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Fluorescent columnar bis(borondifluoride) complexes derived from tetraketonates

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Supporting Information

1. Experimental Section

(2Z,4Z)-3,4-Dihydroxy-1,6-bis(4-(hexyloxy)phenyl)hexa-2,4-diene-1,6-dione 2a (n = 6)

Yield 66%; mp 127.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, 6H, −CH_3, *J* = 6.4 Hz), 1.31−1.82 (m, 16H, −CH_2), 4.02 (t, 4H, −OCH_2, *J* = 6.6 Hz), 6.95 (d, 4H, Ar–H, *J* =9.0 Hz), 7.05 (s, 2H, −CCHCO), 7.99 (d, 4H, Ar–H, *J* =8.7 Hz) , 15.76 (s, 2H, -OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.01, 22.56, 25.63, 29.03, 31.51, 68.36, 95.06, 114.54, 128.09, 130.23, 163.73, 172.45, 190.81. MS (HRFAB, m/z): calcd: 494.2668. Found: 494.2665 [M^+].

(2Z,4Z)-3,4-Dihydroxy-1,6-bis(4-(decyloxy)phenyl)hexa-2,4-diene-1,6-dione 2a (n = 10)

Yield 67%; mp 118.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, 6H, −CH_3, *J* = 6.6 Hz), 1.26−1.84 (m, 32H, −CH_2), 4.02 (t, 4H, −OCH_2, *J* = 6.6 Hz), 6.95 (d, 4H, Ar–H, *J* = 9.0 Hz), 7.06 (s, 2H, −CCHCO), 7.99 (d, 4H, Ar–H, *J* = 8.7 Hz) , 15.76 (s, 2H, −OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.01, 22.67, 25.96, 29.07, 29.33, 29.54, 31.88, 68.39, 95.07, 114.56, 128.12, 130.24, 163.75, 172.49, 190.83. MS (HRFAB, m/z): calcd: 606.3920. Found: 606.3928 [M^+].

(2Z,4Z)-3,4-Dihydroxy-1,6-bis(4-(dodecyloxy)phenyl)hexa-2,4-diene-1,6-dione 2a (n = 12)

Yield 65%; mp 118.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, 6H, −CH_3, *J* = 6.0 Hz), 1.25−1.82 (m, 40H, −CH_2), 4.02 (t, 4H, −OCH_2, *J* = 6.3 Hz), 6.95 (d, 4H, Ar–H, *J* = 9.0 Hz), 7.05 (s, 2H, −CCHCO), 7.99 (d, 4H, Ar–H, *J* = 8.7 Hz) , 15.76 (s, 2H, −OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.11, 22.68, 25.95, 29.06, 29.34, 29.56, 29.63, 31.90, 68.36, 95.05, 114.53, 128.09, 130.23, 163.73, 172.44, 190.82. MS (HRFAB, m/z): calcd: 662.4546. Found: 662.4555 [M^+].

(2Z,4Z)-3,4-Dihydroxy-1,6-bis(4-(tetradecyloxy)phenyl)hexa-2,4-diene-1,6- dione 2a (n = 14)

Yellow solids. Yield 70%; mp 119.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, 6H, $-CH_3$, J = 6.0 Hz), 1.24−1.82 (m, 48H, $-CH_2$), 4.02 (t, 4H, $-OCH_2$, J = 6.6 Hz), 6.95 (d, 4H, Ar−H, J = 8.7 Hz), 7.05 (s, 2H, −CCHCO), 7.99 (d, 4H, Ar−H, J = 9.0 Hz), 15.76 (s, 2H, −OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.11, 22.69, 25.96, 29.08, 29.35, 29.57, 29.66, 31.92, 68.39, 95.07, 114.57, 130.24, 163.76, 205.97. MS (HRFAB, m/z): calcd: 718.5172. Found: 719.5231 $[M+H]^+$.

(2Z,4Z)-1,6-Bis(3,4-bis(hexyloxy)phenyl)-3,4-dihydroxyhexa-2,4-diene-1,6-dione 2b (n = 6)

Yellow powder. Yield 68%; mp 119.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, 12H, $-CH_3$, J = 7.0 Hz), 1.23−1.50 (m, 24H, $-CH_2$), 1.79−1.89 (m, 8H, $-CH_2$), 4.04–4.09 (m, 8H, $-OCH_2$), 6.89 (d, 2H, Ar−H, J = 8.6 Hz), 7.05 (s, 2H, −CCHCO), 7.55 (sd, 2H, Ar−H, ^4J = 2.0 Hz), 7.63 (dd, 2H, Ar−H, ^3J = 8.5 Hz, ^4J = 2.0 Hz), 15.75 (s, 2H, −OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.00, 22.59, 22.62, 25.67, 28.97, 29.11, 31.53, 69.08, 69.31, 95.26, 111.82, 112.07, 122.75, 128.37, 149.07, 154.16, 171.87, 191.18. MS (HRFAB, m/z): calcd: 694.4445. Found: 694.4449 [M^+].

