

Reversible light induced conductance switching of asymmetric diarylethenes on gold: surface and electronic studies†

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We report on the light-induced switching of conductance of a new generation of diarylethene switches embedded in an insulating matrix of dodecanethiol on Au(111), by using scanning tunneling microscopy (STM). The diarylethene switches we synthesize and study are modified diarylethenes where the thiophene unit at one side of the molecular backbone introduces an intrinsic asymmetry into the switch, which is expected to influence its photo-conductance properties. We show that reversible conversion between two distinguishable conductance states can be controlled *via* photoisomerisation of the switches by using alternative irradiation with UV ($\lambda = 313$ nm) or visible ($\lambda > 420$ nm) light. We addressed this phenomenon by using STM in ambient conditions, based on switching of the apparent height of the molecules which convert from 4–6 Å in their closed form to 0–1 Å in their open form. Furthermore, the levels of the frontier molecular orbital levels (HOMO and LUMO) were evaluated for these asymmetric switches by using Scanning Tunneling Spectroscopy at 77 K, which allowed us to determine a HOMO–LUMO energy gap of 2.24 eV.

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1 Introduction

Molecular electronics utilizes molecules as active or passive elements in electronic devices.¹ Since the pioneering work of Aviram and Ratner,² it has been realized that the properties of electronic components could be defined by the structural aspects of a molecule. The possibility to tune the composition and geometry of molecules provides an opportunity to tailor the charge transport, optical, and structural properties of molecular devices.^{3–5} In particular, a major effort has been directed towards the use of a single or a small ensemble of switchable molecules as active electronic components.^{6,7} Photochromic switches are molecules that upon light excitation undergo a transformation from one stable state to another, each of these

states showing distinctive physical characteristics such as different UV/Vis absorption spectra.⁸ There are several groups of photochromic molecular switches including azobenzenes^{9,10} that reversibly isomerize between *cis* and *trans* forms under photoillumination. This *cis*–*trans* isomerization renders changes in the physical height of the molecule that are expressed as changes in electron conductance for isolated molecules in scanning tunneling microscopy (STM) experiments.^{9–12} As opposed to azobenzenes, diarylethene photochromic switches^{8,13} show little variations of physical height upon switching and the changes in conductance of the two forms solely originate from different electronic structures.⁶ These inherent variations of conductive properties with high thermal stability, excellent addressability and high fatigue resistance^{8,13} of diarylethenes make them excellent candidates for molecular-based switching devices. The so-called “off” and “on” states of diarylethenes incorporated between two metallic electrodes have shown to render different charge transport properties of the device.¹⁴ However, the photoreactivity was hampered as a result of the quenching of the excited state by the metal.¹⁴ Recent studies showed that the photoreactivity of the diarylethenes on a metallic electrode can be preserved when the linker connecting the switching unit to the electrode is carefully selected.^{15–18} Despite the recent advancements in the research of a single molecule's reactivity,^{15,16,19–22} the realization of a controlled repetitive switching of a single molecule upon external excitation remains a challenging task.

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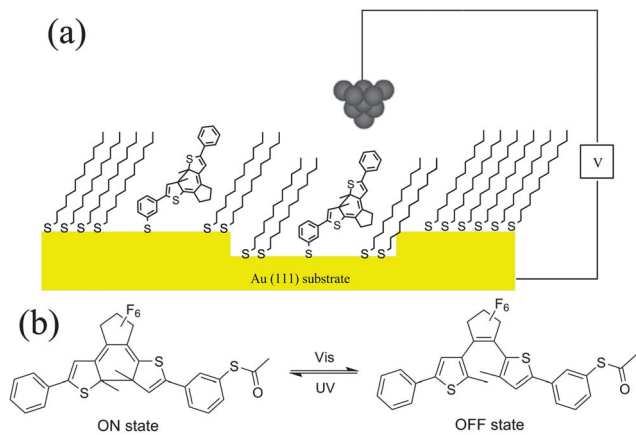


Fig. 1 (a) A mixed self-assembled monolayer (SAM) incorporating dodecanethiol (DT) and As-DE. Individual As-DE molecules are isolated within a matrix of DT. Scanning in constant-current mode shows the more conductive "on" state of As-DE as a different apparent height h_{app} compared with the apparent heights of the "off" state of As-DE and DT. Since h_{app} is a convolution of the physical height and conductance properties, changes in h_{app} of the "on" and "off" states can be attributed qualitatively to molecular switching.²³ (b) The chemical structure of the "on" state (left) and the "off" state (right) of the asymmetric diarylethene switch (abbreviated as As-DE).

