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Au nanoparticle scaffolds modulating intermolecular interactions among the conjugated azobenzenes chemisorbed on curved surfaces: tuning the kinetics of *cis*–*trans* isomerisation†

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π–*π* Intermolecular interactions among adjacent conjugated azobenzenes chemisorbed on (non-)flat Au surfaces can be tuned by varying the curvature of the Au nanoparticles. Here we show that such interactions rule the thermal *cis*–*trans* isomerization kinetics, towards a better control on the azobenzene bistability for its optimal integration as a responsive material.

Photo-switchable molecular systems have attracted great attention in the past few decades due to their tuneable physical and chemical properties paving the route towards their application as switches in (nano)devices and as key components for the fabrication of adaptable/dynamic materials.[1] Among them, azobenzenes are popular scaffolds due to their efficient and reversible photo-isomerisation from a thermodynamically stable *trans* form to a metastable *cis* form. For any potential technological application of azobenzene the rate of isomerization between the two isomers is a crucial characteristic to be controlled. Such a rate is known to depend on the electronic nature of the substituents,[2] the molecular geometry,[3] the solvent,[4] the physical state of the molecule, *etc*. When chemisorbed on Au planar and non-planar surfaces, electronically coupled azobenzenes have been reported not to show isomerization due to the interaction between the surface plasmon resonance (SPR), in particular in the case of gold nano-

particles, and the excited electronic states of the azobenzene, resulting in the quenching of the latter ones.[5] In the case of azobenzene chromophores arranged perfectly perpendicular to the Au surface in highly ordered self-assembled monolayers (SAMs), quenching is less efficient and the optically triggered *trans*–*cis* isomerization can occur. Intermolecular interactions between neighbouring azobenzene molecules in a condensed phase can be expected to play a decisive role in their isomerization, although this aspect is still experimentally unexplored. Moreover, a major limitation for the use of azobenzene in electronics is the metastable nature of the *cis* isomer that can rapidly undergo back-isomerization to the thermodynamically stable *trans* form. Controlling the kinetics of such a back-isomerization process is therefore of great importance.

Here we show that the kinetics of the back *cis* to *trans* isomerization in azobenzene chemisorbed on Au nanoparticles with different sizes depends on the interactions between individual adjacent molecules in the condensed phase of a SAM which can be tuned by modifying the size of the Au nanoparticle acting as a structural scaffold.

In order to gain a direct insight into the role of intermolecular interactions, in particular among the first nearest neighbour molecules, in the *trans*–*cis* isomerisation, we have chosen a thiolated azobenzene derivative (AZO) able to form tightly packed SAMs on planar[6] and non-planar[7] Au surfaces. The AZO molecule has shown an *ca.* 4 times more stable *cis* phase when chemisorbed forming tightly packed SAMs on Au(111) when compared to solution.[6] The observation of an increased stability of the *cis* isomers in SAMs has been rationalized by the presence of π–π interactions between neighbouring azobenzene molecules.[8] A number of researchers including Grzybowski and Klajn have recently demonstrated that SAMs chemisorbed on Au nanoparticles exhibit properties which are dependent on the nanoparticle size, *i.e.* on the curvature of the surface.[9] In the present work, we demonstrate that the AuNP scaffold can be used to regulate the kinetics of *cis* to *trans* isomerization in a fully conjugated azobenzene derivative forming a tightly packed chemisorbed SAM on its surface.

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Unravelling the mechanism ruling such isomerization moreover represents a fundamental step towards the understanding of the switching behaviour in azobenzene materials.

We focussed our attention on two azobenzene-modified Au nanoparticles differing in their size (3 and 15 nm, named AZOAuNP1 and AZOAuNP2, respectively; see Fig. 1) in order to explore the size-dependent properties and the dependence on the curvature, *i.e.* spacing between neighbouring molecules. We previously reported details on their synthesis and characterization.[7] Starting from alkyl-amine AuNPs of the corresponding size as precursors, the coating molecules were substituted with AZO and the obtained particles subsequently dispersed in toluene. These particles exhibit the peculiar characteristic of being photochemically tunable between two different physical states, one featuring a large aggregation (corresponding to the *trans* state), and one exhibiting a colloidal dispersion in an organic medium (toluene, when in the *cis* state).[7] Fig. 1 shows a sketch of the employed systems.

