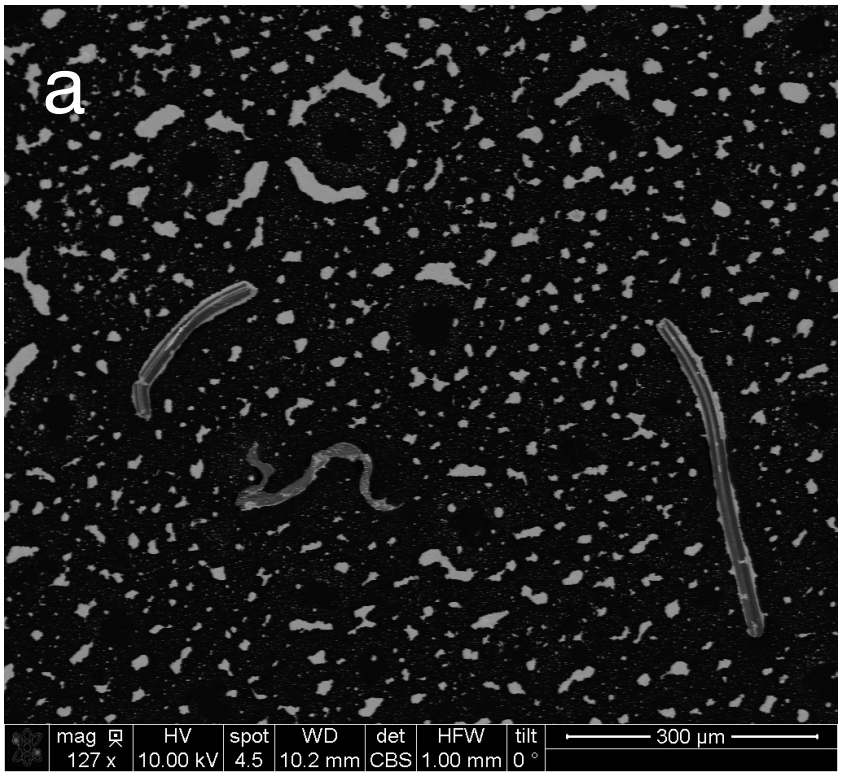
Electronic Supplementary Material (ESI) for Dalton Transactions.

Giant Zirconium-Bisphosphonate Nano-Ribbons and their Liquid Crystalline Phase Behaviour in Water

Dirk Schmelter, Rodolphe Nekui Tagné, Hector Cortes-Sanchez, Jörn Schmedt auf der Günne, Edmund Welter and Horst Hintze-Bruening

Supplementary Information



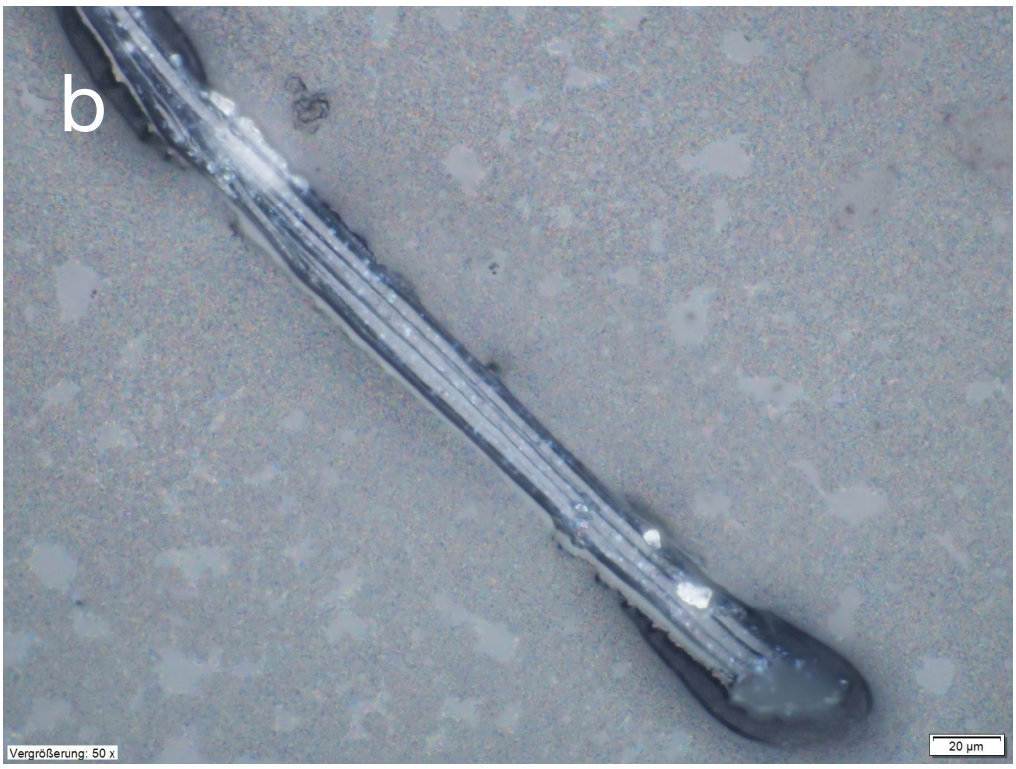


Fig. SI 1: (a) SEM (scale bar 300 microns) and (b) OPM image (scale bar 20 microns) of fibers obtained with hydrothermal synthesis at 120 °C (*Na-2-ht*).

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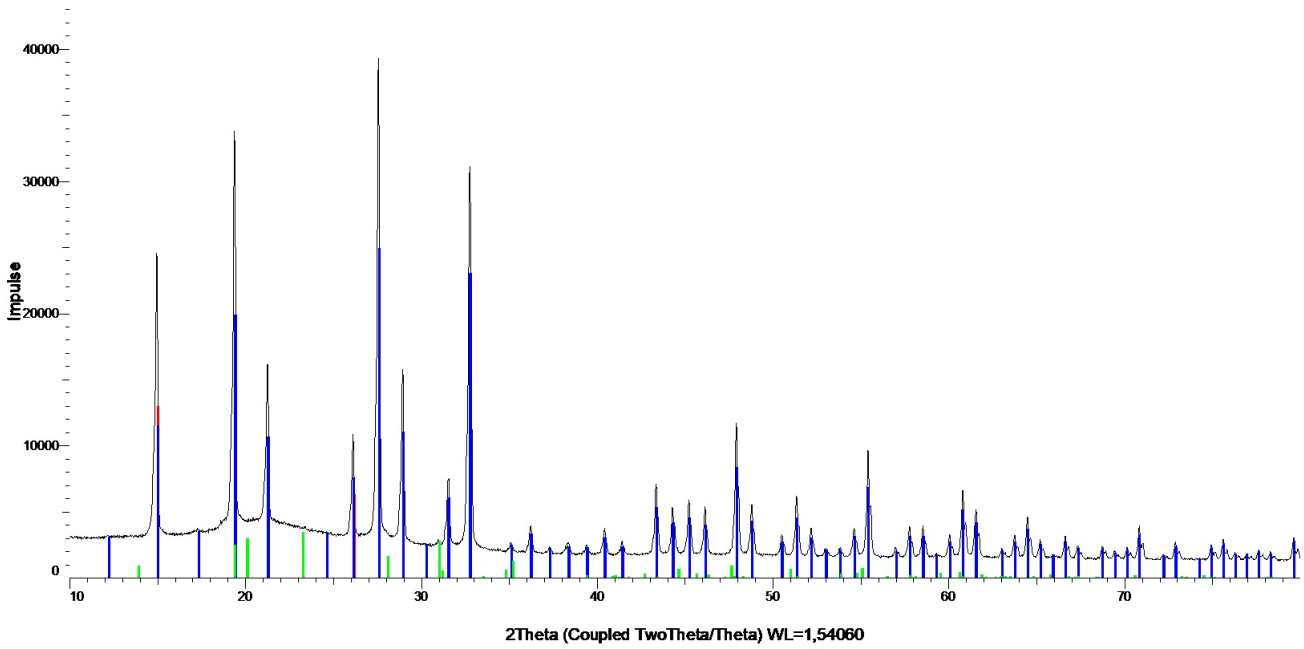


Fig. SI 2: Powder XRD of hydrothermal synthesis product from *Na-2-ht-473*. A good agreement with the reflexes of sodium zirconium phosphate ($NaZr_2(PO_4)_3\,H_2O$) is shown by the blue lines.

