# "Omniphobic "R<sup>F</sup> Paper" Produced by Silanization with Fluoroalkyltrichlorosilanes"

By Ana C. Glavan<sup>1</sup>, Ramses V. Martinez<sup>1†</sup>, Anand Bala Subramaniam<sup>1†</sup>, Hyo Jae Yoon<sup>1</sup>, Rui

M.D. Nunes<sup>1</sup>, Heiko Lange<sup>1</sup>, Martin M. Thuo<sup>1</sup>, and George M. Whitesides<sup>1,2\*</sup>

## **Supporting Information**

#### **Materials and Methods**

**Fabrication of R<sup>H</sup> and R<sup>F</sup> papers.** The silanizing reagents: i) tricholoromethylsilane (CH<sub>3</sub>SiCl<sub>3</sub>, "C1H"), trichlorodecylsilane (CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>SiCl<sub>3</sub>, "C<sub>10</sub><sup>H</sup>"), trichloro(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (CF<sub>3</sub>(CF<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>-CH<sub>2</sub>SiCl<sub>3</sub>, "C<sub>8</sub><sup>F</sup>"), trichloro(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)silane (CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>-CH<sub>2</sub>SiCl<sub>3</sub>, "C<sub>10</sub><sup>F</sup>"), trichloro (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)silane (CF<sub>3</sub>(CF<sub>2</sub>)<sub>9</sub>CH<sub>2</sub>-CH<sub>2</sub>SiCl<sub>3</sub>, "C<sub>12</sub><sup>F</sup>) were purchased from Gelest Inc (Morrisville, PA). All chemicals were used as received without further purification. Paper (Gel Blot paper, Whatman#1, and Whatman#50) was purchased from GE Healthcare (NJ, USA) and used as received, without purification.

The silanization reaction was conducted in a chamber with a volume of 0.01 m<sup>3</sup> at a temperature set at 95 °C. The silanizing reagent is transferred into a glass vial under inert gas atmosphere and placed inside the chamber together with the samples. Each experiment typically required approximately 100 mg of silane in 5 mL of anhydrous toluene. The silane

was vaporized at 95 °C under reduced pressure (~30 mbar, 0.03 atm) and allowed to react for 5 minutes. Diffusion inside the reaction chamber is sufficient for an even distribution of the silane within the chamber.

**Characterization of the wettability of different papers.** Solvents were used as received: Pentane (Sigma-Aldrich, anhydrous,  $\geq$ 99%), diethyl ether (Sigma-Aldrich, anhydrous,  $\geq$ 99%), perfluorodecalin (Sigma-Aldrich, anhydrous,  $\geq$ 99%), anhydrous ethanol (Pharmco-Aaper, 200 proof, absolute), *n*-hexadecane (Sigma-Aldrich, anhydrous,  $\geq$ 99%), DMF (Sigma-Aldrich, anhydrous,  $\geq$ 99%), ethylene glycol (Sigma-Aldrich, anhydrous,  $\geq$ 99%), thiodiglycol (Sigma-Aldrich, anhydrous,  $\geq$ 99%), toluene (Acros, spectrophotometric grade 99+%), dimethylsulfoxide (DMSO, Sigma-Aldrich, anhydrous 99.9%), methanol (Ashland, VLSI). Human heparinized whole blood and human plasma were purchased from Research Blood Components, LLC (Brighton, MA). All surfactants were purchased from Sigma-Aldrich (St. Louis, MO). Water is ultrapure and deionized (resistivity > 18.2 MΩ cm).

**Contact angle measurements.** The contact angle measurements were performed using a contact angle measurement system (Ramé-Hart model 500-F1, Ramé-Hart Instrument Co.) at room temperature (20 - 25 °C) with ~20% relative humidity. The droplet volume for the measurement was ~10 µL (unless otherwise specified). The advancing and receding contact angles were measured by the sessile drop method, which involves expanding or contracting a contact angle droplet by adding or withdrawing fluid in 1 µL increments. The droplet profile was fitted to a spherical profile using the software provided by the system. The advancing contact angles are measured at the leading droplet edge when the value of the contact angle remained constant and solid/liquid interface started to increase; the receding angles were

measured at the trailing droplet edge when the value of the contact angle remained constant and the solid/liquid interface started to decrease.

