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Switchable Molecular Chain Composites: Probing Metal-to-Metal Electron Transfer and Multifunctionality

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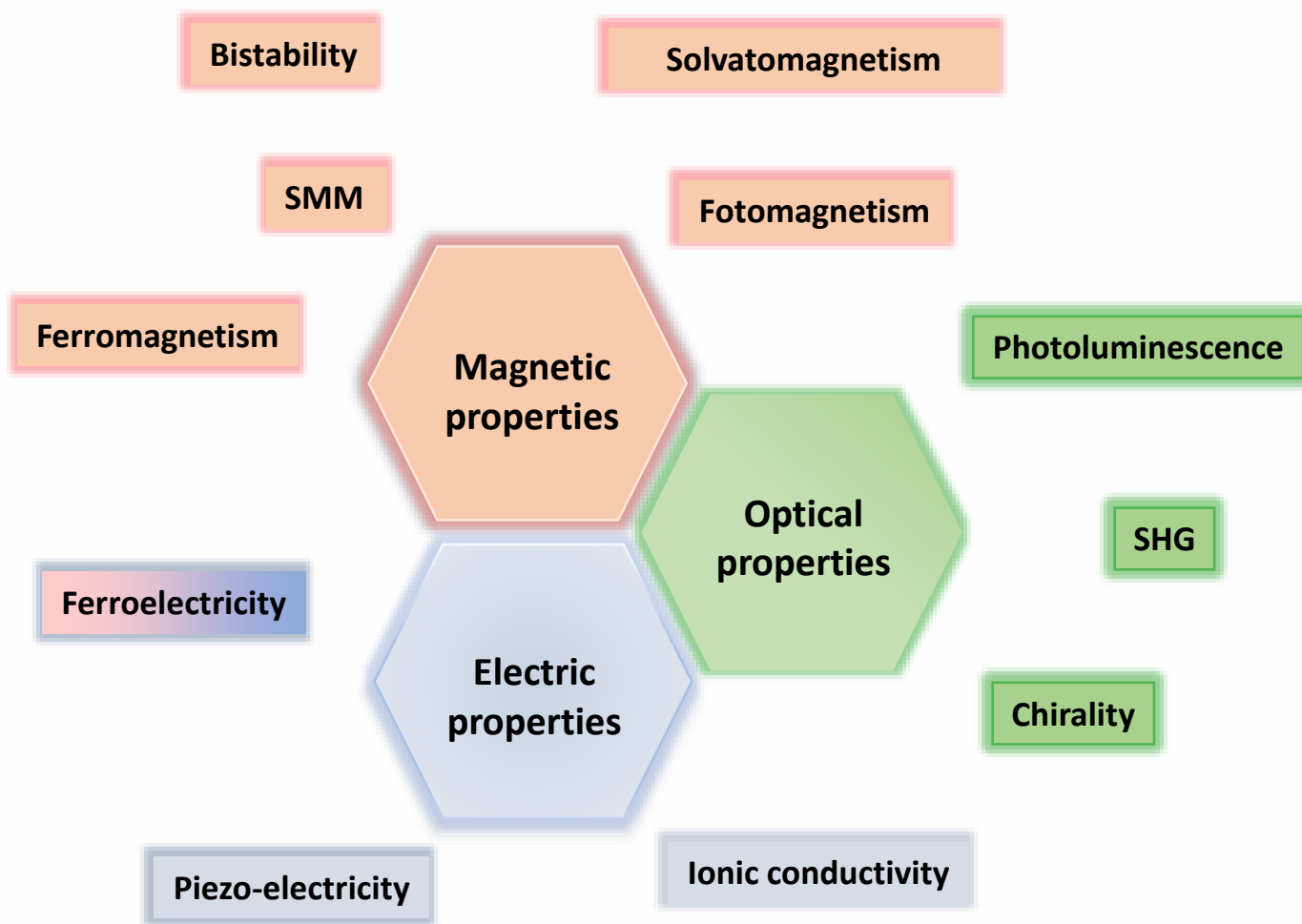
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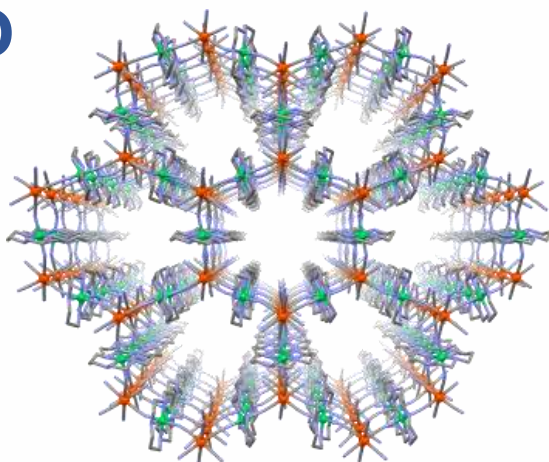
Coordination polymers as molecular functional materials





MMCT chain – $\text{NH}_4[\text{Ni}(\text{cyclam})][\text{Fe}(\text{CN})_6] \cdot 5\text{H}_2\text{O}$

2D

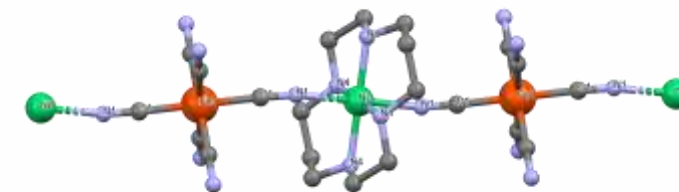
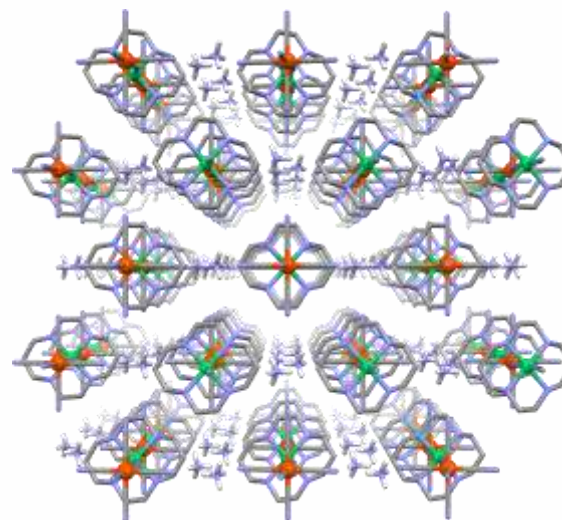


NH_4Cl
solution



time

1D



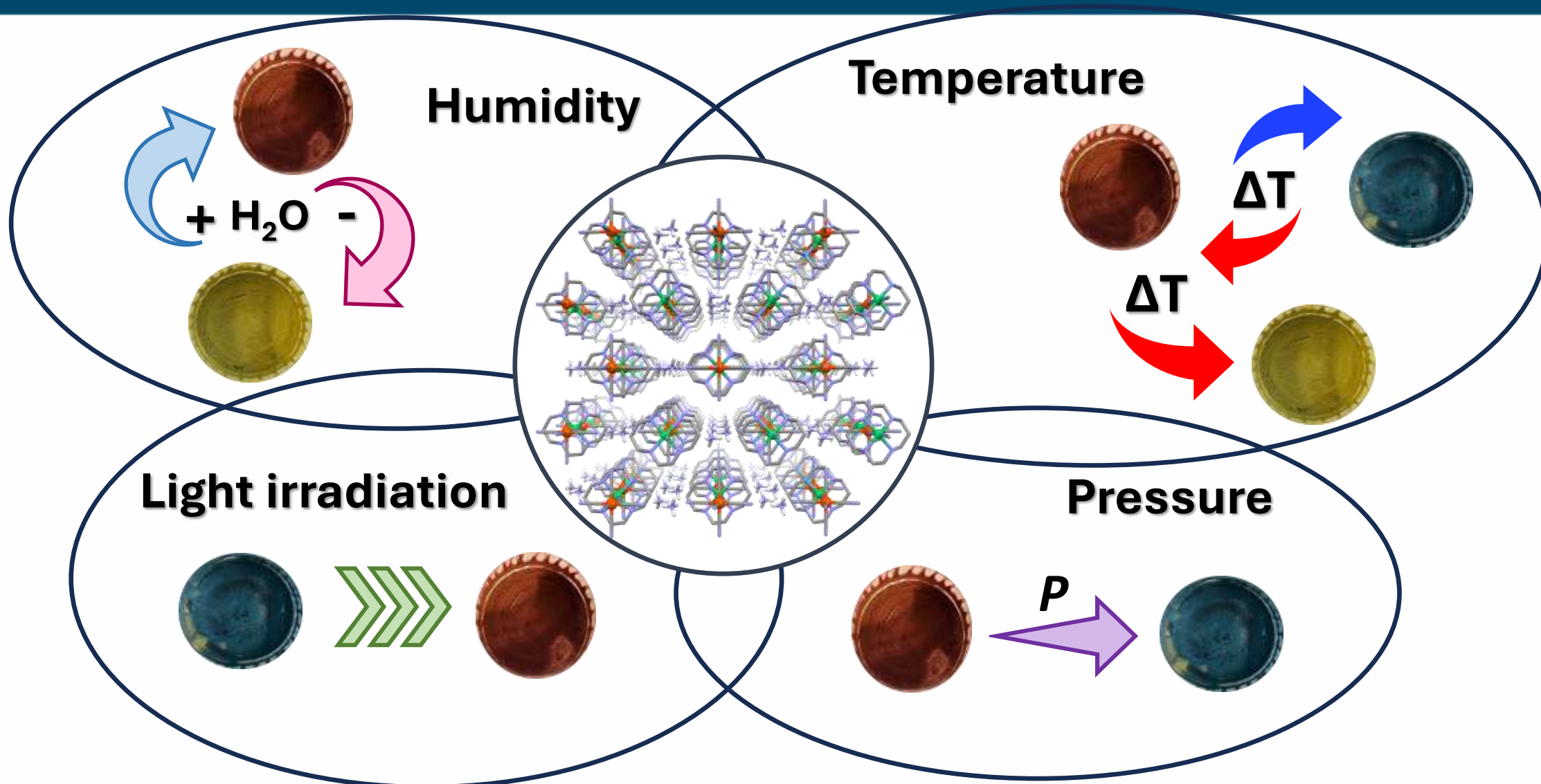
- Switchable structure by varying humidity at RT
- Observed changes in magnetic behaviour below 10K



- Three phases stable at certain temp. and humidity conditions
- multiresponsiveness
- operating at RT
- Fragile and easily disintegrating crystals
- quickly recrystallises in water

