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Chemical Locking in Molecular Tunneling Junctions Enables Nonvolatile Memory with Large On–Off Ratios

Sumit Kumar, Michele Merelli, Wojciech Danowski, Petra Rudolf, Ben L. Feringa, and Ryan C. Chiechi*

This paper describes the reversible chemical locking of spiropyran switches bound to metallic surfaces to enable the encoding of nonvolatile information. Data are encoded spatially by selectively locking the spiropyran moieties in their merocyanine form using a combination of exposure to acid and UV light. Without exposure to acid, the merocyanine form spontaneously converts back to the spiropyran form. Bits are resolved by defining the regions of the monolayer that are exposed to acid, using a “soft punchcard” fabricated from a silicone elastomer. Information is read by measuring the tunneling charge–transport through the monolayer using eutectic Ga–In top-contacts. The merocyanine form is more than three orders of magnitude more conductive than the spiropyran form, allowing the differentiation of bits. Photoelectron spectroscopy shows that the monolayers are undamaged by exposure to light, acid, base, and applied bias, enabling proof-of-concept devices in which an 8-bit ASCII encoded six-character string is written, erased, and rewritten.

Molecular switches couple chemical, optical, and electrical control to the transport and physicochemical properties of molecular systems and devices.^[1,2] Their implementation in logic^[3] and memory^[4,5] devices has long been a driving force for research, from shrinking integrated circuits^[6] to encoding bits in individual molecules.^[7,8] At the length-scale of single-molecules, the dominant mechanism of charge–transport is tunneling and bits are defined by two (or more) different conductance states.^[9] These states arise either through varying the tunneling distance by a conformational change or a modification of the transmission probability when the electronic structure of the switch is altered. However, molecular switches present a thermodynamic challenge when it comes to nonvolatile memory because they will always thermalize back to the ground-state at a rate proportional to the activation barrier separating the states of the switch. In single-molecule switches, this limit manifests as rapid, stochastic switching.^[10] In ensemble

devices, the net change in conductance is proportional to the population of switches in the high-conductance state,^[11] which can depend on quantum yields and molar excitation coefficients and which decays at a rate that increases with temperature.^[12,13]

Spiropyrans (SPs) are a class of molecular switches that ring-open to a zwitterionic merocyanine (MC) upon irradiation with light and ring-close back to the SP form either thermally or by irradiation with bathochromic light.^[14] While the $SP \rightleftharpoons MC$ interconversion is subject to the same thermodynamic constraints discussed above, in solution it can be “locked” in the MC form by exposure to acid, forming MCH^+ .^[15–17] There is a lot of structural diversity in spiropyran switches and some derivatives may not

form merocyanines that are sufficiently stable in their protonated forms to lock, instead behaving like photoacids that ring-close and release a proton upon irradiation.^[18–20] It is an open question how spiropyrans respond to acid when assembled on surface—whether they lock or behave as photoacids. We previously demonstrated that the light-driven switching behavior is preserved in mixed monolayers, which show reversible conductance-switching in tunneling junctions upon exposure to light;^[21] those switches still spontaneously thermalize from the MC form back to the SP form. Mixed monolayers^[22] allow molecules with dissimilar lengths^[23] and/or functionality^[24] to co-exist in a monolayer, allowing fine-grained control over the properties of large-area tunneling junctions;^[25] in the case of SP the mixed monolayer strategy maximizes the switching ratio and minimizes fatigue. Here, we show that switches can be selectively locked in the MC form as MCH^+ , circumventing the thermodynamic constraints inherent to photoswitches and allowing the writing of bits defined by the 10^3 difference in conductance between SP and MC that arises from their different tunneling transmission probabilities. Subsequent unlocking allows bits to be erased by relaxing back to the SP form and then rewritten by repeating the process. This concept is shown schematically in **Figure 1**. The $SP \rightleftharpoons MC$ interconversion is shifted to MC by exposure to UV light (WRITE) and locked (LOCK) in the MC form by exposure to acid, encoding a 1. Exposure to base unlocks (UNLOCK) the conformation such that subsequent exposure to visible light (ERASE) shifts it back to the SP form, encoding a 0. Working with a mixed monolayer is critical, as it alleviates steric hindrance during self-assembly, allowing for

