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Electronic Supplementary Information (ESI)

Microwave-Assisted Synthesis of $NaMnF_3$ Particles with Tuneable Morphologies

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1. Experimental Details

Chemicals

Manganese oxide (MnO, 99.99%), trifluoroacetic acid (CF_3COOH, H-TFA, 98%), sodium trifluoroacetate (CF_3COONa, Na-TFA, 98%), potassium trifluoroacetate (CF_3COOK, K-TFA, 98%), oleic acid ($CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, OA, 90%), poly(acrylic acid) (PAA, #323667), oleylamine ($CH_3(CH_2)_7CH=CH(CH_2)_7CH_2NH_2$, OAm, 70%) and 1-octadecene ($CH_3(CH_2)_{15}CH=CH_2$, ODE, 90%) were purchased from Sigma Aldrich. Ethanol (99%) was purchased from Commercial Alcohols. Acetone and hexane (analytical grade) were purchased from Fischer Chemicals. Toluene (99.8%) was purchased from Fisher Scientific. All chemicals were used as received.

Microwave-assisted synthesis of $NaMnF_3$ particles

The synthesis of the $NaMnF_3$ particles was performed by the microwave-assisted thermal decomposition of manganese trifluoroacetate precursor ($Mn(CF_3COO)_2$, $Mn(TFA)_2$), using a modified version of the protocol previously reported by our group.[1, 2] In brief, 1.25 mmol of MnO were added to 10 mL of a 1:1 TFA-to-H_2O mixture in a 50 mL three-neck round bottom flask. The resulting mixture was stirred at 90 °C until the solution became clear and dried at 60 °C overnight. Subsequently, a stoichiometric amount of Na-TFA was added to the synthesized $Mn(TFA)_2$ along with 2.5 mL of oleic acid, 2.5 mL of oleylamine and 5 mL of 1-octadecene. To investigate the effect of the Na^+-to-Mn^{2+} ion ratio on particle formation, different amounts of Na-TFA were added as following: 1.25 mmol, 1.875 mmol, 2.5 mmol, and 3.75 mmol, yielding metal ion ratios of 1:1, 1.5:1, 2:1, and 3:1, respectively. This mixture was degassed at 120 °C under vacuum for 30 min. Subsequently, the degassed precursor solution was transferred to a 35 mL microwave vessel, purged with N_2 and tightly sealed. The vessel was inserted into a CEM Discovery SP microwave reactor, and the particles were grown by subjecting the reaction mixture under constant stirring to the following temperature profile: (i) slow stirring with rapid increase in temperature to a set nucleation temperature T_a (7 min), (ii) rapid cooling to the growth temperature T_b (15 s), (iii) static heating at T_b (10 min) under slow stirring , and (iv) gradual cooling to 50 °C (6 min). In a typical synthesis, T_a and T_b were 300 °C and 240 °C, respectively. To assess the effect of reaction temperature and time on particle formation and growth, T_a and T_b as well as the holding time at T_b were varied. An overview of all reaction parameters is given in Table S1. Following the synthesis, the reaction mixture containing the synthesized particles was washed with a 1:3 hexane-to-ethanol mixture and centrifuged at 6595 RCF for 20 min. The product was then washed with a 1:3 toluene-to-acetone mixture and centrifuged using the same conditions reported above. After purification, the particles were dispersed and stored in 5 mL toluene. NaF as a potential by-product can be removed by redispersing the particles in 5 mL of ethanol prior to the addition of 5 mL of water, followed by precipitation via centrifugation. Obtained particles were washed one more time with 10 mL of ethanol before being stored in 5 mL of toluene. In case of loss of dispersion stability of the particles following this washing procedure, dispersibility in toluene can be restored by adding 0.2 mL of oleic acid to the particle dispersion and subsequent stirring at room temperature overnight. Alternatively, we recommend a ligand exchange step to replace oleate by poly(acrylic acid), PAA, groups (*vide infra*). This approach does not only result in water-dispersible particles but also yields *in-situ* NaF-free samples without any additional washing, thus, reducing the risk of particle aggregation (Figure S10).

Table S1. Overview of the experimental conditions used in the microwave-assisted synthesis of $NaMnF_3$ particles, as well as their resulting products and morphologies.

