

Supporting Information

Ultralow Surface Energy Self-Assembled Monolayers of Iodo-Perfluorinated Alkanes onto Silica driven by Halogen Bonding

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Wettability studies of monolayers

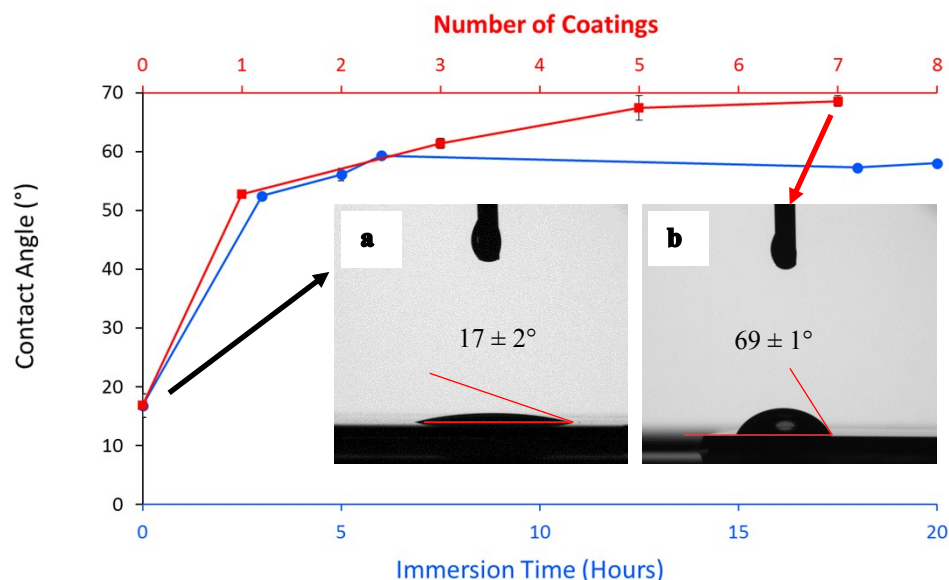


Figure S1: Variation of static contact angle of hexadecane (5 μ L droplet) with increasing cycles of drop-coating of 10 mM I-PFC12 solutions (red square symbols, upper axis) and duration of immersion in solution (blue circles, bottom axis). Error bars indicate standard deviation over at least 6 measurements across 2 samples. Measurements taken at $T = 21.5 \pm 1.0$ °C, relative humidity = 52.6 ± 3.0 %. Inset: Static contact angle of hexadecane on a) clean silicon wafer and b) surface after 7 drop-coats.

As shown in Figure S1, the drop-casting method was found to be an efficient way to form I-PFC12 monolayers on silicon surfaces, driven by the halogen bond: the contact angle of hexadecane on a clean silicon wafer after drop-casting with 10 mM I-PFC12 solution increased from a value of $17 \pm 2^\circ$ to a maximum of $69 \pm 1^\circ$ after 7 cycles. These values are in excellent agreement with those achieved via solution immersion overnight (typically between 15-17 hours). The reached plateau matches the contact angle values measured on plain Teflon films, which are entirely composed of polymeric perfluorocarbon chains.³ The drop-casting technique produces high surface coverage of the molecules after 5 coatings as established from the plateauing of the contact angle values and the procedure takes approximately 5 minutes. Rinsing of the monolayers with the pure solvent following drop-casting led to no changes in the contact angles.

In a few experiments the monolayers were prepared by spin-coating the solution on the silicon wafers. Spin-coating resulted in monolayers with slightly lower contact angle values of hexadecane compared to drop-cast samples (59 - 60°). Therefore, the drop-cast method was used to achieve maximum monolayer coverage.

Monolayers were applied onto surfaces also with micro-contact printing stamps, with channel width and pitch of 20 μ m. The measured contact angle of hexadecane on a micro-contact printed and patterned I-PFC12 surface was $44 \pm 1^\circ$. Using the Cassie Baxter equation, $\cos \theta_c = f_1 \cos \theta_1 + f_2 \cos \theta_2$, and with the surface fractions $f_1 = f_2 = 0.5$ for I-PFC12 and silica, and $\theta_1 = 69^\circ$ on I-PFC12 and $\theta_2 = 17^\circ$ for the clean silicon wafer, the theoretical contact angle of hexadecane was 48.2° . The slight discrepancy between the experimental and calculated values of the contact angle may be explained by the incomplete monolayer formation via micro-

contact printing. We concluded that the formation of SAMs with a PDMS stamp may not be ideally uniform. Indeed when we formed a complete SAMs from a featureless PDMS stamp by “contact transfer”, the SAMs were almost always mixed with impurities and contaminants as revealed by AFM scans.

