Electronic Supplementary Information
for

Light-Triggered Covalent Assembly of Gold Nanoparticles in Aqueous Solution

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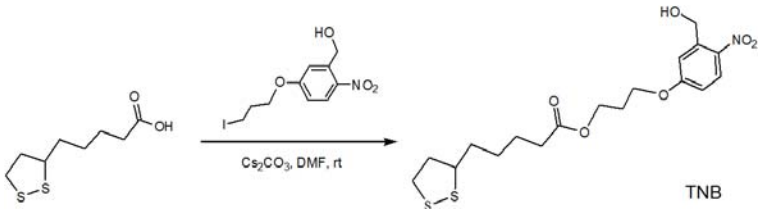
Materials and general methods:

All reagents were purchased from J&K chemical, Sigma-Aldrich or Alfa-Aser, and were used as received. UV-vis absorption spectra were recorded on Hitachi U3900-H absorption spectrophotometer. ^{1}H NMR and ^{13}C NMR were acquired in $CDCl_3$ on Bruker AV400 NMR spectrometer using TMS as an internal standard. Mass spectrometric data were obtained on a Finigan MAT-LCQ mass spectrometry (APCI). Thin-layer chromatography (TLC) was performed on precoated silica gel 60F-254 glass plates. HRTEM was performed on a Tecnai F30 or JEM 2100 electron microscope. Sample preparation was carried out by placing a drop of the freshly prepared colloidal solution on a carbon-coated copper grid and allowing the solution to evaporate. A LINOS für lamp (50 W, UV-A) was used as light source for photochemical reaction. Assembly of Au NPs was carried out by irradiating a sample of Au NPs in fresh PBS (pH7.4) under stirring.

Synthesis of TNB:



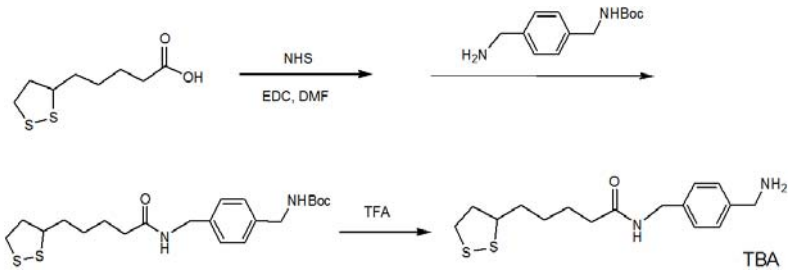
Thioctic acid (TA) (0.206 g, 1.0 mmol), 5-(3-iodoproxy)-2-nitrobenzyl alcohol [S1] (0.338 g, 1.0 mmol) and Cs_2CO_3 (0.325 g, 1.0 mmol) were dissolved in anhydrous *N*,*N*-dimethylformamide (DMF) (30 mL). The mixture was stirred at room temperature for 36 h in dark condition. After removal of the solvent, the resulting mixture was extracted with ethyl acetate and washed with brine (3×50 mL). The organic layer was dried over anhydrous Na_2SO4, filtered, and concentrated *in vacuo*. The product was purified by flash chromatography on a silica gel column using ethyl acetate: hexane (7:3) as eluent (0.373 g, 0.90mmol, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15(d, *J* = 9.2 Hz, 1H), 7.23(d, *J* = 2.8 Hz, 1H), 6.90(dd, *J* = 9.2, 2.8 Hz, 1H), 4.99(s, 2H), 4.28(t, *J* = 6.2 Hz, 2H), 4.16(t, *J* = 6.2 Hz, 2H), 3.50-3.56(m, 1H), 3.06-3.19(m, 2H), 2.40-2.48(m, 1H), 2.33(t, *J* = 7.4 Hz, 2H), 2.16(q, *J* = 6.1 Hz, 2H), 1.84-1.92(m, 1H), 1.59-1.72(m, 1H), 1.38-1.52(m, 1H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.38, 163.36, 140.38, 140.34, 127.96, 114.41, 113.60, 65.18, 62.88, 60.70, 56.34, 40.23, 38.45, 34.54, 33.98, 28.73, 28.40, 24.64 ppm.

