

## Electronic Supplementary Information

### **In situ time-resolved monitoring of mixed-ligand metal organic frameworks (MOFs) mechanosynthesis**

Max Rautenberg,<sup>ab</sup> Biswajit Bhattacharya,<sup>\*a</sup> Julia Witt,<sup>a</sup> Mohit Jain<sup>ac</sup> and Franziska Emmerling<sup>\*ab</sup>

<sup>a</sup>BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11 12489 Berlin, Germany.

<sup>b</sup>Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany.

<sup>c</sup>Department of Materials Science, Technical University of Darmstadt, Karolinenplatz 5, 64289 Darmstadt, Germany.

E-mail: biswajit.bhattacharya@bam.de (BB); franziska.emmerling@bam.de (FE)

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## **Material and Methods**

**Materials.** All reagents were obtained commercially and used without further purification. Cobalt acetate tetrahydrate ( $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ , 98%) was supplied by Carl Roth GmbH, iron chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 98%) was supplied by Applichem GmbH and sodium bicarbonate ( $\text{NaHCO}_3$ , 100%) was bought from VWR International BVBA. 1,4-Phenylenediphosphonic acid ( $\text{H}_4\text{-PhDPA}$ , 98%) was bought from Tokyo Chemical Industries Co. Ltd and 4,4'-bipyridine (4,4'-bipy, 98%) was supplied by Alfa Aesar. Nafion ionomer (98%+) and isopropanol (HPLC grade, 99,8%+) were purchased from Sigma-Aldrich. KOH pellets (85%+) and  $\text{H}_2\text{SO}_4$  (95%+) were supplied by CHEMSOLUTE. Deionized water was purified by a Milli-Q ultrapure water purification system (Merck-Millipore, 18  $\Omega$  resistance at 25°C).

**Mechanochemical synthesis of BAM-1.** In a typical experiment,  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (0.155 mmol, 38.7 mg),  $\text{H}_4\text{-PhDPA}$  (0.155 mmol, 37.0 mg) and 4,4'-bipy (0.155 mmol, 24.3 mg) are placed into a PMMA milling jar (~4 mL). After adding a stainless-steel ball (7 mm diameter) and Milli-Q water (20  $\mu\text{L}$ ) the mixture was ground at a frequency of 50 Hz for 30 min.

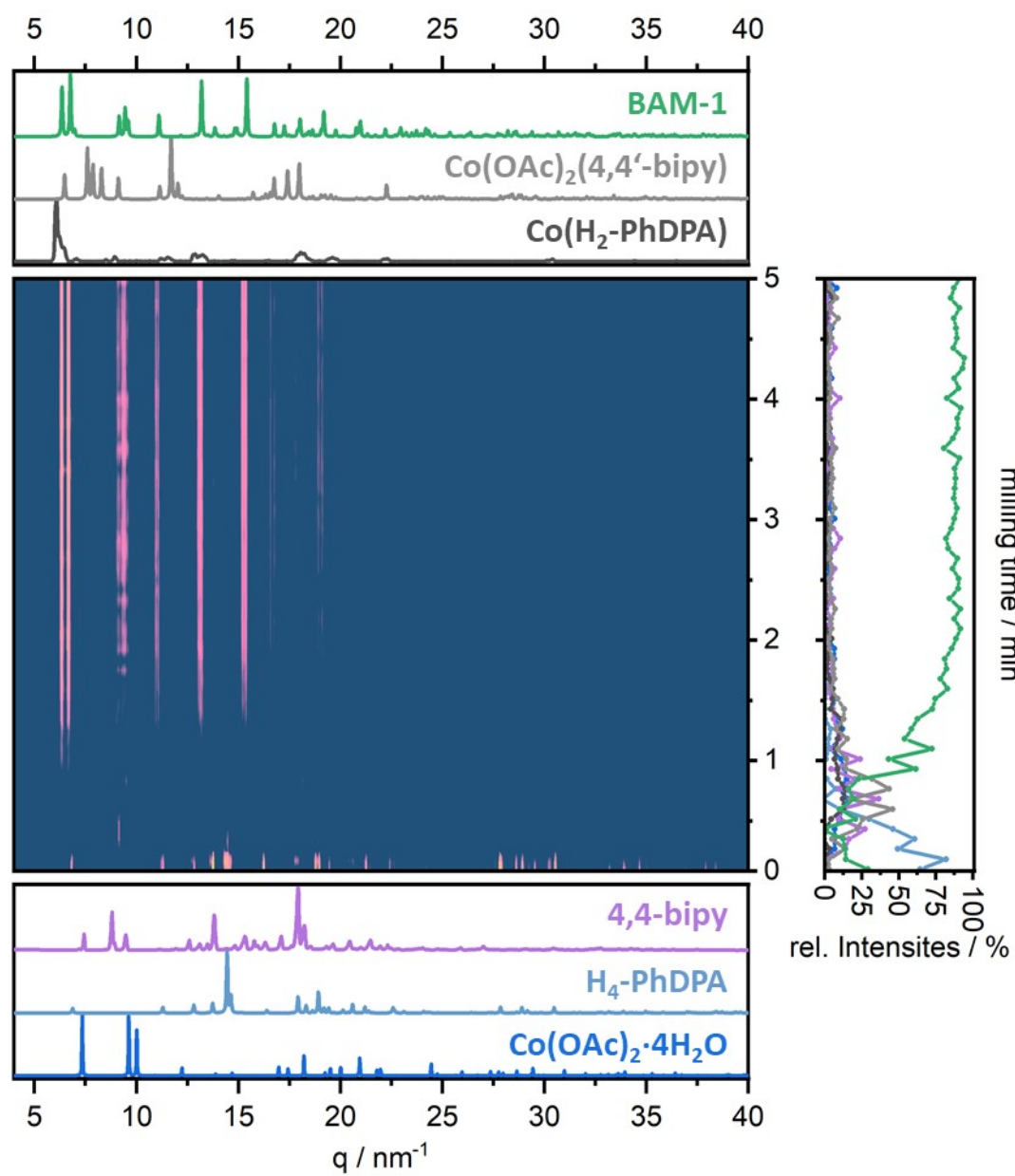
**Mechanochemical synthesis of BAM-2.** In a typical experiment  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (0.131 mmol, 26.1 mg),  $\text{NaHCO}_3$  (0.263 mmol, 22.1 mg),  $\text{H}_4\text{-PhDPA}$  (0.131 mmol, 31.3 mg) and 4,4'-bipy (0.131 mmol, 20.5 mg) are placed into a PMMA milling jar (~4 mL) along with a stainless-steel milling ball (7 mm diameter) and Milli-Q water (20  $\mu\text{L}$ ) and ground at a frequency of 50 Hz for 30 min.

The incremental syntheses were carried out with the ratios of the one pot reactions, while omitting one linker, that is added in the second step with Milli-Q water (20  $\mu\text{L}$ ).

