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## Cooperativity Analysis of the Open-, Closed-and Annulated-Isomers of Diarylethene that form 2-D Ordering at the Liquid/Solid Interface and their Photochemical Interchanges

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## Introduction

- ✓ Control over molecular nanostructure: "bottom-up" strategy<sup>1</sup> for molecular electronic devices
- ✓ 2-D supramolecular self-assembly at interfaces widely studied<sup>2-4</sup>
- ✓ Scanning Tunneling Microscopy (STM): efficient tool for the characterization of Self-assembled Monolayers (SAM)<sup>5</sup>
- ✓ Light as external stimulus: require photo-responsive material
- ✓ Diarylethene: high thermal stability of each isomer, high fatigue resistance<sup>6,7</sup>
- ✓ Diarylethene-pyrene: photoinduced reversible control between 2 orderings<sup>8</sup>
- ✓ Stabilization by H-bond network<sup>9,10</sup>
- ✓ Ordering  $\gamma$  favored / ordering  $\beta$ : after UV,  $\beta$  was never observed<sup>10</sup>

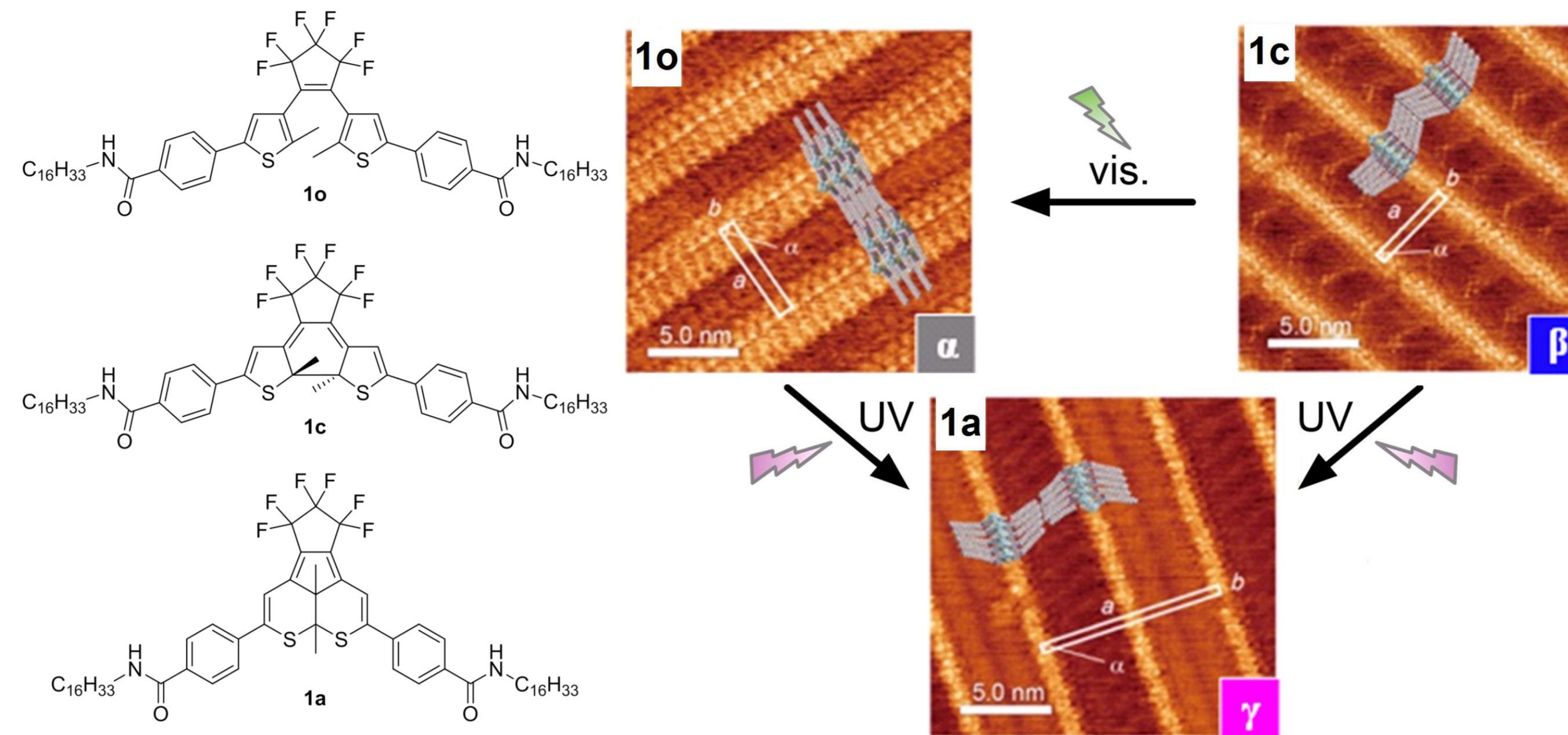


Figure 1. Open-, closed- and annulated-isomers and their 2-D orderings

## Conclusions

- ✓ Adsorption processes were modeled: open-isomer **1o** is isodesmic, closed-isomer **1c** is cooperative and annulated-isomer **1a** has a very high affinity for HOPG ( $K_e > 10^6$ )
- ✓ This work highlighted the existence of mix-crystals **1o/1c** and the "Induced cooperativity" on formation of ordering  $\alpha$  by addition of **1c**.
- ✓ A better understanding of photochemical interchanges became possible: SAM obtained from irradiated solution can be predicted by the model
- ✓ The STM analysis of the in-situ irradiation suggest a modification of photochromic properties at the octanoic acid/HOPG interface

## Results and Discussions

### Photoisomerization

- ✓ Irradiation ( $\lambda=365$  nm) of **1o** solution ( $[1o] = 29.4 \mu\text{M}$ )
- ✓ Ratio  $\Phi_{o \rightarrow c} : \Phi_{c \rightarrow o} : \Phi_{c \rightarrow a}$  is 1 : 0.047 : 0.001
- $\Phi_{o \rightarrow c} = 0.59$  (reported)<sup>11</sup>;  $\Phi_{c \rightarrow o} = 0.028$ ;  $\Phi_{c \rightarrow a} = 0.0006$

