**ADVANCED
OPTICAL
MATERIALS**

Supporting Information

Self-Erasable and Rewritable Optoexcitonic Platform for Antitamper Hardware

Che-Hsuan Cheng, Da Seul Yang, Jinsang Kim, and Parag B. Deotare*

Supplementary Materials

Self-erasable and rewritable optoexcitonic platform

for anti-tamper hardware

AUTHOR NAMES

Che-Hsuan Cheng[1], Da Seul Yang[3], Jinsang Kim[134], Parag B. Deotare[2,]*

AUTHOR ADDRESS

Excitonics and Photonics Laboratory (ExP Lab), University of Michigan, Ann Arbor, MI 48105, USA.

[1]Department of Materials Science and Engineering, [2]Deaprtment of Electrical Engineering and Computer science, [3]Department of Macromolecular Science and Engineering, [4]Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48105, USA.

*Correspondence to: pdeotare@umich.edu

A3 molecules synthesis and preparation

(*E*)-1-(4-((1,3-bis((2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)propan-2-yl)oxy)phenyl)-2-(4-ethylphenyl)diazene (1) was synthesized by a modified procedure reported in the literature[1]. (*E*)-4,4'-(diazene-1,2-diyl)diphenol (0.54 g, 2.4 mmol) was placed in a 100 mL round-bottom flask and dissolved in anhydrous *N*,*N*-dimethylformamide (DMF) under argon atmosphere. K_2CO_3 (1.00 g, 7.3 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 10 minutes, followed by adding 1,3-bis((2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)propan-2-yl methanesulfonate (1.43 g, 3.6 mmol). After refluxing overnight, DMF was evaporated under vacuum. The residue was dissolved in water, acidified with a saturated solution of NH_4Cl, and extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography to give 0.1 g of compound 1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.87 (m, 2H), 7.80 (d, 2H), 7.32 (d, 2H), 7.06 (m, 2H), 4.02-4.19 (m, 3H), 3.45-3.89 (m, 12H), 2.74 (m, 2H), 1.19-1.44 (m, 15H) ppm.

(*E*)-3,3'-((2-(4-((4-ethylphenyl)diazenyl)phenoxy)propane-1,3-diyl)bis(oxy))bis(propane-1,2-diol) (2) was obtained as a yellow oily substance by the deprotection of compound 1 with trifluoroacetic acid (TFA). The general deprotection procedure with TFA is described in the literature[2].

A3 films fabrication through Langmuir-Blodgett (LB) method[3]

Firstly we prepare the amphiphile molecules (A3) that will create a monolayer in a water insoluble solvent. The subphase, typically water, is held in the hydrophobic trough top that provides good subphase containment. When the amphiphile solution is deposited on the water surface with a micro-syringe, the solution spreads rapidly to cover the available area. As the solvent evaporates,

a monolayer forms at the air-water interface and a Langmuir film is created. The software-controlled barriers located at the interface then compress the monolayer until the surface pressure sensor indicates maximum packing density. A compressed, monolayer film can be considered as a two-dimensional solid with a surface area to volume ratio far above that of bulk materials. In these conditions, materials often yield fascinating new properties. Experiment using Langmuir troughs enables inference and understanding about how particular molecules pack when confined in two dimensions[4,5]. The surface pressure-area isotherm can also provide a measure of the average area per molecule and the compressibility of the monolayer.
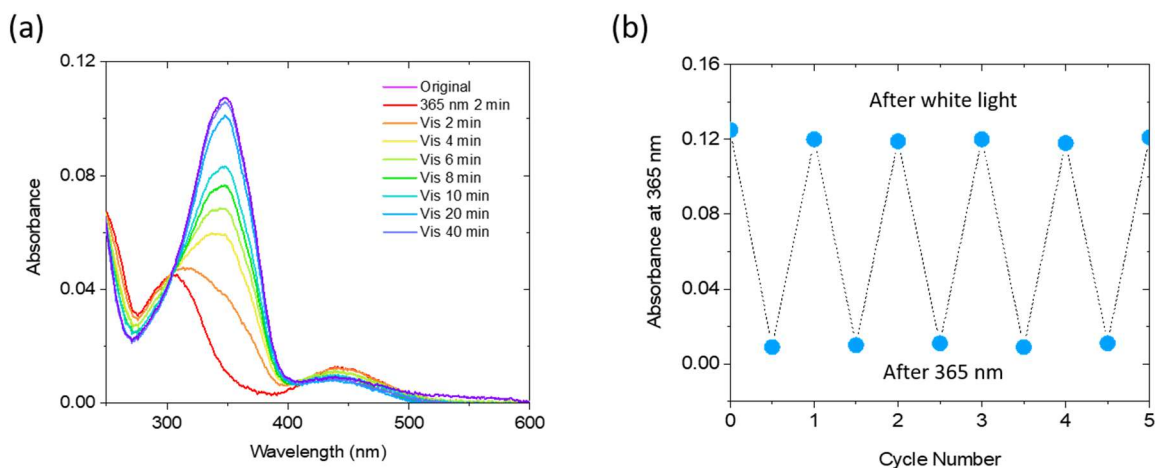