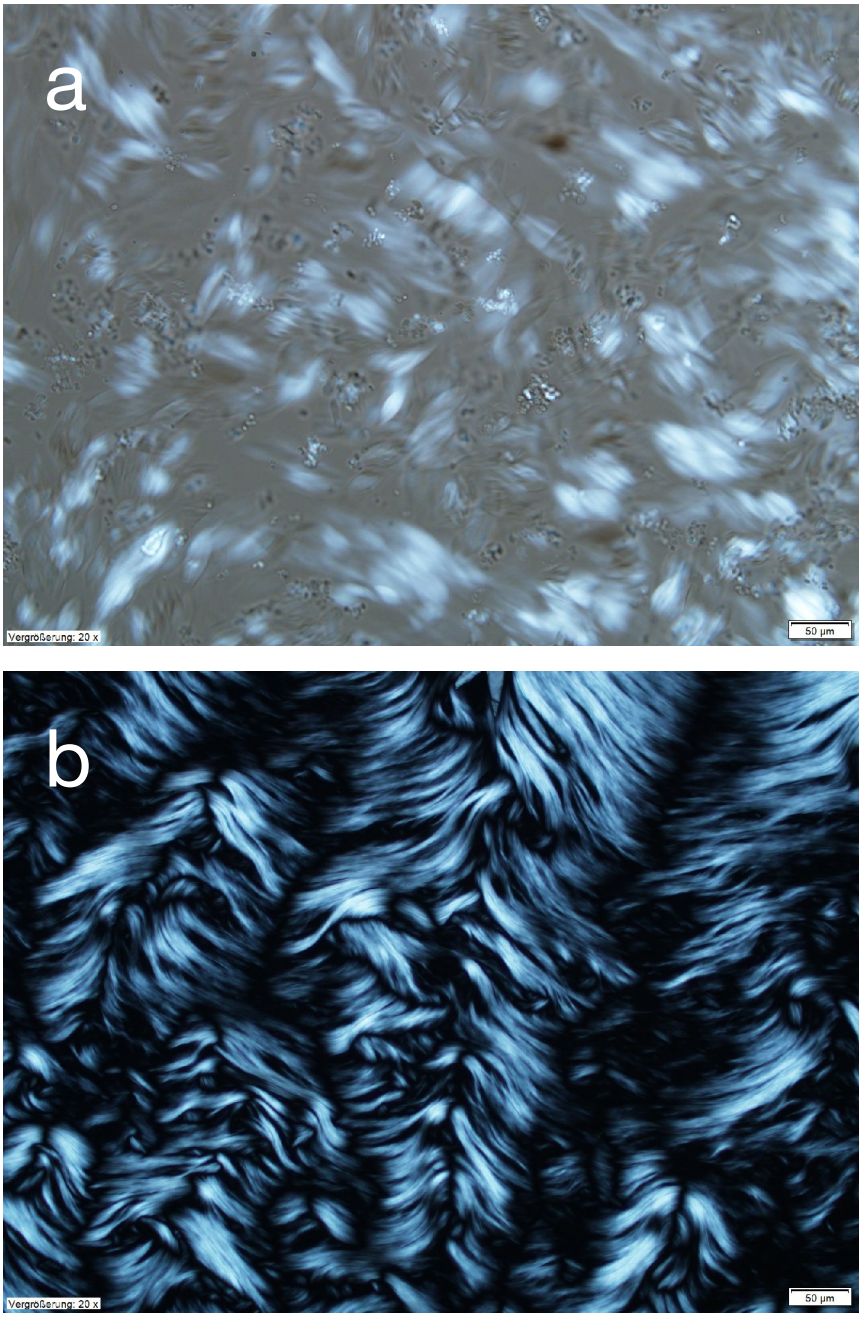
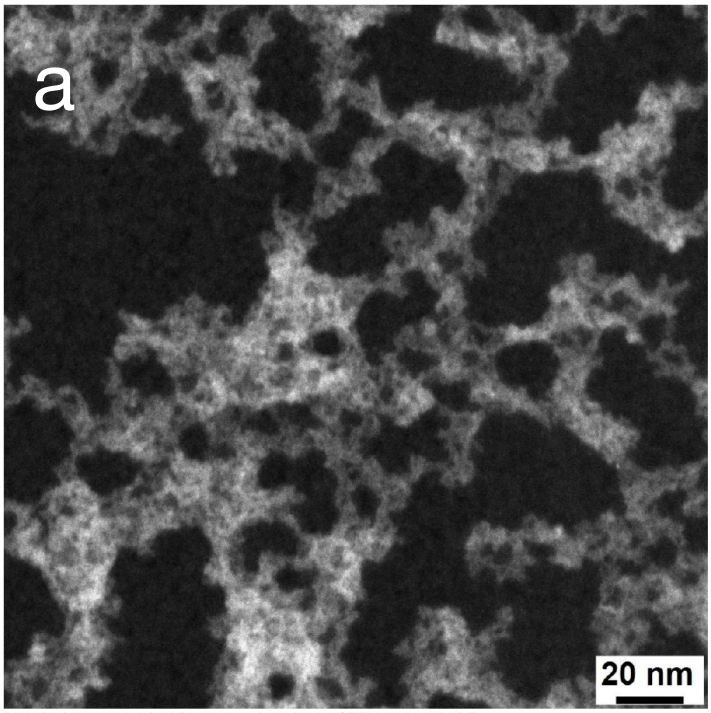


Fig. SI 3: OPM images from dispersions obtained with hydrothermal synthesis of *Li-2-ht* (a) and *A-2-ht* (b), both synthesized at 120 °C. Scale bars are 50 microns.



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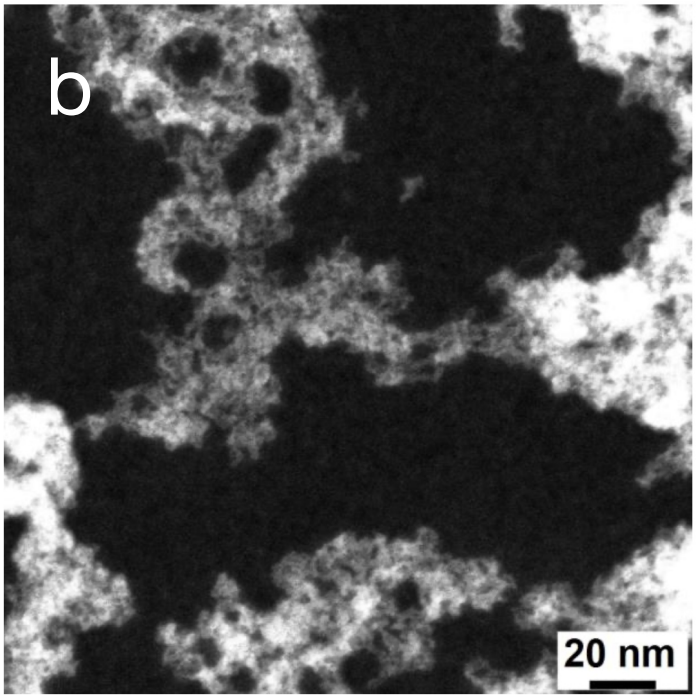

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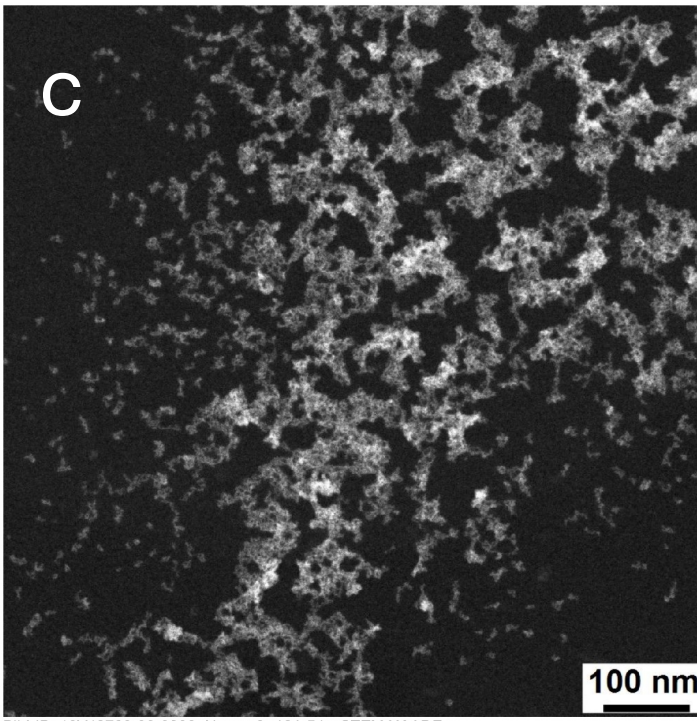

Bild-ID: 19Y42769-03-0008 Name: 3- 121-5 kx STEM HAADF

Fig. SI 4: STEM images from dispersions obtained with hydrothermal synthesis of *K-2-ht* (a), *Li-1-ht* (b) and *A-1-ht* (c), all synthesized at 120 °C.

