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Electronic supplementary information (ESI)

Cholesterol-based non-symmetric liquid crystal dimers: an overview

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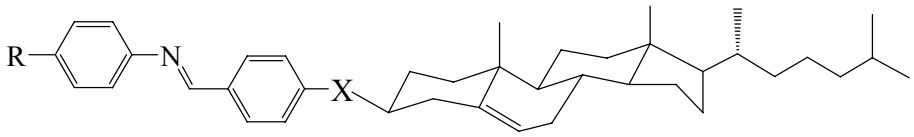
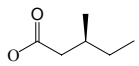
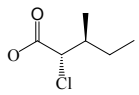
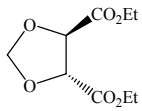
1. Schiff's bases (azomethines)

Table S1: Phase behavior of cholesterol-based dimers having Schiff's base anisometric segment. Cr = crystal; $Sm\tilde{C}$ = two-dimensional modulated smectic C phase (ribbon phase); Sm_{q3} = smectic phase having a periodicity lower than half the molecular length ($q3$ is the wave vector); Sm_{ic} = incommensurate smectic A phase; $Sm_{q1\ LT/HT}$ = smectic phase having a layer spacing close to molecular length ($q1$ is the wave vector; LT = low temperature, HT = high temperature); SmC* = chiral smectic C phase; SmA = smectic A phase; Sm1, Sm2 = smectic (Sm_{q3}) phase; Sm1', Sm2' = tilted commensurate smectic (Sm_{q1}) phase; SmX_1, SmX_2 = unknown smectic phases; TGB = twist grain boundary phase; N* = chiral nematic phase; BPI = blue phase I; BPII = blue phase II; I = isotropic phase; ( ) = monotropic behavior. Generally, dimers are tabulated in the order of their appearance in the literature.

Note: For references mentioned in the last column, see the reference section of the main text.



Dimer	R	X	Phase sequence and transition temperatures in ^oC	Ref.
1-1	*n*-C_4H_9	$O(CH_2)_5COO$	Cr 85 Sm_{ic} 144.5 SmC* 149 SmA_{ic} 151.5 SmC* 165 TGB 168 N* 192 I	15
			Cr 85 Sm_{ic} 144.5 SmC* 149 Sm_{ic} 151.5 SmC* 165 TGB 168 N* 191 BP 192 I	16
			Cr 85 $Sm\tilde{C}$ 97 Sm_{q3} 141 Sm_{ic} 146 Sm_{q1LT} 152 Sm_{q1HT} 164 TGB 168 N* 192 I	17
1-2	*n*-C_4H_9	$O(CH_2)_4COO$	Cr 85 SmC* 134 SmC* 141 TGB 142 N* 153.8 BPI 154.8 BPII 155.6 I	16
1-3	*n*-C_4H_9	$O(CH_2)_7COO$	Cr 148 SmA 151.5 TGB 152.5 N* 172.8 BP 173.5 I	16
1-4	*n*-C_4H_9	$O(CH_2)_{10}COO$	Cr 104 SmA 124.5 TGB 125 N* 140 BPI 140.6 BPII 141.2 I	16
1-5	$CH{=}CHCO_2C_2H_5$	$O(CH_2)_5COO$	Cr 139 Sm_{ic} 140 Sm_{q3} 206 N* 238 I	17

1-6	*n*-C_2H_5	$O(CH_2)_5COO$	Cr 139Sm2 (96) Sm1 157 N* 198 I	18
1-7	*n*-C_3H_7	$O(CH_2)_5COO$	Cr 112 Sm2 (98) Sm1 149 TGB 151 N* 196 I	18
1-8	*n*-C_5H_{11}	$O(CH_2)_5COO$	Cr 70 Sm2' 102 Sm1' 176 N* 190 I	18
1-9	*n*-C_6H_{13}	$O(CH_2)_5COO$	Cr 84 Sm2' 112 Sm1' 181 N* 188 I	18
1-10	*n*-$C_{10}H_{21}$	$O(CH_2)_5COO$	Cr 84 Sm2' 115 Sm1' 184 I	18
1-11	*n*-$C_{12}H_{25}$	$O(CH_2)_5COO$	Cr 63.6 SmC* 104.8 SmA 174.7 I	19
1-12		$O(CH_2)_5COO$	Cr 127.7 SmA 169.1 TGB 169.5 N* 193.2 I	19
1-13		$O(CH_2)_5COO$	Cr 120.7 SmX_1 150.5 SmX_2 165.6 TGB 165.7 N* 185.4 I	19
1-14		$O(CH_2)_5COO$	Cr 105.4 SmC* (84.2) SmA 123.5 N* 148.5 I	19
1-15	*n*-OC_3H_7	$O(CH_2)_5COO$	Cr 117 Sm_{q3} 171 N* 212 I	20
1-16	COCH3	$O(CH_2)_5COO$	Cr 116 Sm_{q1} 156 TGB 160 N* 216 I	20
1-17	CN	$O(CH_2)_5COO$	Cr 160 Sm_{q1}[†]176 TGB 178 N* 216 I	20
1-18	NO_2	$O(CH_2)_5COO$	Cr 178 Sm_{q1}[†] (165) TGB (167) N* 208 I	20
1-19	*n*-C_8H_{17}	$O(CH_2)_5COO$	Cr 130.5 SmC* (124.1) SmA 195.5 N* 197.6 I	21
1-20	$CH_2(CF_2)_6CF_3$	$O(CH_2)_5COO$	Cr 111.9 SmC* 143.7 SmA 235.4 I	21
1-21	*n*-OC_2H_5	$OOC(CH_2)_2COO$	Cr 166.7 N* 256.2 I	22
1-22	*n*-OC_5H_{11}	$OOC(CH_2)_2COO$	Cr 118.5 N* 243.1 I	22
1-23	*n*-OC_7H_{15}	$OOC(CH_2)_2COO$	Cr 132.5 N* 234.1 I	22

[†] The Sm_{q1} phase formed by dimers **1-17** and **1-18** is in fact similar to the SmA_d phase seen for the polar system satisfying the condition $L < d < 2L$

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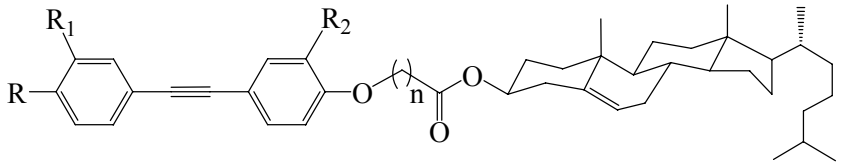
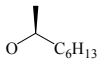
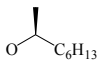
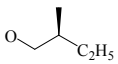
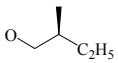
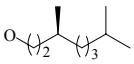
2. Tolanes (diphenylacetylenes)

Table S2[a]: Phase behavior of cholesterol-based dimers consisting of tolane anisometric moiety. TGBA = twist grain boundary phase featuring SmA blocks; TGBC* = twist grain boundary phase having SmC* slabs; BP = blue phase; M_x = Unknown mesophase.



