## **Electronic Supplementary Information**

# Molecular structure of octadecylphosphonic acids during their self-assembly on $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001)

Christian Meltzer<sup>a</sup>, Hui Yu<sup>a</sup>, Wolfgang Peukert<sup>a</sup> and Björn Braunschweig<sup>b</sup>

<sup>a.</sup> Institute of Particle Technology (LFG) and Cluster of Excellence – Engineering of Advanced Materials (EAM), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Cauerstrasse 4, 91058 Erlangen, Germany

<sup>b.</sup> Institute of Physical Chemistry and Center for Soft Nanoscience (SoN), Westfälische Wilhelms University Münster, Corrensstraße 28/30, 48149 Münster, Germany



### 1. Morphology of sample surfaces

**Figure S1** Picture of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (0001) surface after heat treatment (36 h @ 1450°C) taken with an atomic force microscope. Step-bunching, which results from the high miscut of  $< 3^{\circ}$  is visible. RMS roughness is 1.2 nm.

#### 2. Calibration with 2-propanol spectra

Before each measurement a spectrum of 2-propanol on the sample surface was taken. Due to different laser setup and alignment, these spectra have in general the same shape, but different intensity levels also with regard to the spectral contributions (see Figure S2). To correct for this, one 2-propanol spectrum was chosen as reference and a wavenumber dependent correction factor was calculated for each measurement and applied to the data:

calibration factor 
$$(\lambda) = \frac{2 - propanol_{REF}}{2 - propanol_{measurement}} (\lambda)$$



**Figure S2** *SFG spectra of 2-propanol on the clean sample surface taken before different measurements.* 

#### 3. Fitting procedure

To disentangle the different vibrational contributions of the measured SFG spectra, an assumption for the spectral lineshape of the vibrational bands originating from the adsorbed molecules is required. Based on the assumption of homogeneous line broadening the lineshape can be described with a Lorentzian curve.<sup>1</sup> The SFG intensity, which beside the resonant part from the interfacial molecules also consists of a non-resonant part from the substrate, can be described as:<sup>2</sup>

$$I_{SF}(\omega_{IR} + \omega_{VIS}) \propto \left|F_{yyz}\right|^2 \left|\chi_{NR}^{(2)} + \sum_q \chi_q^{(2)}\right|^2 I(\omega_{VIS}) I(\omega_{IR})$$
(S5)

with 
$$\chi_q^{(2)} = \frac{|A_q| \exp(i\varphi_q)}{\omega - \omega_q + i\Gamma_q}$$
 (S6)

With  $\chi_{NR}^{(2)}$  standing for the non-resonant contributions and  $\chi_q^{(2)}$  for the resonant contributions of the vibrational bands q. In the Lorentzian curve, describing  $\chi_q^{(2)}$ ,  $A_q$  represents the amplitude,  $\varphi_q$  the phase,  $\omega_q$  the spectral position and  $\Gamma_q$  the bandwidth of the vibrational mode.  $\omega$  is the frequency of the IR laser beam.

With equation (S5) and (S6), the spectra of an ODPA SAM in air can be fitted, assuming a linear combination of the vibrational bands contributing to the spectrum. For the sapphire substrate used in these experiments, the non-resonant part is negligible. In Table S2 the vibrational bands as well as the fitting parameters used to fit the spectra measured after drying (see Figure S4) are provided.

To extract the vibrational amplitudes of the time-resolved in situ spectra, a more sophisticated approach is required. Due to the overlap of the spectral contributions from ODPA and 2-propanol in the spectral range between 2900 and 3000 cm<sup>-1</sup>, the FR-AS peak was introduced in a former publication and fitted with a Voigt profile (see Supporting Information of <sup>3</sup>). In addition to this Voigt profile we used four Lorentzians to fit the in situ spectra. One for the  $CH_2^{ss}$ , one for the  $CH_3^{ss}$ , one for the methin band and one for the Fermi resonance of the methyl groups (see Table S1 for the fit parameters). This approach was used to fit the spectra measured for ODPA concentrations 0.5, 1 and 2 mM. For 5 and 30 mM it was only used as long as the methine amplitude was contributing to the spectra. Afterwards the Fermi resonance of the methylene group  $(CH_2^F)$  has to be taken into account, to ensure a good fitting result. As  $CH_2^F$  is positioned in close proximity to the mehine amplitude, but has an opposite phase (see Table S1) the methine amplitude has been set to zero for long formation times to avoid arbitrary high amplitudes of this two contributions due to destructive interference.