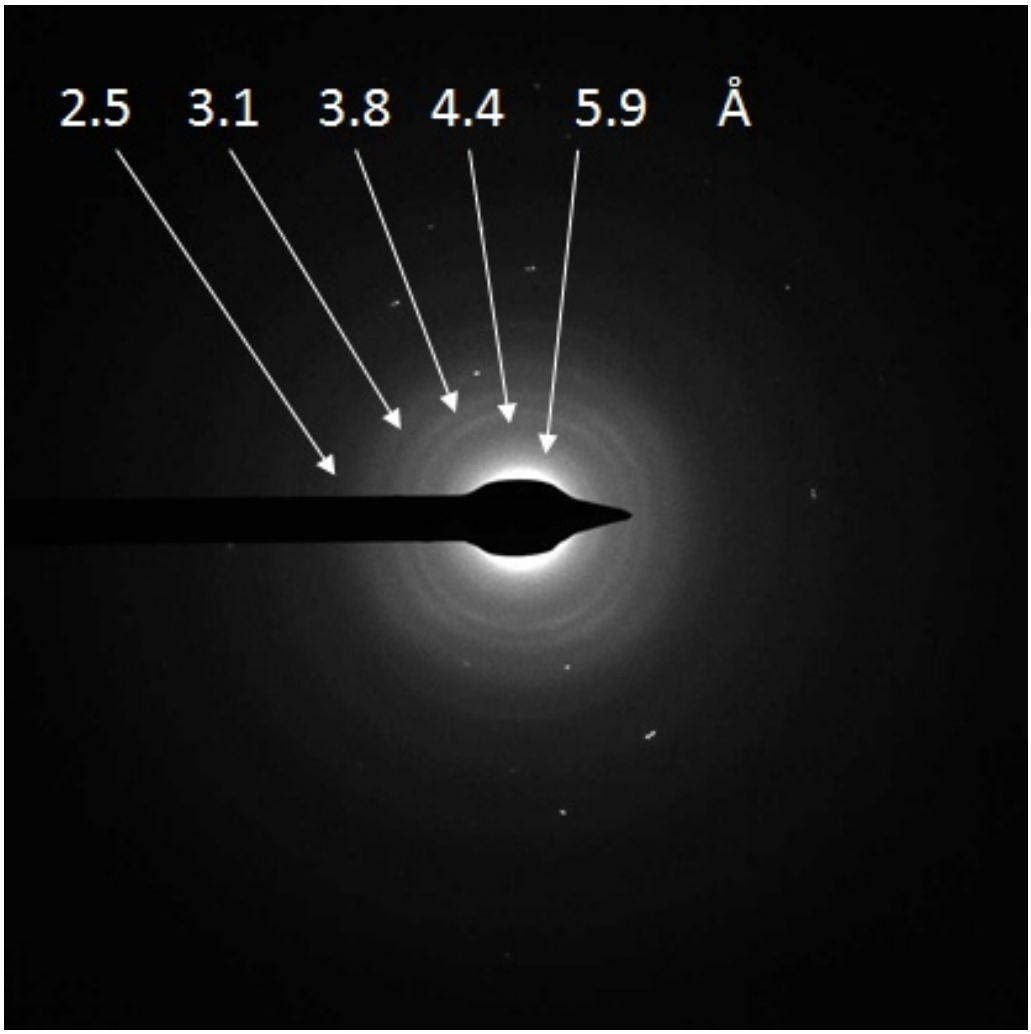

Fig. SI 5: TEM SAD of purified *Na-2* nano-ribbons. Small bright reflexes are from impurities of the sample holder (Cu grid).

Fig. SI 6: Self-supporting film of freeze-dried *Na-2* dispersion.

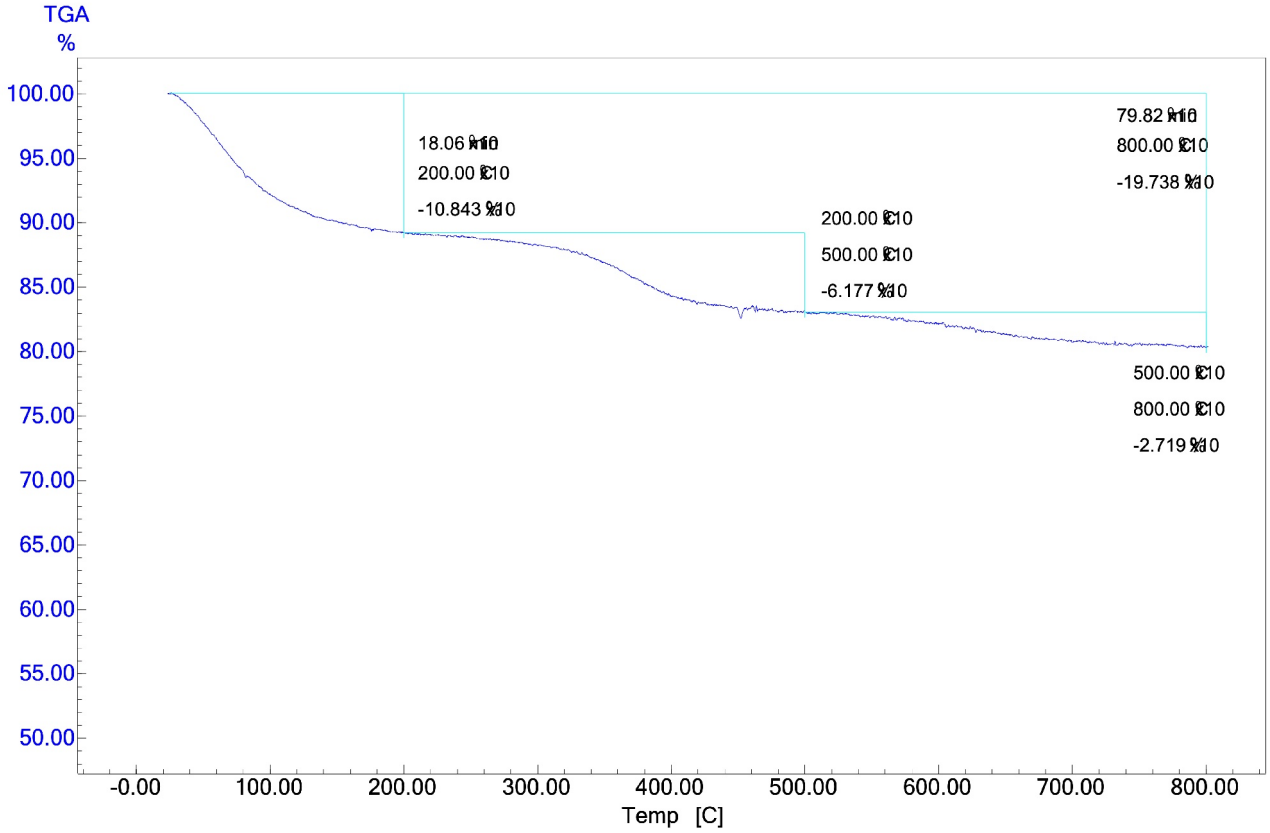

Fig. SI 7: TGA of freeze-dried, TFF-purified *Na-2* dispersion.

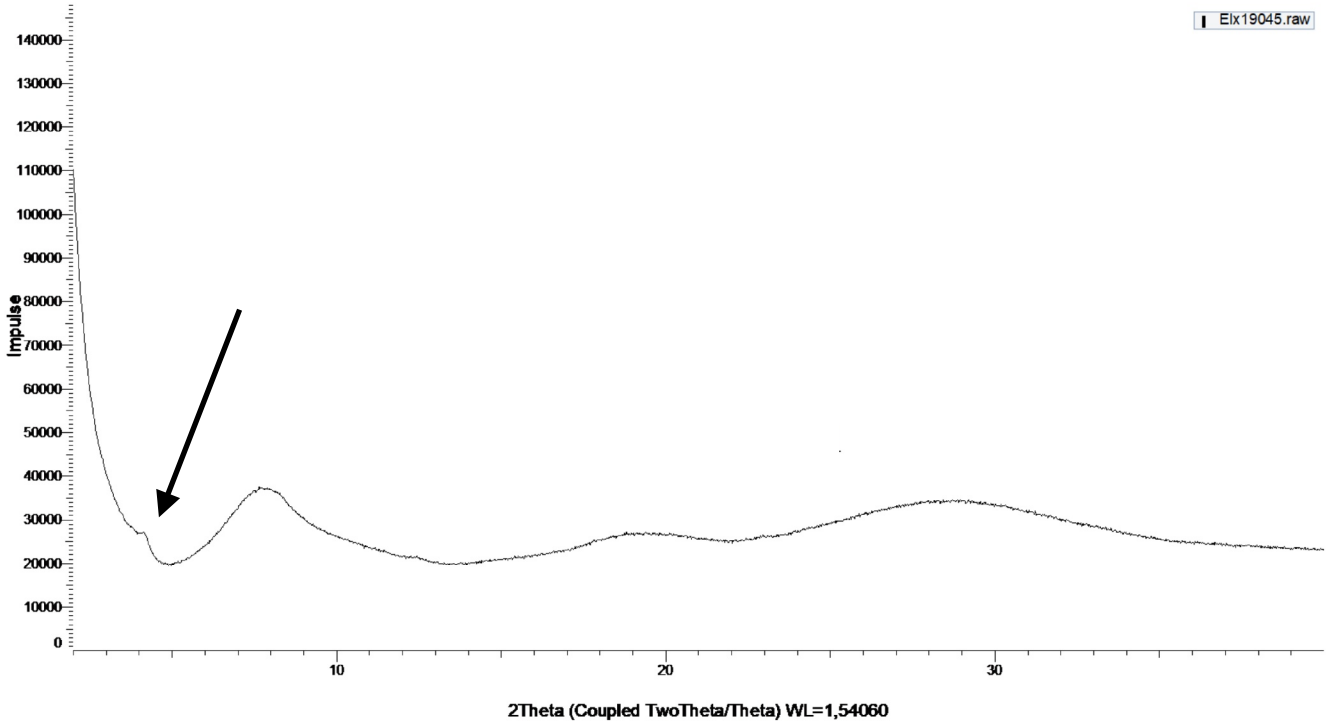

Fig. SI 8: XRD of purified, freeze-dried *Na-2* dispersion. The arrow points to a small hump at *2theta* = 4.2° (*d* = 2.1 nm).