Effect of I-PFC8 solution concentration and light exposure on contact angle

In a few select experiments, solution immersed monolayers of I-PFC8 and Br-PFC10 were prepared. For I-PFC8, a much higher concentration (50 mM) was required to reach a c.a. of hexadecane of 67° .

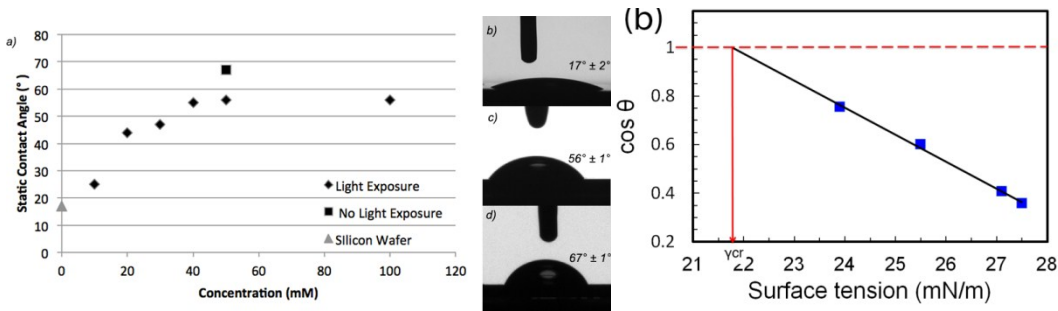


Figure S2 a) Contact angle of hexadecane on a solution immersed monolayer of I-PFC8 exposed to room light (diamonds) or not exposed (square) and on a bare silicon wafer (triangle) vs. I-PFC8 solution concentration. b) Hexadecane droplet on an untreated Si/SiO_x Wafer. c) Contact angle of hexadecane on a I-PFC8 SAM after exposure to lab light for 12 hours. d) Contact angle of hexadecane on a Si/SiO_x wafer that was shielded from light during immersion. (e) Zisman plot relative of I-PFC8 SAM on silicon wafer. Extrapolation of the solid trend line to $\cos \theta = 1$ gives the critical surface tension $\gamma_{cr} = 21.7$ mN/m, with $R^2 = 0.9964$.

Table S1. Static contact angle of hexadecane collected on different hydroxylated substrates solution immersed in I-PFC12, before and after immersion in different solvents for two hours.

I-PFC12 SAM on silicon wafer (native oxide layer 1.8 nm) - immersion in solvent		
Immersion Solvent	Static c.a. (°) of hexadecane before immersion	Static c.a. (°) of hexadecane after immersion
Water	67 ± 2	16 ± 2
Ethanol	64 ± 3	16 ± 3
Acetone	64 ± 1	14 ± 1
Toluene	62 ± 2	60 ± 4
Krytox	55 ± 3	57 ± 2
Silicon oil	60 ± 2	55 ± 2
dioctylphthalate	65 ± 2	6 ± 3
I-PFC12 SAM on thermal oxide silicon wafer (thick oxide layer 200 nm)		
Solvent	Static c.a. (°) of hexadecane before immersion	Static c.a. (°) of hexadecane after immersion
Water	66 ± 1	10 ± 3
Ethanol	62 ± 2	15 ± 2
Acetone	60 ± 3	16 ± 1
Toluene	61 ± 2	60 ± 2
I-PFC12 SAM on glass slide		
Solvent	Static c.a. (°) of hexadecane before immersion	Static c.a. (°) of hexadecane after immersion
Water	60 ± 1	11 ± 2
Ethanol	58 ± 3	15 ± 1
Acetone	61 ± 3	16 ± 3
Toluene	59 ± 2	57 ± 2
I-PFC12 SAMs on mica		
Solvent	Static c.a. (°) of hexadecane before immersion	Static c.a. (°) of hexadecane after immersion
Water	64 ± 1	13 ± 3
Ethanol	63 ± 2	17 ± 3
Acetone	61 ± 3	14 ± 2
Toluene	63 ± 3	62 ± 2

The I-PFC12 SAMs were stable on silicon substrates with thick oxide layer, mica, and glass upon immersion in alkanes, toluene, silicon oil and Krytox-100 for two hours, but were removed by immersion in water, ethanol, acetone and dioctylphthalate.

