

Ultrathin Reduced Graphene Oxide Films as Transparent Top-Contacts for Light Switchable Solid-State Molecular Junctions

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The use of molecules as active electronic components in computational circuitry is a longstanding goal of molecular electronics.^[1] The development of synthetic molecules endowed with desirable functionalities, and the incorporation of these molecules into reliable solid-state electronic devices, have been two major challenges since the dawn of molecular electronics.

From the perspective of functional molecules, species possessing at least two interconvertible molecular states are defined as molecular switches, which have been studied extensively for a broad range of nanoelectronic and nanomechanical applications.^[2] In particular, the successful transduction of different charge or conformational states of the molecules into electrical switching signals show great promise for building memories and logic devices at the molecular level.^[3] Among a number of external stimuli, light offers a non-invasive, low-cost and easilyaddressable way for triggering molecular switches in electrical



been devised, and several well-studied families of photochromic molecules, such as azobenzenes,^[3f,4] diarylethenes^[3b,5] and spiropyrans,^[6] have presented potential opportunities for optoelectronic applications. A less explored photochromic system, the dihydroazulene (DHA)/vinylheptafulvene (VHF) system was introduced in the 1980s.^[7] DHA undergoes a light-induced ring-opening reaction to the corresponding VHF, which in turn undergoes a thermally activated ring-closure reaction back to DHA. The photoreactions of DHA derivatives to the corresponding VHFs are often characterized by higher quantum vields than the trans to cis isomerization of azobenzenes, and it was shown that the absorption maximum of VHFs can be strongly tuned by substituent groups.^[8] Single-molecule electronic measurements on the DHA/VHF system have recently been undertaken,^[9a,b] as well as a first study of DHA/VHF switches immobilized as a monolayer on a gold surface.^[9c]

devices.^[2b,c] To date, a variety of photochromic molecules have

From a device-fabrication perspective, the first step is to unambiguously make contacts to molecular components while retaining their functionality.^[1c,10] While various test beds for contacting and probing single molecules and their ensembles have been reported,^[11] molecular junctions based on self-assembled monolayers (SAMs)^[12] can be constructed and operated in a more reproducible manner, more amenable to mass production and inte-gration.^[13] However, direct vapor deposition of metals onto SAMs has proven to be very invasive and damaging,^[10a,14] normally resulting in a high percentage of short-circuits.^[15] To address this problem, several methods for making soft contacts to SAMs have been developed.^[10a,16] Among these methods introducing a conductive interlayer between metal and SAMs worked well to prevent shorts, achieving high device yield and operational stability.^[11g,13,17] Particularly, by using poly(3,4-ethylenedioxythiophene) stabilized with poly(4-styrenesulphonic acid) (PEDOT:PSS) as the interlayer, a light-controlled solidstate switching device based on monolayers of diarylethenes was successfully constructed,^[5c] which was a breakthrough for large-area functional molecular electronic applications. Nevertheless, for specific optoelectronic applications, PEDOT:PSS (up to 100 nm thick) with an auxiliary semi-transparent top Au contact^[5c] would limit the efficiency of light in addressing the underlying molecules, due to low transmittance.





Figure 1. a) Schematic view of molecular test bed with rGO thin film as transparent top contact. b) Schematic cross section of the molecular junction and molecular structure of DHA 1 and VHF 2 illustrating the thermo-optical switching. Charge transport measurements are made through adjacent micropore junctions in series.

Very recently, our group^[18] as well as Lee et al.^[19] independently reported the successful use of reduced graphene oxide (rGO)^[20] film as the interfacial layer between molecules and top metal electrodes. In particular, benefiting from the high inplane conductivity of rGO films compared with molecular components, we introduced a new test bed in which rGO films can perform as conductive top contacts and interconnects between SAMs in series, obviating the need for an additional top metal contact. Herein, by utilizing the high optical transparency of ultrathin rGO films in the above-mentioned double junction layout, we report a new type of light switchable solid state device based on monolayers of photo switchable molecules (Figure 1). The transparent rGO film and special double junction layout permits the SAMs to be photoswitched in situ while simultaneously enabling charge transport measurements across the molecules. Bidirectional conductance switching events with an average on/off ratio of 5-7 were recorded and ascribed to the structural changes of DHA/VHF isomers. This study is the first demonstration of the use of graphene materials as transparent top-contacts for light switchable solid-state molecular junctions, and highlights the great potential for graphene materials in molecular electronics.