Here, we investigate the photoswitching behaviour of a new class of diarylethene switches, namely, *S,S'*-((4,4'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-4,2-diyl))-bis(4,1-phenylene)) diethanethiolate (As-DE) embedded in an isolated matrix of dodecanethiol (DT) by using STM as depicted in Fig. 1.

We show that individual As-DE molecules can be readily and repeatedly switched between "on" and "off" states. In order to unambiguously assign the STM signals to As-DE and to investigate the electronic structure of these switches, we performed STS measurements at low temperature. HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) were detected²⁴ for the "on" state of switching molecules and the energy gap between the states was determined. The chemical structure of As-DE (Fig. 1b) differs from the previously studied diarylethene switch¹⁵ by the rotation of one thiophene ring with respect to the other. This modifies the conjugation pathway between the "on" and "off" state. In contrast to the previously studied "symmetric" diarylethenes, the "asymmetric" diarylethene As-DE possesses a cross-conjugation in both forms which could lead to different conductive properties with respect to its "symmetric" counterparts.^{25,26}

2 Results and discussion

The electronic spectra and photoswitching behavior of As-DE were investigated in a solution by UV/Vis absorption spectroscopy as shown in Fig. 2a. The spectrum of the "on" state (dotted line) shows a maximum absorption at 503 nm. When the sample is irradiated with visible light ($\lambda > 420$ nm) this absorption band progressively disappears as a consequence of ring opening. The "off" state of As-DE can be subsequently

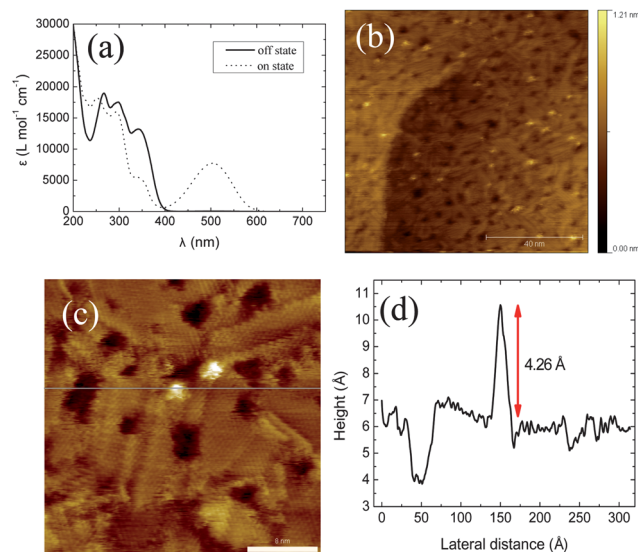


Fig. 2 (a) UV-Vis spectra of As-DE in the "on" (dotted line) and "off" (solid line) states, in *n*-hexane. The broad absorption band at 503 nm is a characteristic feature of the "on" state of the As-DE molecule. (b) STM image showing As-DE switches in the "on" state ($I_t = 8$ pA, $V_{sample} = 1.25$ V). (c) High resolution STM image shows two protrusions indicating the presence of two As-DE molecules in the "on" state ($I_t = 8$ pA, $V_{sample} = 0.7$ V, 31.5×31.5 nm²). (d) The line profile of the corresponding bright protrusion from (c).

converted back to the "on" state when irradiated with UV light. The absorption band with the maximum intensity at 503 nm of the "on" form corresponds to a HOMO–LUMO (π – π^*) optical transition with an energy of 2.46 eV. In addition, we note that the presence of a peak shoulder around 342 nm in the spectrum of the "off" state roughly corresponds to the value of 3.63 eV. Thus, this is in agreement with theoretical calculation which estimates that the HOMO–LUMO gaps of the "on" and "off" form of As-DE are about 2.35 eV and 3.54 eV, respectively (see ESI[†]).

