Supplementary materials

Liquid crystalline cyclic tetramethyltetrasiloxanes containing coumarin moieties

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Characterization of dialkyl malonates (**3**)

Dihexyl malonate (**3**, n=6). Yield: 94%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.89 (6H, t, CH_3), 1.21 ~ 1.46 (12H, m, -$CH_2CH_2CH_2$-), 1.52 ~ 1.78 (4H, m, -CH_2-), 3.36 (2H, s, $OOCCH_2COO$), 4.14 (4H, t, OCH_2).

Diheptyl malonate (**3**, n=7*)*. Yield: 91%. ^{1}H-NMR (ppm, DCl_3): δ = 0.89 (6H, t, CH_3), 1.18 ~ 1.49 (16H, m, -$CH_2CH_2CH_2CH_2$-), 1.52 ~ 1.79 (4H, m, -CH_2-), 3.36 (2H, s, $OOCCH_2COO$), 4.14 (4H, t, -OCH_2-).

Dioctyl malonate (**3**, n=8). Yield: 95%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.89 (6H, t, CH_3), 1.1 ~ 1.54 (20H, m, -$CH_2CH_2CH_2CH_2CH_2$-), 1.54 ~ 1.78 (4H, m, -CH_2-), 3.36 (2H, s, $OOCCH_2COO$), 4.14 (4H, t, OCH_2).

Characterization of alkyl 7-hydroxy-coumarin-3-carboxylate (**4**)

*Ethyl 7-hydroxy-coumarin-3-carboxylate (**4**, n=2)*. Yield: 58%. ^{1}H-NMR (ppm, DMSO): δ = 1.35 (3H, t, CH_3), 4.33 (2H, t, OCH_2), 6.79 (1H, d, phenyl), 6.95 (1H, m, phenyl), 7.75 (1H, d, phenyl), 8.59 (1H, s, -CH=).

*Propyl 7-hydroxy-coumarin-3-carboxylate (**4**, n=3)*. Yield: 35%. ^{1}H-NMR (ppm, DMSO): δ = 0.98 (3H, t, CH_3), 1.67 ~ 1.81 (2H, m, -CH_2-), 4.19 (2H, t, OCH_2), 6.79 (1H, d, phenyl), 6.95 (1H, m, phenyl), 7.75 (1H, d, phenyl), 8.61 (1H, s, -CH=).

*Butyl 7-hydroxy-coumarin-3-carboxylate (**4**, n=4)*. Yield: 39%. ^{1}H-NMR (ppm, CD_3COCD_3): δ = 0.98 (3H, t, CH_3), 1.37 ~ 1.52 (2H, m, -CH_2-), 1.67 ~ 1.81 (2H, m, -CH_2-), 4.29 (2H, t, OCH_2), 6.79 (1H, d, phenyl), 6.95 (1H, m, phenyl), 7.75 (1H, d, phenyl), 8.61 (1H, s, -CH=).

*Pentyl 7-hydroxy-coumarin-3-carboxylate (**4**, n=5)*. Yield: 32%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.90 (3H, t, CH_3), 1.35 ~1.77 (6H, m, -CH_2-), 4.33 (2H, t, OCH_2), 6.93 (1H, m, phenyl), 6.95 (1H, d, phenyl), 7.50 (1H, d, phenyl), 7.71 (1H, br, OH), 8.53 (1H, s, -CH=).

*Hexyl 7-hydroxy-coumarin-3-carboxylate (**4**, n=6)*. Yield: 33%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.90 (3H, t, CH_3), 1.3 ~1.77 (8H, m, -CH_2-), 4.33 (2H, t, OCH_2), 6.93 (1H, m, phenyl), 6.95 (1H, d, phenyl), 7.50 (1H, d, phenyl), 7.71 (1H, br s, OH), 8.54 (1H, s, -CH=).

*Heptyl 7-hydroxy-coumarin-3-carboxylate (**4**, n=7)*. Yield: 36%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.88 (3H, t, CH_3), 1.28 ~ 1.77 (10H, m, -CH_2-), 4.33 (2H, t, OCH_2), 6.93 (1H, m, phenyl), 6.95 (1H, d, phenyl), 7.50 (1H, d, phenyl), 7.70 (1H, br, OH), 8.53 (1H, s, -CH=).

