

Control of sample alignment mode for hybrid lamellar systems based on gold nanoparticles

5 **Joanna M. Wolska,* Damian Pocięcha, Jozef Mieczkowski and Ewa Gorecka**

Experimental section

Substrates and solvents were obtained from Sigma-Aldrich. Substrates were used without further purification; solvents were dried over activated 3Å molecular sieves for 24h. 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 vapour. Presented yields refer to chromatographically and spectroscopically (¹H NMR) homogeneous materials.

The ¹H NMR and ¹³C 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 (CDCl₃, 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: H₂O (1.7ppm) and CHCl₃ (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).

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 glass, polymer tapes and metal with the aid of the shearing plates each time with the same pressure and the same direction at different temperatures from 30°C to 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.

IR spectra were recorded on a Nicolet 6700FT-IR spectrometer. The sample was placed on ZnSe plate, aligned by shearing plates 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.

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Synthesis and characterization of promesogenic ligands

Following abbreviations are used:

DIAD - Diisopropylazodicarboxylate

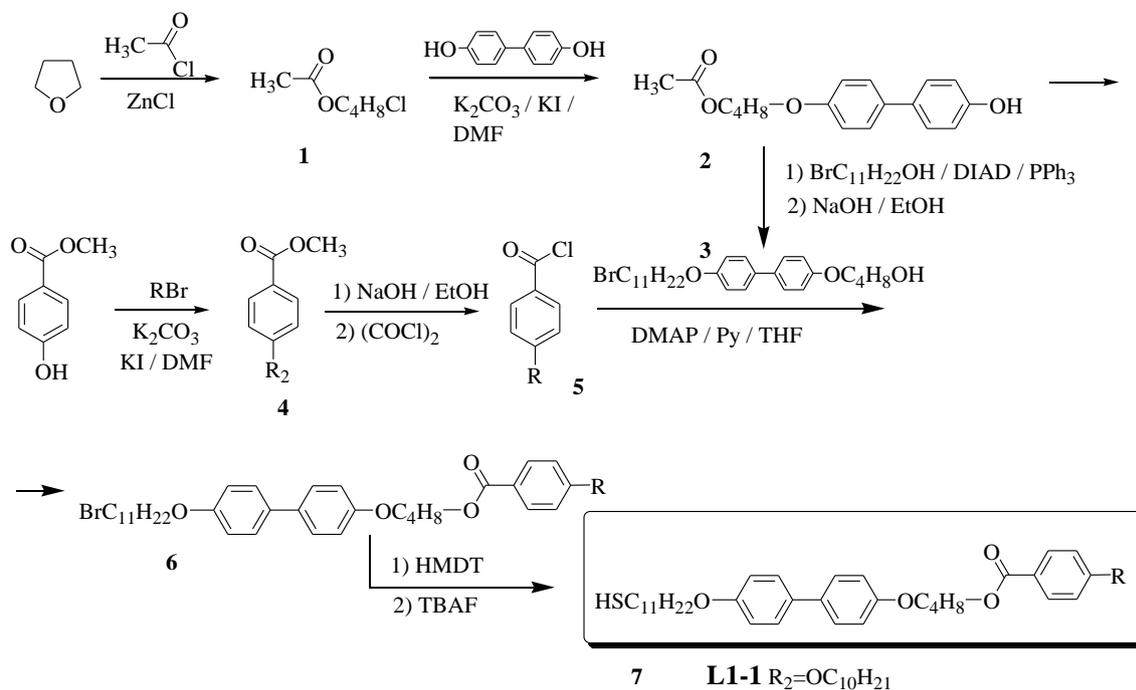
DMAP - 4-Dimethylaminopyridine

10 HMDT - Hexamethyldisilthiane

TBAF - Tetra-n-butylammonium fluoride

The ligands were obtained in the synthetic path presented in Scheme 1. Internal and external parts of the molecules were obtained simultaneously. Tetrahydrofuran was converted to the chloroester and connected to the biphenol via Williamson reaction. Next, into the free hydroxyl group of biphenyl the long spacer was attached via Mitsunobu reaction and the ester group was hydrolyzed. The external moiety was obtained from appropriate methyl hydroxybenzoate via Williamson reaction hydrolyzation and chlorination. Both, external and internal moieties was connected via eteryfication reaction with presence of DMAP and pyridine. Obtained bromide was transformed into thiol derivative with HMDT.

