Supporting Information

Multidimensional structures made by gold nanoparticles with shape-adaptive grafting layer

M. Wojcik, M. Kolpaczynska, D. Pociecha, J. Mieczkowski and E. Gorecka

Experimental procedures

All reactions during synthesis of ligands and nanoparticles were carried out under nitrogen (N_2) atmosphere in dried glassware with efficient magnetic stirring. Purification of reaction products was carried out by column chromatography using Rushan Taiyang silica gel 60 (230-400 mesh). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 (Merck) pre-coated glass plates (0.25 mm thickness) and visualized using iodine vapor and/or UV lamp (254 nm). The solvents used: tetrachloromethane, trichloromethane, dichloromethane, toluene and tetrahydrofuran were of p.a. quality. Unless otherwise specified, substrates were obtained from Sigma-Aldrich and used without further purification. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials. The ^{1}H NMR and ^{13}C NMR spectra were recorded at NMR Varian Unity Plus 500 MHz and 200 MHz respectively. Proton chemical shifts were 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 ($CDCl_3$, 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). It should be noticed that all NMR signals from thiol molecules attached to gold nanoparticles were strongly broaden due to paramagnetic character of metallic core, that allowed for easy control of sample contamination by free ligand molecules (molecules not attached to gold core give sharp signals). In all recorded spectra there are aslo sharp signals coming from small amount of known impurities present in used solvent: H_2O (1.7 ppm) and $CHCl_3$ (7.27 ppm). Mass spectroscopy was performed on Quattro (TOF)-LCT spectrometer.

The small angle X-ray diffraction (SAXRD) patterns for the powder as well as partially aligned samples were obtained with the Bruker Nanostar system. The CuK_α radiation was used, patterns were registered with an area detector VANTEC 2000. The temperature of the sample was controlled with precision of 0.1 K. The signal intensities vs. wavevector q were obtained through integration of the pattern over azimuthal angle. The nanoparticle samples were aligned by shearing of small amount of material placed on the Kapton tape at temperature ~80^{o}C. The same Bruker Nanostar system was also used for the scattering experiments (SAXS). The scattering data from nanoparticle solution in toluene (or hexane) were analyzed using NANOFIT software, assuming spherical form factor for non-interacting gold particles (structure factor S=1) and Shultz distribution (zero particles with zero diameter) of the particle sizes. Gold clusters size was also evaluated from broadening of the x-ray signals from gold crystal lattice using Debye-Schererr model. The broad angle diffraction patterns were collected with Bruker D8 Discover diffractometer (CuK_α radiation) equipped with linear VANTEC 1 detector. For analyzing of the signal broadening TOPAS software was applied. For chosen samples also direct TEM observation were carried on a JEOL JEM 3010 electron microscope operating at an accelerating voltage of 300 kV and SEM pictures taken with Carl Zeiss SMT AURIGA^{TM} CrossBeam.

The optical birefringence of the samples was checked by polarizing optical microscopy and with setup based on photoelastic modulator (Hinds PEM-90).

Synthesis and characterization of mesogenic ligands.

Following abbreviations are used:

DIAD - Diisopropylazodicarboxylate
DMAP - 4-Dimethylaminopyridine
HMDT - Hexamethyldisilthiane
NMP - *N*-Methyl-2-pyrrolidone
TBAF - Tetra-*n*-butylammonium fluoride
TEA - *Triethylamine*
TPP - *Triphenylphosphine*

Synthesis of rod-like mesogenic ligands

General procedure for the synthesis of rod-like mesogenic ligands (compounds 1-8 and 1-9) is presented in Scheme 1.

Synthesis of 4-(bromomethyl)benzoyl chloride (1-1)

To a solution of 68.1 g (0.5 mol) of 4-methylbenzoic acid in $CHCl_3$ (700 mL) 25.7 mL a bromine solution in 50 mL of $CHCl_3$ was added dropwise. During reaction process the whole mixture was vigorously stirred at reflux. After each portion of the bromine solution the mixture was stirred until a loss of red color. Then the reaction mixture was cooled down to room temperature – a precipitate appeared. After that 54.4 mL of thionyl chloride was added. The mixture was stirred at 60 ^{o}C for 6 h until the whole precipitate was dissolved, cooled down and the solvent was evaporated. The crude product was purified by distillation under lowered pressure to afford 78.2 g (67 %) as a white solid.

