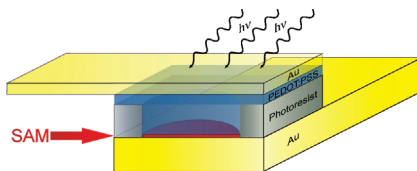


COMMUNICATION

Organic Electronics

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A reliable and reproducible solid-state molecular electronic device that shows bidirectional conductance switching of molecular origin is demonstrated. The devices are manufactured by conventional processing techniques and are based on a molecular monolayer of photochromic diarylethenes, sandwiched between two electrodes, which switches reversibly and in situ between two conductance states via optical addressing.



Reversible Conductance Switching in Molecular Devices

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Reversible Conductance Switching in Molecular Devices**

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In the last decades, the use of organic molecules as active elements in electronic devices has attracted considerable attention, following the theoretical studies of Aviram and Ratner predicting that a single molecule can operate as a diode.^[1] Electronic transport through molecules has been investigated experimentally in many different device geometries including scanning probes, break-junctions, and metallic crossbars.^[2,3] These studies showed that producing good electrical contacts to molecules is very challenging, but of great significance to measure the molecular properties, the interface at the molecular level, and to achieve functional active devices.^[4–6] To realize a molecular electronic circuit, crossbar junctions are required with functional molecules sandwiched between two electrodes. To introduce functionalities into the molecular junctions, molecules should be designed to deliver a specific property to the electronic device, such as rectification^[1,7] or switching.^[8,9] However, the difficulty of making proper electric contacts to molecules has strongly hindered the successful realization of devices of which the incorporated functions can be solely attributed to addressable organic molecules.^[10] Diode-like characteristics can often be explained by instable or unreliable contacts.^[11] Metal filament growth through molecular monolayers is also common^[12] and is, instead of molecular functionalities, an explanation for switching behavior observed in molecular junctions.^[13]

A fundamental problem with electrical molecular switches is that the conductance of the ON and OFF state is not known a priori. As a result, extrinsic effects such as filament formation can easily mask molecular switching properties. Here we present a reliable and reproducible approach that measures the intrinsic conductance switching of a functional molecular

monolayer layer based on photochromic diarylethenes (Fig. 1 and inset Fig. 2A). These molecular switches have two distinct isomers: the ring-closed form is conjugated and the ring-open form nonconjugated. It is expected that both isomers show different conductances, because the conjugation is changed.^[14,15] Theoretical studies show a change in conductance of 1–2 orders of magnitude, subject to the specific substitution pattern around the photochromic core.^[16,17] To realize a solid-state molecular switch, a newly developed processing technique is applied for producing stable and reliable molecular junctions.^[18–20] The so-called large-area molecular junctions are processed in vertical interconnects in an insulating photoresist matrix. The diarylethene monolayer is self-assembled in the individual interconnects and topped off with a highly conductive organic top electrode. This organic top electrode is a key step in the processing and is used to prevent the formation of short-circuits from top to bottom electrode. Then, upon irradiation with a specific wavelength range, the conductance of these devices can be optically switched. The major advantage of this approach is that the two distinct isomers of the diarylethene can be individually synthesized and, therefore, separately assembled in a device. Consequently, the ON and OFF state can be independently measured in the assembled devices, without any involvement of a switching event. Optically induced switching of the conductance of the devices in between these two states then provides a direct proof of the molecular origin of the switching events.

In solution,^[21] mesoscopic,^[22] and crystalline phases,^[23] these compounds demonstrate photochromic behavior and the conjugated and nonconjugated states of the diarylethene can be interconverted, in a fully reversible manner, by exposure to different specific wavelength ranges. In the dark, these switches show low fatigue and high thermal stability.^[21] Ring closure, the transformation to the conjugated state, is achieved upon irradiation of 300–350 nm, and ring opening to the nonconjugated state is realized with 500–600 nm irradiation. This particular molecular switch (Fig. 1) was designed^[24] with the thiolate group at the *meta* position of the phenyl ring to avoid direct conjugation of the diarylethene switching unit with the contacts.^[25]

In a molecular junction, when tunneling is the dominant conduction mechanism, the tunneling current through the closed state is expected to be higher than through the open state. Because of the lowering of the highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gap when the π -conjugation is extended, the tunnel barrier for electrons to flow is effectively lowered. Indeed, this is supported by break-junction experiments,^[14,26] scanning tunneling microscopy

