

## Supplemental Material

for

### Additive and antagonistic effects of substrate and vapors on self-assembly of glycyl-glycine in thin films

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#### Content

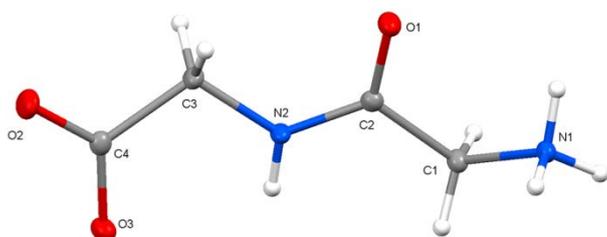
- Single Crystal X-ray Data on  $\alpha$ -phase GlyGly
- Calculated powder diffractograms
- Crystallographic planes of GlyGly crystal
- SEM images of the GlyGly film on silicon plate after saturation with vapors
- AFM images of the GlyGly film on the different substrates before and after saturation with vapors

#### Single Crystal X-ray Data on $\alpha$ -phase GlyGly

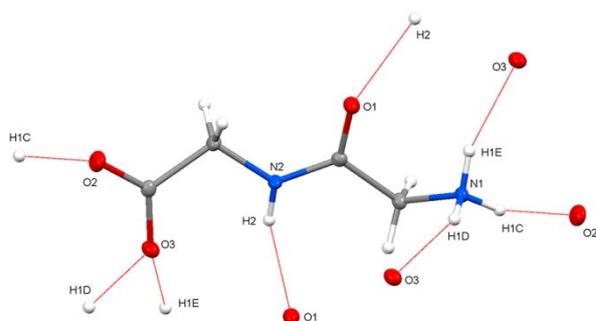
**Table S1.** Crystal data and results of the structure refinement for GlyGly.

Empirical Formula	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>
Mr (g·mol <sup>-1</sup> )	132.12
Crystal color	colorless
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	7.982(3)
<i>b</i> (Å)	9.520(2)
<i>c</i> (Å)	7.759(1)
$\alpha$ (°)	90
$\beta$ (°)	106.21(2)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	566.2(3)
Temperature (K)	100(2)
Crystal size (mm)	0.149×0.232×0.285

$Z$	4
$\rho_{\text{calc.}} (\text{g}\cdot\text{cm}^{-3})$	1.550
$F(000)$	280
$\mu (\text{cm}^{-1})$	1.147
$\theta_{\text{min}} / \theta_{\text{max}} (^{\circ})$	5.77 / 72.50
Reflections measured	8156
Independent refl.	1106 [ $R_{\text{int}} = 0.026$ ]
Number of parameters / restraints	107 / 0
Reflections [ $I > 2\sigma(I)$ ]	1092
$R / wR [> 2\sigma(I)]$	0.027 / 0.067
$R / wR$ (all reflections)	0.028 / 0.068
Goodness-of-fit on $F^2$	1.11
$\rho_{\text{max}} / \rho_{\text{min}} (\text{e}\cdot\text{\AA}^{-3})$	0.40 / -0.23

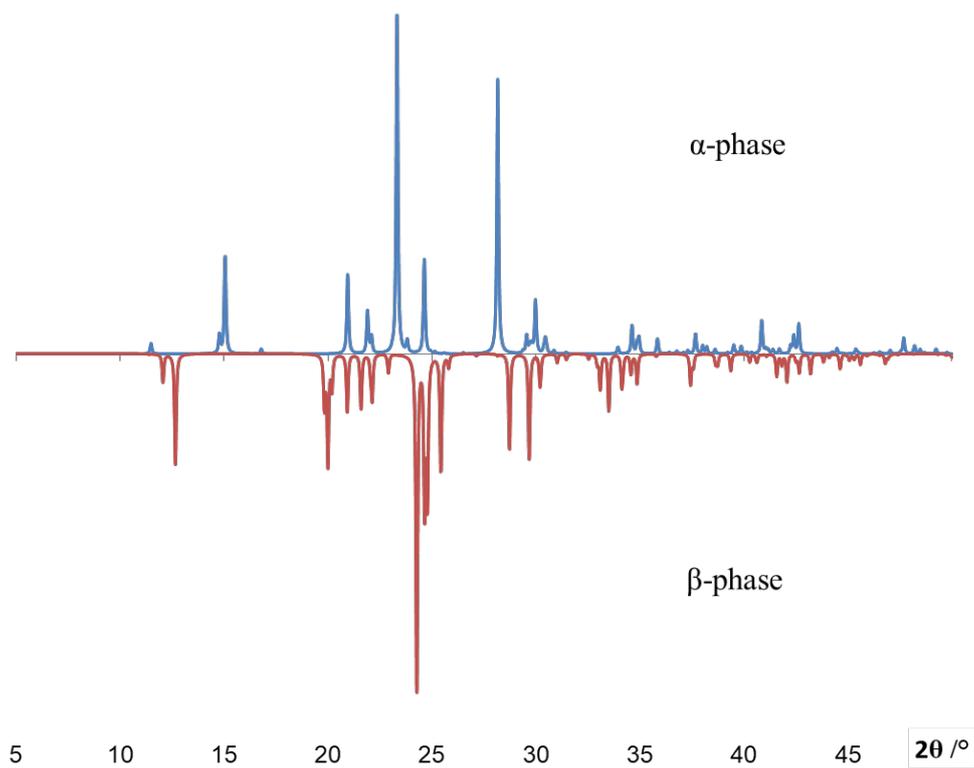


**Figure S1.** The ORTEP plots of GlyGly. Thermal ellipsoids are drawn at the 50% probability level.



**Figure S2.** H-bonding in crystal of GlyGly. Red lines denote the hydrogen bonds. Red and white balls are oxygen and hydrogen atoms of neighboring GlyGly molecules.

