Supporting Information

A Molecular Metal Organic Cage as a Recyclable Sponge for PFOS Removal from Water

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Experimental details

General considerations

All solutions were prepared with ultrapure Millipore deionized water obtained via a Milli-Q Advantage A10 Direct water purification system, with a resistivity of 18.2 MΩ cm at 25.0 °C. The chemicals used for the experiment were used without further purification: palladium chloride (TCI Chemicals, ≥98%), silver chloride (Thermo Scientific Chemicals, ≥99.9%), benzonitrile (Acros Chemical, 98%), sodium hydroxide (VWR, ≥97%), sodium chloride (VWR, ≥99%), sodium sulfate (VWR, anhydrous ≥99.0%), sodium carbonate (VWR, anhydrous ≥99.5%), potassium phosphate tribasic (Thermo Scientific Chemicals, anhydrous, 97%), sodium fluoride (Thermo Scientific Chemicals, 99.99%), sodium nitrate (BeanTown Chemical, 99%), nitric acid (ARISTAR® ACS, VWR Chemicals BDH®, 68-70%), acetonitrile (VWR, anhydrous (max. 0.003% H_2O) ≥99.9%), deuterium oxide (Millipore Sigma, MagniSolv™, 99.9% D), acetonitrile-D3 (Millipore Sigma, 99.8% D), tetraethylammonium perfluorooctane sulfonate (BeanTown Chemical, 98%), perfluorooctanesulphonic acid, potassium salt (Strem Chemicals, 97%). The tetraethylammonium perfluorooctane sulfonate salt was used as the source of PFOS in all experiments except in the DOSY experiments. NMR spectra were collected using a Bruker AVIII HD 400 MHz Nanobay spectrometer for all experiments except for DOSY measurements which used a Bruker AVIII-HD 500 MHz spectrometer. ^{1}H NMR spectra are referenced to the solvent residual peak at 4.79 ppm in D_2O, 1.94 ppm in CD_3CN, and 2.5 ppm in DMSO-d_6, unless otherwise noted.[1] ^{19}F NMR spectra are referenced to C_6F_6.[2] The small benchtop centrifuge used was a Benchmark LC-8 Series, with 12 mL tubes, at 350 rpm.

Synthesis and sample preparations

Synthesis of the organic linker of the MOC. The synthesis was performed following modified literature procedures.[3,4] In a 200 mL round bottom flask, 4-cyanopyridine (3.0 g, 29.1 mmol) was stirred and heated to 90 °C. NaOH power (128 mg, 3.2 mmol) was carefully added to the flask, followed by 3 mL of toluene. The mixture was heated at 145 °C for four days. Any remaining solvent was evaporated, and the resulting solid was washed with pyridine followed by acetone. The solid was then dissolved in ca. 25 mL of 2 M HCl and filtered. The solution was neutralized to pH 7 with 5 M NaOH and a white solid precipitated. The solid was collected and thoroughly washed with water, acetone, and finally diethyl ether. The solid was dried under vacuum to yield 2.2 g (~60%) of white powder. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.95 (d, 2H, J = 4.6 Hz), 8.57 (d, 2H, J = 4.6 Hz).

Synthesis of Pd(bpy)Cl₂. $PdCl_2$ (471 mg, 2.66 mmol) was added to 180 mL of acetonitrile.[5] The mixture was stirred and heated to reflux for one hour at 70 °C. Next, 415 mg (2.66 mmol) of 2,2'-bipyridine were added to the mixture which was further stirred and heated to reflux overnight at 70 °C. After cooling down to room temperature, the reaction was filtered to recover an orange solid. The solid was washed twice with acetonitrile and dried under vacuum. ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) 9.14 (d, 2H, J = 6.8 Hz), 8.58 (d, 2H, J = 7.9 Hz), 8.36 (t, 2H, J = 7.6 Hz), 7.81 (t, 2H, J = 7.3 Hz).

Synthesis of Pd(bpy)(NO$_3$)$_2$. Pd(bpy)Cl$_2$ (500 mg, 1.51 mmol) was dissolved in 140 mL of 1 M HNO$_3$ and heated to 70 °C.[5] Then, silver nitrate (255 mg, 1.51 mmol) was added, and the system was further stirred and heated at 70 °C overnight, shielded from light. A white solid was removed through filtration, yielding a clear yellow filtrate. The solvent was removed under vacuum to yield a solid. The solid was then fully dissolved in ~70 mL boiling 1 M HNO$_3$ and the solution left to crystallize at ca. 5 °C. Three days later, yellow crystals were obtained. The crystals were collected by filtration and dried under vacuum. ^{1}H NMR (DMSO-d$_6$, 400 MHz): δ (ppm) 8.60 (d, 2H, J = 8.0 Hz), 8.45 (t, 2H, J = 7.9 Hz), 8.28 (d, 2H, J = 5.9 Hz), 7.82 (t, 2H, J = 6.0 Hz).

Synthesis of the MOC. Pd(bpy)(NO$_3$)$_2$ (200 mg, 0.56 mmol) and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (109.2 mg, 0.35 mmol) were mixed in 12 mL of a 1:1 water:methanol mixture.[6] The mixture was then heated to 78 °C for 40 minutes, during which time a clear yellow solution was obtained. The solution was then cooled down to room temperature and filtered. The solvent of the filtrate was evaporated and the obtained solid was dried under vacuum. A bright yellow solid was obtained, which was dried under vacuum (283 mg, 91.5% yield). ^{1}H NMR (D$_2$O, 400 MHz): δ (ppm) 9.53 (d, 24H, J = 6.8 Hz), 8.97 (d, 24H, J = 6.8 Hz), 8.56 (d, 12H, J = 8.1 Hz), 8.45 (t, 12Hz, J = 7.9 Hz), 7.77 (d, 12H, J = 6.6 Hz), 7.67 (t, 12H, J = 6.8 Hz).

NMR titration procedure. A stock solution of PFOS (12.6 mM) was prepared in D$_2$O. Separately, a solution (630 µL) in D$_2$O was prepared in a J-Young style NMR tube containing 2 mM of the MOC and 1.9 mM of ethylene carbonate as an internal standard. ^{1}H and ^{19}F NMR spectra were collected initially and after each addition of PFOS (0.25 equivalents for each 25 µL PFOS stock solution addition).

Representative procedure for the preparation of the solid host-guest samples. In a typical experiment, 8 mg of the MOC were dissolved in a minimum amount of water. Separately, 25 mg of PFOS (18 equivalents compared to the MOC) were dissolved in 10 mL of water. The MOC solution was slowly added to the vial containing the solution of PFOS. A white precipitate formed. The mixture was sonicated for ca. 5 minutes. Then the mixture was centrifuged at 350 rpm for about 0.5 to 1 hour. The supernatant was removed, and the solid was then washed three times with water to remove the excess PFOS and counter anions. The solid was dried under vacuum. The solid is insoluble in water but soluble in acetonitrile.

