Advanced functional bio-materials synthesis and applications.

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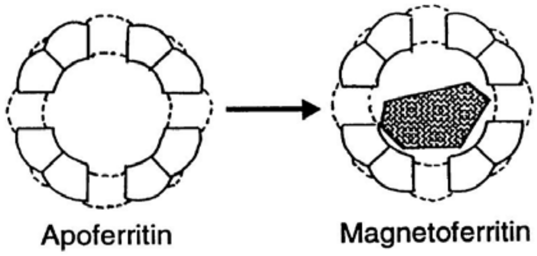
Magnetic Ferritin



Peptide out-shell surrounding ~6 nm iron oxide (Fe_3O_4)

FC Meldrum, BR Heywood, and S Mann, Science, Vol 257, 522-523

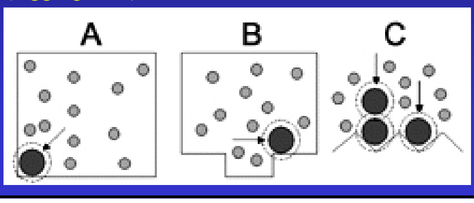
Novel functional materials :Bio-molecules

Entropically Forces

- Self-organization (Folding)
- Self-assembly (Aggregation)

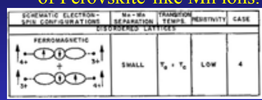
$$\Delta G = \Delta H - TdS$$

$$S = R \ln \Omega$$

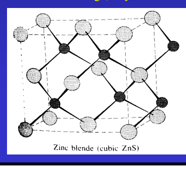


Diluted Magnetic Semiconductor (DMS)

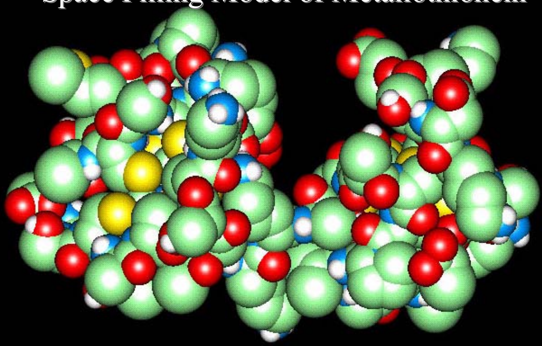
1. Magnetic semiconductors are materials that exhibit both ferromagnetism (or a similar response) and useful semiconductor properties.
2. Silicon substrate are doping with II-Mn-VI A materials, such as $Cd_{(1-x)}Mn_xO$, $Cd_{(1-x)}Mn_xS$, $Cd_{(1-x)}Mn_xSe$ or $Cd_{(1-x)}Mn_xTe$. Where x<0.1.
3. II-Mn-VI A materials are in Zinc blende structure.
4. There d-electrons of Mn may align by a double exchange mechanism of the semi-covalent model of Perovskite-like Mn ions.



John B. Goodenough, Physical Review (1955).

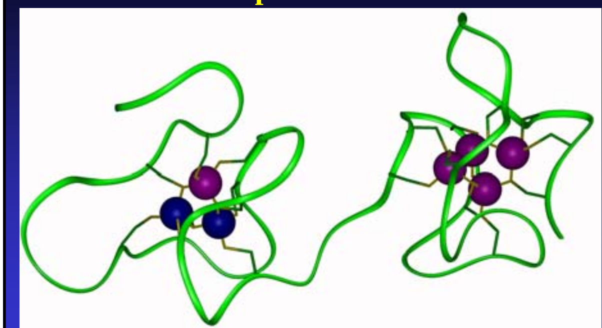


Space Filling Model of Metallothionein



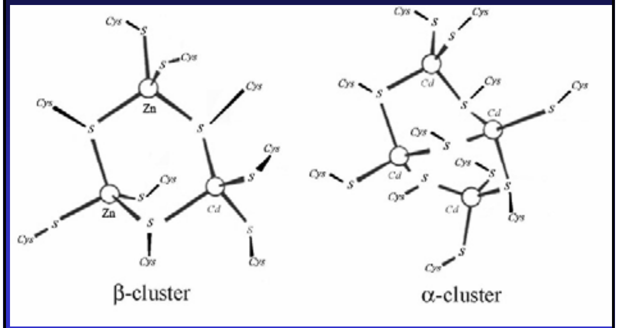
β-domain **α-domain**

Metallothionein-2: native Zn, Cd binding protein.



