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Photochromism of azobenzene-thiol-1,3-diazabicyclo-[3.1.0]hex-3ene on silver nanoparticles



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ABSTRACT

The new azobenzene-thiol terminated photochromic derivatives is designed, synthesized and used to form self-assembled monolayers on silver nanoparticles. The photochromic behavior of 1,3-diazabicyclo-[3.1.0]hex-3-ene joined with surface plasmon resonance absorption band of silver nanoparticles and photoisomerisable azobenzene is presented. The ultraviolet–visible experiments demonstrated that electronic transitions of functionalized silver nanoparticles were shifted as a result of chemical bonding and overlap between absorption bands of photochromic ligands with surface plasmon resonance absorption band of silver nanoparticle. Furthermore, we have also observed that trans \rightarrow cis and cis \rightarrow trans photoisomerization rate by ultraviolet light and thermally induced condition for functionalized silver nanoparticles are noticeably faster than free ligands.

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1. Introduction

The self-assembly of photo-responsive molecules on metal nanoparticles (MNPs) surface has received significant attention in recent years because provides the opportunity of using switching devices as photo-responsive components in optical storage, molecular recognition applications and photoswitchable surface wettability [1–10]. Among these molecules, azobenzene derivatives are most studied due to their higher quantum yields of the photoisomerization in solution, simple molecular structures and relatively good stability of both isomers. These molecules demonstrate a transition from trans configuration to cis configuration upon exposure to UV light and a reversible isomerization under Vis light [2.11]. There has been a significant interest in the properties of azobenzene derivatives in self-assembled monolayers on surfaces. The photochemical and electrochemical reactivity of these systems also have been studied [12-23].

bathochromic shift either in the absorption band of the open ring photoisomers as well in the surface plasmon resonance absorption (SPRA) of AgNPs. Several studies on AgNPs capped with other photochromic molecules were reported and the correlation between the SPRAB and the photochemical property of the photochromic ligands were investigated [26–32]. Here, we are interested to convert the whole nanoparticle as a switch via attaching an interacting photochromic molecule to nanoparticles [14,16]. In this study, AgNPs were immobilized with premade photochromic thiol-terminated 1,3-diazabicyclo[3.1.0]hex-3-ene contained an azobenzene functional group **Az-TTP** and their photochromic behavior was studied. The **Az-TTP** derivatives designed with two different photochromic units in the molecule can serve as multicolor photochromic materials [33]. Photo-isomerization of these photochromic compounds is illustrated

Recently, our group reported photochromism of 1,3diazabicyclo[3.1.0]hex-3-ene with thiol and disulfide groups on

AgNPs surfaces [24,25]. The modified AgNPs showed a pronounced

isomerization of these photochromic compounds is illustrated in Fig. 1. In **Az-TTP** ligands a reversible switching reaction occurred between the close-*E*-photoisomer into the open-*E*photoisomer and open-*Z*-photoisomer under UV irradiation. The latter, upon remaining in the oven or storage in the dark, undergoes the reverse rearrangement to the **Az-TTP** close-*E* starting form.







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Fig. 1. Photochromic performance of Az-TTP close-E to Az-TTP open-Z.

2. Experimental

2.1. Materials and apparatus

The following reagents were purchased from Merck and used without further modification: AgNO₃ (99.9%), H₂NCSNH₂ (99%), polyvinylpyrrolidone (PVP, K30, MW 40,000) and NaBH₄ (99%). The ¹H NMR spectra were obtained on a Bruker Avance 500 and 400 MHz spectrometer. The UV-Vis absorption spectra in the range of 200–800 nm (EtOH, $C = 1.0 \times 10^{-4}$ M) were measured with a Shimadzu UV-2100 spectrometer. The photoinduced (open-Z-photoisomer) was formed upon UV irradiation (Hg lamp DRSh-260+UV-transmitting glass filters). The FT-IR spectra for the samples were obtained using Shimadzu FT-IR-8900 spectrophotometer by using KBr pellets. The X-ray diffraction (XRD) patterns were recorded in a wide angle range $(2\theta = 10-70)$ by Phillips (pw-1840) X-ray diffractometer with Cu-K α 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. (E)-2-Hydroxy-5-(phenyldiazenyl)benzaldehyde (3)

