Single-molecule magnets and composite nanomaterials

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KRAKOWSKA INTERDYSCYPLINARNA SZKOŁA DOKTORSKA

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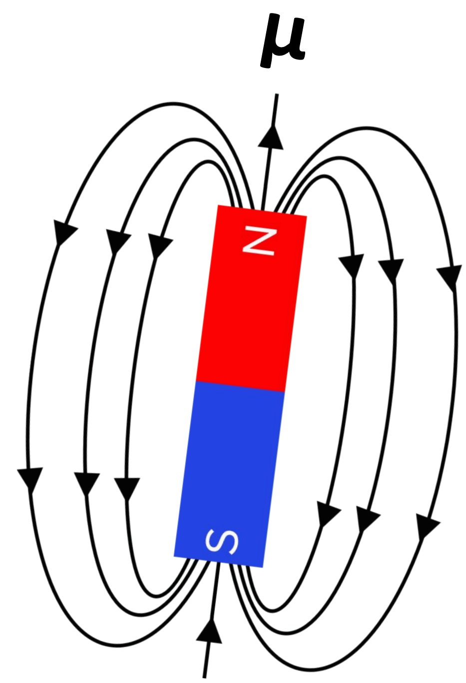
Plan of the talk:

Classical Magnetism

- Compasses
- Speakers/microphones
- Storage Devices (HDD's etc.)
- Medicine (NMR spectroscopy)
- Accelerator physics
- Motors, dynamos, power generators
- Electronics

... just to name a few!

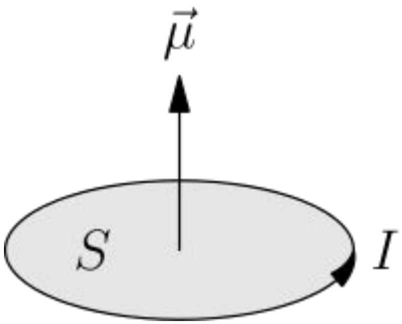


Magnetic field: $\mathbf{H} = \mu_0\mathbf{B}$
Magnetic moment: $\boldsymbol{\mu}$
Magnetization: $\mathbf{M} = d\mathbf{m}/dV$
Susceptibility: $\chi = |\mathbf{M}|/|\mathbf{H}|$

Main types of magnetic materials:
-Diamagnetics: repelled by magnetic field
-Paramagnetics: attracted by magnetic field
-Ferromagnetics: produce their own m.f.

Origins of Magnetism

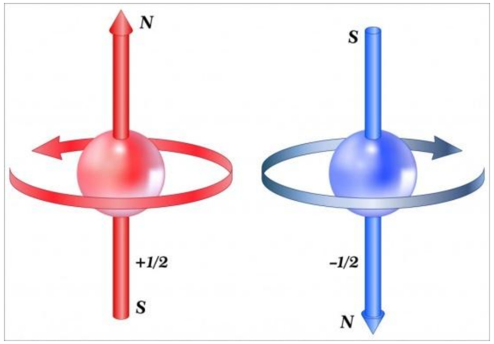
Closed loop with electric current:



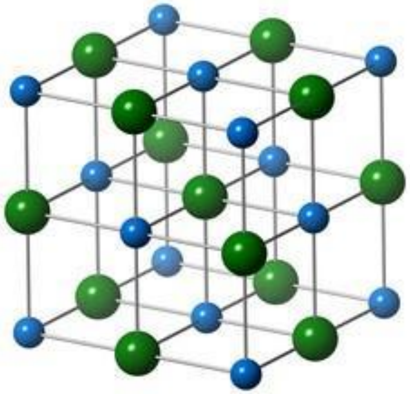
Magnetic moment:

μ = I x S

Spin of an electron:



The crystal lattice:



Every atom in a crystal lattice has its own magnetic moment. Vector sum of these moments tells if the material is dia-, para-, or ferromagnetic (whether they're aligned and sum up, or have different directions and cancel out). Longe-range exchange interactions between magnetic moments can lead to the formation of magnetic DOMAINS and cause the material to be ferromagnetic!

Single-Molecule Magnets (SMM)

- Metal-organic compounds

- Superparamagnetic: every molecule is a 'domain' with its own magnetic moment

- Long-range interactions between moments DO NOT OCCUR!

- They exhibit magnetic hysteresis of PURELY molecular origin

- Possess a large spin in a ground state

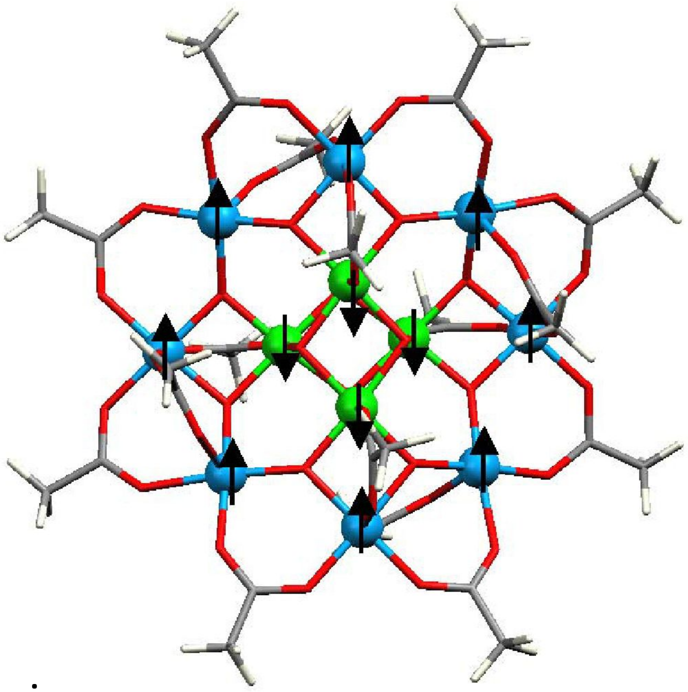
- These (and other) effects are observed below a certain temperature, called 'blocking temperature' $T_\mathbf{B}$

Mn_{12}-ac molecule – the archetypal SMM

- First synthesized by Tadeusz Lis in 1980: '*(…)such a complicated dodecameric unit should have interesting magnetic properties*' (T. Lis, Acta Crystallographica Section B 36 (9) (1980) 2042–2046.)

