### **Electronic Supplementary Information:**

### New 2D networks with a direct fluorine-metal bond: MF(CH<sub>3</sub>COO) (M: Sr, Ba, Pb)

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# Section SI. Chemicals used in the present study

Compound	Origin	Purity
$Ca(CH_3COO)_2 \cdot H_2O$	Sigma-Aldrich	≥99%
Sr(CH <sub>3</sub> COO) <sub>2</sub>	Sigma-Aldrich	≥99%
Ba(CH <sub>3</sub> COO) <sub>2</sub>	Sigma-Aldrich	≥99%
$Pb(CH_3COO)_2 \cdot 3H_2O$	Sigma-Aldrich	≥99%
H <sub>2</sub> (p-BDC)	Sigma-Aldrich	≥99%
NH <sub>4</sub> F	Sigma-Aldrich	≥98%
СН₃СООН	Fluka	≥95%

**Table SI-1.** Chemicals used in the present study.

#### Section SII. Variation of synthesis conditions to obtain pure CaF(CH<sub>3</sub>COO) and SrF(CH<sub>3</sub>COO).

The above discussion and PXRD analysis suggest that it is not possible to obtain pure CaF(CH<sub>3</sub>COO) via Scheme 1(1a). This difficult was further evidenced by the <sup>19</sup>F MAS NMR spectra of the product material. The NMR analysis of the phase pure xerogel of CaF(CH<sub>3</sub>COO) shows two broad <sup>19</sup>F resonances at chemical shifts of  $\delta$  = -104 ppm and  $\delta$  = -108 ppm (SI-1a). Noting that the signal at -108 ppm is typical for <sup>19</sup>F in CaF<sub>2</sub>, this suggests that, despite the absence of obvious contaminants by PXRD analysis, the product is not phase pure. The <sup>19</sup>F signal of the mechanochemical product also exhibits its maximum at -108 ppm, albeit with a notable asymmetric decay in the low-field region. It therefore appears that this sample contains a remarkable quantity of disordered CaF<sub>2</sub>, not visible in the PXRD pattern, and that the signal of CaF(CH<sub>3</sub>COO) (presumably at -104 ppm) is in fact covered by the broad decay.

Previous mechanochemical syntheses<sup>1-5</sup> have demonstrated that small quantities of water can have a remarkable and beneficial influence on the outcome of a mechanochemical preparation of framework materials. The effect of water was tested on the mechanochemical synthesis of CaF(CH<sub>3</sub>COO), with the aim of increasing its purity. For this purpose, water was added (1) dropwise, and (2) through use of a crystal hydrate reactant phase. Regardless of the method of water addition, NMR analysis clearly shows that the quantity of CaF<sub>2</sub> increases with the presence of water, Figure SII-2. The quantity of CaF<sub>2</sub> produced increasing water supply and is considerably higher if the water is added externally (*i.e.* dropwise), Table SII-1. Interestingly, even the presence of atmospheric moisture adversely affects the purity of this mechanochemical synthesis, as has been noted previously <sup>6</sup>. The effect of water was not only observed for the Ca-system, but was also observed in the case of SrF(CH<sub>3</sub>COO) (Fig. SII-2). SrF(CH<sub>3</sub>COO) could only be obtained as the pure phase under inert atmospheric conditions and using dry starting materials.



**Figure SII-1.** Comparison of the experimental (blue) and the simulated (red) <sup>19</sup>F MAS NMR spectrum of milling product obtained by milling of  $Ca(CH_3COO)_2 \cdot H_2O$  with NH<sub>4</sub>F and H<sub>2</sub>(*p*-BDC) (a). The simulated <sup>19</sup>F MAS NMR spectrum is a combination of two single lines (green), representing the two different fluorine species. (b): <sup>19</sup>F MAS NMR spectra of milling products obtained with a different water supply. (red: inert milling with dry starting materials, black: inert milling without pre-drying of starting materials, green: with addition of 130 µL water, blue: with addition of 1.3 mL water).

	Signal intensity	Signal intensity
Reactants and water content	-104 ppm [%]	-108 ppm [%]
$Ca(CH_3COO)_2 \cdot H_2O + 1.3 \text{ mL } H_2O$	43.4	56.6
$Ca(CH_{3}COO)_{2} \cdot H_{2}O + 130 \ \mu L \ H_{2}O$	71.4	28.5
Ca(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	78.9	21.1
Ca(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O, reaction under inert conditions		
dry starting materials	84.5	15.5
$Ca(CH_3COO)_2 \cdot 0.5 H_2O$ , under inert conditions		
without pre-drying	74.2	25.8

**Table SII-1.** Overview about the signal intensities of fluorine species applying different reaction conditions



**Figure SII-2**. Comparison of the experimental (blue) and the simulated (red) <sup>19</sup>F MAS NMR spectrum of the milling product obtained by milling of  $Sr(CH_3COO)_2 0.5 H_2O$  with  $NH_4F$  and  $H_2(p$ -BDC) (a). The simulated <sup>19</sup>F MAS NMR spectrum is combination of 3 single signals (green). representing the 3 different fluorine species. (b): <sup>19</sup>F MAS NMR spectra of milling products obtained with a different water supply. (Red: inert milling with dry starting materials, black: inert milling without pre-drying of starting materials, green: ambient conditions)

