SYNTHESIS AND CONTROL OF SPIN CROSSOVER COMPOUND $[Fe(Htrz)_2(trz)](BF_4)$ NANOSCALE PARTICLES WITH TUBULAR FLOW REACTORS

Pierre-Baptiste Flandrin[1], Karen Robertson[1], Chick C. Wilson[1], Paul R. Raithby[1] Duncan Guthrie[2]

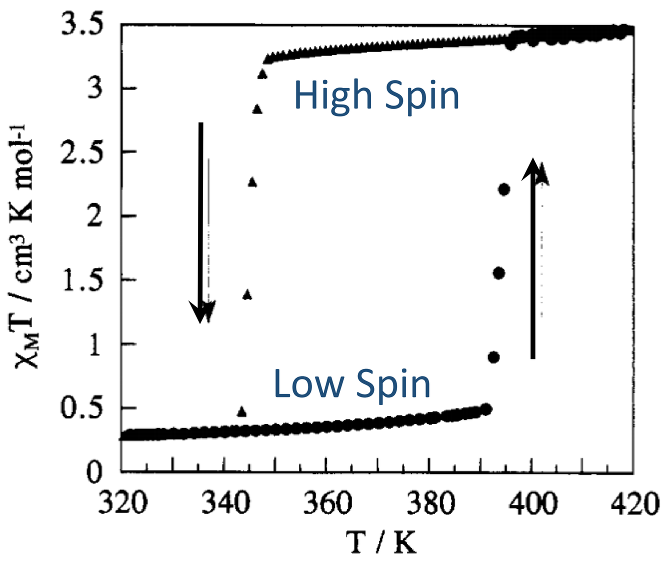
[1] *Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom*
[2] *Vapourtec Ltd, Bury St Edmunds, IP28 6TS, United Kingdom*

Spin-crossover coordination polymers

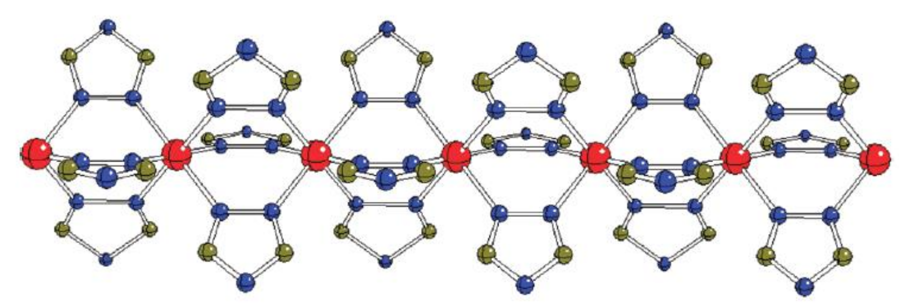
Spin Crossover (SCO) materials switch reversibly between high spin (HS) and low spin (LS) states in response to changes in temperature, pressure and/or light irradiation. The switching process is highly size dependant - need homogenous nanoparticles for reproducible properties.

$[Fe(Htrz)_2(trz)](BF_4)$ changes color in response to the changing spin of the Fe^{IV} ion – upon heating the compound changes from pink to white.

Standard synthesis of this compound is by combination of two aqueous solutions and triazole (Htrz) at room temperature. Depending on mixing conditions the product can have a wide crystal size distribution. We have synthesized this compound in a range of Vapourtec flow reactor and compared the crystal size obtained.



