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Supporting Information

Nanocrystalline FeF_3 and MF_2 (M=Fe, Co, Mn) from Metal Trifluoroacetates and their Li(Na)-ion Storage Properties

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Materials and Methods

$Fe(CF_3COO)_2(CF_3COOH)_2$ $FeCl_2$ (2 g, Sigma-Aldrich, 372870, 98 %) was mixed with trifluoroacetic acid (TFA, 20 mL, Sigma-Aldrich, 299537, ≥99 %) in a 100 mL one-neck round-bottom Schlenk flask. Because of the corrosive nature of TFA this was not performed in a glovebox; therefore short exposure to air could not be avoided. This applies to all syntheses in this work dealing with TFA. The reaction mixture was heated to 85 °C under N_2 flow. At this temperature, the reaction was held for 2 days under reflux. A clear brown solution was obtained. The reaction mixture was passively cooled down in which a colorless powder of $Fe(CF_3COO)_2(CF_3COOH)_2$ crystallized out of solution. The product was collected by filtration under N_2, followed by vacuum drying. By exposure to air, a hydrolyzed form is observed by undergoing a color change from colorless to brown.

$Mn_2(\mu\text{-}CF_3COO)_4(CF_3COOH)_4$ $MnCl_2$ (3.5 g, Merck, 7773-01-5, ≥96 %) and TFA (40 mL, Sigma-Aldrich, 299537, **≥**99 %) were mixed in a 100 mL one-neck flask. The reaction mixture was kept at 82 °C for 2 d under reflux and N_2 flow. A transparent onion colored solution was finally obtained. By cooling to room temperature, $Mn_2(\mu\text{-}CF_3COO)_4(CF_3COOH)_4$ crystalized out. The product was filtrated under N_2 and dried under vacuum. No further purification was executed. If the filtration was carried out under air, a hydrolyzed "$Mn(TFA)_2$" precursor was obtained. This hydrolyzed precursor also provides MnF_2 after decomposition.

"$Co(TFA)_2$" $CoCl_2$ (4 g, Sigma-Aldrich, 60818-50G, ≥ 98 %) and TFA (40 mL, Sigma-Aldrich, 299537, **≥**99 %) were mixed in a 100 mL one-neck flask. Under reflux and N_2 flow the synthesis was kept at 95 °C under stirring for 4 d. A dark blue solution was obtained. After evaporation at RT to 2/3 of the initial volume, 20 mL Toluene was added. This induced the crystallization of the precursor. The solution was heated up to 50 °C and stirred under N_2 flow for 12 hours. The obtained suspension was filtered under inert conditions yielding a pink powder. The pink colored powder was washed with toluene three times. The final product was then dried under vacuum. Both precursors, "$Co(TFA)_2$" and $Co(CF_3COOH)_2(H_2O)_4$, provide CoF_2 after decomposition. $Co(CF_3COOH)_2(H_2O)_4$ can be obtained when "$Co(TFA)_2$" is exposed to air, and is accompanied by a visible color change from pink to baby blue. The powder pattern of "$Co(TFA)_2$" can be seen in Fig. S1.

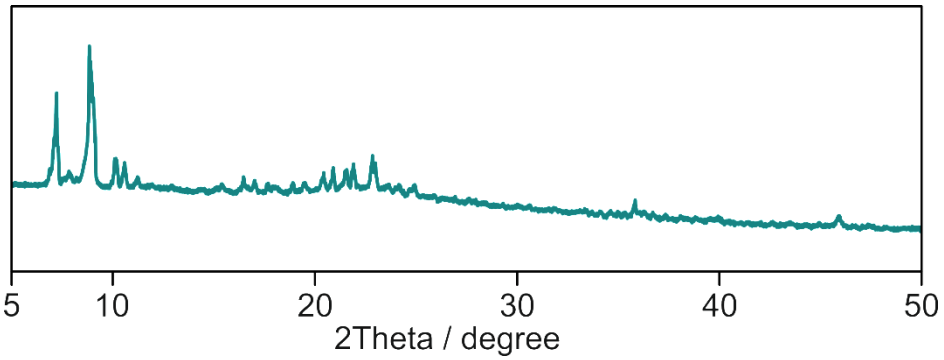

Fig. S1 Powder XRD pattern of "$Co(TFA)_2$".

FeF_2 $Fe(CF_3COO)_2(CF_3COOH)_2$ was used as a precursor to obtain FeF_2 by decomposition. The synthetic procedure followed was the same as that for FeF_3. In this case the decomposition was accomplished at an elevated temperature (285 °C) with the same heating rate and time.

MnF_2 $Mn_2(\mu\text{-}CF_3COO)_4(CF_3COOH)_4$ was used as a precursor for MnF_2. The synthetic procedure followed was the same as that for FeF_3, with small variations. The decomposition took place without a preset drying step. The precursor was placed inside a silica quartz tube and then into a preheated oven at 350 °C. After 10 seconds the release valve connected to a bubbler was opened with no additional gas flow. The duration of the decomposition step was 3 h. The MnF_2 was then used in its obtained state without further purification. Increasing the time of the synthesis at lower temperatures or slowly heating provides larger crystals of MnF_2.

CoF_2 **"**$Co(TFA)_2$" was used as a precursor to obtain CoF_2 by decomposition. The synthetic procedure followed was nearly the same as that for FeF_3. In this case, the decomposition was accomplished by heating the precursor at 295 °C for 20 h with a heating rate of 50 °C h^{-1}.

Structure determination

Crystallographic information for $Fe_3O(CF_3COO)_7(CF_3COOH)$

Several trifluoroacetyl groups are strongly disordered and were described by split positions. A description by anisotropic displacement parameters has not been possible with the TFA-group O50 O51 C52 C53 F54 F55 F56 and the refinement has, therefore, been performed by isotropic displacement parameters. Presumably due to disorder, it was not possible to locate the hydrogen-atom at the oxygen-atom O51/O51A. The hydrogen-atom has been omitted from the refinement.

Table S1 Crystal data and structure refinement for $Fe_3O(CF_3COO)_7(CF_3COOH)$

Empirical formula	$C_{16}HF_{24}Fe_3O_{17}$
Formula weight / g mol^{-1}	1088.72
Temperature / K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	9.7505(11)
b / Å	21.236(2)
c / Å	16.0879(18)
α / °	90
β / °	91.358(2)
γ / °	90
Volume / $Å^3$	3330.2(6)
Z	4
ρ_{calc}g / cm^3	2.171
μ / mm^{-1}	1.495
F(000)	2108.0
Crystal size / mm^3	0.112 × 0.005 × 0.0025
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection / °	3.176 to 55.122
Index ranges	-12 ≤ h ≤ 12, -27 ≤ k ≤ 27, -20 ≤ l ≤ 20
Reflections collected	32972
Independent reflections	7688 [R_{int} = 0.0652]
Data/restraints/parameters	7688/145/588
Goodness-of-fit on F^2	1.154
Final R indexes [I>=2σ (I)]	R_1 = 0.0710, wR_2 = 0.1541
Final R indexes [all data]	R_1 = 0.0884, wR_2 = 0.1631
Largest diff. peak/hole / e $Å^{-3}$	1.28/-1.04

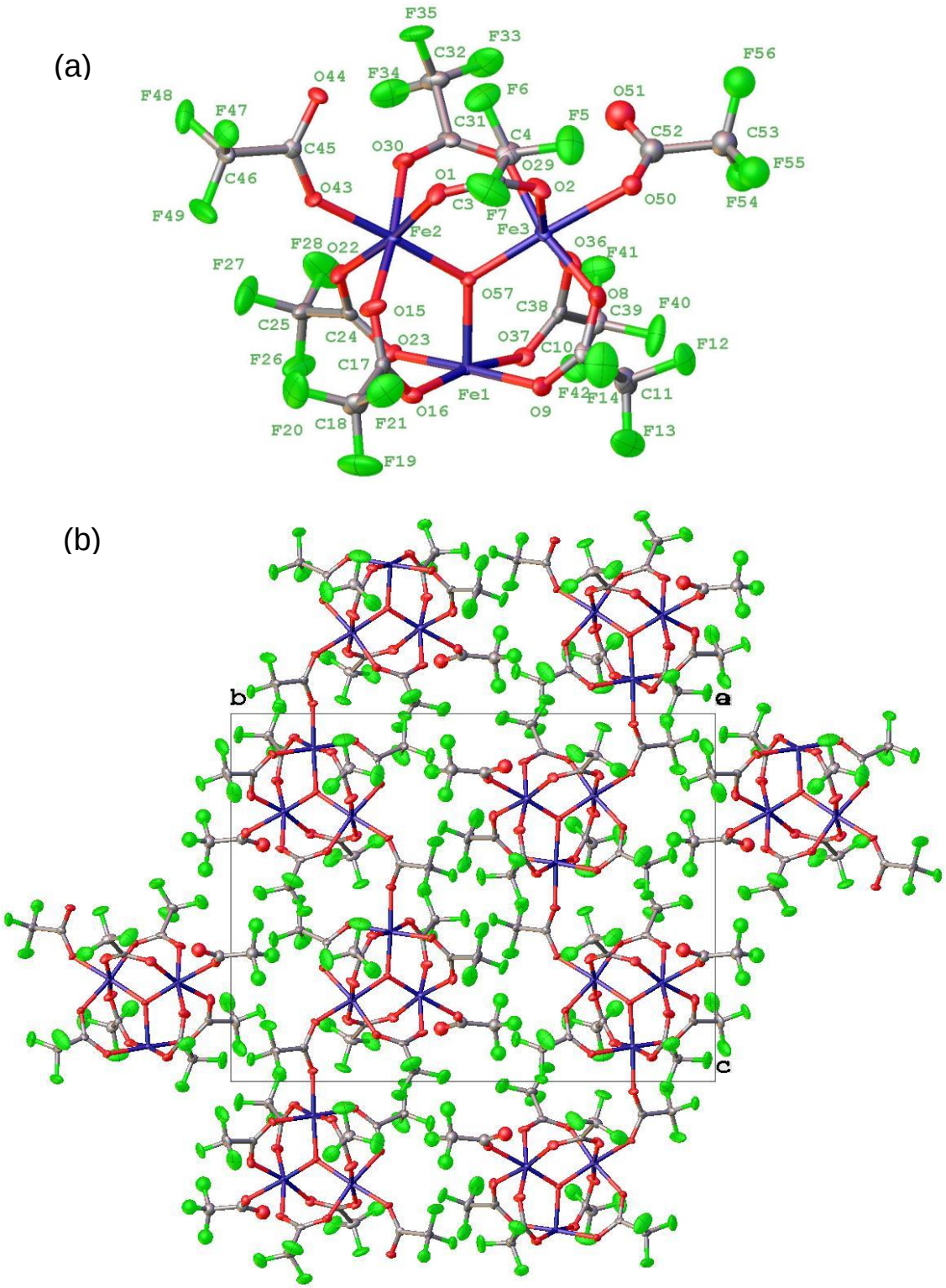

Fig. S2 (a) Structure of $Fe_3O(CF_3COO)_7(CF_3COOH)$. Neutral CF_3COOH molecule present at Fe1 is not shown for clarity. (b) An illustration of the arrangement of such $[Fe_3O]$-based molecules.

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Fe_3O(CF_3COO)_7(CF_3COOH)$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Fe1	103.3(7)	3293.2(3)	4057.6(4)	12.25(16)
Fe2	-167.6(7)	2506.2(3)	2218.8(4)	13.27(16)
Fe3	1308.8(7)	3902.3(3)	2325.7(4)	15.70(17)
F19	-4331(4)	2666(2)	4282(2)	57.6(13)
F20	-4311(4)	1977(2)	3315(3)	57.9(13)
F21	-4736(4)	2928(2)	3021(3)	49.3(11)
F26	1971(5)	1405.8(18)	4942(2)	47.1(11)
F27	1479(5)	883.9(17)	3855(3)	56.0(12)
F28	3187(4)	1500(2)	3871(3)	66.1(15)
F33	4902(4)	2894(2)	1081(3)	57.1(13)
F34	4331(4)	1990(2)	1533(3)	48.9(11)
F35	3529(4)	2311.7(19)	363(2)	37.6(9)
F40	3973(4)	4833.5(16)	4429(3)	44.7(10)
F41	5224(4)	4092(2)	3981(2)	43.0(9)
F42	4252(3)	3996.3(17)	5149(2)	33.1(8)
F47	-2699(3)	1008.1(16)	234(2)	30.0(7)
F48	-999(4)	415.8(15)	600(2)	36.3(9)
F49	-2330(5)	771(2)	1521(2)	51.9(12)
O1	-946(4)	3010.2(17)	1258(2)	23.8(8)
O2	116(4)	3943.6(18)	1306(2)	24.2(8)
O8	166(4)	4584.4(17)	2788(2)	28.0(9)
O9	-774(4)	4145.6(16)	3899(2)	21.2(8)
O15	-2055(4)	2515.9(19)	2684(2)	26.1(9)
O16	-1788(4)	2918.9(17)	3962(2)	20.0(7)
O22	566(4)	1906.0(16)	3081(2)	23.2(8)
O23	974(4)	2443.2(15)	4258(2)	17.5(7)
O29	2719(4)	3350.3(17)	1738(2)	21.6(8)
O30	1666(4)	2414.1(17)	1660(2)	23.0(8)
O36	2816(4)	4042.9(18)	3169(2)	24.4(8)
O37	1930(4)	3694.3(17)	4352(2)	19.3(7)
O43	-804(4)	1743.0(16)	1611(2)	17.0(7)
O44	-214(4)	1689.3(17)	283(2)	19.2(7)
O57	429(3)	3236.9(15)	2861.4(19)	13.5(7)
C3	-737(5)	3563(2)	1027(3)	18.3(10)
C4	-1666(6)	3793(3)	299(3)	25.9(10)
C17	-2447(5)	2677(2)	3380(3)	16.9(10)
C18	-3978(6)	2556(3)	3516(4)	27.1(12)
C24	1064(5)	1982(2)	3791(3)	15.9(10)
C25	1938(6)	1429(3)	4121(3)	23.4(11)
C31	2633(5)	2776(3)	1553(3)	19.6(10)
C32	3889(6)	2484(3)	1124(4)	29.4(13)
C38	2825(5)	3952(2)	3932(3)	18(1)
C39	4099(5)	4217(2)	4396(3)	21.9(11)
C45	-828(5)	1506(2)	909(3)	15.1(9)
C46	-1735(6)	917(3)	822(3)	22.5(11)
F5	-1466(7)	4392(2)	122(4)	50.5(15)
F6	-1397(6)	3477(3)	-379(3)	45.2(14)
F7	-2946(5)	3721(3)	466(4)	56.8(16)
F12	-1165(9)	5625(4)	3107(6)	33.9(17)
F13	-2218(10)	5182(4)	4106(5)	53(2)
F14	-2750(7)	4929(3)	2853(7)	57(2)
F54	4808(9)	5567(4)	2198(5)	47.9(9)
F55	3043(8)	5851(4)	1575(6)	47.9(9)
F56	4531(9)	5524(4)	762(5)	47.9(9)