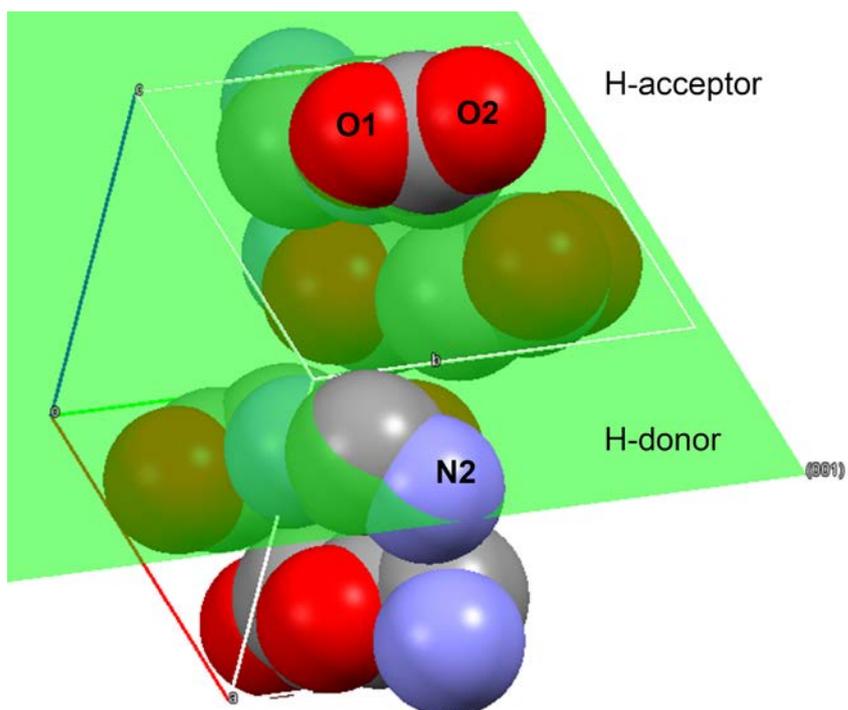
### Calculated powder diffractograms



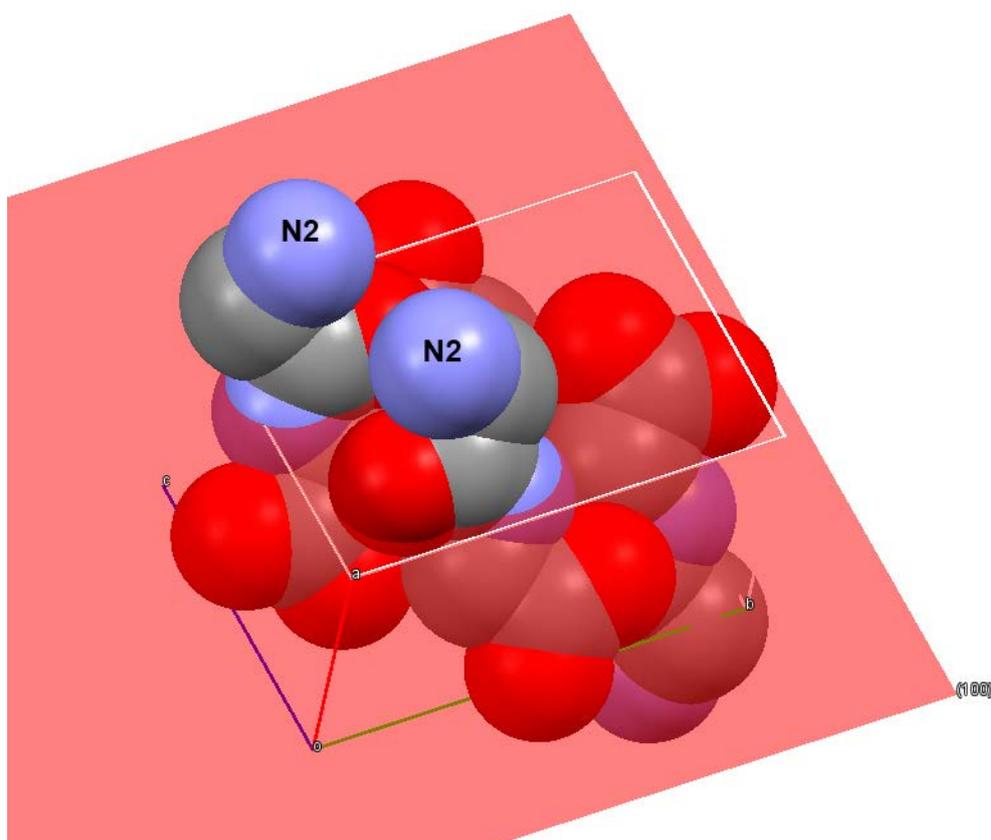
**Figure S3.** X-ray powder diffractograms for  $\alpha$ -phase [1] and  $\beta$ -phase [2] calculated from single crystal X-ray data.

1. J.A. Kwick, A.R. Al-Karaghoul, T.F. Koetzle // *Acta Cryst.*, B33, 3796-3801.
2. E. Hughes, W. J. Moor // *J. Am Chem Soc.*, 1949, 71, 2618–2623.

