

Supplemental Information

Synthesis of bithiazole-based semiconducting polymers via Cu-catalyzed aerobic oxidative coupling

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Materials. All of the chemicals were used as received unless noted. All of the general organic solvents were purchased from Kanto Chemical. Cu(OAc)₂ and *p*-xylene were purchased from Wako Pure Chemical Industries. Thiazole and 2,7-dibromo-9-(1-octylnonyl)carbazole were purchased from Tokyo Chemical Industries (TCI). 4-Methylthiazole, 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene, and 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene were purchased from Sigma-Aldrich. Anhydrous DMAc and toluene were purchased from Kanto Chemical and kept with dry N₂ protection. 1,1,2,2-Tetrachloroethane-*d*₂ was purchased from Acros Organics. To aqueous solution of EDTA·2Na (0.5 M), NaOH was added to adjust at pH = 8. Standard solutions of Cu (1000 mg L⁻¹) were purchased from Wako. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP AI 4083) was purchased from Heraeus, and 2,2',2''-(1,3,5-benzenetriyl)tris(1-phenylbenzimidazole) (TPBi) was purchased from Luminescence Technology Corp.

Instrumentation. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker AVANCE-400 or

AVANCE-600 Spectrometer at 22 °C unless noted. Purifications by recycling preparative high performance liquid chromatography (HPLC) were carried out on a Japan Analytical Industry LC-92XXII NEXT instrument using chloroform as the eluent. Gel permeation chromatography (GPC) measurements were carried out on a Shimadzu prominence GPC system equipped with polystyrene gel columns using chloroform as an eluent at 40 °C after calibration with polystyrene standards. High-temperature GPC measurements were carried out using a HLC-8321 GPC/HT (TOSOH) using *o*-dichlorobenzene as the eluent after calibration with polystyrene standards (140 °C). Elemental analyses were carried out with a Perkin-Elmer 2400-CHN instrument. MALDI-TOF-MS data were recorded on AB SCIEX MALDI TOF/TOF 5800 using PCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene] malononitrile) as a matrix. Air sensitive reactions were carried out in a 25 mL Schlenk tube using a standard Schlenk technique or in a glove box manufactured by Miwa. Ultraviolet visible absorption spectra of the spin coated thin films were recorded on a Hitachi U-3010 spectrophotometer. Photoluminescence spectra were recorded on a Jasco FP-6500 spectrofluorometer. The HOMO energy level was estimated by photoelectron yield spectroscopy (PYS) using a Riken Keiki AC-3 spectrometer. Out-of-plane X-ray diffraction (XRD) measurement was carried out with a MiniFlex600 (Rigaku Corporation). Polymer films on SiO₂ (300 nm) coated Si wafers were thermally annealed at 110 °C for 10 min and were analyzed by XRD using a standard θ -2 θ scan with Cu K α radiation operated at 40 keV and 15 mA. Density functional theory (DFT) calculation was performed at the B3LYP/6-31G(d) level with the Gaussian09 Rev. D.01 program.²

Evaluation of residual amount of Cu.

The amounts of residual Cu in the polymers were determined by ICP-AES using a Shimadzu Optima ICPS 8100 after decomposing the weighed samples in analytical grade nitric acid with heating. Standard curves were prepared with the standard solutions of Cu (0, 1, 5, 10, 50 ppm).

Before a treatment with aqueous solution of EDTA·2Na, **P2** contained a large amount of Cu residue (5300 ppm). After the EDTA treatment, the amount of Cu decreased to 32 ppm.

Fabrication and characterization of OLED.

OLED was fabricated in the following configuration: ITO/PEDOT:PSS/light emitting **P2** layer/electron transporting (hole blocking) TPBi layer/LiF/Al. The patterned indium tin oxide (ITO) glass (conductivity: 10 Ω /square) was pre-cleaned 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 N₂-filled glove box where it was re-dried at 110°C for 10 min on a hot plate. A chloroform solution of **P2** (5 mg/1 mL) was subsequently spin-coated onto the PEDOT:PSS surface to form the light emitting layer (54 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 5×10^{-4} Pa, which provided the devices with an active area of 2×2 mm². Current-voltage characteristics and luminance of the OLED were simultaneously measured using an ADCMT 6246 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.).

Fabrication and characterization of OFETs:

To estimate the hole mobilities of **P4**, OFETs with a top-contact geometry were fabricated and characterized as follows. A glass/Au gate electrode/Parylene-C insulator substrate was prepared according to the previously reported methods.¹ **P4** was spin-coated from *o*-dichlorobenzene (*o*-DCB)

solution onto the Parylene-C layer. The coated substrate was then transferred to a N₂-filled glove box where it was dried for 10 min at 110 °C. Au (40 nm) source-drain electrodes were thermally evaporated onto the substrates through shadow masks. The channel length and width were fixed at 75 μm and 5 mm, respectively. The OFET measurements were conducted using a Keithley 2636A System Source Meter in air.

The electrical parameters were estimated using the standard analytic theory for MOSFETs according to the following equation:

$$I_{D,sat} = \frac{WC_i}{2L} \mu (V_G - V_T)^2$$

where $I_{D,sat}$ is the saturation drain current, V_T is the threshold voltage, V_G is the gate voltage, C_i is the dielectric capacitance of the insulating layer per unit area and μ is the field-effect mobility.

Synthesis of 2,7-bis(4-methylthiazol-5-yl)-9,9-bis(2-ethylhexyl)fluorene (M1).

To a 25 mL Schlenk tube under N₂ atmosphere, Pd(OAc)₂ (6.7 mg, 0.030 mmol), K₂CO₃ (518 mg, 3.8 mmol), 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (822 mg, 1.5 mmol), anhydrous DMAc (6.0 mL), 4-methylthiazole (409 μL, 4.5 mmol), and pivalic acid (51 μL, 0.30 mmol) were added at room temperature. The mixture was stirred at 100 °C for 24 h under N₂. The crude product was extracted with ethyl acetate and hexane (1:1), washed with water and brine, and then dried with Na₂SO₄. Purification by column chromatography (silica gel, ethyl acetate:chloroform = 1:150~1:50) and by HPLC afforded **M1** as a yellow oil (658 mg, 75%). ¹H NMR (400 MHz, CDCl₃): δ 8.71 (s, 2H), 7.76 (d, 2H, *J* = 8.0 Hz), 7.44-7.40 (m, 4H), 2.58 (m, 6H), 2.10-1.94 (m, 4H), 0.94-0.67 (m, 16H), 0.64 (m, 6H), 0.55 (m, 8H). Signal at 2.58 ppm are divided in three peaks as triplet presumably due to the presence of diastereomers. ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 151.2, 150.1, 148.4, 140.5, 132.6, 130.4, 128.4, 125.1, 120.0, 55.2, 44.6, 34.8, 33.9, 28.2, 27.0, 22.7, 16.2, 13.9, 10.3. Signals at 151.2,

148.4, 130.4, 128.4, and 125.1 ppm are divided in three peaks as triplet presumably due to the presence of diastereomers. Signals at 33.9, 28.2, 27.0, 16.2, and 10.3 are divided in two peaks as doublet. MALDI-TOF-MS calcd for $C_{37}H_{48}N_2S_2$ (M) 584.3; Found 584.3. Elemental Analysis: Calculated for $C_{37}H_{48}N_2S_2$: C, 75.98%; H, 8.27%; N, 4.79%; Found: C, 75.91%; H, 8.21%; N, 4.45%.

Synthesis of 2,7-di(5-thiazolyl)-9,9-bis(2-ethylhexyl)fluorene (M2).

To a 25 mL Schlenk tube under N_2 atmosphere, $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), K_2CO_3 (173 mg, 1.3 mmol), 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene (275 mg, 0.50 mmol), anhydrous DMAc (2.0 mL), thiazole (106 μ L, 1.5 mmol), pivalic acid (17 μ L, 0.15 mmol) were added at room temperature. The mixture was stirred at 100 $^{\circ}C$ for 24 h under N_2 . The crude product was extracted with ethyl acetate and hexane (1:1), washed with water and brine, and then dried with Na_2SO_4 . Purification by column chromatography (silica gel, ethyl acetate:chloroform = 1:150 ~ 1:50) and by HPLC afforded **M2** as a yellow solid (188 mg, 68 %). 1H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 2H), 8.12 (s, 2H), 7.73 (d, 2H, J = 8.4 Hz), 7.59-7.57 (m, 4H), 2.06 (m, 4H), 0.87-0.69 (m, 16H), 0.63 (m, 6H), 0.54 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.8, 151.7, 141.0, 140.1, 138.8, 129.6, 126.2, 122.6, 120.5, 55.2, 44.3, 34.8, 33.9, 28.2, 27.2, 22.7, 13.9, 10.40. Signals at 151.7, 129.6, 126.2, and 122.6 ppm are divided in three peaks as triplet presumably due to the presence of diastereomers. Signals at 28.2 and 10.4 are divided in two peaks as doublet. MALDI-TOF-MS calcd for $C_{35}H_{44}N_2S_2$ (M) 556.3; Found 556.5. Elemental Analysis: Calculated for $C_{35}H_{44}N_2S_2$: C, 75.49; H, 7.96; N, 5.03. Found: C, 75.54, H, 8.07; N, 4.81.

Synthesis of 2,7-di(5-thiazolyl)-9-(1-octylnonyl)carbazole (M3).

