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Supporting Information

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Thermolysis of a Hybrid Organic-Inorganic Supramolecular Coordination Assembly: Templating the Formation of Nanostructured Fibrous Materials and Carbon-based Microcapsules

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Thermogravimetric Analysis

In the thermogravimetric analysis of **1** can be interpreted as follows. In the temperature range 25–88ºC, seven of the nine water molecules are lost (Weight loss 10.4 %, theor. 11.0 %). Subsequently, between 240ºC and 378ºC there is a weight loss of 9.6 % corresponding approximately to the loss of the remaining water molecules and two molecules of carbon dioxide (theor. 10.8 %). During this event the formation of sodium carbonate is observed as indicated by infrared spectrophotometric and X-ray powder diffraction data. This also suggests the degradation of the organic ligands is commencing. The third step (380–480ºC) in the TGA represents the combustion of the carboniferous materials and leads to a weight loss of 27.5 % corresponding to the destruction of the ligand. A combination of decomposition products were observed by TG-MS including benzene, naphthalene and carbon oxides. All that remains from the original sample is amorphous carbon (approx. 10 wt%), oxides of iron together with three equivalents of Na_2CO_3. Between 480ºC and 600ºC, further carbon dioxide (3.6 % equiv. to one molecule, theor. 3.9 %) is lost from the sample resulting in the formation of a mixture containing 2 equiv. $NaFeO_2$ and 2 equiv. Na_2CO_3 both of which are visible in the X-ray powder diffraction pattern of samples isolated after heating to 600ºC. Finally, completion of the decomposition of sodium carbonate above 800ºC (approx. 8 % weight loss) leads to the formation of the mixed oxide $Na_2O{\cdot}NaFeO_2$.

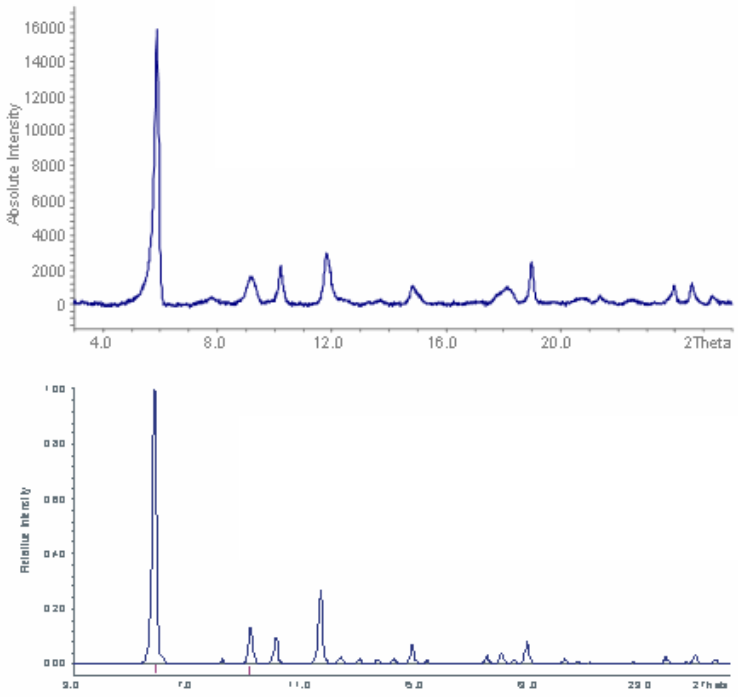


Figure S1. XRD pattern of **1** (top) and pattern generated on the basis of the structural model given Figure 2 (bottom). **1** is isostructural with $K_6[Fe_2(\mu\text{-}O)(\mu\text{-}CO_3)(CHNIDA)_2]\cdot 13.5H_2O$ [11].

