Supporting Information

Electron transfer from the benzophenone triplet excited state directs the photochemical synthesis of gold nanoparticles

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temperature were set to room temperature. The mobile phase consisted of 65/35-Water/Acetonitrile with 0.1% trifluoroacetic acid (TFA) and the flow rate was set to 1.0 mL/min. The injection volume was 10 μL.

Page S8: Table S2. Concentration of benzophenone found by HPLC after 0, 2, 6, and 20 minutes of 368nm LED irradiation of an aqueous solution containing 1.0 mM benzophenone and 0.33mM $HAuCl_4$. Reversed phase analysis was performed on the samples using an Agilent Autosample 1100 with a Zorbax Extend C-18 – reverse phase column (3.5 μm, 80 A; 50 mm x 4.6 mm) C18 column. The autosampler and column temperature were set to room temperature. The mobile phase consisted of 40/60-Water/Acetonitrile and the flow rate was set to 1.0 mL/min. The injection volume was 10 μL. Concentrations were determined using a calibration curve for benzophenone at a wavelength of 260nm.

Page S9: Calculations for BP* and BP$^{+.}$ And Substitution of CH_3CN for CD_3CN

Page S9: Figure S4. Top: Calculated electrostatic potential at the nuclei of the benzophenone triplet excited state (left) and its corresponding cation radical (right). **Bottom**: Graphical representation of the electron spin density on the benzophenone triplet excited state (left) and its corresponding radical cation (right). The length (in Å) of selected bonds is also shown.

Page S9: Figure S5: Effect of substitution of 3% CH_3CN (open points) for 3% CD_3CN (filled points) on the formation of AuNP under 368 nm LED irradiation.

Experimental

All reagents were purchased from commercial sources and used as received unless otherwise stated. Benzophenone (BP) and gold (III) tetrachloroauric acid hydrate (HAuCl$_4$•3H$_2$O) were purchased from Sigma-Aldrich. Aqueous solutions were prepared daily using Milli-Q water, which had been previously treated for 24 hours with Chelex-100 in order to remove any metal traces. Optima grade CH$_3$CN was purchased from Fisher Chemicals and deuterated acetonitrile (CD$_3$CN 99.9%) and deuterated water (D$_2$O 99.9%) were obtained from Cambridge Isotope Laboratories Inc.

Absorption Measurements

Absorption spectra were recorded using a Cary-50 UV-Visible spectrophotometer using 1×1 cm plastic cuvettes.

Synthesis and Characterization of Gold Nanoparticles

Experiments were conducted using a single 368 nm Synjet cooled LED (see Figure S1). The irradiance of which was measured to be 167 W/m^2 with a Luzchem SPR-01 Spectroradiometer. A stock solution of 55 mM benzophenone was prepared in CH$_3$CN from which 1.0 mM, 0.33 mM, and 0.15 mM aqueous solutions of benzophenone were prepared through dilution of an appropriate amount of the benzophenone stock solution with Chelex-100 treated Milli-Q H$_2$O or D$_2$O to a final volume of 15 mL. To all solutions 54 μL of a 91 mM solution of HAuCl$_{4(aq)}$ were added to give a final concentration of 0.33 mM. The HAuCl$_{4(aq)}$ solution was prepared in either H$_2$O or D$_2$O depending on the conditions of the reaction. Irradiation of solutions at 368 nm were carried out under air in polystyrene cuvettes. The solutions were irradiated as 3.0 mL samples and a mini magnetic stirring bar was used to stir the solution. The AuNP formation was followed by UV-Vis, without dilution in the reaction cuvette. Once the intensity of the AuNP SPB had levelled off in the plateau region an aliquot was taken for SEM analysis and the samples were removed from the LED or photoreactor and stored in the dark. pH values recorded during AuNP formation were measured using a pH-meter 2000 (VWR scientific) electrode calibrated daily.

AuNP sizes were determined using a JSM-7500F field emission scanning electron microscope (SEM) from JEOL Ltd. Size distribution histograms and average particle size are based on the measurement of at least 200 particles per sample. Imaging software (ImageJ version 1.45s) was used to measure the size of the particles.

