Electronic Supplementary Information

New and tunable hydroxylated driving agents for the production of tailor-made gold nanorods **

Monique Gabriella Angelo da Silva, Mario Roberto Meneghetti, Audrey Denicourt-Nowicki, and Alain Roucoux**

[a] Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7 (France)

[b] Grupo de Catálise e Reatividade Química GCaR, Instituto de Química e Biotecnologia da Universidade Federal de Alagoas, Av. Lourival de Melo Mota, s/n CEP 57072-970, Maceió, AL (Brazil)

*To whom correspondence should be addressed. E-mail: alain.roucoux@ensc-rennes.fr, audrey.denicourt@ensc-rennes.fr

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1.1- General

Tetrachloroauric acid hydrate, $HAuCl_4.H_2O$ (99.9%), sodium borohydride, (+)-*L*-ascorbic acid (99%), CTAB and silver nitrate - $AgNO_3$ (99%) were used as purchased. The HAAX surfactants were synthesized by a procedure already described.[28-30] Distilled water was used to prepare all solutions. Absorption spectra of the solutions were carried out on a Shimadzu UV-vis-NIR 1800 spectrophotometer, using optical glass cells with length of 1cm. TEM analyses were recorded on a transmission electron microscope (JEOL, JEM 100CX II UHR) at an accelerating voltage of 100 kV.

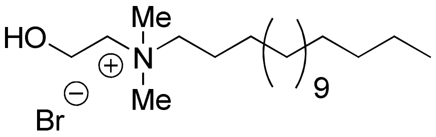
1.2- Synthesis of the Growth-driving agents

Bromohexadecane, (*N*,*N*-dimethylamino)-1-alcohol , *N*,*N*-dimethylhexadecylamine and 1-bromopropane were purchased from Aldrich or Fluka and were used without further purification. The surfactants were prepared as described in the literature or after adapted modification, and characterized. NMR spectra were recorded using a BRUCKER Avance III 400 spectrometer at 400.13 MHz for ^1H and 100.61 MHz for ^{13}C. All magnetic resonance spectra were quoted in parts per million (ppm) measured from tetramethylsilane (TMS) as external reference. The following abbreviations were used to described peak splitting patterns when appropriate: s= singlet, t= triplet, m= multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). All melting points were measured using a Stuart melting point apparatus SMP3. The sample was added in a capillary tube that was accommodated in a heating block. Then, the melting process was observed with the help of bright illumination and a powerful magnifying glass. The CMC measurements were performed using an automatic tensiometer (Krüss K100) and the DuNoüy Ring Method for air-water interface at 298 K. Before each experiment, the platinum ring was cleaned in a water/ethanol mixture and then in a blue colour flame. A concentrated solution 1mg/mL (5 mL) was put in a conic vessel (165.7 mL) and was reduced by the addition of small amounts of ultrapure water. After each addition, the solution is stirred for 120 s. The immersion depth of the ring is 1 mm. Equilibrium surface tension was measured three times at 25°C for each concentration with Harkins and Jordan correction method.

1.2.1- *N,N- dimethyl–N-cetyl–N-(2-hydroxyethyl)ammonium Bromide* - HEA16Br

In a 25mL-flask, 10.7 mL (35.1 mmol, 1.2 eq,) of 1-bromohexadecane and 3,0 mL (29.2 mmol, 1 eq.) of *N,N*-dimethylethanolamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 24h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

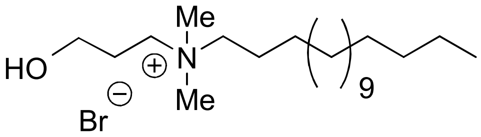
White powder, 92% yield, $C_{20}H_{44}BrNO$ (394.47 g.mol^{-1}), CMC = 0.77 mmol.L^{-1}, m.p. 207-208ºC, ^{1}H NMR (400MHz, $CDCl_3$, 25°C, TMS): δ = 0.85 (t, *J* = 7 Hz, 3H), 1.23 (m, 24H), 1.32 (m, 2H), 1.73 (m, 2H), 3.36 (s, 6H), 3.56 (m, 2H), 3.74 (m, 2H); 4.10 (m, 2H); 5.0 (t, *J* = 5.3 Hz, 1H). ^{13}C NMR (400MHz, $CDCl_3$, 25°C, TMS): δ = 14.1, 22.6- 31.9, 52.1, 55.8, 65.6, 66.0 ppm.



