



# Synthesis and Characterization of Ester Based Azo-Benzene onto the Gold Nanoparticle Surfaces and Their Photo-Switching Ability

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## Abstract

In this paper we have synthesized p-substituted thiol terminal azobenzene liquid crystal embedded with gold nanoparticles and also observed their photoisomerization properties. Different thermal and spectroscopy techniques are used to investigate the synthesized compound properties. The gold nanoparticles surfaces attached thiolated ligand molecules (compound **4**) exhibited smecticA phase. In solution, the synthesized compound shows strong photochromic behaviour. The photosaturation occurred around 9.3 second for compound **4** which indicated *trans*-to-*cis* conversion completely, whereas back relaxation due to *cis*-to-*trans* takes place at 576 minutes. Moreover, the delay back relaxation phenomenon gives us information about storage devices applicability. So, this study might be enhancing the molecular switches application and also be improved the knowledge in the fabrication of optical storage devices.

**Keywords:** Azobenzene; Gold nanoparticles; Photo-isomerisation; Cis-trans isomerisation; Photo-switching

## 1. Introduction

Among the noble metal nanoparticles, gold nanoparticles are the most extensively studied component due to their unique electronic, catalytic and optical properties. In addition, particularly using gold nanoparticles (Au@NPs) to tailor the azo-based liquid crystal properties and has opened up different windows to be applied in several optoelectronic devices and a number of preparation protocols have appeared [1-5]. Compounds with an azo-linkage have received attention due to their unique photo-switchable properties induced by light [6-9]. Azobenzene containing compounds are the most promising materials for photo-switchable devices and photochromic applications. They are highly stable molecules, and a number of structures containing an azo ( $-N=N-$ ) linkage have been reported [10]. For the manipulating of Au@NPs assembly, liquid crystals are the unique choices, as well as their optoelectronic properties for novel nanoscale devices [11-14]. Furthermore, the introducing of Au@NPs may be affected the liquid crystals electrical and optical properties [15]. However, the functionalized Au@NPs could be used as a way to control the alignment of LC molecules and also the effects of textural and alignment properties [16]. Photoswitchable molecules attached to solid surfaces is of a substantial interest for the preparation of advanced nano-systems, leading to a variety of applications, such as information storage, molecular machines, and sensors [17-18].

A recent survey revealed that, p-substituted azobenzene liquid crystals embedded Au@NPs have been reported a very few numbers for photo-switching properties. In this paper, we investigate a new thiol-terminal ester-substituted azobenzene molecules embedded to Au@NPs which exhibits smectic (SmA) phases. Photo

induced effects on this prepared compounds for possible applications in the molecular switches or optical image storing have also been described and may it enhance the properties of optical data storage device and in molecular switches which needs appropriate switching times.

## 2. Materials and Methods

### Materials

Ethyl 4-amino benzoate (Fluka), sodium nitrite (Fluka), phenol (Merck), potassium iodide (Fluka), potassium carbonate (Aldrich), Gold(III) chloride hydrate (Aldrich) and 1, 6-diborobenzene (Fluka) were used. Tetrabutylammonium fluoride (Merck), hexamethyldisilathaine (Merck), silica gel-60 (Merck), tetraoctylammonium bromide (Sigma) and 1-hexanthiol (Sigma) were also used. Other solvents and chemicals were used as received.

### Synthesis

According to the following scheme 1, the desired intermediates and targeted compounds were synthesized. The details synthetic procedure and characterization of ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate (**1**) (yield: 62%). Melting point: 160.2-160.5°C; IR (KBr pellet),  $\nu_{max}$  in  $cm^{-1}$ : 3351 (O-H stretch), 1721 (COOC<sub>2</sub>H<sub>5</sub>), 1601 (aromatic C=C stretch), 1484 (N=N stretch), 1248 (C-O stretch), 1140 (C=C aromatic), 829 (C-H). <sup>1</sup>H (500 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si):  $\delta$  8.12 (d, J=10Hz, 2H, Ar-H), 7.92 (d, J = 5 Hz, 4H, Ar-H), 7.88 (d, J = 5Hz, 2H, Ar-H), 7.14 (d, J = 5 Hz, 2H, Ar-H), 4.42 (q, J = 12.2 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.44 (t, 3H, CH<sub>2</sub>CH<sub>3</sub>) and 1-bromo[4-(4-