Dimer	R	R_1	R_2	n	Phase sequence and transition temperatures in ^oC	Ref.
2-1	*n*-OC_4H_9	H	H	5	Cr 111.5 N* 203.3 I	23
					Cr 113 TGB_{q3} 120 N* 205 I	27
2-2		H	H	4	Cr 85.1 SmA 108.4 I	25
2-3		H	H	5	Cr 89 SmA 146.2 I	25 30
2-4	*n*-OC_6H_{13}	H	H	5	Cr 130.8 TGBC* (105) TGBA (120) SmA 152.5 TGBA 161.2 N* 197.3 I	26
					Cr 129 TGBC* (110) SmA_{q1} 155 $TGBA_{q1}$ 164 N* 199 I	27
2-5	*n*-OC_3H_7	H	H	5	Cr 126 Sm_{q3} 129 TGB_{q3} 131 N* 206 I	27
2-6	*n*-OC_5H_{11}	H	H	5	Cr 125 $TGBA_{q1}$ 151 N* 199 I	27
					Cr 124.8 N* 199.3 I †	31
2-7	*n*-OC_7H_{15}	H	H	5	Cr 114 SmC^*_{q1} (113) SmA_{q1} 168 $TGBA_{q1}$ 170 N* 192 I	27
2-8	*n*-$OC_{10}H_{21}$	H	H	5	Cr 95 SmC^*_{q1} 132 SmA_{q1} 183 N* 186 I	27
2-9	*n*-C_4H_9	H	H	3	Cr 155 SmA 186.8 TGB^b-N* 204.7 I	28 32
2-10	*n*-C_5H_{11}	H	H	3	Cr 153.6 SmC* (81.7) SmA 178.1 TGB^b-N* 195.6 I	28
2-11	*n*-C_6H_{13}	H	H	3	Cr 119.3 SmC* (81.9) SmA 196.4 TGB^b-N* 202.4 I	28 33
2-12	*n*-C_7H_{15}	H	H	3	Cr 82.8 SmA 193.3 TGB^b-N* 196.3 I	28
2-13	*n*-C_4H_9	H	H	4	Cr 118.2 SmA 126.8 TGB^b-N*-BP^b 148.3 I	28

2-14	*n*-C_5H_{11}	H	H	4	Cr 115.8 SmA 134.6 TGB^b-N*-BP^b 150.4 I	28
2-15	*n*-C_6H_{13}	H	H	4	Cr 105.9 SmA 138.1 TGB^b-N* 146.1 I	28
2-16	*n*-C_4H_9	H	H	5	Cr 99 Sm_{q1} 146 TGB_{q1} 150.5 N* 185.4 I	24
					Cr 99.5 SmC* (83.4) SmA 152.5 TGB^b-N* 186.1 I	28
2-17	*n*-C_7H_{15}	H	H	4	Cr 103 SmA 142.2 TGB^b-N*-BP^b 146.5 I	28
2-18	*n*-C_5H_{11}	H	H	5	Cr 114.9 SmC* (84.2) SmA 161.4 TGB^b-N* 185.4 I	28
2-19	*n*-C_6H_{13}	H	H	5	Cr 88.8 SmC* 100.4 SmA 166.7 TGB^b-N* 180.3 I	28
2-20	*n*-C_7H_{15}	H	H	5	Cr 108 SmC* (99.7) SmA 170.8 TGB^b-N* 178.7 I	28
2-21	*n*-C_4H_9	H	H	7	Cr 146.9 SmA (132.6) TGB^b-N* 168.8 I	28
2-22	*n*-C_5H_{11}	H	H	7	Cr 145.7 N* 168.4 I	28
2-23	*n*-C_6H_{13}	H	H	7	Cr 90.9 SmC* 97.9 SmA 167.5 TGB^b-N* 180.3 I	28
2-24	*n*-C_7H_{15}	H	H	7	Cr 128.3 SmC* (98.3) SmA 139.8 TGB 142.4 N* 164.1 I	28
2-25		NO_2	H	5	Cr 86.4 SmA 111.2 N* 113.1 I	29
2-26		F	H	5	Cr 84.4 SmA 145.6 I	29
2-27		H	H	5	Cr 120.8 M_x (63.1) SmA 159.2 TGB^b-N* 182.9 I	29
2-28		H	NO_2	5	Cr 138.6 SmA (134.1) N* 143.8 I	29
2-29		H	H	5	Cr 92.8 SmC* 99.9 SmA 168.3 I	29

[a] The transition between different crystalline forms have been ignored; only the crystalline form (temperature) melting into the mesophase is mentioned. [b] A very short lived phase. [†] The reinvestigation on the reported phase sequence (ref. 31) is in progress

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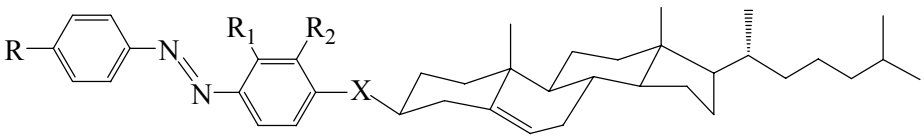
3. Azobenzenes (diphenyldiazenes)

Table S3: Phase behavior of cholesterol-based dimers comprising azobenzene anisometric segment. SmÃ = Two-dimensional modulated smectic A antiphase; Sm = smectic phase; SmX = solid-like phase; Sm1 = Unknown fluid smectic phase



Dimer	R	R_1	R_2	X	Phase sequence and transition temperatures in ^oC	Ref.
3-1	*n*-C_4H_9	H	H	$O(CH_2)_5COO$	Cr 113 SmÃ 137 Sm_{q1} 160 TGB_{q1} 163 N* 194 I	17 24
3-2	*n*-OC_8H_{17}	H	H	$O(CH_2)_5COO$	Cr 112 SmC* 135.7 SmA 187.5 N* 199 I	21
3-3	$OCH_2(CF_2)_6CF_3$	H	H	$O(CH_2)_5COO$	Cr 110.1 SmA 246.9 I	21
3-4	*n*-C_4H_9	H	H	$OOC(H_2C)_8-(C\equiv C)_2-(CH_2)_8COO$	Cr 79 SmA 109 I	34
3-5	*n*-C_7H_{15}	H	H	$OOC(H_2C)_8-(C\equiv C)_2-(CH_2)_8COO$	Cr 89 SmA 112 I	34
3-6	*n*-$C_{12}H_{25}$	H	H	$OOC(H_2C)_8-(C\equiv C)_2-(CH_2)_8COO$	Cr 93 SmA 108 I	34
3-7	*n*-$C_{14}H_{29}$	H	H	$OOC(H_2C)_8-(C\equiv C)_2-(CH_2)_8COO$	Cr 96 SmA 103 I	34
3-8	*n*-$C_{16}H_{33}$	H	H	$OOC(H_2C)_8-(C\equiv C)_2-(CH_2)_8COO$	I 100 SmA 74 Cr	34
3-9	H	H	H	$OOC(H_2C)_8-(C\equiv C)_2-(CH_2)_8COO$	Cr 70 SmA 76 N* 82 I	34
3-10	H	H	H	$OOC(CH_2)_{20}COO$	Cr 97 N* 104 I	34
3-11	H	H	H	$OOC(CH_2)_6COO$	Cr 123.5 N* 153.2 I	35
3-12	H	H	H	$OOC(CH_2)_7COO$	Cr 110.6 Sm 114.9 I	35 36
3-13	H	H	H	$OOC(CH_2)_8COO$	Cr 102 N* 141.5 I	35
3-14	H	H	H	$OOC(CH_2)_9COO$	Cr 109.3 N* 116.8 I	35
3-15	H	H	H	$OOC(CH_2)_{10}COO$	Cr 97.1 N* 131.7 I	35
3-16	H	H	H	$OOC(CH_2)_{11}COO$	Cr 99.9 N* 114.3 I	35