To a 25 mL Schlenk tube under N_2 atmosphere, tris(*o*-methoxyphenyl)phosphine (24 mg, 68 μ mol),

1-adamantanecarboxylic acid (305.8 mg, 1.7 mmol), 2,7-dibromo-9-(*1-octylnonyl*)carbazole (956.2 mg, 1.7 mmol), and thiazole (2.4 mL, 34 mmol) were added. The Schlenk tube was transferred to a glovebox. In the glove box, Pd₂(dba)₃·CHCl₃ (17.6 mg, 17 μmol), Cs₂CO₃ (1.7 g, 5.1 mmol), and anhydrous toluene (17 mL) were added. The mixture was stirred at 100 °C for 24 h under N₂. The crude product was extracted with CHCl₃, washed with water and brine, and then dried with Na₂SO₄. Purification by column chromatography (silica gel, ethyl acetate : hexane = 1:19 ~ 1:5), and by HPLC afforded the product as yellow oil (827.8 mg, 85%). ¹H NMR (400 MHz, CDCl₃) δ 8.79 (s, 2H), 8.17 (s, 2H), 8.10 (m, 2H), 7.76 (s, 1H), 7.57 (s, 1H), 7.46 (d, 2H, *J* = 8.0 Hz), 4.61 (m, 1H), 2.32 (m, 2H), 1.99 (m, 2H), 1.28-1.01 (m, 24H), 0.79 (t, 6H, *J* = 7.0 Hz). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 152.0 (2C), 143.0 (1C), 140.8 (2C), 139.6 (1C), 139.0 (2C), 129.0 (1C), 128.5 (1C), 123.8 (1C), 122.4 (1C), 121.2 (1C), 121.0 (1C), 118.6(2C), 110.0 (1C), 107.3(1C), 56.6(1C), 33.8(2C), 31.7(2C), 29.4(2C), 29.3(2C), 29.2(2C), 26.8(2C), 22.6(2C), 14.1(2C). MALDI-TOF-MS calcd for C₃₅H₄₅N₃S₂ (M) 571.3; Found 571.2. Elemental Analysis: Calculated for C₃₅H₄₅N₃S₂: C, 73.51; H, 7.93; N, 7.35. Found: C, 72.96, H, 7.93; N, 7.32.

Synthesis of 5,5'-di(5-thiazolyl)-4,4'-didodecyl-2,2'-bithiophene (M4).

To a 25 mL Schlenk tube under N₂ atmosphere, tris(*o*-methoxyphenyl)phosphine (20.8 mg, 58 μmol), 1-adamantanecarboxylic acid (263.1 mg, 1.5 mmol), 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene (964.3 mg, 1.5 mmol), and thiazole (2.1 mL, 29 mmol) were added. The Schlenk tube was transferred to a glovebox. In the glove box, Pd₂(dba)₃·CHCl₃ (15.2 mg, 15 μmol), Cs₂CO₃ (1.40 g, 4.4 mmol), and anhydrous toluene (15 mL) were added. The mixture was stirred at 100 °C for 24 h under N₂. The crude product was extracted with CHCl₃, washed with water and brine, and then dried with Na₂SO₄. Purification by column chromatography (silica gel, ethyl acetate : hexane = 1:19 ~ 1:5) and by HPLC afforded the product as orange solid (388.2 g, 40%). ¹H NMR (400 MHz, CDCl₃) δ

8.80 (s, 2H), 7.92 (s, 2H), 7.04 (s, 2H), 2.68 (t, 4H, $J = 7.8$ Hz), 1.64 (m, 4H), 1.37-1.26 (m, 36H), 0.88 (t, 6H, $J = 6.8$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 152.5 (2C), 142.3 (2C), 141.2 (2C), 135.9 (2C), 130.8 (2C), 126.6 (2C), 125.3 (2C), 31.9 (2C), 30.5 (2C), 29.7 (2C), 29.6 (4C), 29.6 (2C), 29.5 (2C), 29.4 (2C), 29.4 (2C), 29.4 (2C), 22.7 (2C), 14.1 (2C). MALDI-TOF-MS calcd for $\text{C}_{38}\text{H}_{56}\text{N}_2\text{S}_4$ (M) 668.3; Found 668.2. Elemental Analysis: Calculated for $\text{C}_{38}\text{H}_{56}\text{N}_2\text{S}_4$: C, 68.21; H, 8.44; N, 4.19. Found: C, 68.30; H, 8.59; N, 4.22.

Synthesis of P1 (Table 1, Entry 1).

To a 25 mL Schlenk tube, 2,7-bis(4-methylthiazol-5-yl)-9,9-bis(2-ethylhexyl)fluorene (**M1**) (152 mg, 0.26 mmol), $\text{Cu}(\text{OAc})_2$ (9.5 mg, 0.052 mmol), and *p*-xylene (1.04 mL) were added. A drying tube with calcium chloride was attached to the Schlenk tube. The mixture was gently stirred and heated at 140 °C for 24 h under air. Volatiles were removed *in vacuo* and organic residues were dissolved in CHCl_3 . To the solution, aqueous solution of $\text{EDTA} \cdot 2\text{Na}$ was added. After stirring for overnight, the organic phase was separated and washed with water. The organic layer was passed through Celite, and concentrated *in vacuo*. Reprecipitation from CHCl_3 /methanol and washing with *n*-hexane yielded **P1** as yellow solid (130 mg, 87%). $M_n = 38500$, $M_w/M_n = 4.48$. ^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, 2H, $J = 7.6$ Hz), 7.54 (m, 4H), 2.64 (s, 6H), 2.04 (br, 4H), 0.98-0.70 (br, 16H), 0.65 (br, 6H), 0.57 (br, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.7, 151.0, 148.7, 140.3, 134.6, 129.9, 127.7, 124.6, 119.8, 54.9, 44.3, 34.3, 33.4, 27.8, 26.6, 22.3, 16.1, 13.5, 9.9. Elemental Analysis: Calculated for $\text{C}_{37}\text{H}_{46}\text{N}_2\text{S}_2$: C, 76.24; H, 7.95; N, 4.81. Found: C, 75.11; H, 8.14; N, 4.63.

Synthesis of P3.

To a 25 mL Schlenk tube, 2,7-di(5-thiazolyl)-9-(9-heptadecyl)carbazole (**M3**) (144 mg, 0.25 mmol),

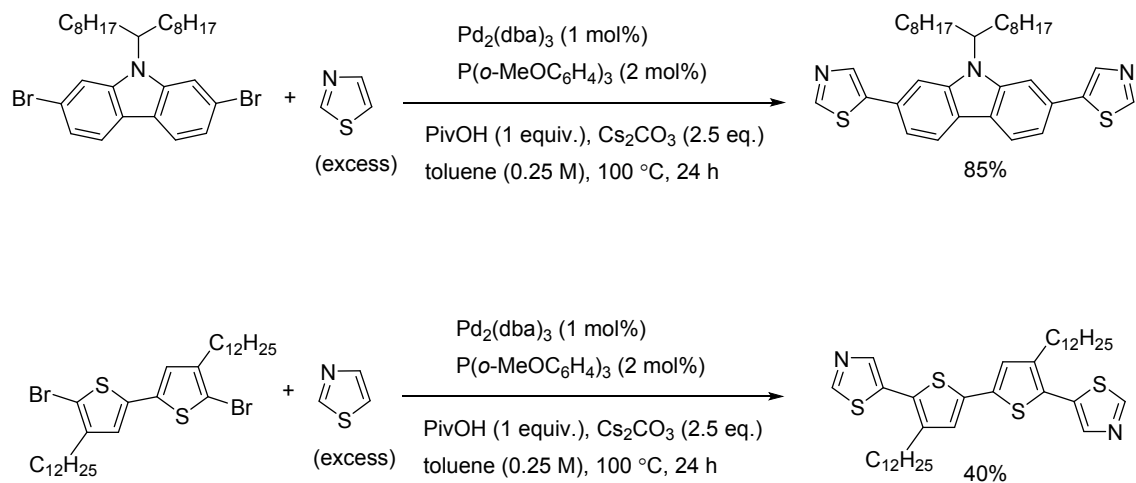
Cu(OAc)₂ (4.6 mg, 0.025 mmol), and *p*-xylene (0.5 mL) were added. A drying tube with calcium chloride was attached to the Schlenk tube. The mixture was gently stirred and heated at 140 °C for 24 h under air. Volatiles were removed *in vacuo* and organic residues were dissolved in *o*-dichlorobenzene. To the solution, aqueous solution of EDTA·2Na was added. After stirring for overnight, the organic phase was separated and washed with water. The solution was then dried under *vacuo*. The crude product was then purified through Soxhlet extraction with methanol and hexane, and collected with *o*-dichlorobenzene (113.8 mg, 80%). ¹H NMR (600 MHz, C₂D₂Cl₄, 393 K): repeating unit δ 8.21 (m, 4H), 7.81 (m, 2H), 7.60 (m, 2H), 4.71 (br, 1H), 2.40 (br, 2H), 2.16 (br, 2H), 1.28-1.44 (m, 26H), 0.90 (m 6H), terminal unit δ 8.83 (s), 8.16 (d, *J* = 8.4 Hz), 7.75 (s), 7.53 (d, *J* = 7.8 Hz). High temperature GPC: *M*_n = 3400, *M*_w/*M*_n = 2.62. NMR-based molecular weight: 3400. Elemental Analysis: Calculated for C₃₅H₄₃N₂S₂: C, 73.77; H, 7.61; N, 7.37. Found: C, 72.53; H, 7.46; N, 7.11.

Synthesis of P4.

To a 25 mL Schlenk tube, 5,5'-di(5-thiazolyl)-4,4'-didodecyl-2,2'-bithiophene (**M4**) (167.3 mg, 0.23 mmol), Cu(OAc)₂ (4.2 mg, 0.023 mmol), and *p*-xylene (0.5 mL) were added. A drying tube with calcium chloride was attached to the Schlenk tube. The mixture was gently stirred and heated at 140 °C for 24 h under air. Volatiles were removed *in vacuo* and organic residues were dissolved in *o*-dichlorobenzene. To the solution, aqueous solution of EDTA·2Na was added. After stirring for overnight, the organic phase was separated and washed with water. The solution was then evaporated and dried under *vacuo*. The crude product was then purified through Soxhlet extraction with methanol and hexane, and collected with *o*-dichlorobenzene (112.1 mg, 73%). ¹H NMR (600 MHz, C₂D₂Cl₄, 393 K): repeating unit δ 7.98 (m, 2H), 7.15 (m, 2H), 2.86 (m, 4H), 1.75 (m, 4H), 1.43-1.51 (m, 18H), 0.90 (m 6H), terminal unit δ 8.83 (s), 2.77 (t, *J* = 7.8 Hz). High temperature

GPC: $M_n = 5100$, $M_w/M_n = 1.75$. NMR-based molecular weight: 5300. Elemental Analysis:

Calculated for $C_{38}H_{54}N_2S_4$: C, 68.42; H, 8.16; N, 4.20. Found: C, 67.11; H, 7.94; N, 4.11.



Scheme S1. Synthesis of **M3** and **M4**.

