Supporting Information

Rim-Differentiated Pillar[5]arene Modified Surfaces for Rapid PFOA/PFOS Detection

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Content

1.   General information

All chemicals for synthesis of pillar-5-arenes were purchased from Sigma-Aldrich. Potassium heptadecafluorooctane-1-sulfonate, pentadecafluorooctanoic acid, were purchased from Sigma Aldrich. 12-Azidododecylphosphonic acid was purchased from Sikemia. All chemicals were used without any further purification unless noted. Porous aluminum oxide substrates with dimensions of 36×8 mm^2 and average pore size of 200 nm were purchased from MicroDish BV.

^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at 298 K. High-resolution mass spectra (HR-MS) were measured on a QTOF micro-spectrometer using electrospray ionization (ESI) in positive mode (ESI+) or in negative mode (ESI-), MeOH was used as solvent. Microwave reaction was performed with Monowave 400 from Anton Paar.

ITC titration was measured by MicroCal VP-ITC isothermal titration calorimeter. A reversed ITC was used due to the poor solubility of PFAS, which does not allow for a run using a normal ITC for 1:10 ratio binding. A 20 mM phosphate buffer with pH 5.6 was used for both host and guest solutions. The host is in syringe and the guest is in the cell. To minimize the error, all experiments were repeated 2 times. All values are an average of duplicate experiments.

XPS was measured by a JEOL JPS-9200 photoelectron spectrometer. Samples were stored in glass vials. All samples were measured by a focused monochromated Al Kα X-ray source (spot size of 300 μm) at a constant dwelling time for survey scan 50 ms and narrow scan of 100 ms and pass energy: survey scan = 50 eV narrow scan = 10 eV. The power of the X-ray source was 240 W (20 mA and 12 kV). Charge compensation was applied during the XPS scans with an accelerating voltage of 2.8 eV and a filament current of 4.8 A.

Infrared reflection absorption spectroscopy (IRRAS) spectra were acquired using a Bruker Tensor 27 FT-IR spectrometer with a variable angle reflection accessory (Auto Seagull, Harrick Scientific). A Harrick grid polarizer was installed in front of the detector to record spectra with p-polarized (parallel 90°) radiation relative to the plane of incidence at the sample surface. The incidence angle was fixed at 55°, with spectra obtained over 1024 scans at a resolution of 1 cm^{-1} per modulation center. A freshly cleaned Al_2O_3 flat surface served as the reference. Data were collected as differential reflectance versus wavelength. All spectra were recorded in a dry environment at room temperature, with a linear baseline correction applied.

Contact angle was measured by a Krüss DSA 100 goniometer. The volume of a drop of demineralized water was 2 μL.
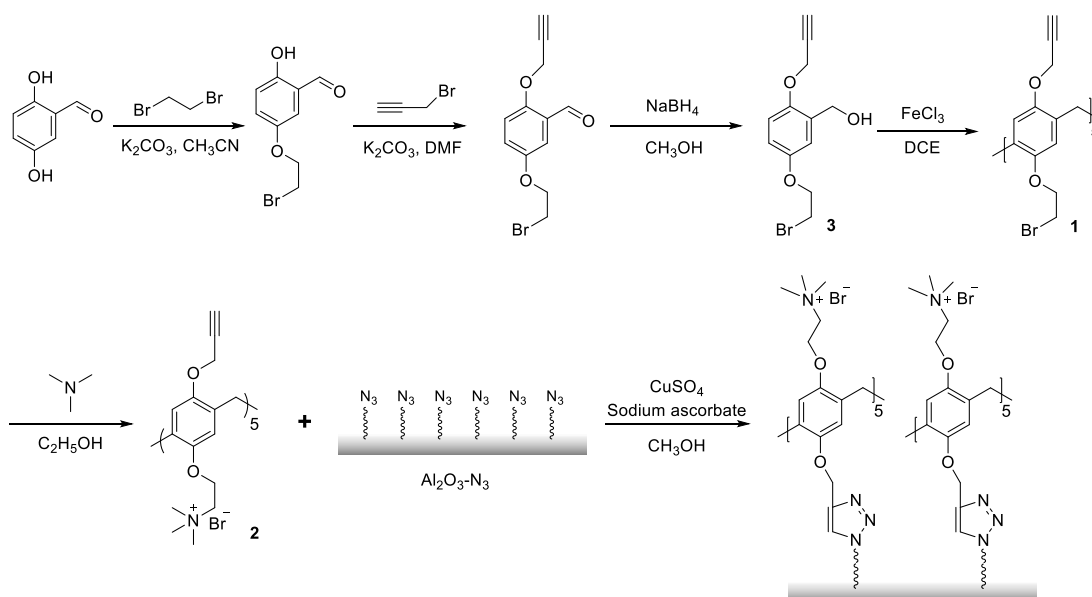
2. Synthesis

Scheme S1. Synthesis route of DAF-P5s.

Compound (3): This compound was synthesized according to previously reported literature procedure.[1]

RD-P5 (1): Compound 3 (1.4 g) was dissolved to 1,2-dicholoroethane (65 mL). FeCl$_3$ (82 mg) was then added to the solution under ambient temperature. The mixture was stirred at ambient temperature for 40 min. After this time, the reaction mixture was quenched by addition of 30 mL of MeOH. Solvent was removed by rotary evaporator. The product is further purified by column chromatography (DCM:PE=1:1). The resulting light yellow solid was dissolved in 1 mL ethyl acetate then MeOH was added dropwise until white precipitate was almost formed, the mixture was let stand for overnight to recrystalize RD-P5 **1**. The white product RD-P5 **1** was dried under vacuum. Yield: 181 mg, 13%. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.92 (s, 5H), 6.82 (s, 5H), 4.58 (d, J=2.4, 10H), 4.21 (t, J = 5.7 Hz, 10H), 3.83 (s, 10H), 3.63 (t, J=5.7, 10H), 2.27 (t, J=2.4, 5H). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 149.7, 149.4, 129.1, 128.9, 116.0, 115.4, 79.4, 69.0, 56.5, 30.89, 29.7. HRMS (ESI) m/z [M+K]$^+$ Calcd. C$_{60}$H$_{55}$O$_{10}$Br$_5$K for 1368.9344, found 1368.9339.

