

Supporting information for

**Photocatalytic Coalescence of Functionalized Gold Nanoparticles**

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## **Experimental section**

**Figure SI-1.-** *Absorption spectrum of AuNP-1*

**Figure SI-2.-**  *$^1\text{H}$ -NMR spectrum of AuNP-1 and pyrene ligand in  $\text{CDCl}_3$*

**Figure SI-3.-** *TEM images of AuNP-1 before and after irradiation in the presence of benzophenone*

**Figure SI-4.-** *Histograms for the nanoparticles shown in Figure SI-3*

**Figure SI-5.-** *Irradiation of AuNP-1 in the presence of 2-metoxibenzophenone (0.5 mM)*

**Figure SI-6.-** *LFP spectrum of AuNP-1 ( $A_{355\text{nm}}=0.25$ ) + 1.9 mM benzophenone under  $\text{N}_2$ .*

**Figure SI-7.-** *LFP spectrum of a deaerated THF solution of benzophenone 1.9 mM.*

**Figure SI-8.-** *TEM image of AuNP-1 after the laser experiments*

**Figure SI-9.-** *Irradiation of decanethiol-derivatized Au NPs in the presence of benzophenone*

## Experimental section

**Materials:** All reagents were commercially available and used as received. Solvents for extraction and chromatography were reagent grade and were used without further purification. Chromatographic separations were performed on silica gel 60 (230-400 mesh) using the indicated solvents.  $^1\text{H}$ -NMR spectra were recorded on a 300 MHz (300 MHz,  $^1\text{H}$ ) spectrometer in  $\text{CDCl}_3$ . The ligand **1** was prepared as already described in the literature.<sup>1</sup>

**Preparation of AuNP-1:** Gold nanoparticles were synthesized as described by Hegmann with a few changes: 120 mg of **1** were dissolved together with 43 mg of  $\text{HAuCl}_4$  in ca 30 mL of anhydrous THF. The mixture was stirred for 10-15 min and then a solution containing 50 mg of  $\text{NaBH}_4$  in 5 mL of deionised water was added at once. The mixture was left under stirring for 2 h. After this time, the volume of the sample was reduced under vacuum and precipitated with ethanol. The precipitation was repeated 5 times to remove any residue of **1** not bonded to the nanoparticles.

**Coalescence experiments:** Samples of AuNPs-**1** in THF (3 mL) were prepared such that they absorbed ca. 0.3 at 355 nm and were placed in quartz cuvettes. Then,  $\mu\text{L}$  of BP 24.7mM were added to obtain the desired final concentration (from 0.16  $\mu\text{M}$  to 1.9 mM). The samples were bubbled with  $\text{N}_2$  during 15 min and irradiated using a photoreactor containing 8 lamps (4 each side; lamps: LZO-UVB, LZO-UVA and LZO-420). The photoreaction was followed by UV-Vis absorption.

**Preparative irradiations:** A sample containing 9 mg of AuNPs-**1** and 7 mg of benzophenone in 200 mL of deaerated THF was irradiated (LZO-UVA, 400 nm  $> \lambda >$  300 nm) for 100 s. Then the nanoparticles were precipitated with ethanol and filtered. The supernatant was concentrated to dryness.  $^1\text{H}$ -NMR showed benzophenone was recovered unchanged.

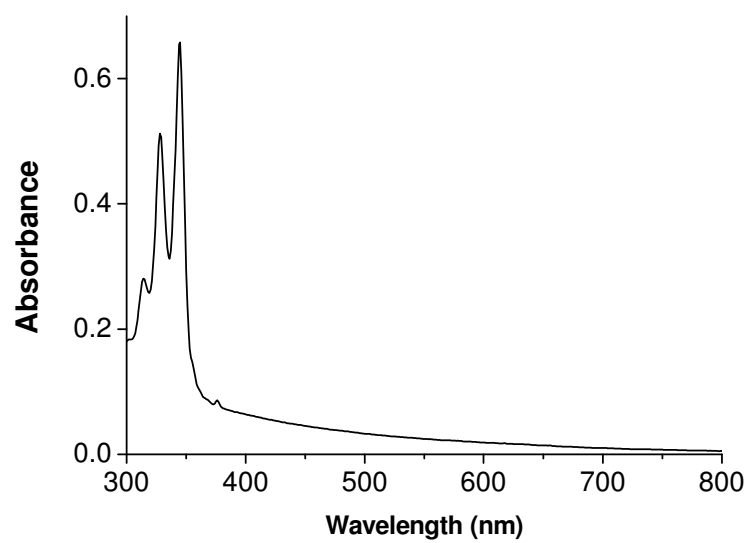
**Characterization:** UV-vis spectra of the samples were recorded using a quartz cuvettes spectrometer. TEM images were registered with a JEOL JEM-1010 microscope operating at 100 kV and equipped with a digital camera (Megaview III). HR-TEM was performed on a TECNAI F20 microscope operating at 200 kV equipped with a CCD GATAN camera.