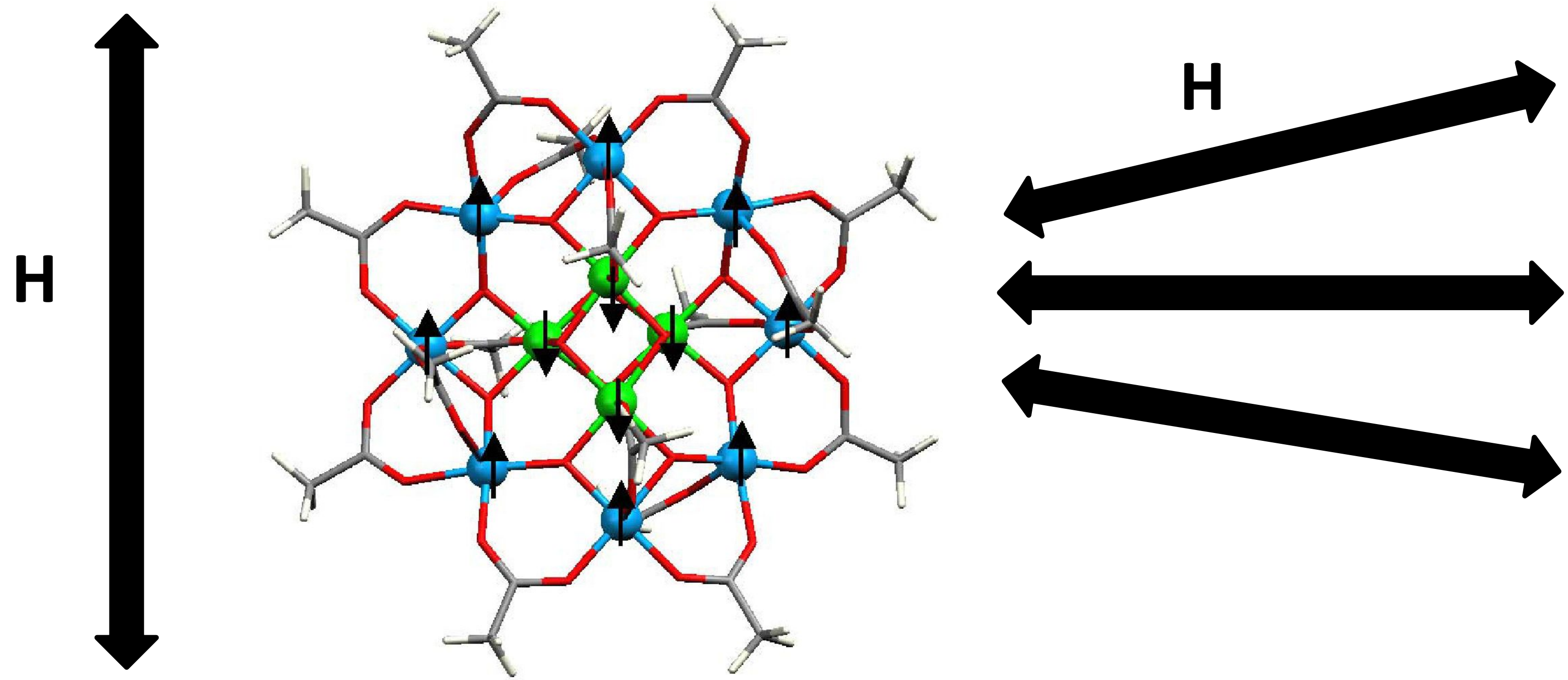
- Recognized as SMM and originated the molecular magnetism field in 1991 (A. Caneschi; D. Gatteschi; R. Sessoli; A.L. Barra; L.C. Brunel; M. Guillot (1991). *Journal of the American Chemical Society*. **113** (15): 5873.)

Ground-state spin:
S = ± 10



Uniaxial Magnetic Anisotropy

In a given material or molecule there exists one, favored direction (so-called easy axis) in which it gets easily magnetized, as opposed to other directions (hard axes), in which it's hard to magnetize (align spin along with the lines of external magnetic field).

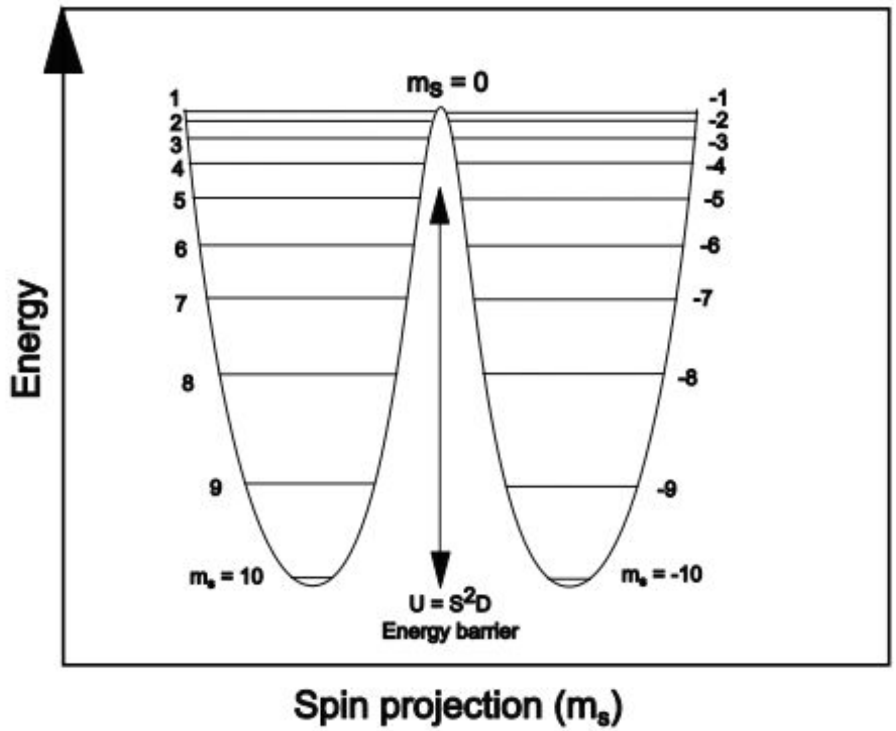


Easy axis of Mn_{12}-ac

Hard axes of Mn_{12}-ac

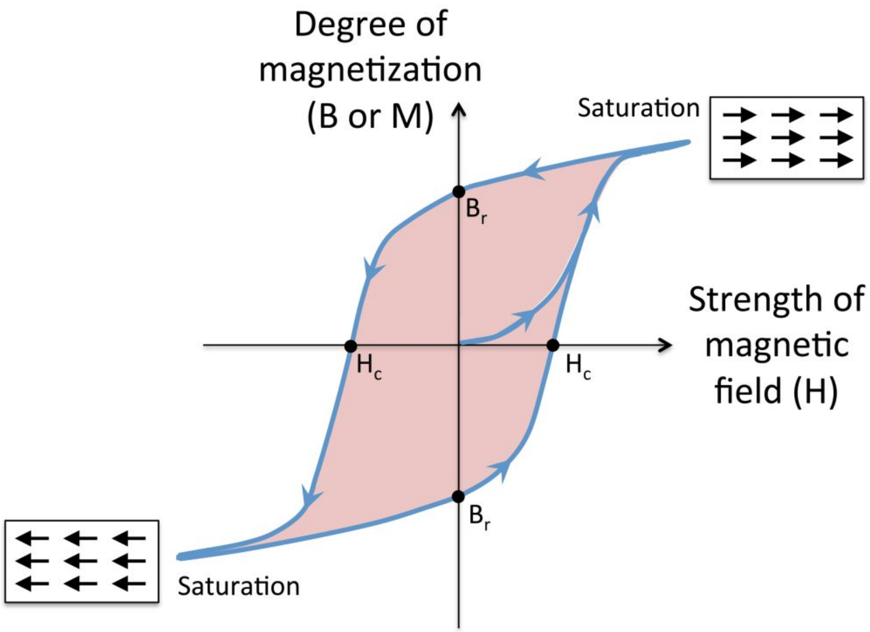
Quantum Tunnelling of Magnetization - QTM

Physical phenomenon by which the quantum mechanical state of magnetization of a nanomagnet is a linear superposition of two states with well-defined and opposite magnetization.

