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Electronic Supplementary Information

U-shaped oligomers with a molecular biaxiality stabilizing blue phases

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1. Spectroscopic data for compounds **I-*5***, **I-*7***, **II-*5***, **II-*7*** and I**I-*8***

1,2-Bis{6-[4-(4-(4-hexylphenyl)-2,3-difluorophenyl)phenyloxycarbonyl]pentyloxy}--benzene (I-*5*)

^{1}H NMR (500MHz, solvent $CDCl_3$, standard TMS) δ_H / ppm : 7.57(dd, 4H, Ar-H, *J* = 8.6 Hz, 1.7 Hz), 7.48(dd, 4H, Ar-H, *J* = 8.3 Hz, 1.7 Hz), 7.27(d, 4H, Ar-H, *J* = 8.0 Hz), 7.24-7.19(m, 4H, Ar-H), 7.17(d, 4H, Ar-H, *J* = 8.6 Hz), 6.91(s, 4H, Ar-H), 4.04(t, 4H, -O-CH_2-, *J* = 6.3 Hz), 2.66(t, 4H, Ar-CH_2-, *J* = 7.7 Hz), 2.63(t, 4H, -OCO-CH_2-, *J* = 7.4Hz), 1.94-1.31(m, 28H, aliphatic-H), 0.90(t, 6H, aliphatic-H, *J* = 6.9 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.0 (**C**=O), 150.7 (**C$_{Ar}$**-O), 149.2 (**C$_{Ar}$**-O), 148.5 (**C$_{Ar}$**-F), 143.2 (**C$_{Ar}$**-C_{Al}), 132.3 (**C$_{Ar}$**-C_{Ar}), 131.9 (**C$_{Ar}$**-C_{Ar}), 130.0 (**C$_{Ar}$**-C_{Ar}), 129.9 (**C$_{Ar}$**-H), 128.7 (**C$_{Ar}$**-H), 128.7 (**C$_{Ar}$**-H), 128.6 (**C$_{Ar}$**-C_{Ar}), 124.7 (**C$_{Ar}$**-H), 124.6 (**C$_{Ar}$**-H), 121.8 (**C$_{Ar}$**-H), 121.3 (**C$_{Ar}$**-H), 114.2 (**C$_{Ar}$**-H), 68.9 (**C**-O), 35.8 (**C$_{Al}$**-C_{Ar}), 34.4 (**C$_{Al}$**-H), 31.8 (**C$_{Al}$**-H), 31.4 (**C$_{Al}$**-H), 29.1 (**C$_{Al}$**-H), 29.1 (**C$_{Al}$**-H), 25.7 (**C$_{Al}$**-H), 24.7 (**C$_{Al}$**-H), 22.6 (**C$_{Al}$**-H), 14.1 (**C$_{Al}$**-H).

IR(KBr) ν_{max} / cm^{-1} : 2927, 2856, 1756, 1460, 1219.

UV-Vis (chloroform, *c* = 10 μM) λmax /nm: 276.

MAS (MALDI – TOF) $C_{68}H_{74}F_4O_6$ $[M + Na]^+$: 1058.24; found: 1058.25.

Elemental anal. Calcd for $C_{66}H_{70}F_4O_6$: C 76.57, H 6.82. Found: C 76.58, H 6.54%.

1,2-Bis{6-[4-(4-(4-hexylphenyl)-2,3-difluorophenyl)phenyloxycarbonyl]heptyloxy}--benzene (I-*7*)