XPS Elemental Composition and MIES analysis of monolayer

The spectrum of the drop-cast I-PFC12 SAM is reported below (**Figure S3**), presenting peaks for O, Si, C, F and Na. The Si and O peaks result from the penetration of x-ray below the surface of the monolayer, up to a depth of 5-10 nm inside the silicon. The excess amount of carbon signal is due to adventitious C, also found in the bare silicon sample (not shown). The low intensity of the iodine peak is discussed in the main text, and is likely due to photodissociation of the iodine. The spectrum of the bare silicon substrate immersed in pure solvent contains peaks for O, Si, C, N, but not for fluorine, which indicates that the perfluorinated solvent has no ability to modify the surface.

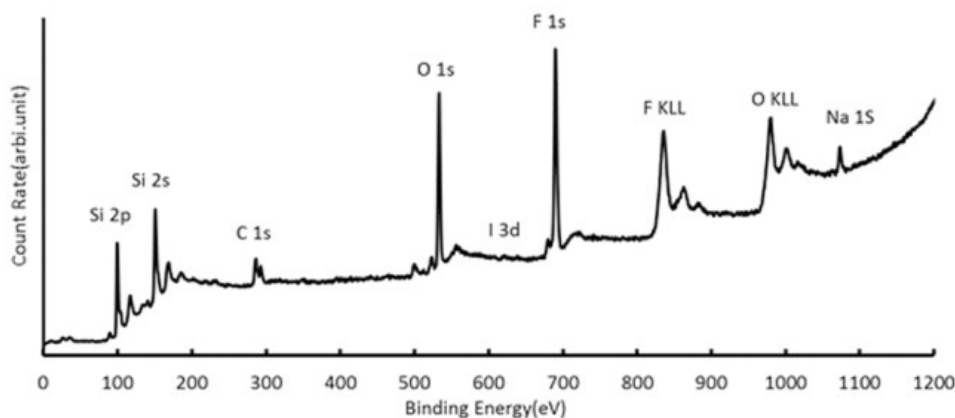


Figure S3 (a) XPS survey spectrum collected on Si/SiO_x substrate immersed for 17 hours in I-PFC12.

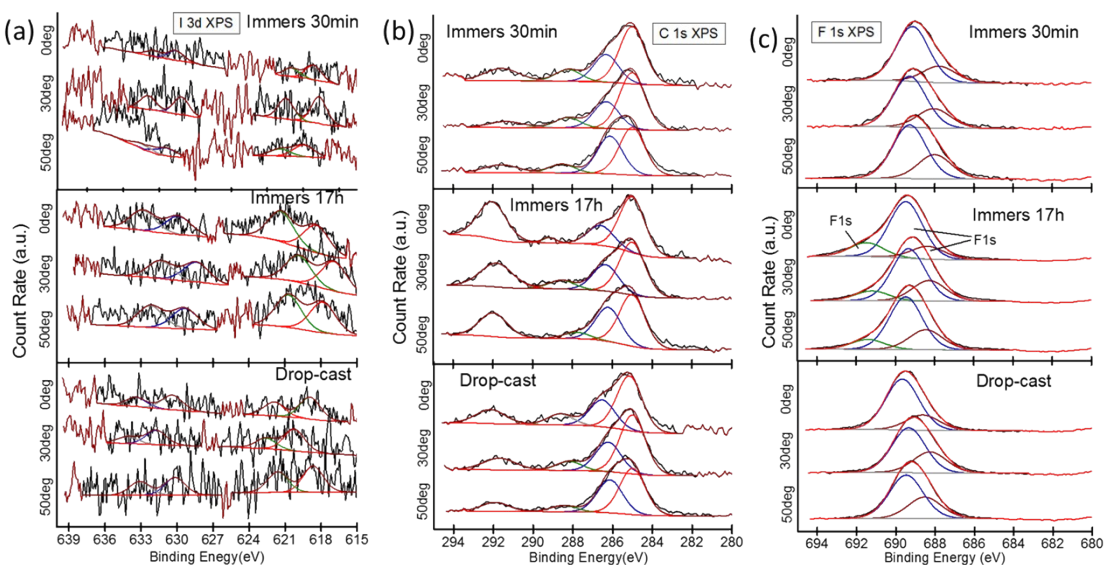


Figure S4 XPS surface elemental concentration on Si/SiO_x substrates immersed in I-PFC12 either for 30 minutes and 17 hours, and drop-cast. (a) Stacked I3d spectra of XPS at various angles. (b) Stacked C1s spectra of XPS at various angles; (c) Stacked F1s spectra of XPS at various angles.

