

# Temperature-controlled liquid crystalline polymorphism of gold nanoparticles

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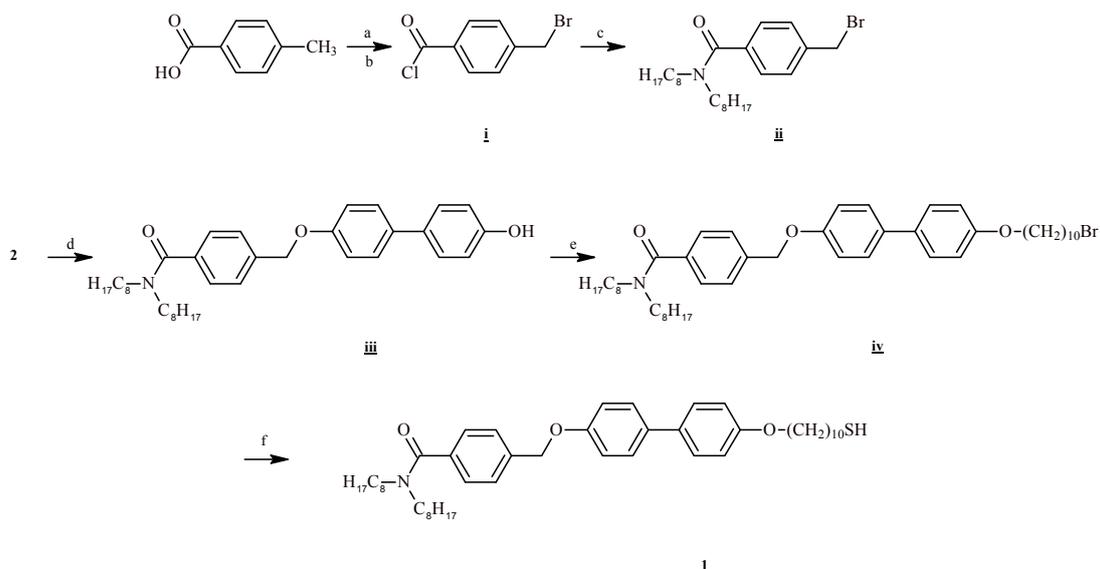
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## Experimental

10 Optical studies were conducted using a Zeiss-Imager A2m polarizing microscope equipped with a Linkam heating stage. Small-angle X-ray diffraction studies were conducted using Bruker NanoStar system with Vantec-2000 detector. The systems used  $\text{CuK}_\alpha$  radiation and was equipped with MRI heating stage. One-surface free samples were prepared on kapton tape and aligned by shearing at slightly elevated temperature ( $\sim 50^\circ\text{C}$ ). IR spectra were recorded on a Nicolet 6700FT-IR spectrometer. The sample was placed on ZnSe plate, aligned by shearing and heated with a Linkam hot stage. 15 The IR polarizer was rotated with respect to the rubbing direction in the sample to obtain variation of IR signal intensities. Visible light absorption due to plasmon resonance was studied using Shimadzu UV-3101PC spectrometer, aligned sample was rotated against polarizer. TEM images 20 were taken in Laboratory of Electron Microscopy, Nencki Institute of Experimental Biology, using JEM 1400 microscope (JEOL).

## Synthesis

### Rod – like mesogenic ligand



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**Scheme 1** . General procedure for the synthesis of rod – like mesogenic ligand (compound 5). **Reagents and conditions:** a)  $\text{Br}_2$ , hv; b)  $\text{SOCl}_2$ ,  $\text{CHCl}_3$ , reflux; c) diocetylamine,  $\text{CHCl}_3$ ; d)  $\text{KI}$ ,  $\text{K}_2\text{CO}_3$ , 4,4' – dihydroxybiphenyl, DMF; e)  $\text{P}(\text{Ph}_3)_3$ , DIAD, 10 – bromodecan – 1 – ol, THF, f) HMDT, TBAF, THF, room temperature.

