nanomaterials

Supplementary Materials

Silver Nanoparticles with Liquid Crystalline Ligands based on Lactic Acid Derivatives

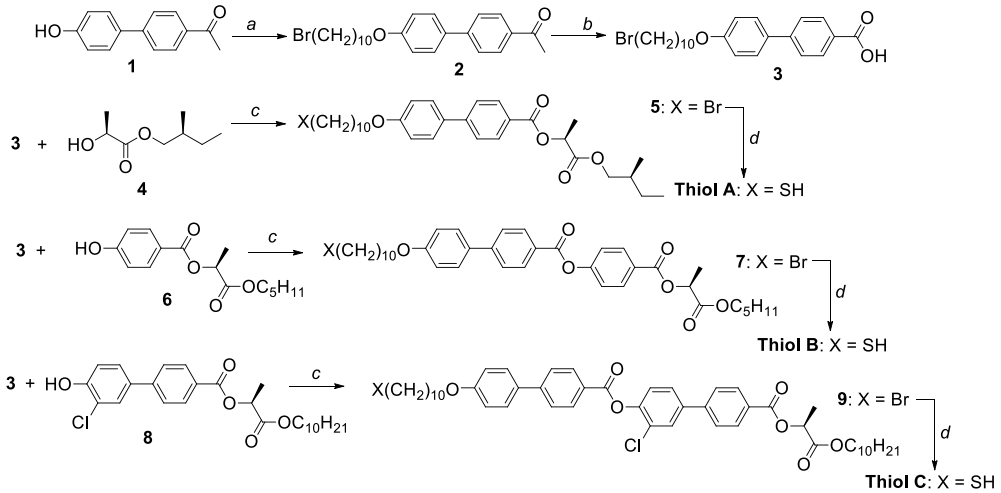
Tinkara Troha [1], Miroslav Kaspar [1], Vera Hamplova [1], Martin Cigl [1], Jaroslav Havlicek [1], Damian Pociecha [2] and Vladimira Novotna [1,*]

[1] Institute of Physics of the Czech Academy of Sciences, Prague 18221, Czech Republic
[2] Faculty of Chemistry, University of Warsaw, ul. Zwirki i Wigury 101, 02-089 Warsaw, Poland
* Correspondence: novotna@fzu.cz

Content

1. Synthesis

Chiral thiol ligands were synthesized by the synthetic routes depicted in **Scheme S1**. Starting phenone **1** was synthesized following a known procedure from literature [S1] and similarly the chiral intermediates **4**, **6**, and 8—see Refs. [S2], [S3], and [S4], respectively. Starting phenone **1** was alkylated using excess of 1,10-dibromodecane. The alkylated phenone **2** was treated with a solution of hypobromite to afford the carboxylic acid **3**. Synthesized carboxylic acid **3** was then esterified by appropriate chiral hydroxy-compound (**4**, **6**, or **8**) via DCC-coupling yielding bromo-esters **5**, **7**, resp. **8**. In the last step, the bromo-esters **5**, **7**, and **8** were refluxed with sodium thiosulfate to obtain appropriate Bunte salt from which the target thiols **A–C** were formed under acidic conditions and under inert atmosphere of argon to prevent oxidation of thiol group.



Scheme S1. Synthesis of thiol ligands **A–C**. Reagents and conditions: (**a**) 1,10-dibromodecane, KOH, dioxane-water, reflux 8 h; (**b**) 1. NaBrO, dioxane; 2. HCl; (**c**) DCC, DMAP, THF-CH_2Cl_2; (**d**) 1. $Na_2S_2O_3$, dioxane-EtOH-H_2O, reflux 12–40 h; 2. HCl, THF, Ar.