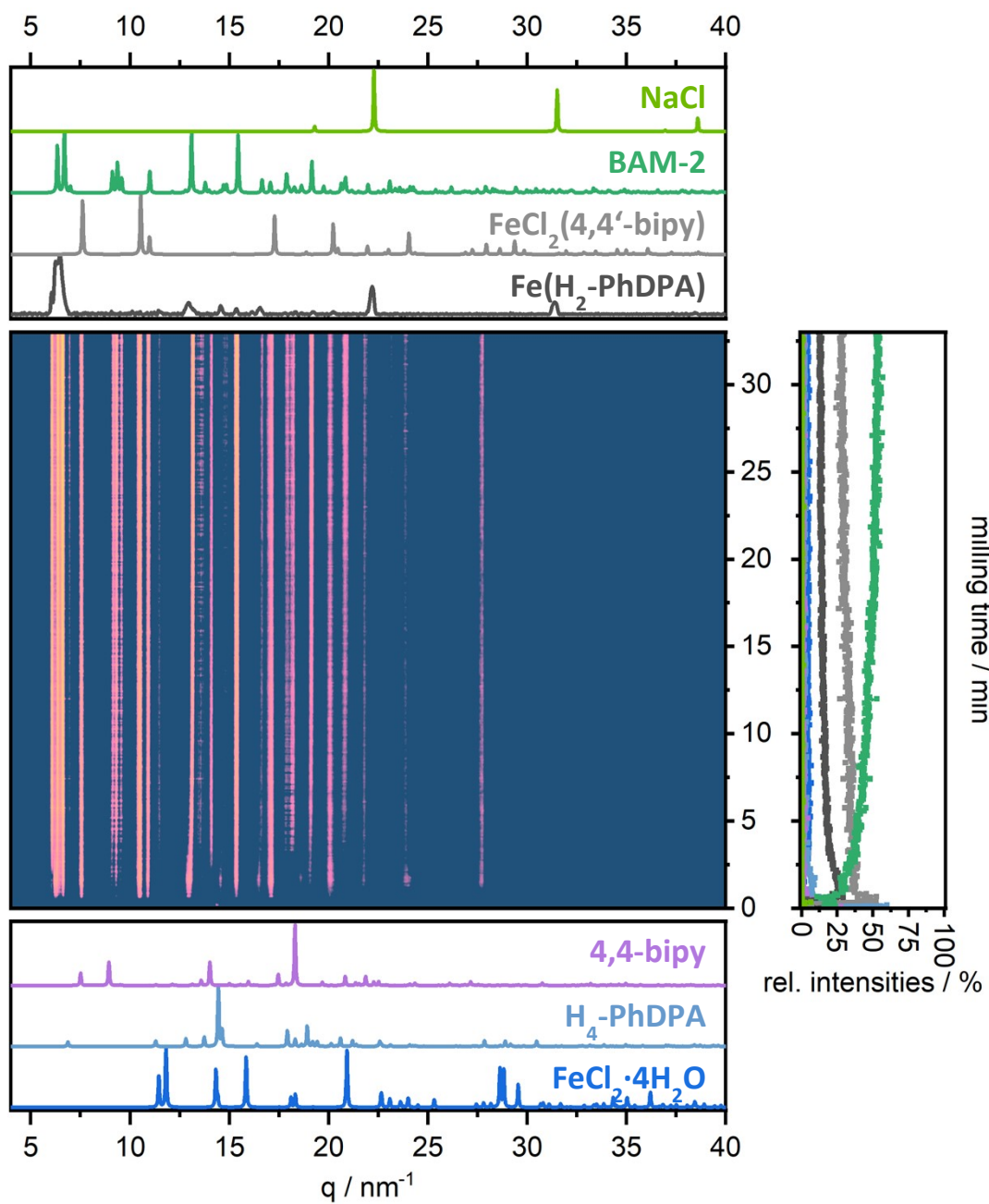
***In situ* PXRD.** *In situ* data were collected at the  $\mu\text{Spot}$  beamline at the BESSY II electron storage ring operated by the Helmholtz-Zentrum Berlin für Materialien und Energie. The utilized beam size was 100  $\mu\text{m}$  at a photon energy of 17.44 keV using a double crystal monochromator (SI 111). To prevent double reflections, the milling jar was positioned in such a way, that the beam passes approximately 50  $\mu\text{m}$  inside of the jar walls. Scattered intensities were collected with a two-dimensional X-ray detector (Eiger 9M, HPC 3110x3269 pixels, 75x75  $\mu\text{m}$  pixel size) with a time resolution of 5 s and a sample-detector distance of 233.5 mm. The obtained scattering images were processed with the program DPDAK.<sup>35</sup> The resulting patterns were background subtracted with a custom-made python script. Analysis, processing, and plotting was done with Origin (Version 2021, OriginLabs Corporation, Northampton, MA, USA). Reference crystal structures were retrieved from the crystallographic databases ICSD or CCDC as .cif files from which all simulated PXRD pattern were simulated using Mercury (Version 4.3.0., CCDC).<sup>36</sup>

## In situ PXRDs

one pot reactions



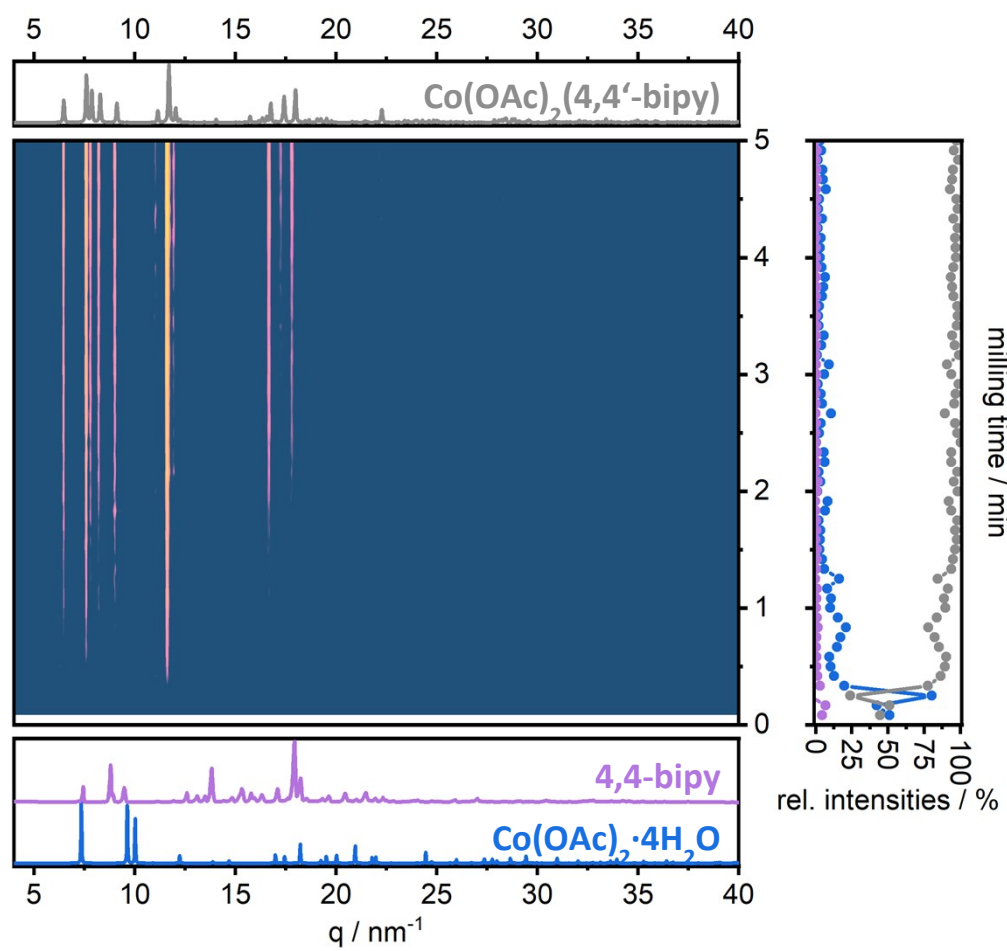
**Fig. S1** TRIS PXRD of the mechanochemical one pot synthesis of BAM-1.



