Supporting Information

Reversible Light Induced Conductance Switching of Asymmetric Diarylethenes on gold: Surface and Electronic Studies

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1. High yield of molecular switches on gold surface using "reverse immersion" method.

Freshly prepared bare gold on mica was fully immersed for 16h into a 0.5 mM solution of As-DE in ethanol for and subsequently the substrate was immersed into a 0.5 mM solution of dodecanethiol in ethanol for 12h. Prior to the immersion steps, we irradiated the As-DE solution using UV light (λ = 313 nm) for 15 min to obtain the closed form of the As-DE molecules. As a result of these two consecutive steps, we embedded a large number of bright spots as shown in figure below. For a comparison, we present a STM image of a sample made using the deposition recipe from Donhausser *et al.*[1]
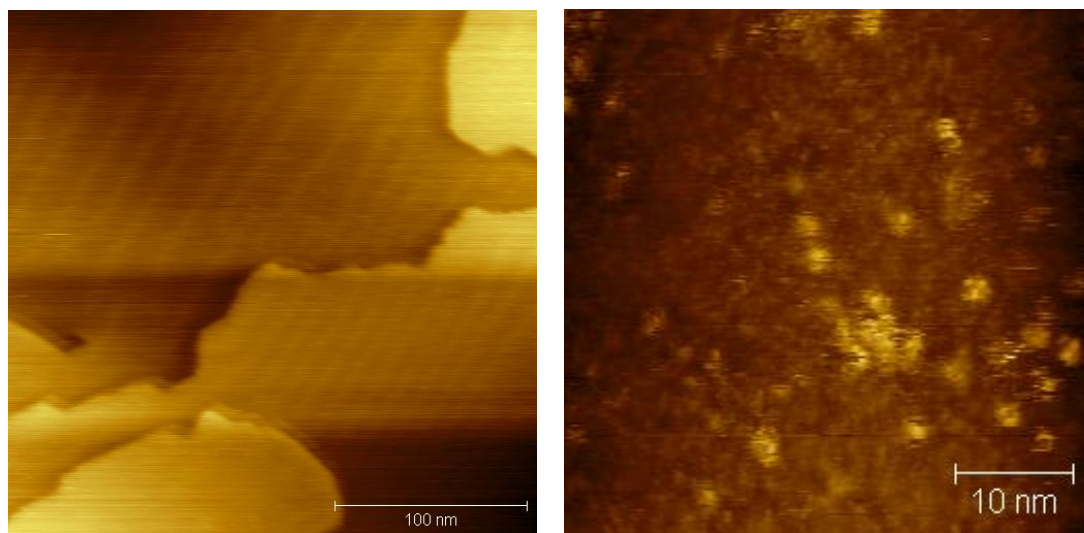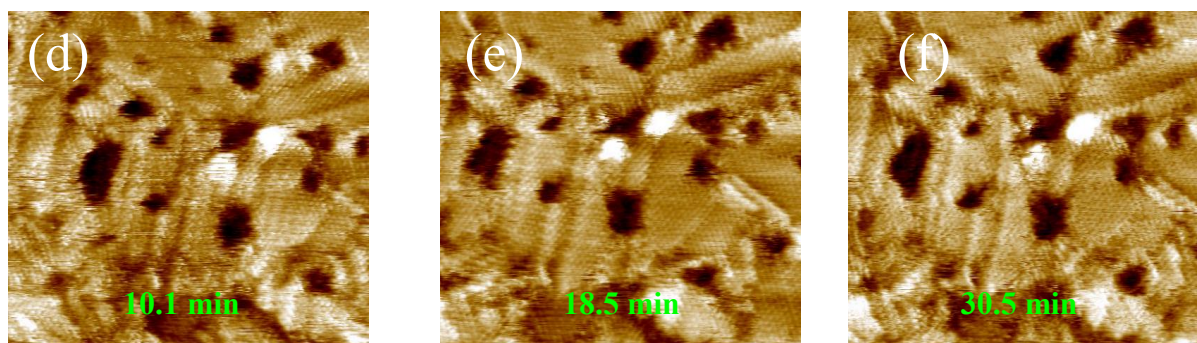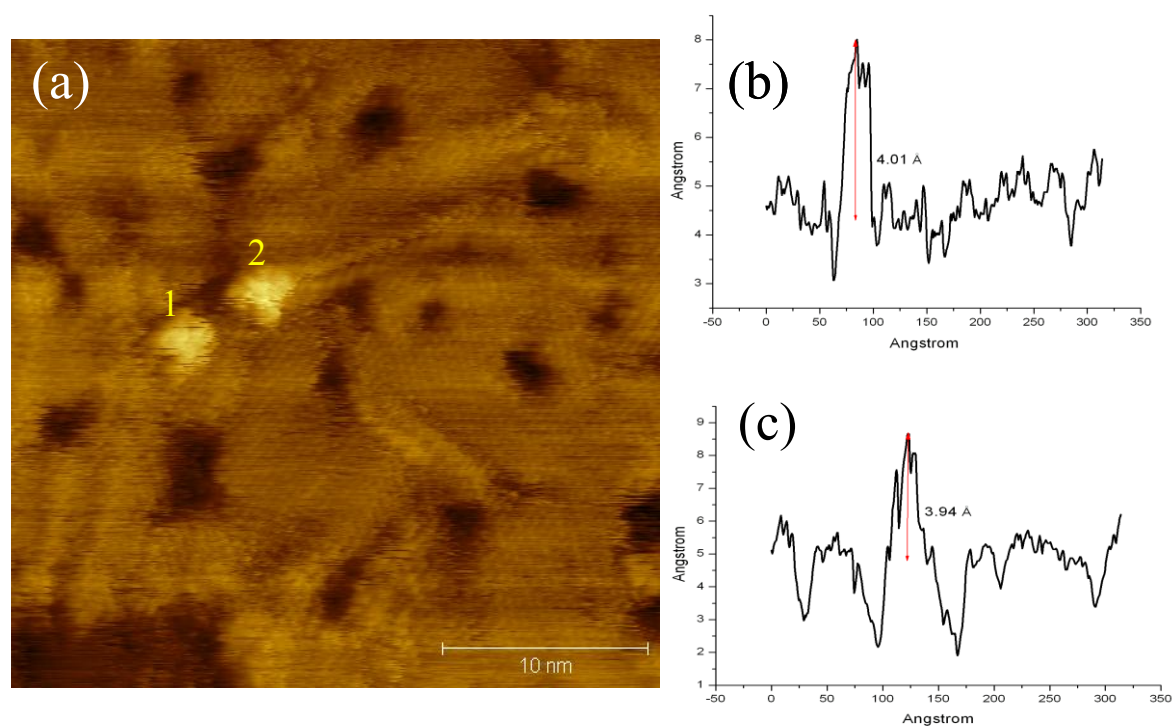

