

Supplementary Information

Photothermal Release of Singlet Oxygen from Gold Nanoparticles

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Materials and Methods

General. All solvents and reagents used for synthesis, chromatography, UV-vis spectroscopy measurements and photolysis studies were purchased from Aldrich or Fisher and used as received, unless otherwise noted. 9-Bromo-10-phenylanthracene was prepared by the bromination of 9-phenylanthracene according to a literature procedure.¹ Diphenylisobenzofuran (**DPBF**) and its endoperoxide (**DPBF-EP**) were prepared according to the literature procedures.² Solvents for NMR analysis were purchased from Cambridge Isotope Laboratories and used as received. Column chromatography was performed using silica gel 60 (230-400 mesh) Silicycle Inc.

Instrumentation. ¹H NMR and ¹³C NMR characterizations of all compounds and synthetic precursors were performed on a Bruker AVANCE 500 TXI inverse ¹H/¹³C/¹⁹F working at 500.19 MHz for ¹H and 125.78 MHz for ¹³C. Chemical shifts (δ) are reported in parts per millions (ppm) relative to tetramethylsilane (TMS) using the residual solvent peak as a reference standard. Coupling constants (J) are reported in hertz (Hz). Multiplicities are reported as: s = singlet, d = double, t = triplet, q = quartet, m = multiplet. UV-vis absorption spectroscopy was performed using a Varian Cary 300 Bio Spectrometer. Infrared (IR) spectra were acquired on a Bomem (Hartmann & Braun, MB-Series) spectrometer. High-resolution mass spectra for the compounds were obtained using an Agilent 6210 TOF LC/MS (ESI+). HPLC chromatograms were obtained on WATERS HPLC instrument equipped with 1515 Isocratic HPLC pump and WATERS 2487 Dual λ absorbance detection using spectroscopic grad CHCl₃ purchased from CALEDON. Temperatures were monitored using and RTD (VWR International, Pt-100 Ω , NIST Traceable) with a resolution of 0.01 °C and accuracy of $\pm 0.1\%$ below 200 °C.

Transmission Electron Microscopy (TEM). TEM images were obtained using a Hitachi 8100 Scanning Electron Microscope operating at 200 keV with a LaB6 source. For the nanoparticles dispersed in chloroform, a small amount of the chloroform dispersion of nanoparticles was drop-cast on a carbon formvar-coated copper grid (200 mesh carbon only, Ted Pella, Part # 070613) and air-dried before

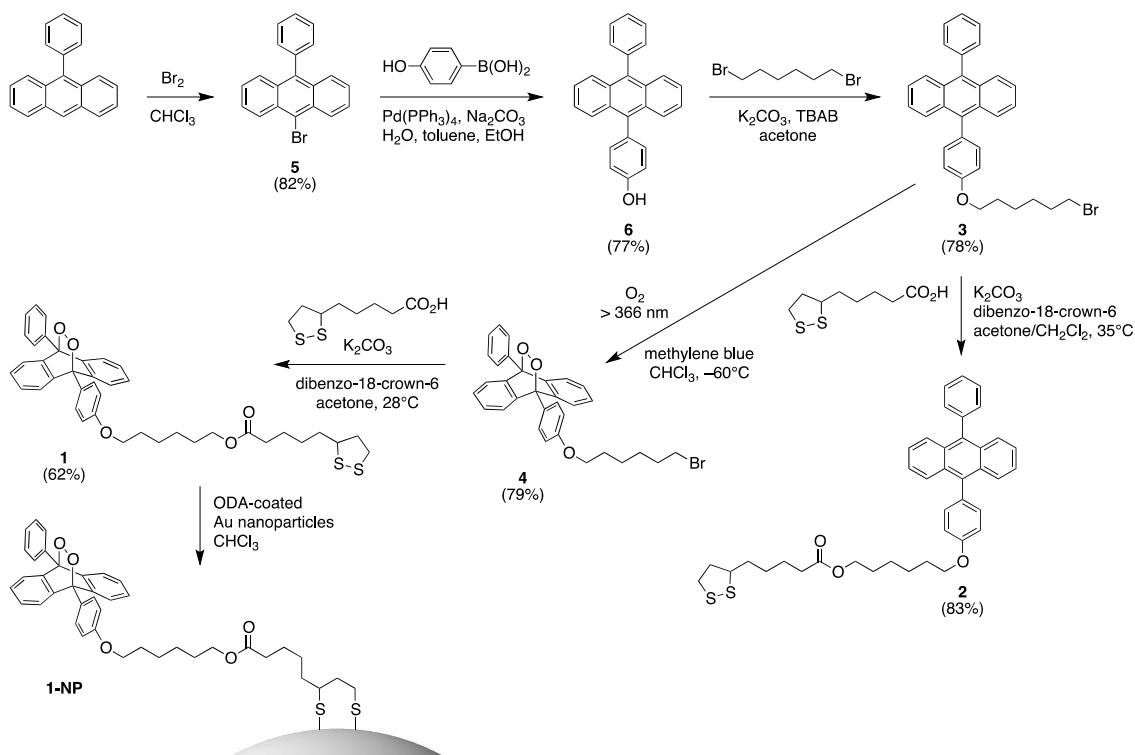
¹ Chung, S.-J.; Kim, K.-K.; Jin, J.-I. *Polymer* **1999**, *40*, 1943.

² Haynes, R.; Peters, J.; Wilmot, I. *Australian Journal of Chemistry* **1980**, *33*, 2653.

imaging. The shape and size of the gold nanoparticles were evaluated from the collected TEM images. The size of the nanoparticles was calculated from over 25 particles located at different areas of the TEM grid. For the nanoparticles dispersed in water, dilute colloids of the nanoparticles (0.1 wt-%) dispersed in ultrapure water (5 mL) were placed on thin, carbon formvar-coated copper grids held by anti-capillary tweezers (Ted Pella, Part # 501-4). Water was then slowly removed under reduced pressure in a vacuum desiccator.