Mixed monolayers composed of aromatic thiols isolated in a matrix of alkylthiols are typically prepared by the immersion of a preformed alkylthiol monolayer into a solution of the aromatic thiol.²⁷ This thiol exchange strategy turned out to be unsuccessful in the case of As-DE. This may be due to the immiscibility of the perfluorinated part of As-DE with the aliphatic chains of the preformed DT monolayer. Therefore we employed a reverse process where gold samples were immersed into a 0.5 mM solution of the "on" form of As-DE overnight in order to form a self-assembled monolayer of As-DE. The cleaving of the acetyl group on aromatic thiols in the presence of gold is a spontaneous and rapid process that does not require an exogenous base, as described previously by Tour *et al.*²⁸ Thus, we expect that the immersion overnight is sufficient to ensure that the As-DE molecules are adsorbed on gold. Crystalline domains of As-DE or individual As-DE molecules were not observable by STM at this stage (see ESI[†]). The sample was subsequently immersed into a 0.5 mM solution of DT that replaces most of the As-DE molecules. A large population of individual As-DE molecules (or their small bundles) embedded within well-ordered crystalline domains of DT on Au(111) was

found following this procedure (Fig. 2b). High resolution STM images reveal that As-DE molecules can be typically found at domain boundaries rather than incorporated within a crystalline domain of DT (Fig. 2c). The typical diameter of these bright spots is 2 nm and their apparent height is between 0.4 and 0.7 nm. This is consistent with the previous examples of aromatic thiols²⁷ and switches¹⁵ incorporated in the DT matrices.

Prior to irradiation experiments the same area of the monolayer was continuously scanned for 30 min in order to exclude stochastic switching phenomena.²⁰ Under the scanning conditions employed, a significant variation of the STM contrasts of the bright spots were not observed without illumination (Fig. 3a–e and S3 in ESI†). Subsequently, the sample was irradiated *in situ* with visible light. After 1 min of irradiation

the bright protrusion disappeared, suggesting that the molecule switched from the “on” to the “off” state (Fig. 3f). Since the apparent heights of the “off” state of As-DE (0.1 nm) are comparable to those of the surrounding DT matrix, the assignment of the STM contrast to the “off” state of As-DE is less straightforward. This is in agreement with the previously studied switches on surfaces.^{27,29,30} Further irradiation with visible light did not trigger further changes in the STM image (Fig. 3g). Subsequently, the sample was exposed to UV light ($\lambda = 313$ nm). Within 4 min of UV irradiation the transition from “off” to “on” state took place and the bright protrusion was restored (Fig. 3h). The reversible switching behavior of individual As-DE molecules is reproducible and was observed over a number of irradiation cycles (Fig. 3i–r), which demonstrates that the switching properties of As-DE molecules were preserved