O50	2295(9)	4686(4)	1764(6)	20.4(11)
O51	4409(10)	4338(5)	1432(7)	43.3(16)
C10	-641(18)	4546(8)	3368(11)	17.5(15)
C11	-1720(20)	5087(6)	3367(12)	29.6(18)
C52	3500(13)	4763(6)	1600(9)	29.1(16)
C53	4036(13)	5442(6)	1520(8)	34(2)
F5A	-950(17)	3860(10)	-353(9)	33(3)
F6A	-2534(18)	3330(9)	39(11)	38(3)
F7A	-2280(20)	4276(9)	479(10)	37(3)
F12A	-1550(40)	5630(20)	2970(30)	32(6)
F13A	-1640(40)	5358(16)	4229(18)	43(6)
F14A	-2890(30)	4967(13)	3340(30)	42(6)
F54A	5153(12)	5489(5)	1969(7)	47.9(9)
F55A	3357(12)	5748(5)	1279(8)	47.9(9)
F56A	5131(13)	5341(5)	786(6)	47.9(9)
O50A	2514(12)	4597(6)	1695(8)	20.4(11)
O51A	4639(14)	4217(6)	1560(9)	43.3(16)
C10A	-770(90)	4620(40)	3340(60)	17.5(15)
C11A	-1750(100)	5190(30)	3430(60)	29.6(18)
C52A	3721(16)	4659(7)	1543(13)	29.1(16)
C53A	4352(18)	5304(8)	1393(11)	34(2)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for $Fe_3O(CF_3COO)_7(CF_3COOH)$. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	16.1(3)	13.9(3)	6.8(3)	-0.5(2)	-0.7(2)	1.8(3)
Fe2	16.2(3)	16.6(3)	7.1(3)	-2.3(2)	1.9(2)	-3.3(3)
Fe3	18.8(4)	18.0(4)	10.2(3)	1.5(3)	-1.6(3)	-6.2(3)
F19	30(2)	108(4)	35(2)	-10(2)	15.8(17)	-11(2)
F20	34(2)	43(2)	98(4)	-13(2)	22(2)	-21.7(18)
F21	26.9(19)	62(3)	58(3)	-10(2)	-8.5(18)	14.8(19)
F26	82(3)	39(2)	19.4(17)	5.0(15)	0.4(18)	30(2)
F27	96(4)	17.7(18)	53(3)	-4.0(17)	-19(2)	11(2)
F28	34(2)	73(3)	92(4)	35(3)	27(2)	32(2)
F33	24.4(19)	73(3)	75(3)	-31(2)	24(2)	-19(2)
F34	35(2)	66(3)	45(2)	-7(2)	0.2(18)	24(2)
F35	34.7(19)	58(2)	20.3(17)	-16.4(16)	9.5(14)	-2.4(17)
F40	49(2)	19.0(17)	64(3)	-7.1(17)	-33(2)	-3.3(16)
F41	22.6(18)	65(3)	41(2)	-11.4(19)	-3.5(16)	-3.6(17)
F42	30.4(18)	43(2)	25.1(17)	4.4(15)	-13.2(14)	-8.1(16)
F47	21.8(16)	35.0(19)	32.7(18)	-1.7(15)	-7.7(14)	-8.4(14)
F48	54(2)	16.1(16)	38(2)	0.9(14)	-20.0(17)	-3.1(15)
F49	74(3)	58(3)	23.9(19)	-5.2(17)	11.3(19)	-48(2)
O1	36(2)	20.0(19)	14.9(17)	-3.2(14)	-7.1(15)	1.8(16)
O2	26(2)	34(2)	12.1(17)	6.7(15)	-5.1(14)	-7.8(17)
O8	39(2)	16.8(18)	28(2)	3.0(15)	8.2(17)	-2.5(16)
O9	31(2)	16.1(17)	16.5(17)	4.3(13)	0.9(15)	7.5(15)
O15	17.9(18)	38(2)	22.4(19)	-14.2(17)	4.9(15)	-5.5(16)
O16	18.5(18)	27.6(19)	13.9(17)	-0.6(14)	2.5(14)	-3.1(15)
O22	43(2)	14.7(17)	11.5(17)	-1.9(13)	-2.6(16)	0.2(16)
O23	24.5(18)	15.5(17)	12.4(16)	-1.1(13)	-2.4(14)	5.4(14)
O29	17.0(17)	27(2)	20.8(18)	-0.4(15)	5.8(14)	-6.2(15)
O30	19.9(18)	26(2)	23.2(19)	-9.6(15)	8.7(15)	-4.8(15)
O36	25(2)	31(2)	16.5(18)	2.7(15)	-5.7(15)	-13.9(16)
O37	19.7(18)	24.9(19)	13.1(16)	-2.9(14)	-4.2(14)	-2.9(15)
O43	24.2(18)	17.5(17)	9.4(15)	-4.9(13)	0.6(13)	-6.5(14)
O44	24.1(18)	23.1(18)	10.3(16)	1.0(14)	1.1(14)	-7.7(15)

O57	17.7(16)	14.5(16)	8.1(15)	-1.0(12)	-1.4(12)	-2.6(13)
C3	18(2)	27(2)	9.6(18)	-2.5(16)	1.4(15)	5.0(18)
C4	27(2)	32(2)	18.5(19)	2.1(16)	-8.3(15)	4.2(16)
C17	19(2)	12(2)	20(2)	-0.1(18)	1.7(19)	-0.4(18)
C18	19(3)	33(3)	30(3)	-5(2)	5(2)	1(2)
C24	19(2)	16(2)	13(2)	2.4(18)	5.8(18)	-1.7(19)
C25	35(3)	21(3)	14(2)	1(2)	4(2)	8(2)
C31	21(3)	29(3)	9(2)	-0.8(19)	-2.0(18)	-5(2)
C32	18(3)	47(4)	23(3)	-10(3)	3(2)	-3(3)
C38	20(2)	11(2)	23(3)	-5.2(19)	-2(2)	0.2(19)
C39	23(3)	21(3)	21(3)	-2(2)	-6(2)	0(2)
C45	11(2)	18(2)	17(2)	0.8(18)	-3.6(18)	2.4(18)
C46	28(3)	24(3)	15(2)	-1(2)	-1(2)	-13(2)
F5	65(3)	40(2)	45(3)	12.2(19)	-29(3)	-3(2)
F6	58(3)	53(3)	24(2)	-5.9(19)	-15.6(19)	21(2)
F7	29(2)	94(4)	47(3)	28(3)	-5.1(18)	7(2)
F12	34(4)	20(2)	48(4)	14(2)	-3(3)	10(3)
F13	61(5)	43(4)	56(3)	17(3)	25(3)	33(3)
F14	37(3)	51(3)	82(6)	10(3)	-33(3)	11(2)
C10	19(4)	17(4)	16(2)	3(2)	-8(2)	1(2)
C11	28(3)	23(4)	38(4)	11(3)	-1(2)	10(3)
F5A	28(5)	55(7)	17(3)	5(3)	-11(3)	4(4)
F6A	40(5)	45(5)	29(6)	2(4)	-16(4)	-3(4)
F7A	42(6)	44(4)	24(5)	-2(3)	-13(4)	16(4)
F12A	23(13)	30(7)	43(9)	12(7)	-12(8)	5(7)
F13A	50(13)	39(11)	40(6)	3(5)	-2(6)	8(9)
F14A	27(5)	34(9)	66(14)	4(8)	-2(6)	6(5)
C10A	19(4)	17(4)	16(2)	3(2)	-8(2)	1(2)
C11A	28(3)	23(4)	38(4)	11(3)	-1(2)	10(3)

Table S4 Bond Lengths for $Fe_3O(CF_3COO)_7(CF_3COOH)$. (^{1}+X,1/2-Y,1/2+Z; ^{2}+X,1/2-Y,-1/2+Z).

Atom	**Atom**	**Length/Å**		**Atom**	**Atom**	**Length/Å**
Fe1	O9	2.016(3)		O22	C24	1.242(6)
Fe1	O16	2.011(4)		O23	C24	1.238(6)
Fe1	O23	2.017(3)		O29	C31	1.258(6)
Fe1	O37	2.021(3)		O30	C31	1.232(6)
Fe1	O44^1	2.003(3)		O36	C38	1.243(6)
Fe1	O57	1.962(3)		O37	C38	1.243(6)
Fe2	O1	2.014(4)		O43	C45	1.236(6)
Fe2	O15	2.003(4)		O44	Fe1^2	2.002(3)
Fe2	O22	2.003(4)		O44	C45	1.247(6)
Fe2	O30	2.030(4)		C3	C4	1.542(7)
Fe2	O43	1.984(3)		C4	F5	1.319(8)
Fe2	O57	1.946(3)		C4	F6	1.312(7)
Fe3	O2	1.991(4)		C4	F7	1.292(8)
Fe3	O8	1.983(4)		C4	F5A	1.283(17)
Fe3	O29	2.054(4)		C4	F6A	1.357(17)
Fe3	O36	1.999(4)		C4	F7A	1.226(17)
Fe3	O57	1.874(3)		C17	C18	1.535(7)
Fe3	O50	2.134(9)		C24	C25	1.539(7)
Fe3	O50A	2.155(13)		C31	C32	1.549(7)
F19	C18	1.308(7)		C38	C39	1.541(7)
F20	C18	1.310(7)		C45	C46	1.537(7)
F21	C18	1.332(7)		F12	C11	1.335(19)
F26	C25	1.322(6)		F13	C11	1.312(18)

F27	C25	1.309(7)		F14	C11	1.33(2)
F28	C25	1.301(7)		F54	C53	1.337(15)
F33	C32	1.321(7)		F55	C53	1.304(15)
F34	C32	1.304(7)		F56	C53	1.334(15)
F35	C32	1.318(6)		O50	C52	1.222(16)
F40	C39	1.316(6)		O51	C52	1.297(9)
F41	C39	1.324(6)		C10	C11	1.557(16)
F42	C39	1.303(6)		C52	C53	1.540(18)
F47	C46	1.332(6)		F12A	C11A	1.23(10)
F48	C46	1.337(7)		F13A	C11A	1.33(9)
F49	C46	1.315(6)		F14A	C11A	1.21(10)
O1	C3	1.249(6)		F54A	C53A	1.26(2)
O2	C3	1.237(6)		F55A	C53A	1.36(2)
O8	C10	1.238(18)		F56A	C53A	1.25(2)
O8	C10A	1.29(9)		O50A	C52A	1.21(2)
O9	C10	1.214(16)		O51A	C52A	1.297(9)
O9	C10A	1.35(7)		C10A	C11A	1.55(8)
O15	C17	1.240(6)		C52A	C53A	1.52(2)
O16	C17	1.236(6)				

Table S5 Bond Angles for $Fe_3O(CF_3COO)_7(CF_3COOH)$. (^{1}+X,1/2-Y,1/2+Z; ^{2}+X,1/2-Y,-1/2+Z).

Atom	**Atom**	**Atom**	**Angle/°**		**Atom**	**Atom**	**Atom**	**Angle/°**
O9	Fe1	O23	178.07(14)		O15	C17	C18	113.9(4)
O9	Fe1	O37	91.14(15)		O16	C17	O15	129.3(5)
O16	Fe1	O9	87.70(15)		O16	C17	C18	116.8(4)
O16	Fe1	O23	92.31(15)		F19	C18	F20	109.3(5)
O16	Fe1	O37	170.55(14)		F19	C18	F21	107.7(5)
O23	Fe1	O37	88.52(15)		F19	C18	C17	112.5(5)
O44^1	Fe1	O9	91.88(14)		F20	C18	F21	106.1(5)
O44^1	Fe1	O16	85.41(14)		F20	C18	C17	110.9(4)
O44^1	Fe1	O23	86.19(14)		F21	C18	C17	110.1(5)
O44^1	Fe1	O37	85.25(14)		O22	C24	C25	114.8(4)
O57	Fe1	O9	90.50(14)		O23	C24	O22	129.0(5)
O57	Fe1	O16	94.03(14)		O23	C24	C25	116.2(4)
O57	Fe1	O23	91.43(13)		F26	C25	C24	111.9(4)
O57	Fe1	O37	95.36(14)		F27	C25	F26	107.1(5)
O57	Fe1	O44^1	177.53(14)		F27	C25	C24	112.4(5)
O1	Fe2	O30	91.78(16)		F28	C25	F26	108.2(5)
O15	Fe2	O1	87.05(17)		F28	C25	F27	108.5(5)
O15	Fe2	O22	93.68(17)		F28	C25	C24	108.6(4)
O15	Fe2	O30	173.32(15)		O29	C31	C32	116.4(5)
O22	Fe2	O1	172.53(14)		O30	C31	O29	128.2(5)
O22	Fe2	O30	86.64(16)		O30	C31	C32	115.4(5)
O43	Fe2	O1	87.04(14)		F33	C32	C31	111.0(5)
O43	Fe2	O15	85.02(15)		F34	C32	F33	108.6(5)
O43	Fe2	O22	85.62(14)		F34	C32	F35	108.9(5)
O43	Fe2	O30	88.36(14)		F34	C32	C31	110.7(5)
O57	Fe2	O1	94.96(14)		F35	C32	F33	108.4(5)
O57	Fe2	O15	93.39(14)		F35	C32	C31	109.2(4)
O57	Fe2	O22	92.42(14)		O36	C38	C39	114.1(4)
O57	Fe2	O30	93.25(14)		O37	C38	O36	128.1(5)
O57	Fe2	O43	177.39(14)		O37	C38	C39	117.7(4)
O2	Fe3	O29	91.74(16)		F40	C39	F41	107.4(5)
O2	Fe3	O36	163.48(15)		F40	C39	C38	107.9(4)
O2	Fe3	O50	82.9(3)		F41	C39	C38	110.5(4)
O2	Fe3	O50A	84.0(4)		F42	C39	F40	109.2(4)

O8	Fe3	O2	87.38(17)		F42	C39	F41	108.6(4)
O8	Fe3	O29	167.85(15)		F42	C39	C38	113.1(4)
O8	Fe3	O36	92.69(17)		O43	C45	O44	127.8(5)
O8	Fe3	O50	81.5(2)		O43	C45	C46	114.4(4)
O8	Fe3	O50A	89.6(3)		O44	C45	C46	117.8(4)
O29	Fe3	O50	86.4(2)		F47	C46	F48	107.5(4)
O29	Fe3	O50A	78.2(3)		F47	C46	C45	109.9(4)
O36	Fe3	O29	84.72(16)		F48	C46	C45	111.2(4)
O36	Fe3	O50	80.7(3)		F49	C46	F47	108.9(5)
O36	Fe3	O50A	79.4(4)		F49	C46	F48	107.0(5)
O57	Fe3	O2	98.48(14)		F49	C46	C45	112.2(4)
O57	Fe3	O8	96.38(15)		C52	O50	Fe3	129.9(8)
O57	Fe3	O29	95.74(14)		O8	C10	C11	113.0(11)
O57	Fe3	O36	97.93(14)		O9	C10	O8	131.1(11)
O57	Fe3	O50	177.4(3)		O9	C10	C11	115.8(14)
O57	Fe3	O50A	173.6(3)		F12	C11	C10	110.8(14)
C3	O1	Fe2	131.9(3)		F13	C11	F12	108.3(10)
C3	O2	Fe3	130.2(3)		F13	C11	F14	108.1(14)
C10	O8	Fe3	127.4(7)		F13	C11	C10	112.2(14)
C10A	O8	Fe3	135(3)		F14	C11	F12	109.1(14)
C10	O9	Fe1	131.7(8)		F14	C11	C10	108.3(11)
C10A	O9	Fe1	138(4)		O50	C52	O51	128.1(13)
C17	O15	Fe2	130.3(3)		O50	C52	C53	118.2(9)
C17	O16	Fe1	133.0(3)		O51	C52	C53	113.6(11)
C24	O22	Fe2	132.8(3)		F54	C53	C52	107.7(11)
C24	O23	Fe1	130.2(3)		F55	C53	F54	102.6(10)
C31	O29	Fe3	128.4(3)		F55	C53	F56	105.1(11)
C31	O30	Fe2	133.4(4)		F55	C53	C52	111.3(10)
C38	O36	Fe3	129.4(3)		F56	C53	F54	120.7(11)
C38	O37	Fe1	133.1(3)		F56	C53	C52	109.2(10)
C45	O43	Fe2	141.4(3)		C52A	O50A	Fe3	135.3(11)
C45	O44	$Fe1^{2}$	152.9(3)		O8	C10A	O9	116(5)
Fe2	O57	Fe1	121.10(16)		O8	C10A	C11A	124(6)
Fe3	O57	Fe1	119.47(16)		O9	C10A	C11A	120(7)
Fe3	O57	Fe2	119.43(16)		F12A	C11A	F13A	112(6)
O1	C3	C4	115.3(5)		F12A	C11A	C10A	116(7)
O2	C3	O1	128.2(5)		F13A	C11A	C10A	106(7)
O2	C3	C4	116.5(5)		F14A	C11A	F12A	112(8)
F5	C4	C3	112.5(5)		F14A	C11A	F13A	106(7)
F6	C4	C3	110.1(5)		F14A	C11A	C10A	104(6)
F6	C4	F5	106.2(6)		O50A	C52A	O51A	126.1(17)
F7	C4	C3	111.0(5)		O50A	C52A	C53A	121.8(12)
F7	C4	F5	107.9(6)		O51A	C52A	C53A	111.9(15)
F7	C4	F6	109.0(6)		F54A	C53A	F55A	108.0(14)
F5A	C4	C3	109.6(8)		F54A	C53A	C52A	114.1(15)
F5A	C4	F6A	100.1(12)		F55A	C53A	C52A	110.8(13)
F6A	C4	C3	110.8(8)		F56A	C53A	F54A	100.2(14)
F7A	C4	C3	111.6(8)		F56A	C53A	F55A	107.1(14)
F7A	C4	F5A	112.3(13)		F56A	C53A	C52A	115.8(15)
F7A	C4	F6A	111.9(13)					

Table S6 Torsion Angles for $Fe_3O(CF_3COO)_7(CF_3COOH)$. (^{1}+X,1/2-Y,-1/2+Z).