Synthesis of gold nanoparticles. All glassware and stirrers used in the synthesis of gold nanoparticles were cleaned with aqua regia, washed with distilled water and kept in distilled water overnight. Just prior to use, they were rinsed with acetone or absolute EtOH and dried. All reactions and measurements involving ligand **1** and diphenylisobenzofuran (**DPBF**) were performed under red light illumination and at an ambient temperature below 22 °C due to the sensitivity of the materials to light and elevated temperatures. The purification of the decorated gold nanoparticles (**1-NP**) by centrifugation was also performed at a temperature below 4 °C.

Synthetic Scheme



Synthesis of 9-bromo-10-phenylanthracene (5). A solution of 9-phenylanthracene (2.0 g, 7.9 mmol) in CHCl_3 (30 mL) was treated with a solution of bromine (0.40 mL, 7.9 mmol) in CHCl_3 (9.6 mL) drop wise over a period of 10 min at room temperature. The reaction was stirred for 75 min, at which time it was quenched with a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL). The organic layer was removed and washed with aqueous Na_2CO_3 (1 M, 100 mL) and water (2×100 mL). The organic layer dried over MgSO_4 , filtered and evaporated under reduced pressure. Recrystallization from a

mixture of CH₂Cl₂ and hexanes (1:1) on rotary evaporator yielded 2.1 g (82%) of the product as yellow crystals.

M.p. = 154–155 °C. ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.61 (d, *J* = 8.8 Hz, 2H), 7.56–7.66 (m, 7H), 7.37–7.41 (m, 4H). ¹³C NMR (CD₂Cl₂, 500 MHz): δ 138.8, 138.5, 131.6, 131.5, 130.7, 128.9, 128.3, 128.1, 127.9, 127.5, 126.1, 122.9. HRMS (CI) *m/z* calculated for C₂₀H₁₃Br (M+H⁺) 332.0201, found 333.1.

Synthesis of 4-(10-phenylanthracen-9-yl)phenol (6). A solution of 9-bromo-10-phenylanthracene (0.50 g, 1.5 mmol) in toluene (10 mL) was mixed with a solution of (4-hydroxyphenyl)boronic acid (0.27 g, 1.9 mmol) in EtOH. This mixture was treated with an aqueous solution of Na₂CO₃•H₂O (2.1 mL, 2 M). The resulting suspension was purged for 30 min with a stream of N₂ and treated with Pd(PPh₃)₄ (7 mg, 0.060 mmol). The mixture was heated to reflux under N₂ atmosphere for 7 h, at which time the heating source was removed and the reaction was allowed to cool to room temperature. Water (30 mL) was added and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure. Purification by column chromatography using silica gel (20% EtOAc in hexanes) afforded 0.40 g (77%) of the product as a yellow solid.

M.p. = 245–247 °C. IR (diamond ATR): $\tilde{\nu}$ = 3427 cm⁻¹ (OH). ¹H NMR (CD₂Cl₂, 500 MHz): δ 7.71–7.76 (m, 2H), 7.64–7.69 (m, 2H), 7.59–7.64 (m, 2H), 7.54–7.59 (m, 1H), 7.44–7.48 (m, 2H), 7.30–7.37 (m, 6H), 7.06–7.11 (m, 2H), 5.21 (s, 1H, OH). ¹³C NMR (CD₂Cl₂, 500 MHz): δ 155.7, 139.4, 137.4, 137.3, 133.0, 131.7, 131.5, 130.6, 130.3, 128.9, 127.9, 127.4, 127.3, 125.4, 125.4. HRMS (CI) *m/z* calculated for C₂₆H₁₈O (M+H⁺) 346.1358, found 347.1419.

Synthesis of 9-(4-((6-bromohexyl)oxy)phenyl)-10-phenylanthracene (3). A solution of 4-(10-phenylanthracen-9-yl)phenol (6) (0.32 g, 0.94 mmol) in acetone (25 mL) was treated with 1,6-dibromohexane (1.0 mL, 6.7 mmol), K₂CO₃ (0.23 g, 1.7 mmol) and tetra-*n*-butylammonium bromide (3 mg, 9 mmol). The suspension was heated to reflux under N₂ atmosphere for 48 h at which time the heating source was removed and the reaction was allowed to cool to room temperature. Any solids were filtered off under vacuum and the filtrate was evaporated to dryness using a rotary evaporator. The residue was triturated with EtOH and the yellow solids were filtered and washed with cold ethanol and dried under vacuum to afford 0.37 g (78%) of the product as yellow solid.

M.p. = 128–130 °C. IR (diamond ATR): $\tilde{\nu}$ = 1239 (C–O). ¹H NMR (CD₂Cl₂, 500 MHz): δ 7.71–7.77 (m, 2H), 7.64–7.70 (m, 2H), 7.59–7.64 (m, 2H), 7.54–7.59 (m, 1H), 7.43–7.49 (d, *J* = 7.1 Hz, 2H), 7.29–7.39 (m, 6H), 7.11–7.17 (d, *J* = 8.2 Hz, 2H), 4.12 (t, *J* = 6.4 Hz, 2H, O–CH₂), 3.49 (t, *J* = 6.7 Hz, 2H, CH₂–Br), 1.89–1.96 (m, 4H), 1.58–1.59 (m, 4H). ¹³C NMR (CD₂Cl₂, 500 MHz): δ 159.2, 139.6, 137.5, 137.4, 132.8, 131.8, 131.3, 130.7, 130.4, 128.9, 128.0, 127.5, 127.3, 125.5, 125.4, 114.9, 68.5, 34.6, 33.3, 29.7, 28.5, 25.9. HRMS (CI) *m/z* calculated for C₃₂H₂₉BrO (M+H⁺) 508.1402, found 510.1393. C₃₂H₂₉BrO: calcd C 75.44, H 5.74; found C 75.39, H 5.90.

