

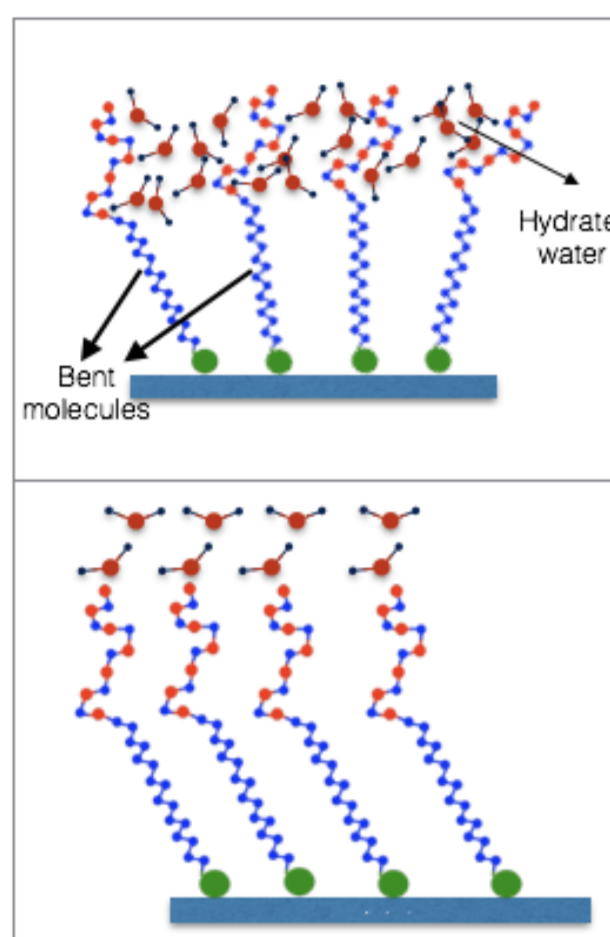
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## Motivation

To get a better understanding of the mechanism behind the inertness of oligo(ethylene glycol), with respect to biofouling and protein adsorption.

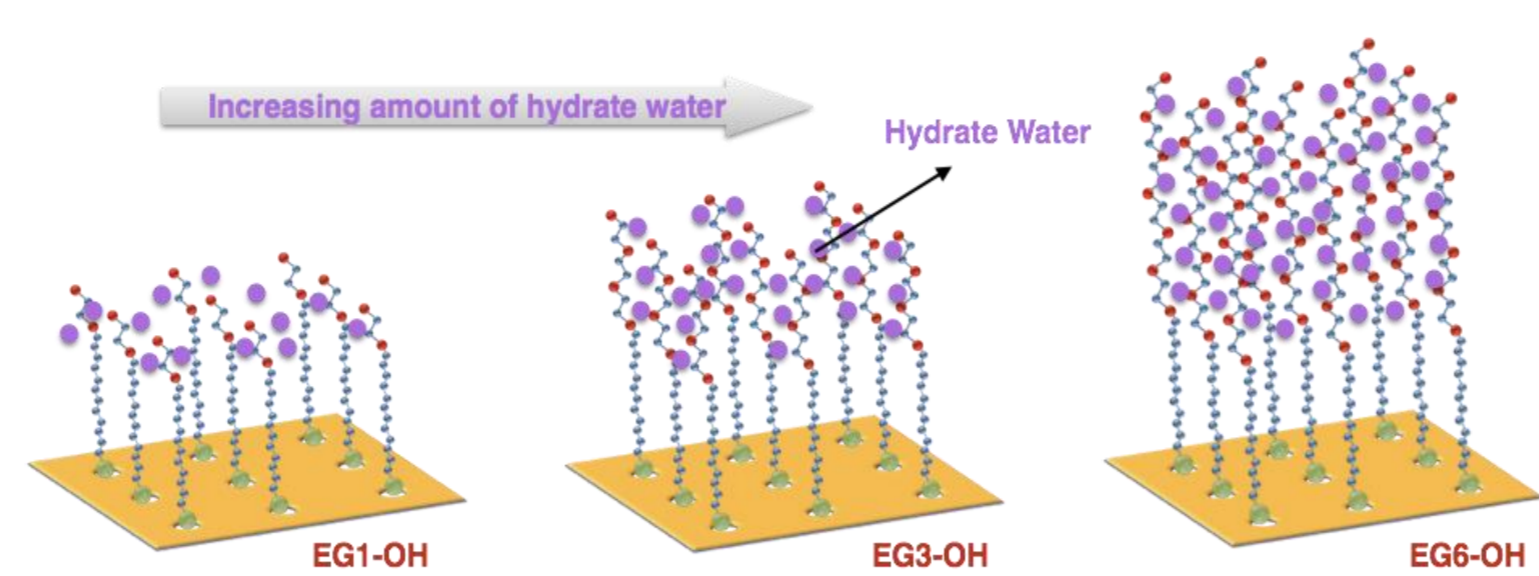


Most theories assume a key role of water adsorption properties related to protein repelling.

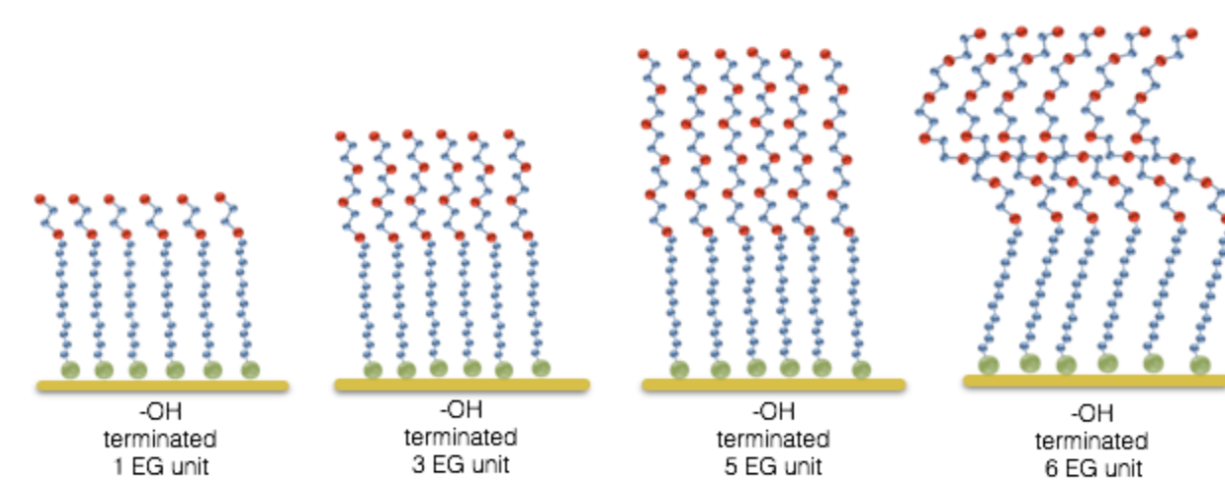
Focus on:

- Kinetics and thermodynamics of water adsorption and desorption.
- Monitoring the transfer from hydration to wetting regime.
- The bonding character of hydration phase.
- The structure and morphology of the interfacial phase.

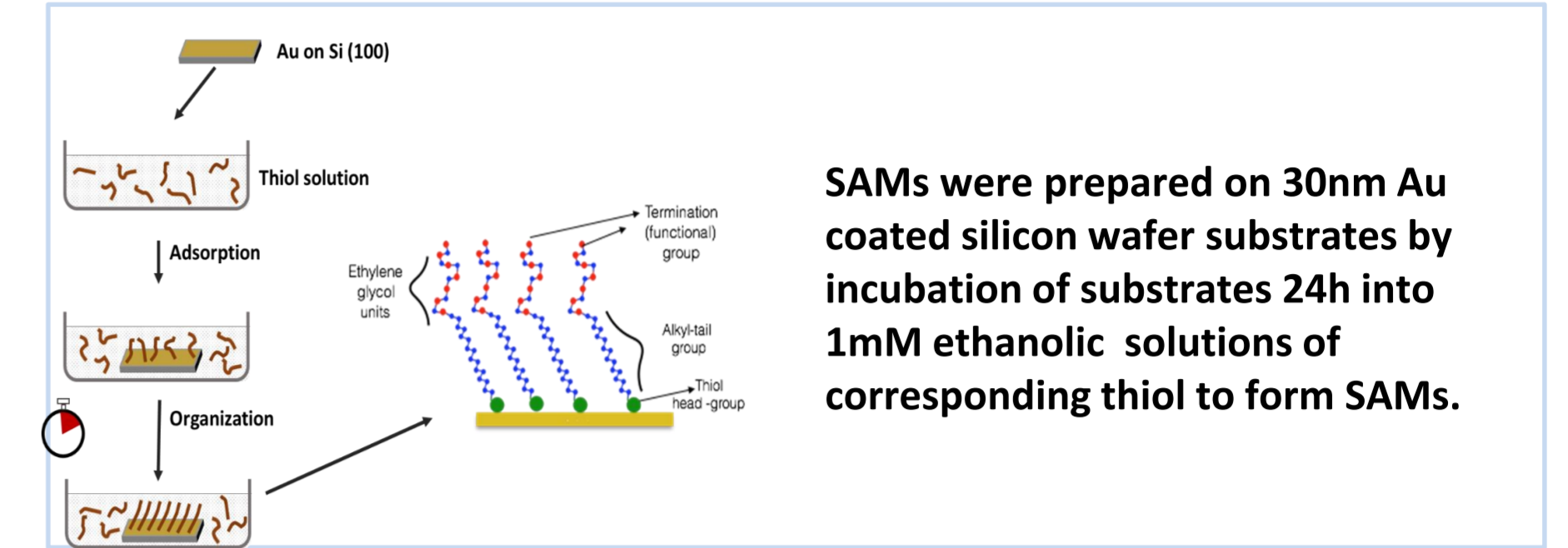
## Model system



The key factor for the bio-inertness is presumably the extent of hydration



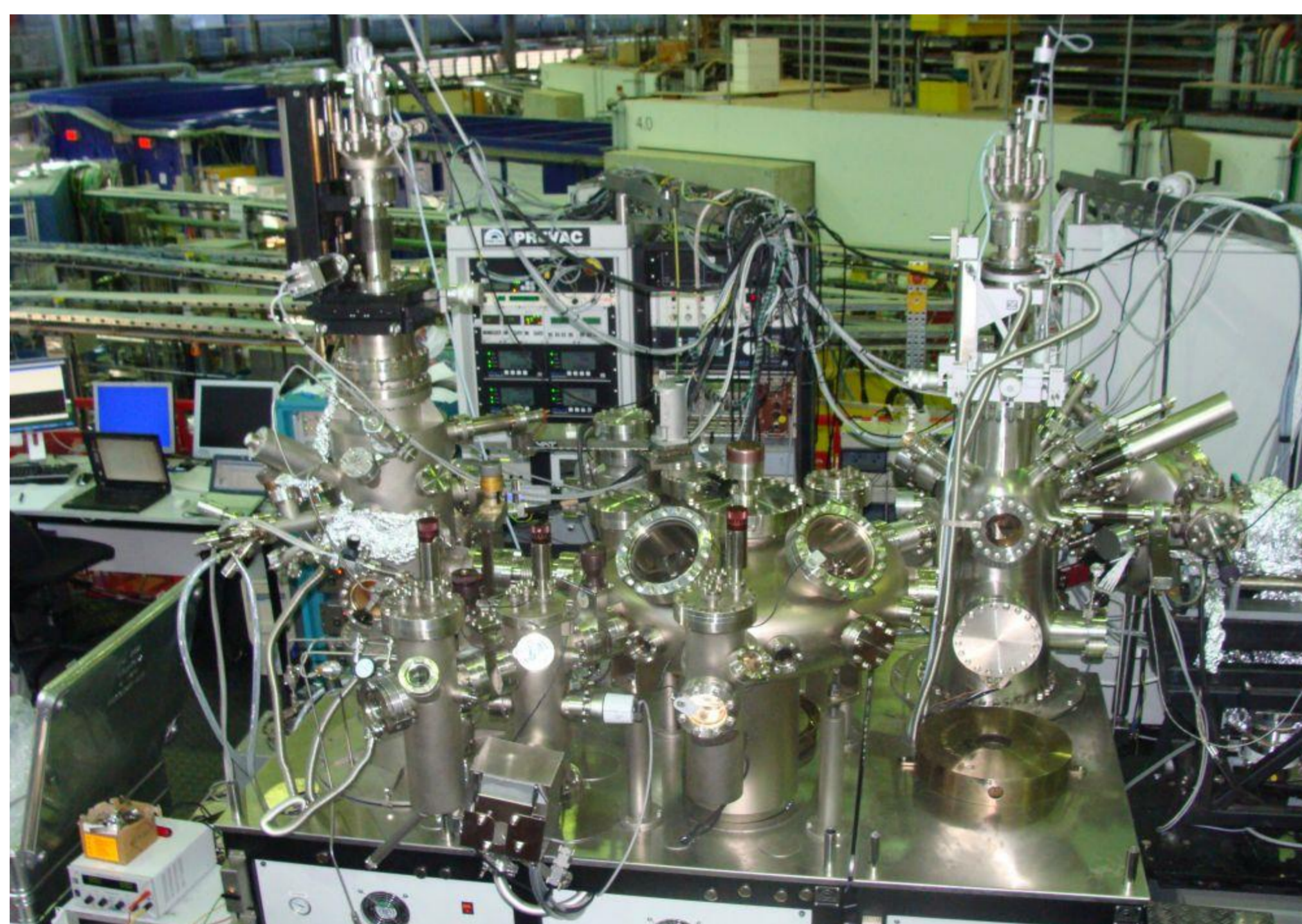
## OEG-SAM Preparation



SAMs were prepared on 30nm Au coated silicon wafer substrates by incubation of substrates 24h into 1mM ethanolic solutions of corresponding thiol to form SAMs.

