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Supporting Information for

Super-Hydrophobic Covalent Organic Frameworks for Chemical Resistant Coatings, Hydrophobic Paper and Textile Composites

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1. Materials and methods

Synthesis of monomers: Tris(4-formylphenyl)amine was synthesized following our earlier reported procedure.^[38]

p-phenylenediamine was purchased from Sigma Aldrich used without any other purification.

Preparation of 2,4,6-Tris(4-aminophenyl)-s-triazine: In a typical synthesis, trifluoromethanesulfonic acid was added to 100mL of CHCl₃ in a two neck round bottom flask maintained at 0°C under a N₂ atmosphere. The solution was stirred for 2hrs. Separately, 4-aminobenzonitrile (4gm, 0.033mol) was dissolved in 80mL of CHCl₃ in an inert atmosphere. The latter was added drop by drop to the trifluoromethanesulfonic acid solution at 0°C under a blanket of N₂. The reaction mixture was warmed up to room temperature and was allowed to stir under N₂ for 48hrs. Completeness of the reaction was monitored using TLC. The contents were neutralized by adding about 250 mL of 2M NaOH solution. Upon neutralization, a pale yellow precipitate was obtained, which was filtered and washed with copious amounts of distilled water. Yield: 94%. Product was characterized by ¹H and ¹³C NMR.

¹H NMR (400 MHz, DMSO-D6): δ = 8.37 (d, J = 8.7 Hz, 6H), 6.70 (d, J = 8.6 Hz, 6H), 5.96 (s, 6H). ¹³C NMR (101 MHz, DMSO-D6): δ = 170.09 (s), 152.95 (s), 130.50 (s), 122.96 (s), 113.18 (s).

Terephthaldehyde was purchased from Sigma Aldrich used without any further purification.

Synthesis of IISERP-COF2-\beta or 1: The COF was prepared by a slight modification of our earlier procedure.^[38] Tris(4-formylphenyl)amine (80 mg, 0.24mmol) and 1,4-diaminobenzene (40 mg, 0.38mmol) were weighed into a Pyrex tube and dissolved in ethanol (3.0 mL), to this o-dicholorobenzene (o-DBC) (3.0mL) was added and stirred until a clear yellow solution was observed. Following this, 0.25 mL of aqueous acetic acid (3 M solution) was added to this mixture. Then the Pyrex tube was flash frozen in a liquid nitrogen bath and sealed. The Pyrex tube along with its contents was placed in an oven at 120°C for 3 days. The product, yellow fluffy powder was obtained in about 86% yield. (Formula for COF: C₂₄₀N₃₂H₁₆₈, M. Wt. 3500.2g/mol, CHN **Obsd.** C = 77.15; H = 4.355; N = 10.85. **Calc.** 82.36; H = 4.84; N = 12.81%).

Synthesis of HSERP-COF4 or 2: About 17mg of terephthalaldehyde (0.127mmol) was dissolved in 3mL of analytical grade ethanol in a Pyrex tube, to this, 3.0mL of O-dicholorobenzene was added and stirred until a clear solution was observed. Then, about 30mg of 2,4,6-Tris(4-aminophenyl)-s-triazine (0.085mmol) and 0.25 mL of aqueous acetic acid (3 M) were added to the reaction mixture and contents were stirred for 30mins. The pyrex tube along with its contents was flash frozen in a liquid nitrogen bath and sealed. The tube was placed in an oven and heated to 120°C and was left undisturbed for 3 days. The product, a yellow powder was washed with copious amounts of MeOH, DMF, Acetone, dioxane and THF. Yield 54%. Formula for IISERP-COF4: $C_{66}N_{12}H_{42}$, M. Wt. 1003.14 g/mol, CHN Obsd. C = 72.93; H = 3.51; N = 15.07%. Calc. C = 79.0; H = 4.22; N = 16.76%. Note: the discrepancy in the CHN values can be attributed to the presence of some unreacted terminal aldehyde and amines and this can be estimated to be about 7% and their presence is evidenced also from the peaks observed in the IR and SSNMR spectra.