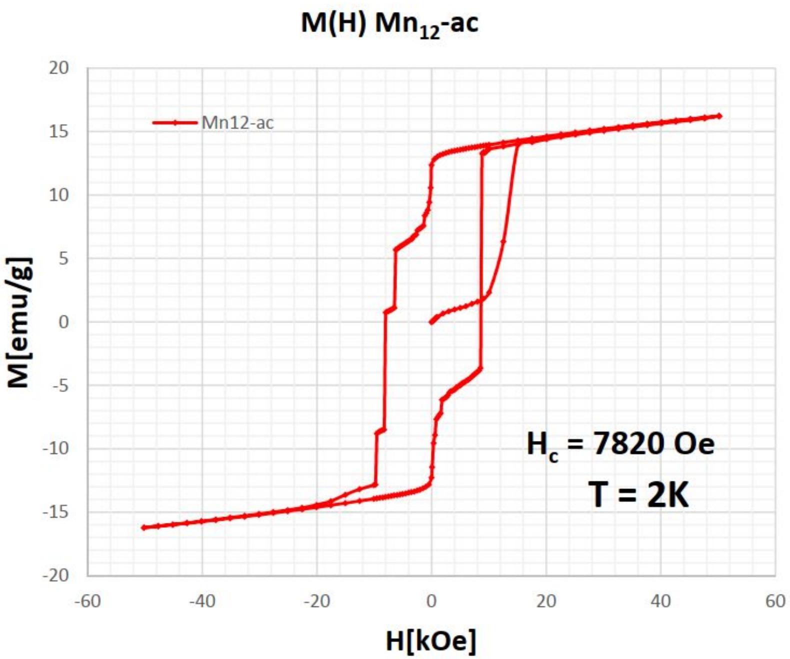


$\mathbf{U}_{eff}$ – energy barrier, **D** - axial zero field splitting parameter

M vs H dependence of a classical magnetic material



M vs H dependence of a Single-molecule magnet



Magnetization of such small entities like single-molecule magnets can be measured using the SQUID magnetometry technique!

Blocking Temperature T_B

The temperature below which the relaxation of the magnetization becomes slow compared to the time scale of a particular investigation technique. There is typically a correlation between increasing an SMM's blocking temperature and energy barrier. The average blocking temperature for SMMs is 4K.

Relaxation Time τ

Time that it takes to reverse the direction of magnetization. In the temperature range below T_B SMMs relaxation time can be in order of months, or even years. This means that below T_B SMMs remain stable with one state of magnetization and do not flip (unless purposedly acted upon with external magnetic field).

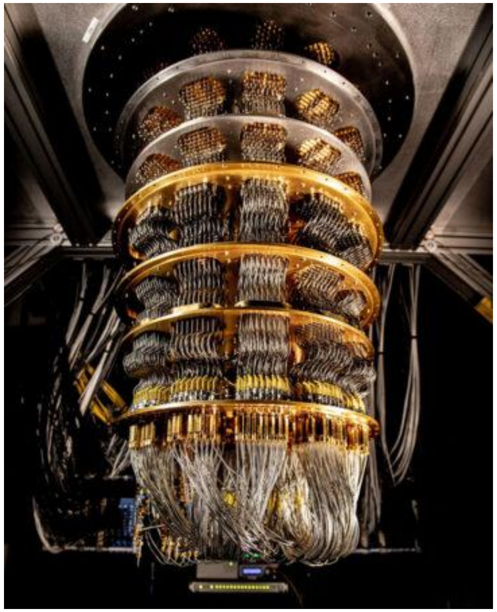
Possible applications of SMMs

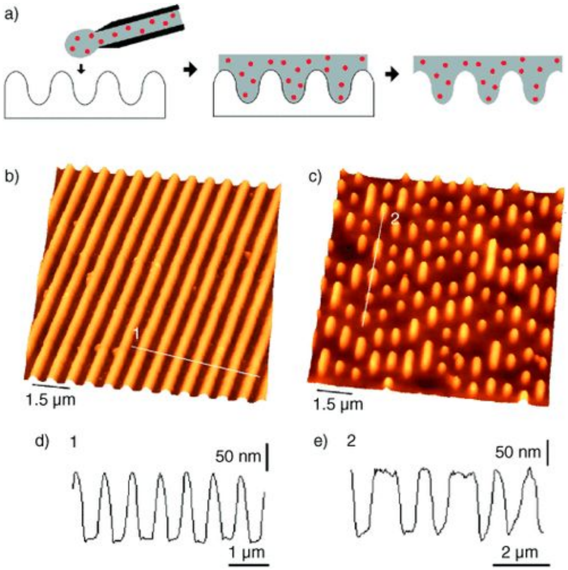
-Qubits for quantum computing

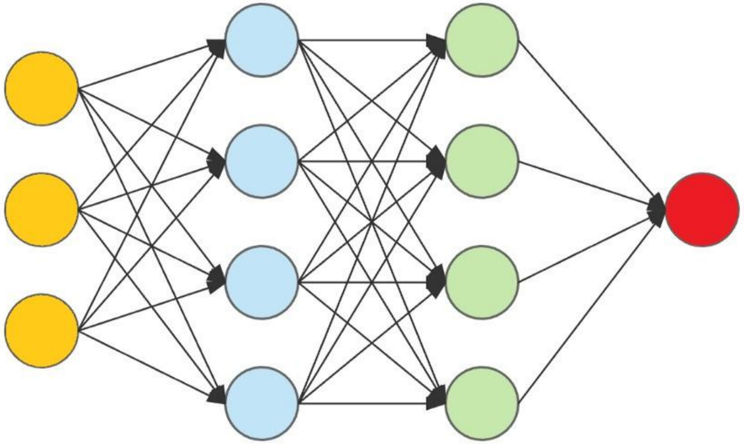
-Ultra-high density data storage devices

- Spintronic devices

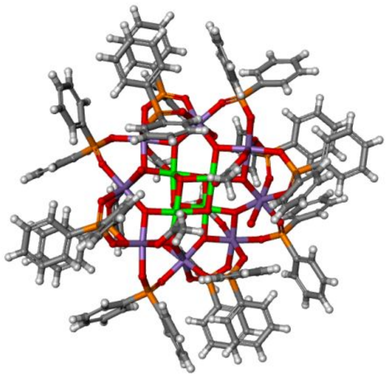
- Molecular neural networks??



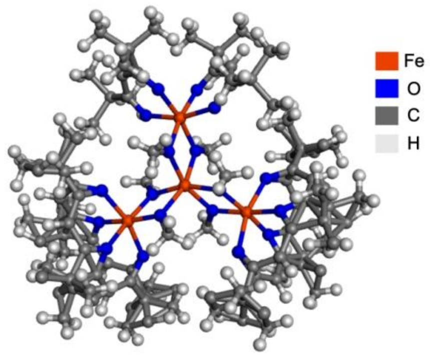




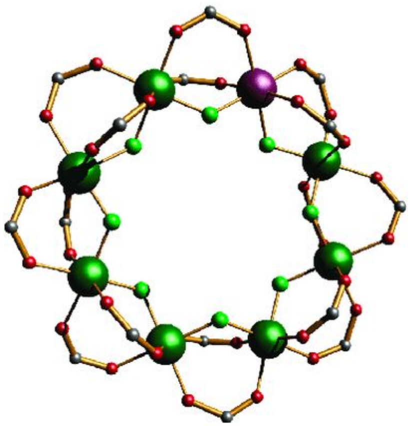
Other types of Single-Molecule Magnets



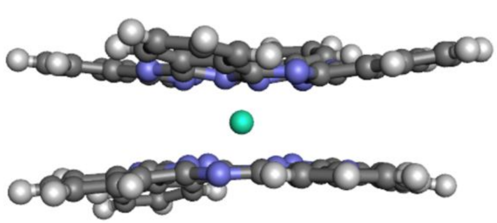
Mn_{12}-dphn (diphenylphosphonate)



Fe_4-tacn „iron star”



Cr_7Ni heterometallic wheel



$LnPc_2$ „double-decker” single-ion magnet

Obtaining Single-Molecule Magnets

Straight-forward, wet chemistry method – crystal growth from a solution

We need only 3 reagents!

- Manganese acetate tetrahydrate: $(Mn(CH_3CO_2)_2 \cdot 4H_2O)$
- Potassium permanganate: $KMnO_4$
- 60% acetic acid: CH_3COOH

With proper proportions, one just needs to mix the ingredients together and leave the solution for ~4 days, isolated from any external disturbances, in order for Mn_{12} crystals to grow.