**Laser flash photolysis (LFP) studies:** Experiments were performed on a pulsed Nd:YAG laser, using 355 nm as exciting wavelength. The pulses width was ca. 10 ns, and the energy was ca. 12 mJ/pulse. A xenon lamp was employed as the detecting light source. The apparatus consisted of the pulsed laser, the Xe lamp, a monochromator, and a photomultiplier (PMT) system. The output signal from the oscilloscope was transferred to a personal computing machine.

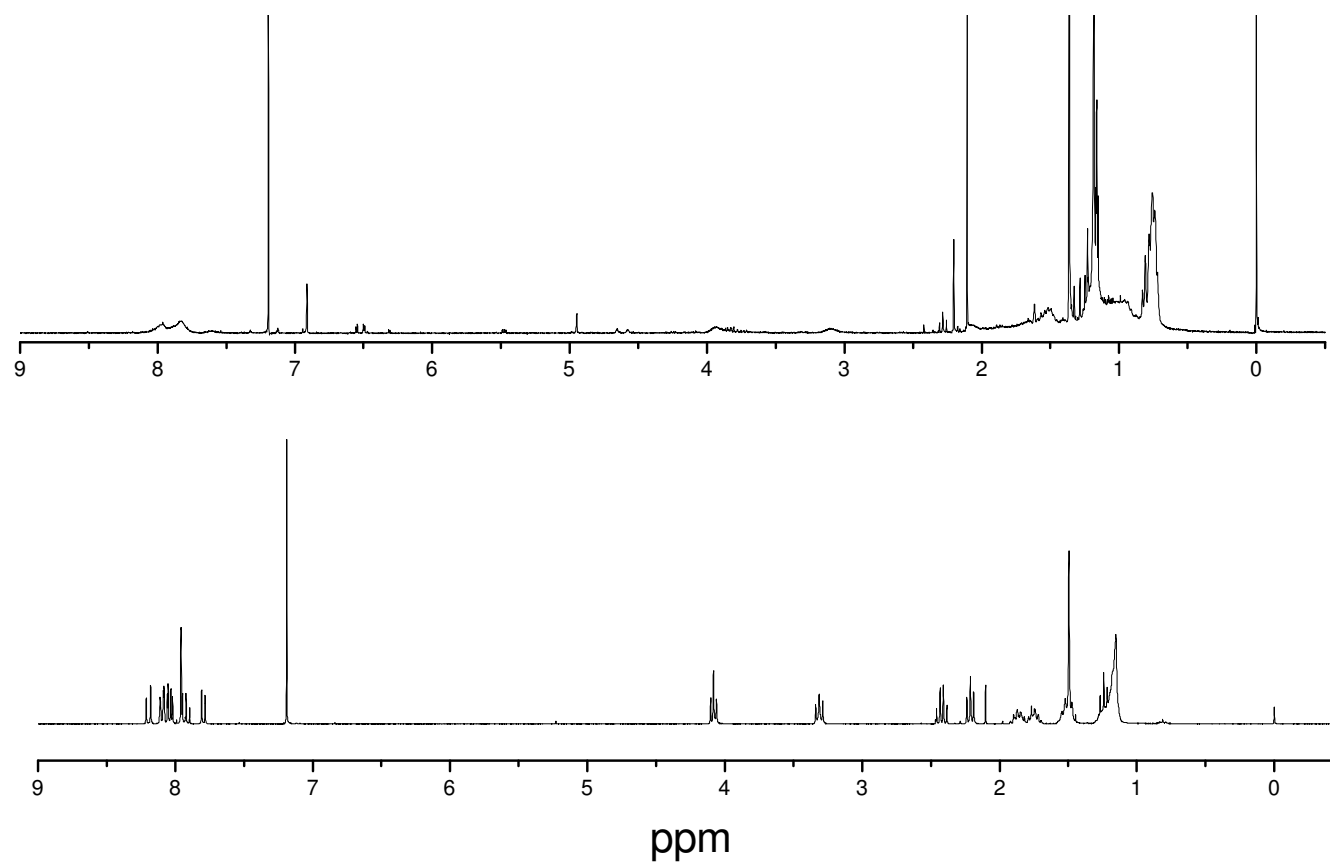
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<sup>1</sup> Montalti, M.; Prodi, L.; Zaccheroni, N.; Baxter, R.; Teobaldi, G.; Zerbetto, F. *Langmuir*, 2005, 19, 5172.

