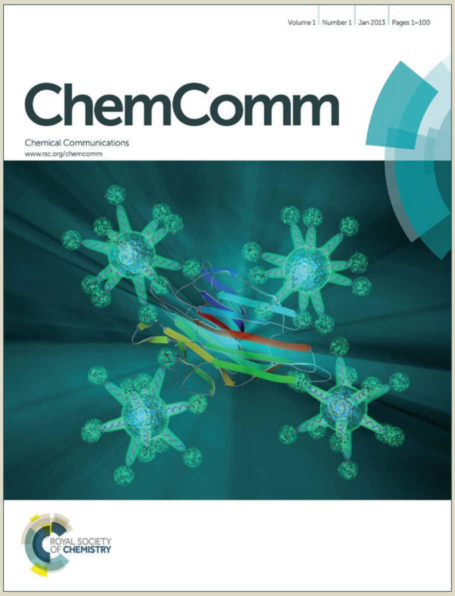
ChemComm

Accepted Manuscript



ROYAL SOCIETY
OF **CHEMISTRY**

www.rsc.org/chemcomm

Journal Name

COMMUNICATION

Reversible Photoisomerization of Azobenzene Molecules on Single Gold Nanoparticle Surface

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

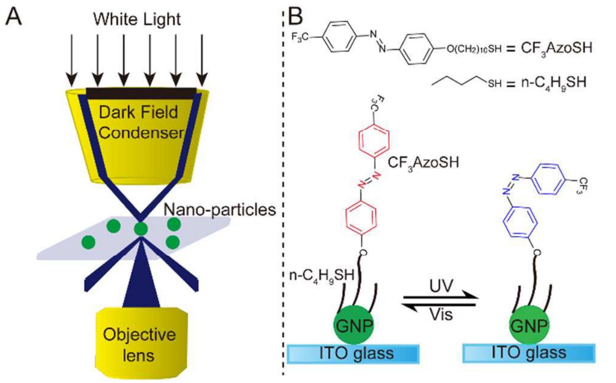
www.rsc.org/

Heng Song, Chao Jing, Wei Ma, Tao Xie, Yi-Tao Long*

We demonstrate reversible photoisomerizaton of azobenzene molecules on a single gold nanoparticle surface with alternating UV and visible irradiation, which is monitored by Plasmon Resonance Rayleigh Scattering spectroscopy and stimulated by discrete-dipole approximation method.

Photochromic switches undergo reversible conformational changes, which affect their structural, electronic, and optical properties in response to photo-stimuli.[1] Photochromic molecules have attracted enormous interests for their versatile property, among them azobenzene is one of the most widely studied photochromic molecules due to its perfect photoisomerization property.[2] The thermodynamically favoured *trans* form is readily converted into the *cis* form upon UV light excitation The reverse reaction occurs easily at room temperature through UV/visible light irradiation. For their excellent optical features, azobenzene and its derivatives have been applied in reversible phase transfer catalysis,[3] self-assembly vesicles,[4] and molecular devices.[5] Placement, addressability become possible once azobenzene molecules are assembled on surface. Therefore, many attempts have been taken to study azobenzene photoisomerization on surface and apply its property to construct functional surface such as controllable wettability surface and reactivated biointerface.[6-8] Scanning tunnelling microscope (STM) tip,[9] contact angle measurement[10] and electrochemistry method[11] are generally applied to monitoring azobenzene molecular reaction and conformation change on surface. According to our knowledge, there are few reports on reversible photoswitch of azobenzene molecules on a single nanoparticle surface. [12] It is a challenge to obtain the signal of hundreds of molecules reaction and conformation change on a single nanoparticle surface. Particularly, plasmonic noble metal nanoparticles including gold, silver and copper, have attracted considerable attentions owing to their unique optical and chemical properties. With the development of dark-field microscopy (DFM), it enables the observation of Plasmon resonance Rayleigh scattering (PRRS) spectroscopy of a single nanoparticle. As the plasmon resonance bands of plasmonics are highly sensitive to the size, shape, and local dielectric environment, PRRS provides a novel method for monitoring molecular reaction,[13] catalyst event,[14] and morphologic variation[15] on single nanoparticle surface. Moreover, photoisomerization of the azobenzene between two conformers provides chemical unit mimics that ascribe to the "0" and "1" states in computers,[16] reversible photoswitch of azobenzene on a single nanoparticle surface may performed as a nano size "write-read" device.

