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## 1 VO 1

The definition of functional materials represents a material's capacity to execute a "function" in response to a certain stimuli.

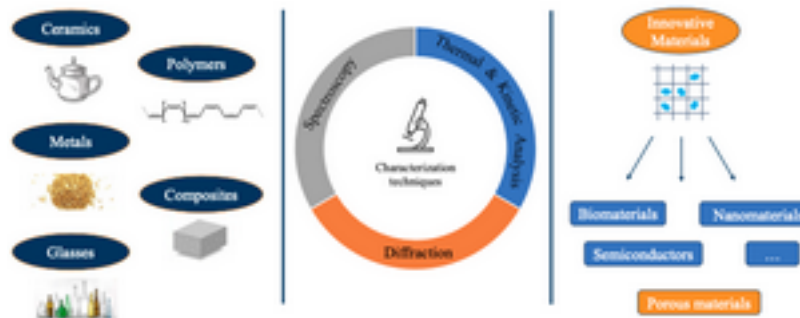


Figure 1: 954cb97fd78a7153aab8a46b2971f879.png

## 1.1 Ceramics - one of the oldest functional material

“Ceramic” is the technical term for a variety of inorganic non-metallic materials. They are almost non-soluble in water and with at least of 30 % crystallinity

Ceramic materials are brittle, hard strong in compression and weak in shearing and tension. They can withstand the chemical erosion, may be subjected to acidic or caustic environment. Furthermore ceramics can withstand very high temperatures ranging from 1.000 - 1.600 °C

### Synthesis

Normally the raw materials are formed at  $RT$  for example:

- Silicates
- Oxides
- SiC
- BN
- $B_4C$
- WC
- AlN

and then via a sintering process converted into ceramics

### Bonding Situation and Properties

- Large range of possible structures and compositions
- almost all elements
- almost all type of bonds (mainly ionic and covalent)
- various levels of crystallinity

### Classification

- Oxides: Alumina, Zirconia, Ceria
- Non-Oxides: Carbides, Silicides, Borides, Nitrides
- Composites

### Mechanical Properties

- Poor toughness due to bond type

- Pores as stress concentrators

### Electrical Properties

- Semiconductors
- Superconductors
- Ferroelectricity & supersets
- Positive Thermal coefficient

### Optical Properties

- Transmission of light in vis and IR Range
- Translucent Alumina

### Some Technical Ceramics

For the resulting properties of ceramic materials, not only the raw materials but even more the synthesis processes are of outmost importance

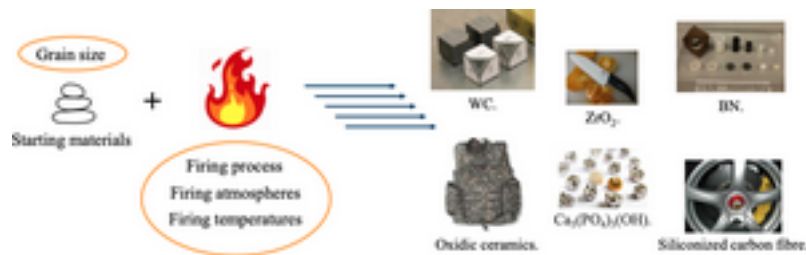


Figure 2: 4cb68b93802ad4a6adc44d34c8d1c345.png

Ceramics have several advantages over metals for practical applications, including low density, high compressive strength (hardness) and resistance to corrosion. However, they have a fatal weakness when used as engineering materials - **they fracture after undergoing a very small deformation**

## 1.2 Metals -old but gold

Metals are designated as materials that show a lustrous appearance, and high electrical and thermal conductivity. Further they are ductile and malleable

### 1.2.1 Bonding Models

#### 1.2.1.1 Electron Sea Model

Positively Charged Atomic bodies surrounded by freely mobile negatively charged valence electrons

#### 1.2.1.2 Electronic Band Structure

Describes the range of energy levels that electrons may have within it, as well as the ranges of energy that they may not have.