^{1}H NMR (500MHz, solvent $CDCl_3$, standard TMS) δ_H / ppm : 7.58(dd, 4H, Ar-H, *J* = 8.6 Hz, 1.7 Hz), 7.49(dd, 4H, Ar-H, *J* = 8.0 Hz, 1.7 Hz), 7.28(d, 4H, Ar-H, *J* = 8.0 Hz), 7.24-7.20(m, 4H, Ar-H), 7.17(d, 4H, Ar-H, *J* = 6.9 Hz), 6.89(s, 4H, Ar-H), 4.01(t, 4H, -O-CH_2-, *J* = 6.6 Hz), 2.66(t, 4H, Ar-CH_2-, *J* = 7.7 Hz), 2.59(t, 4H, -OCO-CH_2-, *J* = 7.5 Hz), 1.88-1.30(m, 36H, aliphatic-H), 0.90(t, 6H, aliphatic-H, *J* = 7.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.1 (**C**=O), 150.7 (**C$_{Ar}$**-O), 149.3 (**C$_{Ar}$**-O), 148.5 (**C$_{Ar}$**-F), 143.2 (**C$_{Ar}$**-C_{Al}), 132.2 (**C$_{Ar}$**-C_{Ar}), 131.9 (**C$_{Ar}$**-C_{Ar}), 130.0 (**C$_{Ar}$**-C_{Ar}), 129.9 (**C$_{Ar}$**-H), 128.7 (**C$_{Ar}$**-H), 128.7 (**C$_{Ar}$**-H), 128.6 (**C$_{Ar}$**-C_{Ar}), 124.7 (**C$_{Ar}$**-H), 124.6 (**C$_{Ar}$**-H), 121.8 (**C$_{Ar}$**-H), 121.1 (**C$_{Ar}$**-H), 114.2 (**C$_{Ar}$**-H), 69.2 (**C**-O), 35.8 (**C$_{Al}$**-C_{Ar}), 34.4 (**C$_{Al}$**-H), 31.8 (**C$_{Al}$**-H), 31.4 (**C$_{Al}$**-H), 29.3 (**C$_{Al}$**-H), 29.1 (**C$_{Al}$**-H), 29.1 (**C$_{Al}$**-H), 29.1 (**C$_{Al}$**-H),

25.9 (**C**$_{Al}$-H), 24.9 (**C**$_{Al}$-H), 22.6 (**C**$_{Al}$-H), 14.1 (**C**$_{Al}$-H).

IR(KBr) ν_{max} / cm^{-1} : 2928, 2855, 1755, 1461, 1222.

UV-Vis (chloroform, *c* = 10 μM) λmax /nm: 276.

MAS (MALDI – TOF) $C_{70}H_{78}F_4O_6$ $[M + Na]^+$: 1114.35.24; found: 1113.96.

Elemental anal. Calcd. for $C_{70}H_{78}F_4O_6$: C 77.04, H 7.20. Found: C 77.14, H 6.84%.

2,2'-Bis{5-[4-(4-(4-hexylphenyl)-2,3-difluorophenyl)phenyloxycarbonyl]pentyloxy} -1,1'-biphenyl (II-*5*)

^{1}H NMR (500MHz, solvent $CDCl_3$, standard TMS) δ_H / ppm : 7.58(dd, 4H, Ar-H, *J* = 8.6 Hz, 1.7 Hz), 7.49(dd, 4H, Ar-H, *J* = 8.3 Hz, 1.7 Hz), 7.30-7.19(m, 12H, Ar-H), 7.16(d, 4H, Ar-H, *J* = 8.6 Hz), 6.99(t, 2H, Ar-H, *J* = 7.4 Hz), 6.96(d, 2H, Ar-H, *J* = 8.0 Hz), 3.95(t, 4H, -O-CH_2-, *J* = 6.3 Hz), 2.66(t, 4H, Ar-CH_2-, *J* = 7.7 Hz), 2.50(t, 4H, -OCO-CH_2-, *J* = 7.4 Hz), 1.73-1.30(m, 28H, aliphatic-H), 0.90(t, 6H, aliphatic-H, *J* = 7.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.0 (**C**=O), 156.6 (**C**$_{Ar}$-O), 150.6 (**C**$_{Ar}$-O), 148.5 (**C**$_{Ar}$-F), 143.2 (**C**$_{Ar}$-C_{Al}), 132.3 (**C**$_{Ar}$-C_{Ar}), 131.8 (**C**$_{Ar}$-C_{Ar}), 131.6 (**C**$_{Ar}$-H), 130.0 (**C**$_{Ar}$-C_{Ar}), 129.9 (**C**$_{Ar}$-H), 128.7 (**C**$_{Ar}$-H), 128.7 (**C**$_{Ar}$-H), 128.6 (**C**$_{Ar}$-C_{Ar}), 128.5 (**C**$_{Ar}$-C_{Ar}), 128.4 (**C**$_{Ar}$-H), 124.7 (**C**$_{Ar}$-H), 124.6 (**C**$_{Ar}$-H), 121.8 (**C**$_{Ar}$-H), 120.3 (**C**$_{Ar}$-H), 112.5 (**C**$_{Ar}$-H), 68.2 (**C**-O), 35.8 (**C**$_{Al}$-C_{Ar}), 34.3 (**C**$_{Al}$-H), 31.8 (**C**$_{Al}$-H), 31.3 (**C**$_{Al}$-H), 29.1 (**C**$_{Al}$-H), 28.9 (**C**$_{Al}$-H), 25.6 (**C**$_{Al}$-H), 24.6 (**C**$_{Al}$-H), 22.6 (**C**$_{Al}$-H), 14.1 (**C**$_{Al}$-H).

