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Supporting Information for

Dibenzo[a,e]pentalene-Embedded Dicyanomethylene-Substituted Thienoquinoidal for n-Channel Organic Semiconductors: Synthesis, Properties, and Device Characteristics

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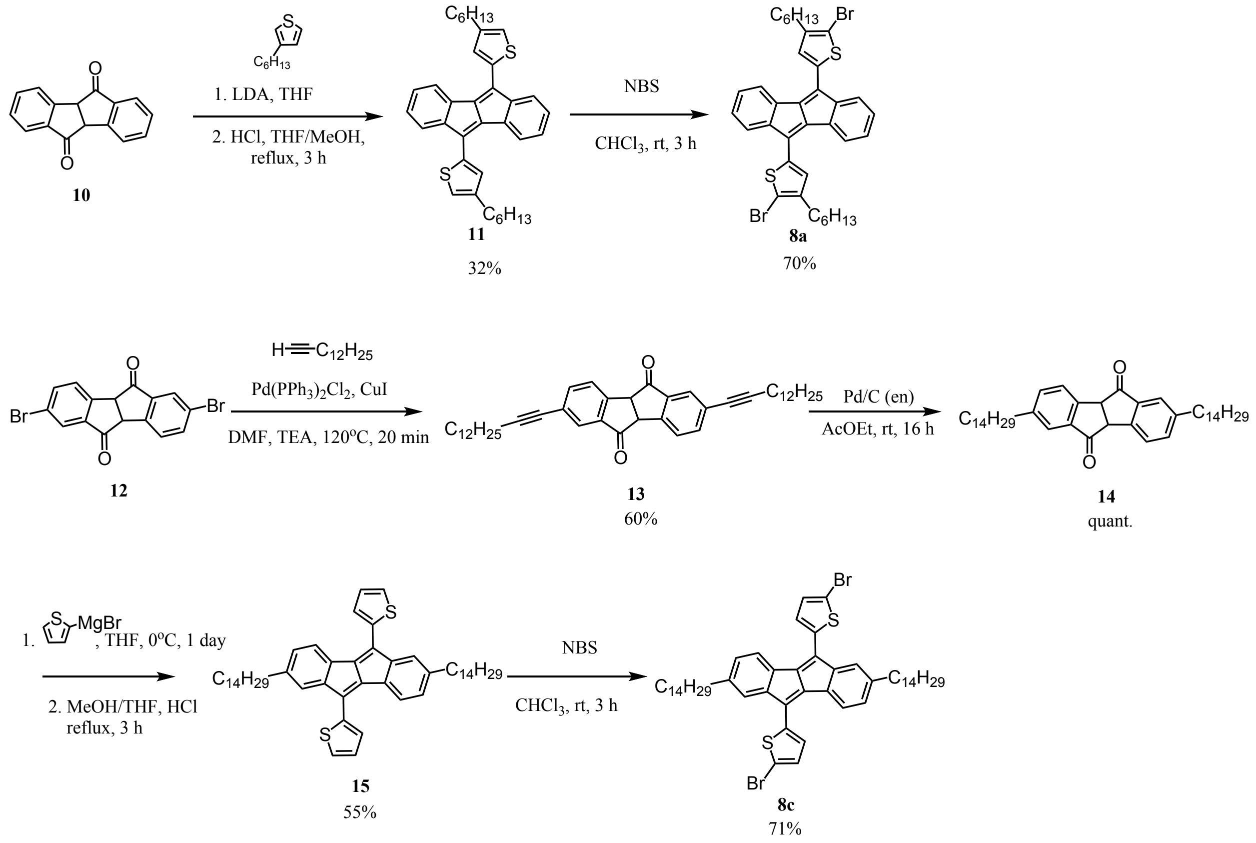
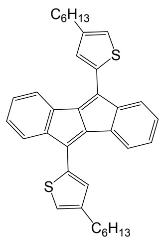
1. Synthesis of 8a and 8c



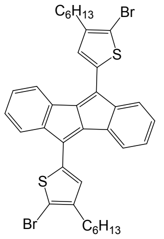
Scheme S1. Synthesis of **8a** and **8c**.

5,10-Bis[2-(4-hexyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (11)



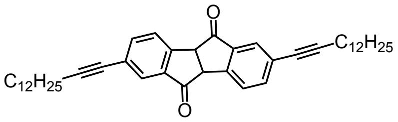
Lithium diisopropylamide solution freshly prepared by adding *n*-butyllithium solution (1.61 M hexane solution, 2.0 mL, 3.22 mmol) to diisopropylamine (0.5 mL, 3.54 mmol) in tetrahydrofuran (28 mL) under argon atmosphere was added to a solution of 3-icosylthiophene (3.65 g, 10 mmol) and 4b,5,9b,10-tetrahydrodibenzo[*a*,*e*]pentalene-5,10-dione **10** (0.58 g, 2.5 mmol) in tetrahydrofuran (5 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. 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/tetrahydrofuran (1:1, v/v , 100 mL). To the solution was added hydrochloric acid (2 M, 1.25 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[2-(4-hexyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene **11** (0.426 g, 32% yield) as a brown solid; Mp 88–89 °C; ^{1}H NMR (400 MHz) δ 0.90 (t, *J* = 7.2 Hz, 6H), 1.33–1.39 (m, 12H), 1.68 (quin, *J* = 7.2 Hz, 4H), 2.67 (t, *J* = 7.2 Hz, 4H), 6.91 (t, *J* = 6.5 Hz, 2H), 6.95 (t, *J* = 6.5 Hz, 2H), 7.07 (s, 2H), 7.30 (d, *J* = 7.0 Hz, 2H), 7.32 (s, 2H), 7.62 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz) δ 14.3, 22.8, 29.2, 30.6, 30.7, 31.9, 122.1, 122.2, 123.0, 127.8, 127.9, 130.3, 133.4, 134.9, 135.1, 142.7, 144.1, 149.0; EI-MS (70 eV) = 534 (M^+); HRMS (APCI): Calcd for $C_{36}H_{38}S_2$: 534.24094 [M^+]. Found: 534.24052.

5,10-Bis[2-(5-bromo-4-hexyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (8a)



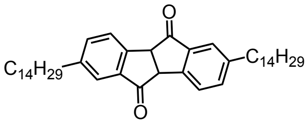
5,10-Bis[2-(4-hexyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene **11** (0.534 g, 1.0 mmol) and *N*-bromosuccinimide (0.378 g, 2.1 mmol) was dissolved in chloroform (100 mL). The mixture was stirred for 3 h at rt. After evaporation of the solvent, the residue was purified by column chromatography on silica gel eluted with dichloromethane/hexane (1:1, v/v) to give 5,10-bis[2-(5-bromo-4-hexyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene **8a** (0.483 g, 70% yield) as a brown solid; Mp 106–107 °C; ^{1}H NMR (400 MHz) δ 0.91 (t, *J* = 7.4 Hz, 6H), 1.34–1.41 (s, 12H), 1.65 (quin, *J* = 7.4 Hz, 4H), 2.64 (t, *J* = 7.4 Hz, 4H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 2H), 7.18 (s, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz) δ 14.3, 22.8, 29.2, 30.6, 30.7, 31.9, 122.1, 122.2, 123.0, 127.8, 130.3, 133.4, 134.9, 135.1, 142.8, 144.1, 149.0; EI-MS (70 eV) = 691 (M^+); HRMS (APCI): Calcd for $C_{36}H_{37}Br_2S_2$: 691.06979 [MH^+]. Found: 691.07147.

2,7-Di(tetradecyn-1-yl)dihydrodibenzo[*a*,*e*]pentalene-5,10-dione (**13**)



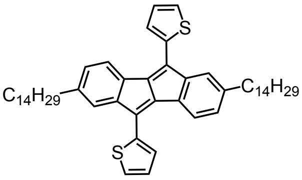
To a 10-20 mL microwave pressurized vial equipped with a stirring bar, 2,7-dibromodihydrodibenzo[*a,e*]pentalene-5,10-dione **12** (0.392 g, 1 mmol), bis(triphenylphosphine)palladium(II) dichloride (70 mg, 0.1 mmol), copper iodide (38 mg, 0.2 mmol), triethylamine (7 mL) and dimethylformamide (7 mL) were added. Then the tube was sealed and refilled with argon. Reaction tube was put into microwave reactor and heated to 120 °C for 20 min. The precipitated solid was separated from the cooled reaction mixture by suction filtration, washed with acetone (20 mL × 2). Recrystallization from dichloromethane/methanol gave a 2,7-di(tetradecyn-1-yl)dihydrodibenzo[*a,e*]pentalene-5,10-dione **13** (0.371 g, 60% yield) as a white solid: Mp 98–99 °C; ^{1}H NMR (400 MHz) δ 0.87 (t, *J* = 6.4 Hz, 6H), δ 1.26–1.48 (m, 36H), 1.58 (quin, *J* = 6.4 Hz, 4H), 2.38 (t, *J* = 6.4 Hz, 4H), 4.34 (s, 2H), 7.65 (d, *J* = 8.1 Hz, 4H), δ 7.69 (s, 2H), 7.54 (d, *J* = 8.1 Hz, 4H); ^{13}C NMR (100 MHz) δ 14.0, 19.4, 22.6, 28.6, 28.7, 28.9, 29.3, 29.51, 29.52, 29.6, 29.7, 31.9, 52.8, 92.8, 108.8, 118.7, 125.9, 135.0, 138.8, 155.8, 157.2, 200.4; IR (KBr) ν= 1709 cm^{-1} (C=O); EI-MS (70 eV) = 619 (M$^+$); HRMS (APCI): Calcd for $C_{44}H_{59}O_2$: 619.45096, [MH$^+$]. Found: 619.45184.

2,7-Ditetradecyldihydrodibenzo[*a,e*]pentalene-5,10-dione (**14**)



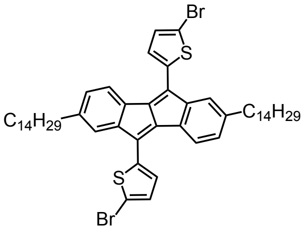
A solution of 2,7-di(tetradecyn-1-yl)dihydrodibenzo[*a,e*]pentalene-5,10-dione **13** (0.371 g, 0.6 mol) in ethyl acetate (30 mL) was degassed and flushed with argon three times. After that palladium-activated carbon-ethylenediamine complex (Pd 5%, 400 mg) was added and the solution was degassed again with argon. A balloon of hydrogen was attached and the reaction mixture was stirred at rt for 16 h. The mixture was filtered through a pad of celite was washed with dichloromethane (20 mL × 2). The solution was concentrated to afford essentially pure 2,7-ditetradecyldihydrodibenzo[*a,e*]pentalene-5,10-dione **14** (376 mg, quantitative yield) as a white solid: Mp 92–93 °C; ^{1}H NMR (400 MHz) δ 0.88 (t, $J = 7.6$ Hz, 6H), 1.25–1.28 (m, 44H), 1.58 (quin, $J = 7.6$ Hz, 4H), 2.62 (t, $J = 7.6$ Hz, 4H), 4.31 (s, 2H), 7.45 (d, $J = 8.0$ Hz, 4H), 7.49 (s, 2H), 7.80 (d, $J = 8.0$ Hz, 4H); ^{13}C NMR (100 MHz,) δ 13.97, 14.03, 22.7, 29.2, 29.3, 29.5, 29.6, 31.2, 31.9, 35.6, 52.8, 124.0, 124.1, 126.3, 135.2, 136.4, 136.4, 144.4, 147.7, 201.7; IR (KBr) ν= 1717 cm^{-1} (C=O); EI-MS (70 eV) = 627(M$^+$); HRMS(APCI): Calcd for $C_{44}H_{67}O_2$: 627.51356, [MH$^+$]. Found: 627.51440.

