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Supporting Information for

Novel dibenzo[*a*,*e*]pentalene-besed conjugated polymers

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Contents

1. Experimental

1-1. General

All chemicals and solvents are of reagent grade unless otherwise indicated. THF were purified with a standard procedure prior to use. 4b,5,9b,10-tetrahydrodibenzo[*a*,*e*]pentalene-5,10-dione (**5**) were synthesized as reported.[S1] Melting points were uncorrected. All reactions were carried out under nitrogen atmosphere. Nuclear magnetic resonance spectra were obtained in deuterated chloroform ($CDCl_3$) with TMS as internal reference unless otherwise stated; chemical shifts (δ) are reported in parts per million. IR spectra were recorded using a KBr pellet for solid samples. EI-MS spectra were obtained using an electron impact ionization procedure (70 eV). The molecular ion peaks of the bromine or sulfur containing compounds showed a typical isotopic pattern, and all the mass peaks are reported based on ^{77}Br. HRMS measurements were carried out at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. Elemental analysis was measured by Yanaco MT-6 CHN CORDER at the Materials Characterization Support Unit in RIKEN Advanced Technology Support Division. UV-Vis absorption spectra were measured using a Shimadzu UV-3600 spectrometer. Cyclic voltammograms (CVs) were recorded on an ALS Electrochemical Analyzer Model 612D in dichloromethane containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as supporting electrolyte at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. All the potentials were calibrated with the standard ferrocene/ferrocenium redox couple (Fc/Fc^+: $E_{1/2}$ = +0.47 V measured under identical conditions). Ionization potential (IP) was determined from the onset of photoelectron spectra measured by using a photoelectron spectrometer MODEL AC-2 in air (RIKEN KEIKI CO., LTD). AFM images were obtained on a Nanotechnology, Inc. scanning probe microsope Nanocute system. Grazing incidence X-ray diffraction (GIXD) experiments were conducted at the SPring-8 on beamline BL19B2. The sample was irradiated at a fixed incident angle on the order of 0.12° through a HUBER diffractometer and the GIXD patterns were recorded on a 2-D image detector (PILATUS 100K) with an X-ray energy of 12.39 keV (λ = 1 Å). Two images were taken in each measurement due to the limited range of the detector, and thus two images are layered to show the entire pattern; a lateral black line in each GIXD image is to show the changeover. Samples for the GIXD measurements were prepared by drop-casting the polymer on the FDTS-modified Si/SiO_2 substrate.

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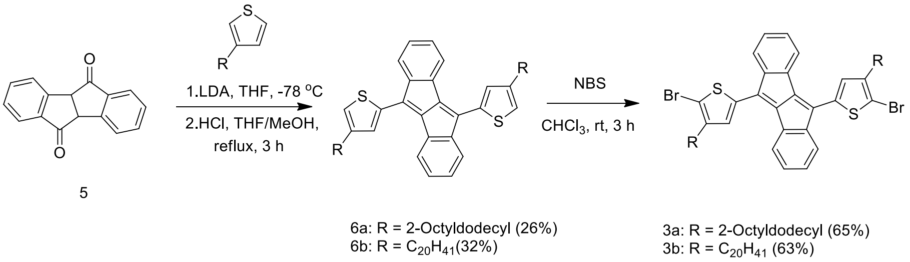
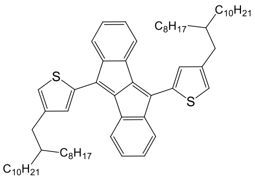
1-2. Synthesis

Synthesis of PDTDBP2Ts



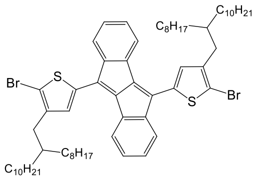
Scheme. S1. Synthesis of monomer units of PDTDBP2T.

5,10-Bis[4-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (6a)



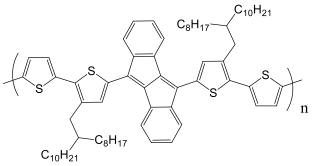
Lithium diisopropylamide (LDA) solution freshly prepared by slowly adding *n*-butyllithium solution (1.61 M hexane solution, 4.0 mL, 6.44 mmol) to diisopropylamine (1.00 mL, 7.08 mmol) in dry THF (28 mL) under argon atmosphere was added to a solution of 3-(2-octyldodecyl)thiophene (7.29 g, 20 mmol) and 4b,5,9b,10-tetrahydrodibenzo[*a*,*e*]pentalene-5,10-dione (**5**) (1.17 g, 5 mmol) in THF (9 mL) at 25 °C within 15 min. The reaction mixture was stirred for 3 h at rt and was then poured into ice containing hydrochloric acid (12 M), and the resulting solution was extracted with ethyl acetate (30 mL × 2). The combined extracts were concentrated in vacuo, and the residue was dissolved in methanol (100 mL). To the solution was added hydrochloric acid (2 M, 2.5 mL), and the mixture was refluxed gently for 3 h, and during this treatment, dark brown oil was separated out. Then, the solvent was disposed by decantation and then evaporated in vacuo. The residual oil was purified by column chromatography on silica gel eluted with dichloromethane-hexane (1:1, v/v) to give **6a** (1.20 g, 26%) as brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.7 Hz, 12H), 1.25–1.31 (m, 64H), 1.67 (sept, *J* = 6.7 Hz, 2H), 2.62 (d, *J* = 6.7 Hz, 4H), 6.92 (t, *J* = 6.5 Hz, 2H), 6.96 (t, *J* = 6.5 Hz, 2H), 7.06 (s, 2H), 7.31 (d, *J* = 7.0 Hz, 2H), 7.32 (s, 2H), 7.63 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.82, 22.83, 26.9, 29.49, 29.50, 29.51, 29.80, 29.81, 29.84, 29.9, 30.19, 30.20, 32.06, 33.57, 33.58, 35.09, 39.3, 122.2, 122.9, 123.0, 127.7, 127.8, 130.8, 133.4, 134.9, 135.0, 142.7, 142.8, 149.1; HRMS (APCI): Calcd for $C_{64}H_{94}S_2$: 926.67915 [M$^+$]. Found: 926.67767.

5,10-Bis[5-bromo-4-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (3a)



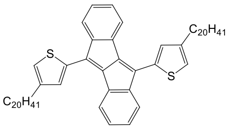
5,10-Bis[4-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (**6a**, 0.927 g, 1.0 mmol) and *N*-bromosuccinimide (0.378 g, 2.1 mmol) was dissolved in $CHCl_3$ (100 mL). The mixture was stirred for 3 h at rt. After evaporation of the solvent, the residue was purified by column chromatography on silica gel eluted CH_2Cl_2 / hexane (1:1, v/v) to give 5,10-bis[5-bromo-4-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (**3a**, 0.705 g, 65%) as brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.1 Hz, 12H), 1.25–1.31 (m, 64H), 1.72 (sept, *J* = 7.1 Hz, 2H), 2.56 (d, *J* = 7.1 Hz, 4H), 6.93 (t, *J* = 7.3 Hz, 2H), 6.96 (t, *J* = 7.3 Hz, 2H), 7.14 (s, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.83, 22.84, 26.8, 29.49, 29.50, 29.79, 29.83, 30.18, 30.20, 32.05, 32.06, 33.64, 34.45, 38.80, 122.0, 122.3, 122.8, 128.1, 130.5, 132.6, 134.6, 134.7, 142.2, 143.0, 148.6; HRMS (APCI): Calcd for $C_{64}H_{92}Br_2S_2$: 1082.50017 [M$^+$]. Found: 1082.49841.

PDTDBP2T-OD



To a 2–5 mL microwave pressurized vial equipped with a stirring bar, 5,10-bis[5-bromo-4-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (**3a**, 0.109 g, 0.1 mmol), $Pd(PPh_3)_2Cl_2$ (1.7 mg, 0.025 mmol), toluene (5 mL) were added. Then the tube was sealed and refilled with argon. Reaction tube was put into microwave reactor and heated to 180 °C for 40 min. After cooling to rt, the reaction mixture was poured into 100 mL of methanol containing 2 mL of hydrochloric acid (12 M) and stirred for 5 h. Then the precipitate was subjected to sequential Soxhlet extraction with methanol and hexane to remove low molecular weight fractions. The residue was extracted with chloroform, precipitated in 100 mL of methanol to yield a dark blue solid (99.7 mg, 91%). ^1H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2) δ 0.87 (t, J = 6.7 Hz, 12H), 1.25–1.36 (m, 64H), 1.81 (br, 2H), 2.84 (d, J = 6.7 Hz, 4H), 6.97 (br, 4H), 7.16 (d, J = 4.0 Hz, 2H), 7.20 (d, J = 4.0 Hz, 2H), 7.36 (s, 2H), 7.38 (d, J = 6.9 Hz, 2H), 7.69 (d, J = 6.9 Hz, 2H); Anal. Calcd for $(C_{72}H_{98}S_4)_n$: C, 79.21; H, 9.05%. Found: C, 79.20; H, 8.93%. The solubility of PDTDBP2T-OD was not sufficient for measuring ^{13}C NMR spectra.

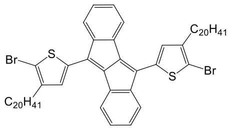
5,10-Bis(4-icosylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (6b)



Lithium diisopropylamide (LDA) solution freshly prepared by adding *n*-butyllithium solution (1.61 M hexane solution, 4.0 mL, 6.44 mmol) to diisopropylamine (1.00 mL, 7.08 mmol) in dry THF (28 mL) under argon atmosphere was added to a solution of 3-icosylthiophene (7.29 g, 20 mmol) and 4b,5,9b,10-tetrahydrodibenzo[*a*,*e*]pentalene-5,10-dione (**5**) (1.17 g, 5 mmol) in THF (9 mL) at 25 °C within 15 min. The reaction mixture was stirred for 3 h at rt and then poured into ice containing hydrochloric acid (12 M).The resulting solution was extracted with ethyl acetate (30 mL × 2). The combined extracts were concentrated in vacuo, and the residue was dissolved in methanol

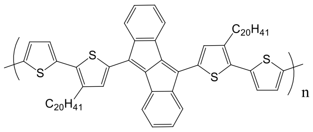
(100 mL). To the solution was added hydrochloric acid (2 M, 2.5 mL), and the mixture was refluxed gently for 3 h, and during this treatment, dark brown solid was separated out. The crude solid was collected by filtration and recrystallization from chloroform-methanol to afford 5,10-bis(4-icosylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (**6b**, 1.48 g, 32% yield) as a brown solid. Mp 88–89 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.2 Hz, 6H), 1.25 (s, 68H), 1.69 (q, *J* = 7.2 Hz, 4H), 2.69 (t, *J* = 7.2 Hz, 4H), 6.92 (t, *J* = 7.4 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 2H), 7.09 (s, 2H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.34 (s, 2H), 7.64 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.8, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 30.6, 30.7, 32.1, 122.1, 122.2, 123.0, 127.8, 127.9, 130.2, 133.4, 134.9, 135.1, 142.8, 144.1, 149.0; HRMS (APCI): Calcd for $C_{64}H_{94}S_2$: 926.67915 [M^+]. Found:926.67700.

5,10-Bis(5-bromo-4-icosylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (3b)



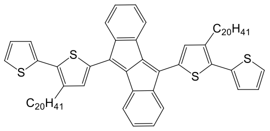
5,10-Bis(4-icosylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (**6b**, 1.09 g, 1.0 mmol) and *N*-bromosuccinimide (0.378 g, 2.1 mmol) was dissolved in chloroform (100 mL). The mixture was stirred for 3 h at rt. After evaporation of the solvent, the residue was purified by column chromatography on silica gel eluted with dichloromethane / hexane (1:1, v/v) to give 5,10-bis(5-bromo-4-icosylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (**3b**, 0.683 g, 63% yield) as brown solid. Mp 97–98°C ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.6 Hz, 6H), 1.25 (s, 68H), 1.65 (q, *J* = 7.6 Hz, 4H), 2.64 (t, *J* = 7.6 Hz, 4H), 6.92 (t, *J* = 7.4 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 2H), 7.18 (s, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.8, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 30.1, 30.2, 30.7, 111.4, 122.3, 122.8, 128.1, 128.2, 129.9, 132.6, 134.6, 143.0, 143.1, 148.6; HRMS (APCI): Calcd for $C_{64}H_{92}Br_2S_2$: 1082.50017 [M^+]. Found: 1082.49866.

PDTDBP2T-C20



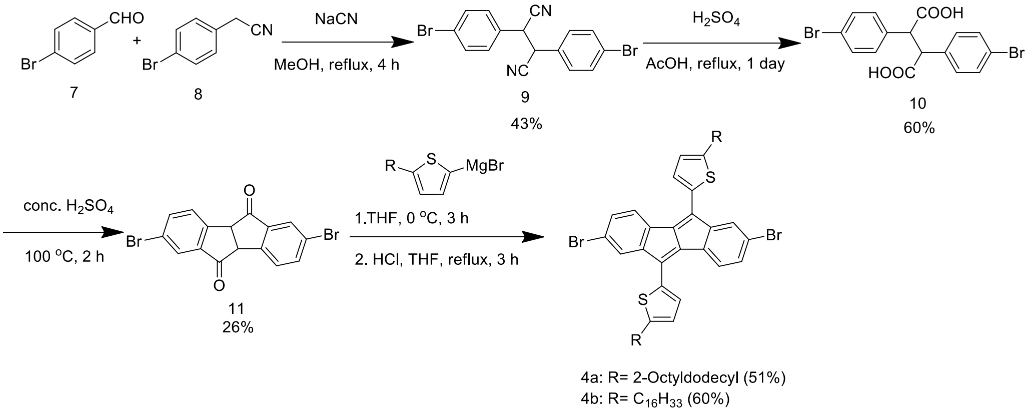
To a 2–5 mL microwave pressurized vial equipped with a stirring bar, 5,10-bis(5-bromo-4-icosylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (**3b**, 0.109 g, 0.10 mmol), $Pd(PPh_3)_2Cl_2$ (1.7 mg, 0.025 mmol), toluene (5 mL) were added. Then the tube was sealed and refilled with argon. Reaction tube was put into microwave reactor and heated to 180 °C for 40 min. After cooling to rt, the reaction mixture was poured into 100 mL of methanol containing 2 mL of hydrochloric acid (12 M) and stirred for 5 h. The precipitate was subjected to sequential Soxhlet extraction with methanol and hexane to remove low molecular weight fractions. The residue was extracted with chloroform, precipitated in 100 mL of methanol yield a dark blue solid (97.1 mg, 89%). ^1H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2) δ 0.91 (t, J = 6.9 Hz, 6H), 1.30–1.51 (m, 68H), 1.82 (br, 4H), 2.94 (br, 4H), 7.02 (br, 4H), 7.21 (br, 2H), 7.25 (br, 2H), 7.41–7.44 (m, 4H), 7.72 (d, J = 6.9 Hz, 2H); Anal. Calcd for $(C_{72}H_{98}S_4)_n$: C, 79.21; H, 9.05%. Found C, 79.15; H, 8.77%: The solubility of compound PDTDBP2T-C20 was not sufficient for measuring ^{13}C NMR spectra.

5,10-Bis[4-icosyl-5-(2-thienyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (1b)



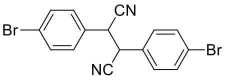
hTo a 2–5 mL microwave pressurized vial equipped with a stirring bar, 5,10-bis(5-bromo-4-icosylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (**3b**, 0.109 g, 0.10 mmol), $Pd(PPh_3)_2Cl_2$ (1.7 mg, 0.025 mmol), toluene (5 mL) were added. Then the tube was sealed and refilled with argon. Reaction tube was put into microwave reactor and heated to 180 °C for 40 min. After cooling to rt, the reaction mixture was poured into 100 mL of methanol containing hydrochloric acid (12 M, 2 mL) and stirred for 5 h. The crude product was precipitated by dilution with water and recrystallization from chloroform-methanol to afford 5,10-bis[4-icosyl-5-(2-thienyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (**1b**, 0.971 g, 89% yield) as a reddish brown solid. Mp 87–88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.8 Hz, 6H), 1.25–1.28 (m, 68H), 1.72 (quin, *J* = 7.8 Hz, 4H), 2.84 (t, *J* = 7.8 Hz, 4H), 6.95 (t, *J* = 7.4 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 2H), 7.11 (t, *J* = 3.7 Hz, 2H), 7.22 (d, *J* = 3.7 Hz, 2H), 7.35–7.39 (m, 6H), 7.70 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.8, 29.51, 29.53, 29.6, 29.7, 29.80, 29.81, 29.83, 29.84, 29.9, 30.5, 31.8, 32.1, 120.8, 122.5, 123.0, 124.6, 125.0, 128.1, 129.1, 132.9, 134.0, 142.6, 144.8, 148.8, 149.7; HRMS (APCI): Calcd for $C_{72}H_{98}S_2$: 1090.65459 [M^+]. Found: 1090.65161.

