

Electronic Supplementary Information

Perylene Diimide-Tagged *N*-Heterocyclic Carbene-Stabilized Gold Nanoparticles: How Much Ligand Desorbs from Surface in Presence of Thiols?

Marilyne Bélanger-Bouliga, Raja Mahious, Poulomsongo I. Pitroipa and Ali Nazemi*

Department of Chemistry, Université du Québec à Montréal, C.P.8888, Succursale Centre-Ville, Montréal, QC, H3C 3P8, Canada

E-mail: nazemi.ali@uqam.ca

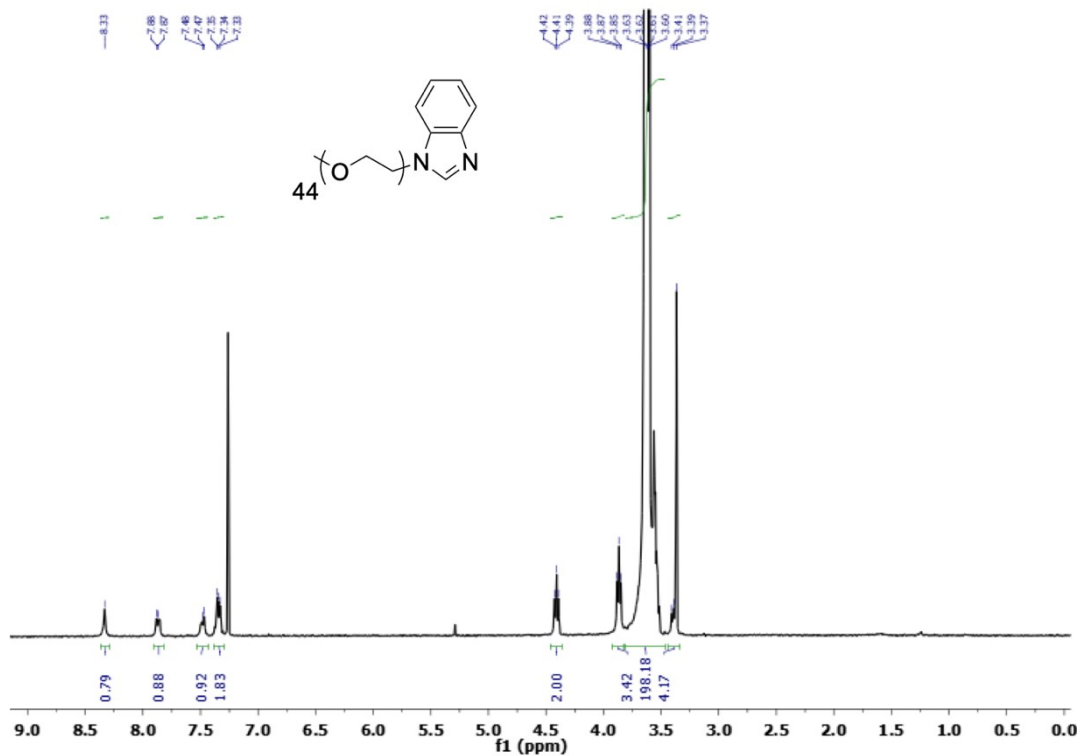


Fig. S1: ^1H NMR spectrum of compound **2** (300 MHz, CDCl_3).

