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Manipulating the magnetism of $NiPS_3$ via organic ions intercalation

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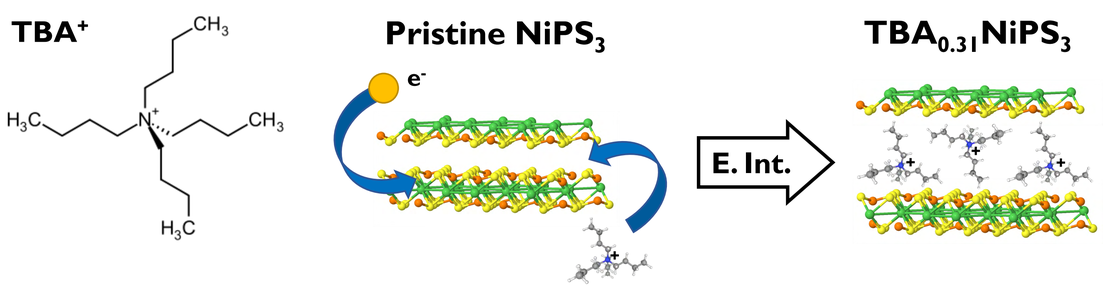
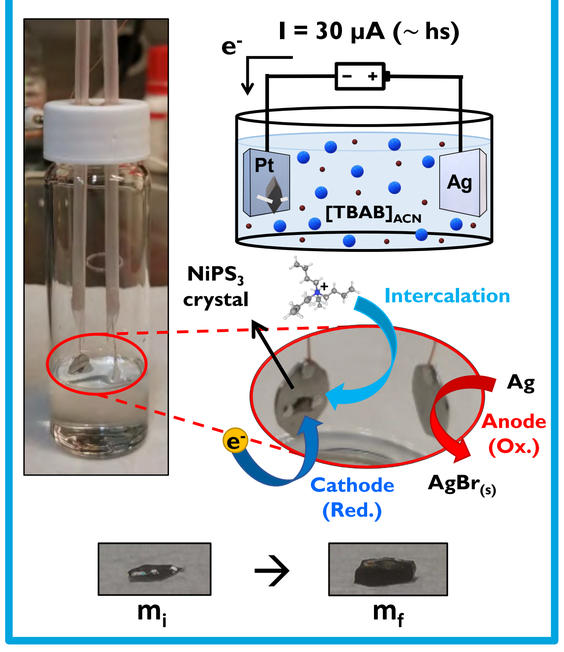
Motivation

Molecular intercalation is a powerful technique to tailor the physical properties of layered materials, both in bulk and in exfoliated flakes [1].
Transition metal phosphorous trisulfides (MPS_3) is a class of layered materials characterized by antiferromagnetic properties [2].
Is it possible to tune the magnetic properties of transition metal phosphorous trisulfides through molecular functionalization?