APCI-MS *m/z*: 415.1 calc., found 415.3 $(M-H)^-$.

Synthesis of TBA:



Thioctic acid (0.206 g, 1.0 mmol), NHS (0.132 g, 1.2 mmol) were mixed in DMF. EDC·HCl (0.231 g, 1.2 mmol) was added under argon at 0°C. After 3 h, 4-(aminomethyl)-1-*N*-Boc-aniline (0.23 mg, 1.0 mmol) was added. The mixture was stirred for 15 h at room temperature and filtered. After removal of the solvent, the resulting mixture was extracted with 30 mL DCM and washed with brine (3×50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and

concentrated to 1 mL. This cure product was added to a solution of trifluoroacetic acid (1 mL) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 1.5 h. It was then concentrated under vacuum, redissolved in CH_2Cl_2, washed with saturated NaHCO3, dried over Na_2SO_4, and concentrated to a residue. The product was purified by flash chromatography on a silica gel column using ethyl acetate: methanol (95:5) as eluent (0.253 g, 0.78mmol, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23(s, 2H), 5.68(s, 1H), 4.42(d, *J* = 5.6 Hz, 2H), 3.86(s, 2H), 3.56(m, 1H), 3.14(m, 2H), 2.44(m, 1H), 2.22(t, *J* = 7.4 Hz, 2H), 1.91(m, 2H), 1.69(m, 4H), 1.52(m, 5H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) 172.40, 142.73, 136.88, 128.10, 127.49, 126.76, 56.40, 46.16, 43.38, 40.23, 38.47, 36.47, 34.62, 29.69, 28.87, 25.37 ppm.

APCI-MS *m/z*: 324.1 calc., found 325.1 $(M+H)^+$.

Preparation of Citrate-Au NPs:

Au NPs were prepared by reducing tetrachloroauric acid with trisodium citrate. Briefly, trisodium citrate (1%, 1.75 mL) was added rapidly to an aliquot of 0.01% $HAuCl_4$ (100 mL) that was heat under refluxing. The heating was continued for an additional 8 min, during which time the color changed to deep red. The solution was set aside to cool to room temperature.

Preparations of TNB-Au NPs and TBA-Au NPs:

To the preparation of TNB-Au NPs, TA (103 mg, 0.5 mmol) and TNB (2.1 mg, 5 μmol) were added to a solution of 50 mL as-prepared citrate–Au NPs. After refluxing for 5 min, the mixture was cool to room temperature and repeated centrifugation and redispersion in H_2O for 3 times to remove the unbounded ligands. Finally, the solution was diluted to a volume of 50 mL. The **TBA-Au NPs** was prepared by the similar procedure expect that TBA (1.7 mg, 5 μmol) was used to instead of TNB.

Note: In order to stabilize the Au NPs and minimize the reaction sites on NPs surface, TA was employed as a stabilizing agent along with TNB and TBA. The molar ratio of TA to corresponding thiol used in the preparation was 100:1. Since their similar thiol structure, the TA and functionalized thiols (TNB and TBA) were considered to have same affinities to Au NPs. Thus,

after ligand exchanging, the molar ratios of TA to the functionalized thiols loaded on per nanoparticle were estimated to be 100:1.

