20 mmol), and 4-methylstyrene (45.8 µL, 0.40 mmol) was stirred in anhydrous DMF (2.4 mL) for 4 h at 100 ˚C under nitrogen atmosphere in the dark. Then the reaction mixture was cooled to room temperature. The mixture was dissolved in dichloromethane (40 mL) and ethylenediamine (1.6 mL). The organic layer was washed with distilled water (40 mL x 3) and dried over sodium sulfate. The product was purified by column chromatography on silica gel using chloroform as an eluent and High Performance Liquid Chromatography (HPLC). Monoalkenylated compound (**3a**) was obtained as a white solid (18.1 mg, 35%). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 8.68 (d, *J* = 4.8 Hz, 2H), 7.99 (d, *J* = 16.3 Hz, 1H), 7.77 (dd, *J* = 3.1, 1.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.90 (d, *J* = 16.3 Hz, 1H), 6.65 (t, *J* = 0.9 Hz, 1H), 6.31 (t, J = 3.4 Hz, 1H), 2.34 (s, 3H). GC-MS calcd. for $C_{17}H_{15}N_3$: 261.13; found: 261.1. The spectral data of **3a** are shown in Figures S24, S25.

Nonstoichiometric polyaddition

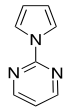
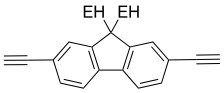
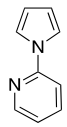
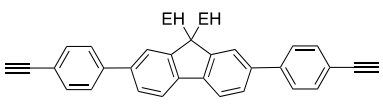
Table S1. Nonstoichiometric hydroarylation polyaddition for Paa with longer reaction time [a]



Entry	**1a** : **2a**	Time [min]	Yield [b] [%]	M_n [c]	M_n (Calcd) [d]	PDI [c]	Regioselectivity [e]
1	2 : 1	90	81	52,000	2,200	4.3	92 : 8
2	2 : 1	120	-[f]	-	-	-	-
3	5 : 1	30	53	20,000	1,100	2.3	92 : 8
4	5 : 1	40	-[f]	-	-	-	-

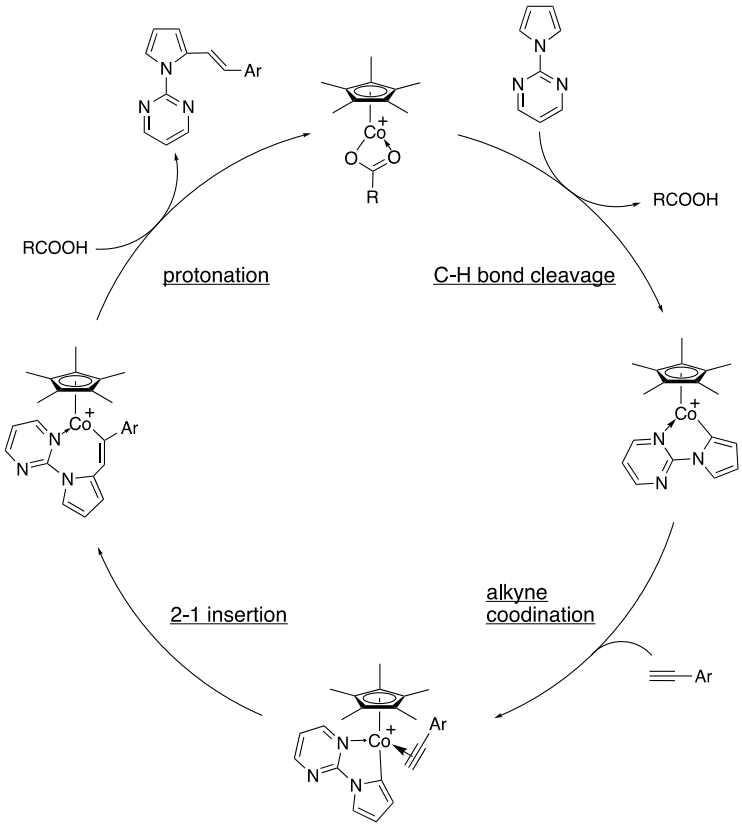
[a] $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (2 mol%), neodecanoic acid (NDA, 30 mol%), 1,2-dichloroethane (DCE, 1.5 mL) were used. [b] The products were obtained by reprecipitation from DCE-CH_3OH. The yields were calculated on the basis of the feeding quantity of **2a**. [c] Estimated by GPC calibrated on polystyrene standards using THF at 40 ˚C. [d] Calculated by Carothers equation.[7] [e] The ratio of 1,2-vinylene to 1,1-vinylidene calculated from the ^1H NMR spectrum. [f] Gelation of the reaction mixture was observed.

Table S2. Nonstoichiometric hydroarylation polyaddition of other aromatic monomers

Entry	**1**	**2**	**1 : 2**	Time [min]	Yield [a] [%]	M_n [b]	M_n (Calcd) [c]	PDI [b]
1			1 : 1	270	61	8,300	-	1.6
2	 1a	 2b	2 : 1	30	51	1,900	1,800	1.5
3			2 : 1	60	68	5,500	1,800	1.8
4			2 : 1	90	83	28,000	1,800	2.7
5	 1b	 2a	1 : 1	25	76	32,000	-	2.5
6			2 : 1	25	67	24,000	2,200	2.4

[a] The products were obtained by reprecipitation from DCE-CH_3OH. The yields were calculated on the basis of the feeding quantity of **2a** or **2b**. [b] Estimated by GPC calibrated on polystyrene standards using THF at 40 ˚C. [c] Calculated by Carothers equation.[7]

(a) General catalytic cycle of hydroarylation of alkynes



(b) Intramolecular catalyst transfer in the Co-catalyzed hydroarylation

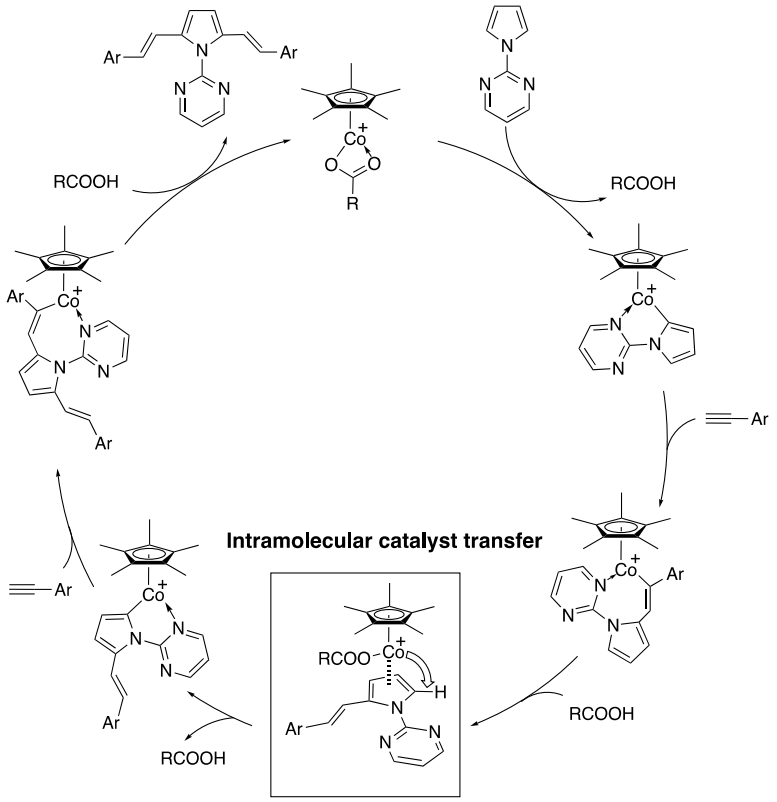
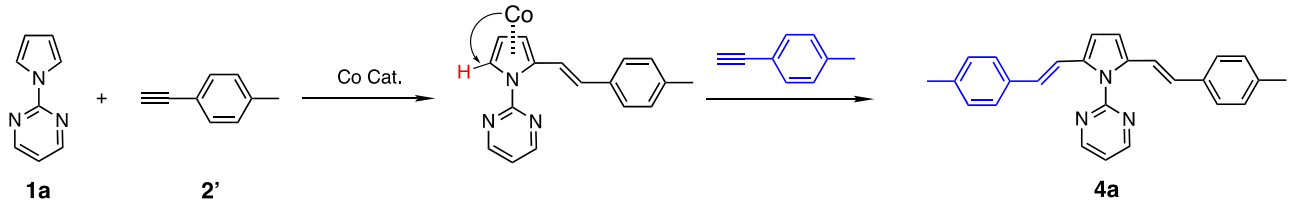
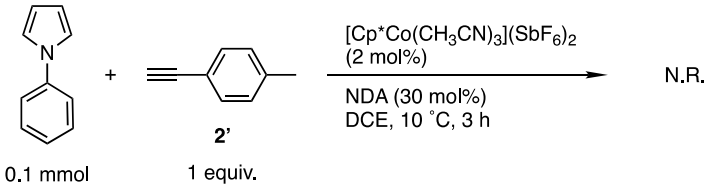


Figure S1. Catalytic cycles of hydroarylation of alkynes.

