

Supporting information for

CO₂ Switchable Nanoparticles: Reversible Water/Organic-Phase Exchange of Gold Nanoparticles by Gas Bubbling

Salvador Pocoví-Martínez, Laura Francés-Soriano, Elena Zaballos-García, Juan C. Scaiano, María González-Béjar* and Julia Pérez-Prieto*

Page S2: Experimental methods: general, characterization and synthesis of Au@OA.

Page S3: Figure S1: ¹H-NMR spectrum of Au@OA in deuterated chloroform.

Page S3: Figure S2: ¹H-NMR spectrum of OAA in deuterated chloroform under nitrogen.

Page S4: Figure S3: ¹³C-NMR spectrum of OAA in deuterated chloroform under nitrogen.

Page S4: Figure S4: UV-Visible spectra of OAA at different concentrations up to 0.075 M in chloroform.

Page S5: Figure S5: Absorbance vs OAA concentrations to calculate OAA molar absorption coefficient at 520 nm of OAA in chloroform.

Page S5: Figure S6: UV-Visible spectra of OAA at different concentrations up to 0.075 M in toluene.

Page S6: Figure S7: UV-Visible spectra of Au@OA in the absence and in the presence of different concentrations of OAA (up to 74.9 mM) in chloroform.

Page S6: Figure S8: ¹H-NMR spectrum of OAAB in deuterated water under CO₂.

Page S7: Figure S9: ¹³C-NMR spectrum of OAAB in deuterated water under CO₂.

Page S7: Figure S10: Photographs of (a) oleylamine-capped Au@OA in toluene; (b) mixture of Au@OA and OAA in toluene under air; (c) sample b and water under air; (d) sample c purged with CO₂ until toluene evaporation; (e) addition of 2 mL of toluene and (f) sample e purged with nitrogen.

Page S8: Figure S11: ¹H-NMR spectrum of a mixture of Au@OA and OAA in deuterated chloroform under N₂.

Page S8: Figure S12: ¹H-NMR spectrum of a mixture of Au@OA and OAAB (OAA has been transferred from chloroform to deuterated water by bubbling CO₂).

Page S9: Figure S13: Left: UV-Visible spectra of Au@OAA in chloroform after each cycle up to cycle 15. The UV-Visible spectrum of the initial Au@OA in the presence of OAA has been added for comparison. Right: Absorbance at the SPB maximum wavelength vs cycle number.

Page S9: Table S1. Surface Plasmon Band (SPB) features of Au@OAA in the chloroform phase (wavelength maximum, λ_{max} , absorbance at the SPB maximum, A_{SPB} , A_{SPB}/A_{450} ratio, and full width at half maximum, FWHM) after each cycle up to cycle 15.

Page S10: Figure S14: UV-Visible spectra of a mixture of Au@OA and OAA, Au@OA re-dissolved after centrifugation of the previous mixture (precipitate), and the supernatant of the same centrifugation in chloroform.

Experimental methods

General

All reagents were used as received from Sigma-Aldrich. Oleylamine technical grade (70%, but 98% primary amines), *N,N*-Dimethylacetamide dimethyl acetal (90%), dimethylamine solution (2M in THF), gold chloride trace metal basis (99.9%). Solvents were used without further purification. Chloroform (99.5% with 0.5% ethanol as stabilizer) Multisolvant® HPLC Grade ACS ISO UV-VIS and toluene (99.8%) HPLC Grade were purchased from Scharlau. Carbon dioxide (99.8%) was purchased from “Carbueros Metálicos” (Air Products Group).

Characterization

¹H NMR and ¹³C NMR (CDCl₃ or D₂O) spectra were recorded on an AVANCE 400 MHz Bruker spectrometer. NMR data are reported in ppm, coupling constants in Hz and multiplicity as follows: singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). UV-Vis spectra were recorded using a quartz cuvette (1x1x4 cm) in an Agilent-8543 spectrometer. Centrifugation was carried out in an Eppendorf Centrifuge 5804 R. Further sample characterization was performed by transmission electron microscopy (TEM) with a JEOL JEM-1010 instrument operated at 100 kV. To prepare TEM samples, a few drops of gold nanoparticles solution on carbon-coated copper grids (300 mesh), which was subsequently dried. Nanoparticle sizes were calculated by using ImageJ software.¹

Synthesis of gold nanoparticles. AuNPs were synthesized as previously described.² Briefly, AuCl (10 mg, 0.043 mmol) and oleylamine (395.9 μL, 0.860 mmol) were dissolved in CHCl₃ (2.15 mL) and heated at 67°C under reflux during 24 h. The resulting nanoparticles were precipitated with acetone (5 mL) and centrifuged at 8000 rpm for 5 min. The supernatant was removed, CHCl₃ (1 mL) and acetone (8 mL) were added again and the suspension was centrifuged under similar conditions. Once supernatant was removed, gold nanoparticles capped with oleylamine (Au@OA) were obtained and ready to be dissolved in the desired organic solvent.

