

†The Supplementary Data of

**Reversible Photoisomerization of Azobenzene Molecules on Single Gold
Nanoparticle Surface**

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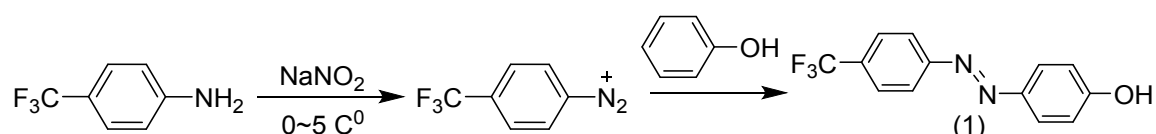
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S-1 Experimental section

Chemicals, Materials and Instrumentations

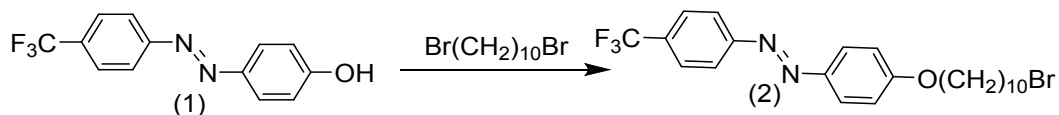
Materials: All the chemicals were of analytic grade and used as received. All solutions were prepared with ultrapure water (18 MΩ cm) from a Millipore system. ¹H NMR and ¹³C NMR were acquired on BRUKER AVANCE 500 spectrometer using TMS as an internal standard. HRMS were obtained on HP5989 mass spectrometer.

Synthesis of 4-(4-trifluoromethyl-phenylazo)-phenol (1)



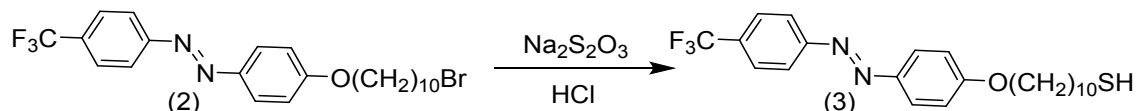
Compound (1) was synthesized according to the literature,¹ the crude product was used without further purification for the next step.

Synthesis of [4-(10-bromo-decyloxy)-phenyl]-(4-trifluoromethyl-phenyl)-diazene (2)



Compound (2) was synthesized according to the literature.² ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 1.32-1.50 (12H, m, [CH₂]₄), 1.84 (4H, m, [CH₂]₂), 3.42 (2H, t, CH₂Br), 4.06 (2H, t, CH₂O), 7.02 (2H, d, ArH ortho to phenolic group), 7.75 (2H, d, ArH ortho to CF₃) and 7.93-7.96 (4H, m, ArH ortho to -N=N-).

Synthesis of 10-[4-(4-trifluoromethyl-phenylazo)-phenoxy]-decane-1-thiol (3)



Compound (3) was synthesized according to the literature.³ ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 1.31-1.52 (12H, m, [CH₂]₄), 1.58-1.65 (2H, m, CH₂), 1.79-1.85 (2H, m, CH₂), 2.52 (d t, 2H, SCH₂), 4.06 (2H, t, CH₂O), 7.02 (2H, m, ArH ortho to phenolic group), 7.75 (2H, d, ArH ortho to CF₃) and 7.92-7.96 (4H, m, ArH ortho to -N=N-). ESI-MS: m/z 439.81 [MH⁺].

Synthesis of 10-(4-phenylazo-phenoxy)-decane-1-thiol

The same procedures were used to synthesize 10-(4-phenylazo-phenoxy)-decane-1-thiol (termed AzoSH). ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 1.45-1.84 (16H, m, [CH₂]₈), 2.52 (dt, 2H, SCH₂), 4.04 (2H, t, CH₂O), 7.01 (2H, d), 7.47 (3H, m) and 7.90 (4H, m). HESI-MS: m/z 371.2233 [MH⁺].

Synthesis of 60 nm gold nanoparticles

50 mL of 0.01 wt% HAuCl₄ was heated to reflux with vigorous stirring and then 5 mL sodium citrate (38.8 mM) was added quickly to the solution. The mixed solution was continued to heat for 15 min, stopped heating and kept stirring for an additional 15 min. The resulting solution of colloidal particles was filtered and characterized by an absorption maximum at 519 nm using an Ocean optical USB 2000+ UV-Vis spectrometer. These particles were then used as seed particles for the synthesis of 60 nm gold particles. To 25 mL of water, 1 mL of preformed seed gold particles and 100 μ L of 0.2 M NH₂OH·HCl was mixed. The mixture was stirred vigorously at room temperature and 3.0 mL of 0.1 wt% HAuCl₄·3H₂O was added drop-wise. Diameters were characterized by UV-Vis and SEM.