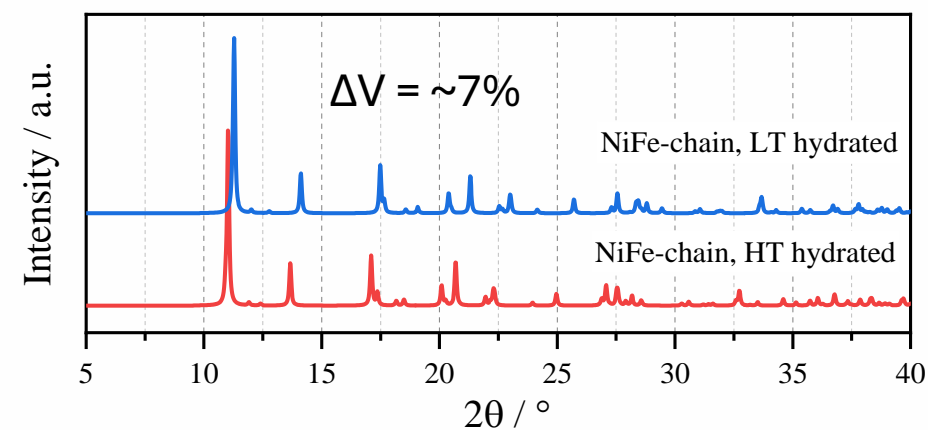
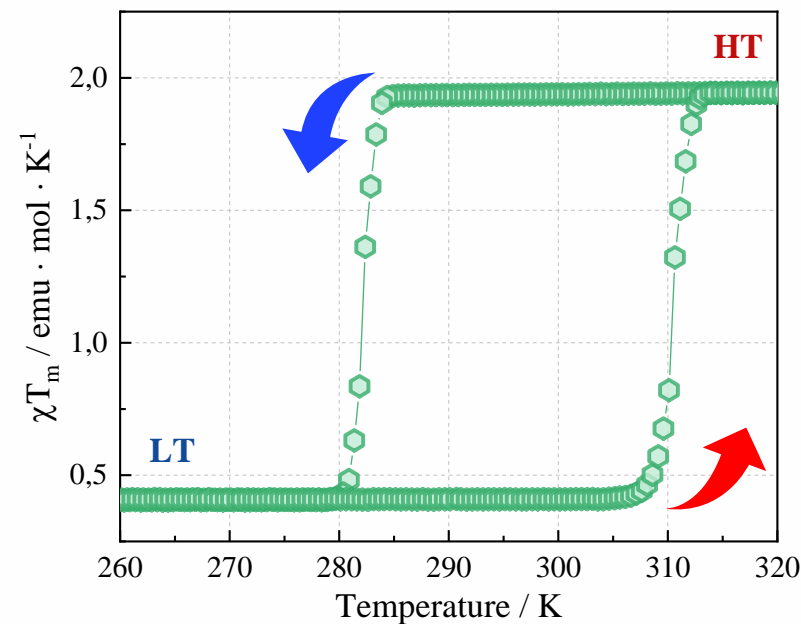
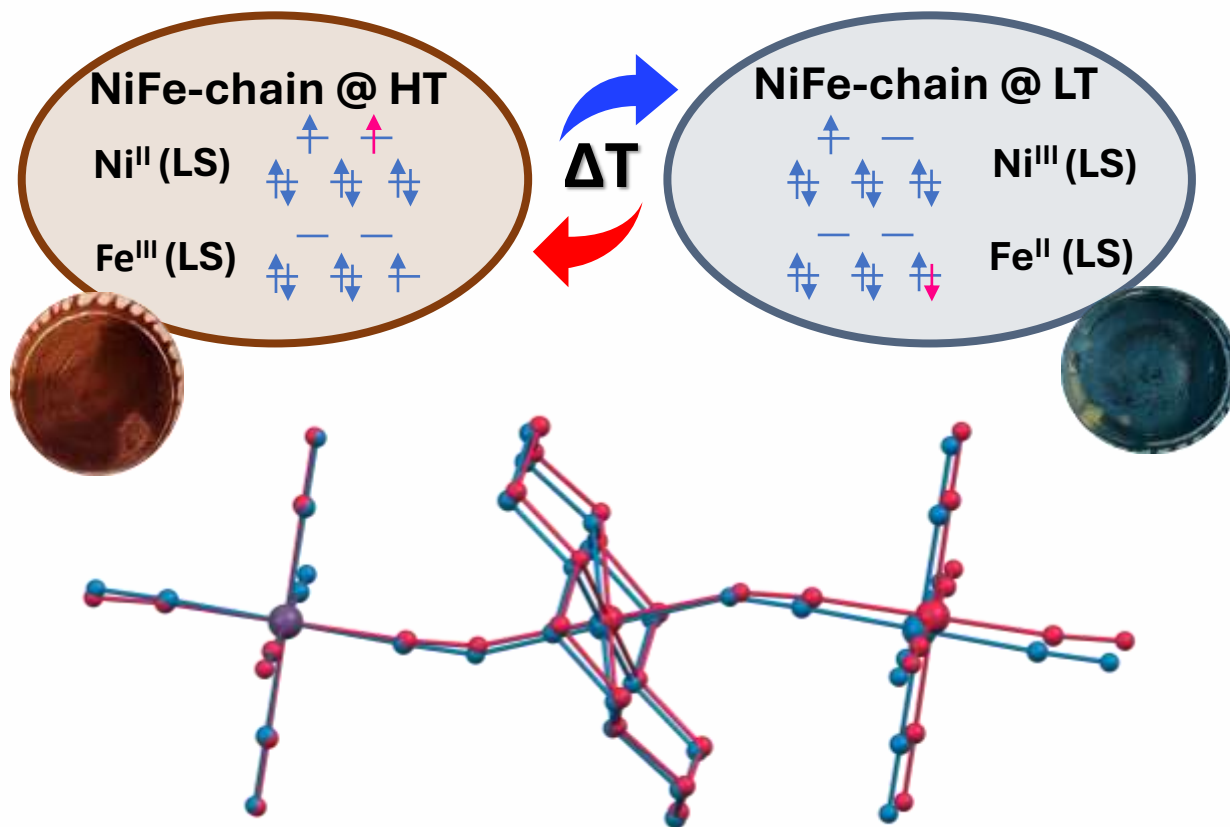


NiFe-chain – external stimuli



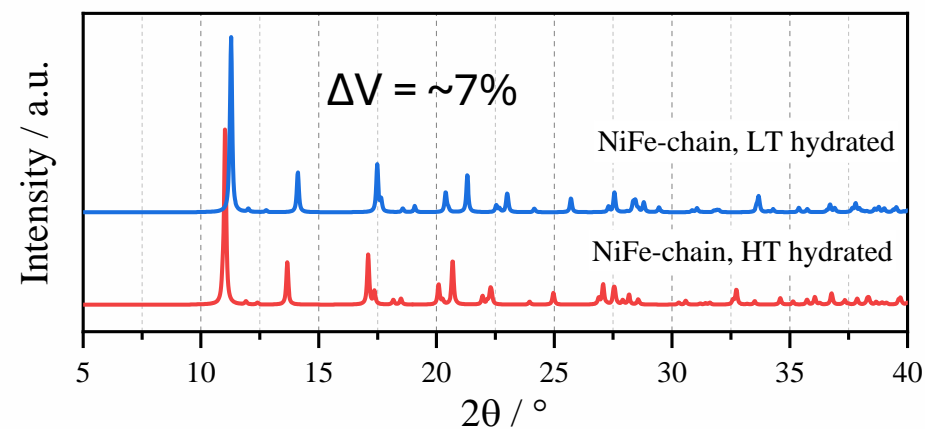
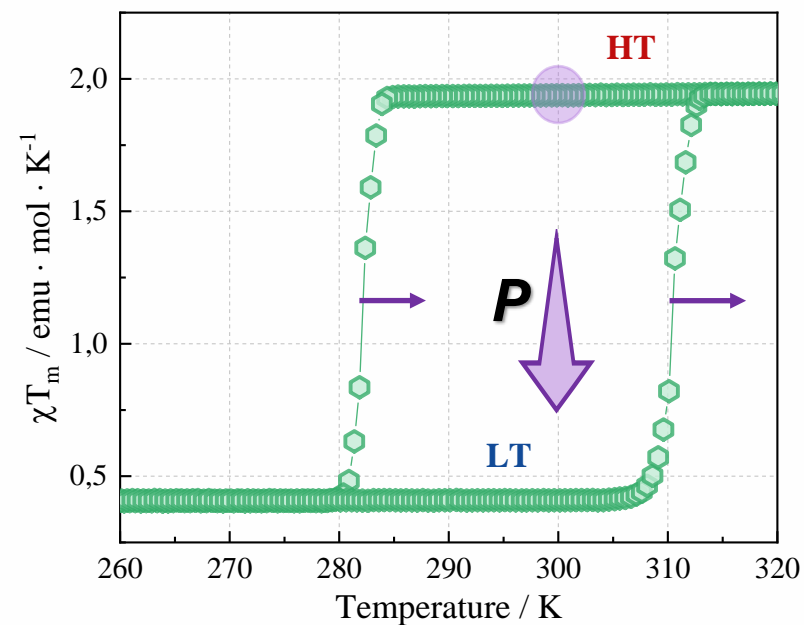
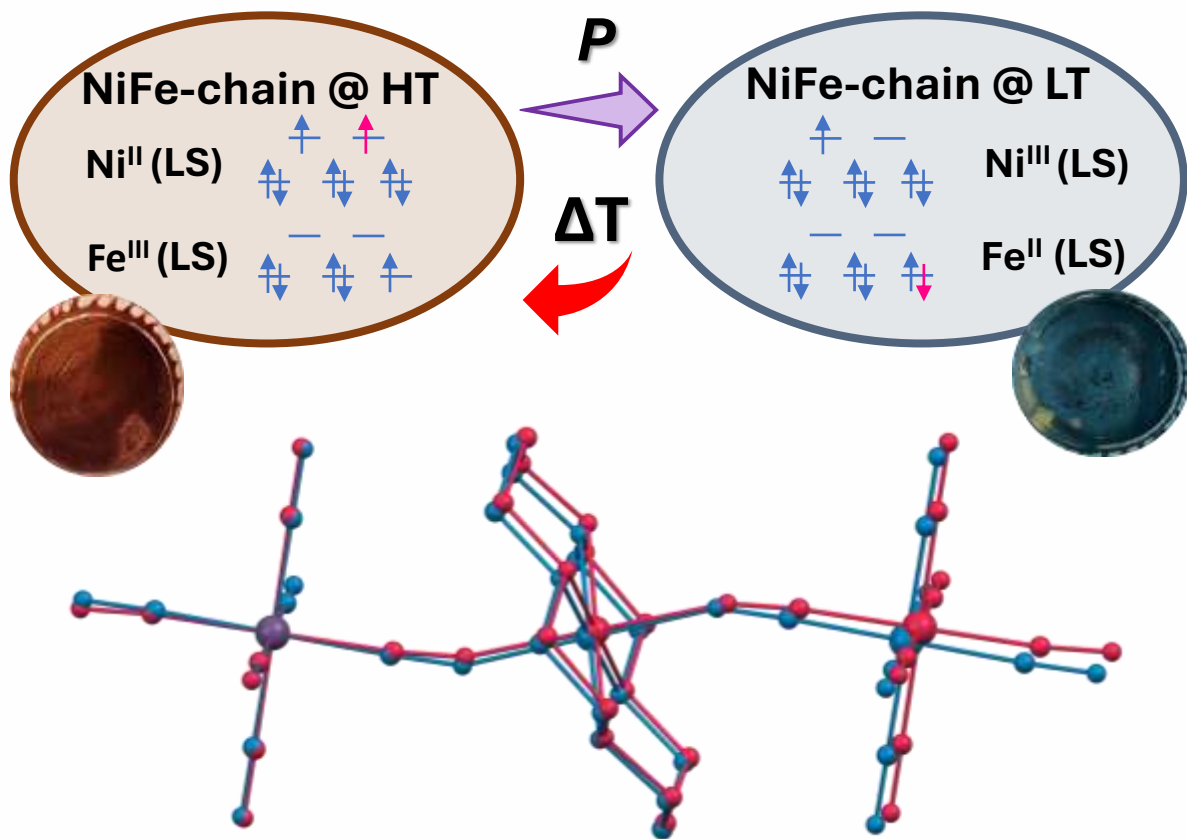


NiFe-chain – MMCT active phases



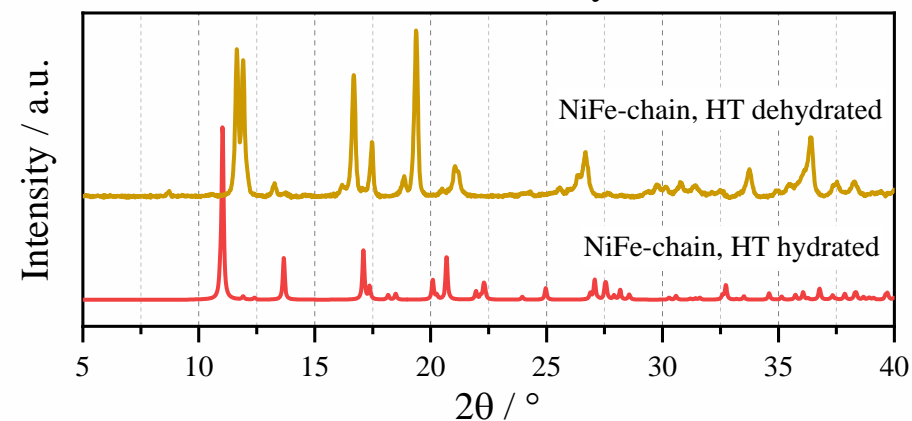
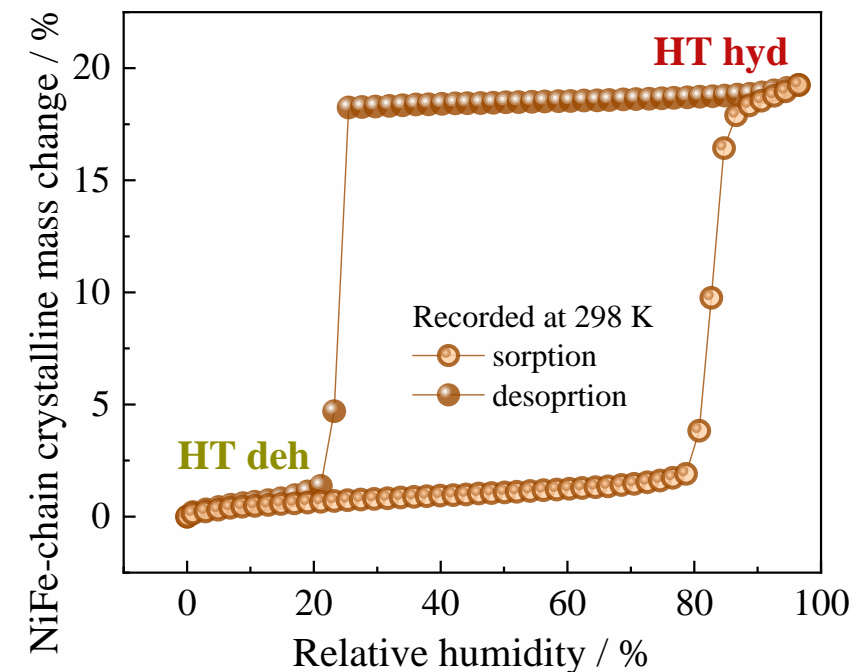
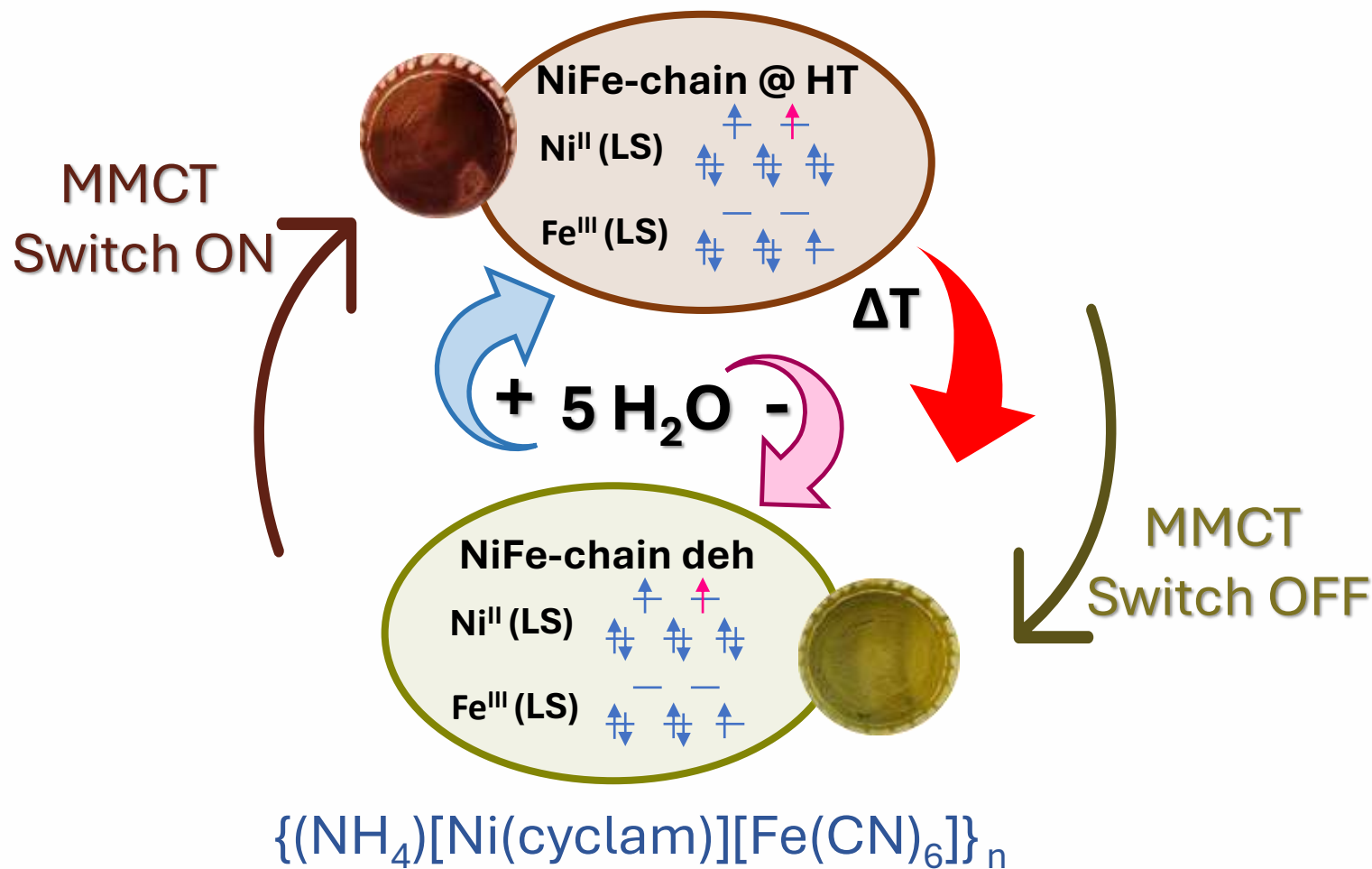