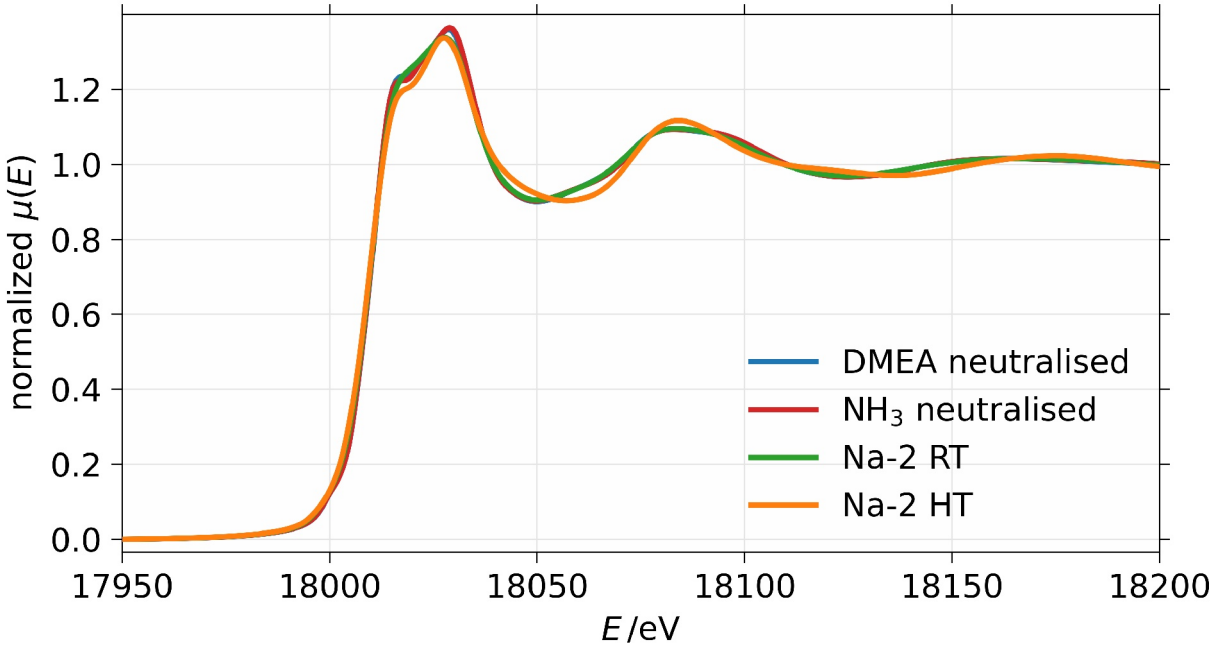

Fig. SI 9a: XANES region recorded in transmission at room temperature of the purified *Na-2* dispersion (Na-2 RT) as well as of its NH_3 and DMEA neutralized derivatives (note: the blue and red curve are congruent). The curve denoted Na-2 HT is obtained from the hydrothermal synthesis product *Na-2-ht-473*, which was identified as $NaZr_2(PO_4)_3xH_2O$ (cf. Fig. SI 2).

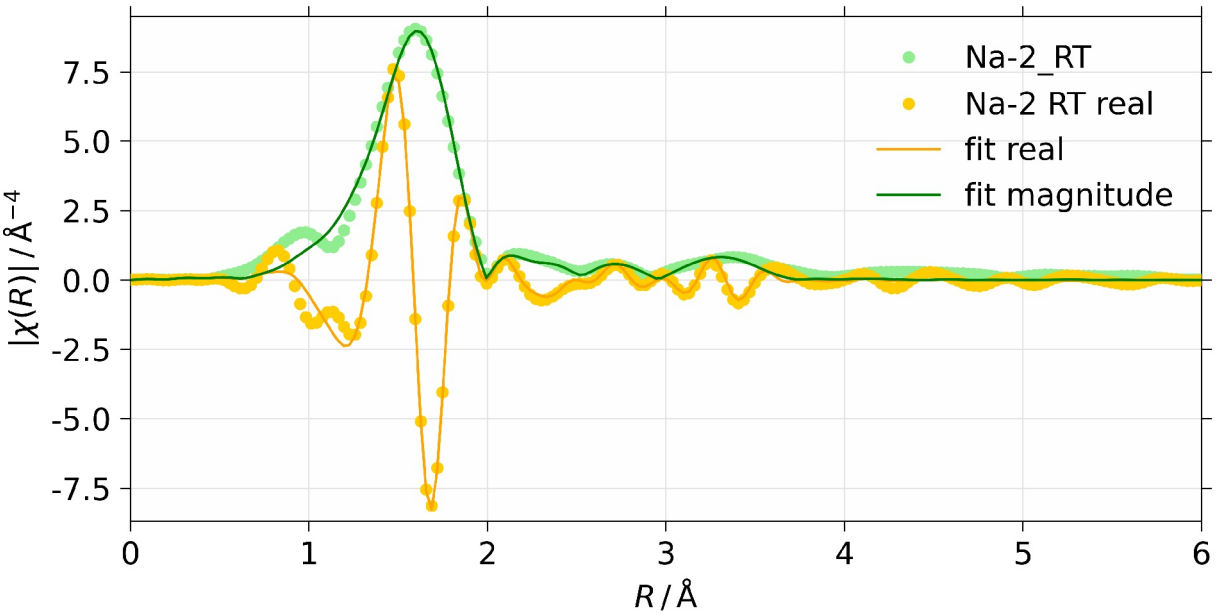

Fig. SI 9b: Overlay of the fitted magnitude and the fitted real part of the Fourier transform data of *Na-2* (Na-2 RT). The structural model is shown in figure SI 10, the fit parameters are listed in table SI 1.

EXAFS fitting

The basic steps of data reduction for the EXAFS fitting were done using the Larch XASviewer.[1] E0 was set to the first maximum of the first derivative at 18011.36 eV, Rbkg was set to 1, the resulting k^3Chi(k) spectrum was Fourier transformed in the k-range between 2.640 $Å^{-1}$ and 13.447 $Å^{-1}$.

EXAFS fits were performed using Artemis from the Demeter software package.[2] The experimental spectrum was fitted in the range of 1.1– 3.7 Å. This results in 17 independent points (Nyquist). Although a number of constraints were made the number of fitted variables was 14 and 12 for the fit of *Na-2* and NH_3 neutralized *Na-2*, respectively, stretching the number of independent data points to the limit.

[1] M. Newville, Larch: An Analysis Package for XAFS and Related Spectroscopies, *Journal of Physics: Conference Series* **430** (2013) 012007
[2] B. Ravel and M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT, *J. Synchr. Rad.* **12** (2005) 537

Fitting model (cf. figure SI 10, tabls SI 1 and table Si 2)

The oxygen atoms in the nearest neighbour shell were divided into two groups, with 7 O-atoms at an initial distance of 2.1504 Å and 1 O-atom at an initial distance of 2.1760 Å. However, only 2 common free parameters one for the distance and one for the mean square radial displacement σ^2 were used in the fit to reduce the number of free variables. Fitting models with 2 or 3 O-atoms at larger distance or with 8 O-atoms all at the same distance yielded inferior results. For the fitting of Na-2 an additional light atom (either oxygen or nitrogen can be used) at a distance of 2.7 Å was included in order to improve the quality of the fit.

One three legged multiple scattering path is included in the fit. To avoid introducing new variables the half path length of this path was calculated from the fitted length of the relevant single scattering paths, the angle between the fitted Zr-O bonds was measured in the original model and used to calculate the O-O distance. The σ2 values of the MS paths were set to fixed reasonable values.

