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Metal-Organic Frameworks III

Lecture 38

Metal-organic frameworks: surfaces and host-guest chemistry

Lecture 39

Metal-organic frameworks: magnetic, electronic ion transport and spin switching properties

Current and future applications of MOFs

1) Separations
2) Catalyses
3) Storage
4) Sensing
5) Data Storage
6) Magnets
7) Molecular Switches/Computers
8) Mechanical Properties
9) Stereoregular Polymerisation
10) Molecular Hosts
11) Controlled Release
12) Optical Properties
13) Conductors/Wires
14) Light-Harvesting

Combinations of some of these in the one material

Long-range Magnetic Order

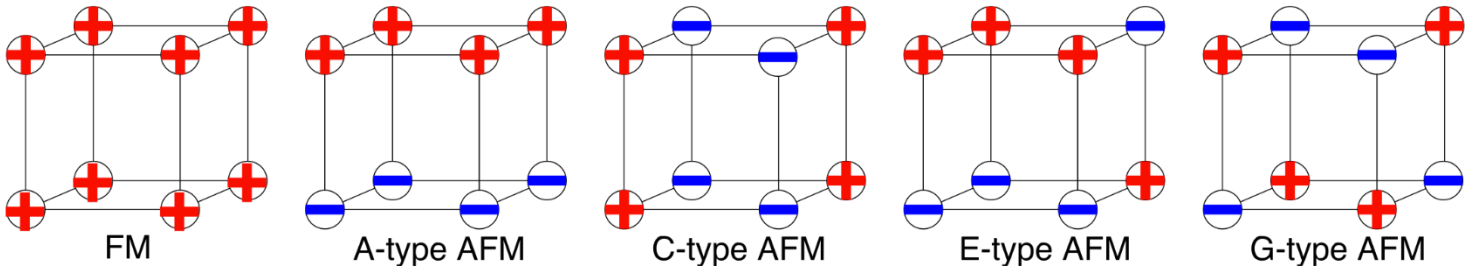
Magnetic atoms arranged in periodic lattices (crystals) have the potential for **long-range magnetic order.**

Most applications of solid-state magnetic materials exploit long-range-ordered, rather than paramagnetic or diamagnetic, states.

↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ ↑ **Ferromagnetic (FM)**

↑ ↓ ↑ ↓ ↑ ↓ ↑ ↓ ↑ **Antiferromagnetic (AFM)**

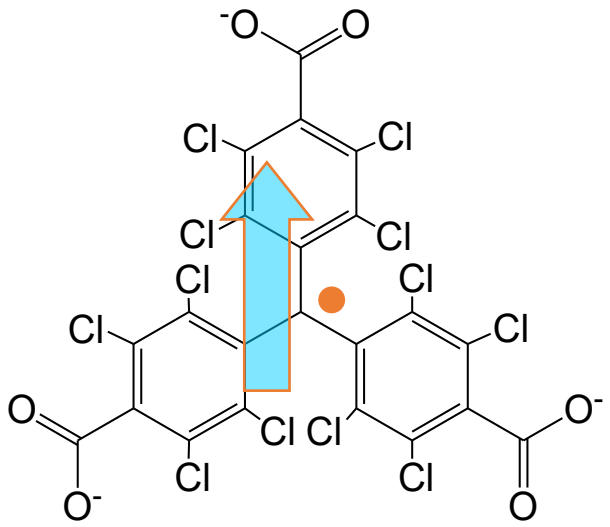
There are a huge variety of possible types of magnetic order in 3D materials. E.g., even for the simplest case of a cubic unit cell with parallel spins of equal magnitude we can have:

