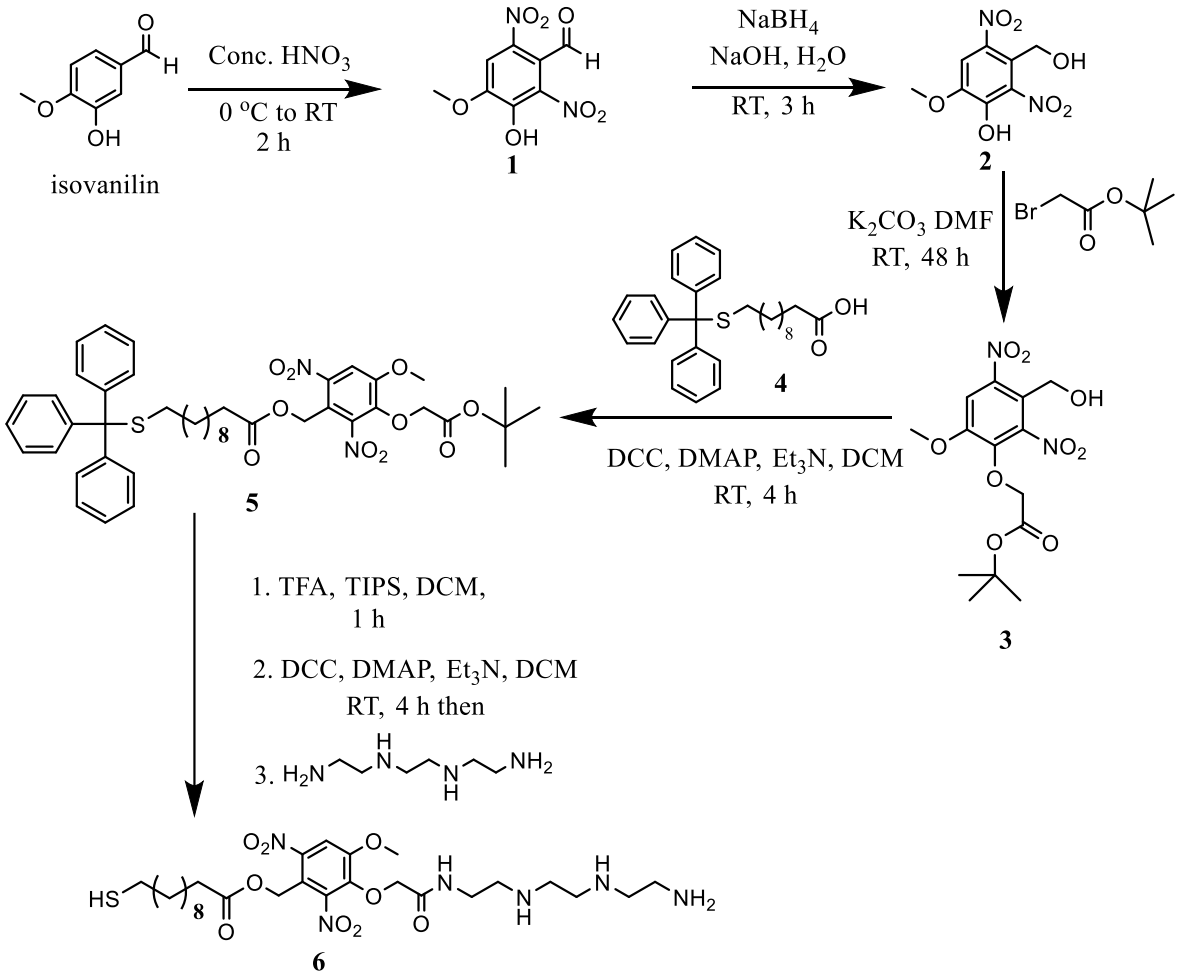
Supporting information

Photo-regulation of gold nanoparticles stabilized in a diacetylenic nanocapsule

All materials were used as received unless otherwise noted. Chlorotriphenylmethane (99.5%), acetone (HPLC grade), hydrochloric acid (HCl, 37%), isovanillin, nitric acid (HNO_3, 65%), potassium carbonate (K_2CO_3, >99%), sodium borohydride ($NaBH_4$, >98%), sodium hydroxide (NaOH, >99%), tert-butyl bromoacetate, triethylamine (99%), and triisopropylsilane (TIPS, 99%) were purchased from Merck Chemicals. Gold (III) Chloride trihydrate ($HAuCl_4$, 49%), 1-dodecanethiol (>98%), 4-(dimethylamino) pyridine (DMAP, >98%), N,N'-dicyclohexylcarbodiimide (DCC, >98%), N,N'dimethylformamide (DMF), 11-mercaptoundecanoic acid (95%), and tetraoctylammonium bromide (98%), Triethylene tetraamine were purchased from Sigma-Aldrich. Dichloromethane (DCM, 99.5%), ethanol (99.9%), sodium chloride (NaCl), and anhydrous sodium sulfate (Na_2SO_4) were purchased from Quality Reagent Chemical. Toluene (99.9%) and trifluoroacetic acid (TFA, 99%) was purchased from RCI Labscan Limited.

