Electronic Supplementary Information

For

Thermal Decomposition of Hybrid Ultramicroporous Materials (HUMs)

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1) Thermogravimetric Analysis (TGA)

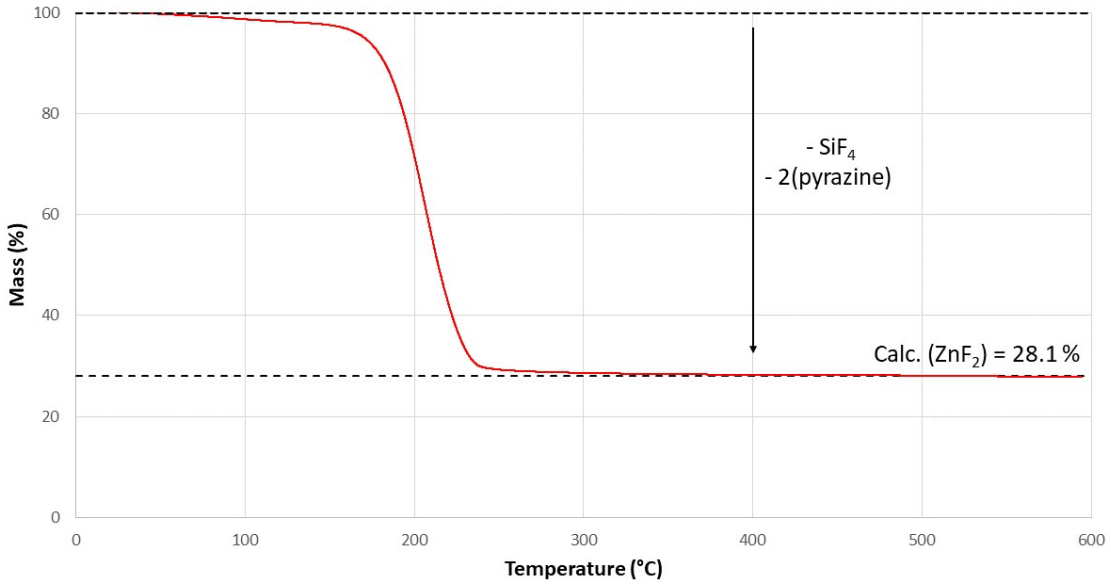

Figure S1 – TGA trace of [SIFSIX-3-Zn] under constant heating at 10 °C/min under N_2 atmosphere.

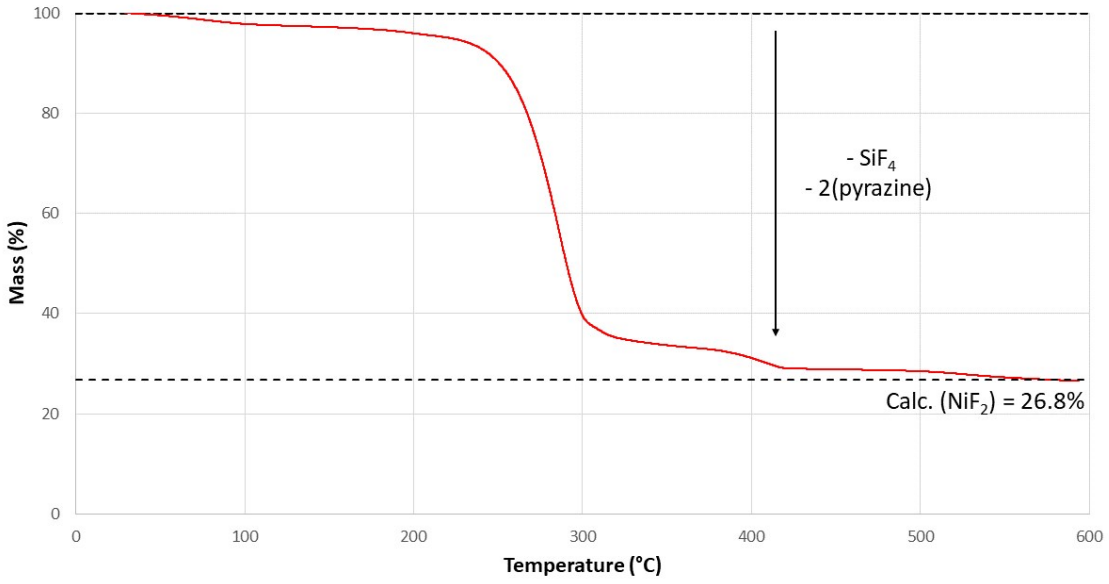

Figure S2 – TGA trace of [SIFSIX-3-Ni] under constant heating at 10 °C/min under N_2 atmosphere.

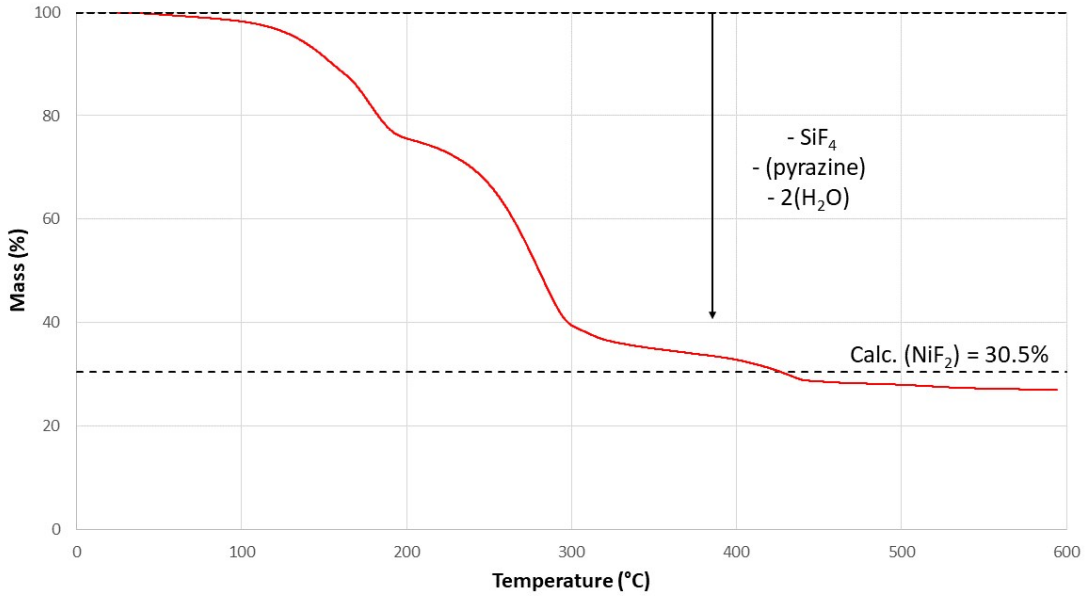

Figure S3 – TGA trace of $[Ni(SiF_6)(pyrazine)(H_2O)_2]$ under constant heating at 10 °C/min under N_2 atmosphere.