S. Kumar, M. Merelli, W. Danowski, Prof. P. Rudolf, Prof. B. L. Feringa, Prof. R. C. Chiechi
Zernike Institute for Advanced Materials
Nijenborgh 4, 9747 AG Groningen, The Netherlands
E-mail: r.c.chiechi@rug.nl

S. Kumar, M. Merelli, W. Danowski, Prof. B. L. Feringa, Prof. R. C. Chiechi
Stratingh Institute for Chemistry
University of Groningen
Nijenborgh 4, 9747 AG Groningen, The Netherlands

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.201807831>.

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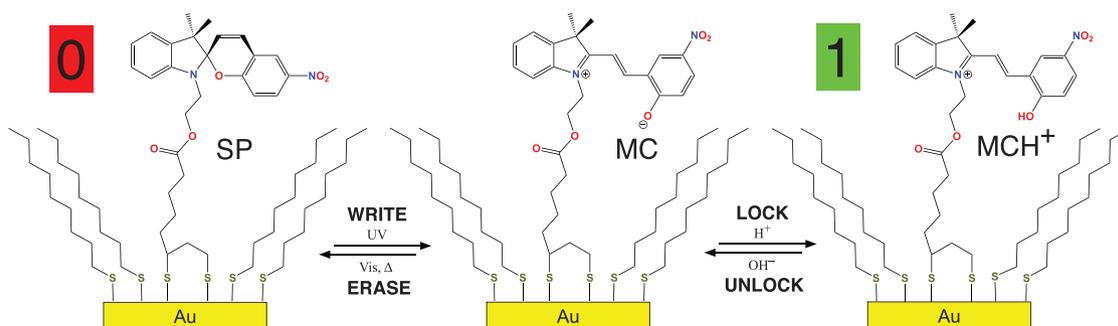


Figure 1. The SP form (left) represents a 0. Upon exposure to UV light (WRITE), the equilibrium shifts to the MC form, which is locked in place by exposure to acid to encode a 1. Subsequent exposure to base unlocks the MC form, allowing the bit to be erased by exposure to visible light (ERASE).

well-ordered self-assembled monolayers (SAMs) in which the chromophores^[26] are physically isolated, thus preventing irreversible side-reactions^[16] and imparting reversibility.^[21]

X-ray photoelectron spectroscopy (XPS) allows the examination of the monolayers before and after switching and (un) locking to determine if SP or MC undergo side-reactions and/or if the monolayer is damaged. Specifically, the N 1s spectrum and core level region tracks the $SP \rightleftharpoons MC$ interconversion, while the S 2p core level region reflects the quality of the monolayer.^[21,27–29] It is not possible to observe pure MC by XPS because switching is never 100% efficient and it thermalizes back to SP during sample preparation, however, a small peak of N^+ in the N 1s spectrum^[21,27,30] is indicative of the presence of MC in the monolayer.

Locking in the MCH^+ form requires an acid strong enough to protonate MC, but the acid dissociation constant (pK_a) does not readily translate to surface-chemistry and an ethanolic solution of triflic acid (TFA) is required to form MCH^+ in detectable quantities. SAMs of pure SP show no signs of damage from treatment with TFA, but undergo irreversible dimerization upon irradiation with 365 nm light. These experiments are described in detail in Section S1 in the Supporting Information.