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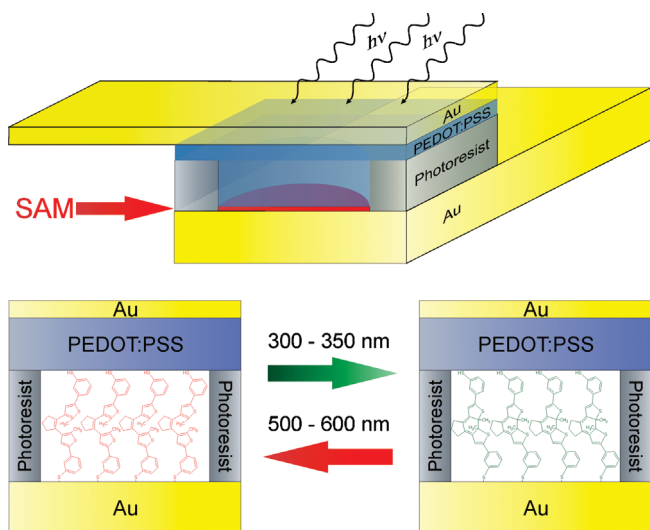


Figure 1. Schematic cross section of the device layout of a large-area molecular junction in which the diarylethene is sandwiched between Au and poly(3,4-ethylenedioxythiophene): poly(4-styrenesulphonic acid) (PEDOT:PSS)/Au. Using UV (312 nm) illumination the open, nonconjugated isomer (in red) can be converted to the closed, conjugated isomer (in green). Visible irradiation of 532 nm reverses the photoisomerization process.

(STM) measurements,^[15] experiments with carbon nanotube electrodes,^[27] and data from Au nanoparticle networks.^[28] However, reversible switching behavior solely based on molecular characteristics still has to be demonstrated in solid-state electronic devices in which the ON and OFF states can be independently assembled and characterized.

The large-area molecular junctions containing a self-assembled monolayer (SAM) of diarylethenes were processed according to a previously reported method.^[18–20] In short, gold bottom electrodes, 60 nm thick, were thermally evaporated on a silicon wafer after deposition of a 1 nm chromium adhesion layer. Circular vertical interconnects with a diameter of 10–100 μm were prepared in insulating photoresist on top of the electrodes by conventional spin-coating and UV lithography. Subsequently, the wafer was immersed in a 1 mM ethanol solution of molecular switches for at least 36 h. The thioacetyl end-group spontaneously dissociates to form a gold surface-bound thiolate during the self-assembly process.^[29] After the formation of a homogeneous SAM, a 90 nm thick organic top electrode consisting of poly(3,4-ethylenedioxythiophene) and poly(4-styrenesulphonic acid) (PEDOT:PSS) was spin-coated on top of the SAM. Finally, an auxiliary semitransparent 20 nm top gold contact was thermally evaporated onto the junctions, and utilized as a self-aligned reactive ion etching mask for the removal of redundant PEDOT:PSS to electronically isolate discrete devices (Fig. 1).

The formation of the SAM on identically prepared Au samples was investigated by X-ray photoelectron spectroscopy (XPS). Angular dependent measurements were performed with angles of 10°, 45°, and 90° between the sample surface and the detector. These angles give rise to an information depth of approximately 2, 7, and 10 nm, respectively. The elements

