

Electronic Supplementary Information for

Dual-Responsive Nanoparticles that Self-Assemble under the Simultaneous Action of Light and CO₂

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1. General information

Solution ¹H and ¹³C NMR spectra were recorded at room temperature on Bruker 300 MHz spectrometer. Chemical shifts (δ) are reported in p.p.m.; multiplicities are indicated by ‘s’ (singlet), ‘d’ (doublet), ‘t’ (triplet), ‘q’ (quartet), ‘quint’ (pentet), ‘m’ (multiplet) or ‘br’ (broad). Coupling constants (*J*) are reported in Hz. Spectra were referenced to residual chloroform (¹H: δ = 7.26 p.p.m.; ¹³C: δ = 77.00 p.p.m.). High-resolution mass spectra were recorded at 60-70 eV on a Waters Micromass Q-TOF spectrometer (ESI, Ar; Waters). TEM was performed on a CM120 Super Twin TEM (Philips) operating at 120 kV. For ultraviolet irradiation, we used a 4-W hand-held UV lamp (UVP, LLC; model number UVGL-25; light intensity \sim 0.7 mW/cm²) or a 100-W UV lamp (UVP, LLC; model number B-100AP; light intensity \sim 10 mW/cm²). As a visible light source, we used a fluorescent bulb (light intensity \sim 1.0 mW/cm²). Ultraviolet-visible spectra were recorded on a Shimadzu UV-3600 spectrometer. Dynamic light scattering (DLS) analysis was carried out on a Malvern ZetaSizer Nano.

2. Synthesis and functionalisation of gold nanoparticles (AuNPs)

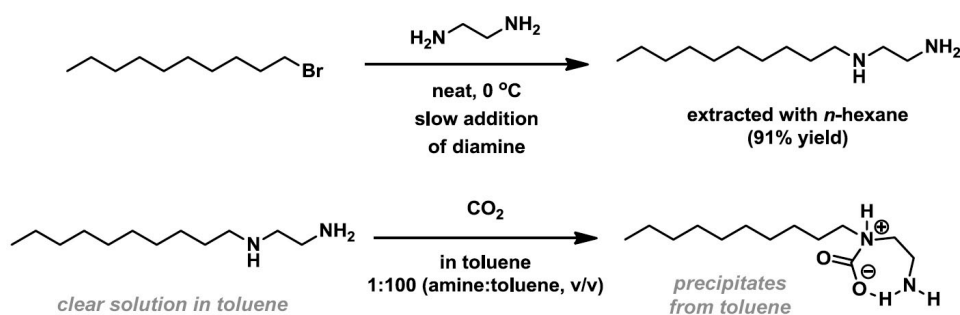
Relatively monodisperse 5.5 nm AuNPs were prepared based on a literature procedure (T. Zdobinsky *et al.*, *J. Am. Chem. Soc.* **2014**, *136*, 2711-2714). DDAB (didodecyldimethylammonium bromide, 925 mg) was dissolved in 20 mL toluene (*stock solution A*). 50 mg of HAuCl₄·3H₂O and 450 mg DDA (dodecylamine) were added to 12.5 mL of stock solution **A** and sonicated until all reagents are dissolved. 125 mg of TBAB (tetra-*n*-butylammonium borohydride) was dissolved in 5 mL of the stock solution **A** and the obtained solution was added to the gold (III) solution under vigorous stirring via rapid injection. Thus prepared solution of \sim 2.6 nm NPs (“seeds”) was aged for 24 hours. Growth solution (**B**) was prepared by adding to 50 mL of pure toluene the following reagents, in the following order: 1) 1.00 g DDAB, 2) 1.85 g DDA, 3) 200 mg of HAuCl₄·3H₂O, 4) 7 mL of the aged seed solution. Finally, 131 μ L of hydrazine dissolved in 20

mL of the DDAB stock solution was added dropwise (~1 drop / sec) to the growth solution under vigorous stirring. Thus prepared NPs were kept in a solution and were stable for up to several months.

Preparation of mixed ligand solution: Prior to the preparation of ligand solutions, diamine **3** was stored under reduced pressure at 40 °C to avoid any CO₂ complexation. Total concentration of the thiol ligand mixture was always kept at $c = 6.28$ mM. Due to the low solubility of the diamine **3** in toluene, a minute amount of CHCl₃ was often added. Otherwise, prolonged sonication (5 min) was applied to dissolve the ligand in pure toluene. The prepared ligand solution was used immediately for NP functionalisation to minimize any disulfide formation and concentration changes.

Functionalisation of gold NPs with mixed monolayers of thiolate ligands. The number of binding sites on the surface of NPs was calculated assuming that a single thiolate ligand occupies a surface area of 0.214 nm². For each experiment, 0.5 mL of gold NP solution ($c = 0.00727$ mol/L in terms of Au atoms) was mixed with equal volume of methanol to precipitate NPs under continuous shaking for 30 minutes. The resulting black precipitate was collected by decantation without centrifugation and redissolved in 5 mL of toluene before adding a solution of thiols ($c = 6.28$ mM, 0.5 mL, 10 equiv of RSH with respect to the number of binding sites on the surface of the NPs). After addition of the ligands solution, ligand exchange reactions were conducted for 18-24 h (longer reaction times led to NP aggregation. 5-7 mL of methanol and 0.5 mg of DDAB were added, the mixture was centrifuged, the precipitate was collected and washed with methanol twice. The resulting NPs were dried under vacuum and dissolved in toluene (0.5 mL).

3. Synthesis of *N*-decylethylenediamine and its CO₂ complexation properties



In a one-neck round bottom flask (100 mL), 1,2-ethylenediamine (24 mL, 30 equiv) was placed with a magnetic stirring bar, and decyl bromide (2.4 mL) was added via syringe slowly for 1 hr at 0 °C. After finishing the addition, the reaction mixture was warmed to room temperature and left undisturbed for an additional one hour. 30 mL of hexane was added into the reaction mixture, which was stirred vigorously overnight. The hexane layer was decanted and dried under reduced pressure to afford the product with a 91% yield. **CAUTION:** the product is sensitive to air (CO₂), therefore should be kept under inert gas and used after heating at 40 °C under reduced pressure (10-20 mbar) to ensure no complexation with CO₂.