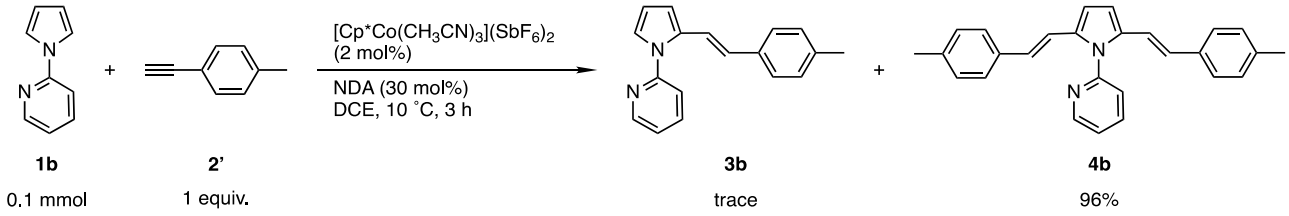
Model reaction



Scheme S2. Intramolecular catalyst transfer on 1a in the equimolar model reaction



Scheme S3. Equimolar model reaction of 1-phenylpyrrole with 4-ethynyltoluene



Scheme S4. Equimolar model reaction of 1b with 4-ethynyltoluene

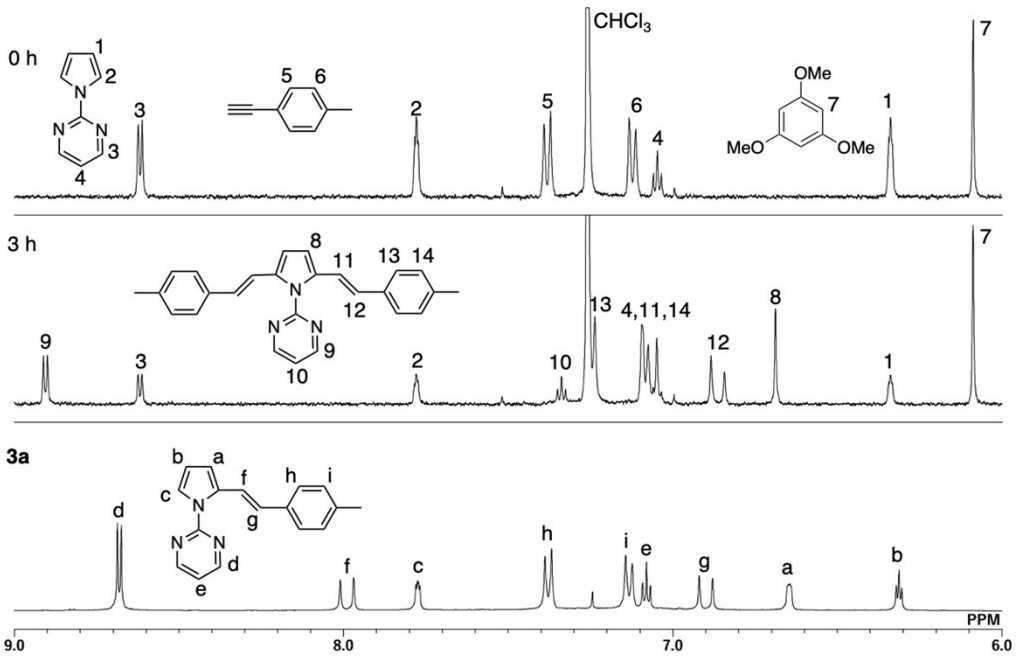


Figure S2. ^{1}H NMR spectra of equimolar model reaction of 1a with 4-ethynyltoluene and 3a (Scheme 2, 400 MHz, $CDCl_3$, r.t.).

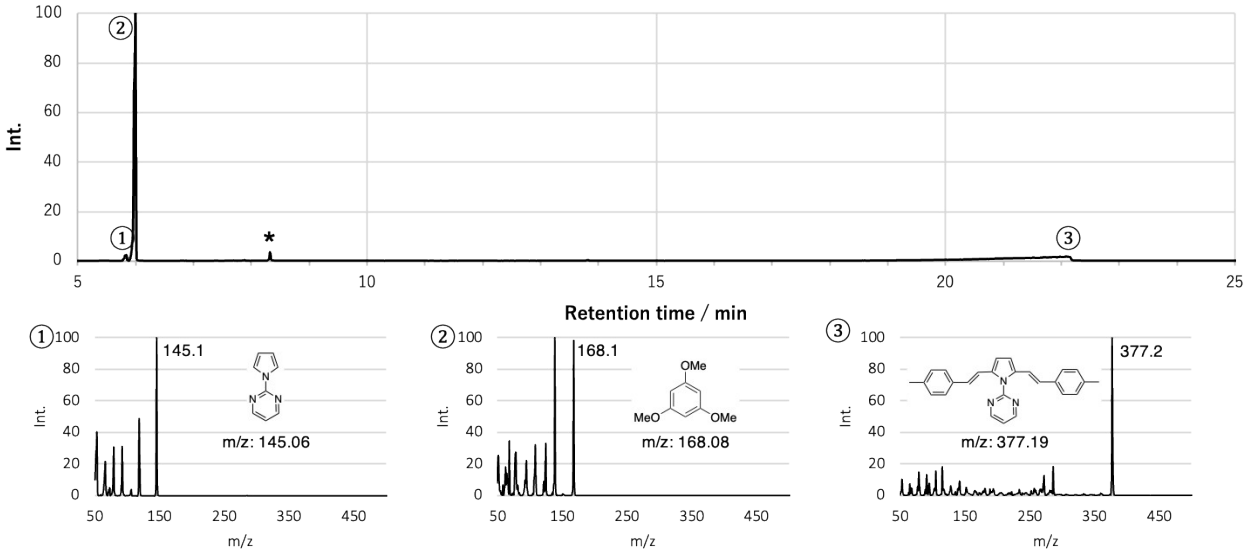
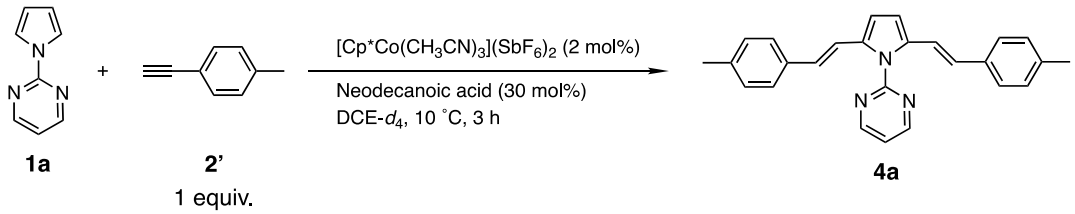
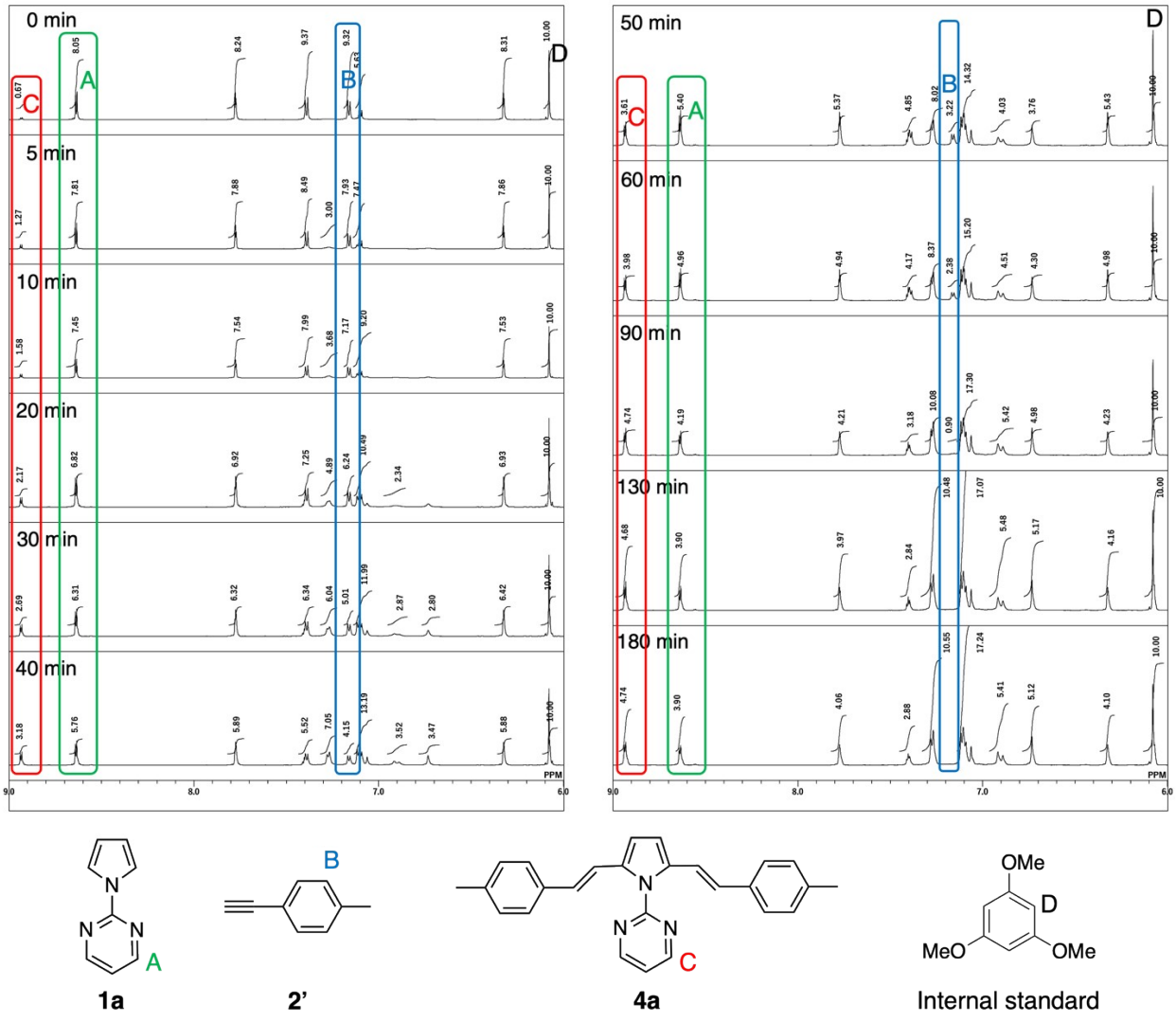


Figure S3. GC-MS of the reaction crude after the equimolar model reaction of 1a with 4-ethynyltoluene (Scheme 2). * Impurities from operations.



1a + **2'** (1 equiv.) → **4a**



1a **2'** **4a** Internal standard

Figure S4. ^{1}H NMR spectra of the time course model reaction of 1a (600 MHz, $C_2D_4Cl_2$, 283 K).