1.1. General Experimental

^{1}HNMR spectra were recorded on Varian VNMRS 300 instrument (Varian, Inc., Palo Alto, CA, USA). Deuteriochloroform ($CDCl_3$) and hexadeuteriodimethyl sulfoxide (DMSO-d_6) were used as solvents and signals of the solvent served as internal standard. Chemical shifts (δ) are given in ppm, and J values are given in Hz. The signals were identified by APT, gCOSY, and gHMBC experiments. The purity of the final compound was checked by HPLC analysis (high-pressure pump ECOM Alpha; column WATREX Biospher Si 100, 250 mm × 4 mm, 5 μm; detector WATREX UVD 250) and were found to be >99.8 %. Column chromatography was carried out using Merck Kieselgel 60 (60–100 μm). Enantiomeric purity of chiral compounds was confirmed by chiral HPLC system (chiral column: Daicel Chiralpak AD-3 (Chiral Technologies Europe SAS, Illkirch – Cedex, France), 150 mm× 4.6 mm I.D., 3 μm).

1.2. Synthetic Procedures

1. -(4'-((10-Bromodecyl)oxy)-[1,1'-biphenyl]-4-yl)ethanone (2)

A mixture of 1-(4'-hydroxy-[1,1'-biphenyl]-4-yl)ethanone (**1**) (42.4 g, 0.2 mol) 1,10-dibromodecane (120.0 g, 0.4 mol) and potassium hydroxide (12.3 g, 0.22 mol) in dioxane (400 mL)–water (40 mL) mixture was refluxed with intensive stirring for 8 h. When cooled to room temperature, the resulting mixture was poured into water (500 mL) and the precipitate filtered off, washed with water, and dried. Crude product was recrystallized from toluene (500 mL) yielding pure phenone **2** 54.3 g (63 %). ^{1}H NMR (DMSO-d_6): 8.08 (2 H, d, *J* = 8.2, H-3, H-5), 7.76 (2 H, d, *J* = 8.2, H-2, H-6), 7.69 (2 H, d, *J* = 8.5, H-2′, H-6′), 7.04 (2 H, d, *J* = 8.5, H-3′, H-5′), 4,0 (2 H, t, *J* = 6.5, OCH_2), 3.52 (t, 2 H, *J* = 6.7, CH_2Br), 2.58 s, 3 H, ($COCH_3$), 1.69–1.83 (m, 4 H, C**H**$_2$$CH_2O$, C**H**$_2$$CH_2Br$), 1.20–1.48 (m, 12 H $(CH_2)_6$).

4. '-((10-Bromododecyl)oxy)-[1,1'-biphenyl]-4-carboxylic acid (3)

Phenone **2** 52.0 g (0.11 mol) dissolved in dioxane (1.0 l) was slowly treated at 40 °C with a solution of sodium hypobromite prepared by mixing of bromine (20 mL, 0.39 mol) with solution of sodium hydroxide (300 mL, 20%) at 0 °C. After 4 h of stirring at 40 °C, the reaction mixture was allowed to cool to room temperature and the precipitate filtered off and washed with water (200 mL), acidified with hydrochloric acid (100 mL, 1:1), and washed with water again. After drying in vacuum drier, the crude product was boiled with toluene, and solid was filtered and further recrystallized from isopropanol. Yield 40.2 g (76 %). ^{1}H NMR (DMSO-d_6): 7.96 (2 H, d, *J* = 8.2, H-3, H-5), 7.73 (2 H, d, *J* = 8.2, H-2, H-6), 7.65 (2 H, d, *J* = 8.8, H-2′, H-6′), 7.01 (2 H, d, *J* = 8.8, H-3′, H-5′), 3,99 (2 H, t, *J* = 6.5, OCH_2), 3.54 (t, 2 H, *J* = 6.7, CH_2Br), 1.67–1.84 (m, 4 H, C**H**$_2$$CH_2O$, C**H**$_2$$CH_2Br$), 1.21–1.45 (m, 12 H $(CH_2)_6$).

