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Light-modulation of the charge injection in a polymer thin-film transistor by functionalizing electrodes with bi-stable photochromic self-assembled monolayers

Thomas Mosciatti, Maria G. del Rosso, Martin Herder, Johannes Frisch, Norbert Koch, Stefan Hecht^{}, Emanuele Orgiu^{*}, Paolo Samorì^{*}*

Dr. T. Mosciatti, Dr. M.G. del Rosso, Dr. E. Orgiu, Prof. P. Samorì

ISIS & icFRC, Université de Strasbourg & CNRS, 8 allée Gaspard Monge, 67000 Strasbourg, France. E-mail: samori@unistra.fr, orgiu@unistra.fr

Dr. M. Herder, Prof. S. Hecht

Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany. E-mail: sh@chemie.hu-berlin.de

Dr. J. Frisch, Prof. N. Koch.

Institut für Physik & IRIS Adlershof, Humboldt Universität zu Berlin, Brook-Taylor-Straße 6, 12489 Berlin, Germany.

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The fabrication and optimization of organic and polymeric optoelectronic devices have been the focus of an active research endeavor during the last few years.^[1, 2] The integration of multiple components into a single device naturally opens the door to multifunctionality.^[3] The latter can be envisioned by considering an Organic Thin-Film Transistor (OTFT) as a basic unit for electronics, and by designing device architectures, in which several interfaces could be decorated with functional molecular systems. This includes the interface between different components blended as semiconducting materials and the interface between the active material with either the gate electrode^[4] or the source and drain electrodes.^[5] The main advantage of such an approach is to be able to use an independent stimulus, *e.g.* light, to address the individual components by changing their properties, thereby attaining control over the operation of the current flowing in the transistor channel. The ultimate goal is to develop approaches for the realization of devices that combine facile processability,^[6] flexibility^[7] and most importantly, implementing straightforward multifunctional character.^[5] More specifically, multifunctional character is intended as the capability of modulating the electrical output of an electric device with external stimuli, *e.g.* light. Among the several families of photochromic molecules, diarylethenes (DAEs) certainly provide unique properties.^[8] Upon irradiation at distinct wavelengths, DAEs are able to undergo isomerization between two stable isomers that possess very different electronic structures. The isomerization is accompanied by a minor change in the molecular geometry, and distinct DAEs can be designed such that they present a high fatigue resistance to multiple switching.^[9, 10] A straightforward strategy, which has been intensely explored by several groups, is to take advantage of both DAEs and semiconducting organic materials, upon blending, to generate a photo responsive bi-component layer.^[11, 12, 13, 14, 15] A different option is to employ thiolated photochromic molecules chemisorbed as self-assembled monolayers (SAMs) on gold electrodes, to reversibly modulate their work function^[16] or to change the

charge injection by varying the tunnelling barrier by using light irradiation at defined wavelengths.^[17] In particular, this approach offers the advantages of an easy and accurate control over the position of the photochromic units in the device and absence of the thermodynamically driven phase segregation of the different components. It also enables to directly modulate with a light stimulus a well-defined physical property of a device, *i.e.* the charge injection. This solution has been first exploited on azobenzene SAMs integrated in a bottom-contact bottom-gate device. It proved that irradiation with UV light triggering the isomerization of the azobenzene from the *E* to the *Z* form was accompanied by a modification of the charge injection at the electrode-semiconductor interface thus inducing a current modulation. Unfortunately azobenzenes suffer from two major problems: the speed of the isomerization is quite slow compared to other photochromic systems and one of the two states, *i.e.* the *cis*-isomer, has a very limited kinetic stability, therefore lacking bi-stability.

Here we show how to obtain high performance and low-fatigue bi-stable OTFTs with source and drain gold electrodes functionalized with DAE SAMs. We used a thiolated DAE ^[8, 18] which we specifically designed for this purpose by exposing a thiophenol group in the α -position and a 3,5-bis(*tert*-butyl)phenyl group in the ω -position (**Figure 1a**). This molecule's absorption band is centered at around 313 nm in the open form (o-DAE) and at 365 and 540 nm in the closed form (c-DAE). Upon irradiation at these wavelengths, it is possible to trigger almost quantitative interconversion between the two isomers (see Supporting Information). After a thorough study of the optical, energetic, and electrical properties of Au planar surfaces functionalized with thiolated-DAE SAMs, DAE monolayers were chemisorbed on gold source and drain electrodes of OTFTs and their optical switching behaviour in the devices was explored. To maximize the effective injection area, we utilized a top-gate bottom-contact device geometry.^[19] P(NDI2OD-T2), *i.e.* a well-known n-type polymer semiconductor, was employed because it exhibited high field-effect mobilities when