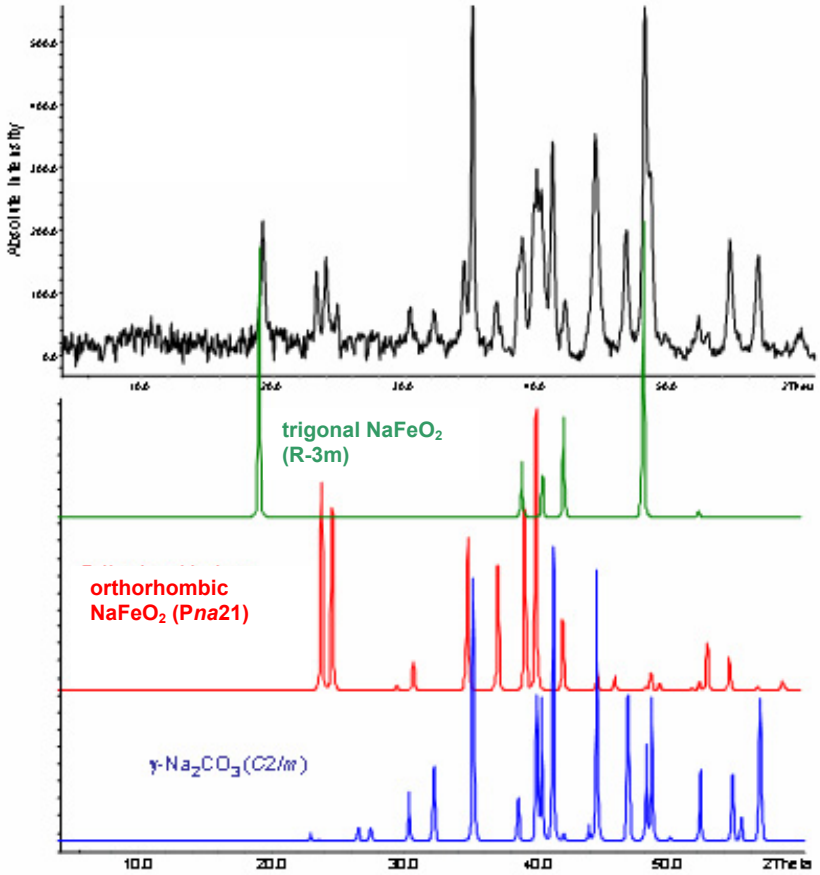


Figure S2. XRD pattern of samples of **1** thermolyzed at 600˚C (top). Identification of components by comparison with generated XRD patterns of trigonal $NaFeO_2$ (green), orthorhombic $NaFeO_2$ (red) and γ-Na_2CO_3.

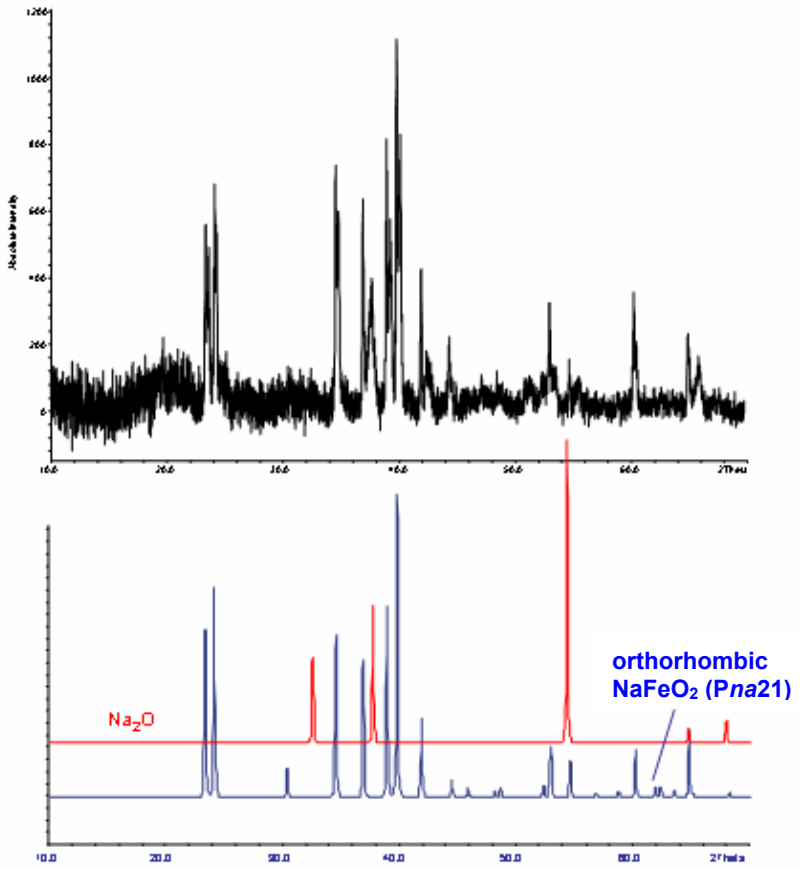


Figure S3. XRD pattern of samples of **1** thermolyzed at 1000˚C (top). Comparison with generated XRD patterns of orthorhombic $NaFeO_2$ (red) and Na_2O (blue).