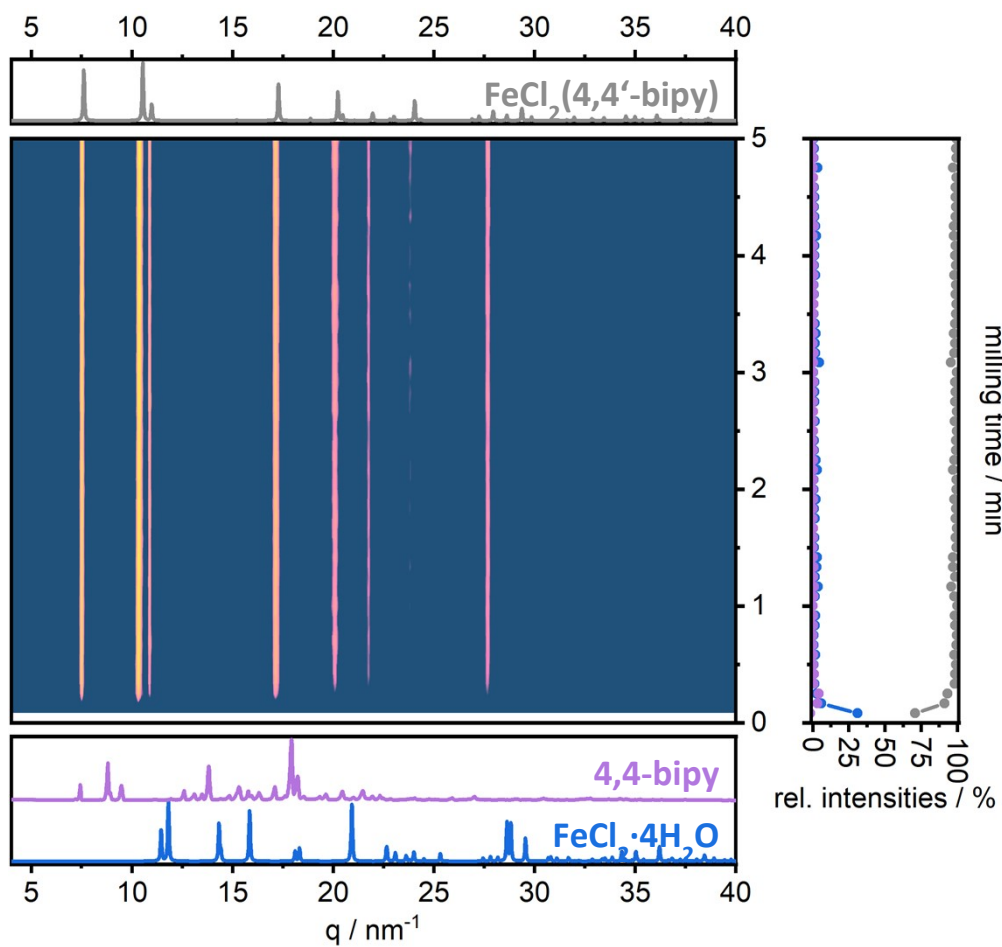
**Fig. S2** TRIS PXRD of the mechanochemical one pot synthesis of BAM-2.