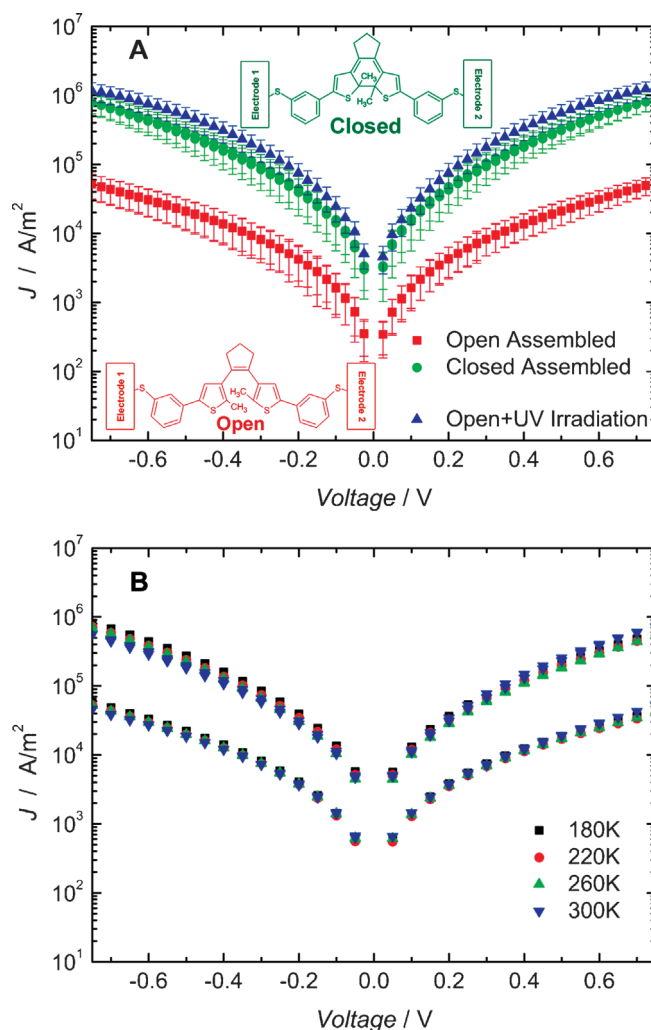


Figure 2. A) J - V characteristics of the closed (green) and open (red) isomers as self-assembled in the molecular junctions, and J - V characteristics of the junctions with the open isomer self-assembled and subsequently photoisomerized to the closed isomer with UV irradiation (blue). Averaged data (at least 35 devices) from devices with diameters of 10–100 μm . Error bars by standard deviation. B) Temperature dependence of the J - V characteristics of the open (lower curves) and closed isomeric state (upper curves). Averaged data for each temperature of at least 35 devices with diameters of 10–100 μm .

present at the surface were identified first, while the atomic concentrations of these elements were determined from narrow-scan measurements. For all samples, measurements were obtained in duplicate. The raw data of the measurements at 45° are listed in Table 1, while the data for the different angles are similar and in good agreement with each other, indicating that a homogeneous layer is present on the Au surface. As reference, a cleaned gold substrate was used which was prepared in the same vapor deposition batch as the substrates used for the monolayers of both the open and the closed isomer.

To extract more useful parameters, the results from Table 1 were analyzed by means of a model calculation,^[30] assuming the following three layers: the Au substrate, the Au–thiol

Table 1. Raw atomic concentrations (at %) on the surface of the XPS samples measured directly from peak areas at 45° angle.

Sample	Au 4f		C 1s				O 1s		S 2p		
	C _x H _y	C–O	C=O	O–C=O	Shake	SO _x	C–S ^H	Au–S			
Reference	71.4	20.3	3.5	1.1	1.5	–	2.2	–	–	–	–
Reference	71.6	20.8	2.2	1.4	1.7	–	2.3	–	–	–	–
Closed-1	37.5	46.0	4.6	2.1	0.7	–	2.5	0.3	4.2	2.0	–
Closed-2	37.8	46.4	4.2	1.4	1.8	–	2.1	0.2	4.2	2.0	–
Open-1	32.1	48.2	5.9	1.2	1.3	–	3.4	0.3	5.5	2.1	–
Open-2	32.3	48.0	6.0	1.6	0.9	–	3.2	0.3	5.4	2.3	–

bonds, and all other components of the organic layer (Table 2). The theoretically calculated length of the molecules, and thus the layer thicknesses for a 0° tilt angle along the surface normal, are 2.0 and 1.9 nm for the closed and open switches, respectively. The terminal S–H bond length was subtracted from the end-to-end distance and the Au–S distance of 2.3 Å was added. The correspondence between the calculated and measured layer thickness of the SAMs indicate, together with the similarity of data obtained for the various angles, that indeed a homogeneous monolayer of molecular switches is present on the Au surface.