1. C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nat. Methods*, 2012, **9**, 671-675.
2. X. Lu, H.-Y. Tuan, B. A. Korgel and Y. Xia, *Chem. Eur. J.*, 2008, **14**, 1584-1591.

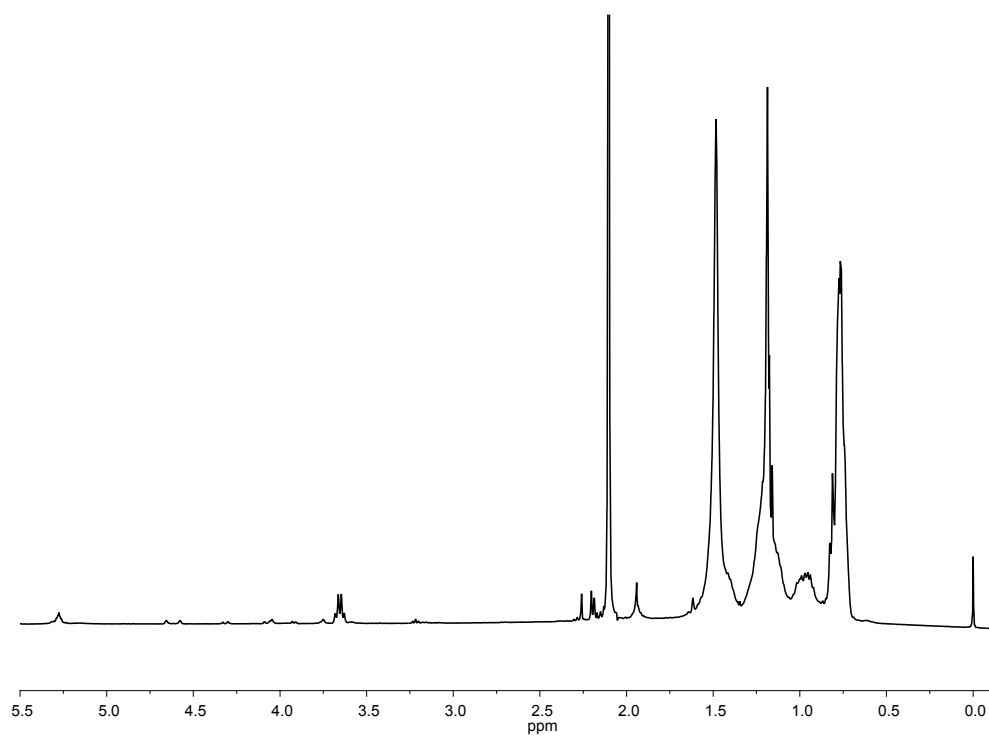


Figure S1. ^1H -NMR spectrum of Au@OA in deuterated chloroform.

