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Synthesis and characterization of azobenzene-based gold nanoparticles for photo-switching properties

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ABSTRACT

A series of new azobenzene based thiolated liquid crystals modified with gold nanoparticles were synthesized and characterized using a different mode of delegated tools e.g. FTIR, NMR and FESEM–EDX measurements for the structural properties of synthesized compounds. Polarized optical microscopy studies have revealed all the studied compounds having liquid crystalline properties, as a typical nematic phase. These liquid crystal capped gold nanoparticles' size was determined by TEM experiment. In addition, azobenzene-based gold nanoparticles containing flexible spacers showed photochromic behavior upon UV irradiation. These molecules exhibited strong photoisomerisation behavior in solutions and their *trans* to *cis* isomerisation took about 44 s whereas the reverse process almost took place ranging from 82 to 125 min.

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1. Introduction

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 [1–2]. A photoswitchable molecule can be converted from one form to another with light of one wavelength and can either revert thermally to the original state or can be reverted by irradiation with light of a different wavelength. In recent years, the photo-responsive molecules on metal nanoparticle surface has received significant attention due to the opportunity of using switching devices as photo-responsive components in optical storage, switching, photo-switchable surface wettability and molecular recognition applications [3–16]. Moreover, the hybrid or composite nanomaterials consisting of inorganic nanoparticle and photoactive organic molecules may provide light-controlled nano-devices [17–21]. For optical switching applications, one of the most used organic chromophores is mostly azobenzene or its derivatives. Generally, 'azobenzene' refers only to the parent molecule, though the term is now repeatedly used to refer to the entire class of substituted azo molecules. The unique commonality among the azobenzene molecules (azo's) is the clean and efficient photochemical isomerization that can occur about the azo linkage when the chromophore absorbs a photon. Azobenzene, a photochromic T-type system, exhibits a reversible isomerisation process between its *trans* and *cis*

isomers of different stability [22]. In addition, azobenzene containing compounds have two geometric isomers (*Z/E*) around the N–N double bond; the *trans* isomer (*E*) is more stable than the *cis* isomer (*Z*). In this process, without any bond breaking, the photoreaction occurs due to the simple rearrangement of the electronic and nuclear structure of the molecule. The photo isomerism process (*cis* to *trans*) can be carried out either by heating or by irradiation with visible light [23]. The energetically more stable *trans* configuration will turn into the *cis* configuration when UV light of wavelength 365 nm shines on azobenzene systems and reversible to the original configuration is brought about either by keeping it in the dark (terms as called thermal back relaxation) or by illuminating with white light of higher wavelength (450 nm). According to the literature, gold nanoparticles derived using as biological molecules investigation such as DNA, protein have gained much interest in liquid crystal research as biosensor [24].

The present study focuses on the synthesis and photo-isomerization behavior of four new gold nanoparticles (Gold-NPs) decorated azo-based liquid crystals having azobenzene chromophores connected via a flexible–CH₂–spacer. In this paper, substituted azo-derivatives capping thiol groups were employed for the preparation of decorated Gold-NPs and the photoisomerization performance of their solution phase have been investigated by UV–vis absorption spectroscopy. Interestingly, thermal back relaxation of the studied compounds were increased with respect to the flexible spacer size (–CH₂–) increased. The morphology and photo-responsive properties of the gold nanoparticles modified azobenzene derivatives having different flexible spacers were characterized via FESEM and UV/vis spectroscopy. In this article, we report a preparation of the gold nanoparticles cover with a layer of

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photoresponsive azo-based liquid crystals by Au–S covalent bonds and its liquid crystal properties and photo responsive behavior were discussed.

2. Experimental details

2.1. Materials

4-Nitro aniline (Fluka), sodium nitrite (Fluka), phenol (Merck), 1,3-dibromopropane (Fluka), 1,4-dibromobutane (Fluka), 1,5-dibromopentane (Fluka), 1,6-dibromohexane (Fluka), potassium carbonate (Aldrich), Gold(III) chloride hydrate (Aldrich), tetrabutylammonium fluoride (Merck), hexamethyldisilathiane (Merck), tetraoctylammonium bromide, silica gel-60 (Merck) were used as received. Phosphorus pentoxide (Merck) was used to reflux the acetone and distilled out before used. Other solvents and chemicals were used as received.