Synthesis of 9-(4-((6-bromohexyl)oxy)phenyl)-10-phenyl-9,10-dihydro-9,10-epidioxyanthracene (4). In a photo-oxidation apparatus, a solution of 9-(4-((6-bromohexyl)oxy)phenyl)-10-phenylanthracene (**3**) (0.37 g, 0.74 mmol) and methylene blue (27 mg, 0.07 mmol) in CHCl₃ (500 mL) was cooled to -60 °C. A slow stream of oxygen gas was bubbled under the surface of the reaction mixture through a needle while the mixture was irradiated with light of wavelengths greater than 366 nm using Hanovia 697A36 mercury arc lamp (450 W). A constant stream of N₂ was also used to dilute the concentration of oxygen gas in the reaction mixture. The reaction was monitored by TLC, which confirmed the completion of the reaction after 2 h. The gas flow and light source were turned off and the reaction mixture was allowed to slowly warm to room temperature. The mixture was washed with water (2 × 200 mL), the colourless organic layer was removed and dried over MgSO₄, filtered and evaporated under reduced pressure. Purification by column chromatography on silica gel (10:1 hexanes:EtOAc) in the dark afforded 310 mg (79%) of the product as white crystals.

M.p. = 144–146 °C. IR (diamond ATR): $\tilde{\nu}$ = 1242 cm⁻¹ (C–O). ¹H NMR (CD₂Cl₂, 500 MHz): δ 7.62–7.69 (m, 4H), 7.54–7.60 (m, 3H), 7.20–7.26 (m, 4H), 7.13–7.20 (m, 6H), 4.09 (t, *J* = 6.4 Hz, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 1.87–1.95 (m, 4H), 1.55–1.58 (m, 4H). ¹³C NMR (CD₂Cl₂, 500 MHz): δ 159.54, 141.20, 140.87, 133.54, 129.16, 128.89, 128.83, 128.14, 128.10, 128.01, 125.21, 123.87, 123.82, 114.81, 84.40, 84.37, 68.51, 34.65, 33.36, 29.69, 28.52, 25.88. HRMS (CI) *m/z* calculated for C₃₂H₂₉BrO₃ (M+H⁺) 540.1300 found 543.1373. C₃₂H₂₉BrO₃: calcd C 70.98, H 5.40; found C 70.75, H 5.59.

Synthesis of 6-(4-(10-phenyl-9,10-dihydro-9,10-epidioxyanthracen-9-yl)phenoxy)hexyl 5-(1,2-dithiolan-3-yl)pentanoate (1). A suspension of α -lipoic acid (27 mg, 0.13 mmol), dibenzo-18-crown-6 (18 mg, 51 μ mol) and K₂CO₃ (42 mg, 0.30 mmol) in acetone (2.5 mL) was purged for 30 min with a stream of N₂ and then treated with 9-(4-((6-bromohexyl)oxy)phenyl)-10-phenyl-9,10-dihydro-9,10-epidioxyanthracene (**4**) (55 mg, 0.10 mmol). The mixture was heated at 28 °C for 69 h using an oil bath, at which time the heating source was removed and the reaction was allowed to cool to room temperature. H₂O (20 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure. Purification by column chromatography on silica gel (20% EtOAc in hexanes) afforded 42 mg (62%) of the product as a yellow solid.

M.p. = 48–50 °C. IR (KBr): $\tilde{\nu}$ = 1732 cm⁻¹ (C=O). ¹H NMR (CD₂Cl₂, 500 MHz): δ 7.66–7.72 (m, 4H), 7.58–7.63 (m, 3H), 7.16–7.29 (m, 10H), 4.08–4.11 (m, 4H), 3.54–3.60 (m, 1H), 3.07–3.19 (m, 2H), 2.41–2.47 (m, 1H), 2.32 (t, *J* = 7.4, 2H), 1.86–1.91 (m, 3H), 1.45–1.73 (m, 12H). ¹³C NMR (CD₂Cl₂, 500 MHz): δ 173.92, 159.60, 141.25, 140.92, 133.58, 129.19, 128.91, 128.85, 128.16, 128.11, 128.04, 125.23, 123.90, 123.85, 114.85, 84.44, 84.41, 68.61, 64.79, 57.03, 40.82, 39.09, 35.19, 34.63, 29.79, 29.34, 29.23, 26.37, 25.33. HRMS (CI) *m/z* calculated for C₄₀H₄₂O₅S₂ (M+H⁺) 666.8885 found 667.2535.

Synthesis of 6-(4-(10-phenylanthracen-9-yl)phenoxy)hexyl 5-(1,2-dithiolan-3-yl)pentanoate (2). A suspension of α -lipoic acid (15 mg, 0.07 mmol), dibenzo-18-crown-6 (17 mg, 0.07 mmol) and K_2CO_3 (13 mg, 0.1 mmol) in acetone (0.50 mL) was purged for 30 min with a stream of N_2 and then treated with a solution of 9-(4-((6-bromohexyl)oxy)phenyl)-10-phenylanthracene (**3**) (25 mg, 0.049 mmol) in CH_2Cl_2 (0.50 mL). The mixture was heated at 35 °C for 48 h using an oil bath, at which time the heating source was removed and the reaction was allowed to cool to room temperature. H_2O (5 mL) was added and the mixture was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. Purification by column chromatography on silica gel (20% EtOAc in hexanes) afforded 26 mg (83%) of the product as a yellow solid.