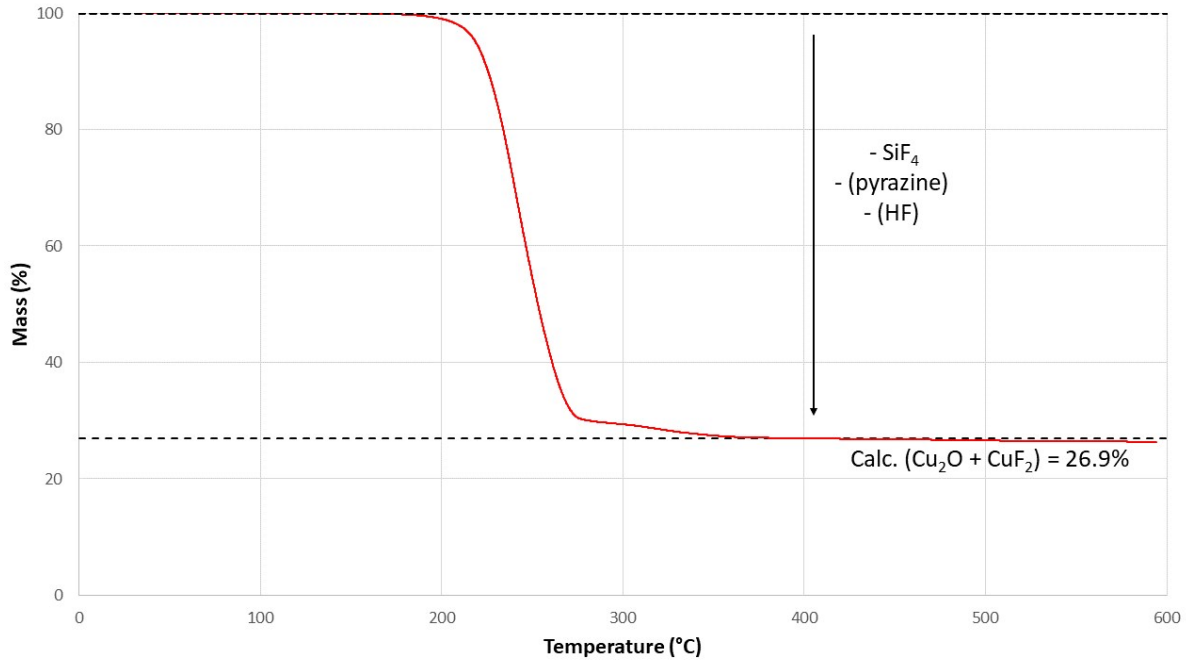

Figure S4 – TGA trace of $[Cu(SiF_6)(pyrazine)(H_2O)_2]$ under constant heating at 10 °C/min under N_2 atmosphere. The quoted residual weight (26.9%) is calculated assuming a 50:50 mixture of Cu_2O and CuF_2.

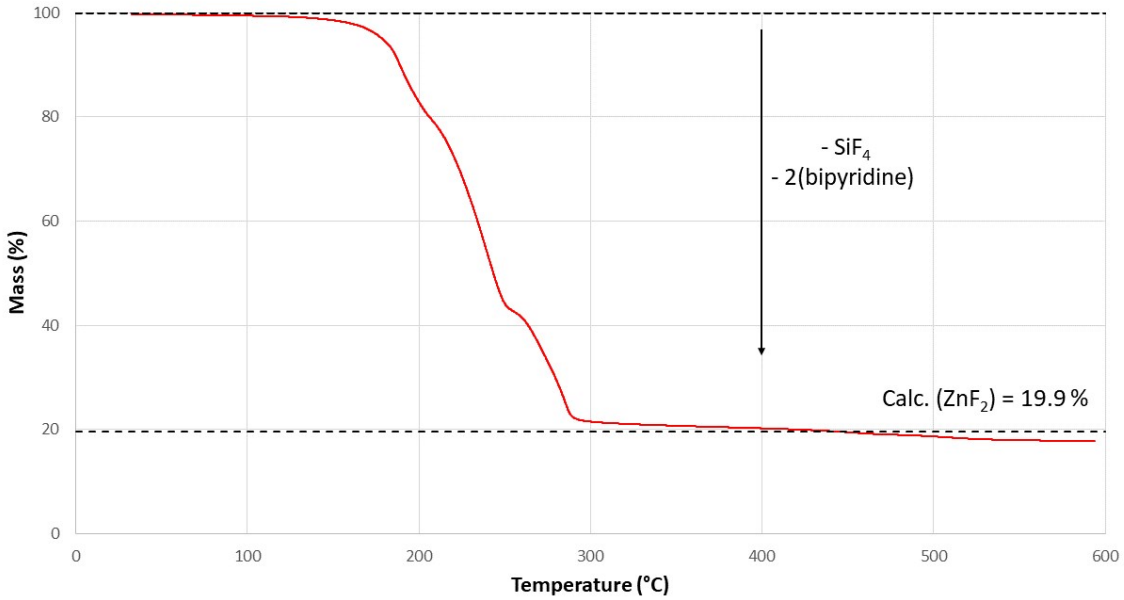

Figure S5 – TGA trace of [SIFSIX-1-Zn] under constant heating at 10 °C/min under N_2 atmosphere.

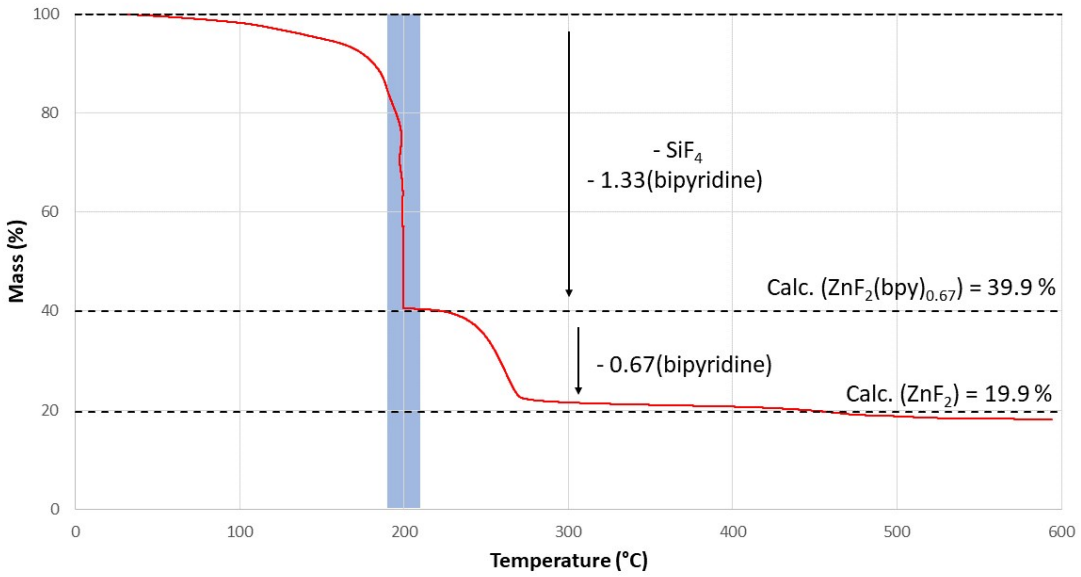

Figure S6 – Ramp-hold-ramp TGA trace of [SIFSIX-1-Zn] under N_2 atmosphere. The sample was heated to 200 °C at a constant rate of 10 °C/min, held at this temperature for 30 minutes (indicated by blue region), and subsequently ramped to 600 °C at a constant rate of 10 °C/min.