*Octyl 7-hydroxy-coumarin-3-carboxylate (**4**, n=8)*. Yield: 40%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.88 (3H, t, CH_3), 1.28 ~ 1.77 (12H, m, -CH_2-), 4.33 (2H, t, OCH_2), 6.93 (1H, m, phenyl), 6.95 (1H, d, phenyl), 7.50 (1H, d, phenyl), 7.70 (1H, br, OH), 8.54 (1H, s, -CH=).

Characterization of vinyl terminated molecules with coumarin units (**V**)

Methyl 7-[4-(pent-4-eneoxy)benzoyloxy]-coumarin-3-carboxylate (**V1**). Yield: 78%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 1.82 ~ 2.40 (4H, m, CH_2), 3.97 (3H, s, CH_3), 4.08 (2H, t, OCH_2), 5.05(2H, m, CH_2=), 5.86 (1H, m, =CH-), 6.98 (2H, d, phenyl), 7.23 (2H, m, phenyl), 7.66 (1H, d, phenyl), 8.14 (2H, m, phenyl), 8.59 (1H, s, -CH=). Elemental analysis: Calc. for $C_{23}H_{20}O_7$: C, 67.64; H, 4.94 percent. Found: C, 67.65; H, 4.73 percent.

Ethyl 7-[4-(pent-4-eneoxy)benzoyloxy]-coumarin-3-carboxylate (**V2**). Yield: 60%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 1.39 (3H, t, CH_3), 1.82 ~ 2.40 (4H, m, CH_2), 4.08 (2H, t, CH_2), 4.42 (2H, t, $COOCH_2$), 5.05(2H, m, CH_2=), 5.86 (1H, m, =CH-), 6.98 (2H, d, phenyl), 7.23 (2H, m, phenyl), 7.66 (1H, d, phenyl), 8.14 (2H, m, phenyl), 8.55 (1H, s, -CH=). Elemental analysis: Calc. for $C_{24}H_{22}O_7$: C, 68.23; H, 5.25 percent. Found: C, 68.28; H, 5.25 percent.

Propyl 7-[4-(pent-4-eneoxy)benzoyloxy]-coumarin-3-carboxylate (**V3**). Yield: 89%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 1.04 (3H, t, CH_3), 1.92 ~ 2.42 (4H, m, CH_2), 4.08 (2H, t, CH_2), 4.42 (2H, t, $COOCH_2$), 5.05(2H, m, CH_2=), 5.86 (1H, m, =CH-), 6.98 (2H, d, phenyl), 7.23 (2H, m, phenyl), 7.66 (1H, d, phenyl), 8.14 (2H, m, phenyl), 8.53 (1H, s, -CH=). Elemental analysis: Calc. for $C_{25}H_{24}O_7$: C, 68.79; H, 5.54 percent. Found: C, 68.99; H, 5.42 percent.

Butyl 7-[4-(pent-4-eneoxy)benzoyloxy]-coumarin-3-carboxylate (**V4**). Yield: 63%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.99 (3H, t, CH_3), 1.32 ~ 2.40 (6H, m, CH_2), 4.08 (2H, t, CH_2), 4.36 (2H, t, $COOCH_2$), 5.05(2H, m, CH_2=), 5.86 (1H, m, =CH-), 6.98 (2H, d, phenyl), 7.23 (2H, m, phenyl), 7.66 (1H, d, phenyl), 8.14 (2H, m, phenyl), 8.53 (1H, s, -CH=).

Elemental analysis: Calc. for $C_{26}H_{26}O_7$: C, 69.32; H, 5.81 percent. Found: C, 69.51; H, 5.66 percent.

Pentyl 7-[4-(pent-4-eneoxy)benzoyloxy]-coumarin-3-carboxylate (**V5**). Yield: 69%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.89 (3H, t, CH_3), 1.4 (4H, m, $(CH_2)_2$), 1.85 (2H, m, CH_2), 1.93 (2H, m, CH_2), 2.26 (2H, m, CH_2), 4.08 (2H, t, OCH_2), 4.35 (2H, t, $COOCH_2$), 5.05(2H, m, CH_2=), 5.85 (1H, m, =CH-), 6.98 (2H, d, phenyl), 7.22 (2H, m, phenyl), 7.65 (1H, d, phenyl), 8.16 (2H, m, phenyl), 8.53 (1H, s, -CH=). Elemental analysis: Calc. for $C_{27}H_{28}O_7$: C, 69.81; H, 6.08 percent. Found: C, 70.02; H, 6.00 percent.