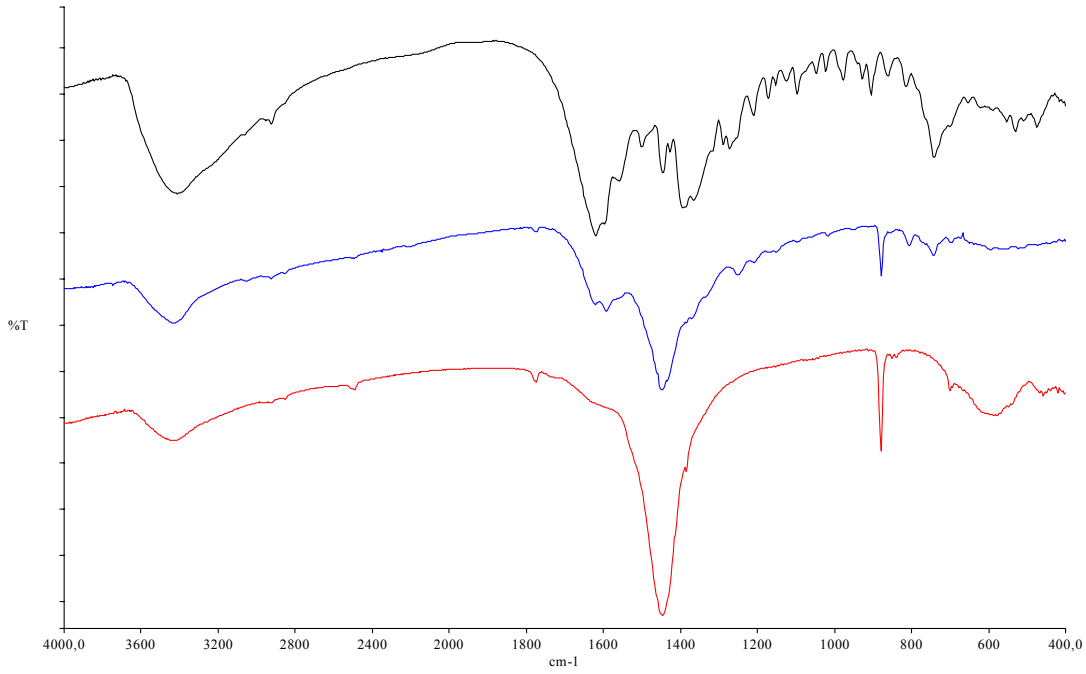


Figure S4. FT-IR spectrum of **1** (top). Comparison with FT-IR spectra of samples of **1** thermolyzed at 350˚C (blue) and 450˚C (red).