M.p. = 121–123 °C. IR (diamond ATR): $\tilde{\nu} = 1731\text{ cm}^{-1}$ (C=O). 1H NMR (CD_2Cl_2 , 500 MHz): δ 7.72–7.76 (m, 2H), 7.64–7.70 (m, 2H), 7.59–7.64 (m, 2H), 7.55–7.59 (m, 1H), 7.45–7.48 (m, 2H), 7.30–7.39 (m, 6H), 7.11–7.16 (m, 2H), 4.09–4.13 (m, 4H), 3.56–3.59 (m, 1H), 3.07–3.18 (m, 2H), 2.43–2.46 (m, 1H), 2.32 (t, $J = 7.52$, 2H), 1.87–1.91 (m, 3H), 1.49–1.73 (m, 12H). ^{13}C NMR (CD_2Cl_2 , 500 MHz): δ 173.94, 159.31, 139.66, 137.61, 137.47, 132.89, 131.86, 131.34, 130.79, 130.48, 128.99, 128.04, 127.55, 127.42, 125.54, 125.46, 114.97, 68.62, 64.82, 57.03, 40.82, 39.09, 35.20, 34.64, 29.88, 29.34, 29.26, 26.41, 25.34. HRMS (CI) m/z calculated for $C_{40}H_{42}O_3S_2$ ($M+H^+$) 634.8897 found 635.2643.

Synthesis of 14 nm citrate-coated gold nanoparticles. The citrate coated gold nanoparticles were synthesized according to the literature.³ A solution of $HAuCl_4$ (1.0 mM in ultrapure water) at reflux in 250 mL round-bottomed flask was rapidly treated with an aqueous solution of preheated sodium citrate (10 mL, 39 mM) while the mixture was vigorously stirring. The heating was continued for 10 min. The color of the reaction changed from yellow to burgundy. The reaction was cooled down to room temperature over 15 min with vigorous stirring. This dispersion was stored in a clean glass vial and used without any further purification. The UV-vis spectrum of this aqueous solution of citrate-coated gold nanoparticles showed an intense absorption band centered at 520 nm, which corresponds to what is reported in the literature. The TEM images of these nanoparticles showed that they have an average size of 13.8 ± 1.4 nm. The concentration of citrate-coated gold nanoparticles was estimated by drying 1 mL of the nanoparticle solution under high vacuum and weighing the residue. This afforded a value of 1.29 mg/mL.

Synthesis of 15 nm octadecylamine-coated (ODA) gold nanoparticles. The citrate-coated gold nanoparticles were transferred from the aqueous to the organic phase according to the literature procedure.⁴ The aqueous solution of citrate-coated gold nanoparticles (1.0 mL) was carefully layered on top of a $CHCl_3$ solution of octadecylamine (ODA) (2.0 mL, 0.75 mM) in a centrifuge tube, followed by the addition of ultrapure water (1 mL). The two-phase mixture was mixed vigorously for

³ Lakshminarayana, P.; Qing-Hua, X. *Nanotechnology* **2009**, *20*, 185606.

⁴ Karg, M.; Schelero, N.; Oppel, C.; Gradzielski, M.; Hellweg, T.; von, K. R. *Chem.-Eur. J.* **2011**, *17*, 4648.

3 min using vortex. The organic layer was carefully removed and its volume reduced to half using a rotary evaporator. This solution of ODA-coated gold nanoparticles was used without any further purification. The UV-vis spectrum of this CHCl₃ solution showed an intense absorption band centered at 525 nm. The TEM images of these nanoparticles showed that they have an average size of 14.6 ± 0.9 nm. The concentration of ODA-coated gold nanoparticles was estimated by drying 1 mL of the nanoparticle solution under high vacuum and weighing the residue. This afforded a value of 0.45 mg/mL.

Synthesis of endoperoxide decorated nanoparticles (1-NP). An aliquot amount of the CHCl₃ stock solution of the ODA-coated nanoparticles (2.5 mL) was diluted to 3 mL with CHCl₃ in a clean vial. This solution was treated with a solution of 6-(4-(10-phenyl-9,10-dihydro-9,10-epidioxyanthracen-9-yl)phenoxy)hexyl 5-(1,2-dithiolan-3-yl)pentanoate (**1**) in CHCl₃ (1.5 mL, 1.5 mM) with stirring at 20 °C. The stirring was continued for 18 h while the reaction mixture was protected from light. After this time, 0.75 mL of crude mixture was transferred to six centrifuge tubes and each was treated with CH₃OH (0.25 mL). The mixtures were centrifuged at 14600 rpm (20000 g) for 15 min at 4 °C. The supernatants were carefully removed and the precipitate was re-dispersed in CHCl₃ (0.20 mL). The purification process was repeated once more. The combined CHCl₃ dispersions of the decorated gold nanoparticles (**1-NP**) were protected from light and stored at 0 °C until use. This process obtained 1 mL of **1-NP** where the UV-vis spectrum of the particles showed an intense absorption band centered at 538 nm. The TEM images of these nanoparticles showed that they have an average size of 14.2 ± 1.4 nm. The concentration of ODA-coated gold nanoparticles was estimated by drying 1 mL of the nanoparticle solution under high vacuum and weighing the residue. This afforded a value of 0.23 mg/mL.

Trapping the released singlet oxygen using the singlet oxygen trapping agent diphenylisobenzofuran (DPBF). In a 0.6 mL cuvette and under red light, 0.2 mL of **DPBF** (0.013 mM) in CHCl₃ was added to 0.2 mL of **1-NP** and then the mixture was topped with 0.2 mL of CHCl₃. The UV-vis spectrum of the sample was taken where the λ_{max} of nanoparticles and **DPBF** were to be 536 and 410 nm, respectively. The mixture was irradiated with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) every 20 s for a total of 180 s and the absorption spectra were recorded.

