Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012

Electronic Supporting Information

Design of Liquid-Crystalline Gold Nanoparticles by Click Chemistry

Sylvain Mischler, Sebastiano Guerra and Robert Deschenaux*

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, 2000 Neuchâtel, Switzerland.

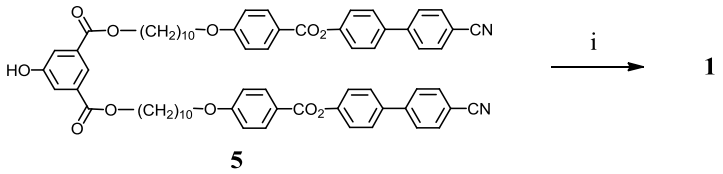
Materials. For the click reactions, the solvents were degassed prior to use. Compounds **5**,[1] **6**,[1] **7**,[2,3] gold nanoparticles stabilized with decanethiol (**8**),[4] and bromo-functionalized gold nanoparticles (**9**)[5-7] were prepared following literature procedures.

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 N_2 pressure. ^{1}H and ^{13}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 CH_2Cl_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: Mikroelementaranalytisches Laboratorium EHT-Zürich.

Liquid-crystalline properties. Transition temperatures (onset point) and enthalpies: differential scanning *Mettler DSC 822^e* calorimeter, under N_2/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; *N,N'*-dicyclohexylcarbodiimide = DCC; 4-pyrrolidinopyridine = 4-ppy; column chromatography = CC; gold nanoparticles = AuNPs; broad singlet = br. s.

Synthesis of compound 1.

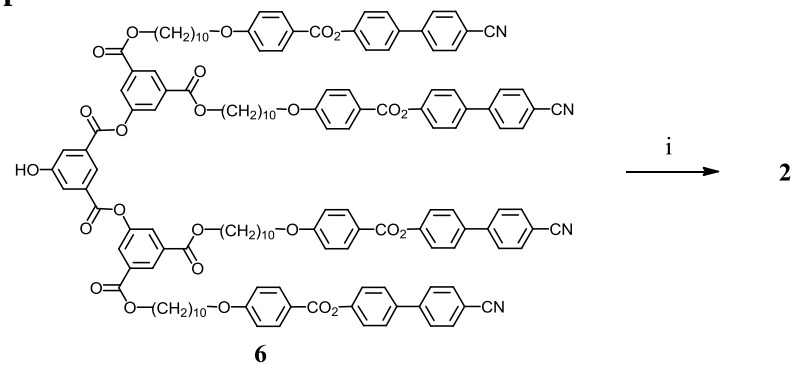


Scheme S1. *Reagents and conditions:* (i) 4-pentynoic acid, DPTS, DCC, 4-ppy, CH_2Cl_2, room temperature, 24 h.

To a solution of **5** (1.00 g, 0.92 mmol) and 4-pentynoic acid (108 mg, 1.10 mmol) in dry CH_2Cl_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 (CH_2Cl_2). Dissolution of the solid residue in a minimum of CH_2Cl_2 and precipitation from CH_3OH gave compound **1** as a white solid (670 mg, 62 %). ^{1}H-NMR (δ in ppm, $CDCl_3$, 400 MHz): 8.57 (t, 1H, $H_{arom.}$); 8.16 (d, 4H, $H_{arom.}$); 7.95 (d, 2H, $H_{arom.}$); 7.73 and 7.70 (2d, 8H, $H_{arom.}$); 7.64 (d, 4H, $H_{arom.}$); 7.33 (d, 4H, $H_{arom.}$); 6.98 (d, 4H, $H_{arom.}$); 4.35 (t, 4H, CH_2O_2C); 4.05 (t, 4H, CH_2O); 2.86 (t, 2H, CH_2CO_2);

2.65 (td, 2H, C*H*$_2$C≡C); 2.06 (t, 1H, *H*C≡C); 1.86-1.75 (m, 8H, C*H*$_2$CH$_2$O and C*H*$_2$CH$_2$O$_2$C); 1.50-1.35 (m, 24H, *H*$_{aliph.}$). ^{13}C-NMR (δ in ppm, CD_2Cl_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. Calcd for $C_{73}H_{72}N_2O_{12}$ (1169.38 g·mol^{-1}): C 74.98, H 6.21, N 2.40. Found: C 74.93, H 6.12, N 2.37.