Table S2. XPS elemental composition data collected on two samples: a silicon substrate immersed in the FC-72 solvent without the I-PFC12 molecule; and a silicon substrate covered with I-PFC12 monolayer. *Adventitious element.

Silicon wafer immersed in pure FC-72 solvent			
Label	Peak binding energy (eV)	Atomic content (%)	Total atomic content (%)
O1s	538.08	32.31	32.31
Si2p	107.08	54.68	54.68
C1s	296.58	11.91	11.91
N1s	406.58	1.1	1.1
Silicon wafer immersed in I-PFC12 solution overnight (10 mM)			
Label	Peak binding energy (eV)	Atomic content (%)	Total atomic content (%)
C1s A	285.07	3.47	9.56
C1s B	286.57	1.1	
C1s C	288.07	0.52	
C1s D	289.20	1.16	
C1s E	291.66	2.87	
C1s F	293.95	0.44	
O1s	538.28	28.65	28.65
F1s	698.28	9.94	9.94
Si2p3 A	106.88	41.9	51.27
Si2p B	106.88	9.37	
I3d5	624.98	0.05	0.05
Na1s*	1077.08	0.55	0.55

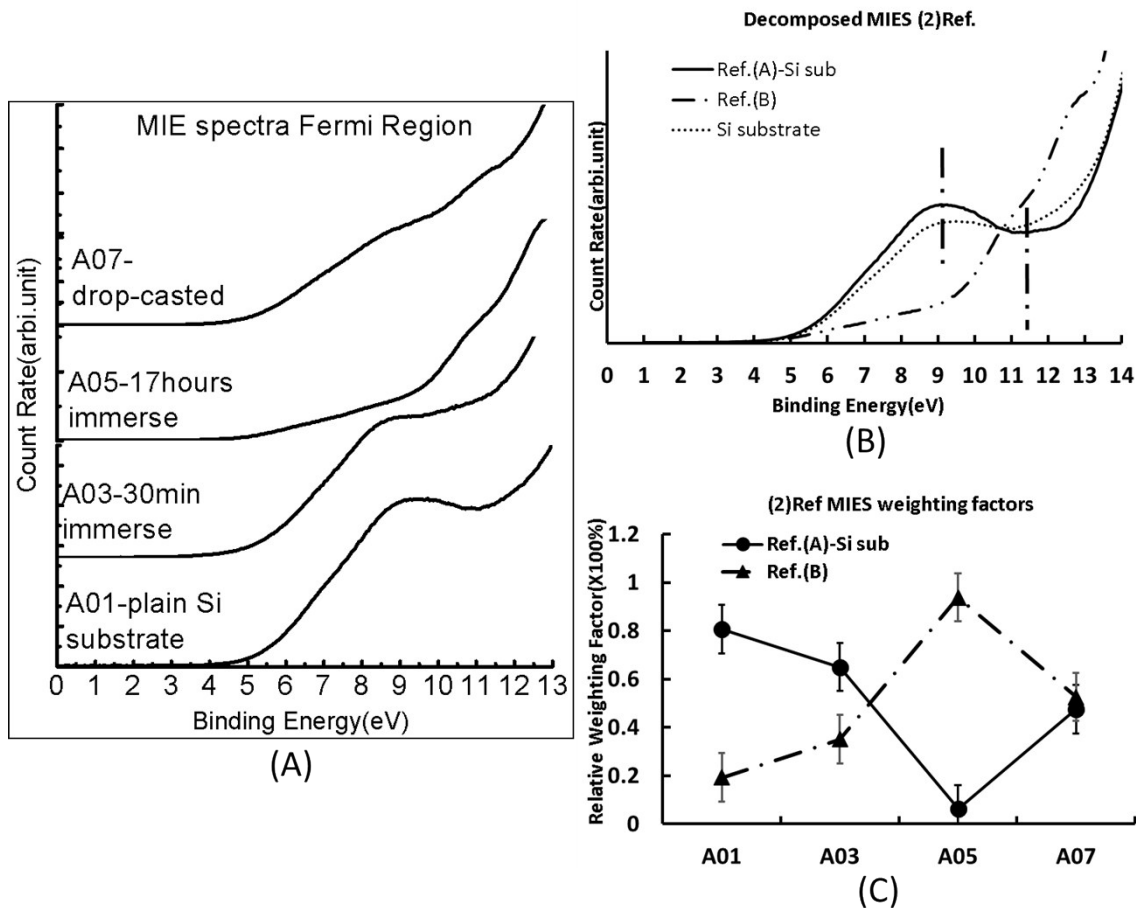


Figure S5 The Fermi Region of silicon wafer and different I-PFC12 samples of monolayers investigated by MIES; (B) The application of SVD results in two individual reference spectra; (C) The weighting factors of reference spectra.

Metastable impact electron spectroscopy (MIES) probed the composition of the outermost 1 nm of the layer. Valence electron spectra of the outermost layer as measured with MIES are shown in Figure S4, which quantify the fraction of the surface covered with the perfluorinated molecules: the weighting factor for the fluorinated chains was 0.2 ± 0.1 in the plain silicon sample (the factor can be expected to be 0. However, when the reference spectrum is rather featureless the