1.2.2 - *N,N- dimethyl–N-cetyl–N-(2-hydroxypropyl)ammonium Bromide* - HPA16Br

In a 25mL-flask, 10.7 mL (35.1 mmol, 1.2 eq,) of 1-bromohexadecane and 3,5 mL (29.2 mmol, 1 eq.) of N,N-dimethylpropanolamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 24h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

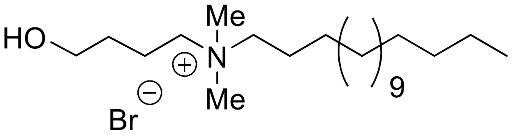
White powder, 92% yield, $C_{21}H_{46}BrNO$ (408.50 g.mol^{-1}), CMC = 0.77 mmol.L^{-1}, m.p.196-197ºC, ^{1}H NMR (400MHz, $CDCl_3$, 25°C, TMS): δ = 0.80 (t, *J* =7 Hz, 3H), 1.22 (m, 24H,), 1.29 (m, 2H), 1.70 (m, 2H), 1.94 (m, 2H), 3.06 (s, 6H), 3.30 (m,2H), 3.34 (m, 2H), 3.61 (m, 2H); 3.62 (m, 2H); 4.71 (t, *J* = 5.3 Hz, 1H). ^{13}C NMR (400MHz, $CDCl_3$, 25°C, TMS): δ = 14.0, 22.6- 32.5, 47.5, 61.5, 62.0, 66.0 ppm



1.2.3 *N,N- dimethyl–N-cetyl–N-(2-hydroxybutyl)ammonium Bromide* -HBA16Br

In a 25mL-flask, 10.7 mL (35.1 mmol, 1.2 eq,) of 1-bromohexadecane and 4,0 mL (29.2 mmol, 1 eq.) of *N,N*-dimethylbutanolamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 24h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

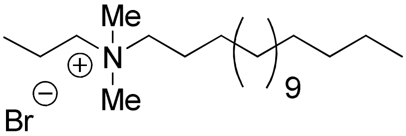
White powder, 80% yield, $C_{22}H_{48}BrNO$ (422.53 g.mol^{-1}), CMC = 0.69 mmol.L^{-1}, m.p. 135-136ºC, ^{1}H NMR (400MHz, $CDCl_3$, 25°C, TMS): δ = 0.81 (t, *J* = 7 Hz, 3H), 1.22 (m, 24H), 1.31 (m, 2H), 1.48 (m, 2H), 1.67 (m, 2H), 1.75 (m, 2H), 3.0 (s, 6H), 3.30 (m, 2H), 3.55 (m, 2H); 3.60 (m, 2H); 5.14 (t, *J* = 5.3 Hz, 1H). ^{13}C NMR (400MHz, $CDCl_3$, 25°C, TMS): δ = 14.0, 19.4, 23.1- 32.5, 47.5, 63.0, 66.0 ppm.



1.2.4 *N,N- dimethyl–N-cetyl–N-propylammonium Bromide* -PA16Br

In a 25mL-flask, 2,7 mL (29.2 mmol, 1 eq.) of 1-bromopropane and 12 mL (35.1 mmol, 1.2 eq,) of *N,N*- dimethylhexadecylamine were added in ethanol (15 mL) and the reaction mixture was stirred under reflux for 24h. After solvent removal, the solid is washed twice with diethyl ether and filtered.

White powder, 92% yield, $C_{21}H_{46}BrN$ (392.50 g.mol^{-1}), CMC = 0,64 mmol.L^{-1}, , m.p.71-72ºC, ^{1}H NMR (400MHz, $CDCl_3$, 25°C, TMS): δ =0.90 (t, *J* = 6.7 Hz, 3H, H-16'), 1.22 (m, 24H, H-14'-H-3'), 1.30 (m, 2H- H-15'), 1.70 (m, 2H, H-2'), 2.21 (m, 2H), 3.05 (s, 6H), 3.20 (m,2H), 3.24 (m, 2H, H-1'); ^{13}C NMR (400MHz, $CDCl_3$, 25°C, TMS): δ = 14.0, 23.1- 32.5, 66.0, 68.0 ppm



1.3 Gold Nanorods synthesis

To prepare AuNRs by the seed-mediated method, the process consists on preparing two solutions: i) the seed solution and ii) the growth solution.

