Supporting Information

Molecular Design of Naphthalene- and Carbazole-Based Monomers for Regiospecific Synthesis of Poly(arylenevinylene)s via Co-catalyzed Hydroarylation Polyaddition

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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 (**2a**), 1-phenylpyrazole (**1b**), 4,4'-diethynylbiphenyl (**7c**), and 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenylbenzimidazole) (TPBi) were purchased from Tokyo Chemical Industry. Neodecanoic acid (NDA) was purchased from Wako Pure Chemical Industries. 2-Phenylpyridine (**1a**) and 4-*tert*-butylphenylacetylene (**2b**) were purchased from Sigma Aldrich. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP AI 4083) was purchased from Heraeus. The other regents were also purchased from Kanto Chemical, Tokyo Chemical Industry, and Sigma Aldrich. TPBi was purified by thermal sublimination before use. 2,7-Bis(4-ethynylphenyl)-9,9-bis(2-octyldodecyl)fluorene (**7a**), 2,7-bis(4-ethynylphenyl)-9,9-di(*n*-octyl)fluorene (**7b**), and $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ were synthesized by the same methods as our previous reports.[1]

General methods

NMR spectra were recorded on a Bruker AVANCE-400 and AVANCE-600 NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured with $CHCl_3$ (7.26 ppm for ^1H NMR), C_2HDCl_4 (6.00 ppm for ^1H NMR), and $CDCl_3$ (77.0 ppm for ^{13}C NMR) as an internal reference. DFT calculations were performed by Gaussian at the B3LYP/6-31G(d) level. Crystal Structure Determination Intensity data were collected on a Bruker SMART APEX II ULTRA with Mo Kα radiation. 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 spectra 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. Elemental analyses were carried out with Yanaco CHN coder MT-6 or MT-5. UV-vis absorption spectra in solution states were recorded on a Hitachi U-3900H or a JASCO V-630. PL spectra in solution states were recorded on a Hitachi F-2700 fluorescence spectrophotometers. UV-vis absorption spectra and PL spectra for the spin-coated films were recorded on a Hitachi U-3010 and JASCO FP-6500 spectrophotometer, respectively. PLQYs of the spin-coated films were measured using a JASCO FP-6500 spectrophotometer with an integrating sphere. The HOMO energy levels were estimated by PYS using an AC-3 spectrometer (Riken Keiki). The surface morphologies of the polymer films were observed using AFM (5100N and 5000II, Hitachi High-Tech Corporation). XRD measurements were performed using MiniFlex600 (Rigaku Corporation, Cu Kα radiation). High-resolution mass spectroscopy (HRMS) was carried out with an APCI-Direct Probe of Bruker micrOTOF II. All of the manipulations for the reactions were performed under a nitrogen atmosphere using Schlenk techniques.

Small molecular model reaction of mono-substituted benzene (Figure 1)

To a stirred solution of a mono-substituted benzene (**1a**-**1e**, 0.10 mmol), 4-ethynyltoluene (**2a**, 26.6 μL, 0.21 mmol), and 1,3,5-trimethoxybenzene (11.2 mg, 0.067 mmol) in anhydrous THF (1.0 mL) was added $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (3.94 mg, 0.0050 mmol) and NDA (11.4 μL, 0.060 mmol). The reaction mixture was stirred for 24 h at 30 °C under nitrogen atmosphere. A portion of the reaction mixture was sampled at 0 and 24 h. The NMR yield was calculated from the integral value of the signal for the product on the basis of the internal standard (1,3,5-trimethoxybenzene).

Small molecular model reaction of naphthalene- and carbazole-based monomers

To a stirred solution of an aromatic monomer (0.10 mmol), 4-*tert*-butylphenylacetylene (**2b**, 37.4 μL, 0.21 mmol), and 1,3,5-trimethoxybenzene (11.2 mg, 0.067 mmol) in anhydrous THF (2.0 mL) was added $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (3.94 mg, 0.0050 mmol) and NDA (18.9 μL, 0.10 mmol). The reaction mixture was stirred for 24 h at 30 °C under nitrogen atmosphere. A portion of the reaction mixture was sampled at 0 and 24 h. The NMR yield was calculated from the integral value of the signal for the product on the basis of the internal standard (1,3,5-trimethoxybenzene). Isolation of the product is described below.

Synthesis of 6ab (Scheme 2a)

2,6-Di(1-pyrazolyl)naphthalene (**5a**, 52.0 mg, 0.20 mmol) was used as the aromatic monomer. The reaction mixture was diluted with $CHCl_3$ (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 product was isolated by silica gel column chromatography using hexane : ethyl acetate (9:1 → 4:1) as an eluent. **6ab** was obtained as a yellow solid in 82% yield (94.6 mg). ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 8.16 (s, 2H), 7.98 (s, 2H), 7.84 (d, *J* = 1.7, 2H), 7.78 (d, *J* = 2.2, 2H), 7.38 (s, 8H), 7.11 (d, *J* = 16.1, 2H), 7.02 (d, *J* = 16.2, 2H), 6.53 (t, *J* = 2.1, 2H), 1.33 (s, 18H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, r.t.): *δ* 151.43, 140.97, 138.11, 134.29, 132.90, 132.00, 131.88, 131.69, 126.62, 125.66, 124.58, 123.29, 106.86, 34.69, 31.27. Anal. calcd. for $C_{40}H_{40}N_4$: C 83.30, H 6.99, N 9.71; found: C 83.12, H 6.76, N 9.69.

Synthesis of 6cb (Scheme S2)

9-(2-Ethylhexyl)-3,6-di(1-pyrazolyl)carbazole (**5c**, 82.3 mg, 0.20 mmol) was used as the aromatic monomer. The reaction mixture was diluted with $CHCl_3$ (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 product was isolated by silica gel column chromatography using hexane : ethyl acetate (1:0 → 4:1) as an eluent. **6cb** was obtained as a yellow solid in 73% yield (106 mg). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 8.02 (s, 2H), 7.79 (s, 2H), 7.67 (s, 4H), 7.36 (s, 8H), 7.07 (d, *J* = 16.4, 2H), 6.91 (d, *J* = 16.4, 2H), 6.48 (d, *J* = 1.9, 2H), 4.22 - 4.40 (m, 2H), 2.05 - 2.27 (m, 1H), 1.39 - 1.50 (m, 8H), 1.32 (s, 18H), 0.99 (t, *J* = 7.2, 3H), 0.92 (t, *J* = 7.1, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, r.t.): *δ* 151.11, 141.86, 140.40, 134.44, 132.62, 132.14, 132.12, 130.45, 126.45, 125.60, 124.24, 121.97, 118.76, 106.24, 105.72, 47.51, 39.43, 34.64, 31.26, 31.00, 28.87, 24.55, 23.03, 14.13, 11.00. Anal. calcd. for $C_{50}H_{57}N_5$: C 82.49, H 7.89, N 9.62; found: C 82.47, H 8.03, N 9.57.

Deuterium exchange experiment (Scheme 3)

To a stirred solution of a naphthalene derivative (0.10 mmol) and 1,3,5-trimethoxybenzene (11.2 mg, 0.067 mmol) in anhydrous THF (2.0 mL) was added $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (3.94 mg, 0.0050 mmol) and CD_3COOD (11.4 μL, 0.20 mmol). The reaction mixture was stirred for 24 h at 30 °C under nitrogen atmosphere. A portion of the reaction mixture was sampled at 0 and 24 h. The deuterium ratio was calculated from the integral value of the signal for the product on the basis of the internal standard (1,3,5-trimethoxybenzene).

Synthesis of Paa (Scheme 4a)

To a stirred solution of **5a** (26.0 mg, 0.10 mmol) and 2,7-bis(4-ethynylphenyl)-9,9-bis(2-octyldodecyl)fluorene (**7a**, 92.8 mg, 0.10 mmol) in anhydrous THF (5.0 mL) were added $[Cp^*Co(CH_3CN)_3](SbF_6)_2$ (3.94 mg, 0.0050 mmol) and NDA (18.9 μL, 0.10 mmol). The reaction mixture was stirred for 24 h at 30 °C under a nitrogen atmosphere in the dark. Then, the reaction mixture was diluted with $CHCl_3$ (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 × 2). The organic layer was dried over sodium sulfate and filtered through a Celite plug. The solution of $CHCl_3$ was concentrated and reprecipitated into methanol. The precipitate was filtered and a polymeric product (**Paa**) was obtained as a yellow solid in 96% yield (114 mg, M_n = 4.1 × 10^4, PDI = 3.9). ^{1}H NMR (600 MHz, $C_2D_2Cl_4$, 373 K): δ 8.27 (s, 2H), 8.07 (s, 2H), 7.92 (s, 2H), 7.88 (s, 2H), 7.82 (d, J = 7.4, 2H), 7.48 - 7.77 (m, 12H), 7.20 (s, 4H), 6.62 (s, 2H), 2.16 (s, 2H), 0.71 - 1.40 (m, 80H). Anal. calcd. for $C_{85}H_{110}N_4$: C 85.95, H 9.33, N 4.72; found: C 85.07, H 9.30, N 4.74.

Synthesis of Pcb (Scheme 4b)

Pcb was obtained by the same procedure as **Paa**.

5c (41.2 mg, 0.10 mmol) and 2,7-bis(4-ethynylphenyl)-9,9-di(*n*-octyl)fluorene (**7b**, 59.1 mg, 0.10 mmol) were used as the monomers. The reaction was carried out at 30 °C for 24 h, giving **Pcb** as an yellow solid in 73% yield (73.4 mg, M_n = 1.1 × 10^4, PDI = 2.8). The reaction was also carried out at 30 °C for 48 h, giving **Pcb** as a yellow solid in 71% yield (71.4 mg, M_n = 2.3 × 10^4, PDI = 3.4). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.): δ 8.10 (s, 2H), 7.86 (s, 2H), 7.45 - 7.84 (m, 18H), 7.19 (d, J = 16.3, 2H), 7.06 (d, J = 16.0, 2H), 6.56 (s, 2H), 4.37 (m, 2H), 1.92 - 2.33 (m, 5H), 0.63 - 1.55 (m, 44H). Anal. calcd. for $C_{71}H_{79}N_5$: C 85.07, H 7.94, N 6.99; found: C 85.28, H 7.67, N 6.71.

Synthesis of Pcc (Scheme S3)

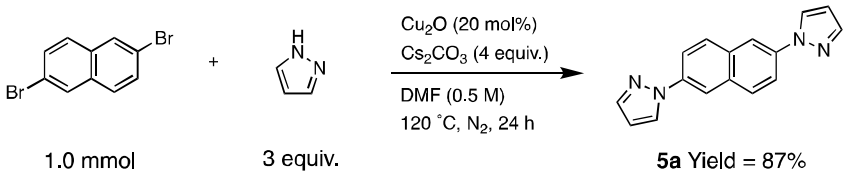
5c (41.2 mg, 0.10 mmol) and 4,4'-diethynylbiphenyl (**7c**, 20.2 mg, 0.10 mmol) were used as the monomers. The reaction was carried out at 30 °C for 24 h, and precipitates were corrected by filtration. The obtained solid was purified via Soxhlet extraction with methanol and tetrachloroethane. The solution of tetrachloroethane was concentrated and reprecipitated into *n*-hexane. The precipitate was filtered and a polymeric product (**Pcc**) was obtained as a red solid in 75% yield (45.7 mg). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, r.t.): δ 8.08 (s, 2H), 7.84 (s, 2H), 7.77 (s, 4H), 7.39 - 7.70 (m, 8H), 7.15 (d, J = 15.7, 2H), 7.03 (d, J = 15.9, 2H), 6.56 (s, 2H), 4.34 (m, 2H), 2.06 - 2.30 (m, 1H), 1.24 - 1.55 (m, 8H), 0.79 - 1.11 (m, 6H).

Fabrication and Characterization of OLED.

OLED was fabricated in the following configuration: ITO/PEDOT:PSS/light-emitting **Paa** layer/electron transporting (hole blocking) TPBi layer/LiF/Al. The patterned indium tin oxide (ITO) glass (conductivity: 10 Ω/square) was precleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet-ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated onto the ITO at 3000 rpm and air-dried at 110 °C for 10 min on a hot plate. The substrate was then transferred to a N_2-filled glovebox where it was redried at 110 °C for 10 min on a hot plate. A chloroform solution of **Paa** (5 mg/1 mL) was subsequently spin-coated onto the PEDOT:PSS surface to form the light-emitting layer (47 nm). TPBi (40 nm), LiF (1 nm), and Al (100 nm) were then deposited onto the active layer with conventional thermal evaporation at a chamber pressure lower than 5 x 10^{-4} Pa, which provided the devices with an active area of 2 x 2 mm^2. Current−voltage characteristics and

luminance of the OLED were simultaneously measured using an ADCMT 6245 DC voltage current source/monitor (ADC CORPORATION) and an LS-100 luminance meter (KONICA MINOLTA JAPAN, INC.), respectively. The EL spectra and the coordinates of the CIE chromaticity were measured using an array spectrometer (MCPD-9800-311C, Otsuka Electronics Co, Ltd.).

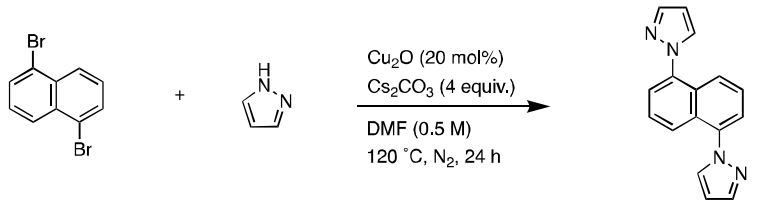
Synthesis of 2,6-di(1-pyrazolyl)naphthalene (**5a**, Figure S23)[2]



1.0 mmol 3 equiv. **5a** Yield = 87%

A solution of 2,6-dibromonaphthalene (286 mg, 1.0 mmol), pyrazole (204 mg, 3.0 mmol), Cu_2O (28.6 mg, 0.20 mmol), and Cs_2CO_3 (1.30 g, 4.0 mmol) in DMF (2.0 mL) was stirred for 24 h at 120 °C under nitrogen atmosphere. The crude mixture was dried under vacuum and dissolved in dichloromethane. The solution filtered through a Celite plug, and rinsed with dichloromethane. The product was isolated by silica gel column chromatography using hexane : ethyl acetate (3:1 → 1:1) as an eluent. 2,6-di(1-pyrazolyl)naphthalene (**5a**) was obtained as a white solid in 87% yield (227 mg). ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 8.15 (d, J = 1.9, 2H), 8.08 (d, J = 2.1, 2H), 7.98 (d, J = 8.8, 2H), 7.95 (dd, J = 1.9, 8.8, 2H), 7.80 (d, J = 1.3, 2H), 6.54 (t, J = 2.0, 2H). Anal. calcd. for $C_{16}H_{12}N_4$: C 73.83, H 4.65, N 21.52; found: C 73.59, H 4.43, N 21.67. **5b** and **5c** were obtained by the same procedure.