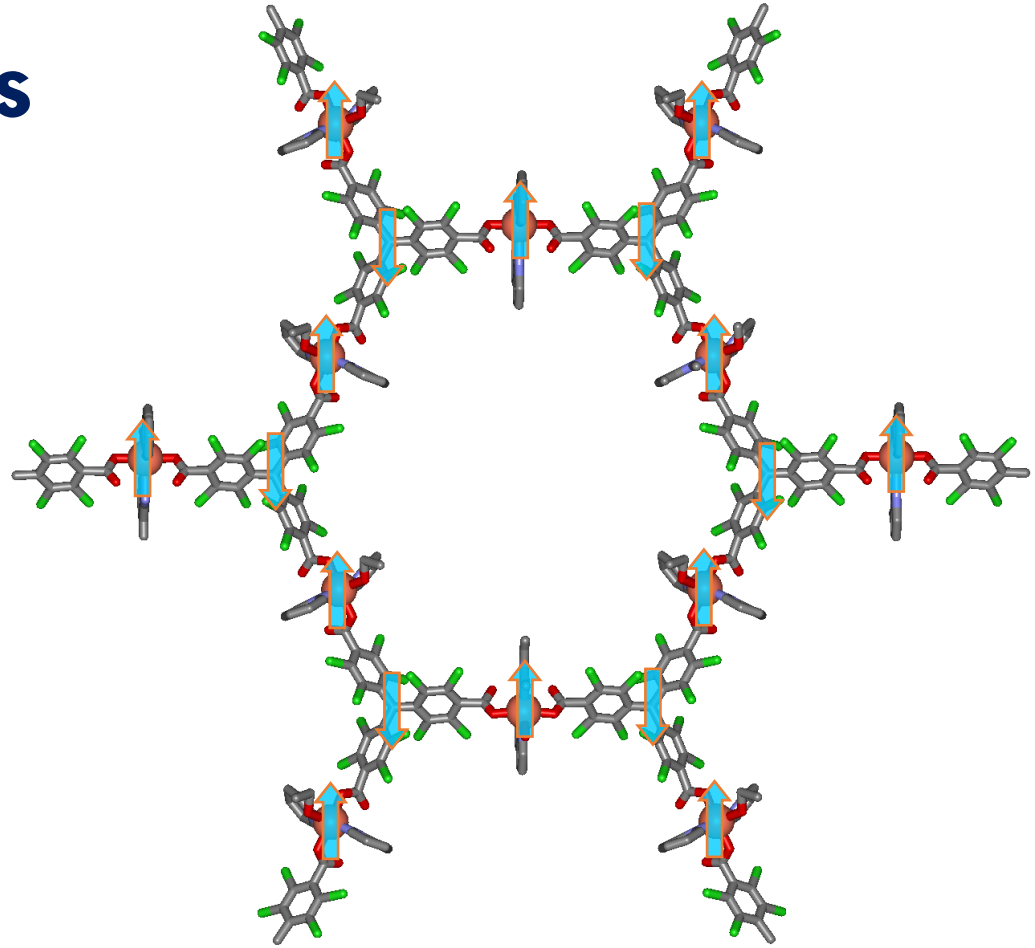


Nanoporous magnetic MOFs

E.g., $Cu_3(PTMTC)_2(py)_6(EtOH)_2(H_2O)$

PTMTC = polychlorinated triphenylmethane tricarboxylate



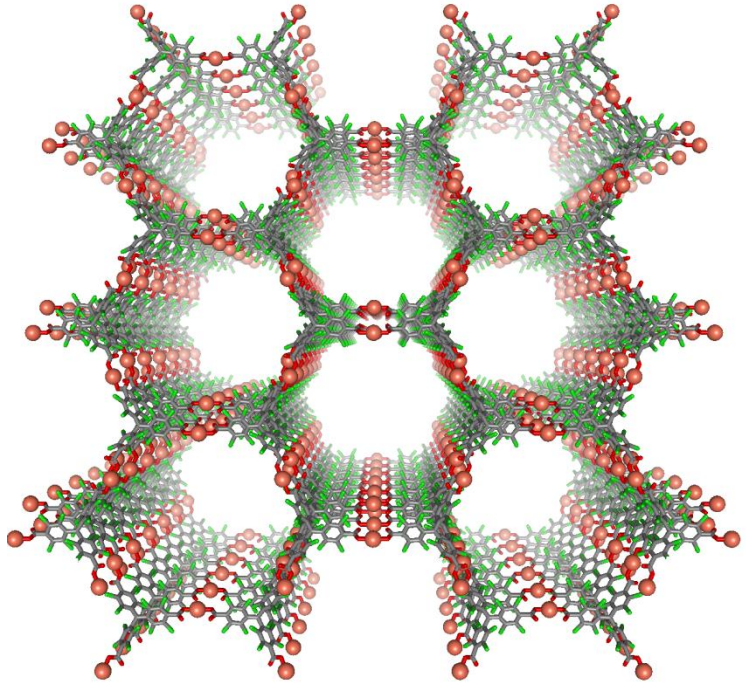


- The ligand is a stable radical with S = ½.
- The metal is Cu(II) (d^9) with 1 unpaired electron, S = ½.
- Antiferromagnetic coupling between the metal and the ligand, but stoichiometry of the antiparallel moments do not cancel out, making this a ferrimagnetic material with a net magnetisation.

Nature Mater., ***2***, *190 (2005).*

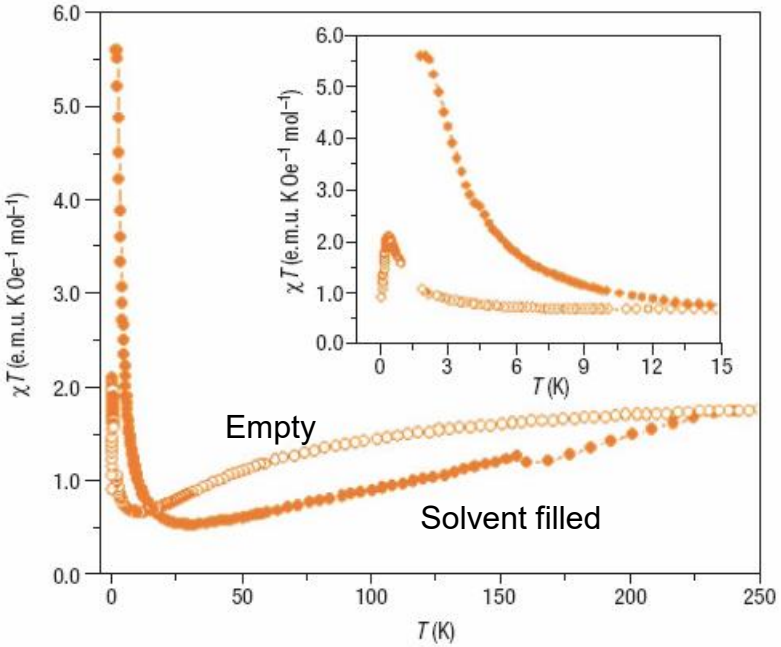
Nanoporous magnetic MOFs

E.g., $Cu_3(PTMTC)_2(py)_6(EtOH)_2(H_2O)$



- The structure consists of hexagonal grids that stack on top of one another.
- The structure is highly porous and contains 30 Å pores that lie perpendicular to the hexagonal layers.

Magnetism



- The magnetic properties change slightly when the guests are removed from the framework.

<u>Potential applications:</u>

- Molecular sensors
- Separation of magnetic and non-magnetic materials

Nature Mater., ***2***, *190 (2005).*

Trends in Electronic Conductivity

Transition Metal Oxides: Rhenium vs. Tungsten

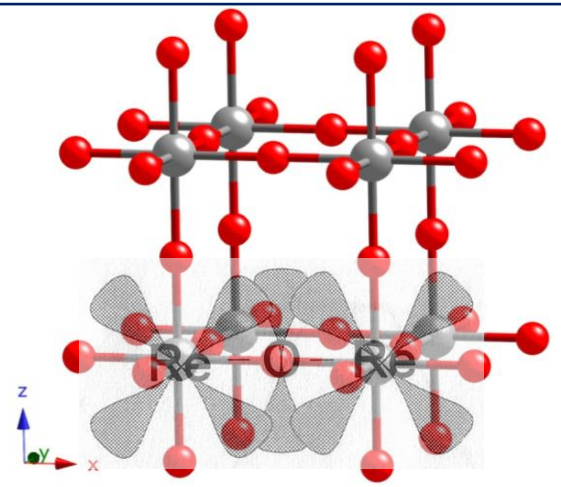
ReO_3 and WO_3 have the *same* crystal structure but *different* electronic structure.