Water treatment procedure. A stock solution of PFOS was prepared by dissolving the solid PFOS in ultrapure water. A solution of dilute PFOS in water was prepared, and the concentration of PFOS was measured by ion-exchange chromatography. The MOC was added to the PFOS solution. The mixture was sonicated for 30 minutes to 1 hour, then centrifuged at 350 rpm for 30-45 minutes, depending on scale. The concentration of PFOS left in the solution was measured again by ion-exchange chromatography.

***MOC recycling procedure*.** Example procedure: a 1.68 mM PFOS solution was prepared by dissolving 425 mg of PFOS in 400 mL of water. Separately, 95.9 mg of the MOC was dissolved in 5 mL of water. The solution of MOC was slowly added dropwise to the PFOS solution, causing the formation of a white precipitate. Once the addition was completed, the mixture was quickly stirred and then sonicated for 5 minutes. Next, the mixture was centrifuged (at 350 rpm for 40-60 minutes) to help the solid settle. The solution was removed, and water was added to the solid and the mixture centrifuged once more to wash the solid. The supernatant was removed, and the solid was collected and dried under vacuum.

The solid was then dissolved in dry acetonitrile (ca. 100 mL) and slowly added into a 5 mL solution of dry acetonitrile containing $TBANO_3$. This immediately led to the formation of a precipitate. The mixture was quickly stirred to mix thoroughly. Next, the mixture was centrifuged, the supernatant removed, and the solid washed once with dry acetonitrile. The obtained solid was dried under vacuum. This affords the clean initial MOC with nitrate counter anions.

The whole procedure was repeated two more times with the recovered MOC, and at the end of the 3 cycles, 90.7 mg of MOC were recovered (94.6%). ^{1}H NMR showed the presence of the initial MOC resonances in D_2O, while no resonances were seen in ^{19}F NMR data, which confirms that the recovered MOC is free of PFOS (Figure S12-S13).

Titration and competition experiments

^{1}H NMR data of the MOC titration with PFOS in D_2O

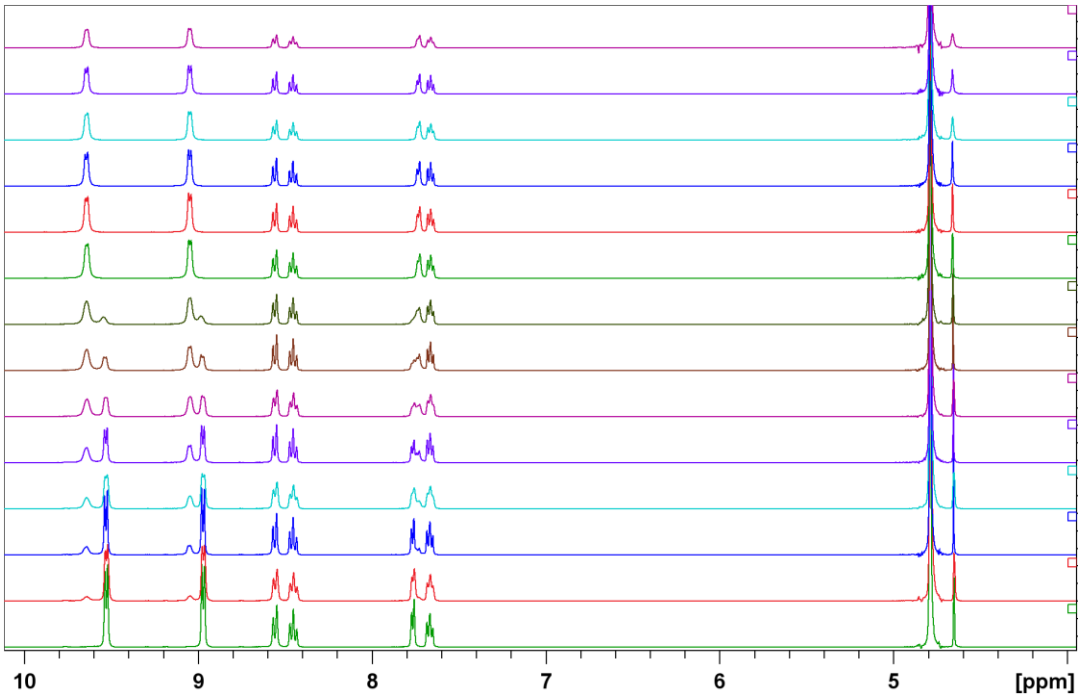

Figure S1. ^{1}H NMR (400 MHz) spectra of the MOC in the absence (green, bottom) and in the presence of increasing equivalents of PFOS (from red, bottom, to top): 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 equivalents. Solids started appearing in the tube at 2.5 equivalents and became more prominent as the titration progressed.

Job Plot

Based on the titration data, the mole fraction of the guest PFOS (χ) was plotted as a function of $\frac{n}{n+m} \times [MOC]_0$ in which n is the peak integration value of the host-guest complex, m is that of the pure MOC, and $[MOC]_o$ is the initial concentration of the MOC host.[7]

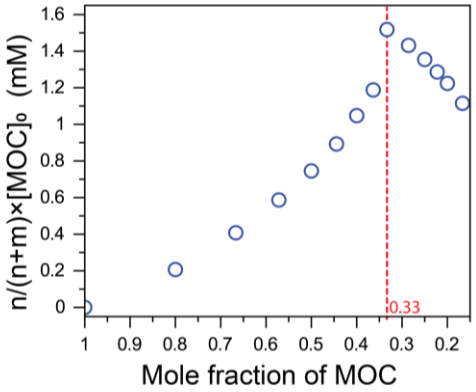

Figure S2. Job Plot for titration of the MOC with PFOS, based on ^{1}H NMR resonance at 9.53 ppm. A stoichiometry of complexation of 2 guests for every host is calculated, *i.e.* 2 PFOS per MOC.

Estimation of the binding constant

Based on the stoichiometry determined, the associated equilibrium constant *K* for the formation of the host-guest complex is expected to be of the form:

$$K = \frac{[complex]}{[MOC][PFOS]^2}$$

A quickly established equilibrium, with slow exchange on the time scale of the NMR experiment, is expected based on the two distinct sets of peaks observed during the titration. For a slow exchange, the concentration of the host-guest complex [$\boldsymbol{C}$] can be determined by:[7]

$$[\boldsymbol{C}] = \frac{\boldsymbol{1}}{\boldsymbol{a}} \times \left(\frac{\boldsymbol{n}}{\boldsymbol{m+n}}\right) \times [H]_0$$

In this equation, [*C*] is the concentration of the host-guest complex at equilibrium at each titration point, $[H]_0$ is the initial concentration of host *i.e.* the MOC, and *a* is the stoichiometric coefficient for the host $a = 1$.