30 General procedure for the synthesis of rod – like mesogenic ligand (compound 1) is presented in Scheme 1.

### Synthesis of 4 – (bromomethyl)benzoyl chloride (i).

35 To a solution of 69,5g (0,51mol) of 4 – methylbenzoic acid in  $\text{CHCl}_3$  (600mL) 26,7mL a bromine solution in 25mL of  $\text{CHCl}_3$  was added dropwise. During reaction process the whole mixture was vigorously stirred at reflux. After each portion of the bromine solution mixture was stirred until a loss of color. After the reaction mixture was cooled down to room temperature a precipitate appeared. Then 37mL of thionyl chloride and pirydine (a few drops) was added. The mixture was stirred at  $60^\circ\text{C}$  for 5 hours until the whole precipitate was dissolved, cooled down and the solvent was 40 evaporated. The crude product was purified by distillation under lowered pressure to afford 87g (73%) as a white solid.  $^1\text{H}$ NMR ( $\text{CDCl}_3$ ; 200MHz)  $\delta$ : 8,12 (d, 2H,  $J=8.5\text{Hz}$ ), 8,07 (d, 2H,  $J=8.6\text{Hz}$ ), 4,63 (s, 2H). MS (TOF MS ES+): m/z 256,4 [ $\text{M}+\text{Na}^+$ ], 272.0 [ $\text{M}+\text{K}^+$ ]

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**Synthesis of N, N – dioctyl – 4 – (bromomethyl) benzamide (ii).**

To 39,2mL (0,13mol) of N,N – dioctylamine, a solution of 15g (0,064mol) of (i) in 150mL of CHCl<sub>3</sub> was added dropwise. During reaction process the mixture was stirred vigorously at room temperature. The reaction was complete in 18 hours. The crude product was purified by column chromatography (eluent: CHCl<sub>3</sub>) to give 30,2g (53%) of compound ii.

<sup>1</sup>H NMR (200 MHz; CDCl<sub>3</sub>): δ 7,78 (2H; d; J = 8,3 Hz); 6,98 (2H; d; J = 8,3 Hz); 4,59 (2H; s); 3,30 (4H; br); 1,91 – 1,72 (4H, m); 1.69-1.14 (20H; m); 0,90 (6H; m).

MS (TOF MS ES+): m/z 461,2 [M+Na<sup>+</sup>].

**Synthesis of N,N – dioctyl – 4 – [(4' – hydroxybiphenyl – 4 – ylo)xymethyl] benzamide (iii).**

A mixture of 11,2g (0,06mol) of 4, 4' – dihydroxybiphenyl, 16,6g (0,12mol) of K<sub>2</sub>CO<sub>3</sub> and 20,0g (0,12mol) of KI in N, N – dimethylformamide (250mL) was stirred at 45°C for 15 minutes. Then a solution of 21,5g (0,049mol) of ii in N, N – dimethylformamide was added quickly. The mixture was stirred at 90°C for 14h. After that it was cooled down to a room temperature and added to 500mL of distilled water. A brown solid was filtrated and dried at room tempertaure. The crude product was purified by column chromatography (eluent: CHCl<sub>3</sub>) to get 11,72g (44%) of compound iii.

<sup>1</sup>H NMR (200 MHz; d – THF): 7,48 (2H; d; J = 8,5 Hz); 7,44 (4H; m); 7,37 (2H; d, J=8.0Hz); 7.04-6.96 (4H; m); 5.12 (2H; s); 3,31 (4H; br); 1,90 – 1,72 (4H, m); 1.68-1.16 (20H; m); 0,91 (6H; m).

MS (TOF MS ES+): m/z 567,4 [M+Na<sup>+</sup>].

**Synthesis of N,N – dioctyl – 4 – [(4' – (10-bromodecyloxy)biphenyl – 4 – ylo)xymethyl] benzamide (iv).**

To a solution of 9,2g (0,017mol) of iii in THF, 4,98g (0,019mol) of TPP and 5,9g (0,025mol) of 10 – bromodecan – 1 – ol was added. The mixture was stirred for 20 minutes and then 3,56g (0,018mol) of DIAD was added. The mixture was stirred at room temperature for 15h. The crude product was purified by column chromatography (eluent: CHCl<sub>3</sub>) to get 4,4g (36%) of iv.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): 7,48 (2H; d; J = 8,5 Hz); 7,44 (4H; m); 7,37 (2H; d, J=8.0Hz); 7.02 (2H, d, J=8.8Hz)-6.94 (2H; d, J=8.8Hz); 5.12 (2H; s); 3.98 (2H; t; 7,4Hz); 3.41 (2H, t, J= 6,8 Hz); 3,31 (4H; br); 1,92 – 1,72 (6H, m); 1.68-1.16 (34H; m); 0,90 (6H; m).

MS (TOF MS ES+): m/z 785,4 [M+Na<sup>+</sup>].