CCCCCCCCCCCCNCCN ¹H NMR (300 MHz, CDCl₃), $\delta = 0.87$ (t, 3H, $J = 6.7$ Hz), 1.21 (m, 6H), 1.41 (m, 2H), 2.60 (m, 2H), 2.66 (t, 2H, $J = 5.9$ Hz), 2.81 (t, 2H, $J = 5.7$ Hz) ppm. ¹³C NMR (75 MHz, CDCl₃), $\delta = 14.22, 22.79, 27.51, 29.44, 29.69, 29.70, 29.73, 30.37, 32.01, 42.01, 50.12, 52.84$ ppm.

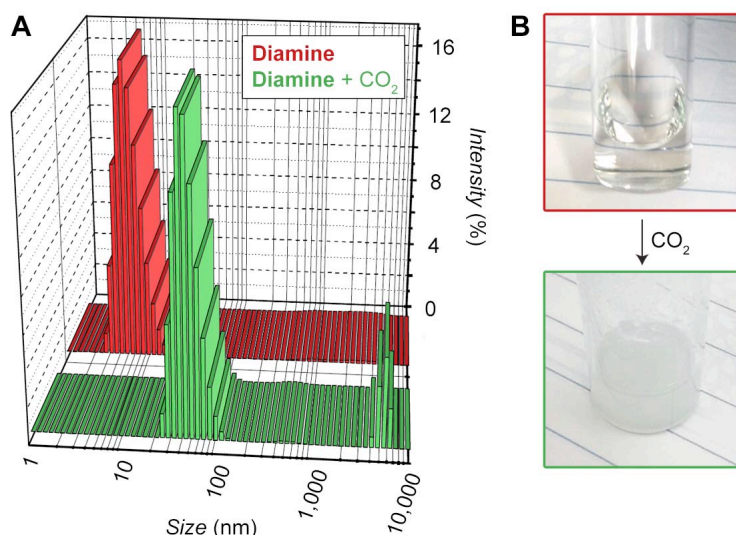
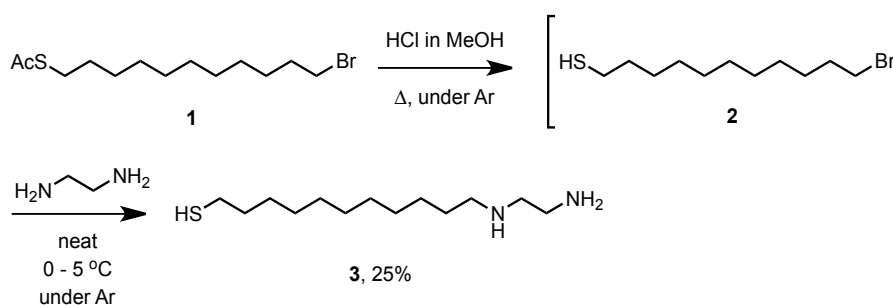


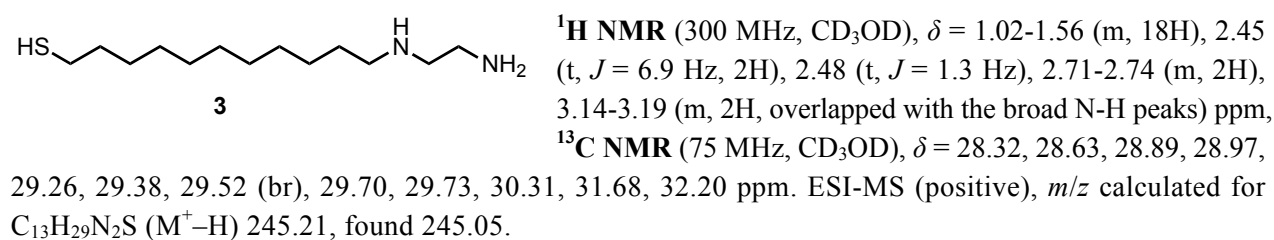
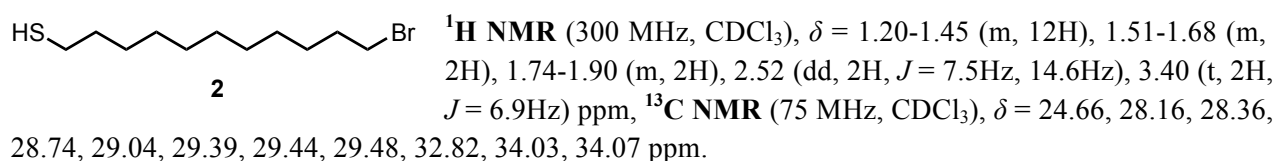
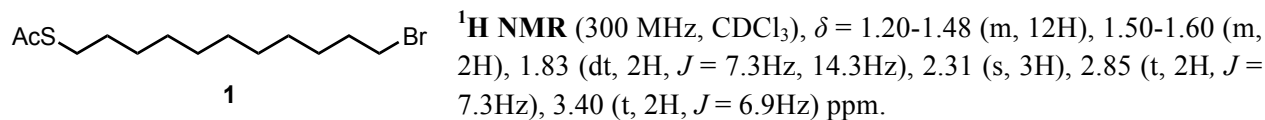
Figure S1. Control reactions with *N*-decylethylenediamine for CO₂-responsiveness. Dynamic light scattering (DLS) data (A) and photographs (B) of toluene solutions of the diamine before and after bubbling CO₂ (addition of a minute amount of dry ice had the same effect).

4. Synthesis of diamine ligand 3



Synthesis of 11-bromoundecane-1-thiol (2): In a two-neck round-bottom flask (100 mL) equipped with a magnetic stirring bar and a reflux condenser, thioacetate **1** (1 mmol, 309 mg) (see H. Yang, Y. Kwon, T. Kwon, H. Lee, B. J. Kim, *Small* **2012**, *8*, 3161-3168) was placed, evacuated under reduced pressure and charged with argon. Then concentrated 1 mL of HCl solution (34%, aqueous) and 14 mL of MeOH were added and bubbled with argon for 30 min with moderate stirring. Then the reaction mixture was refluxed for 1 hr and cooled down to room temperature, then evaporated under reduced pressure (*CAUTION: reaction mixture contains a strong thiol odour*). The remaining aqueous phase was further evaporated following the addition of a small quantity of methanol. The desired product was obtained with quantitative yield (less than 2% of disulfide was detected by NMR) after the residual solvent was removed using high vacuum, and it was used for the next step without further purification.