The structural difference between interconvertible DHA 1 and VHF 2 in solution, with regard to conjugation, spatial shape, and dipole moment, was reflected by significantly different UV-vis absorption maxima of the two species (Figure 2a). DHA 1 exhibited an absorption maximum (λ_{max}) at 358 nm while VHF 2 exhibited a red-shifted absorption maximum at 476 nm. The reverse reaction occurred thermally and was significantly accelerated by increasing the temperature. Reversible conformational change between DHA 1 and VHF 2 can be induced by alternating light irradiation and heat treatment. The compounds were stable enough to survive several cycles without any sign of decomposition. Similar UV-vis absorption spectra for other DHA/VHF couples have been reported previously,^[8,21] however, very little is known about the photochromic properties of DHA/VHF molecules in the solid state. We employed Raman spectroscopy to probe the interconvertible molecular states of DHA 1 and VHF 2 in the form of solid-state powders. A part of the Raman spectrum of the DHA 1 powders is shown in Figure 2b. The Raman band arising from the -CN groups was observed at 2246 cm⁻¹ and had a FWHM of \approx 6 cm⁻¹. After recording the Raman spectrum, the powders were exposed to UV light. Upon UV exposure, a distinct color

change was observed going from transparent to red (Figure 2c). Furthermore, the powder initially exhibited a bright blue fluorescence (see Supporting Information), which rapidly disappeared during photoconversion. A new spectrum after UV exposure showed a small peak at 2211 cm⁻¹ from VHF 2 in addition to the original peak at 2246 cm⁻¹ arising from DHA 1, indicating the DHA 1 had been partially converted into VHF 2. The ratio between the integrated CN-peaks from DHA 1 and VHF 2 in this spectrum is 2:1. Our theoretical calculations indicate that the peak from VHF 2 is roughly 10 times more intense than the peak from DHA 1, leading to the conclusion that the majority of the powder was still present as DHA 1. Most likely, the photoconversion only took place in the top molecular layers of the powder and the system would slowly convert back to initial DHA 1, evidenced by a decreased intensity of the VHF 2 peak over time (see Supporting Information). In order to fully photoconvert the material, DHA 1 powder was dissolved in toluene and placed under UV exposure for 15 min. The solution shifted from colorless to deep red (Figure 2a). The solution was dropcast on a metal surface and set to dry in the dark. When dry, another Raman spectrum was recorded. All the DHA 1 seemed to have converted into VHF 2 since the peak at 2246 cm⁻¹ had disappeared and only a peak at 2209 cm⁻¹ with a FWHM of $\approx 16 \text{ cm}^{-1}$ was present (Figure 2b). The experimental Raman spectroscopy data match closely the theoretical Raman spectroscopy calculation on the DHA 1 and VHF 2 (ab initio calculations, see Supporting Information).

After characterizing the DHA 1/VHF 2 couple in solution and as powders, the next crucial step is to assemble them as SAMs on metal surfaces without losing their photoswitching ability. The acetyl-protected thiolate anchoring group was synthesized in a meta configuration on a phenylene unit to decouple the photochromic core from the electrodes in an effort to reduce surface quenching (Figure 1). The SAM was formed on clean and flat Au substrates. Electrochemical characterization by cyclic voltammetry (CV) indicated that the surface properties of the Au substrate were significantly changed by the coverage of VHF 2 SAMs (see Supporting Information). X-ray photoelectron spectroscopy (XPS) was employed to determine the quality of the SAMs. The measurements were performed with angles of 0° , 40° and 60° between the sample surface and the detector. The data for different angles indicated that clean and uniform monolayers were present on the Au surface. Figure 3a depicts the S 2p spectrum for VHF 2 SAMs at 0° . No obvious changes

