Supporting information

Optical properties of thiophene-containing liquid crystalline and hybrid liquid crystalline materials

Jerzy Romiszewski,[a] Zita Puterová-Tokarová,*[a,b] Jozef Mieczkowski [a] and Ewa Gorecka[a]

*[*a]Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland. Tel:+4822 8220211; E-mail: z.puterova@chem.uw.edu.pl*
[b]Department of Chemistry, University of SS Cyril and Methodius, Nám. J. Herdu 2, 917-01 Trnava, Slovakia. Fax:+421335921403; Tel:+421335921408; E-mail: zita.tokarova@ucm.sk

Contents

1 Experimental section p. 1
2 Synthesis and characterization of compounds p. 2
2.1 General procedures p. 2
2.1.1 Synthesis of compounds of Series A – the stilbene containing thiohenes p. 2-4
2.1.2 Synthesis of compounds of Series B – the azobenzene containing thiophenes p. 4-5
2.1.3 Synthesis of compounds of Series C – bromo-substituted precursor L1 and thiol-ended ligand L2, gold nanoparticle p. 6
3 Figures p. 7-10

1 Experimental section

All reactions were carried out under an argon atmosphere in dried glassware with efficient magnetic stirring. 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 30 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. Unless otherwise specified, substrates were obtained from Sigma-Aldrich and used without further purification. Presented yields refer to chromatographically and spectroscopically (1H NMR) homogeneous materials. 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). TheNMR signals from thiol ligand attached to gold nanoparticles were strongly broaden due to paramagnetic character of metallic core, which allowed for easy control of sample contamination by free ligand molecules (molecules not attached to gold core give sharp signals). Compositions of the synthesized compounds weredetermined by elemental analysis (FlashEA 1112, Thermo Finnigan, FChPT, STU, Bratislava, Slovakia).
Identification of the liquid crystalline phases was based on the type of texture exhibited by the compound. The textures were observed with a polarizing optical microscope Zeiss Axio Imager A2m equipped with a Linkam hot stage. The identification was confirmed by X-ray studies carried out on a Bruker GADDS system equipped with VANTEC 2000 area detector and a hot stage controlled by Linkam controller. CuKα radiation was used. Phase transition temperatures, enthalpies and melting points were determined by differential scanning calorimetry measurements on TA Instruments DSC Q 200. Uv-visible absorption spectra were recorded using a Shimadzu UV-3100 PC spectrometer for solutions of appropriate compounds in dichloromethane ($c \sim 5.10^{-5}$ mol.dm^{-3}). Fluorescence measurements were performed for dilute solutions in dichloromethane using FluoroLog HORIBA Jobin Yvon spectrometer equipped with a TBX-04 PMT detector. Fluorescence lifetimes were measured by time-correlated single-photon counting using the same FluoroLog HORIBA JobinYvon instrument.
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 of 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 a small amount of material placed on the Kapton tape at the temperature of ca. 100 °C.

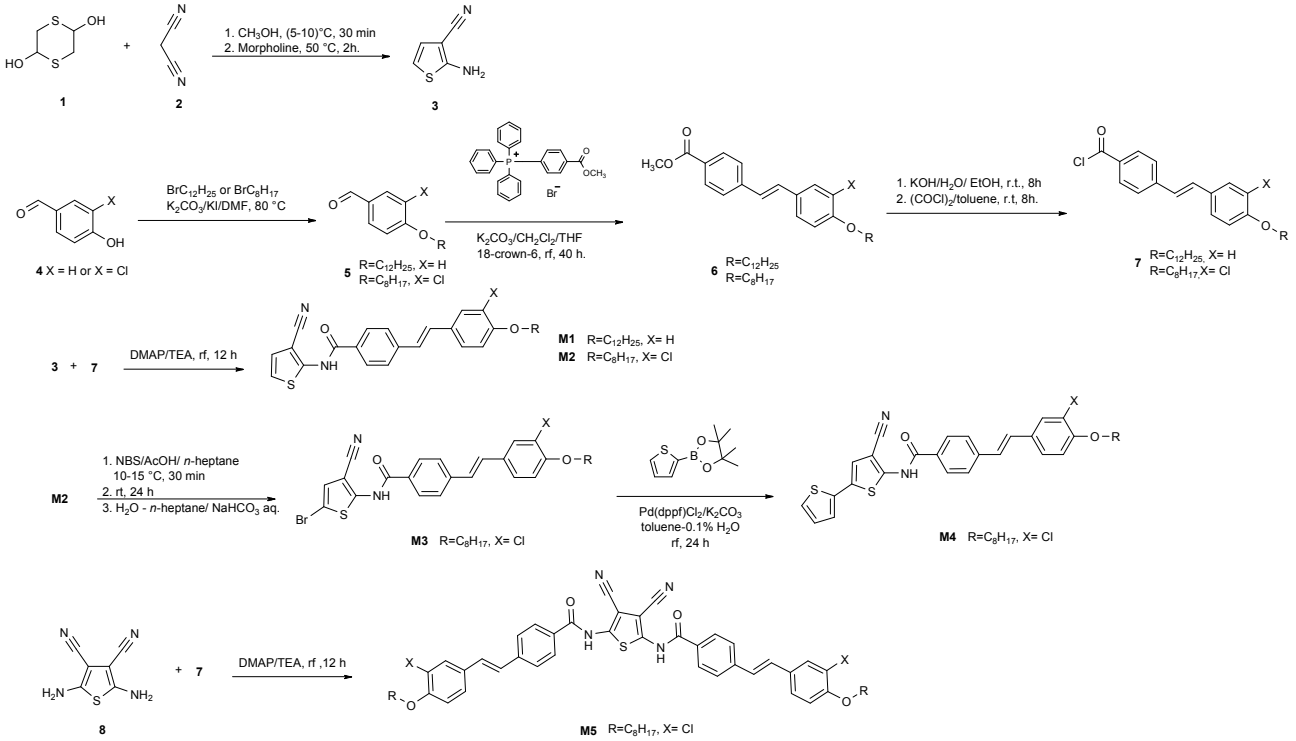
2 Synthesis and characterization of compounds

Following abbreviations were used:
AcOH – Acetic acid
DMAP – 4-Dimethylaminopyridine
dppf –1,1'-Bis(diphenylphosphino)ferrocene
EtOH – Ethanol
HMDT - Hexamethyldisilthiane
NBS – *N*-bromosuccinimide
NHS – succinimide
TBAF – Tetra-*n*-butylammonium fluoride
TEA – Triethylamine
THF – tetrahydrofurane

2.1 General procedures

The general procedure of the synthesis of mesogenic and pro-mesogenic compounds of *series A*–stilbene-containing thiophenes **M1-M5** is outlined in Scheme S1, of *series B*–azobenzene-containing thiophenes **M6-M9** is outlined in Scheme S2, and of *series C* – pro-mesogenic bromide **L1** and thiol ended ligand **L2** is outlined in Scheme S3. For synthesis of series A and B of compounds the synthesis is described for **M1-M5** and **M6**; ligands **M7-M8** were synthesized according to the same manner as for mentioned compounds, so their synthesis in detail is excluded. Intermediate **8** – diaminothiophene-3,4-dicarbonitrile could be prepared from tetracyanoethylene [W.J. Middleton, 1963] or purchased from Sigma-Aldrich and its preparation is not described herein. Preparation of Compound **4** – 3-chloro-4-hydroxybenzaldehyde was prepared previously in our group and its synthesis can be found in [J. Mieczkowski et al., 2002].

2.1.1 Synthesis of compounds of Series A – the stilbene-containing thiophenes



Scheme S1. Synthesis of compounds of Series A – the stilbene containing thiophenes (**M1-M5**).

Synthesis of compound 3

Into the solution of 2,5-dihydroxy-1,4-dithiane **1** (0.065 mol, 10g) in methanol (20 mL) 2 equiv. of malononitrile **2** (0.131 mol, 8.7 g) was added. To the stirred mixture morpholine (0.06 mol, 7.0 mL) was added dropwise at the temperature 10 °C over 30 minutes. After stirring at 30-40 °C for 2 hours, the mixture was cooled down to room temperature and the precipitate was filtrated and recrystallized from *n*-heptane. A 12 g (69 %) of ***2-aminothiophene-3-carbonitrile*** as a pale-brown solid was obtained. M.p. = 103-105 °C.