2,7-Ditetradecyl-5,10-di(2-thienyl)dibenzo[*a,e*]pentalene (15)



Under an atmosphere of argon, 2-bromothiophene (360 mg, 2.2 mmol) dissolved in tetrahydrofuran (10 mL) was slowly added to a refluxing mixture of magnesium (176 mg, 7.1 mmol) and iodine (catalytic amount) in tetrahydrofuran (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-ditetradecyldihydrodibenzo[*a,e*]pentalene-5,10-dione **14** (376 mg, 0.6 mmol) in tetrahydrofuran (20 mL) at 0 °C. The reaction mixture was stirred for 3 h at rt and then poured into ice containing hydrochloric acid and isolated by extraction with ethyl acetate (100 mL × 2). The combined extracts were concentrated in vacuo, and the residue was dissolved in methanol/tetrahydrofuran (1:1, v/v , 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 suspension was separated out. Then, the crude product was collected by suction filtration and purified by recrystallization from dichloromethane/methanol to afford 2,7-ditetradecyl-5,10-di(2-thienyl)-dibenzo[*a,e*]pentalene **15** (250 mg, 55% yield) as a dark red solid: Mp 109–110 °C; ^{1}H NMR(400 MHz) δ 0.87 (t, $J = 7.0$ Hz, 6H), 1.25–1.30 (m, 44H), 1.55 (t, $J = 7.0$ Hz, 4H), 2.48 (t, $J = 7.0$ Hz, 4H), 6.71 (d, $J = 8.0$ Hz, 2H), 7.09 (s, 2H), 7.22 (t, $J = 8.0$ Hz, 2H), 7.48–7.50 (m, 6H); ^{13}C NMR (100 MHz) δ 14.5, 23.0, 29.8, 29.94, 29.97, 30.0, 30.7, 30.9, 32.2, 122.3, 122.4, 123.1, 127.9, 128.0, 130.4, 133.5, 135.1, 135.2, 142.9, 144.3, 149.1; EI-MS (70 eV) = 759 (M$^+$); HRMS (APCI): Calcd for $C_{52}H_{71}S_2$: 759.49917, [MH$^+$]. Found: 759.50079.

5,10-Bis[2-(5-bromo)thiophen-2-yl]-2,7-ditetradecyldibenzo[*a,e*]pentalene (8c)



2,7-ditetradecyl-5,10-di(2-thienyl)dibenzo[*a,e*]pentalene **15** (0.759 g , 1 mmol) and *N*-bromosuccinimide (0.378 g, 2.1 mmol) was dissolved in chloroform (100 ml). The mixture was stirred for 3 h at room temperature. After evapolation of the solvent, the residue was purified by column chromatography on silica gel eluted dichloromethane/hexane (1:1, v/v) to give 5,10-bis[2-(5-bromo)thiophen-2-yl]-2,7-ditetradecyldibenzo[*a,e*]pentalene **8c** (0.577 g, 63% yield) as a brown solid: Mp 116–117 °C; ^{1}H NMR(400 MHz) δ 0.88 (d, *J* = 7.1 Hz, 6H), 1.26–1.31 (m, 44H), 1.57 (quin, *J* = 7.1 Hz, 4H), 2.48 (t, *J* = 7.1 Hz, 4H), 6.69 (d, *J* = 7.4 Hz, 2H), 6.99 (s, 2H), 7.14 (d, *J* = 4.0 Hz, 2H), 7.19 (d, *J* = 4.0 Hz, 2H), 7.39 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 14.1, 22.8, 29.5, 29.7, 29.8, 29.9, 31.3, 32.1, 36.3, 114.1, 123.1, 127.7, 127.8, 130.7, 131.6, 132.0, 137.6, 143.6, 144.2, 149.3; HRMS (APCI): Calcd for $C_{52}H_{69}Br_2S_2$: 915.32020, [MH$^+$]. Found: 915.32269.

2. Absorption spectra of 7a and 7b.

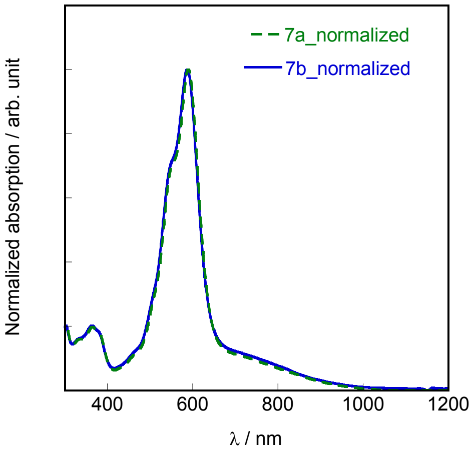


Figure S1. Normalized solution absorption spectra of **7a** and **7b**.

3. TD-DFT calculation of 7b' and 7c'

Table S1. TD-DFT calculated vertical excitation energy (in nm) and corresponding oscillator strength of **7b'** and **7c'** (RB3LYP/6-31G*).

		7b'		
#Transition	*λ*/ nm	*f*	Main monoexcitations	Weight / %
1	889.7	0.0944	HOMO-2→LUMO	44
			HOMO→LUMO	50
2	615.3	0.0000	HOMO→LUMO+1	56
3	599.0	1.3778	HOMO→LUMO	32
			HOMO-1→LUMO	49
4	523.4	0.0054	HOMO-2→LUMO	43
			HOMO-1→LUMO+1	49
5	444.2	0.0293	HOMO-1→LUMO+1	44
6	413.6	0.0320	HOMO-3→LUMO	65
7	403.8	0.3917	HOMO-2→LUMO+1	62
8	398.1	0.0001	HOMO-4→LUMO	56
9	389.6	0.0001	HOMO-5→LUMO	70
10	374.6	0.1644	HOMO-6→LUMO	65
11	357.4	0.0096	HOMO-8→LUMO	56
12	346.2	0.1014	HOMO-5→LUMO+2	62
13	319.7	0.0597	HOMO-9→LUMO	47
			HOMO-1→LUMO+2	46
14	318.3	0.0000	HOMO-3→LUMO+1	65

15	311.3	0.0265	HOMO-8→LUMO+1	60
16	308.0	0.0333	HOMO→LUMO+3	62
17	304.6	0.0000	HOMO→LUMO+4	39
18	298.1	0.0077	HOMO-6→LUMO+1	62
19	288.9	0.0000	HOMO-1→LUMO+3	53
20	288.5	0.0820	HOMO→LUMO+5	50

2c’

#Transition	λ/ nm	f	Main monoexcitations	Weight / %
1	985.1	0.0638	HOMO-2→LUMO	37
			HOMO→LUMO	55
2	632.1	0.0000	HOMO→LUMO+1	60
3	596.6	1.3582	HOMO→LUMO	25
			HOMO-1→LUMO	53
4	535.7	0.0064	HOMO-2→LUMO	49
5	443.3	0.0313	HOMO-1→LUMO+1	48
6	429.2	0.0000	HOMO-3→LUMO	69
7	418.2	0.0325	HOMO-4→LUMO	66
8	403.4	0.4205	HOMO-2→LUMO+1	63
9	391.2	0.0051	HOMO-4→LUMO	57
10	358.5	0.1144	HOMO-5→LUMO	63
11	350.7	0.0071	HOMO-6→LUMO	60
12	346.9	0.2011	HOMO→LUMO+2	59
13	328.7	0.0265	HOMO-3→LUMO+1	65
14	324.4	0.0483	HOMO-8→LUMO	47
15	319.8	0.0000	HOMO-3→LUMO+1	65
16	310.8	0.0417	HOMO-4→LUMO+1	52
17	305.5	0.0015	HOMO→LUMO+2	63
18	298.9	0.0195	HOMO→LUMO+4	44
19	291.8	0.2230	HOMO→LUMO+4	45
20	285.7	0.0000	HOMO-2→LUMO+2	65

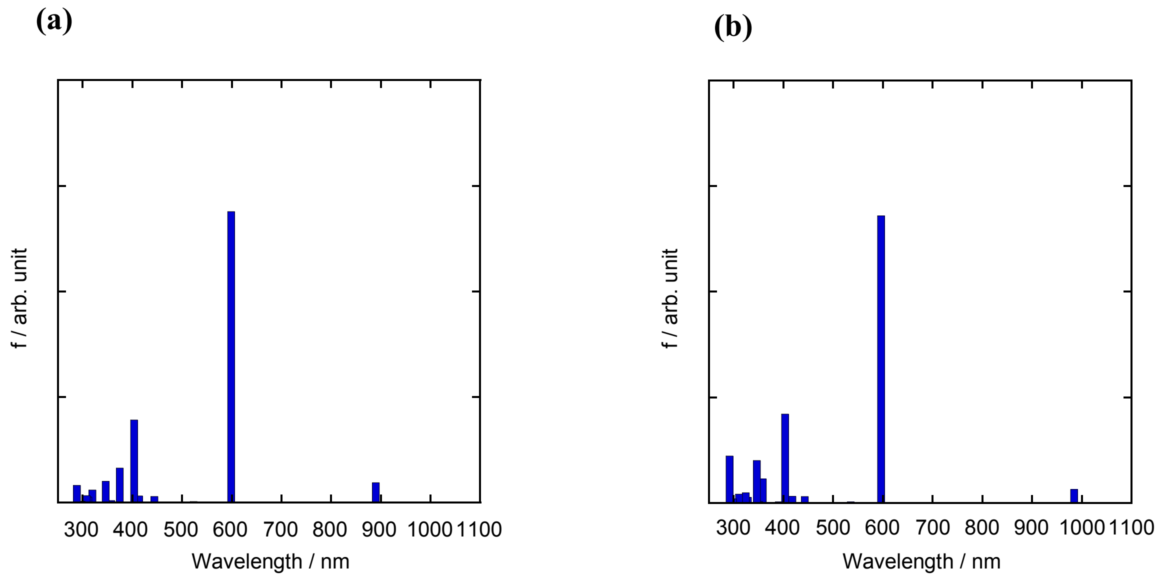


Figure S2. TD-DFT calculated electron spectra of **7b’** (a) and **7c’** (b) (RB3LYP/6-31G*).