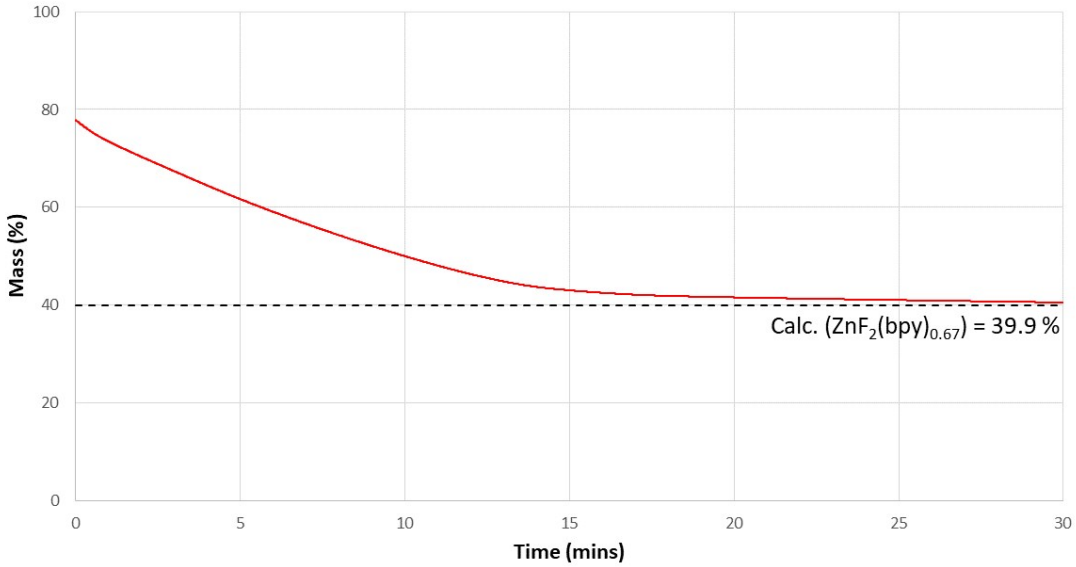

Figure S7 – Time course of the isothermal portion of Figure S6, showing a plateau in mass loss. Sample was held isothermally at 200 °C for 30 minutes under N_2 atmosphere.

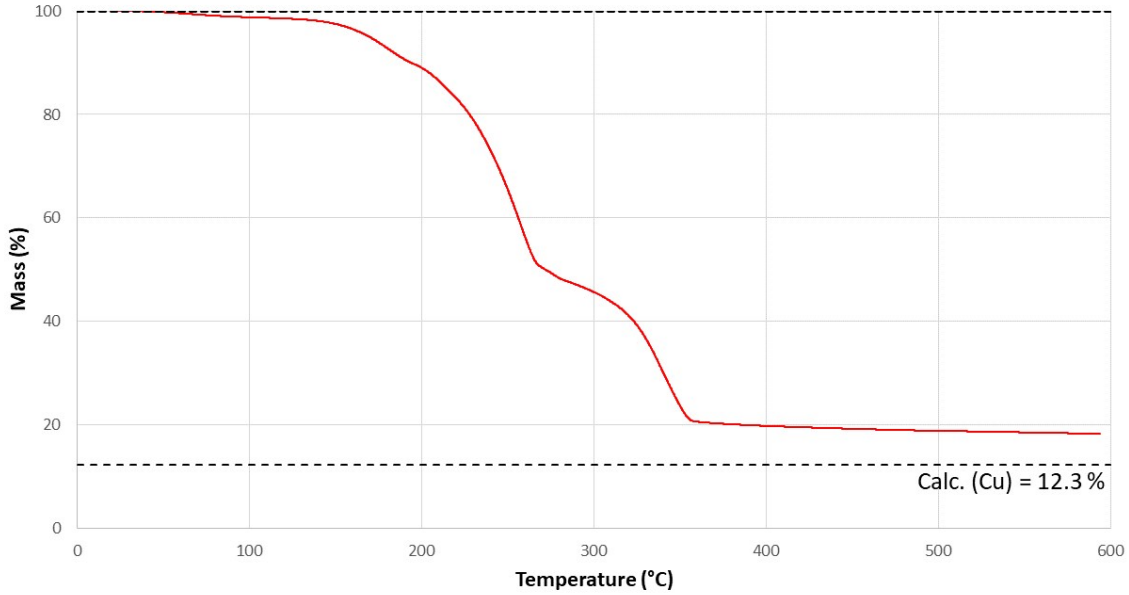

Figure S8 – TGA trace of [SIFSIX-1-Cu] under constant heating at 10 °C/min under N_2 atmosphere. This sample was activated at 150 °C for 30 minutes at ambient pressure before analysis. PXRD analysis (see below) indicates that metallic Cu is present in the residue, not CuF_2. The additional mass is assigned as amorphous carbon.

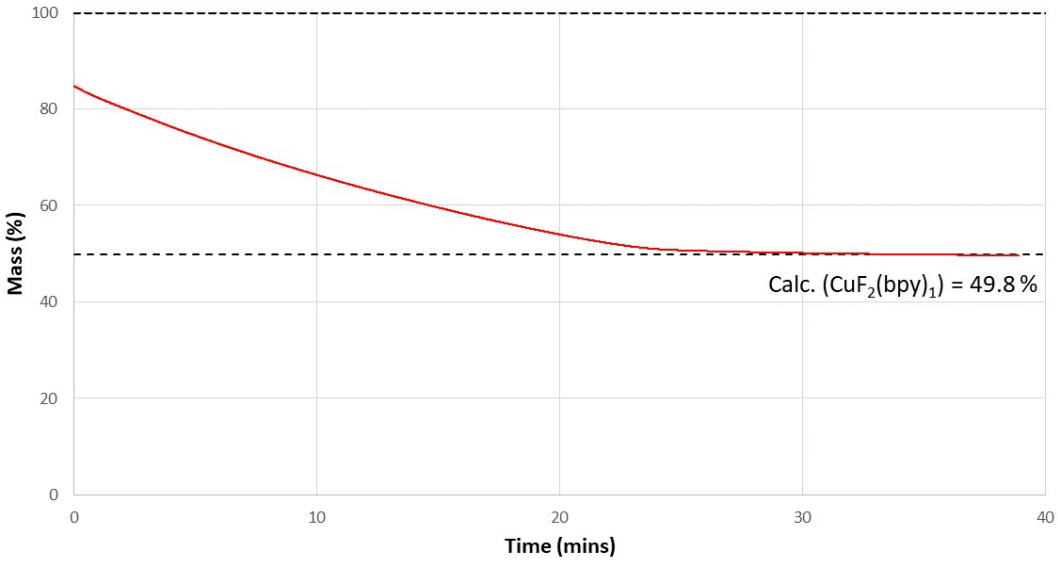

Figure S9 – Time course TGA of [SIFSIX-1-Cu] held at 210 °C under N_2 atmosphere for 40 minutes. This sample was activated at 150 °C for 30 minutes at ambient pressure before analysis.