Table S3. Data of time course model reaction of 1a with 2'[8]

Time (min)	Conversion of **2'** (%)	**3a** (%)	**4a** (%)	**4a**/(**3a**+**4a**)
0	0	0	0	-
5	15	0	7.5	1
10	23	0	11	1
20	33	0	19	1
30	46	0	25	1
40	55	0	31	1
50	65	0	37	1
60	74	0	41	1
90	90	0	51	1
130	100	0	50	1
180	100	0	51	1

[a] Calculated by 100 x (1 - [**2'**]$_t$ / [**2'**]$_0$). [b] Calculated by 100 x [**4a**]$_t$ / [**1a**]$_0$.

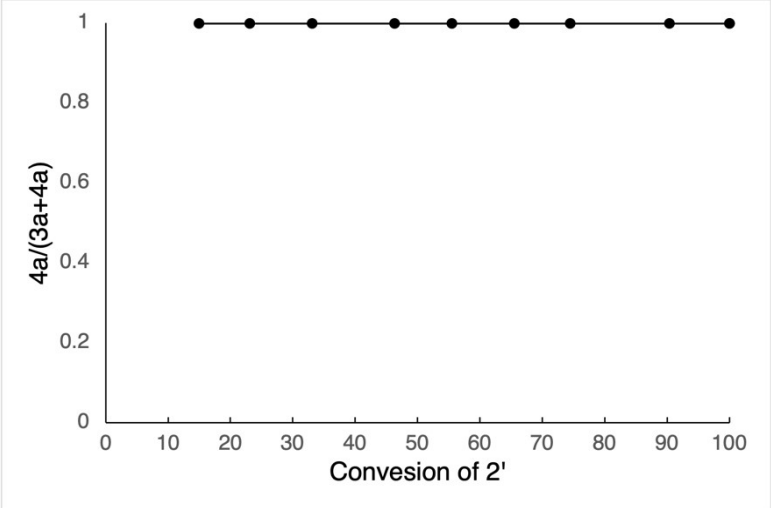


Figure S5. Plot of product (4a) ratio vs percent conversion of 2'[8]

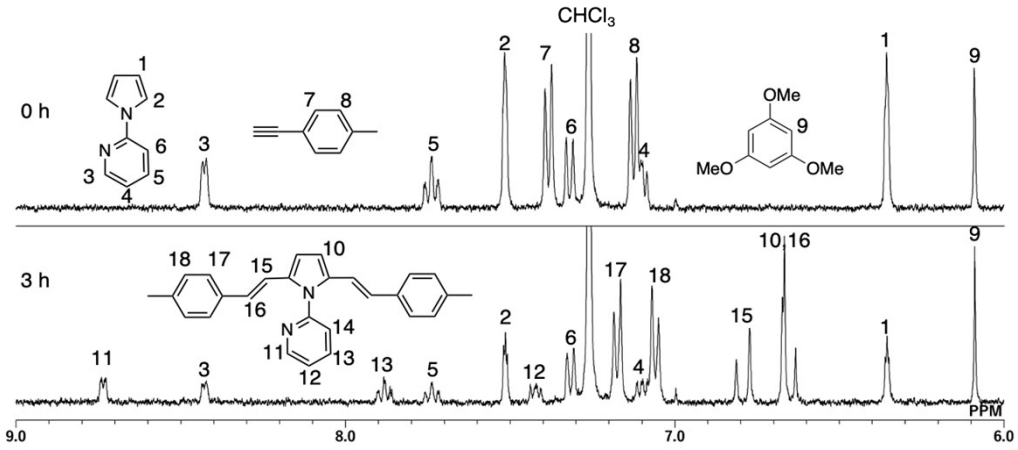


Figure S6. ^{1}H NMR spectra of equimolar model reaction of 1b with 4-ethynyltoluene (Scheme S4, 400 MHz, $CDCl_3$, r.t.).

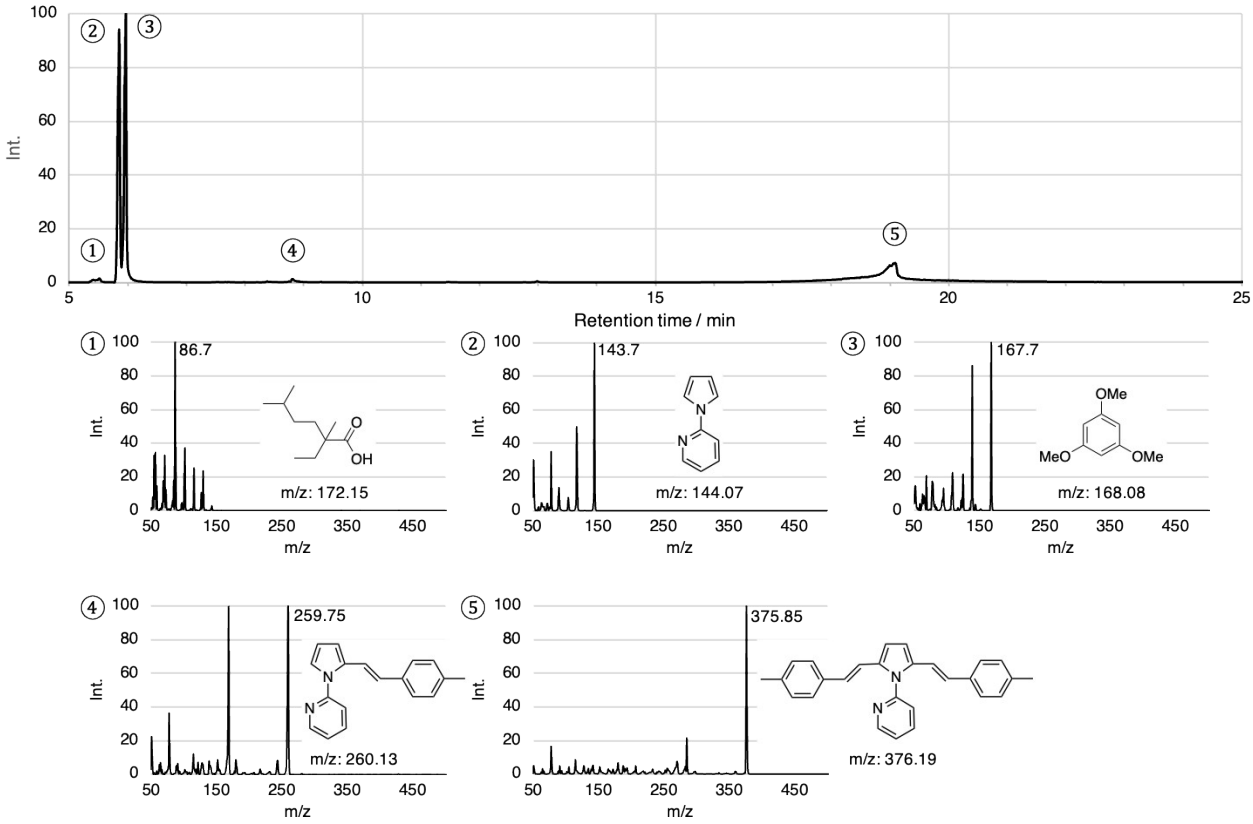


Figure S7. GC-MS of the reaction crude after the equimolar model reaction of 1b with 4-ethynyltoluene (Scheme S4).

^{1}H NMR and MS spectra

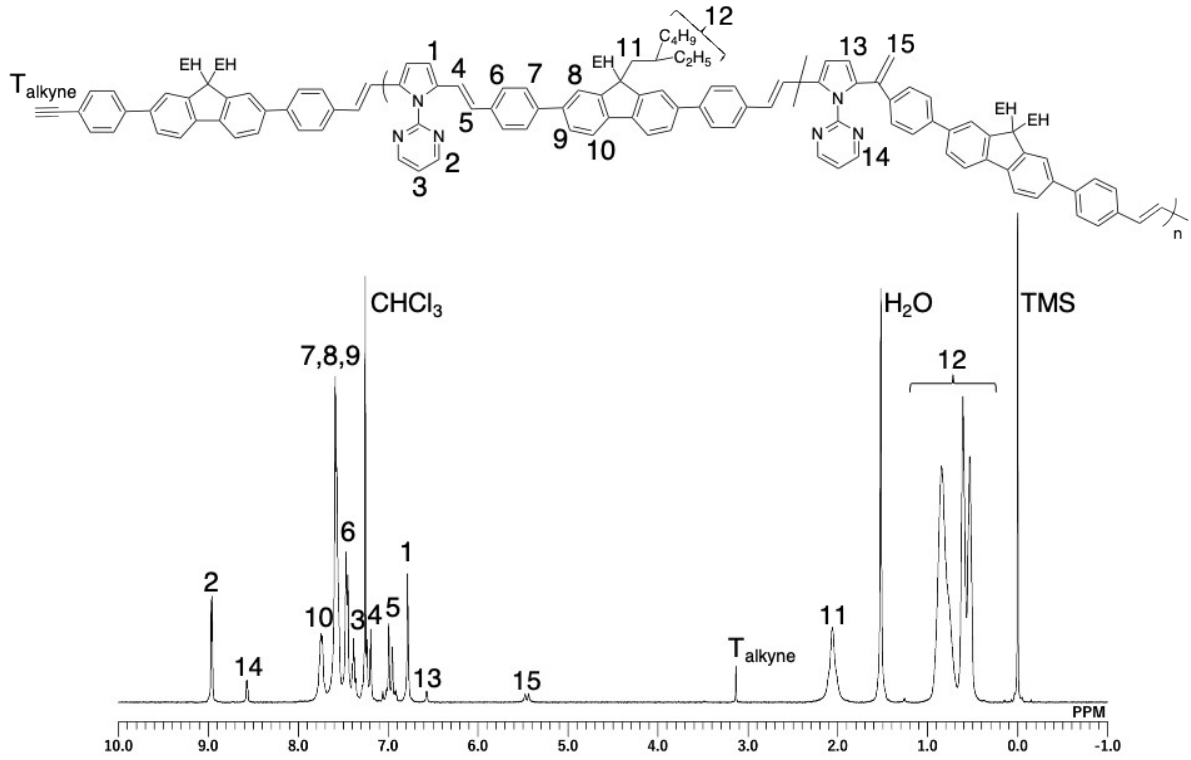


Figure S8. ^{1}H NMR spectrum of Paa under the stoichiometric conditions (1a : 2a = 1:1, Table 1, Entry 1, 400 MHz, $CDCl_3$, r.t.).