Magnetic susceptibility as a function of temperature *Chem. Mater.* **1994,** *6,* 1404-1412

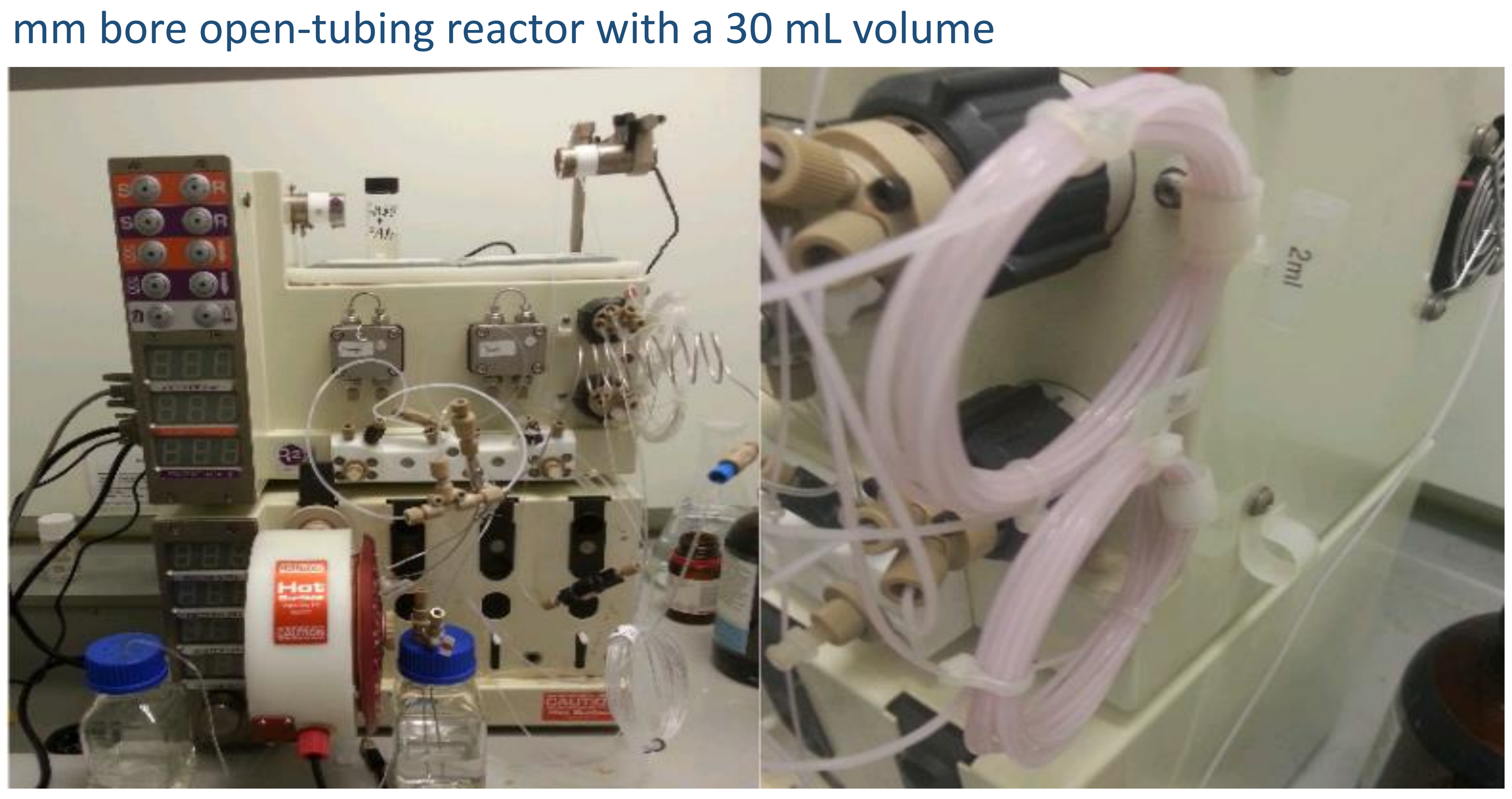


Coordination polymer chain: Fe (red); N (blue); C (brown). $[BF_4]^-$ counterion not shown for clarity. *Phys. Chem. C* **2011,** *115,* 1323–1329

Spin crossover (SCO) compounds are of great interest for data storage materials due to their highly reversible switching between spin states.

