

## **Combinatorial Near-Edge X-ray Absorption Fine Structure: Simultaneous Determination of Molecular Orientation and Bond Concentration on Chemically Heterogeneous Surfaces**

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**Introduction:** We show that information about the chemistry (including bond concentration) and molecular orientation on chemically heterogeneous surfaces can be collected by simultaneously utilizing near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and rastering the X-ray beam on the probed specimen. This rastering produces serially two-dimensional NEXAFS images in space and energy with sub-millimeter planar spatial resolution and sub-monolayer molecular sensitivity. We call this technique combinatorial NEXAFS.

**Methods and Materials:** We formed double molecular gradients of t-F8H2,  $F(CF_2)_8(CH_2)SiCl_3$ , on silica substrates using a variant of the methodology proposed by Chaudhury and Whitesides [1]. The NEXAFS experiments were carried out at the NIST/Dow soft X-ray materials characterization facility at the NSLS BNL. The partial-electron-yield (PEY) signal is collected using a channeltron electron multiplier with an adjustable entrance grid bias. The NIST/Dow materials characterization end-station is equipped with a computer controlled stepping motor actuated sample holder, which controls the orientation of the sample with respect to the polarization vector of the X-rays and enables rapid horizontal and vertical sample motion. The combinatorial NEXAFS experiments were conducted by scanning the sample in the vertical direction with 0.5 mm increments, after each step a new NEXAFS spectrum was recorded.

**Results:** The top panels in Figure 1 show the carbon K edge PEY NEXAFS spectra collected from a homogeneous F8H2 SAM sample measured at  $\theta=20^\circ$ ,  $50^\circ$ , and  $90^\circ$ , where  $\theta$  is the angle between the sample normal and the electric field vector of the X-ray beam. The dashed lines in Figure 2 denote the positions of the  $1s \rightarrow \sigma^*$  transitions for the C-F ( $E=292.0$  eV), and C-C ( $E=295.4$  eV) bonds. The combinatorial NEXAFS experiments on the double gradient sample were carried out by vertically moving the sample in the X-ray beam (increments 0.5 mm). After each vertical increment, a carbon K edge PEY NEXAFS spectrum was taken at photon energies around the C-F and C-C signals. In addition, PEY NEXAFS data were collected at the carbon ionization pre-edge ( $E=280.0$  eV) and post-edge ( $E=320.0$  eV). The corresponding normalized PEY NEXAFS intensities as a function of the incident photon energy beam and the position on the substrate are shown in the bottom panel of Figure 1. In Figure 2 we plot the concentration of the F8H2 molecules (solid circles) and the molecular tilt of F8H2,  $\langle\tau_{F8}\rangle$  (open circles). Close to the diffusing sources, F8H2 forms complete SAMs with the molecules oriented roughly perpendicular to the sample surface, similar to the situation in a homogeneous t-F8H2 SAM [2,3]. At larger distances from the diffusing sources, the concentration of the F8H2 molecules decreases; the functional dependence resembles that of typical diffusion profiles.  $\langle\tau_{F8}\rangle$  increases as one moves into the center of the double gradient, suggesting that the F8H2 molecules start tilting away from the sample normal. However, because  $\langle\tau_{F8}\rangle$  determined from NEXAFS represents only an *average* value, there is no straightforward way to discriminate between the case of all F8H2 molecules homogeneously tilting by the same angle and the case of a disordered system with a broad distribution of tilt angles. Complementary measurements of another physical property along the gradient – such as the density and/or the thickness – are required.