Figure S1. Photoisomerization of A3 molecule solutions.

Figure S1 shows the absorption spectra of A3 molecule solution (concentration of 10mg/mL) after 365 nm exposure (the trans isomer shows strong absorption between 300 and 400 nm with a peak at 365 nm,) and followed by a sequence of white light relaxation. Since we use a commercial UV lamp with rather lower fluences, it takes 2 minutes of UV irradiation for the original trans isomer (purple) to convert to cis isomer (red). The complete transition can be achieved faster using a UV source with higher intensity. We have lengthened the UV treatment to 5, 10, and 15 minutes, respectively, and no further spectral change is observed. The reversible photoisomerization

response is also demonstrated in Figure S1. We monitor the absorption intensity at 365 nm of the UV-Vis spectrum upon alternate irradiation of 2 minutes of 365 nm UV light and 60 minutes of white lights for 5 complete cycles. The absorption intensity remains fairly constant throughout each cycle.
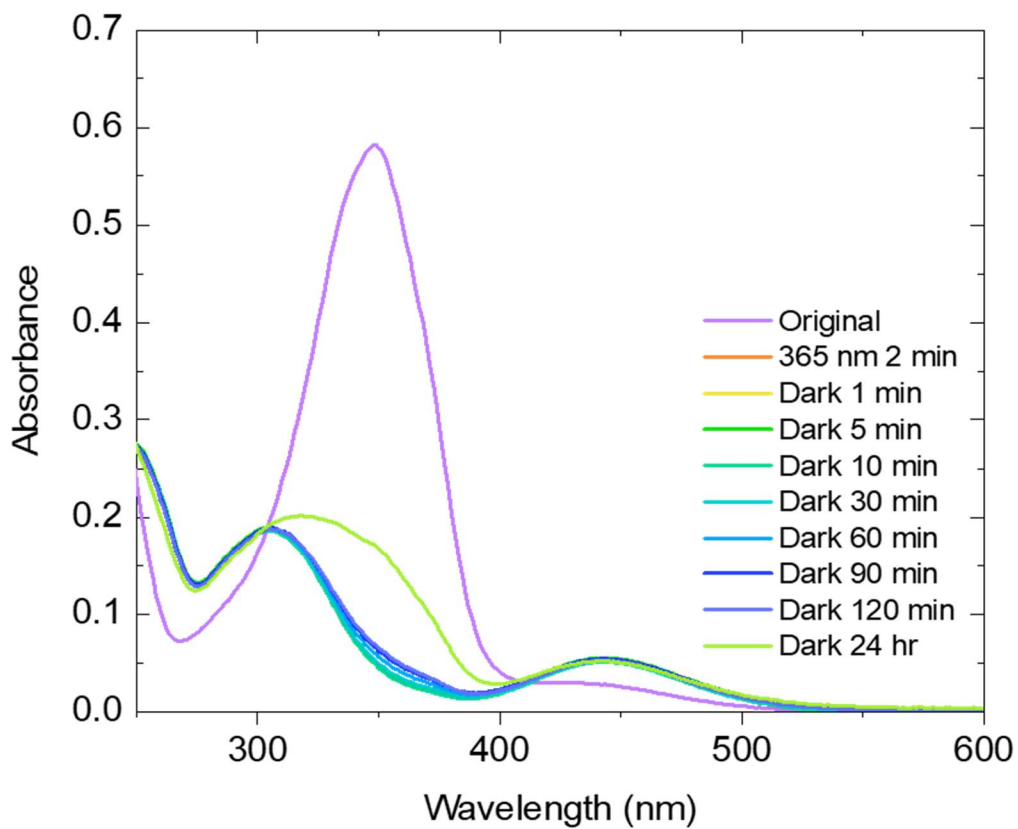