NiFe-chain – MMCT active phases



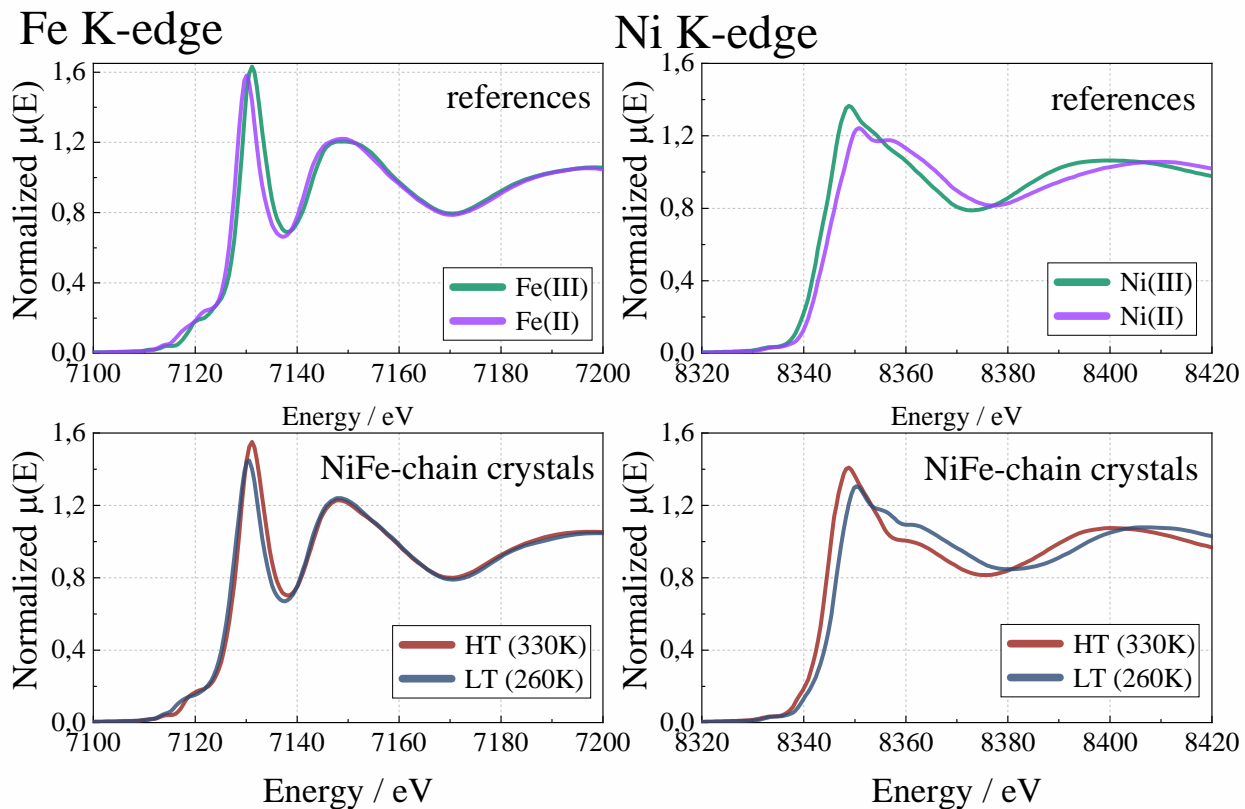


NiFe-chain – MMCT ON/OFF

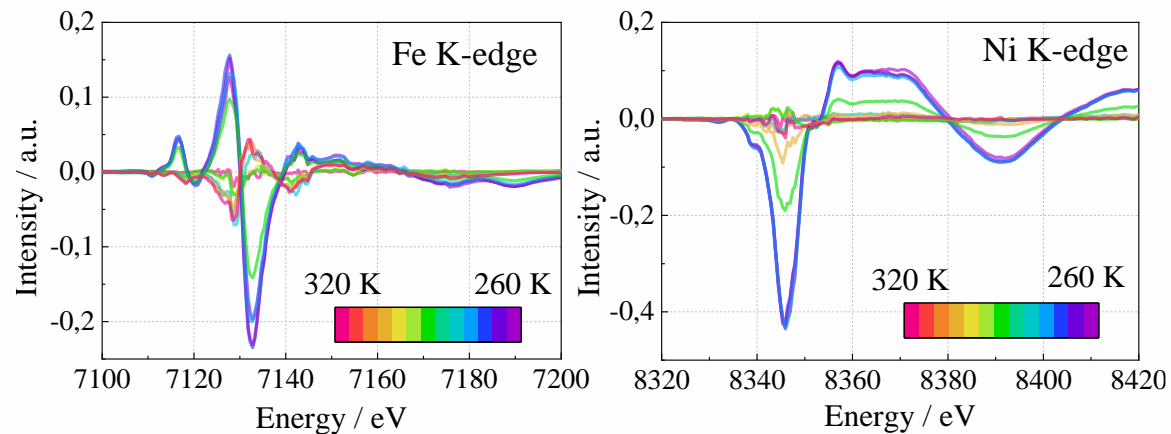
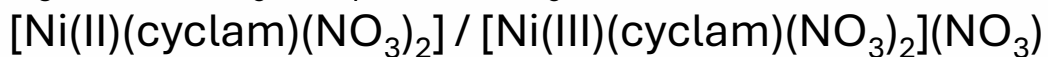
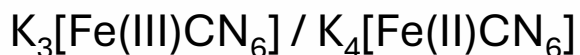




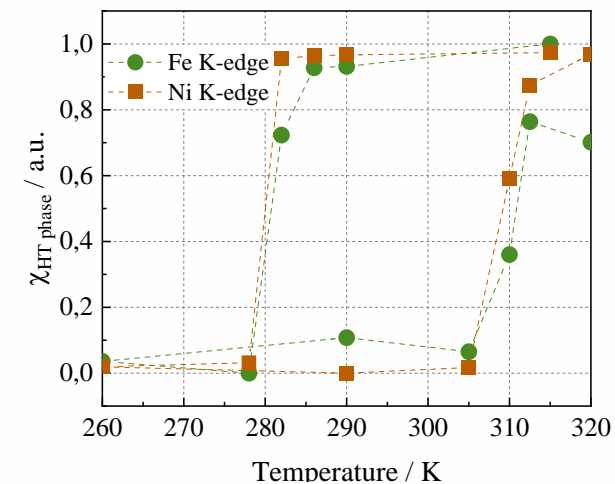
NiFe-chain MMCT – XANES studies



References:

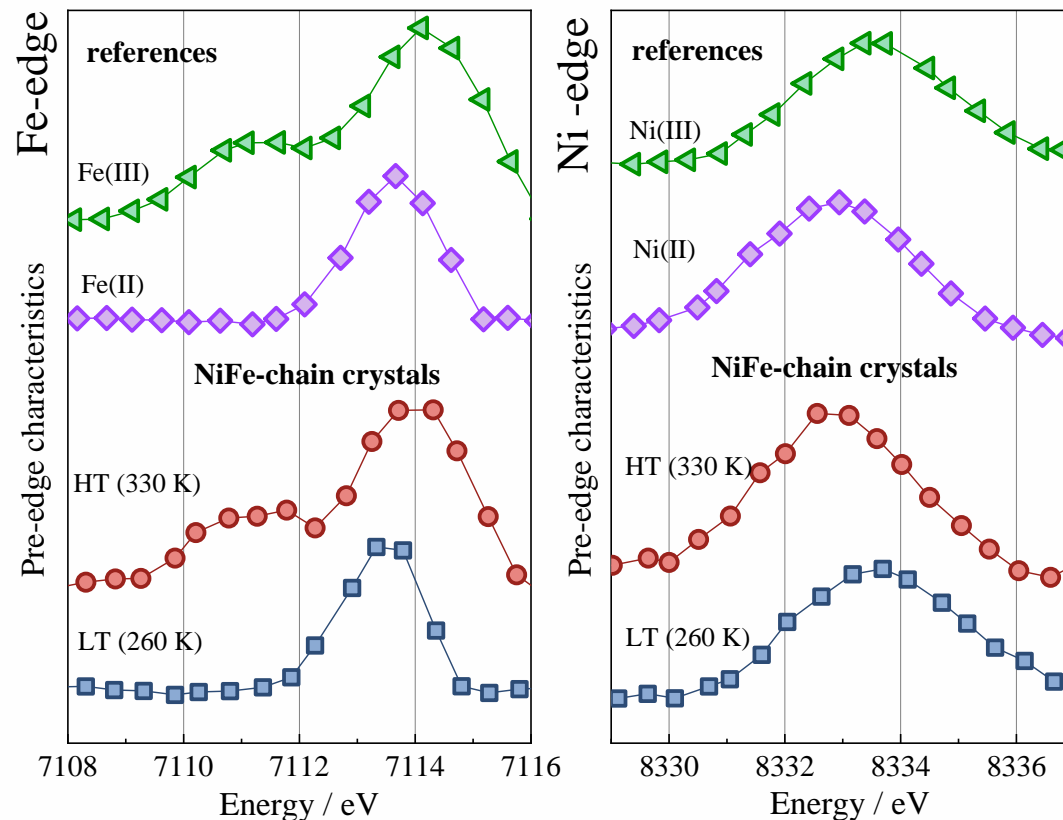
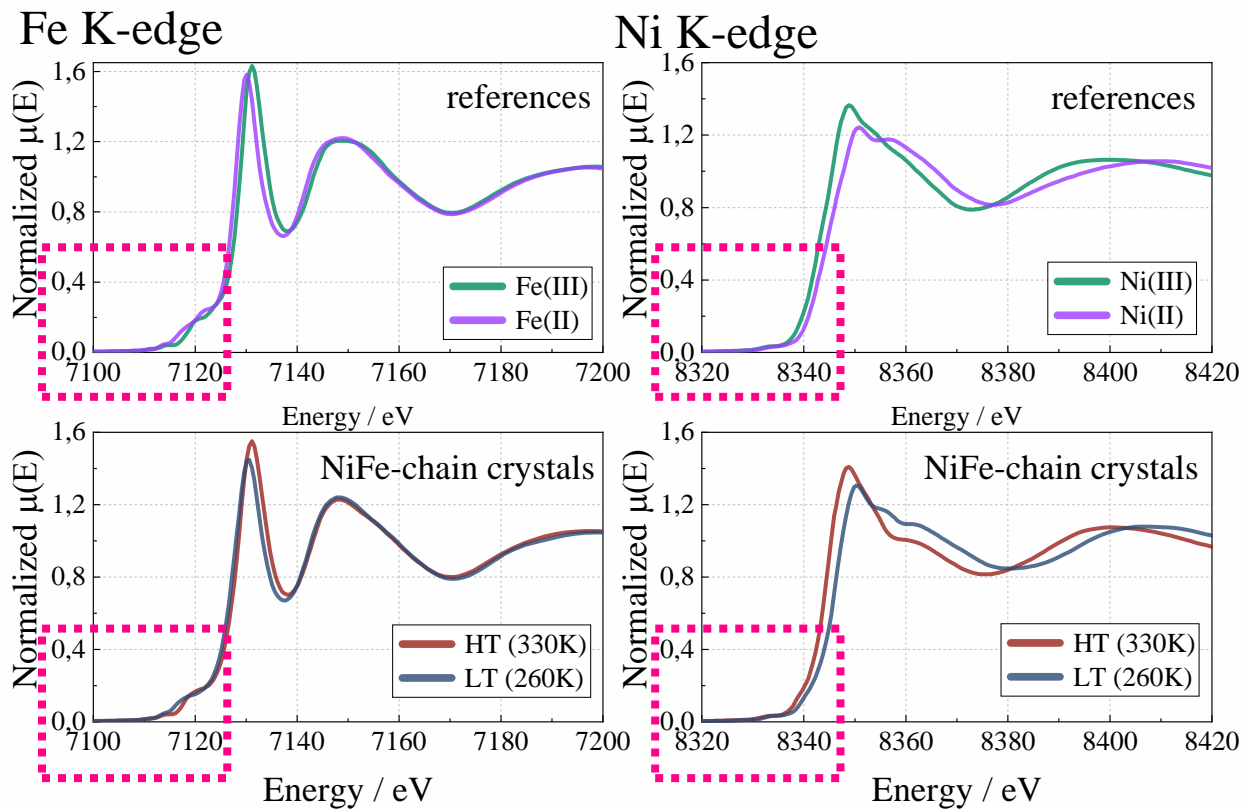