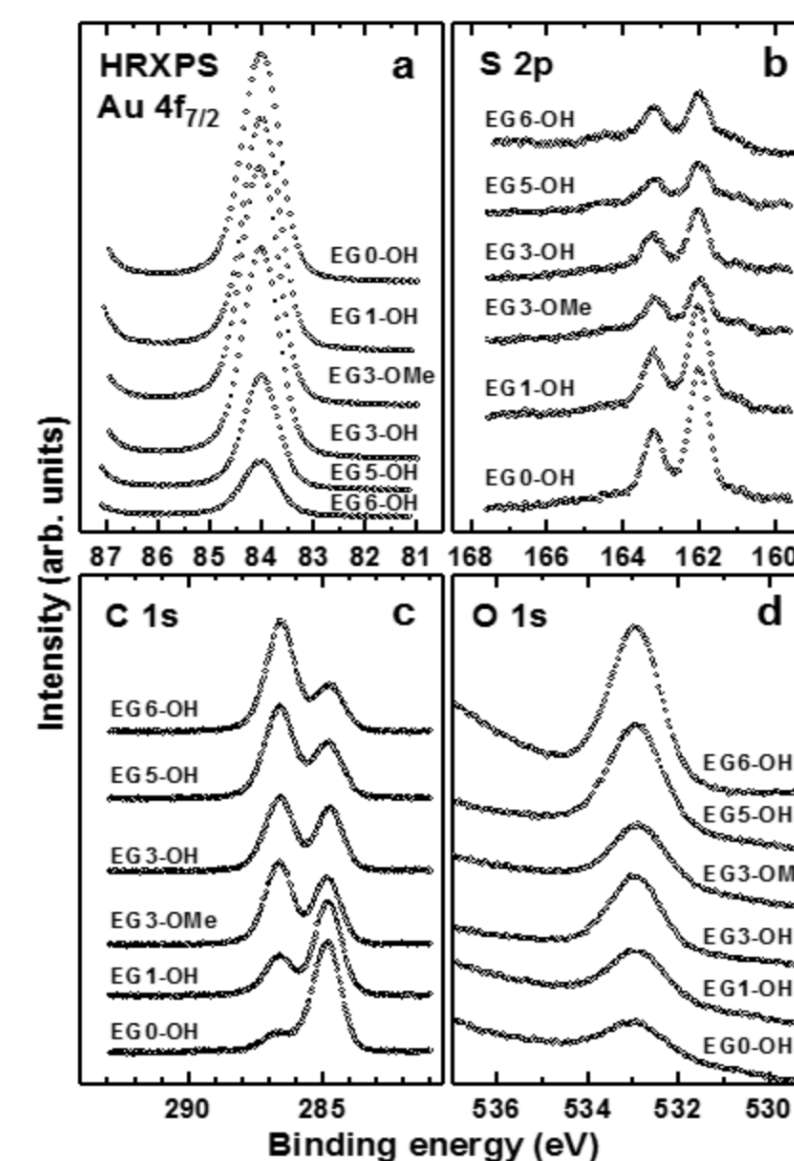
Monolayer	Packing density (molecules/cm <sup>2</sup> )	Thickness from XPS (Å)	Thickness from ellipsometry (Å)	Static water contact angle
EG0-OH	4.5·10 <sup>14</sup>	12±3	16±2	28±2°
EG1-OH	4.0·10 <sup>14</sup>	13±3	16.5±2	33±2°
EG3-OH	4.2·10 <sup>14</sup>	16±3	18±2	31±2°
EG3-OMe	4.3·10 <sup>14</sup>	16±3	18±2	61±2°
EG5-OH	4.0·10 <sup>14</sup>	21±3	23±2	34±2°
EG6-OH	4.2·10 <sup>14</sup>	24±3	25±2	33±2°