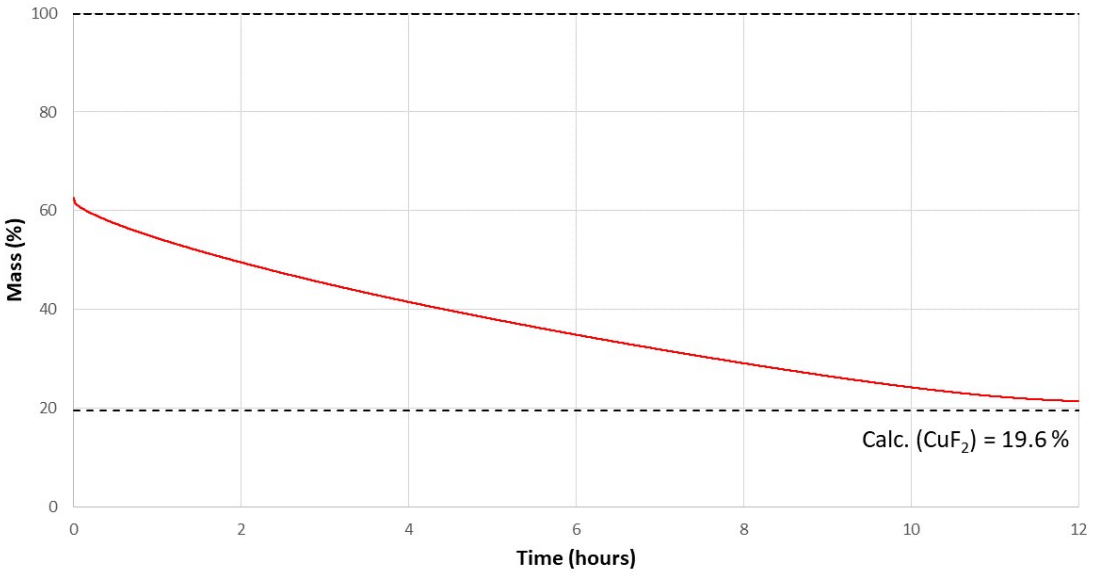

Figure S10 – Time course TGA of [SIFSIX-1-Cu] held at 250 °C under N_2 atmosphere for 12 hours. This sample was activated at 150 °C for 30 minutes at ambient pressure before analysis.

2) Powder X-ray Diffraction (PXRD)

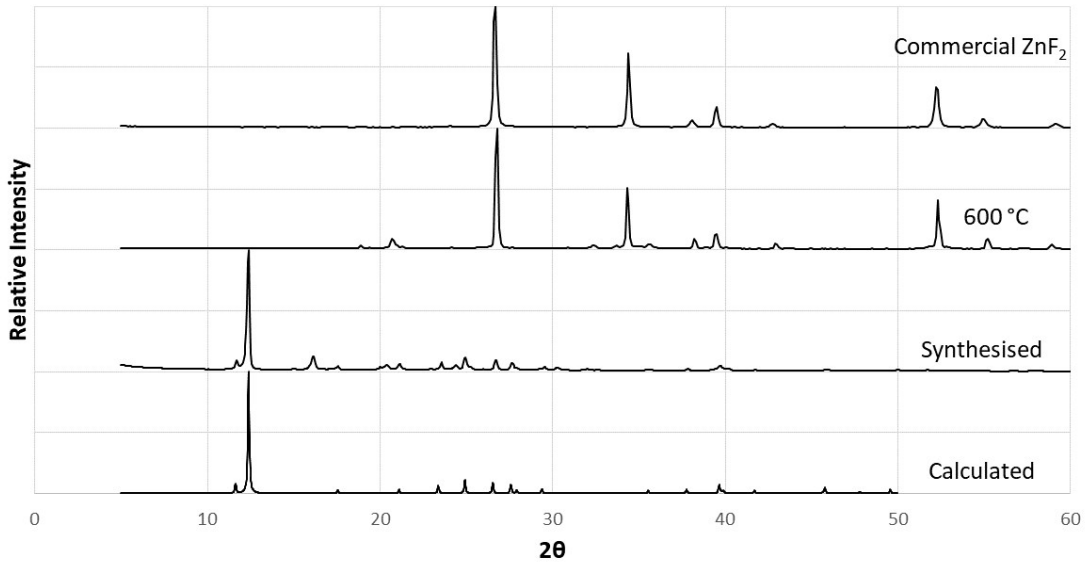

Figure S11 – PXRD spectra of [SIFSIX-3-Zn] as calculated from single crystal data; as synthesised; residue isolated by heating [SIFSIX-3-Zn] samples at 10 °C/min under N_2 atmosphere to the quoted temperature, and a commercial sample of ZnF_2.

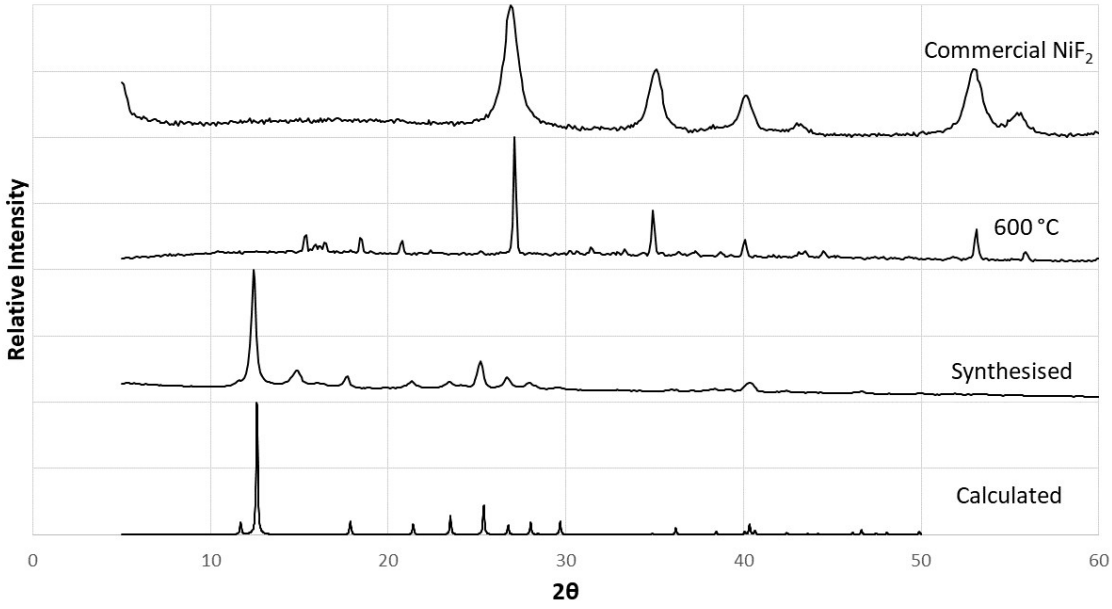

Figure S12 – PXRD spectra of [SIFSIX-3-Ni] as calculated from single crystal data; as synthesised; residue isolated by heating [SIFSIX-3-Ni] samples at 10 °C/min under N_2 atmosphere to the quoted temperature, and a commercial sample of NiF_2.