Aniline (0.28 g, 3 mmol), water (1.5 mL) and HCl (2.5 mL, 37%) were stirred for 5 min in an ice bath to give an amine salt. To this mixture, sodium nitrite (0.21 g, 3 mmol) dissolved in water (1.0 mL), after cooling to 0-5 °C, was added dropwise over 15 min. The mixture was stirred for 30 min in an ice bath to obtain colorless diazonium salt solution. In a second flask, salicylaldehyde (0.32 mL, 3 mmol) was dissolved in water (15 mL) containing sodium hydroxide (0.12 g, 3.0 mmol) and sodium carbonate (2.2 g, 21 mmol) and cooled to 0 °C in an ice bath. The diazonium solution was slowly added to the phenolate solution over 30 min. The solution was stirred at 0 °C for 1 h, during which a brown precipitate formed, and then was stirred for 7 h at room temperature. The precipitate was collected and was washed with water and then was poured into water and acidified (pH = 6-7) by addition of diluted HCl. The precipitate obtained was filtered, washed with cool water and recrystallized in EtOH to afford desired product as a brown solid 3 (53 g, 78%). M.p.: 128–129 °C. IR (KBr, cm⁻¹): 3200 (O-H stretch), 3030 (aromatic C–H stretch), 1660 (aromatic aldehyde C=

2.3. (E)-2-(4-Bromobutoxy)-5-(phenyldiazenyl)benzaldehyde (2)

(*E*)-2-hydroxy-5-(phenyldiazenyl)benzaldehyde **3** (2.26 g, 10 mmol), 1,4-dibromobutane (7.1 mL, 60 mmol) and KOH (1.12 g, 20 mmol) were added to absolute EtOH (150 mL) and the mixture was refluxed at 90 °C for 24 h under N₂. The EtOH was removed under reduced pressure. The resulting dark brown residue was dissolved in 200 mL of *n*-hexane and precipitate was filtered off. The excess amount of MeOH was added to orange filtrate solution and cooled in deepfreeze overnight. The orange precipitate was collected and recrystalized using toluene and MeOH to yield orange solid **2** (1.52 g, 42%). M.p.: 145–147 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.83–1.94 (m, 4H), 3.44 (t, 2H, *J* = 5.9 Hz), 4.14 (t, 2H, *J* = 6.7 Hz), 7.17 (d, 1H, *J* = 8.2 Hz), 7.55 (t, 1H, *J* = 7.5 Hz), 7.60 (t, 2H, *J* = 6.9 Hz), 7.92 (d, 2H, *J* = 7.6 Hz), 8.19 (s, 1H), 8.24 (d, 1H, *J* = 7.9 Hz), 10.05 (s, 1H). Anal. Calcd for C₁₇H₁₇BrN₂O₂: C, 56.52; H, 4.74; N, 7.75; Found: C, 56.31; H, 4.57; N, 7.44.

2.4. (E)-2-(4-Mercaptobutoxy)-5-(phenyldiazenyl)benzaldehyde (1)

A solution of (*E*)-2-(4-bromobutoxy)-5-(phenyldiazenyl)benzaldehyde 3 (0.21 g, 0.57 mmol) and thiourea (0.22 gg, 2.89 mmol) in EtOH (10 mL) was heated under reflux for 12 h. After cooling down to r.t, a solution of KOH (0.19 g, 3.47 mmol) in water (10 mL) was then added into the reaction mixture and continued to reflux for another 3 h. The reaction mixture acidified (pH = 1) by addition of diluted HCl (1 N) and then was extracted twice with Et₂O. The organic phase was combined, washed with brine, dried over MgSO₄ and removed. The crude residue was chromatographed over silica gel using a mixture of EtOAc/hexane (1:5) to give thiol 1 as a viscose liquid (0.12 g, 65%). ¹H NMR (500 MHz, CDCl₃): δ 1.41 (t, 1H, J = 7.4 Hz), 1.65–1.84 (m, 4H), 2.55 (q, 2H, J = 7.5 Hz), 4.12 (t, 2H, J = 7.6 Hz), 7.15 (d, 1H, J = 8.1 Hz), 7.52 (t, 1H), 7.57 (t, 2H, J = 7.2 Hz), 7.93 (d, 2H, J = 7.9 Hz), 8.18 (s, 1H), 8.22 (d, 1H, J = 7.9 Hz), 9.90 (s, 1H). Anal. Calcd for C₁₇H₁₈N₂O₂S: C, 64.94; H, 5.77; N, 8.91; Found: C, 64.24; H, 5.37; N, 8.71.