<u>*Seed solution:*</u> In a 25 mL-flask, a Au^{3+} solution (0.1 mL, 1% w/v) were added to an aqueous solution of surfactant (7.4 mL, 0.2M). The solution color changed to dark or light yellow depending on the surfactant. Then, a ice cold solution of sodium borohydride (5 x 10^{-1} mmol, 0.6 mL, 0.01 mol.L^{-1}) was added. The solution color immediately turned to brown. The system remained under stirring for 2 min. and kept at room temperature for at least 2 h.

<u>*Growth Solution:*</u> In a 25 mL-flask, a Au^{3+} solution (0.2 mL, 1% w/v) were added to a surfactant solution (7.3 mL, 0.2M). The solution color changed to dark or light yellow depending on the surfactant in question. Then, silver nitrate (0.150 mL, 0.40 mmol.L^{-1}) was added under stirring, followed by ascorbic acid (and 0.070 mL, 0.0788 M). The system turned to colorless, proving the reduction of Au^{3+} to Au^{+}.

<u>*Growing process of AuNRs:*</u> 0.060 mL of seed particles were added to the growth solution freshly prepared. The system remained under stirring for just 10 s. Then it is allowed to stand for 4 h prior to characterization to ensure the system stability. The solution darkens slowly between 10 to 15 min. to a dark brown colour.

2- TEM and UV-Vis/near-IR characterization

Transmission Electron Microscopy images were obtained on a Microscope JEOL TEM 100CXII operating at 100kV. The samples were prepared with a thin film of the gold nanorods solution on a copper grid coated with carbon film at minimum of 24 hours before analysis to dry sufficiently maintained in a dissector. The analyses of UV-Vis/near-IR measurements were carried out on a Schimadzu UV-vis 1800 spectrophotometer. The set-up was configured to fix the baseline of distilled water absorption band from 400 to 1000 nm, using optical glass cells with length of 1cm.

2.1- Gold Nanorods produced with CTAB

Pictures obtained from samples prepared with 24 hours.

Mean size: 40.8 nm x 12.4 nm (±4.8 nm x 2.3 nm)

Aspect ratio: 3.3

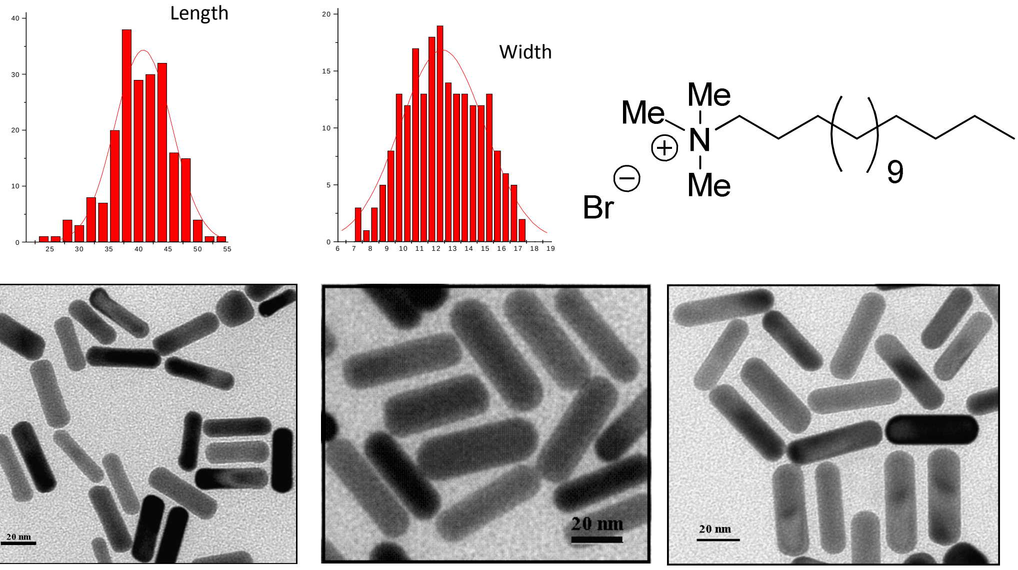


Figure S1: TEM images and size distributions of AuNR@CTAB

2.2 Gold Nanorods produced with HEA16Br

Pictures obtained from samples prepared with 24 hours.

