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Nano-electronic switches: Light-induced switching of the conductance of molecular systems

Tibor Kudernac, Nathalie Katsonis, Wesley R. Browne* and Ben L. Feringa*

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This Highlight reviews recent advances in developing light-controlled molecular switches that can be of use for molecular and organic electronics.

Introduction

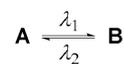
Perhaps the most basic of molecular devices is a molecule that can be switched^{1,2} between states of low and high conductivity, *i.e.* on/off functionality. The recent announcements by Stoddart, Heath and coworkers³ of a 160-kilobit memory based on 'wired-up' organic molecular switches, and of Blom, de Boer and Feringa⁴ of a light-driven solid-state molecular switching device based on monolayers of photochromic molecules, have demonstrated the viability of the bottom-up approach to molecular components into electronic circuitry; an

approach promulgated by Richard Feynman almost half a century earlier⁵ and realized conceptually by Aviram and Ratner in their seminal work in the 1970s.⁶ The field of molecular based nano-electronics is not only emerging rapidly, but also reveals numerous fascinating phenomena at the interface between the hard (semiconductor) and soft (molecular) worlds.⁷ In this Highlight we discuss recent advances in the development of photoswitchable molecules that can be applied to molecular and organic electronics.

isomeric forms exhibit different geometries and physical properties such as colour, hydrophobicity, redox chemistry, *etc.* Advantages which photochromic systems present include ease of tuning structure at the molecular level, addressability, reversibility and short response times.⁸ These open up the possibility of controlling local and bulk properties with light. Indeed, the versatile nature of photochromic molecular systems has seen their application in molecular memory devices,⁹ molecular electronics,¹⁰ smart surfaces, responsive materials,¹¹ actuators¹² and in the control

Molecular photoswitching

Photochromic molecular switches are a class of compounds capable of undergoing a reversible photo-induced transformation between two stable states (**A** and **B**), whose absorption spectra are distinctly different (Scheme 1).^{1,8} The two



Scheme 1 Optical molecular switching: if the direction of switching is wavelength-dependent, then a system employing the molecule will be photoswitchable in a reversible manner.

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Tibor Kudernac

Tibor Kudernac obtained his PhD at the University of Groningen (The Netherlands), under the guidance of Prof. B. L. Feringa and Prof. B. J. van Wees, on the design, synthesis and applications of photochromic molecular switches. In 2007 he joined the research group of Prof. S. De Feyter at K. U. Leuven (Belgium), investigating self-assembly phenomena at solid-liquid interfaces. Since 2009 he has been a postdoctoral research fellow in

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Nathalie Katsonis

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of supramolecular organization, to name but a few areas.¹³

Photochromic molecules present many challenges, as well as opportunities, in their application in functioning devices. In particular, the translation of the changes in molecular structure, which accompany photochromism, to changes in molecular conductivity requires that photochromic systems be held as components in electronic circuits and that their charge transport properties are affected significantly when irradiated. Further issues faced are photochemical stability (fatigue), quantum yields, switching times, selectivity, readout, compatibility and defects. Importantly, the effects of surface confinement and immobilization on molecular properties are critical.¹⁴

However, to exploit fully the potential of responsive molecular components in electronic devices we need to consider two distinct contributions that molecular systems make towards the charge transport across the electrode–electrode gap: the effect on tunneling between the metallic contacts, *i.e.* by modification of the density of states at the surfaces of the two electrodes and the resonant tunneling mediated through the molecular orbitals of the responsive molecule.¹⁵ In the latter case the photochemically induced change in the molecule affects the occupied and unoccupied frontier orbitals of the molecule.^{1,2,16}

Photoswitching of conductance

The simplest approach to measuring changes in molecular conductivity (in terms of resonant tunneling) is to examine the changes to the electronic absorption spectrum that occur upon photo-switching. In general, a blue or red shift in the lowest electronic absorption band would indicate an increase or decrease in the HOMO–LUMO gap of the molecule, respectively, which can be viewed simplistically as a decrease or increase, respectively, in the conjugation pathlength of the molecule. However, this interpretation must be made with caution, as the effect that a change in conjugation has on ‘molecular conductivity’ requires more detailed information regarding the absolute changes in the free energy of the HOMO and LUMO orbitals.

Electrochemistry is a powerful tool towards the non-destructive readout of the molecular state of photochromic molecules. For example, the open and closed forms of diarylethenes give distinguishably different signals (see below).¹⁷ By using cyclic voltammetry it is possible to monitor not only the change in the HOMO–LUMO gap (the origin of the change in electronic absorption upon photoreaction) but also to gain insight as to whether it is the HOMO or LUMO orbital or both which changes in energy – a factor critical to understanding changes in resonant tunneling *via* these orbitals.

For example, two well-known classes of photochromic molecules, the diarylethenes and the spiropyran, show very similar changes in their electronic absorption spectra upon irradiation, as a result of the change in the HOMO–LUMO gap.

However, electrochemical measurements show that in the case of the spiropyran¹⁸ (for a typical example of the structure of spiropyran, see Fig. 14) the HOMO levels are essentially unaffected by the ring opening and closing while the LUMO changes in energy considerably. By contrast, for the dithienylethenes the increase in conjugation pathlength upon photochemical ring closure results in a decrease in the bandgap by increasing the HOMO energy and decreasing the LUMO energy.¹⁹

Are changes in bonding necessary for switching conductivity?

Photochromic behavior is not limited to changes in intramolecular bond connectivity. Changes in molecular shape can drive changes in electronic structure also. This is exemplified in two recent examples. In the case of bis-thiaxanthylidene²⁰ the steric crowding between the four phenyl rings forces the molecule to adopt one of several conformations (Fig. 1) In this case the *anti*-folded state is most stable and is the only state observed at



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Wesley R. Browne is an Assistant Professor at the Stratingh Institute for Chemistry. He obtained a PhD under the guidance of Prof. Han Vos in 2002 at Dublin City University (Ireland) followed by postdoctoral research jointly with Prof. J. G. Vos and Prof. John J. McGarvey (Queens University Belfast, UK) in 2002–03. In 2003, he was appointed as a postdoctoral research fellow in the group of Prof. Ben L. Feringa. In 2007 he was awarded a VIDI research

grant by the Netherlands Organization for Scientific Research. His current research interests include transition metal based oxidation catalysis, electrochromic materials and responsive surfaces.



Ben L. Feringa

Ben L. Feringa obtained his Ph.D. degree in 1978 at the University of Groningen under the guidance of Professor Hans Wynberg. After working as a research scientist at Shell, he was appointed Full Professor at the University of Groningen in 1988 and named the distinguished Jacobus H. van't Hoff Professor of Molecular Sciences in 2004. He is a foreign honorary member of the American Academy of Arts and Sciences, and a member of the Royal

Netherlands Academy of Sciences (KNAW). In 2008 he was appointed as Academy Professor of the KNAW. His research interests include stereochemistry, organic synthesis, asymmetric catalysis, molecular switches and motors, self-assembly and nanosystems.

