Effect of end-groups on simultaneous oleophobicity/hydrophilicity and anti-fogging performance of nanometer-thick perfluoropolyethers (PFPEs)

*Yongjin Wang, James Knapp, Aleigh Legere, Jacob Raney and Lei Li**

Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261

*: Corresponding author. Email: lel55@pitt.edu

Supporting Document

- Thickness of PFPE nanofilms

The thickness of PFPE nanofilms was measured using a J.A. Woollam alpha-SETM Ellipsometer and the detailed procedure was described elsewhere.[1] The average thickness based on three repeats at different samples, are 1.6 ± 0.2 nm, 1.7 ± 0.2 nm and 2.0 ± 0.2 nm for Z-03, Zdol and Z-tetraol, respectively, as shown in Table S1.

Table S1 The thickness of PFPE nanofilms on silica surfaces

PFPE nanofilm	Concentration of solution for dip-coating (g/L)	Thickness (nm)
Z-03	2.0	1.6 ± 0.2
Zdol	1.5	1.7 ± 0.2
Z-tetraol	0.4	2.0 ± 0.2

- Topography of PFPE nanofilms

Atomic force microscopy (AFM) images of PFPE nanofilms were obtained with a Veeco MultilMode V scanning probe microscopy (SPM) and the images are shown in Figure S1. The surface roughness (R_a) is 0.134 nm, 0.126 nm and 0.184 nm for Zdol/Si, Z-03/Si and Z-tetraol /Si, respectively. These results show that these PFPE nanofilms have similar topography and are all very smooth.

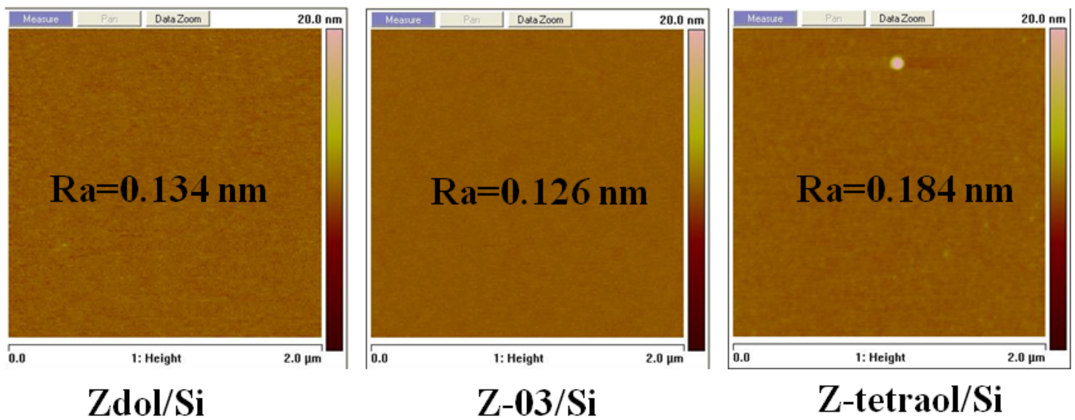


Figure S1 AFM images of PFPE nanofilms on silica surfaces

- Evaporation effect on time-dependent contact angles (CA)

Although time-dependent contact angle tests were conducted in a "sealed" system, it did not completely stop the evaporation. Bourges-Monnier has showed that, during the evaporation of a liquid droplet, the diameter of the droplet decreases with time.[2] As shown in Table S2 the diameter of water droplet decreased a little bit during 24 hours in the time-dependent water contact angle (WCA) experiments, indicating that there has been slight evaporation. On the contrary, the hexadecane droplet does not evaporate as shown previously by thermogravimetric analysis (TGA).[3] More interestingly, the diameter of hexadecane droplet on Zdol 1.8nm/Si actually increased by 0.35 mm after 24 hours as shown in Table S2, indicating that the change of hexadecane contact angle (HCA) is due to the "penetrating" instead of evaporation of hexadecane.

Table S2 The decrease of diameter of water and hexadecane droplet

	Droplet Diameter Decrease (mm)	
	Water	Hexadecane
Z-03 1.7nm/Si	0.06	0.00
Zdol 1.8nm/Si	0.08	-0.35
Z-tetraol 2.2nm/Si	0.03	0.00

- XPS peaks assignment

Zdol (m=n=21)

$HOC^3H_2C^2F_2O\text{-}[C^1F_2C^1F_2O]_m\text{-}[C^2F_2O]_n\text{-}C^2F_2C^3H_2OH$

Z-tetraol (m=n=9)

$HOC^3H_2C^3HC^3H_2OC^3H_2C^2F_2O\text{-}[C^1F_2C^1F_2O]_m\text{-}[C^2F_2O]_n\text{-}C^2F_2C^3H_2OC^3H_2C^3HC^3H_2OH$