In this communication, we aimed to monitor photoresponsive behaviour of azobenzene molecules on a single gold nanoparticle (GNP) surface. PRRS spectroscopy as a novel technique was used to track the isomerization process of azobenzene molecules upon irradiation by (~365 nm) UV light and (~450 nm) visible light (as shown in scheme 1). Benefitting from the high spatial and temporal resolution, we could easily monitor the nano-environment change surrounding the single GNP surface in real-time. We found that under UV/Vis



Scheme 1 A) Setup of dark-field microscopy and scattering spectroscopy. B) Schematic illustration of photo-induce azobenzene isomerize on a single gold nanoparticle.

---

*Key Laboratory for Advanced Materials & Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, P. R. China. *E-mail: ytlong@ecust.edu.cn*

† Electronic Supplementary Information (ESI) available: [Synthesis and structure characterizations of compounds, additional optical spectra]. See DOI: 10.1039/x0xx00000x

irradiation, the isomerization of azobenzene molecules on GNP surface between *trans* and *cis* form would induce the scattering spectra peak red and blue shift respectively. The spectral shift may be due to that the conformation change of azobenzene molecules caused the change of local environment surrounding the GNP surface. Furthermore, Discrete-dipole approximation (DDA) simulations[17] were performed to verify the relationship between these photoresponsive process on GNP surface and the corresponding scattering spectra shift. The good agreement between calculation and experimental results suggests that this local environment change surrounding the GNP surface is resulted from the reversible photoisomerization of azobenzene molecules.

To realize the photocontrolled monolayer on a single GNP surface, we synthesized the azobenzene derivatives 10-(4-(4-trifluoromethylphenyldiazenyl)phenoxy)decane-1-thiol (shown in Scheme 1, denoted CF_3AzoSH, the synthesis method described in ESI†). The principle of photo-induced azobenzene molecules isomerize on a single GNP surface is outlined in Scheme 1. GNP was selected as the substrate to maintain the CF_3AzoSH molecules, due to that it could form stable Au-S bond (as showed in Figure S2 of the ESI†) and has perfect photostability property. In addition, the PRRS spectroscopy of single GNP is proportion to the local refractive index.[18] Upon irradiation of UV light, the CF_3AzoSH molecules transform from *trans* to *cis*, which would enhance the refractive index of the local environment surrounding the GNP surface inducing the spectral red shift. When exposure to visible light, the *trans* CF_3AzoSH molecules convert to *cis* isomer, the local environment surrounding the GNP surface would closely recover back to the initial state with spectral blue shift. Thus, it is possible to monitor the reversible isomerization process of CF_3AzoSH molecules on a single GNP surface by tracing the scattering spectra of corresponding particle.

As shown in Figure 1, the CF_3AzoSH molecules exhibited perfect reversible photoswitch property in ethanol solution, upon UV irradiation of CF_3AzoSH solution there was a remarkable change of the absorption spectra. Continuous UV irradiation the absorption band at 352 nm got further decreased. In the meantime, the absorption band at 440 nm increased slightly. For the absorption band at 352 and 440 nm are attributed to π-π* and n-π* transitions of CF_3AzoSH molecules respectively. This change of spectral clearly exhibits the isomerization of CF_3AzoSH molecules from *trans* to *cis* isomer. When exposure to visible light, the π–π* absorption recovered back with a slight decrease in the n–π* absorption, which shows that CF_3AzoSH molecules transformed from *cis* to *trans* state. Upon repeated alternating irradiation by UV and visible light, this reversible photoisomerization process in solution could be recycled by several times.

Most studies of azobenzene molecules switch have been carried out in solution, in which azobenzene molecules are randomly distributed without orders, on single GNP surface azobenzene molecules could form self-assembled monolayer and be addressed separately. To modify dispersed azobenzene molecules, a spacer molecules n-C_4H_9SH was selected. We applied the following procedure to form the mixed self-assembled monolayers (SAMs) of n-C_4H_9SH/CF_3AzoSH on GNP surface. GNPs with an average diameter of 60 nm were immobilized on ITO glass slide to act as substrate. Then immersing of the ITO glass slide in octane-1-thiol ethanol solution for 5 min to take up some sites of GNP surface. After that, immerse the above treated substrate in CF_3AzoSH ethanol solution for 24 hours. Finally, rinse the prepared slides with ethanol for several times to remove the free CF_3AzoSH molecules to obtain a mixed monolayers. The mixed monolayers of GNP provides more free space for photoisomerization of CF_3AzoSH molecules between *trans* and *cis* form on GNP surface.