Mean size: 30 nm x 10 nm (±5.5 nm x 1.3 nm)

Aspect ratio: 3.0

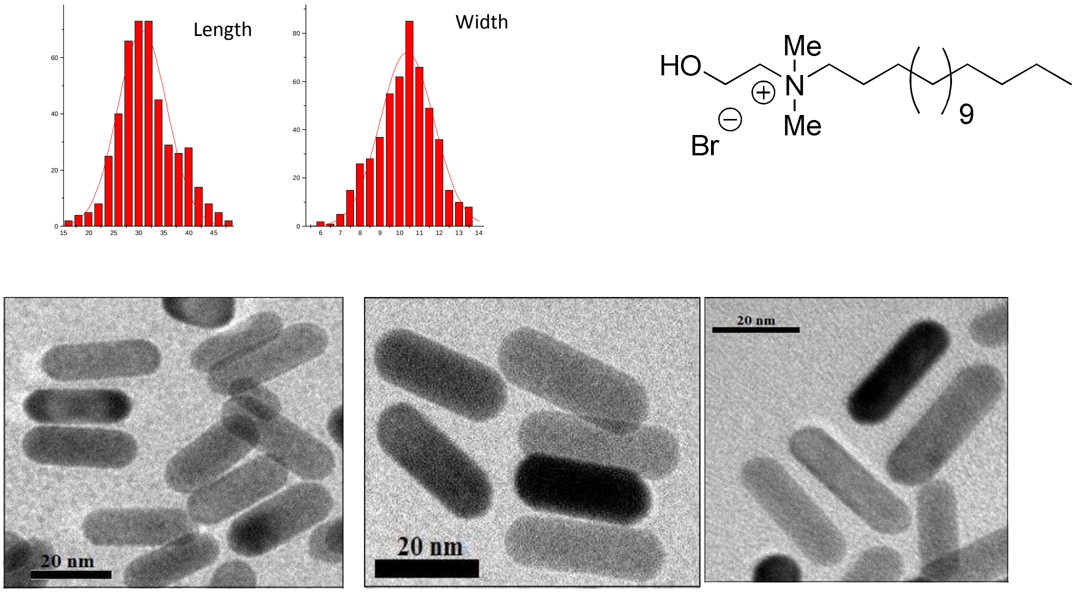


Figure S2: TEM images and size distributions of AuNR@HEA16Br

2.3 Gold Nanorods produced with HPA16Br

Pictures obtained from samples prepared with 24 hours.

Mean size: 30.2 nm x 7.2 nm (±3.0 nm x 0.8 nm)