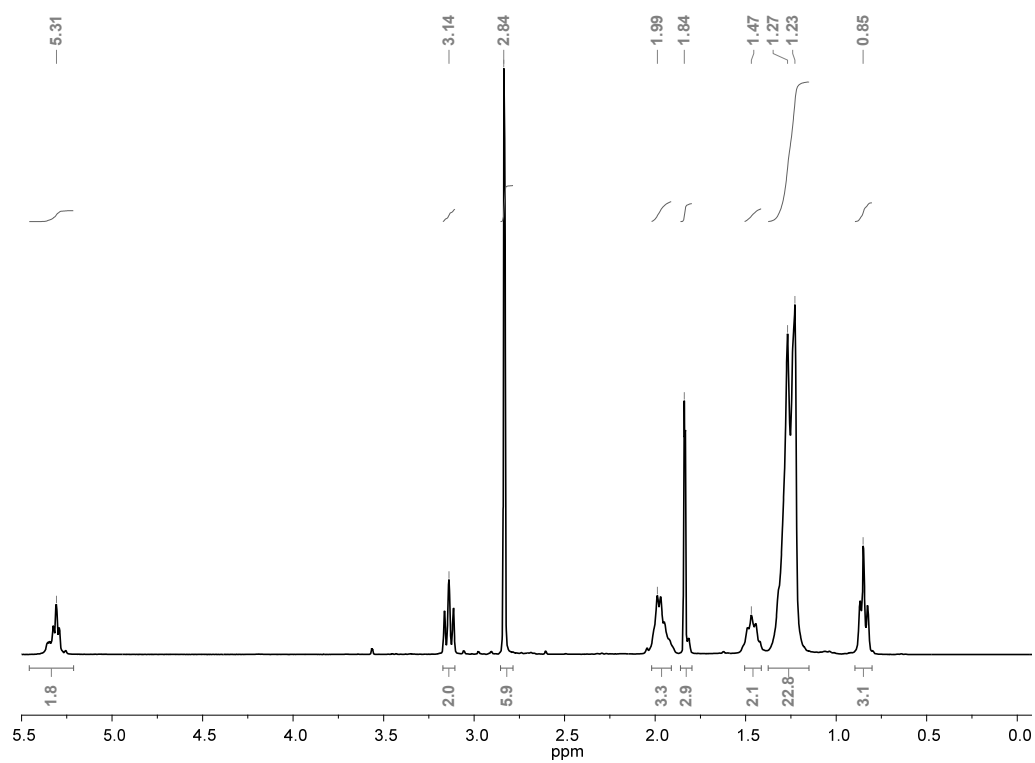


Figure S2. ^1H -NMR spectrum of OAA in deuterated chloroform under nitrogen.

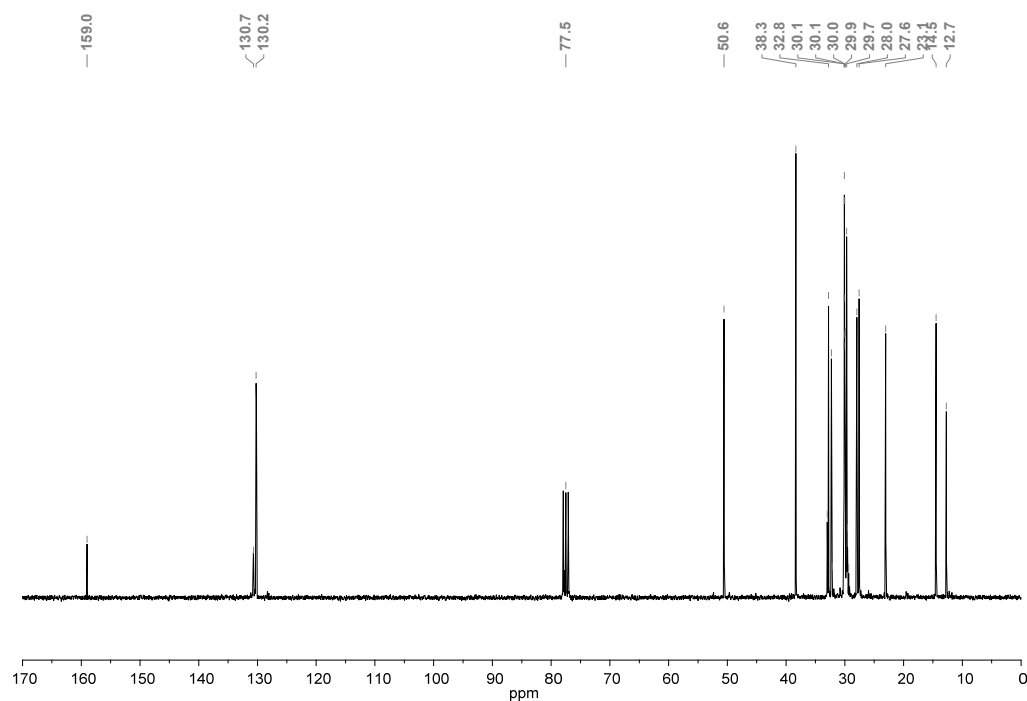


Figure S3. ^{13}C -NMR spectrum of OAA in deuterated chloroform under nitrogen.

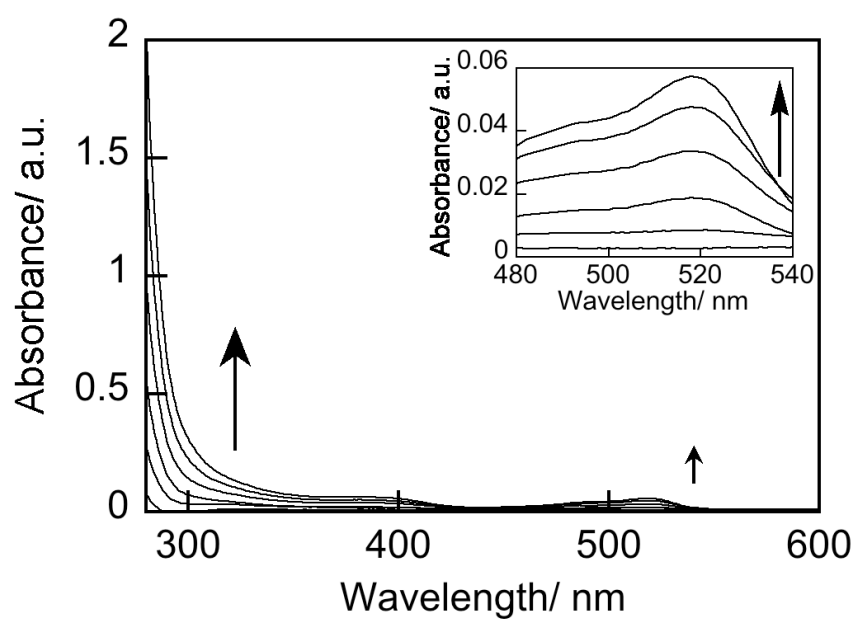


Figure S4. UV-Visible spectra of OAA at different concentrations: 0, 3.9, 22.6, 37.4, 56.1 and 74.9 mM in chloroform.