Table S1 Results of polycondensation reactions of **M1**

Entry	Atmosphere	Cat. /mol%	conc. /M	Additive	Yield /% ^a	M_n^b	M_w/M_n^b
1 ^c	Air	20	0.25		87	38500	4.48
2	O ₂ balloon	10	0.50		67	14000	2.75
3	O ₂ balloon	10	0.50		18	4600	1.10
4	O ₂ balloon	10	0.50		trace	oligomer	-
5	O ₂ balloon	10	0.50	K ₂ CO ₃	-	-	-
6	O ₂ balloon	10	0.50	AcOH	-	-	-

^a The products were obtained by reprecipitation from CHCl₃/CH₃OH ^b Estimated by GPC calibrated on polystyrene standards. ^c Table 1, Entry 1. In entries 2, 3, and 4, the reactions under same reaction conditions were conducted, but reproducible results were not obtained.

Table S2 Results of polycondensation reactions of **M2**

Reaction scheme showing the polymerization of monomer **M2** to polymer **P2** using $\text{Cu}(\text{OAc})_2$ in *p*-xylene at $140\text{ }^\circ\text{C}$, 0.5 M , under Air or O_2 .

Entry	Atmosphere	Cat. /mol%	Time / h	Yield / % ^a	M_n^b	M_w/M_n^b
1 ^c	Air (CaCl ₂ tube)	10	24	98	19800	3.73
2	O ₂ balloon	10	24	75	4000	1.22
3	O ₂ balloon	10	48	26	oligomer	-

^a The products were obtained by reprecipitation from CHCl₃/CH₃OH ^b Estimated by GPC calibrated on polystyrene standards. ^c Table 1, Entry 4.

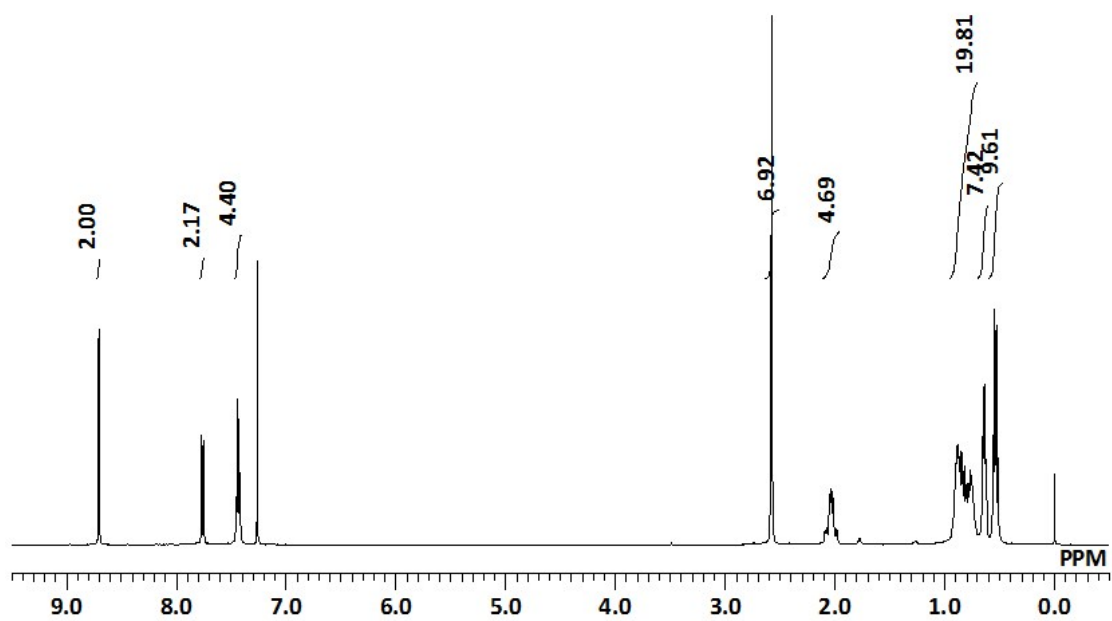


Fig. S1 ^1H NMR spectrum of **M1** (CDCl_3 , 400 MHz)

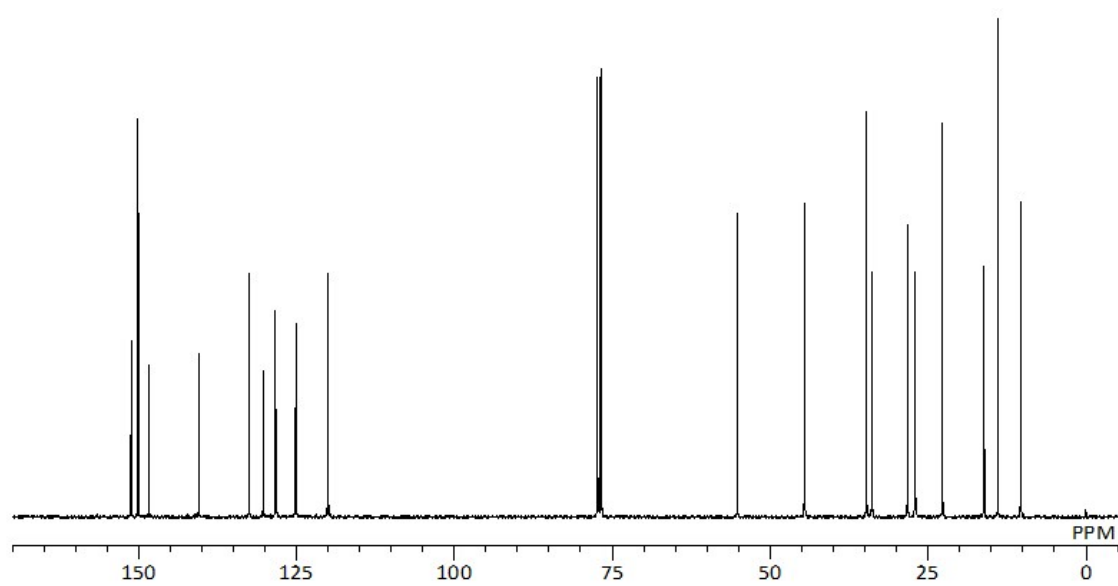


Fig. S2 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **M1** (100 MHz, CDCl_3).

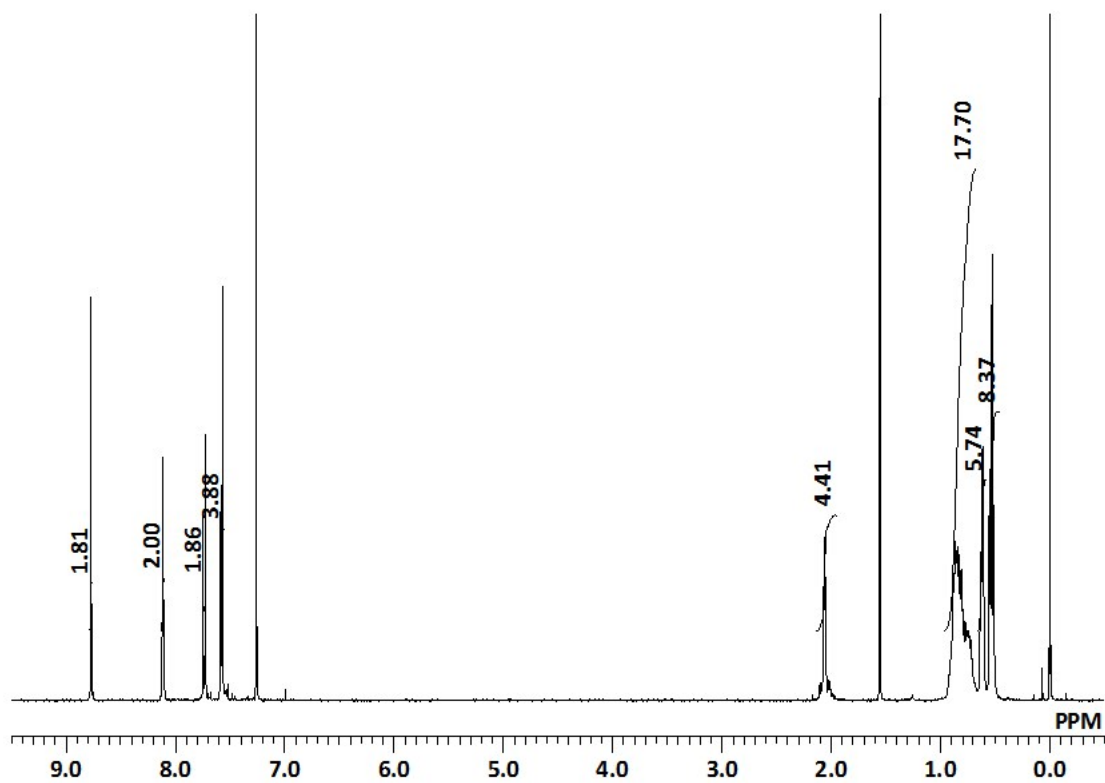


Fig. S3 ^1H NMR spectrum of **M2** (CDCl_3 , 400 MHz).

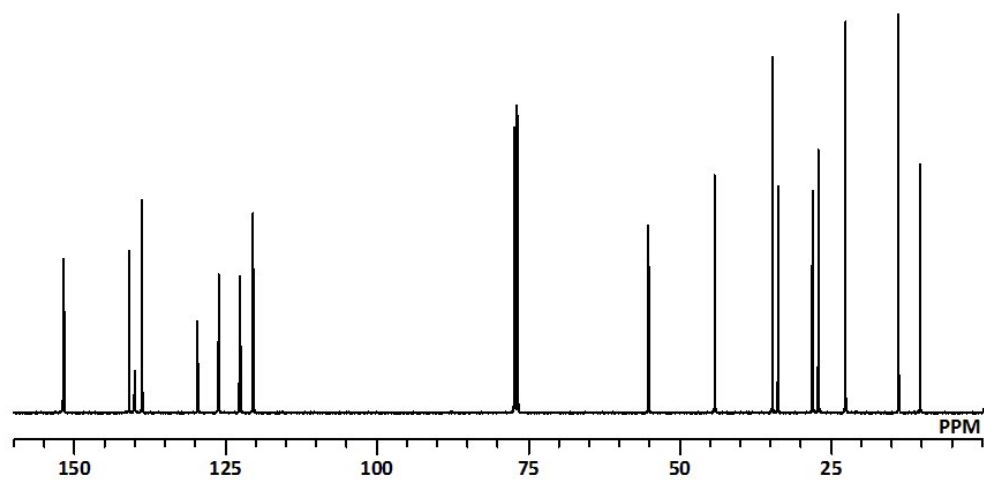


Fig. S4 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **M2** (CDCl_3 , 100 MHz).