Aspect ratio: 4.2

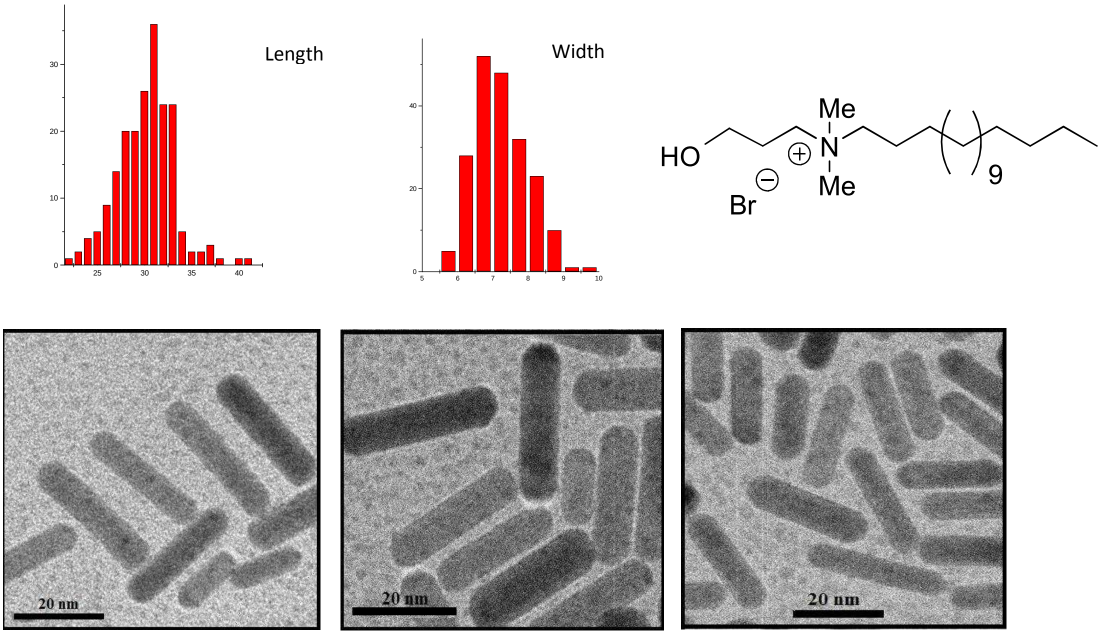


Figure S3: TEM images and size distributions of AuNR@HPA16Br

2.4 Gold Nanorods obtained with HBA16Br

Pictures obtained from samples prepared with 24 hours.

Mean size: 38.6 nm x 8.8 nm (±6.4 nm x 1.2 nm)

Aspect ratio: 4.4

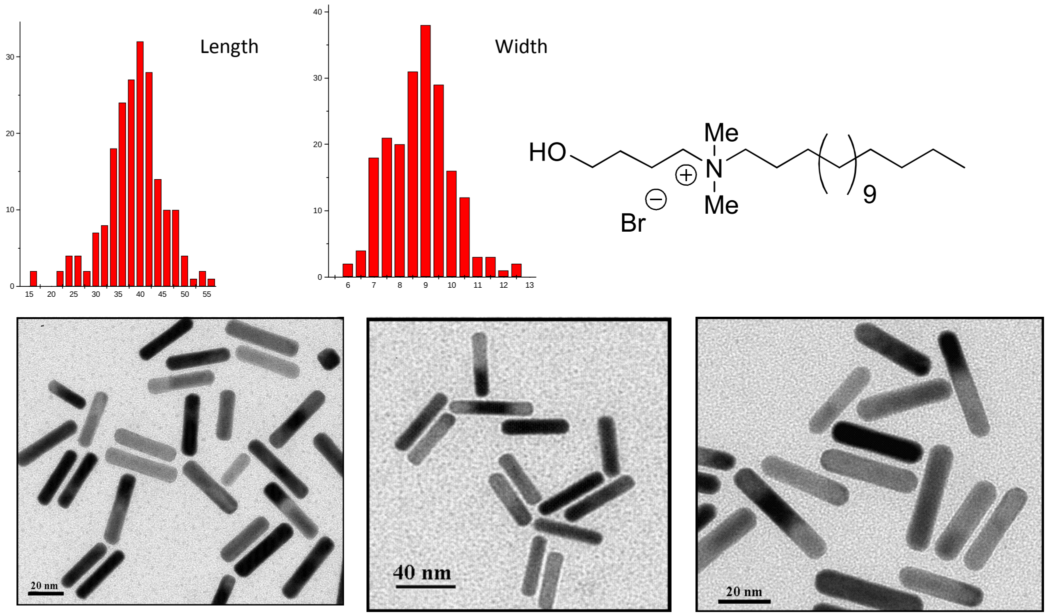


Figure S4: TEM images and size distributions of AuNR@HBA16Br

2.5 Gold Nanoparticles obtained with PA16Br

Pictures obtained from samples prepared with 24 hours.