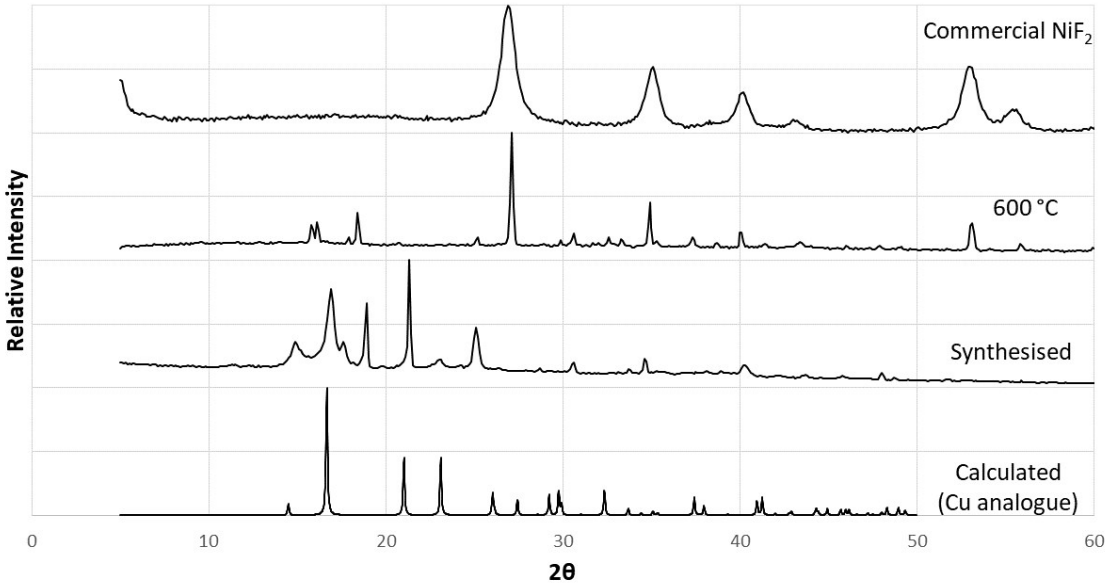

Figure S13 – PXRD spectra of $[Ni(SiF_6)(pyrazine)(H_2O)_2]$ as calculated from single crystal data (Cu analogue); as synthesised; residue isolated by heating $[Ni(SiF_6)(pyrazine)(H_2O)_2]$ samples at 10 °C/min under N_2 atmosphere to the quoted temperature, and a commercial sample of NiF_2.

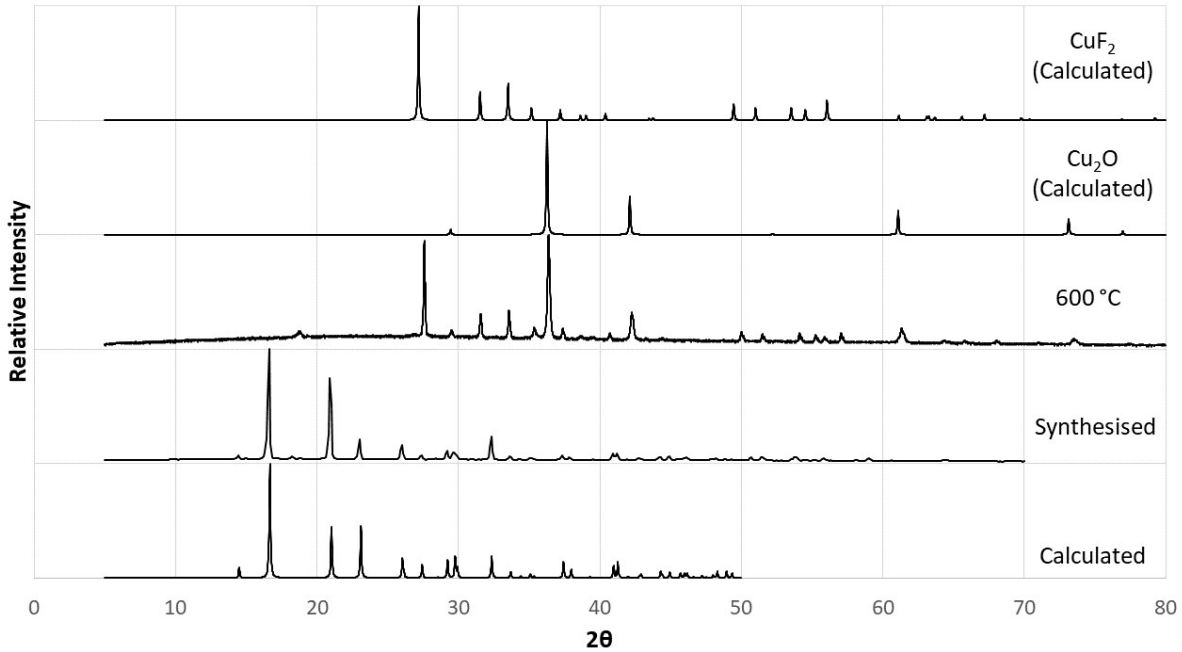

Figure S14 – PXRD spectra of $[Cu(SiF_6)(pyrazine)(H_2O)_2]$ as calculated from single crystal data; as synthesised; residue isolated by heating $[Cu(SiF_6)(pyrazine)(H_2O)_2]$ samples at 10 °C/min under N_2 atmosphere to the quoted temperature, and; Cu_2O and CuF_2 as calculated from literature data.