Proton nuclear magnetic resonance (^{1}H-NMR) analysis of these two differently coated nanoparticles revealed different chemical shifts of the azobenzene's aromatic protons depending on their size (Fig. S1 in the ESI†) providing evidence for their dissimilar chemical environment. This experimental result, together with the theoretical and high resolution microscopic reports by other groups,[10] made it possible to model the real geometric shape of the nanoparticles not as a perfectly hairy sphere, but rather as a sphere coated with polycrystalline architectures. The size of the crystalline domains within which the molecule interacts by π–π stacking thus strongly depends on the NP size.[11]

Since the system undergoes simultaneous isomerisation (having a known first order kinetics) and aggregation (having unknown order kinetics) the concentration of azobenzenes on the AuNPs undergoing irradiation was kept constant. The temperature of the solution was stepwise increased up to 95–100 °C to ensure complete dissolution of the as-synthesized *trans*-AZOAuNPs (Fig. S2†). Samples featuring equal absorbances in the *trans* state were then prepared since no dependence of the extinction coefficient of the azobenzene on the curvature was found.
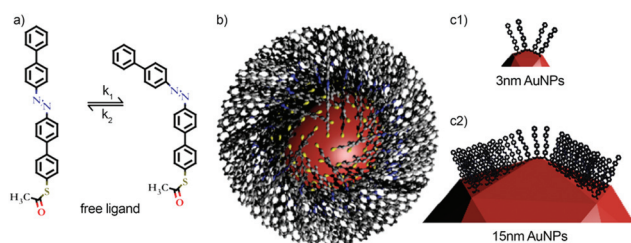
Different complementary techniques including ^{1}H-NMR, UV-Vis and Surface Enhanced Raman Spectroscopy (SERS) were employed to prove the reversible and over-time reliable switch of the AZO molecules grafted on the AuNP surfaces. Albeit the UV-Vis technique allows the monitoring of the SPR band while irradiating, it does not provide easy access to the isomerisation state of the coating AZO moieties because of the spatial overlap of the peaks attributed to the AZO in the *trans* and *cis* form. On the other hand, the ^{1}H-NMR enables the identification of the AZO isomers separately (at least for the molecules dissolved in solution) but (i) it cannot give information on the SPR of the AuNP, (ii) the integral dependence on the actual amount of molecules is still debated,[12] and (iii) the spectra of the different nanoparticles depend drastically on their sizes to an extent that no isolated peaks for the smaller particles could be obtained. In addition, SERS experiments can provide evidence for the switching but, due to the different aggregation among the adjacent NPs, it cannot provide reliable integrals to be compared.

Although the use of the aforementioned techniques singularly does not offer sufficient information making it possible to achieve full characterization, the complementary use of all of them allows the full characterization of the hybrid system and enables a timescale cross-checking of the results obtained. Fig. 2 shows different spectra corresponding to the *cis* and the *trans* forms. The kinetic rate constants were evaluated *via* UV-Vis spectroscopy. The time required for the acquisition of each spectrum, at the chosen concentrations, was *ca.* 3 min.

All the systems showed a reversible first order kinetic behaviour (Fig. S6†). The reaction was monitored under UV irradiation and in the dark to evaluate the stability of the *cis* phase in the dark. First the kinetics of the precipitation process was studied giving overall bigger precipitation rates for larger AuNPs. The investigation of a system subjected to physical state variation is a great challenge. However, if one takes into account different aspects involved, including the concomitant azobenzene switch and aggregation/disaggregation, together with an in-depth statistical analysis, the acquisition of reliable results is possible. While irradiating different processes can occur such as (i) the sudden disaggregation of individual nanoparticles more external in the overall cluster, or (ii) the simultaneous disaggregation of smaller aggregates of AuNPs from the biggest ones, both phenomena causing great
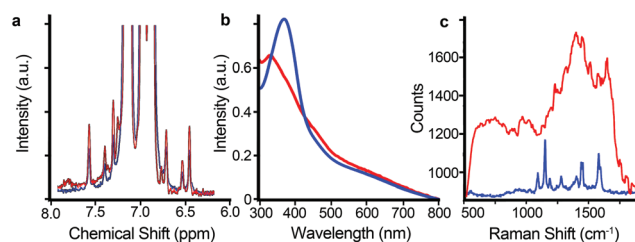

Fig. 1 (a) 4′-[(1,1′-Biphenyl)-4-yl]diazenyl-(1,1′-biphenyl)-4-ethanethioate (acetyl protected AZO) reaction between the *trans* (left) and the *cis* (right) forms and kinetic constants involved. (b) Cartoon of AuNPs. (c1) Sketch of the π-stacking on a 3 nm sized particle, and (c2) sketch of the π-staking on a 15 nm sized particle.