ReO_3 is metallic

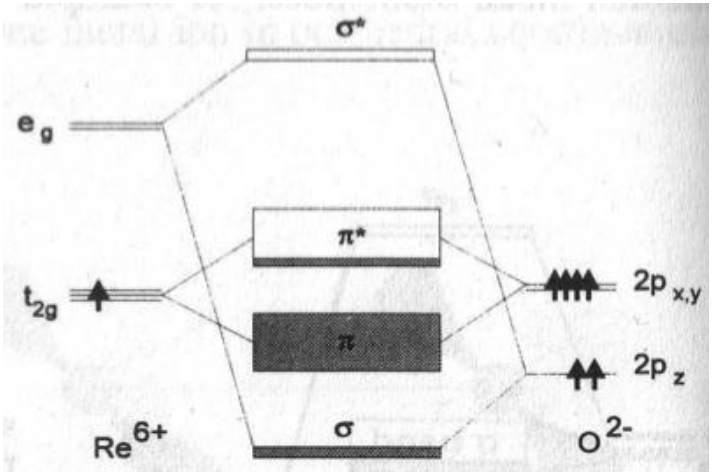
- Re^{6+} has one *5d*-electron that can delocalise throughout the band formed by the π-type overlap of t_{2g} orbitals on the transition metal cation and *p* orbitals on the O anion.

WO_3 is an insulator

- W^{6+} has no *5d*-electrons, so this band is empty.



Crystal structure of ReO_3 and WO_3



Band structure of ReO_3

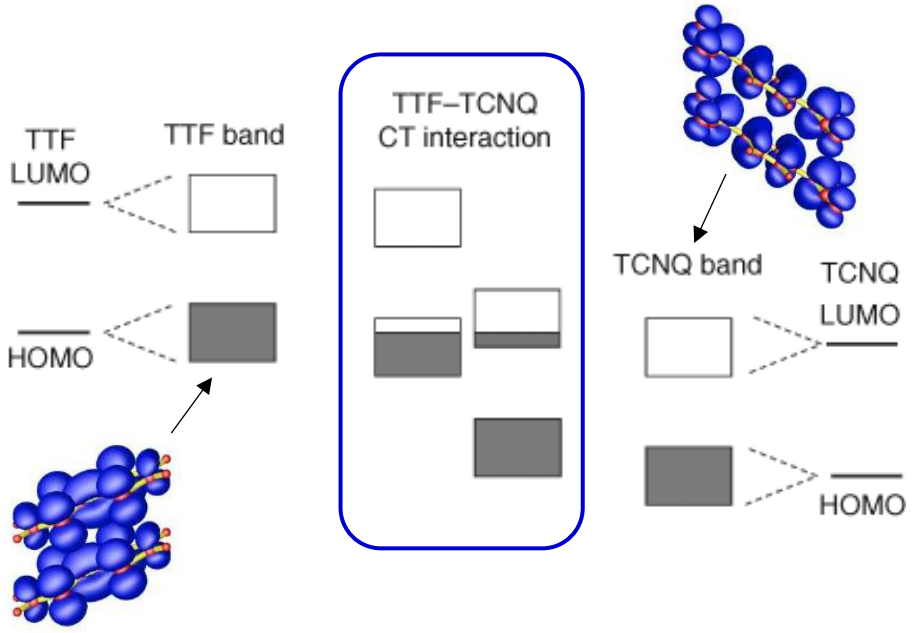
Figures from Weller "Inorganic Materials Chemistry"

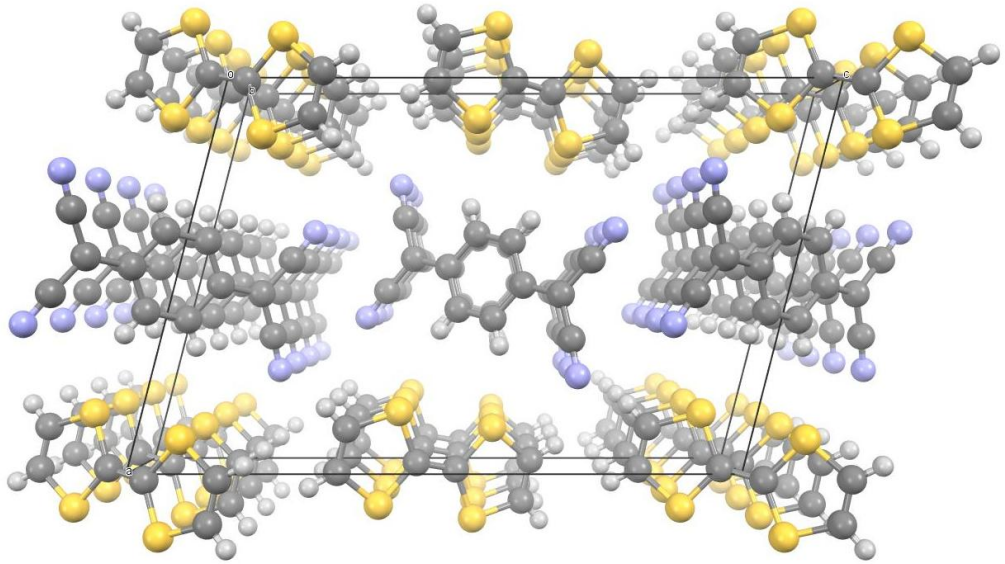
1-D Conductors

TTF-TCNQ: "The first organic metal" (1973)

Two insulating molecules can be combined to form a crystal structure (1-D chains running into the screen) that exhibits conductivity in 1-D.

Orbital overlap and charge transfer, from electron donator to electron acceptor, creates a partially-filled band and a band structure characteristic of a metal.

