

Supplementary Information (SI)

**Thiolate-mediated photoreduction and aerobic oxidation cycles in bismuth-bismuth oxide nanosystem towards the thiol-to-disulfide photocatalytic transformation**

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**Part 1. Experimental details**

**Photoreduction of Bi(SR)<sub>3</sub> in toluene via laser irradiation**

**(1) Preparation of Bi(SR)<sub>3</sub> toluene solution**

The toluene solution of Bi(SR)<sub>3</sub> (R=C<sub>n</sub>H<sub>2n+1</sub>, n=4, 6 and 8) was prepared at first. In a typical procedure for Bi(SC<sub>8</sub>H<sub>17</sub>)<sub>3</sub> toluene solution, for instance, 0.1 mmol Bi<sub>2</sub>O<sub>3</sub> (0.0465 g) was dissolved in 1 mL 1-octanethiol (C<sub>8</sub>H<sub>17</sub>SH) by ultrasonic and then mixed with 3 mL toluene in a glass vessel to form a transparent, yellow, homogeneous solution of Bi(SC<sub>8</sub>H<sub>17</sub>)<sub>3</sub>. This procedure was applied as well to the preparation of the toluene solution of other Bi(III) alkanethiolates (n=4, 6, 10 and 12), including Bi(SC<sub>4</sub>H<sub>9</sub>)<sub>3</sub> and Bi(SC<sub>6</sub>H<sub>13</sub>)<sub>3</sub> by using 1-butanethiol (HSC<sub>4</sub>H<sub>9</sub>) and 1-hexanethiol (HSC<sub>6</sub>H<sub>13</sub>). All of 1-alkanethiols of interest were purchased from Aladdin Scientific (Shanghai, China) and used without any treatments.

**(2) Isolation of Bi(SR)<sub>3</sub> (R=C<sub>n</sub>H<sub>2n+1</sub>, n= 8, 10 and 12) polycrystalline powders**

The toluene solution of Bi(SR)<sub>3</sub> was prepared by the method described in **(1)**. Afterwards, a large volume of ethanol was added to the toluene solution of Bi(SR)<sub>3</sub> (v/v > 5:1), and Bi(SR)<sub>3</sub> was flocculated and precipitated from solution, which can be isolated by centrifugation (>3000 r/min). Bi(SR)<sub>3</sub> solid powders could be further purified by twice of dispersing into ethanol and centrifugation and were dried at room temperature in a vacuum oven for further characterization. Bi(SC<sub>8</sub>H<sub>17</sub>)<sub>3</sub> solid powder was more easily flocculated and obtained at a relatively low temperature (e.g., 10–20 °C).

**(3) Photoreduction of Bi(SR)<sub>3</sub> in toluene**

2 mL Bi(SR)<sub>3</sub> (n=4, 6 and 8) toluene solution prepared in **(1)** was transferred into a capped quartz cuvette (1 × 1 × 4 cm<sup>3</sup>) or a glass bottle of suitable size and then photo-irradiated by commercialized LED lasers of different wavelength and output power, including 365 nm (50 mW), 420 nm (150 mW), 532 nm (150 mW) and 650 nm (150 mW). The photoreduction of Bi(SR)<sub>3</sub> in toluene to black Bi colloids and RSSR could be triggered under 365 and 420 nm light irradiation or even sunlight that contains UV-blue light of <450 nm. The observation of a black suspension meant the beginning of the photoreduction. The solution would become completely black with the irradiation time (2–3 min for 420 nm, ~10 min for 365 nm). The black suspension of Bi colloids would disappear and the solution turned yellow and transparent by turning off the laser and then shaking the solution. Such a cycle could repeat several to more than ten times dependent on the irradiation time, the volume ratio of the black/yellow solution, and the concentration of thiol/toluene. A low value for these three factors was found to increase the number of the Bi-Bi<sub>2</sub>O<sub>3</sub> photoredox cycles. When the solution kept black and could not turn yellow after multiple cycles, the black Bi colloids were isolated by centrifugation and washed with ethanol two times; the supernatant after the first time of centrifugation was preserved for the GC-MS measurements.

