Electronic Supplementary Material (ESI) for CrystEngComm.

Fluorine Magic: One new Organofluorine Linker leads to three new Metal-Organic Frameworks

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SUPPORTING INFORMATION

Overview

1. **Single-crystal X-ray crystallographic studies**
2. **Powder X-ray diffraction patterns of UHM-31, UHM-32 and UHM-33**
3. **Thermo-gravimetric studies on UHM-31, UHM-32 and UHM-33**
4. **^{1}H-NMR and ESI-MS studies on UHM-31**
5. **Literature**

1. Single-crystal X-ray crystallographic studies

Crystal data and structure refinement for UHM-31.

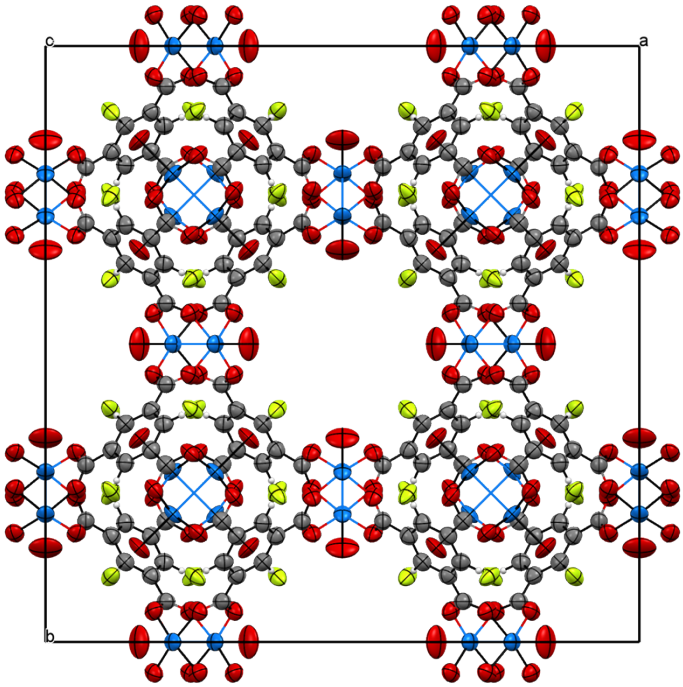


Figure S1: ORTEP-like plot of UHM-31 (cell content, probability level 25 %)

SQUEEZE/PLATON[1] was used in order to account for the electron density from disordered DMA solvent molecules, which could not be resolved. The contributions of 2334 electrons were removed from the unit-cell contents. In the space group Fm-3m 2334/192 = 12.2 electrons were removed from the asymmetric unit. With Z being 16, 194 electrons would be associated with one formula unit, consistent with 4 DMA solvent molecules per formula unit.

Identification code	UHM-31
Empirical formula	C34 H37 Cu3 F2 O19
Formula weight	978.26
Temperature	153(2) K
Wavelength	154.178 pm
Crystal system	Cubic
Space group	F m -3 m

Unit cell dimensions	a = 2631.360(10) pm	α= 90°.
	b = 2631.360(10) pm	β= 90°.
	c = 2631.360(10) pm	γ = 90°.
Volume	18.21968(12) nm^3	
Z	16	
Density (calculated)	1.427 Mg/m^3	
Absorption coefficient	2.306 mm^{-1}	
F(000)	7968	
Crystal size	0.10 x 0.10 x 0.07 mm^3	
Theta range for data collection	4.75 to 68.74°.	
Index ranges	0<=h<=18, 0<=k<=22, 2<=l<=31	
Reflections collected	908	
Independent reflections	908 [R(int) = 0.0000]	
Completeness to theta = 68.74°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8552 and 0.8021	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	908 / 0 / 42	
Goodness-of-fit on F^2	1.146	
Final R indices [I>2sigma(I)]	R1 = 0.0599, wR2 = 0.2127	
R indices (all data)	R1 = 0.0668, wR2 = 0.2212	
Largest diff. peak and hole	0.352 and -0.324 e.$Å^{-3}$	

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (pm^2x 10^{-1}) for UHM-31. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	0	2145(1)	2145(1)	123(1)
O(1)	519(1)	1825(1)	2569(1)	144(1)
O(2)	0	1579(2)	1579(2)	265(6)
C(1)	680(3)	2030(2)	2970(2)	132(2)
C(2)	1116(3)	1778(2)	3222(2)	137(2)
C(3)	1342(2)	1995(3)	3659(2)	136(2)
F(1)	1096(3)	2477(4)	3904(3)	153(4)

Crystal data and structure refinement for UHM-32.