$$\chi_{HT\ phase} = \frac{(A_T - A_{LT})}{(A_{HT} - A_{LT})}$$





NiFe-chain MMCT – XANES studies

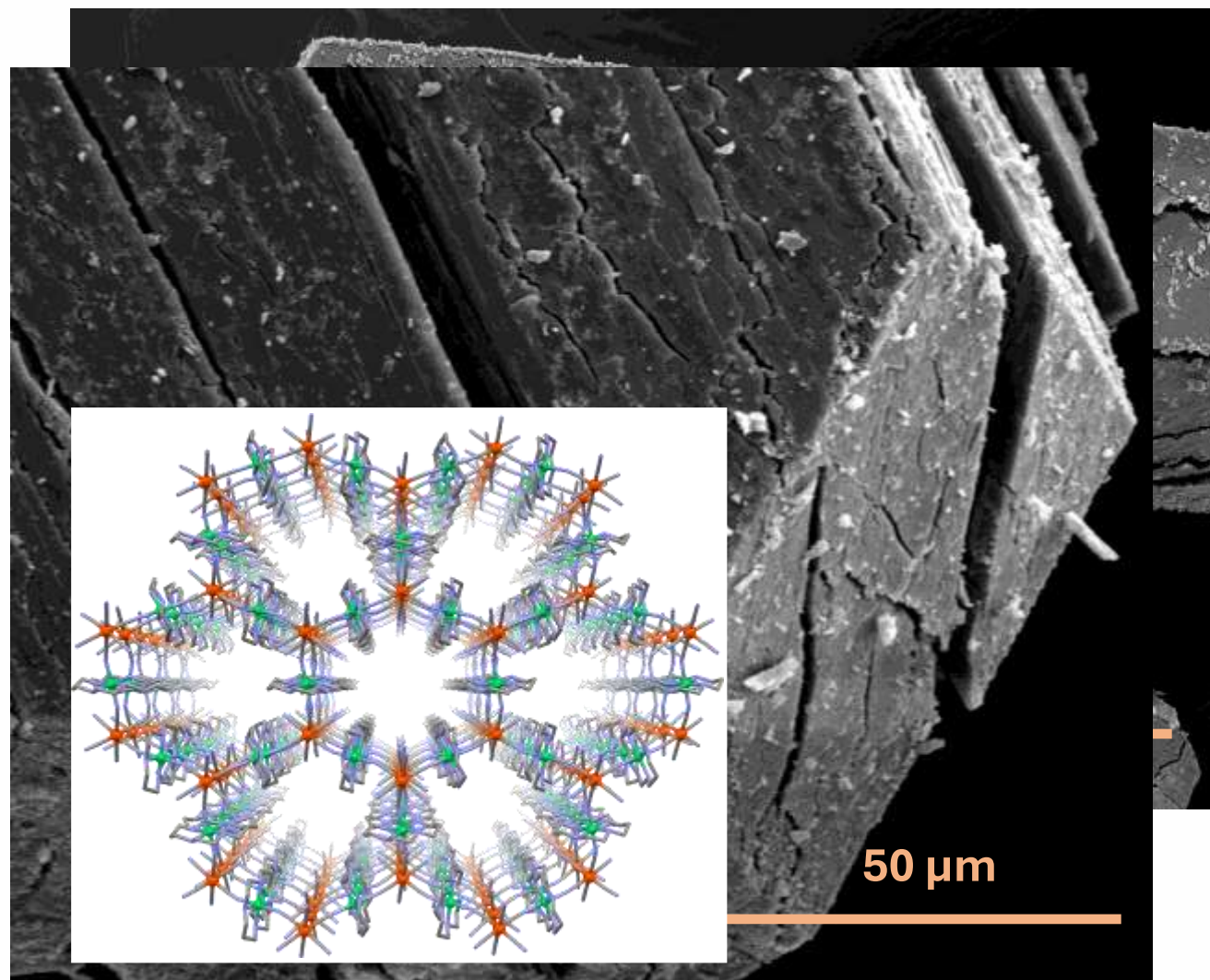




Limitations of NiFe-chain crystals

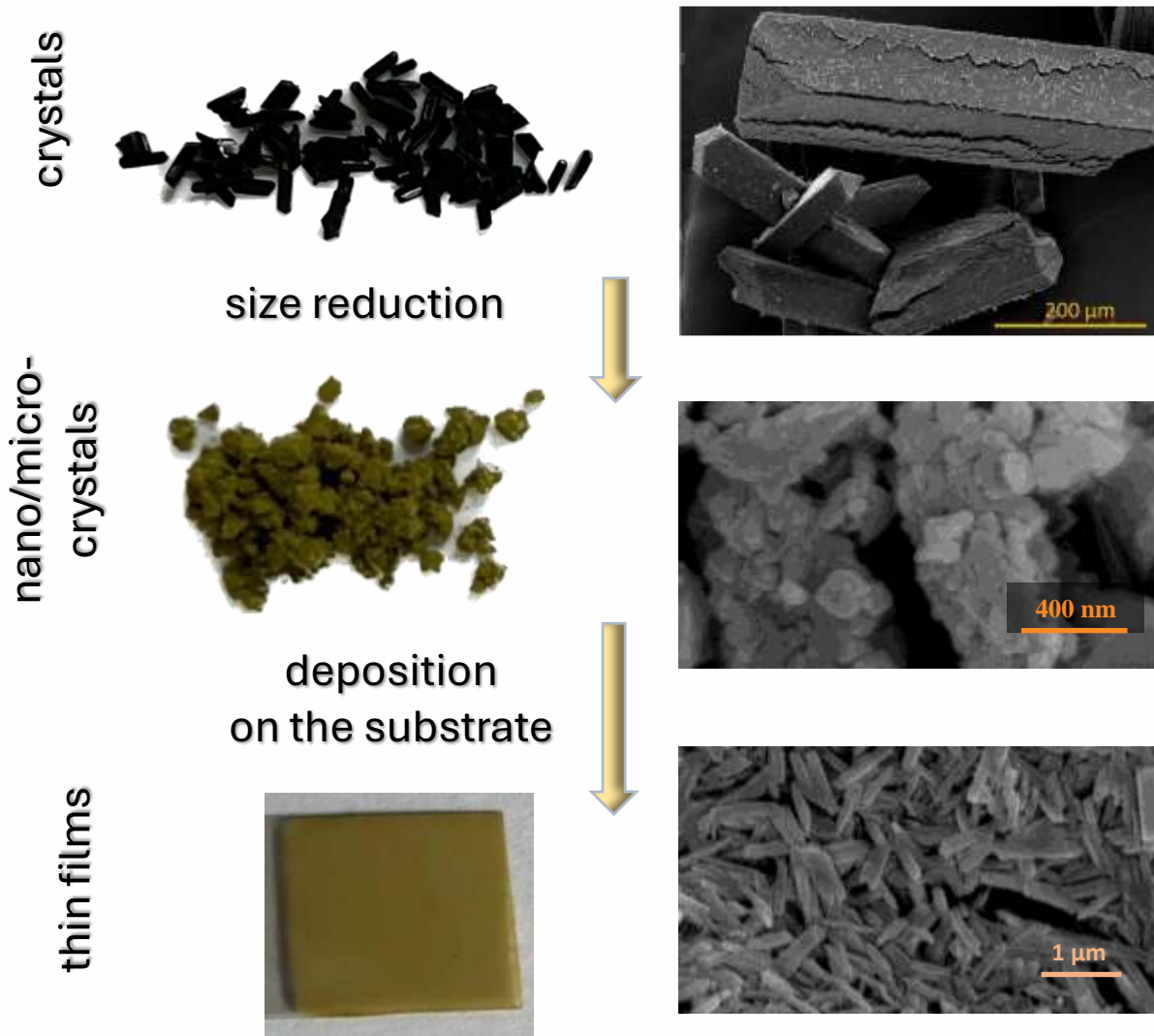


- Crystals collapse in the 1st thermal cycle
- When heated over 40°C or placed in vacuum crystal dehydrate and disintegrate
- Quickly recrystalizes in water/alcohol