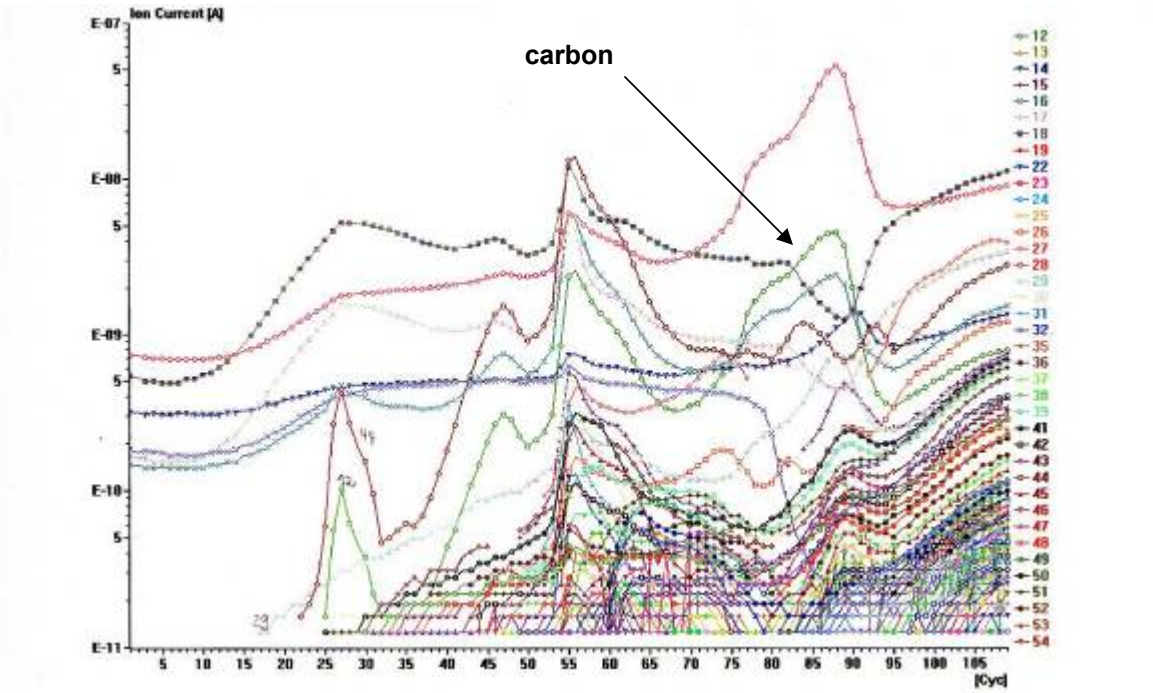


Figure S5. TGA-MS analysis of a sample of **1**. Identified decomposition products with a molecular weight between 12 and 54 g/mol (For time–temperature correlation see Figure S9).