integrated into top-gate OTFTs.^[20] Importantly, P(NDI2OD-T2) was shown to form films possessing two strong optical absorption bands at 400 and 700 nm that do not overlap with those of the thiolated-DAE, making it an ideal candidate for this system.^[21]

Figure 1 a) Cartoon of the thiolated-DAEs based SAM chemisorbed on a planar gold surface, in its *open* (o-DAE) and *closed* (c-DAE) form. b) *In-situ* interconversion of a DAE SAM grown on a thin transparent gold electrode (15 nm thick) from the open (i.e. o-DAE) to the closed form (i.e. c-DAE) as followed with UV–Vis absorption spectroscopy by subtraction of subsequent spectra obtained after different irradiation times at 313 nm (0.14 mW/cm²). c) *In-situ* interconversion of c-DAE (black curve) grown on the same thin transparent Au electrode to o-DAE (red and blue curves) and then to c-DAE again (green curve) as followed by UV–Vis absorption by subtraction of subsequent spectra obtained after different irradiation times at 540 nm (0.42 mW/cm²) and 313 nm, respectively.

SAMs of the thiolated-DAE on gold have been prepared as described in the Experimental Section of the Supporting Information. We first confirmed by XPS (see SI) the presence of chemisorbed DAEs on the surface of the gold. Then UV-Vis absorption spectra were recorded during irradiation with UV light of Au films coated with a SAM of o-DAE. By subtraction of consecutive spectra (before and after irradiation) in order to remove the

contribution of the gold surface plasmon resonance, it is possible to observe characteristic bands. In particular, we observed the increase of the 540 nm absorption band, corresponding to the c-DAE, and for the first time with this technique, the increase of the band at 365 nm and the decrease in absorbance at 313 nm (**Figure 1b**). In this way, the complete cycle from the closed to the open form and back again by using visible light followed by UV light can be observed (**Figure 1c**). The absence of noticeable fatigue demonstrates the DAEs ability to undergo multiple switching cycles as SAM on gold.^[22]

In view of our ultimate goal of integrating DAE functionalized gold electrodes into top gate OTFTs to maximize switching efficiency we explored the electrical properties of mono-component thiolated-DAE based SAMs on gold. Three major factors play a role on charge injection in OTFTs based on a DAE SAM coated Au source and drain electrodes: (i) conductance of the SAM, (ii) work function shift as a result of photoisomerization, and (iii) wettability inducing changes in morphology.^[23]

Regarding the first factor, the difference in conductance between the closed and open form of DAEs SAMs are well known and have been widely studied by STM,^[24, 25, 26] AFM^[27] and molecular devices.^[28] In order to better understand and to prove different electrical contributions of the two forms of the thiolated-DAE SAM, we performed current density measurements in metal | SAM | metal junctions relying on liquid compliant Gallium-Indium (E-GaIn)/thiolated-DAE SAM/Au, respectively. This technique allows for reproducible, non-destructive, high throughput current density–voltage (J–V) measurements.^[29, 30] We found a difference of two orders of magnitude in conductance between the open and the closed form, which is consistent with both theoretical^[26] and experimental^[28, 31] reports. The closed form has an extended π -conjugation with respect to the o-DAE, hence the transport of charges across the monolayer is favored.^[32] We also observed a lower switching ratio in SAMs using the c-DAE isomer as the starting form, a result that can be ascribed to a tighter molecular

packing within the SAM of c-DAE compared to o-DAE (see Supporting Information).^[28]

Hence, all transistors tested in this work were prepared by chemisorption onto the Au electrodes of the DAE in its open form.