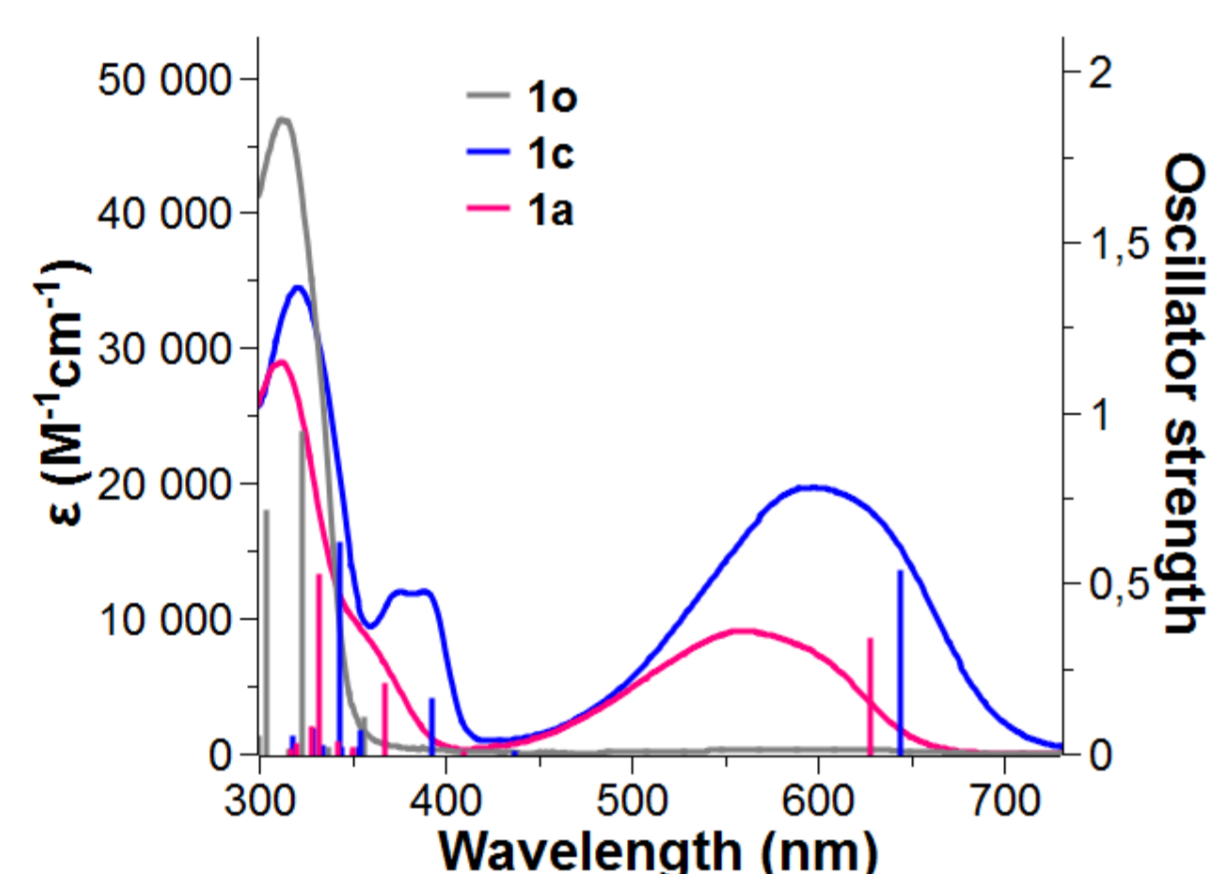


Figure 2. Absorption spectra in octanoic acid

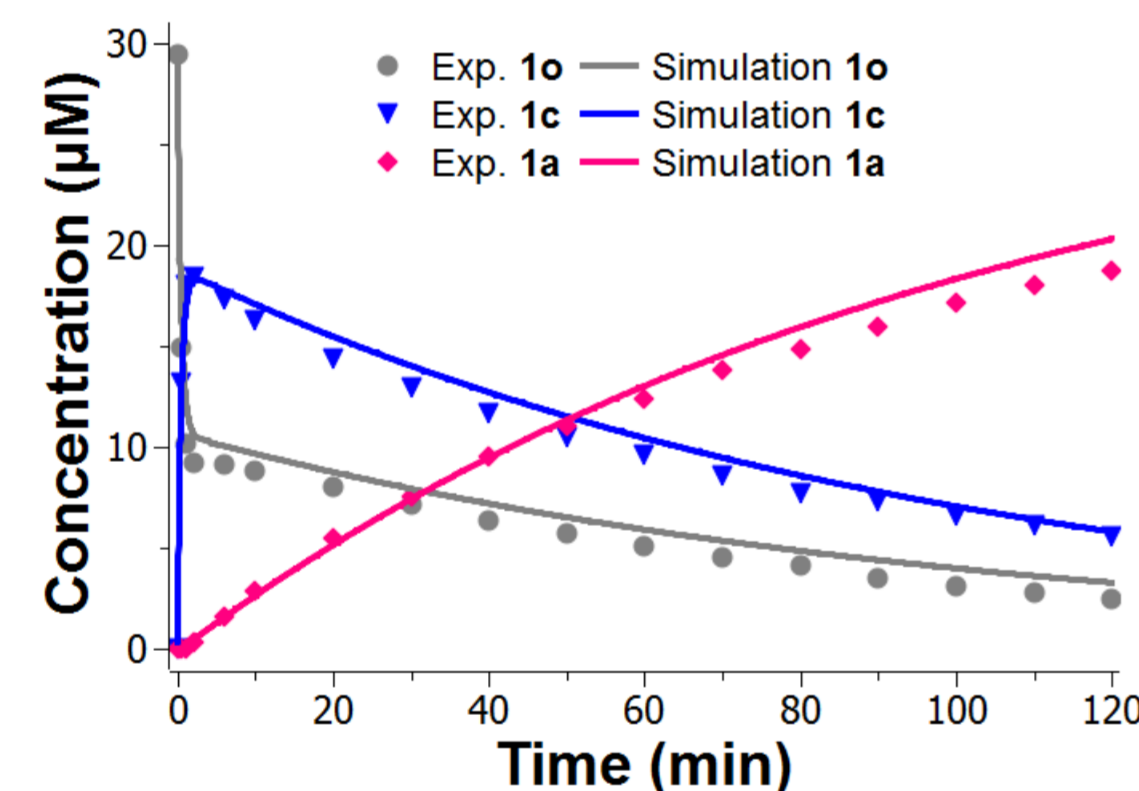


Figure 3. Evolution of concentrations upon irradiation with UV light

### Mono-component adsorption parameters

- ✓ Cooperative supramolecular polymer<sup>12-13</sup>
- ✓ Cooperative model at the octanoic acid/highly oriented pyrolytic graphite (HOPG) interface<sup>10</sup>