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Scheme 1. Synthetic cycle of the ligands presented for series 1 (L1). 7 – compound **L1-1** ($R_2=OC_{10}H_{21}$) in a main text

Synthesis of 4-chlorobutyl acetate (1)

Into the cooled mixture of 33.2g (420mmol) acetyl chloride in 41g (579mmol) tetrahydrofuran 1g (7mmol) of zinc chloride was added. The mixture was cooled in a water bath until the termination of the exothermic process and refluxed for 15 minutes. Next 150ml of water was added. The organic layer was separated and the water layer was extracted with toluene (3x30ml). The organic layers were washed with saturated solution of NaHCO₃ and dried by anhydrous CaCl₂. The solvent was evaporated to dryness and the product was distilled under reduced pressure (89 – 93°C / 20mmHg) affording pure product (50.5 g) with 80% yield.

Elemental analysis for C₆H₁₁ClO₂ (M = 150.0): calc. C 47.85, H 7.36; found C 47.82, H 7.32%; ¹H NMR δH (CDCl₃): 4.10 (2H, t, J~6.1Hz), 3.58 (2H, t, J~6.3Hz), 2.06 (3H, s), 1.95 – 1.70 (4H, m)

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Synthesis of 4-[(4'-hydroxybiphenyl-4-yl)oxy]butyl acetate (2)

Into the solution of 21.7g (0.124mol) of 4,4'-dihydroxybiphenyl in 500ml of DMF a 13.75g (0.1mol) of anhydrous K₂CO₃ and 12.4g (0.07mol) of KI was added. Next 7.5g (0.049mol) of **1** was added. The mixture was vigorously stirred in temperature of 80°C for 24h. After cooling to the room temperature the mixture was poured into the 1000ml of cold water with ice. The precipitate was filtered, recrystallized twice from methanol and chromatographed on silica gel (eluent: CHCl₃ / 2% methanol), affording **2** as a white solid (11.2g) with 75% yield.

Elemental analysis for C₁₈H₂₀O₄ (M = 300.1): calc. C 71.98, H 6.71%; found C 71.82, H 6.53%; ¹H NMR δH (CDCl₃): 7.52 – 7.36 (4H, m), 7.00 – 6.82 (4H, m), 5.08 (1H, br-s), 4.25–4.11 (2H, m), 4.1–3.92 (2H, m), 2.06 (3H, s), 2.00–1.70 (4H, m)

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Synthesis of 4-({4'-[(11-bromoundecyl)oxy]biphenyl-4-yl}oxy)butan-1-ol (3)

5.71g (21.8mmol) of triphenylphosphine and 6.38g (25.4mmol) of 1-bromo-11-hydroxyundecane was added to 5.45g (18.2mmol) of compound **2** dissolved in dry THF. Mixture was stirred for 30 min and then 4.4ml (21.8mmol) of DIAD was added dropwise. The reaction was stirred at 70 °C for 16 hours after which the mixture was evaporated to dryness and chromatographed on silica gel eluted with dichloromethane. Next 7.5g (14mmol) of white solid was dissolved in THF and solution of 5.62g (140mmol) of NaOH in 30ml of ethanol was added. The mixture was stirred at room temp. for 24 hours. After cooling to the room temperature the precipitate was filtrated and recrystallized twice from methanol; the filtrate was concentrated, poured into the water, filtrated and chromatographed on silica gel eluted with solution of 2% methanol in dichloromethane affording pure product (6.5 g) with 95% yield.