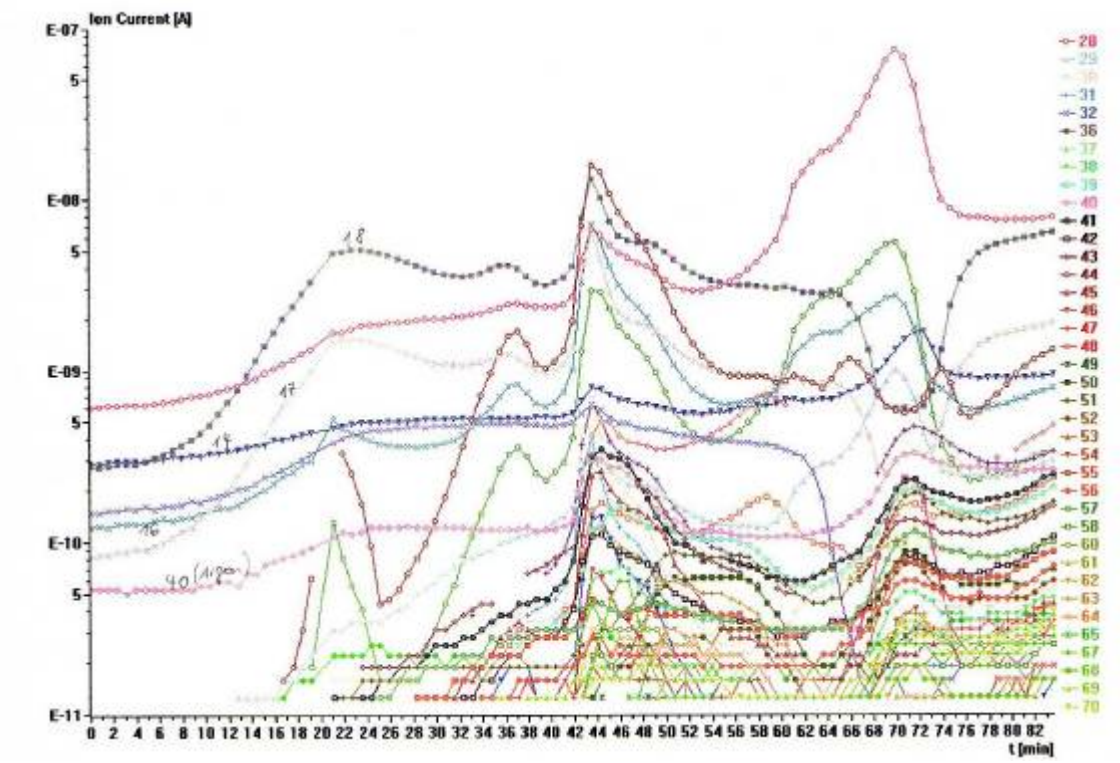


Figure S6. TGA-MS analysis of a sample of **1**. Identified decomposition products with a molecular weight between 28 and 70 g/mol (For time–temperature correlation see Figure S9).

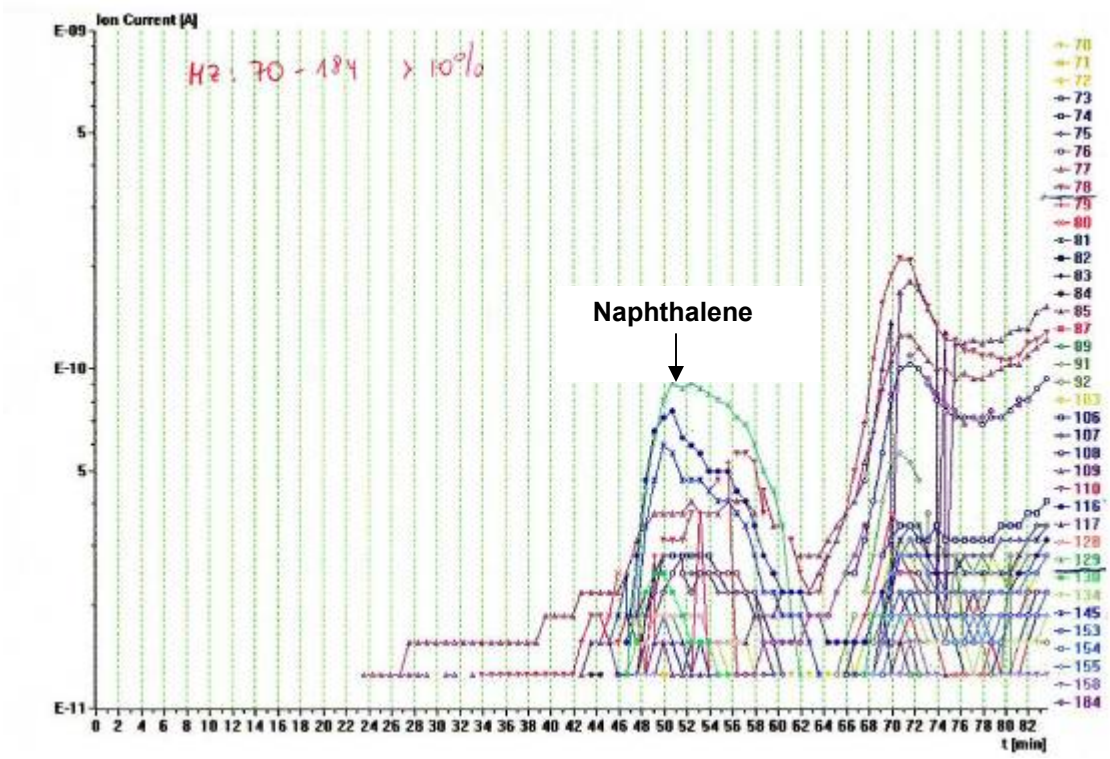
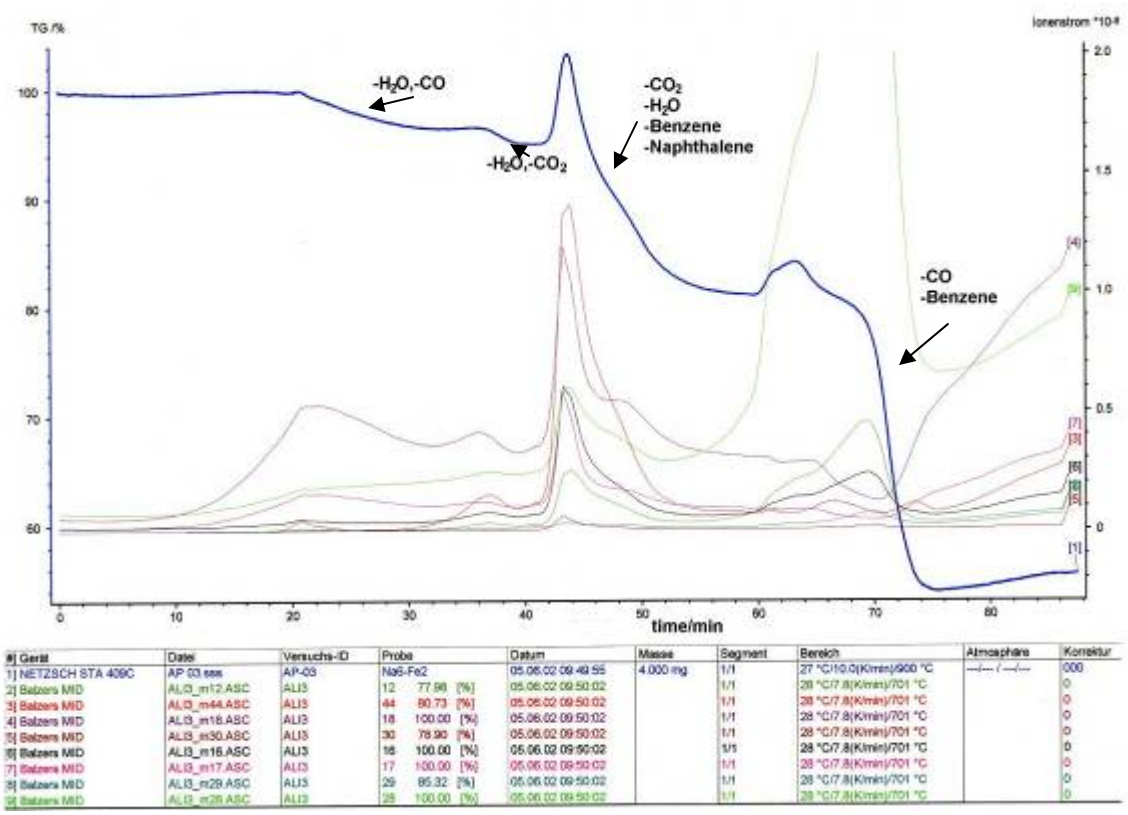


