# Responsive Functional Materials

Ass.-Prof. Dr. Heidi A. Schwartz

*Photoactive Hybrid Materials*

Universität Innsbruck

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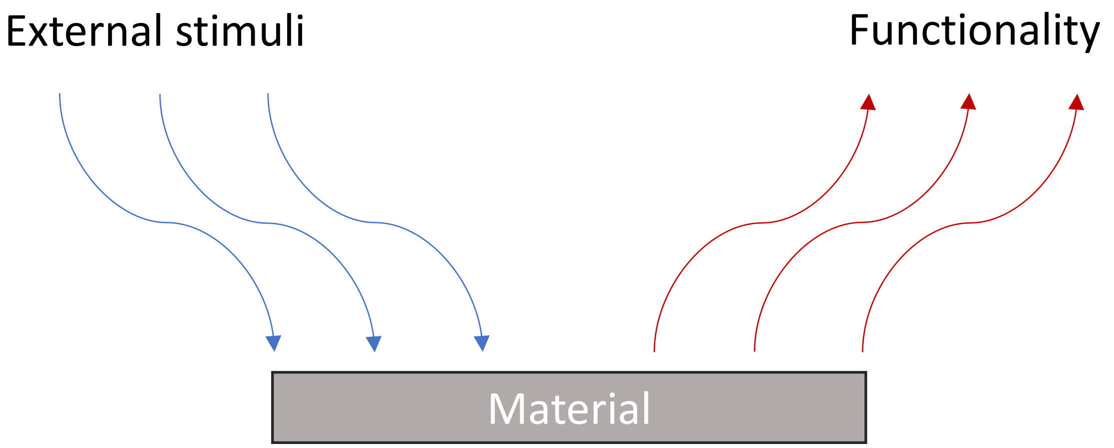


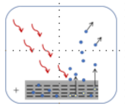
# Outline for today´s lecture

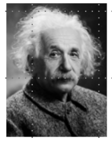
1. Short conclusion of last lecture

Diffraction / no change in electronic structure

- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)

Ejection of Electrons



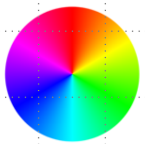


- XPS (AES) and UPS

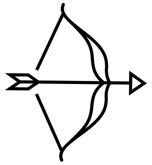
Vibrations and Rotations

- IR and Raman

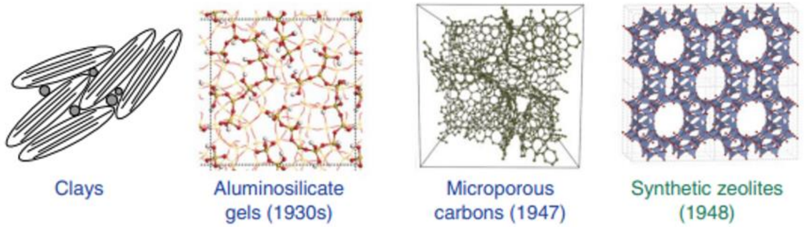
Electronic, nuclear transitions



- XAS spectroscopy
- UV/Vis spectroscopy
- NMR spectroscopy

2. Learning objectives 

- Porous Materials (Zeolites, COFs) – History, Properties, Synthesis
- Next time: MOFs – History, Properties, Synthesis



# Short recap from last time…

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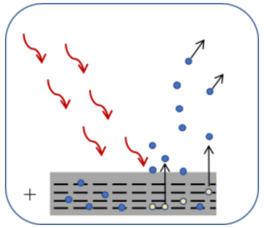
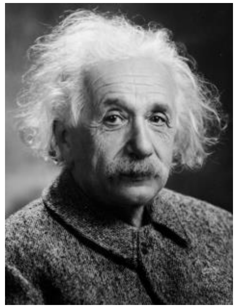
There are various methods to determine the average and the local structure: diffraction and spectroscopic methods.

**Diffraction / no change in electronic structure**

- X-ray diffraction
- Neutron diffraction
- Pair Distribution Function (PDF)

**Ejection of Electrons**



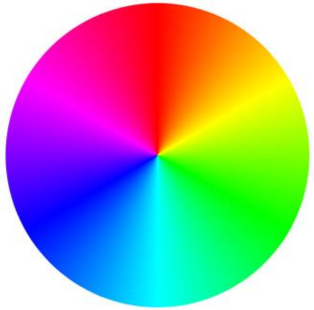


- XPS (AES) and UPS

**Vibrations and Rotations**

- IR and Raman

**Electronic, nuclear transitions**

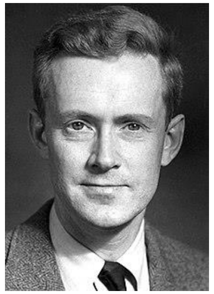


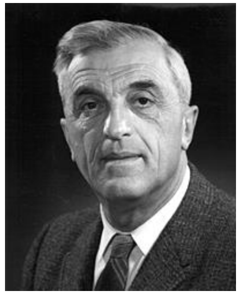
- XAS spectroscopy
- UV/Vis spectroscopy
- NMR spectroscopy

Further methods: EDX, mass spectrometry, DSC-TGA, BET.

# Core competence – NMR spectroscopy

In nuclear magnetic resonance ( = NMR) spectroscopy, the magnetic properties of atomic nuclei are used to obtain information on the structure of molecules/compounds.





E. M. Purcell (left) and F. Bloch (right)
Independent discovery of NMR in 1945
Awarded with Nobel Prize in 1952.

NMR Spectroscopy (msu.edu) (29th March, 2023)

**White Board**

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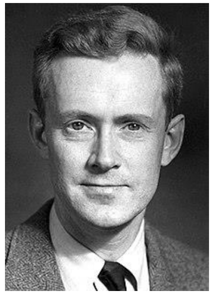
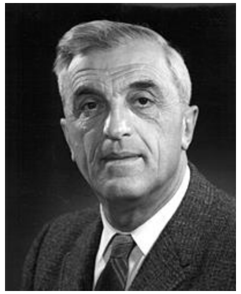

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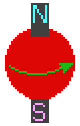


- $^{1}H$ has an angular momentum P
- The rotating nucleus induces a magnetic field and has a magnetic moment ($\mu$) proportional to the spin

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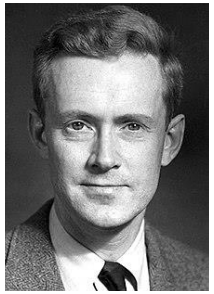

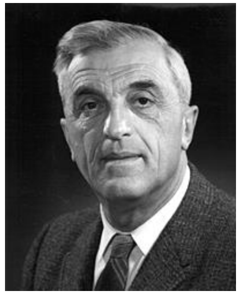

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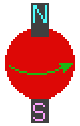


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**When is a nucleus magnetic?**

Sum of number of protons + number protons and neutrons is even: **no magnetic moment**.

Sum of number of protons + number protons and neutrons is odd: **magnetic moment**.

**Nuclei with a magnetic moment $\mu$ are NMR active!**

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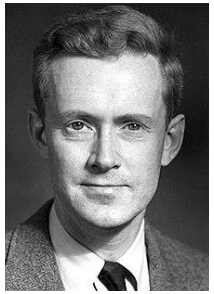
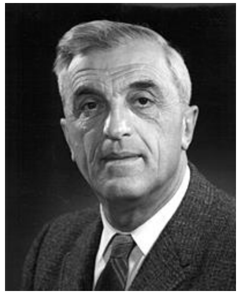

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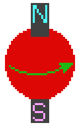


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Angular momentum is a quantum mechanical property:

$$P = \sqrt{I\ (I+1)} \cdot \frac{h}{2\pi}$$

h = Planck´s constant
I = nuclear spin quantum number (0, ½, 1, …, 6)

**When is a nucleus magnetic?**

**Sum** of number of protons + number protons and neutrons is **even**: **no magnetic moment**.

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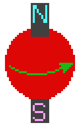
# Relation between P and $\mu$: gyromagnetic ratio $\gamma$

The magnitude of a magnetic moment generated by a nucleus with a spin is proportional to the angular momentum of the nucleus.

$$\mu = \gamma \cdot \mathrm{P} = \gamma \cdot \sqrt{I\,(I+1)} \cdot \frac{h}{2\pi}$$

**$\gamma$ is characteristic for each isotope/element!**

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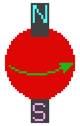


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**Absence of an external magnetic field**

- All nuclei (same isotope) have same magnetic energy in the ground state
- From quantum mechanics: magnetic energy state is 2 I + 1 times degenerated

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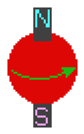


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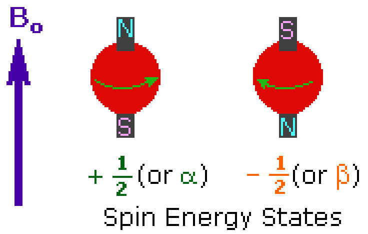


- two spin states exist, **+½** and **-½**
- Never totally align with $B_o$ because of P: complex rotational motion: **precession!**

**Absence of an external magnetic field**

- All nuclei (same isotope) have same magnetic energy in the ground state
- From quantum mechanics: magnetic energy state is 2 I + 1 times degenerated

**Presence of an external magnetic field $B_0$**

- Degeneration is cancelled: +½ is favored
- Splitting of the magnetic energy states in 2 I + 1 energy niveaus: **Zeeman effect**

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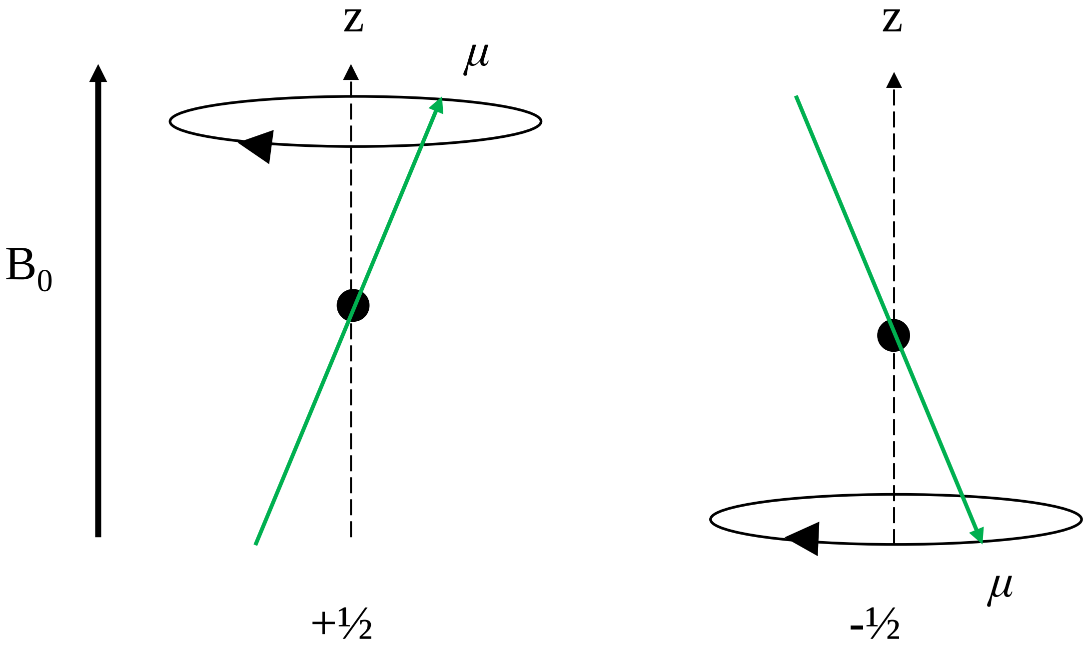
# Larmor frequency $\omega_0$







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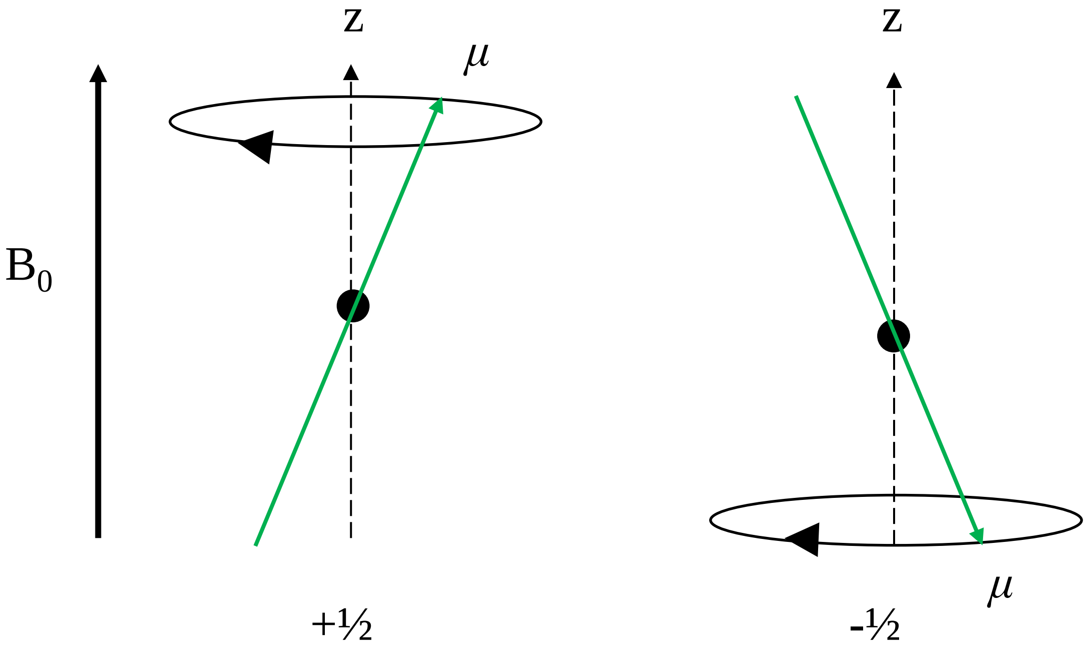
# Larmor frequency $\omega_0$

Precession around *z* direction has a specific frequency, it is called the **Larmor frequency** with the unit $\omega_0$.

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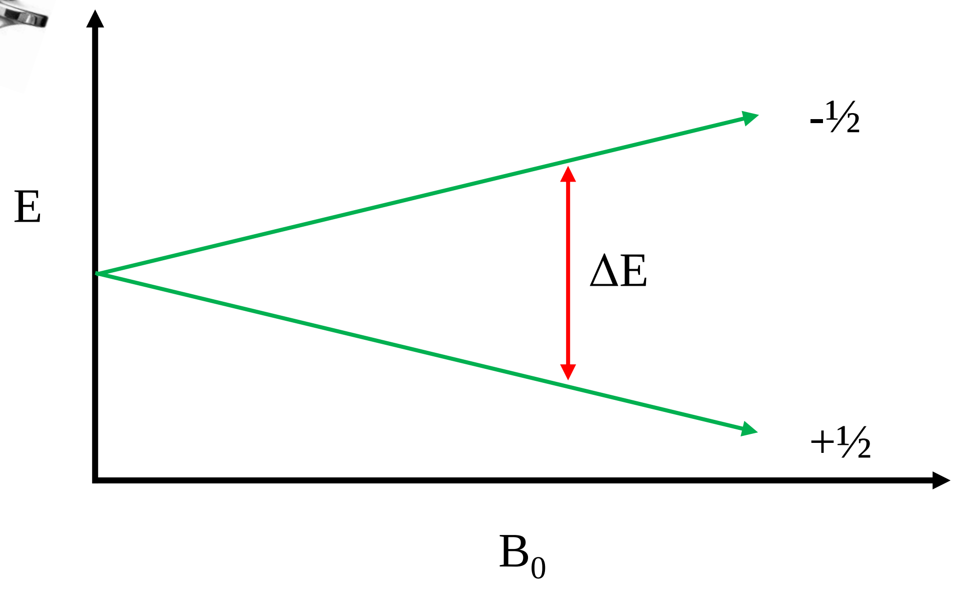


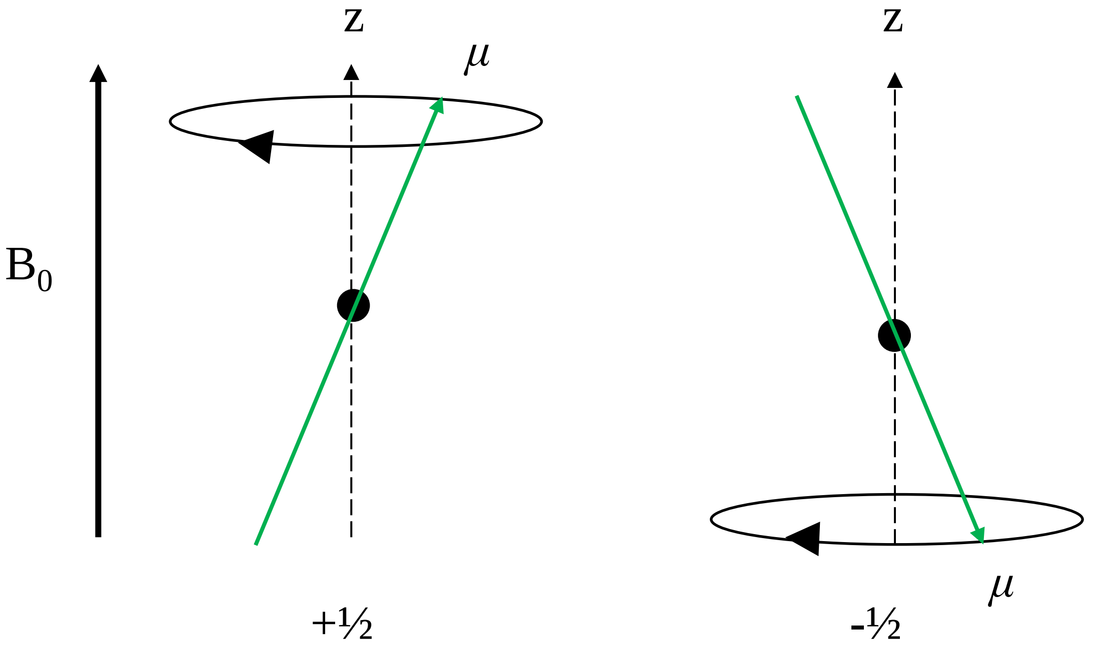


Larmor frequency rises with $B_0$ by the factor $\gamma$

$$\omega_0 = \gamma \cdot B_0$$

And with ΔE connected to $\omega_0$:

$$\Delta E = h \cdot \nu_0 = \frac{h}{2\,\pi} \cdot \omega_0 = \gamma \cdot \hbar \cdot B_0$$


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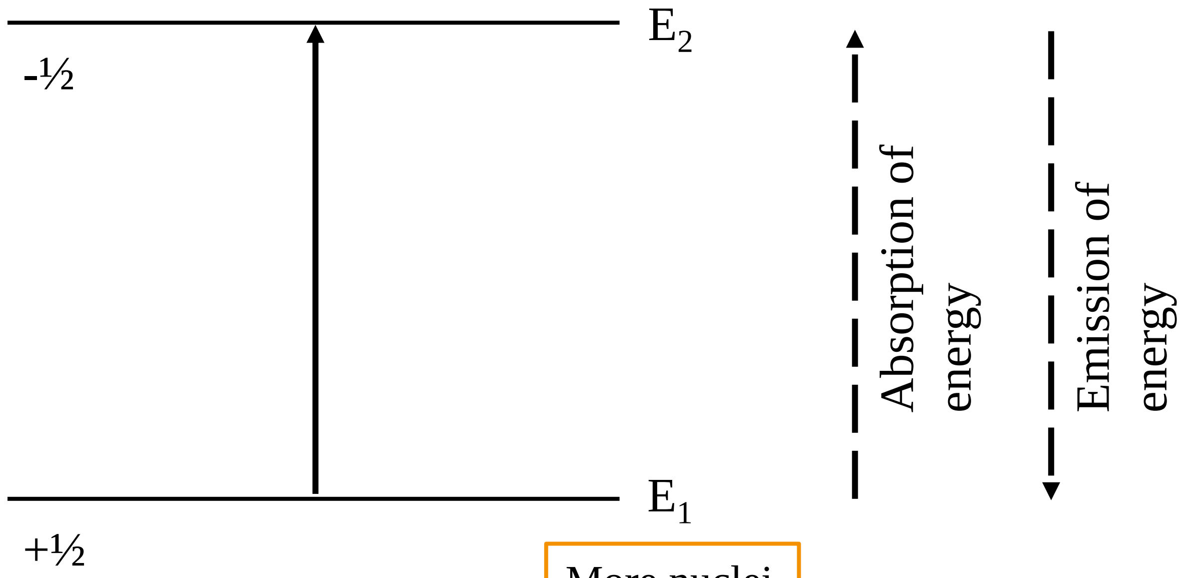
# And how is this useful for NMR?