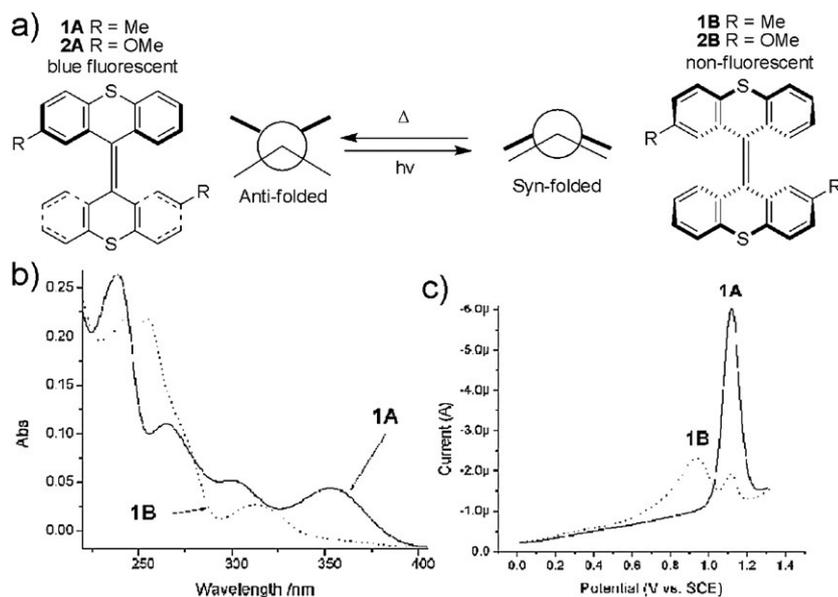


Fig. 1 a) Changes in conformation between the *anti*-folded and *syn*-folded states. b) UV/Vis spectrum showing the *anti*-folded and *syn*-folded states. c) Differential pulse voltammetry of the *anti*-folded and *syn*-folded states. (Reproduced with permission from ref 20. Copyright ACS 2007).

room temperature. Irradiation of this compound in solution at 263 K results in a change in geometry, a pronounced hypsochromic shift in the absorption spectrum and a complete quenching of its fluorescence. However, in contrast to spiropyrans and diarylethenes, this change is not due to a change in bonding but instead to a change in the conformation of the molecule *i.e.* to a *syn*-folded state (Fig. 1). Importantly the formal conjugation in this system is not affected. However, the electrochemical properties of the molecule change also, with a cathodic shift in the first oxidation process upon irradiation (Fig. 1). As would be expected, the conversion to a conformationally less stable state implies that the ground state of the molecule is destabilised, *i.e.* the HOMO energy increases. The blue shift in the absorption spectrum however shows that the destabilisation of the LUMO is much more pronounced than that of the HOMO. This is remarkable as there is no simple change in conjugation involved in this system but only a change in conformation. Furthermore, the blue shift in the absorption spectrum could be expected to indicate a decrease in conjugation, however, in this case HOMO-mediated superexchange process would be enhanced rather than reduced.²¹ This is again in contrast to the diarylethenes.

Hence a basic frontier orbital approach, *i.e.* drawing double bonds, says little about the charge transport ability of a system. In the previous example the change in electronic properties was driven by a change in molecular conformation. However, such changes can be effected by using photochromic units, which are electronically separated from the unit of interest (Fig. 2). The photochromic azobenzene unit in the system of Roncali and co-workers is linked covalently to a tetrathioether moiety.²²

The changes in energy of the HOMO level, although modest, are due to the

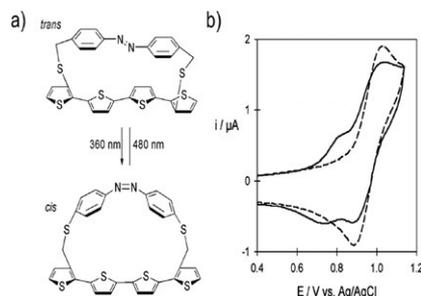


Fig. 2 a) Photomechanical manipulation of the electronic properties of a linear π -conjugated system. b) Cyclic voltammogram of the *trans* form before irradiation (dashed line) and after 2 h of irradiation at 360 nm (solid line) (Reproduced with permission from ref. 22. Copyright ACS 2003).

change in conformation imposed on the tetrathioether by the photochromic azobenzene unit. The mechanically induced distortion results in the reversible switching of the HOMO–LUMO gap of the tetrathioether as indicated by cyclic voltammetry (Fig. 2). The effect of mechanical distortions on conductance are known²³ and have important implications for molecular junctions.

Electrochemical read-out following photochemistry on surfaces

Electronics based on molecular systems can be defined as technology exploiting the properties and functionality of molecules as components in electronic devices.^{2,24} However, the molecular component must be “wired up” using other functional units (*e.g.*, thiol or thioacetate groups for metallic surfaces, $\text{Si}(\text{OH})_3$ for silicon-based surfaces, *etc.*) and must be addressable independently of other switchable molecules and functional units in proximity to it.

The electrochemical properties of many photochromic systems on surfaces have been noted for some time, in particular with respect to the change in surface conductivity which accompanies changes in molecular state.²⁵ In particular, interfacing biomolecules with electrode surfaces *via* photochromic switches allows control of electronic communication such as on/off switching or modulation of, *e.g.*, protein binding or redox enzyme activity.²⁶ Recently, electrochemistry has been applied as both a complementary switching method as well as a read-out method for immobilised photochromic switches.^{17,27,28}

However, in immobilising photochromic switches it is essential to understand that in addition to direct electronic interactions between the surface and the molecule²⁹ (which can quench photochemistry, change in molecular orbital structure *etc.*), other effects can be important. These include, besides the nature of the surface material, steric effects, *i.e.* decreases in conformational freedom, intermolecular interactions, changes to rates of intermolecular electron and energy transfer. For example, in the case of some dithienylcyclopentenes in solution, the state can be switched in both

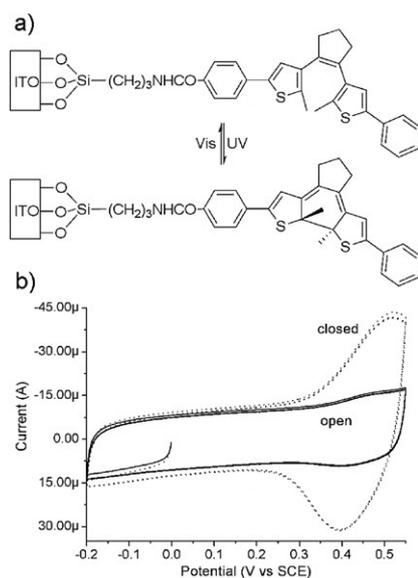


Fig. 3 a) The open (top) and closed (bottom) form of a diarylethene-modified ITO electrode. b) Cyclic voltammetry of the open and closed form covalently attached to ITO electrodes.

directions by UV and visible irradiation but is effective only in one direction by electrochemical stimulation.¹⁹ When immobilised on an ITO surface (Fig. 3), no change in its photochemical properties occur, however, it can be switched in both directions electrochemically.¹⁷ The change in electrochemical behaviour from solution to surface is not due to changes in intrinsic properties of the molecular species or by orbital interactions with the surface. It is due to a change in observed intermolecular electron transfer rates between the individual molecules now held close together on the surface instead of diffusing randomly in solution.

