

A Self-Assembled Iron(II) Metallacage as a Trap for Per- and Poly-fluoroalkyl Substances in Water

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Supporting Information

Table of Contents

<i>I. FeMOP Synthesis</i>	<i>S2</i>
<i>II. FeMOP Solubility.....</i>	<i>S3</i>
<i>III. Per- and polyfluoroalkyl Substances Chemical Structure</i>	<i>S4</i>
<i>IV. LC/MS/MS Method for the analysis of 20 PFAS.....</i>	<i>S5</i>
<i>V. ^{19}F NMR titration spectra and Binding Models.....</i>	<i>S6</i>
<i>VI. ^{19}F NMR spectra for Job plot</i>	<i>S9</i>

VII. ^{19}F Variable Temperature (VT) NMR spectra	S10
VIII. ^1H and ^{19}F DOSY NMR spectra.....	S11
References.....	S14

I. FeMOP Synthesis

FeMOP¹ was self-assembled in gram-scale using the following procedure. 5.000 g (10.15 mmol) 4,4'-diaminobiphenyl-2,2'-disulfonic acid, 2.170 g (20.30 mmol) 2-formylpyridine, 3.685 g (20.33 mmol) tetramethylammonium hydroxide pentahydrate, and 1.880 g (6.750 mmol) iron(II) sulfate heptahydrate were added to a 500 mL Schlenk flask and evacuated for 15 min. Then, 125 mL degassed deionized H₂O was added to the flask. The mixture was stirred under N₂ for 20 h at 50 °C. The mixture was then filtered and the product was precipitated by adding 250 mL acetone. After recrystallization in 500 mL 1:2 (H₂O:acetone mixture), 5.65 g of pure product was isolated at quantitative yield. The FT-IR spectrum for the synthesized powder is shown in Figure 6. The ^1H NMR spectrum is shown in Figure 2. ^1H NMR (400 MHz, D₂O, 25 °C): δ (ppm) = 9.34 (s, 12H, imine), 8.71 (d, 12H, $^3\text{J} = 7.9$ Hz, 3-pyridine), 8.40 (t, 12H, $^3\text{J} = 8.1$ Hz, 4-pyridine), 7.77 (t, 12H, 5-

pyridine), 7.54 (d, 12H, $^3J = 5.5$ Hz, 6-pyridine), 7.14 (d, 12H, $^3J = 8.4$ Hz, 6,6'-benzidine),

6.44 (s, 12H, 3,3'-benzidine), 5.84 (d, 12H, $^3J = 3.6$ Hz, 5,5'-benzidine), 7.14 (s, [NMe₄]⁺).

FT-IR (ATR, cm⁻¹): 3407 (w), 1640 (w), 1608 (w), 1582 (w), 1553 (w), 1491 (w), 1471

(w), 1431 (w), 1397 (w), 1356 (w), 1302 (w), 1225 (w), 1184 (w), 1140 (w), 1091 (w), 1080

(w), 1041 (w), 1025 (w), 997 (w), 951 (w), 935 (w), 906 (w), 832 (w), 767 (w), 750 (w),

729 (w), 701 (w), 672 (w), 620 (w), 581 (w), 550 (w).

II. FeMOP Solubility

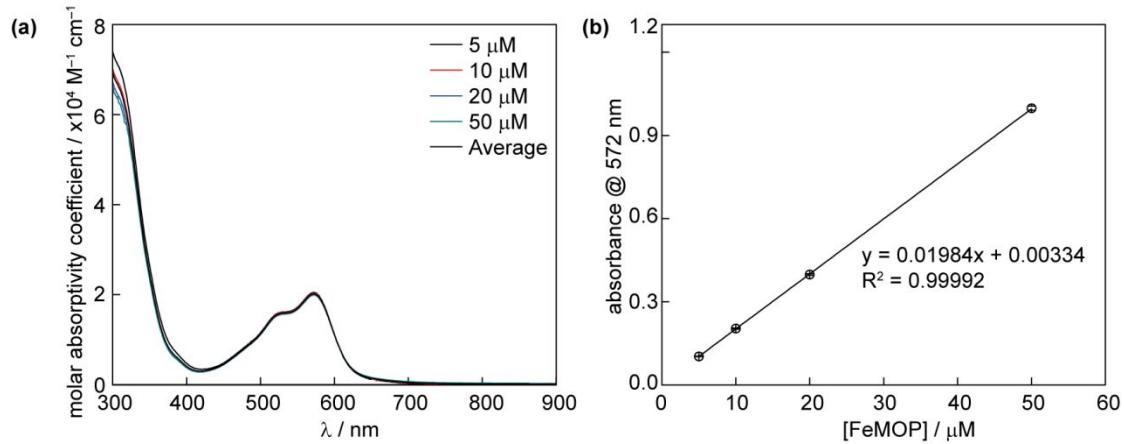


Figure S1. (a) Molar absorptivity coefficient spectra of aqueous **FeMOP** at 5, 10, 20, and 50 μM concentrations and (b) calibration curve using absorbances of **FeMOP** at 572 nm to extrapolate the molar solubility.

