Supporting Information for:

Covalent Diamond-Gold Nanojewels Hybrids via Photochemically Generated Carbenes

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Contents

Experimental

Commercial Solvents and Reagents Used

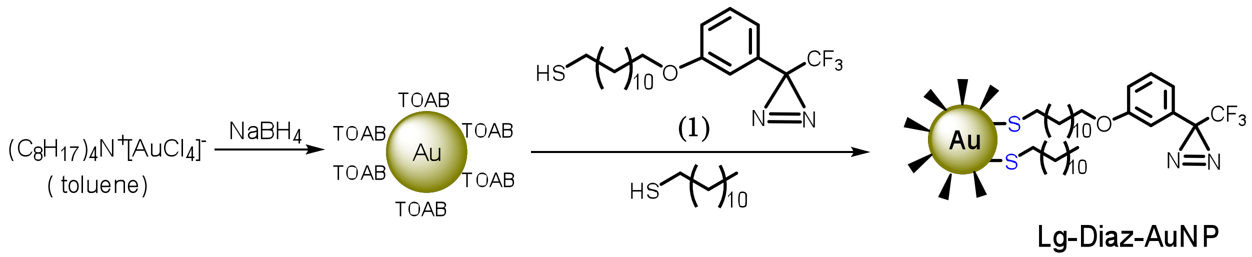
Deuterated chloroform ($CDCl_3$) and dichloromethane (CD_2Cl_2) (Cambridge Isotope Laboratories) were used as received. The compounds dodecanethiol, hydrogen tetrachloroaurate(III), tetraoctylammonium bromide (TOAB), 1,12-dibromododecane, 3-bromoanisole, n-butyllithium, hydroxylamine hydrochloride, (N, N-dimethylamino) pyridine, p-toluenesulfonylchloride, silver (I) nitrate, boron tribromide, potassium thioacetate, acetyl chloride and Diamond powder (Aldrich, monocrystalline, ca. 1 micron) were used as received from the suppliers.

General instrumentation

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on either a Varian Inova or Mercury 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz, and ^{19}F: 376 MHz) and chemical shifts are reported in ppm relative to internal TMS (0.00 ppm) or the signals from the NMR solvent ($CHCl_3$: δ 7.26 ppm for ^{1}H NMR, δ 77.0 ppm for ^{13}C NMR; and $CFCl_3$: δ 0 ppm for ^{19}F NMR). Mass spectra and exact mass were recorded on a MAT 8200 Finnigan High Resolution Mass Spectrometer. Infrared spectra were recorded on a Bruker Vector 33 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). The light source used for the photochemical reactions was a Hanovia medium pressure mercury lamp (PC 451050 /805221). Transmission electron microscopy (TEM) images were recorded on a Philips CM-10 TEM operating at 100 kV. Scanning electron microscopy images were recorded on a LEO (Zeiss) 1540XB FIB/SEM. UV-Visible absorption spectra were recorded on a Cary 100 spectrometer in spectroscopic grade THF and CH_2Cl_2. An Inel MPD (Multi-Purpose Diffractometer) with a curved CPS 120 detector was used to collect x-ray powder diffraction data (XRD). The pattern was taken in the range of 5 and 120 degrees 2theta with copper radiation. DRIFT analysis was performed using a Bruker IFS 55 infrared spectrometer equipped with an MCT detector. A Spectra Tech Baseline™ Diffuse Reflectance attachment with a micro sampling cup was used in the main box. A mirror was used to collect the background. The powder was analysed without any further sample preparation. The XPS analyses were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al K(alpha) source (15mA, 14kV). XPS can detect all elements except hydrogen and helium, probes the surface of the sample to a depth of 5-7 nanometres, and has detection limits ranging from 0.1 to 0.5 atomic percent depending on the element. The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f7/2 line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p3/2 line of metallic copper. The Kratos charge neutralizer system was used on all specimens. Survey scan analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 160 eV. High resolution analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 20 eV. Spectra have been charge corrected to the main line of the carbon 1s spectrum (adventitious carbon) set to 284.8 eV. Spectra were analysed using CasaXPS software (version 2.3.14).