HPLC Analysis of Reaction Mixtures

i) Benzophenone Degradation: Aqueous solutions containing 1.0 mM benzophenone and 0.33 mM HAuCl$_4$ were irradiated with 368 nm LED light for varying periods of time corresponding to the induction period, linear growth phase, and plateau phase of AuNP growth, i.e. 2.0, 6.0 and 20 min, respectively. LED irradiations were conducted in the same fashion as described in the previous section (see Figure S1). The samples were transferred to 15 mL polystyrene centrifuge tubes and centrifuged at 3000 rpm for 20 min. The supernatant was then filtered through a 0.22 μm syringe filter, of which 250 μL was diluted with 4.75 mL of Milli-Q H$_2$O to give a final volume of 5.0 mL. 1.8 mL of the solution was then transferred to an HPLC vial. Reverse phase analysis was performed on the samples using an Agilent Autosample 1100 with a Zorbax Extend C-18 – reverse phase column (3.5 μm, 80 Å; 50 mm x 4.6 mm) C18 column. The autosampler and column temperature were set to 25 °C. The mobile phase consisted of 40/60-water/acetonitrile and the flow rate was set to 1.0 mL/min. The injection volume was 10 μL and the detection wavelengths used were 220, 230, 260 and 285 nm. Benzophenone was followed at 260 nm.

ii) Oxidation Products: To examine the oxidation products obtained upon irradiation of aqueous solutions containing benzophenone and HAuCl$_4$ we have analyzed the products obtained following 20 min of 368 nm LED irradiation of an air equilibrated acetonitrile:H$_2$O solution containing 1.0 mM and 0.33 mM HAuCl$_4$. After irradiation the sample was centrifuged at 3000 rpm for 20 minutes and 900 μL of the supernatant was then diluted with 900 μL of acetonitrile in an HPLC vial. Reverse phase analysis was performed on the samples using an Agilent Autosample 1100 with a Zorbax Extend C-18 – reverse phase column (3.5 μm, 80 Å; 50 mm x 4.6 mm) C18 column. The autosampler and column temperature were set to 25 °C. The mobile phase consisted of 65/35-Water/Acetonitrile with 0.1% trifluoroacetic acid (TFA) and the flow rate was set to 1.0 mL/min. The injection volume was 10 μL and the detection wavelengths used were 220, 240, 260 and 285 nm.

HPLC Calibration Curve and Standards

A 15 mL solution of a 1.0 mM benzophenone solution was prepared as described in the previous section. This stock solution was diluted to 50 μM in Milli-Q H$_2$O and from here a series of dilutions provided 40, 30, 20, and 10 μM solutions which were analyzed via HPLC under the same conditions described above to construct a calibration curve for benzophenone at 260 nm. 50 μM solutions of 4-chlorobenzophenone, 4-hydroxybenzophone, and benzoic acid, as well as a 16.5 μM solution of HAuCl$_4$ were also submitted for HPLC analysis under the same conditions to determine their retention times. The concentrations of benzophenone, 4-hydroxybenzophenone, and benzoic acid found in the oxidation product study were determined from their molar absorptivity coefficient at 230nm.

Computational Details

The geometrical optimization of both the benzophenone triplet excited state and the radical cation formed after the electron transfer was done using the Amsterdam Density Functional (ADF) code. Both molecular structures were fully optimized by an analytical energy gradient method as implemented by Verluis and Ziegler, using the hybrid functional

B3LYP with the triple-ξ quality double plus polarization function (TZ2P) for all atoms.[1] In all cases, frequency analyses were performed after the geometry optimization, in which we obtained only positive frequencies, thus verifying local minima.

After the optimization procedure, the spin density was plotted by calculating the alpha spin density minus the beta spin density. Finally the electrostatic potential (EP) at each nucleus was determined by calculating the Coulomb potential of the molecule at the nuclear positions, where the contribution from the nucleus itself is omitted; in that way we obtained the EP at the nuclei due to valence electrons and other nuclei.

