

Gold nanoparticle catalysis of the *cis*–*trans* isomerization of azobenzene†Cite this: *Chem. Commun.*, 2013, **49**, 10073Received 5th March 2013,
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Ablated, “pseudo-naked” gold nanoparticles (AuNPs) catalyze the *cis*–*trans* isomerization of substituted azobenzenes. *para*-Substitution was found to affect the rate of isomerization, suggesting the participation of AuNP-mediated electron transfer in the isomerization mechanism.

Azobenzene isomerization has gained considerable interest as a photochromic switch due to its versatile applications in electronics, energy storage and molecular devices.^{1–5} The thermodynamically favoured *trans* isomer is easily converted into the *cis* isomer upon UV-light excitation (Fig. S1, ESI†).⁶ The reverse reaction is somewhat less energetically demanding occurring efficiently at room temperature either through visible light excitation or a thermal mechanism.⁶ In contrast to the structurally similar stilbene, the activation energy for dark (thermal) *cis*–*trans* isomerization is considerably lower (23 kcal mol^{–1}),⁷ occurring readily at room temperature and can be easily monitored using UV-visible spectroscopy.⁸

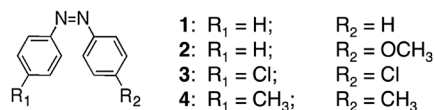
The coupling of photochromic molecules and nanoparticles has been widely studied as a way of developing novel nanoswitches and electronic devices. However, the majority of these studies, in particular those involving AuNPs or gold clusters,^{1,3–6,9,10} have focused on the direct attachment of the photochromic moiety to

the nanoparticle surface and UV or visible irradiation of the azobenzene to induce isomerization. In such cases, the nanostructure is viewed as an external factor and discussion is mainly focused on how photoisomerization of the photochromic component influences nanomaterial properties (*i.e.*, aggregation upon molecular conformational change).^{1,4,10}

In our system, the dark *cis*–*trans* isomerization is readily detected using UV-visible absorption spectroscopy. This communication discusses the propensity for pseudo-naked, ~12 nm spherical, ablated AuNPs, generated photochemically,¹¹ to effectively promote thermal *cis*–*trans* azobenzene isomerization in the dark and examine the effects of *para*-substitution (Scheme 1) on the rate of *cis*–*trans* conversion.

Briefly, the AuNPs were prepared from HAuCl₄ using H₂O₂ as a reducing agent in a process initiated by HAuCl₄ photolysis. This method yields pseudo-naked AuNPs (only Cl[–] left on the surface)¹² that are polymorphic and polydisperse. This can be corrected by 532 nm laser ablation, which in our laboratory we performed using the laser drop technique (Fig. S2, ESI†).^{11,13} For additional details see the ESI.†

Initial studies carried out using azobenzene **1** are presented in Fig. 1. Following the addition of 100 μL of ablated AuNPs (*ca.* 192 pM) to the aqueous azobenzene solution, the absorption spectrum of the photochromic molecule slowly began to change as a function of time. Three isosbestic points at 235, 270 and 380 nm, along with a shift in the maximum absorption wavelength from 295 nm (*cis*) to 320 nm (*trans*) and the disappearance of the 420 nm absorption band, assigned to the *n*– π^* transition of the *cis* isomer, are indicative of efficient *cis*–*trans* azobenzene isomerization.¹⁴ The growth of the *trans* isomer was monitored as a function of time (Fig. 1 inset). From the Fig. 1 inset, the growth of *trans*-azobenzene occurs with a rate constant of $0.14 \pm 0.03 \text{ min}^{-1}$ and is complete



Scheme 1 Molecules to be examined in this work.

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† Electronic supplementary information (ESI) available: Experimental details; *cis*–*trans* azobenzene spectra, SEM of AuNP; control experiments; UV-vis spectra of AuNP over time and in the presence of azobenzene, effects of [AuNP] on *cis*–*trans* isomerization and qualitative simulation of free catalytic site availability for variable AuNP concentrations; batch-to-batch reproducibility. See DOI: 10.1039/c3cc41669k

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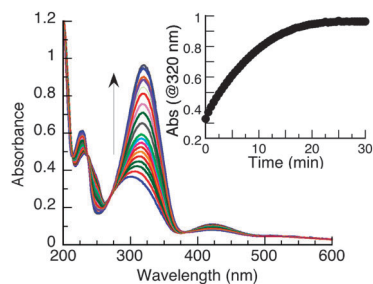


Fig. 1 Time resolved UV-visible spectra of a 48 μM aqueous solution of azobenzene **1** recorded after addition of 100 μL of pseudo-naked AuNPs (ca. 192 pM). Inset illustrates the growth of the *trans* isomer monitored at 320 nm.

after 30 minutes. Control experiments for azobenzene only and in the presence of 3.3 mM H_2O_2 , 33 μM Au^{3+} and 33 μM HCl (Fig. S3, ESI[†]) show no appreciable changes in the absorption spectra, indicating that AuNPs are required to induce the isomerization reaction.