Photochromism on metallic nanoparticles

Metallic (and in particularly gold) nanoparticles offer tremendous help in understanding molecular surface interactions due to the range of nanoparticle sizes which can be accessed by simple preparation techniques.³⁰ As such, they offer a convenient model system for mimicking properties of bulk solids, with the additional benefit of being able to tune size-dependent properties, in particular surface plasmon energies.³¹ Of particular interest are self-assembled monolayers (SAMs) of photoactive molecules formed on the surface of gold nanoparticles. Due

to the high surface-to-volume ratio, the concentration of photoactive compounds compared to the number of gold atoms allows for standard characterization techniques such as UV-vis or FTIR spectroscopy to be employed to detect photochromic switching.

The effect of self-assembly of photo-switches on metallic nanoparticle surfaces can be seen in two major contributions. Firstly, a direct electronic coupling of a nanoparticle core with a chromophore due to their proximity,^{29,30b} which might result in complete quenching of the photoreactivity. Secondly, effects of steric constraints, which limit conformational freedom of the molecular entities.

Trans-cis isomerization of azobenzenes and stilbenes chemisorbed on gold nanoparticles *via* alkylthiol linkers with a range of chain lengths have been reported.³² The quantum yields for the photoisomerization from *trans* to *cis* isomers were found to be dependent on the length of the alkyl chain and was attributed to distance-dependent quenching of the excited state by the metallic core. By contrast, *trans*-to-*cis* isomerization of an analogous stilbene monolayer on planar gold was not observed because of the high crystallinity and dense packing of the monolayer.³³ This demonstrates the importance of conformational restrictions on the photoreactivity of photochromic molecules. More recently, non-symmetric azobenzene disulfides were employed in an attempt to realize highly efficient isomerization on colloidal gold surfaces.³⁴ In the SAMs formed, the free volume for photoreaction of azobenzenes was determined by a 50% dilution due to the presence of the second alkyl leg of the disulfide (Fig. 4). As a result of the dilution both *trans*-to-*cis* and the *cis*-to-*trans* isomerizations were relatively free of steric restrictions in contrast to that obtained on the planar gold surface.³⁵

The *cis-trans* isomerization on gold nanoparticles has also been studied recently in the so-called light-driven unidirectional molecular motors³⁶ (Fig. 5). A sequence of two energetically uphill photochemical isomerization steps each followed by an energetically downhill irreversible thermal helix inversion step results in a full 360° rotation around the double bond. Separation of the motor molecules from the gold surface by two

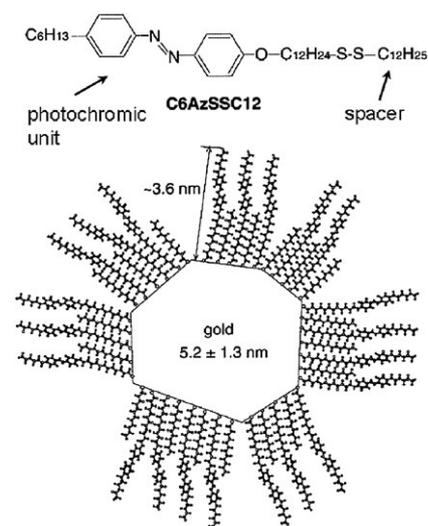


Fig. 4 Molecular structure of an azobenzene disulfide and schematic drawing of the azobenzene-capped gold nanoparticle. (Adapted with permission from ref. 34. Copyright ACS 2003).

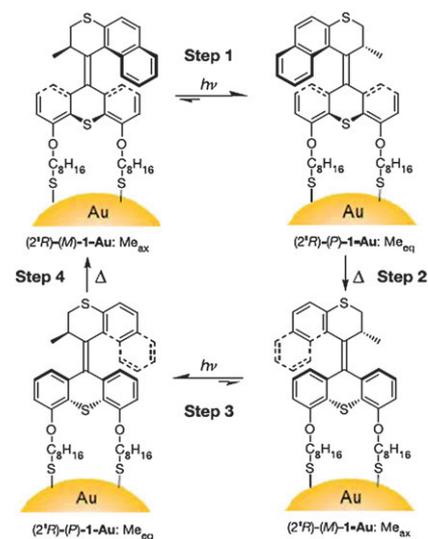


Fig. 5 The four-state unidirectional rotation of a motor-functionalized nanoparticle is shown ($h\nu$, photochemical step; Δ , thermal step). The photoisomerizations were induced by irradiation at $\lambda \geq 280$ nm or $\lambda = 365$ nm. Me_{ax} indicates the pseudo-axial orientation of the methyl substituent, Me_{eq} indicates the unstable pseudo-equatorial orientation of the methyl substituent. (Reproduced from ref 36. Copyright Nature 2005).

eight-methylene-unit linkers was chosen to ensure that the function of the motor observed in solution is retained upon grafting to the gold surface. The barrier for thermal isomerization of molecules grafted on gold nanoparticles was found

to be slightly higher than for the molecules in solution, a change which was attributed to the decrease in the molecules' degrees of freedom.

In the previous examples, direct electronic coupling and steric restrictions contribute to the change in photochemistry observed upon immobilisation. For diarylethenes, however, steric effects arising from closed packing in SAMs should not significantly alter photochemistry since the photoswitching is not accompanied by dramatic geometrical changes and photochemistry is preserved even in crystalline states.³⁷ An early attempt to investigate photoswitching of diarylethenes self-assembled on a surface of gold nanoparticles showed that when the switching unit is isolated from the surface by a linker based on pentamethylene alkyl chain (Fig. 6), the photochromic behavior is retained.³⁸ Both ring-closing and ring-opening processes of molecules grafted on gold nanoparticles resembled those of free molecules in solution.