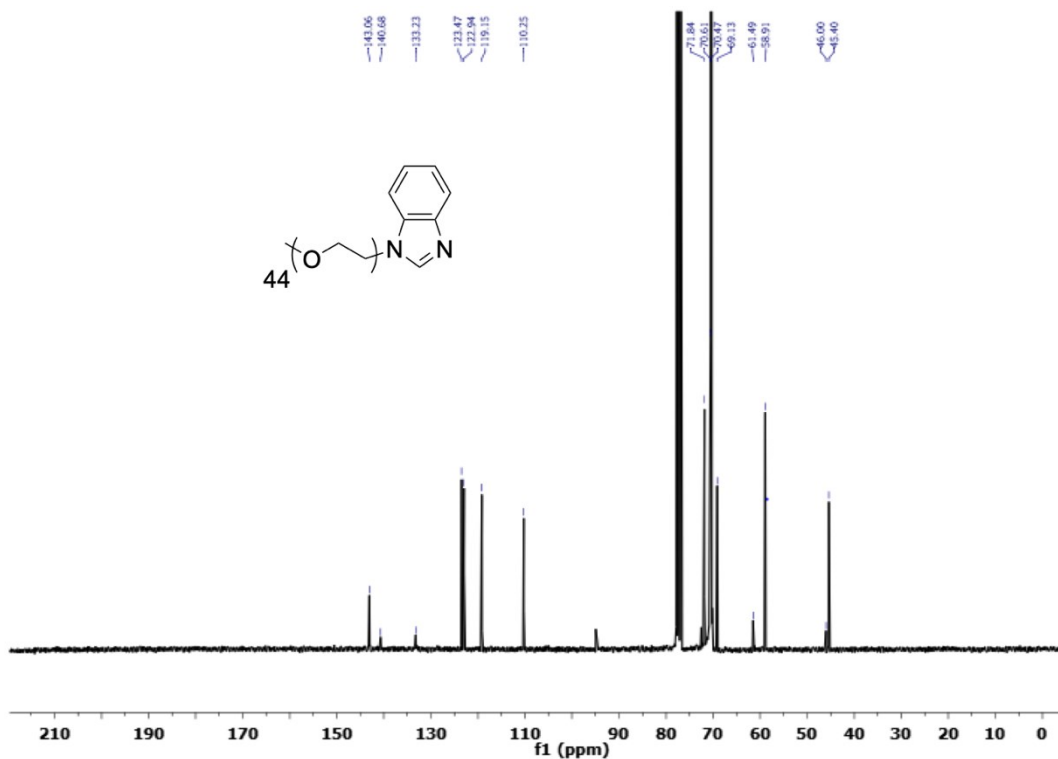
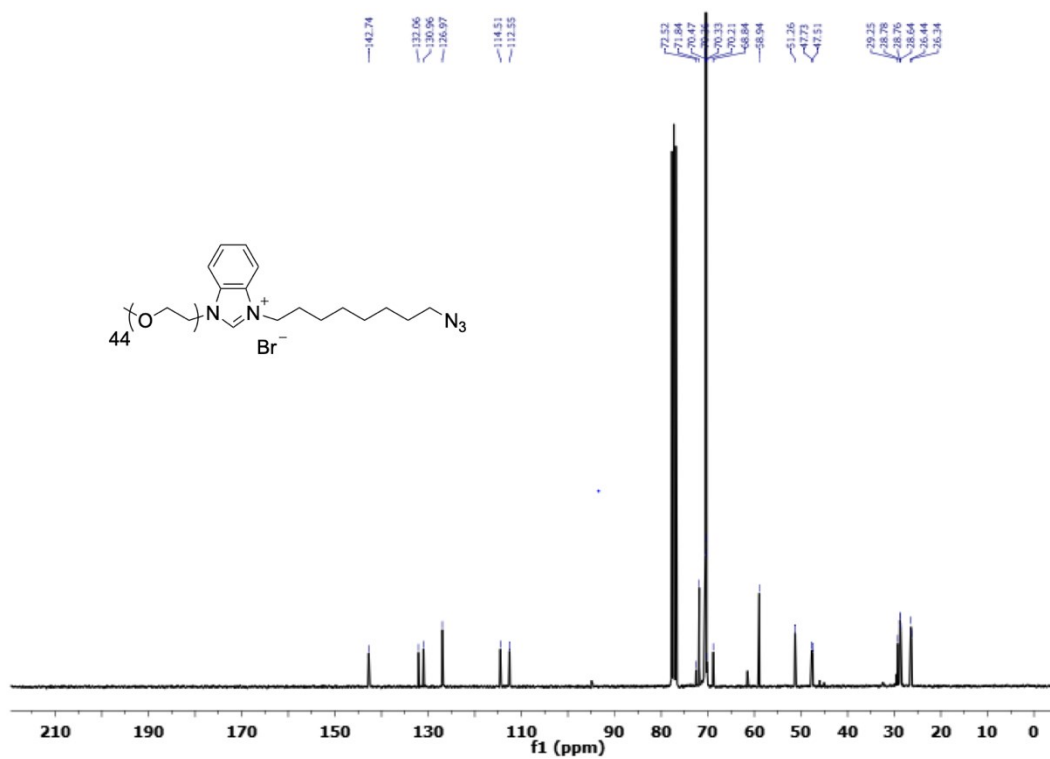
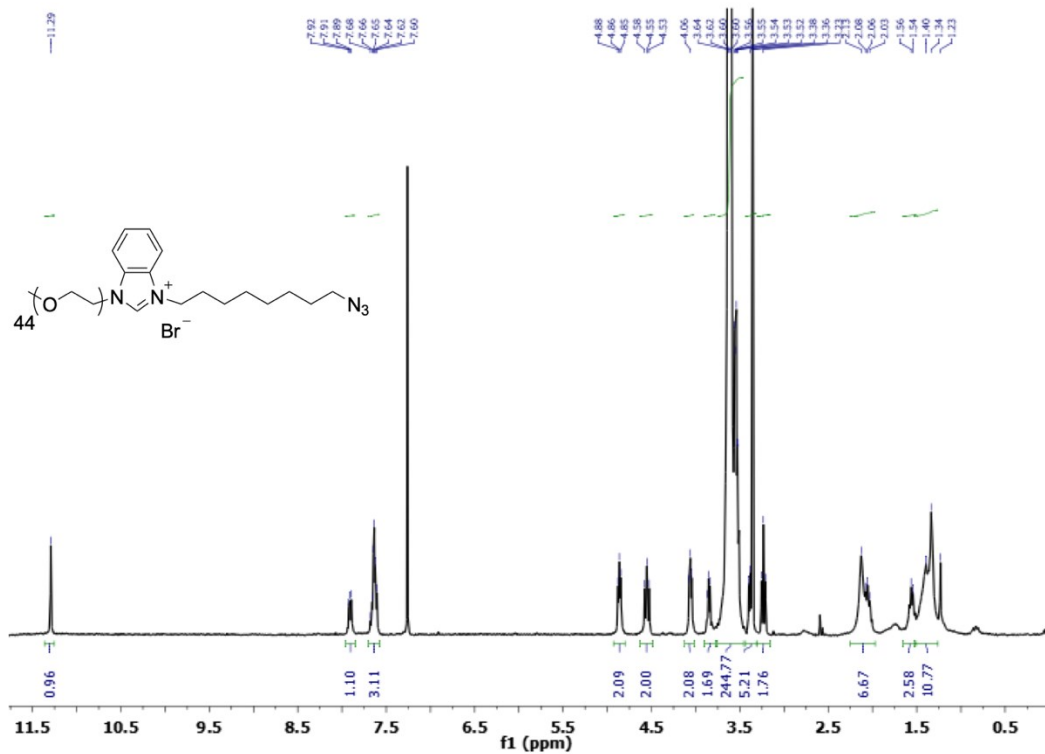
