Electronic Supporting Information

Design of Liquid-Crystalline Gold Nanoparticles by Click Chemistry

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Materials. For the click reactions, the solvents were degassed prior to use. Compounds \( 5 \), \( 6 \), \( 7 \), gold nanoparticles stabilized with decanethiol \( 8 \), and bromo-functionalized gold nanoparticles \( 9 \) were prepared following literature procedures.

Techniques. Column chromatography used silica gel (Chemie Brunschwig, Bâle, Switzerland, 63-200 µm, 60 Å). Ultrafiltration: Millipore solvent-resistant ultrafiltration device with 30 kDa regenerated cellulose ultrafiltration membrane under 0.6 bar \( \text{N}_2 \) pressure. \( ^1 \text{H} \) and \( ^{13} \text{C} \)-NMR spectra: Brucker 400 spectrometer with the solvent as internal reference. Mass spectra: Finnigan LCQ. UV-vis spectra: Uvikon 930 spectrophotometer. The samples for Transmission Electron Microscopy (TEM) analyses were prepared by drop casting a dilute gold nanoparticles solution in \( \text{CH}_2\text{Cl}_2 \) onto a 300-mesh carbon-coated copper grid. TEM images were obtained using a Philips C200 transmission electron microscope operated at 200 kV, and analyzed with the help of Image J program. IR spectra: PerkinElmer Spectrum One FT-IR spectrometer using samples drop cast onto powdered KBr. Elemental analyses: Mikroelementaranalysisches Laboratorium EHT-Zürich.

Liquid-crystalline properties. Transition temperatures (onset point) and enthalpies: differential scanning Mettler DSC 822° calorimeter, under \( \text{N}_2/\text{He} \), 10°C/min. Optical studies: Zeiss-Axioscope polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage.

Abbreviations: 4-(dimethylamino)pyridinium toluene-para-sulfonate = DPTS; \( \text{N,N}’ \)-dicyclohexylcarbodiimide = DCC; 4-pyrrolidinopyridine = 4-ppy; column chromatography = CC; gold nanoparticles = AuNPs; broad singlet = br. s.

Synthesis of compound 1.

\[ \text{Scheme S1. Reagents and conditions: (i) 4-pentynoic acid, DPTS, DCC, 4-ppy, CH}_2\text{Cl}_2, \text{room temperature, 24 h.} \]

To a solution of \( 5 \) (1.00 g, 0.92 mmol) and 4-pentynoic acid (108 mg, 1.10 mmol) in dry \( \text{CH}_2\text{Cl}_2 \) (150 mL) at 0°C, were added DPTS (270 mg, 0.92 mmol), DCC (569 mg, 2.76 mmol) and 4-ppy (spatula tip). The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under vacuum and the crude material purified by CC (\( \text{CH}_2\text{Cl}_2 \)). Dissolution of the solid residue in a minimum of \( \text{CH}_2\text{Cl}_2 \) and precipitation from \( \text{CH}_3\text{OH} \) gave compound 1 as a white solid (670 mg, 62 %). \( ^1 \text{H} \)-NMR (δ in ppm, CDCl\(_3\), 400 MHz): 8.57 (t, 1H, \( \text{H}_{\text{arom.}} \)); 8.16 (d, 4H, \( \text{H}_{\text{arom.}} \)); 7.95 (d, 2H, \( \text{H}_{\text{arom.}} \)); 7.73 and 7.70 (2d, 8H, \( \text{H}_{\text{arom.}} \)); 7.64 (d, 4H, \( \text{H}_{\text{arom.}} \)); 7.33 (d, 4H, \( \text{H}_{\text{arom.}} \)); 6.98 (d, 4H, \( \text{H}_{\text{arom.}} \)); 4.35 (t, 4H, \( \text{CH}_2\text{O}_2\text{C} \)); 4.05 (t, 4H, \( \text{CH}_2\text{O} \)); 2.86 (t, 2H, \( \text{CH}_2\text{CO}_2 \));
2.65 (td, 2H, CH$_2$C≡C); 2.06 (t, 1H, H/C≡C); 1.86-1.75 (m, 8H, CH$_2$CH$_2$O and CH$_2$CH$_2$O$_2$C); 1.50-1.35 (m, 24H, H$_{aliph}$). $^{13}$C-NMR (δ in ppm, CD$_2$Cl$_2$, 400 MHz): 170.60; 165.38; 165.29; 164.34; 152.26; 151.22; 145.26; 137.28; 133.23; 133.12; 132.75; 128.86; 128.31; 128.23; 127.38; 123.13; 121.84; 119.37; 114.92; 111.61; 82.53; 69.82; 69.02; 66.34; 33.93; 30.04; 30.01; 29.89; 29.80; 29.66; 29.19; 26.53; 26.51; 14.84.