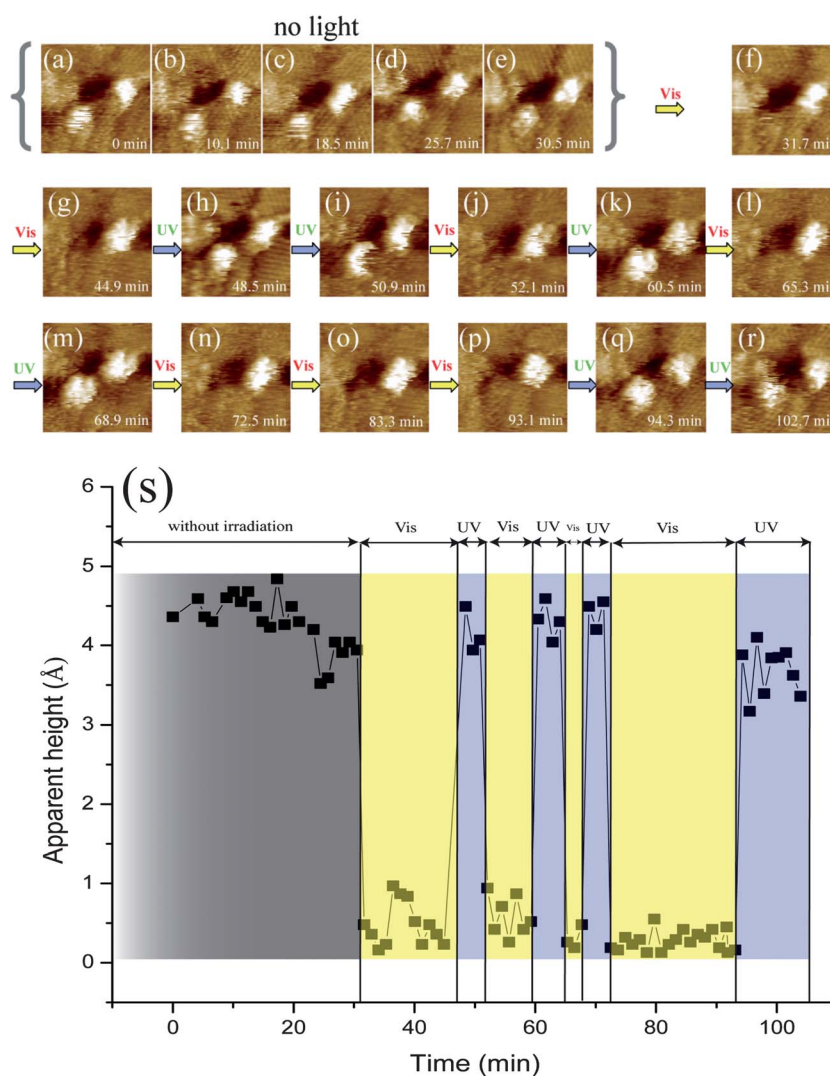


Fig. 3 Cropped sequential STM images of the molecular photoswitching event in an area of 100 nm^2 ($I_t = 20 \text{ pA}$; $V_{\text{sample}} = 0.8 \text{ V}$; Z-scale = 0.8 nm). In order to evaluate the stability of the molecular switches signature, we scanned continuously the same area without irradiation for 30 min (a to e). The apparent height is reduced upon irradiation with visible light for 13 min (f and g). UV light irradiation was used to switch As-DE molecules back to the “on” state. Consequently, we recover the apparent height of 0.4 nm as shown in (h) and (i). In (j), the molecular conductance is switched back to its “off” state. In this cycle, the sample was irradiated with visible light for 8.2 min, however no significant fluctuation in the apparent heights was observed. Subsequently, the procedure was repeated to maintain the “on” state for a longer period of time and indeed no appreciable changes in the apparent height value were observed. (s) The variation of apparent height as a function of time and irradiation.

throughout the experiment. To illustrate the reversibility of the light conductance switching, variations of the apparent height of the bright spot were plotted as a function of time (Fig. 3s). This graph shows that the conductance of the As-DE can be controlled reversibly by using UV and visible light. A high conductance state is associated with a typical apparent height value of 0.4–0.7 nm. As the As-DE is converted to the “off” form, evidence for the formation of the low conductance state comes from the absence of the bright STM signal. To emphasize that these switching events are reproducible, we present a similar finding where the initial state is the “off” state (see Fig. S5 in the ESI†).

In contrast to the discussed reversible switching of the conductivity of As-DE molecules, we also observed bright protrusions in the scanned area that did not display switching under irradiation. These unresponsive protrusions most likely consist of As-DE molecules whose switching is inhibited due to confinement by the rigid DT matrix.¹¹ The observation that this inhibited switching is only displayed for a part of the As-DE molecules can be explained by variations in the ordering of the DT matrix, *i.e.* some As-DE molecules have more free space in which they can perform their switching action than others. Besides the proposed DT confinement, another possibility causing this undesired event is the quenching of the closed form of As-DE by the gold surface as previously mentioned by Dulic *et al.*¹⁴

Predicting typical switching rates of diarylethenes on a gold surface and comparing it to solution photochemistry are far from trivial as surface confinement effects need to be taken into account. However, we estimate that the intensities of the UV/visible light are not very different, so we can conclude that the observed switching time in solution is between 1 and 3 seconds and on the gold surface is less than 90 seconds (this value is an upper bound because of the scanning time needed to scan one full STM image). In conclusion, the switching time of As-DE in solution is comparable to a molecule on gold. In addition, the switching times that we found for As-DE are comparable with the previous experiments of the symmetric DE on gold surfaces.¹⁵