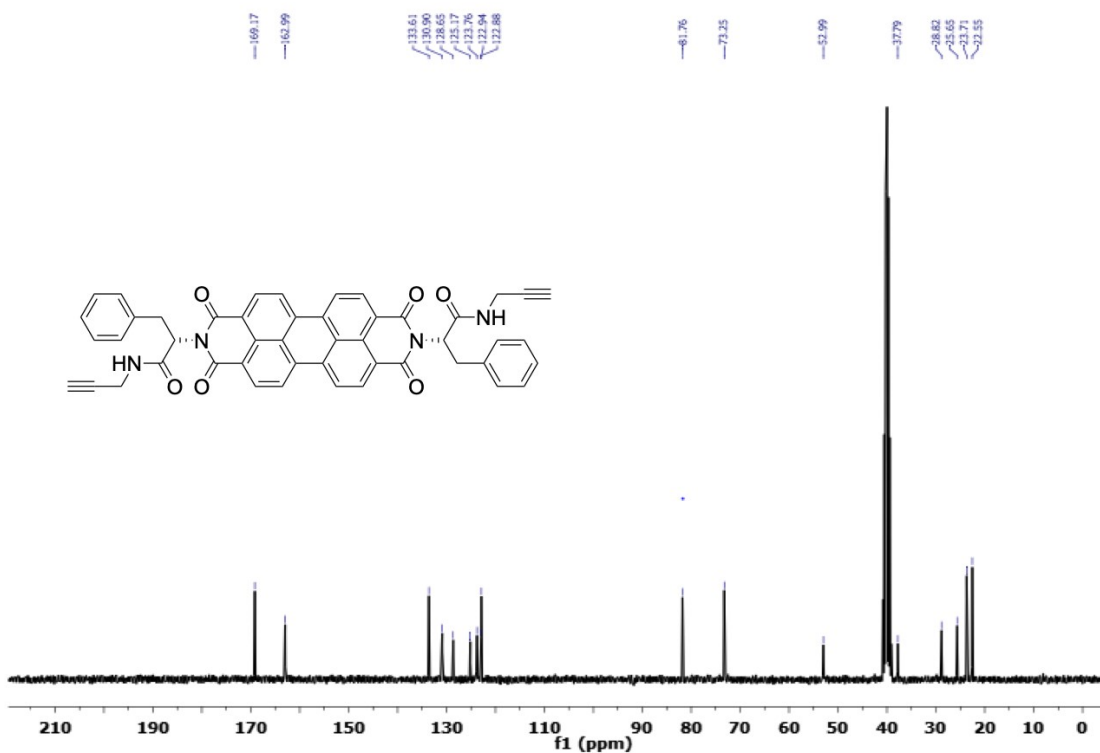
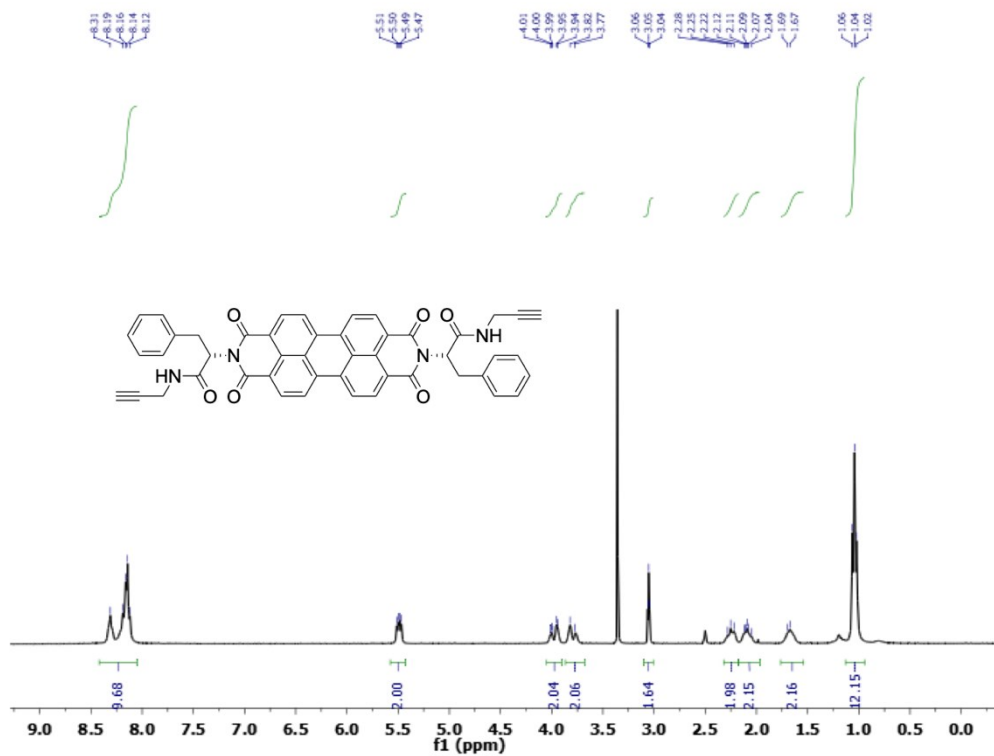