Another key approach for tuning the charge injection in a device is the shift in work function (WF) due to Au functionalization with a SAM.^[33, 34] By using specifically designed photochromic moieties equipped with a terminal thiol group to grow the SAM it is possible to tune the electrode's work function with light.^[35] To explore this aspect ultraviolet photoelectron spectroscopy (UPS) was performed on o-DAE SAMs and c-DAE SAMs on gold. Pristine gold exhibited a work function of (5.3 ± 0.05) eV. Gold functionalized with either o-DAE SAM or c-DAE SAM featured WFs of (4.32 ± 0.05) eV and (4.35 ± 0.05) eV, respectively (see **Figure S8a and S8b**). Within experimental error there seems to be no difference in WF between the two DAE isomers. Further, the P(NDI2OD-T2) is Fermi level (E_F) pinned at the conduction band in both cases, therefore, the almost negligible WF difference of the two SAMs cannot account for the current change recorded in devices. Taking into account the E_F pinned polymer levels and the very similar WF of both SAM/Au electrodes, it is apparent that the polymer has the same effective electron injection barrier in both cases. However, the o-DAE SAM has its LUMO level significantly above the Fermi level, whereas the c-DAE SAM has its LUMO level very close to E_F (see **Figure S9a and S9b**). By considering the significant tunnelling barrier for electrons introduced by the thickness of the molecular SAM (ca. 1.5 nm), the c-DAE SAM form allows for essentially resonant electron tunnelling from the metal through the c-DAE LUMO while for o-DAE the huge energy barrier enforces non-resonant tunnelling (see **Scheme 1**). This may well explain the increase in device current observed.

Scheme 1 Measured energy levels by UPS for the a) o-DAE SAM, and b) c-DAE SAM.

Further, PhotoElectron Yield counter operated in Ambient conditions (PEYA) and macroscopic Kelvin Probe (macroKP) measurements were employed to measure the WF under ambient conditions for both o-DAE and c-DAEs SAMs in the very same samples. The former technique exhibited a value of WF of (4.50 ± 0.05) eV for the o-DAE and (4.62 ± 0.05) eV for c-DAE SAMs [Figure S7 – details on how the experiments were carried out in order to avoid to activate the isomerization within the SAM when irradiating the samples with the UV light of the photoelectron spectrometers (PEYA and UPS) are discussed in the SI], while the latter method gave a net shift of (125 ± 24) meV. The combination of the three measurement techniques allows us to conclude that the change in WF due to the isomerization between open to closed form, albeit rather small, is consistent and in the same direction with respect to the vacuum level, with the c-DAE form having the higher work function. However, we believe that the increased current measured when the DAE SAM is in its closed form stems predominantly from the resonant vs. non-resonant tunnelling injection through the c-DAE vs. o-DAE SAM into the polymer.

Water Contact Angle (WCA) measurements were performed on SAMs of both DAE forms. The measurements indicated the hydrophobic nature of both surfaces featuring a contact angle of $(108 \pm 5)^\circ$ and $(100 \pm 6)^\circ$ for o-DAE SAM and c-DAE SAM, respectively. While such a photo-triggered change in contact angle of the SAMs is negligible, the change in wettability

with respect to the pristine gold surface ($53\pm4^\circ$) is remarkable. This suggests that the morphology of the polymer at the interface remains unchanged after isomerization, also because of the absence of a major geometrical/conformational rearrangement occurring between the two isomers. In **Table S2** all WF values and contact angles for the differently functionalized surfaces are reported, including mono-phenylthiol (MPT) as SAM on gold. We decided to characterize MPT for the same parameters in order to have a comparison with a non-photoresponsive SAM coating the Au electrodes, making it possible to rule out any contribution on current changes coming from the irradiation itself. Values obtained for MPT functionalized gold, both the WF (5.05 eV) and contact angle (79°), are in agreement with previous studies.^[23]

Figure 2 a) Schematic representation of the employed top-gate OTFTs with a scheme of the switching of the thiolated-DAE SAM interface between the open and closed form. b) Output characteristics of the o-DAE device before (black) and after (violet) UV irradiation. c) Transfer characteristic ($V_{ds} = 40$ V) of the o-DAE device after UV irradiation (in red) and after subsequent 540 nm light irradiation to reactivate the original state (in blue). Channel length (L) = 100 μm , and W = 10 mm.