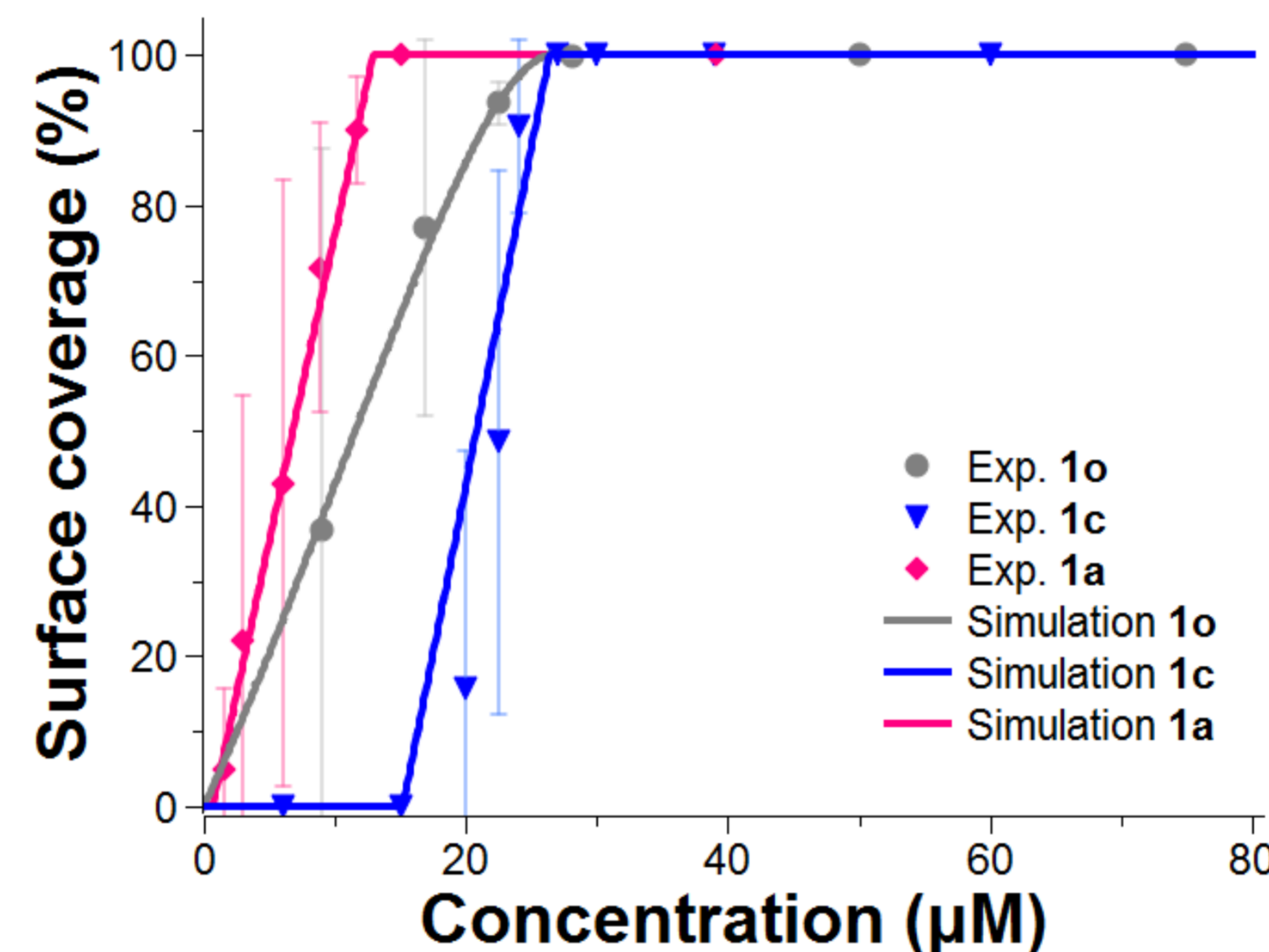


Figure 4. Concentration dependence of the surface coverage

Table 1. Best-fitting adsorption parameters for **1o**, **1c** and **1a**

Compound	$K_e$ ( $M^{-1}$ )	$K_n$ ( $M^{-1}$ )	$\sigma$
<b>1o</b>	$6.7 \pm 0.2 \times 10^4$	$6.7 \pm 0.2 \times 10^4$	1
<b>1c</b>	$6.5 \pm 0.3 \times 10^4$	$\leq 6.5 \pm 0.3 \times 10^{-2}$	$\leq 10^{-6}$
<b>1a</b>	$1.5 \pm 0.5 \times 10^6$	$\leq 1.5 \pm 0.5$	$\leq 10^{-6}$

### SAM obtained from irradiated solutions

- ✓ Irradiation ( $\lambda=365$  nm) of **1o** solution ( $[1o] = 28.7 \mu\text{M}$ )
- ✓ Exact composition (UV-Vis): calculated fractional coverage values (cooperative model)
- ✓ Experimental fractional coverage values (STM)
- ✓ Experimental  $\theta_\beta >$  Calculated  $\theta_\beta$ ;  $\alpha$  not observed
- ✓ Co-crystallization ?