IR(KBr) ν_{max} / cm^{-1} : 2927, 2855, 1758, 1460, 1206.

UV-Vis (chloroform, *c* = 10 μM) λmax /nm: 277.

MAS (MALDI – TOF) $C_{72}H_{74}F_4O_6$ $[M + Na]^+$: 1134.34; found: 1134.44.

Elemental anal. Calcd for $C_{72}H_{74}F_4O_6$: C 77.81, H 6.71. Found: C 77.83, H 6.42%.

2,2'-Bis{7-[4-(4-(4-hexylphenyl)-2,3-difluorophenyl)phenyloxycarbonyl]heptyloxy} -1,1'-biphenyl (II-*7*)

^{1}H NMR (500MHz, solvent $CDCl_3$, standard TMS) δ_H / ppm : 7.58(dd, 4H, Ar-H, *J* = 8.6 Hz, 1.7 Hz), 7.49(dd, 4H, Ar-H, *J* = 8.3 Hz, 1.7 Hz), 7.30-7.21(m, 12H, Ar-H), 7.18(d, 4H, Ar-H, *J* = 8.6 Hz), 6.97(t, 2H, Ar-H, *J* = 7.5 Hz), 6.94(d, 2H, Ar-H, *J* = 8.0 Hz), 3.91(t, 4H, -O-CH_2-, *J* = 6.6 Hz), 2.66(t, 4H, Ar-CH_2-, *J* = 8.0 Hz), 2.55(t, 4H, -OCO-CH_2-, *J* = 7.7 Hz), 1.72(qui, 4H, aliphatic-H, *J* = 7.5 Hz), 1.68-1.31(m, 32H, aliphatic-H), 0.90(t, 6H, aliphatic-H, *J* = 7.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2 (**C**=O), 156.6 (**C$_{Ar}$**-O), 150.7 (**C$_{Ar}$**-O), 148.5 (**C$_{Ar}$**-F), 143.3 (**C$_{Ar}$**-C$_{Al}$), 132.3 (**C$_{Ar}$**-C$_{Ar}$), 131.9 (**C$_{Ar}$**-C$_{Ar}$), 131.6 (**C$_{Ar}$**-H), 130.0 (**C$_{Ar}$**-C$_{Ar}$), 129.9 (**C$_{Ar}$**-H), 128.7 (**C$_{Ar}$**-H), 128.7 (**C$_{Ar}$**-H), 128.6 (**C$_{Ar}$**-C$_{Ar}$), 128.4 (**C$_{Ar}$**-C$_{Ar}$), 128.3 (**C$_{Ar}$**-H), 124.7 (**C$_{Ar}$**-H), 124.6 (**C$_{Ar}$**-H), 121.8 (**C$_{Ar}$**-H), 120.0 (**C$_{Ar}$**-H), 112.3 (**C$_{Ar}$**-H), 68.4 (**C**-O), 35.8 (**C$_{Al}$**-C$_{Ar}$), 34.4 (**C$_{Al}$**-H), 31.8 (**C$_{Al}$**-H), 31.4 (**C$_{Al}$**-H), 29.2 (**C$_{Al}$**-H), 29.1 (**C$_{Al}$**-H), 29.0 (**C$_{Al}$**-H), 28.9(**C$_{Al}$**-H), 25.9 (**C$_{Al}$**-H), 24.8 (**C$_{Al}$**-H), 22.6 (**C$_{Al}$**-H), 14.1 (**C$_{Al}$**-H)

IR(KBr) ν_{max} / cm^{-1} : 2929, 2855, 1757, 1461, 1210.

UV-Vis (chloroform, *c* = 10 μM) λmax /nm: 277.

MAS (MALDI – TOF) $C_{76}H_{82}F_4O_6$ $[M + Na]^+$: 1190.44; found: 1190.59.