Synthesis of *i*PDTDBP2Ts



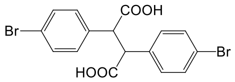
Scheme S2. Synthesis of the monomer units of *i*PDTDBP2T.

2,3-Bis(4-bromophenyl)succinonitrile (9)



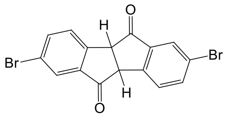
Sodium cyanide (53.5 g, 1.09 mol) and distilled water (85 mL) was added in a three-necked flask, and the mixture was warmed with stirring for about 15 minutes while the sodium cyanide was dissolved. Then methanol (340 mL) was added, and the mixture was rapidly heated to gentle reflux. To the mixture was added 4-bromobenzylnitrile (**8**) (70.9 g, 0.361 mol) in one portion, and then 4-bromobenzaldehyde (**7**, 80.0 g, 0.432 mol) and additional 4-bromobenzylnitrile (**8**, 44.0 g, 0.224 mol) were added in each three portion during 30 min. During the addition, the reaction mixture turned into green from yellow in color, and was gently refluxed for 30 min. After cooling to rt, a crude product was precipitated from solution, collected by filtration, washed successively with 75% aqueous methanol, water, ether, and dried in air overnight. Recrystallization from dichloromethane-methanol gave 2,3-bis(4-bromophenyl)succinonitrile (**9**, 72.8 g, 0.187 mol, 43% yield) as a white solid. Mp 236–237 °C (melt with decomposition); IR (KBr) ν = 2246 cm^{-1} (C≡N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 (s, 2H), δ 7.08 (d, *J* = 8.4 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.7, 116.5, 124.4, 129.4, 130.1, 132.8; EI-MS (70 eV) = 388 (M^+); HRMS (APCI): Calcd for $C_{16}H_{13}N_2Br_2Cl$: 422.89047 [MCl^-]. Found: 422.89099.

2,3-Bis(4-bromophenyl)succinic acid (10)



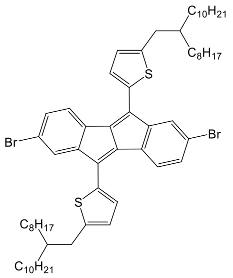
A suspension of 2,3-bis(4-bromophenyl)succinonitrile (**9**, 39 g, 0.10 mol) in a mixture of sulfuric acid (98%, 175 mL), water (200 mL), and acetic acid (250 mL) was refluxed for 24 h. The reaction mixture was cooled, diluted with water (500 mL) to precipitate 2,3-bis(4-bromophenyl)succinic acid (**10**) as a white solid, which was collected by filtration. The product was then dissolved in aqueous potassium hydroxide solution (10 wt%, 500 mL), and the solution was filtered. The filtrate was neutralized by addition of hydrochloric acid (6M, ca. 500 mL) to precipitate **10** (25.6 g, 0.060 mol, 60%) as a white solid. Mp 213–214 °C; IR (KBr) ν= 1707 cm^{-1} (C=O); ^{1}H NMR(500 MHz, $CDCl_3$) δ 4.19 (s, 2H), 6.97 (d, *J* = 8.3 Hz, 4H), 7.32 (d, *J* = 8.3 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 54.2, 122.6, 130.0, 132.3, 133.1, 181.8; EI-MS (70 eV) *m/z* = 428 (M^+); HRMS (APCI): Calcd for $C_{16}H_{13}O_4Br_2$: 426.91751 [MH^+]. Found: 426.91623.

2,7-Dibromo-4b,5,9b,10-tetrahydrodibenzo[*a,e*]pentalene-5,10-dione (11)



2,3-Bis(4-bromophenyl)succinic acid (**10**, 25 g, 58.4 mmol) was slowly added to sulfuric acid (98%, 370 mL) at rt. The mixture was heated to 100 °C and stirring for 2 h. The resulting light brown solution was cooled and poured onto crashed ice (ca. 500 g) to precipitate a white solid, which was collected, washed with water, and dried in air. The crude product was purified by recrystallization from THF-hexane to afford 2,7-dibromo-4b,5,9b,10-tetrahydrodibenzo[*a*,*e*]pentalene-5,10-dione (**11**) (5.95 g, 26%) as a white solid. Mp 247–248 °C; IR (KBr) ν = 1722 cm^{-1} (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (s, 2H), 7.79 (m, 4H), 7.84 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3, 123.9, 127.9, 128.2, 136.6, 138.9, 148.0, 199.6; EI-MS (70 eV) *m/z* = 392 (M^+); HRMS (APCI): Calcd for $C_{16}H_8O_2Br_2$: 389.88856 [M^+]. Found: 389.88885.

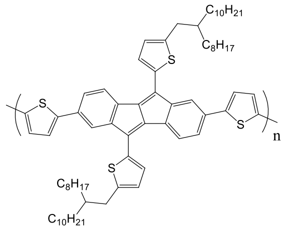
2,7-Dibromo-5,10-bis[5-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (4a)



Under an argon atmosphere, a solution of 2-bromo-5-(2-octyldodecyl)thiophene (2.8 g, 7.6 mmol) dissolved in THF (10 mL) was slowly added to a refluxing mixture of magnesium (0.615 g, 25 mmol) and catalytic amount of iodine in THF (20 mL). The reaction mixture was refluxed for 1 h to complete generation of the corresponding thienyl magnesium bromide. The Grignard reagent was then added dropwise to a solution of 2,7-dibromo-4b,5,9b,10-tetrahydrodibenzo[*a*,*e*]pentalene-5,10-dione (**11**) (0.823 g, 2.1 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred for 3 h at rt, then poured into ice containing hydrochloric acid, extracted with ethyl acetate (30 mL × 2). The combined extracts were dried and concentrated, and the resulting residue was dissolved in methanol (100 mL). To the solution was added a hydrochloric acid solution (2 M, 2.5 mL) and the mixture was refluxed gently for 3 h. The crude product was precipitated by dilution with water (50 mL), collected by filtration, and purified by recrystallization from chloroform-methanol (1:1, v/v) to afford 2,7-dibromo-5,10-bis[5-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (**4a**, 1.13 g, 51%) as a brown solid. Mp 61–62 °C; ^{1}H NMR (500MHz, $CDCl_3$) δ 0.86 (t, *J* = 8.0 Hz, 6H), 0.87 (t, *J* = 6.7 Hz, 6H), 1.26–1.33 (m, 64H), 1.70 (sept, *J* = 6.7 Hz, 2H), 2.83 (t, *J* = 6.7 Hz, 4H), 6.86 (d, *J* = 3.5 Hz, 2H), 7.07 (dd, *J* = 1.7 and 8.0 Hz, 2H), 7.30 (d, *J* = 3.5 Hz, 2H), 7.43 (d, *J* = 1.7 Hz, 2H), 7.50

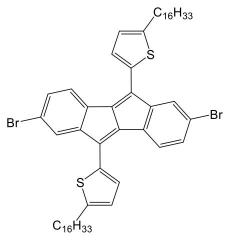
(d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.8, 26.80, 29.49, 29.52, 29.79, 29.81, 29.83, 30.12, 30.14, 32.07, 32.09, 33.45, 33.46, 24.9, 40.2, 121.8, 123.3, 126.2, 126.3, 129.2, 130.3, 132.3, 132.7, 133.4, 142.0, 147.9, 150.7; HRMS (APCI): Calcd for $C_{64}H_{92}Br_2S_2$: 1082.50017 [M^+]. Found: 1082.49854.

*i*PDTDBP2T-OD



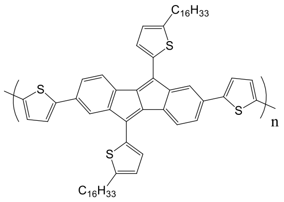
To a 2–5 mL microwave pressurized vial equipped with a stirring bar, 2,7-bibromo-5,10-bis[5-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (**4a**, 0.109 g, 0.10 mmol), $Pd(PPh_3)_2Cl_2$ (1.7 mg, 0.025 mmol), toluene (5 mL) were added. Then the tube was sealed and refilled with argon. The reaction tube was put into microwave reactor and heated to 180 °C for 40 min. After cooling to room temperature, the reaction mixture was poured into 100 mL of methanol containing 2 mL of hydrochloric acid (12 M) and stirred for 5 h. Then the precipitate was subjected to sequential Soxhlet extraction with methanol and hexane to remove low molecular weight fractions. The residue was extracted with chloroform, precipitated in 100 mL of methanol to afford a dark red solids (98.2 mg, 90%). ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-*d*$_2$) δ 0.93 (br, 6H), 1.35–1.48 (m, 64H), 1.84 (br, 2H), 2.96 (br, 4H), 6.97 (br, 2H), 7.17–7.25 (m, 6H), 7.45 (br, 2H), 7.64 (s, 2H), 7.70 (br, 2H); Anal. Calcd for $(C_{72}H_{98}S_4)_n$: C, 79.21; H, 9.05%. Found: C, 78.99; H, 8.92%. The solubility of ***i*PDTDBP2T-OD** was not sufficient for measuring ^{13}C NMR spectra.

2,7-Dibromo-5,10-bis(5-hexadecylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (4b)



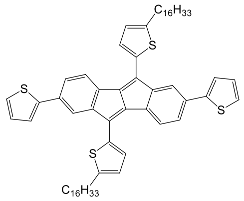
Under argon atmosphere, 2-bromo-5-hexadecylthiophene (2.35 g, 7.6 mmol) in THF (10 mL) was slowly added to a refluxing mixture of magnesium (0.615 g, 25 mmol) and iodine (catalytic amount) in THF (20 mL). The reaction mixture was stirred at gentle reflux for 1 h. The Grignard reagent was then added dropwise to a solution of 2,7-dibromo-4b,5,9b,10-tetrahydrodibenzo[*a*,*e*]pentalene-5,10-dione (**11**) (0.823 g, 2.1 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred for 3 h at rt, then poured into ice containing hydrochloric acid, extracted with ethyl acetate (30 mL × 2). The combined extracts were dried and concentrated, and the resulting residue was dissolved in methanol (100 mL). To the solution was added a hydrochloric acid solution (2M, 2.5 mL) and the mixture was refluxed gently for 3 h. The crude product was precipitated by dilution with water (50 mL), collected by filtration, and purified by recrystallization from chloroform-methanol (1:1, v/v) to afford 2,7-dibromo-5,10-bis(5-hexadecylthienyl)dibenzo[*a*,*e*]pentalene (**4b**) (1.21 g, 60%) as a brown solid: Mp 109–110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.7 Hz, 6H), 1.26–1.43 (m, 52H), 1.75 (t, *J* = 7.7 Hz, 4H), 2.90 (t, *J* = 7.7 Hz, 4H), 6.89 (d, *J* = 3.5 Hz, 2H), 7.07 (dd, *J* = 1.7 and 8.0 Hz, 2H), 7.29 (d, *J* = 3.5 Hz, 2H), 7.43 (d, *J* = 1.7 Hz, 2H) 7.50 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125MHz, $CDCl_3$) δ 14.3, 22.83, 29.3, 29.5, 29.7, 29.79, 29.80, 29.82, 29.84, 30.5, 31.7, 32.1, 121.9, 123.3, 125.3, 126.2, 129.3, 130.3, 132.1, 133.4, 142.0, 149.3, 150.7; HRMS(APCI): Calcd for $C_{56}H_{76}Br_2S_2$: 970.37497, [M$^+$]. Found: 970.37408.

***i*PDTDBP2T-C16**



To a 2–5 mL microwave pressurized vial equipped with a stirring bar, 2,7-dibromo-5,10-bis(5-hexadecylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (**4b**) (0.097 g, 0.10 mmol), $Pd(PPh_3)_2Cl_2$ (1.7 mg, 0.025 mmol), toluene (5 mL) were added. Then the tube was sealed and refilled with argon, put into a microwave reactor, and heated to 180 °C for 40 min. After cooling to rt, the reaction mixture was poured into 100 mL of methanol containing 2 mL of hydrochloric acid and stirred for 5 h. Then the precipitate was subjected to sequential Soxhlet extraction with methanol, hexane and chloroform to remove low molecular weight fractions. The residue was extracted with PhCl, precipitated in 100 mL of methanol to afford a dark red solid (39.2 mg, 42%). ^{1}H NMR (400MHz, 1,1,2,2-Tetrachloroethane-d_2) δ 0.93 (br, 6H), 1.35–1.48 (m, 64H), 1.84 (br, 2H), 2.96 (br, 4H), 6.97 (br, 2H), 7.17–7.25 (m, 6H), δ 7.45 (br, 2H), δ 7.64 (br, 2H), δ 7.70 (br, 2H); Anal. Calcd for $(C_{64}H_{82}S_4)_n$: C, 78.47; H, 8.44%. Found C, 78.36; H, 8.63%. The solubility of *i*PDTDBP2T-C16 was not sufficient for measuring ^{13}C NMR spectra.

5,10-Bis(5-hexadecylthiophen-2-yl)-2,7-di(2-thienyl)dibenzo[*a*,*e*]pentalene (2b)



To a 2–5 mL microwave pressurized vial equipped with a stirring bar, 2,7-dibromo-5,10-bis(5-hexadecylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (**4b**, 0.109 g, 0.10 mmol), $Pd(PPh_3)_2Cl_2$ (1.7 mg, 0.025 mmol), toluene (5 mL) were added. Then the tube was sealed and refilled with argon, put into a microwave reactor, and heated to 180 °C for 40 min. After cooling to rt, the reaction mixture was poured into 100 mL of methanol containing 2 mL of hydrochloric acid (12 M) and stirred for 5 h. The crude product was precipitated by dilution with water (10 mL), and recrystallization from chloroform-methanol to afford **2b** (0.083 g, 85% yield) as a brown solid. Mp 114–115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, J = 7.6 Hz, 6H), 1.25–1.45 (m, 52H), 1.72 (quin, J = 7.6 Hz, 4H), 2.92 (t, J = 7.6 Hz, 4H), 6.92 (d, J = 3.4 Hz, 2H), 7.06 (t, J = 3.5 Hz,2H), 7.20 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 3.4 Hz, 2H), 7.29 (d, J = 3.5 Hz, 2H), 7.38 (d, J = 3.5 Hz, 2H), 7.61 (s, 2H), 7.68 (d, J = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.3, 22.8, 29.4, 29.5, 29.6, 29.7, 29.8, 29.81, 29.82, 29.85, 30.8, 32.1, 122.3, 123.0, 126.1, 127.7, 127.8, 127.9, 132.2, 132.8, 133.0, 134.9, 135.8, 140.3, 142.8, 148.7; HRMS(APCI): Calcd for $C_{72}H_{98}S_2$: 978.52939, [M$^+$]. Found: 978.52771.

1-3. OFET Fabrication and Measurement.

OFET devices were fabricated in a "top-contact" configuration on heavily doped n$^+$-Si (100) wafers with 200 nm-thick thermally grown SiO_2 (Ci = 17.3 nF/cm^2). The Si/SiO_2 substrates were carefully cleaned and then treated with 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane (FDTS) vapor in a closed desicaator to form a self-assembled monolayer (SAM). Polymer layers were then spin-coated from warm (~120 °C) chlorobenzene solution (3 g/L) with a spinning rate of 2500 rpm for 45 sec. On top of the polymer thin films, Au drain and source electrodes (thickness 80 nm) were deposited in vacuum through a shadow mask, where the drain-source channel length (L) and width (W) are 50 µm and ca. 1.5 mm, respectively. Current-voltage characteristics of the OFET devices were measured at rt in air with a Keithly 4200-SCS semiconductor characterization system. Field-effect mobilities were calculated in the saturation regime (V_d = –60 V) of the I_d using the following equation,

$$I_d = (WC_i/2L)\ \mu\ (V_g - V_{th})^2$$

where C_i is the capacitance of the SiO_2 dielectric, I_d is the source–drain current, and V_g, and V_th are the gate and threshold voltages, respectively. Current on/off ratios ($I_\mathrm{on}/I_\mathrm{off}$) were determined from the minimum current at around V_g = 0–20 V (I_off) and the current at V_g = –60 V (I_on).

