SUPPORTING INFORMATION FOR

Dynamic self-assembly of metal nanoparticles using thermotropic liquid crystals

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1. Materials and methods

Solvents and substrates were obtained from Sigma-Aldrich. Before use solvents were dried over activated 3Å molecular sieves for 24h. Substrates were used without further purification. All reactions were carried out under nitrogen (N₂) atmosphere in dried glassware and assuring efficient magnetic stirring. Purification of reaction products was carried out by column chromatography using RushanTaiyang silica gel 60 (230-400 mesh) at atmospheric pressure or by crystallization if possible. Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 (Merck) pre-coated glass plater (0.25 mm thickness) and visualized using iodine vapor and/or UV lamp (254 nm). Yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials.

The ¹H NMR spectra were recorded at either 200 MHz or 500 MHz NMR Varian Unity Plus. The ¹³C NMR spectra were recorded at NMR Varian Unity Plus 200 MHz.

Proton chemical shifts are reported in ppm (δ) relative to the internal standard – tetramethylsilane (TMS δ=0.00 ppm). Carbon chemical shifts are reported in ppm (δ) relative to the residual solvent signal (CDCl₃, δ=77.0 ppm). Data are presented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q =

quartet, br = broad, m = multiplet), and coupling constant (Hz). In all recorded spectra there are also sharp signals coming from small amount of known impurities present in used solvent: H₂O (1.7 ppm) and CHCl₃ (7.27 ppm).

The small angle X-ray diffraction (SAXRD) patterns for the powder as well as partially aligned samples were obtained with the BrukerNanostar system. The CuK α radiation was used, patterns were registered with an area detector VANTEC2000. The temperature of the sample was controlled with precision of 0.1 K. Kapton tape was used as a substrate for nanoparticle measurements. The nanoparticle samples were first heated up to 150 oC, quickly aligned by shearing and cooled to room temperature. The same BrukerNanostar system was also used for the scattering experiments (SAXS). The scattering data from nanoparticle solution in toluene were analyzed using NANOFIT software, assuming spherical form factor for non-interacting particles (structure factor S=1) and Shultz distribution of the particle sizes.

Transmission electron microscopy was performed using Zeiss Libra 120 microscope, with LaB6 cathode, equipped with OMEGA internal columnar filters and CCD camera.

2. Promesogenic ligand synthesis (L)

Supplementary Figure 1: Synthetic route for the preparation of promesogenic ligand. (i) a. SOCl_2 , DMF, CH_2Cl_2 ; b. $\text{Cl}_3\text{CCH}_2\text{OH}$, NaHCO_3 ; (ii) 2-octyl-1-chlorodecanol, PPh_3 , DIAD, THF; (iii) a. KOH , EtOH , rfx; b. $(\text{COCl})_2$, toluene, rfx; (iv) 2,2,2-trichloroethyl 4-hydroxybenzoate 1, TEA, DMAP, toluene, rfx; (v) a. Zn (powder), acetic acid, THF; b. $(\text{COCl})_2$, toluene, rfx; (vi) hydroquinone, TEA, DMAP, THF, rfx; (vii) 16-mercaptohexadecanoic acid, DCC, DMAP, CH_2Cl_2 .

Synthesis of 2,2,2-trichloroethyl ester of 4-hydroxybenzoic acid (S1):

50.0 g (362 mmol) of 4-hydroxybenzoic acid in 500 ml of dry DMF and 100 ml of dry CH₂Cl₂ were stirred at room temperature for 30 min. Next, 39.5 ml (543 mmol) thionyl chloride was added dropwise to the mixture while stirring. Stirring was continued for 30 min. After that time, excess amount of 2,2,2-trichloroethanol was added dropwise and reaction (5 mol eq. of 4-hydroxybenzoic acid) was left under stirring for 48 hours. Next to quench the reaction, 150 ml of saturated aqueous solution of sodium dicarbonate was added and mixture was stirred for 40 minutes. Then 100 ml of distilled water was added, the organic phase was separated and the aqueous phase was extracted four-times using chloroform (15 mL). All organic phases were combined, dried over anhydrous MgSO₄ and evaporated. The white precipitate was washed with cyclohexane. The crude product was crystallized from hexane affording pure product with 65% yield.

Synthesis of the ethyl ester of 4-decyl(2'-octyl)oxy benzoic acid (S2):

16.88 g (102 mmol) of the ethyl ester of 4-hydroxybenzoic acid, 30.33 g (102 mmol) of 2-octyl-1-chlorodecan, 28.38 g (1006 mmol) of triphenylphosphine and 250 ml of THF were put together in a round-bottom flask. Then, the reaction mixture was cooled to 0°C and 20 mL (102 mmol) of diisopropyl azodicarboxylate (DIAD) was added dropwise. Reaction was left under stirring for 24 hours. Next, solvent was evaporated on a rotary evaporator. The crude product was chromatographed on silica gel eluted with dichloromethane affording almost pure product in the form of clear oil.