Parameter Studied	Ion Ratio (Na^+-to-Mn^{2+})	T_a[1]	T_b	t (Tb)	Product	Predominant Morphology
Ion Ratio (Na^+-to-Mn^{2+})	1:1	300 °C	240 °C	10 min	$NaMnF_3$[2]	Rods
	1.5:1					Ribbons
	2:1					Plates
	3:1					Plates
Reaction Temperature	2:1	260 °C	240 °C	10 min	NaF	/
		270 °C				
		280 °C			$NaMnF_3$	Irregular Shape
		290 °C				
		300 °C				Plates
		300 °C	240 °C	10 min	$NaMnF_3$	Plates
			250 °C			Irregular Shape
			280 °C			
Reaction Time	1:1	300 °C	240 °C	1 min	$NaMnF_3$	Rods + Increasing Number of Plates
				5 min		
				10 min		
				20 min		
	2:1			1 min	$NaMnF_3$ $NaMn_3F_7$	Plates + Nanoparticles
				5 min	$NaMnF_3$	Plates
				10 min		
				20 min		

[1] Holding time at growth temperature T_a: 1 s

[2] All $NaMnF_3$ particles listed in this table crystallized in the orthorhombic phase

Microwave-assisted synthesis of $KMnF_3$ particles

The synthesis of the $KMnF_3$ particles followed the same protocol as described above for the $NaMnF_3$ particles, by replacing the Na-TFA by K-TFA. The $Mn(TFA)_2$ precursor was prepared following the aforementioned protocol. Subsequently, different amount of K-TFA (1.25 mmol or 2.5 mmol, yielding metal ion ratios of 1:1 and 2:1, respectively) was added to the synthesized precursor along with 2.5 mL of oleic acid, 2.5 mL of oleylamine, and 5 mL of 1-octadecene. This mixture was degassed at 120 °C under vacuum for 30 min. The T_a and T_b used in the microwave reactor were 300 °C and 240 °C (holding time: 10 min), respectively. The subsequent washing procedures were the same as described above for the $NaMnF_3$ particles.

Surface modification with poly(acrylic acid) (PAA)

PAA was used to replace oleate groups on the surface of $MMnF_3$ (M = Na, K) particles using a modified version of the protocol previously reported in the literature.[1] To prepare PAA-capped particles, 80 mg of PAA were dispersed in 10 mL of ethanol, and 50 mg of $MMnF_3$ particles were dispersed in 5 mL of chloroform. The two solutions were mixed together and stirred at room temperature for 1 h. Subsequently, the particles were precipitated with acetone (acetone to particle dispersion ratio: 8:1) and centrifuged at 6595 RCF for 20 min. The recovered solids were dispersed in ethanol for further use.

Characterization techniques

To determine the crystalline phase of the $NaMnF_3$ particles, powder X-ray diffraction (XRD) analysis was performed using a Rigaku Ultima IV Diffractometer (Cu Kα, λ = 1.5401 Å), operating at 44 kV and 40 mA (step size: 0.02°, scan speed: 0.7° min^{-1}). The particles were deposited on a glass slide from their suspension. The morphology and size distribution of the obtained particles were investigated by transmission electron microscopy (TEM, FEI Tecnai Spirit) and scanning electron microscopy (SEM, JEOL JSM-7500F FESEM). For TEM observations, the samples were dispersed on a Formvar/carbon film supported on a 300-mesh copper TEM grid. Size distributions (mean size ± standard deviation) of the samples were derived from TEM images using the software ImageJ. The respective size distributions were obtained analysing 150 particles per sample. The SEM analysis was conducted on samples drop-casted on a 5 mm x 5 mm silicon wafer after gold-sputtering (3 nm gold layer thickness) in a vacuum coater (Leica EM ACE200). Energy dispersive X-ray (EDX) measurements were performed on a Zeiss GeminiSEM 500 equipped with a Bruker EDX detector. The presence of the PAA ligands at the particles' surface was investigated by Fourier-transform infrared (FTIR) spectroscopy, using a Cary 630 FTIR spectrometer in ATR mode (Diamond ATR crystal), with acquisition of 128 scans and resolution of 4 cm^{-1}. Thermogravimetric analysis (TGA) of the PAA-capped samples was carried out using a TGA Q500/Discovery under N_2 atmosphere and at a heating rate of 10 °C/min. The Mn^{2+} ion concentration in the samples used for time-domain nuclear magnetic resonance (NMR) relaxivity measurements was determined with an Agilent ICP-OES spectrometer. Flow conditions of the Agilent ICP-OES spectrometer were as follows: nebulizer flow = 0.7 L/min, plasma flow = 12 L/min, auxiliary flow = 1 L/min. The same instrument was used to estimate the yield of $NaMnF_3$ as a function of Na^+-to-Mn^{2+} ratio as well as reaction time. Yields based on the determined Mn^{2+} ion concentration in the solid product are given in Table S2 (see Section 2 of ESI). Finally, the proton relaxation times of PAA-capped $NaMnF_3$ and $KMnF_3$ in phosphate-buffered saline (PBS) (pH = 7.4) suspensions were measured using a time domain NMR relaxometer. R_1 and R_2 relaxation rates (in s^{-1}) were obtained from T_1 and T_2 relaxation times (in s) determined at 40 °C on a Bruker Minispec mq20 instrument (Bruker, Billerica, MA) operating at 0.47 T and 20 MHz, equipped with a temperature control unit. T_1 was obtained with an inversion-recovery sequence with the following parameters: first pulse separation time = 40 ms, final pulse separation time = 10000 ms, fifteen data points separated by exponentially increasing intervals were recorded, acquisition scans = 4. T_2 was obtained by a Carr-Purcell-Meiboom-Gill sequence with the following parameters: 90° - 180° pulse separation time (tau) = 5 ms, 3000 data points were acquired, acquisition scans = 4. Relaxivities r_1 and r_2 and their statistical difference (p-value) were obtained from the linear fit of the plots of R_1 and R_2 against the molar concentration of Mn^{2+} ions of the tested particle dispersions (obtained from inductively coupled plasma optical emission spectroscopy, ICP-OES), carried out with Minitab 19 (Minitab LLC, State College, PA).