RD-P5 (2): RD-P5 **2** (1.0 g) was dispersed to EtOH (60 mL). Trimethylamine (10 mL of 3.2 M solution in MeOH) was added to the solution under ambient temperature. The mixture was heated to reflux and refluxed at stirring for 12 hours. After this time all solvents were removed by rotary evaporator. The product was washed with 100 mL of diethyl ether for 3 times and 100 mL of acetone for 3 times. White product **3** was dried under vacuum. Yield: 1.2 g, 94%. ^{1}H NMR (400 MHz, Methanol-d$_4$) δ = 7.01 (s, 5H), 6.73 (s, 5H), 4.52 (s, 10H), 4.34 (s, 10H), 4.03 (s, 10H), 3.86 (s, 10H), 3.38 (s, 45H), 2.59 (s, 5H). ^{13}C NMR (101 MHz, Methanol-d$_4$) δ = 151.1, 150.7, 131.0, 130.3, 117.6, 116.6, 80.3, 76.9, 67.1, 64.5, 58.0,

55.0, 30.6. HRMS (ESI) m/z [M-4Br]$^{4+}$ Calcd. $C_{75}H_{100}N_5O_{10}Br$ for 327.4158, found 327.4157.

Surface modification of Al$_2$O$_3$:   Al$_2$O$_3$ surfaces were sonicated in acetone, hexane and dichloromethane for 5 min each. After that 10 surfaces were immersed in a freshly prepared mixture of 37% hydrochloric acid (10 mL) and methanol (10 mL) (1:1 v/v) in a beaker for 30 min. After that Al$_2$O$_3$ surfaces were immersed in a 1 mM solution of 12-azidododecylphosphonic acid in absolute ethanol for 30 min at 60 °C and kept for 16 h at room temperature. Afterward, surfaces were rinsed with absolute ethanol and heated at 100 °C under vacuum for 1 h. Thus obtained Al$_2$O$_3$ surfaces were rinsed and sonicated in absolute ethanol (twice for 5 min) and dichloromethane (5 min) and dried under a flow of nitrogen or argon to obtain the azido-terminated Al$_2$O$_3$ surfaces (**Al$_2$O$_3$-N$_3$**).

Copper-Catalyzed Azide−Alkyne Cycloaddition (CuAAC) Reaction on Al$_2$O$_3$-N$_3$: A solution of 10.2 mg of RD-P5 **2**, 3.2 mg of CuSO$_4$•5H$_2$O, and 2.5 mg of sodium ascorbate in 2.5 mL ultrapure water was placed in a reaction tube together with a Al$_2$O$_3$-N$_3$ surface. The reaction tube is heated in a microwave oven at 50 °C for 60 min under stirring. After the reaction, the substrate was thoroughly rinsed, sonicated in water (5 min), ethanol (5 min) and dichloromethane (5 min), and dried in air.

3. Interpretation of ITC result

Interpretation of binding constants K_a.

For 1:1 binding, K_a value is defined by the equation (1):

$$K_a = \frac{[HG]}{[H][G]} \tag{1}$$

For 1:2 or higher stoichiometry number, K values can be defined by equations (2) or (3):

$$K_1 = \frac{[HG]}{[H][G]} \quad K_2 = \frac{[HG_2]}{[HG][G]} \quad \dots \quad K_n = \frac{[HG_n]}{[HG_{n-1}][G]} \tag{2}$$

$$K_a = \frac{[HG_n]}{[H][G]^n} \tag{3}$$

The unit of K_n in (2) is M^{-1} whereas the unit of K_a in (3) is M^{-n}. And relation between these two binding constants is:

$$K_a = K_1 \times K_2 \times \dots \times K_n \tag{4}$$

The K_n in (2) and K_a in (3) have different units, K_n in (2) has a unit of M^{-1}, which is comparable with the K_a for 1:1 ratio binding. But K_a in (3) has a unit of M^{-n}, which is not comparable with the K_a for 1:1 ratio binding.

In the ITC titration data, each peak corresponds to the heat change caused by each injection. Integrating peaks, we can get the heat change q_i for injection number i. The heat change will decrease due to the gradually saturation of host.

$$\Delta q_i = q_i - q_{i-1} \tag{5}$$

In the mean time Δq_i also represent not all guest are bound to host, we set the amount of guest that bound to host as $[G]_{bound}$, and we acquire equation (6).

$$\Delta q_i = \Delta[G]_{bound} \times V_{cell} \times \Delta H \tag{6}$$

Then we introduce the saturation degree Y_i to connect Δq_i and K_a.

$$Y_i = \frac{[HG]}{[H]_{unbound} + [HG]} = \frac{K_a \times [G]}{1 + K_a \times [G]} \tag{7}$$

So Δq_i can also be written as:

$$\Delta q_i = n\Delta[H] \times V_{cell} \times \Delta H \times Y_i \tag{8}$$

The trend of Δq_i should fit the nonlinear regression according to (8):

$$Y_i^2 - \left(1 + \frac{1}{nK_a[H]} + \frac{[G]}{n[H]}\right) \times Y_i + n[H][G] = 0 \tag{7}$$