MS (ESI(+)): 1191 [M+Na]$^+$. Anal. C$_{73}$H$_{72}$N$_2$O$_{12}$ (1169.38 g·mol$^{-1}$): C 74.98, H 6.21, N 2.40. Found: C 74.93, H 6.12, N 2.37.

Synthesis of compound 2.

![Scheme S2. Reagents and conditions: (i) 4-pentyne acid, DPTS, DCC, 4-ppy, CH$_2$Cl$_2$, room temperature, 24 h.](image)

From 6 (1.00 g, 0.43 mmol) and 4-pentyne acid (46 mg, 0.47 mmol); 63 % yield after purification; for the reaction conditions, see the synthesis of 1. $^1$H-NMR (δ in ppm, CD$_2$Cl$_2$, 400 MHz): 8.91 (t, 1H, Harom.); 8.64 (t, 2H, Harom.); 8.24 (d, 2H, Harom.); 8.14 (d, 8H, Harom.); 8.10 (d, 4H, Harom.); 7.72 and 7.70 (2d, 16H, Harom.); 7.63 (d, 8H, Harom.); 7.32 (d, 8H, Harom.); 6.97 (d, 8H, H$_{arom}$); 4.36 (t, 8H, C$_2$H$_2$O$_2$C); 2.90 (t, 2H, CH$_2$CO$_2$); 2.68 (td, 2H, CH$_2$C≡C); 2.08 (t, 1H, H/C≡C); 1.83-1.78 (m, 16H, CH$_2$CH$_2$O and CH$_2$CH$_2$O$_2$C); 1.47-1.34 (m, 48H, H$_{aliph}$). $^{13}$C-NMR (δ in ppm, CD$_2$Cl$_2$, 400 MHz): 170.06; 164.84; 164.78; 163.85; 163.13; 151.77; 151.24; 150.73; 144.76; 136.78; 132.84; 132.75; 132.27; 131.38; 129.12; 128.71; 128.37; 128.18; 127.74; 126.89; 122.64; 121.36; 118.92; 114.43; 111.13; 81.94; 69.49; 68.53; 65.96; 33.47; 29.55; 29.52; 29.40; 29.32; 29.17; 28.71; 26.05; 26.02; 14.36. MS (ESI(+)): 2426 [M+Na]$^+$. Anal. C$_{149}$H$_{142}$N$_4$O$_{26}$ (2404.77 g·mol$^{-1}$): C 74.42, H 5.95, N 2.33. Found: C 74.26, H 5.99, N 2.31.

Synthesis of AuNPs 3.

![Scheme S3. Reagents and conditions: (i) NaN$_3$, CH$_2$Cl$_2$/DMSO (1:1), room temperature, 2 d.](image)