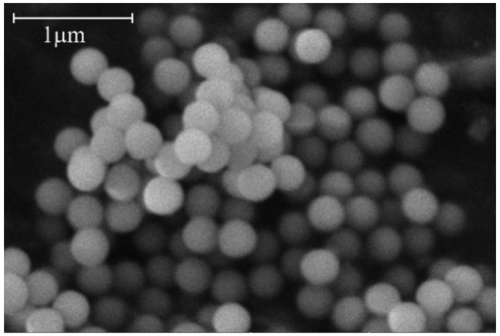
Mn_{12}-ac crystals synthesized in our lab.

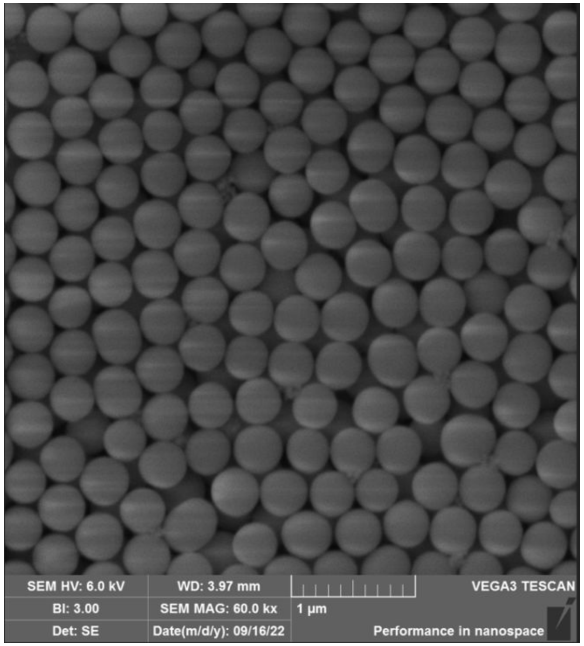
Functionalization – creating a functional, composite nanomaterial

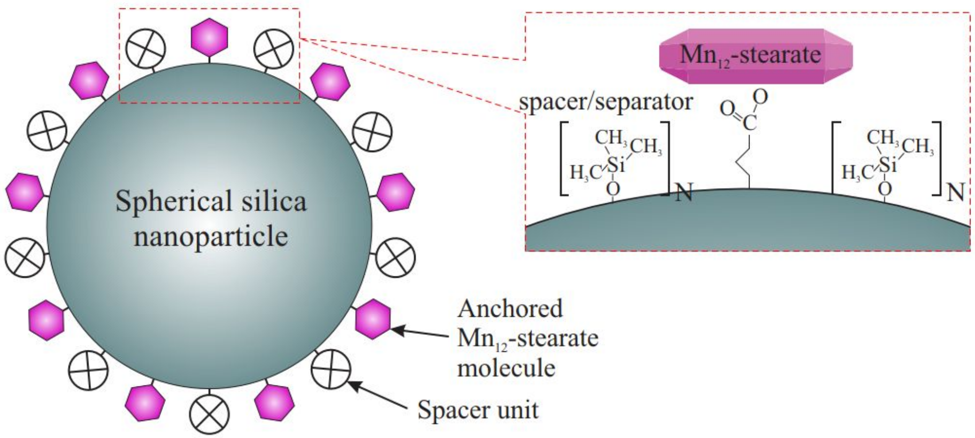
In order to get SMMs to work – we need to place them somewhere.

Spherical SiO_2 nanoparticles (d = 75 – 450 nm):

- Excellent thermal and mechanical stability,
- Easy and not expensive to produce,
- Large specific surface area -> more room for nanomagnets to accommodate!







Laskowska, M.; Pastukh, O.; Konieczny, P.; Dulski, M.; Zalsiński, M.; Laskowski, L. Magnetic Behaviour of Mn_{12}-Stearate Single-Molecule Magnets Immobilized on the Surface of 300 nm Spherical Silica Nanoparticles. *Materials* **2020**, *13*, 2624

Obtaining spherical silica nanoparticles

The Stöber method

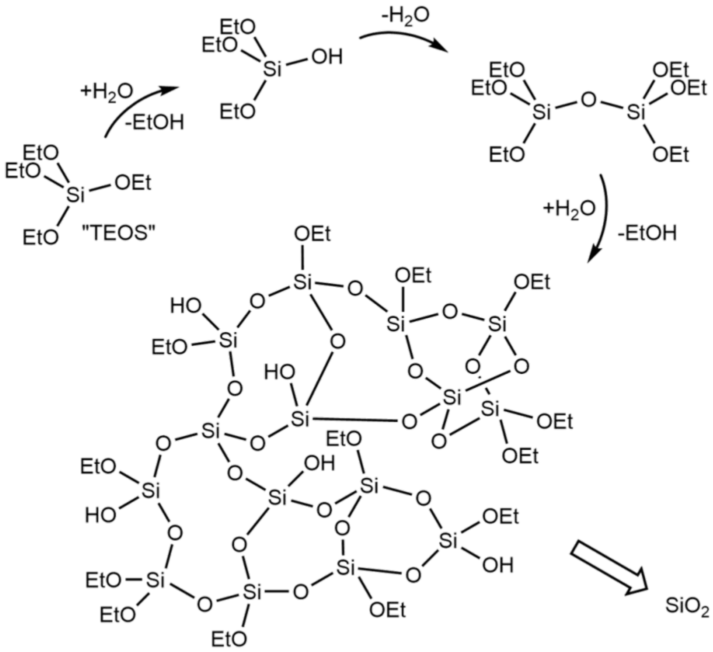
A convenient, sol-gel process of synthesizing spherical silica NPs with controllable and uniform size (d = 50 – 2000 nm, depending on conditions).

Precursor: tetraethylortosilicate (TEOS)

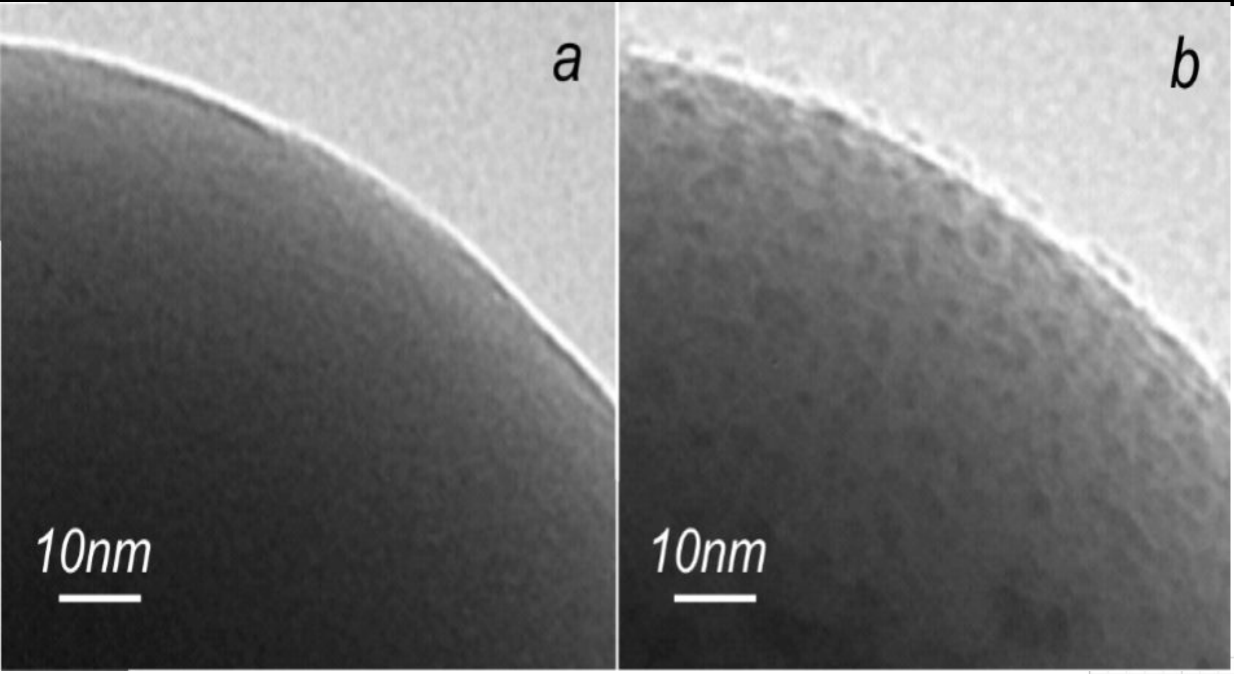
Hydrolysis and condensation with water in ethyl alcohol environment

