Gold nanoparticles grafted with chemically incompatible ligands

Joanna M. Wolska, Aleksandra Błażejewska, Martyna Tupikowska, Damian Pociecha and Ewa Górecka

1. 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 Bruker AVANCE 300MHz. 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 (1.7 ppm) 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 free ligand molecules (molecules not attached to gold core give sharp signals). TEM images were taken using Zeiss Libra 120 microscope.

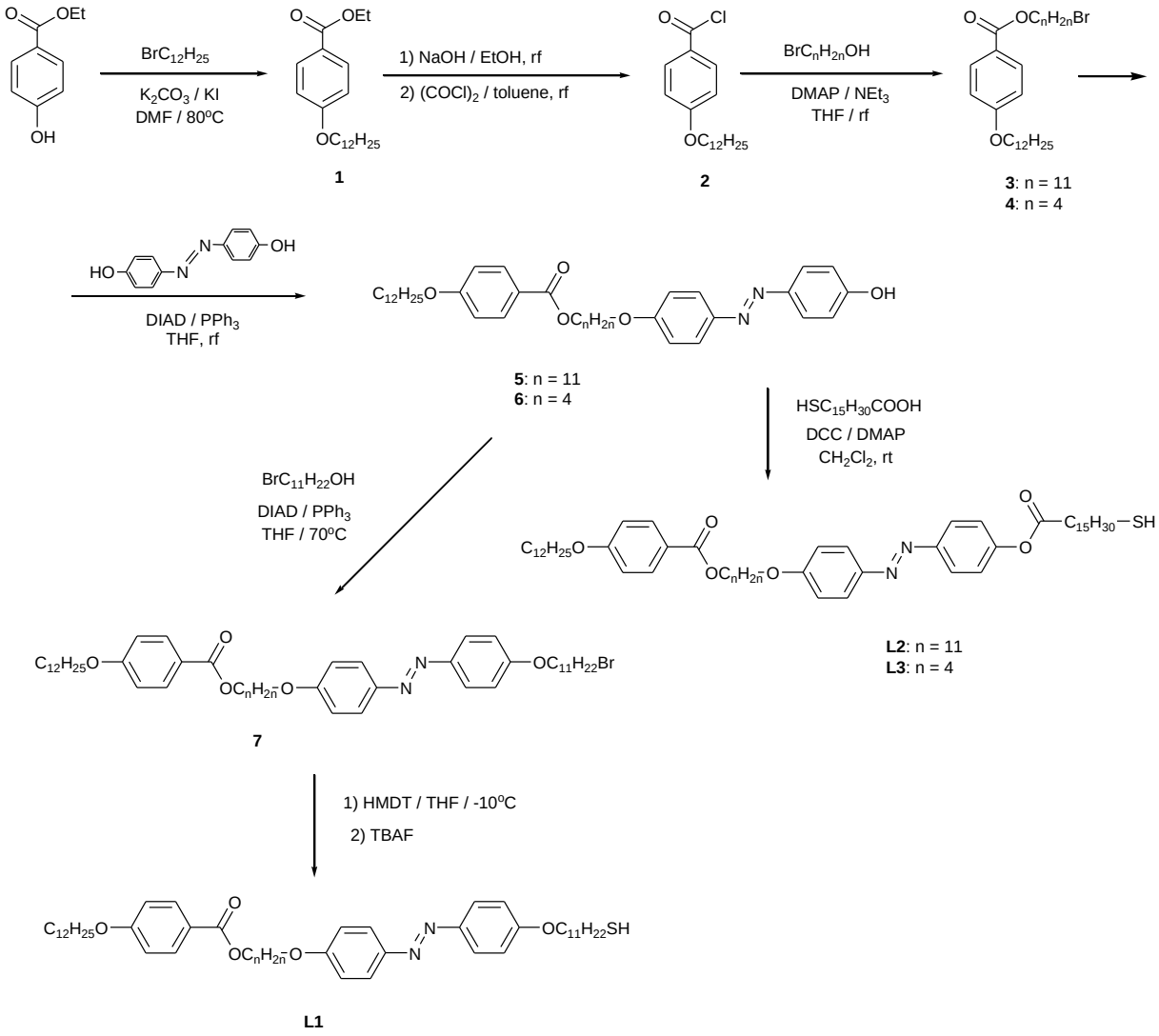
Presented reactions were carried out under an argon atmosphere with using a magnetic stirring hotplate. All products were purified by column chromatography with Merck silica gel 60 (230-400 mesh). Analytical thin-layer chromatography (TLC) was performed using Silica Gel 60 Å F254 (Merck) pre-coated plastic/alumina 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: dichloromethane, chloroform, hexane, toluene, tetrahydrofuran, N,N-dimethyloformamide, trimethylamine, dimethyl sulfoxide, ethanol and methanol. As a substrates were used Sigma-Aldrich or TCI products without further purification. Presented yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.