To validate the change of contributing bands for 5 and 30 mM within the fitting procedure of the time-resolved in situ spectra, results have been compared within the region of the change. In Figure S3 (a) the resulting amplitudes of the methine band and the  $CH_2^F$  band are plotted. The comparison shows, that once the methine amplitude reaches zero, the  $CH_2^F$  band starts to grow. Before that point, arbitrary values of the  $CH_2^F$  bands result. Comparing the  $CH_2^{ss}/CH_3^{ss}$  amplitude ratio in Figure S3 (b) for the two procedure also shows a good agreement of both at the time the methine amplitude reaches zero.

Table S1	_			C <sub>ODPA</sub>		
		0,5	1	2	5	30
	$\omega/cm^{-1}$	2844.6	2839.8	2843.0	2844.5	2844.5
$CH_2^{ss}$	Г/ <b>ст<sup>-1</sup></b>	10.5	10.5	10.5	10.5	10.5
	$oldsymbol{arphi}$	1	1	1	1	1
	$\omega/cm^{-1}$	2864.9	2865.9	2865.9	2868.6	2868.6
$CH_3^{ss}$	Г/ <i>ст</i> <sup>-1</sup>	10.3	10.3	10.3	10.3	10.3
	$oldsymbol{arphi}$	1	1	1	1	1
	$\omega/cm^{-1}$	2900.7	2905.9	2905.3	2905.3	2905.3
СН	Г/ <i>ст</i> <sup>-1</sup>	15.0	15.0	15.0	15.0	15.0
	$oldsymbol{arphi}$	1	1	1	1	1
	$\omega/cm^{-1}$				2911.0	2911.0
$CH_2^F$	Г/ <i>ст</i> <sup>-1</sup>				12.5	12.5
_	$oldsymbol{arphi}$				0	0
	$\omega/cm^{-1}$	2925.0	2925.0	2925.0	2931.0	2931.0
$CH_3^F$	Г/ <i>ст</i> <sup>-1</sup>	13.7	13.7	13.7	11.6	11.6
	$oldsymbol{arphi}$	1	1	1	1	1
	$\omega_V/cm^{-1}$	2959.0	2961.3	2961.3	2960.9	2960.9
FR-AS	$\gamma/cm^{-1}$	2.0	2.0	2.0	2.0	2.0
	σ/ <i>cm</i> <sup>−1</sup>	15.2	15.2	15.2	15.2	15.2
	φ	0	0	0	0	0

**Table S2** Parameters of the vibrational bands used to fit the SFG spectra shown in Figure S4.  $\varphi$  is given in multiples of  $\pi$ . Concerning the position of the vibrational modes consult (Nishi et al. 2003; Lambert et al. 2005; Lu et al. 2005).

$\omega/cm^{-1}$ 2846.0 $\Gamma/cm^{-1}$ 15	
$CH_2^{SS}$ $\Gamma/cm^{-1}$ 15	
$\overline{\varphi}$ 1	
$\omega/cm^{-1}$ 2872.0	
$CH_{3}^{ss}$ $\Gamma/cm^{-1}$ 10.3	
φ 1	
$\omega/cm^{-1}$ 2905.0	
$CH_2^F$ $\Gamma/cm^{-1}$ 14.4	
φ 0	
$\omega/cm^{-1}$ 2934.0	
$CH_3^F$ $\Gamma/cm^{-1}$ 11.6	
$\varphi$ 1	
$\omega/cm^{-1}$ 2960.0	
$CH_3^{as}$ $\Gamma/cm^{-1}$ 10	
φ 1	



**Figure S3** Results of the fitting procedures used for the time-resolved in situ SFG spectra measured during SAM formation for 5 mM (red symbols) and 30 mM (black symbols) ODPA solution concentration. At beginning of the SAM formation the methin amplitude was considered for the fit, while  $CH_2^F$  was set to zero (squares). Once the methin amplitude reached zero, it was set to zero in the fit an replaced by  $CH_2^F$ . In (a) the respective amplitudes are shown for both procedures, in (b) the  $CH_2^{SS}/CH_3^{SS}$  amplitude ratio. The time at which the methin amplitude was set to zero and the  $CH_2^F$  unequal zero is marked in (b) with vertical lines.

#### 4. Spectra measured after drying



**Figure S4** Spectra measured after the sample was dried in a stream of nitrogen (ODPA concentration 5 mM, formation time 17 h). The first spectrum was taken directly after drying; time between each spectrum is 10 min.

#### References

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