Gold nanoparticles with flexible mesogenic grafting layers

Joanna M. Wolska, Damian Pociecha, Jozef Mieczkowski and Ewa Gorecka

Experimental section

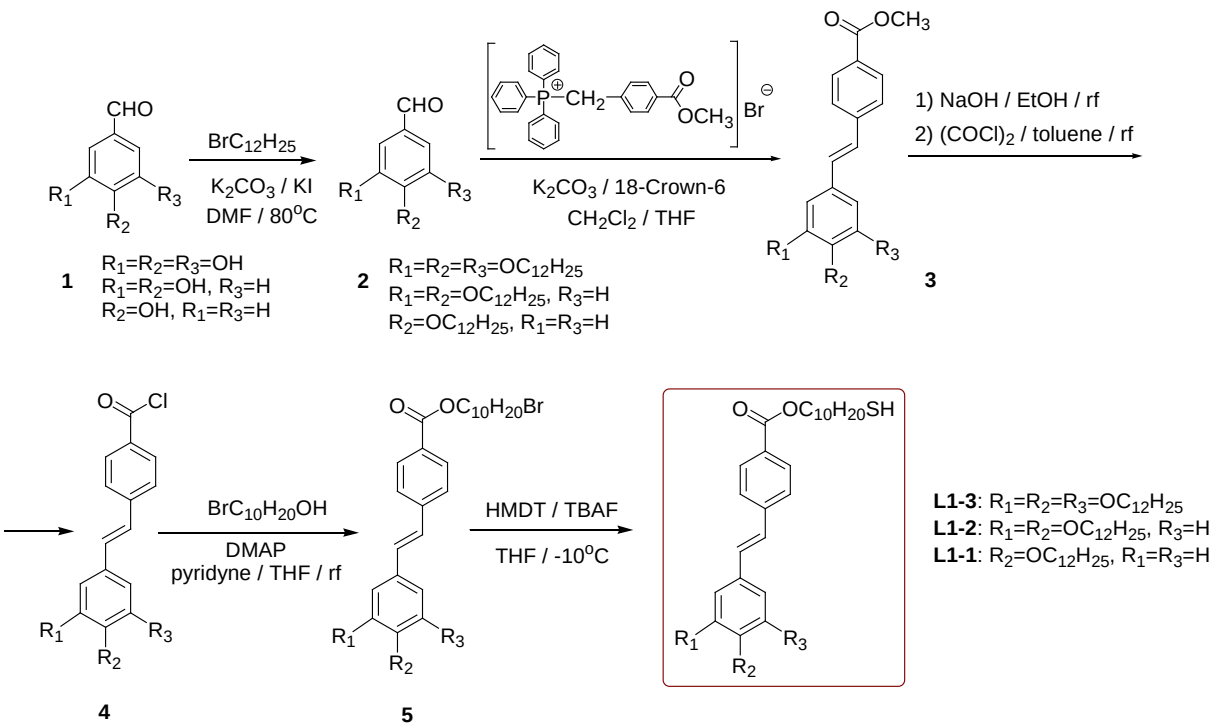
The small angle X-ray diffraction patterns were obtained by Bruker Nanostar system with an area detector VANTEC 2000 and CuKα radiation. The temperature of the sample was controlled with precision 0.1 degree. The signal intensities vs. wavevector q were obtained through integration of the pattern over azimuthal angle. The nanoparticle samples were aligned by shearing of small amount of material placed on the Kapton tape at temperature ~70°C or ~100°C. 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 (CuKα radiation) equipped with linear VANTEC 1 detector. For analysing of the signal broadening TOPAS software was applied. The optical birefringence was measured using setup built with photoelastic modulator (PEM-90), He-Ne laser photodiode (PIN-20) and lock-in amplifier (EG&G 7265). The ^{1}H NMR and ^{13}C NMR spectra were recorded at NMR Varian Unity Plus 200 MHz respectively. Proton chemical shifts were reported in ppm (δ) relative to 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). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz). In all recorded spectra there are sharp signals coming from impurities present in used solvent: H_2O (1.7ppm) and $CHCl_3$ (7.27 ppm). 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 freeligand molecules (molecules not attached to gold core give sharp signals). 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. The IR polarizer was rotated with respect to the rubbing direction in the sample to obtain variation of IR signal intensities. TEM images were taken using Zeiss Libra 120 microscope.