(2Z,4Z)-1,6-Bis(3,4-bis(dodecyloxy)phenyl)-3,4-dihydroxyhexa-2,4-diene-1,6-dione 2b (n = 12)

Yellow powder. Yield 65%; mp 115.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (m, 12H, $-CH_3$, J = 6.6 Hz), 1.24−1.47 (m, 72H, $-CH_2$), 1.82−1.86 (m, 8H, $-CH_2$), 4.04–4.08 (m, 8H, $-OCH_2$), 6.89 (d, 2H, Ar−H, J = 8.7 Hz), 7.05 (s, 2H, −CCHCO), 7.55 (sd, 2H, Ar−H, ^4J = 2.1 Hz), 7.63 (dd, 2H, Ar−H, ^3J = 8.6 Hz, ^4J = 2.0 Hz), 15.75 (s, 2H, −OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.10, 22.68, 25.59, 25.94, 25.99 28.99, 29.14, 29.35, 29.60, 31.91, 67.96, 69.07, 69.30, 95.24, 111.83, 112.08, 122.73, 128.35, 149.06, 154.15, 171.86, 191.16. MS (HRFAB, m/z): calcd: 1030.8201. Found: 1030.8210 [M^+].

(2Z,4Z)-3,4-Dihydroxy-1,6-bis(3,4,5-tributoxyphenyl)hexa-2,4-diene-1,6-dione 2c (n = 4)

Yellow powder. Yield 66%; mp 113.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93–0.99 (m, 18H, $-CH_3$), 1.48–1.53 (m, 12H, $-CH_2$), 1.69–1.75 (m, 4H, $-CH_2$), 1.78–1.83 (m, 8H, $-CH_2$), 4.03–4.07 (m, 12H, $-OCH_2$), 7.03 (s, 2H, –CCHCO), 7.22 (s, 4H, Ar–H), 15.76 (s, 2H, –OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.80, 19.11, 19.25, 31.38, 32.34, 69.13, 73.29, 95.35, 106.73, 130.36, 143.58, 153.23, 173.01, 191.04. MS (HRFAB, m/z): calcd: 726.4343. Found: 726.4350 [M^+].

(2Z,4Z)-3,4-Dihydroxy-1,6-bis(3,4,5-tris(dodecyloxy)phenyl)hexa-2,4-diene-1,6-dione 2c (n = 12)

Yellow powder. Yield 61%; mp 61.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (t, 18H, $-CH_3$, J = 6.9 Hz), 1.25–1.50 (m, 108H, $-CH_2$), 1.70–1.76 (m, 4H, $-CH_2$), 1.79–1.84 (m, 8H, $-CH_2$), 4.02–4.06 (m, 12H, $-OCH_2$), 7.02 (s, 2H, –CCHCO), 7.22 (s, 4H, Ar–H), 15.77 (s, 2H, –OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.08, 22.68, 26.05, 26.10, 29.36, 29.55, 29.63, 29.70, 30.37, 31.93, 69.48, 73.69, 95.36, 106.77, 130.36, 143.62, 153.23, 173.04, 191.05. MS (HRFAB): calcd: 1399.1855. Found: 1399.1866 [M^+].

2. Single Crystal Data

Table S1. Bond lengths [Å] and angles [°] crystal **2a** (n = 6) and **1a** (n = 14)

Crystal **2a** (n = 6)			
Bond distances			
O(1)-C(1)	1.3230(15)	O(2)-C(3)	1.2628(14)
C(1)-C(2)	1.3582(18)	C(2)-C(3)	1.4360(18)
C(1)-C(1)	1.479(2)		
Bond angles			
O(1)-C(1)-C(2)	123.20(12)	O(1)-C(1)-C(1)	114.65(14)
C(2)-C(1)-C(1)	122.15(14)	C(1)-C(2)-C(3)	120.12(11)
O(2)-C(3)-C(2)	119.51(12)	O(2)-C(3)-C(4)	118.66(11)
C(2)-C(3)-C(4)	121.83(11)		
Crystal **1a** (n = 14)			
Bond distances			

B(1)-F(2)	1.3546(14)	B(1)-F(1)	1.3584(13)
B(1)-O(1)	1.4707(13)	B(1)-O(2)	1.5029(12)
O(1)-C(1)	1.3042(12)	O(2)-C(3)	1.2930(12)
C(1)-C(2)	1.3600(13)	C(2)-C(3)	1.4097(14)
Bond angles			
F(2)-B(1)-F(1)	111.11(9)	F(2)-B(1)-O(1)	109.69(9)
F(1)-B(1)-O(1)	109.14(9)	F(2)-B(1)-O(2)	108.21(9)
F(1)-B(1)-O(2)	108.02(8)	O(1)-B(1)-O(2)	110.66(8)
C(1)-O(1)-B(1)	120.94(8)	C(3)-O(2)-B(1)	123.75(8)
O(1)-C(1)-C(2)	124.12(9)	C(1)-C(2)-C(3)	118.94(9)
O(2)-C(3)-C(2)	119.53(9)	O(2)-C(3)-C(4)	116.56(8)