Hexyl 7-[4-(pent-4-eneoxy)benzoyloxy]-coumarin-3-carboxylate (**V6**). Yield: 63%. ^{1}H-NMR (ppm, $CDCl_3$): δ= 0.91 (3H, t, CH_3), 1.3 ~ 1.5 (6H, m, $(CH_2)_3$), 1.85 (2H, m, CH_2), 1.93 (2H, m, CH_2), 2.26 (2H, m, CH_2), 4.08 (2H, t, OCH_2), 4.35 (2H, t, $COOCH_2$), 5.05(2H, m, CH_2=), 5.85 (1H, m, =CH-), 6.98 (2H, d, phenyl), 7.22 (2H, m, phenyl), 7.65 (1H, d, phenyl), 8.16 (2H, m, phenyl), 8.53 (1H, s, -CH=). Elemental analysis: Calc. for $C_{28}H_{30}O_7$: C, 70.27; H, 6.32 percent. Found: C, 70.50; H, 6.34 percent.

Heptyl 7-[4-(pent-4-eneoxy)benzoyloxy]-coumarin-3-carboxylate (**V7**). Yield: 70%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.89 (3H, t, CH_3), 1.2 ~ 1.5 (8H, m, $(CH_2)_4$), 1.80 (2H, m, CH_2), 1.95 (2H, m, CH_2), 2.29 (2H, m, CH_2), 4.08 (2H, t, OCH_2), 4.35 (2H, t, $COOCH_2$), 5.05(2H, m, CH_2=), 5.85 (1H, m, =CH-), 6.98 (2H, d, phenyl), 7.22 (2H, m, phenyl), 7.65 (1H, d, phenyl), 8.16 (2H, m, phenyl), 8.53 (1H, s, -CH=). Elemental analysis: Calc. for $C_{29}H_{32}O_7$: C, 70.71; H, 6.55 percent. Found: C, 70.88; H, 6.52 percent.

Octyl 7-[4-(pent-4-eneoxy)benzoyloxy]-coumarin-3-carboxylate (**V8**). Yield: 75%. ^{1}H-NMR (ppm, $CDCl_3$): δ= 0.89 (3H, t, CH_3), 1.2 ~ 1.5 (10H, m, $(CH_2)_5$), 1.85 (2H, m, CH_2), 1.93 (2H, m, CH_2), 2.26 (2H, m, CH_2), 4.08 (2H, t, OCH_2), 4.35 (2H, t, $COOCH_2$), 5.05(2H, m, CH_2=), 5.85 (1H, m, =CH-), 6.98 (2H, d, phenyl), 7.22 (2H, m, phenyl), 7.65 (1H, d, phenyl), 8.16 (2H, m, phenyl), 8.53 (1H, s, -CH=). Elemental analysis: Calc. for $C_{30}H_{34}O_7$: C, 71.12; H, 6.76 percent. Found: C, 71.11; H, 6.86 percent.

Characterization of cyclic tetramethyltetrasiloxanes with coumarin moieties (**CS**)

CS1. Yield: 20.3%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.11 (12H, br s, $SiCH_3$), 0.59 (8H, br m, $SiCH_2$-), 1.41~1.52 (16H, m, -CH_2CH_2-), 1.67~ 1.95 (8H, m, -CH_2-), 4.02 (12H, s, $COOCH_3$), 4.11 (8H, m, OCH_2), 6.94 (8H, br m, phenyl), 7.22 (8H, br m, phenyl), 7.66

(4H, d, phenyl), 8.10 (8H, m, phenyl), 8.56 (4H, s, -CH=). IR (KBr disk, cm^{-1}): 1763, 1732, 1703 (carbonyl, esters). Elemental analysis: Calc. for $C_{96}H_{96}O_{32}Si_4$: C, 61.52; H, 5.16 percent. Found: C, 61.29; H, 5.15 percent.