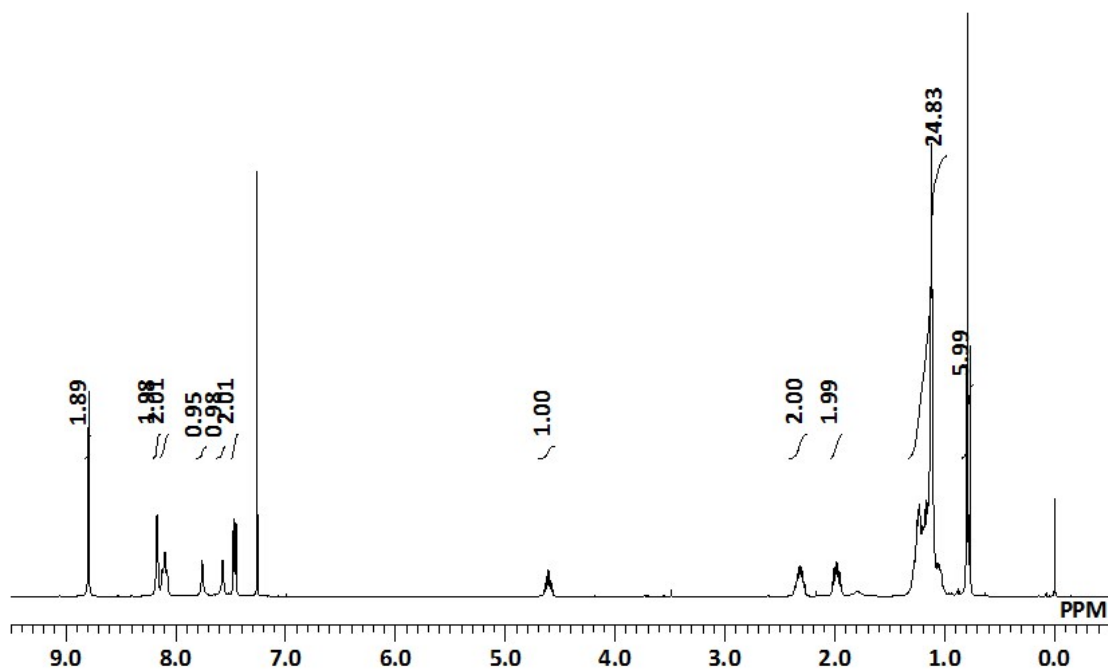


Fig. S5 ¹H NMR spectrum of **M3** (CDCl₃, 400 MHz).

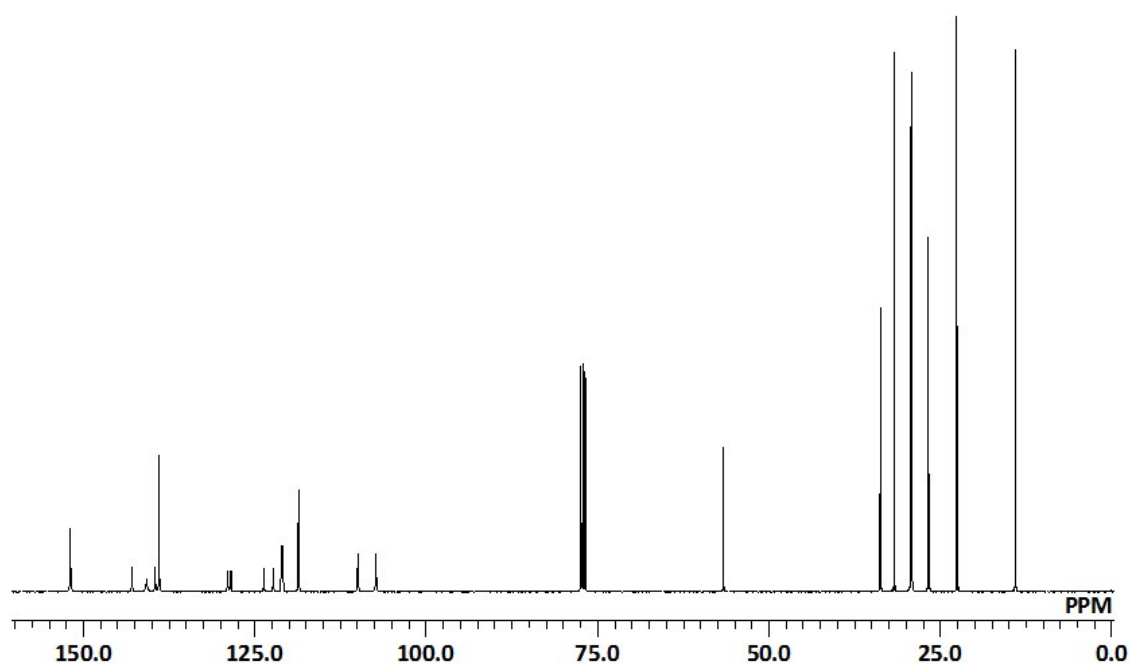


Fig. S6 ¹³C{¹H} NMR spectrum of **M3** (CDCl₃, 100 MHz).

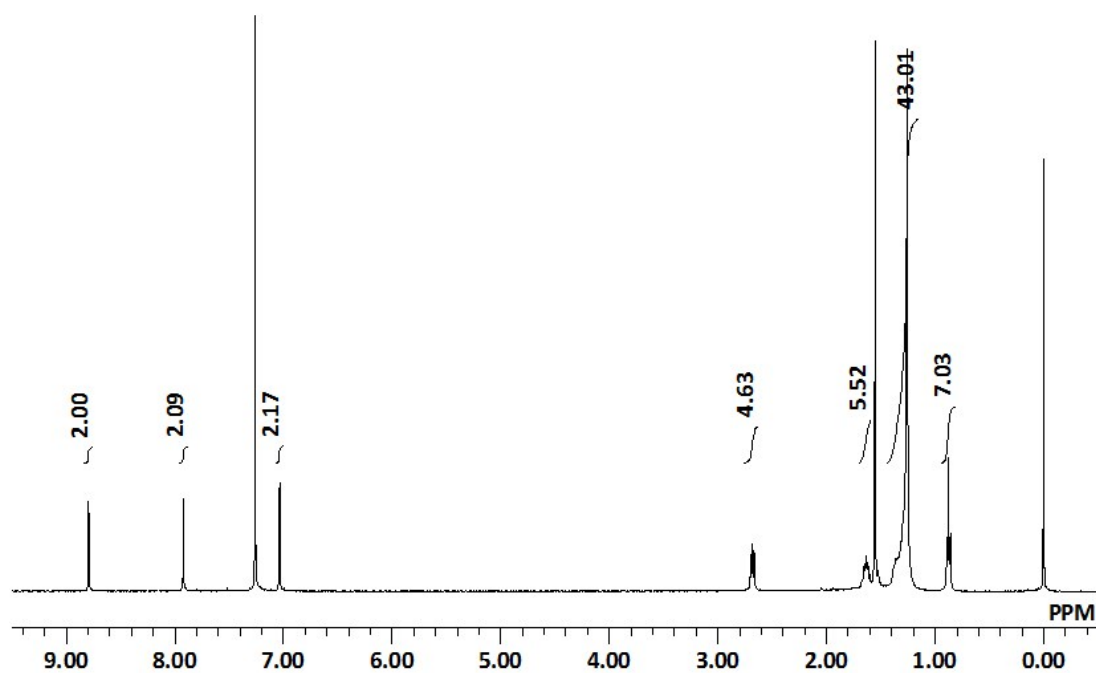


Fig. S7 ^1H NMR spectrum of **M4** (CDCl_3 , 400 MHz).

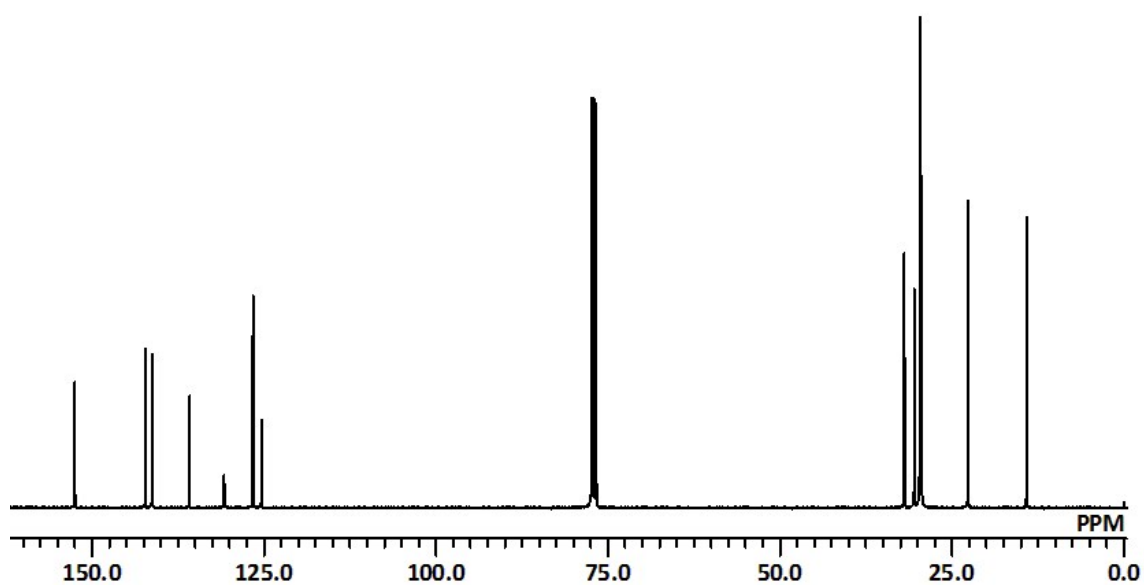


Fig. S8 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **M4** (CDCl_3 , 100 MHz).