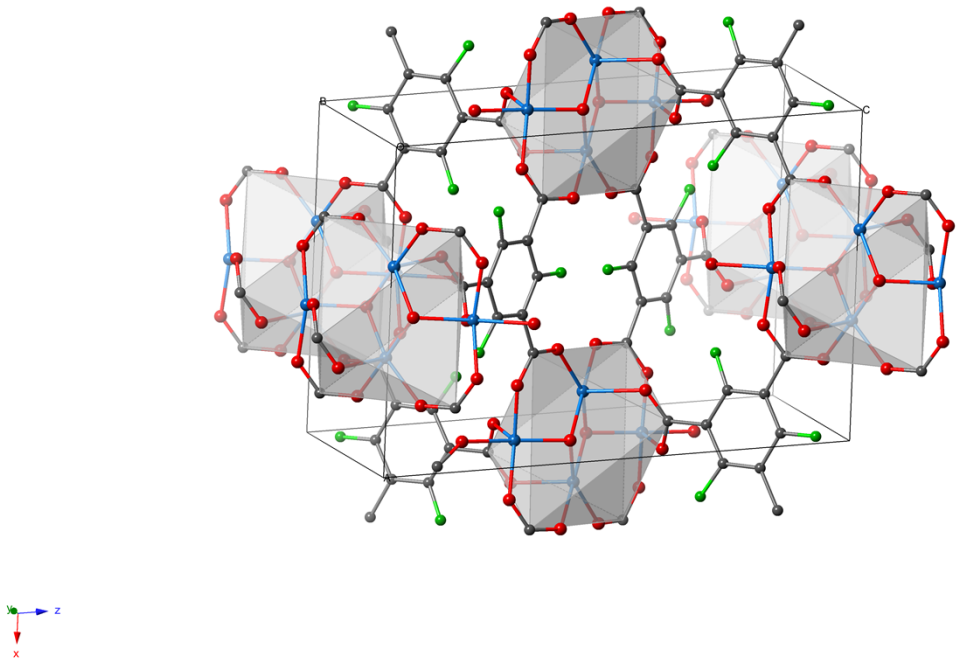


Figure S2a: Slightly extended view of the unit cell of UHM-32, overall SBU of the inorganic cluster shown as semitransparent grey octahedral. Solvent molecules and hydrogen atoms were omitted for clarity reasons.

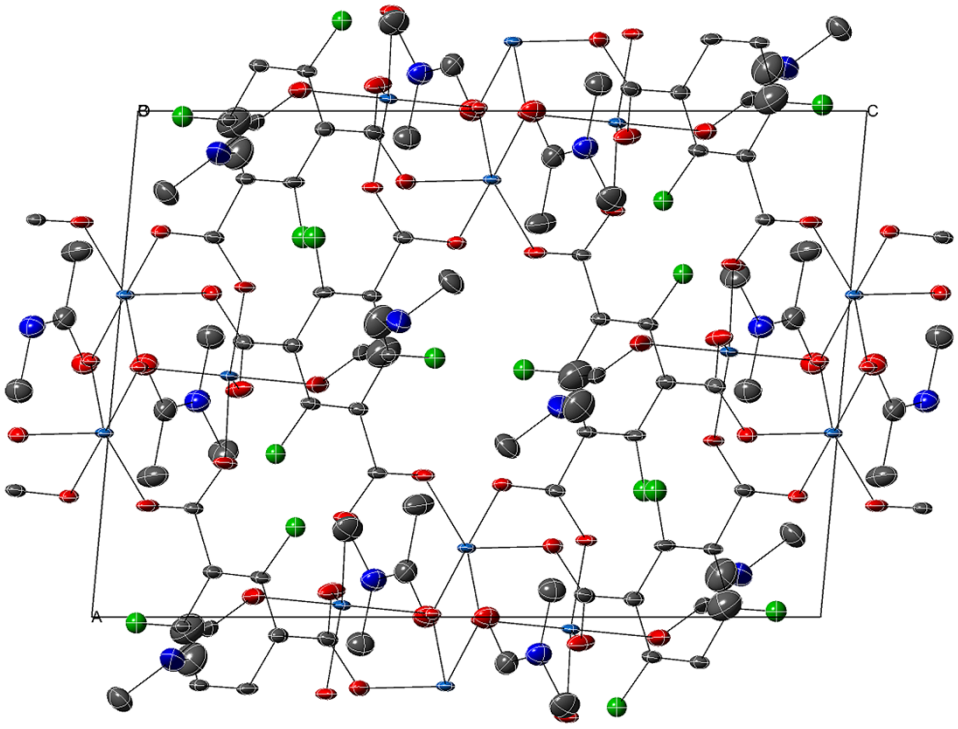


Figure S2b: ORTEP-like plot of the slightly extended unit cell of UHM-32 (probability level 40 %), view along the *b* axis. Hydrogen atoms were omitted for clarity reasons.