2.2. Preparation of 4-(4-nitrophenylazo)phenol (**1**)

4-Nitroaniline (10.0 g, 72.4 mmol) was dissolved in methanol (150 mL) and water (30 mL) with 18 mL of conc. hydrochloric acid and the mixture was cooled to 2–5 °C. Sodium nitrite (7.493 g, 108.6 mmol) in water (30 mL) was added dropwise and the mixture was stirred for 1 h. Then phenol (6.813 g, 72.4 mmol) in acetone (100 mL) and water (50 mL) was added and the pH 8–9 was adjusted using sodium hydroxide solution, which was further stirred for another 2 h. Then, dilute hydrochloric acid (ca. 60 mL, 10%) and water (800 mL) were added and the resulting precipitate was collected by filtration. The product, compound **1** was crystallized twice using methanol and ethanol, respectively. A reddish colored solid; yield: 68%. IR (KBr), $\nu_{\max}/\text{cm}^{-1}$ 3429 (O–H stretch), 3283 (aromatic C–H stretch), 1618, 1585 (aromatic C C stretch), 1458 (N N stretch), 1282 (C–O stretch). δ_{H} (500 MHz; CDCl₃; Me₄Si) 8.46 (dd, 4H, Ar–H), 8.08 (d, 2H, Ar–H), 7.97 (d, 2H, Ar–H), 9.40 (s, 1H, Ar–OH).

2.3. 1-bromo-4-(4-nitrophenylazo)phenoxypropane (**2a**)

Compound **1** (2.0 g, 8.23 mmol) was dissolved in dry acetone (110 mL) followed by potassium carbonate (9 g, 82.2 mmol), potassium iodide (30 mg) as well as 10-fold excess of 1,3-dibromopropane (16.61 g, 82.27 mmol) were added and the mixture was refluxed for 24 h under argon. The reaction mixture was filtered at hot state and the acetone was removed under reduced vacuumed pressure. Then, hexane was added to remove excess 1,3-dibromopropane, the product was insoluble in hexane. The product was collected by filtration and was dissolved in dichloromethane and water (1:1). The organic phase was washed with dilute hydrochloric acid (ca. 50 mL, 10%), sodium carbonate solution (ca. 50 mL, saturated) and water successively. The organic fraction was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure. The product (compound **2a**) was re-crystallized from ethanol. Compound **2a**: yellow-reddish colored solid; yield 60%. IR (KBr), $\nu_{\max}/\text{cm}^{-1}$ 3283 (aromatic C–H stretch), 1618, 1585 (aromatic C C stretch), 1458 (N N stretch), 1282 (C–O stretch). δ_{H} (500 MHz; CDCl₃; Me₄Si): 8.37 (d, 2H, Ar–H), 7.98 (d, 4H, Ar–H), 7.05 (d, 2H, Ar–H), 4.23 (t, 2H, OCH₂), 3.64 (t, 2H, CH₂Br), 2.36–2.41 (m, 4H, CH₂).

2.3.1. 1-bromo-4-(4-nitrophenylazo)phenoxybutane (**2b**)

Compound **1** (2.0 g, 8.23 mmol) was dissolved in dry acetone (130 mL) and potassium carbonate (9.09 g), potassium iodide (30 mg) and a 10-fold excess of 1,4-dibromobutane (17.9 g) were added and the reaction was carried out by the same method used for synthesis of **2a**. Work-up procedure was also followed by the same method of **2a**. Solid yellow-reddish colored, yield 65%, mp. 90 °C. IR (KBr), $\nu_{\max}/\text{cm}^{-1}$ 3283 (aromatic C–H stretch), 1618, 1585 (aromatic

C C stretch), 1458 (N N stretch), 1282 (C–O stretch). δ_{H} (500 MHz; CDCl₃; Me₄Si) 8.37 (d, 2H, Ar–H), 7.98 (d, 4H, Ar–H), 7.03 (d, 2H, Ar–H), 4.12 (t, 2H, OCH₂), 3.52 (t, 2H, CH₂Br), 2.08–2.13 (m, 2H, CH₂), 2.00–2.03 (m, 2H, CH₂).

