Supporting Information

Generation of Singlet Oxygen by Photoexcited $Au_{25}(SR)_{18}$ Clusters

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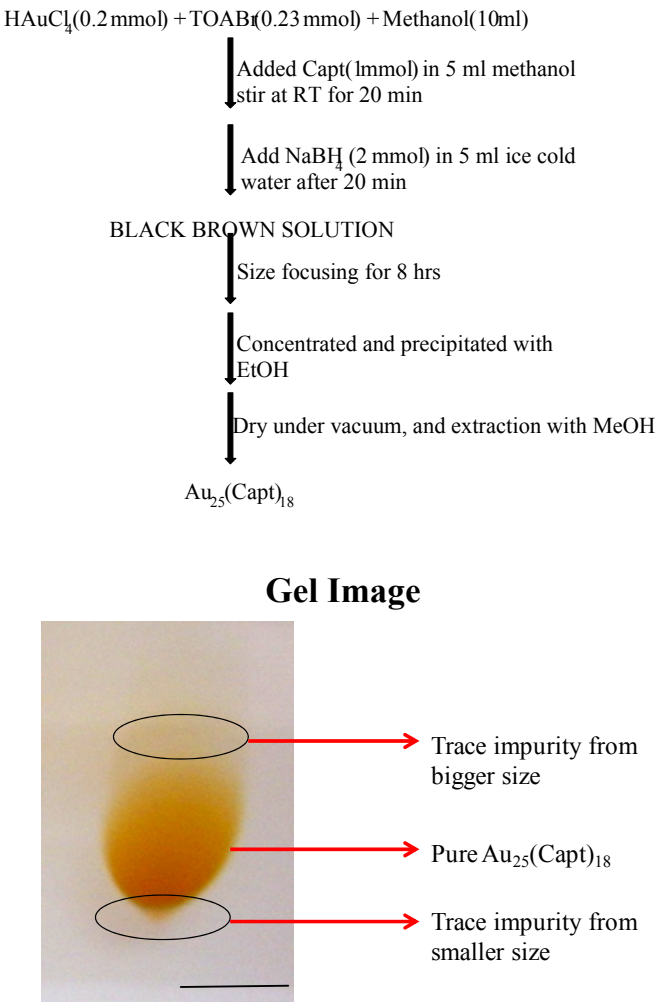


Figure S1 The synthetic scheme of $Au_{25}(Capt)_{18}^-$. The high purity of as-synthesized clusters was confirmed through polyacrylamide gel electrophoresis (PAGE) separation. The length of black bar is 2 cm.

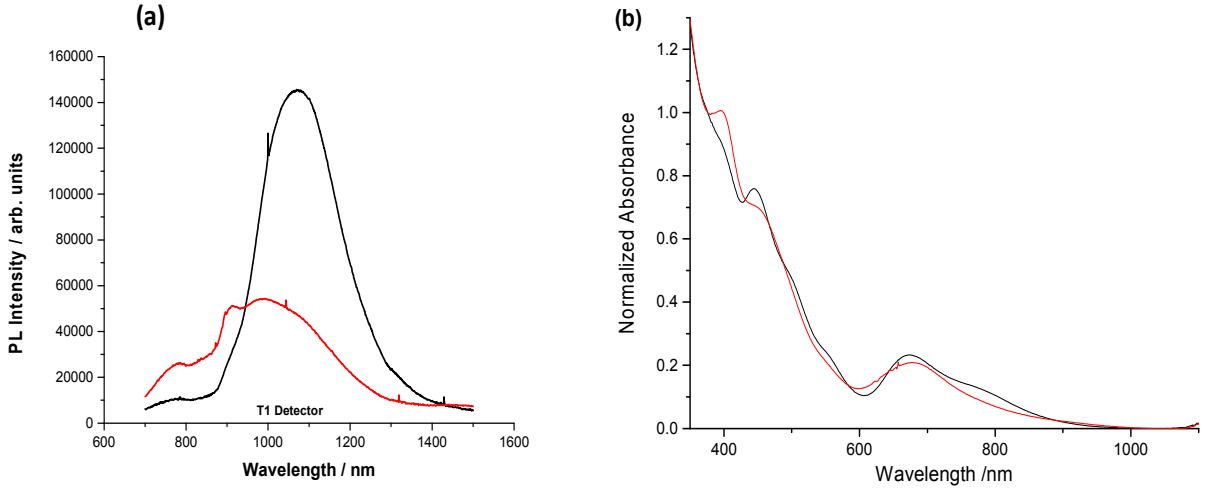


Figure S2 (a) NIR photoluminescence of $Au_{25}(Capt)_{18}^{-}$ in a D_2O solution. Spectra were collected with a liquid N_2 cooled InGaAs detector using 447 nm excitation. A 550 nm long-pass optical filter was placed between the sample and the detector to block overtones from the 447 nm excitation source from reaching the detector. Black line: N_2 purging-solution before illumination and red line: O_2 purging-solution after illumination. (b) Absorbance spectra of $Au_{25}(Capt)_{18}^{-}$ in a D_2O solution. before and after illumination. Black line: solution after N_2 purging, and red line: solution after O_2 purging. Black line: N_2 purging-solution before illumination and red line: O_2 purging-solution after illumination.