CS2. Yield: 36.5%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.11 (12H, br s, $SiCH_3$), 0.59 (8H, br m, $SiCH_2$-), 1.41~1.88 (36H, m, $-CH_2CH_2CH_2-$ and CH_3), 4.03 (8H, br m, OCH_2), 4.38 (8H, q, $COOCH_2$), 6.92 (8H, br m, phenyl), 7.22 (8H, br m, phenyl), 7.65 (4H, d, phenyl), 8.06 (8H, m, phenyl), 8.52 (4H, s, -CH=). IR (KBr disk, cm^{-1}): 1763, 1732, 1705 (carbonyl, esters). Elemental analysis: Calc. for $C_{100}H_{104}O_{32}Si_4$: C, 62.22; H, 5.43 percent. Found: C, 62.17; H, 5.47 percent.

CS3. Yield: 34.5%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.11 (12H, br s, $SiCH_3$), 0.59 (8H, br m, $SiCH_2$-), 1.15 (12H, t, CH_3), 1.62~1.96 (32H, m, $-CH_2CH_2CH_2-$ and $-CH_2-$), 4.03 (8H, br m, OCH_2), 4.38 (8H, t, $COOCH_2$), 6.92 (8H, br m, phenyl), 7.22 (8H, br m, phenyl), 7.65 (4H, d, phenyl), 8.06 (8H, br m, phenyl), 8.63 (4H, s, -CH=). IR (KBr disk, cm^{-1}): 1763, 1732, 1705 (carbonyl, esters). Elemental analysis: Calc. for $C_{104}H_{112}O_{32}Si_4$: C, 62.88; H, 5.68 percent. Found: C, 62.81; H, 5.81 percent.

CS4. Yield: 27.5%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.11 (12H, br s, $SiCH_3$), 0.59 (8H, br m, $SiCH_2$-), 0.98 (12H, t, CH_3), 1.43~1.85 (40H, m, $-CH_2CH_2CH_2-$ and $-CH_2CH_2-$), 4.03 (8H, br m, OCH_2), 4.38 (8H, t, $COOCH_2$), 6.92 (8H, br m, phenyl), 7.22 (8H, br m, phenyl), 7.65 (4H, d, phenyl), 8.06 (8H, br m, phenyl), 8.50 (4H, s, -CH=). IR (KBr disk, cm^{-1}): 1763, 1732, 1705 (carbonyl, esters). Elemental analysis: Calc. for $C_{108}H_{120}O_{32}Si_4$: C, 63.51; H, 5.92 percent. Found: C, 63.69; H, 6.02 percent.

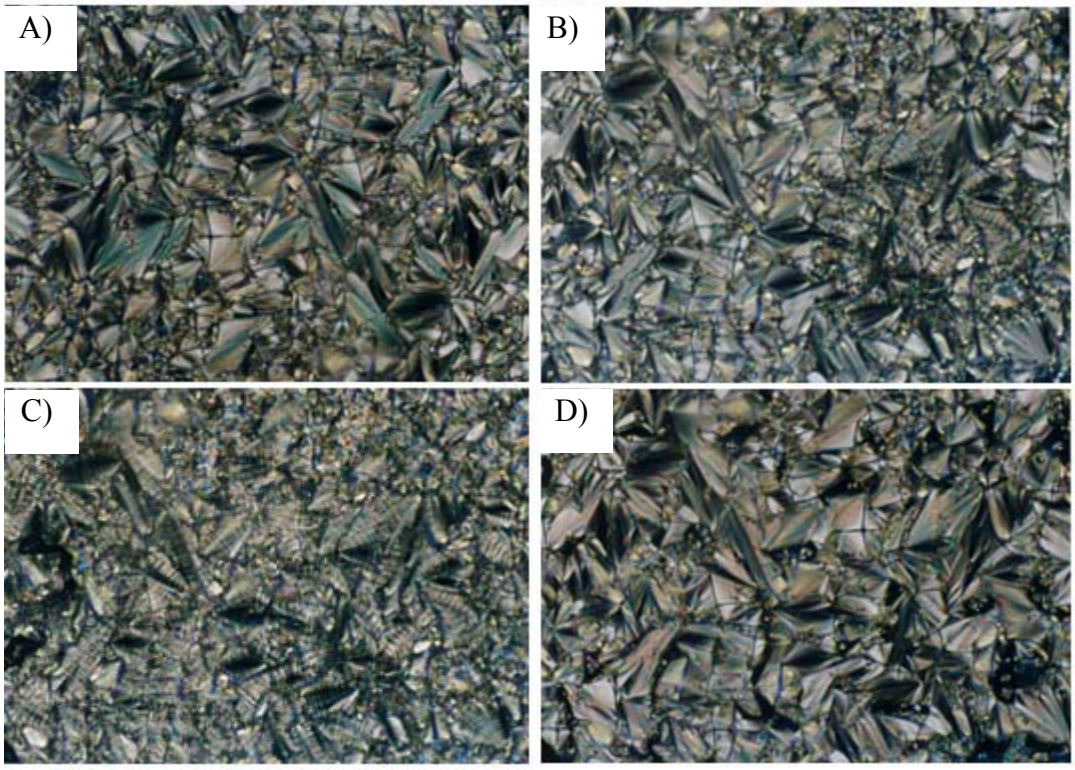
CS5. Yield: 24.8%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.11 (12H, br s, $SiCH_3$), 0.59 (8H, br m, $SiCH_2$-), 0.92 (12H, t, CH_3), 1.3 ~1.84 (48H, m, $-CH_2CH_2CH_2-$ and $-CH_2CH_2CH_2-$), 4.04 (8H, br m, OCH_2), 4.34 (8H, t, $COOCH_2$), 6.95 (8H, br m, phenyl), 7.24 (8H, br m, phenyl), 7.65 (4H, d, phenyl), 8.11 (8H, m, phenyl), 8.53 (4H, s, -CH=). IR (KBr disk, cm^{-1}): 1763, 1736, 1704 (carbonyl, esters). Elemental analysis: Calc. for $C_{112}H_{128}O_{32}Si_4$: C, 64.09; H, 6.14 percent. Found: C, 64.37; H, 6.25 percent.

