

SUPPORTING INFORMATION

Measurement of conformational switching of azobenzenes from macro- to atomolar scale in self-assembled 2D and 3D nanostructures

Chemical structure of the two azobenzene molecules

Molecular Mechanics

All calculations based on semi-empirical molecular orbital theory have been carried out using HyperChem Release 8.0.6 molecular modeling software. The structures of the investigated azobenzene molecules in ground state were optimized using AM1 and PM3 semi-empirical methods with restricted Hartree-Fock (RHF) basis.¹

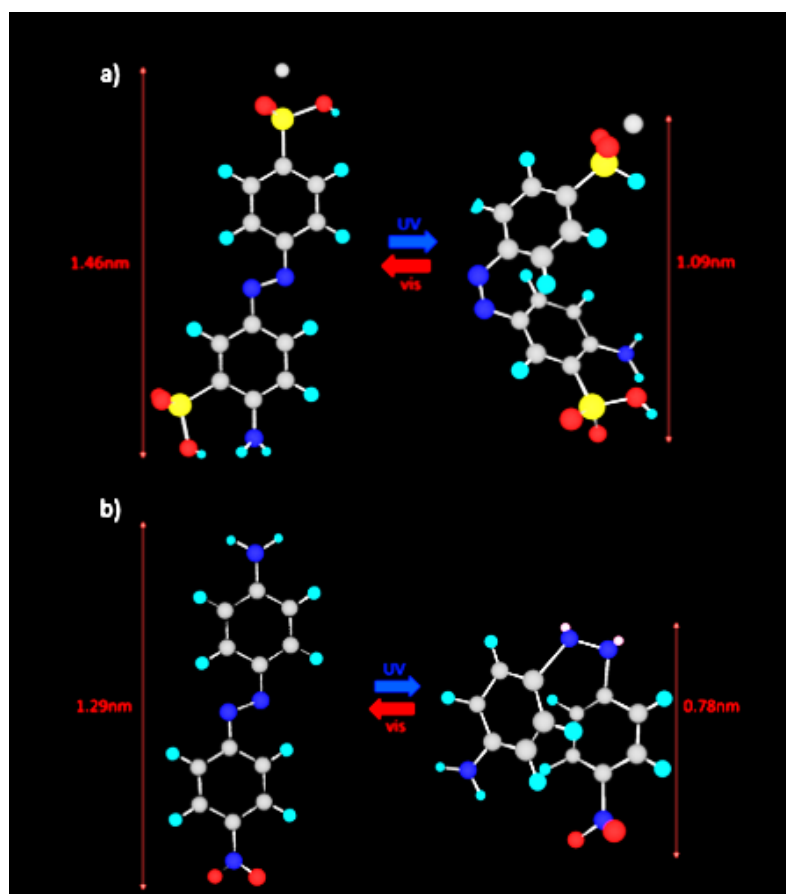


Fig. S1. Optimized molecular structures and height of a) AZO1 and b) AZO2 in trans and cis conformation, in ground state (S_0), computed by AM1 method.

In addition to HyperChem semi-empirical calculations (AM1 and PM3), the Gaussian program has been employed for more accurate computations of the geometrical parameters in ground state:

TD-DFT calculations

Table S1 reports the ground state energies calculated by Time-Dependent Density Functional Theory (TD-DFT) for the different systems. The different polarity of the solvents produces a stabilization of the different compounds. Conversely, the energy difference between cis and trans isomers does not depend significantly on neither the solvent nor the nature of the substituents (AZO1 vs AZO2). The frontier energetic levels do not depend strongly on the solvent polarity. The AZO2 molecule features a lower bandgap than AZO1 due to the stronger donor character of the nitro (NO_2) respect the (SO_3) electron donating group, and the presence electron withdrawing (NO_2) groups in the chemical structure.

TD-DFT calculations allowed us to assign the contributions of the electronic states in the absorption properties of AZO1 and AZO2. The calculated TD-DFT spectra of compound AZO1 for the different solvents are represented in fig. S1. All simulated spectra for the trans isomers presents the main absorption signatures for the trans-azobenzenes, with the $\pi \rightarrow \pi^*$ transition ($\text{H} \rightarrow \text{L}$) at 390 nm dominating the absorption. On the other hand, the cis isomer spectra display the typical characteristics of cis-azobenzenes with the lowest energy $n \rightarrow \pi^*$ transition ($\text{H} \rightarrow \text{L}$) at 480 nm and higher energy transitions ($\text{H}-1 \rightarrow \text{L}$) around 335 nm (see Table 2). All absorption bands described before are slightly blue shifted and lowered in intensity when increasing the polarity of the solvent.