Having established that TFA by itself does not negatively influence monolayer of SP, we repeated the XPS experiments on mixed monolayers of SP and hexanethiolate (SP-h), prepared by immersing pure Au substrates supporting pure SAMs of SP in solution of hexanethiol in ethanol for 24 h.^[21] Figure 2a,b shows the N 1s and S 2p XPS spectra of the mixed monolayers of SP-h after exposure to TFA and 365 nm light for 20 min followed by 24 h of white light. In the absence of TFA, exposure to white light would shift the $SP \rightleftharpoons MC$ interconversion back to 100% SP. In contrast to the pure SAM of SP shown in Figure S1 in the Supporting Information, the mixed monolayers of SP-h show three distinct peaks in the N 1s region; the indole N of SP (399.4 eV),^[27] the N^+ of MCH^+ (400.6 eV),^[31] and the NO_2 group (406.0 eV).^[27] The $SP:MCH^+$ ratio is about 1:1 as indicated by the fact that the intensities of the respective fingerprint contributions make up 29% and 28% of the total N 1s signal, respectively; hence the switching-efficiency of the combination of acid and UV light (the LOCK operation) is 50%, even after exposure to white light for 12 h. The N 1s core level spectrum proves that MCH^+ is stable to irradiation with white light, which further confirms that the switching of spiropyrans is irreversible in

pure SAMs, in contrast to switching in acidified solutions.^[18,19] The S 2p spectra show that the mixed monolayer of SP-h was not damaged, with only the doublet at 161.8 eV and peak at 163.6 eV corresponding to S chemisorbed to bulk Au and either S–S or physisorbed S. Control experiments on pure SAMs of hexanethiolate do not exhibit a peak at 163.6 eV after exposure to the same conditions (Figure S2, Supporting Information), thus we tentatively ascribe the peak to S–S formed from the intramolecular dimerization of the anchoring groups of SP. Overall, the LOCK operation does stress the mixed monolayers more than the light-driven switching process by itself.^[21] This stress could be (re)dimerization of the thiolate anchors of SP or surface rearrangement. In either case, SP (and MCH^+) remain bound to the surface and, importantly, there is no evidence of higher oxidation states of S (e.g., SO_2). Although this additional stress is likely to fatigue mixed monolayers of SP-h with repeated switching cycles, none of the sulfur species associated with the peak at 163.6 eV are the result of irreversible processes like the formation of oxides.

Figure 2c,d shows spectra for mixed monolayers of SP-h treated identically as above (i.e., the LOCK operation) and then immersed in ethanolic solutions of triethylamine (TEA) under exposure to white light for 3 h (i.e., the UNLOCK operation). The N 1s spectrum shows only two sharp peaks at 399.5 and 406.0 eV, corresponding to indole N of SP and NO_2 respectively. The S 2p spectrum (Figure 3d) is unaffected. Thus, the spectra in Figure 2 show that the LOCK operation results in a mixed monolayer in which 50% of the chromophores are in the SP form and 50% in the MCH^+ form and that the subsequent UNLOCK operation produces a mixed monolayer in which 100% are in the SP form. Although there are signs of the formation of S–S or physisorbed S during the LOCK operation, the mixed monolayer is completely unperturbed by the UNLOCK operation and shows no signs of catastrophic damage—contrary to pure SAMs of SP.

We previously demonstrated that mixed monolayers of SP-h in tunneling junctions with top-contacts of eutectic Ga–In (EGaIn)^[32] show a reversible change in conductance when switched with light.^[21] One of the advantages of EGaIn is that it forms large-area junctions ($\approx 500 \mu m^2$) nondestructively and reversibly, allowing for the use of XPS in between conductance measurements to prove that applying a bias of ± 1 V is innocuous. Thus, neither light and acid nor applied bias damage mixed monolayers of SP-h.