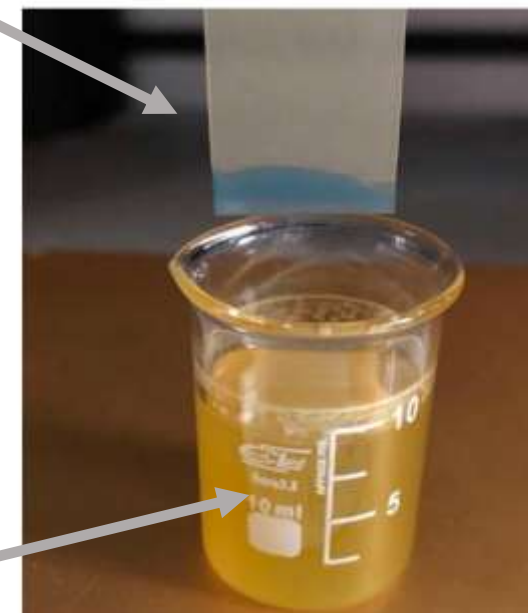
MMCT thin films preparation



Dip-coating deposition

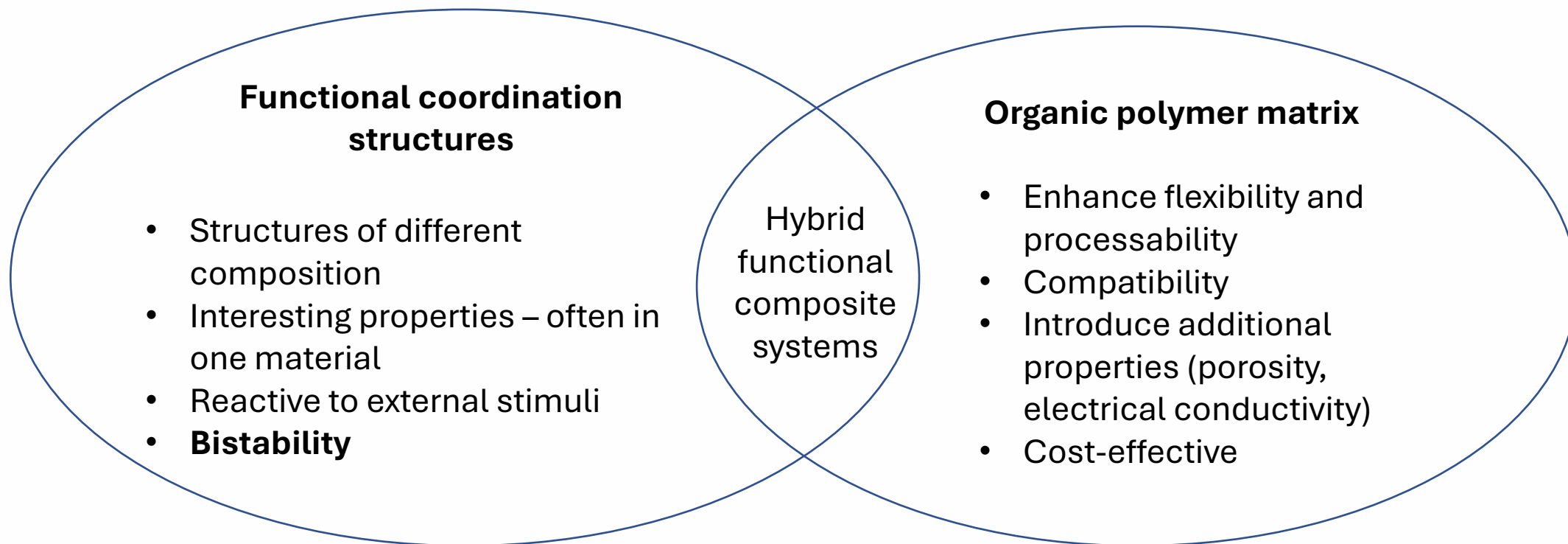
Thin film deposited on PET/ITO surface

Suspension of MMCT material



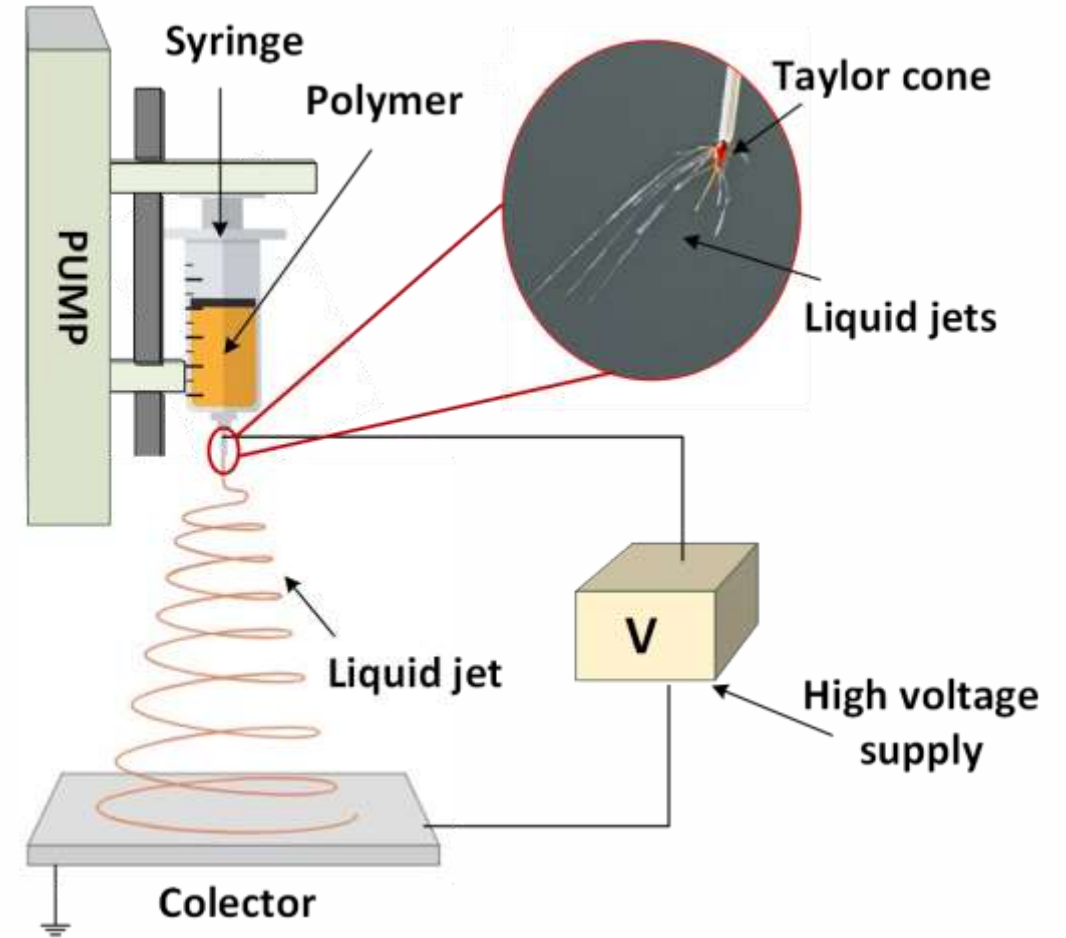
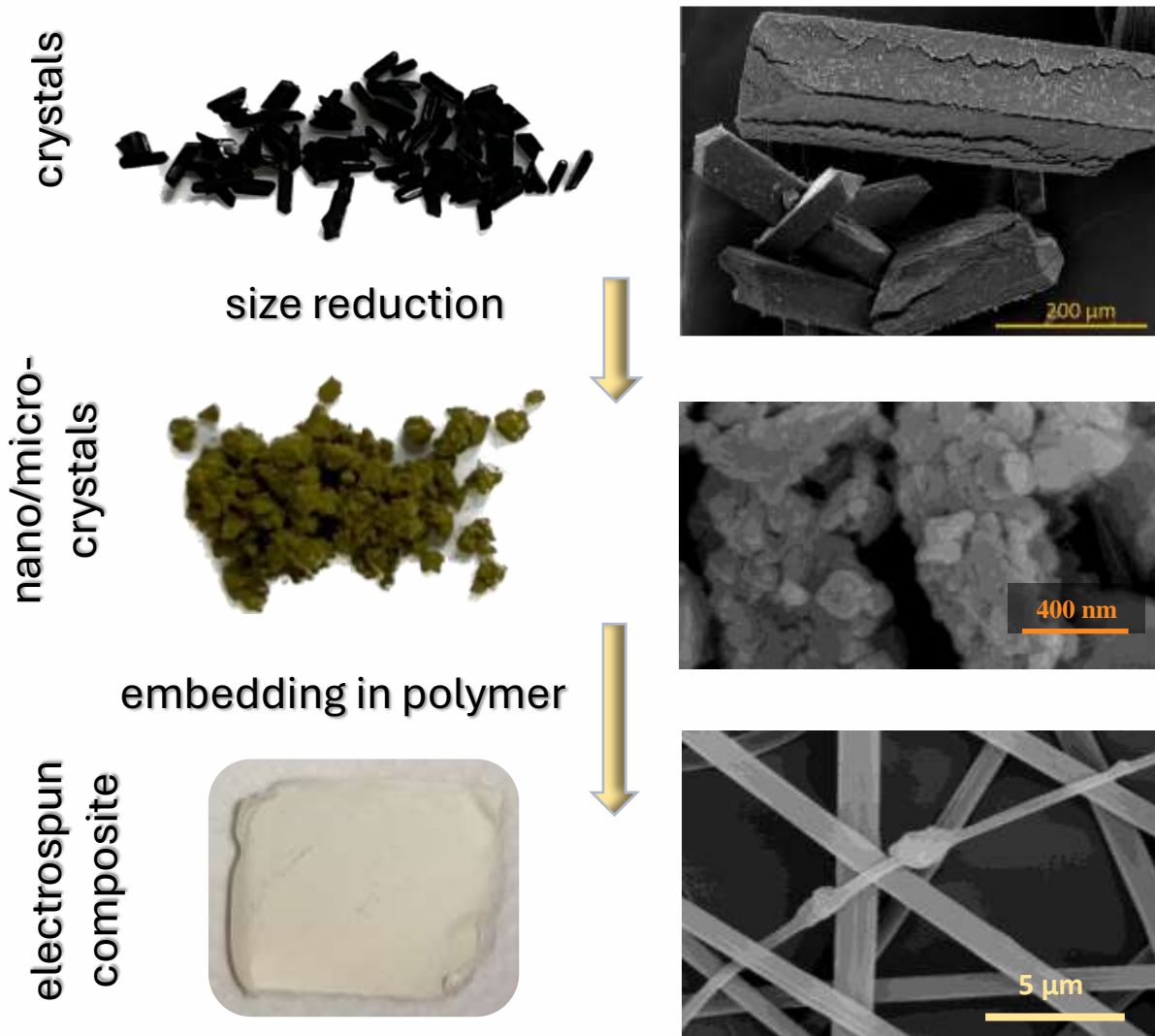


Introducing molecular materials into the flexible polymer matrix and producing composite materials





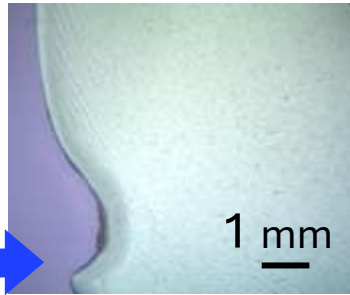
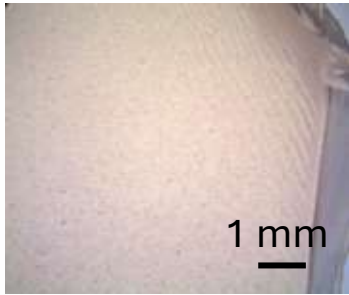
MMCT electrospun composite preparation



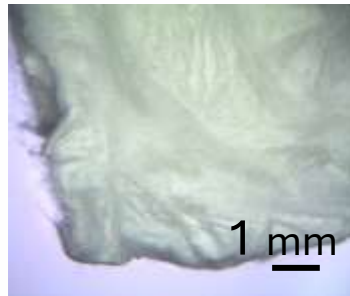
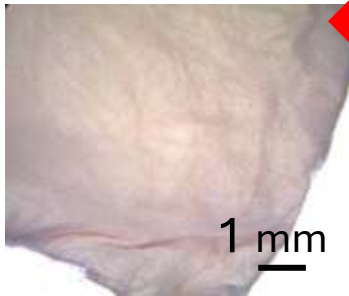


Bistability in MMCT electrospun composite

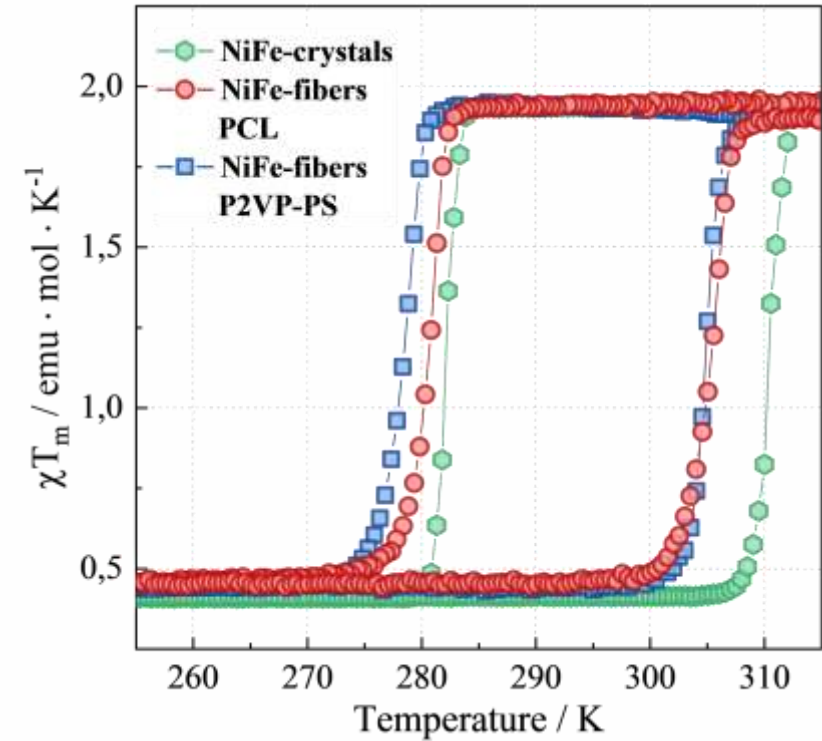
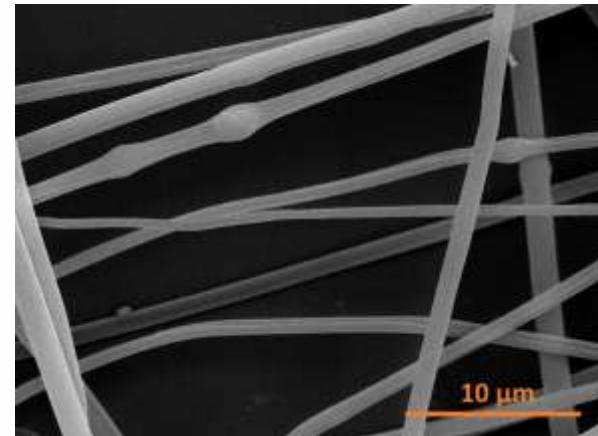
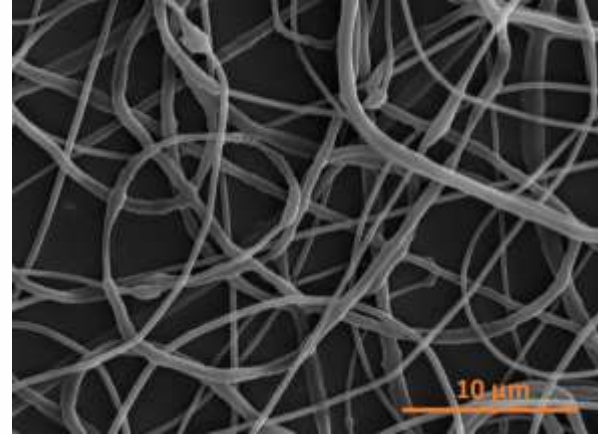
PCL fibers