## **Characterisations**

### *UV-Vis Absorption Spectra*

UV-vis spectra were obtained on a UV-visible spectrophotometer (UV-2600, Shimadzu). The UV-vis-NIR spectra of Bi(SR)<sub>3</sub> toluene solution were collected in an absorbance mode within a range of 200–800 nm.

### *Powder X-ray Diffraction*

Room-temperature powder XRD data were collected on a D8 ADVANCE diffractometer with graphite-monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ , Bruker-AXS) within a  $2\theta$  range of 2–70° or 10–70° and a scan rate of 7°(2 $\theta$ )/min and 0.02° per step. The MDI JADE 6.0 software package was used to analyse the XRD data.

### *X-ray photoelectron spectroscopic (XPS) Spectra*

XPS measurements were carried out on an ESCALAB 250Xi X-ray photoelectron spectrometer using an Al K $\alpha$  excitation source ( $h\nu = 1486.6 \text{ eV}$ , Thermo Fisher Scientific). No any treatments for the samples were carried out before and during XPS analysis.

### *Transmission Electron Microscopy*

TEM images were recorded on a JEM-2100 electron microscope (JEOL, Japan) operated at an accelerating voltage of 200 kV. The sample for TEM observation was prepared by dropping an ethanol dispersion of Bi NPs onto a carbon-coating Cu TEM grid.

#### *Thermogravimetry and Differential Scanning Calorimetry*

TG–DSC data were collected on a NETZSCH STA 449 F3 thermal analyzer. The heating rate was 10 K/min and the purge and protection N<sub>2</sub> flows were fixed at 60 and 20 mL/min, respectively.

#### *Nuclear Magnetic Resonance Measurements*

<sup>1</sup>H NMR spectrum of Bi(SC<sub>8</sub>H<sub>17</sub>)<sub>3</sub> was collected at room temperature on a Bruker UltraShield™ 400 MHz NMR spectrometer. CDCl<sub>3</sub> was used as the solvent for the <sup>1</sup>H NMR data collection.