Figure S1. Subsequent STM images which shows the morphology of Au (111) substrate before and after molecular deposition of As-DE at room temperature. (a) Constant current STM image of bare Au (111) deposited on mica with scan area 273.2 x 273.2 nm^2 (I = 0.25 nA; V_{sample} = -0.125 V). Typical herringbone structure was found on a fresh deposited gold that measured at room temperature. (b) Formation of a disordered monolayer of As-DE on Au (111) after overnight immersion procedure (scan area 43.8 x 43.8 nm^2, I = 10 pA; V_{sample} = -0.750 V)
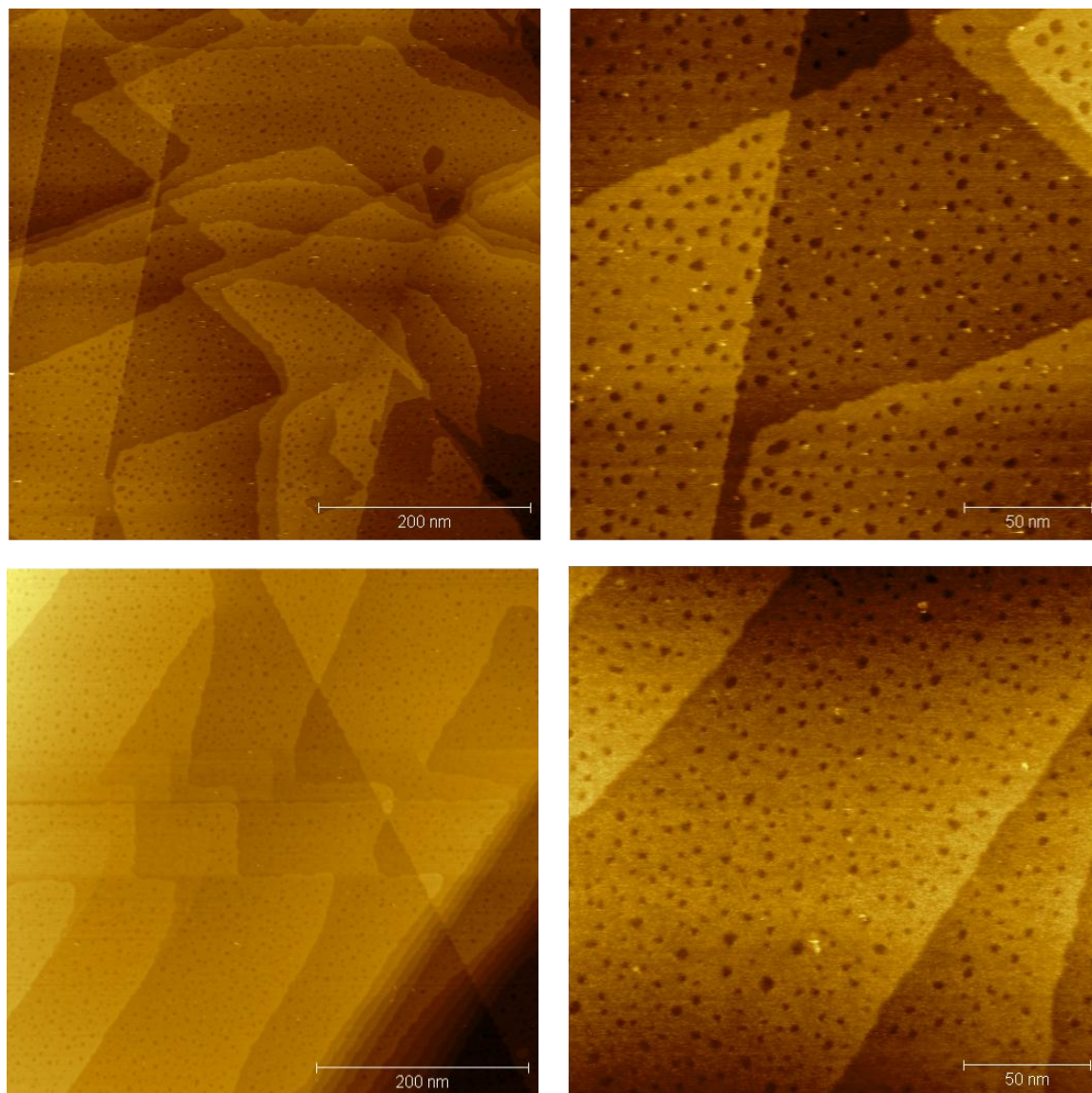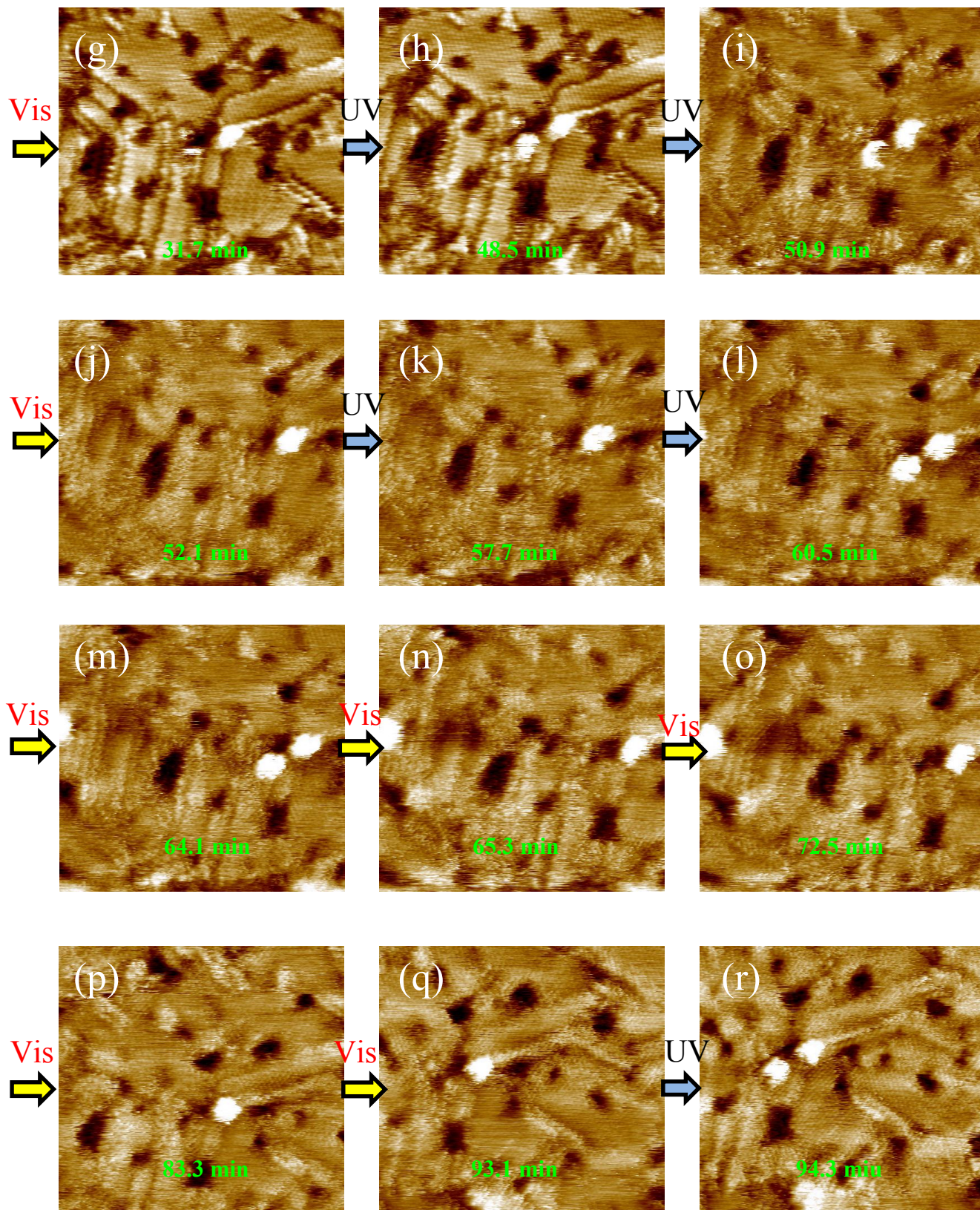
Figure S2. A structural comparison of the normal *versus* the reverse immersion procedure to create 2D nanostructure constriction of As-DE switches in mixed C12 monolayers. (a) Constant current STM image showing topographic information in a large scanning area of 0.5 μm x 0.5 μm. (b) Smaller scan image which depicted a large yield population of bright spots on gold surface with scan area 208 nm x 208 nm (Tunneling parameters are I_t = 12 pA and V_{sample} = 1.2 V). Both figures represent the reverse immersion procedure while fig (c) and (d) are representative STM images prepared using the normal procedure. The tunneling parameters are I_t = 40 pA; V_{sample} = 0.8 V.