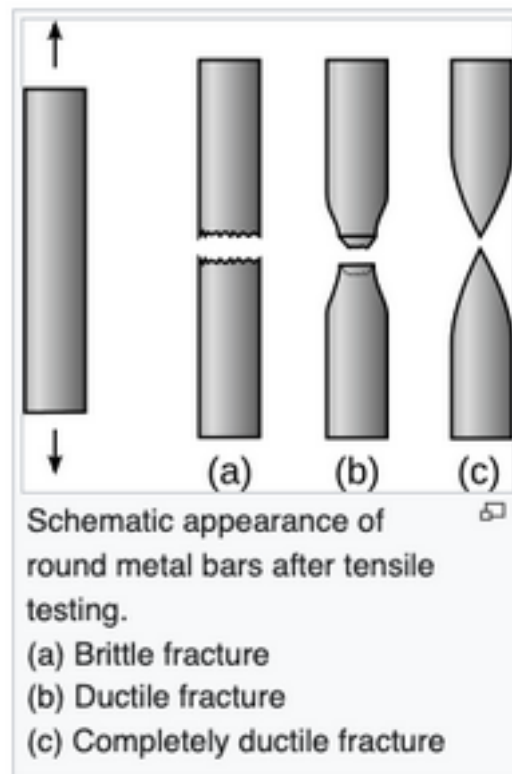


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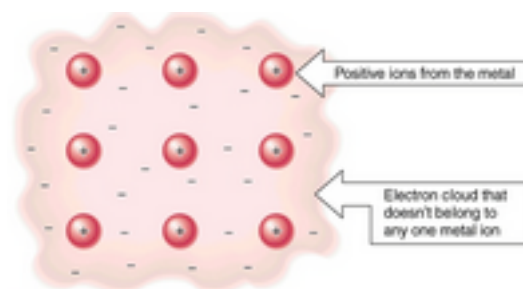
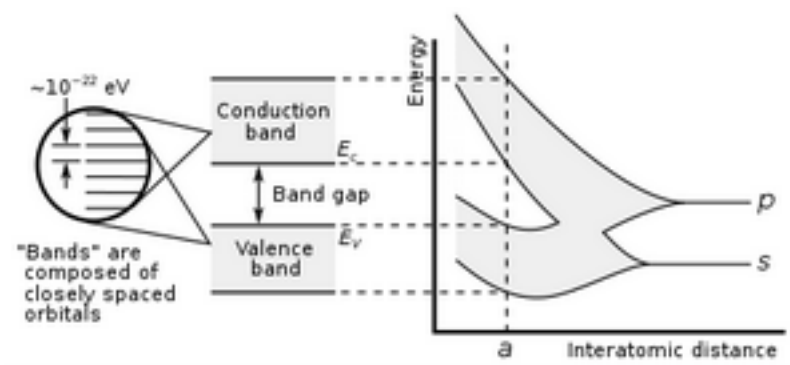


Figure 4: eca88f8ce79d1c6ba6517b366ff813e9.png

Band theory derives these bands and band gaps by examining the allowed quantum mechanical wave functions for a electron in a large periodic lattice of atoms or molecules



A hypothetical example of band formation when a large number of carbon atoms is brought together to form a diamond crystal. The right graph shows the energy levels as a function of the spacing between atoms. When the atoms are far apart (right side of graph) the eigenstates are the atomic orbitals of carbon. When the atoms come close enough (left side) that the orbitals begin to overlap, they hybridize into molecular orbitals with different energies. Since there are many atoms, the orbitals are very close in energy, and form continuous bands. The [Pauli exclusion principle](#) limits the number of electrons in a single orbital to two, and the bands are filled beginning with the lowest energy. At the actual diamond crystal cell size denoted by  $a$ , two bands are formed, separated by a 5.5 eV band gap.

Figure 5: 989a16dfa1228b958b16db894b853802.png

This results in the properties:

- Lustrous
- Malleable
- Ductile
- Good conductors for electricity and heat

### 1.2.2 Applications of Metals

Pure metals are used for wires because of their high electric conductivity. In further applications, metals are applied as alloys or inter-metallic phases

## 1.3 Alloys - better together

An alloy is a combination of chemical elements possessing the characteristic properties of a metal. The production of alloys is of great

importance, as it is one of the main processes used to modify the properties of pure metallic elements

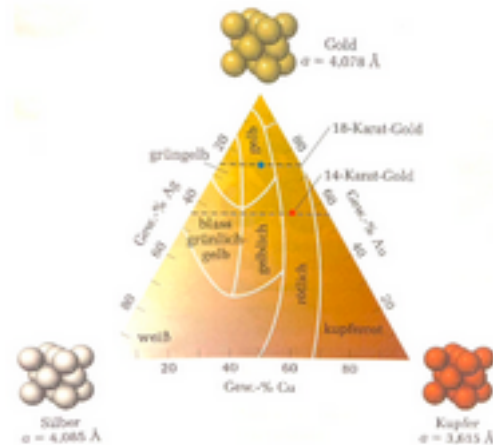


Figure 6: 0612f0332a208423bdad85bb24054ead.png

Example would we gold:

- Pure gold is 24 karat
- Ag, Cu and Au all have fcc structure and almost same radii

### 1.3.1 Different types of alloys

#### 1.3.1.1 Substitutional Solid Solution Alloy

- Solute atoms replace solvent atoms in crystal lattice
- Requires similar atomic sizes and chemical properties
- Properties like conductivity and strength are intermediate

#### 1.3.1.2 Interstitial Solid solution alloy

- Smaller solute atoms fit into the gaps of the solvent's lattice
- Solute atoms are typically much smaller
- Often increases hardness and strength due to lattice distortion

#### 1.3.1.3 Heterogenous Alloys

- Non-uniform mixtures where components are not fully dissolved
- Examples include cast iron (Fe-C)
- Properties vary locally

#### 1.3.1.4 Intermetallic Compounds

- Ordered compounds with fixed stoichiometry and distinct crystal structures
- Exhibit high melting points, strength and brittleness due to strong ionic/covalent bonds

### 1.3.2 Example Steel

Steel is an alloy of iron and carbon with improved strength and fracture resistance compared to other forms of iron

