Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Calculated and Experimental Powder Patterns of Samples Used for Magnetic Studies

Experimental powder X-ray patterns of the bulk samples were compared with powder patterns calculated from the single crystal structures determined in the study, or from structures reported in the literature, in order to determine if the single crystal is representative of the bulk sample, and to ensure that the samples used for the magnetic studies were pure. The experimental powder patterns are shown in red and the calculated patterns are given in black.

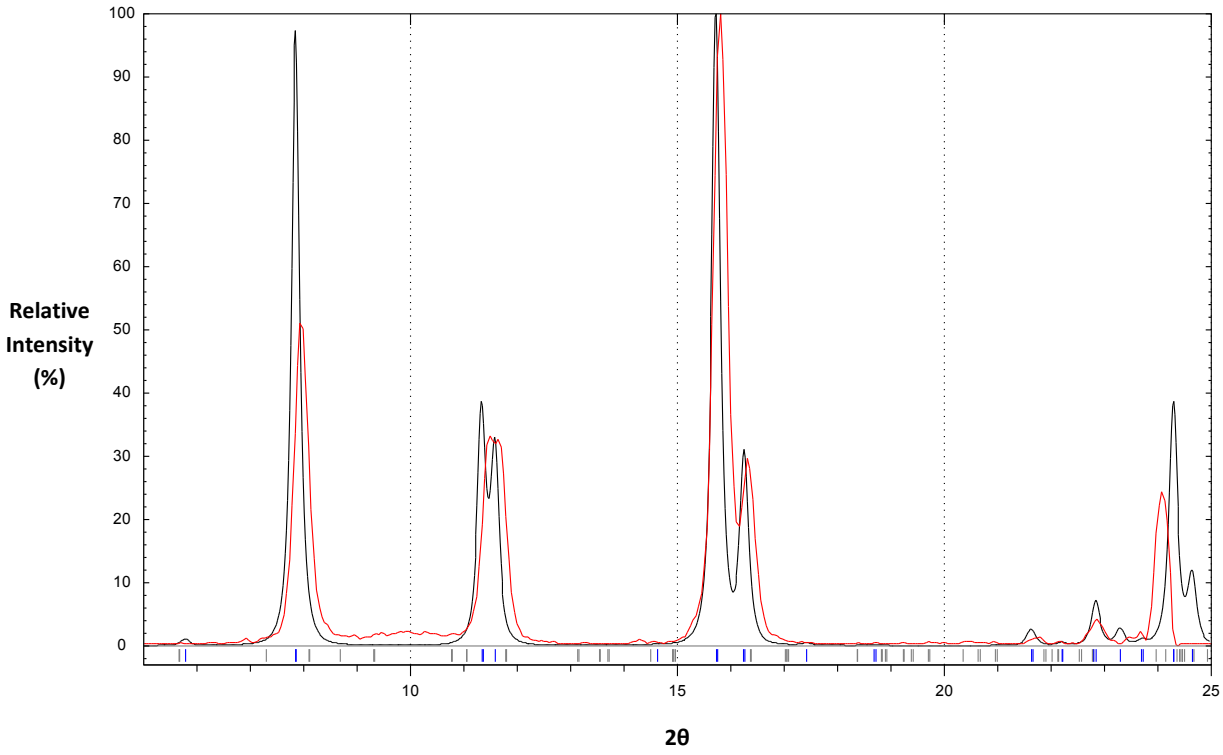

Figure S1: Calculated **inicCuCla** powder X-ray diffraction (black) vs experimental pattern (red).