III. Per- and polyfluoroalkyl Substances Chemical Structure

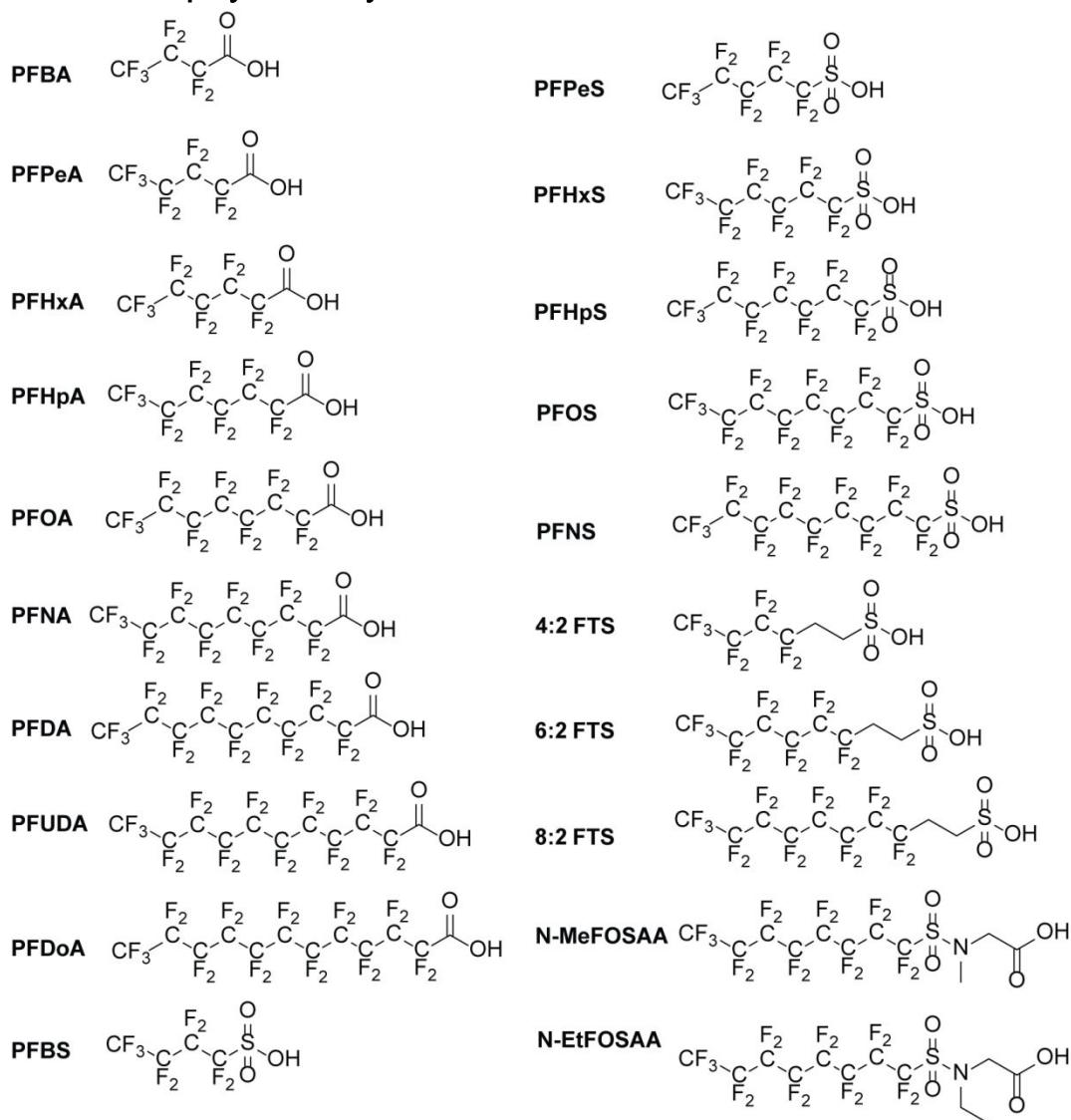


Figure S2. List of per- and polyfluoroalkyl substances (PFASs) included in this work, namely, perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PPPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUDA), perfluorododecanoic acid (PFDoA), perfluorobutanesulfonic acid (PFBS), perfluoropentanesulfonic acid (PPPeS), perfluorohexanesulfonic acid (PFHxS), perfluoroheptanesulfonic acid (PFHpS), perfluorooctanesulfonic acid (PFOS), perfluorononanesulfonic acid (PFNS), 4:2 fluorotelomer sulfonate (4:2 FTS), 6:2 fluorotelomer sulfonate (6:2 FTS), 8:2 fluorotelomer

sulfonate (8:2 FTS), 2-(*N*-Methylperfluorooctanesulfonamido)acetic acid (N-MeFOSAA), and 2-(*N*-Ethylperfluorooctanesulfonamido)acetic acid (N-EtFOSAA).

IV. LC/MS/MS Method for the analysis of 20 PFAS

A method using a triple quadrupole liquid chromatography with tandem mass spectrometry system [Agilent Technologies HPLC 1200 Series with Thermo Scientific TSQ Quantum Ultra MS] operated under selected reaction monitoring (LC/MS/MS) was optimized for the simultaneous analysis of PFASs compounds. The method uses a Waters X-BridgeTM C18 (3.5 µm particle size, 2.1 mm i.d., 150 mm length) with a mobile phase consisting of water with 5 mM ammonium acetate (mobile phase A) and acetonitrile (mobile phase B). Gradient elution was carried out at a flow rate of 200 µL min⁻¹ starting with 5% mobile phase B, held for 1 min, followed by a 20-min linear gradient to 90% mobile phase B, held for 2 min, and then brought back to initial conditions in 1 min and equilibrated for 10 min before next injection. The sample injection volume was 10 µL. Summary of the LC/MS/MS parameters for the PFASs included in this study is shown in the table below.

Table S1. LC/MS/MS parameters for the 20 PFASs showing ions monitored [for quantitation (Quan) and for verification (qual)], retention time and instrument linear range.

