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Direct Photopatterning of Light-Activated Gold Nanoparticles

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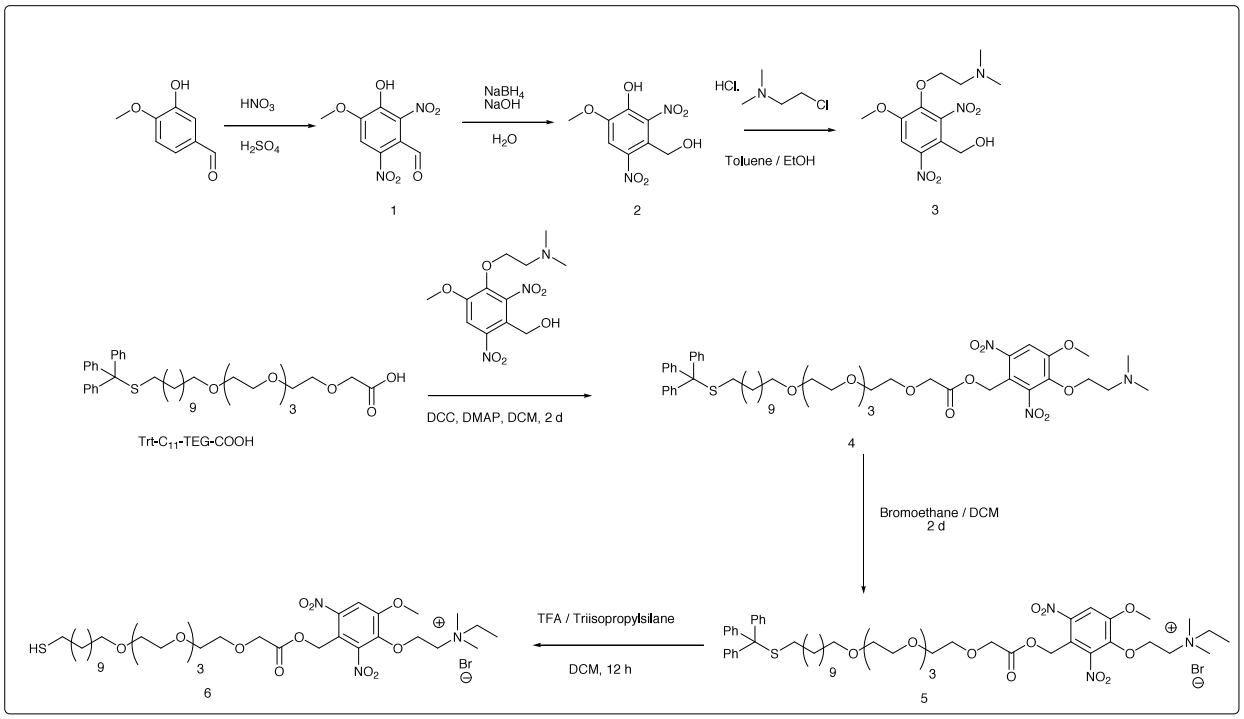

Scheme-S1. Synthetic scheme for the synthesis of compound **6**.

Synthesis of compound **1**

Isovanilin (4.6 gr, 30 mmol) was placed in a 100 mL round bottom flask, which was cooled with ice bath. Concentrated HNO_3 was added to the solid under stirring dropwise. The white solid was turned to dark with the generation of brown NO_2. After addition, the mixture was stirred for 1h, then the mixture poured into ice water. After filtration, the solid was recrystalized from water (~400 mL) to obtain Compound **1** as a yellow needle. Yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.48 (s, 1H), 7.84 (s, 1H,), 4.10 (s, 3H,).

