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Bistable molecular systems in electrospun polymer fibres

24.03.2023, Kraków

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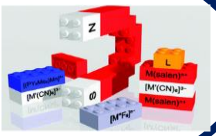
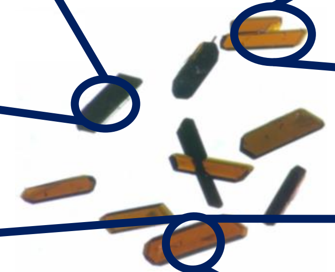
Coordination polymers as molecular functional materials

Tunable structures
Building frameworks
like Lego blocks



Multi-responsivness
Temperature, pressure, light,
guest molecules



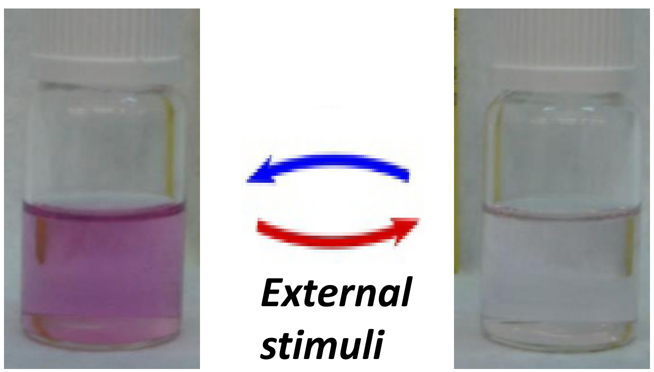
Combination of **various properties** at the molecular level
(magnetism + sorption)

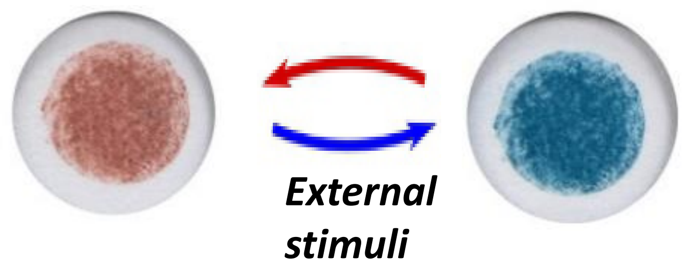
Bistability and
hysteretic behaviour
(memory of the material)

Switching abilities in molecular systems

Bistability

ability of the system to switch between two stable states under external stimuli



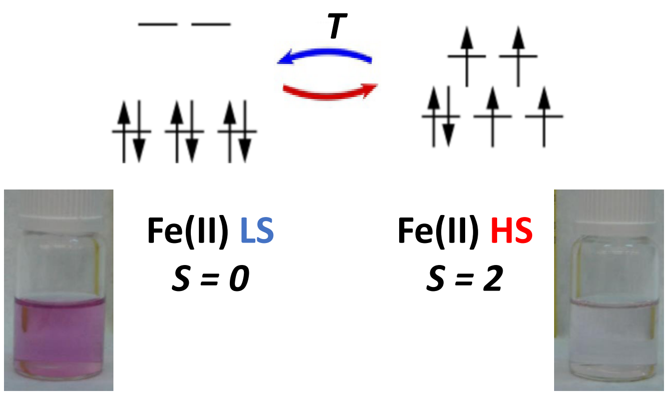


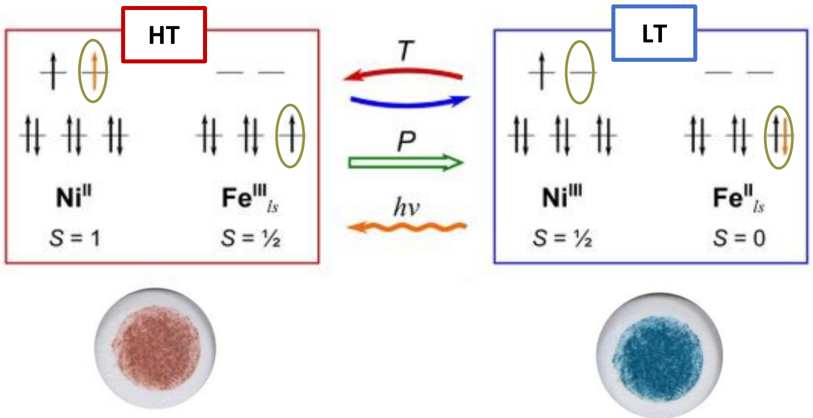
Switch „ON/OFF”