3-17	H	H	H	$OOC(CH_2)_{12}COO$	Cr 112.7 N* 121.9 I	35
3-18	H	H	H	$OOC(CH_2)_{13}COO$	Cr 100.3 N* 112.3 I	35
3-19	H	H	H	$OOC(CH_2)_{14}COO$	Cr 96.6 N* 120.1 I	35
3-20	*n*-C_7H_{15}	H	H	$OOC(CH_2)_7COO$	Cr 122.7 SmA 125.4 N* 145.7 I	36
3-21	*n*-C_7H_{15}	H	H	$OOC(CH_2)_8COO$	Cr 86.6 SmC* 110.6 SmA 126.2 N* 159.3 I	37
3-22	*n*-OC_8H_{17}	H	H	$O(CH_2)_4COO$	Cr 119.2 SmA 161.2 N* 167.6 I	38
3-23	*n*-OC_8H_{17}	H	H	$O(CH_2)_6COO$	Cr 132.7 SmA (41.7) N* 162.6 I	38
3-24	*n*-OC_8H_{17}	H	H	$O(CH_2)_7COO$	Cr 145.7 SmA 153.6 N* 180.9 I	38
3-25	*n*-OC_8H_{17}	H	H	$O(CH_2)_{10}COO$	Cr 118.5 SmA (45.2) N* 153.7 I	38
3-26	*n*-OC_8H_{17}	H	H	$O(CH_2)_{11}COO$	Cr 128.5 SmA 147 N* 160 I	38
3-27	$OCH_2(CF_2)_6CF_3$	H	H	$O(CH_2)_4COO$	Cr 123.6 SmA 231.3 I	38
3-28	$OCH_2(CF_2)_6CF_3$	H	H	$O(CH_2)_6COO$	Cr 110.5 SmA 214 I	38
3-29	$OCH_2(CF_2)_6CF_3$	H	H	$O(CH_2)_7COO$	Cr 110.3 SmA 221.8 I	38
3-30	$OCH_2(CF_2)_6CF_3$	H	H	$O(CH_2)_{10}COO$	Cr 101.3 SmC* (95.4) SmA 190 I	38
3-31	$OCH_2(CF_2)_6CF_3$	H	H	$O(CH_2)_{11}COO$	Cr 80.1 SmA 184.2 I	38
3-32	*n*-OC_8H_{17}	F	F	$O(CH_2)_4COO$	Cr 88.4 SmA (75.2) N* 149 I	39
3-33	*n*-OC_8H_{17}	F	F	$O(CH_2)_5COO$	Cr 89.5 SmX (60.2) SmÃ 127 SmC* 139 N* 184 I	39
3-34	*n*-OC_8H_{17}	F	F	$O(CH_2)_6COO$	Cr 105 SmX (72.8) N* 143 I	39
3-35	*n*-OC_8H_{17}	F	F	$O(CH_2)_7COO$	Cr 100 TGBC (96.6) SmC* 131 N* 170 I	39
3-36	*n*-OC_8H_{17}	F	F	$O(CH_2)_8COO$	Cr 107 SmX 115 N* 140 I	39
3-37	*n*-OC_8H_{17}	F	F	$O(CH_2)_9COO$	Cr 99.6 TGBC (87.9) Sm1 126 SmC* 142 N* 156 I	39
3-38	*n*-OC_8H_{17}	F	F	$O(CH_2)_{10}COO$	Cr 96.1 SmX (38.5) N* 140 I	39
3-39	*n*-OC_8H_{17}	F	F	$O(CH_2)_{11}COO$	Cr 99.6 SmX (74.1) TGBC (86.3) SmC* 140 N* 150 I	39
3-40	*n*-OC_8H_{17}	F	F	$O(CH_2)_{12}COO$	Cr 80.3 SmX (48.1) N* 136 I	39
3-41	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_4COO$	Cr 73.6 SmA 211 I	39
3-42	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_5COO$	Cr 111 SmA 224 I	39
3-43	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_6COO$	Cr 70.6 SmA 189 I	39

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3-44	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_7COO$	Cr 85.6 SmA 207 I	39
3-45	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_8COO$	Cr 69.8 SmA 178 I	39
3-46	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_9COO$	Cr 92.4 SmA 187 I	39
3-47	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_{10}COO$	Cr 75.3 SmA 169 I	39
3-48	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_{11}COO$	Cr 97.9 SmA 175 I	39
3-49	$OCH_2(CF_2)_6CF_3$	F	F	$O(CH_2)_{12}COO$	Cr 75.5 SmA 160 I	39
3-50	NO_2	H	H	$OOC(CH_2)_2COO$	Cr 197.1 N* 240.9 I	40
3-51	NO_2	H	H	$OOC(CH_2)_4COO$	Cr 130.5 N* 220 I	40
3-52	NO_2	H	H	$OOC(CH_2)_6COO$	Cr 147.5 N* 194.8 I	40
3-53	NO_2	H	H	$OOC(CH_2)_8COO$	Cr 145.8 N* 183.7 I	40

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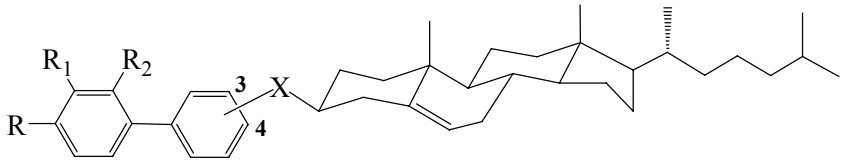
4. Biphenyls (phenyl benzenes)

Table S4[a]: Phase behavior of cholesterol-based dimers comprising biphenyl mesogenic moiety. The compounds are generally listed as per their order of appearance in the literature. SmE = Smectic E phase (this is not a true smectic phase and therefore it is regarded as crystal E phase in recent times); SmX = Unidentified smectic phase, N^*_{re} = reentrant chiral nematic phase.