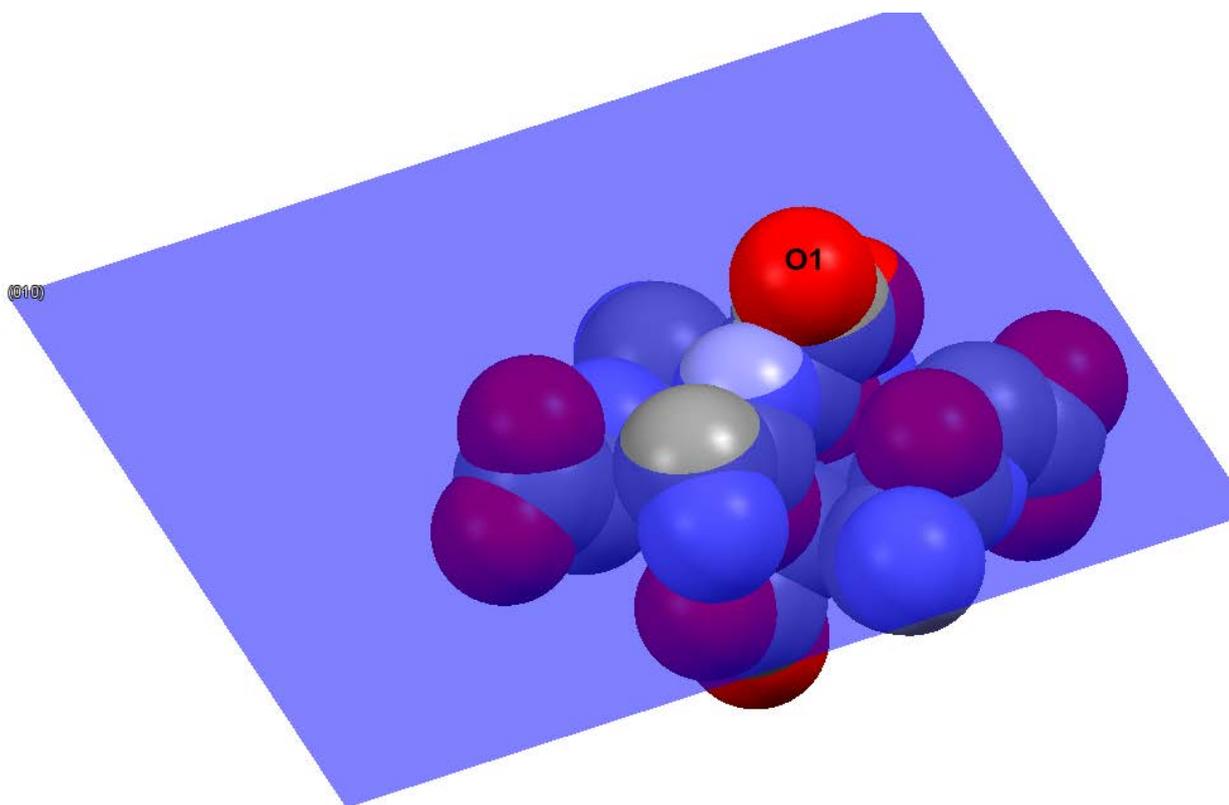
## Crystallographic planes of GlyGly crystal



**Figure S4.** Charged carboxylate ( $-\text{COO}^-$ ) and ammonium ( $-\text{NH}_3^+$ ) groups which are in the plane (001)