The calculated spectra of compound AZO2 are considerably red shifted respect the spectra of AZO1 due to the energy gap decrease described in the first paragraph (see fig. S2). Since this red-shift is higher in the case of the trans form (94 nm vs 36 nm for trans and cis isomers), the lowest energy absorption bands for both isomers in AZO2 (trans $\pi \rightarrow \pi^*$ and cis $n \rightarrow \pi^*$ bands) are overlapping, thus hindering the resolution of both isomers in the experimental data.

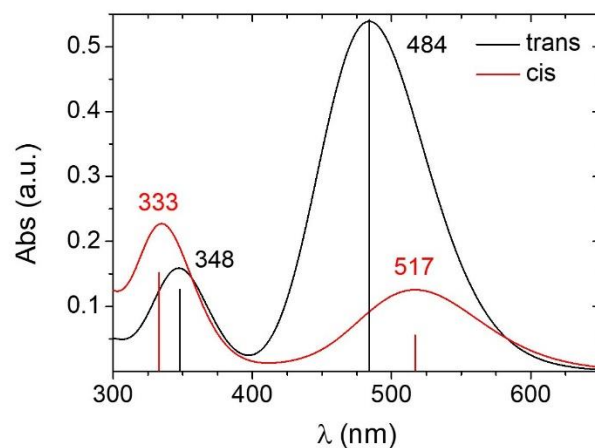


Fig. S2. Calculated TD-DFT spectra of the trans (red) and cis (black) isomers of AZO2 in DMF solvent.

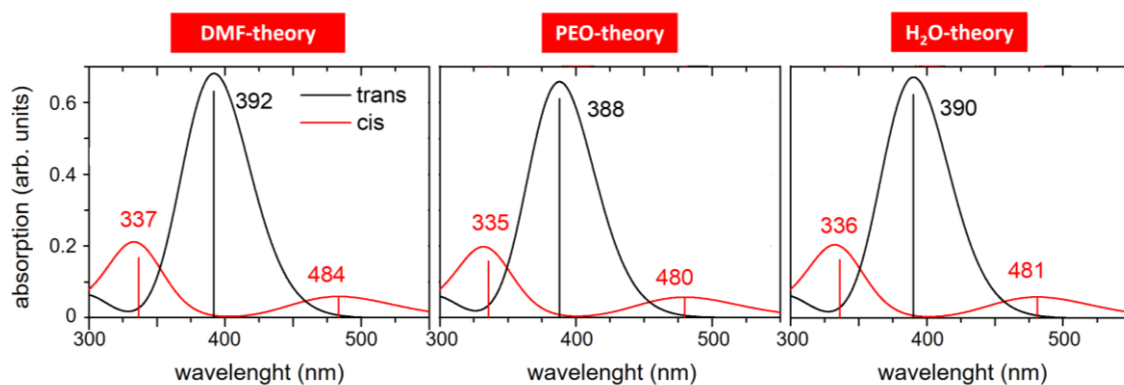


Fig. S3. Calculated TD-DFT spectra of the trans (red) and cis (black) isomers of AZO1 in DMF, PEG and water solvents.

Table S1. Ground state properties for the different systems under study: relative energy (ΔE_{rel}) respect the less stable compound (cis- isomers in PEG and DMF for AZO1 and AZO2 respectively), difference in energy ($\Delta E_{cis-trans}$) between isomers, Lowest/Highest Un-/Occupied molecular orbital (LUMO/HOMO) level energies, electronic bandgap and dipole magnitude.