2. The direct evidence of the reversible photoswitching behavior of As-DE

The following sequential STM images illustrate the reversible light-controlled conductance switching event as shown in the main text. Noticeably, a large bright spot population was detected in various locations. The light induced experiments were performed several times at different areas.

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(g)

Vis ➡

31.7 min

(h)

UV ➡

48.5 min

(i)

UV ➡

50.9 min

(j)

Vis ➡

52.1 min

(k)

UV ➡

57.7 min

(l)

UV ➡

60.5 min

(m)

Vis ➡

64.1 min

(n)

Vis ➡

65.3 min

(o)

Vis ➡

72.5 min

(p)

Vis ➡

83.3 min

(q)

Vis ➡

93.1 min

(r)

UV ➡

94.3 min

Figure S3. Constant current STM images which display a reproducible on-off transition of the light conductance switching observation in their respective observation time. These STM images (31.5 x31.5 nm^2) are obtained with the tunneling parameters $I_t = 8pA$, $V_{sample} = 600$ mV, and z-scale 0.6 nm. Fig. (a) represents the baseline observation for several STM frames without the use of light (we assigned it as 0 min for our reference). Typical STM image which shows the switches (labeled no. 1 and 2) with their corresponding cross section in fig (b) and (c). We continuously monitored the same area for about 30 min, then we irradiated the sample with visible light and successfully switched the As-DE molecules from an on to an off state (as shown in fig. (d) and (e)). The signature of the closed form of the switches started to decrease as depicted in fig. (f), and finally decayed as shown in fig. (g). In order to recover the closed form, we used UV light ($\lambda = 313$ nm) to change their conductance state, causing the bright spot to arise again. Interestingly, we are able to modulate the low and high conductance state in a controllable manner by irradiating the sample at two different wavelengths. Furthermore, the reversible transitions of three consecutive cycles (on-off-on states) are clearly demonstrated in temporal and spatial resolution. For instance, this photoconversion can be found from the image series in fig. (h) to (l) which indicated that the whole light-driven conductance demonstration is a reversible and controllable process.
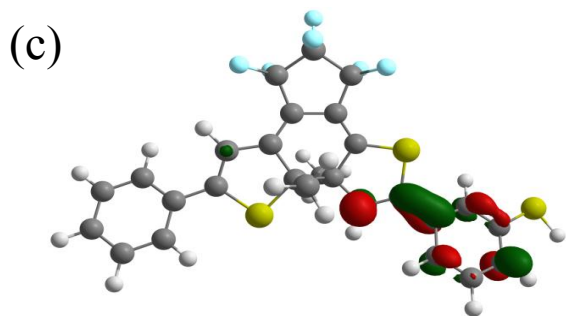
## 3. The electronic density map of the frontier molecular orbitals of As-DE.

(c)
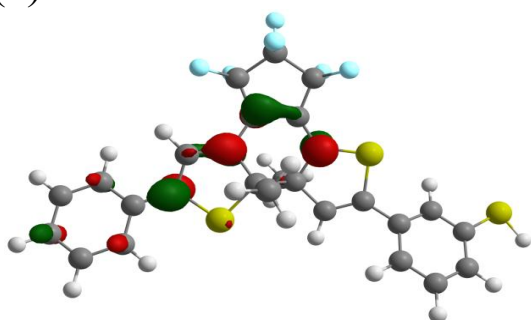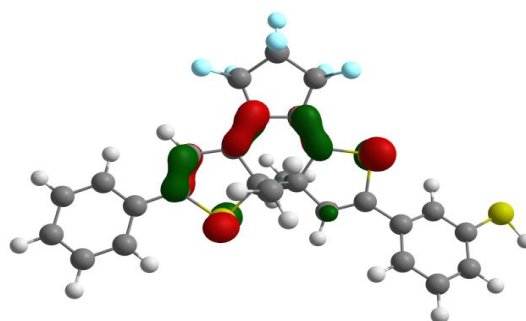
Figure S4. (a) The electron density map of the "on" form of As-DE calculated for the lowest unoccupied frontier molecular orbital (LUMO). (b) Second lowest unoccupied molecular orbital (LUMO+1) and highest occupied molecular orbital (HOMO) (c). The grey, white, yellow, and blue spheres represent carbon, hydrogen, sulfur, and fluorine atoms, respectively. The wave function phases are colored red and green and are plotted with an isovalue of 0.06.