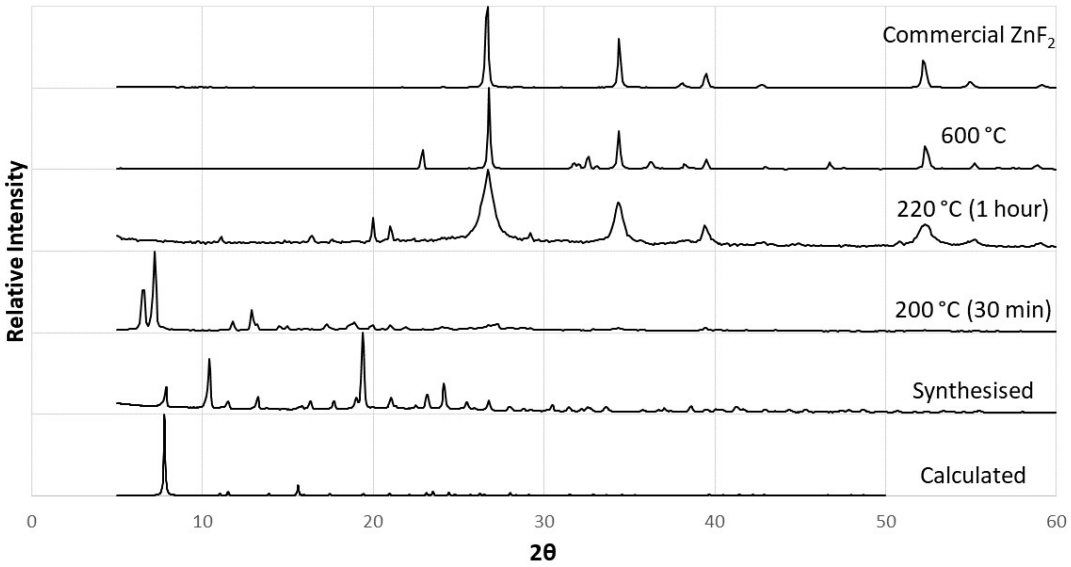

Figure S15 – PXRD spectra of [SIFSIX-1-Zn] as calculated from single crystal data; as synthesised; residues isolated by heating [SIFSIX-1-Zn] samples at 10 °C/min under N_2 atmosphere to the quoted temperatures (and hold times), and; ZnF_2.

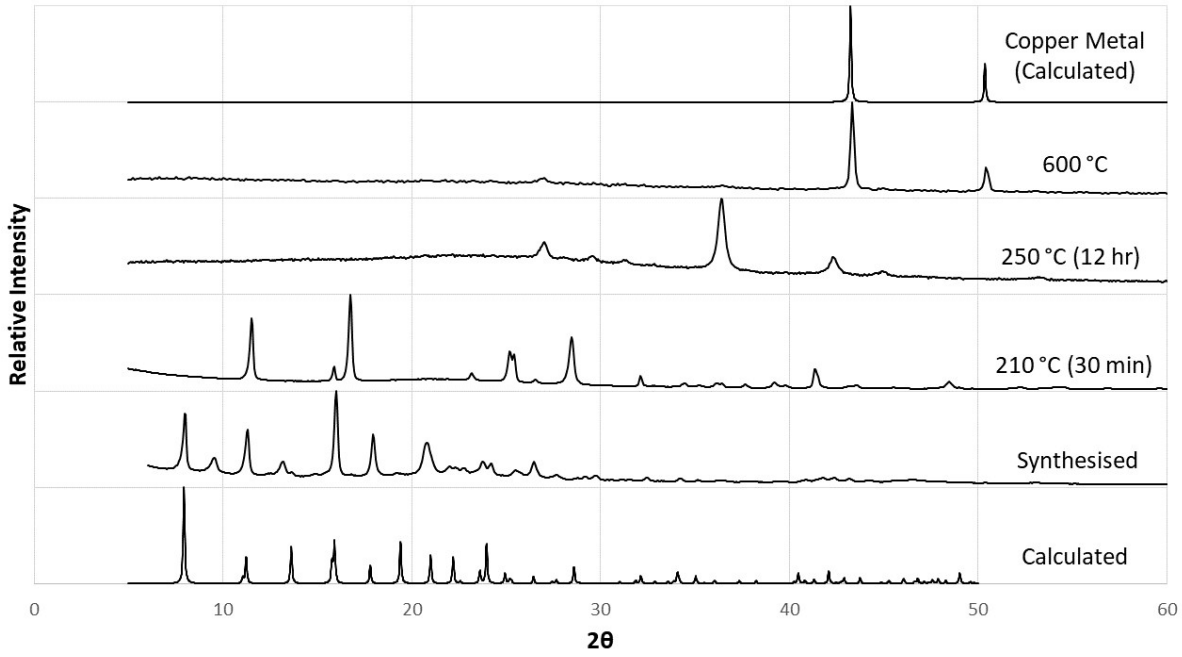

Figure S16 – PXRD spectra of [SIFSIX-1-Cu] as calculated from single crystal data; as synthesised; residues isolated by heating [SIFSIX-1-Cu] samples at 10 °C/min under N_2 atmosphere to the quoted temperatures (and hold times), and; copper metal.

3) Infrared (IR) Spectroscopy

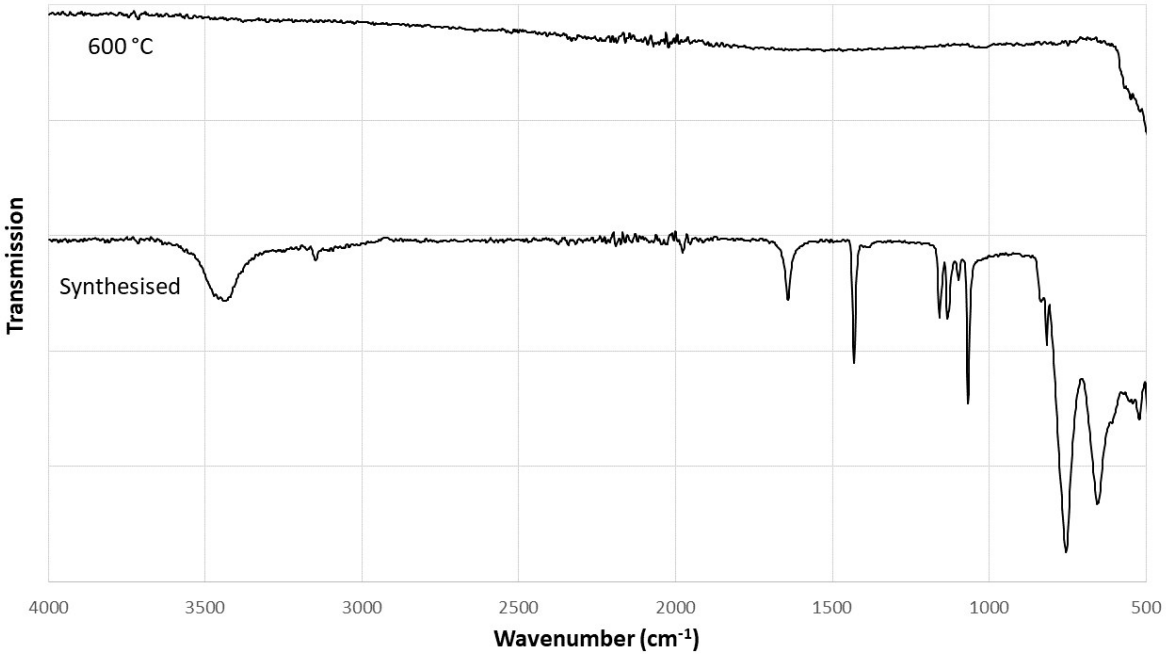

Figure S17 – IR spectra of [SIFSIX-3-Zn] as synthesised and the residue prepared by heating [SIFSIX-3-Zn] samples at 10 °C/min under N_2 atmosphere to the quoted temperature.