Table SII-2.	Overview	about the sig	nal intensities	s of different	fluorine s	species apply	ving different	reaction (	conditions
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	Signal intensity at	Signal intensity at	Signal intensity at
Reactants and water content	-80 ppm [%]	-83 ppm [%]	-88 ppm [%]
Sr(CH <sub>3</sub> COO) <sub>2</sub> ·0.5H <sub>2</sub> O	80.1	12.1	7.8
$Sr(CH_3COO)_2 \cdot 0.5H_2O$ , reaction under inert conditons	100	0	0

### Section SIII: Results of elemental analysis of BaF(CH<sub>3</sub>COO), SrF(CH<sub>3</sub>COO) and PbF(CH<sub>3</sub>COO)

The elemental composition of the material produced by both synthetic procedures are in good agreement, and match well with the expected composition. The slightly increased carbon content results from residual acetic acid, which is still on the surface of the coordination polymer. No more nitrogen can be detected in the samples, which points to a complete conversion of the fluorinating agent. In principle, halogenated compounds attack the combustion reactor and the column material. This leads to asymmetric peaks, which complicates the evaluation and does not allow an exact determination of the composition.

		C[%]	H[%]	F[%]	N[%]
	obtained by milling	14.4	1.3	8.3	0
BaF(CH <sub>3</sub> COO)	xerogel	12.6	1.3	-	0
	calculated	11.2	1.4	8.8	0
	obtained by milling	18.3	1.7	9.2	0
SrF(CH <sub>3</sub> COO)	xerogel	12.6	1.8	-	0
	calculated	14.5	1.8	11.5	0
PbF(CH <sub>2</sub> COO)	obtained by milling	8.4	1.1	6.6	0
	calculated	8.4	1.0	6.7	0

Table SIII-1. Results of elemental analysis of BaF(CH<sub>3</sub>COO), SrF(CH<sub>3</sub>COO) and PbF(CH<sub>3</sub>COO).

Section SIV. BET plot of nitrogen on BaF(CH<sub>3</sub>COO)



Figure SIV-1. Linear isotherm plot of nitrogen on BaF(CH<sub>3</sub>COO) obtained by milling taken at 77 K.



Figure SIV-2. Linear isotherm plot of

#### Section SV. Crystal structure supported by IR spectroscopy

The FTIR spectra (Fig. SV-1) of BaF(CH<sub>3</sub>COO), SrF(CH<sub>3</sub>COO), and PbF(CH<sub>3</sub>COO) show the symmetric and asymmetric vibration bands of the carboxylic groups (BaF(CH<sub>3</sub>COO):  $v_s$ =1419 cm<sup>-1</sup>,  $v_{as}$ =1550 cm<sup>-1</sup>; SrF(CH<sub>3</sub>COO):  $v_s$ =1433 cm<sup>-1</sup>,  $v_{as}$ =1554 cm<sup>-1</sup>; PbF(CH<sub>3</sub>COO):  $v_s$ =1392 cm<sup>-1</sup>,  $v_{as}$ =1510 cm<sup>-1</sup>). The FTIR spectra of BaF(CH<sub>3</sub>COO), SrF(CH<sub>3</sub>COO and PbF(CH<sub>3</sub>COO) suggest the presence of a connection between the metal cations and acetate groups. This stems from a softening of vibration band of the asymmetric stretching of the carboxylic groups as compared to free acetic acid ( $v_{as}$ =1740 cm<sup>-1</sup>).<sup>7</sup>

Whereas the FTIR spectra of the xerogels and milling products of Sr- and Ba-acetate fluorides agree very well, the spectra of the Ca-compound show, as already expected from the PXRD and solid-state NMR results, a superposition of contributions from different components present in the sample.



**Figure SV-1.** IR spectra of the products  $MF(CH_3COO)$  (M= Ba, Sr, Ca and Pb) obtained by milling (green), xerogel (blue) along with the reactants  $M(CH_3COO)_2$  and  $H_2(p$ -BDC) (black).

### Section SVI. Scalar coupling between <sup>19</sup>F and <sup>207</sup>Pb in the <sup>19</sup>F MAS NMR spectrum



**Figure SVI-1**. Comparison of the experimental (blue) and simulated (red) <sup>19</sup>F MAS NMR spectra of PbF(CH<sub>3</sub>COO). The simulated <sup>19</sup>F MAS NMR spectrum is a superposition different contributions representing different fluoride ion environments; green:  $[F^{207}Pb_0Pb_4]$ , violet:  $[F^{207}Pb_1Pb_3]$ , turquoise  $[F^{207}Pb_2Pb_2]$ .

|--|

Options of local units from [FPb <sub>4</sub> ]	Probabilities in %
[FPb <sub>4</sub> ]	35.8
[F <sup>207</sup> Pb <sub>1</sub> Pb <sub>3</sub> ]	41.9
$[F^{207}Pb_2Pb_2]$	18.4
[F <sup>207</sup> Pb <sub>3</sub> Pb <sub>1</sub> ]	3.6
[F <sup>207</sup> Pb <sub>4</sub> ]	0.3





Figure SVII-1. Thermoanalytical curves of barium fluoride acetate (BaF(CH<sub>3</sub>COO)); m/z=18: H<sub>2</sub>O, and H<sub>2</sub>O, m/z=44: CO<sub>2</sub>).



**Figure SVII-2.** Thermoanalytical curves of strontium fluoride acetate (SrF(CH<sub>3</sub>COO)); m/z=18: H<sub>2</sub>O, m/z=19: F, m/z=44: CO<sub>2</sub>).



**Figure SVII-3**. Thermoanalytical curves of lead fluoride acetate (PbF(CH<sub>3</sub>COO)) prepared by milling for 8 h; m/z=18:  $H_2O$ , m/z=19:F, m/z=44:  $CO_2$ ).

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