Presented reactions were carried out under an argon atmosphere with using a magnetic stirring hotplate. All products were purified by column chromatography with Rushan Taiyang silica gel 60 (230-400 mesh). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 (Merck) pre-coated plastic/alumina plates (0.25 mm thickness) and visualized using UV lamp (254 nm) and iodine vapor. During the synthesis following solvents of p.a. quality were used: trichloromethane, dichloromethane, hexane, toluene, tetrahydrofuran, ethanol and methanol. As a substrates were used Sigma-Aldrich products without further purification. Presented yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.

Synthesis and characterization of promesogenic ligands

Following abbreviations are used:
DIAD - Diisopropylazodicarboxylate
DMAP - 4-Dimethylaminopyridine
HMDT - Hexamethyldisilthiane
TBAF - Tetra-n-butylammonium fluoride

The general procedure of obtaining ligands of series L1, L2, L3 are presented on Scheme 1, Scheme 2 and Scheme 3 respectively. The preparative part for ligands is presented on example of compounds containing two terminal chains in positions 3 and 4 (L1-2, L2-2, L3-2).



Scheme 1. Synthesis of ligands of series L1 (L1-3, L1-2, L1-1).

Synthesis of the compound 2:

Into the solution of 15g (0.1mol) of 3,4-dihydroxybenzaldehyde in 500ml of DMF a 37,5g (0.27mol) of anhydrous K_2CO_3 and 45,1g (0.27mol) of KI was added. Next 67,7g (0.27mol) of 1-bromododecane was added dropwise. The mixture was vigorously stirred in temperature of 80°C for 24h. After cooling to the room temperature the mixture was poured into the 1 L of cold water with ice. The precipitate was filtrated and recrystallized twice from ethanol. A 43,5g (84%) of product was obtained as a white solid.

^{1}H NMR: (200MHz, $CDCl_3$) δ 9,82 (1H;s); 7,41 – 7,39 (2H;m); 6,94 (1H; d; J=8,1Hz); 4,06 (4H; q; J=5,6Hz); 1,92 – 1,77 (4H; m); 1,54 – 1,2 (36H; m); 0,88 (6H;m)

Synthesis of the compound 3:

Into the solution of 24,2g (49mmol) of (4-methoxycarbonyl-benzyl)-triphenylphosphonium bromide in 170 ml of CH_2Cl_2 and 200 ml of THF 19,4 (0.14mol) of anhydrous K_2CO_3 and catalytic amount of 18-crown-6 was added in one portion. After 15 minutes to the vigorously stirred mixture a compound **2,** diluted in CH_2Cl_2, was added. The reaction mixture was refluxed for 48h and next cooled down to the room temperature. An inorganic compounds was filtrated and solvents was removed. The crude product was recrystallized from ethanol and purified by chromatography column (eluent $CHCl_3$) to give 17,8 g (70%) white solid.

^{1}H NMR: (200MHz, $CDCl_3$) δ8,0 (2H; d; J=8,6); 7,52 (2H; d; J=8,6Hz); 7,14 (1H; d; J=16,3Hz); 7,09 – 7,02 (2H; m); 6,96 (1H; d; J=16,2Hz); 6,86 (1H; m); 4,03 (4H; q; J=6,8Hz); 3,91 (3H, s); 1,92 – 1,74 (4H; m) 1,58 – 1,2 (36H; m); 0,88 (6H;m); ^{13}C NMR (50MHz, $CDCl_3$) δ 167.13; 149.91; 149.47; 131.38; 130.2; 130.01; 128.62; 126.12; 125.58; 120.73; 113.73; 111.86; 69.57; 69.4; 52.22; 32.13; 29.9; 29.85; 29.63; 29.58; 29.44;26.26; 26.23; 22.89; 14.31

