Uni- and bi-directional light-induced switching of diarylethenes on gold nanoparticles†

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Photochromic studies of diarylethenes with their switching unit linked to the surface of gold nanoparticles *via* a conjugated aromatic spacer show linker-dependent switching behavior.

A major challenge of molecular electronics is to design useful devices based on addressable molecular structures and to incorporate these into integrated circuits.[1] As a result of decades of research into this area substitutes for conventional switches,[2a] rectifiers,[2b] wires[2c] and transistors[2d,e] have been introduced. The necessity to respond to external stimuli places molecular switches among the most challenging systems.[3] Photochromic molecular switches[3] meet this requirement, and specifically 1,2-dithienyl-ethenes hold a prominent position among others because of their reversible photo-induced transformations that modulate electrical conductivity and their exceptional thermal stability and fatigue resistance.[4]

Despite the noticeable progress in designing new molecular electronic components their incorporation into integrated circuits remains a challenge. A common approach is based on anchoring molecules to metal electrodes.[2b,5] However, in the case of photochromic molecules, the situation is more complicated since the presence of a metal surface may influence optical processes in photoactive molecules.[6] Recently we and others published experimental and theoretical papers[7] focused on photochromic and electronic properties and very recently on the electrochemical properties[8] of diarylethenes at the interface of metallic electrodes. Switching behavior depends critically on the nature, length and position of the spacer linking the switching unit to the anchoring group. Uni- or bi-directional switching has been observed. This triggers the demand for a fast and reliable method to test the photochromic properties of molecules attached to a metal. Here we show that monolayer-protected metallic nanoparticles[9] may help us to explore events happening at the molecule–metal interface. These systems hence fill the gap between ordinary solution-phase measurements and highly advanced molecular device techniques demanding expensive and time-consuming nanofabrications.

We report a study of the photochromic properties of three different dithienylethene derivatives, anchored to gold

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nanoparticles showing spacer-dependent uni- and bi-directional light-induced switching. In a recent paper dealing with the photochemistry of dithienylethenes attached to gold nanoparticles,[10] the photochromic unit was isolated from the metal core to some extent by an alkyl chain. The same held for related studies concerning other types of photoswitches.[11] However, to make molecular switching devices feasible, low on-state resistances (and high on–off ratios) are essential. This requires a certain level of communication between the metal electrodes and the switching unit. Therefore, we decided to explore the photochromism of molecules with an anchoring sulfur atom which is connected to the switching unit *via* an aromatic spacer in a linearly- or cross-conjugated fashion (Scheme 1 and 2). In particular, assembly of these molecules on gold nanoparticles provides a useful model system mimicking molecule–gold electrode interactions.‡
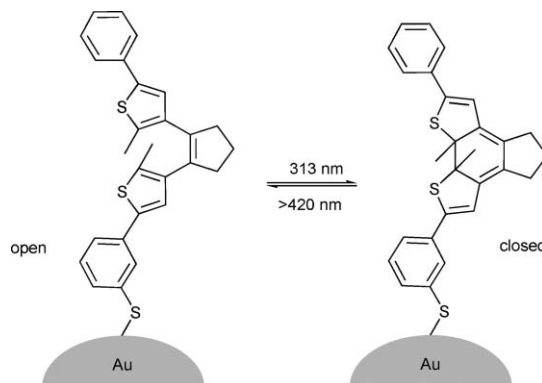
Scheme 1 Photoisomerization between **1o**- and **1c**-anchored on gold nanoparticles.
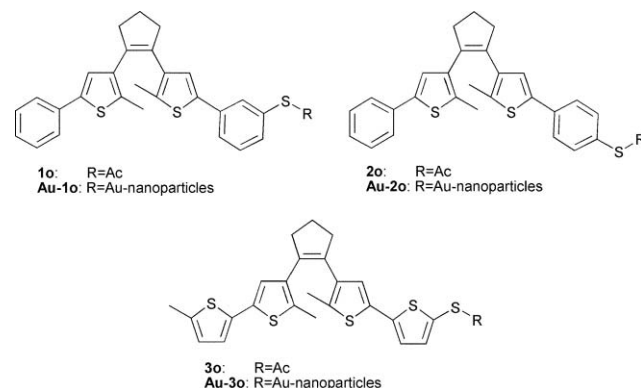
Scheme 2 Molecular structures and molecule-capped nanoparticle systems used in this study.