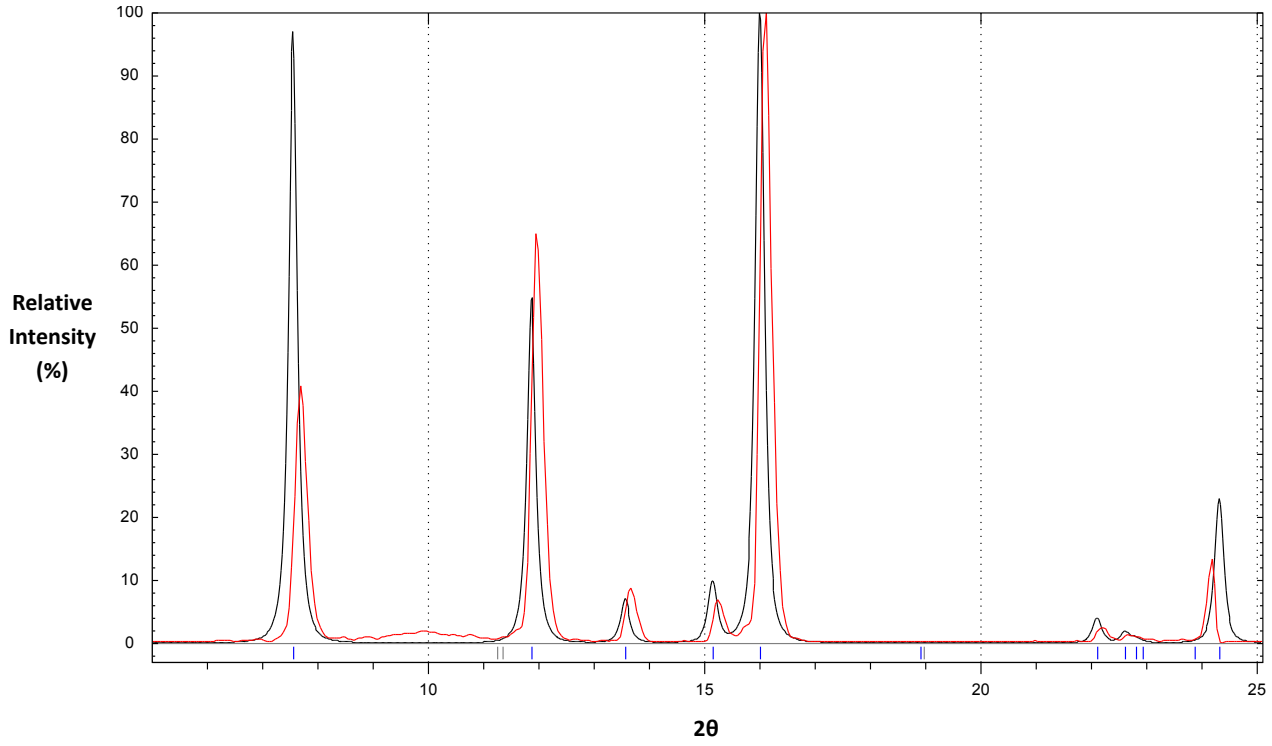

Figure S2: Calculated **inicCuClb** powder X-ray diffraction (black) vs experimental pattern (red).

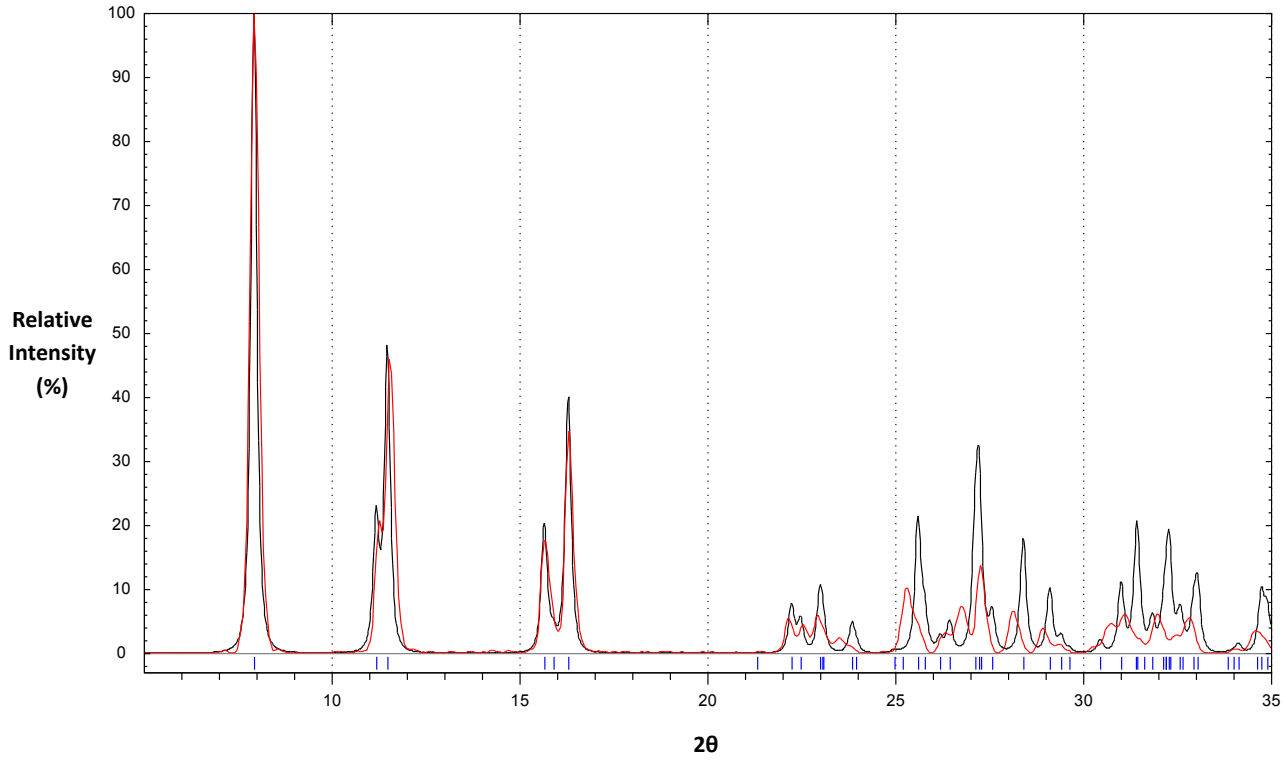

Figure S3: Calculated **inicCuBra** powder X-ray diffraction (black) vs experimental pattern (red).

