Fast and Reversible Photo-Responsive Wettability on TiO_2 based hybrid surfaces

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Electronic Supplementary information (ESI)

I Theoretical absorption spectra of *Trans*- and *Cis*-AzoC11 acid in THF

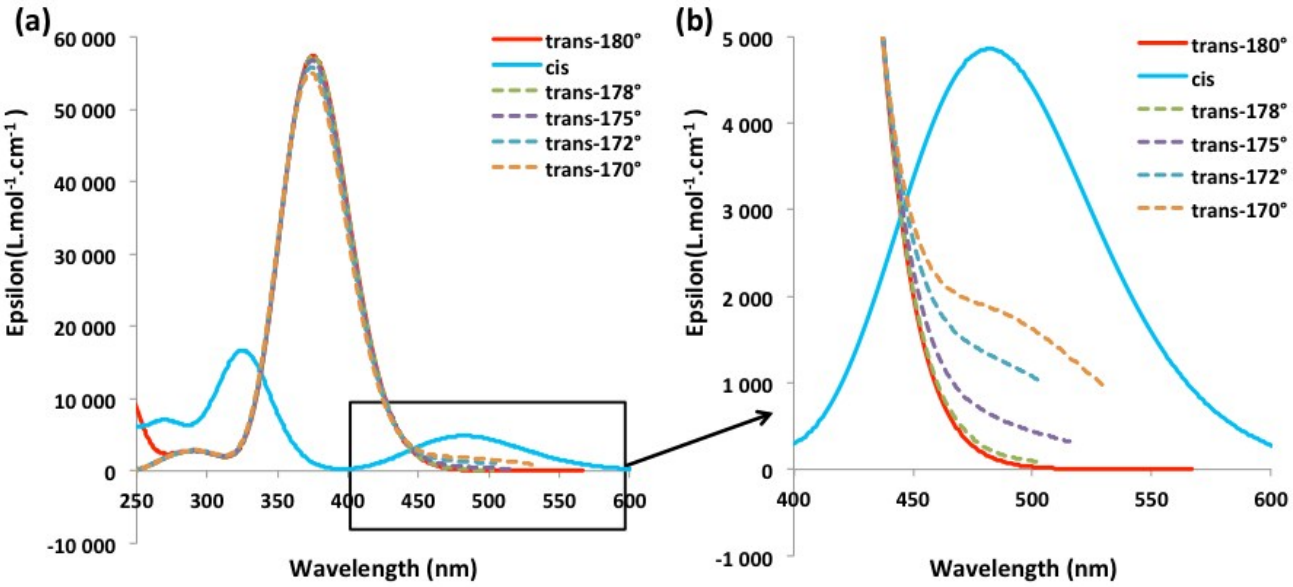

Figure S1: Theoretical absorption spectra of *Trans*- and *Cis*-AzoC11 acid in THF. Compared to the perfectly planar *Trans*-isomer (indicated as *Trans*-180°), small deformations from the planarity around the N=N bond are simulated and reported as *Trans*-180°, 178°, 175°, 172° and 170°. The n→π transition at 500 nm, which is forbidden for *Trans*-180° (red plot) is shown to become less forbidden with deviation from π -backbone planarity.