## Incremental reactions

### Reactions I a

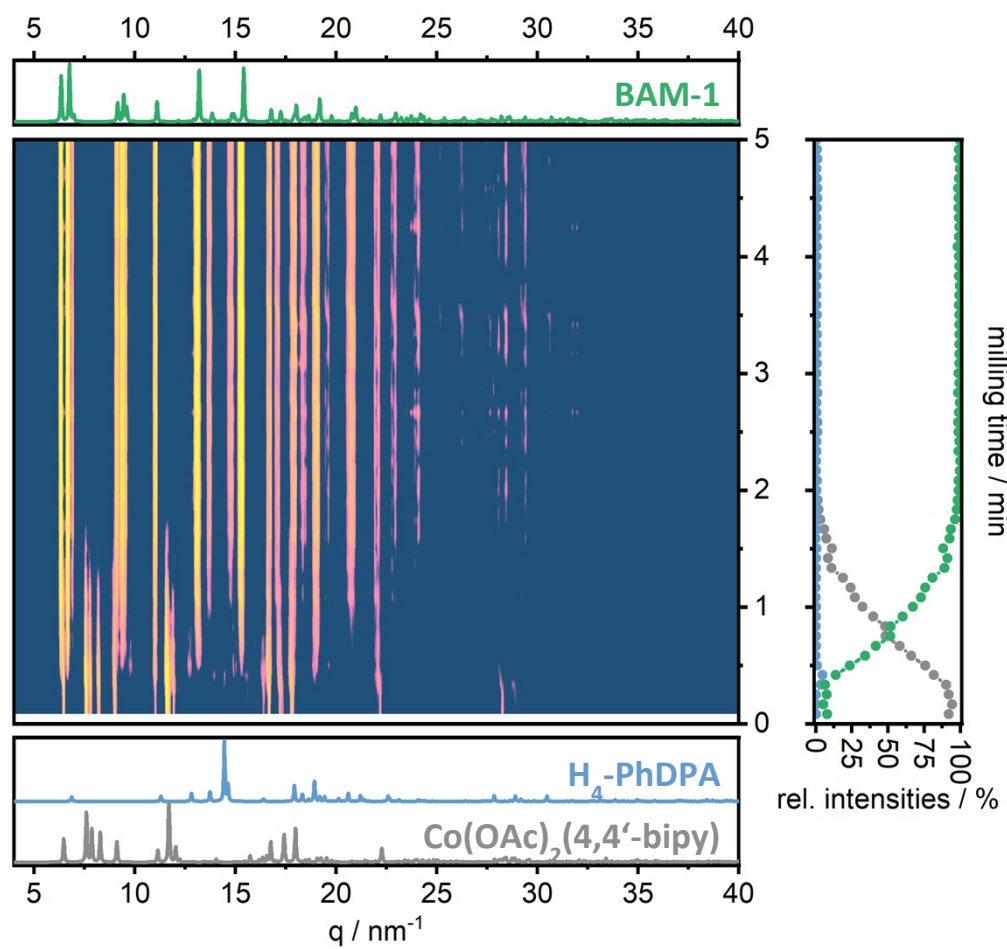


**Fig. S3** TRIS PXRD of the mechanochemical reaction I a of BAM-1.

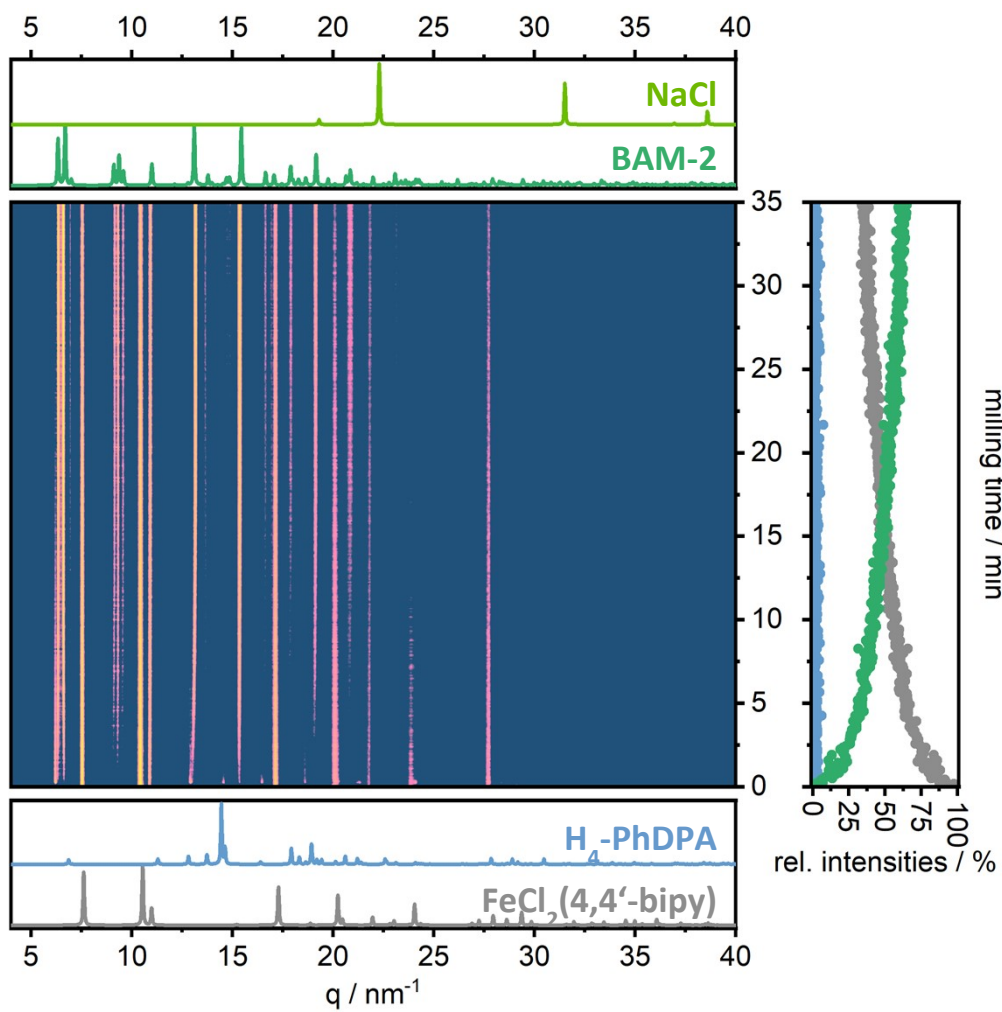


**Fig. S4** TRIS PXRD of the mechanochemical reaction I a of BAM-2.

**Reactions I b**



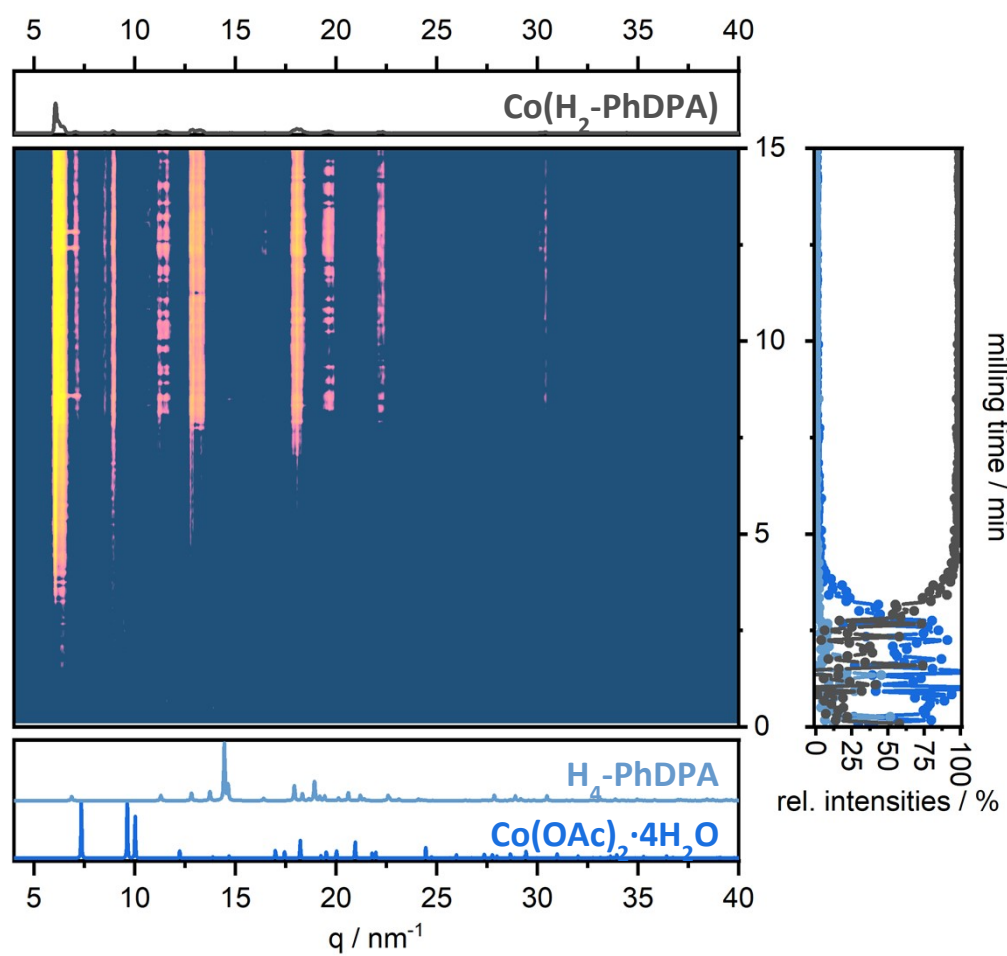
**Fig. S5** TRIS PXRD of the mechanochemical reaction I b of BAM-1.



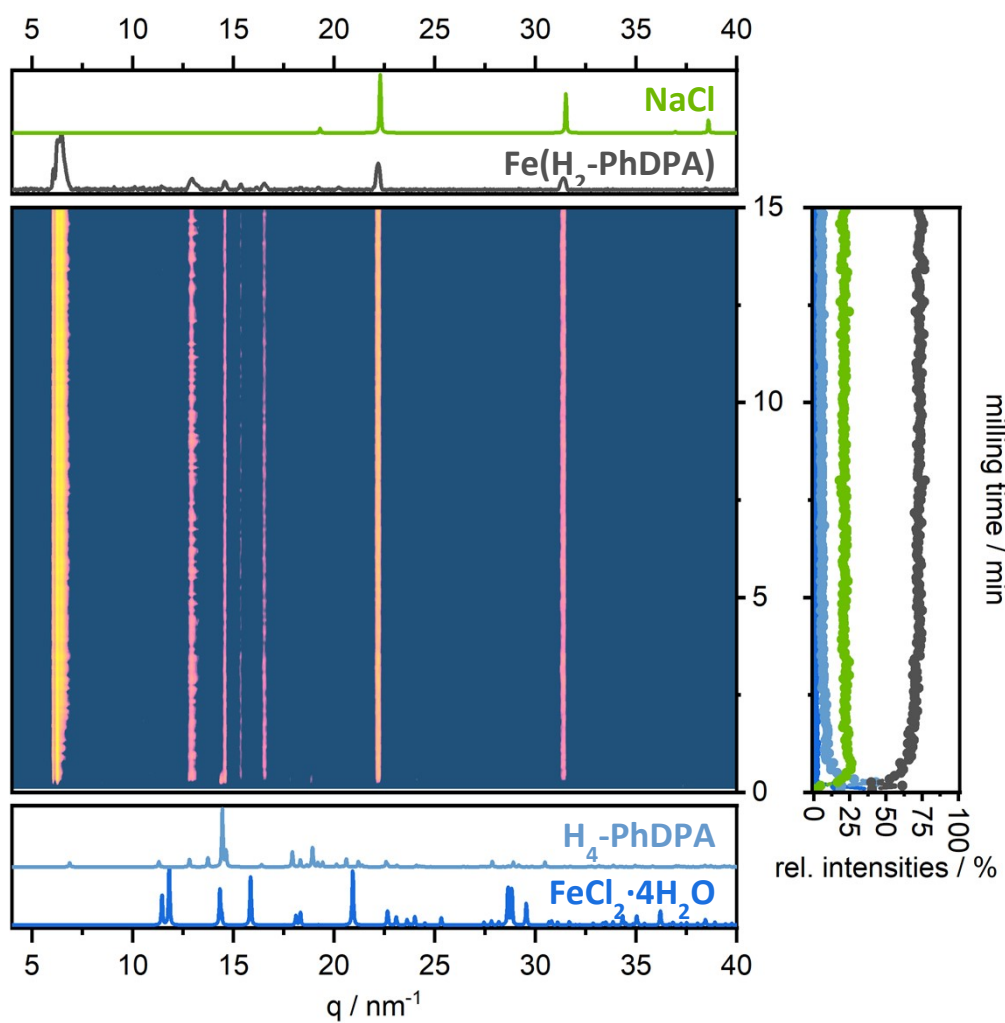
**Fig. S6** TRIS PXRD of the mechanochemical reaction I b of BAM-2.