**Applying a radio frequency pulse**

In an NMR experiment, the transition of the nuclei from one spin state to the other is induced by another (electro-) magnetic field $B_1$, which has a frequency in the region of radio waves.




More nuclei in $E_1$ state.

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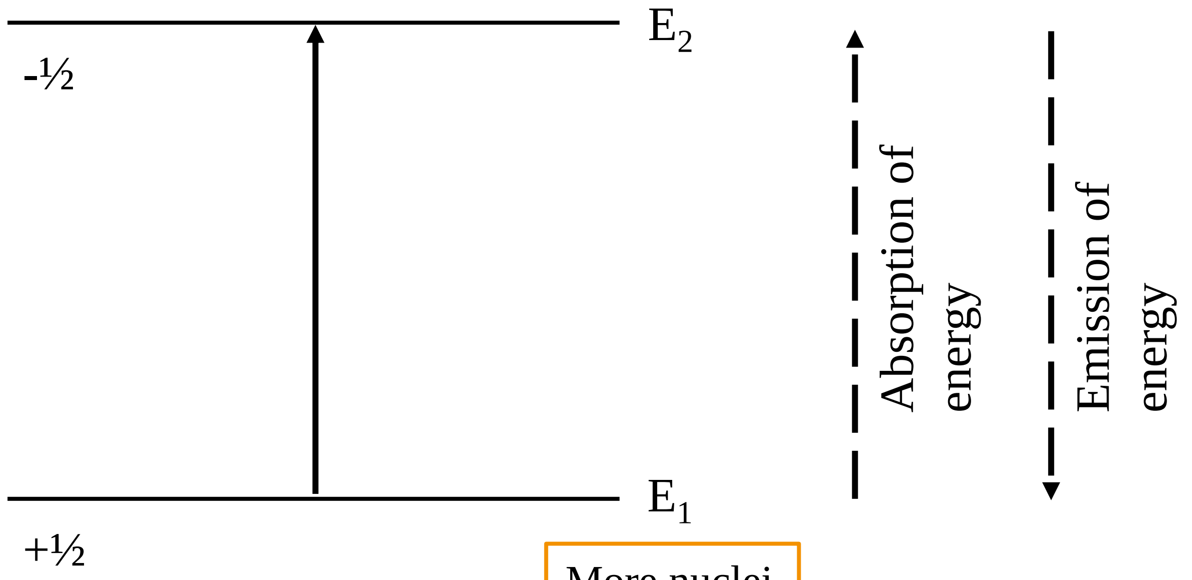


More nuclei in $E_1$ state.

If the frequency of $B_1$ is exactly the Larmor frequency: **resonance occurs**!

If the absorption is plotted against the frequency of $B_1$, a peak occurs, which corresponds to $\omega_0$ of the studied nucleus.

Resonance is not only dependent on $\gamma$ but also on the chemical environment: **chemical shift**!


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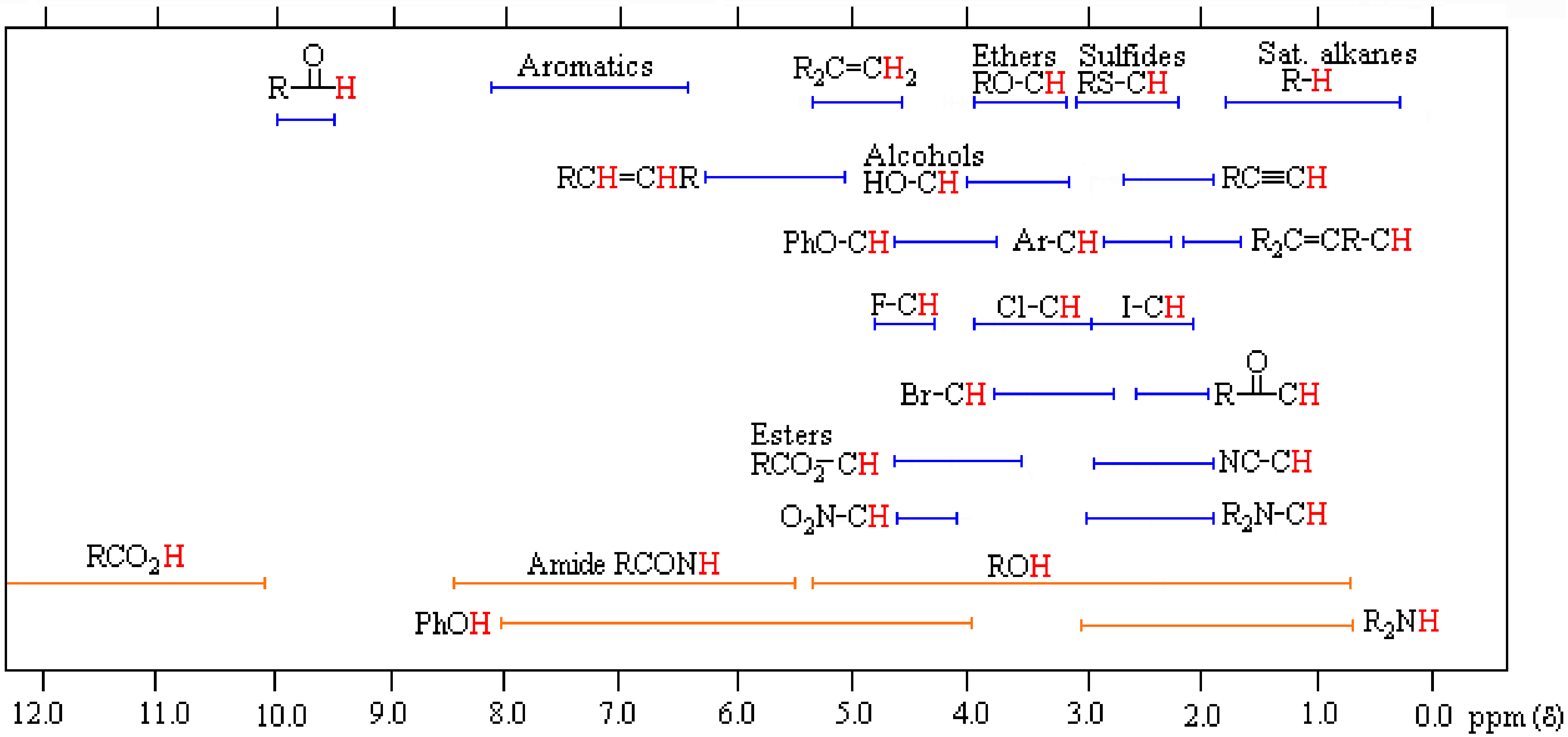
# To account for the spectrometer frequency

Separation of NMR signals is dependent on the magnetic field: To correct frequency differences for their field dependence, they are divided by the spectrometer frequency: the **chemical shift**!
Is multiplied by million to obtain the chemical shift $\delta$ with the unit ppm!




NMR Spectroscopy (msu.edu) (29th March, 2023)

# Moving from liquid to solid state

**Main difference to liquid-state NMR**
In solid state, spins are oriented and not randomly distributed: broad signals as a result of nuclear spin interactions (these are dipolar coupling, chemical shift anisotropy (orientation dependence of chemical shift) and quadrupolar interactions).


University of Ottawa NMR Facility Blog: 1H NMR Spectra of Solids (3rd March, 2025)
Solid-state NMR spectroscopy | Nature Reviews Methods Primers (3rd March, 2025)
Solid-state nuclear magnetic resonance – Wikipedia (3rd March, 2025)

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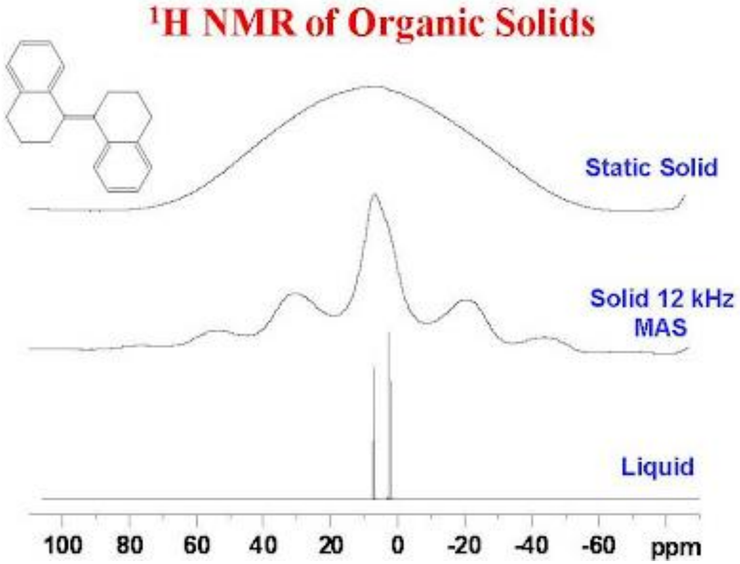
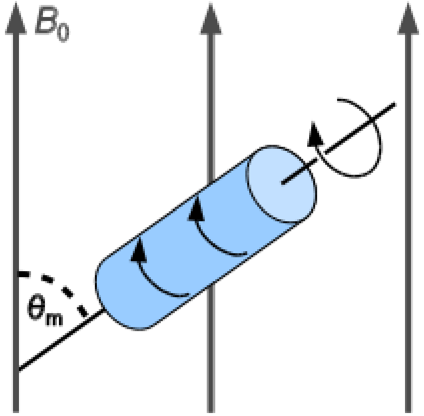



**Magic Angle Spinning**

Sample is rotated at the magic angle of 54.74 ° with respect to the magnetic field.




Resolution improved, but not as good as in solution!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# Mass spectrometry – analyzation of fragments

Analytical method to measure masses of atoms (historically) and molecules and with that to solve structure and composition of substances.

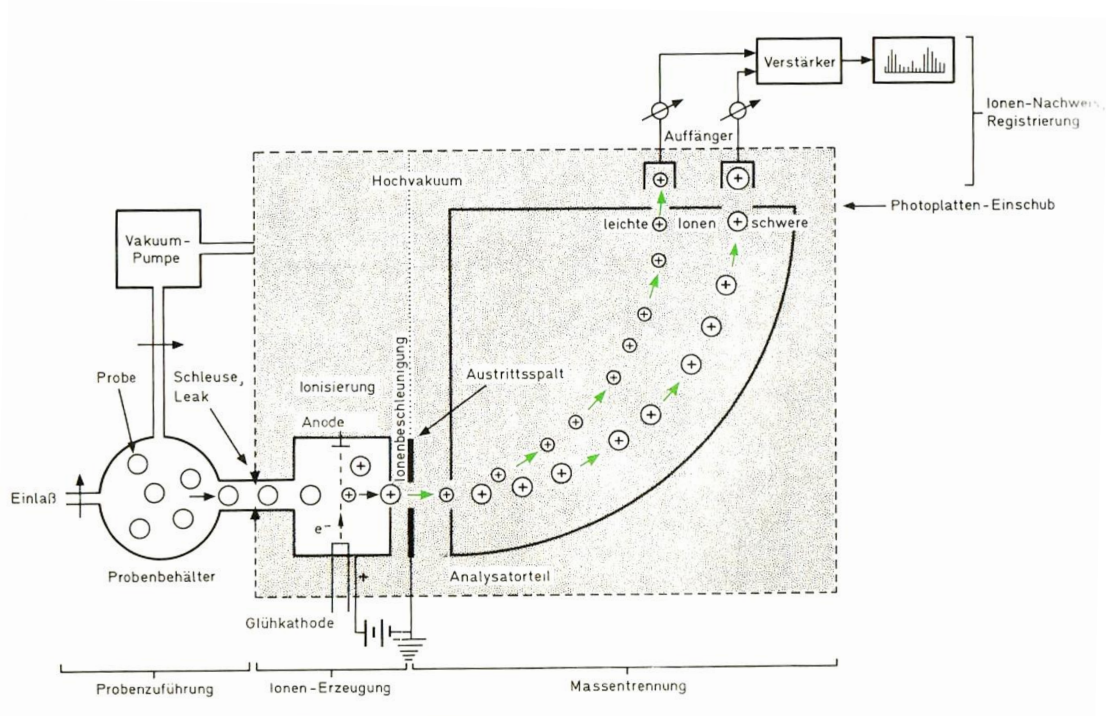


**Abb. 4.1** Schematische Darstellung eines Massenspektrometers

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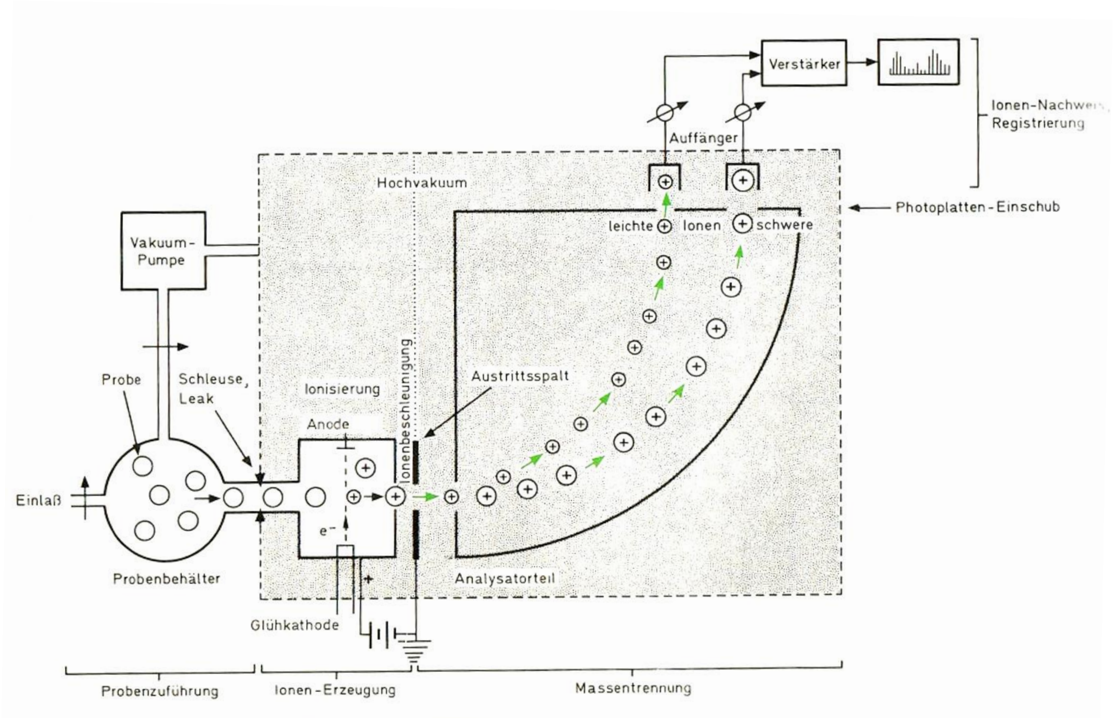

**Abb. 4.1** Schematische Darstellung eines Massenspektrometers

1. **Sample insertion**
   gas inlet (liquid or gaseous samples) or direct inlet (crystalline samples)

2. **Ion production**
   analyte is being ionized *via* various methods

3. **Mass separation**
   ions are separated by mass in the field of an electromagnet (mass-to-charge-ratio, *m*/*z*)

4. **Ion detection**

M. Hesse, H. Meier, B. Zeeh, Spektroskopische Methoden in der organischen Chemie, 3. Auflage, **1987**, *Georg Thieme Verlag*, Stuttgart

# When it´s getting hot: DSC/TGA measurements

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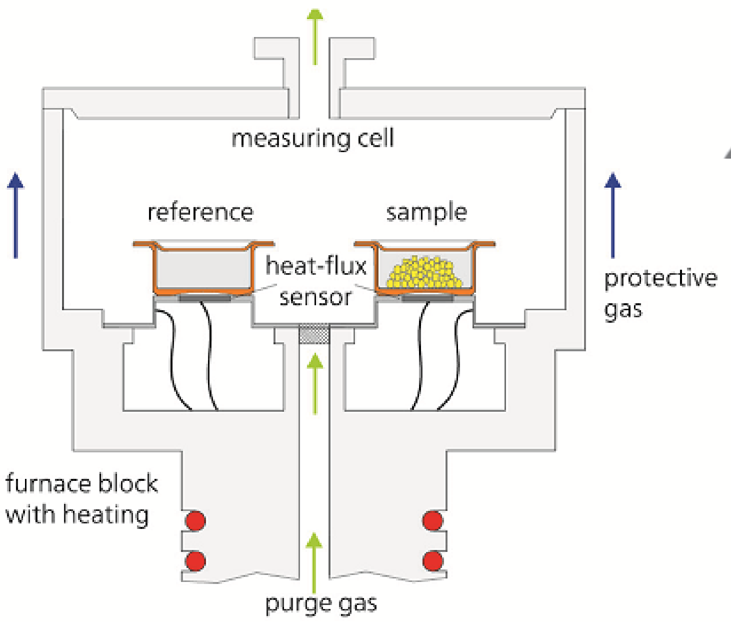
Differential scanning calorimetry (DSC) is a method for measuring the amount of heat given off/absorbed by a sample during isothermal operation, heating or cooling.




Schematic representation of a DSC from *NETZSCH*.