In order to address this bulky photoreaction could take place on the single GNP surface, scattering spectra of single GNP was employed to monitoring the photoresponsive behaviour of CF_3AzoSH molecules on a single GNP surface under UV/Vis irradiation (Figure 2A). Scattering spectra were

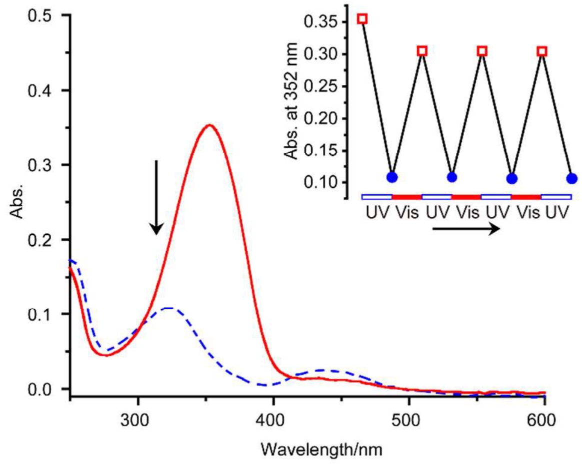


Figure 1 UV/Vis spectra of CF_3AzoSH ethanol solution before (red solid line) and after (blue dash line) UV irradiation (c=1.25 × 10^{-5}M). Inset the changes of CF_3AzoSH molecules absorption band at 352 nm upon alternating irradiation by UV and visible light. The concentration of CF_3AzoSH is 1.25 × 10^{-5}M.

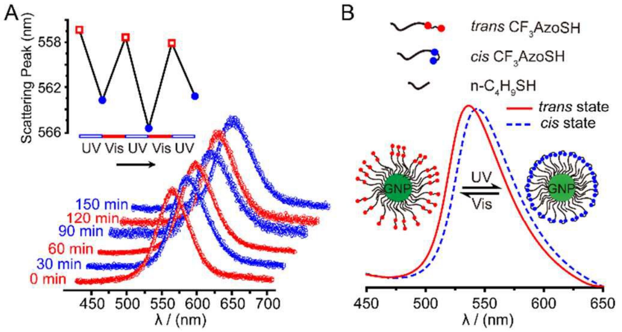


Figure 2 A) The reversible shift of Plasmon resonance Rayleigh scattering spectra of single mix n-C_4H_9SH/CF_3AzoSH functionalized GNP (60 nm) obtained at different times upon alternating irradiation by UV and visible light (from bottom to top 0, 30, 60, 90, 120, 150 min). Inset The reversible shift of scattering spectra peak of single mix n-C_4H_9SH/CF_3AzoSH functionalized GNP (60 nm) obtained at different times upon alternating irradiation by UV and visible light. B) The simulation model of CF_3AzoSH molecules photoisomerizing on a single GNP surface and the corresponding simulated scattering spectra of the model.

recorded at 30 min interval between 0 min and 150 min during reversible light control by repeated UV/Vis irradiation. Before light irradiation, the scattering spectra peak of the n-C_4H_9SH/CF_3AzoSH SAMs modified GNP was 557 nm. After exposure to UV light (~365 nm) for 30 min, its scattering spectra peak red shifted to 563 nm. This should be attributed to the increasing of surrounding refractive index induced by the molecules conformation change as shown in Figure 2B. After continuous UV irradiation, there was no further red shift of scattering spectra. After exposure to visible light, spectral blue shift of GNP was observed, which suggests that visible light induced the local environment surrounding the GNP nearly recovered back to the initial state. Upon repeated alternating irradiation by UV and visible light, the $\Delta\lambda_{max}$ of scattering spectra were 6~7 nm (as showed in Figure 2A inset). Meanwhile, in the same conditions the $\Delta\lambda_{max}$ of scattering spectra of n-C_4H_9SH modified GNP were 1~2 nm (see in Figure S3 of the ESI†). This reversible shift of scattering spectra might due to the reversible photoisomerization of CF_3AzoSH molecules on GNP surface between *trans* and *cis* isomer, which caused the change of dielectric constant of the SAMs immobilized on GNP surface.

