

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

Fiorella Callari,<sup>a</sup> Salvatore Petralia<sup>b</sup> and Salvatore Sortino<sup>a\*</sup>

<sup>a</sup>Dipartimento di Scienze Chimiche, Università di Catania, I-95125 Catania, Italy;

E-mail: [ssortino@unict.it](mailto:ssortino@unict.it);

<sup>b</sup>LoC R&D, Microfluidic Division-CPG ST Microelectronics, Catania, Italy

## Supplementary Information

### Chemicals and general procedures.

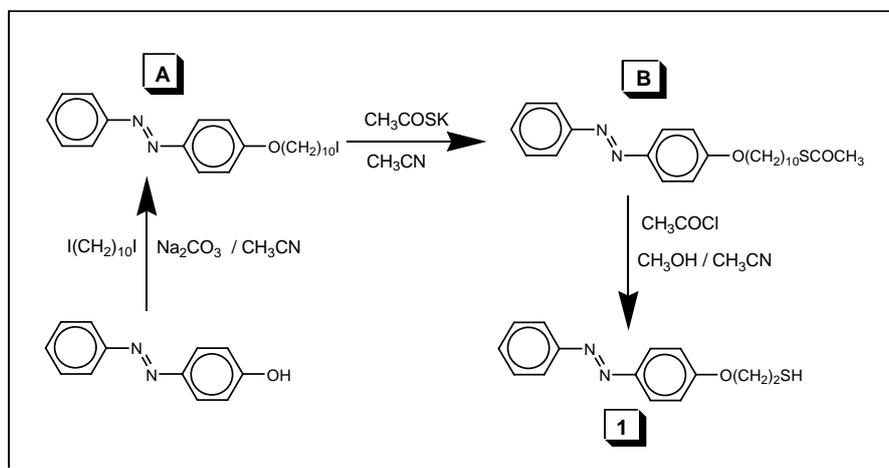
4-(phenylazo)phenol (98%), 1,10 diiododecane (95%), sodium carbonate and potassium thioacetate were purchased from Sigma-Aldrich (Milan) and used as received. All solvent used (from Carlo Erba, Milan) were analytical grade. Syntheses were carried out under a low intensity level of vis light.

### Instrumentation.

<sup>1</sup>H 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, N<sub>2</sub> (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-{4-[(*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-iododecyl)oxy]phenyl]-2-phenyldiazene (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%).  $H^1$ -NMR  $CDCl_3-d_1$  (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,  $J=7.3$ ), 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)***

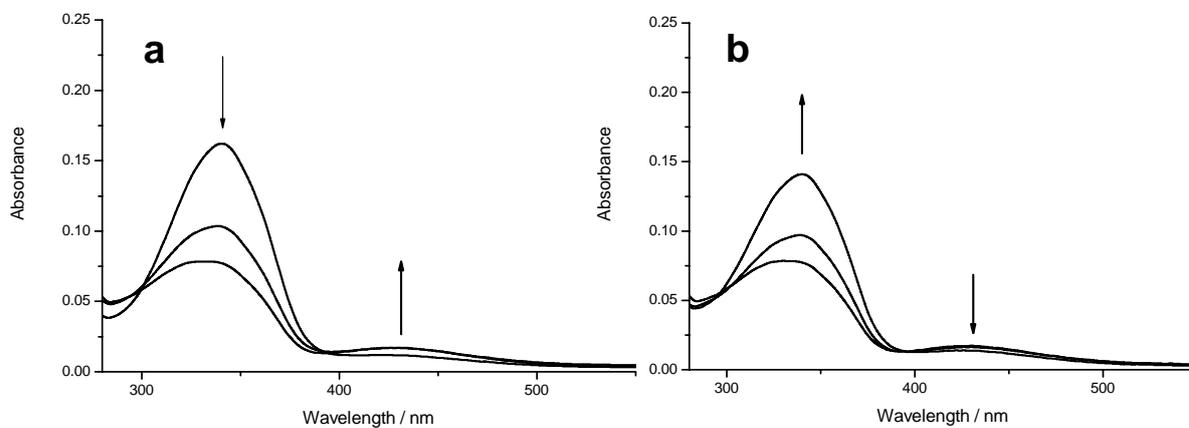
A mixture of **A** (0.46 g, 1 mmol) and MeCOSK (0.60 g, 5 mmol) in acetonitrile (500 mL) was heated for 6 h under reflux and  $N_2$ . After cooling down to ambient temperature, the solvent was distilled off under reduced pressure. The residue was suspended in  $CH_2Cl_2$  and filtered. The organic solution 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;  $H^1$ -NMR  $CDCl_3-d_1$  (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,  $J=7.4$ ) 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  $\mu$ l, 1.4 mmol) was added dropwise to a solution of **B** (40 mg, 0.1 mmol) in methanol/acetonitrile (1:4) maintained at  $-78^\circ C$  under  $N_2$ . 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;  $H^1$ -NMR  $DMSO-d_6$  (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**