1-4. DFT and NICS calculations

Geometry optimization and normal mode calculations and nucleus-independent chemical sifts (NICS) calculations of compound **1** and **2** were performed at the B3LYP/6-31G(d) level using the Gaussian03 program package. [S2, S3]

2. AFM images of thin films of DBP-based polymers

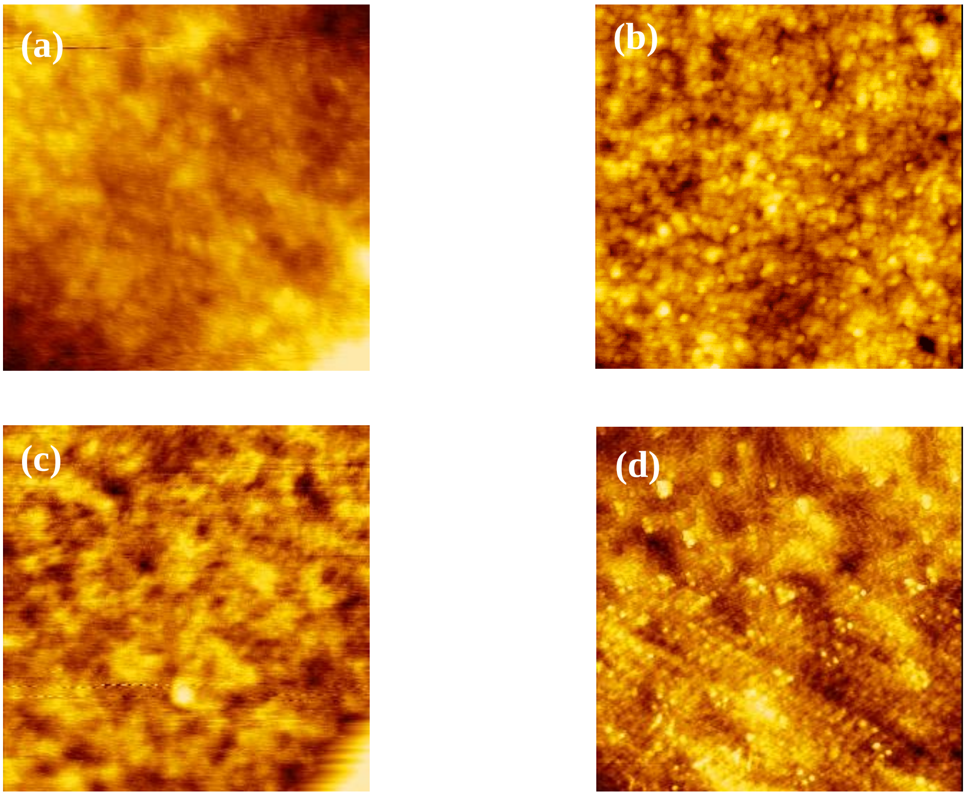


Figure S1. AFM images (2 × 2 μm) of spin-coated thin films of (a) PDTDBP2T-OD, (b) PDTDBP2T-C20, (c) *i*PDTDBP2T-OD, and (d) *i*PDTDBP2T-C16 on the Si/SiO$_2$ substrate.

3. Logarithmic absorption spectra of 1b and 2b

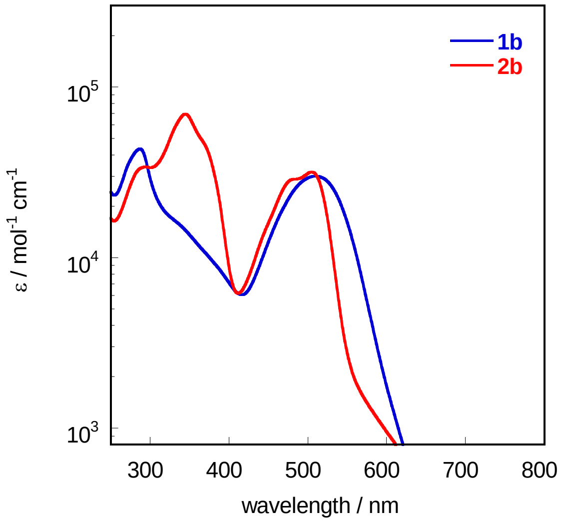


Figure S2. Logarithmic absorption spectra of **1b** and **2b**.

4. TD-DFT calculations of 1a and 2a

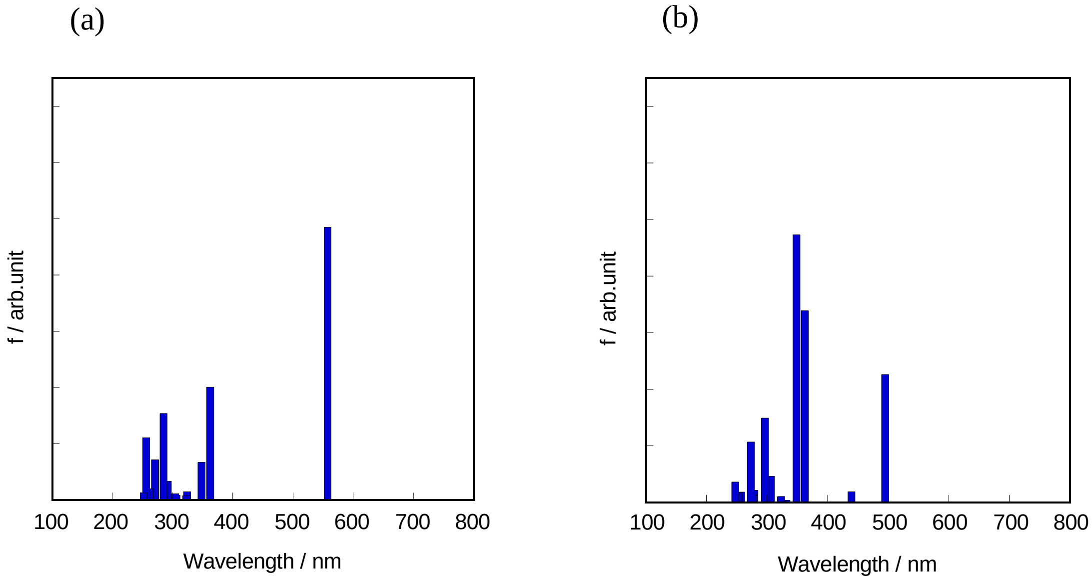


Figure S3. TD-DFT calculated electro spectra of **1a** (a) and **2a** (b) (B3LYP/6-31G*).

Table S1. TD-DFT calculated vertical excitation energy (in nm) and corresponding oscillator strength (f, in a.u.) of **1a** (a) and **2a** (b) (B3LYP/6-31G*).

		1a		
#Transition	λ / nm	f	Main monoexcitations	Weight / %
1	621.0	0.0000	HOMO−1→LUMO	64
2	557.6	0.9695	HOMO→LUMO	63
3	443.2	0.0000	HOMO−2→LUMO	66
4	410.6	0.0000	HOMO−3→LUMO	66
5	368.1	0.0000	HOMO→LUMO+2	64
6	362.5	0.4009	HOMO−1→LUMO+1	61
7	348.1	0.1340	HOMO→LUMO+2	59
8	340.1	0.0000	HOMO−1→LUMO+2	68
9	324.8	0.0000	HOMO−6→LUMO	60
10	324.0	0.0299	HOMO−4→LUMO	62
11	322.6	0.0148	HOMO−7→LUMO	56
12	322.6	0.0000	HOMO−5→LUMO	55
13	311.7	0.0000	HOMO→LUMO+3	69
14	306.7	0.0163	HOMO−8→LUMO	53

15	306.2	0.0000	HOMO−9→LUMO	62
16	304.5	0.0227	HOMO−2→LUMO+1	54
17	291.8	0.0671	HOMO−10→LUMO	50
18	287.9	0.0000	HOMO−3→LUMO+1	62
19	284.7	0.3076	HOMO−1→LUMO+3	53
20	284.2	0.0000	HOMO−2→LUMO+2	64
21	276.4	0.0000	HOMO−11→LUMO	62
22	270.7	0.1429	HOMO−3→LUMO+2	58
23	261.9	0.0399	HOMO−1→LUMO+4	49
24	261.1	0.0000	HOMO→LUMO+5	57
25	256.4	0.1429	HOMO−3→LUMO+3	42
26	256.3	0.2212	HOMO→LUMO+6	37
27	256.0	0.0000	HOMO−1→LUMO+6	54
28	252.8	0.0000	HOMO→LUMO+10	40
29	252.3	0.0255	HOMO−12→LUMO	34
30	250.4	0.0000	HOMO→LUMO+9	54

2a

#Transition	λ / nm	f	Main monoexcitations	Weight / %
1	673.1	0.0000	HOMO→LUMO	67
2	495.0	0.4526	HOMO−1→LUMO	62
3	439.5	0.0379	HOMO−2→LUMO	69
4	370.3	0.0000	HOMO−3→LUMO	60
5	362.1	0.6787	HOMO−5→LUMO	48
6	361.2	0.0001	HOMO−4→LUMO	59
7	348.3	0.9465	HOMO−5→LUMO	45
			HOMO→LUMO+1	46
8	341.9	0.0001	HOMO−1→LUMO+1	67
9	332.6	0.0003	HOMO−6→LUMO	70
10	332.0	0.0071	HOMO−7→LUMO	68
11	324.1	0.0044	HOMO−8→LUMO	69
12	323.1	0.0205	HOMO−9→LUMO	69
13	309.2	0.0001	HOMO→LUMO+2	60
14	306.0	0.0934	HOMO→LUMO+3	68
15	303.5	0.0000	HOMO−9→LUMO	56
16	296.4	0.2978	HOMO−1→LUMO+2	64
17	292.4	0.0000	HOMO→LUMO+4	52
18	290.4	0.0001	HOMO−2→LUMO+1	54
19	279.6	0.0001	HOMO−2→LUMO+5	30

20	278.9	0.0428	HOMO−11→LUMO	59
21	277.7	0.0259	HOMO−1→LUMO+4	50
			HOMO→LUMO+5	39
22	273.1	0.2141	HOMO−11→LUMO	33
			HOMO−1→LUMO+4	34
			HOMO→LUMO+5	40
23	264.7	0.0001	HOMO−1→LUMO+5	56
24	256.8	0.0363	HOMO−3→LUMO+2	45
			HOMO−2→LUMO+3	46
25	253.2	0.0269	HOMO−4→LUMO+1	57
26	253.1	0.0005	HOMO−5→LUMO+1	45
27	252.2	0.0350	HOMO−3→LUMO+1	42
28	249.6	0.0002	HOMO−2→LUMO+2	59
29	247.3	0.0721	HOMO−12→LUMO	49
30	243.8	0.0023	HOMO→LUMO+6	54

5. TG and DSC curves of DBP derivatives

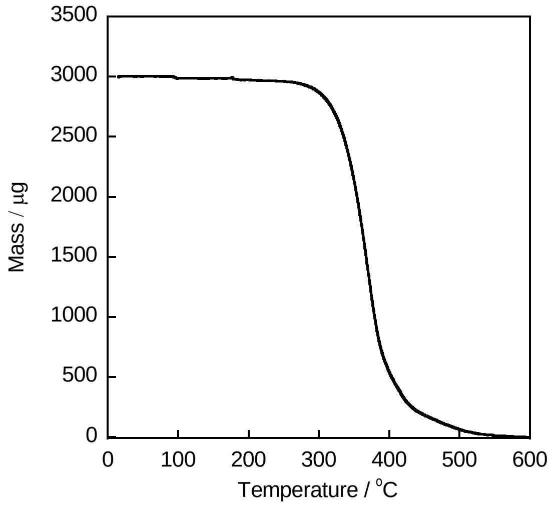


Figure S4. TG curves of 5,10-di(2-thienyl)dibenzo[*a*,*e*]pentalene.

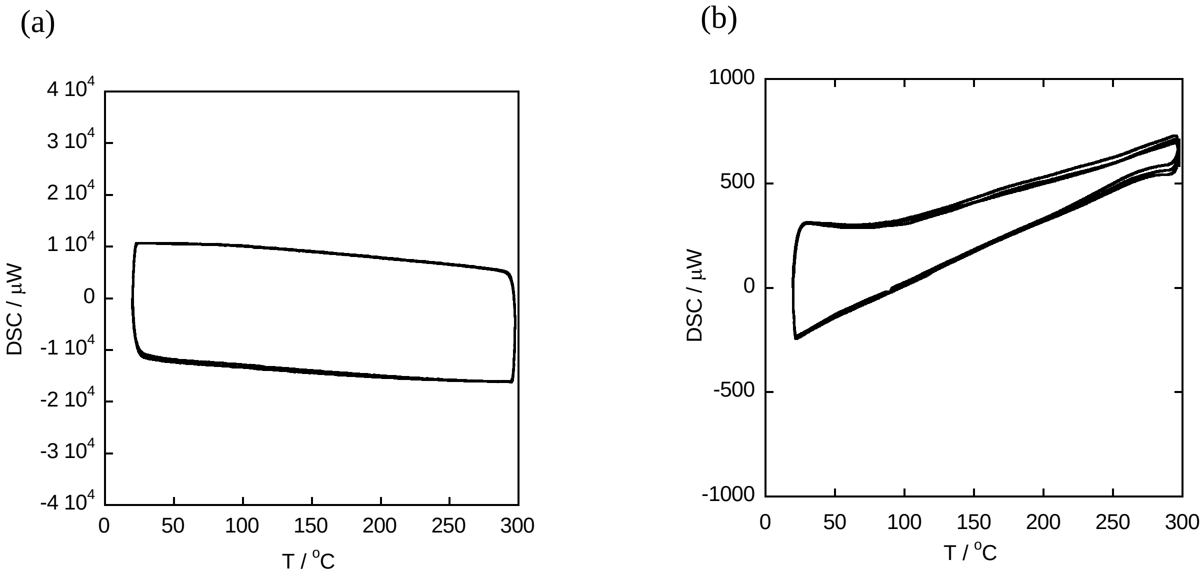


Figure S5. DSC curves of PDTDBP2T-OD (a) and *i*PDTDBP2T-OD (b).

6. Time dependent UV-vis absorption spectra

The photostability of the DTDBP derivatives were investigated by measuring time dependent UV-vis absorption spectra under ambient conditions and room light. There were no spectral changes in all absorption spectra.

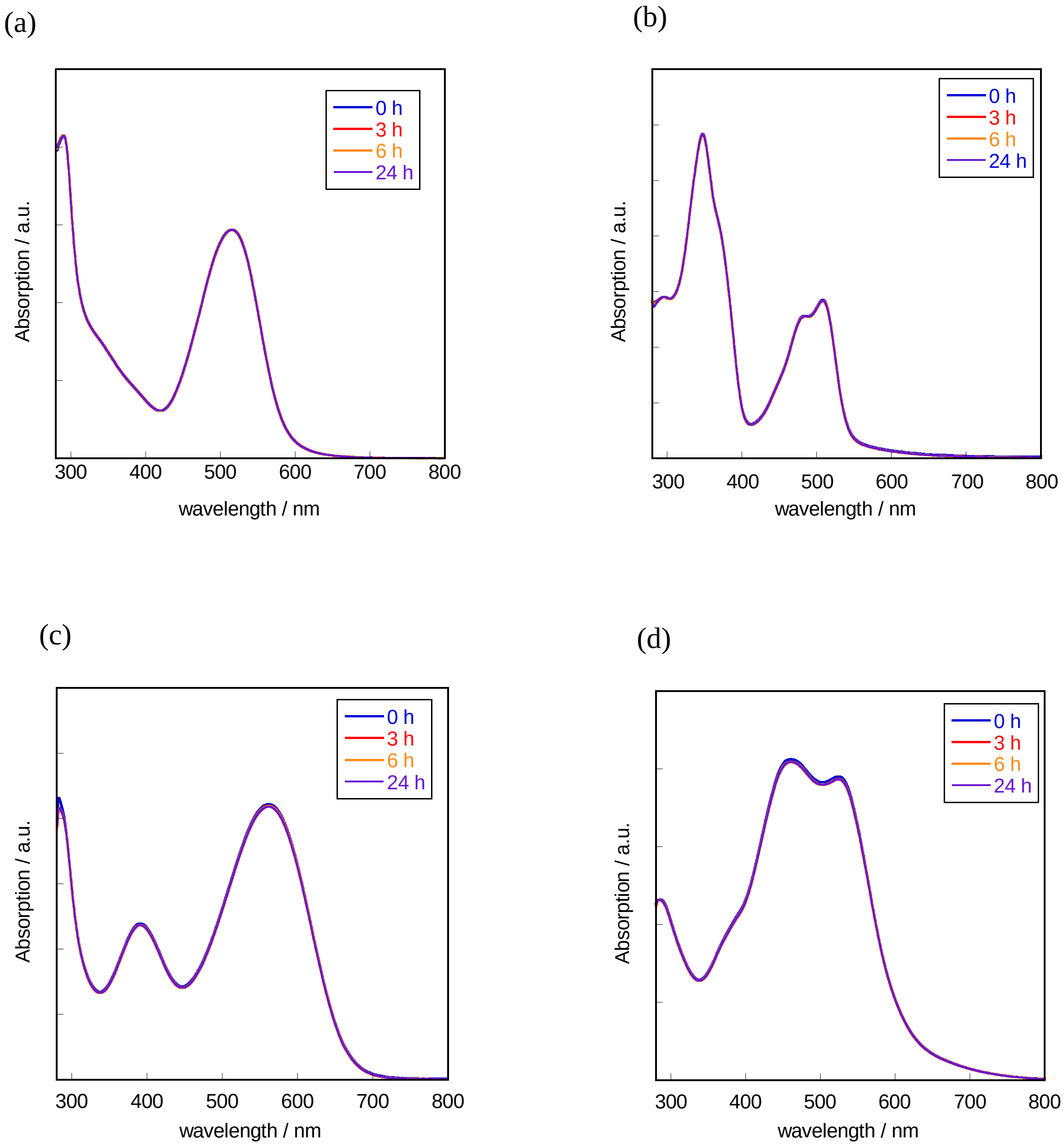


Figure S6. Time dependent UV-vis absorption spectra of **1b** (a), **2b** (b), PDTDBP2T-OD (c), and *i*PDTDBP2T-OD (d) in chlorobenzene solution with ambient condition under room light.