4. FET characteristics of 7b.

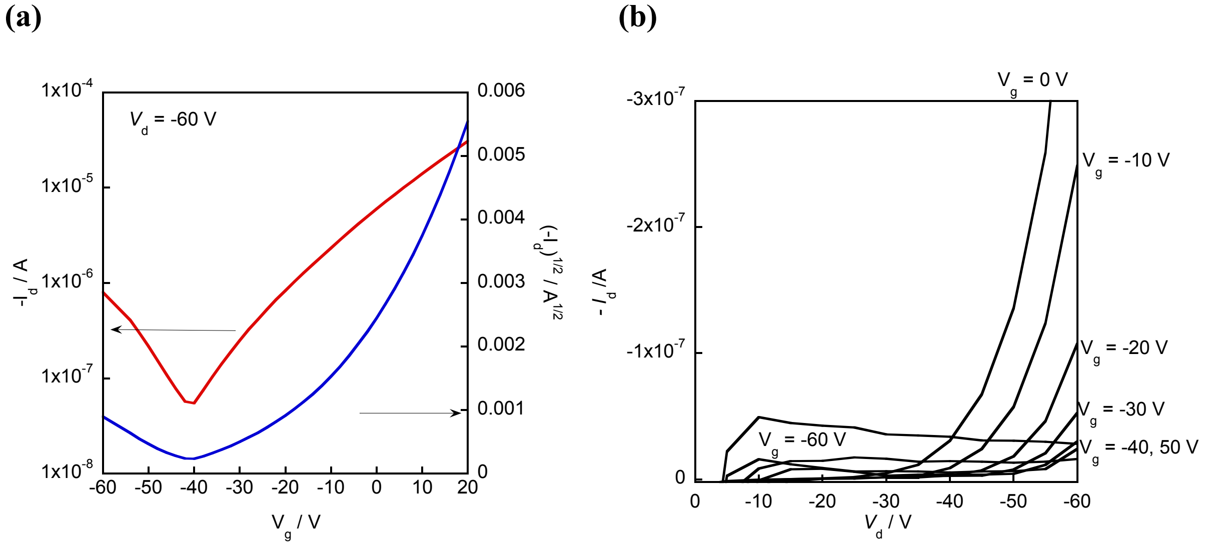


Figure S3. Transfer (a) and output (b) curves of **7a** (V_d = -60V).

5. AFM images of thin films of 7b and 7c on Si/SiO$_2$ substrate

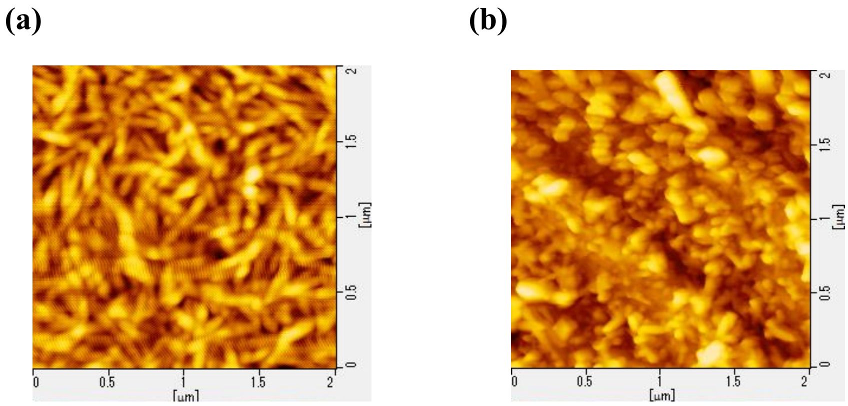


Figure S4. AFM images of the thin films of 7b (a) and 7c (b) on Si/SiO$_2$ substrate.

6. Out-of-plane and in-plane XRD patterns of the drop-casted film of 7a together with the simulated powder pattern from the bulk single crystal

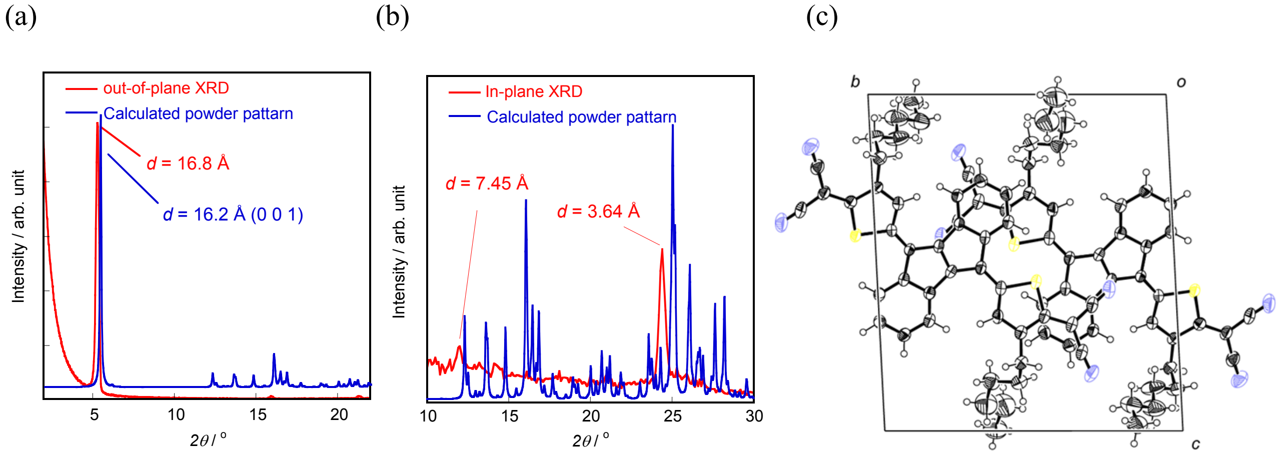
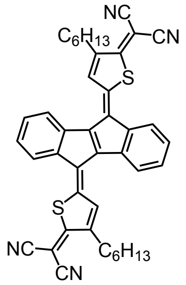
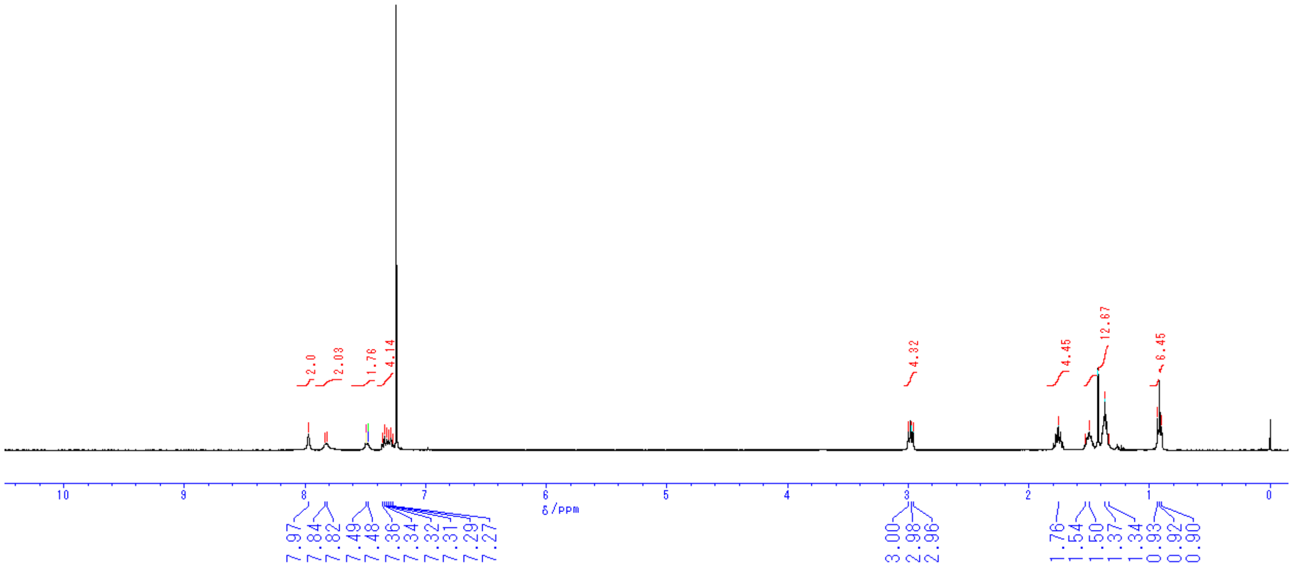


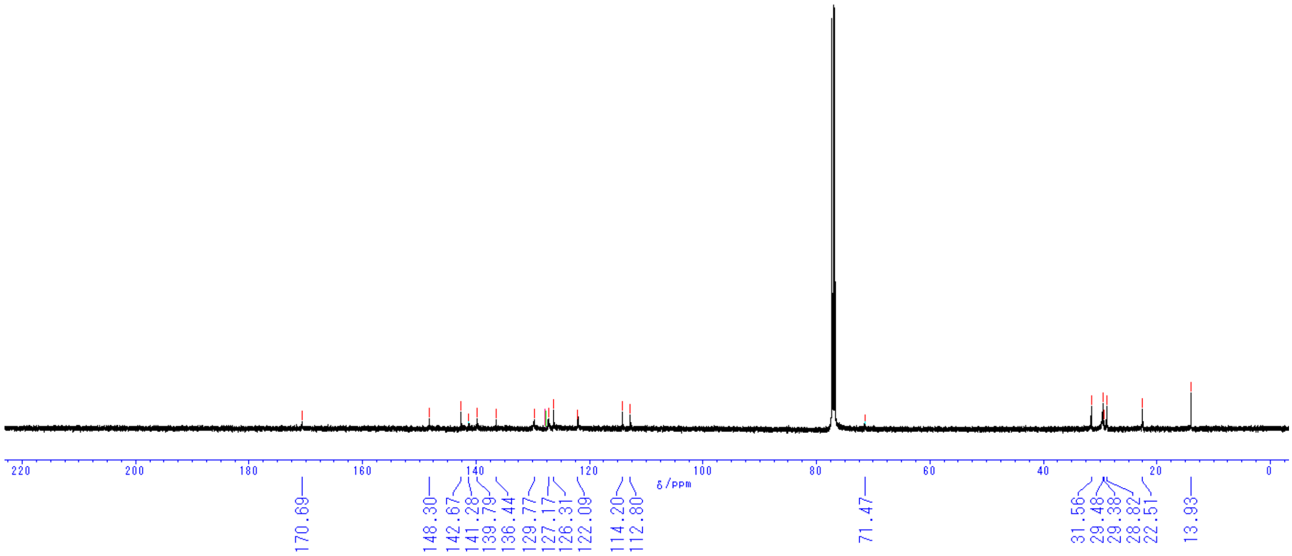
Figure S5. Comparison of the XRD patterns of **7a** thin film with the simulated powder pattern from the single crystal data of **7a**; out-of-plane (a) and in-plane XRD (b), and the crystallographic *a*-axis projection of **7a** in the bulk single crystal structure: Although the first peak in out-of-plane XRD pattern (16.8 Å), at a glance, is close to the 001 peak in the simulated powder pattern (16.2 Å), they do not correspond to each other (a). Also two in-plane peaks can not be indexed by the simulated powder pattern (b). The crystallographic *a*-axis projection of the packing structure of **7a** also demonstrates that the length of the alkyl groups does not affect the *c*-axis length, since the alkyl groups point up or down in the perpendicular manner to the π-plane (or the crystallographic *bc*-plane).