(S,S)-1-(2-methylbutoxy)-1-oxopropan-2-yl 4'-((10-bromodecyl)oxy)-[1,1'-biphenyl]-4-carboxylate (5)

To a mixture of acid **3** (31.0 g, 71.53 mmol) and chiral phenol **4** (11.46 g, 72.40 mmol) in dichloromethane-THF mixture (150 mL + 150 mL) cooled to 2–8 °C was added *N,N′*-dicyclohexylcarbodiimide (DCC, 15.0 g, 72.70 mmol) and *N,N*-(dimethylamino)pyridine (2.2 g, 18.16 mmol). The reaction mixture was stirred for 6 h, during which the temperature was allowed to reach the room temperature. Precipitate was filtered off, and the filtrate evaporated under reduced pressure. The residue was purified by means of column chromatography on silica using dichloromethane-acetone (99:1) as eluent. Yield 18.70 g (45 %).^{1}H NMR ($CDCl_3$): 8.12 (2 H, d, H-3, H-5), 7.60 (4 H, m, H-2, H-6, H-2′, H-6′), 7.00 (2 H, d, H-3′, H-5′), 5.38 (1 H, q, *J* = 7.04, CH*), 3.93–4.11 (4 H, m, CH_2OAr, CH_2C*), 3.40 (2 H, t, CH_2Br), 1.20–1.80 m (19 H, CH_2, CH), 0.84–0.92 m (6 H, 2 × CH_3).

(S,S)-1-(2-methylbutoxy)-1-oxopropan-2-yl 4'-((10-sulfanyldecyl)oxy)-[1,1'-biphenyl]-4-carboxylate (Thiol A)

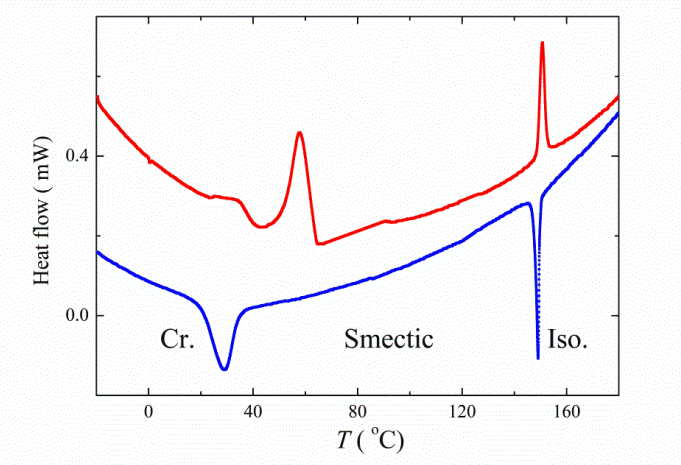


Figure S4. Thermograph for NP2 shows the second heating (red colour) and the second cooling runs.

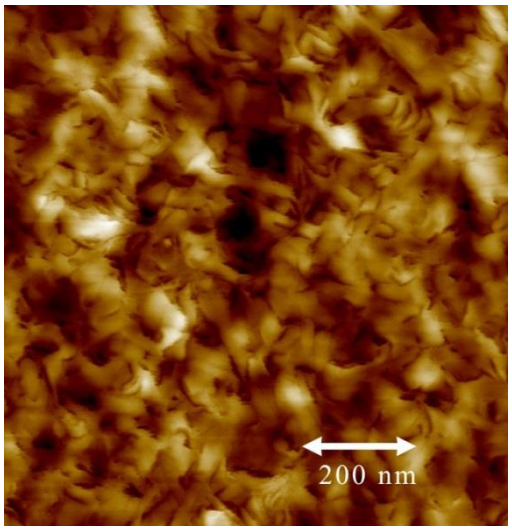


Figure S5. Atomic force microscopy (AFM) image on film created from NP4 at the room temperature, freely evaporated from a solution in toluene.