Synthesis of diazirine-modified AuNPs (Diaz-AuNP, 3.9 ± 0.9 nm)

Diaz-AuNPs were prepared using modified two phase Brust-schiffrin method (scheme S1). Hydrogen tetrachloroaurate (III) trihydrate (88.6 mg, 0.24 mmol) was dissolved in 7.5 mL distilled water (resulting in a bright yellow solution) and then added to a solution of tetraoctylammonium bromide (TOAB) (0.574 g, 1.05 mmol) in 21 mL toluene. The contents were stirred for 20 min at room temperature in order to facilitate the phase transfer of the hydrogen tetrachloroaurate (III) trihydrate into the toluene layer. After phase transfer, the aqueous layer was removed and a fresh solution of sodium borohydride (90.8 mg, 2.4 mmol) in 12 mL water was slowly added to the vigorously stirring toluene solution over 10 min. The reaction mixture was stirred for 2 h. The aqueous layer was removed, dodecanethiol (93 mg, 0.46 mmol) and diazirinethiol (93 mg, 0.23 mmol), synthesized as previously reported,[3] were added to the organic layer and stirred overnight. The aqueous layer was removed and the wine-red toluene layer was washed with 3 x 10 mL distilled water and evaporated to reduce the volume to ~ 2 cm^3. The resulting Diaz- AuNPs were suspended in 100 ml of 95 % ethanol and placed in the refrigerator overnight during which time they precipitated from the solution. The supernatant was decanted and the precipitate was dissolved in 100 mL of toluene/ethanol (2:3 v/v) and sonicated for 1 min and re-precipitated. The dissolving and re-precipitation procedure was repeated five times. The Diaz-AuNP mixture was evaporated to dryness, dissolved in toluene, and stored in the refrigerator.



Scheme 2. Schematic representation of preparation of Lg-Diaz-AuNPs

Figure S1 shows the ^{1}H NMR spectrum of free diazirinethiol and Diaz-AuNP. As can be seen, good alignment of the chemical shifts between diazirinethiol and the Diaz-AuNPs implies the successful exchange reaction and incorporation of diazirinethiol onto the AuNP. The lack of sharp signals in the ^{1}H NMR spectra of Diaz-AuNP confirms the purity of product AuMPNs; otherwise the sharp peaks due to impurities such as unattached diazirinethiol, dodecanethiol or TOAB would appear in the ^{1}H NMR spectrum. In addition ^{19}F NMR spectrum of the Diaz-AuNPs shows a single peak at -65 ppm assignable to the fluorine of the CF_3 group of diazirinethiol, a further indication of incorporation of diazirinethiol onto the AuNP (Figure S1).

Synthesis of Non-functionalized AuNP

Non-functionalized AuNPs (AuNPs without diazirinethiol) were prepared as described for Diaz-AuNP except that only the dodecanethiol was used as a protecting ligand.

Fenton Treatment of Micro-Diamond

Ferrous sulfate (15 g) was added to the suspension of micro-diamond (300 mg) in 50 mL of distilled water. The mixture was stirred for 30 min to dissolve ferrous sulfate. Concentrated sulfuric acid (15 mL) was added and the mixture was cooled in an iced-bath. Hydrogen peroxide (15 mL, 30 v/v %) was slowly dropped while observing evolution of CO_2. The slurry was sonicated in an ice-bath for 2 h. Additional amounts of concentrated sulfuric acid (10 mL) and hydrogen peroxide (10 mL) were added to the mixture and sonication was continued for 2 more hours. The contents were stirred for overnight at room temperature. The excess of ferrous sulfate, acid, and hydrogen peroxide were removed by several consecutive centrifugation-dispersion cycles with Milli-Q water. The diamond powder was dried in an oven at 120 ^{0}C for 4 h.