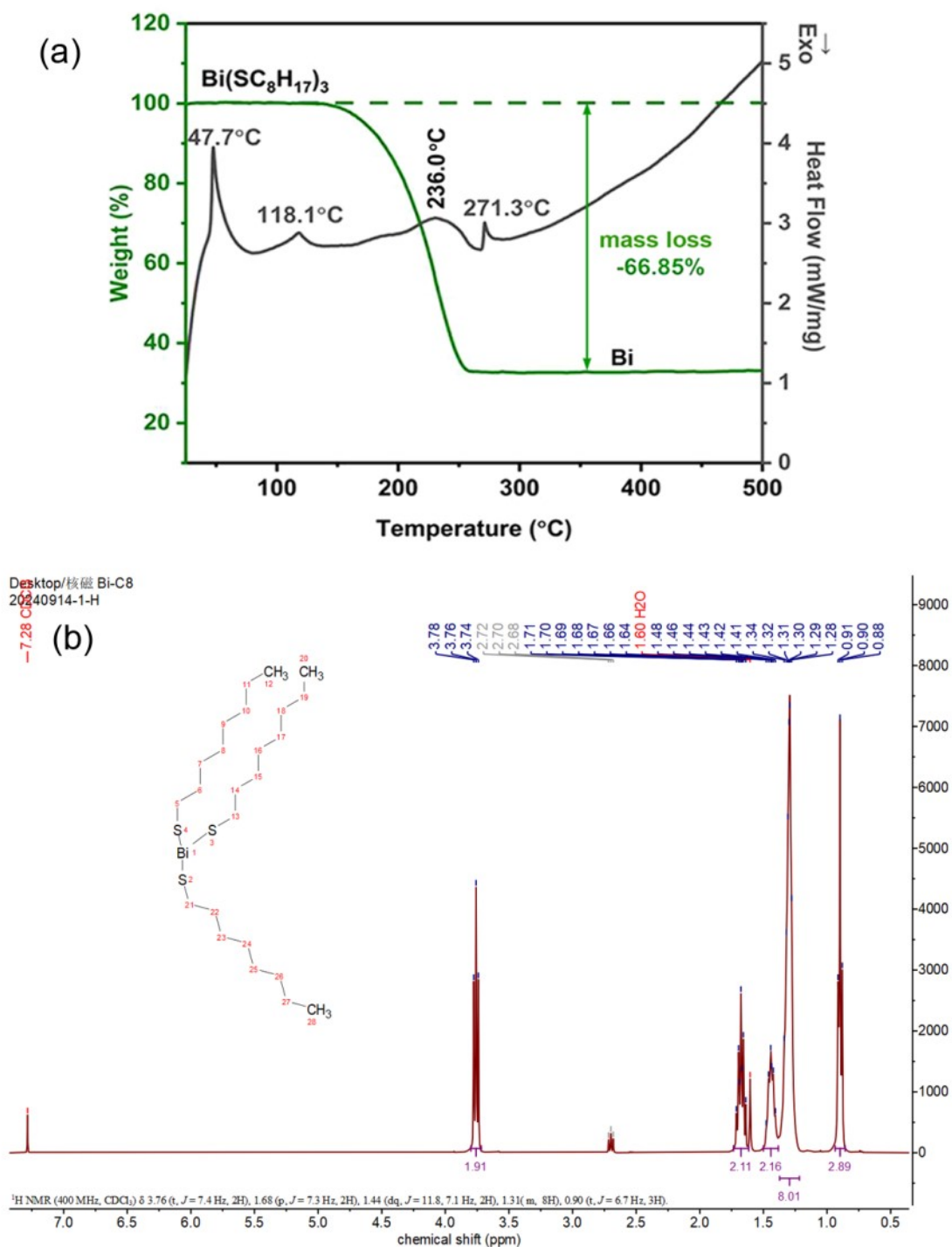
#### *Gas Chromatography/Mass Spectrometry*

GC-MS data were obtained by using Shimadzu-QP2010 Ultra GC-MS Spectrometry. A Restek Rtx-5ms chromatography column (30m × 0.25mm × 0.25μm; –60–350 °C) was used to separate the organic components soluble in the solution. The carrier gas (He) flow was 1 mL/min. The MS data was collected using a single-quadrupole scan mode and an ion source temperature of 230 °C with an m/z range of 35–600. The original solution was diluted to 1/100–1/10000 for a more accurate measurement. The injection volume of 10 μL diluted solution was injected into each GC/MS analysis.

#### *Electron Spin Resonance Measurements*

ESR measurements were carried out on a Bruker A300-10/12 ESR spectrometer. A glass capillary filled with Bi(SR)<sub>3</sub> toluene solution was connected to the detection feeler and the ESR signals were probed at ambient temperature under laser irradiation or not.