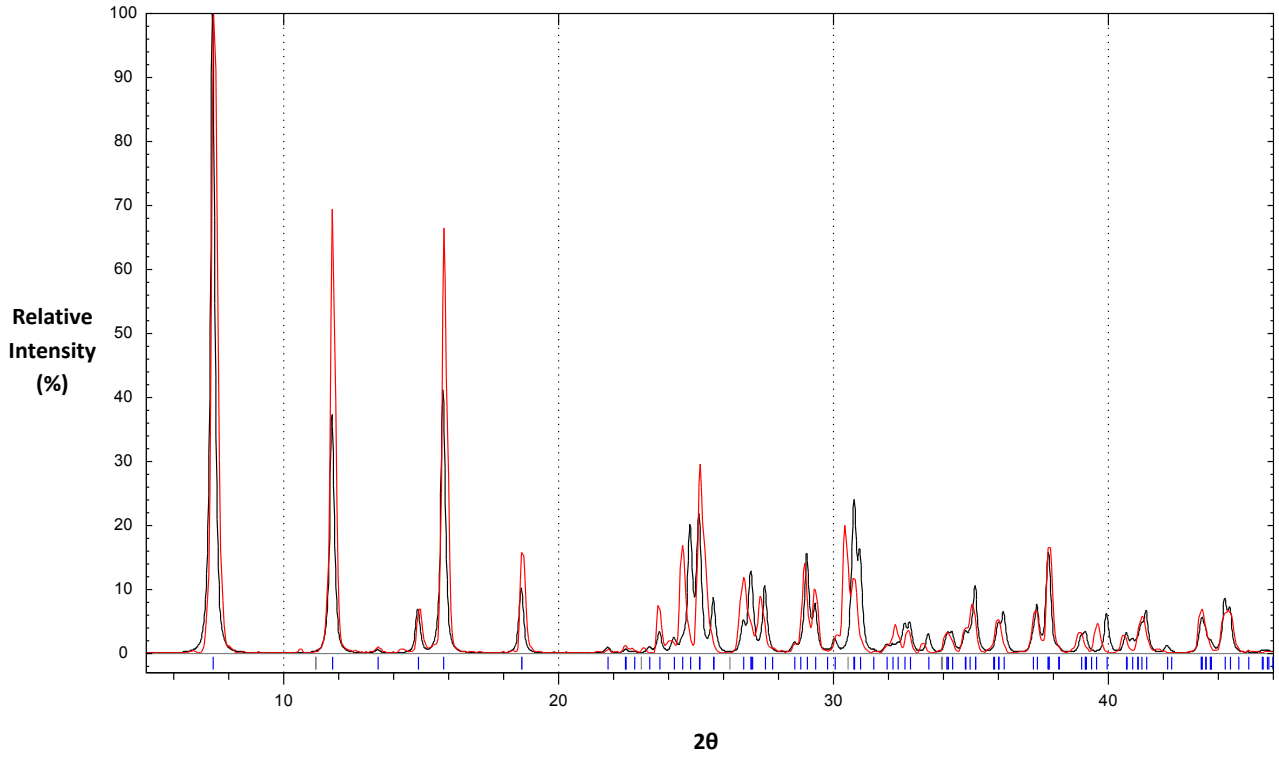

Figure S4: Calculated **inicCuBrb** powder X-ray diffraction (black) vs experimental pattern (red).