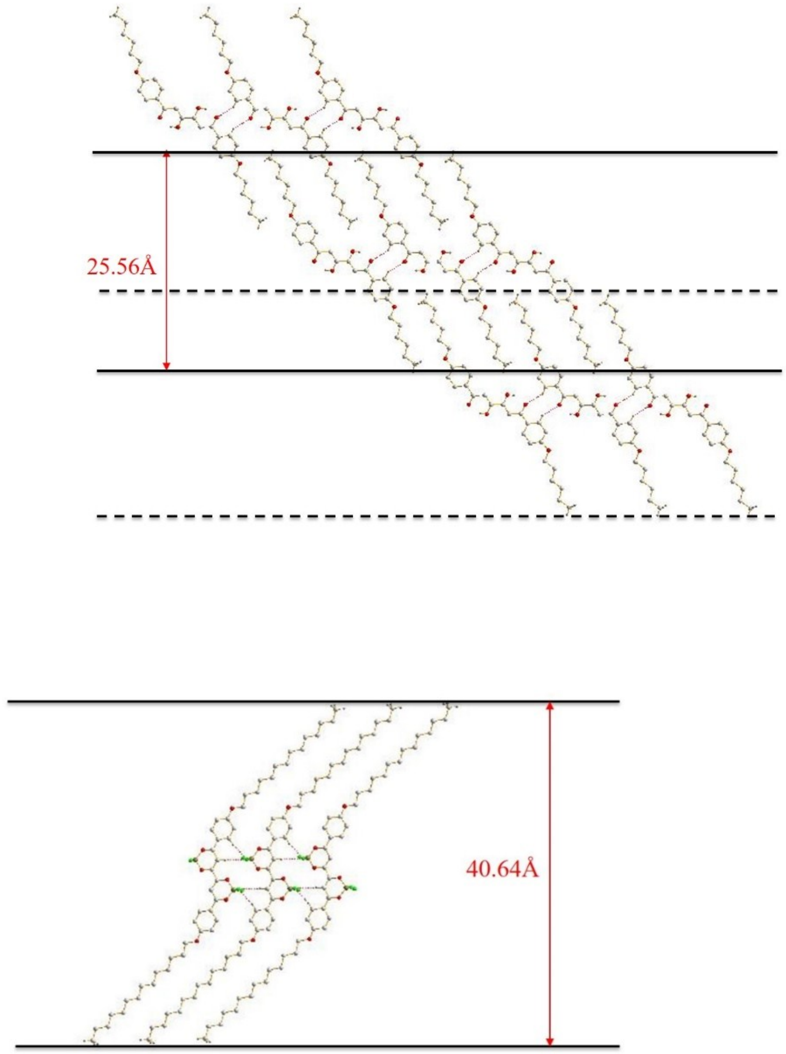

Fig. S1 Layered structures formed in crystal lattice by crystal **2a** (n = 6, top plot) and **1a** (n = 14, bottom plot). Solid and dash line represent the neighboring layers in the crystal lattice. The distance between layers is 25.56 Å in **2a** and 40.64 Å in **1a**.

3. Bar Graph of Phase Behavior

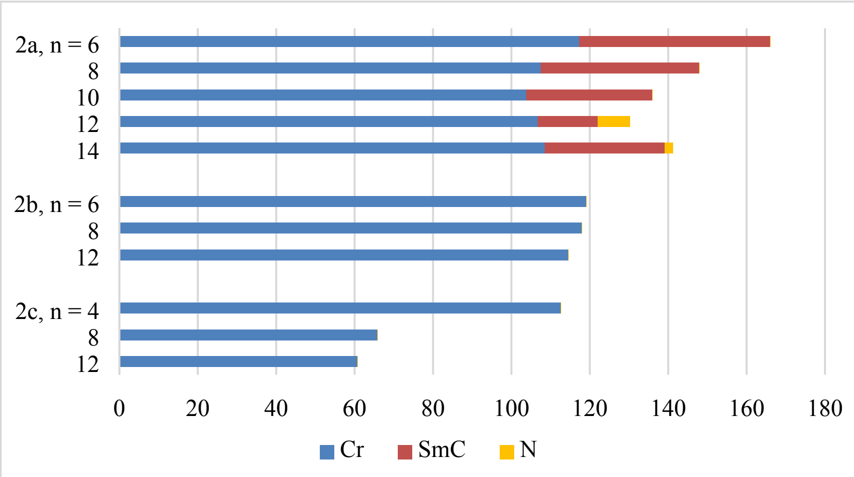

Fig. S2 Bar graphs showing the phase behavior of compounds **2a–2c**. The temperatures of compounds **2a** (n = 6–14) were taken from cooling process, and the temperatures of compounds **2b** (n = 6–12) and **2c** (n = 4–12) were taken from heating process.

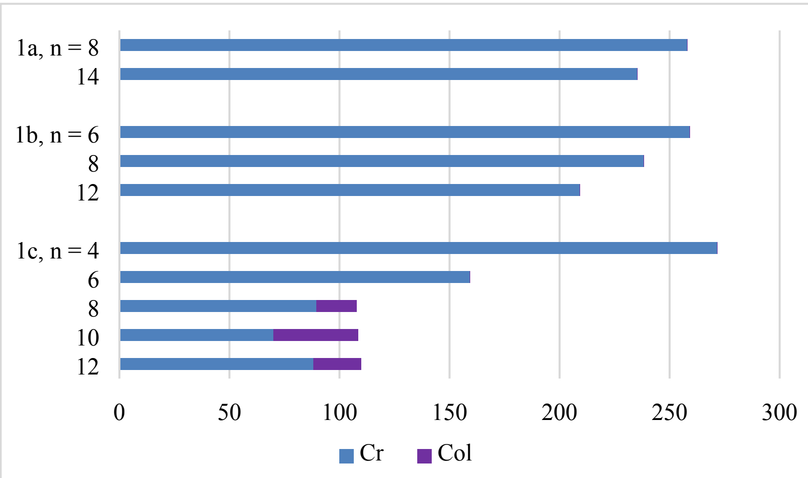

Fig. S3 Bar graphs showing the phase behavior of compounds **1a–1c**. The temperatures of compounds **1a** (n = 8, 14), **1b** (n = 6–12) and **1c** (n = 4, 6) were taken from heating process. The temperatures of compounds **1c** (n = 8–12) were taken from cooling process.