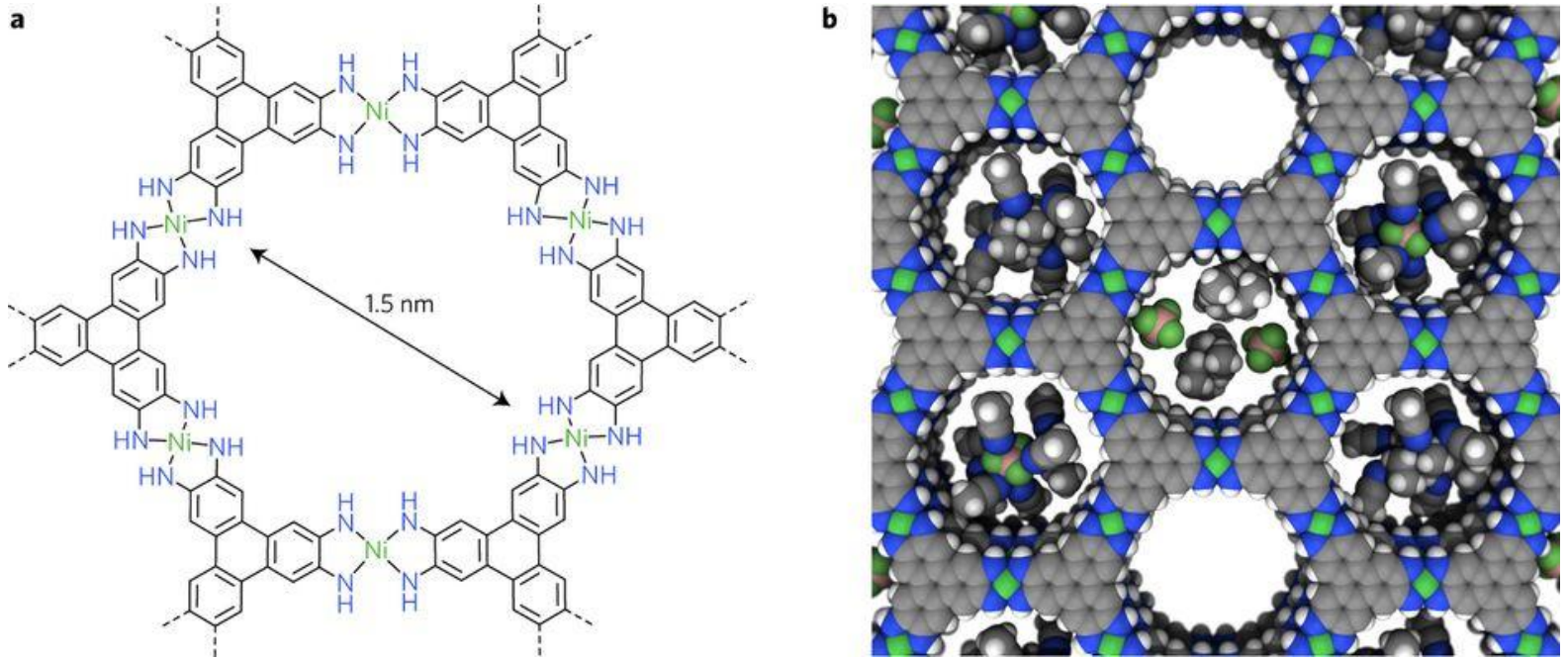




$(TTF)^{\delta+}(TCNQ)^{\delta-}$

Electron conducting MOFs

E.g., Ni_3(2,3,6,7,10,11-hexaiminotriphenylene)$_2$ ($Ni_3(HITP)_2$)



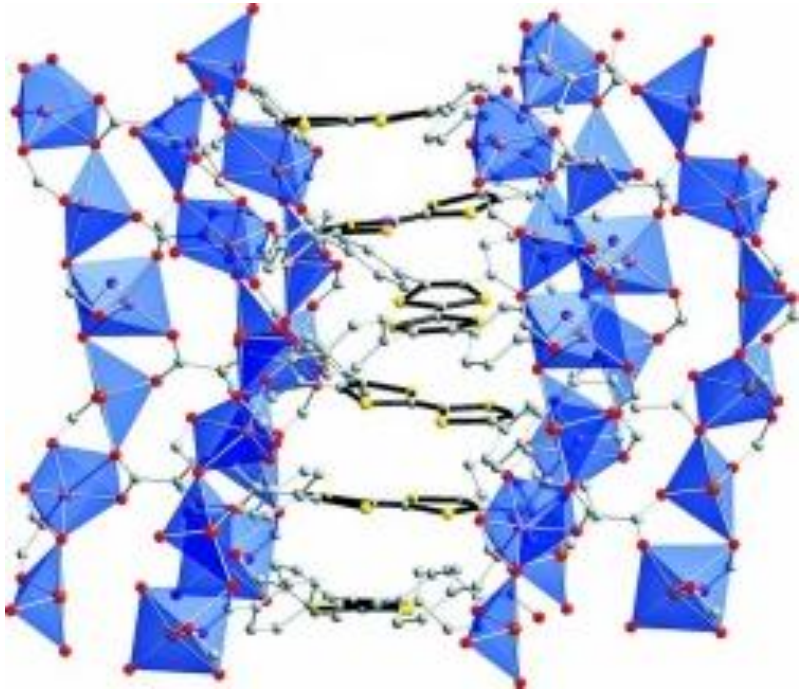
- Electronic delocalisation over large aromatic ligands.
- Overlap between orbitals of metal (Ni) and the ligand creates **framework electron delocalisation.**

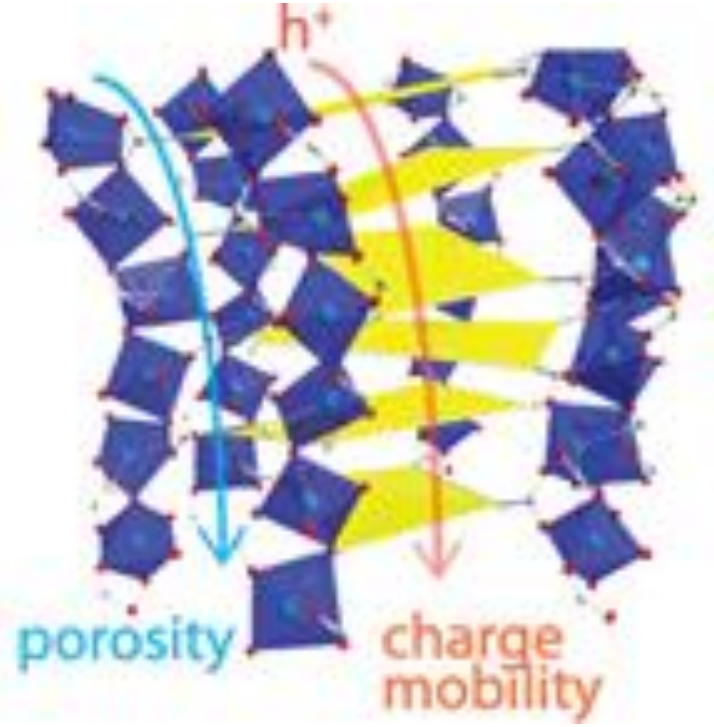
Nature Materials **16,** 220–224 (2017)

Electron conducting MOFs

E.g., Zn_2(TTFTB)

- Pores of the MOF are filled with electron donor TTF arranged in layers.
- Charge delocalisation through overlapping bands of neighbouring TTF gives 1D conduction through the structure