The synthesis is adapted from a literature procedure.$^6$ AuNPs 9 were dissolved in CH$_2$Cl$_2$ to yield a 10 mg/mL solution. To the latter, was added an equal volume of a 0.25 M NaN$_3$ solution in DMSO. The mixture was stirred under Ar at room temperature for 2 days, water was added, and
the dark brown organic layer was recovered. The organic phase was dried (MgSO$_4$), filtered and the solvent removed under vacuum. The resulting AuNPs were precipitated from ethanol. The AuNPs were washed (ethanol, 20 x 100 mL) through regenerated cellulose membrane filters (pore size: 0.2 µm) and redissolved by adding a minimum of a heptane/acetone (1:1) solution. The solvents were removed under vacuum, and pure AuNPs 3 were obtained (mass yield: 87 %; by $^1$H-NMR spectroscopy, the following ligands distribution was obtained: 30% of N$_3^-$, 20% of Br$^-$, and 50% of CH$_3$-terminated ligands). $^1$H-NMR (δ in ppm, CD$_2$Cl$_2$, 400 MHz): 3.41 (br. s, CH$_2$Br); 3.26 (br. s, CH$_2$N$_3$); 1.86 (br. s, CH$_2$CH$_2$Br); 1.28 (br. s, H$_{\text{aliph.}}$); 0.89 (br. s, CH$_3$). UV-vis: weak plasmon band at 520 nm. IR (ν in cm$^{-1}$, KBr): 2095 (N$_3$).  

**Synthesis of AuNPs 4-G1 and 4-G2.**

![Scheme S4. Reagents and conditions: (i) 1 or 2, CuSO$_4$·5H$_2$O, sodium ascorbate, THF/H$_2$O (1:1), 30°C, 3 d.]

General procedure. AuNPs 3 were dissolved in THF to yield a 10 mg/mL solution. Three equivalents of 1 or 2 were added. At 0°C, a solution of CuSO$_4$·5H$_2$O (6 equivalents) in water was added, followed by dropwise addition of a freshly prepared solution of sodium ascorbate (12 equivalents) in water; the quantities were adjusted to obtain a 1:1 THF/H$_2$O ratio. The mixture was stirred under Ar at 30°C for 3 days. THF was removed under vacuum. CH$_2$Cl$_2$ and an aqueous ammonia solution (1M) were added. The mixture was stirred for 10 minutes in order to remove copper complexes trapped inside the AuNPs. The organic phase was recovered, washed (2 x H$_2$O), dried (MgSO$_4$) and filtered. The solvent was removed under vacuum. To remove the alkyne substrate in excess, the AuNPs were purified by ultrafiltration (CH$_2$Cl$_2$, 15 x 50 mL). The AuNPs were redissolved with CH$_2$Cl$_2$ and recovered from the ultrafiltration system. Removal of the solvent under vacuum gave pure AuNPs 4-Gn (n = 1 or 2) (mass yield: 85 %). $^1$H-NMR spectroscopy indicated that: a) AuNPs 4-G1 were covered with 30% of G1-cyanobiphenyl dendron moieties, 20% of Br$^-$, and 50% of CH$_3$-terminated ligands, and b) AuNPs 4-G2 with 10% of G2-cyanobiphenyl units, 20% of N$_3^-$, 20% of Br$^-$, and 50% of CH$_3$-terminated ligands.  

**Data of 4-G1.** $^1$H-NMR (δ in ppm, CD$_2$Cl$_2$, 400 MHz): 8.49 (br. s, H$_{\text{arom.}}$); 8.11 (br. s, H$_{\text{arom.}}$); 7.90 (br. s, H$_{\text{arom.}}$); 7.67 (br. s, H$_{\text{arom.}}$); 7.30 (br. s, H$_{\text{arom.}}$); 6.97 (br. s, H$_{\text{arom.}}$); 4.30 (br. s, CH$_2$O$_2$C and CH$_2$N); 4.02 (br. s, CH$_2$O); 3.41 (br. s, CH$_2$Br); 3.09 (br. s, CH$_2$CH$_2$CO$_2$); 3.02 (br. s, CH$_2$CH$_2$CO$_2$); 1.77 (br. s, CH$_2$CH$_2$Br, CH$_2$CH$_2$O and CH$_2$CH$_2$O$_2$C); 1.32 (br. s, H$_{\text{aliph.}}$); 0.89 (br. s, CH$_3$). TG: percentage of weight loss = 46 %; particles thermally stable until 255°C. UV-vis: weak plasmon band at 520 nm. TEM: particles diameter = 1.6 ± 0.6 nm. IR (ν in cm$^{-1}$, KBr): 2225 (C≡N), 1725 (C=O).  