Synthesis of the compound 4:

Into the mixture of 15 g (24mmol) of compound **3** in 250ml of ethanol a 25,5g (0.45mol) of KOH diluted in 10ml of distillated water was added in portions. The reaction mixture was stirred under reflux for 12h. After cooling to the room temperature the precipitate was filtrated and dried under vacuum for 24h to give a 15,5g (100%) of white solid. A 7g (10mmol) of dry product was dissolved in unhydrous toluene. Into the mixture 10ml (0.11mol) of oxalyl chloride was added dropwise. The reaction mixture was stirred under reflux for 8h. The cooled mixture was filtrated to separate inorganic wastes and solution was concentrated to give bright yellow residue which was dried under vacuum and used in next reaction without any purification. Yield 6,8g (100%).

Synthesis of the compound 5:

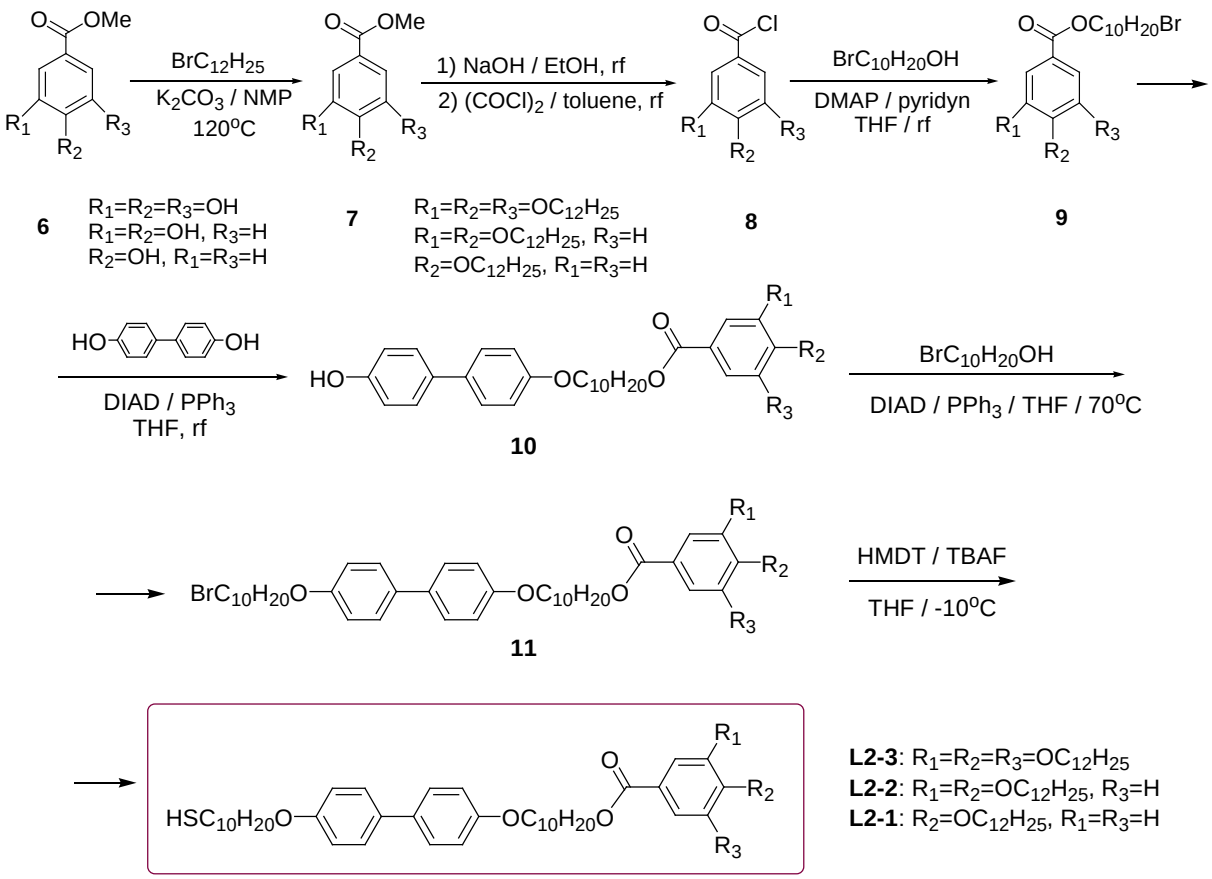
Into the solution of 4g (16.9mmol) of the 10-bromodecan-1-ol in 10ml of dry THF 2ml of dry pyridine and catalytic amount of DMAP was added. Next the solution of 7g (11.4mmol) of compound **4** was added dropwise. The mixture was stirred at 70°C for 16h. The solvent was removed and the residue was purified by column chromatography (eluent: $CHCl_3$) and recrystallized with ethanol to yield 5,5 g (60%) of white solid.