7. Cyclic voltammograms of repeat scans

We check electrochemical behavior of the DBP derivatives by repeated cyclic voltammetry. Repeated cycles of **1b** and **2b** gradually afforded new peaks in the voltamogram, indicating that electrochemical polymerization on the working electrode occurred via their vacant thiophene α-position (Figure S7). In fact, dark-colored insoluble material was deposited on the surface of the working electrode. In the case of PDTDBP2T-OD and *i*PDTDBP2T-OD, which have no vacant thiophene α-position, their repeated voltammograms show no change of oxidation peak in shape. On the other hand, emergence of new peaks at relatively high reduction potentials (Figure S8, PDTDBP2T-OD: -1.43 V vs Ag/AgCl, PDTDBP2T-OD: -1.34 V vs Ag/AgCl) were observed after negative scans. However, the same solution showed the original reduction process after wiping the working electrode, which indicates that the new peaks likely originate from the partially reduced DTDBP-based polymers adsorbed on the electrode.

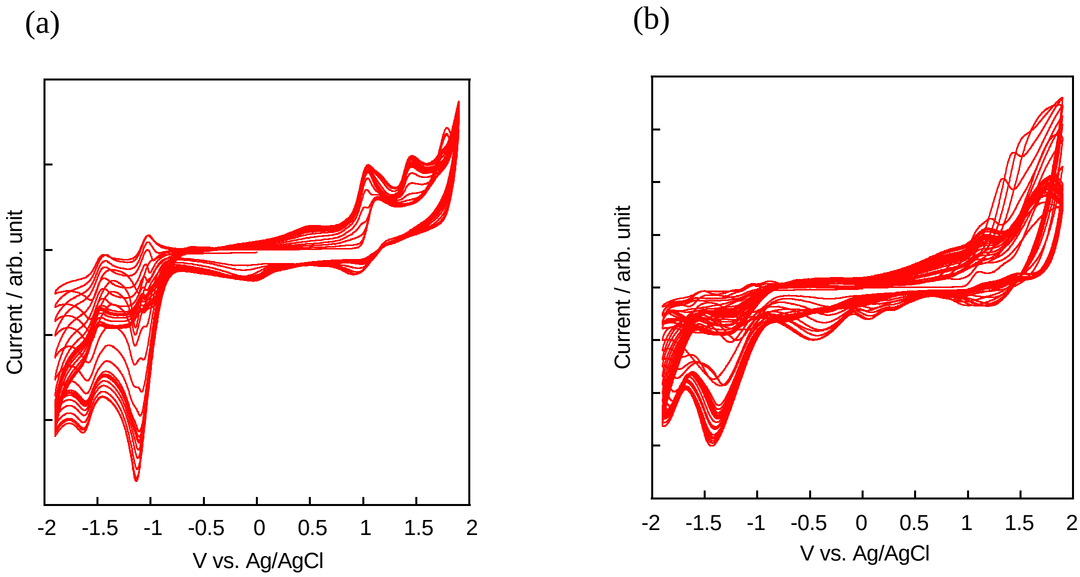


Figure S7. Cyclic voltammograms of repeat scans of **1b** (a) and **2b** (b) in dichloromethane solution (30 segments).

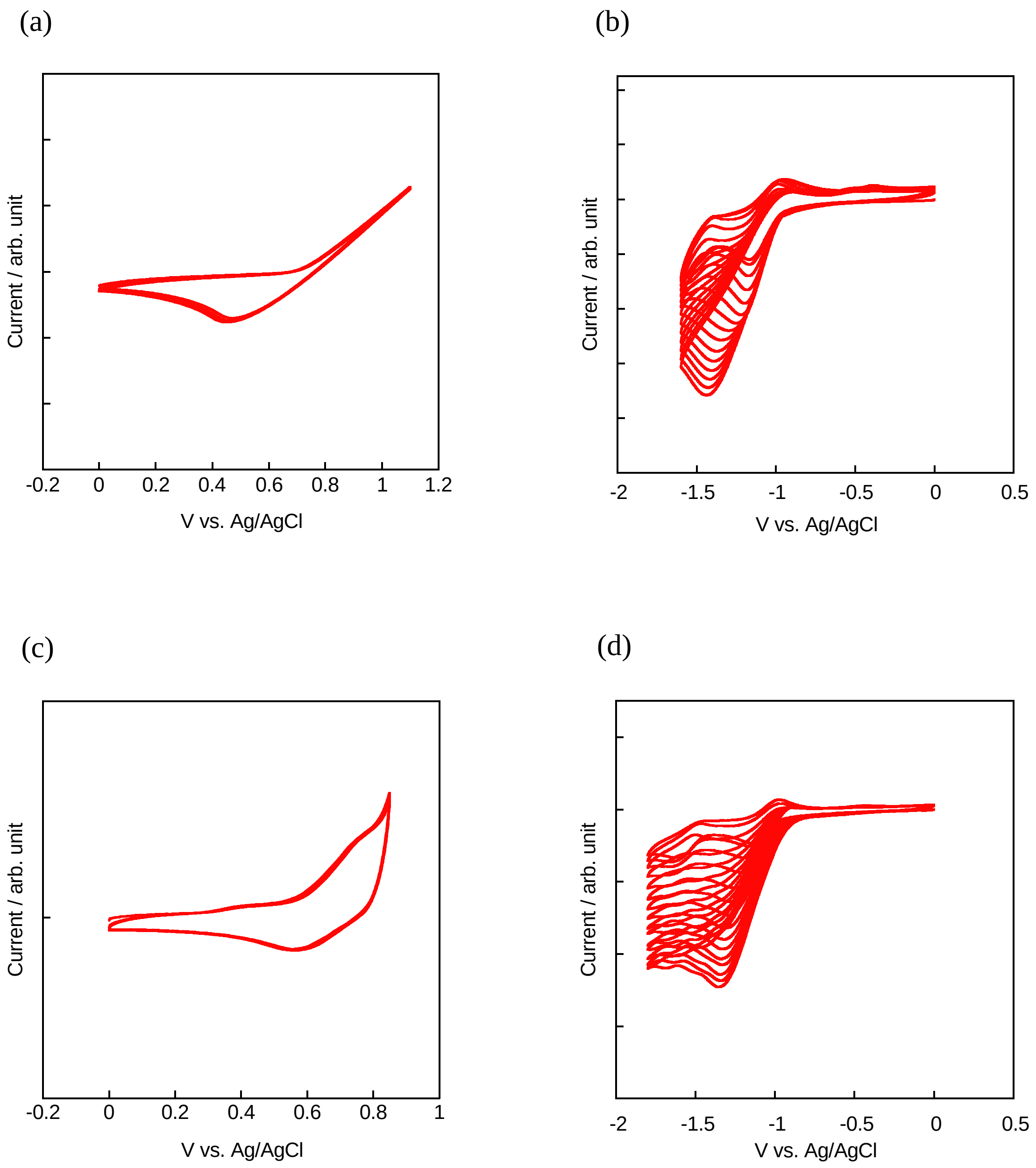


Figure S8. Cyclic voltammograms of repeat scans (chlorobenzene/benzonitrile solution, 30 segments) of PDTDBP2T-OD scanned between 0 to 1.1 V (a), and 0 to -1.6 V (b), of *i*PDTDBP2T-OD scanned between 0 to 0.85 V (c), and 0 to -1.8 V (d).

8. Fluorescence spectra of DTDBP-based polymers

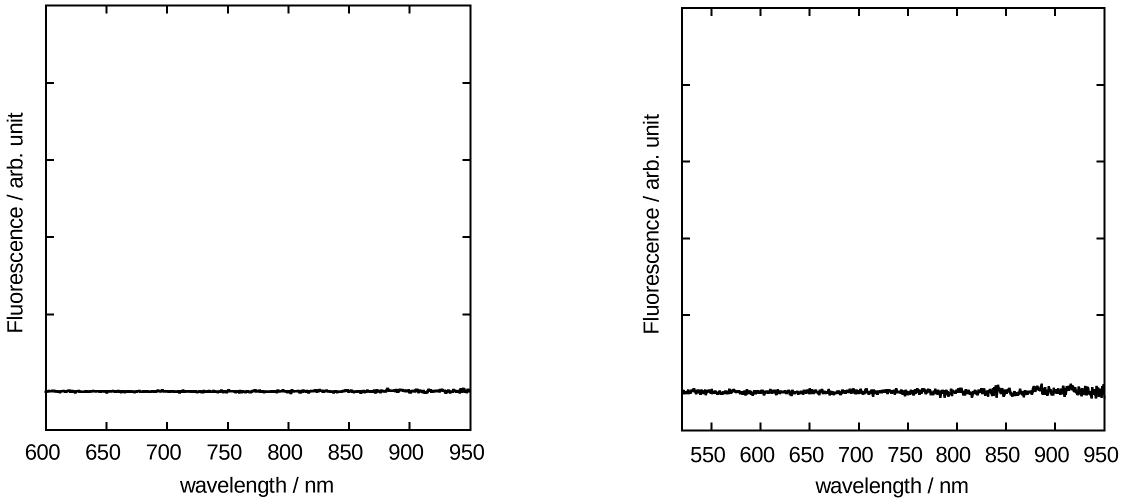


Figure S9. Fluorecence spectra of PDTDBP2T-OD (a) and *i*PDTDBP2T-OD (b) in chlorobenzene solution (λ_{Ex} = 580 and 500 nm, respectively).

9. Absorption spectra of PDTDBP2T-C20 and *i*PDTDBP2T-C16

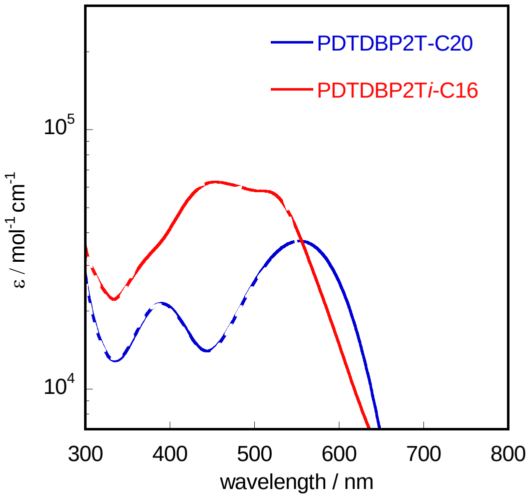


Figure S10. Absorption spectra of PDTDBP2T-C20 and *i*PDTDBP2T-C16 in hot chlorobenzen solution (100 °C).

10. References

S1. (a) Roser W, *Lieb. Ann*. **1888**, *247*, 153. (b) Mittal, R. S. D., Sothi, S. C. *Tetrahedron* **1973**, *29*, 1321.

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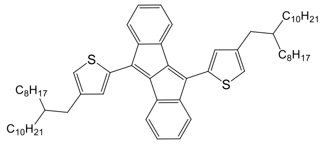
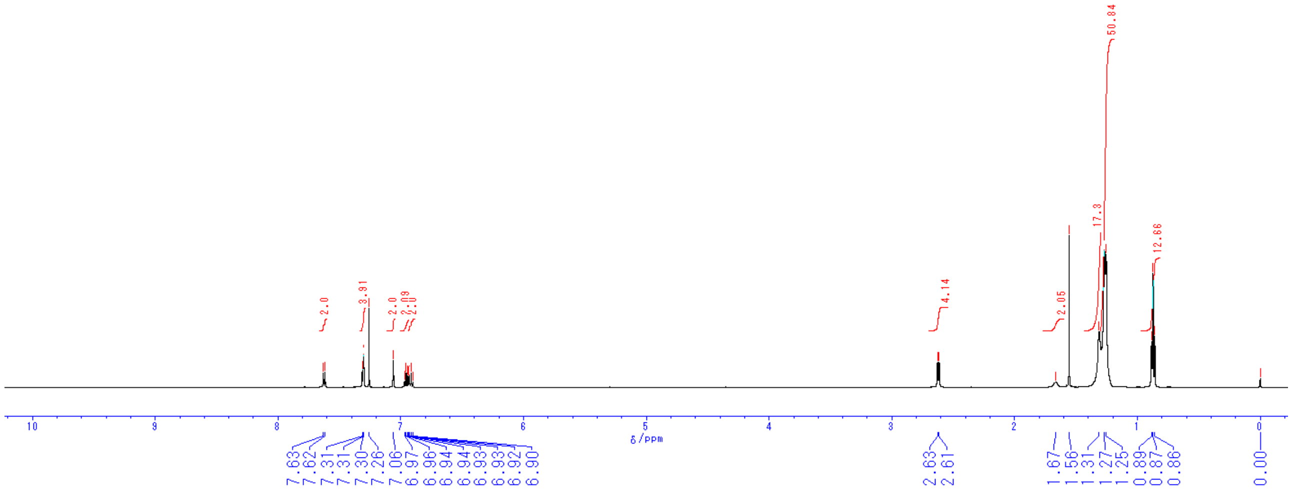
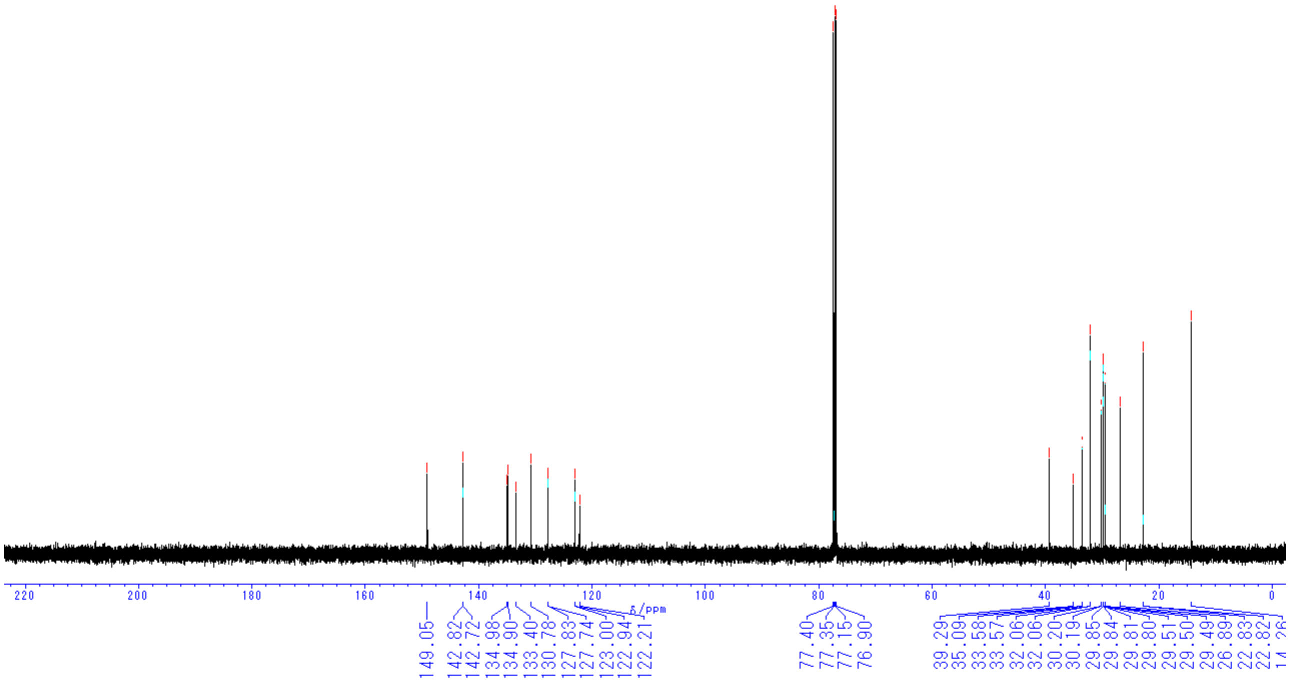
10. NMR spectra

5,10-Bis[4-(2-octyldodecyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (6a)