**Reactions II a**

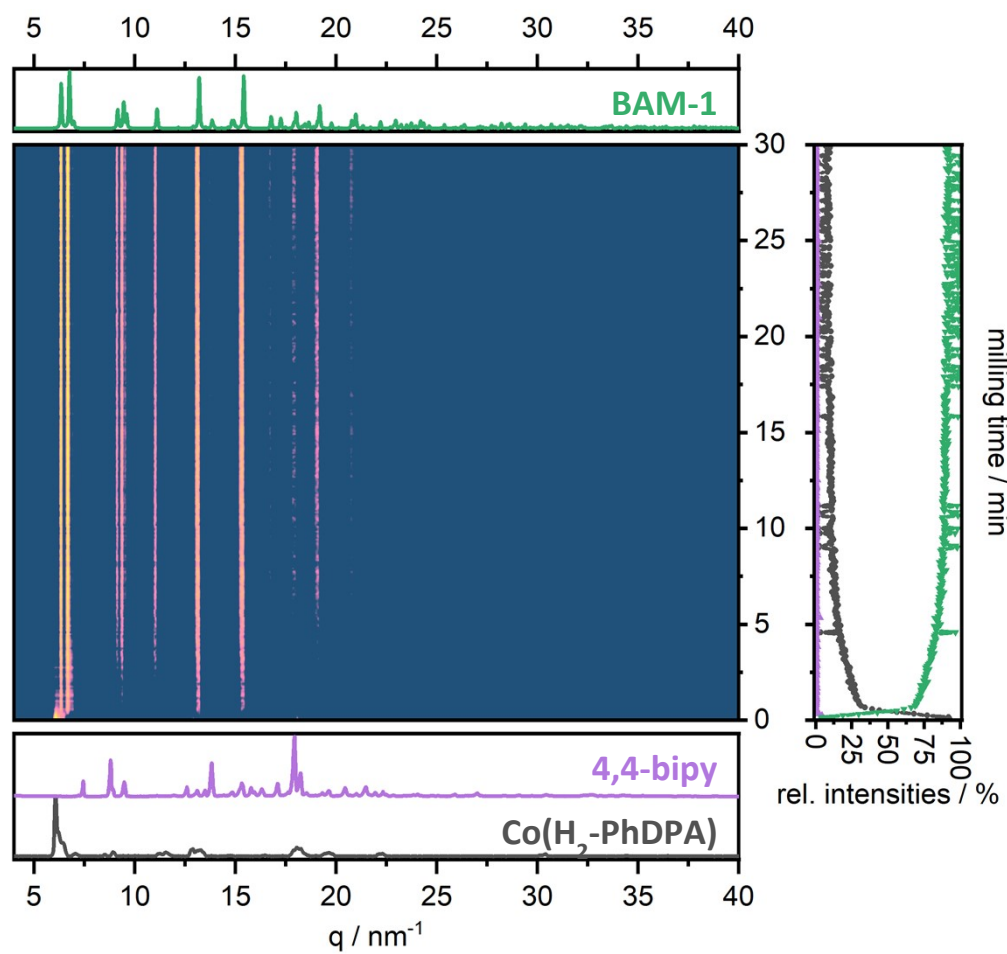


**Fig. S7** TRIS PXRD of the mechanochemical reaction II a of BAM-1.

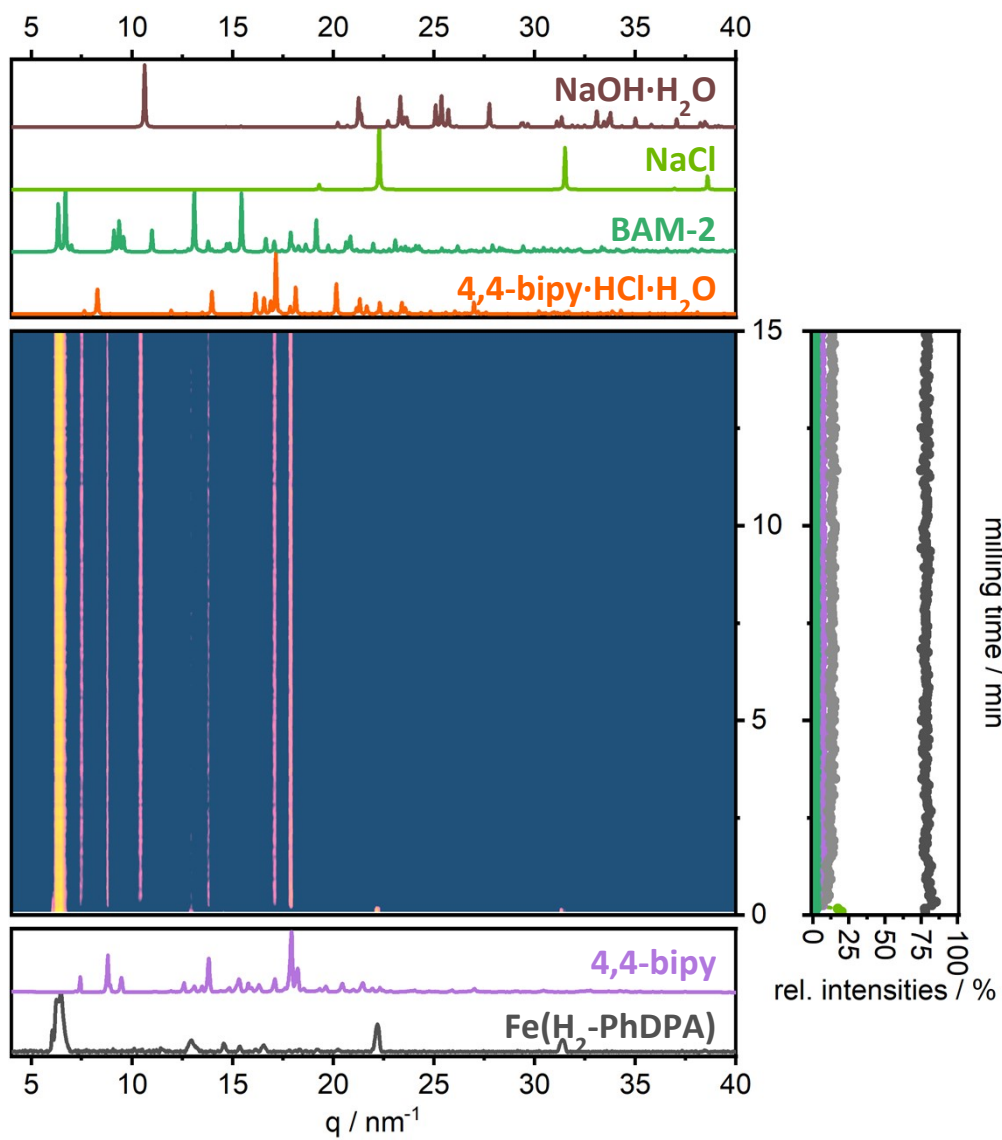


**Fig. S8** TRIS PXRD of the mechanochemical reaction II a of BAM-2. The starting material  $\text{NaHCO}_3$  was omitted due to not being visible during milling.