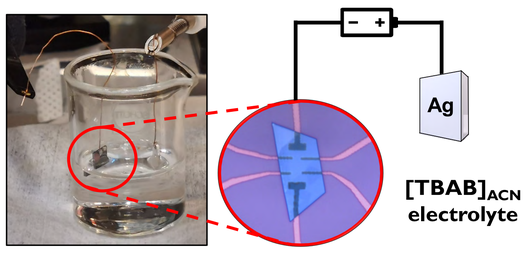
Electrochemical intercalation



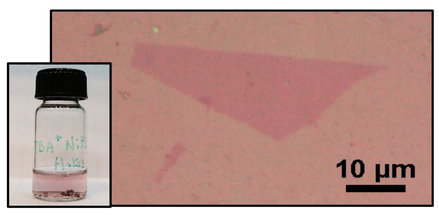
Intercalation in bulk

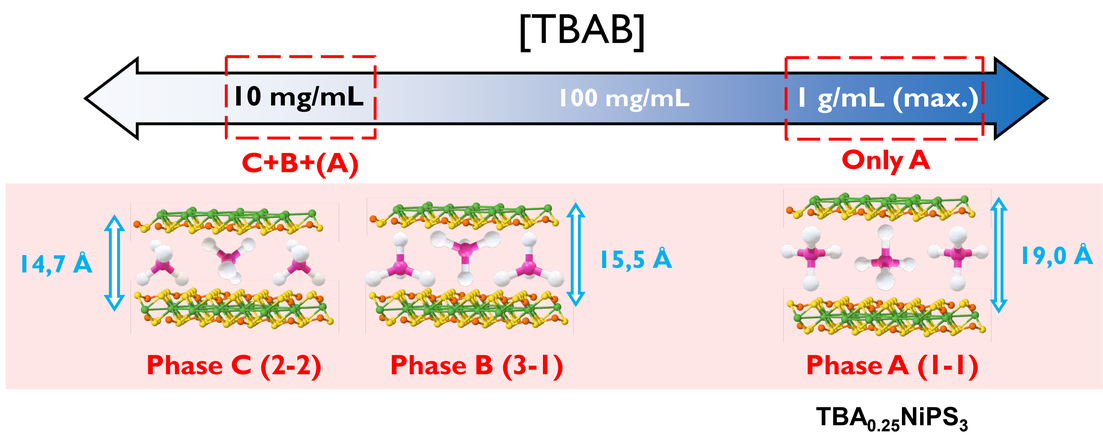


Intercalation in flake



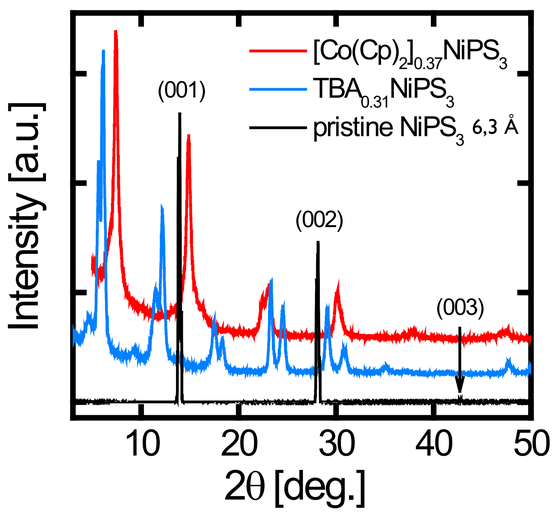
Exfoliation





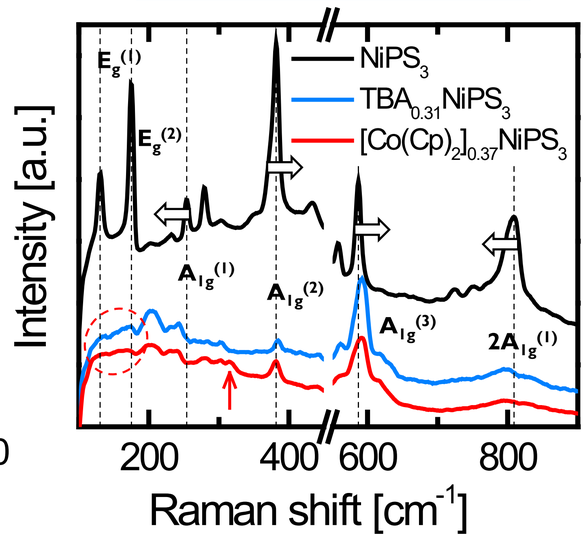
Characterizations

X-ray diffractometry



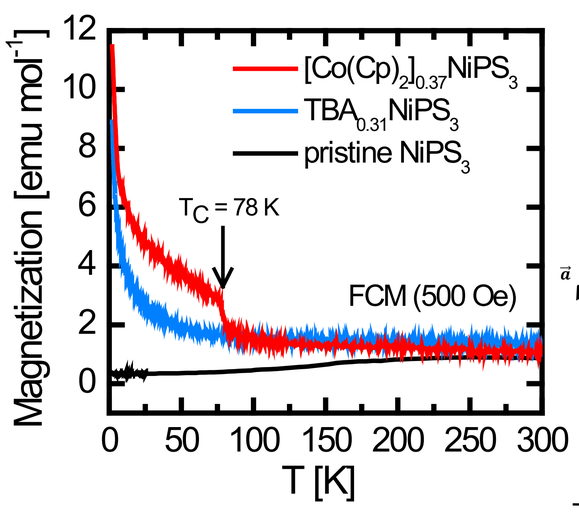
Effectiveness of both the intercalation processes is demonstrated by the appearance of new crystallographic phases in the XRD pattern.