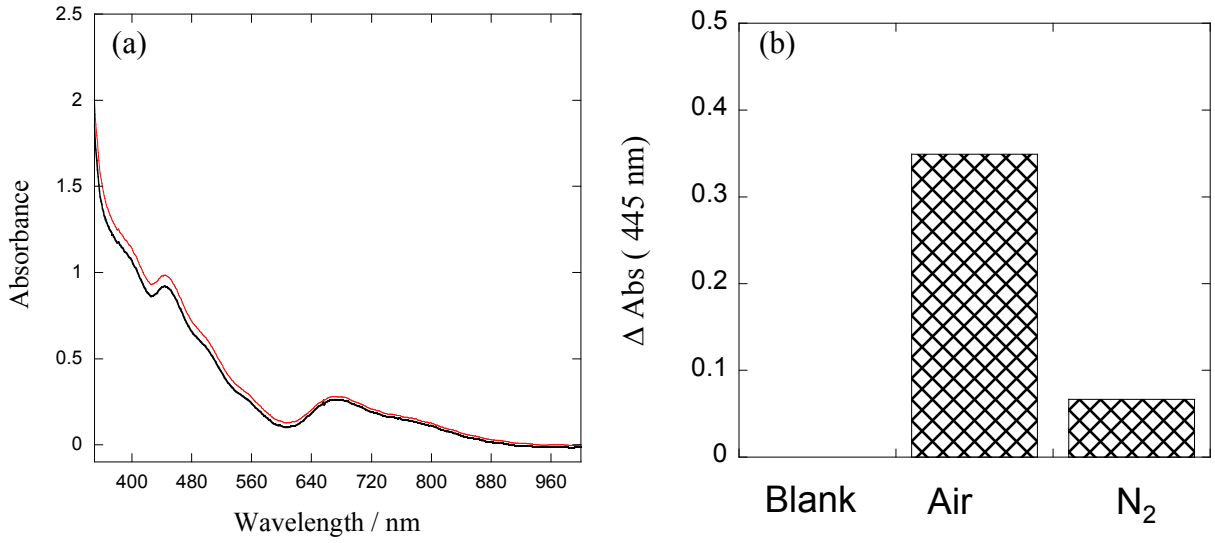


Figure S3 (a) Absorption spectra of a DAB-containing solution of $Au_{25}(Capt)_{18}^-$ in D_2O under a N_2 gas atmosphere before (black) and after (red) irradiation at 532nm (50mW) for 10 min. $[Au_{25}]$= 35 μM, [DAB] = 500 μM. (b) Change in absorbance at 445 nm of a DAB-containing solution of $Au_{25}(Capt)_{18}^-$ in D_2O after irradiation at 532nm (50 mW) for 10 min under N_2 and air atmospheres. As a blank experiment, the absorbance change at 445 nm in a D_2O solution containing only DAB under air atmosphere is shown.

Note: If the singlet oxygen generated by the $Au_{25}(Capt)_{18}^-$ in fact causes the oxidation of DAB, the change in the rate of DAB absorbance would depend on the concentration of oxygen dissolved in the D_2O. Removal of such oxygen by N_2 purging resulted in significantly smaller changes in the absorbance spectrum. It should be noted that there was still a slight change in the absorbance of DAB, even in the N_2 atmosphere, indicating that there was a small contribution from a photocatalytic effect of $Au_{25}(Capt)_{18}^-$ without the involvement of oxygen.