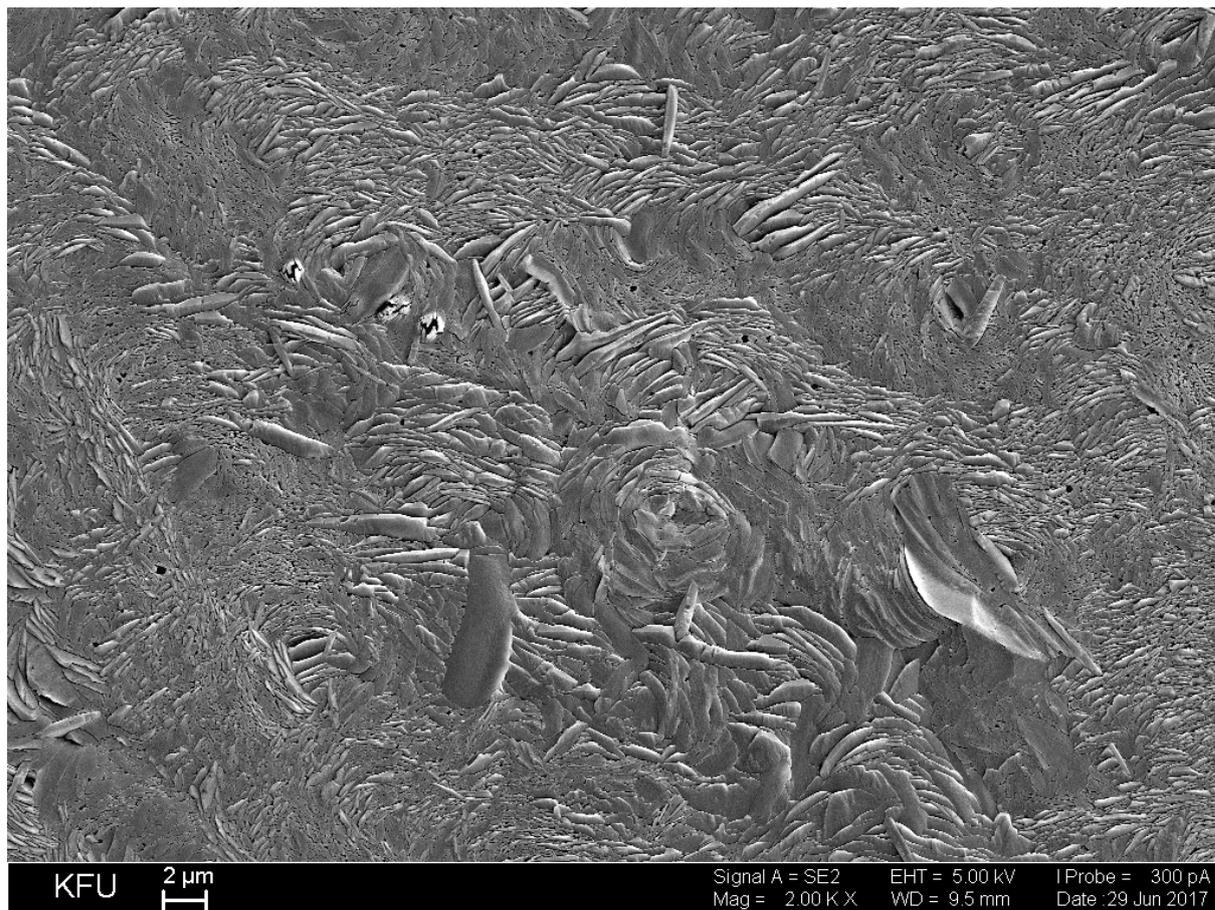


**Figure S5.** Positively charged ammonium ( $-\text{NH}_3^+$ ) groups which are in the plane (100).

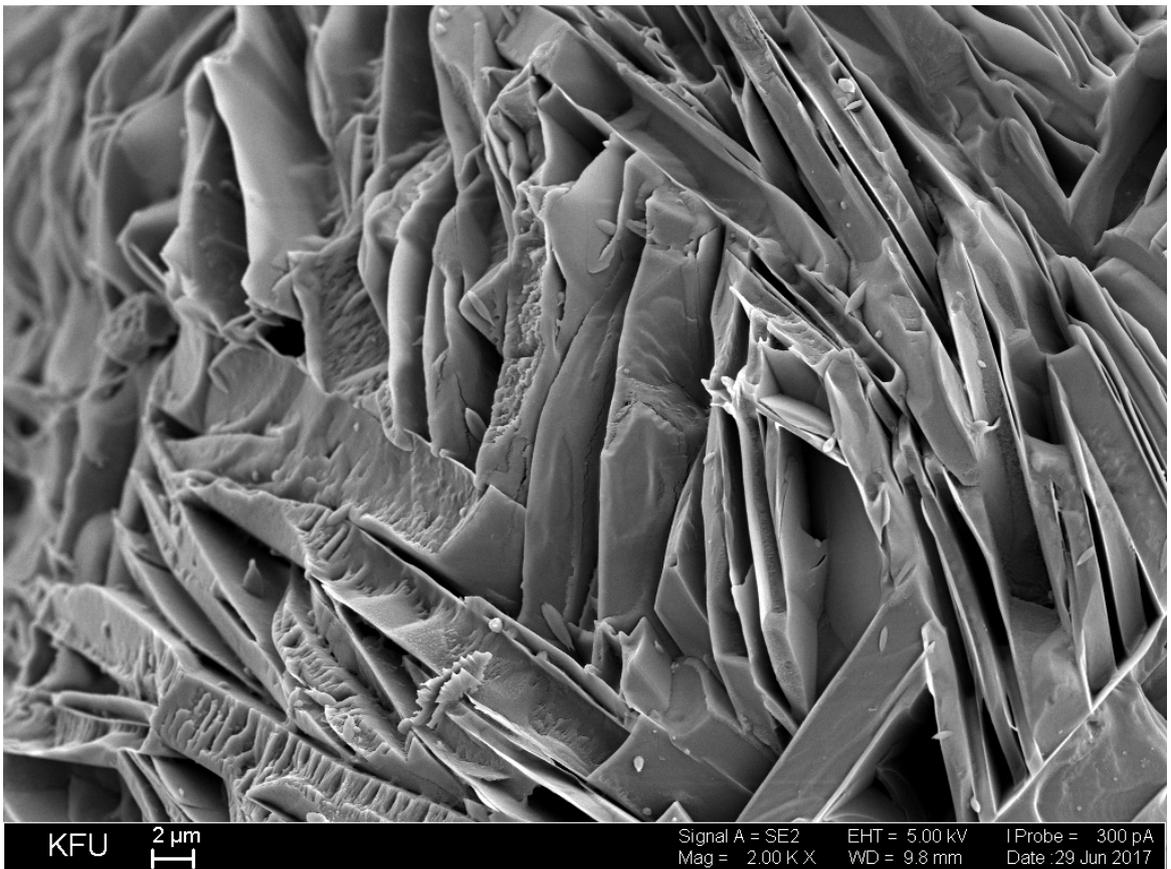
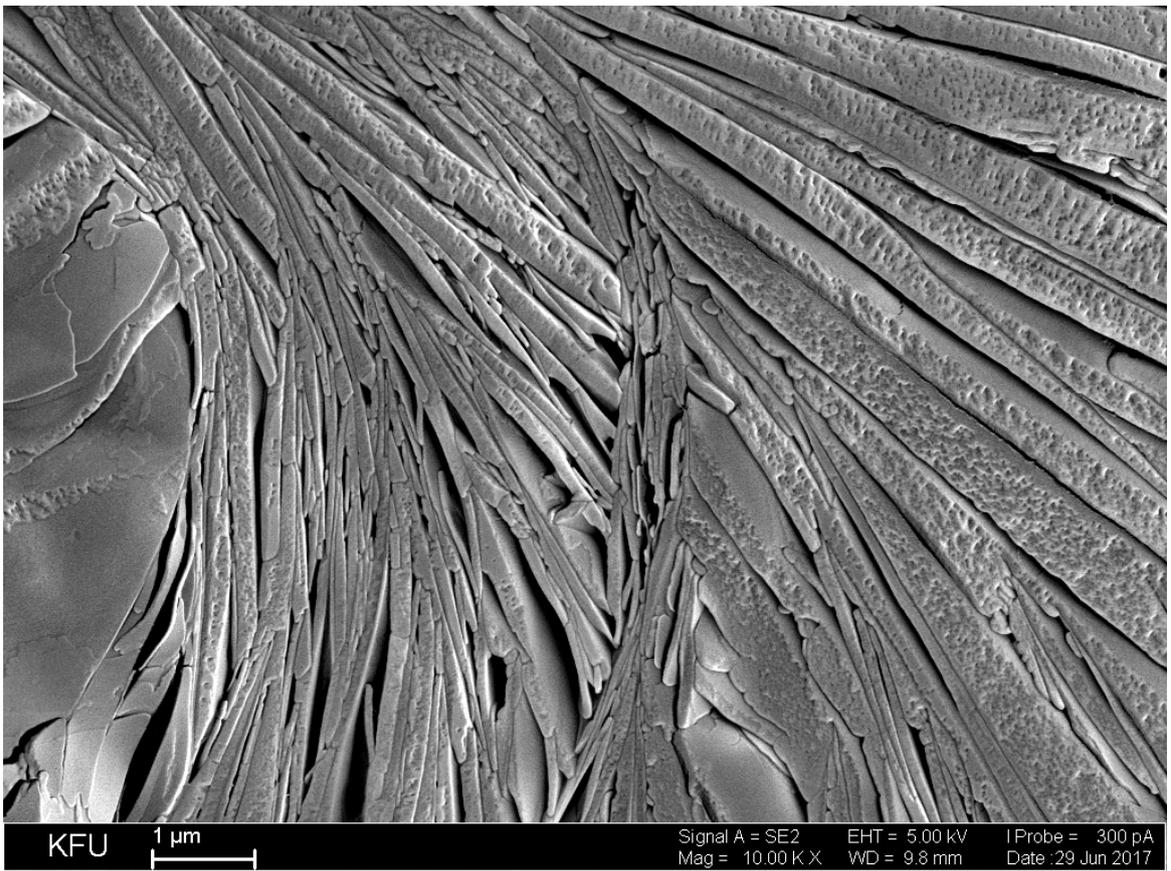