Synthesis of 11-((2-aminoethyl)amino)undecane-1-thiol (3): In a two-neck round-bottom flask (100 mL), 1,2-ethylenediamine (6 mL; excess) was added and frozen using ice-water bath. The solid diamine was degassed under reduced pressure and the flask was warmed to room temperature. The liquid diamine was bubbled with Ar for 30 min then kept at a low temperature (0-5 °C) during the slow addition of bromide **2** (840 mg) over the course of 1 hour. Once the slow addition was completed, the reaction mixture was warmed to room temperature and left undisturbed for 1 hour. Then, 20 mL of diethyl ether was added into the reaction mixture, which was stirred vigorously overnight. The resulting two-phase mixture was extracted with diethyl ether twice and the combined organic layers were dried under reduced pressure to afford product **3** with 25% yield over two steps. The obtained compound was kept under inert gas at a low temperature (<5 °C).



5. Additional control reactions and tailoring the stimuli-responsiveness of AuNPs by the composition of the mixed monolayer

Control reaction 1: We prepared AuNPs functionalised with a mixed monolayer of 1-dodecanethiol (C_{12}SH) and (AzoSH) (1:1). DLS measurements (Fig. S2) showed that while these NPs responded to UV and visible light in a reversible fashion, exposure to CO_2 did not affect the sizes of free NPs or NP aggregates.

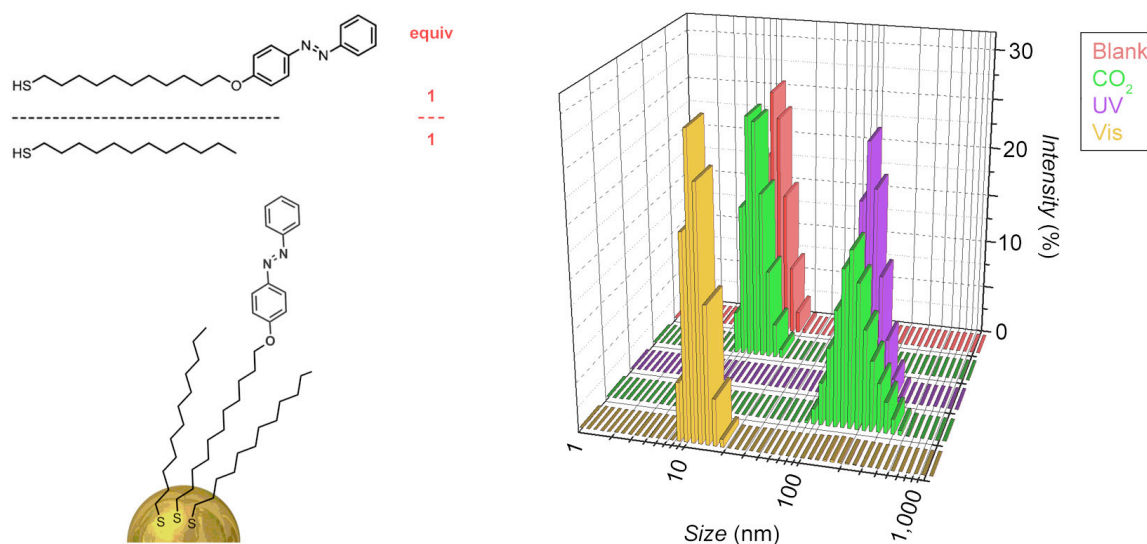


Figure S2. AuNPs co-functionalised with C_{12}SH and C_6SH (1:1) and their (lack of) CO_2 -responsiveness.

Control reaction 2: We prepared AuNPs functionalised with a mixed monolayer of 1-dodecanethiol ($C_{12}SH$) and 1-hexanethiol (C_6SH) (1:1). DLS measurements (Fig. S2) showed no response of these particles to CO_2 .

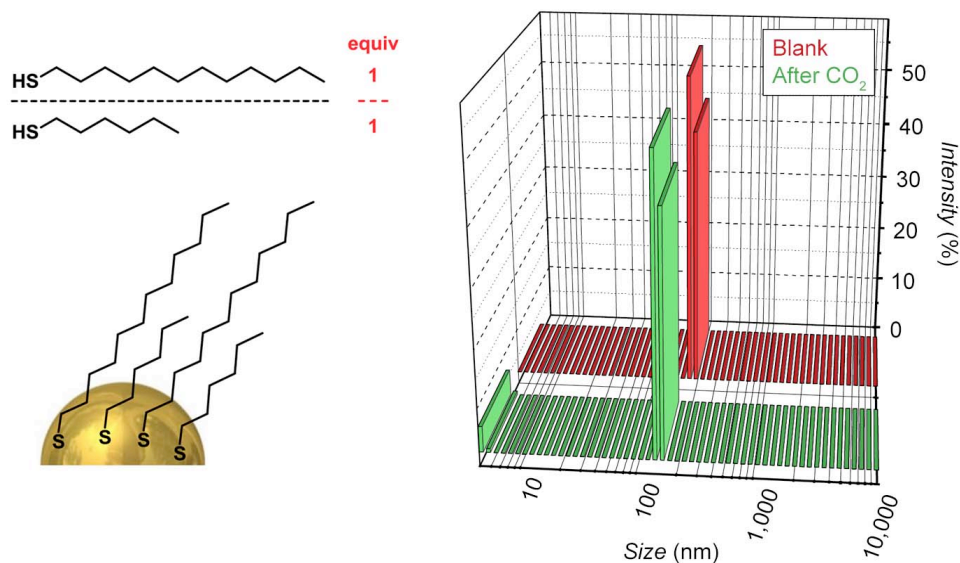


Figure S3. AuNPs co-functionalised with $C_{12}SH$ and C_6SH (1:1) and their (lack of) CO_2 -responsiveness.

Control reaction 3: We prepared AuNPs co-functionalised with a ternary monolayer comprising $C_{12}SH$, C_6SH and diamine **3** (2:2:1). DLS measurements showed that the NPs aggregated in response to CO_2 (Figure S3). We verified that NPs were also not affected by UV light.