4. TGA Analysis

Table S2. The decomposition temperature[a] of compounds **1a–2c** by TGA analysis

Compd.	T_{dec} (°C)
2a (n = 8)	225.2
2b (n = 8)	247.8
2c (n = 8)	282.6
1a (n = 8)	314.5
1b (n = 8)	313.9
1c (n = 8)	311.1

[a]: Temperatures taken with a 5% weight loss.

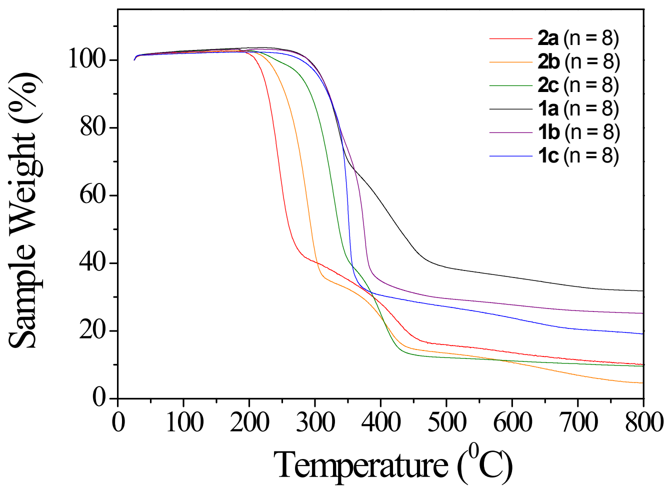

Fig. S4 TGA thermograms of compounds **1a–2c** (all n = 8).

5. X–ray Diffraction Study

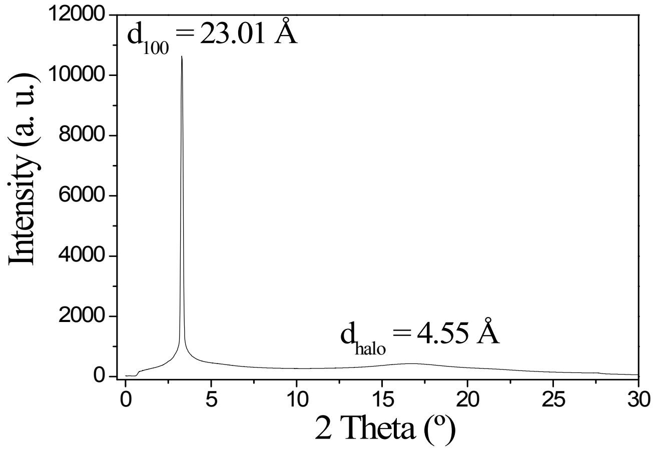

Fig. S5 The powder X–ray diffraction plots of **1c** (n = 8) at 99 °C.

6. Photophysical Property

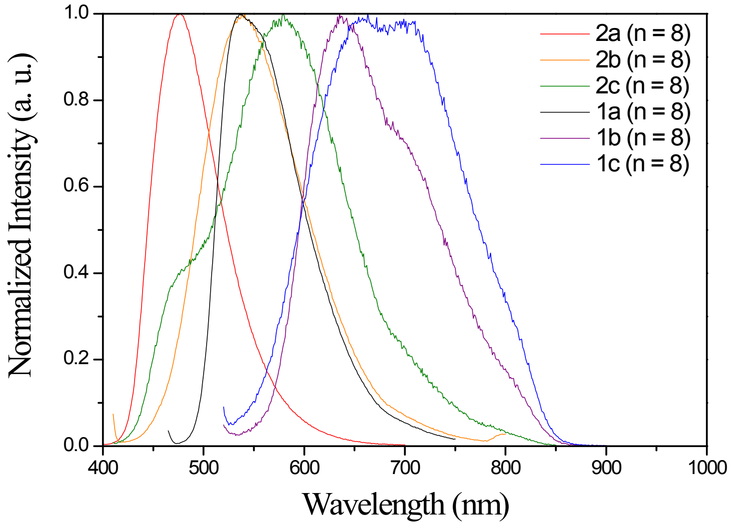

Fig. S6 Normalized fluorescent spectra of compounds **1a**–**2c** (n = 8). The PL spectra were excited at 459 nm (for **1a**, n = 8), 502 nm (for **1b**, n = 8), 497 nm (for **1c**, n = 8), 377 nm (for **2a**, n = 8), 401 nm (for **2b**, n = 8) and 397 nm (for **2c**, n = 8).