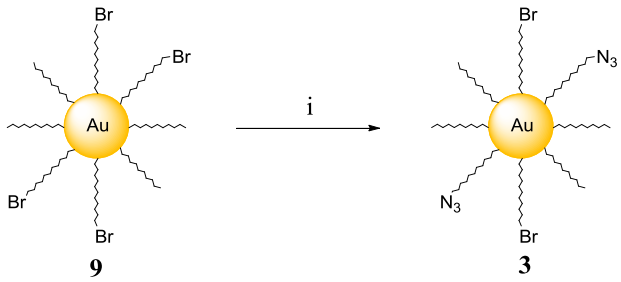
Synthesis of compound 2.



Scheme S2. *Reagents and conditions:* (i) 4-pentynoic acid, DPTS, DCC, 4-ppy, CH_2Cl_2, room temperature, 24 h.

From **6** (1.00 g, 0.43 mmol) and 4-pentynoic 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_2Cl_2, 400 MHz): 8.91 (t, 1H, *H*$_{arom.}$); 8.64 (t, 2H, *H*$_{arom.}$); 8.24 (d, 2H, *H*$_{arom.}$); 8.14 (d, 8H, *H*$_{arom.}$); 8.10 (d, 4H, *H*$_{arom.}$); 7.72 and 7.70 (2d, 16H, *H*$_{arom.}$); 7.63 (d, 8H, *H*$_{arom.}$); 7.32 (d, 8H, *H*$_{arom.}$); 6.97 (d, 8H, *H*$_{arom.}$); 4.36 (t, 8H, C*H*$_2$O$_2$C); 4.04 (t, 8H, C*H*$_2$O); 2.90 (t, 2H, C*H*$_2$CO$_2$); 2.68 (td, 2H, C*H*$_2$C≡C); 2.08 (t, 1H, *H*C≡C); 1.83-1.78 (m, 16H, C*H*$_2$CH$_2$O and C*H*$_2$CH$_2$O$_2$C); 1.47-1.34 (m, 48H, *H*$_{aliph.}$). ^{13}C-NMR (δ in ppm, CD_2Cl_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. Calcd for $C_{149}H_{142}N_4O_{26}$ (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.

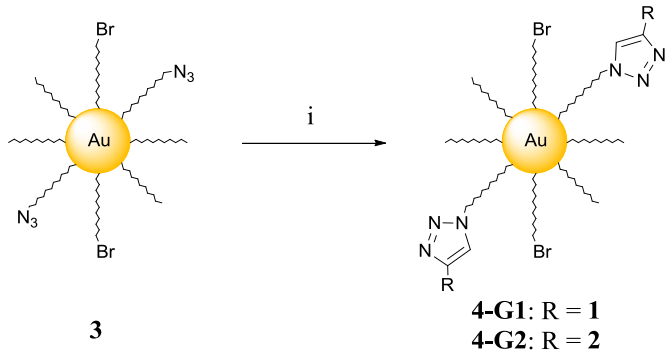


Scheme S3. *Reagents and conditions:* (i) NaN_3, CH_2Cl_2/DMSO (1:1), room temperature, 2 d.

The synthesis is adapted from a literature procedure.[6] AuNPs **9** were dissolved in CH_2Cl_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_2Cl_2, 400 MHz): 3.41 (br. s, C*H*$_2$Br); 3.26 (br. s, C*H*$_2$N$_3$); 1.86 (br. s, C*H*$_2$CH$_2$Br); 1.28 (br. s, *H*$_{aliph.}$); 0.89 (br. s, C*H*$_3$). UV-vis: weak plasmon band at 520 nm. IR (*v* in cm^{-1}, KBr): 2095 (N_3).