2. $NaMnF_3$ Yield

Table S2. Overview of the yield of $NaMnF_3$ particles obtained using different metal ion ratios and reaction times.

Parameter Studied	Ion Ratio (Na^+-to-Mn^{2+})	T_a	T_b	t $_{(Tb)}$	Yield
Ion Ratio (Na^+-to-Mn^{2+})	1:1	300 °C	240 °C	10 min	50.6 %
	1.5:1				81.3 %
	2:1				78.1 %
	3:1				83.6 %
Reaction Time	1:1	300 °C	240 °C	1 min	48.9 %
				5 min	56.2 %
				10 min	50.6 %
				20 min	59.0 %
	2:1			1 min [a]	/
				5 min	51.6 %
				10 min	78.1 %
				20 min	76.8 %

[a] After 1 min, a phase-mixture of $NaMnF_3$ and $NaMn_3F_7$ was obtained, hence, no yield for $NaMnF_3$ could be determined.

As summarized in Table S2, using a 1:1 Na^+-to-Mn^{2+} ratio resulted in a lower yield (50.6 %) compared to higher Na^+-to-Mn^{2+} ratios yielding 78 % to 83.6 %. In the microwave-assisted synthesis, sodium trifluoroacetate (Na-TFA) not only acts as a reagent but also to enrich the reaction medium with ions able to absorb microwave energy providing the system the energy required for $NaMnF_3$ crystallization (oleic acid/octadecene/oleylamine alone being rather poor microwave absorbers).[2, 3] Therefore, excess Na-TFA likely increases the energy intake from the microwave into the reaction, ultimately yielding more product.

Moreover, the yield was assessed in light of reaction time. At a 2:1 Na^+-to-Mn^{2+} ratio, the yield increased when the reaction time was prolonged from 5 to 10 min, without further increase after 20 min. No significant change in morphology and size was observed under these conditions (Figure 3D, main text). These findings indicate that, at sufficiently high metal ion ratio, time is the key aspect to increase the reaction's yield at a 5-10 min scale and once the phase mixture observed after 1 min was transformed into a phase-pure product. In contrast, at a metal ion ratio of 1:1, no obvious correlation between reaction time and yield was observed, with yields not exceeding 60 % even after 20 min of microwave irradiation. The lack of increase in yield with time indicates that formation of rod-like particles takes place at the initial stages of the reaction, followed by their subsequent transformation into plate-like structures upon longer reaction times (Figure 3B, main text).