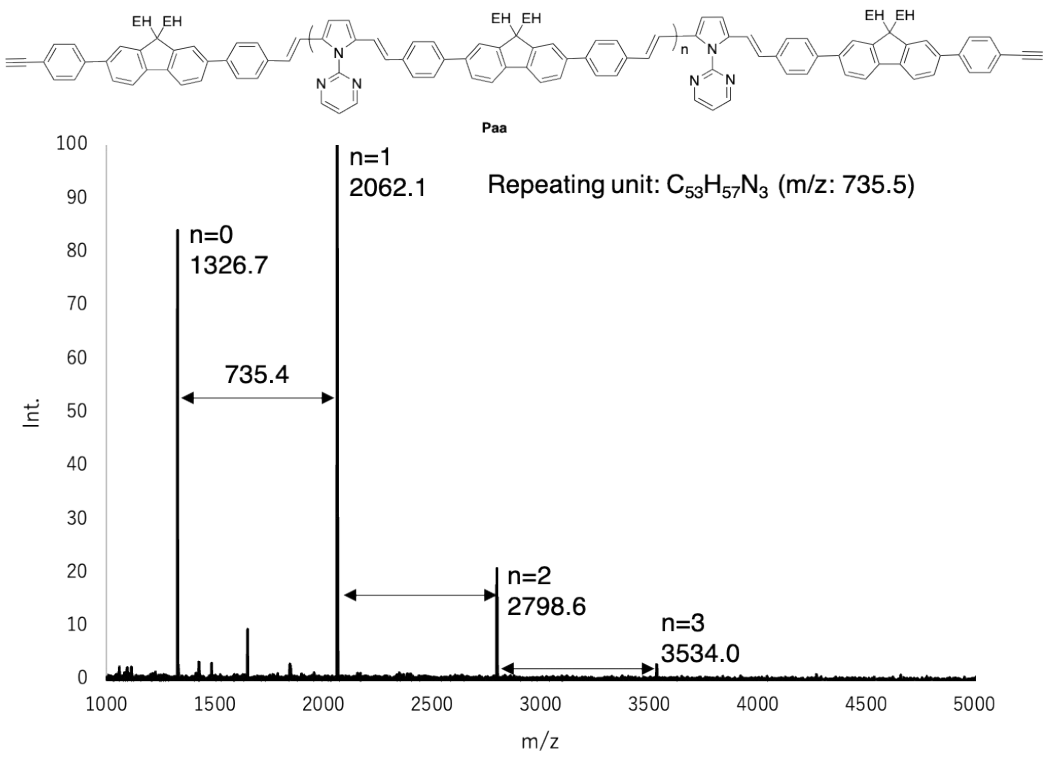


Figure S9. MALDI-TOF-MS of Paa under the stoichiometric conditions (1a : 2a = 1:1, Table 1, Entry 1).

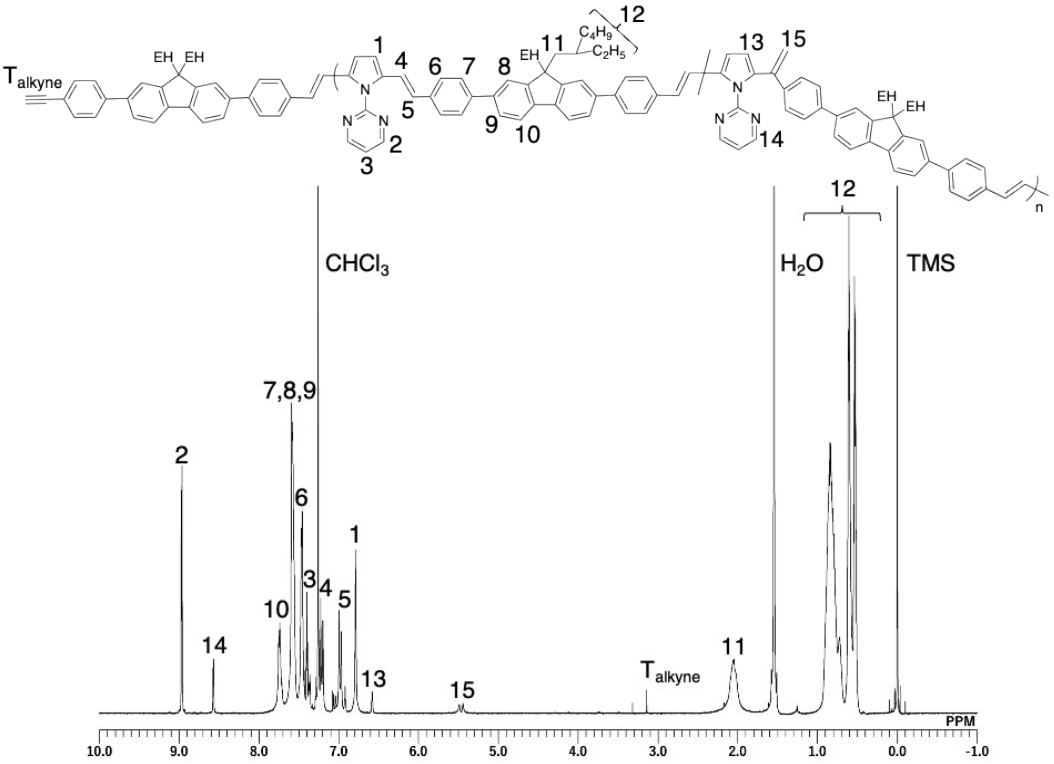


Figure S10. ^{1}H NMR spectrum of Paa under the nonstoichiometric conditions (1a : 2a = 2:1, Table 1, Entry 3, 600 MHz, $CDCl_3$, r.t.).

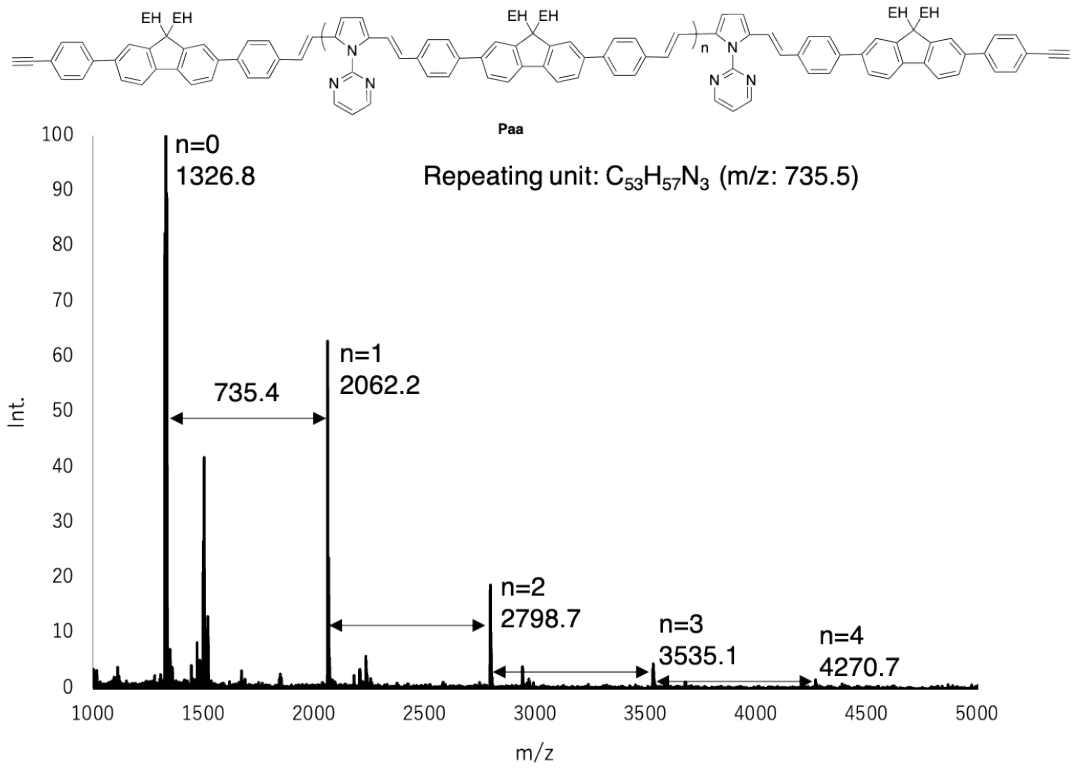


Figure S11. MALDI-TOF-MS of Paa under the nonstoichiometric conditions (1a : 2a = 2:1, Table 1, Entry 3).