[G] is the total concentration of guest added until injection number i. And K_a represent the strength of each binding sites on the host to the guest. The stoichiometry number is n, meaning the amount of binding site that each host has. The obtained K_a values from ITC for multivalent binding are the average of K_1, K_2, K_3, K_4....K_n and it is comparable with the K_a for 1:1 binding model.[2]

4. Crystallographic details

Table S1. Crystal data and structure refinement for **2**.

|	
Identification code	rd-p5-2
Empirical formula	C161.80 H256.40 Br10 N10 O37
Formula weight	3732.85
Temperature	150.00(10) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 26.50453(14)$ Å $\quad \alpha = 90°.$
	$b = 14.53119(6)$ Å $\quad \beta = 114.2663(7)°.$
	$c = 25.82392(16)$ Å $\quad \gamma = 90°.$
Volume	$9067.12(9)$ Å^3
Z	2
Density (calculated)	1.367 Mg/m^3
Absorption coefficient	3.214 mm^{-1}
F(000)	3886
Crystal size	0.768 x 0.426 x 0.061 mm^3
Theta range for data collection	3.574 to 73.117°.
Index ranges	-32<=h<=32, -17<=k<=17, -32<=l<=27
Reflections collected	211614
Independent reflections	18049 [R(int) = 0.0449]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.118
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18049 / 252 / 1294
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0972
R indices (all data)	R1 = 0.0395, wR2 = 0.0993
Extinction coefficient	n/a
Largest diff. peak and hole	1.158 and -0.776 e.Å^{-3}
CCDC	**2359089**