3. Supplementary Figures

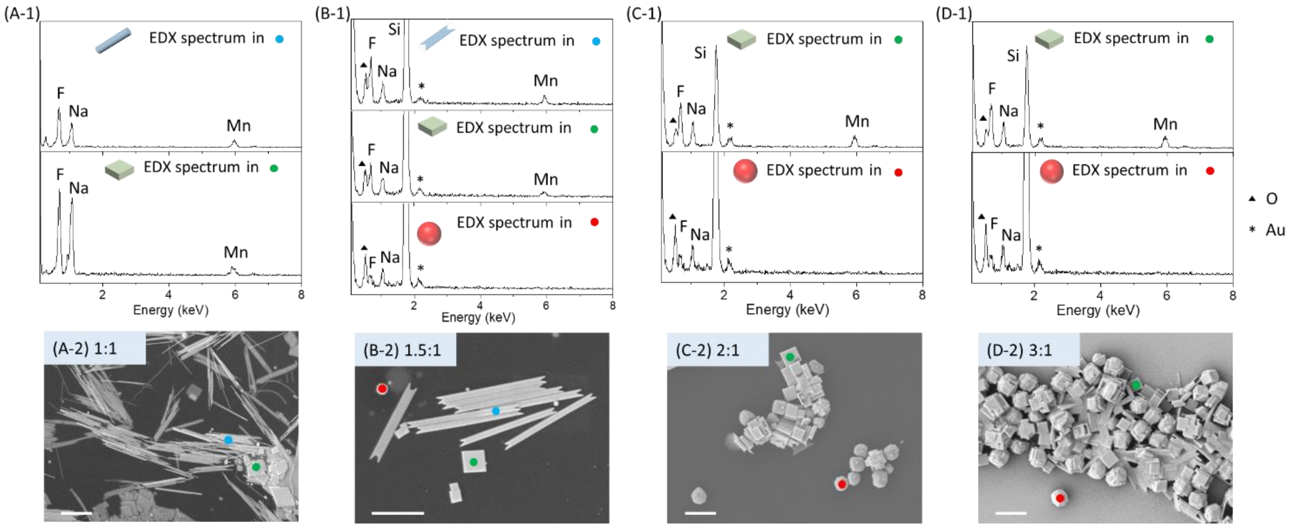

Figure S1. Energy dispersive X-ray (EDX) spectra (1) and the corresponding SEM images (2) of the particles obtained using different Na^+-to-Mn^{2+} ratios: (A) 1:1, (B) 1.5:1, (C) 2:1, and (D) 3:1. Reaction temperature: T_a = 300 °C, T_b = 240 °C; reaction time = 10 min. Scale bars: 1 µm.

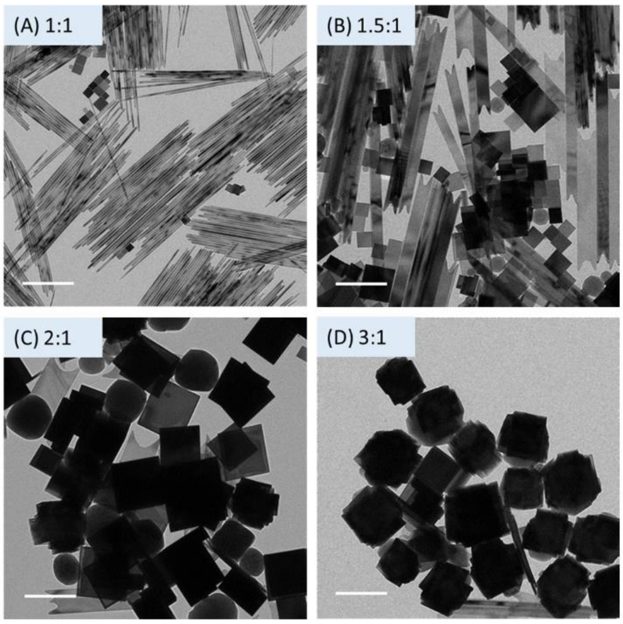

Figure S2. Transmission electron microscopy (TEM) images of $NaMnF_3$ particles synthesized using different Na^+-to-Mn^{2+} ratios: (A) 1:1, (B) 1.5:1, (C) 2:1 and (D) 3:1. Reaction temperature: T_a = 300 °C, T_b = 240 °C; reaction time = 10 min. Scale bars: 500 nm.