Procedure for coating of COFs on glass slides: In a typical coating, about 30mg of Poly(methyl methacrylate) (PMMA) was dissolved in 2ml of dichloromethane. This solution was coated on the glass plate using a spin coater (1000 rpm, dropped over 10mins). This upon UV curing gives a transparent coating of PMMA. Immediately after the UV curing, a dispersion of 100mg of COF in 5ml of methanol, prepared by sonicating for about 2h, was spin-coated on to this PMMA surface. The COF dispersion was added using a micropipette on to the PMMA coated glass that was spun at 1000rpm and the addition was carried out over a period of 30 mins. Finally the coating was dried in a UV-curer over 12hrs. *Important remark:* The PMMA coating on its own did not show any hydrophobic property it merely improves the adherence of the COF. A contact angle measurement carried out on this neat PMMA coated glass indicated contact angles of ~41 \pm 3°.

Self-cleaning studies:

For self-cleaning property investigations, fine dispersion of dust particles (ground dry grass collected from natural habitat, ~20-25mg) on the COF coated glass surface was prepared. To this about 5mL of water was added by using a syringe (Supporting Video S6).

Composite preparation: In all cases, the composite using paper or textile were prepared by dipcoating. In a typical experiment, a slurry was made by mixing the COF (\sim 25mg) and 50µL of epoxy resin (paint adhesive) in 5mL toluene. The paper or textile was dipped in this slurry for 2 mins and then dried. The dried composite was thoroughly washed in water and even squeeze-dried. No powder or flakes peeled off from the composite. This was dried under a UV-lamp for about 3hrs. All composites turned yellow when coated with the COF and the colour remained unchanged even after the UV treatment.

Important: The epoxy resin on its own was exceptionally hydrophilic and a coating made only with neat epoxy resin on a glass did not have any hydrophobic character.

2. Analytical characterizations

The complete characterization of the COF was done employing a series of analytical techniques. Powder X-ray diffraction (PXRD) was carried out using a Rigaku Miniflex-600 instrument and processed using PDXL software and/or were carried out using a full-fledge Bruker D8 Advance instrument.

Thermogravimetric Analysis (TGA) was carried out on NETSZCH TGA-DSC system. The routine TGAs were done under N_2 gas flow (20ml/min) (purge + protective) and samples were heated from RT to 900°C at 2K/min.

Infrared spectra were recorded using Bruker FT-IR (ATR mode) spectrophotometer in the range of 4000-600 cm⁻¹. NMR spectra were recorded on a 400 MHz Jeol ECS-400 and Bruker 500MHz.

Field Emission Scanning Electron Microscopy images were collected using Ultra Plus Field Emission Scanning Electron Microscope with integral charge compensator and embedded EsB and AsB detectors. Oxford X-max instruments 80 mm². (Carl Zeiss NTS, Gmbh), Imagin conditions: 2kV, WD=2mm, 200kX, Inlens detector. Adsorption measurements were carried out using a Quanta Chrome pore and surface area analyzer, Model IQ dual port. High resolution transmission electron microscopy images were collected from a FEI (Jeol FEG 2100F is the model) high resolution transmission electron microscope (HRTEM) equipped with field emission source operating at 300 KeV was used.

Computation: The COF's PXRD pattern indexing, space group determination, atomic manipulations, refinements and the final structure and geometry optimizations were done using the Materials Studio V.6.0 of the *Accelrys* program.



Figure S1. Structures of the α and β phases of IISERP-COF2. The α form has planar layers π -stacked in a perfectly eclipsed configuration with an interlayer distance of 3.4Å, while the β has buckled layers due to the flexibility at the sp³ nitrogen centers. This gives rise to a pseudo-three dimensional structure to the β phase with 22Å pores in the interlayer spaces.



Figure S2. A comparison of the simulated and experimental powder pattern for the eclipsed and staggered (*ABCABC*... stacking) for IISERP-COF4 or **2**. The highlighted part shows the peak corresponding to the $(0\ 0\ 2)$ reflection and the relative intensity of this peak matches much better for the slipped layers.



Figure S3. A Pawley refinement fit for slipped model of IISERP-COF4 with a *ABCABC*...stacking. Unit cell in P1: a = 38.434; 37.173; 10.147Å; α = 89.98°; β = 90.01°; γ = 119.96°; Rp = 3.90%; wRp = 5.10%.



