Electronic Supporting Information

Liquid-crystalline fullerene-gold nanoparticles

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Materials and intruments. For general information, see reference 1. Compounds **4**,[1] **7**[2] and gold nanoparticles **2**[3] were prepared following literature procedures. [60]Fullerene (99,9%) was purchased from MER Corporation, Tucson (AZ), USA. All other reagents were purchased from Sigma-Aldrich and used as received. All solvents were distilled prior to use. MALDI-TOF-MS: MS-service, Department of Chemistry, University of Fribourg. Elemental microanalysis: Mikroelementaranalytisches Laboratorium ETH – Zürich, Switzerland.

Abbreviations: Column chromatography = CC; 4-(dimethylamino)pyridinium *p*-toluenesulfonate = DPTS; N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide = EDC; 1,8-diazabicyclo[5,4,0]undec-7-ene = DBU; broad signal = br. s, δ in ppm.

Synthetic procedures and analytical data.

Compound 6. A mixture of 10-undecyn-1-ol (**5**) (301 mg, 1.79 mmol) and Meldrum acid (258 mg, 1.79 mmol) was heated at 95 °C for 5 hours (under Ar). The mixture was cooled to room temperature and evaporated to dryness. Compound **6** was obtained as a slightly yellow oil (430 mg, 95%). ^{1}H-NMR ($CDCl_3$): δ 4.19 (t, 2H, $C\mathit{H}_2O_2CCH_2CO_2H$), 3.45 (s, 2H, $O_2CC\mathit{H}_2CO_2H$), 2.22-2.15 (m, 2H, $HC{\equiv}CC\mathit{H}_2$), 1.94 (t, 1H, $\mathit{H}C{\equiv}C$), 1.72-1.65 (m, 2H, $C\mathit{H}_2CH_2O_2CCH_2CO_2H$), 1.58-1.46 (m, 2H, $HC{\equiv}CCH_2C\mathit{H}_2$), 1.43-1.26 (m, 10H, $\mathit{H}_{\mathrm{aliph.}}$). MS (ESI+): 277.50 [calcd. $(M+Na)^+$ = 277.05].

Compound 8. A mixture of **7** (682 mg, 0.50 mmol) and **6** (140 mg, 0.55 mmol) in CH_2Cl_2 (50 mL) was cooled to 0°C. DPTS (118 mg, 0.40 mmol) and EDC (210 mg, 1.35 mmol) were added. The mixture was allowed to warm up to room temperature, stirred for 18 hours (under Ar), washed (H_2O), dried ($MgSO_4$) and evaporated to dryness. Purification of the solid residue by CC (CH_2Cl_2 then CH_2Cl_2/AcOEt 100:2) and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) gave pure **8** (610 mg, 76%). ^{1}H-NMR (CD_2Cl_2): δ 8.55 (t, 1H, $\mathit{H}_{\mathrm{arom.}}$), 8.13 and 8.12 (2d, 6H, $\mathit{H}_{\mathrm{arom.}}$), 8.04 (d, 2H, $\mathit{H}_{\mathrm{arom.}}$), 7.78-7.70 (d, 8H, $\mathit{H}_{\mathrm{arom.}}$), 7.67 (d, 4H, $\mathit{H}_{\mathrm{arom.}}$), 7.32 (d, 4H, $\mathit{H}_{\mathrm{arom.}}$), 7.0 (d, 2H, $\mathit{H}_{\mathrm{arom.}}$), 6.98 (d, 4H, $\mathit{H}_{\mathrm{arom.}}$), 4.34 (t, 4H, $ArCO_2C\mathit{H}_2$), 4.11 and 4.10 (2t, 4H, $C\mathit{H}_2O_2CH_2CO_2C\mathit{H}_2$), 4.08-4.00 (m, 6H, $C\mathit{H}_2OAr$), 3.34 (s, 2H, $O_2CC\mathit{H}_2CO_2$), 2.18-2.14 (m, 2H, $HC{\equiv}CC\mathit{H}_2$), 1.95 (t, 1H, $\mathit{H}C{\equiv}C$), 1.87-1.73 (m, 10H, $C\mathit{H}_2CH_2O$), 1.68-1.58 (m, 4H, $C\mathit{H}_2CH_2OCO$), 1.55-1.26 (m, 48H, $\mathit{H}_{\mathrm{aliph.}}$). ^{13}C-NMR ($CD_2Cl_2$): δ 166.71, 164.99, 164.76, 164.53, 164.00, 163.81, 151.73, 151.27, 144.71, 136.72, 132.72, 132.53, 132.35, 132.25, 128.35, 127.71, 127.60, 127.19, 122.63, 121.30, 120.84, 118.87, 114.49, 114.41, 111.08, 84.76, 68.55, 68.51, 67.97, 65.83, 65.59, 41.75, 29.55, 29.51, 29.42, 29.40, 29.31, 29.28, 29.22, 29.16, 29.08, 28.79, 28.70, 28.60, 28.55, 26.05, 26.02, 26.01, 25.86, 25.84, 18.35. MALDI-TOF MS (+): 1624.10; calcd.

$(M+Na)^+$ = 1623.78. Anal. Calcd for $C_{99}H_{112}N_2O_{17}$ (1601.98): C, 74.23; H, 7.05; N, 1.75. Found. C, 74.33; H, 7.02; N, 1.82.