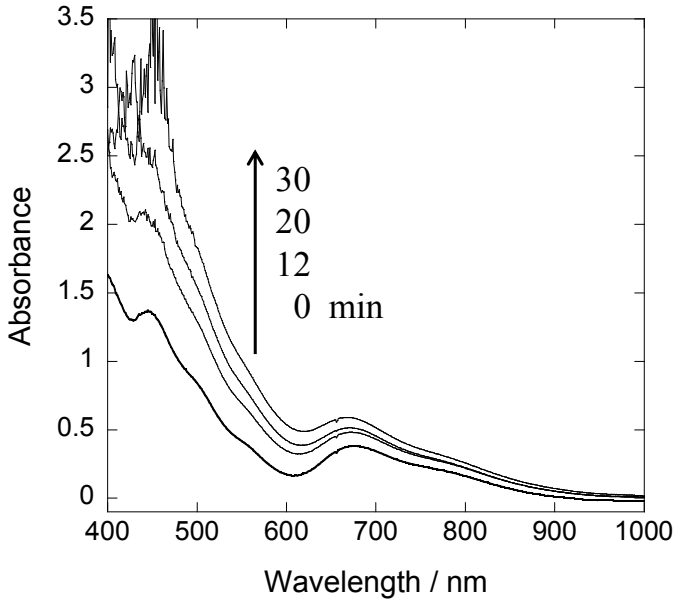


Figure S4 Absorption spectra of a DAB-containing solution of $Au_{25}(Capt)_{18}^{-}$ in D_2O after light irradiation at 650 nm (50 mW) for 30 min. [DAB] = 500 μM.

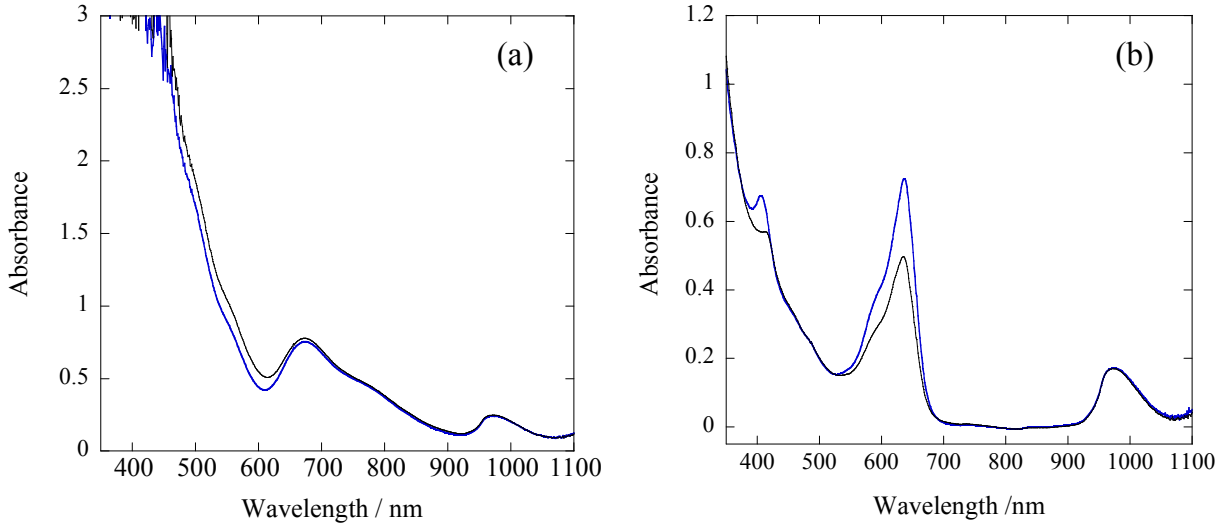


Figure S5 (a) Absorption spectra of $Au_{25}(Capt)_{18}^{-}$ in human serum containing DAB before (blue line) and after (black line) irradiation at 650 nm (50mW) for 10 min. [DAB] = 500 μM. (b) Absorption spectra of NMB in human serum containing DAB before (blue line) and after (black line) irradiation at 650 nm (50mW) for 10 min. [DAB] = 500 μM. The concentration of NMB was adjusted to be the same absorbance (~0.65) at 650 nm as that of $Au_{25}(Capt)_{18}^{-}$. *Note: the peak at ~970 is from water.