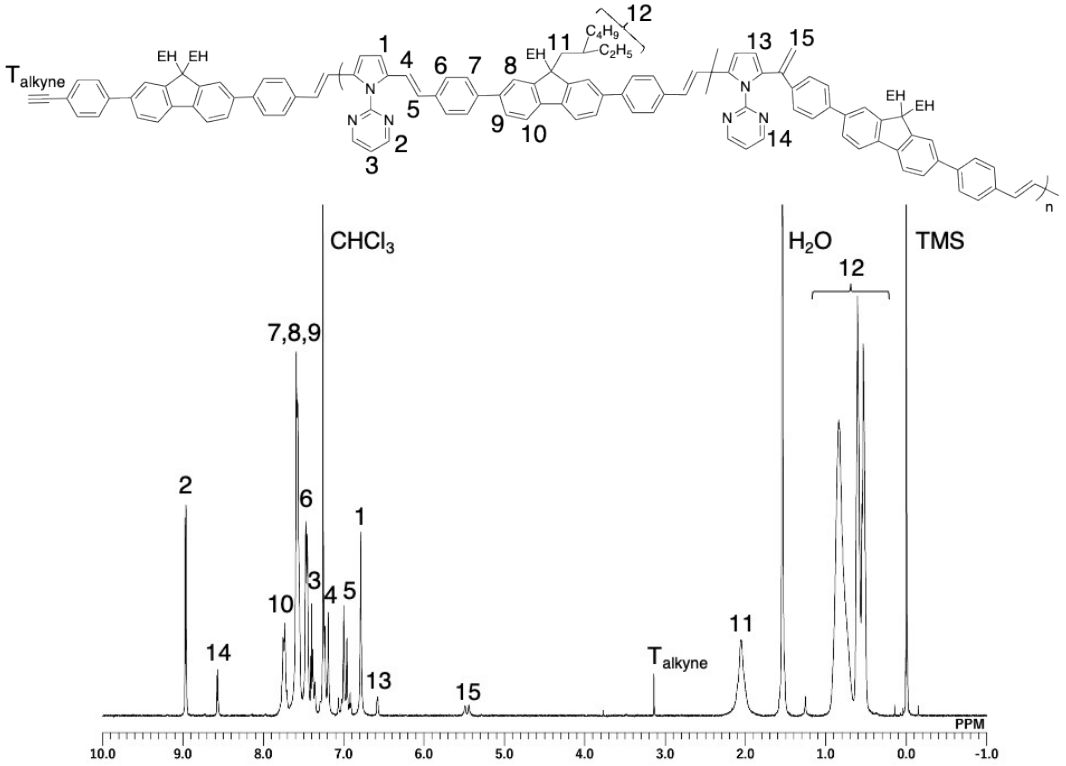


Figure S12. ^{1}H NMR spectrum of Paa under the nonstoichiometric conditions (1a : 2a = 5:1, Table 1, Entry 4, 400 MHz, $CDCl_3$, r.t.).

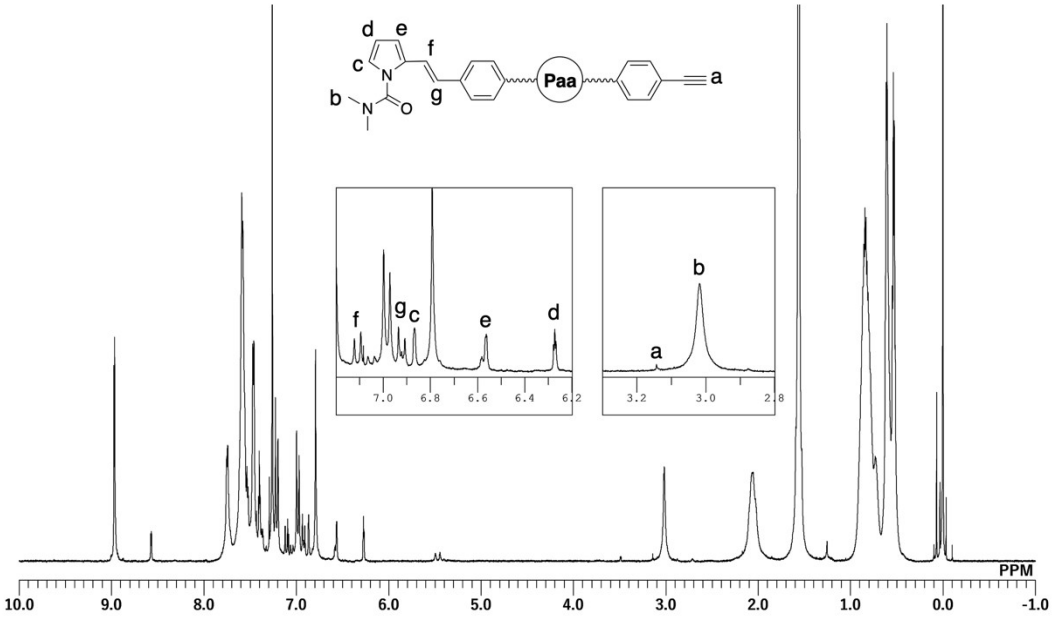


Figure S13. ^{1}H NMR spectrum of Paa modified by 1c (Scheme 3, 600 MHz, $CDCl_3$, r.t.).

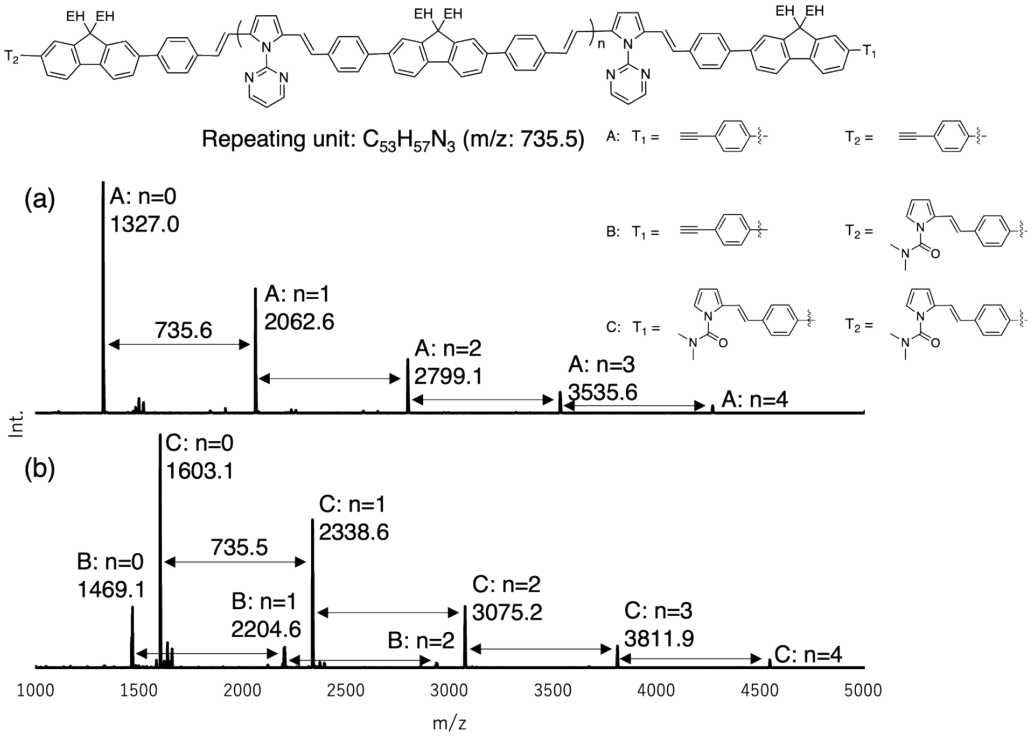


Figure S14. MALDI-TOF-MS of Paa modified by 1c (Scheme 3).

(a) Before the end-capping reaction (b) After the end-capping reaction

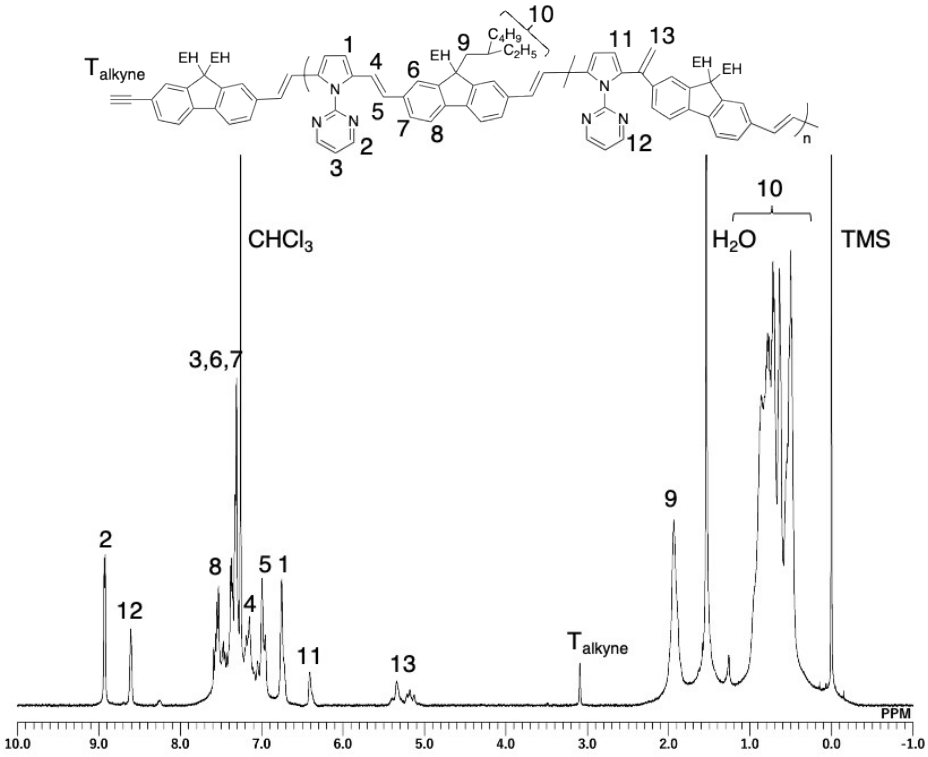


Figure S15. ^{1}H NMR spectrum of Pab under the stoichiometric conditions (1a : 2b = 1:1, Table S2, Entry 1, 400 MHz, $CDCl_3$, r.t.).