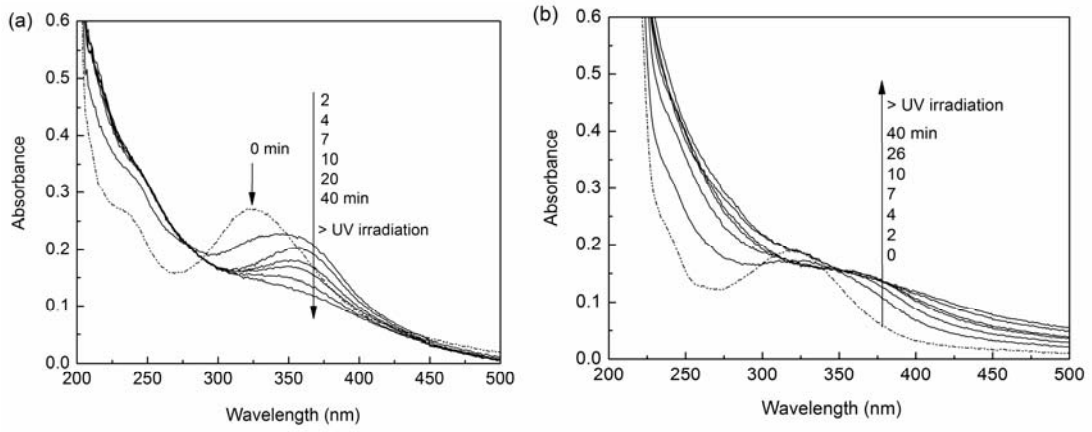


Fig. S1 Overlaid UV-visible absorption spectra of TNB without (a) and with (b) TBA in pH7.4 PBS after various periods of irradiation using UV light.

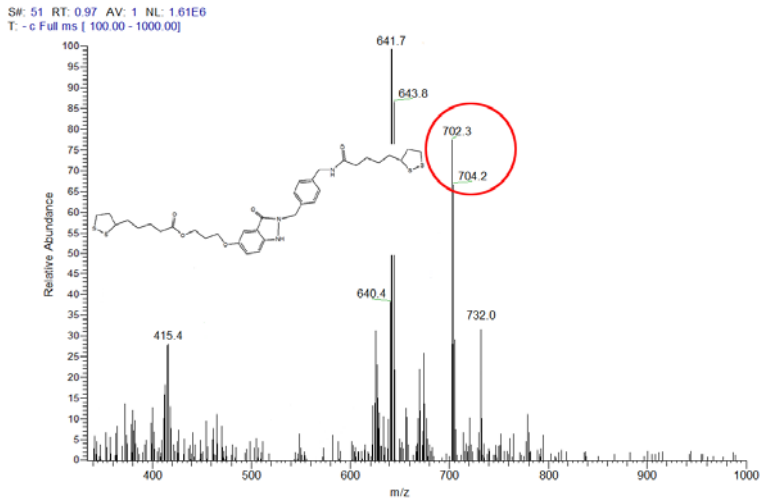


Fig. S2 APCI-MS characterization of the reaction mixture after a 40 min of UV irradiation. The inset shows the structure of the anticipative product with a molecular weight of 704.5.

Note: As shown in Fig. S1a, irradiating TNB in phosphate buffered saline (PBS) solution at pH7.4 induced the absorption band at 325 nm shift to 360 nm quickly. A further irradiation led to a decrease of the absorption band at 360 nm by degrees which indicated the photolysis of TNB. In contrast, photolysis of the mixture of TNB and TBA led to a different spectra change. As the photochemical reaction processed, the absorption band of TNB at 325 nm was red shift and extended to a broad band from 350 nm to 500 nm (Fig. S1b), indicating the formation of an

indazalone product which was further confirmed by the APCI-MS analysis (calc. 704.5, found 704.20, $(M-H)^-$) which shown in Fig. S2. These results demonstrated the light-triggered crosslinking properties of TNB and TBA in aqueous solution.

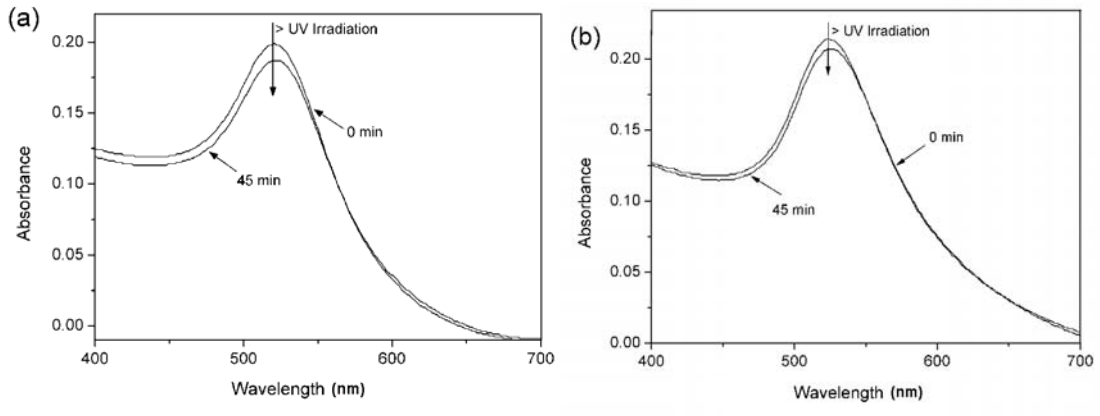


Fig. S3 Absorption spectra of TNB-Au NPs (a) and TBA-NPs (b) in pH7.4 PBS after respective UV irradiations.