I - V and dI/dV spectra were investigated to gain a deeper insight into the charge transport properties of As-DE as shown in Fig. 4. Fig. 4a displays typical I - V spectra of the “on” form of As-DE. The negative and positive bias regimes are asymmetric with respect to each other. The differential conductance spectra of the “on” form of the As-DE (Fig. 4b) exhibit three main features: a distinctive peak at -0.67 V and two less pronounced peaks at -1.44 V and 1.57 V respectively. The peak at the value of -0.67 V was assigned to the LUMO level of the molecule and the peak at -1.44 V to the LUMO + 1 level. Similarly, the resonance peak of the HOMO level of the As-DE is assigned to the feature at 1.57 V. The HOMO–LUMO gap can be extracted from the peak to peak difference of the outmost frontier orbitals, giving here the value of 2.24 eV. The I - V spectra of the open form could not be obtained. We were unable to measure those data for a combination of two reasons. First, the STM apparent heights of the open form (so-called “off-state”) are similar to the apparent heights of the dodecanethiol matrix, also in

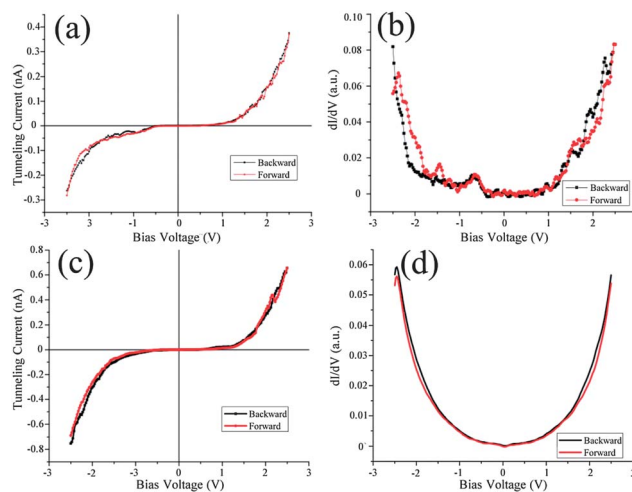


Fig. 4 I - V characteristics and dI/dV spectra taken simultaneously using the lock-in technique at 77 K (the bias voltage V is applied to the tip and the sample is grounded). (a) I - V spectra of As-DE; 160 traces were obtained from four different locations and averaged to give the resulting curve. (b) dI/dV of As-DE. (c) I - V spectra of DT; 1500 traces were obtained from five different points and averaged to give the resulting curve. (d) dI/dV spectra of DT.

accordance with previous studies.^{15,20,29} Second, the lack of optical access in our UHV-STM setup. Therefore we could not switch to the open form of As-DE.

The I - V characteristics of the surrounding DT matrix are symmetric within the range of the measured bias (Fig. 4c). No peaks were found in the dI/dV spectra of the DT matrix that could be associated with the molecular orbitals of the DT (Fig. 4d). Since I - V s of the DT matrix are symmetric at the same tunneling conditions, the asymmetry of the I - V s of As-DE must originate from the structure of the molecule. The As-DE switch is designed with the same thiol-linkage at the end of the molecular backbone as the DT molecules. The major difference between As-DE and DT can be found in terms of partially conjugated electron density of the molecular backbone. Hence the higher conductance of As-DE is rendered by the resonant tunneling through the molecular orbitals within the measured range. The asymmetry of the I - V s of As-DE is then a consequence of the higher density of states at the negative bias regime.

3 Conclusions

In conclusion, we have incorporated a newly designed asymmetric diarylethene molecular switch into an insulating matrix at room temperature. The light-controlled conductance switching phenomenon was successfully demonstrated and simultaneously probed using STM. The number of photo-switching cycles of As-DE as well as the rates of switching is improved with respect to the previously studied symmetric diarylethenes. In addition, the local electronic properties of As-DE were measured with high spatial resolution using a lock-in technique at 77 K. The evolution of resonant tunneling conductance peaks in the STS spectra yielded information on the frontier orbital energies. As a result, we were able to determine that the HOMO–LUMO gap of the “on” state is 2.24 eV.