Transmission Electron Microscopy (TEM)

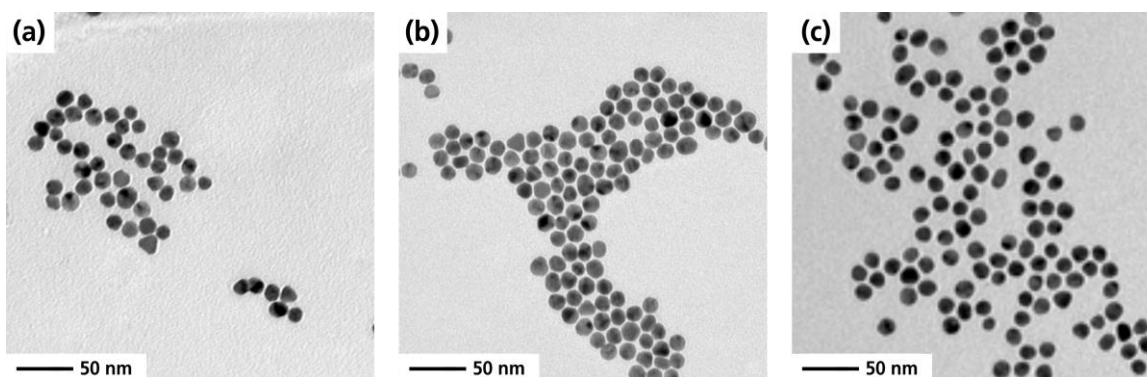


Figure S1. TEM images of (a) a water dispersion of citrate-coated gold nanoparticles (1.29 mg/mL) (average diameter = 13.8 ± 1.4 nm), (b) a CHCl_3 dispersion of octadecylamine-coated gold nanoparticles (0.45 mg/mL) (average diameter = 14.6 ± 0.9 nm), and (c) a CHCl_3 dispersion of decorated gold nanoparticles **1-NP** (0.23 mg/mL) (average diameter = 14.2 ± 1.4).

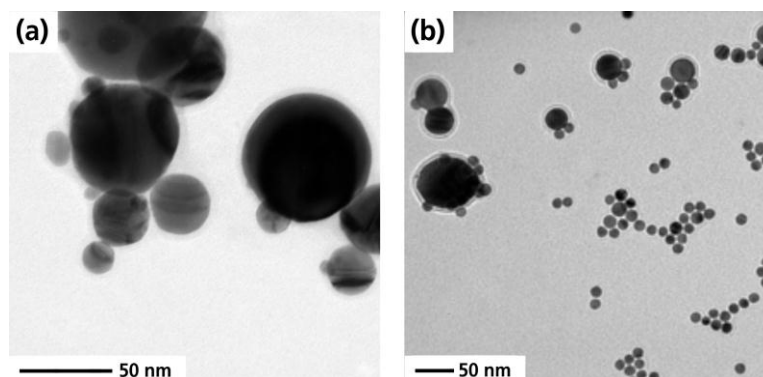


Figure S2. (a) TEM image of a CHCl_3 dispersion of decorated gold nanoparticles **1-NP** after irradiation with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) for a total of 140 s (average diameter = 43.6 ± 31.0 nm). (b) TEM image of a CHCl_3 dispersion of octadecylamine-coated gold nanoparticles after irradiation with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) for a total of 140 s (average diameter = 20.4 ± 15.1 nm).

Estimating the loading of ligand 1 in 1-NP. The amount of endoperoxide ligand **1** decorated on the surface of the gold nanoparticles was estimated by comparing the number of molecules of endoperoxide **1** in an aliquot amount of the CHCl_3 stock solution of **1-NP** to the number of particles in a similar aliquot of solution of **1-NP**. The sample (0.4 mL) of the stock solution of **1-NP** was diluted to 0.5 mL with CHCl_3 and then treated with a CHCl_3 solution of dithiothreitol (0.5 mL, 0.10 M) to remove all the ligands from the nanoparticles. The mixture was stirred vigorously for 10 min at room temperature followed by sonication for 15 min. The mixture was treated with CH_3OH (0.5 mL) and centrifuged for 15 min at 14600 rpm. The supernatant was carefully removed from nanoparticle pellet and evaporated under reduced pressure.

The solid residue was re-dissolved in CHCl_3 (0.5 mL), CH_3OH (0.5 mL) was added and centrifugation was repeated followed by drying the supernatant under reduced pressure. The anthracene endoperoxide ligand **1** has no absorption bands at wavelengths greater than 300 nm, therefore solid residue was taken up in CHCl_3 , heated to reflux until the change in absorption intensity at 395 nm corresponding to anthracene ligand **2** stopped increasing. The concentration of anthracene ligand **2** was calculated to be 0.028 mM based on its molar absorptivity (see table below).

calculated number of nanoparticles in 400 μL of 1-NP		
average radius of nanoparticle (cm)		$= 7.10 \times 10^{-7}$
volume of particle (cm^3) using $v = 4/3\pi r^3$	$= 4/3 \times 3.14 \times (7.10 \times 10^{-7})^3$	$= 1.50 \times 10^{-18}$
density of gold (g/cm^3)		$= 19.30$
mass of one single particle (g)	$= 19.30 \times 1.50 \times 10^{-18}$	$= 2.89 \times 10^{-17}$
weight of residue in 400 μL of 1-NP (g)		$= 9.00 \times 10^{-5}$
number of nanoparticles in 400 μL of 1-NP	$= 9.00 \times 10^{-5} / 2.89 \times 10^{-17}$	$= 3.11 \times 10^{12}$
calculated number of molecules of 1 in 400 μL of 1-NP by quantifying ligand 2		
ϵ at 395 nm of ligand 2 in CHCl_3 ($\text{M}^{-1}\text{cm}^{-1}$)		$= 3.45 \times 10^3$
absorbance at 395 nm of ligand 2 from nanoparticle		$= 0.0974$
concentration of 2 solution (M)	$= 0.0974 / 3.45 \times 10^3 \times 0.5$	$= 5.64 \times 10^{-5}$
moles of ligand 2 in 400 μL of 1-NP	$= 5.64 \times 10^{-5} \times 4.00 \times 10^{-4}$	$= 2.26 \times 10^{-8}$
number of molecules of 1 in 400 μL of 1-NP	$= 2.26 \times 10^{-8} \times 6.022 \times 10^{23}$	$= 1.36 \times 10^{16}$
number of molecules of 1 per nanoparticle	$= 1.36 \times 10^{16} / 3.11 \times 10^{12}$	$= 4371$