Dimer	R	R_1	R_2	X	Position of X	Phase sequence and transition temperatures in ^oC	Ref.
4-1	CN	H	H	$O(CH_2)_2COO$	4	Cr 152 SmA 157 N* 168 I	41 42
4-2	CN	H	H	$O(CH_2)_3COO$	4	Cr 160 SmA 202 N* 226 I	41 42
4-3	CN	H	H	$O(CH_2)_4COO$	4	Cr 118 SmA 144 N* 168 I	41 42
4-4	CN	H	H	$O(CH_2)_5COO$	4	Cr 128 SmA 168 N* 205 I	41 42
4-5	CN	H	H	$O(CH_2)_6COO$	4	Cr 103 SmA 118 N* 160 I	41 42
4-6	CN	H	H	$O(CH_2)_7COO$	4	Cr 127 SmA 139 N* 185 I	41 42
4-7	CN	H	H	$O(CH_2)_{10}COO$	4	Cr 97 SmA 92 N* 151 I	41 42
4-8	CN	H	H	OCH_2COO	4	Cr 176 SmA 210 I	42
4-9	$COOC_4H_9$	H	H	$O(CH_2)_5COO$	4	Cr 110 SmA 162.8 N* 178.2 I	43
4-10	$COOC_4H_9$	H	H	$O(CH_2)_7COO$	4	Cr 86.7 SmA 155.8 N* 159.7 I	43
4-11	$COOC_4H_9$	H	H	$O(CH_2)_{10}COO$	4	Cr 82 SmA 120.4 N* 127.4 I	43
4-12	$COOC_5H_{11}$	H	H	$O(CH_2)_5COO$	4	Cr 118 SmA 154.5 N* 174.5 I	43
4-13	$COOC_5H_{11}$	H	H	$O(CH_2)_7COO$	4	Cr 121.9 SmA 151.2 N* 158.9 I	43

4-14	$COOC_5H_{11}$	H	H	$O(CH_2)_{10}COO$	4	Cr 98.4 SmA 117.7 N* 126.2 I	43
4-15	$COOC_6H_{13}$	H	H	$O(CH_2)_5COO$	4	Cr 132 SmX (99) SmC* (111) SmA 160.5 N* 166.7 I	43
4-16	$COOC_6H_{13}$	H	H	$O(CH_2)_7COO$	4	Cr 137.8 SmE (68) SmA 143.2 N* 151.8 I	43
4-17	$COOC_6H_{13}$	H	H	$O(CH_2)_{10}COO$	4	Cr 82 SmA 111.7 N* 120.4 I	43
4-18	*n*-OC_6H_{13}	H	H	$O(CH_2)_3COO$	4	Cr 160 SmA 198 N* 207 I	44 45
4-19	*n*-OC_6H_{13}	H	H	$O(CH_2)_4COO$	4	Cr 127 SmA 133 N* 148 I	44 45
						Cr 127.2 SmA 136.1 TGB 137.6 N* 150.7 I	46
4-20	*n*-OC_6H_{13}	H	H	$O(CH_2)_5COO$	4	Cr 136 SmA 162 N* 181 I	44 45
						Cr 134.3 SmA 158.3 TGB 164.3 N* 182.1 I	46
4-21	*n*-OC_6H_{13}	H	H	$O(CH_2)_6COO$	4	Cr 103 N* 123 I	44 45
4-22	*n*-OC_6H_{13}	H	H	$O(CH_2)_7COO$	4	Cr 110 SmA 161 N* 168 I	44 45
4-23	*n*-OC_6H_{13}	H	H	$O(CH_2)_{10}COO$	4	Cr 95 SmA 130 N* 138 I	44 45
4-24	*n*-OC_6H_{13}	H	H	$O(CH_2)_3COO$	3	Cr 58 N* (19) I	44
4-25	*n*-OC_6H_{13}	H	H	$O(CH_2)_4COO$	3	Cr 82 SmA (59) I	44
4-26	*n*-OC_6H_{13}	H	H	$O(CH_2)_5COO$	3	Cr 47 N* (33) I	44
4-27	*n*-OC_6H_{13}	H	H	$O(CH_2)_6COO$	3	Cr 66 N* (36) I	44
4-28	*n*-OC_6H_{13}	H	H	$O(CH_2)_7COO$	3	Cr 54 N* (33) I	44
4-29	*n*-OC_6H_{13}	H	H	$O(CH_2)_{10}COO$	3	Cr 63 N* (42) I	44
4-30	*n*-OC_4H_9	H	H	$O(CH_2)_3COO$	4	Cr 171 SmA 169 N* 215 I	45
4-31	*n*-OC_4H_9	H	H	$O(CH_2)_4COO$	4	Cr 104 N* 152 I	45
						Cr 104 N* 153.1 I	46
4-32	*n*-OC_4H_9	H	H	$O(CH_2)_5COO$	4	Cr 118 SmA 171 N* 194 I	45
						Cr 116.6 SmA 166.5 N* 190.6 I	46
4-33	*n*-OC_4H_9	H	H	$O(CH_2)_6COO$	4	Cr 92 N* 142 I	45
4-34	*n*-OC_4H_9	H	H	$O(CH_2)_7COO$	4	Cr 112 SmA 166 N* 177 I	45
4-35	*n*-OC_4H_9	H	H	$O(CH_2)_{10}COO$	4	Cr 99 SmA 130 N* 144 I	45

4-36	*n*-OC_5H_{11}	H	H	$O(CH_2)_3COO$	4	Cr 174 SmA 188 N* 206 I	45
4-37	*n*-OC_5H_{11}	H	H	$O(CH_2)_4COO$	4	Cr 117 SmA 126 N* 148 I	45
						Cr 119.6 SmA 124.4 TGB 129.6 N* 150 I	46
4-38	*n*-OC_5H_{11}	H	H	$O(CH_2)_5COO$	4	Cr 143 SmA 169 N* 187 I	45
						Cr 145.2 SmA 170.8 TGB 171 N* 188.5 I	46
4-39	*n*-OC_5H_{11}	H	H	$O(CH_2)_6COO$	4	Cr 86 N* 141 I	45
4-40	*n*-OC_5H_{11}	H	H	$O(CH_2)_7COO$	4	Cr 95 SmA 165 N* 171 I	45
4-41	*n*-OC_5H_{11}	H	H	$O(CH_2)_{10}COO$	4	Cr 99 SmA 131 N* 142 I	45
4-42	*n*-OC_7H_{15}	H	H	$O(CH_2)_4COO$	4	Cr 112.3 SmA 139.4 TGB 140.5 N* 146.1 I	46
4-43	*n*-OC_8H_{17}	H	H	$O(CH_2)_4COO$	4	Cr 107.8 SmA 144.7 TGB 145.2 N* 147.8 I	46
4-44	*n*-OC_7H_{15}	H	H	$O(CH_2)_5COO$	4	Cr 139.7 SmA 167.2 TGB 168 N* 179.4 I	46
4-45	*n*-OC_8H_{17}	H	H	$O(CH_2)_5COO$	4	Cr 111.5 SmA 172.2 TGB 172.4 N* 177.5 I	46
4-46	*n*-OC_8H_{17}	F	F	$O(CH_2)_3COO$	4	Cr 127 SmC* (92.8) SmA 177.1 TGB^b-N* 179.9 I	47
4-47	*n*-$OC_{10}H_{21}$	F	F	$O(CH_2)_3COO$	4	Cr 81.4 SmC* 105.8 SmA 174.3 I	47
4-48	*n*-OC_8H_{17}	F	F	$O(CH_2)_4COO$	4	Cr 80.1 SmA 119.7 TGB^b-N* 125.5 I	47
4-49	*n*-$OC_{10}H_{21}$	F	F	$O(CH_2)_4COO$	4	Cr 83.4 SmA 121 TGB^b-N* 121.7 I	47
4-50	*n*-OC_8H_{17}	F	F	$O(CH_2)_5COO$	4	Cr 67.4 SmC* 92.5 SmA 151.2 TGB^b-N* 161.1 I	47
4-51	*n*-$OC_{10}H_{21}$	F	F	$O(CH_2)_5COO$	4	Cr 62.1 SmC* 103.6 SmA 154.9 TGB^b-N* 156.8 I	47
4-52	*n*-OC_8H_{17}	F	F	$O(CH_2)_7COO$	4	Cr 77.1 TGBC* 85.8 SmA 117.5 TGB 124 N* 145 I	47
4-53	*n*-$OC_{10}H_{21}$	F	F	$O(CH_2)_7COO$	4	Cr 101.9 SmC* (94.2) SmA 132.4 TGB^b-N* 142 I	47
4-54	CN	H	H	$O(CH_2)_3O$	4	Cr 139 SmA (110) N* (118) I	48
4-55	CN	H	H	$O(CH_2)_4O$	4	Cr 151 SmA 178 N* 210 I	48
4-56	CN	H	H	$O(CH_2)_5O$	4	Cr 111 SmA 119 N* 146 I	48
4-57	CN	H	H	$O(CH_2)_6O$	4	Cr 105 SmA 150 N* 188 I	48
4-58	CN	H	H	$O(CH_2)_7O$	4	Cr 119 SmA (106) N* 147 I	48
4-59	CN	H	H	$O(CH_2)_8O$	4	Cr 130 SmA (129) N* 172 I	48

