



STRUCTURE-PROPERTIES RELATIONSHIPS IN LIQUID CRYSTAL THIOLS

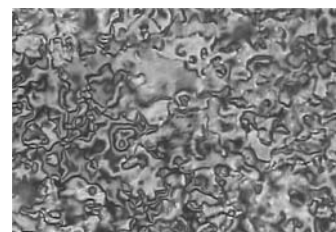
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Two new series of thiols were studied in order to establish the structure-properties relationships. First series consists of compounds with three or four aromatic rings as rigid part of mesogen and the second contains thiols with a flexible chain attached to side on or end of the rigid part of molecules. The molecular structures of compounds were confirmed by elemental analysis and NMR. The mesomorphic properties and thermal stabilities of compounds were studied by DSC, OPM and XRD. All the thiols are liquid crystals; thiols with side on chain show nematic phase, and thiols with end on chain show nematic phase and also, smectic A and C phases.



INTRODUCTION

In recent years, increasing attention has been paid to gold colloidal particles due to the practical and fundamental interest in such systems with potential applications in the area of optoelectronic,¹⁻³ catalysis^{3,4} and biomedical.^{3,5-7} One of the major challenges is to control the size and monodispersity of gold nanoparticles and to organise them into nanostructured devices. In order to obtain stable and monodispersed gold nanoparticles with a desired particles size and properties it is important to synthesize thiol surfactants with tuneable size.⁸⁻¹² The thiols play an important role in the formation of self-assembled monolayers on gold surfaces, thereby the possibility of getting multifunctional nanoparticles is extended and the stability in air of nanoparticles is assured. For this purpose, a logical way is to design and study liquid crystal properties of thiol series. A combination of molecular rigidity and flexibility, and anisotropic forces of attractions serve to dictate the occurrence of mesomorphism. The changes on rigidity or flexibility of molecule can be achieved by: (i) varying the length or nature

of end or side groups; (ii) increasing or decreasing the number of phenyl rings of rigid core.¹³⁻¹⁶

Here, we report the synthesis and characterization of four thiols, but also the relationships between structure and liquid crystal properties. However, the selection of these structure¹⁷ has not been done randomly. The compounds with similar base structures of our show smectic and/or nematic phases and also they have been found to promote nematic or smectic phase behaviour in organic-inorganic hybrids,¹⁸⁻²² polymeric²³⁻²⁵ and dendrimeric systems.²⁶⁻²⁸ These thiols contain three or four aromatic rings and one spacer positioned end or side-on. The spacer has five or eleven methylene groups which can assure a suitable degree of decoupling of the rigid aromatic structure from the gold core.

RESULTS AND DISCUSSION

The phase transition temperatures and the transition enthalpy values of the compounds determined by DSC are given in Table 1.

Table 1

Phase transition temperatures (°C) and associated enthalpy changes ($\Delta H/\text{kJ mol}^{-1}$, in the brackets). Cr = crystalline phase; N = nematic phase; SmC = smectic C phase, SmA = smectic A phase, Iso = isotropic phase

Compound	Transition temperatures, °C (kJ mol ⁻¹)
4	CrI 98.7 (11.4) CrII 112.5 (51.3) SmA 165.4 (4.0) N 173.3 (3.9) Iso Iso 172.4 (4.3) N 164.2 (3.73) SmA 97.9 (53.53) CrI
5	CrI 95.3(74.5)CrII 117.8 (7.9) SmC142.0 SmA160.9(2.5) N 166.1(2.1) Iso Iso165.5 (2.5) N 160.5 (2.2) SmA 141 SmC 117.0 (7.4) CrI 74.7 (22.8) CrII
11	Cr 53.8 (73.7) N 72.3 (1.9) Iso Iso 72.2 (1.9) N -4.0 Cr
12	Cr 47.0 (78.5) N 62.4 (1.3) Iso Iso 60.2 (1.3) N -10.0 Cr
13	Cr 40.5 (90.5) N 67.6 (1.2) Iso Iso 65.5 (1.2) N -30.0 Cr
14	Cr 63.9 (99.6) Iso Iso 61.3 (1.7) N -20.0 Cr
16	Cr 87.5 (53.5) N 143.4 (1.3) Iso Iso 142.0 (1.8) N -3.0 Cr
17	Cr 69.8 (65.8) Cr I 81.3 (4.0) N 139.5 (1.3) Iso Iso 138.1 (1.2) N 45.6 (55.1) Cr

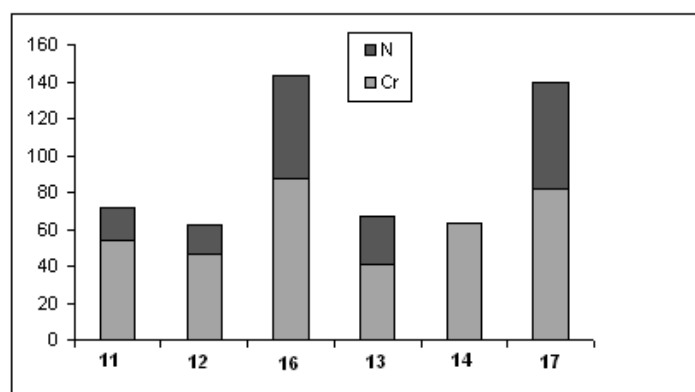


Fig. 1 – Melting points, transition temperatures (on heating) and morphology of phases of **11**, **12**, **13**, **14**, **16** and **17**.