Modification Procedure of mix SAMs n-C₄H₉SH /CF₃AzoSH on GNPs surface

ITO slides surfaces were cleaned by rinsing the slides with soapy water, acetone, ethanol, distilled water, respectively. The cleaned slides were dried, and immersed in a dilution 40 times of aqueous gold nanoparticle (60 nm) solution for 4 min. Then the GNPs modified ITO slides were dipped in a solution of the n-C₄H₉SH (10 μ M in ethanol) for 5 minutes, rinsed extensively with ethanol. After that, the obtained substrate were immersed into the solution of CF₃AzoSH (10 μ M in ethanol) for 24 hours, then sufficient rinsed with ethanol and dried under a stream of high-purity nitrogen.

Single nanoparticle DFM imaging and scattering spectroscopy measurements

The dark-field measurements were carried out on an inverted microscope (eclipse Ti-U, Nikon, Japan) equipped with a dark-field condenser (0.8 <NA<0.95) and a 40 \times objective lens (NA=0.8). The GNPs functionalized ITO slides were immobilized on a platform, and a white light source (100 W halogen lamp) was used to excite GNPs and generate plasmon resonance scattering light. The scattered light was split by a monochromator (Acton SP2300i, PI, USA) that was equipped with a grating (grating density: 300 lines/mm; blazed wavelength: 500 nm) and recorded by a spectrograph CCD (CASCADE 512B, Roper Scientific, PI, USA) to generate the scattering spectra. The scattering spectra from individual nanoparticle were corrected by subtracting the background spectra taken from the adjacent regions without GNPs and dividing with the calibrated response curve of the entire optical system.

The SERS sample prepared procedure and SERS spectroscopy measurements

To prepare the SERS sample, Au NPs were first functionalized via a 5 min incubation with 10 mM C₄H₉SH and then washed three times to remove excess C₄H₉SH. After that, Au NPs/C₄H₉SH were functionalized with CF₃AzoSH via 24 h incubation with 10 mM solution of CF₃AzoSH at ambient temperature. The excess CF₃AzoSH was removed through centrifugation and subsequent washing (three times). The SERS spectroscopy tests were performed similar as our published method⁴

S-2 Calculated Spectra of mix SAMs n-C₄H₉SH/CF₃AzoSH modified gold Nanoparticle

In order to farther prove the scattering spectra reversible shift of mix SAMs n-C₄H₉SH/CF₃AzoSH modified GNP was caused by CF₃AzoSH molecules reversible photoisomerize on GNP surface, discrete dipole approximation (DDA) is adopted to simulate the scattering efficiency of gold nanoparticle. For this calculation, a DDA code developed by Draine and Flatau is performed to characterize the core-shell case with a finite target. In spite of the complex electric field, incident wave is regard as a deformation of the monochromatic electromagnetic field unless stated otherwise. The propagation direction of the incident light is assumed to be perpendicular to the x-axis of the nanoparticle. The target type is specified by CONELLIPS in ddscat.par and considered to have a geometry of a gold core with mix SAM n-C₄H₉SH/CF₃AzoSH shell. We considered spheres with a gold core of radius $R = 30$ nm, a dielectric shell of thickness $t = 25.2$ Å (according to the chemdraw stimulation of CF₃AzoSH molecule length), and refractive index n of dielectric shell was related to the shell compositions, refractive index of CF₃AzoSH and C₄H₉SH/H₂O molecule were expected to be $n_1 = 1.55$, $n_2 = 1.33$ respectively.

$$n = \frac{n_1 V_1 + n_2 V_2}{V_1 + V_2} \quad (\text{Equation S1})$$

$$V = \frac{4\pi((R + t)^3 - R^3)}{3} \quad (\text{Equation S2})$$

Based on the surface areas of CF₃AzoSH molecule and GNP, the average number of CF₃AzoSH molecules per GNP could be calculated to be 3×10^4 , beside, the volume of CF₃AzoSH molecule was 123 Å³ (according to the chemdraw3D stimulation data). The volume of the CF₃AzoSH molecules on single GNP surface $V_1 = 3690$ nm³ and volume of the shell $V_1 + V_2 = 7201.53094$ nm³. According to the above equations, the initial refractive index n of dielectric shell was 1.44435133. When exposure to UV irradiation, the CF₃AzoSH molecules on GNP surface transformed from *trans* to *cis*, the volume of the shell $V_1 + V_2$ was changed to 5584.02538 nm³, which increased the refractive index n of dielectric shell to 1.47650849.

