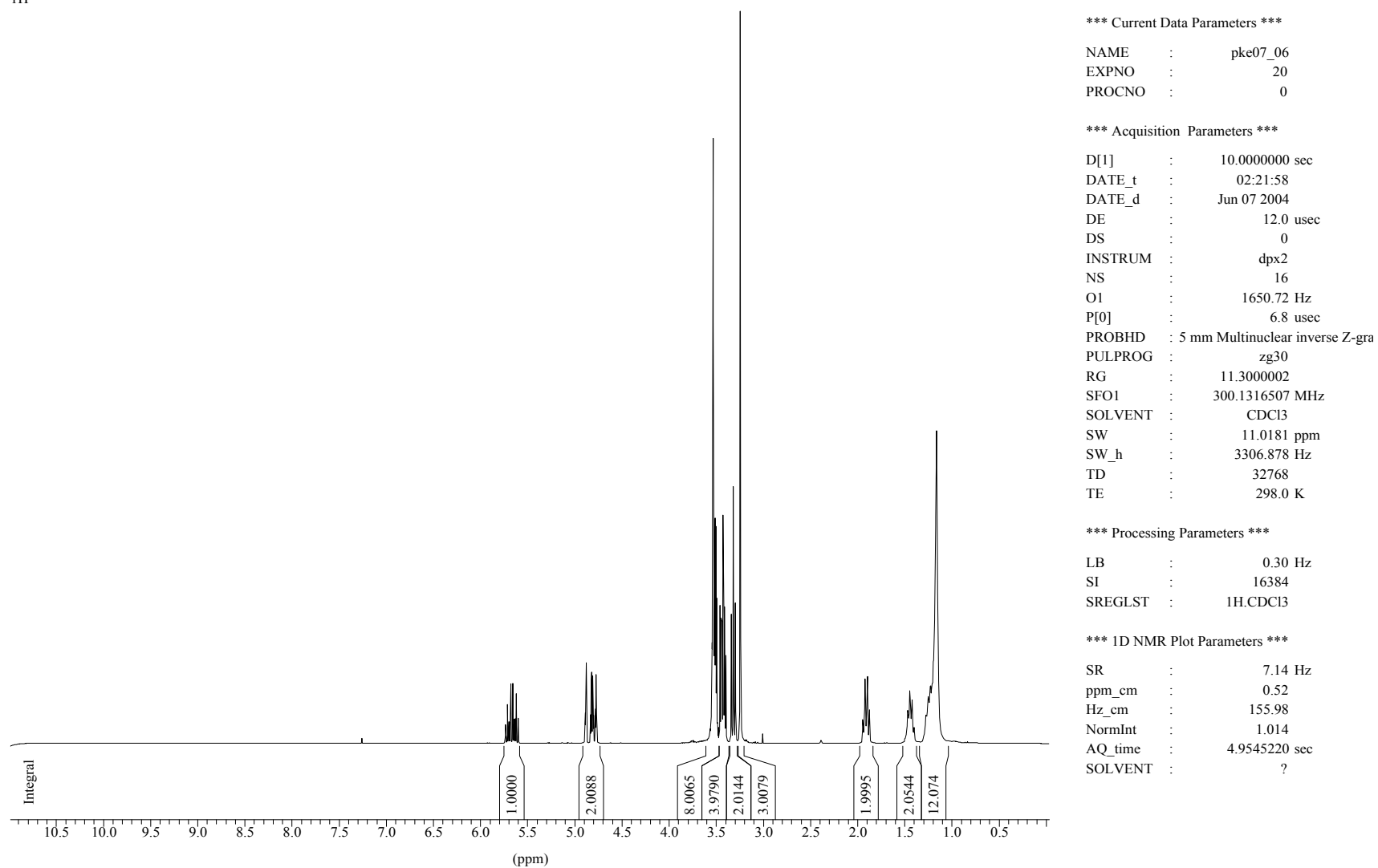


1H

Figure S1. ^1H NMR spectrum of 11-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)undec-1-ene (**1**).