	<i>solvent</i>	<i>isomer</i>	ΔE_{rel} (eV)	$\Delta E_{cis-trans}$ (eV)	HOMO (eV)	LUMO (eV)	Bandgap (eV)	$\mu(D)$
AZO1	PEG	trans	-0.62	0.62	-5.93	-2.47	3.45	8.81
		cis	0		-5.82	-2.26	3.56	12.86
	DMF	trans	-0.78	0.63	-5.93	-2.48	3.45	8.69
		cis	-0.14		-5.82	-2.26	3.56	15.76
	H ₂ O	trans	-0.82	0.63	-5.92	-2.45	3.47	8.87
		cis	-0.19		-5.81	-2.25	3.56	15.91
AZO2	DMF	trans	-0.61	0.61	-5.63	-2.9	2.73	14.08
		cis	0		-5.63	-2.67	2.95	10.24

Table S2. Excited state properties in the UV-VIS region for the two azobenzene compounds under study: wavelengths (λ), oscillator strengths (f), major contributions and related percentage (%) of the main optical transitions.

	<i>solvent</i>	<i>isomer</i>	λ (nm)	f	<i>Mayor Cont</i>	%
AZO1	PEG	trans	392	1.26	H \rightarrow L	70.5
		cis	484	0.11	H \rightarrow L	64
			337	0.34	H-1 \rightarrow L	59.3
	DMF	trans	390	1.24	H \rightarrow L	70.6
		cis	481	0.11	H \rightarrow L	63.7
			336	0.32	H-1 \rightarrow L	59.2
	H ₂ O	trans	388	1.22	H \rightarrow L	70.3
		cis	480	0.11	H \rightarrow L	63.5
			336	0.32	H-1 \rightarrow L	59
AZO2	DMF	trans	484	1.22	H \rightarrow L	70.7
			348	0.28	H-1 \rightarrow L	67.4
		cis	517	0.13	H \rightarrow L	63.1
			333	0.34	H-1 \rightarrow L+1	52.2

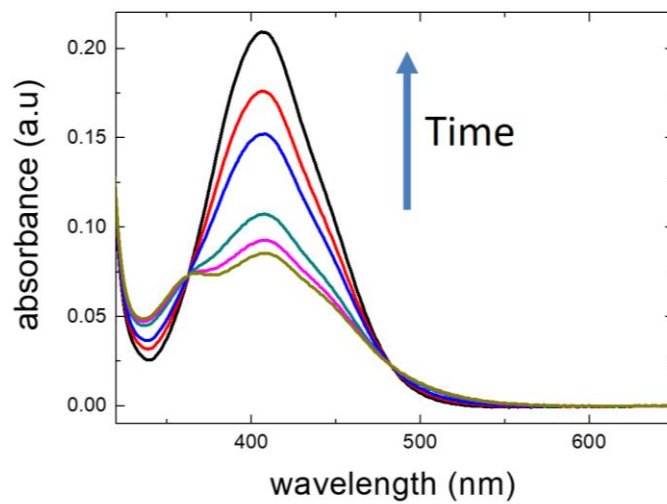


Fig. S4. Changes in the absorption spectra of AZO1 in DMF upon darkness. The Arrow indicates the changes upon irradiation time. The different spectra have been recorded at 10 seconds time steps.

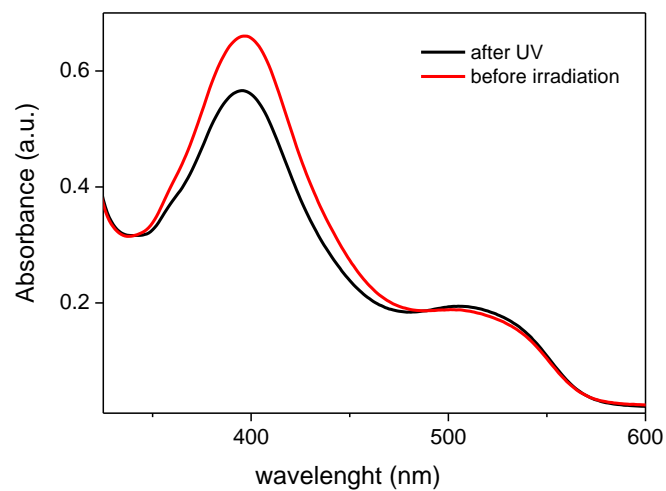


Fig. S5. Changes in the absorption spectra of AZO1 in IPA before and after UV irradiation.

Histogram analysis

Intrinsic surface roughness

Let's consider an AFM image with two materials: i) the substrate and ii) a deposited nanostructure (island), which of them with measured roughness values: $R_{RMS,1}$ and $R_{RMS,2}$, respectively. The roughness of the deposited nanostructure depends on the substrate's one. For this reason, we introduce the *intrinsic roughness of the island*: σ_{island} , which is decoupled from the substrate one and defined as the roughness of the nanostructure deposited on infinitely flat substrate ($R_{RMS,1} = 0$).