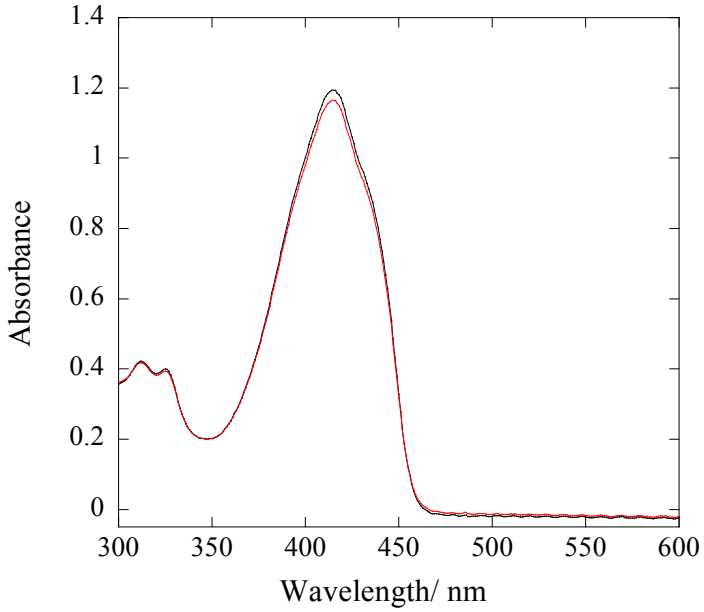


Figure S6 Absorption spectra of DPBF in a DMF solution before (black) and after (red) irradiation at 532nm (1 mW) for 60 min in the *absence* of $Au_{25}(PET)_{18}^{-}$; [DPBF] = 50 μM.

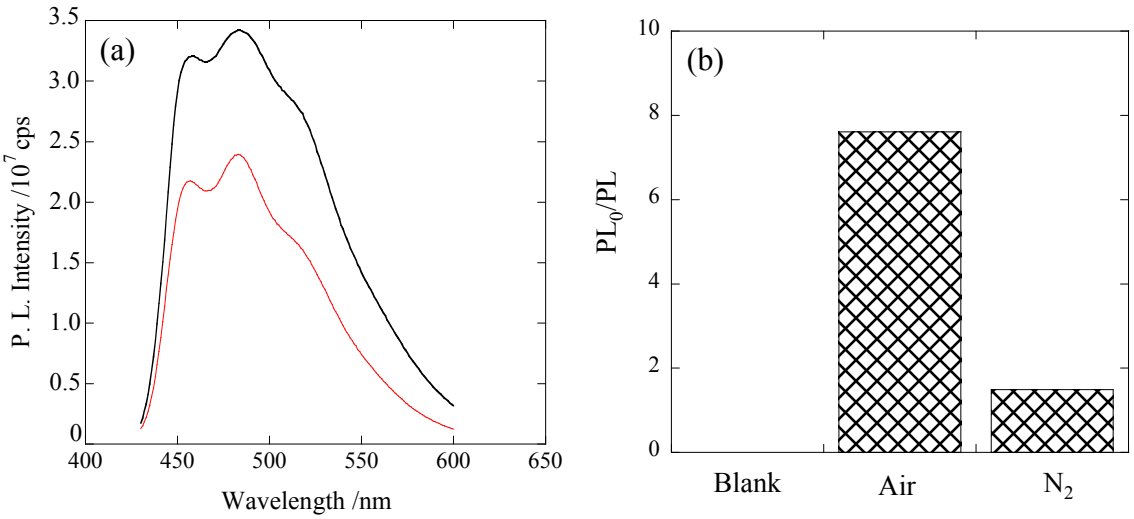


Figure S7 (a) Fluorescence spectra at an excitation of 410 nm of a DPBF-containing solution of $Au_{25}(PET)_{18}^{-}$ in DMF under a N_2 atmosphere before (black) and after (red) irradiation at 532nm (1 mW) for 15 min. (b) Relative fluorescence(PL_0/PL) at 455 nm in a DMF solution containing DPBF after irradiation at 532nm (1mW) for 15 min under N_2 and air atmospheres. PL_0 and PL are the fluorescence peak intensities at 455 nm before and after light irradiation, respectively. As a blank experiment, results from a DMF solution containing only DPBF under an air atmosphere are shown. [Au_{25}]= 35μM, [DPBF] = 10 μM.