Bistability in coordination polymer

Spin crossover effect

Charge transfer - MMCT





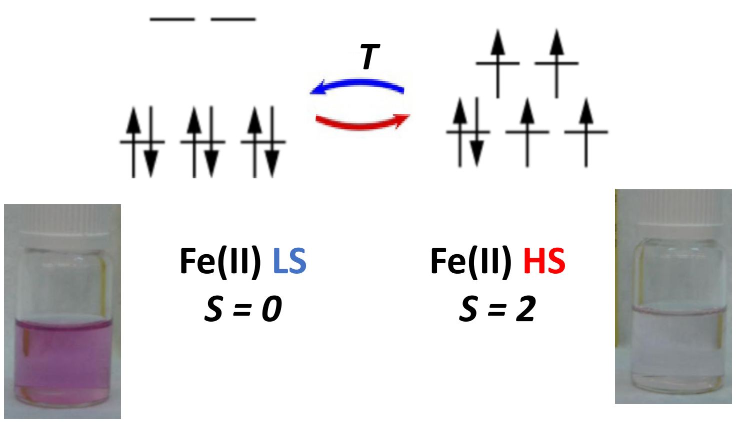
Change of spin state

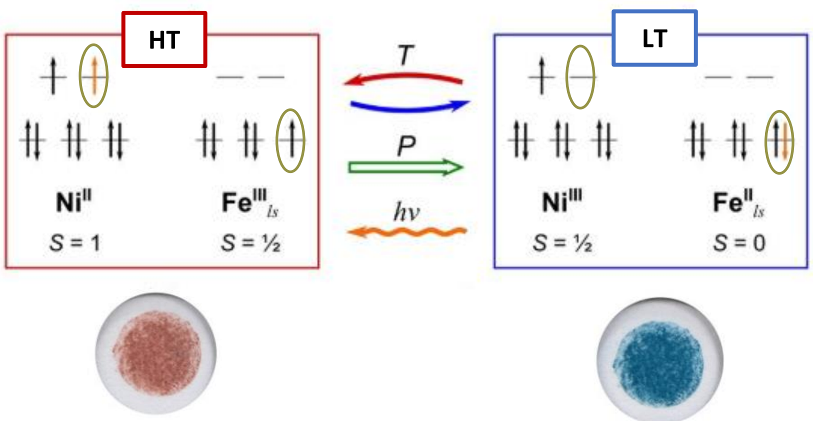
Change of oxidation states

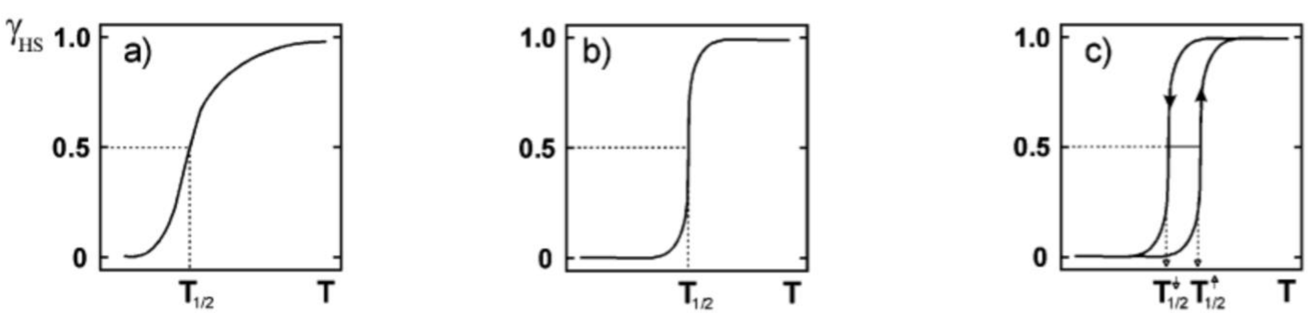
Bistability in coordination polymer

Spin crossover effect

Charge transfer - MMCT



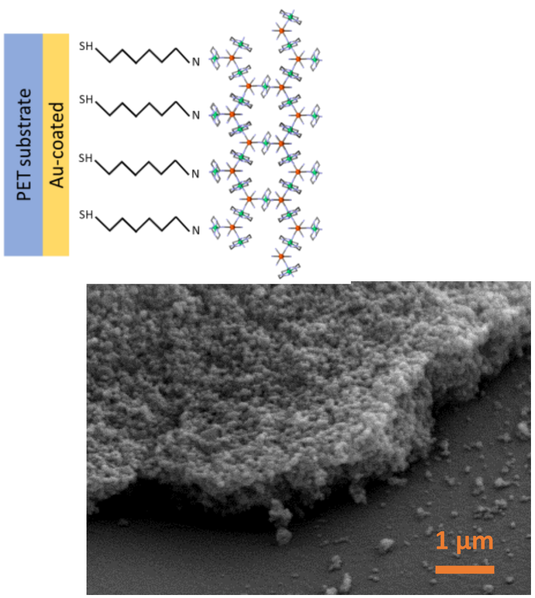




Top. Curr. Chem., 2004, **233**, 1.

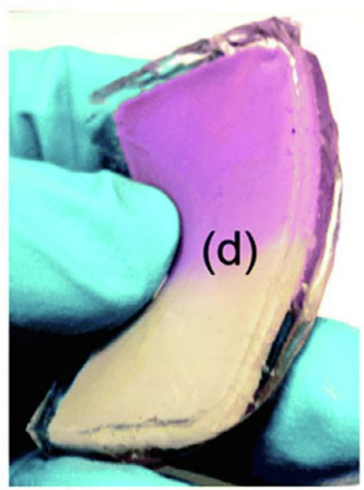
How to make them more processable?

Deposition on surfaces

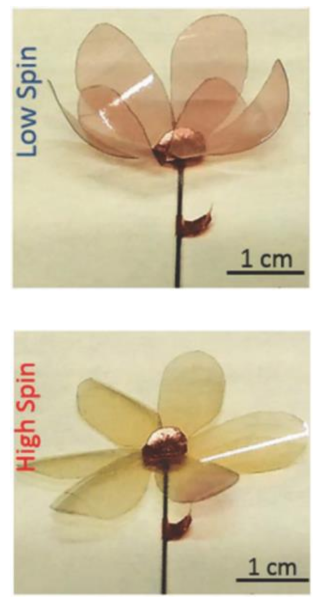


Adv. Mater. Interfaces 2023, **10**, 2201834.

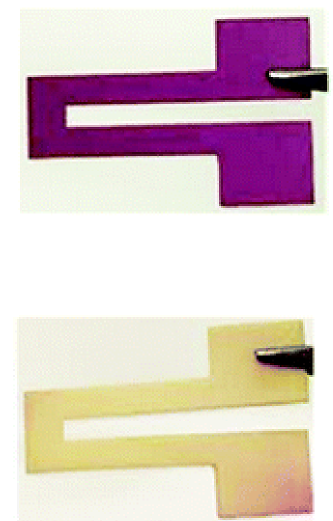
Combining with more flexible materials – <u>polymer matrix</u>



Inorg. Chem. Front., 2018, **5**, 2140.



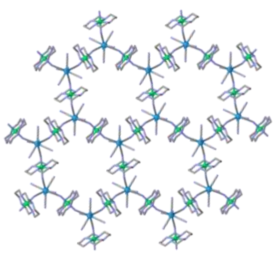
Adv. Funct. Mater. 2018, **28**, 1801970.

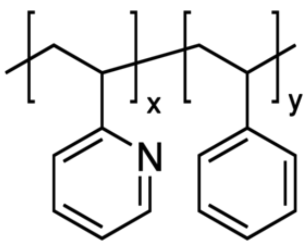


J. Mater. Chem. C, 2020, **8**, 6001.

Goal

Introducing brittle bistable molecular materials into the flexible polymer matrix





Functional coordination structures

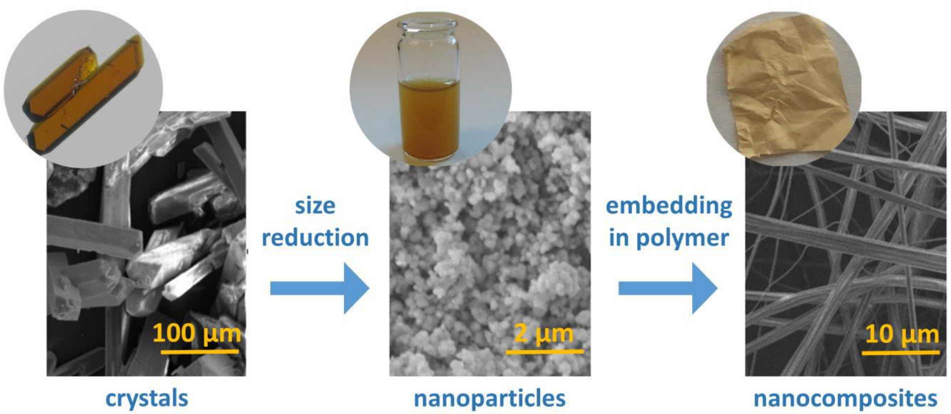
- Structures of different composition
- Interesting properties – often in one material
- Reactive to external stimuli
- Bistability