II Absorption onset on the UV-Vis spectra

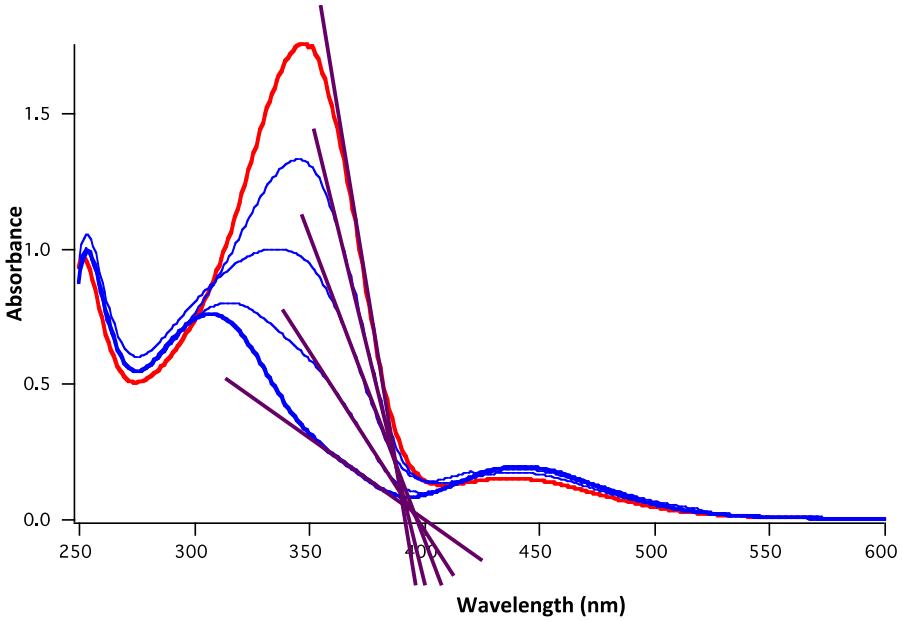

Figure S2: Absorption onset on the UV-Vis spectra of AzoC11 acid solution

III Theoretical estimation of molecular-areas.

Considering the maximum distances along the two short-axes directions (1.8Åx7.3 Å and 5.1Åx5.6Å respectively for the *Trans*- and *Cis*-isomers), and by adding one hydrogen van der Waals radii (1.2 Å) to each dimension, molecular areas of roughly 0.26 nm^2 and 0.43 nm^2 respectively can be deduced. While being close to the experimental results, the theoretical values correspond to pure *Trans*- and *Cis* isomers. However, small mixing cannot be excluded in the *Cis*- experimental state as suggested by the absorption spectra in THF. By arbitrary considering the value of 5-10 % of *Trans*-mixing in the *Cis*-isomer after UV irradiation, effective molecular area of 41-42 nm^2 can be found for the *Cis*-isomer, in good agreement with the experimental result.

IV Expression of surface ratio

The surface ratio of the AzoC11 acid on the nanoparticles was estimated with this following relation:

$$\text{Surface ratio} = \frac{\text{Area}_{\text{AzoC11 acid}} \times N_a \times \frac{\text{m}_{\text{AzoC11 acid}}}{\text{M}_{\text{AzoC11 acid}}}}{\text{Area}_{\text{TiO}_2} \times \text{m}_{\text{TiO}_2}}$$

The numerator represented the total area of the AzoC11 acid molecules and the denominator represented total area of the nanoparticles.

$\text{Area}_{\text{AzoC11 acid}}$: area molecular of the AzoC11 acid,

N_a: Avogadro constant,

$\text{m}_{\text{AzoC11 acid}}$: weight of the AzoC11 acid,

$\text{M}_{\text{AzoC11 acid}}$: Molar weight of the AzoC11 acid,

$\text{Area}_{\text{TiO2}}$: specific area of TiO_2 nanoparticles P25 (55 m^2/g),

m_{TiO2}: weight of TiO_2 nanoparticles.

V values of wetting study

Surface Ratio	0%	39%	62%	77%	116%	193%
θ_{init}	<10°	26.7°±2.7°	136.7°±2.4°	146.0°±2.1°	152.8°±3.4°	156.5°±2.4°
$\theta_{after\ UV}$	<10°	<10°	35.9°±3.4°	21.2°±3.9°	117.2°±2.1°	139.6°±1.8°
θ_{init}-$\theta_{after\ UV}$	0°	16.7°±2.7°	100.8°±5.8°	124.8°±6.0°	35.6°±5.5°	16.9°±4.2°

Table S1: Initial water contact-angle, contact angle after 12 min of UV irradiation and the variation of the contact angles between before- and after the UV irradiation

VI Comparison of contact angle variations versus the irradiation conditions

The following table reports some results in the literature concerning the contact angle variations ($\Delta\theta°$) and irradiation conditions.

$\Delta\theta$ (°)	The power of the UV source	Irradiation Time	References
12°	25 Watt	5 min	1
50°	10 Watt	60 min	2
121°	8 Watt	13 hours	3
124°	**15 Watt**	**12 min**	**This study**
138°	300 Watt	10 min	4
156°	150 Watt	2 hours	5

Table S2: Contact angle variations versus the irradiation conditions

References

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