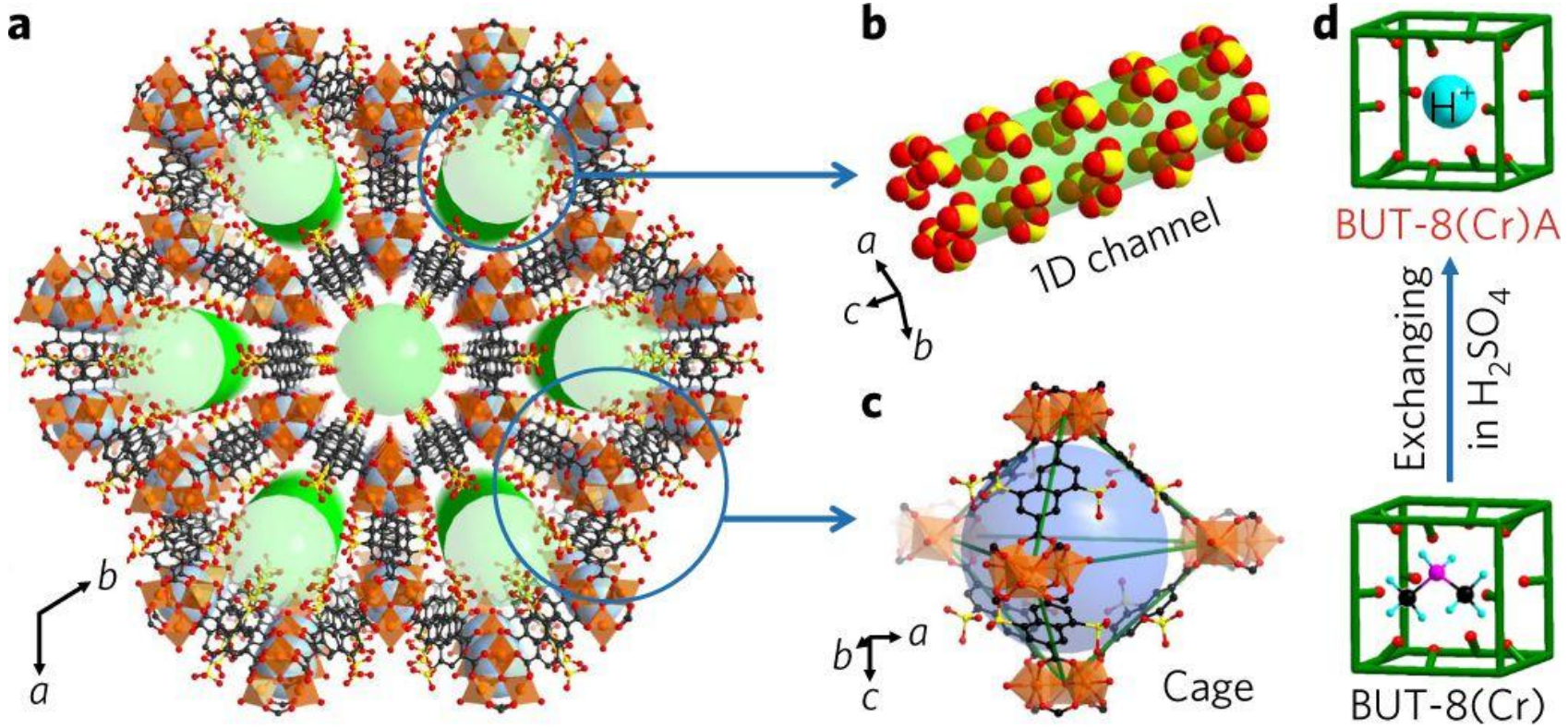


<u>Potential applications:</u>

- Molecular sensors (guest would change conductivity)
- Electrocatalysis (redox reactions inside pores of MOF)

J. Am. Chem. Soc., ***134***, *12932 (2012).*

Proton conducting MOFs

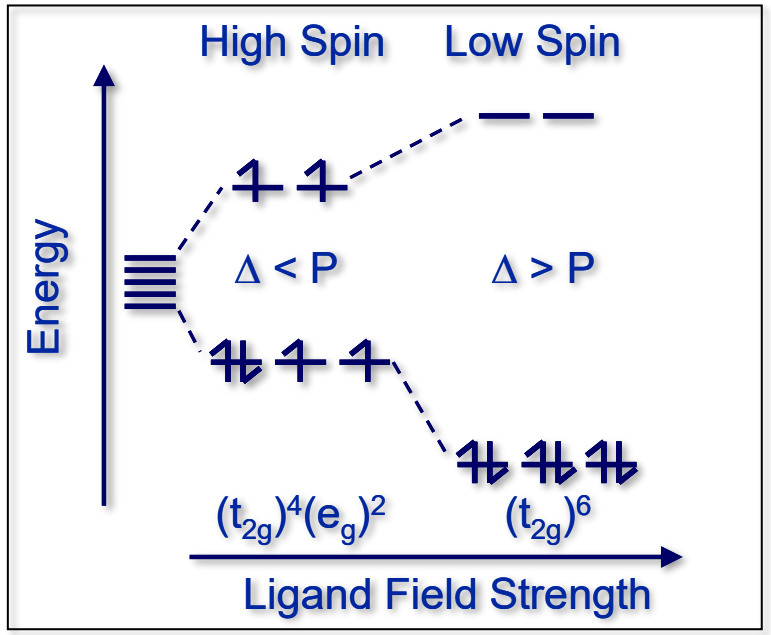


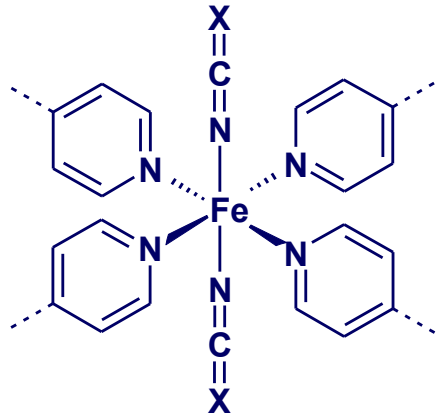
- Surface sulfonate groups lead to high proton conductivity:
  1.27×10^{-1} S cm^{-1} at 100% RH and 80 °C