7. NMR spectra

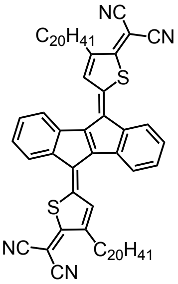
5,10-Bis[5-(dicyanomethylene)-4-hexyl-2(5*H*)-thienylidene]-5,10-dihydrodibenzo[*a,e*]pentalene (7a)

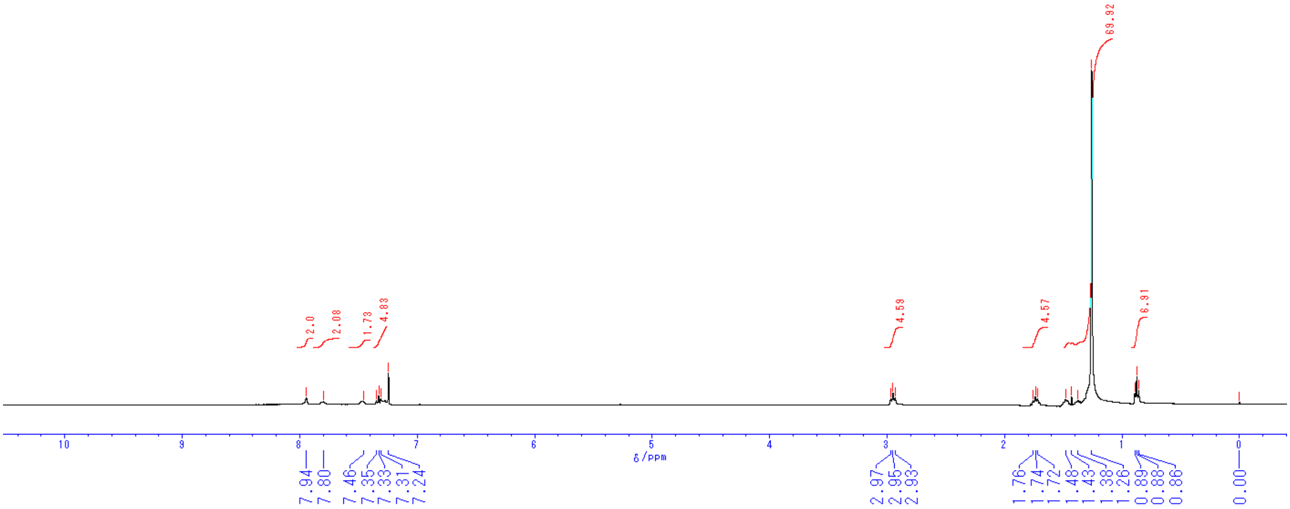


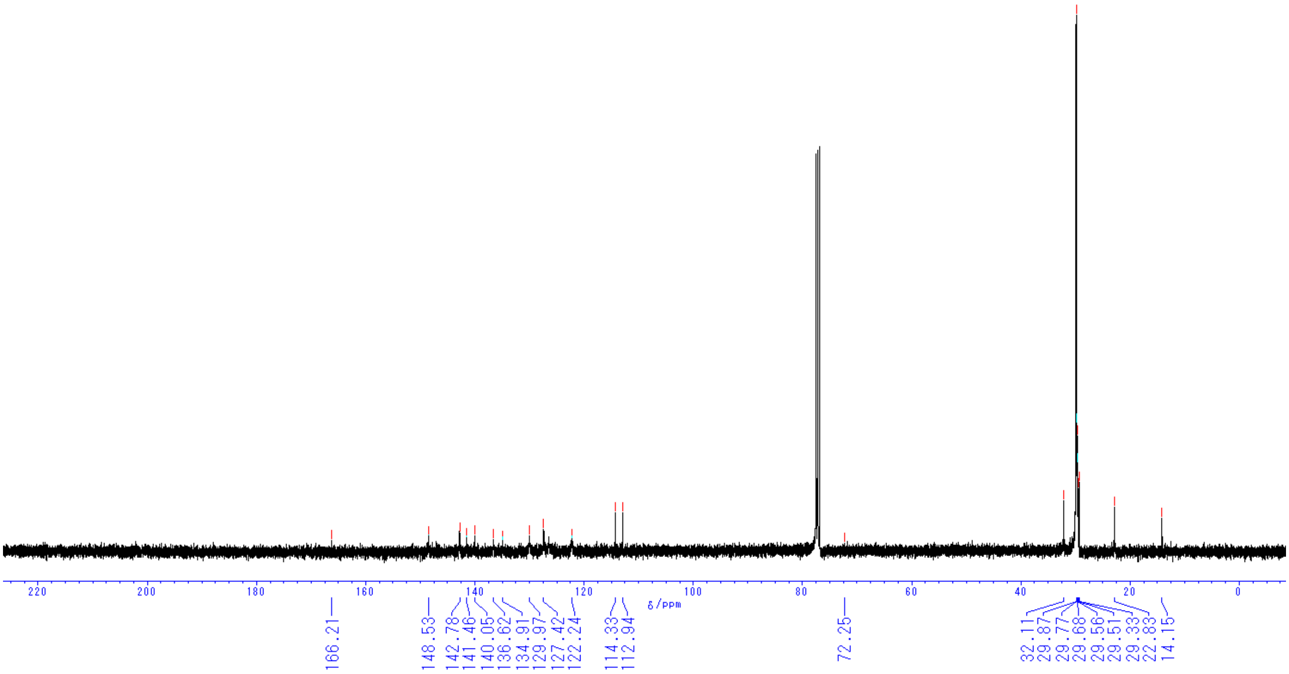




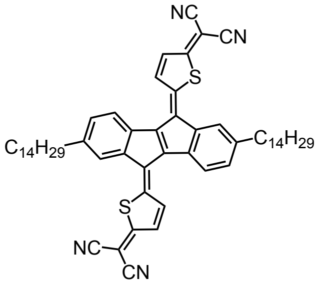
5,10-Bis[5-(dicyanomethylene)-4-eicoxyl-2(5*H*)-thienylidene]-5,10-dihydrodibenzo[*a,e*]pentalene (7b)