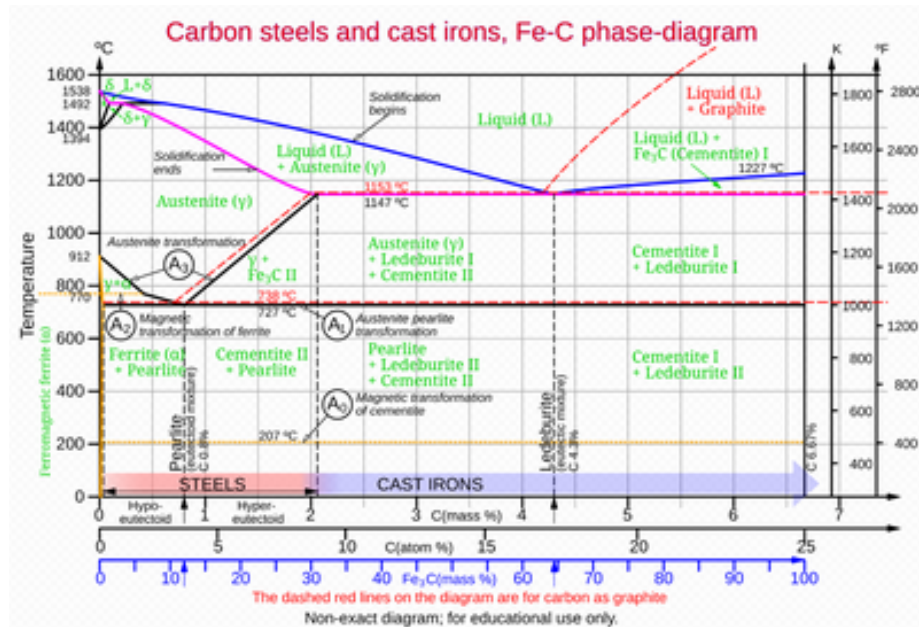


Figure 7: b37306101c697f95fd2e1ee10ecb459d.png

Normally a steel is a alloy of max 2.14 % carbon with additional elemental doping resulting in defined properties. The metal lattice becomes harder stronger and less ductile

**Stainless Steel with 0.4 % carbon 18% chromium and 1% nickel**

|            |   |
|------------|---|
| aluminum   | Increases desoxygenation and ferrite stabilization                                    |
| boron      | Increases yield strength, strength, brittleness and heat resistance                   |
| chromium   | Increases cooling rate, wear resistance, heat resistance, tensile strength, hardness  |
| cobalt     | Increases strength, heat resistance   |
| molybdenum | Increases hardenability, tensile strength, weldability, ductility, heat resistance    |
| nickel     | Increases tensile strength, hardness, strength, yield strength, ferrite stabilization |

Figure 8: b7eb3465f6ec4dd3ea8085a7a89a4dfa.png

### 1.3.3 Note on Intermetallic Compounds

Intermetallic Compounds are solid phases with  $\geq 2$  metallic elements possessing an ordered structure with well defined stoichiometry

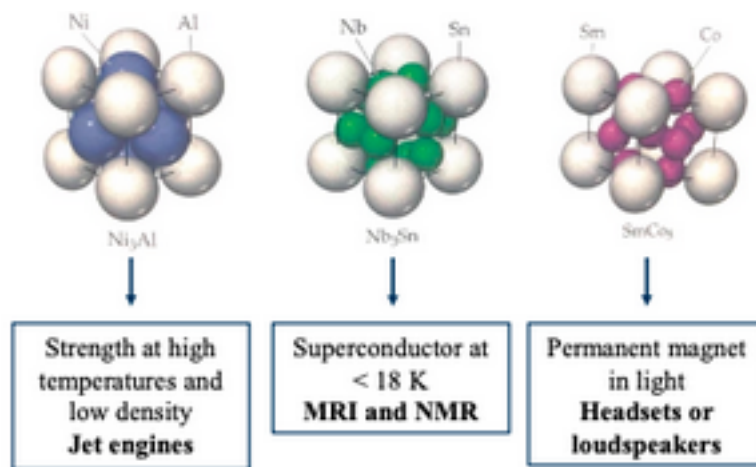


Figure 9: f56973c754ca2b408f61bfb890c9997f.png

#### 1.4 Pyrochlore Magnets - No thermal expansion

A pyrochlore magnet is an alloy of the four metals  $Zr$ ,  $Nb$ ,  $Fe$  and  $Co$  which expands only 0,0001% over a 400 °C temperature range

The reason behind this zero thermal expansion is the heterogeneous lattice structure. Parts within the structure react thermally and magnetically different.

**Thermal treatment** partial contraction and repulsion with net-balance zero

#### 1.5 Amorphous Metals Metallic Glasses

Amorphous metals or metallic glasses are alloys with a disordered atomic structure (no long-range crystalline order) achieved by rapid cooling to prevent crystallization

High viscosity in molten state which prevents the atoms to form an ordered lattice

##### Formation

- extremely rapid cooling
- Mechanical alloying
- Ion radiation

##### Properties

- Low shrinkage when cooling
- Wear resistance
- Less corrosion due to missing grain boundaries
- Great hardness
- Best magnetic soft materials



## 2 VO 2

### 2.1 Polymers

Polymers are chemical compounds, which are built up from repetitively connected macromolecules. They are divided into biopolymers and synthetic polymers

#### Homopolymer

Made up only of one type of monomer with a simple uniform structure. Properties depend on the single monomer used

- Polyethylene (PE)
- Polypropylene (PP)
- Polystyrene

#### Copolymer

Made from two or more different types of monomers, have a more complex structure leading to varied properties

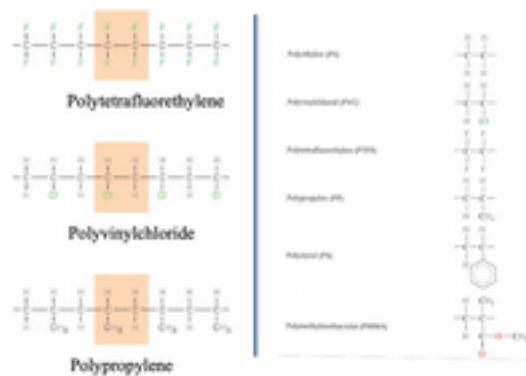


Figure 10: d3081b49082ac607b1d9f999b4ba0153.png

#### 2.1.1 Basic Polymer Structures

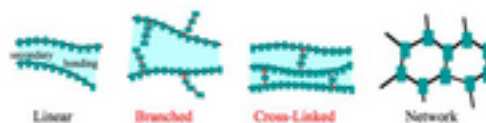


Figure 11: de76593d37e2c6f0ea55493f9631020e.png

##### Linear

- Van der Waals or H-Bonding
- Material can be remolded by heating
- thermoplastics