**Synthesis of N, N – dioctyl – 4 – [(4' – (10-mercaptodecyloxy)biphenyl – 4 – ylo)xymethyl] benzamide (I).**

To a cooled solution of 4,4g (5,8mmol) of iv in dry tetrahydrofuran under argon atmosphere 1,30mL (6,09mmol) of HMDT was added quickly. After 5 minutes 6,38mL (1M solution in tetrahydrofuran) of TBAF was added. The reaction mixture was stirred at room temperature for 1h. Then to the reaction mixture 80mL of CH<sub>2</sub>Cl<sub>2</sub> was added and washed with

saturated water solution of NH<sub>4</sub>Cl (three times using 40mL).

Afterwards mixture was dried under MgSO<sub>4</sub> and the solvent was evaporated. The crude product was purified by column chromatography (eluent: CHCl<sub>3</sub>) to get 3,12g (75%) of I.

<sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>): 7,48 (2H; d; J = 8,5 Hz); 7,45 (4H; m); 7,37 (2H; d, J=8.0Hz); 7.01 (2H, d, J=8.8Hz)-6.94 (2H; d, J=8.8Hz); 5.12 (2H; s); 3.98 (2H; t; 7,4Hz); 3,32 (4H; br); 2.52 (2H, m); 1,92 – 1,72 (6H, m); 1.68-1.16 (34H; m); 0,90 (6H; m).

MS (TOF MS ES+): m/z 739,5 [M+Na<sup>+</sup>].

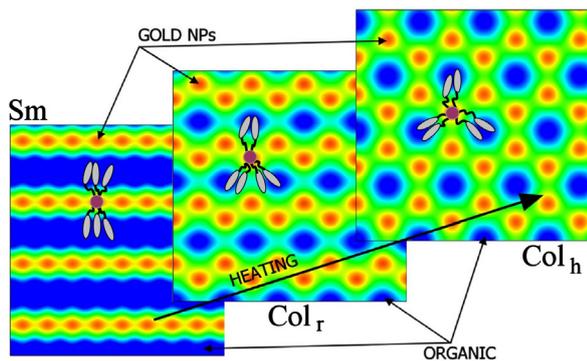
<sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>) δ 172.85, 160.24, 160.21, 138.70, 136.14, 133.46, 129.33, 128.72, 127.97, 126.37, 116.25, 115.62, 70.96, 69.66, 45.61, 31.73, 29.15, 29.04, 28.80, 28.69, 27.75, 27.64, 26.58, 14,00.

**Gold nanoparticles**

The gold nanoparticles were synthesized using a modified method reported before<sup>1</sup>. Only difference was using tricaprylmethylammonium chloride instead of methyltrioctylammonium bromide. All the conditions and synthetic procedure of preparation hybrid materials was carried as in the mentioned articles except crude material purification where the ligand exchange mixture was stirred for 72 h at room temperature, then evaporated to 1-2 mL in a rotary evaporator and mixed with of 25 mL of acetone to precipitate nanoparticles. The resulting gel-like mixture was sonicated for 60 s and left overnight at room temperature for nanoparticles to precipitate. The precipitate was carefully centrifuged, washed with small amount of acetone and re-dissolved in a small amount of toluene (1-2 mL). Further purifying procedure was repeated three times, but in the second repetition absolute ethanol was used instead of acetone. In the final hybrid material no trace of excess of thiol was found, as determined by 1H NMR spectra and TLC. For the ligand exchange reaction the same conditions (time, amount of primary gold nanoparticles, concentration of exchanging ligand and temperature) were applied as it was reported before.<sup>1-4</sup>

Both NMR and MALDI-MS analytical data proved that nanoparticles were successfully covered with mesogenic thiols. Basing on 1H NMR, thermogravimetry and elemental analysis data the aspect ratio of the mesogenic molecules to n-butanethiol in the nanoparticle covering layer was estimated to be ~ 1:1. The exact procedure for determining composition of organic grafting layer was described in details before.<sup>4</sup>

## Structure studies



5 **Figure 1.** Schematic drawing showing distribution of  
promesogenic ligands (gray ellipses) around gold nanoparticles  
in liquid crystalline phases: smectic (Sm), columnar rectangular  
(Col<sub>r</sub>) and columnar hexagonal (Col<sub>h</sub>). As a background  
electron density maps are used, obtained from x-ray diffraction  
10 data by reverse Fourier transform.

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