7. The ^{1}H and ^{13}C NMR Spectra of Compounds 1a-c

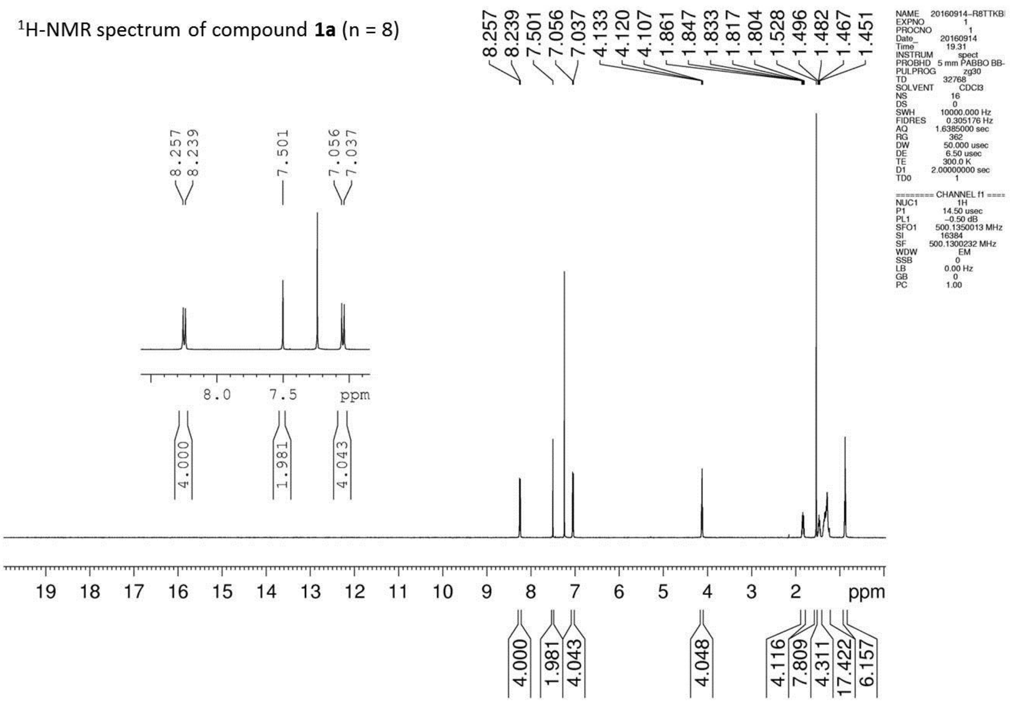

Fig. **S7** The ^{1}H-NMR spectrum of compound **1a** (n = 8).

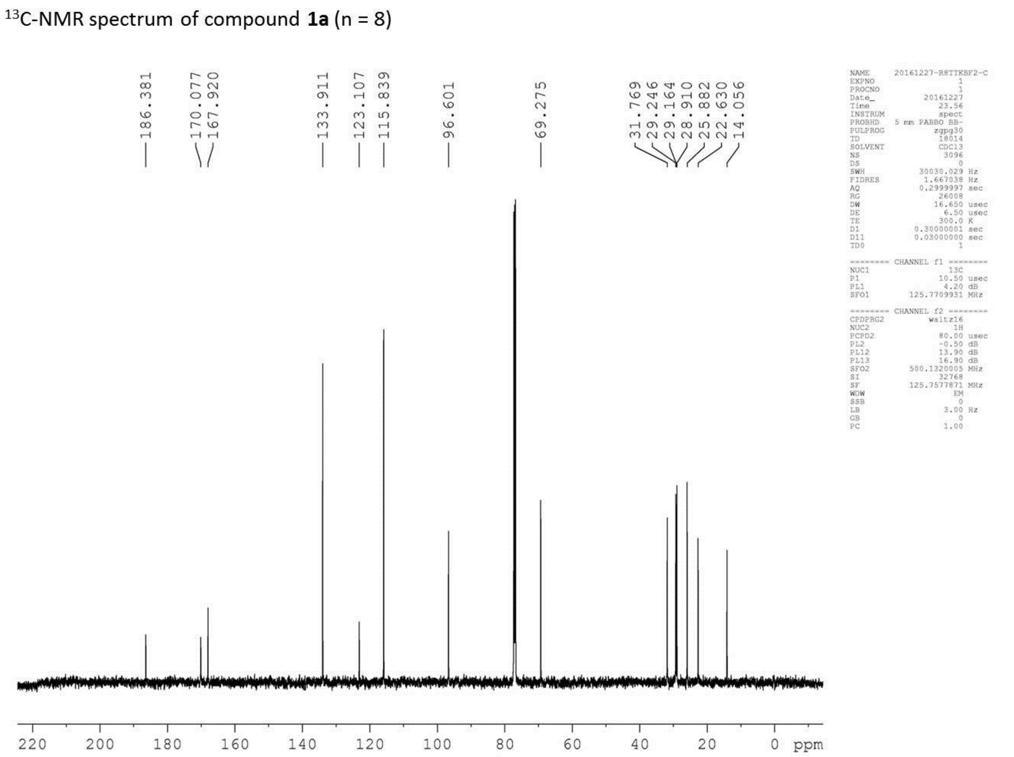

Fig. **S8** The ^{13}C-NMR spectrum of compound **1a** (n = 8).

^{1}H-NMR spectrum of compound **1b** (n = 8)