Compound 3. To a solution of C_{60} (158.4 mg, 0.22 mmol) in toluene (330 mL), were added **8** (320 mg, 0.20 mmol), iodine (61 mg, 0.24 mmol) and DBU (61 mg, 0.40 mmol). The mixture was stirred at room temperature for 4 hours and filtered through a silica gel plug eluting with toluene to remove the excess of C_{60} and then with AcOEt to recover compound **3**. The solvent was evaporated to dryness. Purification of the solid residue by CC [Biobeads SX-1 (toluene) and SiO_2 (CH_2Cl_2/AcOEt 100:0 to 100:1)] and precipitation (dissolution in CH_2Cl_2 and precipitation by pouring the solution into MeOH) gave pure **3** (184 mg, 40%) ^{1}H-NMR (CD_2Cl_2)*:* δ 8.55 (t, 1H, $H_{arom.}$), 8.13 (d, 6H, $H_{arom.}$), 8.05 (d, 2H, $H_{arom.}$), 7.77-7.70 (m, 8H, $H_{arom.}$), 7.67 (d, 4H, $H_{arom.}$), 7.32 (d, 4H, $H_{arom.}$), 6.99 (d, 6H, $H_{arom.}$), 4.48 and 4.47 [2t, 4H, $C_{60}C(CO_2CH_2)_2$], 4.34 (t, 4H, $ArCO_2CH_2$), 4.04 (t, 6H, CH_2OAr), 2.19-2.14 (m, 2H, $HC{\equiv}CCH_2$), 1.95 (t, 1H, $HC{\equiv}C$), 1.88-1.73 (m, 14H, CH_2CH_2OAr and $CO_2CH_2CH_2$), 1.51-1.25 (m, 48H, $H_{aliph.}$). ^{13}C-NMR (CD_2Cl_2): δ 164.97, 164.74, 164.51, 163.98, 163.80, 163.55, 151.72, 151.24, 145.66, 145.57, 145.25, 145.17, 144.85, 144.71, 144.68, 144.58, 143.85, 143.08, 143.00, 142.97, 142.21, 141.91, 140.96, 139.06, 138.93, 136.72, 132.72, 132.52, 132.38, 132.24, 128.34, 127.71, 127.61, 127.18, 122.62, 121.29, 120.84, 118.86, 114.50, 114.40, 111.06, 84.74, 71.89, 68.54, 68.50, 68.02, 67.53, 65.82, 29.62, 29.58, 29.54, 29.51, 29.46, 29.39, 29.31, 29.26, 29.15, 29.05, 28.83, 28.70, 28.61, 26.11, 26.05, 26.00, 18.37. MALDI-TOF MS (+): 2342.77; calcd. $(M+Na)^+$ = 2341.78. UV-vis [CH_2Cl_2, λ_{max} in nm (ε in $L{\cdot}mol^{-1}{\cdot}cm^{-1}$)]: 427 (2985), 490 (1658), 688 (199). IR (KBr, υ in cm^{-1}): 2226 (nitrile), 1725 (ester). Anal. Calcd for $C_{159}H_{110}N_2O_{17}$ (2320.62): C, 82.29; H, 4.78; N, 1.21. Found. C, 82.37; H, 4.68; N, 1.27.

Synthesis of AuNPs 2. The synthesis is adapted from a literature procedure.[1,3] ^{1}H-NMR (CD_2Cl_2): δ 3.26 (br. s, CH_2N_3), 1.29 (br. s, $H_{aliph.}$), 0.91 (br. s, CH_3). UV-vis (CH_2Cl_2): weak plasmon band at 520 nm. IR (KBr, υ in cm^{-1}): 2095 (N_3). TEM: 1.5 ± 0.4 nm.

Synthesis of AuNPs 1. A solution of AuNPs **2** (20 mg, 0.0120 mmol of azide group) in THF (2 mL) was added to a solution of **3** (8.35 mg, 0.0036 mmol) and **4** (37.88 mg, 0.0324 mmol) in THF (2 mL). At 0 °C, a solution of sodium ascorbate (28.50 mg, 0.1440 mmol) in water (0.5 mL) was added into a solution of anhydrous $CuSO_4$ (11.52 mg, 0.0720 mmol) in water (0.5 mL). The copper solution was then added dropwise into the THF solution. The mixture was stirred at 30 °C for 3 days (under Ar). THF was removed under vacuum and the residue was dissolved in CH_2Cl_2. The latter organic phase was washed with an aqueous NH_3 solution (1M) and with H_2O. To remove the alkyne derivatives **3** and **4**, the organic phase was then purified by ultrafiltration (CH_2Cl_2). Removal of the solvent under vacuum gave pure **1** (mass yield: 60%). **Data of 1**. ^{1}H-NMR (CD_2Cl_2): δ 8.51 (br. s, $H_{arom.}$), 8.18-7.95 (br. s, $H_{arom.}$), 7.89 (br. s, $H_{arom.}$), 7.79-7.45 (br. s, $H_{arom.}$), 7.28 (br. s, $H_{arom.}$), 6.94 (br. s, $H_{arom.}$), 4.43 [br. s, $C_{60}C(CO_2CH_2)_2$], 4.31 (br. s, $ArCO_2CH_2$), 3.99 (br. s, CH_2OAr), 3.07 (br. s, $CH_2CH_2CO_2$), 3.00 (br. s, $CH_2CH_2CO_2$), 1.75 (br. s, CH_2CH_2O et $CH_2CH_2O_2C$), 1.46-1.10 (br. s, $H_{aliph.}$), 0.85 (br. s, CH_3). UV-vis (CH_2Cl_2, λ_{max} in nm): 427 (weak). IR (KBr, υ in cm^{-1}): 2225 (nitrile), 1725 (ester). TEM: 1.5 ± 0.4 nm.