##### Branched

- Shorter chains
- Less dense than linear polymer
- material can be remolded by heating
- thermoplastics

#### Cross-Linkes

- Resemble ladders with linked chains
- covalent bonds
- thermosets

#### Network

- heavily links
- nearly impossible to soften → degradation
- Thermosets

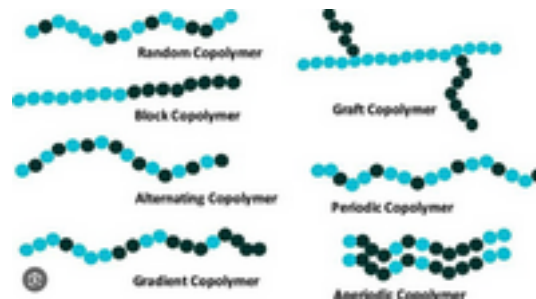


Figure 12: 8104a4fa57f492c41a715c2474292f30.png

## 2.2 Biopolymers

Biopolymers are polymers produced by living organisms. Three main classes of biopolymers include: Polynucleotides, Polypeptides and Polysaccharides

## 3 VO 8

### 3.1 Porous Liquids

Microporous liquids are a new class of materials that exhibit accessible and permanent porosity of a porous solid and fluid like properties

#### 3.1.1 Type I

Neat porous liquids, the molecules themselves form permanent pores in the liquid state

#### 3.1.2 Type II

Solutions of molecular porous species in pore-excluded solvents, consist of discrete porous molecules dissolved in a solvent that is too large to enter the pores

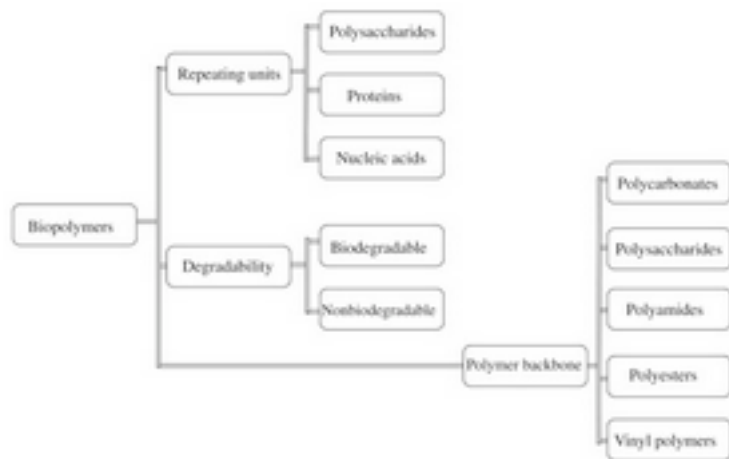


Figure 13: 91a1940b52ec3a7cb9b69fc43a9bc65c.png

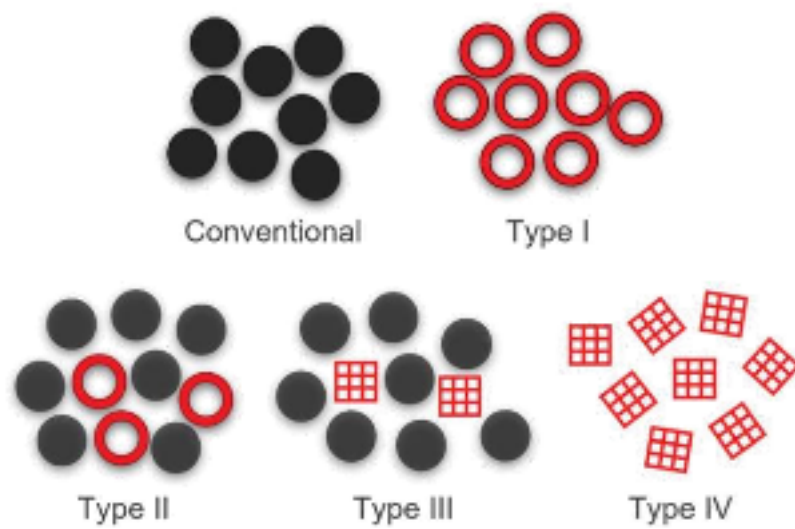


Figure 14: a5e6dbcc475b6db332407fc3aa07e300.png

### 3.1.3 Type III

Dispersions of microporous solids in pore excluded liquids. The liquid is too bulky to enter the pores of the dispersed solid

### 3.1.4 Type IV

Meltable microporous extended frameworks, these frameworks maintain their porosity in the liquid state due to strong physical interactions

### 3.1.5 Characterisation of porous liquids

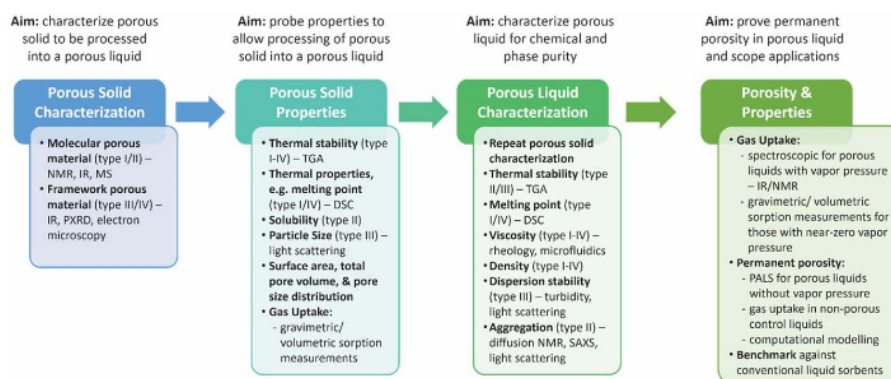


Figure 15: d3fb54fa6b3f8e21e9a548bb0da5abed.png

### 3.1.6 Applications of porous liquids

**Gas uptake and selective gas separation:**

- Porous liquids can be an alternative absorbend for carbon capture
- Uptake of  $CO_2$  by these systems has been reported