Reference

- 1 X. Chen, L. Wang, C. Li, J. Xiao, H. Ding, X. Liu, X. Zhang, W. He and H. Yang, *Chem. Commun.*, 2013, **49**, 10097–10099.
- 2 C.-W. Tseng, D.-C. Huang and Y.-T. Tao, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9528–9536.
- 3 H. Wolf, H. Ringsdorf, E. Delamarche, T. Takami, H. Kang, B. Michel, C. Gerber, M. Jaschke, H.-J. Butt and E. Bamberg, *J. Phys. Chem.*, 1995, **99**, 7102–7107.
- 4 D.-W. Li, L.-L. Qu, K. Hu, Y.-T. Long and H. Tian, *Angew. Chemie Int. Ed.*, 2015, **54**, 12758–12761.

S-1 Figures S1-S10

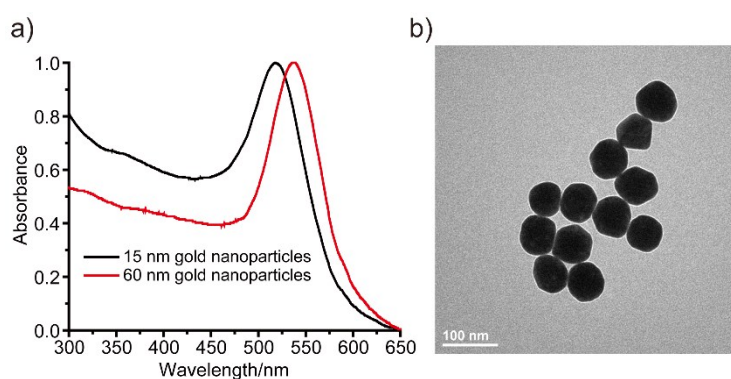


Figure. S1. a) UV-Vis spectrum of 14 nm and 60 nm gold nanoparticles; b) TEM image of 60 nm gold nanoparticles.

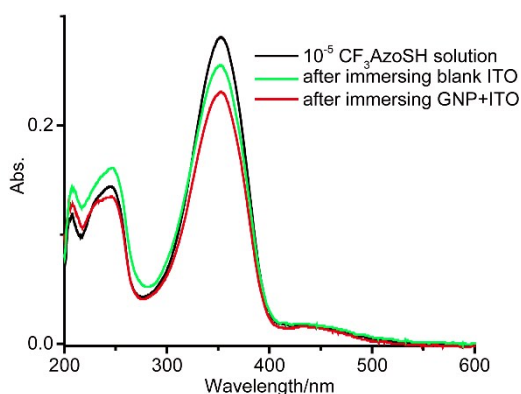


Figure. S2. a) UV/Vis spectra of CF_3AzoSH solution before (black line) and after immersing blank ITO (green line), immersing $n\text{-C}_4\text{H}_9\text{SH}$ modified GNP+ITO (red line).

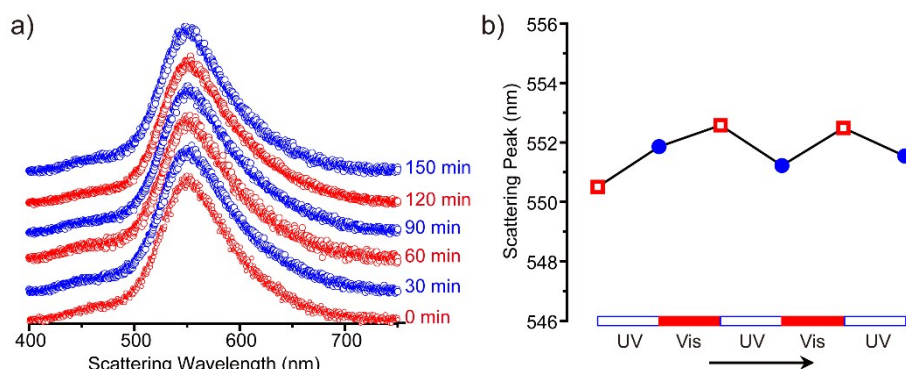


Figure. S3. a) The reversible shift of Plasmon resonance Rayleigh scattering spectra of single n-C₄H₉SH functionalized GNP (60 nm) obtained at different times upon alternating irradiation with UV and visible light (from bottom to top 0, 30, 60, 90, 120, 150 min). b) The reversible shift of scattering spectra peak of single n-C₄H₉SH functionalized GNP (60 nm) upon alternating irradiation with UV and visible light.