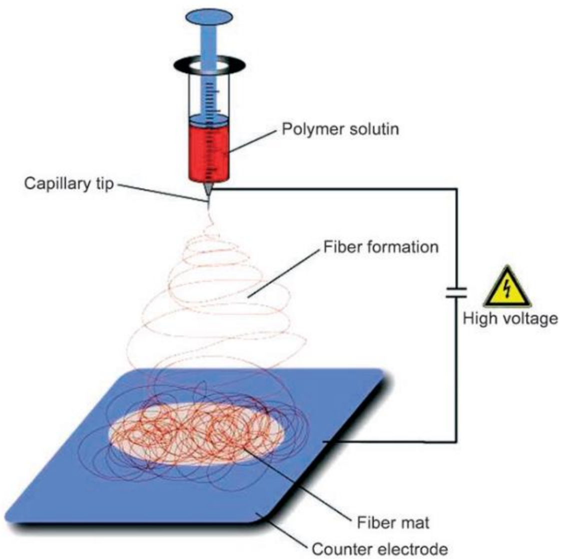
Bistable composite systems

Organic polymer matrix

- Flexibility
- Compability
- Without any suport
- Easy to produce

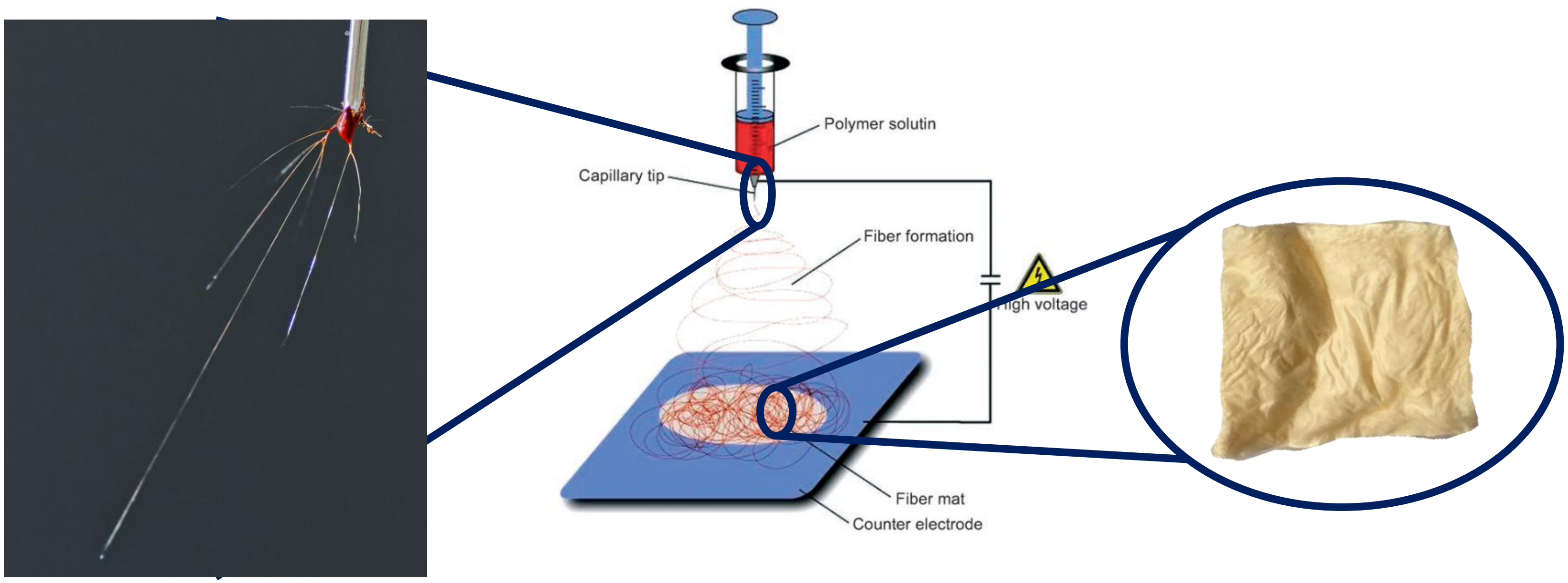
Preparation of composite materials - electrospinning





Electrospinning process

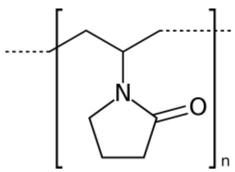
Preparation of composite materials - electrospinning



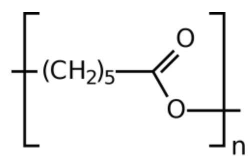
Preparation of composite materials

- Polymers used:

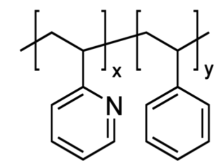
Polyvinylopirrolidone - PVP

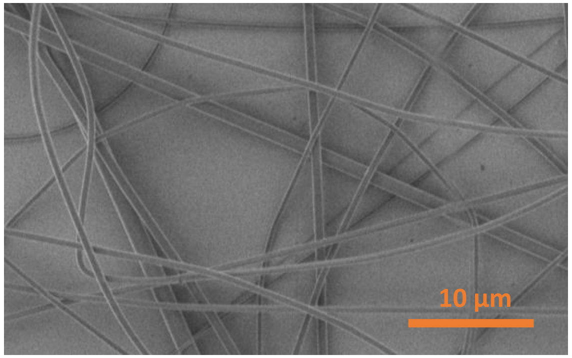


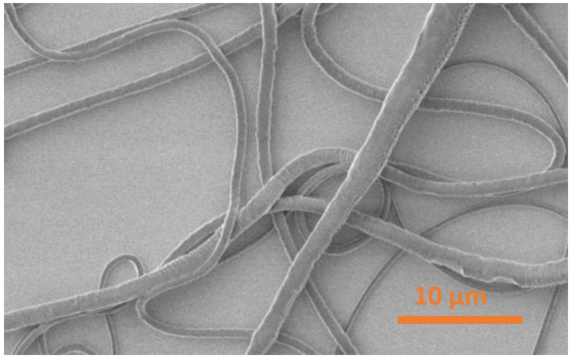
Poly(Ɛ – lactone) - PCL

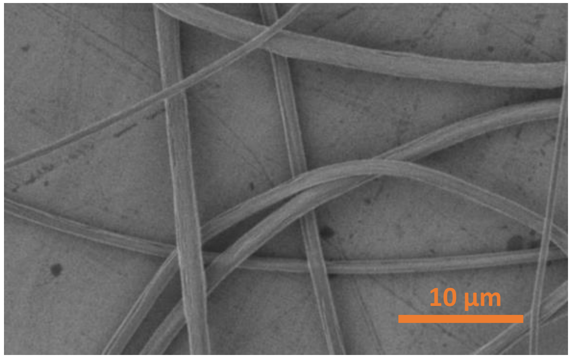


Poly(2-vinylpiridine-co-styrene) – P2VP-PS

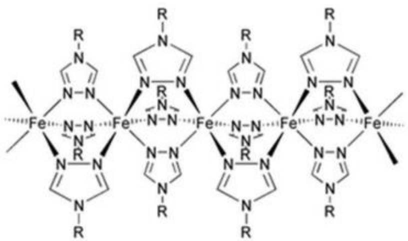


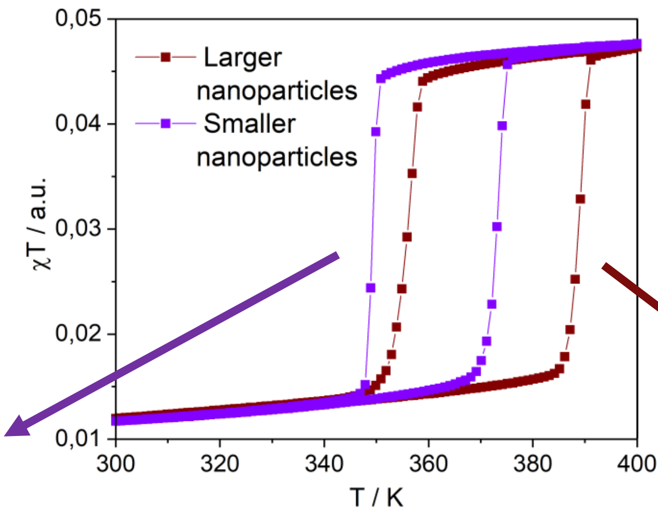


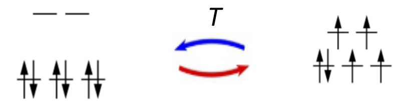




Nanoparticles of $[Fe(Htrz)_2(trz)](BF_4) \cdot H_2O$

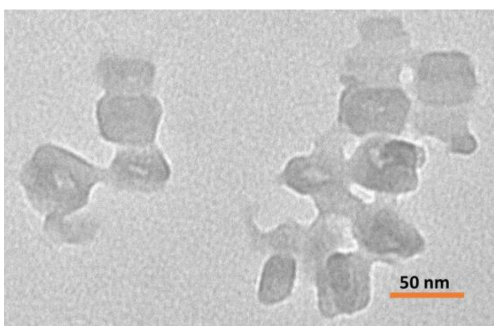


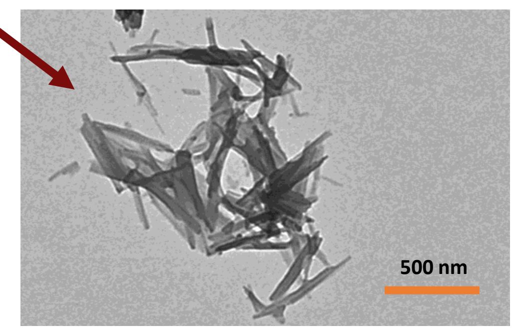




Fe(II) LS
S = 0

Fe(II) HS
S = 2



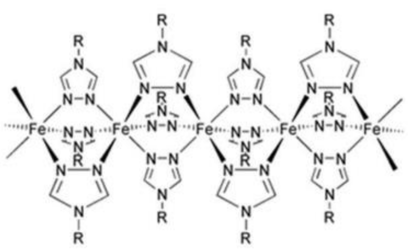


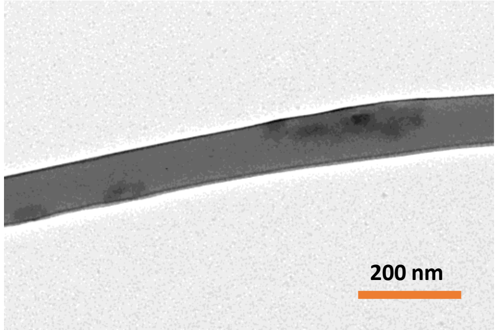
*J. Am. Chem. Soc.***,** 1993, **115**, 9810