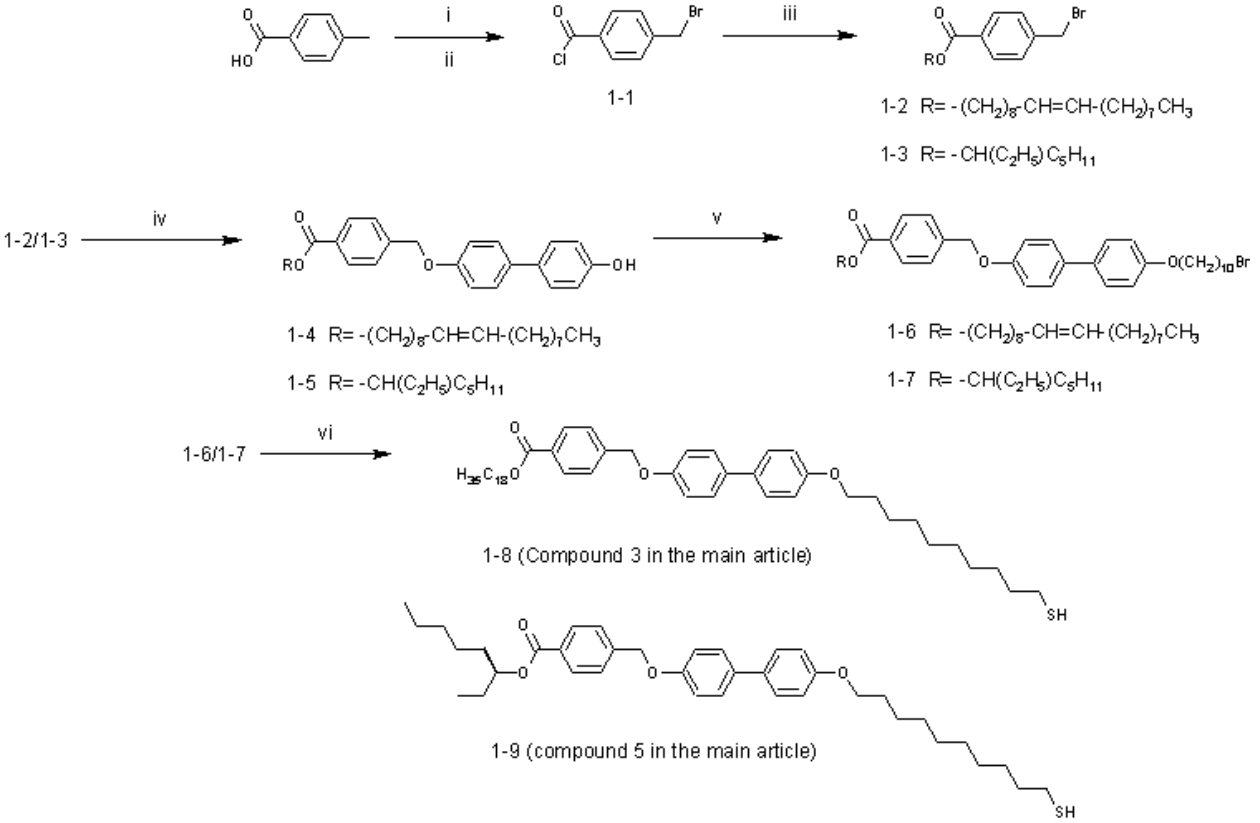
^{1}H-NMR ($CDCl_3$, 200MHz) δ 8.12-8.11 (d, 2H), 8.09-8.06 (d, 2H), 4.63 (s, 2H).MS (TOF MS ES+): m/z 256.4 [M+Na^+]

Synthesis of (9Z)-octadec-9-en-1-yl 4-(bromomethyl)benzoate (1-2)

To a solution of 94 mL (0.3 mol) of cis-9-octadecen-1-ol in toluene (300 mL), 20.15 mL of pyridine (0.25 mol) and 1.5 g of DMAP was added. To the resulting solution 1-1, 58.4 g (0.25 mol) was added slowly at -10 ^{o}C. The reaction mixture

was stirred at -10 °C for 20 minutes and then at room temperature for 1 h. The solvent was removed and the crude mixture was filtrated through a short pad of silica (eluent haxane/toluene 1:1). Removing the solvent yielded 107,1 g (92%) as a colorless liquid (1-2).

^{1}H-NMR (CDCl3, 200MHz) δ 8.18 (2H, d, J=8.0Hz); 7.45 (2H, d, J=8.2Hz); 5.41-5.31 (2H, m); 4.61 (2H, s); 3.45 (2H, t, J=7.0); 2.09-1.91 (4H, m); 1.82-1.69 (2H, m);1.49-1.21 (22H, m), 0.88 (3H, t, J=6.8); MS (TOF MS ES+): m/z 488.5 [M+Na$^+$]



Scheme 1 General procedure for the synthesis of rod-like mesogenic ligands (compounds 1-8 and 1-9). *Reagents and conditions:* (i) Br_2, hv; (ii) SOCl2, $CHCl_3$, reflux; (iii) *cis*-9-octadecen-1-ol, pyridine, toluene, DMAP; (iv) KI, K_2CO_3, NMP, 4,4`-biphenol, 110°C; (v) $P(Ph)_3$, DIAD, THF, 10-bromodecan-1-ol ; (vi) HMDT, TBAF, THF, -10°C.

