Supporting Information

Improving the rate of the copper-catalyzed Henry reaction by surface plasmon excitation of Au nanoparticles

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Henry reaction conducted with Cu(OAc)2/bipyridine

Cu(OAc)₂ (3.9 mg, 0.0215 mmol, 0.1 eq.) and 2,2'-bipyridine (4 mg, 0.0258 mmol, 0.12 eq) were mixed in DMF (1 mL) for 20 min. Then, to the mixture was added nitrobenzaldehyde (NBA, 32.2 mg, 0.212 mmol, 1 eq.) and nitromethane (NM, 10 eq., 117 μ L). The solution was stirred for 16 h at room temperature. Then the mixture was extracted with ethyl acetate, washed with water and brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure to yield the corresponding nitroaldol. A ¹H NMR was recorded on the crude to calculate the conversion of the reaction by integration of the corresponding nitroaldol protons. Then, purification by preparative layer chromatography (ethyl acetate/petroleum ether (1/9, v/v) afforded the compound and the yield was calculated.

Henry reaction conducted with only sodium citrate

A mixture of nitrobenzaldehyde (NBA, 32.2 mg, 0.212 mmol, 1 eq.) and nitromethane (NM, 10 eq., 117 μ L) was prepared in DMF (1 mL) and to that mixture was added sodium citrate (2 mg, 0,00688 mmol, 3 mol%). The solution was stirred for 5 h at room temperature. Then the

mixture was extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4 , filtered and concentrated under reduced pressure to yield the corresponding nitroaldol. A ¹H NMR was recorded on the crude to calculate the conversion of the reaction by integration of the corresponding nitroaldol protons.

Henry reaction conducted with the complex C1

A 1 mM solution of copper complex C1 in DMF was prepared beforehand. A mixture of nitrobenzaldehyde (NBA, 32.2 mg, 0.212 mmol, 1 eq.) and nitromethane (NM, 10 eq., 117 μ L) was prepared in DMF (1 mL) and to that mixture was added 20 μ L of the C1 solution in DMF. The solution was stirred for 16 h at room temperature. Then the mixture was extracted with ethyl acetate, washed with water and brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure to yield the corresponding nitroaldol. A ¹H NMR was recorded on the crude to calculate the conversion of the reaction by integration of the corresponding nitroaldol protons. Then, purification by preparative layer chromatography (ethyl acetate/petroleum ether (1/9, v/v) afforded the compound and the yield was calculated.



Figure S1. UV-visible spectrum of the copper(II) complex in DMF at 5 mM. λ max = 677 nm (transition d-d)



Figure S2. ¹H NMR spectrum of nitrobenzaldehyde recorded in CDCl₃.



Figure S3. ¹H NMR spectrum of the corresponding nitroaldol recorded in CDCl₃.



Figure S4. Emission spectra of the commercial LED used in this work, and compared with absorption spectrum of the Au NPs in DMF and the corresponding lumens for blue, green and red LEDs. The emission spectra of the LEDs are recorded using an Avaspec - 2048L spectrophotometer from Avantes. The light is collected with a fiber optic and a CCD camera is used as detector. Two accumulations were performed with a measurement time of 100 ms for each accumulation.



Figure S5. UV-visible spectrum of Au NPs in water synthesized in that work, and the corresponding TEM image and size distribution calculated from TEM images.





Figure S6. UV-visible spectra of Au NPs in water with various color, and the corresponding TEM images and DLS histograms.



Figure S7. Evolution of the ¹H NMR spectrum of the mixture while irradiated under green LED in the presence of Ncat.



Where N represents the number of nuclei represented by the peaks chosen

Equation S1. Conversion of the reaction by integration of the protons on NBA and NNBOH



Figure S8. Home-made set-up for the temperature measurement with a thermal camera



Figure S9. Temperature measurements with the set-up described in Figure Sx of (i) DMF (grey curve), (ii) Au NPs (green curve) and (iii) Henry reaction performed with Ncat under LED irradiation



Figure S10. Time monitoring of Raman spectra during the Henry reaction with Ncat under green irradiation (see UV-visible spectra of Figure S6-b for the Au NPs used in this experiment).



Figure S11. Time monitoring of Raman spectra during the Henry reaction with Ncat under dark conditions (see UV-visible spectra of Figure S6-b for the Au NPs used in this experiment).



Figure S12. Principal component analysis



Figure S13. UV-Vis spectra of the Au NPs after each run of the recycling experiments



Figure S14. UV-Vis spectra of Ncat after each run of the recycling experiments