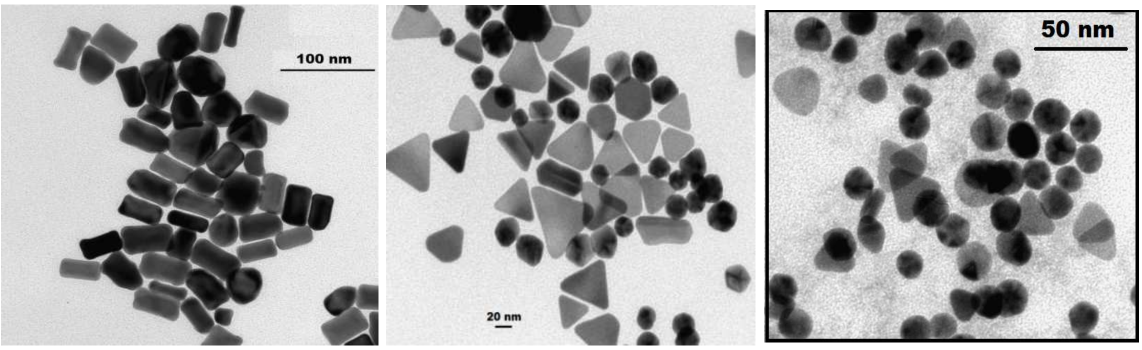


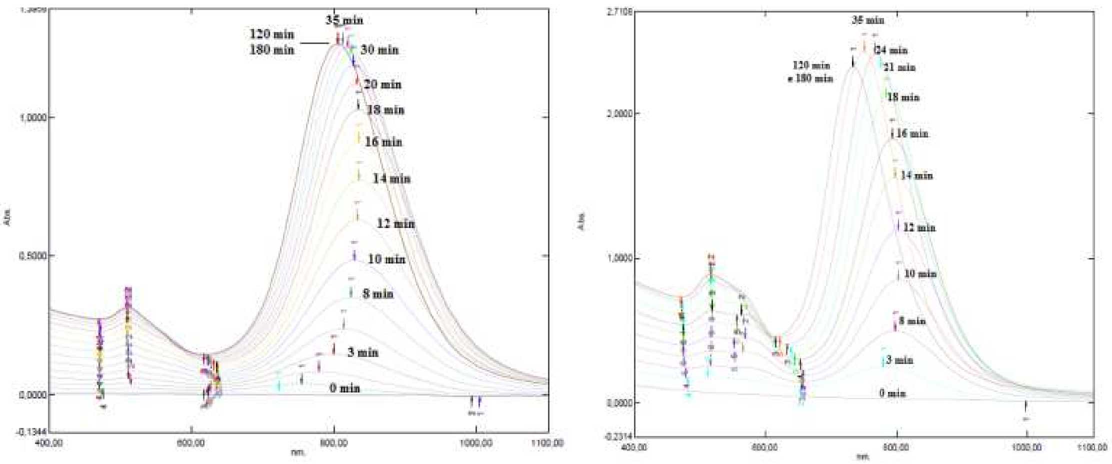
Figure S5: TEM images of AuNR@PA16Br

3. Kinetic study of Gold Nanorods formation

The growth process has been followed since the seed particles were added to the growth solution and during four hours, to evaluate when the systems are stable (the moment when the initial formation stops, it also means no more evolution of the spectra). After that, the systems were monitored every day for one month to observe their evolution.