Figure S2. Photoisomerization of A3 molecule films (~6nm) under dark condition. We note that 99% of the molecules remain in *cis* state within first 120 minutes and only 20% of the molecules relax back to *trans* state after 24 hours.
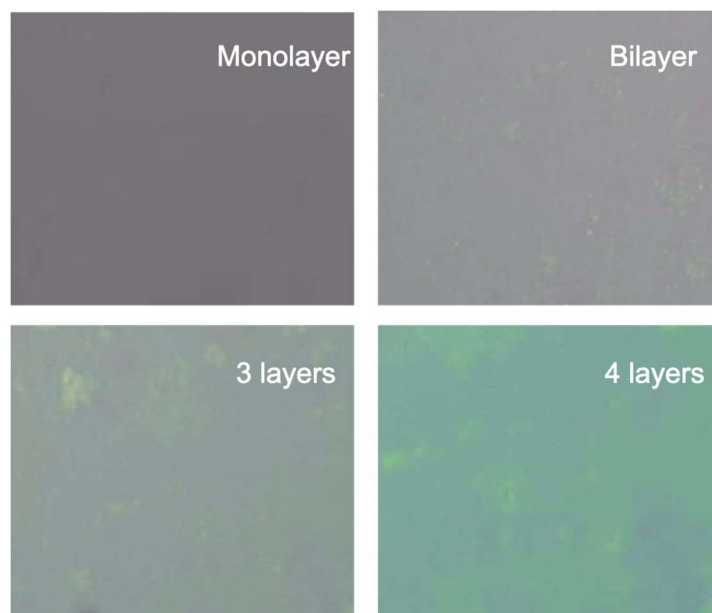
Figure S3. Optical microscope images of A3 films of various numbers of layers on Si/SiO$_2$ substrates fabricated using Langmuir-Blodgett (LB) method.
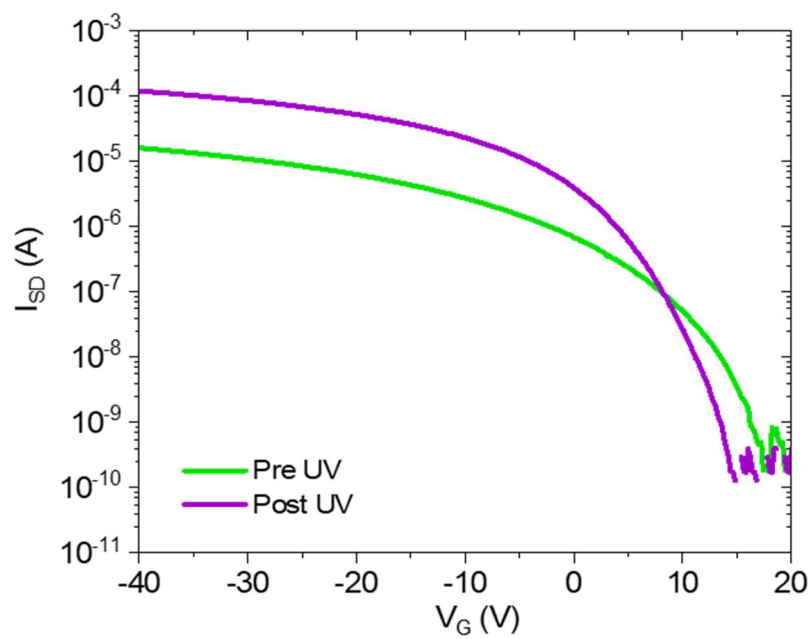
Figure S4. Electrical transfer characteristics of monolayer WSe_2 on bilayer A3 films. A clear shift of turn on voltage confirms higher p-doping from *trans* A3 molecules.
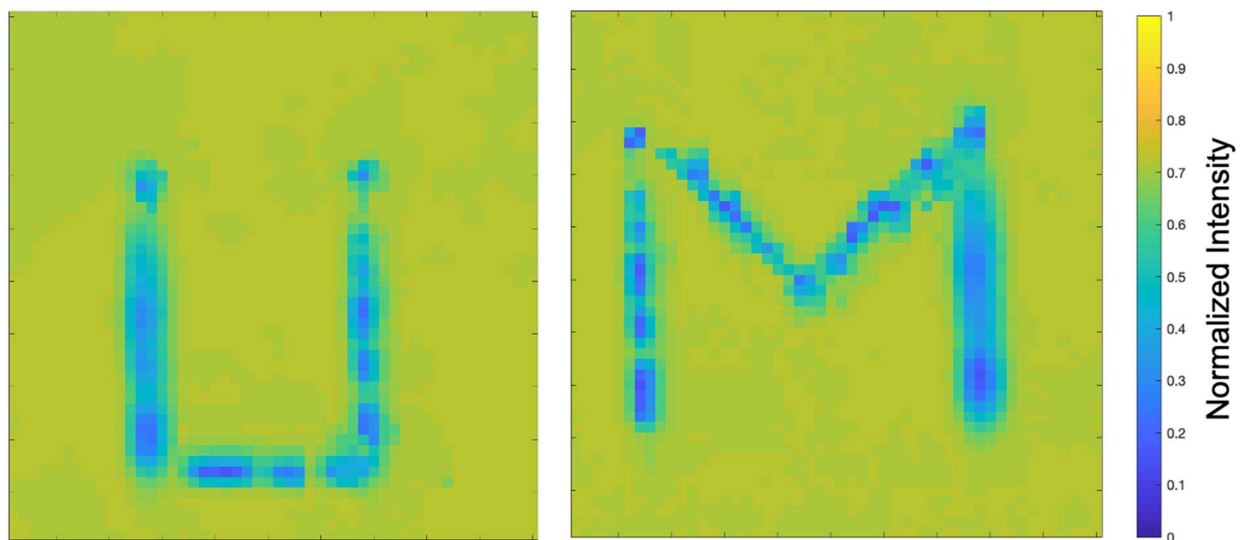
Figure S5. PL intensity maps of the written letters U and M shown in Figure 5. The intensity drop is consistent with our findings as described in the main text.
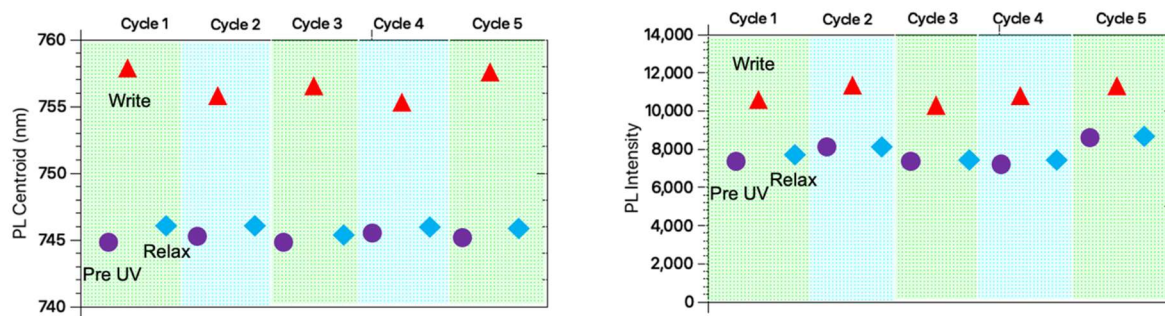
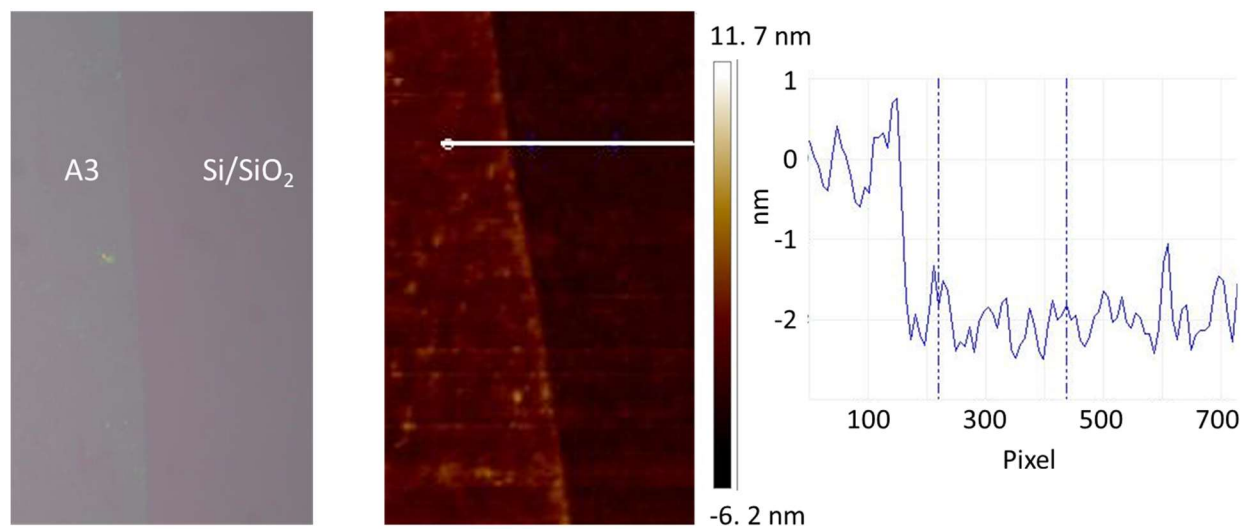Figure S6: PL wavelength and intensity of "Pre UV" , "Write", and "Relax 40 mins" steps over 5 cycles.