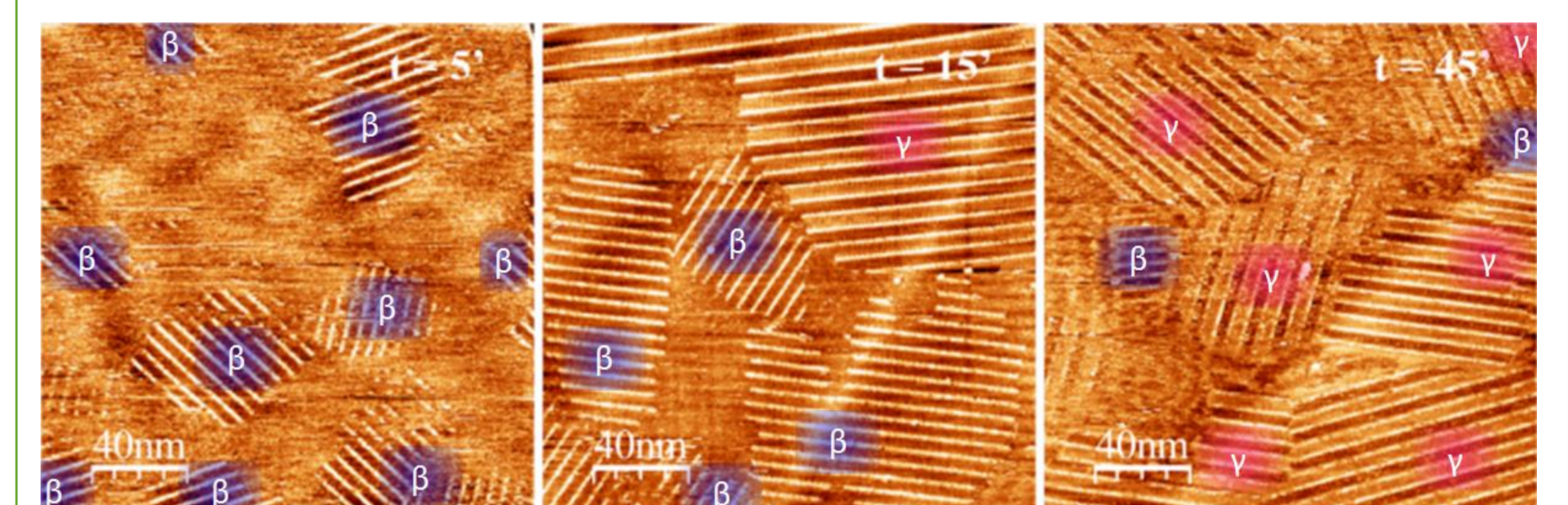


Figure 5. STM image from an irradiated solution of **1o**

Table 2. Calculated and experimental fractional coverage

	Calc. $\theta_\alpha$	Exp. $\theta_\alpha$	Calc. $\theta_\beta$	Exp. $\theta_\beta$	Calc. $\theta_\gamma^*$	Exp. $\theta_\gamma$
5 min	0.40	0	0.08	0.35	0.09	0
15 min	0.33	0	0.02	0.18	0.26	0.32
45 min	0.21	0	0	0.005	0.87	0.79