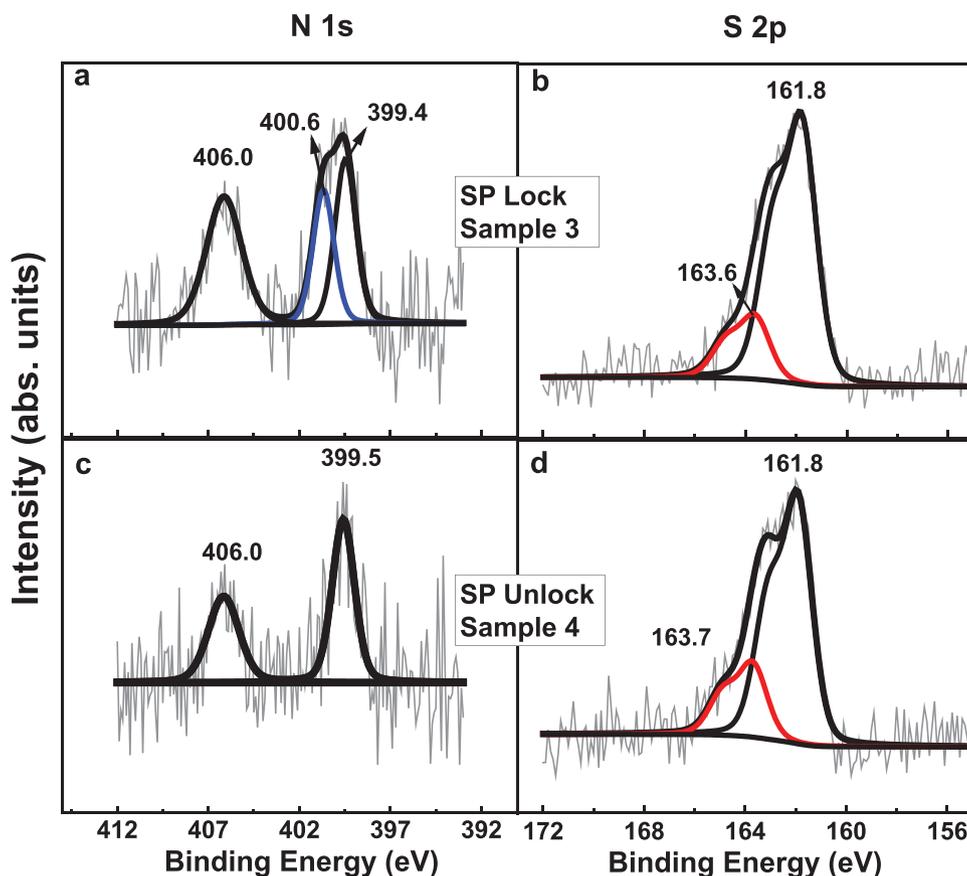


Figure 2. The XPS spectra of the N 1s a,c) and S 2p b,d) core level regions for mixed SAMs of SP and hexanethiolate on Au. Top panels: after immersion in ethanolic TFA under UV light for 20 min, drying and exposure to white light for 12 h before measurement. The three indicated peaks in the N 1s spectrum a) correspond to an approximately 1:1 mixture of SP and MCH⁺. Bottom panels: spectra relative to a second sample, treated identically and then exposed to ethanolic TEA and white light for 3 h shows two sharp peaks in the N 1s spectrum c) and no change in the S 2p spectrum d) indicating that 100% of the molecules switched back to SP.

To characterize the effect of the LOCK and UNLOCK operations (i.e., exposure to combinations of acid/base/light) on the conductance of mixed monolayers of SP-h, we recorded current–density versus voltage (J/V) sweeps between ± 1.0 V after LOCK and UNLOCK operations in a controlled atmosphere of 1.5 ppm O₂ and <5% relative humidity.^[33] The green J/V curve in Figure 3a is a control experiment on a mixed monolayer of SP-h after exposure to 365 nm light for 20 min to switch it to the MC form and then white light for 12 h to switch back to the SP form. The red J/V curve was recorded on the same mixed monolayer shown in Figure 2a,b (Sample 3) and shows that exposure to acid, followed by 365 nm light for 20 min (LOCK) increases the conductance by a factor of 10³. The black J/V curve was recorded after subsequent exposure to white light for 12 h and demonstrates that the acid treatment locks the mixed monolayer in the high-conductance state. The blue J/V curve was recorded on the same mixed monolayer shown in Figure 2c,d (Sample 4) and proves that exposure to acid, followed by 365 nm light for 20 min (LOCK), followed by base, and then white light for 12 h (UNLOCK) returns the mixed monolayer to the initial, low-conductance state. (Two different samples were necessary because a single sample did not survive the cumulative stress of LOCK and UNLOCK cycling

plus being taken in/out of ultrahigh vacuum for two XPS measurements.)