## XPS/NEXAFS Endstation at BESSY II



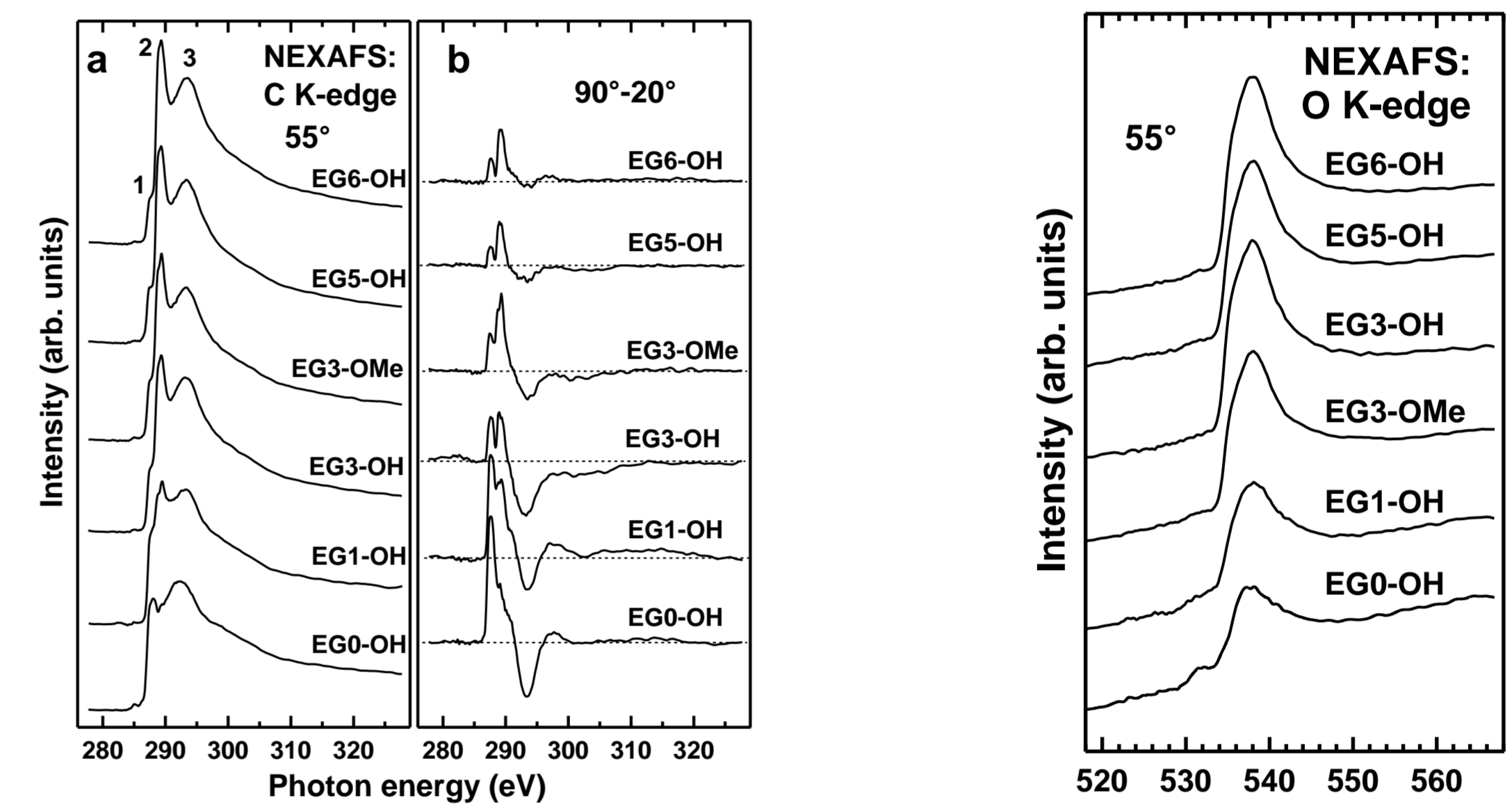
## Characterization of the pristine SAMs

### XPS



Au 4f<sub>7/2</sub> (a), S 2p (b), C 1s (c), and O 1s (d) XPS spectra of the EG<sub>n</sub>-OH (n=0,1,3,5,6) and EG3-OMe SAMs. The C 1s spectra are normalized to the maximum intensity. The Au 4f<sub>7/2</sub> and S 2p spectra were measured at a photon energy of 350 eV; the C 1s and O 1s spectra were measured at a photon energy of 580 eV.