^{1}H NMR (200 MHz, $CDCl_3$) δ 6.94 (1H; d; J = 5.6 Hz), 6.38 (1H; d; J = 5.6 Hz), 4.80 (2H; br s). ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.0, 130.1, 128.8, 115.3, 111.0.

Synthesis of compounds 5

Into the solution of 12 g (0.1 mol) of 4-hydroxybenzaldehyde or 16 g (0.1 mol) of 3-chloro-4-hydroxybenzaldehyde in 500 ml of DMF a 37.5 g (0.27 mol) of anhydrous K_2CO_3 and 45.1 g (0.27 mol) of KI were added. Next, to the solution of 4-hydroxybenzaldehyde 67.7 g (0.27 mol) of 1-bromododecane and to the solution of 3-chloro-4-hydroxybenzaldehyde 52.1 g (0.27 mol) 1-bromooctane was added dropwise. The mixture was vigorously stirred at temperature of 80 °C for 24 hours. After cooling to the room temperature the mixture was poured into a 1 L of cold water with ice. The aqueous phase was extracted with

dichloromethane (3 × 30 mL). The organic layer was washed twice with aq. NaOH (10 % mol), water and dried with $MgSO_4$. After evaporation of solvent the corresponding products were obtained subsequently used without purification.
A 25.0 g (86 %) of ***4-(dodecyloxy)benzaldehyde*** (R = $C_{12}H_{25}$, X = H) was obtained as yellowish oil. Analytical data correspond to those published for 4-(dodecyloxy)benzaldehyde, $C_{19}H_{30}O_2$ (290.44 g·mol^{-1}) [Z. Puterová et al., 2012].
A 23.0 g (85 %) of ***3-chloro-4-(octyloxy)benzaldehyde*** (R = C_8H_{17}, X = Cl) was obtained as brownish oil. Analytical data correspond to those published for 3-chloro-4-(octyloxy)benzaldehyde, $C_{15}H_{21}ClO_2$ (268.78 g·mol^{-1}) [K. Gomola, et al., 2009].

Synthesis of compounds 6

Into the solution of 6.0g (12.0 mmol) of methyl(4-triphenylphosphoniummethyl)-benzoate bromide in 70 ml of CH_2Cl_2 and 70 ml of THF 8.4 g (61.0 mmol) of anhydrous K_2CO_3 and a catalytic amount of 18-crown-6 were added in one portion. After 1 hour to the vigorously stirred mixture a diluted solution of compound **5** (18.0 mmol) in CH_2Cl_2 was added. The reaction mixture was heated at the boiling point temperature for 48 hours and then cooled down to the room temperature. After filtration of inorganic salts formed during the Witting reaction, the solvents were evaporated and the crude product was recrystallized from ethanol to obtain appropriate pure (*E*)-stilbene.
A 3.4 g (45.0 %) of ***(E) 4-[2-(4-dodecyloxy-phenyl)-vinyl]-benzoic acid methyl ester*** (R = $C_{12}H_{25}$, X = H) was obtained as white solid. Analytical data correspond to those published for (*E*) 4-[2-4-(dodecyloxy-phenyl)-vinyl]-benzoic acid methyl ester, $C_{23}H_{38}O_3$ (422.60 g·mol^{-1}) [Z. Puterová et al., 2012].
A 2.8 g (52.0 %) of ***(E) [3-chloro-2-(4-octyloxy-phenyl)-vinyl]-benzoic acid methyl ester*** (R = C_8H_{17}, X = Cl) was obtained as white solid. Analytical data corresponds to those published for (*E*) 4-[3-chloro-2-(4-octyloxy-phenyl)-vinyl]-benzoic acid methyl ester, $C_{24}H_{29}ClO_3$ (400.94 g·mol^{-1}) [K. Gomola, et al., 2009].

Synthesis of compounds 7

To a solution of the appropriate (*E*) 4-[2-(4-alkyloxy-phenyl)-vinyl]-benzoic acid methyl ester **6** (7.0 mmol) in ethanol (200 mL), a solution of potassium hydroxide (1.6 g, 28.0 mmol) in water (20 mL) was added and the mixture was heated at the boiling temperature of ethanol for 8 h. After cooling the solution, the crude product was isolated by suction filtration as the potassium salt. After drying under vacuum, the obtained salt was suspended in toluene (200 mL) and treated with an excess of oxalyl chloride (6.0 mL). The reaction mixture was heated at 110 °C for 8 h. After filtration of the precipitated potassium chloride, the remaining solution was evaporated to dryness. The products slowly solidified at room temperature and were subsequently used without further purification and characterization in the next step.
A 2.8 g (95 %) of ***(E) 4-[2-(4-dodecyloxy-phenyl)-vinyl]-benzoyl chloride*** (R = $C_{12}H_{25}$, X = H), $C_{27}H_{35}ClO_2$ (427.02 g·mol^{-1}) was obtained as light yellow powder.
A 2.8 g (95 %) ***(E) 4-[2-(3-chloro-4-octyloxy-phenyl)-vinyl]-benzoyl chloride*** (R = C_8H_{17}, X = Cl), $C_{23}H_{26}Cl_2O_2$ (405.36 g·mol^{-1}) was obtained as light yellow powder.

Synthesis of stilbene-containing thiophenes M1 and M2

To a solution of 2-aminothiophene-3-carbonitrile **3** (5.0 mmol, 621.0 mg), DMAP (0.3 mmol, 37.0 mg), and triethylamine (2-3 drops) in toluene (100 mL) the appropriate 4-[2-(4-alkyloxy-phenyl)-vinyl]-benzoyl chloride **7** (6.0 mmol): (*E*) 4-[2-(4-dodecyloxy-phenyl)-vinyl]-benzoyl chloride (R = $C_{12}H_{25}$, X = H) (2.6 g); (*E*) 4-[2-(3-chloro-4-octyloxy-phenyl)-vinyl]-benzoyl chloride (R = C_8H_{17}, X = Cl) (2.4 g), respectively was added. The reaction mixture was stirred at boiling temperature of toluene for 24 hours. After cooling down to room temperature the excess of solvent was evaporated and the remaining crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with dichloromethane.
A 1.5 g (60.0 %) of ***(E) N-(3-cyano-thiophen-2-yl)-4-[2-(4-dodecyloxy-phenyl)-vinyl]-benzamide*** **M1** was obtained as a pale yellow solid. M.p. = 179-181 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.05 (1H; br s), 7.92 (2H; d; J = 8.4 Hz), 7.63 (2H; d; J = 8.6 Hz), 7.48 (2H; d; J = 8.6 Hz), 7.14 (1H; d; J = 13.6 Hz), 7.03 (1H; d; J = 13.6 Hz), 7.01 (2H; d; J = 8.4 Hz), 6.98 (1H; d; J = 7.4 Hz), 6.90 (1H; d; J = 7.4 Hz), 3.99 (2H; d; J = 6.4 Hz), 1.78 (2H; q; J = 6.4 Hz), 1.27 (16H, br s), 0.88 (3H; t; J = 6.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.0, 157.9, 149.1, 138.3, 132.8, 128.0, 127.5, 126.8, 126.4, 126.1, 124.4, 118.2, 115.8, 114.1, 96.6, 74.3, 32.7, 30.9, 30.5, 29.9, 24.0, 15.2. Elemental analysis: calcd. for $C_{32}H_{28}N_2O_2S$ (514.72 g.mol^{-1}), C% 74.67, H% 7.44, N% 5.44; found C% 74.82, H% 7.62, N% 5.60.
A 1.4 g (55.0 %) of ***(E) 4-[2-(3-chloro-4-octyloxy-phenyl)-vinyl]-N-(3-cyano-thiophen-2-yl)-benzamide*** **M2** was obtained as a pale yellow solid. M.p. = 155-158 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.07 (1H; br s), 7.92 (2H; d; J = 8.6 Hz), 7.61 (1H; d; J = 8.4 Hz), 7.35 (1H; d; J = 6.2 Hz), 7.13 (1H; d; J = 14.2 Hz), 7.06 (1H; d; J = 14.2 Hz), 7.03 (1H; d; J = 6.2 Hz), 6.94 (2H; d; J = 8.4 Hz), 6.91 (2H; d; J = 8.6 Hz), 4.05 (2H; t; J = 6.4 Hz), 1.85 (2H; q; J = 6.6 Hz), 1.31 (10H; br s), 0.89 (3H; t; J = 6.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.5, 159.0, 150.3, 138.6, 132.9, 127.8, 127.4, 127.2, 126.6, 125.1, 124.8, 119.6, 118.0, 116.7, 114.9, 96.6, 74.3, 33.0, 30.8, 30.2, 26.2, 24.3, 13.6. Elemental analysis: calcd. for $C_{28}H_{29}ClN_2O_2S$ (493.06 g.mol^{-1}), C% 68.21, H% 5.93, N% 5.68; found C% 68.28, H% 6.14, N% 5.74.