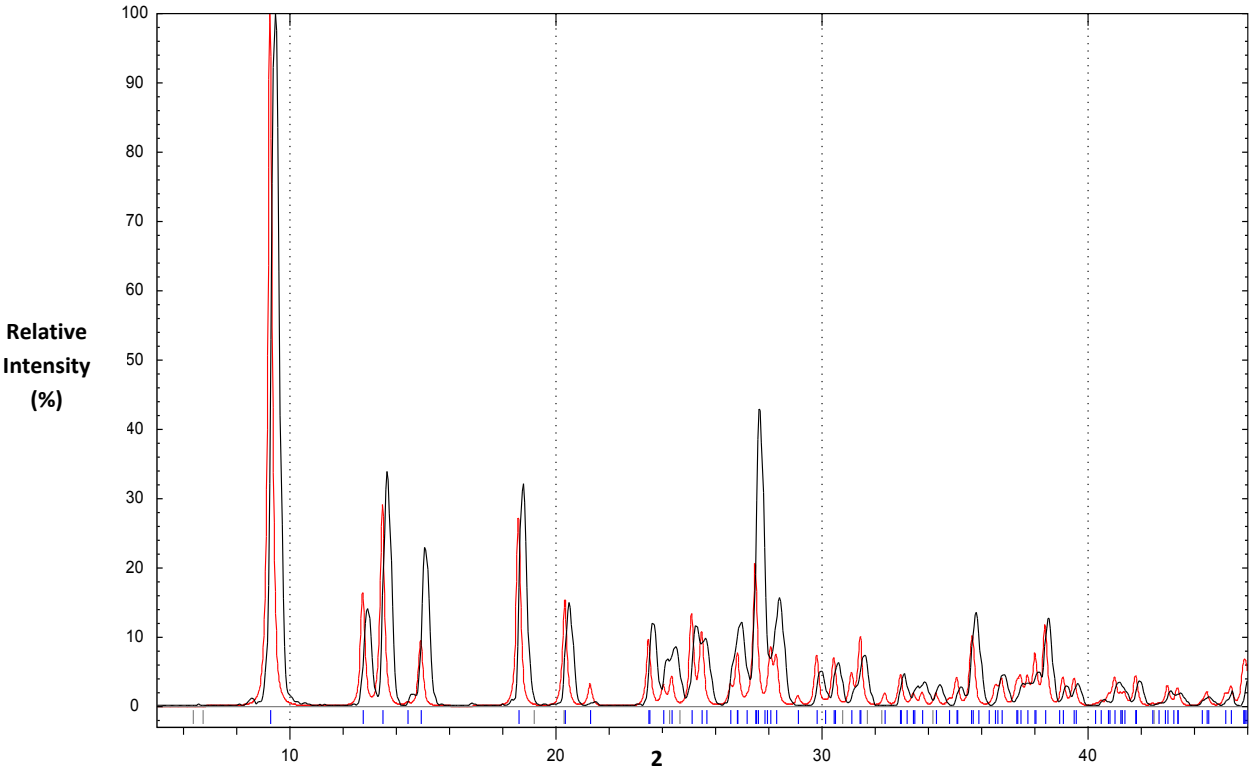

Figure S5: Calculated **nicCuCl** (OCEROG[1]) powder X-ray diffraction (black) vs experimental pattern (red).

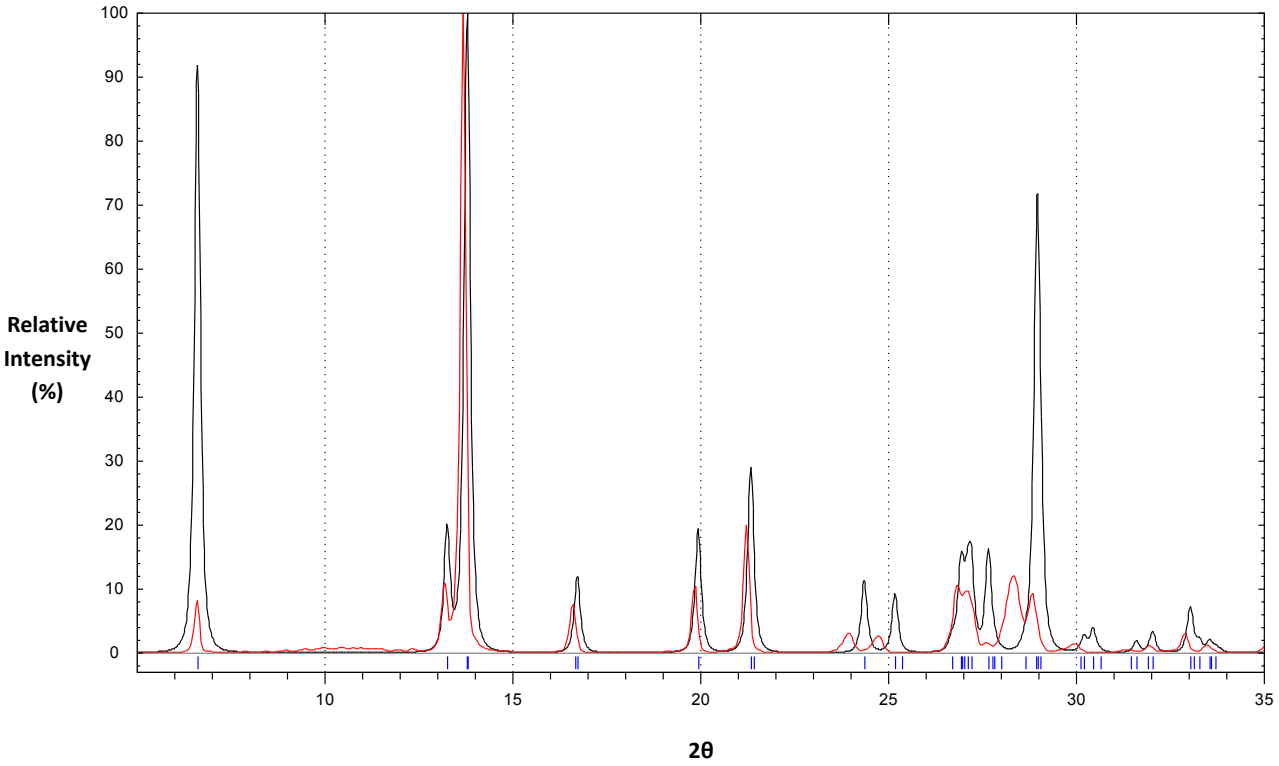

Figure S6: Calculated **nicCuBr** powder X-ray diffraction (black) vs experimental pattern (red).