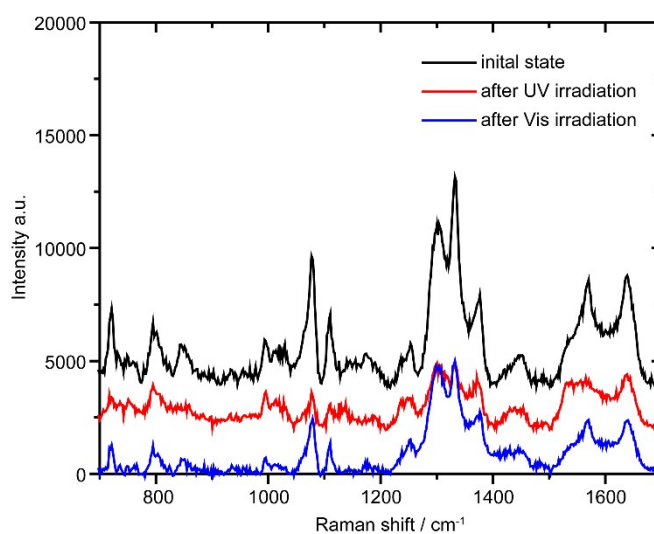


Figure. S4. SERS spectra of mix C₄H₉SH/CF₃AzoSH functional AuNPs initial (black line) and after UV irradiation (red line), after Vis irradiation (blue line).

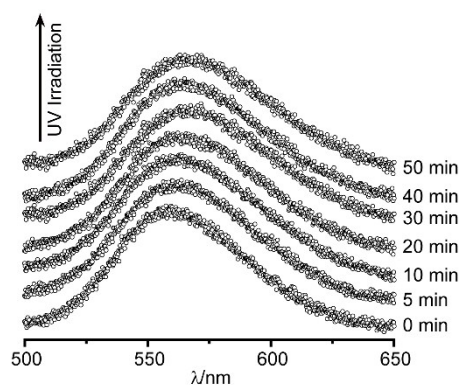


Figure. S5. The change of Plasmon resonance Rayleigh scattering spectra of single mix n- C_4H_9SH/CF_3AzoSH functionalized GNP (60 nm) obtained in increasing irradiation time by UV light (from bottom to top 0, 5, 10, 20, 30, 40, 50 min).

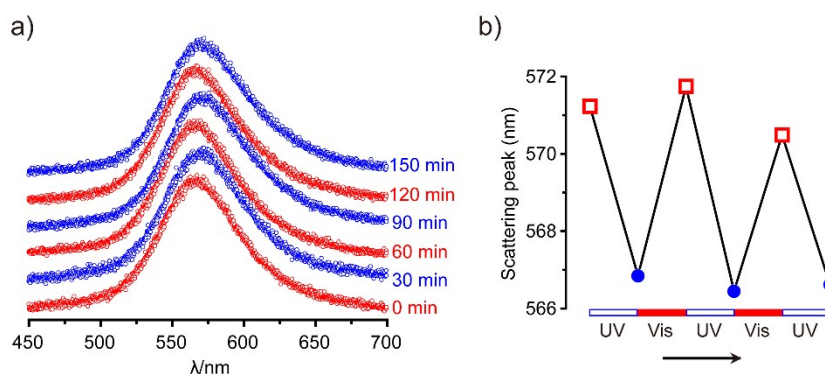


Figure. S6. a) The reversible shift of Plasmon resonance Rayleigh scattering spectra of single mix n- $C_4H_9SH/AzoSH$ functionalized GNP (60 nm) obtained at different times upon alternating irradiation by UV and visible light (from bottom to top 0, 30, 60, 90, 120, 150 min). b) The reversible shift of scattering spectra peak of single mix n- $C_4H_9SH/AzoSH$ functionalized GNP (60 nm) obtained at different times upon alternating irradiation by UV and visible light.

Figure S7~S11 are the 1H NMR, ^{13}C NMR and MS characterization of target compound and Intermediate