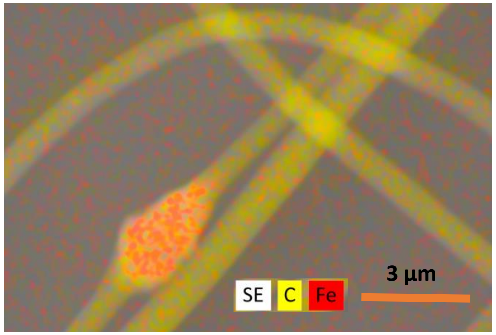
Adv. Mater., 2007, **19**, 1359

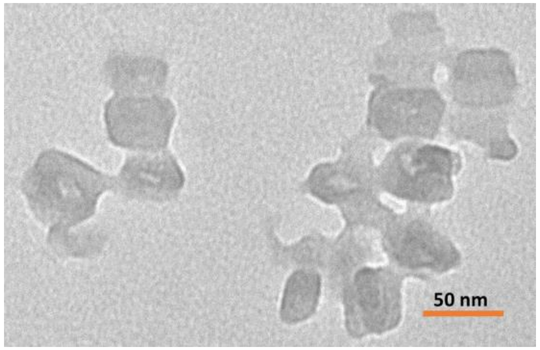
*Dalton Trans.***,** 2019, **48**, 15465

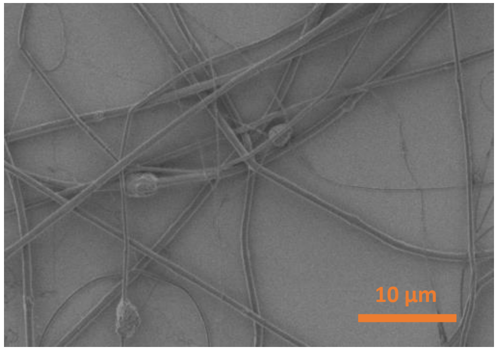
Nanoparticles of $[Fe(Htrz)_2(trz)](BF_4) \cdot H_2O$ in PVP fibers