Controlled experiments were carried out by irradiating a solution that contained TNB-Au NPs or TBA-Au NPs only in pH7.4 PBS solution. As shown in Fig. S3a, a 45 min of irradiation of UV light leads to a slight decrease in the surface plasmon band of TNB-Au NPs at 520 nm, which may attribute to the photolysis of thiol ligands and the UV light droved fusion and fragmentation of Au NPs, while neglectable increase at the band longer than 530 nm indicates that no aggregation of the Au NPs was observed. Fig. S3b shows a similar result for TBA-Au NPs.

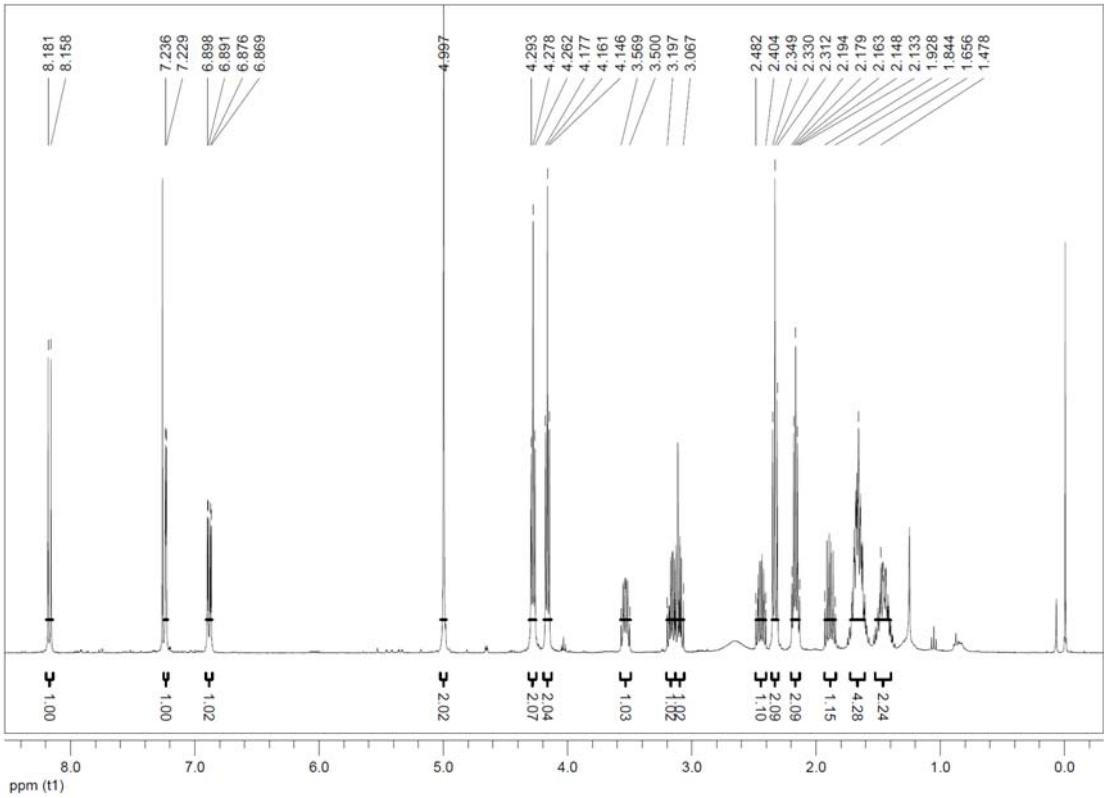


Fig. S4 H-NMR characterization of TNB

Reference

S1 K. C. Nicolaou, N. Winssinger, J. Pastor, F. Deroose, *J. Am. Chem. Soc.* **1997**, *119*, 449-450.