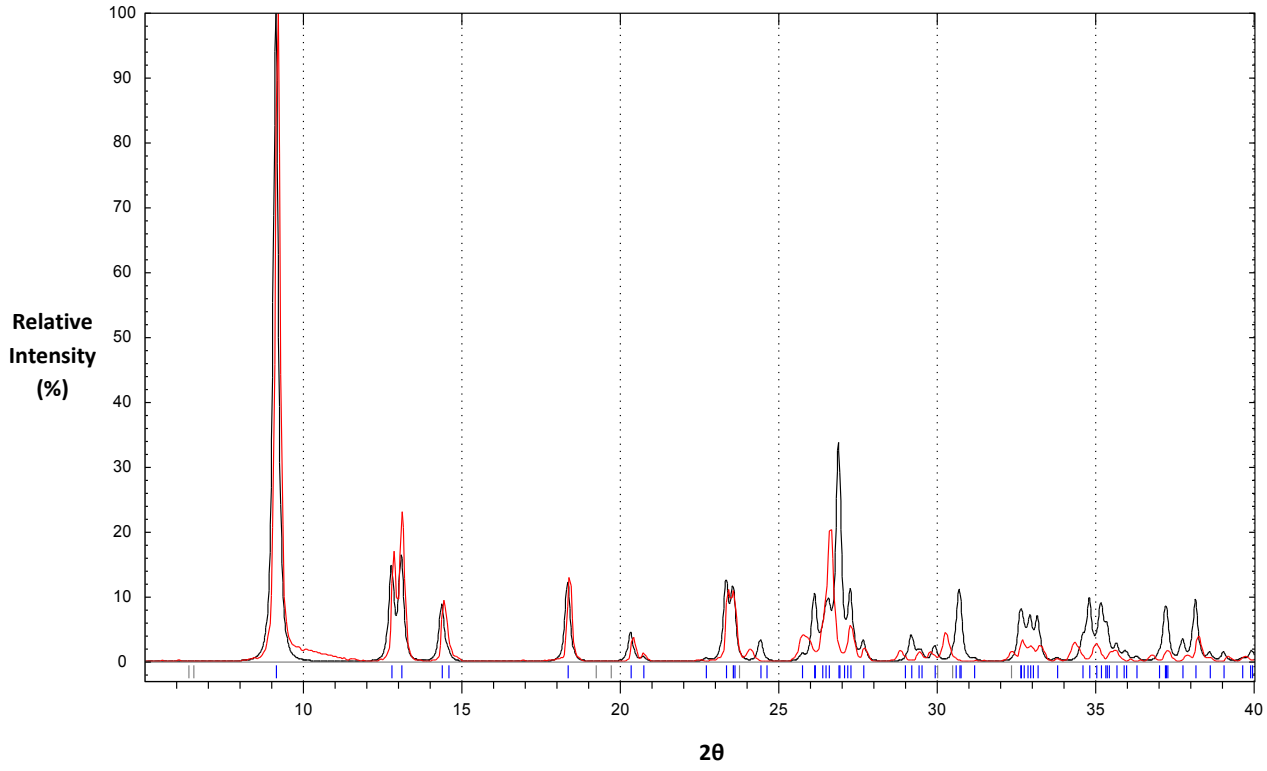

Figure S7: Calculated **pyrCuCl** powder X-ray diffraction (black) vs experimental pattern (red).