Quenching of Benzophenone by HAuCl$_4$

The triplet quenching experiments by HAuCl$_4$ were performed using a Nd-YAG laser (355 nm, ca 10 ns, 10 mJ/pulse) in a LFP-111 laser-flash photolysis (LFP) system (Luzchem Inc., Ottawa, Canada) and 1×1 cm LFP-Luzchem cuvettes. Samples of benzophenone were prepared in solutions of 3% acetonitrile:water with a total volume of 3 mL and an absorbance of ~0.1 at 355 nm. The samples were degassed with N$_2$ for 30 minutes prior to use. The solution of HAuCl$_4$ used for the quenching study was prepared as a 91 mM solution in H$_2$O, which was also degassed for the duration of the experiment. Through serial additions of the quencher the quenching of the benzophenone triplet and the bleaching of the gold salt at 520 nm and 320 nm were monitored, respectively. From this the quantum yield of the one electron reduction, Φ_{et}, of Au^{3+} to Au^{2+} was determined as follows:

$$\Phi_{et} = \frac{I_{abs}}{Electron\_transfer} = \frac{\dfrac{\Delta OD_{520nm}}{\varepsilon_{520nm}}}{\dfrac{\Delta OD_{320nm}}{\varepsilon_{320nm}}}$$

Where I$_{abs}$ and Electron_transfer are defined as the amount of light absorbed by benzophone and the number of Au^{+3} reduced by the triplet excited state, respectively. We have replaced those by ΔOD at 520 nm and 320 nm respectively that correspond to the maximum absorption for the benzophenone triplet excited state and HAuCl$_4$ ground state absorption. e$_{520nm}$ (5800 M^{-1} cm^{-1})^2 and e$_{320nm}$ (2051 M^{-1} cm^{-1}) correspond to the molar extinction coefficient for the benzophenone triplet excited state and ground state Benzophenone/HAuCl$_4$ in 3% acetonitrile/water respectively. In our calculation we have worked in conditions where almost 90% of the benzophenone triplet excited state is quenched by the gold salt.

Apparatus used for 368nm LED irradiation

Photographs of the apparatus which was utilized in the 368 nm LED irradiation of aqueous solutions containing benzophenone and $HAuCl_4$ is shown in Figure S1.
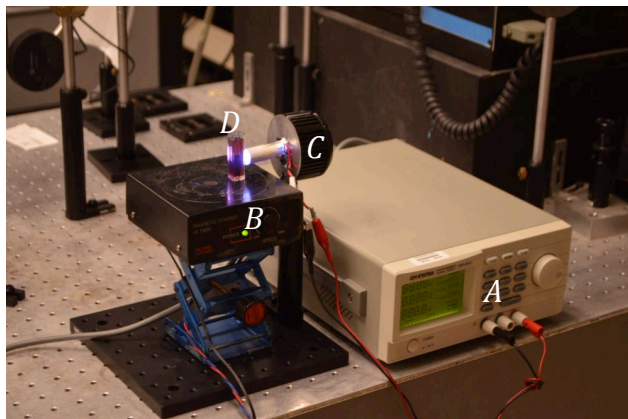
Figure S1. Photograph illustrating the experimental setup used for 368nm LED irradiation. The solutions were irradiated as 3.0 mL samples in polystyrene cuvettes and a mini magnetic stirring bar was used to agitate the solution. *A* is the power supply for the LED, *B* is a magnetic stirrer, *C* is the synjet cooled 368nm LED fitted with a tubular foil light colimator, and *D* is a polystyrene cuvette which contains the solution to be irradiated and a mini magnetic stir bar.