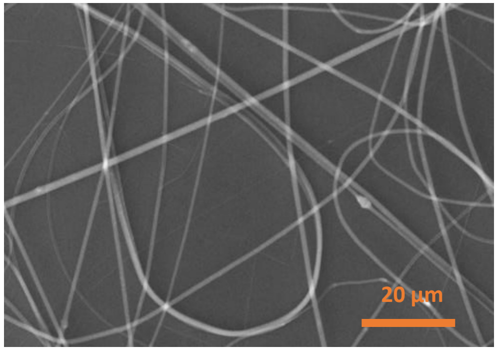




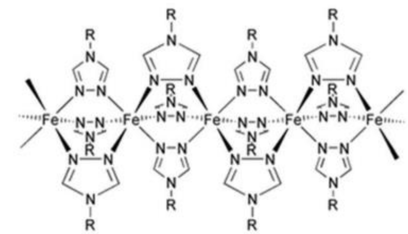


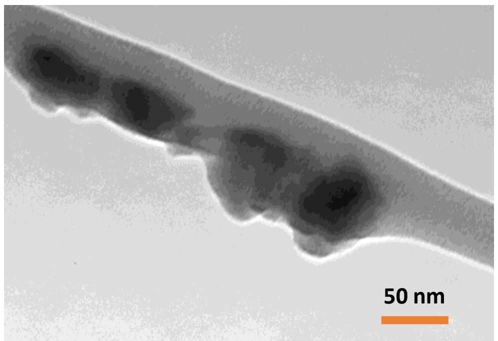


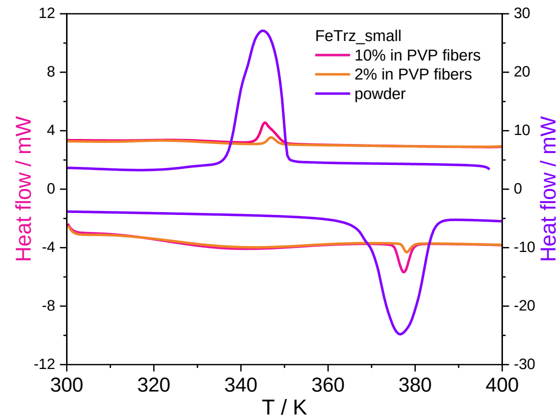




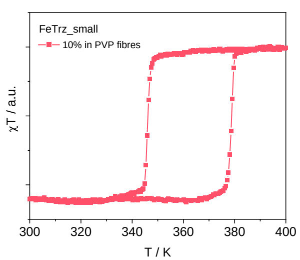
Bistability of FeTrz NP in PVP fibers

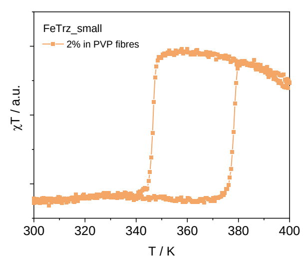


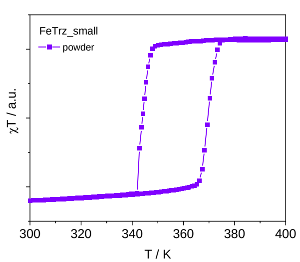


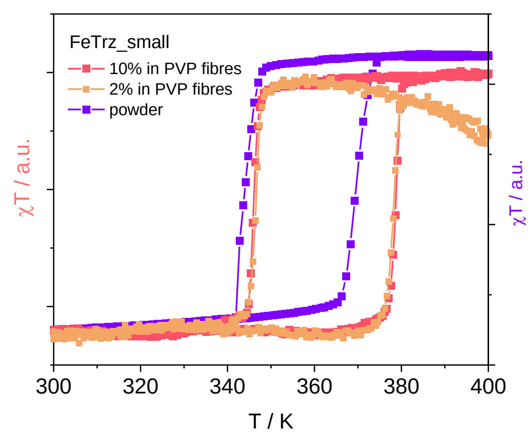


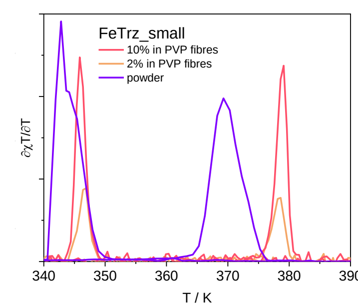
Calorimetric measurements





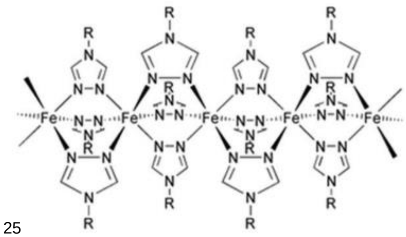


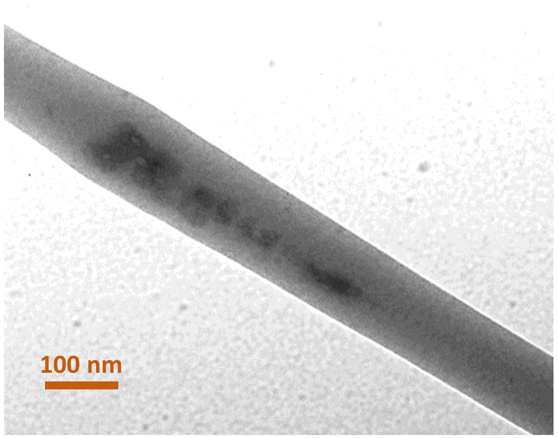


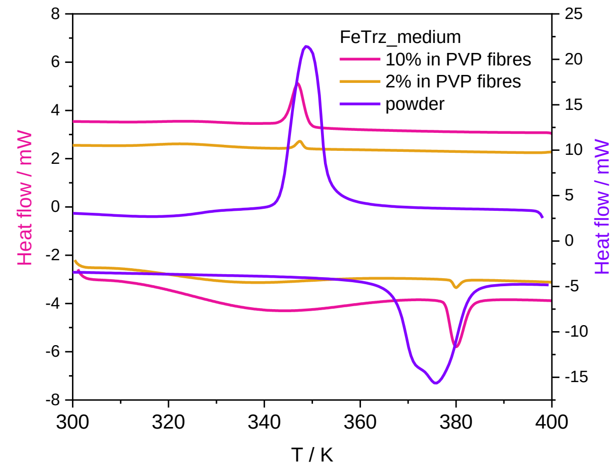


Magnetic measurements

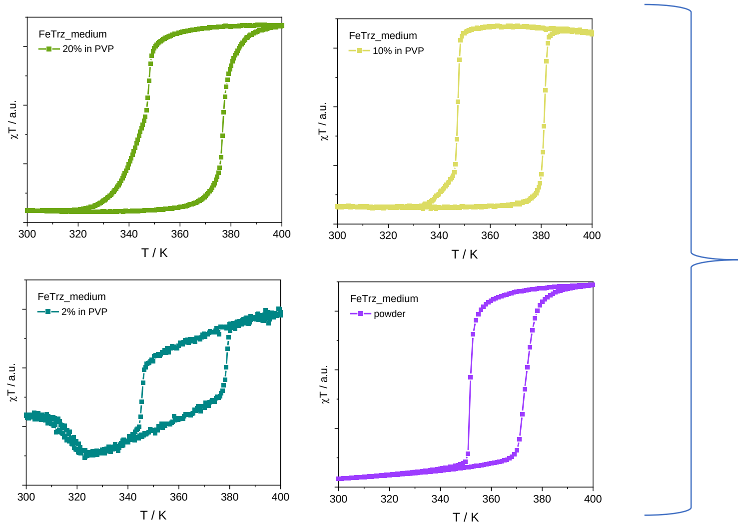
Bistability of FeTrz NP in PVP fibers

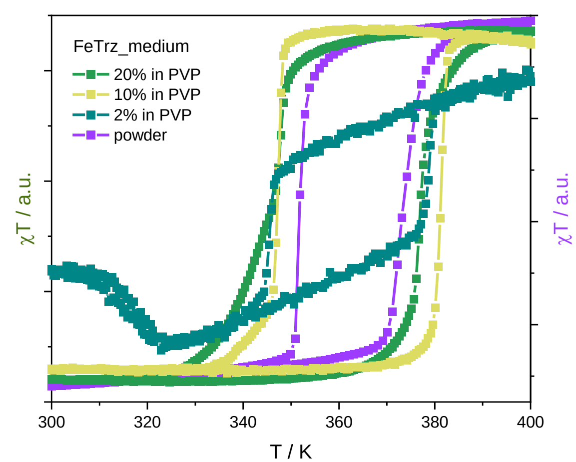