2. Synthesis and characterization of promesogenic ligands

Following abbreviations are used:
DCC - N,N′-Dicyclohexylcarbodiimide
DIAD - Diisopropylazodicarboxylate
DMAP - 4-Dimethylaminopyridine
HMDT - Hexamethyldisilthiane

TBAF - Tetra-n-butylammonium fluoride

The general procedure of obtaining ligands L1-L3 and L4 are presented on Scheme 1 and Scheme 2 respectively. The preparative part for ligands is presented on example of compounds containing 11 carbons in internal flexible chain (n=11).



Scheme 1. Synthesis of ligands L1, L2 and L3

Synthesis of the 4-dodecyloxybenzoic acid ethyl ester (1):

Into the solution of 10g (0,06mol) of ethyl 4-hydroxybenzoate in 300ml of DMF a 12,5g (0,09mol)of anhydrous K_2CO_3 and 15g (0,09mol)of KI was added. Next 17,9g (0,07mol)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 from ethanol. Product was purified by column chromatography with chloroform as an eluent to yield 20,6 g (90%) of white solid.

^{1}H NMR: (300MHz, $CDCl_3$) δ: 7,98 (d, 2H, J = 8,7Hz); 6,91 (d, 2H, J = 8,7 Hz); 4.38 (2H, q, J=7.2Hz); 4,00 (t, 2H, J = 6,60 Hz); 1,8 – 1,68 (m, 2H); 1,51 – 1,42 (m, 2H); 1.39 (3H, t, J=7.2Hz); 1,35 – 1,18 (m, 16H); 0,88 (t, 3H, J = 6,30 Hz)

Synthesis of the 4-dodecyloxybenzoyl chloride (2):

Into the mixture of 15,8g (0,05mol) of compound **1** in 250ml of ethanol a 9,5g (0,23mol)of NaOH diluted in 10ml of distillate water was added in portions. The reaction mixture was stirred under reflux for 12h. After cooling the precipitate was filtrated and dried under vacuum for 24h to give a 12,5g (95%) of white solid. A 5,9g (0,018mol) of dry product was dissolved in unhydrous toluene. Into the mixture 10ml (0.12mol) 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 5,3g (100%).

Synthesis of the 4-dodecyloxybenzoic acid 11-bromoundecyl ester (3):

Into the solution of 2g (8,1mmol) of the 11-bromoundecan-1-ol in 10ml of dry THF 2ml of dry trimethylamine and catalytic amount of DMAP was added. Next the solution of 3,16g (9,8mmol)of compound **2** in 10ml of THF 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: toluene) and recrystallized with ethanol to yield 2,6 g (60%) of white solid.

^{1}H NMR: (300MHz, $CDCl_3$) δ: 7,98 (d, 2H, J = 8,71Hz); 6,90 (d, 2H, J = 8,71 Hz); 4,28 (t, 2H, J = 6,60 Hz); 4,00 (t, 2H, J = 6,60 Hz); 3,53 (t, 2H, J = 6,60 Hz); 1,88 – 1,68 (m, 6H); 1,51 – 1,38 (m, 6H); 1,38 – 1,18 (m, 26H); 0,88 (t, 3H, J = 6,30 Hz)

NMR for the 4-dodecyloxybenzoic acid 4-bromobutyl ester (4):

^{1}H NMR: (300MHz, $CDCl_3$) δ: 7,97 (d, 2H, J = 9,01 Hz); 6,90 (d, 2H, J = 9,01 Hz); 4,33 (t, 2H, J = 6,00 Hz); 4,00 (t, 2H, J = 6,60 Hz); 3,61 (t, 2H, J = 6,00 Hz); 2,01 – 1,88 (m, 4H); 1,87 – 1,72 (m, 2H); 1,51 – 1,39 (m, 2H); 1,39 – 1,18 (m, 16H); 0,88 (t, 3H, J = 6,30 Hz)