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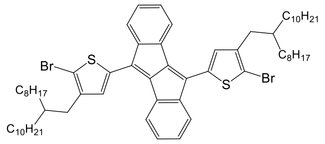
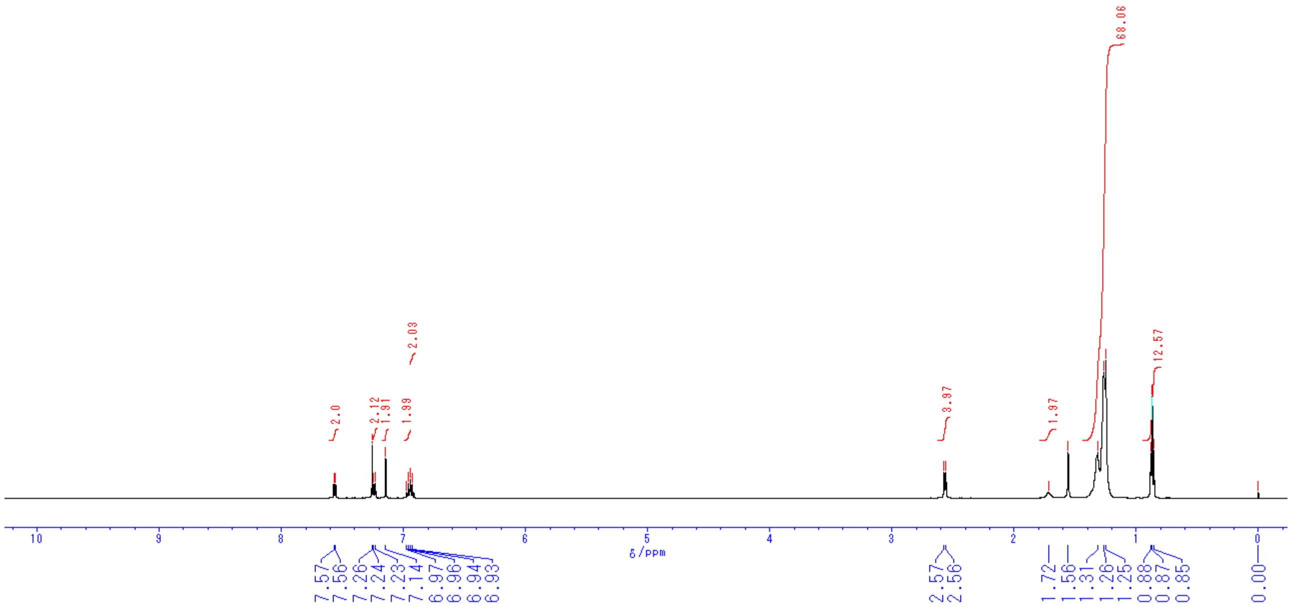
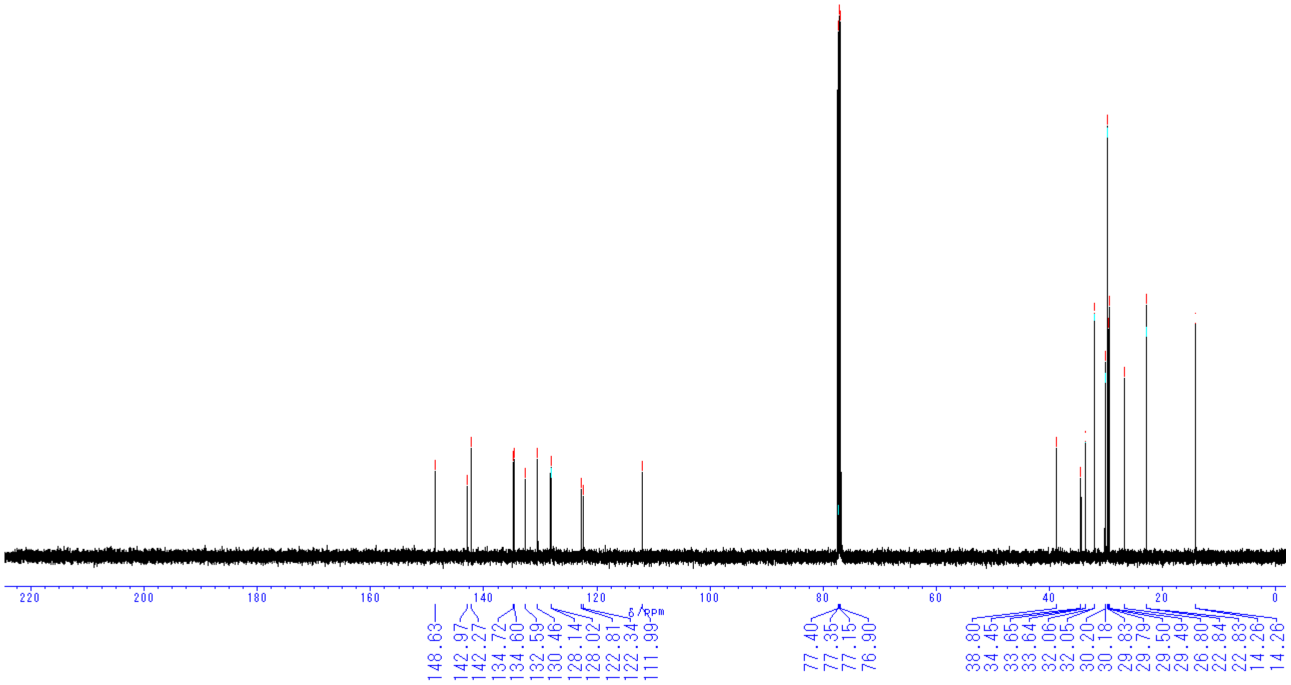
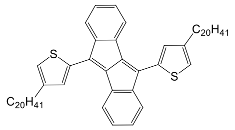
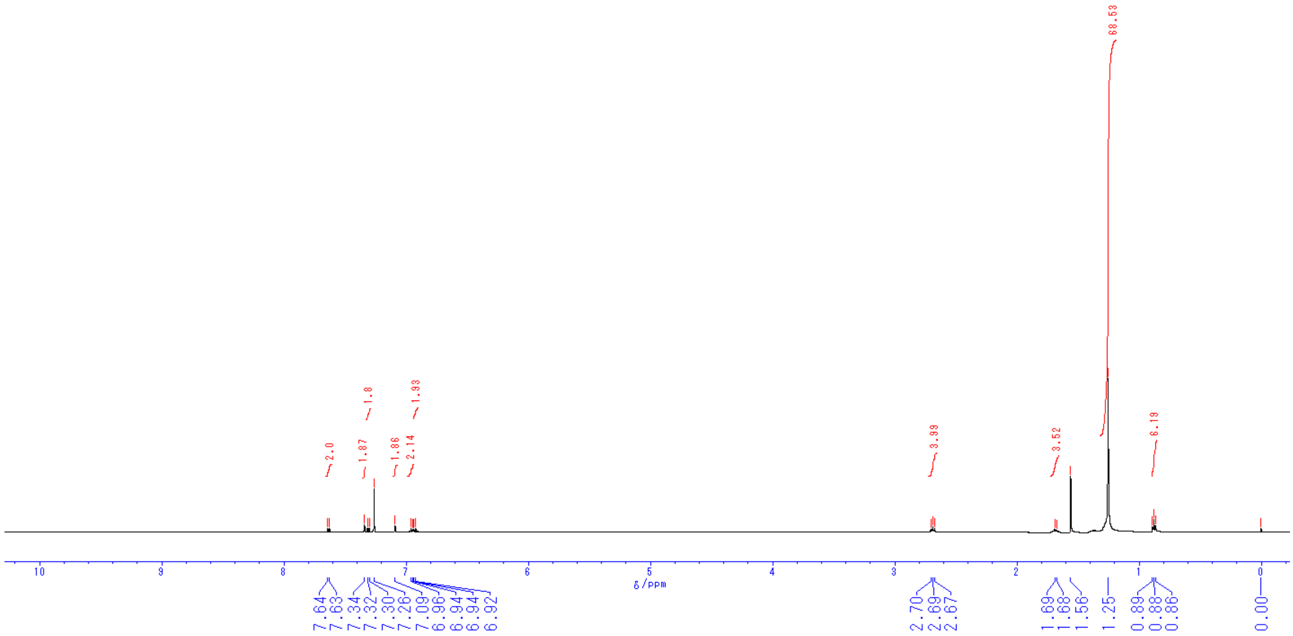


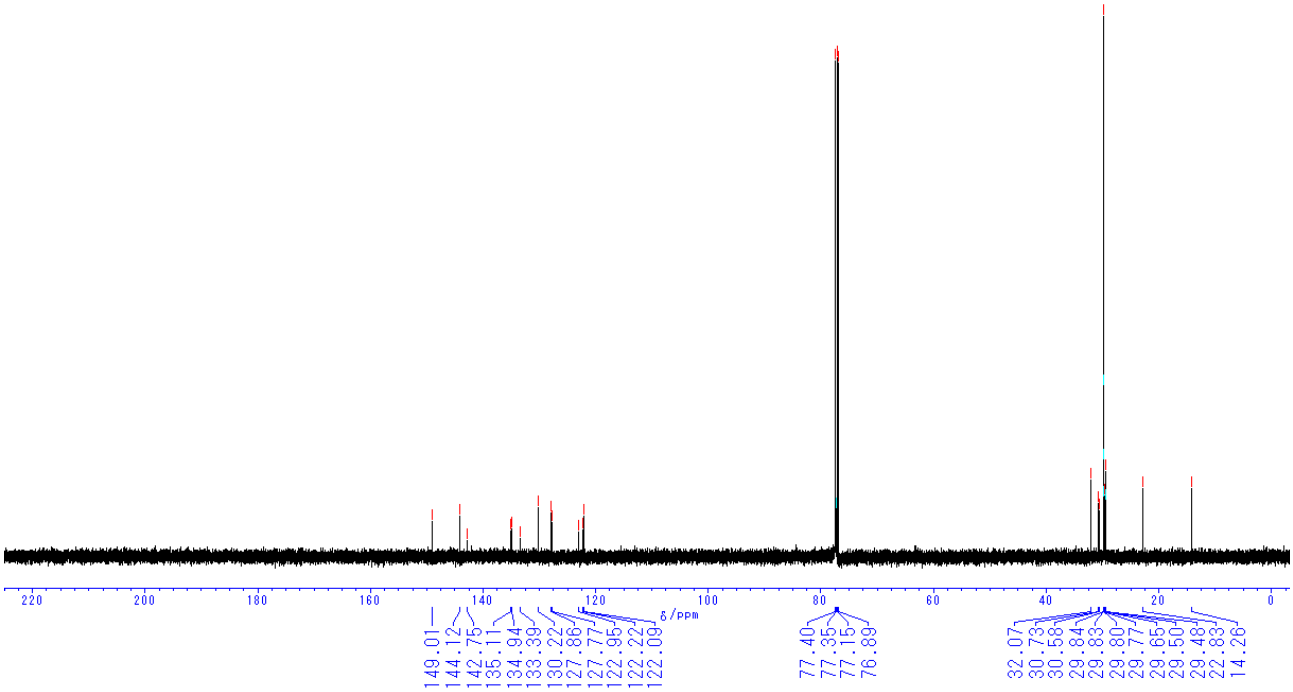




5,10-Bis(4-icosylthiophen-2-yl)dibenzo[*a*,*e*]pentalene (6b)







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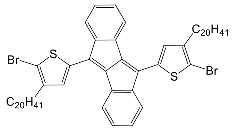