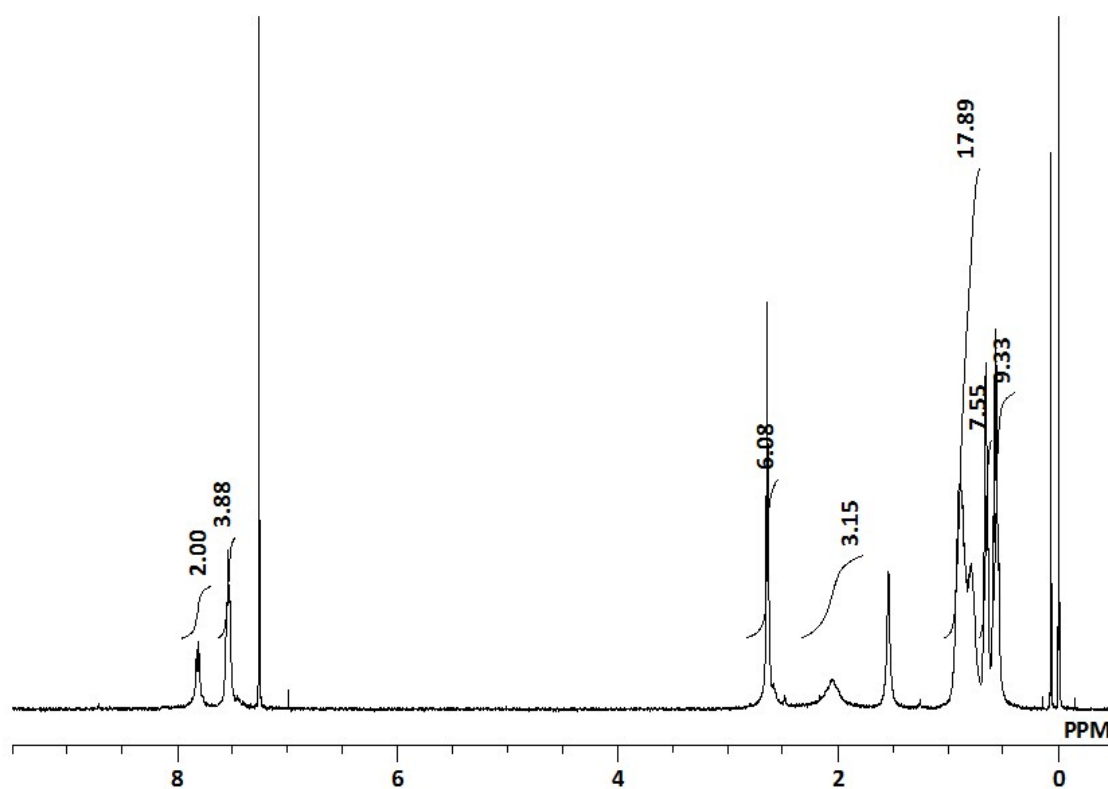


Fig. S9 ^1H NMR spectrum of **P1** (CDCl_3 , 400 MHz).

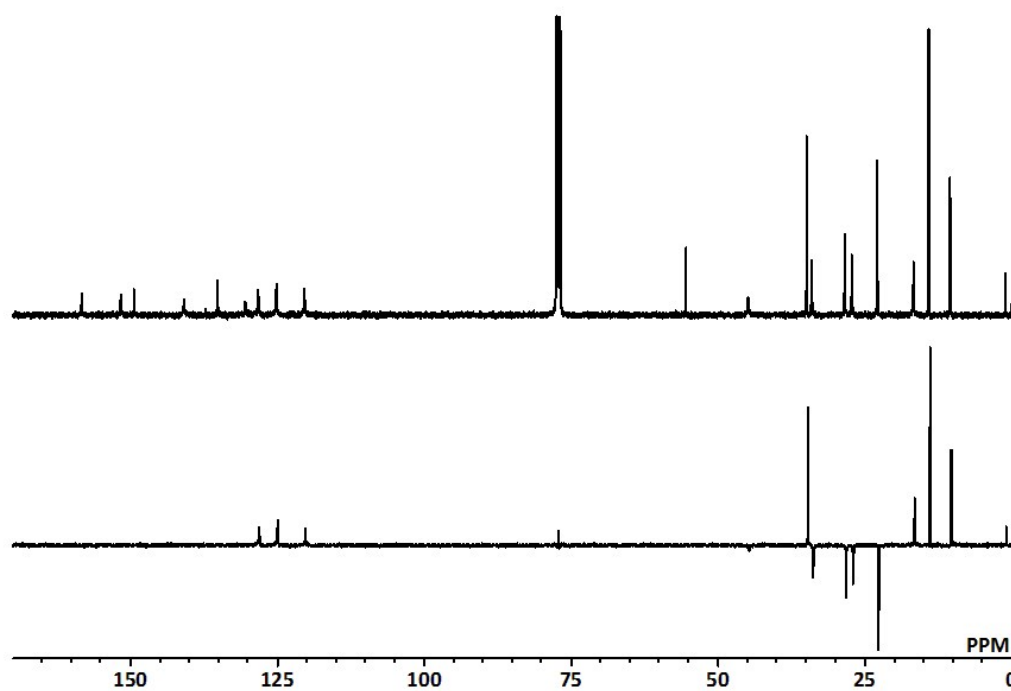


Fig. S10 $^{13}\text{C}\{^1\text{H}\}$ and DEPT NMR spectra of **P1** (CDCl_3 , 100 MHz).

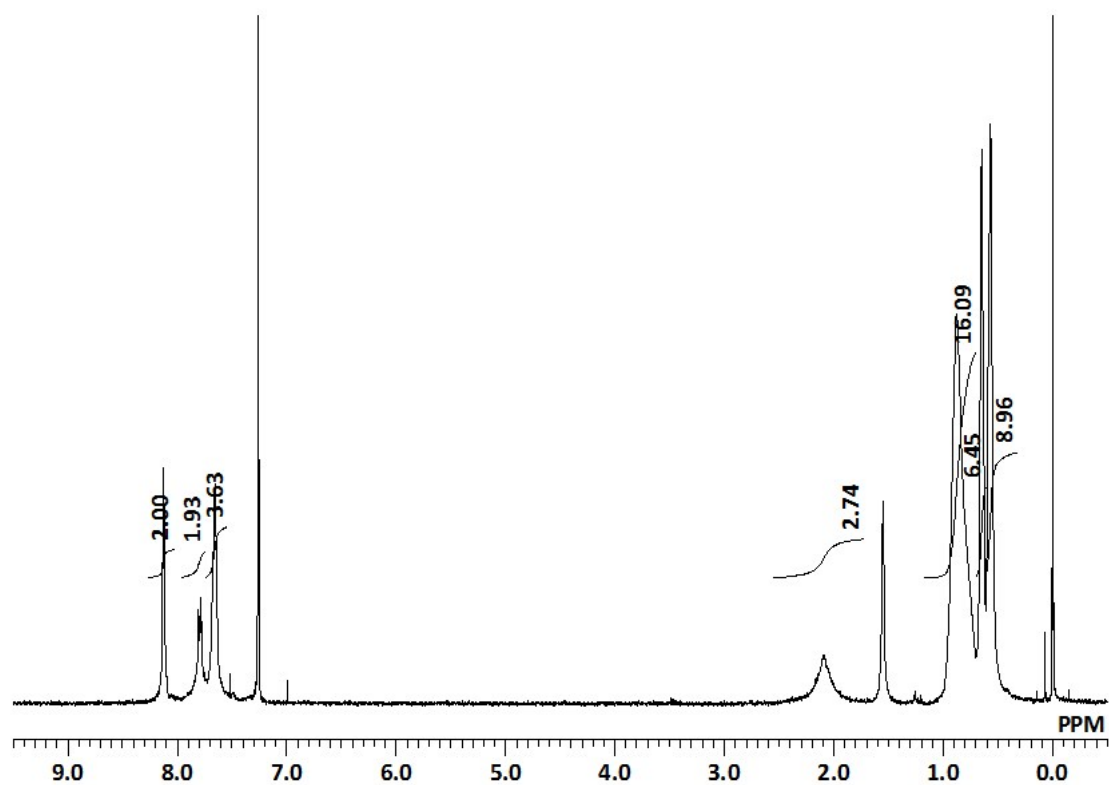


Fig. S11 ^1H NMR spectrum of **P2** (CDCl_3 , 400 MHz).

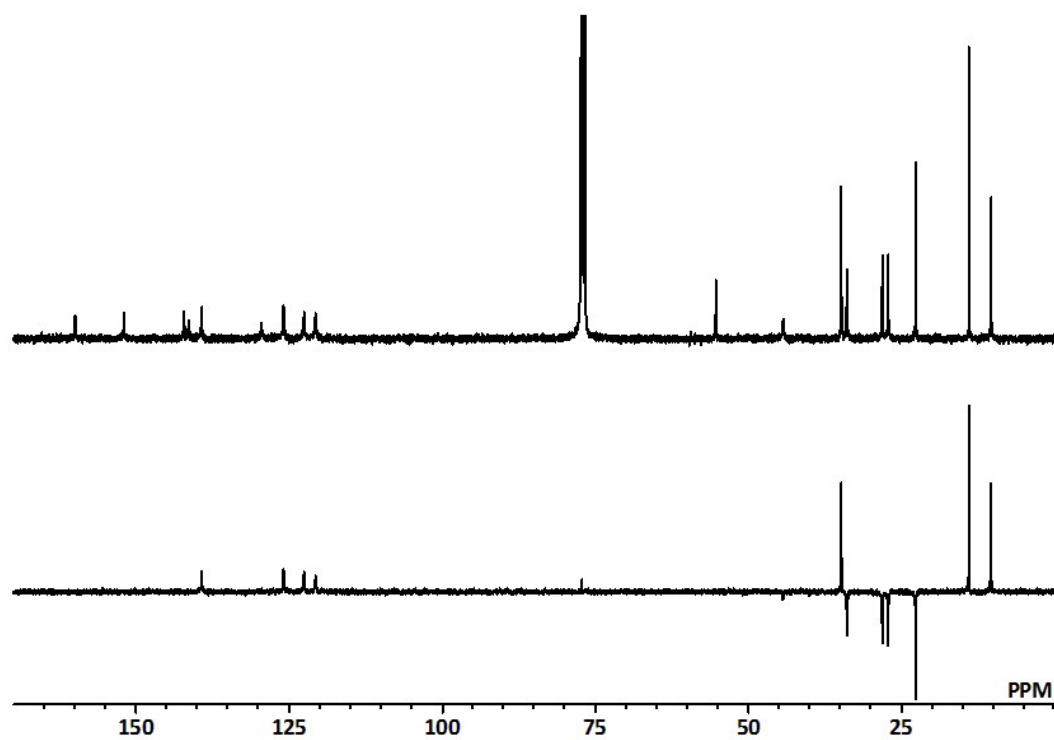


Fig. S12 $^{13}\text{C}\{^1\text{H}\}$ and DEPT NMR spectra of **P2** (CDCl_3 , 100 MHz).