As discussed above, a simple way to preserve photochemistry upon grafting on metallic surfaces is isolation of the switching unit by a non-conjugated linker. However, this might have negative implications on charge transport properties since a certain level of communication between the switching unit and the metallic surface is essential in order to make molecular switching devices feasible. Hence photochromic behavior of diarylethenes with their switching unit connected to the surface of gold nanoparticles *via* different conjugated aromatic spacers was investigated.³⁹ By varying spacer units the ring-opening process stayed intact (Fig. 7). However

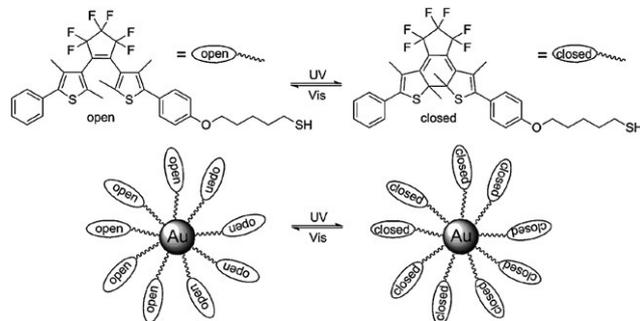


Fig. 6 Photochromic interconversions of a thiol-terminated diarylethene derivative unbound (top) and bound to gold nanoparticles (bottom). (Reproduced with permission from ref. 38. Copyright CSJ 2004).

ring-closing showed strong linker-dependent behavior. The quantum yields for *meta*- and *para*-substituted benzene units were the same. This indicates that a variation of the π -conjugation pathway from cross- to linearly-conjugated does

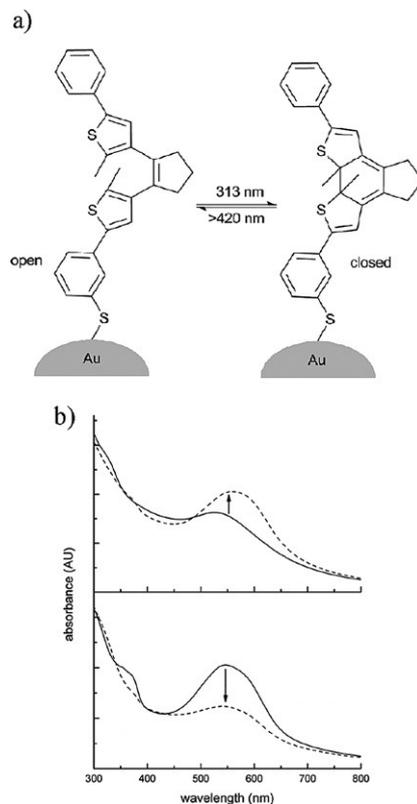


Fig. 7 a) Photoisomerization between an open and closed switch anchored on gold nanoparticles. b) UV/Vis spectra of the open form measured in dry toluene before (—) and after (---) irradiation at 313 nm (top). UV/Vis spectra of the closed form measured in dry toluene before (—) and after (---) irradiation at >420 nm. (Reproduced with permission from ref. 39. Copyright RSC 2006).

not alter the electronic coupling of the chromophore with the Au surface. However, if a thienyl moiety was used as a linker no evidence for ring-closing was obtained.⁴⁰ Since the distance of the photoswitching unit for all spacers is comparable, we can reasonably assume that the origin of the different switching behaviors lies in different proximity of states and consequently different mixing of energy levels of gold nanoparticles and photoswitches. Similar results were obtained on flat gold electrodes.²⁹

Light switching of conductance of monolayers

Light-induced switching of individual azobenzenes physisorbed on Au(111) was investigated under ultra-high vacuum conditions.⁴¹ *tert*-Butyl groups lift the switching unit off of the substrate (Fig. 8), thereby increasing the photoreactivity of the molecules by decreasing molecule–surface coupling. If the molecule contained none or two *t*-butyl legs, isomerization was not observed due to the stronger electronic coupling of the switching unit with the substrate. The “transition” that was observed from quenched to active photomechanical behavior reveals the importance of electro-mechanical coupling between a molecule and substrate in determining single-molecule photoswitching.

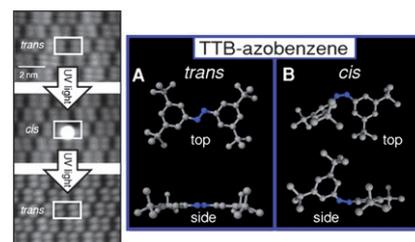


Fig. 8 a) Reversible photo-induced switching is observed for a single TTB-azobenzene molecule. The same individual TTB-azobenzene molecule (identified by white boxes in three successive panels) is shown before and after two successive exposures to UV light. The molecule initially in the *trans* state (top panel) is then switched to the *cis* state after the first exposure to UV light (middle panel), and is then switched back to the *trans* state after a second exposure to UV light (bottom panel). Simulated *trans*- and *cis*-TTB-azobenzene structures. (A) Calculated *trans* geometry. (B) Calculated *cis* geometry (Adapted with permission from ref. 41. Copyright APS 2007).

Light switching of conductance of individual molecules

In the frame of development of optoelectronic molecular devices, a crucial milestone would be direct observation of photoinduced conductance switching under conditions similar to those confronted by molecules in real devices, *i.e.* molecules assembled on nanoscopic metallic electrodes under ambient conditions. Fundamental questions related to charge transport in molecules (*i.e.* stability of molecule–electrode contact *versus* conductance, stochastic conformational changes *versus* conductance changes, stochastic switching *versus* controlled switching) can be addressed with techniques allowing for measurements of individual molecules, in particular scanning tunneling microscopy⁴² (STM) and mechanically controlled break-junction⁴³ (MCBJ).

In one of the first reported experiments designed to correlate photochromic switching to changes of conductance for individual molecules, azobenzene derivatives were embedded in *n*-dodecanethiol SAMs formed on Au(111).⁴⁴ The STM tip was used as a nanoscale probe for the charge transport properties of the switch. Direct evidence of light-induced switching for individual azobenzene molecules was achieved by comparing unequal apparent STM heights for the *trans* and *cis* isomers. When azobenzenes undergo a *cis*–*trans* isomerization, the physical height of the molecules is altered (Fig. 9), albeit without significant change of the conductance of the molecule. The apparent changes in conductivity observed by STM are thus attributed to the switching of height of the molecules rather than to an internal structural modification leading to a modification of molecular resistance. Additionally, it was shown that even in the absence of light, conductance switching was observed, and this was attributed to the reversible *trans*–*cis* isomerization driven by an external electric field and current flow. By controlling the potentials employed, this voltage-induced switching could be suppressed.