The increasing length of the lateral alkyl chain in *ortho*- position to -COO- group has as effect the decrease of the melting points and the transition temperatures. It was observed that the number of aromatic rings/molecule influences both the transition temperatures and isotropisation temperatures. Thus, the compounds with four aromatic rings/molecule show an increase of both the

transition temperature and isotropisation temperatures comparative to the compound with three aromatic rings/molecule, as can be noticed in Fig. 1.

Optical morphology of **11**, **12**, **13**, **14**, **16** and **17** show nematic phase, with a *schlieren* texture (Fig. 2) of **11**, **13**, **14**, **16** and **17** and *marbled* texture (Fig. 3) of **12**.



Fig. 2 – Optical texture (schlieren) of a nematic phase of **17** at 132.8 °C.

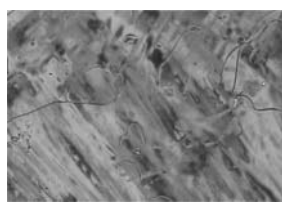


Fig. 3 – Optical texture (marbled) of a nematic phase of **12** at 60.5 °C.

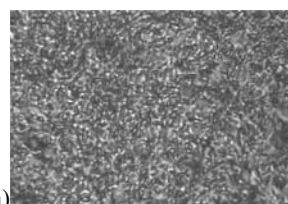


Fig. 4 – Optical micrograph of **4**: a) – smectic A phase at 155.5 °C; b) – nematic phase (*marbled* texture) at 166.2 °C.

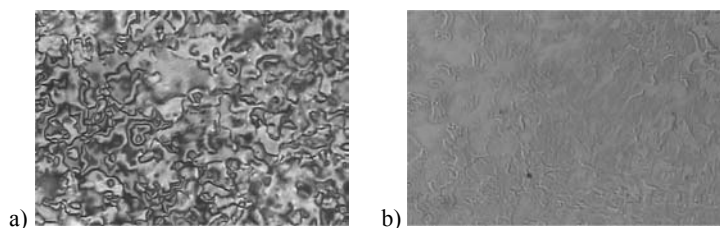


Fig. 5 – Optical micrography of **5**: a) – nematic phase (*schlieren* texture) at 165.0 °C; b) – smectic C phase at 130.2 °C.

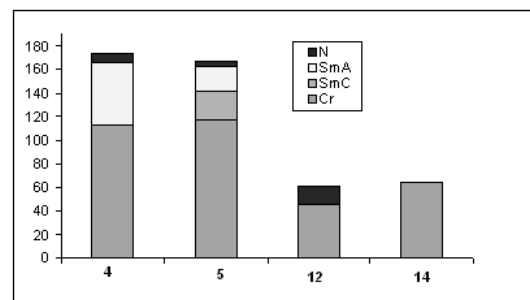


Fig. 6 – Melting points, transition temperatures (on heating) and morphology of mesophases of **4**, **5**, **12** and **14** compounds.

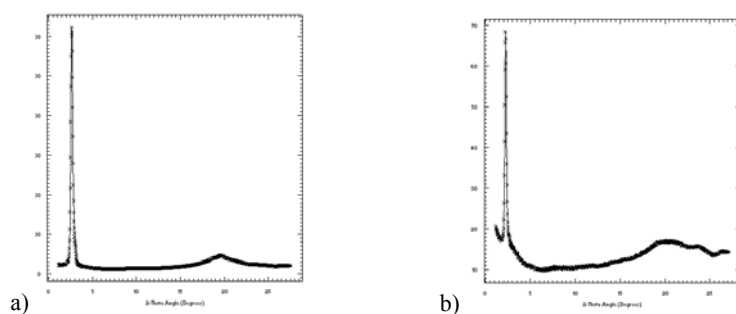


Fig. 7 – X-Ray diffraction patterns of compound **4** (a) and **5** (b) in the SmA phase.