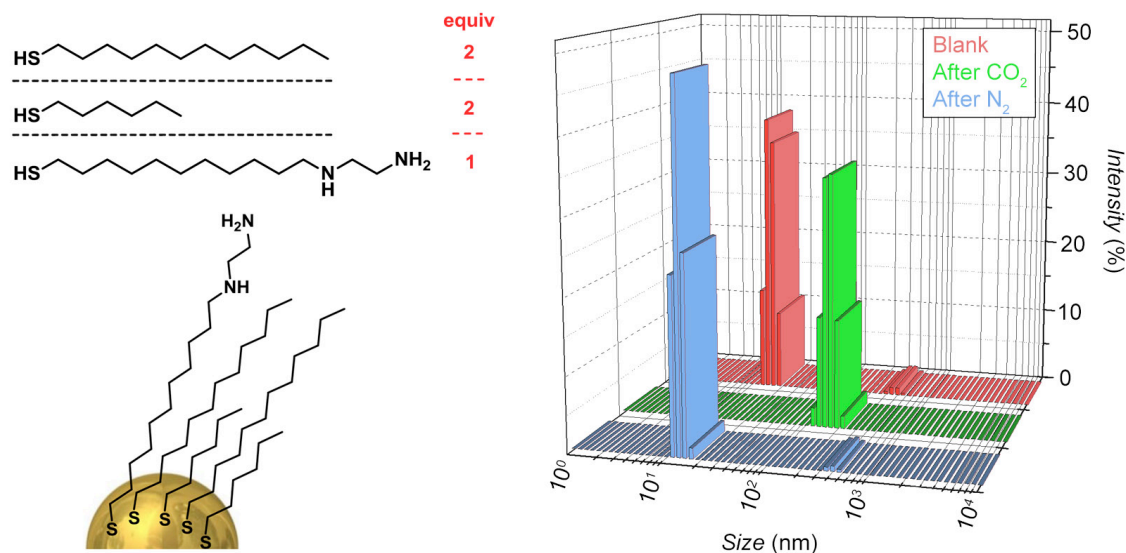
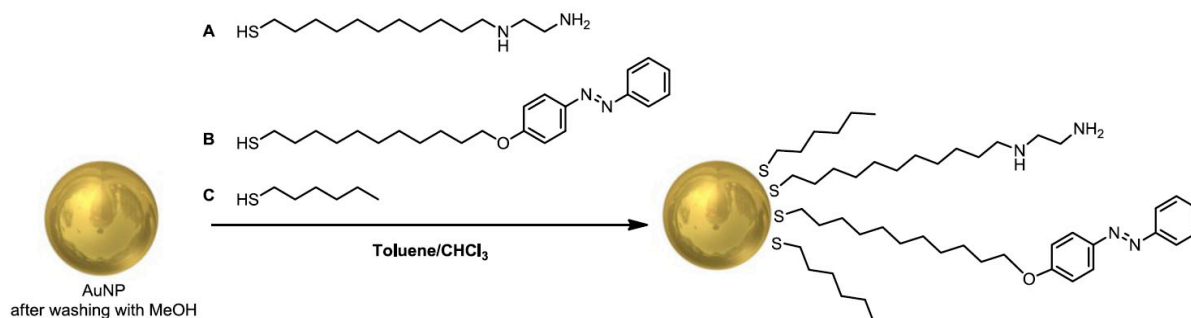


Figure S4. $C_{12}SH$ - and C_6SH - and diamine **3**-functionalised AuNPs and their reversible CO_2 -responsiveness.

Optimisation of ligand ratio for dual-responsive AuNPs with C_6SH as the dummy ligand



Entry	Molar ratio of ligands			Soluble in toluene?	Responsiveness?		Remarks
	A	B	C		UV	CO ₂	
1	1	1	1	X	n/a	n/a	
2	1	1	0	X	n/a	n/a	
3	2	1	2	*	V	X	* Partially aggregated
4	1	2	1	*	V	V**	* Partially aggregated ** Aggregation is irreversible (see Fig. S4)
5	1	1	2	V	X	V	
6	10	1	10	X	n/a	n/a	

Table S1. Properties of AuNPs functionalised with mixed monolayers comprising C_6SH . Responsiveness to either UV or CO₂ was verified independently by DLS, absorption spectroscopy, and visual inspection.

Conclusions: Solubility of NPs in toluene was enhanced by **B** (**AzoSH**) and decreased by **A** (diamine **3**). Minimum amounts of **A** and **B** were necessary to induce CO₂- and UV-responsiveness, respectively. NPs coated with 25% **A** and 50% **B** responded to both light and CO₂, however aggregation was not reversible, most likely due to poor steric stabilisation of the NPs by C_6SH .

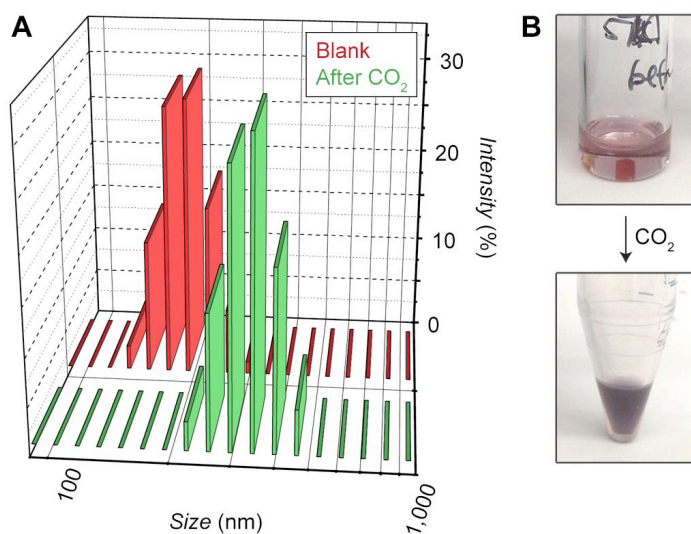
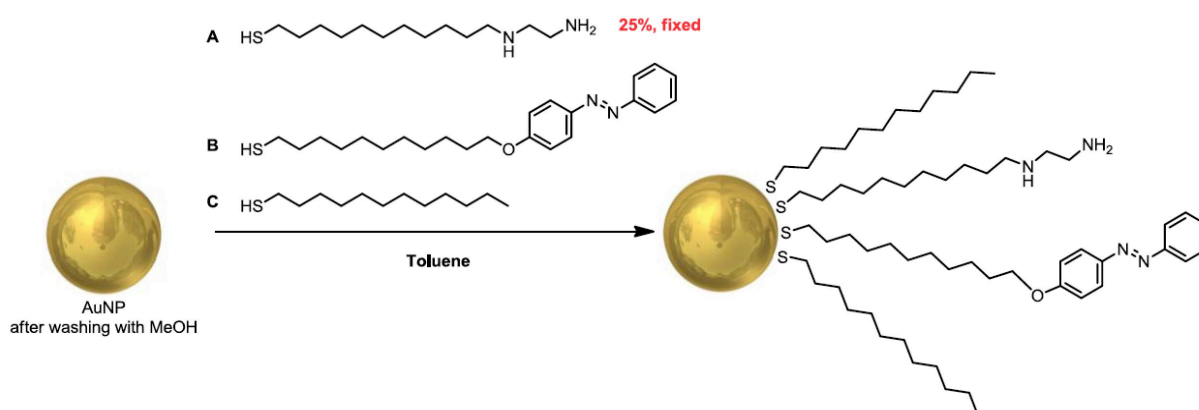


Figure S5. DLS (A) and photographs (B) of toluene solutions of AuNPs (entry 4, Table S1) before and after delivering CO₂. The process was irreversible.