Identification code	UHM-32	
Empirical formula	C17 H21 Cu2 F N2 O9	
Formula weight	543.44	
Temperature	153(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.83040(10) Å	α= 90°.
	b = 11.99850(10) Å	β= 95.2270(10)°.
	c = 15.4960(2) Å	γ = 90°.
Volume	2005.31(4) $Å^3$	
Z	4	
Density (calculated)	1.800 Mg/m^3	
Absorption coefficient	3.204 mm^{-1}	
F(000)	1104	
Crystal size	0.20 x 0.20 x 0.12 mm^3	
Theta range for data collection	4.67 to 76.39°.	

Index ranges	-13<=h<=13, -14<=k<=15, -19<=l<=19
Reflections collected	36617
Independent reflections	4186 [R(int) = 0.0503]
Completeness to theta = 76.39°	99.5 %
Max. and min. transmission	0.6998 and 0.5667
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4186 / 1 / 289
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1144
R indices (all data)	R1 = 0.0488, wR2 = 0.1168
Largest diff. peak and hole	1.368 and -0.951 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for UHM-32. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5238(1)	8712(1)	1587(1)	21(1)
Cu(2)	6363(1)	9962(1)	-58(1)	16(1)
O(1)	5062(2)	8983(2)	338(1)	17(1)
O(2)	7799(2)	9303(2)	630(2)	25(1)
O(3)	6959(2)	8287(2)	1639(2)	29(1)
O(4)	12387(2)	9037(2)	464(1)	20(1)
O(5)	13484(2)	8466(2)	1688(2)	30(1)
O(6)	9493(2)	5490(2)	3258(2)	36(1)
O(7)	11402(2)	6029(2)	3761(1)	24(1)
C(1)	7849(3)	8655(2)	1262(2)	18(1)
C(2)	9109(3)	8233(3)	1603(2)	20(1)
C(3)	9217(3)	7445(3)	2266(2)	21(1)
F(3)	8223(5)	7147(5)	2682(4)	25(1)
C(4)	12502(3)	8596(3)	1202(2)	20(1)
C(5)	10361(3)	7014(3)	2584(2)	22(1)
C(6)	11414(3)	7396(3)	2226(2)	23(1)
F(6)	12498(4)	6849(3)	2421(3)	31(1)
C(7)	10429(3)	6111(3)	3264(2)	24(1)
C(8)	11344(3)	8183(3)	1560(2)	20(1)
C(9)	10180(3)	8587(3)	1248(2)	20(1)

F(9)	10115(10)	9347(9)	618(7)	28(2)
O(8)	5408(3)	8171(4)	2806(2)	70(1)
C(10)	4773(4)	7830(8)	3371(3)	131(5)
C(11)	3377(4)	8031(4)	4512(3)	42(1)
C(12)	4768(5)	6554(5)	3670(4)	65(1)
N(1)	4157(4)	8330(6)	3840(3)	89(2)
C(13)	4169(6)	9644(4)	3586(4)	61(1)
O(9)	5011(2)	3118(2)	415(2)	34(1)
C(14)	5902(4)	3676(3)	750(2)	34(1)
N(2)	5733(3)	4614(3)	1180(2)	35(1)
C(15)	4469(4)	4978(3)	1280(3)	40(1)
C(16)	7222(4)	3310(4)	661(3)	48(1)
C(17)	6740(4)	5288(4)	1600(3)	48(1)

Crystal data and structure refinement for UHM-33.