DSC 214 Polyma - NETZSCH Analyzing & Testing (29th March, 2023)

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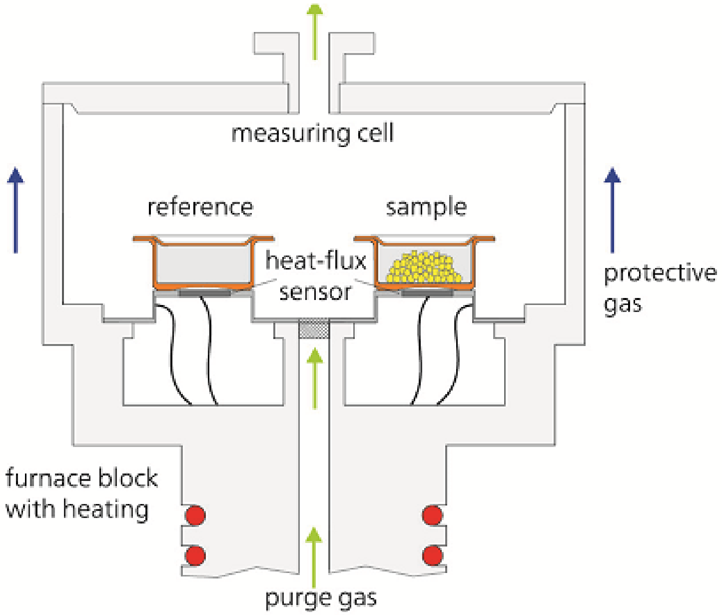


Schematic representation of a DSC from *NETZSCH*.

Thermogravimetric Analysis (TGA) is a method for measuring the change in mass of a sample as a function of temperature and time.

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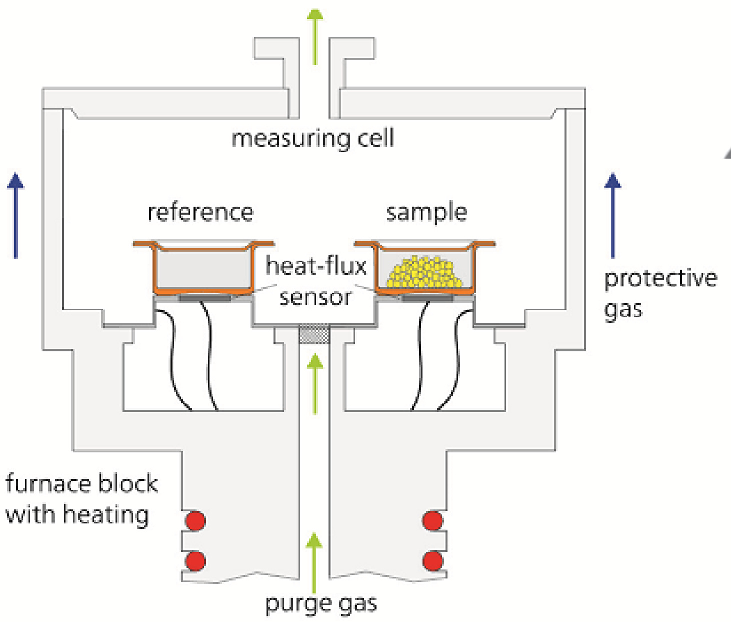



Schematic representation of a DSC from *NETZSCH*.

**Measurement principle**

Two crucibles: (a) reference and (b) sample crucible

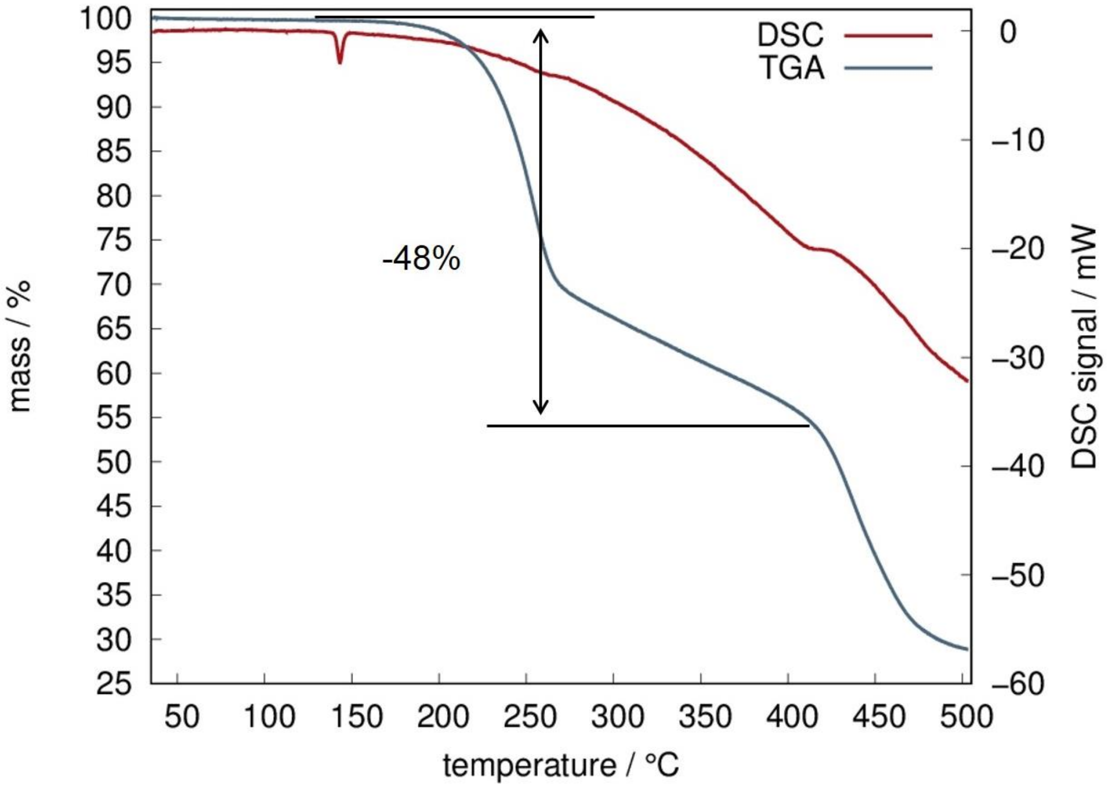
- Both are weighed before the temperature profile starts
- During in-/decrease of T, the heat flux is measured for both (a) and (b) as a function of T
- During in-/decrease of T, changes in mass are measured for both (a) and (b) as a function of T

Thermogravimetric Analysis (TGA) is a method for measuring the change in mass of a sample as a function of temperature and time.

DSC 214 Polyma - NETZSCH Analyzing & Testing (29th March, 2023)

# When it´s getting hot: DSC/TGA measurements

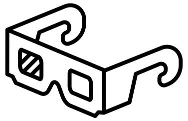
Differential scanning calorimetry (DSC)  and thermogravimetric analysis (TGA) are often combined for deeper understanding of samples under changing T profiles.




**Interpretation of data**

*DSC curve*

- Signal down: endothermic process / heat is required for *e.g.*, phase transitions or release of fragments / molecules
- Signal up: exothermic process



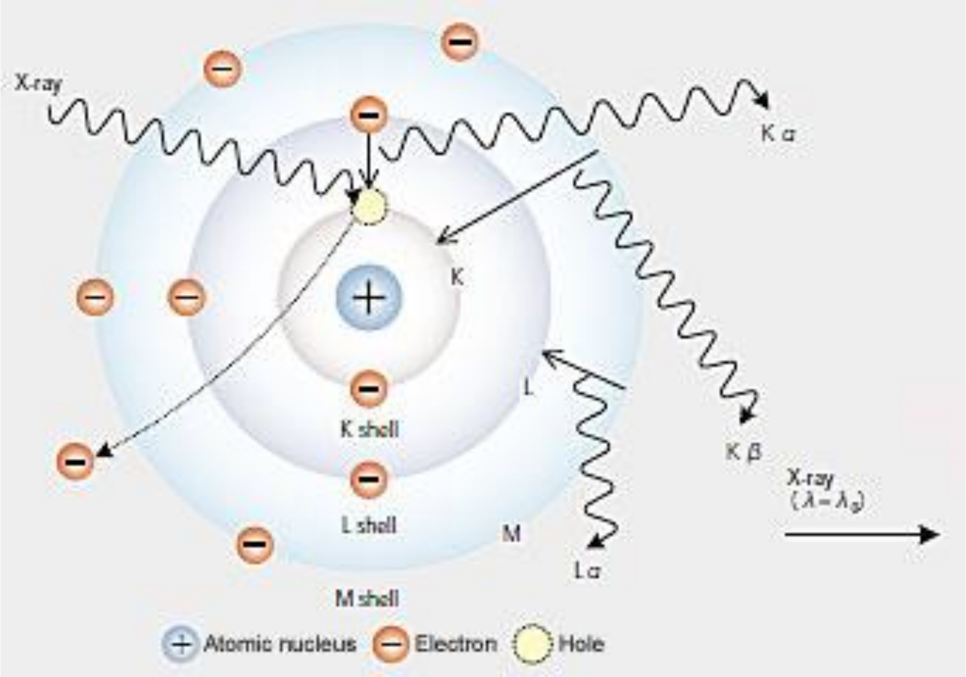
*TGA curve*

- Flat line: no changes in mass
- Decreasing line: mass loss
- Increasing line: gain of mass

Information on: thermal stability, phase transitions, composition.

# Energy-dispersive X-ray spectroscopy

By Energy-dispersive X-ray spectroscopy (EDX), the elemental composition of a sample is determined *via* detection of emitted X-rays of this probe.




Energiedispersive_Röntgenspektroskopie (chemie.de) (29th March, 2023)
EDX-7000P / EDX-8000P | SHIMADZU SWEDEN (29th March, 2023)
Gesetz von MOSELEY | LEIFIphysik (29th March, 2023)

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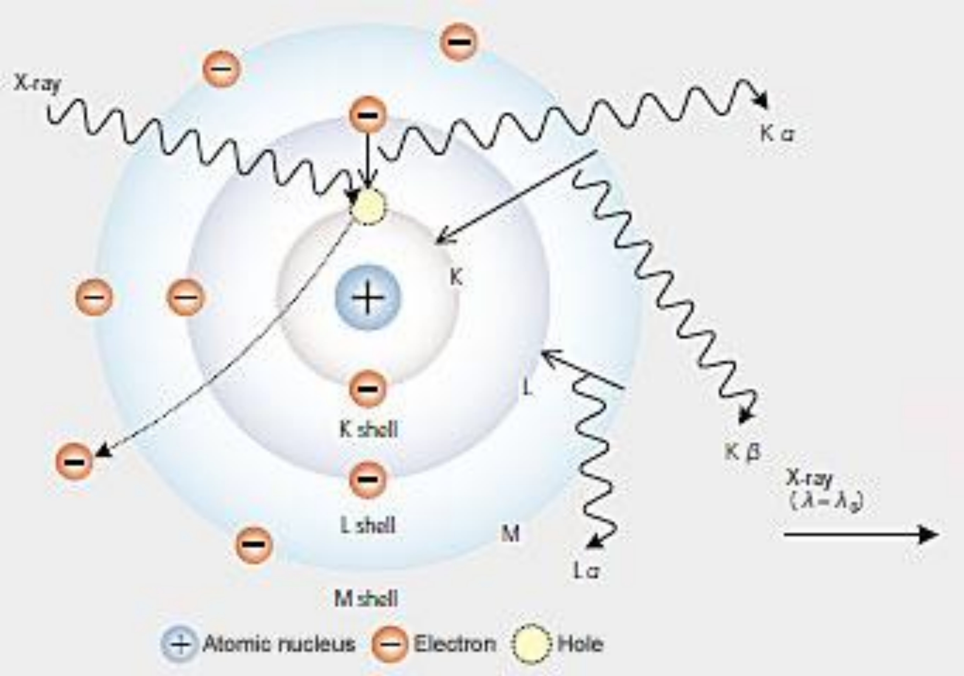


**Fluorescent X-ray generation**

Generally: same principle as for X-ray diffraction, but inverse

- Sample is irradiated with X-rays or electrons
- X-rays cause generation of "unique" X-rays, which are emitted from the sample (as a result of unique atomic structure)
- These fluorescent X-rays are characteristic for each element

[Energiedispersive_Röntgenspektroskopie (chemie.de)](Energiedispersive_Röntgenspektroskopie (chemie.de)) (29th March, 2023)
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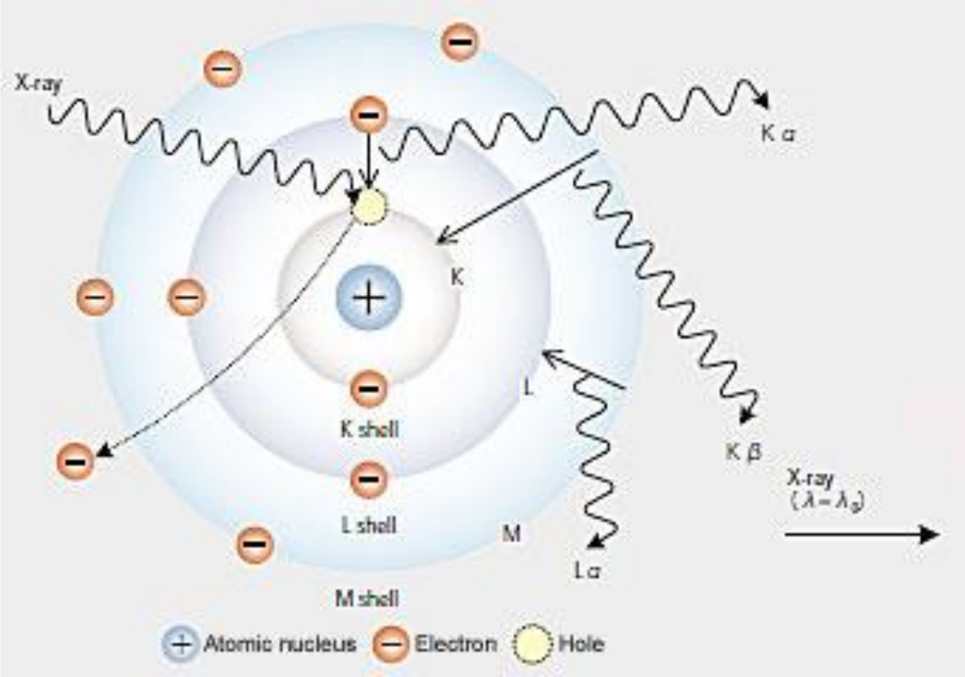


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Moseleys law: Relation of wavelength of $K_a$ and atomic number Z:

$$\frac{1}{\lambda_{K_\alpha}} = (Z-1)^2 \cdot R_\infty \cdot \frac{3}{4}$$

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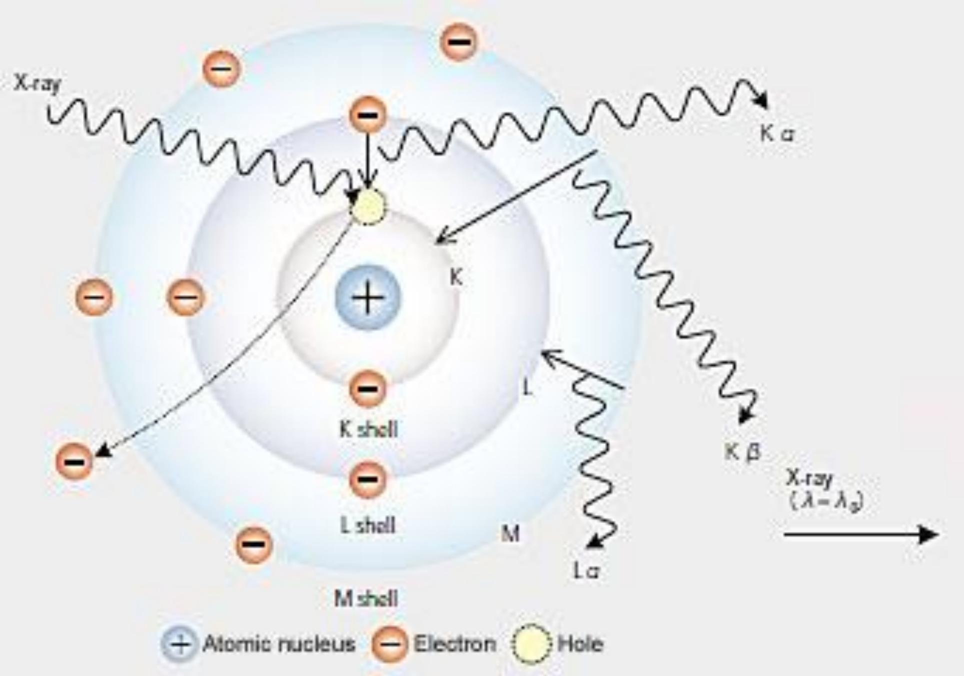


Information on: qualitative and quantitative elemental composition.

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# BET – Brunauer, Emmett and Teller

Brunauer-Emmett-Teller method, BET method, is a procedure for determining the specific surface area (in $m^2/g$) of powders and porous adsorbents, developed by S. Brunauer, P.H. Emmett, and E. Teller in 1938. In this method, a measuring gas ($N_2$, Ar, or Kr) is gradually introduced to the adsorbent at a constant temperature. The amount of gas adsorbed, $m$m, is determined by weighing, while the equilibrium pressure, $p$p, is measured.

BET surface area – Andy Connelly (wordpress.com) (25th April, 2023)
Adsorption of Gases in Multimolecular Layers | Journal of the American Chemical Society (3rd March, 2025)
How Reproducible are Surface Areas Calculated from the BET Equation? - Osterrieth - 2022 - Advanced Materials - Wiley Online Library (3rd March, 2025)
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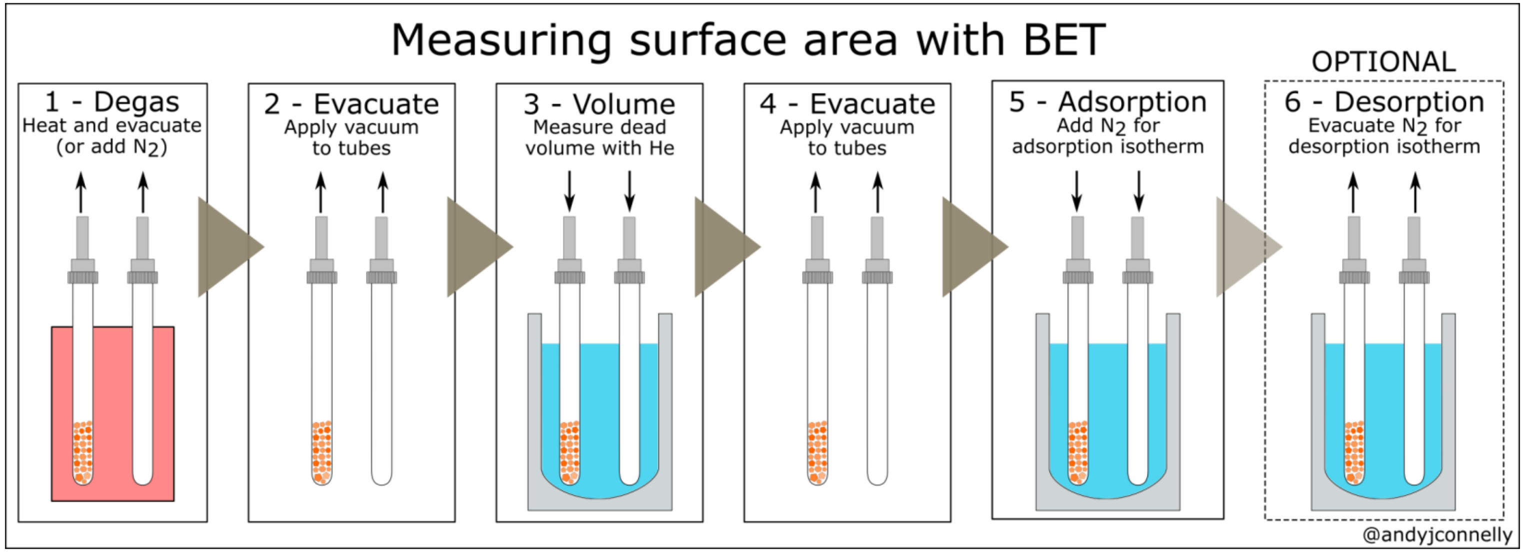


**Measurement principle**

In principle, the smallest pores are filled first during gas adsorption. As the pressure or relative pressure increases, the larger pores are successively filled. The volume of gas is measured at the boiling point.