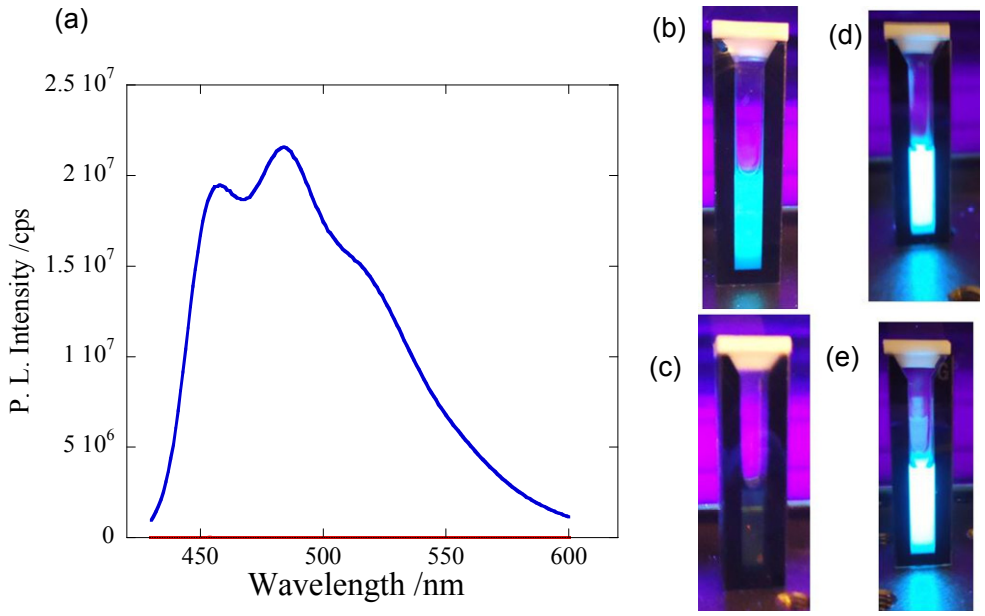


Figure S8. (a) Fluorescence spectra (excitation at 410 nm) of a DPBF-containing DMF solution of $Au_{25}(PET)_{18}^{-}$ before (blue) and after (red) irradiation at 532 nm (50 mW) for 5 min. Photographs of the DPBF-containing DMF solution in the *presence* of $Au_{25}(PET)_{18}^{-}$ at excitation of 350 nm (b) before and (c) after irradiation at 532 nm (50 mW) for 2 min. Photographs of a DPBF-containing DMF solution in the *absence* of $Au_{25}(PET)_{18}^{-}$ at excitation of 350 nm (d) before and (e) after irradiation at 532 nm (50 mW) for 2 min.