acetylphenylazo)phenoxy]alkane (yellow-reddish colored solid compound 2), yield ~60%. IR (KBr),  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3283 (aromatic C–H stretch), 2939 and 2870 (C–H stretching), 1601, 1579 (aromatic C=C stretch), 1489 (N=N stretch), 1270 (C–O stretch).  $\delta\text{H}$  (500 MHz, Chloroform-d, Me4Si)  $\delta$  8.18 (d,  $J = 8.4$  Hz, 2H), 7.92 (dd,  $J = 20.0, 8.7$  Hz, 4H), 7.10 – 6.93 (m, 2H), 4.41 (d,  $J = 7.2$  Hz, 2H), 4.06 (t,  $J = 6.4$  Hz, 2H), 3.44 (t,  $J = 6.8$  Hz, 2H), 2.03 – 1.73 (m, 4H), 1.61 – 1.52 (m, 5H), 1.43 (t,  $J = 7.1$  Hz, 3H) are reported in our published article [19].

Furthermore, to synthesis the thiolated azo-derivative (3), 10mL dry THF was placed in a round bottom flask and dissolved the compound 2. Now a mixture of tetrabutylammonium fluoride (TBAF, 1.3 equiv.) and hexamethyldisilathiane (HMDST, 1 equiv.) in THF (5mL) was added slowly with mild stirring. The mixture was stirred continuously another 12 h, monitor the reaction progress using TLC paper, poured onto dilute aqueous sodium chloride (2 mL; 1 M), and extracted with ethyl acetate (3×20mL). The product yield was 65.5% (compound 3) as a yellowish solid. IR, ( $\nu_{\text{max}}/\text{cm}^{-1}$ ) 2947 (CH<sub>2</sub>), 2870 (CH<sub>2</sub>), 1674 (C=O), 1592, 1480 (C=C, aromatic), 1391 (OH), 1362 (CH<sub>3</sub>), 1245, 1132 (C–O), 844 (CH).  $\delta\text{H}$  NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  8.22 – 7.97 (m, 1H), 7.89 (dd,  $J = 10.6, 8.5$  Hz, 2H), 7.13 (d,  $J = 8.9$  Hz, 1H), 4.08 (t,  $J = 6.5$  Hz, 1H), 2.73 (t,  $J = 7.2$  Hz, 1H, -CH<sub>2</sub>-SH), 1.91 – 1.31 (m, 2H). Now 1-hexanthiol capped gold nanoparticles were synthesized using the biphasic liquid-liquid system method [20]. Detail procedure is illustrated in our earlier publication [21]. Finally, ligand exchange reaction procedure [22] was followed to obtain the target compound 4. Typically hexanthiol decorated gold nanoparticles is dissolved in toluene (5mL) and kept in a 50mL round bottom flask. Then thiolated compound (3) was also dissolved in toluene and added with stirring vigorously and left 24h to complete the exchange procedure. After that the mixture was kept in a refrigerator (-18°C) with excess amount of methanol and obtained the precipitate with methanol using centrifugation and sonication repeatedly. It is confirmed by taking the  $^1\text{H}$  NMR spectra. Yield: 40%, blackish brown colour, mesophase. The purification procedure was carried out until no trace of excess -SH containing liquid crystal could be found in proton NMR spectrum (absence of 1.5ppm peak responsible for SH) and TLC of compound 4.

### 3. Results and Discussion

All the studied compounds illustrated in cheme 1 were confirmed by FTIR,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR. From the FTIR analysis, the absorption bands at ~2870 and 2939  $\text{cm}^{-1}$  assigned C–H symmetric stretching vibration of alkanes means spacer group (-CH<sub>2</sub>-) was successfully introduced to the phenolic compounds 1. The FTIR profile suggested that CH<sub>2</sub> spacer group was successfully attached the phenolic compound 1 means the compound 2 is prepared.