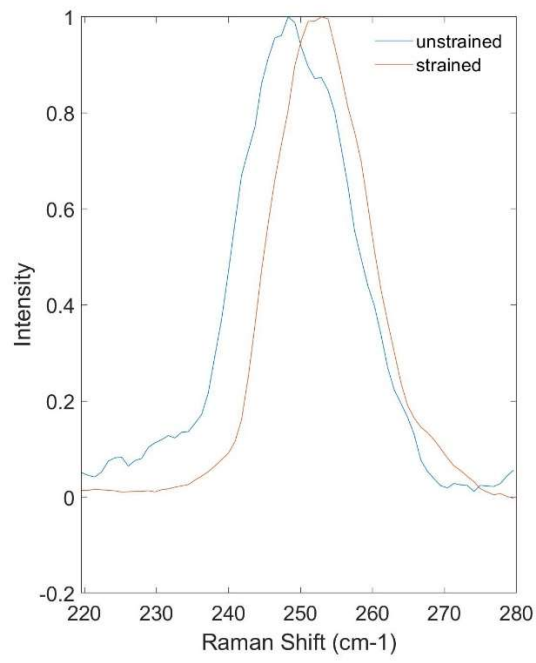Figure S7: AFM image on a monolayer A3 film. The film thickness was measured to be ~ 2nm.