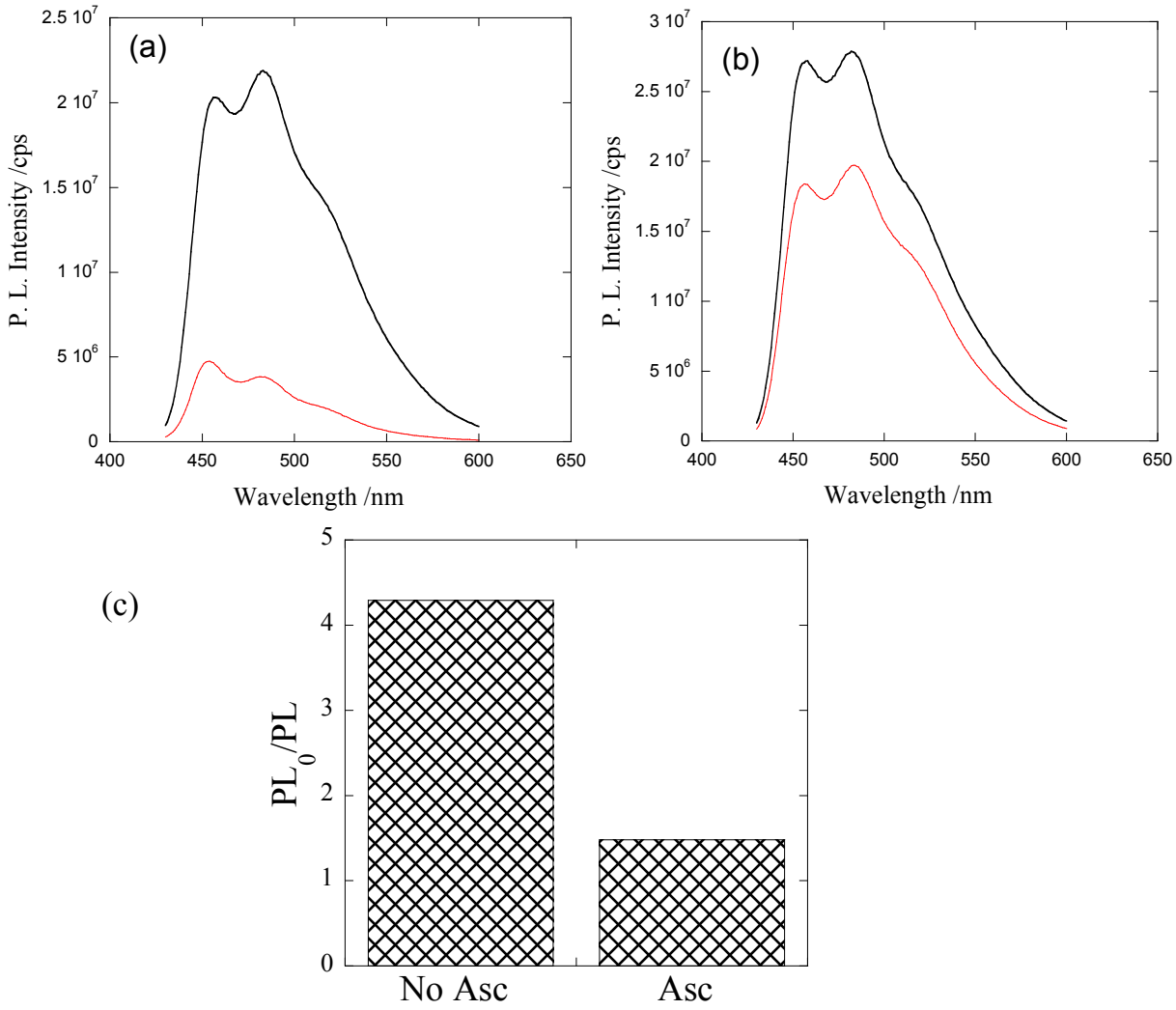


Figure S9. Fluorescence spectra (at excitation of 410 nm) of a DPBF-containing DMF solution of $Au_{25}(PET)_{18}^{-}$ before (black) and after (red) irradiation at 532 nm (1 mW) for 10 min (a) in the *presence* of ascorbic acid (5 mM) and (b) in the *absence* of ascorbic acid. (c) Relative fluorescence (PL_0/PL) at 455 nm in the DPBF-containing DMF solution after irradiation at 532 nm (1 mW) for 10 min in the *presence* of ascorbic acid (denoted "Asc") and in the *absence* of ascorbic acid (denoted "No Asc"). PL_0 and PL are the fluorescence peak intensities at 455 nm before and after light irradiation, respectively.

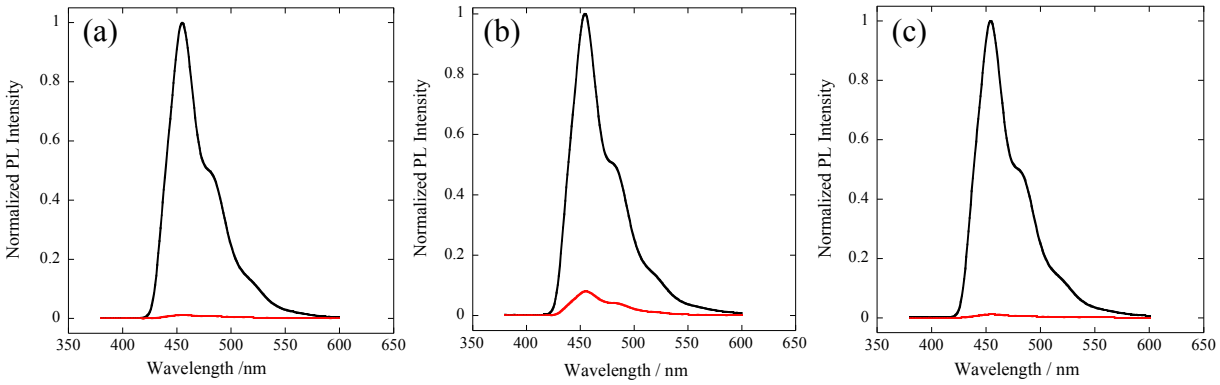
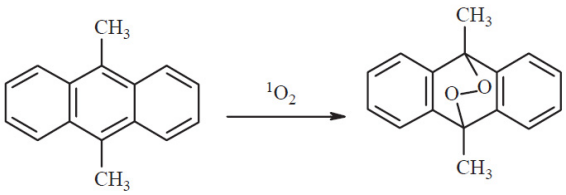


Figure S10. Fluorescence spectra (at excitation of 360 nm) of a DMA-containing solution (0.7 mg/mL) of $Au_{25}(PET)_{18}^-$ in DMF under air atmosphere before (black) and after (red) irradiation at (a) 532 nm (38 mW/cm^2), (b) 650 nm (41 mW/cm^2), and (c) 808 nm (65 mW/cm^2) for 30 min. [Au_{25}]= 45 μM. All fluorescence measurements were conducted in an hour after the preparation of the DMA-containing solution of $Au_{25}(PET)_{18}^-$ in DMF.

Note: 9,10-Dimethylanthracene (DMA) is known to be a fluorescent compound that reacts selectively with $^1O_2$ to produce the non-fluorescent 9,10-endoperoxide.