Synthesis of the 4-dodecyloxybenzoic acid 4-[4-(4-hydroxy-phenylazo)-phenoxy]- undecyl ester (5):

Into the solution of 2g (9,4mmol)of 4 4'-dihydroxyazobenzene in 150ml of DMF 1,76g (12,8mmol)of K_2CO_3 and 2,12g (12,8mmol) KI were added. Next 2,29g (4,3mmol)of compound **3** diluted in DMF was added dropwise. Reaction mixture was stirred at 80°C for 10h. After cooling down the mixture was poured into the water with ice. The precipitate was filtrated and dried under the vacuum. The crude product was purified by column chromatography (chloroform) to give a 1,3g (45%) of yellow solid.

^{1}H NMR: (300MHz, $CDCl_3$) δ: 7,98 (d, 2H, J = 9,01 Hz); 7,91 – 7,78 (m, 4H); 7,04 – 6,83 (m, 6H); 4,29 (t, 2H, J = 6,60 Hz); 4,00 (q, 4H, J = 6,60 Hz); 1,88 – 1,68 (m, 6H); 1,53 – 1,39 (m, 6H); 1,39 – 1,18 (m, 26H); 0,88 (t, 3H, J = 6,30 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ: 166,74; 162,93; 161,20; 157,95; 147,12; 146,82; 131,53; 124,5; 124,31; 122,55; 115,74; 114,65; 114,04; 68,31; 68,20; 64,90; 31,90; 29,63; 29.61; 29.57; 29.53; 29,48; 29,33; 29,26; 29,19; 29,09; 28,75; 26,02; 25.99; 25,96; 22,67; 14,11

NMR for the **4-dodecyloxybenzoic acid 11-[4-(4-hydroxyphenylazo)-phenoxy]-butyl ester** (**6**)

^{1}H NMR: (300MHz, $CDCl_3$) δ: 7,97 (d, 2H, J = 9,01 Hz); 7,91 -7,78 (m, 4H); 7,05 – 6,81 (m, 6H); 4,45 – 4,33 (m, 2H); 4,18 – 4,05 m, 2H); 3,98 (t, 2H, J = 6,60 Hz); 2,06 – 1,92 (m, 4H); 1,85 – 1,7 (m, 2H); 1,5 – 1,38 (m, 2H);1,38 – 1,18 (m, 16H); 0,88 (t, 3H, J = 6,60 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ: 166,65; 163,03; 160,93; 157,98; 147,01; 146.95; 131,55; 124,54; 124,35; 122,27; 121,49; 117,33; 116,47; 115,74; 114,66; 114,08; 68,22; 67,56; 64,33; 31,89; 29,63; 29.61; 29.57;29.53; 29,33; 29,08; 25,98; 25.95; 25,49; 22,67; 14,11

Synthesis of the 4-dodecyloxybenzoic acid 11-{4-[4-(11-bromoundecyloxy)-phenylazo]-phenoxy}-undecyl ester (7):

Into the 0,5g (0,74mmol)of compound **5**, 0,22g (0,89mmol)11-bromoundecan-1-ol and 0,21g (0,82mmol)of triphenylphosphine dissolved in 100ml of dry THF cooled to the 0°C 0,16ml (0,82mmol) 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 0,57g (85%).

^{1}H NMR: (300MHz, $CDCl_3$) δ: 7,98 (d, 2H, J = 9,01 Hz); 7,86 (d, 4H, J = 9,01 Hz); 6,98 (d, 4H, J = 9,01 Hz); 6,89 (d, 2H, J = 9,01 Hz); 4,28 (t, 2H, J = 6,60 Hz); 4,07 – 3,94 (m, 6H); 3,40 (t, 2H, J = 6,60 Hz); 1,91 – 1,68 (m, 10H); 1,54 – 1,39 (m, 10 H); 1,39 – 1,18 (m, 36H); 0,88 (t, 3H, J = 6,60 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ: 166,49; 162,85; 161,14; 161.13; 146,91; 131,48; 124,27; 122,66; 114,63; 113,99; 68,28; 68,18; 64,76; 34,03; 32,81; 31,90; 29,63; 29.61; 29.57; 29.53; 29.48; 29.43; 29.3929.33; 29.26; 29.19; 29,10; 28,76; 28.74; 28,15;26. 03; 25,99; 25.96; 22,67; 14,11