Alternative fit for the C1s XP narrow scan

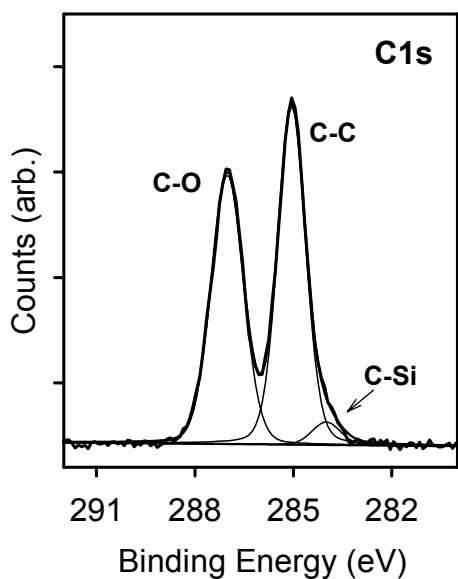


Figure S2. XP narrow scans of the carbon 1s region of Si(111) derivatized with $C_{11}EO_3Me$.

Alternatively to the fit shown in the paper, the C1s narrow scan could be deconvoluted into three peaks corresponding to the C-O (287.0 eV), C-C (285.0 eV) and C-Si (283.9 eV) species. The area of the C-Si peak was consistent with expectation when taking the attenuation due to the overlying monolayer into account. The ratio of C-O bonded carbons to the remaining carbons of the molecule was essentially the same as that determined from the fit shown in the paper.

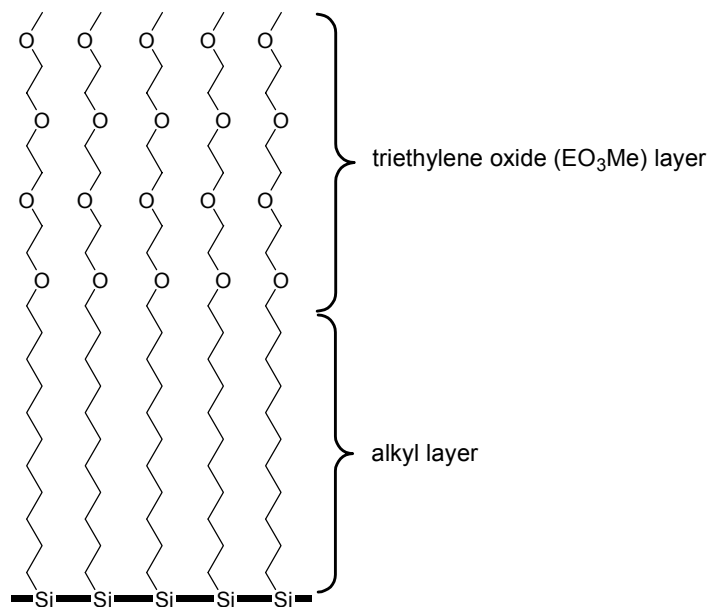


Figure S3. Bilayer model of the Si-C linked monolayer. The photoelectrons from the top (EO₃Me) layer are attenuated within the top layer itself. The photoelectrons from the bottom (alkyl) layer are attenuated within the bottom layer itself and also attenuated by the top layer.

Correction of peak areas for attenuation

The basis of the following considerations to calculate the expected ratio of the peak area at 285.0 eV (C-C linked carbons) to that at 287.0 eV (C-O linked carbons) is a “bilayer” model of the monolayer (Fig. S2). In this model the triethylene oxide moieties form a separate “layer” on top the alkyl “layer”, i.e. there is no intermixing of the two different moieties.