No.	Compound Name	Acronym	Precursor Ions	Product Ions, Quan/qual	Retention Time, min	Instrument Linear Range, $\mu\text{g L}^{-1}$	Linear Correlation, R^2
1	Perfluorobutanoic acid	PFBA	213	169/115	8.9	3-250	0.993
2	Perfluoropentanoic acid	PPPeA	263	219/187	9.5	3-250	0.997
3	Perfluorohexanoic acid	PFHxA	313	269/297	9.8	3-150	0.994
4	Perfluoroheptanoic acid	PFHpA	363	319/169	10.2	3-150	0.991
5	Perfluoroctanoic acid	PFOA	413	369/169	10.5	3-150	0.992
6	Perfluorononanoic acid	PFNA	463	419/219	10.9	3-150	0.997
7	Perfluorodecanoic acid	PFDA	513	469/269	11.3	3-150	0.995
8	Perfluoroundecanoic acid	PFUdA	563	519/269	11.9	3-150	0.999
9	Perfluorododecanoic acid	PFDoA	613	569/319	12.5	3-150	0.998
10	Perfluorobutanesulfonic acid	PFBS	299	80/99	10.1	5-150	0.992
11	Perfluoropentanesulfonic acid	PPPeS	349	80/99	10.4	5-150	0.994
12	Perfluorohexanesulfonic acid	PFHxS	399	80/99	10.8	5-150	0.996
13	Perfluoroheptanesulfonic acid	PFHpS	449	80/99	11.2	5-150	0.993
14	Perfluoroctanesulfonic acid	PFOS	499	80/99	11.7	5-150	0.999
15	Perfluorononanesulfonic acid	PFNS	549	80/99	12.1	5-150	0.999
16	2-(N-Methylperfluorooctanesulfonamido)acetic acid	N-MeFOSAA	570	419/483	11.3	5-250	0.992
17	2-(N-Ethylperfluorooctanesulfonamido)acetic acid	N-EtFOSAA	584	419/526	11.5	5-250	0.999
18	Fluorotelomer sulfonic acid 4:2	4:2 FTS	327	307/80	9.7	5-250	0.994
19	Fluorotelomer sulfonic acid 6:2	6:2 FTS	427	407/80	10.3	3-250	0.995
20	Fluorotelomer sulfonic acid 8:2	8:2 FTS	527	507/80	11.1	3-250	0.992

V. ^{19}F NMR titration spectra and Binding Models

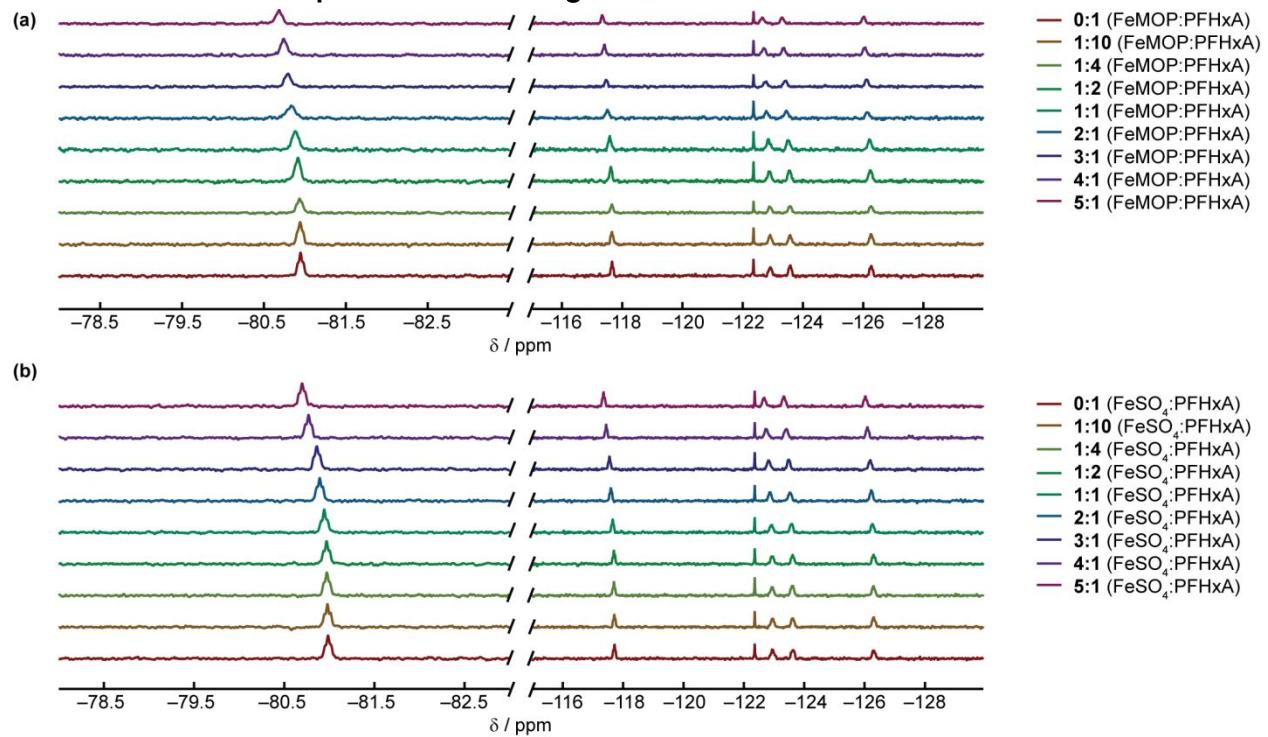


Figure S3. ^{19}F NMR spectra of 0.5 mL D_2O solution titration of (a) FeMOP and (b) FeSO_4 in 1.0 mM PFHxA referenced at -122.36 ppm using 5.00 mM NaF solution in D_2O .