Finally, we employed the DAE SAM functionalized Au as source and drain electrodes of the OTFT. We used a top-gate bottom-contact device architecture, employing a UV-transparent quartz slide as a support as depicted in **Figure 2a**. This choice enables to irradiate the device from the bottom (15-nm thick Au electrodes) as well as to maximize the isomerization yield of the DAE SAMs and consequently their effect on charge injection. In fact, the use of this geometry implies that a larger portion of the electrode surface is involved in charge injection with respect to the bottom-contact configuration. Further, P(NDI2OD-T2) has been found to exhibit higher mobilities in top-gate bottom-contact configuration.^[20] Cytop was used as dielectric layer.

All devices were tested in nitrogen atmosphere (glove box) and exhibited very good n-type characteristics, responding with an almost ideal spacing between curves at different gate voltages (see Supporting Information). Pristine P(NDI2OD-T2) OTFTs reached mobility values of up to $0.35 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The measured threshold voltage amounted to 4.5 V and 12 V in the linear and saturation regime, respectively. The $I_{\text{on}}/I_{\text{off}}$ ratio resulted in the range 10^4 - 10^5 and negligible hole transport was observed. All these characteristics and performances are in line with those previously reported on this material.^[36]

In addition to devices integrating pristine Au source and drain electrodes coated with the polymer semiconductor, devices with MPT-functionalized electrodes were tested because (i) the limited contour length of MPT should help to minimize the tunnelling resistance with respect to the pristine Au; (ii) the WF of MPT SAMs (on Au) is very close to that of pristine gold; and (iii) they improve the electrode wettability.^[23] The mobility values measured in devices with MPT-functionalized electrodes were lower than those of devices using pristine Au source and drain. The mobility decrease is approximately two-fold for the saturation regime mobility and of 20% for linear regime mobility in line with previous reports.^[23] The extracted mobility, V_{th} , and $I_{\text{on}}/I_{\text{off}}$ values are reported in **Table S3**.

Electrical characterization of o-DAE functionalized devices showed a very good reproducibility. In this case mobility values were found to be decreased on average by two-fold in the linear regime and saturation regime with respect to pristine devices based on uncoated Au electrodes, with an average value of $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and a maximum value of $0.17 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. On the other hand, an average increase of $I_{\text{on}}/I_{\text{off}}$ by up to ten-fold was observed. On the same time, V_{th} for o-DAE devices shifts towards more negative values, indicating that OTFTs bearing SAM-functionalized electrodes turn on at lower voltages with respect to the pristine ones. In other words, o-DAE electrodes at a given gate voltage are capable of injecting a higher current density with respect to the devices based on non-functionalized electrodes. This finding is in agreement with WF values reported above, showing that the WF of o-DAE functionalized gold is closer to the P(NDI2OD-T2) LUMO level with respect to bare gold, hence the barrier the charges have to overcome is lower. The devices were then irradiated with UV light (313 nm, $0.5 \text{ mW}/\text{cm}^2$) to promote the isomerization to c-DAE. We found that 10 minutes of irradiation are sufficient to record the maximum change in electrical performance. The c-DAE devices have a maximum source-drain current increase both in the output (**Figure 2b**) and transfer characteristics (**Figure 2c**). An irradiation at 540 nm for 20 minutes at very low intensity ($6 \text{ mW}/\text{cm}^2$) is enough to fully recover the initial electrical characteristics, indicating a complete back-switching of the molecules to the o-DAE isomer.

Figure 3 a) Normalized maximum drain-source current I_{ds} registered from the transfer characteristics with $V_g = +30$ V and $V_d = +10$ V for the linear regime (in brown) and $V_d = +40$ V for saturation regime (in blue) during irradiation of the device with UV (313 nm, 10 min) and visible (540 nm, 20 min) light. The constant ratio of the shift is highlighted by the dotted line, the green representing the o-DAE SAM and the violet the c-DAE SAM states of the device. Mobility and V_{th} values extracted from b) linear and c) saturation regime transfer curves for consecutive irradiation cycles performed. Channel length (L) = 100 μm and $W = 10$ mm.