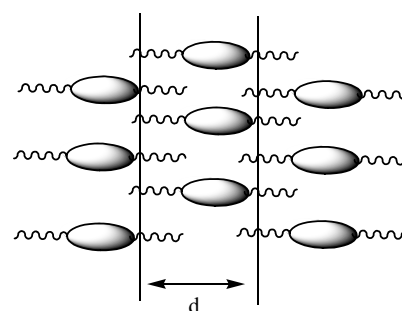


Fig. 8 – Sketch of the intercalated SmA phase exhibited by **4** and **5**.

The compounds with alkyl chain in *para* position to $-\text{COO}-$ group (**4** and **5**) show mesomorphic properties. **4** exhibits smectic A phase (Fig. 4a) and a nematic phase (*marbled* texture) (Fig. 4b). Compound **5** exhibits a smectic A phase (homeotropic arrangement) and a nematic phase (*schlieren* texture) (Fig. 5a) on heating and an extra smectic C phase (Fig. 5b) on cooling.

The comparative studies of the mesomorphic properties of compounds **4** or **5**, unsubstituted compounds in the *ortho* position to ester group, with compounds **12** or **14**, substitute on the *ortho* position to ester group, show that a laterally group suppresses a smectic phase and decreases the temperature of the nematic phase (Fig. 6). This behaviour is due to the bulkier size of the molecules (**12** and **14**) and to the suppression of the interactions between terminal chains, which usually promote the smectic phases.²⁹

2.1. X-ray diffraction studies

Diffraction patterns of the N and SmA phases of all the compounds show a diffuse peak in the wide angle region, in a direction normal to that of the magnetic field. It has a spacing of about 4.5 Å that corresponds to the average lateral separation of the molecules in these fluid phases. In the SmA phase a reflection at $2\theta = 2.64^\circ$ (for **4**) and 2.28°

(for **5**) were observed in the small angle region, corresponding to the spacing (*d*) of 33 Å and 43 Å, respectively (Fig. 7). The difference of 10 Å between corresponding spaces of **4** and **5** is too bigger to be only due to the extra bond C-S. The value of this length is 1.8 Å, which means the difference of 10 Å is also due to the lower packing of the molecules. The molecular lengths were calculated to be 45 Å for **4** and 46 Å for **5** by the MM2 method. Highlighting an homeotropic orientation of **5** in the range 141–117 °C excludes the possibility of a tilted phase.^{30,31} Based on these results we propose a SmA packing model with interdigitating alkyl tails as presented in Fig. 8.

The compound **5** shows a SmC phase in the range 141–117 °C, as is proved by OPM (Fig. 5b) and X-ray diffraction (Fig. 9b). The DSC thermogram does not show this transition.

The XRD at 138 °C on cooling on the small angle shows an extra spot, which is not present at 144 °C. This is due to the ordering on the molecules into the tilt layers. The spacing is 38 Å, with 5 Å the smallest in the SmA phase. The XRD at 138 °C looks like a mixture of SmA and SmC phases. Purity of thiol was proved by NMR and EA, thus the suspicion of impure compound is eliminated. This behaviour can be explained only by the contact surface phenomenon; molecules contact the glass capillary move in this range of temperature.

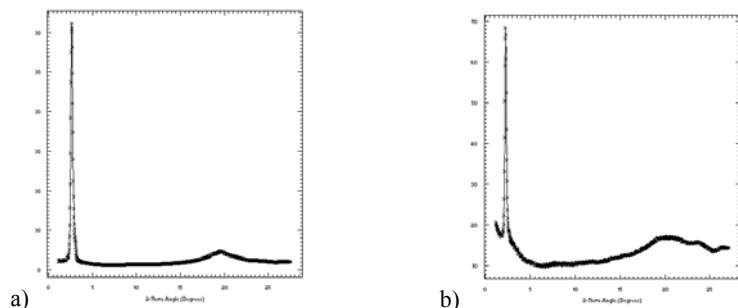


Fig. 7 – X-Ray diffraction patterns of compound **4** (a) and **5** (b) in the SmA phase.

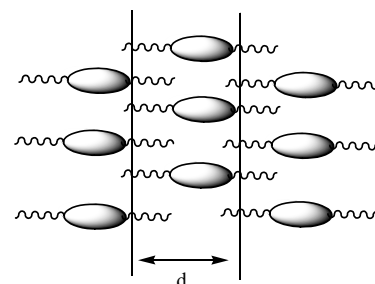


Fig. 8 – Sketch of the intercalated SmA phase exhibited by **4** and **5**.