data analysis algorithm has a larger uncertainty for the weighting factors of such spectra). The weighting factor for the fluorinated chains increased to 0.38 ± 0.1 for the 30 minutes immersed sample, and then increased to 0.95 ± 0.1 in the 17 hours immersed sample, demonstrating an almost complete surface coverage in this case. The drop-cast sample showed a weighting factor for fluorine of 0.5 ± 0.1 . Importantly, the trend in weighting factors of the fluorinated chain component reflected that of the work function of the samples, described later.

The MIE spectra can be decomposed by applying SVD into two reference spectra. The measured spectra can be written as

$$S_{meas}^i = \sum_j a_j^i \times S_{ref,j} \quad \text{with} \quad \sum_j a_j^i = 1 \quad (1)$$

The two reference spectra are shown in Figure S4. Reference spectrum A can be identified with the silicon substrate because it shows the same features as the spectrum of the plain substrate, and Ref (B) can be identified with the fluorinated chain which is the only component on the surface. Plotting the weighting factors in part (c), the trend in coverage with the amount of fluorine was determined and the result is in accordance with the XPS outcome.

Table S3 Measured thickness and scattering length density for three samples of I-PFC12 monolayers prepared by solution immersion for 17 hours, as measured by x-ray reflectometry.

Sample	Measured thickness (\AA) before immersion in solvent	Scattering length density before immersion ($\times 10^{-5} \text{\AA}^{-2}$)
1	10.3	15.5
2	19.9	15.5
3	19.9	15.5

