



HAL
open science

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

Denis Frath, Takeshi Sakano, Yohei Imaizumi, Soichi Yokoyama, Takashi Hirose, Kenji Matsuda

► To cite this version:

Denis Frath, Takeshi Sakano, Yohei Imaizumi, Soichi Yokoyama, Takashi Hirose, et al.. 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. Annual Meeting of the Japanese Photochemistry Association, Oct 2014, Sapporo, Japan. hal-02103593

HAL Id: hal-02103593

<https://hal.science/hal-02103593>

Submitted on 3 May 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Introduction

- ✓ Control over molecular nanostructure: "bottom-up" strategy¹ for molecular electronic devices
- ✓ 2-D supramolecular self-assembly at interfaces widely studied²⁻⁴
- ✓ Scanning Tunneling Microscopy (STM): efficient tool for the characterization of Self-assembled Monolayers (SAM)⁵
- ✓ Light as external stimulus: require photo-responsive material
- ✓ Diarylethene: high thermal stability of each isomer, high fatigue resistance^{6,7}
- ✓ Diarylethene-pyrene: photoinduced reversible control between 2 orderings⁸
- ✓ Stabilization by H-bond network^{9,10}
- ✓ Ordering γ favored / ordering β : after UV, β was never observed¹⁰

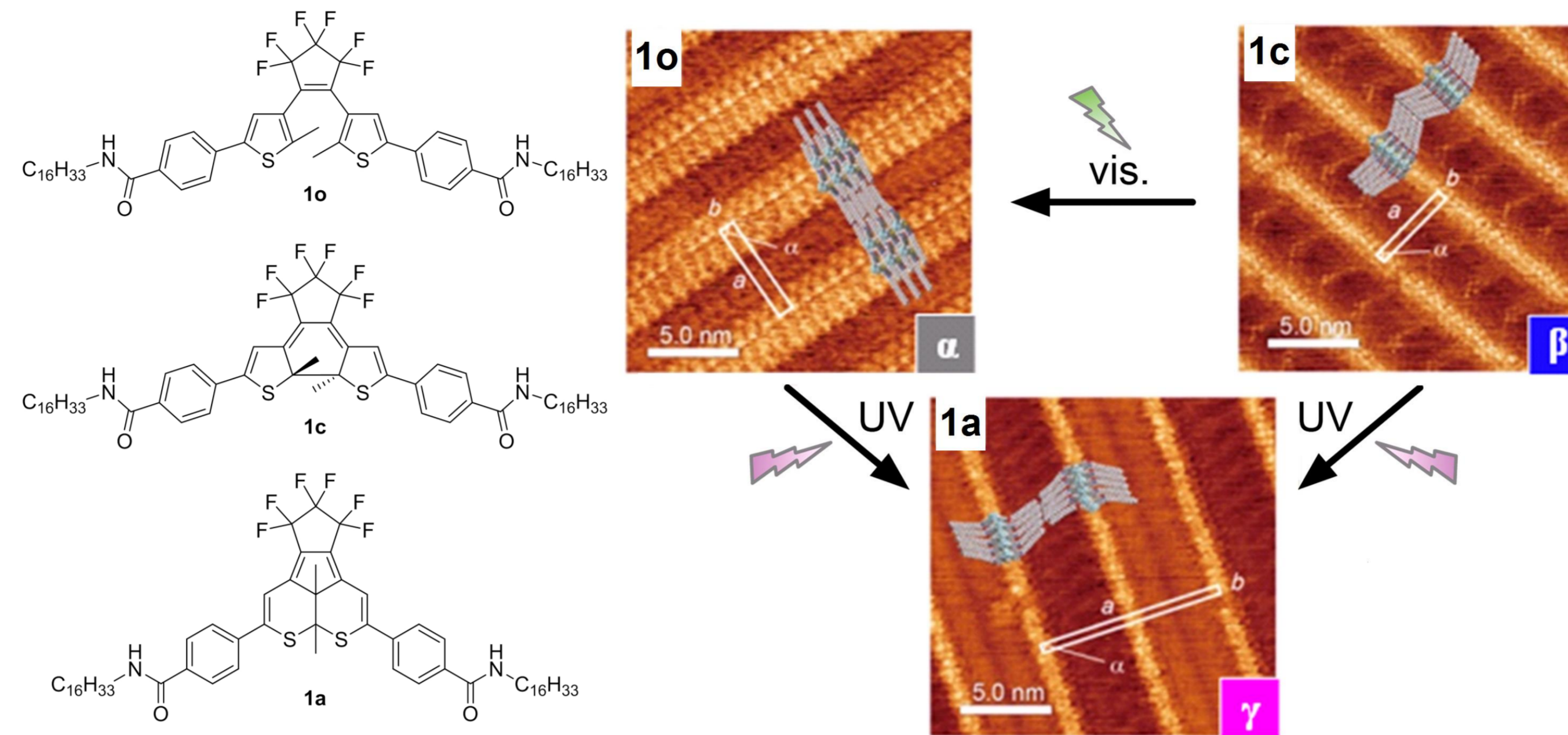


Figure 1. Open-, closed- and annulated-isomers and their 2-D orderings

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 α 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)¹¹; $\Phi_{c \rightarrow o} = 0.028$; $\Phi_{c \rightarrow a} = 0.0006$