Synthesis of compound **2**

Compound **1**(7.26 g, 30 mmol) was suspended in 150 mL H_2O and NaOH (1.2 g, 30 mmol) was added to this solution under stirring. The solution became clear in few minutes and turns dark yellow in color. After 10 min, $NaBH_4$ (0.6 g, 15 mmol) was added and the mixture was stirred at r.t for 3h. Then, 1M HCl was added to adjust the p^H value at ~2. Some dark brown solid was formed. The solid was extracted with EtOAc. The organic layer was washed thoroughly with H_2O and brine. After drying over Na_2SO_4 and

removal of the solvent, Compound **2** was obtained as a dark yellow solid. Yield: 94%. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.69 (s, 1H), 4.80 (s, 2H), 4.07 (s, 3H), 2.75 (br, 1H).

Synthesis of compound **3**

Compound **2** (1.220 g, 5 mmol), 2-(dimethylamino)ethylchloride.HCl (0.86 g, 6 mmol) and NaOH (0.44 g, 11 mmol) were suspended in a mixture of tolune (50 mL) and ethanol (10mL). The reaction mixture was heated to reflux and stirred for 48h. After cooling to r.t, the dark solution was poured into water (~300 mL). The organic layer was isolated and water phase was washed with tolune. The organic layer was combined and washed successively with $NaHCO_3$, H_2O and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, the residue was dissolved in minimum amount of CH_2Cl_2 and a large amount of hexane was added to the solution. Crystals of the pure compound **3** was formed from the solution after standing the solution in cold temperature. Yield: 18%. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.70 (s, 1H), 4.73 (s, 2H), 4.34 (t, J = 5.8 Hz, 2H), 4.01 (s, 3H), 2.68 (t, J = 5,8 Hz, 2H), 2.31 (s, 6H).

Synthesis of compound **4**

Trt-C11-TEG-COOH[1] (325 mg, 0.43 mmol) was dissolved in dry DCM that was placed in an ice bath. *N,N′*-Dicyclohexylcarbodiimide (DCC, 118 mg, 0.57 mmol) and 4-Dimethylaminopyridine (DMAP, 29 mg, 0.33 mmol) was then added to the solution was stirred at 0 ^{0}C for about 10 min. Then, compound **3** was added subsequently. The reaction mixture was allowed to reach r.t and stirred for 2 days. The precipitate was removed by filtration and the filtrate was concentrated. The residue was charged on SiO_2 column (eluent: 50% methanol in DCM v/v) to obtained compound **4**. Yield: 80%. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.46-7.40 (m, 6H), 7.32-7.26 (m, 6H), 7.24-7.18 (m, 3H), 5.40 (s, 2H), 4.34 (t, J = 5.7 Hz, 2H), 4.14 (s, 2H), 4.02 (s, 3H), 3.74-3.62 (m, 14H), 3.61-3,56 (m, 2H), 3.45 (t, J = 6.8 Hz, 2H), 2.69 (t, J = 5.6 Hz, 2H), 2.32 (s, 6H), 2.14 (t, J = 7.2 Hz, 2H), 1.62-1.53 (m, 2H), 1.44-1.36 (m, 2H), 1.34-1.10 (m, 14H).

Synthesis of compound **5**

Compound **4** (200 mg, 0.20 mmol) was dissolved in dry DCM (10 mL) and bromoethane (1.2 mL, 4 mmol) was added subsequently. The mixture was stirred at room temperature under dark for 2 days. Then, the solvent and the excess bromoethane was removed under a reduced pressure. The residue was washed thoroughly with diethyl ether. After drying under high vacuum compound **5** was obtained. Yield 85%. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.45-7.37 (m, 6H), 7.32-7.23 (m, 6 H), 7.22-7.16 (m, 3H), 5.36 (s, 2H), 4.73 (t, J = 3.9 Hz, 2H), 4.24 (t, J = 4.0 Hz, 2H), 4.10 (s, 2H), 4.00 (s, 3H), 3.80 (q, J = 7.2 Hz, 2H), 3.72-3.60 (m, 14H), 3.58-3.54 (m, 2H), 3.50-3.40 (m, 8H), 2.13 (t, J = 7.3 Hz, 2H), 1.62-1.51 (m, 2H), 1.46 (t, J = 7.2 Hz, 3H), 1.42-1.32 (m, 2H), 1.31-1.10 (m, 14H).