Vapourtec R-Series

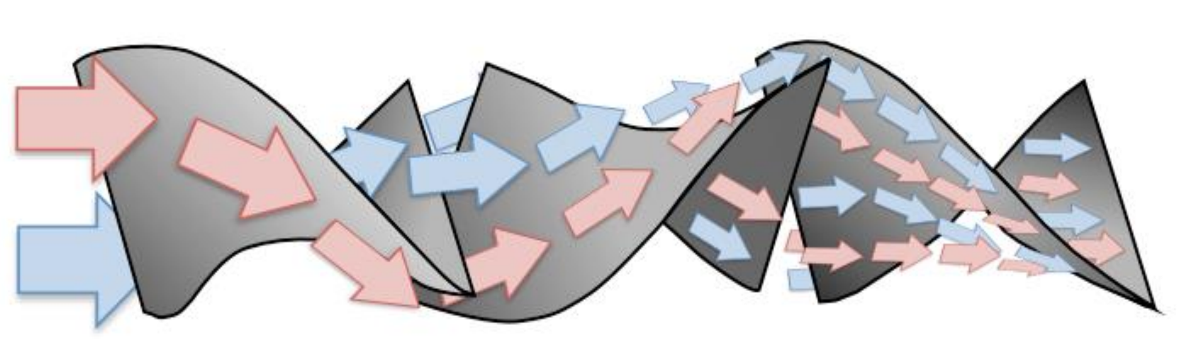
- Homogenous crystal shape and size is achieved in the different reactor size
- Design of Experiment was pursued to control and target particle size, the response surface model was used to create a mapping of the particle target
- Experiments were carried out with a Vapourtec R-Series kit equipped with different reactors
- A 1 mm bore open-tubing reactor with a 30 mL volume



- 3 mm and 6 mm bore tubing (respectively 64 mL and 140 mL volume) equipped with static mixer