To verify the plasmon resonance scattering spectra reversible shift is corresponding to the photoisomerization of CF_3AzoSH molecules on GNP surface, we performed careful calculation to simulate this process. Considering the dielectric environment of core/shell system have been extensively studied by discrete-dipole approximation (DDA) method,[19] and the dielectric constant **m** of the model in Figure 2B |**m**| < 2,[17] we chose DDA method to simulate the scattering spectra (the calculation detail see in ESI†). The mixed self-assembled monolayers (SAMs) of n-C_4H_9SH/CF_3AzoSH was considered to be the shell cover the finite metal core, the incident light went through the shell medium to the metal core surface and been converted into the localized surface plasmon resonance oscillations. Therefore, the CF_3AzoSH molecules in the SAMs transformed from *trans* to *cis* upon the UV irradiation, which would change the thickness and refractive index of the shell. The change of dielectric constant **m** of shell medium would cause the scattering spectra shift. The calculation results suggested that when CF_3AzoSH molecules on GNP surface isomerized from *trans* to *cis* state with UV irradiation, the scattering spectra of GNP would red shift (Figure 2B), which is in good agreement with the experimental results. This indicated that CF_3AzoSH molecules could reversibly photoisomerize on single GNP surface and alter the refractive index of the surrounding environment.

In order to further confirm the photoisomerization process of CF_3AzoSH molecules on GNP surface. surface-enhanced Raman spectroscopy (SERS) was performed according to the published method.[20] As shown in Figure S4 in the ESI†, after exposure the sample to UV irradiation for 30 min, the intensity of the entire SERS spectra decreased compared with the initial SERS spectra of CF_3AzoSH molecules. In addition, the peaks at 1571, 1171 and 1110 cm^{-1} that may be ascribed to *trans* isomer became weak and some new peaks at 1531, 1138 and 1130 cm^{-1} may be ascribed to *cis* isomer occurrence. After irradiation by visible light for 30 min, the intensity of the entire SERS spectra of CF_3AzoSH molecules got some recovered and concomitantly the peaks of SERS spectra at 1571, 1171 and 1110 cm^{-1} nearly recovered back, and meanwhile, the peaks at 1531, 1138 and 1130 cm^{-1} disappeared. These results demonstrated the photoisomerization process of CF_3AzoSH molecules on GNP surface is convinced.

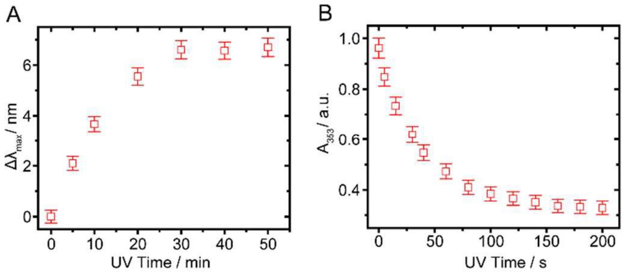


Figure 3 A) The peak shift of scattering spectra of single mix n-C_4H_9SH/CF_3AzoSH functionalized GNP (60 nm) obtained in increasing irradiation time by UV light. B) UV/Vis spectra absorbance measured at 353 nm (A_{353}) during the course of *trans–cis* isomerization of CF_3AzoSH molecules in solution.

To get further insights into the relationship of the photoisomerization process and scattering spectra shift. The scattering spectra of mix n-C_4H_9SH/CF_3AzoSH functionalized GNP at different UV irradiation time were studied. As shown in Figure 3A, the scattering spectra gradually red shift as the UV irradiation went on during 50 min. The rate change trend of scattering spectra red shift occurred similarly with the change of photoisomerization rate of CF_3AzoSH molecules in solution (Figure 3B). Furthermore, the kinetic constant of scattering spectra red shift is 4.39 $min^{-1}/10^2$, that is about 36 times less than the photoisomerization kinetic constant of CF_3AzoSH molecules in solution (k_p = 2.67 $s^{-1}/10^2$).[21] Which intrinsically reflects the quench effect for photoisomerization of CF_3AzoSH molecules from the GNP surface. The results reveal that the rate of scattering spectra red shift should be dependent on the kinetic of CF_3AzoSH molecules transformed from *trans* to *cis* isomer on GNP surface.