Table SI 1 - Fit Parameter of NH_3 neutralized *Na-2* (cf. figure 9b,c)

Path	**Degeneracy**	**Half path length / Å**	**σ^2 / Å²**	**ΔE_0 / eV**	**S_0^2**	**R-factor**
Zr – O1 – Zr	7	2.093(12)	0.005(1)	-3.2(18)	0.95(15)	0.0082
Zr – O2 – Zr	1	2.261(43)	0.002(3)			
Zr – N – Zr[c]	1	2.787(50)	0.002(5)			
Zr – P – Zr	1	3.665(42)	0.002(3)			
Zr – O3 - Zr	2	3.248(83)	0.010(10)			
Zr – Zr1 – Zr	2	3.573(20)	0.019(20)			
Zr- O1 – O1 - Zr[a]	2	*3.313*	*0.0130*[b]			

[a] Angle O – Zr – O: 71.35°, [b] defined as $3*\sigma^2$(O2), the degeneracy of each path is set to the tabulated value, parameters of multiple scattering paths set in italics are defined using fitted parameters of the involved single scattering paths, [c] the N-atom is not shown in the model shown in figure SI 10.

Table SI 2 - Fit Parameter of *Na-2* (cf. figure SI 9b)

Path	**Degeneracy**	**Half path length / Å**	**σ^2 / Å²**	**ΔE_0 / eV**	**S_0^2**	**R-factor**
Zr – O1 – Zr	7	2.100(11)	0.005(1)	1.8**(**15**)**	1.05(15)	0.0098
Zr – O2 – Zr	1	2.293(45)	0.002(3)			
Zr – P – Zr	1	2.932(48)	0.0011(6)			
Zr – O3 – Zr	2	3.272(20)	0.001(2)			
Zr – Zr1 – Zr	2	3.652(49)	0.015(6)			
Zr – O1 – O1 – Zr[a]	2	*3.419*	*0.015*[b]			

[a] Angle O – Zr – O: 71.35°, [b] defined as $3*\sigma^2$(O2). the degeneracy of each path is set to the tabulated value, parameters of multiple scattering paths set in italics are defined using fitted parameters of the involved single scattering paths,

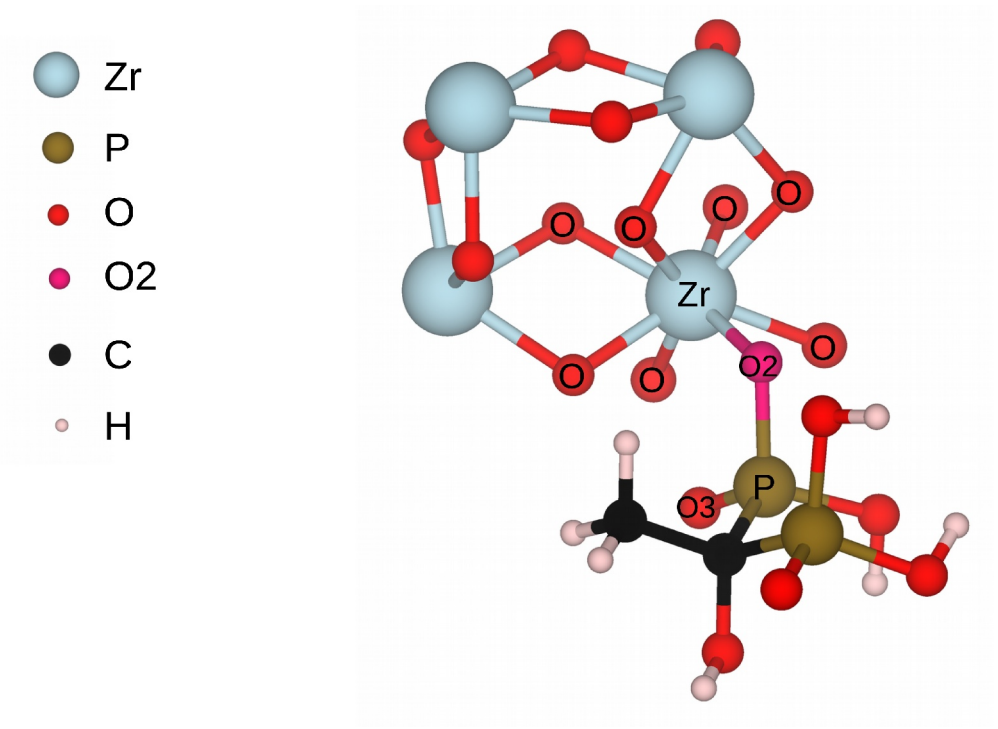

Fig. SI 10: Structural increment of the nano-ribbons: a tetranuclear zirconium cluster with one mono-dentate HEDP attached to each zirconium, only one full coordination being shown for clarity. Since EXAFS is agnostic of more remote parts of the molecule, only atoms with distances < 3.6 Å were included in the EXAFS fitting and labeled in this plot. This model was used for the fitting of the EXAFS data of *Na-2* and of the NH_3 neutralized *Na-2*, respectively. The additional back-scattering light atom (oxygen or nitrogen) at a Zr-O(N) distance of 2.7 Å, which yields better fits of the *Na-2* data is not shown.

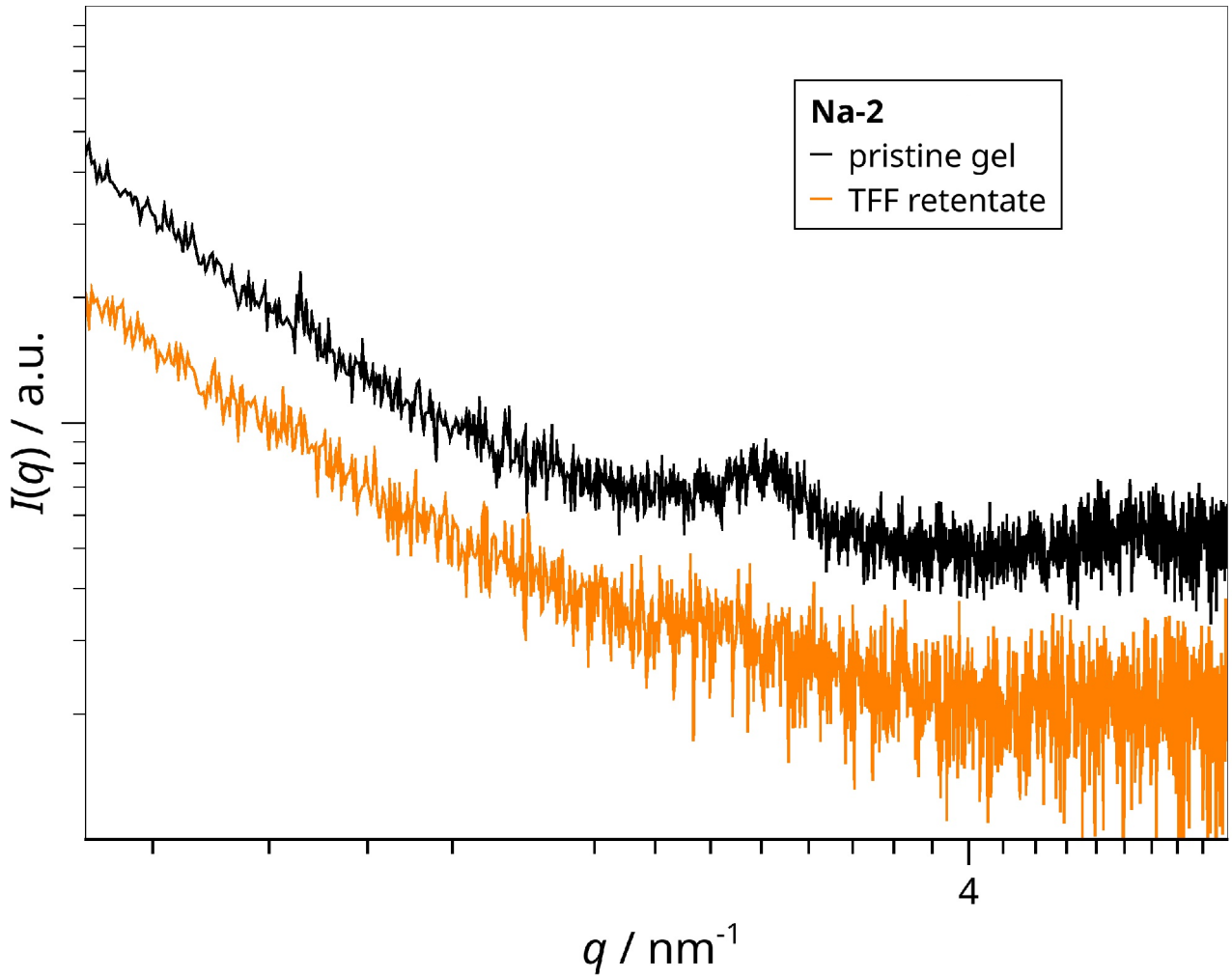

Fig. SI 11: SAXS of diluted pristine gel and of TFF-purified ribbons of *Na-2* measured under flow at the DESY beamline. The zoomed WAXS section shows the peak for d = 2.1 nm^{-1} in the diluted gel. In the curve of the TFF-purified ribbons a broad, very modest intensity hump, slightly shifted to lower q-values might be seen. Nevertheless, XRD of the corresponding freeze-dried dispersion shows that a minor part of the ribbons retained that repeat distance (cf. fig. SI 8). Both dispersions had 1 weight-% solid content.