Conductance switching of azobenzene derivatives relies inherently on switching of the shape and length of the molecule rather than direct switching of their intrinsic conductance. This means that

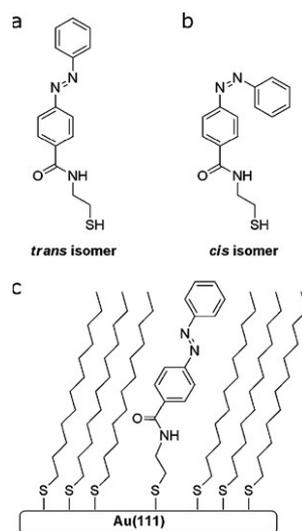


Fig. 9 Schematic structures of an azobenzene derivative which can be grafted on a surface through a S–Au bond: (a) *trans* isomer, (b) *cis* isomer. (c) The *trans* isomer was inserted in a SAM of *n*-dodecanethiol, forming a mixed azobenzene/*n*-dodecanethiol monolayer.

a technique sensitive to height switching would have to be employed if azobenzenes are to be used for switching devices. On the other hand, in the case of diarylethene switches rearrangement of double and single bonds after photoswitching was expected to be accompanied by a significant modification of conductance, while their physical height is not significantly altered. The potential of 1,2-dithienylethenes in molecular electronics was demonstrated first by studying the conductivity of a dithienylethene switch with thiophene groups as spacers and functionalized by two thiol groups chemisorbed on each of the mechanically controllable break junction (MCBJ) electrodes (Fig. 10).⁴⁰ It should be emphasized that such a trapping of single molecule between nanoscale electrodes remains experimentally challenging. These experiments revealed that switching a molecule from the closed to the open form results in a resistance increase of three orders of magnitude. This constitutes an additional indication that closed and open forms are characterized by intrinsically different charge transport properties. However, once the switch is connected to gold *via* the Au–S bond, it could only be switched from the closed to the open form. These results were subsequently corroborated

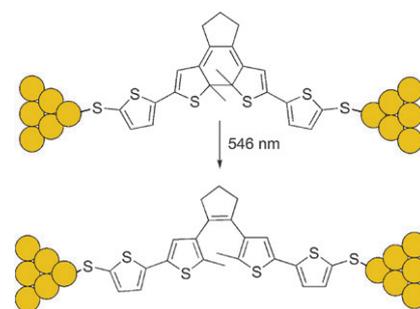


Fig. 10 Schematic representation of the switching from the closed to the open form by visible irradiation for a single diarylethene molecule.

by measuring a monothiol analogue of the switch by STM.⁴⁵

The lack of reversibility in those systems (the same behavior was observed for the monothiol derivative on gold nanoparticles) was investigated theoretically and attributed to the quenching of the excited state of the open form by gold.⁴⁶ More specifically, density functional theory (DFT) calculations suggested that the quenching observed may result from the alignment of the Fermi-level of gold with the open isomers. The deep-lying HOMO level at a high metal density of states offers the opportunity for many possible electron transfer events, thus reducing the lifetime of the hole created after an excitation. In contrast, the HOMO of the closed isomer is higher in energy within the low density of states of gold, and ring-opening can take place. Recently an alternative explanation has been proposed in which the relative order of photoactive and photo-inactive states are inverted through mixing distortion of molecular orbitals by interaction with the metal surface.⁴⁷

A slightly modified diarylethene derivative with one CH₂ group separating the aromatic part of the switch from the gold surface was investigated using a repetitive break junction method using an STM tip (Fig. 11).⁴⁸ Extensive statistical analysis of the conductance properties of the single switch is possible as a gold tip is repeatedly pushed towards a gold surface and withdrawn again to form each time a transient metal–molecule–metal junction (Fig. 11). Markedly different resistances of 526 MΩ in the open form and 4 MΩ in the closed form were found. The isolation of the switching unit with only a partly conjugated linker allowed for the

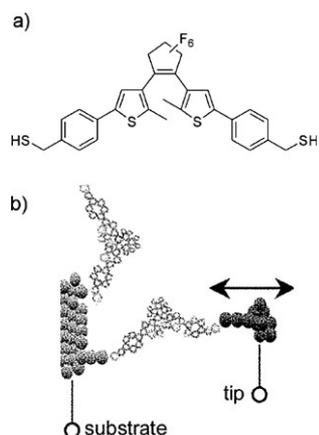


Fig. 11 a) Dithiolated diarylethene switch. b) Schematic representation of the set-up for conductance measurements. (Reproduced with permission from ref. 48. Copyright 2005 IOP Publishing Ltd).

retention of reversible photochromism. A more recent example of this approach was taken by the group of Guo and Nuckolls using carbon nanotubes as electrodes in place of gold.⁴⁹ The importance of the latter study is the use of electrodes which avoid issues such as atom migration on the electrode surface.

Direct observation of reversible switching was realized recently for individual photochromic molecules grafted on gold.⁵⁰ The switches were embedded in *n*-dodecanethiol SAMs formed on Au(111) (Fig. 12). Reversible light-induced switching accompanied by a significant change in conductance was observed on a single-molecule level. In contrast to MCBJ techniques, this approach allows for a statistical analysis of switching events and for a direct observation of the state of the molecule and its surroundings.

Switching devices based on photochromic molecules

An important objective of molecular electronics is to create devices based on molecules. A “macroscopic” switching device based on diarylethene photochromic molecules has been realized previously.⁵¹ A conductive polymer based on diarylethenes was sandwiched between metallic and ITO electrodes. These experiments using different metals as the electrode highlighted the importance of the material that is used as an electrode in the assembly of organic electronic

devices. The overall reversibility of current switching was found to be poor. However, this was not a direct consequence of a loss of reversibility in photochemical switching, judging from the reversible changes in the fluorescence emission intensity. Instead, it was attributed to the instability of the junction or interface structure upon irradiation. This is not surprising since the surface morphology for a single crystal of diarylethene can be changed following photo-reactions.³⁷ The instability of the interface in the sandwiched photoswitching polymer devices can be overcome by using a non-photochromic polystyrene polymer doped with diarylethene molecules.⁵² The domination of photochromic dopants in charge transport in non-conducting polymers was emphasized by the fact that the switch molecule with a donor-acceptor structure exhibited the highest conductance profile (the conductance increases by a factor of two when the molecule is converted from the closed to the open form).

Performance of large-scale devices

Recently μm -sized devices based on a network of nanoparticles deposited between interdigitated nanogapped Au electrodes (Fig. 13) was reported.⁵³ Nanoparticles were encapsulated by switchable diarylethene molecules connecting pairs of nanoparticles. Fully reversible conductance switching was achieved by a sequence of UV and visible irradiation cycles. Switching times were long, however (10 h for the maximum ON/OFF ratio).