**Figure S6.** Negatively charged carboxylate (-COO<sup>-</sup>) group which is in the plane (010).

**SEM images of the GlyGly film on silicon plate after saturation with vapors**

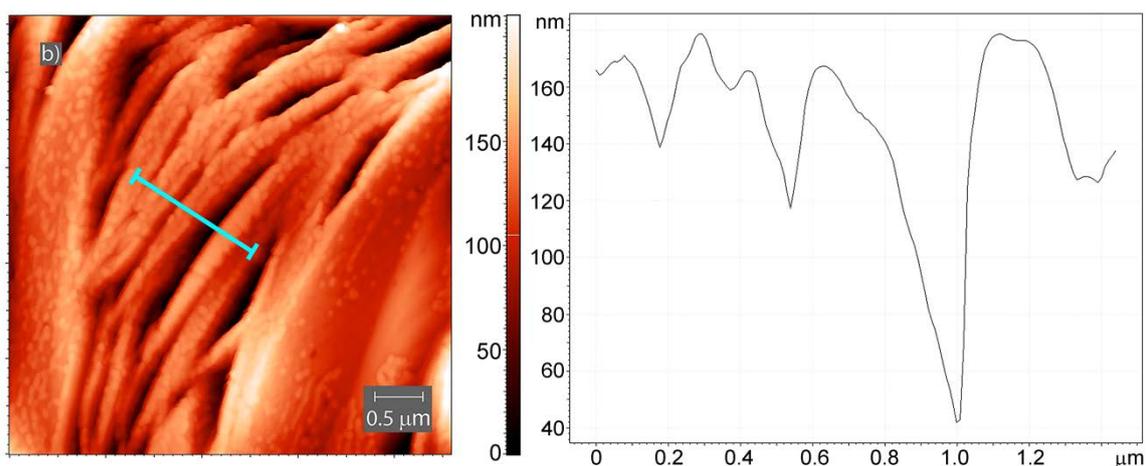


**Figure S7.** SEM images of the GlyGly film deposited on silicon after the saturation with mehtanol vapors.

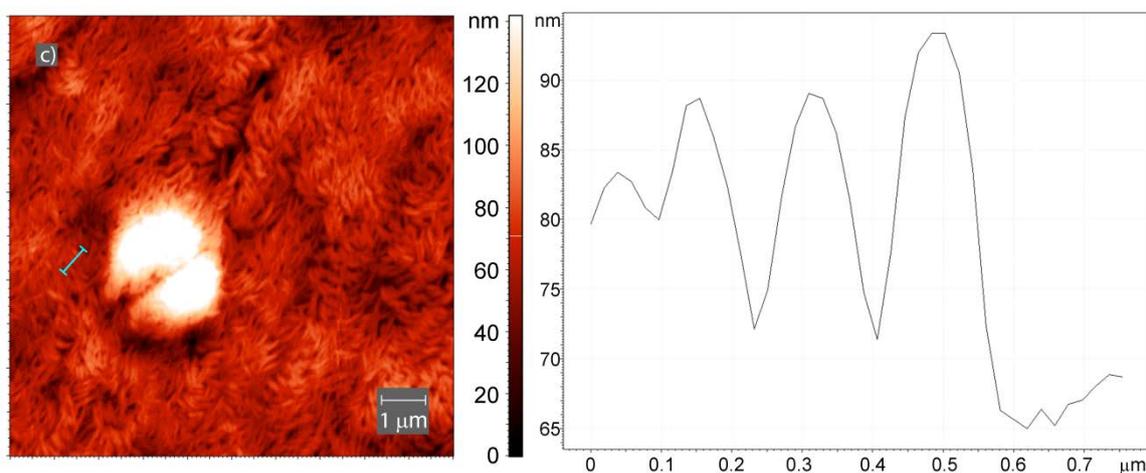


**Figure S8.** SEM images of the GlyGly film deposited on silicon after the saturation with ethanol vapors.

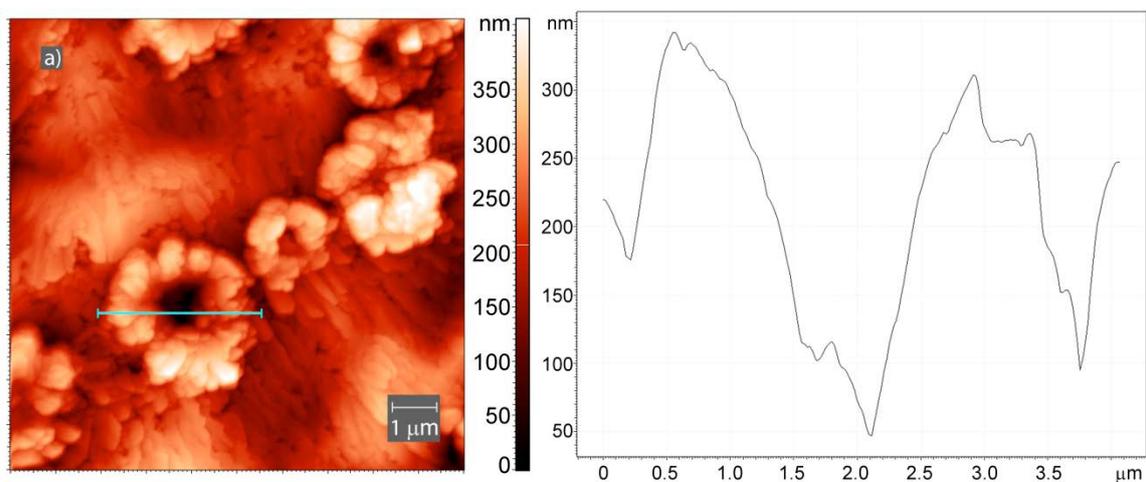
## AFM images of the GlyGly film on the different substrates before and after saturation with vapors