### NEXAFS

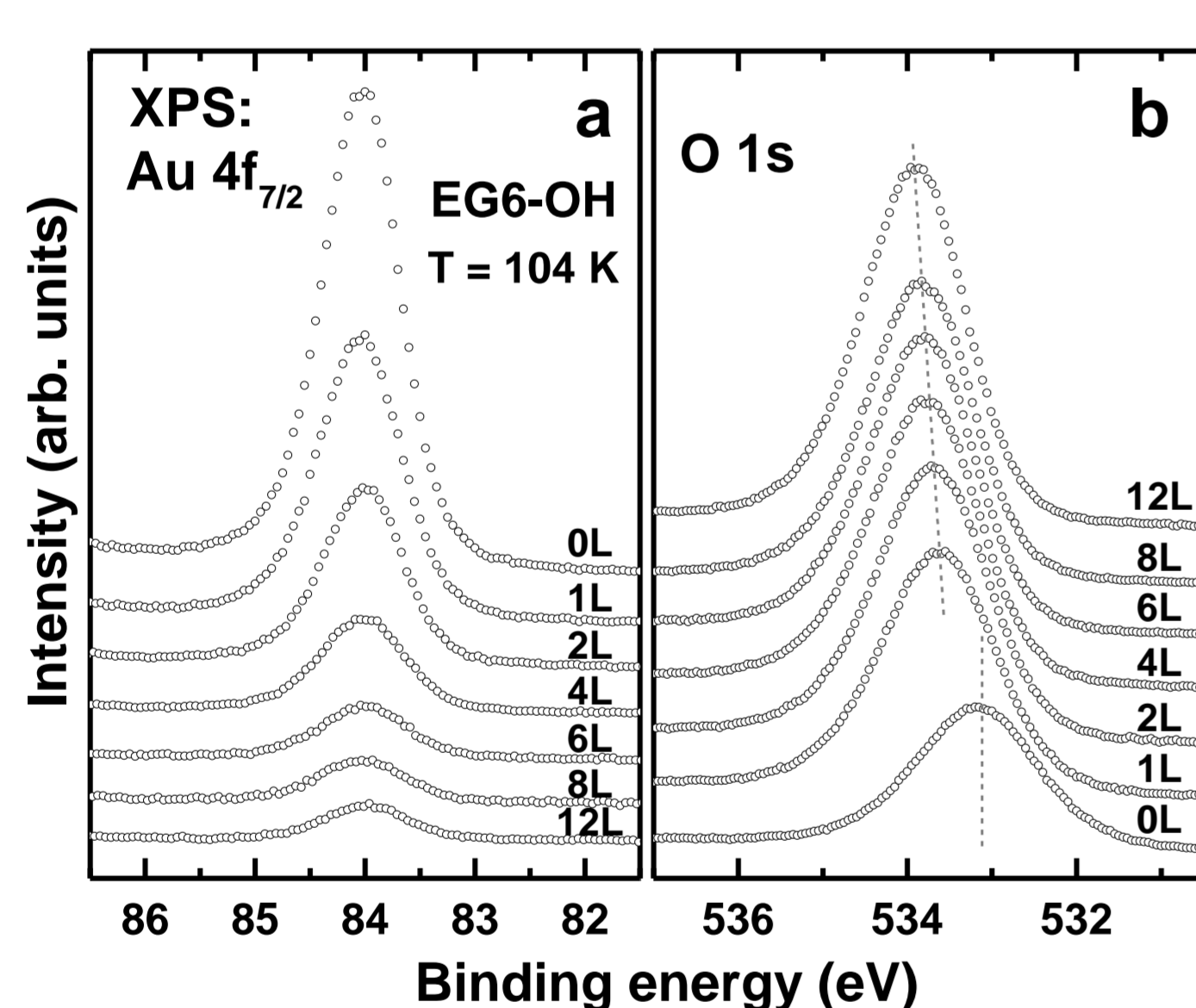


C K-edge NEXAFS data for the EG<sub>n</sub>-OH (n=0,1,3,5,6) and EG3-OMe SAMs, including the spectra acquired at an X-ray incidence angle of 55° (a) and the difference between the spectra measured at X-ray incidence angles of 90° and 20° (b).

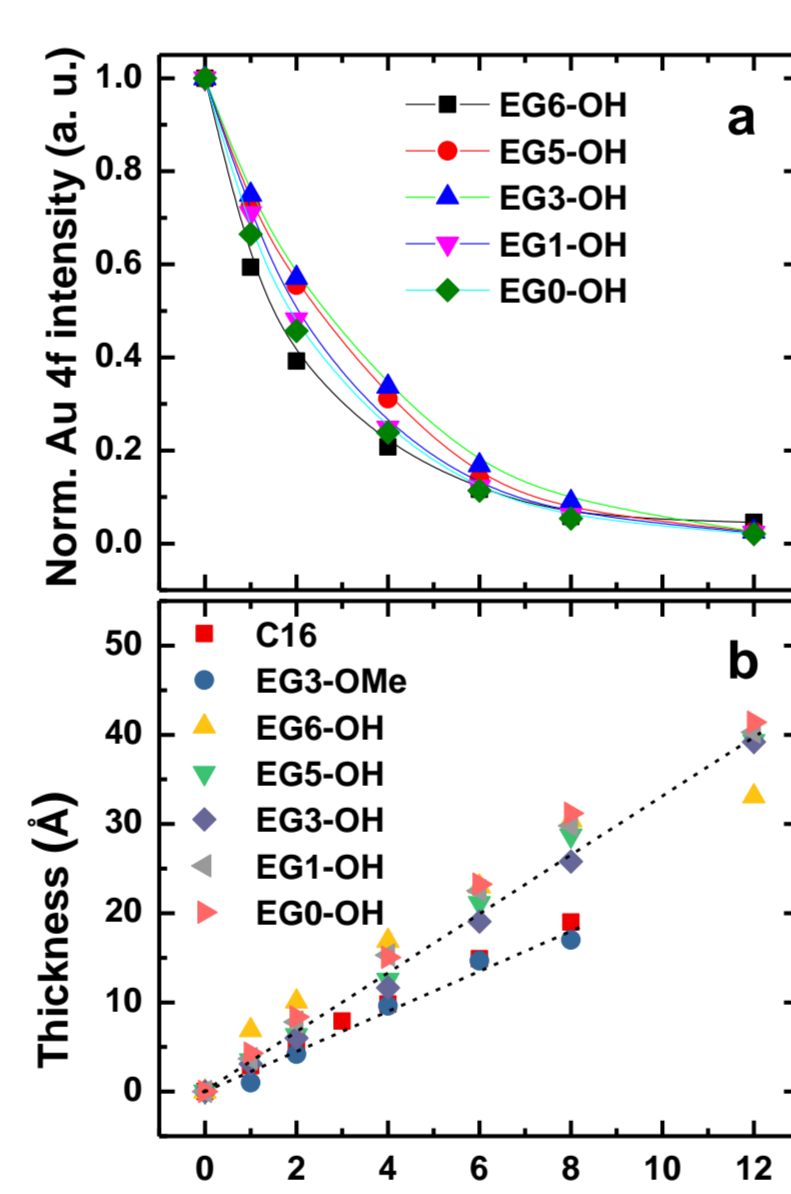
O K-edge NEXAFS spectra of the EG<sub>n</sub>-OH (n=0,1,3,5,6) and EG3-OMe SAMs acquired at an X-ray incidence angle of 55°.