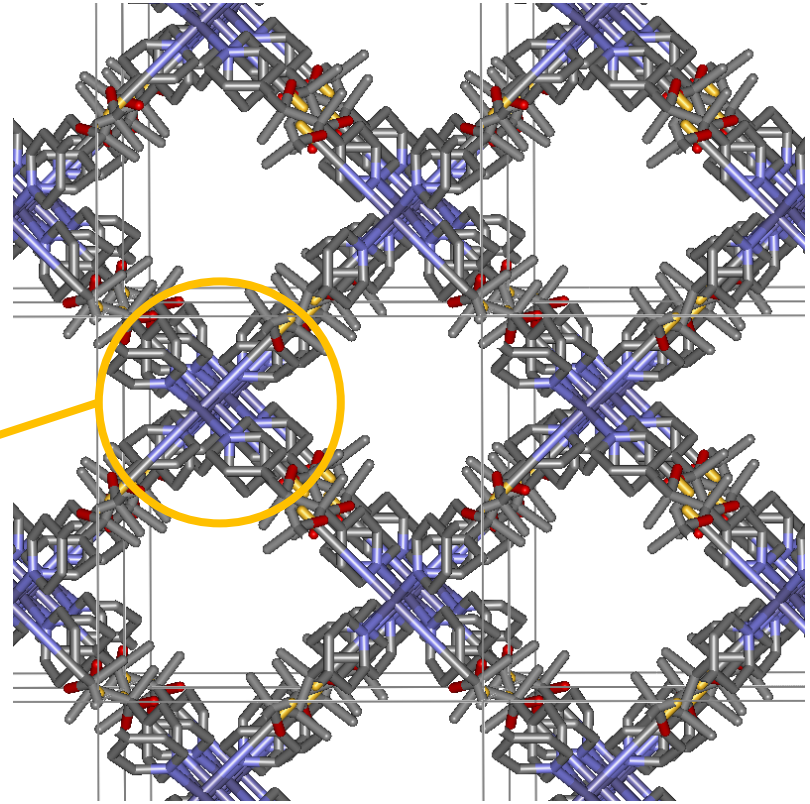
Nature Energy **2**, 877–883 (2017)

Spin switching MOFs

A material is a spin switch if a stimuli like light, temperature, or pressure can be used to manipulate the intrinsic spin of electrons.