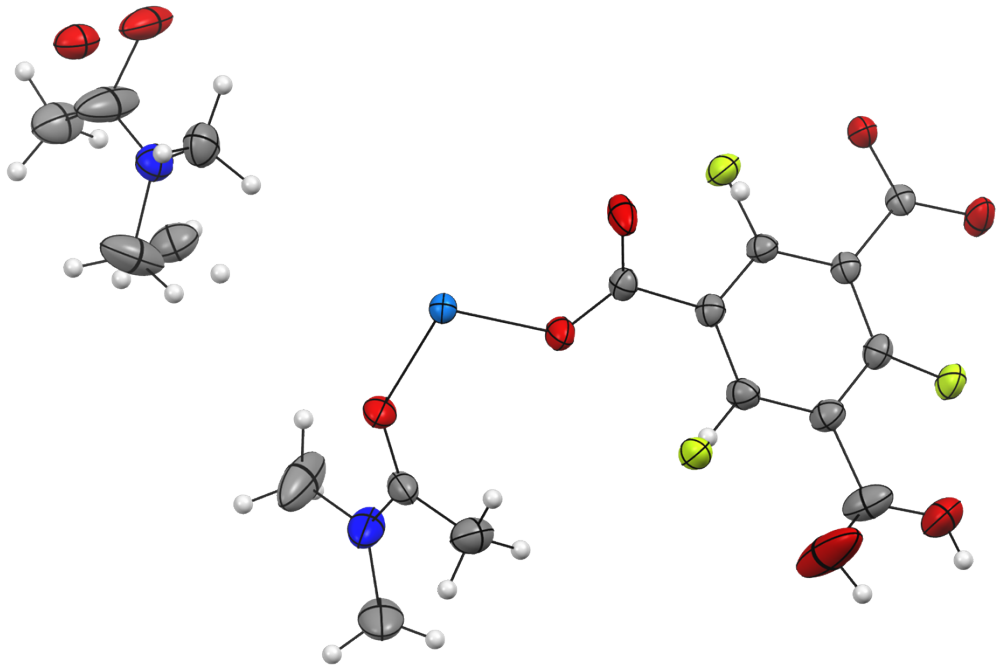


Figure S3: ORTEP-like plot of the asymmetric unit of UHM-33 (probability level 50 %).

Identification code	UHM-33	
Empirical formula	C17 H21 Cu F N2 O8	
Formula weight	463.90	
Temperature	153(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.89060(10) Å	α= 90°.
	b = 11.62620(10) Å	β= 91.6710(10)°.
	c = 14.50100(10) Å	γ = 90°.
Volume	2003.80(3) $Å^3$	
Z	4	
Density (calculated)	1.538 Mg/m^3	

Absorption coefficient	2.054 mm^{-1}
F(000)	956
Crystal size	0.20 x 0.12 x 0.10 mm^3
Theta range for data collection	3.72 to 76.31°.
Index ranges	-14<=h<=14, -14<=k<=14, -18<=l<=18
Reflections collected	39591
Independent reflections	4185 [R(int) = 0.0208]
Completeness to theta = 76.31°	99.6 %
Absorption correction	Numerical
Max. and min. transmission	0.8210 and 0.6842
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4185 / 0 / 308
Goodness-of-fit on F^2	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1095
R indices (all data)	R1 = 0.0436, wR2 = 0.1099
Largest diff. peak and hole	0.744 and -0.932 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for UHM-33. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	5821(1)	5784(1)	88(1)	20(1)
O(1)	4882(1)	6321(2)	1095(1)	33(1)
O(2)	3460(1)	9652(2)	4073(1)	31(1)
O(3)	4849(2)	8361(2)	4217(1)	40(1)
O(4)	3505(2)	5029(2)	945(1)	38(1)
O(5)	-5(2)	6731(4)	3766(2)	113(2)
O(6)	-4(2)	5671(2)	2538(2)	59(1)
F(1)	4923(3)	7704(4)	2433(3)	34(1)
F(2)	1621(2)	8121(3)	4107(2)	33(1)
F(3)	1573(8)	5574(8)	1660(6)	35(2)
C(1)	3956(2)	5897(2)	1302(1)	22(1)
C(2)	3328(2)	6493(2)	2044(1)	23(1)
C(3)	2208(2)	6229(2)	2195(2)	27(1)
C(4)	1613(2)	6779(2)	2881(2)	29(1)

C(5)	2164(2)	7620(2)	3415(2)	27(1)
C(6)	3289(2)	7884(2)	3290(2)	23(1)
C(7)	3855(2)	7316(2)	2603(2)	24(1)
C(8)	3919(2)	8705(2)	3912(1)	23(1)
C(9)	432(2)	6399(3)	3055(2)	44(1)
C(10)	8798(2)	6094(3)	132(2)	41(1)
C(11)	-2848(3)	6492(3)	3040(3)	57(1)
O(7)	7034(1)	7083(1)	308(1)	31(1)
C(12)	8080(2)	7066(2)	457(2)	31(1)
N(1)	8571(2)	7921(2)	921(2)	50(1)
C(13)	7887(3)	8858(3)	1280(4)	85(2)
C(14)	9792(3)	8056(3)	1045(3)	62(1)
O(8A)	-1678(3)	5413(3)	4186(3)	41(1)
O(8B)	-1728(4)	4806(5)	3356(5)	62(2)
C(15)	-2630(3)	5453(3)	3644(4)	76(1)
N(2)	-3443(2)	4833(2)	3921(2)	36(1)
C(16)	-3239(3)	3836(2)	4508(2)	42(1)
C(17A)	-4567(6)	4992(7)	3545(5)	49(2)
C(17B)	-4566(10)	5398(11)	3968(9)	68(3)