Synthesis of AuNPs 4-G1 and 4-G2.



Scheme S4. *Reagents and conditions:* (i) **1** or **2**, $CuSO_4{\cdot}5H_2O$, sodium ascorbate, THF/H_2O (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 $CuSO_4{\cdot}5H_2O$ (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_2O ratio. The mixture was stirred under Ar at 30°C for 3 days. THF was removed under vacuum. CH_2Cl_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_2O), 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_2Cl_2, 15 x 50 mL). The AuNPs were redissolved with CH_2Cl_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_2Cl_2, 400 MHz): 8.49 (br. s, *H*$_{arom.}$); 8.11 (br. s, *H*$_{arom.}$); 7.90 (br. s, *H*$_{arom.}$); 7.67 (br. s, *H*$_{arom.}$); 7.30 (br. s, *H*$_{arom.}$); 6.97 (br. s, *H*$_{arom.}$); 4.30 (br. s, C*H*$_2$O$_2$C and C*H*$_2$N); 4.02 (br. s, C*H*$_2$O); 3.41 (br. s, C*H*$_2$Br); 3.09 (br. s, CH$_2$C*H*$_2$CO$_2$); 3.02 (br. s, C*H*$_2$CH$_2$CO$_2$); 1.77 (br. s, C*H*$_2$CH$_2$Br, C*H*$_2$CH$_2$O and C*H*$_2$CH$_2$O$_2$C); 1.32 (br. s, *H*$_{aliph.}$); 0.89 (br. s, C*H*$_3$). 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 (*v* in cm^{-1}, KBr): 2225 (C≡N), 1725 (C=O). **Data of 4-G2**. ^{1}H-NMR (δ in ppm, CD_2Cl_2, 400 MHz): 8.85 (br. s, *H*$_{arom.}$); 8.58 (br. s, *H*$_{arom.}$); 8.09 (br. s, *H*$_{arom.}$); 7.68 (br. s, *H*$_{arom.}$); 7.28 (br. s, *H*$_{arom.}$); 6.94 (br. s, *H*$_{arom.}$); 4.26 (br. s, C*H*$_2$O$_2$C and C*H*$_2$N); 3.98 (br. s, C*H*$_2$O); 3.41 (br. s, C*H*$_2$Br); 3.26 (br. s, C*H*$_2$N$_3$); 3.07 (br. s, CH$_2$C*H*$_2$CO$_2$ and C*H*$_2$CH$_2$CO$_2$); 1.75 (br. s, C*H*$_2$CH$_2$Br, C*H*$_2$CH$_2$O and

C*H*$_2$CH$_2$O$_2$C); 1.30 (br. s, *H*$_{aliph.}$); 0.89 (br. s, C*H*$_3$). UV-vis: weak plasmon band at 520 nm. IR (*v* in cm^{-1}, KBr): 2095 (N$_3$), 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 ligands[11,12]). 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 [$CH_3(CH_2)_8CH_2S$] = 173 g/mol (AuNPs **8** were stabilized with decanethiol ligands).