Figure S4. A variable temperature PXRD analysis of IISERP-COF2 showing the transformation of α -phase to β upon desolvation, the shrinking of the a-axis and expansion of the c-axis during this irreversible phase transformation is shown using dotted lines.



Figure S5. (A) A schematic representation of the different unique carbon atoms in the COF. Solid state ¹³C-MASNMR spectrum of the B) IISERP-COF2- α ; C) IISERP-COF2- β or 1.



Figure S6. (A) A schematic representation of the different unique carbon atoms in **2** and its corresponding solid state ¹³C-MASNMR spectrum.



Figure S7. Comparison of the IR Spectra of **1** and its corresponding monomers. Note: Band at 1619 cm⁻¹ are assigned to the C=N of the Schiff bond and one at 1168 cm⁻¹ corresponds to the sp³ tetrahedral C-N bond in **1**.



Figure S8. Comparison of the IR Spectra of **2** and its corresponding monomers. The stretching bands at 1621cm⁻¹ and 1598 cm⁻¹ correspond to C=N Schiff and aromatic triazine C=N bonds, respectively. Note: Bands present at 3400 cm⁻¹ (N-H str.) and 2850 cm⁻¹ (C-H str.) indicate the presence of unreacted terminal terephthaldehyde and amine groups.

3. Microscopy



Figure S9. FESEM images of 1 showing hexagonal sheets which aggregated into spheres.



Figure S10. FESEM Images of 2 showing spherical balls which self-aggregate into wooly fibers.



Figure S11. HRTEM images: (a) showing **1** growing as thin wafers, some of which fold up like paper. (b) Larger flakes which seems to curl inwards along the edges resembling a dry leaf.



Figure S12. HRTEM image of 2 (after sonication) showing the aggregate of flaky structures.

IISERP-COF2

Spectrum processing : Peaks possibly omitted : 0.524, 2.627 keV Processing option : All elements analysed

(Normalised) Number of iterations = 3 Standard :

- C CaCO3 1-Jun-1999 12:00 AM
- N Not defined 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
СК	81.74	83.93
NK	18.26	16.07
Totals	100.00	







Figure S13. Energy dispersive X-ray Analysis (EDAX) and elemental mapping for 1 obtained from FESEM.

IISERP-COF4

Spectrum processing :

Peaks possibly omitted : 2.625 keV Processing option : All elements analyzed (Normalised) Number of iterations = 3 Standard : C CaCO3 1-Jun-1999 12:00 AM

N Not defined 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
ск	78.84	83.46
NK	21.16	16.54
Totals	100.00	



Electron Image 1



Elemental mapping



Electron Image 1

Figure S14. Energy dispersive X-ray Analysis (EDAX) and elemental mapping for 2 obtained from FESEM.

4. Adsorption and porosity analysis



Figure S15. a) Pore size distribution of 1 obtained using a non-localized DFT (NLDFT on carbon) fit carried out on a 77K N_2 isotherm. b) The DFT fit to the 77K N_2 isotherm.



Figure S16. A BET and Langmuir fit for as-synthesized 1 obtained from 77K N₂ isotherms.

CO₂ adsorption in **2**:

IISERP-COF4, **2**, showed very low N₂ uptake even at 77K and the isotherm represented a non-porous character and no model (Barrett-Joyner-Halenda (BJH), BET or NLDFT) could be fitted with satisfactory R² values. Fortuitously, **2** exhibited a moderate CO₂ uptake of 2.7mmol/g at 195K with a characteristic type-I isotherm (Figure S14). A NLDFT model (slit pore, Carbon) yielded an acceptable fit with a surface area of 337 m²/g and suggested the presence of ultra-micropores of size ~ 3.5 Å with a pore volume of 0.066 m²/g (Figure S15). It is to be noted that these values need to be considered only with a moderate confidence as the employed DFT model is not perfected for 195K CO₂ isotherms. However, this strategy of utilizing 195K CO₂ isotherms for surface area determinations has been accepted in case of ultra-microporous MOF, which tend to exhibit only CO₂ uptakes.[1S]



Figure S17. CO₂ adsorption isotherms of 2.



Figure S18. Pore size distribution of **2** obtained using a non-localized DFT (NLDFT on carbon) fit carried out using the 195K CO₂ isotherm. The resulting surface area was $337m^2/g$.