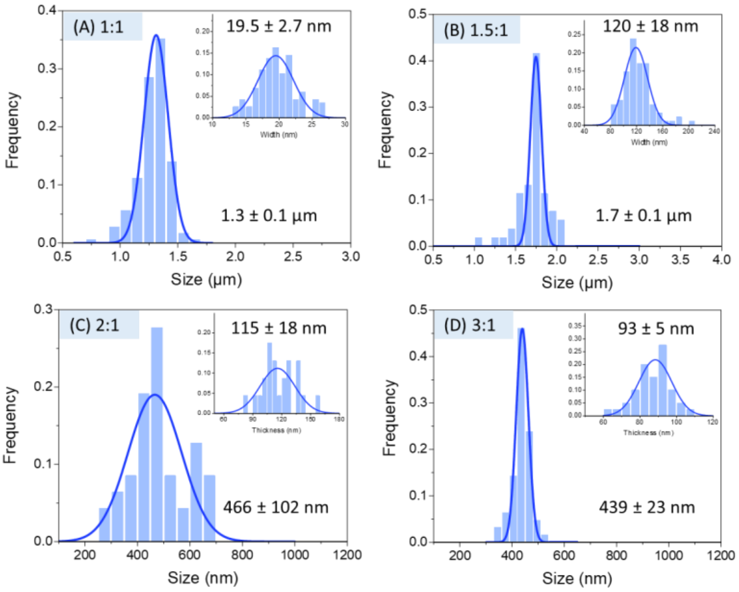

Figure S3. Size distributions of $NaMnF_3$ particles shown in Figure S2 synthesized using different Na^+-to-Mn^{2+} ratios: (A) 1:1, (B) 1.5:1, (C) 2:1, and (D) 3:1. The insets in (A) and (B) provide the width distributions for the rods and ribbons obtained; insets in (C) and (D) provide the thickness distributions for the plates obtained. Reaction temperature: T_a = 300 °C, T_b = 240 °C; reaction time = 10 min.

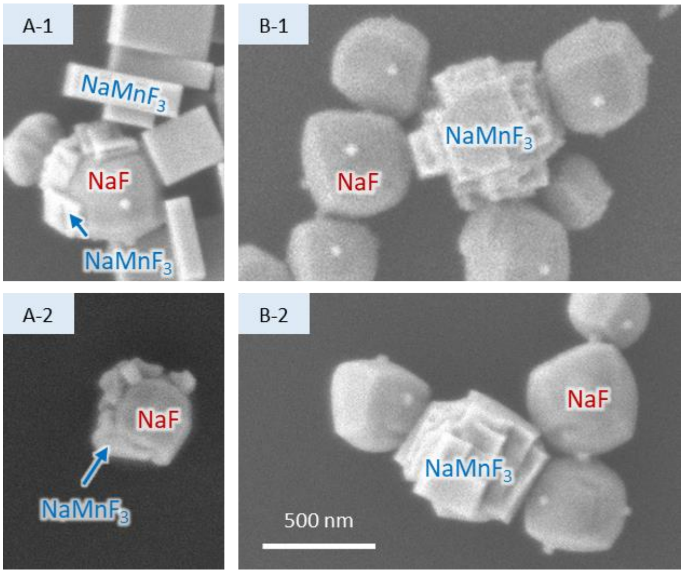

Figure S4. SEM images of the particles obtained using a 2:1 Na^+-to-Mn^{2+} ratio providing evidence for the proposed assembly of $NaMnF_3$ plates around NaF spheres – (A) partial and (B) full coverage of the spheres. The scale bar given in (B-2) applies to all four images. Upon further increase of the metal ion ratio to 3:1, SEM and TEM images showed an increasing number of these box-like assemblies.

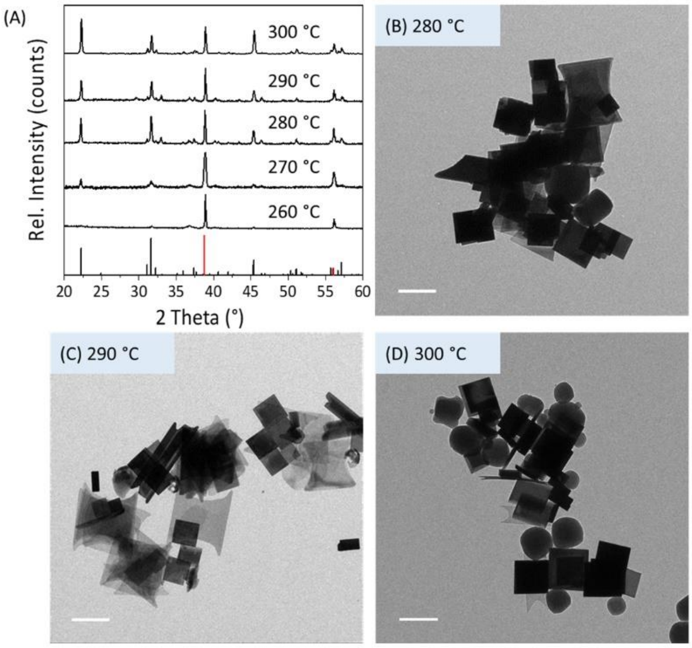

Figure S5. (A) X-ray diffraction (XRD) patterns of $NaMnF_3$ particles obtained by a microwave-assisted thermal decomposition using a 2:1 Na^+-to-Mn^{2+} ratio and a nucleation temperature T_a of 260 °C, 270 °C, 280 °C, 290 °C, and 300 °C, respectively (growth temperature T_b = 240 °C; reaction time = 10 min). References: black line – orthorhombic $NaMnF_3$, PDF card [01-072-0291]; red line – NaF, PDF card [00-001-1184]. (B-D) Transmission electron microscopy (TEM) images of particles obtained at T_a of (B) 280 °C, (C) 290 °C, and (D) 300 °C. Scale bars: 500 nm.