^{1}H NMR: (200MHz, $CDCl_3$) δ8,0 (2H; d; J=8,6); 7,53 (2H; d; J=8,1Hz); 7,15 (1H;d; J=16,3Hz); 7,1 – 7,02 (2H; m); 6,96 (1H; d; J=16,3Hz); 6,86 (1H; d; J=8Hz); 4,36 (2H; m); 4,03 (4H; q; J=7Hz); 3,49; (2H; t; J=6,1Hz); 2,14 – 1,74 (8H; m); 1-58 – 1,18 (48H; m); 0,88 (6H;m); ^{13}C NMR (50MHz, $CDCl_3$) δ 166.6; 149.94; 149.49; 142.5; 131.47; 130.21; 130; 128.67; 126.24; 125;57; 120.79; 113;73; 111.84; 69.59; 69.42; 64.24; 64.1; 33.38; 32.16; 29.89;29.66; 29.6; 27.66; 26.27;22.92;14.35;

Synthesis of the compound L1-2:

To a cooled solution of 1g (1.2mmol) of the compound **5** in 20ml of anhydrous THF 0,3ml (1.4mmol) of HMDT was added. After 5 minutes of stirring 1,3ml (1.3mmol, 1M solution in THF) of TBAF was added dropwise. The reaction mixture was stirred at -10°C for 0,5h and at room temperature for 1h. Next 30ml of CH_2Cl_2 was added and the solution was washed with 50ml of saturated solution of NH_4Cl in water. The crude product was dried over anhydrous $MgSO_4$ and purified by column chromatography (toluene/cyclohexane, 7:3) to give 0,7g (75%), as a white solid.

^{1}H NMR: (200MHz, $CDCl_3$) δ8,0 (2H; d; J=8,1); 7,53 (2H; d; J=8,1Hz); 7,23 – 7,02 (3H;m); 6,97 (1H; d; J=16,3Hz); 6,87 (1H; d; J=8,1Hz); 4,29 (2H; m) 4,11 – 3,95 (4H; m); 2,52 (2H; q; J=7,19); 1,93 – 1,69 (8H; m); 1,53 – 1,75 (48H; m); 0,88 (6H; m); ^{13}C NMR (50MHz, $CDCl_3$) δ 166.54; 149.7; 149.28; 142.1; 131.12; 129.98; 129.04; 128.86; 128.23; 125.98; 125.46; 125.3; 120.54; 113.54; 111.64; 69.39; 69.22; 65.04; 34.04; 31.94; 29.67; 29.39; 29.52; 28.74; 28.37; 26.04; 24.67; 22.7. 14.13; MS (TOF MS ES+): m/z 787,3 [M+Na+]



Scheme 2. Synthesis of the ligands of series L2 (L2-3, L2-2, L2-1)

Synthesis of the compound 7:

Synthesis procedure, conditions and molar ratio leading to the compound **7** were the same as used for preparation of compound **2**. Yield 90 %.

^{1}H NMR: (200MHz, $CDCl_3$) δ7,63 (1H; dd; J=8,5Hz; J=2Hz); 7,53 (1H; d; J=2Hz); 6,86 (1H; d; J=8,3Hz); 4,03 (4H; m); 3,88 (3H; s); 1,87 – 1,79 (4H; m); 1,51 – 1,21 (36H;m); 0,88 (6H; m);

Synthesis of the compound 9:

Compound **9** was obtained in the same synthesis procedure, conditions and molar ratio as used for compound **5**.