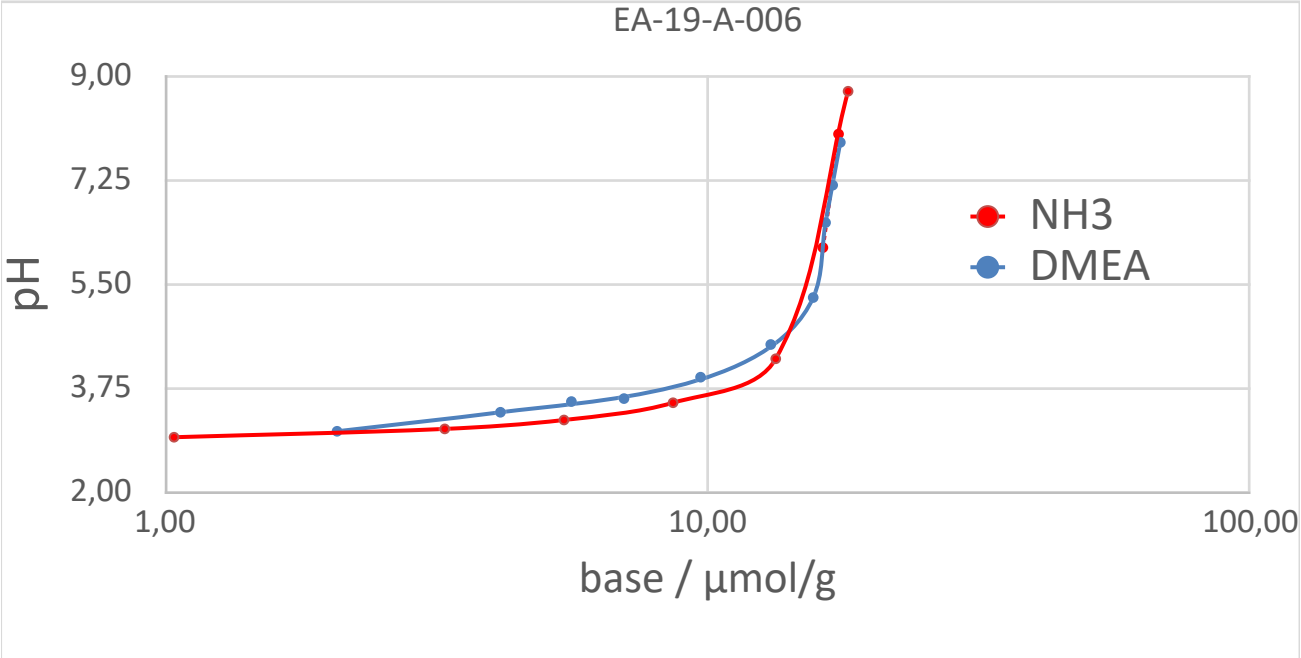

Fig. SI 12: Titration curves for the neutralization of the dispersion with TFF-purified ribbons of *Na-2* with aqueous ammonia and DMEA, respectively.

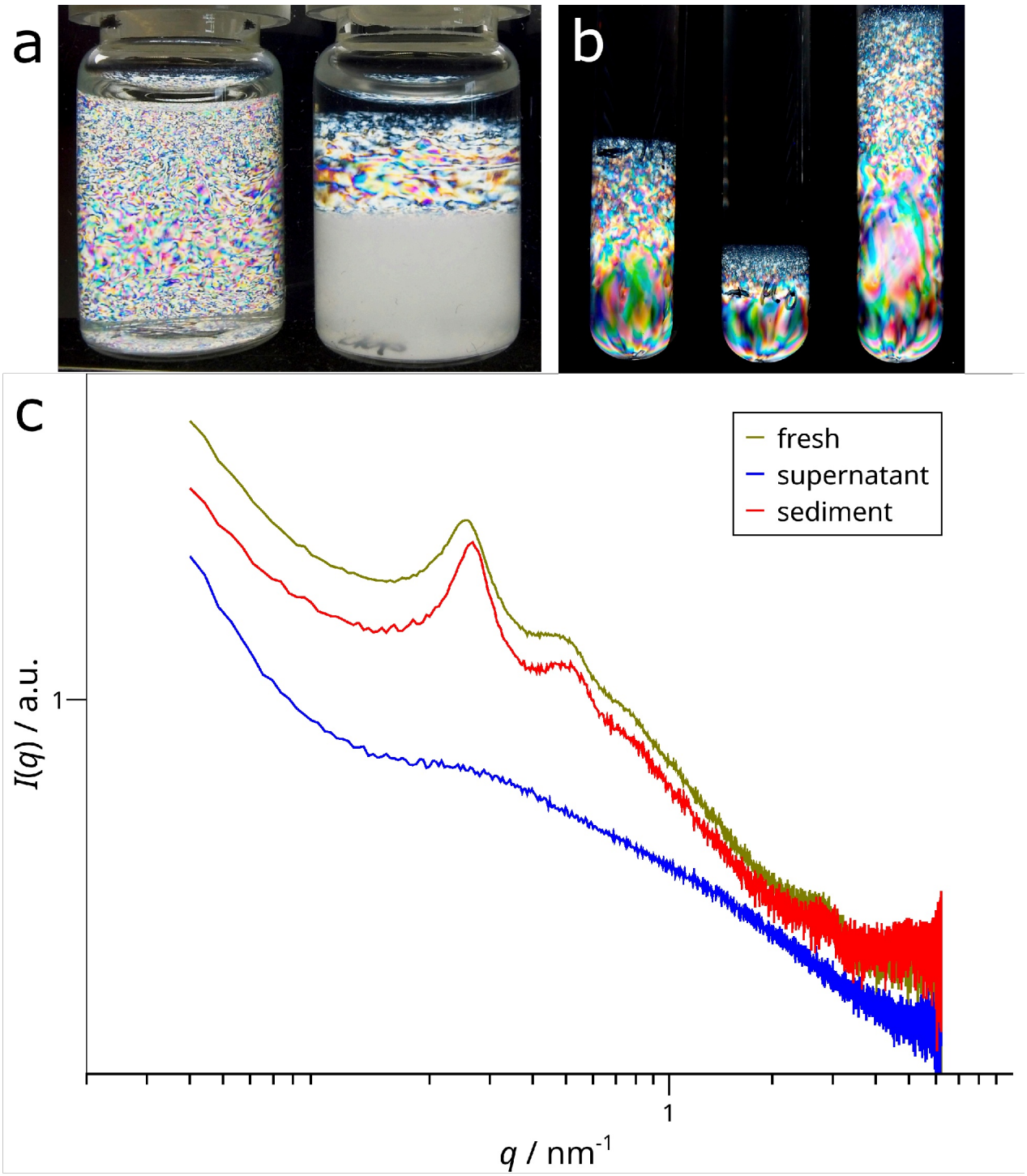

Fig. SI 13: (a) Vials of TFF-purified *Na-2*, neutralized with DMEA (left) and NH_3 (right) to pH 8 and aged for 3 months. (b) TFF-purified *Na-2* after dilution (0.5 weight-%): sediment (left), supernatant (middle), directly after dilution (right). (c) SAXS of TFF-purified *Na-2* (1 weight-%) neutralized with NH_3 to pH 8. Measured under flow at the DESY beamline. Fresh actually denotes an ageing of roughly one week, whereas the supernatant and the sedimented liquid crystalline phase were taken from the three months aged sample.