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Fe1	O9	C10	O8	-7(3)		O8	C10A	C11A	F12A	-2(13)
Fe1	O9	C10	C11	168.3(9)		O8	C10A	C11A	F13A	-127(9)
Fe1	O9	C10A	O8	-13(12)		O8	C10A	C11A	F14A	121(9)
Fe1	O9	C10A	C11A	174(4)		O9	C10	C11	F12	148.2(17)
Fe1	O16	C17	O15	10.7(8)		O9	C10	C11	F13	27(2)
Fe1	O16	C17	C18	-168.9(4)		O9	C10	C11	F14	-92.2(19)
Fe1	O23	C24	O22	-4.7(8)		O9	C10A	C11A	F12A	170(8)
Fe1	O23	C24	C25	173.8(3)		O9	C10A	C11A	F13A	46(10)
Fe1	O37	C38	O36	1.1(8)		O9	C10A	C11A	F14A	-66(10)
Fe1	O37	C38	C39	178.9(3)		O15	C17	C18	F19	173.0(5)
Fe1^1	O44	C45	O43	-163.9(5)		O15	C17	C18	F20	50.2(7)
Fe1^1	O44	C45	C46	16.1(10)		O15	C17	C18	F21	-66.9(6)
Fe2	O1	C3	O2	6.2(8)		O16	C17	C18	F19	-7.4(7)
Fe2	O1	C3	C4	-173.9(3)		O16	C17	C18	F20	-130.2(5)
Fe2	O15	C17	O16	5.7(8)		O16	C17	C18	F21	112.7(5)
Fe2	O15	C17	C18	-174.8(4)		O22	C24	C25	F26	-154.2(5)
Fe2	O22	C24	O23	18.6(8)		O22	C24	C25	F27	-33.7(6)
Fe2	O22	C24	C25	-160.0(4)		O22	C24	C25	F28	86.4(6)
Fe2	O30	C31	O29	-4.2(8)		O23	C24	C25	F26	27.0(7)
Fe2	O30	C31	C32	176.7(4)		O23	C24	C25	F27	147.6(5)
Fe2	O43	C45	O44	10.1(9)		O23	C24	C25	F28	-92.4(6)
Fe2	O43	C45	C46	-169.9(4)		O29	Fe3	O57	Fe1	130.52(19)
Fe3	O2	C3	O1	-10.4(8)		O29	Fe3	O57	Fe2	-50.3(2)
Fe3	O2	C3	C4	169.7(3)		O29	C31	C32	F33	4.5(7)
Fe3	O8	C10	O9	16(3)		O29	C31	C32	F34	125.2(5)
Fe3	O8	C10	C11	-159.8(9)		O29	C31	C32	F35	-115.0(5)
Fe3	O8	C10A	O9	22(11)		O30	C31	C32	F33	-176.2(5)
Fe3	O8	C10A	C11A	-165(5)		O30	C31	C32	F34	-55.6(6)
Fe3	O29	C31	O30	2.2(8)		O30	C31	C32	F35	64.3(6)
Fe3	O29	C31	C32	-178.7(3)		O36	Fe3	O57	Fe1	45.1(2)
Fe3	O36	C38	O37	7.3(8)		O36	Fe3	O57	Fe2	-135.7(2)
Fe3	O36	C38	C39	-170.6(3)		O36	C38	C39	F40	74.0(6)
Fe3	O50	C52	O51	28(2)		O36	C38	C39	F41	-43.1(6)
Fe3	O50	C52	C53	-156.4(9)		O36	C38	C39	F42	-165.1(5)
Fe3	O50A	C52A	O51A	18(3)		O37	C38	C39	F40	-104.1(5)
Fe3	O50A	C52A	C53A	-155.3(13)		O37	C38	C39	F41	138.7(5)
O1	C3	C4	F5	175.5(5)		O37	C38	C39	F42	16.8(7)
O1	C3	C4	F6	-66.3(7)		O43	C45	C46	F47	121.5(5)
O1	C3	C4	F7	54.5(7)		O43	C45	C46	F48	-119.6(5)
O1	C3	C4	F5A	-110.6(11)		O43	C45	C46	F49	0.2(7)
O1	C3	C4	F6A	-1.1(11)		O44	C45	C46	F47	-58.5(6)
O1	C3	C4	F7A	124.4(12)		O44	C45	C46	F48	60.4(6)
O2	Fe3	O57	Fe1	-136.85(19)		O44	C45	C46	F49	-179.9(5)
O2	Fe3	O57	Fe2	42.3(2)		O50	C52	C53	F54	106.1(14)
O2	C3	C4	F5	-4.6(7)		O50	C52	C53	F55	-5.6(18)
O2	C3	C4	F6	113.6(6)		O50	C52	C53	F56	-121.2(13)
O2	C3	C4	F7	-125.7(6)		O51	C52	C53	F54	-77.5(14)
O2	C3	C4	F5A	69.3(12)		O51	C52	C53	F55	170.8(11)
O2	C3	C4	F6A	178.8(10)		O51	C52	C53	F56	55.2(15)
O2	C3	C4	F7A	-55.8(13)		O50A	C52A	C53A	F54A	109(2)
O8	Fe3	O57	Fe1	-48.6(2)		O50A	C52A	C53A	F55A	-13(2)
O8	Fe3	O57	Fe2	130.6(2)		O50A	C52A	C53A	F56A	-135.1(19)
O8	C10	C11	F12	-35(2)		O51A	C52A	C53A	F54A	-65(2)
O8	C10	C11	F13	-156.6(16)		O51A	C52A	C53A	F55A	172.8(15)
O8	C10	C11	F14	84.1(19)		O51A	C52A	C53A	F56A	51(2)

Table S7 Atomic Occupancy for $Fe_3O(CF_3COO)_7(CF_3COOH)$.

Atom	***Occupancy***		**Atom**	***Occupancy***		**Atom**	***Occupancy***
F5	0.782(6)		F6	0.782(6)		F7	0.782(6)
F12	0.82(2)		F13	0.82(2)		F14	0.82(2)
F54	0.577(9)		F55	0.577(9)		F56	0.577(9)
O50	0.577(9)		O51	0.577(9)		C10	0.82(2)
C11	0.82(2)		C52	0.577(9)		C53	0.577(9)
F5A	0.218(6)		F6A	0.218(6)		F7A	0.218(6)
F12A	0.18(2)		F13A	0.18(2)		F14A	0.18(2)
F54A	0.423(9)		F55A	0.423(9)		F56A	0.423(9)
O50A	0.423(9)		O51A	0.423(9)		C10A	0.18(2)
C11A	0.18(2)		C52A	0.423(9)		C53A	0.423(9)

Crystallographic information for $Fe(CF_3COO)_2(CF_3COOH)_2$

The crystals were extremely hygroscopic, very soft and sensitive to mechanical treatment. Therefore, they were protected by a layer of poly-fluorinated polyether oil and selected in a glove box under argon atmosphere. Any attempts to cut the crystals lead to complete splitting along the needle axis and bending of the crystals. Therefore, after carefully selecting and isolating a crystal from the inter-grown aggregates, the more than 1mm long needles were directly used for the data set collection without further shaping in order to avoid damage. Nevertheless, all crystals investigated, showed significant smearing of the reflections in the h0l-layer of the reconstructed precession images. Moreover, all crystals examined were twinned by a 180 deg. rotation around the [301] direction in real space, which corresponds to the [100] direction in reciprocal space. The volume ratio of the two domains of the crystal under investigation crystal is 0.453:0.547. All CF_3-are disordered and were described by two sets of fluorine atoms each. The hydrogen atom at O4 has been found in the difference Fourier map and the refinement was done according to the riding model.

Table S8 Crystal data and structure refinement for $Fe(CF_3COO)_2(CF_3COOH)_2$

Empirical formula	$C_8H_2F_{12}FeO_8$
Formula weight / g mol^{-1}	509.95
Temperature / K	150.0
Crystal system	monoclinic
Space group	*C*2/*c*
a / Å	19.658(6)
b / Å	9.753(3)
c / Å	8.341(3)
α / °	90
β / °	98.571(4)
γ / °	90
Volume / Å^3	1581.3(8)
Z	4
ρ_{calc}g / cm^3	2.142
μ / mm^{-1}	1.129
F(000)	992.0
Crystal size / mm^3	1.0 × 0.43 × 0.228
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection / °	4.19 to 63.094
Index ranges	-28 ≤ h ≤ 27, 0 ≤ k ≤ 13, 0 ≤ l ≤ 12
Reflections collected	2370
Independent reflections	2370 [R_{int} = 0.052]
Data/restraints/parameters	2370/114/190
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0508, wR_2 = 0.1333
Final R indexes [all data]	R_1 = 0.0580, wR_2 = 0.1408
Largest diff. peak/hole / e Å^{-3}	1.56/-0.54

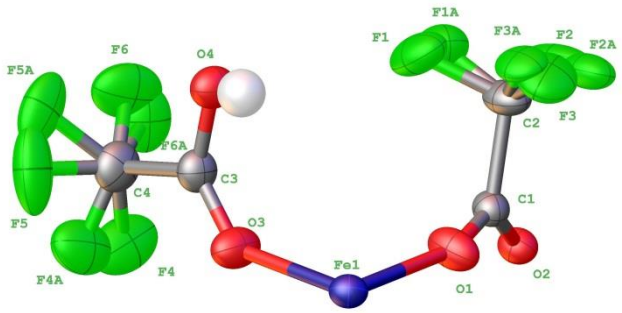

Fig. S3 Structure of $Fe(CF_3COO)_2(CF_3COOH)_2$.

Table S9 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for $Fe(CF_3COO)_2(CF_3COOH)_2$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Fe1	5000	6084.5(5)	7500	24.76(16)
O1	4484.0(11)	4606(3)	8598(3)	41.4(5)
O2	4142.4(10)	3653(2)	10745(2)	28.2(4)
O3	4540.1(12)	7659(3)	8815(3)	41.9(6)
O4	3509.3(11)	8111(2)	7393(3)	38.8(5)
C1	4059.6(14)	4089(3)	9319(3)	28.0(5)
C2	3325.8(16)	3957(3)	8393(4)	40.0(7)
C3	3996.4(15)	8256(3)	8582(3)	32.3(6)
C4	3835.1(19)	9350(4)	9804(4)	43.3(7)
F1	3052(4)	5224(8)	8212(8)	59.9(13)
F2	2927(3)	3230(14)	9200(13)	73(3)
F3	3348(5)	3447(12)	6954(10)	69.3(19)
F4	4243(4)	9171(10)	11208(6)	74(2)
F5	3963(7)	10542(5)	9280(9)	86(3)
F6	3210(3)	9252(10)	10094(12)	75(2)
F1A	2942(11)	4890(30)	8570(40)	57(4)
F2A	3039(12)	2820(20)	8750(30)	48(4)
F3A	3281(12)	3820(30)	6800(30)	43(4)
F4A	4346(7)	9780(20)	10730(30)	70(4)
F5A	3533(13)	10462(16)	9023(14)	65(4)
F6A	3362(12)	8970(20)	10530(30)	61(4)

Table S10 Anisotropic Displacement Parameters ($Å^2\times10^3$) for $Fe(CF_3COO)_2(CF_3COOH)_2$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	23.6(2)	31.2(3)	19.5(2)	0	3.6(2)	0
O1	40.4(11)	53.9(14)	29.1(10)	8.5(9)	2.9(9)	-14.8(10)
O2	28.5(9)	33.2(9)	22.5(9)	2.2(7)	2.8(7)	-2.6(7)
O3	39.2(11)	50.7(13)	34.1(12)	-13.2(9)	0.2(9)	9.6(9)
O4	36.9(11)	42.5(12)	36.6(11)	-8.7(9)	4.5(9)	6.0(8)
C1	28.8(11)	28.6(11)	25.7(12)	0.2(9)	0.9(9)	-1.9(9)
C2	31.5(13)	48.3(17)	36.9(17)	10.6(12)	-6.3(11)	-5.4(11)
C3	36.4(13)	33.1(13)	29.0(13)	-4.5(10)	9.8(10)	1.6(10)
C4	53.2(17)	43.2(17)	35.2(15)	-9.6(13)	11.7(13)	6.8(14)

F1	41(2)	63(3)	74(3)	27(2)	3.0(17)	13.1(18)
F2	33(2)	106(6)	76(4)	45(4)	-11(2)	-25(3)
F3	74(3)	77(5)	47(2)	-14(3)	-23(2)	1(3)
F4	89(3)	92(5)	38(2)	-26(2)	-4(2)	33(3)
F5	162(7)	34.6(17)	72(3)	-14.8(17)	54(4)	-10(3)
F6	54(2)	102(5)	74(5)	-37(4)	19(2)	16(2)
F1A	40(6)	58(7)	72(10)	3(6)	2(5)	3(5)
F2A	30(6)	59(6)	52(8)	14(5)	-9(5)	-11(4)
F3A	38(6)	54(8)	31(4)	11(4)	-13(4)	2(5)
F4A	62(5)	79(9)	67(8)	-40(6)	5(4)	4(5)
F5A	116(10)	45(5)	37(5)	-9(3)	19(5)	30(5)
F6A	82(8)	58(7)	53(8)	-9(5)	38(7)	2(6)

Table S11 Bond Lengths for $Fe(CF_3COO)_2(CF_3COOH)_2$. ([1]1-X,+Y,3/2-Z; [2]1-X,1-Y,2-Z; [3]+X,1-Y,-1/2+Z).