Figure S8: Raman shift (E_{2g}^{1+}) for strained and unstrained case. We observe a centroid Raman shift of 2.76 cm^{-1} from the unstrained case that corresponds to an effective strain of ~ 1.38 %.
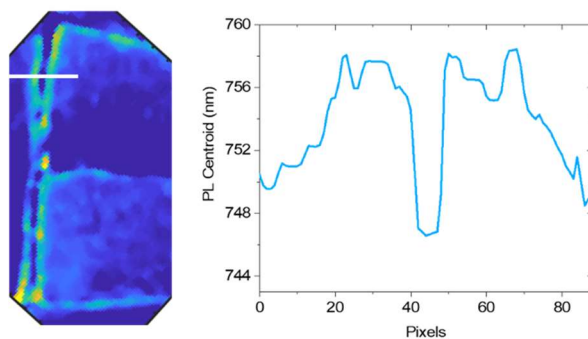
Figure S9: PL centroid for an over exposed write cycle, i.e.. the laser spot is irradiated for extended time. This causes most of the molecules in the center to relax and hence generates a flat-topped Gaussian distribution of relaxed molecules. We observe that PL shift in this case is observed at two regimes along the exposed line as shown in figure. The maximum shift occurs when 50% molecules are relaxed. The right panel shows the PL centroid along the while line drawn in the left panel.

We note that the estimate tensile strain is an effective strain measured from our PL measurements. This is because, the PL is taken from a diffraction limited spot and hence it is a statistically averaged value over the spot. Since the excitation laser spot is a Gaussian, we can assume similar distribution for the probabilities of molecules to be relaxed during the writing phase. The probability that all molecules are relaxed being 1 at the center of the spot and almost 0 near the edge. In either of the extreme cases, the WSe_2 monolayer will be effectively unstrained. In the intermediate region, the measured PL will be a weighted distribution of PL emission over the excited spot from strained and unstrained region. Hence, we use centroid and not peak values in the manuscript.

Figure S9 confirms the hypothesis where the laser spot is irradiated for an extended time. This causes most of the molecules in the center to relax and hence generates a flat-topped Gaussian distribution of relaxed molecules. We observe that PL shift in this case is observed at two regimes along the exposed line as shown in figure. The maximum shift should occur when 50% molecules are relaxed.

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