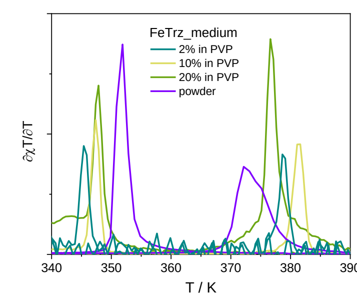




Calorimetric measurements

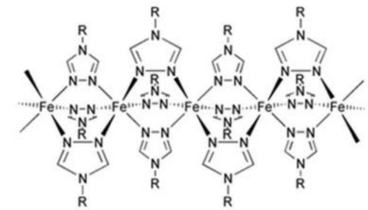


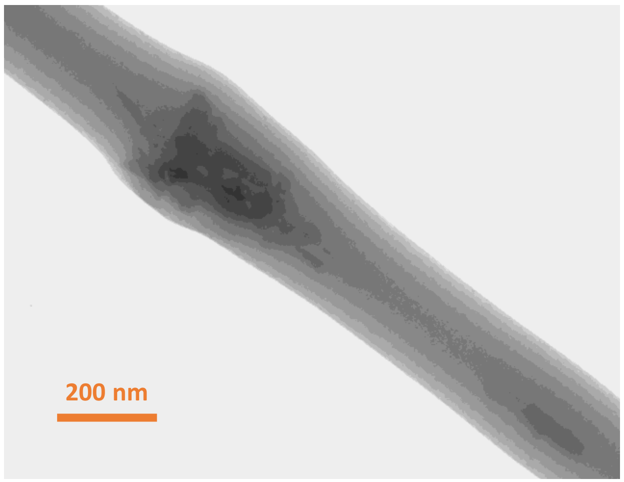


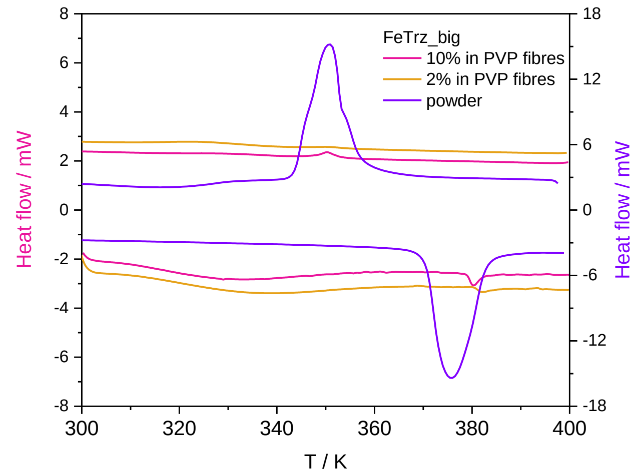


Magnetic measurements

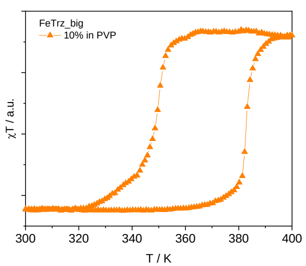
Bistability of FeTrz NP in PVP fibers

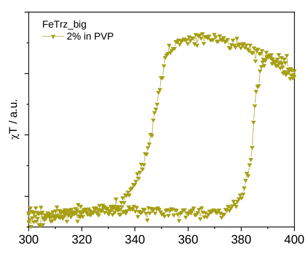


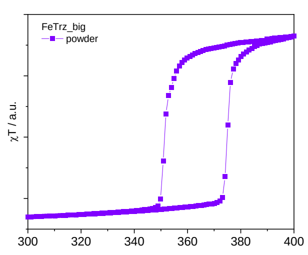


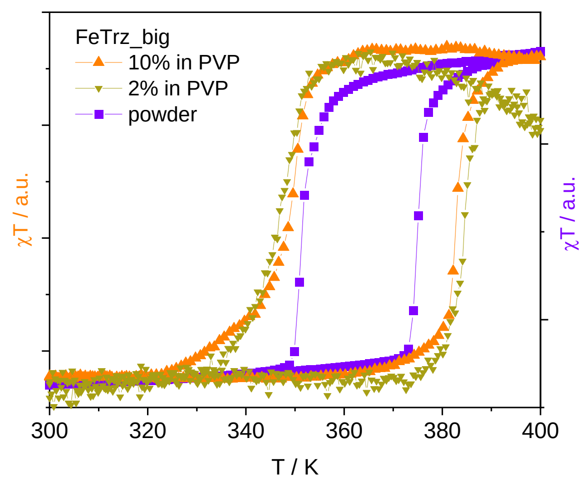


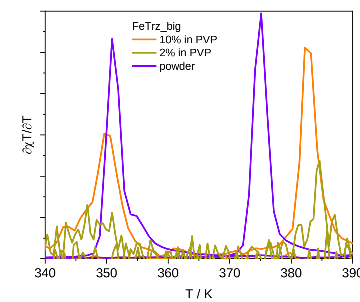
Calorimetric measurements





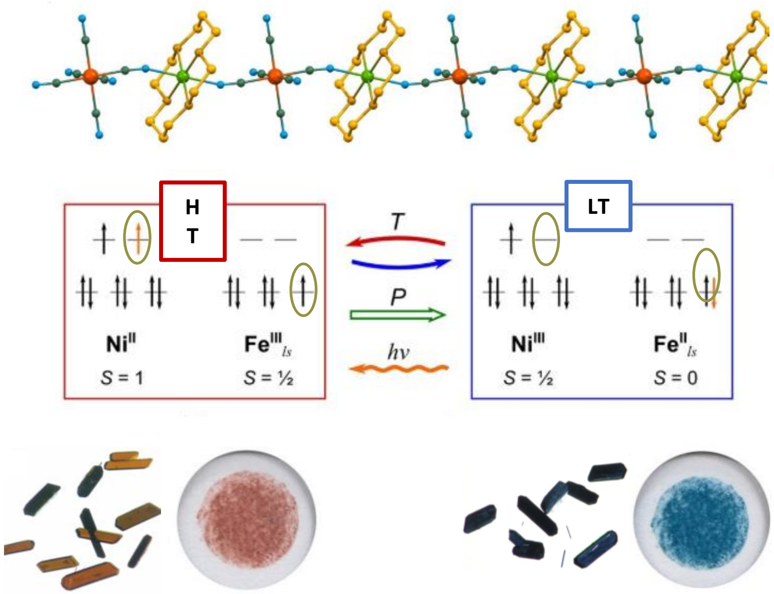


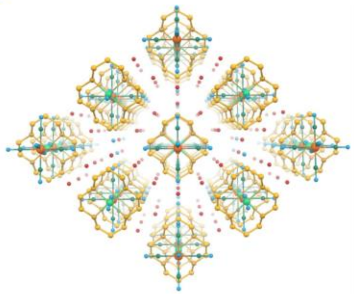


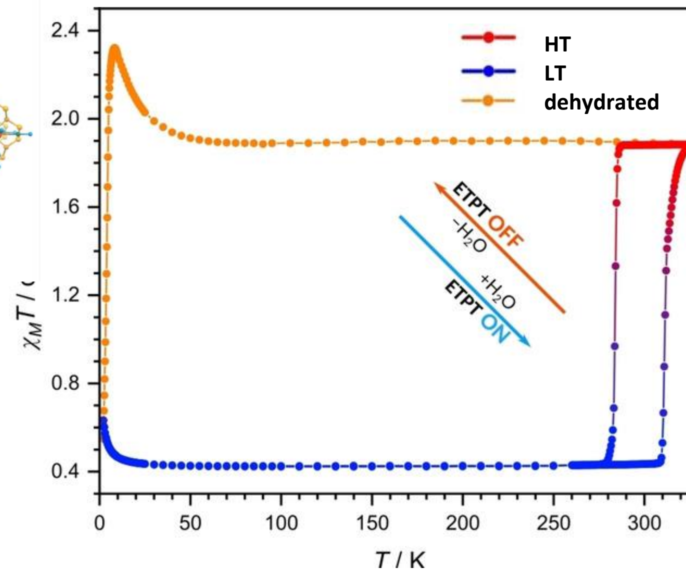


Magnetic measurements

MMCT chain – $NH_4[Ni(cyclam)][Fe(CN)_6] \cdot 5H_2O$