4-60	CN	H	H	$O(CH_2)_9O$	4	Cr 89 SmA 97 N* 144 I	48
4-61	CN	H	H	$O(CH_2)_{10}O$	4	Cr 109 SmA 115 N* 160 I	48
4-62	CN	H	H	$O(CH_2)_{11}O$	4	Cr 86 SmA 89 N* 140 I	48
4-63	CN	H	H	$O(CH_2)_{12}O$	4	Cr 106 SmA (105) N* 151 I	48
4-64	*n*-OC_4H_9	H	H	$O(CH_2)_4O$	4	Cr 160 N* 189 I	48
4-65	*n*-OC_4H_9	H	H	$O(CH_2)_5O$	4	Cr 119 N* 133 I	48
4-66	*n*-OC_4H_9	H	H	$O(CH_2)_6O$	4	Cr 128 SmA 148 N* 175 I	48
4-67	*n*-OC_4H_9	H	H	$O(CH_2)_7O$	4	Cr 92 N* 135 I	48
4-68	*n*-OC_4H_9	H	H	$O(CH_2)_8O$	4	Cr 120 SmA 158 N* 167 I	48
4-69	*n*-OC_4H_9	H	H	$O(CH_2)_9O$	4	Cr 111 SmA 116 N* 139 I	48
4-70	*n*-OC_6H_{13}	H	H	$O(CH_2)_5O$	4	Cr 113 SmA (106) N* 131 I	48
4-71	*n*-OC_6H_{13}	H	H	$O(CH_2)_6O$	4	Cr 143 SmA 151 N* 174 I	48
4-72	*n*-OC_6H_{13}	H	H	$O(CH_2)_7O$	4	Cr 109 N* 131 I	48
4-73	*n*-OC_6H_{13}	H	H	$O(CH_2)_8O$	4	Cr 122 SmA 155 N* 161 I	48
4-74	*n*-OC_6H_{13}	H	H	$O(CH_2)_9O$	4	Cr 99 SmA 117 N* 135 I	48
4-75	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_4O$	4	Cr 103 SmC* (98) SmA 182 I	49
4-76	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_5O$	4	Cr 67 SmC* 78 SmA 120 I	49
4-77	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_6O$	4	Cr 100 SmC* 113 SmA 162 I	49
4-78	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_7O$	4	Cr 68 SmC* 79 SmA 114 N* 116 I	49
4-79	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_8O$	4	Cr 89 SmC* 105 SmA 138 N* 143 I	49
4-80	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_9O$	4	Cr 88 SmC* 90 SmA 110 N* 122 I [c]	49
4-81	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_{10}O$	4	Cr 126 SmA 127 N* 137 I	49
4-82	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_{11}O$	4	Cr 113 SmA (98) N* 120 I	49
4-83	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_{12}O$	4	Cr 128 N* (125) I	49
4-84	*n*-$OC_{12}H_{25}$	H	H	$O(CH_2)_{10}COO$	4	Cr 116 N^*_{re} (103) TGB (110) N* 127 I	49

[a] The transition between different crystalline forms have not been considered; only the crystalline form (temperature) melting into the mesophase is mentioned. [b] A very short lived phase. [c] For this compound, the authors describe a N*-TGB-SmA-TGB-N* sequence during the cooling cycle, although transitions temperatures are not mentioned.

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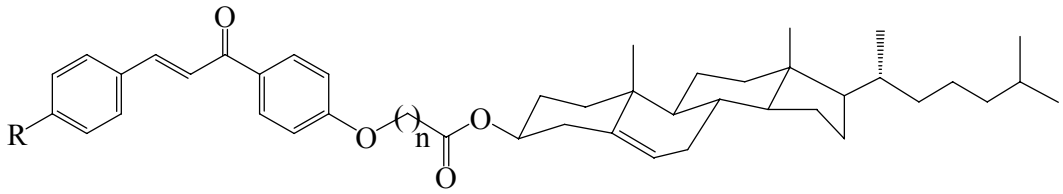
5. Chalcones (1,3-diphenylpropenones).

Table S5 [a]: Phase sequence and transition temperatures of cholesterol-based dimers consisting of chalcone core.



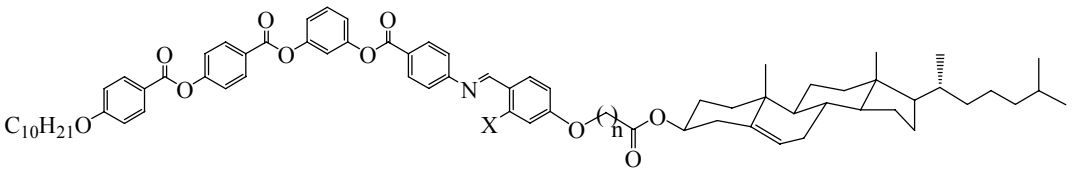
Dimers	R	n	Phase sequence and transition temperatures in ^{o}C	Ref.
5-1	*n*-$OC_{10}H_{21}$	4	Cr 118.9 TGBC* (81.6) TGBA 124.4 I	50 51
5-2	*n*-$OC_{11}H_{23}$	4	Cr 114.2 TGBC* (83.6) TGBA 125.4 I	50 51
5-3	*n*-$OC_{12}H_{25}$	4	Cr 116.3 TGBC* (82.5) TGBA 125.9 I	50 51
5-4	*n*-OC_2H_5	3	Cr 171.9 N* (167.6) BP (168.8) I	51
5-5	*n*-OC_4H_9	3	Cr 162.6 N* (154.1) BP (156.6) I	51
5-6	*n*-OC_5H_{11}	3	Cr 158.2 N* (152.3) BP (153.7) I	51
5-7	*n*-OC_6H_{13}	3	Cr 141.2 SmA (125)-TGB[b]-N* (138.7) BP (140) I	51
5-8	*n*-OC_7H_{15}	3	Cr 153.8 SmA (143.7) TGB (144.7) N* (150.7) BP (151.9) I	51
5-9	*n*-OC_8H_{17}	3	Cr 148.8 SmA 152.8 N* (146.7) BP (148) I	51
5-10	*n*-OC_9H_{19}	3	Cr 145.8 SmA 150.5-TGB[b]-N*-(BP)[b]-151.2 I	51
5-11	*n*-$OC_{10}H_{21}$	3	Cr 140.8 SmA- N*[b]-(BP)[b]-150.8 I	51
5-12	*n*-$OC_{11}H_{23}$	3	Cr 138.1 SmA 150.5 I	51
5-13	*n*-$OC_{12}H_{25}$	3	Cr 136.8 SmA 151.8 I	51
5-14	*n*-OC_2H_5	4	Cr 125.3 N* 128.1 BP 132.4 I	51
5-15	*n*-OC_4H_9	4	Cr 117.5 N* 121.0 BP (122.3) I	51