Control experiments were also run in the presence of higher AuNP concentrations (1.92 nM) to allow for observation of the surface plasmon absorption and to access the stability of the AuNP during the isomerization of **1** (Fig. S4b, ESI[†]). Following 15 minutes of reaction, no change in the surface plasmon absorption or aggregation of the AuNPs was observed.

The AuNP-mediated isomerization of *para* substituted azobenzenes **2**, **3** and **4** was also examined to investigate the role of substituents in the isomerization reaction. As shown in Fig. 2, the UV-visible spectra for the (a) 4-methoxy, (b) 4,4'-dichloro and (c) 4,4'-dimethyl substituted azobenzenes show a shift in the absorption maxima of the starting material upon addition of AuNPs to the reaction mixture. For azobenzene **2**, the major absorption band shifts from 320 to 345 nm. Such a remarkable shift in the spectral properties of azobenzene **3** was not observed, where the formation of the *trans* isomer was inferred from the appearance of a shoulder absorption at 390 nm (comparison with standard samples). Isomerization of azobenzene **4** shows the disappearance of the 305 nm *cis*

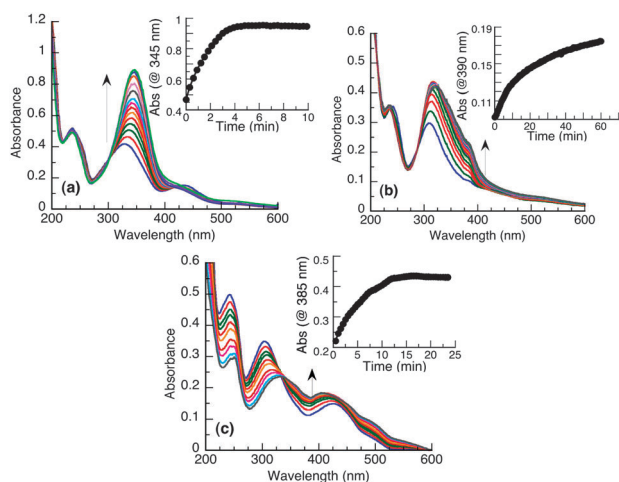


Fig. 2 UV-visible spectra of (a) *cis*-4-methoxyazobenzene (**2**), (b) *cis*-4,4'-dichloroazobenzene (**3**) and (c) *cis*-4,4'-dimethylazobenzene (**4**) in the presence of ablated AuNPs (ca. 192 pM). Insets depict the growth of the *trans* isomers as a function of time monitored at 345 nm for **2**, 390 nm for **3** and 385 nm for **4**.

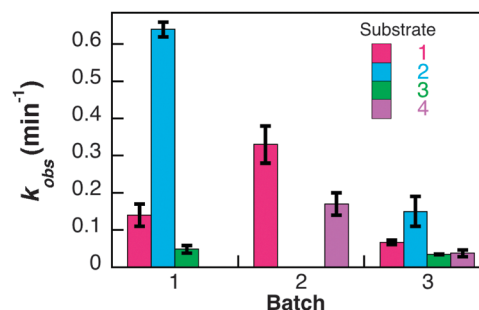


Fig. 3 Catalytic activity of three separate batches of AuNPs prepared at different times, as measured by the kinetics of *cis-trans* isomerization of azobenzenes **1-4**.

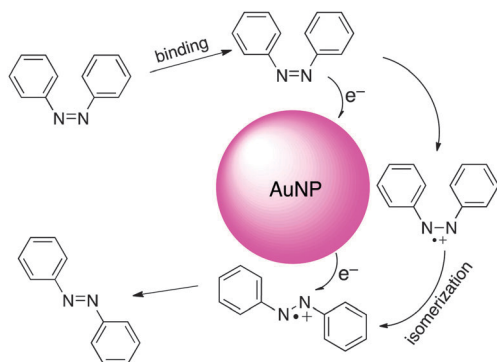
isomer absorption concomitant with a growth of absorption at 385 nm, ascribed to the *trans* isomer. Control experiments, similar to those described above for **1** revealed no observable conversion of the *cis* to *trans* stereoisomers in the absence of AuNPs.

Table S1 (ESI[†]) summarizes the rate constants for isomerization, as well as k_{rel} calculated with respect to **1**. From the k_{rel} values, **2** converts to the *trans* stereoisomer rapidly compared to **1**. Reactivities follow the order $2 \gg 1 > 4 \approx 3$. Several batches of AuNPs were required for the completion of all measurements; these various batches show variability in their catalytic activity, but the order of reactivity remains constant and independent of the absolute activity of the catalyst, see Fig. 3.