Synthesis of bromo-substituted stilbene-containing thiophene M3

Starting (*E*) 4-[2-(3-chloro-4-octyloxy-phenyl)-vinyl]-*N*-(3-cyano-thiophen-2-yl)-benzamide **M2** (4.0 mmol, 2.0 g) was diluted in glacial acetic acid – *n*-heptane (1:1, 150 mL) and resulting solution was cooled down to 10-15 °C *via* vigorous stirring. The NBS (5.0 mmol, 560 mg) was added to this solution in portions over 30 minutes. The reaction mixture was stirred at room temperature for 24 hours. Afterward the mixture was diluted with water – *n*-heptane (1:1, 100 mL) and stirred for additional 15 minutes, while formed succinimide completely dissolved in water and formed brominated compound in *n*-heptane. The organic layer was separated and the water layer extracted with another portion of *n*-heptane (2 × 30 mL). Combined organic phases were dried with $MgSO_4$ and the solvent evaporated. Crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with dichloromethane.
A 1.65 g (72.0 %) of ***N-(5-bromo-3-cyano-thiophen-2-yl)-4-[2-(3-chloro-4-octyloxy-phenyl)-vinyl]-benzamide*** **M3** was obtained as yellow solid. M.p. = 198-200 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.07 (1H; br s), 8.04 (2H; d; J = 8.8 Hz), 7.99 (2H; dd; J = 14.4 Hz), 7.97 (2H; d; J = 8.8 Hz), 7.28 (1H; d; J = 8.8 Hz), 7.04 (3H; m; J = 8.8 Hz), 4.06 (2H; t; J = 6.6 Hz), 1.82 (2H; q; J = 6.8 Hz), 1.28 (10H; br s), 0.88 (3H; t; J = 6.6 Hz).^{13}C NMR (50 MHz, $CDCl_3$) δ 166.8, 160.1, 153.3, 140.0, 133.4, 131.8, 128.2, 127.6, 127.1,

126.0, 124.9, 124.6, 120.2, 117.0, 114.8, 105.6, 98.3, 72.1, 33.0, 31.1, 30.4, 29.8, 24.0, 14.4. Elemental analysis: calcd. for $C_{28}H_{28}BrClN_2O_2S$ (571.96 g.mol^{-1}), C% 58.80, H% 4.93, N% 4.90; found C% 58.96, H% 5.08, N% 4.96.

Synthesis of stilbene-containing bithiophene M4 *via* palladium catalyzed cross coupling

A dry round bottomed flask was degassed through 3 freeze–pump–thaw cycles using liquid nitrogen and then **M3** (2.5 mmol, 1.4 g) and thiophene-2-boronic acid pinacol ester (3.0 mmol, 0.6 g) were dissolved in dry toluene (100 mL). To the above mixture was added an aqueous solution of potassium carbonate (17.5 mmol, 2.4 g) *via* syringe followed by addition of a catalytic amount of $Pd(dppf)Cl_2$. The resultant reaction solution was further degassed through three freeze–pump–thaw cycles, purged with argon, stirred at 95 °C in the inert atmosphere for 48 h. The reaction mixture was then allowed to cool down to room temperature and diluted with water (50 mL), washed with 5 % solution of $NaHCO_3$ and extracted with dichloromethane (3 × 30 mL). Combined organic phases were dried with MgSO4, solvent evaporated and crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with the mixture of toluene:dichloromethane (7:3).

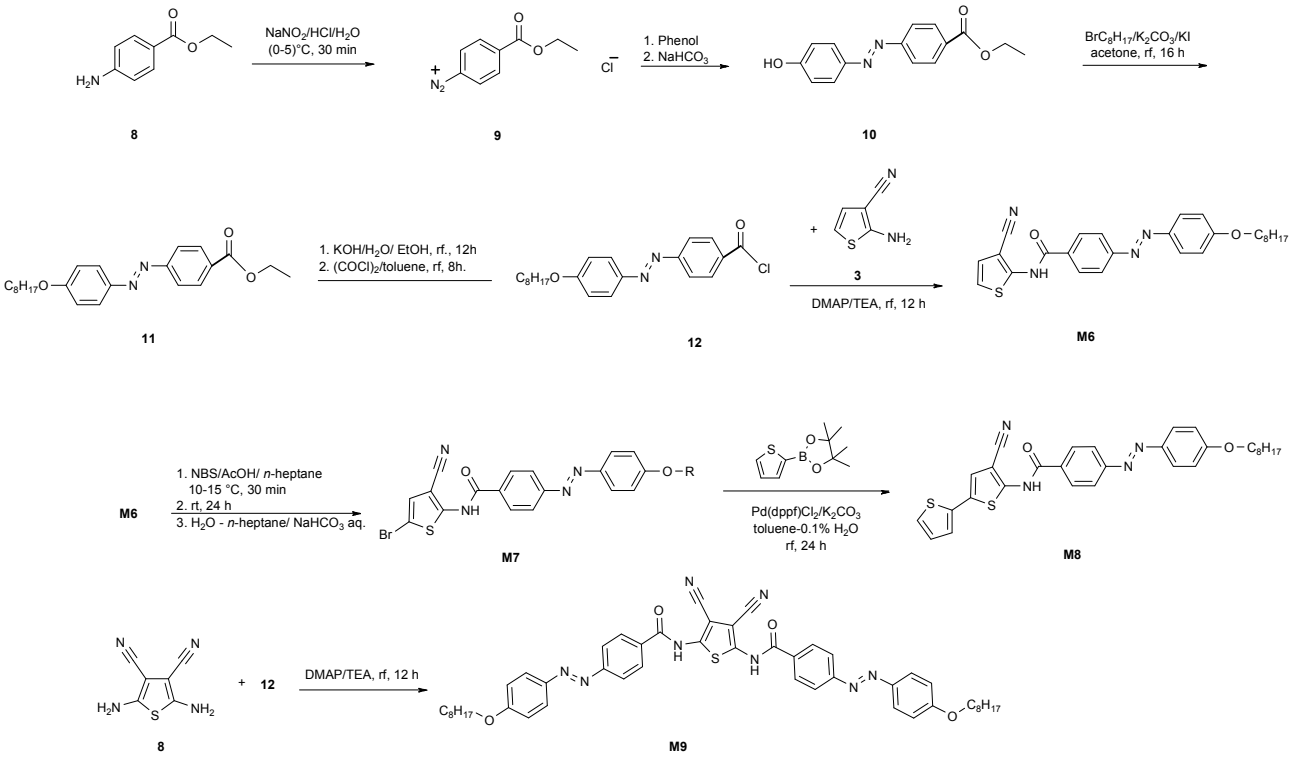
A 600 mg (43 %) of ***4-[2-(3-chloro-4-octyloxy-phenyl)-vinyl]-N-(4-cyano-2,2'-bithiophenyl-5-yl)-benzamide*** was obtained as yellow powder. M.p. = 160-162 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.00 (1H; br s), 7.91 (2H; d; J = 8.4 Hz), 7.62 (2H; d; J = 8.4 Hz), 7.37 (1H; d; J = 8.6 Hz), 7.25 (1H; d; J = 14.8 Hz), 7.21 (1H; t; J = 7.4 Hz), 7.20 (1H; d; J = 14.8 Hz), 7.11 (1H; d; J = 8.6 Hz), 7.09 (1H; d; J = 7.4 Hz), 7.03 (1H; d; J = 7.4 Hz), 7.01 (1H; s), 6.92 (1H; d; J = 8.6 Hz), 4.06 (2H; t; J = 6.4 Hz), 1.84 (2H; q; J = 6.4 Hz), 1.31 (2H; s), 1.29 (10H; s), 0.89 (3H; q; J = 6.4 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 166.1, 159.4, 149.1, 143.6, 139.4, 135.1, 133.1, 128.3, 127.9, 127.4, 127.2, 126.7, 126.5, 126.3, 125.8, 125.0, 124.6, 123.6, 122.4, 119.7, 116.4, 115.5, 97.4, 72.3, 32.8, 31.1, 30.5, 30.1, 27.4, 24.2, 13.9. Elemental analysis: calcd. for $C_{32}H_{31}ClN_2O_2S_2$ (575.18 g.mol^{-1}), C% 66.82, H% 5.43, N% 4.87; found C% 66.90, H% 5.52, N% 4.96.