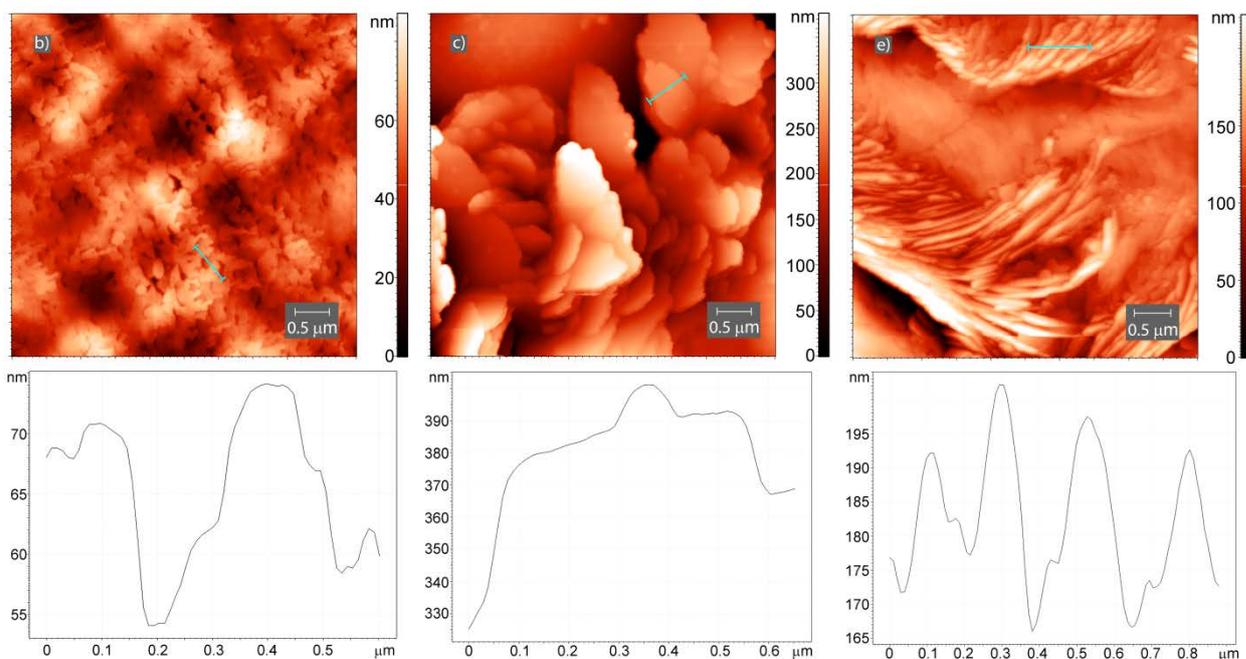
**Figure S9.** AFM image with cross section for Figure 2b (GlyGly film deposited on a silicon substrate from a MeOH/H<sub>2</sub>O solution (53 mg mL<sup>-1</sup>).



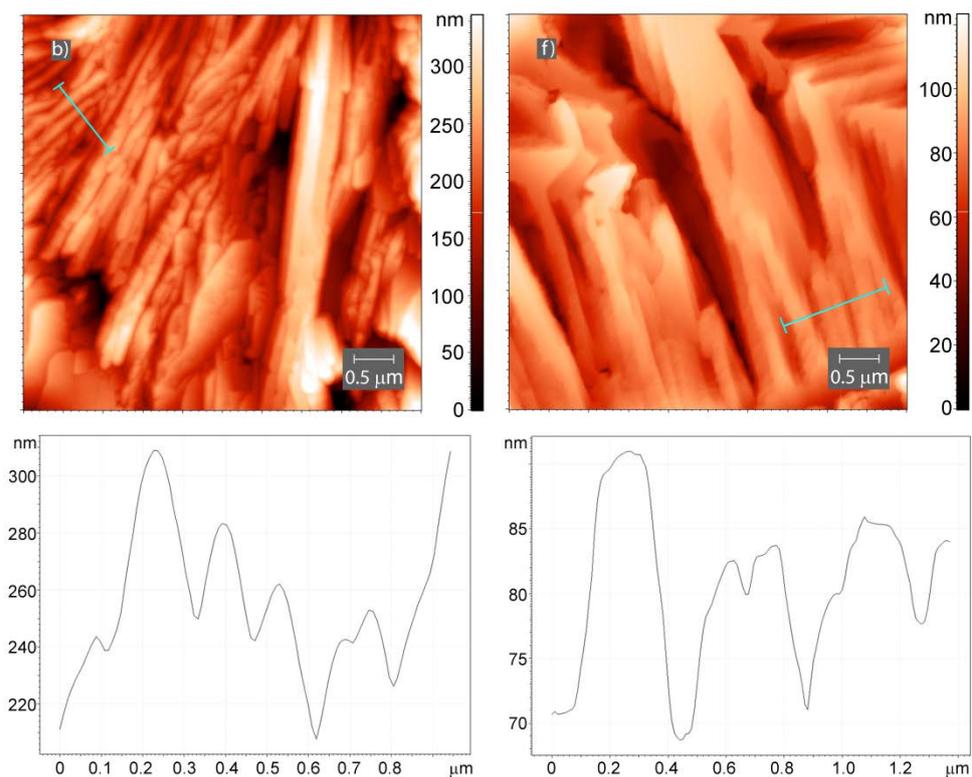
**Figure S10.** AFM image with cross section for Figure 3c (GlyGly films deposited on silicon from H<sub>2</sub>O/MeOH solution with concentration 1 mg mL<sup>-1</sup>).