Synthesis procedure, conditions and molar ratio leading to the compound 1-3 were the same like for preparation of compound 1-2. Yield 90 %.

Synthesis of (9Z)-octadec-9-en-1-yl 4-{[(4`-hydroxybiphenyl-4-yl)oxy]methyl}benzoate (1-4)

A mixture of 21.2 g (114 mmol) of biphenyl-4,4`-diol, 42.9 g (304 mmol) of K_2CO_3 and 50.5 g (304 mmol) of KI in 180 mL of N-methyl-2-pyrrolidone was vigorusly sttired at 40 °C for 20 minutes. After that 35,5 g (76 mmol) of compound 1-2 was quickly added. The mixture was stirred at 70 °C for 12 h and cooled down to a room temperature. Cooled mixture was added to 500 mL of distilled water. A brown deposit was separated by filtration and dried under lowered pressure at 78 °C. The target compound was purified by column chromatography (eluent - firstly $CHCl_3$, then 1 % CH_3OH in $CHCl_3$) and was crystallized in CH_3OH to give 18.65 g of compound 1-4. Yield 43 %.

Synthesis procedure, conditions and molar ratio leading to the compound 1-5 were the same like for preparation of compound 1-4. Yield 43 %.

^{1}H-NMR (CDCl3, 200MHz) δ 8.08 (2H, d, J=8.2Hz); 7.56-7.36 (6H,m); 7.00 (2H, m); 6.89 (4H, m); 5.40-5.32 (2H, m); 5.15 (2H, s); 4.32 (2H, t); 2.08-1.96 (4H, m); 1.74 (2H, tt, J=7.1Hz, J=7.2Hz); 1.51-1.22 (22H, m); 0.88 (3H, t, J=6.7Hz).MS (TOF MS ES+): m/z 593.9 [M+Na$^+$]

Synthesis of (9Z)-octadec-9-en-1yl-4-({[4`-(10-bromodecyloxy)biphenyl-4-yl]oxy}methyl)benzoate (1-6)

To a solution of 17.1 g (30 mmol) of compund 1-4 THF (125 mL) 8.65 g of triphenylphosphine (33 mmol; 1.1 eq.) and 10.67 g of 10-bromodecan-1-ol (45 mmol, 1.5 eq) was added. The mixture was stirred at this temperature for 15 minutes and a solution of 6.67 g diisopropyl azodicarboxylate in 10 mL of THF was added successively at room temperature. The reaction was complete in six hours at room temperature. Crude product was purified by column chromatography (eluent toluene). Solution after column chromatography was concentrated to afford 1-6 (20.62 g, 26 mmol), which can be used for thiol preparation in the next step. Yield – 86%.

^{1}H-NMR (CDCl3, 200MHz) δ 8.07 (2H, dd, J=6.6Hz, J=1.9Hz); 7.54-7.42 (6H, m);
7.04-6.88 (4H, m); 5.44-5.30 (2H, m); 5.16 (2H, s); 4.32 (2H, t, J=6,8); 3.98 (2H, t, J=6.6Hz); 3.41 (2H, t, J=6,8); 2.08-1.94 (4H, m); 1.89-1.68 (8H, m); 1.52-1.22 (32H, m); 0.89 (3H, t, J=6.8);
^{13}C NMR (125 MHz, $CDCl_3$) δ 166.40; 158.35; 157.55; 142.17; 134.09; 133.10; 130.04; 129.99; 129.86; 129.80; 127.76; 127.69; 126.93; 115.11; 114.77; 69.45; 68.06; 65.15; 34.00; 32.83; 31.91; 29.77; 29.74; 29.71; 29.67; 29.53; 29.44; 29.43; 29.36; 29.36; 29.34; 29.32; 29.30; 29.27; 29.22; 28.75; 28.73; 28.16; 27.23; 27.19; 26.05; 22.69; 14.12. MS (TOF MS ES+): m/z 813.0 [M+Na^+]

Synthesis procedure, conditions and molar ratio leading to the compound 1-7, 2-14 and 2-15 were the same like for preparation of compound 1-6. Yield 81-88 %.

Synthesis of (9Z)-octadec-9-en-1-yl-4-({[4`-(10-sulfanyldecyloxy)biphenyl-4-yl]oxy}methyl)benzoate (1-8)