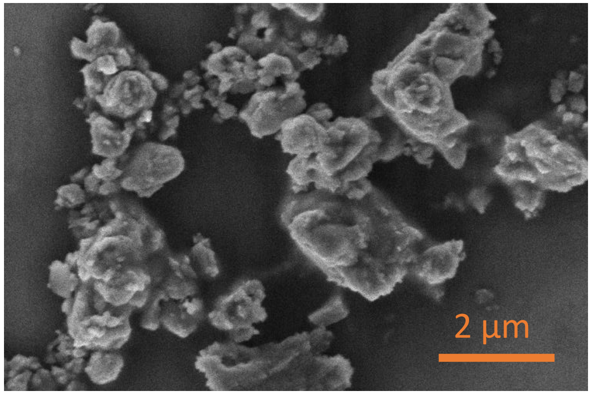




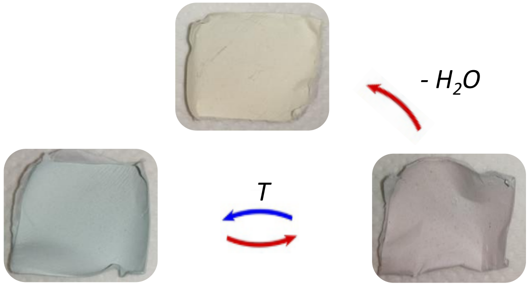


Angewandte Chemie Inter. Ed, 2021, **60**, 2330

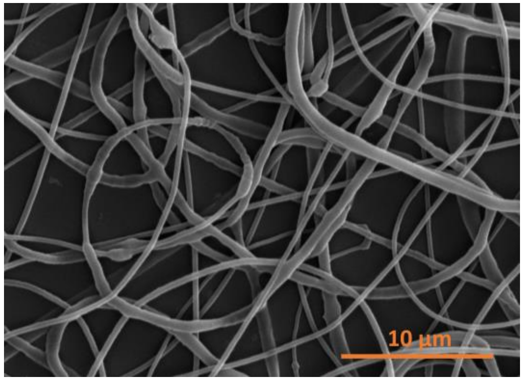
Miniaturised
by sonification

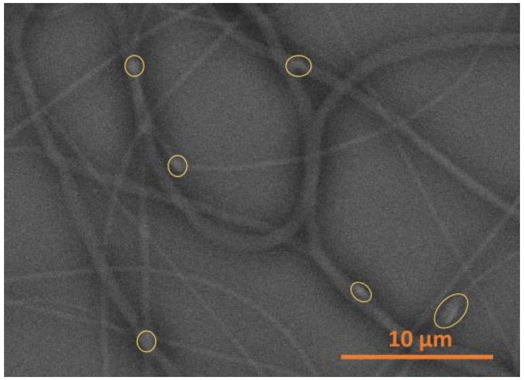


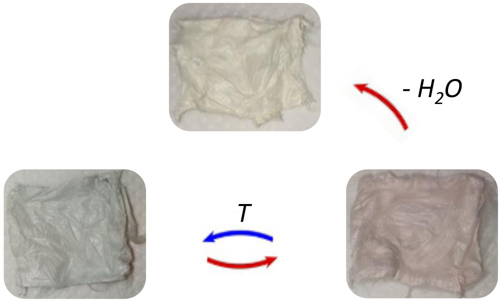
SEM – outside and inside the fibers



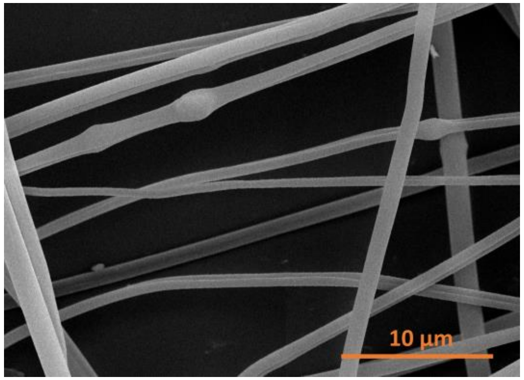
~14% of NiFe-chain in **PCL fibers**

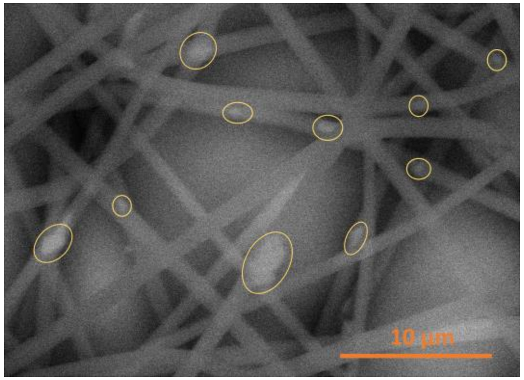




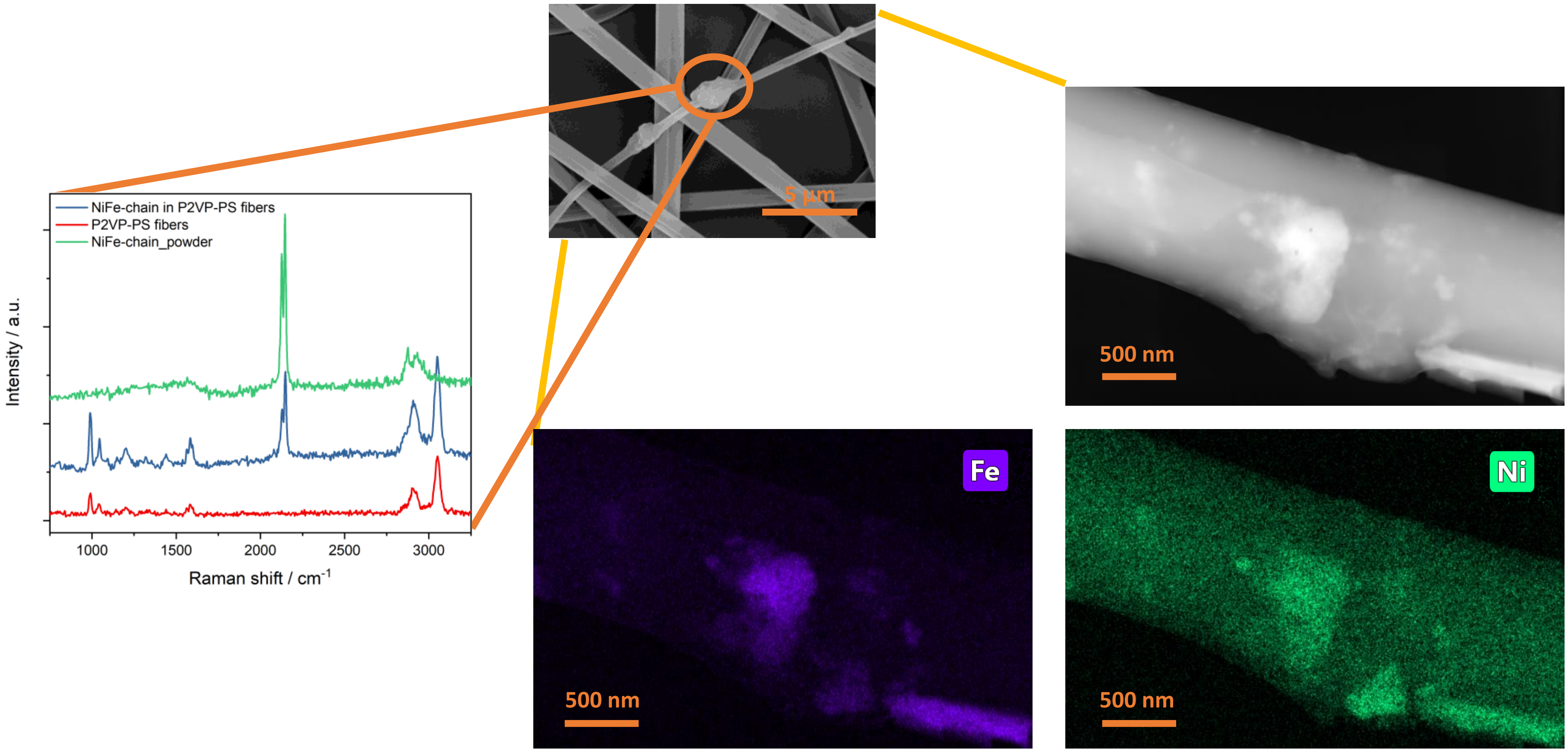


~14% of NiFe-chain in **P2VP-PS fibers**

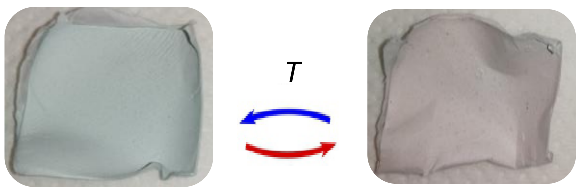




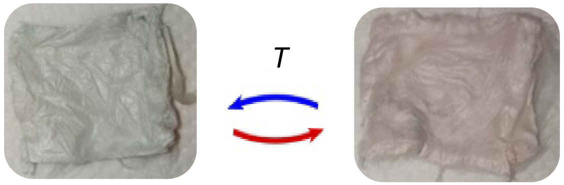
NiFe-chain vs the fibers



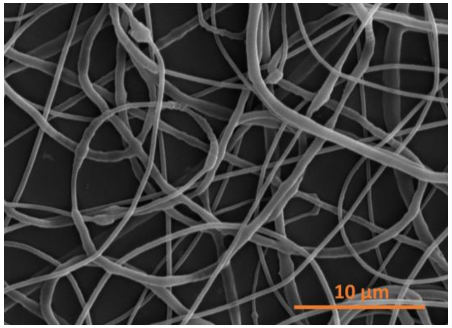
Bistability of fibers – magnetic measurment