**Scanning electron imaging.** Scanning electron microscope (SEM) images (Fig. 2 B, C inset) of the paper microfluidic device was acquired with a Zeiss Supra 55 VP FESEM at 2 kV at a working distance of 6 mm. Before SEM imaging, the sample was sputter coated with Pt/Pd at 60 mA for 15–45 s.

**RMS Roughness measurements of paper.** We measured the height RMS roughness with a Taylor-Hobson CCI HD Optical Profiler according to the ISO25178 norm. The CCI method is based on the cross-coherence analysis of two low-coherence light sources, the beam reflected from our sample and a reference beam reflected from a reference mirror. Paper has a low reflectance that hinders the application of interferometry techniques. To improve the reflectance of paper we deposited a conformal thin layer of Au (~4 nm) using a Cressington 208HR sputter coater. In each experiment, at least seven 0.4 µm x 0.4 µm areas were analyzed.

**Preparation of SLIPS**. Lubricating fluid (Dupont<sup>TM</sup> Krytox® GPL 105), was added to the surfaces (~50  $\mu$ L/cm<sup>2</sup>) by pipette to impregnate the paper and form a coating film. The fluid spontaneously spread onto the whole substrate through capillary wicking. Tilting the surface and mildly applying compressed air removed the excess of lubricating fluid.

$$CF_3(CF_2)_2O$$
- $[CF-CF_2O]_nCF_2CF_3$   
 $| CF_3$  n=10-60

Dupont<sup>™</sup> Krytox<sup>®</sup> GPL 105: molecular structure



**Figure S1:** Schematic representation of the process used for surface modification of paper surfaces *via* silanization.



**Figure S2:** Optical profilometry images of Whatman #1 (W1), Whatman #50 (W50), Gel Blot paper (Blot)



**Figure S3:** Droplets of water and hexadecane on Whatman #1 functionalized with alkyl and fluoroalkyl trichlorosilanes. The volume of each droplet is  $10 \mu L$ .



**Figure S4:** Static contact angles (filled symbols) and hysteresis (hollow symbols) for several buffers commonly used in biological applications: PBS (pH 7.2), Tris (pH 7.4), LB, DMEM, Tris-Gly Buffer (pH 8.3), and 1x OneTaq MasterMix (typical PCR buffer) on functionalized Gel Blot, Whatman #1 and Whatman #50 paper. The 1x OneTaq Mastermix is an aqueous solution that notably wets the non-fluorinated surfaces. Error bars represent standard deviation (N=30).



**Figure S5:** Static contact angles (filled symbols) and hysteresis (hollow symbols) of aqueous solutions of detergent commonly used in molecular biology on functionalized Blotting, Whatman#1 and Whatman#50 paper. The non-fluorinated surfaces are wetted by 0.05% TritonX, 0.07% Tween 20 and 0.05% IGEPAL@CA630. Error bars represent standard deviation (N=30).



**Figure S6**: Origami Designs: Crease pattern for the fabrication of a multiwell plate. Mountain and valley folds are indicated by solid green and dashed red lines, respectively. The mechanical flexibility of the omniphobic paper allowed us to form 3-D structures by folding the sheet of paper before or after functionalization.

![](_page_9_Figure_0.jpeg)

**Figure S7**: Origami designs for paper SLIPS: Crease pattern for the fabrication of channels and switches. Mountain and valley folds are indicated by green and red dashed lines, respectively. The mechanical flexibility of the omniphobic paper allowed us to form 3-D structures by folding the sheet of paper after impregnation with a perfluoropolyether (Krytox® GPL105).