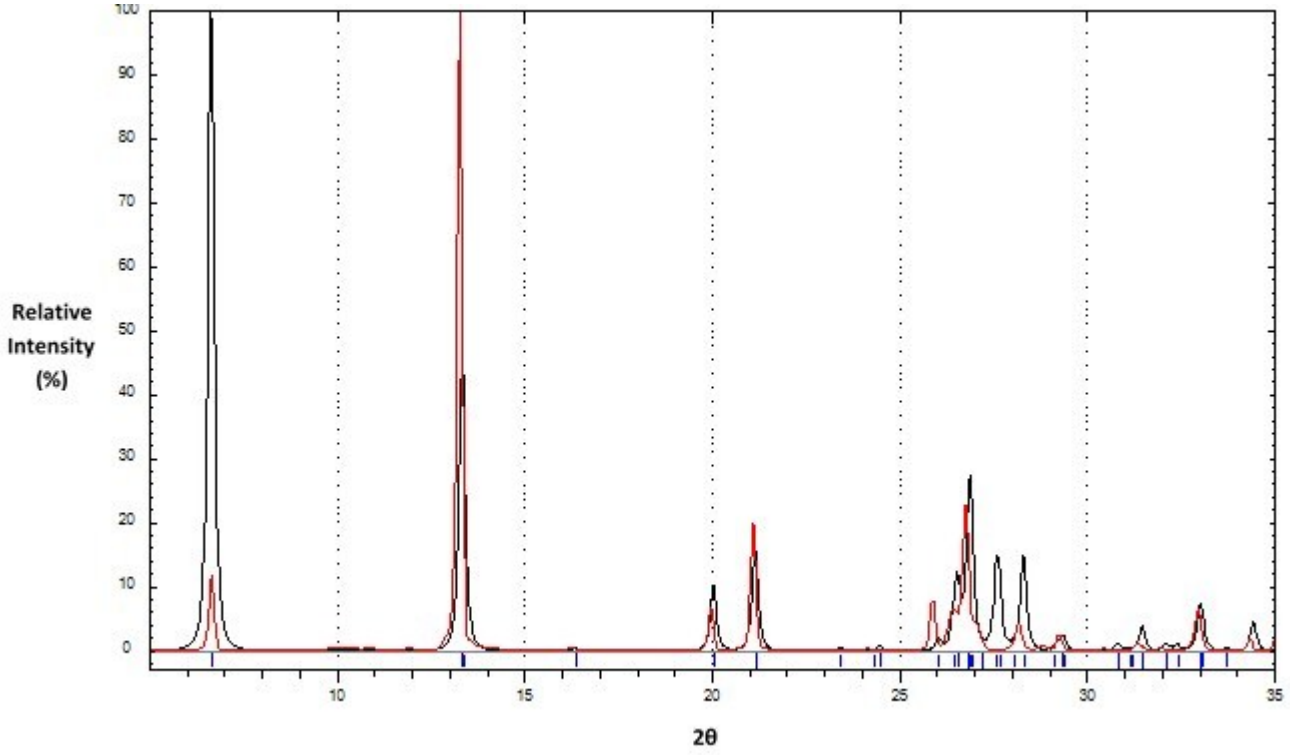

Figure S8: Calculated **pyrCuBr** powder X-ray diffraction (black) vs experimental pattern (red).

Powder Patterns of Heated Samples

A selection of samples were heated to 325°C, a temperature at which the thermal event observed in the TGA curves has been completed for all the compounds. Powder samples of a selection of the compounds were heated to 325°C on a Linkham hot stage, whereafter the samples were cooled back to room temperature, and analysed by powder X-ray diffraction at room temperature. The obtained powder X-ray patterns were matched against patterns in the ICDD PDF-2 database[2] employing the Bruker software EVA. It was found that for the chlorido-containing compounds, the residue remaining after the thermal event corresponds to CuCl, whereas the remaining residue is CuBr in the case of the bromido-containing materials. The experimental powder patterns are shown in black, and the peaks corresponding to CuCl or CuBr are indicated in red. The PDF files in the PDF-2 database are PDF 00-001-0793[3] for CuCl and PDF 01-077-1997[4] for CuBr.

