Highly photoresponsive monolayer-protected gold clusters by self-assembly of a cyclodextrin-azobenzene derivative supramolecular complex

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Supplementary Information

Chemicals and general procedures.
4-(phenylazo)phenol (98%), 1,10 diiododecane (95%), sodium carbonate and potassium thioacetate were purchased from Sigma-Aldrich (Milan) and used as received. All solvent used (from Carlo Erba, Milan) were analytical grade. Syntheses were carried out under a low intensity level of vis light.

Instrumentation.
1H NMR spectra were recorded on a VARIAN INOVA 200 spectrometer, using TMS as internal standard. ESI-MS spectra were recorded on an Agilent 1100 Series ESI/MSD spectrometer. Experimental conditions were as follows: capillary voltage, 3.5 KV; fragmentor, 100 V; source temperature, 350 °C; drying gas, N2 (10 L/min), carrier solvent, methanol (0.4 mL/min). The samples were dissolved in a mixture methanol:acetonitrile. UV/vis absorption spectra were recorded with a Beckman DU 650 spectrophotometer.

Synthetic procedures.
10-{(E)-phenyldiazenyl}phenoxy}decane-1-thiol (1) was synthesized in a three step synthesis as reported in Scheme 1S

![Scheme 1S]
(E)-1-{4-[10-iiododecyl]oxy[phenyl]-2-phenyldiazen (A).

4-(phenylazo)phenol (0.40 g, 2.0 mmol), 1,10 diiododecane (3.94 g, 10 mmol) and sodium carbonate (3.0 g) were refluxed in 100 ml of acetonitrile for 3 days. After cooling down to ambient temperature, the resulting precipitate was washed with water and acetonitrile and dried under vacuum to give A (yield 55 %). ESI-MS m/z: [M+H]+ 465.3 (100%). H1-NMR CDCl3-d1 (200 MHz) 7.9 (2H d, J=8.0) 7.7 (2H d, J=7.5) 7.5 (3H t J=7.5) 7.0 (2H d, J=8.0) 4.0 (2H t, J=7.3), 3.28 (2H t, J=7.4) 2.76 (2H m, J=7.2) 1.82 (2H m, J=7.4) 1.24 (12H s broad).

S-(10-{4-[E-phenyldiazenyl]phenoxy}decyl)ethanethioate (B).

A mixture of A (0.46 g, 1 mmol) and MeCOSK (0.60 g, 5 mmol) in acetonitrile (500 mL) was heated for 6 h under reflux and N2. After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was suspended in CH2Cl2 and filtered. The organic solution was concentrated under reduced pressure and purified by column chromatography (dichloromethane:cyclohexane 2:1) to give B (yield 85%) as a yellowish powder.

ESI-MS m/z: [M+H]+ 413.5; H1-NMR CDCl3-d1 (200 MHz) 7.9 (2H d, J=8.0) 7.7 (2H d, J=7.5) 7.5 (3H t J=7.6) 7.0 (2H d, J=8.0) 4.0 (2H t, J=7.3), 2.8 (2H t, J=7.3) 2.76 (2H m, J=7.2), 2.3 (3H, s) 1.36 (2H m, J=7.4) 1.24 (12H s broad).

10-{4-[E-phenyldiazenyl]phenoxy}decane-1-thiol (1)

Acetyl chloride (100 μl, 1.4 mmol) was added dropwise to a solution of B (40 mg, 0.1 mmol) in methanol/acetonitrile (1:4) maintained at -78°C under N2. After 15 min, the mixture was allowed to warm up to ambient temperature in 3 h. The solvent was distilled off under reduced pressure to afford 1 (yield 82 %) as a yellowish powder.

ESI-MS m/z: [M+H]+ 371.5; H1-NMR DMSO-d6 (200 MHz) 7.87 (2H d, J=9.0), 7.82 (2H d, J=8.6), 7.54 (3H t J=8.5), 7.12 (2H d, J=9.0), 4.07 (2H t, J=6.6), 2.8 (2H t, J=7.0), 2.3 (1H s broad), 1.73 (2H m, J=6.5), 1.44 (2H m, J=6.9), 1.26 (12H s).
Photoisomerization of 1. Figure 1S shows the absorption spectra of a DMF solution of 1 recorded at different interval of UV (340 nm) (a) and Vis (440 nm) (b) irradiation. The spectra were recorded under ambient conditions using a quartz cell with an optical pathway of 10 mm.

Fig. 1S