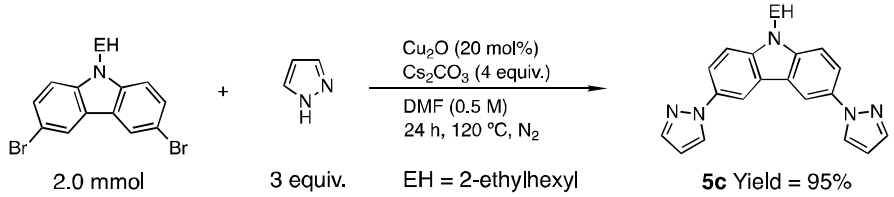
Synthesis of 1,5-di(1-pyrazolyl)naphthalene (**5b**, Figure S24)



1.0 mmol 3 equiv. **5b** Yield = 85%

1,5-Dibromonaphthalene (286 mg, 1.0 mmol) was used instead of 2,6-dibromonaphthalene. The reaction was also carried out at 120 °C for 24 h, giving 1,5-di(1-pyrazolyl)naphthalene (**5b**) as a white solid in 85% yield (221 mg). ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 7.90 (d, J = 8.4, 2H), 7.87 (d, J = 1.3, 2H), 7.81 (d, J = 2.2, 2H), 7.55 - 7.62 (m, 4H), 6.57 (t, J = 2.0, 2H). Anal. calcd. for $C_{16}H_{12}N_4$: C 73.83, H 4.65, N 21.52; found: C 73.92, H 4.52, N 21.73.

Synthesis of 9-(2-ethylhexyl)-3,6-di(1-pyrazolyl)carbazole (**5c**, Figure S25)

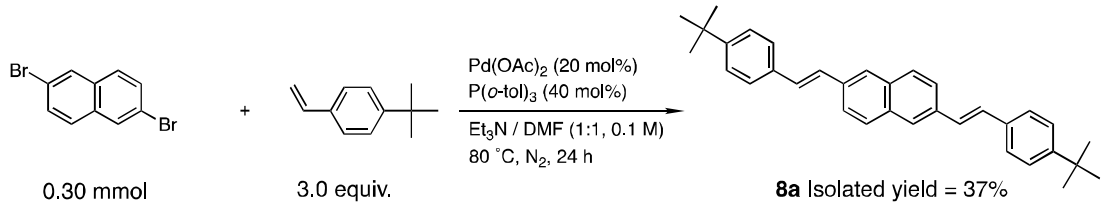


2.0 mmol 3 equiv. EH = 2-ethylhexyl **5c** Yield = 95%

9-(2-Ethylhexyl)-3,6-dibromocarbazole (437 mg, 1.0 mmol) was used instead of 2,6-dibromonaphthalene. The reaction was also carried out at 120 °C for 24 h, giving 9-(2-ethylhexyl)-3,6-di(1-pyrazolyl)carbazole (**5c**) as a colorless oil in 95% yield (391 mg). ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 8.37 (d, J = 1.8, 2H), 7.98 (d, J = 2.5, 2H),

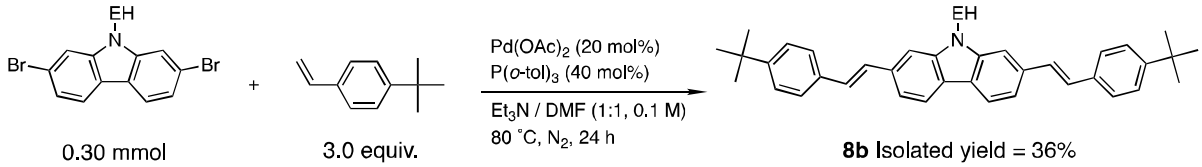
7.79 - 7.87 (m, 2H), 7.77 (s, 2H), 7.45 (d, J = 8.8, 2H), 6.45 - 6.56 (m, 2H), 4.13 - 4.28 (m, 2H), 2.01 - 2.15 (m, 1H), 1.17 - 1.48 (m, 8H), 0.93 (t, J = 7.4, 3H), 0.86 (t, J = 7.0, 3H). HRMS (APCI): *m/z* calculated for $C_{26}H_{30}N_5^+$ [M+H$^+$]: 412.2496, found: 412.2509.

Synthesis of 2,6-bis((*E*)-4-*tert*-butylstyryl)naphthalene (**8a**, Figure S26)[3]



To a stirred solution of 2,6-dibromonaphthalene (85.8 mg, 0.30 mmol), $Pd(OAc)_2$ (13.5 mg, 0.060 mmol), and tris(*o*-tolyl)phosphine (36.5 mg, 0.12 mmol) in anhydrous DMF (1.5 mL) was added 4-*tert*-butylstyrene (164 μL, 0.90 mmol) and triethylamine (1.5 mL). The reaction mixture was stirred for 24 h at 80 °C under nitrogen atmosphere. The crude mixture was filtered through a Celite plug, and rinsed with toluene. The toluene solution was poured into water, and washed with water and brine. The organic layer was dried over sodium sulfate, and filtered through a Celite plug. The product was isolated by silica gel column chromatography using hexane : chloroform (1:0 → 1:1) as an eluent, followed by washing with methanol and recrystallization with chloroform and hexane. 2,6-bis((*E*)-4-*tert*-butylstyryl)naphthalene (**8a**) was obtained as a white solid in 37% yield (49.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 7.82 (d, J = 1.4, 2H), 7.80 (d, J = 8.5, 2H), 7.73 (dd, J = 1.3, 8.6, 2H), 7.51 (d, J = 8.4, 4H), 7.41 (d, J = 8.5, 4H), 7.23 (s, 4H), 1.35 (s, 18H). Anal. calcd. for $C_{34}H_{36}$: C 91.84, H 8.16; found: C 91.68, H 8.26.

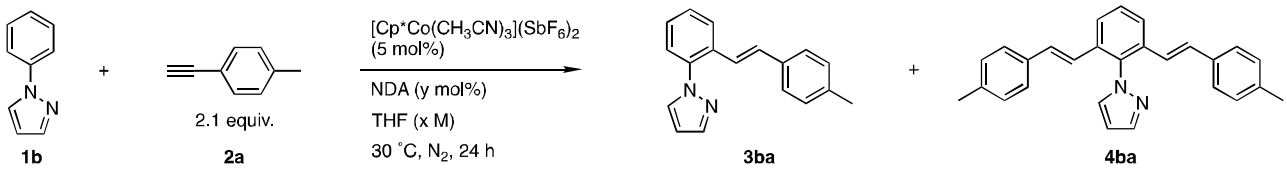
Synthesis of 9-(2-ethylhexyl)-2,7-bis((*E*)-4-*tert*-butylstyryl)carbazole (**8b**, Figure S27)[3]



To a stirred solution of 9-(2-ethylhexyl)-2,7-dibromocarbazole (131 mg, 0.30 mmol), $Pd(OAc)_2$ (13.5 mg, 0.060 mmol), and tris(*o*-tolyl)phosphine (36.5 mg, 0.12 mmol) in anhydrous DMF (1.5 mL) was added 4-*tert*-butylstyrene (164 μL, 0.90 mmol) and triethylamine (1.5 mL). The reaction mixture was stirred for 24 h at 80 °C under nitrogen atmosphere. The crude mixture was filtered through a Celite plug, and rinsed with toluene. The toluene solution was poured into water, and washed with water and brine. The organic layer was dried over sodium sulfate, and filtered through a Celite plug. The product was isolated by silica gel column chromatography using hexane : ethyl acetate (1:0 → 4:1) as an eluent, followed by high performance liquid chromatography (HPLC) and recrystallization with chloroform and hexane. 9-(2-ethylhexyl)-2,7-bis((*E*)-4-*tert*-butylstyryl)carbazole (**8b**) was obtained as a white solid in 36% yield (63.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$, r.t.): δ 8.01 (d, J = 8.1, 2H), 7.52 (d, J = 8.3, 4H), 7.43 - 7.46 (m, 4H), 7.41 (d, J = 8.4, 4H), 7.26 (d, J = 16.9, 2H), 7.21 (d, J = 16.2, 2H), 4.09 - 4.33 (m, 2H), 2.09 - 2.17 (m, 1H), 1.29 - 1.50 (m, 8H), 1.35 (s, 18H), 0.96 (t, J = 7.4, 3H), 0.91 (t, J = 7.3, 3H). Anal. calcd. for $C_{44}H_{53}N$: C 88.68, H 8.97, N 2.35; found: C 88.65, H 9.01, N 2.22.

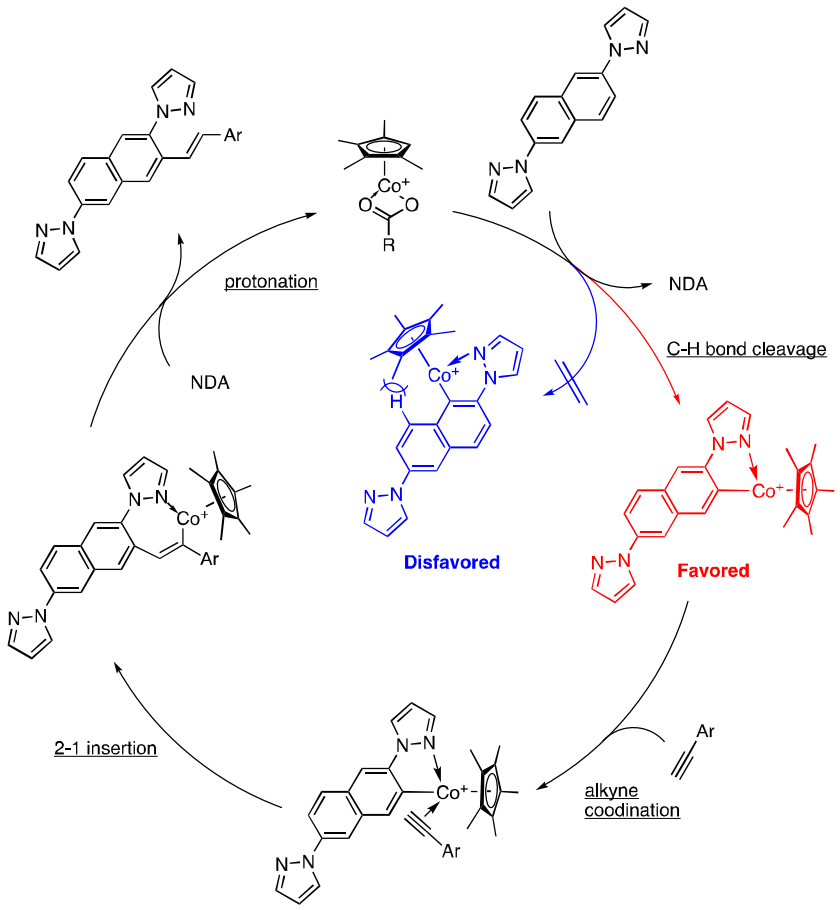
Model reactions and hydroarylation polyaddition

Table S1. Optimization of hydroarylation reaction of 1b with 2a [a]

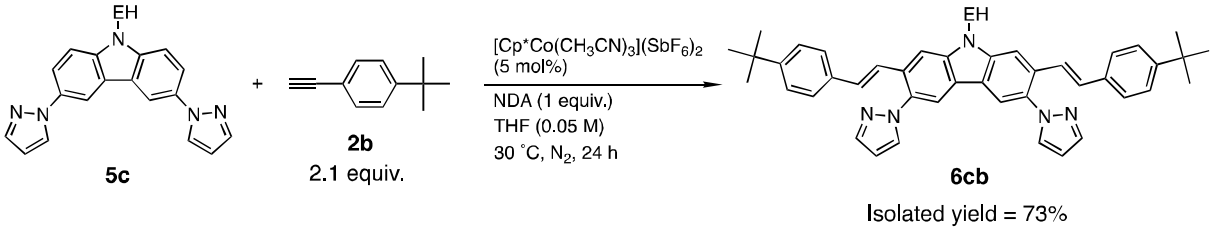


Entry	x [M]	y [mol%]	Conversion of **1b** [%] [b]	Yield of **3ba** [%] [b]	Yield of **4ba** [%] [b]
1	0.10	60	80 (49) [c]	62	18
2	0.05	60	97 (62) [c]	70	27
3	0.05	30	54 (32) [c]	45	9.1
4	0.05	100	96 (66) [c]	61	35

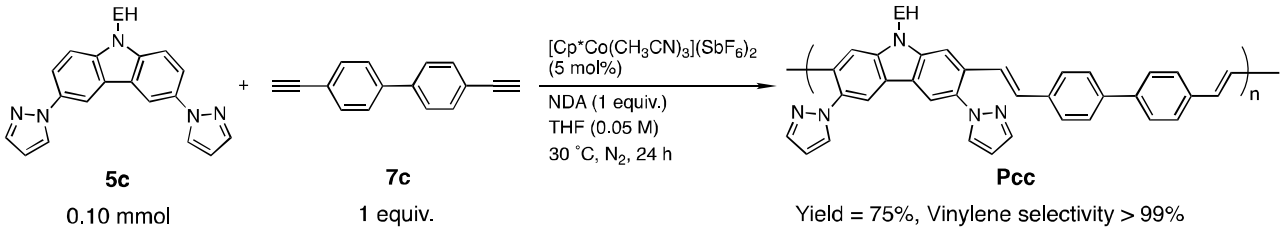
[a] Reaction conditions: **1b** (1.0 equiv., 0.10 mmol), **2a** (2.1 equiv., 0.21 mmol), $[Cp^*Co(CH_3CN)](SbF_6)_2$ (5 mol%), Neodecanoic acid (NDA, 30-100 mol%), and tetrahydrofuran (THF, 1.0 or 2.0 mL), 24 h under N_2 atmosphere at 30 °C. [b] Conversions and yields were calculated by ^1H NMR analyses using 1,3,5-trimethoxybenzene as an internal standard. [c] Consumption of C-H bonds adjacent to an 1-pyrazole group.



Scheme S1. Proposed catalytic cycle of the hydroarylation reaction of 5a.



Scheme S2. Hydroarylation reaction of 5c with 2b



Scheme S3. Hydroarylation polyaddition of 5c with 7c

NMR and MS spectra

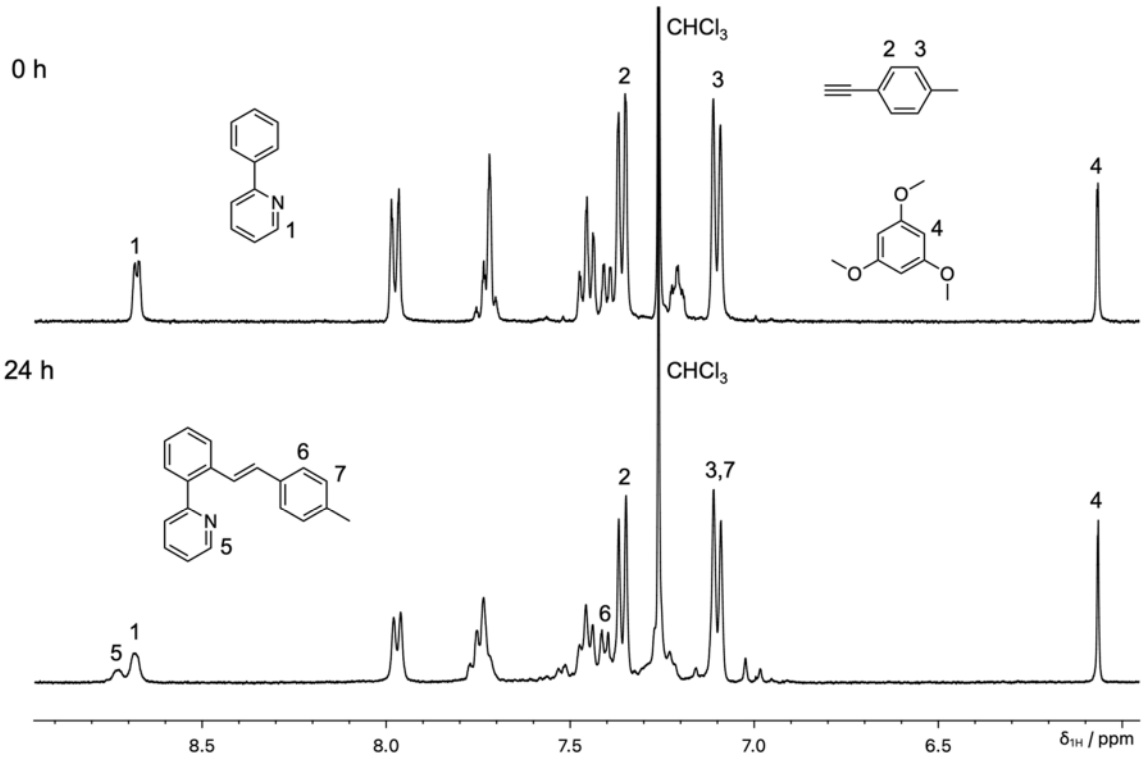


Figure S1. ^{1}H NMR spectra of the model reaction of 1a with 2a (400 MHz, $CDCl_3$, r.t.).