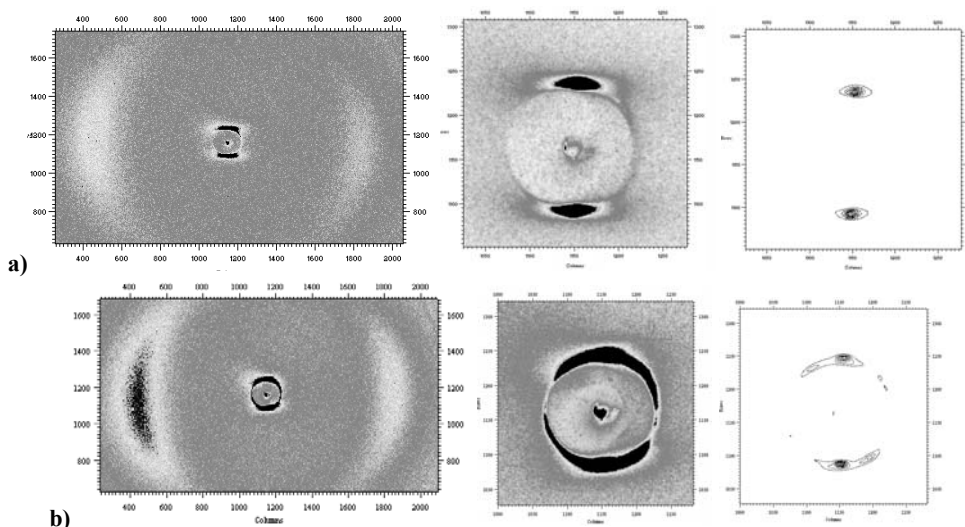


Fig. 9 – XRD patterns of **5** on cooling: a) in the SmA phase at 144 °C; b) in the SmC phase at 138 °C.

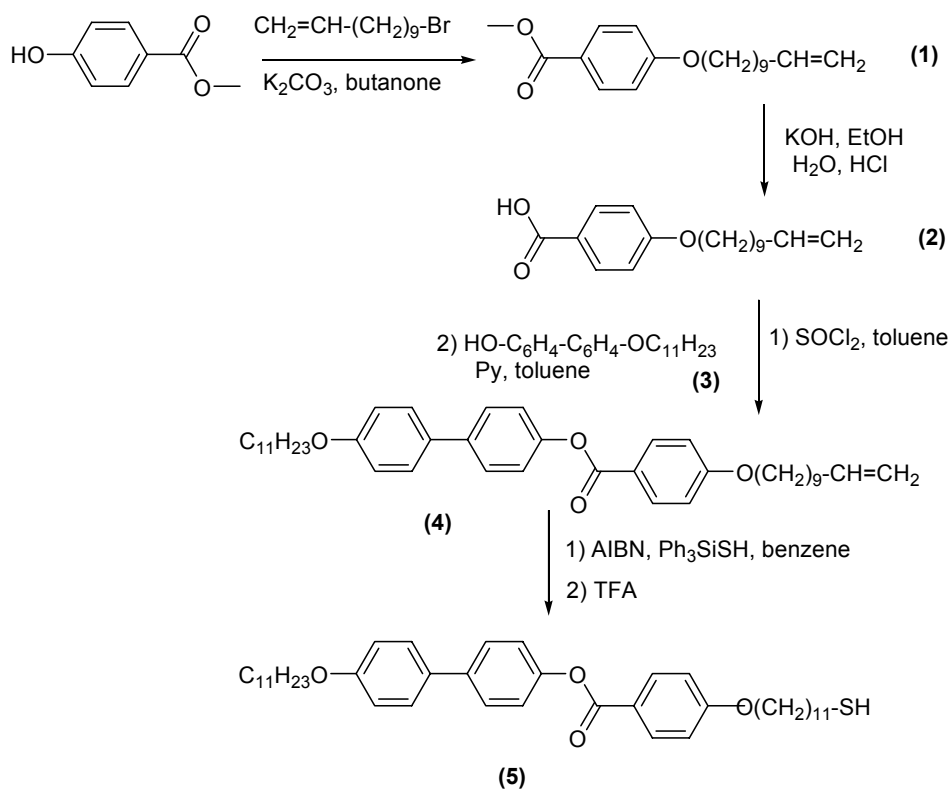
EXPERIMENTAL

1. Measurements: Structural characterization of the compounds was carried out through a combination of $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ (Jeol JNM-ECP 400) and elemental analysis (Perkin-Elmer 2400). NMR spectra were recorded using deuterated chloroform or benzene as solvent. Tetramethylsilane (TMS) was used as an internal standard. The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (DSC 882e, Mettler Toledo) which was operated at a scanning rate $10^\circ\text{C}/\text{min}$ both on heating and cooling. The apparatus was calibrated using an indium standard. Phase identification was performed by polarised light microscopy using an Olympus BH-2 optical microscope equipped with Mettler Toledo FP82Ht hot stage and a FP90Central processor. Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software *Studio Capture* was used for image capturing. X-ray diffraction measurements were performed on an MAR345 diffractometer with a two-dimensional Marresearch image plate detector ($\text{CuK}\alpha$ radiation, graphite monochromator, $\lambda = 1.54 \text{ \AA}$). The samples were heated in the presence of a magnetic field using a home-built capillary furnace.