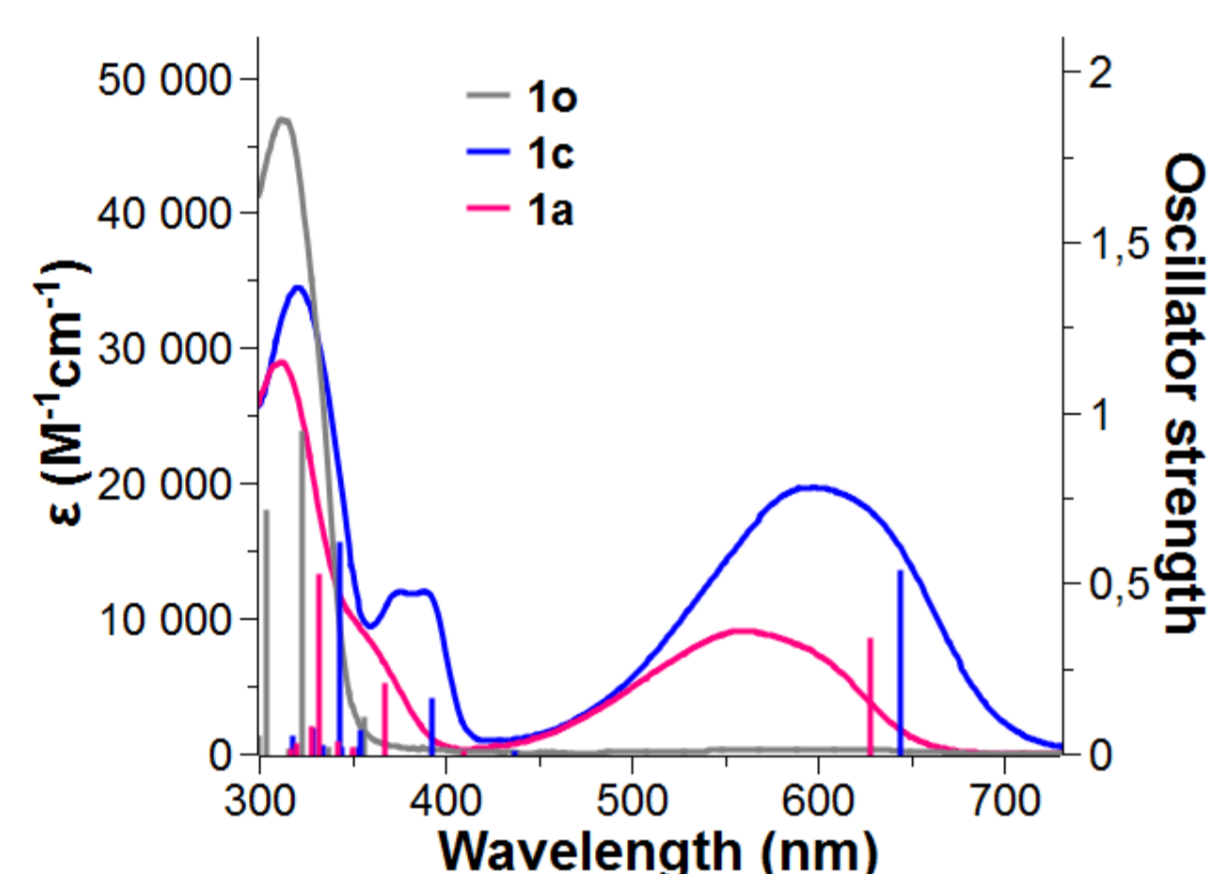


Figure 2. Absorption spectra in octanoic acid

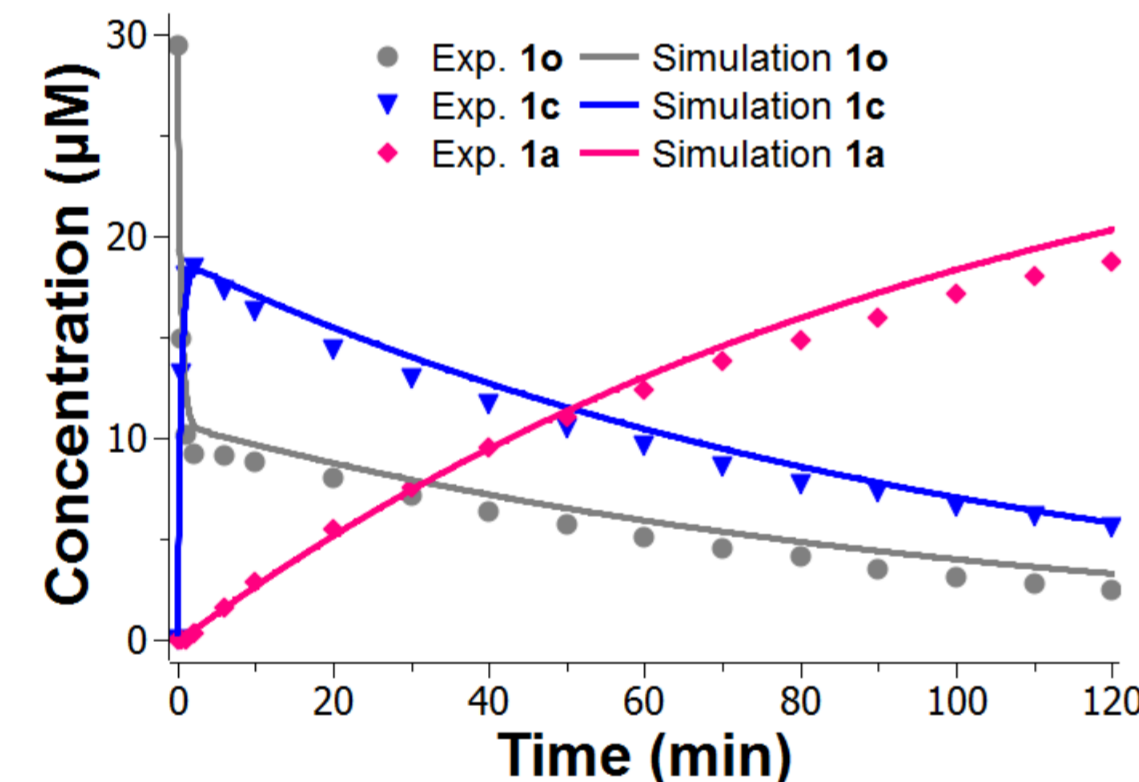


Figure 3. Evolution of concentrations upon irradiation with UV light

Mono-component adsorption parameters

- ✓ Cooperative supramolecular polymer¹²⁻¹³
- ✓ Cooperative model at the octanoic acid/highly oriented pyrolytic graphite (HOPG) interface¹⁰