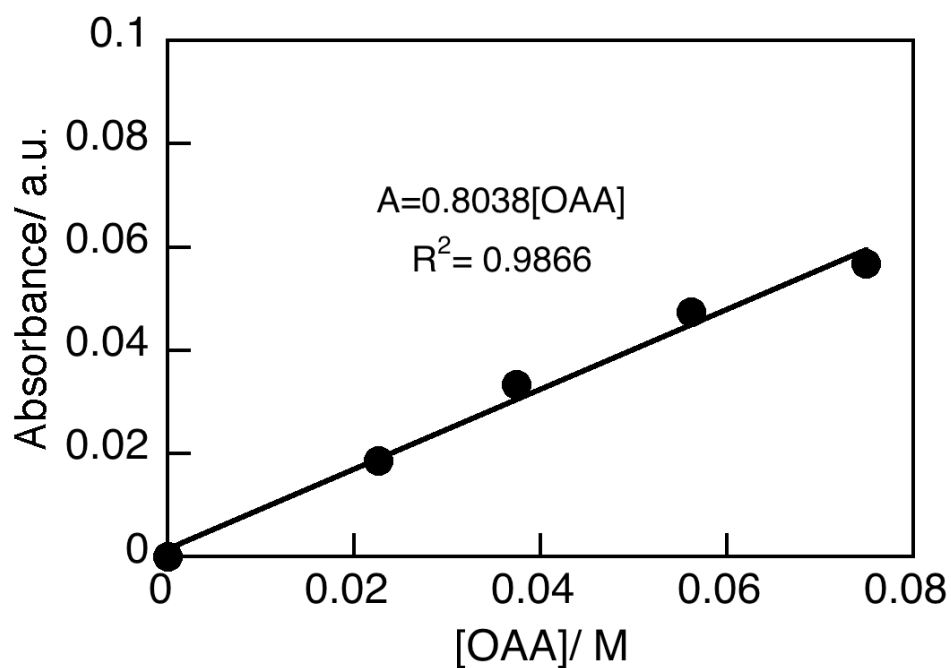


Figure S5. Molar absorption coefficient at 520 nm of OAA in chloroform.

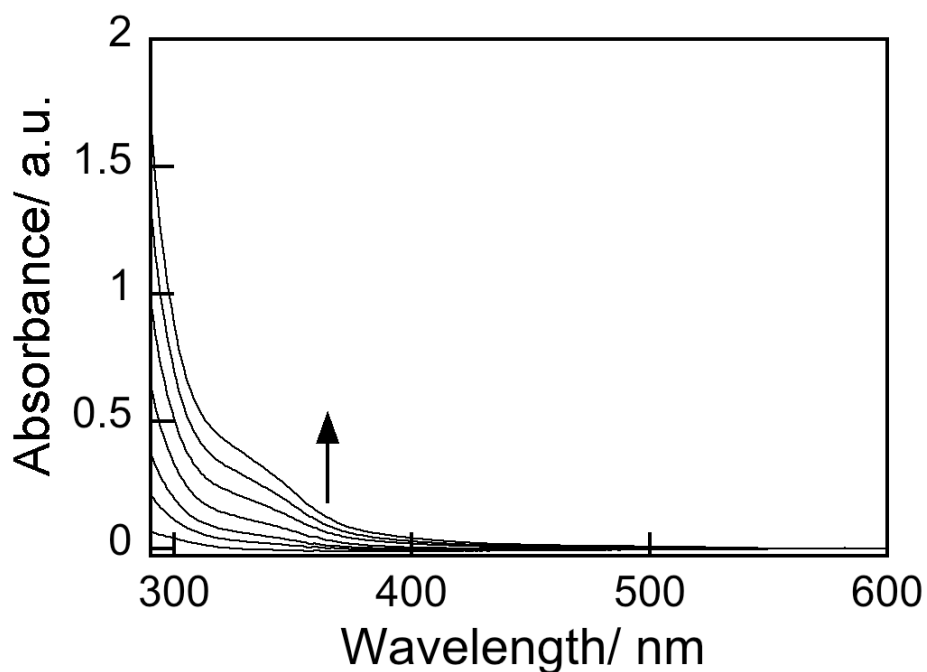


Figure S6. UV-Visible spectra of OAA at different concentrations: 0, 3.9, 11.3, 22.6, 37.4, 56.1 and 74.9 mM in toluene.