9,10-Dimethylanthracene Endoperoxide

Fluorescent Non-fluorescent

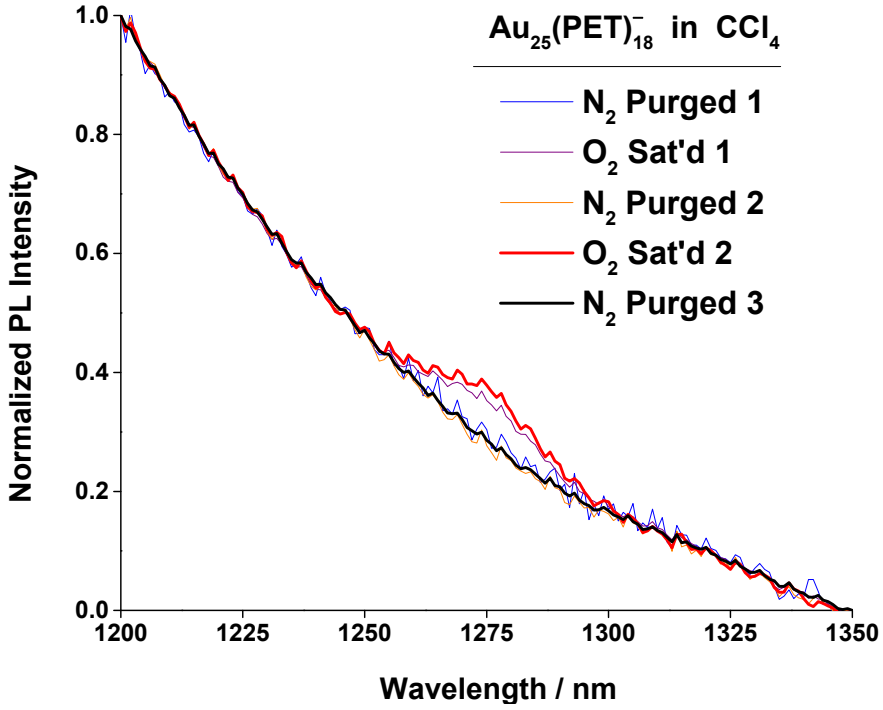
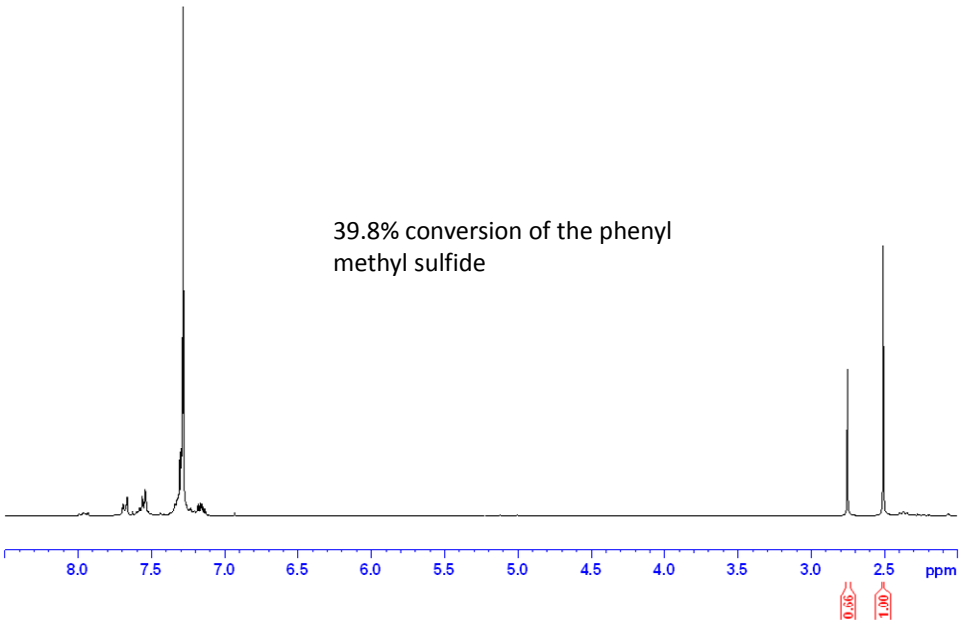


Figure S11. Photoluminescence spectra of $Au_{25}(PET)_{18}^-$ in CCl_4 after several N_2 purging and O_2 saturation cycles. This data shows the $^1O_2$ PL peak at 1276 nm is reversible and reproducible.