Synthesis of the 4-dodecylox-benzoic acid 11-{4-[4-(11-mercaptoundecyloxy)-phenylazo]-phenoxy}-undecyl ester (L1):

Into a cooled solution of 0,484g (0,535 mmol) of the compound **7** in 10ml of anhydrous THF 134,5µl (0,642 mmol) of HMDT was added. After 5 minutes of stirring 0,154g (0,589mmol, 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 NH_4Cl in water. The crude product was dried over anhydrous $MgSO_4$ and purified by column chromatography (toluene) to give 0,53g (65%), as a yellow solid.

^{1}H NMR: (300MHz, $CDCl_3$) δ: 7,98 (d, 2H, J = 9,01 Hz); 7,86 (d, 4H, J = 8,71 Hz); 6,98 (d, 4H, J = 9,01 Hz); 6,90 (d, 2H, J = 9,01 Hz); 4,28 (t, 2H, J = 6,60 Hz); 4,09 – 3,95 (m, 6H); 2,52 (q, 2H, J = 7,51 Hz); 1,88 – 1,69 (m, 8H); 1,69 – 1,55 (m, 2H); 1,53 – 1,42 (m, 10H); 1,42 – 1,17 (m, 36H); 0,88 (t, 3H, J = 6,30 Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ 166.66;163.01;161.29, 147.07; 131.63; 124.42; 122.82; 114.79; 114.16; 68.45; 68.34; 64.92; 32.19; 32.05; 29.77; 29.72; 29.69; 29.63; 29.5; 29.42; 29.35; 29.25; 29.2; 28.92; 28.51; 26.16; 25.12; 24.8; 22.82; 14.26;

Synthesis of the 4-dodecyloxybenzoic acid 11-{4-[4-(16-mercaptohexadecanoyloxy)-phenylazo]-phenoxy}-undecyl ester (L2):

0,2g (0,298mmol) of compound **5**, 0,095g (0,3278mmol) of 16-mercaptohexadecanoic acid, (0,074g, 0,3576mmol) of DCC and catalytic amount of DMAP were dissolved in 15ml of anhydrous CH_2Cl_2. Reaction mixture was stirred at room for 24h. The precipitate was filtrated and the crude product was purified by column chromatography (hexane : dichloromethane 3:7) to give a 155mg (55%) of yellow solid.