^{1}H NMR: (200MHz, $CDCl_3$) δ7,62 (1H; dd; J=8,3Hz; J=2Hz); 7,53 (1H; d; J=2Hz); 6,86 (1H; d; J=8,4Hz); 4,32 (2H; m); 4,04 (4H; m);3,49 (2H; m); 2,13 – 1,72 (8H; m); 1,58 – 1,12 (48H;m); 0,88 (6H; m);

Synthesis of the compound 10:

Into the solution of 2g (10,8 mmol) of 4,4'-biphenol in 350ml of DMF 0,9g (6,5 mmol) of K_2CO_3 and 1g (6 mmol) were added. Next 3g (4,2 mmol) of compound **9** diluted in mixture of DMF and acetone (1:1) was added dropwise. Reaction mixture was stirred at 100°C for 24h. After cooling down the mixture was poured into the water with ice. The precipitate was filtrated and filtrate was three times extracted with toluene. An organic layer was dried over anhydrous $MgSO_4$, filtrated and evaporated to dryness. The crude product was gathered and purified by column chromatography ($CHCl_3$/ $CHCl_3$ + 0,5% methanol) to give a 2,6g (75%) of white solid.

^{1}H NMR: (200MHz, $CDCl_3$) δ7,62 (1H; dd; J=8,0Hz; J=2Hz); 7,55 (1H; d; J=2Hz); 7,43 (2H; d; J=6,5Hz); 7,40 (2H; d; J=8,6Hz); 6,92 (2H; d; J=8,5Hz); 6,88 (2H; d; J=8,5Hz); 6,83 (1H; d; J=8,0Hz); 5,46 (1H, br, s,) 4,39 (2H; m); 4,03 (6H; m); 2,01 – 1,77 (8H; m); 1,5 – 1,21 (48H;m); 0,88 (6H; m); ^{13}C NMR (50MHz, $CDCl_3$) δ 167.08; 158.2; 155.17; 153.47; 148.7; 133.6; 128.1; 127.89; 123.82; 122.63; 115.87; 114.96; 11448; 112.09; 69.55; 69.25; 67.6; 64.8; 32.17; 29.9; 29.62; 29.39; 29.27;26.25; 25.81; 22.93; 14.37

Synthesis of the compound 11:

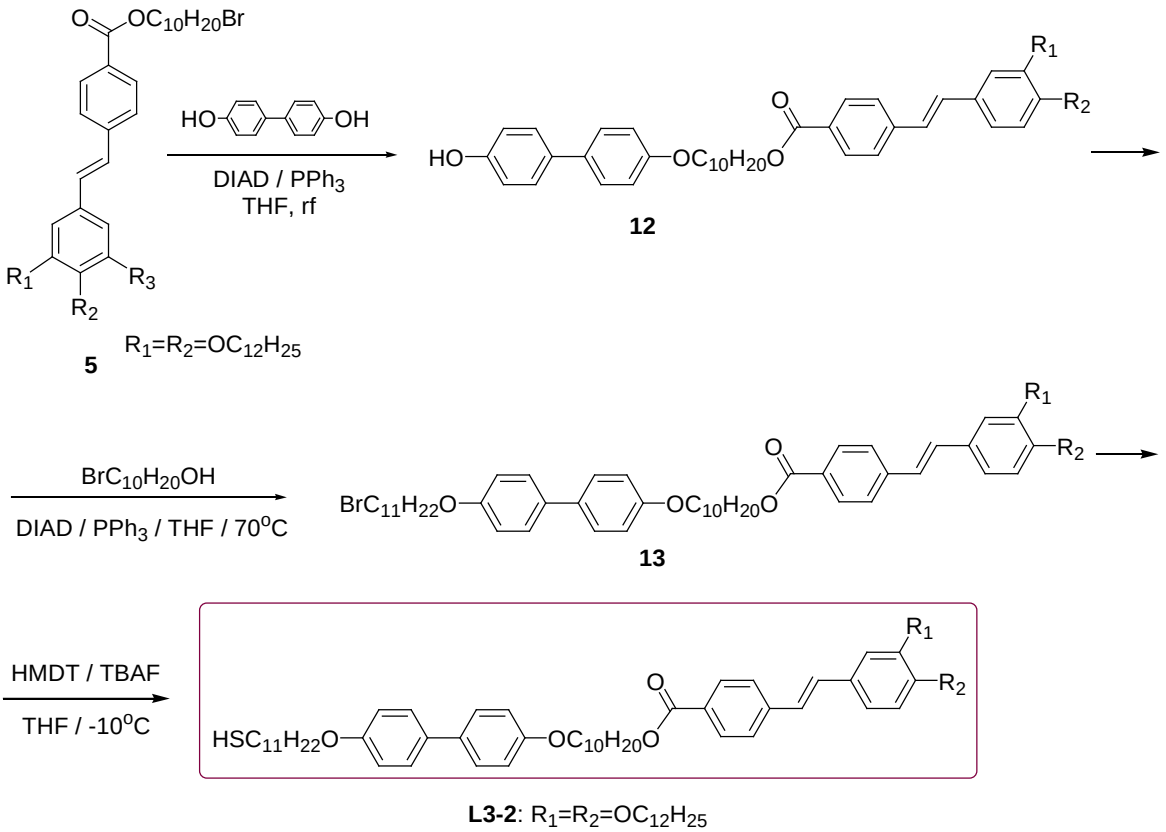
Into the 1,71g (2,1mmol) of compound **10**, 0,7g (2,7mmol) 10-bromodecan-1-ol and 0,7g (2,7mmol) of triphenylphosphine dissolved in 40ml of dry THF cooled to the 0°C 0,53ml (2,7mmol) of DIAD wad added dropwise. The reaction mixture was stirred at 70°C for 12h. The solvent was removed and the crude product was purified by chromatography column (toluene), yield 1,5g (70%).

^{1}H NMR: (200MHz, $CDCl_3$) δ7,61 (1H; dd; J=8,6Hz; J=2Hz); 7,54 (1H; d; J=2,1Hz); 7,46 (4H; d; J=8,6Hz); 6,94 (4H; d; J=8,7Hz); 6,83 (1H; d; J=8,6Hz); 4,37 (2H; m); 4,02 (8H; m); 3,44 (2H; t; J=6,8); 2,03 – 1,72 (12H; m); 1,54 – 1,18 (60H;m); 0,88 (6H; m); ^{13}C NMR (50MHz, $CDCl_3$) δ 166.56; 158.24; 157.99; 153.2; 148.5; 133.51; 133.24; 127.67; 123.48; 122.53; 114.73; 114.26; 111.87; 69.29; 68.98; 68.04; 67.38; 64.4; 34.07; 32.82; 31.93; 29.64; 29.38; 29.07; 28.75; 28.16; 26.03; 25.58; 22.7; 14.13;

Synthesis of the compound L2-2:

Synthesis procedure, conditions and molar ratio leading to the compound **L2-2** were presented for compound **L1-2**. Yield 85%.

^{1}H NMR: (200MHz, $CDCl_3$) δ7,61 (1H; dd; J=8,6Hz; J=2Hz); 7,53 (1H; d; J=2Hz); 7,45 (4H; d; J=8,6Hz); 6,94 (4H; d; J=8,6Hz); 6,83 (1H; d; J=8,4Hz); 4,38 (2H; m); 4,01 (8H; m); 2,52 (2H; q; J=7,2Hz); 2,08 – 1,7 (12H; m); 1,68 – 1,1 (61H; m); 0,88 (6H; m); ^{13}C NMR (50MHz, $CDCl_3$) δ 166.76; 158.19; 153.4; 148.7; 133.72; 133.44; 127.86; 123.69; 122.73; 114.93; 114.47; 112.06; 69.5; 69.19; 68.26; 67.58; 64.62; 34.25; 32.14; 29.84; 29.59; 29.34; 29.27; 28.58; 26.27; 25.79; 24.87; 22.91; 14.34; MS (TOF MS ES+): m/z 1009,4 [M+Na+]



L3-2: $R_1=R_2=OC_{12}H_{25}$

Scheme 3. Synthesis of the compound of series L3

Synthesis of the compound 12:

Synthesis procedure, conditions and molar ratio leading to the compound **12** were presented for compound **10**. Yield 80%.