Fe1	**O1**[1]	**2.055(2)**		**C2**	**F2**	**1.314(6)**
Fe1	O1	2.055(2)		C2	F3	1.307(8)
Fe1	O2[2]	2.077(2)		C2	F1A	1.204(19)
Fe1	O2[3]	2.077(2)		C2	F2A	1.300(19)
Fe1	O3[1]	2.162(2)		C2	F3A	1.33(2)
Fe1	O3	2.162(2)		C3	C4	1.541(4)
O1	C1	1.209(3)		C4	F4	1.329(6)
O2	Fe1[2]	2.077(2)		C4	F5	1.280(6)
O2	C1	1.251(3)		C4	F6	1.292(7)
O3	C3	1.207(4)		C4	F4A	1.246(13)
O4	C3	1.279(4)		C4	F5A	1.355(12)
C1	C2	1.537(4)		C4	F6A	1.241(18)
C2	F1	1.347(7)				

Table S12 Bond Angles for $Fe(CF_3COO)_2(CF_3COOH)_2$. ([1]1-X,+Y,3/2-Z; [2]+X,1-Y,-1/2+Z; [3]1-X,1-Y,2-Z).

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O1[1]	Fe1	O1	90.89(15)		F3	C2	C1	109.6(5)
O1	Fe1	O2[2]	89.86(8)		F3	C2	F1	108.3(6)
O1[1]	Fe1	O2[2]	100.08(8)		F3	C2	F2	111.7(7)
O1	Fe1	O2[3]	100.08(8)		F1A	C2	C1	115.7(11)
O1[1]	Fe1	O2[3]	89.86(8)		F1A	C2	F2A	108.5(13)
O1	Fe1	O3[1]	174.81(8)		F1A	C2	F3A	104.4(15)
O1[1]	Fe1	O3[1]	90.06(11)		F2A	C2	C1	111.2(10)
O1[1]	Fe1	O3	174.81(8)		F2A	C2	F3A	100.3(14)
O1	Fe1	O3	90.05(11)		F3A	C2	C1	115.4(11)
O2[3]	Fe1	O2[2]	165.86(11)		O3	C3	O4	127.9(3)
O2[2]	Fe1	O3[1]	84.95(8)		O3	C3	C4	119.5(3)
O2[3]	Fe1	O3[1]	85.02(8)		O4	C3	C4	112.7(3)
O2[2]	Fe1	O3	85.02(8)		F4	C4	C3	109.6(4)
O2[3]	Fe1	O3	84.95(8)		F5	C4	C3	109.4(3)
O3[1]	Fe1	O3	89.46(14)		F5	C4	F4	107.3(5)
C1	O1	Fe1	159.6(2)		F5	C4	F6	111.9(5)
C1	O2	Fe1[3]	127.25(18)		F6	C4	C3	111.6(5)
C3	O3	Fe1	133.5(2)		F6	C4	F4	107.0(5)
O1	C1	O2	127.8(3)		F4A	C4	C3	114.8(7)
O1	C1	C2	116.8(3)		F4A	C4	F5A	106.3(9)
O2	C1	C2	115.4(2)		F5A	C4	C3	110.8(5)
F1	C2	C1	108.0(4)		F6A	C4	C3	111.2(11)
F2	C2	C1	112.0(4)		F6A	C4	F4A	113.0(13)

F2	C2	F1	107.1(5)		F6A	C4	F5A	99.6(10)

Table S13 Torsion Angles for $Fe(CF_3COO)_2(CF_3COOH)_2$. ([1]1-X,1-Y,2-Z).

A	B	C	D	Angle/°		A	B	C	D	Angle/°
Fe1	O1	C1	O2	-107.9(6)		O2	C1	C2	F1A	87(2)
Fe1	O1	C1	C2	71.5(7)		O2	C1	C2	F2A	-37.8(15)
Fe1[1]	O2	C1	O1	9.7(4)		O2	C1	C2	F3A	-151.2(13)
Fe1[1]	O2	C1	C2	-169.62(19)		O3	C3	C4	F4	-19.3(7)
Fe1	O3	C3	O4	-0.5(5)		O3	C3	C4	F5	98.1(8)
Fe1	O3	C3	C4	-179.9(2)		O3	C3	C4	F6	-137.6(6)
O1	C1	C2	F1	-70.4(5)		O3	C3	C4	F4A	17.4(15)
O1	C1	C2	F2	171.9(9)		O3	C3	C4	F5A	137.8(13)
O1	C1	C2	F3	47.3(7)		O3	C3	C4	F6A	-112.5(12)
O1	C1	C2	F1A	-93(2)		O4	C3	C4	F4	161.2(6)
O1	C1	C2	F2A	142.7(14)		O4	C3	C4	F5	-81.4(7)
O1	C1	C2	F3A	29.4(13)		O4	C3	C4	F6	42.9(7)
O2	C1	C2	F1	109.0(5)		O4	C3	C4	F4A	-162.2(15)
O2	C1	C2	F2	-8.7(9)		O4	C3	C4	F5A	-41.7(13)
O2	C1	C2	F3	-133.3(7)		O4	C3	C4	F6A	68.0(12)

Table S14 Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Fe(CF_3COO)_2(CF_3COOH)_2$.

Atom	*x*	*y*	*z*	U(eq)
H4	3641	7599	6691	58

Table S15 Atomic Occupancy for $Fe(CF_3COO)_2(CF_3COOH)_2$.

F1	**0.79(3)**		**F2**	**0.79(3)**		**F3**	**0.79(3)**
F4	0.731(19)		F5	0.731(19)		F6	0.731(19)
F1A	0.21(3)		F2A	0.21(3)		F3A	0.21(3)
F4A	0.269(19)		F5A	0.269(19)		F6A	0.269(19)

Crystallographic information for $Mn_2(CF_3COO)_4(CF_3COOH)_4$

Several CF_3- groups show significant disorder.

Table S16 Crystal data and structure refinement for $Mn_2(CF_3COO)_4(CF_3COOH)_4$.

Empirical formula	$C_{16}H_4F_{24}Mn_2O_{16}$
Formula weight / g mol^{-1}	1018.07
Temperature / K	100
Crystal system	triclinic
Space group	*P*-1
a / Å	10.3229(17)
b / Å	13.518(2)
c / Å	13.940(2)
α / °	105.172(2)
β / °	111.289(2)
γ / °	107.081(2)
Volume / $Å^3$	1577.4(5)
Z	2
ρ_{calc} g / cm^3	2.143
μ / mm^{-1}	1.012
F(000)	988.0
Crystal size / mm^3	0.426 × 0.215 × 0.133
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection / °	3.444 to 56.958
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Reflections collected	16256
Independent reflections	7786 [R_{int} = 0.0289]
Data/restraints/parameters	7786/171/631
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1126
Final R indexes [all data]	R_1 = 0.0708, wR_2 = 0.1262
Largest diff. peak/hole / e $Å^{-3}$	0. 92/-0.39

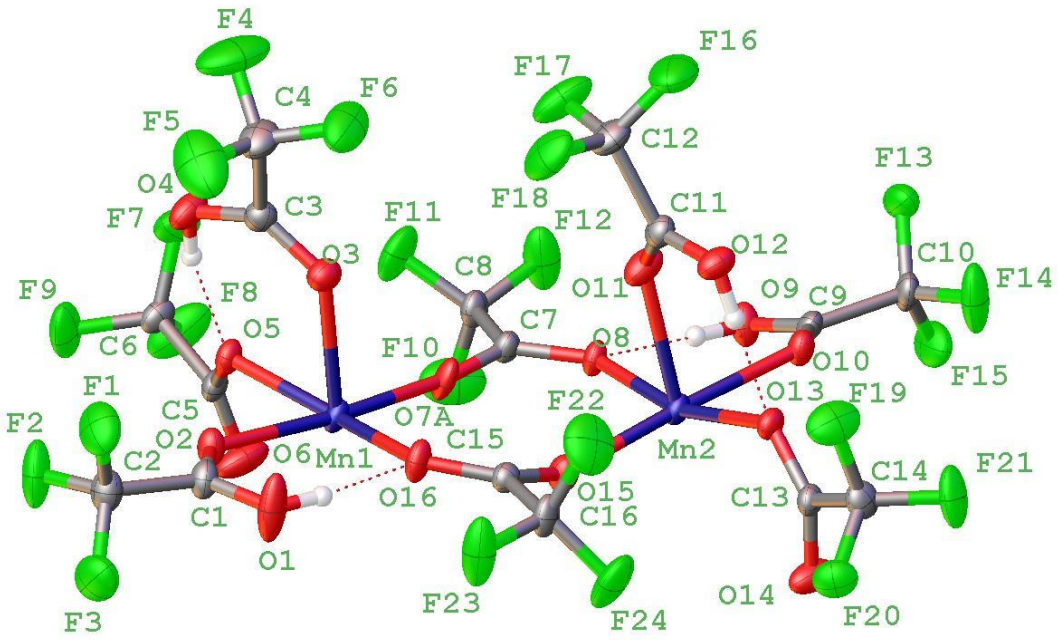

Fig. S4 Structure of $Mn_2(CF_3COO)_4(CF_3COOH)_4$.

Table S17 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Mn_2(CF_3COO)_4(CF_3COOH)_4$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Mn1	10113.2(5)	6194.9(3)	6613.8(4)	18.26(11)
Mn2	8428.6(5)	8810.4(3)	5481.6(3)	17.36(11)
F1	14342(3)	6741(2)	10521.9(17)	45.8(6)
F2	13770(3)	5279.6(17)	9126.4(19)	49.9(6)
F3	15696(2)	6836(2)	9672(2)	48.0(6)
F7	6233(2)	2510.5(17)	5155(2)	43.1(5)
F8	6293(3)	1924(2)	3617.2(18)	58.1(7)
F9	7812(3)	1823.5(17)	5057(2)	49.7(6)
F10	6062(3)	4550(2)	3038(2)	58.8(7)
F11	5472(3)	4260.0(16)	4279.5(18)	45.1(6)
F12	4414(2)	5048.5(17)	3319(2)	52.1(7)
F16	6691(3)	9505(2)	8760(2)	56.6(7)
F17	6405(3)	7846.4(19)	7885.7(18)	51.4(6)
F18	8559(3)	9039(2)	9298.7(18)	49.8(6)
F22	12173(3)	10525.0(19)	8770(2)	56.8(7)
F23	13955(2)	10001.6(17)	8846(2)	52.8(7)
F24	13011(3)	10597.1(18)	7604(2)	49.4(6)
O1	13840(3)	7825(2)	9065(2)	50.1(8)
O2	12003(2)	6057.2(16)	7943.2(17)	22.6(4)
O3	9295(2)	6295.9(17)	7885.9(18)	25.8(5)
O4	8541(3)	4551.5(19)	7847(2)	31.0(5)
O5	8884(2)	4365.8(16)	6042.1(17)	20.9(4)
O6	8753(3)	3771(2)	4353(2)	40.9(6)
O8	6913(2)	6993.5(16)	4524.8(17)	20.3(4)
O9	4786(3)	7248.3(18)	3029.7(19)	27.9(5)
O10	6369(2)	8986.6(17)	4436.6(18)	23.3(4)

O11	7609(3)	8672.7(18)	6738.6(18)	30.6(5)
O12	8750(3)	10424.2(18)	8114.8(19)	26.8(5)
O13	9492(2)	10622.7(16)	6539.4(17)	20.4(4)
O14	10897(3)	11240.9(19)	5761(2)	34.8(6)
O16	11582(2)	8006.7(16)	7619.6(17)	25.1(5)
C1	13233(4)	6743(2)	8739(3)	24.0(6)
C2	14282(4)	6384(3)	9524(3)	28.5(7)
C3	8897(3)	5624(2)	8257(3)	22.9(6)
C4	8828(5)	6036(3)	9359(3)	35.6(7)
C5	8396(3)	3643(2)	5068(2)	20.5(6)
C6	7165(4)	2453(2)	4726(3)	24.1(6)
C7	7048(3)	6159(2)	4698(2)	19.8(6)
C8	5719(3)	4986(2)	3820(3)	23.4(6)
C9	5218(3)	8320(2)	3566(3)	21.8(6)
C10	4004(4)	8692(3)	2957(3)	26.6(6)
C11	7933(3)	9338(3)	7649(2)	22.4(6)
C12	7378(4)	8926(3)	8418(3)	29.8(7)
C13	10469(3)	11364(2)	6471(2)	19.7(5)
C14	11250(4)	12577(2)	7386(3)	26.1(6)
C15	11432(3)	8785(2)	7346(2)	18.6(5)
C16	12688(4)	9997(2)	8159(3)	26.0(6)
F4	7605(11)	5298(5)	9299(7)	73(2)
F5	10058(10)	6181(9)	10185(5)	71(2)
F6	8718(11)	7014(5)	9568(7)	54.6(17)
F13	2681(4)	8149(4)	2927(4)	36.1(9)
F14	4452(5)	9781(3)	3445(5)	55.8(13)
F15	3704(5)	8425(5)	1881(3)	43.3(11)
F19	11049(9)	12571(5)	8301(5)	43.3(16)
F20	12786(7)	12983(8)	7763(7)	33.3(14)
F21	10762(9)	13255(5)	7064(6)	43.9(18)
O7A	8220(40)	6190(30)	5360(30)	28(3)
O15	10439(7)	8688(4)	6450(7)	25.1(13)
F4A	8370(20)	5246(8)	9692(10)	61(3)
F5A	10290(12)	6668(12)	10207(9)	56(3)
F6A	8110(19)	6625(15)	9321(12)	63(3)
F13A	2670(20)	8007(17)	2540(18)	34(3)
F14A	4230(20)	9671(14)	3802(14)	32(3)
F15A	4320(20)	9050(20)	2294(18)	44(3)
F19A	10552(15)	12747(7)	7959(12)	46(2)
F20A	12675(13)	12935(13)	8011(11)	32(2)
F21A	11107(12)	13291(7)	6802(9)	30.8(18)
O7	8030(20)	6135(14)	5508(18)	28(3)
O15A	10210(20)	8716(14)	6712(18)	25.1(13)

Table S18 Anisotropic Displacement Parameters ($Å^2×10^3$) for $Mn_2(CF_3COO)_4(CF_3COOH)_4$. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	19.5(2)	14.1(2)	17.7(2)	8.70(17)	6.00(17)	4.71(16)
Mn2	20.1(2)	13.8(2)	17.5(2)	8.31(16)	7.80(17)	6.16(16)
F1	60.1(14)	58.8(14)	27(1)	23.4(10)	17.1(10)	35.6(12)
F2	56.3(14)	22.6(10)	44.2(13)	12.4(9)	-2.3(11)	18.5(10)
F3	29.2(11)	61.9(15)	56.7(14)	35.2(12)	14.8(10)	22.4(11)
F7	41.0(12)	33.4(11)	64.0(15)	23.5(11)	35.6(11)	10.9(9)
F8	55.1(14)	44.4(13)	27.5(11)	8.7(10)	6.1(10)	-14.6(11)
F9	39.6(12)	21.6(10)	80.2(17)	25.8(11)	17.7(12)	12.9(9)
F10	62.2(16)	39.5(13)	49.5(14)	-7.5(11)	33.8(13)	4.3(11)
F11	51.4(13)	20.9(10)	44.8(12)	18.8(9)	11.9(10)	2.2(9)
F12	24.9(10)	25(1)	67.5(16)	14.1(11)	-6.9(10)	3.5(8)
F16	81.9(18)	66.3(16)	70.8(17)	44.7(14)	63.7(16)	44.3(15)
F17	59.1(15)	36.9(12)	36.9(12)	14.5(10)	23.7(11)	-6(1)