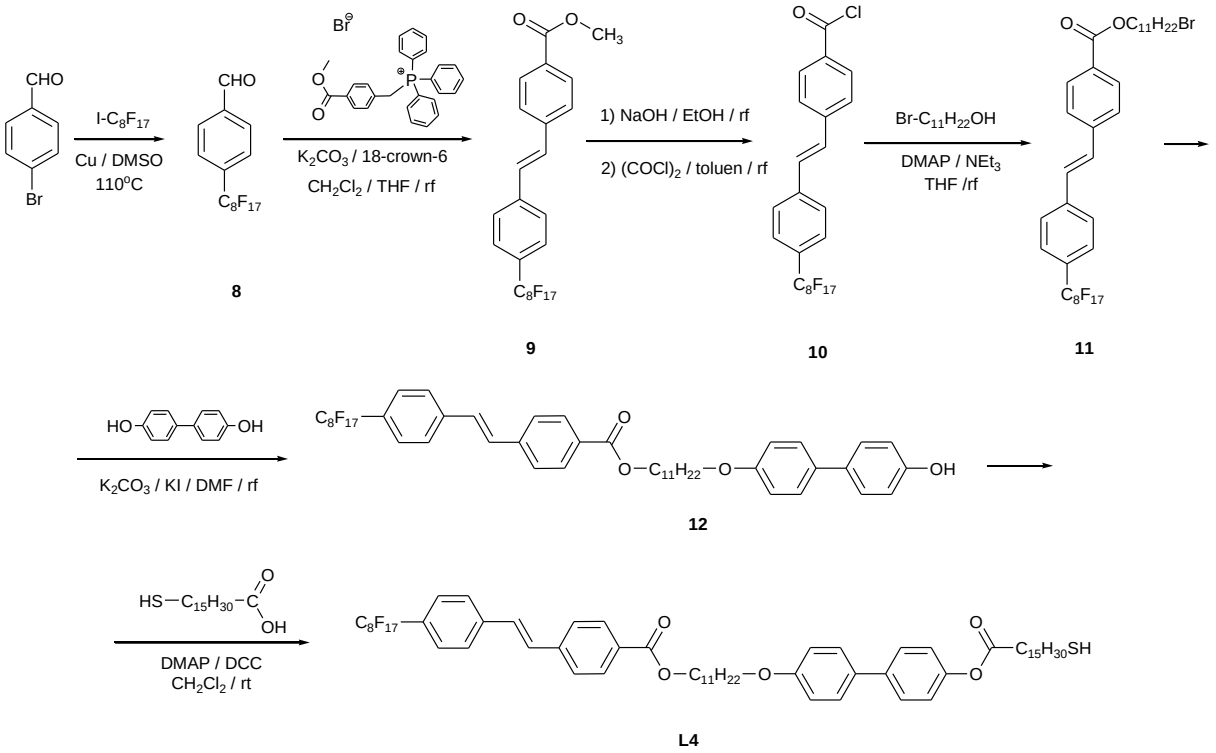
^{1}H NMR: (300MHz, $CDCl_3$) δ: 7,98 (d, 2H, J = 8,71 Hz); 7,94 – 7,84 (m, 4H); 7,21 (d, 2H, J = 9,01 Hz); 7,00 (d, 2H, J = 9,01 Hz); 6,90 (d, 2H, J = 8,71 Hz); 4,28 (t, 2H, J = 6,60 Hz); 4,10 – 3,94 (m, 4H); 2,64 – 2,46 (m, 4H); 1,89 – 1,69 (m, 8H); 1,69 – 1,57 (m, 2H); 1,51 – 1,31 (m, 8H); 1,31 – 1,13 (m, 46H); 0,96 – 0,79 (m, 3H); ^{13}C NMR (75MHz, $CDCl_3$) δ: 172.19; 166.56;163.13;161.65, 152.42; 150.45; 147.11; 131.7; 124.45; 122.52; 122.27;

114.85; 114.2; 68.35; 67.82; 64.36; 34.57; 34.21; 32.05; 29.78; 29.72; 29.69; 29.66; 29.59; 29.48; 29.39; 29.24; 28.9; 28.51; 26.16; 26.13; 25.65; 25.05; 24.81; 22.86; 14.25;

Synthesis of the 4-dodecyloxybenzoic acid 11-{4-[4-(16-mercaptohexadecanoyloxy)-phenylazo]-phenoxy}-butyl ester (L3):

Synthesis procedure, conditions and molar ratio leading to the compound **L3** were presented for compound **L2**. Yield 60%.

^{1}H NMR: (300MHz, $CDCl_3$) δ:7,98 (d, 2H, J = 9,01 Hz); 7,93 – 7,84 (m, 4H); 7,22 (d, 2H, J = 8,71 Hz); 7,00 (d, 2H, J = 9,01 Hz); 6,89 (d, 2H, J = 9,01 Hz); 4,44 – 4,3 (m, 2H); 4,17 – 4,08 (m, 2H); 3,98 (t, 2H, J = 6,60 Hz); 2,63 – 2,46 (m, 4H); 2,05 – 1,94 (m, 4H); 1,87 – 1,71 (m, 4H); 1,70 – 1,52 (m, 6H); 1,50 – 1,13 (m, 36H); 0,94 – 0,8 (m, 3H); ^{13}C NMR (75MHz, $CDCl_3$) δ: 172.18 166.56;163.12;161.62, 152.4; 150.44; 147.01; 131.67; 124.91; 124.45; 123.81; 122.52; 114.81; 114.02; 68.53; 67.8; 64.34; 34.58; 34.2; 32.05; 29.77; 29.72; 29.69; 29.66; 29.59; 29.49; 29.40; 29.24; 28.52; 26.13; 25.66; 25.04; 24.8; 22.82; 14.26;



Scheme 2. Synthesis of the ligand L4

Synthesis of the 4- perfluorooctylbenzaldehyde (8):