To prove this method not confined to CF_3AzoSH molecule model and address the effect of substituent group trifluoromethyl, the azobenzene derivatives 10-(4-(phenyldiazenyl)phenoxy)decane-1-thiol was synthesized (denoted AzoSH, the synthesis method described in ESI†) to study its photoisomerization process on a single GNP surface based on PRRS spectra. From the scattering spectra in Figure S6, we know the reversible photoisomerization of AzoSH molecules on a single GNP surface could also cause the reversible shift of scattering spectra. The $\Delta\lambda_{max}$ of scattering spectra were 4~5 nm less than the scattering spectral change of mix n-C_4H_9SH/CF_3AzoSH functionalized GNP. This result could be attributed to the substituent group trifluoromethyl increased the refractive index surrounding the GNP surface which induced the red shift of scattering spectra of GNPs. Thus, CF_3AzoSH functionalized GNPs showed more obvious scattering peak shift and enhanced the signal to noise ratio compare with AzoSH functionalized GNPs.

In conclusion, we designed and studied photoresponsive behaviour of CF_3AzoSH molecules on individual GNP surface. The results suggested that the reversible photoisomerization process of CF_3AzoSH molecules on single GNP surface is relative to the single-particle spectra reversible shift. Furthermore, the experimental observations could be explained well via theoretical models using DDA simulations. In addition, from the rate of scattering spectra red shift, we could constitutionally illustrate the photoisomerization kinetic of CF_3AzoSH molecules on a single GNP surface and the quench effect from the GNP surface. Besides, this method not prohibited to the model molecule CF_3AzoSH and could also be applied to study the photoisomerization process of other azobenzene molecules on single GNP surface. The findings of this investigation demonstrate PRRS spectroscopy has great potential in studying molecular behaviour at single nanoparticle level. Moreover, the study of photoisomerization process on single nanoparticle level offers great importance in developing nano size "write-read" devices.

This research was supported by the National Natural Science Foundation of China (21421004, 21327807), and Fundamental Research Funds for the central Universities (Grant 222201313004) Y.-T. Long thanks the support by Shanghai Science and Technology Committee (12JC1403500) and Eastern Scholar at Shanghai Institutions of Higher Learning.