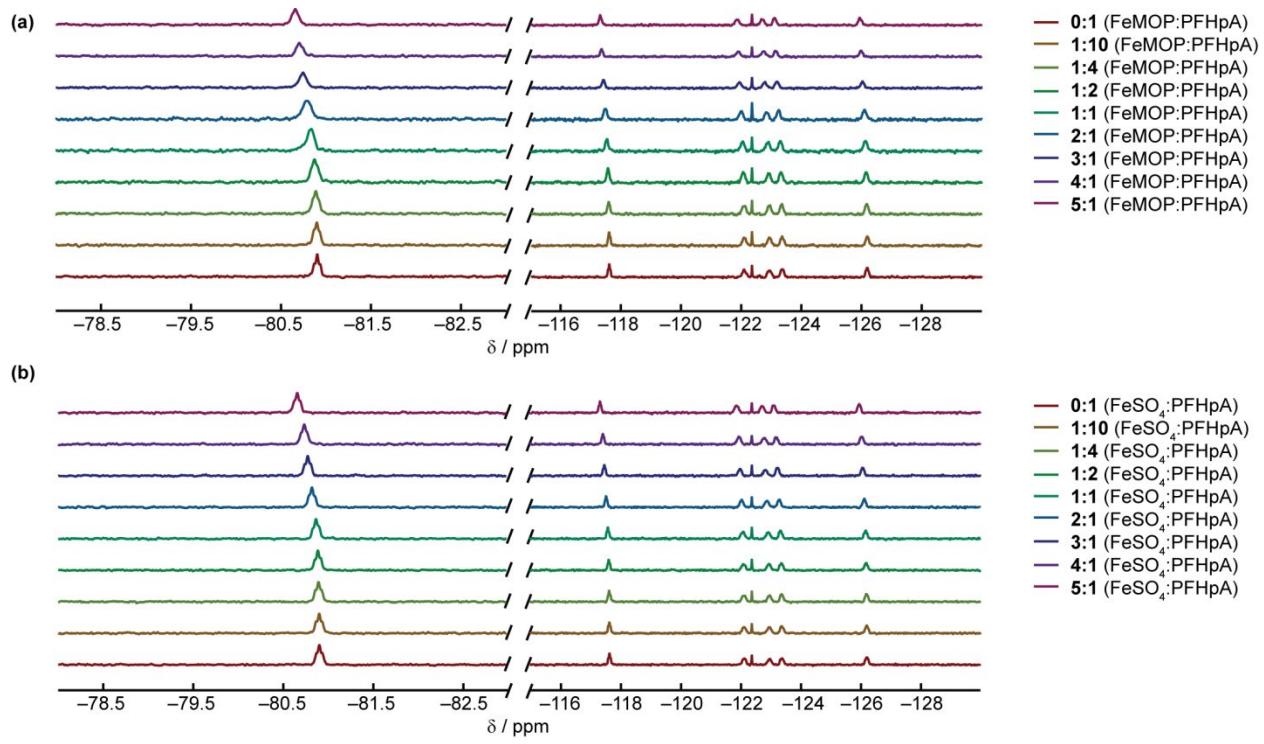


Figure S4. ^{19}F NMR spectra of $0.5 \text{ mL D}_2\text{O}$ solution titration of (a) FeMOP and (b) FeSO_4 in 1.0 mM PFHpA referenced at -122.36 ppm using 5.00 mM NaF solution in D_2O .

Table S2. Summary of remaining PFHpA concentration in solution after addition of FeMOP

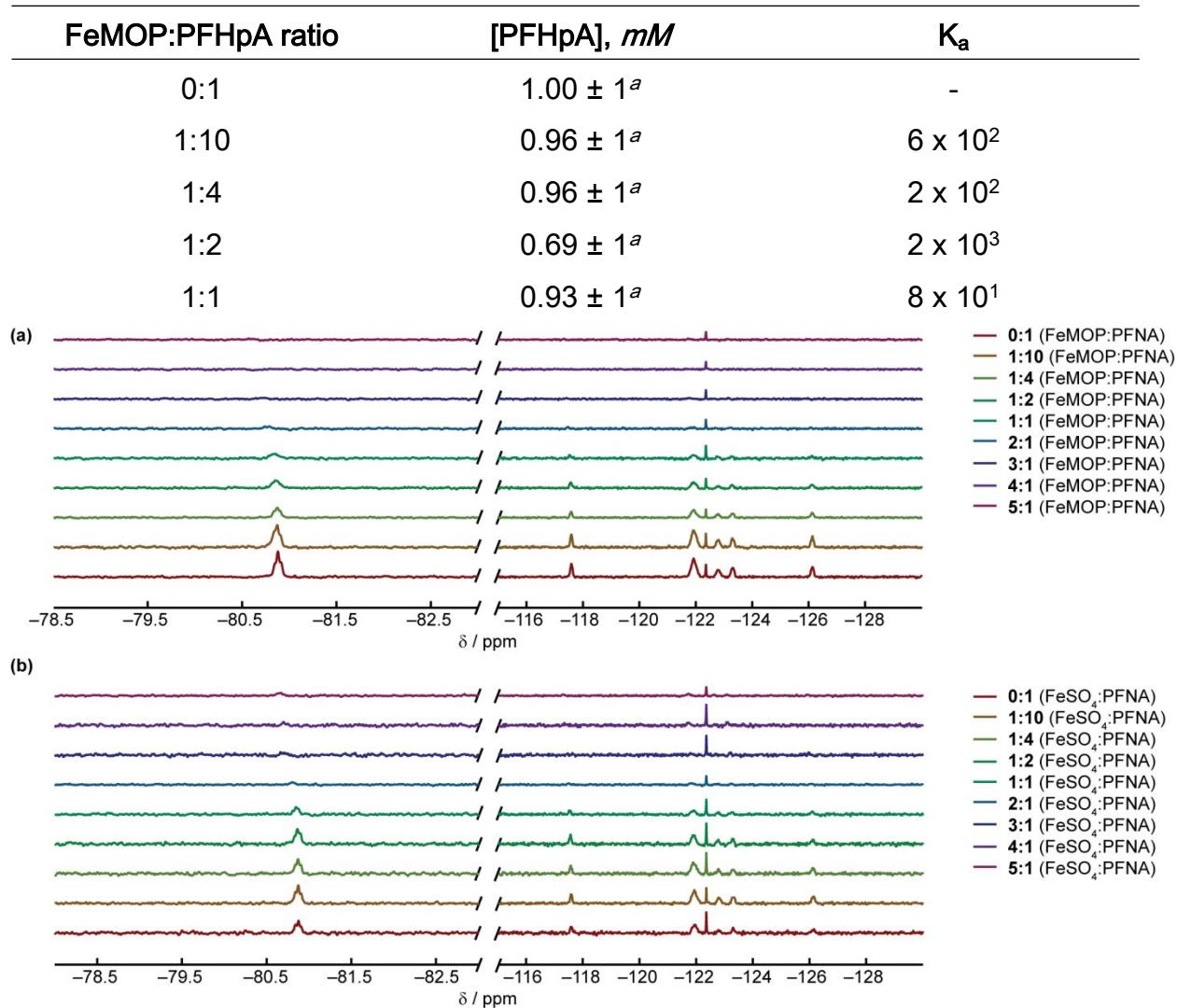


Figure S5. ¹⁹F NMR spectra of 0.5 mL D₂O solution titration of (a) FeMOP and (b) FeSO₄ in 1.0 mM PFNA referenced at -122.36 ppm using 5.00 mM NaF solution in D₂O.