Optical Characterization

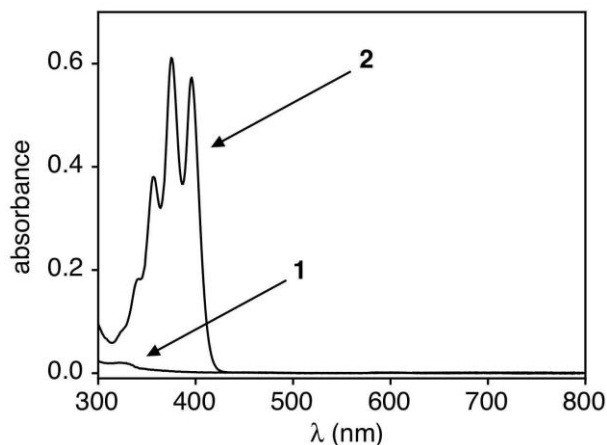


Figure S3. UV-vis absorption spectra of tetrachloroethane solutions of ligands **1** and **2** (30×10^{-6} M) in at 20 °C.

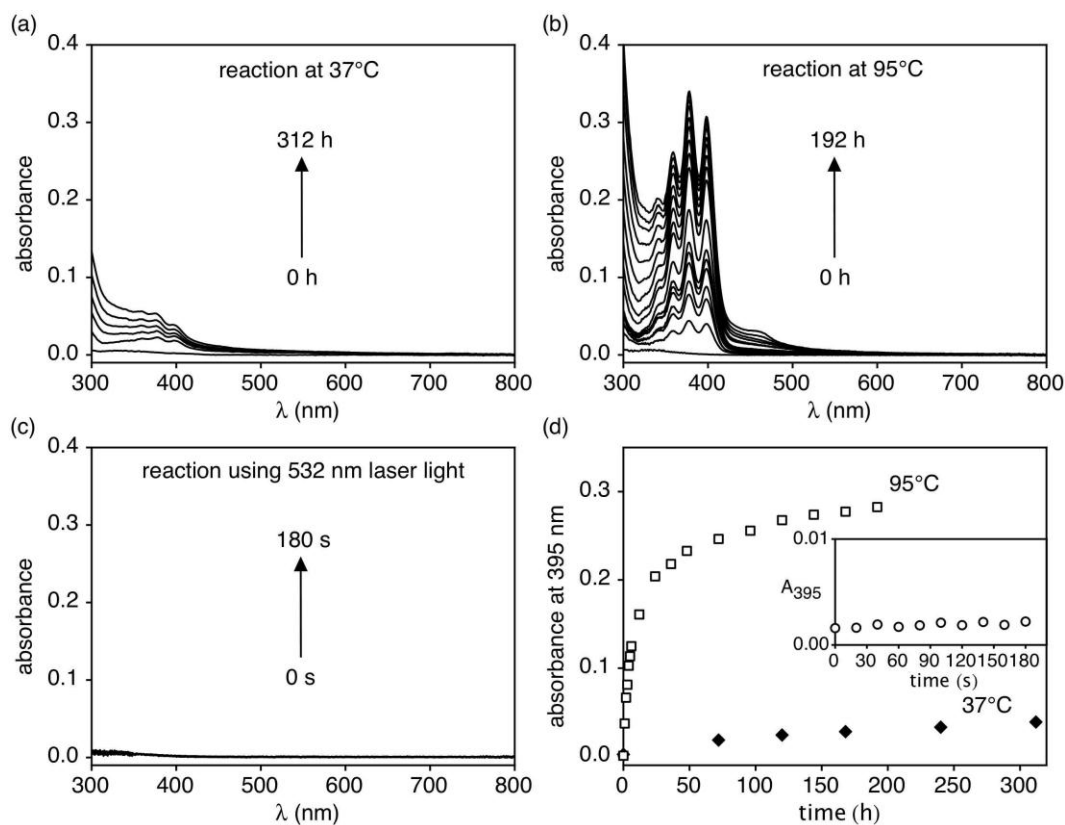


Figure S4. Changes in UV-vis absorption spectra of tetrachloroethane solutions of ligand **1** (30×10^{-6} M) at (a) 37 °C, (b) 95 °C and (c) during irradiation with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) at 20 °C. (d) The changes in absorption intensity at 395 nm for the same solutions as they are heated at 37 °C (black

diamonds) and 95 °C (empty squares) and irradiated with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) (inset, empty circles).

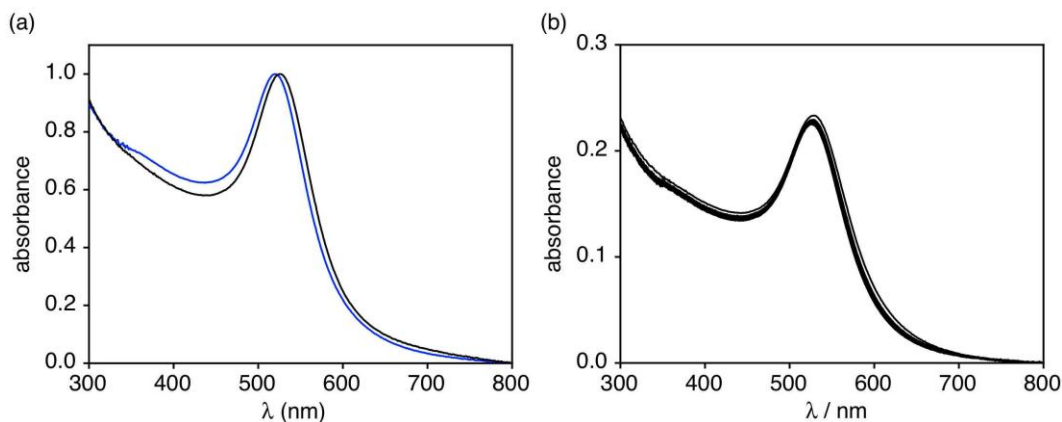


Figure S5. (a) Normalized UV-vis absorption spectra of dispersions of citrate-coated gold nanoparticles in H₂O (1.29 mg/mL, 13.8 ± 1.4 nm) (blue line) and octadecylamine-coated gold nanoparticles in CHCl₃ (0.45 mg/mL, 14.6 ± 0.9 nm) (black line). (b) Changes in the UV-vis absorption spectra of CHCl₃ dispersions of gold nanoparticles as they are irradiated with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) for a total of 120 s.