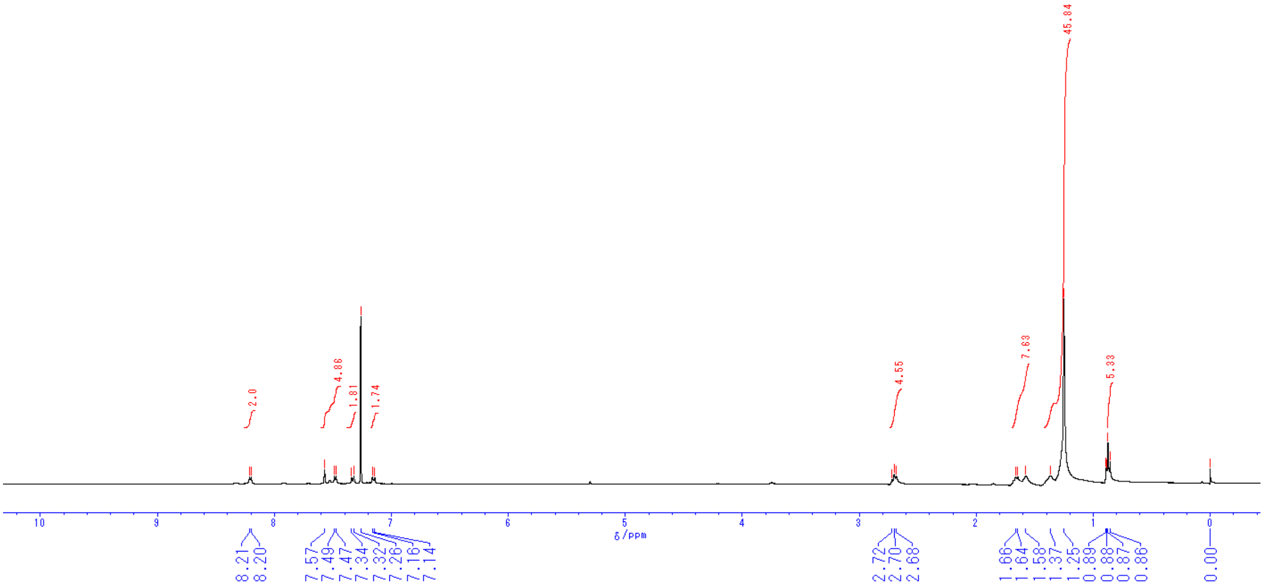


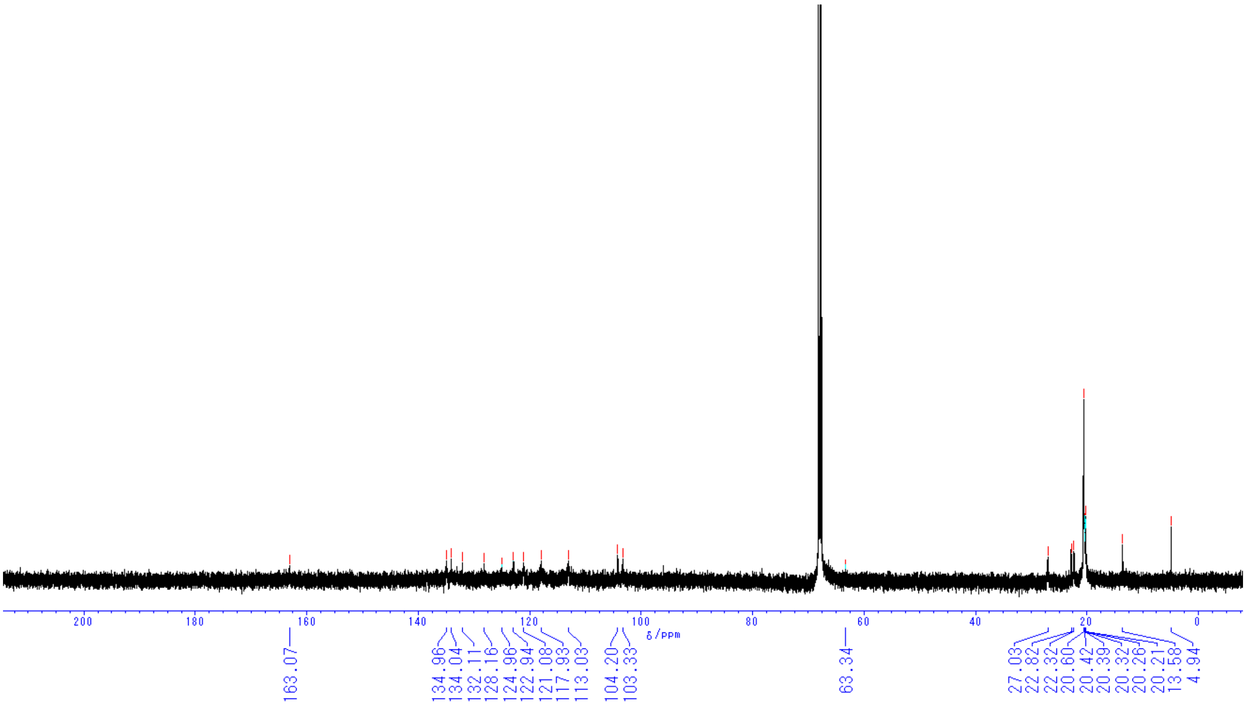




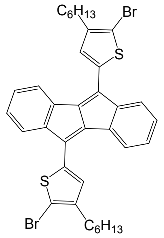
5,10-Bis[5-(dicyanomethylene)-2(5*H*)-thienylidene]-5,10-dihydro-2,7-tetradecyldibenzo[*a,e*] pentalene (7c)

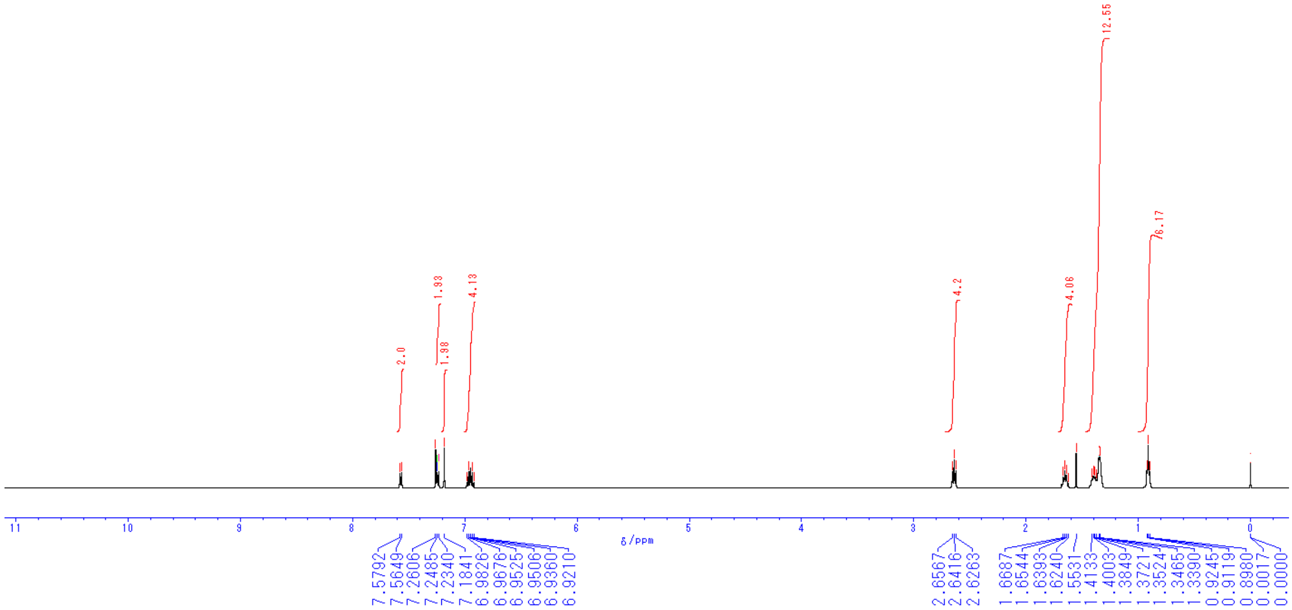


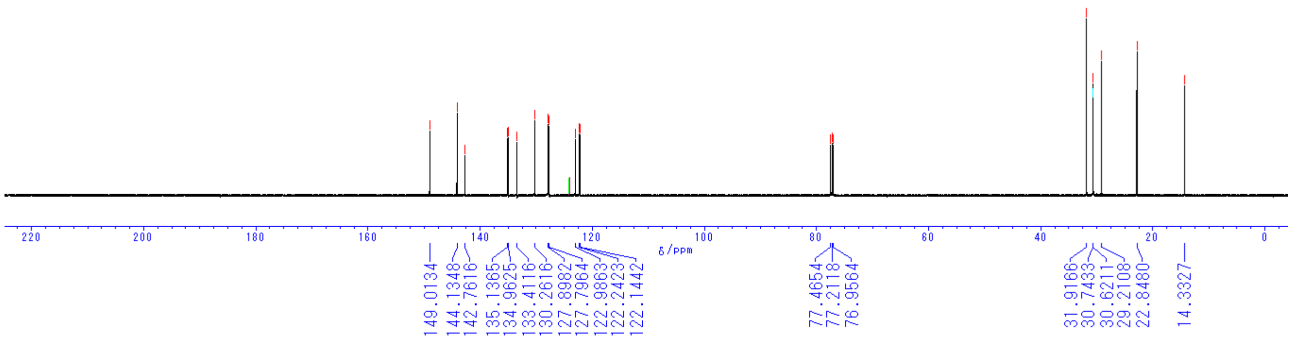




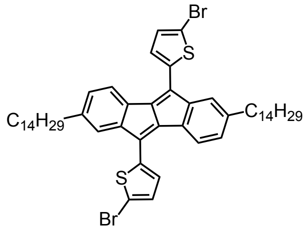
5,10-Bis[2-(5-bromo-4-hexyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (8a)

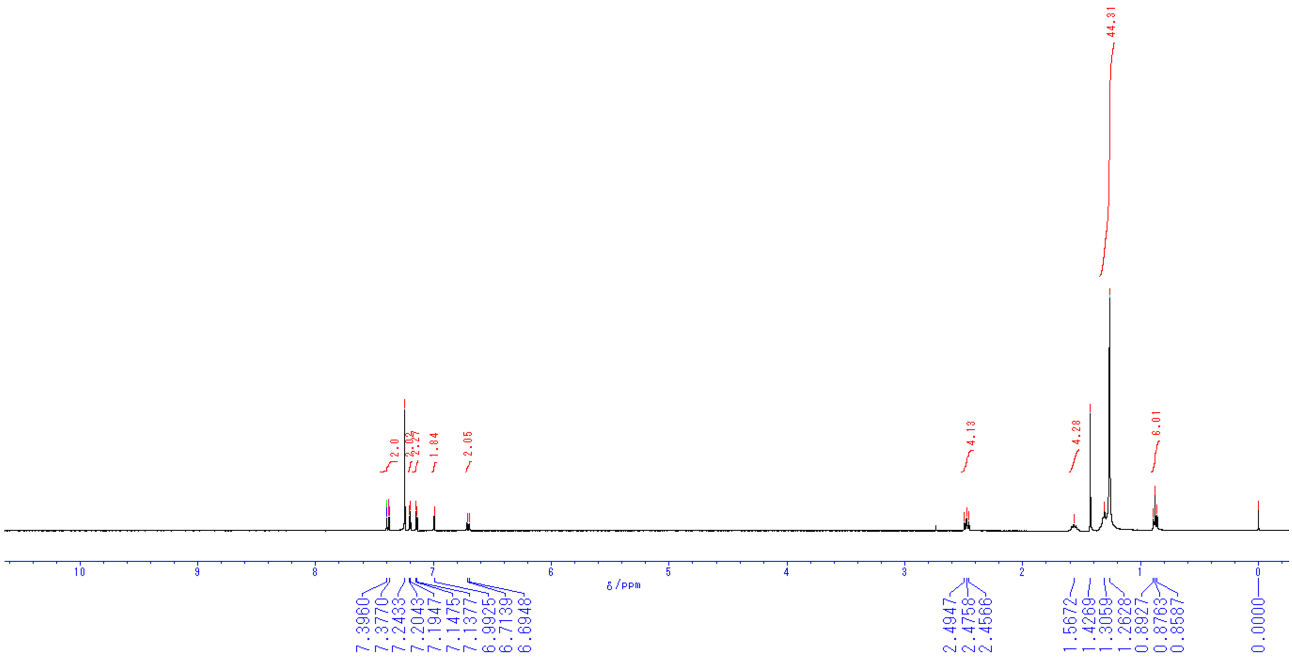


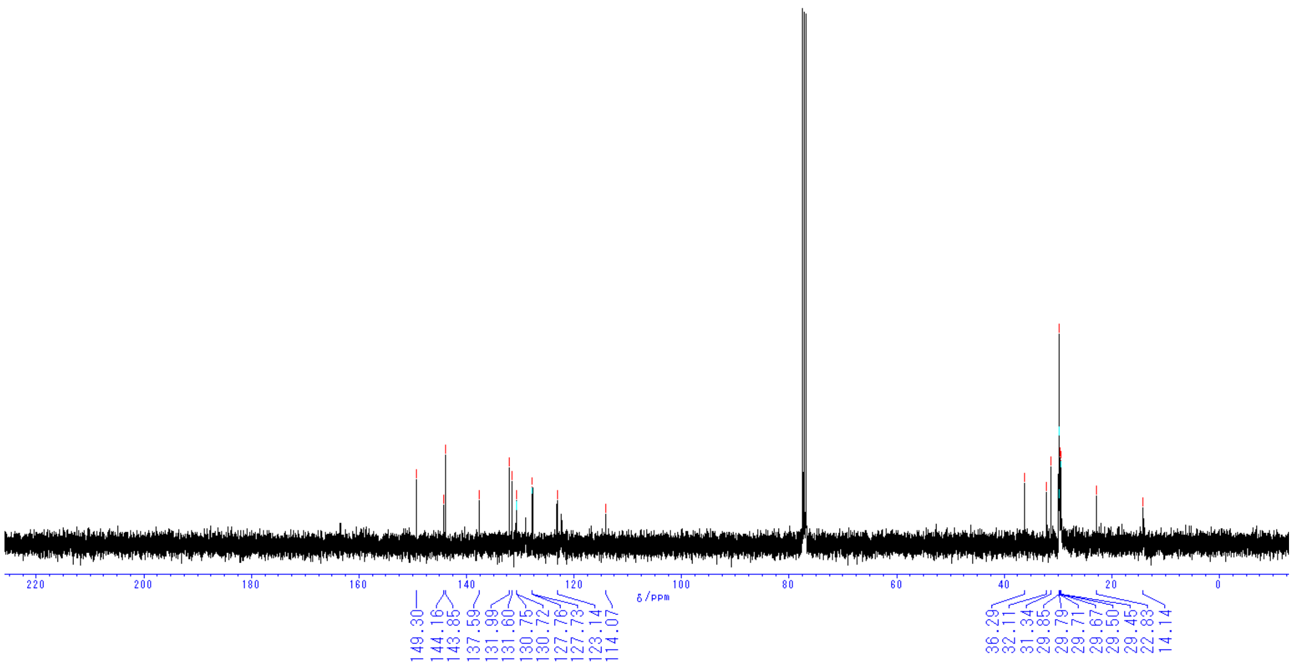




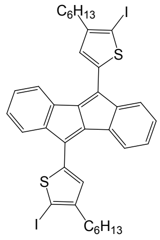
5,10-Bis[2-(5-bromo)thiophen-2-yl]-2,7-tetradecyl-dibenzo[*a*,*e*]pentalene (8c)