Into the solution of 30g (0,16mol) of 4-bromobenzaldehyde in 100ml of DMSO a 51,5g (0,81mol)of copper powder and 115g (0,21mol) of heptadecafluoro-1-iodooctane was added. The mixture was stirred in temperature of 110°C for 12h. After cooling worm mixture was filtered and the filtrate was poured into the 300ml of cold water. The precipitate was filtrated and recrystallized from hexane several times to yield 44g (65%) of white solid. ^{1}H NMR: (300MHz, $CDCl_3$) δ: 10.12 (1H; s); 8.05 (2H; d; J=8.7Hz); 7.79 (2H; d; J=8,7Hz); ^{13}C NMR (75MHz, $CDCl_3$) δ: 191.06; 138.78; 134.31 (t, J=24Hz); 129.64; 127.75 (t; J=6.41Hz); 119.04; 118.87; 115.45; 115.22; 111.28; 110.79; 108.13; 107.16; ^{19}F NMR (282MHz, $CDCl_3$) δ: -81.01 (3F; t; J=7.9Hz); -111.37 (2F; t; J=13.6Hz); -121.31 (2F, m); -121.84 and -122.02 (6F, m); -122.81 (2F, m); -126.31 (2F; m)

Synthesis of the 4-[(E)-2-(4-perfluorooctyl-phenyl)-vinyl]-benzoic acid methyl ester (9):

Into the solution of 23,4g (47,7mmol) of (4-methoxycarbonyl-benzyl)-triphenylphosphonium bromide in 170 ml of dichloromethane and 200 ml of tetrahydrofuran 9,21g (66,8mmol) of anhydrous potassium carbonate and catalytic amount of 18-crown-6 were added in one portion. After 15 minutes to the vigorously stirred mixture a 10g (19mmol) of compound **8**, diluted in 30ml of dichloromethane, 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 chloroform) to give 8,7 g (70%) of white solid.

^{1}H NMR: (300MHz, $CDCl_3$) δ: 8.05 (2H; d; J=8.7Hz); 7.66 – 7.45 (6H; m); 7.27 – 7.24 (2H; m); 3,91 (3H, s); ^{13}C NMR (75MHz, $CDCl_3$) δ: 166.3; 140.87; 140.43; 130.34; 130.06; 130.0; 129.39; 128.14 (t; J=24Hz); 127.3 (t; J=6.4Hz); 126.75; 126.59; 119.04; 118.87; 115.45; 115.22; 111.28; 110.79; 108.13; 107.16; 51.06

^{19}F NMR (282MHz, $CDCl_3$) δ: -81.69 (3F; t; J=7.9Hz); -110.62 (2F; t; J=14Hz); -121.19 (2F, m); -121.81 (6F, m); -122.69 (2F, m); -126.11 (2F; m)

Synthesis of the 4-[(E)-2-(4-perfluorooctyl-phenyl)-vinyl]-benzoyl chloride (10):

Into the mixture of 5 g (7,62mmol) of compound **9** in 150ml of ethanol a 6g (0.16mol) of NaOH diluted in 10ml of distilled water was added in portions. The reaction mixture was stirred under reflux for 12h. After cooling to the room temperature the precipitate was filtered and dried under vacuum for 24h. A 3,88g (5,95mmol) of dry product was dissolved in anhydrous toluene. Into the mixture 10ml (0.056mol) 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 3,86g (100%).

Synthesis of the 4-[(E)-2-(4-perfluorooctyl-phenyl)-vinyl]- benzoic acid 11-bromoundecyl ester (11):

Into the solution of 0,91g (3,63mmol) of the in 50ml of dry THF 2ml of dry trimethylamine and catalytic amount of DMAP was added. Next the solution of 2g (3mmol) of chloride derivative **10** in 25ml of dry THF was added dropwise. The mixture was stirred at 75°C for 12h. The solvent was removed and the residue was purified by column chromatography (eluent: $CHCl_3$) to yield 1,94 g (65%) of white solid.