For further analysis of the electronic data obtained on these molecular switches, as discussed later in this Communication, we would like to emphasize the fact that the planar closed switch has a lower grafting density than the open switch. Furthermore, the calculated layer thickness for the closed switch (2.0 nm) is higher than that calculated for the open switch (1.9 nm), whereas the measured layer thicknesses show the opposite effect, that is, the closed switch (2.0 nm) forms a thinner layer than the open switch (2.4 nm). This effect can be explained by a difference in tilt angle in correlation with the packing density, similar to alkanethiols on Au and Ag.^[31] The grafting of the sulfur head group on the underlying Au surface (with a Au–Au spacing of 2.88 Å) and the mutual interactions (π – π stacking, van der Waals interactions) of the molecular switches determine the energetically most favorable packing density and tilt angle. Because the grafting density of the closed switch is lower according to XPS measurements (most likely the closed, conjugated isomer will form a herringbone-like packing^[32]), the molecules have to increase their off-normal tilt angle to optimize the interactions with neighboring molecules and to minimize their free energy. In this manner

Table 2. Results of the standard model calculations: thickness (*d*), coverage of sulfur (N_S), and composition of the organic top layer.

Sample	<i>d</i> [nm]	N _S [cm ⁻²]	C 1s		O 1s		S 2p		
			C _x H _y	CO _x	SO _x	C–S ^H	Au–S		
Reference	0.6	–	71.6	21.3	6.7	–	–	–	–
Reference	0.6	–	73.7	19.0	6.9	–	–	–	–
Closed-1	2.0	4.4 10 ¹⁴	72.3	11.7	3.4	0.6	7.0	5.0	–
Closed-2	2.0	4.3 10 ¹⁴	73.2	11.7	2.9	0.3	7.0	5.0	–
Open-1	2.4	5.4 10 ¹⁴	69.4	12.2	4.4	0.4	8.3	5.2	–
Open-2	2.4	5.7 10 ¹⁴	69.3	12.3	4.2	0.4	8.1	5.6	–

the molecules will adopt conformations that allow high degrees of interactions with their neighboring molecules and, therefore, a closer packing of the molecular backbone. Consequently, the effective layer thickness is smaller than anticipated from the calculated end-to-end distance. Vice versa, the bulky and noncoplanar open isomer occupies more conformational space (free volume) and interacts with its neighboring molecules even without any canting. The free energy is minimized by using its internal rotational freedom to optimize the interactions with the neighboring open isomers.

After the verification of the SAM formation, as a first step in the electronic characterization of the molecular switches, separate current density versus voltage (*J*–*V*) characteristics were measured of large-area molecular junctions in which molecules exclusively in the open or closed states are self-assembled between the electrodes. The as-assembled open (OFF) and closed (ON) switches determine the lower and higher limits, respectively, and thus the maximum possible current density ratio between the OFF and ON state (Fig. 2A). During all *J*–*V* measurements up and down sweeps were performed. No hysteresis was observed for any of the devices. Average current densities are calculated from at least 35 devices for both isomers with device diameters ranging from 10–100 μm. The values obtained for the current density through the open, insulating state are in good agreement with measurements on alkanedithiols with comparable layer thickness (20 Å, HS–C₁₄H₂₈–SH) in the same junctions. At low bias the current increases linearly with applied voltage, while at higher bias an exponential increase is observed. The conductance through the closed, more-conducting state of the switch is shown to be 16 times higher at 0.75 V bias. These reference measurements demonstrate that the resistance of this specific switch can be varied by more than 1 order of magnitude by changing the isomeric (or conjugated) state of the molecules. Furthermore, the current densities through both open and closed switches are temperature-independent in the range 180–300 K (Fig. 2B). This observation, together with the exponential *J*–*V* characteristics, confirms (nonresonant) tunneling as the dominant transport mechanism in these junctions. It should be noted that for the closed, conjugated form of the molecule other transport mechanisms could also play a role.^[33] Apart from information about the transport mechanism, temperature-independent transport infers that minor heating of the devices while irradiating will not influence the conductance of the molecular devices. This eliminates the assignment of current changes to small temperature fluctuations during irradiation.