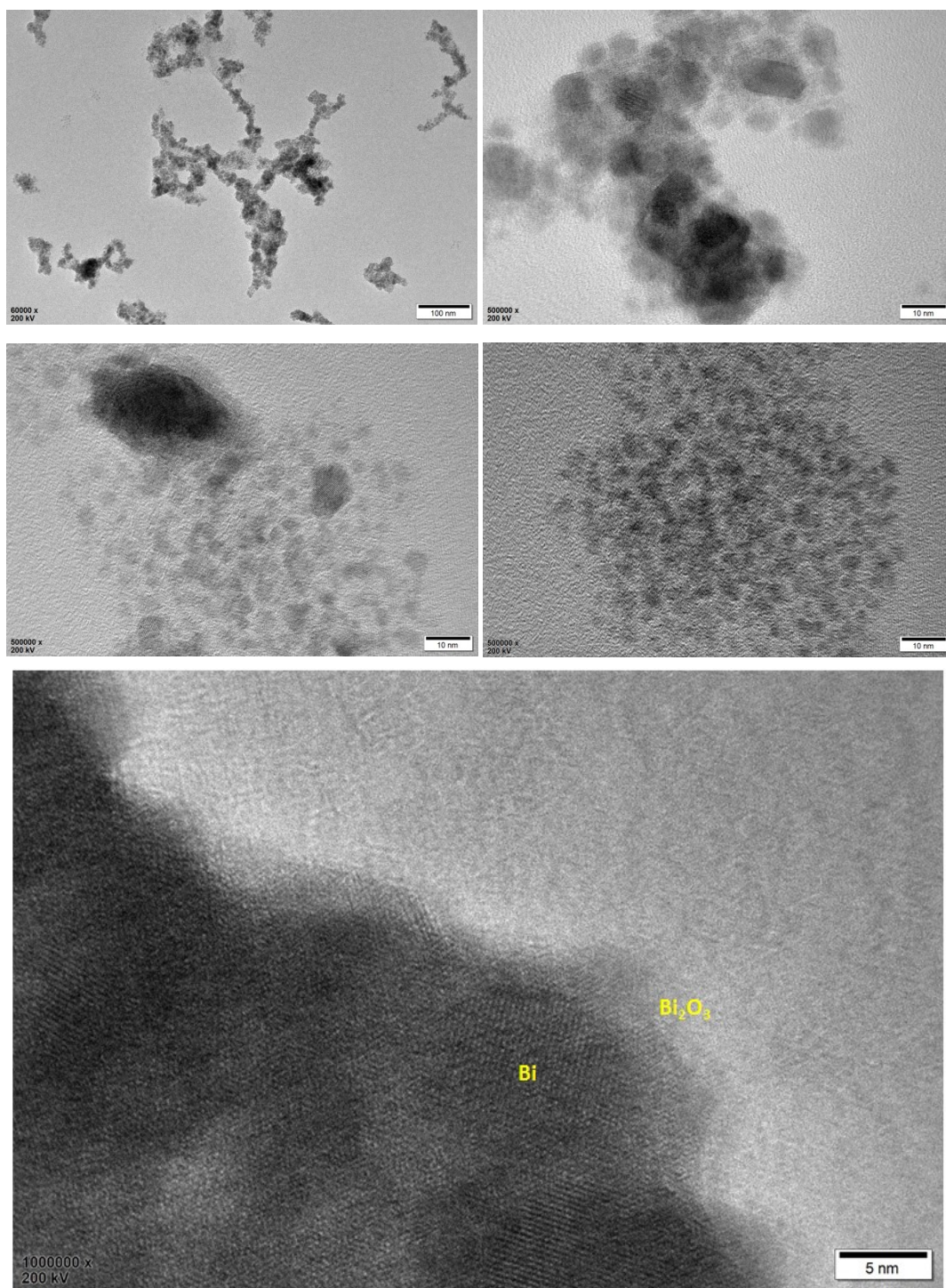
## Part 2. Supporting Figures



**Fig. S1** (a) TG-DSC results of solventless thermolysis of Bi(SC<sub>8</sub>H<sub>17</sub>)<sub>3</sub>. A single-step decomposition event is detected by TG. The measured total mass loss 66.85% agrees well with the theoretical mass loss of Bi(SC<sub>8</sub>H<sub>17</sub>)<sub>3</sub> to Bi (67.59%), indicating a 1:3 Bi/SC<sub>8</sub>H<sub>17</sub> molar ratio. The DSC endothermic peaks at 47.7 and 271.3 °C are due to