3.2 mm bore tubing reactor

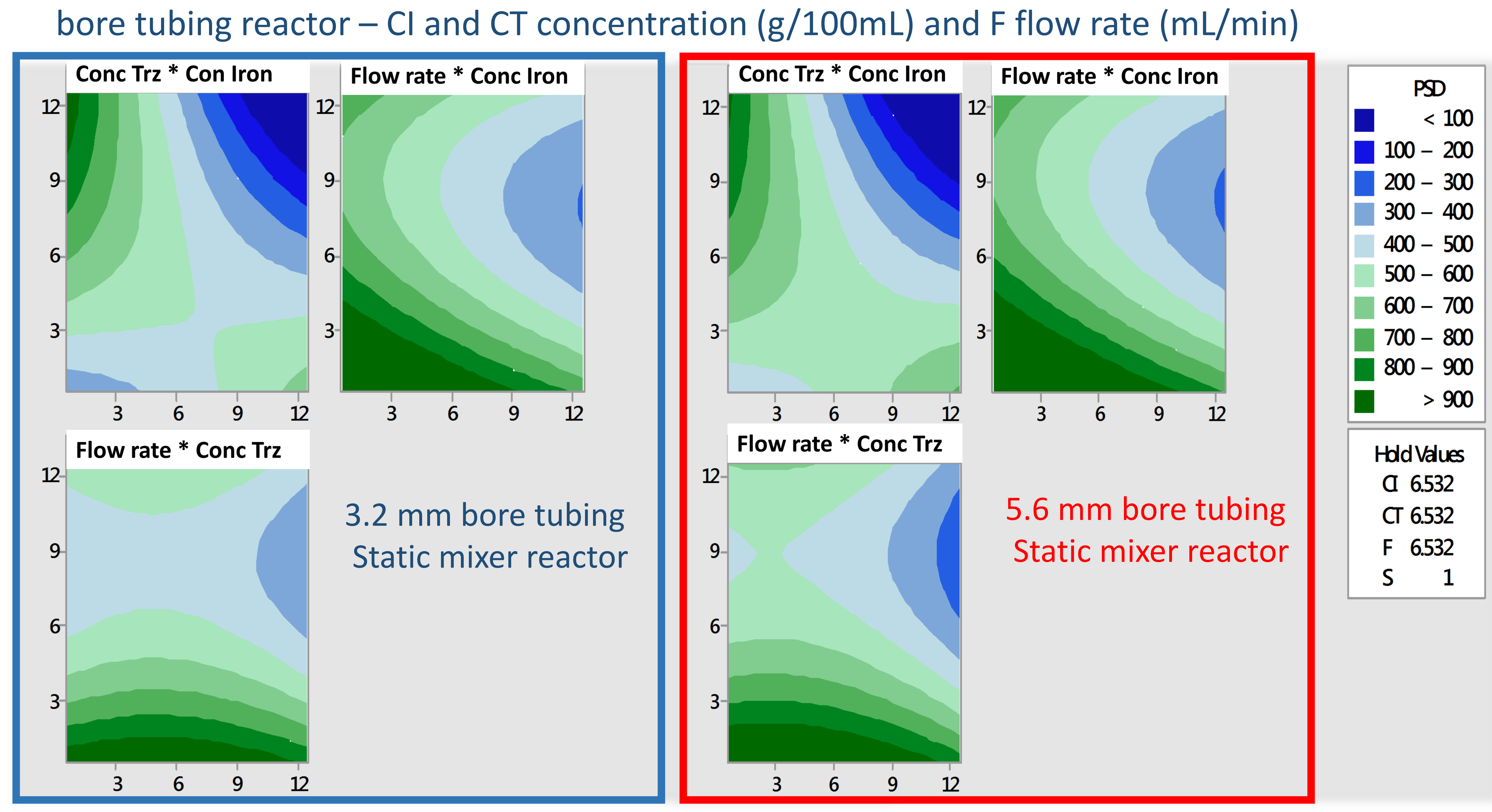
5.6 mm bore tubing reactor

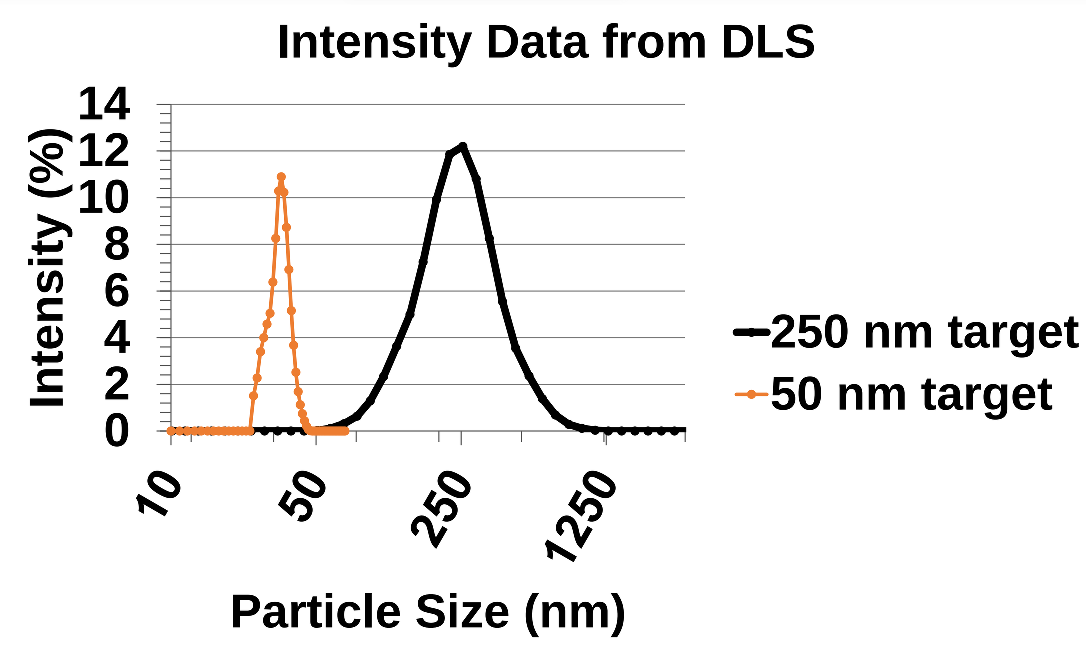


Flow division inside the reactor due to helicoidal static mixers

Particle size targeting with DOE

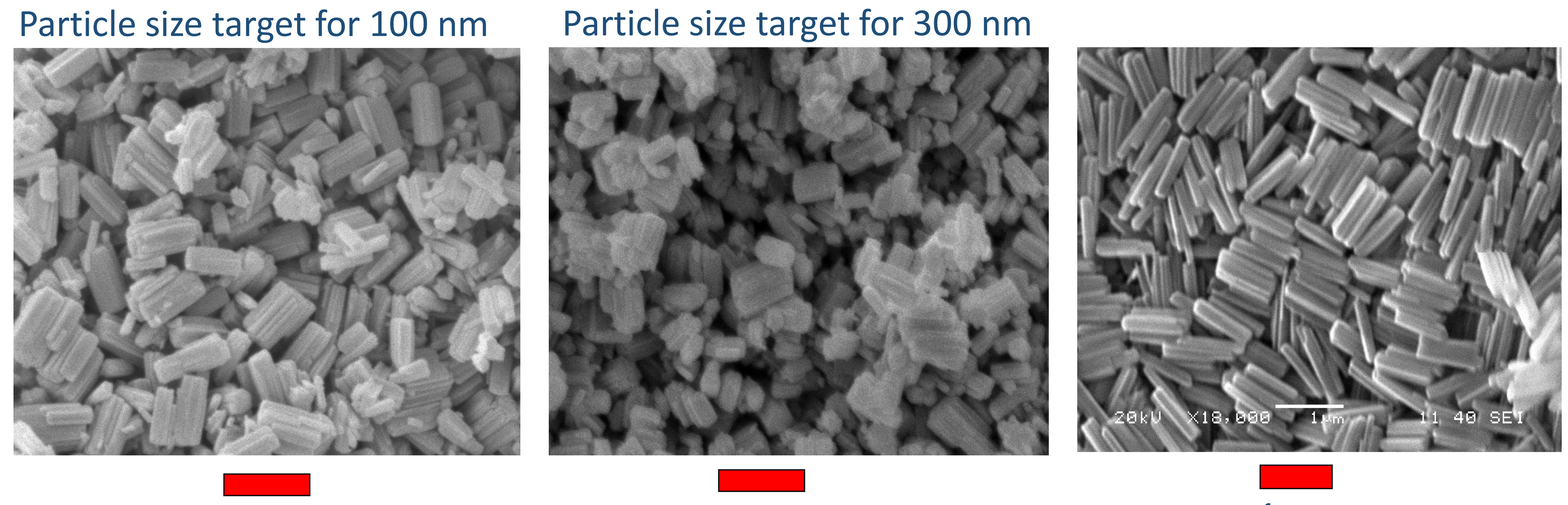
- DOE was employed with 40 experiments on 2 different reactors with static mixers (3.2 mm and 5.6 mm bore tubing).
  - 4 Factors were used; three continuous factors – concentration $Fe(BF_4)_4{\cdot}6H_2O$, concentration of Htrz and flow rate; one categorical 2 level factor – size of reactor (3.2 or 5.6 mm bore)
- The software Minitab® was used in order to create surface response plots of the variables to target a range of different particle size
  - Mapping of the particle size average distribution(PSD) of the 3.2 mm (left) and 5.6 mm (right) bore tubing reactor – CI and CT concentration (g/100mL) and F flow rate (mL/min)