2.5. (E)-4-(2-(6-(4-Nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0] hex-3-en-2-yl)-4-(phenyldiazenyl)phenoxy)butane-1-thiol (**Az-TTP** 1)

3-(4-Nitrophenyl)aziridin-2-yl (phenyl)methanone 7 [34] (0.26 g, 1 mmol), 2 (0.31 g, 1 mmol) and NH₄OAc (0.4 g, 5 mmol) were dissolved in 2 mL of DMF and stirred at r.t. The reaction was completed after overnight. The reaction mixture was filtered, washed with EtOH and dried in air to give orange solid 1 (0.43 g, 76%), M.p.: 168–170 °C. IR (KBr, cm⁻¹): 3066 (aromatic C-H stretch), 2946–2841 (aliphatic C–H stretch), 2558 (–SH stretch), 1598 (C=N stretch), 1510 (NO₂ asymmetric stretch), 1500 (aromatic C=C stretch), 1465 (N=N stretch), 1342 (NO₂ symmetric stretch), 1286 and 1248 (C-O stretch), 739, 691 (aromatic out of plane bend). ¹H NMR (500 MHz, CDCl₃): δ 1.63 (t, 1H, J = 7.5 Hz), 1.78 (m, 2H), 1.94-1.97 (m, 2H), 2.61-2.68 (m, 2H), 2.74 (s, 1H), 3.98 (s, 1H), 4.12 (t, 2H, J = 6.6 Hz), 6.84 (s, 1H), 7.06 (d, 1H, J = 8.2 Hz), 7.43 (t, 1H, J = 7.6 Hz), 7.48 (t, 2H, J = 7.3 Hz), 7.55–7.61 (m, 3H), 7.63–7.67 (m, 2H), 7.75 (d, 2H, J = 7.9 Hz), 7.87 (d, 2H, J = 8.4 Hz), 7.98 (d, 2H, J = 8.8 Hz), 8.25 (d, 2H, J = 8.8 Hz). UV–Vis (EtOH) λ_{max}/nm : 265,



Fig. 2. (a,b) The TEM image of Ag-Az-TTP 1 and Ag-Az-TTP 2, respectively and (c,d) XRD patterns of Ag-Az-TTP 1 and Ag-Az-TTP 2, respectively.

387 nm before and after irradiation. Anal. Calcd for $C_{32}H_{29}N_5O_3S$: C, 68.19; H, 5.19; N, 12.42; Found: C, 68.11; H, 5.36; N, 12.91.

2.6. (E)-4-(2-(6-(3-Nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0] hex-3-en-2-yl)-4-(phenyldiazenyl)phenoxy)butane-1-thiol (**Az-TTP 2**)

Yield: 72% (0.41 g), M.p.: 174–176 °C, yellow solid. IR (KBr, cm^{-1}): 3077 (aromatic C–H stretch), 2978–2838 (aliphatic C–H

stretch), 2555 (-SH stretch), 1598 (C=N stretch), 1529 (NO₂ asymmetric stretch), 1480 (aromatic C=C stretch and N=N stretch), 1347 (NO₂ symmetric stretch), 1251 (C-O stretch), 731, 688 (aromatic out of plane bend). ¹H NMR (500 MHz, CDCl₃): δ 1.64 (t, 1H), 1.78–1.84 (m, 2H), 1.97 (m, 2H), 2.51–2.55 (m, 2H), 2.70 (s, 1H), 3.97 (s, 1H), 4.13 (t, 2H, *J* = 6.7 Hz), 6.84 (s, 1H), 7.07 (d, 1H, *J* = 8.0 Hz), 7.43 (t, 1H, *J* = 7.8 Hz), 7.48 (t, 2H, *J* = 7.7 Hz), 7.76 (d, 2H, *J* = 7.7 Hz), 7.88 (t, 1H, *J* = 7.3 Hz), 8.01 (d, 2H, *J* = 7.8 Hz), 8.09 (s, 1H), 8.21 (d, 1H, H, J = 7.8 Hz), 8.01 (d, 2H, *J* = 7.8 Hz), 8.09 (s, 1H), 8.21 (d, 1H, J)



Fig. 3. FT–IR spectra of **Az-TTP 1** (black line) and **Ag-Az-TTP 1** (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

J = 7.6 Hz), 8.26 (s, 1H). UV–Vis (EtOH) λ_{max}/nm : 254, 373 nm before and after irradiation. Anal. Calcd for $C_{32}H_{29}N_5O_3S$: C, 68.19; H, 5.19; N, 12.42; Found: C, 68.45; H, 5.71; N, 12.23.