^{1}H-NMR spectra was recorded using a Varian Mercury Plus 400 spectrometer. UV-vis spectra were recorded using a Shimadzu, UV-1800. Fluorescent Spectra were measured using fluorescence spectrometry (JASCO, FP-8200). Dynamic light scattering (DLS) was measured using a Zetasizer Nano ZS.



Scheme S1 Synthetic scheme for the preparation of photocleavable cationic ligand **6** [1]

Synthesis of compound 1

Isovanilin (18.3 g, 120 mmol) was placed in a 250 mL round bottomed flask. The flask was cooled to 0 °C in an ice bath. Then, HNO_3 (40 mL) was added dropwise to the isovanilin with stirring. The reaction mixture changed into to a dark yellow solution and finally turned brown. This mixture was kept at room temperature and further stirred for 2 h. The reaction mixture was then poured into 200 mL of water at 0 ^oC, filtered, and evaporated under vacuum to yield compound **1** 17.8671 g (61.52% yield).

^{1}H-NMR (400 MHz, CDCl3): δ 10.48 (s, 1H, −CHO), 7.85 (s, 1H, HAr), 4.10 (s, 3H, −OCH3).

Synthesis of compound 2

Compound **1** (7.26 g, 30 mmol) was dissolved in water (150 mL) in a 250 mL round bottomed flask. NaOH pellets (0.17 g, 4.3 mmol) were added to the solution of compound **1**. $NaBH_4$ (1.2 g, 30 mmol) was then added to the solution after 10 min of stirring. The reaction mixture was further stirred at room temperature for 3h. Then, 1 M HCl was used to adjust the pH of the solution to ~2. A dark brown solid was precipitated from the acidic solution. This solid was extracted using ethyl acetate (3x 100 mL). The organic layers were combined and washed with water and brine. After drying over Na_2SO_4, ethyl acetate was removed under reduced pressure to produce compound **2** 5.0453 g (68.22% yield). Compound **2** was used in the next step of the reaction with no further purification.

^{1}H-NMR (400 MHz, CDCl3): δ 7.70 (s, 1H, HAr), 4.80 (s, 2H, −PhCH_2O−), 4.07 (s, 3H, −OCH3)

Synthesis of compound 3

K_2CO_3 (10.5 g, 76 mmol) was suspended in dry DMF (100 mL). Compound **2** (2.8 g, 11.5 mmol) was added to the suspended solution of K_2CO_3. This mixture was stirred for 1 h and then *tert*-butyl bromoacetate (2.54 g, 13 mmol) was added to the solution. The reaction

mixture was stirred for 48 h at room temperature. The resulting insoluble solid was removed by filtration. The filtrate was transferred into water (~300 mL). The mixture was extracted with ethyl acetate (3x150 mL). The ethyl acetate layers were combined, washed with a saturated solution of brine (100 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The product was purified using silica-gel chromatography (eluent: 50% ethyl acetate in hexane v/v) to produce compound **3** 2.3111 g (56.09% yield).

^{1}H-NMR (400 MHz, CDCl3): δ 7.70 (s, 1H, HAr), 4.79 (s, 2H, −$OCH_2C(O)$−), 4.72 (d, J = 7.32 Hz, 2H,−$PhCH_2O$−), 3.97 (s, 3H, −OCH3), 2.69 (t, J = 7.44 Hz, 1H, Benzyl−OH), 1.45 (s, 9H, −C(CH3)3).

Synthesis of Trt-mercaptoundecanoic acid (4)

Mercaptoundecanoic acid (1 g, 4.58 mmol) was dissolved in DCM (10 mL) and placed in a 100 mL round bottomed flask. NaH (0.1214 g, 5.05 mmol) was added to the clear solution and stirred for 10 min. Chlorotriphenylmethane (2.8212 g, 10.11 mmol) was added into the mixture of mercaptoundecanoic acid. The reaction mixture was further stirred at room temperature for 3 h. The solvent was removed under reduced pressure. The product was purified using silica-gel chromatography (eluent: a gradient eluent of hexane to ethyl acetate) to yield Trt-mercaptoundecanoic acid 0.78 g (37% yield).