**Molecular separation of non-gaseous molecules**

**Absorption of volatile organic compounds**

**Introduction of catalytic compounds**

## 3.2 Combining organic and inorganic parts

### Definition Coordination Polymer

A coordination polymer is a compound with repeating coordination entities extending in 1,2 or 3 dimensions

### Definition Coordination Network

A coordinatio compound extending through repeating coordination entities, in one dimension but with cross links between two or more individual chains, loops or spiro like links

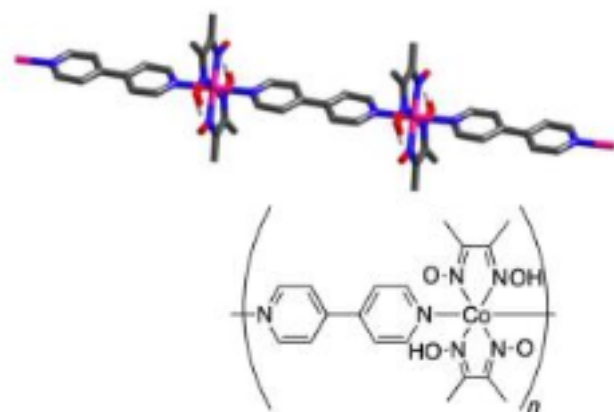


Figure 16: 9f1e943629e763ce08609baeb4f627f6.png

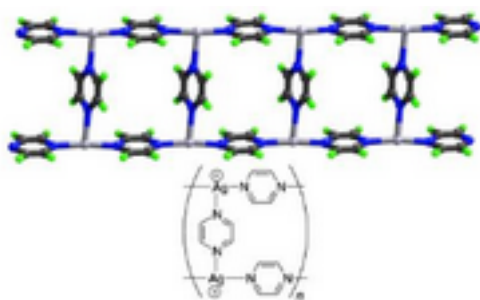


Figure 17: 310603d8652f23c62d91b80c888ae136.png

### 3.2.1 MOF - Metal Organic Framework

A Metal organic framework, abbreviated to MOF, is a coordination network with organic ligands containing potential voids

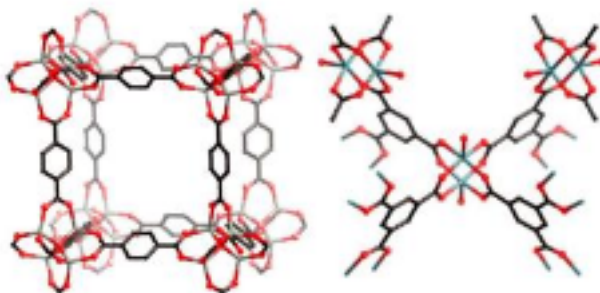


Figure 18: 1e6ecb4c05684e87e3593e33011d1d24.png

A combination of a metal-salt and any at least bifunctional organic molecules gives a MOF

- Extremely high surface areas
- tunable properties
- Used for gas storage, separation, catalysis and drug deliver
- Exceptionally porous
- Can be systematically functionalized and therefore modified for targeted applications

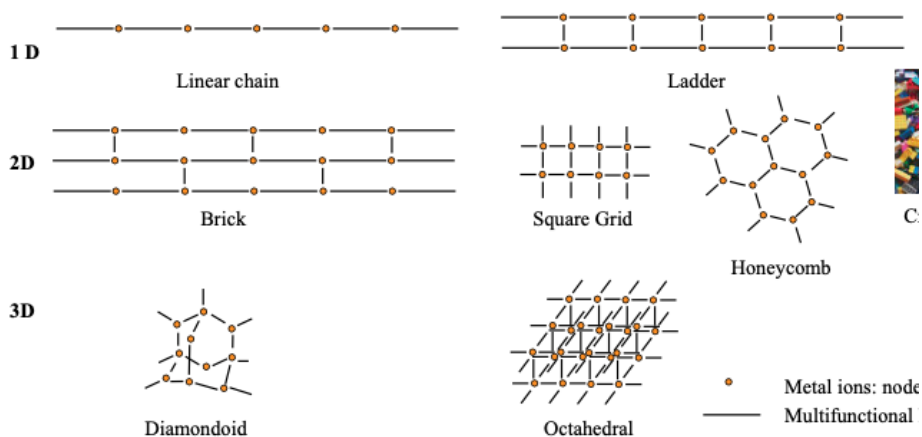


Figure 19: b377a4faaabdd81159d0a493ab18816a.png

#### 3.2.1.1 Systematic structure assembly

#### 3.2.1.2 Synthesis Methods Microwave assisted method

With the help of microwave process, small metal and oxide particles are produced. Microwave converts electromagnetic energy into thermal energy, per-

manent dipole moment of molecules is connected with an applied electric field, which rapidly heats the liquid mixture. Applying right frequency will cause molecules to collide it is efficient.

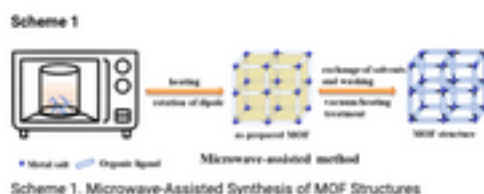


Figure 20: 36e22bce571161678ed658a09715ab05.png

### Electrochemical methods

Electrochemical method uses electrons as a source of metal ions that are passed through a reaction mixture, which contains the dissolved organic linker and an electrolyte via anodic dissolution as the metal source instead of metal salt.