5. NMR data
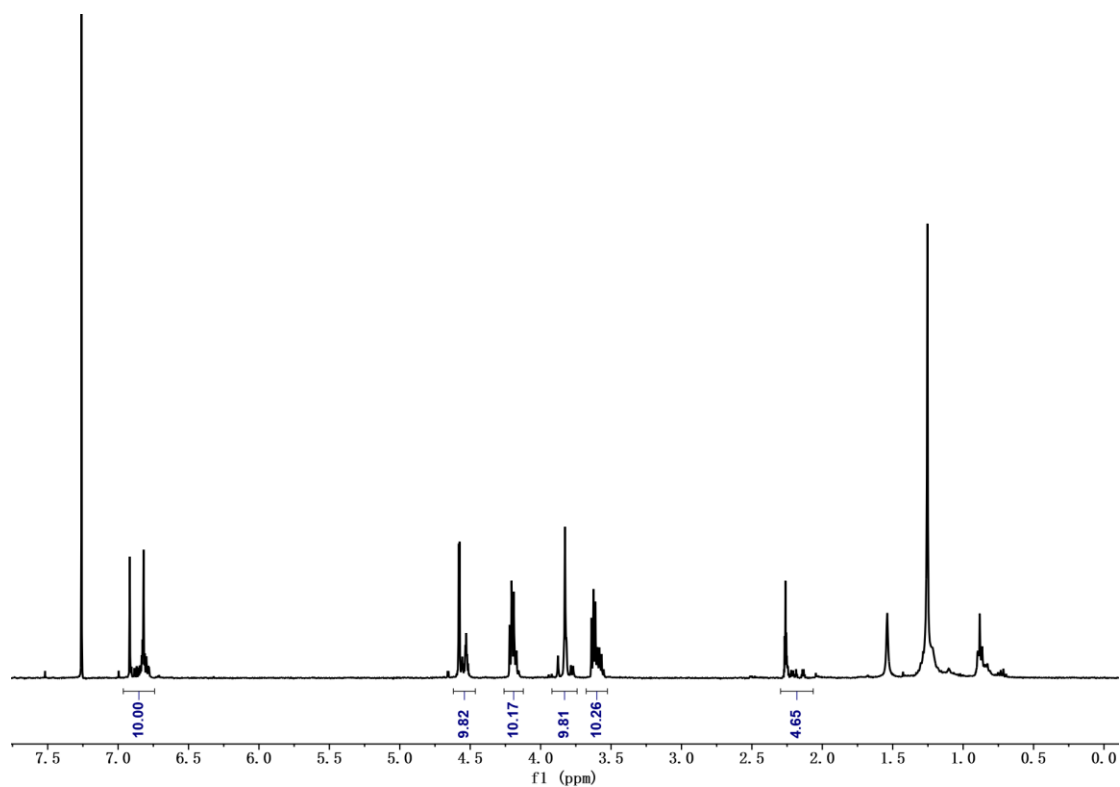
Figure S1 ^{1}H NMR (400 MHz, CDCl$_3$) of RD-P5 **1** crude reaction mixture after MeOH work-up.
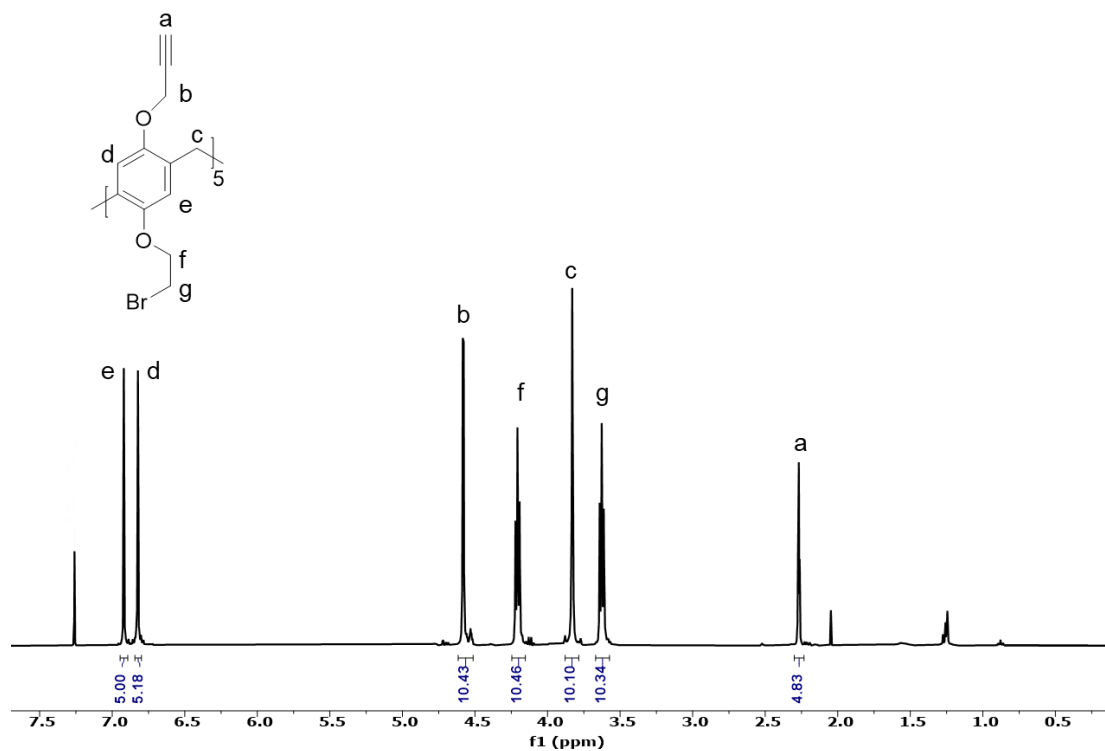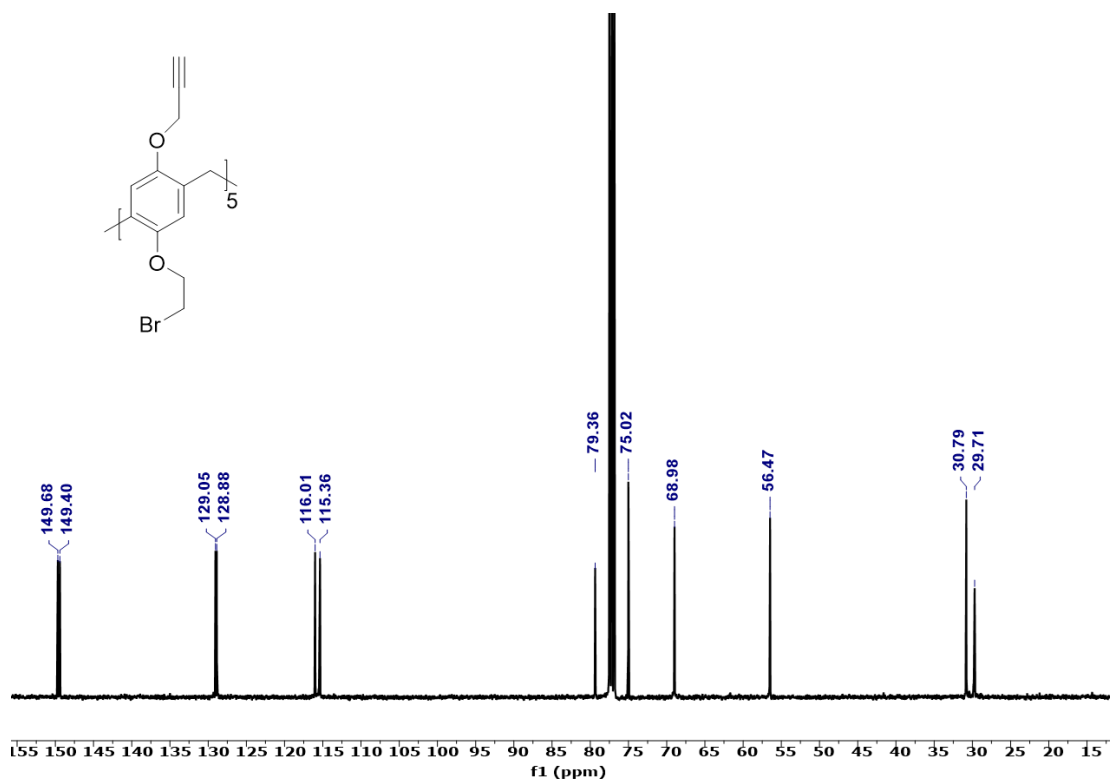