Synthesis of *bis*-stilbene containing thiophene M5

To a solution of diamino-thiophene-3,4-dicarbonitrile **8** (2.5 mmol, 410.0 mg), DMAP (0.15 mmol, 18.5 mg), and triethylamine (2-3 drops) in toluene (100 mL) (*E*) [3-chloro-2-(4-octyloxy-phenyl)-vinyl]-benzoyl chloride (R = C_8H_{17}, X = Cl) (6.0 mmol, 2.4 g) was added. The reaction mixture was stirred at boiling temperature of toluene for 24 hours. After cooling down to room temperature the excess of solvent was evaporated and the remaining crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with dichloromethane diluted with 0.5 % methanol.

A 790 mg (35 %) of ***(E) bis{4-[2-(3-chloro-4-octyloxy-phenyl)-vinyl]-N-(3-cyano-thiophen-2-yl)-benzamide}*** was isolated as a yellow solid. M.p. = 310 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.11 (2H; br s), 7.96 (4H; d; J = 8.4 Hz), 7.71 (2H; d; J = 8.6 Hz), 7.17 (2H; d; J = 14.6 Hz), 7.10 (2H; d; J = 14.6 Hz), 6.98 (4H; d; J = 8.6 Hz), 6.92 (4H; d; J = 8.4 Hz), 4.02 (4H; t; J = 6.2 Hz), 1.88 (4H; q; J = 6.2 Hz), 1.27 (20H; br s), 0.91 (6H; t; J = 6.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.5, 157.7, 142.4, 139.0, 133.1, 128.1, 127.3, 127.0, 126.5, 125.9, 124.6, 124.1, 120.1, 116.5, 115.8, 97.4, 74.3, 32.1, 30.0, 26.4, 22.8, 15.1. Elemental analysis: calcd. for $C_{52}H_{54}Cl_2N_4O_4S$ (901.98 g.mol^{-1}), C% 69.24, H% 6.03, N% 6.21; found C% 69.40, H% 5.97, N% 6.26.

2.1.2 Synthesis of compounds of Series B – the azobenzene-containing thiophenes



Scheme S2. Synthesis of compounds of Series B – the azobenzene containing thiophenes (**M6-M9**).

Synthesis of azo-compound 10
A solution of sodium nitrite (2.27 g, 32.0 mmol in 15.7 mL of water) was added drop wise to a suspension of ethyl *p*-aminobenzoate **8** (26.7 mmol, 4.5 g) in a mixture of 10 mL of HCl and 30 mL of water, keeping the temperature below 5 ºC. After 30 min. of vigorous stirring, the diazonium salt (**9**) was formed. To this dark solution phenol (32.0 mmol, 3.05 g) was added in one portion. The reaction was stirred for 1 hour at room temperature, after which the solution was made basic with 100 mL of a saturated solution of $NaHCO_3$. A brown solid precipitated, which was filtered off and washed with distilled water. The product was isolated by recrystallization with ethanol. A 4.7 g (65 %) of ***(E) 4-(4-hydroxy-phenylazo)-benzoic acid ethyl ester*** was obtained as dark-red powder. Analytical data correspond to those published for 4-(4-hydroxy-phenylazo)-benzoic acid ethyl ester, $C_{14}H_{35}N_2O_3$ (270.28 $g \cdot mol^{-1}$) [F. Vera et al., 2007].

Synthesis of octyloxy substituted azo-compound 11
4-(4-Hydroxy-phenylazo)-benzoic acid ethyl ester **10** (9.25 mmol, 2.5 g), anhydrous K_2CO_3 (18.5 mmol, 2.6 g) and KI (0.1 g) were dissolved in 100 mL of acetone. After 10 minutes of stirring 1-bromo-*n*-octane (11.0 mmol, 2.12 g) was added dropwise *via* syringe while the solution was refluxing. The mixture was stirred overnight under reflux. After cooling down to room temperature, 200 mL of water was added. The product was extracted with dichloromethane. The organic layer was dried with $MgSO_4$ and filtered, and then the solvent was evaporated. The product was recrystallized with ethanol.
A 2.9 g (83 %) of ***(E) 4-(4-octyloxy-phenylazo)-benzoic acid ethyl ester*** was obtained as orange powder. Analytical data correspond to those published for 4-(4-octyloxy-phenylazo)-benzoic acid ethyl ester, $C_{23}H_{30}N_2O_3$ (382.5 $g \cdot mol^{-1}$) [O. Hiroshi et al., 1997].

Synthesis of compound 12
To a solution of (*E*) 4-(4-octyloxy-phenylazo)-benzoic acid ethyl ester **11** (7.0 mmol, 2.7 g) in ethanol (200 mL), a solution of potassium hydroxide (1.6 g, 28.0 mmol) in water (20 mL) was added and the mixture was heated at the boiling temperature of ethanol for 12 h. After cooling the solution, the crude product was isolated by suction filtration as the potassium salt. After drying under vacuum, the obtained salt was suspended in toluene (200 mL) and treated with an excess of oxalyl chloride (6.0 mL). The reaction mixture was heated at 110 °C for 8 h. After filtration of the precipitated potassium chloride, the remaining solution was evaporated to dryness. The products slowly solidified at room temperature and were subsequently used without further purification and characterization in the next step.
A 2.2 g (85 %) of ***(E) 4-(4-octyloxy-phenylazo)-benzoyl chloride*** **12**, $C_{21}H_{25}ClN_2O_2$ (372.89 $g \cdot mol^{-1}$) was obtained as orange powder.

Synthesis of azobenzene containing thiophene M6
Reaction leading to substance **M6** was provided in a similar way to the synthesis of **M1** and **M2** with (*E*) 4-(4-octyloxy-phenylazo)-benzoyl chloride **12** (6.0 mmol, 2.2 g) as a substrate. Crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with dichloromethane diluted with 0.5 % methanol.
A 1.2 g (51 %) of ***N-(3-cyano-thiophen-2-yl)-4-(4-octyloxy-phenylazo)-benzamide*** was obtained as dark orange powder. M.p. = 187-189 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.12 (1H; br s), 8.14 (2H; d; J = 8.4 Hz), 8.01 (2H; d; J = 8.6 Hz), 7.77 (2H; d; J = 8.6 Hz), 7.01 (2H; d; J = 8.4 Hz), 6.75 (1H; d; J = 7.4 Hz), 6.65 (1H; d; J = 7.4 Hz), 3.93 (2H; d; J = 6.4 Hz), 1.81 (2H; q; J = 6.4 Hz), 1.27 (10H, br s), 0.88 (3H; t; J = 6.2 Hz). Elemental analysis: calcd. for $C_{26}H_{28}N_4O_2S$ (406.59 $g.mol^{-1}$), C% 67.80, H% 6.13, N% 12.16; found C% 67.94, H% 6.17, N% 12.20.

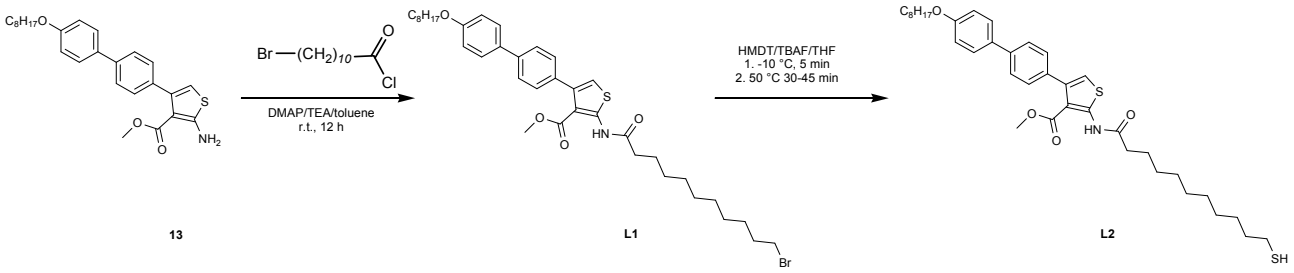
Synthesis of bromo-substituted azobenzene containing thiophene M7
Reaction leading to substance **M7** was provided in a similar way to the synthesis of **M3** with *N*-(3-cyano-thiophen-2-yl)-4-(4-octyloxy-phenylazo)-benzamide **M6** (4.0 mmol, 1.8 g) as substrate. Crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with dichloromethane diluted with 0.5 % methanol.
A 1.5 g (70 %) of ***N-(5-bromo-3-cyano-thiophen-2-yl)-4-(4-octyloxy-phenylazo)-benzamide*** was obtained as red powder. M.p. = 198-199 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.17 (1H; br s), 8.14 (2H; d; J = 8.8 Hz), 8.21 (2H; d; J = 8.8 Hz), 7.82 (2H; d; J = 8.4 Hz), 7.04 (1H; d; J = 8.4 Hz), 6.87 (1H; s), 4.03 (2H; t; J = 6.6 Hz), 1.80 (2H; q; J = 6.8 Hz), 1.28 (10H; br s), 0.91 (3H; t; J = 6.6 Hz). Elemental analysis: calcd. for $C_{26}H_{27}BrN_4O_2S$ (539.49 $g.mol^{-1}$), C% 57.88, H% 5.04, N% 10.39; found C% 57.90, H% 5.10, N% 10.42.