^{1}H NMR: (200MHz, $CDCl_3$) δ7,99 (2H; d; J=8,3Hz); 7,5 (2H; d; J=8,2Hz); 7,48 – 7,38 (4H; m); 7,19 – 6,82 (9H; m); 4,88 (1H; s); 4,41 (2H; m); 4,14 – 3,96 (6H; m); 2,06 – 1,74 (8H;m); 1,57 – 1,19 (48H; m); 0,88 (6H; m); ^{13}C NMR (50MHz, $CDCl_3$) δ 166.82; 158.23; 154.83; 149.92; 149.43; 142.39; 133.88; 131.36; 130.2; 129.7;

129.11; 128.15; 127.91; 126.21; 122.14; 120.83; 115.82; 114.97; 113.71; 111.93; 69.66; 67.54; 64.82; 32.14; 29.87; 29.6; 26.28; 25.73; 22.91; 14.35;

Synthesis of the compound 13:

Synthesis procedure, conditions and molar ratio leading to the compound **13** were presented for compound **11**. Yield 85%.

^{1}H NMR: (200MHz, $CDCl_3$) δ8,0 (2H; d; J=8,1Hz); 7,51 (2H; d; J=8,6Hz); 7,46 (4H; d; J=8,8Hz); 7,2 – 6,83 (9H; m); 4,41 (2H; m); 4,14 – 3,91 (8H; m); 3,4 (2H; t; J=6,8); 2,0 (4H; m); 1,94 – 1,71 (8H;m); 1,58 – 1,17 (62H; m); 0,88 (6H; m); ^{13}C NMR (50MHz, $CDCl_3$) δ 166.88; 158.46; 158.18; 149.91; 149.48; 142.39; 133.74; 131.38; 130.2; 129.72; 129.13; 128.17 127.89; 126.21; 125.62; 120.77; 115.85; 114.95; 113.72; 111.89; 69.42; 68.27; 67.57; 64.8; 34.3; 33.05; 32.15; 29.89; 29.6; 28.98; 28.4; 26.28; 25.77; 22.92; 14.35

Synthesis of the compound L3-2:

Synthesis procedure, conditions and molar ratio leading to the compound **L3-2** were presented for compound **L1-2**. Yield 75%.

^{1}H NMR: (200MHz, $CDCl_3$) δ8,0 (2H; d; J=8,3Hz); 7,51 (2H; d; J=8,6Hz); 7,46 (4H; d; J=8,6Hz); 7,2 – 6,82 (9H; m); 4,41 (2H; m); 4,13 – 3,91 (8H; m); 2,52 (2H; q; J=7,6); 2,0 (4H; m); 1,92 – 1,71 (8H;m); 1,7 – 1,1 (63H; m); 0,88 (6H; m); ^{13}C NMR (50MHz, $CDCl_3$) δ 166.88; 158.47; 158.19; 149.91; 149.48; 142.39; 133.77; 131.38; 130.21; 129.72; 128.17 127.9; 126.22; 125.62; 120.78; 114.95; 113.72; 111.82; 69.58; 68.28; 67.56; 64.81; 34.27; 32.15; 29.88; 29.6; 29.28; 28.6; 26.27; 25.76; 24.89 22.92; 14.35; MS (TOF MS ES+): m/z 1125,2 [M+Na+]

Table 1. Characterization of bromide derivatives.