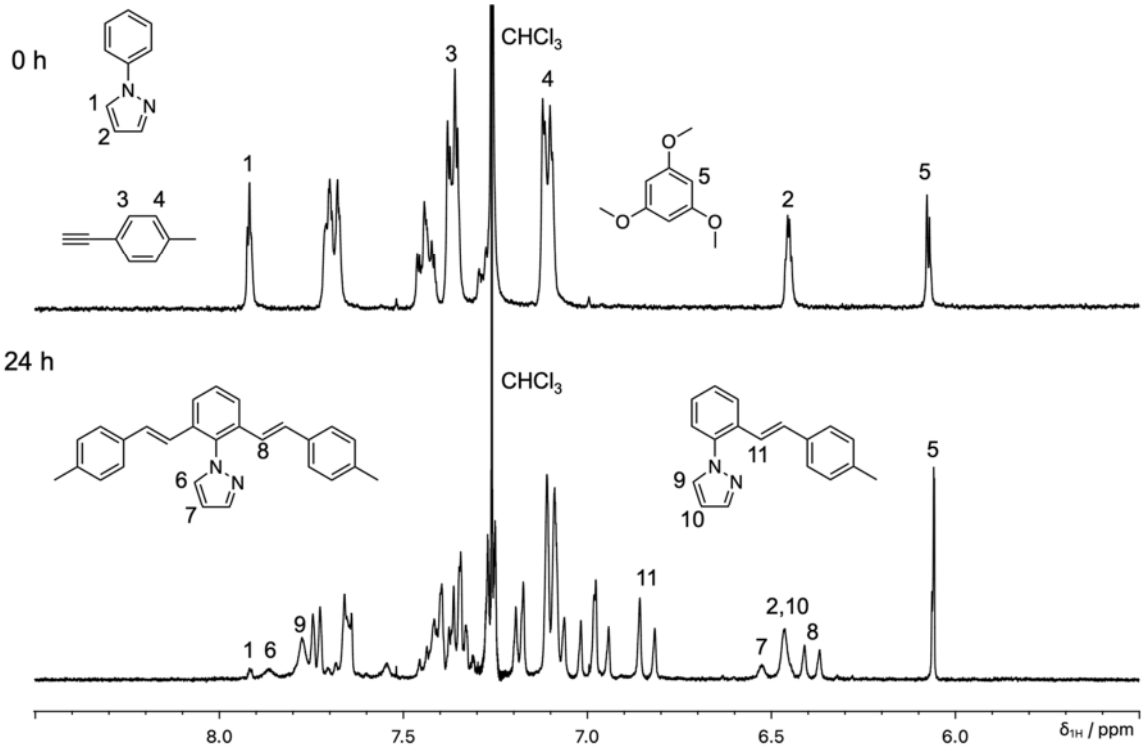


Figure S2. ^{1}H NMR spectra of the model reaction of 1b with 2a (400 MHz, $CDCl_3$, r.t.).

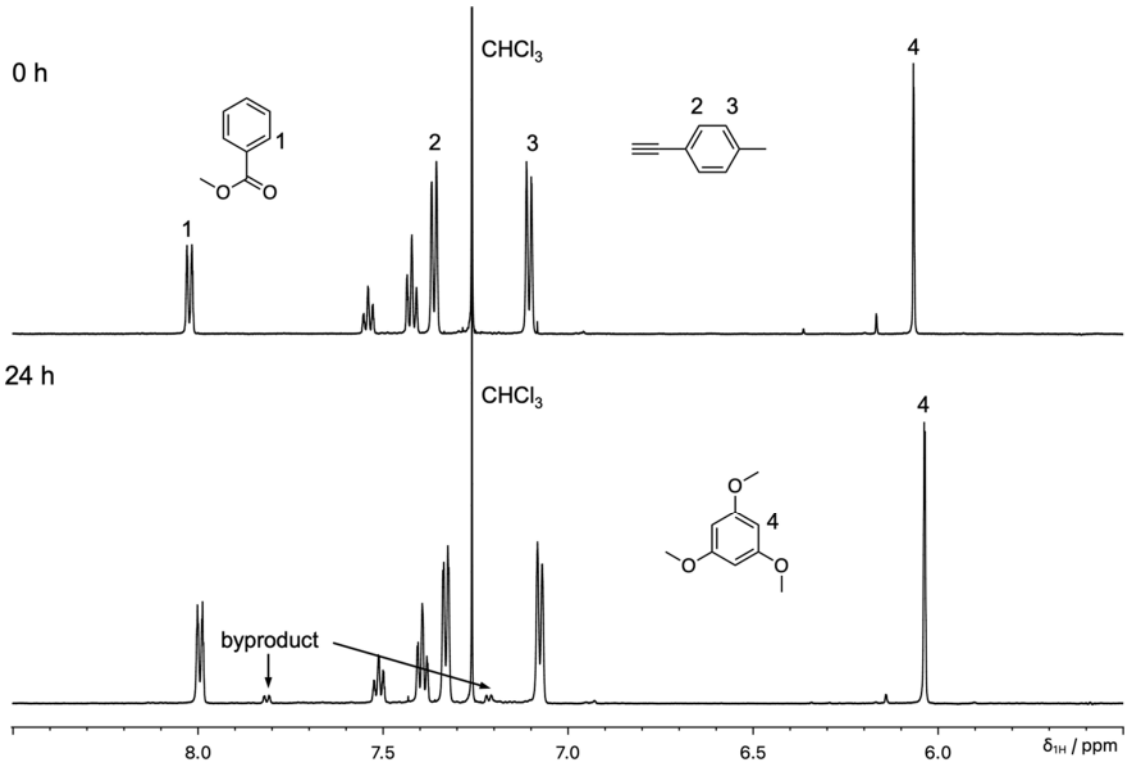


Figure S3. ^{1}H NMR spectra of the model reaction of 1c with 2a (600 MHz, $CDCl_3$, r.t.).

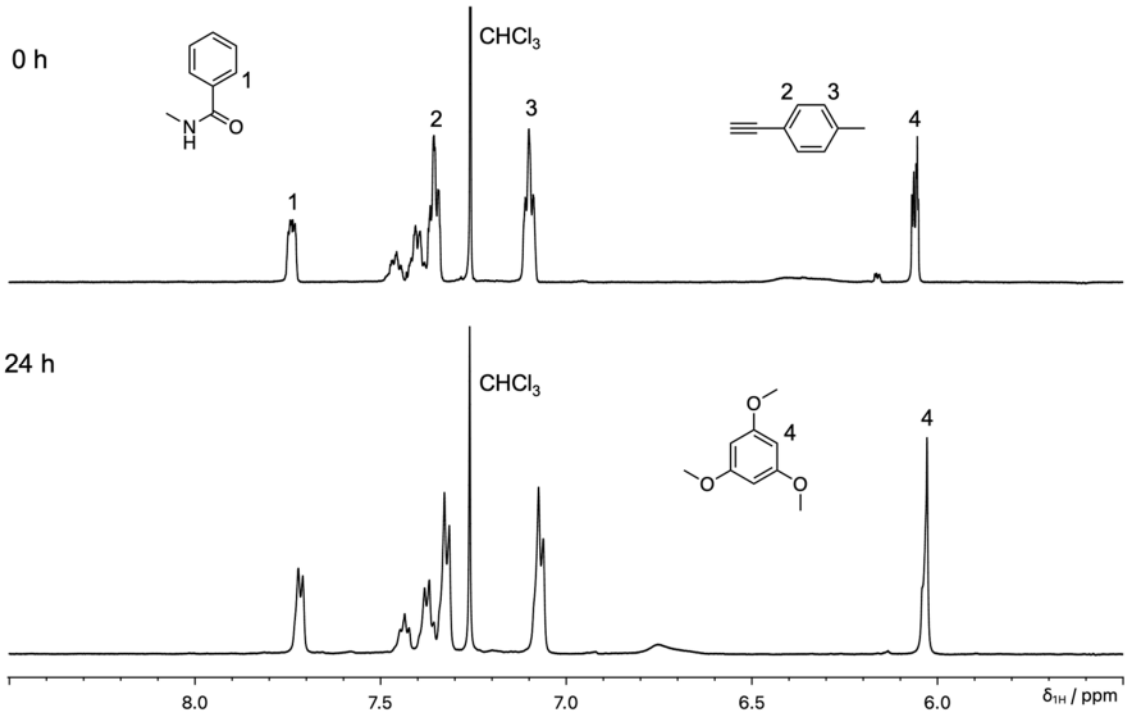


Figure S4. ^{1}H NMR spectra of the model reaction of 1d with 2a (600 MHz, $CDCl_3$, r.t.).

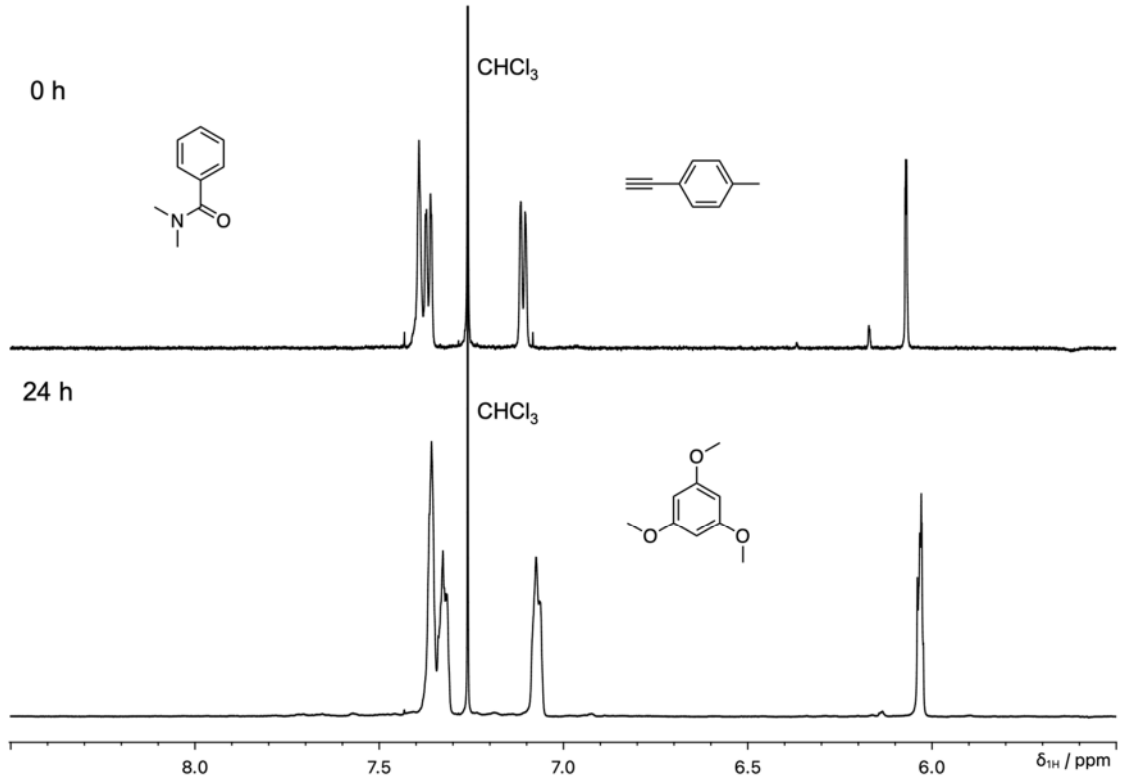


Figure S5. ^{1}H NMR spectra of the model reaction of 1e with 2a (600 MHz, $CDCl_3$, r.t.).

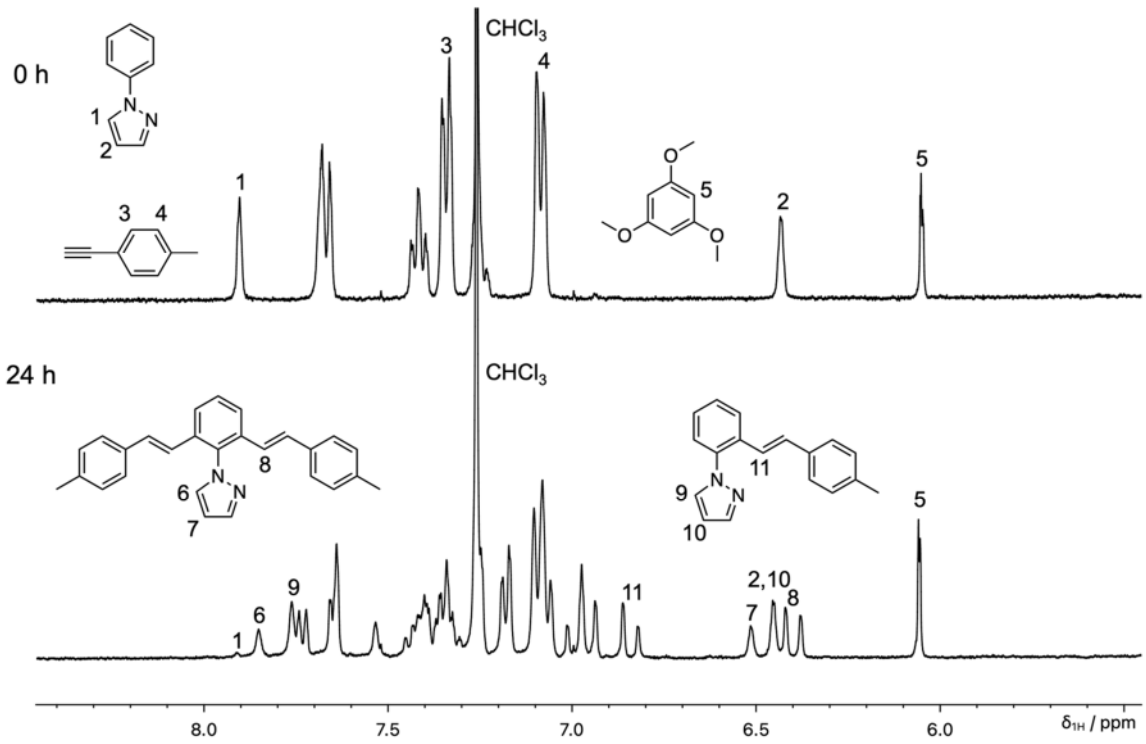


Figure S6. ^{1}H NMR spectra of the model reaction of 1b with 2a under the optimized conditions (Table S1 Entry 4, 400 MHz, $CDCl_3$, r.t.).