Figure 3b shows histograms of $\log|J|$ at 1.0 V for the red, black, and blue J/V curves in Figure 3a. The data are distributed log-normal with no significant outliers and there is no overlap between the high- and low-conductance states, which is important for the READ operation because it is performed by briefly measuring the current at a fixed bias (as opposed to extracting values from histograms of repeated measurements). Strongly skewed or unusually broad distributions decrease the likelihood of a READ successfully distinguishing between a mixed monolayer (bit) in the high- (1) or low-conductance (0) states. The datapoints and error bars in Figure 3a represent the peak value and variance of histograms for each voltage. The complete lack of overlap in the histograms is due to the unprecedented switching ratio of 10³, which is the highest reported for in-place switching of a molecular tunneling junction. Light-driven switching alone gives a ratio of 35,^[21] but chemical locking either increases the fraction of switches in the MC form or further increases their tunneling transmission probabilities. In either case, a ratio of 10³ is large enough for potential technological applications.

An advantage of SAMs (and mixed monolayers) is that they spontaneously form one-molecule-thick films over arbitrarily

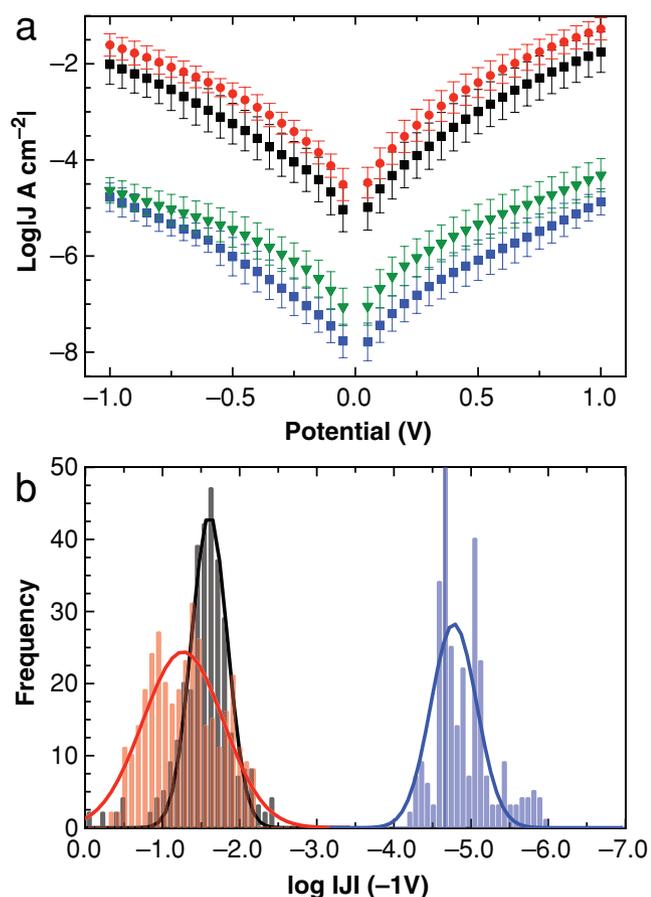


Figure 3. a) J/V curves of the mixed monolayers shown in Figure 2 measured using conical EGaln top-contacts. Red (Sample 1): exposure to acid, followed by 365 nm light for 20 min (LOCK). Black (Sample 1): after subsequent exposure to white light for 12 h. Blue (Sample 2): exposure to acid, followed by 365 nm light for 20 min (LOCK), followed by base (UNLOCK), and then white light for 12 h. Green: after exposure to 365 nm light for 20 min followed by white light for 12 h. b) Histograms of $\log|J|$ at 1 V for the red, black, and blue curves. The datapoints and error bars in panel (a) are the peak value and variance of histograms for each voltage.