\*Calculated using cooperative parameters

### Bi-component adsorption parameters

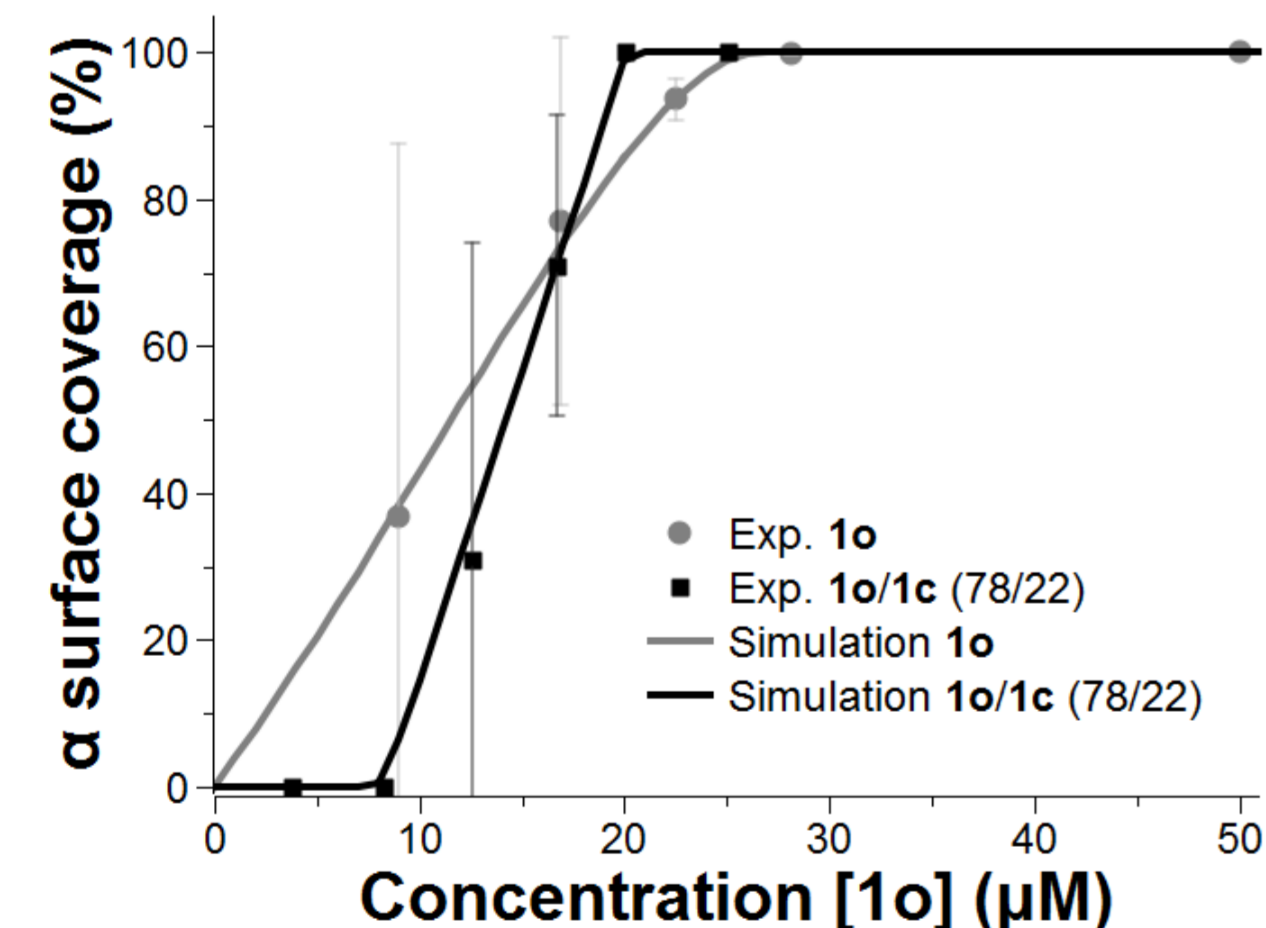


Figure 6.  $[1o]$  dependence of the surface coverage

- ✓ Modification of adsorption properties for bi-component systems: mix-crystals **1o/1c**
- ✓ Depending of the ratio: ordering  $\alpha$  or ordering  $\beta$ , both never observed together
- ✓ Induced cooperativity on the formation of  $\alpha$  by addition of **1c** to solutions of **1o**