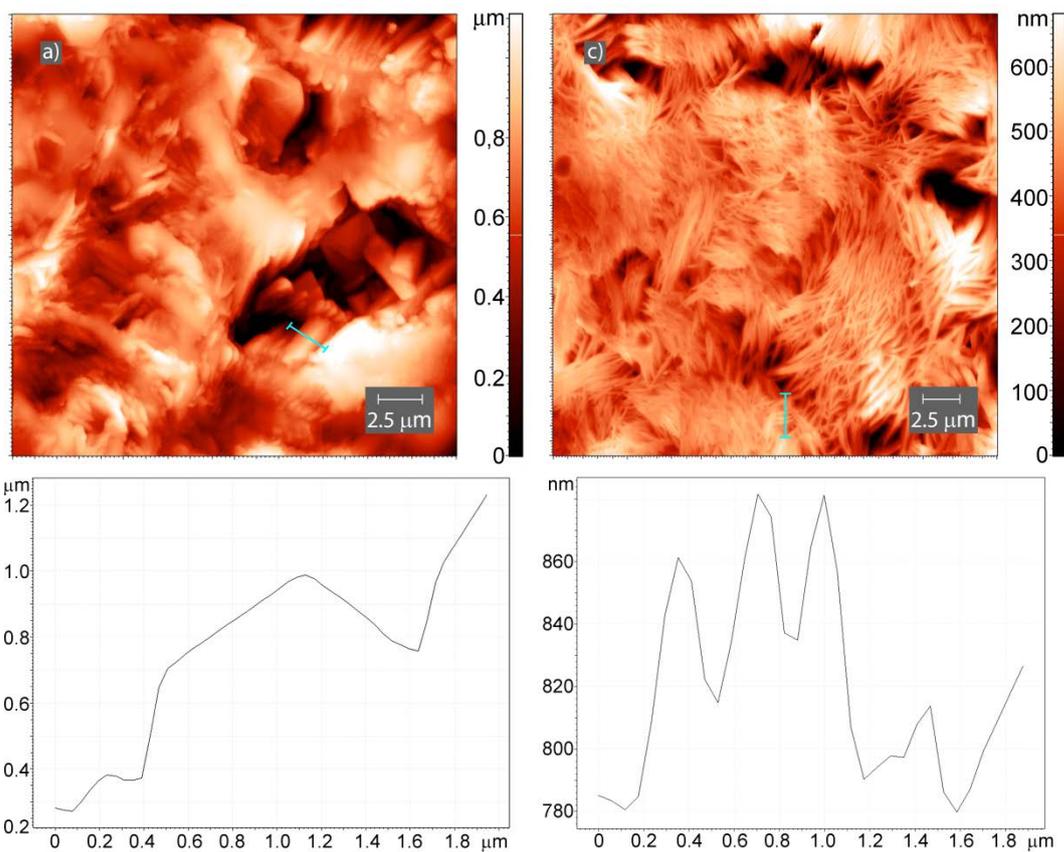
**Figure S11.** AFM image with cross section for Figure 6a (GlyGly film deposited on HOPG after the saturation with methanol vapors).



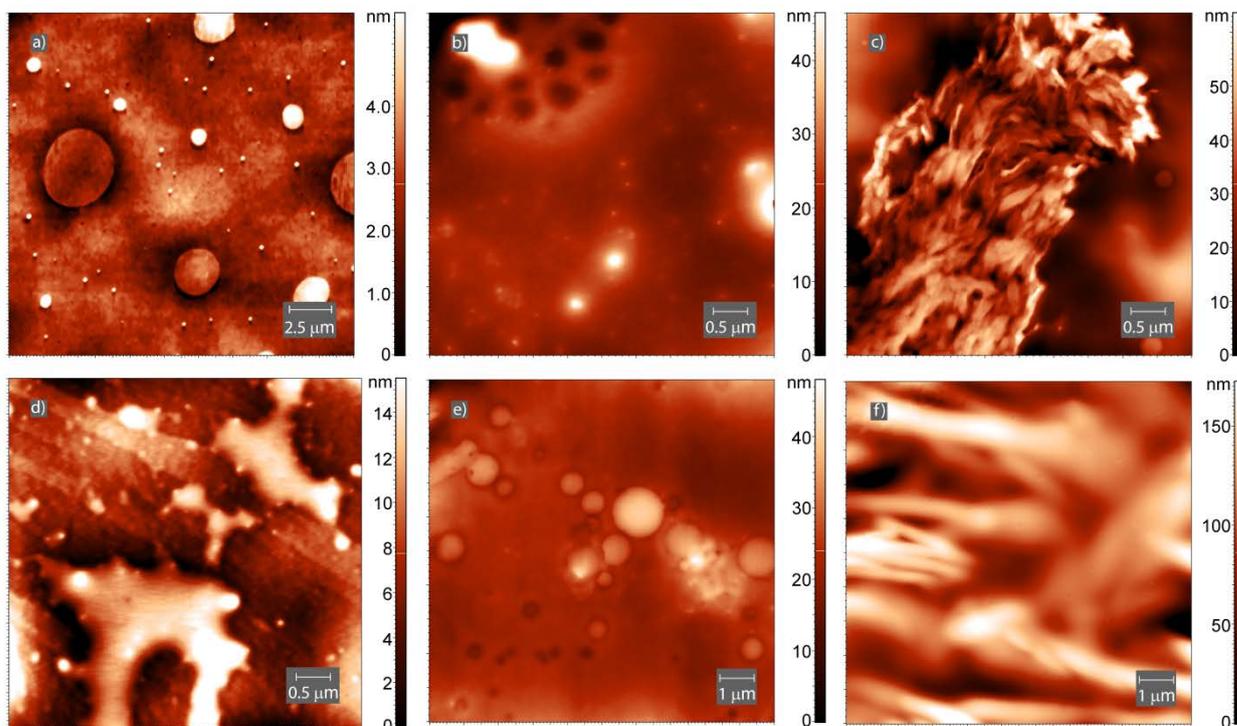
**Figure S12.** AFM images with cross section for Figures 8b (GlyGly film deposited on HOPG), 8c (GlyGly film deposited on mica), 8e (GlyGly film deposited on silicon) after the saturation with ethanol vapors.