Molecular switches **1**–**3** (Scheme 2) used in this work all contain the central dithienyl cyclopentane part responsible for light-driven transformations. In order to achieve better switching properties,[4] conjugation is extended by an aromatic moiety on each side of the central switching unit. Variation of *meta*- or *para*-substituted benzene rings in compounds **1** and **2**, respectively, and a thiophene group in compound **3** provides slight modifications in the final electronic structure of the switch. All three compounds display a typical photochromic behavior when present freely in solution. Initial colourless open isomers in toluene turn coloured when exposed to light with a wavelength of 313 nm (see the solution spectra in the ESI†). Similarly, an inverse process occurs upon irradiation with light above 420 nm and the original open isomers are regained, thus demonstrating the reversibility of the whole process.§ Monolayer-protected gold nanoparticles were prepared by a modified Brust's two-phase procedure.[12] Acetyl-protected thiol groups of compounds **1**–**3** in both open and closed forms were deprotected with ammonium hydroxide in THF under an inert atmosphere immediately before the nanoparticle preparation in order to avoid an undesired oxidative dimerization. The preparation itself was performed in a mixture of toluene and water containing HAuCl$_4$, tetraoctylammonium bromide (TOAB), deprotected thiol and NaBH$_4$. Purification of nanoparticle samples is essential since any traces of unbound switches could affect the photochemical experiments. Multiple precipitation or size-exclusion chromatography were employed to obtain a clean sample of nanoparticles free from thiols and TOAB. Although both methods lead to a high purity, the multiple precipitation results in significant losses due to the partial solubility in appropriate solvents. The functionalized nanoparticles have an average diameter of 2 nm, as established by transmission electron microscopy (TEM; see ESI†). The nature of the organic shell encapsulating the nanoparticles was confirmed by reflection FT-IR spectroscopy, showing similar spectral band characteristics compared to those of unattached molecules.

Fig. 1a shows the absorption spectra of the **Au-1o** cluster in toluene (see Scheme 2). Its absorption is a superposition of the spectral bands of the organic shell and a broad absorption of the gold colloids, extending from the UV into the visible region. An additional absorption at 525 nm corresponds to the surface plasmon absorption which is typical for gold nanoclusters of 2 nm diameter in dimension.[13] Upon irradiation with light of 313 nm, the visible spectral band increases and a new maximum is found at 558 nm, indicating the formation of the closed isomer. Compared with the unbound molecules, the ring-closure process is less efficient. The quantum yield of this process was found to be 0.07, which should be compared with 0.4 for the unattached molecule.[14] Spectral characteristics and light-induced transformations of **Au-2o** (Fig. 1b) are similar to those observed for **Au-1o** with the same quantum yield. The absorption profile of **Au-3o** (Fig. 1c) resembles the absorption profiles of **Au-1o** and **Au-2o** with a UV absorption maximum at 336 nm. Contrary to **Au-1o** and **Au-2o**, cluster **Au-3o** does not show any absorption changes after the irradiation of 313 nm light. The quantum yield of ≪0.01 reflects this observation.¶ This indicates that each excitation of the molecules, arising from light absorption, is effectively quenched by the presence of the gold core and does not lead to the photoreaction.

In contrast to the ring-closure process, ring-opening does not vary going from phenyl to thiophene spacer. All three clusters
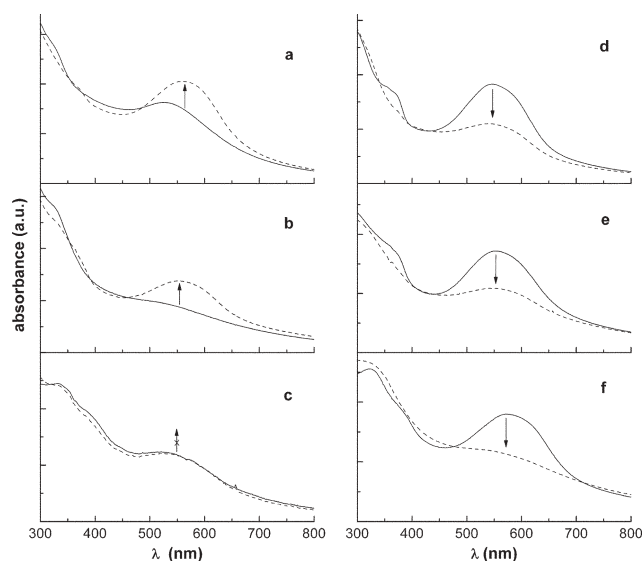
Fig. 1 UV/Vis spectra of a) **Au-1o**, b) **Au-2o** and c) **Au-3o** measured in dry toluene before (—) and after (---) irradiation at 313 nm. UV/Vis spectra of d) **Au-1c**, e) **Au-2c** and f) **Au-3c** measured in dry toluene before (—) and after (---) an irradiation at >420 nm.