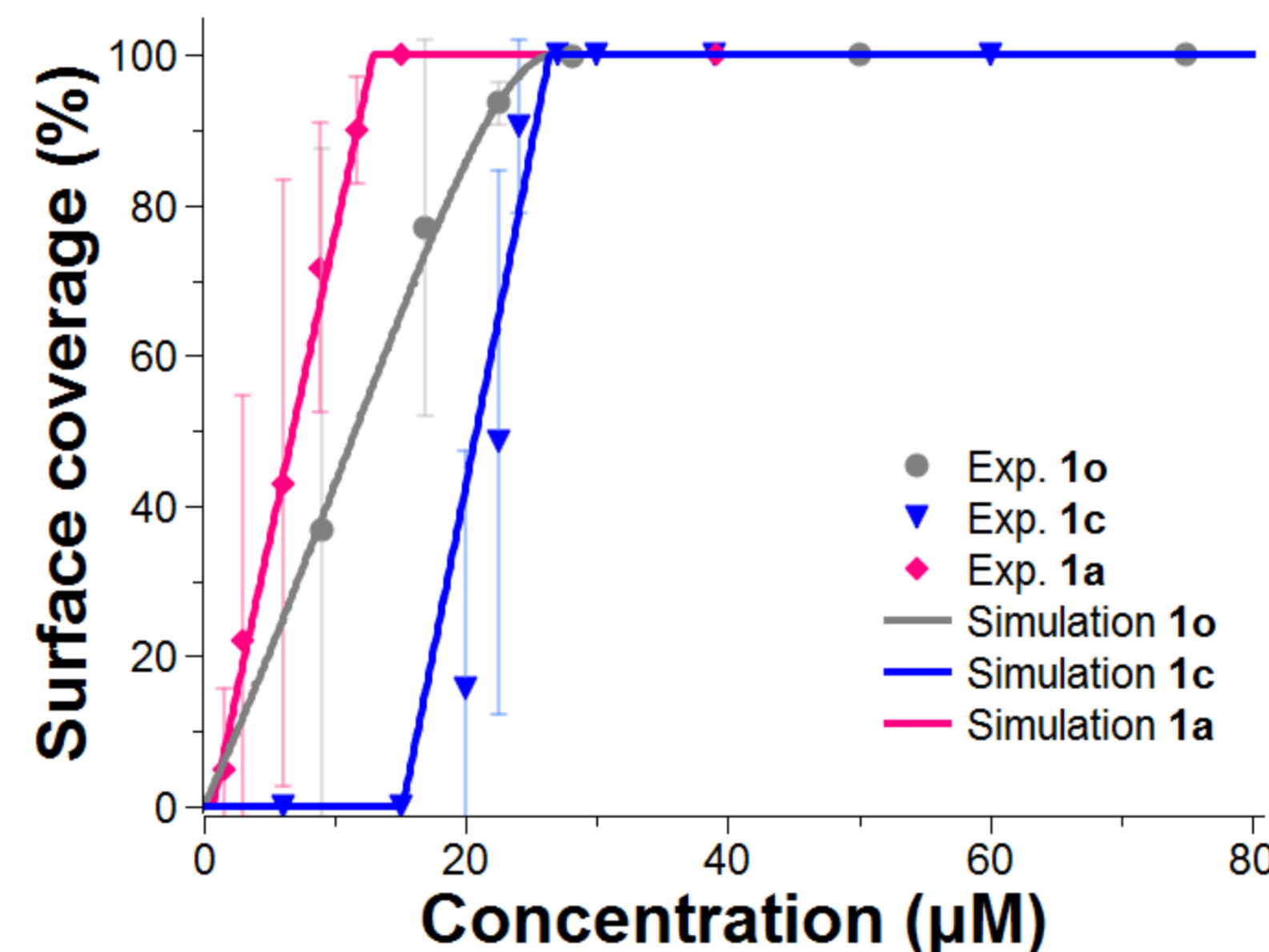


Figure 4. Concentration dependence of the surface coverage

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

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

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 θ_β ; α not observed
- ✓ Co-crystallization ?

