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# Synthesis and photochromic properties of disulfide-1,3-diazabicyclo [3.1.0]hex-3-ene functionalized silver nanoparticles

Q1 Atefeh Ghavidast, Nosrat O. Mahmoodi\*, Mohammad Ali Zanjanchi

Q2 Department of Chemistry, Faculty of Science, University of Guilan, P.O. Box, 41335-1914 Rasht, Iran

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## ABSTRACT

The new 1,3-diazabicyclo[3.1.0]hex-3-ene derivative with disulfide bond to modify silver nanoparticle (AgNP) surface was synthesized. The photochromism of the packed ligand on AgNPs showed a pronounced bathochromic shift in the absorption band of the open ring photoisomers and also in the surface plasmon resonance absorption (SPRA) of AgNPs.

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Self-assembled monolayer (SAM)

## 1. Introduction

Metal nanoparticles (MNPs) protected by self-assembled monolayers are of increasing interest in areas such as tunable optical devices [1,2], sensor technologies [3,4], and drug delivery [5–8]. Self-assembled monolayers (SAMs) have been intensively studied in recent years because they provide a simple method to engineer surface properties for a variety of applications [9,10]. In particular, SAMs derived from thiols (–SH) and disulfides (–S–S–) on metal surfaces such as gold and silver surfaces have been extensively studied [11–14]. Thiols are well-known ligand molecules because they are able to form SAMs on the MNPs surface through a strong metal–sulfur covalent bond. The disulfide bond is a very valuable functional group in a variety of chemical and biological agents that display effective reactivity or biological activities [15]. A disulfide bond undergoes S–S bond cleavage and formed a thiolate bond at the nanoparticle surfaces [6,13,16,17].

Surface plasmon resonance absorption (SPRA) is a key optical property of MNPs. SPRA occurs in MNPs when light drives the oscillation of the free electrons in the nanoparticles [18]. Due to the unique and tunable SPRA properties, protected nanoparticles can be applied as materials for surface-enhanced spectroscopy, optical filters, waveguides and sensors.

SAMs of photochromic molecules have recently attracted considerable interest due to their potential applications in the field of molecular electronics [19–26]. The incorporation of photochromic molecules on

the nanoparticle surface leads to photo-responsive systems which their properties can be manipulated by light. 1,3-Diazabicyclo [3.1.0] hex-3-ene, one of the typical photochromic molecule species, can undergo suprafacial photo-cleavage of the aziridine ring and formation of a double charged imine ylide under UV irradiation [26–33]. This allows a reversible switching reaction between colorless close photoisomer **a** into colored open photoisomer **b**. The open photoisomer **b** upon visible light undergoes the back rearrangement to the closed form **a**. These products change their colors in both powder and solution form. The designed thiol **1a** and disulfide **2a** both exhibit obvious photo-responsive properties with different colors **1b** and **2b** upon UV irradiation (Fig. 1).

## 2. Experimental

## 2.1. Materials and apparatus

The following reagents were purchased from Merck and used without further modification: AgNO<sub>3</sub> (99.9%), H<sub>2</sub>NCSNH<sub>2</sub> (99%), polyvinylpyrrolidone (PVP, K30, MW 40,000), NaBH<sub>4</sub> (99%), NaI and H<sub>2</sub>O<sub>2</sub>. The <sup>1</sup>H NMR spectra were obtained on a Bruker Avance 500 and 400 MHz spectrometer. The UV–vis absorption spectra in the range of 200–600 nm (EtOH, C = 1.0 × 10<sup>−4</sup> M) were measured with a Shimadzu UV-2100 spectrometer. The photoinduced (open-photoisomer) **b** was formed upon UV irradiation (Hg lamp DRSh-260 + UV-transmitting glass filters). Visible light was generated by a 500 W Xenon lamp with a standard band-pass filter 550 AF10 (Omega). The FT-IR spectra for the samples were obtained using Shimadzu FT-IR-8900 spectrophotometer by using KBr pellets. Elemental analysis was performed on a Carlo-Erba EA1110 CNNO-S analyzer and agreed with the calculated values. The X-ray diffraction (XRD)

\* Corresponding author. Tel./fax: +98 1313233262.

E-mail addresses: [mahmoodi@guilan.ac.ir](mailto:mahmoodi@guilan.ac.ir), [nosmahmoodi@gmail.com](mailto:nosmahmoodi@gmail.com) (N.O. Mahmoodi).