2. Chemical synthesis: Methyl 4-hydroxybenzoate and methyl 2,4-dihydroxybenzoate were purchased from Merck. All reagents used were of analytical grade and were purchased from Merck, Sigma-Aldrich or Scharlau. The synthesis of the thiols *4'-(undecyloxy)biphenyl-4-yl 4-(11-mercapto-undecyloxy)benzoate* **5**, *4'-(undecyloxy)biphenyl-4-yl 2-(5-mercaptopentyl)-4-(octyloxy)benzoate* **13**, *4'-(undecyloxy)biphenyl-4-yl-2-(11-mercapto-undecyloxy)-4-(octyloxy)benzoate* **14** and *4'-(4-(octyloxy)benzoyloxy)biphenyl-4-yl 2-(11-mercapto-undecyloxy)-4-(octyloxy)benzoate* **17** is outlined in Schemes 1 and 2. Alkylation of methyl 4-hydroxybenzoate or 2,4-dihydroxybenzoate by a Williamson etherification,^{17,32} followed by deprotection of carboxylic group leads to intermediates *4-(undec-10-enoxy)benzoic acid* **2**, *4-(octyloxy)-2-(pent-4-enoxy)benzoic acid* **9** and *4-(octyloxy)-2-(undec-10-enoxy)benzoic acid* **10**.^{17,33} Esterification of *4-hydroxy-4'-undecyloxybiphenyl* **3** with one of the intermediates **2**, **9** or **10** forms the compounds *4'-(undecyloxy)biphenyl-4-yl 4-(undec-10-enoxy)benzoate* **4**, *4'-(undecyloxy)biphenyl-4-yl 4-(octyloxy)-2-(pent-4-enoxy)benzoate* **11** or *4'-(undecyloxy)biphenyl-4-yl 4-(octyloxy)-2-(undec-10-enoxy)benzoate* **12** containing three aromatic rings. The compound *4'-(4-(octyloxy)benzoyloxy)biphenyl-4-yl 4-(octyloxy)-2-(undec-10-enoxy)benzoate* **16** containing four aromatic rings was obtained by esterification of **10** with *(4'-hydroxy)biphenyl 4-octyloxybenzoate* **15**. The thiol group is introduced by radical addition reaction³⁴ on the compounds **4**, **11**, **12** or **16**. The thiols were isolated by column chromatography (SiO_2) as white solid product with 34-53 % yields.

2.1. 4'-(undecyloxy)biphenyl-4-yl 4-(undec-10-enoxy)benzoate (4). The product was purified by column (SiO_2 , DCM/hexane = 6/4, Rf = 0.60). After recrystallization from CHCl_3 /methanol a white solid was obtained. Yield 63 %. **E.A.:** Calc.: C 80.35 %, H 9.21 %; Found: C 80.21 %, H 9.05 %; $^1\text{H-NMR}$ 400 MHz, CDCl_3/δ [ppm]: 8.09 (m, 2H, H^{ar}); 7.51 (m, 2H, H^{ar}); 7.44 (m, 2H, H^{ar}); 7.18 (m, 2H, H^{ar}); 6.91 (m, 2H, H^{ar}); 6.89 (m, 2H, H^{ar}); 5.74 (m, 1H, $\text{CH}_2=\text{CH-}$); 4.89 (m, 2H, $\text{CH}_2=\text{CH-}$); 3.97 (t, 2H, $-\text{O-CH}_2-$); 3.92 (t, 2H, $-\text{O-CH}_2-$); 1.97 (v, 2H, $\text{CH}_2=\text{CH-CH}_2-$); 1.73 (m, 4H, $-\text{O-CH}_2-\text{CH}_2-$); 1.14-1.46 (m, 28H, $-\text{CH}_2-$); 0.79 (t, 3H, $-\text{CH}_3$).

The thiol group is introduced by radical addition reaction³⁴ on the compounds **4**, **11**, **12** or **16**. The thiols were isolated by column chromatography (SiO_2) as white solid product with 34-53 % yields.



Scheme 1

2.2. Methyl 4-(octyloxy)-2-(undec-10-enoxy)benzoate (8). The crude product was used in the next reaction without further purification ($R_f = 0.51$, DCM) Yield 95 %. $^1\text{H-NMR}$ 400 MHz, CDCl_3/δ [ppm]: 7.82 (dd, 1H, H^{ar}); 6.46 (d, 1H, H^{ar}); 6.44 (d, 1H, H^{ar}); 5.75-5.85 (m, 1H, $\text{CH}_2=\text{CH}-$); 4.90-5.01 (m, 2H, $\text{CH}_2=\text{CH}-$); 3.98 (t, 4H, $-\text{O}-\text{CH}_2-$); 3.84 (s, 3H, $-\text{O}-\text{CH}_3$); 2.03 (v, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2$); 1.74-1.86 (m, 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-$); 1.21-1.50 (m, 22H, $-\text{CH}_2-$); 0.88 (t, 3H, $-\text{CH}_3$).