General assumption: Gas condenses on the surface in a monolayer fashion – amount of adsorbed gas is correlated to the total surface area and pores by utilization of the BET method.


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# Sorption Isotherms

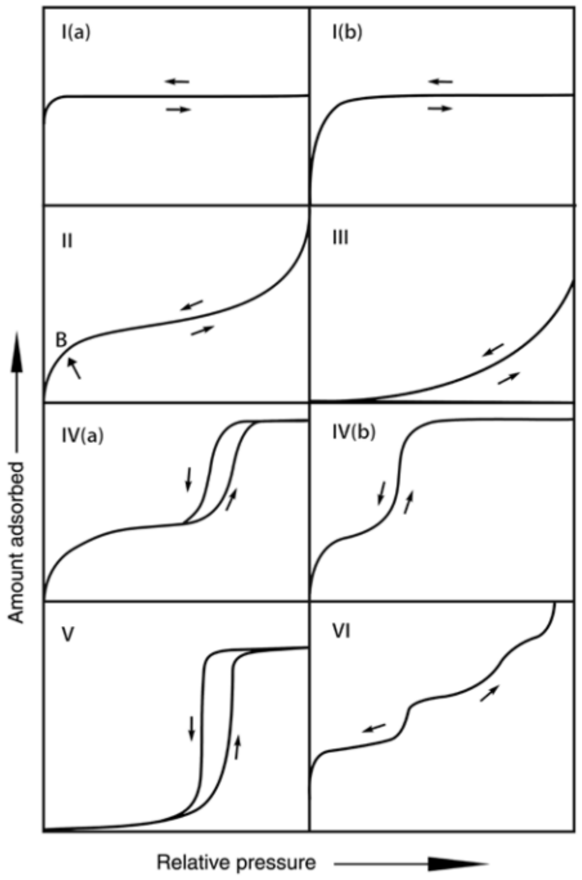



**Fig. 2:** Classification of physisorption isotherms.

Reversible Type I: a) **microporous** solids with narrow micropores
b) **microporous** solids with wider micropores + narrow nanopores

Reversible Type II: **nonporous** or **macroporous** adsorbents

Reversible Type III: no monolayer formation (point B is missing)

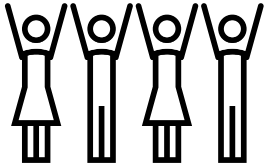
Type IV: **mesoporous** adsorbents
a) capillary condensation with hysteresis (pores exceed critical width)
b) reversible, smaller pore width

Type V: hydrophobic **microporous** and **mesoporous** adsorbents: most **MOFs!**

Type VI: layer-by-layer adsorption on a uniform **nonporous** surface

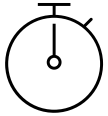
Macropores: > 50 nm; Mesopores: 2 nm – 50 nm; Micropores: ≤ 2 nm.

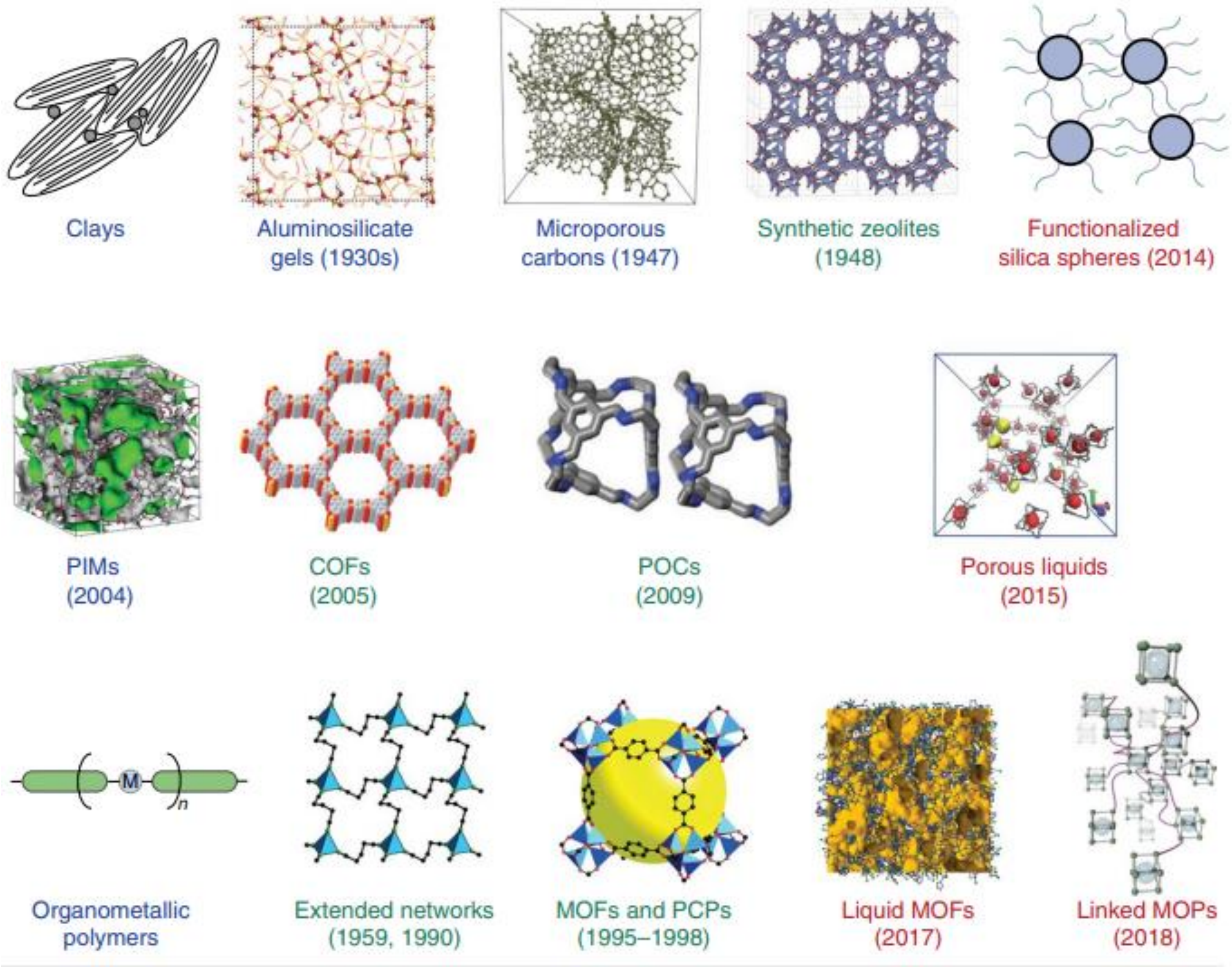
S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, *2*, 309–319.
M. Thommes et al., *Pure Appl. Chem.* **2015**, *87* (9-10): 1051–1069.
BET theory – Wikipedia (25th April, 2023)



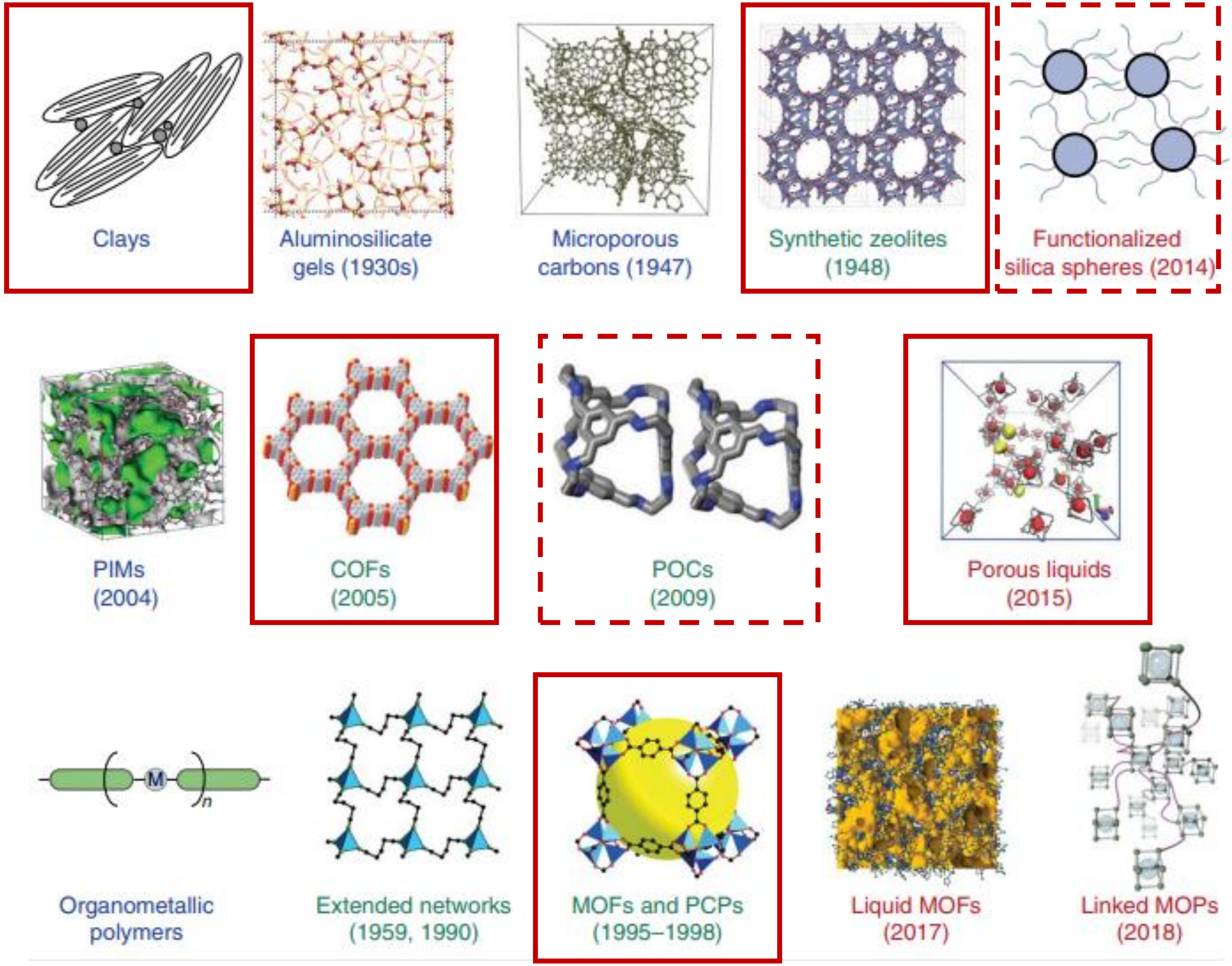
# Plenum

# Methods-Table: Finalization

 15 min



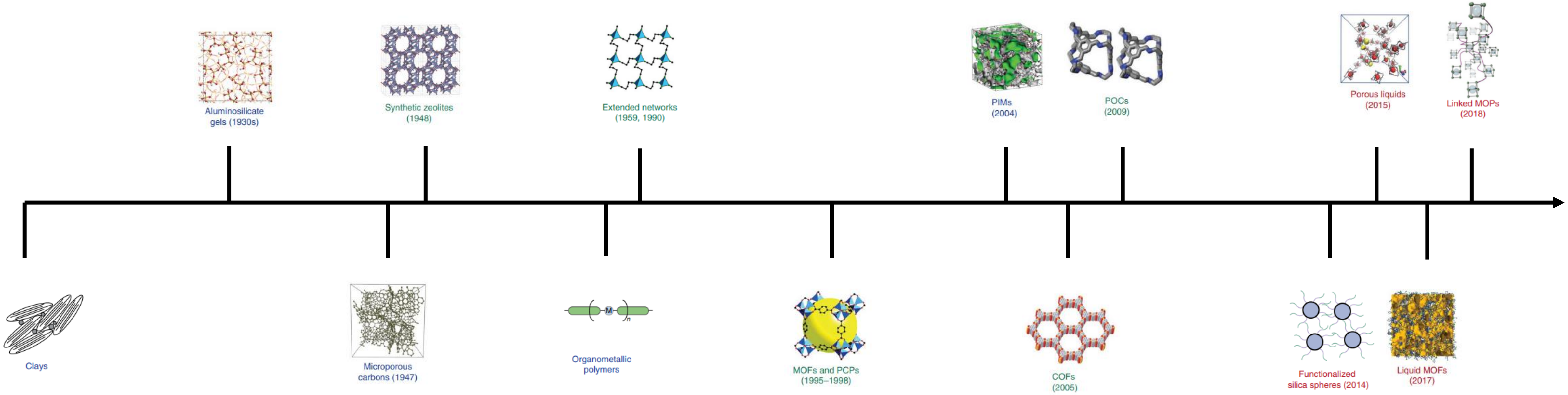

# Porous materials




# Porous materials

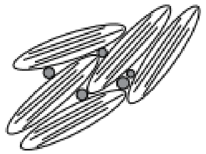
# Evolution of porous materials

"Porous materials contain regions of empty space into which guest molecules can be selectively adsorbed or chemically transformed. They can be of organic, inorganic or hybrid nature."

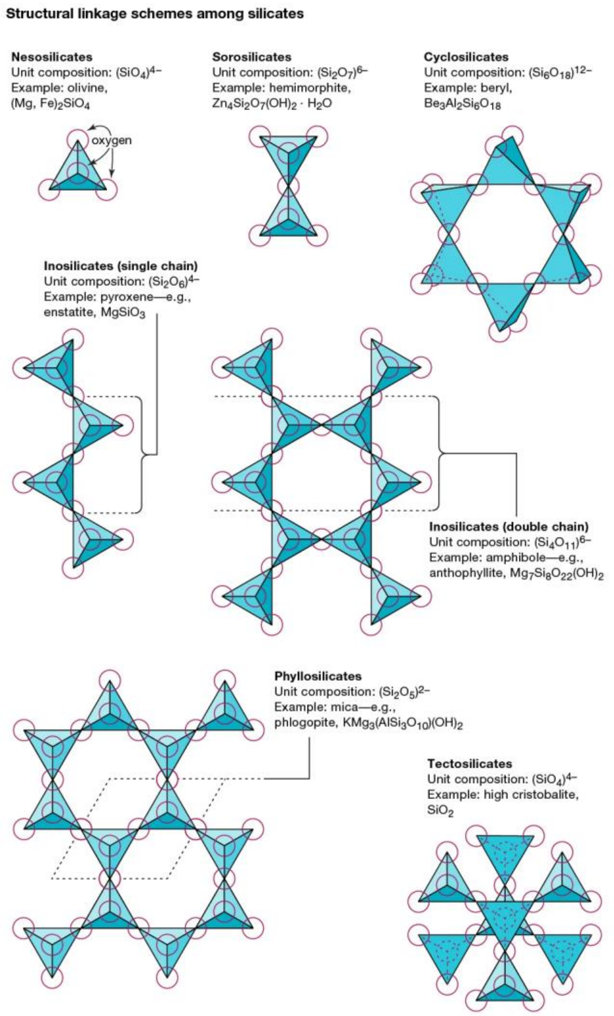



T. D. Bennett, F.-X. Coudert, S. L. James, A. Cooper, *Nat. Mater.* **2021**, *20*, 1179–1187.

# Clays – already used by the Mayan people




**Clay** is a type of natural soil containing clay minerals, which are hydrous aluminium **phyllosilicates** *e.g.*, palygorskite or attapulgite.




[Maya blue – Wikipedia]() (17th April, 2023)
[Phyllosilicate | Structure & Facts | Britannica]() (17th April, 2023)

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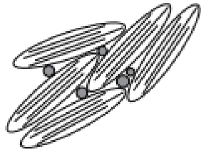

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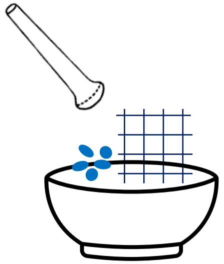
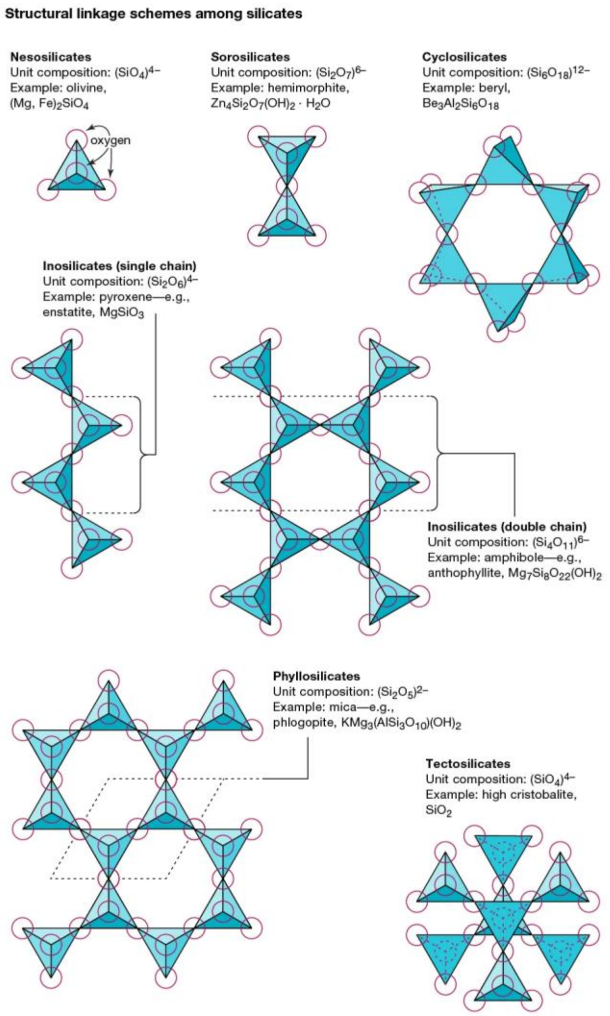


Mayan blue painting containing indigo as coloring agent and clay as stabilizer

Chemical sum formula of palygorskite:
$(Mg,Al)_2Si_4O_{10}(OH) \cdot 4\,(H_2O)$

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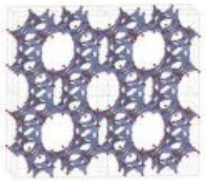
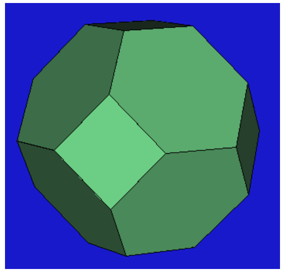
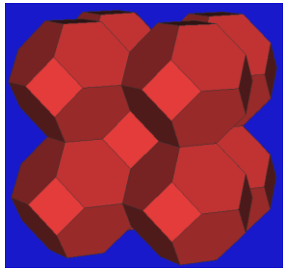
# Framework Silicates (Tectosilicates)



Synthetic zeolites (1948)



b-cage



Sodalith
$Na_4[Al_3Si_3O_{12}]Cl$

Lapislazuli (Lapis Lazuli) is a deep-blue metamorphic rock primarily composed of lazurite (**$Na_4[Al_3Si_3O_{12}]S_x$**, where $x$ = 2-3). It belongs to the **ultramarine group**, which also includes synthetically produced blue pigments. A well-known example of a synthetic ultramarine pigment is the **typical blue color seen on Nivea tins**.