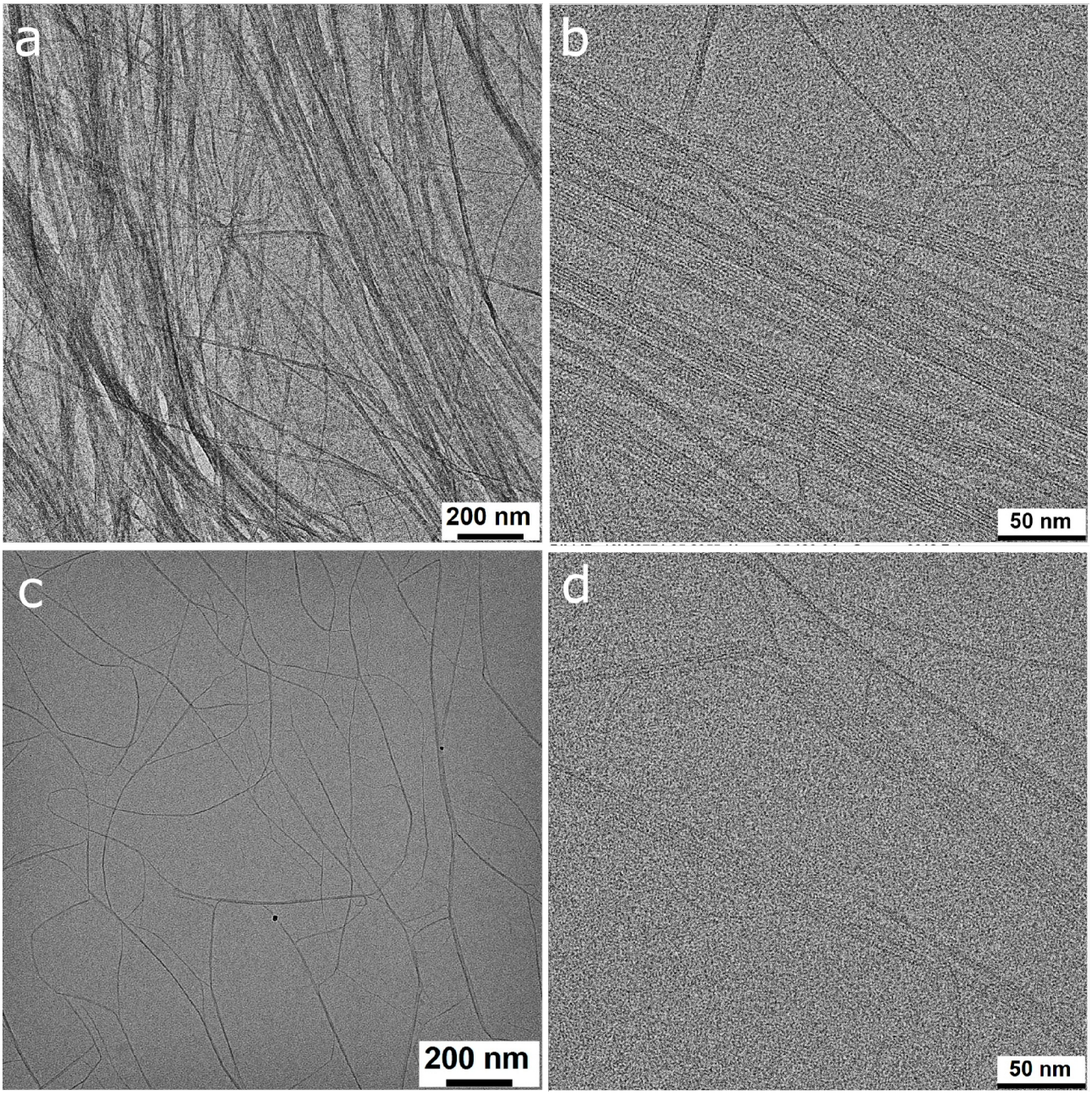

Fig. SI 14: HRTEM brightfield images of dried dispersions of (a, b) NH_3 and (c, d) DMEA neutralized purified *Na-2* ribbons (1 weight-%, pH 8). Scale bars 200 nm (a,c) and 50 nm (b, d). Despite identical sample preparation only few ribbons could be retrieved from the DMEA treated dispersion.

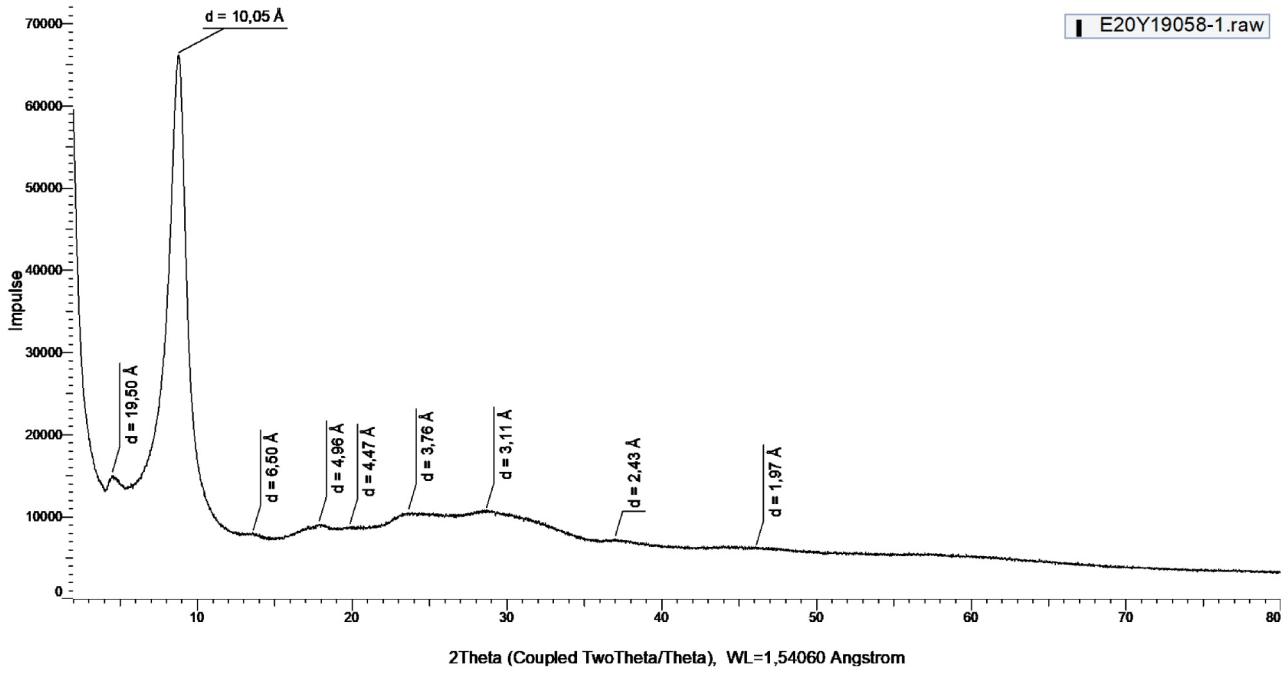

Fig. SI 15: XRD of the dried, NH_3 neutralized dispersion of purified *Na-2*.

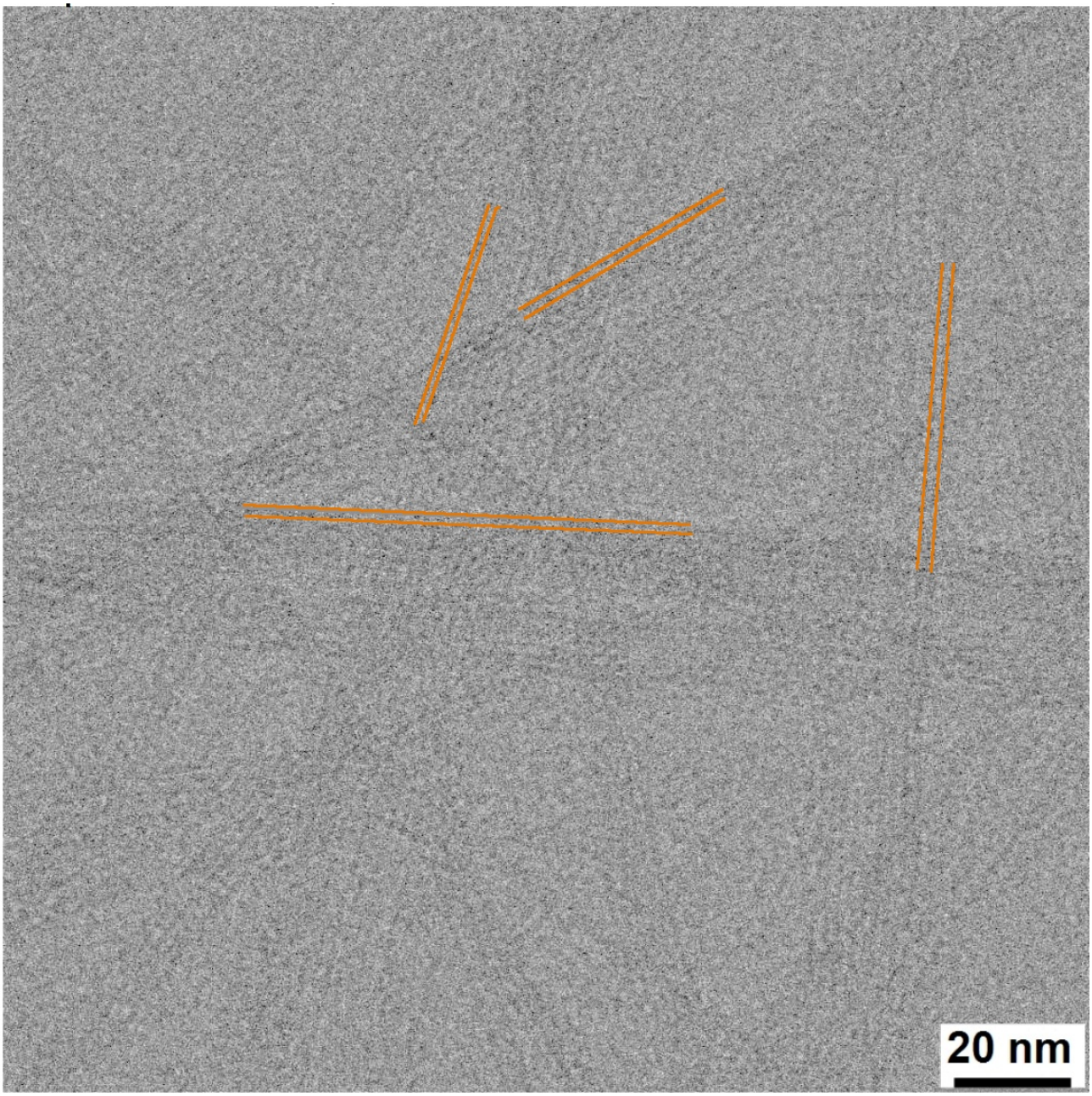

Fig. SI 16: Low dose HRTEM brightfield image of the dried dispersion of NH_3 neutralized purified *Na-2* ribbons (1 weight-%, pH 8) recorded over five seconds using the direct electron detector Falcon in EC mode. Fast Fourier transformation detects a distance of 2 nm. Orange lines highlight some single filaments and are guidance to the eyes.