Fig. S2: ^{13}C NMR spectrum of compound **2** (75 MHz, CDCl_3).





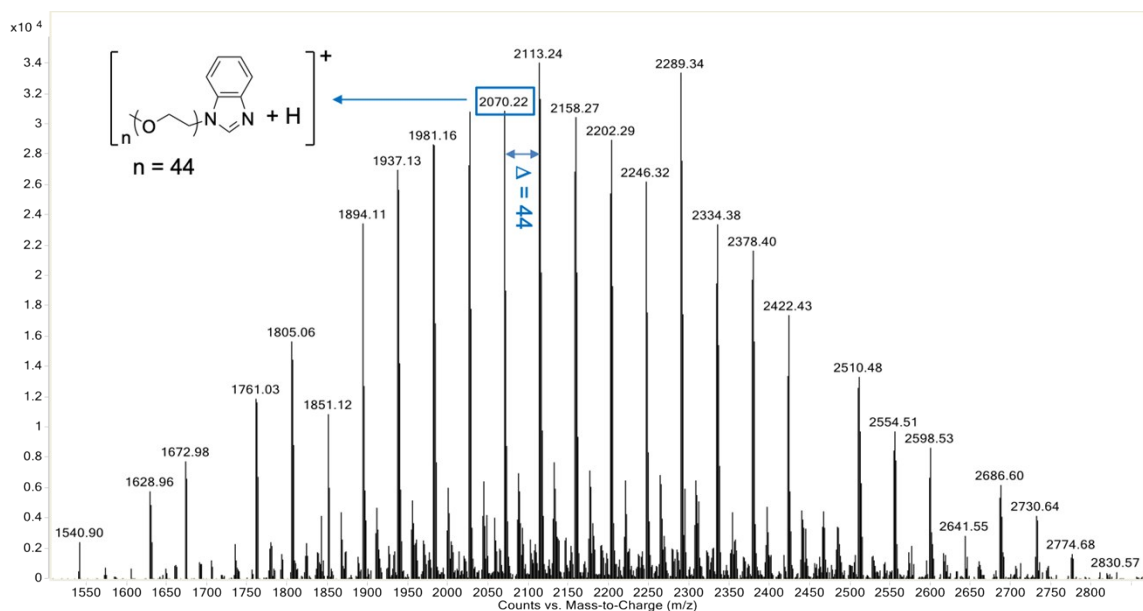


Fig. S9: HRMS spectrum of compound **2**. The second population results from the Na salt of compound **2**.

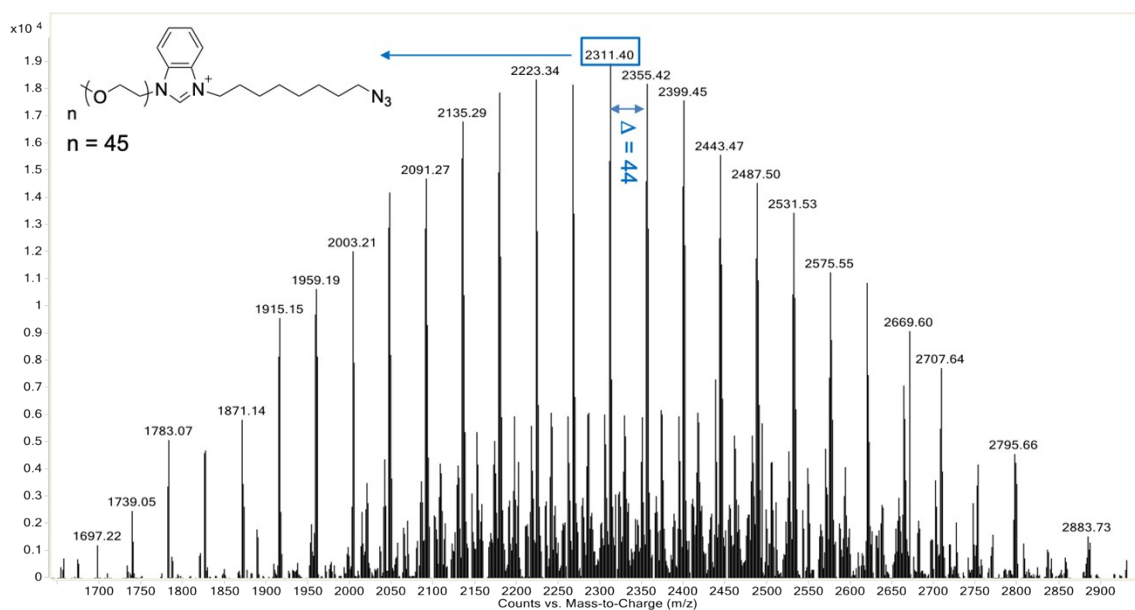


Fig. S10: HRMS spectrum of compound **4**. The second population results from N_2 loss from the azide group in compound **4**.