Table S3. Summary of fit parameters for the titration binding modeling of FeMOP and FeSO₄ association with PFHxA, PFHpA, and PFNA

Complex	Model	K_{a1}	K_{a2}	Sum of squares	Standard Error	Covariance of fit
FeMOP:PFHx	1:1	28.01 ±		0.00115		0.0032529
		63% ^a	-	6	0.006107	37
A	1:2	26.43 ^b	-14.17 ^c	0.00110		0.0030943
				1	0.006508	82
FeMOP:PFHp	1:1	37.52 ^b	-	0.00104		0.0033382
		37.52 ^b	-	5	0.005805	04
A	1:2	28.87 ±		0.00102		0.0032571
		50% ^a	31.24 ^b	0	0.006262	88
FeMOP:PFNA	1:1			0.00305		0.0878690
		606.25 ^b	-	6	0.012683	86

VI. ^{19}F NMR spectra for Job plot

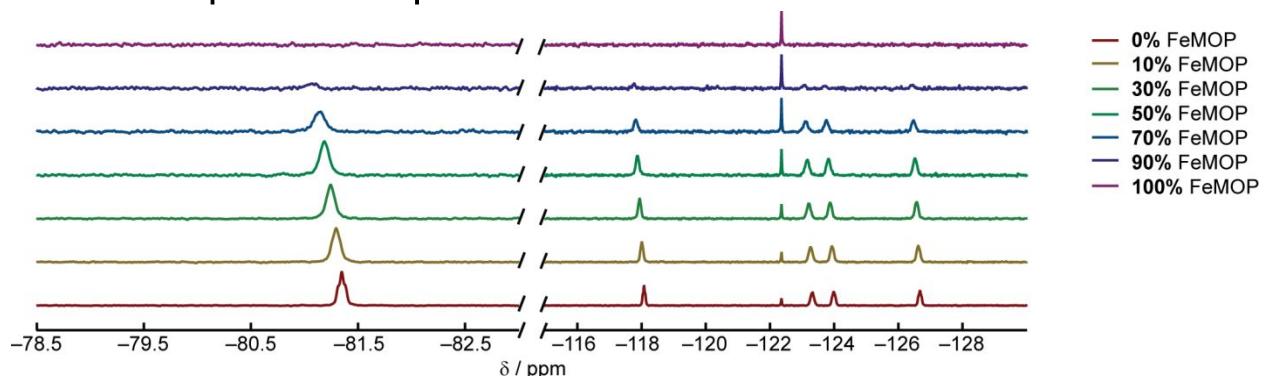


Figure S6. ^{19}F NMR spectra of 0.5 mL D_2O solutions of FeMOP and PFHxA at varying ratios and a total concentration of 5.00 mM referenced at -122.36 ppm using 10.0 mM NaF solution in D_2O for Job plot.

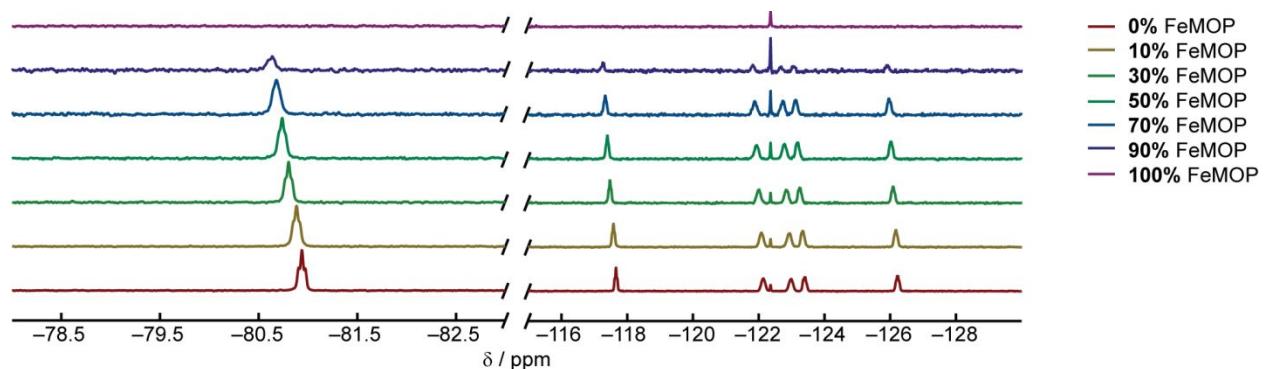


Figure S7. ^{19}F NMR spectra of 0.5 mL D_2O solutions of FeMOP and PFHpA at varying ratios and a total concentration of 5.00 mM referenced at -122.36 ppm using 10.0 mM NaF solution in D_2O for Job plot.

