Controlling the lifetimes of dynamic nanoparticle aggregates by spiropyran functionalization

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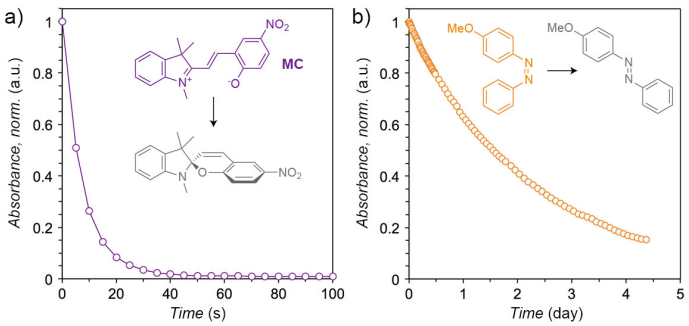
Electronic Supplementary Information

1. General information

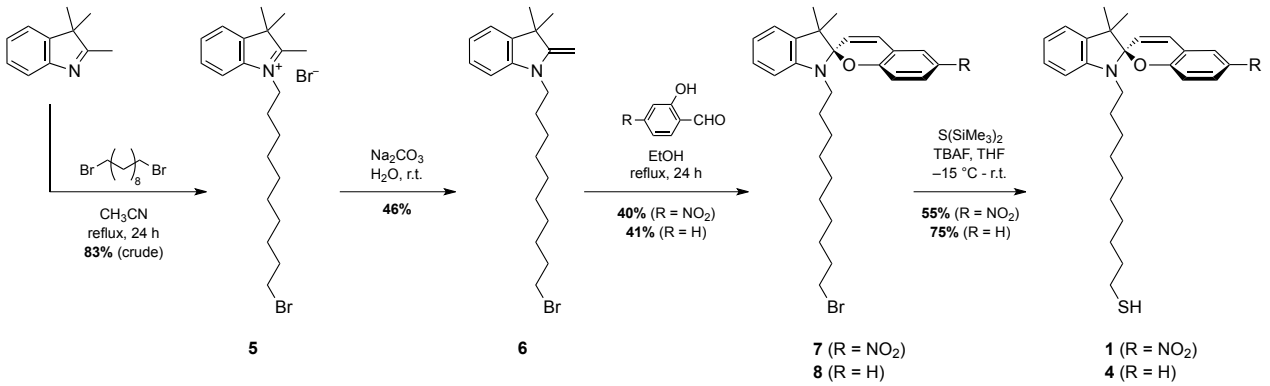
All reagents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C Nuclear magnetic resonance (NMR) spectra were recorded at room temperature on Bruker 300 MHz and 500 MHz spectrometers (Bruker). Chemical shifts (δ) are reported in p.p.m.; multiplicities are indicated 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 (^{1}H: δ = 7.26 p.p.m.; ^{13}C: 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). Scanning electron microscopy (SEM) was performed on an ULTRA 55 field emission SEM and on a SUPRA 55VP field emission SEM (both Carl Zeiss Microscopy, LLC), both operating at 5 kV. Transmission electron microscopy (TEM) was performed on a CM120 Super Twin TEM (Philips) operating at 120 kV. UV/vis spectra were recorded on Shimadzu UV-2700 and UV-3600 spectrophotometers (Shimadzu). UV and visible light sources used are described in Section 6 of the Electronic Supplementary Information (ESI). Dynamic light scattering (DLS) was measured with Zetasizer Nano ZS (Malvern). Femtosecond transient absorption studies were performed on a Spectra Physics Tsunami system based on a mode-locked Ti:sapphire oscillator pumped by a CW diode-pumped Nd:YVO_4 laser (Millennia X).

2. Studying thermal relaxation of merocyanine and *cis*-azobenzene

In these experiments, we initially exposed toluene solutions of a model merocyanine (MC in Fig. **a** below) and *trans*-azobenzene (here, 4-methoxyazobenzene; Fig. **b** below) to UV light until a photo-stationary state was reached. Next, we monitored the thermal back-isomerization using UV/vis spectroscopy. As the figure below shows, the UV-generated MC and cis-azobenzene relaxed with vastly different kinetics (note the units on the x-axes).



3. Synthesis of 10-(3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indolin]-1′-yl)decane-1-thiol **1**



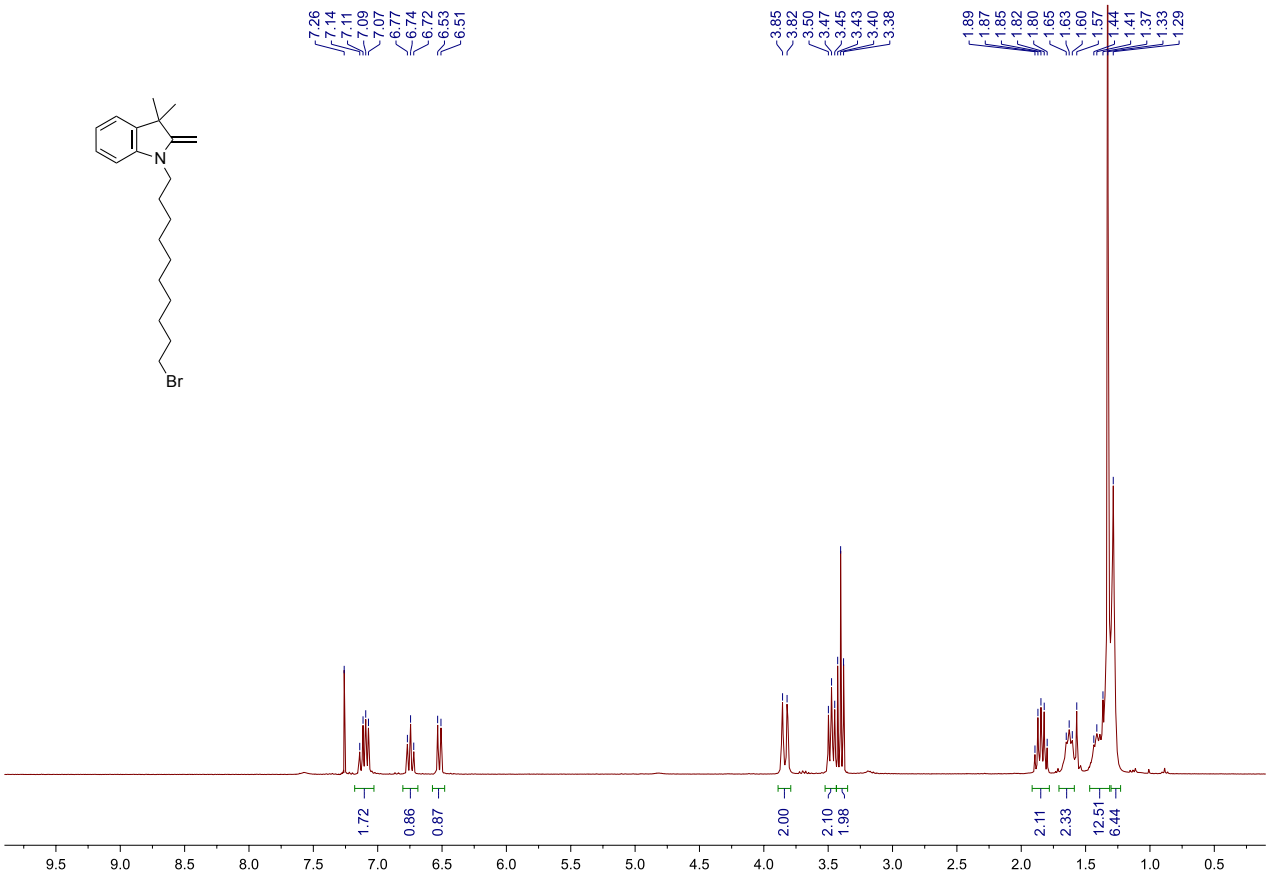
5 **6** **7** (R = NO_2) **8** (R = H) **1** (R = NO_2) **4** (R = H)

3a. Synthesis of 1-(10-bromodecyl)-3,3-dimethyl-2-methyleneindoline **6**:

A two-necked, round-bottomed flask equipped with a reflux condenser was charged with 1,10-dibromodecane (10.4 g, 34.6 mmol). The contents of the flask were dissolved in acetonitrile (20 mL) under a nitrogen atmosphere and the solution was brought to reflux. Then, a solution of 2,3,3-trimethylindoline (5 g, 31.4 mmol) in acetonitrile (5 mL) was added very slowly over the course of 2 h to the refluxing reaction mixture. After continuing the reflux for another 24 h, the reaction mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was triturated with diethyl ether to afford a sticky, semi-solid material, which was washed thoroughly with ether and dried under high vacuum to yield the crude product **5** (12 g, 83%).