The equilibrium constant calculation becomes:

$$\boldsymbol{K} = \frac{[\boldsymbol{C}]}{([\boldsymbol{H}]_\boldsymbol{0} - [\boldsymbol{C}]) \times ([\boldsymbol{G}]_\boldsymbol{0} - \boldsymbol{2}[\boldsymbol{C}])^\boldsymbol{2}}$$

In this equation, $[G]_0$ is the initial concentration of the guest *i.e.* PFOS, and the concentration of free PFOS at equilibrium each titration point is $[\boldsymbol{G}]_\boldsymbol{0} - \boldsymbol{2}[\boldsymbol{C}]$.

The analysis requires access to the integration values of the free MOC and of the MOC interacting with PFOS. Clear signals for both populations corresponding to the peaks initially at 9.53 and 8.97 ppm are observed. The analysis was thus performed for those two resonances and repeated at in a range where free MOC signals are still observed from 0.25 to 1.75 equivalents of PFOS added.

Table S1. Binding constant values obtained from NMR data.

Entry	Added equivalents of PFOS	Binding constant based on the specified resonances (M^{-2})	
		peak at 9.53 ppm	peak at 8.97 ppm
1	0.25	2.71×10^7	3.00×10^7
2	0.50	2.31×10^7	2.24×10^7
3	0.75	1.73×10^7	1.69×10^7
4	1.0	1.38×10^7	1.35×10^7
5	1.25	1.28×10^7	1.27×10^7
6	1.5	1.71×10^7	1.69×10^7
7	1.75	2.38×10^7	2.38×10^7
Average value of *K*:		1.93 (±0.54) $\times10^7$	1.95 (±0.54) $\times10^7$

Of note, the experimental conditions mean that the value obtained represents crude estimation of the lower limit for *K*.

Competition experiment with β-CD

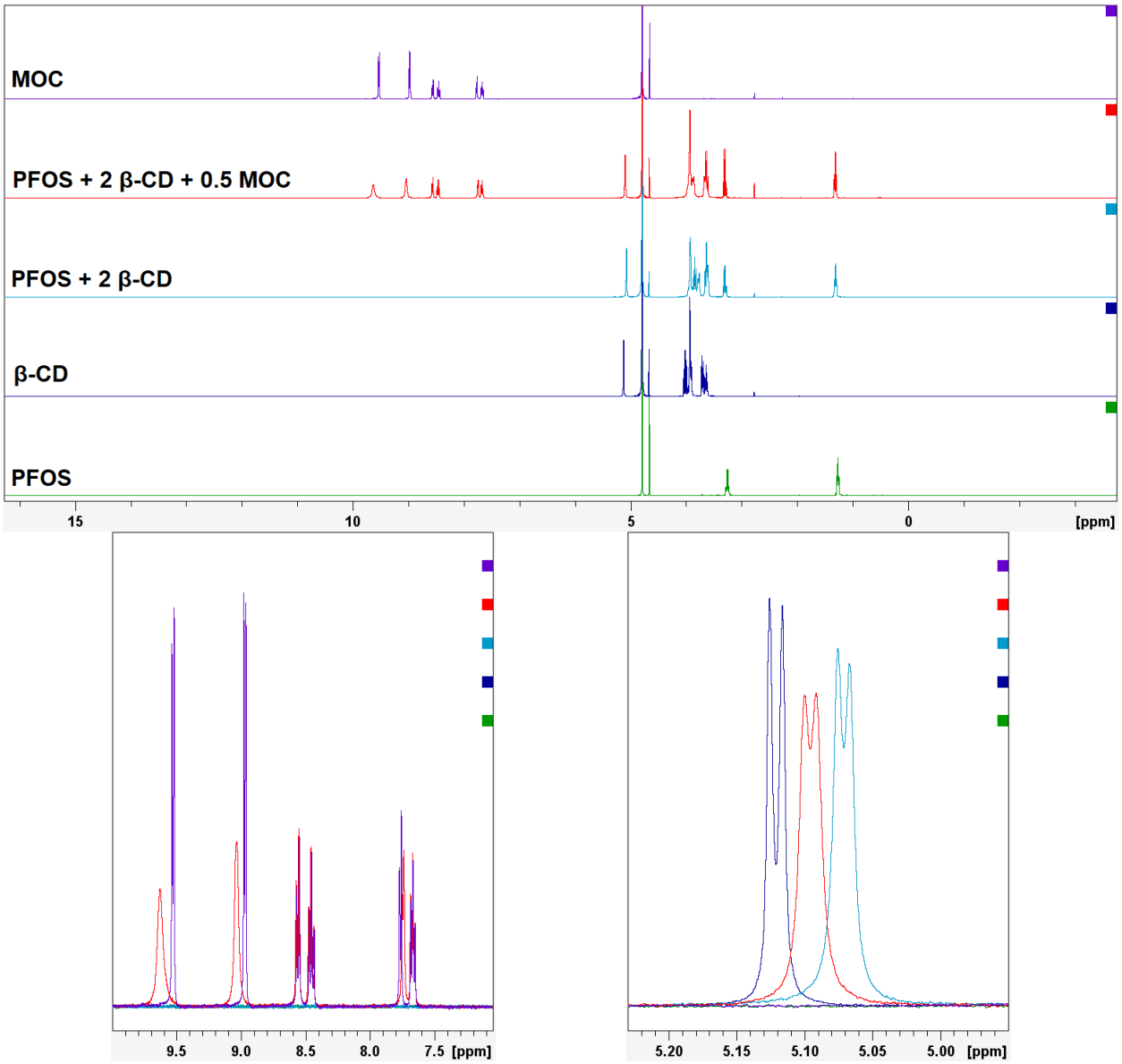

Figure S3. ^{1}H NMR data (400 MHz, D_2O) of PFOS (green, NEt_4^+ counter ions are seen), β-CD (dark blue, 8 mM), β-CD (8 mM) with 0.5 eq of PFOS (light blue, 4 mM), β-CD (8 mM) with 0.5 eq of PFOS (4 mM) and 0.25 eq of MOC (red, 2 mM), pure MOC (purple, 2 mM). Full spectra top) and zooms in the aromatic region showing the MOC, and on a characteristic doublet for the β-CD. All traces have ethylene carbonate as an internal standard (1.80 mM in dark blue, 1.59 mM in light blue and red, and 1.90 mM in purple).

The 2:1 complex of β-CD to PFOS (light blue) has a binding affinity reported at $5.95\pm1.70\times10^4$ M^{-1}.[8] When 0.5 equiv. of MOC is added to it, the resonance at ca. 5.1 ppm for β-CD in the 2:1 complex shifts back towards free β-CD (from light blue to red, compared to dark blue) indicating a weakening of the interaction between β-CD and PFOS. Meanwhile, the resonances for the MOC (7.5 to 9.6 ppm range) shift similarly to what is observed for a 2:1 PFOS to MOC complex.