4 Experimental

A mixed monolayer of dodecanethiol and As-DE was self-assembled on Au(111). Dodecanethiol was used as received (Aldrich). The synthesis of the As-DE is reported elsewhere.³¹ 150 nm thick Au(111) films on mica and SAMs were prepared by procedures similar to those reported previously.²⁰ Thin mica sheets were heated for 16 hours at $T = 375\text{ }^{\circ}\text{C}$ under a typical pressure of $P = 3 \times 10^{-7}$ mbar in a home-made vacuum deposition system. Gold was deposited on the pre heated mica substrate at a constant rate of 0.01 nm s^{-1} to form a semi-transparent (20 nm) Au(111) layer, followed by 150 nm Au(111) layers at a rate varying between 0.01 nm s^{-1} and 0.1 nm s^{-1} . After deposition the substrates were kept at $T = 375\text{ }^{\circ}\text{C}$ for 1 hour and subsequently the temperature was gradually decreased in order to reach room temperature for 5 hours. The fresh gold thin film was used immediately after removal from vacuum. We employed two different As-DE immersion procedures in our experiments, namely normal and reverse procedures. In the normal procedure, freshly prepared Au(111) samples were inserted into a solution of diarylethene (approximately 0.5 mM) with varied immersion time from 12 h up to 2 days. The samples were subsequently rinsed three times with ethanol (Uvasol, Merck) and dried under a flow of nitrogen gas. The second step consisted of immersing the samples into a 0.5 mM solution of DT in ethanol overnight. The solution was subsequently heated at $40\text{ }^{\circ}\text{C}$ for 5 h, rinsed with ethanol and dried under a flow of nitrogen. In the reverse procedure, the gold samples were fully immersed into a DT solution in ethanol overnight followed by the same heating and cleaning treatment as performed in the normal procedure. Then, the gold-containing DT matrix was inserted into a solution of diarylethene overnight. In the end, the sample is rinsed with ethanol and cleaned by the flow of nitrogen. Irradiation of the SAMs and As-DE was carried out with a 300 W Xe lamp (LOT-Oriel), with appropriate filtering and fiber optics. The typical output was 433 mW cm^{-2} and 63.7 mW cm^{-2} for UV and visible light, respectively. We estimate the number of photons for these intensities as 1.34×10^{17} photons per cm^2 per second and 6.82×10^{17} photons per cm^2 per second for UV and visible light, respectively. The sample and fiber optic output were 7 cm apart. A cut-off filter was used to deliver visible light ($\lambda > 420\text{ nm}$), whereas a band-pass filter was used to deliver UV light ($\lambda = 313\text{ nm}$).

The UV-vis spectroscopy spectra of the molecular switches in *n*-hexane were recorded at room temperature using a JASCO V-630 spectrometer with a 1 cm path length quartz cuvette.

STM measurements were carried out using a PicoLE STM (Agilent) equipped with a low tunneling current STM scanner head (type: N9501-A) and a digital instrument from Agilent Technologies (model N960A). Tips were obtained by mechanically cutting a 0.25 mm Pt_{0.8}Ir_{0.2} wire (Goodfellow). The STM images were acquired in constant current operating mode, in air at room temperature. Typical scanning parameters for obtaining STM images of As-DE and DT matrix surface structures are in the range of 10 to 15 pA with the tip bias voltage ranging from -0.8 to -1.2 V . Scanning Tunneling Spectroscopy (STS) data were acquired using a Variable Temperature Ultra High Vacuum (VT-UHV) Omicron STM with a base pressure of

1.5×10^{-10} mbar and a temperature of 77 K. The measurements were performed in $I(V)$ mode and in the LT-STM system used the bias voltage V_b is applied to the tungsten tip and the sample is grounded. Briefly, the tip-sample distance was adjusted at a specific tunneling current and bias voltage set point and the feedback loop mechanism was disabled temporarily. During this period, the tunneling current variation for both molecules (As-DE and DT matrix) was obtained. In the experiments, the sweeping voltage range was held between -2.5 V and 2.5 V . In addition, the lock-in technique was used to measure the tunneling conductance spectra (dI/dV) and the $I-V$ curve acquisitions simultaneously. The amplitude voltage and modulation frequency (ω) were 26 mV and 1 kHz, respectively.