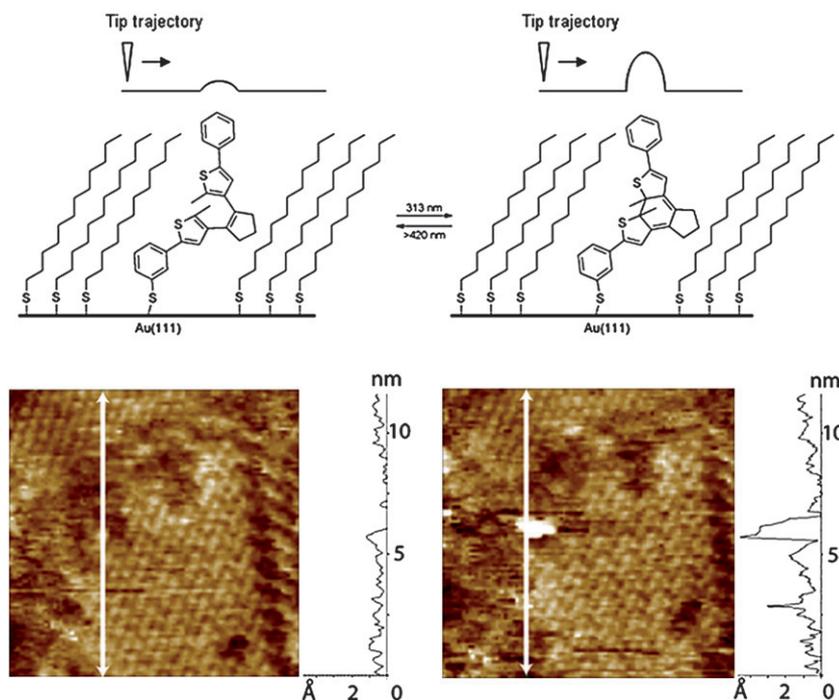


Fig. 12 (Top) Schematic description of a tip trajectory over individual open and closed states of the diarylethene switch incorporated within a matrix of a dodecanethiol monolayer on gold. (Bottom) STM images of the same area before (left) and after (right) the UV light-induced molecular transition. (Reproduced with permission from ref. 50. Copyright Wiley 2007).

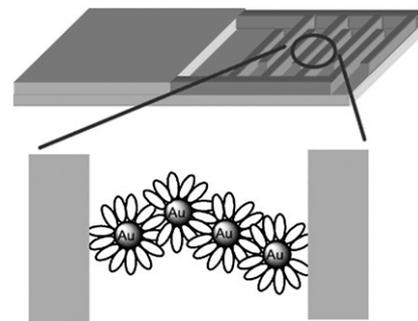


Fig. 13 The diarylethene-Au nanoparticle network on an interdigitated nano-gap Au electrode. (Reproduced with permission from ref. 53. Copyright RSC 2007).

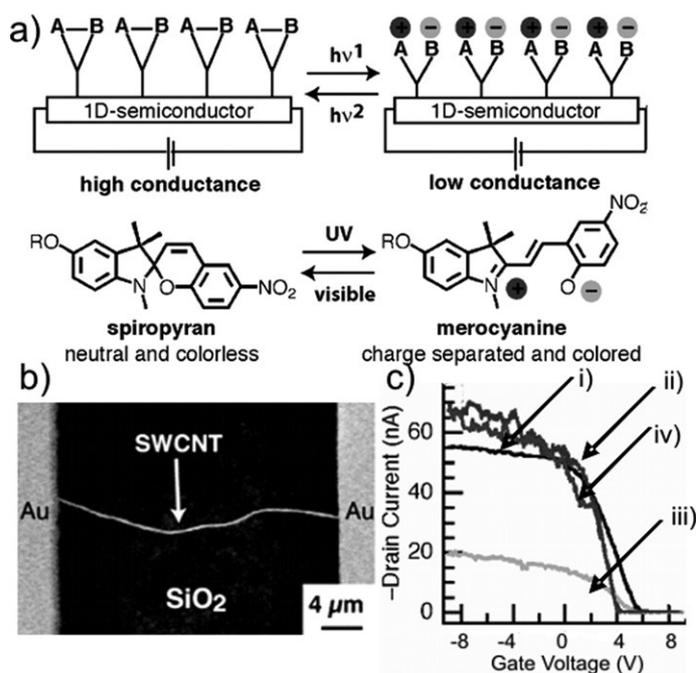


Fig. 14 a) A SAM-coated one-dimensional semiconductor. The spiroyrans SAM is switched between neutral and zwitterionic states by light. b) Scanning electron micrograph image of a single carbon nanotube between two Au/Cr contacts. c) Change in drain current of an individual SWCNT device as a function of V_g . i) before assembly; ii) after assembly of the spiropyran; iii) after irradiation with UV light; iv) after irradiation with visible light. (Reproduced with permission from ref. 54. Copyright ACS 2005).

A field effect transistor (FET) based on an isolated single-walled carbon nanotube (SWCNT) functionalized with spiropyran photochromic molecules was reported by Nuckolls and coworkers (Fig. 14).⁵⁴ Pyrene- or alkane-tethered spiropyran molecules were self-assembled on a SWCNT. The single nanotube was contacted on each side to Au electrodes (Fig. 14b). Alternating UV and visible light irradiation allows for the devices to be switched back-and-forth between low and high conductance. The reversible conductance switching in the functionalized SWCNT FETs was attributed to the photoswitching of the tethered molecules. Two possible explanations of the phenomenon were proposed. One possibility is that the charge-separated state of the merocyanine (Fig. 14a) introduces scattering sites for the carriers by creating localized dipole fields around the tubes. These sites then scatter charge when it flows in the nearby SWCNT channel and thereby reduces charge mobility in the devices. Another possibility is that the proximal phenoxide ion quenches the p-type carriers in the nanotubes and behaves like a charge trap.

Finally, the functioning of a large device based on diarylethene switches self-assembled on gold was recently reported.^{4a} The photochromic monolayer was covered with a layer of a conducting polymer layer, followed by deposition of a top gold electrode layer. In this setup short circuits through the photoactive SAM were prevented by the polymer layer^{4b} and excellent reversible photoswitching of conductance was demonstrated, although issues including stability and switching efficiency remain to be addressed.

Summary

In summary, the future of molecular electronic systems based on photo-switchable components looks increasingly bright, but many challenges remain in order to make the leap from fundamental science to applied technologies. The demonstration of a working redox device based on rotaxanes by Stoddart, Heath and coworkers³ and more recent example of a light-driven solid-state molecular switching device based on monolayers of photochromic diarylethenes⁴ have paved the way for this transition (Fig. 15).

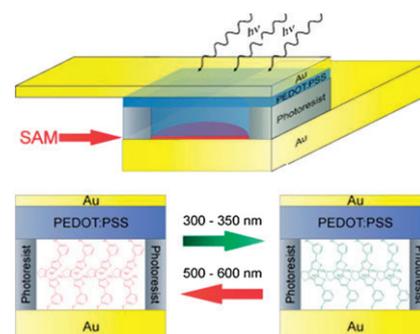


Fig. 15 Schematic cross-section of the device layout of a large-area molecular junction in which the diarylethene is sandwiched between Au and PEDOT:PSS/Au. (Reproduced with permission from ref. 4a. Copyright Wiley 2008).