Figure S2 ^{1}H NMR (400 MHz, CDCl$_3$) of isolated RD-P5 **1**, after crystallization.
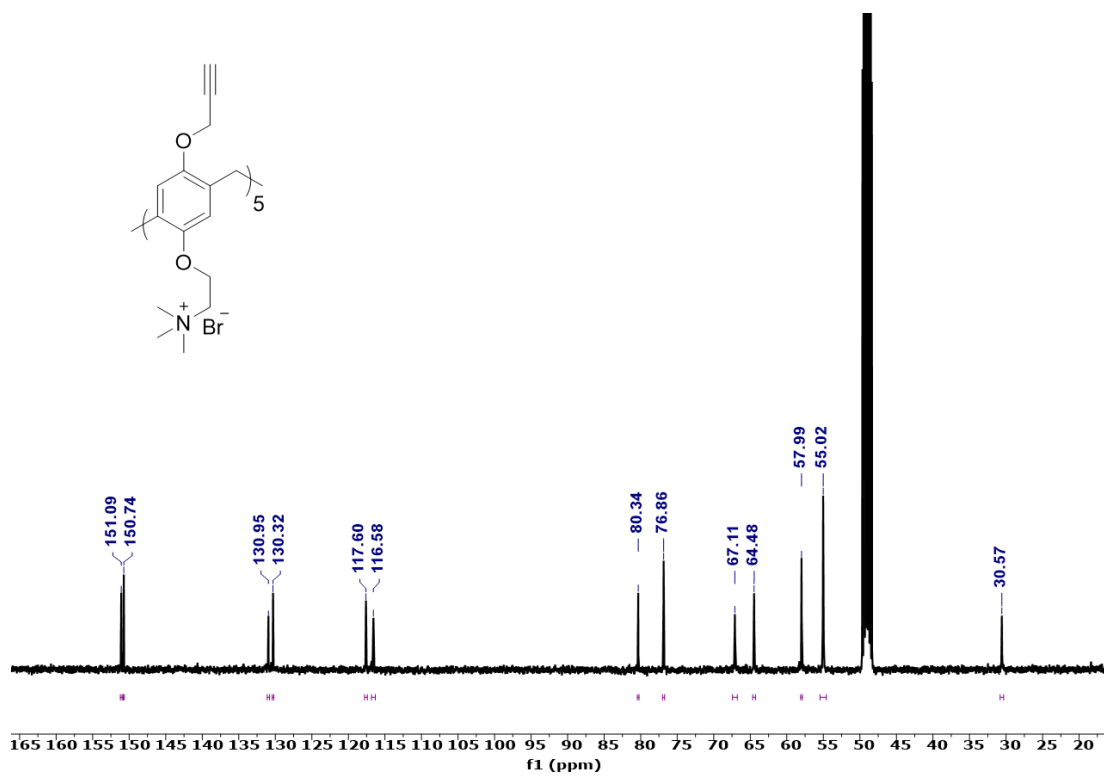
Figure S3 ^{13}C NMR (101 MHz, CDCl$_3$) of isolated RD-P5 **1**, after crystallization.

Figure S4 ^{1}H NMR (400 MHz, MeOD-d_4) of RD-P5 **2**.
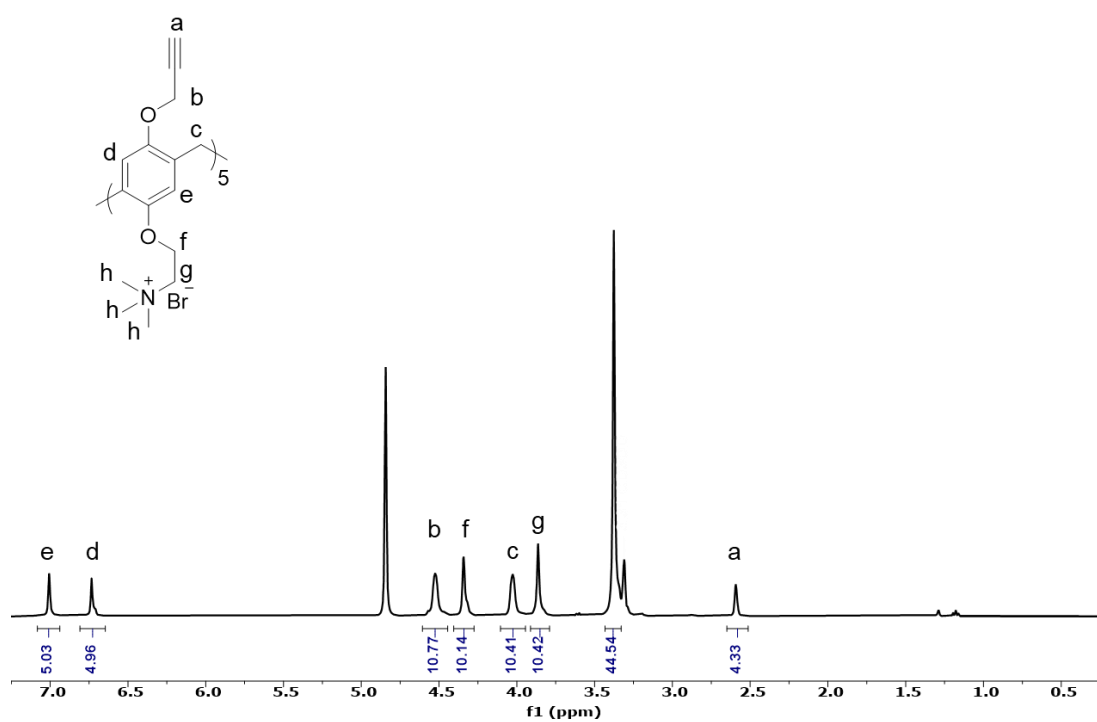
Figure S5 ^{13}C NMR (101 MHz, MeOD-d_4) of RD-P5 **2**.