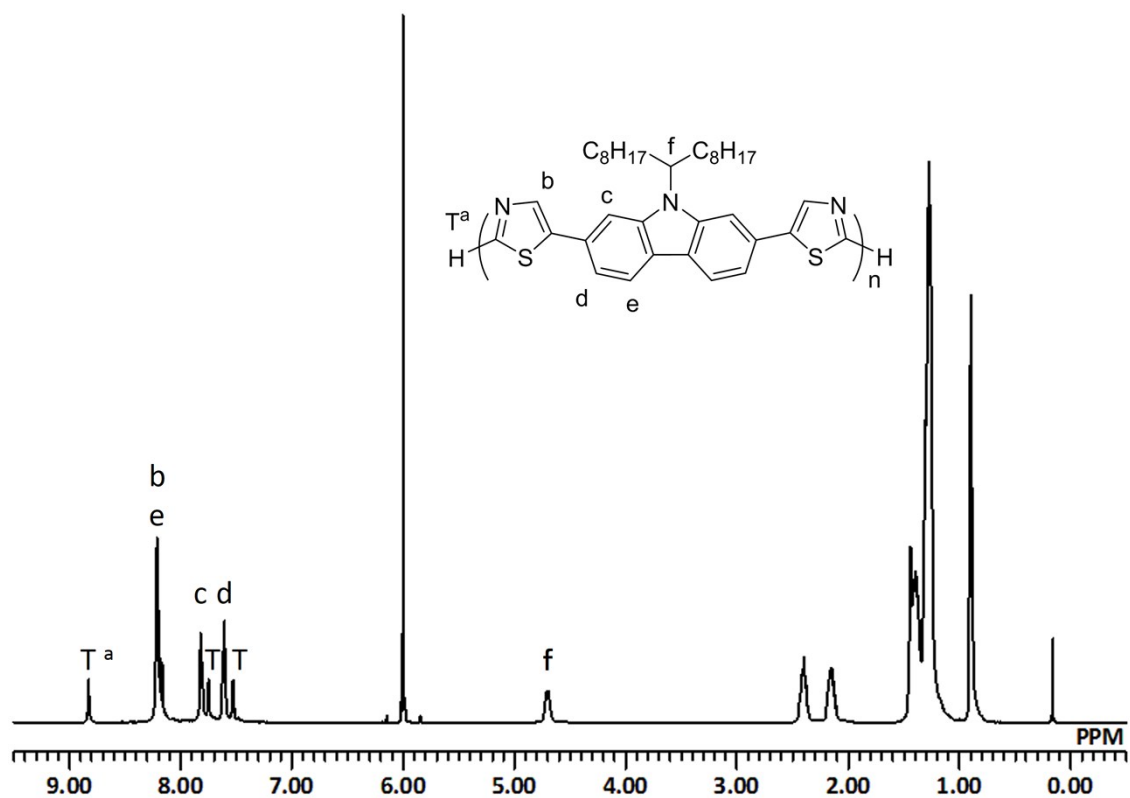


Fig. S13 ^1H NMR spectrum of **P3** ($\text{C}_2\text{D}_2\text{Cl}_4$, 600 MHz, 393 K).

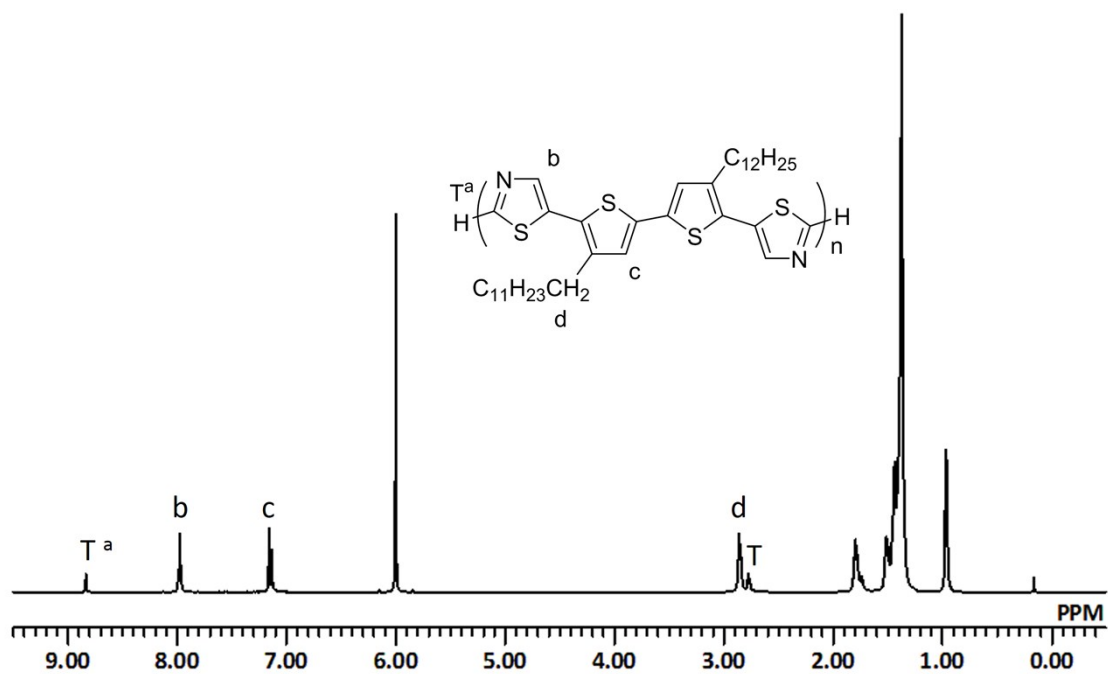
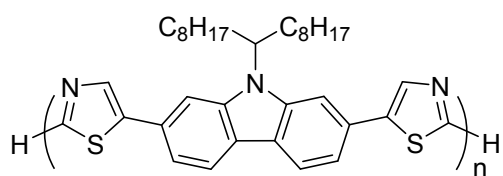


Fig. S14 ^1H NMR spectrum of **P4** ($\text{C}_2\text{D}_2\text{Cl}_4$, 600 MHz, 393 K).



$n = 3, m/z = 1710.89$
 $n = 4, m/z = 2280.18$
 $n = 5, m/z = 2850.47$

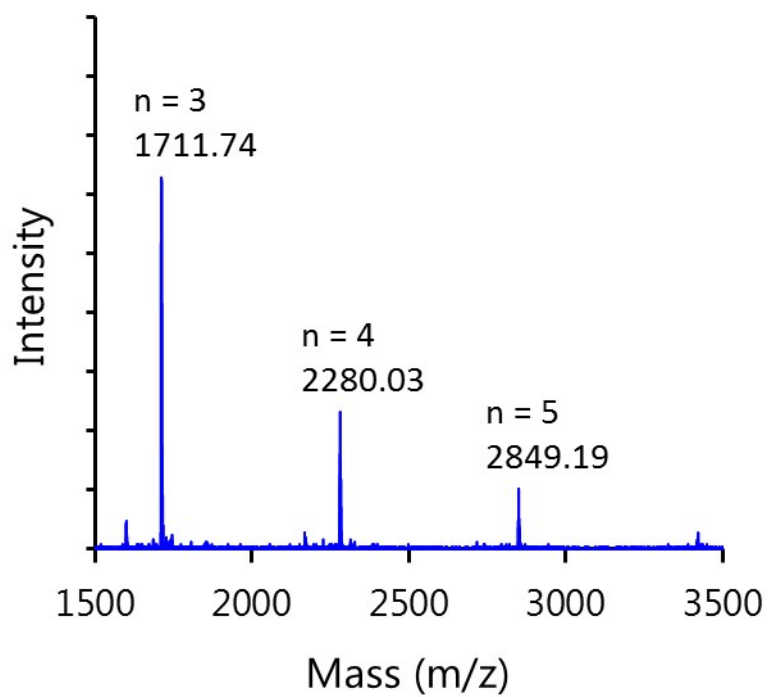
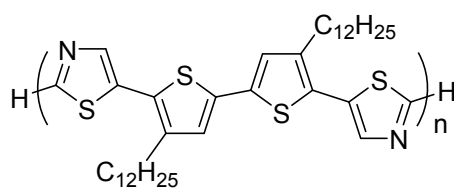


Fig. S15 MALDI-TOF-MS spectrum of **P3** and calculated mass.



$n = 3$, $m/z = 2001.97$

$n = 4$, $m/z = 2668.29$

$n = 5$, $m/z = 3337.60$

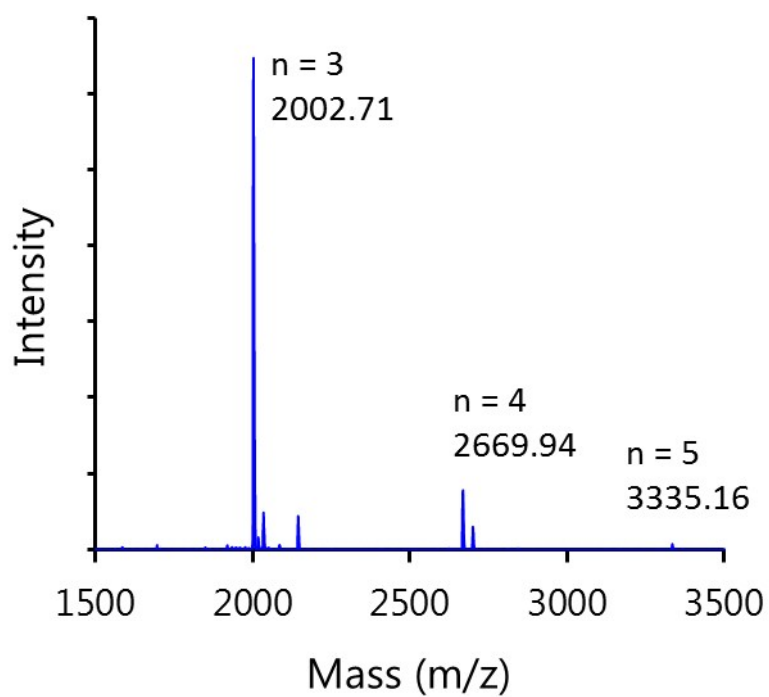


Fig. S16 MALDI-TOF-MS spectrum of **P4** and calculated mass.