## Reactions II b



**Fig. S9** TRIS PXRD of the mechanochemical reaction II b of BAM-1.



**Fig. S10** TRIS PXRD of the mechanochemical reaction II b of BAM-2.

## **Raman spectroscopy**

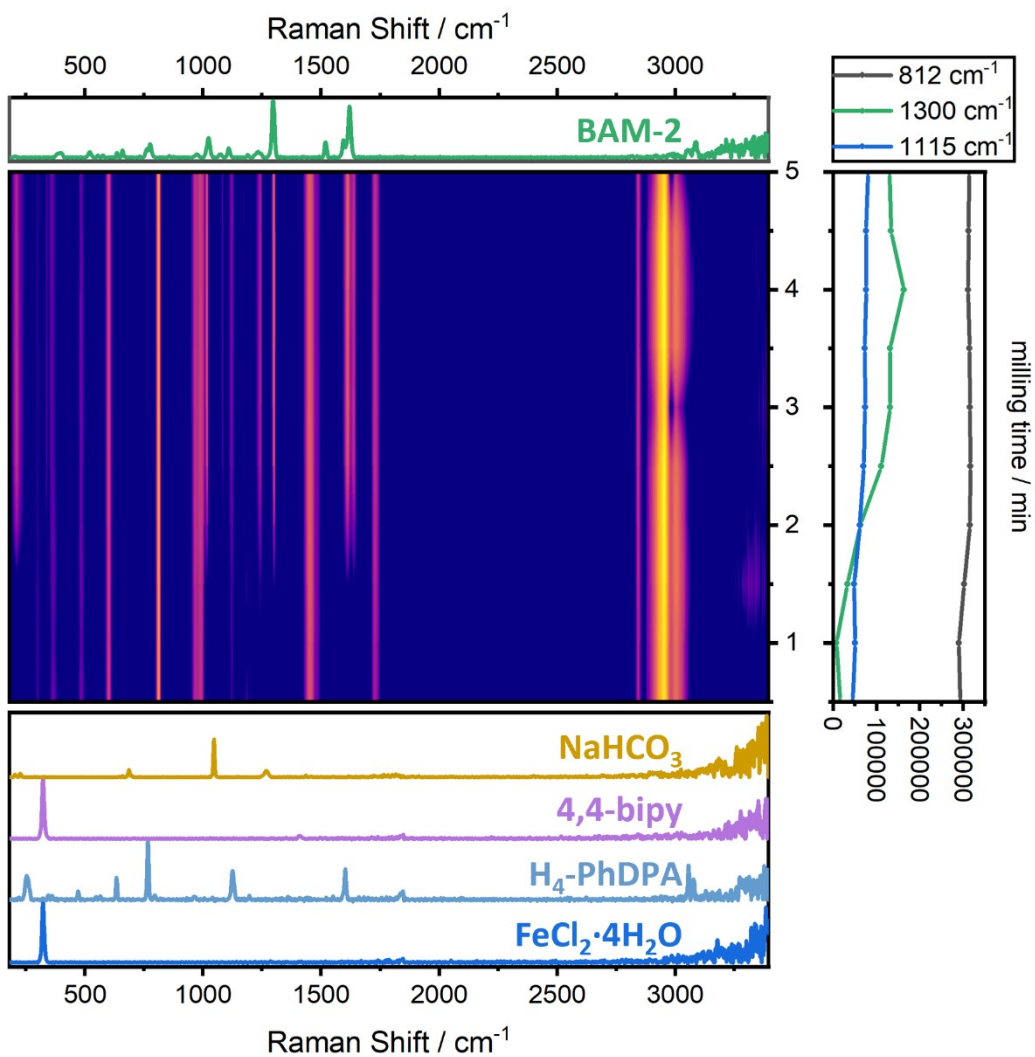
Raman spectra were collected with a RAMAN RXN1 analyzer (Kaiser Optical systems, France). The non-contact probe was adjusted to a working distance of 6 cm and employed an excitation wavelength of  $\lambda = 785$  nm. A dark scan of 30 s was acquired prior to every measurement, followed by accumulation of five measurements of 5 s acquisition time. *Ex-situ* Raman spectra were taken on CaF<sub>2</sub> discs, while *in-situ* measurements were performed within custom-made Perspex jars.

The band at 812 cm<sup>-1</sup> is present and unchanged in intensity during all five monitored reactions. Its absence in Raman spectra recorded on CaF<sub>2</sub> discs indicates that it belongs to the Perspex jar. A vibration at 1300 cm<sup>-1</sup> arises in reactions where Iron(II) compounds and 4,4'-bipy are present, thus it can be assumed it corresponds to a Fe-N<sub>4,4'-bipy</sub> vibration. Similarly, a vibration at 1115 cm<sup>-1</sup> is visible when Iron(II) and H<sub>2</sub>-PhDPA are co-present in a milling mixture, making it likely belong to a Fe-O<sub>phosphono</sub> vibration.

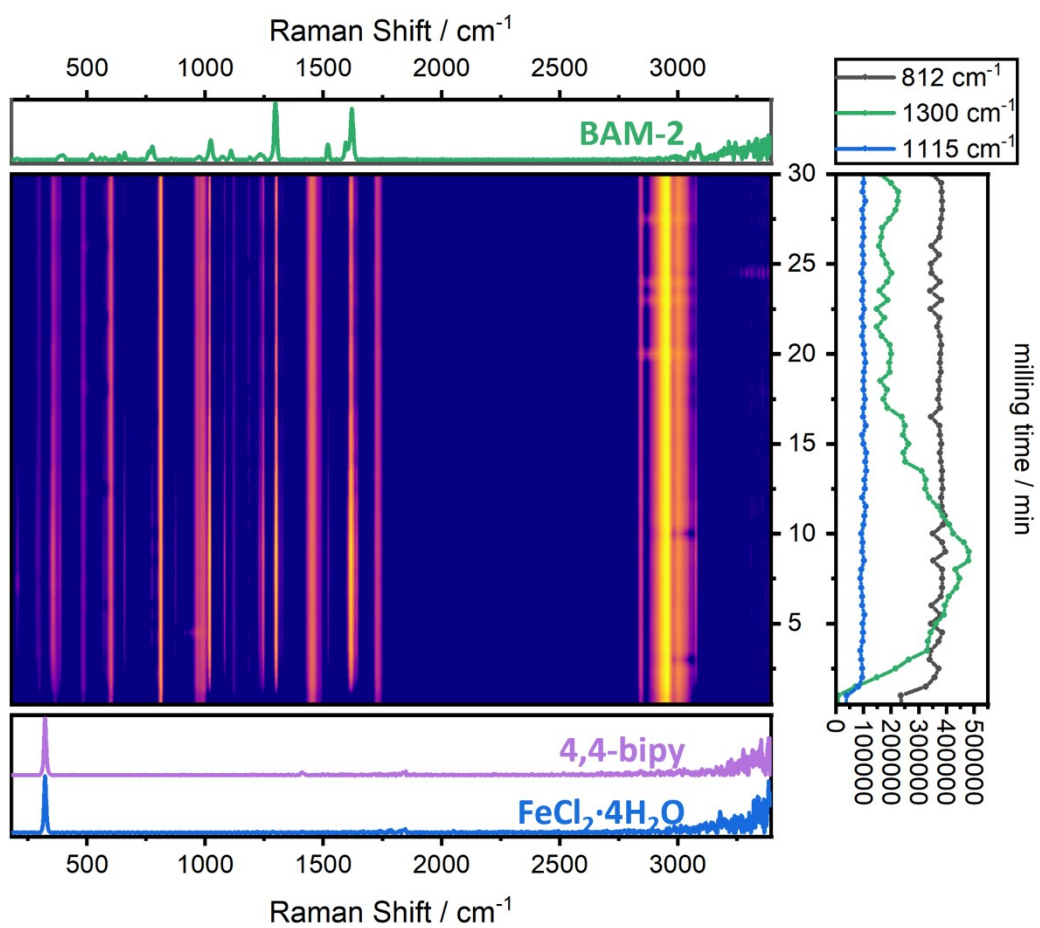
The data suggests the formation of Fe-N<sub>4,4'-bipy</sub> and Fe-O<sub>phosphono</sub> vibrations in the one-pot reactions. Furthermore, during the incremental reactions, the vibration of Fe(II) with the newly added ligand become visible. Thus, TRIS Raman data corroborate the findings from TRIS PXRD data.

A shortcoming of the acquired TRIS Raman data is, it doesn't allow for differentiation of the FeN<sub>4,4'-bipy</sub> source. Thus, BAM-2 and the intermediate FeCl<sub>2</sub>(4,4'-bipy) show the same FeN<sub>4,4'-bipy</sub> vibrations. Although the final Raman spectra of reactions I b, II b and III look similar (Fig. S16a), PXRD reveals the low conversion towards BAM-2 for the reactions II b and III (Fig. S16b).