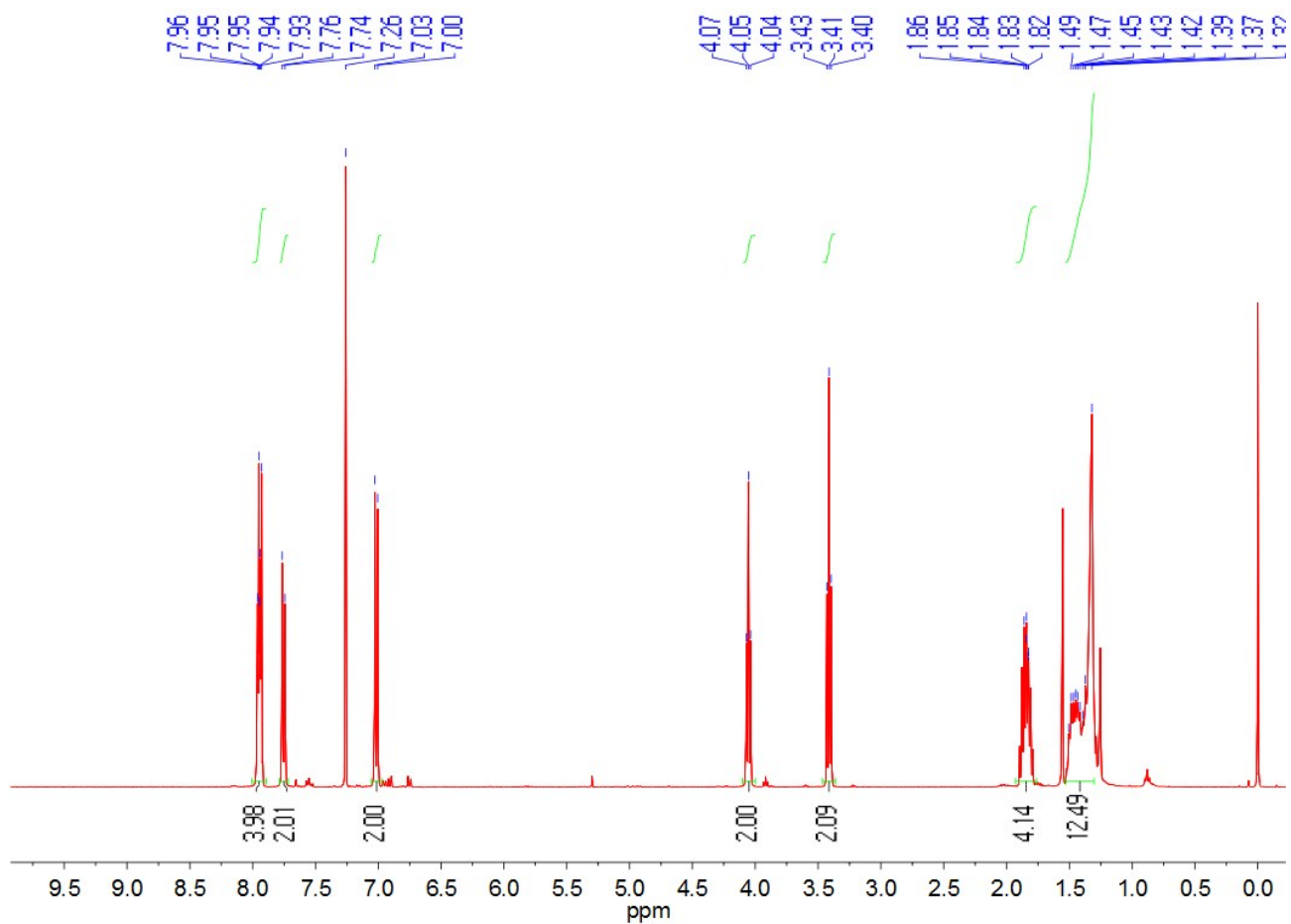


Figure. S7. ^1H NMR spectrum of [4-(10-bromo-decyloxy)-phenyl]-(4-trifluoromethyl-phenyl)-diazene (2).