(a)



(b)

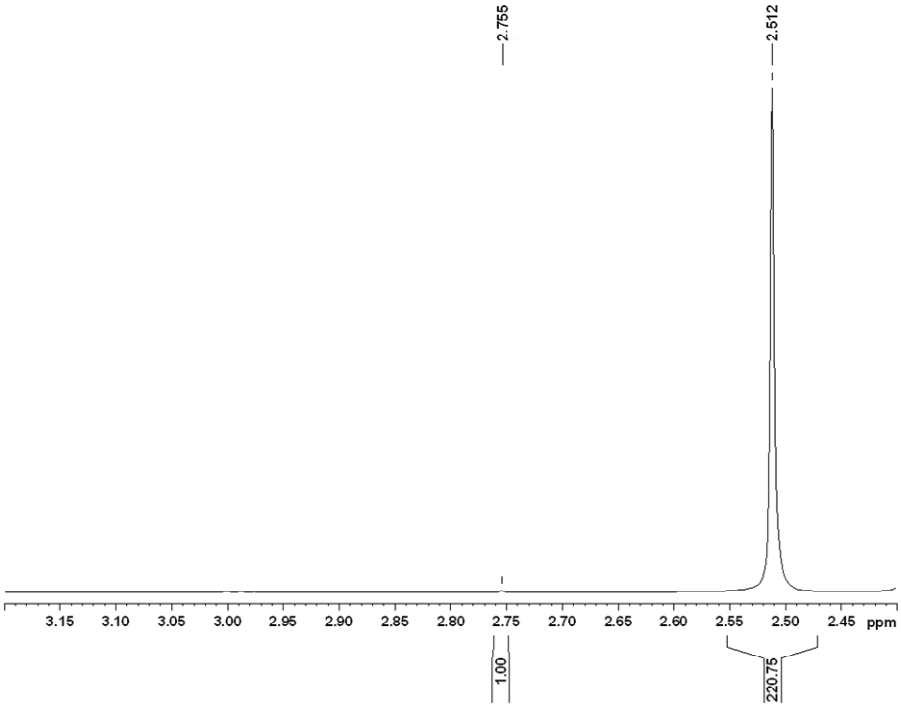


Figure S12. ^{1}H NMR of sulfide, sulfoxide and sulfone (-CH_3 of sulfide at 2.52, sulfoxide at 2.76 and sulfone at 3.08 ppm). (a): Table 1, entry 5; (b) Table 1, entry 2 (blank).

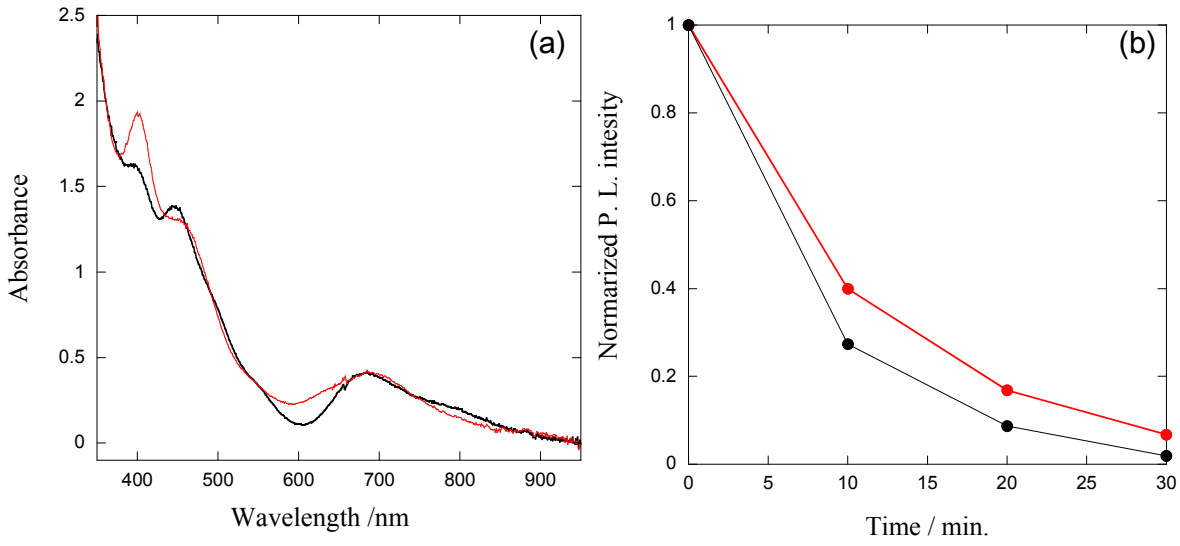


Figure S13. (a) Absorption spectra of $Au_{25}(PET)_{18}^{-}TOA^{+}$ (black line) and $Au_{25}(PET)_{18}^{0}$ (red line). (b) Normalized fluorescence intensity (PL/PL_0) of DPBF at 455 nm in a DMF solution containing $Au_{25}(PET)_{18}^{-}TOA^{+}$ (black line) and $Au_{25}(PET)_{18}^{0}$ (red line) after irradiation at 532nm (1mW) for 30 min, showing similar changes of the DPBF fluorescence during light irradiation at 532 nm for 30 min. PL_0 and PL are the fluorescence peak intensities before and after light irradiation, respectively. [DPBF] = 10 μM.