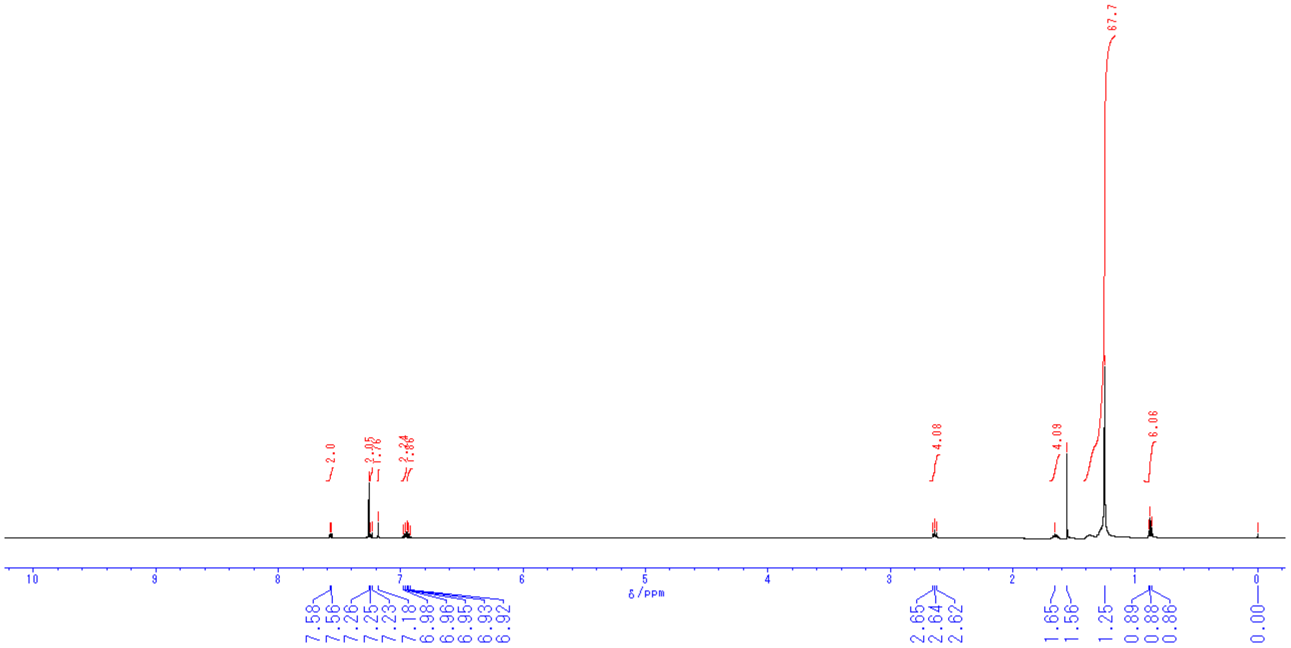

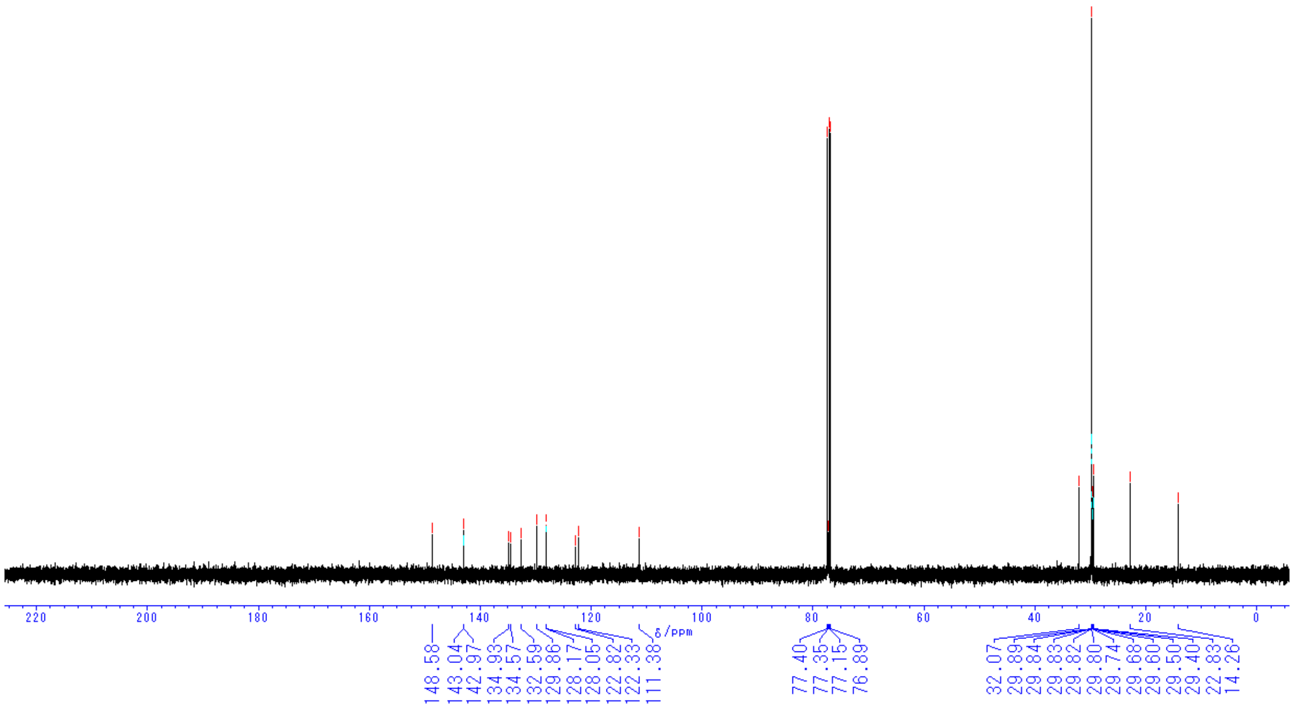

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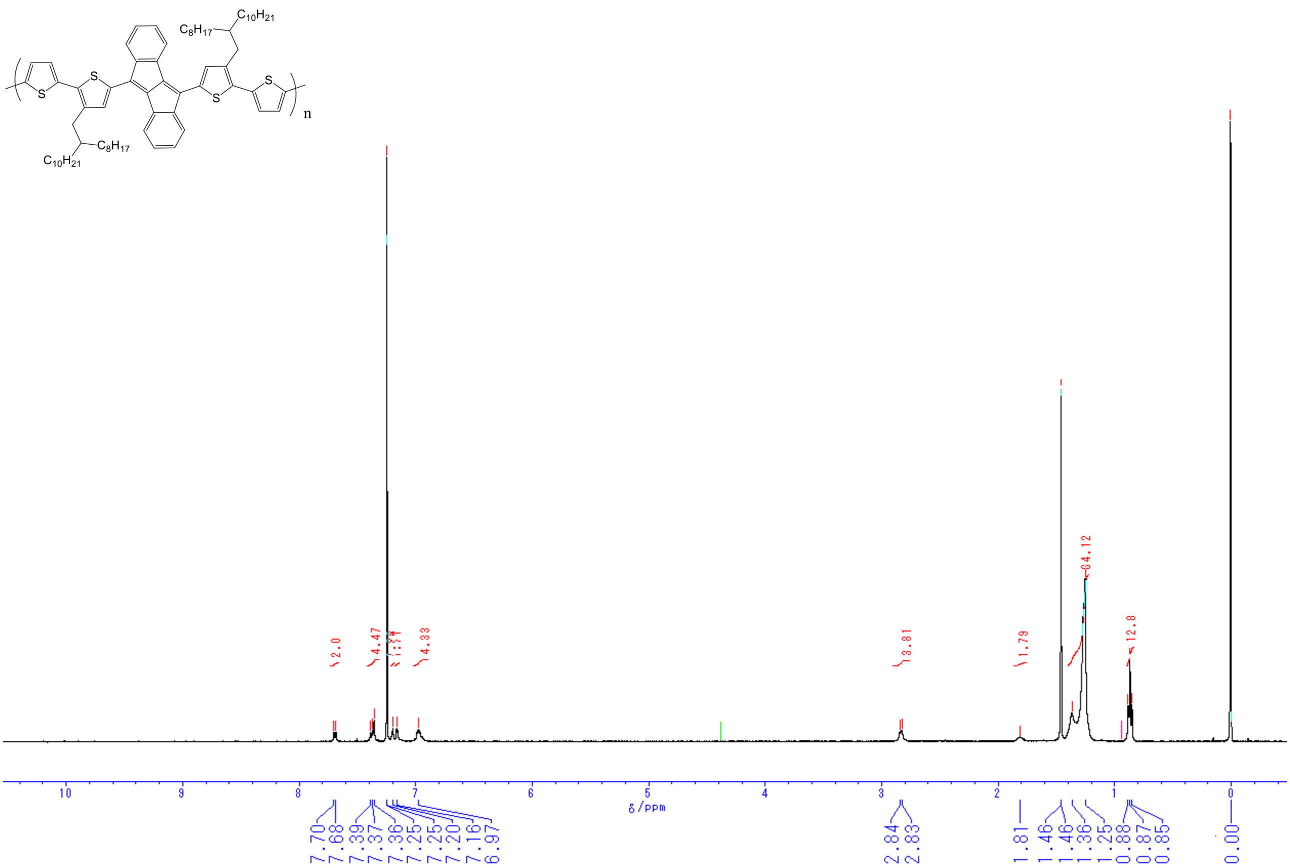
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S
S
S
S
n
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4.33
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1.79
64.12
12.8
10
9
8
7
6
5
4
3
2
1
0
δ/ppm
7.70
7.68
7.39
7.37
7.36
7.25
7.25
7.20
7.16
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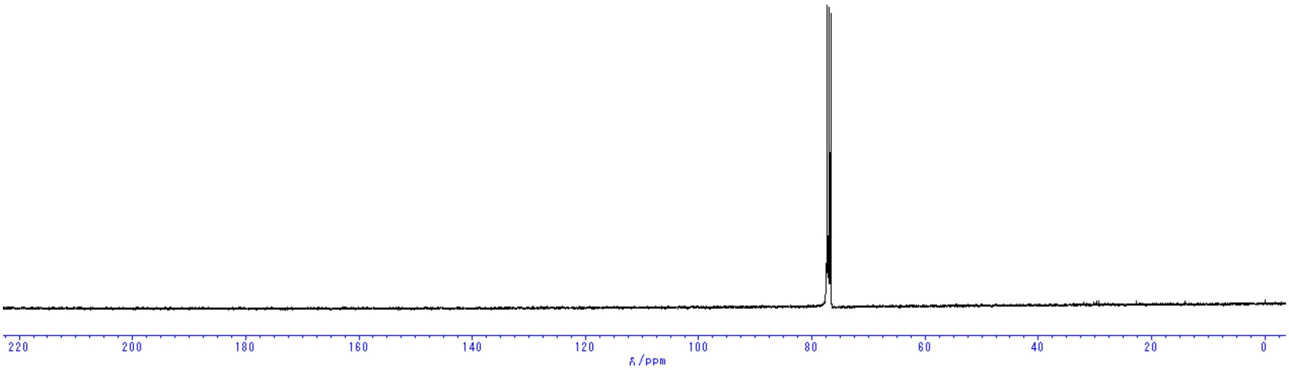
0.85
0.00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100
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0
δ/ppm

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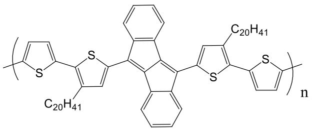

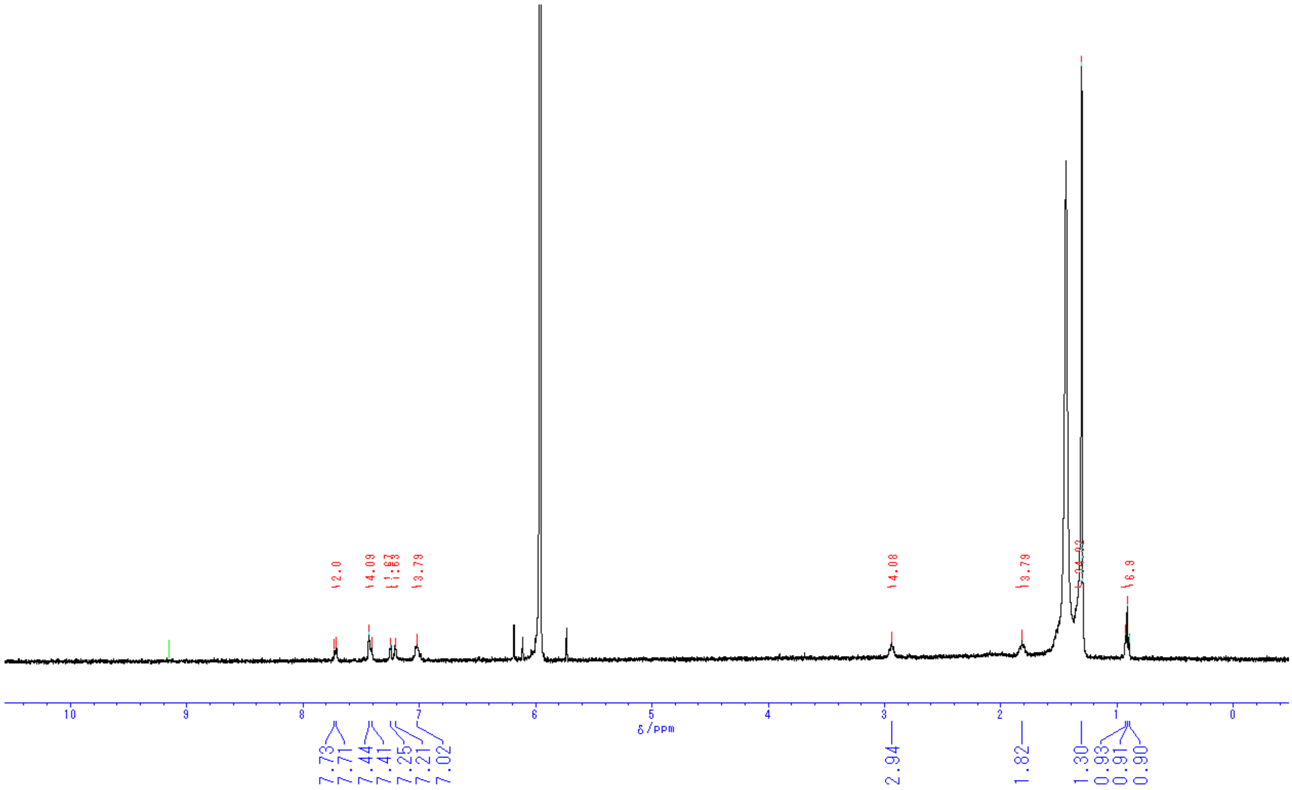

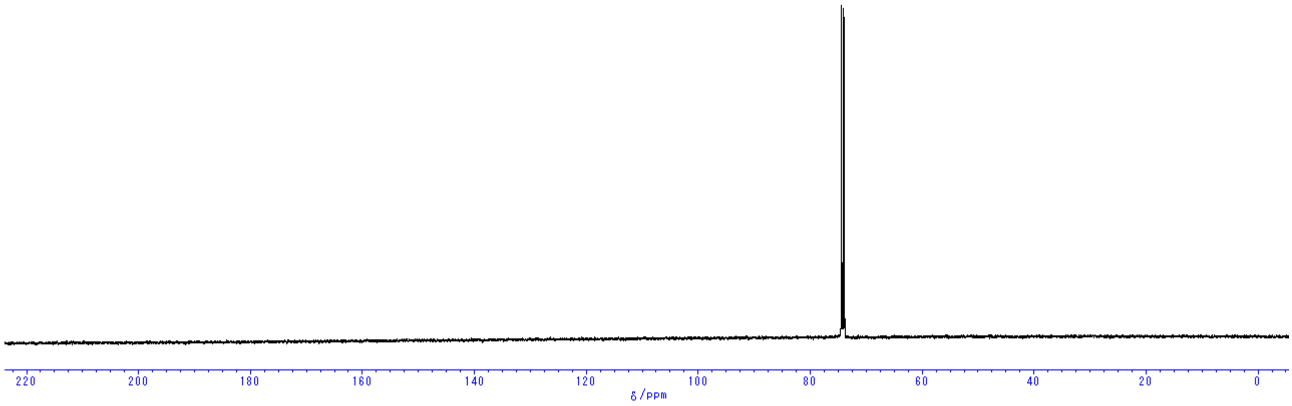

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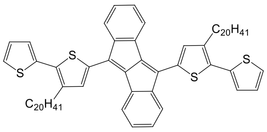
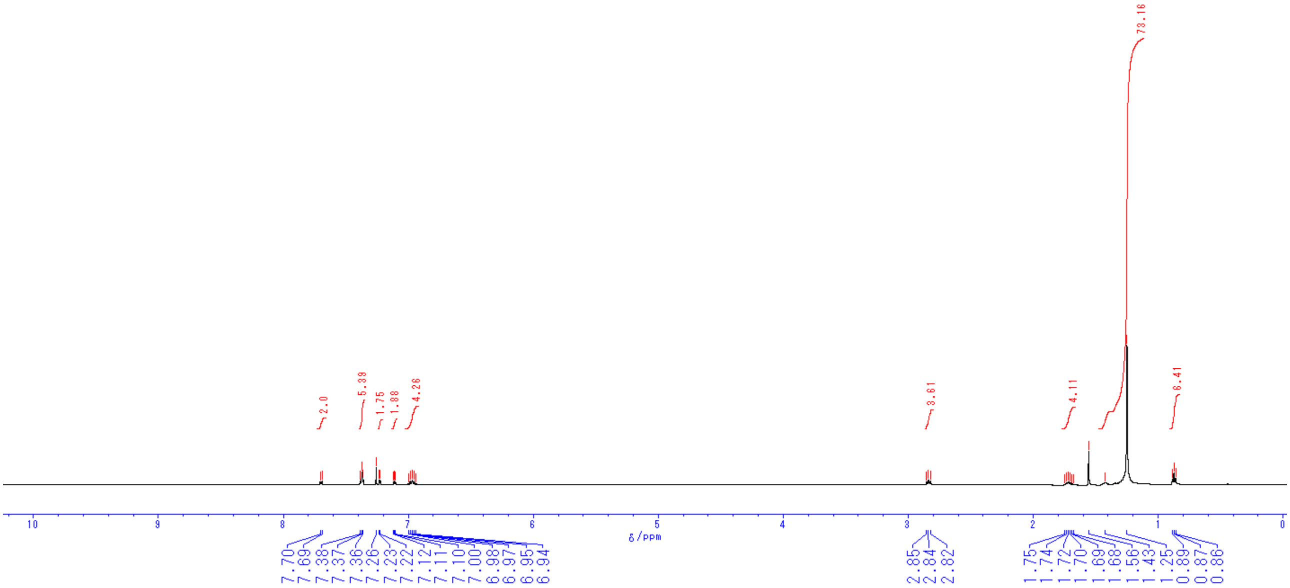
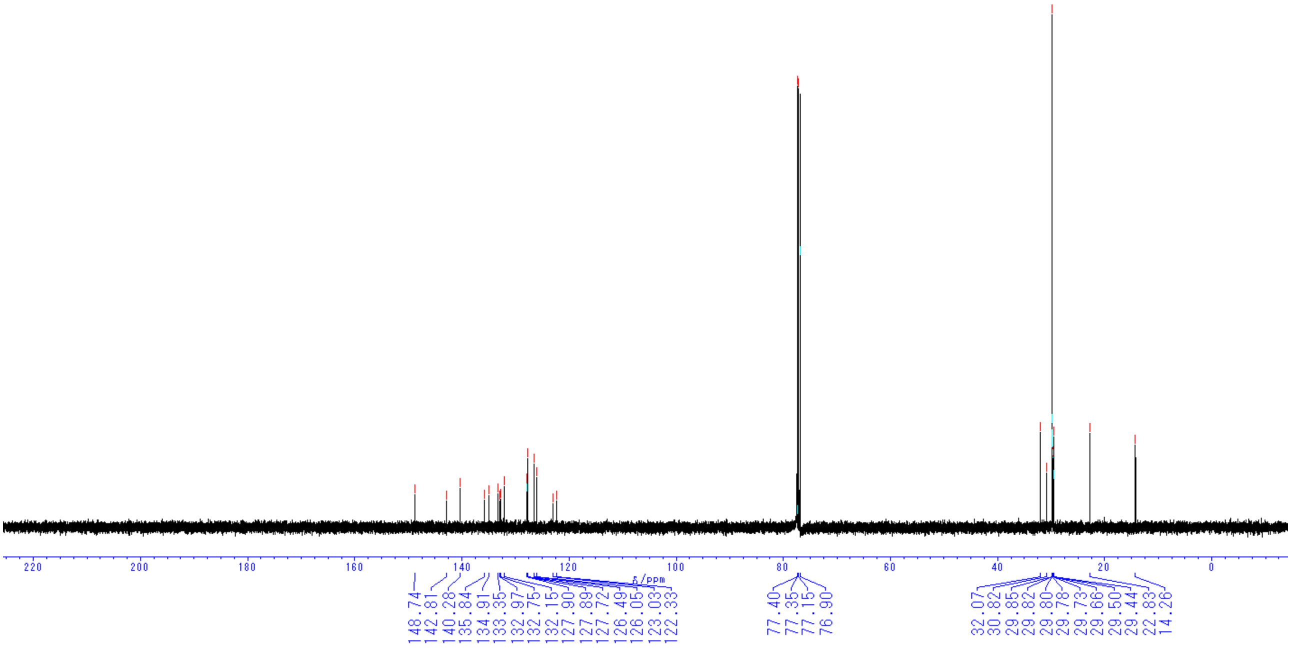
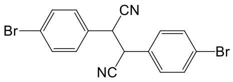
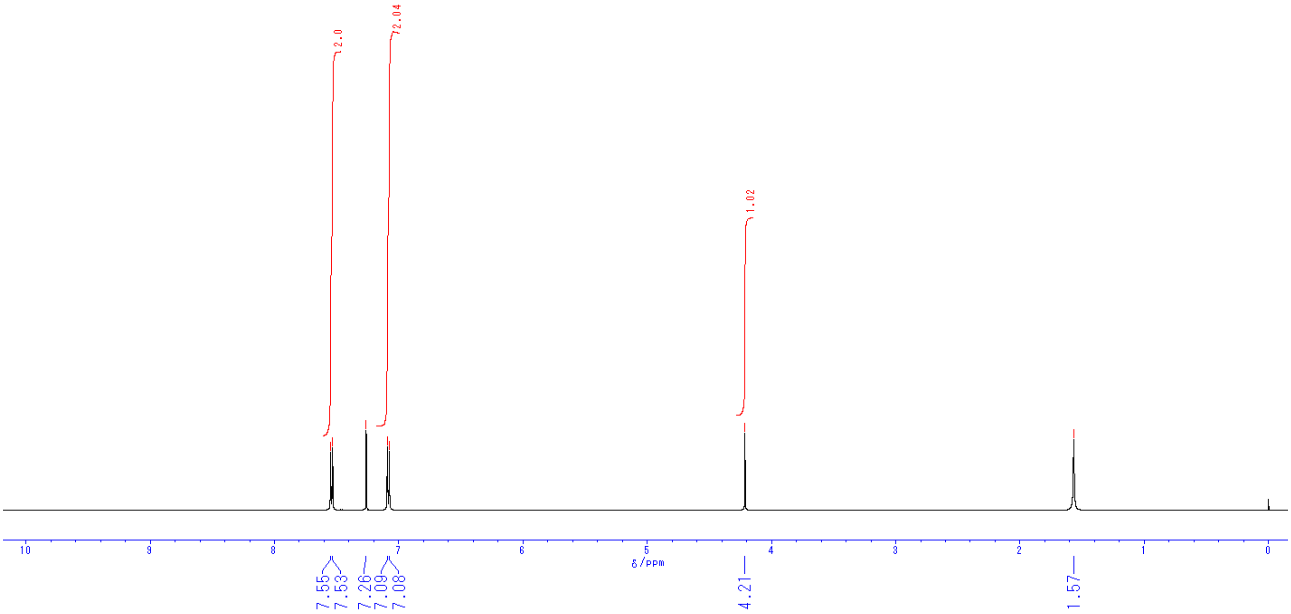