6. ITC data
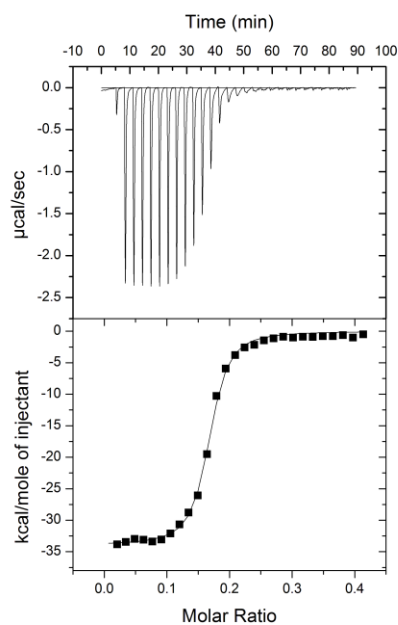
Figure S6. ITC of RD-P5 **2-PFOS**. [H]= 0.2 mM [G]= 0.1 mM, reversed ITC titration was applied to this experiment. Ka= (2.59±0.37) ×10^6 M^{-1}, n=5.64±0.017
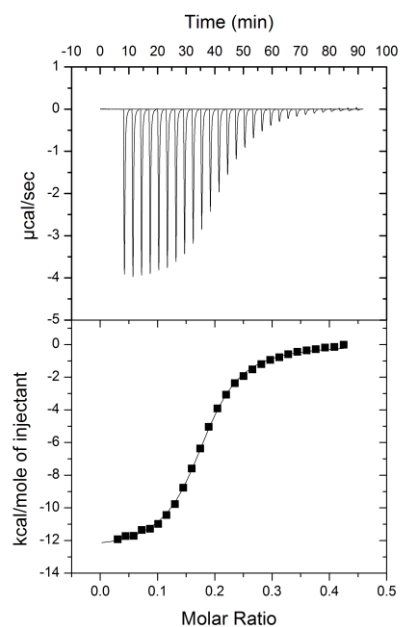

Figure S7. ITC of RD-P5 **2-PFOS -PFOA**. [H]= 1 mM [G]= 0.5 mM, reversed ITC titration was applied to this experiment. Ka= (2.6±0.89) × 10^4 M^{-1}, n=5.93±0.030

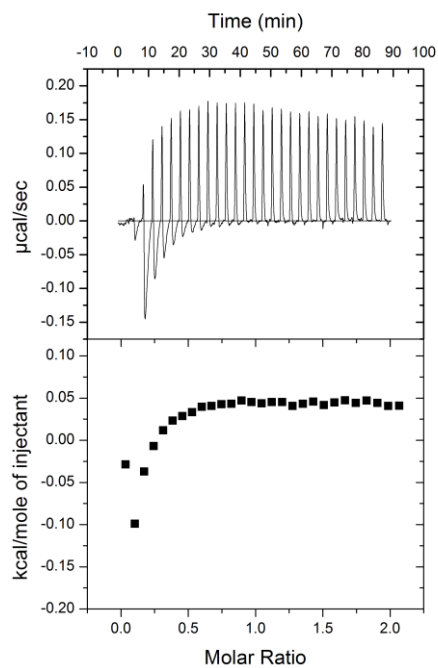**Figure S8** ITC of RD-P5 **2-OA**. [H]= 1 mM [G]= 10 mM, normal ITC titration was applied to this experiment.

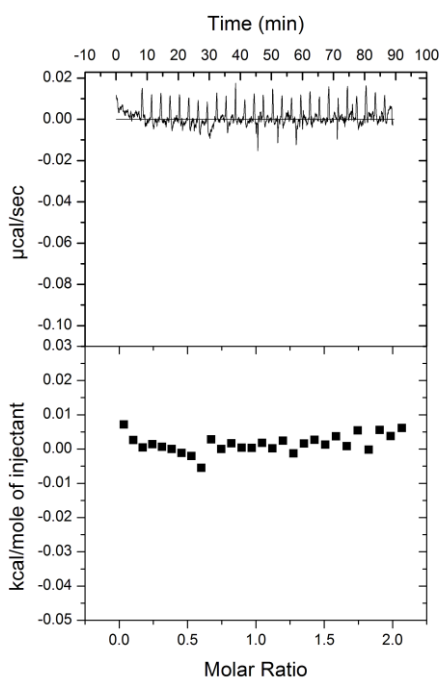**Figure S9** ITC of RD-P5 **2-OSA**. [H]= 1 mM [G]= 10 mM, normal ITC titration was applied to this experiment.

7. PFAS detection experiments

Contact Angle measurement: the RD-P5 **2**-modified Al_2O_3 surface was submerged in 20 mL of PFOA/PFOS/salt solution for 5 minutes. Subsequently, the surface was rinsed with Milli-Q water for 10 seconds, followed by drying under argon flow for contact angle measurement. The volume of drop is 2 µL, the measurement start after the droplet is stably formed. Contact angle is measured in 3 different places on surfaces to eliminate error.

Environmental sample preparation: Water taken from Yitong River was filtered with 5 µm Nylon filter then measured by the method as mentioned above(YR). Water taken from Nederrijn river in Wageningen was filtered with 5 µm Nylon filter to remove the insoluble particles(NR). Then 1 mL of 100 µg/L PFOS solution was added to 999 mL of Nederrijn water to form NR-1. And 10 mL of 10 mg/L PFOS solution was added to 990 mL of Nederrijn water to form NR-2.

Repeated use of Al_2O_3-2 surface: To demonstrate the reusability of the Al_2O_3-**2** surface, the surface was submerged in 20 mL of aqueous PFOS solution (10 mg/L) for 5 minutes. Subsequently, the surface was rinsed with Milli-Q water for 10 seconds, followed by drying under argon flow for contact angle measurement. After that the surface was submerged in 20 mL of acetone, sonicated for 5 min and flushed with EtOH for 10 seconds, followed by drying under argon flow for next round contact angle measurements. We repeated measurement-washing procedure for 10 cycles. No significant change in contact angle response was observed after 10 cycles. Notably, the regeneration can only recover the surface to hydrophilic state, not to superhydrophilic state. XPS further confirmed there is 2.3% F remaining on the surface (Figure S14).
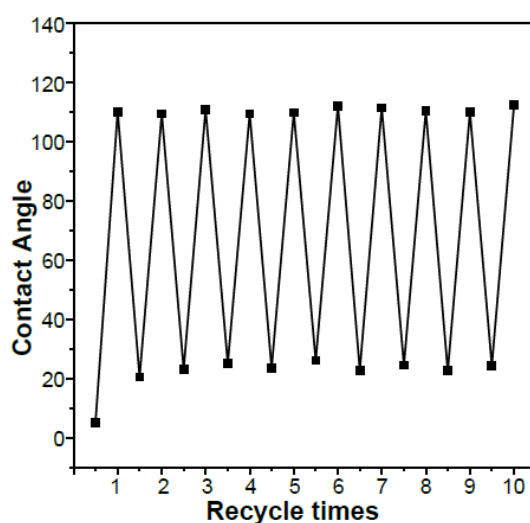