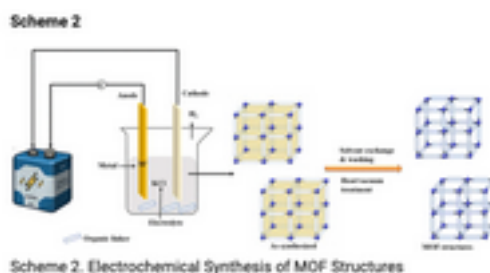


Figure 21: 20539dc421963682b5c5b867960cae3d.png

### Solvothermal Method

Widely used for the preparation of MOFS. Metal Salts and organic ligands are stirred in protic or aprotic organic solvents which contain formamide functionality.

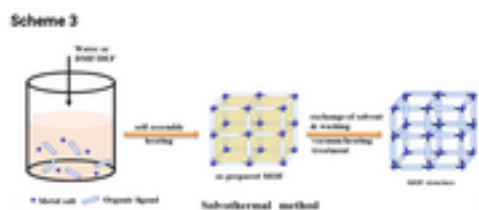


Figure 22: f8077fc7ab23fb70996c1672ce2dfdea.png

### Mechanochemical Method

Concentrates on responses between solids usually for the most part started just using mechanical energy. Combination of metal salt and organic ligand is ground in a ball mill or pestle and mortar approach (Very science)

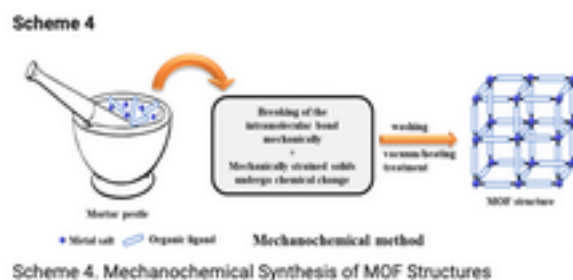


Figure 23: 69b487393f711ce7b2e5246fec3cf2e9.png

### Sonochemical Method

Rapid synthesis of MOFs, decreases the time for crystallization through ultra-radiation. A cyclic mechanical vibration is used for the synthesis of the MOF

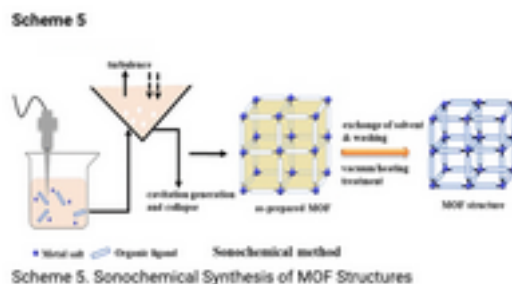


Figure 24: 7a7f05436320cbf967f31d70efaf142c.png

## 4 VO 9

### 4.1 Introduction Stimuli and Inducing Change

Nature of stimulus is highly variable. The same is also true for the response and the type of responsive species, which can be of inorganic or organic nature

**Response can change:**

- Structural change
- Magnetic Properties
- Electrical properties
- Molecular motion
- Acidity
- Optical properties

**Definition Chromism**

Chromism refers to a reversible change in the color of a material in response to an external stimulus. These color changing properties are often linked to structural or electronic changes in the material at the molecular level



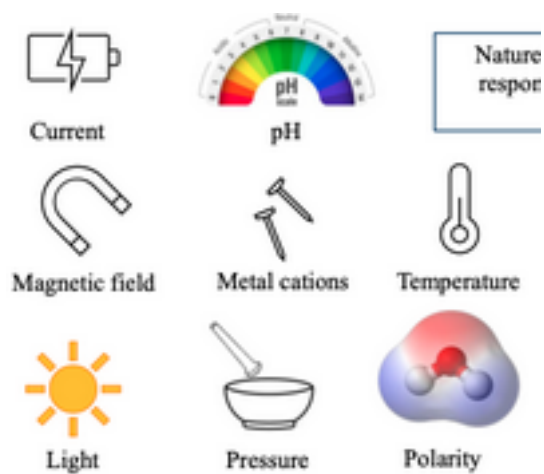


Figure 25: 4bc237ad471feaed6cb4e23b2151e142.png

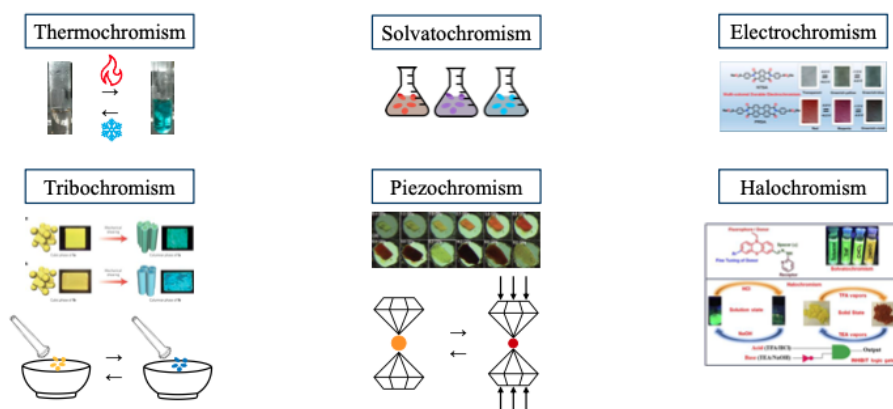


Figure 26: 271bcf2928f29ab96c02c281805424fc.png

## 4.2 Photochromism

Photochromism is defined as the reversible transformation of a molecule between its two or more photoisomers upon irradiation with light of a specific wavelength, which show different absorption properties