Au-1c, **Au-2c** and **Au-3c**‖ exhibit a decrease in absorption around 560 nm (Fig. 1d–f), demonstrating that opening of the switching unit takes place.

Nevertheless, the efficiency of the ring-opening process is also influenced and slowed down compared with molecules in solution, just as was observed in the case of ring-closure of **Au-1o** and **Au-2o**. A number of factors probably contribute to this phenomenon including a reduced effective interaction with light due to the restricted motion in a packed monolayer and a deteriorated transparency of the medium due to the presence of light absorbing clusters. However, the most important contribution is presumably partial and, in the case of the **Au-3o** ring-closure, complete quenching of the excited state. Quenching of the excited states of organic chromophores anchored to gold nanoparticles is well known and is usually atributed to resonance energy transfer.[9b,15] In energy transfer the efficiency of the process is related to the strength of the coupling between chromophores. This strength is determined by the proximity of energy states. As the HOMO–LUMO gap of **3** is expected to be smaller, compared with **1** and **2**,[7b] we can reasonably assume that its LUMO lies closer to the lowest unoccupied orbital of gold nanoparticles, so that mixing is stronger. We suggest that this effect is at the origin of the differences in the observed switching quantum yields. More detailed studies of the quenching mechanism are currently under investigation. The fact that ring-closure of **Au-1o** and **Au-2o** has the same quantum yield indicates that the effect of linear- *versus* cross-conjugated attachment does not play an important role in the switching enhancement on gold.

In conclusion, photochromic behavior of diarylethenes directly linked to gold nanoparticles *via* an aromatic spacer has been investigated. Depending on the spacer, uni- (**3**) or bi-directionality (**1**,**2**) has been observed. This demonstrates that small changes in the molecular structure can have an enormous impact on the overall photochemistry. More generally, it shows that monolayer-protected gold colloids form a convenient tool for

fast screening of properties of functional molecules grafted on gold surfaces.

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Notes and references

‡ The solubility of nanoparticles in some organic solvents and a relatively high ratio between molecules and gold atoms enables easily accessible analytical tools such as absorption spectroscopy to be employed.

§ The absence of absorption in the visible region for the open form, together with the fact that a ring-closure has a typically larger quantum yield[3] allows high selectivity for a ring-closure (providing a photostationary state with undetectable amounts of the open isomer as determined by proton NMR) and complete selectivity for ring-opening.

¶ Further attempts to employ light with different wavelengths ranging from 220 nm to even far visible wavelenghts in order to overcome an unexpected inhibition of the photoreaction, failed.

‖ Closed forms of **1**, **2** and **3** were prepared by irradiation in solution before grafting on gold nanoparticles (for more details see ESI†).