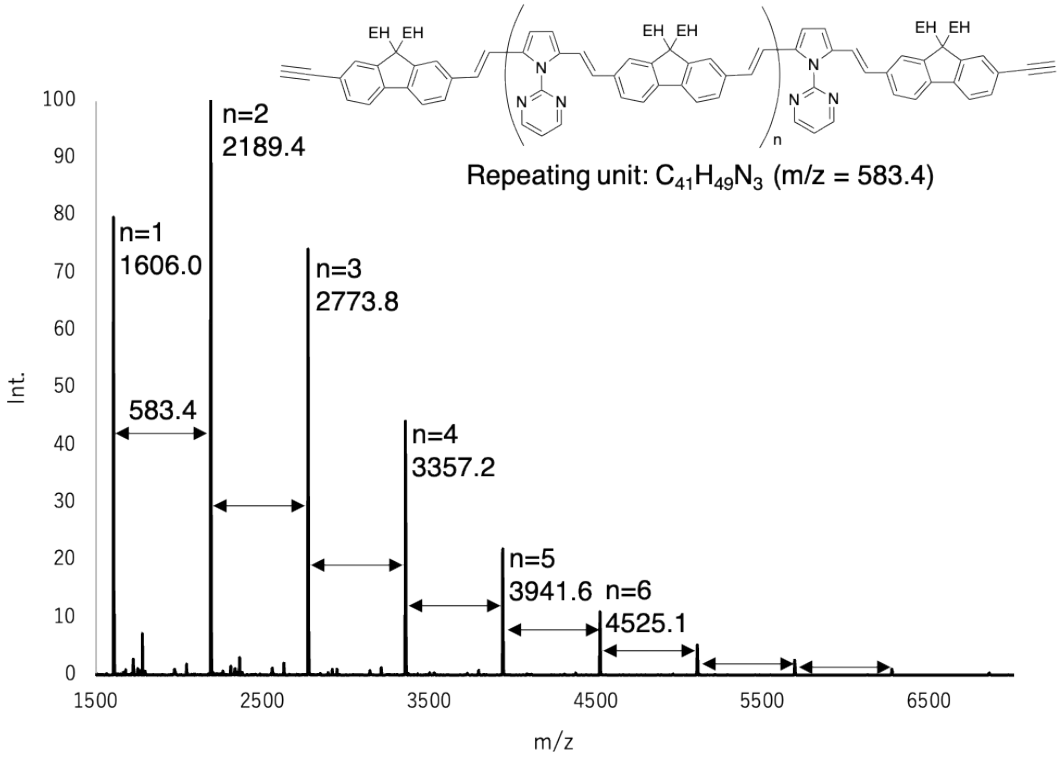


Figure S16. MALDI-TOF-MS of Pab under the stoichiometric conditions (1a : 2b = 1:1, Table S2, Entry 1).

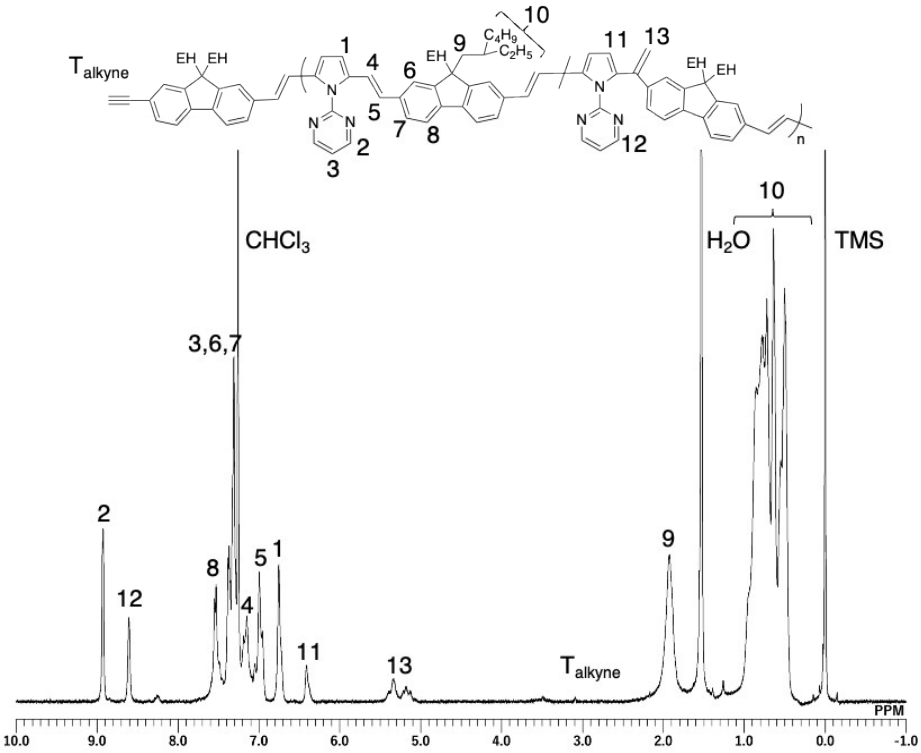


Figure S17. ^{1}H NMR spectrum of Pab under the nonstoichiometric conditions (1a : 2b = 2:1, Scheme 4a , 400 MHz, $CDCl_3$, r.t.).

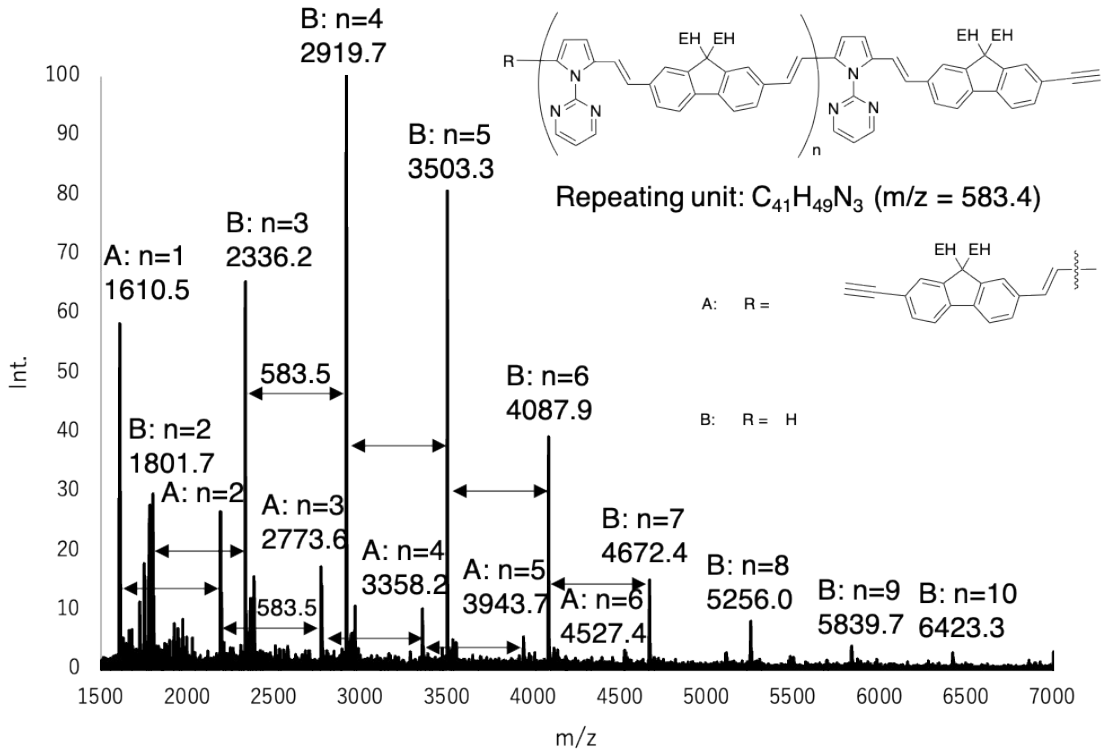


Figure S18. MALDI-TOF-MS of Pab under the nonstoichiometric conditions (1a : 2b = 2:1, Scheme 4a).

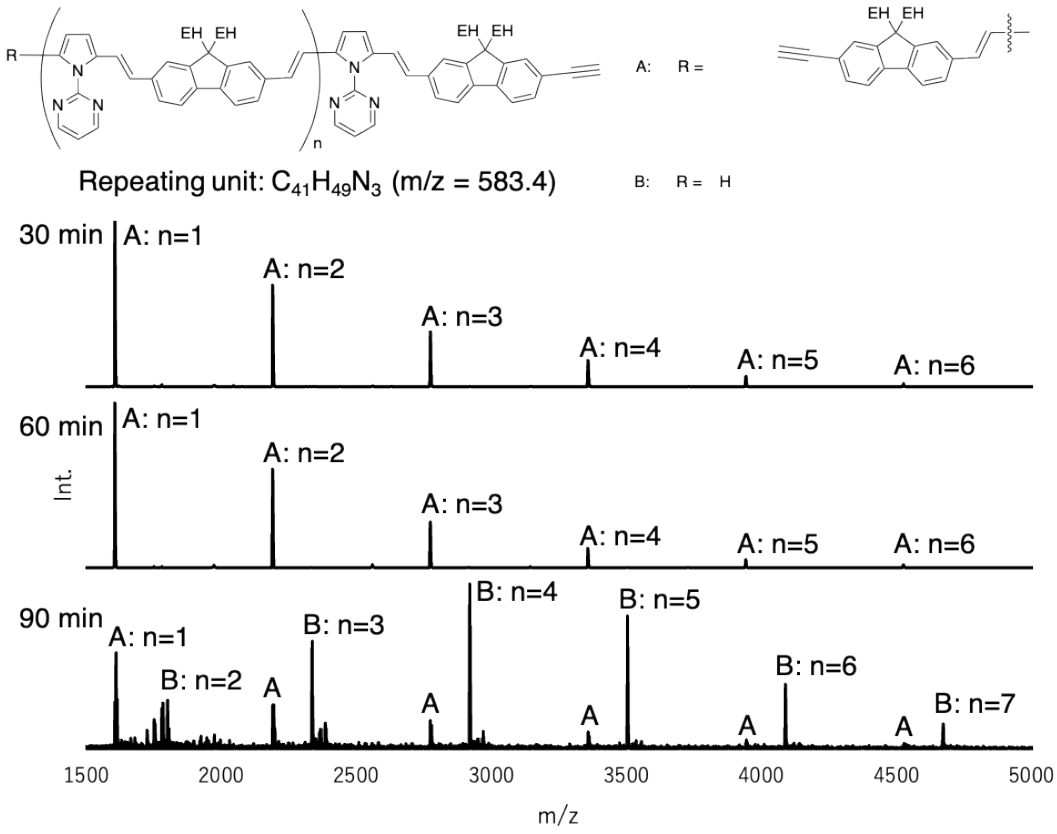


Figure S19. MALDI-TOF-MS of Pab under the nonstoichiometric conditions with various reaction time (1a : 2b = 2:1, 30 min: Table S2, Entry 2; 60 min: Table S2, Entry 3; 90 min: Scheme 4a).