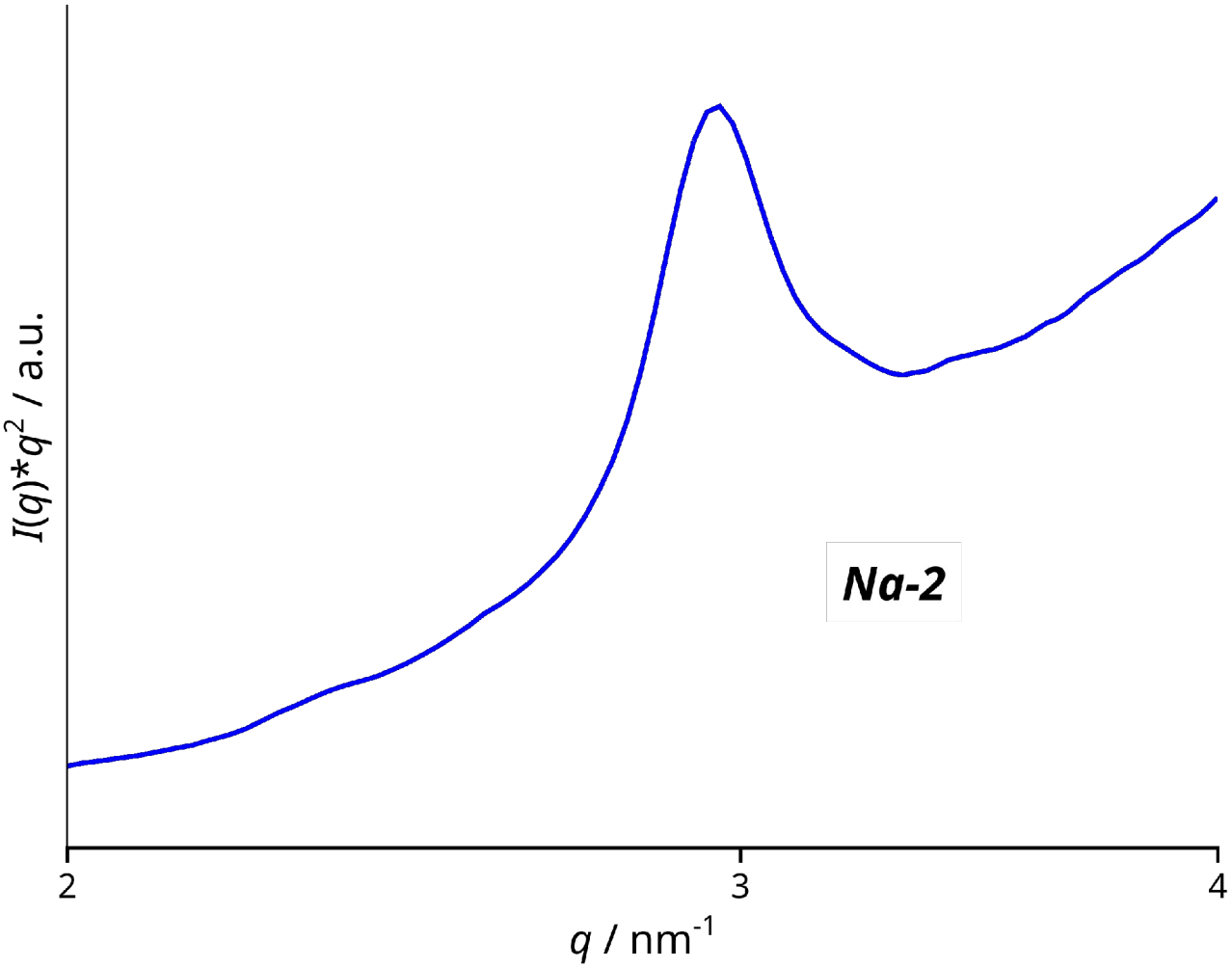

Fig. SI 17: Kratky plot of the first harmonic SAXS peak at q = 2.94 nm^{-1} of the *Na-2* curve shown in figure 1 of the manuscript. The tail at the larger q-value side and increasing intensity confirm the asymmetry of the scattering object.

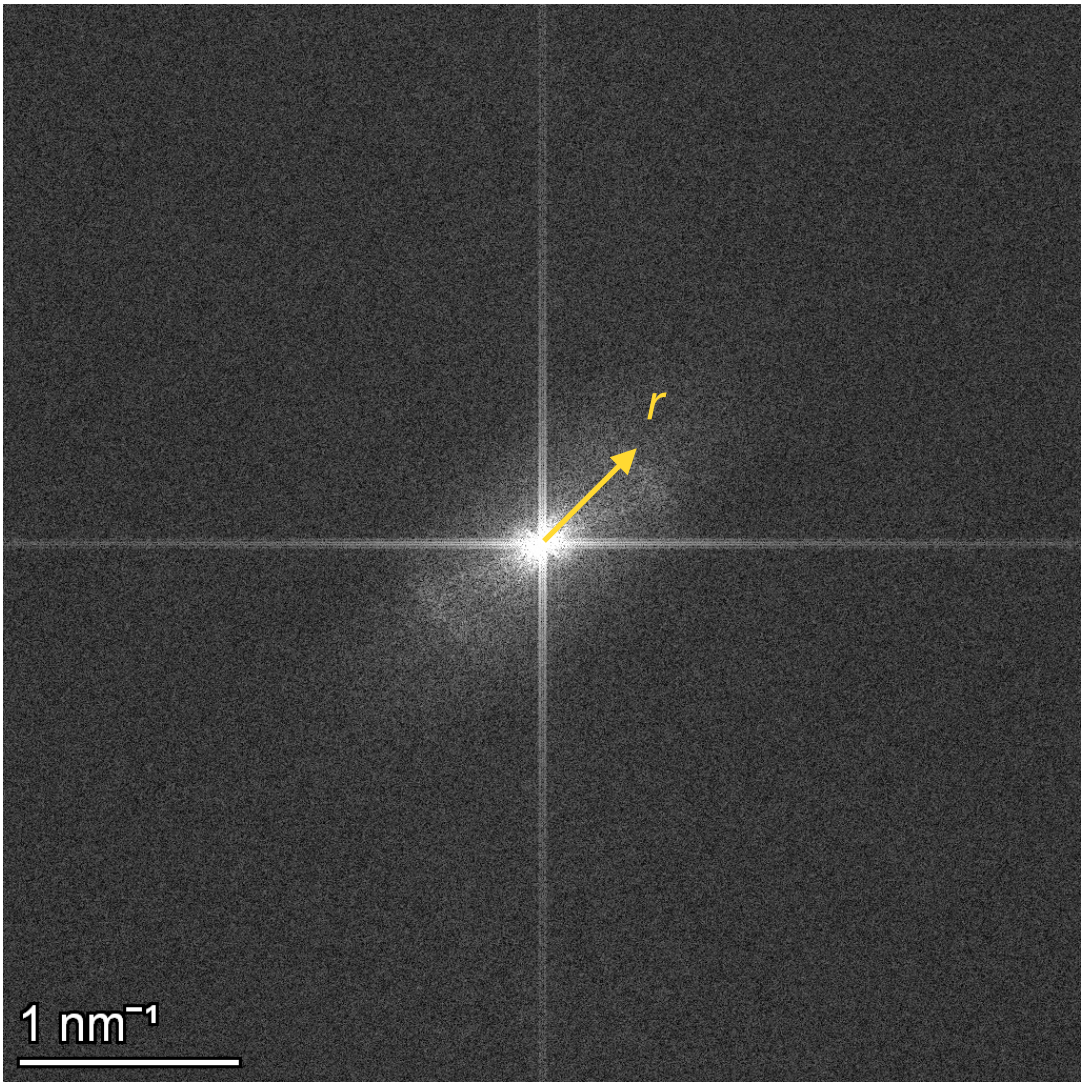

Fig. SI 18: Fast Fourier transform (FFT) of the whole image that is shown in figure 3b of the manuscript. The average distance in real space between the lines that can be spotted in the TEM picture is confirmed to be: $d=1/r$ =1/0.5= 2nm.