Thus, the substrate roughness can be treated as a sort of disorder that disturbs the molecular packing. Using the convolution theorem it is simple to obtain that the intrinsic roughness of the nanostructure is given by:

$$R_{RMS,island} = \sqrt{R_{RMS,2}^2 - R_{RMS,1}^2} \quad (S1)$$

Mean height value

HFD describes the height distribution of AFM image.

For a given nanostructure, the mean thickness $\langle h \rangle$ is given by the equation:

$$\langle h \rangle = \sum_{h_{min}}^{h_{max}} h \cdot HFD, \text{ where } \sum_{h_{min}}^{h_{max}} HFD = 1 \quad (S2)$$

Scanning Probe Microscopy images

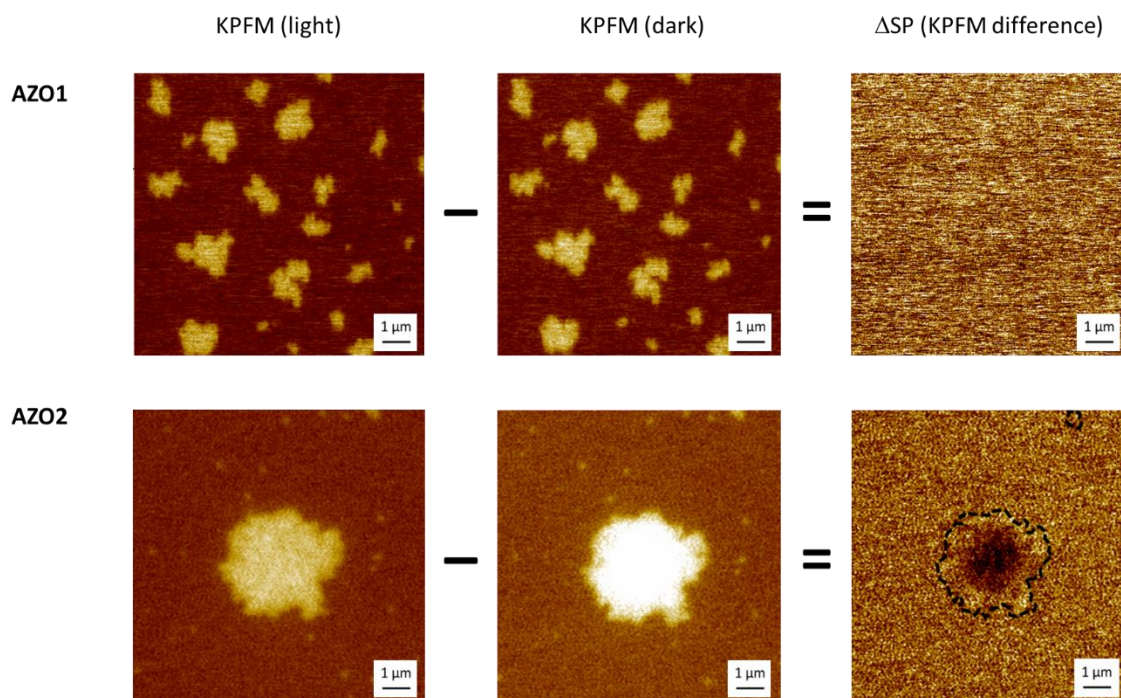


Fig. S6. KPFM images of AZO1 and AZO2 islands self-assembled on silicon. Z-ranges: (KPFM images) 70 mV, (Δ SP images) 30 mV.