Figure 27: bbcbl1dfd87f4ef91c584b9e96ab1a1f1.png

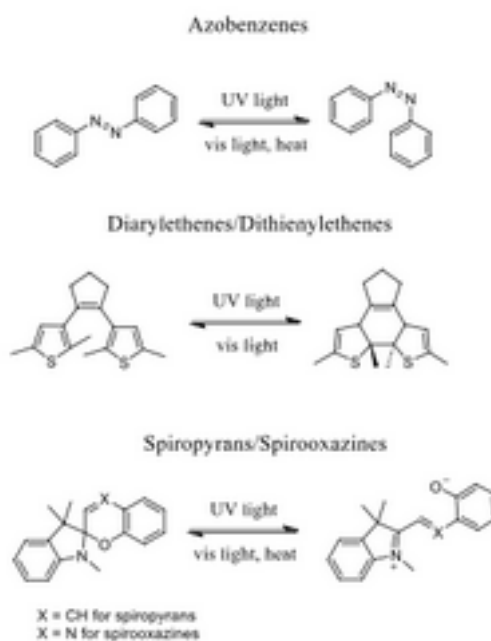


Figure 28: 9bb6a7ce5e3ac47348dcf62b3ec0626f.png

### Example Diarylethens

Diarylethens and Dithienylethenes are one of the rare examples showing photochromism in solid state

#### 4.2.1 General Definitions and Concepts

In the example above **A** is the thermodynamically stable form **B** is less stable.

Reorganization into the ground state either:

- solely by light (P-type photochromism)

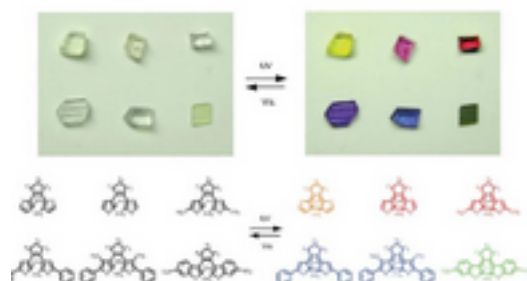


Figure 29: 09a433d5a45d30aee535571fe797b442.png

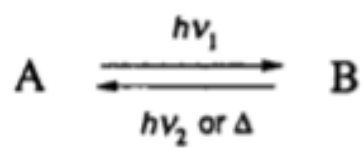
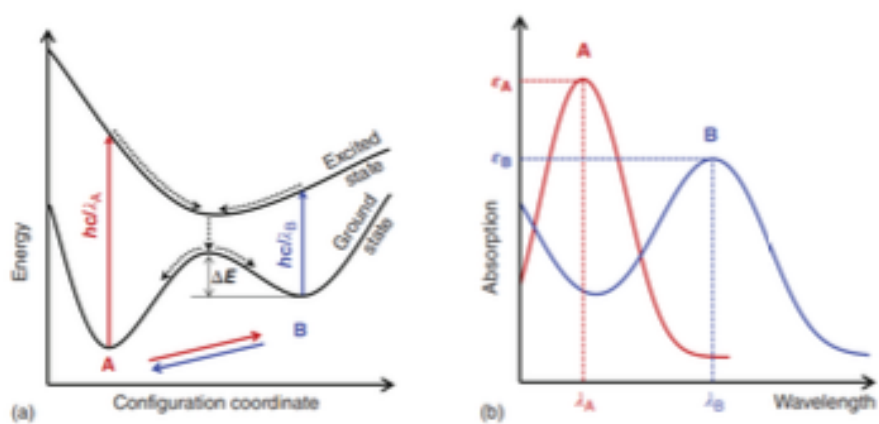


Figure 30: c1d0602aae07d514fd7ce1fc2bc81224.png

- Or by heat supply (T-Type Photochromism)

**Positive Photochromism**  $\lambda_{max}(A) < \lambda_{max}(B)$

**Negative Photochromism**  $\lambda_{max}(A) > \lambda_{max}(B)$

Most of these photochromic processes involve one photon mechanism:

B is formed from the singlet  $^1A^*$  or triplet  $^3A^*$  excited states or both

#### 4.2.2 Families of organic photochromic compounds

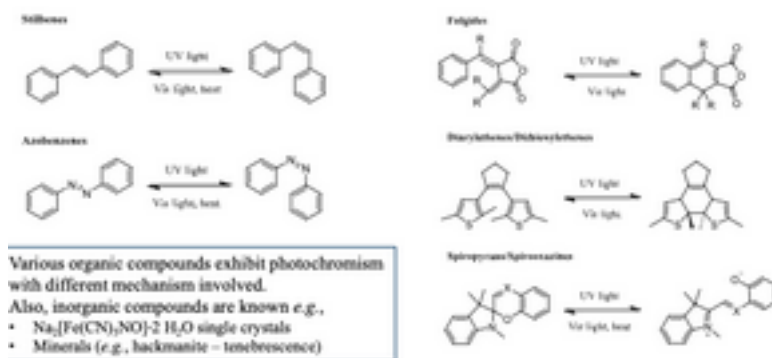


Figure 31: 0165cea7ebdd4212f0b626d93d52ace6.png

#### 4.3 Inorganic Photoswitch by Linkage Isomers

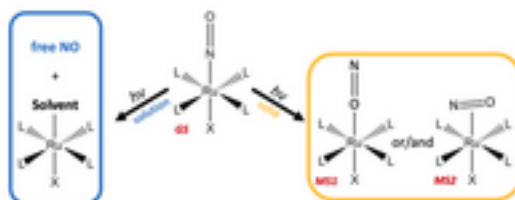


Figure 32: fb35af431dc675ba536ee7b4d9bb1868.png

Input some stuff about the talk from bro here

#### 4.4 E-to-Z Isomerisation

E-to-Z isomerization is described as a change in the absolute stereochemistry of double bonds in organic molecules