OH OH

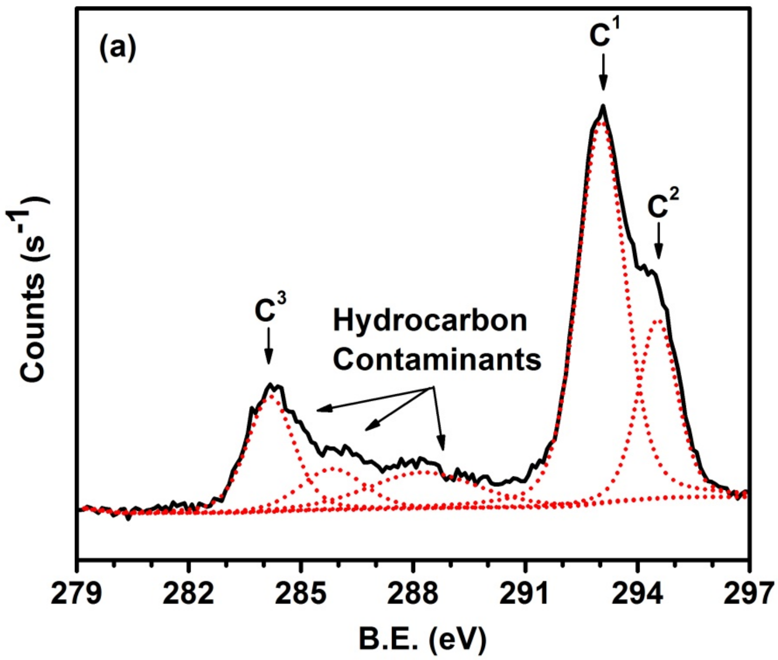
Z-03 (m=n=21)

$C^1F_3C^1F_2O\text{-}[C^1F_2C^1F_2O]_m\text{-}[C^2F_2O]_n\text{-}C^1F_2C^1F_3$

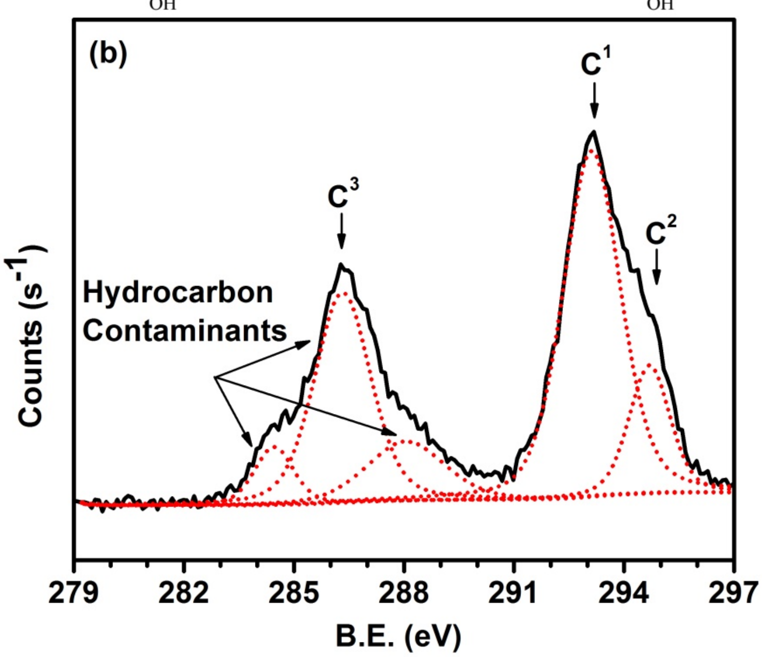
Figure S2 Molecular formula of PFPEs

Note: Not all the C^3 in Z-tetraol are exactly the same. However, these carbons have very similar binding energy [4] and are labeled as the "same" carbon here.

$HOC^3H_2C^2F_2O\text{-}[C^1F_2C^1F_2O]_m\text{-}[C^2F_2O]_n\text{-}C^2F_2C^3H_2OH$



$HOC^3H_2C^3H(OH)C^3H_2OC^3H_2C^2F_2O\text{-}[C^1F_2C^1F_2O]_m\text{-}[C^2F_2O]_n\text{-}C^2F_2C^3H_2OC^3H_2C^3H(OH)C^3H_2OH$