The absorption spectra in Figure 3 of the open and closed switch demonstrate the possibility to utilize distinctly different wavelengths for switching from the open to the closed state (300–350 nm) and vice versa (500–600 nm). The ability to optically access the molecules in the junctions imposes restraints on the thickness of the top contact. The 20 nm thickness of the gold top electrode ensures sufficient optical transmission through the layers of PEDOT:PSS (90 nm) and Au (20 nm), namely 19% and 43% in the 300–350 nm and

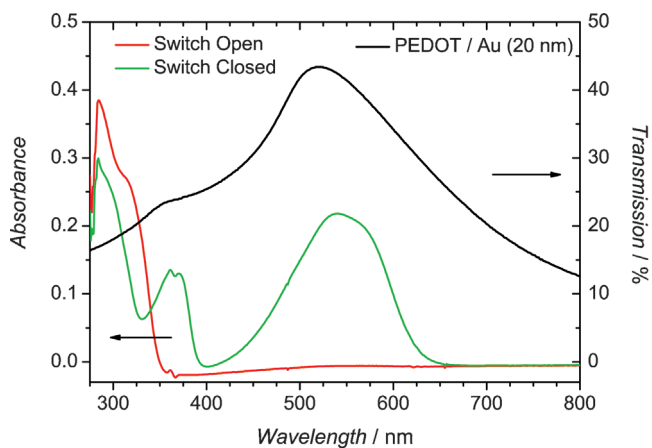


Figure 3. Absorbance of the open (red) and closed (green) isomers obtained in toluene compared with the transmission (black) of the top electrode stack PEDOT:PSS (90 nm)/Au (20 nm).

500–600 nm regimes, respectively, for illumination of the molecules inside the devices (Fig. 3). Wafers with the open isomer of the switch self-assembled in the devices were illuminated for 15 min with 312 nm UV irradiation to convert the molecular switches in the devices to the closed isomer. The J - V characteristics of the converted open-state isomer after UV irradiation show an increase of the conductance through the monolayer, as expected from the as-assembled devices with closed isomers present (Fig. 2A). Following UV irradiation and consecutive measurements, these devices were illuminated with 532 nm irradiation (visible light; see Supporting Information). The quantum efficiency for ring opening of these switches is known to be appreciably lower than for ring closure.^[21] Therefore, an illumination time of 45 minutes was chosen for visible light to achieve ring opening of the switches in the SAM. The observed J - V characteristics show a significant decrease (by a factor 3) of the conductance upon visible light irradiation, but the conductance of the as-assembled open state isomer is not fully recovered (see Supporting Information). This might be a consequence of the ring opening kinetics, molecular conformation, packing of the self-assembled monolayer, or perhaps the inherent energetic structure of the electrode–molecule system is such that not all molecular switches can be switched back after ring closure.

Conversely, no change in conductance upon visible illumination is observed when our starting point of the experiments is the as-assembled closed isomer. An explanation can possibly be found in a partial conversion of the monolayers. When partially converting the monolayer from the open state to the closed state, the conductance will quickly be dominated by the smaller fraction of closed isomer. In the conversion from closed to open a larger fraction of the monolayer should be switched before the open isomers start to dominate the conductance. However, since the devices with the UV-irradiated open assembled isomers so uniquely reproduce the J - V characteristics of the closed assembled devices, we argue that the observed phenomenon stems from a different packing of the molecules in the SAM.^[34] In the monolayer, this packing

is imposed by the underlying gold surface in contrast to packing in crystals. While the closed state isomer is conjugated, less flexible, and more planar, the open state is nonconjugated and preferably both halves adopt a nonplanar (strongly twisted out of plane) conformation. The planarity and rigidity of the closed state results in a denser packing of the molecular backbone in the monolayer on the gold surface, even though the grafting density is lower, as explained before in the discussion of the XPS data. Consequently, no sufficient conformational freedom is present for the out-of-plane bending during the conrotatory ring-opening process owing to steric hindrance of surrounding molecules. As the open state isomer requires more space, a less dense monolayer is formed, which allows for conformational and rotational freedom (more free volume), and as a consequence a reversible switching process is possible. This reversible process is in accordance with reversible optical switching of diarylethenes in solution and a variety of condensed phases.^[15,21–23,25,28]