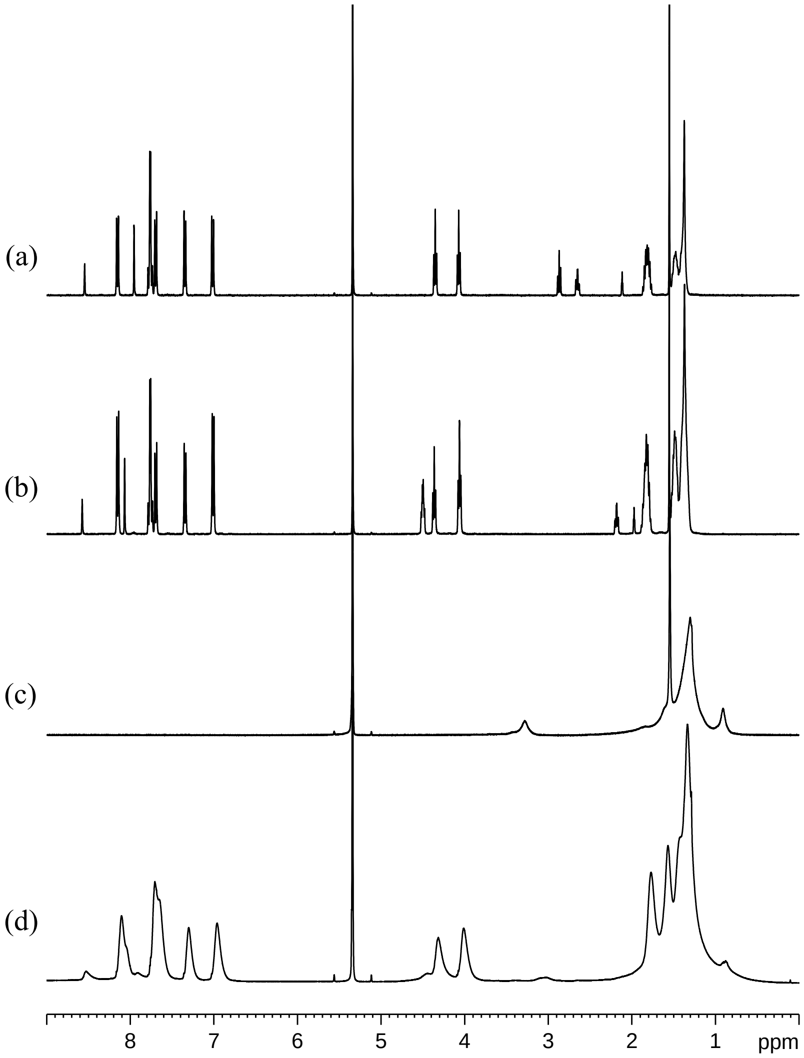

Figure S1. ^{1}H-NMR spectra of **4** (a), **3** (b), **2** (c) and **1** (d) in CD_2Cl_2.

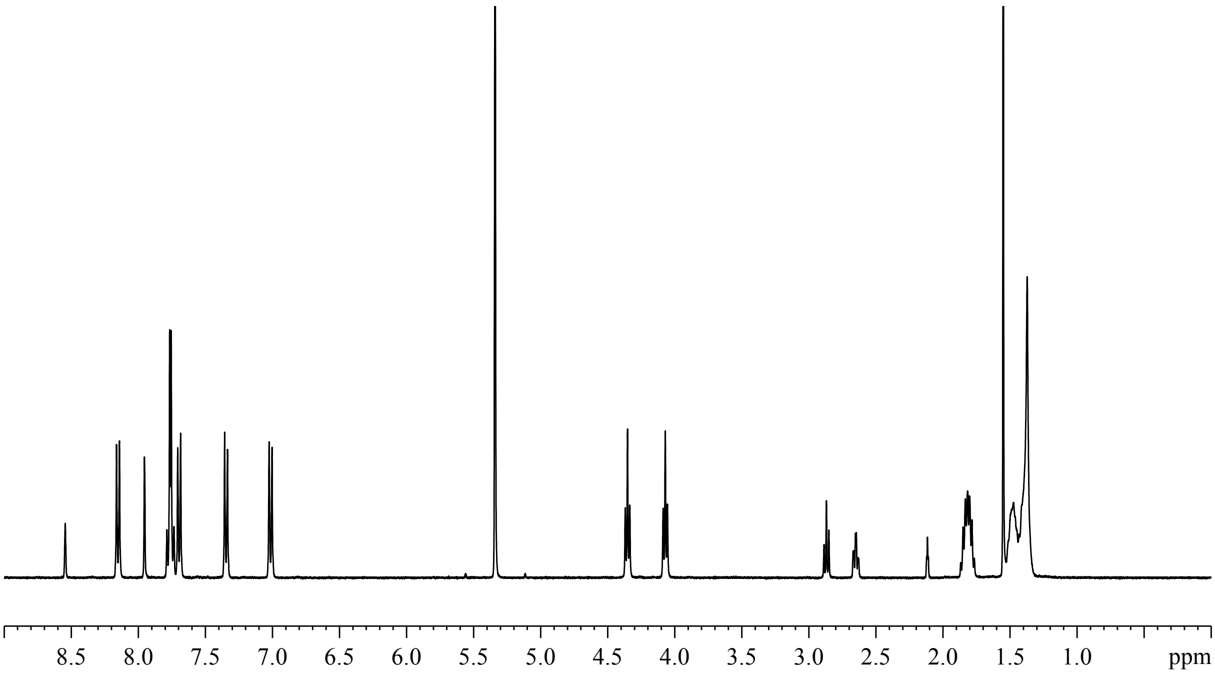

Figure S2. ^{1}H-NMR spectrum of **4** in CD_2Cl_2.