2.3. Methyl 4-(octyloxy)-2-(undec-10-enoxy)benzoic acid (10). The white product was recrystallized from hexane. Yield 75 %. $^1\text{H-NMR}$ 400 MHz, CDCl_3/δ [ppm]: 10.78 (u, 1H, $-\text{OH}$); 8.12 (d, 1H, H^{ar}), $J_o = 8.80$; 6.62 (dd, 1H, H^{ar}), $J_o = 8.80$, $J_m = 2.20$; 6.51 (d, 1H, H^{ar}), $J_m = 2.20$; 5.82 (m, 1H, $\text{CH}_2=\text{CH}-$); 4.95 (m, 2H, $\text{CH}_2=\text{CH}-$); 4.20 (t, 2H, $-\text{O}-\text{CH}_2-$); 4.02 (t, 2H, $-\text{O}-\text{CH}_2-$); 2.06 (v, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-$); 1.89 (q, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2-$); 1.80 (q, 2H, $-\text{O}-\text{CH}_2-\text{CH}_2-$); 1.24-1.53 (m, 22H, $-\text{CH}_2-$); 0.90 (t, 3H, $-\text{CH}_3$).

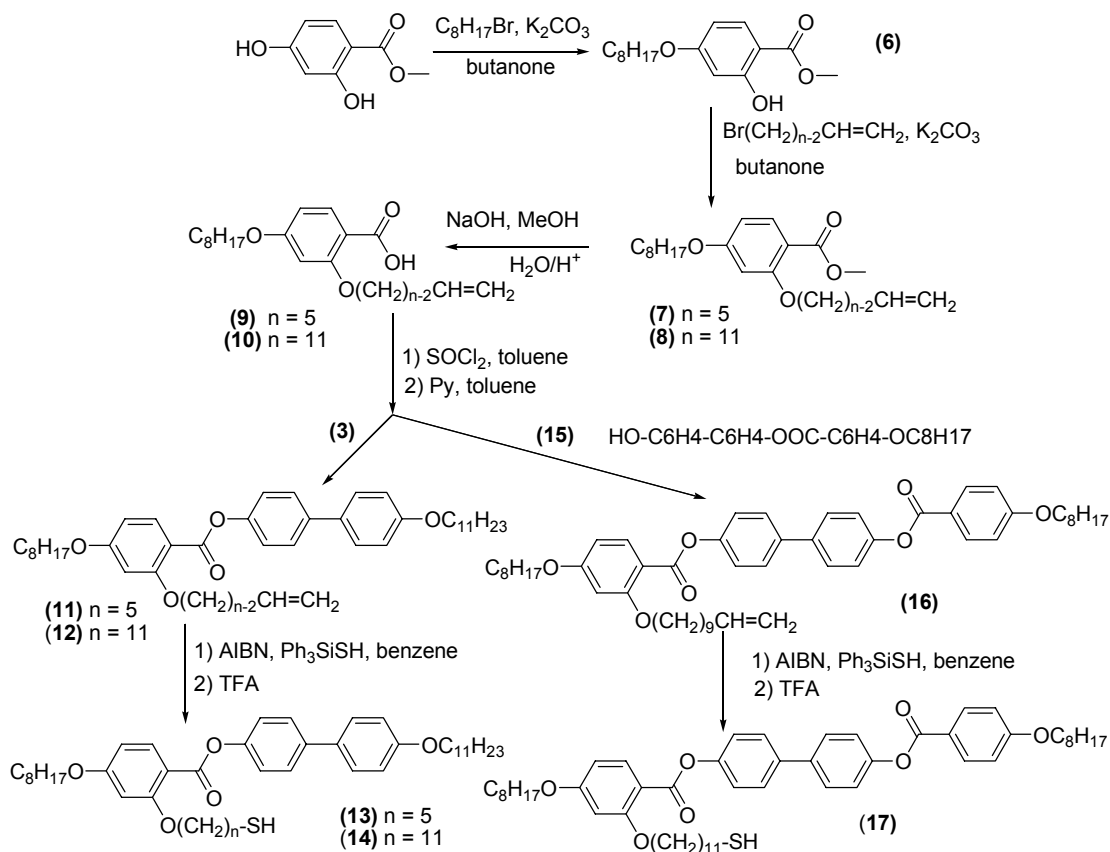
2.4. 4'-(undecyloxy)biphenyl-4-yl 4-(octyloxy)-2-(undec-10-enoxy)benzoate (12). White solid. Yield 80 %. $\text{C}_{49}\text{H}_{72}\text{O}_5$; $M = 741.09$; **A.E.:** Calc.: C 79.41 %, H 9.79 %; Found: C 79.70 %, H 10.00 %; $^1\text{H-NMR}$ 400 MHz, CDCl_3/δ [ppm]: 7.95 (d, 1H, H^{ar}); 7.48 (m, 2H, H^{ar}); 7.42 (m, 2H, H^{ar}); 7.16 (m, 2H, H^{ar}); 6.89 (m, 2H, H^{ar}); 6.45 (dd, 1H, H^{ar}); 6.43 (d, 1H, H^{ar}); 5.70 (m, 1H, $\text{CH}_2=\text{CH}-$); 4.87 (m, 2H, $\text{CH}_2=\text{CH}-$); 3.94 (m, 6H, $-\text{O}-\text{CH}_2-$); 1.93 (v, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-$); 1.73 (m, 6H, $-\text{O}-\text{CH}_2-\text{CH}_2-$); 1.13-1.46 (m, 38H, $-\text{CH}_2-$); 0.80 (m, 6H, $-\text{CH}_3$).