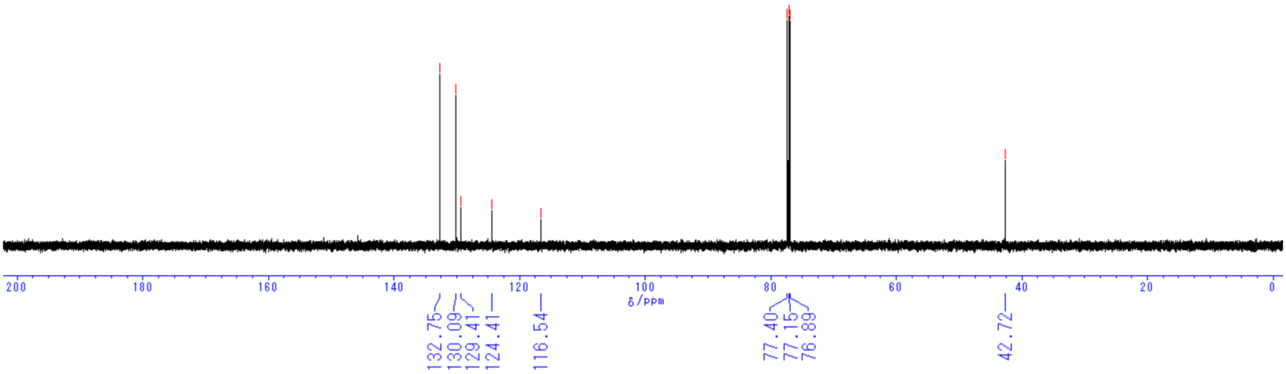




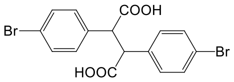
2,3-Bis(4-bromophenyl)succinonitrile (9)

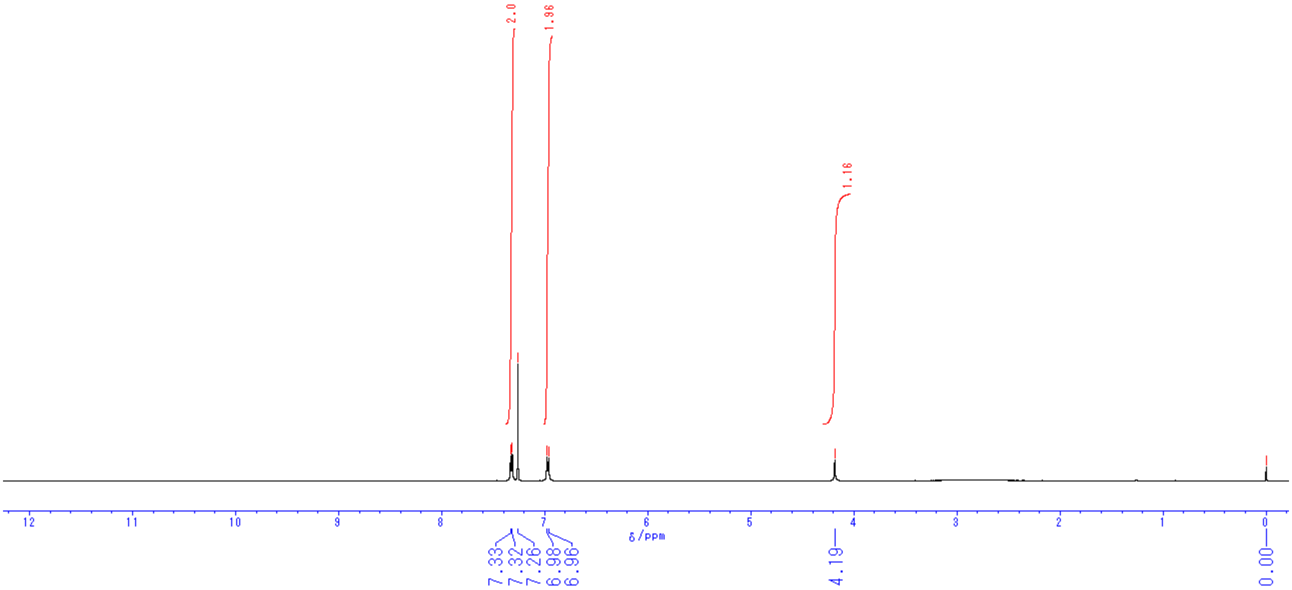


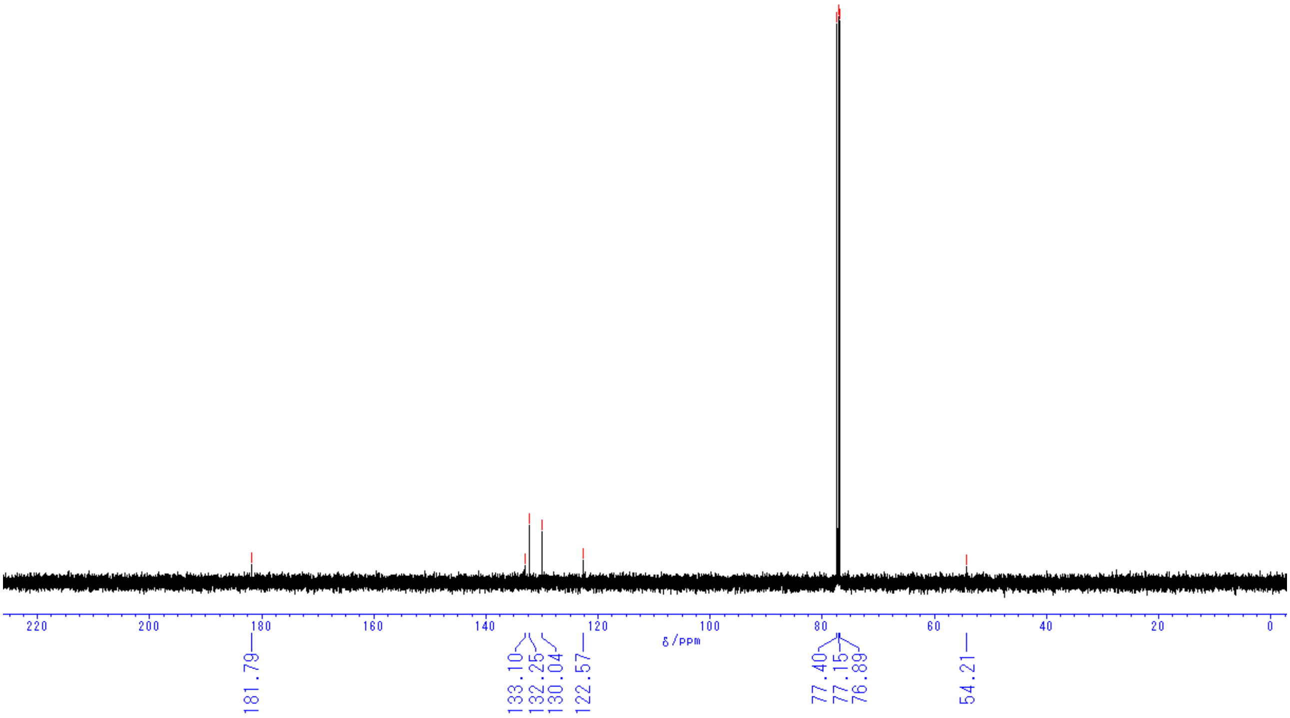




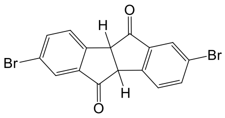
2,3-Bis(4-bromophenyl)succinic acid (10)

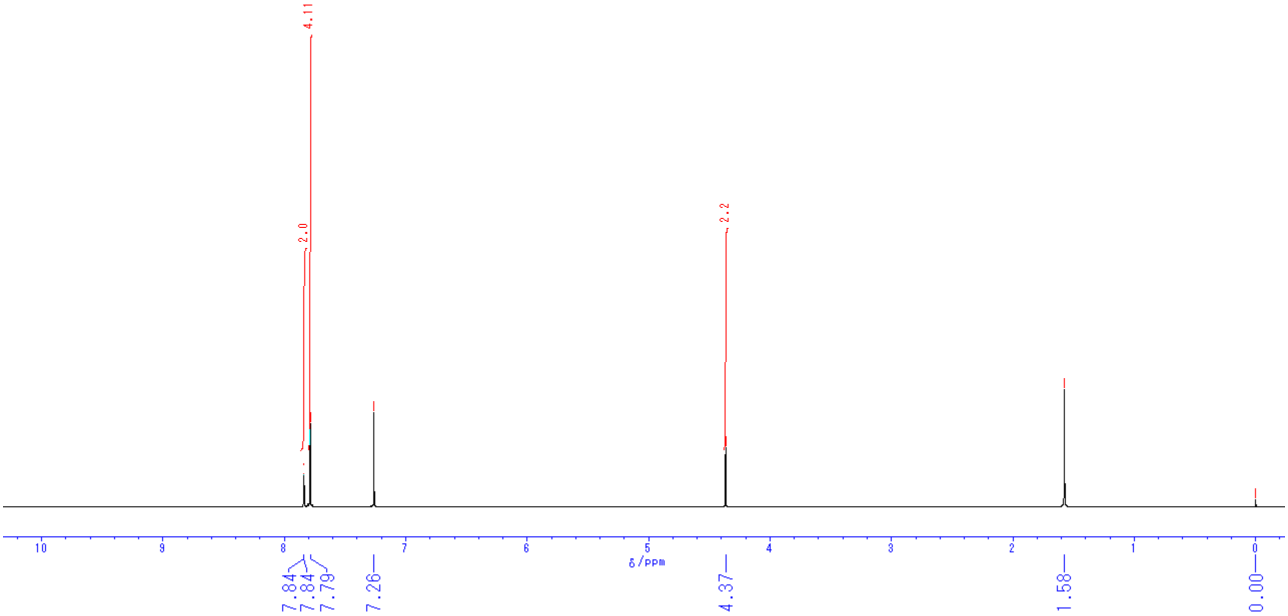


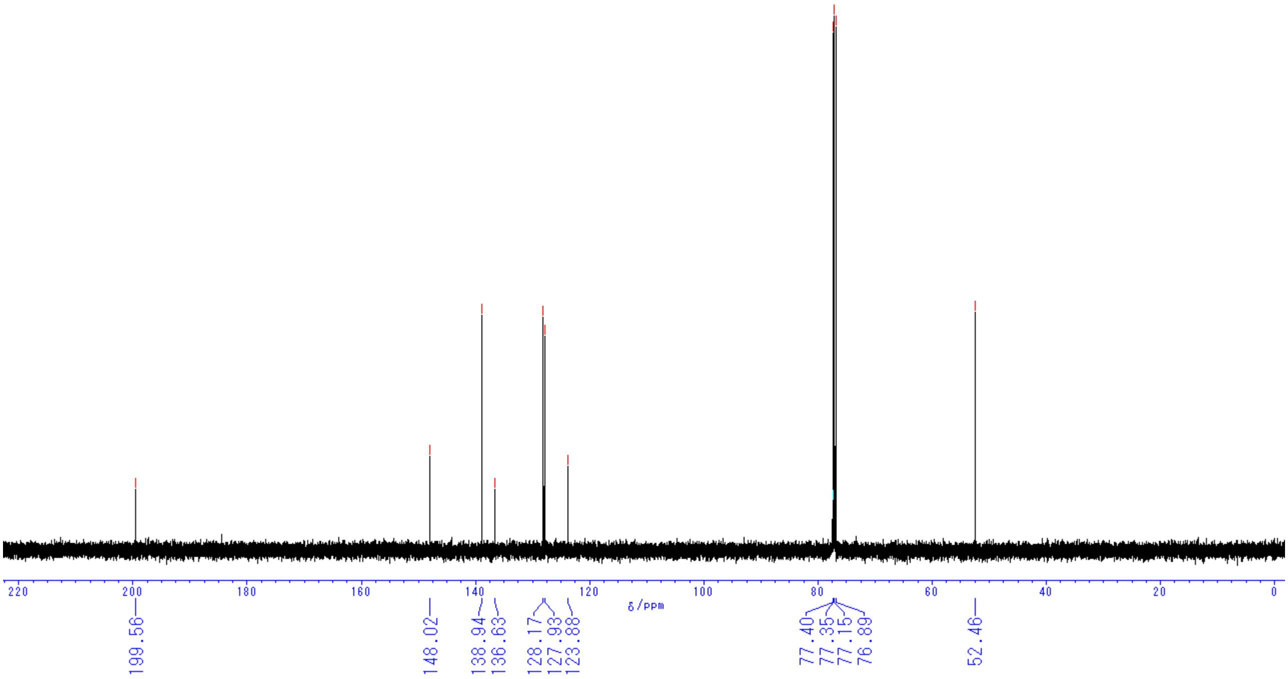




2,7-Dibromo-4b,5,9b,10-tetrahydrodibenzo[*a*,*e*]pentalene-5,10-dione (11)







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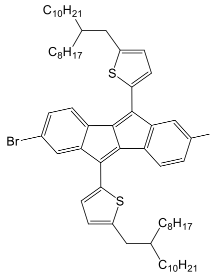

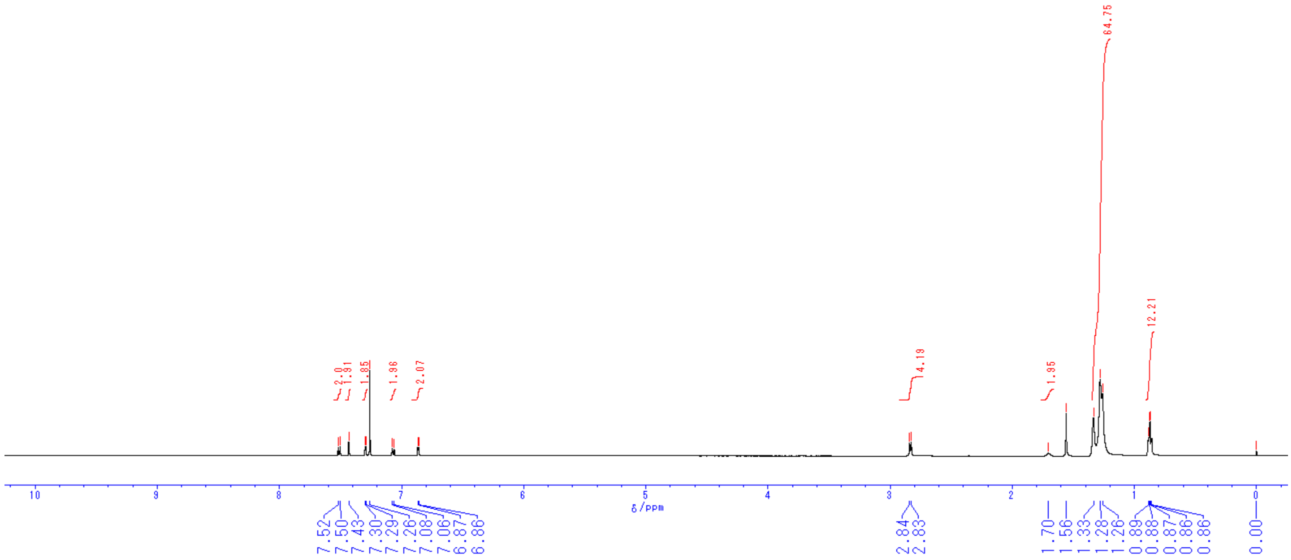

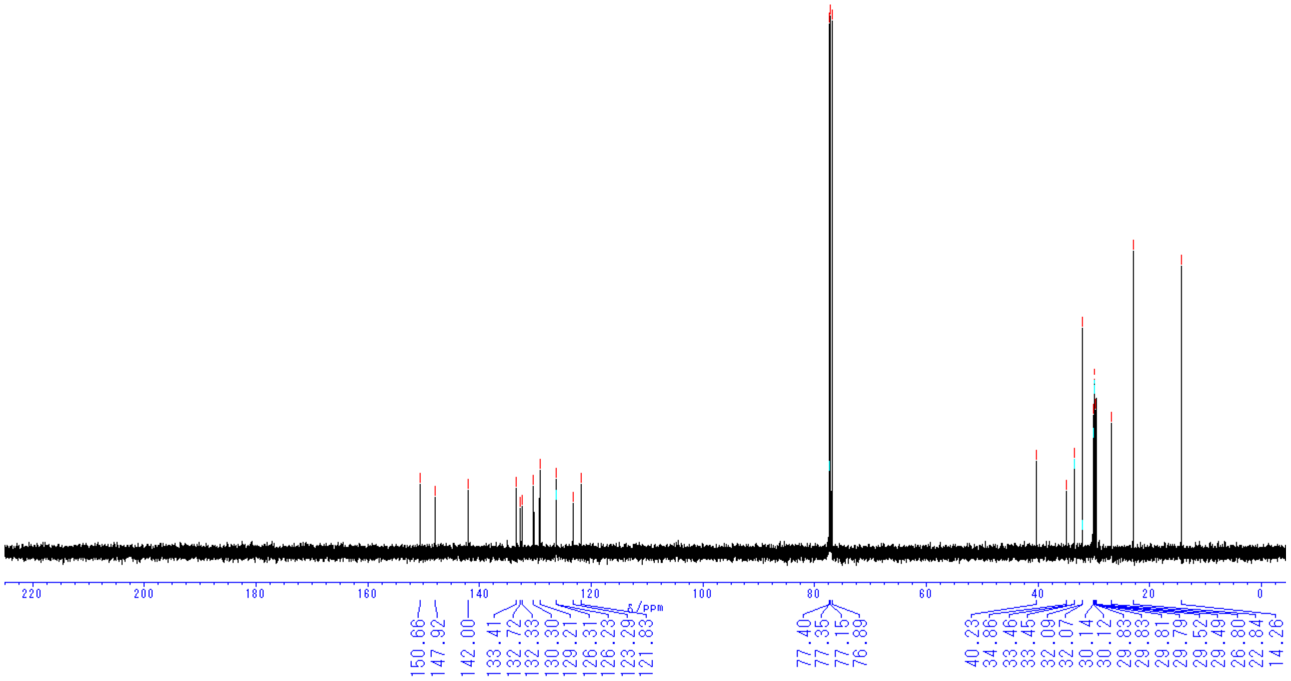

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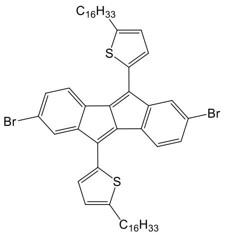