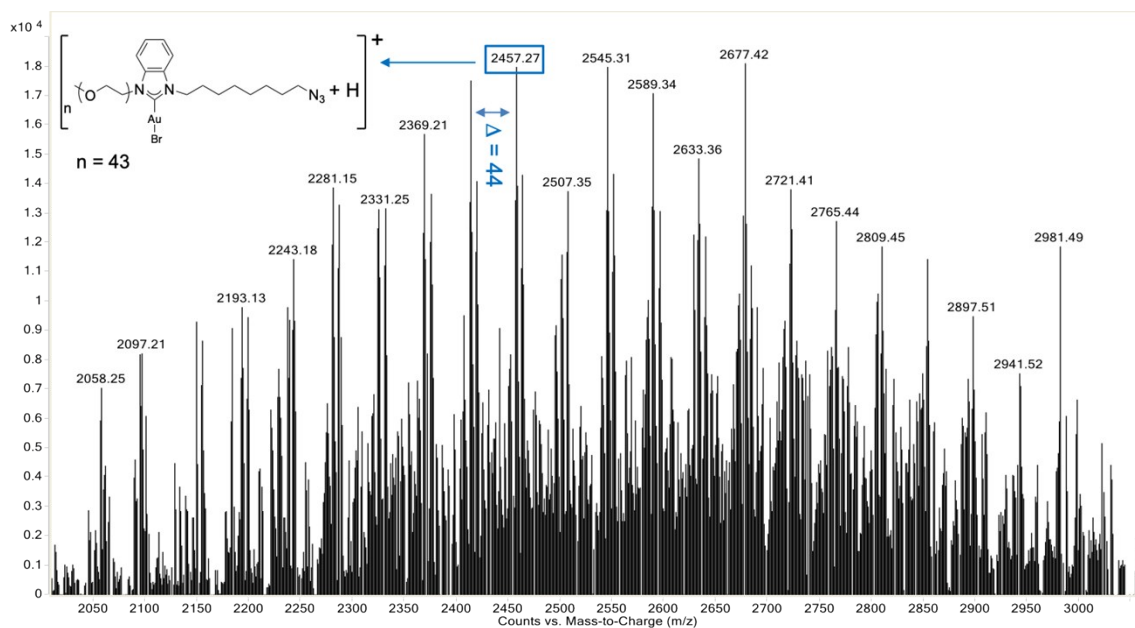


Fig. S11: HRMS spectrum of compound **5**. The relatively noisy baseline is a result of combinations of Na salt of **5**, N₂ loss from azide group, and more complex isotope pattern as a result of Au and Br incorporation.

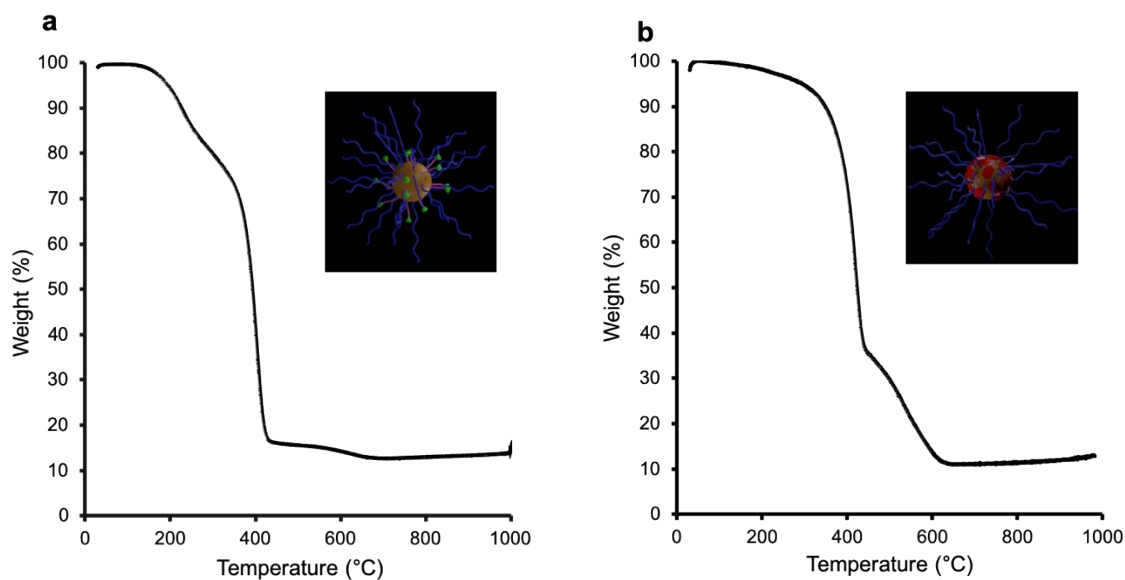


Fig. S12: TGA curves of (a) AuNP@N₃ and (b) AuNP@PDI demonstrating that 10% (w/w) of the AuNPs was comprised of the Au core while the organic surface component accounts for the remaining 90% (w/w) of the nanoparticle's mass. The insets demonstrate cartoon representations of AuNP@N₃ (a) and AuNP@PDI (b).