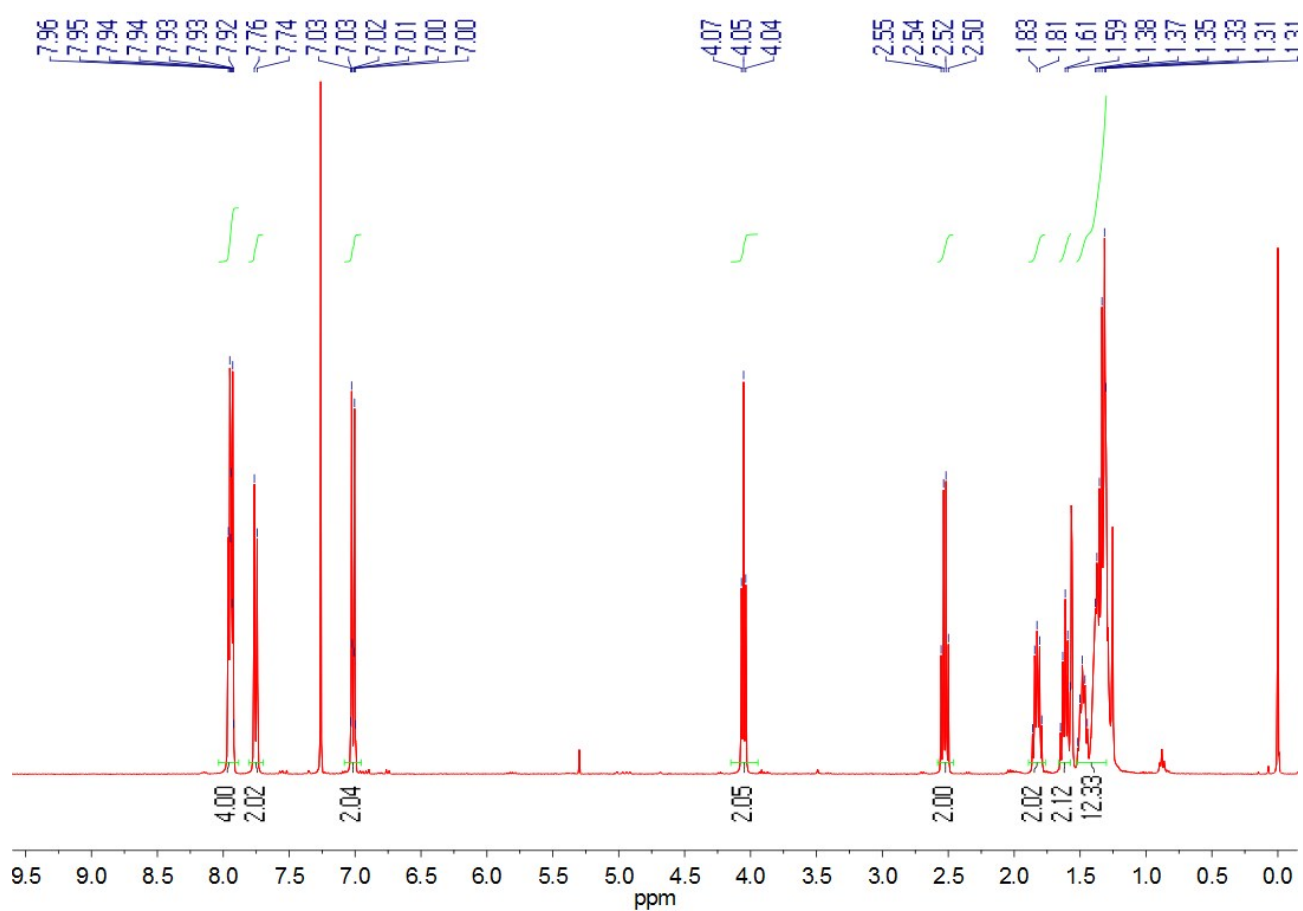


Figure. S8. ¹H NMR spectrum of 10-[4-(4-trifluoromethyl-phenylazo)-phenoxy]-decane-1-thiol (3).