Elemental analysis for C₂₇H₃₉BrO₃ (M = 490.2): calc. C 80.59, H 10.82; found C 80.27, H 10.63%; ¹H NMR δH (CDCl₃): 7.52 – 7.39 (4H, m), 7.00 – 6.87 (4H, m), 4.1 – 3.92 (4H, m), 3.81 – 3.67 (2H, m), 3.41 (2H, t, J ~ 6.8Hz), 2.00 – 1.68 (8H, m), 1.50 – 1.22 (14H, m), ¹³C NMR δC (CDCl₃): 158.43, 158.11, 133.76, 133.41,

127.89, 127.86, 114.92, 68.24, 68.01, 62.79, 45.41 34.29, 33.01, 32.83, 29.71, 29.64, 29.56, 29.49, 29.07, 28.94, 28.36, 27.07, 26.23, 26.03

Synthesis of methyl 4-dodecyloxybenzoate (4)

5 Into the solution of 15g (0.1mol) of methyl 4-hydroxybenzoate in 500ml of DMF a 17.7g (0.128mol) of anhydrous K_2CO_3 and 21.2g (0.128mol) of KI was added. Next 24.3g (0.128mol) 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 1000ml of cold water with ice. The precipitate was filtered and recrystallized twice from ethanol affording 26.5g (90.8%) of product was obtained as a white solid.

10 Elemental analysis for $C_{18}H_{28}O_3$ (M = 292.2): calc. C 73.93, H 9.65%; found C 73.64, H 9.45%; 1H NMR δH ($CDCl_3$): 7.97 (2H, d, J ~ 9.0Hz), 6.89 (2H, d, J ~ 9.0), 3.98 (2H, t, J ~ 6.3Hz), 3.87 (3H, s), 1.91 – 1.68 (2H, m), 1.54 – 1.16 (14H, m), 0.96 – 0.78 (3H, m)

Synthesis of 4-dodecyloxybenzoyl chloride (5)

15 Into the mixture of 26.5g (0.09mol) of compound **4** in 250ml of ethanol a 36.3g (0.9mol) of NaOH diluted in 50ml 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 to give a 27g (100%) of white solid. A 7g (23mmol) of dry product was suspended in anhydrous toluene and excess of oxalyl chloride (10.5 ml) was added dropwise. Reaction mixture was stirred under reflux for 8h. The cooled mixture
20 was filtered 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 4-({4'-[(11-bromoundecyl)oxy]biphenyl-4-yl}oxy)butyl 4-(dodecyloxy)benzoate (6)

Into the solution of 1.4g (2.84mmol) of compound **3** in 20ml of dry THF 2ml of dry pyridine and catalytic
25 amount of DMAP was added. Next the solution of 1.32g (4.54mmol) of compound **5** in 25ml of dry 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) affording 1.28 g (60%) of white solid.

Elemental analysis for $C_{44}H_{63}BrO_5$ (M = 750.4): calc. C 70.29, H 8.45%; found C 70.01, H 8.30%; 1H NMR δH ($CDCl_3$): 7.97 (2H, d, J ~ 9.0Hz), 7.46 (4H, d, J ~ 8.8Hz), 6.94 (4H, d, J ~ 8.8Hz), 6.88 (2H, d J ~ 9.0Hz), 4.43 –
30 4.30 (2H, m), 4.12 – 3.90 (6H, m), 3.52 (2H, t, J ~ 6.6Hz), 2.03 – 1.91 (4H, m), 1.88 – 1.68 (6H, m), 1.56 – 1.20 (28H, m), 0.95 – 0.81 (3H, m), ^{13}C NMR δC ($CDCl_3$): 166.67, 163.15, 158.43, 133.44, 131.72, 127.88, 122.62, 114.93, 114.25, 68.38, 68.23, 68.58, 64.52, 34.26, 32.16, 29.76, 29.58, 29.52, 29.28, 28.59, 26.27, 26.18, 24.88, 22.89, 14.33