2.5. 4'-(4-(octyloxy)benzoyloxy)biphenyl-4-yl 4-(octyloxy)-2-(undec-10-enoxy)benzoate (16). The white product was purified by column chromatography (SiO_2 , DCM/hexane = 4/1,

$R_f = 0.66$). Yield 82 %. $\text{C}_{53}\text{H}_{70}\text{O}_7$; $M = 819.12$; **A.E.:** Calc.: C 77.71 %, H 8.61 %; Found: C 78.00 %, H 8.89 %; $^1\text{H-NMR}$ 400 MHz, CDCl_3/δ [ppm]: 8.08 (dd, 2H, H^{ar}), $J_o = 8.98$; 7.97 (d, 1H, H^{ar}), $J_o = 8.61$; 7.54 (m, 4H, H^{ar}); 7.20 (m, 4H, H^{ar}); 6.90 (dd, 2H, H^{ar}), $J_o = 8.98$; 6.48 (d, 1H, H^{ar}), $J_m = 2.38$; 6.44 (dd, 1H, H^{ar}); 5.71 (m, 1H, $\text{CH}_2=\text{CH}-$); 4.88 (m, 2H, $\text{CH}_2=\text{CH}-$); 3.97 (m, 6H, $-\text{O}-\text{CH}_2-$); 1.93 (v, 2H, $\text{CH}_2=\text{CH}-\text{CH}_2-$); 1.74 (m, 6H, $-\text{O}-\text{CH}_2-\text{CH}_2-$); 1.14-1.45 (m, 32H, $-\text{CH}_2$); 0.82 (t, 6H, $-\text{CH}_3$); $^{13}\text{C-NMR}$ CDCl_3/δ [ppm]: 165; 164.5; 164; 163.5; 161.5; 150.5 (2); 139; 138 (2); 134.5; 132.5; 128 (2); 122.5 (2); 121.5; 114 (2); 111; 105; 100; 69; 68; 34; 32; 29.5 (3); 29 (4); 26; 22.5; 14.

2.6. General method of synthesis of thiols: A stirred solution of alkene (1.4 mmol), triphenylsilanethiol (0.49 g, 1.7 mmol) and azoisobutyronitrile (AIBN) (0.065 g, 0.4 mmol) in benzene (6 ml) was warmed until reflux. After 2 days the mixture was cooled to room temperature. Trifluoroacetic acid (TFA) (1.48 ml, 7 mmol) was added and allowed to react 30 min. The solvent was removed give crude product which was purified by column (SiO_2).

2.6.1. 4'-(undecyloxy)biphenyl-4-yl 4-(11-mercaptoundecyloxy)benzoate (5). Col. eluent: DCM/hexane = 4/6 ($R_f = 0.22$). Yield 52 %. $\text{C}_{41}\text{H}_{58}\text{O}_4\text{S}$; $M = 646.96$; **A.E.:** Calc.: C 76.12 %, H 9.04 %, S 4.96 %; Found: C 76.43 %, H 9.15 %, S 4.85 %; $^1\text{H-NMR}$ 400 MHz, CDCl_3/δ [ppm]: 8.14 (m, 2H, H^{ar}); 7.56 (m, 2H, H^{ar}); 7.49 (m, 2H, H^{ar}); 7.23 (m, 2H, H^{ar}); 6.96 (m, 4H, H^{ar}); 4.01 (m, 4H, $-\text{O}-\text{CH}_2-$); 2.51 (dt, 2H, $-\text{CH}_2-\text{SH}$); 1.81 (m, 4H, $-\text{O}-\text{CH}_2-\text{CH}_2-$); 1.59 (m, 2H, $-\text{CH}_2-\text{CH}_2-\text{SH}$); 1.20-1.54 (m, 31H, $-\text{CH}_2-$, $-\text{SH}$); 0.87 (t, 4H, $-\text{CH}_3$).