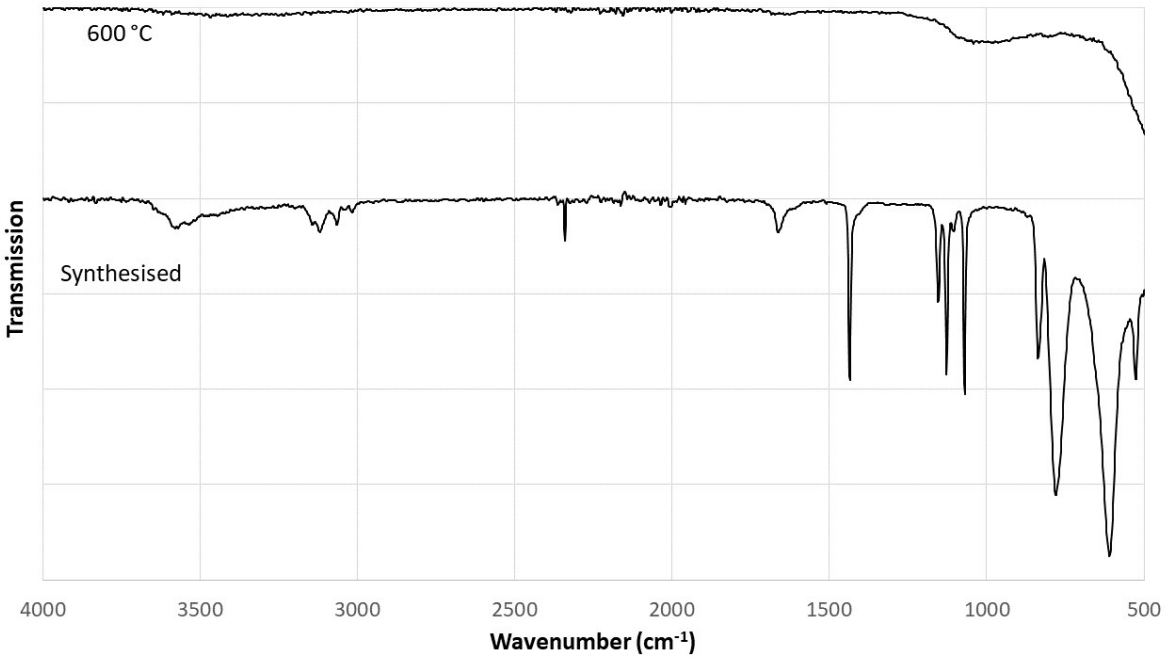

Figure S18 – IR spectra of [SIFSIX-3-Ni] as synthesised and the residue prepared by heating [SIFSIX-3-Ni] samples at 10 °C/min under N_2 atmosphere to the quoted temperature.

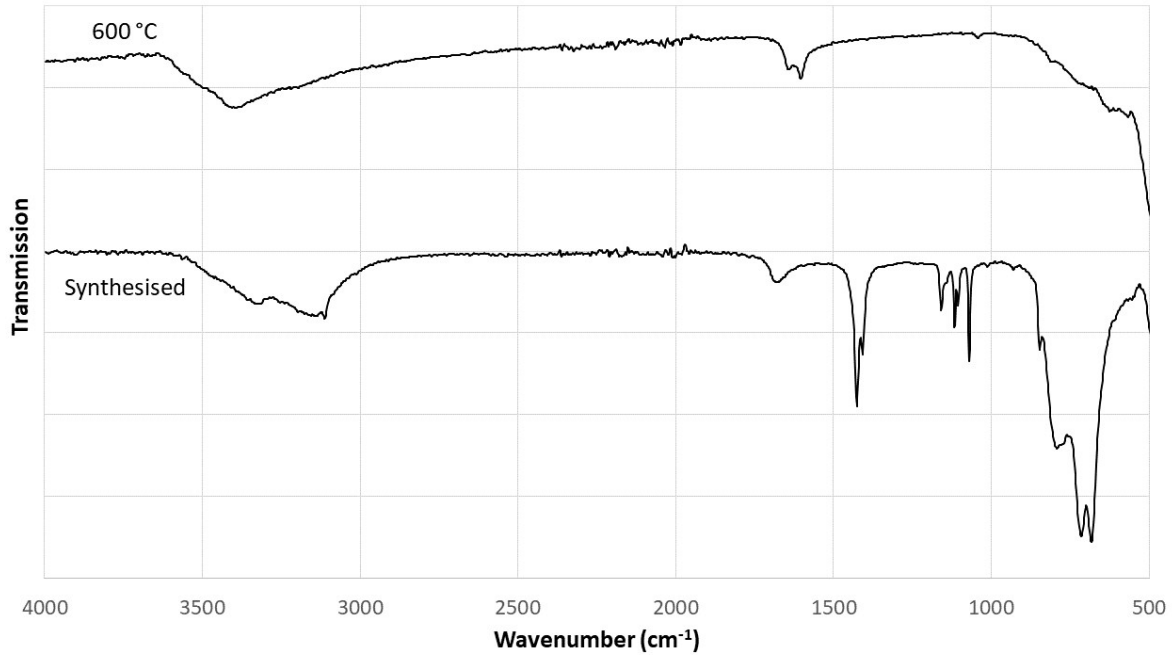

Figure S19 – IR spectra of $[Ni(SiF_6)(pyrazine)(H_2O)_2]$ as synthesised and the residue prepared by heating $[Ni(SiF_6)(pyrazine)(H_2O)_2]$ samples at 10 °C/min under N_2 atmosphere to the quoted temperature.