Figure S100 Repeated use experiment performed with 10 mg/L PFOS solution.
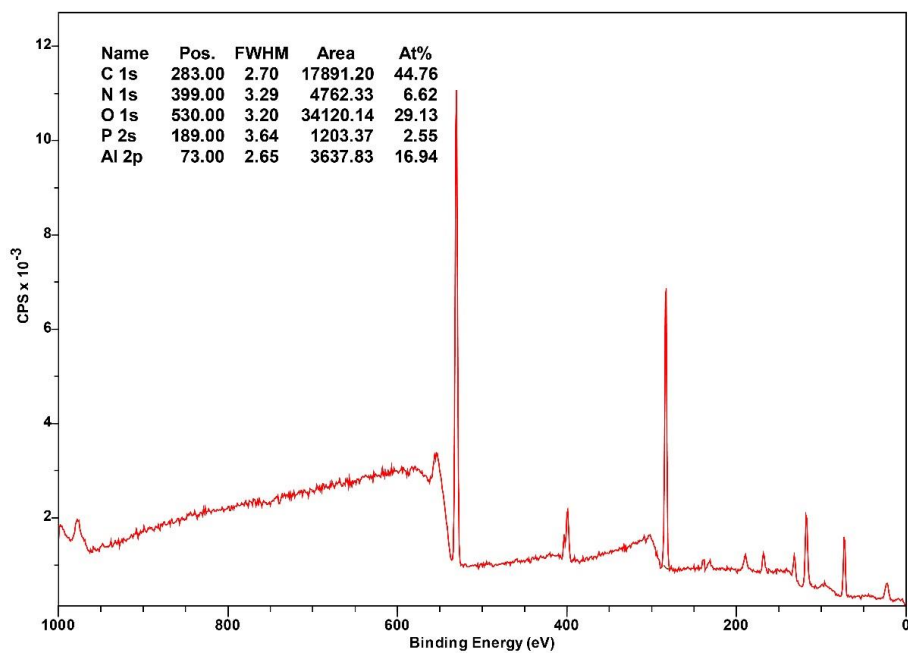
8. XPS and IRRAS data

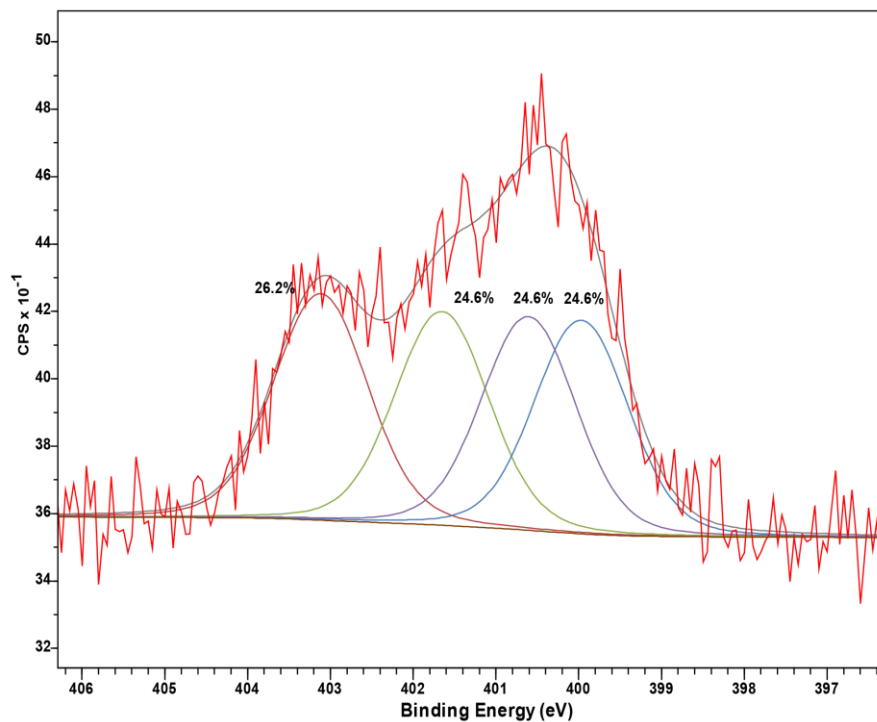| Name	Pos.	FWHM	Area	At%
C 1s	283.00	2.70	17891.20	44.76
N 1s	399.00	3.29	4762.33	6.62
O 1s	530.00	3.20	34120.14	29.13
P 2s	189.00	3.64	1203.37	2.55
Al 2p	73.00	2.65	3637.83	16.94

Figure S111 Survey scan of Al_2O_3-N_3.