Synthesis of 4-({4'-[(11-sulfanylundecyl)oxy]biphenyl-4-yl}oxy)butyl 4-(dodecyloxy)benzoate (7)

To a cooled solution of 0.82g (1.1mmol) of the compound **6** in 20ml of anhydrous THF 0.28ml (1.3mmol) of HMDT was added. After 5 minutes of stirring 1.31ml (1.2mmol, 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 CH₂Cl₂ was added and the solution was washed with 50ml of saturated solution of NH₄Cl in water. The crude product was dried over anhydrous MgSO₄ and purified by column chromatography (toluene/cyclohexane, 3:7) to give 0,58g (75%), as a white solid.

Elemental analysis for C₄₄H₆₄O₅S (M = 704.5): calc. C 74.96, H 9.15%; found C 74.67, H 8.92%; ¹H NMR δH (CDCl₃): 7.97 (2H, d, J ~ 9.0Hz), 7.46 (4H, d, J ~ 8.8Hz), 6.94 (4H, d, J ~ 8.8Hz), 6.73 (2H, d J ~ 9.0Hz), 4.43 – 4.31 (2H, m), 4.13 – 3.91 (6H, m), 2.52 (2H, q, J ~ 7.0Hz), 2.05 – 1.91 (4H, m), 1.89 – 1.70 (6H, m), 1.68 – 1.18 (28H, m), 0.95 – 0.82 (3H, m), ¹³C NMR δC (CDCl₃): 166.67, 163.15, 158.45, 133.46, 131.75, 127.88, 122.63, 114.93, 114.25, 68.40, 68.27, 68.59, 64.51, 34.26, 29.76, 29.59, 29.52, 29.28, 28.59, 26.27, 26.18, 25.77, 24.88, 22.89, 14.33

15 Synthesis of the gold nanoparticles

The gold nanoparticles coated with n-alkyl thiols as a *primary* grafting layer were synthesized according to modified Brust-Schiffrin method [1]. Into the aqueous solution of hydrogen tetrachloroaurate (90ml, 30mmol/dm³) a solution of methyltriethylammonium chloride (4,8g, 12mmol) in toluene was added and stirred vigorously for 2h. Next, toluene layer was separated and 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, cold H₂O) was added. The mixture was stirred for 3h and organic phase was separated, washed twice with deionised water and concentrated to 5ml. Than 200ml of absolute alcohol was added and the mixture was kept for 12h 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 ¹H NMR spectra and TLC. The SAXS measurements as well as direct microscopic TEM observations and analysis of broadening of x-ray diffraction signals coming from crystal lattice of gold consistently show that metal cluster diameter is close to 2 ± 0,5 nm.

30 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 (L) 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, sonicated for 1min. and

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 acetone and centrifuged (13000 rpm, 15 min). The purification was controlled by TLC and proceeded until the final hybride was absolutely pure. Finally, all samples were redissolved in toluen (20 ml) and centrifuged (13000 rpm, 5 min) to remove any aggregates. The purity of the final compounds was determined by TLC and ¹H NMR spectra. The NMR spectra and elemental analysis confirms an exchange of primary ligands to mesogenic molecules in the nanoparticle covering layer with ratio 1:1.

10 Table 1. Elemental analysis results for chosen compounds obtained in two consecutive experiments

Compound	%C	%H
AuL1-1	29.81; 30.02	4.00; 4.03
AuL2-1	34.94; 35.09	4.57; 4.37
AuL3-1	35.38; 35.19	4.98; 5.05

15 The ¹H NMR spectra indicated that the ligands are attached to the AuNPs. The signals from the ligands attached to the metal are broad (Fig. 1b) compared to the same signals of the free ligands (Fig. 1a). This is a clear signature of the grafting of ligands on AuNP surfaces; no free ligands were detected in final hybrides.