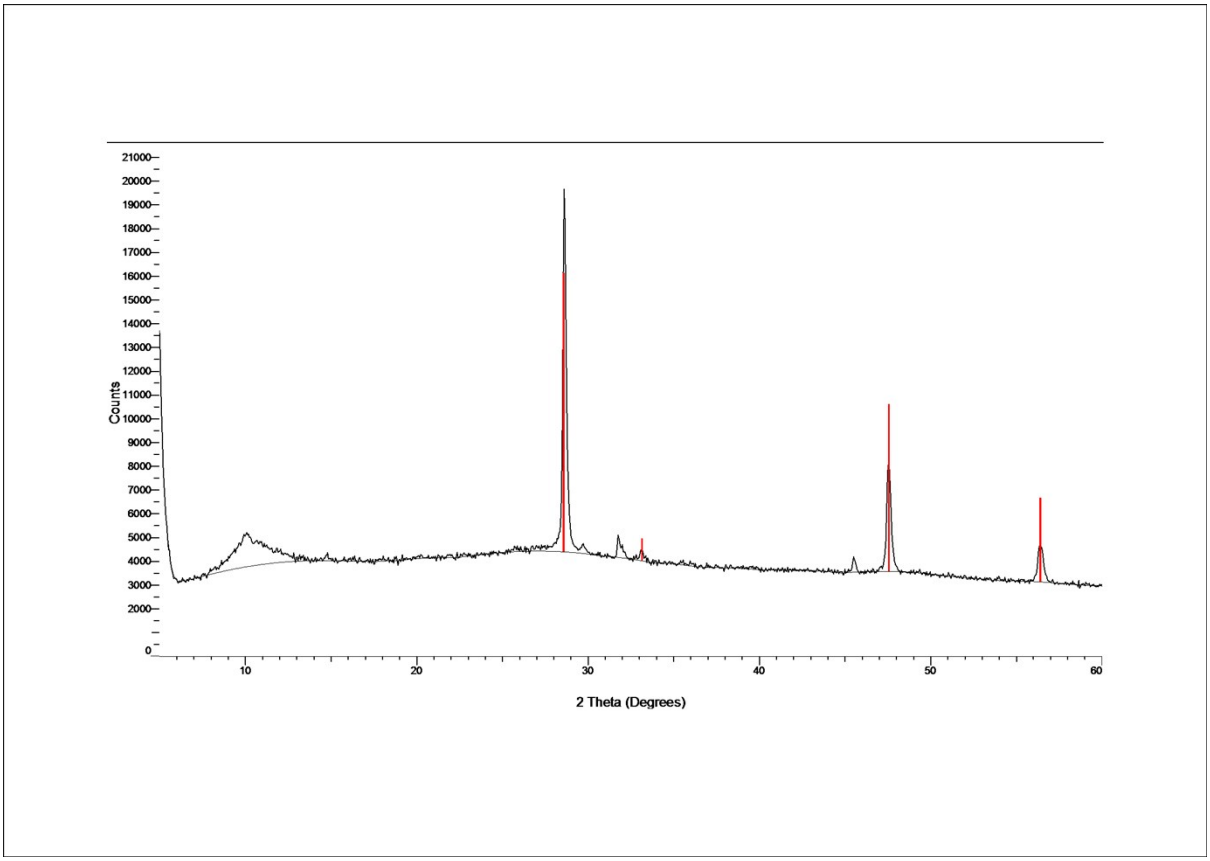

Figure S9: Experimental powder pattern of **inicCuClb** heated to 325°C (black), matched with the pattern of $CuCl^3$ (red lines).

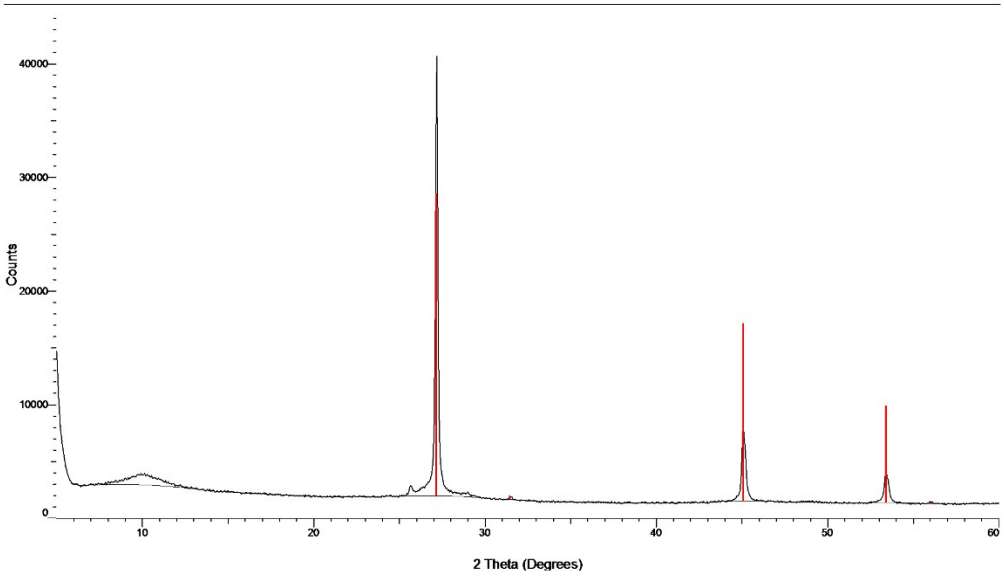

Figure S10: Experimental powder pattern of **inicCuBra** heated to 325°C (black), matched with the pattern of $CuBr^4$ (red lines).