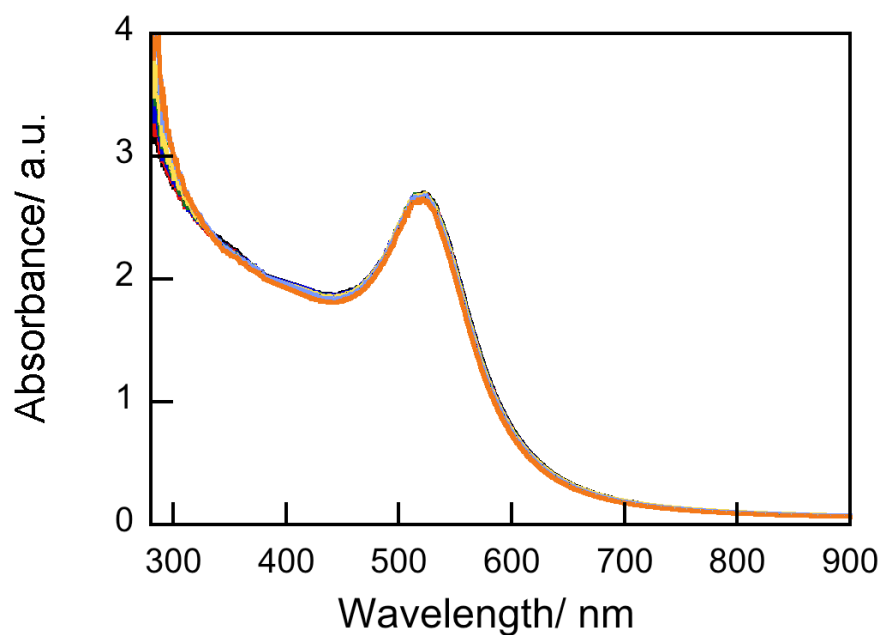


Figure S7. UV-Visible spectra of Au@OA in the absence and in the presence of different concentrations of OAA (up to 74.9 mM) in chloroform.

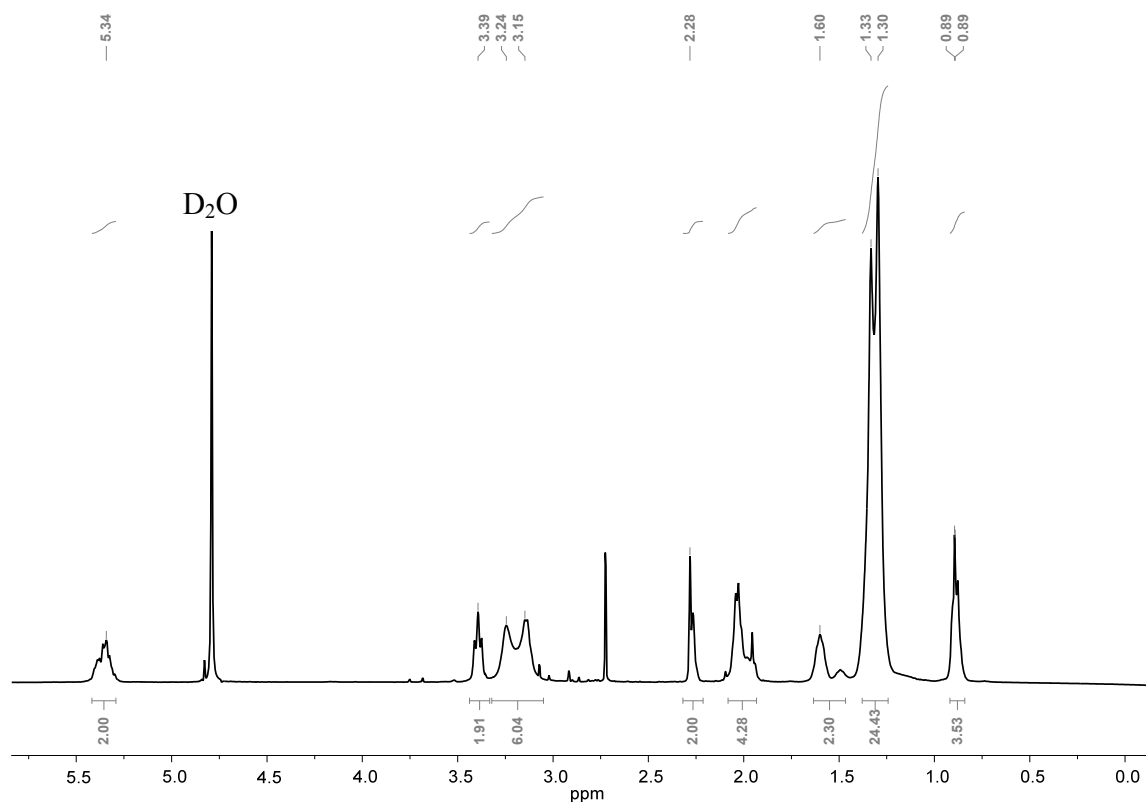


Figure S8. ^1H -NMR spectrum of OAAB in deuterated water under CO_2 .