Diffusion-ordered spectroscopy (DOSY) NMR Data

^{1}H NMR DOSY of pure MOC

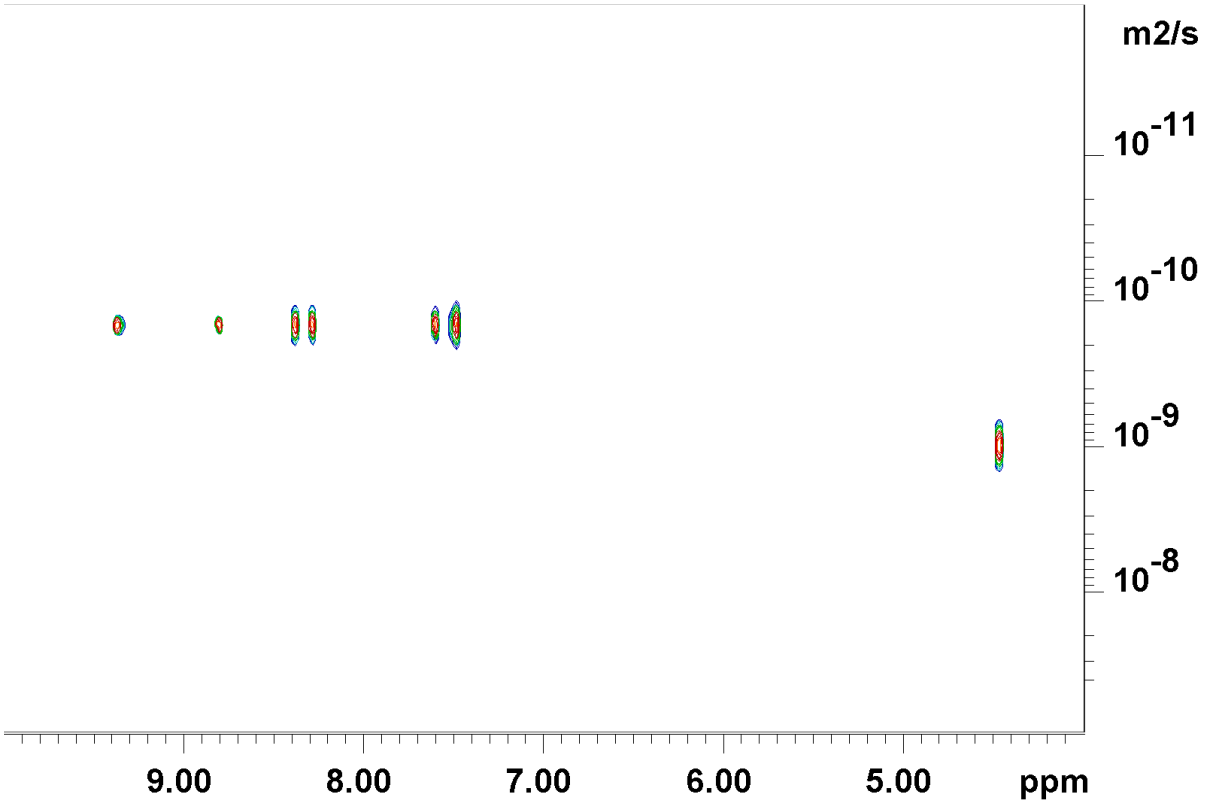

Figure S4. ^{1}H NMR (500 MHz) DOSY of pure MOC 2 mM in D_2O in the presence of an ethylene carbonate internal standard. The ^{1}H NMR trace is unreferenced: the resonances at 9.35 and 8.79 ppm correspond to the organic linker of the MOC, while the resonances at 8.38, 8.27, 7.59, and 7.49 ppm are from the bipyridine part of the metal nodes. The resonance at 4.48 ppm is due to the internal standard ethylene carbonate.

Table S2. Diffusion coefficients obtained for the MOC in D_2O.

Entry	Peak (ppm)	Diffusion Coefficient (m^2/s)	Average Diffusion Coefficient (m^2/s)
1	9.35	1.45×10^{-10}	$1.45(\pm0.002)\times10^{-10}$
2	8.79	1.46×10^{-10}	
3	8.38	1.45×10^{-10}	
4	8.27	1.45×10^{-10}	
5	7.59	1.45×10^{-10}	
6	7.49	1.46×10^{-10}	
7	4.48	1.00×10^{-9}	(ethylene carbonate standard)