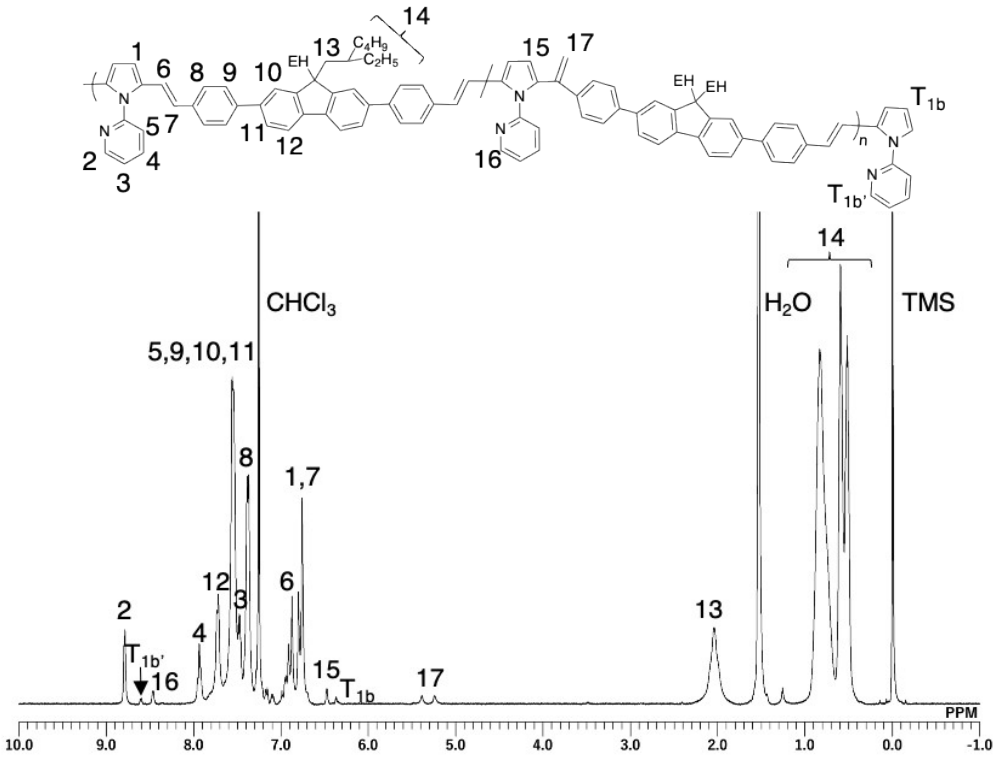


Figure S20. ^{1}H NMR spectrum of Pba under the stoichiometric conditions (1b : 2a = 1:1, Table S2, Entry 5, 400 MHz, $CDCl_3$, r.t.).

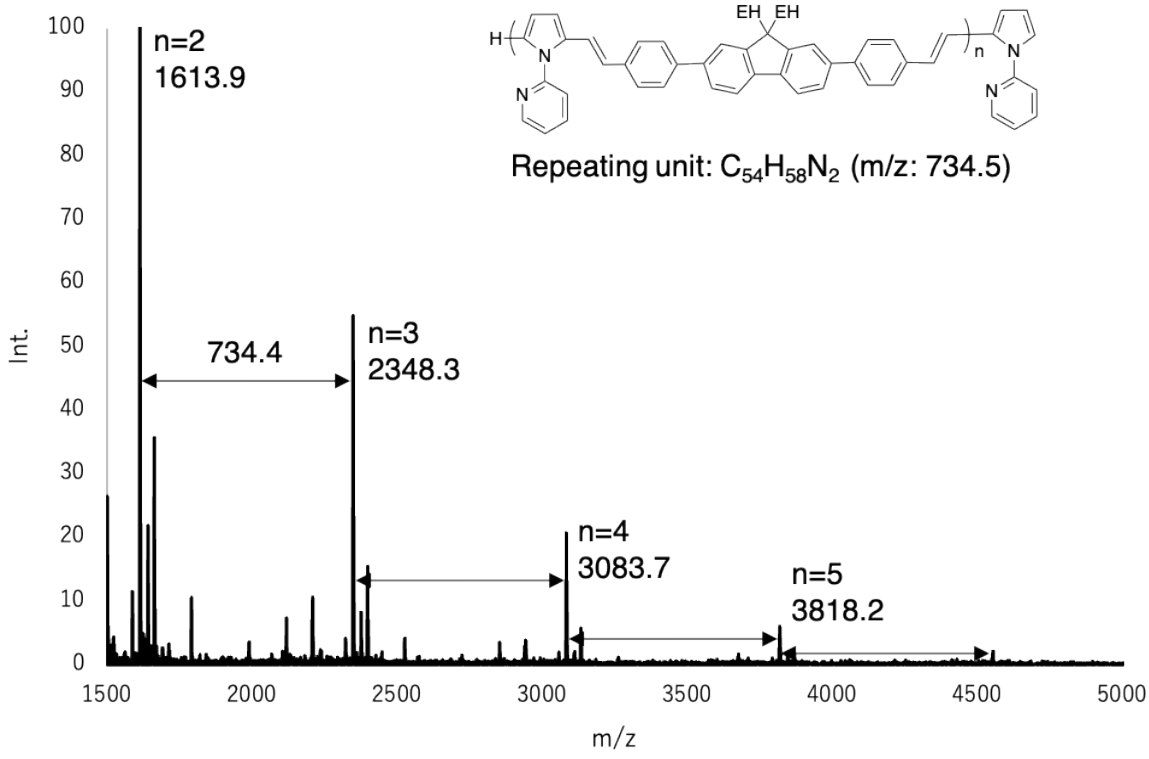


Figure S21. MALDI-TOF-MS of Pba under the stoichiometric conditions (1b : 2a = 1:1, Table S2, Entry 5).

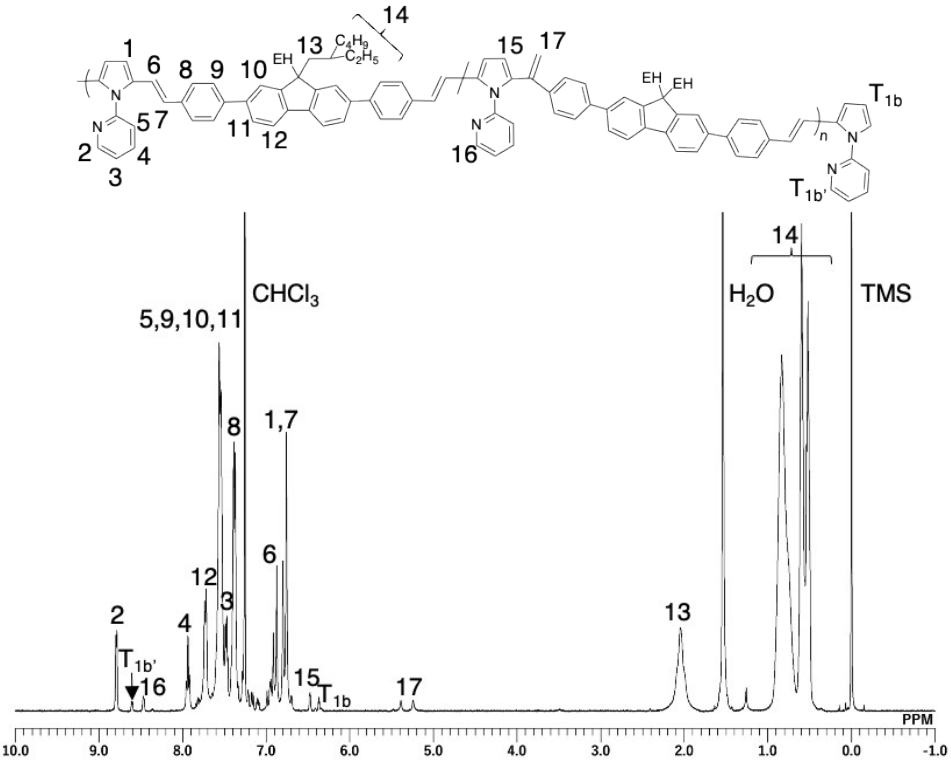


Figure S22. ^{1}H NMR spectrum of Pba under the nonstoichiometric conditions (1b : 2a = 2:1, Scheme 4b , 400 MHz, $CDCl_3$, r.t.).