4. The light induced switching experiment with the OFF state as the initial observation.
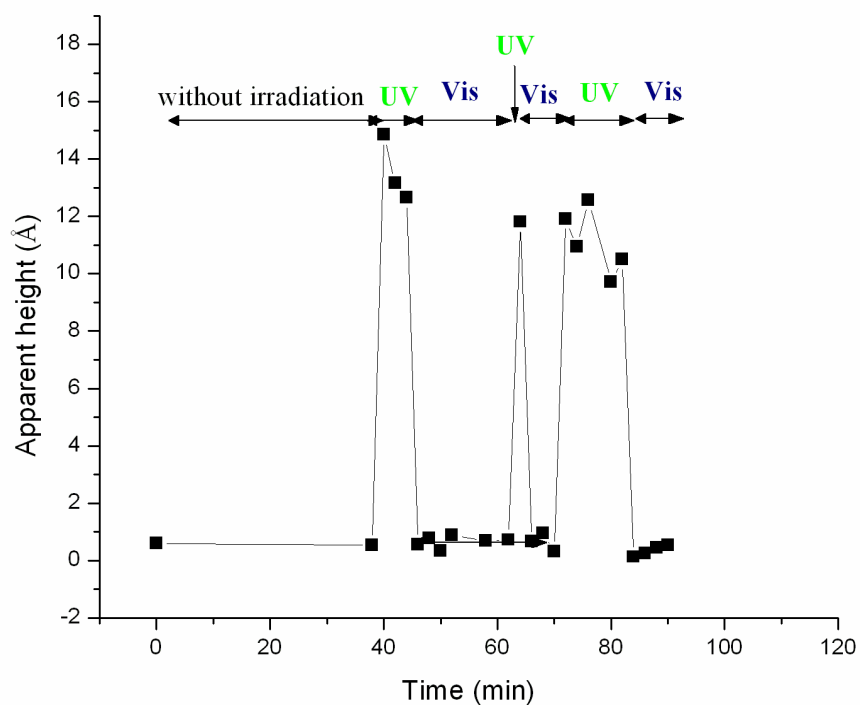
Figure S5. The second evidence of the light-induced switching of As-DE at room temperature. The low apparent height at t=0 min indicates the "off" state of As-DE. The same area was probed for 40 min and

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the sample was immediately irradiated with UV light and consequently a bright spot was appeared. Further, the visible light is used to convert As-DE to its off state. A repetition of this experiment was demonstrated to clarify that the switching behavior is reproducible for few cycles.

5. Quantum chemical calculations

The geometry optimization and the subsequent Density Functional Theory (DFT) single point calculation were performed using the B3LYP hybrid functional (using VWN formula 5 correlation) and a 6-311G(2d,p) basis set with spherical harmonic d functions. The calculations were performed using the Firefly QC package, which is partially based on the GAMESS (US) source code. We note that the calculation is based on the deprotected form of As-DE (in which the acetyl group is replaced by a hydrogen atom) and that the calculation was carried out in the gas phase.

6. The intensities of UV and visible light calculations.

The intensities of visible and UV light sources on the sample plane are estimated based on the typical output for UV and visible light: 433 mW/cm^2 and 63.7 mW/cm^2. To convert them into number of photon per seconds, we assume that the number of photons in a Joule of monochromatic light of wavelength (λ) can be calculated by:$E = hc/\lambda$ joules

Where:

h = Planck's constant (6.626 x 10^{-34} J s)

c = Speed of light (2.998 x 10^8 m s^{-1})

λ = Wavelength in m

Thus, the number of photons per joule is:

$N_{p\lambda} = \lambda$ x 5.03 x 10^{15} where λ is in nm

Therefore we can estimate for respective output light:

Φ_p UV = 63.7 10^{-3} x 420 x 5.03 10^{15} = 1.34 10^{17} photons/cm^2 second

Φ_p Vis = 433 10^{-3} x 313 x 5.03 10^{15} = 6.82 10^{17} photons/cm^2 second

7. References

(1) Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L.A. Bumm, J. D. Monnell, J. J. Stapleton, D. W.

Price Jr. , A. M. Rawlett, D. L. Allara, J. M. Tour, and P. S. Weiss, Science, 2001, **292**, 2303–2307.

(2) Alex A. Granovsky, Firefly version 7.1.G, www.http://classic.chem.msu.su/gran/firefly/index.html .

(3) M. W. Schmidt, K. K. Baldridge, J. A. S. T. Boatz, Elbert, M. S. Gordon, J. H. Jensen,

S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery,

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