F18	45.7(13)	60.4(15)	34.8(12)	33.1(11)	10.2(10)	12.0(11)
F22	78.9(18)	36.7(13)	43.4(13)	1(1)	26.3(13)	28.1(13)
F23	35.8(12)	22.4(10)	52.8(14)	13.1(10)	-15.3(10)	2.1(9)
F24	43.6(12)	33.7(11)	55.6(14)	31.4(11)	12.9(11)	0.1(9)
O1	41.5(15)	16.6(12)	49.6(17)	13.6(11)	-12.6(13)	3.2(11)
O2	20.8(10)	18.1(10)	22.7(10)	8.7(8)	4.2(8)	8.1(8)
O3	29.3(11)	22.3(10)	29.0(11)	11.5(9)	16.9(10)	10.7(9)
O4	43.6(14)	21.7(11)	29.7(12)	12.6(10)	21.8(11)	9.6(10)
O5	24.3(10)	13.4(9)	22.3(10)	8.9(8)	8.5(8)	6.6(8)
O6	52.3(16)	27.6(12)	36.2(13)	9.6(11)	30.0(13)	0.7(11)
O8	22.4(10)	14.2(9)	22.3(10)	10.2(8)	7.2(8)	7.3(8)
O9	27.0(12)	20.3(11)	28.4(12)	8.7(9)	5.1(10)	11.8(9)
O10	22.3(10)	19.5(10)	28.1(11)	13.6(9)	9.2(9)	9.2(8)
O11	42.4(13)	22.7(11)	26.0(11)	11.2(9)	18.9(10)	9(1)
O12	31.8(12)	23.4(11)	26.2(11)	11.1(9)	17.4(10)	8.0(9)
O13	25(1)	14.5(9)	24.6(10)	10.1(8)	13.3(9)	8.6(8)
O14	48.3(14)	21.7(11)	36.5(13)	8.8(10)	30.5(12)	7.6(10)
O16	28.9(11)	13.2(9)	24.7(11)	9.1(8)	5.6(9)	6.6(8)
C1	27.6(15)	20.2(14)	22.1(14)	10.0(12)	8.0(12)	11.4(12)
C2	28.6(16)	24.2(15)	25.2(16)	10.2(13)	5.8(13)	11.0(13)
C3	20.1(13)	23.2(14)	24.2(13)	10.1(11)	10.4(11)	8.0(11)
C4	51.7(18)	37.5(16)	29.8(14)	17.2(13)	27.2(13)	21.8(14)
C5	23.5(14)	16.1(13)	24.1(14)	11.5(11)	11.4(12)	8.5(11)
C6	27.3(15)	17.4(13)	23.5(14)	8.3(12)	12.2(13)	4.6(12)
C7	19.1(13)	17.1(13)	22.9(14)	10.9(11)	8.5(12)	6.9(11)
C8	24.7(15)	14.6(13)	27.3(15)	9.3(12)	9.0(13)	7.5(11)
C9	22.6(13)	21.8(14)	28.8(15)	17.4(12)	14.1(12)	10.8(11)
C10	26.2(13)	24.8(13)	34.6(15)	20.2(12)	11.7(12)	14.5(11)
C11	22.9(14)	24.4(14)	22.4(14)	13.8(12)	10.0(12)	10.8(12)
C12	36.0(18)	31.4(17)	22.7(15)	14.4(13)	16.0(14)	10.1(14)
C13	24.6(13)	15.6(12)	22.6(13)	9.8(10)	12.0(11)	10.8(10)
C14	26.7(13)	16.9(12)	28.8(14)	5.5(11)	10.9(11)	8.6(10)
C15	20.7(13)	15.6(13)	19.2(13)	7.0(11)	9.6(11)	7.6(11)
C16	28.4(16)	14.0(13)	26.9(15)	9.1(12)	5.7(13)	7.1(12)
F4	91(4)	63(3)	68(4)	18(2)	65(3)	10(3)
F5	97(4)	93(5)	30.0(19)	22(3)	23(2)	61(4)
F6	95(5)	42(2)	57(3)	24(2)	55(3)	40(3)
F13	28.2(12)	48.8(18)	50(2)	33.8(18)	22.5(14)	23.0(12)
F14	46.1(19)	21.3(12)	68(3)	16.6(14)	-3.4(17)	15.4(12)
F15	46(2)	66(3)	39.5(16)	37.4(18)	20.9(15)	38(2)
F19	55(3)	30(2)	31(2)	0.3(16)	25(2)	7.6(19)
F20	24.5(16)	33(2)	30(3)	9(2)	9.8(16)	4.9(14)
F21	48(3)	18.2(17)	44(3)	5.7(17)	2(2)	19(2)
O7A	24(4)	23.6(18)	30(4)	20(2)	4(3)	7(2)
O15	20.4(18)	23.1(12)	27(3)	13.1(15)	6.3(15)	7.7(12)
F4A	96(7)	54(4)	51(5)	28(3)	53(5)	27(4)
F5A	60(3)	61(5)	29(3)	12(3)	19(2)	13(3)
F6A	86(6)	79(6)	51(5)	27(5)	42(5)	57(6)
F13A	28(3)	30(4)	45(6)	20(4)	12(3)	17(3)
F14A	41(6)	30(4)	35(4)	23(3)	14(4)	26(4)
F15A	55(7)	49(7)	47(5)	35(5)	28(5)	29(6)
F19A	55(4)	25(3)	52(4)	1(3)	36(4)	10(3)
F20A	30(3)	23(3)	30(4)	8(3)	7(2)	8(2)
F21A	37(4)	19(2)	39(3)	13(2)	16(3)	15(2)
O7	24(4)	23.6(18)	30(4)	20(2)	4(3)	7(2)
O15A	20.4(18)	23.1(12)	27(3)	13.1(15)	6.3(15)	7.7(12)

Table S19 Bond Lengths for $Mn_2(CF_3COO)_4(CF_3COOH)_4$. ([1]2-X,1-Y,1-Z; [2]2-X,2-Y,1-Z).

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Mn1	O2	2.246(2)		O10	C9	1.203(4)
Mn1	O3	2.215(2)		O11	C11	1.203(4)
Mn1	O5	2.1795(19)		O12	C11	1.290(4)
Mn1	O6[1]	2.082(2)		O13	C13	1.248(3)
Mn1	O16	2.177(2)		O14	Mn2[2]	2.081(2)
Mn1	O7A	2.09(3)		O14	C13	1.214(4)
Mn1	O7	2.102(16)		O16	C15	1.241(3)
Mn2	O8	2.184(2)		C1	C2	1.528(4)
Mn2	O10	2.220(2)		C3	C4	1.527(4)
Mn2	O11	2.231(2)		C4	F4	1.318(6)
Mn2	O13	2.176(2)		C4	F5	1.285(7)
Mn2	O14[2]	2.082(2)		C4	F6	1.326(6)
Mn2	O15	2.107(5)		C4	F4A	1.303(9)
Mn2	O15A	2.072(17)		C4	F5A	1.351(11)
F1	C2	1.319(4)		C4	F6A	1.235(12)
F2	C2	1.306(4)		C5	C6	1.544(4)
F3	C2	1.319(4)		C7	C8	1.543(4)
F7	C6	1.314(4)		C7	O7A	1.21(3)
F8	C6	1.321(4)		C7	O7	1.232(17)
F9	C6	1.304(4)		C9	C10	1.538(4)
F10	C8	1.314(4)		C10	F13	1.327(4)
F11	C8	1.320(3)		C10	F14	1.301(4)
F12	C8	1.313(4)		C10	F15	1.338(4)
F16	C12	1.311(4)		C10	F13A	1.216(19)
F17	C12	1.312(4)		C10	F14A	1.416(16)
F18	C12	1.312(4)		C10	F15A	1.251(14)
F22	C16	1.324(4)		C11	C12	1.537(4)
F23	C16	1.308(4)		C13	C14	1.533(4)
F24	C16	1.314(4)		C14	F19	1.365(6)
O1	C1	1.283(4)		C14	F20	1.351(7)
O2	C1	1.204(4)		C14	F21	1.272(6)
O3	C3	1.201(3)		C14	F19A	1.276(8)
O4	C3	1.290(4)		C14	F20A	1.260(12)
O5	C5	1.254(3)		C14	F21A	1.423(9)
O6	Mn1[1]	2.082(2)		C15	C16	1.537(4)
O6	C5	1.216(4)		C15	O15	1.238(6)
O8	C7	1.249(3)		C15	O15A	1.210(18)
O9	C9	1.292(4)				

Table S20 Bond Angles for $Mn_2(CF_3COO)_4(CF_3COOH)_4$. ([1]2-X,1-Y,1-Z; [2]2-X,2-Y,1-Z)

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O3	Mn1	O2	80.48(8)		O5	C5	C6	116.0(2)
O5	Mn1	O2	84.91(7)		O6	C5	O5	127.9(3)
O5	Mn1	O3	83.97(8)		O6	C5	C6	116.1(3)
O6[1]	Mn1	O2	91.31(10)		F7	C6	F8	106.6(3)
O6[1]	Mn1	O3	170.48(10)		F7	C6	C5	111.9(2)
O6[1]	Mn1	O5	100.19(9)		F8	C6	C5	111.0(2)
O6[1]	Mn1	O16	88.38(9)		F9	C6	F7	108.7(3)
O6[1]	Mn1	O7A	91.1(8)		F9	C6	F8	107.6(3)
O6[1]	Mn1	O7	100.4(9)		F9	C6	C5	110.8(3)
O16	Mn1	O2	82.40(8)		O8	C7	C8	115.6(2)
O16	Mn1	O3	85.79(8)		O7A	C7	O8	125.0(15)
O16	Mn1	O5	164.85(8)		O7A	C7	C8	118.0(16)
O7A	Mn1	O2	175.0(8)		O7	C7	O8	129.5(8)
O7A	Mn1	O3	97.5(8)		O7	C7	C8	114.7(8)

O7A	Mn1	O5	90.3(9)		F10	C8	F11	107.3(3)
O7A	Mn1	O16	102.1(9)		F10	C8	C7	109.7(2)
O7	Mn1	O2	166.9(8)		F11	C8	C7	112.0(2)
O7	Mn1	O3	88.3(8)		F12	C8	F10	108.1(3)
O7	Mn1	O5	87.3(5)		F12	C8	F11	107.2(3)
O7	Mn1	O16	103.6(4)		F12	C8	C7	112.3(2)
O8	Mn2	O10	83.50(8)		O9	C9	C10	110.7(3)
O8	Mn2	O11	85.36(8)		O10	C9	O9	128.3(3)
O10	Mn2	O11	91.50(8)		O10	C9	C10	120.9(3)
O13	Mn2	O8	165.97(8)		F13	C10	C9	110.4(3)
O13	Mn2	O10	88.63(8)		F13	C10	F15	106.4(3)
O13	Mn2	O11	83.25(8)		F14	C10	C9	111.9(3)
O14^{2}	Mn2	O8	89.02(8)		F14	C10	F13	108.8(4)
O14^{2}	Mn2	O10	89.42(9)		F14	C10	F15	108.1(3)
O14^{2}	Mn2	O11	174.16(8)		F15	C10	C9	110.9(3)
O14^{2}	Mn2	O13	102.54(8)		F13A	C10	C9	115.2(10)
O14^{2}	Mn2	O15	88.6(3)		F13A	C10	F14A	107.0(12)
O15	Mn2	O8	97.96(13)		F13A	C10	F15A	114.2(12)
O15	Mn2	O10	177.5(3)		F14A	C10	C9	105.4(7)
O15	Mn2	O11	90.6(3)		F15A	C10	C9	110.1(8)
O15	Mn2	O13	90.34(15)		F15A	C10	F14A	103.8(10)
O15A	Mn2	O8	98.4(5)		O11	C11	O12	127.9(3)
O15A	Mn2	O10	168.1(7)		O11	C11	C12	120.6(3)
O15A	Mn2	O11	77.0(7)		O12	C11	C12	111.6(3)
O15A	Mn2	O13	87.0(5)		F16	C12	F17	108.3(3)
O15A	Mn2	O14^{2}	102.4(7)		F16	C12	F18	109.5(3)
C1	O2	Mn1	133.55(19)		F16	C12	C11	111.1(3)
C3	O3	Mn1	131.4(2)		F17	C12	F18	107.4(3)
C5	O5	Mn1	124.66(18)		F17	C12	C11	110.9(3)
C5	O6	Mn1^{1}	161.1(3)		F18	C12	C11	109.6(3)
C7	O8	Mn2	130.68(18)		O13	C13	C14	117.3(3)
C9	O10	Mn2	131.40(19)		O14	C13	O13	127.6(3)
C11	O11	Mn2	133.3(2)		O14	C13	C14	115.0(3)
C13	O13	Mn2	124.67(18)		F19	C14	C13	110.4(3)
C13	O14	Mn2^{2}	173.2(2)		F20	C14	C13	108.5(5)
C15	O16	Mn1	126.25(19)		F20	C14	F19	105.8(4)
O1	C1	C2	110.9(3)		F21	C14	C13	114.2(4)
O2	C1	O1	127.6(3)		F21	C14	F19	107.7(4)
O2	C1	C2	121.5(3)		F21	C14	F20	109.9(6)
F1	C2	F3	108.0(3)		F19A	C14	C13	113.8(5)
F1	C2	C1	109.6(3)		F19A	C14	F21A	103.7(6)
F2	C2	F1	107.9(3)		F20A	C14	C13	114.4(7)
F2	C2	F3	109.0(3)		F20A	C14	F19A	112.0(7)
F2	C2	C1	111.5(3)		F20A	C14	F21A	105.9(8)
F3	C2	C1	110.7(3)		F21A	C14	C13	106.0(5)
O3	C3	O4	127.5(3)		O16	C15	C16	116.7(3)
O3	C3	C4	119.4(3)		O15	C15	O16	127.1(3)
O4	C3	C4	113.1(3)		O15	C15	C16	115.9(3)
F4	C4	C3	110.6(4)		O15A	C15	O16	123.6(9)
F4	C4	F6	106.8(5)		O15A	C15	C16	115.7(9)
F5	C4	C3	109.6(4)		F22	C16	C15	109.3(3)
F5	C4	F4	110.0(5)		F23	C16	F22	108.5(3)
F5	C4	F6	108.4(5)		F23	C16	F24	109.0(3)
F6	C4	C3	111.3(4)		F23	C16	C15	112.2(2)
F4A	C4	C3	115.0(5)		F24	C16	F22	106.4(3)
F4A	C4	F5A	100.0(7)		F24	C16	C15	111.3(3)
F5A	C4	C3	107.8(6)		C7	O7A	Mn1	173(2)
F6A	C4	C3	110.2(7)		C15	O15	Mn2	153.0(8)
F6A	C4	F4A	113.6(8)		C7	O7	Mn1	162(2)
F6A	C4	F5A	109.4(8)		C15	O15A	Mn2	166.0(17)

Table S21 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $Mn_2(CF_3COO)_4(CF_3COOH)_4$.

Atom	*x*	*y*	*z*	U(eq)
H1	13250(60)	8000(40)	8690(40)	71(17)
H4	8660(60)	4390(50)	7280(50)	81(18)
H9	5430(60)	7110(40)	3450(50)	72(17)
H12	9140(40)	10590(30)	7710(30)	38(11)

Table S22 Atomic Occupancy for $Mn_2(CF_3COO)_4(CF_3COOH)_4$.