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Figure 2. a) UV-vis absorption spectroscopy of DHA 1 and VHF 2 in MeCN. Irradiation of DHA 1 (1.0×10^{-5} M) with UV light (365 nm) induces ring-opening reaction to VHF 2. The initial DHA 1 and final VHF 2 absorption spectra are indicated by thick lines. VHF 2 undergoes a thermally-induced ring-closure reaction back to DHA 1. b) Raman spectra of solid-state powders composed of DHA 1 only, a mixture of DHA 1 and VHF 2, and VHF 2 only. c) Upon UV exposure, the color of the powders changed from transparent to deep red. Initially bright blue fluorescence was also observed which rapidly disappeared during photoconversion. The scale bar is 20 μ m.

were observed after thermal annealing at 70 °C for 0.5 h (DHA 1 SAMs, not shown). Under both conditions, the S 2p signals showed only one doublet with S $2p_{3/2}$ at 162 eV attributed to an S atom bound to Au. No signal was observed at 164 eV (from S–C or S–H bonds) and no peak appeared at 168 eV for oxidized S. At higher detection angles, where XPS is the most surface sensitive, traces of S at 164 eV were detected and traces of oxidized S from air annealed sample were observed. The data thus verified that the molecules were bound to the surface via S–Au for both DHA 1 and VHF 2 SAMs. Data analysis revealed a negligible change of SAM thickness (*d*) for the as-prepared VHF 2 sample and the after-annealing sample (DHA 1), both yielding thicknesses around *d* = 1.4–1.5 nm (further XPS information).

Calculations have revealed that the dipole moment of VHF is about twice that of DHA ($\mu_{DHA} = 6.0$, $\mu_{s-cis-VHF} = 11.6$,

 $\mu_{\text{s-trans-VHF}} = 15.7$ Debye).^[22] Thus, the hydrophobicity of the SAM surface should be reduced when converting DHA to VHF.^[23] The contact angle of VHF 2 SAM was found to be $63 \pm 1^{\circ}$. It reached $82 \pm 2^{\circ}$ after 30 min thermal treatment at 70 °C, and reverted to its initial state after exposure to UV light (365 nm) for 2 h. Optical images in Figure 3b depict a visible change of surface wettability triggered by external stimuli. This interconvertible change ($\approx 19^\circ$) was attributed to two distinct molecular states (VHF 2 and DHA 1) of the SAM. Reversible wettability transitions can be reproduced for at least 5 cycles by alternating heating and UV irradiation (Figure 3b), albeit with prolonged UV exposure in the last few rounds (likely due to degradation of the SAM). Collectively, XPS and water contact angle measurement confirmed that the DHA 1/VHF 2 couple can be immobilized onto an Au surface as high-quality SAMs with their thermo-optical activity retained.

For the fabrication of reliable molecular junctions, welldefined junction areas, minimized parasitic leakage current and non-destructive contacts to the molecules are important considerations. An insulating layer of aluminium oxide (\approx 30 nm) was patterned by electron beam lithography (EBL) to define Au bottom contacts in micropores (2 and 4 µm in diameter). In this way, the molecules were only assembled inside the pores (Figure 1). The presence of a SAM inside the micropore cavity was confirmed by Kelvin-probe force microscopy (see Supporting Information). The preparation of rGO thin films as a soft top contact was described in our previous work, where they were shown to form reliable (>90% yield) and highly uniform contacts in the applied micropore devices.^[18,24] rGO thin films have been studied extensively as a transparent and flexible electronic material.^[20a,c] In the present work, we transferred the rGO films onto quartz (Figure 3c, inset) and recorded optical transmission spectra of the films with varied thickness (Figure 3c). These ultrathin films (<10 nm) were confirmed to have fairly high and uniform light transmittances across the UV-vis region. A decrease of transmittance with increased film thickness was also observed, as expected. Conversely, thicker films normally possess higher in-plane conductivity.^[18,20c] Concerning both optical and electrical properties, we chose \approx 5 nm thick rGO films with up to 25 000 S m⁻¹ in-plane conductivity and higher than 80% transmittance for device fabrication. The optical transmittance of these rGO films are found to be superior to the previously applied PEDOT:PSS Au contacts (See Suporting Information for comparison). After the molecules were self-assembled onto Au bottom electrodes inside micropores, the rGO thin films were transferred onto the SAMs as a top contact. The hydrophilic aluminium oxide, low aspect-ratio (<1:50) holes, and flexibility of rGO films all facilitated the transfer process. Figure 3d shows optical and atomic force microscopy (AFM) images of a working device covered by a rGO film. The rGO thin film follow the topography of the substrate very well making up potentially an ideal contact to the SAM at the bottom of the micro well.