^{1}H NMR: (300MHz, $CDCl_3$) δ: 8.05 (2H; d; J=8.7Hz); 7.67 – 7.45 (6H; m); 7.28 – 7.23 (2H; m); 4.32 (2H; t; J=6.6Hz); 3.52 (2H; t; J=6.9Hz); 1.92 – 1.79 (4H; m); 1.52 – 1.36 (4H, m); 1.36 – 1.21 (10H; m); ^{13}C NMR (75MHz, $CDCl_3$) δ: 166.3; 140.87; 140.43; 130.34; 130.06; 130.0; 129.39; 128.14 (t; J=24Hz); 127.3 (t; J=6.4Hz); 126.75; 126.59; 65.19;45.16; 34.01; 32.81; 32.63; 29.46; 29.42; 29.41; 29.3929.24; 28.87; 28.74; 8.71; 28.15; 26.87; 26.02; ^{19}F NMR (282MHz, $CDCl_3$) δ: -81.78 (3F; t; J=7.9Hz); -110.69 (2F; t; J=14Hz); -121.21 (2F, m); -121.83 (6F, m); -122.7 (2F, m); -126.11 (2F; m)

Synthesis of the 4-[(E)-2-(4-perfluorooctyl-phenyl)-vinyl]- benzoic acid 11-(4'-hydroxy-biphenyl-4-yloxy)-undecyl ester (12):

Into the solution of 0,9g (4,86 mmol) of 4,4'-biphenol in 100ml of DMF 0,8g (5,82 mmol) of K_2CO_3 and 0,97g (5,82 mmol) KI were added. Next 1,7g (1,94 mmol) of compound 11 diluted in mixture of DMF was added dropwise. Reaction mixture was stirred at 80°C for 12h. After cooling down the mixture was poured into the water

with ice. The precipitate was filtrated and dried under the vacuum. The crude product was purified by column chromatography (toluene) to give a 1,16g (65%) of white solid.

^{1}H NMR: (500MHz, THF-d) δ: 8.02 (2H; d; J=8.5Hz); 7.80 (2H; d; J=8.5Hz); 7.73 – 7.62 (4H; m); 7.46 – 7.38 (4H; m); 7.34 (2H; d; J=8.5Hz); 6.89 (2H; d; J=8.5Hz); 6.76 (2H; d; J=8.5); 4.29 (2H; t; J=6.5Hz); 3.96 (2H; t; J=6.5Hz); 1.82 – 1.75 (4H; m); 1.53 – 1.43 (4H, m); 1.43 – 1.31 (10H; m); ^{13}C NMR (125MHz, THF-d) δ: 166.0; 158.96; 157.57; 142.12; 141.97; 134.30; 132.77; 131.35; 130.84; 130.47; 129.99; 127.95; 127.88; 127.74; 127.35; 116.07; 115.14; 86.33; 67.73; 65.33; 30.37; 30.31; 30.20; 30.14; 30.09; 29.75; 29.55; 26.86; 26.82; 25.61; ^{19}F NMR (470MHz, THF-d) δ: -81.72 (3F; t; J=8.0Hz); -110.96 (2F; t; J=14.6Hz); -121.73 (2F, m); -122.33 and 122. 43 (6F, m); -123.25 (2F, m); -126.75 (2F; m)

Synthesis of the 4-[(E)-2-(4-perfluorooctyl-phenyl)-vinyl]- benzoic acid 11-[4'-(16-mercapto-hexadecanoyloxy)-biphenyl-4-yloxy]-undecyl ester (L4):

Synthesis procedure, conditions and molar ratio leading to the compound **L4** were presented for compound **L2**. The product was purified by column chromatography (toluene) to give a 113mg (60%) of white solid.

^{1}H NMR: (300MHz, $CDCl_3$) δ: 7.97 (2H; d; J=8.4Hz); 7.59 – 7.47 (6H; m); 7.43 (3H; d; J=8.7Hz); 7.38 (2H; d; J=8.7Hz m); 7.19 (2H; m); 7.03 (2H; d; J=8.7Hz); 6.87 (2H; d; J=9);4.32 (2H; t; J=6.6Hz); 3.99 (2H; t; J=6.6Hz); 2.62 – 2.48 (4H; m); 1.8 – 1.65 (6H; m); 1.65 – 1.52 (6H, m); 1.51 – 1.17 (34H; m);

^{13}C NMR (75MHz, $CDCl_3$) δ: 166.01; 157.57; 154.46; 142.23; 142.02; 134.32; 132.75; 131.4; 130.84; 130.39; 129.99; 127.95; 127.88; 127.74; 127.35; 116.07; 115.14; 86.33; 67.73; 65.33; 30.37; 30.31; 30.20; 30.14; 30.09; 29.75; 29.55; 26.86; 26.82; 25.61;