^{1}H-NMR (400 MHz, CDCl3): δ 7.41 (m, 6H, Ar-H), 7.27 (m, 6H, Ar-H), 7.20 (m, 3H, Ar-H), 2.30 (t, 2H, -S-CH_2-), 2.10 (t, 2H, -CH_2-C(O)OH), 1.80-1.85 (m, 4H, -CH_2-), 1.50-1.70 (m, 12H, -$(CH_2)_6$.

Synthesis of Compound 5

Trt-mercaptoundecanoic acid (0.7 g, 1.52 mmol) was dissolved in DCM (25 mL) and placed in a 100 mL round bottomed flask forming a clear solution after 10 min of stirring. DCC (0.3357 g, 1.67 mmol), NEt_3 (0.23 mL, 0.1689 mmol), DMAP (cat.) were added to a suspended solution of Trt-mercaptoundecanoic acid. Compound **3** (0.5446 g, 1.52 mmol) was

suspended in DCM (20 mL) and added into the reaction mixture of Trt-mercaptoundecanoic acid. The mixture was stirred for 4 h. The solvent was removed under reduced pressure and the residue was purified using silica-gel chromatography (eluent: a gradient eluent of hexane to ethyl acetate) to yield compound **4** 0.5417 g (44.5% yield).

^{1}H-NMR (400 MHz, CDCl3): δ 7.65 (s, 1H, Ar-H), 7.41 (m, 6H, Ar-H), 7.27 (m, 6H, Ar-H), 7.20 (m, 3H, Ar-H), 5.30 (s, 2H, O-CH_2-Ph-), 4.75 (s, 2H, -O-CH_2-C(O)), 3.95 (s, 3H, CH_3-O), 2.25 (t, 2H, -S-CH_2-), 2.10 (t, 2H, -CH_2-C(O), 1.58 (m, 2H, -$(CH_2)_2$-), 1.45 (9H, $(CH_3)_3$-C-), 1.39 (m, 2H, -$(CH_2)_2$-), 1.10-1.35(m, 12H, -$(CH_2)_6$-).

Synthesis of Compound 6

Compound **5** (0.5 g, 0.625 mmol) was suspended in DCM (5 mL) and placed in a 25 mL round bottomed flask. Trifluoroacetic acid (TFA, 0.5 mL, 0.688 mmol) was added to the solution which caused it to turn yellow. Triisopropylsilance (TIPS) was carefully added to the reaction mixture and the mixture slowly became colorless. The reaction was continued for 1 h at room temperature with stirring. The volatile components (solvent, TFA and TIPS) were distilled under a reduced pressure. A pale yellow residue was further purified by washing it with hexane (4x15mL). The solvent was removed under reduced pressure to yield 0.24 g (78.86% yield) and which was used in the next step.

^{1}H-NMR (400 MHz, CDCl3): δ 7.65 (s, 1H, Ar-H), 5.30 (s, 2H, O-CH_2-Ph-), 4.90 (s, 2H, -O-CH_2-C(O)), 3.99 (s, 3H, CH_3-O), 2.5 (m, 2H, -S-CH_2-), 2.22 (t, 2H, -CH_2-C(O), 1.65-1.50 (m, 4H, -$(CH_2)_2$-), 1.42-1.10 (m, 12H, -$(CH_2)_6$-).

After deprotection, compound **5** (0.5 g, 0.99 mmol) was dissolved in 10 mL of DCM. Then DCC (0.233 g, 1.12 mmol) was added to the solution. Subsequently, N-hydroxysuccinimide (0.1140 g, 0.99 mmol) dissolved in 10 mL of DCM was added to the reaction mixture. Next, Et_3N (1.37 mL, 0.99 mmol) and DMAP (cat.) were added and stirred for 4 h at room temperature and then the reaction mixture was filtered. After filtration, the

mixture was added to the solution of Triethylenetetramine (0.9132 g, 6.24 mmol) in DCM (90 mL). The mixture was stirred for 24 h. Next, the organic solvent was removed under a reduced pressure. The resulting residue was purified using silica-gel chromatography (eluent: 5% methanol:DCM) to yield compound **6** 0.1541 g (25.8 % yield).