Synthesis of azobenzene containing bithiophene M8 *via* palladium catalyzed cross coupling
Reaction leading to substance **M8** was provided in a similar way to the synthesis of **M4** with *N*-(5-bromo-3-cyano-thiophen-2-yl)-4-(4-octyloxy-phenylazo)-benzamide **M7** (2.5 mmol, 1.3 g) as substrate. Crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with dichloromethane diluted with 0.5 % methanol.
A 530 mg (39 %) of *N*-(4-cyano-2,2'-bithiophenyl-5-yl)-4-(4-octyloxy-phenylazo)-benzamide was obtained as red powder. M.p. = 96-98 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.13 (1H; br s), 8.16 (2H; d; J = 8.4 Hz), 8.10 (2H; d; J = 8.4 Hz), 7.73 (2H; d; J = 8.6 Hz), 7.21 (1H; d; J = 7.4 Hz), 7.01 (1H; t; J = 7.4 Hz), 6.97(1H; d; J = 7.4 Hz), 6.94 (2H; d; J = 8.6 Hz), 6.7 (1H; s), 3.99 (2H; t; J = 6.2 Hz), 1.81 (2H; q; J = 6.4 Hz), 1.29 (2H; s), 1.26 (10H; s), 0.87 (3H; q; J = 6.4 Hz). Elemental analysis: calcd. for $C_{30}H_{30}N_4O_2S_2$ (542.71 $g.mol^{-1}$), C% 66.39, H% 5.57, N% 10.32; found C% 66.44, H% 5.60, N% 10.30.

Synthesis of *bis*-(azobenzene-containing thiophene) M9
Reaction leading to substance **M9** was provided in a similar way to the synthesis of **M5** with (*E*) 4-(4-octyloxy-phenylazo)-benzoyl chloride **12** (2.5 mmol, 1.4 g) as substrate. Crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with dichloromethane diluted with 0.5 % methanol.
A 324 mg (31 %) of ***bis*{*N-(3-cyano-thiophen-2-yl)-4-(4-octyloxy-phenylazo)-benzamide}*** was obtained as red powder. M.p. = 231-235 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 9.14 (2H; br s), 8.16 (4H; d; J = 8.4 Hz), 8.05 (2H; d; J = 8.4 Hz), 7.88 (4H; d; J = 8.6 Hz), 6.92 (4H; d; J = 8.6 Hz), 3.96 (4H; t; J = 6.2 Hz), 1.81 (4H; q; J = 6.2 Hz), 1.27 (20H; br s), 0.94 (6H; t; J = 6.2 Hz). Elemental analysis: calcd. for $C_{48}H_{52}N_8O_4S$ (837.04 $g.mol^{-1}$), C% 68.88, H% 6.26, N% 13.39; found C% 69.10, H% 6.32, N% 13.44.

Note: Because of lowered solubility of presented compounds from series B in $CDCl_3$ the 13C NMR spectra were excluded.

2.1.3 Synthesis of compounds of Series C – bromo-substituted precursor L1 and thiol-ended ligand L2, gold nanoparticle



Scheme S3. Synthesis of compounds of Series C – the pro-mesogenic bromide **L1** and mesogenic thiol **L2**.

Synthesis of compound 13

The preparation of ***2-amino-4-(4'-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester*** **13** ($C_{26}H_{31}NO_3S$, 437.59 $g \cdot mol^{-1}$) was already described by us and herein it was prepared in the same manner as published [Z. Puterová, et al., 2012].

Synthesis of compound L1 – the pro-mesogenic bromide

To a solution of 2-amino-4-(4'-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester **13** (5.0 mmol, 2.2 g) in THF (50 mL) an excess of 11-bromo-undecanoyl chloride (5 mL) and a catalytic amount of pyridine (5 drops) were added. The reaction mixture was left to stir at room temperature for 72 hours. After the reaction was completed the solvent and excess of unreacted 11-bromo-undecanoyl chloride were evaporated. The crude product was purified by column chromatography on silica gel (previously absorbed with 1% TEA) eluting with dichloromethane.

A 2.1 g (62 %) of ***2-(11-bromo-undecanoylamino)-4-(4'-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester*** was obtained as white solid. M.p. = 68-69 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 11.26 (1H; br s), 7.54 (2H; d; J = 8.6 Hz), 7.51 (2H; d; J = 8.6 Hz), 7.30 (2H; d; J = 8.2 Hz), 6.94 (2H; d; J = 8.2 Hz), 6.58 (1H; s), 3.96 (2H; t; J = 6.6 Hz), 3.60 (3H; s; $COO\underline{CH_3}$), 3.36 (2H; t; J = 6.8 Hz; $\underline{CH_2}Br$), 2.48 (2H; t; J = 7.2 Hz; $\underline{CH_2}CONH$), 1.76 (2H; q; J = 6.8 Hz; J = 7.2 Hz), 1.26 (10H; s), 1.22 (16H; s), 0.84 (3H; t; J = 6.8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.0, 164.2, 156.7, 148.1, 144.1, 137.2, 134.8, 128.8, 128.5, 128.0, 127.7, 127.4, 116.3, 115.1, 111.0, 71.2, 51.3, 35.0, 33.6, 32.8, 32.3, 30.8, 30.4, 30.1, 29.7, 29.2, 28.4, 26.8, 23.4, 13.6. Elemental analysis: calcd. for $C_{37}H_{50}BrNO_4S$ (684.77 $g.mol^{-1}$), C% 64.90, H% 7.36, N% 2.05; found C% 64.95, H% 7.32, N% 2.12.

Synthesis of compound L2 – the mesogenic thiol

To a 50 mL three necked round-bottom flask 2-(11-bromo-undecanoylamino)-4-(4'-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester **L1** (1.3 mmol, 900 mg, 1 eq.) and anhydrous THF (5 mL) were added. The mixture was stirred under argon at room temperature for 10 minutes. Precipitate formed during the cooling was dissolved by addition of another portion of anhydrous THF (10-15 mL). The resulting solution was cooled to –10 °C and HMDT (hexamethyldisilathiane) (1.6 mmol, 288 mg, 1.2 eq.) was injected using syringe. After 5 minutes dry TBAF (tetra-*n*-butylammonium fluoride) (1.5 mmol, 356 mg, 1.1 eq) was added with vigorous stirring. After 40 minutes the reaction mixture was allowed to warm gradually to room temperature and stirred over 30 minutes under inert atmosphere of argon. The reaction was monitored by TLC (DCM) which showed that only traces of final thiol were formed while bromo-precursor was still major in the reaction mixture. The reaction was heated up to 50 °C and stirred for 45 minutes while monitoring over 5 minutes the reaction progress on TLC (DCM). When in the reaction mixture the side-product – the *bis* thiol derivate started to appear (on TLC in DCM as a spot on the bottom of the plate) the reaction was turned off and allowed to cool down to room temperature. To a slightly green solution 70 mL of CH_2Cl_2 was then added followed by washing with saturated solution of NH_4Cl (3 x 50 mL) and with pure water (2 x 50 mL). Afterwards mixture was dried with $MgSO_4$. The solvent was evaporated and the crude compound was purified twice by column chromatography on silica gel (previously absorbed with 1% TEA) eluting first with dichloromethane and then with the mixture of hexanes:ethylacetate (8:2).