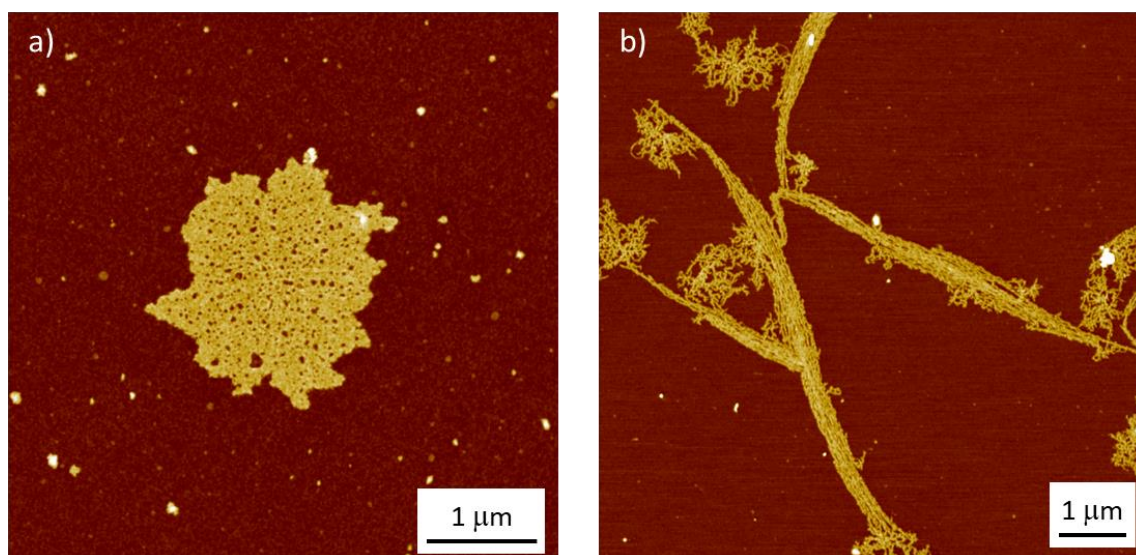


Fig. S7. AFM images of AZO2 structures self-assembled on silicon using: a) DMF solvent, conc. = 2 mg/L, b) THF solvent, conc. = 10 mg/L. Z-ranges: (a) 6 nm, (b) 12 nm.

Reflectance spectra

Once the diffuse reflectance optical accessory is properly aligned, a background spectrum of the cleaned silicon substrate can be obtained. Prior to each sample measurements the background spectrum has been collected under identical conditions to the sample spectrum and then subtracted from the sample one. In this case the spectrum of the silicon substrate is reported for clarification.

As is shown in fig.S7 the difference in the spectra before and after UV exposure for 60 minutes can be neglected. Meaning that there is no interference with the results obtained in fig. 7 c) and d).

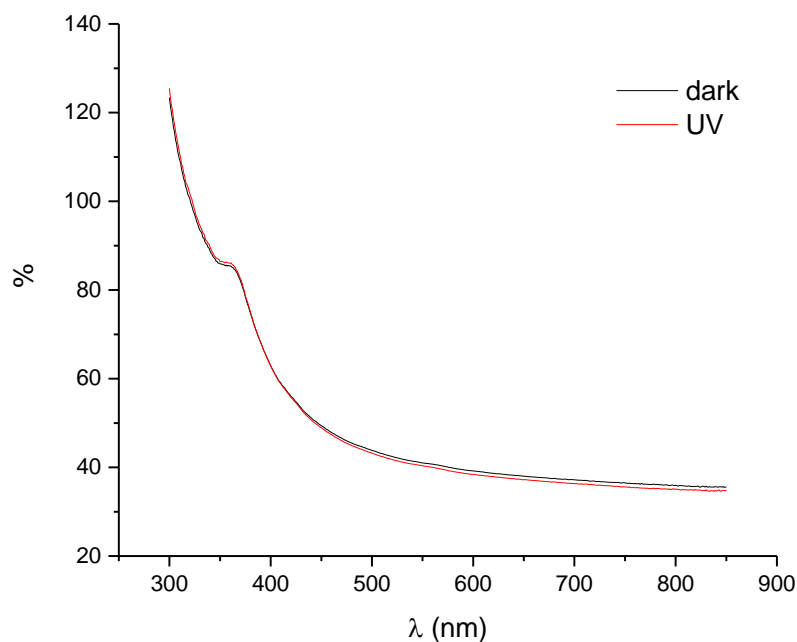


Fig. S8. Reflectance spectra of freshly cleaned silicon substrate acquired in dark (black) and after UV illumination (red) for 60 min.

References

1. Ludwig, S. & Bayley, H. Photoisomerization of an individual azobenzene molecule in water: An on-off switch triggered by light at a fixed wavelength. *J. Am. Chem. Soc.* **128**, 12404–12405 (2006).