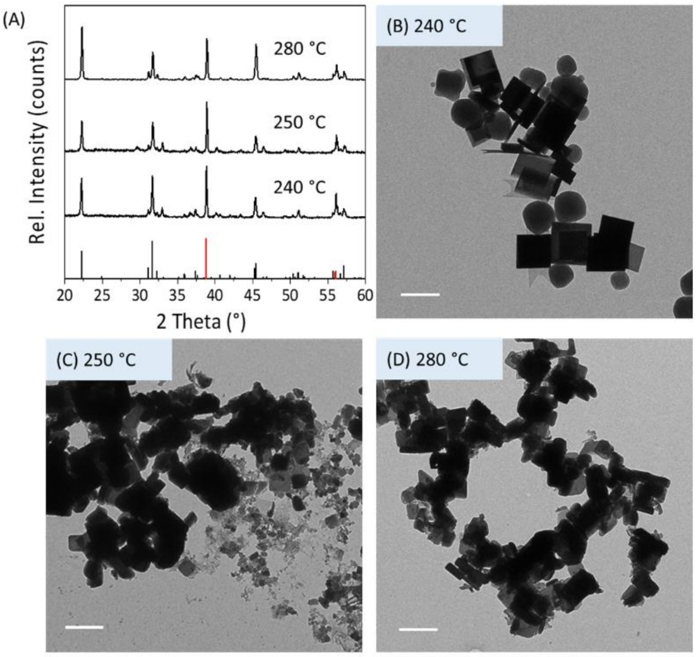

Figure S6. (A) XRD patterns of $NaMnF_3$ obtained by a microwave-assisted thermal decomposition using a 2:1 Na^+-to-Mn^{2+} ratio and a particle growth temperature T_b of 240 °C, 250 °C, and 280 °C, respectively (nucleation temperature T_a = 300 °C; reaction time = 10 min). Reference: black line – orthorhombic $NaMnF_3$, PDF card [01-072-0291]; red line – NaF, PDF card [00-001-1184]. (B-D) TEM images of materials obtained at (B) 240 °C, (C) 250 °C, and (D) 280 °C. Scale bars: 500 nm.

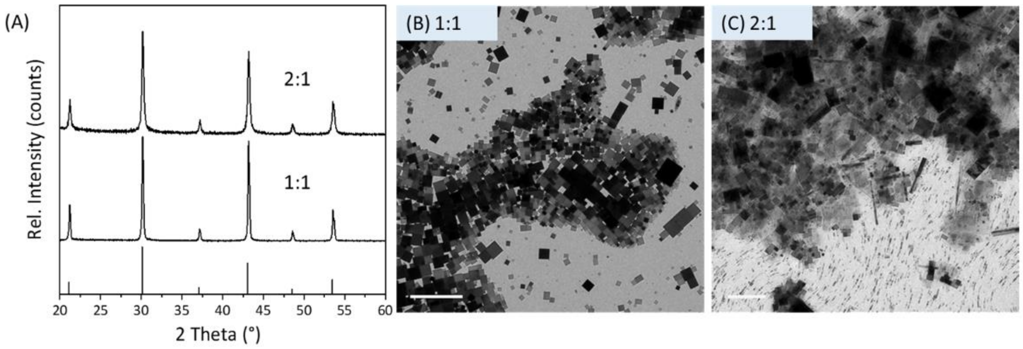

Figure S7. (A) XRD patterns of cubic-phase $KMnF_3$ particles synthesized by a microwave-assisted approach using K^+-to-Mn^{2+} ratios of 1:1 and 2:1. Reference: black line – cubic $KMnF_3$, PDF card [00-017-0116]. (B) and (C) show the corresponding TEM images of $KMnF_3$ particles obtained at K^+-to-Mn^{2+} ratios of (B) 1:1 and (C) 2:1. Reaction temperature: T_a = 300 °C, T_b = 240 °C; reaction time = 10 min. Scale bars: 500 nm.