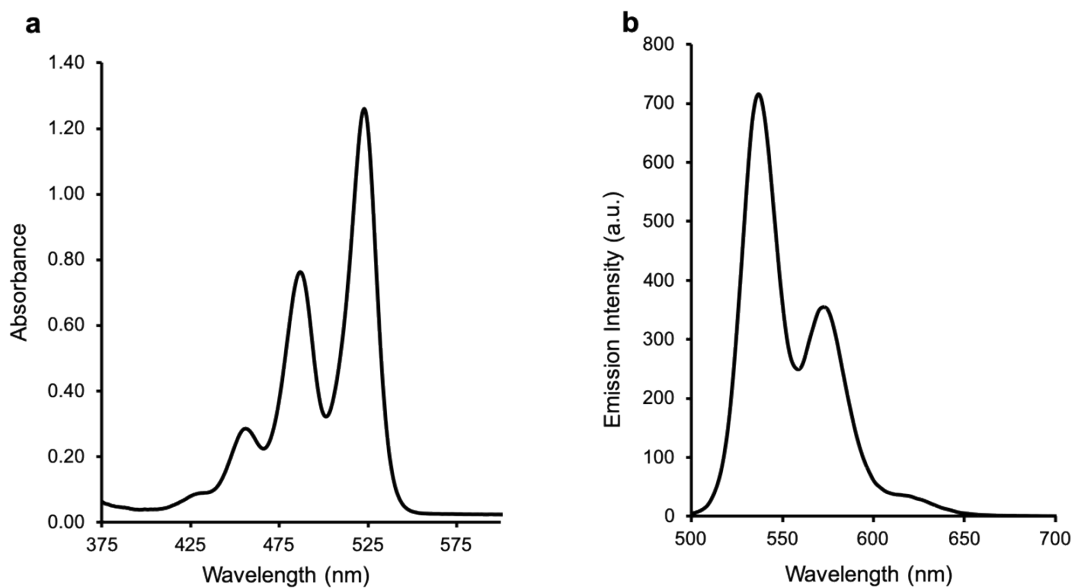


Fig. S13: (a) UV-vis absorption and (b) fluorescence emission spectra of compound 7 in THF at concentrations of 15 μM and 1.5×10^2 nM, respectively. Excitation wavelength to obtain the fluorescence emission was at 503 nm.

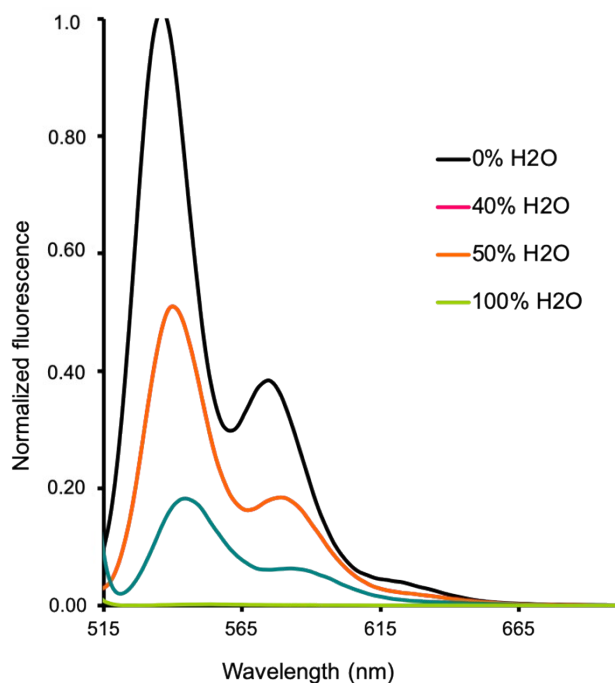
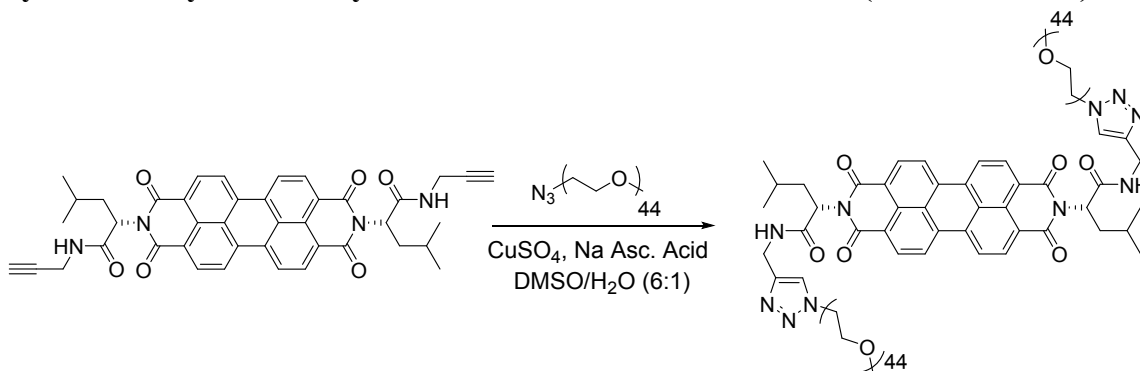
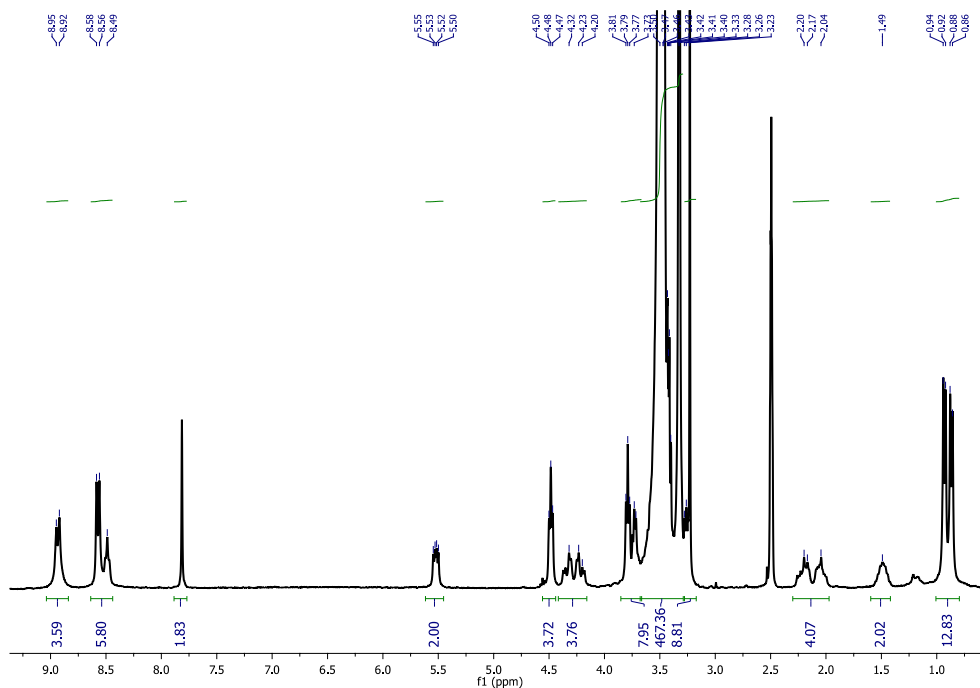


Fig. S14: Fluorescence emission spectra of AuNP@PDI in THF/H₂O mixtures. Excitation wavelength = 503 nm.