Scheme 2

2.6.2. 4'-(undecyloxy)biphenyl-4-yl 2-(5-mercaptopentyl)-4-(octyloxy)benzoate (**13**). Col. eluent: DCM/hexane = 4/1 (Rf = 0.69). Yield 37%. C₄₃H₆₂O₅S; M = 691.02; **A.E.**: Calc.: C 74.74 %, H 9.04 %, S 4.64 %; Found: C 75.00 %, H 9.30 %, S 4.46 %; ¹H-NMR 400 MHz, C₆D₆/δ [ppm]: 8.31 (d, 1H, H^{ar}); 7.42 (m, 2H, H^{ar}); 7.37 (m, 2H, H^{ar}); 7.30 (m, 2H, H^{ar}); 6.91 (dd, 2H, H^{ar}); 6.53 (d, 1H, H^{ar}); 6.38 (dd, 1H, ar); 3.69 (t, 2H, -O-CH₂-); 3.61 (m, 4H, -O-CH₂-); 2.09 (dt, 2H, -CH₂-SH); 1.65 (m, 4H, -O-CH₂-CH₂-); 1.50 (q, 2H, -O-CH₂-CH₂-); 1.26-1.37 (m, 30H, -CH₂-); 1.04 (t, 1H, -SH); 0.92 (t, 6H, -CH₃).

2.6.3. 4'-(undecyloxy)biphenyl-4-yl 2-(11-mercaptoundecyloxy)-4-(octyloxy)benzoate (**14**). Col. eluent: DCM/hexane = 6/4 (Rf = 0.43). Yield 34%. C₄₉H₇₄O₅S; M = 775.17; **A.E.**: Calc.: C 75.92 %, H 9.62 %, S 4.14 %; Found: C 75.80 %, H 9.50 %, S 4.19 %; ¹H-NMR 400 MHz, C₆D₆/δ [ppm]: 8.31 (d, 1H, H^{ar}); 7.42 (m, 2H, H^{ar}); 7.38 (m, 2H, H^{ar}); 7.32 (m, 2H, H^{ar}); 6.93 (m, 2H, H^{ar}); 6.57 (dd, 1H, H^{ar}); 6.39 (d, 1H, H^{ar}); 3.71 (m, 4H, -O-CH₂-); 3.62 (t, 2H, -O-CH₂-); 2.15 (dt, 2H, -CH₂-SH); 1.66 (m, 6H, -O-CH₂-CH₂-); 1.10-1.55 (m, 42H, -CH₂-); 1.08 (t, 1H, -SH); 0.92 (t, 6H, -CH₃).

2.6.4. 4'-(4-(octyloxy)benzoyloxy)biphenyl-4-yl 2-(11-mercaptoundecyloxy)-4-(octyloxy)benzoate (**17**). Col. eluent: DCM/hexane = 7/3 (Rf = 0.53). Yield 37%. C₅₃H₇₂O₅S; M = 853.20; **A.E.**: Calc.: C 74.61 %, H 8.51 %, S 3.76 %; Found: C 74.30 %, H 8.83 %, S 3.66 %; ¹H-NMR 400 MHz, C₆D₆/δ [ppm]: 8.30 (m, 2H, H^{ar}); 7.30 (m, 6H, H^{ar}); 7.20 (m, 2H, H^{ar}); 6.77 (m, 2H, H^{ar}); 6.57 (s, 1H, H^{ar}); 6.39 (dd, 1H, H^{ar}); 3.92 (t, 2H, -O-CH₂-); 3.63 (t, 2H, -O-CH₂-); 3.51 (t, 2H, -O-CH₂-); 2.16 (dt, 2H, -CH₂-SH); 1.46-1.74 (m, 6H, -O-CH₂-CH₂-);

1.18-1.40 (m, 36H, -CH₂-); 1.10 (t, 1H, -SH); 0.92 (t, 6H, -CH₃).

CONCLUSIONS

There were synthesized and characterized new compounds (**4**, **5**, **13**). A series of structurally different side- or end-on alkene and thiols were been investigated. The end-on compounds show smectic and nematic phases, and the compounds side-on show only nematic phase. Also, the melting point of side-on compounds is decreasing compared to the similar end-on compounds. The introduction of thiolic group has as effect the decrease of the transition temperatures and the increase of the range for the nematic phases of side-on compound. All these thiols form monolayers on gold surface, but the full characterization of these self-assembled monolayers have been presented elsewhere^{11,12,21} or are currently being considered for publication.

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