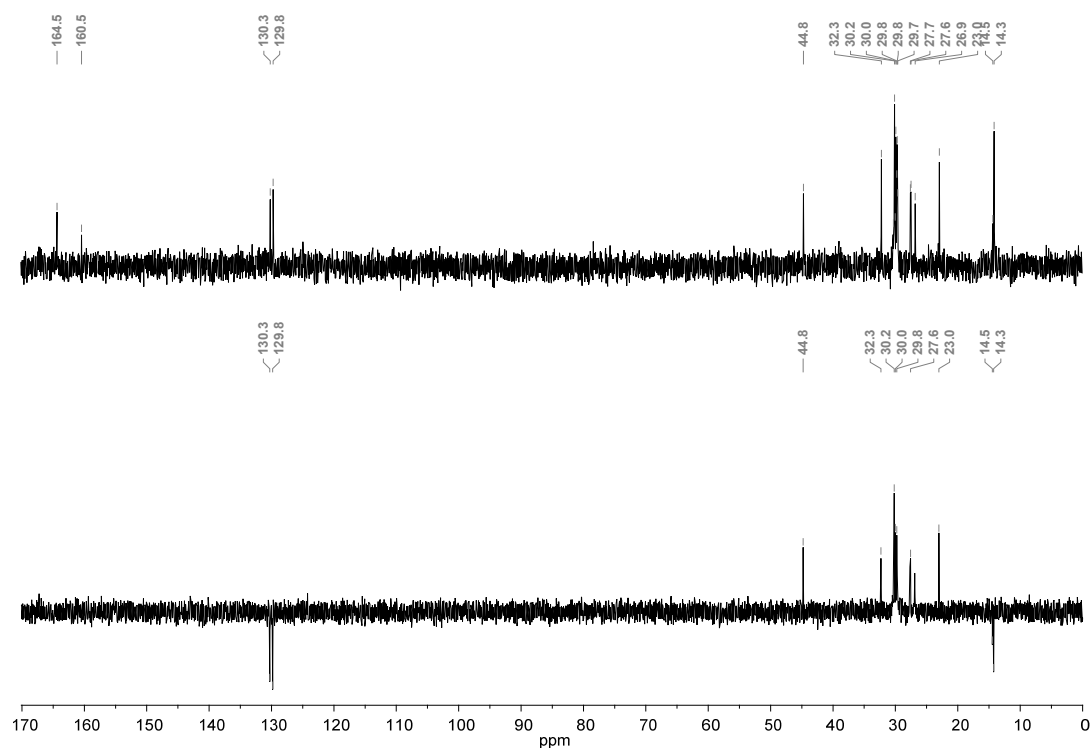


Figure S9. ^{13}C -NMR and DEPT spectrum of OAAB in deuterated water under CO_2 .

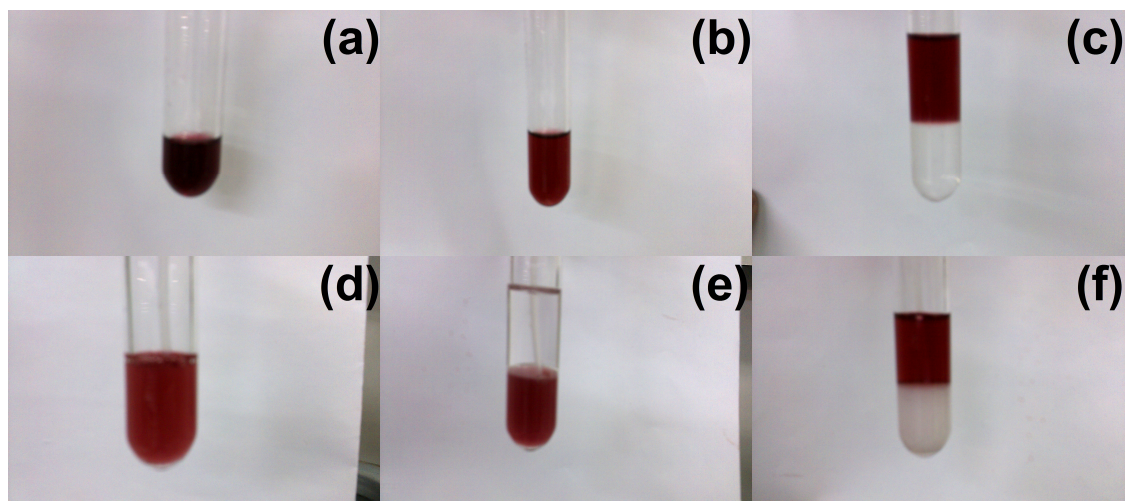


Figure S10. Photographs of (a) Au@OA in toluene; (b) mixture of Au@OA and OAA in toluene under air atmosphere; (c) addition of water to solution b under air; (d) sample c purged with CO_2 until complete removal of toluene; (e) addition of 2 mL of toluene to sample d; and (f) sample e purged with nitrogen.