Estimation of the Surface Free Energies of the Functionalized Papers. The method developed by Owens–Wendt–Rabel–Kaelble allows us to calculate the polar and disperse components of the surface energy and uses a geometric mean of these in the expression for  $\gamma_{LA}$ . We estimate the surface energy of the different R<sup>F</sup> and R<sup>H</sup> modified papers using the geometric mean equation:

$$(1 + \cos\theta_{app})\gamma_{LA} = 2[(\gamma_{SA}^{d}\gamma_{LA}^{d})^{1/2} + (\gamma_{SA}^{p}\gamma_{LA}^{p})^{1/2}]$$
(1)

 $\theta_{app}$  is the static apparent contact angle, and  $\gamma_{SA}$  and  $\gamma_{LA}$  are the interfacial free energies with air of the solid and liquid, respectively. The superscripts *d* and *p* refer to the dispersive and polar components of surface energy, respectively.

By solving Equation (1) for diiodomethane and pure water as test liquids, we obtained total apparent surface free energies between 7 and 11 mN/m for surfaces treated with the fluoroalkyl silanes, below the 18-20 mN/m reported value for polytetrafluoroethylene (PTFE). Based on the typical values for surface energies of exposed  $-CF_2$ - (18mN/m) and  $-CF_3$ (6 mN/m) groups,<sup>[1, 2]</sup> the calculated values for the surface free energies of fluorinated paper would indicate a high ratio of CF<sub>3</sub> groups to exposed CF<sub>2</sub> groups. The trend corresponds to what is expected from the chemical nature of the surface.

![](_page_11_Figure_0.jpeg)

**Figure S8:** Dispersive and polar components of the apparent surface free energy for Gel Blot paper (Blot), Whatman #1 (W1) and Whatman #50 (W50) paper functionalized with alkyl trichlorosilane ( $C_1^{H}$  and  $C_{10}^{H}$ ) and fluoroalkyl trichlorosilane ( $C_8^{F}$ ,  $C_{10}^{F}$  and  $C_{12}^{F}$ ). Error bars represent standard deviation (N=30).

#### Disposability of the fluorinated paper surfaces: estimate of products formed upon

**incineration.** Combustion of fluoroalkanes occurs at temperatures above 1500°C <sup>[3-6]</sup> under atmospheric pressure. The distribution of products includes  $\text{COF}_2$ ,  $\text{CF}_4$ , CO, and  $\text{CO}_2$ ,<sup>[4]</sup> with  $\text{COF}_2$  and  $\text{CO}_2$  being the most abundant when the combustion occurs with 20%  $\text{O}_2$ .<sup>[3, 4]</sup> The toxic volatile compounds,  $\text{COF}_2$  and HF, have threshold limits for short-term exposure of 2ppm (5.4 mg/m<sup>3</sup>) for  $\text{COF}_2$  and 2 ppm (1.7 mg/m<sup>3</sup>) for HF.

We used a FLIR (Forward Looking Infrared) camera (B400, FLIR Systems Inc.) to record the burning of paper with different surface treatments, and recorded the maximum temperatures in each individual image. In the case of untreated paper, paper treated with  $C_1^{H}$ , and paper treated with  $C_{10}^{H}$ , the maximum temperatures are ~ 630°C between ~ 670°C, respectively. In the case of paper functionalized with  $C_8^{F}$ ,  $C_{10}^{F}$  and  $C_{12}^{F}$ , the maximum temperatures are between ~ 450°C and ~ 490°C. The R<sup>F</sup> papers burned more slowly, and generated flames of lower temperatures, than untreated paper and R<sup>H</sup> paper.

If the R<sup>F</sup> paper is burned in a simple set-up, with no high-temperature combustion catalyst present in the system when the paper is burned, the temperature of the flame is likely not high enough to allow the decomposition of the fluoroalkyl chains. It is, however, sufficiently high <sup>[7]</sup> to allow the breaking of the C-Si bond and the oxidation of the terminal carbon atom to yield terminally oxidized fluoroalkyl species.