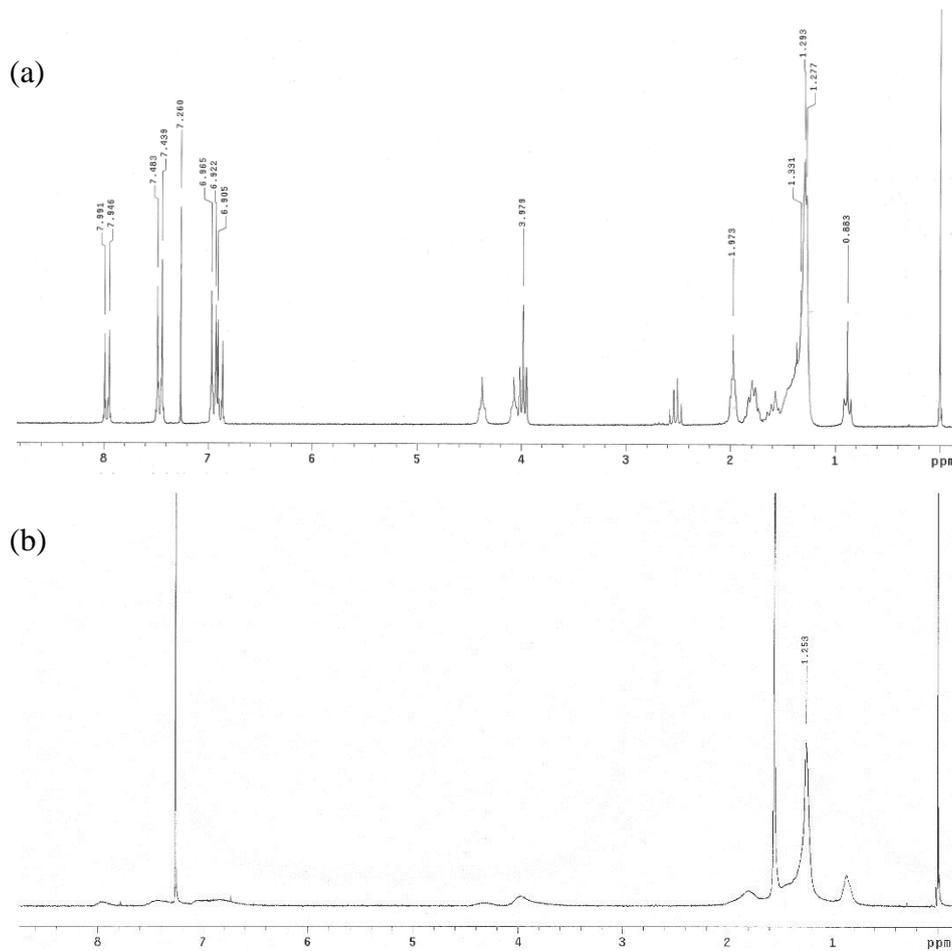
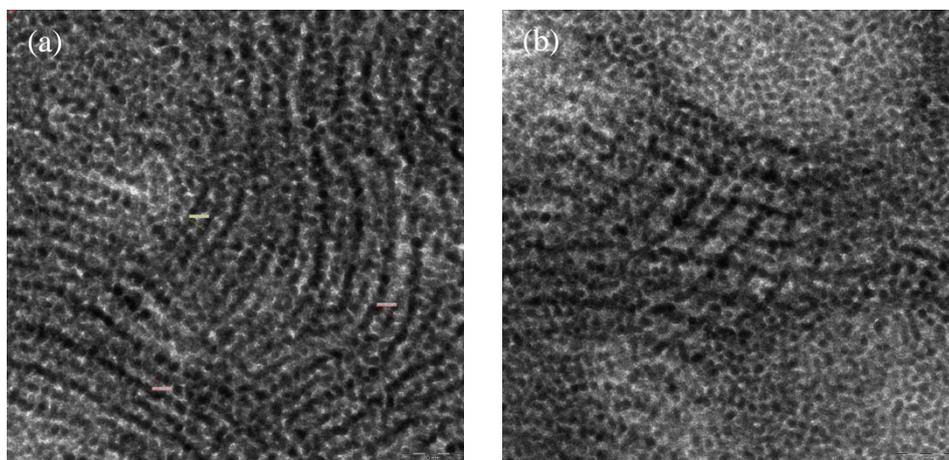