Table S1. The melting points (m.p.) taken on the second heating, the phase transition temperature smectic-isotropic, T_{iso}, and the crystallization temperature, T_{cr}, on the second cooling in °C and corresponding enthalpy changes, ΔH, in J/g, are in brackets at the corresponding temperature. The symbol * shows that the crystallization is not fully completed on the second cooling, and an additional crystallization peak appears on subsequent heating.

	m.p. [H]	**T_{iso} on heating [H]**	**T_{iso} on cooling [H]**	**T_{cr} [H]**
NP2	53 [+13.8]	150 [+5.07]	150 [−4.10]	34 [−10.2]
NP4	58 [+25.5]	180 [+0.82]	180 [−0.80]	40 [−1.52]*

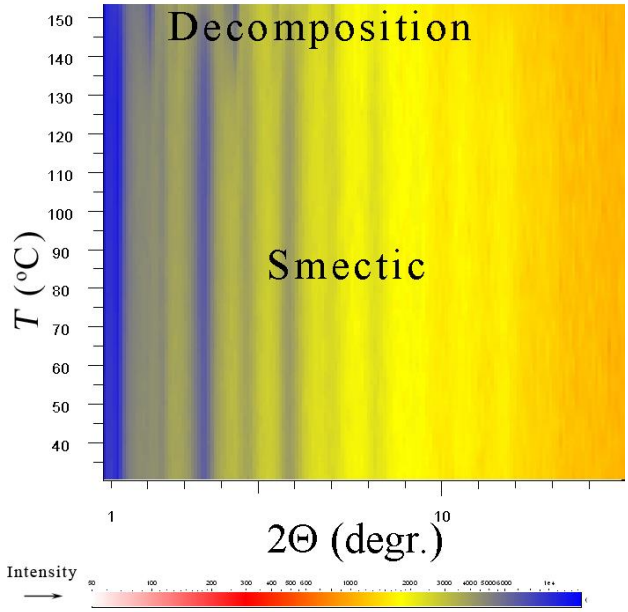


Figure S6. Dependences of the X-ray intensity (corresponding colours are below the graph) for compound NP2. The figure shows a distinct smectic-like mesophase on heating and decomposition at higher temperatures above 140ºC.

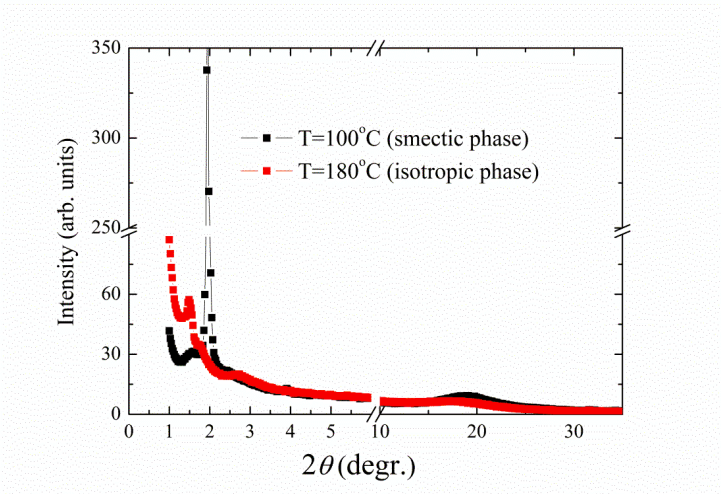


Figure S7. Intensity profile with respect to the scattering angle for NP2 in the smectic phase at T = 100 °C and in the isotropic phase at T = 180 °C for comparison.

5. References

1. V. Novotná, M. Kašpar, V. Hamplová, M. Glogarová, P. Bílková, V. Domenici, D. Pociecha, *Liq. Cryst.*, 2008, **35**, 287–298.
2. M. Kašpar, V. Hamplová, V. Novotná, M. Glogarová, D. Pociecha, P. Vaněk. New series of ferroelectric liquid crystals with two or three chiral centers exhibiting antiferroelectric and hexatic phases. *Liq. Cryst.* 2001, 28, 1203–1209.
3. M. Kašpar, V. Hamplová, S. A. Pakhomov, A. M. Bubnov, F. Guittard, H. Sverenyak, I. Stibor, P. Vaněk, M. Glogarová, *Liq. Cryst.*, 1998, **24**, 599–605
4. V. Novotná, V. Hamplová, N. Podoliak, M. Kašpar, M. Glogarová, D. Pociecha, E. Gorecka. *J. Mater. Chem.*, 2011, **21**, 14807–14814.