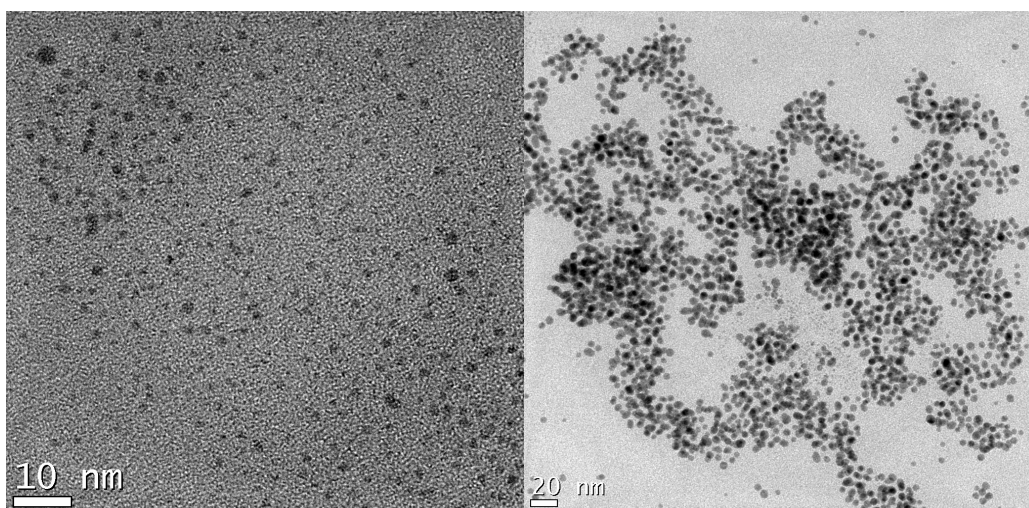
Samples of AuNP-1 in THF (3 mL) were prepared such that they absorbed *ca.* 0.3 at 355 nm and they were bubbled with N<sub>2</sub>. Microliters of a 24.7mM solution of benzophenone were added and its ketyl radical formation monitored.



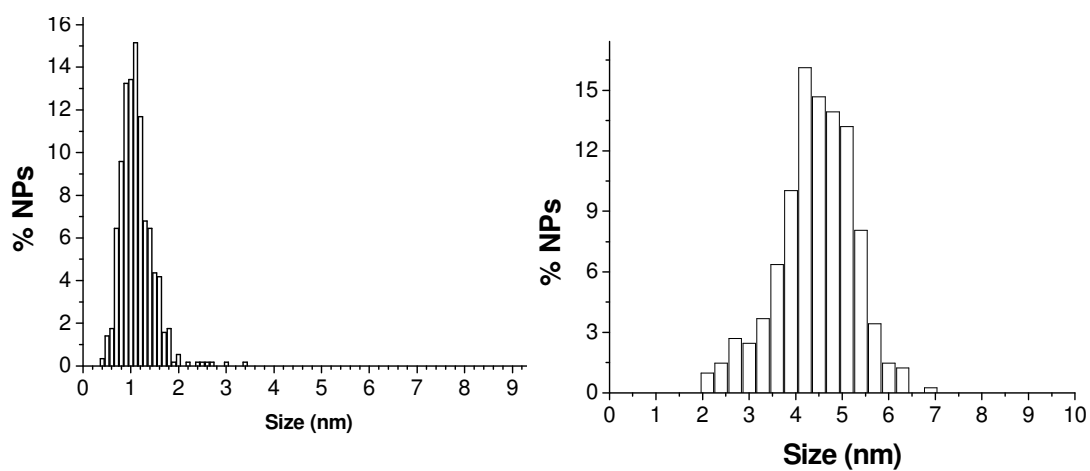
**Figure SI-1.-** Absorption spectrum of **AuNP-1**