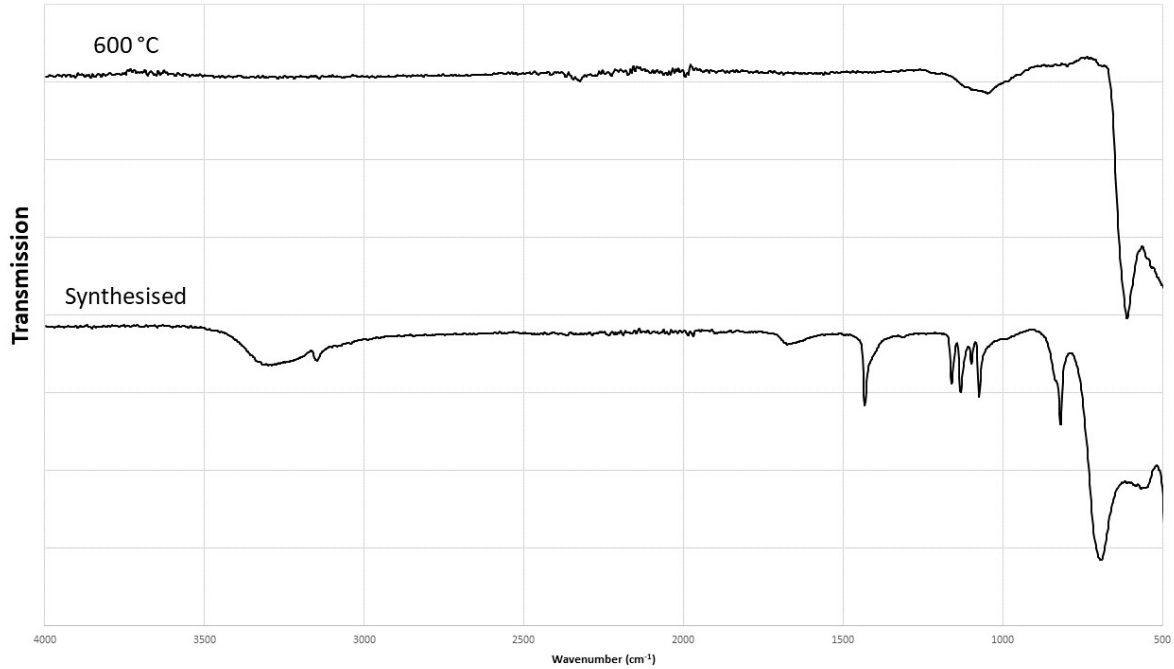

Figure S20 – IR spectra of $[Cu(SiF_6)(pyrazine)(H_2O)_2]$ as synthesised and the residue prepared by heating $[Cu(SiF_6)(pyrazine)(H_2O)_2]$ samples at 10 °C/min under N_2 atmosphere to the quoted temperature.

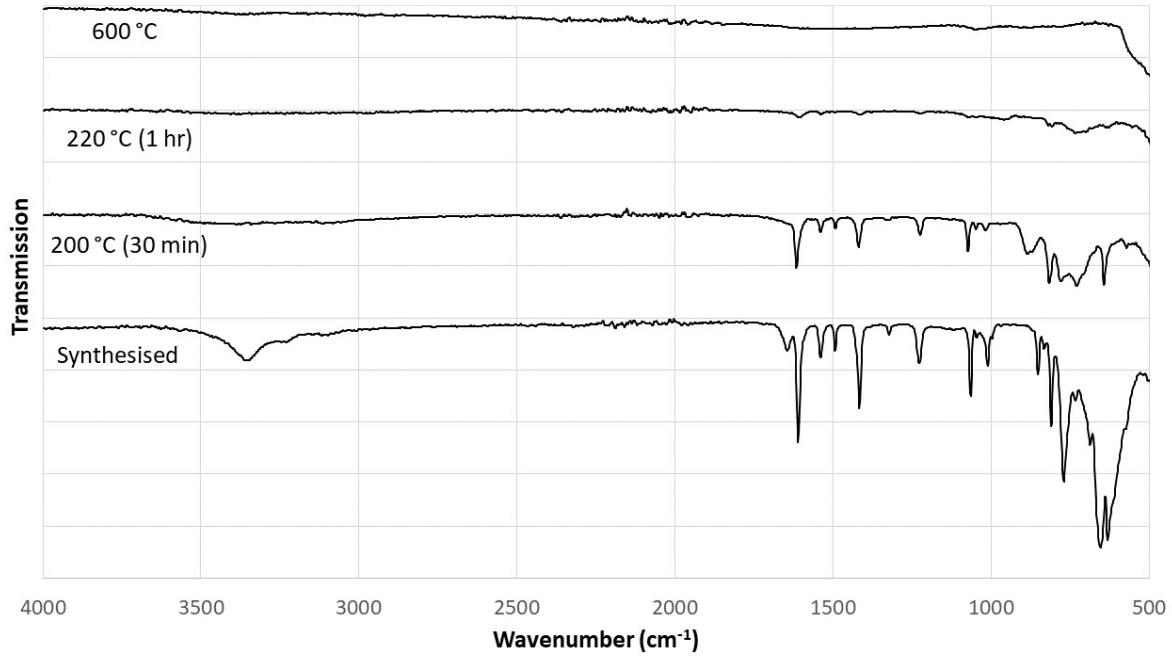

Figure S21 – IR spectra of [SIFSIX-1-Zn] as synthesised and the residues prepared by heating [SIFSIX-1-Zn] samples at 10 °C/min under N_2 atmosphere to the quoted temperatures (and hold times).

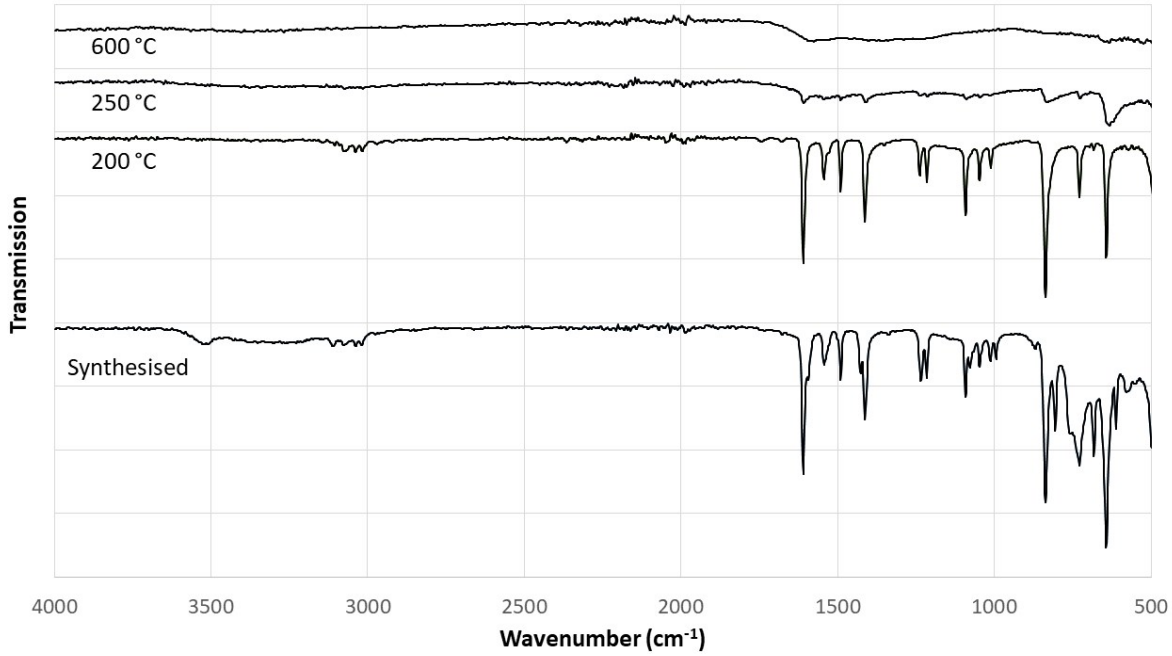

Figure S22 – IR spectra of [SIFSIX-1-Cu] as synthesised and the residues prepared by heating [SIFSIX-1-Cu] samples at 10 °C/min under N_2 atmosphere to the quoted temperatures.