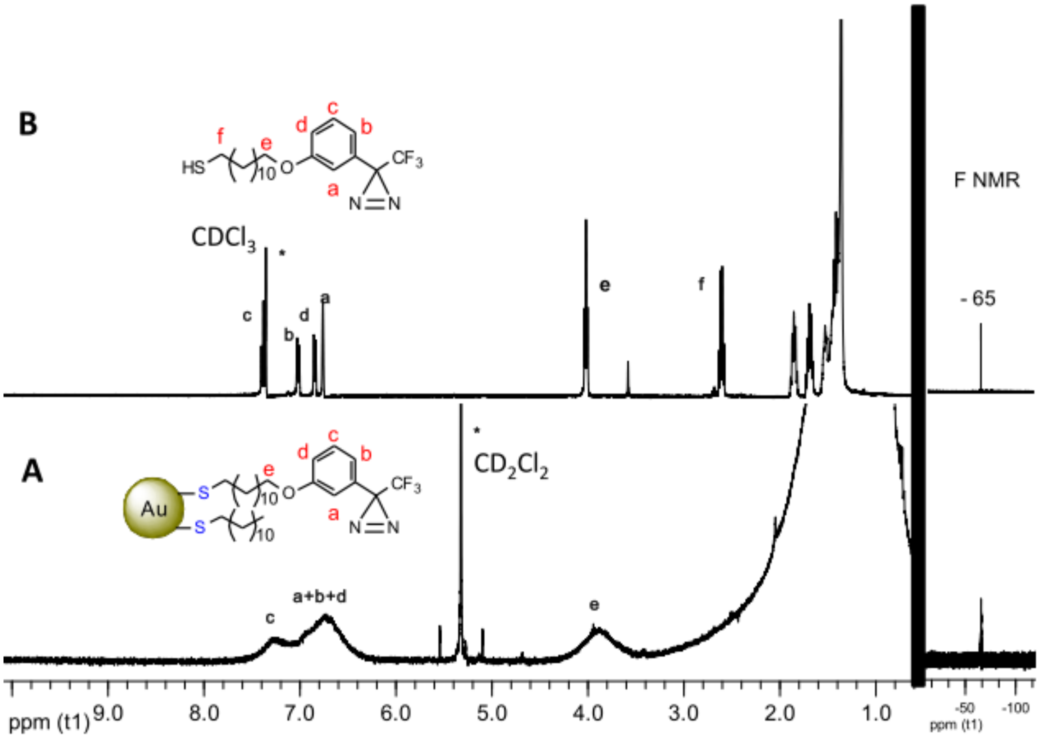


Figure S1. ^{1} HNMR spectra of A) Diaz-AuNPs and B) Diazirinethiol

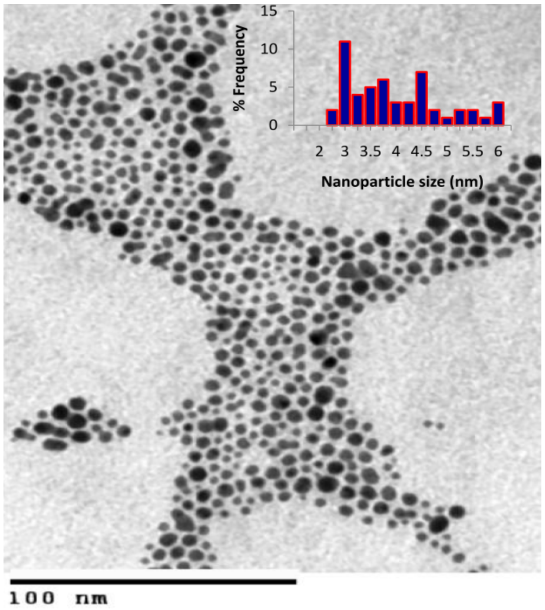


Figure S2. TEM image of Diaz-AuNPs (inset: statistical size distribution)

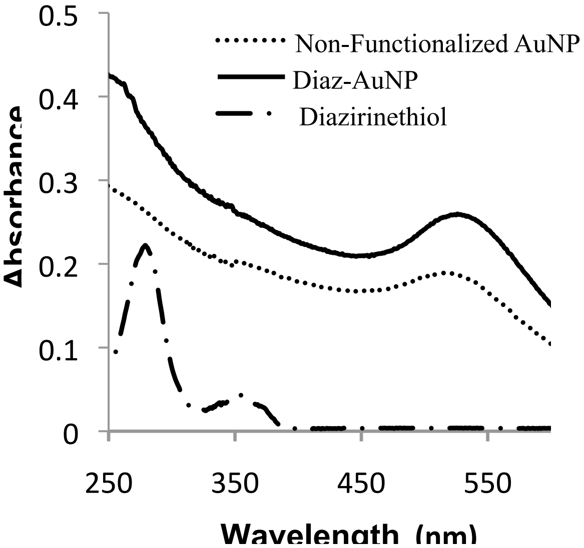


Figure S3. Absorption spectra of Diaz-AuNP, non-functionalized AuNPs and Diazirinethiol in THF