##### 4.4.1 Example Stilbenes

A **stilbene** is a 1,2-diphenylethene and is present in two photoisomers. Where the **E-stilbene** is colorless and the **Z-Stilbene** is slightly yellow in color



Figure 33: 09857835a92e8b6b04ad7da1473ff507.png

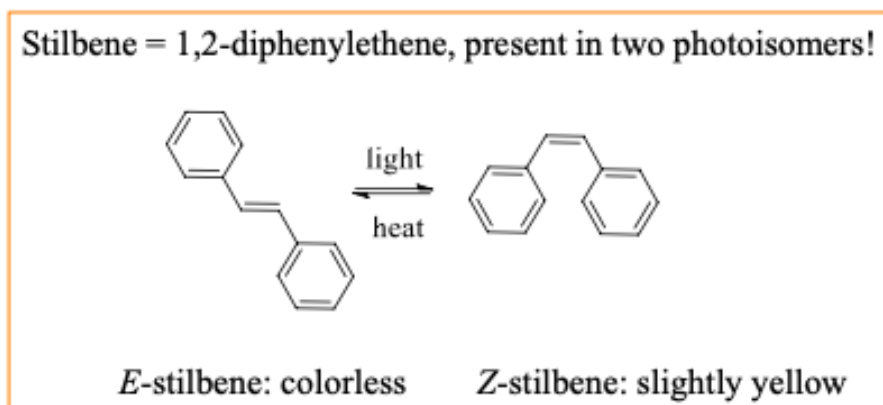


Figure 34: 3c347dbbb837ce4e4065804323b3e36a.png

#### 4.4.2 Azobenzenes

An **Azobenzene** is a diphenyldiazene and also present in two photoisomer. **E-AZB** is orange, **Z-AZB** is slightly orange

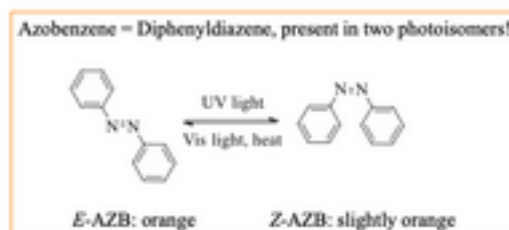


Figure 35: 0ba2f05cde992f476d7b742ef738bef9.png

#### 4.4.3 Fluorinated Derivatives

Introduction of ortho-fluorine atoms lowers energy of n-orbital of *Z* isomer. The change in  $n \rightarrow \pi^*$  transition when irradiated with light

Fluorine is highly electronegative, lowers the energy of the lone pair n-orbital. Transition energy  $n \rightarrow \pi^*$  is altered enabling the molecule to respond to visible light instead of UV-light

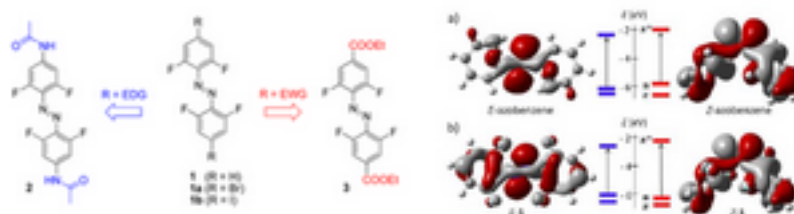


Figure 36: 86daf49fdaf77859c8f6ea14e9c626f5.png

Normally azobenzene switches between trans and cis forms under UV-light, these fluorination allows for quantitative photoswitching with visible light

#### 4.4.4 Ring Opening-Ring closing Reactions

Pericyclic reactions, these can be or concerted or non-concerted nature take place in various photochromic compounds including:

- Fulgides or Diarylethenes for **ring closing** reactions
- Spiropyrans or Spirooxazines for **ring opening reactions**

##### Definition Concerted Reaction

Bond-Breaking and Bond-Formation occur in a single step

##### Definition Non-Concerted Reaction

Bond breaking and bond formation occur in distinct steps

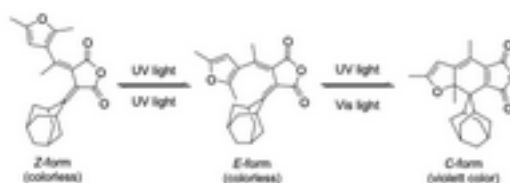


Figure 37: fd4bf3eafaf8a3404a79ad24b29ff8cf.png

**4.4.4.1 Fulgides and Fulgimides** Fulgides can only be switched by light and are thermally stable - **P-type chromophores**

Origin of the color is the formation of a planar conjugated molecule

#### 4.4.4.2 Diarylethenes and Dithienylethenes

Again the simplest representative is stilbene! Replacement of the hydrogens ortho to the carbon carbon double bond by groups that cannot be removed during oxidation! Thiophene rings

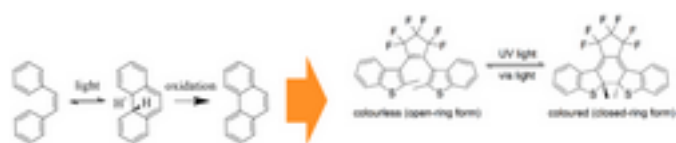


Figure 38: dcac72a5d0d0d691182aeb11d4710779.png