large areas, greatly simplifying the formation of metal/molecule/metal tunneling junctions. A disadvantage is that the

switching/locking phenomenon shown in Figure 1 occurs everywhere in the SAM. The most straightforward way to encode information is to pattern the locked regions of the SAM spatially, by rasterizing the light used to induce switching while exposing the entire SAM to an acid or patterning the acid and exposing the entire SAM to light. Bitstreams can be (de)coded from physical media patterned with a spiral of bits, for example, pits in optical media and magnetic domains in hard disks. Data storage based on conductance switching typically arranges bits into grids and cubes, such as in solid-state disks (SSDs). Encoding or decoding information using mixed monolayers of SP requires physical access for WRITE/ERASE operations, but not READ operations. Thus, a hybrid approach like a Millepede drive, in which bits are (en)coded in parallel by arrays of atomic force microscope (AFM) tips could be employed.^[34] Combined with conducting-probe AFM^[35] (for READ) and dip-pen lithography^[36] (for LOCK/UNLOCK), such a device could theoretically yield a bit density on the order of 1 Tb mm⁻².^[37] However, for proof-of-concept, we chose the simple, “soft punchcard” device shown in Figure 4 into which information is encoded similar to patterned masks used to encoding information in trains of microdroplets.^[38] Mixed monolayers of SP-h are grown on ultrasmooth^[39] Au (Au^{TS}) that is patterned into eight columns and six rows, which is sufficient to (de)encode six bytes. A complementary rigid master is formed from the same mask used to pattern the Au^{TS} from which poly[dimethylsiloxane] (PDMS) monoliths are cast. Information is encoded by punching holes in the PDMS above each recession that will encode a 1. When the mask is placed over the Au^{TS} bearing mixed monolayers of SP, it makes a conformal seal such that the entire chip can be exposed to acid and light, flipping all of the bits to 1, but only locking the bits exposed to acid through the punched holes. Thus, the WRITE and LOCK operations happen simultaneously, in parallel and only in bit-positions defined in the soft punchcard.

Six bytes is sufficient to encode rclab as 7-bit ASCII characters padded with one bit. For example, the bottom row of bits in Figure 4 encodes b as 01100010 (binary representations of the other letters are shown in Table S1, Supporting Information). The pristine mixed monolayers are in the less conductive, SP form, thus, all elements of the 6 × 8 matrix shown in Figure 4 contain 0 initially. In order to differentiate bits, we recorded J/V sweeps for mixed monolayers in the SP and MC forms to

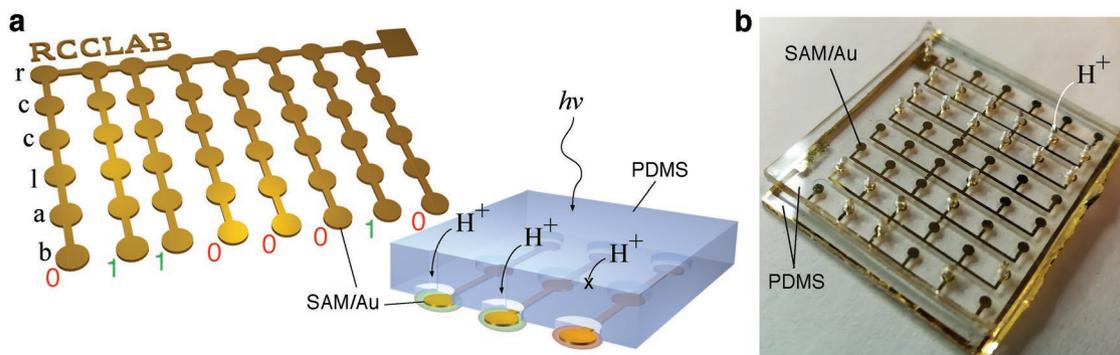


Figure 4. a) Scheme of the gold array patterned by shadow mask deposition. Each line corresponds to an alphanumeric character (the binary code at the bottom corresponds to the character b (lowercase)). Lower right corner: A cross-section of the PDMS slab showing two open and one closed cavity. Holes are punched where a “1” bit is desired. The acidic solution and vapor can then flow inside these cavities, changing the transport properties of the SAM. b) A photograph of a 1 cm² chip including the soft punchcard.