The amounts of perfluoroalkylcarboxylic acid, HF and  $\text{COF}_2$ , released as by-product upon burning paper functionalized with  $C_{12}^{\ \ F}$  are estimated based on the elemental analysis (wt % C, F, Si) performed by the Intertek QTI Laboratory (Whitehouse, NJ). The results of the elemental analysis are summarized in Table S1.

Type of paper	Basis weight (mg/cm <sup>2</sup> )	wt % C	wt % F	wt % Si
Whatman #50	~9.3	42.7 ± 0.3	0.5 ± 0.5	$0.0018 \pm 0.0005$
Whatman #1	~8.6	42.8 ± 0.3	0.6 ± 0.5	0.0019 ± 0.0005
Gel Blot paper	~49.3	42.3 ± 0.3	0.6 ± 0.5	0.0041 ± 0.0005

Table S1: Elemental analysis (wt%) of papers functionalized with C<sub>12</sub><sup>F</sup>

We can estimate, based on the Si content, that one cm<sup>2</sup> of Gel Blot paper functionalized with  $C_{12}^{F}$  contains ~7 × 10<sup>-8</sup> moles  $C_{12}^{F}$ , corresponding to ~4 × 10<sup>16</sup> molecules  $C_{12}^{F}$  per cm<sup>2</sup> of paper. Similarly, one cm<sup>2</sup> of functionalized Whatman #1 and Whatman #50 papers contain~6 × 10<sup>-9</sup> moles or ~4 × 10<sup>15</sup> molecules  $C_{12}^{F}$  per cm<sup>2</sup> of paper.

Thus, the incineration of 1 cm<sup>2</sup> of Gel Blot paper functionalized with  $C_{12}^{F}$  will produce at most 34 µg of perfluoroalkylcarboxylic acid ( $C_{12}H_3F_{21}O_2$ ), corresponding to a maximum of ca. 29 µg of HF, or a maximum of ca. 49 µg of COF<sub>2</sub>. The amounts of fluorinated products released by the incineration of 1 cm<sup>2</sup> of Whatman #1 and Whatman #50 papers are maximum ca. 3 µg of perfluoroalkylcarboxylic acid, or ca. 2.6 µg of HF and ca. 4.3 µg of COF<sub>2</sub>. **Cost of materials.** An average of 12 sheets of 20 cm x 25 cm paper can be functionalized during one silanization experiment, conducted in a chamber with a volume of 0.01 m<sup>3</sup> at a temperature set at 95°C. Each experiment typically required approximately 100 mg of organosilane in 10 mL of anhydrous toluene. The cost of one 20 cm x 25 cm sheet of Whatman#1 paper is ~\$0.27, making the cost of 1 m<sup>2</sup> Whatman#1 paper ~\$5.4.

Table S2: Cost of silanizing reagents as purchased at laboratory scale

Organosilane	C <sub>1</sub> <sup>H</sup>	C <sub>10</sub> <sup>H</sup>	C <sub>8</sub> <sup>F</sup>	C <sub>10</sub> <sup>F</sup>	<b>C</b> <sub>12</sub> <sup>F</sup>
Cost of 100 mg reagent (\$)	0.05	0.18	0.27	0.35	0.47
Cost reagent (\$/m <sup>2</sup> )	0.08	0.30	0.45	0.58	0.78

### References

[1] A. W. Adamson, A. P. U. Gast, *Physical Chemistry of Surfaces*, Wiley, 1997.

[2] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, Y. Ueda, *Langmuir* 1999, *15*, 4321.

[3] E. A. Fletcher, D. Kittelso, *Combust. Flame* **1968**, *12*, 164.

[4] C. H. Douglass, H. D. Ladouceur, V. A. Shamamian, J. R. McDonald, *Combust. Flame* **1995**, *100*, 529.

[5] L. E. Fuller, E. A. Fletcher, *Combust. Flame* **1969**, *13*, 434.

- [6] R. A. Matula, D. I. Orloff, J. T. Agnew, *Combust. Flame* **1970**, *14*, 97.
- [7] R. L. Schalla, UNT Digital Library 1954, Doc. ID:19930087991.