Zeolite Database Help (iza-structure.org) (17th April, 2023)
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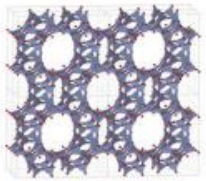

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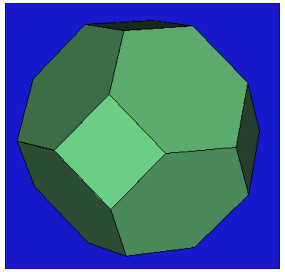

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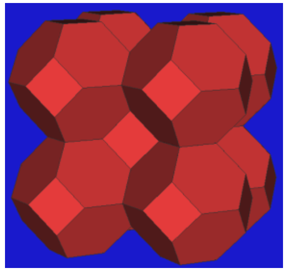

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Ultramarine blue

Ultramarine middle

Ultramarine purple

Ultramarine red


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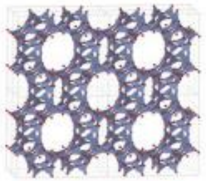
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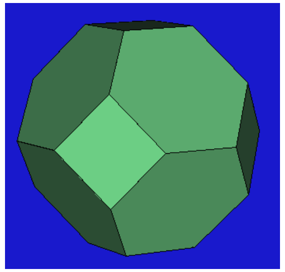
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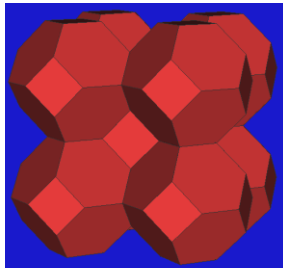
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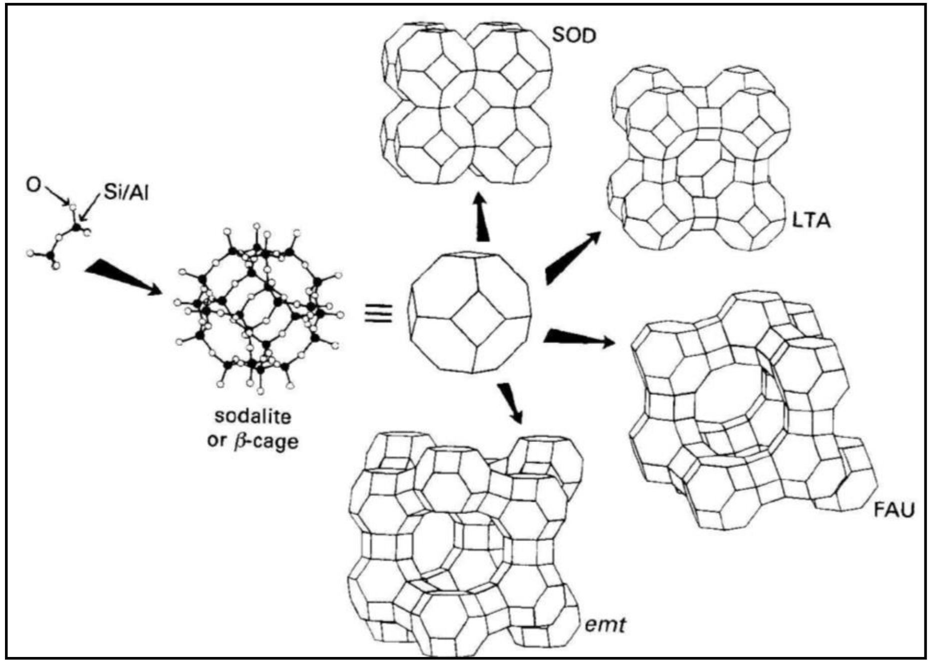


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# The boiling stones - zeolites

**Definition of Zeolites**
- Crystallized hydrated aluminosilicates
- Can be synthetic or natural (≈ 40 types)
- Rigid framework structures made of $SiO_4$ and $AlO_4$ tetrahedra
- Defined periodic cavities and/or channels
- Cavities contain chemically exchangeable metal cations *e.g.*, alkali or alkaline earth metal ions
- Cavities can also contain water or other gas molecules

**Discovery**
- In 1756, the Swedish Baron **Axel Cronstedt** discovered minerals that released water when heated → "boiling stones" → *zeo* = "I boil", *lithos* = "stone"
- In 1949, **Milton at Union Carbide** synthesized the first artificial zeolites


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**General Composition**
- Derived from **$SiO_2$ (silicon dioxide)**
- Partial replacement of **$Si^{4+}$ by $Al^{3+}$**
- This creates **excess charges**, which are compensated by incorporated metal ions

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot m\ H_2O$$

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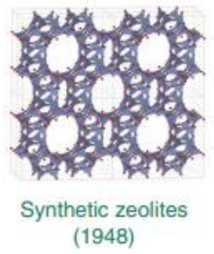
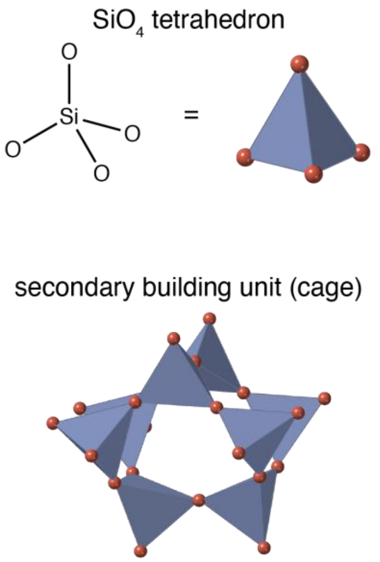


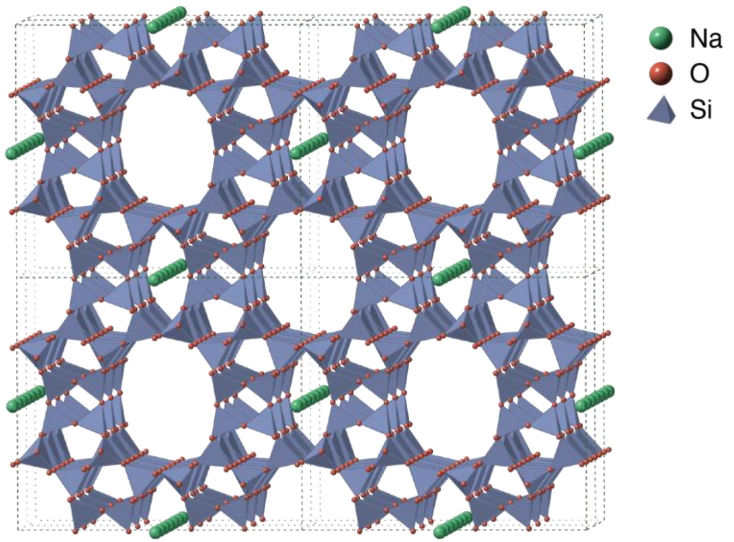

Database of zeolite structures:
"Classically, zeolites are defined as aluminosilicates with open 3-dimensional framework structures composed of corner-sharing $TO_4$ tetrahedra, where T is Al or Si."

Zeolite means: boiling stone.

Natural (Natrolite) and synthetic zeolite.

| Name | N(Si) : N(Al) |
|---|---|
| Zeolite A | 1:1 |
| Zeolite X | 1.2:1 |
| Chabazite | 2:1 |
| ZSM-5 | 30:1 |




Mordenite (MOR framework)

General sum formula of zeolites:
$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot m\, H_2O$

**White Board**


Zeolite Database Help (iza-structure.org) (17th April, 2023)
Zeolite – Wikipedia (17th April, 2023)
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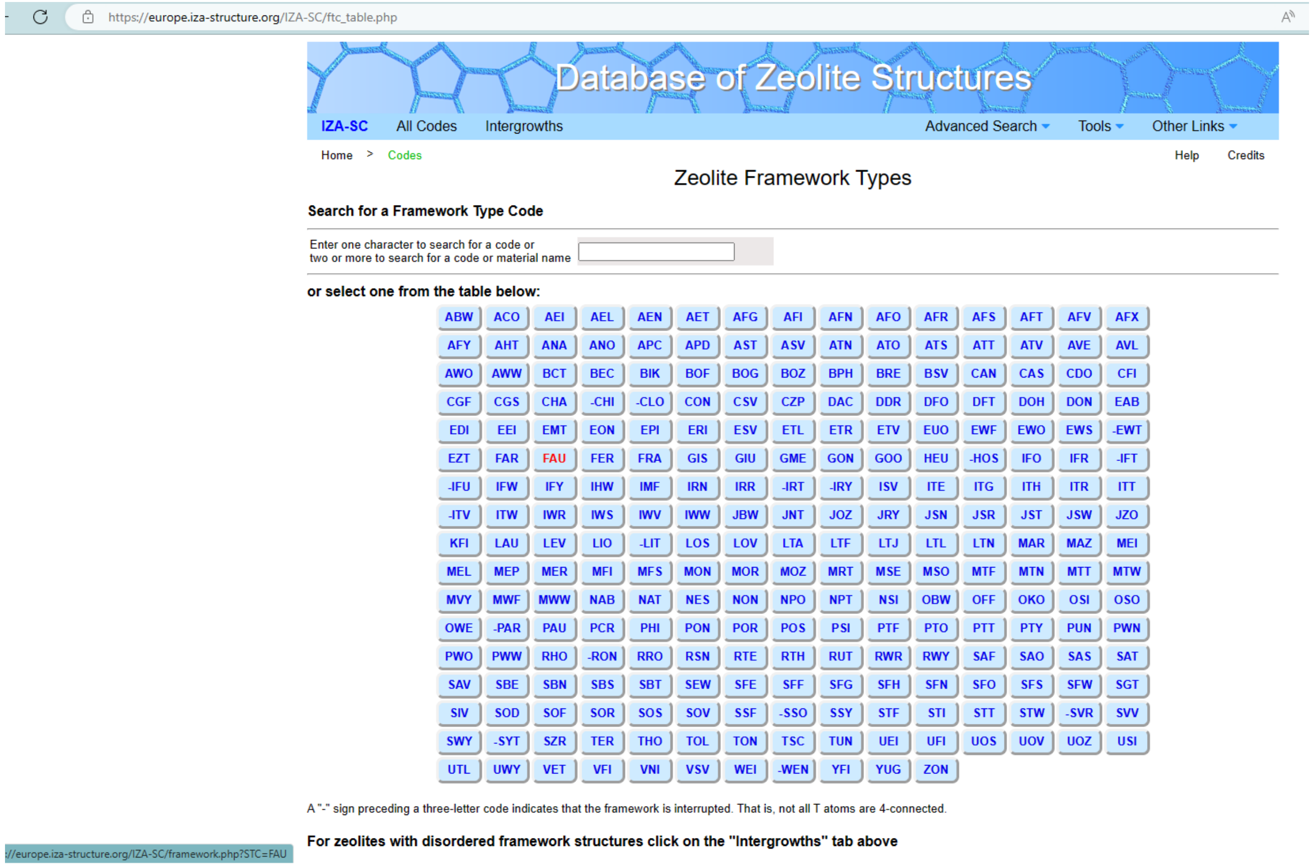
# Classification of zeolites

There are 251 ordered and 9 disordered Zeolite Framework Types classified to date by the IZA-SC.




[Zeolite Database Help (iza-structure.org)]

[Zeolite – Wikipedia] (17th April, 2023)

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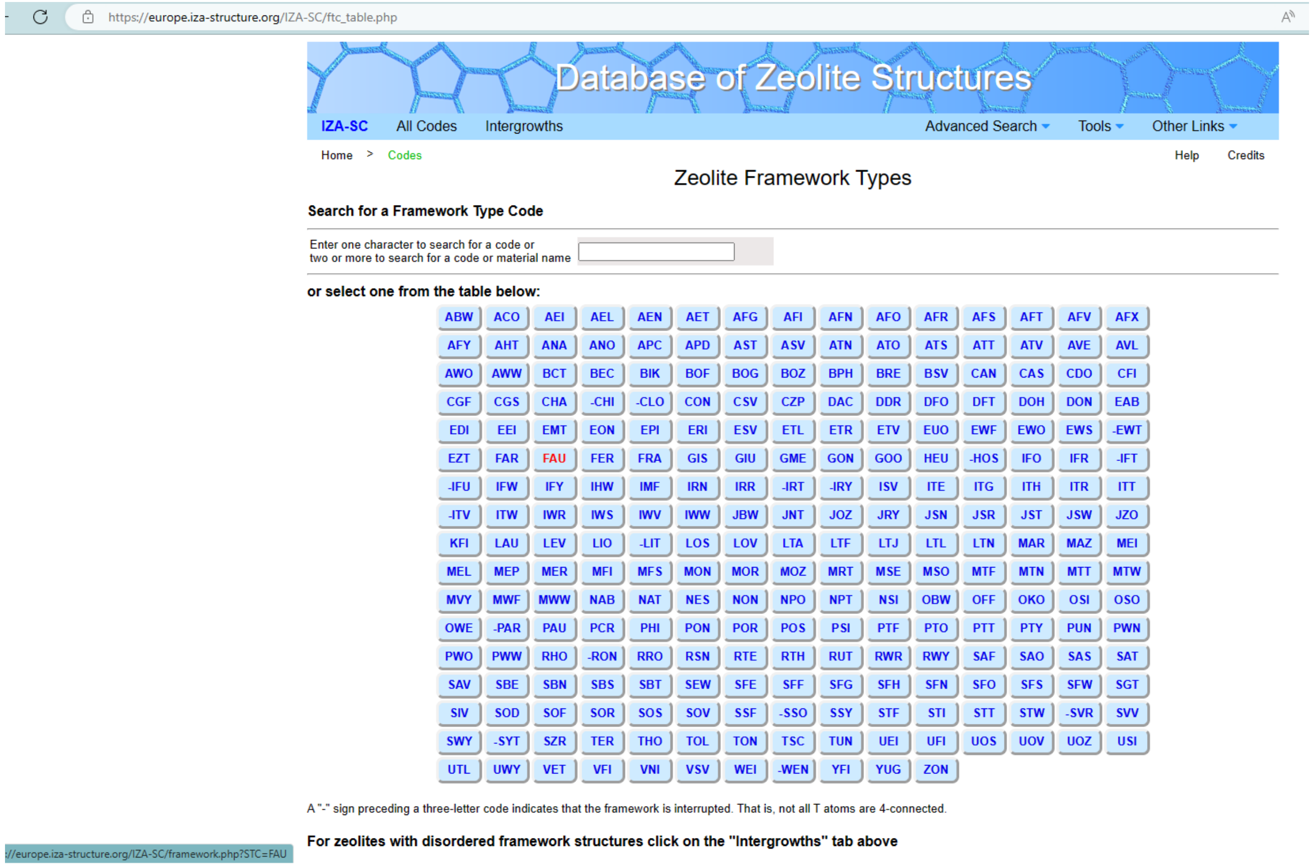
https://europe.iza-structure.org/IZA-SC/ftc_table.php

Database of Zeolite Structures

IZA-SC All Codes Intergrowths Advanced Search Tools Other Links

Home > Codes Help Credits

Zeolite Framework Types

**Search for a Framework Type Code**

Enter one character to search for a code or two or more to search for a code or material name

**or select one from the table below:**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ABW | ACO | AEI | AEL | AEN | AET | AFG | AFI | AFN | AFO | AFR | AFS | AFT | AFV | AFX |
| AFY | AHT | ANA | ANO | APC | APD | AST | ASV | ATN | ATO | ATS | ATT | ATV | AVE | AVL |
| AWO | AWW | BCT | BEC | BIK | BOF | BOG | BOZ | BPH | BRE | BSV | CAN | CAS | CDO | CFI |
| CGF | CGS | CHA | -CHI | -CLO | CON | CSV | CZP | DAC | DDR | DFO | DFT | DOH | DON | EAB |
| EDI | EEI | EMT | EON | EPI | ERI | ESV | ETL | ETR | ETV | EUO | EWF | EWO | EWS | -EWT |
| EZT | FAR | FAU | FER | FRA | GIS | GIU | GME | GON | GOO | HEU | -HOS | IFO | IFR | -IFT |
| -IFU | IFW | IFY | IHW | IMF | IRN | IRR | -IRT | -IRY | ISV | ITE | ITG | ITH | ITR | ITT |
| -ITV | ITW | IWR | IWS | IWV | IWW | JBW | JNT | JOZ | JRY | JSN | JSR | JST | JSW | JZO |
| KFI | LAU | LEV | LIO | -LIT | LOS | LOV | LTA | LTF | LTJ | LTL | LTN | MAR | MAZ | MEI |
| MEL | MEP | MER | MFI | MFS | MON | MOR | MOZ | MRT | MSE | MSO | MTF | MTN | MTT | MTW |
| MVY | MWF | MWW | NAB | NAT | NES | NON | NPO | NPT | NSI | OBW | OFF | OKO | OSI | OSO |
| OWE | -PAR | PAU | PCR | PHI | PON | POR | POS | PSI | PTF | PTO | PTT | PTY | PUN | PWN |
| PWO | PWW | RHO | -RON | RRO | RSN | RTE | RTH | RUT | RWR | RWY | SAF | SAO | SAS | SAT |
| SAV | SBE | SBN | SBS | SBT | SEW | SFE | SFF | SFG | SFH | SFN | SFO | SFS | SFW | SGT |
| SIV | SOD | SOF | SOR | SOS | SOV | SSF | -SSO | SSY | STF | STI | STT | STW | -SVR | SVV |
| SWY | -SYT | SZR | TER | THO | TOL | TON | TSC | TUN | UEI | UFI | UOS | UOV | UOZ | USI |
| UTL | UWY | VET | VFI | VNI | VSV | WEI | -WEN | YFI | YUG | ZON | | | | |

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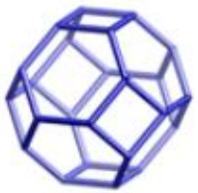
**For zeolites with disordered framework structures click on the "Intergrowths" tab above**