Elemental anal. Calcd. for $C_{76}H_{82}F_4O_6$: C 78.19, H 7.08. Found: C 78.39, H 6.67%.

2,2'-Bis{8-[4-(4-(4-hexylphenyl)-2,3-difluorophenyl)phenyloxycarbonyl]octyloxy}-1,1'-biphenyl (II-*8*)

^{1}H NMR (500MHz, solvent $CDCl_3$, standard TMS) δ_H / ppm : 7.58(dd, 4H, Ar-H, *J* = 8.6 Hz, 1.7 Hz), 7.49(dd, 4H, Ar-H, *J* = 8.3 Hz, 1.7 Hz), 7.29-7.21(m, 12H, Ar-H), 7.18(d, 4H, Ar-H, *J* = 8.6 Hz), 6.97(t, 2H, Ar-H, *J* = 7.5 Hz), 6.94(d, 2H, Ar-H, *J* = 8.6 Hz), 3.90(t, 4H, -O-CH_2-, *J* = 6.6 Hz), 2.66(t, 4H, Ar-CH_2-, *J* = 7.7 Hz), 2.57(t, 4H, -OCO-CH_2-, *J* = 7.5 Hz), 1.75(qui, 4H, aliphatic-H, *J* = 7.5 Hz), 1.69-1.28(m, 32H, aliphatic-H), 0.90(t, 6H, aliphatic-H, *J* = 7.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2 (**C**=O), 156.6 (**C$_{Ar}$**-O), 150.7 (**C$_{Ar}$**-O), 148.5 (**C$_{Ar}$**-F), 143.3 (**C$_{Ar}$**-C$_{Al}$), 132.3 (**C$_{Ar}$**-C$_{Ar}$), 131.9 (**C$_{Ar}$**-C$_{Ar}$), 131.6 (**C$_{Ar}$**-H), 130.0 (**C$_{Ar}$**-C$_{Ar}$), 129.9 (**C$_{Ar}$**-H), 128.7 (**C$_{Ar}$**-H), 128.7 (**C$_{Ar}$**-H), 128.6 (**C$_{Ar}$**-C$_{Ar}$), 128.4 (**C$_{Ar}$**-C$_{Ar}$), 128.3 (**C$_{Ar}$**-H), 124.7 (**C$_{Ar}$**-H), 124.6 (**C$_{Ar}$**-H), 121.8 (**C$_{Ar}$**-H), 120.0 (**C$_{Ar}$**-H), 112.3 (**C$_{Ar}$**-H), 68.4 (**C**-O), 35.8 (**C**-C$_{Ar}$), 34.4 (**C**-H), 31.8 (**C**-H), 31.4 (**C**-H), 29.2 (**C**-H), 29.2 (**C**-H), 29.1 (**C**-H), 29.1 (**C**-H), 29.0 (**C**-H), 25.9 (**C**-H), 24.9 (**C**-H), 22.6 (**C**-H), 14.1 (**C**-H).

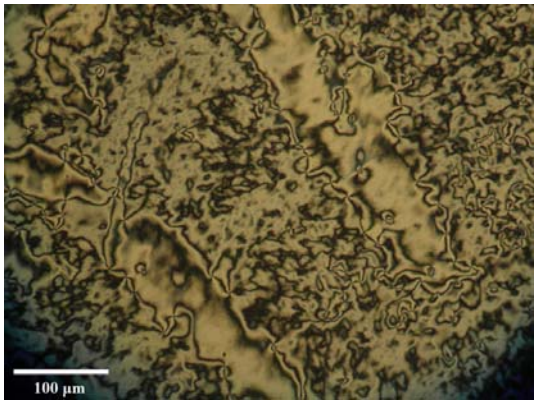
IR(KBr) ν_{max} / cm^{-1} : 2929, 2854, 1757, 1461, 1210.

UV-Vis (chloroform, *c* = 10 μM) λmax /nm: 277.