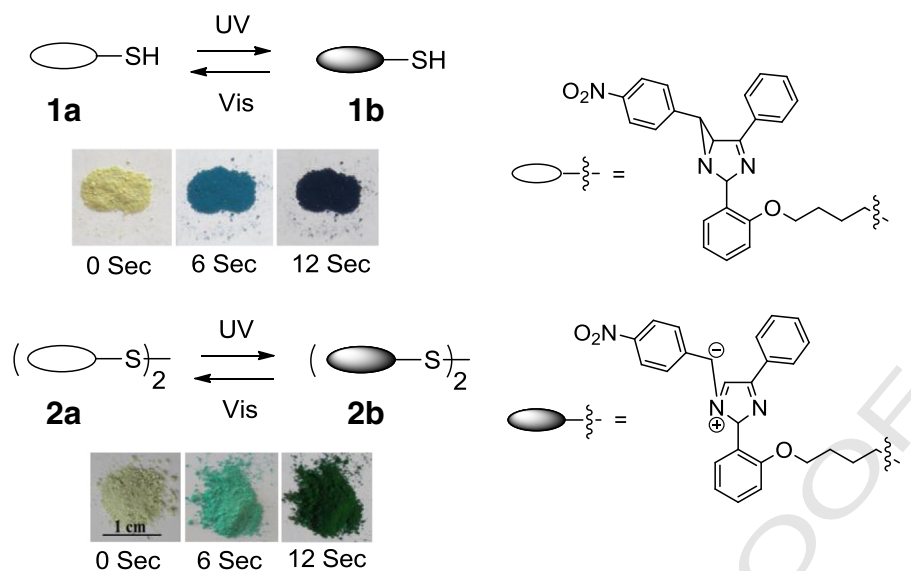


Fig. 1. Photochromic performance of thiol **1** and disulfide **2**.

patterns were recorded in a wide angle range ( $2\theta = 10\text{--}70$ ) by Phillips (pw-1840) X-ray diffractometer with Cu-K $\alpha$  radiation. The morphology and particle sizes of synthesized powder were characterized by transmission electron microscope (TEM) images on a Phillips CM-10 instrument with an accelerating voltage of 100 kV.

## 2.2. Synthesis of 2-(4-bromobutoxy)benzaldehyde **5**

K<sub>2</sub>CO<sub>3</sub> (1.15 g, 7.6 mmol), 2-hydroxybenzaldehyde (0.92 g, 7.6 mmol) and 1,4-dibromobutane (8.2 g, 38 mmol) were added to acetone (48 mL) and the mixture was refluxed for 6 h under N<sub>2</sub>. The reaction mixture was cooled to r.t and after the removal of the solid part by filtration; organic solvent was removed under reduced pressure. Then H<sub>2</sub>O (20 mL), 2 M HCl (20 mL) and CH<sub>2</sub>Cl<sub>2</sub> (80 mL) were added. The organic phase was collected and washed with 10% Na<sub>2</sub>CO<sub>3</sub> (2  $\times$  10 mL). The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to oil. The crude product was chromatographed over silica gel using a mixture of EtOAc/Hexane (1:3) to give yellow oil (0.17 g, 68% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.98–2.08 (m, 4H), 3.42 (t,  $J = 6.1$  Hz, 2H), 4.23 (t,  $J = 6.4$  Hz, 2H), 7.03 (d,  $J = 8.4$  Hz, 1H), 7.08 (t,  $J = 7.4$  Hz, 1H), 7.58 (t,  $J = 7.8, 0.9$  Hz, 1H), 7.86 (d,  $J = 7.8$  Hz, 1H), 10.54 (s, 1H, CHO). Anal. Calcd. for C<sub>11</sub>H<sub>13</sub>BrO<sub>2</sub>: C, 51.38; H, 5.10, found: C, 51.31; H, 5.18.

## 2.3. Synthesis of 2-(4-mercaptobutoxy)benzaldehyde **4**

2-(4-Bromobutoxy)benzaldehyde **5** (1.28 g, 5 mmol) and thiourea (5.2 mmol) were dissolved in 95% EtOH (10 mL) and the reaction mixture was refluxed for 3 h. After cooling down to r.t., a solution of 2.5 mol/L NaOH (10 mL) was then added into the reaction mixture and continued to reflux for another 3 h. The reaction mixture acidified (pH = 1) by the addition of diluted HCl and then was extracted twice with Et<sub>2</sub>O. The organic phase was combined, washed with brine, dried over MgSO<sub>4</sub> and removed. The crude residue was chromatographed over silica gel using a mixture of EtOAc/petroleum ether (1:5) to give **4** as yellow viscous liquid (0.12 g, 58% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.36 (s, 1H, SH), 1.74–1.76 (m, 2H), 1.86–1.93 (m, 2H), 2.56 (t,  $J = 6.7$  Hz, 2H, CH<sub>2</sub>-SH), 4.24 (t,  $J = 6.9$  Hz, 2H), 7.05 (d,  $J = 7.4$  Hz, 1H), 7.10 (t,  $J = 7.8$  Hz, 1H), 7.60 (t,  $J = 8.6$  Hz, 1H), 7.88 (d,  $J = 7.5$  Hz, 1H), 10.56 (s, 1H, CHO). Anal. Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>S: C, 62.83; H, 6.71, found: C, 62.76; H, 6.62.