We then performed multiple irradiation cycles to test reproducibility and fatigue effects. Each irradiation step consisted of 10 minutes of irradiation at 313 nm to switch to c-DAE and 20 minutes of irradiation at 540 nm for switching back to o-DAE, at the above-mentioned power. As shown in **Figure S11** it is possible to perform multiple cycles with no performance degradation, constant modulation of current, and full recovery of the electrical characteristics. The photo-triggered increase in maximum source-drain current is very constant through the irradiation cycles and it amounts to about 50% for saturation regime and 65% for the linear regime (**Figure 3a**). These results demonstrate a very effective and reproducible

photomodulation of the charge injection. The obtained values are the highest ever reported for OTFTs with a photochromic SAM on the device electrodes. It is worth to point out that previous examples of OTFTs based on light modulated charge injection achieved an output current modulation of only 20% with longer irradiation time.^[17]

The higher modulation is achieved in the linear regime because contact effects that govern charge injection are more pronounced at low source-drain voltage. In addition, full recovery of the original value is obtained after irradiation at $\lambda = 540$ nm for all cycles performed. A more detailed analysis was carried out by extracting mobility and V_{th} values from reported curves in **Figure S11** in the Supporting Information for the linear and saturation regime, respectively (**Figure 3b** and **3c**). The V_{th} was found to be constant throughout the entire measurement sequence suggesting that the difference in conductance between the isomers is responsible for the light induced modulation of the device current. In spite of the increased device mobility of about 70% for the c-DAE state, we believe that the increase in current cannot be ascribed to an improved charge transport within the polymer but, instead, it is favoured by the higher conductivity across the injecting c-DAE molecular layer.

Furthermore, the system is perfectly stable in both configurations and no thermal relaxation was observed for the closed form after many days. After 313 nm irradiation, the sample was left in the dark and tested again after 14 hours, after 90 days, and then after 150 days, showing no changes in the maximum source-drain current in both linear and saturation regime (**Figure S13**). These measurements prove that c-DAE SAM isomer is stable for over five months, suggesting a potential application of our transistors as memory devices. As reported in the Supporting Information, similar irradiation cycles performed on devices integrating either uncoated or MPT functionalized Au electrodes showed no changes of the electric output of the OTFTs thereby fully supporting the idea that the modulation of device

performance upon irradiation stems from the differences between the two isomeric thiolated-DAE SAM chemisorbed on gold.

Such increase in performance, stability, and responsivity with respect to azobenzene-based systems can be explained by the following reasons: (i) the use of bottom-gate configuration determines only a modest current change as a result of the optical stimuli because of the reduced injection area decorated by the photo-responsive molecules; (ii) the *Z* isomer tends to thermally relax to the *E* form, thereby impeding the generation of both an all-optical control and a bi-stable device that could be switched numerous times; (iii) azobenzene switching mechanism is typically rather slow in condensed media due to the necessary large geometrical rearrangement.^[17]

This also means that the here proposed solution of top-gate geometry could be further extended to p-type semiconductors (small molecules or polymers). Even if the energy alignment will not be optimal, the increase of the injection area achieved using this specific device geometry could be an asset to the overall performances and bistability of multifunctional OTFTs integrating DAE SAMs coated electrodes.

In conclusion, we designed and fabricated a photo-responsive top-gate bottom-contact OTFT integrating thiolated-DAE-functionalized gold source and drain electrodes. Such a functionalization guaranteed a light tunable charge injection at the electrode-semiconductor interfaces. Introduction of the thiolated-DAEs SAM layer did not severely affect the electrical characteristics, enabling us to obtain high-performance transistors with mobilities exceeding $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Moreover, by taking advantage of the photochromic nature of thiolated-DAEs, we imparted multifunctional character to the OTFTs. Light control of isomerization is bi-directional and is directly coupled to modulation of charge injection and thus to current output and device mobility. Notably, we obtained the maximum switching ratio ever for OTFTs with DAE-functionalized electrodes without detectable fatigue during

the course of the performed switching cycles. More importantly, both states, *i.e.* o-DAE and c-DAE, are stable for over five months. All the improvements presented here were achieved by a careful design of both molecular structure and transistor geometry. Finally, our results indicate that the different degree of conjugation between the DAE isomers affects the tunnelling of charges through the SAM, which can be resonant or non-resonant depending on the photo-controlled isomeric state. Our findings take the concept of electrode functionalization to a new level, demonstrating that a high-performance transistor with an optically modulable bi-stable charge injection can be easily obtained with standard laboratory facilities. Our approach holds potential for being harnessed for the fabrication of light-controllable logic circuits and memories.

Supporting Information

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

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