## D<sub>2</sub>O adsorption

### XPS

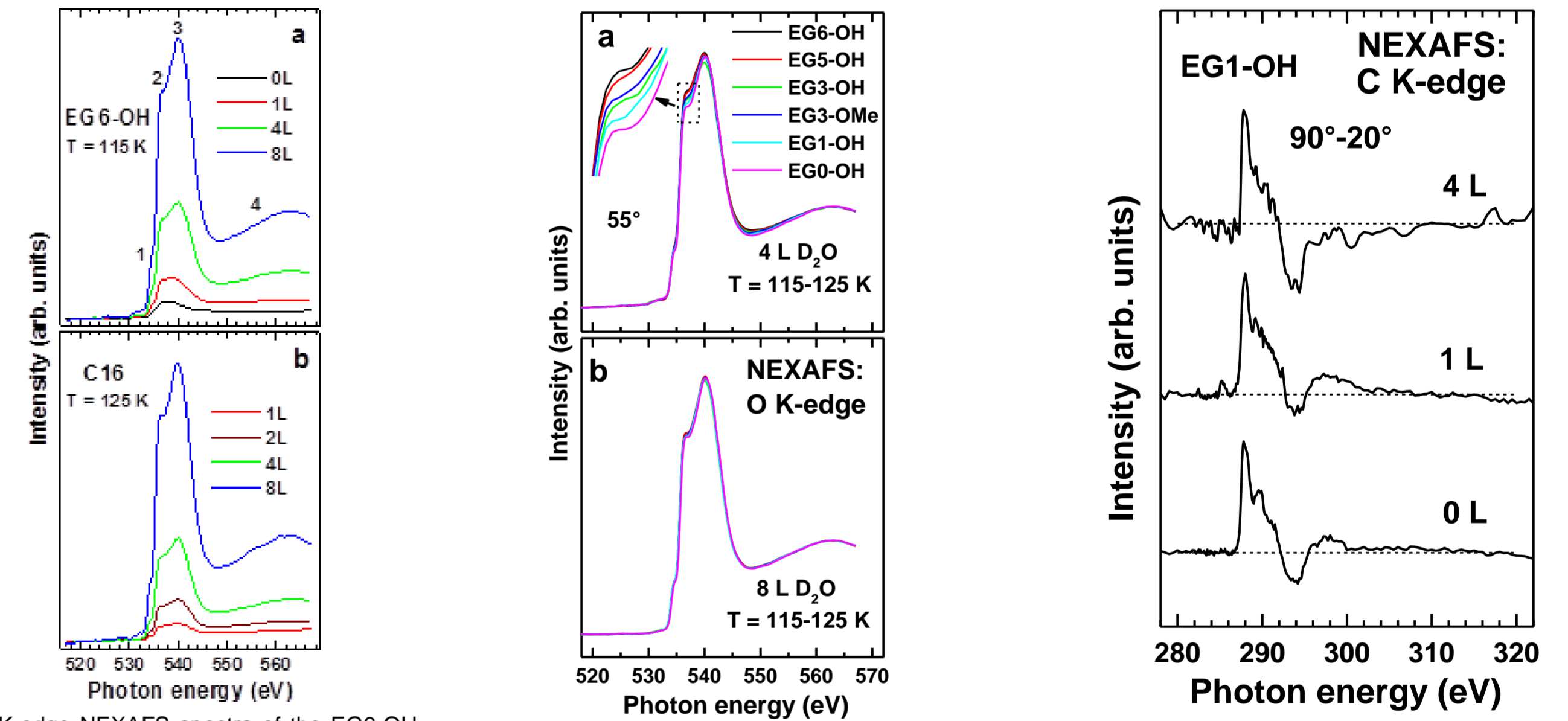


Evolution of the Au 4f<sub>7/2</sub> (a) and O 1s (b) XPS spectra of the EG6-OH SAM in the course of the D<sub>2</sub>O adsorption. The spectra were measured at a photon energy of 580 eV. The doses are marked at the respective spectra. The dashed straight lines are guides to the eyes.



(a) Normalized intensity of the Au 4f<sub>7/2</sub> signal in the course of the D<sub>2</sub>O adsorption onto the EG<sub>n</sub>-OH SAMs (n=0,1,3,5,6); (b) the derived thicknesses of the D<sub>2</sub>O films as functions of the D<sub>2</sub>O dose, including the values for the C16 and EG3-OMe SAMs.

### NEXAFS



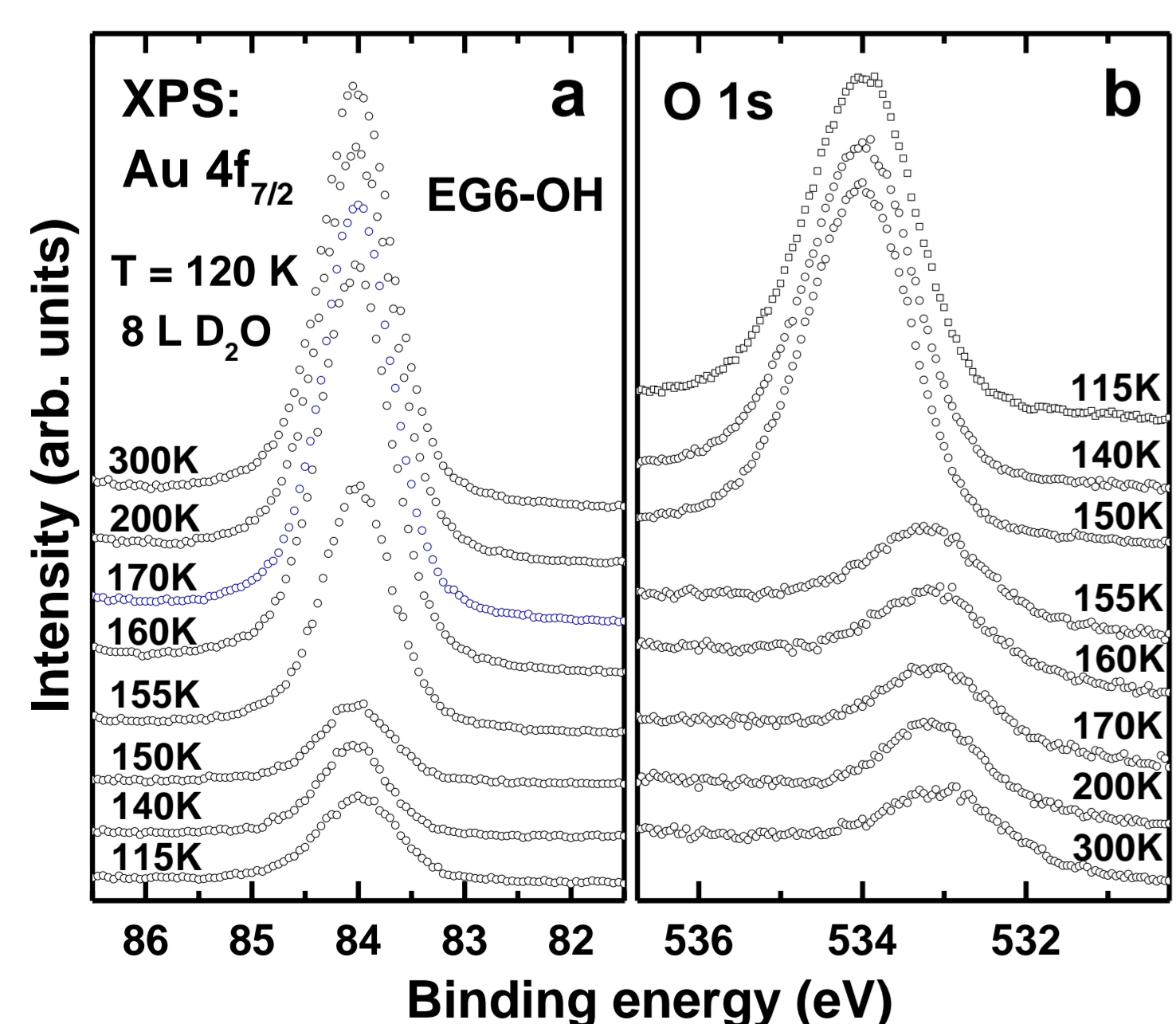
The O K-edge NEXAFS spectra of the EG6-OH (a) and C16 (b) SAMs. The spectra were measured at an X-ray incidence angle of 55°, they are normalized to the pre-edge intensity to reflect an increase of the signal from the growing ice film.