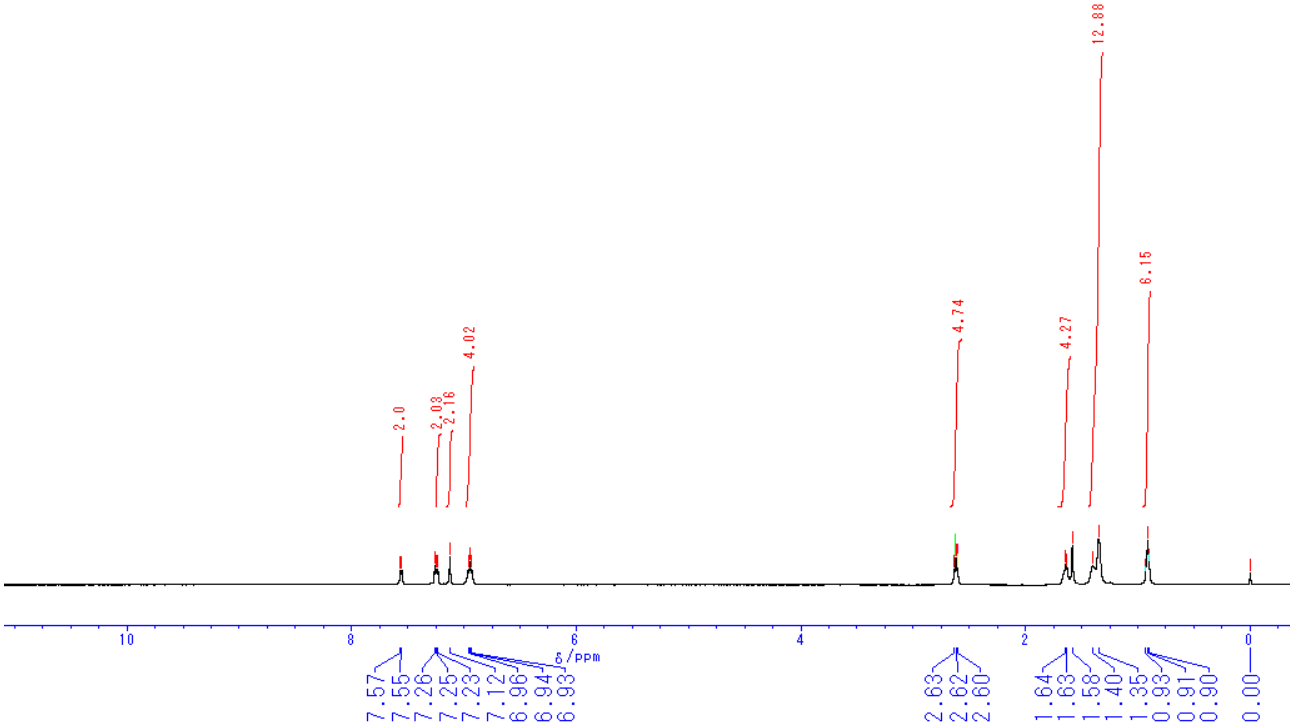


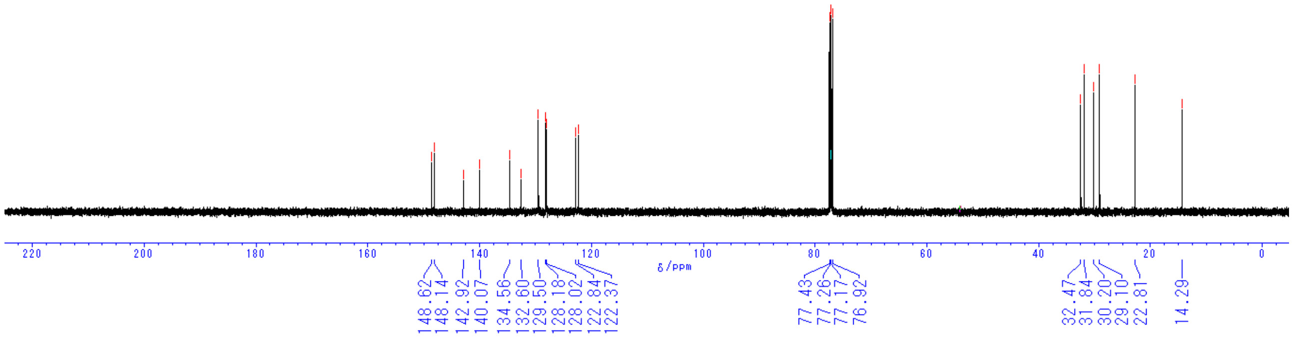




5,10-Bis[2-(5-iodo-4-hexyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (9a)







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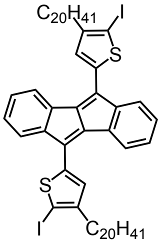
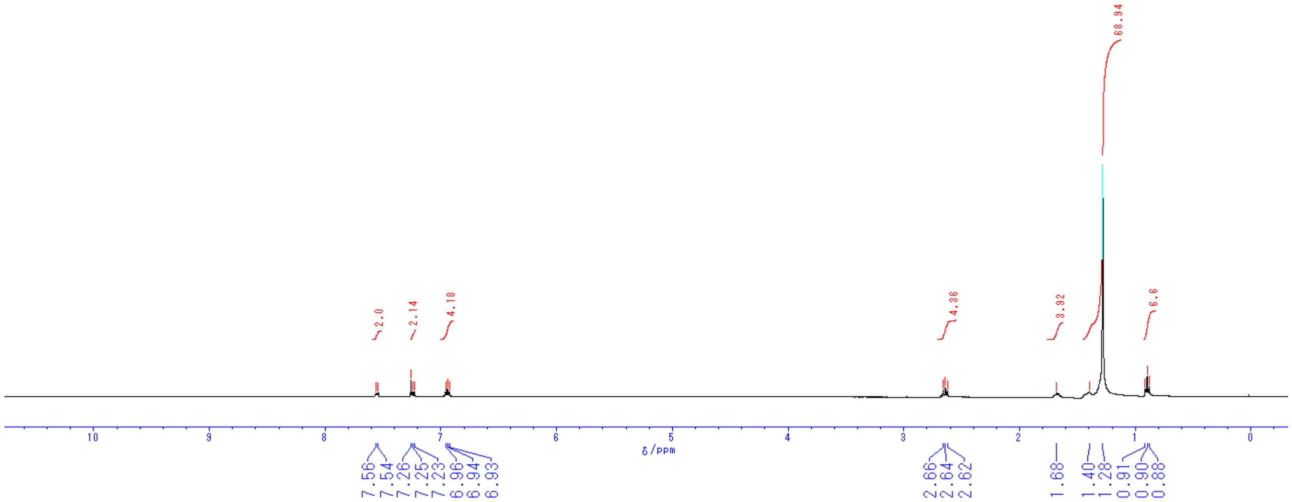
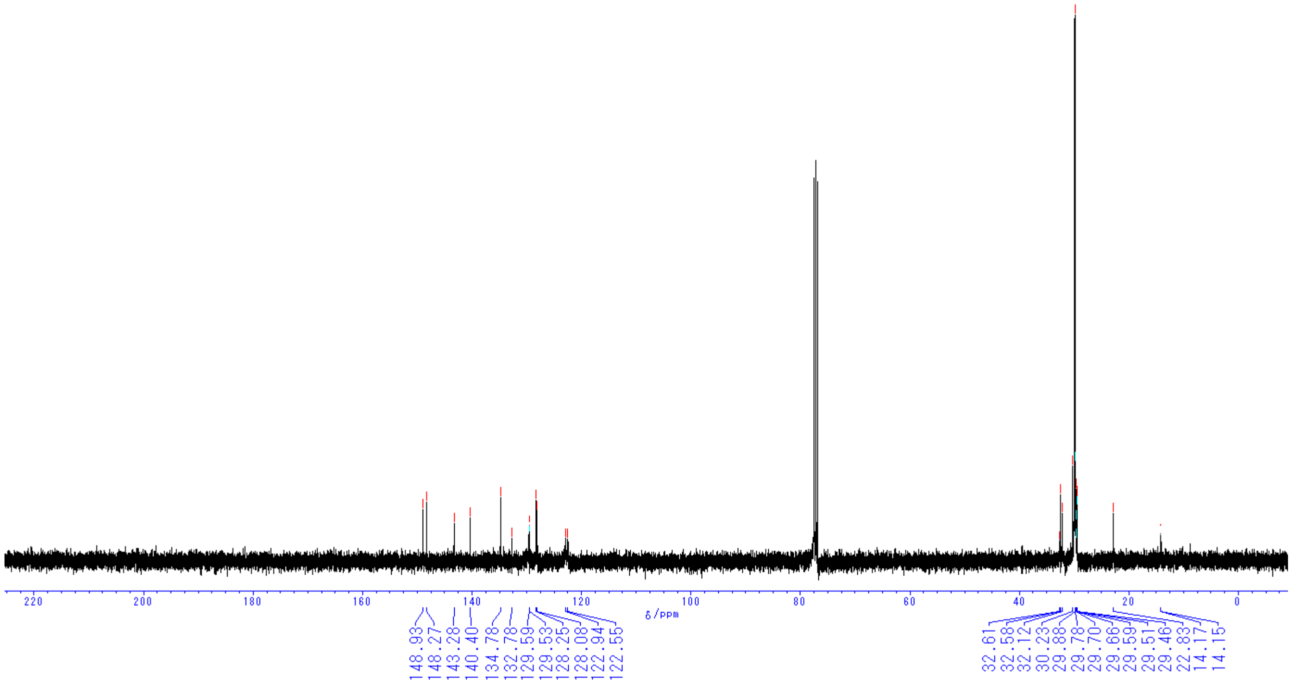
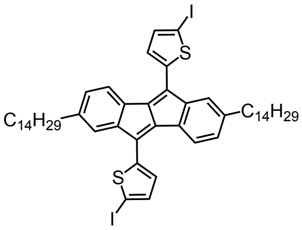
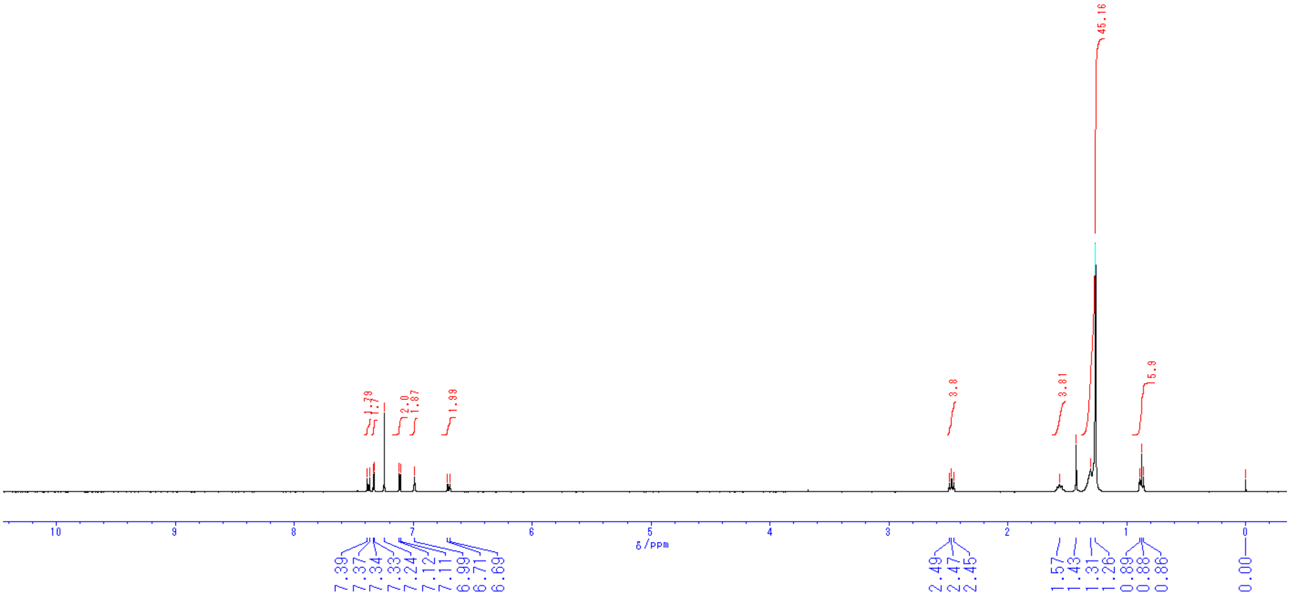