^{19}F NMR (282MHz, $CDCl_3$) δ: -80.73 (3F; t; J=8.0Hz); -110.38 (2F; t; J=14.6Hz); -120.91 (2F, m); -121.57 (6F, m); -122.43 (2F, m); -125.85 (2F; m)

3. Additional results

Thermogravimetric analysis of H5 material (Fig. S1) revealed that ca. 63% mass of the hybrid particle can be ascribed to the organic matter. Two regions of mass loss were observed, below and above 250 °C, coming from dodecanethiol and (pro)mesogenic ligands, respectively, as previously shown [W. Lewandowski, K. Jatczak, D. Pociecha, and J. Mieczkowski, *Langmuir*, 2013, **29**, 3404]. The mass losses were 13% and 50%, which corresponds to 146 dodecanethiol molecules and 90 to 135 (pro)mesogenic ligands (if we assume L4 or L3 is exclusively present on the Au surface, respectively). A 1:1 ratio between the (pro)mesogenic ligands can be assumed based on the initial concentrations of these ligands in the reaction mixture, as well as similar chemical structure at the molecular end by which these molecules bind to the surface of nanoparticles. With this assumption it can be calculated that 54 molecules of each (pro)mesogenic ligand are attached to a single nanoparticle.

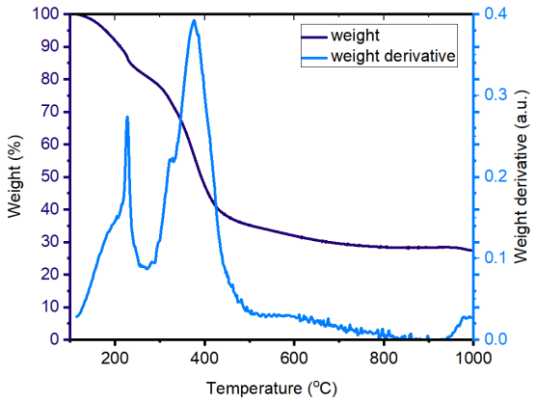


Figure S1. Thermogravimetric curves (weight loss and its derivative) for H5 hybrid material.

TEM imaging was performed for hybrid H5 material. Samples were dropcasted onto carbon coated TEM grids and heated to 150 deg. C; afterwards they were quenched to room temperature. Analysis of the images (Fig. S2) revealed an anisotropic arrangement of NPs, lines appearing in the images can be ascribed to vertically oriented NP layers. An inter-layer distance of ca. 6.5 nm was commonly found in the sample, which correlates to the distance between metallic core rich sublayers determined for H5 samples by x-ray diffraction.

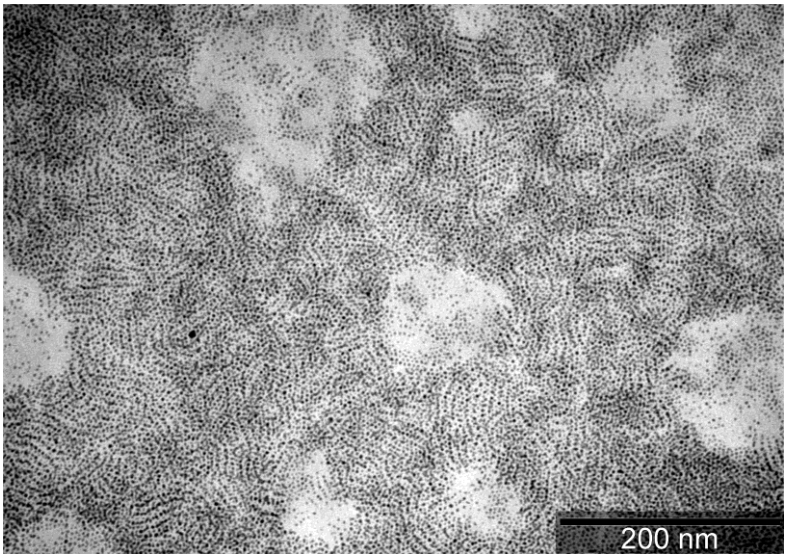


Figure S2. TEM image of hybrid H5 sample.