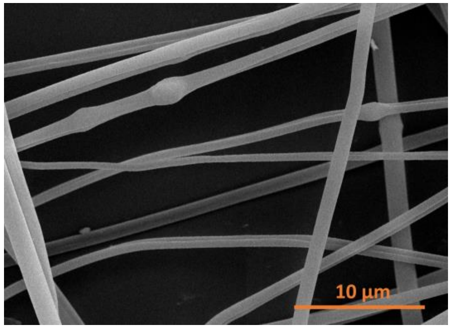


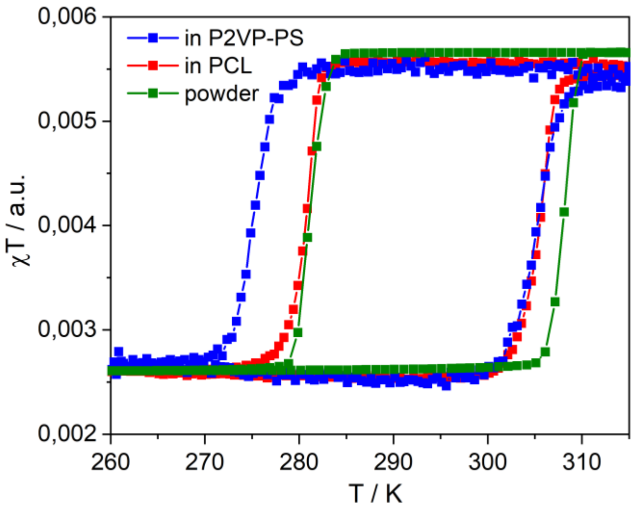
~14% of NiFe-chain in PCL fibers



~14% of NiFe-chain in P2VP-PS fibers



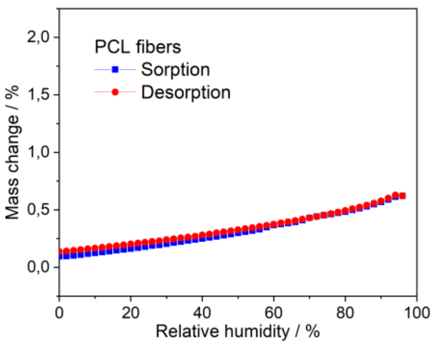


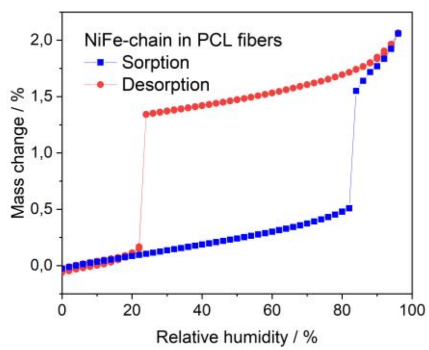


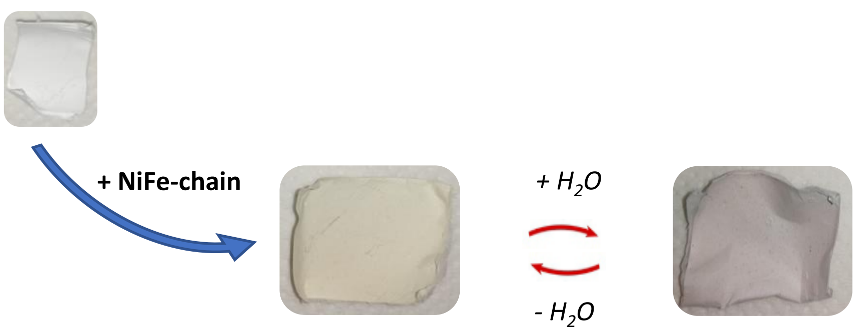
	In P2VP-PS	In PCL	powder
$T_{½}$ ↓	274 K	281 K	281 K
$T_{½}$ ↑	306 K	306 K	308 K

Sorption properties

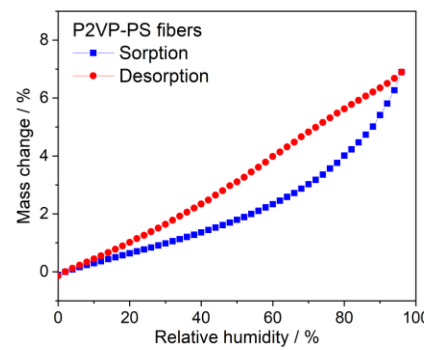
PCL fibers

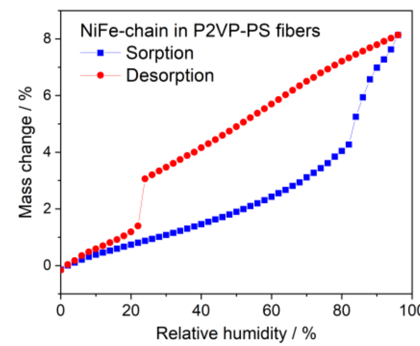


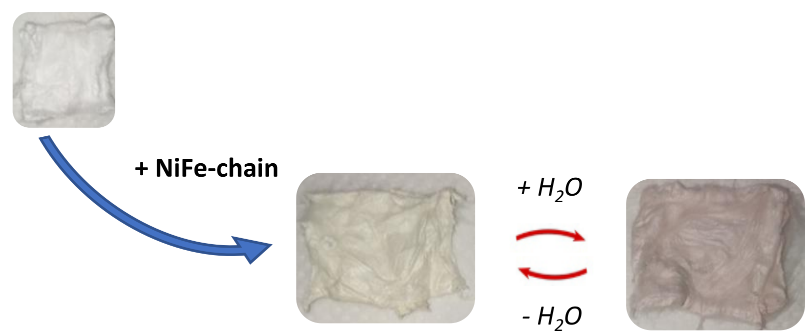




P2VP-PS fibers

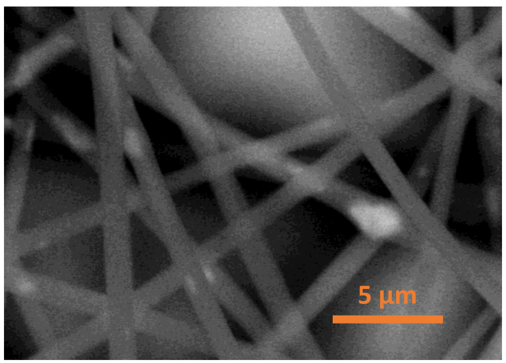




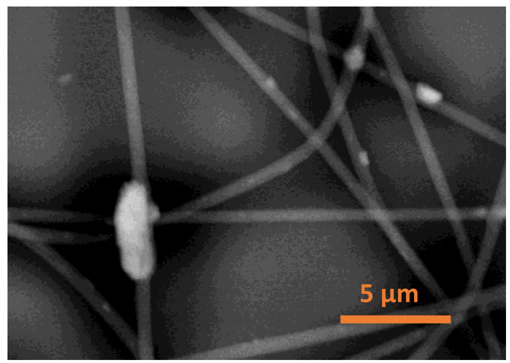


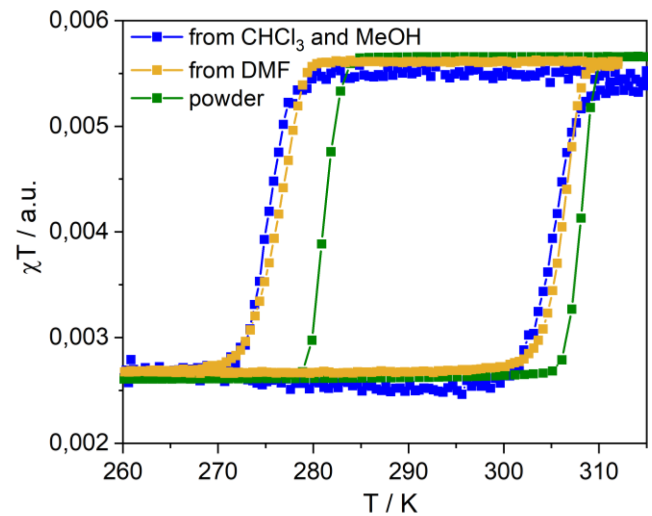
Change of solvent for P2VP-PS fibers

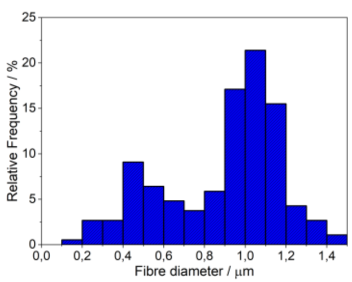
Fibers from $CHCl_3$ and MeOH

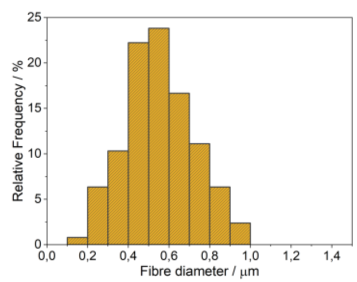


Fibers from DMF









	from $CHCl_3$ + MeOH	from DMF	powder
$T_{1/2}$ ↓	274 K	277 K	281 K
$T_{1/2}$ ↑	306 K	306 K	308 K

Conclusions

- We were able to incorporate two different systems into the polymer matrix in the form of electrospun fibers (1D confinement).
- The obtained materials retain the switching abilities of fillers (coordination systems).
- For the composites with NiFe-chain we discovered that the polymer matrix secures the fragile bistable material from external conditions (keeps the NiFe-chain sub-micro particles in the hydrated form in which shows bistability).
- The functional coordination materials in the form of composites (electrospun fibers) are more processable and it is easier to take advantage of their switching abilities on a bigger scale.

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