5-16	*n*-OC_5H_{11}	4	Cr 126.1 N* (116.5) BP (124.1) I	51
5-17	*n*-OC_6H_{13}	4	Cr 132.2 N* (114.8) BP (116) I	51
5-18	*n*-OC_7H_{15}	4	Cr 132.5 N* (112.9) BP (120) I	51
5-19	*n*-OC_8H_{17}	4	Cr 149.1 SmA (145.4) N* 149 BP 149.8 I	51
5-20	*n*-OC_9H_{19}	4	Cr 144.2 SmA 148.9-TGB^b-N*-$(BP)^b$-150.5 I	51
5-21	*n*-OC_2H_5	5	Cr 189.9 I	51
5-22	*n*-OC_4H_9	5	Cr 156.1 N* (146.4) BP (147.7) I	51
5-23	*n*-OC_5H_{11}	5	Cr 150.7 N* (141.5) BP (142.9) I	51
5-24	*n*-OC_6H_{13}	5	Cr 148.3 N* (135.9) BP (137.3) I	51
5-25	*n*-OC_7H_{15}	5	Cr 147 N* (138.5) BP (139.8) I	51
5-26	*n*-OC_8H_{17}	5	Cr 144.5 N* (136.8) BP (138.7) I	51
5-27	*n*-OC_9H_{19}	5	Cr 141.5 N* (134.9) BP (136.8) I	51
5-28	*n*-$OC_{10}H_{21}$	5	Cr 138 SmA (132.9) N* (133.4) BP (135.7) I	51
5-29	*n*-$OC_{11}H_{23}$	5	Cr 136.4 SmA (134.3) N* (135.2) I	51
5-30	*n*-$OC_{12}H_{25}$	5	Cr 135.1 SmA 137.2 I	51
5-31	*n*-OC_2H_5	7	Cr 151 N* (136.5) BP (140.8) I	51
5-32	*n*-OC_4H_9	7	Cr 161.1 N* (147.7) I	51
5-33	*n*-OC_5H_{11}	7	Cr 148.1 N* (128.2) BP (131.2) I	51
5-34	*n*-OC_6H_{13}	7	Cr 152.2 N* (128.8) BP (130.2) I	51
5-35	*n*-OC_7H_{15}	7	Cr 128.4 N* BP (129) 130 .2 I	51
5-36	*n*-OC_8H_{17}	7	Cr 126.6 N* BP (128.8) 129.7 I	51
5-37	*n*-OC_9H_{19}	7	Cr 123.7 SmA –TGB^b-N^{*b} BP (126.7) 128 I	51
5-38	*n*-$OC_{10}H_{21}$	7	Cr 119.8 SmA 125.5 N* -BP^b 128 I	51
5-39	*n*-$OC_{11}H_{23}$	7	Cr 116 SmA 117.8-TGB^b-N* 121 BP 122.5 I	51
5-40	*n*-$OC_{12}H_{25}$	7	Cr 121 SmA 120.9-TGB^b-N* 123 BP 123.9 I	51

[a] The transition between different crystalline forms have not been considered; only the crystalline form melting (temperature) into the mesophase is mentioned. [b] A very short lived phase.

6. Bent-core (banana-shaped) systems

Table S6: Thermal behavior of cholesterol-based dimers comprising five-ring bent-core system. BP = Blue phase III; M_{x1}, M_{x2} and M_{x3} = unknown tilted smectic mesophases; Col_{r1} and Col_{r2} = rectangular columnar phases.



Dimers	n	X	Phase sequence and transition temperatures in °C	Ref.
6-1	3	H	Cr 145.6 M_{x1} (124.1) N* 153 BP 171.5 I	52
6-2	3	OH	Cr 158.1 M_{x1} (154.2) N* 167 BP 186.3 I	52
6-3	4	H	Cr 122 Col_r 137.8 I	52
6-4	4	OH	Cr 141.9 Col_r 149.5 I	52
6-5	5	H	Cr 145.9 M_{x2} (108.9) Col_{r2} (112.6) Col_{r1} (118.4) N* 153 BP 164.2 I	52
6-6	5	OH	Cr 151.2 M_{x3} (52) N* 160 BP 175.5 I	52 53
6-7	7	H	Cr 122.6 Col_r (114.7) N* 140 BP 152.6 I	52
6-8	7	OH	Cr 156.8 Col_r (138.9) N* (144) BP 163.5 I	52

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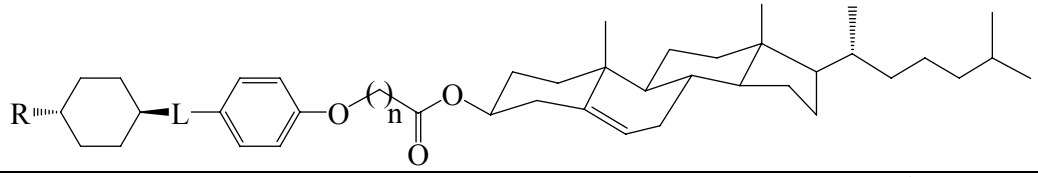
7. Cyclohexanes

Table S7: Phase behavior of cholesterol-based dimers having cyclohexane-aromatic mesogenic segment.