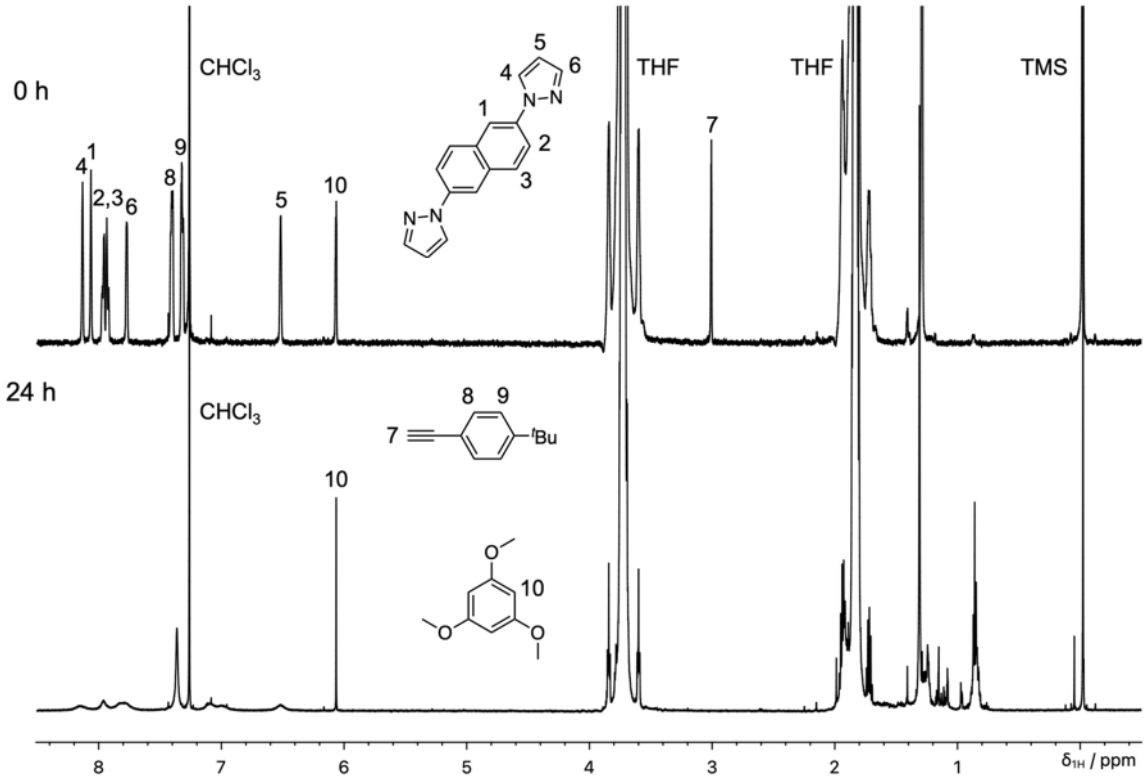


Figure S7. ^{1}H NMR spectra of the model reaction of 5a with 2b (600 MHz, $CDCl_3$, r.t.).

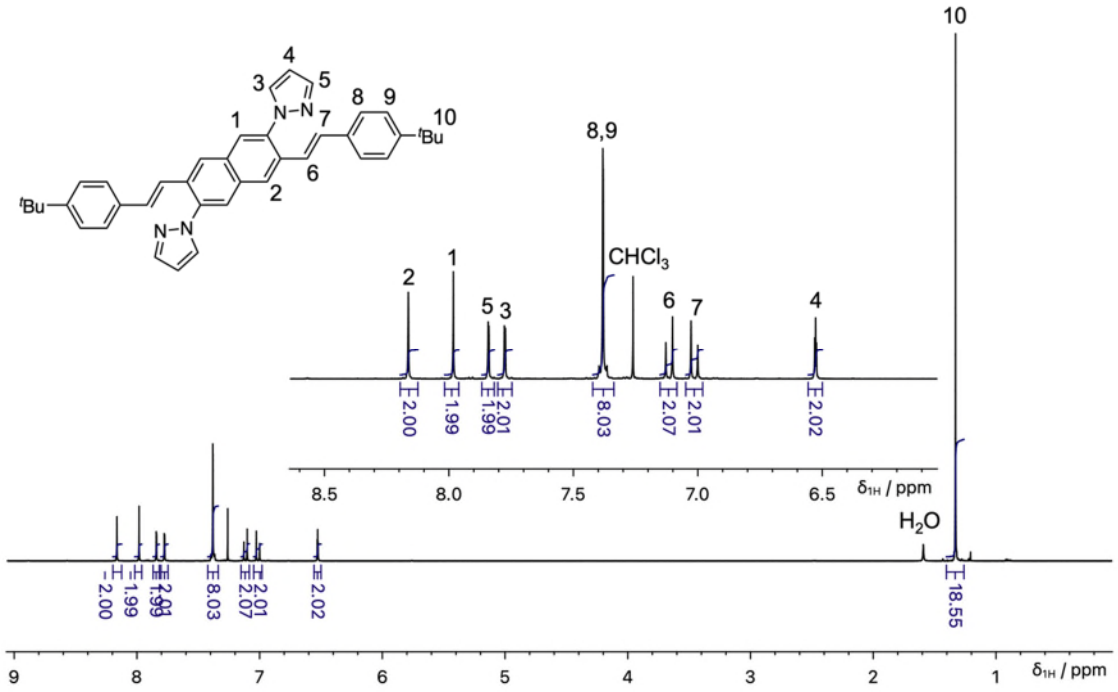


Figure S8. ^{1}H NMR spectrum of 6ab (600 MHz, $CDCl_3$, r.t.).

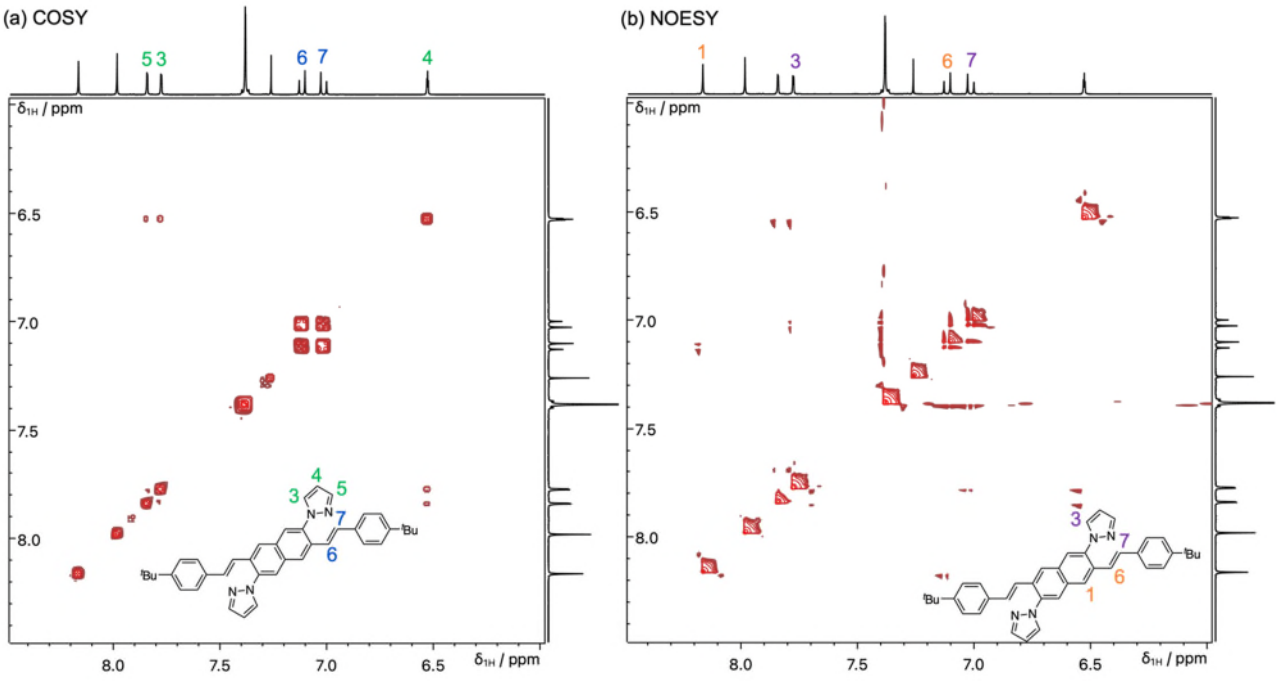


Figure S9. 2D ^{1}H NMR spectra of 6ab (600 MHz, $CDCl_3$, r.t.). (a) COSY NMR. (b) NOESY NMR.

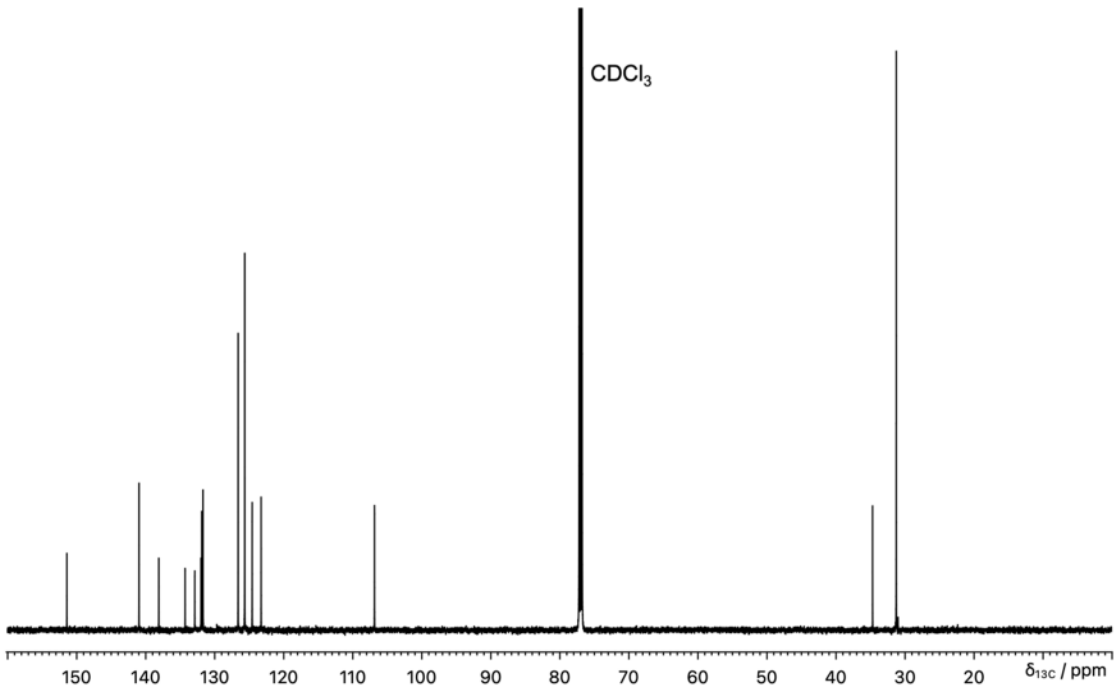


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of 6ab (150 MHz, $CDCl_3$, r.t.).

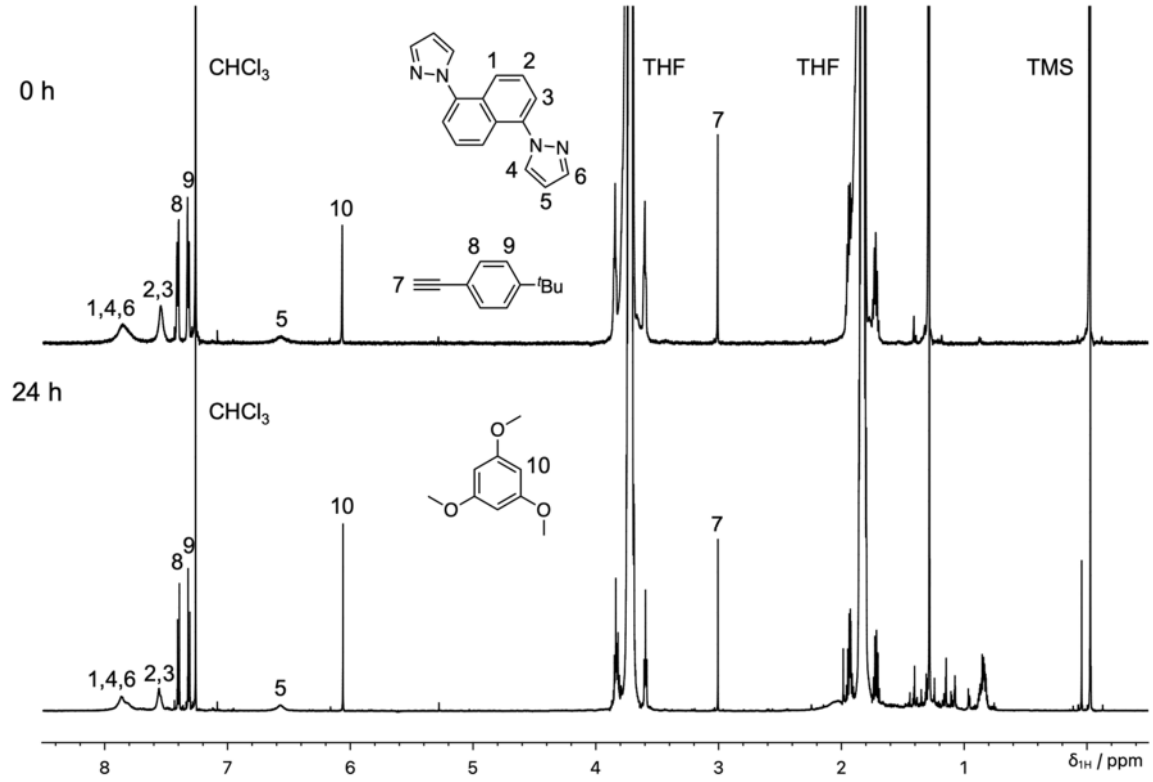


Figure S11. ^{1}H NMR spectra of the model reaction of 5b with 2b (600 MHz, $CDCl_3$, r.t.).