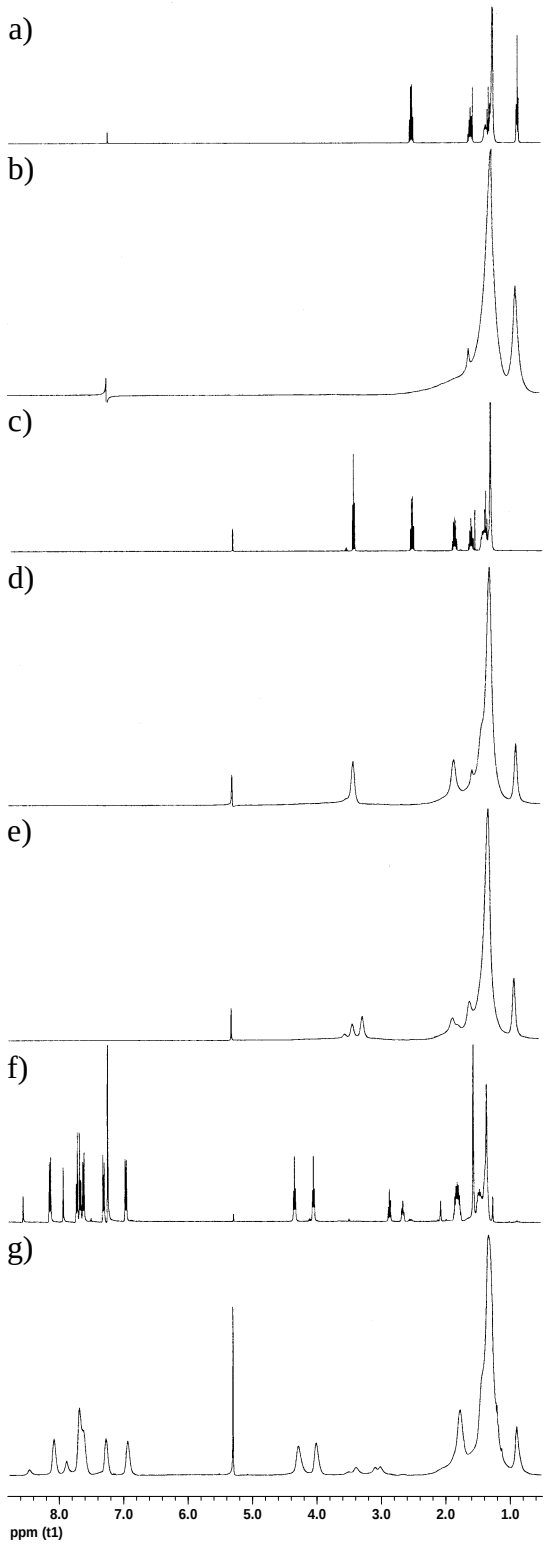
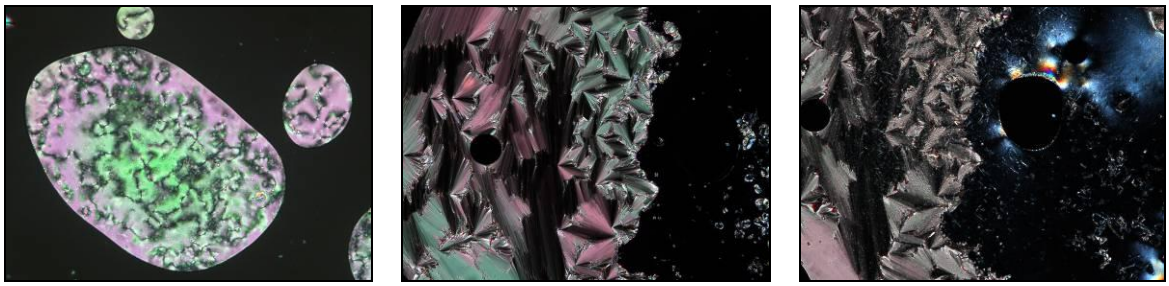


Figure S1. ^{1}H-NMR spectra of: a) decanethiol, b) AuNPs **8**, c) 11-bromo-1-undecanethiol (**7**), d) AuNPs **9**, e) AuNPs **3**, f) G1-cyanobiphenyl alkyne **1**, g) AuNPs **4-G1**.



a) b) c)

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.

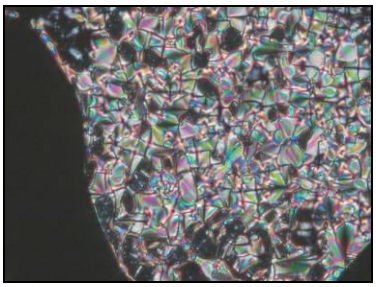


Figure S3. Thermal polarized optical micrograph of the smectic A phase displayed by **2** (172°C) upon cooling the sample from the isotropic liquid.