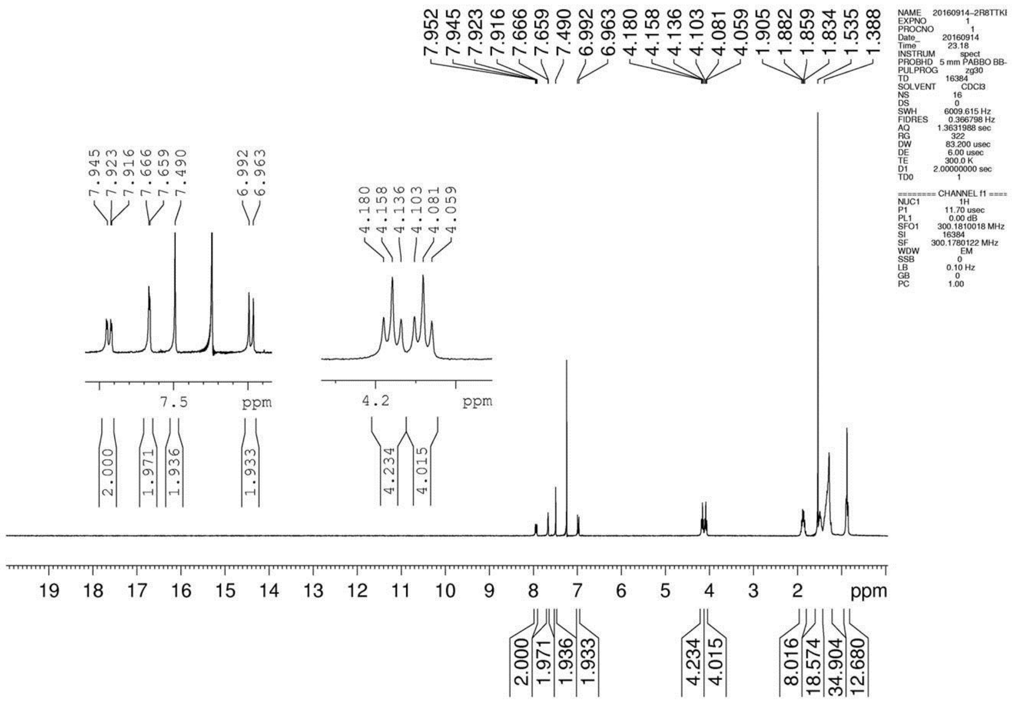

Fig. **S9** The ^{1}H-NMR spectrum of compound **1b** (n = 8).

^{13}C-NMR spectrum of compound **1b** (n = 8)

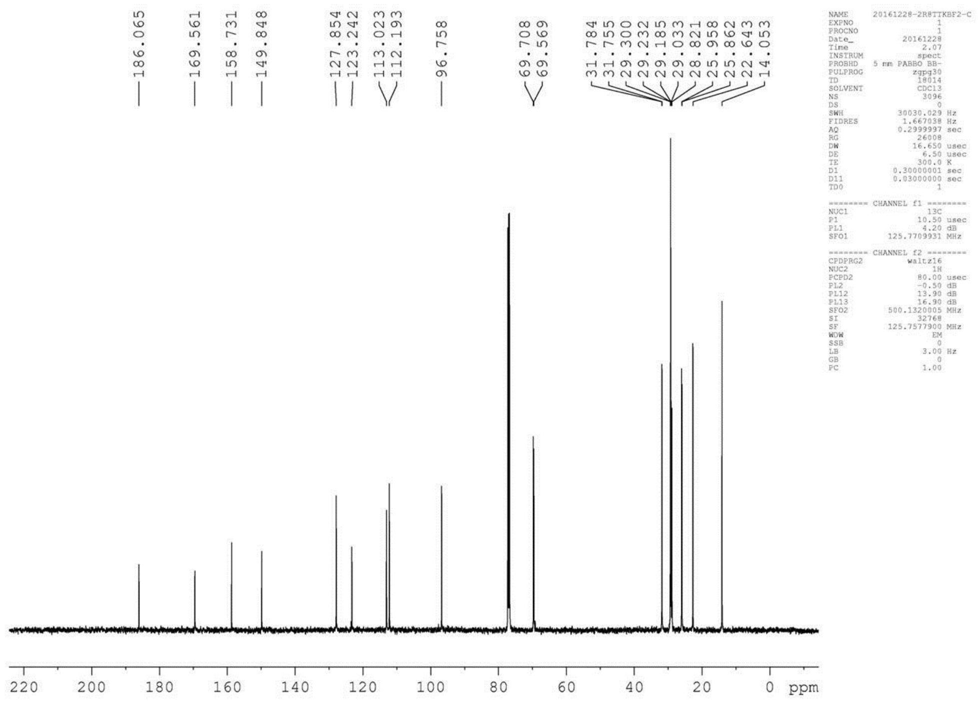

Fig. **S10** The ^{13}C-NMR spectrum of compound **1b** (n = 8).

^{1}H-NMR spectrum of compound **1c** (n = 10)