[1]H NMR DOSY of MOC with PFOS

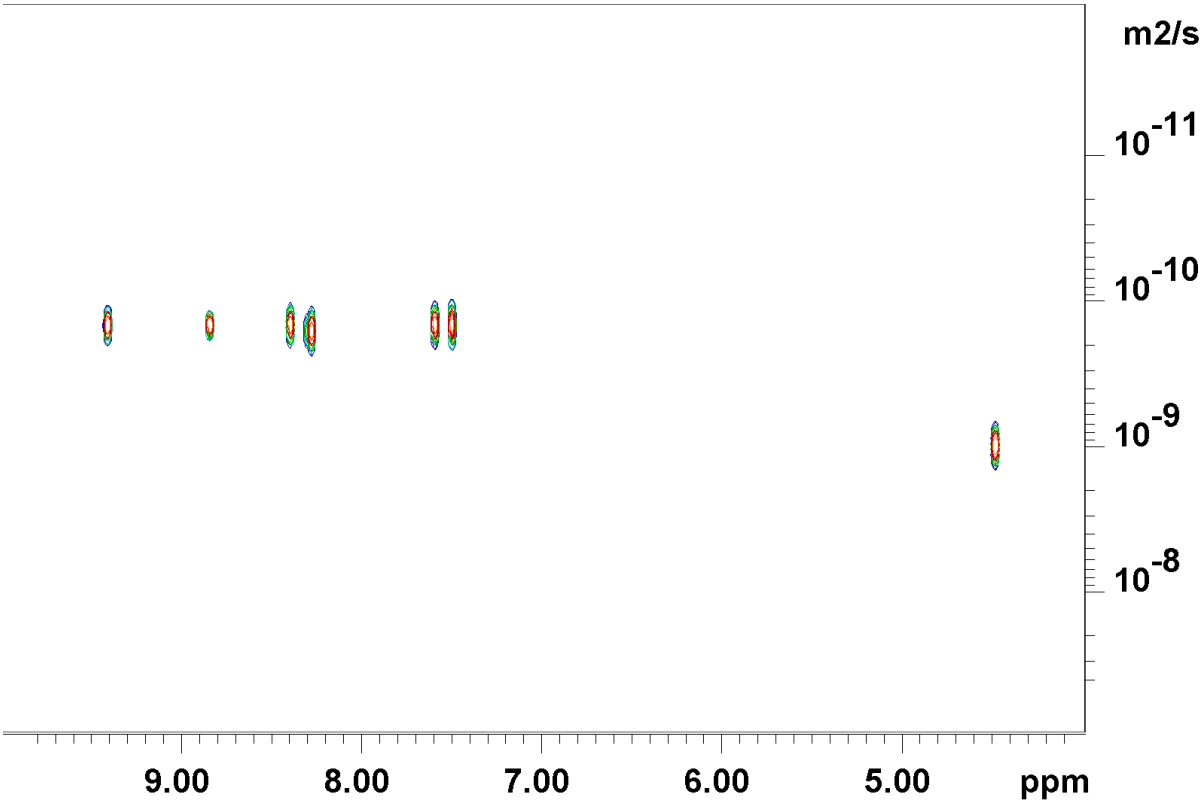

Figure S5. ^{1}H NMR (500 MHz) DOSY of the MOC (2 mM) with two equivalents of PFOS (4 mM) in D_2O in the presence of an ethylene carbonate internal standard. The ^{1}H NMR trace is unreferenced: the resonances at 9.40 and 8.83 ppm correspond to the organic linker of the MOC, while the resonances at 8.38, 8.28, 7.59, and 7.49 ppm are from the bipyridine part of the metal nodes. The resonance at 4.48 ppm is due to the internal standard ethylene carbonate.

Table S3. Diffusion coefficients obtained for the MOC in D_2O in the presence of 2 eq. of PFOS.

Entry	Peak (ppm)	Diffusion Coefficient (m^2/s)	Average Diffusion Coefficient (m^2/s)
1	9.40	1.53×10^{-10}	$1.52(\pm0.009)\times10^{-10}$
2	8.83	1.51×10^{-10}	
3	8.38	1.53×10^{-10}	
4	8.28	1.58×10^{-10}	
5	7.59	1.53×10^{-10}	
6	7.49	1.53×10^{-10}	
7	4.48	1.00×10^{-9}	(ethylene carbonate standard)

^{19}F NMR DOSY of free PFOS

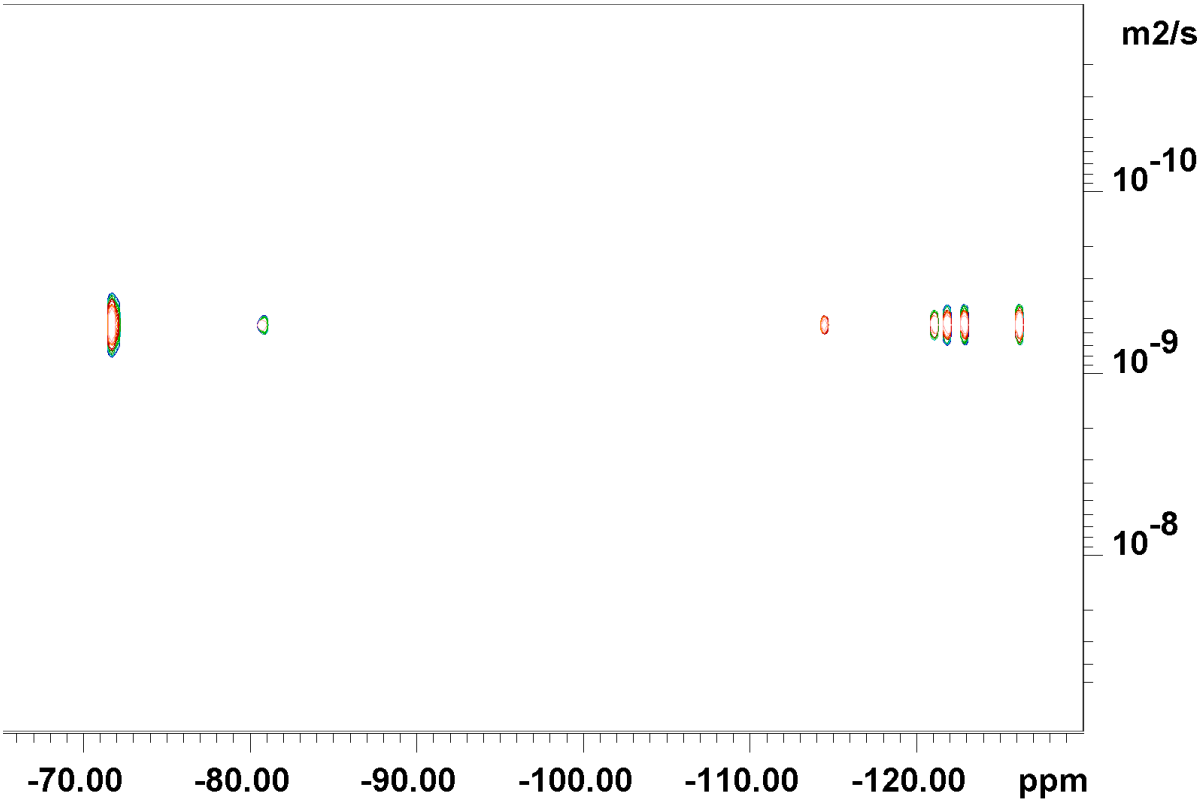

Figure S6. ^{19}F NMR (500 MHz) DOSY of free PFOS (4 mM) in D_2O.

Table S4. Diffusion coefficients obtained for free PFOS in D_2O.

Entry	Peak (ppm)	Diffusion Coefficient (m^2/s)	Average Diffusion Coefficient (m^2/s)
1	–71.93	5.24×10^{-10}	$5.39(\pm0.026) \times 10^{-10}$
2	–80.81	5.41×10^{-10}	
3	–114.4	5.40×10^{-10}	
4	–120.9	5.42×10^{-10}	
5	–121.9	5.41×10^{-10}	
6	–122.8	5.45×10^{-10}	
7	–126.1	5.43×10^{-10}	