Powder X-ray diffraction patterns of UHM-31, UHM-32 and UHM-33

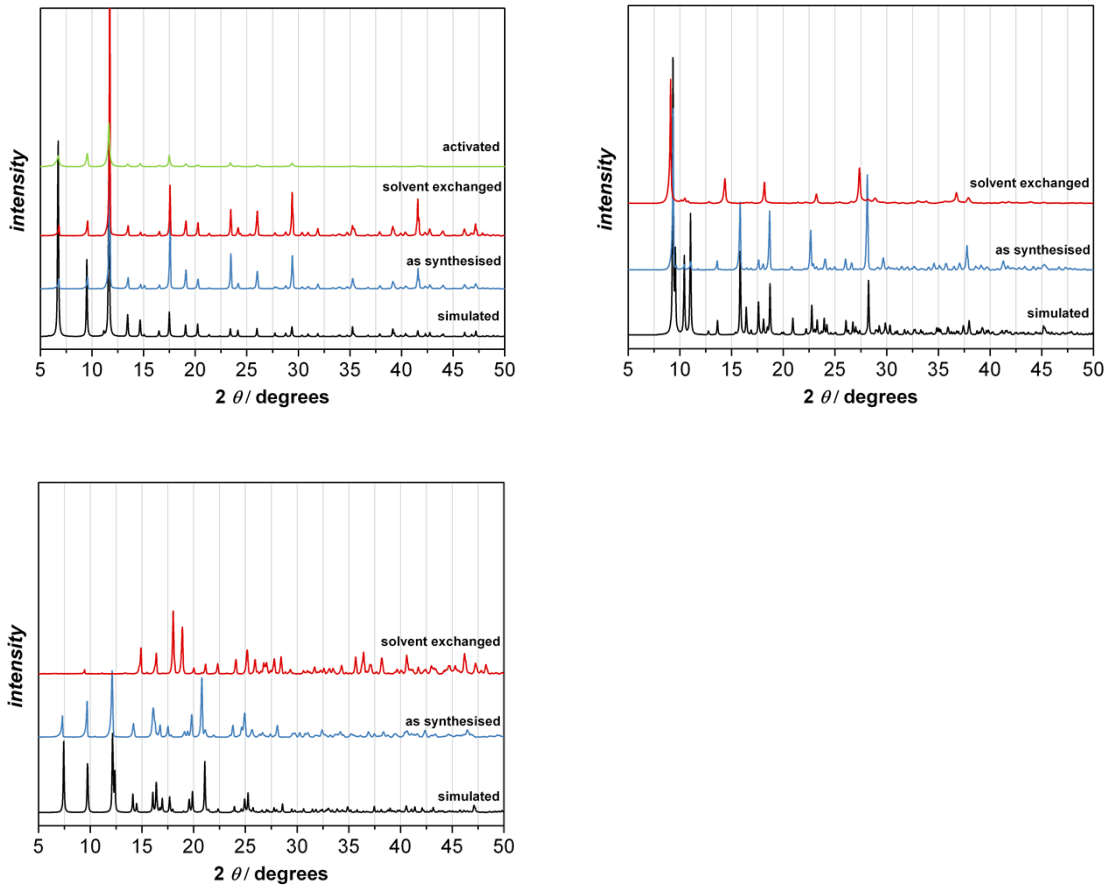


Figure S4: Powder X-ray diffraction patterns of UHM-31 (top, left), UHM-32 (top, right) and UHM-33 (bottom). Powder XRD patterns of the balk phases (blue) are compared with diffractograms simulated from the X-ray single-crystal data (black). In all three cases structural identity of the microcrystalline and the single-crystal phase can be confirmed. Furthermore the diffractogram of the MOFs after solvent exchange with ethanol are given (red). For UHM-31 the as synthesised structure remains, UHM-32 and UHM-33 show a structure change. After thermal treatment in vaccum the crystallinity of UHM-31 is reduced (green).