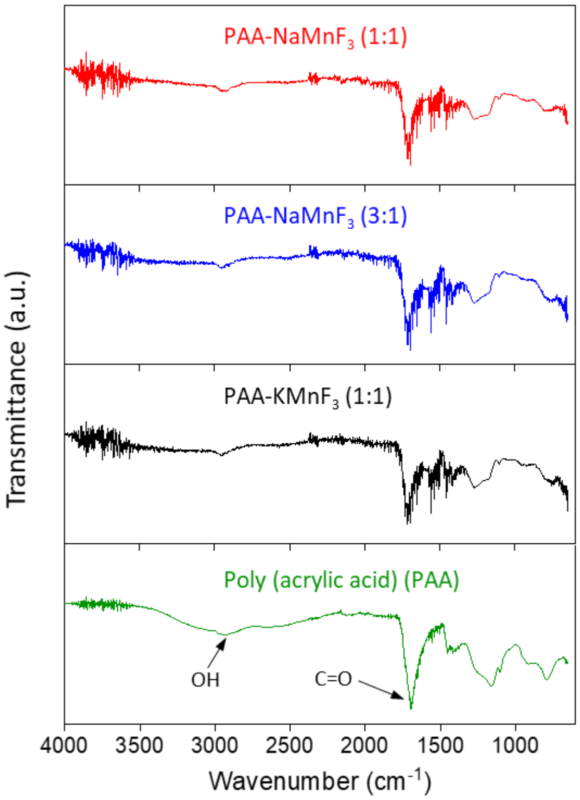

Figure S8. FTIR spectra of PAA-capped $MMnF_3$ (M = Na, K) particles and PAA used as reference.

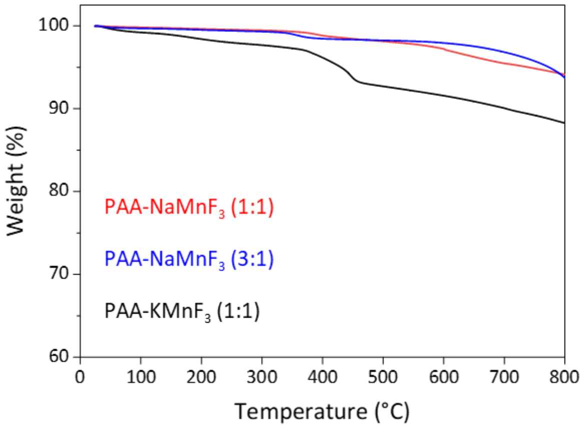

Figure S9. TGA profiles of PAA-capped $MMnF_3$ (M = Na, K) particles showing mass loss ascribed to PAA surface groups at temperatures up to ca. 500 °C. Comparable amounts of PAA were found for $NaMnF_3$ needles and plates obtained at Na^+-to-Mn^{2+} ratios of 1:1 and 3:1, exhibiting a mass loss of 2.4 % and 2.0 %, respectively. A larger amount of PAA (4.7 %) was observed for $KMnF_3$ particles, which may be explained by the particles' smaller size, thus, larger surface area.