^{1}H-NMR (400 MHz, CDCl3): δ 7.65 (s, 1H, Ar-H), 5.30 (s, 2H, O-CH_2-Ph-), 4.90 (s, 2H, -O-CH_2-C(O)), 3.99 (s, 3H, CH_3-O), 3.39 (br m, 12H, –CH_2N–), 2.5 (m, 2H, -S-CH_2-), 2.22 (t, 2H, -CH_2-C(O), 1.65-1.50 (m, 4H, -$(CH_2)_2$-), 1.42-1.10 (m, 12H, -$(CH_2)_6$-).

Synthesis of 2-nm gold nanoparticle (Au_C12)[2]

Hydrogen tetrachloroaurate (0.3275 g) was suspended in 30 mL of DI water and placed in a 250 mL round bottomed flask. Tetraoctylammonium bromide (2.1900 g) in 80 mL of toluene was added to this solution. Then 170 mg of 1-dodecanethiol and sodium borohydride (0.3833 g) in 25 mL of DI water were added to the reaction. The reaction mixture was stirred for 3 h and using separatory funnel that selected the organic layer and then the toluene was removed using a rotary evaporator. 400 mL of ethanol was added to wash away excess thiol. Next, the organic solvent was evaporated under reduced pressure. The resulting nanoparticles was named as to Au_C12. Gold nanoparticles were characterized using transmission electron microscopy (FEI Tecnai G2 20) and UV-Vis spectophotometer (Shimadzu, UV-1800).

Synthesis of AuPCNH$_2$ [3]

Compound **6** (0.3 g) was dissolved in 5 mL of DCM and methanol (1 mL). Then, 5 mL of TFA was added to the solution and stirred for 30 minute**.** After 30 minutes, the solvent was evaporated under a reduced pressure. Au_C_{12} was dissolved in 5 mL of DCM and placed in a solution of compound 5. Sodium borohydride (0.02 g) was added to the reaction mixture and stirred for 48 h at room temperature. Then this solution was evaporated under reduced pressure and washed using hexane (10 mL x 3 times) and DCM (10 mL x 1

time). Next, a mixture of methanol and DI water was added and stirred overnight. The solution containing methanol was evaporated under a reduced pressure and the solution filtered through a nylon membrane (0.45 μm).

Morphology of Au_C12

Figure S1 (a) showed the TEM image of Au_C12. The Au_C12 have sizes between 2.1± 0.75 nm which were determined from randomly selected images using the Image J program. The size distribution of Au_C12 is shown in Figure S1 (b). It was found that the Au_C12 were well dispersed and no aggregation of nanoparticles was observed.

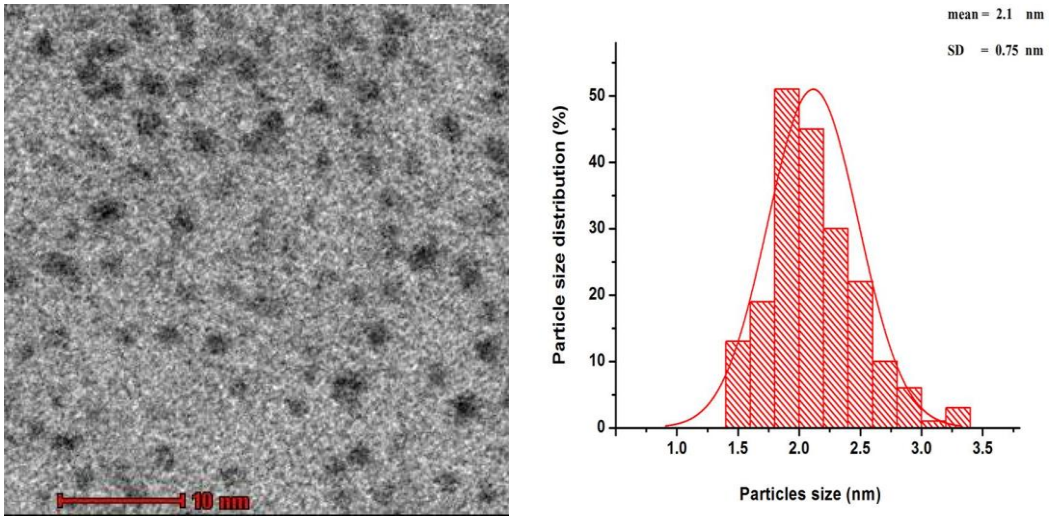


Figure S1: (a) TEM images of Au_C12 (b) the size distribution of Au_C12 calculated using the program, Image J, and 100 randomly selected particles.

References

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