The azo-based liquid crystal compounds decorated with Au@NPs (compound 4) did not show any trace of thiol (absence of the sharp signal at 1.52 ppm) and representative HNMR for compound 4. Followed by column chromatography with silica gel and re-crystallization procedure was maintained to purify the all synthesized compounds.  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses were used to characterize all prepared compounds. The cited alkyl spacer containing azo-mesogens decorated Au@NPs structure was found to be confirmed through the spectroscopic and analytical data in Scheme 1.

A mesomorphic property of the studied compound (4) was observed by polarizing optical microscopy (POM). The hot stage was used to measure the phases with different temperatures and the rate was used at 10°C min<sup>-1</sup>. Figure 1 showing the SmA (smectic) phase of the compound at 83°C. The compound displays typical Batonnets Smectic-A phase upon cooling from the isotropic phase. Therefore, this compound showed the liquid crystal characteristics having SmA phase.

Field emission electron microscopy (FESEM, JEOL, JSM-7800F) was used to obtain the micrographic image of compound 4 and Au

metal particles observed homogeneously distributed. For more evaluation Electron dispersive X-ray spectroscopy (EDX) was used to know the quantitative presence of all elements in the prepared ligand capped Au@NPs. Figure 2 for compound 4 indicates the presence of carbon (43.94 % wt), nitrogen (6.26 % wt), oxygen (14.28 %wt), sulphur (5.58 %wt) and gold (29.95 %wt) composition in the nanomaterials compound. The spectrum also shown the presence of C, N, S, O and Au peaks which indicated that mesogenic azo-compound remains attached to the gold particles surfaces. A similar result was observed and reported for gold nanoparticles [23] and Cu nanoparticles [24].

#### Photoswitching Studies

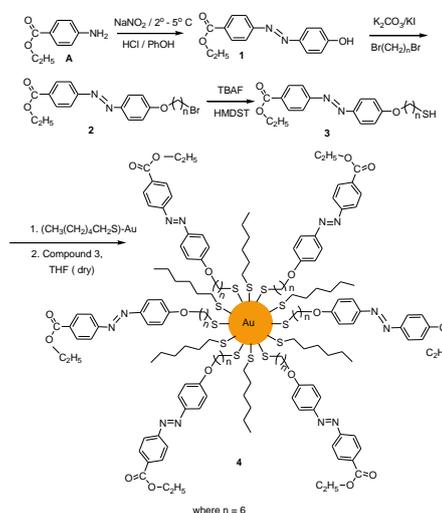
Au@NPs decorated liquid crystal solution ( $C = 1.2 \times 10^{-5}$  mol L<sup>-1</sup>) in THF was used to observe the photo-switching studies. In figure 3, the observed absorption spectra for compound 4 were shown after the UV illumination. At different time intervals, compound 4 was illuminated with UV light with 365 nm filter having intensity 5mW/cm<sup>2</sup> and quickly absorption spectra were recorded. The absorption maximum at 378 nm (responsible for  $\pi$ - $\pi^*$  transition, S<sub>2</sub> state) decreases due to E isomer transformed to Z isomer. After ~9.3 sec illumination, there is no much change in absorption spectrum confirms the saturation of E-to-Z isomerization process.

Now, the solution is shined continuously for reaching photo stationary state (~10sec) and kept in the dark and then at subsequent time intervals spectral data were recorded. Figure 4 shows the Z-to-E absorption for compound 4 as a function of the subsequent time intervals for the back relaxation period. Peak wavelength is plotted as a function of recovery time at 378 nm which obtained from back relaxation absorption spectra. About 576 minutes time was taken to relax back to their original state (cis-to-trans, E/Z) for the compound 4. The lengthening of back relaxation may be due to the multiple attachments of azobenzene moieties onto the Au@NPs surfaces and to be developed of sterically hindered and restricts the free rotation and mobility of molecules within the system [23].