SEM images of AuNP and corresponding size histograms

SEM images of AuNP obtained upon 368 nm LED irradiation of air equilibrated aqueous solutions containing 0.33 mM $HAuCl_4$ and varying concentrations of benzophenone.
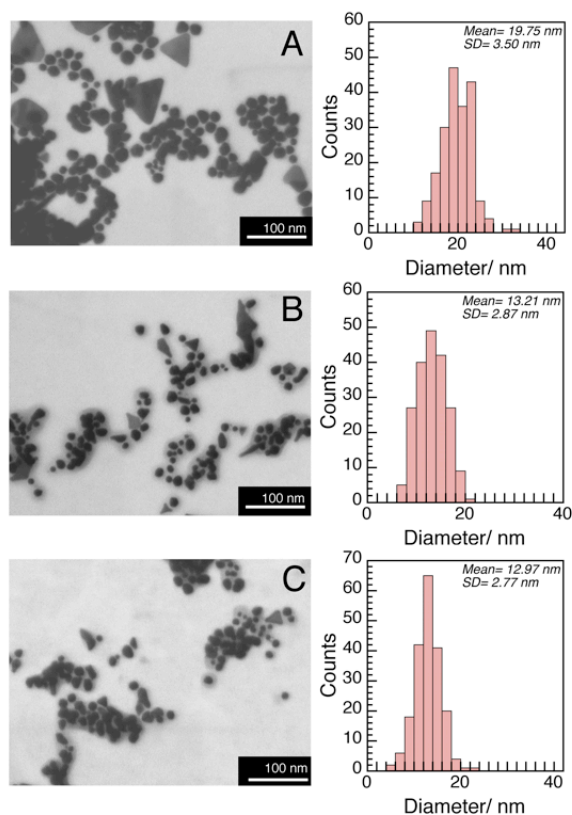
Figure S2. SEM images of AuNP prepared by 368nm LED irradiation of aqueous solutions containing 0.33 mM $HAuCl_4$ and 0.15 mM (A), 0.33 mM (B) and 1.0 mM (C) of benzophenone (left) and corresponding size distribution histogram (right).

## Changes in pH upon 368 nm LED irradiation of aqueous solutions containing HAuCl$_4$ and benzophenone

As previously mentioned in the main text one of the oxidation products, found upon 368 nm LED irradiation of aqueous solutions containing HAuCl$_4$ and benzophenone, is 4-hydroxybenzophenone. It is proposed that this oxidation product is formed via a hydroxy-cyclohexyldienyl radical mediated gold salt reduction. Oxidation of the radical would result in 4-hydroxybenzophenone and the release of a proton, which would most likely form HCl in solution resulting in a progressively more acidic solution as irradiation is continued. In good agreement with this are the pH of solutions containing 0.15, 0.33, or 1.0 mM benzophenone and 0.33mM HAuCl$_4$ upon 368nm LED irradiation shown below in Table S1.

1.0 mM Benzophenone		0.33 mM Benzophenone		0.15 mM Benzophenone	
Time (min)	pH	Time (min)	pH	Time (min)	pH
0	3.46	0	3.41	0	3.42
5	3.28	5	3.2	5	3.26
10	3.19	10	3.04	10	3.25
15	2.98	15	2.93	15	3.12
20	2.90	20	2.90	20	3.06
25	2.87	25	2.89	25	2.98
30	2.87	30	2.90	30	2.96

Table S1. Changes in the pH of aqueous solutions containing 1.0 mM, 0.33 mM, or 0.15 mM benzophenone and 0.33mM HAuCl$_4$ upon irradiation with 368nm LED.