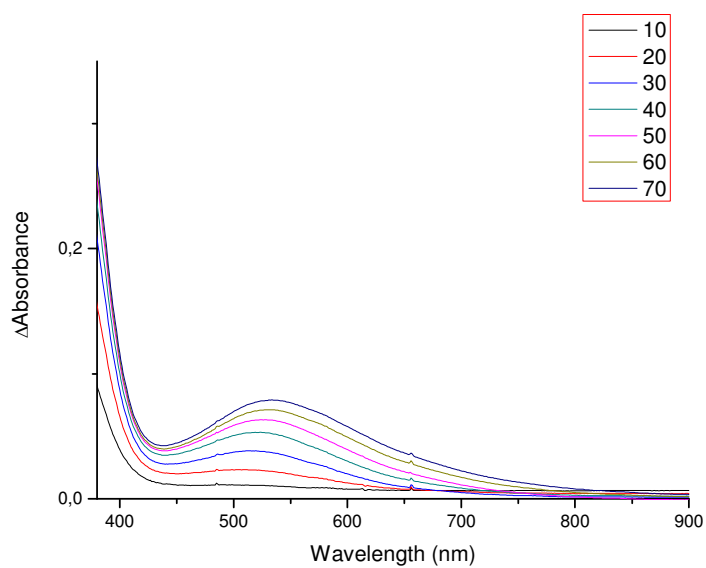
**Figure SI-2.**  $^1\text{H}$ -NMR spectra in  $\text{CDCl}_3$  of: A) **AuNP-1**, B) pyrene-thiol ligand **1**.



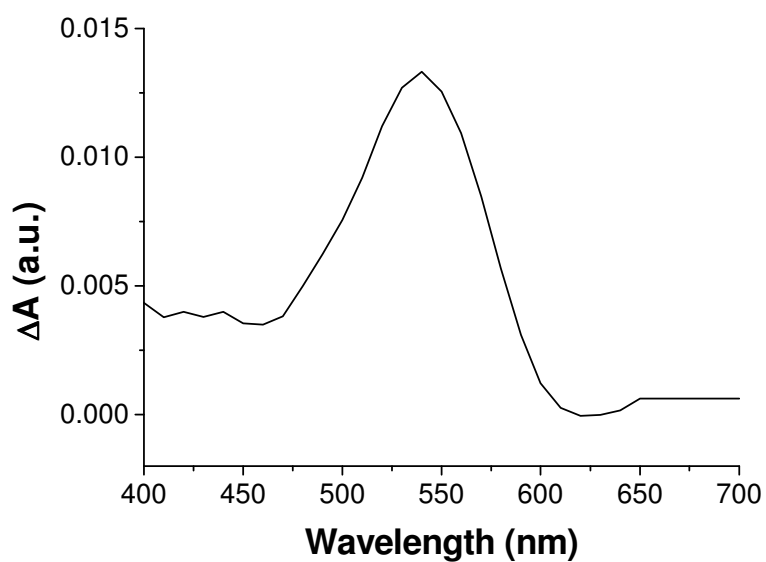
**Figure SI-3.-** TEM images of **AuNP-1** before (left) and after (right) irradiation in the presence of benzophenone (0.2 mM). Please note that the scale in the left is 10 nm and that in the right is 20 nm.



**Figure SI-4.** Histograms of the nanoparticles shown in Figure SI-3. More than 500 NP were measured for the preparation of these histograms.