Synthesis of symmetrically PEO-functionalized PDI derivative (PEO-PDI-PEO):



Compound **7** (30 mg, 40 μmol) and an azide-functionalized PEO_{2000} (0.26 g, 0.13 mmol) were dissolved in DMSO (6 mL) in a 10 mL round bottom flask. The solution was stirred before adding CuSO_4 (5.0 mg, 20 μmol) as a solution in DI water (0.50 mL). Finally, sodium ascorbate (9.0 mg, 40 μmol) was added as a solution in DI water (0.50 mL). The reaction was stirred at room temperature for 24 h. The pure product was obtained after being dialyzed in a 12-14K MWCO membrane in DI water for one day with multiple dialysate changes (yield = 90%). The chemical structure was confirmed by ^1H NMR ($\text{DMSO}-d_6$, 300 MHz): δ (ppm) 9.03-8.85 (m, 3H, H), 8.64-8.43 (m, 5H, H), 7.82 (s, 2H), 5.55-5.50 (m, 2H), 4.49 (t, $J = 6.0$ Hz, 4H), 4.40-4.15 (m, 4H), 3.79 (t, $J = 6.0$ Hz, 4H), 3.63-3.29 (m, 352H), 3.24 (s, 6H), 2.30-1.95 (m, 4H), 1.58-1.40 (m, 2H), 0.95-0.86 (d, $J = 6.0$ Hz, 12H). The ^1H NMR spectrum is shown below:



Stability of PEO-PDI-PEO in presence of glutathione (4 mM):

To ensure that the changes we observed in the intensity of the fluorescence spectra are only due to the displacement of the ligand by GSH and not due to the instability of PDI moieties in presence of GSH, we prepared five solutions of the PEO-PDI-PEO model compound different concentrations (3.3 $\mu\text{g/mL}$, 6.6 $\mu\text{g/mL}$, 9.9 $\mu\text{g/mL}$, 13 $\mu\text{g/mL}$, 16 $\mu\text{g/mL}$ and 19 $\mu\text{g/mL}$) and added GSH to each solution so that the final concentration of GSH is 4 mM. 3 mL solutions were prepared at different concentrations from a stock solution of 0.5 mg/mL. Fluorescence spectra of these solutions at 0 h, 1 h, and 3 days after addition of GSH were obtained which revealed no change in their intensity demonstrating that GSH does not interfere with the PDIs, but strictly interact with the gold surface.

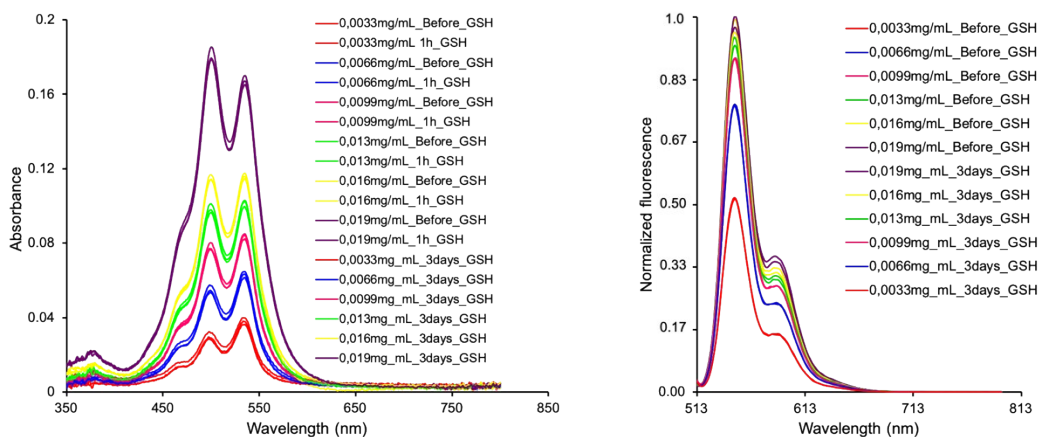


Fig. S15: UV-vis absorption (left) and normalized fluorescent (right) spectra of PEO-PDI-PEO, as a model water-soluble PDI derivative, of varying concentrations in GSH solution (4 mM) for 3 days demonstrating photochemical stability of PDI core to GSH.

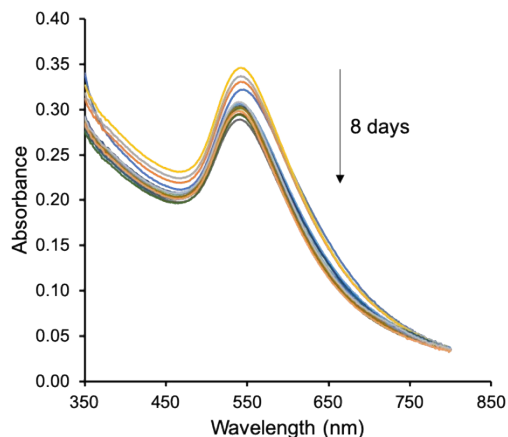


Fig. S16: UV-vis spectra of AuNP@N₃ (15 $\mu\text{g mL}^{-1}$) in GSH solution (4 mM).