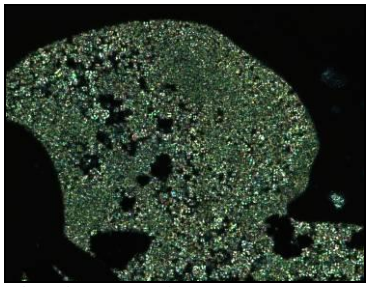


Figure **S4.** Thermal polarized optical micrograph of the focal-conic fan texture displayed by **4-G2** (139°C) upon cooling the sample from the isotropic liquid.

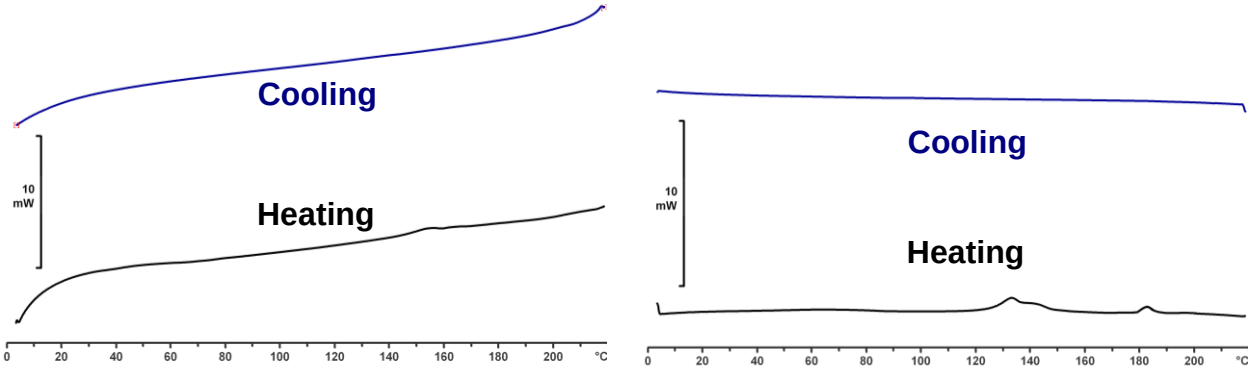


Figure S5. Differential scanning thermograms of **4-G1** (left) and **4-G2** (right).

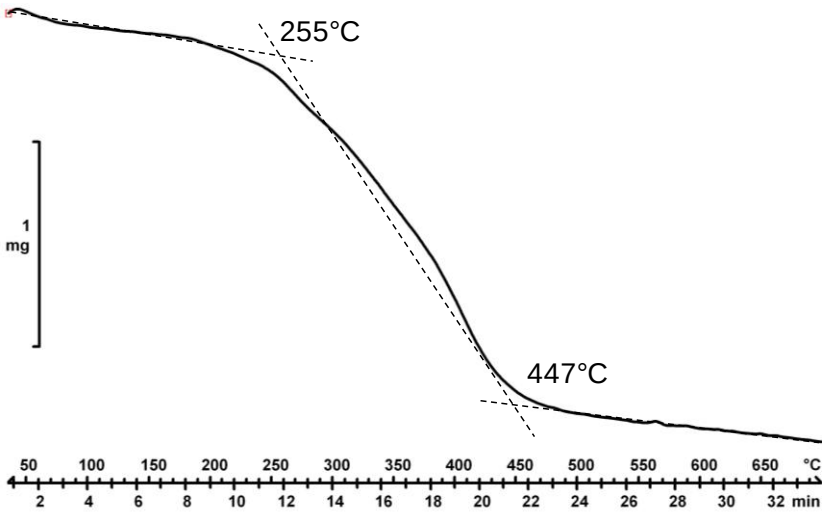


Figure S6. TG thermogram of **4-G1**.

