Supporting Information

Reversible Photoisomerization of Spiropyran on the Surfaces of Au$_{25}$ Nanoclusters

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Reversible Photoisomerization of Spiropyran on the Surfaces of Au$_{25}$ Nanoclusters

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1. Methods

UV-Vis absorption spectra were recorded on a UV-3600 spectrophotometer (Shimadzu). Fluorescence spectra were recorded on an RF-5401PC spectrofluorophotometer (Shimadzu). All absorption and fluorescence spectra were recorded in THF unless indicated otherwise. Dynamic light scattering (DLS) experiments were performed with a Zetasizer Nano ZS (Malvern). All DLS measurements were done in toluene. Mass spectrometry studies on ligand-protected gold nanoclusters were conducted on an AB SCIEX 5800 MALDI TOF/TOF system (Applied Biosystems Intl., Inc.) equipped with a Nd:YAG 355 nm laser with a 1 kHz pulse used for desorption ionization. Typical delay times employed were on the order of 550 ns. Accelerating voltage was ~12 kV. Mass spectra were collected in the negative ion mode and were averaged over 200 shots. The matrix and the analyte were both dissolved in THF. As the matrix, trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used. Matrix-to-analyte mole ratios varied from 250:1 to 1000:1 at 40 mM DCTB. The solutions of the matrix and the clusters were mixed and 1–2 µL of the resulting mixtures were applied onto the sample plate and allowed to dry under ambient conditions.

2. Synthesis of thiolated spiropyran SP

The target compound, 10-(3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indolin]-1′-yl)decane-1-thiol (SP) was synthesized as follows:

Synthesis of 1-(10-bromodecyl)-3,3-dimethyl-2-methyleneindoline 2:

A two-neck round-bottom flask equipped with a reflux condenser was charged with 1,10-dibromodecane (10.4 g; 34.6 mmol), which was dissolved in acetonitrile (20 mL) under a nitrogen atmosphere. The solution was brought to reflux temperature and a solution of 2,3,3-
trimethylindoline (5.0 g; 31.4 mmol) in acetonitrile (5 mL) was added slowly to the refluxing reaction mixture over the course of two hours. After having been refluxed for an additional 24 hours, the reaction mixture was cooled down to room temperature. The solvent was evaporated under reduced pressure and the resulting residue was triturated with diethyl ether to afford a sticky material, which was dried under high vacuum to afford the crude product 1 (12 g; 83%). The crude product was dissolved in water (110 mL). To the stirred solution was slowly added an aqueous solution of Na$_2$CO$_3$ (60 mL, c = 0.5 M), and stirring was continued for an additional 30 min. The product was extracted three times with diethyl ether. Combined organic fractions were dried over MgSO$_4$, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica using a diethyl ether-hexane (10:90 v/v) mixture to afford the desired product 2 (4.6 g, 46%) as yellowish-brown oil, which slowly turned pink.

$^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) 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 (ppm) 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$_8$Br [M+H]$^+$ 380.1776, found 380.1780.

**Figure S1 | $^1$H NMR spectrum of 1-(10-bromodecyl)-3,3-dimethyl-2-methyleneindoline (300 MHz, CDCl$_3$).**
Synthesis of 1′-(10-bromodecyl)-3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indoline] 3:

Compound 2 (1.3 g, 3.4 mmol) and 5-nitrosalicylaldehyde (575 mg, 3.4 mmol) were dissolved in ethanol (70 mL) under a nitrogen atmosphere and refluxed with stirring for 24 h. The reaction mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The solid residue was then purified by column chromatography on silica using a dichloromethane-hexane mixture (1:1 v/v) as the eluent to afford the desired product 3 (720 mg, 40%) as a yellowish solid.