Fig. 2 (a) ^{1}H-NMR, (b) UV-Vis, (c) SERS for the *trans* (blue) and the *cis* (red) isomerization states of the AZO molecule when coating with AuNP1.

variation of UV-Vis spectral features. The same processes, but involving aggregation steps, can take place when the reversed isomerization from *cis* to *trans* is considered. The kinetics of the precipitation process being variable with the nanoparticles' size, a normalization for the integral of the SPR was used to guarantee a comparison of an equal amount of AZO on the surface (Fig. S3–S6†), thereby ensuring an accurate determination of the *cis* to *trans* ratio in the system. From the absorbance at the maximum wavelength of the *trans*, which changes from sample to sample, and through the subtraction of the absorbance of the SPR at the same wavelength, it was possible to obtain the graphs of the different concentrations *vs.* time (Fig. S6†). From the concentration *vs.* time plots one can estimate the kinetic constants involved in the process (k_1 and k_2); in our particular case, in view of the characteristics of the system, only the back *cis* to *trans* kinetic constant (k_2) could be fully determined. (Fig. S6†). The precipitation kinetics in the early stage regime show a different behaviour compared with the overall process, although the trend with the size is consistent over the whole process. Since at the early stage the system is more dependent on the actual interaction among the molecules and less subjected to other external phenomena such as temperature changes and aggregation, the early stage has been considered in this work.

Fig. 3 displays the comparison between the obtained *cis* to *trans* kinetic constants with those obtained in the case of a SAM absorbed on flat gold. Higher variability was found for the azobenzene absorbed on flat gold (error bar not shown) and for the larger gold nanoparticles considered due to the smaller concentration of azobenzene in the optical pathway giving higher variability from measurement to measurement, and due to the high heterogeneity of the system. The error presented takes into account both the standard deviation between

different samples and the fitting error. The graph reveals a correlation between the kinetic constant and the size of the nanoparticles. This means that the kinetic constant can be modulated by varying the size of the crystalline domains, therefore it depends on the spatial extension of π–π stacking between the azobenzene molecules. This proves that the higher thermal stability of the *cis* form for the SAM absorbed on flat surfaces can be attributed to the extended π–π stacking between the adjacent molecules due to the intrinsic nature of the molecules involved. It is also important to mention an opposite trend between different sized nanoparticles for what concern the precipitation kinetics. This opposite behaviour might be a reason why direct evaluation of the rate of the reaction results not being possible.

The precipitation rate has also been calculated by extracting the SPR integral at each period in time to prove that in the chosen timescale the isomer state (*cis vs. trans*) of the AZO coating the two NP sizes is associated with the different relaxation mechanisms and not with mechanical/weight related reasons. The two precipitation processes are, in fact, absolutely equivalent in the early stage of the reactions (an example of the spectra from which the data were extracted is reported in the ESI in Fig. S3†).

Due to the complexity of the system under investigation a giant statistical analysis has been carried out. Out of the overall 25 full kinetics tested under the same conditions, 68% (17) complies with the behaviour described here. Both processes exhibit for early reaction times a linear behaviour following a first order (or pseudo first-order kinetic law). For longer times a quasi-linear behaviour is shown but with a different slope, indicating different stages in the process.

Conclusions

In summary, we have carried out a quantitative analysis that provided unambiguous evidence for the key role played by intermolecular interactions in the kinetics of the *cis–trans* isomerization in azobenzene SAMs exhibiting a variable size of the crystalline domains. We found a variation of the precipitation kinetics of the nanoparticles depending on their size and, most importantly, a trend for the *cis* state stability depending on the degree of π–π stacking. These results are particularly relevant in view of the key role played by weak interactions in physical processes such as light-switching, thereby providing additional proof of the importance of achieving full control over the self-assembly of single molecules as a route to modulate the macroscopic properties of a responsive material. Future effort in our laboratories will be addressed to the unravelling of the cooperative nature of the isomerisation process.
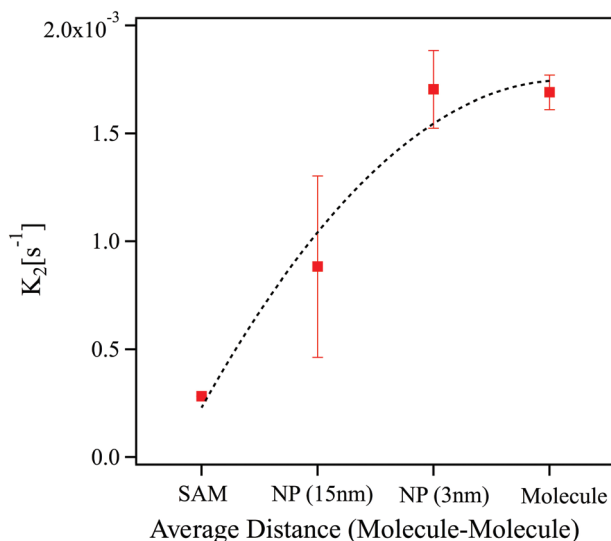

Fig. 3 Dependence of the k_2 kinetic constant on the π-stacking distance between the adjacent azobenzene molecules, from higher (SAM on flat gold) to lower (molecule solvated).