Synthesis of compound **6**

Compound **5** (250 mg, 0.23 mmol) was dissolved in dry DCM (10 mL) and trifluoroacetic acid (TFA, 0.18 mL) and triisopropylsilane (0.05 mL) was added successively in the argon atmosphere. The reaction mixture was stirred at room temperature for 6h. All the DCM and excess TFA was removed under a reduced pressure. The residue was washed with diethyl ether for several times. After drying under high

vacuum, pale yellow oil was obtained. Yield 90%. ^{1}H NMR ($CDCl_3$): δ 7.70 (s, 1H), 5.38 (s, 2H), 4.72 (b, 2H), 4.21 (b, 2H), 4.11 (s, 2H), 4.10 (s, 3H), 3.76-3.60 (m, 16H), 3.59-3.54 (m, 2H),), 3.43 (t, J = 6.8 Hz, 2H), 3.37 (s, 6H), 2.52 (q, J = 7.2 Hz, 2H), 1.66-1.52 (m, 4H), 1.46 (t, J = 7.0 Hz, 3H), 1.40-1.16 (m, 14H).

Construction of photocleavable gold nanoparticle (**NP-PC**)

The photocleavable gold nanoparticle was prepared by Murray place-exchange reaction[2] of 1-dodecanethiol protected 6 nm gold nanoparticle (NP-C12) with thiolate ligand **6**. Briefly, NP-C12 (d ~ 6 nm, 20 mg) were dissolved in 8 mL of DCM (60 mL) and ligand **6** (15 mg) in DCM (15 mL) was added to the nanoparticle solution. The mixture was stirred at room temperature for 2~3 days. The precipitates formed were collected by centrifugation and washed thoroughly with DCM to remove free ligands. The dark solid was dried under high vacuum to remove the solvent.