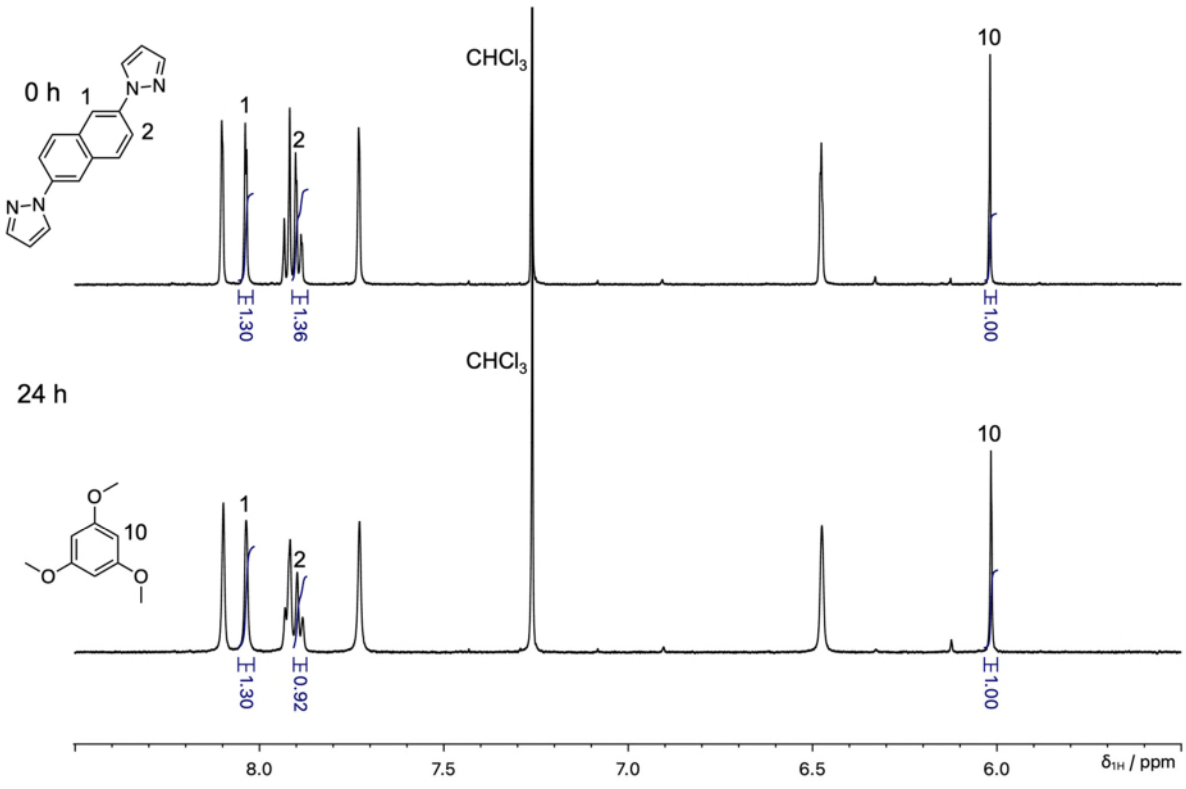


Figure S12. ^{1}H NMR spectra of the deuterium exchange experiment of 5a (600 MHz, $CDCl_3$, r.t.).

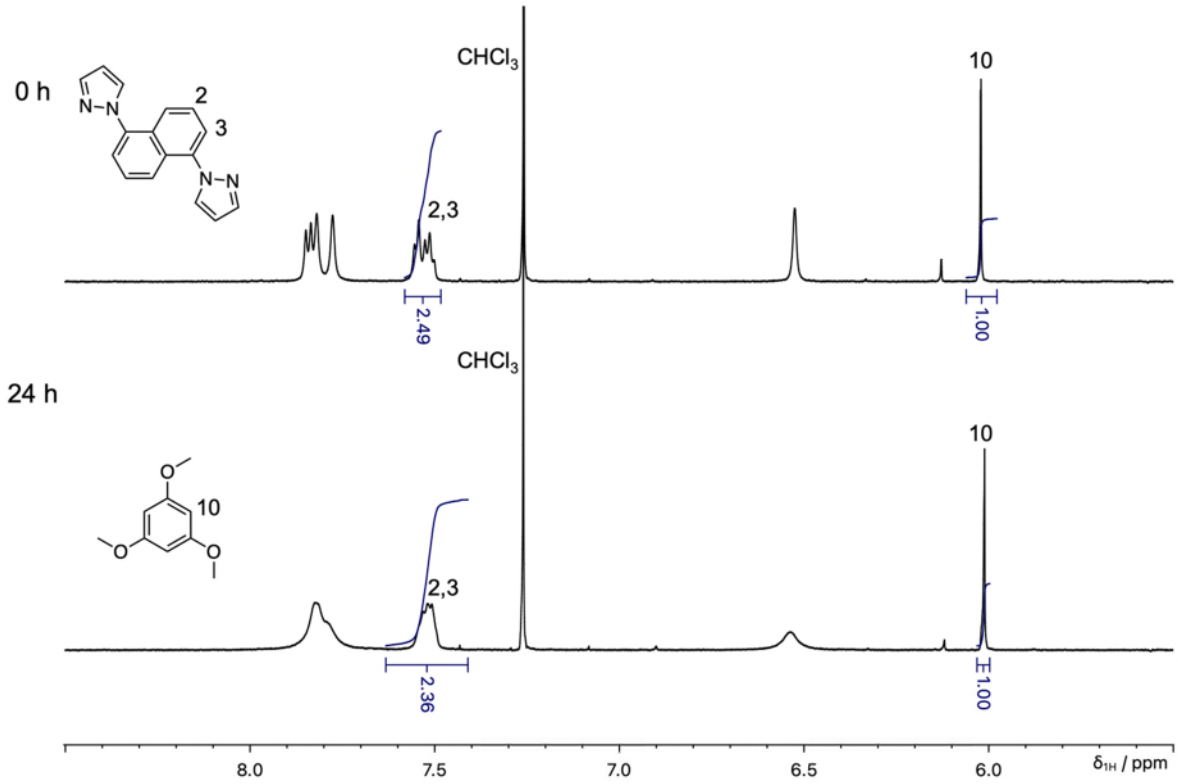


Figure S13. ^{1}H NMR spectra of the deuterium exchange experiment of 5b (600 MHz, $CDCl_3$, r.t.).

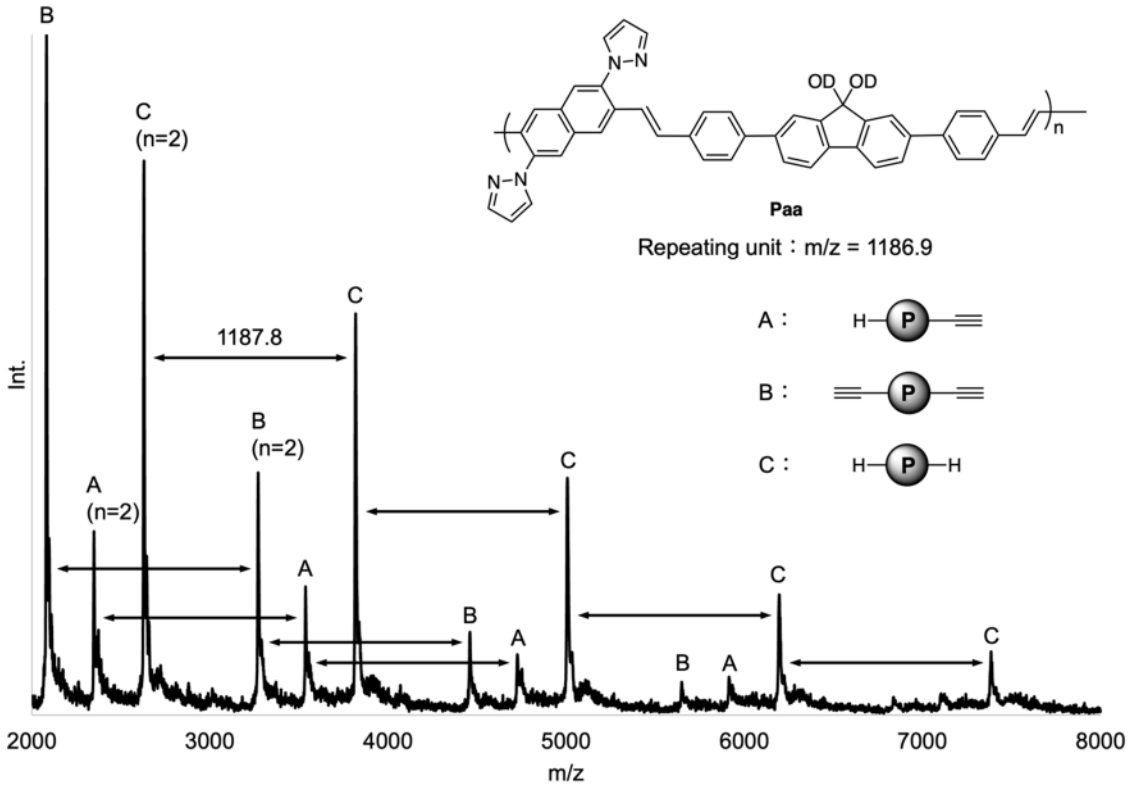


Figure S14. MALDI-TOF MS of Paa

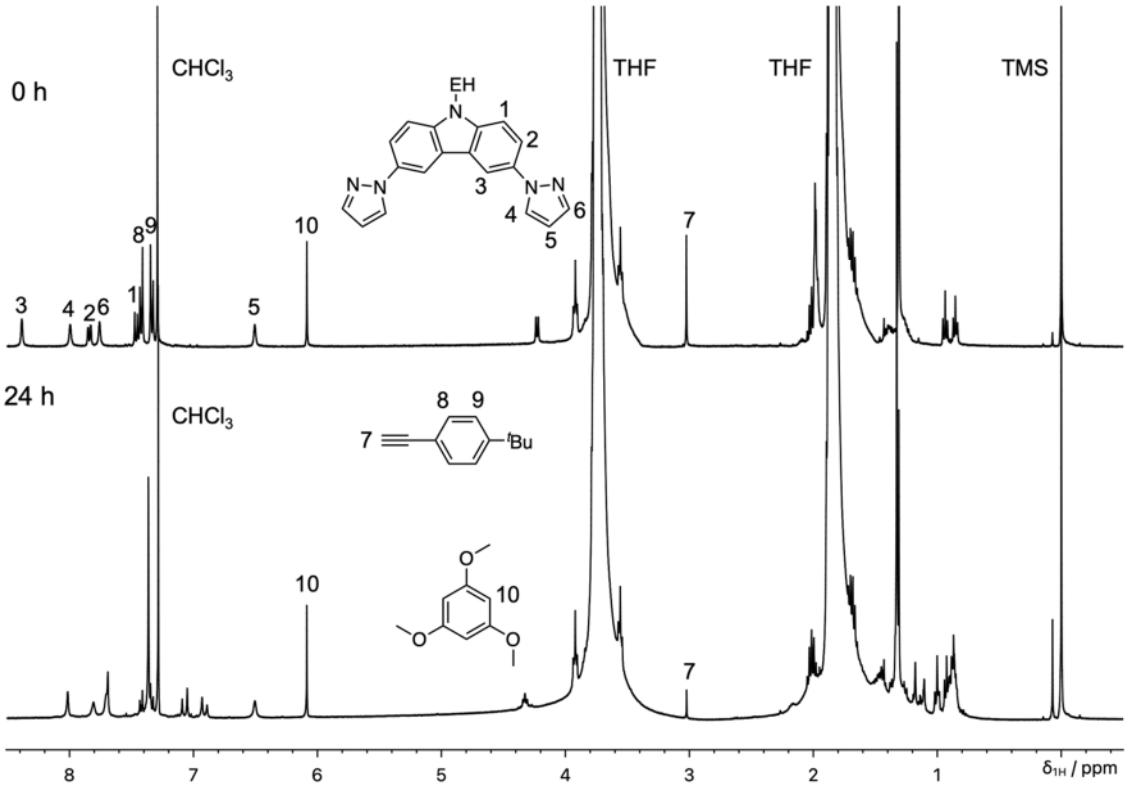


Figure S15. ^{1}H NMR spectra of the model reaction of 5c with 2b (400 MHz, $CDCl_3$, r.t.).

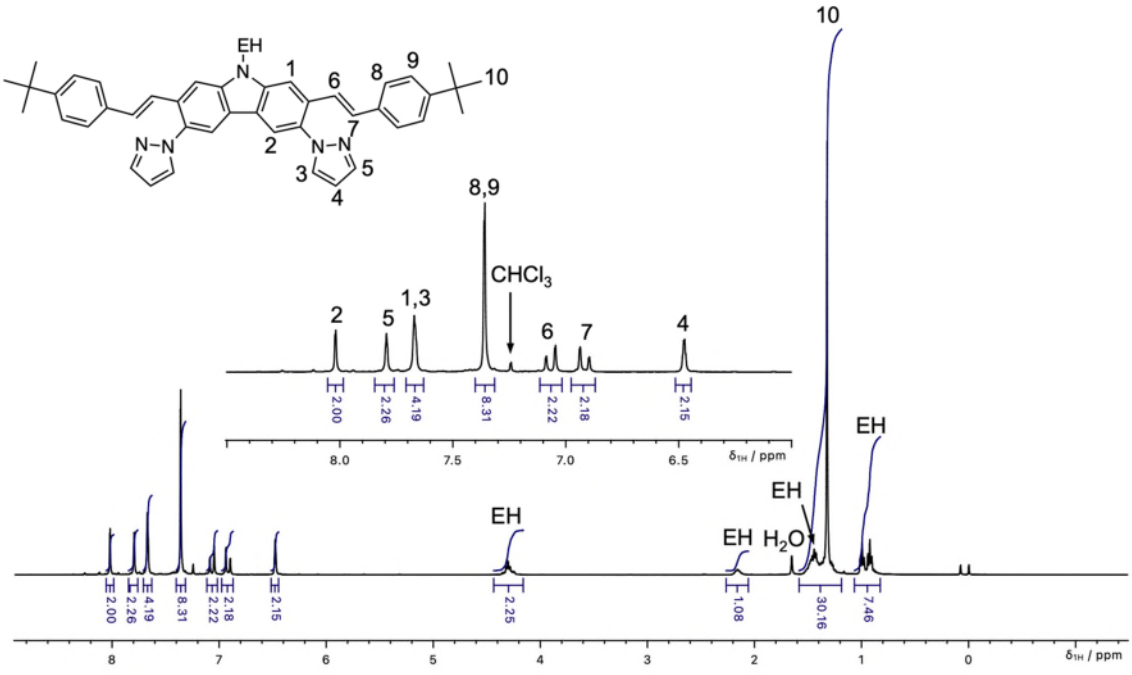


Figure S16. ^{1}H NMR spectrum of 6cb (600 MHz, $CDCl_3$, r.t.).