Bromide 1-6 (2.5 g, 3.16 mmol) was dissolved under argon atmosphere in dry and degassed THF (30 mL). Mixture was cooled and hexamethyldisilthiane (0.683 mL, 3.31 mmol, 1.05 eq.) was added quickly. After 5 minutes 2.5 mL (1M solution in THF) of tetr-n-butylammonium fluoride was added. The reaction mixture was stirred at -10 ^{o}C for 30 minutes and after that at a room temperature for another 30 minutes. To a slightly green solution 70 mL of CH_2Cl_2 was added and then mixture was washed with saturated water solution of NH_4Cl (three times using 50 mL). Afterwards mixture was dried ($MgSO_4$) and the solvent was evaporated. The residue was purified by column chromatography (eluent – hexane and toluene 1:1). Removing the solvent yielded 1-8 (1.90 g, 2.55 mmol, 81 %) as a white solid.
^{1}H-NMR (CDCl3, 200MHz) δ 8.07 (2H, d, J=8.9Hz); 7.54-7.41 (6H, m); 7.04-6.89 (4H, m); 5.44-5.30 (2H, m); 5.16 (2H, s); 4.32 (2H, t, J=6,7); 3.98 (2H, t, J=6.6Hz); 2.52 (2H, m); 2.08-1.94 (4H, m); 1.89-1.68 (8H, m); 1.52-1.22 (32H, m); 0.89 (3H, t, J=6.8); ^{13}C NMR (125 MHz, $CDCl_3$) δ, 166.41; 158.34; 157.54; 142.16; 134.09; 133.09; 130.45; 130.25; 130.08; 129.98; 129.85; 129.79; 127.76; 127.69; 126.93; 115.10; 114.76; 69.46; 68.07; 65.17; 39.19; 34.03; 32.60; 32.57; 31.92; 31.90; 29.76; 29.72; 29.69; 29.65; 29.60; 29.51; 29.49; 29.42; 29.31; 29.35; 29.31; 29.29; 29.26; 29.21; 29.17; 29.04; 28.72; 28.51; 28.35; 27.21; 27.18; 26.03; 24.64; 22.67; 14.10; MS (TOF MS ES+): m/z 766.1 [M+Na^+]

Synthesis procedure, conditions and molar ratio leading to the compounds 1-9, 2-17 and 2-18 were the same like for preparation of compound 1-8. Yield 79 %, 81 %, 70 %.

Compound 1-9

^{1}H-NMR (CDCl3, 200MHz) δ 8.06 (2H, d, J=8.2Hz); 7.54-7.41 (6H, m); 7.04-6.90 (4H, m); 5.16-5.11 (3H, m); 3.98 (2H, t, J=6.5); 2.52 (2H, m); 1.84-1,54 (12H, m); 1.52-1.24 (12H, m); 0.88 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ, 166.13; 165.95; 158.35; 157.56; 142.05; 134.08; 133.10; 130.49; 130.44; 129.86; 129.84; 127.76; 127.69; 126.94; 126.90; 115.12; 114.77; 69.47; 68.07; 39.20; 36.07; 34.04; 33.65; 31.74; 29.70; 29.67; 29.49; 29.44; 29.36; 29.30; 29.22; 29.16; 29.05; 28.51; 28.37; 27.08; 26.05; 25.41; 25.03; 24.65; 22.70; 22.59; 22.54; 20.08; 14.13; 14.06; 14.10; 9.65. MS (TOF MS ES+): m/z 627.3 [M+Na^+]

Compound 2-17

^{1}H NMR (500 MHz w CDCl3) δ 7.68(1H, m); 7.60-7.57 (2H, m); 7.53-7.50 (3H, m); 7.25- 7.23 (2H, m); 6.98-6.93 (3H, m); 4.08 (4H, m); 4.00 (2H, t, J= 6.1 Hz); 2.66-2.49 (2H, m); 1.90-1.78 (8H, m); 1.52-1.27 (48H, m); 0.91-0.87 (6H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.19; 158.73; 153.78; 150.01; 148.62; 138.53; 132.80; 129.11; 127.68; 124.38; 122.01; 121.55; 114.79; 114.55; 111.88; 69.33; 69.06; 69.05; 34.10; 32.82; 31.83; 31.82; 29.71; 29.45; 29.38; 29.36; 29.35; 29.29; 29.27; 29.17; 29.05; 28.76; 28.17; 26.05; 26.01; 25.98; 22.69; 14.13. MS (TOF MS ES+): m/z 868.3 [M+Na^+]

Compound 2-18

^{1}H NMR (500 MHz w CDCl3) δ 7,61-7,49 (4H, m); 7,42 (2H, m); 7,21(2H, m); 6,99-6,95 (2H, m); 4,09-3,97 (8H, m); 2,67-2,50 (2H, m); 1,87-1,75 (10H, m); 1,50-1,26 (66H, m); 0,90-0,86 (9H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.16; 158.78; 152.97; 149.95; 138.66; 132.75; 128.11; 127.71; 123.93; 121.96; 114.82; 108.55; 73.59; 69.26; 68.08; 34.05; 31.94; 30.36; 29.72; 29.68; 29.50; 29.42; 29.38; 29.30; 29.07; 28.37; 26.09; 24.66; 22.71; 14.13. MS (TOF MS ES+): m/z 1052.6 [M+Na^+]

Synthesis of polycatenar ligands

Polycatenar ligands (**2-16**, **2-17** and **2-18**) were synthesized according to general route presented in Scheme 2.