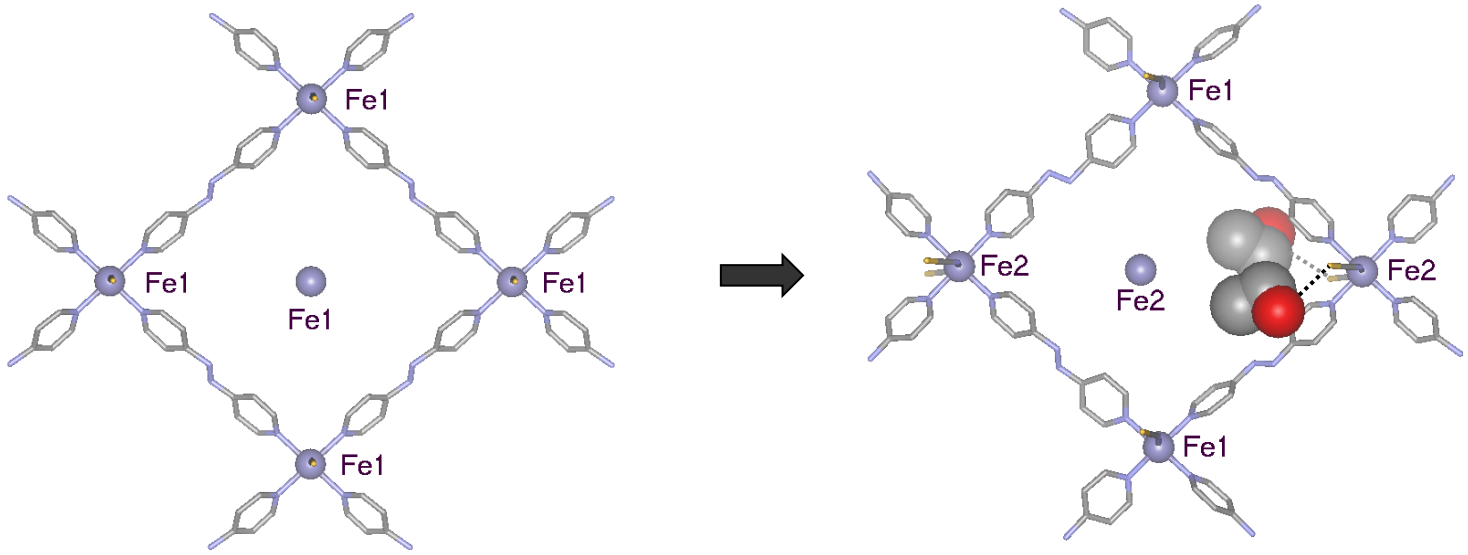






Spin switching MOFs

E.g., $[Fe(azpy)_2(NCS)_2]\cdot\frac{1}{2}(EtOH)$



$[Fe(azpy)_2(NCS)_2]$ $[Fe(azpy)_2(NCS)_2]\cdot\frac{1}{2}(EtOH)$

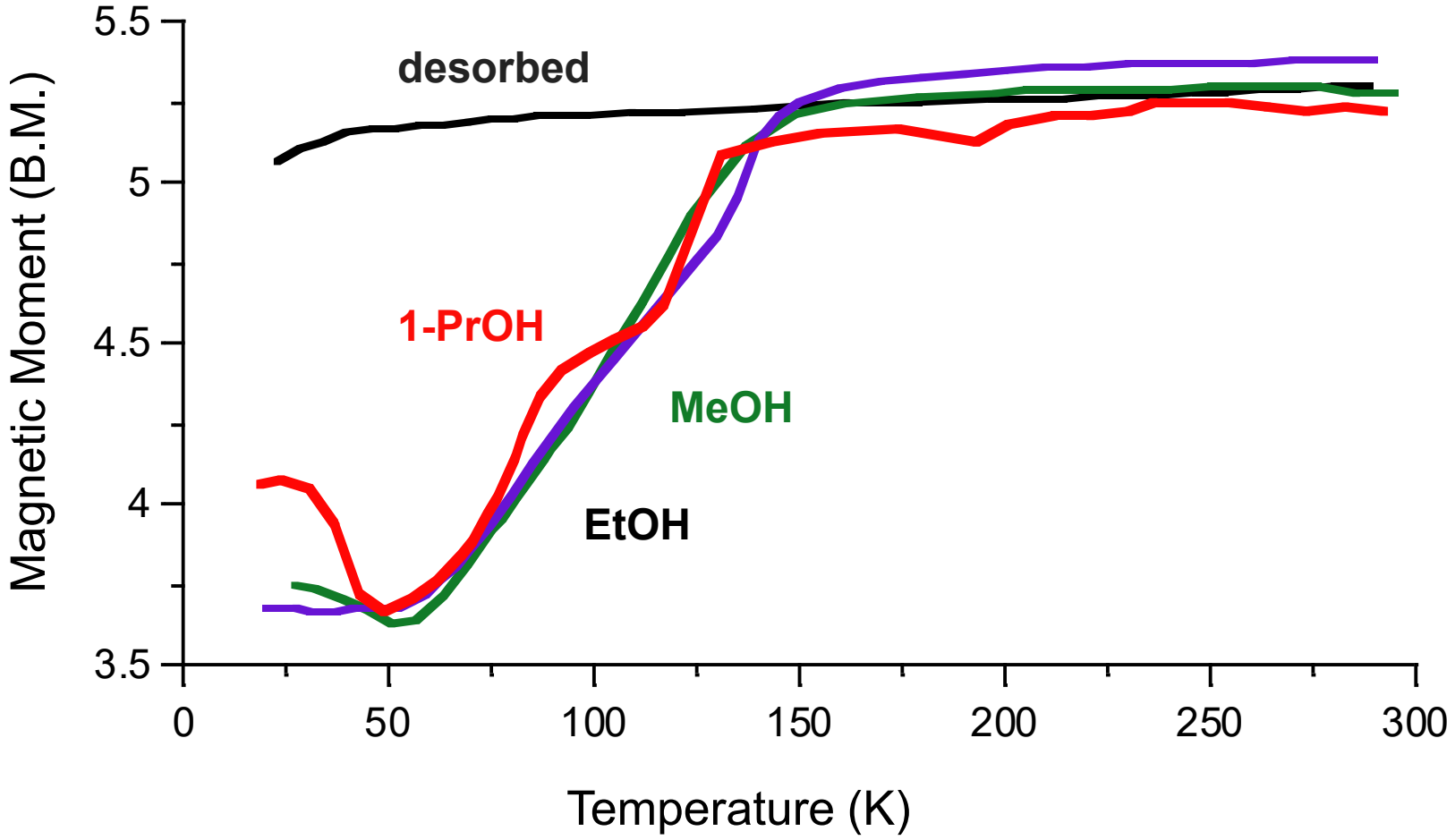
- The structure of the MOF changes depending on whether there is gas molecules (e.g., ethanol) in the pores.

Science, ***298***, *1762 (2002).*

Spin switching MOFs

E.g., $[Fe(azpy)_2(NCS)_2]\cdot\frac{1}{2}(EtOH)$

- The structure influences the magnetic properties.
- The desorbed material does not undergo spin switching.
- Absorbed materials undergo spin switching with the magnetic behaviour dependent on the guest, i.e., a chemical sensor.



Science, ***298***, *1762 (2002)*.

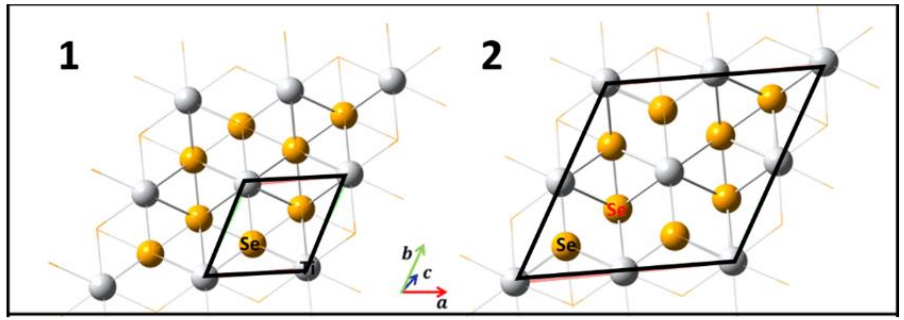
Learning outcomes

After this lecture you should be able to

- Understand how the following properties can be incorporated into MOFs, and appreciate the broad reasons for why this is scientifically and technologically important:
  - Magnetic ordering
  - Electron delocalisation
  - Proton conduction
  - Spin switching

Practice exam questions

SA1: The material $TiSe_2$ is metallic at room temperature but on cooling converts to an insulator in which the structure distorts very slightly. This distortion causes a doubling of the size of the hexagonal unit cell along both the *a* and the *b* axes (see figure: 1 = high temperature; 2 = low temperature).



Describe how the X-ray diffraction pattern is expected to change on cooling through the transi
the larger unit cell. (3 marks)

(Lecture 6 + worksheet)

SA1: *This question is mainly testing your understanding that spacing of diffraction peaks is inversely related to the spacing of Miller planes – there are multiple ways to answer it. Related important concepts here include the directions of the diffraction spots and what information is present in their intensities.*

Since the diffraction pattern is inversely related to the structure (it is the reciprocal), the doubling along a and b will cause a halving of the distance between diffraction spots along the associated diffraction directions.

(Or more technically: the reciprocal lattice vectors a* and b* will each halve and c* will remain unchanged, causing … etc.)

Very good answer: Since there is only very small movement of the atoms away from the high symmetry structure, the extra difffraction peaks caused by the distortion will be very weak, i.e., the diffraction pattern will look very similar, but with extra very weak peaks midway between the main peaks along a* and b*.

{By the way, this type of metal-insulator transition is called a 'charge density wave' (CDW), and arises for the same reason as Jahn-Teller distortions – the delocalised electrons move to lower energy with the opening of a band gap associated with slight deformation of the structure.}

Practice exam questions

SA2: The materials $Li^{I}F$, $Ca^{II}O$, $Al^{III}N$, $Ni^{II}O$ and $Cs^{I}I$ all adopt the rock-salt structure type. On the basis of the Born-Mayer equation below, place these in order of increasing ΔH^0_L. Briefly justify your answer. (4 marks)

$$\Delta H_L^0 = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right) A$$

(Lecture 7 + tutorial week 4)

SA2: (This is similar to a week 4 tute question)

CsI < LiF < CaO < NiO < AlN

The only things varying across these compounds are zA, zB and d. The charges z have a larger influence on the enthalpy than changes in d and so are considered first. The values of zA x zB are 1 (CsI & LiF; CsI has larger d), 4 (CaO & NiO; CaO has larger d) and 9 (AlN).