Crude **5** was dissolved in 110 mL of water. To the stirred solution was added slowly an aqueous solution of Na_2CO_3 (60 mL, 0.5 M) and the mixture was stirred for another 30 min at room temperature. The mixture was then extracted 3 times with diethyl ether. The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica using diethyl ether-hexane (10:90) as the eluent to afford the desired product **6** (4.6 g, 46%) as yellowish-brown oil, which slowly turned pink in solution.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14-7.07 (m, 2H), 6.75 (t, 1H, *J* = 7.4 Hz), 6.52 (d, 1H, *J* = 7.8 Hz), 3.84 (d, 2H, *J* = 10.5 Hz), 3.47 (t, 2H, *J* = 7.4 Hz), 3.40 (t, 2H, *J* = 6.8 Hz), 1.89-1.80 (m, 2H), 1.69-1.60 (m, 2H), 1.47-1.33 (m, 12H), 1.29 (s, 6H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 161.6, 146.0, 137.5, 127.4, 121.7, 118.1, 105.0, 72.8, 44.1, 42.2, 33.9, 32.8, 30.0, 29.4, 29.4, 29.3, 28.7, 28.1, 27.2, 26.0; **HRMS (ESI) m/z**: Exact mass calculated for $C_{21}H_{33}N^{81}Br$ $[M+H]^+$ 380.1776, found 380.1780.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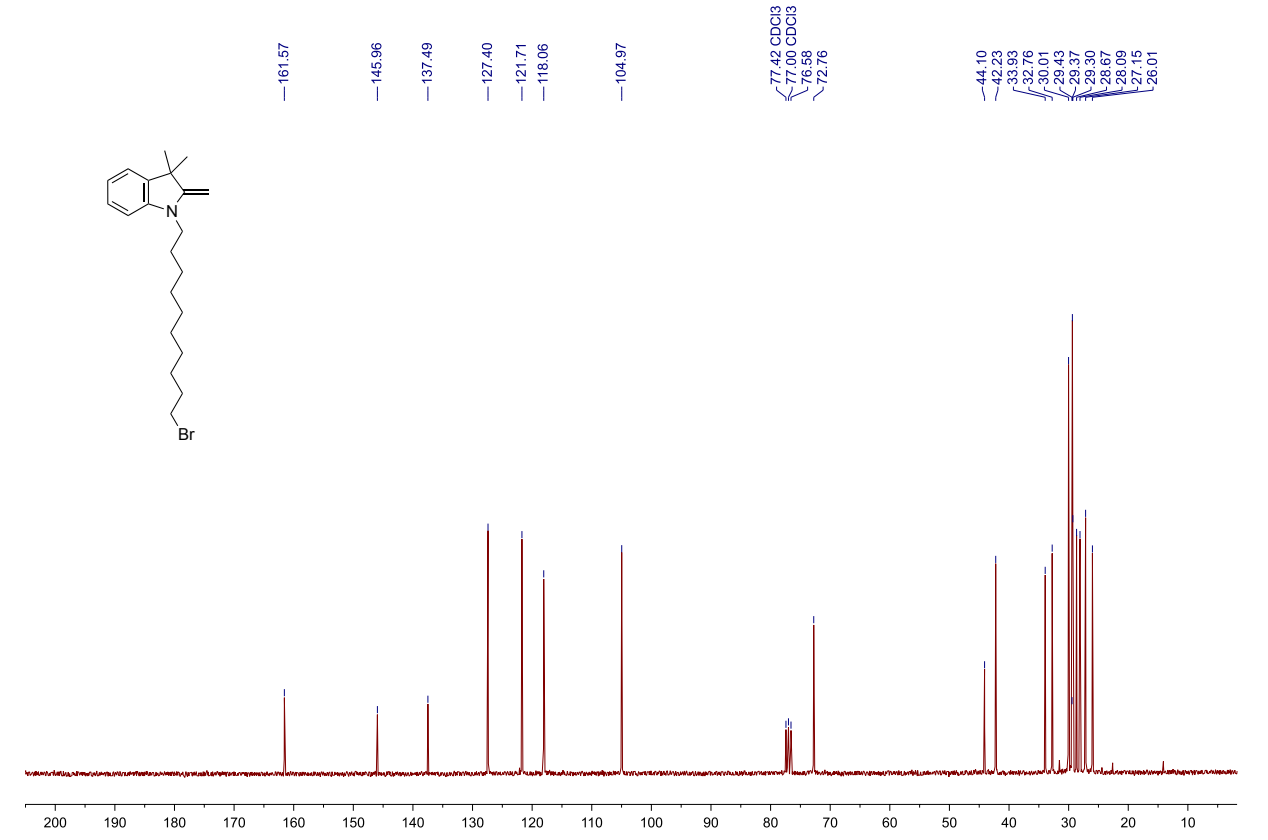
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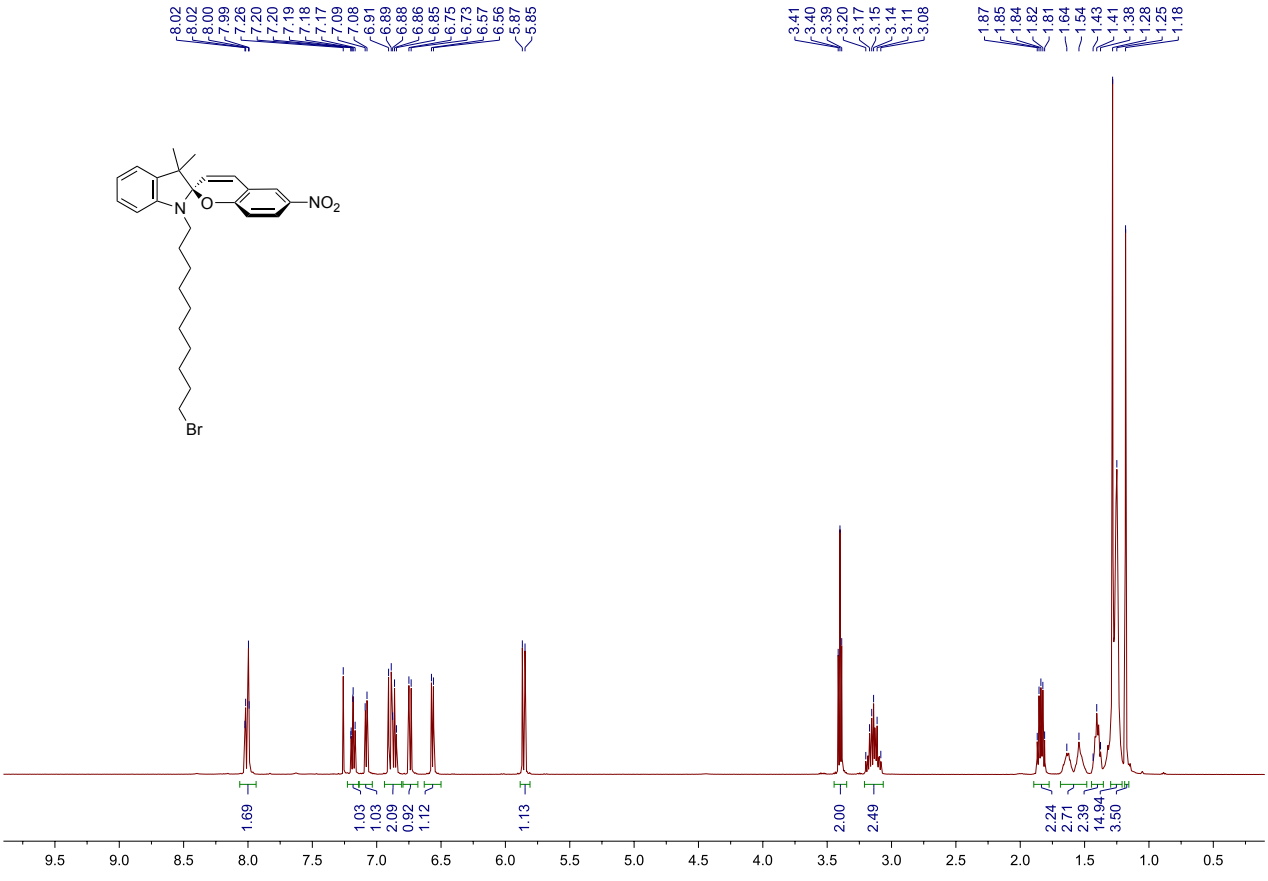
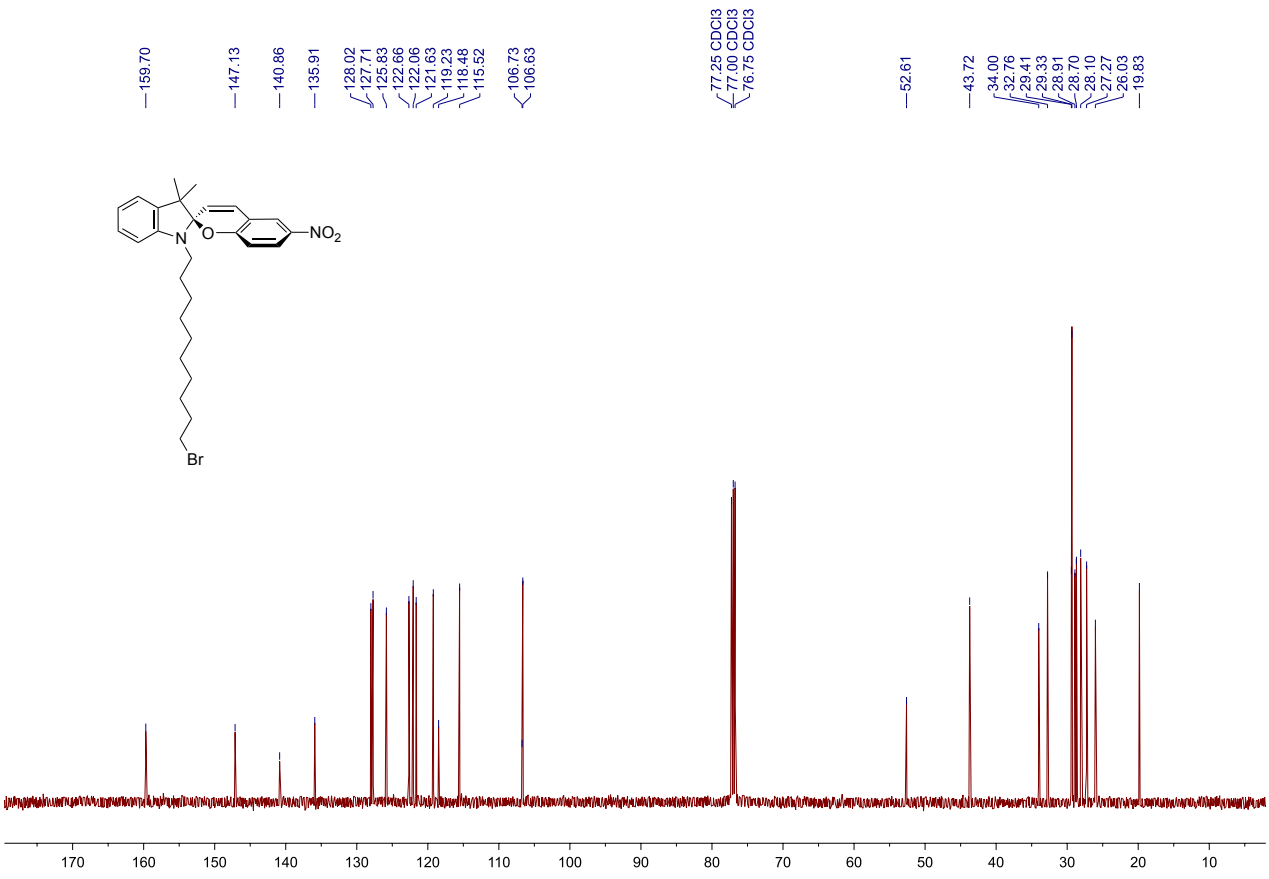
3b. Synthesis of 1′-(10-bromodecyl)-3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indoline] **7**:

Compound **6** (1.3 g, 3.4 mmol) and 5-nitrosalicylaldehyde (575 mg, 3.4 mmol) were dissolved in EtOH (70 mL) and the solution was refluxed with stirring for 24 h under a nitrogen atmosphere. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The solid residue was then purified by column chromatography on silica using CH_2Cl_2-hexane (1:1) to afford the desired product **7** (720 mg, 40%) as a yellowish solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02-7.99 (m, 2H), 7.20-7.17 (m, 1H), 7.08 (d, 1H, J = 7.2 Hz), 6.91- 6.85 (m, 2H), 6.74 (d, 1H, J = 8.7 Hz), 6.57 (d, 1H, J = 7.8 Hz), 5.86 (d, 1H, J = 10.4 Hz), 3.40 (t, 2H, J = 6.9 Hz), 3.20-3.08 (m, 2H), 1.87-1.81 (m, 2H), 1.68-1.50 (m, 2H), 1.43-1.18 (m, 18H).
^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 147.1, 140.9, 135.9, 128.0, 127.7, 125.8, 122.7, 122.1, 121.6, 119.2, 118.5, 115.5, 106.7, 106.6, 52.6, 43.7, 34.0, 32.8, 29.4, 29.3, 28.9, 28.7, 28.1, 27.3, 26.0, 19.8.
HRMS (ESI) m/z: Exact mass calculated for $C_{28}H_{35}N_2O_3BrNa$ $[M+Na]^+$ 549.1729, found 549.1710.

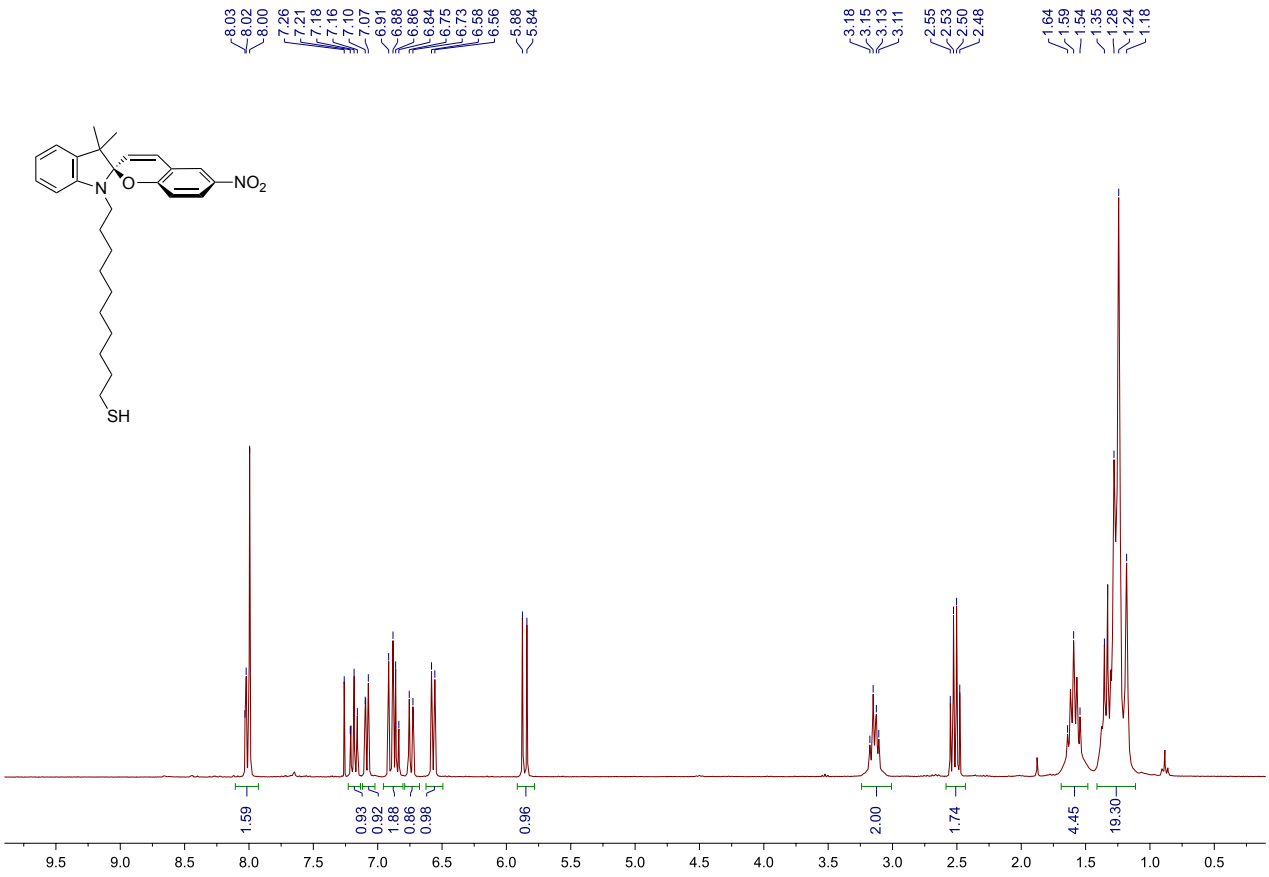




3c. Synthesis of 10-(3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indolin]-1′-yl)decane-1-thiol **1**:

Compound **7** (395 mg, 0.75 mmol) was dissolved in freshly dried and degassed (with N_2) THF (18 mL) and the solution was cooled to –15 °C with an NaCl-ice mixture under a nitrogen atmosphere. Bis(trimethylsilyl) sulfide (0.21 mL, 1 mmol) was added to the mixture and after stirring for 5 min, and tetra-*n*-butyl ammonium fluoride (820 µL, 1 M in THF) was added dropwise. The temperature of the reaction mixture was raised to 0 °C gradually over the course of 30 min by adding water into the NaCl-ice bath. The cooling bath was then removed and stirring was continued for another 2.5 h at room temperature. The reaction mixture was quenched with a saturated solution of NH_4Cl (40 mL) and the crude product was extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica using dichloromethane-hexane (3:2) to afford the desired product **1** (200 mg, 55%) as yellowish solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03-8.00 (m, 2H), 7.21-7.16 (m, 1H), 7.08 (d, 1H, *J* = 7.2 Hz), 6.92-6.84 (m, 2H), 6.74 (d, 1H, *J* = 8.6 Hz), 6.57 (d, 1H, *J* = 7.7 Hz), 5.86 (d, 1H, *J* = 10.4 Hz), 3.22-3.08 (m, 2H), 2.51 (q, 2H, *J* = 7.2 Hz), 1.70-1.46 (m, 4H), 1.42-1.13 (m, 19H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 159.7, 147.1, 140.8, 135.9, 128.0, 127.7, 125.8, 122.6, 122.0, 121.6, 119.2, 118.4, 115.5, 106.7, 106.6, 52.6, 43.7, 33.9, 29.4, 29.4, 29.3, 29.0, 28.9, 28.3, 27.2, 26.0, 24.6, 19.8. **HRMS (ESI) m/z**: Exact mass calculated for $C_{28}H_{36}N_2O_3SNa$ $[M+Na]^+$ 503.2344, found 503.2334.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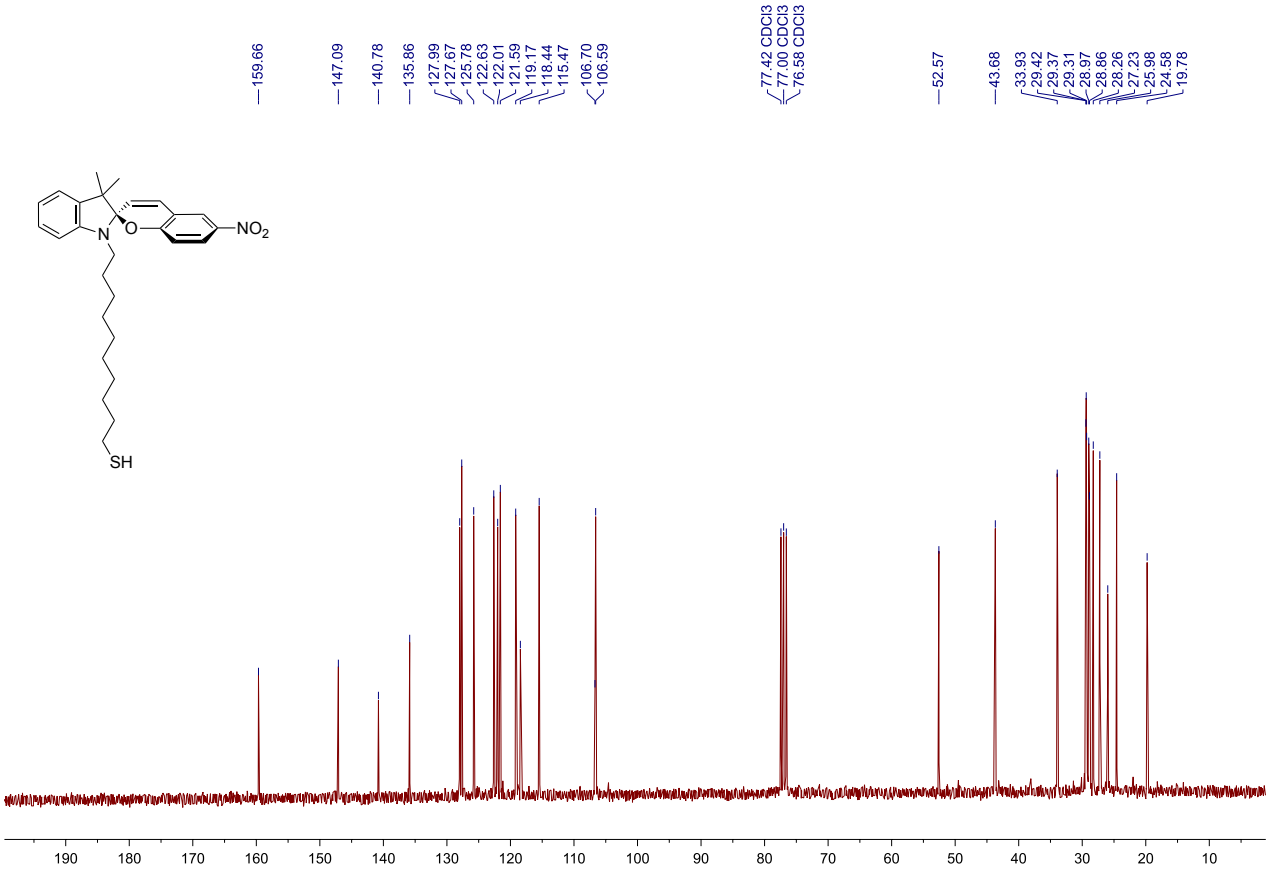
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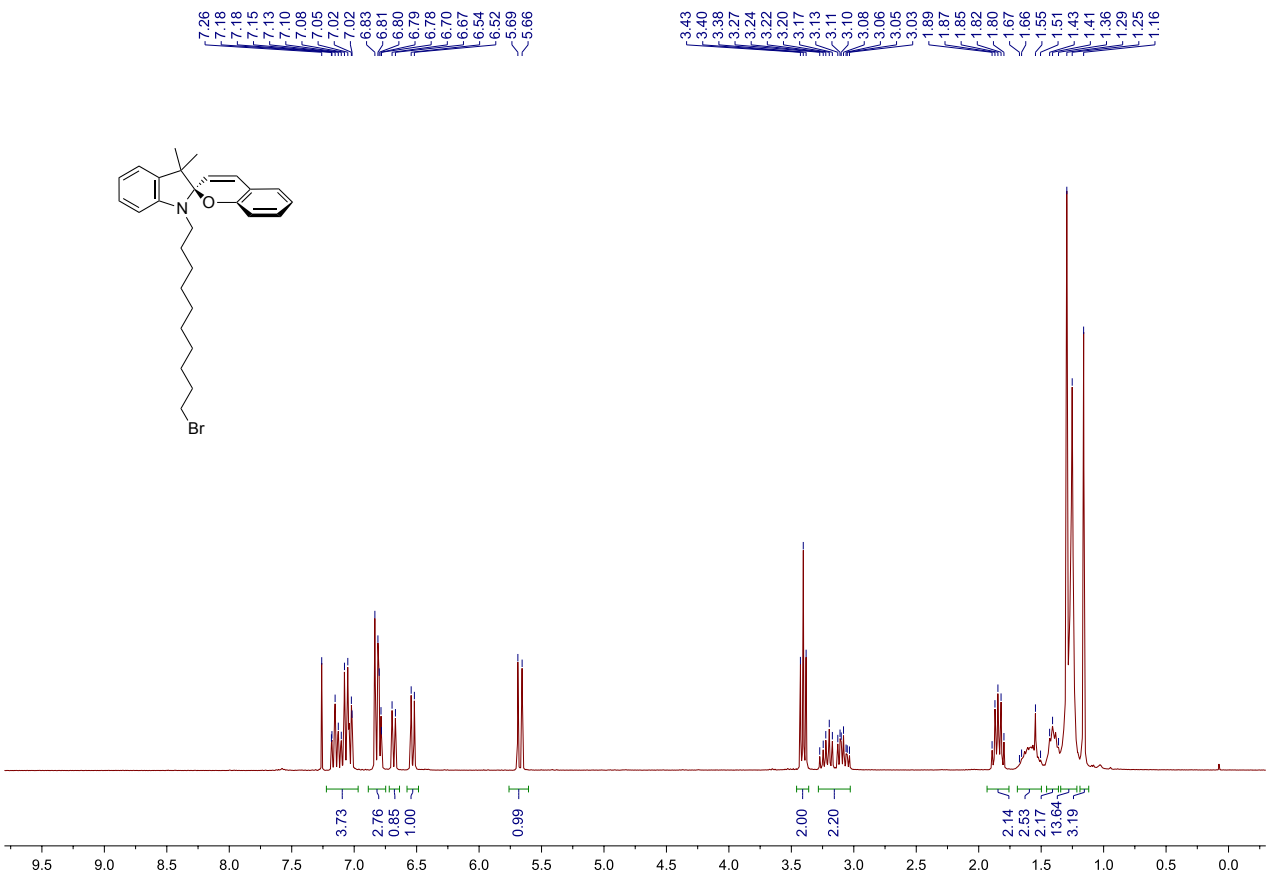
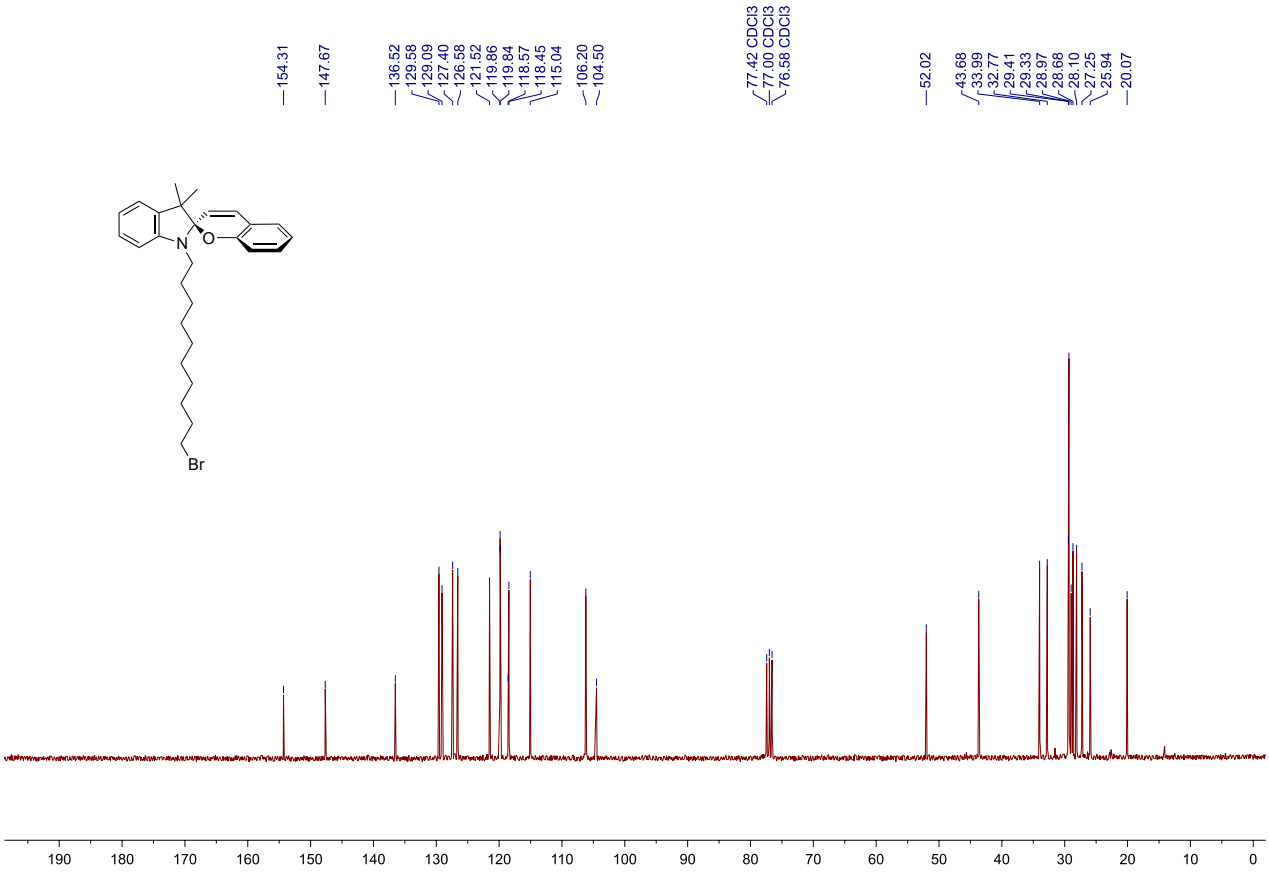
4. Synthesis of 10-(3′,3′-dimethylspiro[chromene-2,2′-indolin]-1′-yl)decane-1-thiol **4**