Figure S7. TGA-MS analysis of a sample of **1**. Identified decomposition products with a molecular weight between 70 and 184g/mol. (For time–temperature correlation see Figure S9).



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2]	Balzers MID	ALI3_m12.ASC	ALI3	12 77.98 [%]	05.06.02 09:50:02		1/1	28 °C/7.8(K/min)/701 °C		0
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5]	Balzers MID	ALI3_m30.ASC	ALI3	30 78.90 [%]	05.06.02 09:50:02		1/1	28 °C/7.8(K/min)/701 °C		0
6]	Balzers MID	ALI3_m16.ASC	ALI3	16 100.00 [%]	05.06.02 09:50:02		1/1	28 °C/7.8(K/min)/701 °C		0
7]	Balzers MID	ALI3_m17.ASC	ALI3	17 100.00 [%]	05.06.02 09:50:02		1/1	28 °C/7.8(K/min)/701 °C		0
8]	Balzers MID	ALI3_m29.ASC	ALI3	29 85.32 [%]	05.06.02 09:50:02		1/1	28 °C/7.8(K/min)/701 °C		0
9]	Balzers MID	ALI3_m28.ASC	ALI3	28 100.00 [%]	05.06.02 09:50:02		1/1	28 °C/7.8(K/min)/701 °C		0

Figure S8. TGA-MS analysis of a sample of **1**. Thermogravimetric analysis (blue line) and selected decomposition products.