2.7. Synthesis of Ag-Az-TTP 1 and Ag-Az-TTP 2

An aqueous solution of AgNO₃ (0.082 g, 0.48 mmol) in ultrapure H₂O (10 mL) was mixed with 0.051 g PVP in 5.0 mL ultrapure H₂O. The mixture was stirred heavily for 30 min in an ice bath under N₂ gas. A solution of Az-TTP 1 or Az-TTP 2 (0.27 g, 0.48 mmol) in toluene (10 mL) was added to the reaction vessel. The two-phase mixture was vigorously stirred for further 30 min. A solution of NaBH₄ (0.018 g, 0.48 mmol) in ultrapure H₂O (6 mL) was added dropwise to the below solution, the color of the aqueous phase suddenly turned bright yellow, attributed to the formation of AgNPs. Then, the color of the aqueous phase turned to red. On complete addition of NaBH₄, the resulting mixture was further stirred for 4 h at r.t under N₂ gas. In this period of time, all of the photochromic ligand was transferred into the aqueous phase, which became deep red and then turned to black color while the organic phase became colorless. The organic layer was evaporated. The residue was poured into EtOH (50 mL) and was kept in a refrigerator overnight. The obtained suspension was then centrifuged at 18,000 rpm for 15 min and the precipitate washed three times with double distilled H₂O to remove any water soluble impurity. After that, the precipitate formed was washed 2-3 times by dispersion and centrifugation using toluene to remove excess organic ligand. The precipitate was then dried in oven at 60 °C for 8 h and the black powder Ag-Az-TTP 1 and Ag-Az-TTP 2 was obtained.

3. Results and discussion

The new azobenzene-thiol-1.3-diazabicvclo-[3.1.0]hex-3-ene derivatives (Az-TTP) were synthesized and used to form selfassembled monolayers (SAMs) on AgNPs surface as shown in Scheme 1. In this effort, aniline **4** was reacted with NaNO₂ in aqueous HCl to give diazonium salt followed by coupling with salicylaldehyde to obtain azosalicylaldehyde 3. The azosalicylaldehyde 3 was alkylated with an excess of 1,4-dibromobutane to obtain the brominated product 2. The brominated product 2 was converted to thiol **1** by reacting with thiourea in basic media. Reaction of thiol **1** with premade ketoaziridine **5** or **6** [34] in the presence of excess NH₄OAc and DMF afforded the desired Az-TTP 1 and Az-TTP 2, respectively. Then, 1.0 equivalent solution of Az-TTP derivatives in toluene was added to 1 equitant solution of AgNO₃ in ultrapure H₂O and PVP as a capping agent stirring under stream of nitrogen gas. Subsequently, a modified Brust reaction [35] was carried out through the addition of excess amount of NaBH₄ as a reducing agent that led to the formation of the selfassembled monolayer on the AgNPs. In order to reduce all of the Ag⁺ ions to metallic silver the molar ratio of metal to the reducing agent was selected as 0.5:1. The prepared Ag-Az-TTP 1 and Ag-Az-TTP 2 exhibit reversible photochromic conversion in the EtOH solution.

3.1. TEM imaging and XRD

The morphology of the **Ag-Az-TTP 1** and **Ag-Az-TTP 2** were investigated by TEM (Fig. 2a and b). The TEM image shows that the particles are fairly uniform in diameter and spherical in shape and the approximate size of the AgNPs was found to be in the range of <40 nm. The phase of the **Ag-Az-TTP 1** and **Ag-Az-TTP 2** was investigated by X-ray diffraction technique. As shown in Fig. 2c and d; the resultant product has shown all the major peaks of metallic silver with *fcc* structure. The mean crystallite diameter using Scherrer's formula was calculated to be 24 and 26 nm, respectively. This value is in good agreement with the TEM image. The intensity of peaks reflected the high degree of crystallinity of the AgNPs.