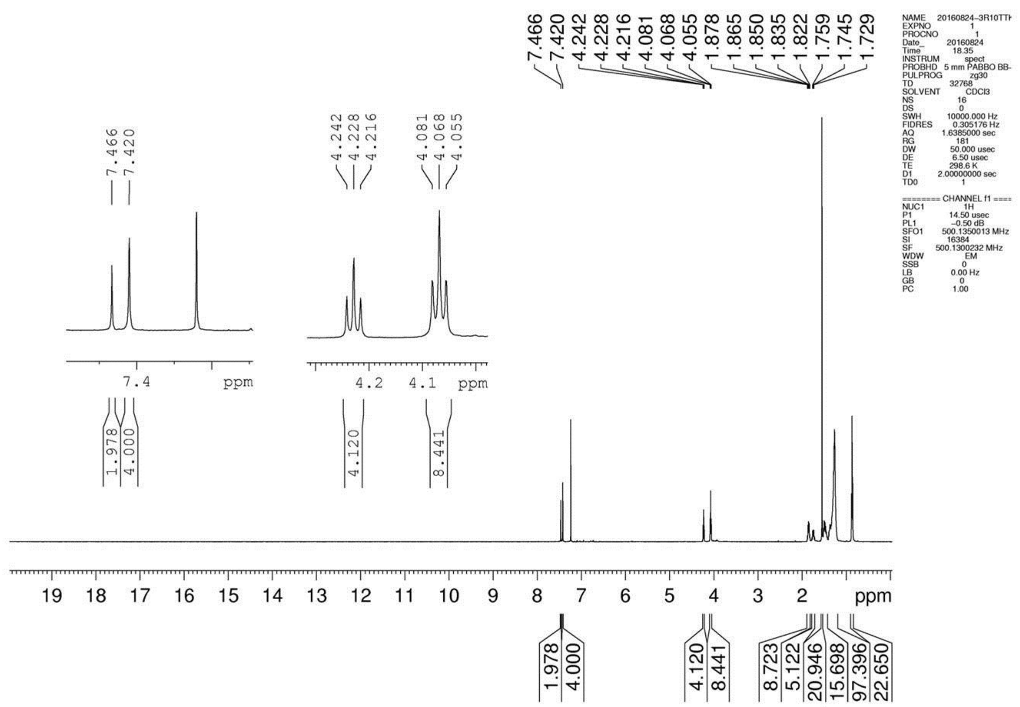

Fig. **S11** The ^{1}H-NMR spectrum of compound **1c** (n = 10).

^{13}C-NMR spectrum of compound **1c** (n = 10)

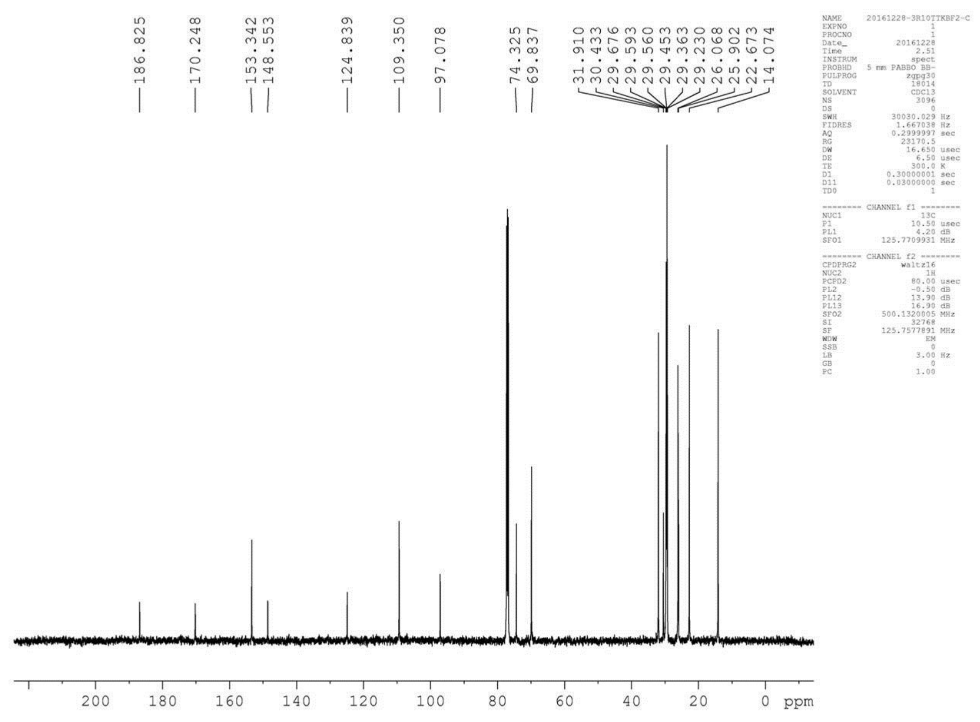

Fig. **S12** The ^{13}C-NMR spectrum of compound **1c** (n = 10).

8. DSC Thermographs of Compounds 1a–c

DSC curve of compound **1a** (n = 8)

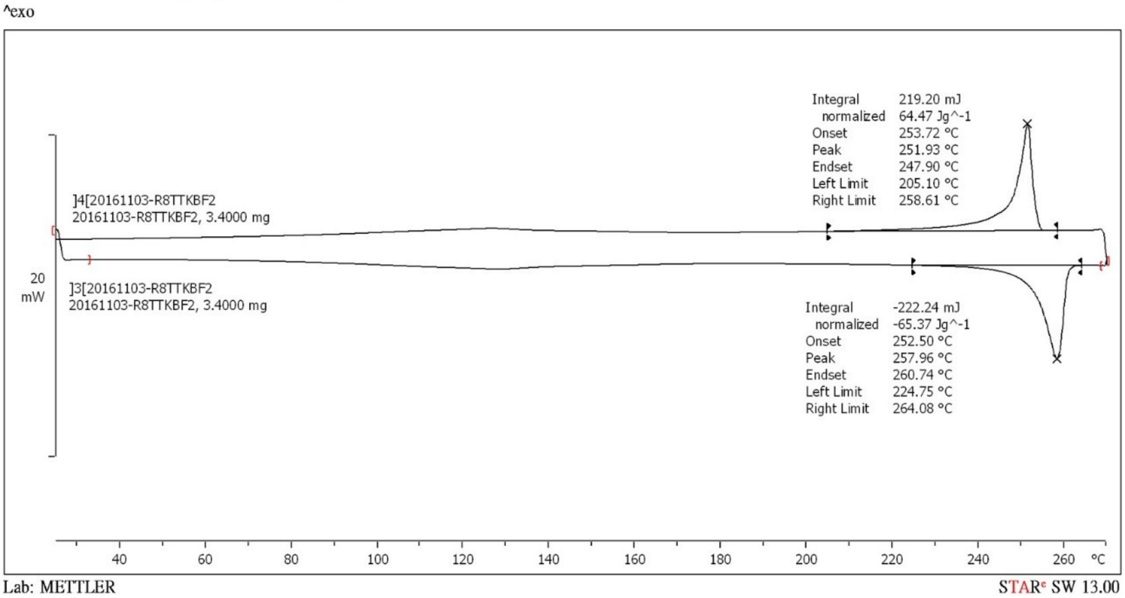

Fig. **S13** DSC thermograph of compound **1a** (n = 8).