O K-edge NEXAFS spectra of the ice (D<sub>2</sub>O) films deposited onto the EG<sub>n</sub>-OH (n=0,1,3,5,6) and EG3-OMe SAMs with a dose of 4 L (a) and 8 L (b). The spectra were measured at an X-ray incidence angle of 55°. Panel (a) also contains a magnified part of these spectra emphasizing difference between the different SAMs.

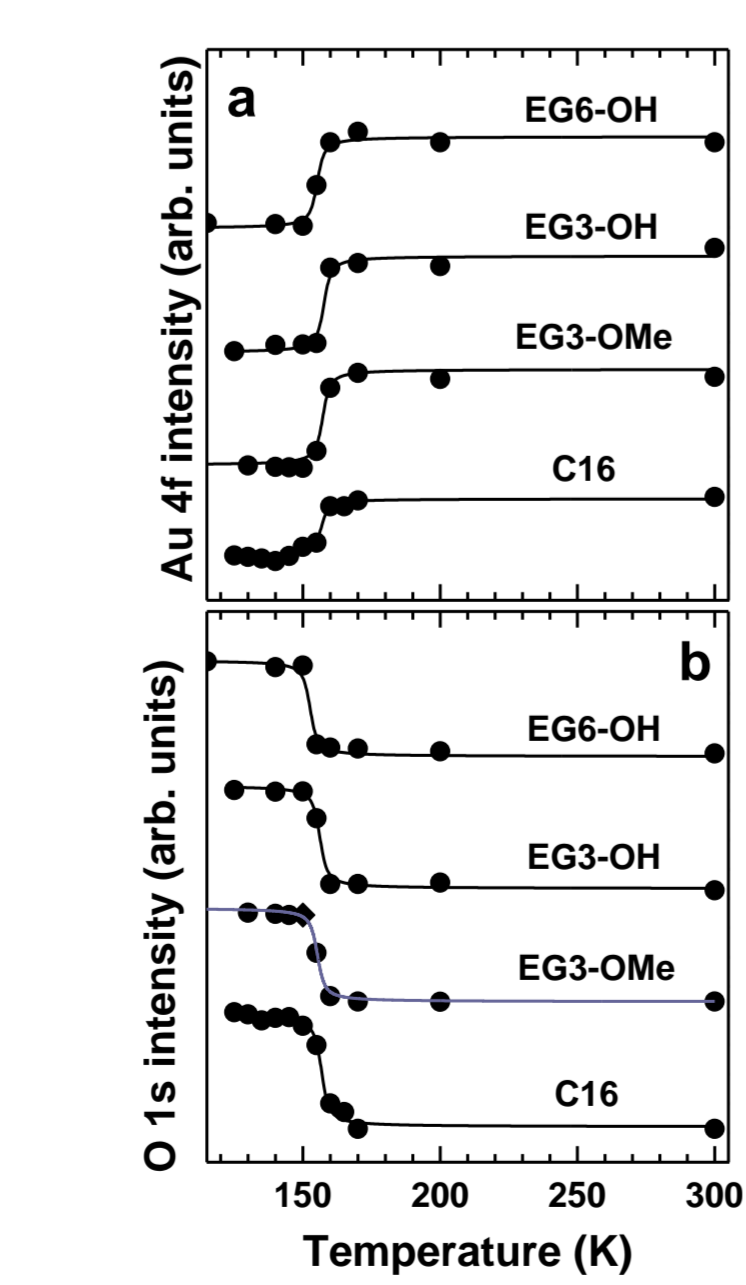
C K-edge NEXAFS difference (90°-20°) spectra of the EG1-OH SAM in the pristine state and after D<sub>2</sub>O exposure with doses of 1 and 4 L. The doses are given at the respective spectra. Horizontal dashed lines correspond to zero.