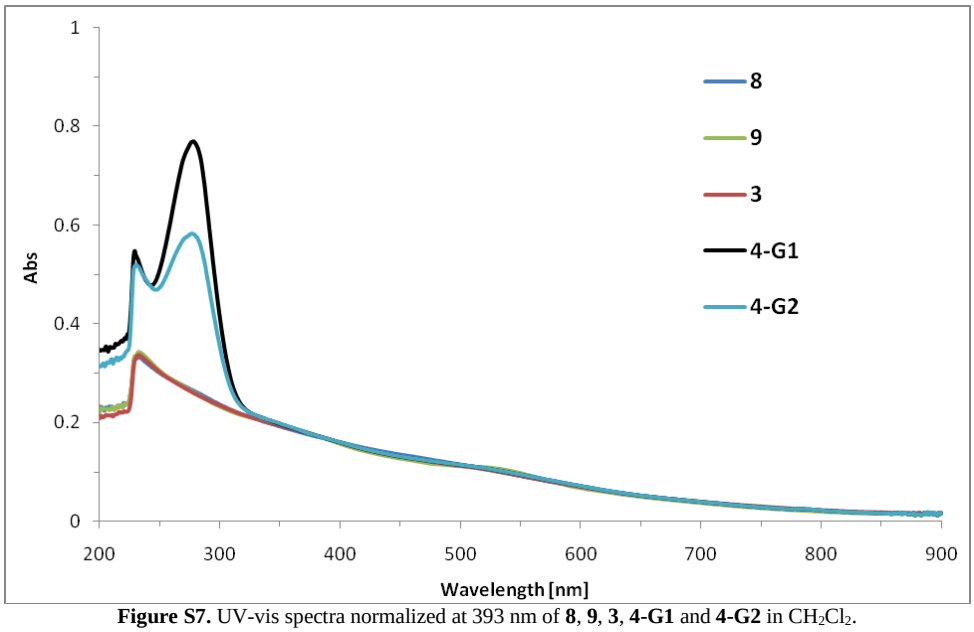


Figure S7. UV-vis spectra normalized at 393 nm of **8**, **9**, **3**, **4-G1** and **4-G2** in CH_2Cl_2.

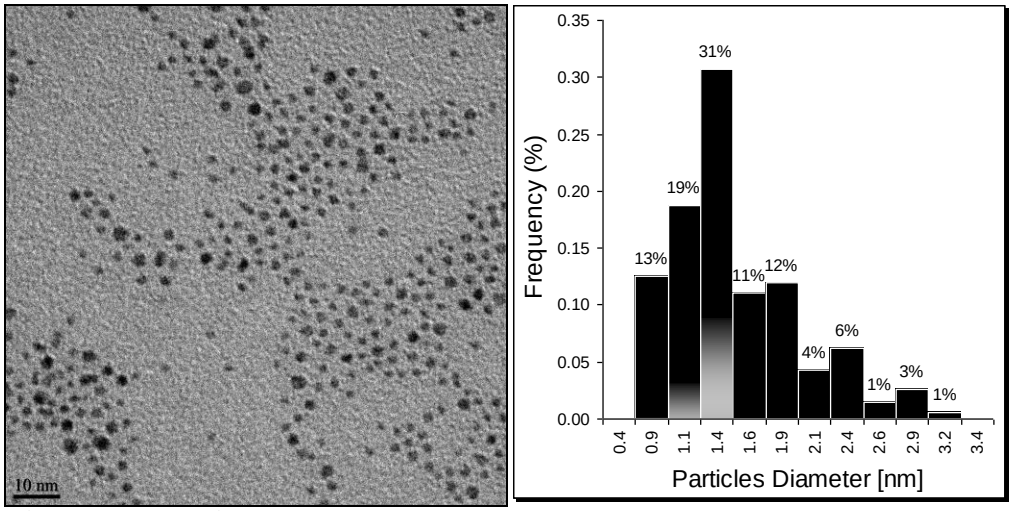


Figure S8. Left: TEM micrograph of **3** (scale bar = 10 nm). Particles diameter: 1.5 ± 0.5 nm. Right: Histogram showing the distribution of the sizes. Size and size distribution were estimated from an image containing 355 particles.