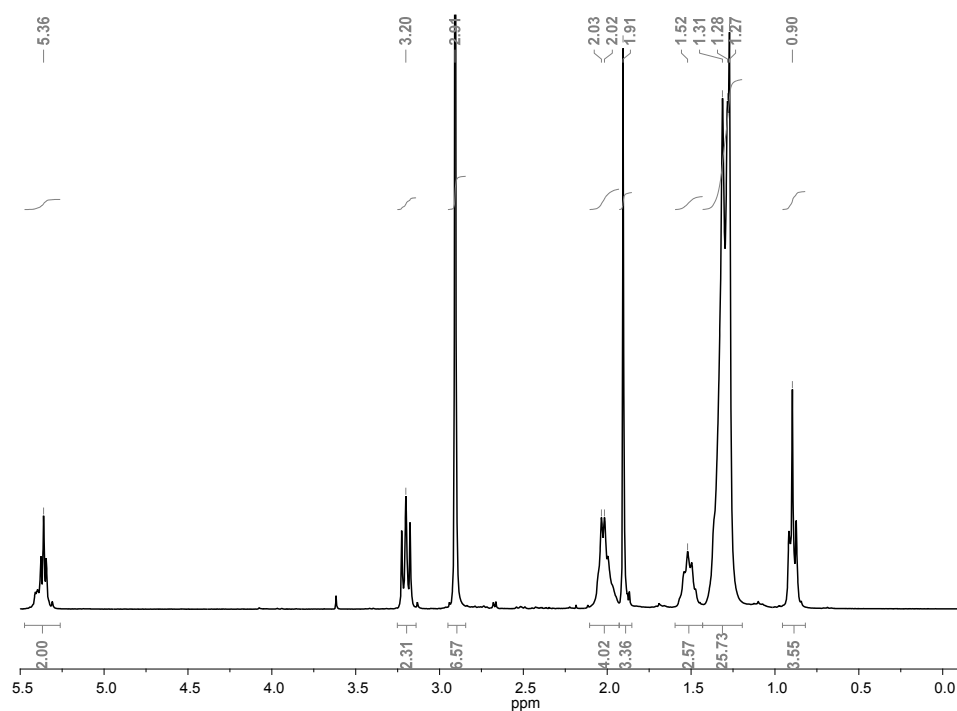


Figure S11. ^1H -NMR spectrum of a mixture of Au@OA and OAA in CDCl_3 under N_2 .

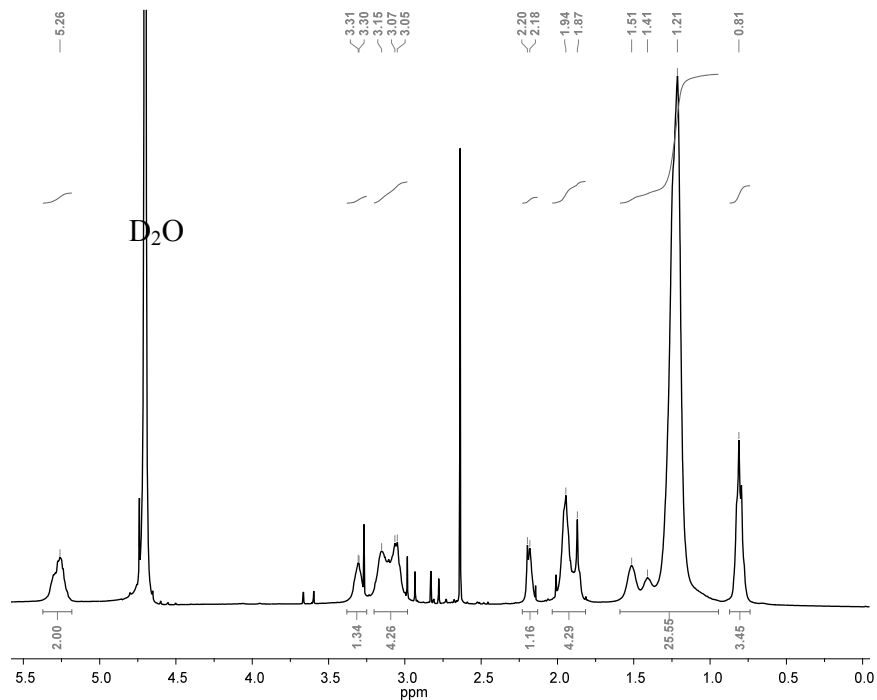


Figure S12. ^1H -NMR spectrum of a mixture of Au@OA and OAAB (OAA has been transferred from chloroform to deuterated water by bubbling CO_2).