Atom	Occupancy		Atom	Occupancy		Atom	Occupancy
F4	0.642(16)		F5	0.642(16)		F6	0.642(16)
F13	0.832(11)		F14	0.832(11)		F15	0.832(11)
F19	0.625(19)		F20	0.625(19)		F21	0.625(19)
O7A	0.34(7)		O15	0.77(3)		F4A	0.358(16)
F5A	0.358(16)		F6A	0.358(16)		F13A	0.168(11)
F14A	0.168(11)		F15A	0.168(11)		F19A	0.375(19)
F20A	0.375(19)		F21A	0.375(19)		O7	0.66(7)
O15A	0.23(3)						

Crystallographic information for $Co(CF_3COO)_2(H_2O)_4$

While cooling form 275 K to 100 K the crystal experiences a phase transition to an ordered phase, where the rotation of the trifluoromethyl-groups freezes. The crystal system changes from monoclinic to triclinic, the resulting crystal at 100 K is twinned with a volume ratio of the individuals of about 1:1. All hydrogen atom positions were found in the difference Fourier map and refined freely.

Table S23 Crystal data and structure refinement for $Co(CF_3COO)_2(H_2O)_4$.

Empirical formula	$C_4H_8CoF_6O_8$
Formula weight / g mol^{-1}	357.03
Temperature / K	103(5)
Crystal system	triclinic
Space group	*P*-1
a / Å	8.1360(4)
b / Å	9.0331(7)
c / Å	9.2695(5)
α / °	75.139(6)
β / °	64.574(6)
γ / °	71.426(6)
Volume / Å^3	577.49(7)
Z	2
ρ_{calc}g / cm^3	2.053
μ / mm^{-1}	1.604
F(000)	354.0
Crystal size / mm^3	0.33 × 0.23 × 0.16
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection / °	5.954 to 65.152
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13
Reflections collected	7011
Independent reflections	7011 [R_{int} = 0.033]
Data/restraints/parameters	7011/0/203
Goodness-of-fit on F^2	0.985
Final R indexes [I>=2σ (I)]	R_1 = 0.0308, wR_2 = 0.0694
Final R indexes [all data]	R_1 = 0.0413, wR_2 = 0.0712
Largest diff. peak/hole / e Å^{-3}	1.07/-0.51

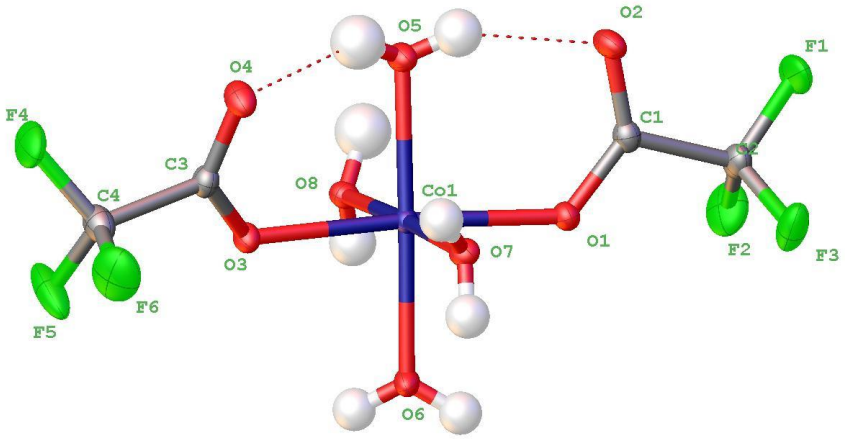

Fig. S5 Structure of $Co(CF_3COO)_2(H_2O)_4$.

Table S24 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Co(CF_3COO)_2(H_2O)_4$. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Co1	1605.2(3)	5941.2(3)	1123.9(3)	12.74(7)
F2	-1078.9(17)	1651.8(13)	4463.3(15)	36.4(3)
F6	3653.5(19)	10415.5(15)	-2964.7(14)	42.6(3)
F4	4546.2(16)	11004.2(13)	-1362.1(15)	32.1(3)
F1	-3628.8(17)	3058.2(14)	5940.5(13)	34.6(3)
F3	-3201.1(17)	2938.7(15)	3518.3(13)	34.1(3)
O2	-2126.9(17)	5515.8(14)	4622.6(13)	19.9(3)
O1	-131.2(16)	4338.1(13)	2443.0(13)	15.6(2)
O4	1584.9(16)	9723.5(13)	532.0(15)	21.1(3)
O7	-293.7(16)	7135.0(14)	-12.3(15)	15.1(2)
O8	3589.2(16)	4734.9(14)	2148.7(15)	14.5(2)
O5	320.5(18)	7358.2(15)	2924.6(16)	18.1(3)
O6	2994.6(18)	4461.7(15)	-631.9(15)	17.8(3)
C1	-1460(2)	4434.8(19)	3802.3(19)	15.5(3)
C3	2981(2)	8904.9(19)	-383(2)	15.9(3)
C4	4341(2)	9802(2)	-1811(2)	22.4(4)
F5	6031.0(16)	8895.4(13)	-2454.8(16)	43.3(4)
O3	3433.1(15)	7437.0(12)	-348.0(13)	15.2(2)
C2	-2355(3)	2996(2)	4452(2)	20.7(4)

Table S25 Anisotropic Displacement Parameters ($Å^2×10^3$) for $Co(CF_3COO)_2(H_2O)_4$. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	11.74(11)	11.18(11)	13.36(11)	-2.23(7)	-1.98(8)	-3.77(8)
F2	40.9(7)	16.1(5)	49.3(8)	3.9(5)	-16.6(6)	-10.4(5)
F6	55.7(9)	46.1(8)	26.3(7)	13.9(6)	-17.5(6)	-24.7(7)
F4	32.3(6)	20.0(6)	40.1(7)	-2.3(5)	-3.8(5)	-16.9(5)
F1	42.2(7)	42.3(7)	17.4(5)	-2.0(5)	4.4(5)	-31.3(6)
F3	46.1(7)	44.8(7)	26.3(6)	6.2(5)	-17.9(5)	-32.9(6)
O2	21.3(6)	17.7(6)	14.7(6)	-3.3(5)	0.7(5)	-6.6(5)
O1	15.6(6)	16.1(6)	14.1(6)	-2.6(5)	-2.3(5)	-6.5(4)
O4	18.0(6)	12.6(6)	25.1(7)	-2.8(5)	-1.5(5)	-3.4(5)
O7	16.8(6)	11.1(6)	16.1(6)	-2.7(5)	-5.0(5)	-2.9(5)
O8	14.4(6)	13.4(6)	13.3(6)	-2.6(5)	-3.5(5)	-2.3(5)
O5	19.4(7)	15.5(6)	16.9(6)	-4.3(5)	-2.1(5)	-6.3(5)
O6	13.3(6)	18.0(6)	20.7(6)	-8.6(5)	-0.2(5)	-6.2(5)
C1	15.1(8)	15.6(8)	15.1(8)	1.0(6)	-5.9(6)	-5.0(6)
C3	17.1(8)	14.7(8)	16.8(8)	0.5(6)	-6.6(7)	-6.7(6)
C4	20.2(9)	15.9(8)	24.3(9)	-0.7(7)	-2.3(7)	-5.8(7)
F5	23.2(6)	20.4(6)	55.2(8)	-4.1(6)	13.6(6)	-6.0(5)
O3	14.8(6)	11.0(5)	17.2(6)	-1.7(4)	-2.9(5)	-4.2(4)
C2	24.5(9)	22.3(9)	16.2(8)	1.1(7)	-5.1(7)	-13.3(7)

Table S26 Bond Lengths for $Co(CF_3COO)_2(H_2O)_4$.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Co1	O1	2.1213(11)		F1	C2	1.3247(19)
Co1	O7	2.1006(12)		F3	C2	1.335(2)
Co1	O8	2.0882(12)		O2	C1	1.2309(19)
Co1	O5	2.0646(12)		O1	C1	1.2611(18)
Co1	O6	2.0703(12)		O4	C3	1.231(2)
Co1	O3	2.1192(11)		C1	C2	1.552(2)
F2	C2	1.323(2)		C3	C4	1.549(2)
F6	C4	1.332(2)		C3	O3	1.2539(19)
F4	C4	1.337(2)		C4	F5	1.322(2)

Table S27 Bond Angles for $Co(CF_3COO)_2(H_2O)_4$.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
O7	Co1	O1	88.49(5)		O1	C1	C2	113.49(14)
O7	Co1	O3	90.87(5)		O4	C3	C4	116.11(14)
O8	Co1	O1	92.83(5)		O4	C3	O3	128.89(15)
O8	Co1	O7	177.35(5)		O3	C3	C4	114.96(14)
O8	Co1	O3	87.64(4)		F6	C4	F4	106.86(15)
O5	Co1	O1	92.74(5)		F6	C4	C3	109.74(15)
O5	Co1	O7	93.57(5)		F4	C4	C3	111.54(14)
O5	Co1	O8	88.67(5)		F5	C4	F6	108.01(16)
O5	Co1	O6	177.10(6)		F5	C4	F4	107.33(15)
O5	Co1	O3	91.80(5)		F5	C4	C3	113.10(15)
O6	Co1	O1	87.47(5)		C3	O3	Co1	123.78(10)
O6	Co1	O7	89.32(5)		F2	C2	F1	107.61(15)
O6	Co1	O8	88.44(5)		F2	C2	F3	107.50(15)
O6	Co1	O3	88.02(5)		F2	C2	C1	111.55(14)

O3	Co1	O1	175.44(4)		F1	C2	F3	107.51(14)
C1	O1	Co1	127.49(10)		F1	C2	C1	112.23(14)
O2	C1	O1	128.43(15)		F3	C2	C1	110.23(14)
O2	C1	C2	118.06(14)					

Table S28 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for $Co(CF_3COO)_2(H_2O)_4$.

Atom	*x*	*y*	*z*	U(eq)
H6A	4050(30)	4400(30)	-1130(30)	31
H6B	2530(30)	3850(30)	-670(30)	31
H8A	4140(30)	3910(30)	1880(30)	37(7)
H5A	-590(30)	7140(30)	3560(30)	39(7)
H8B	3190(30)	4660(30)	3270(30)	53(8)
H5B	440(30)	8240(30)	2560(30)	50(8)
H7A	-40(30)	6880(30)	-900(30)	33(6)
H7B	-680(30)	8140(30)	-130(30)	32(6)

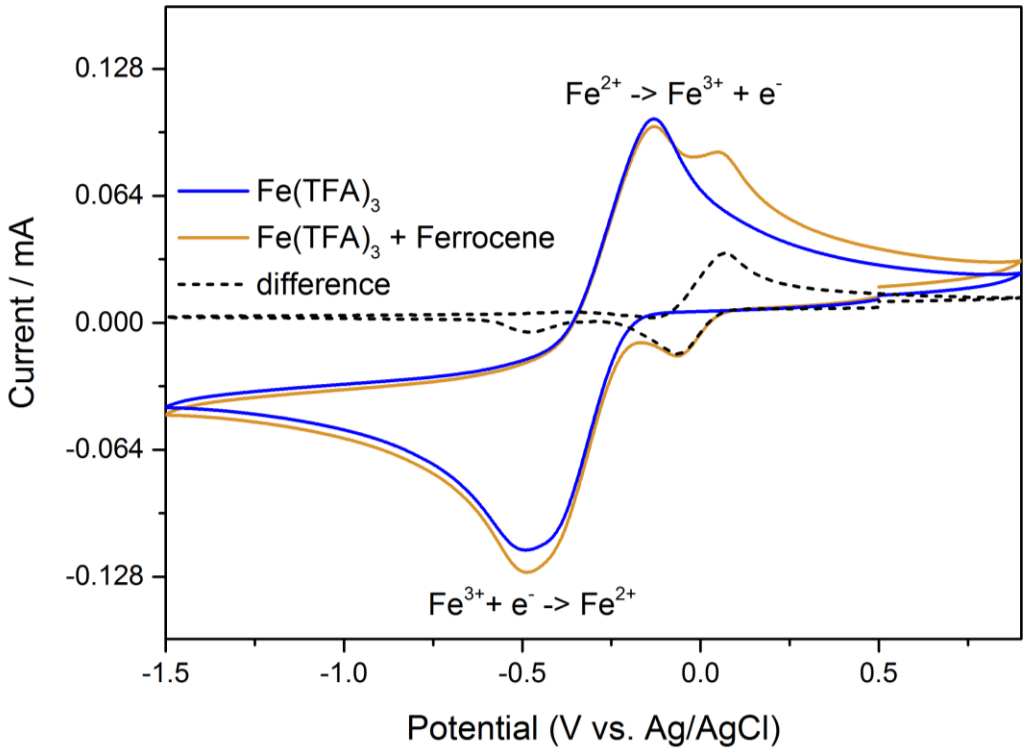

Fig. S6 Linear sweep voltammetric measurement of the "$Fe(TFA)_3$" precursor solved in DMSO. As a reference, ferrocene was added in a second measurement. The difference plot of these two measurements shows a slightly higher area for the reduction of Fe^{3+} than for the reverse oxidation of Fe^{2+} due to irreversible processes. Because the Fe^{3+} reduction and the reverse Fe^{2+} oxidation integrals are similar (or even Fe^{3+} slightly larger) it is evident that only Fe^{3+} is present in the starting "$Fe(TFA)_3$" precursor.

Table S29 Unit cell parameters of $Fe(CF_3COO)_2(CF3COOH)_2$, $Co(CF_3COO)_2(H_2O)_4$, $Mn_2(CF_3COO)_4(CF_3COOH)_4$ and $Fe_3O(CF_3COO)_7(CF_3COOH)$

formula	a / Å	b / Å	c / Å	α / °	β / °	γ / °	V / Å^3	Z
$Fe(CF_3COO)_2(CF3COOH)_2$	19.658(6)	9.753(3)	8.341(3)	90	98.571(4)	90	1581.3(8)	4
$Co(CF_3COO)_2(H_2O)_4$	8.1360(4)	9.0331(7)	9.2695(5)	75.139(6)	64.574(6)	71.426(6)	577.49(7)	2
$Mn_2(CF_3COO)_4(CF_3COOH)_4$	10.3229(17)	13.518(2)	13.940(2)	105.172(2)	111.289(2)	107.081(2)	1577.4(5)	2
$Fe_3O(CF_3COO)_7(CF_3COOH)$	9.7505(11)	21.236(2)	16.0879(18)	90	91.358(2)	90	3330.2(6)	4