\[ ^1H \text{ NMR (500 MHz, CDCl}_3\]: } \delta \text{ (ppm)} \text{ 8.02-7.99 (m, 2H), 7.20-7.17 (m, 1H), 7.08 (d, 1H, } J = 7.2 \text{ Hz), 6.91-6.85 (m, 2H), 6.74 (d, 1H, } J = 8.7 \text{ Hz), 6.57 (d, 1H, } J = 7.8 \text{ Hz), 5.86 (d, 1H, } J = 10.4 \text{ Hz), 3.40 (t, 2H, } J = 6.9 \text{ 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).} \]

\[ ^13C \text{ NMR (125 MHz, CDCl}_3\]: } \delta \text{ (ppm)} \text{ 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_{33}N_{3}O_{3}BrNa [M+Na]^+ 549.1729, found 549.1710.
Figure S3 | $^1$H NMR spectrum of 1'-{(10-bromodecyl)-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]} (500 MHz, CDCl$_3$).

Figure S4 | $^{13}$C NMR spectrum of 1'-{(10-bromodecyl)-3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indoline]} (125 MHz, CDCl$_3$).
Synthesis of 10-(3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indolin]-1′-yl)decane-1-thiol SP:

A solution of compound 3 (395 mg, 0.75 mmol) in freshly dried and degassed THF (18 mL) was cooled down to −15 °C (using an ice-NaCl mixture) under a nitrogen atmosphere. Bis(trimethylsilyl) sulfide (0.21 mL, 1 mmol) was added to the reaction mixture and, after having been stirred for 5 min, tetra-n-butylammonium fluoride (820 µL, 1 M in THF) was added dropwise. The temperature was raised to 0 °C gradually over a period of 30 min by adding water into the ice-NaCl bath. The cooling bath was then removed and stirring was continued for an additional 2.5 h at room temperature. The reaction mixture was quenched with a saturated solution of ammonium chloride in water (40 ml), and the product was extracted with CH$_2$Cl$_2$. 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 a dichloromethane-hexane mixture (3:2 v/v) to afford the desired product SP (200 mg, 55%) as a yellowish solid.

$^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) 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 (ppm) 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, 29.3, 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$_2$O$_3$SNa [M+Na]$^+$ 503.2344, found 503.2334.

Figure S5 | $^1$H NMR spectrum of SP (300 MHz, CDCl$_3$).
3. Synthesis of [Au$_{25}$(PET)$_{18}$] TOA$^+$

[Au$_{25}$(PET)$_{18}$] TOA$^+$ was prepared based on a previously published procedure.$^{[15c]}$ HAuCl$_4$·3H$_2$O (80 mg; 0.203 mmol) was dissolved in 15 mL of THF. Tetra-$n$-octylammonium bromide (TOAB) (129 mg; 0.235 mmol) was added and the mixture was stirred vigorously for 15 min; the color turned from yellow to orange. The stirring speed was reduced and the reaction mixture was cooled to 0 °C on an ice bath. PET (140 µL; 1.02 mmol; Au:S molar ratio = 1:5) was added dropwise over a period of about 2 min. During the addition of PET, the solution turned pale yellow and then colorless. Once the solution became colorless, the stirring speed was increased and a freshly prepared, ice-cold aqueous solution of NaBH$_4$ (77 mg; 2.03 mmol, Au:NaBH$_4$ molar ratio = 1:10) in 5 mL of water was immediately added. The reaction mixture quickly turned black and was stirred for an additional 7 hours. THF was then removed under reduced pressure, resulting in a mixture of an aqueous phase and a black oil. The aqueous fraction was removed with a syringe and the black oil was collected and washed with deionized water three times. Then 15 mL of methanol was added and Au nanoclusters were precipitated out overnight in the freezer. Supernatant was discarded and the precipitate was washed with methanol several times. Finally, the black solids were dissolved in acetonitrile and the resulting solution was centrifuged at ~5,000 rpm for 15 min, allowing for the removal of Au(I)-PET species, whereas pure [Au$_{25}$(PET)$_{18}$] TOA$^+$ remained dissolved. Next, the supernatant was collected and the solvent was evaporated under reduced pressure at room temperature. The resulting solids were readily soluble in toluene. Figure S7 shows a UV-Vis spectrum of the resulting nanoclusters; a MALDI spectrum is shown in Fig. S8.
4. Synthesis of spiropyran-functionalized Au$_{25}$