The solid-state molecular junctions were measured in a double-junction configuration, as illustrated in Figure 1b. rGO thin films not only made a non-destructive contact to the SAMs, but also acted as the conductive interconnect allowing measurements on SAMs in series. More significantly, transparent rGO allows incident light to easily access the underlying







Figure 3. a) S 2p XPS signals for VHF 2 SAMs. b) Optical images of water droplets on surfaces of DHA 1 (left) and VHF 2 (right) SAMs, and reversible wettability transitions as a function of alternating thermal treatment and UV irradiation. c) Optical transmission spectra of rGO films with a series of film thicknesses. Inset, a \approx 7 nm-thick rGO film transferred onto quartz for transmission measurement. d) Optical and AFM images of rGO films transferred onto bottom electrodes. The ultrathin flexible rGO film follows the topography of the electrode patterns and ensures a good contact to the SAMs at the bottom of the microholes. The texture of the film is clearly visible.

molecules. The measurement started from junctions based on VHF 2 SAMs. As the photochromic molecules were sensitive to light while in solution, it was more straightforward to use fully converted VHF 2 for the SAM formation rather than pure DHA 1. Both 2 μ m and 4 μ m diameter junctions were measured.

The current density versus applied voltage (I-V) characteristics for molecular junctions based on VHF 2 monolayers before and after thermal annealing (70°C for 0.5 h, DHA 1) is shown in Figure 4a. The data is averaged from at least 24 junctions (both 2 µm and 4 µm diameter junctions) of the same batch. An increase in *I* was observed after thermal treatment. Statistics based on more than 200 junctions confirmed that SAMs of DHA 1 showed higher conductivity than that of VHF 2 (Figure 4b). Conductance values were calculated from linear fits of the lowbias region (-0.3 V \leq V \leq 0.3 V), and the corresponding histogram indicates an averaged conductance on/off ratio of 5-7 (Figure 4b). Exposure to UV irradiation in turn resulted in a decrease of I and these bidirectional conductance switching characteristics were reproduced by alternating thermal treatment and UV irradiation (Figure 4c). We emphasize the fact that UV irradiation normally did not fully recover the low-conducting state of VHF 2 SAMs (see Supporting Information), resulting in a decrease of the on/off ratio (Figure 4c, inset). To confirm that the conductance switching is intrinsically due to structural changes of the molecular components in the devices,

independent control experiments were conducted. J-V characteristics of junctions without SAMs (rGO only), with SAMs of non-switching C12 alkane thiols and conjugated OPE3 are shown in Figure 4d-f, respectively. For rGO-only junctions, ohmic behavior was observed and the current densities were orders of magnitude higher. Neither thermal treatment nor UV irradiation influenced the I-V characteristics. For junctions with a monolayer of non-switchable molecules (Au/C12/ rGO/C12/Au and Au/OPE3/rGO/OPE3/Au), the influence of UV irradiation was also negligible, while thermal treatment resulted in a slight increase of conductivity of less than a factor of 2 (Figure 4e,f). This small irreversible thermal annealing effect is the only change that was observed in monolayers of the non-switchable molecules, and optical switching was observed only for the DHA/VHF couple. Collectively, it is evident that the observed conductance switching is a molecular feature, that is to say due to the interconversion between DHA 1 and VHF 2 isomers induced by optical and thermal stimuli.

The current magnitude of the DHA/VHF devices is in the range expected for molecular junctions, as observed by the two reference systems (C12 and OPE). The rGO electrode, on the other hand, is orders of magnitude more conducting^[18] thus ruling out changes in the rGO conductance as the origin of the observed device response. In previous measurements on single molecules coupled only to one electrode with a tunnel-ling gap to the other, the VHF isomer was shown to be more