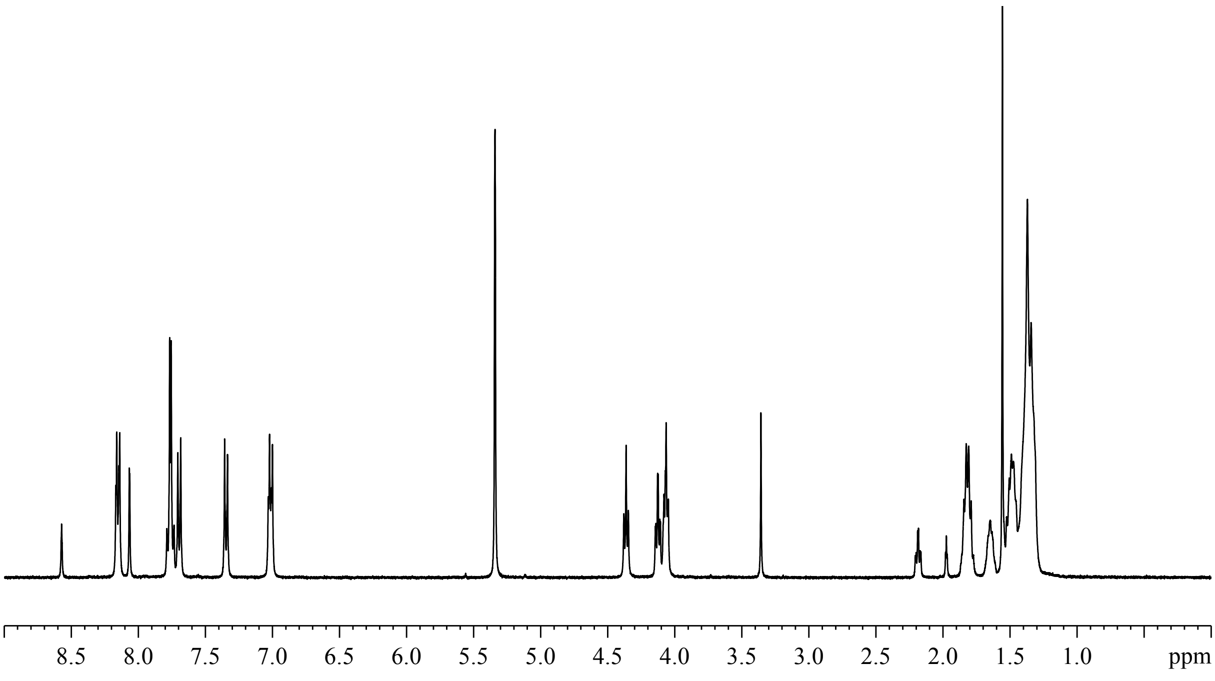

Figure S3. ^{1}H-NMR spectrum of **8** in CD_2Cl_2.

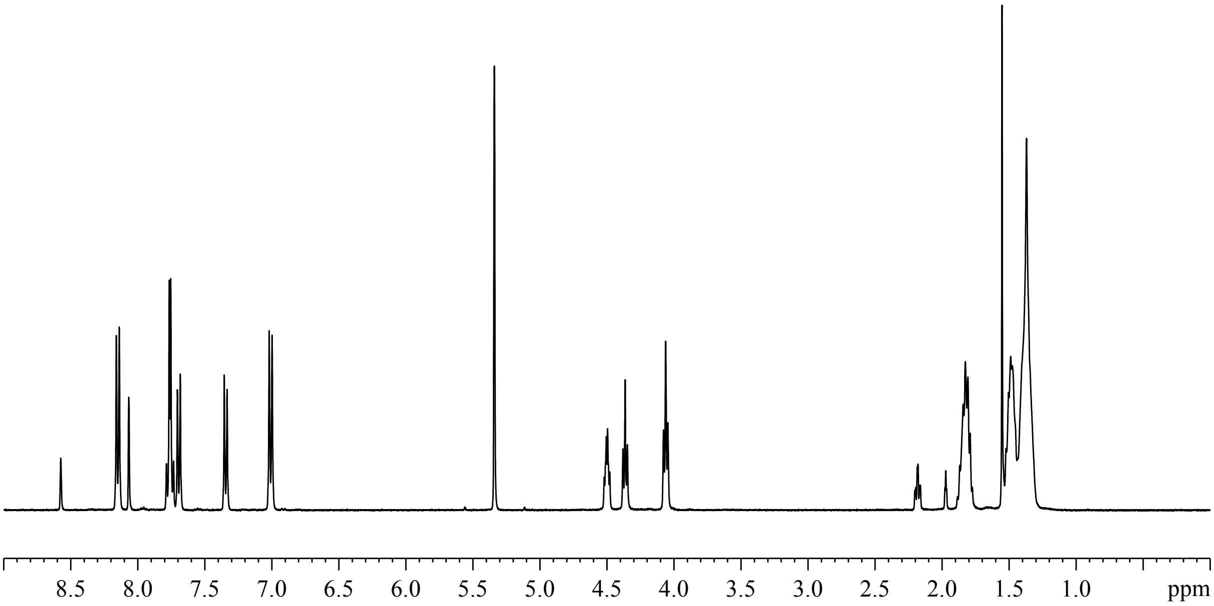

Figure S4. ^{1}H-NMR spectrum of **3** in CD_2Cl_2.