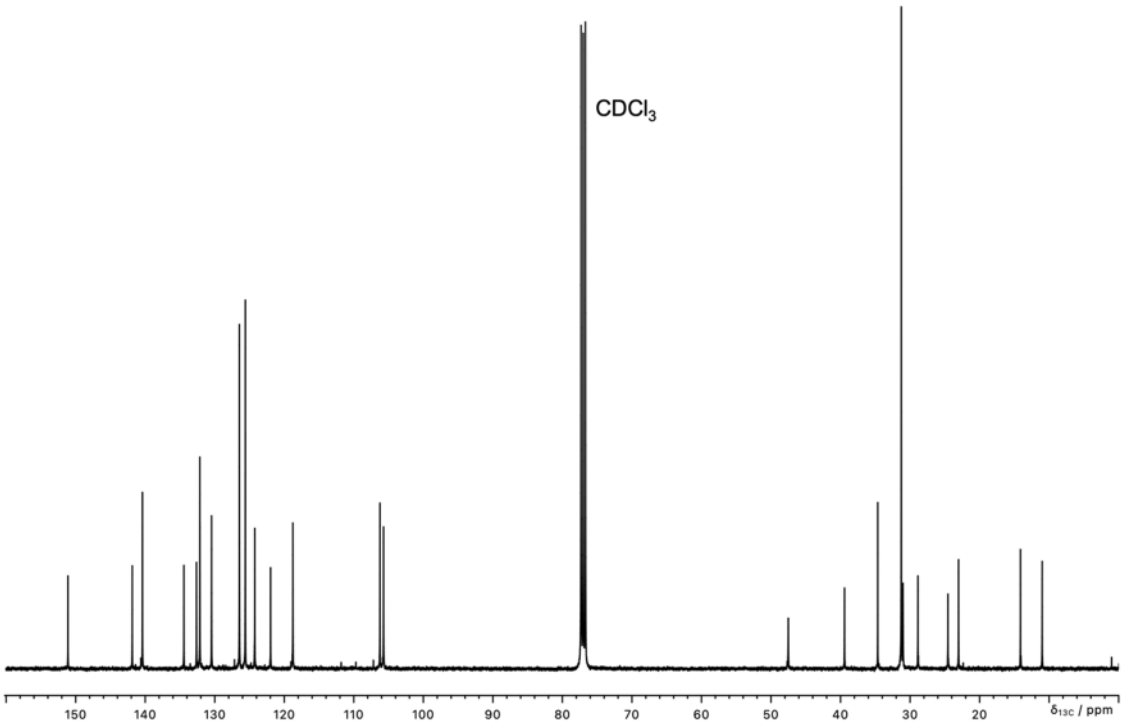


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of 6cb (150 MHz, $CDCl_3$, r.t.).

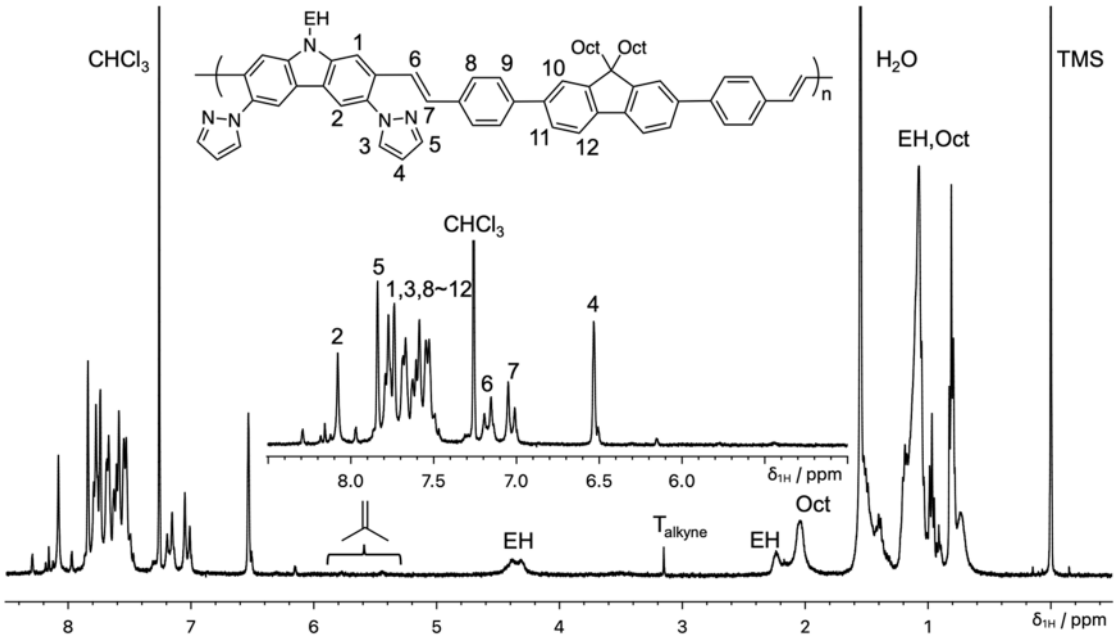


Figure S18. ^{1}H NMR spectrum of Pcb; reaction time of 24 h (400 MHz, $CDCl_3$, r.t.).

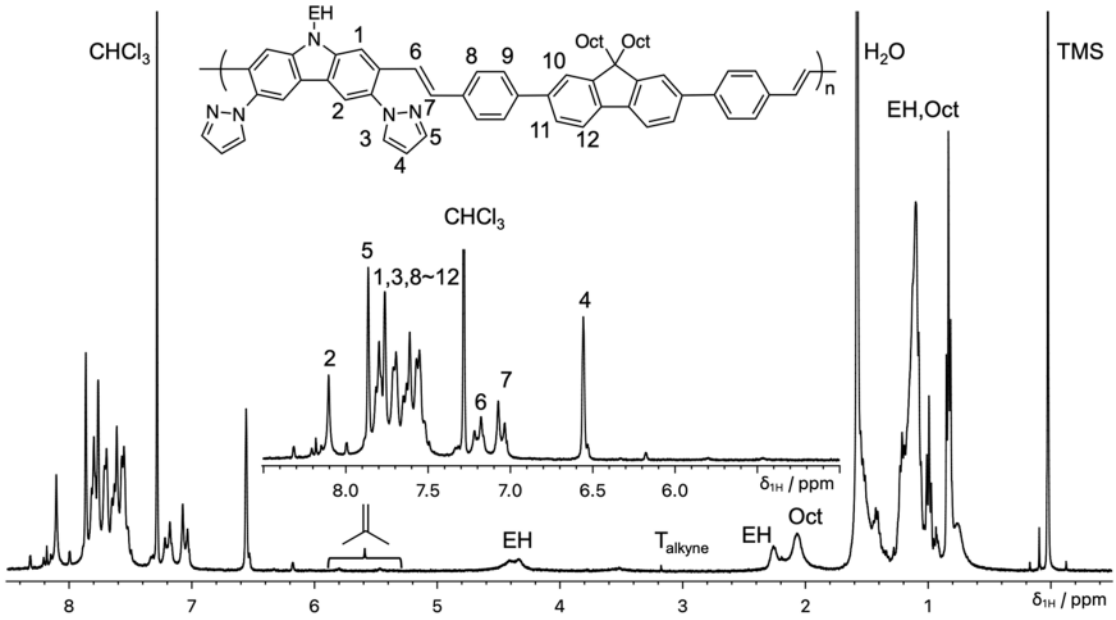


Figure S19. ^{1}H NMR spectrum of Pcb; reaction time of 48 h (400 MHz, $CDCl_3$, r.t.).

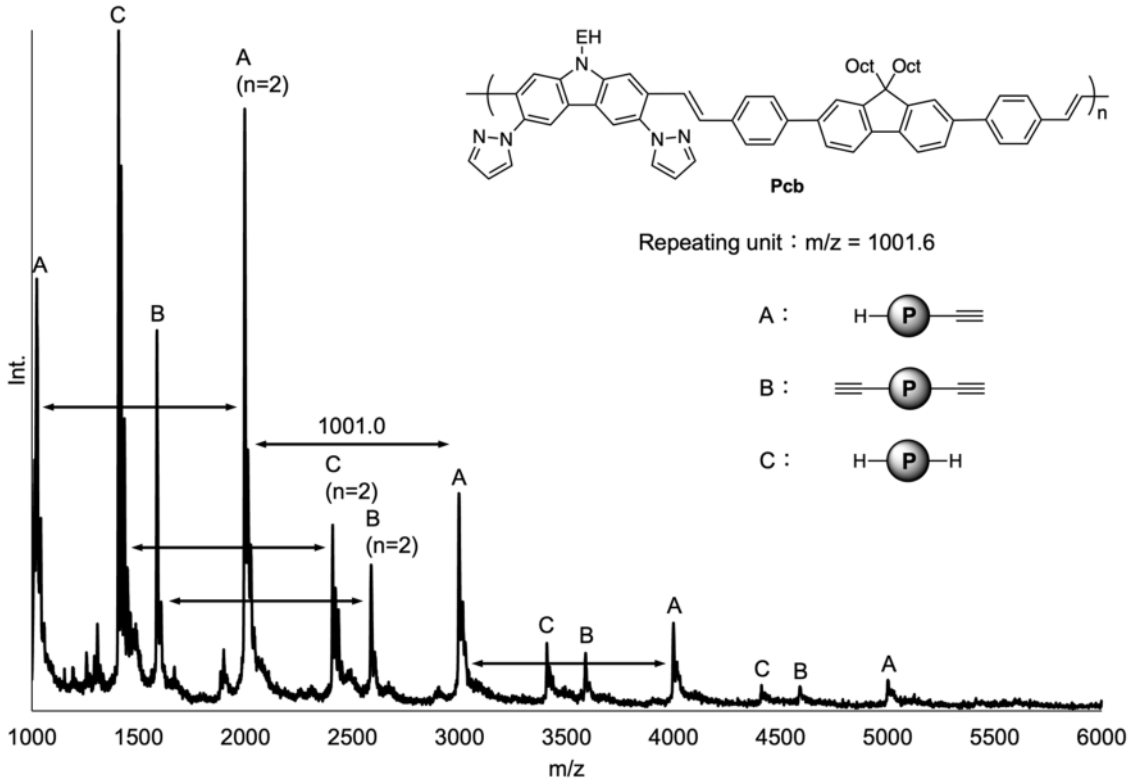


Figure S20. MALDI-TOF MS of Pcb

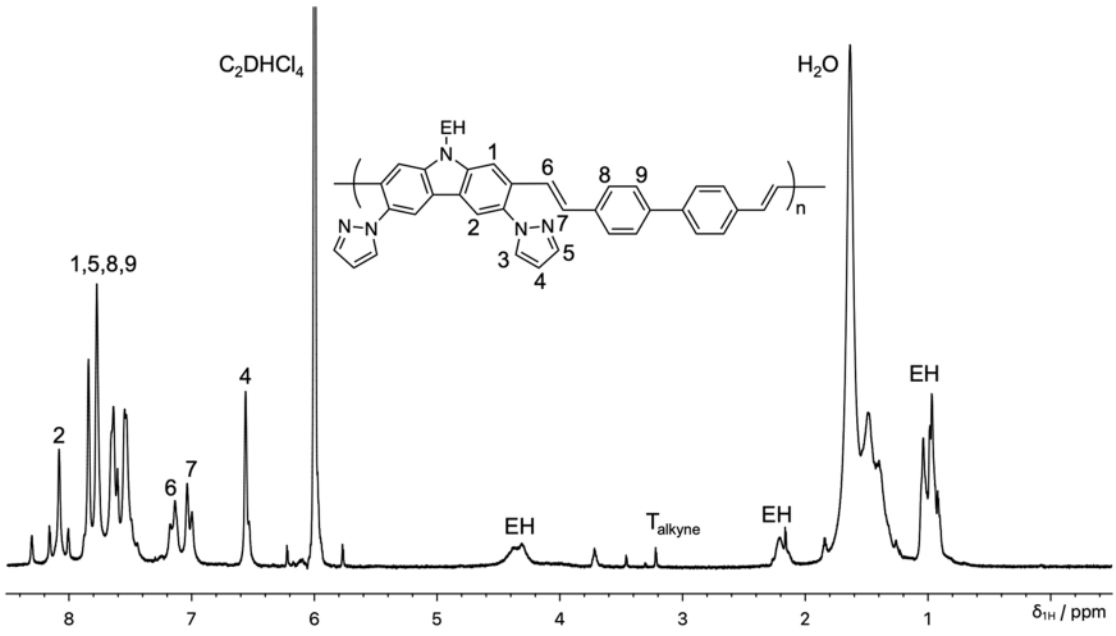


Figure S21. ^{1}H NMR spectrum of Pcc (400 MHz, $C_2D_2Cl_4$, r.t.).

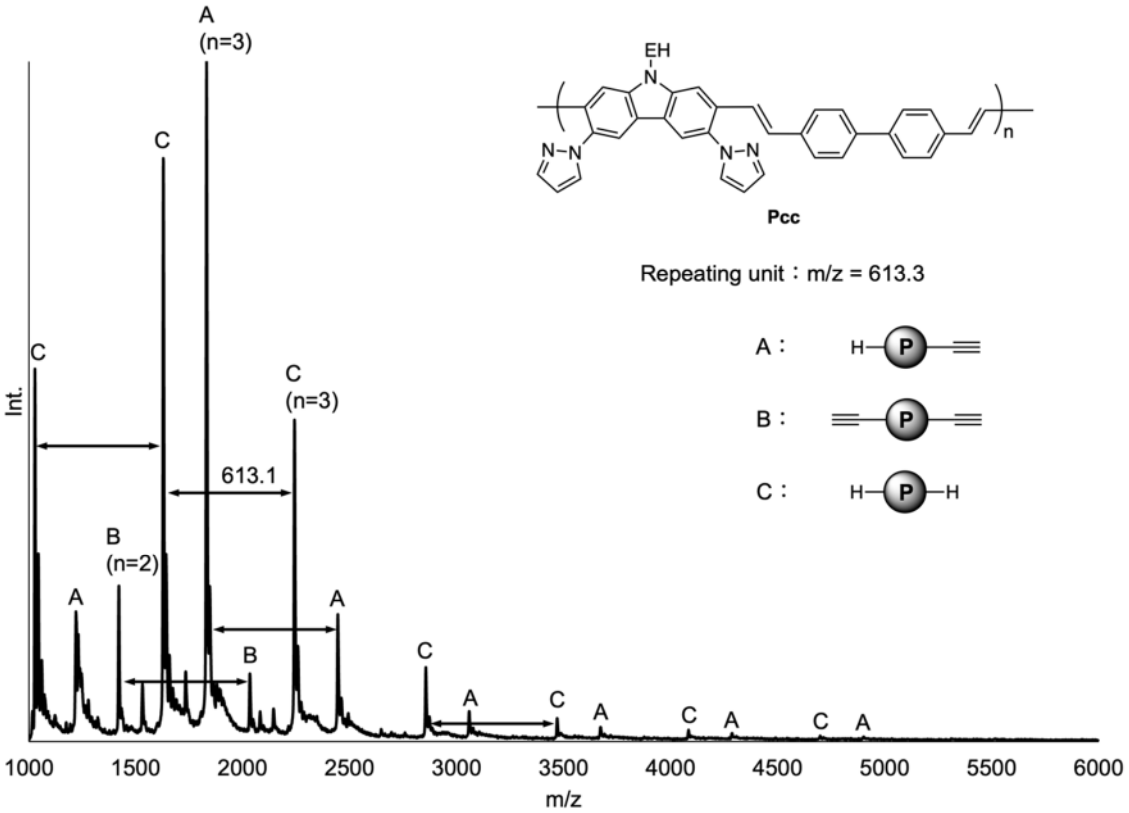


Figure S22. MALDI-TOF MS of Pcc

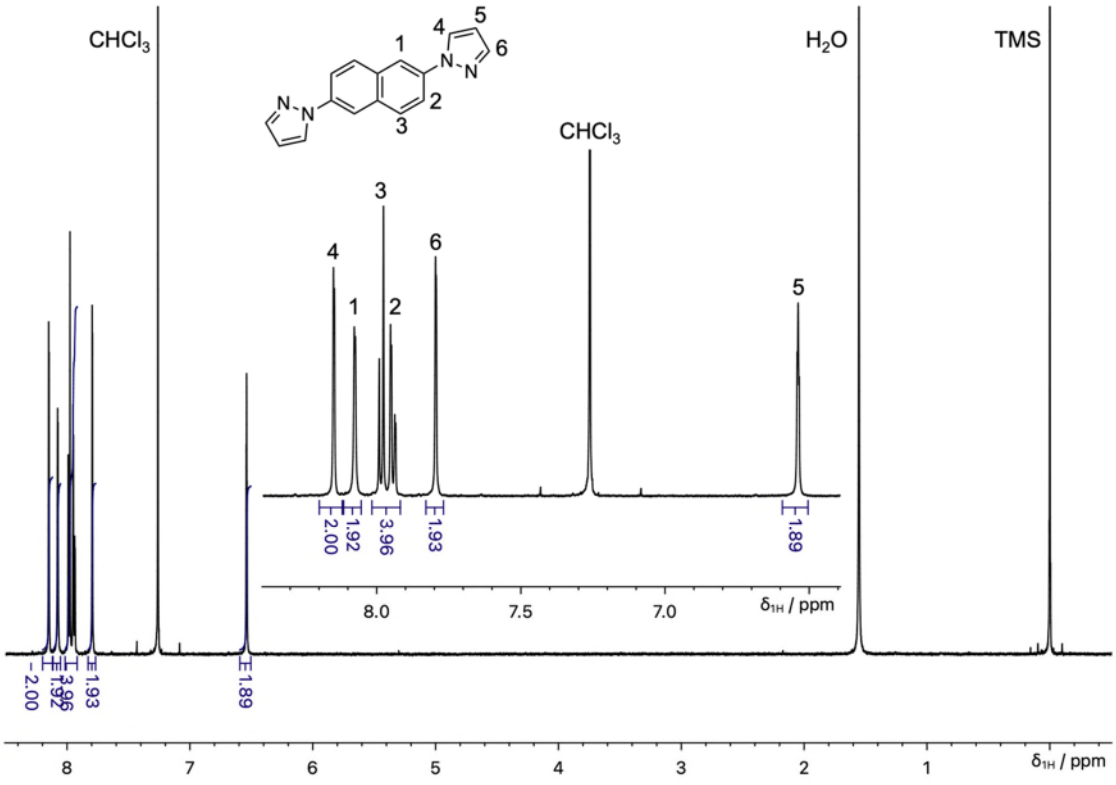


Figure S23. ^{1}H NMR spectrum of 5a (600 MHz, $CDCl_3$, r.t.).