However, to realize the full potential of photochromic systems, fundamental questions on change of this conductivity for connected molecules remain to be resolved.⁵⁵ Also response times and read-out rate are critical factors for molecular electronics, and regarding these properties many improvements are still required prior to applications. Among the most significant problems are also those associated with stability in interfacing molecular systems with the macroscopic world, and the understanding of the relative contributions of photochromic responses to changes in tunneling and resonant tunneling contributions to charge transport over the gap bridged by these systems.

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References

- (a) *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001; (b) J. C. Crano and R. Guglielmetti, *Organic Photochromic and Thermochromic Compounds Vol. 1*, Plenum Press, New York, 1999.
- (a) R. L. Carroll and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2002, **41**, 4378; (b) C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541–548.
- J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. Johnston-Halperin,

- E. Delonno, Y. Luo, B. A. Sheriff, K. Xu, Y. S. Shin, H.-R. Tseng, J. F. Stoddart and J. R. Heath, *Nature*, 2007, **445**, 414–417.
- 4 (a) A. J. Kronemeijer, H. B. Akkerman, T. Kudernac, B. J. van Wees, B. L. Feringa, P. W. M. Blom and B. de Boer, *Adv. Mater.*, 2008, **20**, 1467–1473; (b) E. C. P. Smits, S. G. J. Mathijssen, P. A. van Hal, S. Setayesh, T. C. T. Geuns, K. A. H. A. Mutsaers, E. Cantatore, H. J. Wonderegem, O. Werzer, R. Resel, M. Kemerink, S. Kirchmeyer, A. M. Muzafarov, S. A. Ponomarenko, B. de Boer, P. W. M. Blom and D. M. de Leeuw, *Nature*, 2008, **455**, 956–959.
- 5 R. P. Feynman, *The Pleasure of Finding Things Out*, Perseus Books, Cambridge, MA, 1999, (Chapter 5). Richard Feynman's original lecture "There's plenty of room at the bottom" can read at www.its.caltech.edu/~feynman.
- 6 A. Aviram and M. Ratner, *Chem. Phys. Lett.*, 1974, **29**, 277–283.
- 7 E. A. Weiss, J. K. Kriebel, M. A. Rampi and G. M. Whitesides, *Philos. Trans. R. Soc. London, Ser. A*, 2007, **365**, 1509.
- 8 (a) H. Tien and Y. Feng, *J. Mater. Chem.*, 2008, **18**, 1617–1622; (b) N. Katsonis, M. Lubomska, M. M. Pollard, B. L. Feringa and P. Rudolf, *Prog. Surf. Sci.*, 2007, **82**, 407–434.
- 9 (a) K. Uchida, M. Saito, A. Murakami, T. Kobayashi, S. Nakamura and M. Irie, *Chem. Eur. J.*, 2005, **11**, 534–542; (b) M. Irie, *Applied Photochromic Polymer Systems*, ed. C. B. McArdle, Blackie, Glasgow, 1991, pp. 174–206; (c) T. Ikeda and O. Tsutsumi, *Science*, 1995, **268**, 1873–1875; (d) S. Shinkai, *Pure Appl. Chem.*, 1987, **59**, 425–430.
- 10 S. L. Gilat, S. H. Kawai and J.-M. Lehn, *Chem. Eur. J.*, 1995, **1**, 275–284.
- 11 K. Uchida, N. Izumi, S. Sukata, Y. Kojima, S. Nakamura and M. Irie, *Angew. Chem., Int. Ed.*, 2006, **45**, 6470.
- 12 (a) S. Kobatake, S. Takami, H. Muto, T. Ishikawa and M. Irie, *Nature*, 2007, **446**, 778–781; (b) K. Uchida, S. I. Sukata, Y. Matsuzawa, M. Akazawa, J. J. D. de Jong, N. Katsonis, Y. Kojima, S. Nakamura, J. Areephong, A. Meetsma and B. L. Feringa, *Chem. Commun.*, 2008, **3**, 326–328.
- 13 (a) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch and B. L. Feringa, *Science*, 2004, **304**, 278–281; (b) R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. M. Bastiaansen, D. J. Broer and B. L. Feringa, *Nature*, 2006, **440**, 163–163.
- 14 W. R. Browne and J. J. McGarvey, *Coord. Chem. Rev.*, 2007, **251**, 454–473.
- 15 X.-Y. Zhu, *Surf. Sci. Rep.*, 2004, **56**, 1.
- 16 T. Albrecht, A. Guckian, A. M. Kuznetsov, J. G. Vos and J. Ulstrup, *J. Am. Chem. Soc.*, 2006, **128**, 17132–17138.
- 17 (a) J. Areephong, W. R. Browne, N. H. Katsonis and B. L. Feringa, *Chem. Commun.*, 2006, 3930–3932; (b) G. Guirado, C. Coudret, M. Hliwa and J. P. Launay, *J. Phys. Chem. B*, 2005, **109**, 17445–17459; (c) B. Gorodetsky, H. D. Samachetty, R. L. Donkers, M. S. Workentin and N. R. Branda, *Angew. Chem., Int. Ed.*, 2004, **43**, 2812.
- 18 (a) M. Campredon, G. Giusti, R. Guglielmetti, A. Samat, G. Gronchi, A. Alberti and M. Benaglia, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2089; (b) A. S. Saraç, B. Ustamehmetoglu, A. Leiminer, B. Stephan and A. Mannschreck, *Electrochim. Acta*, 1997, **42**, 3629–3635; (c) J. F. Zhi, R. Baba, K. Hashimoto and A. Fujishima, *Ber. Bunsen. Phys. Chem.*, 1995, **99**, 32–39.
- 19 (a) W. R. Browne, J. J. D. de Jong, T. Kudernac, M. Walko, L. N. Lucas, K. Uchida, J. H. van Esch and B. L. Feringa, *Chem. Eur. J.*, 2005, **11**, 6414–6429 and references cited therein; (b) W. R. Browne, J. J. D. de Jong, T. Kudernac, M. Walko, L. N. Lucas, K. Uchida, J. H. van Esch and B. L. Feringa, *Chem. Eur. J.*, 2005, **11**, 6430–6441 and references cited therein.
- 20 W. R. Browne, M. M. Pollard, B. de Lange, A. Meetsma and B. L. Feringa, *J. Am. Chem. Soc.*, 2006, **128**, 12412–12413.