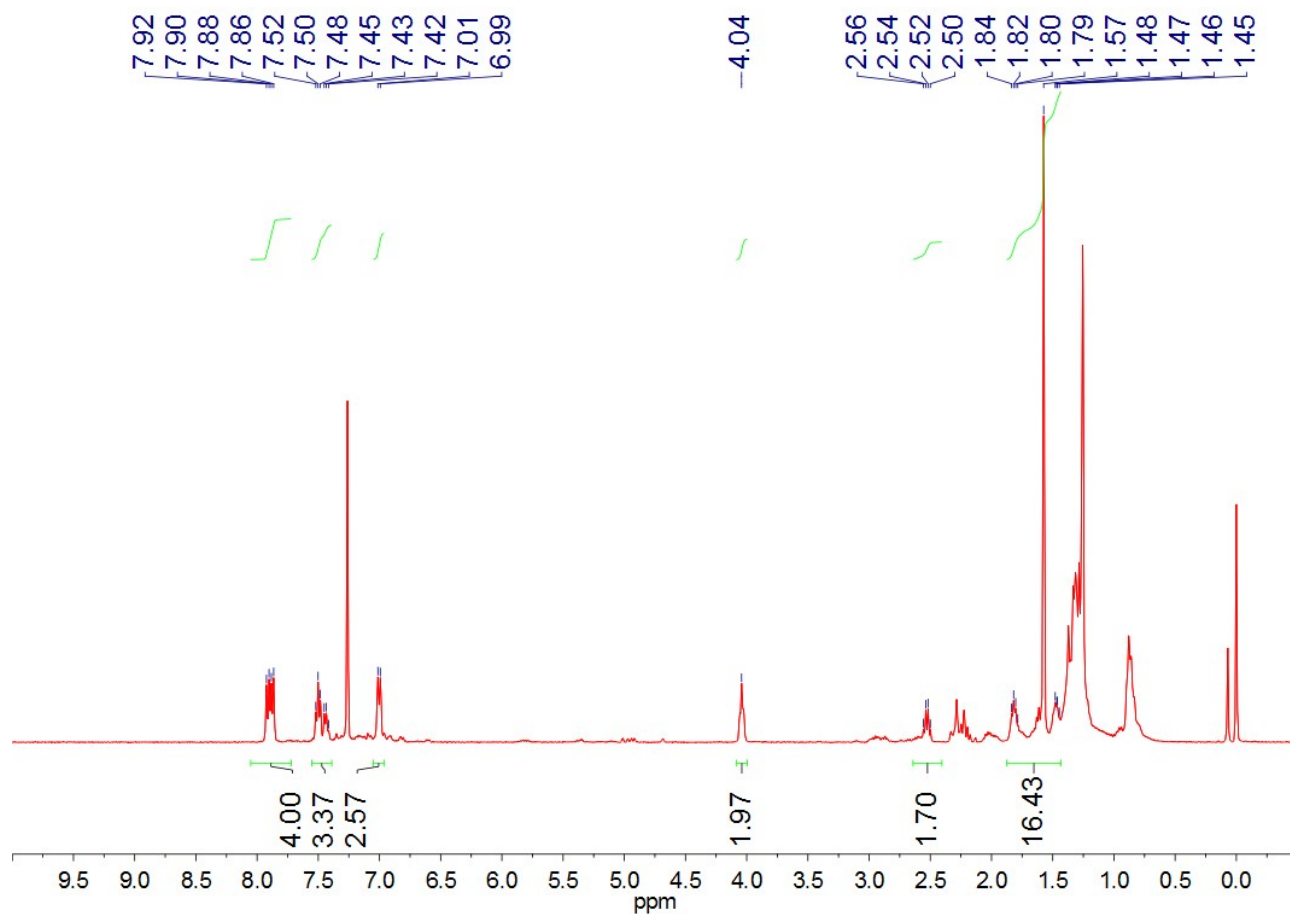


Figure. S9. ^1H NMR spectrum of 10-(4-phenylazo-phenoxy)-decane-1-thiol.

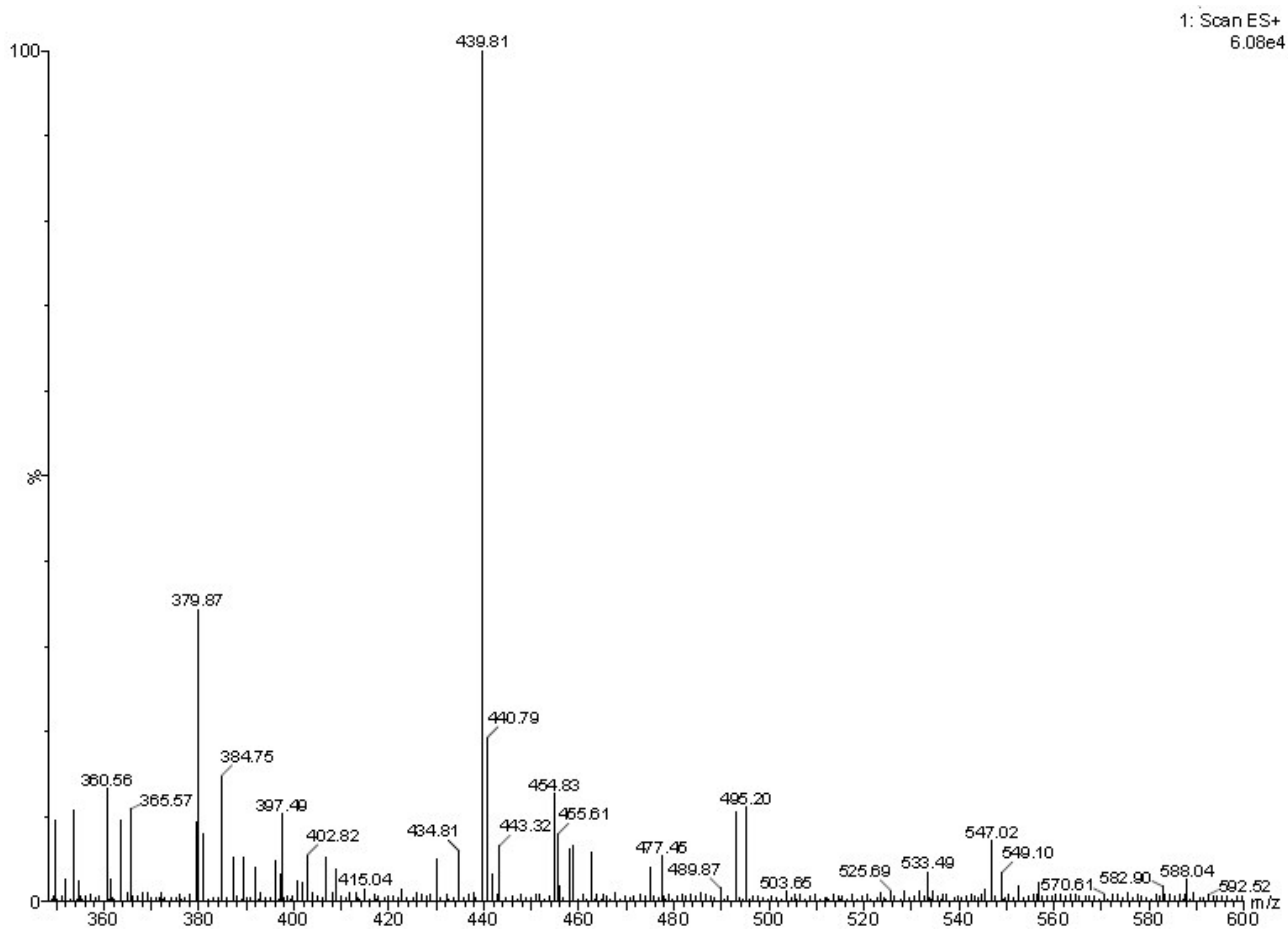


Figure. S10. Mass spectrum (ESI⁺) of 10-[4-(4-trifluoromethyl-phenylazo)-phenoxy]-decane-1-thiol (3).