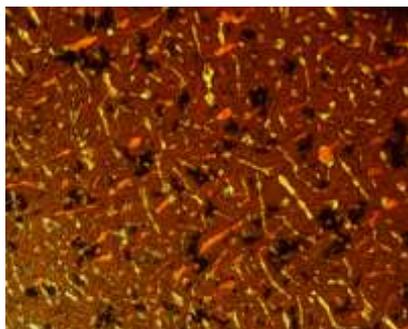
Using the equation (1) reported by Lutfor et al [25] rate constant was also calculated for the trans-cis isomerisation behavior at room temperature for the studied compound.

$$\ln \frac{A_{\infty} - A_t}{A_{\infty} - A_0} = -kt \quad (1)$$

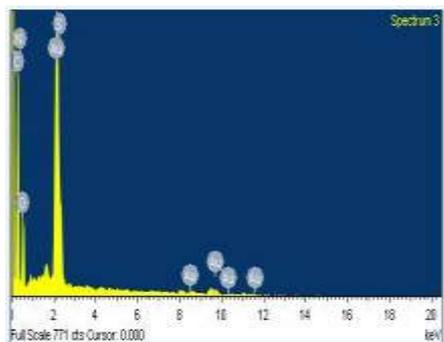
Where, A<sub>0</sub>, A<sub>t</sub> and A<sub>∞</sub> are the absorbance at 378 nm at time zero, time t, and infinite time (photostationary state), respectively. A typical first order plot was observed using the rate equation (1) at 25°C for compound 4 and it also showed first order exponential decay in solutions.



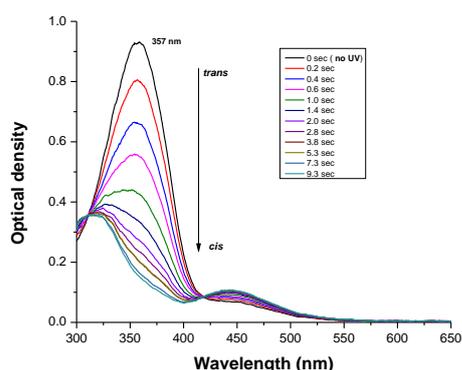
**Scheme 1:** Illustrated the synthetic procedure of the thiol-terminal p-substituted azo-ester embedded gold nanoparticles.



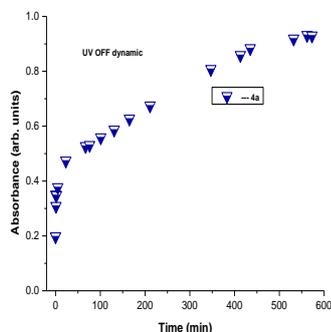
**Figure 1:** Optical textures of compounds **4** on cooling from the isotropic liquids (A) SmA phase Batonnets texture taken at 83°C.



**Figure 2:** Typical EDX micrograph of Au@NPs attached compound **4**.



**Figure 3:** Spectra show the absorbance behaviour of the gold embedded compound **4** when UV light is shined on the sample. Data were taken before shining UV light (NO UV) and with subsequent time intervals.



**Figure 4:** Photoisomerization dynamic curve of Z isomer (**4**) as a function of recovery time when UV light is illuminated until it reaches photo-saturation and followed by measuring back relaxation time.

## 4. Conclusion

We have successfully synthesized and studied the photochromism behaviour of gold decorated p-substituted azobenzene

containing thiol-terminal molecule in solution. The compound shows smectic (SmA) phase irrespective of gold capped mesogen. Moreover, Au@NPs containing azo-based molecule exhibited strong photochromic behaviour. The observed thermal back relaxation about ~ 10 h (576 minutes) value has potential advantage in the field of optical data storage devices. Thus, the presence of the azo-linkage in this liquid crystal molecule is suitable for nanoparticles based optical storage device applications.

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