^{19}F NMR DOSY of PFOS with MOC

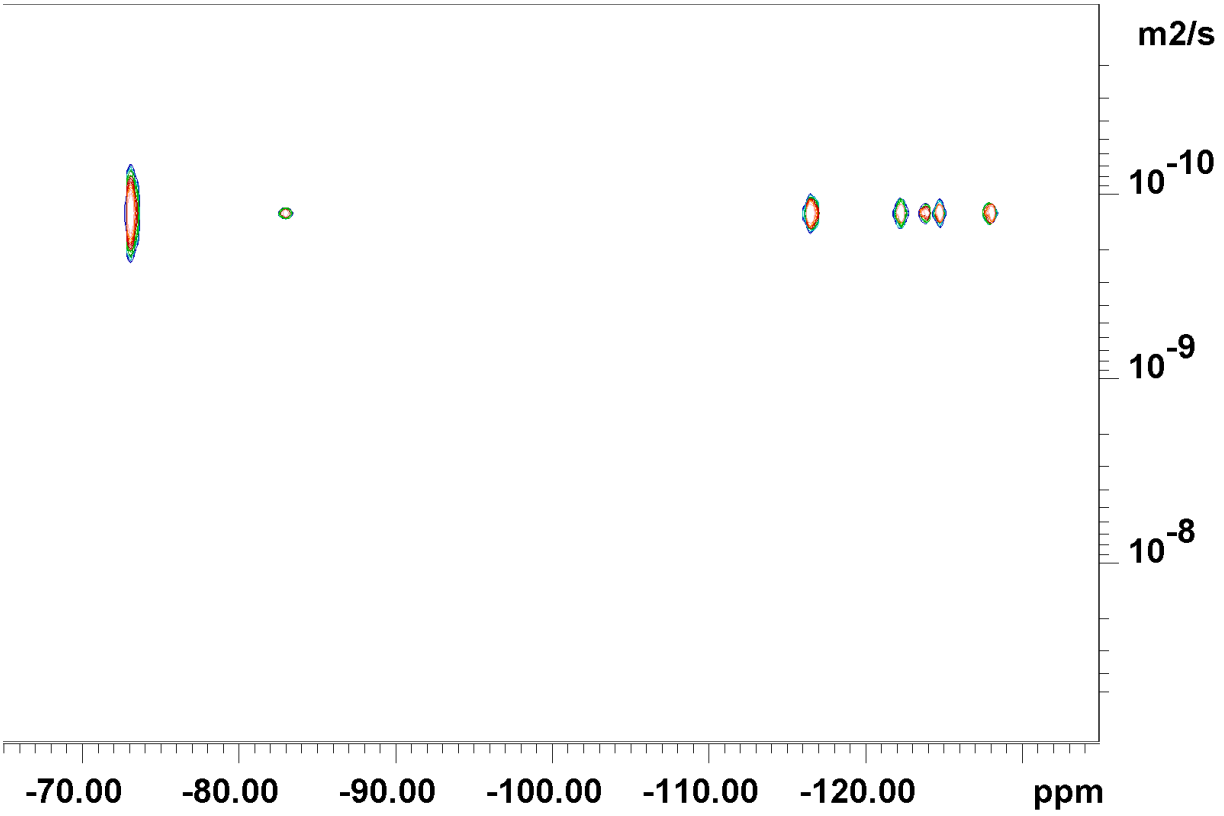

Figure S7. ^{19}F NMR (500 MHz) DOSY of PFOS (4 mM) in the presence of the MOC (2 mM) in D_2O.

Table S5. Diffusion coefficients obtained for PFOS in D_2O in the presence of 2 eq. of MOC.

Entry	Peak (ppm)	Diffusion Coefficient (m^2/s)	Average Diffusion Coefficient (m^2/s)
1	–73.2	1.27×10^{-10}	$1.31(\pm0.012) \times 10^{-10}$
2	–83.0	1.30×10^{-10}	
3	–116.5	1.28×10^{-10}	
4	–122.2	1.35×10^{-10}	
5	–123.8	1.29×10^{-10}	
6	–124.7	1.29×10^{-10}	
7	–127.9	1.25×10^{-10}	

Ion-exchange chromatography data

***Ion-Exchange Chromatography Method*.** Ion exchange chromatography data was collected with a Metrohm 930 IC Flex instrument, using a MetroSil RP 3 - 150/4 column and a conductivity detector. The eluent was a boric acid and acetonitrile solution obtained by mixing a 20 mM boric acid solution (adjusted to pH 8 with NaOH) with acetonitrile (HPLC grade) in a ratio of 62% boric acid solution to 38% acetonitrile by volume. The flow rate was 1.0 mL/min, and the injection loop was 20 µL. Before injection, enough sample was added to a volumetric flask containing 0.1 mL of a 2 mM borate buffer (pH 8) to reach 10 mL.

Calibrations Plots

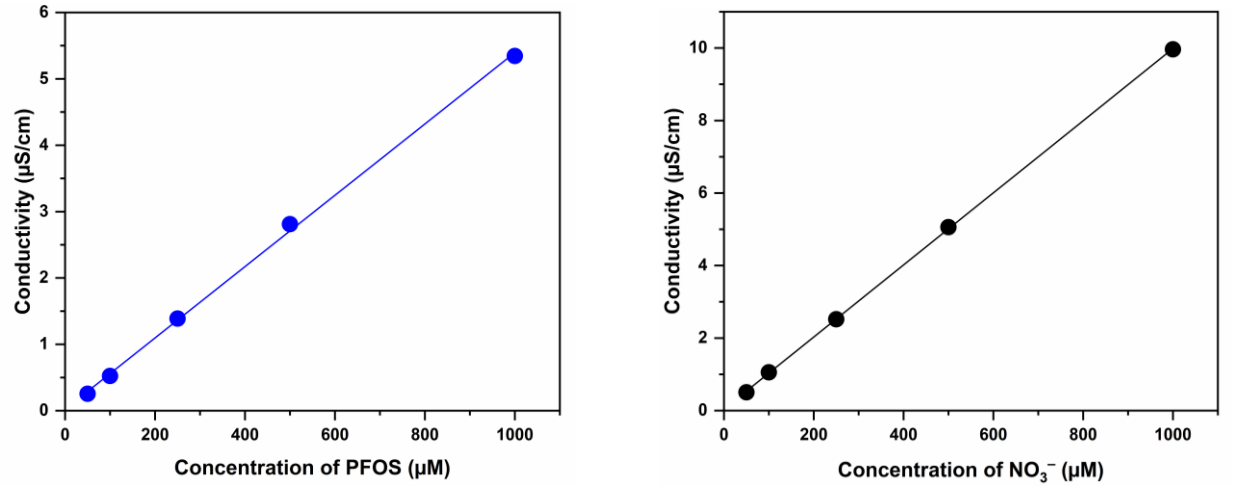

Figure S8. Calibration plots in the concentration range of 50 to 1000 µM for solutions containing both PFOS (left, R^2 = 0.999, slope = 5.37 10^{-3} S cm^{-1} M^{-1}) and nitrate (right, R^2 = 0.999, slope = 9.94 10^{-3} S cm^{-1} M^{-1}).

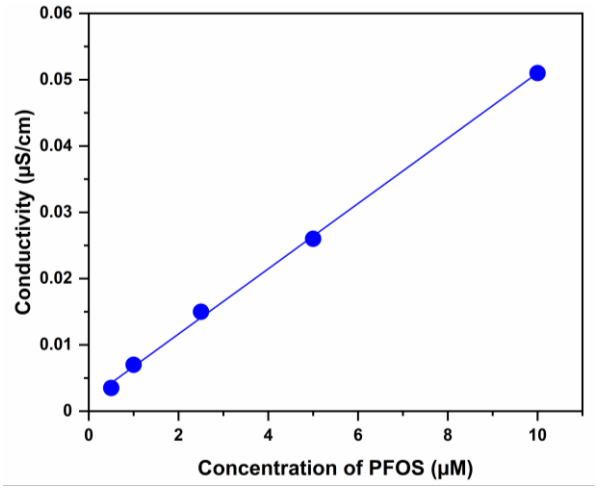

Figure S9. Calibration plot for PFOS in the concentration range of 0.5 to 10 µM (R^2 = 0.999, slope = 4.92 10^{-3} S cm^{-1} M^{-1}).