determine the threshold current-density J_{thr} (e.g., the value of J at the READ voltage in Figure 3). This number can vary between monolayers and experimental platforms, but must be constant for a particular device in order to differentiate bits. In our case $J_{\text{thr}} = 0.63 \text{ A cm}^{-2}$; values above J_{thr} at 1.0 V are read as 1, values below as 0.

To encode information, holes are made in a soft punchcard corresponding to the matrix elements that will encode a 1. The punchcard is aligned with the patterned Au^{TS} supporting a mixed monolayer of SP-h, an acidic solution is placed on top and the entire chip is irradiated with 365 nm light (Figure S3, Supporting Information and related discussion). As shown in Figure 1, the exposure to light shifts the $\text{SP} \rightleftharpoons \text{MC}$ conversion toward MC across the entire SAM, amounting to a WRITE operation on every bit. However, the matrix elements exposed to acid through the soft punchcard undergoes an additional LOCK operation to form MCH^+ ; the remaining areas of the mixed monolayer relax back to SP thermally, assisted by visible light. To read a bit, a sharp EGaIn tip is brought into contact with the mixed monolayer at one of the circular regions of the patterned Au^{TS} and biased at 1.0 V for 5 s before recording the current; Figure 5 shows the results of reading the entire matrix after encoding rclab. This method of reading produces a much larger spread in J than the J/V sweep method we use for characterizing the tunneling transport properties, but it is a better representation of how data are read in conductance-based memory devices. As is clear from Figure 3b, the mean values of J extracted from multiple J/V sweeps result in 100% accuracy as is shown for c in Figure S4 in the Supporting Information. Nonetheless, using single READ operations at fixed bias produced only three erroneous bits; two on the wrong side of J_{thr}

and one that could not be read. Even though three erroneous READ operations corresponds to a 7.2% error rate, because they occurred in three different rows, 50% of the ASCII characters were read incorrectly. Commercial devices are far from error-free and incorporate error-correction strategies that are well beyond the scope of this proof-of-concept work. For example, commercial SSDs based on NAND gates can tolerate a 3% error rate.^[40]

A nonvolatile memory must be able to be erased and rewritten; to demonstrate this ability, we erased the entire matrix (reset all bits to 0) and wrote ardra (the sixth náksatra in Hindu astrology). To perform an UNLOCK operation, we immersed the entire array in basic solution, followed by an ERASE operation with visible light, and then a LOCK/WRITE operation as before, but with a soft punchcard patterned for ardra. As is shown in Figure 5, 100% of bits were successfully erased and there was only one erroneous bit after rewriting, corresponding to an error rate of 2.8%.

Locking SP in the MCH^+ form by acid is well-studied, but somewhat controversial because of the difficulties of interpreting solution-phase spectroscopic data.^[15–20] We successfully translated this phenomenology to metallic electrodes showing, for the first time, that mixed monolayers of SP can be locked in a high-conductance state by forming MCH^+ on the surface. The combination of tunneling conductance and XPS provide unambiguous evidence both for chemical locking and for reversibility. This process circumvents the spontaneous relaxation of MC back to SP, which we exploit in a proof-of-concept, optically switched, nonvolatile memory device. Exposure to acid, base, light, and applied bias do not damage the monolayers or promote any side-reactions, meaning that there