To confirm that the observed changes in current densities through the junctions are intrinsically due to the molecular switching events in the devices, illumination of reference devices without switchable moieties is mandatory. First, devices were processed omitting the self-assembly of switches, resulting in Au/PEDOT:PSS/Au junctions in the vertical interconnects. As expected, ohmic behavior is observed for these junctions and the current densities are orders of magnitude higher. UV irradiation and subsequent measurements show no change of the electrical characteristics (Fig. 4A). This implies that neither the PEDOT:PSS layer nor the interface PEDOT:PSS/Au is responsible for any increase in conductance upon illumination. To eliminate the possibility of switching caused by the bottom S–Au bond, the top thiol/PEDOT:PSS interface, or some characteristics general to molecules, devices with 1,12-dodecanedithiol ($\text{HS-C}_{12}\text{H}_{24}\text{-SH}$) were processed and irradiated. Again, no change of conductance is observed (Fig. 4B), demonstrating that the isomerization of the diarylethenes is the origin for the observed conductance switching. Moreover, the large-area molecular junctions with alkanedithiols and thin top contact can also be stored for at least 75 days in ambient (light) conditions^[18] and have been measured in ambient light conditions, implying that visible light has no effect on the conduction in these junctions. Clearly, the decrease of the current upon visible irradiation as observed through devices with incorporated switches is of true molecular nature and results from the presence of the molecular monolayer of switches.

To further elucidate the bidirectional switching, multiple in situ illumination cycles were performed (Fig. 5). The modulation of the current density through the devices by multiple irradiation sequences is a compelling demonstration of molecular switching. First, the assembled monolayer of the open isomer is irradiated at 312 nm for 4 min, and a rapid increase of the current density by a factor 7 is observed (Fig. 5A and B), due to the photoisomerization to the closed, conjugated state. After 4 min a current density of $1.5 \times 10^5 \text{ A m}^{-2}$ is achieved. Then, the light source is removed for 60 s and

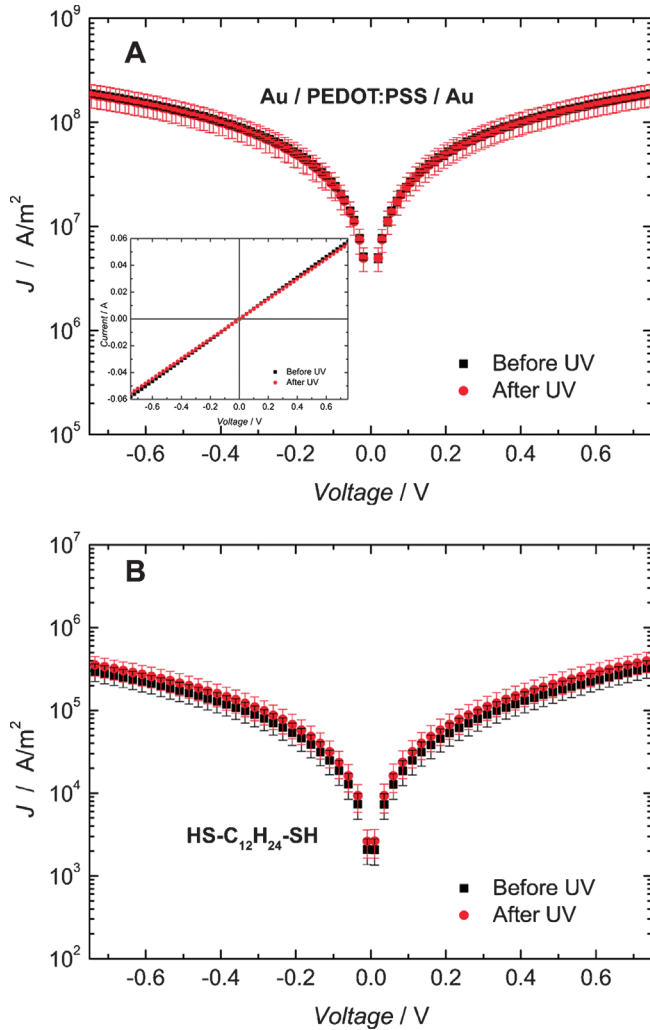


Figure 4. A) Ohmic Au/PEDOT:PSS/Au short-circuited devices show no change of the J - V characteristics upon UV irradiation. B) No switching is observed in the J - V characteristics of devices with a SAM of 1,12-dodecanedithiol in the large-area molecular junctions.