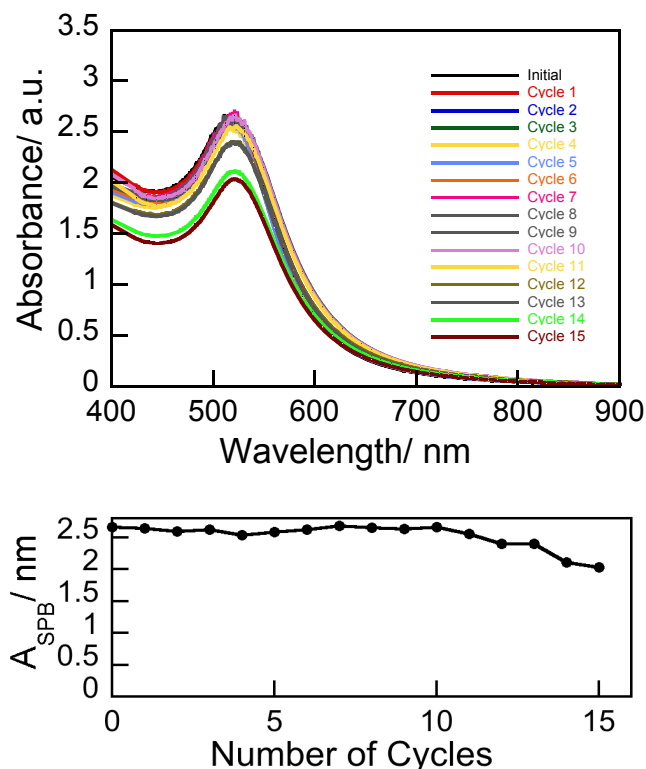


Figure S13. Left: UV-Visible spectra of Au@OAA in chloroform after each cycle up to cycle 15. The UV-Visible spectrum of the initial Au@OA in the presence of OAA has been added for comparison. Right: Absorbance at the SPB maximum wavelength vs the cycle number.

Table S1. Surface Plasmon Band (SPB) features of Au@OAA in the chloroform phase (wavelength maximum, λ_{max} , absorbance at the SPB maximum, A_{SPB} , A_{SPB}/A_{450} ratio, and full width at half maximum, FWHM) after each cycle up to cycle 15.

	SPB (λ_{max} , nm)	A_{SPB}	A_{SPB}/A_{450}	FMHW/2(nm)
Initial	521	2.66	1.39	49
Cycle 1	520	2.64	1.38	58
Cycle 2	519	2.60	1.42	54
Cycle 3	522	2.62	1.44	48
Cycle 4	522	2.54	1.44	48
Cycle 5	518	2.59	1.45	51
Cycle 6	520	2.62	1.45	52
Cycle 7	524	2.69	1.44	48
Cycle 8	523	2.66	1.43	49
Cycle 9	523	2.64	1.45	57
Cycle 10	522	2.66	1.44	56
Cycle 11	523	2.56	1.44	56
Cycle 12	518	2.40	1.42	58
Cycle 13	520	2.40	1.43	56
Cycle 14	521	2.11	1.43	56
Cycle 15	521	2.04	1.44	52

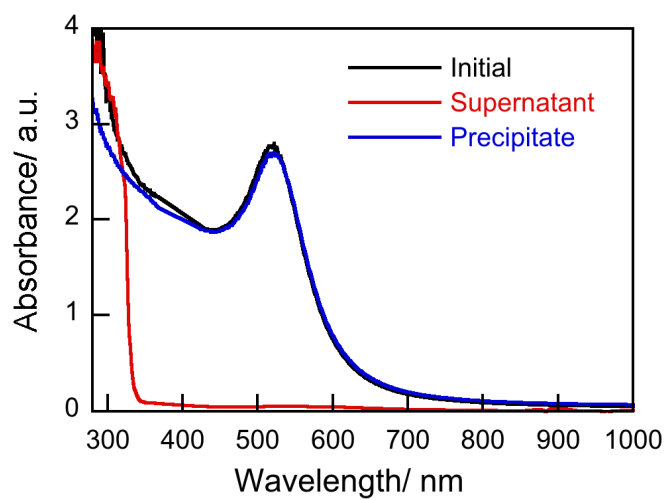


Figure S14. UV-Visible spectra of a mixture of Au@OA and OAA (initial), Au@OA redissolved after centrifugation of the previous mixture (precipitate), and the supernatant of the same centrifugation in chloroform.