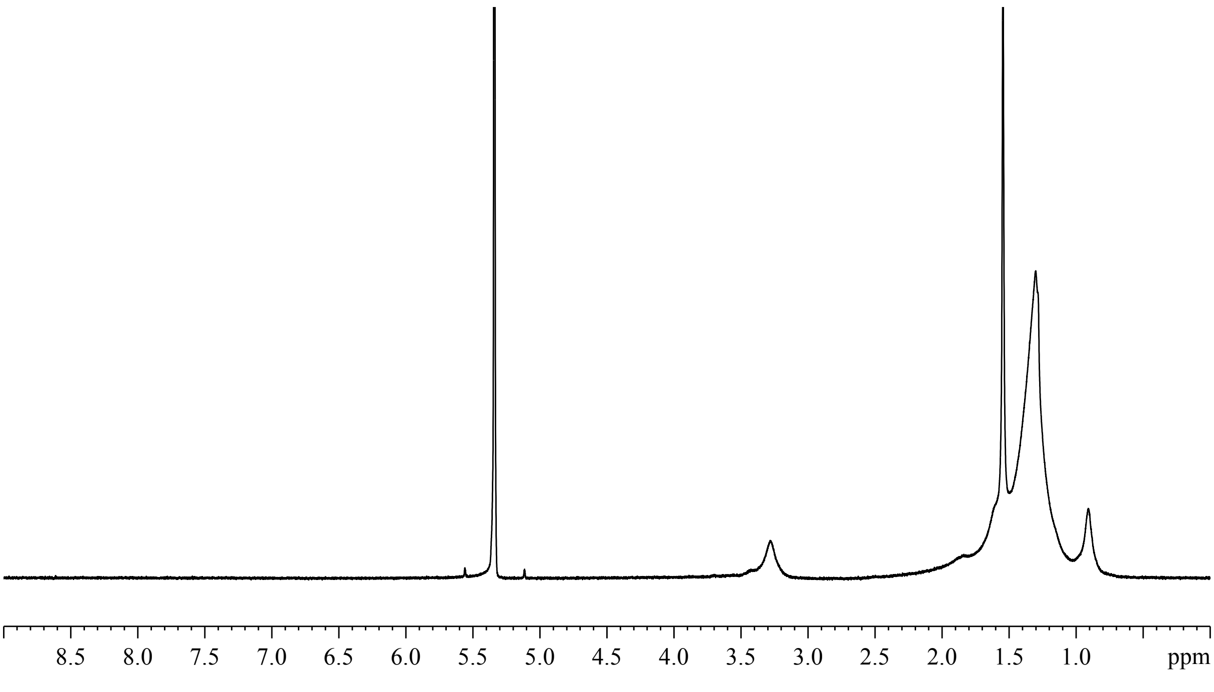

Figure S5. ^{1}H-NMR spectrum of AuNPs **2** in CD_2Cl_2.

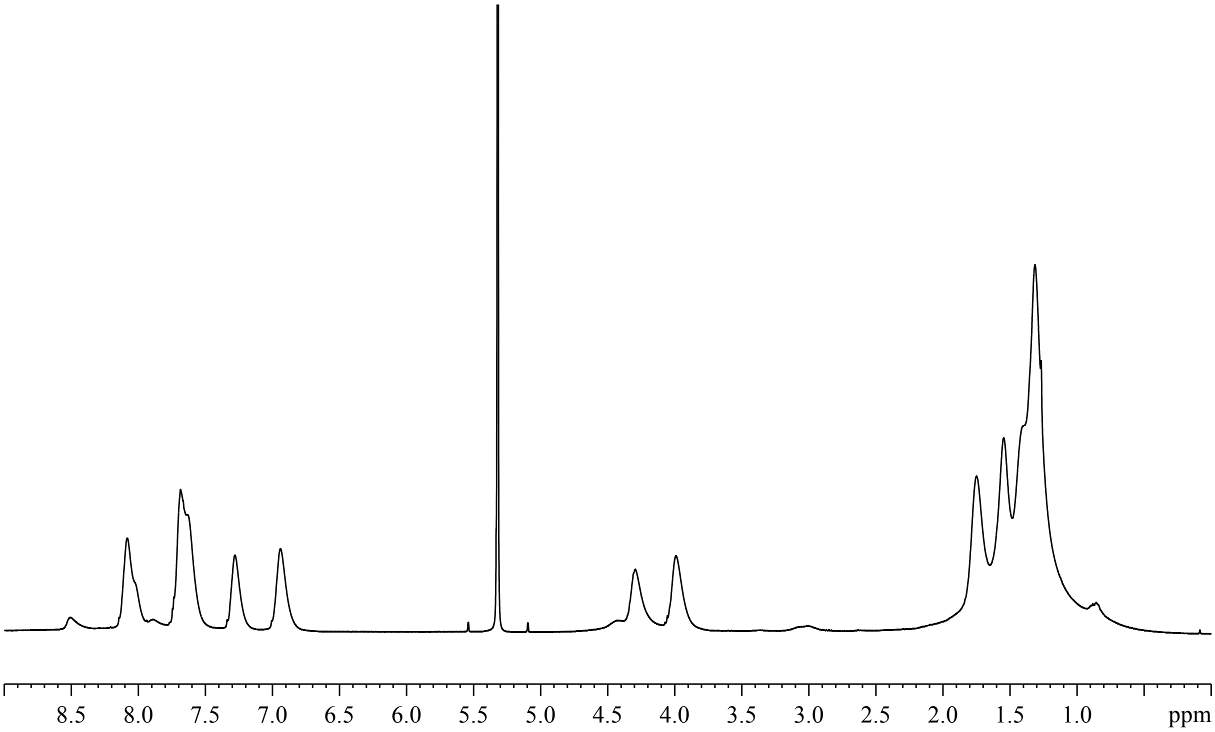

Figure S6. ^{1}H-NMR spectrum of **1** in CD_2Cl_2.