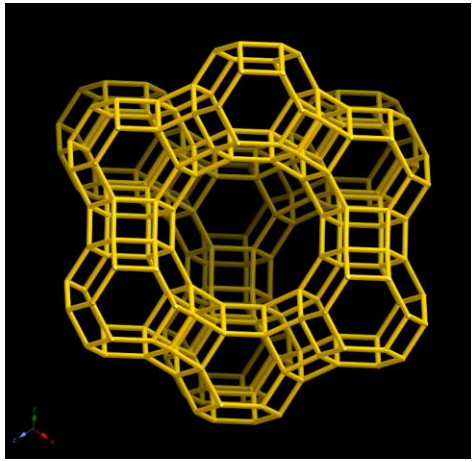
://europe.iza-structure.org/IZA-SC/framework.php?STC=FAU

*d4r (t-cub )*



*sod (t-toc )*

*lta (t-grc )*

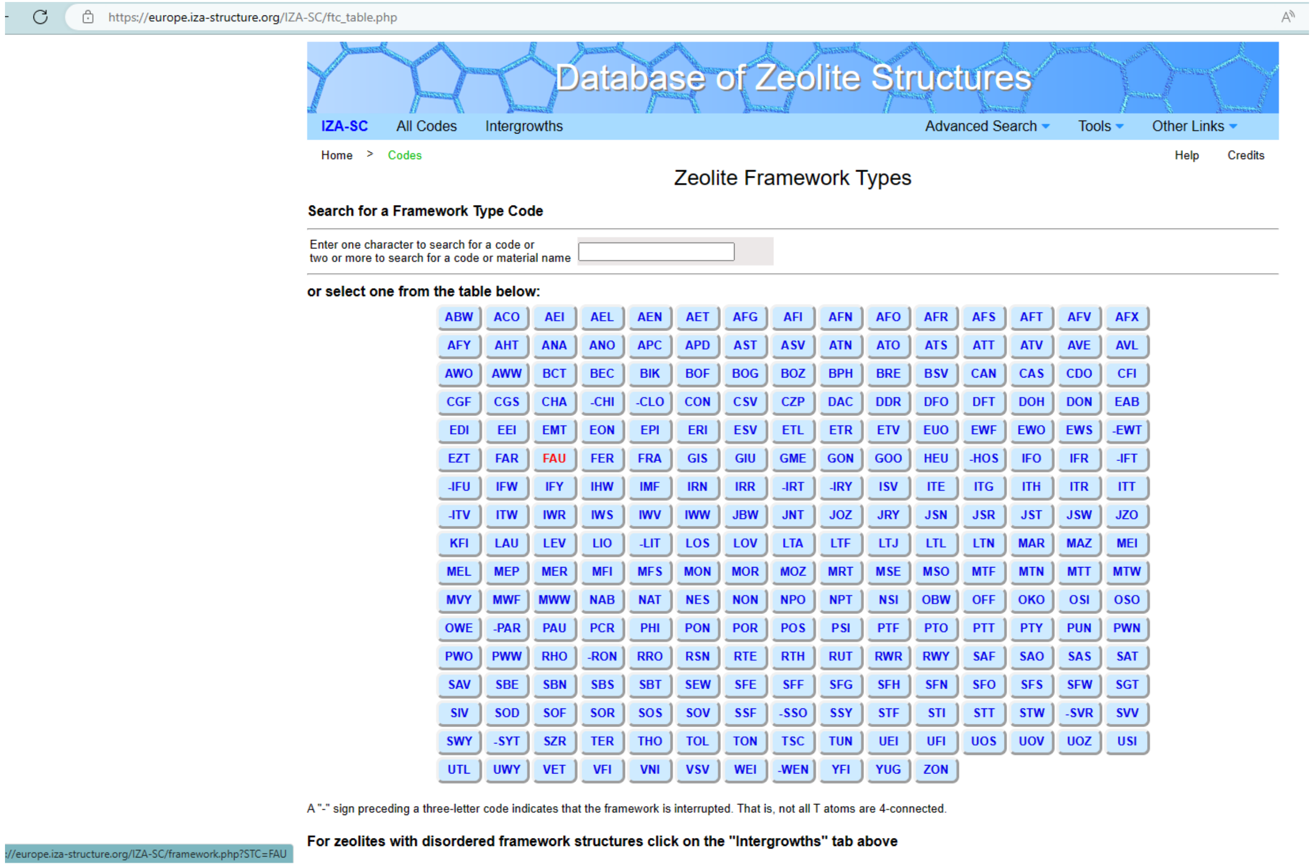


**Faujasite** type
12-ring entrance
Large-pore zeolite

[Zeolite – Wikipedia]() (17th April, 2023)

# Classification of zeolites

There are 251 ordered and 9 disordered Zeolite Framework Types classified to date by the IZA-SC.

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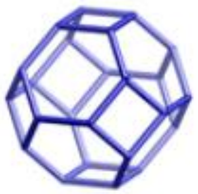

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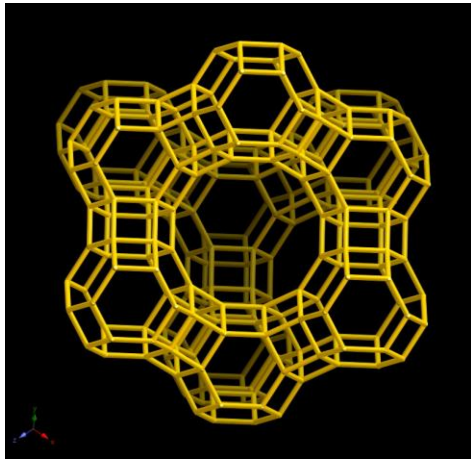

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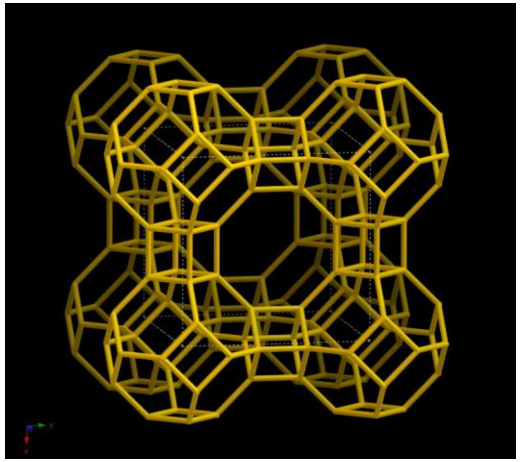

**LTA** type
8-ring entrance
Small-pore zeolite

Zeolite – Wikipedia (17th April, 2023)

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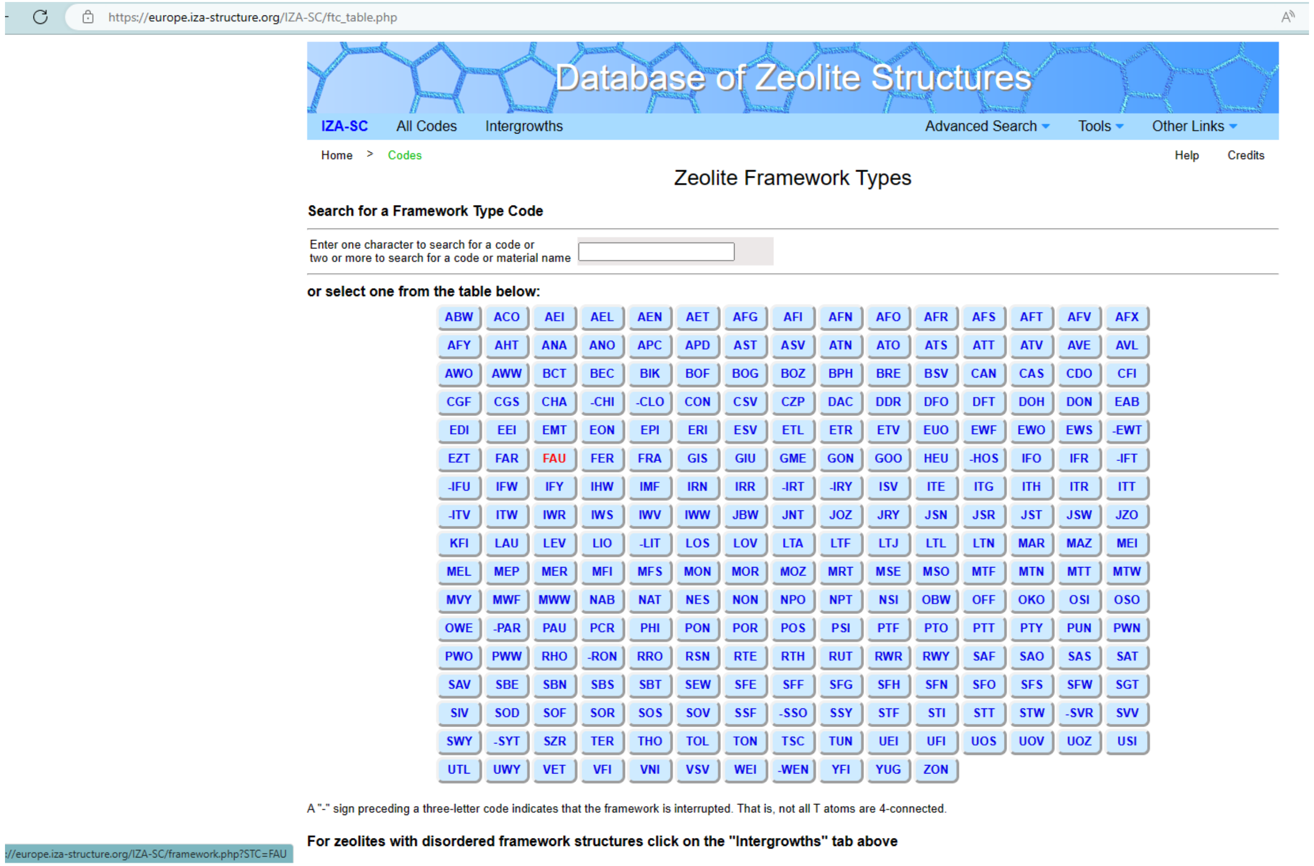

https://europe.iza-structure.org/IZA-SC/ftc_table.php

Database of Zeolite Structures

IZA-SC All Codes Intergrowths Advanced Search Tools Other Links

Home > Codes Help Credits

Zeolite Framework Types

**Search for a Framework Type Code**

Enter one character to search for a code or two or more to search for a code or material name

**or select one from the table below:**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ABW | ACO | AEI | AEL | AEN | AET | AFG | AFI | AFN | AFO | AFR | AFS | AFT | AFV | AFX |
| AFY | AHT | ANA | ANO | APC | APD | AST | ASV | ATN | ATO | ATS | ATT | ATV | AVE | AVL |
| AWO | AWW | BCT | BEC | BIK | BOF | BOG | BOZ | BPH | BRE | BSV | CAN | CAS | CDO | CFI |
| CGF | CGS | CHA | -CHI | -CLO | CON | CSV | CZP | DAC | DDR | DFO | DFT | DOH | DON | EAB |
| EDI | EEI | EMT | EON | EPI | ERI | ESV | ETL | ETR | ETV | EUO | EWF | EWO | EWS | -EWT |
| EZT | FAR | FAU | FER | FRA | GIS | GIU | GME | GON | GOO | HEU | -HOS | IFO | IFR | -IFT |
| -IFU | IFW | IFY | IHW | IMF | IRN | IRR | -IRT | -IRY | ISV | ITE | ITG | ITH | ITR | ITT |
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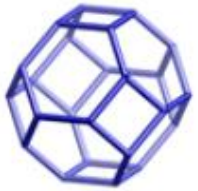

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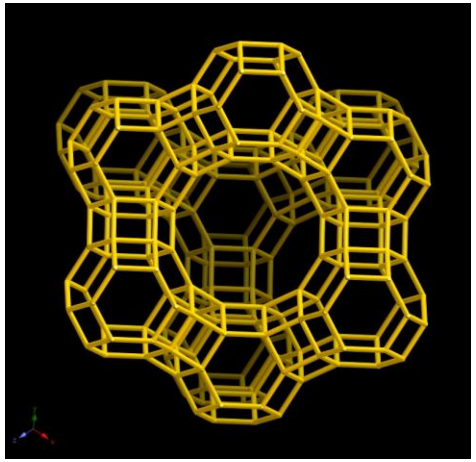
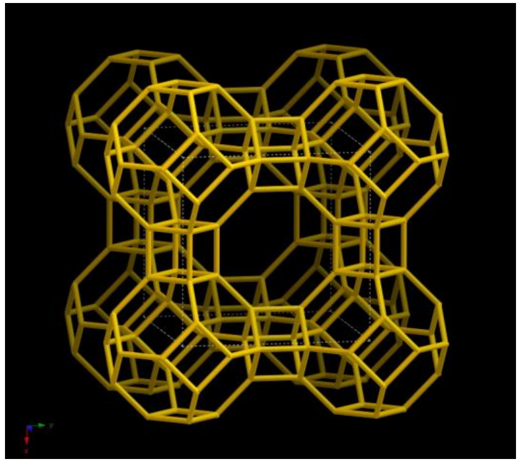


**Faujasite** type
12-ring entrance
Large-pore zeolite



**LTA** type
8-ring entrance
Small-pore zeolite

ZSM-5 (Zeolite Socony Mobile - MFI type) has a 10-ring entrance
Medium-pore zeolite

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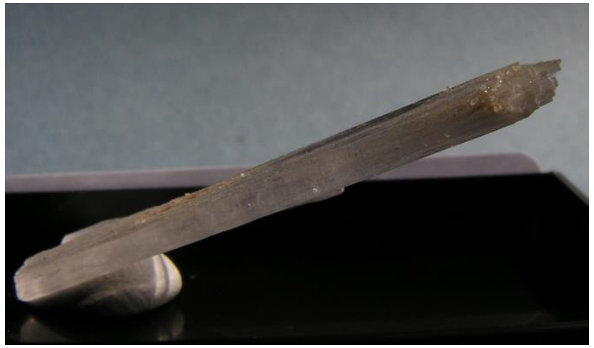
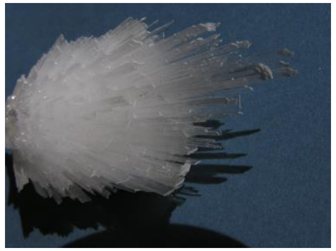
[Zeolite – Wikipedia](https://en.wikipedia.org/wiki/Zeolite) (17th April, 2023)

# Classification of zeolites

1. **Zeolites with one-dimensional channels (fiber zeolites)**
2. Zeolites with two-dimensional channel systems (lamellar zeolites)
3. Zeolites with three-dimensional channel systems (*e.g.*, cube zeolites, pentasils)

Natrolite $Na_2[Al_2Si_3O_{10}]$ . 2 $H_2O$





Skolezite

**Fiber zeolites** have a predominantly one-dimensional channel system. The most well-known examples are zeolites from the **Natrolite/Skolezite group**:

- **Edingtonite** $Ba[Al_2Si_3O_{10}] \cdot 4H_2O$, which has an almost identical structure to the synthetic **Z-F Thomsonite**
- **Thomsonite** $NaCa_2[Al_5Si_5O_{20}] \cdot 6H_2O$ also exhibits a very similar structure.

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.

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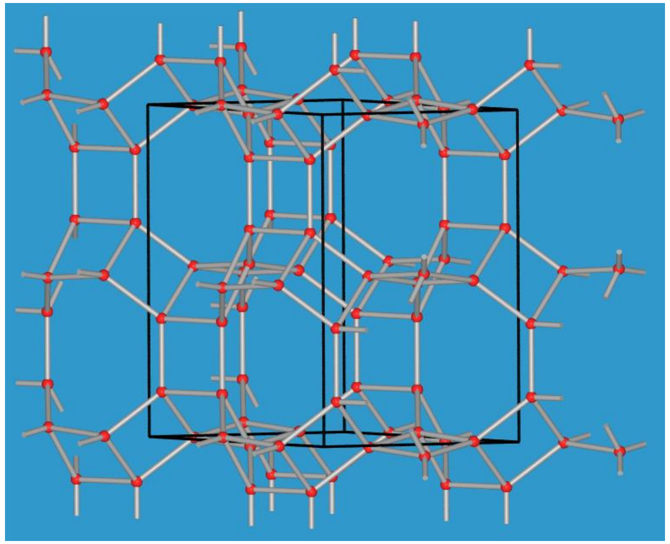
Heulandite



Phillipsite

**Lamellar zeolites** usually have a **platy habit**. The most well-known representatives are:

- **Phillipsite**: $(K,Na)_5[Si_{11}Al_5O_{32}] \cdot 10H_2O$, with tetrahedra and a pure silicon framework.
- **Heulandite**: $Ca[AlSi_3O_8] \cdot 5H_2O$.

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.