VII. ^{19}F Variable Temperature (VT) NMR spectra

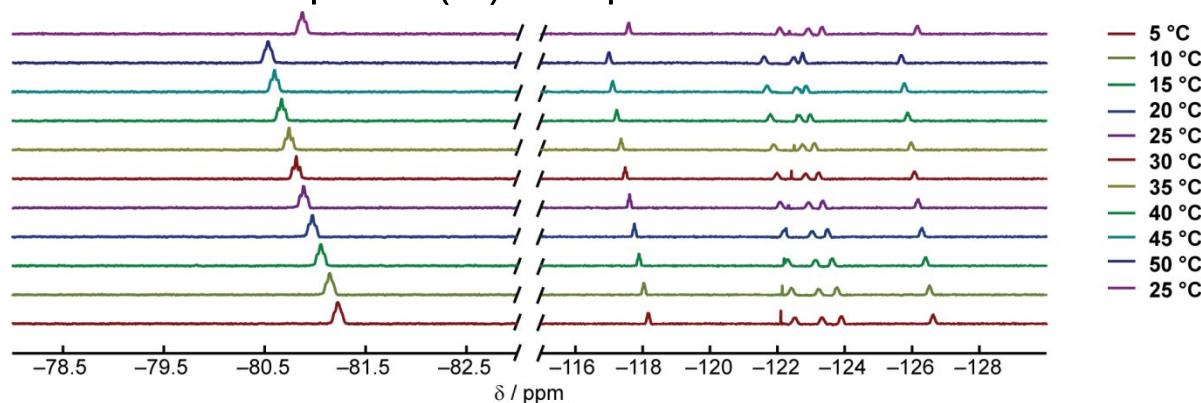


Figure S8. ^{19}F NMR spectra of 0.5 mL D_2O solution of 5.00 mM PFHpA at 5, 10, 15, 20, 25, 30, 35, 40, 45 °C then back to 25 °C for VT NMR method.

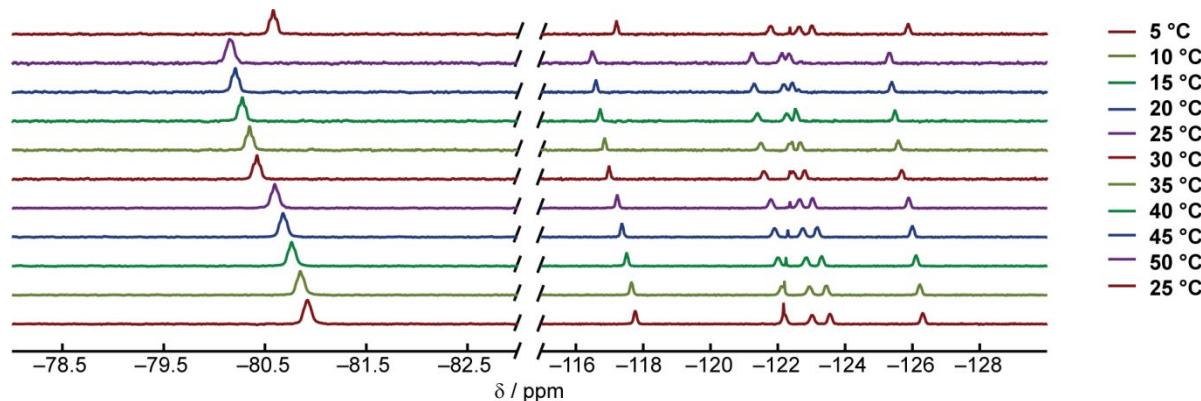


Figure S9. ^{19}F NMR spectra of 0.5 mL D_2O solution of a 10.0 mM total concentration 1:1 (FeMOP:PFHpA) at 5, 10, 15, 20, 25, 30, 35, 40, 45 °C then back to 25 °C for VT NMR method.

Table S4. Summary of fit parameters for the VT NMR modeling of FeMOP association with PFHpA

Peak/R un	A1 ^a	A2 ^a	x0 ^a	dx ^a	R _{adj} ²	T _{1/2} , K	ΔH, kJ mol ⁻¹	ΔS, J mol ⁻¹ K ⁻¹
1/1	111.85 ± 1	99.25 ± 1	0.00332 ± 0.5	2.08 × 10 ⁻⁵ ± 52	0.90902	300.92	4.00 × 10 ²	1.33 × 10 ³
2/1	164.18 ± 13	118.14 ± 4	0.00325 ± 3	1.09 × 10 ⁻⁴ ± 61	0.95666	307.88	7.62 × 10 ¹	2.47 × 10 ²
3/1	111.82 ±	99.92 ±	0.00332 ±	2.00 × 10 ⁻⁵ ±	0.92401	301.12	4.15 × 10 ²	1.38 × 10 ³