Fig. 1. ^1H NMR for compounds: a) ligand L2-2 b) hybrid AuL2-2

5 TEM analysis

AuNPs exhibit the tendency to form lamellar structures; the inlayer and interlayer distance values observed by TEM imaging correspond well to those obtained from XRD studies.



10 Fig. 2 TEM images of gold nanoparticles thermally annealed: a) AuL2-1 b) AuL3-1;

Polarized IR studies

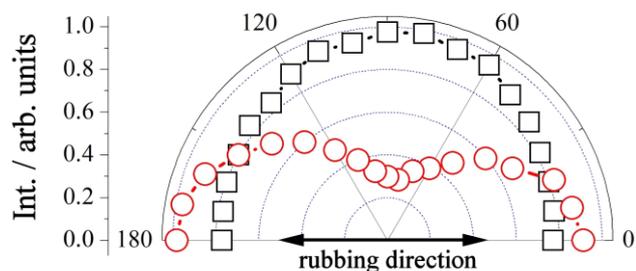
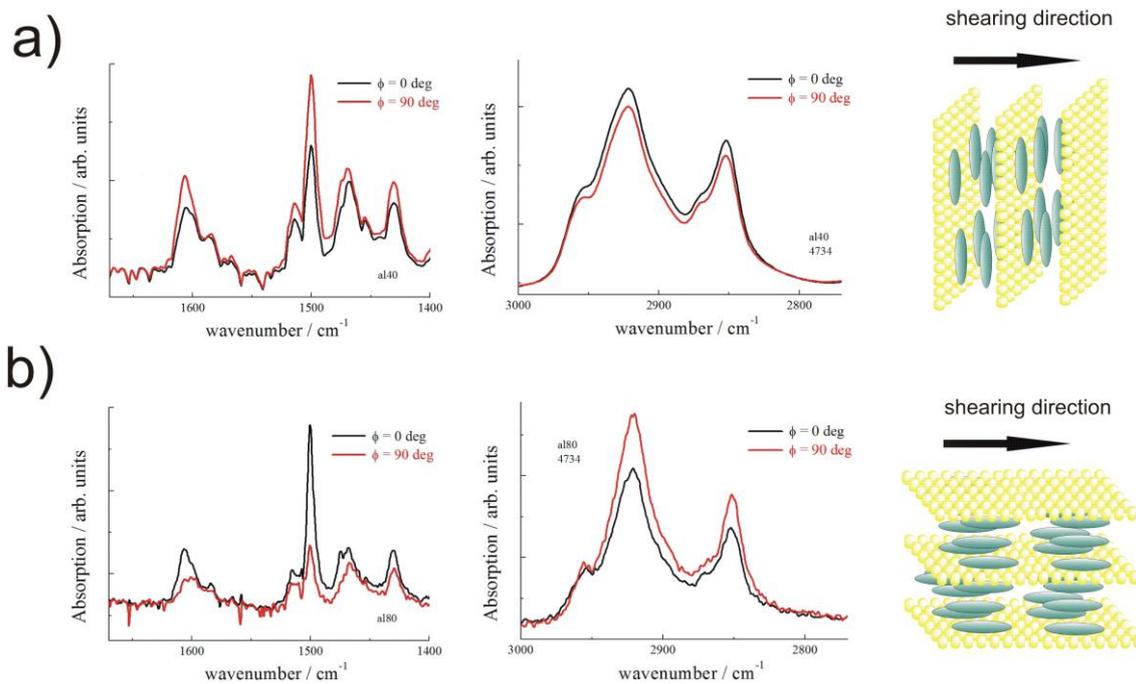