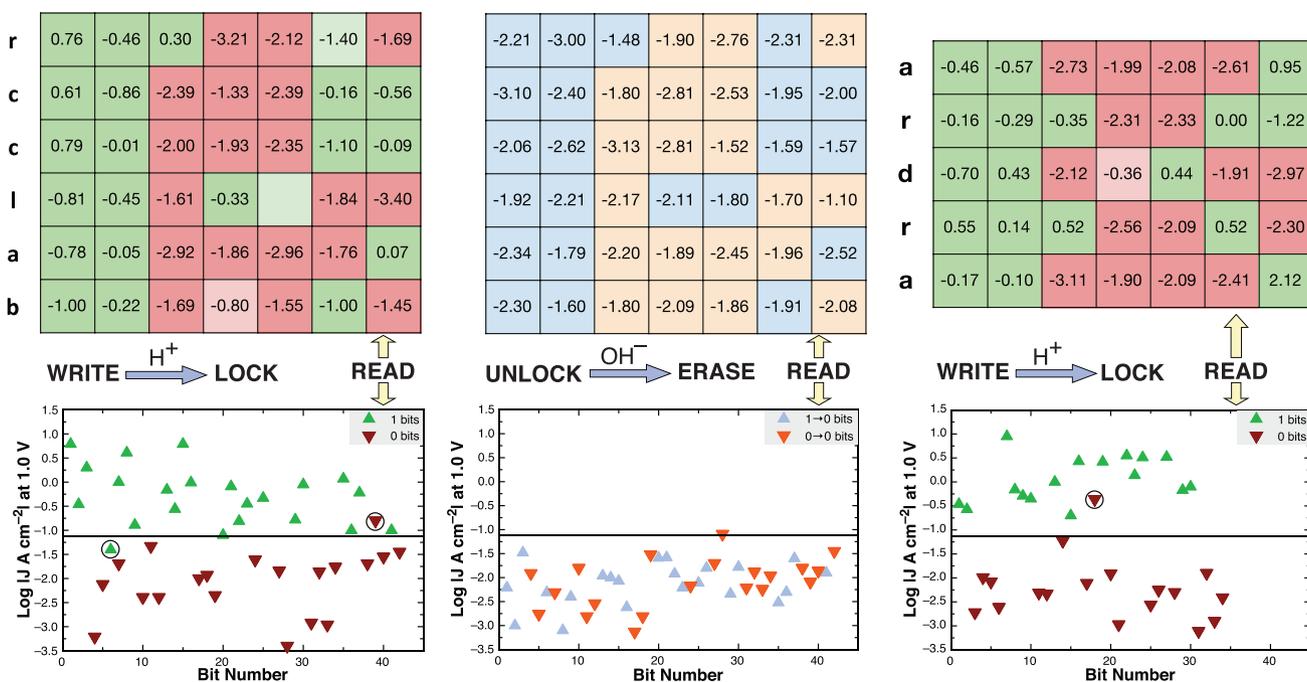


Figure 5. Values of $\log |J| \text{ A cm}^{-2}$ measured at 1.0 V for each bit after WRITE/LOCK to encode rclab (left), UNLOCK/ERASE (center), and a second WRITE/LOCK to encode ardra (right). The top row shows matrices corresponding to the positions of bits. Green and red tiles show bits successfully written as 1 and 0, respectively. Successful erase operation are colored blue for $1 \rightarrow 0$ and yellow for $0 \rightarrow 0$. The bottom row shows plots of the values of $\log |J|$ with a horizontal line marking J_{thr} , the threshold that differentiates bits. Erroneous bits are circled and correspond to lighter colors in the matrices.

is no fundamental limit to the reversibility of the process. The enormous increase in the switching ratio (from 35 with light alone to 10^3 with acid treatment) also creates room for multi-state switching by controlling the light dosage or the pK_a of the acid used to lock the switches. While we demonstrated reading, writing, erasing, rewriting, and rereading six bytes (48 bits) in simple, soft-punchcard devices, the entire process can feasibly be miniaturized using arrays of nanoscale tips capable of coupling light inputs.^[41] Switching to the MC form on surfaces modulates myriad other physical properties, for example, wettability, hydrophobicity, net dipole, polarizability, and absorbance/reflectance, any of which can be patterned and erased using chemical locking.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

EGaIn, memory, molecular electronics, spiropyran, switching

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