2.3.2. 1-bromo-4-(4-nitrophenylazo)phenoxypropane (**2c**)

Compound **1** (2.0 g, 8.23 mmol) was dissolved in dry acetone (110 mL) and potassium carbonate (9 g, 8 equivalent of compound **1**), potassium iodide (30 mg) and a 10-fold excess of 1, 5-dibromopentane (18.97 g) were added and the reaction was carried out by the same method used for synthesis of **2a**. Compound **2c**, yield 65% as a solid yellow-reddish colored, mp. 91 °C. IR (KBr) $\nu_{\max}/\text{cm}^{-1}$ 3283 (aromatic C–H stretch), 1618, 1585 (aromatic C C stretch), 1458 (N N stretch), 1282 (C–O stretch). δ_{H} (500 MHz; CDCl₃; Me₄Si) 8.37 (d, 2H, Ar–H), 7.97 (d, 4H, Ar–H), 7.02 (d, 2H, Ar–H), 4.09 (t, 2H, OCH₂), 3.46 (2H, t, CH₂Br), 1.89–2.00 (m, 2H, CH₂), 1.85–1.89 (m, 2H, CH₂), 1.66–1.70 (m, 2H, CH₂).

2.3.3. 1-bromo-4-(4-nitrophenylazo)phenoxyhexane (**2d**)

Compound **1** (2.0 g, 8.23 mmol) was dissolved in dry acetone (100 mL) and potassium carbonate (8 g, 82.2 mmol), potassium iodide (20 mg) and a 10-fold excess of 1,6-dibromohexane (20 g, 82.3 mmol) were added and the reaction was carried out by the same method used for synthesis of **2a**. The product, **2d** was re-crystallized from ethanol. Yield 60% as a solid. IR (KBr), $\nu_{\max}/\text{cm}^{-1}$ 3283 (aromatic C–H stretch), 1618, 1585 (aromatic C C stretch), 1458 (N N stretch), 1282 (C–O stretch). δ_{H} (500 MHz; CDCl₃; Me₄Si) 8.30 (d, 2H, Ar–H), 7.95 (d, 2H, Ar–H), 7.88 (d, 2H, Ar–H), 7.03 (d, 2H, ArH), 4.05 (t, 2H, OCH₂), 3.38 (t, 2H, CH₂Br), 1.91–1.94 (m, 4H, CH₂), 1.70 (d, 2H, CH₂).

2.4. Synthesis of thiolated azo-derivatives (**3a–d**)

Compound **2a** (250 mg) was dissolved in dry THF (5 mL). Then a mixture of tetrabutylammonium fluoride (TBAF, 1.3 equiv.) and hexamethyldisilathiane (HMDST, 1 equiv.) in THF was added slowly by stirring. The mixture was stirred for 12 h, poured onto dilute aqueous sodium chloride (2 mL; 1 M), and extracted with dichloromethane (2 × 20 mL). The organic layer was separated and dried over anhydrous sodium sulfate and the solvent was evaporated under vacuum at room temperature, and the product was purified by column chromatography [silica; hexane: ethyl acetate (9:1)] and to yield the thiolated compound **3a**, 150 mg, (~60%) as a solid. Compounds **3b**, **3c** and **3d** were synthesized from compound **2b**, **2c** and **2d**, respectively by the same method used for synthesis of **3a**.

2.5. Synthesis of gold nanoparticles capped with azobenzene moieties (representative compound **4d**)

Synthesis begins by dissolving of tetraoctylammonium bromide (TOAB) (0.577 mmol) in 30 mL of toluene. In the second step, the aqueous solution of 40 mg of hydrogen tetrachloroaurate trihydrate (HAuCl₄·3H₂O) in 20 mL deionized water was prepared at room temperature. The organic solution was poured to the aqueous phase and stirred vigorously. Immediately, a two-layer system was formed. The system was kept stirring until the bottom layer (the aqueous phase) became transparent and the top layer (the organic phase) became orange-brown. This assures the transfer of all Au⁺³ from the aqueous phase into the organic phase. During this reaction step, the phase transfer reagent (TOAB) was transferred all AuCl₄[−] from the aqueous phase to organic layer. The organic phase was washed with distilled water (10 mL) several times, and the organic layer is separated. A solution of thiolated azo-compound, **3d** (0.0084 mmol) in toluene (5 mL) was added to the above solution, and the resulting mixture was stirred for 30 min. An aqueous solution of freshly prepared sodium borohydride (NaBH₄) (40 mg) was then added drop-wise, and the mixture was stirred for another 3 h that resulted in the reduction of AuCl₄[−]

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