## D<sub>2</sub>O Thermodesorption

### XPS

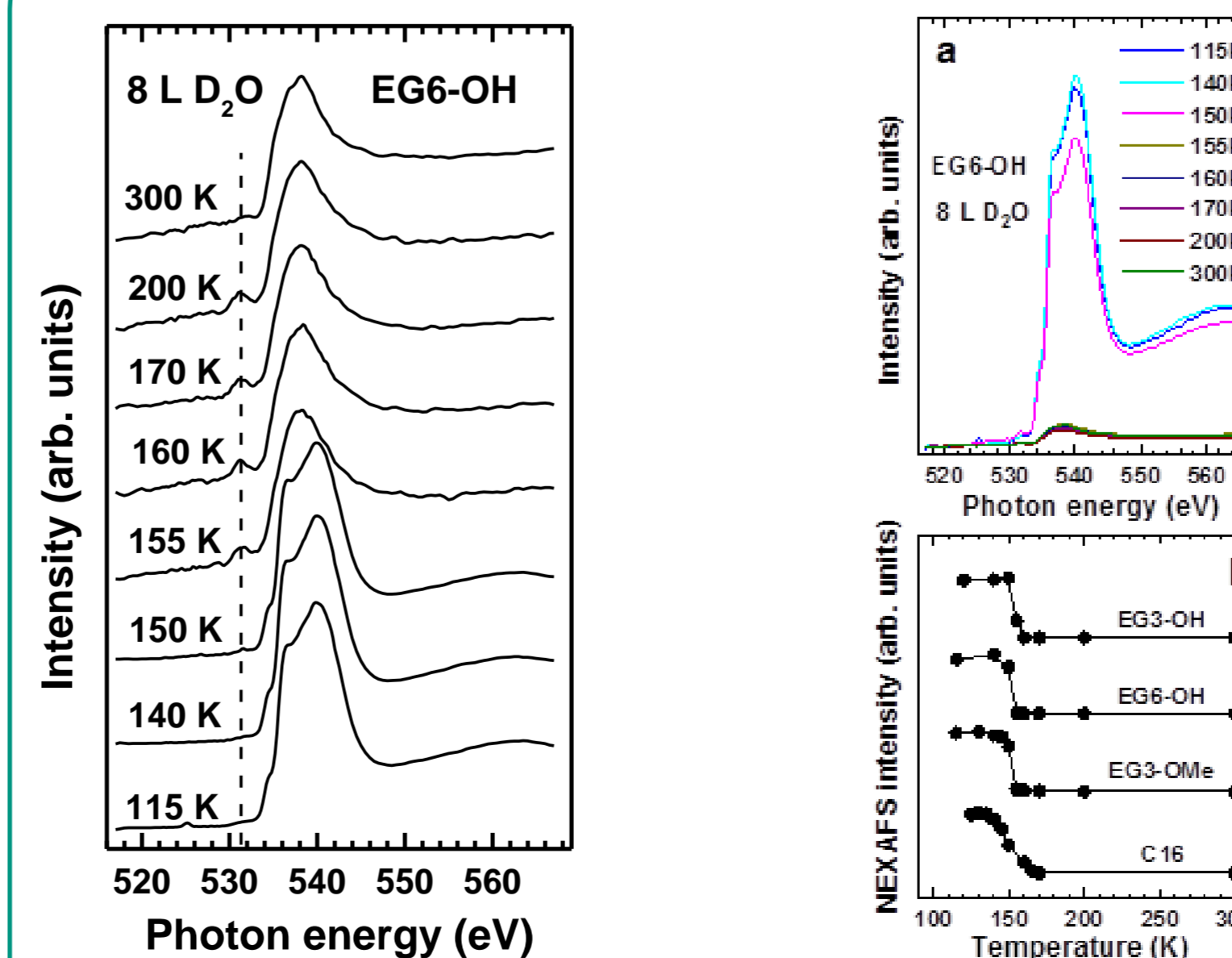


Evolution of the Au 4f<sub>7/2</sub> (a) and O 1s (b) XPS spectra of the EG6-OH SAM exposed to D<sub>2</sub>O (8 L) at 120 K in the course of the temperature-driven desorption of D<sub>2</sub>O. The temperature is marked at the respective spectra.



The Au 4f<sub>7/2</sub> (a) and O 1s (b) intensity for the EG3-OH, EG6-OH, EG3-OMe, and C16 SAMs exposed to D<sub>2</sub>O (8 L) at 115-125 K in the course of the temperature-driven D<sub>2</sub>O desorption.

### NEXAFS



Evolution of the "magic angle" O K-edge NEXAFS spectra of the EG6-OH SAMs exposed to D<sub>2</sub>O (8 L) at 115 K in the course of the temperature-driven D<sub>2</sub>O desorption. The spectra were normalized in the standard fashion.

(a) Evolution of the "magic angle" O K-edge NEXAFS spectra of the EG6-OH SAMs exposed to D<sub>2</sub>O (8 L) at 115 K in the course of the temperature-driven D<sub>2</sub>O desorption. The spectra were normalized to the pre-edge intensity. (b) Evolution of the normalized intensity of the "magic angle" O K-edge NEXAFS spectra of the SAMs exposed to D<sub>2</sub>O (8 L) at 110-125 K. The intensity was measured at the position of the post-edge resonance (3; see above).

## Conclusions

- The D<sub>2</sub>O adsorption was found to occur exclusively onto the SAM surface, without any indication for the penetration of the D<sub>2</sub>O molecules into the hydrogel-like OEG part of the monolayers.
- The thickness of the ice films increased linearly with the D<sub>2</sub>O dose with the same rate for all OH-terminated SAMs and a somewhat lower rate for the CH<sub>3</sub>-terminated monolayers, associated with a lower sticking ability of the latter surfaces and formation of 3D clusters, in contrast to 2D ones in the -OH case.
- The structure of the D<sub>2</sub>O ice films was found to be amorphous-like for all SAM-substrates studied, with only small differences (degree of crystallinity) for the different lengths of the OEG segment.
- At the same time, the first layer of D<sub>2</sub>O on the OH-terminated SAMs exhibited characteristic signatures of strongly distorted and broken hydrogen bonds, associated with the formation of 2D clusters and involvement of most molecules into the bonding to the substrate.
- The temperature-driven desorption experiments showed an abrupt change in the intensity and character of the XPS and NEXAFS spectra at 150-155 K, corresponding to an extensive and subsequently complete desorption of D<sub>2</sub>O.
- No indication of the structural transition (from amorphous-like to crystalline-like) was observed for the OH-terminated SAMs, but the possibility of such a transition, close to or at the desorption temperature, cannot be completely excluded.
- For the CH<sub>3</sub>-terminated SAMs, characteristic signatures of the structural transition were recorded. Specific features observed in the NEXAFS spectra could be interpreted as stemming from temperature-driven diffusion of the adsorbed D<sub>2</sub>O molecules into the hydrogel-like OEG part of the OEG-substituted SAMs, which is associated with a building of a hydration phase, characterized by a higher binding energy than that in the original ice film.