Robbins et al. J Mol Biol. (1991)
Y.-L. Liu et al. Biochem. Biophys. Res. Commun. (2003) C.C. Chang 2005

Metal binding cluster of MT-2



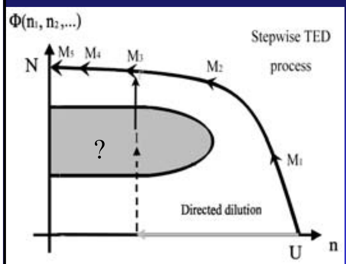
Motivation

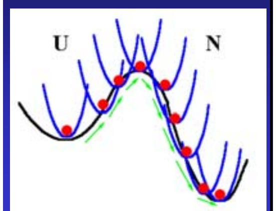
Protein is not a magnetic material in nature. However, if we replace the metal species, (such as Zn, Ca) of metal binding protein with magnetic ions (such as Mn, Ni, Co), we may obtain a novel magnetic material, "magnetic protein".

Objectives

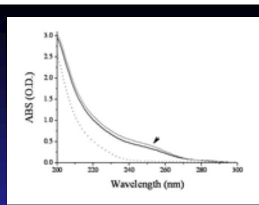
- Creating a room temperature molecular magnet from metal binding protein, MT-2.
- By combining biomaterial and semiconductor techniques we have created novel biomaterial based molecular devices.

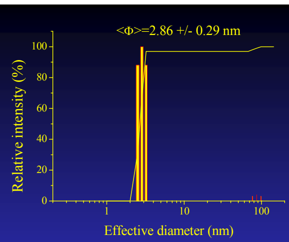
Refolding of metallothionein via an over-critical reaction path.





Liu et al., Biochem. Biophy. Res. Commu. (2003) 306, 59- 63

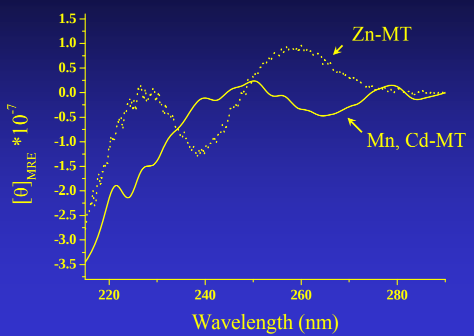




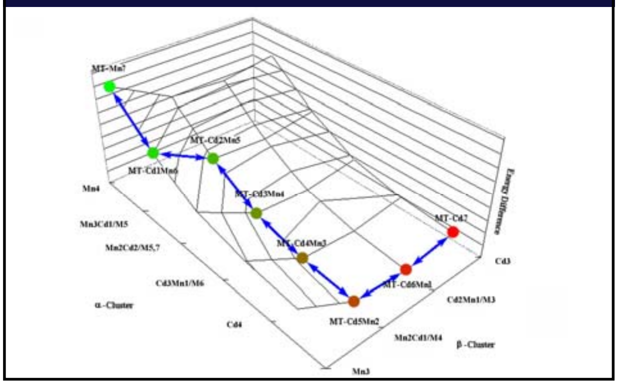
1. ICP mass spectroscopy (sensitivity ~0.01 PPB) analysis indicated that there are two Mn and five Cd ions in each MT molecule. There is no trace Fe containing.
2. The UV spectrum is similar to native MT and this indicated that, when Mn is substituted for Zn, the conformation of metal binding clusters does not change.
3. Dynamic light scattering study indicated that the effective diameter of Mn/Cd bound MT is 2.86 nm and the particle sizes are uniform.

