Nanocylindrical confinement imparts highest structural order in molecular self-assembly of organophosphonates on aluminum oxide

Anshuma Pathak^{1,2}, Achyut Bora^{1,2}, Björn Braunschweig^{3,4}, Christian Meltzer³, Hongdan Yan⁵, Peter Lemmens^{5,5a}, Winfried Daum⁶, Jeffrey Schwartz⁷, Marc Tornow^{1,2*}

1) Institut für Halbleitertechnik, TU Braunschweig, Germany

2) Department of Molecular Electronics, TU München, Germany

3) Institute of Particle Technology, FAU Erlangen-Nürnberg, Germany

4) Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster, Germany

5) Institute for Condensed Matter Physics, TU Braunschweig, Germany

5a) Laboratory for Emergent Nanometrology, LENA, TU Braunschweig, Germany

6) Institut für Energieforschung und Physikalische Technologien, TU Clausthal, Germany

7) Department of Chemistry, Princeton University, NJ, USA

*corresponding author: tornow@tum.de

Supporting Information

Nine figures, one table, and three explanatory paragraphs.



Supporting Information Figure SI 1. CA images of (a) a bare AAO membrane immediately after oxygen plasma cleaning, and (b) a C12P SAM-coated AAO membrane.



Supporting Information Figure SI 2. AFM tapping mode images of C12P SAM-coated (a) AlOx, (b) α -Al₂O₃ (0001) and (c) nanoporous AAO substrates; inset in (c): zoomed image of the porous membrane.



Supporting Information Figure SI 3. Infrared absorption spectra of bare AAO and C12P SAM-coated AAO membranes. The broad peak at ~3500 cm⁻¹ can be attributed to surface hydroxyl groups on the surface ^{1, 2}. A substantial reduction in its intensity in the SAM-coated sample indicates disappearance of such groups, though not completely, on the surface. A sharp band at ~1469 cm⁻¹ can be ascribed to the methylene bending mode of the hydrocarbon chain in the SAM. The lower wavenumber range below 1400 cm⁻¹ appears to be dominated by peaks from the AAO substrate itself thereby making it difficult (even considering difference spectra) to get any (weak) signal from the phosphonate groups of the SAM, whose characteristic peaks lie in this range. An oscillation with period ~75 cm⁻¹ throughout the whole range of the spectra was attributed to internal reflections within the highly ordered, aligned nanopores of AAO ².



Supporting Information Figure SI 4. A comparison of the peak wave numbers of methylene symmetric (top panel) and antisymmetric (bottom panel) stretching bands in the IR absorbance spectra of different aluminum oxide substrates coated with C12P monolayers, extracted from Figure 2.



Supporting Information Figure SI 5. Infrared peak positions of methylene symmetric (top panel) and antisymmetric (bottom panel) stretching vibrations of C18P monolayers on different aluminum oxide substrates.



Supporting Information Figure SI 6. SFG spectra of C8P, C12P, C16P and C18P SAMs on nanoporous AAO membranes. All spectra show two peaks due to the r^+ and r^+ , fr vibrations. A slight increase in intensity with increasing length of the alkyl chains of the SAM constituents can be seen for both peaks. This increase can be attributed to higher interfacial order.



Supporting Information Figure SI 7. SFG spectra of C8P, C12P, C16P and C18P SAMs on single crystalline α -Al₂O₃ (0001). The intensities of the bands (r⁺ and r⁺, fr) are strongest in the C18P spectrum, while in the same spectrum the signature of the methylene vibration cannot be resolved anymore. This indicates highest conformational order in the C18P SAM.

Supporting Information Table T1. FWHM values of the methylene symmetric and antisymmetric bands for C12P SAMs on the different aluminum oxide substrates.