subsequently the switches in the molecular junction are irradiated at 532 nm for 4 min. Immediately, the current density through the monolayer of switches decreases, because the photoisomerization reverses the closed state to the open isomeric state. A current density of $4 \times 10^4 A m^{-2}$ is achieved, which is only a factor of 2 higher than the value obtained for the as-assembled open switch (Fig. 5B). The observed profiles suggest that the majority of the molecules is switched relatively easily and fast, while upon prolonged exposure the current slowly increases. Prolonged illumination with both 312 nm and 532 nm will enhance the ON/OFF ratio, because saturation of the current density has not been reached after 4 minutes, but will approach its maximum asymptotically. Finally, we performed 25 irradiation cycles (alternation of 13 UV cycles of 2 minutes and 12 visible illumination cycles for 4 minutes) on the molecular junctions and measured its current densities at 0.5 V to demonstrate the stability and reversibility of the

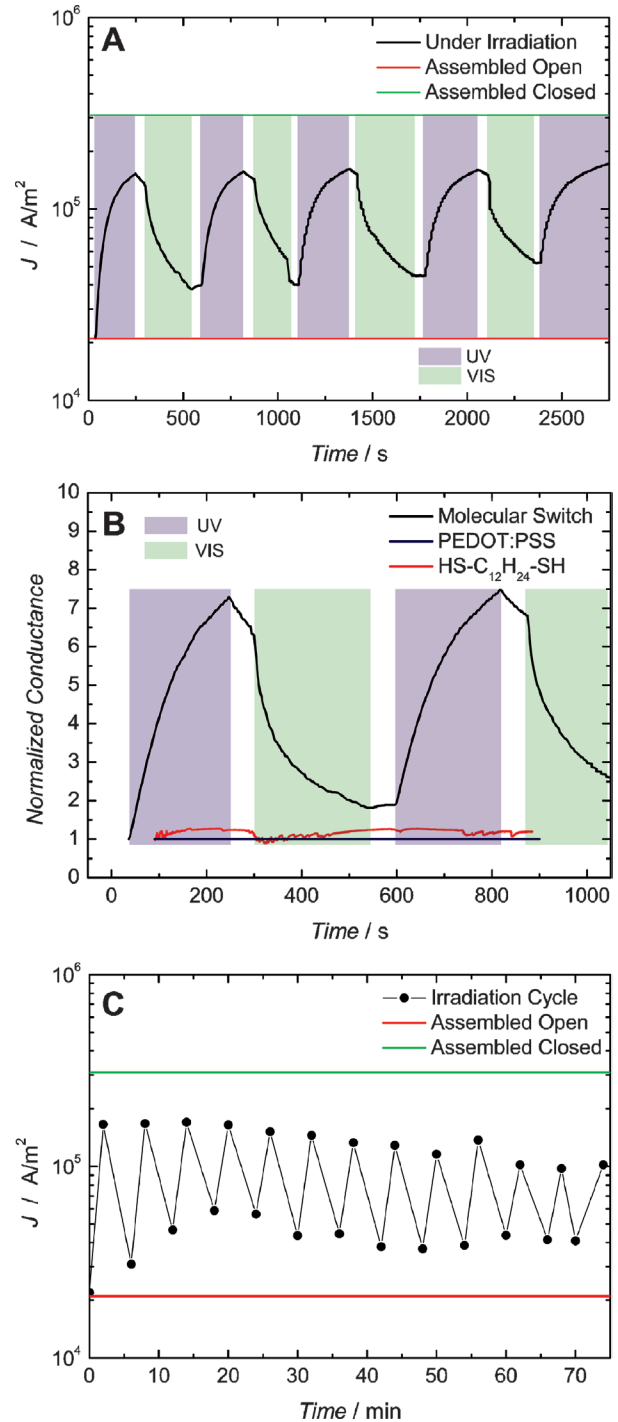


Figure 5. In situ optical switching of a monolayer of diarylethenes at 0.5 V bias results in a direct current modulation of the molecular junctions. A) Comparison of the current densities of the as-assembled devices based on the open (red) and closed (green) isomer with the in situ irradiated molecular junctions (black). B) Comparison of the normalized conductance data from the molecular diarylethene switches with in situ measurements on junctions with non-switchable 1,12-dodecanedithiol and with PEDOT:PSS only. C) Current density (at 0.5 V) vs. time for the in situ optical switching of a monolayer of diarylethenes. Alternation with UV (2 minutes) and visible (4 minutes) illumination results in a direct current modulation through the molecular junctions.

isomeric switches under ambient conditions (Fig. 5C). A distinct ON/OFF ratio is maintained throughout the 25 cycles.