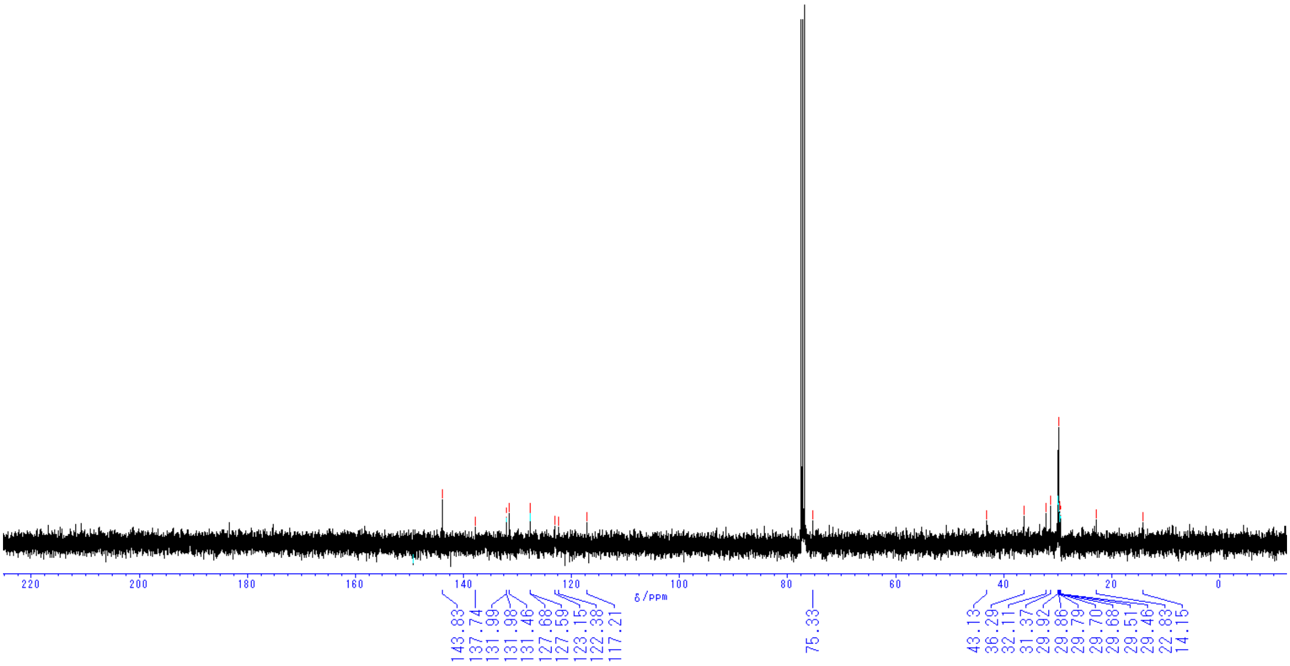




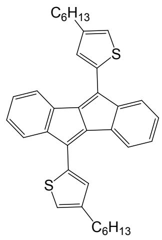
5,10-Bis[2-(5-iodo)thiophen-2-yl]-2,7-tetradecyl-dibenzo[*a,e*]pentalene (9c)

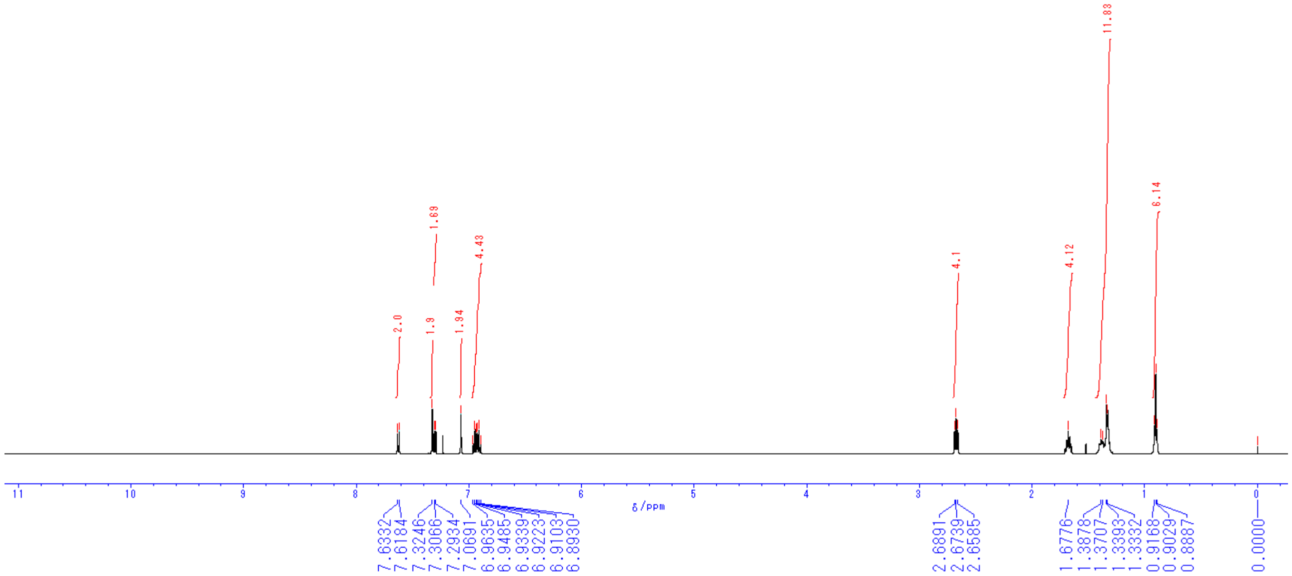


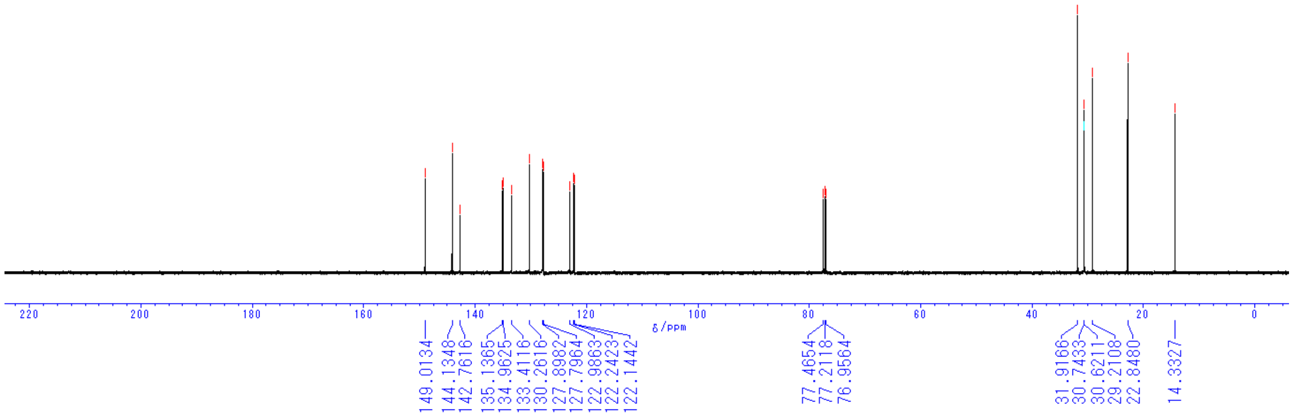




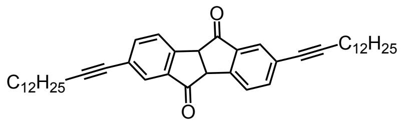
5,10-Bis[2-(4-hexyl)thiophen-2-yl]dibenzo[*a*,*e*]pentalene (11)