Ref: [1S] R. Vaidhyanathan, S. S. Iremonger, K. W. Dawson and G. K. H. Shimizu, Chem. Commun. 2009, 5230.



Figure S19. Solvent sorption isotherms carried out using 1 at 308K.



Figure S20. Virial fit carried out using the water vapor isotherms of **1**. Average error for the fit = 2.7073.



Figure S21. (A) Virial fit carried out using the Benzene sorption isotherms of **1**. Average error for the fit (Benzene) = 5.0952. (B) Virial fit carried out using the Toluene sorption isotherms of **1**. Average error for the fit (Toluene) = 7.4450.



Figure S22. Solvent sorption isotherms carried out using 2 at 308K.



Figure S23. Virial fit carried out using the water sorption isotherms of **2**. Average error for the fit = 2.5936.



Figure S24. Virial fit carried out using the Benzene sorption isotherms of **2**. Average error for the fit = 1.4665.

5. Calculations of hydrophobicity-related parameters of IISERP-COF2 (1) & IISERP-COF4 (2)

Roughness:

$$R = \frac{s + n (2\pi rh)}{s}$$

Roughness, R, for IISERP-COF2 = 1.4239 (radius, r = 5nm; height, h = 27nm; s = 90000nm²); for IISERP-COF4 = 1.5181 (radius= 5.5nm; height= 30 nm; s = 90000nm²). All dimensions from AFM. Meanwhile, the roughess R, can be estimated from contact angle measurements on the bulk sample from the expression $\cos \theta_{rough} = R \cos \theta_{flat}$, which yields values of 3.67 and 2.94 for 1 and 2, respectively.

Solid fraction in contact with surface:

According to Cassie-Baxter model, the surface roughness can create air gap that can be trapped between the nanostructures and the water droplet. The apparent contact angle in this state is described by:

 $\cos \theta_{rough} = \phi_s \left(\cos \theta_{flat} + 1 \right) \text{ - } 1$

For IISERP-COF2: $\phi_s = 0.070$. For IISERP-COF4: $\phi_s = 0.065$.

where ϕ_s is fraction of the solid surface in contact with the water droplet.

'Most stable' apparent contact angle calculated using the advancing and receding contact angles.

 $\cos \theta_{\rm ms} = (\cos \theta_{\rm adv} + \cos \theta_{\rm rec})/2$

For IISERP-COF2: $\cos \theta_{ms} = 159^{\circ}$ For IISERP-COF4: $\cos \theta_{ms} = 161^{\circ}$.

Calculating experimental contact angles (θ) using dimensions from AFM, assuming the surface as being made of asperities with cylindrical shape.

Area used from AFM, $s = L^2 = 300 \times 300 \text{ nm} = 90000 \text{ nm}^2$; radius of the individual cone (approx. to a cylinder) = 5 nm for 1 and 5.5nm for 2, average height of the individual cone ~27nm for 1 and ~30nm for 2.

 $\theta_{\rm W} = \cos^{-1} \left[\left(1 + \frac{n(2\pi rh)}{s} \right) \cos \theta_{\rm y} \right]$ $\theta_{\rm CB} = \cos^{-1} \left[\frac{n(\pi r^2)}{s} \left(\cos \theta_{\rm y} + 1 \right) - 1 \right]$

For IISERP-COF2: $\theta w = \cos^{-1}(-1.35) =$ undefined; $\theta_{CB} = \cos^{-1}(-0.99786) = 176.25^{\circ}$ For IISERP-COF4, $\theta w = \cos^{-1}(-1.45) =$ undefined; $\theta_{CB} = \cos^{-1}(-0.99792) = 176.31^{\circ}$



Figure S25. Represents the AFM image from which the average diameter was determined to be ~ 10 nm for IISERP_COF2 using ImageJ software. B) Shows the representative AFM image obtained by drop casting the sample on the grid, from which the average height was determined to be ~ 27 nm for both COFs. About 8 such images were collected and the height used in the calculations was estimated by averaging these heights.



Figure S26. AFM image from which the average diameter was determined to be ~ 11 nm for IISERP_COF4 using ImageJ software. B) Shows the representative AFM image from which the average height was determined to be ~ 30 nm for both COFs. About 8 such images were collected and the height used in the calculations was estimated by averaging these heights.