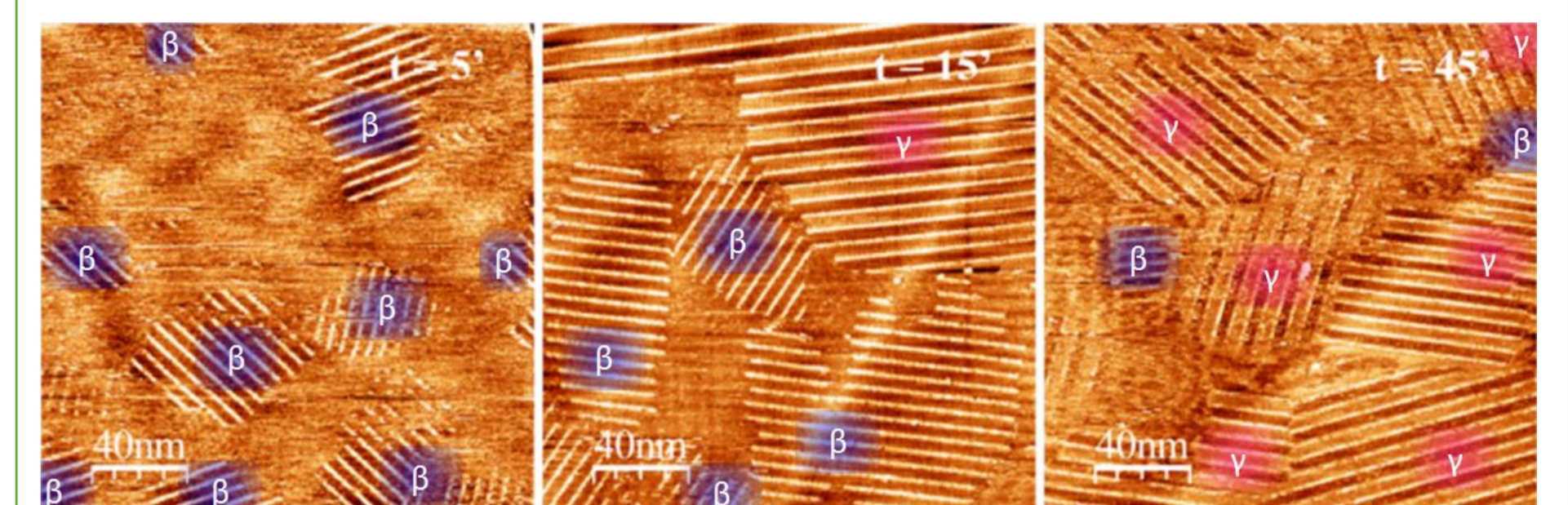


Figure 5. STM image from an irradiated solution of **1o**

Table 2. Calculated and experimental fractional coverage

	Calc. θ_α	Exp. θ_α	Calc. θ_β	Exp. θ_β	Calc. θ_γ^*	Exp. θ_γ
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