4a. Synthesis of 1′-(10-bromodecyl)-3′,3′-dimethylspiro[chromene-2,2′-indoline] **8**:

Following the procedure for synthesizing compound **7**, compound **6** (1.45 g, 3.8 mmol), salicyl-aldehyde (280 μL, 3.85 mmol), and EtOH (80 mL) yielded pure product **8** (750 mg, 41%) as a thick yellowish oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.02 (m, 4H), 6.83-6.78 (m, 3H), 6.68 (d, 1H, *J* = 8.1 Hz), 6.53 (d, 1H, *J* = 7.7 Hz), 5.67 (d, 1H, *J* = 10.2 Hz), 3.41 (t, 2H, *J* = 6.9 Hz), 3.27-3.04 (m, 2H), 1.89-1.80 (m, 2H), 1.67-1.51 (m, 2H), 1.43-1.36 (m, 2H), 1.30-1.25 (m, 13H), 1.16 (s, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 154.3, 147.7, 136.5, 129.6, 129.1, 127.4, 126.6, 121.5, 119.9, 119.8, 118.6, 118.5, 115.0, 106.2, 104.5, 52.0, 43.7, 34.0, 32.8, 29.4, 29.3, 29.0, 28.7, 28.1, 27.3, 25.9, 20.1; **HRMS (ESI) m/z**: Exact mass calculated for $C_{28}H_{37}NOBr$ $[M+H]^+$ 482.2059, found 482.2059.

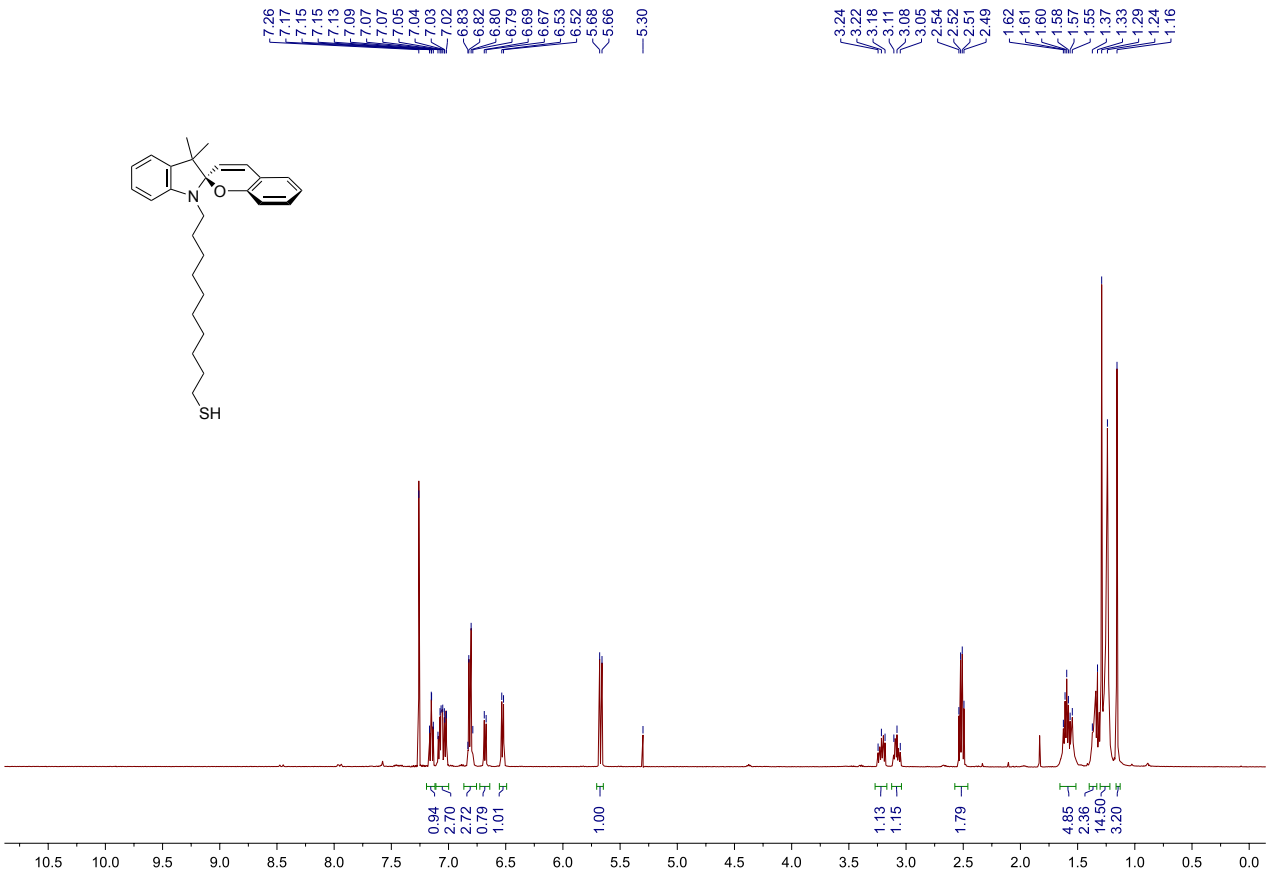




4b. Synthesis of 10-(3′,3′-dimethylspiro[chromene-2,2′-indolin]-1′-yl)decane-1-thiol **4**:

Following the procedure for the synthesizing compound **1**, compound **8** (428 mg, 0.89 mmol), bis(trimethylsilyl) sulfide (242 µL, 1.15 mmol), tetra-*n*-butyl ammonium fluoride (975 µL, 1 M in THF) and THF (20 mL) yielded pure product **4** (290 mg, 75%) as a pale yellowish sticky oil.