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### **References:**

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- [2] J. Genzer et al., *Macromolecules* **33**, 1882 (2000).
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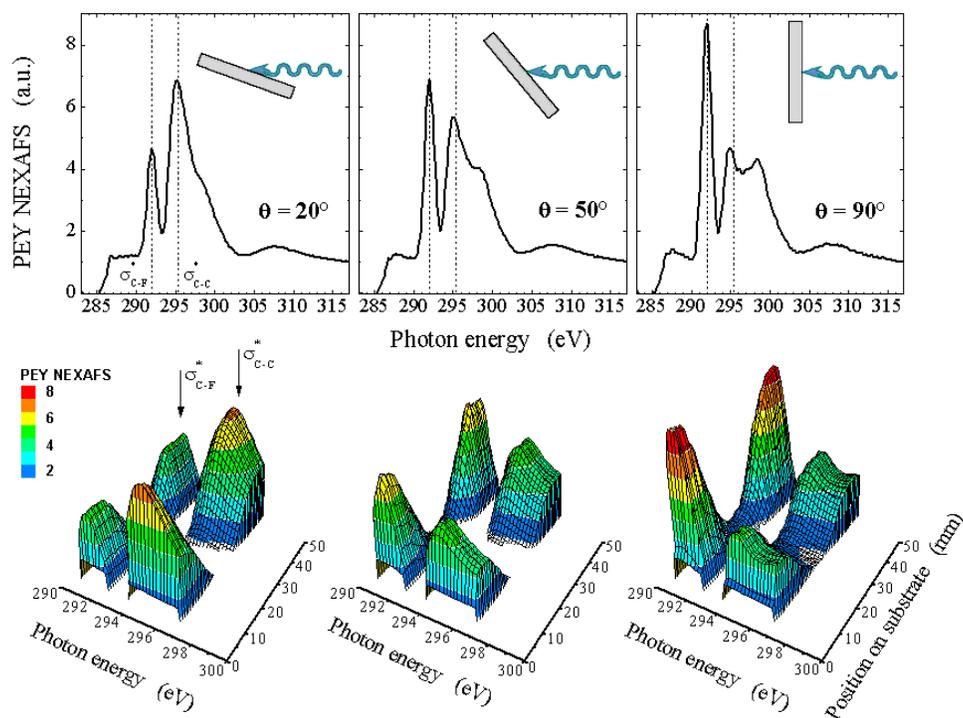


Figure 1 (top panels) Carbon K edge PEY NEXAFS spectra from homogeneous t-F8H2 SAMs collected at  $\theta=20^\circ$ ,  $50^\circ$ , and  $90^\circ$ , where  $\theta$  is the angle between the sample normal and the polarization vector of the X-ray beam. The dashed lines denote the positions of the  $1s \rightarrow \sigma^*$  transitions for the C-F ( $E=292.0$  eV), and C-C ( $E=295.4$  eV) bonds. (bottom panels) Carbon K edge PEY NEXAFS intensities around the C-F ( $291.4$  eV  $\leq E \leq 293.0$  eV) and C-C ( $294.4$  eV  $\leq E \leq 297.0$  eV)  $1s \rightarrow \sigma^*$  signals collected from the double gradient F8H2 samples as a function of the photon energy and the position on the sample at  $\theta=20^\circ$ ,  $50^\circ$ , and  $90^\circ$ .

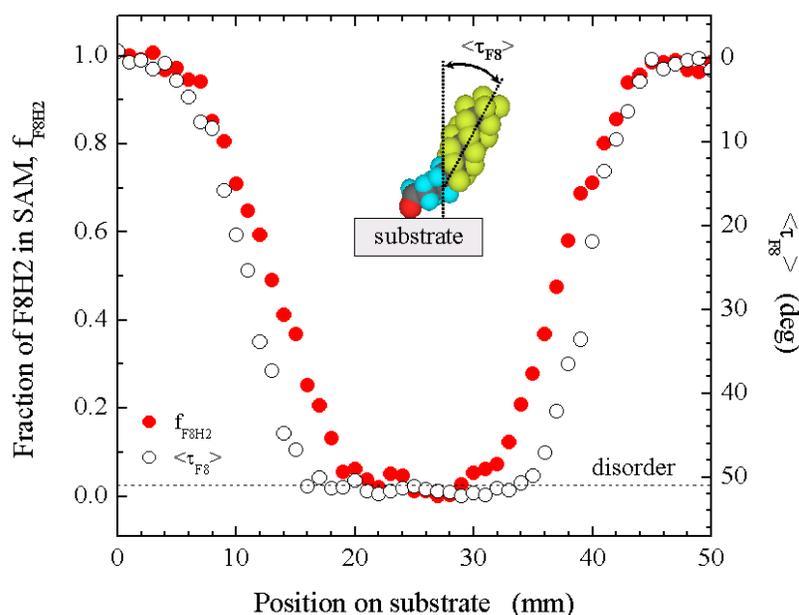


Figure 2 Fraction of F8H2 in the SAM ( $f_{F8H2}$ ) (closed circles) and the molecular orientation ( $\langle \tau_{F8} \rangle$ ) of F8H2 in the molecular double gradient ( $\langle \tau_{F8} \rangle$ ) as a function of the position on the substrate. The inset to the figure shows a schematic of the molecular orientation of a single F8H2 molecule and marks the definition of  $\langle \tau_{F8} \rangle$ .