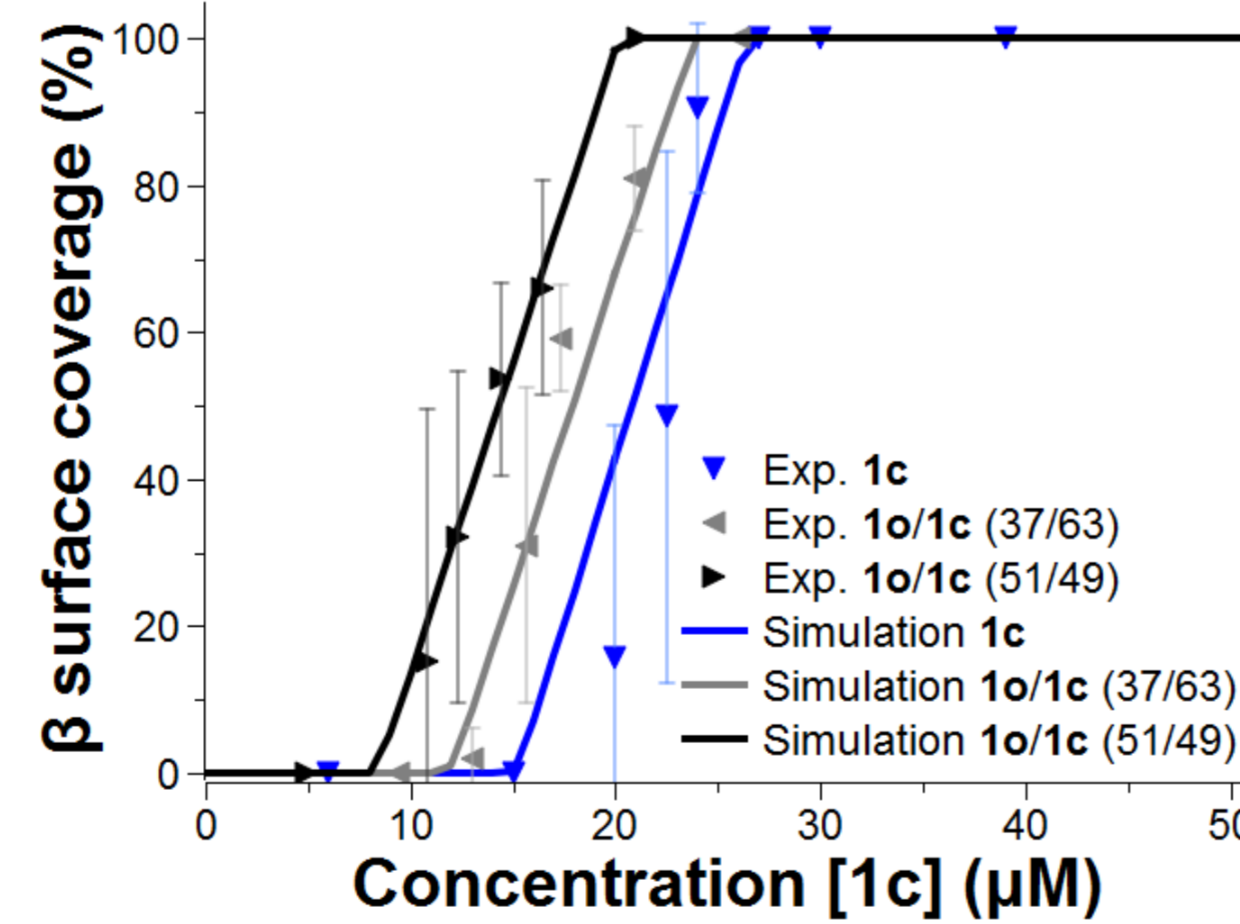


Figure 7.  $[1c]$  dependence of the surface coverage

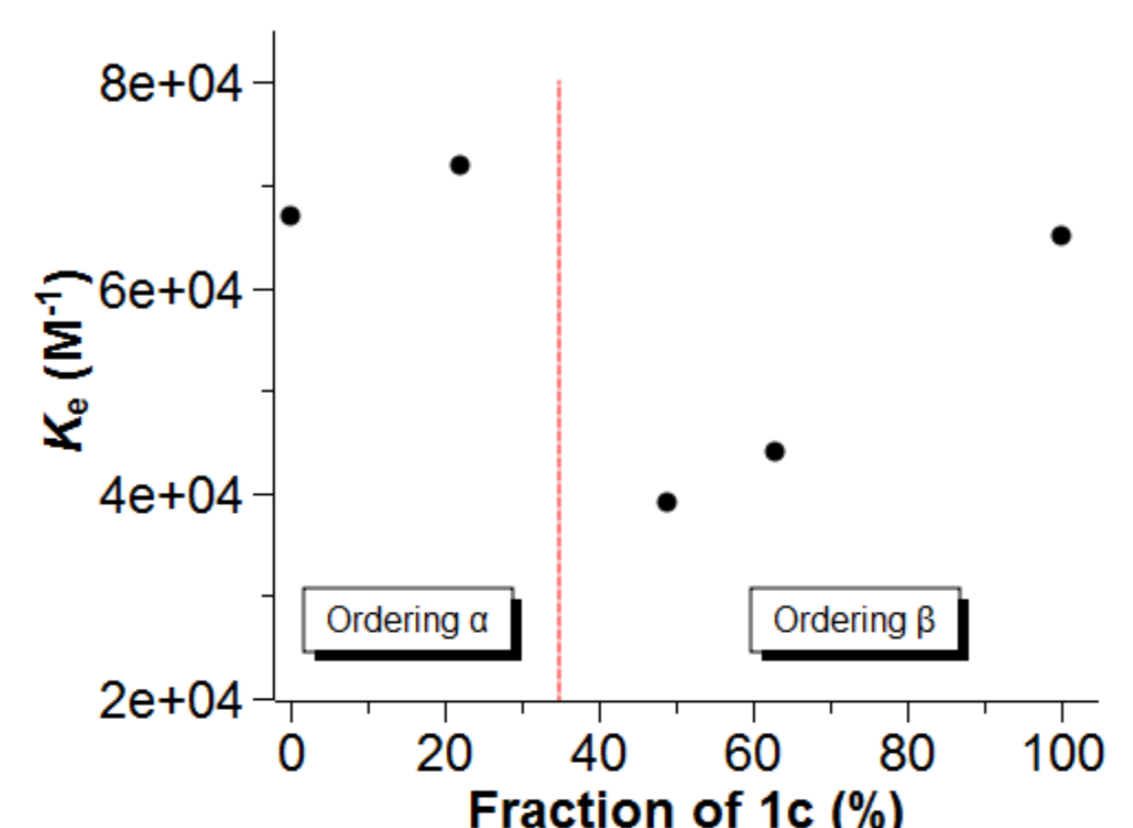


Figure 8.  $1o/1c$  ratio dependence of  $K_e$

### In-situ irradiation of SAM

- ✓ In-situ irradiation of SAM obtained from **1o** solution ( $[1o] = 30.0 \mu\text{M}$ )
- ✓ Progressive disappearance of ordering  $\alpha$
- ✓ Replacement by ordering  $\gamma$
- ✓ After about 1h: only ordering  $\gamma$
- ✓ Reorganization: Ostwald ripening<sup>14,15</sup>
- ✓ Figure 3: ratio in favor of  $\beta$  but it was never observed
- ✓ Modification of photochromic properties at the interface ?