P2VP-PS fibers



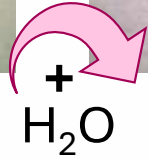
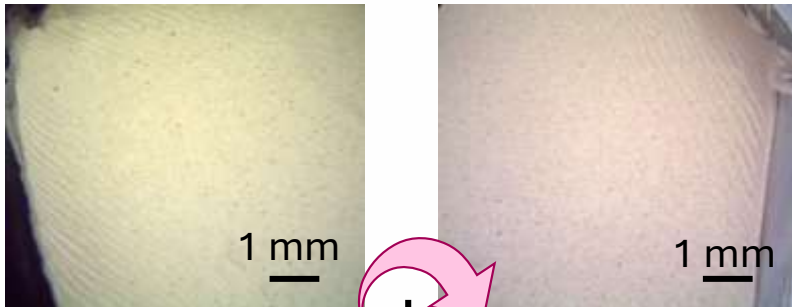
ΔT



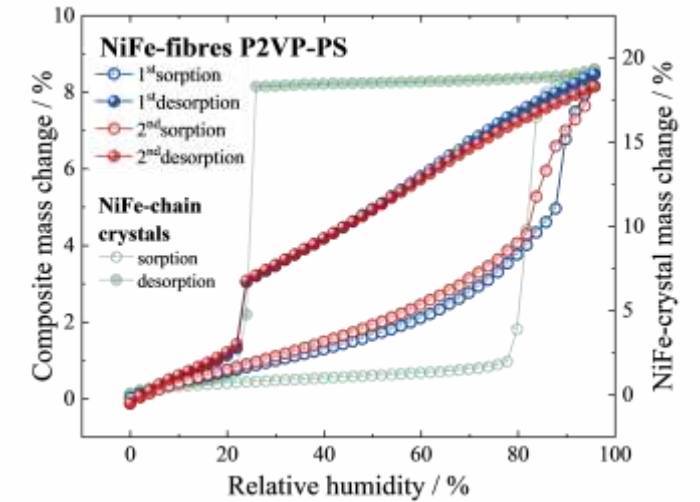
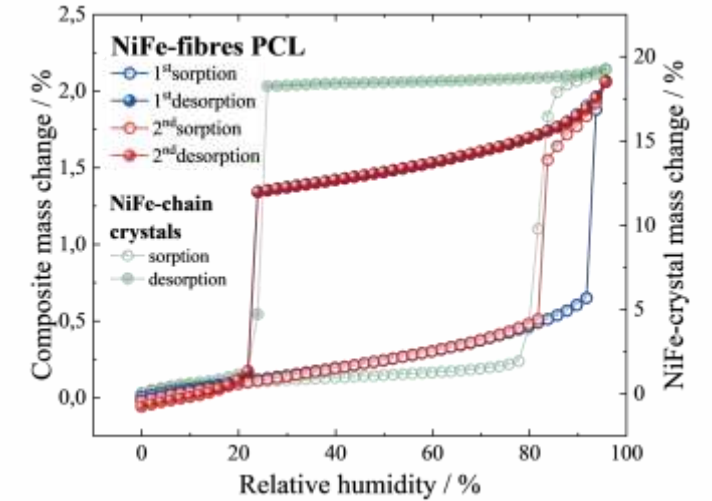
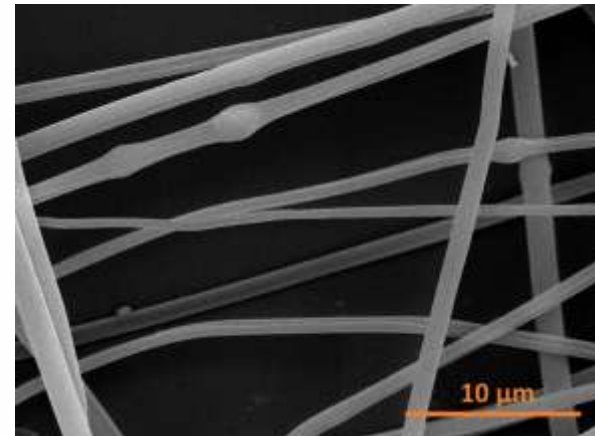
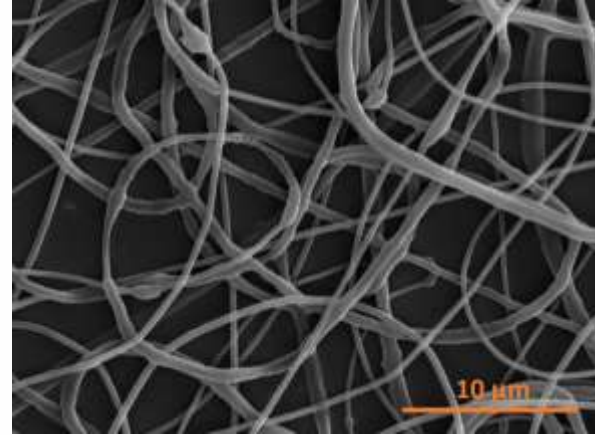


Bistability in MMCT electrospun composite

PCL fibers



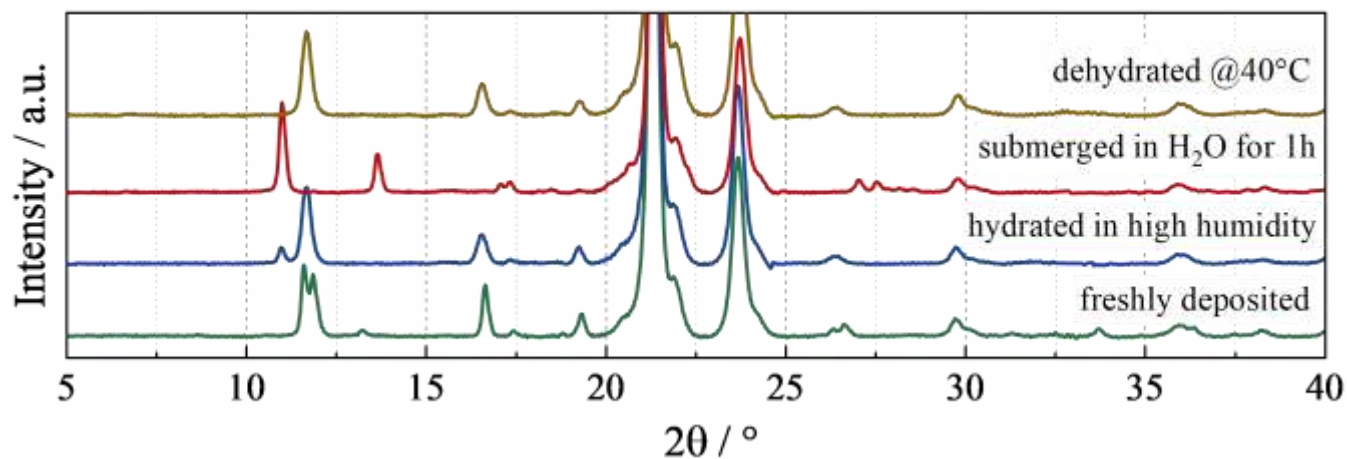
P2VP-PS fibers



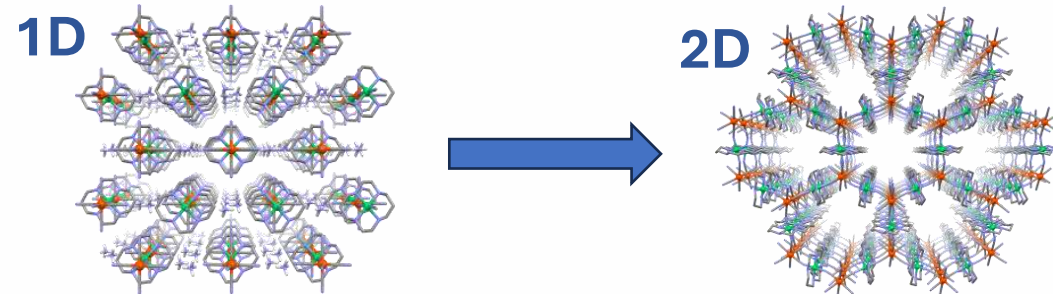
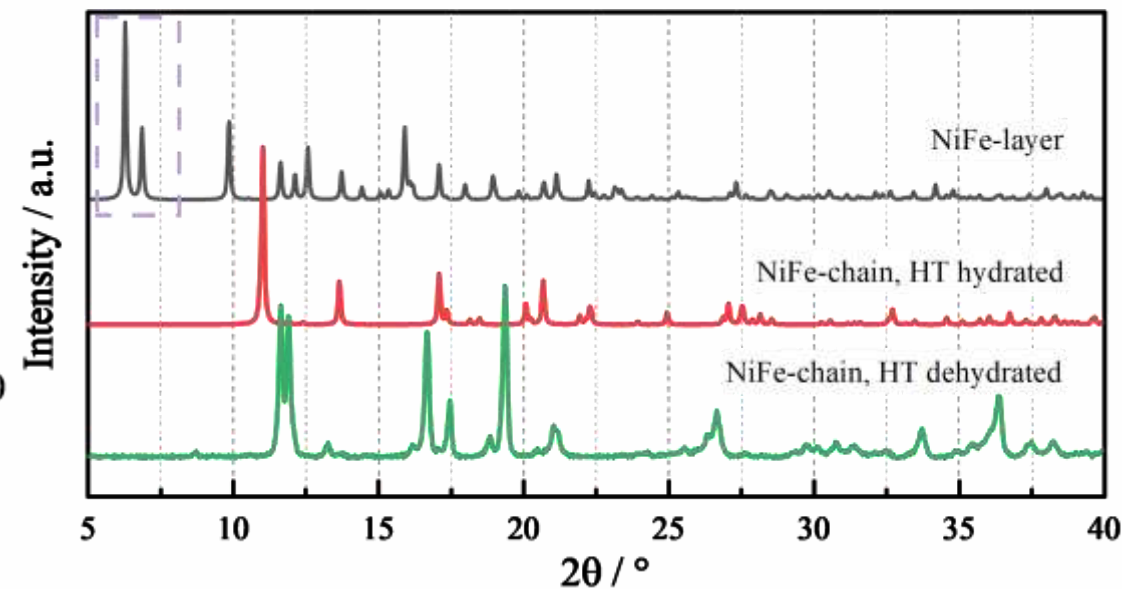
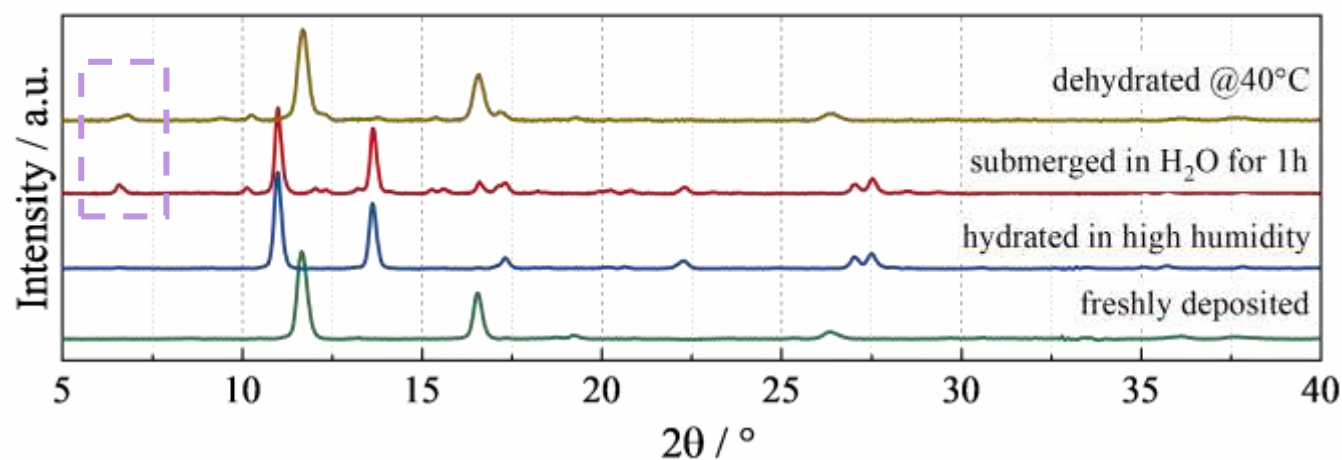