A 274 mg (33 %) of ***2-(11-thiol-undecanoylamino)-4-(4'-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester*** was obtained as a white solid. M.p. = 75-76 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 11.3 (1H; br s), 7.57 (4H; dd; J = 8.6 Hz), 7.33 (2H; d; J = 8.0 Hz), 6.98 (2H; d; J = 8.0 Hz), 6.62 (1H; s), 4.00 (2H; t; J = 6.6 Hz), 3.63 (3H; s; $COO\underline{CH_3}$), 2.53 (2H; dd; J = 7.4 Hz; $\underline{CH_2}CONH$), 2.50 (2H; dd; J = 7.0 Hz; $\underline{CH_2}SH$), 1.79 (2H; dd; J = 7.4 Hz), 1.32 (10H; s), 1.30 (16H; s), 0.89 (3H; t; J = 7.4 Hz).
^{13}C NMR (50 MHz, $CDCl_3$) δ 170.5, 164.0, 158.4, 148.3, 142.6, 137.1, 135.2, 128.7, 128.2, 128.0, 127.7, 127.4, 127.1, 116.6, 115.0, 112.1, 71.1, 51.2, 34.4, 33.8, 32.7, 30.8, 30.2, 29.5, 29.0, 28.7, 28.4, 26.5, 26.0, 22.8, 13.9. Elemental analysis: calcd. for $C_{37}H_{51}NO_4S_2$ (637.94 $g.mol^{-1}$), C% 69.66, H% 8.06, N% 2.20; found C% 70.12, H% 8.12, N% 2.18.

2.1.4 Preparation of gold nanoparticles

Preparation of $Au@SC_{10}H_{22}$

The gold nanoparticles were synthesized using a modified Brust and Schiffrin method [Brust et al., 1994]. An aqueous solution of hydrogen tetrachloroaurate (50 mL, 145 mmol dm^{-3}) was mixed with a solution of methyltrioctylammonium bromide in toluene (50 mL, 125 mmol dm^{-3}). The two-phase mixture was vigorously stirred until all the tetrachloroaurate was transferred into the organic layer, determined by discoloration of water layer. Consequently, phases were separated and decanethiol (l.4 g; 8.0 mmol) was then added to the organic phase and stirred for 20 min. The obtained toluene solution containing a 1:1 mole ratio of decanethiol to $AuCl_4^-$ was reduced at 15 °C with freshly prepared aqueous solution of sodium borohydride (50 mL, 400 mmol dm^{-3}). Solution of borohydride was quickly added with vigorous stirring. After further stirring for 3 h the organic phase was separated, washed with pure water (2 x 100 mL), evaporated to 5 mL in a rotary evaporator and mixed with 200 mL of ethanol to precipitate nanoparticles. The mixture was kept for 12 h at –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. The procedure was repeated until no trace of excess of thiol was found, as determined by ^{1}H NMR spectra and TLC.

Preparation of Au@L2

Ligand-exchange reaction was accomplished via a slight modification of previously reported procedure [Murray et al., 1996]. The incoming thiol mesogenic compound (2-(11-thiol-undecanoylamino)-4-(4'-octyloxy-biphenyl-4-yl)-thiophene-3-carboxylic acid methyl ester **L2**) (66 mmol) and the decanethiolate-protected gold nanoparticles (100 mg) were co-dissolved in toluene (50 mL).
The mixture was stirred for 72 h at room temperature, then evaporated to 5 mL in a rotary evaporator and mixed with 200 mL of ethanol to precipitate nanoparticles. The resulting gel-like mixture was sonicated for 60 s and left overnight at room temperature for nanoparticles to precipitate on the bottom of the flask. The precipitate was carefully collected and dissolved in a small amount of toluene (5 mL). Further purifying procedure was analogous to that described for Au@$SC_{10}H_{22}$ nanoparticles and repeated until no trace of excess of thiol was found, as determined by ^{1}H NMR spectra and TLC.

3 Figures

a) UV-Visible absorption and fluorescence spectra of all prepared compounds

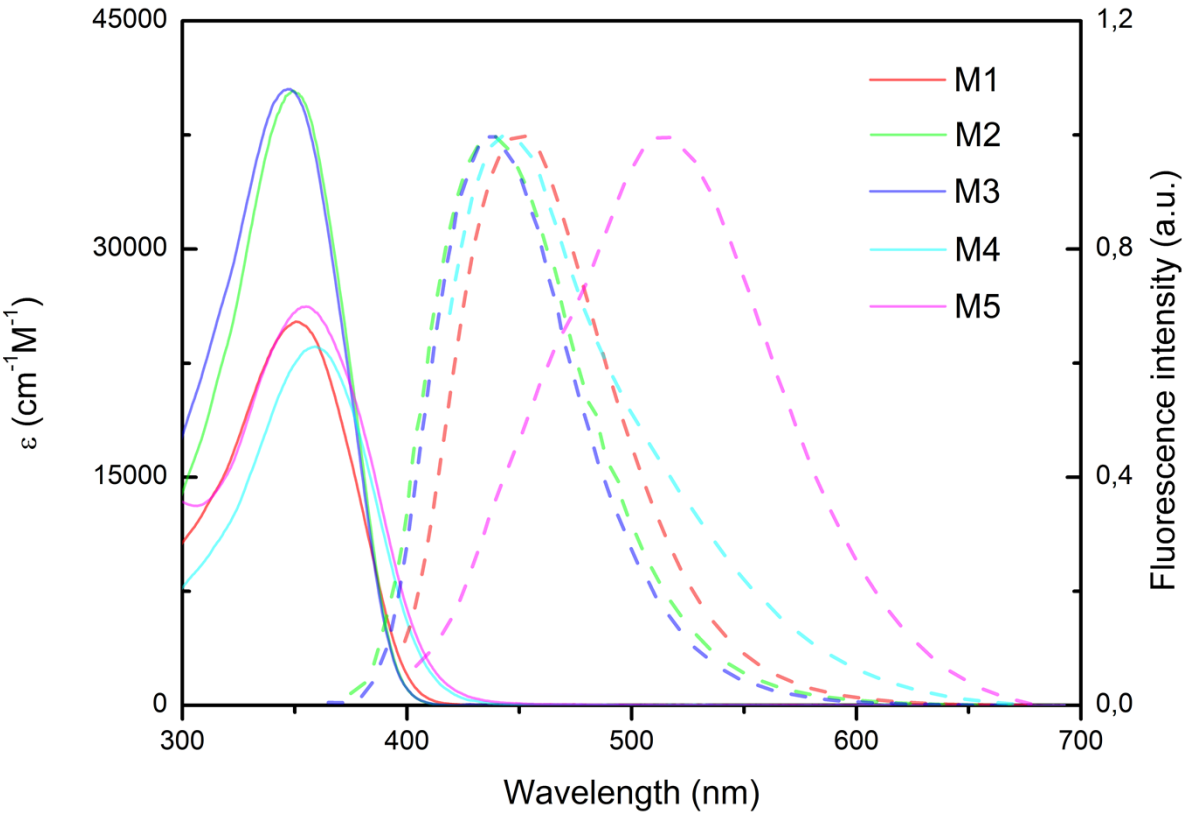


Fig. 1 UV-Visible absorption (solid line) and fluorescence (dashed line) spectra for compounds from *series A* – stilbene containing thiophenes.