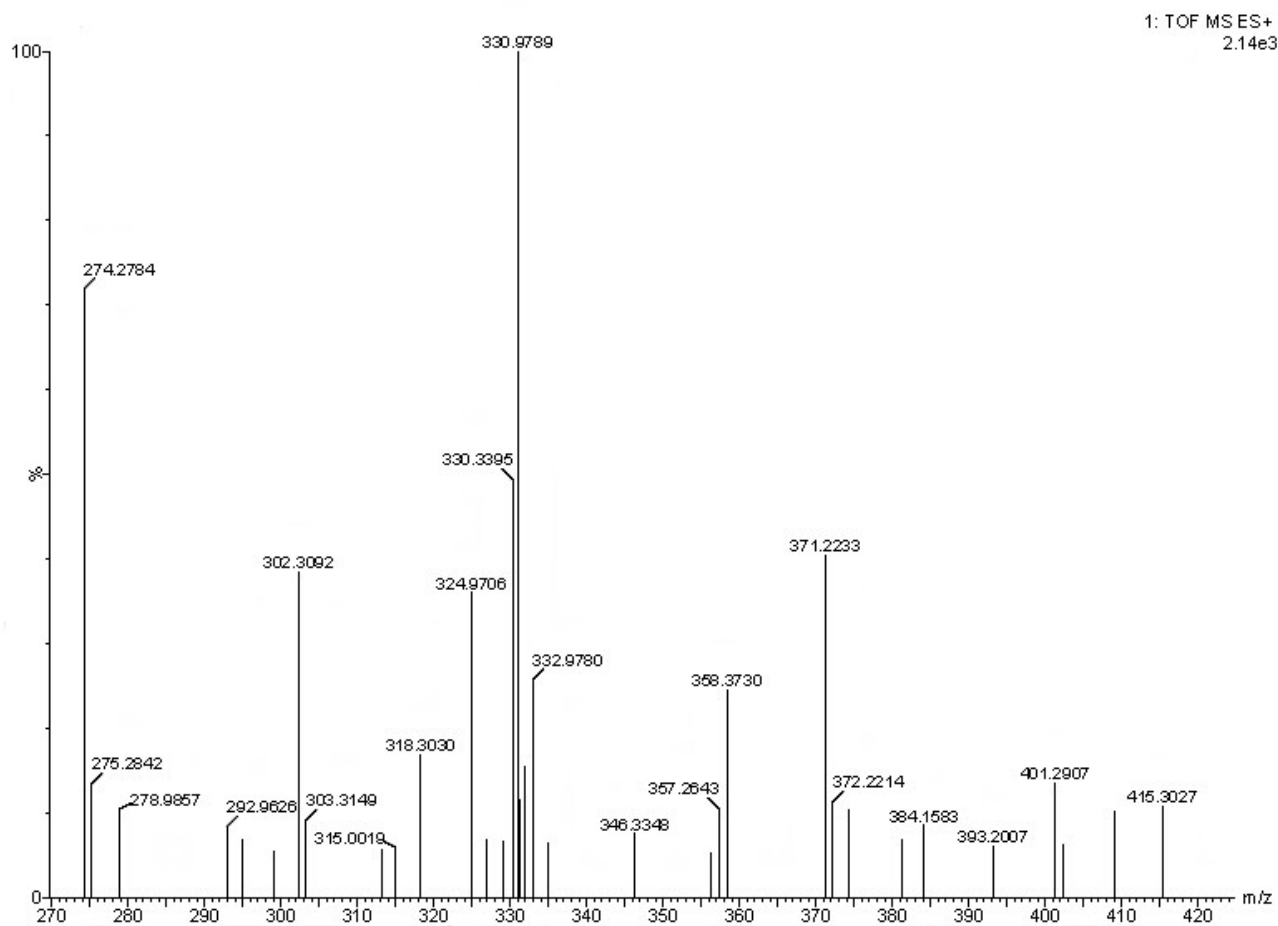


Figure. S11. Mass spectrum (HESI⁺) of 10-(4-phenylazo)-phenoxy]-decane-1-thiol.