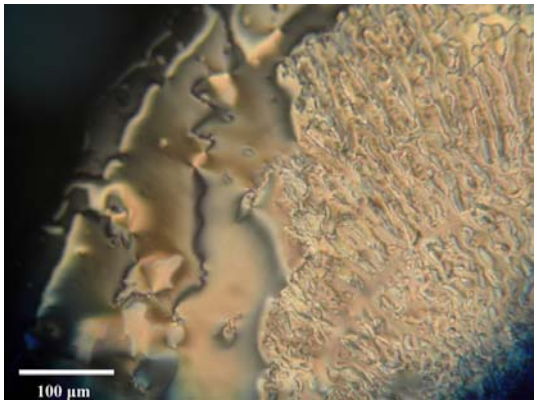
MAS (MALDI – TOF) $C_{78}H_{86}F_4O_6$ $[M + Na]^+$: 1218.50; found: 1218.91.

Elemental anal. Calcd for $C_{78}H_{86}F_4O_6$: C 78.36, H 7.25. Found: C 78.40, H 7.07%.

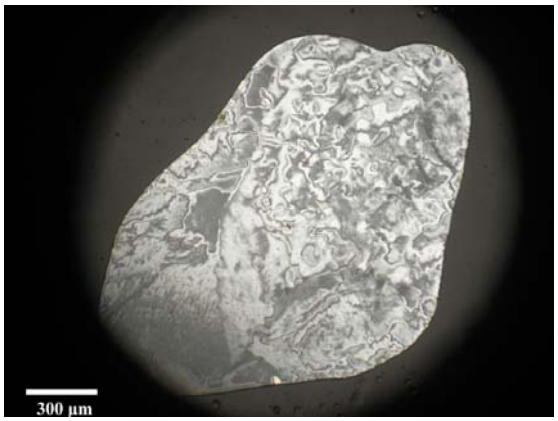
2. Representative textures of the smectic phases of the new compounds



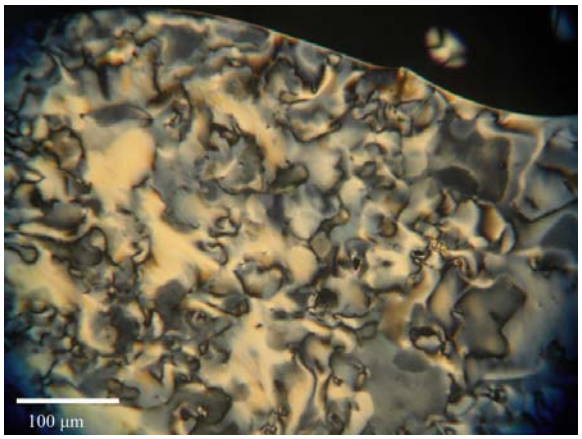
Photomicrograph of the SmC phase of a homeotropically aligned sample of **I-*5*** at 110 °C.



Photomicrograph of **I-*6*** on a glass slide with a cover glass in) the SmC phase at 115.9 °C.



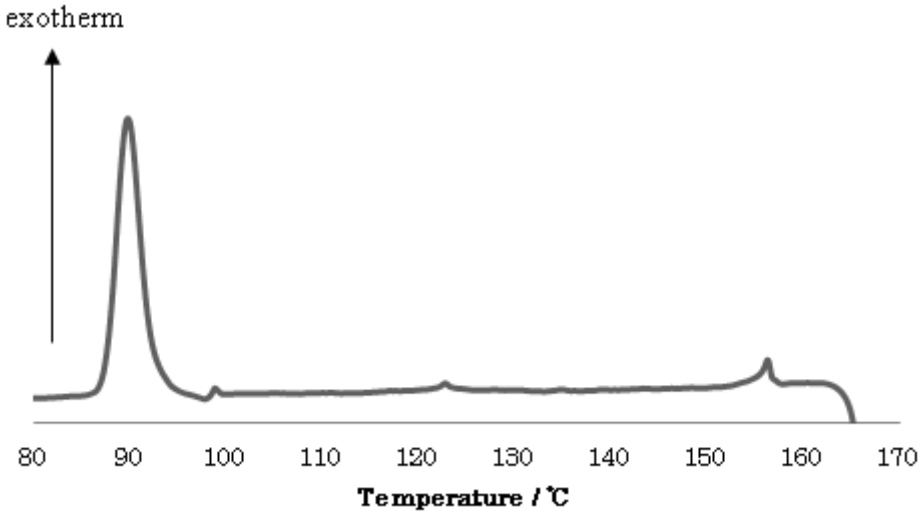
Photomicrograph of **I-*7*** on a glass slide with a cover glass in) the SmC phase at 123.0 °C.