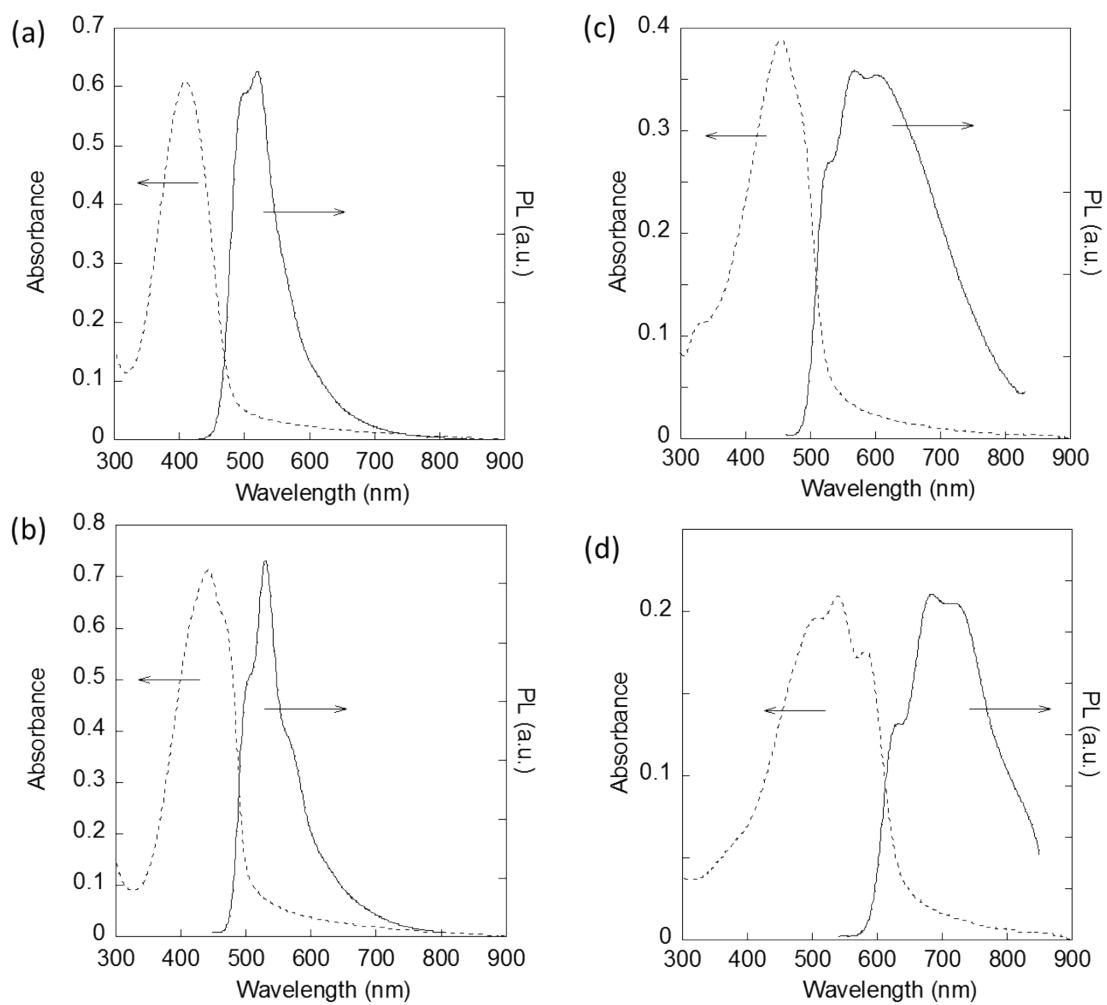


Fig. S17 UV/Vis absorption and photoluminescence spectra of (a) **P1**, (b) **P2**, (c) **P3**, and (d) **P4** in the film state.

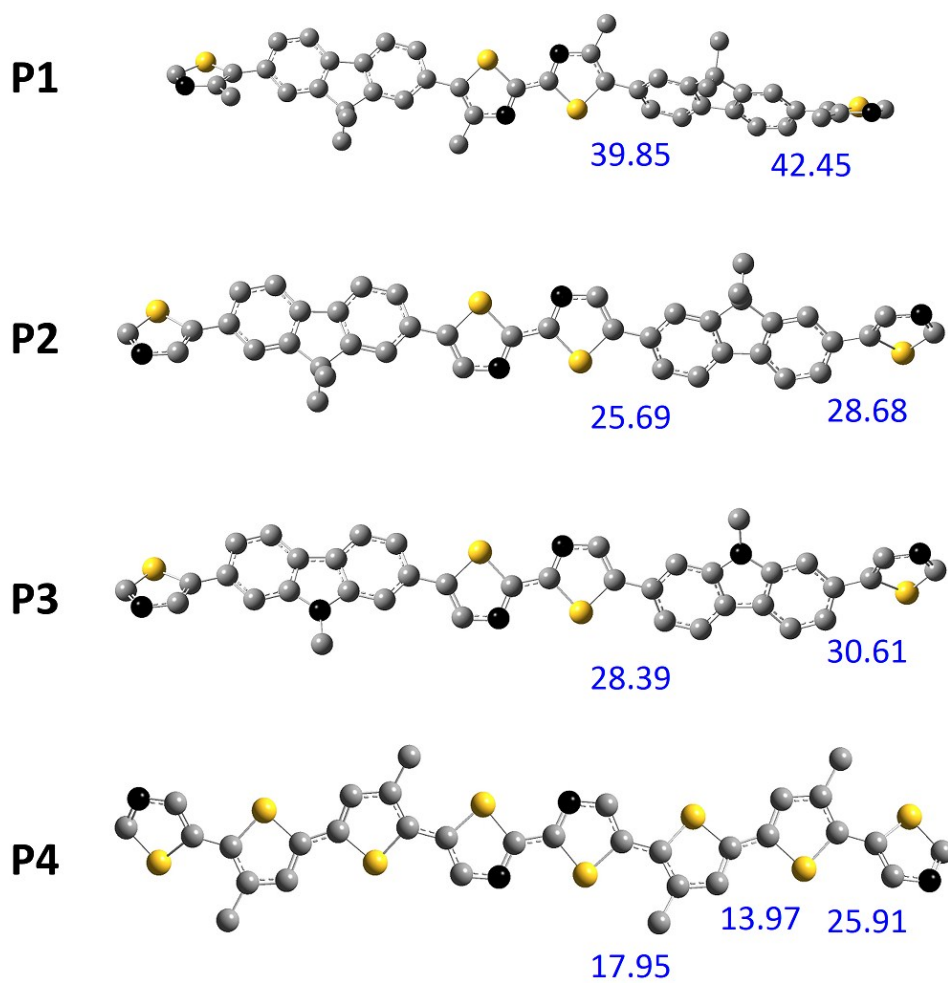


Fig. S18 Energy minimized structures and torsion angles of the model compounds for **P1-P4** obtained by DFT.

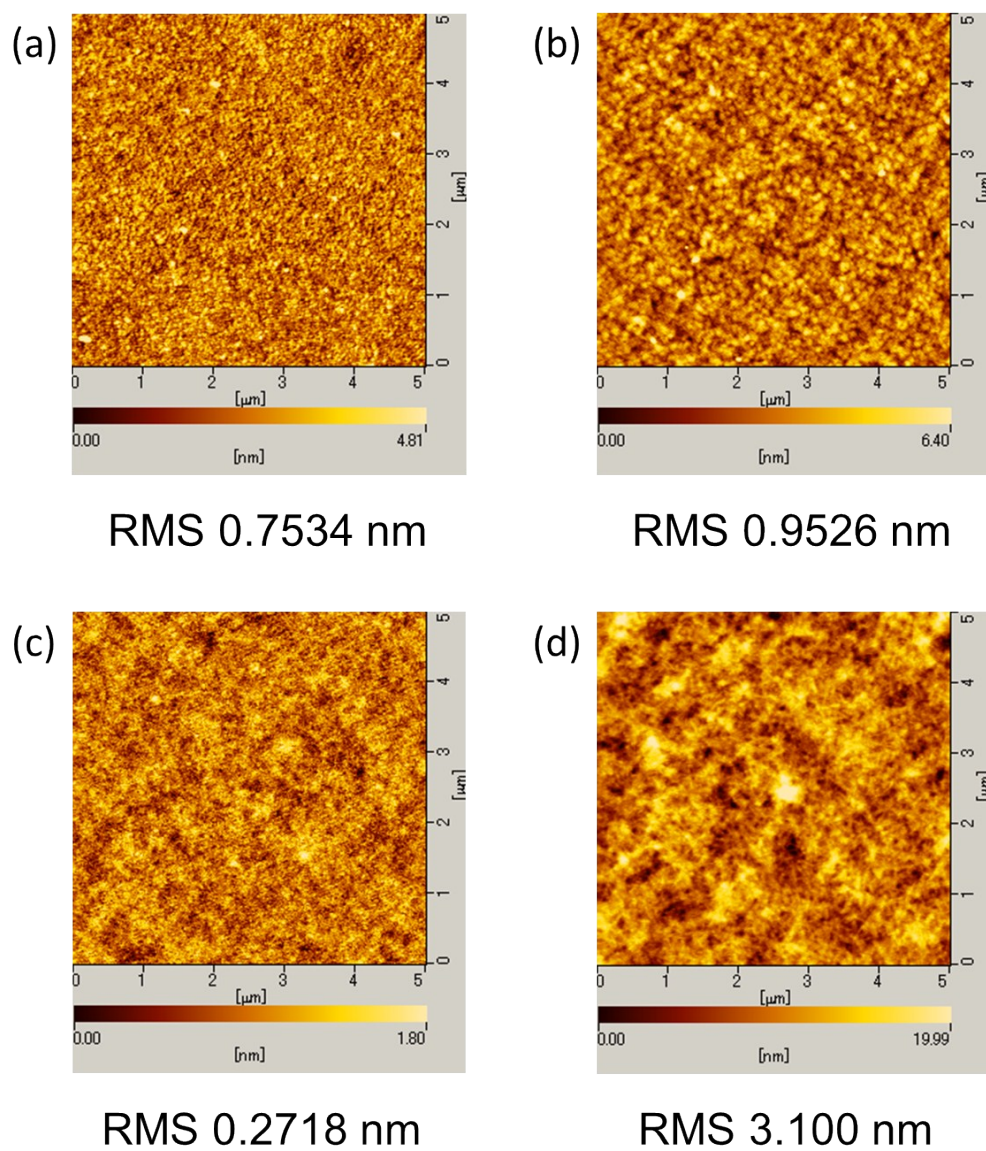


Fig. S19 AFM images ($5 \times 5 \mu\text{m}^2$) of spin coating films. (a) **P1**, (b) **P2**, (c) **P3**, and (d) **P4**.