Raman Spectroscopy

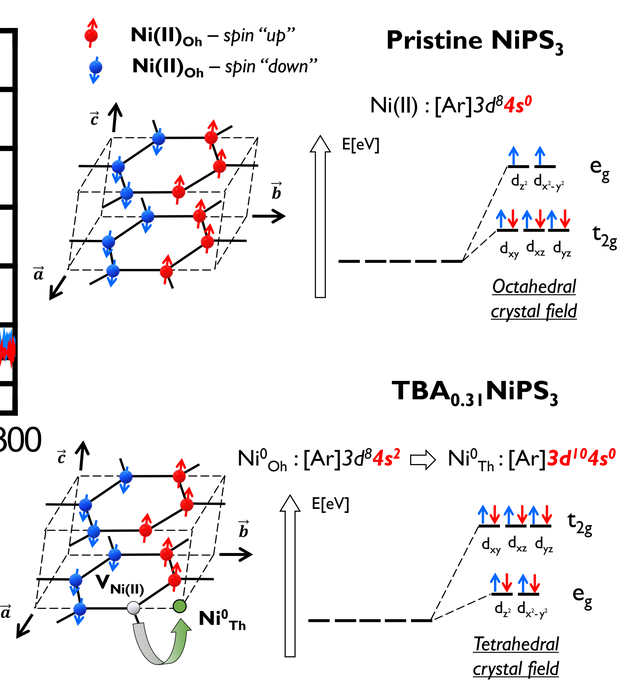


Intercalates' Raman spectra confirm the occurrence of the insertion of TBA^+ and the exchange with $Co(Cp)_2^+$ in between $NiPS_3$ layers [3].

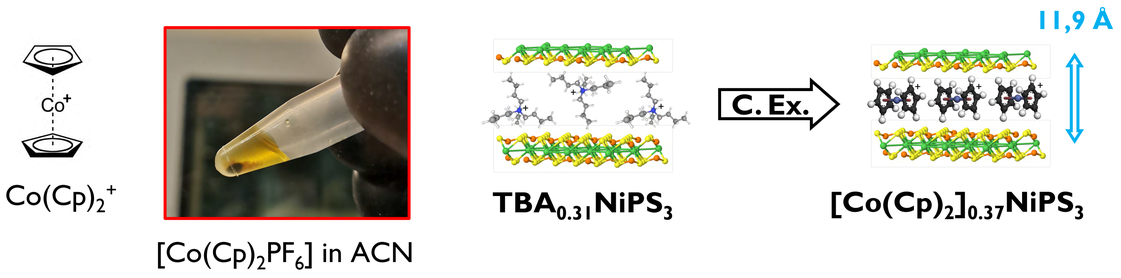
Magnetic properties



Paramagnetism arises from the reduction of Ni(II) to Ni^0 and its migration from an octahedral to a tetrahedral site, leading to a "*low spin*" diamagnetic configuration [4, 5].



Cation exchange



TBA^+ - $[Co(Cp)_2]^+$ cations exchange is thermodynamically allowed and kinetically favored even at RT, within one day.

Conclusions and Outlooks

- $NiPS_3$ can get electrochemically intercalated with TBA^+ organic cations and with $Co(Cp)_2^+$ by cation exchange.
- Antiferromagnetism of pristine $NiPS_3$ is replaced by paramagnetism in the case of $TBA_{0.31}NiPS_3$ and paramagnetism + ferrimagnetism (T_C=78 K) for $[Co(Cp)_2]_{0.37}NiPS_3$;
- Magnetism of other organic-$NiPS_3$ 2D-superlattices will be further explored upon optimization of the processes and meticulous selection of guest molecules.

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References

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