Monolayer formation with Br-PFC10

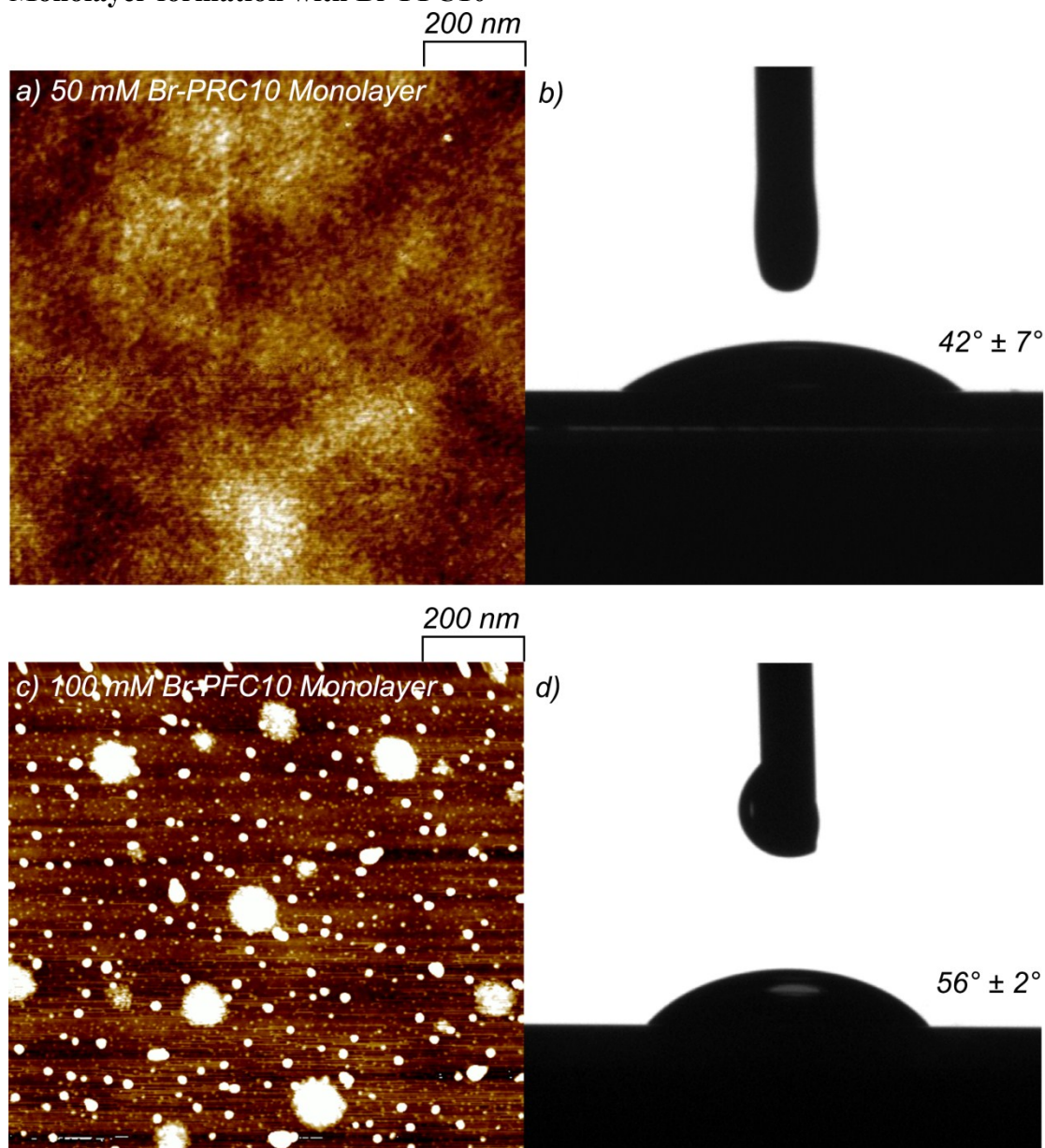


Figure S7 a) AFM scan of Br-PFC10 SAM formed by immersion in a 50 mM solution. RMS is 0.43 ± 0.07 nm. b) A droplet of hexadecane on this surface, with contact angle is $42^\circ \pm 7^\circ$. c) AFM scan of Br-PFC10 SAM formed by immersion a 100 mM solution. The surface is substantially rougher, 3.03 ± 0.99 nm and a large number of aggregates appear. Height scale is 10 nm for both a) and c). d) A droplet of hexadecane on this surface, with contact angle $56^\circ \pm 2^\circ$.