Notes and references

1 F. M. Raymo and M. Tomasulo, Chem. Soc. Rev., 2005, **34**, 327–336.
2 (a) H. M. D. Bandara and S. C. Burdette, Chem. Soc. Rev., 2012, **41**, 1809–1825; (b) Z. F. Liu, K. Hashimoto and A. Fujishima, Nature, 1990, **347**, 658–660; (c) K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki, Langmuir, 1988, **4**, 1214–1216; (d) T. Ikeda and O. Tsutsumi, Science , 1995, **268**, 1873–1875; (e) T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi and A. Kanazawa, Adv. Mater., 2003, **3**, 201–205.
3 L. Peng, M. You, C. Wu, D. Han, I. Öçsoy, T. Chen, Z. Chen and W. Tan, ACS Nano, 2014, **8**, 2555–2561.
4 (a) W. Su, Y. Luo, Q. Yan, S. Wu, K. Han, Q. Zhang, Y. Gu and Y. Li, Macromol. Rapid Commun., 2007, **28**, 1251–1256; (b) Q. Jin, G. Liu, X. Liu and J. Ji, Soft Matter, 2010, **6**, 5589–5595; (c) Y. Liu, C. Yu, H. Jin, B. Jiang, X. Zhu, Y. Zhou, Z. Lu and D. Yan, J. Am. Chem. Soc., 2013, **135**, 4765–4770.
5 (a) W. Browne and B. Feringa, Nat. Nanotechnol., 2006, **3**, 25–35; (b) G. Pace, V. Ferri, C. Grave, M. Elbing, C. von Hänisch, M. Zharnikov, M. Mayor, M. A. Rampi and P. Samorì, Proc. Natl. Acad. Sci. U. S. A., 2007, **104**, 9937–9942; (c) J. M. Mativetsky, G. Pace, M. Elbing, M. A. Rampi, M. Mayor and P. Samorì, J. Am. Chem. Soc., 2008, **130**, 9192–9193.
6 (a) X. J. Feng and L. Jiang, Adv. Mater., 2006, **18**, 3063–3078; (b) S. Wang, Y. Song and L. Jiang, J. Photochem. Photobiol. C Photochem. Rev., 2007, **8**, 18–29.
7 (a) P. Wan, Y. Wang, Y. Jiang, H. Xu and X. Zhang, Adv. Mater., 2009, **21**, 4362–4365; (b) D. Liu, Y. Xie, H. Shao and X. Jiang, Angew. Chem. Int. Ed., 2009, **48**, 4406–4408.
8 (a) B. K. Pathem, S. a Claridge, Y. B. Zheng and P. S. Weiss, Annu. Rev. Phys. Chem., 2013, **64**, 605–630; (b) V. Ferri, M. Elbing, G. Pace, M. D. Dickey, M. Zharnikov, P. Samorì, M. Mayor and M. A. Rampi, Angew. Chem. Int. Ed., 2008, **120**, 3455–3457.
9 M. Alemani, M. V Peters, S. Hecht, K.-H. Rieder, F. Moresco and L. Grill, J. Am. Chem. Soc., 2006, **128**, 14446–14447.
10 (a) O. Nachtigall, C. Kördel, L. H. Urner and R. Haag, Angew. Chem. Int. Ed., 2014, **53**, 9669–9673; (b) A. M. Masillamani, S. Osella, A. Liscio, O. Fenwick, F. Reinders, M. Mayor, V. Palermo, J. Cornil and P. Samori, Nanoscale, 2014, **6**, 8969–8977.
11 (a) Y. Qin, L. Xu, J. Ren, Y. Liu and E. Wang, Chem. Commun., 2011, **47**, 8232–8234; (b) I. Willner, V. Pardo-Yissar, E. Katz and K. T. Ranjit, J. Electroanal. Chem., 2001, **497**, 172–177.
12 R. Klajn, J. F. Stoddart and B. A. Grzybowski, Chem. Soc. Rev., 2010, **39**, 2203–2237.
13 (a) Y. Liu and C. Z. Huang, ACS Nano, 2013, **7**, 11026–11034; (b) L. Shi, C. Jing, W. Ma, D.-W. Li, J. E. Halls, F. Marken and Y.-T. Long, Angew. Chem. Int. Ed., 2013, **52**, 6011–6014; (c) P. F. Gao, B. F. Yuan, M. X. Gao, R. S. Li, J. Ma, H. Y. Zou, Y. F. Li, M. Li and C. Z. Huang, Sci. Rep., 2015, **5**, 15427; (d) C. Novo, A. M. Funston and P. Mulvaney, Nat. Nanotechnol., 2008, **3**, 598–602.
14 Y. Khalavka, J. Becker and C. Sönnichsen, J. Am. Chem. Soc., 2009, **131**, 1871–1875.
15 N. Grillet, D. Manchon, E. Cottancin, F. Bertorelle, C. Bonnet, M. Broyer, J. Lermé and M. Pellarin, J. Phys. Chem. C, 2013, **117**, 2274–2282.
16 T. Niazov, B. Shlyahovsky and I. Willner, J. Am. Chem. Soc., 2007, **129**, 6374–6375.
17 B. T. Draine and P. J. Flatau, J. Opt. Soc. Am. A, 1994, **11**, 1491–1499.
18 W. Wang and N. Tao, Anal. Chem., 2014, **86**, 2–14.
19 (a) V. Amendola, O. M. Bakr and F. Stellacci, Plasmonics, 2010, **5**, 85–97; (b) X. Xu, Z. Yi, X. Li, Y. Wang, X. Geng, J. Luo, B. Luo, Y. Yi and Y. Tang, J. Phys. Chem. C, 2012, **116**, 24046–24053; (c) P. K. Jain, S. Eustis and M. a El-Sayed, J. Phys. Chem. B, 2006, **110**, 18243–18253; (d) T. R. Jensen, M. L. Duval, K. L. Kelly, A. a. Lazarides, G. C. Schatz and R. P. Van Duyne, J. Phys. Chem. B, 1999, **103**, 9846–9853.
20 (a) Y. B. Zheng, J. L. Payton, C.-H. Chung, R. Liu, S. Cheunkar, B. K. Pathem, Y. Yang, L. Jensen and P. S. Weiss, Nano Lett., 2011, **11**, 3447–3452; (b) J. H. Yoon and S. Yoon, Phys. Chem. Chem. Phys., 2011, **13**, 12900–12905; (c) S. I. Yang, K.-H. Kim, D. Kang and S.-W. Joo, Photochem. Photobiol. Sci., 2009, **8**, 31–33.
21 T. Asano and T. Okada, J. Org. Chem., 1986, **51**, 4454–4458.

Graphical Abstract:

Reversible Photoisomerization of Azobenzene Molecules on Single Gold Nanoparticle Surface

By **Heng Song, Chao Jing, Wei Ma, Tao Xie, Yi-Tao Long***

PRRS spectra of single gold nanoparticles shows a reversible shift towards the photoswitchable reaction, which could be verified by DDA simulations.