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References

- 1 J. R. Heath, *Annu. Rev. Mater. Res.*, 2009, **39**, 1–23.
- 2 A. Aviram and M. A. Ratner, *Chem. Phys. Lett.*, 1974, **29**, 277–283.
- 3 C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541–548.
- 4 N. J. Tao, *Nat. Nanotechnol.*, 2006, **1**, 173–181.
- 5 S. M. Lindsay and M. A. Ratner, *Adv. Mater.*, 2007, **19**, 23–31.
- 6 T. Kudernac, N. Katsonis, W. Browne and B. L. Feringa, *J. Mater. Chem.*, 2009, **19**, 7168–7177.
- 7 J. E. Green, J. W. Choi, A. Boukai, Y. Bunimovich, E. J. 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.
- 8 W. R. Browne and B. L. Feringa, *Molecular Switches*, Wiley-VCH, Germany, 2nd edn, 2011.
- 9 A. S. Kumar, T. Ye, T. Takami, B. Y. Yu, A. K. Flatt, J. M. Tour and P. S. Weiss, *Nano Lett.*, 2008, **8**, 1644–1648.
- 10 M. J. Comstock, N. Levy, A. Kirakosian, J. Cho, F. Lauterwasser, J. H. Harvey, D. A. Strubbe, J. M. J. Frechet, D. Trauner, S. G. Louie and M. F. Crommie, *Phys. Rev. Lett.*, 2007, **99**, 038301.
- 11 S. Yasuda, T. Nakamura, M. Matsumoto and H. Shigekawa, *J. Am. Chem. Soc.*, 2003, **125**, 16430–16433.
- 12 K. M. Poulsen, L. Patrone, N. S. Hansen, J. B. Christensen, J.-P. Bourgoin and T. Bjornholm, *Nano Lett.*, 2005, **5**, 783–785.
- 13 M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803–808.
- 14 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. van Wees, *Phys. Rev. Lett.*, 2003, **91**, 207402.

- 15 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.
- 16 J. He, F. Chen, P. A. Liddell, J. Andreasson, 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.
- 17 S. J. van der Molen, J. Liao, T. Kudernac, J. S. Agustsson, L. Bernard, M. Calame, B. J. van Wees, B. L. Feringa and C. Schönenberger, *Nano Lett.*, 2009, **9**, 76–80.
- 18 A. J. Kronemeijer, H. Akkerman, T. Kudernac, B. J. van Wees, B. L. Feringa, P. W. M. Blom and B. de Boer, *Adv. Mater.*, 2008, **20**, 1467–1473.
- 19 N. Katsonis, A. Minoia, T. Kudernac, T. Mutai, H. Xu, H. Uji-i, R. L. S. de Feyter and B. L. Feringa, *J. Am. Chem. Soc.*, 2008, **130**, 386–387.
- 20 Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. P. Junior, A. M. Rawlett, D. L. Allara, J. M. Tour and P. Weiss, *Science*, 2001, **292**, 2303–2307.
- 21 M. Kim, J. N. Hohman, Y. Cao, K. N. Houk, H. Ma, A. K. Jen and P. S. Weiss, *Science*, 2011, **331**, 1312–1315.
- 22 K. Uchida, Y. Yamanoi, T. Yonezawa and H. Nishihara, *J. Am. Chem. Soc.*, 2011, **133**, 9239–9241.
- 23 S. J. van der Molen and P. Liljeroth, *J. Phys.: Condens. Matter*, 2010, **22**, 133001.
- 24 D. A. Bonnell, *Scanning Tunneling Microscopy and Spectroscopy: Theory, Techniques, and Applications*, Wiley-VCH, New York, 1993.
- 25 N. Phelan and M. Orchon, *J. Chem. Educ.*, 1968, **45**, 633–637.
- 26 T. Kudernac, T. Kobayashi, A. Uyama, N. Katsonis, K. Uchida, S. Nakamura and B. L. Feringa, Manuscript in preparation.
- 27 M. T. Cygan, T. D. Dunbar, J. J. Arnold, L. A. Bumm, N. F. Shedlock, T. P. Burgin, L. Jones, D. L. Allara, J. M. Tour and P. S. Weiss, *J. Am. Chem. Soc.*, 1998, **120**, 2721–2732.
- 28 J. M. Tour, L. Jones II, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh and S. V. Atre, *J. Am. Chem. Soc.*, 1995, **117**, 9529–9534.
- 29 L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour and P. S. Weiss, *Science*, 1996, **271**, 1705–1707.
- 30 S. van der Molen, H. van der Vegte, T. Kudernac, I. Amin, B. L. Feringa and B. J. van Wees, *Nanotechnology*, 2006, **17**, 310–314.
- 31 T. C. Pijper, T. Kudernac, W. R. Browne and B. L. Feringa, submitted.