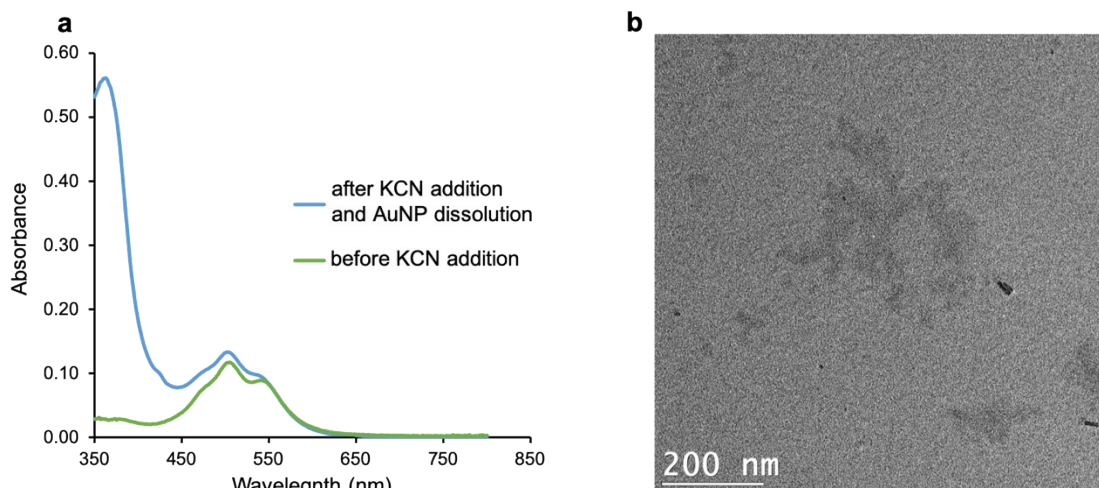


Fig. S17: (a) UV-vis spectra of AuNP@PDI solution ($15 \mu\text{g.mL}^{-1}$) before and after the addition of KCN. (b) TEM image of AuNP@PDI after Au core dissolution using KCN showing no AuNPs present.

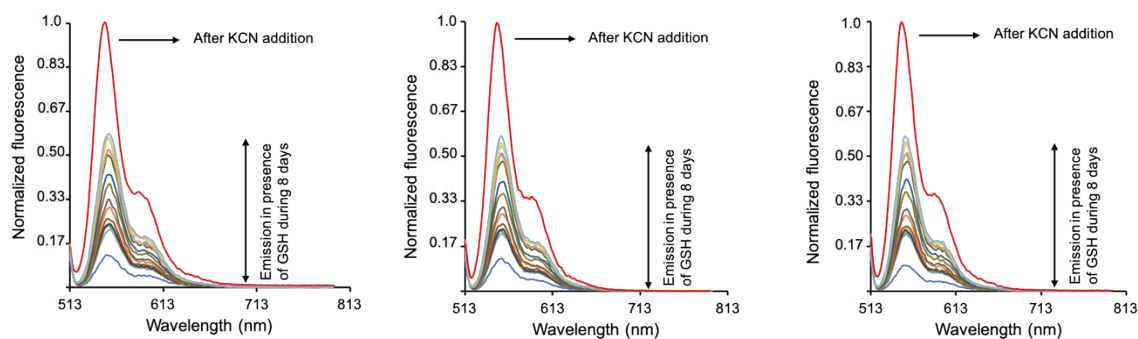


Fig. S18: Normalized fluorescence emission spectra of AuNP@PDI ($15 \mu\text{g.mL}^{-1}$) in presence of GSH (4 mM) before and after Au core dissolution using KCN. Experiments were carried out in triplicate.

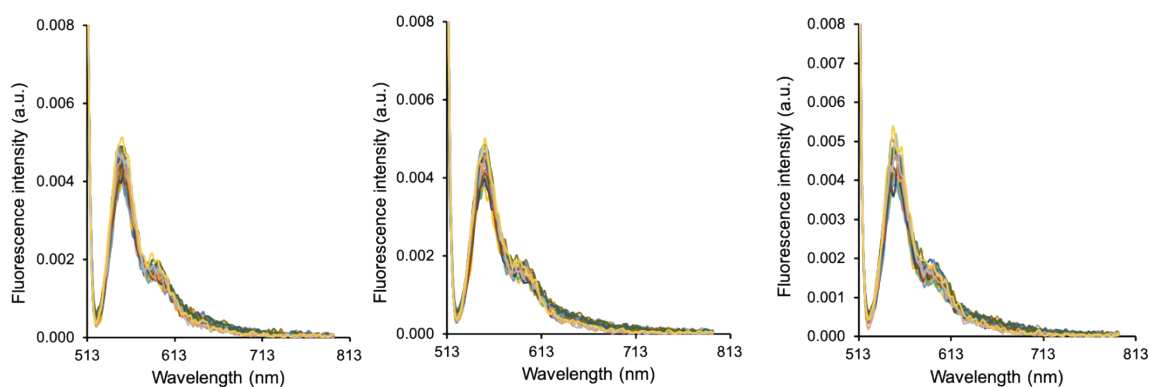


Fig. S19: Normalized fluorescence emission spectra of AuNP@PDI ($15 \mu\text{g.mL}^{-1}$) in absence of GSH over a period of 8 days demonstrating no significant increase in their fluorescence intensities. Experiments were carried out in triplicate.