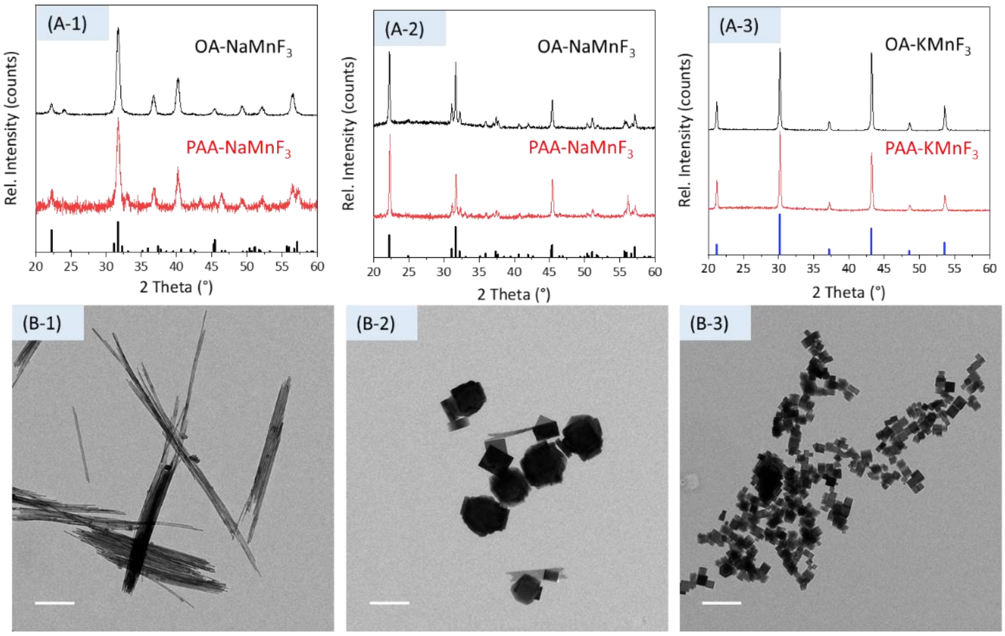

Figure S10. (A-1) and (A-2): XRD patterns of oleate (OA)-capped $NaMnF_3$ particles (black lines) obtained by the microwave-assisted approach using Na^+-to-Mn^{2+} ratios of (A-1) 1:1 and (A-2) 3:1 and their respective PAA-capped samples (red lines). (A-3): XRD patterns of OA-$KMnF_3$ synthesized using a 1:1 K^+-to-Mn^{2+} ratio (black line) and the corresponding PAA-capped particles (red line). Reference: black line – orthorhombic $NaMnF_3$, PDF card [01-072-0291]; blue line – cubic $KMnF_3$, PDF card [00-017-0116]. Reaction temperature: T_a = 300 °C, T_b = 240 °C; reaction time: 10 min. (B-1) to (B-3) show the corresponding TEM images of the PAA-capped samples. Scale bars: 500 nm.

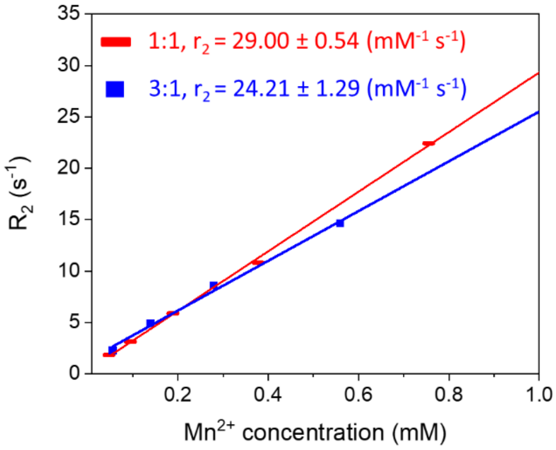

Figure S11. Relaxation rate R_2 of water protons plotted against the molar concentration of Mn^{2+} for PAA-capped $NaMnF_3$ particles synthesized using Na^+-to-Mn^{2+} ratios of 1:1 (red data points) and 3:1 (blue data points) under 0.47 T. Solid lines are linear fits.

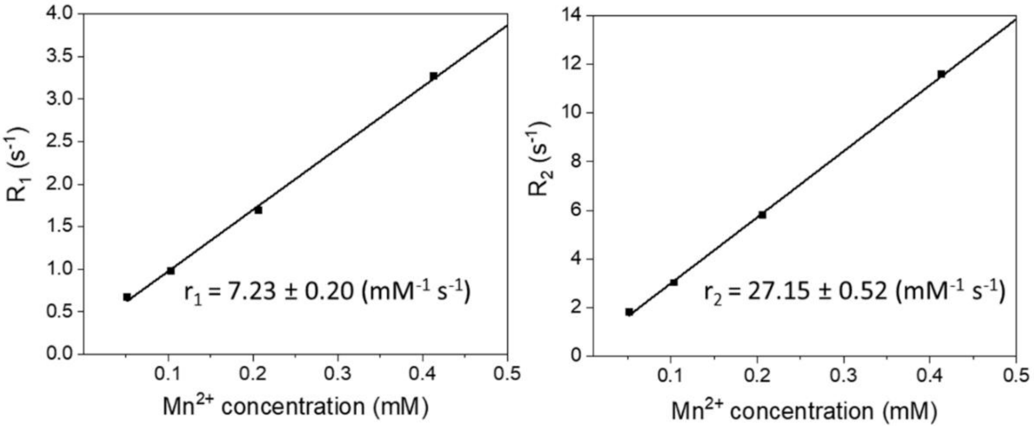

Figure S12. Relaxation rates R_1 and R_2 of water protons plotted against the molar concentration of Mn^{2+} for PAA-capped $KMnF_3$ particles (synthesized using a 1:1 K^+-to-Mn^{2+} ratio) under 0.47 T. Solid lines are linear fits.

4. References

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2. I. Halimi, E. M. Rodrigues, S. L. Maurizio, H.-Q. T. Sun, M. Grewal, E. M. Boase, N. Liu, R. Marin and E. Hemmer, *J. Mater. Chem. C*, 2019, **7**, 15364.
3. I. Bilecka and M. Niederberger, *Nanoscale*, 2010, **2**, 1358.