Optimisation of ligand ratio for dual-responsive AuNPs with $C_{12}SH$ as the dummy ligand



Entry	Molar ratio of ligands			Percentage of B	Solubility in toluene?	Responsiveness?			Δ_{size} (nm)
	A	B	C			UV	CO ₂	UV+CO ₂	
1	1	1	2	25%	✓	✗	✗	✗	n/a
2	1	1.2	1.8	30%	✓	✗	✗	✗	n/a
3	1	1.25	1.75	31.25%	✓	✗	✗	✗	n/a
4	1	1.3	1.7	32.5%	✓	✗	✗	✗	n/a
5	1	1.35	1.65	33.75%	✓	✗	✗	✓	6
6	1	1.4	1.6	35%	✓	✗	✗	✓	1,008
7	1	1.6	1.4	40%	✓	✓	✗	n/a	109
8	1	1.8	1.2	45%	✓	✓	✗	n/a	85
9	1	2	1	50%	✓	✓	✗	n/a	68

Table S2. Properties of AuNPs functionalised with mixed monolayers comprising $C_{12}SH$. Molar percentage of A was fixed at 25%. Δ_{size} is the increase in the DLS size after CO₂ was applied to samples pre-irradiated with UV.

Conclusions: In general, replacing C_6SH with $C_{12}SH$ as the dummy ligand improved the solubility of AuNPs. NPs covered with 25% of A (entries 1-9) were soluble in toluene, and remained soluble after the addition of CO₂. By controlling the molar ratio of AzoSH and $C_{12}SH$, we found that NPs functionalised with 33-35% AzoSH (entries 5, 6) aggregated only when both UV and CO₂ were delivered simultaneously. Those NPs that were covered with less than 33% of AzoSH did not aggregate even in the presence of both stimuli, whereas NPs containing more than 35% of AzoSH aggregated when UV-irradiated even in the absence of CO₂. The behaviour of these three types of NPs, exemplified by entries 1, 6, and 7, is shown below:

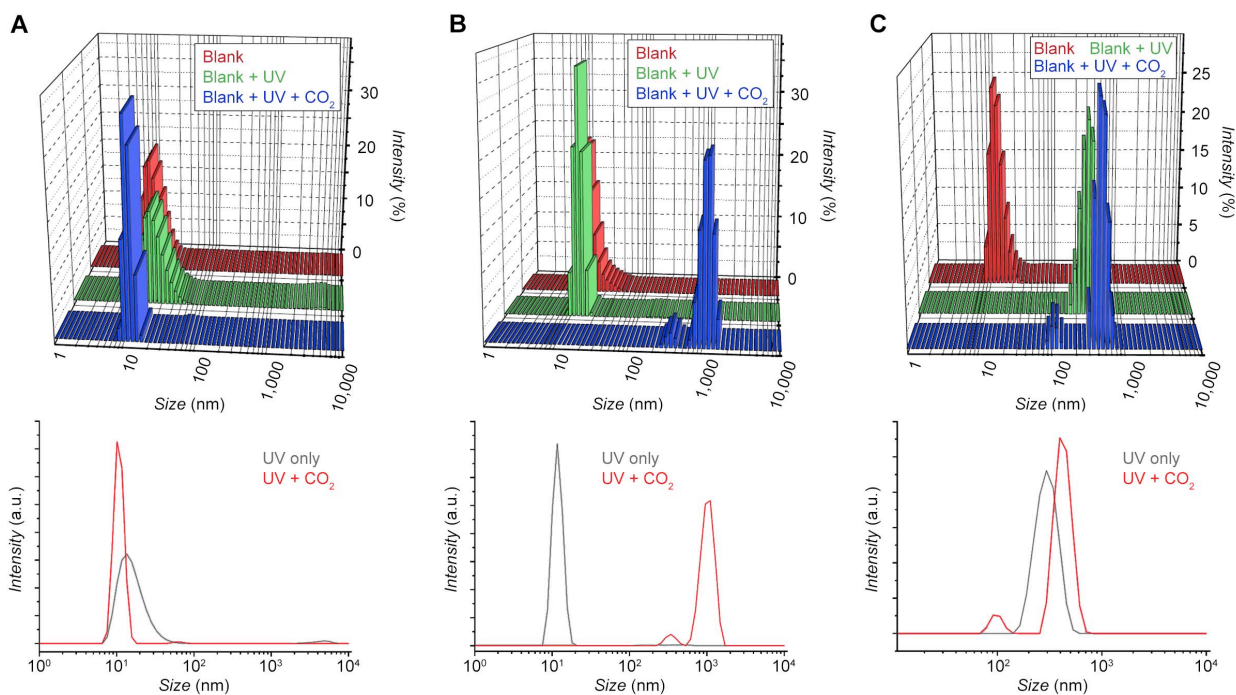


Figure S6. DLS measurements on AuNPs functionalised with 25% of diamine **3** and increasing amounts of **AzoSH**: 25%, 35%, 50% (entries 1, 6, 7, respectively, in Table S2) before and after UV light, and after a simultaneous exposure to UV and CO₂. None of the samples aggregated when exposed to CO₂ only.