Synthesis of methyl 4-(octyloxy)benzoate (2-4)

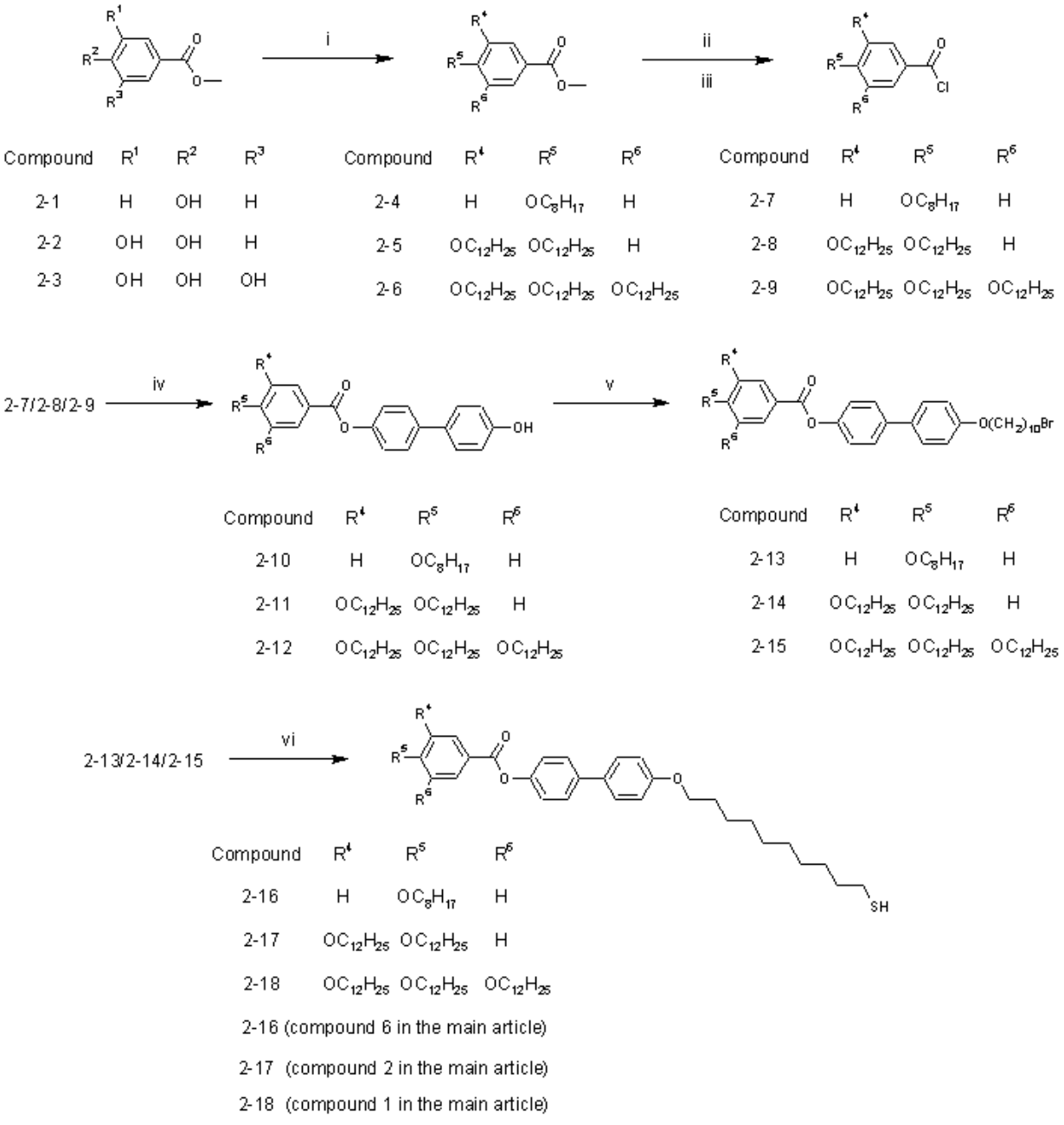
To a solution of methyl 4-hydroxybenzoate (5 g, 33 mmol, 1 eq.) in 200 mL of N-methyl-2-pyrrolidone at 40 ^{o}C, 21.8 g (132 mmol, 4 eq.) of KI and 18.2 (132 mmol, 4 eq) of K_2CO_3 were added . The solution was stirred for 30 minutes and 12.7 g (66 mmol, 2 eq.) of n-octyl bromide was added. The reaction mixture was heated up to 110 ^{o}C and vigorously stirred for 10 h and then allowed to cool down to a room temperature. After that the mixture was added to 400 mL of water with ice and cooled down to 4 ^{o}C. The gray deposit was filtrated and dried on air. Crude product was dissolved in 200 mL of $CHCl_3$ and dried again using $MgSO_4$. The solvent was concentrated and the product purified by column chromatography (eluent toluene) yielding **2-4** (7.2 g, 83%).
^{1}H-NMR (CDCl3, 200MHz) δ 7.97 (2H, d, J= 8.0 Hz); 6.88 (2H, d, J= 8.6 Hz); 3,97 (2H, t, J= 7.4 Hz); 3.86 (3H, s); 1.81-1.71 (2H, m); 1.48-1.20 (10H, m); 0.88 (3H, t, J1 = 7.0). MS (TOF MS ES+): m/z 287.2 [M+Na^+]

Synthesis procedure, conditions and molar ratio leading to the compounds **2-5** and **2-6** were the same like for preparation of

compound **2-4,** except eluents composition used in column chromatography. Yield 78 % (2-5), 85% (2-6).