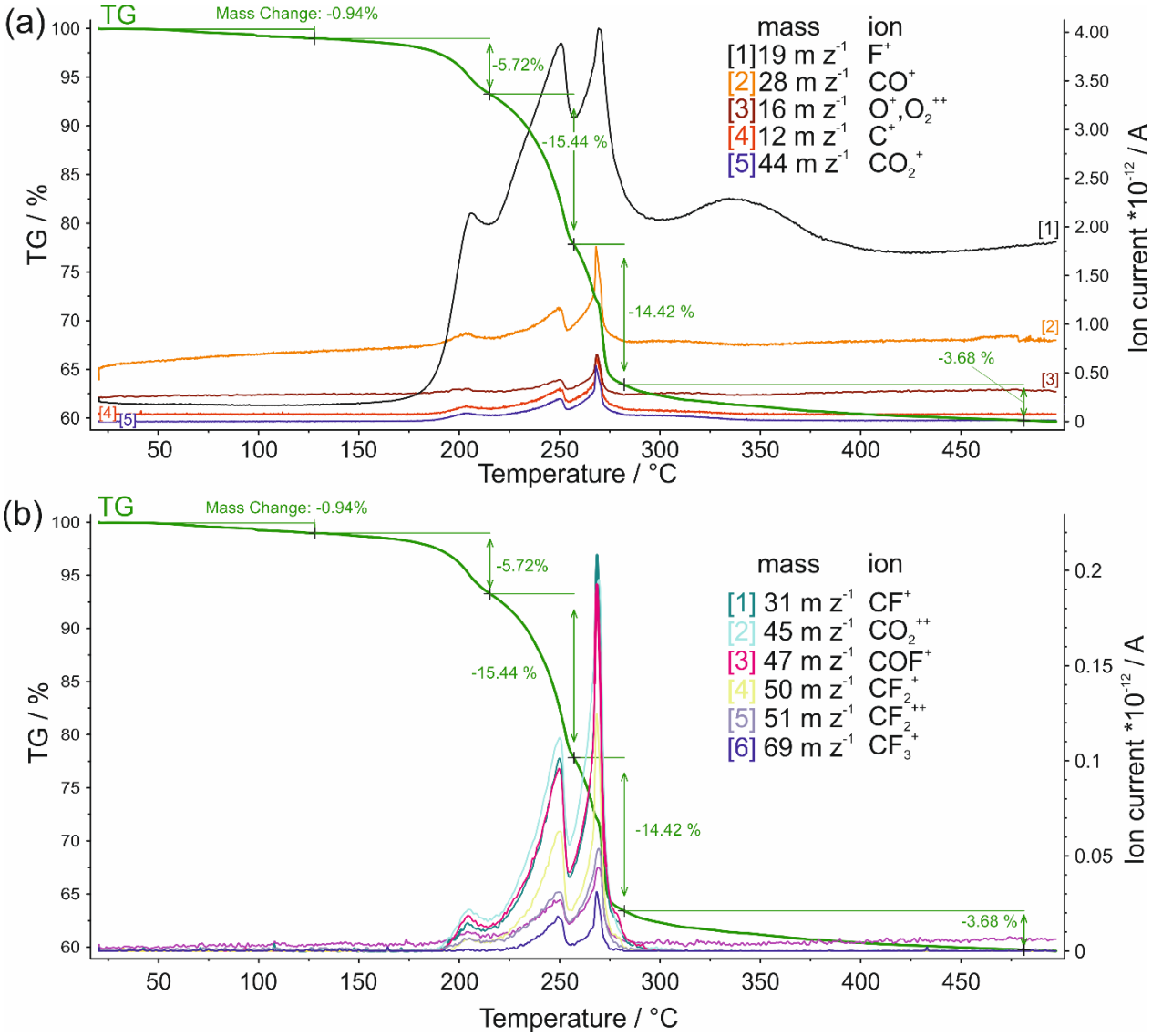

Fig. S7 TGA-MS measurement of the decomposition of "$Fe(TFA)_3$" to FeF_3 under vacuum. (a) and (b) are the same measurement but presented at different ion currents to improve the visibility. The decomposition takes part in three main steps at around 200 °C, 250 °C and 270 °C. Observed ions in mass spectroscopy (Balzers MID) may be related to decomposition side products as F, CO, CO_2, COF, $CF_{x=1-3}$. The dark green line is presenting the thermogravimetric analysis (NETZSCH, STA 409 C/CD) with the white losses in percent to initial weight (13.5 mg).

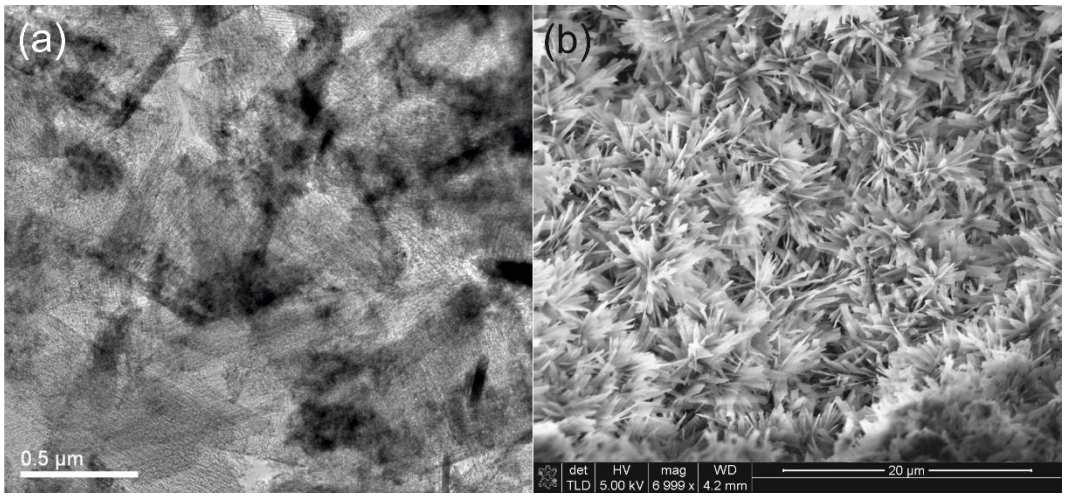

Fig. S8 Low resolution images (a) TEM image of FeF_3; (b) SEM image of FeF_3

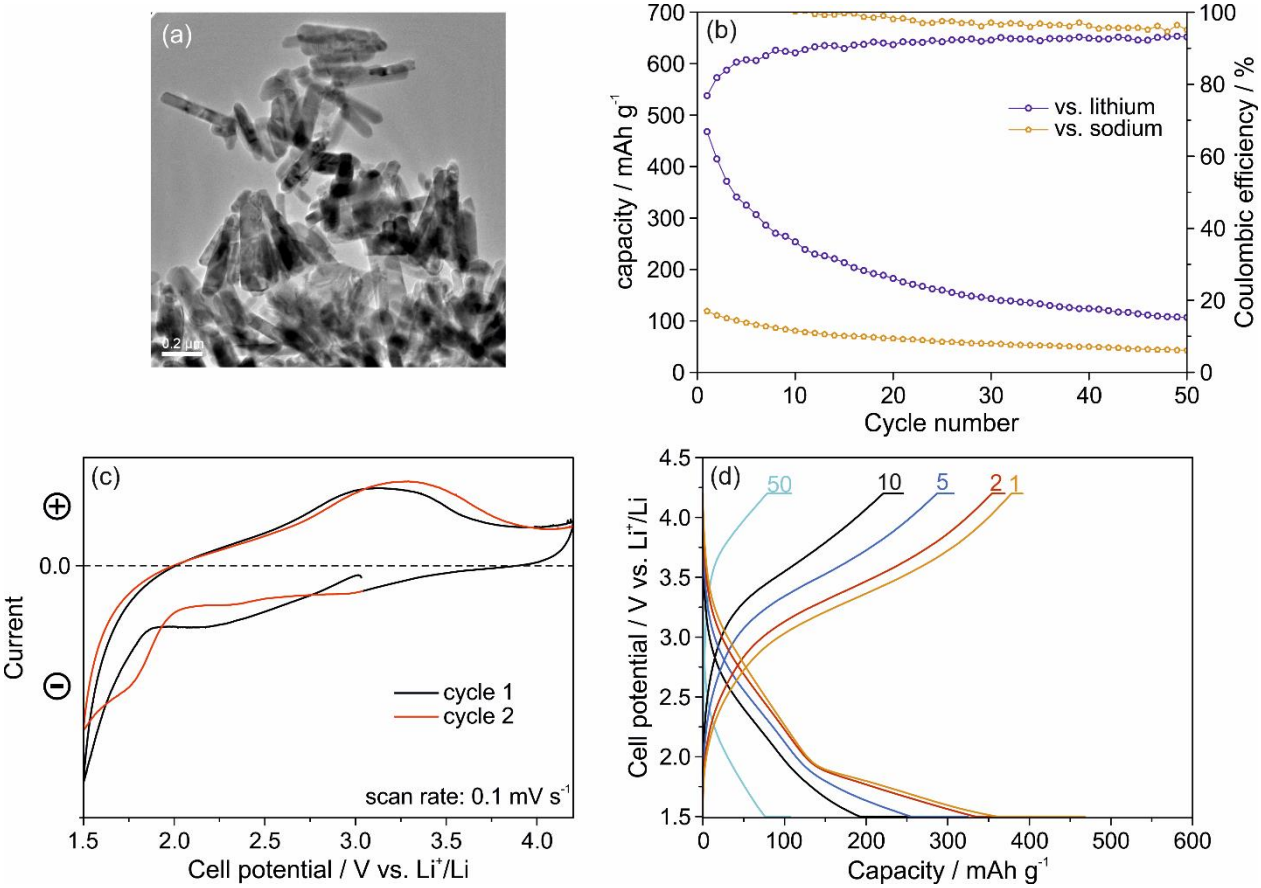

Fig. S9 Electrochemical results obtained with FeF_2 as active material. (a) TEM image of FeF_2; (b) Galvanostatic cycling towards lithium (1.5-4.2 V) and sodium (1.2-4.0 V) with a current rate of 100 mAh/g; (c) Cycling voltammetry between 1.5 V and 4.2 V versus lithium. (d) Voltage - capacity plot towards lithium.

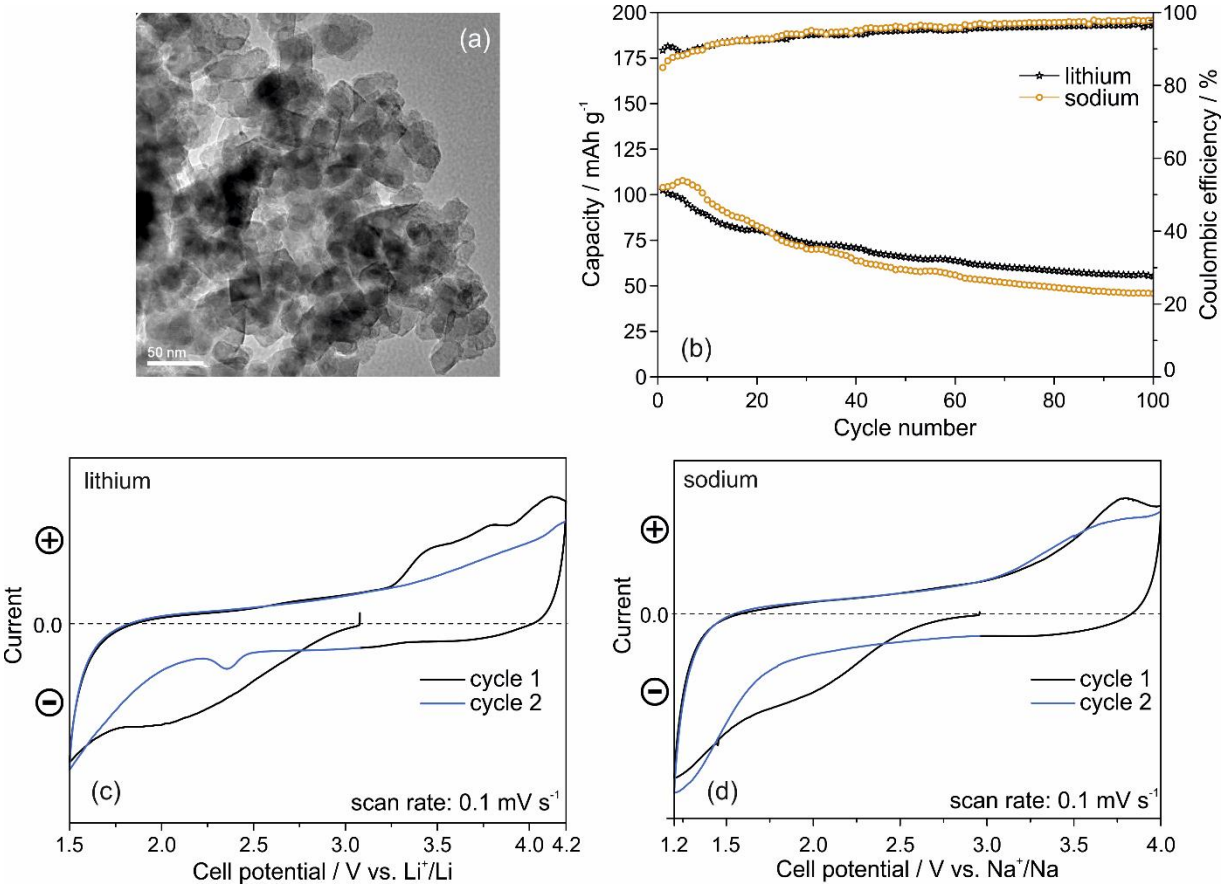

Fig. S10 Electrochemical results and TEM image from MnF_2. (a) TEM image of MnF_2. (b) Galvanostatic measurements measured against lithium (1.5-4.2 V) and sodium (1.2-4.0 V) with a current rate of 100 mA/g. (c) Cycling voltammetry towards lithium between 1.5 V and 4.2 V. (d) Cyclic voltammetry towards sodium between 1.2 V and 4.0 V.

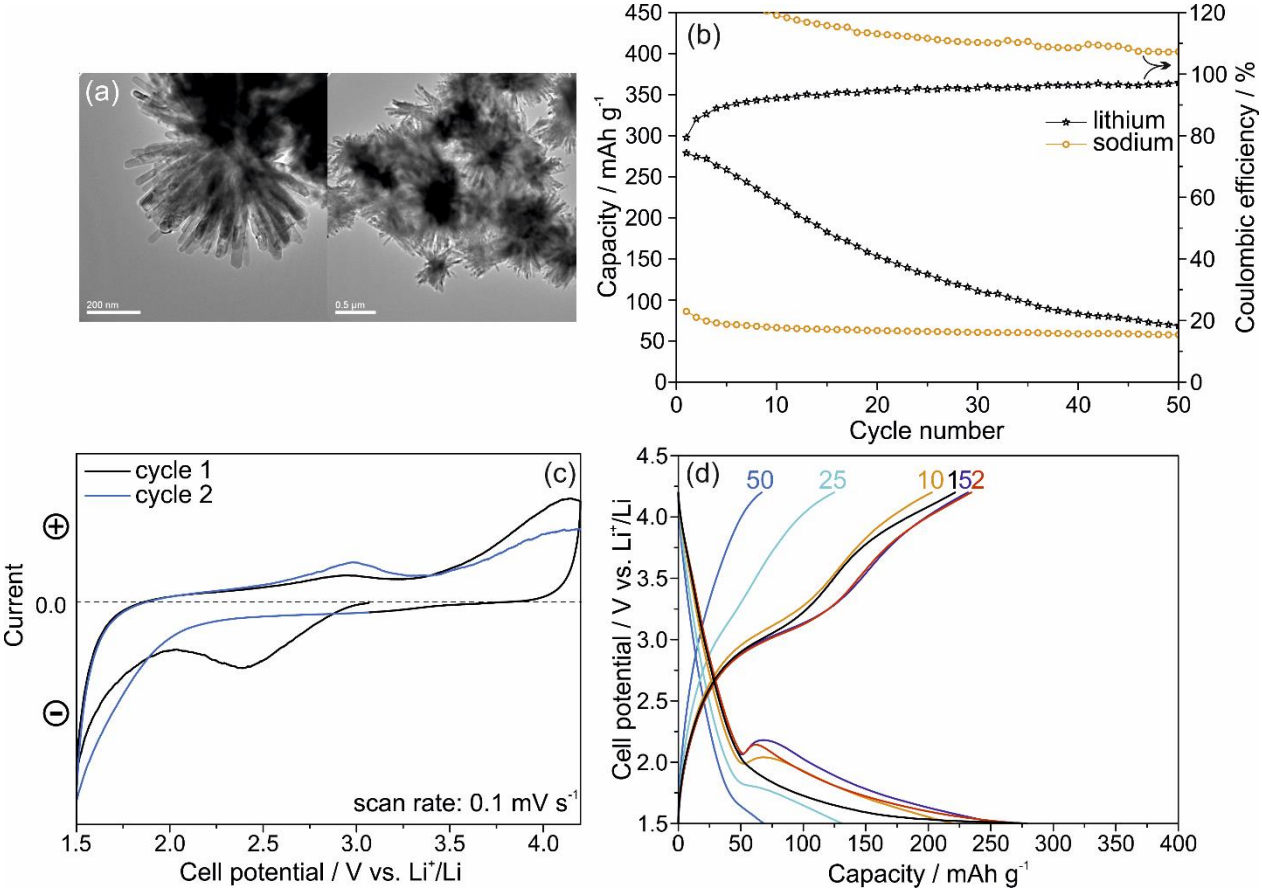

Fig. S11 Electrochemical results obtained with CoF_2 as active material. (a) TEM images of CoF_2 (b) Galvanostatic cycling towards lithium (1.5-4.2 V) and sodium (1.2-4.0 V) with a current rate of 100 mAh/g (c) Cyclic voltammetry between 1.5 V and 4.2 V. (d) Voltage - capacity plot towards lithium.