Dimers	R	L	n	Phase sequence and transition temperatures in ^{o}C	Ref.
7-1	*n*-C_5H_{11}	COO	3	Cr 126.4 TGBC* (101.2) SmA 163.4 TGB 167.5 N* 210 I	54
7-2	*n*-C_5H_{11}	COO	4	Cr 94.8 N* 157.3 I	54
7-3	*n*-C_5H_{11}	COO	5	Cr 94.6 TGBC* 133.8 N* 190 I	54
7-4	*n*-C_5H_{11}	COO	7	Cr 136 N* 174 4.I	54
7-5	*n*-C_3H_7	-	3	Cr 145.5 N* 187.6 I	55
7-6	*n*-C_4H_9	-	3	Cr 103.8 SmA 146.9 N* 186.7 I	55
7-7	*n*-C_5H_{11}	-	3	Cr 122.3 SmA 164.0 N* 192.8 I	55
7-8	*n*-C_6H_{13}	-	3	Cr 106.3 SmA 163.3 N* 183.2 I	55
7-9	*n*-C_7H_{15}	-	3	Cr 128.5 SmA 172.7 N* 185.2 I	55
7-10	*n*-C_8H_{17}	-	3	Cr 138.0 SmA 177.3 N* 184.0 I	55
7-11	*n*-C_9H_{19}	-	3	Cr 116.7 SmA 162.1 N* 172.5 I	55
7-12	*n*-C_3H_7	-	4	Cr 105.8 N* 114.8 I	55
7-13	*n*-C_4H_9	-	4	Cr 64.1 N* 98.5 I	55
7-14	*n*-C_5H_{11}	-	4	Cr 82.5 SmA 107.0 N* 132.3 I	55
7-15	*n*-C_6H_{13}	-	4	Cr 97.3 SmA 109.7 N* 129.0 I	55
7-16	*n*-C_7H_{15}	-	4	Cr 85.0 SmA 126.1 N* 134.0 I	55
7-17	*n*-C_8H_{17}	-	4	Cr 96.0 SmA 121.1 N* 134.1 I	55
7-18	*n*-C_9H_{19}	-	4	Cr 71.1 SmA 128.0 N* 133.2 I	55
7-19	*n*-C_3H_7	-	5	Cr 103.3 N* 141.1 I	55
7-20	*n*-C_4H_9	-	5	Cr 101.8 N* 164.0 I	55
7-21	*n*-C_5H_{11}	-	5	Cr 84.9 N* 172.8 I	55
7-22	*n*-C_6H_{13}	-	5	Cr 99.7 SmA 138.2 N* 169.4 I	55
7-23	*n*-C_7H_{15}	-	5	Cr 123.0 SmA 138.5 N* 161.2 I	55
7-24	*n*-C_8H_{17}	-	5	Cr 111.1 SmA 152.1 N* 166.8 I	55
7-25	*n*-C_9H_{19}	-	5	Cr 97.7 SmA 155.5 N* 165.0 I	55

7-26	*n*-C_3H_7	-	7	Cr 116.5 N* 154.7 I	55
7-27	*n*-C_4H_9	-	7	Cr 103.7 N* 154.3 I	55
7-28	*n*-C_5H_{11}	-	7	Cr 98.1 N* 157.6 I	55
7-29	*n*-C_6H_{13}	-	7	Cr 91.4 N* 154.6 I	55
7-30	*n*-C_7H_{15}	-	7	Cr 85.6 N* 152.0 I	55
7-31	*n*-C_8H_{17}	-	7	Cr 77.8 SmA 125.1 N* I	55
7-32	*n*-C_9H_{19}	-	7	Cr 91.2 SmA 130.7 149.3 I	55

8. Phenylbenzoates (esters)

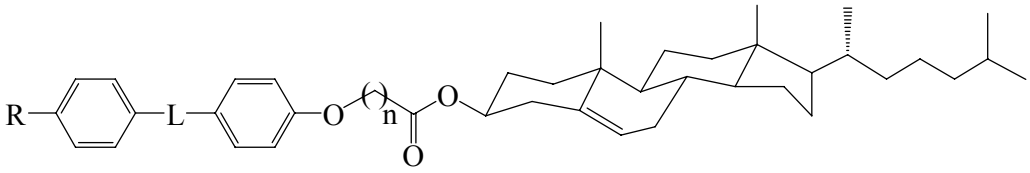


Table S8: Phase behavior of cholesterol-based dimers having phenylbenzoate core

Dimers	R	L	n	Phase sequence and transition temperatures in ^oC	Ref.
8-1	*n*-C_4H_9	COO	5	Cr 119 Sm_{q1} 142 TGB_{q1} 144 N* 180.8 I	24
8-2	*n*-C_4H_9	OOC	5	Cr 85 N* 175.5 I	24
8-3	CN	COO	3	Cr 120.8 SmA 201.5-TGB[a]-N* 224.6 I	54
8-4	CN	COO	4	Cr 108.6 SmA 159.1-TGB[a]-N* 179.1 I	54
8-5	CN	COO	5	Cr 84.2 SmC* (58.6) SmA 178.2-TGB[a]-N* 212.7 I	54
8-6	CN	COO	7	Cr 96 SmA 148.5-TGB[a]-N* 187.2 I	54

[a] An enantiotropic transient phase;

9. Salicylaldimines

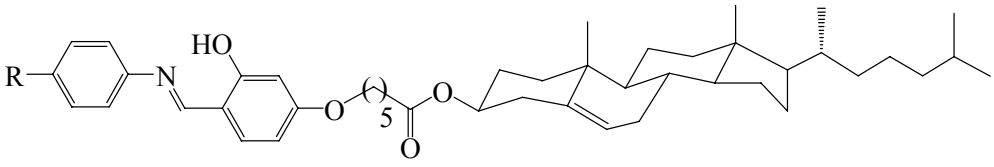
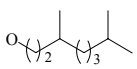


Table S9: Thermal behavior of cholesterol-based dimers having salicylaldimine segment.

Dimers	R	Phase sequence and transition temperatures in ^oC	Ref.
9-1	*n*-C_4H_9	Cr 130.1 SmA 74.9 N* 203 I	56 57
9-2	*n*-$C_{10}H_{21}$	Cr 120.3 SmC* 153.6 SmA 185.6 N* 187.2 I	56 57
9-3		Cr 116.7 SmC* 146.4 SmA 176.5 N* 179.6 I	56 57

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10. Stilbenes (*trans*-1,2-diphenylethylenes)

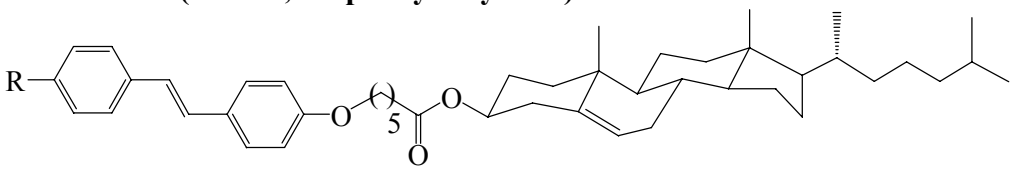


Table S10: Phase behavior of cholesterol-based dimers comprising stilbene moiety.