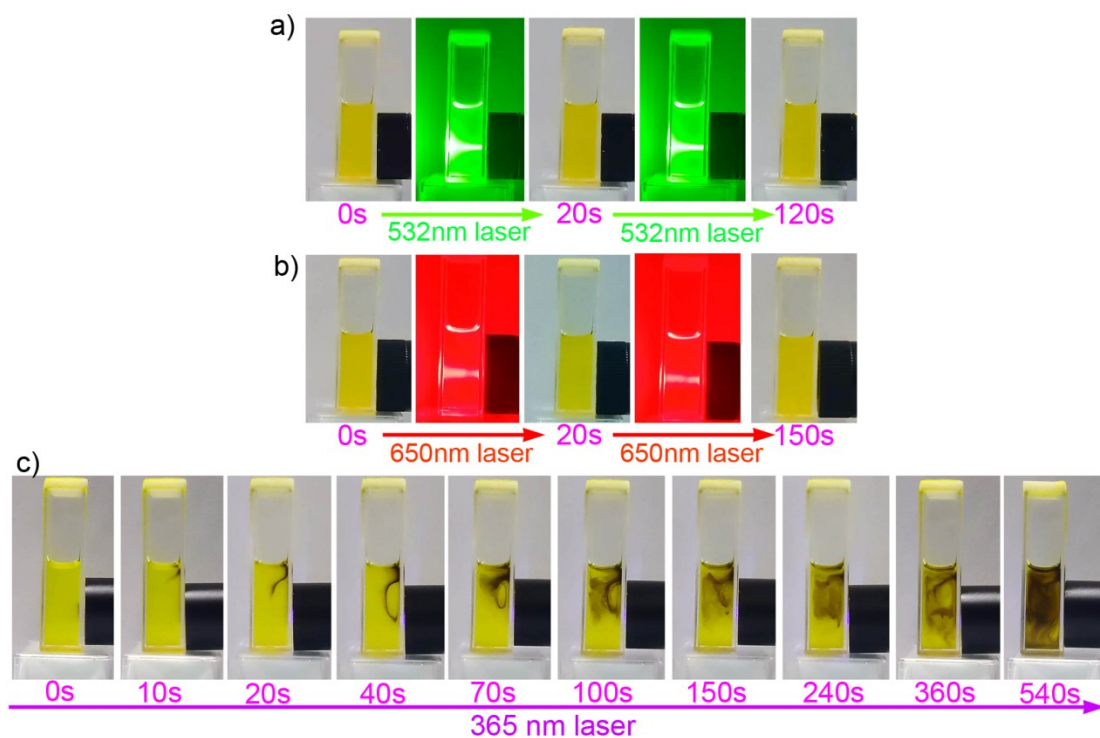
the melting of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  and Bi, the one at 236.0 °C due to the evaporation of decomposed organic products, and the one at 118.1 °C probably due to the decomposition of a small portion of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  to Bi during heating.

(b)  $^1\text{H}$  NMR (room temperature in  $\text{CDCl}_3$ ) spectrum of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$ : 7.28 ppm, H in  $\text{CHCl}_3$  (s); 1.60 ppm, H in  $\text{H}_2\text{O}$  impurity (s); 3.76 ppm, 2H in  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (t); 1.68 ppm, 2H in  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (m); 1.44 ppm, 2H in  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (m); 1.31 ppm, 8H in  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (m); 0.90 ppm, 3H in  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  (t). The different  $^1\text{H}$  NMR chemical shifts indicate the differences in the chemical environments of H atoms in long-chain  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  ligand. The numerical ratios of H atoms with different chemical shifts are 2:2:2:8:3, showing there are 17 H atoms in one ligand, consistent with the molecular formula of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  after 17 H atoms multiply by 3 for the total 3 ligands.