Synthesis of 4-(octyloxy)benzoyl chloride (2-7)

To a suspension of methyl 4-octylbenzoate (7.2 g, 27 mmol) in absolute ethanol (150 mL) solution of 7.5 g (136 mmol) of potassium hydroxide in 30 mL of ethanol was added. The reaction mixture was heated at reflux for 4 h and then cooled down to a room temperature. The suspension was filtrated and washed with absolute ethanol. The remaining crude potassium salt was then dried under lowered pressure. Dried salt (7.0 g)was then used without any purification to obtain suspension



Compound	R^1	R^2	R^3
2-1	H	OH	H
2-2	OH	OH	H
2-3	OH	OH	OH

Compound	R^4	R^5	R^6
2-4	H	OC_8H_{17}	H
2-5	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H
2-6	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$

Compound	R^4	R^5	R^6
2-7	H	OC_8H_{17}	H
2-8	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H
2-9	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$

Compound	R^4	R^5	R^6
2-10	H	OC_8H_{17}	H
2-11	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H
2-12	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$

Compound	R^4	R^5	R^6
2-13	H	OC_8H_{17}	H
2-14	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H
2-15	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$

Compound	R^4	R^5	R^6
2-16	H	OC_8H_{17}	H
2-17	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H
2-18	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$

2-16 (compound 6 in the main article)

2-17 (compound 2 in the main article)

2-18 (compound 1 in the main article)

Scheme 2 Synthetic route to ligands 2-17 and 2-18. *Reagents and conditions:* (i) KI, K_2CO_3, NMP, $C_nH_{2n+1}Br$; (ii) KOH, EtOH, reflux; (iii) CH_2Cl_2, $(COCl)_2$, reflux; (iv); TEA, DMAP, 4,4`-biphenol; (v) $P(Ph)_3$, DIAD, THF, 10-bromodecan-1-ol; (vi) HMDT, TBAF, THF, -10ºC;

in 100 mL of toluene. To the mixture 5.5 mL (64 mmol)of oxalyl chloride was added. After addition of oxalyl chloride the reaction mixture was refluxed for 10 h. The cooled mixture was filtrated to separate inorganic wastes and solution was concentrated to give the yellow residue of **2-7** (6.9 g, 25.7 mmol, 95 %) which was used in next reaction without any purification.

Synthesis procedure, conditions and molar ratio leading to the compound **2-8 and 2-9** were the same like for preparation of compound **2-7**. Yield 94% (2-8), 95% 2-9).

Synthesis of 4`-hydroxybiphenyl-4-yl 4-octyloxybenzoate (2-10)

In a clean and dried round-bottom flask biphenyl-4,4`-diol (6.7 g, 36 mmol, 2 eq.), 8 mL triethylamine (5.8 mmol) and 50 mg (catalytic amount) of 4-dimethylaminopyridine were added. The reaction mixture was stirred for 30 minutes at room temperature and then 4.8 g (18 mmol) 4-(octyloxy)benzoyl chloride in 30 mL of toluene was carefully added. The reaction mixture was refluxed for 4 h and cooled down to room temperature and solid wastes were filtrated. A liquid residue was evaporated and redissolved in a small amount of $CHCl_3$, then 40 mL of methanol was added and the reaction mixture was heated under reflux. White precipitated solid was filtrated and the liquid residue was cooled down to 4 ^oC. A new white solid appeared, it was filtrated and washed using cold methanol. Crude product was filtrated by flash chromatography and the solvent was removed in vacuum to yield 6.7 g (89 %) of white solid **2-10**.

^{1}H-NMR (CDCl3, 200MHz) δ 8.16 (2H, d, J= 8.8 Hz); 7.56 (2H, d, J= 8.6 Hz); 7.46 (2H, d, J= 8.6 Hz); 7.20 (2H, d, J=7.8); 6.98 (2H, d, J=8.8 Hz); 6.89 (2H, d, J= 8.6 Hz); 4.05 (2H, t, J= 6.4Hz); 1.90-1.75 (2H, m); 1.47-1.30 (10H, m); 0.90-0.86 (3H, m). MS (TOF MS ES+): m/z 441.5 [M+Na^+]

Synthesis procedure, conditions molar ratio, but slightly modified purification methods, leading to the compound **2-11** and **2-12** were the same like for preparation of compound **2-10**. Yield 80% (**2-11**), 84% (**2-12**).