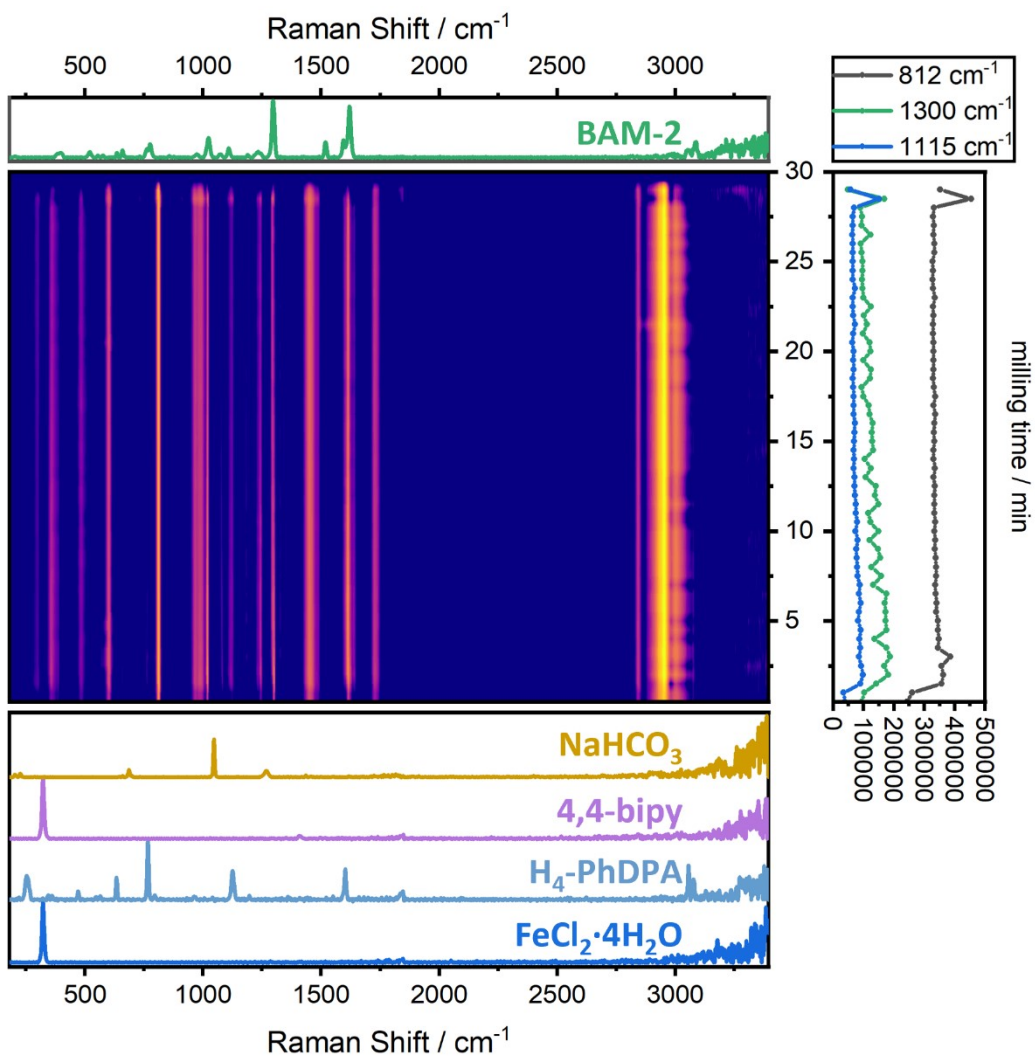
Raman spectra were not recorded for BAM-1 as the Co(OAc)<sub>2</sub>·4H<sub>2</sub>O showed fluorescence that saturated the detector, overlapping any Raman signals.