3.1 Kinetic study during the first three hours

AuNR@CTAB **AuNR@HEA16Br**



AuNR@HPA16Br **AuNR@HBA16Br**

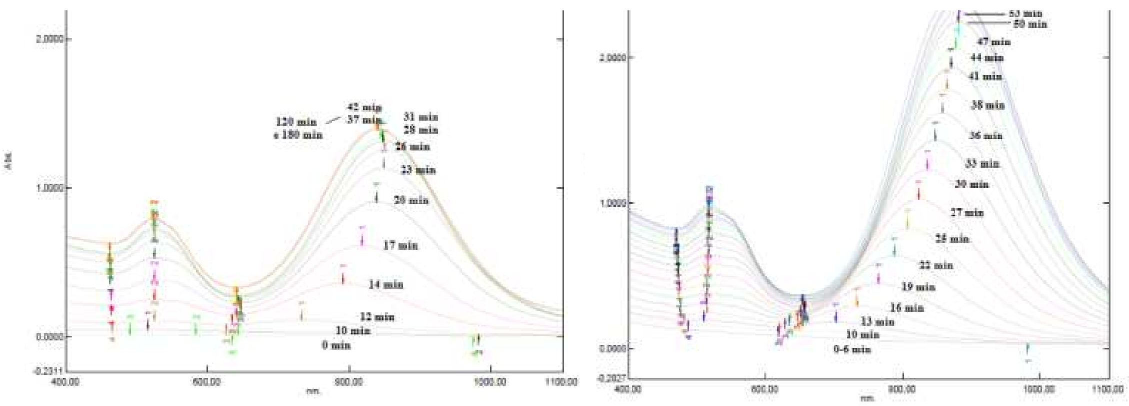
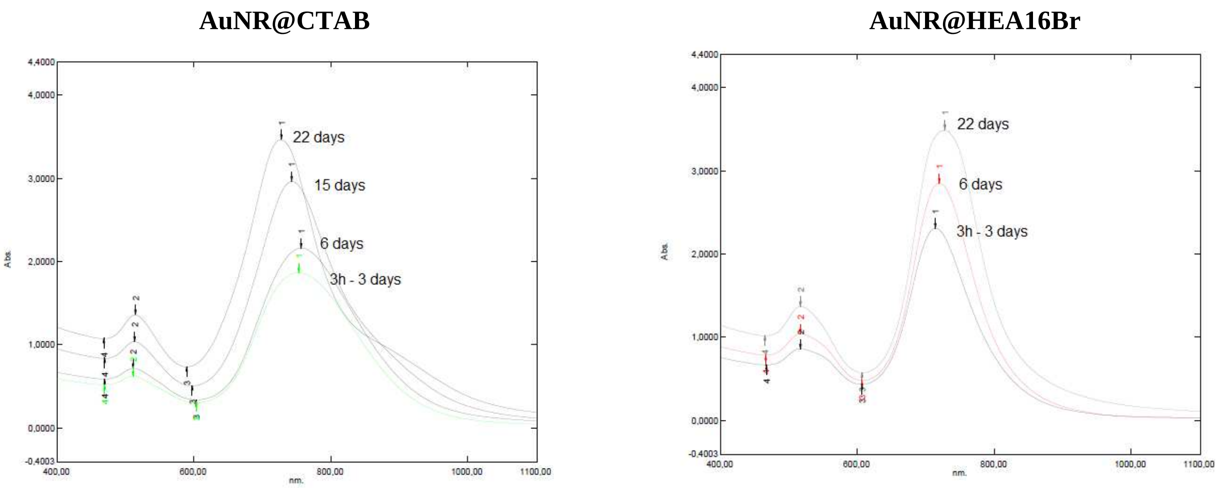


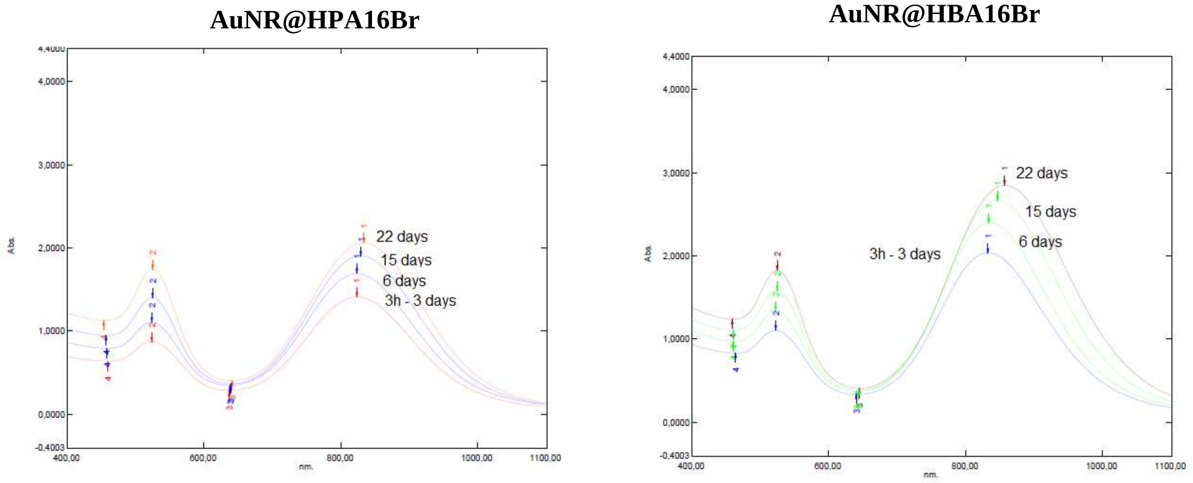
Figure S6: UV-vis spectra of the colloids obtained from various growth-driving agents, collected during the first 3 hours of the NPs formation

3.2 Kinetic study from 3h to 22 days



AuNR@CTAB

AuNR@HEA16Br



AuNR@HPA16Br

AuNR@HBA16Br

Figure S7: UV-vis spectra of the gold nanorods systems (3 hours to 22 days)