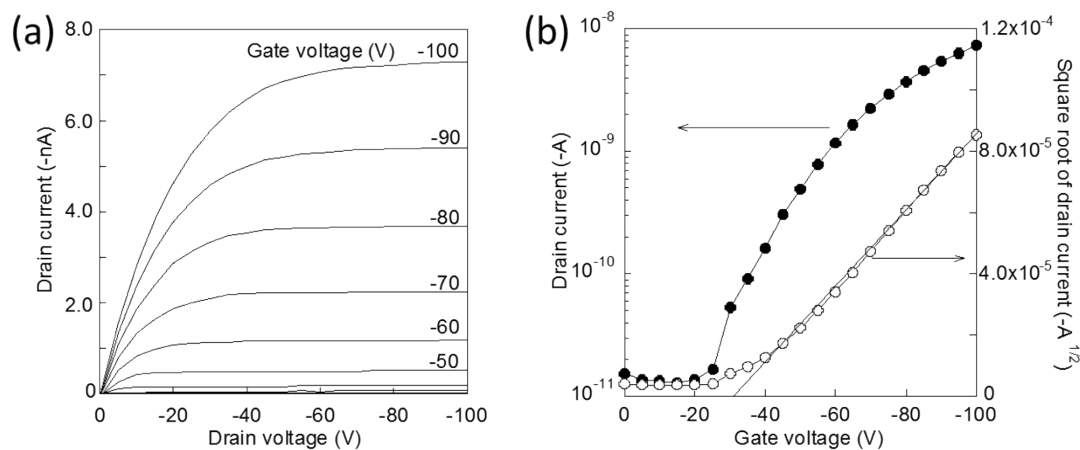


Fig. S20 Typical (a) output and (b) transfer characteristics (measured at drain voltage of -100 V) of the top-contact OFETs for **P4**.

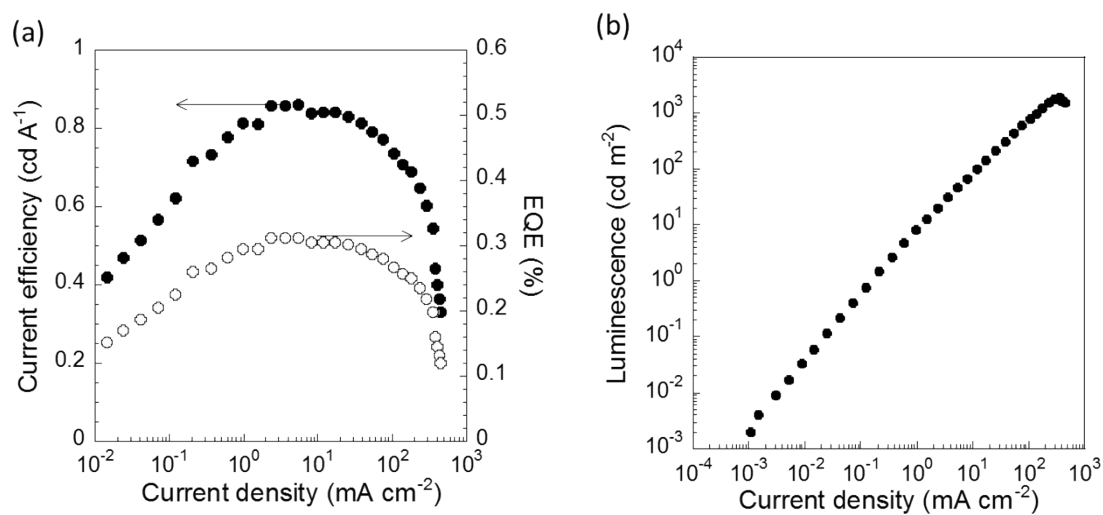


Fig. S21 (a) Current efficiency, EQE and (b) luminescence characteristics of the device with **P2**.

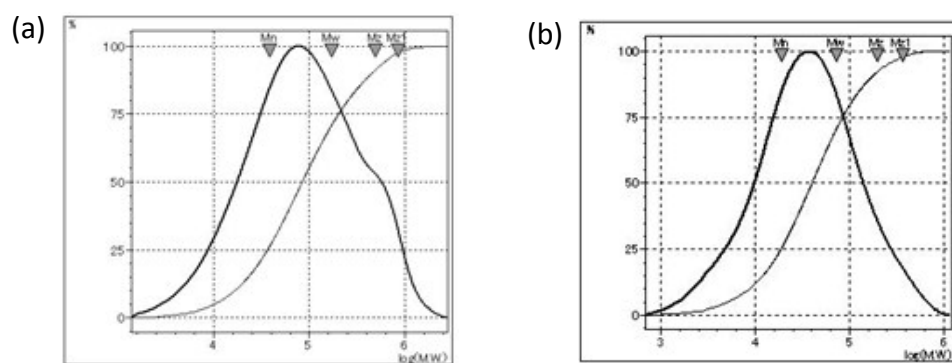


Fig. S22 GPC traces of (a) **P1** and (b) **P2** listed in Table 1.

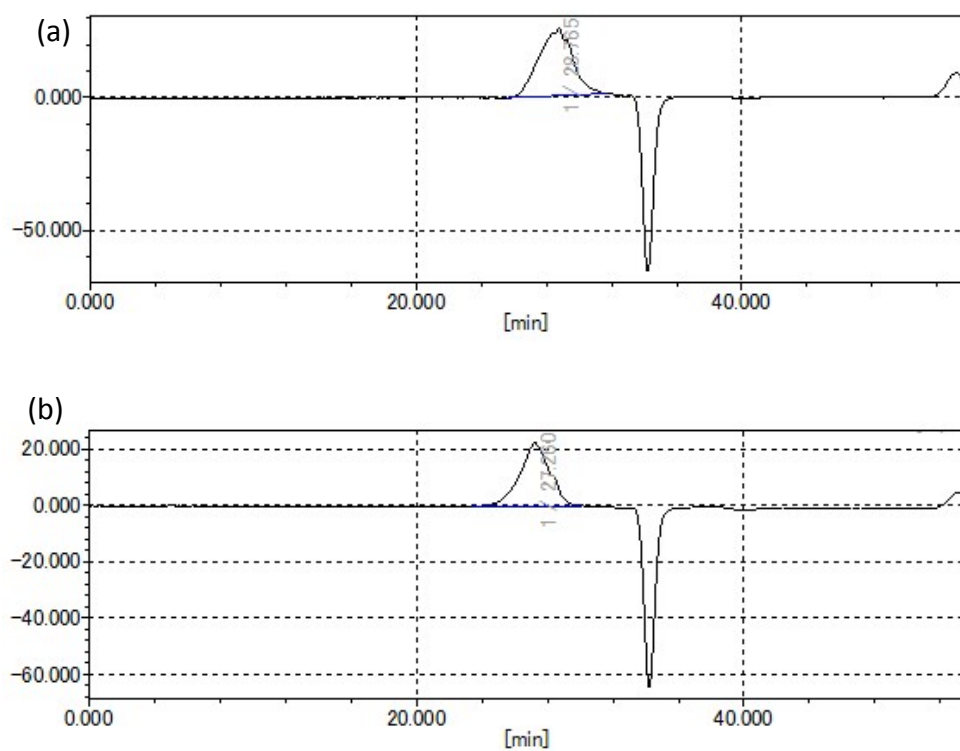


Fig. S23 High temperature GPC traces of (a) **P3** and (b) **P4**.

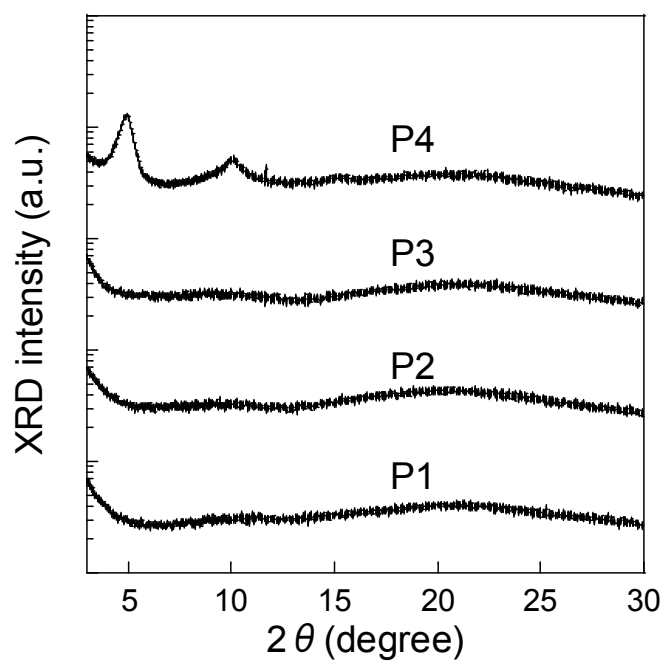


Fig. S24 XRD patterns of **P1** - **P4** after annealing at 110 °C for 10 min.

Table S1 Degree of polymerization

	M_n	Degree of polymerization
P1	38500 ^a	66
P2	19800 ^a	36
P3	3400 ^b	6
P4	5100 ^b	8

^a Based of GPC, ^b Based on NMR.

References

- 1 H. Nagashima, M. Saito, H. Nakamura, T. Yasuda and T. Tsutsui, *Org. Electron.*, 2010, **11**, 658–663.
- 2 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.