C.C. Chang 2005

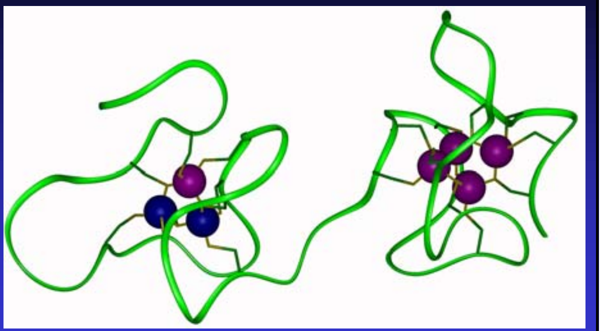
Circular Dichroism spectra of MTs



Molecular simulation of Mn,Cd-MT



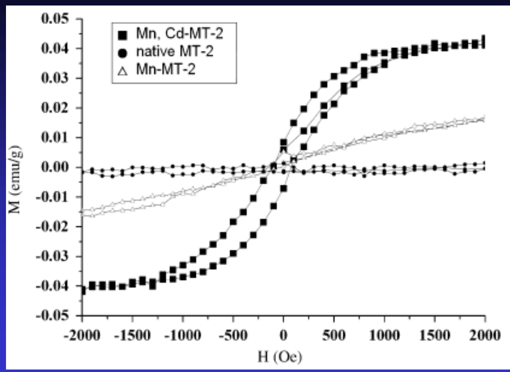
Mn,Cd-Metallothionein.



C.C. Chang et al. Biochem. Biophys. Res. Commun. (2006)

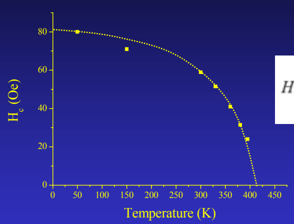
C.C. Chang 2005

Magnetization measurement of MTs by SQUID



Chang C.-C, et. al (2006) Applied Physics Letters.

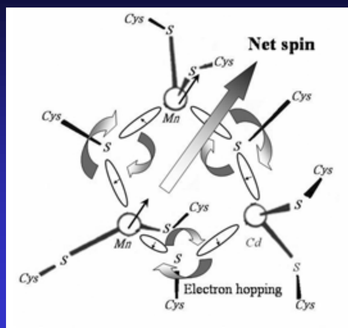
Temperature versus Corecive field of Mn,Cd-MT-2



$$H_c(T)=H_0 m(\tau)\left\{1-\left[\frac{k_B T}{E_0 m^2(\tau)}\ln(t/t_0)\right]^{1/\alpha}\right\}$$

This can fit with modified Neel Brown's model very well and it's α value is about 0.5. Namely, it is a magnetic nanoparticle.

Modified semi-covalent model of Perovskite-like Mn ions.

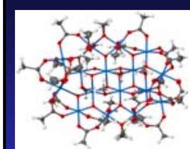


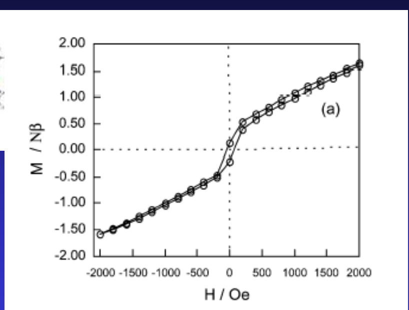
John B. Goodenough, Physical Review (1955)

C.-C. Chang et al. Biochem. Biophys. Res. Commun. (2006)

Conventional molecular magnet

Magnetic ions clustered via VI A elements linkage

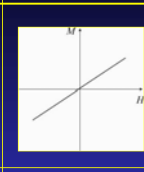
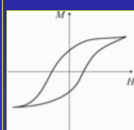