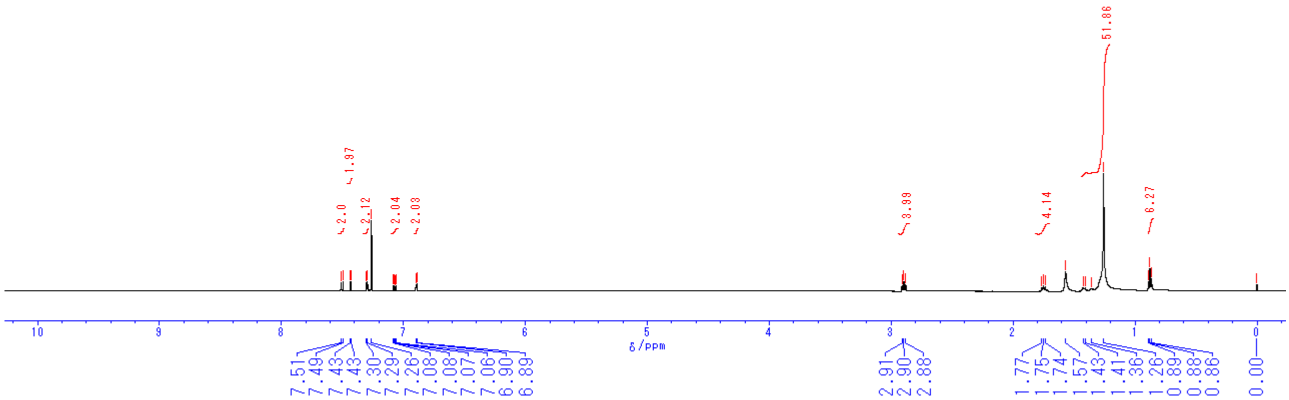

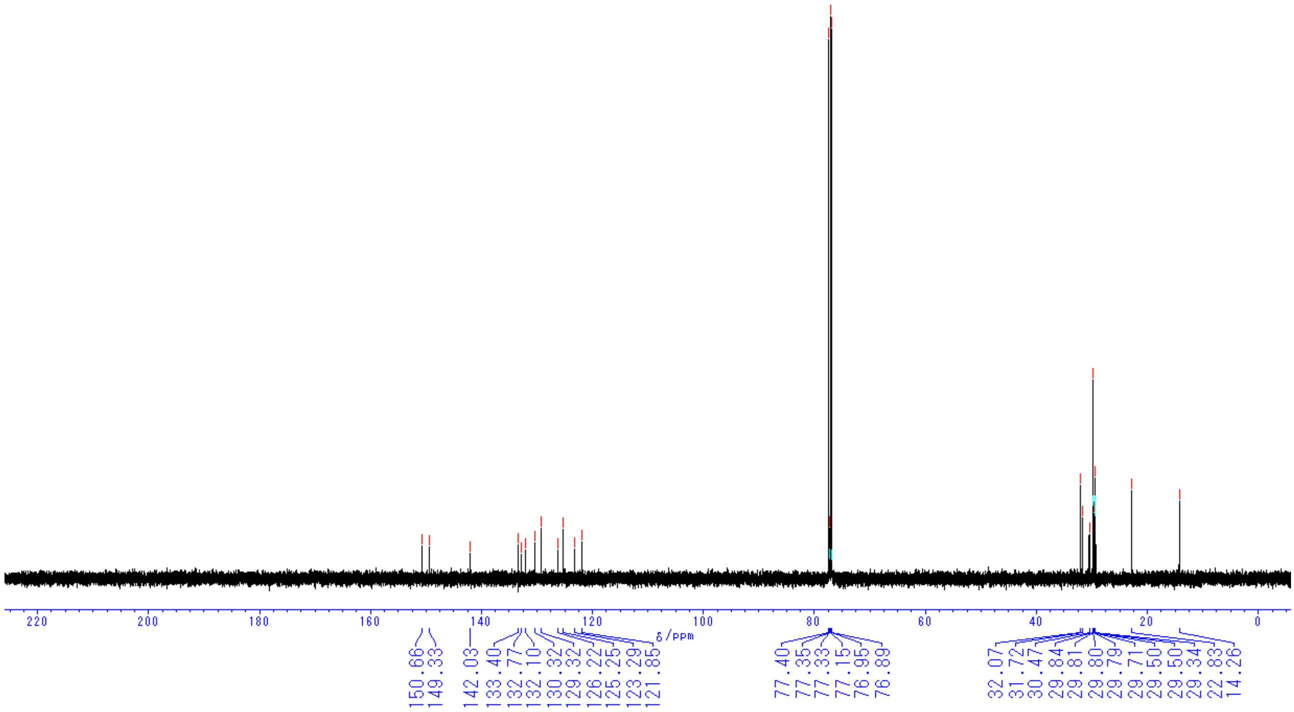

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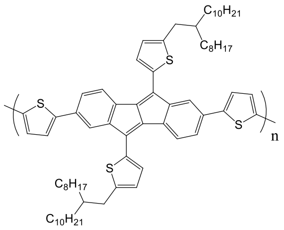

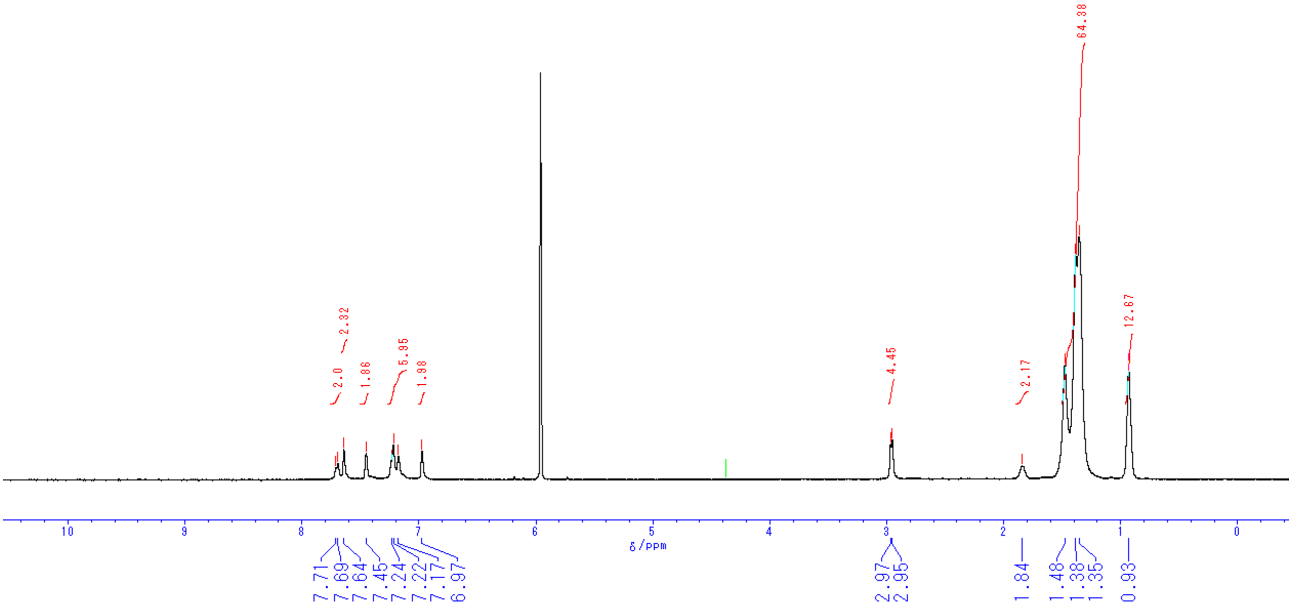

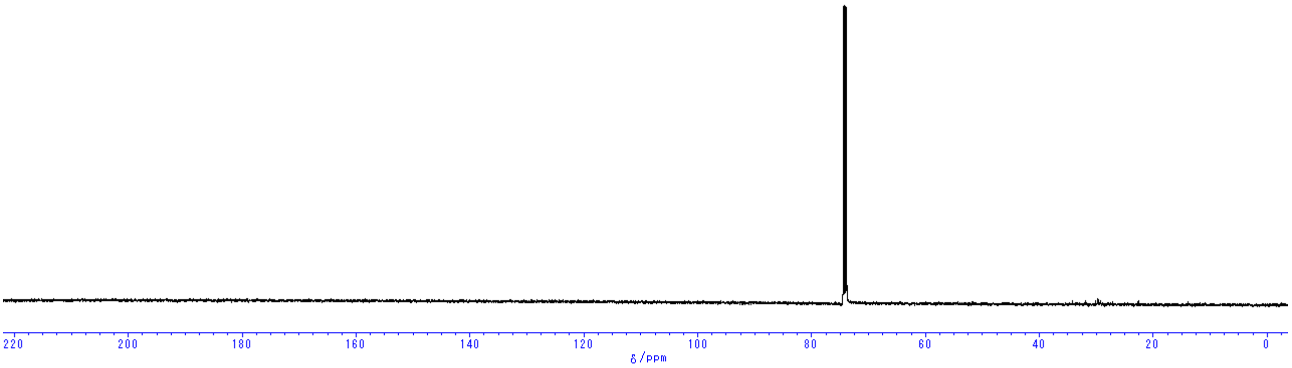

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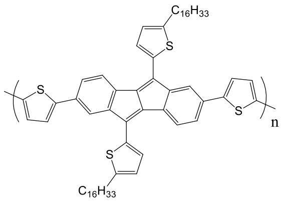

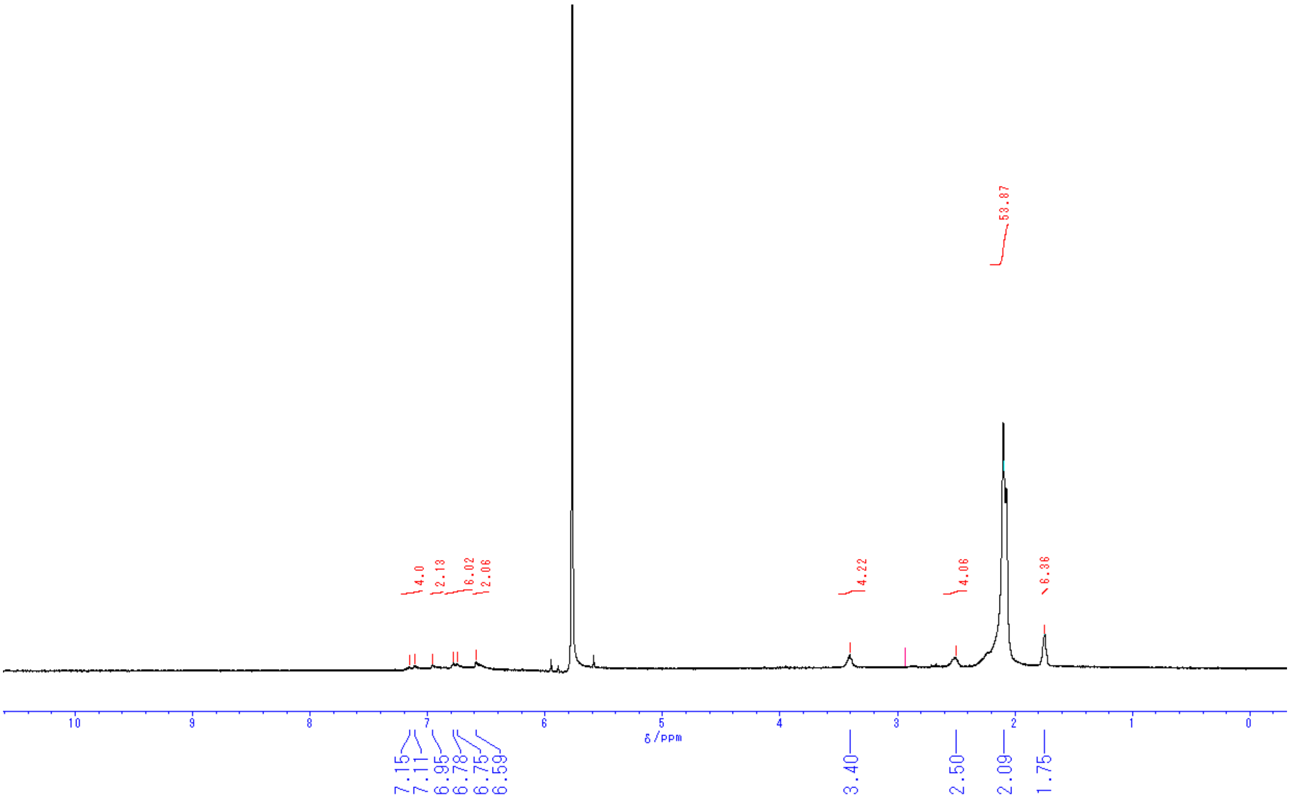

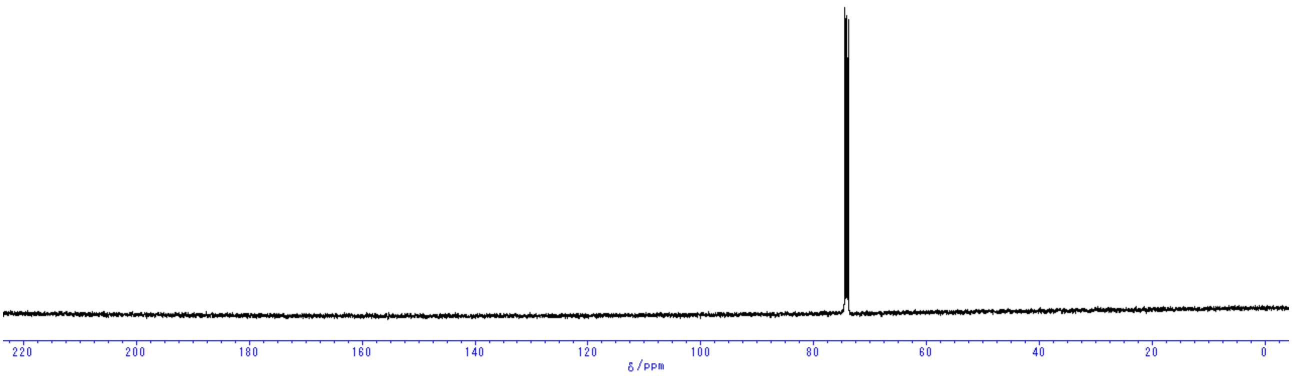

5,10-Bis(5-hexadecylthiophen-2-yl)-2,7-di(2-thienyl)dibenzo[*a*,*e*]pentalene (2b)