Thermo-gravimetric studies on UHM-31, UHM-32 and UHM-33

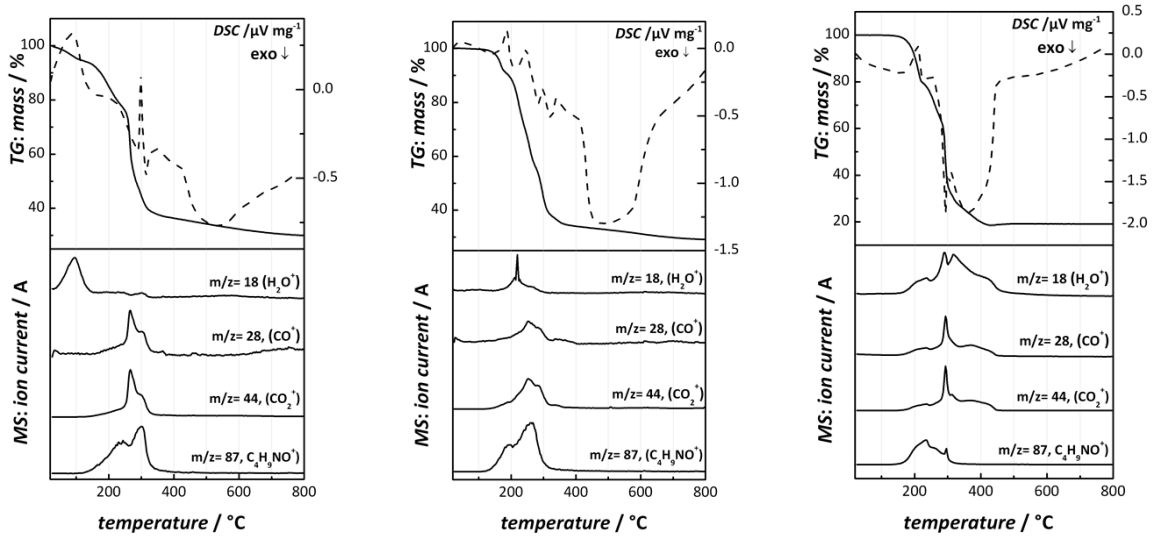
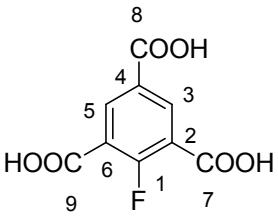


Figure S5: TG-DTA studies coupled with mass spectrometry. Left: UHM-31, middle: UHM-32, right: UHM-33. The overall mass decrease of UHM-31 can be roughly divided into three parts. Between 50 and 150 °C the dehydration of the material (m/z: 18) can be detected. The second step shows the detection of DMA (m/z: 87) between 200 and 260 °C. The third weight change occurs in the temperature interval of 260 to 400 °C and is accompanied by the detection of CO (m/z: 28), CO_2 (m/z: 44) and water (m/z: 18), which are generated by the thermal decomposition of the network. UHM-32 and UHM-33 do not show the effect of dehydration. Therefore the overall mass decrease of these two MOFs can be described in two steps. In UHM-32 the loss of DMA can be detected between 125 and 210 °C, in UHM-33 between 175 and 260 °C. In both cases the step of DMA loss goes directly into the degradation step as well.