Particle size target for 100 nm

Particle size target for 300 nm



100 nm

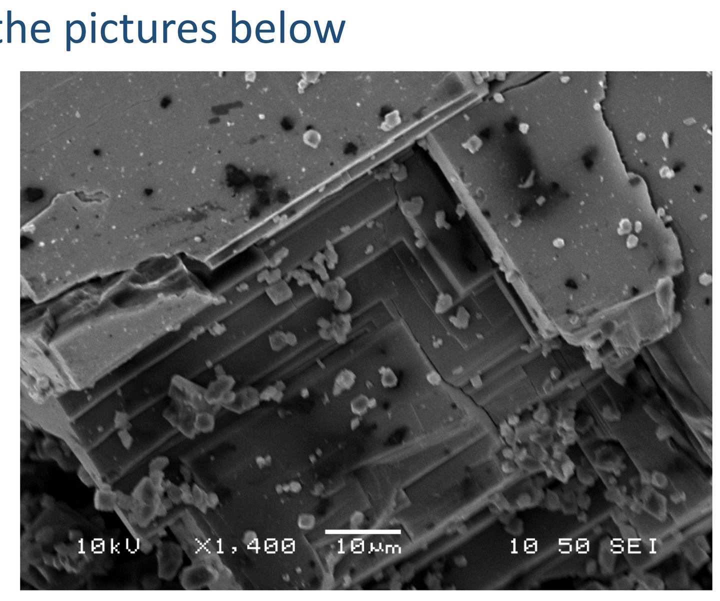
200 nm

1 µm

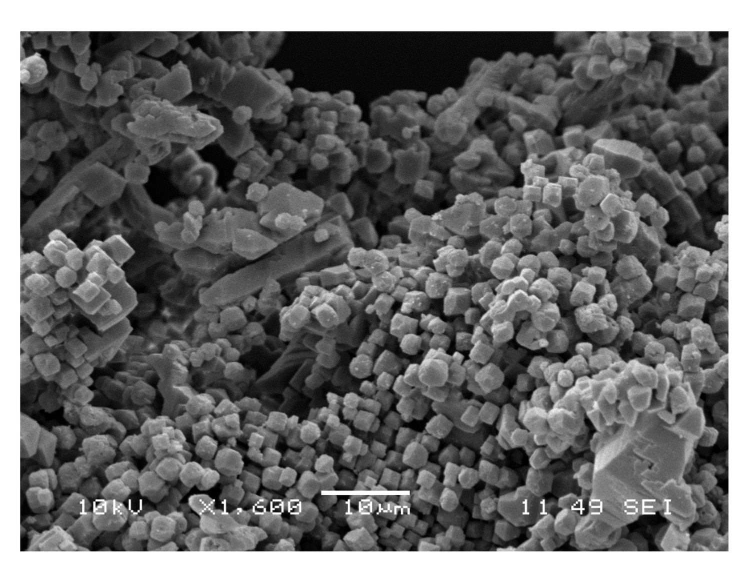
SEM for 3.2 mm (left), 5.6 mm (center) bore tubing with static mixers and 1 mm tubing (right)

Future Work

- Investigating other SCO compounds to see their magnetic behaviour depending on their particle size
- The anti-solvent precipitation reaction *via* diethyl ether of $Fe(BF_4)_2{\cdot}6H_2O$ with 2,6-Bi(pyrazol-1-yl)-pyridine (1-BPP) gives $[Fe(1\text{-}BPP)_2][BF_4]_2$ was achieved with a tube-in-tube reactor consisting of a perforated PFA inner tubing and a PFA outer tubing
- The solution produced is flowed through the inner tube and precipitate out in the outer tubing after entering in contact with diethyl ether *via* the perforated holes
- Initial results show a large improvement in particle size distribution compare to batch as shown on the pictures below



10 µm



Particles from batch (left) and tube-in-tube reactor from Vapourtec (right)

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