DSC curve of compound **1b** (n = 8)

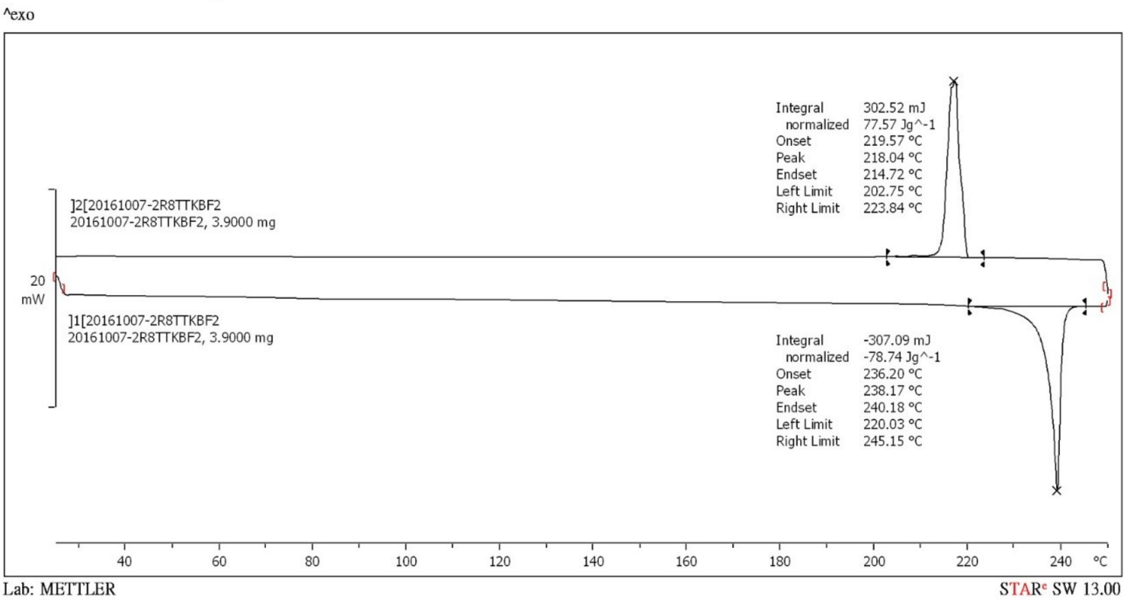

Fig. **S14** DSC thermograph of compound **1b** (n = 8).

DSC curve of compound **1c** (n = 8)

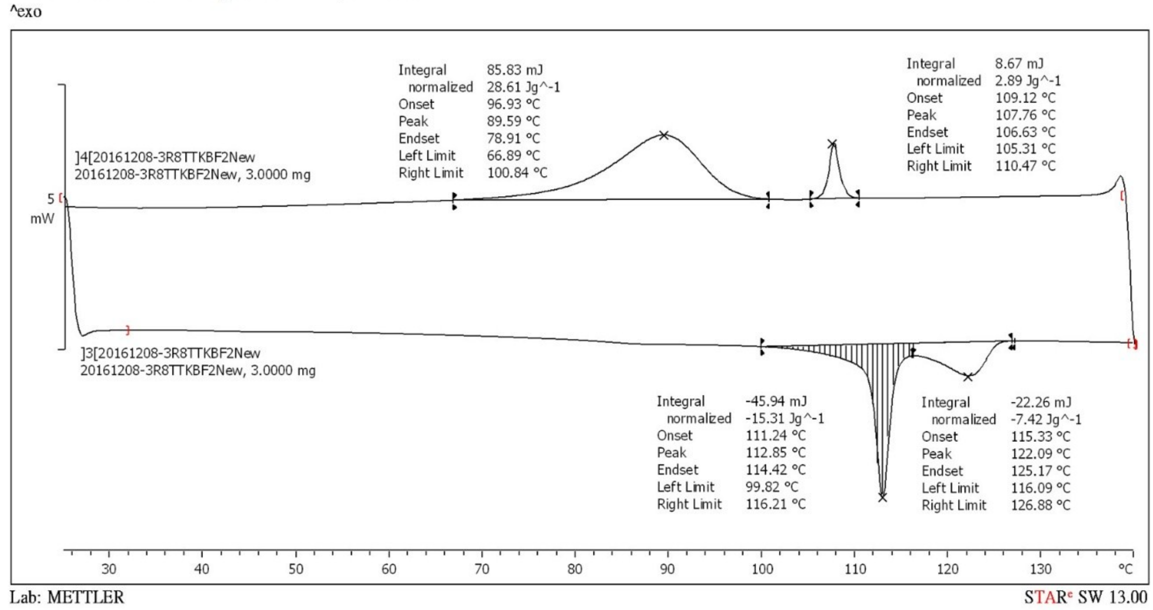

Fig. **S15** DSC thermograph of compound **1c** (n = 8).