Comments on the roughness and Wenzel vs CB model based contact angles of the COFs: It has been shown in systems with controllable surface roughness, tungsten on Teflon, [ref. 61 of the maintext] that the contact angles related to increasing surface roughness of a CB state shows a linear relationship with the fraction of surface in contact with the liquid (φ_s). And based on this linear relationship, it can be expected that the large contact angle of these COFs should result in a φ_s of ~0.1 and in fact, the φ_s calculated from the equation: $\cos \theta_{rough} = \varphi_s (\cos \theta_{flat} + 1) - 1...$ Equn. 3, associated with typical CB state, turns out to be ~0.1.

The contact angles can be estimated from the experimentally observed dimensions of the asperities assuming either a Wenzel state, equation 3: $\theta_w = cos^{-1} \left[\left(1 + \frac{n(2\pi\rho h)}{s} \right) cos\theta_y \right]$, or

a CB state, equation 4: $\theta_{CB} = \cos^{-1} \left[\frac{n(\pi \rho^2)}{s} (\cos \theta_y + 1) - 1 \right].$

In our case, we could not get a meaningful fit following the Wenzel equation, but the CB equations yielded apparent contact angles of 159 and 176° for **1** and **2**, respectively. These agree with the values determined from the contact angle measurements.

References:

Correlation between surface roughness and hydrophobicity of GLAD RF sputtered PTFE/W/Glass nanorod thin films, A. Bayat, M. Ebrahimi, A.Z. Moshfegh, *Vacuum*, **2014**, *101*, 279-282.

6. Contact angle measurements



Figure S27. Experimental measurement of the contact angle for water droplet on the surface of a packed powder of **1**. The contact angles are obtained from Image J.

	Low Bond Axisymme	tric Drop Shape A	nalysis	2
DROP PARAM	ETERS			
				Optimize
b [pixels]			315	V
c [m-2]	water	-	1.35E5	M
x0 [pixels]			942	r
y0 [pixels]			353	M
h [pixels]	\frown		477	~
d [pixels]			996	
Relative appro	oximation: 105 %			
DROP PROPER	RTIES			
Contact angle Contact angle	e (Canvas): e subpixel:	163.064		
Drop Volume:	1.36E1 mm^3	Drop Surface: 2	2.55E1 mm	n^2
Surface of co	ntact: 2.37E0 mm^2			
Region En	ergy	Q	Gradi	ent Energy
	Un	ified		54 % gradier
Table	Settings	About		Close

Figure 28. Experimental measurement of the contact angle for water droplet on the surface of a packed powder of 2.



Figure S29. Image of a water droplet on the glass coated with (a) **1** and (b) **2**. The water droplet could be dragged along the surface without losing its shape and retains a very high dynamic contact angle as shown. Please see the attached Video S5 for a real time experiment.



Figure S30. Image obtained after dropping benzene on the surface of the COF powders, (a) 1 and (b) **2**. As can be seen the benzene contact angle on both COFs seem to be close to 0° .

	DROP PARAMETERS
	Optimize
	b [pixels] 77 🔽
	c [m-2] water 1.35E5
	x0 [pixels] 773 🖌
	y0 [pixels] 591 🖌
	h [pixels] 147 🖌
	d [pixels] 768
· · · ·	Relative approximation: 7 %
	DROP PROPERTIES
	Contact angle (Canvas): 162.504
	Contact angle subpixel: Drop Volume: 2.65E-1 mm^3 Drop Surface: 1.94E0 mm^2
\rightarrow	Surface of contact: 5.74E-2 mm ²
	OPTIMIZATION
	Region Energy Gradient Energy
	Unified 50 % gradient
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DROP PARAMETERS
Optimize
b (pixels) 132 🕑
c [m-2] water 1.35E5
x0 [pixels] 370 🗹
 y0 [pixels] 499 🕑
h [pixels] 240 🗹
d [pixels] 768
Relative approximation: 21 %
DROP PROPERTIES
Contact angle (Canvas): 158.685
Contact angle subpixel:
Drop Volume: 1.28E0 mm^3 Drop Surface: 5.42E0 mm^2 Surface of contact: 2.92E 4 mm/2
Destant Factor
Region Energy Gradient Energy
Unified 50 % gradient
Table Settings About Close

Figure S31. Image of water droplets on the surface of **2**. Calculated hysteresis from contact angles, Hw = contact angle of big drop (volume = 1.28 E0 mm^3) - contact angle of small drop (volume = 2.65 E-1 mm^3)= 3.8° .