Synthesis of n-octyl-4-({[4`-(bromodecyloxy)biphenyl-4-yl]oxy}methyl)benzoate (2-13)

To a solution of 10.33 g (25 mmol) of compound **2-10** in THF (425mL) 7.21 g of triphenylphosphine (27.5 mmol; 1.1 eq.) and 8.90 g of 10-bromodecan-1-ol (37.5 mmol, 1.5 eq) were added . The mixture was stirred at this temperature for 15 minutes and a solution of 5.91 g diisopropyl azodicarboxylate (27.5 mmol, 94% solution, 1.1 eq.) in 10 mL of THF was added successively at room temperature. The reaction mixture was refluxed for 4 h and cooled down to room temperature and solid wastes were filtrated. Crude product was recrystallized using methanol. White precipitate was separated and used for thiol preparation in the next step. Yield 54 %.

^{1}HNMR (500 MHz w CDCl3) δ 8,17-8,14 (2H, m); 7,60-7,57 (2H, m); 7,52-7,50 (2H, m); 7,24-7,23 (2H, m); 6,99-6,95 (4H, m); 4,04 (2H, t, J=6.6 Hz); 3.99 (2H, t, J= 6.6Hz); 3,41 (2H, t, J= 6.8 Hz); 1,90- 1,76 (6H, m); 1,51-1,26 (22H, m); 0,90 (3H, t, 7.0 Hz). MS (TOF MS ES+): m/z 660.7 [M+Na^+]

Synthesis of n-octyl-4-({[4`-(sulfanyldecyloxy)biphenyl-4yl]oxy}methyl)benzoate (2-16)

Bromide **2-13** (2.70 g, 4.23 mmol) was dissolved under argon atmosphere in dry and degassed THF (200 mL) and hexamethyldisilthiane (0.924 mL, 4.44 mmol, 1.05 eq.) was added quickly at room temperature. After 5 minutes 4.44 mL (1M solution in THF) of tetr-n-butylammonium fluoride was added. The reaction mixture was stirred at room temperature. After 60 minutes, the organic solution was concentrated. White precipitate was filtrated, dissolved in 300 mL of trichloromethane and mixed with 20 g of silicagel. Solvent was removed and dry mixture of crude product was used to prepare column chromatography (eluent – 2 % methanol in trichloromethan). Removing the solvent yielded **2-16** (1.90 g, 2.55 mmol, 76 %) as a white solid.

^{1}HNMR (500 MHz w CDCl3) δ 8,17-8,14 (2H, m); 7,59-7,56 (2H, m); 7,52-7,50 (2H, m); 7,24-7,23 (2H, m); 6,99-6,94 (4H, m); 4,04 (2H, t, J=6.5 Hz); 3.98 (2H, t, J= 6.8Hz); 2.52 (2H, m); 1,90- 1,76 (6H, m); 1,51-1,26 (22H, m); 0,89 (3H, t, 6.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.09; 163.55; 158.72; 149.98; 138.53; 132.81; 132.30; 128.11; 127.70; 122.01; 121.52; 114.79; 114.29; 68.34; 68.05; 34.11; 32.83; 31.82; 29.46; 29.37; 29.35; 29.28; 29.24; 29.11; 28.76; 28.17; 26.05; 26.00; 22.68; 14.13. MS (TOF MS ES+): m/z 213.9 [M+Na^+]

Synthesis of gold clusters

Series of gold clusters with n-alkyl thiols of different length in *primary* grafting layer was synthesized according to modified Brust method [2]. To keep similar conditions of obtaining gold nanoclusters the starting toluene solution of tetrachloroaurate ions was prepared. An aqueous solution of hydrogen tetrachloroaurate (90 mL, 30 mmol dm^{-3}) was extracted (three times with 200 mL) with toluene solution of methyltrioctylammonium bromide (5.38 g, 1.38 mmol) to transfer tetrachloroaurate ions to the organic layer. Alkanethiol was added to the toluene solution (2:1 mole ratio of alkanethiol to $AuCl_4^-$) and mixture was reduced at 15 °C with freshly prepared aqueous solution of sodium borohydride (1.40 g, 30 mmol in 10 mL of deionised H_2O). Solution of borohydride was quickly added under vigorous stirring. After further stirring for 3 h the organic phase was separated, washed with pure water (2x50 mL), evaporated to 5 mL in a rotary evaporator and mixed with 200 mL of absolute ethanol to precipitate nanoparticles. The mixture was kept for 12 h at -4 ^oC. The dark brown precipitate was sonicated for 60 s and centrifuged (5 min, 13 000 rpm). Again precipitate was dissolved in a small amount of toluene (5 mL), precipitated with ethanol (100 mL) and centrifuged. Finally, all samples were dissolved in 20 mL of hexane and centrifuged for 5 minutes. Samples with $C_{18}H_{37}SH$, as a *primary* ligand, showed a big amount of aggregated gold nanoparticles which were separated from hexane solution. The procedure was repeated until no trace of excess of thiol was found, as determined by ^{1}H NMR spectra and TLC.