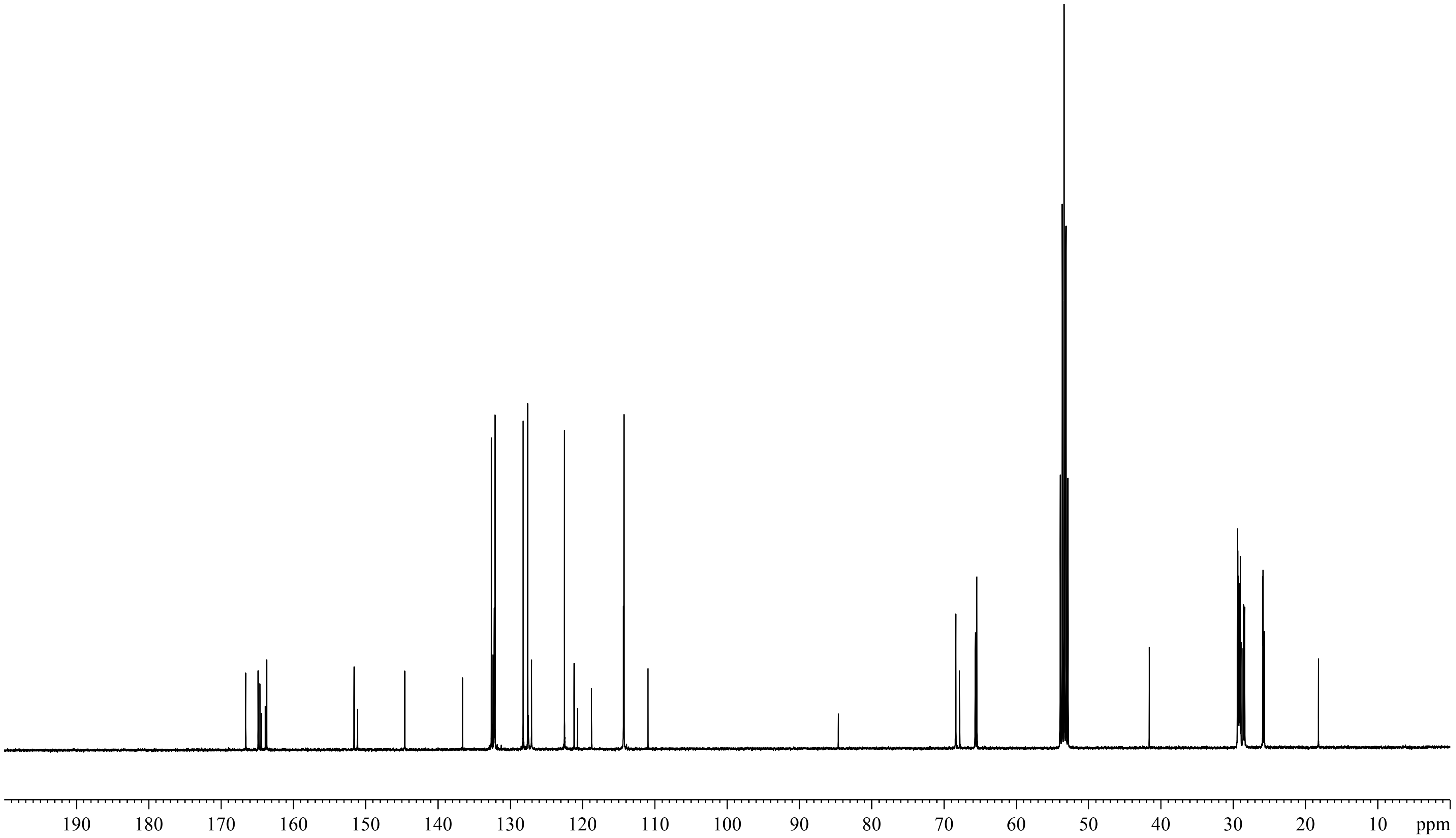

Figure S7. ^{13}C-NMR spectrum of **8** in CD_2Cl_2.