T_c=2 K

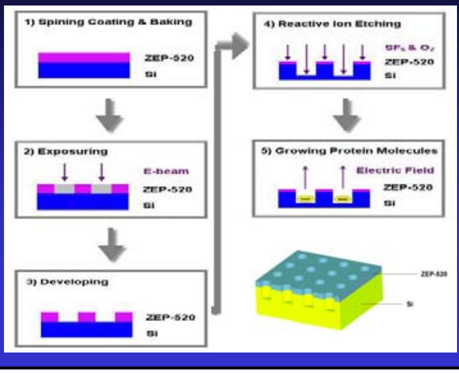
$[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3]\ 6H_2O$

D.J. Price, S.R. Batten, B. Moubaraki and K.S. Murray, Chem. Comm., 2002, 762-763

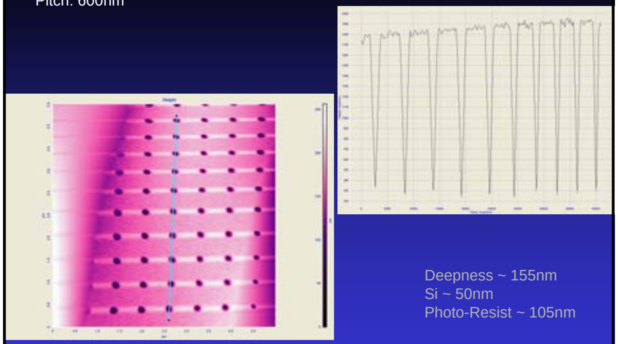
		Dipole Flip Energy	Hysteresis Loop
In Solvent		Small	
Dry powder		Large	

Discrete finite size Heisenberg model simulated by Monte Carlo method

Flow chart of the lithography, etching process and growth of protein molecules.

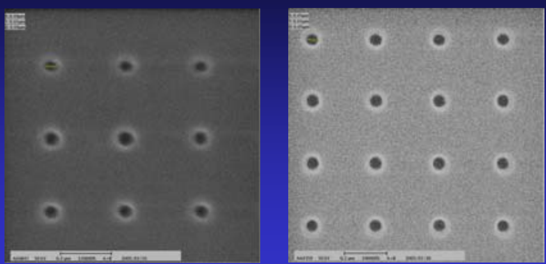


Pitch: 600nm



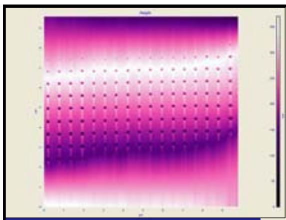
Deepness ~ 155nm
Si ~ 50nm
Photo-Resist ~ 105nm

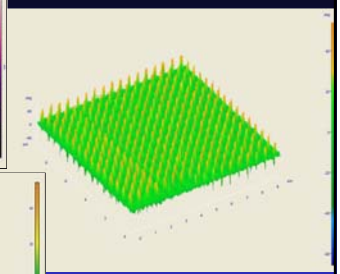
SEM image of the nanopores on a Si (001) substrate

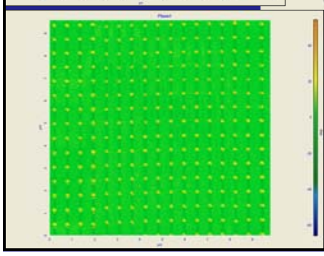


after e-beam lithography process after reactive ion etching process

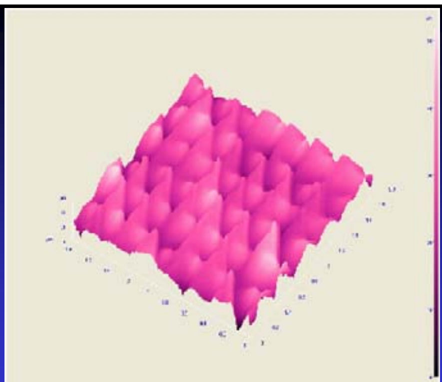
Pore size is 40~130 nm and pitch size is 300 ~600 nm.