Catalyst: ammonia (NH_3)

After mixing the mixture is centrifuged and the products are dried

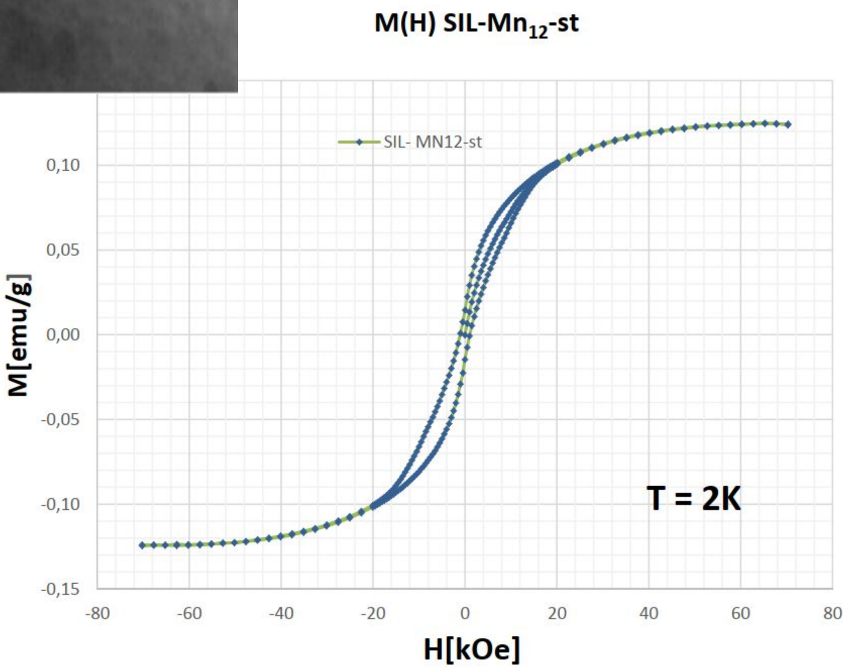


Hydrolysis and condensation of TEOS
(https://en.wikipedia.org/wiki/Stöber_process)



TEM images of a single silica sphere a) before and b) after functionalization

Hysteresis loop for 300nm silica spheres functionalized with single-molecule magnets. It is the proof, that magnetic properties remain after the process of functionalization!



Problems:

- Mn_{12} mass is ~1% of a total nanomaterials mass, which is why characterization of its properties is usually challenging
-Aspiration to improve the magnetic performance of the nanomaterial

Solution:

Optimization of the nanomaterial by manipulating the size of a silica substrate!

In the meantime...

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Synthetic Opals or Versatile Nanotools—A One-Step Synthesis of Uniform Spherical Silica Particles

by Magdalena Laskowska [1], Agnieszka Karczmarska [1], Mateusz Schabikowski [1], Michał Adamek [1], Alexey Maximenko [2], Katarzyna Pawlik [3], Oliwia Kowalska [4], Zbigniew Olejniczak [1] and Łukasz Laskowski [1,*]

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(This article belongs to the Section Molecular Nanoscience)

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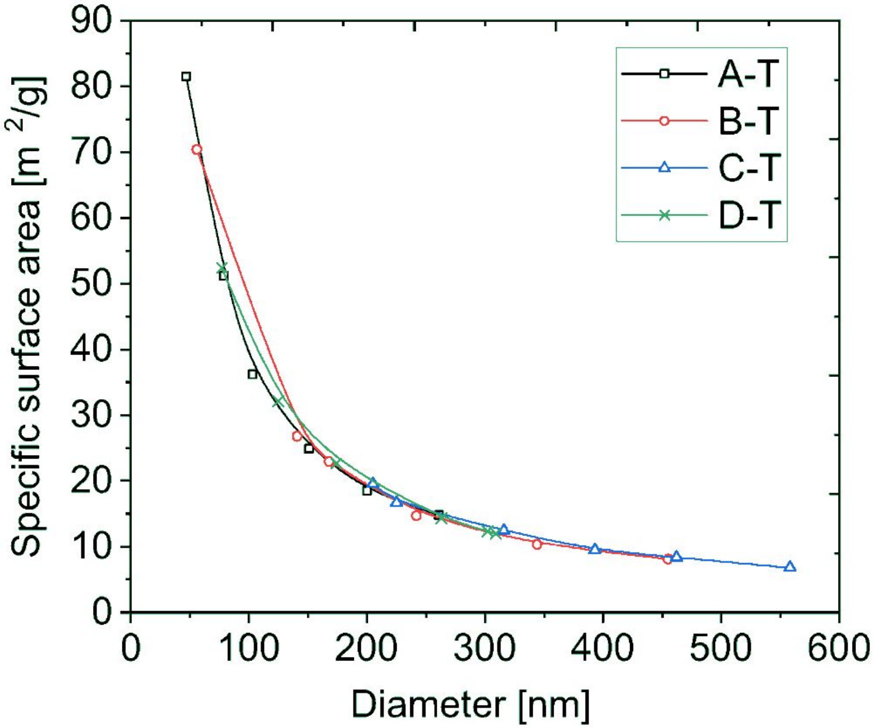
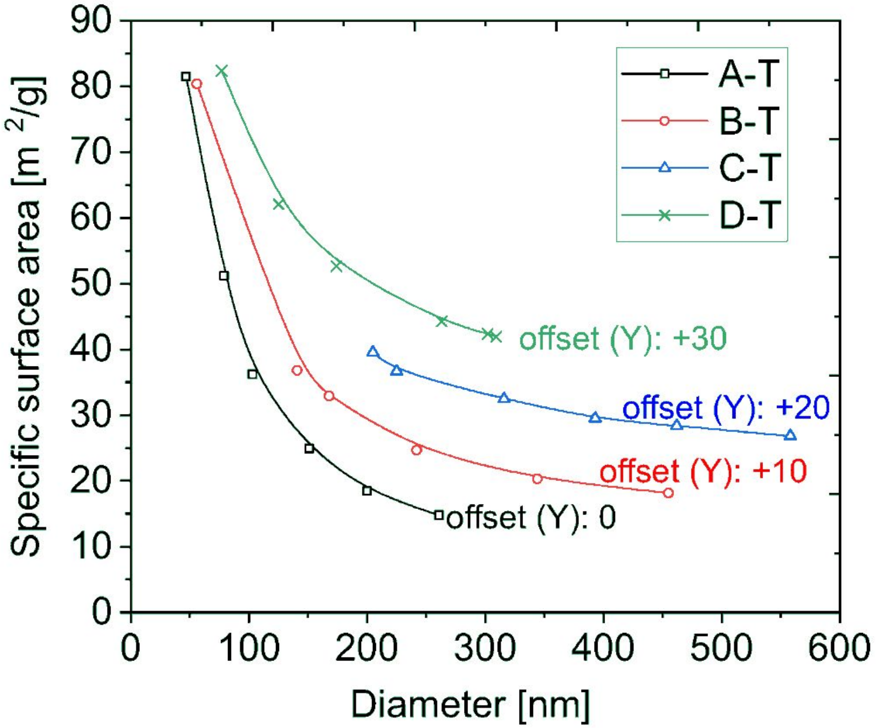




The dependence of the specific surface area on the diameter of the nanoparticles.
Left: native results, right: offset applied for better visibility.