Variable catalytic activity among batches of nanoparticles is not unprecedented and has been ascribed to small changes in nanoparticle concentration,¹⁵ age,¹⁶ surface chemistry,¹⁷ reactive binding sites¹⁶ and, as observed in this work, laser beam homogeneity. Two lasers of the same type and age (Surelite II Nd/YAG) gave catalysts with different activities, with the one having the better quality beam giving the better material. Using the concentrated beam from a laser with 'hot spots' we were able to prepare AuNPs virtually devoid of catalytic activity (not included in Table S1, ESI[†]).

As the AuNPs have been deemed essential for the dark isomerization process, their active participation in the isomerization mechanism must be anticipated. From the data presented in Table S1 (ESI[†]) and in Fig. 2 and 3, a faster conversion to the *trans* isomer is observed in the presence of a 4- OCH_3 substituent (*i.e.*; **2**). In contrast, the presence of the two, equivalent *para* substituents (**3** and **4**) slows down the process. In all cases, AuNPs can be considered truly catalytic in nature, since pM concentrations are sufficient to catalyze the reaction.

The specific pathway of azobenzene isomerization has involved discussions of a rotational *versus* inversion-type mechanism about the central $\text{N}=\text{N}$ bond,^{2-4,7,14,18,19} with the latter being favoured. However, *cis-trans* isomerization has been suggested to be largely environment dependent, dictated by both solvent polarity and molecular substituents.^{4,7} AuNPs have long been shown to act favourably as electron sinks and participate in redox reactions.²⁰ The influence of the azobenzene substituents on the rate constants of thermal *cis-trans* isomerization is quite evident. However, electronic substituent effects cannot be the dictating factor, as one would expect a trend where azobenzene **4** ($\sigma_p^{21} = -0.34$)²² would undergo *cis-trans* isomerization the fastest, followed by **2** ($\sigma_p = -0.27$)²² and **3** being the slowest ($\sigma_p = 0.44$),²² considering the additive electronic substituent effects of the di-substituted substrates.²³ Both **3** and **4**



Scheme 2 Proposed mechanism for dark *cis-trans* azobenzene isomerization mediated by pseudo-naked AuNPs.

give similar relative rate constants for isomerization. An additional, and more likely, consideration is the influence of the molecular dipole moment of substrates 2–4 in the AuNP-mediated isomerization pathway. Qualitative evaluation of the dipole moments illustrates that azobenzene 2 should have a strong dipole moment due to the electron donating contributions of the 4-OCH₃ moiety, while azobenzenes 3 and 4 would have similar dipole moments, due to the symmetrical substitution on the aryl rings resulting in an overall electronic contribution close to zero. Given that polarity of a molecule can strongly dictate its interaction with the AuNP surface, azobenzene 2, for example, would be considerably more polar due to its enhanced dipole moment and promote closer proximity and binding to the AuNP surface. The reduced distance between the substrate and catalyst would manifest as accelerated isomerization and more effective electron transfer (eT) between AuNP and azobenzene.

We propose that eT from the catalyst surface plays a key role in the isomerization mechanism (Scheme 2), though the exact role of the AuNPs within the azobenzene activation has yet to be defined. As such, Scheme 2 is used to simply illustrate the participation of eT in the isomerization mechanism. These results suggest an electron transfer from azobenzene to the AuNP, resulting in the formation of an azobenzene radical cation intermediate and supporting a rotational mechanism about the N=N bond, corroborated by the significant effects of the molecular dipole moments and corresponding rate constants (Fig. 3). While such experimental results seem to argue against inversion-type isomerization, typically unaffected by azobenzene functionalization,^{7,19} we note that this is not an ‘azobenzene’ isomerization, but rather a radical-cation reaction where almost all spin density is in the N=N system and virtually none on the aromatic rings.²⁴

Preliminary studies on the effects of AuNP concentration have shown non-linear acceleration of the isomerization in the presence of AuNPs at concentrations of up to 0.5 nM (Fig. S6 and S7, ESI†). The behaviour can be understood qualitatively by assuming that the less soluble *trans* isomer is capable of blocking active catalytic sites as a consequence of a larger association constant with AuNPs compared with the *cis* isomer.

Monodisperse, spherical AuNPs prepared by laser ablation have been shown to effectively promote the thermal *cis-trans* isomerization of azobenzenes in the absence of light. To the

best of our knowledge, this is the first report focusing on AuNP mediated azobenzene isomerization in the absence of direct irradiation of the photochromic moiety. Functionalization of azobenzene and the resultant variations in the molecular dipole moments of the substrates were found to largely influence the isomerization process. These results suggest the participation of strong nanoparticle surface binding and an azobenzene-AuNP electron transfer in the catalytic pathway. Initial eT, followed by azobenzene radical cation formation and rotation about an activated N=N bond is suggested to be the most likely pathway for AuNP-mediated azobenzene *cis-trans* isomerization.

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