[1]H-NMR and ESI-MS studies on UHM-31



M = 228.13 g/mol

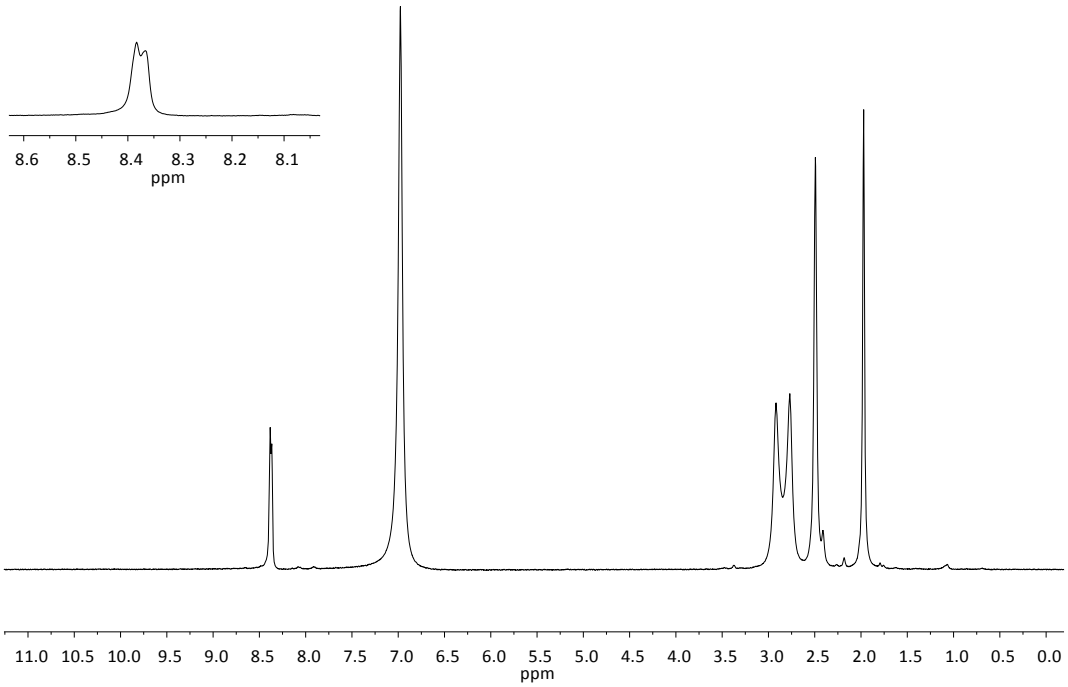


Figure S6: UHM-31 was digested with DCl in DMSO for [1]H-NMR (DMSO-*d*6, 400 MHz) analysis to prove that the fluorine substituent remained during the MOF synthesis. The linker signal at 8.38 ppm (*d*, $^4J_{H,F}$ = 5.3 Hz, 2H, H-3/H-5) still shows the typical H-F coupling. Further signals: δ (ppm) = 2.50 (*m*, DMSO); 1.97, 2.77, 2.92 (*s*, DMA); 6.98 (*s*, H_2O). Compared to the NMR spectrum of the pure linker (see Figure S7) this NMR sprecturm shows broader peaks and a smaller coupling constant for the H-F coupling, this is due to the paramagnetism induced by the copper ions.

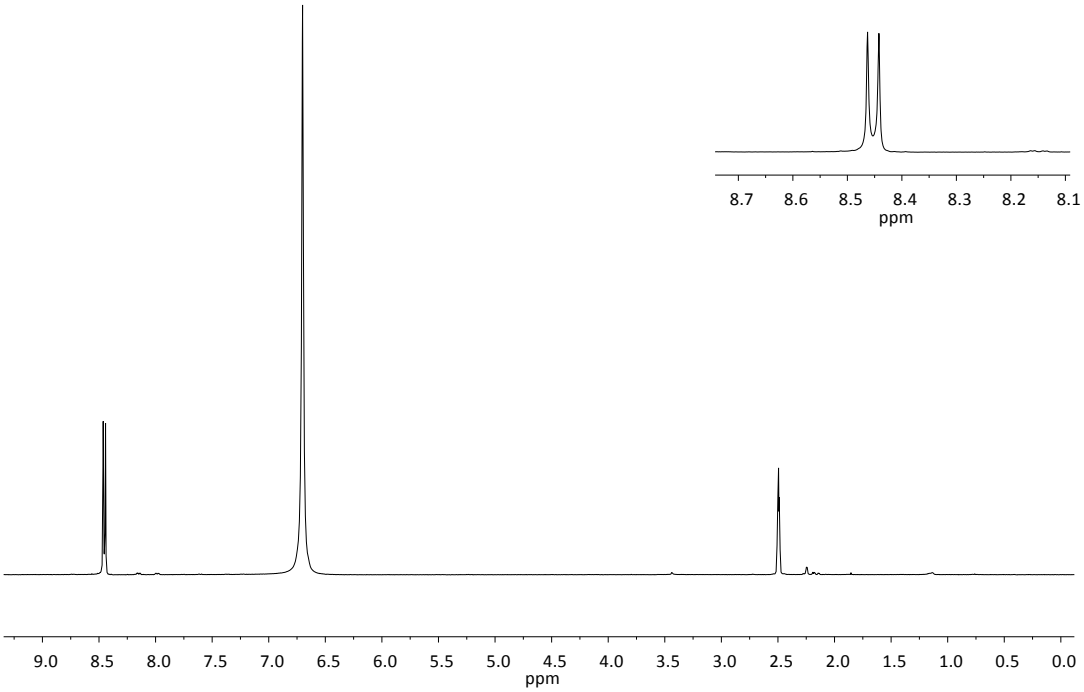


Figure S7: ^{1}H-NMR (DMSO-*d*6, 400 MHz) spectrum of the pure Fbtc linker: δ (ppm) = 8.45 (*d*, $^{4}J_{H,F}$ = 6.2 Hz, 2H, H-3/H-5). Further signals: δ (ppm) = 2.50 (*m*, DMSO); 5.42 (*s*, H_2O).