- 21 W. R. Browne, N. M. O'Boyle, J. J. McGarvey and J. G. Vos, *Chem. Soc. Rev.*, 2005, **34**, 641–663.
- 22 B. Joussemle, P. Blanchard, N. Gallego-Planas, J. Delaunay, M. Allain, P. Richomme, E. Levillain and J. Roncali, *J. Am. Chem. Soc.*, 2003, **125**, 2888–2889.
- 23 C. Joachim, J. K. Gimzewski, R. R. Schlittler and C. Chavy, *Phys. Rev. Lett.*, 1995, **74**, 2102–2105.
- 24 Y. Wada, *Pure Appl. Chem.*, 1999, **71**, 2055–2066.
- 25 (a) I. Willner, A. Doron and E. Katz, *J. Phys. Org. Chem.*, 1998, **11**, 546–560; (b) I. Willner, V. Prado-Yissar, E. Katz and K. T. Ranjit, *J. Electroanal. Chem.*, 2001, **497**, 172–177.
- 26 E. Katz, B. Willner and I. Willner, *Biosens. Bioelectron.*, 1997, **12**, 703.
- 27 R. Baron, A. Onopriyenko, E. Katz, O. Lioubashevski, I. Willner, S. Wang and H. Tian, *Chem. Commun.*, 2006, 2147.
- 28 I. Willner, B. Basnar and B. Willner, *Adv. Funct. Mater.*, 2007, **17**, 702–717.
- 29 W. R. Browne, T. Kudernac, N. Katsonis, J. Areephong, J. Hjelm and B. L. Feringa, *J. Phys. Chem. C*, 2008, **112**, 1183–1190.
- 30 (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.
- 31 M. Brust and C. J. Kiely, *Colloids Surf. A: Physicochem. Eng. Asp.*, 2002, **202**, 175–186.
- 32 (a) J. Hu, J. Zhang, F. Liu, K. Kittredge, J. K. Whitesell and M. A. Fox, *J. Am. Chem. Soc.*, 2001, **123**, 1464; (b) J. Zhang, J. K. Whitesell and M. A. Fox, *Chem. Mater.*, 2001, **13**, 2323.
- 33 M. O. Wolf and M. A. Fox, *Langmuir*, 1996, **12**, 955.
- 34 A. Manna, P.-L. Chen, H. Akiyama, T.-X. Wei, K. Tamada and W. Knoll, *Chem. Mater.*, 2003, **15**, 20–28.
- 35 K. Tamada, H. Akiyama and T. X. Wei, *Langmuir*, 2002, **18**, 5239–5246.
- 36 R. A. van Delden, M. K. J. ter Wiel, M. M. Pollard, J. Vicario, N. Koumura and B. L. Feringa, *Nature*, 2005, **437**, 1337–1340.
- 37 (a) S. Kobatake, S. Takami, H. Muto, T. Ishikawa and M. Irie, *Nature*, 2007, **446**, 778–781; (b) M. Irie, S. Kobatake and M. Horichi, *Science*, 2001, **291**, 1769–1772; (c) K. Uchida, S. I. Sukata, Y. Matsuzawa, M. Akazawa, J. J. D. de Jong, N. Katsonis, Y. Kojima, S. Nakamura, J. Areephong, A. Meetsma and B. L. Feringa, *Chem. Commun.*, 2008, 326–328.
- 38 K. Matsuda, M. Ikeda and M. Irie, *Chem. Lett.*, 2004, **33**, 456–457.
- 39 T. Kudernac, S. J. van der Molen, B. J. van Wees and B. L. Feringa, *Chem. Commun.*, 2006, 3597–3599.
- 40 (a) D. Dulic, 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**, 207402.
- 41 M. J. Comstock, N. Levy, A. Kirakosian, J. Cho, F. Lauterwasser, J. H. Harvey, D. A. Strubbe, J. M. J. Fréchet, D. Trauner, S. G. Louie and M. F. Crommie, *Phys. Rev. Lett.*, 2007, **99**, 038301.
- 42 (a) P. Jiang, G. M. Morales, W. You and L. Yu, *Angew. Chem., Int. Ed.*, 2004, **43**, 4471; (b) J. He, Q. Fu, S. M. Lindsay, J. W. Cizek and J. M. Tour, *J. Am. Chem. Soc.*, 2006, **128**, 14828–14835; (c) L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara and P. S. Weiss, *J. Phys. Chem. B*, 1999, **103**, 8122–8127; (d) B. Xu and N. J. Tao, *Science*, 2003, **301**, 1221–1223.
- 43 (a) C. Kergueris, J.-P. Bourgoin, S. Palacin, D. Esteve, C. Urbina, M. Magoga and C. Joachim, *Phys. Rev. B*, 1999, **59**, 12505–12513; (b) M. Mayor, H. B. Weber, J. Reichert, M. Elbing, C. von Hänisch, d. Beckmann and M. Fisher, *Angew. Chem., Int. Ed.*, 2003, **42**, 5834; (c) J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor and H. von Lohneysen, *Phys. Rev. Lett.*, 2002, **88**, 176804.
- 44 S. Yasuda, T. Nakamura, M. Matsumoto and H. Shigekawa, *J. Am. Chem. Soc.*, 2003, **125**, 16430–16433.
- 45 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.
- 46 (a) J. Li, G. Speyer and O. F. Sankey, *Phys. Rev. Lett.*, 2004, **93**, 248302; (b) M. Zhuang and M. Ernzerhof, *Phys. Rev. B*, 2005, **72**, 073104.
- 47 (a) K. Yoshizawa, T. Tada and A. Staykov, *J. Am. Chem. Soc.*, 2008, **130**, 9406–9413; (b) A. Staykov and K. Yoshizawa, *J. Phys. Chem. C*, 2009, **113**, 3826–3834.
- 48 J. He, F. Chen, P. A. Liddell, J. Andreasoon, S. D. Straight, D. Gust, T. A. Moore, A. L. Moore, J. Li, O. F. Sankey and S. M. Lindsay, *Nanotechnology*, 2005, **16**, 695–702.
- 49 A. C. Whalley, M. L. Steigerwald, X. Guo and C. Nuckolls, *J. Am. Chem. Soc.*, 2007, **129**, 12590–12591.

-
- 50 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.
- 51 T. Kawai, Y. Nakashima, T. Kunitake and M. Irie, *Curr. Appl. Phys.*, 2005, **5**, 139–142.
- 52 E. Kim, M. Kim and K. Kim, *Tetrahedron*, 2006, **62**, 6814–6821.
- 53 M. Ikeda, N. Tanifuji, H. Yamaguchi, M. Irie and K. Matsuda, *Chem. Commun.*, 2007, 1355–1357.
- 54 X. Guo, L. Huang, S. O'Brien, P. Kim and C. Nuckolls, *J. Am. Chem. Soc.*, 2005, **127**, 15045–15047.
- 55 (a) E. A. Weiss, R. C. Chiechi, G. K. Kaufman, J. K. Kriebel, Z. F. Li, M. Duati, M. A. Rampi and G. M. Whitesides, *J. Am. Chem. Soc.*, 2007, **129**, 4336–4349; (b) E. Tran, M. Duati, V. Ferri, K. Mullen, M. Zharnikov, G. M. Whitesides and M. A. Rampi, *Adv. Mater.*, 2006, **18**, 1323–1328.