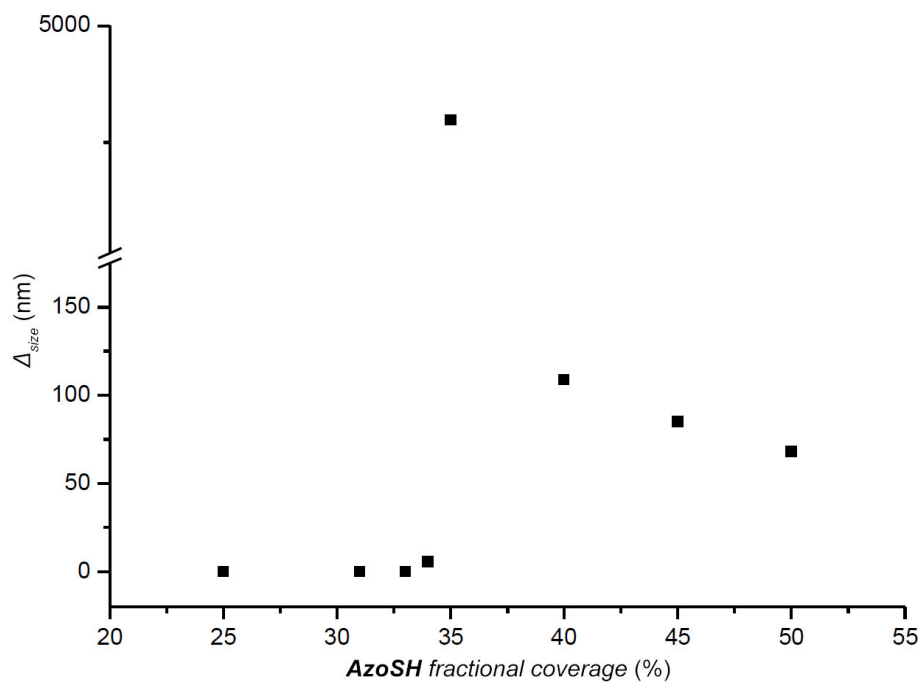
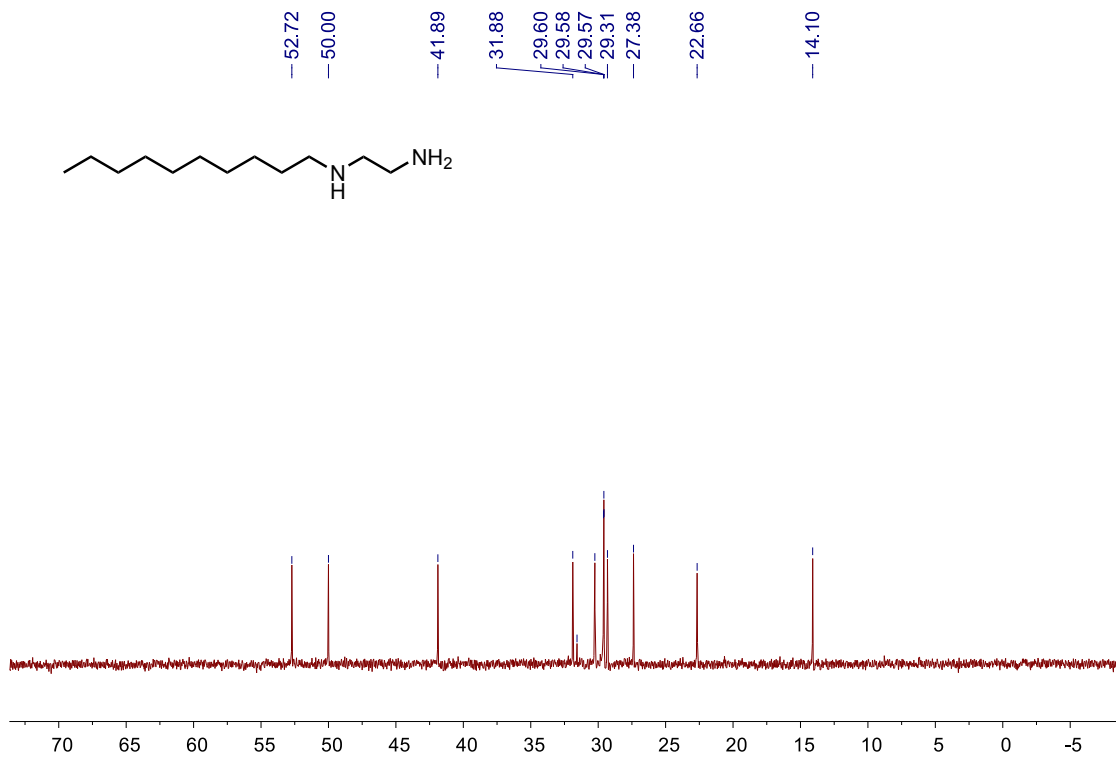
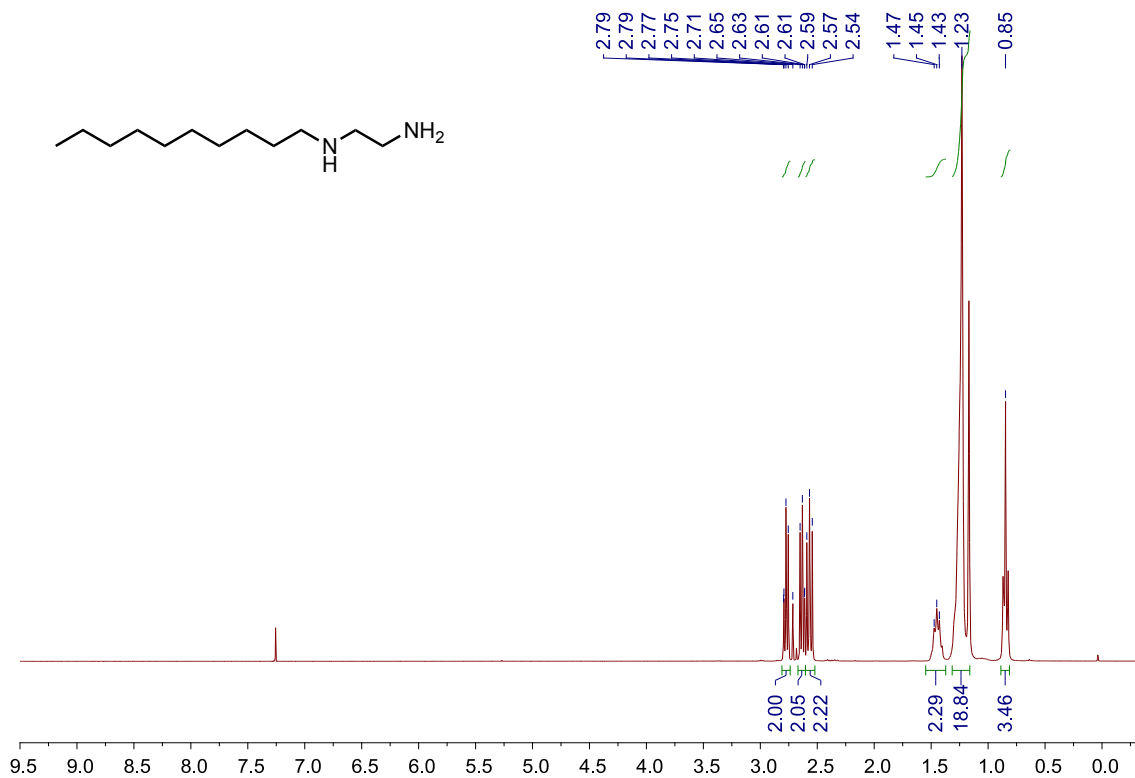
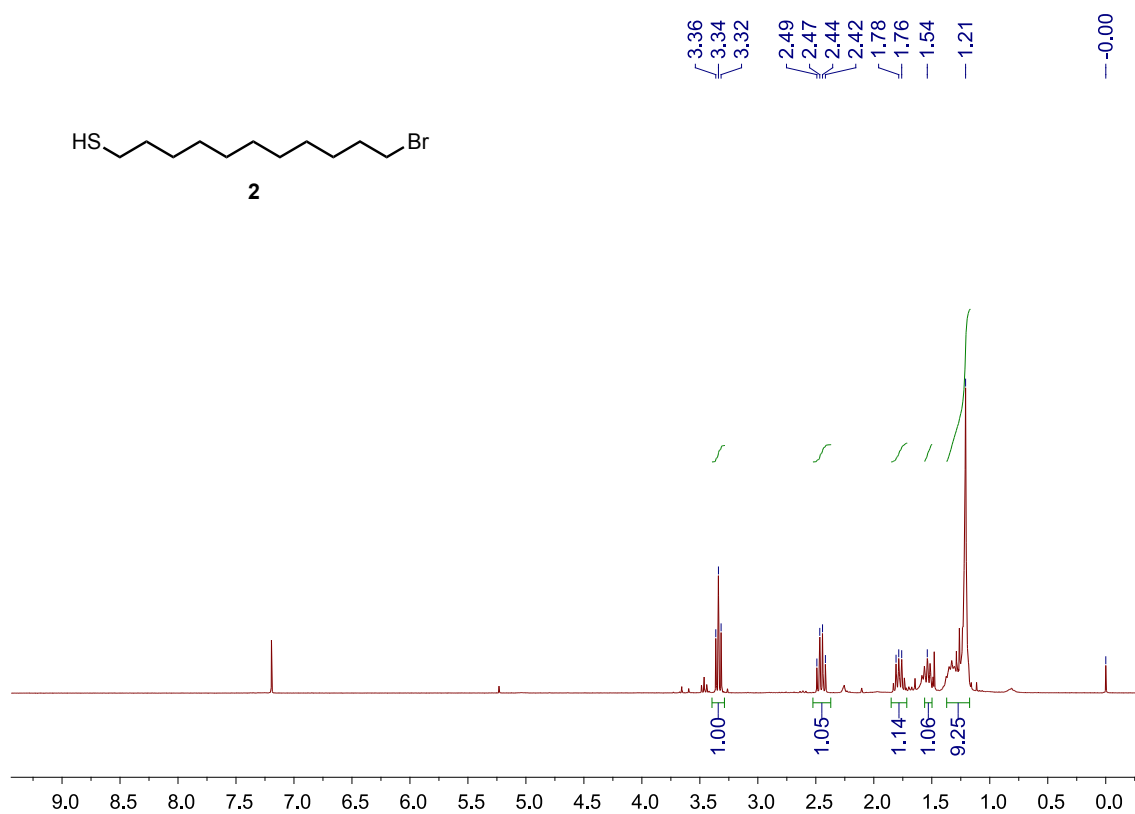
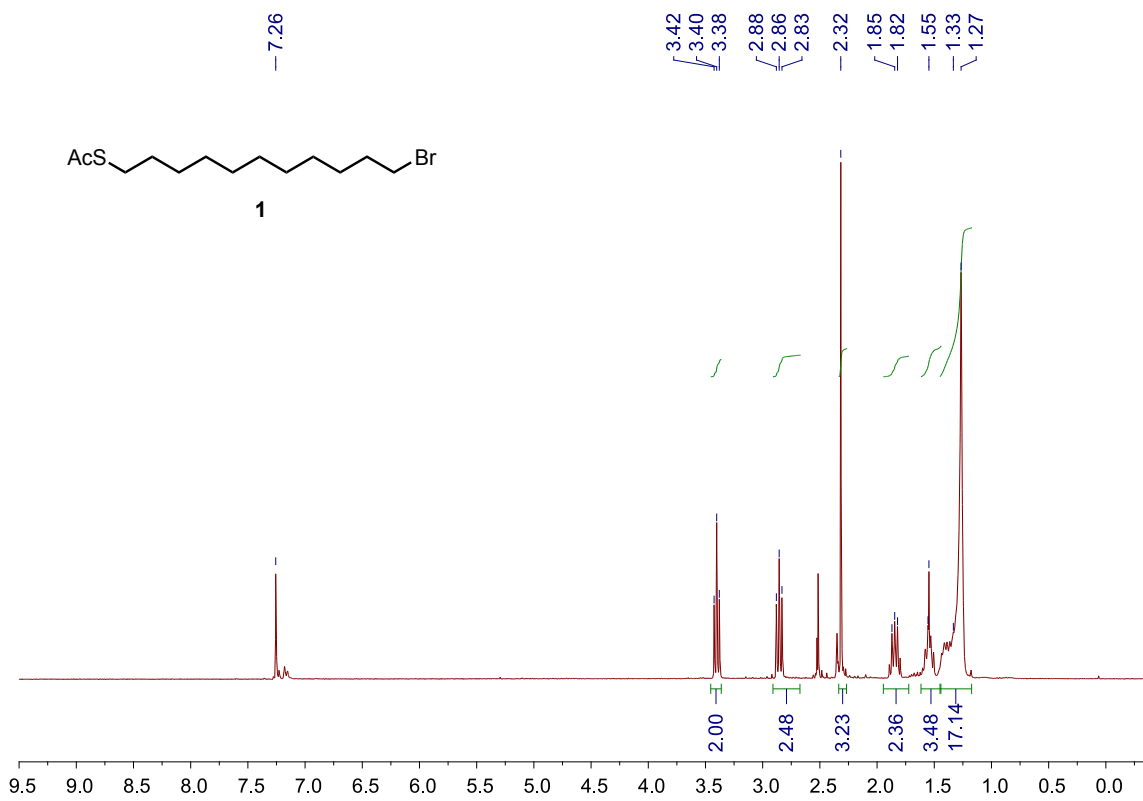