Practice exam questions

SA3: Azafullerene, NC_{59}, has the same soccer-ball structure as C_{60} but has one carbon atom replaced ('doped') by a nitrogen atom. (6 marks)

(i) Assuming that the solid state packing is the same as that of C_{60}, predict the electron conducting behaviour of azafullerene. Include in your answer a description and explanation of how the conductivity might be expected to change upon cooling. (3 marks)

(ii) Predict how the electrical conductivity of this material would be expected to change if Na^+ ions were intercalated into the octahedral holes of the structure. Give a justification for this prediction. (3 marks)

(Lectures 8 & 9)

SA3: (i) NC59 has 1 more valence electron than C60 (same as C60(-)). It would therefore lead to a partially-filled valence band (1/6-filled t(1u)), and so be metallic. For metals, the conductivity increases on cooling due to the lower vibrational amplitudes leading to less electron scattering. The material might be expected to superconduct at very low temperature, but this could depend on the extent of the overlap of the orbitals.

(ii) NaNC59 would add 1 extra electron per NC59, and so would increase the band filling from 1/6 up to 1/3. Given the general shape of density of states curves, this might be expected to increase the density of states at the Fermi level, leading to an increase in the conductivity.

{Note: if you research azafullerene you'll see there are some additional complexities, all of which can't be readily foreseen and so certainly not expected if this was an actual exam question}

Practice exam questions

SA4: There are a number of similarities and differences in the ways that electric dipoles (e.g., polar materials) behave in electric fields and the way that magnetic dipoles (e.g., unpaired electron spins) behave in magnetic fields. List *one* similarity and *one* difference, and briefly describe and explain each. (4 marks)

(Lectures 10 & 11)

SA4: Examples of similarities:

- Ferroelectric & ferromagnetic – both involve spontaneous dipoles in zero field and exhibit hysteresis loops when the field is cycled in the positive and negative directions, and require negative fields (coercive fields) to reverse the dipole alignment. Both can occur in domains, and transition to randomised states on heating.
- Paraelectric & paramagnetic – both involve gradual alignment of thermally-randomised dipoles with increasing electric/magnetic field strength, reaching saturation at high field and/or low temperature.
- Electric and magnetic susceptibilities are analogous in giving the relative ease with which materials become polarised/magnetised in an electric/magnetic field. Polarisation and magnetisation are analogous in giving the extent to which electric and magnetic dipoles are induced in the material.
- {Not mentioned in L10, but can have antiferroelectric materials, like antiferromagnetic.}

Both a similarity and a difference:

- Dipole ordering occurs due to electrostatic interactions, and/but in the case of electric dipoles this is through the electric field of the the dipoles (and results in an attractive interaction – as seen in intermolecular forces) whereas in magnetic dipoles it is through exchange coupling (e.g., superexchange, double exchange). Some differences:

Examples of differences:

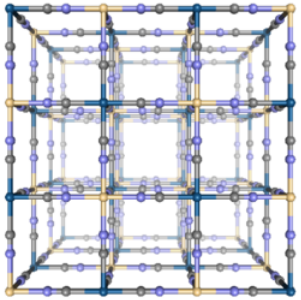
- Electric dipoles arise from symmetry/structural arrangements of ionic charges; magnetic dipoles aren't related to structural change. As such, the structures of electric dipole materials change in response to an electric field, whereas the structures of magnetic materials don't change {at least, at most only very slightly … beyond examinable since I didn't mention this in the lectures, but there can be a very weak effect called magnetostriction.}
- There is no electric dipole equivalent of diamagnetism. All atoms are slightly repelled by a magnetic field (superconductors are very strongly repelled), whereas there is no similar effect for electric fields.
- Electric dipoles can exist across a very wide range of molecule and materials since they just require a net imbalance in the direction/displacement of positive and negative charges, whereas magnetic materials require unpaired electrons and so generally (but not solely) involve metal ions.

Practice exam questions

SA5: Answer *one* of the following two questions (i.e., choose **A** *or* **B** for a total of 8 marks):

A) Metal-organic frameworks (MOFs) show potential for the storage of methane gas. Briefly describe the features of these materials that make them suitable for this application. List and briefly discuss one challenge that needs to be overcome to enable their technological use. (8 marks)

B) Prussian Blue analogues of the form $M^{II}Pt^{IV}(CN)_6$ (M^{II} = transition metal ion; see picture) display negative thermal expansion (NTE) behaviour.



(i) Explain why most materials expand upon warming. (2 marks)

(ii) Explain the origin of the NTE behaviour of these Prussian Blue analogues. (3 marks)

(iii) Explain how can the coefficient of thermal expansion can be varied. (3 marks)

(Lectures 37 & 38)

A) Very high surface areas achieved through construction of porous frameworks, leading to very high methane gas uptake both volumetrically and gravimetrically. Ability to optimise the interaction energy of the methane molecules with the surface of the framework, thereby leading to gas uptake and release at ideal conditions (i.e., room temperature, pressures up to 250 atm). Design approaches include the use of bare metal sites to bind the methane molecules.

Examples of challenges:

- Optimise the MOF-methane interaction energy to allow uptake and release in the right temperature and pressure range. This should not be too low, since high pressures/low temperature would be needed, but also not too high, since this would cause the uptake/release to be highly exo/endothermic.
- Maximise the surface area – this involves the construction of highly open framework, which requires the use of large, light building units. A particular challenge here is making such frameworks sufficiently chemically and mechanically stable to withstand gas sorption/desorption cycles.
- Densification – ie. work out how to pack as much MOF into a given volume as possible, thereby maximising the gas storage capabilities. Ideas here include processing of the crystals (which has been shown to decrease their uptake ability) and sol-gel processing.

B) (i) Longitudinal vibration at higher temperatures causes an average lengthening of bonding interactions due to the asymmetry of the interaction potential.

(ii) Transverse vibration (like a skipping rope) of the Pt-CN-M bridges leads to the Pt…M distance getting shorter at higher temperatures due to the tranverse vibrational amplitude increasing.

(iii) Changing the metal ion M^{II} leads to a change in the strength of the M^{II}-N bond, which changes the 'stiffness' of the Pt-CN-M bridges. Strong bonding (eg. associated with large crystal field stabilisation energies, e.g. Ni(II) > Zn(II)) leads to decreased NTE since the amplitude of the transverse vibration is less. (Could alternatively talk about the role of adsorbed guest molecules in the pores.)