Fig. 3. Intensity of the IR absorption band at 1600 cm^{-1} vs. angle between the polarization plane of the incident IR beam and the shearing direction for AuL2-1 prepared at 100°C (red circles represents phenyl rings stretching, black squares represent $-\text{CH}_2-$ groups stretching)



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Fig 4. Intensity of the IR absorption band related to phenyl rings stretching (left) and methylene groups stretching (right) for the compound AuL2-2 sheared at: a) 40°C and b) 80°C with schematic drawing of obtained alignment of layers and ligand molecules for a) *transverse* and b) *perpendicular* mode. ϕ is the angle between the shearing direction and polarization of IR light. An arrow shows the shearing direction

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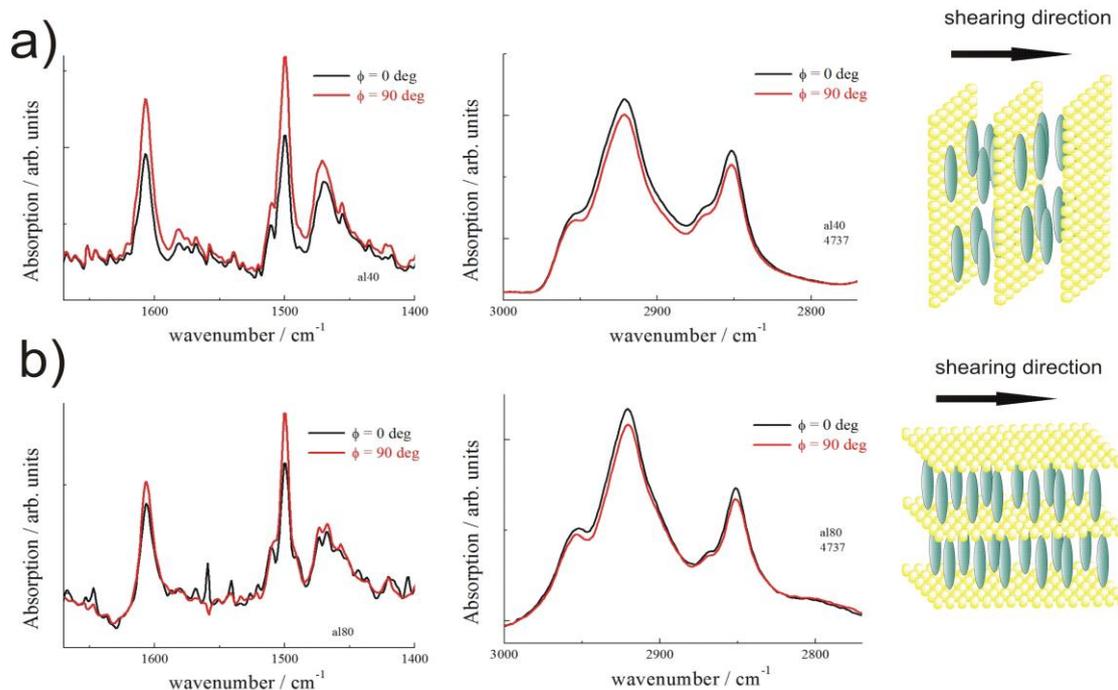


Fig 4. Intensity of the IR absorption band related to phenyl rings stretching (left) and methylene groups stretching (right) for the compound AuL2-1 sheared at: a) 40°C and b) 80°C with schematic drawing of obtained alignment of layers and ligand molecules for a) *transverse* and b) *perpendicular* mode. Note the different orientation of ligand molecules vs layers in b). ϕ is the angle between the shearing direction and polarization of IR light. An arrow shows the shearing direction.

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