HPLC analysis of benzophenone degradation and resulting oxidation products

To better understand the mechanism by which benzophenone reduces $HAuCl_4$ upon 368nm LED irradiation we set out to monitor the degradation of benzophenone and the resulting oxidation products by HPLC. In Figure S4, one can find HPLC chromatograms extracted at a wavelength of 230 nm for (**A**) a standard mixture of starting materials (benzophenone and $HAuCl_4$) and possible oxidation products (4-hydroxybenzophenone and benzoic acid) and for (**B**) a 1mM benzophenone and 0.33mM $HAuCl_4$ aqueous solution which had been irradiated with a 368nm LED for 20 minutes. In comparing the retention times of the standards with those from the actual reaction mixture, it can be seen that after irradiation there are peaks corresponding to benzophenone, 4-hydroxybenzophenone, and benzoic acid. The degree of degradation of benzophenone with respect to time upon 368nm LED irradiation of a 1mM benzophenone and 0.33mM $HAuCl_4$ aqueous solution was also monitored by HPLC, the results of which can be found in Table S2. As stated in the main text, after 20 minutes of irradiation approx. 30% of the benzophenone has been degraded. The concentrations of benzophenone and its oxidation products used to determine percent composition were determined using the molar absorptivity coefficient of each of the compounds at a wavelength of 230nm. Sample prep and HPLC conditions for each of the HPLC analyses can be found in the corresponding figure caption or in the experimental section of the main text.
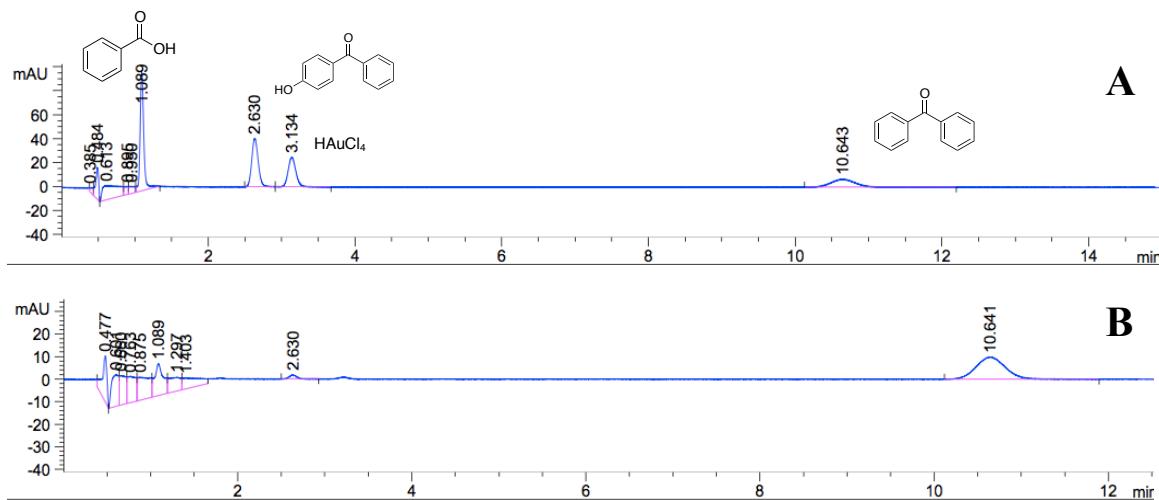

Figure S3. HPLC chromatograms for (**A**) standard solution containing benzophenone [10.643 min], $HAuCl_4$ [3.134 min], 4-Hydroxybenzophenone [2.630 min], and benzoic acid [1.089 min] and (**B**) 1.00 mM benzophenone and 0.33mM $HAuCl_4$ aqueous solution irradiated for 20 minutes with 368 nm LED under air followed by 20 minutes of centrifugation at 3000 RPM and a 50:50 dilution in acetonitrile. Chromatograms were extracted at a wavelength of 230nm. Reversed phase analysis was performed on the samples using an Agilent Autosample 1100 with a Zorbax Extend C-18 – reverse phase column (3.5 μm, 80 A; 50 mm x 4.6 mm) C18 column. The autosampler and column temperature were set to room temperature. The mobile phase consisted of 65/35-Water/Acetonitrile with 0.1% trifluoroacetic acid (TFA) and the flow rate was set to 1.0 mL/min. The injection volume was 10 μL.

Time (min)	[Benzophenone] mM
0	1.00
2	0.83
6	0.82
20	0.70

Table S2. Concentration of benzophenone found by HPLC after 0, 2, 6, and 20 minutes of 368nm LED irradiation of an aqueous solution containing 1.0 mM benzophenone and 0.33mM $HAuCl_4$. Reversed phase analysis was performed on the samples using an Agilent Autosample 1100 with a Zorbax Extend C-18 – reverse phase column (3.5 μm, 80 A; 50 mm x 4.6 mm) C18 column. The autosampler and column temperature were set to room temperature. The mobile phase consisted of 40/60-Water/Acetonitrile and the flow rate was set to 1.0 mL/min. The injection volume was 10 μL. Concentrations were determined using a calibration curve for benzophenone at a wavelength of 260nm.