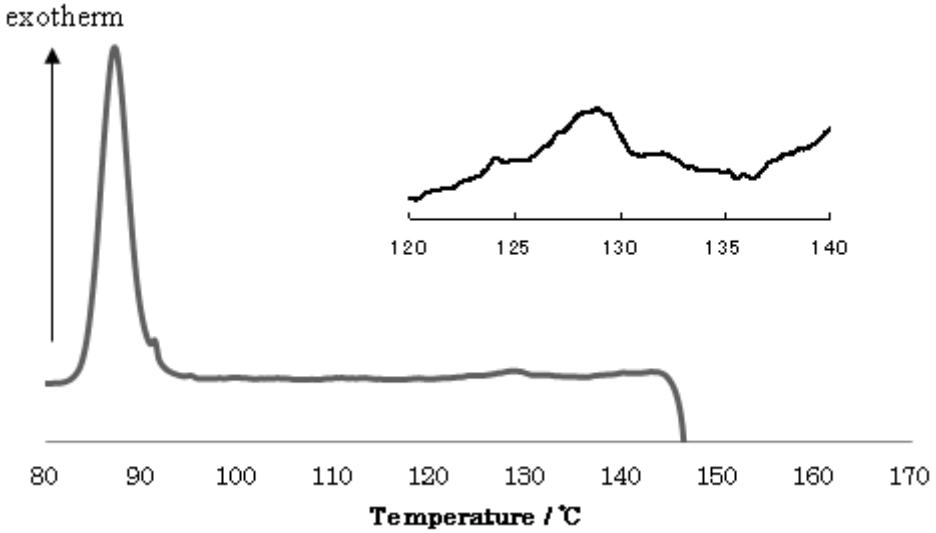
Photomicrograph of **II-*8*** on a glass slide with a cover glass in) the SmC phase at 79.4 °C.

3. DSC thermograms of compound **I-*6*** and compound **I-*6*** doped with 10 wt% of **ISO-(6OBA)$_2$**

(a)



(b)



DSC thermograms of (a) compound **I-*6*** and (b) compound **I-*6*** doped with **ISO-(6OBA)$_2$** (10 wt%) on cooling from the isotropic liquid at a scanning rate of 5°C min^{-1}.

4. Two sets of *L*/*D* ratio according to the short axis for the U-shaped derivatives.

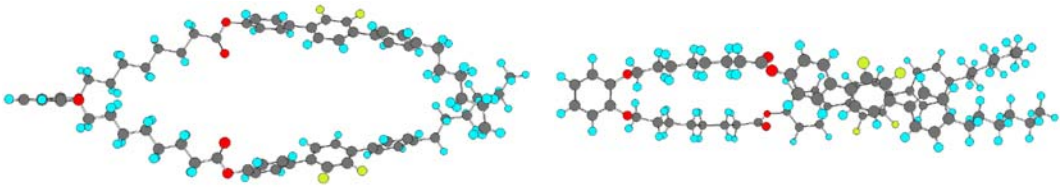
(1) **I-*5***

(a) (b)

(a) The short axis is parallel to the catechol plane. *L*/*D* is 3.32. (b) The short axis is perpendicular to the catechol plane. *L*/*D* is 4.20. Bond angles of Caromatic-O-Caliphatic (ether) are 115.8° and 115.9°, those of Ccarbonyl-O-Caromatic (ester) are 116.5° and 118.2°, and those of Caromatic-Caliphatic-Caliphatic are 110.6° and 115.1°.

(2) **I-*7***

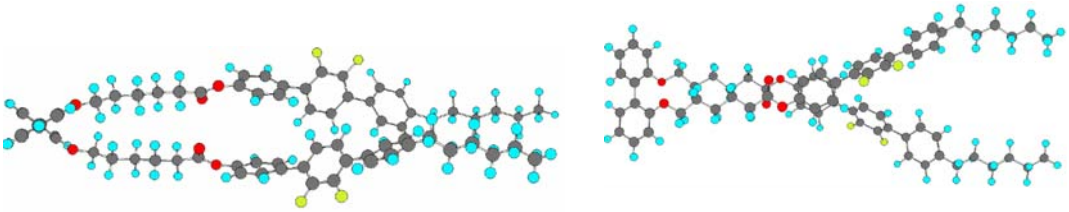
(a) (b)



(a) The short axis is parallel to the catechol plane. *L*/*D* is 2.90. (b) The short axis is perpendicular to the catechol plane. *L*/*D* is 4.35. Bond angles of Caromatic-O-Caliphatic (ether) are 114.4° and 114.4°, those of Ccarbonyl-O-Caromatic (ester) are 117.0° and 117.3°, and those of Caromatic-Caliphatic-Caliphatic are 110.0° and 114.3°.