Dimers	R	Phase sequence and transition temperatures in ^{o}C	Ref.
10-1	*n*-C_4H_9	Cr 125 Sm_{q3} 190 TGB_{q3} 191.7 N* 206.5 I	24
10-2	*n*-OC_8H_{17}	Cr 133.6 SmA 204.7 N* 210.9 I	21
10-3	*n*-$OCH_2(CF_2)_6CF_3$	Cr 143.8 SmA 251.9 I	21

11. Diphenylbutadienes

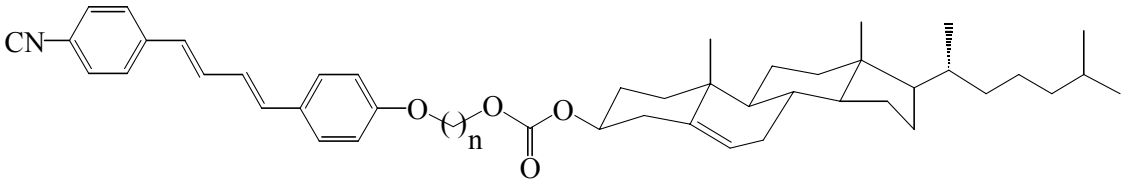


Table S11: Liquid crystal behavior of cholesterol-based dimers having diphenylbutadiene core. Cr_1 and Cr_2 = Crystalline states.

Dimers	*n*	Phase sequence and transition temperatures in ^{o}C	Ref.
11-1	8	Cr_1 99.5 SmA 112.8 Cr_2 131.9 SmA 134 TGBA 138 N* 202.9 I	58
11-2	11	Cr 120.9 SmA 145.5 N* 175 I	58
11-3	12	Cr_1 109.4 SmA 112.8 Cr_2 129.5 N* 188.1 I	58

12. Terphenyls

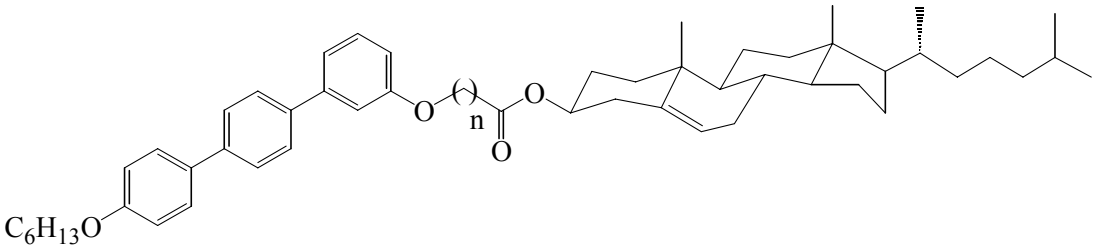


Table S12: Phase transitional properties of cholesterol-based dimers featuring terphenyl segment.

Dimers	n	Phase sequence and transition temperatures in ^{o}C	Ref
12-1	3	Cr 120 SmA 112 I	44
12-2	4	Cr 113 SmA 153 I	44
12-3	5	Cr 107 SmA 117 I	44
12-4	6	Cr 101 SmA 139 I	44
12-5	7	Cr 88 SmA 115 I	44
12-6	10	Cr 94 SmA 124 I	44

13. Sydnones

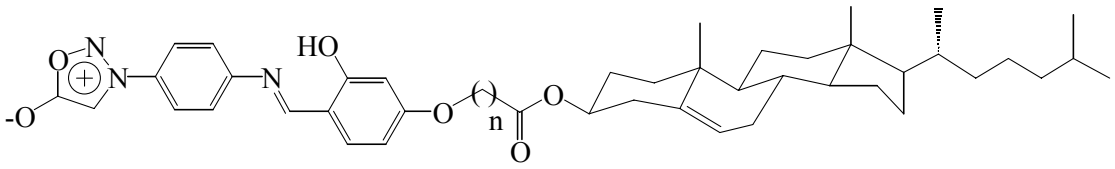


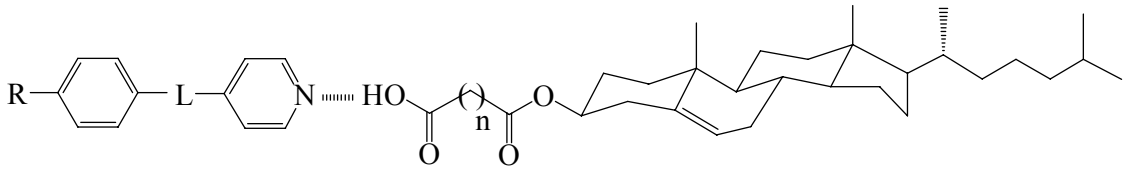
Table S13: Phase behavior of cholesterol-based dimers possessing sydnone core.

Dimers	n	Phase sequence and transition temperatures in ^{o}C	Ref
13-1	3	Cr 230 SmA 265[a]	59
13-2	4	Cr 162 SmA 210[a]	59
13-3	5	Cr 170 SmA 215[a]	59
13-4	7	Cr 242 SmA 270[a]	59

[a] SmA – I has not been ascertained by either microscopy or calorimetric techniques, owing to thermal degradation above this temperature.

14. Supramolecular (H-bonded) systems

Table S14 [a]: Thermal behavior of supramolecular cholesterol-based dimers.
Sm_{LT} = Low temperature smectic phase; Sm_{HT} = High temperature smectic phase



Dimers	R	L	n	Phase sequence and transition temperatures in °C	Ref
14-1	4-(*n*-OCH_3)C_6H_4COO	CH=CH	2	Cr 133.7 SmC* 190 N* 229.3 I	22
14-2	4-(*n*-OC_2H_5)C_6H_4COO	CH=CH	2	Cr 152.2 SmC* 186 N* 234.6 I	22
14-3	4-(*n*-OC_3H_7)C_6H_4COO	CH=CH	2	Cr 145.6 SmC* 187 N* 224.4 I	22
14-4	4-(*n*-OC_4H_9)C_6H_4COO	CH=CH	2	Cr 157 SmC* 183 N* 231.4 I	22
14-5	4-(*n*-OC_5H_{11})C_6H_4COO	CH=CH	2	Cr 149.2 SmC* 185 N* 226.4 I	22
14-6	4-(*n*-OC_6H_{13})C_6H_4COO	CH=CH	2	Cr 148.5 SmC* 190 N* 222.3 I	22
14-7	4-(*n*-OC_7H_{15})C_6H_4COO	CH=CH	2	Cr 150.7 SmC* 187.2 N* 219.1 I	22
14-8	4-(*n*-OC_8H_{17})C_6H_4COO	CH=CH	2	Cr 151.8 SmC* 195.3 N* 218.7 I	22
14-9	4-(*n*-$OC_{10}H_{21}$)C_6H_4COO	CH=CH	2	Cr 148.8 SmC* 190.6 N* 209.1 I	22
14-10	*n*-OC_2H_5	N=CH	2	Cr 113.8 SmA 126 N* 156.6 I	22
14-11	*n*-OC_5H_{11}	N=CH	2	Cr 103.1 SmA 140 N* 149.6 I	22
14-12	*n*-OC_7H_{15}	N=CH	2	Cr 115.4 N* 144.9 I	22
14-13	*n*-$OC_{10}H_{21}$	N=CH	2	Cr 110 SmA 120 N* 141.4 I	22
14-14	4-(*n*-OC_4H_9)C_6H_4COO	N=CH	4	Cr 126 Sm_{LT} (116) Sm_{HT} 145 N* I	60
14-15	4-(*n*-$OC_{10}H_{21}$)C_6H_4COO	N=CH	4	Cr 126 Sm 135 N* 192 I	60

[a] The transition between different crystalline forms have not been considered; only the crystalline form (temperature) melting into the mesophase is mentioned