Calculations for BP* and BP+•
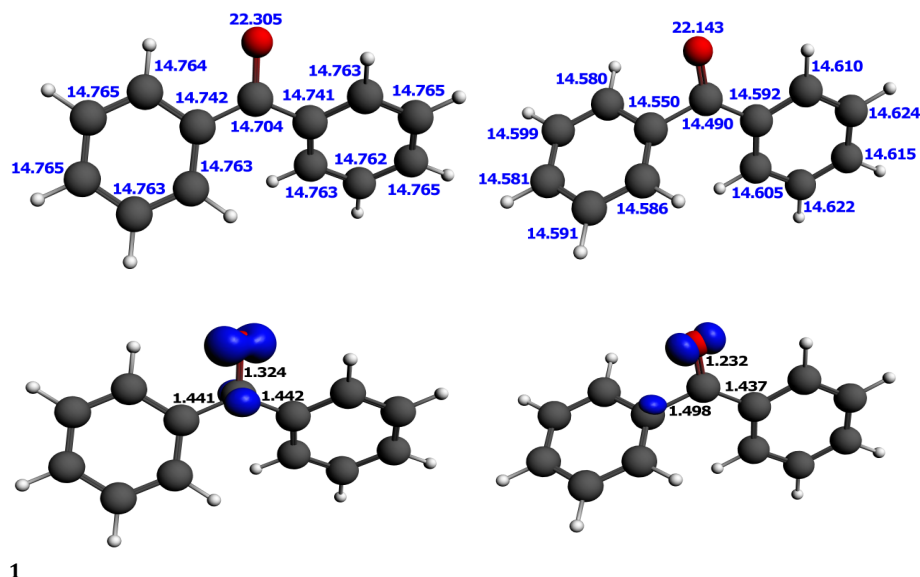
Figure S4. **Top:** Calculated electrostatic potential at the nuclei of the benzophenone triplet excited state (left) and its corresponding cation radical (right). **Bottom**: Graphical representation of the electron spin density on the benzophenone triplet excited state (left) and its corresponding radical cation (right). The length (in Å) of selected bonds is also shown.

Substitution of CH$_3$CN for CD$_3$CN

Figure S6 shows that substitution of 3% CH$_3$CN for 3% CD$_3$CN has no significant effect on AuNP plasmon band formation. The same observation (i.e., AuNP formation) was made in pure water, although under these conditions it is difficult to establish the exact concentration of BP in the saturated solution.
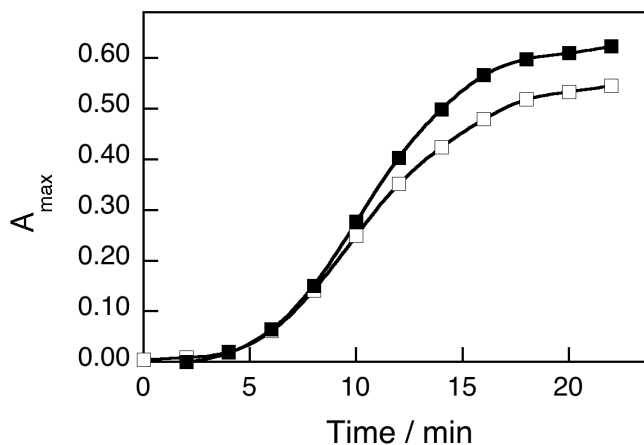
Figure S5. Effect of substitution of 3% CH$_3$CN (open points) for 3% CD$_3$CN (filled points) on the formation of AuNP under 368 nm LED irradiation.

1.   S. Grimme, Semiempirical GGA-type density functional constructed with a long-range dispersion correction, J. Comput. Chem., 2006, 27, 1787-1799.
2.   R. V. Bensasson and J.-C. Gramain, Benzophenone triplet properties in acetonitrile and water. Reduction by lactams, J. Chem. Soc., Faraday Trans.1, 1980, 76, 1801-1810.