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Figure 4. a) J-V characteristics of VHF 2 (as prepared) and DHA 1 (70 °C for 0.5 h) isomers self-assembled in the molecular junctions. The data are averaged from at least 24 junctions of the same batch. b) Conductance on/off ratio histogram (purple bars) based on more than 200 junctions. SAMs of DHA 1 show a higher conductivity than that of VHF 2 by an averaged factor of 5–7. The blue and red bars correspond to non-switchable OPE3 and dodecanethiol molecular junctions, respectively. c) Representative bidirectional conductance switching characteristics induced by alternatingheating and UV irradiation. UV irradiation normally does not fully recover the low-conducting state of VHF 2 and thus results in a decrease of the on/off ratio (inset). d,e,f) J-V characteristics of junctions without SAMs (rGO only), with a SAM of dodecanethiol and with a SAM of OPE3, respectively.

conducting than DHA.^[9] In the present case, through-bond tunnelling along the molecular backbone is expected to dominate the charge-transport. Moreover, the junction conductivity is an average of many molecules in a monolayer. The increased backbone flexibility of the VHF **2** isomer gives rise to a larger number of possible molecular conformations in the SAM, compared with the much more constricted conformations of DHA **1**. This difference in conformational freedom is supported by ab initio calculations (see Supporting Information). Hence, the surface morphology could play a significant role in determining the conductivity of the device, as the different molecular conformers will have varying coupling strengths to the physisorbed top electrode. Specifically, the reduced conformational flexibility in DHA 1 means that all the conformations are of approximately similar height, that is to say, all the molecules are equally close to the top contact and can contribute to the charge transport. Conversely, for VHF 2 the transmission through the conformations corresponding to relatively short

www.advmat.de tunnelling length (possibly more highly conducting states, for example, injection through the cyano group) could be partially screened by taller conformations (lower conductive states, for example, injection into the 7-membered ring). Thus, the monolayer DHA/VHF device can be considered an electromechanical switch, differing from individual single-molecule electronic measurements. It is in this regard interesting to make a comparison with the conducting AFM studies of SAMs of cis/transisomeric azobenzenes on a Au substrate.^[3f] These studies reveal that the *cis*-isomer is more highly conducting than the trans-isomer due to a smaller tunnelling barrier length. The effective length of the *cis*-isomer is only from the Au-S bond to the exposed azo group, touching the AFM tip, while it is the full length of the molecule for the trans-isomer. In contrast, calculations reveal that trans-azobenzenes are significantly more conducting than cis-azobenzenes in regards to transport through the entire molecules.^[25] We anticipate that the rGO top-contact test bed can be employed generally for a wide range of light-

molecules and their monolayers. In summary, we have studied the reversible photoisomerization of DHA/VHF derivatives 1/2 in solution, in the solid state and in SAMs, and analyzed its effect on the SAM thickness, surface wettability, and electrical conductivity. More significantly, by using solution-processed ultrathin rGO films as a transparent, soft top-contact, we successfully constructed solid-state conductance switches operated by thermo-optical stimuli. The flexible, conductive and transparent rGO films permit molecular monolayers to be photoswitched in situ while simultaneously enabling charge transport measurements across the molecules. The double-junction geometry with well-defined electrode area and spacing obviates the need for an additional top metal contact and provides a simple reproducible architecture. Experimental results showed that SAMs of DHA 1 displayed a higher conductivity than that of VHF 2 with an average current on/off ratio of 5-7 (or >3 when accounting for thermal annealing effects). By alternating thermal annealing and UV irradiation, bidirectional conductance switching could be achieved. Independent control experiments confirmed that the conductance switching properties were due to the intrinsic structural change of photochromic molecules. These results demonstrate the immense potential of graphene materials for molecular electronic applications, for example, by exploiting the high transparency, high conductivity and the mechanical flexibility of the material.

switchable monolayer junctions, some of which could exhibit

improved device performances depending on the nature of the

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The work was supported by the Danish-Chinese Center for Molecular Nanoelectronics, funded by the Danish National Research Foundation, the Center for Synthetic Biology funded by the UNIK research initiative



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of the Danish Ministry of Science, Technology and Innovation (Grant 09-065274), the European Union seventh Framework Programme (FP7/2007–2013) under the grant agreement n° 270369 ("ELFOS") and the Lundbeck Foundation. The authors thank Dr. Tue Hassenkam for fruitful discussions.

Received: February 5, 2013 Revised: April 9, 2013 Published online:

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