1 C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541–548; R. L. Carroll and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2002, **41**, 4378.
2 (*a*) S. Fraysse, Ch. Coudret and J.-P. Launay, *Eur. J. Inorg. Chem.*, 2000, 1581–1590; B. Jousselme, P. Blanchard, N. Gallego-Planas, E. Levillain, J. Delaunay, M. Allain, P. Richomme and J. Roncali, *Chem.–Eur. J.*, 2003, **9**, 5297; (*b*) M.-K. Ng and L. Yu, *Angew. Chem., Int. Ed.*, 2002, **41**, 3598–3601; (*c*) N. Robertson and C. A. McGowan, *Chem. Soc. Rev.*, 2003, **32**, 96–103; (*d*) H. Yu, Y. Luo, K. Beverly, J. F. Stoddart, H.-R. Tseng and J. R. Heath, *Angew. Chem., Int. Ed.*, 2003, **42**, 5706–5711; (*e*) A. Babel and S. A. Jenekhe, *J. Am. Chem. Soc.*, 2003, **125**, 13 656–13 657.
3 *Molecular switches*, ed. B. L. Feringa, Wiley, Weinheim, Germany, 2001.
4 M. Irie, in *Molecular switches*, ed. B. L. Feringa, Wiley, Weinheim, Germany, 2001, pp. 37–62; M. Irie, *Chem. Rev.*, 2000, **100**, 1685; H. Tian and S. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85.
5 C. Kergueris, J.-P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga and C. Joachim, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 12 505–12 513; M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänisch, D. Beckmann and M. Fisher, *Angew. Chem., Int. Ed.*, 2003, **42**, 5834–5838.
6 K. W. Kittredge, M. A. Fox and J. K. Whitesell, *J. Phys. Chem. B*, 2001, **105**, 10 594; A. Ishida, Y. Sakata and T. Majima, *Chem. Commun.*, 1998, 57.
7 (*a*) D. Dulić, S. J. van der Molen, T. Kudernac, H. T. Jonkman, J. J. D. de Jong, T. N. Bowden, J. van Esch, B. L. Feringa and B. J. van Wees, *Phys. Rev. Lett.*, 2003, **91**, 207 402; S. J. van der Molen, H. van der Vegte, T. Kudernac, I. Amin, B. L. Feringa and B. J. van Wees, *Nanotechnology*, 2006, **17**, 310; J. He, F. Chen, P. A. Liddell, J. Andréasoon, S. D. Straight, D. Gust, T. A. Moore, A. L. Moore, J. Li, O. F. Sankey and S. M. Lindsay, *Nanotechnology*, 2005, **16**, 695; N. Katsonis, T. Kudernac, M. Walko, S. J. van der Molen, B. J. van Wees and B. L. Feringa, *Adv. Mater.*, 2006, **18**, 1397–1400; (*b*) J. Li, G. Speyer and O. F. Sankey, *Phys. Rev. Lett.*, 2004, **93**, 248 302; (*c*) G. Speyer, J. Li and O. F. Sankey, *Phys. Status Solidi B*, 2004, **241**, 2326; M. Zhuang and M. Ernzerhof, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **72**, 073 104.
8 R. Baron, A. Onopriyenko, E. Katz, O. Lioubashevski, I. Willner, S. Wang and H. Tian, *Chem. Commun.*, 2006, 2147–2149.
9 (*a*) M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293–346; (*b*) K. G. Thomas and P. V. Kamat, *Acc. Chem. Res.*, 2003, **36**, 888–898.
10 K. Matsuda, M. Ikeda and M. Irie, *Chem. Lett.*, 2004, **33**, 456–457.
11 J. Zhang, J. K. Whitesell and M. A. Fox, *Chem. Mater.*, 2001, **13**, 2323–2331; A. Manna, P.-L. Chen, H. Akiyama, T.-X. Wei, K. Tamada and W. Knoll, *Chem. Mater.*, 2003, **15**, 20–28; J. Hu, J. Zhang, F. Liu, K. Kittredge, J. K. Whitesell and M. A. Fox, *J. Am. Chem. Soc.*, 2001, **123**, 1464–1470.
12 T. Teranishi, S. Hasegawa, T. Shimizu and M. Miyake, *Adv. Mater.*, 2001, **13**, 1699–1701.
13 M. J. Hostetler, J. E. Wingate, C.-J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans and R. W. Murray, *Langmuir*, 1998, **14**, 17–30.
14 Details of the procedure used for quantum yield measurement can be found in P. R. Hania, R. Telesca, L. N. Lucas, A. Pugzlys, J. van Esch, B. L. Feringa, J. G. Snijders and K. Duppen, *J. Phys. Chem. A*, 2002, **106**, 8498.
15 E. Dulkeith, A. C. Morteani, T. Niedereichholz, T. A. Klar, J. Feldmann, S. A. Levi, F. C. J. M. van Veggel, D. N. Reinhoudt, M. Möller and D. I. Gittins, *Phys. Rev. Lett.*, 2002, **89**, 203 002.