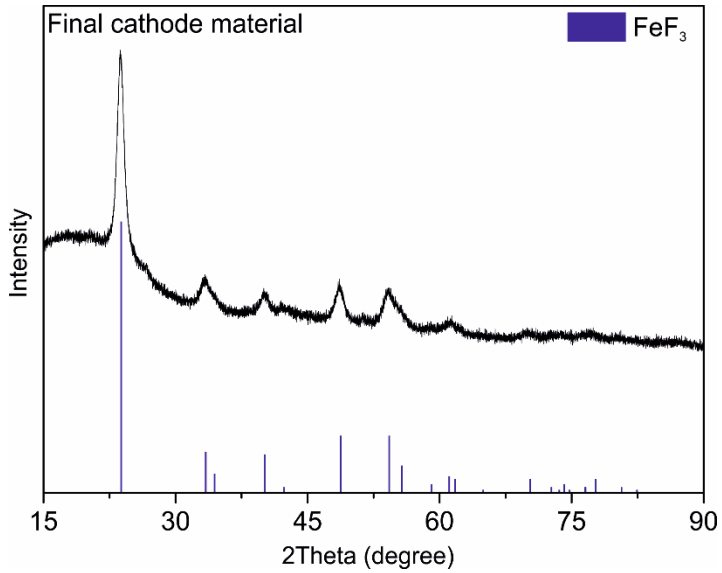

Fig. S12 Powder XRD pattern of the cathode material (FeF_3/CB/GO) after wet ball milling. No sign of reduction of FeF_3 (PDF 033-0647) is observable.

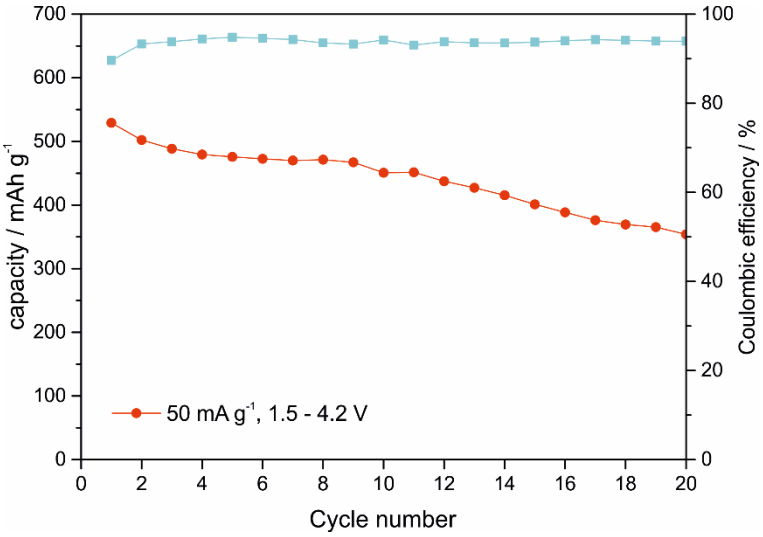

Fig. S13 Galvanostatic cycling of FeF_3 within 1.5-4.2 V with a current density of 50 mA/g. In this half-cell a different cathode composition was used but with the same method of preparation. The cathode material has a ratio of 40% FeF_3, 50 % CB, 10 % pVdF. The observed coulombic efficiency is lower as well as the cycling retention compared to the intercalation reaction only between 2-4.2 V.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) spectra were measured for FeF_3-Li half cells cycled at 0.1 A g^{-1} and 1 A g^{-1} (Fig. S14a, b). The cells were assembled and pre-cycled in the same manner as those used in galvanostatic measurements shown in Fig. 5. An EIS spectrum was taken every day, after the cell was charged and allowed to rest for 3 min. Overall, all EIS spectra show a shift on the Z` axis (real part of the impedance), followed by two depressed and strongly merged semicircle,s spanning from the high frequency (HF) to the middle frequency (MF) range, followed by an incline line at low frequency (LF).

To obtain quantitative results (Tab. S30) the spectra were fitted with an equivalent electrical circuit (EES, Fig. S14c) that includes: R_e – electrolyte resistance; R_{sf} – surface-film resistance; CPE_{sf} – surface-film constant phase element; R_{ct} - charge-transfer resistance; CPE_{dl} - double-layer capacitance; CPE_{diff} - lithium diffusion constant phase element. They delineate the impedances within the electrode as follow: Re is the resistance within the electrolyte related to the HF shift on the real axis. R_{sf} and CPE_{sf} values correspond to the surface film of the cathode, which is built at first contact between the electrolyte and the cathode and is related to the depressed semicircle at HF. R_{ct} describes the charge transfer resistance from the electron transfer to the lithium/conductive matrix and CPE_{dl} is the double-layer capacitance due to charge separation. R_{ct} and CPE_{dl} are related to the semicircle at MF. Finally, CPE_{diff} delineate the diffusion of lithium within the electrode known as Warburg impedance related to the LF. The values for CPE_{dl} and CPE_{sf} are given directly as pseudo capacitance in farad. The EIS spectra were fitted only until 1.6 Hz in order to obtain more precise fit of the semicircles as no strong variation of the steepness at incline line (Warburg impedance) was observed. Re and remains constant at around 4 Ohm for both cell measured at low (0.1 A g^{-1}) and high (1 A g^{-1}) currents. CPE_{diff} also remain stable.

Fig. S15 underlines the observation that the total resistance is reduced over cycling at high current (1 A g^{-1}). This effect is based on decrease of R_{sf} over cycling at high current in comparison with lower rates.[1, 2] The removal (faradaic reaction) of this surface-film resistance seems to stabilize the R_{ct}, which is known as a destructive effect for the cyclic stability of a battery.[3]

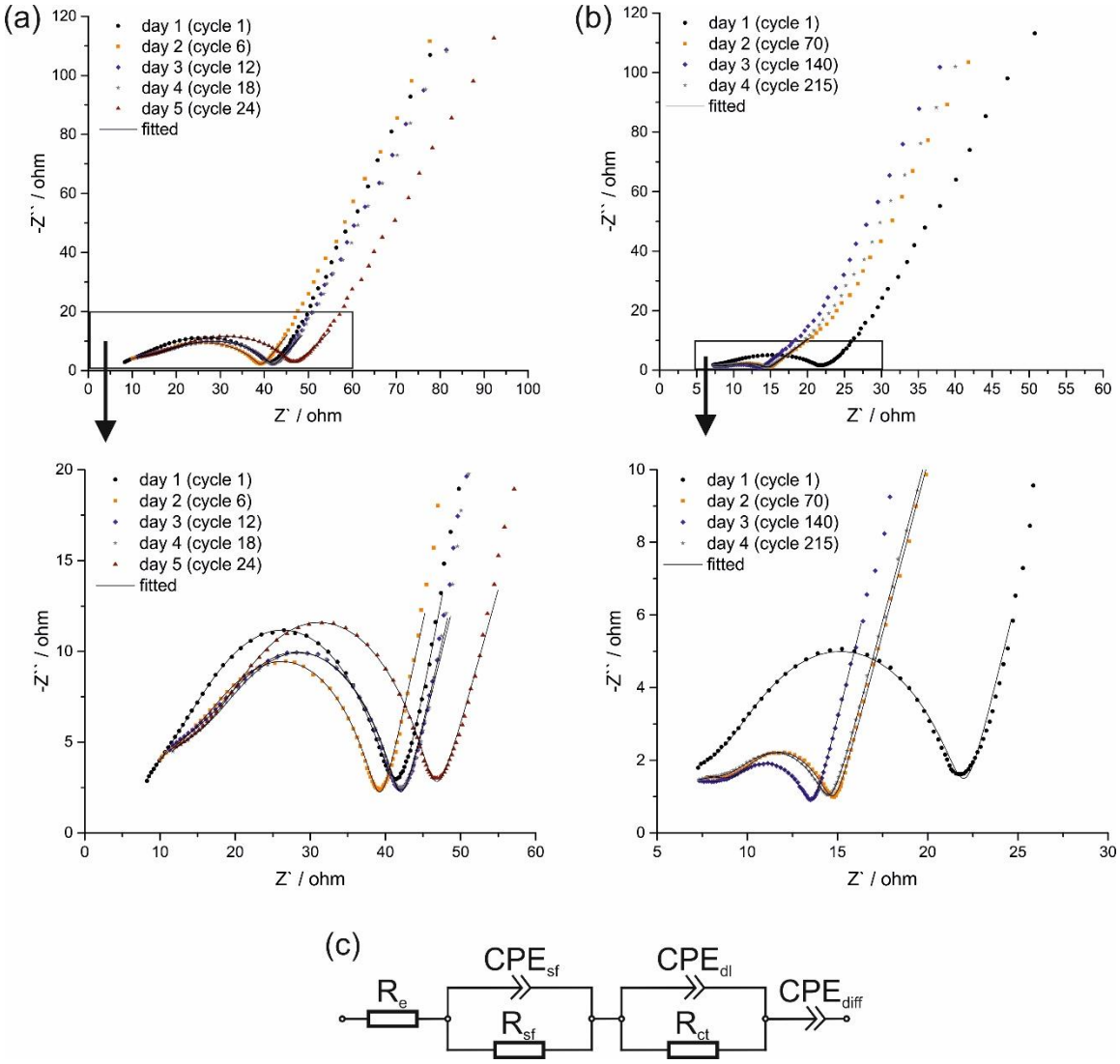

Fig. S14 EIS measurements during the galvanostatic cycling of two Li-ion half-cells at current densities of (a) 0.1 A g^{-1} and (b) 1 A g^{-1}. Every day an EIS measurement was performed. (c) Equivalent electrical circuit.

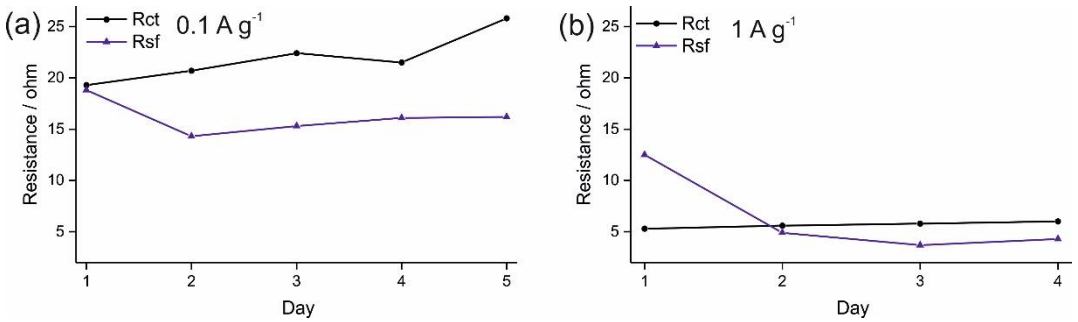

Figure S15. Evolution of the R_{ct} and R_{sf} values over several days of cycling at (a) 0.1 A g^{-1} and (b) 1 A g^{-1} in the voltage range of 2-4.2 V.

Tab. S30 Impedance parameters of half-cells cycled with a current rate of 0.1 A g^{-1} and 1 A g^{-1}. *(R_e+R_{sf}+R_{ct})

charge density 0.1 A g^{-1}					
day	**1**	**2**	**3**	**4**	**5**
cycle	1	6	12	18	24
total resistance*	42.2	39.1	41.8	41.8	46.3
R_e / ohm	4.1	4.0	4.2	4.3	4.3
C_{sf} / µF	1.0	0.2	0.1	0.1	0.1
R_{sf} / ohm	18.8	14.3	15.3	16.1	16.2
C_{ct} / µF	5.7	3.8	3.2	3.4	3.0
R_{ct} / ohm	19.3	20.7	22.4	21.5	25.8
CPE_{diff} / mF $s^{(a-1)}$	12.6	14.3	15.0	15.1	14.2
a	0.73	0.70	0.68	0.67	0.63
charge density 1 A g^{-1}					
day	**1**	**2**	**3**	**4**	
cycle	1	70	140	215	
total resistance*	21.9	14.6	13.5	14.5	
R_e / ohm	4.1	4.1	4.0	4.2	
C_{sf} / µF	6.0	14.0	21.7	18.4	
R_{sf} / ohm	12.5	4.9	3.7	4.3	
C_{ct} / µF	0.2	0.1	0.2	0.2	
R_{ct} / ohm	5.3	5.6	5.8	6.0	
CPE_{diff} / mF $s^{(a-1)}$	15.7	15.7	16.2	16.3	
a	0.72	0.69	0.71	0.69	

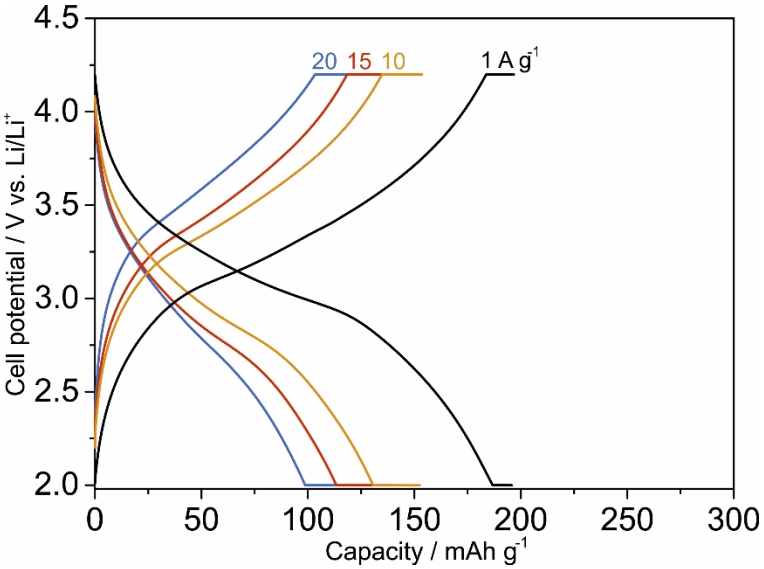

Fig. S16 Voltage-capacity plot of galvanostatic measurements in the voltage window 2.0 – 4.2 V towards lithium. Different current speeds (1, 10, 15, 20 A g^{-1}) were applied. The 5th cycle is presented for each measurement.

Reference

1. S. S. Zhang, K. Xu and T. R. Jow, *J. Electrochem. Soc.*, 2002, **149**, A1521-A1526.
2. P. C. Goonetilleke, J. P. Zheng and D. Roy, *J. Electrochem. Soc.*, 2009, **156**, A709-A719.
3. Zhaofeng Deng, Zhian Zhang, Yanqing Lai, Jin Liu, Jie Li and Y. Liua, *J. Electrochem. Soc.*, 2013, **160**, A553-A558.