3.2. FT-IR spectra

In Fig. 3 the FT–IR spectra of **Az-TTP 1** and **Ag-Az-TTP 1** were compared. In both spectra, the similar signals in the CH– (aromatic) and CH₂ (aliphatic) stretch regions at 3066 and 2946–2841 cm⁻¹ of **Az-TTP 1** and 3066 and 2946–2841 cm⁻¹ of **Ag-Az-TTP 1** were observed. The signals at 1510, 1342, 1465 and 1598 cm⁻¹ are attributed to the asymmetric and symmetric stretch of NO₂, N=N



Fig. 4. The UV–Vis spectra of (a) Az-TTP 1 and (b) Az-TTP 2 before and after UV light irradiation for various times in EtoH ($C = 1.0 \times 10^{-4}$ M, 293 K).

 Table 1

 UV-Vis absorption data for photochromic new compounds.

Entry	$\lambda_{\max}(nm)$
Azo-TTP 1	265, 387
Azo-TTP 2	254, 373
Ag-Az-TTP 1	262, 413
Ag-Az-TTP 2	259, 402

and C=N vibration, respectively. The S-H stretching band of neat ligand **Az-TTP 1** was observed at 2558 cm⁻¹. These data and the absence of the S-H stretching mode in the FT-IR spectrum of **Ag-Az-TTP 1**, indicate the existence of **Az-TTP 1** on AgNPs surface [36]. Similar results were observed for FT-IR spectra of **Az-TTP 2** and **Ag-Az-TTP 2** (see supplementary data).

3.3. UV–Vis absorption spectra

Fig. 4 shows the UV–Vis spectra of **Az-TTP 1** and **Az-TTP 2** through irradiation with UV light at 254 nm for various times in EtOH. Before light irradiation, the maximum absorption at 265 and 387 nm for **Az-TTP 1** and 254 and 373 nm for **Az-TTP 2** was observed due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of close-*E*-

photoisomer. After the Az-TTP 1 solution was irradiated under UV light at 254 nm for 20 s (Fig. 4a), the absorption intensity at 265 and 387 nm increased. This attributed to the formation of the open-Ephotoisomer. The open photoisomer band of bicyclic aziridinesis typically near 400 nm [37–40], that also corresponds to the $n \rightarrow \pi^*$ transition of the N=N bond in azobenzene. Following subsequent irradiation under UV light for 80 s, the absorption peak intensity at 265 and 387 nm in the solution increased again (orange line (in web version)) due to the increase of population of open-*E*-photoisomer (Fig. 1). After irradiation for 30 min, the absorption peak intensity at 387 nm increased again. Conversely, absorption peak intensity at 265 nm simultaneously decreased. This implies that the open-Zphotoisomer has been formed. Further irradiation for 60 min, the intensity of absorption band at 265 nm significantly reduced. When comparing the spectra of Fig. 4a and b, similar behavior for Az-TTP 2 was observed. While, the azomethine ylide form of Az-TTP 1 is more stabilized than that of **Az-TTP 2** due to the *p*-NO₂ conjugation effect, which account for the longer wavelength of the visible range absorption maximum (Table 1).

In Fig. 5 the absorption spectra for both of **Ag-Az-TTP 1** and **Ag-Az-TTP 2** in EtOH are shown. Before irradiation, the yellow color solution of **Ag-Az-TTP 1**, with a characteristic strong surface plasmon resonance absorption band (SPRAB) for AgNPs at 413 nm and



Fig. 5. The UV–Vis spectra of (a) Ag-Az-TTP 1 and (b) Ag-Az-TTP 2 before and after UV light irradiation for various times in EtoH ($C = 1.0 \times 10^{-4}$ M, 293 K).



Fig. 6. The growth of the open-Z photoisomer of (a) AZ-TTP 1 at 387 nm, (b) AZ-TTP 2 at 373 nm, (c) Ag-AZ-TTP 1 at 413 nm and (d) Ag-AZ-TTP 2 at 402 nm.



Fig. 7. The UV–Vis absorption spectra of (a) **Az-TTP 1**, (b) **Az-TTP 2**, (c) **Ag-Az-TTP 1** and (d) **Ag-Az-TTP 2** before and after remaining in the oven at 60 °C for various times in EtOH ($C = 1.0 \times 10^{-4}$ M).