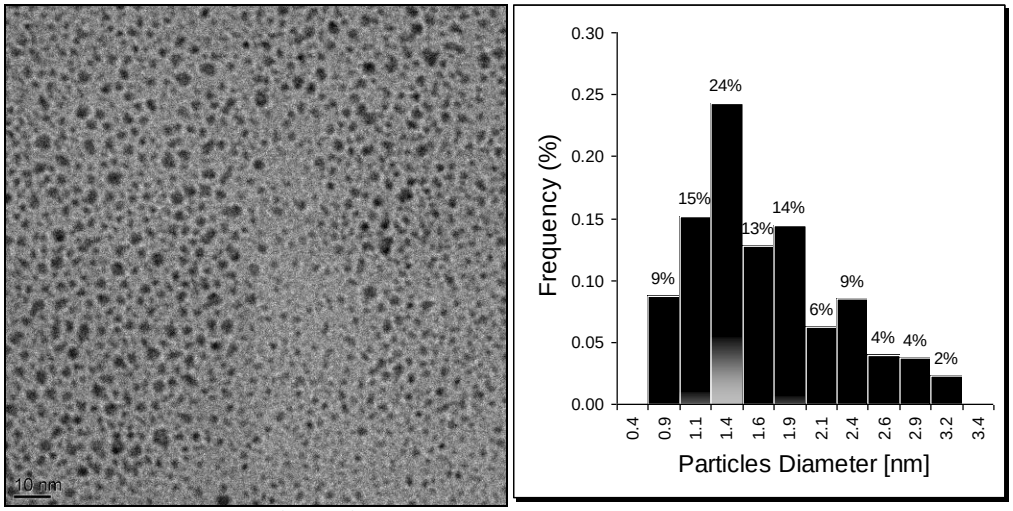


Figure S9. TEM image and the distribution of sizes of **4-G1** (scale bar = 10 nm). Particles diameter: 1.6 ± 0.6 nm. Size and size distribution were estimated from a micrograph of 705 particles.

References.

1. B. Dardel, D. Guillon, B. Heinrich and R. Deschenaux, *J. Mater. Chem.*, 2001, **11**, 2814.
2. A. R. Rothrock, R. L. Donkers and M. H. Schoenfisch, *J. Am. Chem. Soc.*, 2005, **127**, 9362.
3. W. J. Sommer and M. Weck, *Langmuir*, 2007, **23**, 11991.
4. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.
5. A. Kassam, G. Bremner, B. Clark, G. Ulibarri and R. B. Lennox, *J. Am. Chem. Soc.*, 2006, **128**, 3476.
6. E. Boisselier, L. Salmon, J. Ruiz and D. Astruc, *Chem. Commun.*, 2008, 5788.
7. D. A. Fleming, C. J. Thode and M. E. Williams, *Chem. Mater.*, 2006, **18**, 2327.
8. Y. Yamamoto and H. Hori, *Rev. Adv. Mater. Sci.*, 2006, **12**, 23.
9. A. S. Barnard and L. A. Curtiss, *Chem. Phys. Chem.*, 2006, **7**, 1544.
10. D. V. Leff, P. C. Ohara, J. R. Heath and W. M. Gelbart, *J. Phys. Chem.*, 1995, **99**, 7036.
11. H. Tan, T. Zhan and W. Y. Fan, *J. Phys. Chem. B*, 2006, **110**, 21690.
12. A. Badia, W. Gao, S. Singh, L. Demers, L. Cuccia and L. Reven, *Langmuir*, 1996, **12**, 1262.