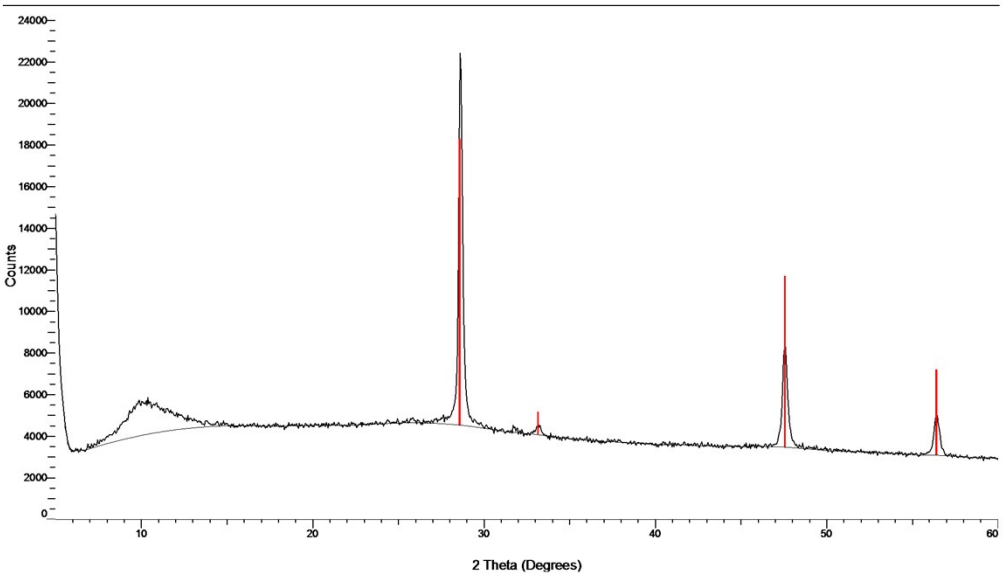

Figure S11: Experimental powder pattern of **nicCuCl** heated to 325°C (black), matched with the pattern of $CuCl^3$ (red lines).

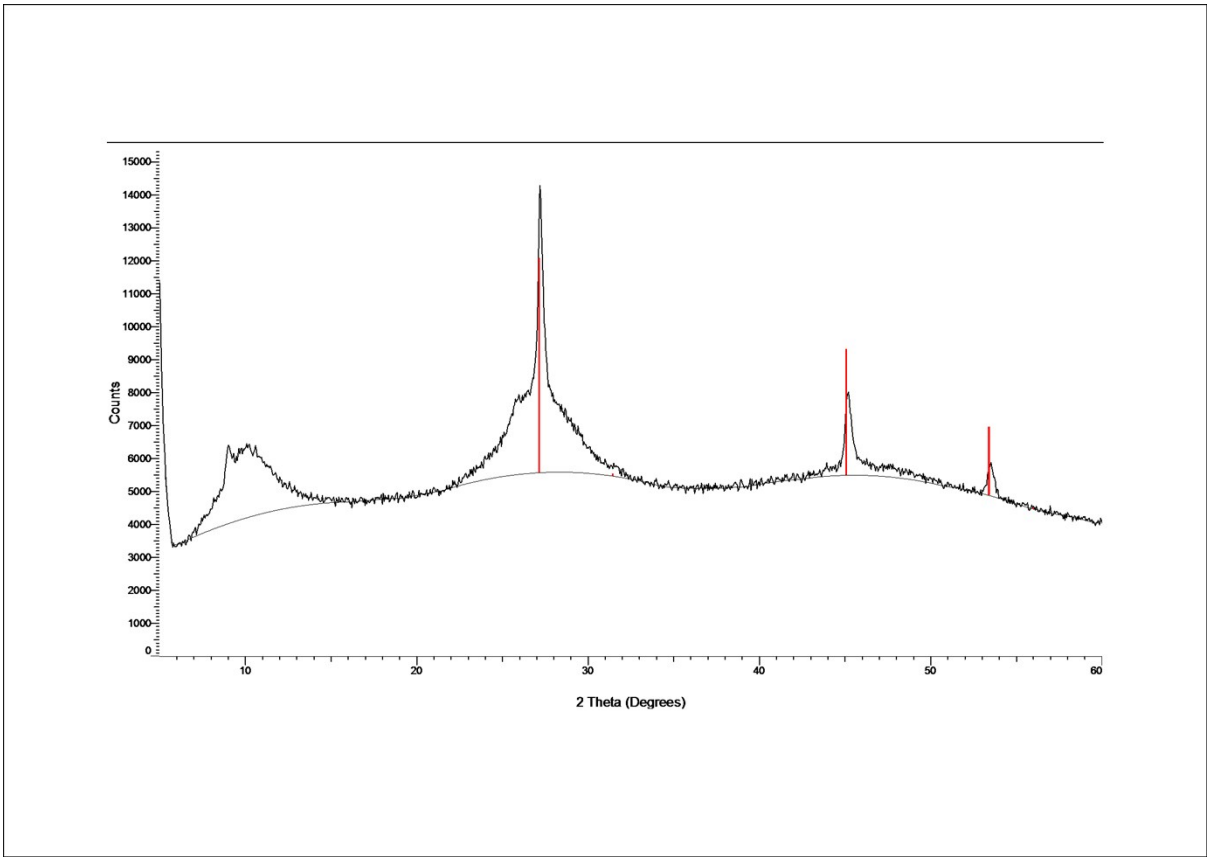

Figure S12: Experimental powder pattern of pyr**CuCl** heated to 325°C (black), matched with the pattern of $CuCl^3$ (red lines).

References:

1. S. M. Fellows and T. J. Prior, *Cryst. Growth. Des.*, 2017, 17, 106.

2. International Centre for Diffraction Data (2018). ICDD Products/PDF-2, http://www.icdd.com/index.php/pdf-2/

3. J. Hanawalt, H. W. Rinn and L. K. Frevel, *Anal. Chem*., 1938, 10, 457.

4. J.-C. Monier, R. Kern, *C. R. Hebd. Seances Acad. Sci.*, 1955, 241, 69.