VIII. ^1H and ^{19}F DOSY NMR spectra

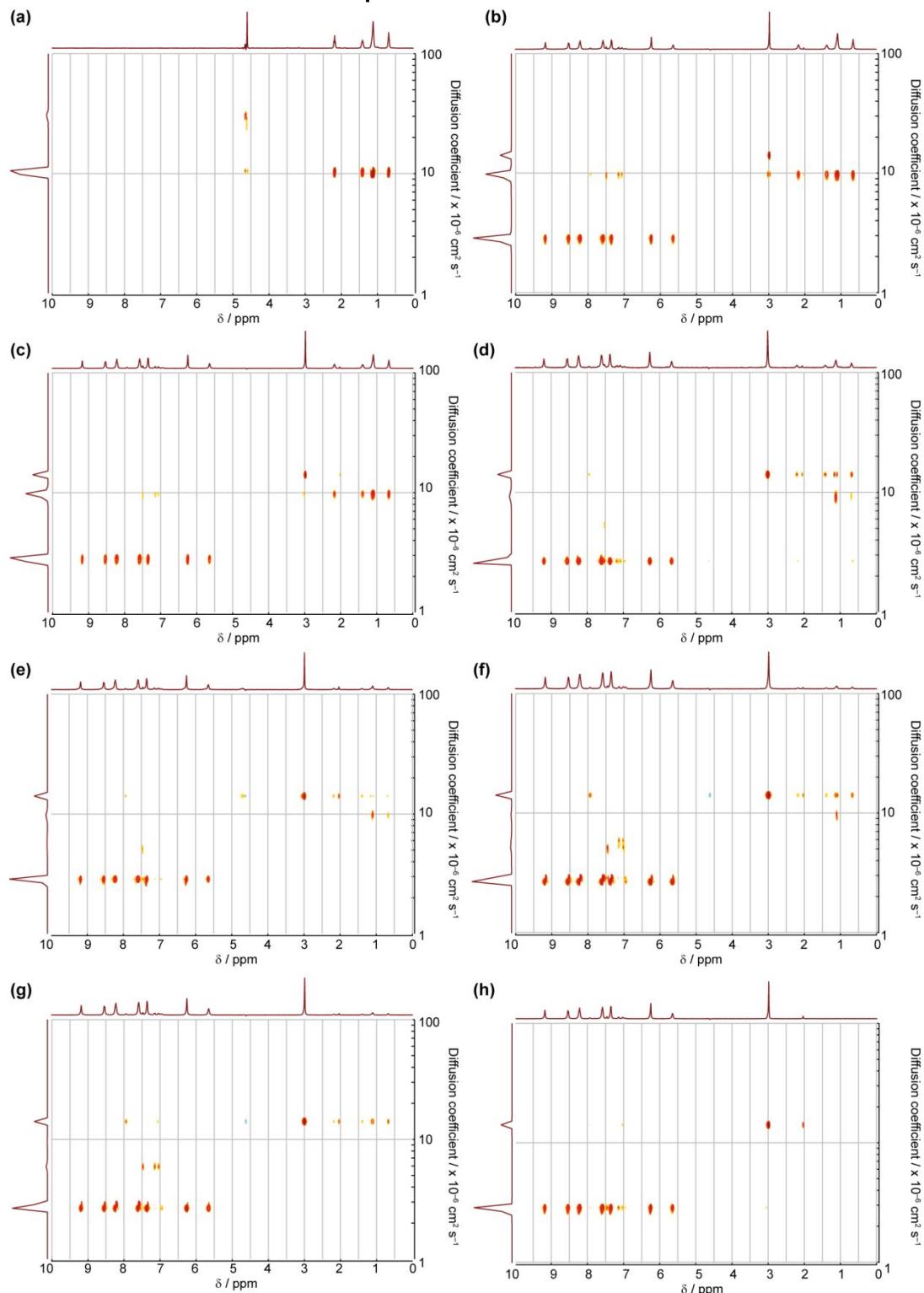


Figure S10. ^1H DOSY NMR spectra of (a) heptanoic acid, (b) 1:4 (FeMOP:heptanoic acid), (c) 1:3 (FeMOP:heptanoic acid), (d) 1:2 (FeMOP:heptanoic acid), (e) 1:1

(FeMOP:heptanoic acid), (f) 2:1 (FeMOP:heptanoic acid), (g) 3:1 (FeMOP:heptanoic acid) at 2.5 mM heptanoic acid concentration, and (h) 2.5 mM FeMOP in D₂O.

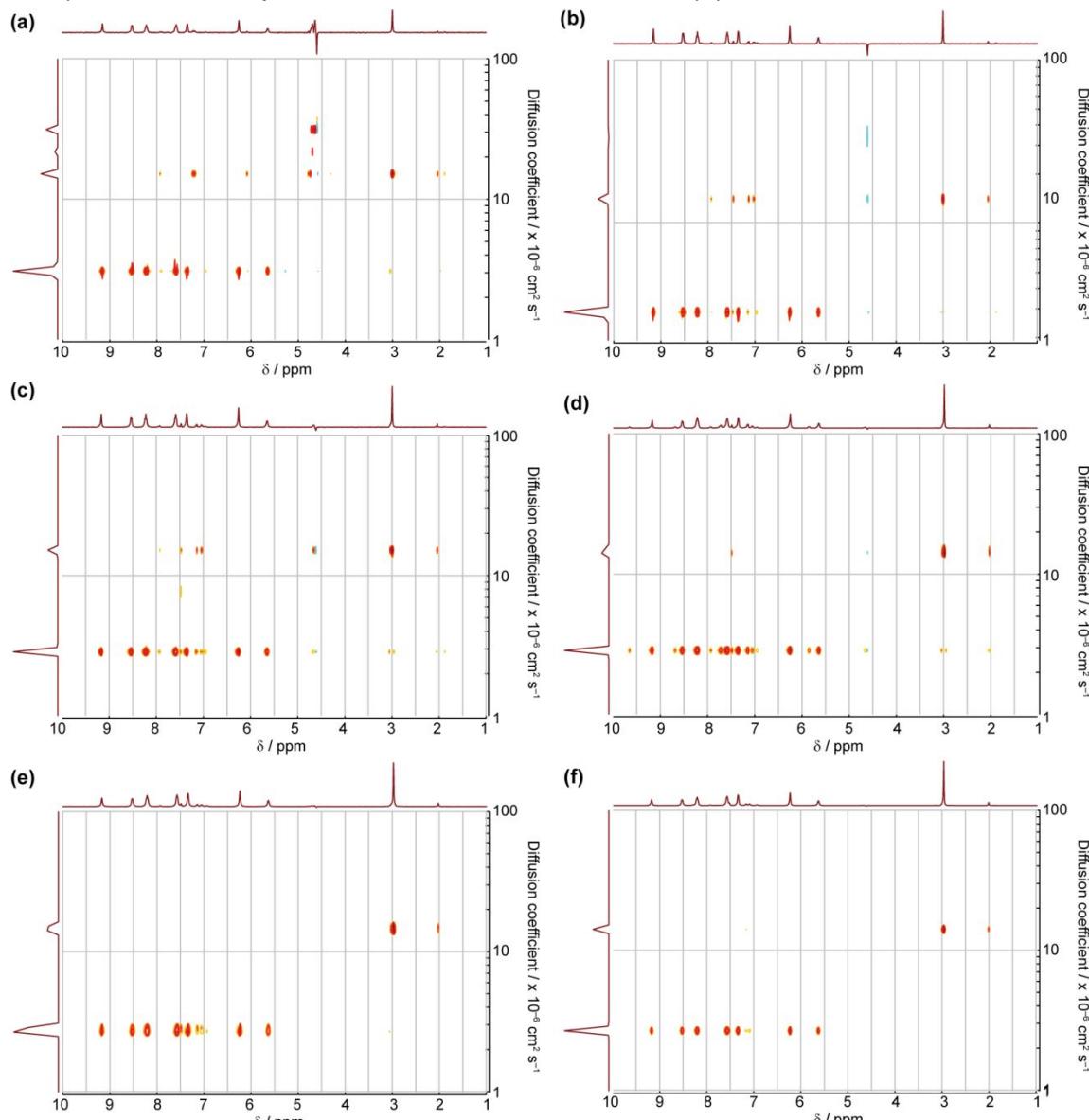


Figure S11. ¹H DOSY NMR spectra of (a) 1:4 (FeMOP:PFHpA), (b) 1:2 (FeMOP:PFHpA), (c) 1:1 (FeMOP:PFHpA), (d) 2:1 (FeMOP:PFHpA), (e) 3:1 (FeMOP:PFHpA), and (f) 4:1 (FeMOP:PFHpA) D₂O solutions at 1.0 mM PFHpA concentration.