## 2.4. Synthesis of 2,2'-((disulfaneyldiylbis(butane-4,1-diyl))bis(oxy))dibenzaldehyde **3**

The solution of the thiol **4** (0.21 g, 1 mmol) in EtOH (3 mL) was added with NaI (0.001 g, 0.01 mmol) and 30% H<sub>2</sub>O<sub>2</sub> (0.11 mL, 1 mmol) and the mixture was stirred at r.t for 6 h. Sat. aq Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (15 mL) was added. The precipitated was collected by filtration and re-crystallized from EtOH to afford the pure disulfide **3** as white powder (0.34 g, 82% yield). IR (KBr, cm<sup>-1</sup>): 3069, 2939, 2858, 2760, 1681, 1594, 1460, 1389, 1293, 1245, 759. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.78–1.80 (m, 2H), 1.88–1.96 (m, 2H), 2.69 (t,  $J = 6.5$  Hz, 2H, CH<sub>2</sub>-SH), 4.25 (t,  $J = 7.0$  Hz, 2H), 7.07 (d,  $J = 7.5$  Hz, 1H), 7.16 (t,  $J = 7.6$  Hz, 1H), 7.62 (t,  $J = 8.5$  Hz, 1H), 7.88 (d,  $J = 7.6$  Hz, 1H), 10.57 (s, 1H, CHO). Anal. Calcd. for C<sub>52</sub>H<sub>48</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: C, 68.10; H, 5.28; N, 9.16, found: C, 68.25; H, 5.14; N, 9.10.

## 2.5. Synthesis of 1,2-bis(4-(2-(6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-en-2-yl)phenoxy)butyl)disulfane **2**

(3-(4-Nitrophenyl)aziridin-2-yl)(phenyl)methanone **7** [27] (0.26 g, 1 mmol), **3** (0.42 g, 1 mmol) and NH<sub>4</sub>OAc (0.4 g, 5 mmol) were dissolved in 2 mL of DMF and stirred at r.t. The reaction was completed after overnight. A color change in the reaction mixture from orange into pale green is characteristic for the formation of target product **2**. The reaction mixture was filtered, washed with EtOH and dried in air to give a pale yellow solid **2** (0.67 g, 73% yield), M.p > 200 °C. IR (KBr, cm<sup>-1</sup>): 3065, 2936, 2860, 1601, 1516, 1342, 1241, 754. Closed-form 65%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.65 (t,  $J = 7$  Hz, 2H), 1.82–1.84 (m, 2H, b-H), 2.55 (t,  $J = 4.4$  Hz, 2H, d-H), 2.71 (s, 1H, f-H), 3.71 (s, 1H, e-H), 3.93–4.04 (m, 2H, a-H), 6.97 (d,  $J = 7.6$  Hz, 1H), 7.03 (t,  $J = 7.4$  Hz, 1H), 7.11 (s, 1H, g-H), 7.32 (t,  $J = \text{Hz}$ , 1H), 7.38–7.742 (m, 1H), 7.49–7.53 (m, 3H), 7.57–7.61 (m, 2H), 8.01 (d,  $J = 7.2$  Hz, 2H), 8.07 (d,  $J = 7.2$  Hz, 2H, i-H). After irradiation with UV light the color of **2** converts to deep green (open-form, 35%): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.65 (t,  $J = 7$  Hz, 2H), 1.98–2.02 (m, 2H, b'-H), 2.61 (t,  $J = 6$  Hz, 2H, d'-H), 2.81 (s, 1H, f'-H), 3.77 (s, 1H, e'-H), 4.06–4.10 (m, 2H, a'-H), 6.49 (s, 1H, g'-H), 6.93–6.96 (m, 1H), 7.03 (t,  $J = 7.4$  Hz, 1H), 7.32 (t,  $J = \text{Hz}$ , 1H), 7.38–7.742 (m, 1H), 7.49–7.53 (m, 3H), 7.57–7.61 (m, 2H), 8.01 (d,  $J = 7.2$  Hz, 2H), 8.16 (br, 2H, i'-H). Anal. Calcd. for C<sub>52</sub>H<sub>48</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub>: C, 68.10; H, 5.28; N, 9.16, found C, 68.18; H, 5.34; N, 9.25.

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