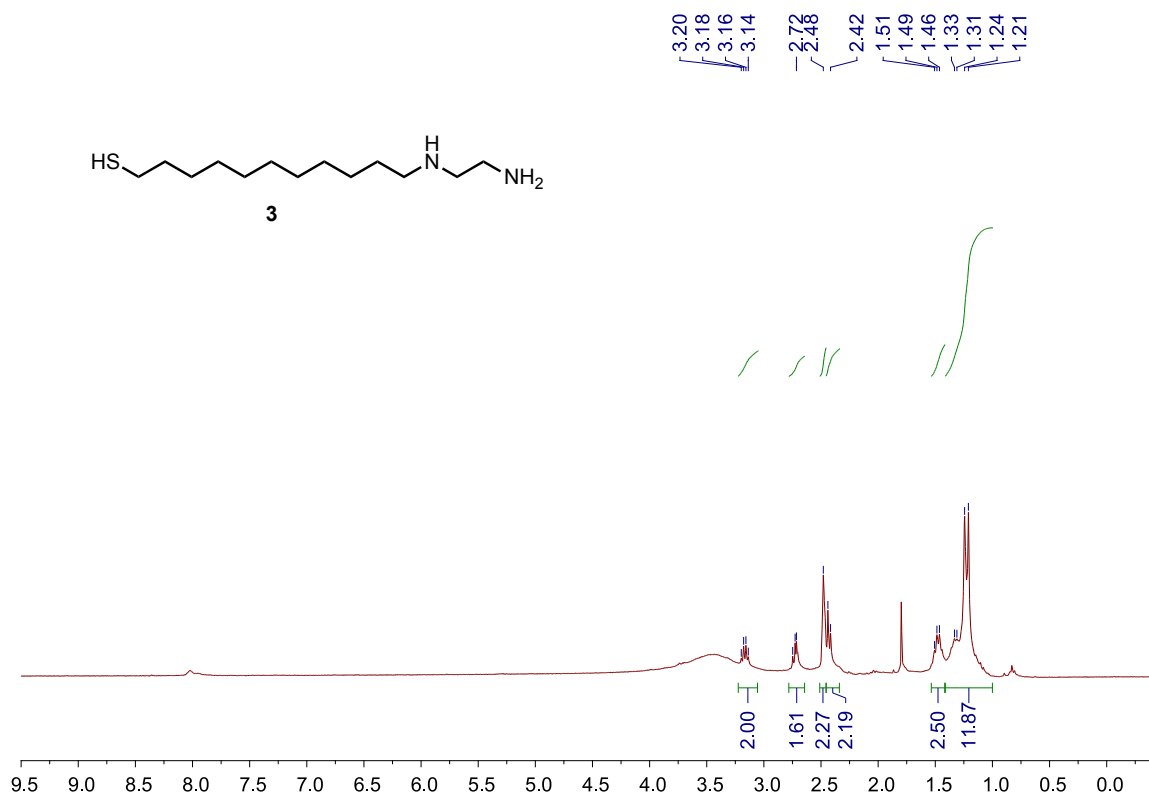
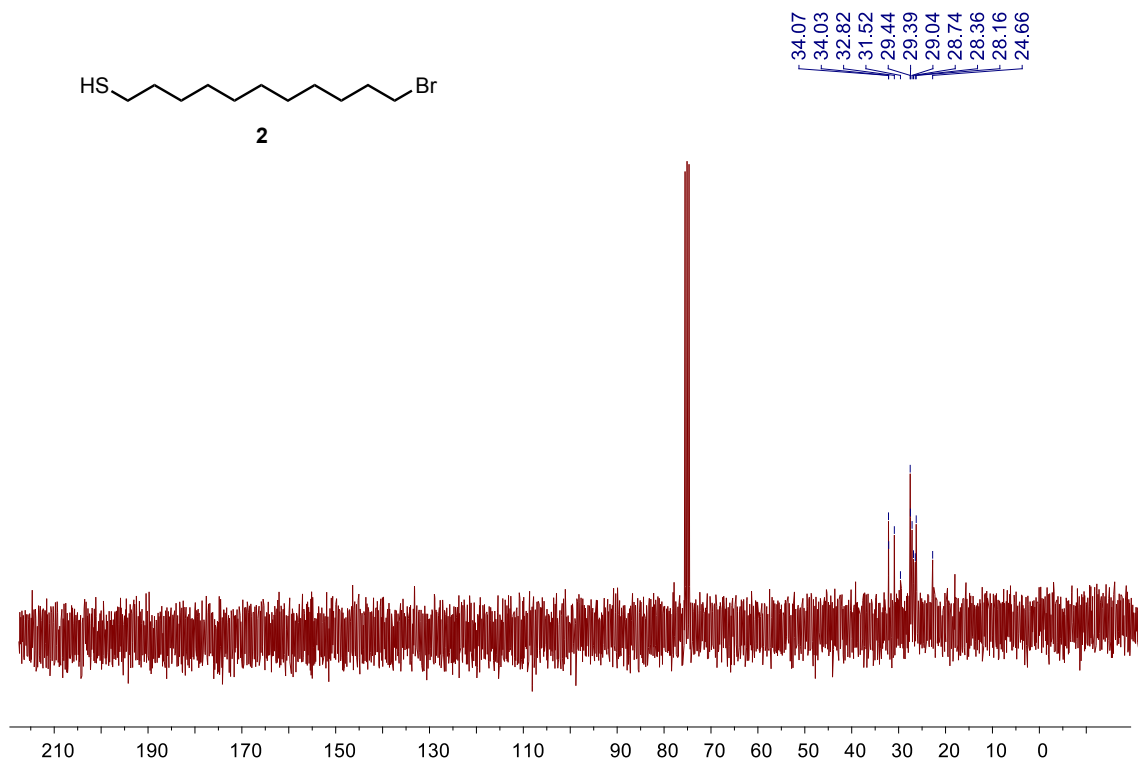


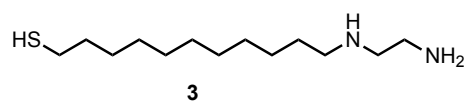
Figure S7. Δ_{size} , defined as the increase in the DLS size after CO₂ was applied to samples pre-irradiated with UV, as a function of the surface concentration of azobenzene on NPs.

6. NMR spectra









32.20
31.68
29.73
29.70
29.52
29.38
29.26
28.97
28.89
28.63
28.23