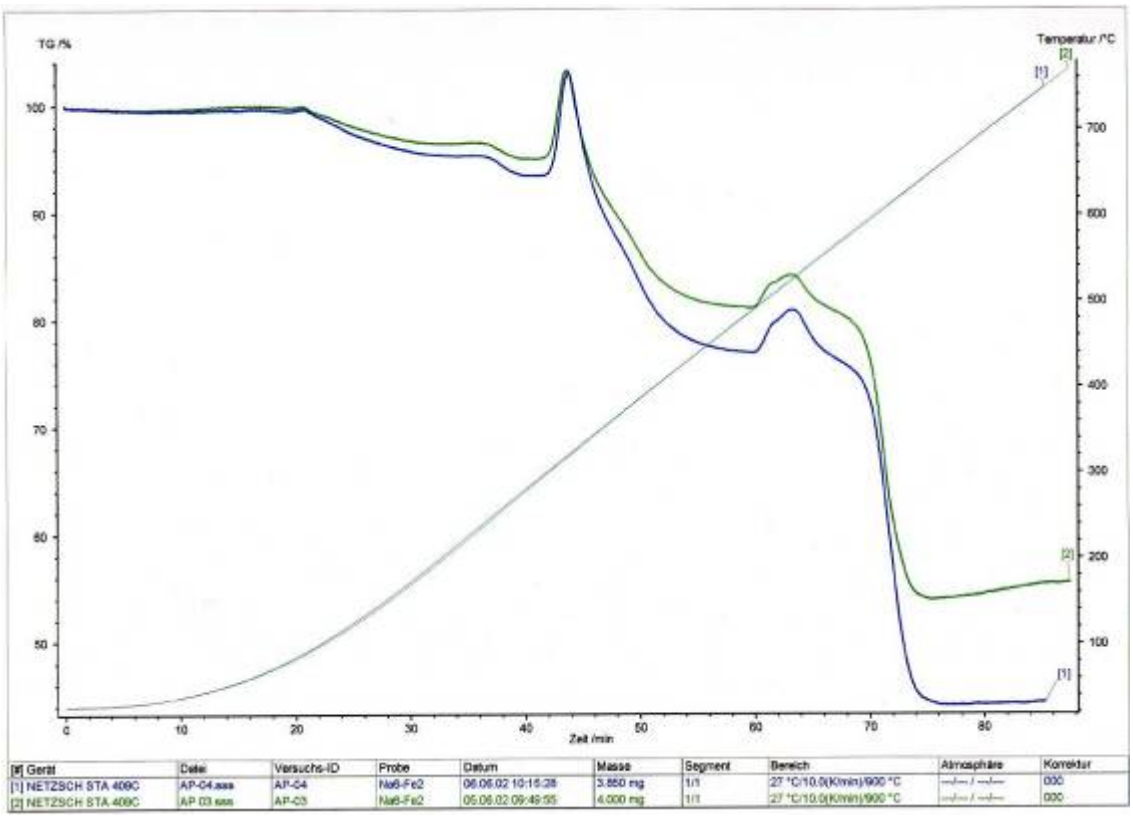

Figure S9. TGA-MS analysis of a sample of **1**. Thermogravimetric analysis and time – temperature correlation for the experiment.