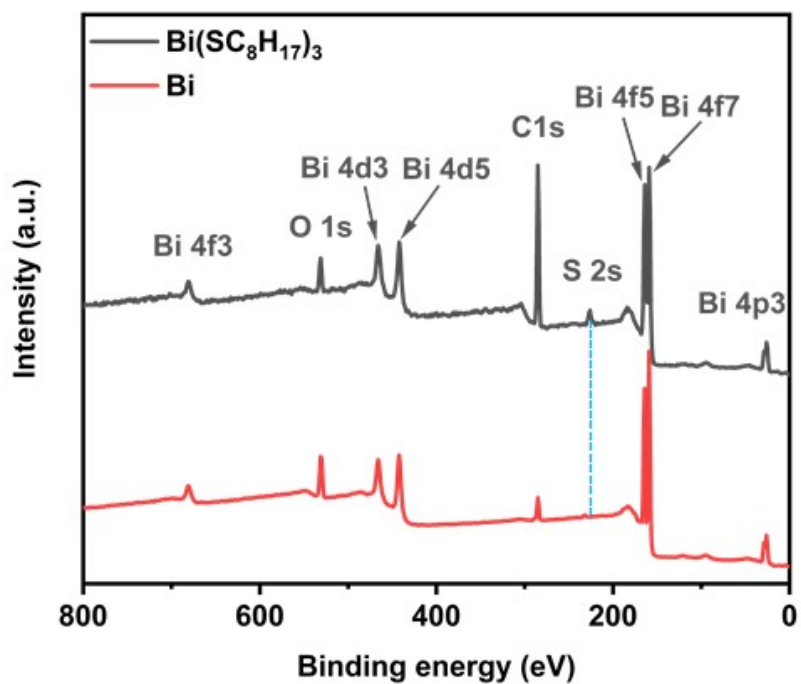


**Fig. S2** TEM and HRTEM images of Bi colloids obtained after 12 times of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$ -mediated Bi-Bi<sub>2</sub>O<sub>3</sub> photoredox cycles. The core-shell structure can be clearly observed in some Bi NPs by HRTEM imaging.



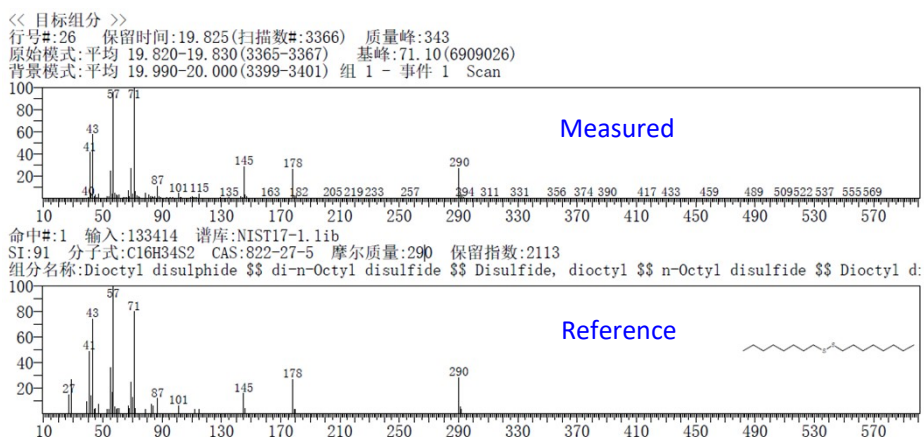
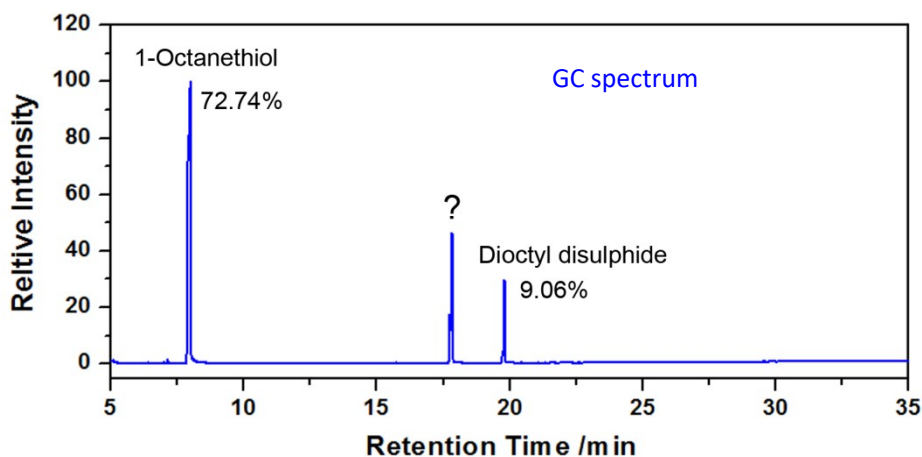