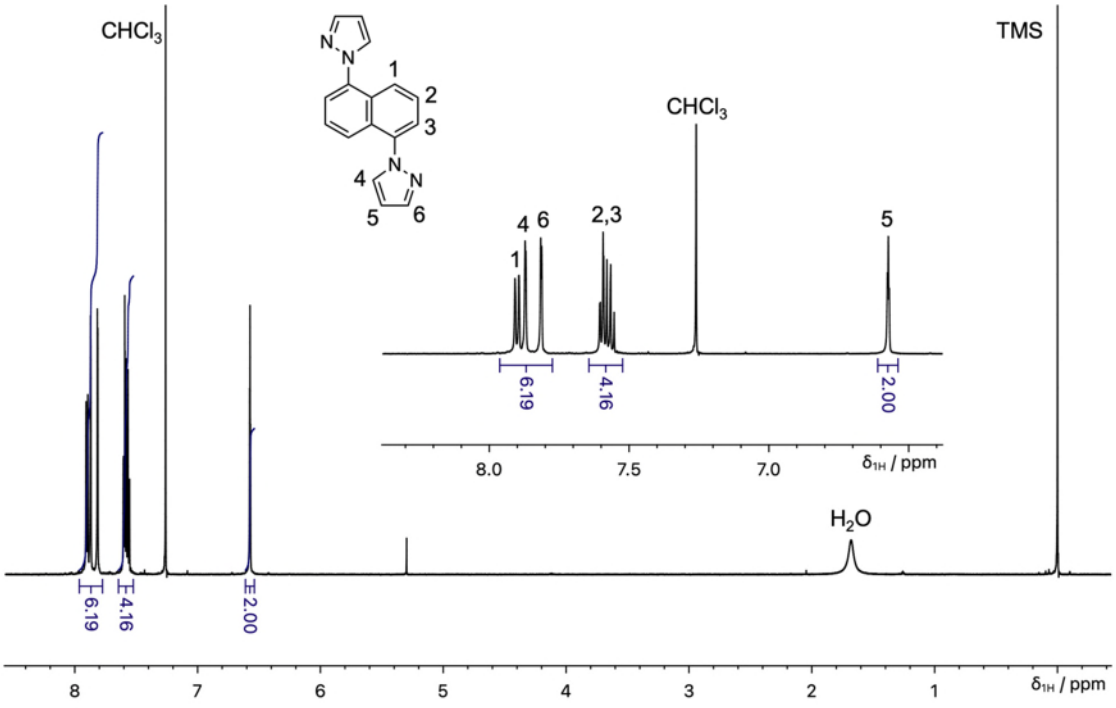


Figure S24. ^{1}H NMR spectrum of 5b (600 MHz, $CDCl_3$, r.t.).

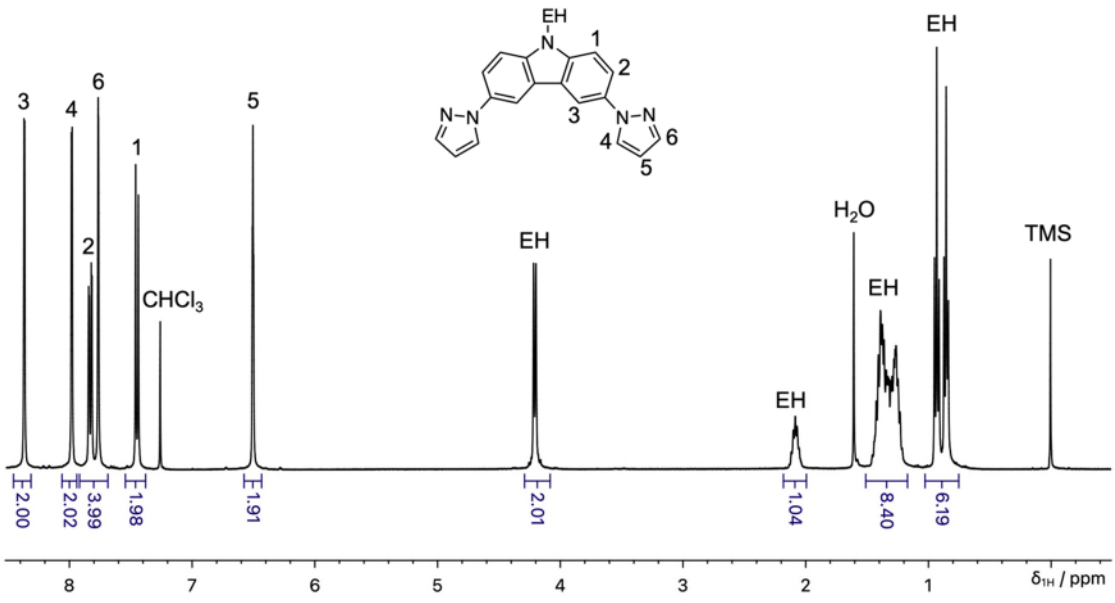


Figure S25. ^{1}H NMR spectrum of 5c (600 MHz, $CDCl_3$, r.t.).

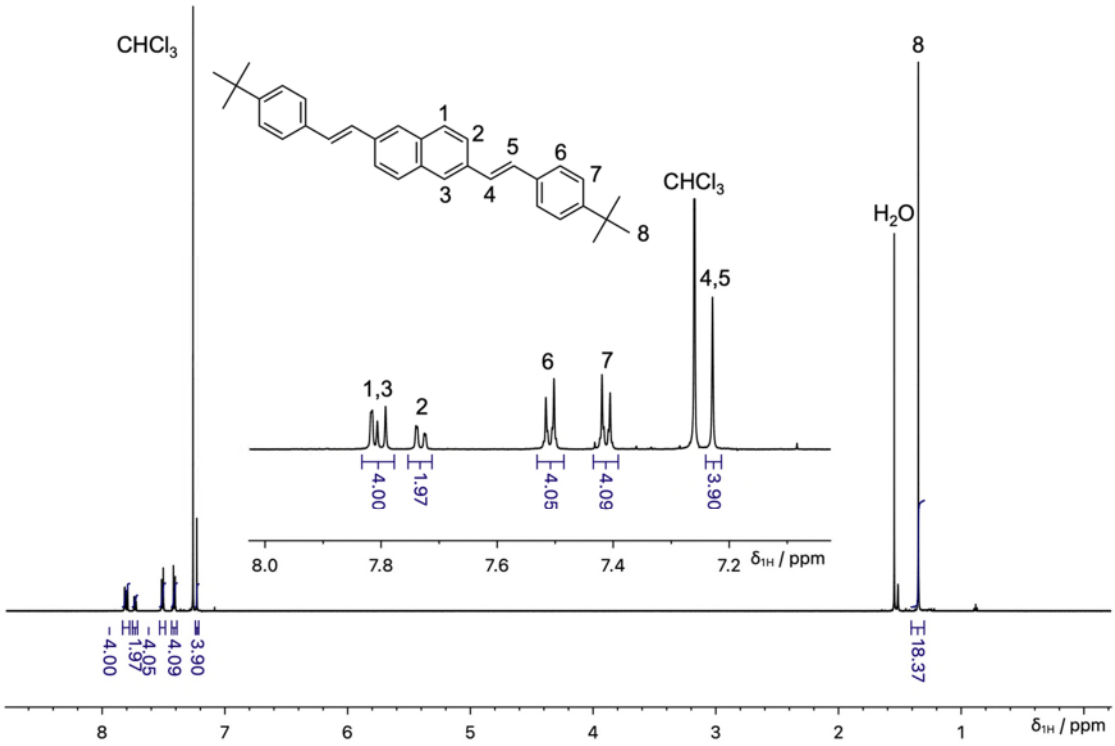


Figure S26. ^{1}H NMR spectrum of 8a (600 MHz, $CDCl_3$, r.t.).

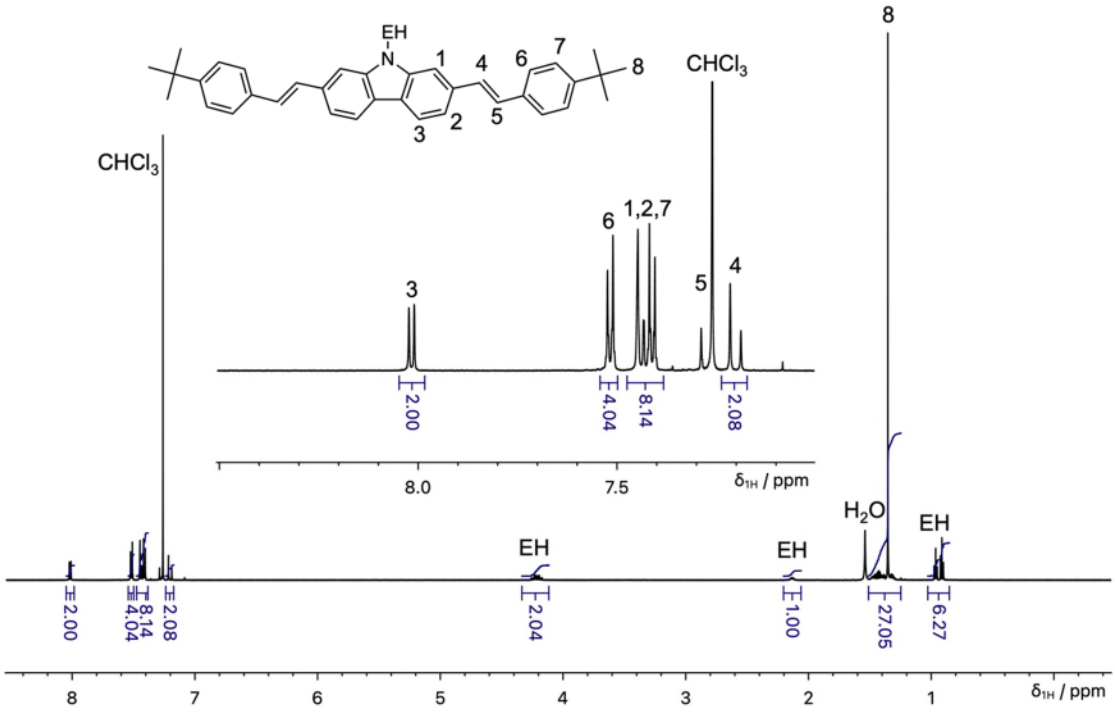


Figure S27. ^{1}H NMR spectrum of 8b (600 MHz, $CDCl_3$, r.t.).

GPC charts

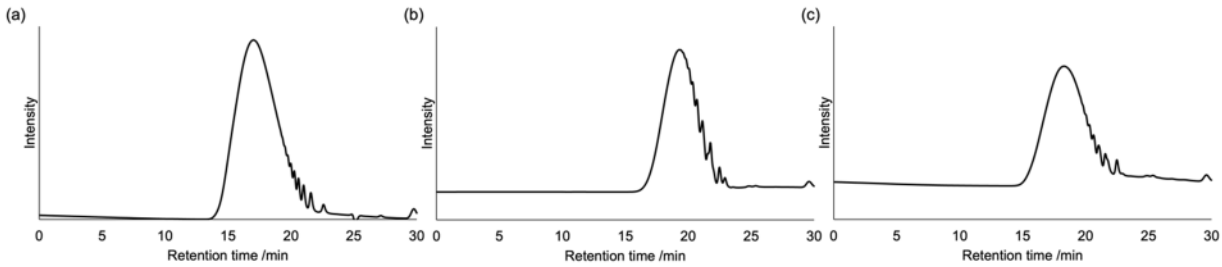


Figure S28. GPC charts of synthesized PAVs.

(a) Paa. (b) Pcb; Reaction time = 24 h. (c) Pcb; Reaction time = 48 h.