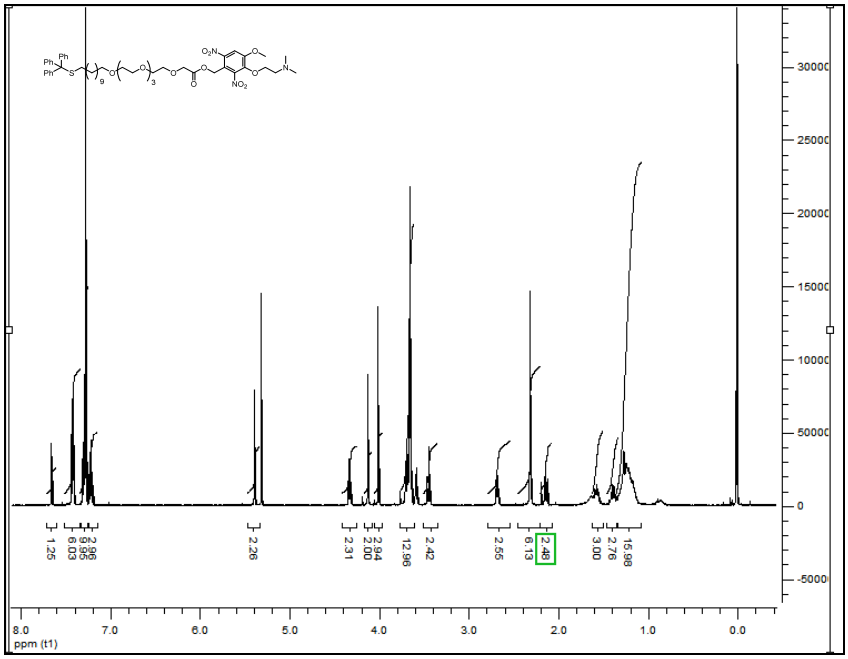

Figure S1. ^{1}H NMR spectrum of compound **4**

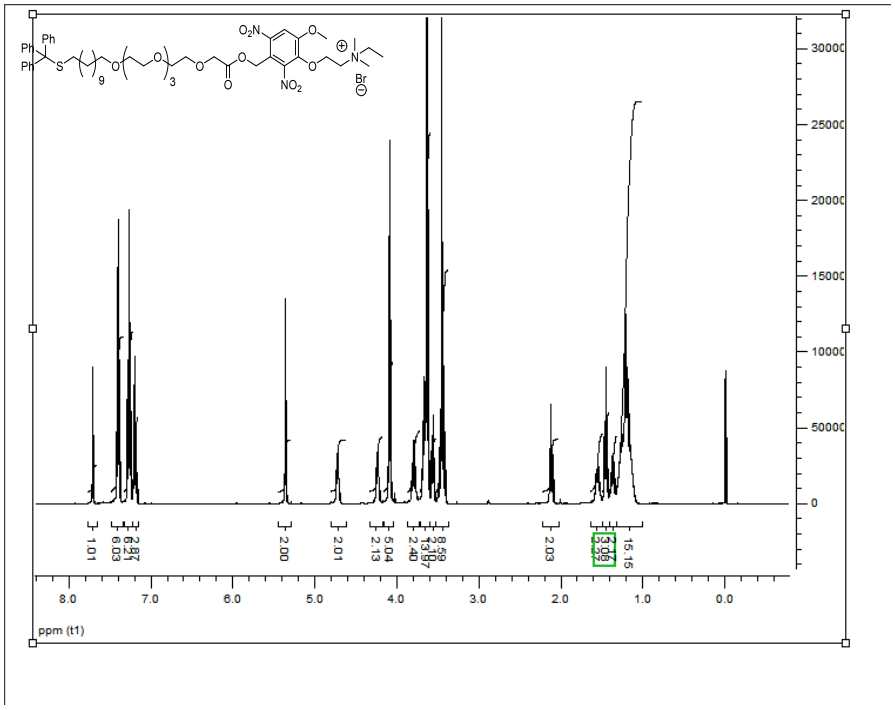

Figure S2. ^{1}H NMR spectrum of compound **5**

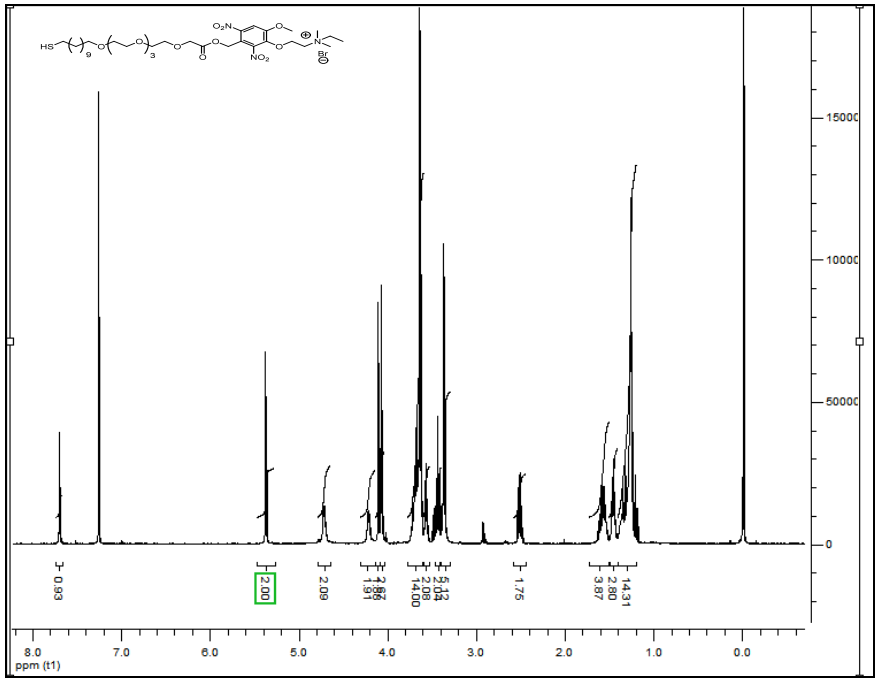

Figure S3. ^{1}H NMR spectrum of compound **6**

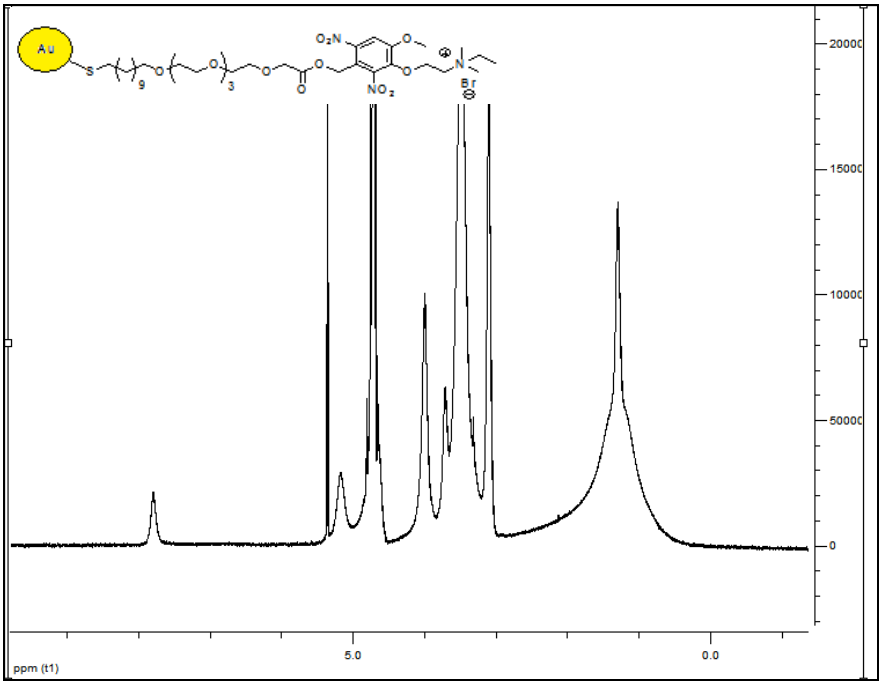

Figure S4. ^{1}H NMR spectrum of **NP-PC** in D_2O