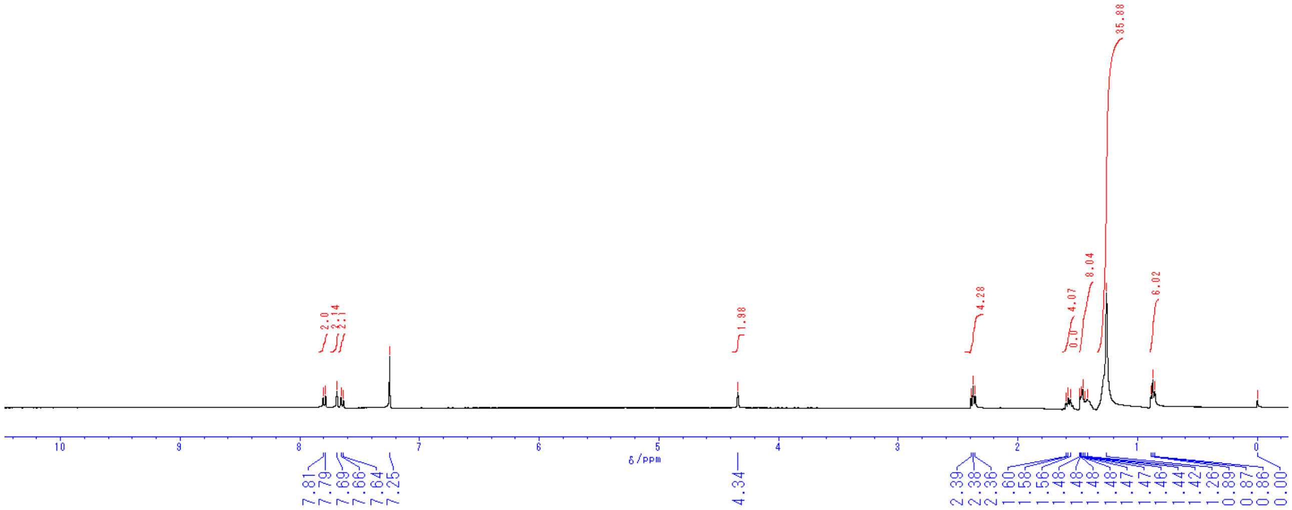


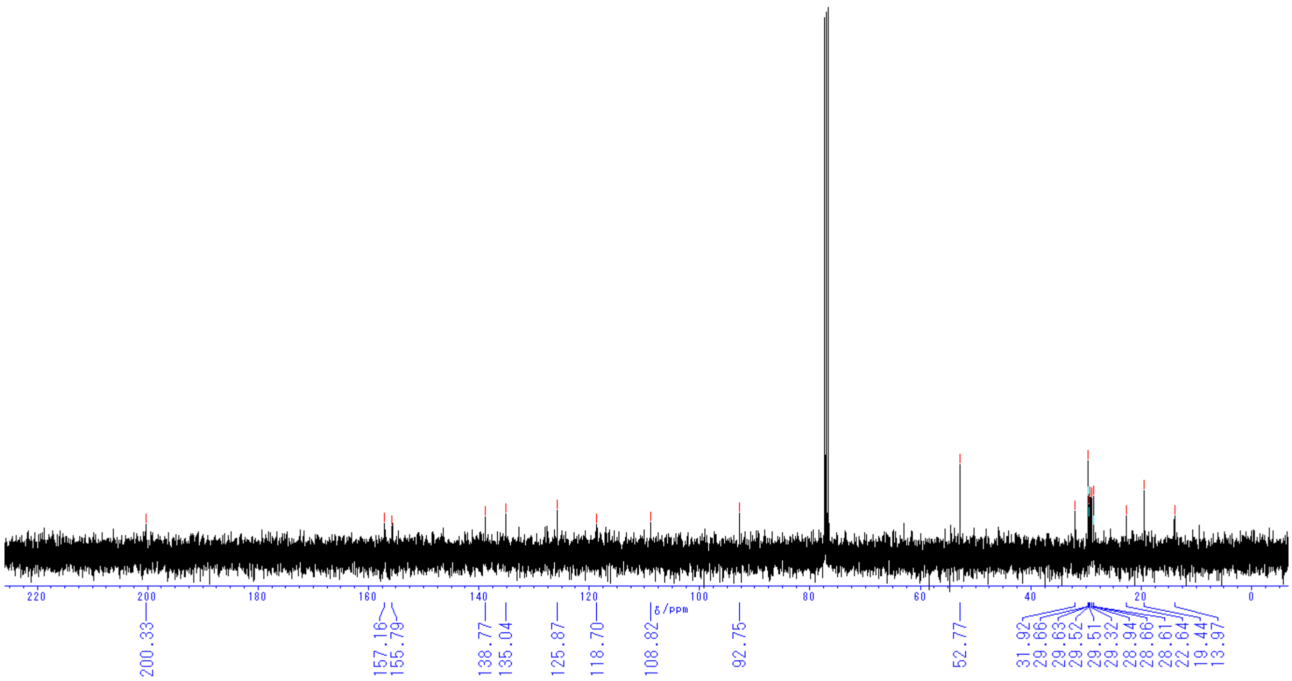




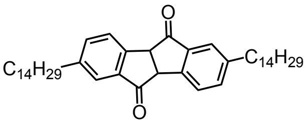
2,7-Di(tetradecyn-1-yl)dihydrodibenzo[*a,e*]pentalenedione-5,10-dione (13)

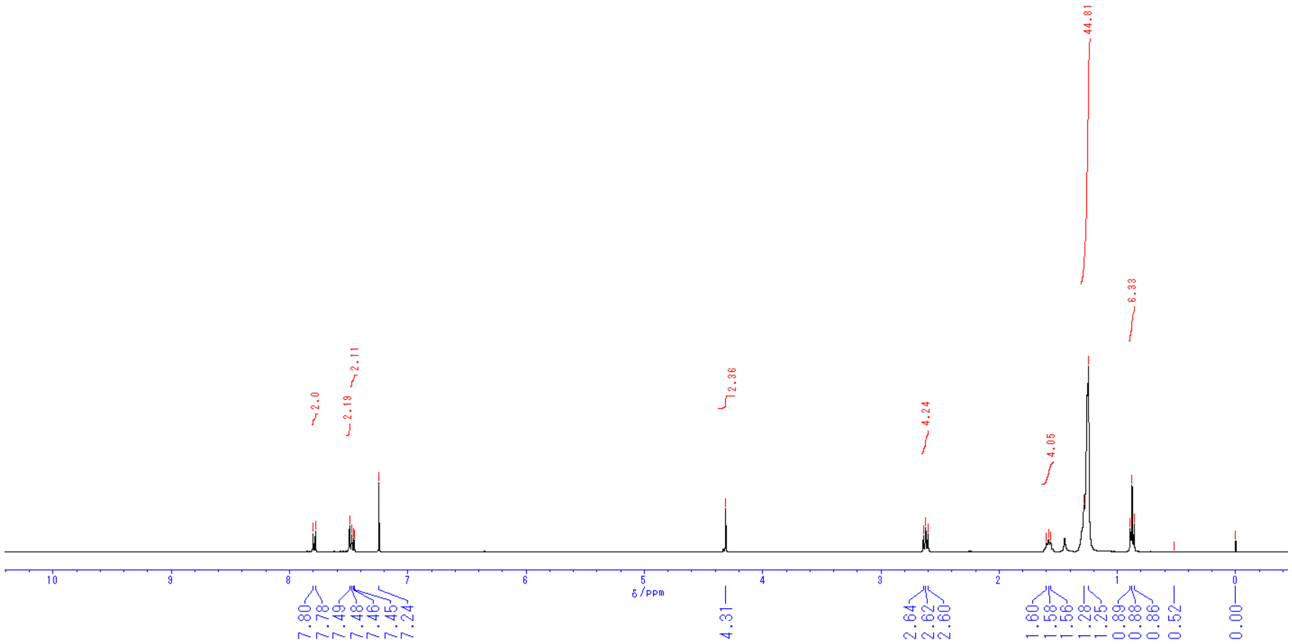


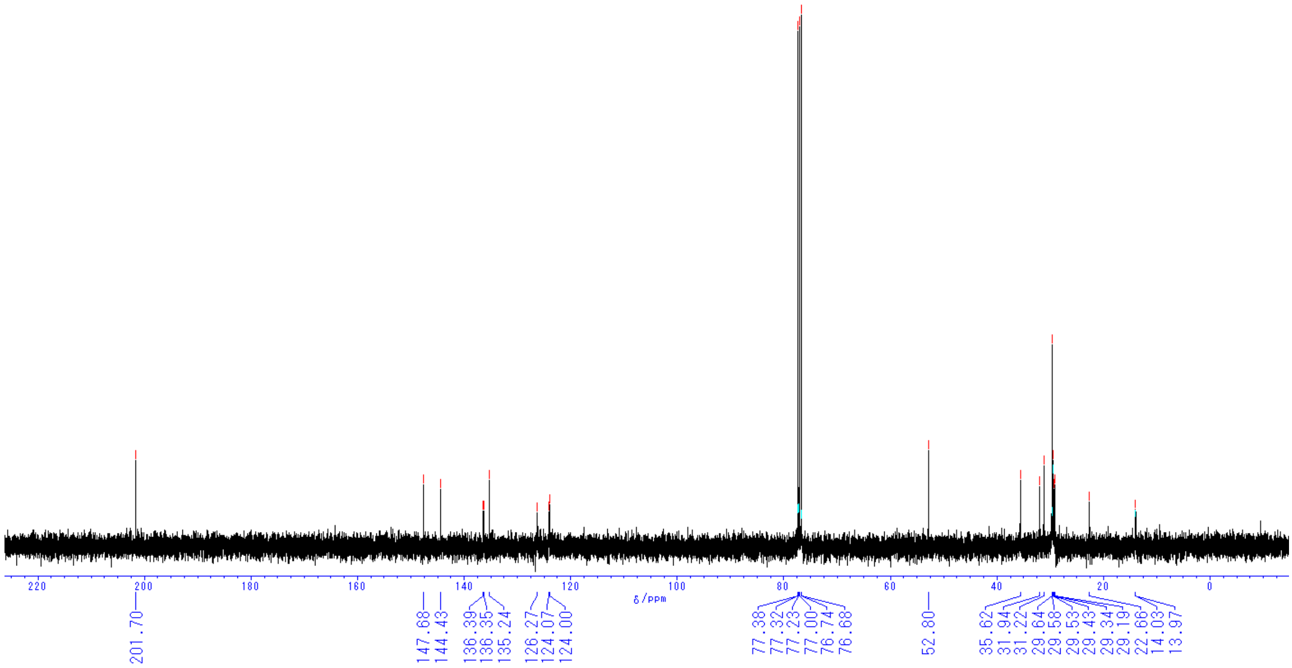




2,7-Ditetradecyldihydrodibenzo[*a,e*]pentalene-5,10-dione (14)







2,7-Ditetradecyl-5,10-di(2-thienyl)-dibenzo[a,e]pentalene (15)