Synthesis of 4-decylo(2'-octyl)oxybenzoic acid chloride (**S3**):

56 g (124 mmol) of the ethyl ester of 4-decyl(2'-octyl)oxy benzoic acid **2** was dissolved in 460 mL of ethanol. Then, 46 g (807 mmol) of potassium hydroxide in ethanol (230 ml) was added. The reaction mixture was heated under reflux for 5 hours. Excess of KOH was filtered out and solvent was rotary evaporated. 89.9 g of potassium salt contaminated with small amounts of KOH, was obtained.

Next, potassium salt was dissolved in 1150 ml of toluene and excess of oxalyl chloride (80,0 ml) was added dropwise. Reaction was heated under reflux for 3 hours. Then, potassium chloride was filtered on Schott's funnel. Toluene and oxalyl chloride were rotary evaporated and dried using vacuum pump for 2 hours. 63g of product **3** was obtained.

*Synthesis of bicyclic ester (**S4**):*

TEA (90 ml) was added to the solution of **1** (17.50 g, 65 mmol) and DMAP (catalytic amount) in 1000 ml of anhydrous toluene. Then, chloric acid **3** was added dropwise. The reaction mixture was stirred for 3 h at reflux. The progress of the reaction was monitored with TLC chromatography. The resulting precipitate was filtered out and solvents were rotary evaporated. 33g of light brown, clear oil was obtained. Next, column chromatography was performed using gradient elution with mixture of toluene and hexane affording pure product with 62 % yield in the form of light yellow, clear oil.

*Synthesis of acid chloride of 4 - {[4' - (decyl (2'-octyl) oxy) benzoyl] oxy} benzoic acid (**S5**):*

20.0 g (31 mmol) of ester **4**, 340 ml of THF, 17.5 g (268 mmol) of zinc powder and 68 ml of acetic acid were stirred at room temperature for 12 h. The progress of the reaction was monitored with TLC chromatography. Inorganic precipitate was filtered

out, 600 ml of toluene was added to the mixture and evaporated to dryness (to remove acetic acid) yielding crude product. The obtained Zn salt was washed with hexane. In next step 15.00 g (13,8 mmol) of Zn salt was dissolved in 600 ml of toluene and 15 ml (139 mmol) of oxalyl chloride was added. Reaction mixture was heated under reflux for 6h. Toluene and excess of oxalyl chloride were rotary evaporated affording product **5** which was used without purification in the next step of synthesis.

Synthesis of tricyclic compound with a branched lateral chain (S6):

In the next step, compound **5** (44,1g; 72 mmol) was dissolved in 800 mL of THF. Then, 19g (173 mmol) of hydroquinone in 100 mL of THF, TEA (13.8 ml) and DMAP (catalytic amount) were added. The reaction mixture was stirred for 3 h at reflux and evaporated to dryness. The resulted precipitate of trimethylamine chloride was filtrated out. TLC chromatography evidenced synthesis of two products: mono- and di-substituted esters of hydroquinone. THF was rotary evaporated. Crystallization in methanol (200 mL) was performed to obtain grey precipitate and brown filtrate. Column chromatography from grey precipitate was performed, using mixture of methylene chloride and methanol as eluent, with progressively increasing proportions of methanol (from 2% to 10%). Fractions containing still partially contaminated product **6** were rotary evaporated. Crystallization of the collected material from approximately 100 ml of methanol was performed affording pure product with 42% yield.

¹HNMR (500MHz, CDCl₃) [ppm]: 0,84 (m; 6H); 1,23-1,42 (m; 28H); 1,18 (m; 1H); 3,88 (d; 2H); 6,78 (m; 2H,ArH); 6,98 (m; 2H,ArH); 7,22 (d; 2H,ArH); 7,32 (d; 2H,ArH); 8,12 (d; 2H,ArH); 8,22 (d; 2H,ArH)

Synthesis of ligand L1 with a branched lateral chain (S7):

631 mg (1.05 mmol) of compound **6** was dissolved in 4 ml of anhydrous dichloromethane. Then, mercaptohexadecanoic acid (300 mg; 1.05 mmol) and DMAP (30 mg; 0.24 mmol) were added and solution was stirred until all precipitates were dissolved. The mixture was degassed by connecting the flask to water pump. Then the flask was placed in ice bath and 260 mg (1.26 mmol) of DCC dissolved in 1 ml of anhydrous dichloromethane was added, using a syringe. Reaction was stirred for 5 minutes, then ice bath was removed and reaction was left under stirring for 12 hours. A resulting white precipitate (DCU – dicyclohexyl urea) was filtered out. The filtrate was rotary evaporated. The obtained crude product was chromatographed twice on silica gel eluted with methylene chloride affording pure product with 58% yield.

¹HNMR (500MHz, CDCl₃) [ppm]: 0,84 (m; 6H); 1,20-1,82 (m; 28H); 2,64(t; 2H); 2,82(q; 2H); 3,89 (d; 2H); 6,95 (d; 2H, ArH); 7,16 (m; 2H, ArH); 7,22 (m; 2H, ArH); 7,33 (d; 2H, ArH); 8,12 (d; 2H, ArH); 8,23 (d; 2H, ArH)