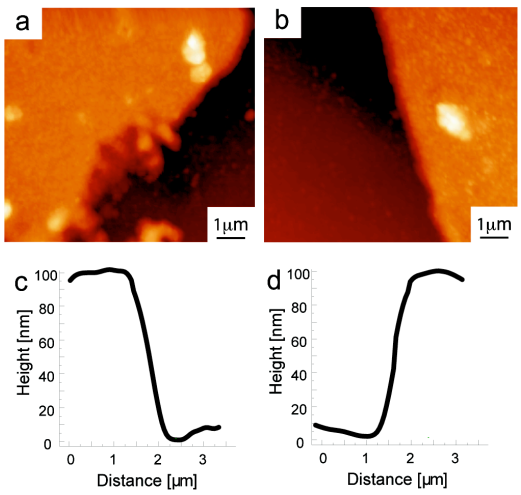

Figure S5. AFM imaging of a) spin-coated film, b) developed film after UV exposure, c) and d) are the thicknesses of spin-coated film and developed film after UV exposure respectively.

References:

1. B. T. Houseman, M. Mrksich, *J. Org. Chem*. **1998**, 63, 7552-7555.

2. M. J. Hostetler, A. C. Templeton, R. W. Murray, *Langmuir* **1999**, 15, 3782-3789.