^{1}H NMR (after 10 min of heating with visible light irradiation; see Section 5 below) (500 MHz, $CDCl_3$): δ 7.17-7.13 (m, 1H), 7.09-7.02 (m, 3H), 6.83-6.79 (m, 3H), 6.68 (d, 1H, *J* = 8.2 Hz), 6.53 (d, 1H, *J* = 7.7 Hz), 5.67 (d, 1H, *J* = 10.3 Hz), 3.25-3.05 (m, 2H), 2.52 (q, 2H, *J* = 7.3 Hz), 1.62-1.55 (m, 4H), 1.37-1.1.29 (m, 2H), 1.29-1.24 (m, 14H), 1.16 (s, 3H). **^{13}C NMR (after 10 min of heating with visible light irradiation; see Section 5 below) (125 MHz, $CDCl_3$)**: δ 154.4, 147.7, 136.6, 129.6, 129.1, 127.4, 126.6, 121.6, 119.9, 119.9, 118.6, 118.5, 115.1, 106.2, 104.5, 52.1, 43.7, 34.0, 29.5, 29.4, 29.4, 29.0, 28.3, 27.3, 26.0, 24.6, 20.1. **HRMS (ESI) m/z**: Exact mass calculated for $C_{28}H_{38}NOS$ $[M+H]^+$ 436.2674, found 436.2677.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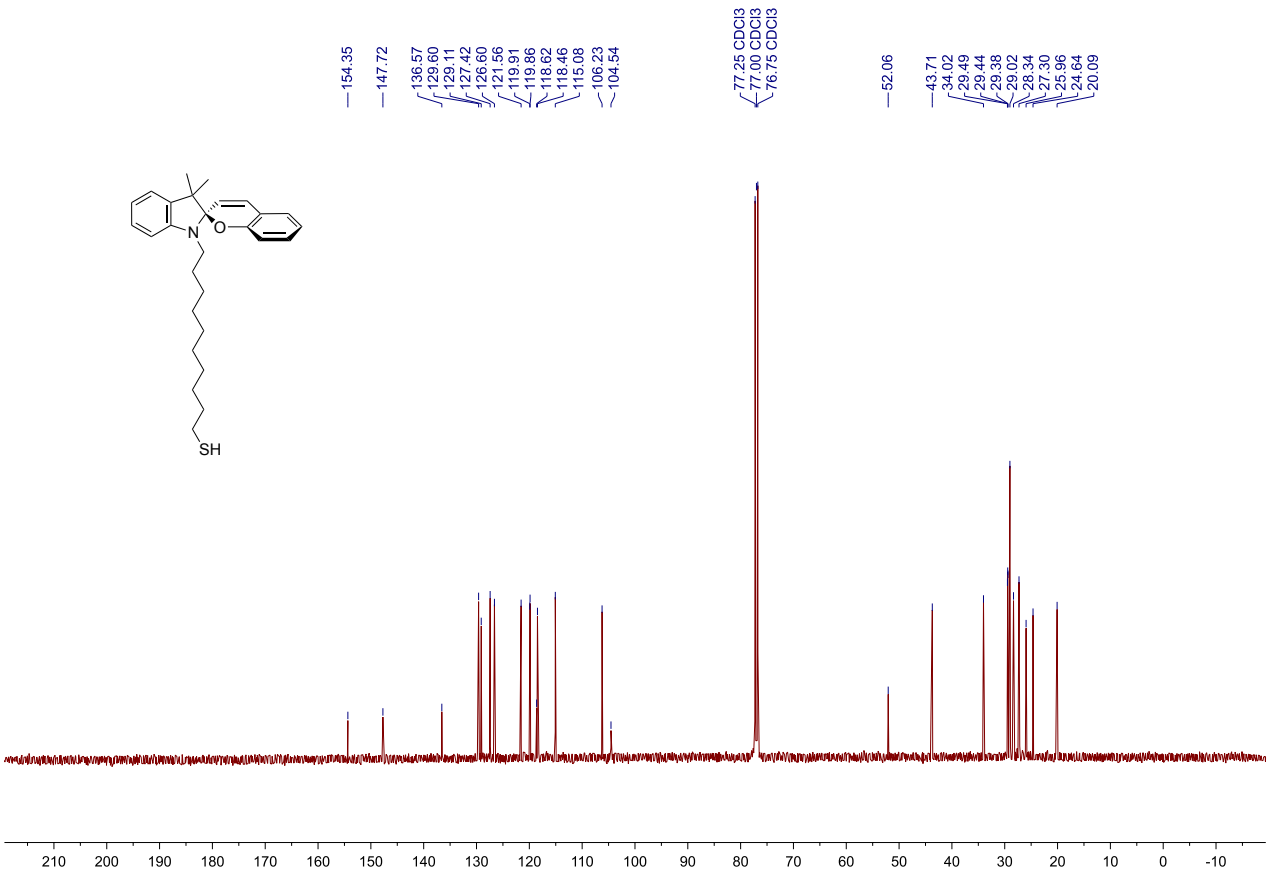
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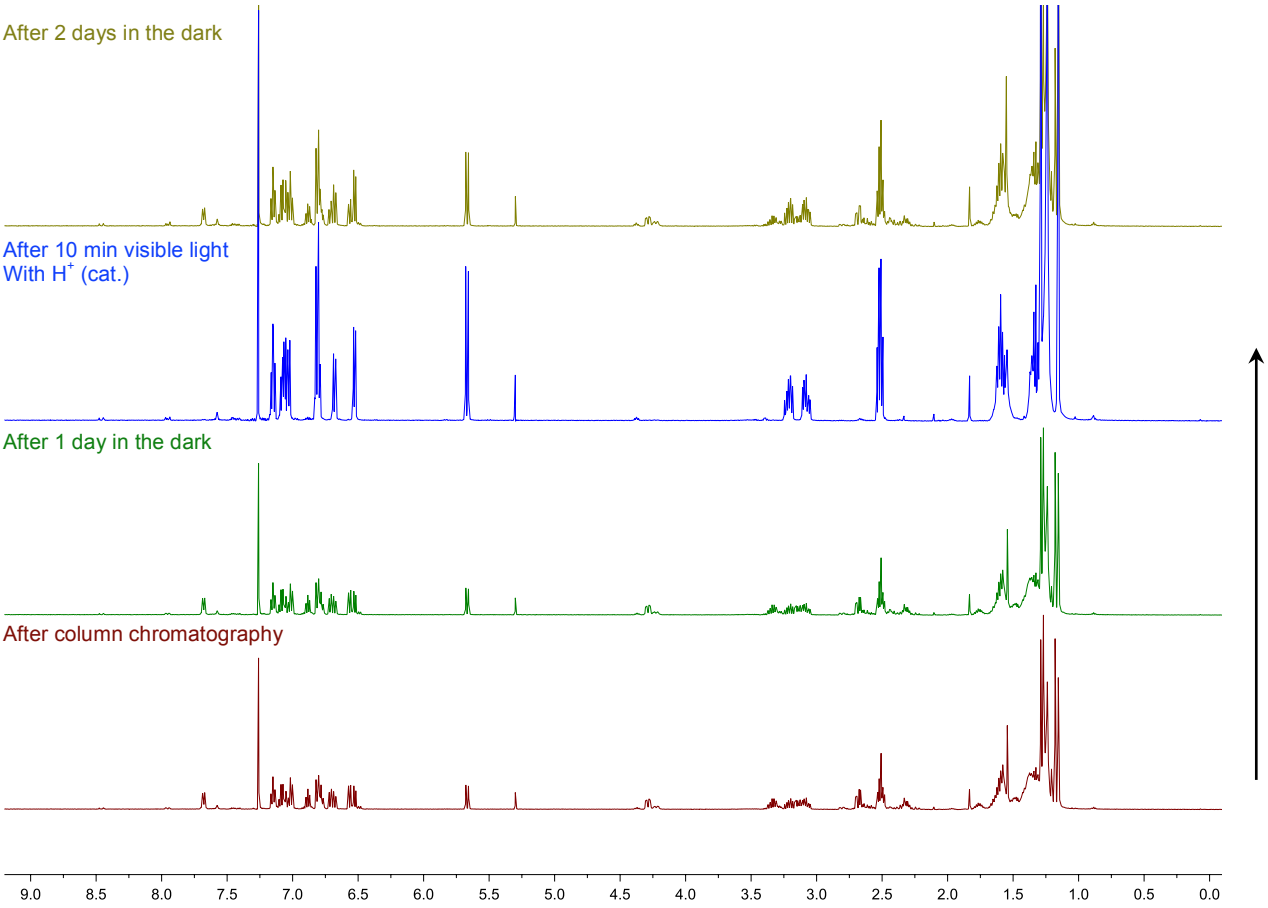
5. NMR spectra of **4**



To our surprise, column chromatography purification of crude **4** (relatively pure) resulted in a partial (~50%) conversion to a by-product (the spectrum shown above in maroon). The spectrum was not affected by dark storage (green). However, exposure to *either* UV or visible light for 10 min eliminated the undesired by-product, affording pure **4** (blue) (as a visible light source, we used a regular desk lamp equipped with a 50 W fluorescent bulb). We found that the presence of a small amount of acid in $CDCl_3$ was essential for the light-induced transformation: upon the addition of trimethylamine, the green spectrum above did not change upon visible light irradiation. In addition, a solution of **4** in toluene-d_8 (which is free of acid traces) was not affected by visible light (however, changes could be induced following the addition of a small amount of HCl to toluene-d_8). Upon dark storage, the undesired side product was re-generated (olive). The by-product most likely results from a nucleophilic attack of the thiolate group on the *spiro* carbon atom.