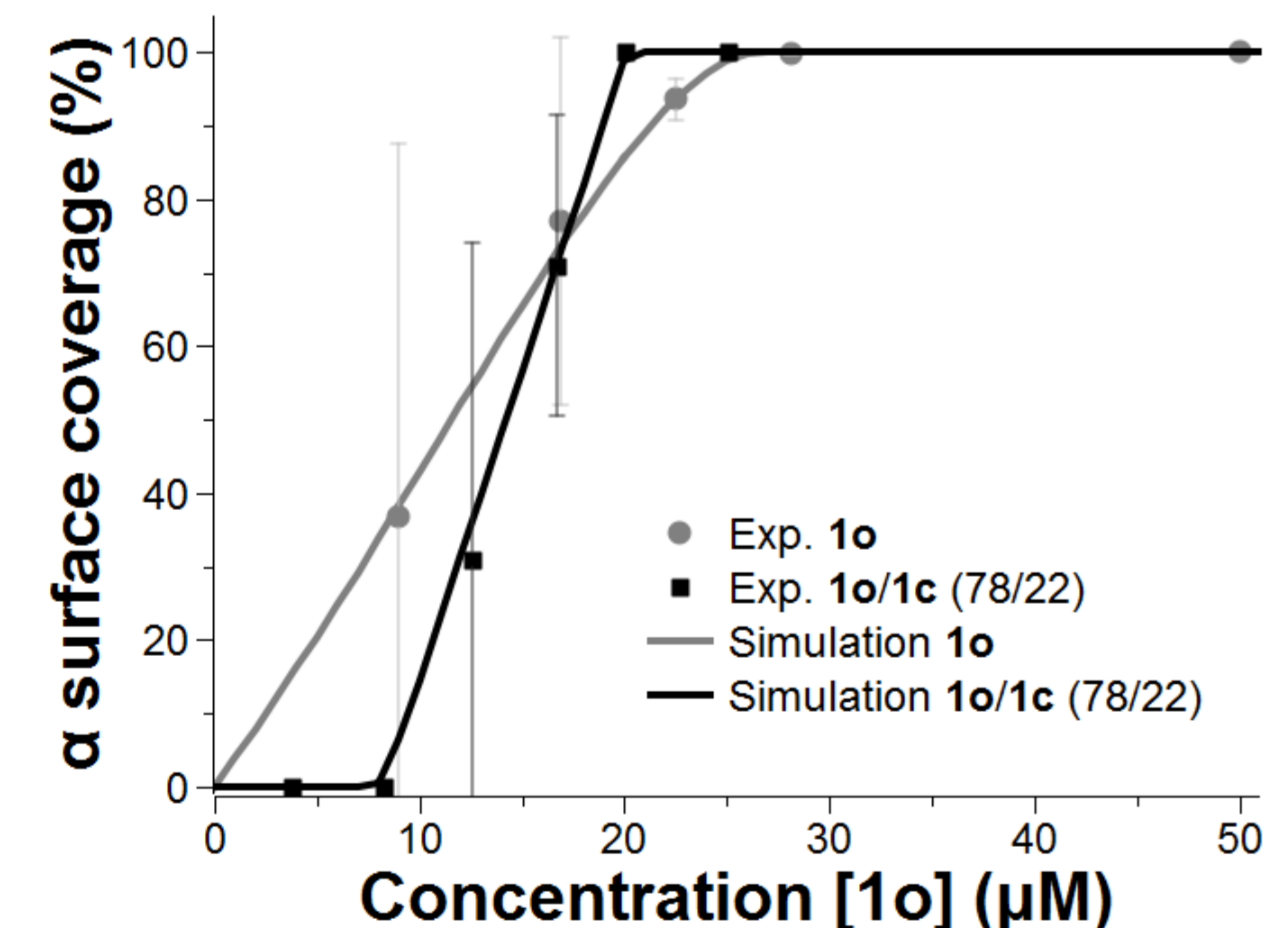


Figure 6. $[1o]$ dependence of the surface coverage

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

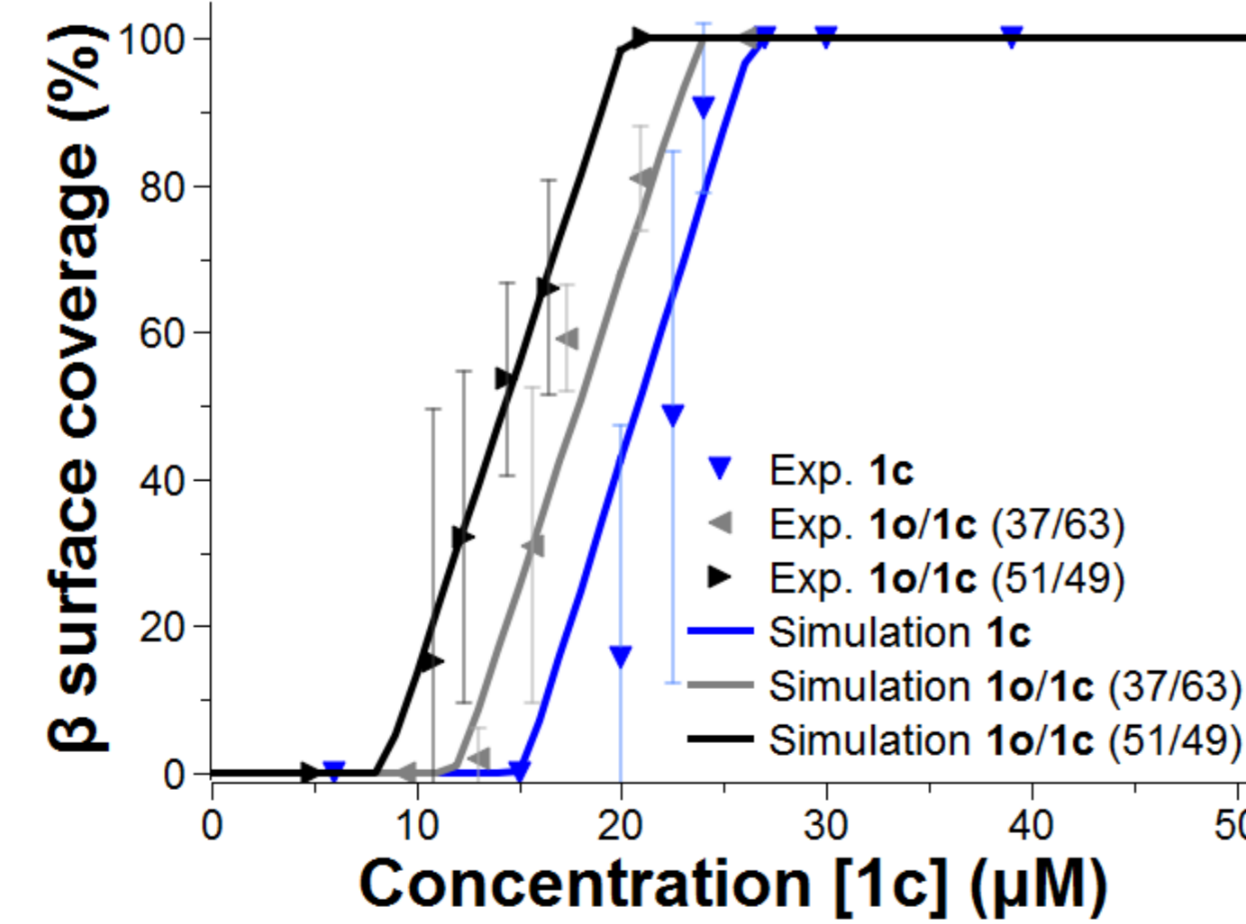


Figure 7. $[1c]$ dependence of the surface coverage

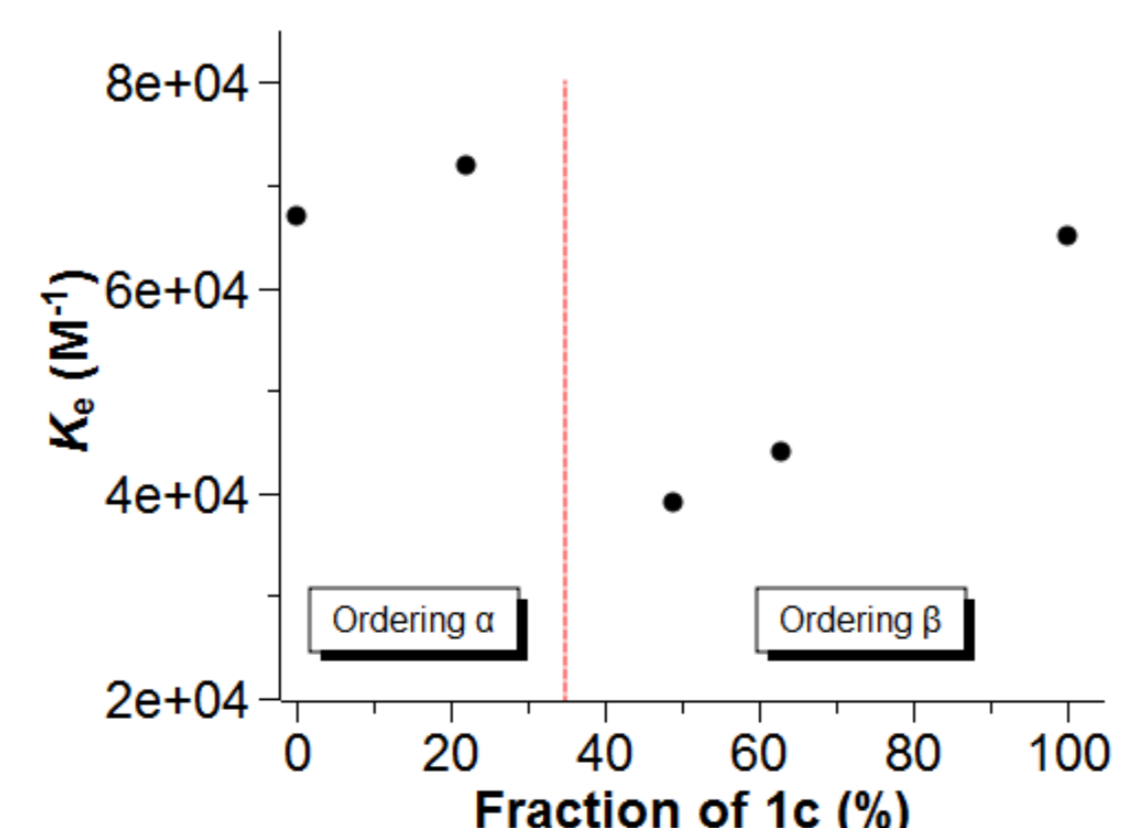


Figure 8. $1o/1c$ ratio dependence of K_e

In-situ irradiation of SAM

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

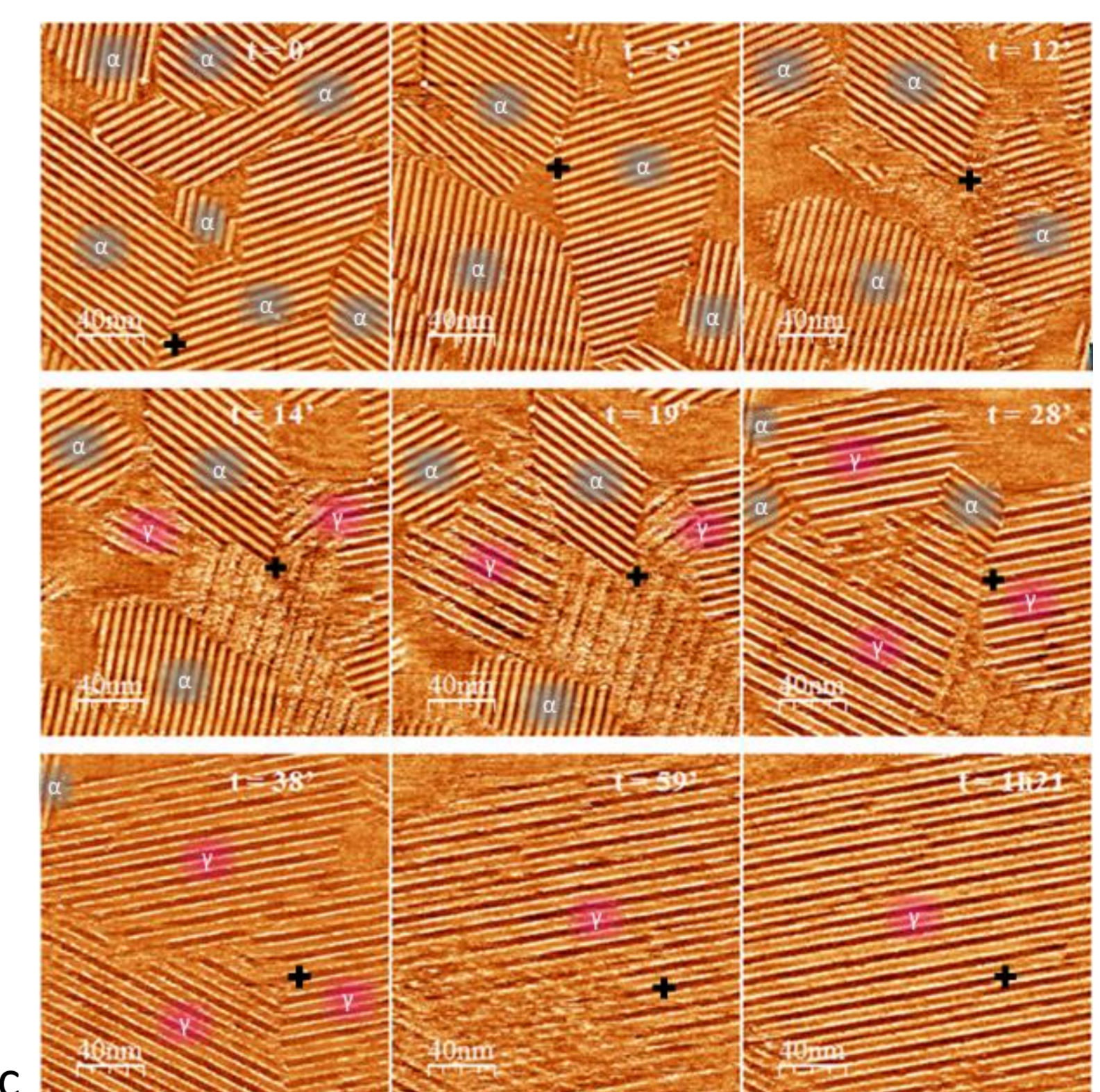


Figure 9. STM images of the in-situ photoirradiation

Contact

Dr. Denis Frath, JSPS postdoctoral fellow