Fig. 8. The growth of the close-E photoisomer of (a) AZ-TTP 1 at 387 nm, (b) AZ-TTP 2 at 373 nm, (c) Ag-AZ-TTP 1 at 413 nm and (d) Ag-AZ-TTP 2 at 402 nm.

electronic transitions of the trans isomer at 262 nm and around of the SPRAB due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ showed a red-shifted compared to the absorption band of close-*E*-photoisomer of free **Az-TTP 1**. This shift attributed to the chemical bonding of **Az-TTP 1** on the AgNP surface and overlap between absorption bands of close-*E*-photoisomer with SPRAB. After irradiation for 10 and 20 s, similar to **Az-TTP 1** increase of absorption intensity was detected and on 30–50 s irradiation, absorption intensity band at 262 nm decreases and absorption intensity band at 413 nm increases. These results demonstrated that **Ag-Az-TTP 1** carried out very fast trans \rightarrow cis photoisomerization with 265 nm light within 30–50 s. The same phenomena previously were reported [15,41]. Similar behavior for **Ag-Az-TTP 2** was observed. The intensity of absorption spectra in **Ag-Az-TTP** was small (Fig. 5 vs. Fig. 4). This suggests that the formation of open-*E*-photoisomer and open-*Z*-photoisomer of **Az-TTP** was heavily quenched by AgNPs due to the energy transfer from the **Az-TTP** to the AgNPs and the overlap between absorption of **Az-TTP** and SPRAB of AgNPs [28].

Fig. 6 shows the kinetics of the photoisomerization of AZ-TTP 1 at 387 nm (Fig. 6a), Az-TTP 2 at 373 nm (Fig. 6b), Ag-Az-TTP 1 at 413 nm (Fig. 6c) and Ag-Az-TTP 2 at 402 nm (Fig. 6d) via the corresponding Ln[A] *versus* time plots and the rate constants were calculated to be $0.008 (s^{-1})$ for Az-TTP 1, $0.009 (s^{-1})$ for Az-TTP 2 and 0.012 and $0.011 (s^{-1})$ for Ag-Az-TTP 1 and Ag-Az-TTP 2, respectively. It is clear that an increase in rate (1.5 times) occurs when photochromic ligands are anchored on the AgNP surface.

We have also studied the thermally induced isomerization of photochromic materials. The change in absorption over time for all compounds in EtOH solution that had been isomerized by remaining in the oven at 60 °C is shown in Fig. 7. The $\pi \to \pi^*$ absorption band of the close-*E* photoisomer gains intensity, while the $n \rightarrow \pi^*$ band of the open-Z photoisomer loses intensity. The kinetics of the thermally isomerization of AZ-TTP 1 at 387 nm (Fig. 8a), Az-TTP 2 at 373 nm (Fig. 8b), Ag-Az-TTP 1 at 413 nm (Fig. 8c) and Ag-Az-TTP 2 at 402 nm (Fig. 8d) via the corresponding Ln[A] versus time plots were obtained and the rate constants were calculated to be 0.003 (min⁻¹) for Az-TTP 1 and Az-TTP 2 and 0.013 and 0.019 (min⁻¹) for Ag-Az-TTP 1 and Ag-Az-TTP 2, respectively. A notably increase in constant rate (5-6 times) for AgNPs functionalized was detected. Therefore, both of clos- $E \rightarrow \text{open-}Z$ photoisomerization rate and open- $Z \rightarrow \text{close-}E$ thermal isomerization rate become accelerated when Az-TTP is anchored on the AgNPs surface.

The maximum absorption wavelength of **Az-TTP 1**, **Az-TTP 2**, **Ag-Az-TTP 1** and **Ag-Az-TTP 2** in EtOH are shown in Table 1.

4. Conclusion

Here, photochromic thiol-terminated bicyclic aziridine derivatives with the azobenzene moiety which was applied as a functional agent on AgNPs was successfully synthesized and photochromic properties of AgNPs functionalized have been considered. Absorbance bands of 1,3-diazabicyclo[3.1.0]hex-3ene, azobenzene and SPRAB of AgNPs are matching and appeared typically near 400 nm. The UV–Vis experiments demonstrated that trans→cis photoisomerization rate with 265 nm light and cis→trans thermally isomerization for Ag-Az-TTP 1 and Ag-Az-TTP 2 solutions is noticeably faster than free ligand Az-TTP 1 and Ag-Az-TTP 2 were also shifted as a result of chemical bonding and overlap between absorption bands of Az-TTP with SPRA of AgNPs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.03.014.

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