6. Nanoparticle synthesis, functionalization, and light-induced self-assembly

Synthesis of 2.6 nm gold nanoparticles: Didodecyldimethylammonium bromide (DDAB) stock solution was first prepared by dissolving DDAB (833 mg; 1.80 mmol) in toluene (18 mL) (with sonication). $HAuCl_4 \cdot 3H_2O$ (50 mg; 125 µmol) and dodecylamine (DDA) (450 mg; 2.43 mmol) were added to 12.5 mL of the stock solution and sonicated until completely dissolved. Gold(III) was then reduced by rapidly adding tetrabutylammonium borohydride (TBAB) (125 mg; 486 µmol) in DDAB stock solution (5 mL) under vigorous stirring at room temperature, and stirring was continued for an additional 30 min.

Synthesis of 5.5 nm gold nanoparticles: A DDAB stock solution was first prepared by dissolving 925 mg DDAB in 20 mL toluene. Fifty mg of $HAuCl_4 \cdot 3H_2O$ and 450 mg DDA were added to 12.5 mL of the stock solution and sonicated until dissolved. Gold(III) was then reduced by rapid injection of 125 mg of TBAB in 5 mL of the DDAB stock solution under vigorous stirring. A solution of ~2.6 nm NPs ("seeds") prepared this way was aged for 24 hours. Growth solution 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 $HAuCl_4 \cdot 3H_2O$, and 4) 7 mL of the aged seed solution. Finally, 131 μL of hydrazine dissolved in 20 mL of the DDAB stock solution was added dropwise (~1 drop / s) to the growth solution under vigorous stirring, and the resulting mixture was stirred overnight. Prior to functionalization with thiols, an aliquot of as-prepared gold NPs was briefly purified from an excess of surfactants (DDA + DDAB) by mixing with one volume of methanol, decantation (after the NPs have sedimented; ca. 1 hr) (without removing the solvent to dryness), and redissolution in pure toluene.

Synthesis of 11 nm silver nanoparticles: 110 mg of high-purity (≥99.99%) silver trifluoroacetate was stirred in 2 mL of 1,2-dichlorobenzene (DCB) at 50 °C for 30 min. Next, 500 μL of oleylamine was added and the mixture was sonicated for 1 min. The resulting solution was injected all at once into 6 mL of refluxing DCB under a nitrogen atmosphere, and the solution was kept under reflux for an additional 30 min. The reaction mixture was allowed to cool down to room temperature under a nitrogen atmosphere. Nanoparticles were precipitated by adding 12 mL of methanol, followed by centrifuging. The resulting black solids were washed several times with ethanol and finally dissolved in pure toluene.

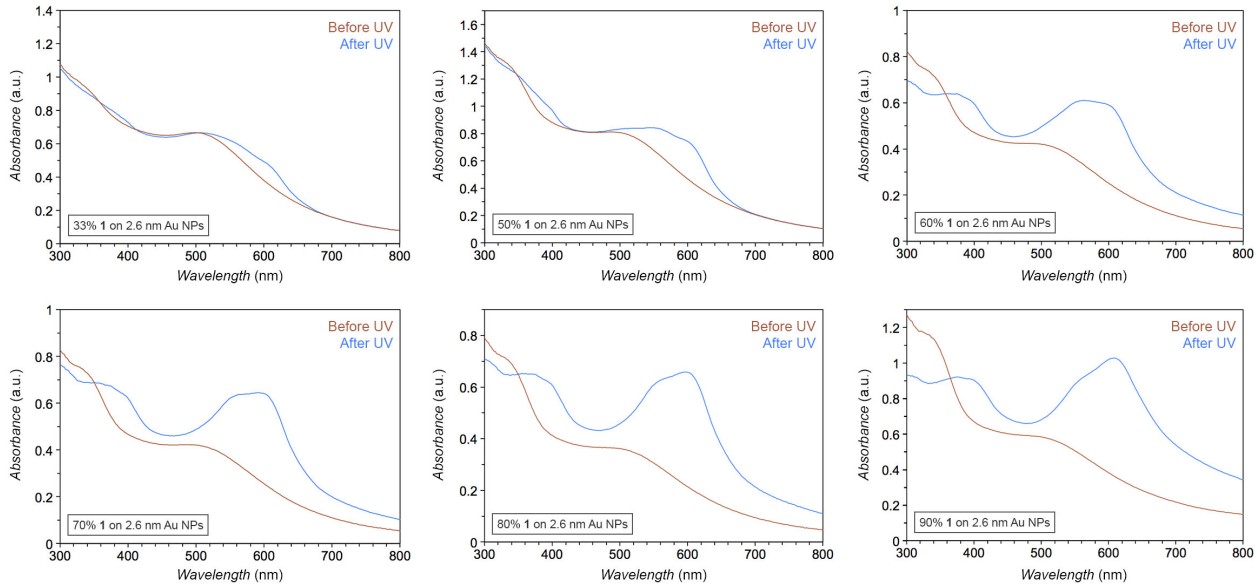
Nanoparticle functionalization: To a given amount of NP solution was added a mixture of **1**+**2** or **4**+**2** (for Au NPs) or **1**+**3** (for Ag NPs) dissolved in a small volume of toluene, such that the total number of thiol molecules corresponded to a 10-fold excess over the number of the binding sites on Au/Ag, assuming that a single thiolate moiety occupies an area of 0.214 nm^2 on the surface of Au/Ag). After six hours, the functionalized NPs were purified by precipitating with one volume of methanol, centrifugation, copious washing with methanol, and drying. Finally, the NPs were dispersed in pure toluene. In all cases, we confirmed that the molar ratio of the thiols in solution was retained on the NPs. The relative molar content of spiropyran on the NP surfaces, $n_{\mathbf{spiropyran}}/(n_{\mathbf{spiropyran}} + n_{\mathbf{background\ ligand}})$, is denoted as χ.

UV light-induced NP self-assembly: Toluene solutions of **1**-functionalized NPs were exposed to low-intensity UV light (we used a UVP UVGL-25 hand-held lamp; $\lambda \approx 365$ nm and $I \approx 0.7$ mW/cm^2) for different periods of time, after which they were analyzed by UV/vis absorption spectroscopy, DLS, TEM, and SEM.

Blue light-induced NP self-assembly: To a toluene solution of **4**-functionalized 5.5 nm Au NPs was added a solution of HCl in dioxane, such that the molar ratio of HCl to **4** was 10 (for example, to 1 mL of $\chi_{\mathbf{4}} = 0.35$ NPs prepared from 0.167 mL of the original Au NP solution was added 0.5 μL of 4 mM HCl in dioxane; the addition of HCl induced NP aggregation). The samples were exposed to low-intensity blue light (we used a Prizmatix mic-LED 420 nm light-emitting diode; light intensity ~1.0 mW/cm^2) for ca. 1 min, after which they were analyzed by UV/vis spectroscopy, DLS, and TEM.

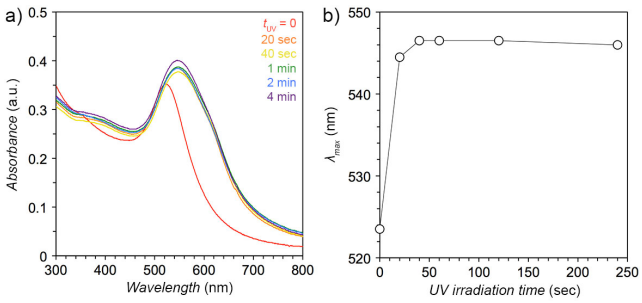
7. UV-induced isomerization on nanoparticles functionalized with different amounts of **1**

To establish the smallest number of ligands **1** per NP to induce the self-assembly of **1**-functionalized 2.6 nm Au NPs, we prepared NPs carrying different ratios of **1** and the background ligand **2**. Whether the NPs (in toluene) self-assembled was followed by monitoring the absorbance at 800 nm, as well as by DLS. As can be seen from the figure below, the transition in the aggregation behavior of the NPs occurred at $0.5 < \chi_{\mathbf{1}} < 0.6$, corresponding to 49–59 molecules of **1** per NP. We note that the actual number of the MC units per NP required to induce self-assembly is lower than that, as not all ligands **1** undergo a ring-opening reaction; we estimated, using UV/vis absorption spectroscopy, that the photostationary state for free **1** in toluene under low-intensity UV light comprises ~70% of the MC isomer (however, the composition of the photostationary state may be different for **1** residing on NP surfaces).