In a typical ligand exchange reaction, 5 mg of Au$_{25}$(PET)$_{18}$]TOA$^+$ was dissolved in 2 mL of toluene and purged with nitrogen for 10 min. The reaction mixture was cooled to 0 °C and a freshly prepared solution of SP in toluene (29 mg in 500 µL) was added. Ligand exchange reaction was allowed to proceed for 16 hours in the dark while a temperature of 0 °C and the dark condition were maintained. (Reactions taking place at higher temperatures resulted in a greater extent of the ligand exchange reaction, although the nanoclusters showed signs of decomposition.) The solvent was evaporated under reduced pressure and the resulting solid was washed with ice-cold ethanol twice to remove any small molecules. The resulting solid was further purified by size exclusion chromatography (using BioBeads S-X1 as reported before in S. Knoppe et al., Anal. Chem. 2011, 83, 5056-5061) to afford Au$_{25}$(PET)$_{18-}(SP)$]TOA$^+$. 

5. Synthesis of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospirow[2H-1-benzopyran-2,2′-(2H)-indole]

A solution of 2,3,3-trimethylindolenine (7.7 g; 48.4 mmol) and methyl iodide (7.5 mL; 120.5 mmol) in acetonitrile (90 mL) was refluxed for 18 h under a nitrogen atmosphere. The solvent was removed under reduced pressure and the residue was triturated with diethyl ether to yield a powder. Next, the solid was collected by filtration, washed with diethyl ether, and dried under a high vacuum. The resulting solid was added to a solution of KOH in water and stirred for 30
min. Finally, the product was extracted with diethyl ether and the combined organic extracts were washed with brine, dried over MgSO₄, and evaporated under reduced pressure to afford 1,3,3-trimethyl-2-methyleneindoline (80%) as a yellow oil (which gradually turned pink).

1,3,3-trimethyl-2-methyleneindoline (5.5 g; 31.7 mmol) was dissolved in ethanol (350 mL) and refluxed with 2-hydroxy-5-nitrobenzaldehyde (6.9 g; 41.3 mmol) under a nitrogen atmosphere for 15 h. After the reaction mixture was cooled to room temperature, the solvent was removed under reduced pressure. Next, the residue was dissolved in CH₂Cl₂ and washed three times with an aqueous NaOH solution. The organic layer was dried over MgSO₄ and evaporated under reduced pressure. Finally, the residue was purified by crystallization from ethyl acetate to afford pure spiropyran 1 (75%).

**¹H NMR (300 MHz, CDCl₃):** δ (ppm) 8.04–8.00 (m, 2H), 7.21 (dt, J = 7.5, 1.2 Hz, 1H), 7.09 (dd, J = 7.2, 1.2 Hz, 1H), 6.93 (d, J = 10.3 Hz, 1H), 6.89 (dt, J = 7.3, 0.9 Hz, 1H), 6.77 (d, J = 9.4 Hz, 1H), 6.56 (d, J = 7.5 Hz, 1H), 5.86 (d, J = 10.3 Hz, 1H), 2.74 (s, 3H), 1.30 (s, 3H), 1.19 (s, 3H);

**¹³C NMR (75 MHz, CDCl₃):** δ (ppm) 159.8, 147.6, 140.9, 136.0, 128.2, 127.8, 125.8, 122.6, 121.6, 121.5, 119.7, 118.6, 115.4, 107.0, 106.3, 52.2, 28.8, 25.8, 19.9.

![Figure S9](image-url) **Figure S9** | ¹H NMR spectrum of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (300 MHz, CDCl₃).
Figure S10 | $^{13}$C NMR spectrum of 1',3'-dihydro-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole] (75 MHz, CDCl$_3$).