**Fig. S11:** TRIS Raman spectroscopy of the mechanochemical one pot synthesis (III) of BAM-2.

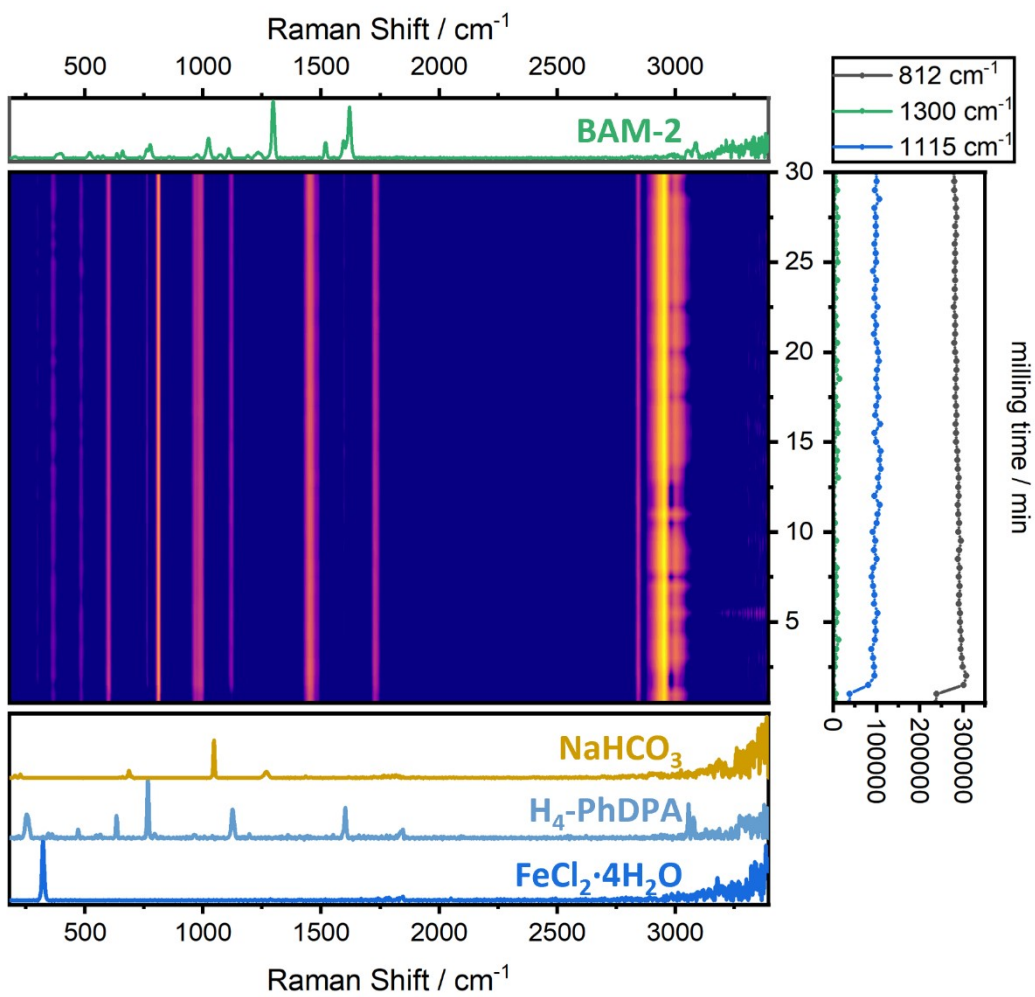


**Fig. S12:** TRIS Raman spectroscopy of the mechanochemical reaction Ia of **BAM-2**.

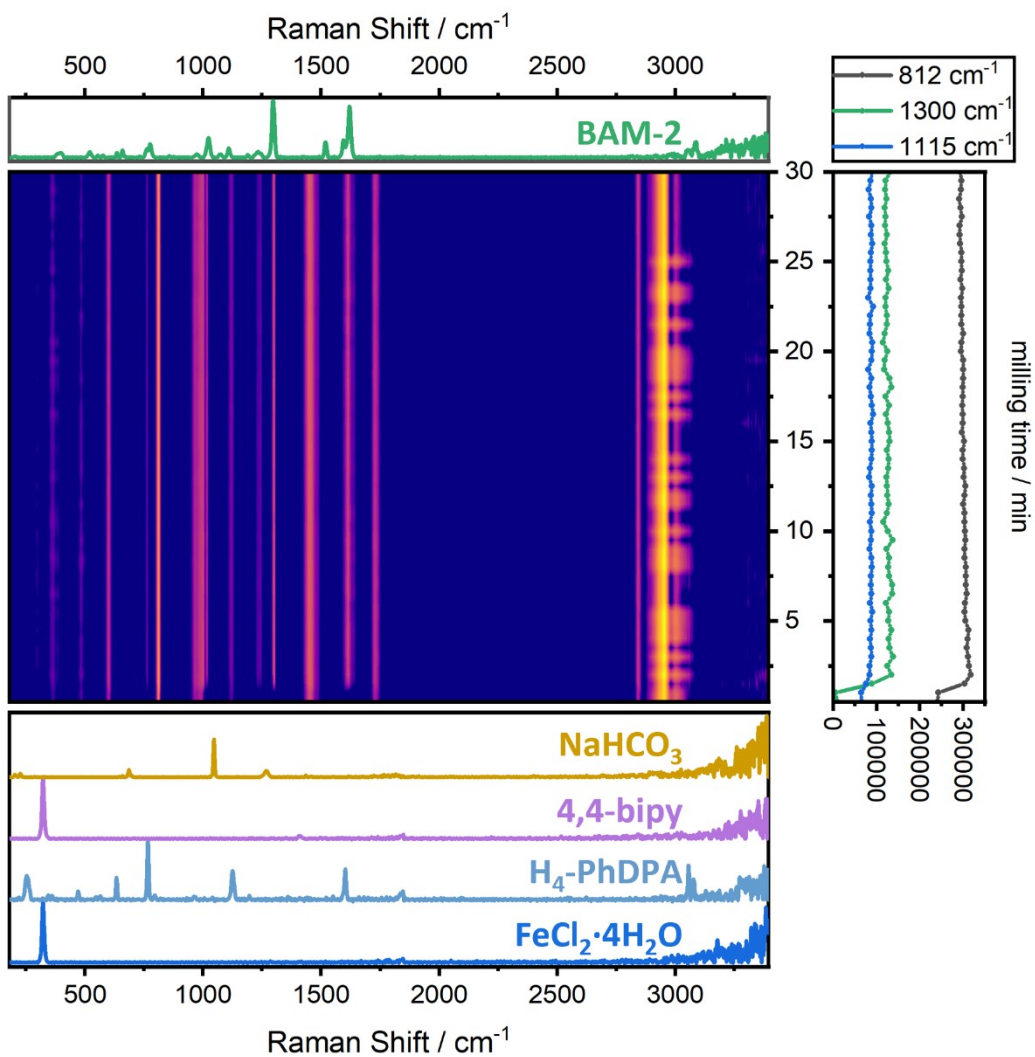


**Fig. S13:** TRIS Raman spectroscopy of the mechanochemical reaction I b of **BAM-2**.

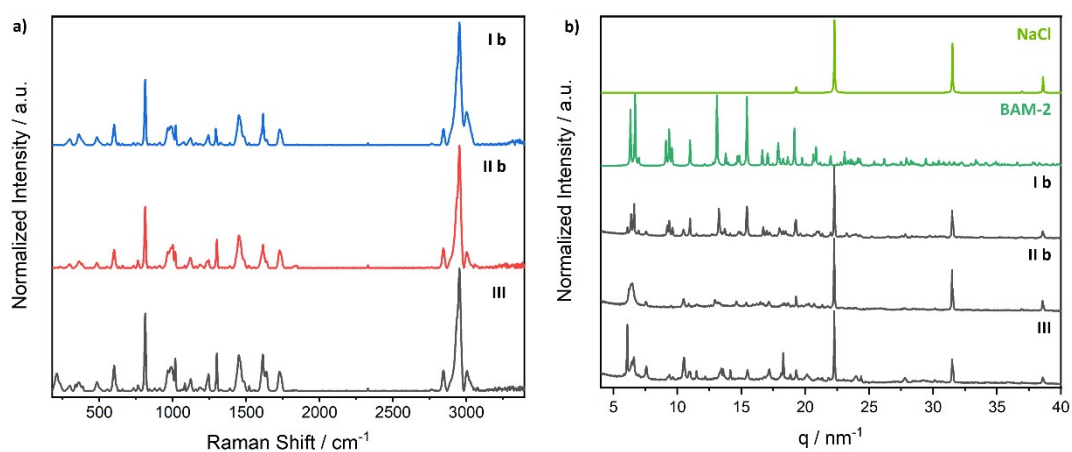




**Fig. S14:** TRIS Raman spectroscopy of the mechanochemical reaction II a of **BAM-2**.



**Fig. S15:** TRIS Raman spectroscopy of the mechanochemical reaction II b of **BAM-2**.



**Fig. S16:** a) Raman spectra and b) XRD of powders received after TRIS Raman monitored reactions.

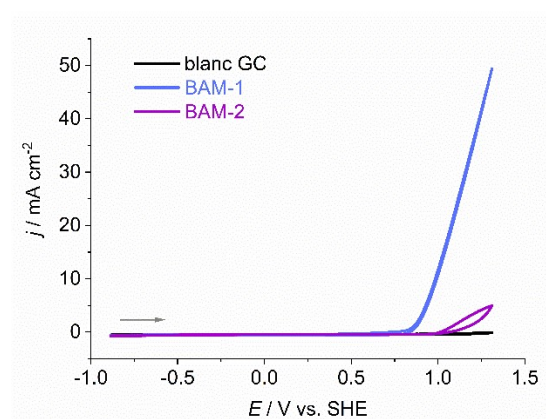
### **Preparation of heterogeneous catalysts and electrochemical characterization**

The ball mill grinded powder samples were loaded on glassy carbon (GC) rotating disk electrode (RDE) using the method described by Garsany *et al.*<sup>37</sup> The method involved initial preparation of a stock solution with 10 mL isopropanol (Sigma Aldrich), 0.2 mL of 5 wt% Nafion ionomer solution (Sigma-Aldrich) and 39.8 mL of deionized water (0.055  $\mu\text{S}/\text{cm}$ , Evoqua, USA). To prepare catalytic inks from the powder samples, 10 mg of **BAM-1** and **BAM-2** were mixed with 10 mL of the stock solution. The inks were stored for 30 min in an ultrasonic bath at 80 Hz. Afterward, the dispersion (10  $\mu\text{L}$ ) was deposited on a clean GC electrode with an area of 0.126  $\text{cm}^2$  and spun at 900 rpm until the liquid was evaporated. Prior to use the GC electrode was polished with 0.3 and 0.05 mm alumina powder followed by sonicating and rinsing with deionized water (0.055  $\mu\text{S}/\text{cm}$ , Evoqua, USA) after each polishing step for 5 min to remove the alumina and abraded particles.

Electrochemical characterizations of the heterogeneous catalyst powders were conducted using a three-electrode setup at a Gamry Reference 600+ potentiostat (Gamry Instruments, USA). Before each measurement, the electrolyte was degassed for 30 min with nitrogen. All measurements were performed in 0.1 M KOH or in 0.1 M  $\text{H}_2\text{SO}_4$  by using a Pt counter electrode and an Ag/AgCl (3 M NaCl) reference electrode. All potentials were corrected with respect to standard hydrogen electrode (SHE). Cyclic voltammetry (CV) experiments were performed in a potential range of +1.1 V to -1.1 V at a scan rate of 50  $\text{mV s}^{-1}$  while the RDE was kept at constant rotation of 1500 rpm. The overpotential was extracted at a current density of 10  $\text{mA cm}^{-2}$  for sample comparison.

### Performance in OER electrocatalysis

Cobalt and Iron-based phosphonates are reportedly active catalysts for the oxidative water splitting. Thus, we examined **BAM-1** and **BAM-2** as electrocatalysts towards the oxygen evolution reaction (OER). The electrocatalytic performance of **BAM-1** and **BAM-2** was studied by cyclic voltammetry (CV) in N<sub>2</sub>-saturated 0.1 M KOH (Fig. S17) using a glassy carbon (GC) rotating disc electrode (RDE). Additionally, a blank GC electrode was used as reference surface (Fig. S17, black line). In alkaline conditions **BAM-2** shows a low activity for OER with an onset potential of 0.96 V (Fig. S17, blue line). On the contrary, **BAM-1** shows a low onset potential of 0.80 V vs SHE for the OER electrocatalysis (Fig. S17, purple line).



**Fig. S17:** Electrochemical characterization of BAM-1 and BAM-2 immobilized on a RDE by cyclic voltammetry in 0.1 M KOH.