We note that a complete switching to the OFF state is difficult to achieve as mentioned above. Furthermore, these measurements establish that the conductance of the high-conducting state is slowly decreasing after switching off the UV light, in contrast to devices with the assembled closed state. This arises from the presence of a constant voltage bias stress of 0.5 V for almost one hour over the samples during these in situ measurements. It has been previously shown that under electrochemically controlled conditions an applied voltage induces switching.^[35] As stated before, other conduction mechanisms can be important for the conduction through the closed monolayer of switches. Charging of the molecules during bias stress is thus a possibility although tunneling is the main transport mechanism. Charged species of the closed isomer, depending on the specific substitution of the photochromic core, can destabilize this isomer, resulting in a complicated ring opening process.^[35] Without any or only shortly applied bias during the illumination, instead of prolonged stress, we do observe a complete switching (Fig. 2A) from the OFF to the ON state. As a further reference experiment, in situ measurements were also performed on devices without any monolayer (Au/PEDOT:PSS/Au in blue) and with 1,12-dodecanedithiol (red) as the SAM (Fig. 5B). No substantial effect is observed upon irradiation of these devices, which enforces our previously stated conclusion that the observed switching is of molecular origin and that any form of photoconduction in these devices is absent.

In conclusion, junctions with a self-assembled monolayer of photochromic diarylethene-based switches clearly demonstrate an ON/OFF ratio of 16 upon irradiation. No switching is observed for devices without a molecular monolayer or with a monolayer of nonswitching alkanedithiol molecules. Therefore, the bidirectional switching and the accompanying modulation of the conductance are truly a manifestation of the structural and electronic changes of the molecular monolayer of the photochromic switches inside the junctions. The macroscopic alteration of the current in these solid-state molecular electronic devices originates from photoisomerization of the molecular monolayer of diarylethenes. These molecular devices can operate as an electronic ON/OFF switch and as a reprogrammable data storage moiety that can be optically written and electronically read. Our results offer exciting prospects toward tailoring existing molecules and incorporation of novel molecular switches, thereby providing a range of functional molecular devices. Finally, the implementation of a molecular monolayer of optical switches in molecular electronic devices, processed by conventional techniques, is a clear leap towards functional molecular electronic applications and integration in circuitry.

Experimental

Large-Area Molecular Junctions: Bottom contacts of 60 nm thick Au were thermally evaporated with 1 nm Cr adhesion layer on p-type silicon wafer with 500 nm thick oxide (Silicon Quest). Next, negative

photoresist (Ma-N 1410, MicroResist) was spin-coated onto the wafer. Patterning of the resist was done with a Süss Maskaligner MA1006, and the resist was developed in ma-D 533S. Next, the wafers were immersed in an 1 mM solution of molecular switches for at least 36 h. After immersion the wafers were rinsed with ethanol, toluene, and 2-propanol and spin-dried. PEDOT:PSS (Baytron P HC V4) was spin-coated onto the wafer and dried in vacuum. A 20 nm thick semitransparent top Au contact was thermally evaporated. As a last step, a reactive ion etching step in oxygen was done with a home-built RIE etcher to remove all exposed and redundant PEDOT:PSS.

I-V measurements were performed in vacuum as well as ambient pressure. For the vacuum measurements, a home-built setup was used. While the devices can all be measured in air, some of the measurements were performed in vacuum to eliminate contributions from water in the PEDOT:PSS. In all cases, a Keithley 4200 Semiconductor Analyzer was used to record the measurements. Temperature dependent measurements were performed by cooling the devices in the home-built vacuum setup with liquid nitrogen to 180 K and heated to 300 K. At every stage the temperature was stabilized for at least 10 minutes to ensure the wafer was at the desired temperature.

Illumination of the devices was performed outside vacuum. For UV irradiation, the 312 nm UV source was used of an 8 Watt 312/364 nm Spectronics Spectroline E-Series UV Handheld lamp. A 5 mW laser pointer (532 nm) was used for the visible irradiation.

X-Ray Photoelectron Spectroscopy: The measurements were carried out in a Quantum from ULVAC-PHI (Q2), using monochromatic Al K α radiation (25 W), with a measuring spot of 100 μm , scanned across an area of 1200 \times 500 μm .

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