Representative Chromatograms

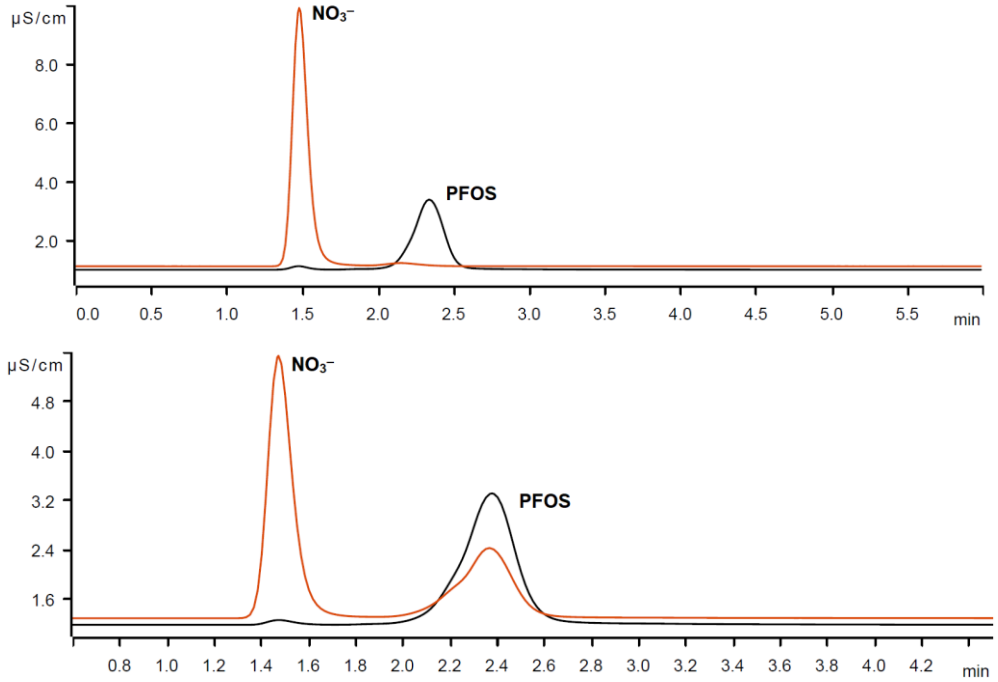

Figure S10. Example Chromatograms of PFOS solutions before (black) and after (orange) treatment with the MOC. Top: 99.3 µM PFOS treated with 8.33 µM of MOC (1:12 molar ratio of MOC to PFOS). Bottom: 100.7 µM PFOS treated with 4.17 µM of MOC (1:24 molar ratio of MOC to PFOS).

Change in nitrate concentration upon treatment with MOC

Table S6. Effect of sponge addition on nitrate concentration.

Entry	MOC (µM)	Initial Nitrate (µM)[a]	Final Nitrate (µM)	Δ[b] Nitrate per MOC
1	4.17	1.33 (± 0.6)	51.3 (± 0.6)	12.0 eq.
2	8.33	1.33 (± 0.6)	102.3 (± 1.1)	12.1 eq.
3	16.7	1.33 (± 0.6)	191.3 (± 1.5)	11.4 eq.

All concentrations are the average of 3 measurements. These entries correspond to the experiments in entries 1-3 of Table 1 in the main text. For entries 4-6 of Table 1 in the main text, we could not track the nitrate concentration at this level as a trace amount of nitrate in water interferes with calibrating the low micromolar range. [a]: Measured from the same solution, split across the different experiments. [b]: change in equivalents of nitrate per equivalent of added MOC.

NMR characterization of the solid complex and the recycled MOC

^{19}F NMR data of the isolated solid complex in CD_3CN

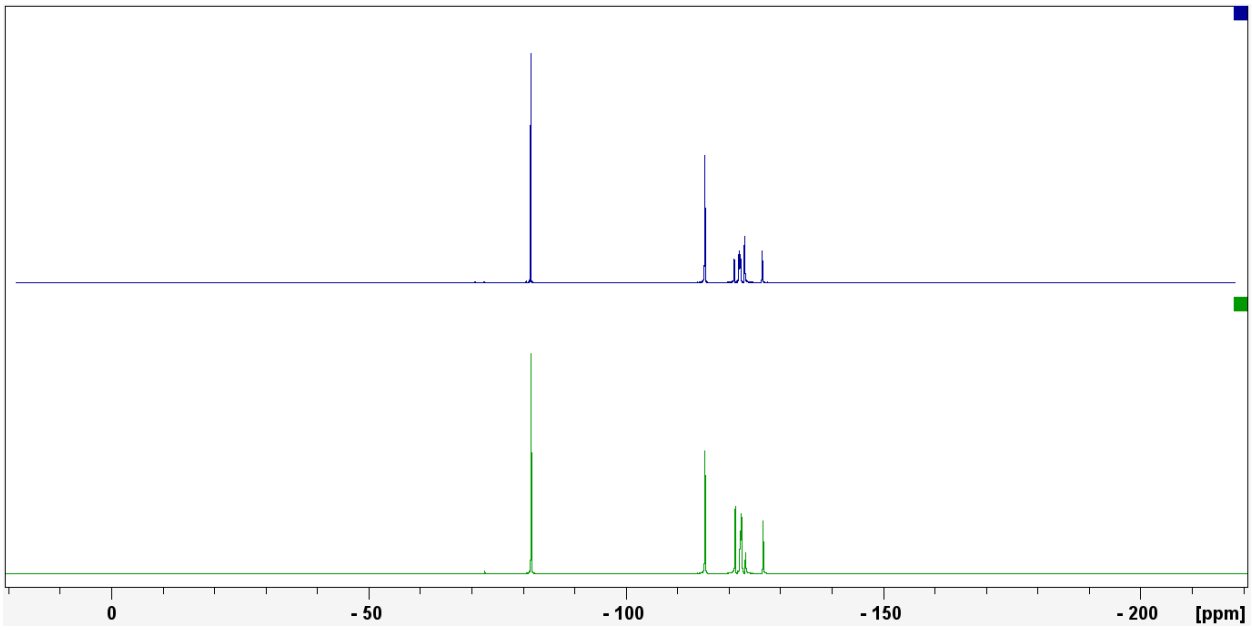

Figure S11. ^{19}F NMR (400 MHz) spectra of the obtained MOC and PFOS solid dissolved in CD_3CN (green, bottom), corresponding to the ^{1}H NMR in Fig. 3 in the main text, and of an authentic PFOS sample in CD_3CN (blue, top).