DFT calculations and X-ray crystallographic data

Crystal structure determination (Figure S30)

Intensity data were collected on a Bruker SMART APEX II ULTRA with Mo Kα radiation. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters using the SIR2002 or the SIR2014 program. CCDC 2334324-2334326 contain the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S2. Crystallographic data of 5a, 5b, and 5c

	5a	**5b**	**5c**
Empirical Formula	$C_{16}H_{12}N_4$	$C_{16}H_{12}N_4$	$C_{19}H_{15}N_5$
Formula Weight	260.30	260.30	313.36
Crystal Color	colorless	colorless	colorless
Crystal Dimensions / mm	0.326 x 0.276 x 0.082	0.050 x 0.050 x 0.020	0.476 x 0.082 x 0.062
Crystal System	triclinic	monoclinic	orthorhombic
Lattice Parameters			
a / Å	3.8226	5.4302(8)	21.810(4)
b / Å	10.5361	18.624(3)	4.1280(7)
c / Å	15.1908	6.5107(10)	8.1510(13)
β / deg.	93.0010	108.056(2)	90.0000
V / Å^3	605.6804	626.03(17)	733.9(2)
Space Group	*P*-1 (#2)	$P2_1/n$ (#14)	$P2_12_12$ (#18)
Z	2	2	2
D / gcm^{-3}	1.427	1.381	1.418
*F*000	272.00	272.00	328.00
μ(MoKα) / cm^{-1}	0.891	0.862	0.888
Reflection/Parameter Ratio	11.52	15.27	14.64
*R*1 ($I > 2.00\sigma(I)$)	0.0409	0.0423	0.0385
R (All reflections)	0.0451	0.0600	0.0398
*wR*2 (All reflections)	0.1272	0.1025	0.1127
Goodness of Fit Indicator	1.098	1.057	1.139
CCDC Number	2334326	2334325	2334324

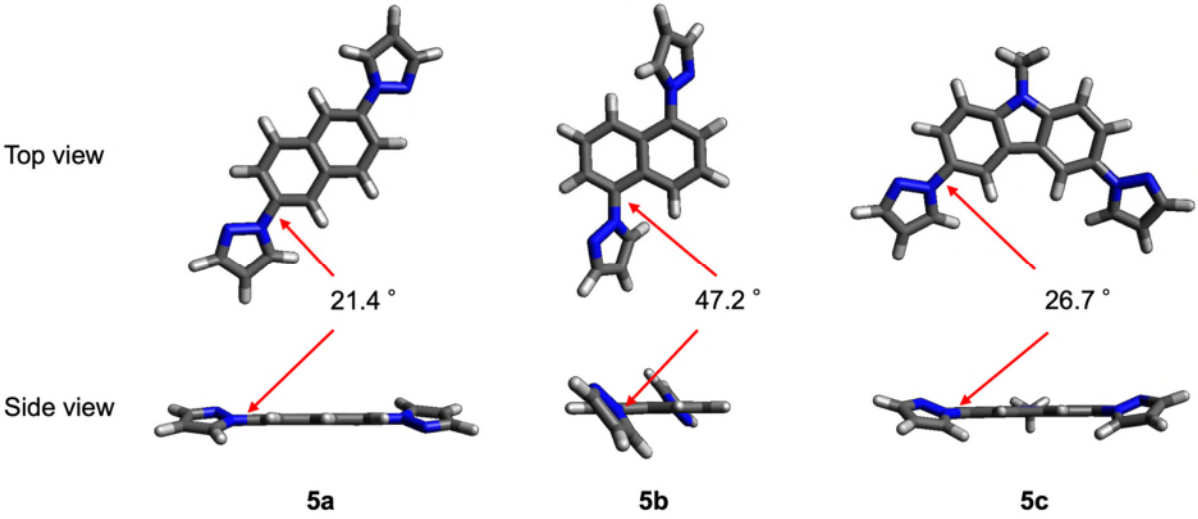


Figure S29. Molecular geometries of 5a, 5b, and 5c optimized by DFT calculations using Gaussian at the B3LYP/6-31G(d) level.

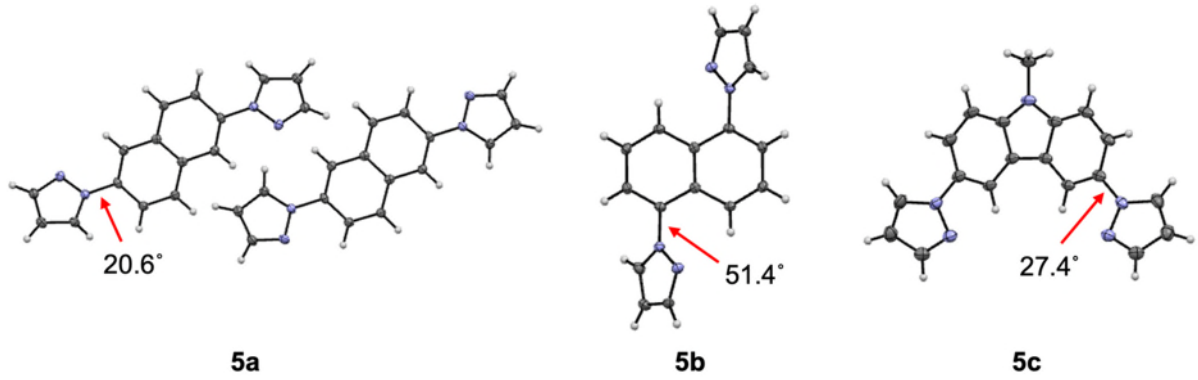


Figure S30. ORTEP drawing of 5a, 5b, and 5c by X-ray crystallographic analyses.

Optical and electronic data

Table S3. Optical properties of monomer, model compounds, and PAVs

Compound	$CHCl_3$ solution [a]			Film state [b]		
	λ_{abs} (nm)	λ_{em} (nm)	PLQY [c] (%)	λ_{abs} (nm)	λ_{em} (nm)	PLQY [c] (%)
5a	267, 308	358	-	-	-	-
6ab	302, 361	425	84	298, 363	459	13
8a	365	418	87	- [d]	- [d]	- [d]
Paa	405	460	80	406	472	20
6cb	283, 375	449	71	282, 373	482	6.5
8b	377	419	79	377	447	5.9
Pcb	406	454	66	408	475	6.0

[a] Concentration of 5.0 x 10^{-6} M. [b] Spin-coated film. [c] Photoluminescence quantum yield. [d] Spin-coated film was not able to fabricate because the solubility of **8a** was quite low.

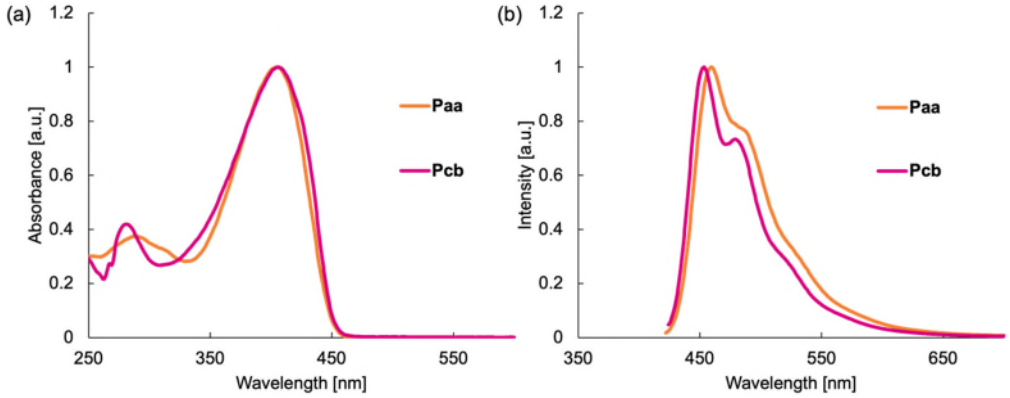


Figure S31. Optical spectra of Paa and Pcb in $CHCl_3$ solutions (5.0 x 10^{-6} M) (a) UV-vis absorption spectra. (b) PL spectra.

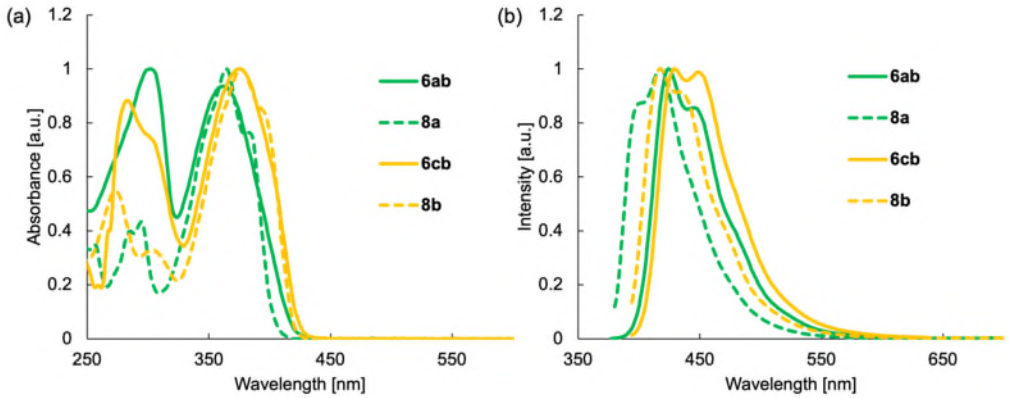


Figure S32. Comparison of optical spectra of the naphthalene- and carbazole-based model compounds in $CHCl_3$ solutions (5.0 x 10^{-6} M). (a) UV-vis absorption spectra. (b) PL spectra.

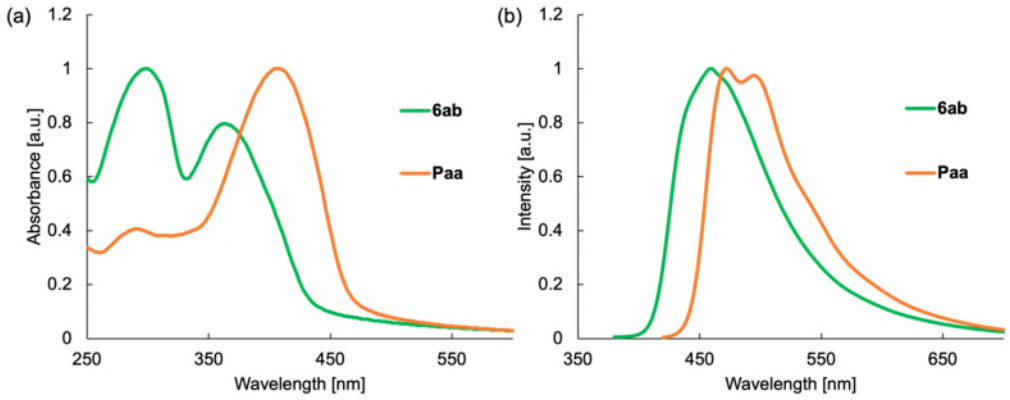


Figure S33. Optical spectra of naphthalene derivatives in the film states.
(a) UV-vis absorption spectra. (b) PL spectra.

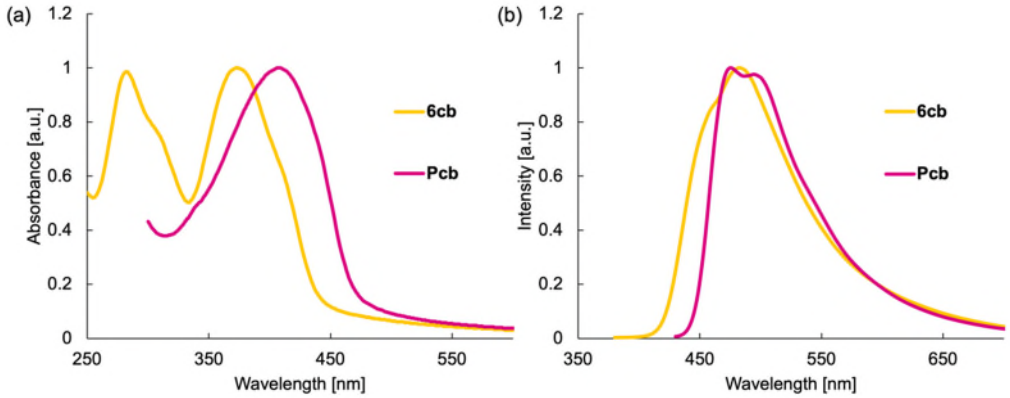


Figure S34. Optical spectra of carbazole derivatives in the film states.
(a) UV-vis absorption spectra. (b) PL spectra.

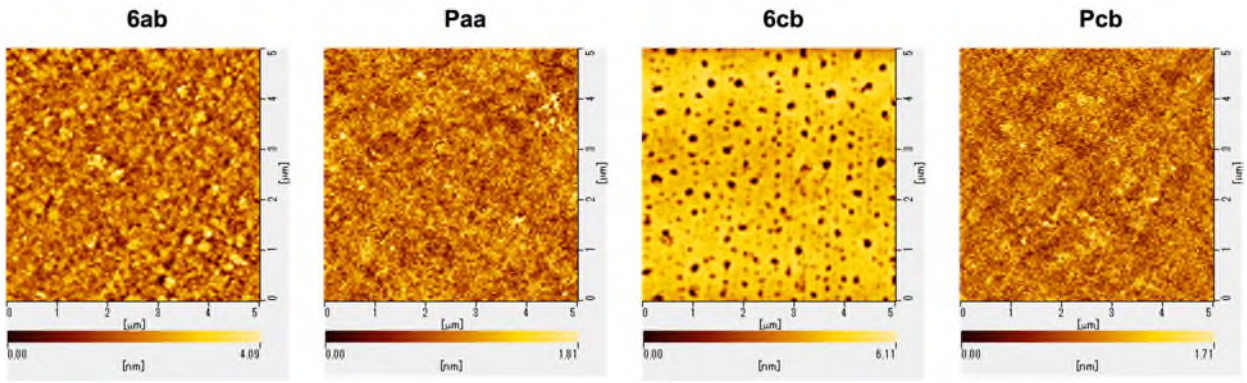


Figure S35. AFM images (5 x 5 µm) of spin-coated films

OLED properties of Paa

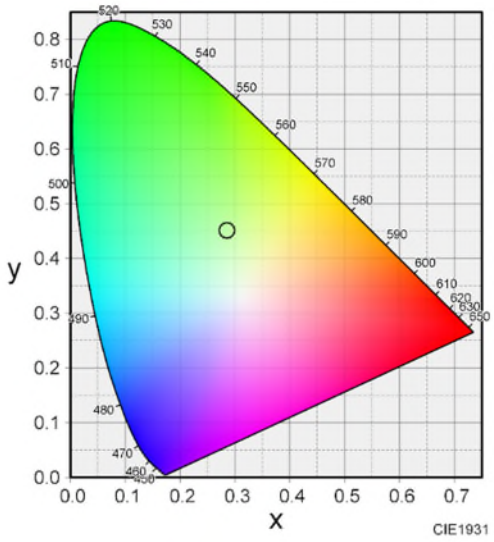


Figure S36. CIE chromaticity diagram from the EL spectrum of Paa.

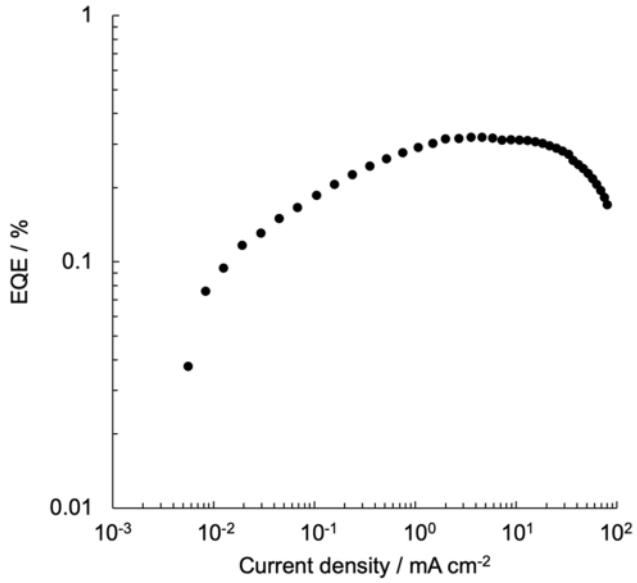


Figure S37. EQE vs current density plots for the fabricated OLED of Paa.
Configuration ITO/PEDOT:PSS (40 nm)/Paa (47 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm).

References

[1] R. Iwamori, R. Sato, J. Kuwabara, T. Yasuda, T. Kanbara, *Macromol. Rapid Commun.* **2021**, *42*, 2100283.

[2] A. Correa, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 2673-2676.

[3] Z. Liu, D. Cao, Y. Chen, Q. Fang, *Dyes Pigments* **2010**, *86*, 63-67.