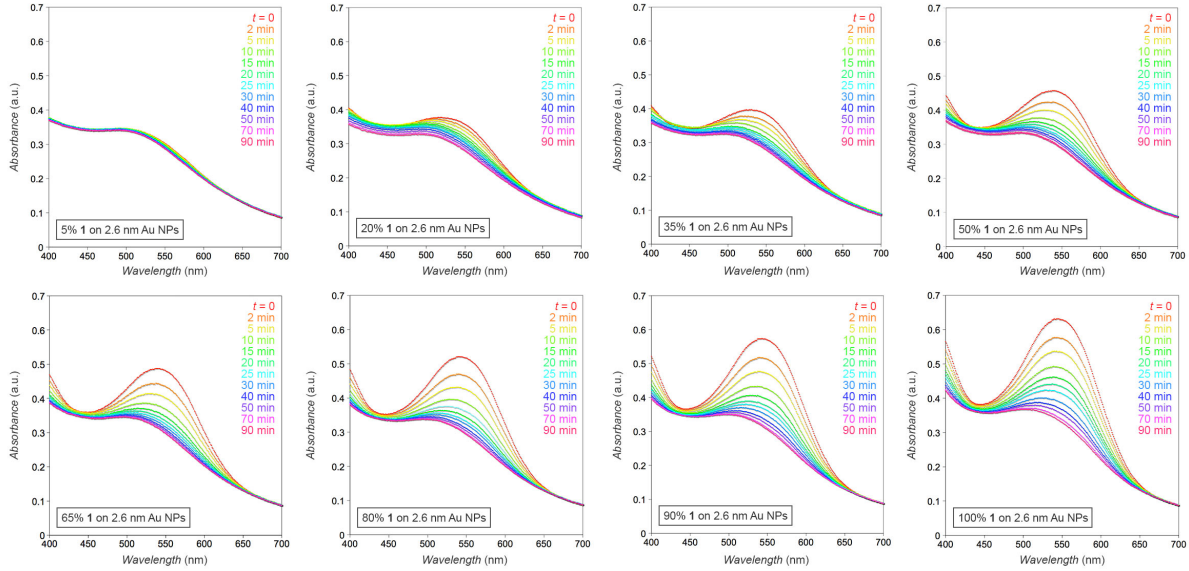
8. Establishing the minimum irradiation time required for completing NP self-assembly

Figure **a** below shows changes in the UV/vis spectra of 5.5 nm Au NPs (at $\chi_{\mathbf{1}} = 0.5$ and $c_{Au} = 0.9$ mM) caused by exposure to UV light. After plotting λ_{max} vs. irradiation time, we concluded that self-assembly is largely complete within 40 sec of UV irradiation.

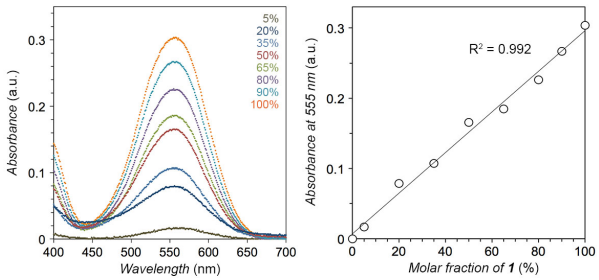


9. Insights from studying **1**-functionalized nanoparticles in $CHCl_3$

We found that chloroform provided good stabilization of both isomers of **1**, such that the UV-induced SP→MC isomerization was not accompanied by NP aggregation. This can be seen in the series of UV/vis spectra below, which were recorded for a series of 2.6 nm NPs (all at the same NP concentration) co-functionalized with **1** and the background ligand **2** at different ratios, all in pure $CHCl_3$. In each case, the spectra in red were recorded immediately (t = 0) after UV-irradiating of the samples for 2 min (longer irradiation times did not induce further changes in the spectra). Subsequent spectra were collected after different times of dark incubation (where the MC→SP back-isomerization took place) until no further changes were seen. The spectra at t = 90 min corresponded to the spectra before UV irradiation.

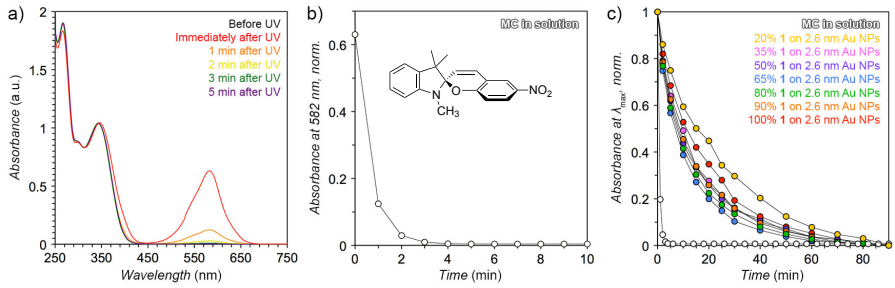


By subtracting the spectra at t = 90 min from the t = 0 spectra, we obtained the optical response of MC as a function of the **1**:**2** molar ratio used for NP functionalization (we note that: *i*) the optical response of the nanoparticle core is the same before and after UV irradiation (no NP aggregation takes place), and that *ii*) the SP form does not absorb in the 400–700 nm region). The linearity of the plot strongly suggests that the **1**:**2** ratio in the solution used for NP surface modification is preserved on the nanoparticles.

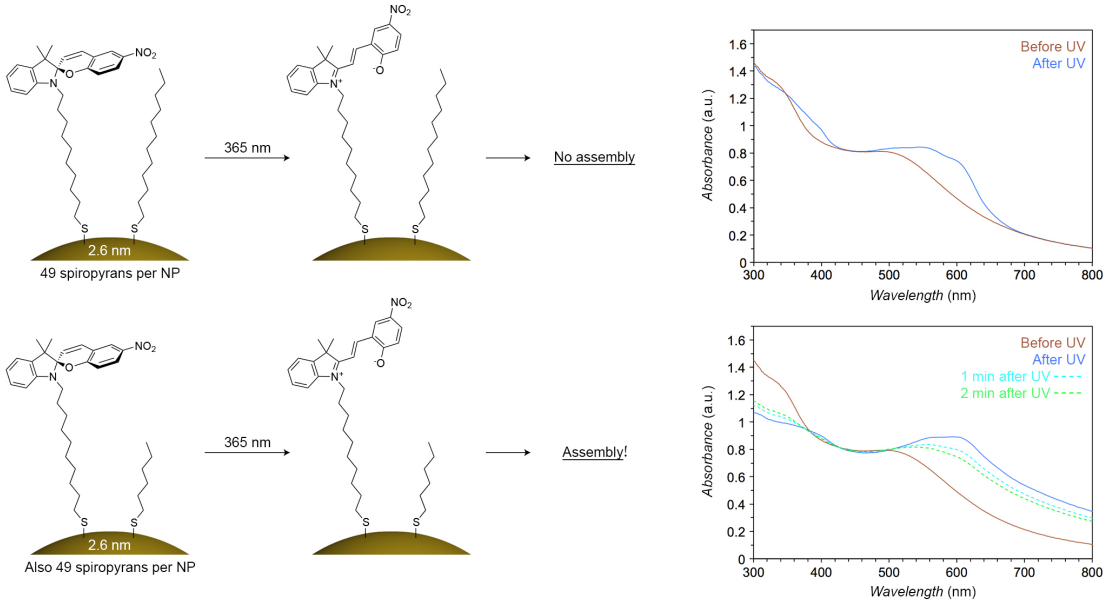


It was also of interest to compare the rates of MC→SP back-isomerization in $CHCl_3$ on NPs (at different values of χ_1) vs. in solution (we worked with the unsubstituted spiropyran, i.e., 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole]; see Section 2 of the ESI). Figure **a** below shows a series of UV/vis spectra of the small-molecule spiropyran irradiated with UV light and after storing in the dark. Notably, λ_{max} of free MC in solution (582 nm) is significantly shifted with respect to the NP-bound MC; λ_{max} = 555 nm (irrespective of χ_1; see the figure above). Interestingly,

free MC back-isomerized considerably faster than on NPs; see Figs. **b** and **c**; suggesting stabilization of the MC form on the NPs. On the other hand, the kinetics of back-isomerization on NPs was largely independent of χ_1, suggesting that MC stabilization is due to binding to NPs rather than to proximity-induced, direct MC-MC interactions.



10. Effect of the background ligand



In order to determine how increased conformational flexibility of spiropyran would affect the behavior of the NPs, we replaced dodecanethiol with a shorter background ligand. To this end, we functionalized 2.6 nm Au NPs with a 1:1 mixture of **1** and 1-hexanethiol (see the bottom panel in the above figure) and compared their properties to the NPs decorated with a 1:1 monolayer of **1** and **2** (top panel). Interestingly, although both types of NPs hosted about the same number of the spiropyran units, only the NPs containing hexanethiol were found to aggregate upon exposure to UV light.

We also found that replacing dodecanethiol with hexanethiol markedly influenced the disassembly behavior of NP aggregates. Whereas the aggregates generated using dodecanethiol as the background ligand rapidly disassembled in the dark, the ones in which hexanethiol was used remained stable in the dark even after several hours (they could, however, be disassembled when exposed visible light). These experiments highlight a deleterious affect of a short background ligand, and are in agreement with earlier studies of Shiraishi and co-workers, who established that exposure to visible light is necessary to re-generate free NPs (Y. Shiraishi, E. Shirakawa, K. Tanaka, H. Sakamoto, S. Ichikawa and T. Hirai, *ACS Appl. Mater. Interfaces* 2014, **6**, 7554-7562).