^{1}H NMR data of the recycled MOC in D_2O

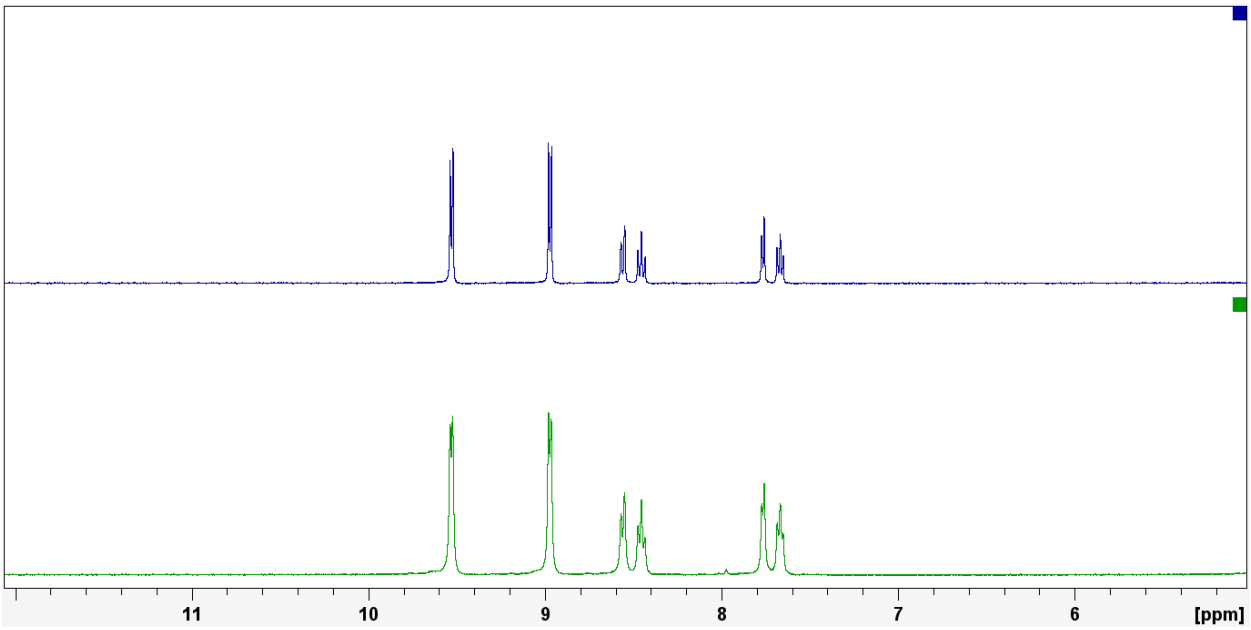

Figure S12. ^{1}H NMR (400 MHz) spectra in D_2O of: an authentic sample of MOC (blue, top) and of the solid obtained after the recycling procedure (green, bottom) confirming the MOC is recovered in the recycling procedure.

^{19}F NMR data of the recycled MOC in D_2O

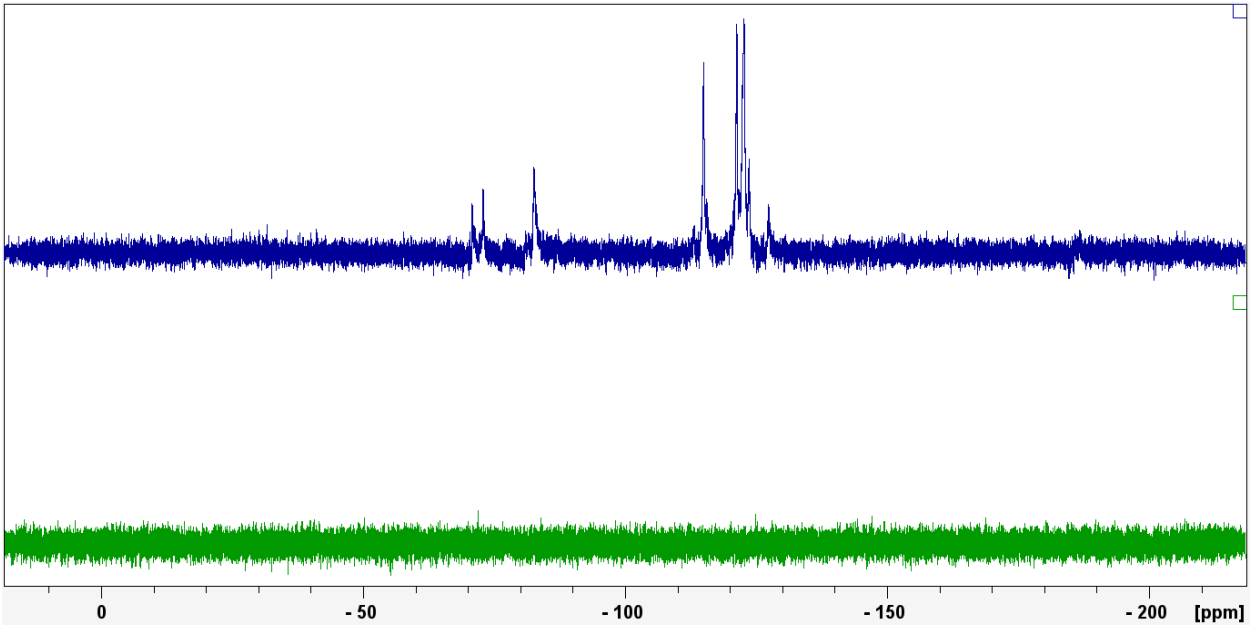

Figure S13. ^{19}F NMR (400 MHz) spectra in D_2O of: an authentic sample of PFOS (blue, top) and of the solid obtained after the recycling procedure (green, bottom) confirming the absence of PFOS in the recycled MOC sample.

Impact of common anions on PFOS treatment with MOC

The possible influence of the presence of common anions on the solubility of the MOC in water was monitored by UV-Vis spectroscopy. The concentration of the MOC used for these experiments was 9 μM. The same procedure was followed for each sample: first, the MOC was dissolved in water. Then, the anion to be tested was added. The solution was centrifuged, and a UV-vis spectrum was recorded. Then, 18 equivalents of PFOS were added, which as expected caused the formation of a precipitate. The sample was centrifuged again before a second UV-vis spectrum of the solution was collected.

The concentration of the anions used was chosen based on the limit or typical level of those respective anions in drinking water obtained from various sources, as referenced in the table.

Table S7. Concentration of anions used in the UV-vis experiments.

Entry	Anions	Limit or typical content in drinking water	Salts Used	Concentration used (mg/L)
1	Chloride	250 mg/L [9]	NaCl	250
2	Sulfate	250 mg/L [9]	Na_2SO_4	250
3	Phosphate	0.05 mg/L[10]	K_3PO_4	0.05
4	Fluoride	2 mg/L [9]	NaF	2
5	Nitrate	10 mg/L[11]	$NaNO_3$	10

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