Recently:

- 4 sizes of SiO_2 substrate were prepared: 75, 150, 300 and 450 nm

- All of them were functionalized with Mn_{12} SMMs

- The resulting 4 variants of our composite nanomaterial were thoroughly characterized by several experimental techniques

- Data were collected, processed and analyzed

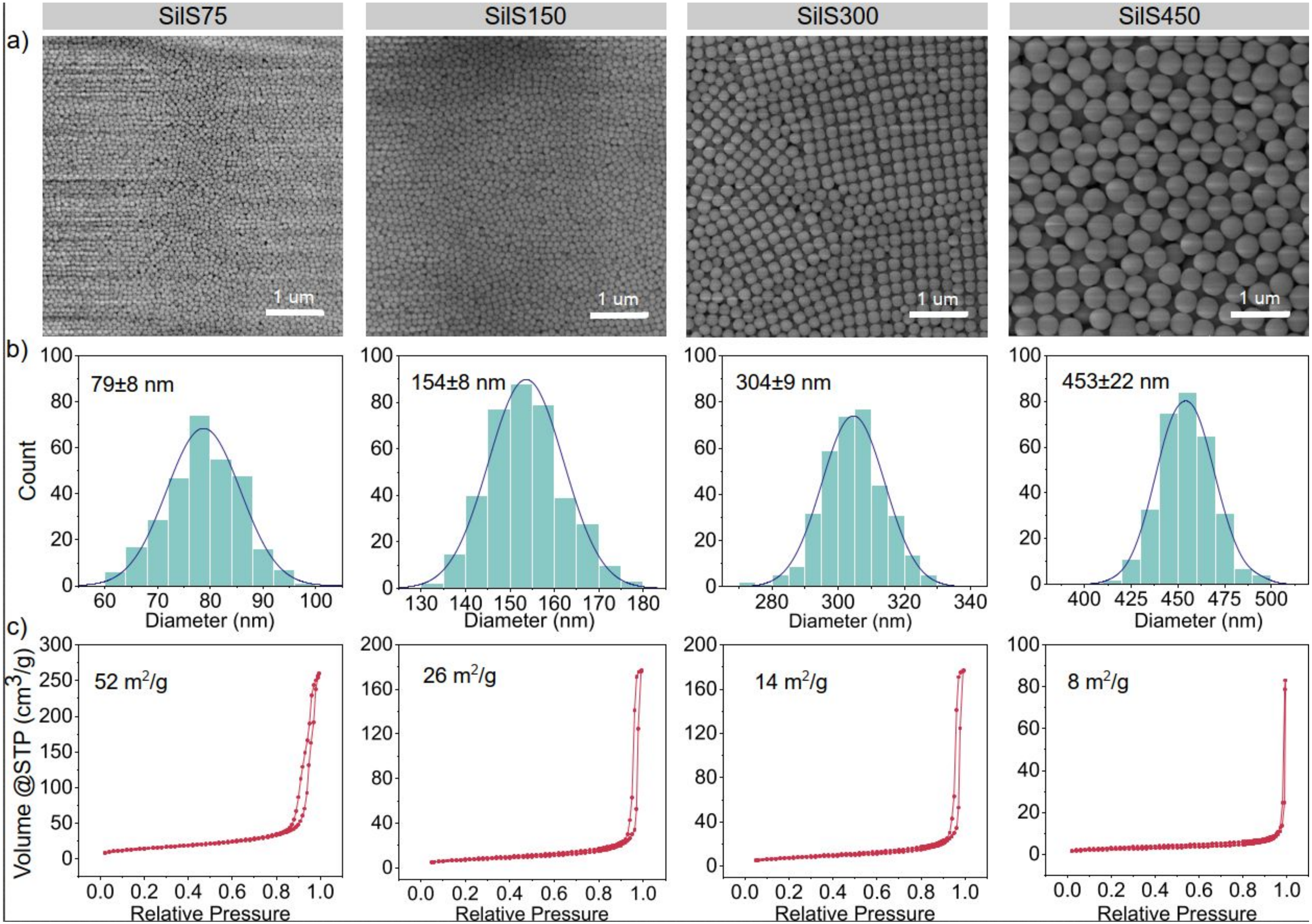
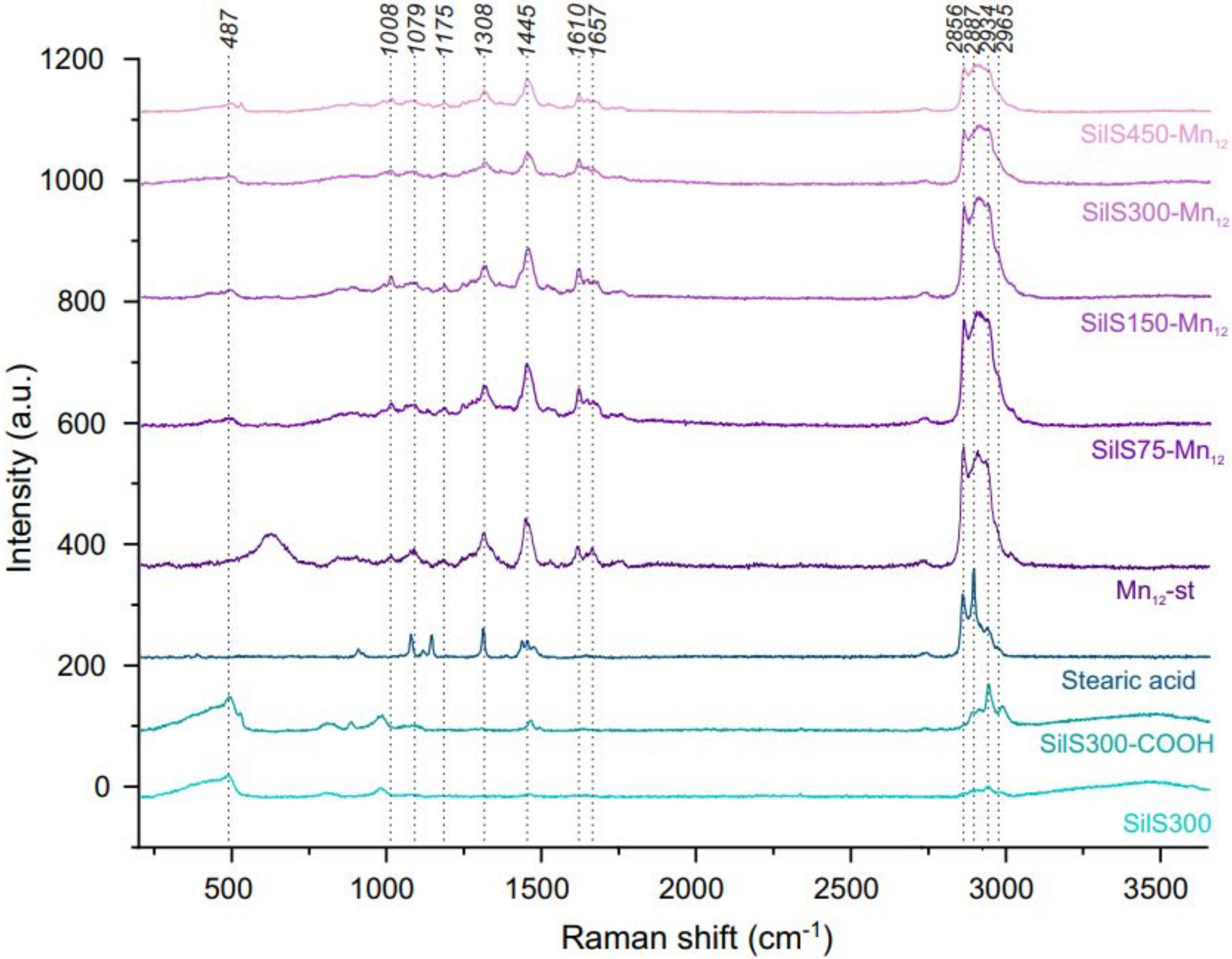
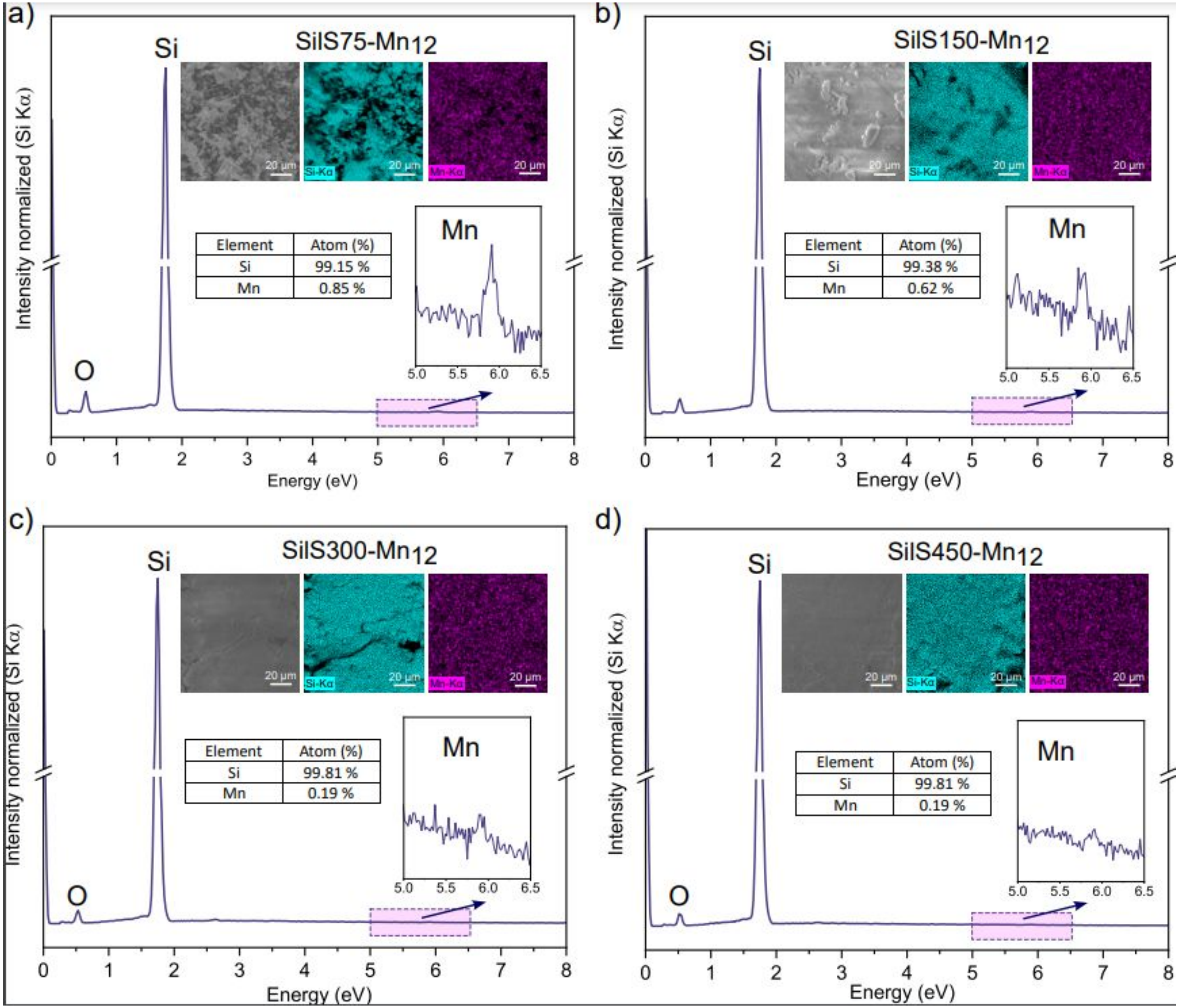
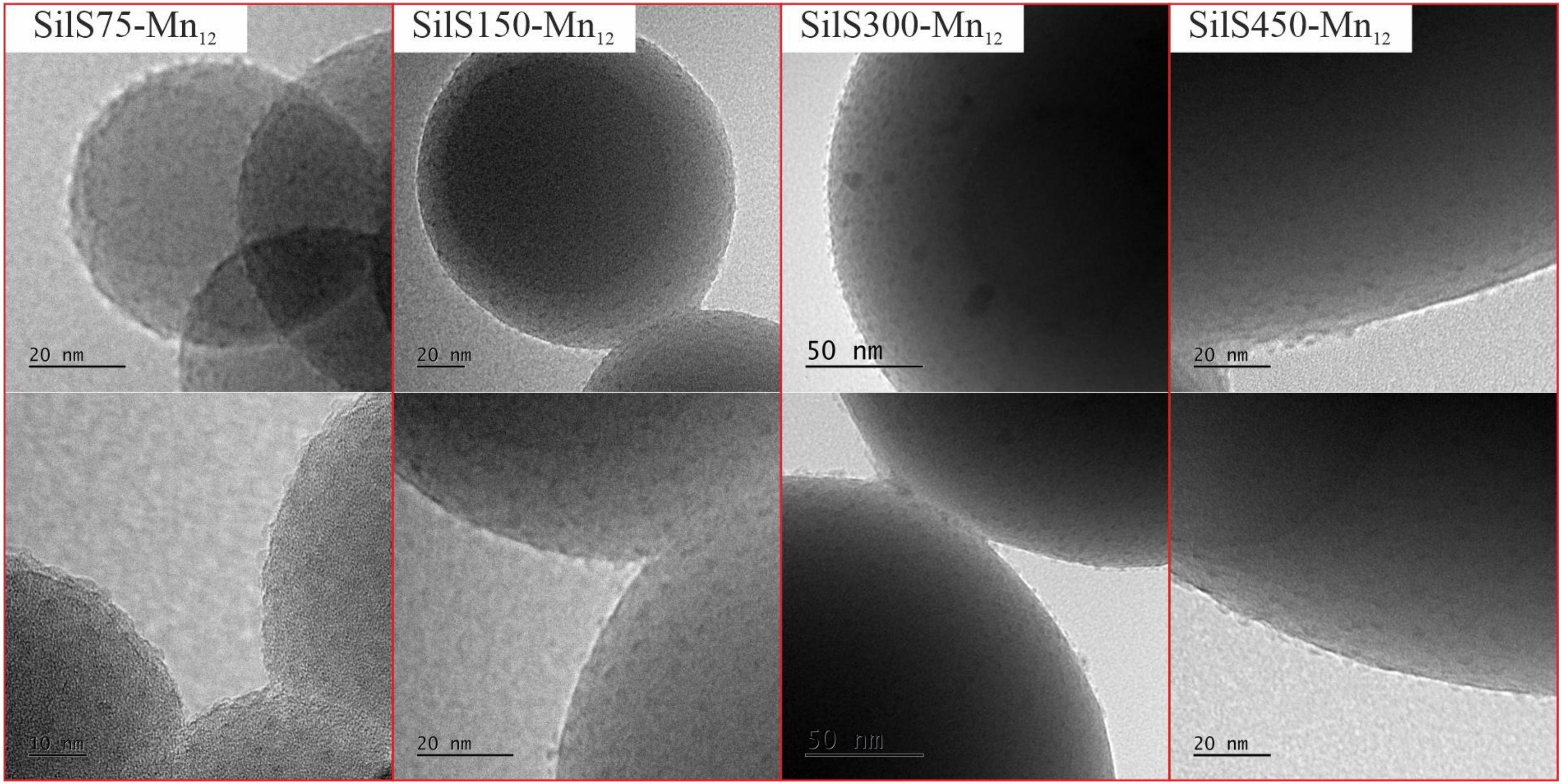