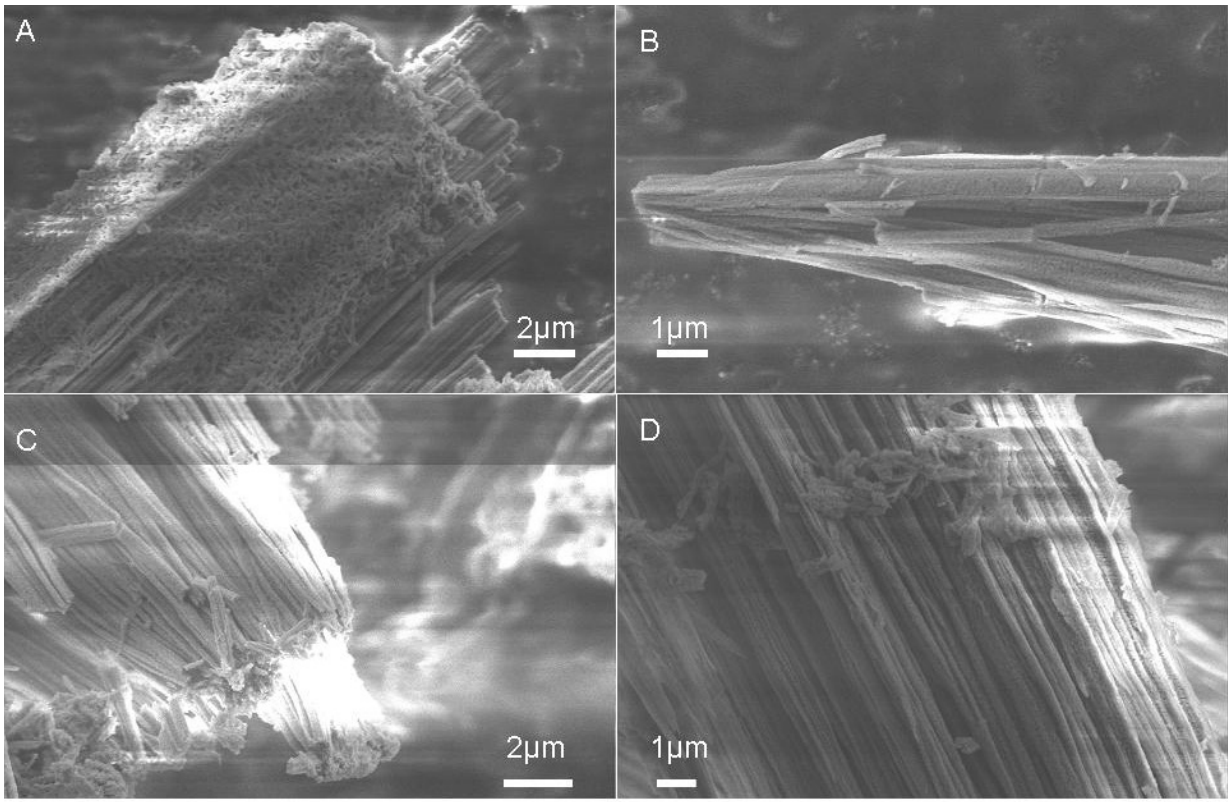

Figure S10. *SEM* micrographs of samples of **1** heated to 250°C. The fibrous material appears less segmented, thicker and often crystalline.

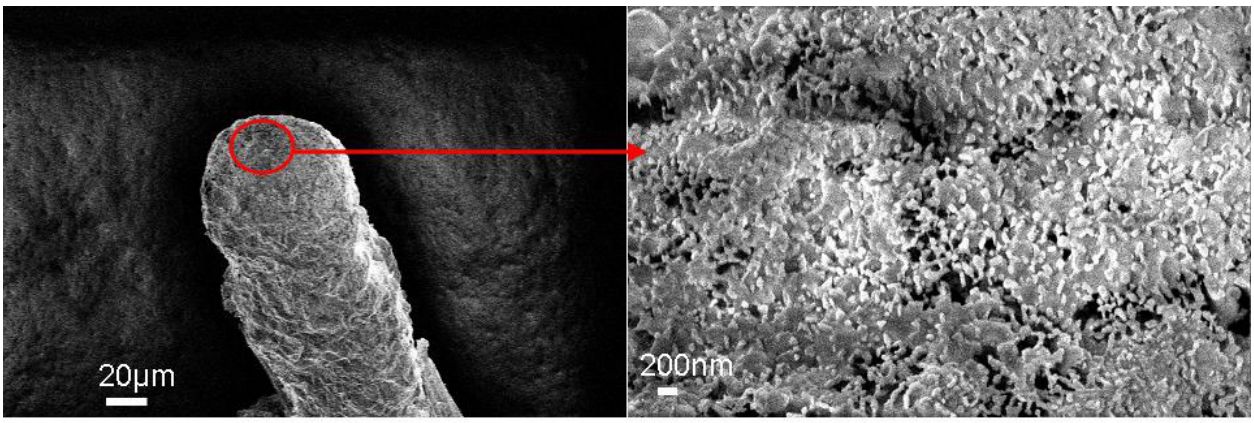

Figure S11. SEM micrographs of a single crystal of **1** heated to 510 °C showing nanosized particulates (EDAX analysis identifies Na, Fe, O) on the surface.