(3) **II-*5***

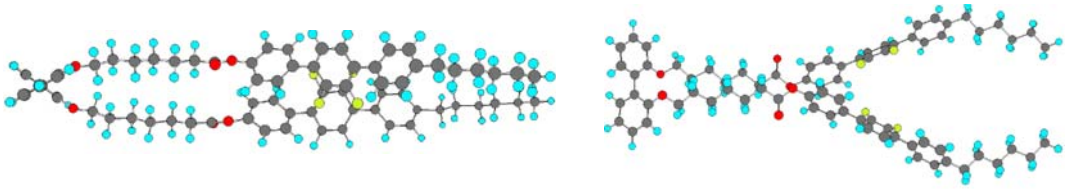
(a) (b)



(a) The short axis is parallel to the biphenyl axis. *L*/*D* is 3.46. (b) The short axis is perpendicular to the biphenyl axis. *L*/*D* is 2.54. Bond angles of Caromatic-O-Caliphatic (ether) are 116.8° and 117.3°, those of Ccarbonyl-O-Caromatic (ester) are 118.2° and 119.7°, and those of Caromatic-Caliphatic-Caliphatic are 111.2° and 111.7°.

(4) **II-*6***

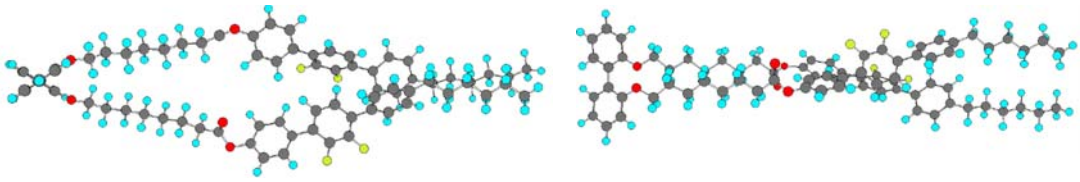
(a) (b)



(a) The short axis is parallel to the biphenyl axis. *L*/*D* is 4.61. (b) The short axis is perpendicular to the biphenyl axis. *L*/*D* is 2.52. Bond angles of Caromatic-O-Caliphatic (ether) are 117.0° and 117.1°, those of Ccarbonyl-O-Caromatic (ester) are 117.6° and 117.8°, and those of Caromatic-Caliphatic-Caliphatic are 111.0° and 111.9°.

(5) **II-*7***

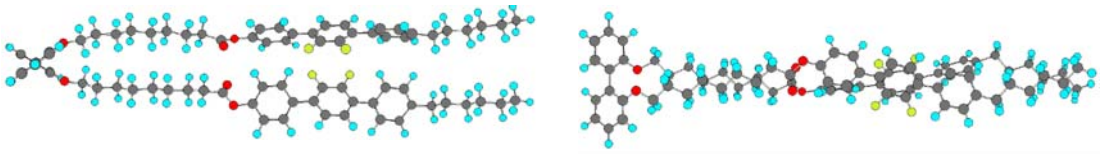
(a) (b)



(a) The short axis is parallel to the biphenyl axis. *L*/*D* is 3.16. (b) The short axis is perpendicular to the biphenyl axis. *L*/*D* is 3.69. Bond angles of Caromatic-O-Caliphatic (ether) are 116.7° and 117.3°, those of Ccarbonyl-O-Caromatic (ester) are 116.2° and 114.4°, and those of Caromatic-Caliphatic-Caliphatic are 115.2° and 116.7°.

(6) **II-*8***

(a) (b)



(a) The short axis is parallel to the biphenyl axis. *L*/*D* is 5.14. (b) The short axis is perpendicular to the biphenyl axis. *L*/*D* is 3.82. Bond angles of Caromatic-O-Caliphatic (ether) are 117.6° and 117.7°, those of Ccarbonyl-O-Caromatic (ester) are 118.7° and 119.9°, and those of Caromatic-Caliphatic-Caliphatic are 115.3° and 116.6°.