SiIS75
SiIS150
SiIS300
SiIS450
a)
1 um
1 um
1 um
1 um
b)
79±8 nm
154±8 nm
304±9 nm
453±22 nm
Count
Diameter (nm)
Diameter (nm)
Diameter (nm)
Diameter (nm)
c)
52 m²/g
26 m²/g
14 m²/g
8 m²/g
Volume @STP (cm³/g)
Relative Pressure
Relative Pressure
Relative Pressure
Relative Pressure

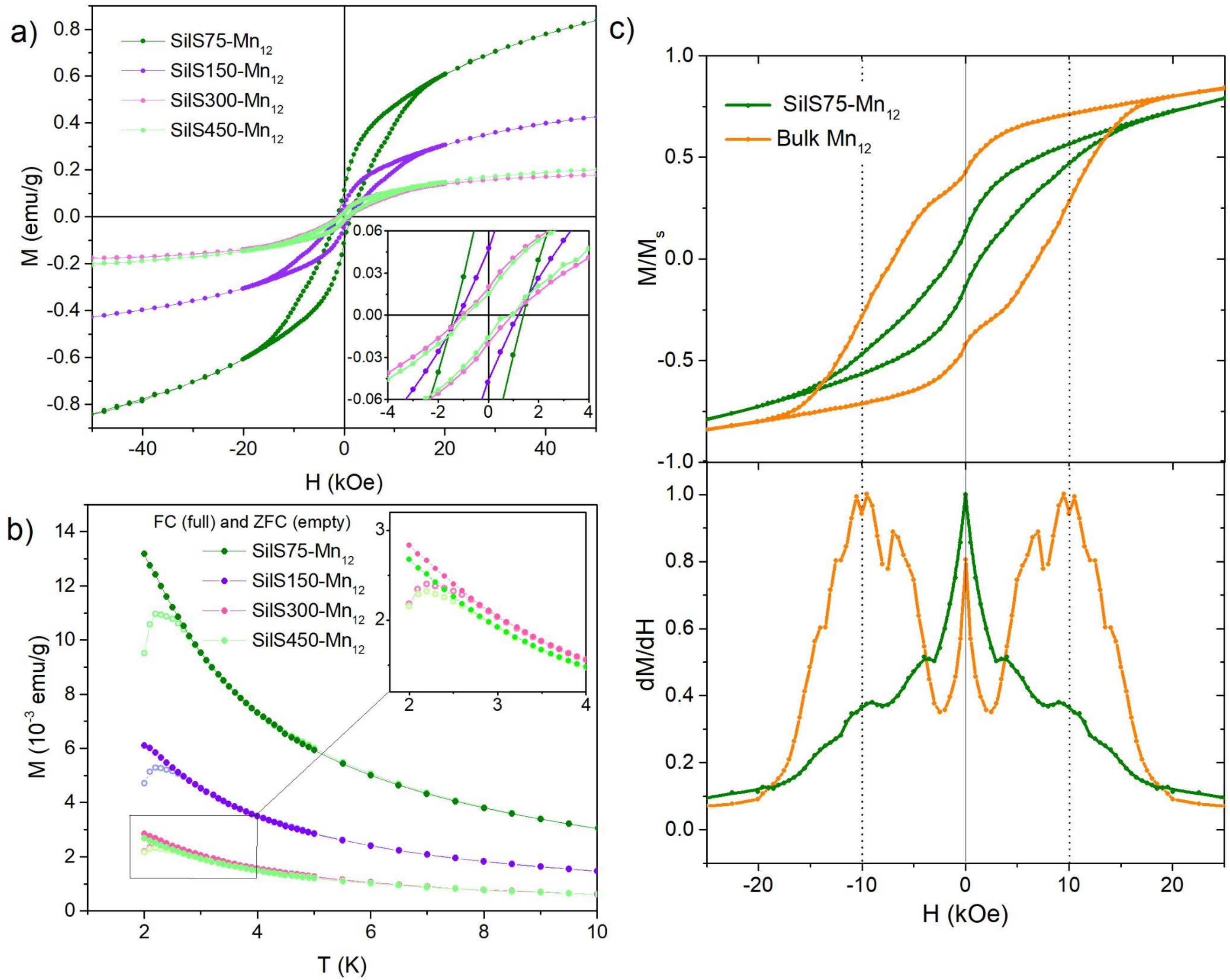
Table 1: Data set illustrating the capacity of different-sized SilS nanoparticles for anchoring Mn_{12}-st molecules.

	BET	AAS		EDS	Theoretical	
	S [m^2/g]	Mn [mg/l]	Mn [mg/m^2]	Mn [%mass]	Mn_{12}-st no. per 1 NP	Mn_{12}-st no. per 1 g
SilS75-Mn_{12}	52,41	5,138	0,09	0,85	5062	8,65
SilS150-Mn_{12}	24,91	3,251	0,13	0,62	20250	4,32
SilS300-Mn_{12}	12,38	1,473	0,11	0,19	81000	2,16
SilS450-Mn_{12}	8,12	1,256	0,16	0,19	182250	1,44


487
1008
1079
1175
1308
1445
1610
1657
2856
2887
2934
2965
1200
1000
800
600
400
200
0
Intensity (a.u.)
500
1000
1500
2000
2500
3000
3500
Raman shift (cm-1)
SilS450-Mn12
SilS300-Mn12
SilS150-Mn12
SilS75-Mn12
Mn12-st
Stearic acid
SilS300-COOH
SilS300


a)
SiIS75-Mn12
Si
O
Mn
Element | Atom (%)
Si | 99.15 %
Mn | 0.85 %
Intensity normalized (Si Kα)
Energy (eV)
b)
SiIS150-Mn12
Si
Mn
Element | Atom (%)
Si | 99.38 %
Mn | 0.62 %
Intensity normalized (Si Kα)
Energy (eV)
c)
SiIS300-Mn12
Si
O
Mn
Element | Atom (%)
Si | 99.81 %
Mn | 0.19 %
Intensity normalized (Si Kα)
Energy (eV)
d)
SiIS450-Mn12
Si
O
Mn
Element | Atom (%)
Si | 99.81 %
Mn | 0.19 %
Intensity normalized (Si Kα)
Energy (eV)


SilS75-Mn_{12}
SilS150-Mn_{12}
SilS300-Mn_{12}
SilS450-Mn_{12}
20 nm
20 nm
50 nm
20 nm
10 nm
20 nm
50 nm
20 nm



a) Hysteresis loops of magnetization recorded at 2.0 K, (b) ZFC and FC magnetization collected in a DC field of H=100 Oe, (c) Normalized magnetization loop of SilS75Mn12 sample in comparison to bulk Mn12 complex and corresponding derivatives of magnetization as a function of field.

Summary

- In contrast to classical magnets, SMM molecules are individual magnets, each having their own incidental magnetic moment,
- We can say that every such molecule is a separate domain,
- SMMs main features are: magnetic anisotropy, quantum tunnelling of spin, blocking temperature and long relaxation time,
- There are many kinds of SMMs, and one can obtain them by means of wet chemistry,
- Their possible applications are quantum computing, spintronics, molecular neural networks,
- Process of functionalization is essential to make them applicable

Summary

- We are able to produce a magnetic composite nanomaterials with spherical nanosilica substrate of different sizes in a controllable manner
- By adjusting the size of a substrate we have optimized our material and improved its performance
- A series of experiments confirm our assumptions about its structure and functioning

Thank you!