7. AFM studies



Figure S32. Top: Micrometer resolved AFM images of **1** showing their tendency to stack. **Bottom:** Nanometer resolved AFM image showing the surface roughness with asperities of hierarchically sized.





Figure 33. AFM images of **2** showing large number of asperities on its surface which contribute to its roughness and to the observed super-hydrophobicity. It shows the presence of nano-sized asperities present on the surface.

9. COF Coatings and their characteristics



Figure S34. 1 coated on a glass surface (orange colour); 2 coated on glass.



Figure S35. HR Microscopy images showing the homogeneous distribution of the COFs coated on the glass surface at 500 micrometer (a) **1** and (b) **2**.



Figure S36. Three-dimensional reconstruction from the Video S1 of the supporting information. Figure shows the bouncing and splitting of water droplets on the surface of the COF coated glass slide. Such phenomenon is typically observed in nano etched metal surfaces touted for extremely high super-hydrophobicity. Note: the water droplet was dropped from just \sim 3-4cm above the surface. For the original video was sliced into small segments and the image was constructed by tracing the shape and size of the droplets.



Figure S37. (A) Change in the color of IISERP-COF4 upon soaking in 3M HCl (aq) for 24hrs. (B) The reddish colored sample was isolated by filtration. (C) the reddish solid turns into yellow color resembling the color of the pristine IISERP-COF4 upon washing with water and methanol. Water droplet contact angles of the acid treated bulk samples are shown in Figure S38.



Figure S38. The water droplet contact angles on the acid treated samples of the COFs. Most of the super-hydrophobicity is retained. Note: The samples were filtered from the acid solution and were dried in air. No washings were done. Notice the homogeneity of the sample and its uniform color, which suggests that it is not partial decomposition of the sample.



Figure S39. Shows 12M NaOH solution sitting on the surface of the COF. After 72hrs the NaOH crystallizes on the COF and no trace of water is found. The water droplet contact angles of this NaOH treated surface is shown below in Figure S40.

		DROP PARAME	TERS			
IISERP-GUFZ						Optimize
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and the second		y0 [pixels]			413	
		h [pixels]			357	V
		d [pixels]	-		768	
	10 m 10 m	Relative approx	cimation: 51 %			
		DROP PROPER	nes			
		Contact angle	Canvas):	158.967		
		Contact angle s	subpixel: 1.82E0 mm^3	Drop Surface: 1	1.29E1 mr	n^2
	-	Surface of con	tact: 9.55E-1 mm^2			
> <		OPTIMIZATION				
	X	Region Ene	ray		Gradie	ent Energy
	1		Unifie	b		50 % gradient
	1	Table	Settings	About		Close
IISERP-COF4						
		DROP PARAMI	TERS			
						Optimize
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		c [m-2]	water	-	1.35E5	
		x0 [pixels]	Q		477	
		y0 [pixels]	-Q		65	~
		h (pixels)			410	
	-	d (pixels)		0	768	
	Concession of the local division of the loca	Relative appro	ximation: 72 %			
		DROP PROPER	THES			
		Contact angle	(Canvas):	160.694		
		Drop Volume:	subpixel: 7.83E0 mm^3	Drop Surface: 1.	.78E1 mm	12
		Surface of co	ntact: 1.45E0 mm^2			
		OPTIMIZATION	L			
		Region En	ergy 📿		Gradie	ent Energy
			Unifie	be		50 % gradient
	الهويد ورشد	Table	Settings	About		Close
		Real Property lies and the second			and because	

Figure S40. Water droplet contact angles measured on samples of **1** and **2** treated with 12M NaOH solution. The crystallized NaOH solid was removed and the same surface was used to measure these contact angles.



Figure S41. Contact angle measurements on the COFs after treatment with vapors of 3M HCl in methanol and 3M NaOH in methanol, in separate experiments. Water droplet contact angle for (A) **1** treated with acidic methanol vapors; (B) **1** treated with basic methanol vapors; (C) **2** treated with acidic methanol vapors; (D) **2** treated with basic methanol vapors.