Kyoto University, Graduate School of Engineering
Email: dfrath@sbchem.kyoto-u.ac.jp
Website: <http://www.sbchem.kyoto-u.ac.jp/matsuda-lab>
Personal page: researchgate.net/profile/Denis_Frath
Phone: 075 383 2746

References

- J. V. Barth, G. Costantini, K. Kern, *Nature* **2005**, *437*, 671–679
- T. Kudernac, S. Lei, J. A. A. W. Elemans, S. De Feyter, *Chem. Soc. Rev.* **2009**, *38*, 402–421
- K. S. Mali, J. Adisojoso, E. Ghijssens, I. De Cat, S. De Feyter, *Acc. Chem. Res.* **2012**, *45*, 1309–1320
- A. G. Slater (nee Phillips), P. H. Beton, N. R. Champness, *Chem. Sci.* **2011**, *2*, 1440–1448
- S. De Feyter, F. C. De Schryver, *Chem. Soc. Rev.* **2003**, *32*, 139–150
- M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716
- K. Matsuda, M. Irie, *J. Photochem. Photobiol. C* **2004**, *5*, 169–182
- R. Arai, S. Uemura, M. Irie, K. Matsuda, *J. Am. Chem. Soc.* **2008**
- S. Yokoyama, T. Hirose, K. Matsuda, *Chem. Commun.* **2014**, *50*, 5964–5966
- T. Sakano, Y. Imaizumi, T. Hirose, K. Matsuda, *Chem. Lett.* **2013**, *42*, 1537–1539
- M. Irie, T. Lifka, S. Kobatake, N. Kato, *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876
- D. Zhao, J. S. Moore, *Org. Biomol. Chem.* **2003**, *1*, 3471–3491
- T. F. A. De Greef, M. M. J. Smulders, M. Wolfs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, *Chem. Rev.* **2009**, *109*, 5687–5754
- R. Heinz, A. Stabel, F. C. De Schryver, J. P. Rabe, *J. Phys. Chem.* **1995**, *99*, 505–507
- G. M. Florio, J. E. Klare, M. O. Pasamba, T. L. Werblowsky, M. Hyers, B. J. Berne, M. S. Hybertsen, C. Nuckolls, G. W. Flynn, *Langmuir* **2006**, *22*, 10003–10008