The SAXS scattering measurements as well as direct microscopic TEM observations and analysis of broadening of x-ray diffraction signals coming form crystal lattice of gold consistently show that metal cluster diameter is close to 2 nm. (Fig.1) The size distribution, taken assuming Shultz distribution, was in the range 20% for all samples (inset

Fig.1).

Ligand exchange reaction at gold cluster surface

Obtained gold nanoclusters, with the average gold core diameter ~2 nm, were a starting material for preparation of hybrid mesogenic nanoparticles. The ligand exchange reaction was carried on by the procedure similar to that described in the reference 3.

A proper organic ligand (20-30 mg) was added to the toluene solution (20-50 mL – depending on ligand solubility) of starting gold NPs (20-25 mg) and the reaction proceeded with stirring at room temperature for ca. 48 h. No precipitation and/or change of color occurred. From this we infer that the ligand-exchange reaction is not accompanied by side-effects

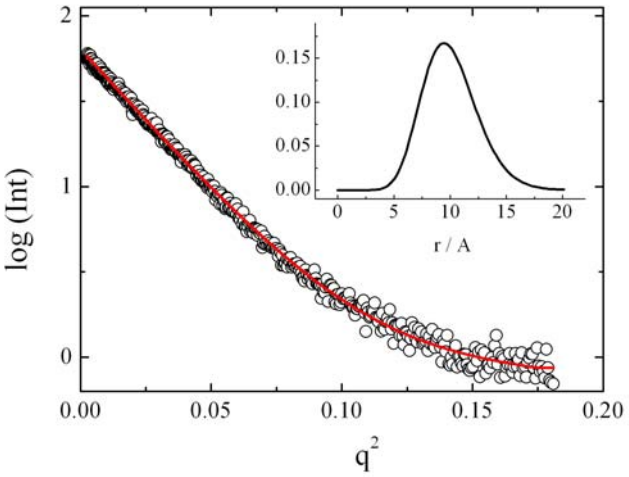


Fig.1 Intensity of x-ray scattering from gold particles with grafting layer of n-hexyl thiol diluted in toluene vs. squared wavevector. The calculated curve (red line) was obtained assuming noninteracting spherical particles of mean radius 1.05 nm. In the inset the nanoparticle radius distribution.

such as irreversible aggregation or significant gold core size modifications. Only in case of ligand **2-16** the reaction mixtures were heated at 60 ^{o}C, because of its poor solubility in toluene, which led to appearance of small amounts of aggregated nanoparticles. The clear burgundy solution obtained after ligand exchange reaction was evaporated and the blackish solid was dissolved in minimum volume of toluene (max. 2 mL). In the next step the nanoparticles were precipitated using a mixture of acetone and absolute ethanol (1:1) and cooled down to 4^{o}C, then after 2h centrifuged (13000 rpm, 5 min). This washing process was repeated twice using different proportions of acetone and ethanol. For organic ligands that were poorly soluble in toluene, larger volume of toluene has been used and centrifugation time has been extended up to 15-25 minutes. After that, all samples have been redissolved in toluene and centrifuged for 5 minutes. Black precipitate was removed and the solution was concentrated.

Lack of metal clusters size changes during ligand exchange reaction was confirmed by results of SAXS experiments performed before and after the reaction.

Based on integration of NMR signals it was deduced that the nanoparticles after ligand exchange reaction are covered by n-alkyl and mesogenic thiol molecules in ratio ~ 1:1. The calculations were performed as follows. Integration of a signal characteristic to mesogenic molecule (for example hydrogens at the aromatic core) allowed to estimate integration of -CH_3 hydrogens from the mesogenic molecules. From the difference between measured integration of -CH_3 hydrogens signal and that expected to come from mesogenic molecule the number of -CH_3 hydrogens from aliphatic thiol molecules was calculated. This enabled to determine relative amount of both thiols. From thermogravimetric analysis (the mass reduction of a sample heated under oxidizing atmosphere) the mass ratio of metallic core and organic shell was estimated that corresponds to ~ 80 thiol molecules at the particle surface. For details see SI in ref. 1.

References

1. M. Wojcik, W. Lewandowski, J. Matraszek, J. Mieczkowski, J. Borysiuk, D. Pociecha, E. Gorecka, *Angew. Chem. Int. Ed.* 2009, **48**, 5167.
2. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman *J. Chem. Soc., Chem. Commun.*, 1994, 801.
3. R. S. Ingram, M. J. Hostetler, R. and W. Murray, *J. Am. Chem. Soc.* 1996, **118**, 4214..