CS6. Yield: 25.3%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.11 (12H, br s, $SiCH_3$), 0.59 (8H, br m, $SiCH_2$-), 0.92 (12H, t, CH_3), 1.3 ~1.84 (56H, m, $-CH_2CH_2CH_2-$ and $-CH_2CH_2CH_2CH_2-$), 4.04 (8H, br m, OCH_2), 4.34 (8H, t, $COOCH_2$), 6.95 (8H, br m,

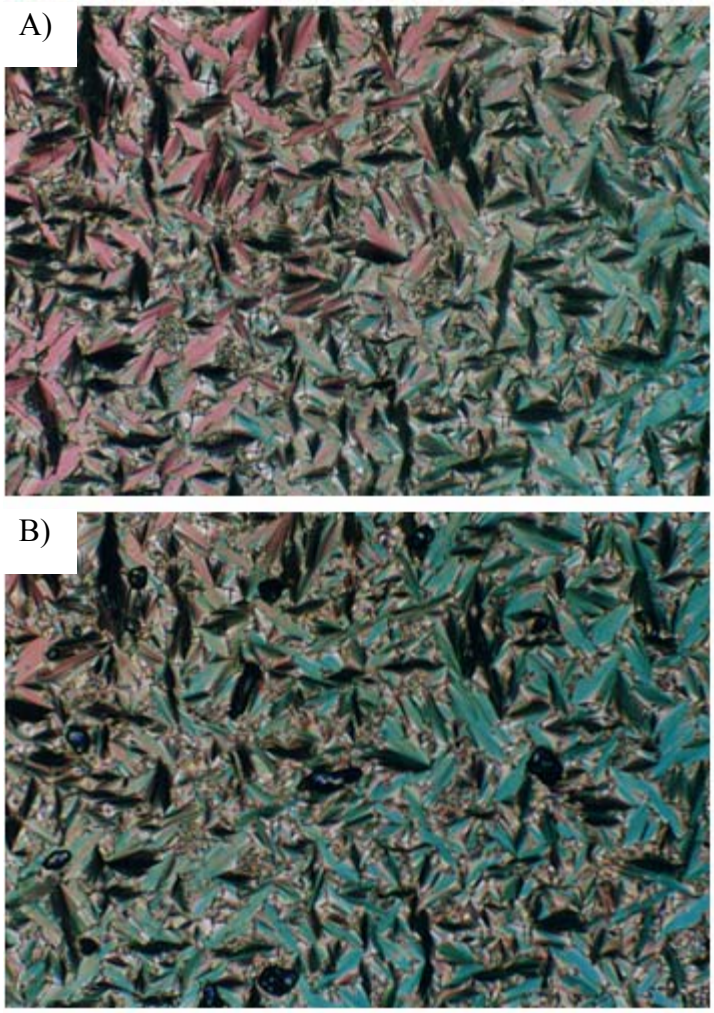
phenyl), 7.24 (8H, br m, phenyl), 7.65 (4H, d, phenyl), 8.11 (8H, m, phenyl), 8.50 (4H, s, -CH=). IR (KBr disk, cm^{-1}): 1763, 1736, 1704 (carbonyl, esters). Elemental analysis: Calc. for $C_{116}H_{136}O_{32}Si_4$: C, 64.66; H, 6.36 percent. Found: C, 64.51; H, 6.42 percent.