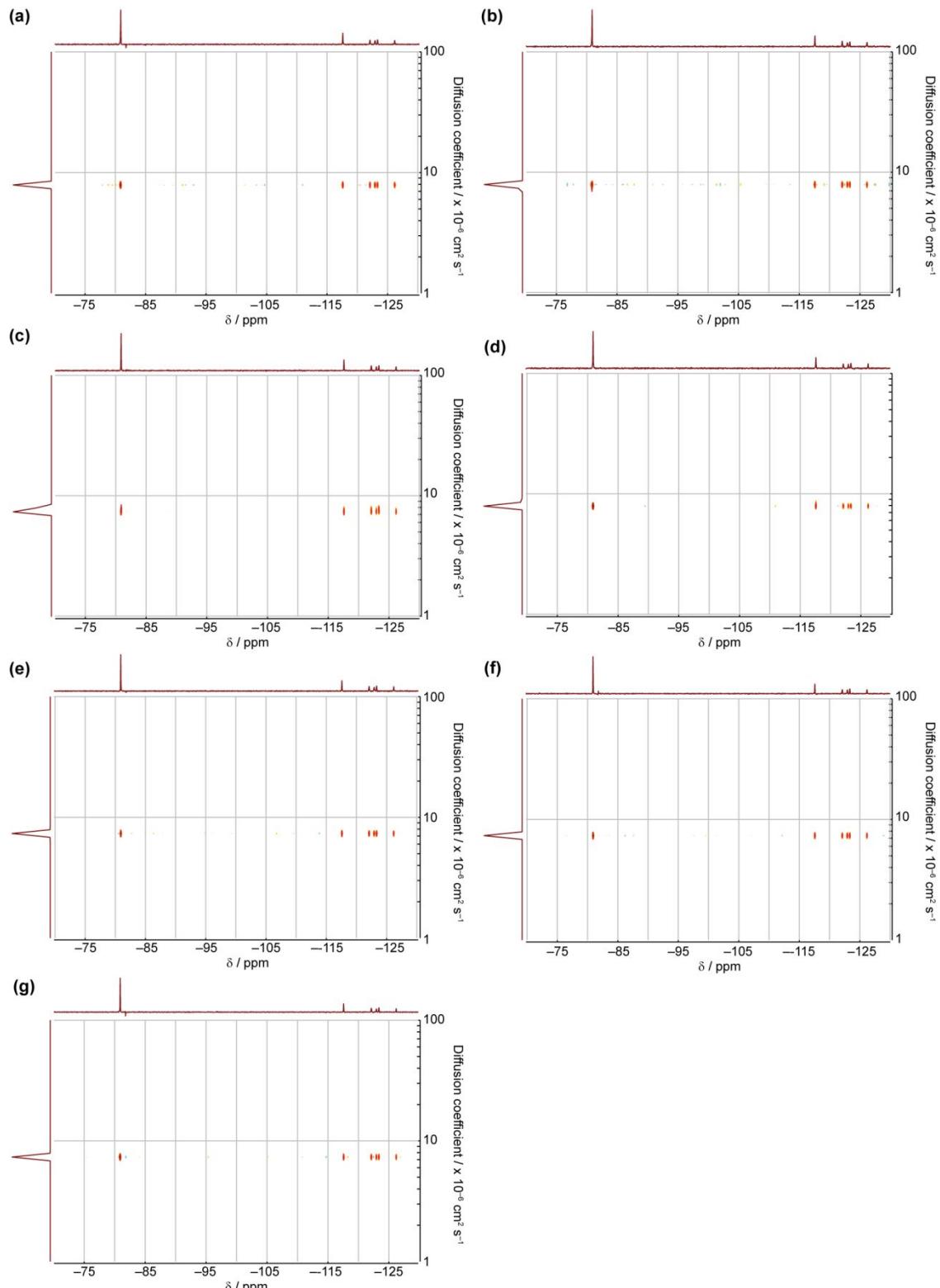


Figure S12. ^{19}F DOSY NMR spectra of (a) PFHpA, (b) 1:4 (FeMOP:PFHpA), (c) 1:2 (FeMOP:PFHpA), (d) 1:1 (FeMOP:PFHpA), (e) 2:1 (FeMOP:PFHpA), (f) 3:1

(FeMOP:PFHpA), and (g) 4:1 (FeMOP:PFHpA) D₂O solutions at 1.0 mM PFHpA concentration.

Table S5. Summary of diffusion coefficients of FeMOP when complexed with heptanoic acid and PFHpA

Solution [FeMOP]/[heptanoic acid]	Diffusion coefficient, $\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$		
	FeMOP	Heptanoic acid	PFHpA
0.00	0	10.5	-
0.25	2.85	9.8	-
0.33	2.86	9.8	-
0.50	2.67	9.22	-
1.00	2.86	9.73	-
2.00	2.66	9.73	-
3.00	2.67	9.73	-
[FeMOP]/[PFHpA]			
0.00	0	-	7.87

References

- (1) Mal, P.; Schultz, D.; Beyeh, K.; Rissanen, K.; Nitschke, J. R., An Unlockable–Relockable Iron Cage by Subcomponent Self-Assembly. *Angew. Chemie. Int. Ed.* 2008, 47, 8297–8301.