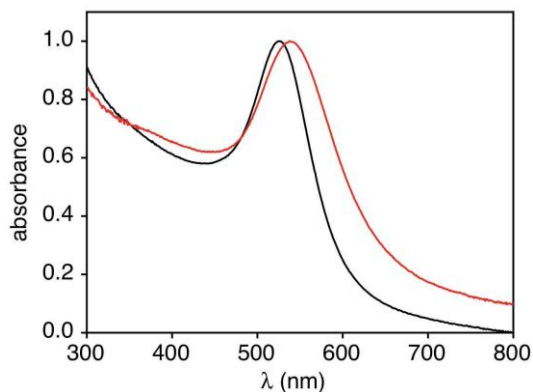


Figure S6. Normalized UV-vis absorption spectra of dispersions of octadecylamine-coated gold nanoparticles in CHCl₃ (0.45 mg/mL, 14.6 ± 0.9 nm) (black line) and of 1-NP in CHCl₃ (0.23 mg/mL, 14.2 ± 1.4 nm) (red line).

Photothermal Release Experiments

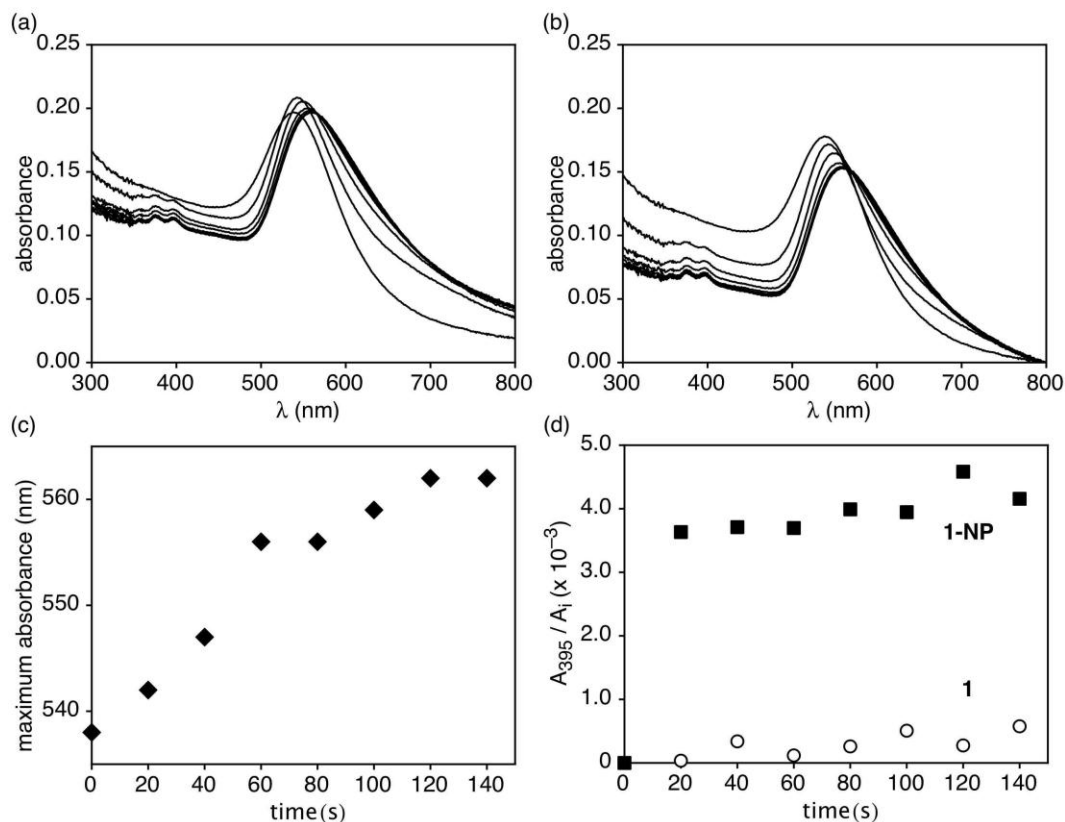


Figure S7. (a) Changes in the UV-vis absorption spectra of a CHCl₃ dispersion of decorated nanoparticles (**1-NP**) as it is irradiated with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) for a total of 140 s. (b) The same spectral data corrected for scatter at 800 nm. (c) The change in the λ_{max} for the absorption band corresponding to the gold nanoparticles during the irradiation period. (d) The change in absorption intensity at 395 nm corresponding to the anthracene product (**2-NP** and **2**) as CHCl₃ dispersions of decorated nanoparticles (**1-NP**) (black squares) and endoperoxide ligand **1** (empty circles) are irradiated with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns).