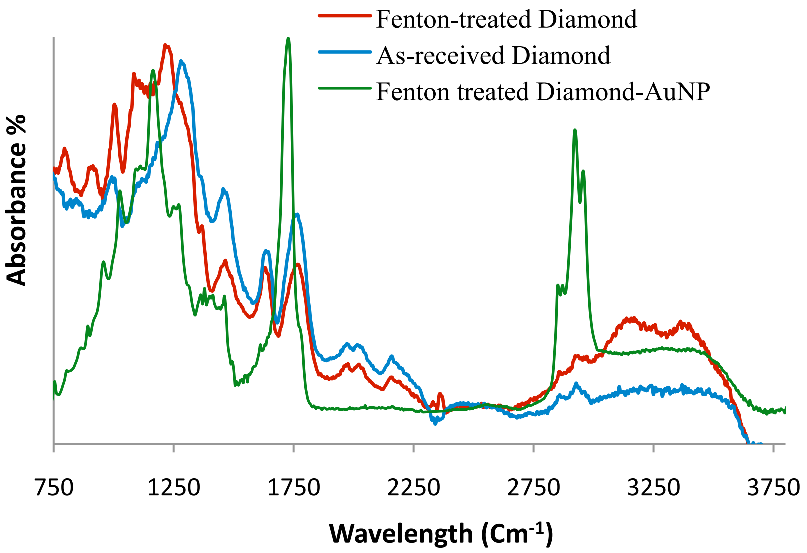


Figure S4. DRIFT-IR spectra of the micro-diamond powder before (blue) and after (red) the Fenton treatment. The green is the IR spectrum of the Fenton-treated diamond-AuNP hybrid material isolated after irradiation.

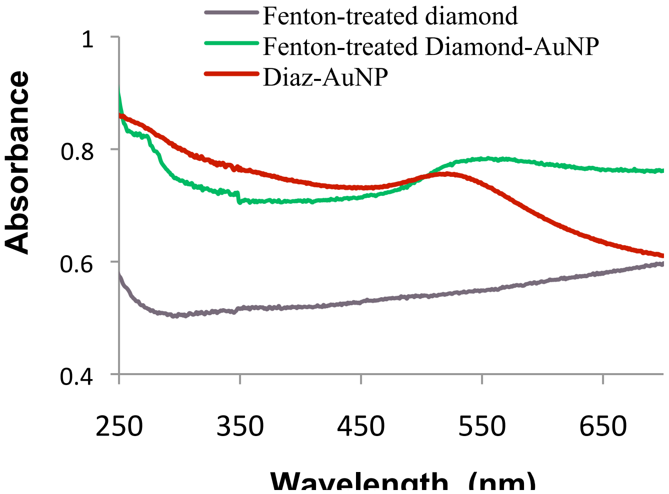


Figure S5. Absorption spectra of Diaz-AuNP, Fenton-treated diamond and Fenton-treated diamond-AuNP hybrid in THF

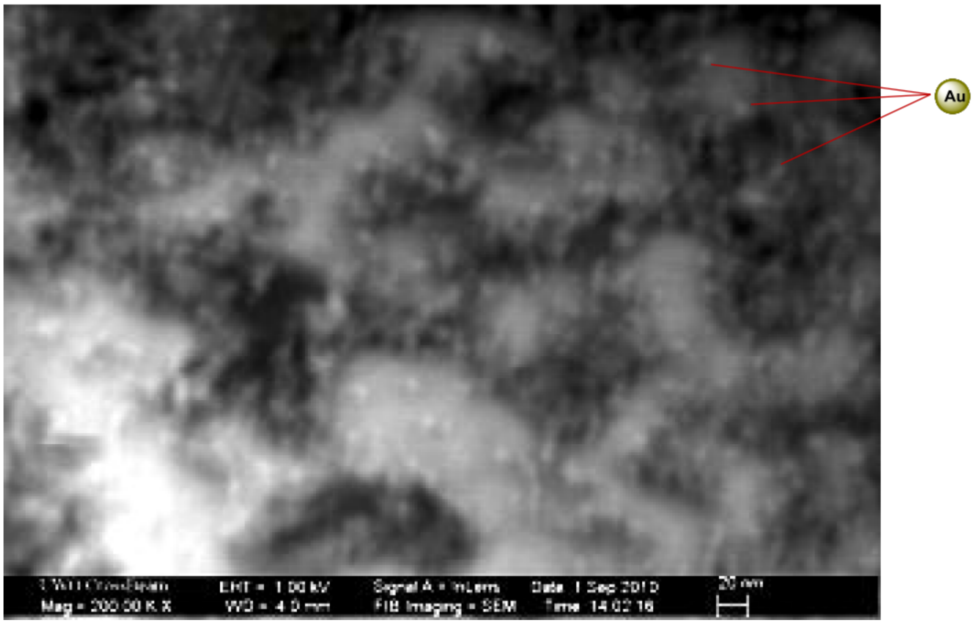


Figure S6. SEM of Diamond-AuNP hybrid.