**Fig. S3** Photographs of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  toluene solution under the laser irradiation of different wavelengths and irradiation times. (a,b) 532 nm green and 650 nm red lasers, which are unable to initiate the photolysis (photoreduction) of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  to black Bi colloids due to no color change during the laser irradiation. (c) 365 nm UV laser, which initiates the photolysis of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  to black Bi colloids as the solution gradually changes from yellow to black. The longer time for the color change from yellow to completely black is due to the low outlet power density of 365 nm UV laser compared to the 420 blue laser. As well, these results demonstrate that the wavelength (photon energy) of light determines whether the photolysis (photoreduction) of  $\text{Bi}(\text{SR})_3$  can proceed or not, while the output power of light determines the speed of the photolysis (photoreduction) of  $\text{Bi}(\text{SR})_3$ . All graphics are extracted from the videos recording the color change of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  solution with increasing irradiation time.

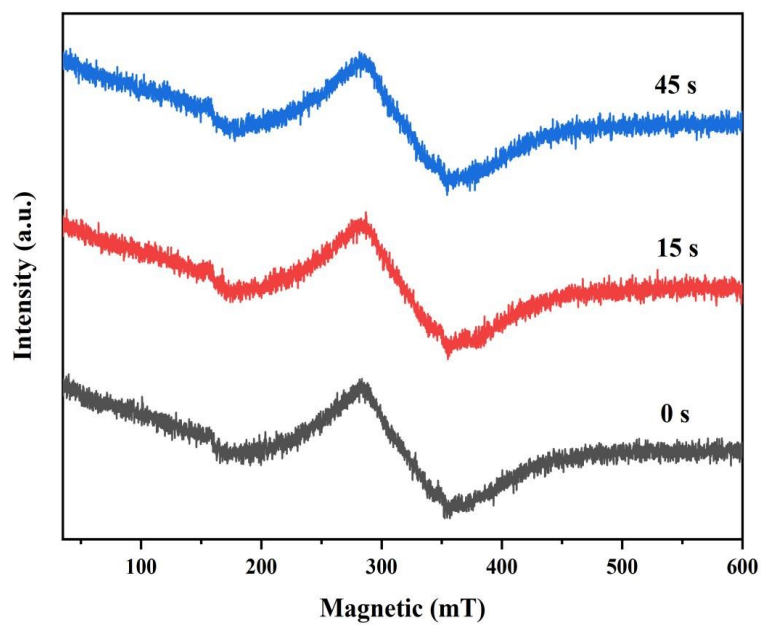


**Fig. S4** XPS survey spectra of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  and Bi NPs. A clear S 2s signal at 226.1 eV is present in  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  and the high carbon content in  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  contribute the strong C 1s signal, compared to the result for Bi NPs.





**Fig. S5** GC-MS results for the organic product obtained after 25 min of 420 nm laser illumination on  $C_8H_{17}SH$  toluene solution (1:3 volume ratio) in the absence of Bi(III) ( $Bi_2O_3$ ). The irradiation time is approximate equal to that for 12 cycles of  $Bi(SC_8H_{17})_3$ -mediated Bi- $Bi_2O_3$  photoredox reaction. The low relative abundance of dioctyl disulfide (9.06%) relative to octanethiol (72.74%) reveals that the thiol-to-conversion is very low compared to the case with Bi(III) catalyst (Fig. 2b,c in the main text). The component for the GC peak marked with “?” is unclear. The m/z peaks measured for dioctyl disulfide are consistent with the reference MS data of dioctyl disulfide from the NIST17-1 spectrum library.



**Fig. S6** ESR spectra of  $\text{Bi}(\text{SC}_8\text{H}_{17})_3$  toluene solution recorded at different periods of irradiation time of 420 nm laser. No obvious signal enhancement is observed during the light irradiation.