(a) Attenuation of photoelectrons from C-O linked carbon

The intensity of photoelectrons originating from the C-O linked carbons, S_{EO}^C , is attenuated within the layer and the area of the corresponding XPS signal is given by

$$S_{EO}^C = C \sigma_C \rho_{EO}^C \lambda_{EO}^C A (1 - e^{-(d_{EO}/\lambda_{EO}^C \sin \theta)}) \quad (1)$$

where:

C is an instrument specific factor,

σ_C is the sensitivity factor for carbon,

ρ_{EO}^C is the density of carbon atoms per unit area in the triethylene oxide layer,

λ_{EO}^C is the inelastic mean free path of photoelectrons derived from carbon in the triethylene oxide layer,

A is the area probed by the X-ray beam,

d_{EO} is the thickness of the triethylene oxide layer, here we assume d_{EO} to be between 6-8 Å,

θ is the angle between the analyzer and the surface (90° for the instrument used in this study).

The peak area without attenuation is equal to

$$S_{EO}^{C,unattenuated} = C \sigma_C \rho_{EO}^C A d_{EO} \quad (2)$$

The measured peak area for the peak at 287.0 eV is therefore multiplied by the following factor to account for the attenuation within the triethylene oxide layer:

$$f_{EO} = S_{EO}^{C,unattenuated} / S_{EO}^C = d_{EO} / [\lambda_{EO}^C (1 - e^{-(d_{EO}/\lambda_{EO}^C \sin \theta)})] \quad (3)$$

(b) Attenuation of photoelectrons from C-C linked carbon

The intensity of the photoelectrons from the C-C linked carbons, S_{alkyl}^C , of the alkyl chains is attenuated by the overlying triethylene oxide layer as well as within the alkyl layer itself. The peak area is given by

$$S_{alkyl}^C = C e^{-(d_{EO}/\lambda_{EO}^C \sin \theta)} \sigma_C \rho_{alkyl}^C \lambda_{alkyl}^C A (1 - e^{-(d_{alkyl}/\lambda_{alkyl}^C \sin \theta)}), \quad (4)$$

where:

ρ_{alkyl}^C is the density of carbon atoms per unit area in the alkyl layer,

λ_{alkyl}^C is the inelastic mean free path of photoelectrons derived from carbon in the alkyl layer,

d_{alkyl} is the thickness of the alkyl layer, here we assume $d_{alkyl} = 9-10 \text{ \AA}$.

The corresponding correction factor is then given by

$$f_{alkyl} = \frac{S_{alkyl}^{C,unattenuated}}{S_{alkyl}^C} = \frac{d_{alkyl}}{e^{-(d_{EO}/\lambda_{EO}^C \sin \theta)} \lambda_{alkyl}^C (1 - e^{-(d_{alkyl}/\lambda_{alkyl}^C \sin \theta)})} \quad (5)$$

(c) Estimation of the inelastic mean free path

The inelastic mean free path λ_k^j is given by [1]

$$\lambda_k^j = \rho_k^{-1} (49 E_k^{-2} + 0.11 E_k^{0.5}), \quad (6)$$

where E_k is the kinetic energy of the photoelectron, and ρ_k is the density of the material in layer k .

The kinetic energy of the photoelectron E_k can be obtained by

$$E_k = h\nu - E_b, \quad (7)$$

where E_b is the binding energy and $h\nu$ the X-ray photon energy.

Based on estimated densities for the alkyl layer (0.78 g cm^{-3}) and the EO₃Me layer (1.03 g cm^{-3}) the attenuation lengths for the carbon derived photoelectrons in the alkyl monolayer were calculated according to Eq. 6 and 7 to give $\lambda_{alkyl}^C = 49 \text{ \AA}$ and $\lambda_{EO}^C = 37 \text{ \AA}$.

(d) Expected ratio for C-C:C-O peak areas

Multiplication of the number of C-C linked carbons (10) and the number of C-O linked carbons (8) with the corresponding correction factors results in a C-C:C-O ratio of 0.98-1.04:1

Reference

[1] M. P. Seah and W. A. Dench. Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surface and Interface Analysis* **1979**, 1, 2-11.