Stability of electrospun composite

NiFe-fibers PCL



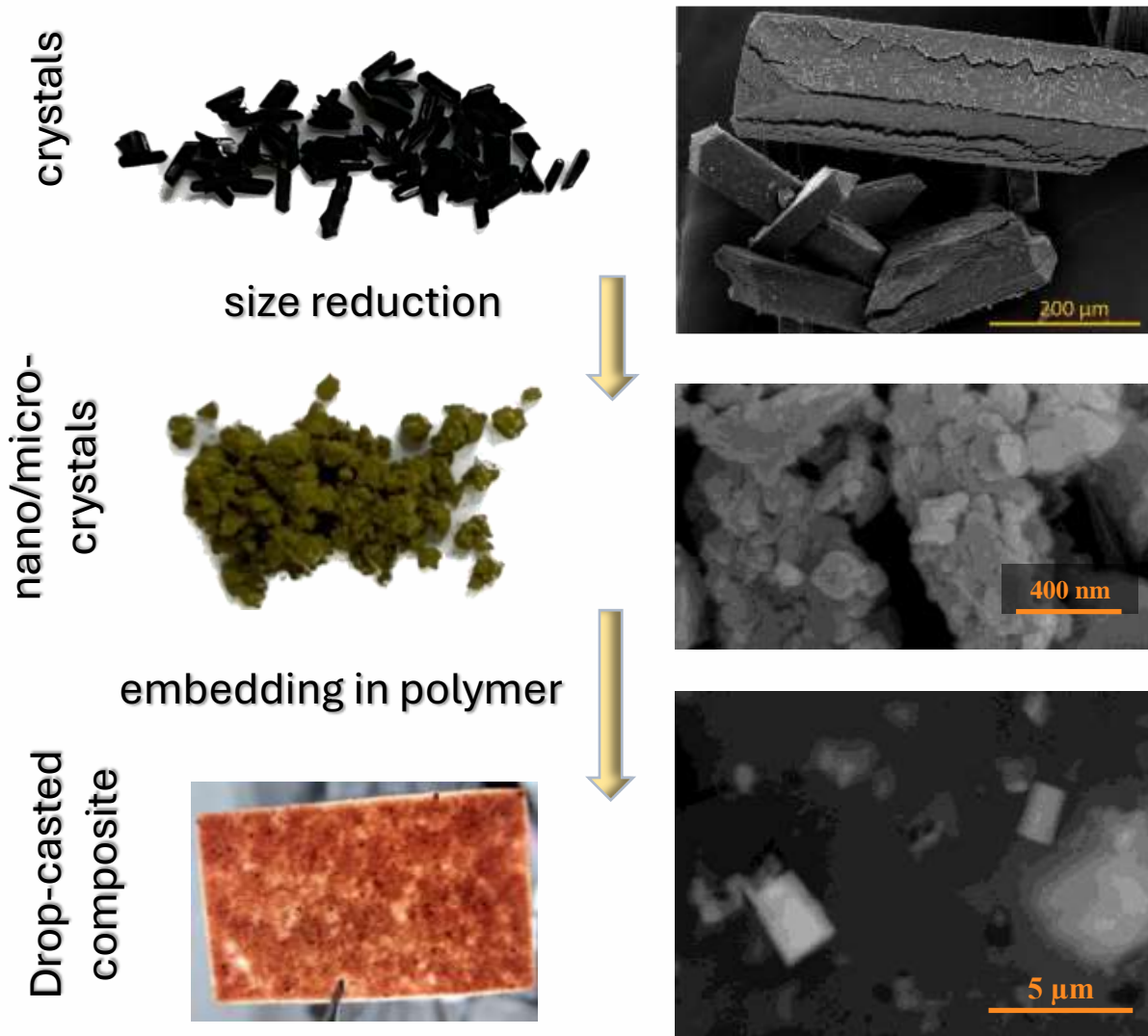
NiFe-fibers P2VP-PS



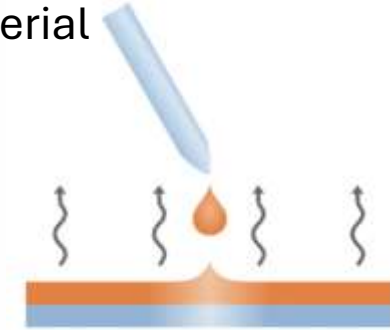
Angew. Chem. Int. Ed. 60, 2021, 2330.



MMCT composite foil preparation



Polymer suspension of MMCT material



Solvent evaporation

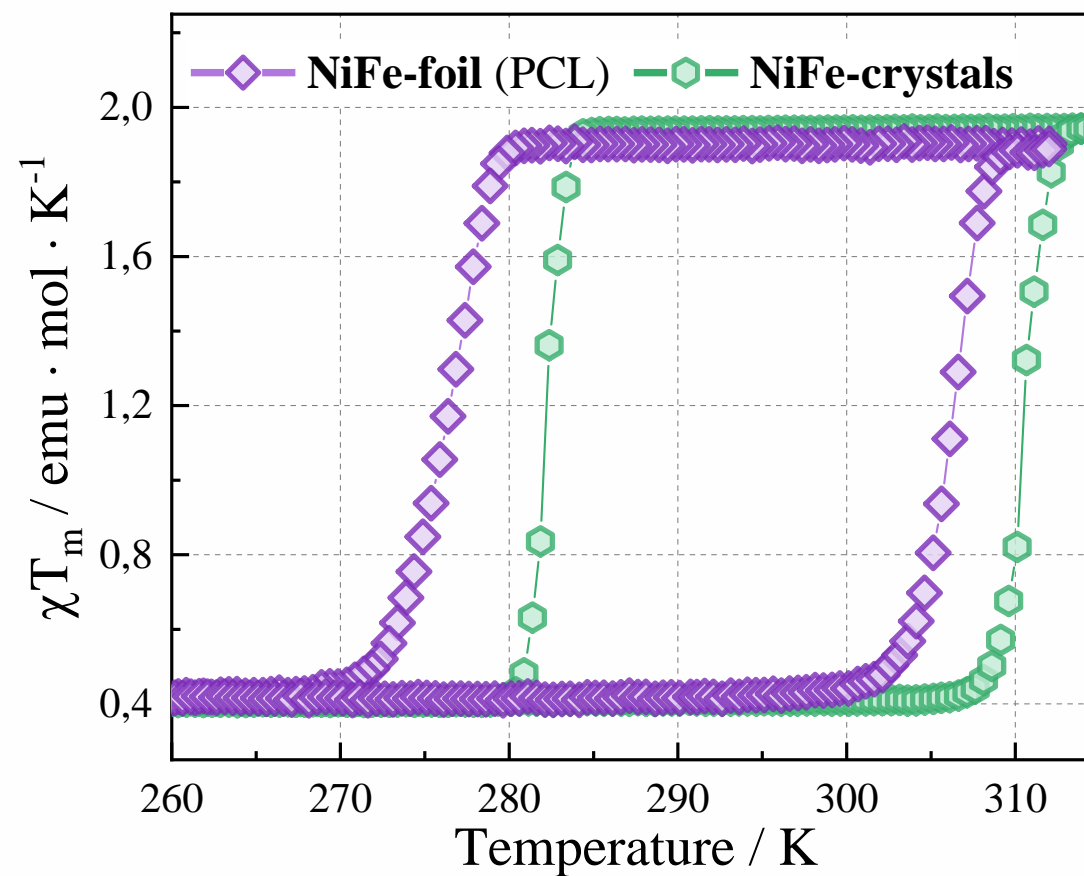
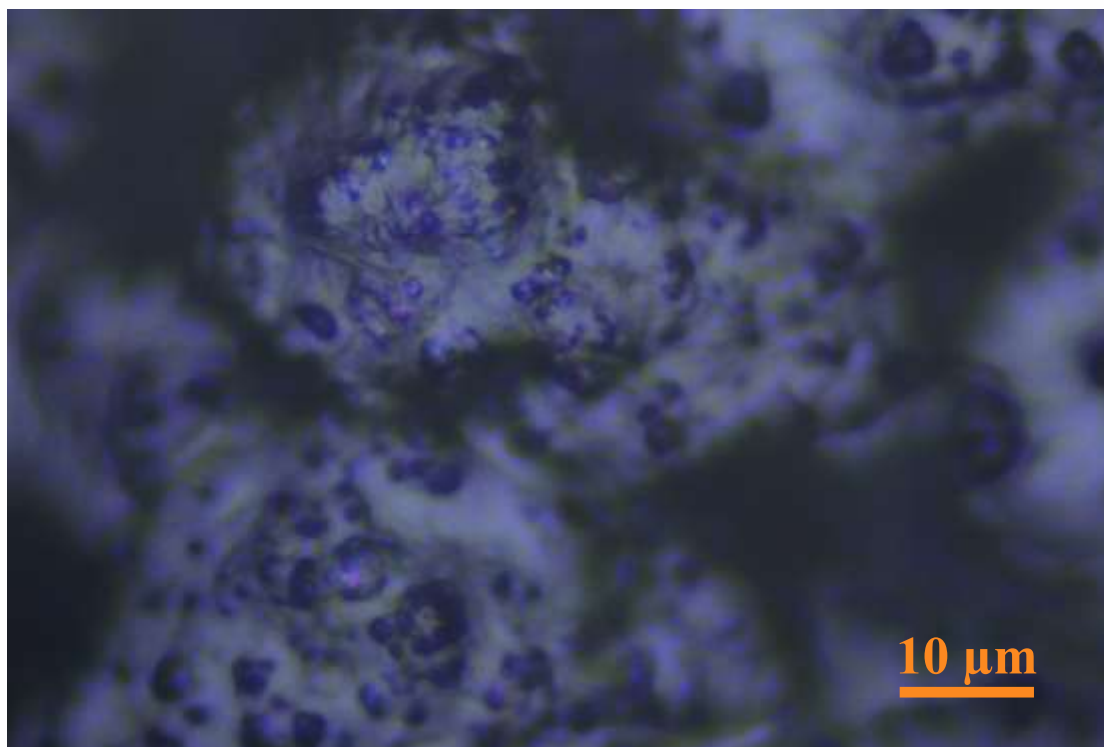


Free-standing NiFe-foil



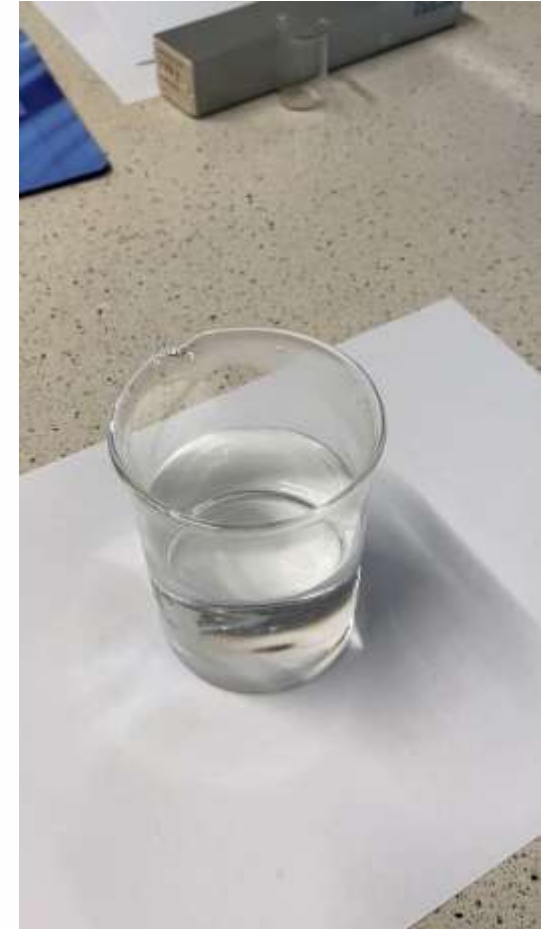
NiFe-foil - functionalities

Thermally-induced LT of **NiFe-foil**



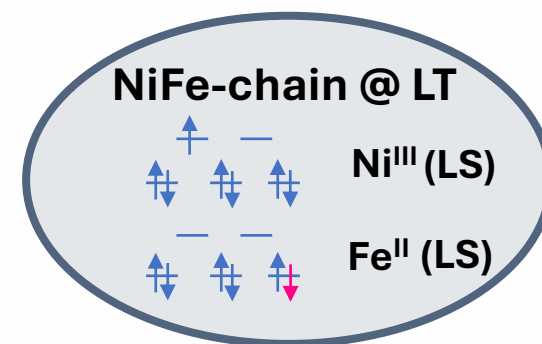
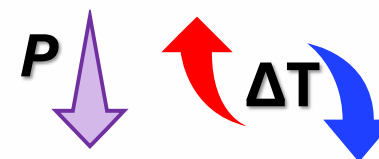
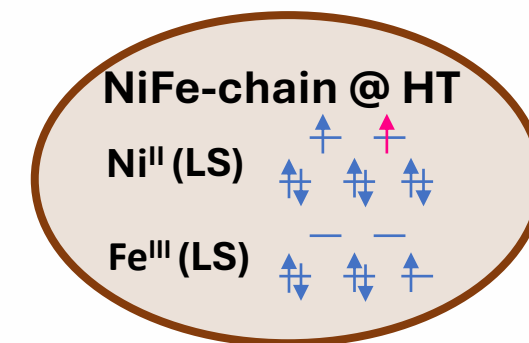
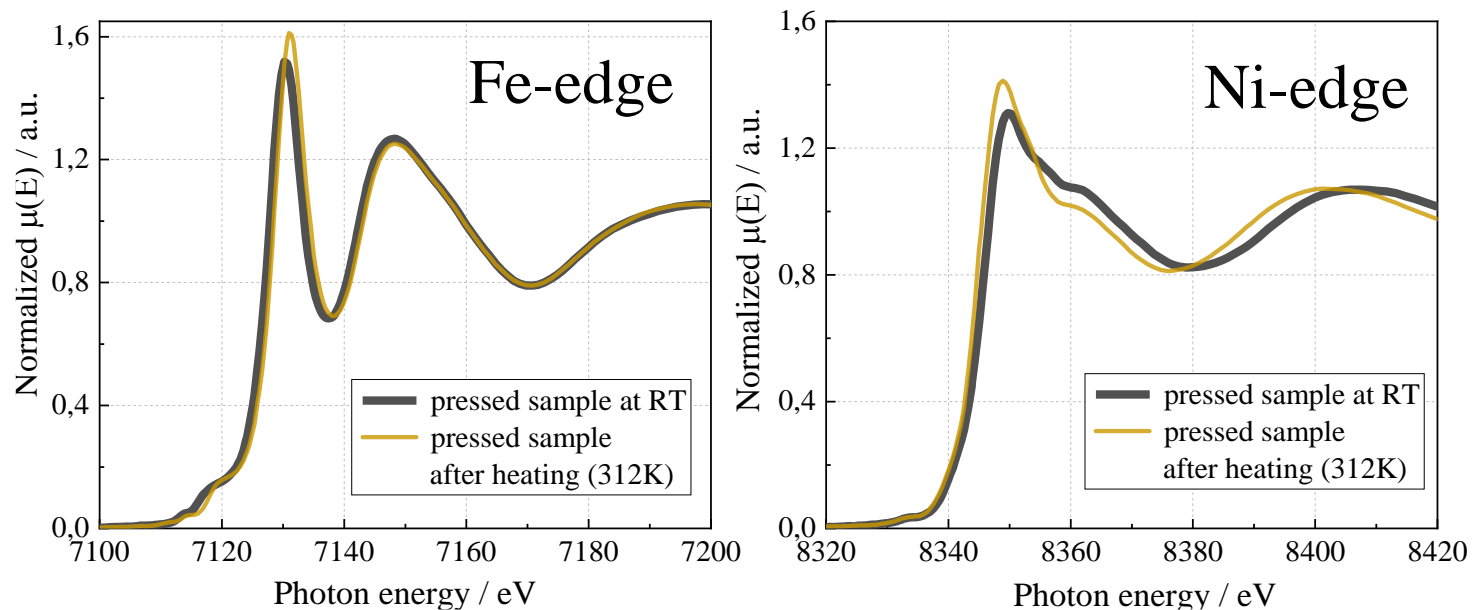