Figure S42. 77K N₂ isotherms of **2** treated with acidic methonolic vapors and basic methanolic vapors. Open circles- adsorption; closed circles- desorption.



Figure S43. Image of a water droplet on the COF coated glass surface, showing the contact angles for water droplets maintained at different acidities: (a) 1 @ pH = 1 (b) 1 @ pH = 7 (c) 1 @ pH = 14 (d) 2 @ pH = 1 (e) 2 @ pH = 7 (f) 2 @ pH = 14.



Figure S44. Trends in the contact angles as a function of pH variation. Note every reading is associated with an average error of ± 2 to 3° .

Effect on the super-hydrophobicity upon prolonged treatment with 12M NaOH:

DROP P.	ARAMETERS				
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c (m-2)	l wate	эг Х	v 1	.35E5	r V
		0			
x0 [pixe	els]			553	V
yū (pixe	els] 🔤	\bigtriangledown		260	×.
h [pixel	ls]	_		359	r
d [pixel	ls] 🗖		\Box	768	
Relative DROP P	e approximatio	m: 52 %			
Contact	t angle (Canva	s):	161.565		
Contact Drop Vo	t angle subpixe olume: 4.83E0	el: mm^3	Drop Surface: 1.30	DE1 mr	n^2
Surface	e of contact: 8.	57E-1 mm^2			
OPTIMIZ	ZATION				
Reg	gion Energy			Gradie	50 % gradient
		Unified	d		50 % graulent
	Table	Settings	About		Close
DROP b [pix c [m- x0 [pi y0 [pi h [pix	PPARAMETERS vels] vels] vels] vels] vels] vels]			384 1.35E5 621 284 391 769	Optimize V V
Relati	ive approximat	tion: 83 %	~	708	
DROP	PROPERTIES				
Conta	act angle (Canv act angle subpi	as): xel:	104.933 104.933		
Drop	Volume: 1.58E	1 mm^3	Drop Surface: 2.4	4E1 m	m^2
Surfa OPTIM	ICE OF CONTACT:	1.03E1 mm*2			
R	egion Energy			Grad	ient Energy
		Unifie	ed		37 % gradient
	Table	Settings	About		Close

Figure S45. Showing difference in contact angle between the COF powder coated surface vs. a smoothened surface (8 ton pressure) of a pellet of **1**. The roughness factor calculated using Wenzel state, $\cos \theta_w = r \cos \theta_Y$; $\theta_Y = 162^\circ$, $\theta_W = 105^\circ$ ($\pm 2^\circ$). The contact angles are obtained from Image J.

	Low Bond Axisymmetric Drop Shape Analysis					
	DROP PARAMETERS					
			Optimize			
ſ	b [pixels]	31	5 🖌			
	c [m-2]	water 1.35E	5 🖌			
		_ Q				
	x0 [pixels]	94	2 🖌			
	y0 [pixels]	35	3 🖌			
	h [pixels]	47	7 🖌			
	d [pixels]	99	6			
	Relative approx	ximation: 105 %				
	DROP PROPER	TIES				
	Contact angle	(Canvas): 163.064				
	Contact angle	subpixel: 1 36E1 mm^3 Drop Surface: 2 55E1 n	um≜2			
	Surface of con	tact: 2.37E0 mm^2				
	OPTIMIZATION					
	Region Ene	rgy Gra	dient Energy			
		Unified	54 % gradient			
	Table	Settings About	Close			



Figure S46. Showing difference in contact angle between the coated surface or powder vs. a smoothened surface of a pellet of **2**. The roughness factor calculated using $\cos \theta_w = r \cos \theta_Y$; $\theta_Y = 163^\circ$, $\theta_W = 109^\circ (\pm 3^\circ)$.



Figure S47. AFM image of a smoothened surface of 2.



Figure S48. Height profiles for the smoothened surface of 2 as observed from AFM images.

Calculation of roughness parameter for the smoothened surface: $S = L^2 = 300 \times 300 = 90000 \text{ nm}^2$; Average height = ~10nm; radius of the asperity = ~5nm. Roughness parameter, R = 1.1.