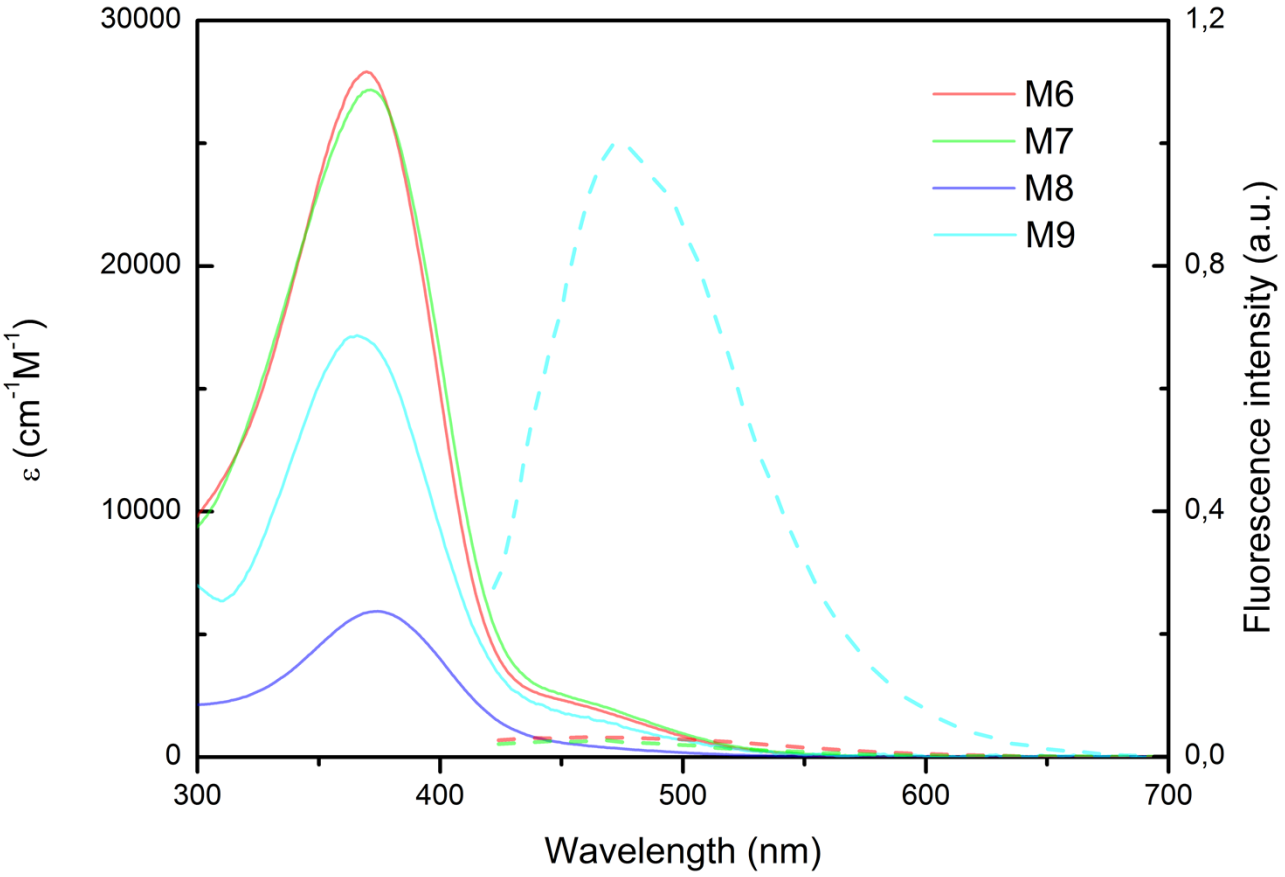


Fig. 2 UV-Visible absorption (solid line) and fluorescence (dashed line) spectra for compounds from *series B* – azobenzene containing thiophenes.

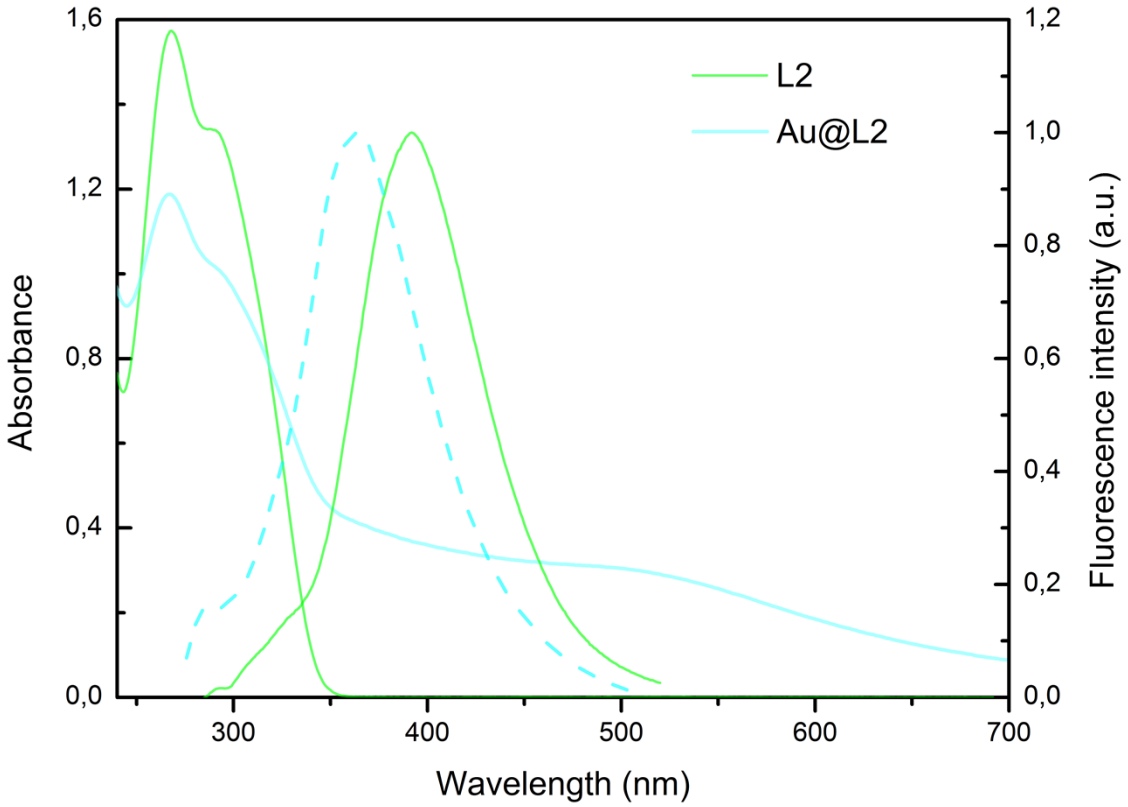


Fig. 3 UV-Visible and fluorescence for compounds from *series C* –thiol-ended ligand (**L2**) and **Au@L2** (in solution).

b) POM images and XRD patterns

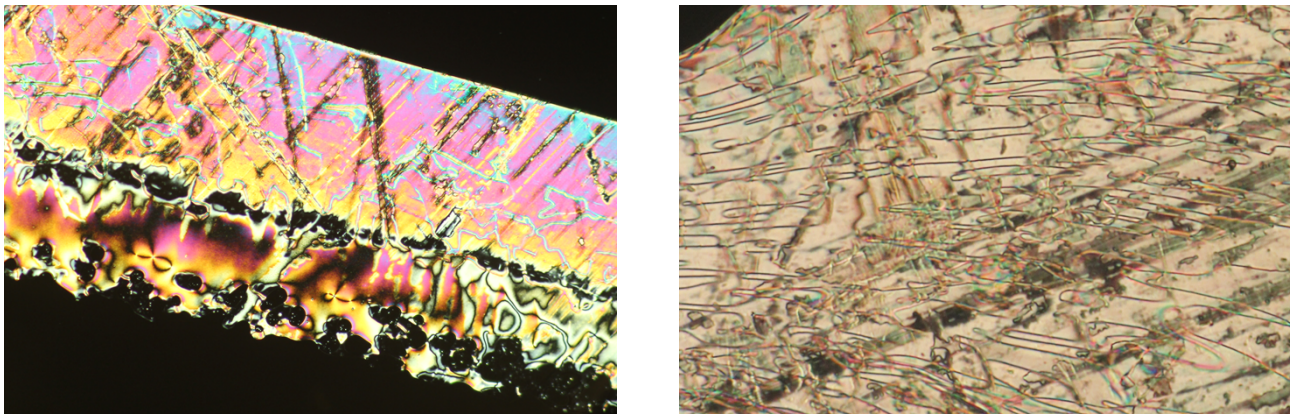


Fig. 4 Nematic texture (on the left) and flow in the nematic state (on the right) of **M2**.