Compound number	R_1	R_2	R_3	Phase sequence
5a	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	Cry 55°C [94,9 Jg^{-1}] Iso
5b	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	Cry 72°C [89,9 Jg^{-1}] Iso
5c	H	$OC_{12}H_{25}$	H	Cry 85°C [53,9Jg^{-1}] SmA 95°C [12,9 Jg^{-1}] Iso
11a	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	Cry 62,5°C [76,5 Jg^{-1}] Iso
11b	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	Cry 79,5°C [61 Jg^{-1}] Iso
11c	H	$OC_{12}H_{25}$	H	Cry 89°C [59 Jg^{-1}] Iso
13	$OC_{12}H_{25}$	$OC_{12}H_{25}$	H	Cry 97°C [66,2 Jg^{-1}] Iso

Synthesis of the gold nanparticles

The gold nanoparticles passivated with n-alkyl thiols as a *primary* grafting layer was synthesized according to modified Brust-Schiffrin method [1]. Into the aqueous solution of hydrogen tetrachloroaurate (90ml, 30mmol/dm^3) a solution of methyltrioctylammonium chloride (4,8g, 12mmol) in toluene was added and stirred vigorously for 2h. Next, two phases was separated and into the organic layer 0,53ml (2,52mmol) of 1-decanethiol was added. The mixture was stirred for 20min. and freshly prepared aqueous solution of sodium borohydride (1.40 g, 30 mmol in 10 ml of deionised H_2O) was added. The mixture was stirred for 3h and organic phase was separated, washed twice with water and concentrated to 5ml. Than 200ml of absolute alcohol was added and the mixture was kept for 10h in 4°C. 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, nanoparticles were dissolved in 20 ml of toluene and centrifuged for 5 minutes. 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 1,5 nm.

Ligand exchange reaction was performed according to Murray reaction [2], with some modification depending on solubility of some secondary ligands (L). For the ligand exchange reaction the same conditions as: concentration, time of reaction temperature and ratio of primary gold nanoparticles to secondary ligands, were applied. Into the solution of 50mg of primary coated gold nanoparticles in 6-10ml of toluene 65mg of thiol ligand dissolved in ca. 10ml of toluene was added. The mixture was stirred at room temperature for 72h. No precipitation or aggregation were observed. Next the solution was concentrated to 2ml and sonicated for 1min. Into the black, gel-like mixture 50ml of acetone was added. After 6h the precipitate was centrifuged (13000 rpm, 15 min). The residue was dissolved in 2ml of toluene, sonicated for 10min., precipitated with hot acetone and immediately centrifuged (13000 rpm, 15 min). The purification was controlled by TLC and proceeded until the final hybride was absolutely pure. The purity of the final compounds was determined by TLC and ^{1}H NMR spectra. The NMR spectra and elemental analysis confirms an exchange of primary ligands to mesogenic molecules in the nanoparticle covering layer with ratio 2:1.

Table 2. Elemental analysis for chosen hybrid materials

Compound	%C	%H
AuL1-2	28.47	4.02
AuL2-2	36.3	5.08
AuL3-2	35.81	4.56

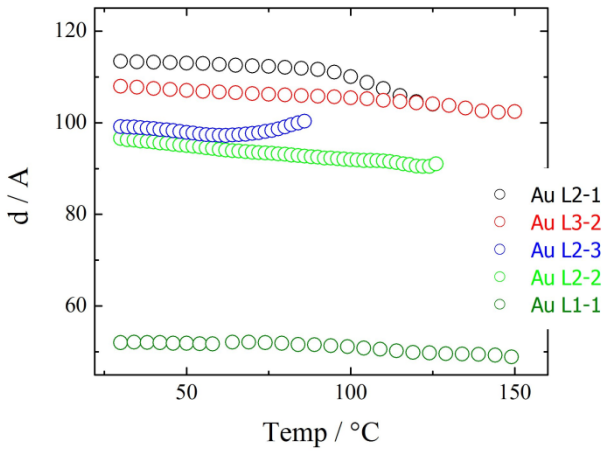


Figure 1. Layer spacing dependence on temperature for lamellar phases of studied hybrid materials.

References

1. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman*J. Chem. Soc., Chem. Commun.*, 1994, 801.
2. R. S. Ingram, M. J. Hostetler, R. and W. Murray, *J. Am. Chem. Soc.* 1996, **118**, 4214