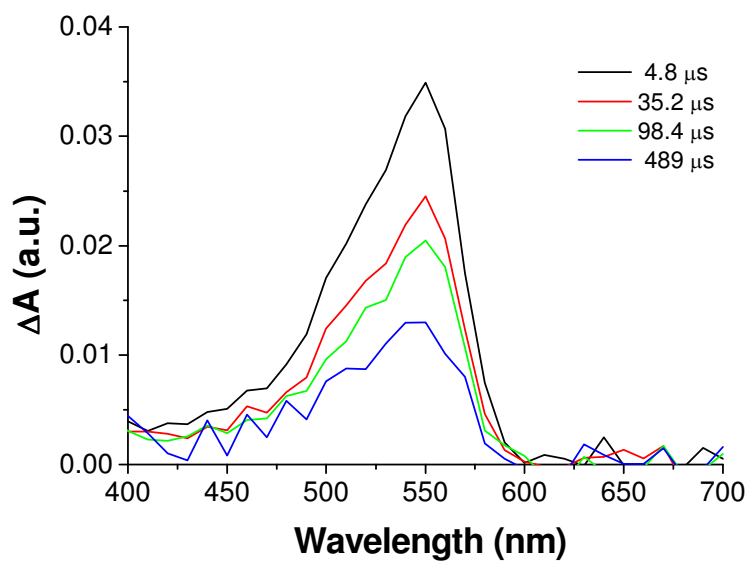


**Figure SI-5.** Irradiation of **AuNP-1** in THF in the presence of 4-metoxibenzophenone (0.5 mM).

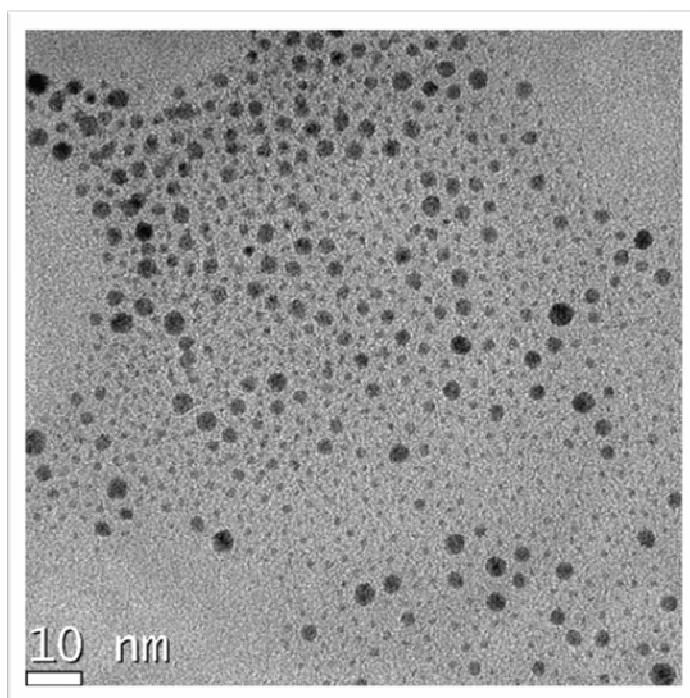


**Figure SI-6.** Laser flash photolysis spectrum of deaerated THF solution of **AuNP-1** ( $A_{355\text{nm}}=0.25$ ) in the presence of benzophenone (1.9 mM) registered 1.6  $\mu\text{s}$  after the laser pulse.

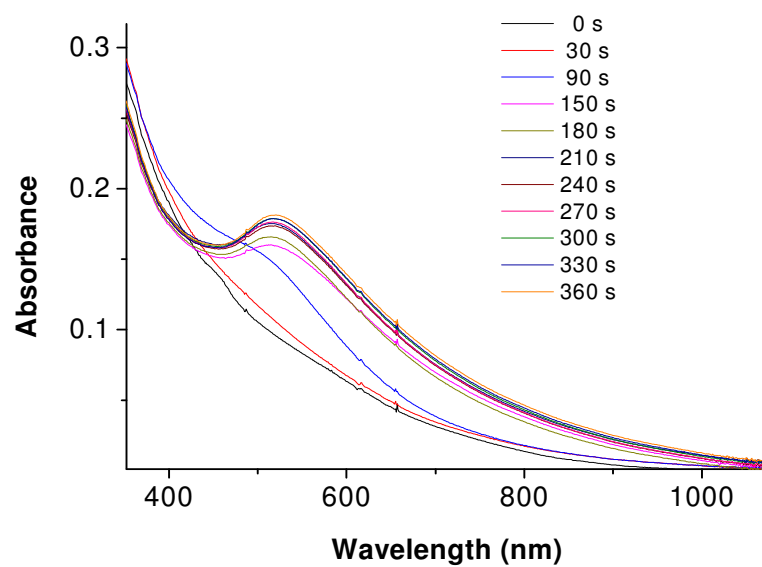




**Figure SI-7.** Transient absorption spectra of deaerated THF solution of benzophenone (1.9 mM) registered 4.8  $\mu\text{s}$  (black), 35.2  $\mu\text{s}$  (red), 98.4  $\mu\text{s}$  (green), and 489  $\mu\text{s}$  (blue) after the laser pulse.



**Figure SI-8.** TEM image evidencing the growth of **AuNP-1** after the laser experiments.



**Figure SI-9.-** UV-vis absorption spectra of the irradiation of decanethiol-derivatized NPs in the presence of BP (0.2 mM).