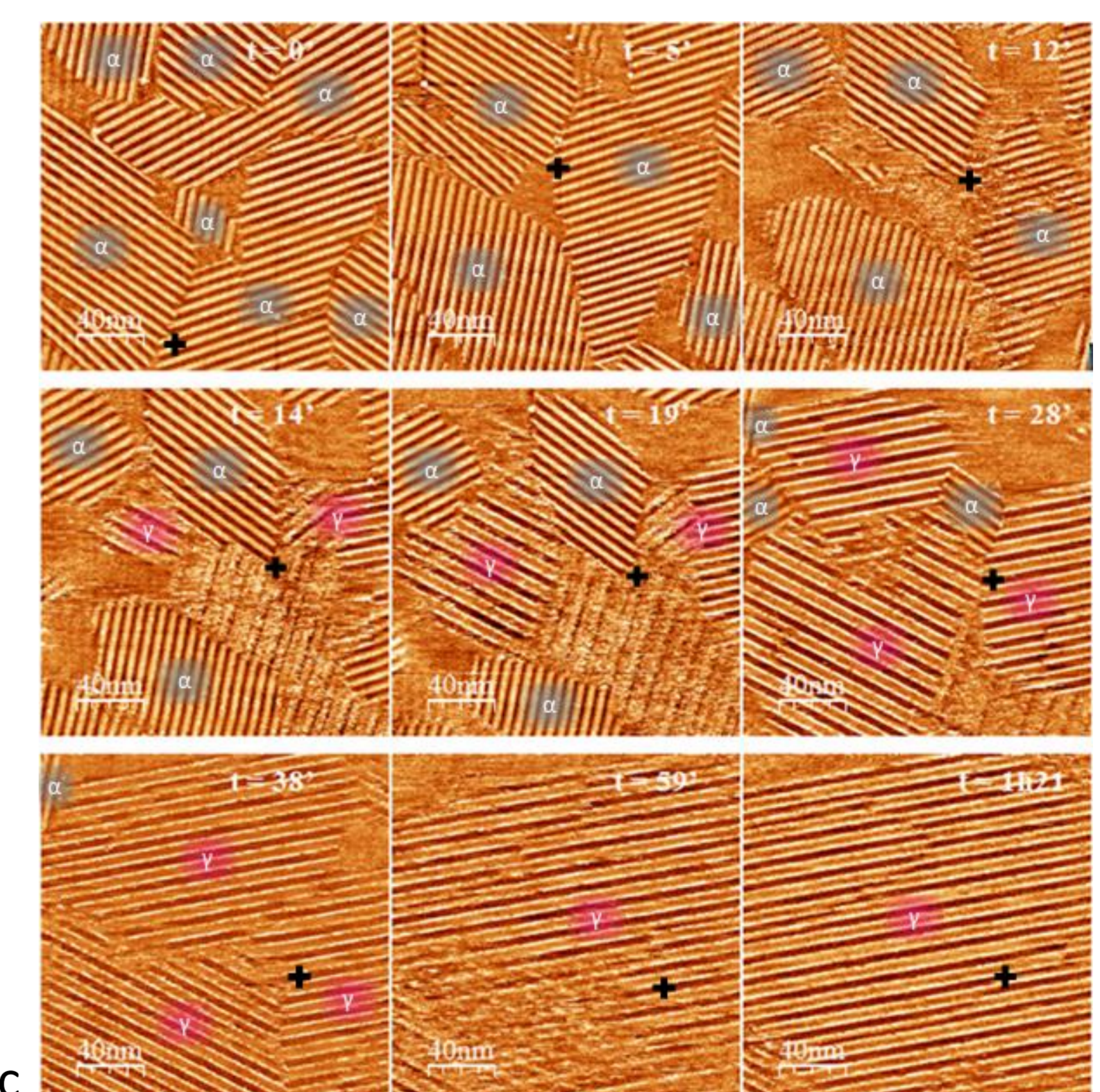


Figure 9. STM images of the in-situ photoirradiation

## Contact

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