Evidence of halogen bonding in I-PFC8

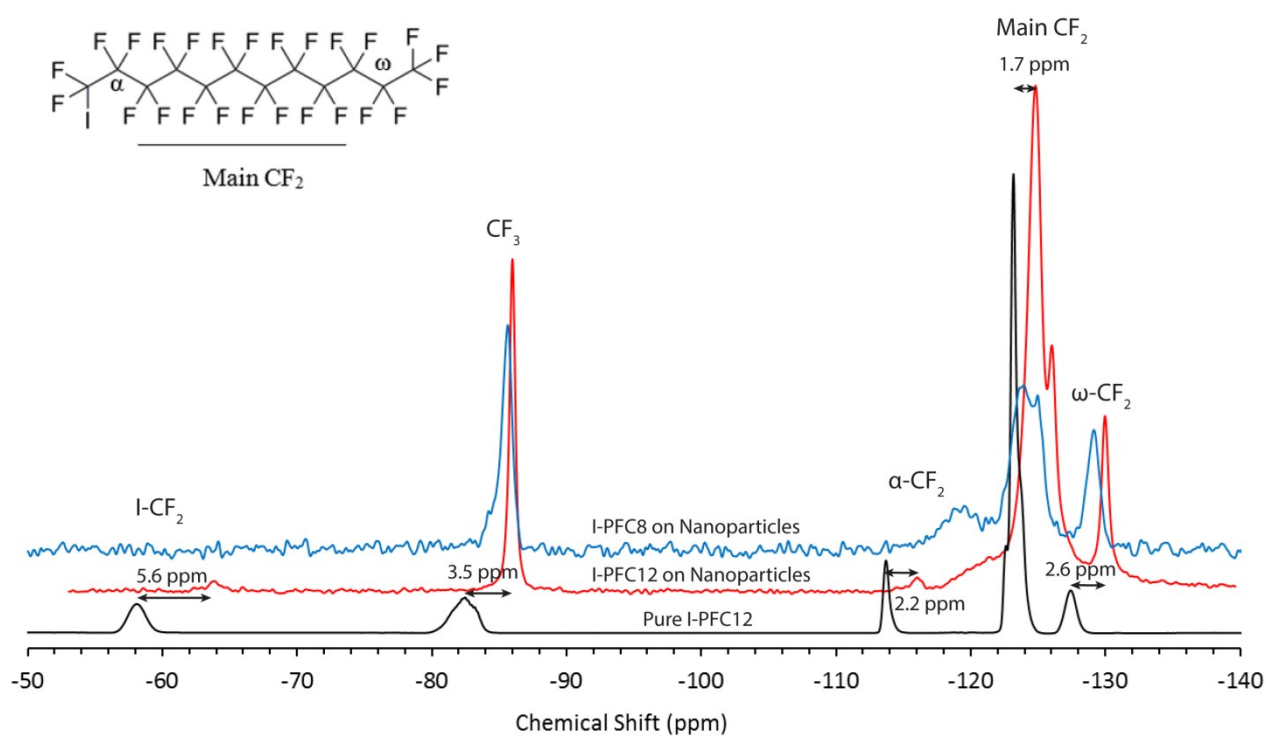


Figure S8 ^{19}F MAS NMR spectra of: a) Pure I-PFC12 (black, recycle delay 10 s; scans = 16), b) I-PFC12 adsorbed to SiO_2 microparticles (red, recycle delay 2 s; scans = 4096), and c) of I-PFC8 adsorbed to SiO_2 microparticles (blue, recycle delay 10 s; scans = 1024). The spectra were acquired at $B_0 = 16.4$ T at ambient temperature with MAS spinning frequency of 60 kHz. Inset: Molecular structure of I-PFC12 with labeled CF_x fragments.

Evidence of photodissociation of pure I-PFC8

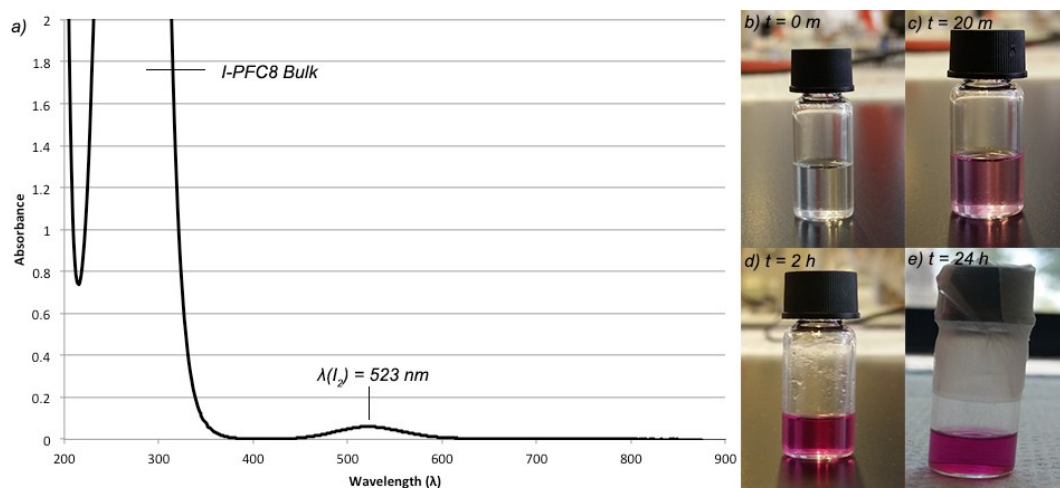


Figure S9: a) UV-Vis spectrum of pure I-PFC8 liquid after ageing in sunlight, showing peak absorbance at 523 nm, characteristic of molecular iodine. b-e) Photographs demonstrating the rapid appearance of a pink color in pure I-PFC8 under standard lab conditions (exposure to sunlight).

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