CS7. Yield: 24.9%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.11 (12H, br s, $SiCH_3$), 0.59 (8H, br m, $SiCH_2$-), 0.92 (12H, t, CH_3), 1.31 ~1.84 (64H, m, -$CH_2CH_2CH_2$- and -$CH_2CH_2CH_2CH_2CH_2$-), 4.04 (8H, br m, OCH_2), 4.34 (8H, t, $COOCH_2$), 6.95 (8H, br m, phenyl), 7.24 (8H, br m, phenyl), 7.65 (4H, d, phenyl), 8.11 (8H, m, phenyl), 8.50 (4H, s, -CH=). IR (KBr disk, cm^{-1}): 1763, 1736, 1704 (carbonyl, esters). Elemental analysis: Calc. for $C_{120}H_{144}O_{32}Si_4$: C, 65.19; H, 6.56 percent. Found: C, 65.16; H, 6.62 percent.

CS8. Yield: 25.9%. ^{1}H-NMR (ppm, $CDCl_3$): δ = 0.11 (12H, br s, $SiCH_3$), 0.59 (8H, br m, $SiCH_2$-), 0.86 (12H, t, CH_3), 1.30~1.82 (72H, m, -$CH_2CH_2CH_2$- and -$CH_2CH_2CH_2CH_2CH_2CH_2$-), 4.04 (8H, br m, OCH_2), 4.34 (8H, t, $COOCH_2$), 6.95 (8H, br m, phenyl), 7.24 (8H, br m, phenyl), 7.65 (4H, d, phenyl), 8.11 (8H, m, phenyl), 8.50 (4H, s, -CH=). IR (KBr disk, cm^{-1}): 1763, 1736, 1704 (carbonyl, esters). Elemental analysis: Calc. for $C_{124}H_{152}O_{32}Si_4$: C, 65.70; H, 6.76 percent. Found: C, 65.74; H, 6.90 percent.



Supplementary Fig. 1. Typical textures of **CS1** at different phases. a) focal-conic texture of smectic A phase at 190°C; b) the texture at the transition from SmA phase to crystal phase at 131°C on cooling; c) the texture of crystal phase at 120°C; d) the texture of smectic A phase at 176°C on the subsequent heating. (magnification: 400x)



Supplementary Fig. 2. Typical textures of **CS8**. a) focal-conic texture of smectic A at 124°C; b) focal-conic texture of the glassy state at room temperature. (magnification: 400x)

Supplementary Table 1 Layer spacing, *d*, as determined by X-ray diffraction and calculated extended molecular length, *L*, by MM2 force field method

Code	Tail length (n)	Measured Layer Spacing (*d*, Å)	Calculated Extended Molecular Length (*L*, Å)	*d/L*
V1	1	*	22.1	*
V2	2	*	22.9	*
V3	3	23.4	24.3	0.96
V4	4	24.5	25.3	0.97
V5	5	24.3	26.6	0.92
V6	6	26.8	27.6	0.97
V7	7	----	29.0	----
V8	8	26.9	30.0	0.90
CS1	1	27.1		1.23
CS2	2	25.8		1.13
CS3	3	25.8		1.06
CS4	4	26.3		1.06
CS5	5	26.1		0.98
CS6	6	25.1		0.91
CS7	7	24.5		0.85
CS8	8	25.1		0.84

*: Not measured because they don't show liquid crystalline properties. ---: Not measured due to its narrow liquid crystalline temperature range.