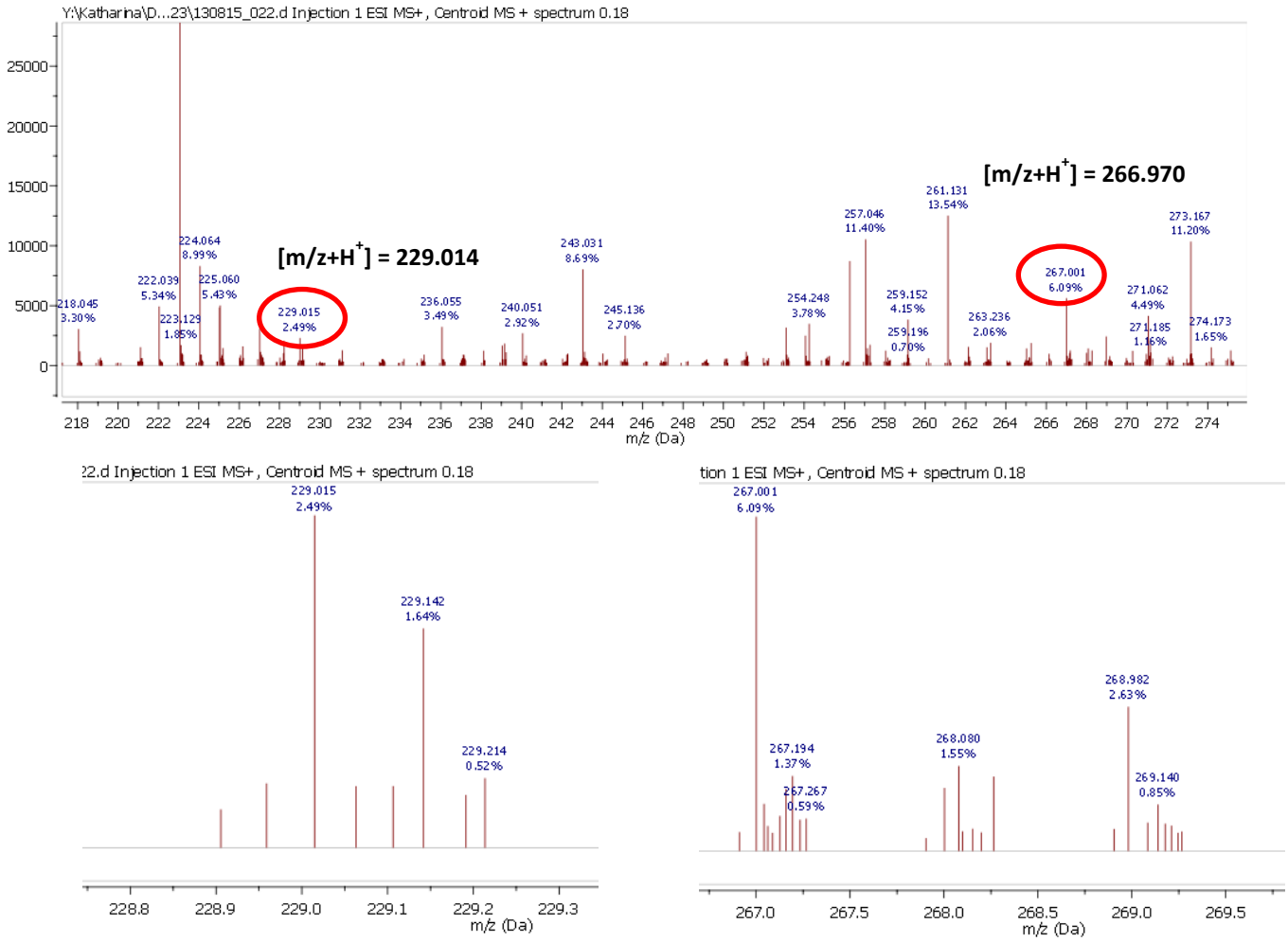


Figure S8: ESI-MS analysis shows the existence of the Fbtc linker as hydrogen adduct [m/z + H^+] = 228.70 and the as potassium adduct [m/z + K^+] = 266.970.

References

[1] A.L.Spek, *Acta Cryst.*, 2009, **D65**, 148.