Figure S122 N 1s narrow scan of Al_2O_3-RD-P5/PFOS.
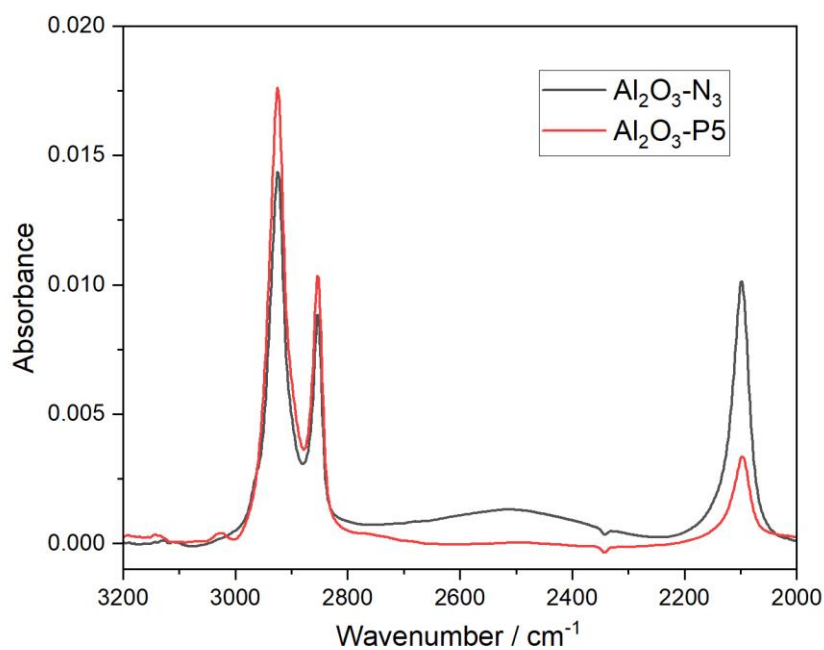
Figure S133 IRRAS spectra of Al_2O_3-**2** (Al_2O_3-P5) and Al_2O_3-N_3 (with baseline correction).

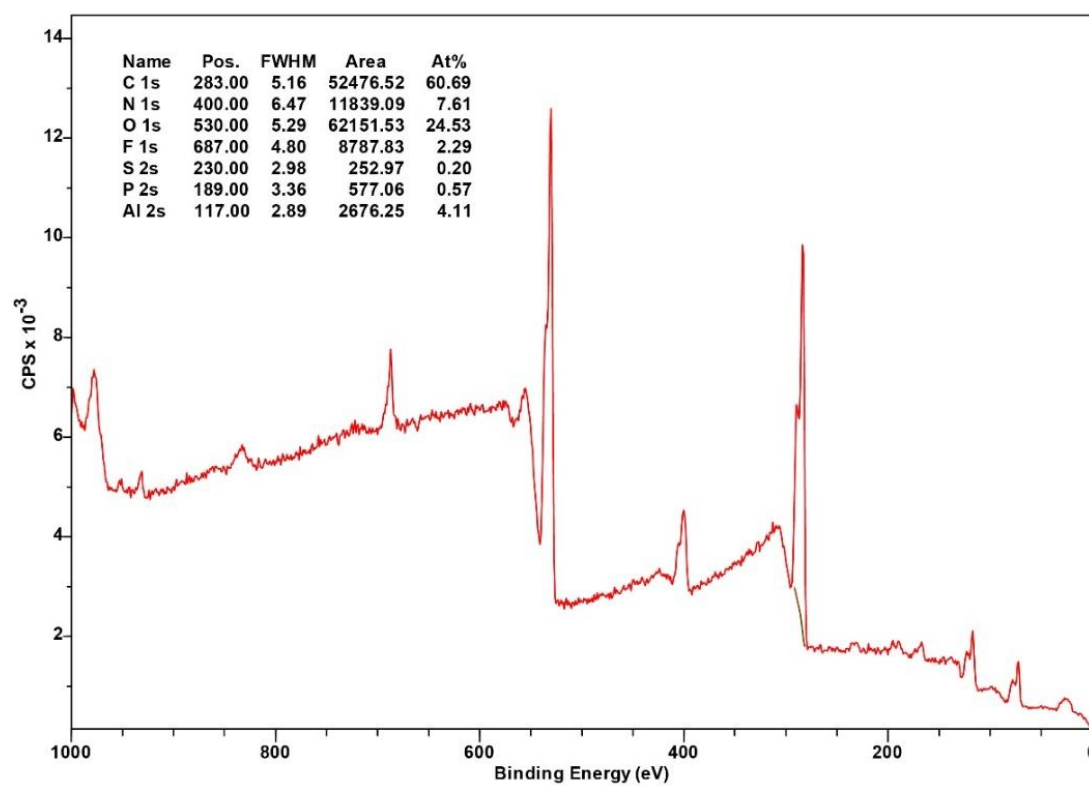| Name	Pos.	FWHM	Area	At%
C 1s	283.00	5.16	52476.52	60.69
N 1s	400.00	6.47	11839.09	7.61
O 1s	530.00	5.29	62151.53	24.53
F 1s	687.00	4.80	8787.83	2.29
S 2s	230.00	2.98	252.97	0.20
P 2s	189.00	3.36	577.06	0.57
Al 2s	117.00	2.89	2676.25	4.11

Figure S144 Survey scan of Al_2O_3-**2** after 10 cycles of PFOS absorption (10 mg/L) and washing with acetone.

9. References

[1]   W. Mao, S. Zhan, B. Zhu, D. Ma, *The Journal of Organic Chemistry* **2018**, 83, 4147.

[2]   I. Jelesarov, H. R. Bosshard, *Journal of Molecular Recognition* **1999**, 12, 3.

[3]   G. Sheldrick, *Acta Crystallographica Section A* **2015**, 71, 3.

[4]   C. B. Hubschle, G. M. Sheldrick, B. Dittrich, *Journal of Applied Crystallography* **2011**, 44, 1281.

[5]   C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *Journal of Applied Crystallography* **2006**, 39, 453.