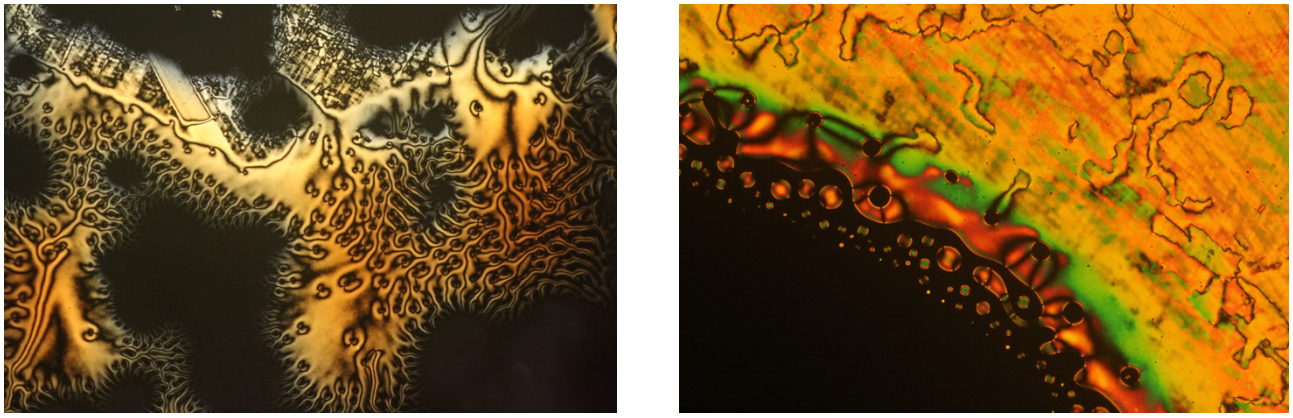


Fig. 5 Nematic texture (on the left) and transition from isotropic to nematic state (on the right) in **M7**.

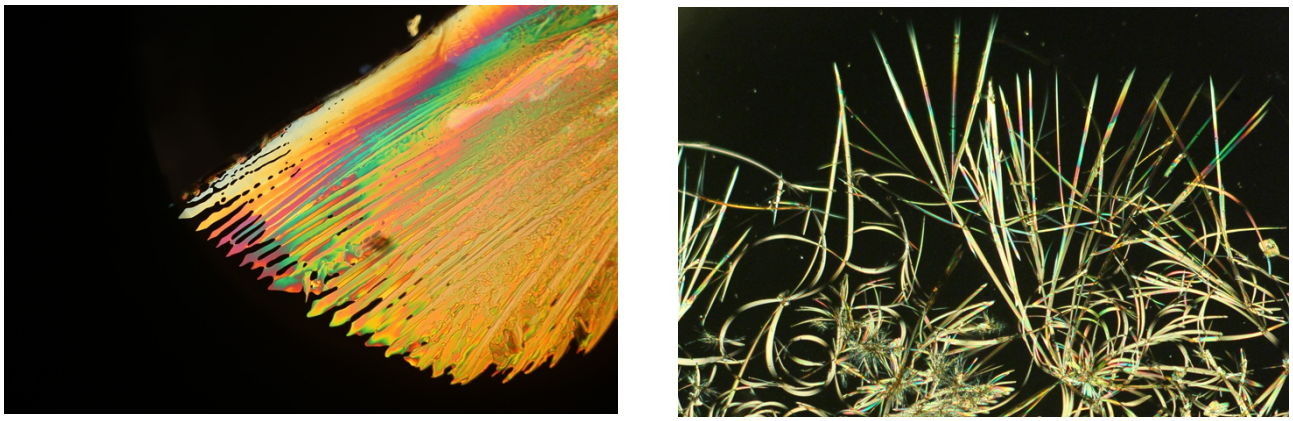


Fig. 6 Crystal growth in **M6** (on the left) and **M8** (on the right).

Fig. 7 Solutions of **M9** (left vial) and **M6** (right vial) irradiated with UV light.

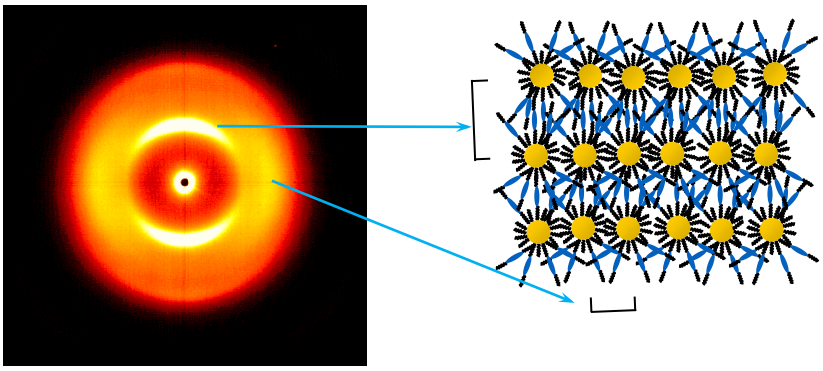


Fig. 8 XRD pattern of shear aligned sample of **Au@L2** and model of particles packing in the structure formed

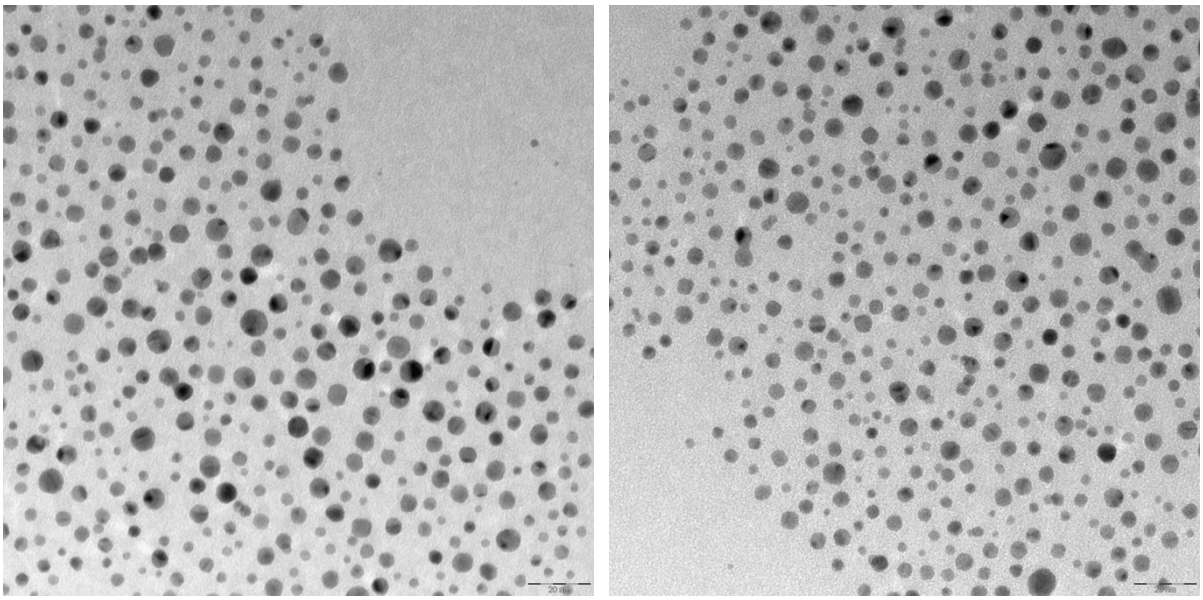


Fig. 9 TEM images of the sample of material **Au@L2**
Note: Our attempts to obtain TEM images of AuNPs layers failed as heating of the sample to temperatures above phase (ordering) transition temperature caused AuNP aggregation (Fig.9). The root causes of this fact we see in relatively limited temperature range of stable smectic AuNPs phase and mainly in the influence of large interface area in so thin samples that dramatically change local environment of AuNPs.

References

1. W. J. Middleton, *Organic Syntheses*, 1963, **Coll. Vol. 4**, 243.
2. J. Mieczkowski, J. Szydlowska, J. Matraszek, D. Pociecha, E. Gorecka, B. Donnio, D. Guillon, *J. Mater. Chem*., 2002, **12**, 3392.
3. Z. Puterová, J. Romiszewski, J. Mieczkowski, E. Gorecka, *Tetrahedron*, 2012, **68**, 8172.
4. K. Gomola, G. Lingfeng, D. Surajti, S. Yoshio, T. Hideo, E. Gorecka, D. Pociecha, J. Mieczkowski, *J. Mater. Chem*. 2009, **19**, 4240.
5. F. Vera, J. Barberá, P. Romero, J. L. Serrano, M. Blanca-Ros, T. Sierra, *Angew. Chem. Int. Ed.*, 2007, **46**, 1873.
6. O. Hiroshi, K. Shigeyoshi, M. Masatoshi, *Bull. Chem. Soc. Jpn*., 1997, **70**, 1649.
7. M. Brust, M. Walker, D. Bethell, J. Schiffrin, R. Whyman, *J. Chem. Soc.Chem. Commun.* 1994, 801.
8. R. S. Ingram, M. J. Hostetler, W. Murray, *J. Am. Chem. Soc*. 1996, **118**, 4214.