**Data of 4-G2.** $^1$H-NMR (δ in ppm, CD$_2$Cl$_2$, 400 MHz): 8.85 (br. s, H$_{\text{arom.}}$); 8.58 (br. s, H$_{\text{arom.}}$); 8.09 (br. s, H$_{\text{arom.}}$); 7.68 (br. s, H$_{\text{arom.}}$); 7.28 (br. s, H$_{\text{arom.}}$); 6.94 (br. s, H$_{\text{arom.}}$); 4.26 (br. s, CH$_2$O$_2$C and CH$_2$N); 3.98 (br. s, CH$_2$O); 3.41 (br. s, CH$_3$Br); 3.26 (br. s, CH$_2$N$_3$); 3.07 (br. s, CH$_2$CH$_2$CO$_2$ and CH$_2$CH$_2$CO$_2$); 1.75 (br. s, CH$_2$CH$_2$Br, CH$_2$CH$_2$O and
CH₂CH₂O₂C); 1.30 (br. s, Hₐliph.); 0.89 (br. s, CH₃). UV-vis: weak plasmon band at 520 nm. IR (ν in cm⁻¹, KBr): 2095 (N₃), 2225 (C≡N), 1725 (C=O).

**Number of ligands per gold nanoparticle.**

1) The AuNPs can be considered as spherical objects.⁸,⁹ Mean number of gold atoms per particle: \(N_{Au} = 4/3\pi(d/2)^3/V_{Au} = 126\); where a) \(V_{Au} = 17 \, Å^3\) (volume of a gold atom),¹⁰ and b) \(d = 16 \, Å\) (average diameter of AuNPs, by TEM).

2) Molar mass of the gold core for one nanoparticle: \(M_{Au} = N_{Au} \cdot A_{Au} = 24822 \, g/mol\); with \(A_{Au} = 197 \, g/mol\).

3) The TG analysis of AuNPs ⁸ indicates that the percentage of weight loss is ca. 23%. This means that ca. 77% of the sample is gold by mass (heating generates only a weight loss of the ligands¹¹,¹²). Molar mass of the ligands for one gold nanoparticle: \(M_L = M_{Au} \cdot (23/77) = 7414 \, g/mol\).

4) Number of ligands per particle: \(N_L = M_L/MW_L = 43\); \(MW_L [CH₃(CH₂)₈CH₂S] = 173 \, g/mol\) (AuNPs ⁸ were stabilized with decanethiol ligands).
Figure S1. $^1$H-NMR spectra of: a) decanethiol, b) AuNPs 8, c) 11-bromo-1-undecanethiol (7), d) AuNPs 9, e) AuNPs 3, f) G1-cyanobiphenyl alkyne 1, g) AuNPs 4-G1.
Figure S2. Thermal polarized optical micrographs of the textures displayed by 1: a) nematic phase (180°C), b) smectic A phase (165°C), c) unidentified mesophase (41°C) upon cooling the samples from the isotropic liquid.

Figure S3. Thermal polarized optical micrograph of the smectic A phase displayed by 2 (172°C) upon cooling the sample from the isotropic liquid.

Figure S4. Thermal polarized optical micrograph of the focal-conic fan texture displayed by 4-G2 (139°C) upon cooling the sample from the isotropic liquid.
Figure S5. Differential scanning thermograms of 4-G1 (left) and 4-G2 (right).

Figure S6. TG thermogram of 4-G1.

Figure S7. UV-vis spectra normalized at 393 nm of 8, 9, 3, 4-G1 and 4-G2 in CH₂Cl₂.
**Figure S8.** Left: TEM micrograph of 3 (scale bar = 10 nm). Particles diameter: 1.5 ± 0.5 nm. Right: Histogram showing the distribution of the sizes. Size and size distribution were estimated from an image containing 355 particles.

**Figure S9.** TEM image and the distribution of sizes of 4-G1 (scale bar = 10 nm). Particles diameter: 1.6 ± 0.6 nm. Size and size distribution were estimated from a micrograph of 705 particles.

**References.**