$C^1F_3C^1F_2O\text{-}[C^1F_2C^1F_2O]_m\text{-}[C^2F_2O]_n\text{-}C^1F_2C^1F_3$

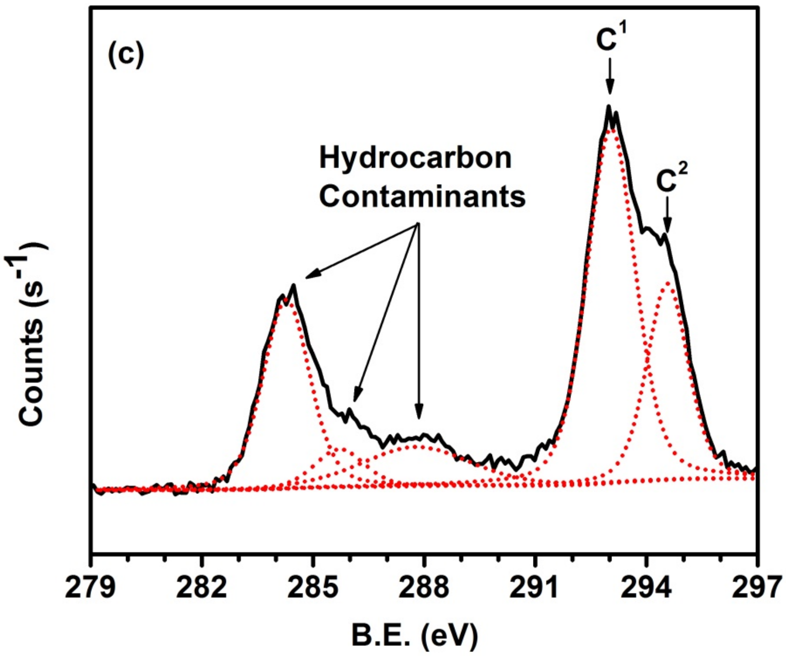


Figure S3 XPS C1s spectra and curve-fitting results (a) Zdol, (b) Z-tetraol, (c) Z-03

- Calculation of the amount (%) of airborne hydrocarbon contaminants

Based on XPS results and the molecular formula of PFPEs, the fluorocarbon% and total hydrocarbon%, including the hydrocarbons from both PFPE end-groups and airborne contaminants, were determined first. Then the airborne hydrocarbon contaminants% is determined by subtracting the hydrocarbon% in end-groups, which is calculated according to the molecular formula of PFPEs and fluorocarbon%, from the total hydrocarbon%. The area% of different C1s peaks (mean value of the three repeats) of PFPEs on different days is shown in Table S3.

Table S3 XPS C1s curve fitting results for different PFPEs coated glass slides on the 1st day (a) and the 14th day (b) after the samples were fabricated

a. 1st day

Peak	Zdol	Z-tetraol	Z-03
Fluorocarbon (%)	74.25 ± 7.53	59.54 ± 2.27	63.63 ± 3.24
Hydrocarbon (%)	25.75 ± 7.53	40.46 ± 2.27	36.68 ± 3.24
Hydrocarbon from end-group (%)	2.19	15.9	0
Hydrocarbon contaminants (%)	23.56 ± 7.53	24.56 ± 2.27	36.68 ± 3.24

b. 14th day

Peak	Zdol	Z-tetraol	Z-03
Fluorocarbon (%)	70.92 ± 1.04	57.64 ± 0.72	49.12 ± 3.74
Hydrocarbon (%)	29.08 ± 1.04	42.36 ± 0.72	50.88 ± 3.74
Hydrocarbon from end-group (%)	2.19	15.9	0
Hydrocarbon contaminants (%)	26.89 ± 1.04	26.46 ± 0.72	50.88 ± 3.74

- Advancing contact angle (ACA) and receding contact angle (RCA)

The dynamic contact angle was measured with a VCA optima XE instrument, the process of adding (advancing) or withdrawing (receding) test liquid to and from an existing test liquid droplet was recorded by a CCD camera (30 images per second). The ACA and RCA were determined by measuring the tangent of the test liquid droplet at the intersection of the air/drop surface while adding (advancing) and withdrawing (receding). The results of dynamic WCA and HCA are shown in Table S4.

Table S4 Dynamic contact angles of PFPEs coated on silica surfaces

	Water_ACA	Water_RCA	Hexadecane_ACA	Hexadecane_RCA
Z-03	51.3 ± 1.5	12.8 ± 0.4	43.0 ± 1.5	7.5 ± 0.2
Zdol	47.5 ±1.4	21.1 ± 1.9	67.7 ± 1.6	32.3 ± 1.7
Z-tetraol	63.3 ± 2.2	33.6 ± 1.5	75.6 ± 3.5	59.9 ± 0.7

- Effect of molecular weight (MW) on contact angle results

The WCA and HCA of Zdol/Si, with the MW of Zdol as 2610 g/mol, 4000 g/mol and 8778 g/mol, respectively, are shown in Table S5. The results show that there is no significant change in both WCA and HCA, which suggests that the molecular weight has little effect on the wetting behavior.

Table S5 WCA and HCA on different Zdol nanofilms with different molecular weights

	Zdol 2610	Zdol 4000	Zdol 8778
WCA	46.9 ± 0.6	46.0 ± 0.9	47.8 ± 0.6
HCA	66.5 ± 0.4	67.0 ± 0.7	67.1 ± 0.4

Reference

(1) Wang, Y.; Sun, J.; Li, L., What is the role of the interfacial interaction in the slow relaxation of nanometer-thick polymer melts on a solid surface? *Langmuir* **2012,** *28* (14), 6151-6156.

(2) Bourges-Monnier, C.; Shanahan, M., Influence of evaporation on contact angle. *Langmuir* **1995,** *11* (7), 2820-2829.

(3) Li, L.; Wang, Y.; Gallaschun, C.; Risch, T.; Sun, J., Why can a nanometer-thick polymer coated surface be more wettable to water than to oil? *J. Mater. Chem.* **2012,** *22* (33), 16719-16722.

(4) http://www.lasurface.com/database/elementxps.php.