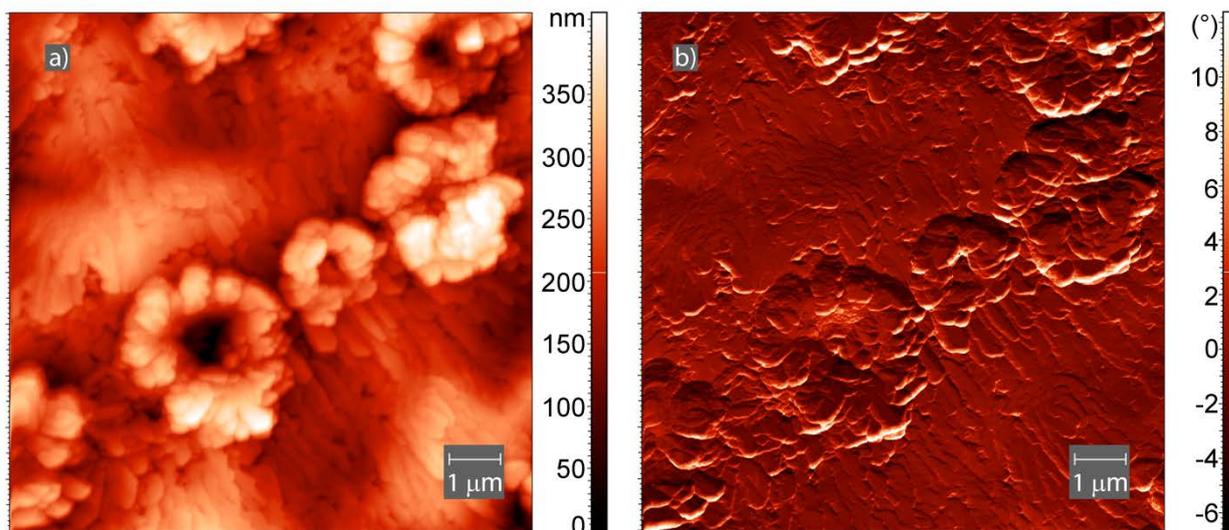
**Figure S13.** AFM images with cross section for Figures 10b (GlyGly film deposited on HOPG) and 10f (GlyGly film deposited on silicon) after the saturation with pyridine vapors.



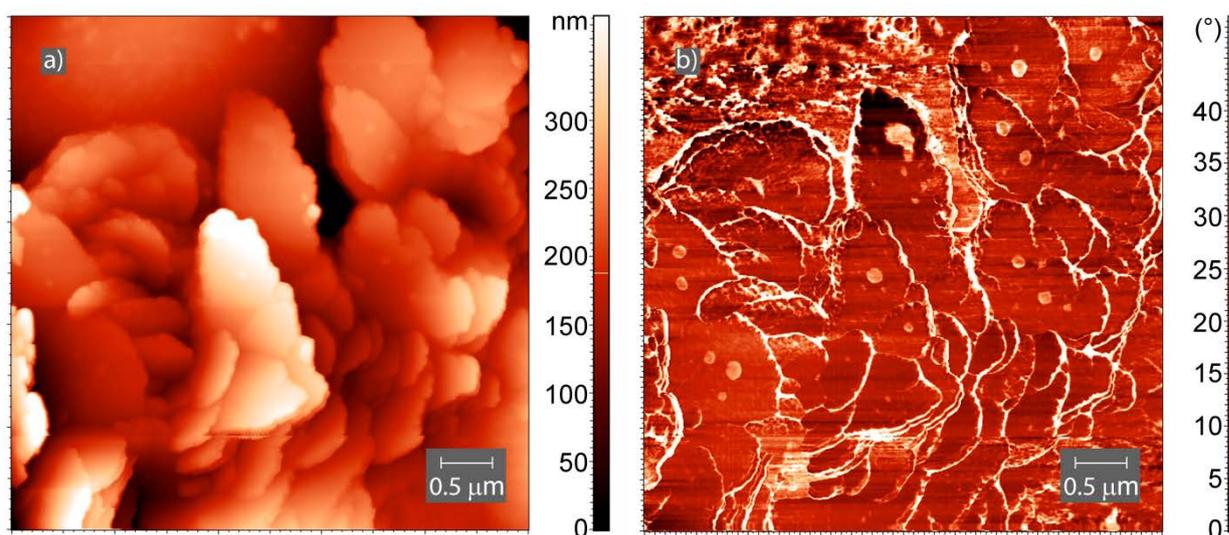
**Figure S14.** AFM images with cross section for Figures 11a (GlyGly film deposited on HOPG) and 11c (GlyGly film deposited on silicon) after the saturation with acetonitrile vapors.



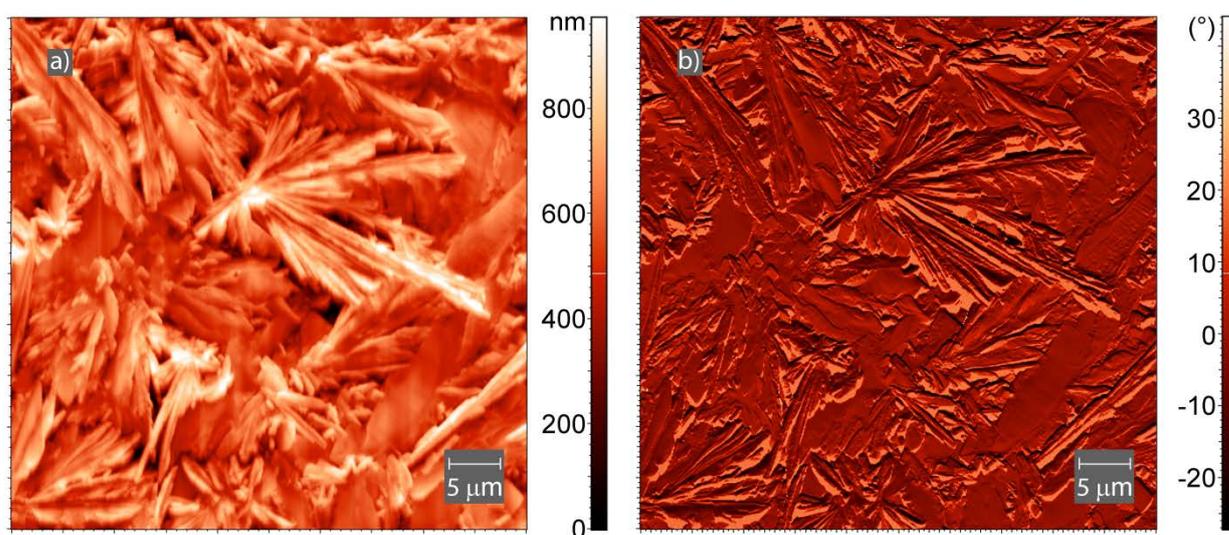
**Figure S15.** AFM images of the GlyGly film deposited on HOPG (a), mica (b) and silicon (c) after the saturation with chloroform (a, b, c) and dichloromethane (d, e, f) vapors.



**Figure S16.** AFM images for Figure 6a in the (a) topography and (b) phase contrast modes.



**Figure S17.** AFM images for Figure 8c in the (a) topography and (b) phase contrast modes.



**Figure S18.** AFM images for Figure 10a in the (a) topography and (b) phase contrast modes.