Pressure-induced MMCT – writing test



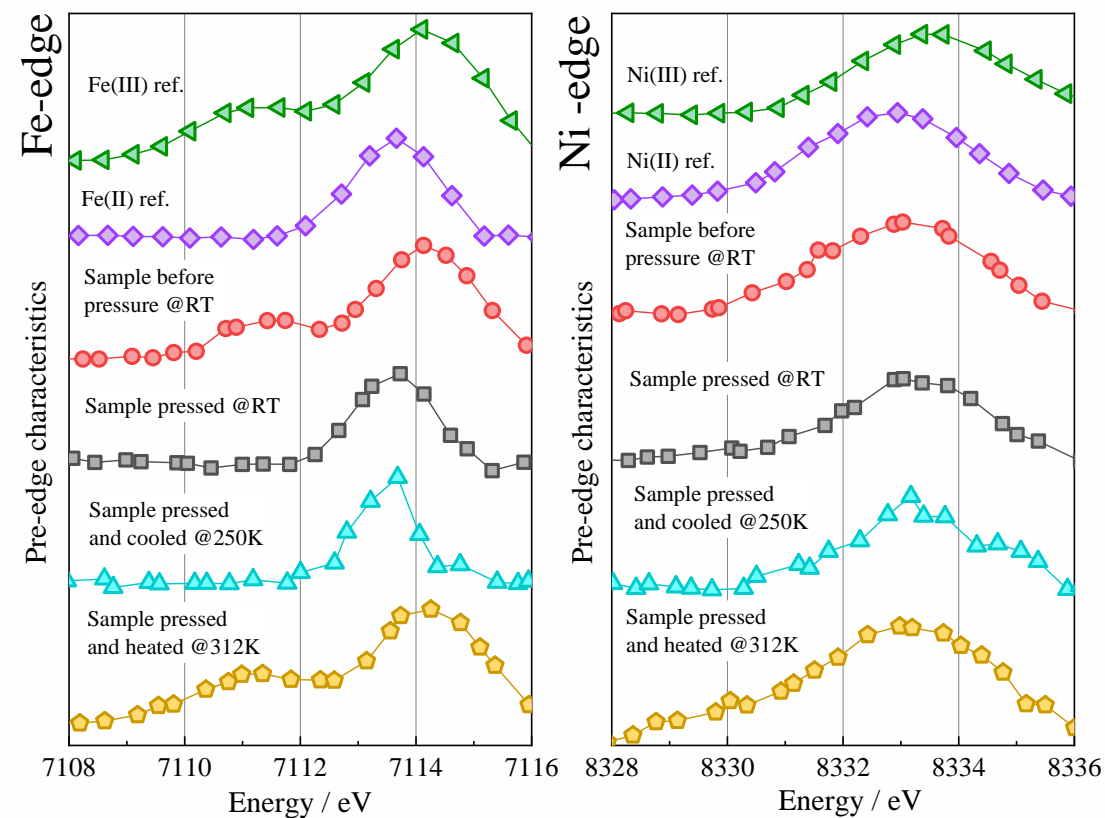
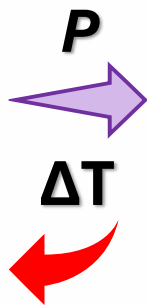
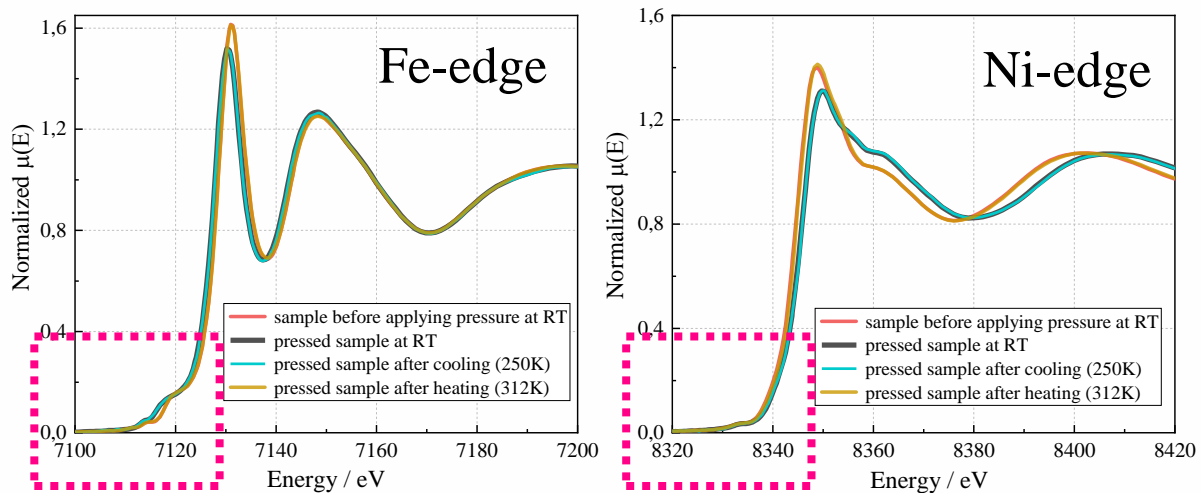


Pressure-induced MMCT – XANES studies



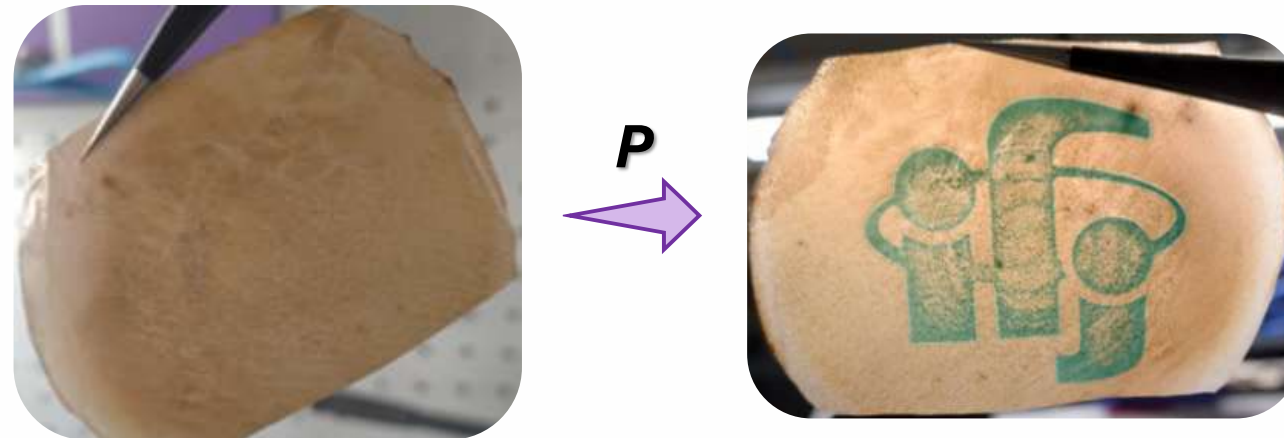
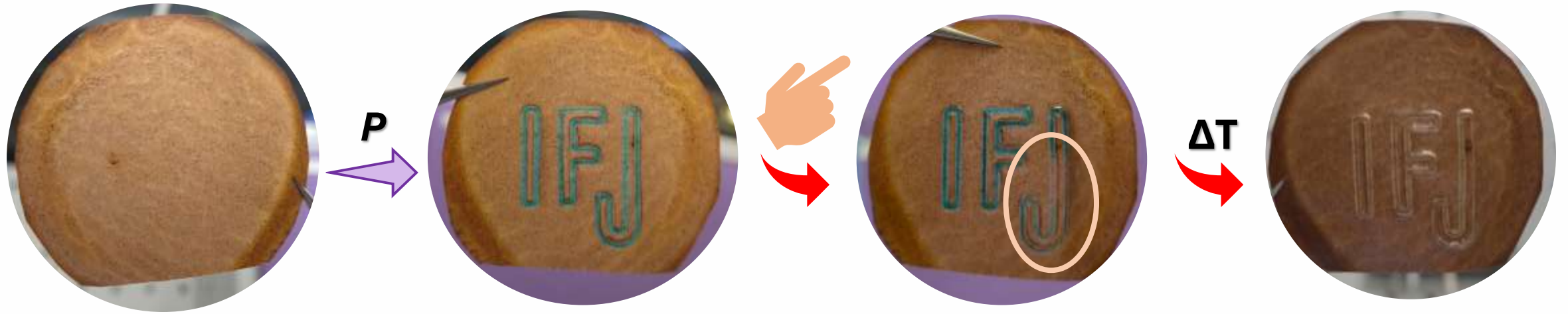


Pressure-induced MMCT – XANES studies





Pressure-induced MMCT – in function

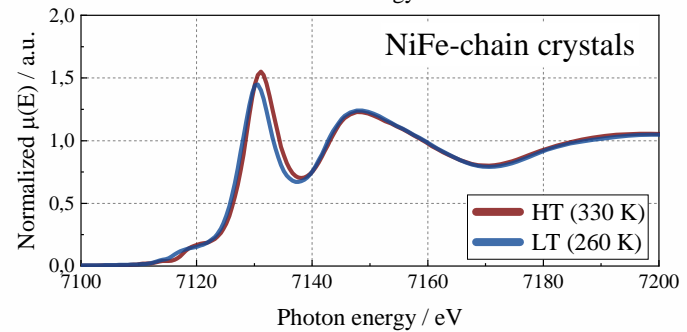
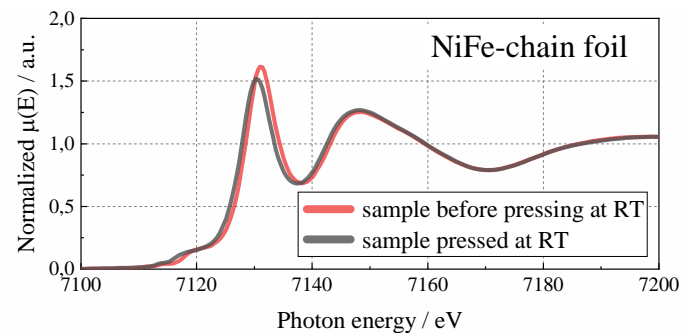




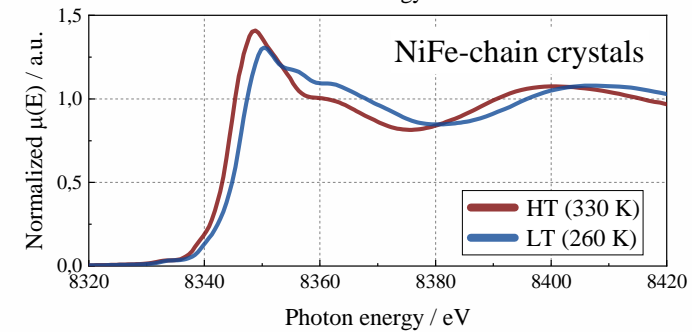
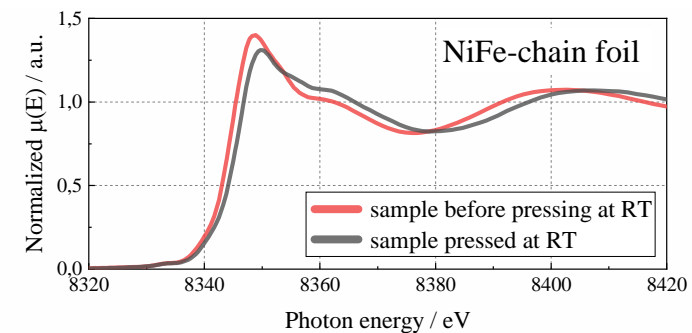
Pressure-induced MMCT – μ XAS



Fe K-edge



Ni K-edge





Conclusions



- Stimuli-responsive molecule-based materials are an interesting field to study with different methods
- New ways to incorporate sensitive and often very fragile crystalline compounds are required
- Embedding switchable coordination compounds into an organic polymer matrix opens new possibilities to harness their functionality



Thank you for your attention!



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