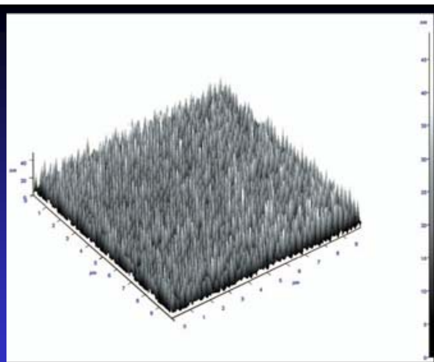




C. -C. Chang et al. (2007). Biomaterials, **Leading opinion.**



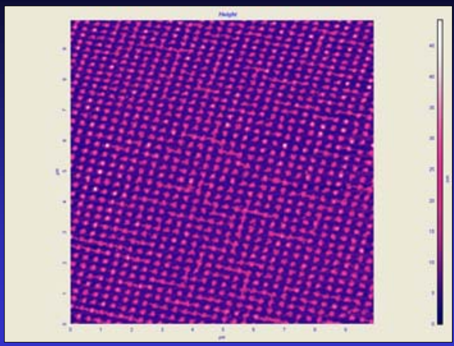
With the AFM operated in contact mode, due to larger scanning force applied on the molecular self-assembly in compared to the taping mode, the nanorods were all bent down and leaned along the tip scanning direction.



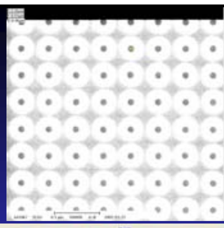
AFM images of the dense molecular self-assembly arrays with a density of approximately 10^{10} cm^{-2}. It is about 100-fold dense than the highest conventional magnetic data storage devices.

Chang C.-C, et. al (2006) Applied Physics Letters **88,** 263104

Two-dimensional AFM image of the patterned MT molecules.

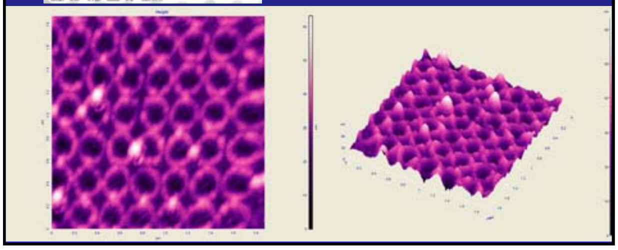


pore size:130 nm; pitch size 300 nm.

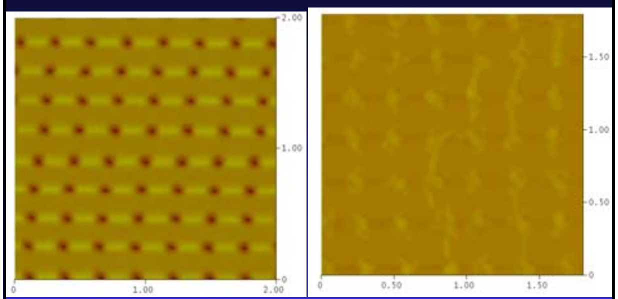


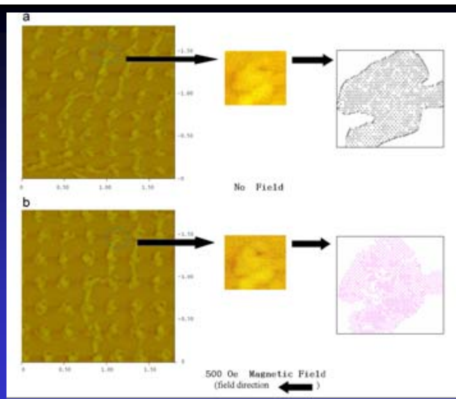
SEM image of the Si template shows a ring shape Si exposed area around the circumference of nanopores.