# Classification of zeolites

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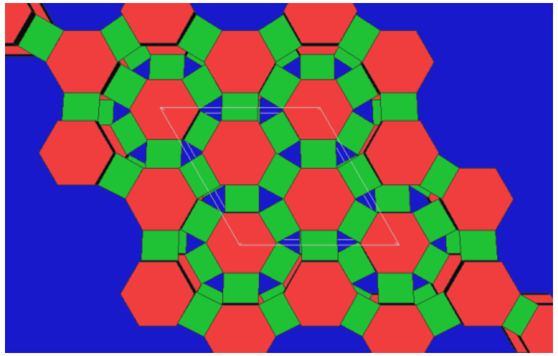
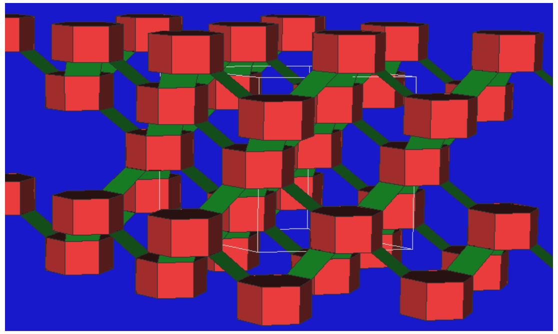
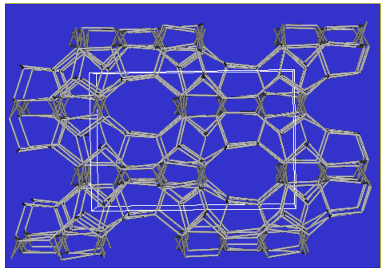
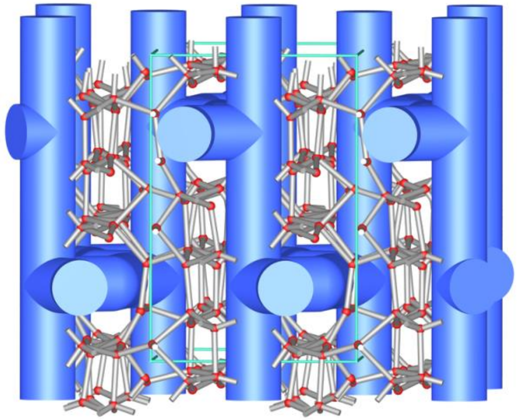
Chabasite



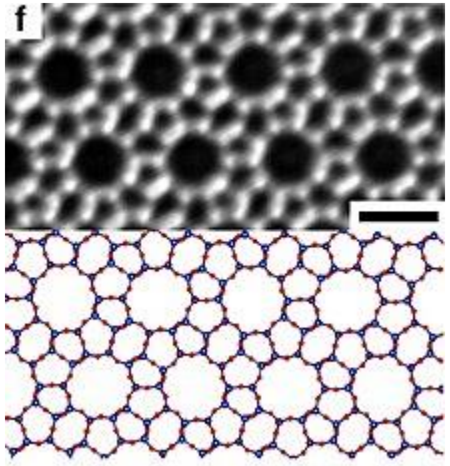




**Zeolites with 3D channels are the largest group of zeolites!**



ZSM-5

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# Synthesis and Applications

Most common synthesis strategies in industry:
- slow crystallization of silica-alumina gel in the presence of alkalis and organic templates
- Sol-gel processing

Zeolite – Wikipedia (17th April, 2023)
Insulated glazing – Wikipedia (17th April, 2023)
3476357eba0.pdf (ki-portal.de) (17th April, 2023)

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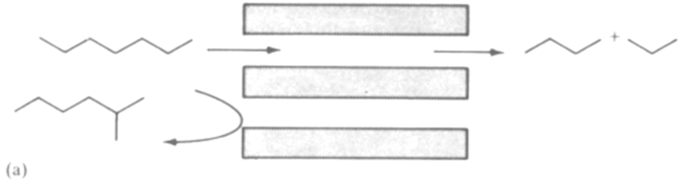
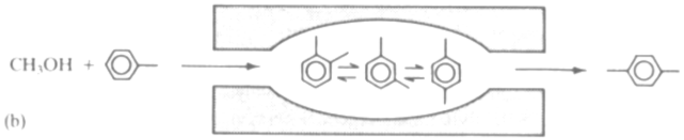
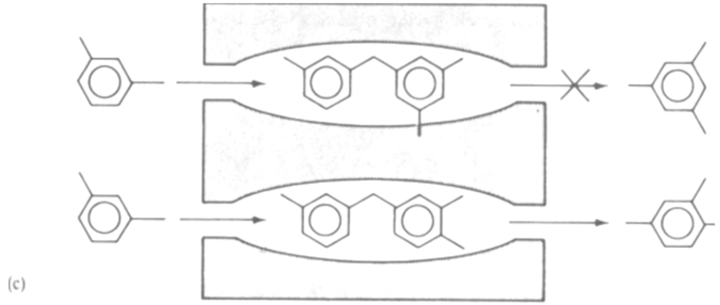
Application in organic syntheses and in catalysis




Reactand selectivity



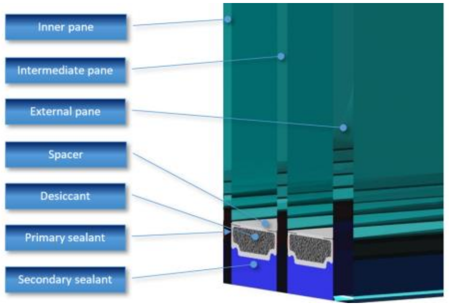

Product selectivity




Selectivity of transition states

Ion exchange in laundry&washing devices


Self-cooling beer barrel.




Drying agent for double windows.


Absorption material in cat litter.

Zeolite – Wikipedia (17th April, 2023)
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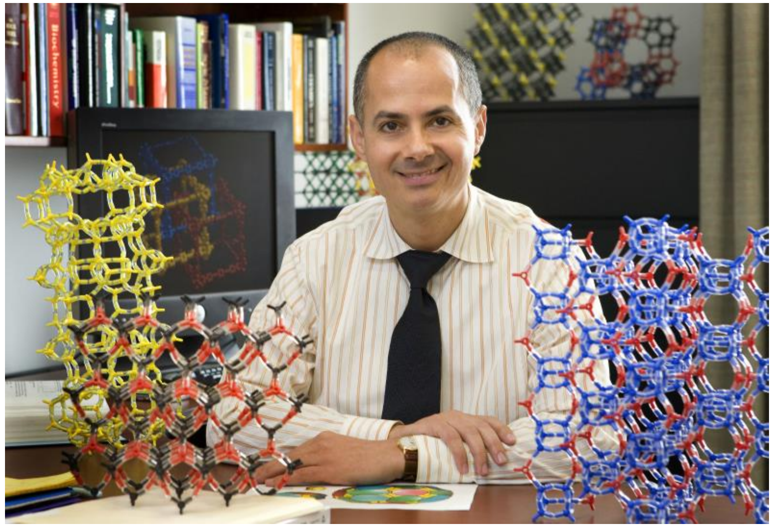
# The father of porosity – Introduction of COFs

**C**ovalent **O**rganic **F**rameworks are porous organic materials, which are ingeniously constructed with organic building blocks *via* strong **covalent** bonds.



O. M. Yaghi: First report on COF together with A. P. Côte in 2005 on a series of 2D COFs.

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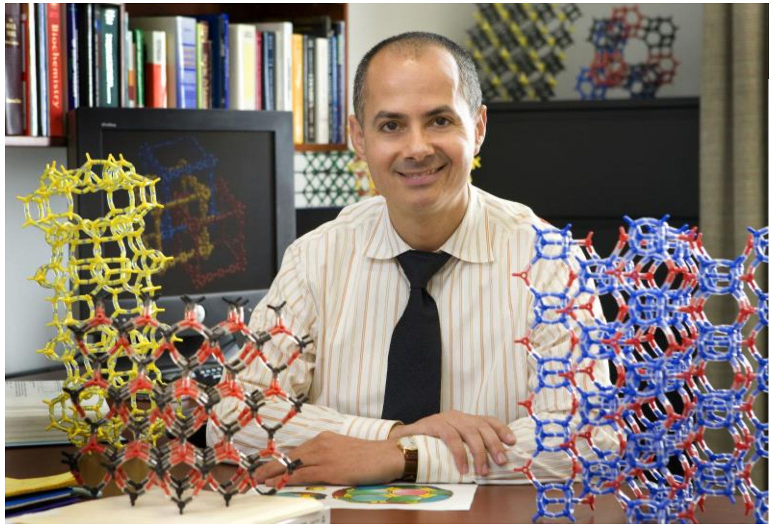

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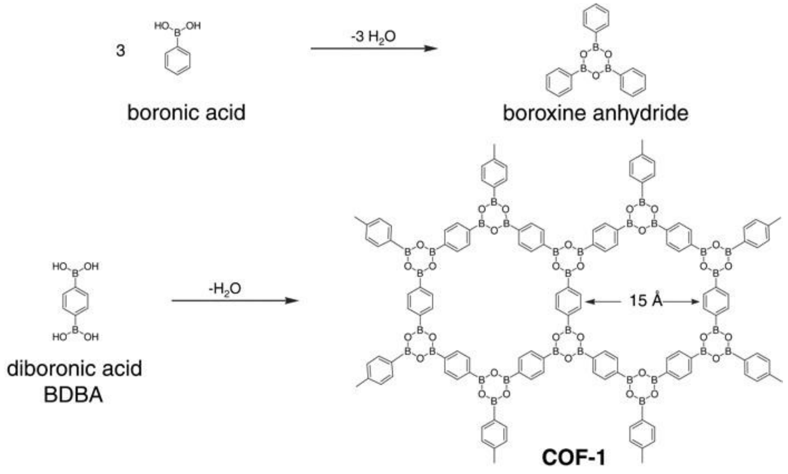


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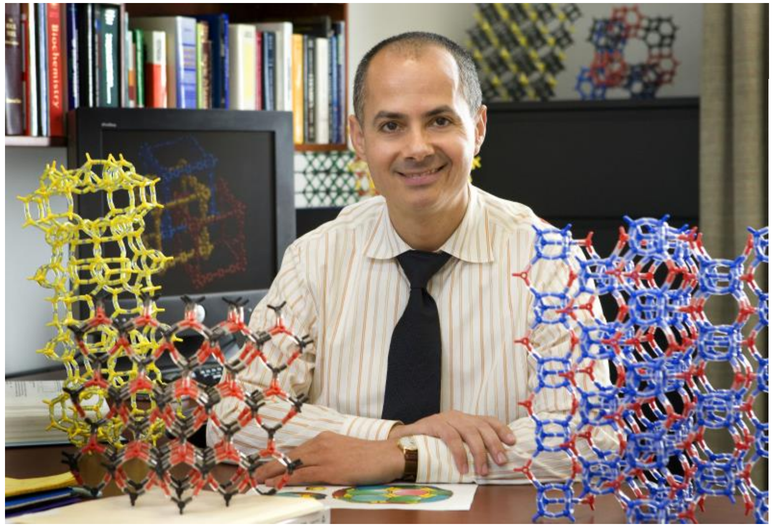

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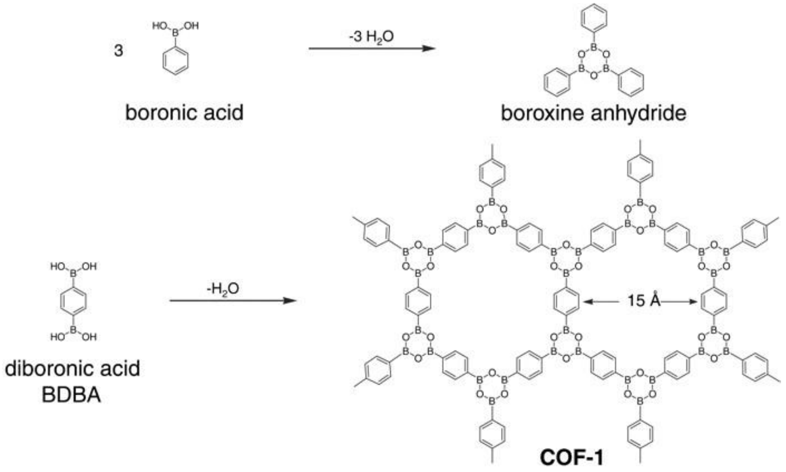


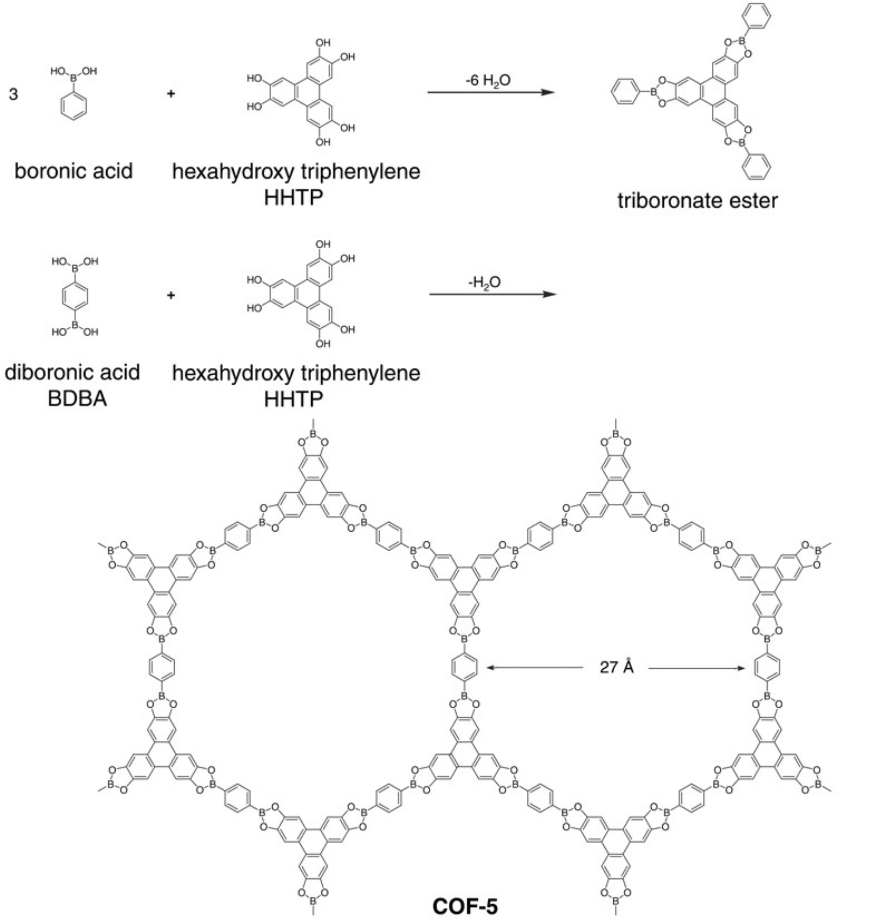


Condensation reactions of boronic acids and HHTP lead to strong covalent bonds.


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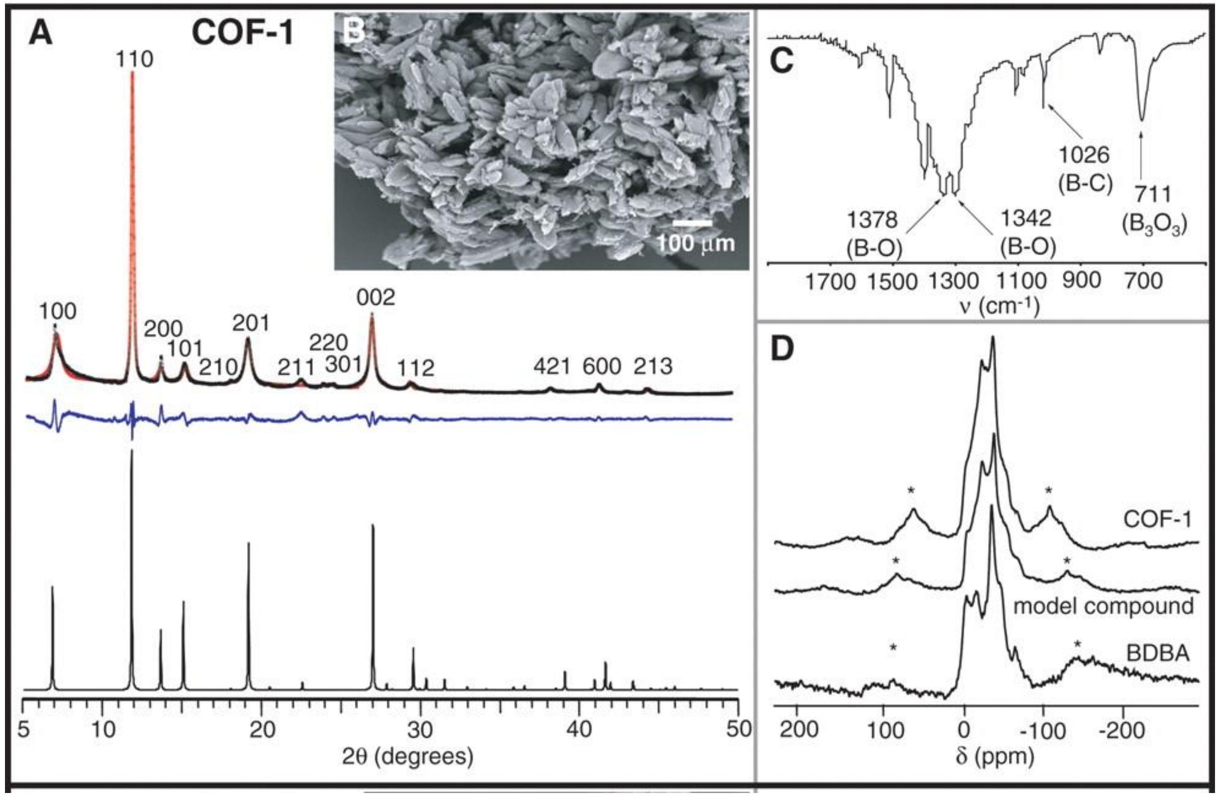
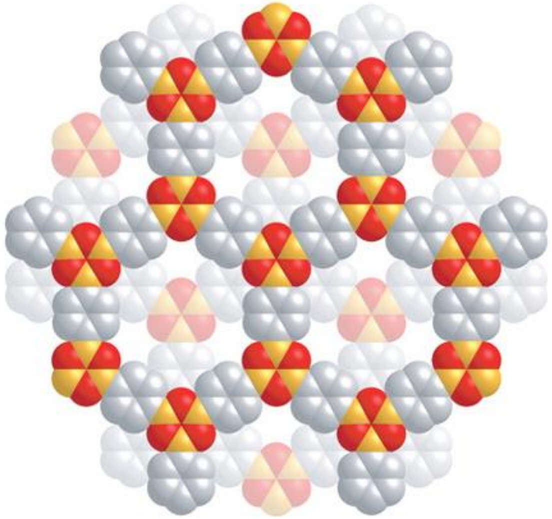
# Crystallinity of porous organic compounds



Structures of the COF-1 framework was modelled and then compared to experimental data from X-ray diffraction and NMR spectroscopy.