	C12P/AIO _x	C12P/Al ₂ O ₃	C12P/AAO
FWHM _{CH2,symm}	11 (±1)	14 (±1)	9 (±0.9)
(cm ⁻¹)			
FWHM _{CH2,antisymm}	24 (±1)	25 (±1)	14 (±0.9)
(cm ⁻¹)			

Supporting Information Paragraph P1. <u>Comparison of the total surface area of an AAO</u> <u>membrane with that of a planar surface.</u>

Here, we calculate the ratio r of the total surface area of the AAO membrane with respect to the area of a planar surface (A_{plan}) of same lateral dimension. The total surface area of the AAO membrane (A_{AAO}) is the sum of the area of the pore inner walls (A_{pore}) and the inter-pore area at the upper surface ($A_{interpore}$). If we consider a rectangular region of length L and width W containing N_{pore} numbers of pores with diameter D, and an AAO template of thickness t, the ratio r can be written as

$$r = \frac{A_{pore} + A_{interpore}}{A_{plan}}$$
$$A_{pore} = \pi N_{pore} Dt$$
$$A_{plan} = LW$$
$$A_{int\,erpore} = LW - \frac{\pi N_{pore} D^2}{4}$$

For example, if we consider a region of 400 x 400 nm^2 of the porous AAO template of thickness 30 μ m comprising a total of ~24 pores with mean diameter of 50 nm (Figure SI 8),

$$A_{pore} = 1.1 \times 10^8 nm^2$$
; $A_{interpore} = 1.1 \times 10^5 nm^2$; $A_{plan} = 1.6 \times 10^5 nm^2$

the ratio will be $r \approx 690$.



Supporting Information Figure SI 8. A 400 nm x 400 nm region of the AAO template used for pore area calculation (yellow dashed line square). This area contains ~24 pores.

100nm Supporting Information Paragraph P2. <u>SFG measurements on metallic surfaces</u>

Measuring SFG on conducting surfaces reduces the number of possible polarization combinations with nonvanishing intensity in SFG spectra. The polarized incident light waves can induce molecular vibrations parallel and perpendicular to the surface, which leads to induced image dipoles in the metal substrate (Figure SI 9). In case of an excitation of molecular vibrations parallel to the surface, e.g., by s-polarized light, the total dipole moment of the vibration is canceled for a perfectly screening metal due to the image dipole in the metal. In contrast, dipole-active vibrations perpendicular to the surface are enhanced by an image dipole ³ (see, Figure SI 9). Because of these selection rules, vibrations on metal surfaces, even when a thin (<10 nm) oxide layer is present, cannot be characterized with SFG in ssp polarization, and SFG spectra on such surfaces must be measured with ppp polarization. However, the metal substrate can contribute to a strong non-resonant background that interferes with the resonant contributions from the interfacial molecules, which makes a comparison between ssp and ppp spectra difficult.



Supporting Information Figure SI 9. (a) A vibrational dipole oriented parallel to a metal surface induces an image dipole of opposite direction in the metal which results in a cancelation of the total dipole moment. (b) Bands of vibrations perpendicular to a metal surface are enhanced due to the induced image dipole moment.

Supporting Information Paragraph P3. <u>Calculation of reduction of intermolecular distance</u> inside AAO pores.

When the SAM of thickness *d* is formed on a cylindrical pore innerwall of radius *r*, the terminal part of the molecules can be imagined to form a cylinder of radius r_{tail} , shown as an inner cylinder (red dashed line) in Figure SI 10.

Circumference of pore inner wall = $2\pi r$

Circumference of inner cylinder = $2\pi r_{tail}$

Therefore, the circumference of the molecular tail part is smaller than that of the wall by an amount of $2\pi d$. This leads to a reduction of distance between two neighboring molecules on the top part of the SAM, which can be expressed as:

Reduction in intermolecular distance $=\frac{2\pi d}{2\pi r} = \frac{d}{r}$

For a 50 nm pore diameter (r = 25 nm) and a SAM thickness of 1.2 ± 0.2 nm (considering a C12P film of same thickness as on a planar AlO_x surface), this translates into a relative reduction of intermolecular distance at the top of the SAM by ~ 5%.



Supporting Information Figure SI 10. A schematic of the cross-section of an AAO pore with the inner wall covered by a SAM. The dashed red circle indicates the circumference formed by the terminal groups of the molecules.

References:

- 1. G. Xiong, J. W. Elam, H. Feng, C. Y. Han, H. H. Wang, L. E. Iton, L. A. Curtiss, M. J. Pellin, M. Kung, H. Kung and P. C. Stair, *Journal of Physical Chemistry B*, 2005, **109**, 14059-14063.
- 2. J. Ter Maat, R. Regeling, C. J. Ingham, C. A. G. M. Weijers, M. Giesbers, W. M. De Vos and H. Zuilhof, *Langmuir*, 2011, **27**, 13606-13617.
- 3. M. Moskovits, *The Journal of Chemical Physics*, 1982, 77, 4408-4416.