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Notes and references

1 (a) A. C. Fahrenbach, S. C. Warren, J. T. Incorvati, A. J. Avestro, J. C. Barnes, J. F. Stoddart and B. A. Grzybowski, *Adv. Mater.*, 2013, **25**, 331–348; (b) A. C. Coleman, J. M. Beierle, M. C. A. Stuart, B. Macia, G. Caroli, J. T. Mika, D. J. van Dijken, J. W. Chen, W. R. Browne and B. L. Feringa, *Nat. Nanotechnol.*, 2011, **6**, 547–552; (c) M. Mas-Torrent, C. Rovira and J. Veciana, *Adv. Mater.*, 2013, **25**, 462–468; (d) R. Klajn, J. F. Stoddart and B. A. Grzybowski, *Chem. Soc. Rev.*, 2010, **39**, 2203–2237; (e) M. M. Russew and S. Hecht, *Adv. Mater.*, 2010, **22**, 3348–3360.

2 K. Gille, H. Knoll and K. Quitzsch, *Int. J. Chem. Kinet.*, 1999, **31**, 337–350.

3 K. Janus, J. Sworakowski and E. Luboch, *Chem. Phys.*, 2002, **285**, 47–54.

4 J. Garcia-Amoros, A. Sanchez-Ferrer, W. A. Massad, S. Nonell and D. Velasco, *Phys. Chem. Chem. Phys.*, 2010, **12**, 13238–13242.

5 R. Klajn, *Pure Appl. Chem.*, 2010, **82**, 2247–2279.

6 M. Elbing, A. Blaszczyk, C. von Haenisch, M. Mayor, V. Ferri, C. Grave, M. A. Rampi, G. Pace, P. Samorì, A. Shaporenko and M. Zharnikov, *Adv. Funct. Mater.*, 2008, **18**, 2972–2983.

7 C. Raimondo, F. Reinders, U. Soydaner, M. Mayor and P. Samorì, *Chem. Commun.*, 2010, **46**, 1147–1149.

8 G. Pace, V. Ferri, C. Grave, M. Elbing, C. von Hanisch, M. Zharnikov, M. Mayor, M. A. Rampi and P. Samorì, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 9937–9942.

9 (a) K. P. Browne and B. A. Grzybowski, *Langmuir*, 2011, **27**, 1246–1250; (b) T. Zdobinsky, P. S. Maiti and R. Klajn, *J. Am. Chem. Soc.*, 2014, **136**, 2711–2714.

10 (a) B. R. Cuenya, *Thin Solid Films*, 2010, **518**, 3127–3150; (b) A. Mayoral, H. Barron, R. Estrada-Salas, A. Vazquez-Duran and M. Jose-Yacaman, *Nanoscale*, 2010, **2**, 335–342; (c) J. Patel, L. Nemcova, P. Maguire, W. G. Graham and D. Mariotti, *Nanotechnology*, 2013, **24**, 245606.

11 (a) O. Balmes, J. O. Malm, N. Pettersson, G. Karlsson and J. O. Bovin, *Microsc. Microanal.*, 2006, **12**, 145–150; (b) M. T. Kumara, B. C. Tripp and S. Muralidharan, *Chem. Mater.*, 2007, **19**, 2056–2064; (c) V. Petkov, Y. Peng, G. Williams, B. H. Huang, D. Tomalia and Y. Ren, *Phys. Rev. B: Condens. Matter*, 2005, **72**, 195402.

12 (a) A. Badia, W. Gao, S. Singh, L. Demers, L. Cuccia and L. Reven, *Langmuir*, 1996, **12**, 1262–1269; (b) O. Kohlmann, W. E. Steinmetz, X. A. Mao, W. P. Wuelfing, A. C. Templeton, R. W. Murray and C. S. Johnson, *J. Phys. Chem. B*, 2001, **105**, 8801–8809; (c) A. C. Templeton, S. W. Chen, S. M. Gross and R. W. Murray, *Langmuir*, 1999, **15**, 66–76; (d) R. H. Terrill, T. A. Postlethwaite, C. H. Chen, C. D. Poon, A. Terzis, A. D. Chen, J. E. Hutchison, M. R. Clark, G. Wignall, J. D. Londono, R. Superfine, M. Falvo, C. S. Johnson, E. T. Samulski and R. W. Murray, *J. Am. Chem. Soc.*, 1995, **117**, 12537–12548; (e) X. Liu, M. Yu, H. Kim, M. Mameli and F. Stellacci, *Nat. Commun.*, 2012, **3**, 1182.