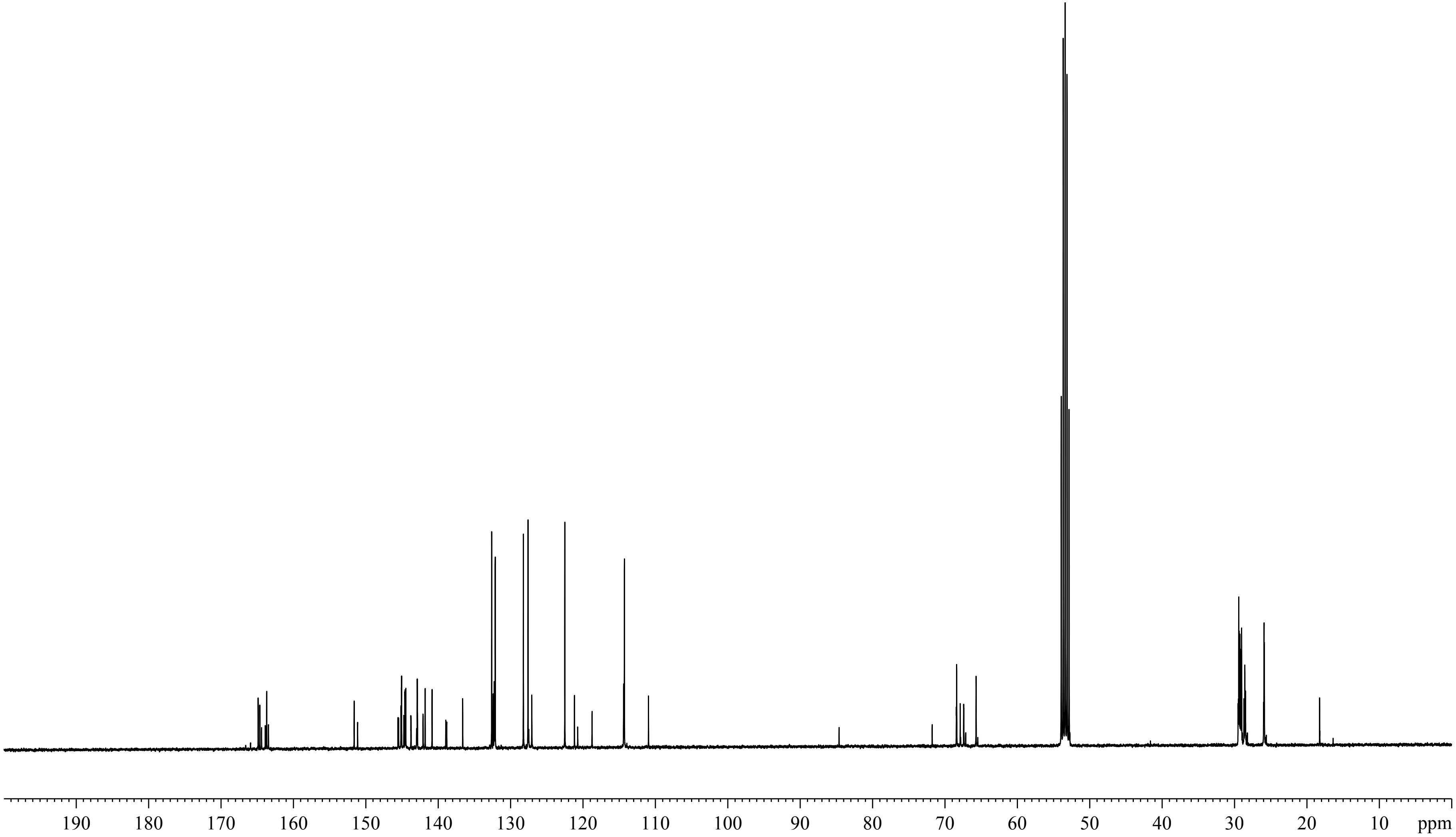

Figure S8. ^{13}C-NMR spectrum of **3** in CD_2Cl_2.

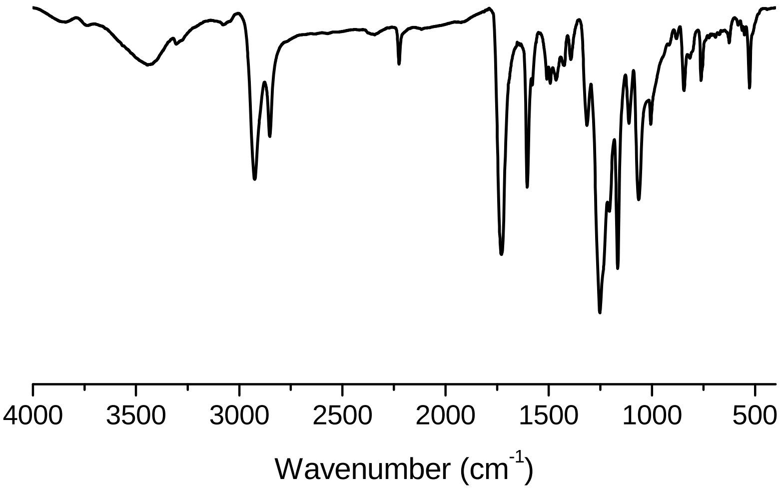

Figure S9. FT-IR spectrum (KBr) of **3**.