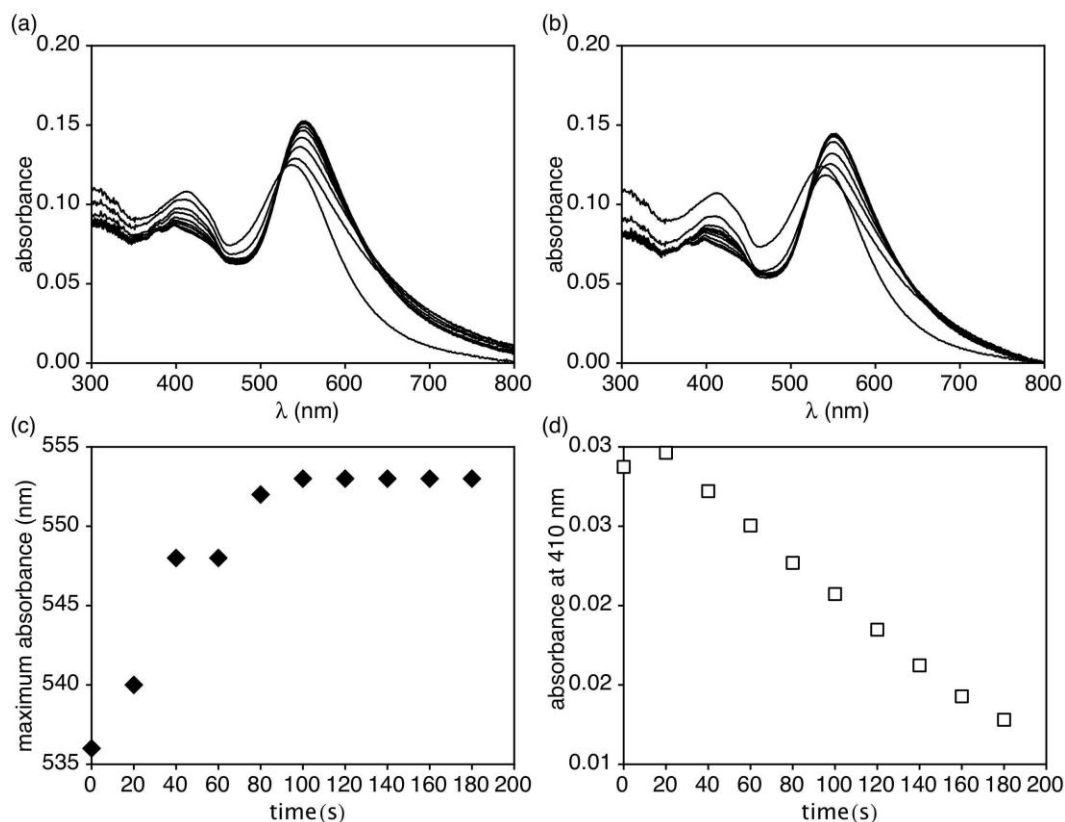


Figure S8. (a) Changes in the UV-vis absorption spectra of a CHCl₃ dispersion of decorated nanoparticles (**1-NP**) with added diphenylisobenzofuran (**DPBF**) as a singlet oxygen trapping agent as it is irradiated with 532 nm pulse laser light (10 Hz, 5 mJ/pulse, 10 ns) for a total of 180 s. (b) The same spectral data corrected for scatter at 800 nm. (c) The change in the λ_{\max} for the absorption band corresponding to the gold nanoparticles during the irradiation period. (d) The change in absorption intensity at 410 nm corresponding to the diphenylisobenzofuran trapping agent as the CHCl₃ dispersion is irradiated with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns). The last set of data was corrected for the absorption at 465 nm

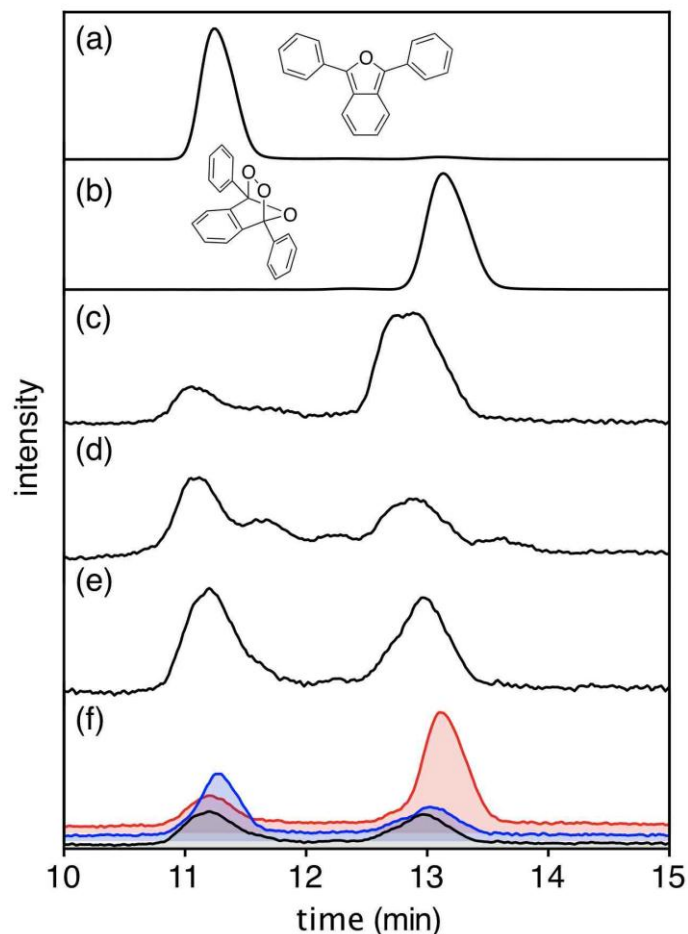


Figure S9. HPLC chromatograms of CHCl_3 solutions of (a) the diphenylisobenzofuran (**DPBF**) singlet oxygen trapping agent and (b) an authentic sample of the endoperoxide product of the trapping agent and singlet oxygen (**DPBF-EP**). (c–e) HPLC chromatograms of three separately filtered CHCl_3 solutions of the endoperoxide-coated nanoparticles **1-NP** after they were irradiated with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) for 180 s. (f) HPLC chromatograms of a fourth filtered CHCl_3 solution of the endoperoxide-coated nanoparticles **1-NP** after it was irradiated with 532 nm pulsed laser light (10 Hz, 5 mJ/pulse, 10 ns) for 180 s (black) and treated with the authentic samples of the diphenylisobenzofuran singlet oxygen trapping agent (blue) and the endoperoxide product of the trapping agent and singlet oxygen (red). All chromatograms were recorded at 254 nm, 1 mL/min and CHCl_3 as a mobile phase.