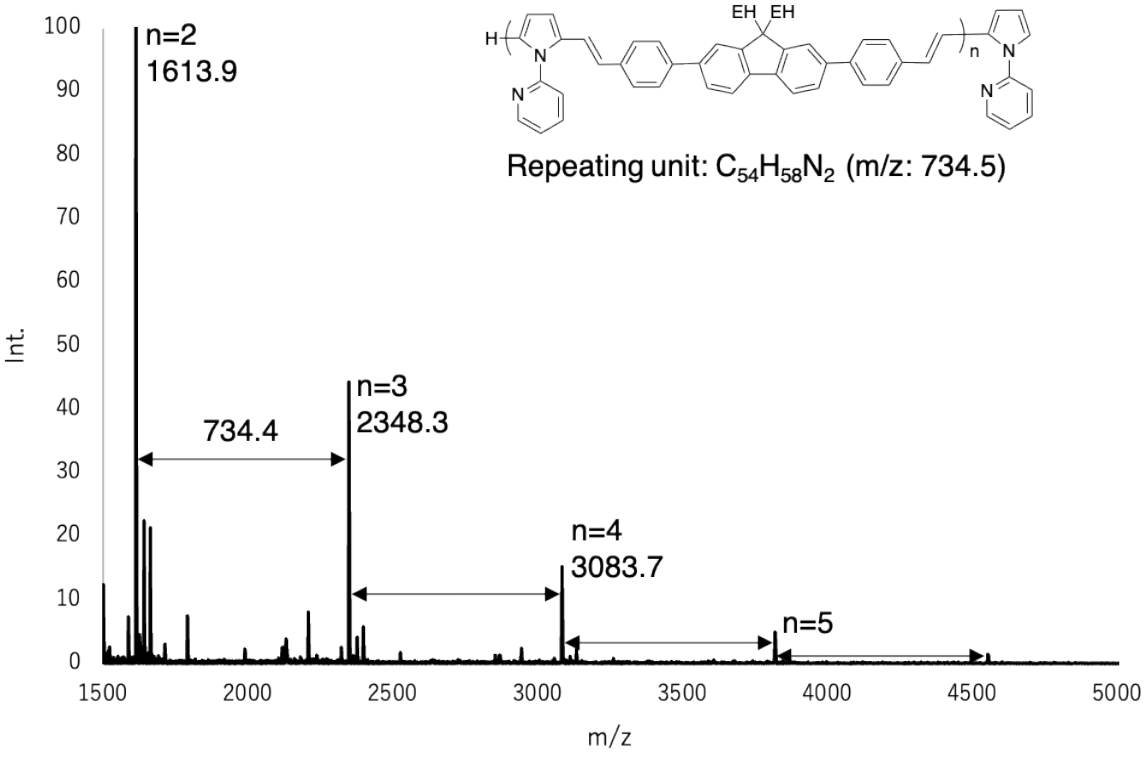


Figure S23. MALDI-TOF-MS of Pba under the nonstoichiometric conditions (1b : 2a = 2:1, Scheme 4b).

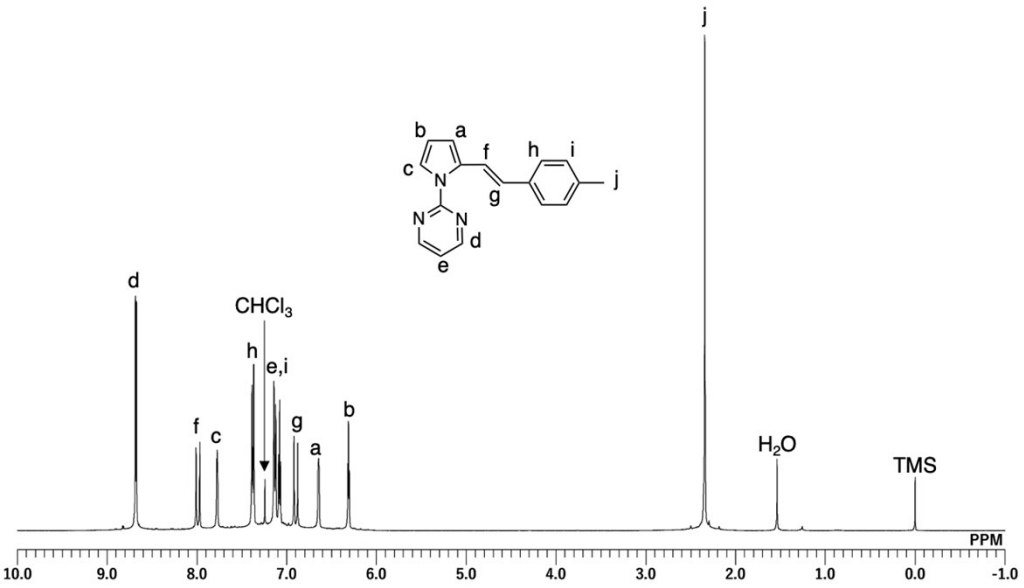


Figure S24. ^{1}H NMR spectrum of 3a prepared by direct alkenylation (Scheme S1, 400 MHz, $CDCl_3$, r.t.).

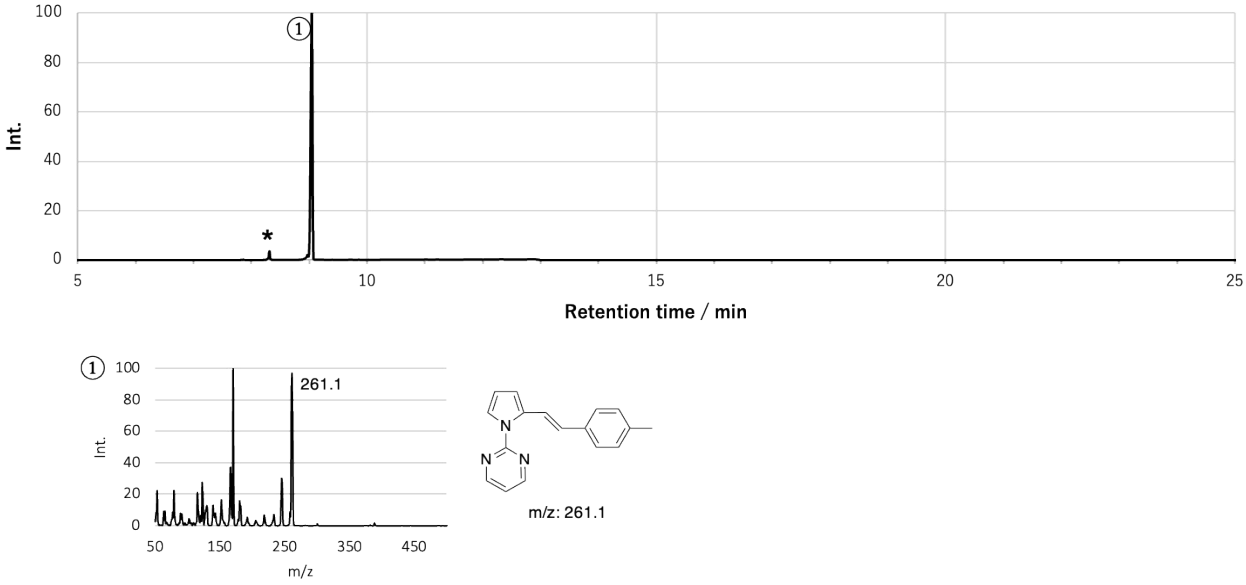


Figure S25. GC-MS of 3a prepared by direct alkenylation (Scheme S1). * Impurities from operations.

Optical data

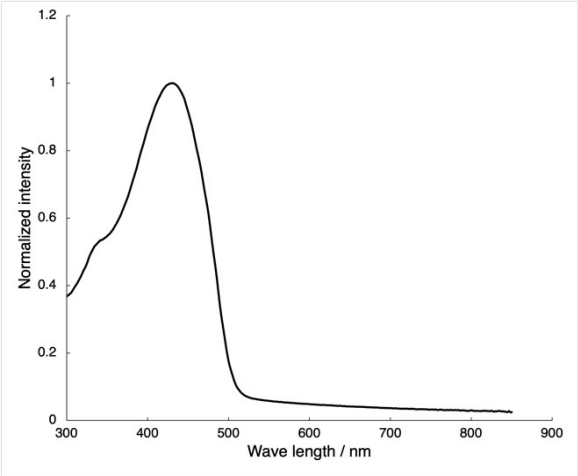


Figure S26. UV absorption spectrum of Paa in the film state (Table 1, Entry 3).

GPC traces

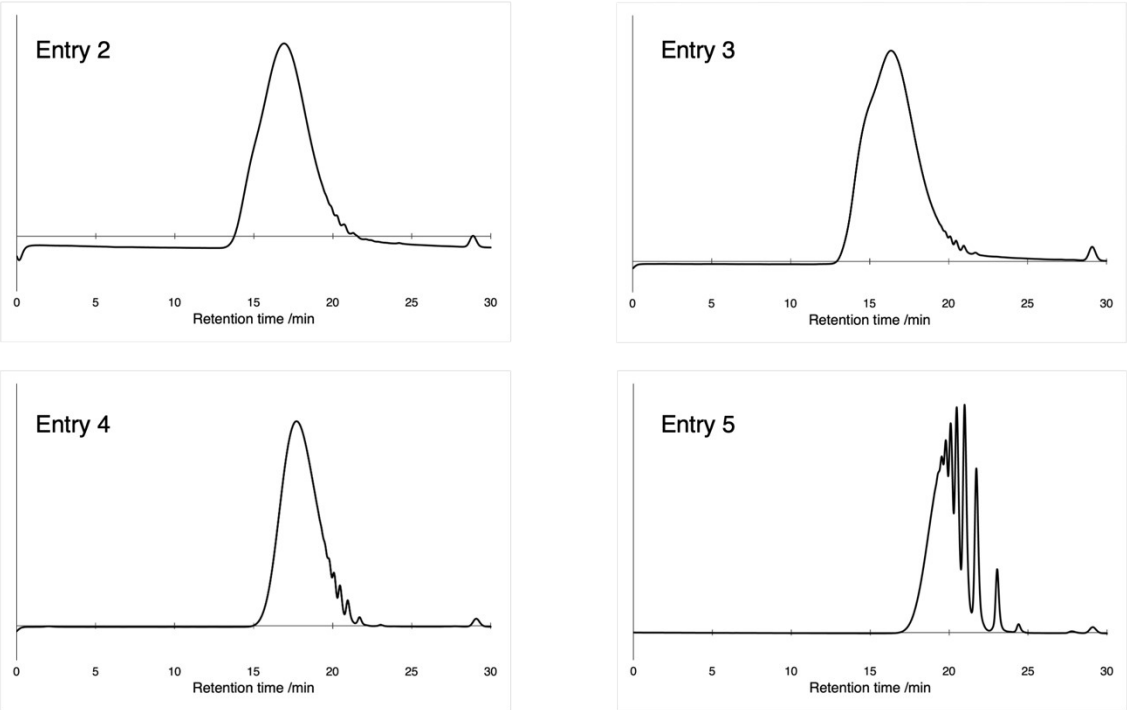


Figure S27. GPC traces of Paa synthesized by nonstoichiometric polyaddition (Table 1).

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