2D and 3D AFM images of the patterned MT-molecules.



AFM image of protein rods array for MFM measurement.



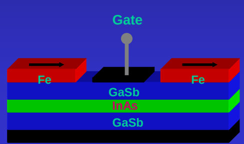


MFM images of nanorods: (a) without the magnetic field; (b) with a 500 Oe magnetic field applied with a field direction from right to left.

Can we create a room temperature magnetic sensing molecular device?

+

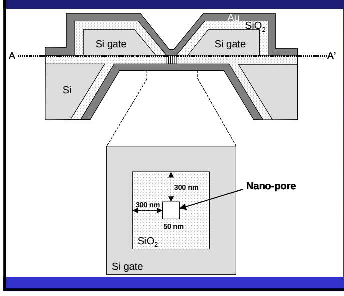
Patterned Molecular Magnets

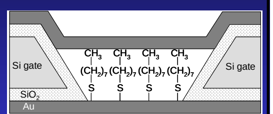


Spin FET

Innovative magnetic protein nanoclusters engineering and applications.

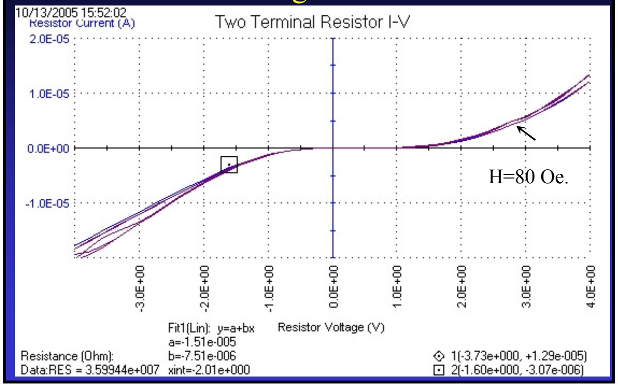
Electric and magnetic field effects on electron conduction through bio-molecules.





Designed by 周亞謙

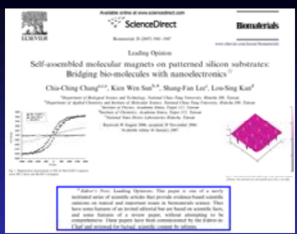
Room temperature molecular magnetic sensing device.



Summary

1. Mn,Cd-MT is a room temperature molecular magnet.
2. MT can be patterned on nanostructured semiconductor surfaces.
3. The shapes of self-assembled MT are depending on the nanostructures patterned on the silicon templates.
4. Using molecular self-assembly and topographical patterning of the semiconductor substrate, we can close the gap between bio-molecules and nanoelectronics built into the semiconductor chip.
5. This magnetic protein may be used in spintronic nano-devices, ultra-high density data storage devices or biomedical image system.
6. This work can be extended to other type of molecules and proteins.

References:



1. **Chang C.-C, Sun K.-W., Lee S.-F., Kan L.-S (2007) Self-assembled Molecular Magnets on Patterned Silicon Substrates: Bridging Bio-molecules with Nanoelectronics. Biomaterials, 28, 1941-7.** **Leading opinion.**
2. **Chang C.-C**, Sun K.-W., Kan L.-S, Kuan C.H. (2006) Guided Three-dimensional Molecular Self-assembly on Silicon Substrates. Applied Physics Letters **88, 263104.**
This paper has been selected in **Virtual Journal of Biological Physics Research** Volume 12, Issue 1 (2006). This paper has been selected in **Virtual Journal of Nanoscale Science & Technology**, Volume 14, Issue 2 (2006), too.
3. **Chang C.-C***, Lee S.-F., Sun K.-W., Ho C.-C., Chen Y.-T., Chang C.-H., Kan L.-S. (2006) Mn,Cd-metallothionein-2: A room temperature magnetic protein. *Biochem. Biophys. Res. Commun.* 340, 1134-1138.

Acknowledgment

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