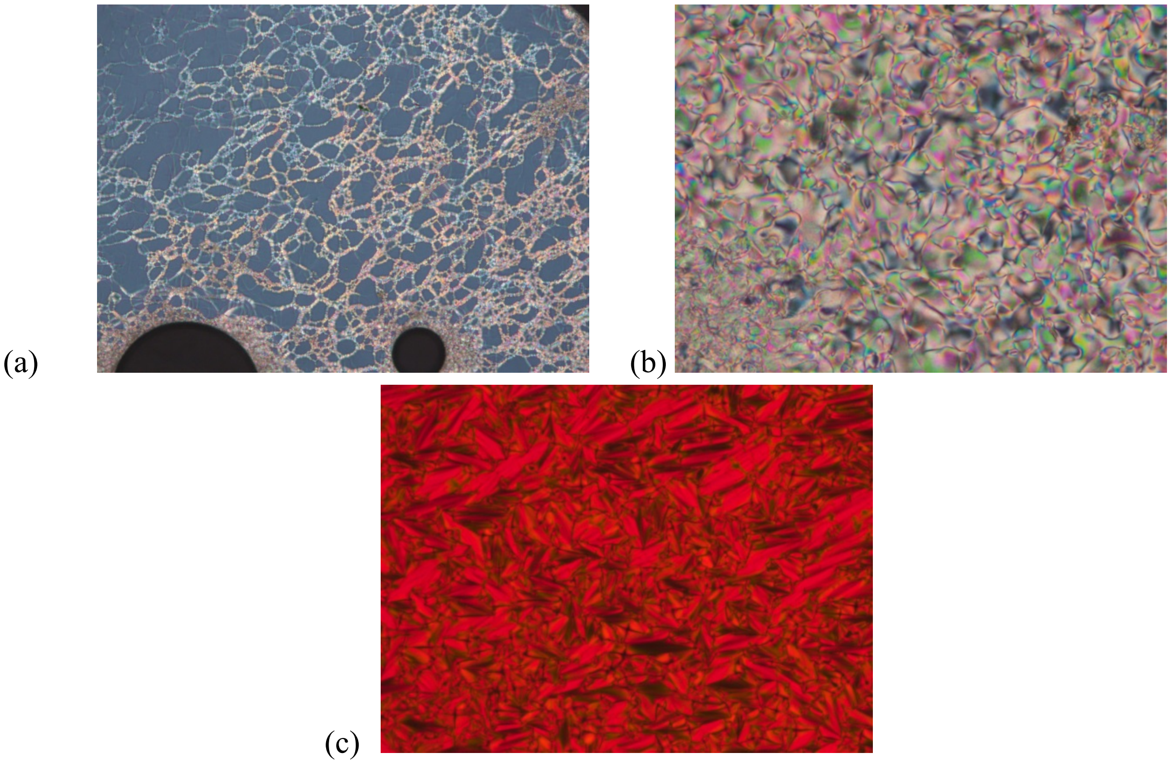

Figure S10. Thermal polarized optical micrographs: (a) smectic A phase displayed by compound **8** at 110 °C, (b) nematic phase displayed by compound **8** at 147 °C, and (c) smectic A phase displayed by compound **3** at 137°C.

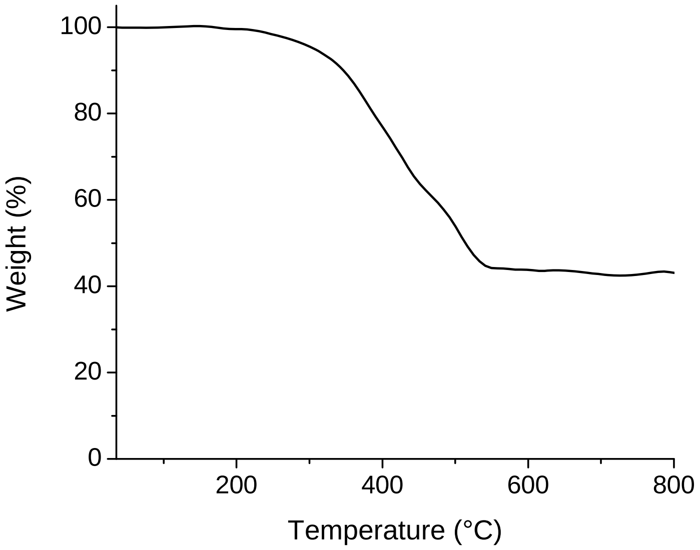

Figure S11. TG curve of AuNPs **1** (10 °C·min^{-1}).

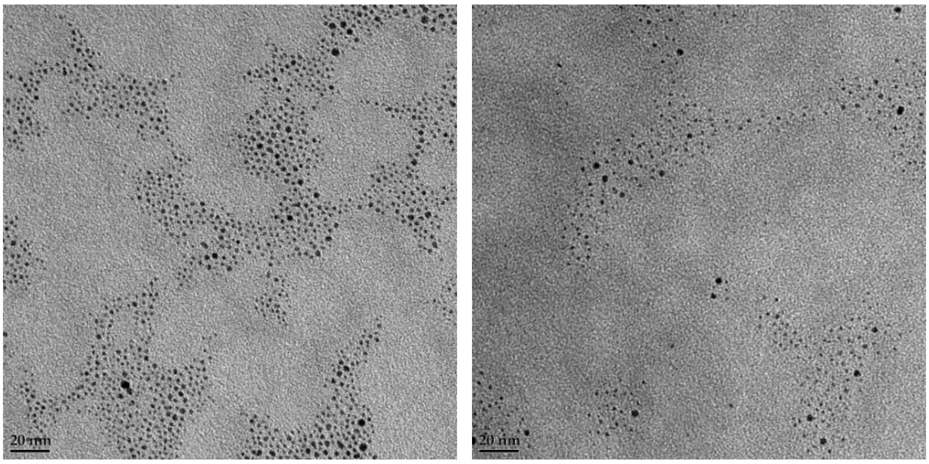

Figure S12. TEM images of **2** (left) and **1** (right).

Notes and references.

1. S. Mischler, S. Guerra and R. Deschenaux*,* *Chem. Commun.*, 2012, **48**, 2183.
2. S. Campidelli, J. Lenoble, J. Barberá, F. Paolucci, M. Marcaccio, D. Paolucci and R. Deschenaux, *Macromolecules*, 2005, **38**, 7915.
3. E. Boisselier, L. Salmon, J. Ruiz and D. Astruc, *Chem. Commun.*, 2008, 5788.