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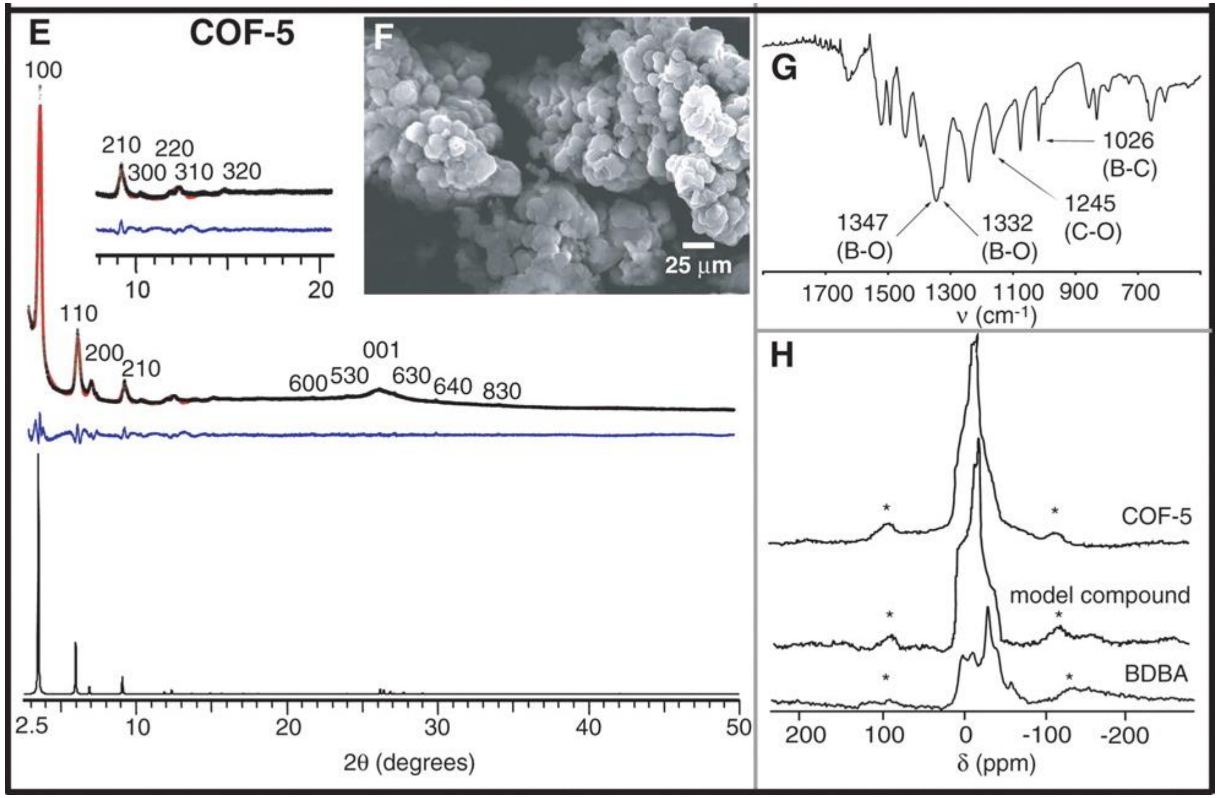


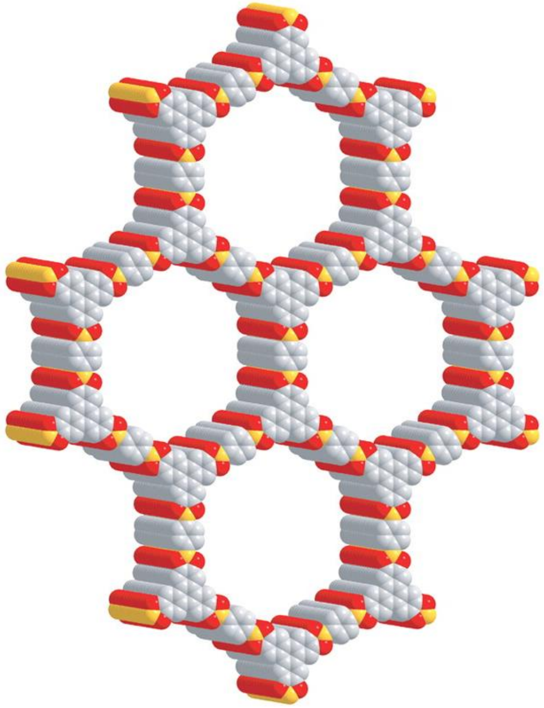

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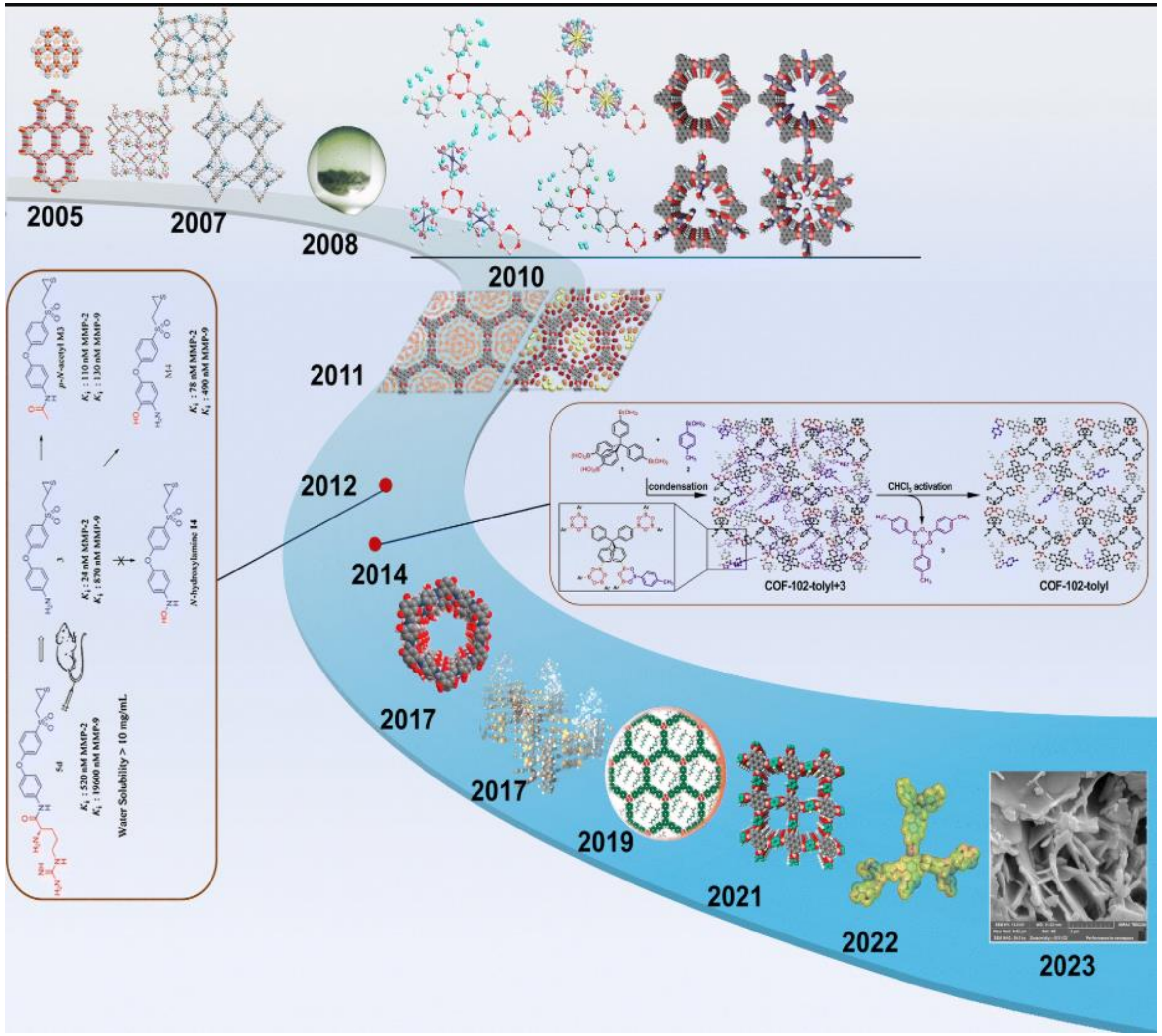
# Evolution of COFs




[A comprehensive review of covalent organic frameworks (COFs) and their derivatives in environmental pollution control - Chemical Society Reviews (RSC Publishing)]() (8th March, 2025)

# Chemical structure and configuration of COFs

Reticular synthesis: Control of topology through selection of precursors that result in characteristic bondings for the final network formation.

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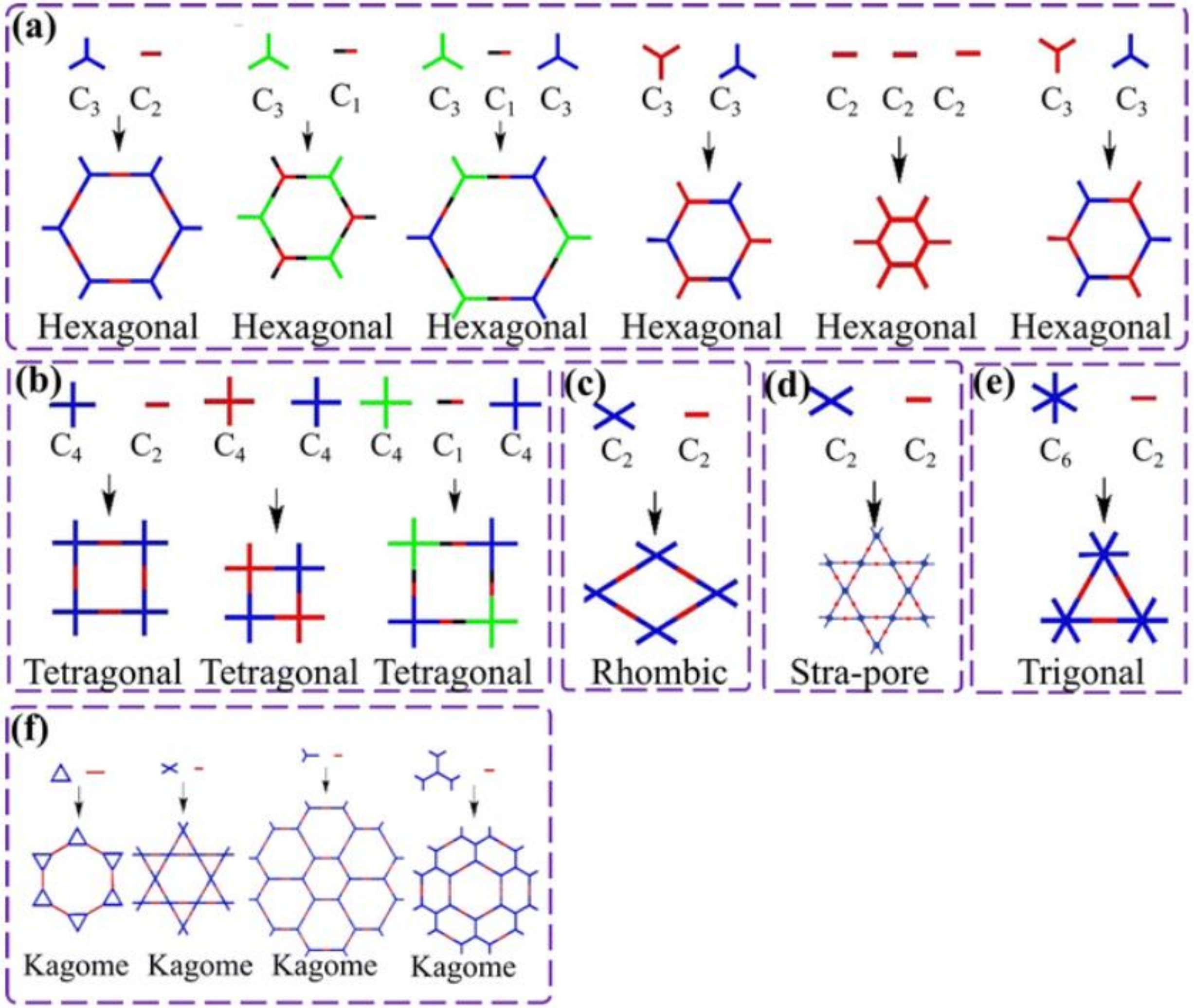


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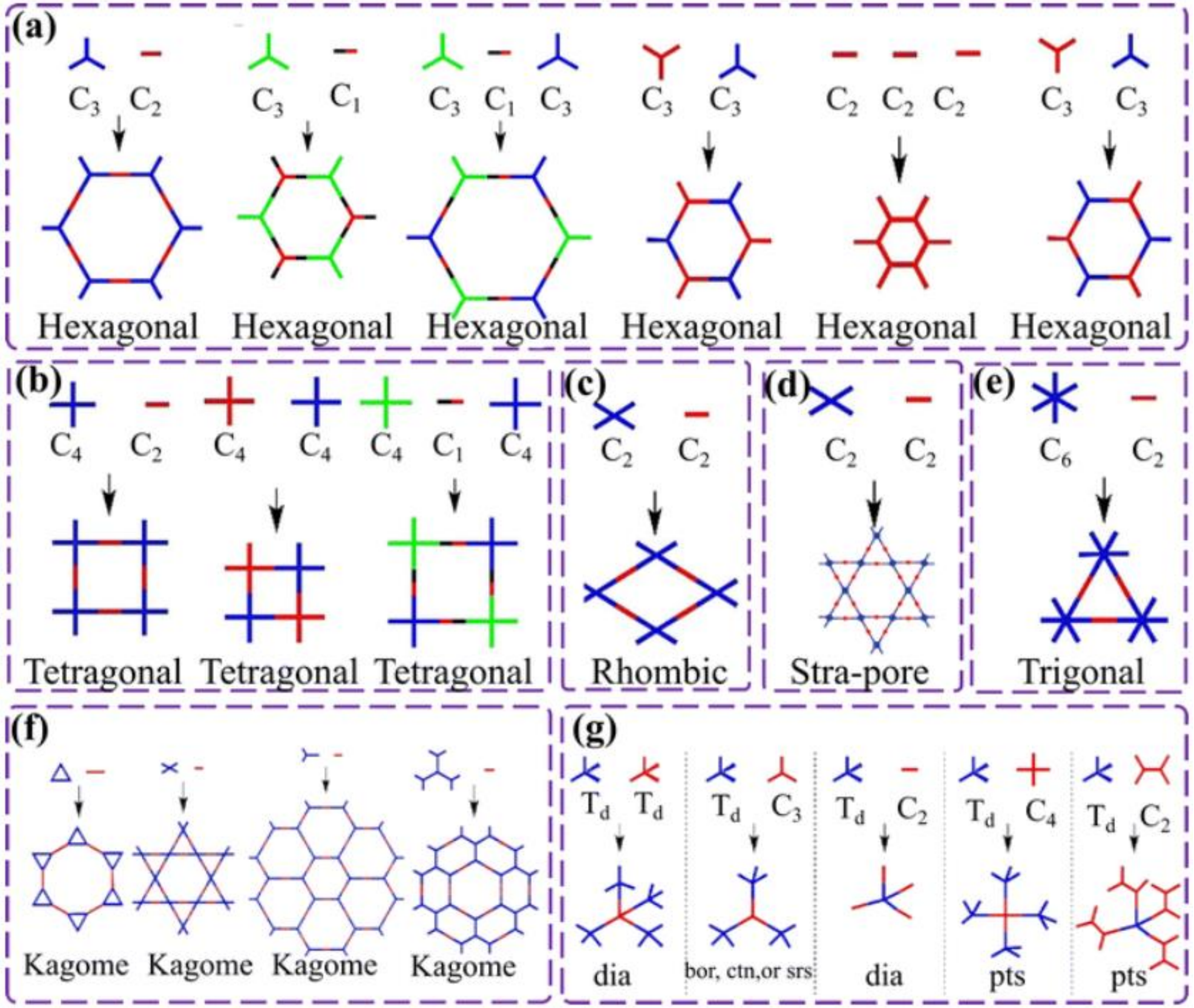


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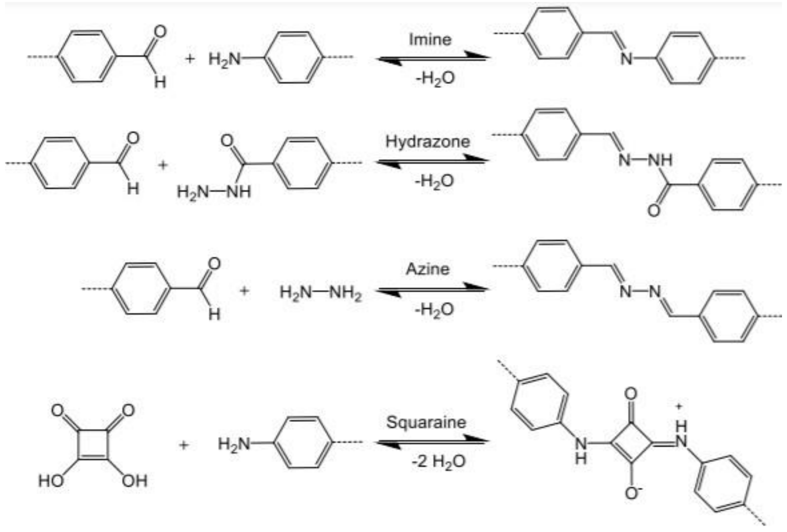
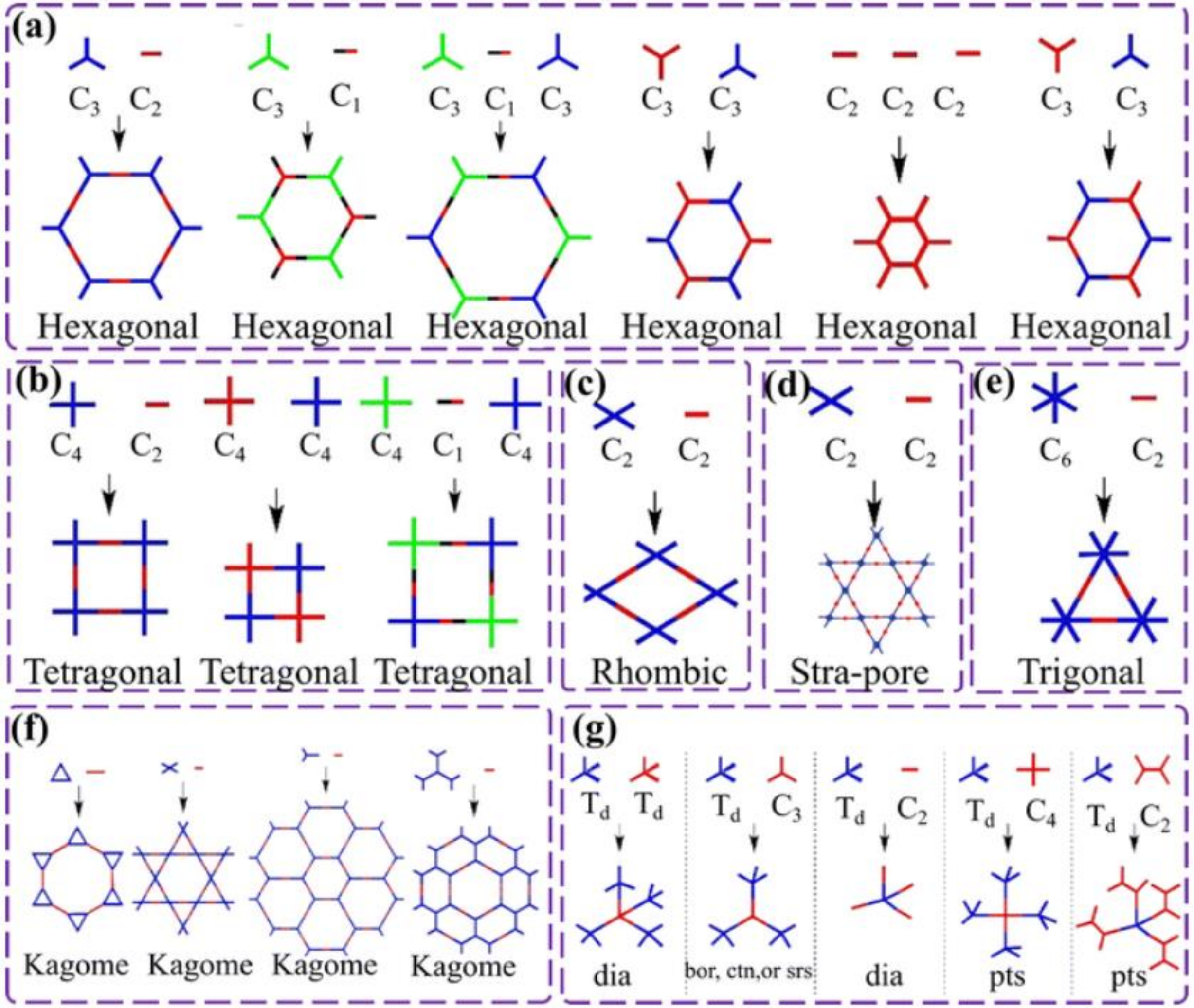



COFs can be synthesized *via* boron-, nitrogen- or other atom linkages. Mainly condensation reactions!





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# Evolution of COF synthesis

universität innsbruck

The synthesis of COFs is highly dependent on the desired application.

**Solvothermal synthesis**

- High temperature and organic solvent as reaction medium

**Microwave-assisted synthesis**

- Rapid heating of reaction mixtures using microwave energy

**Mechanochemical synthesis**

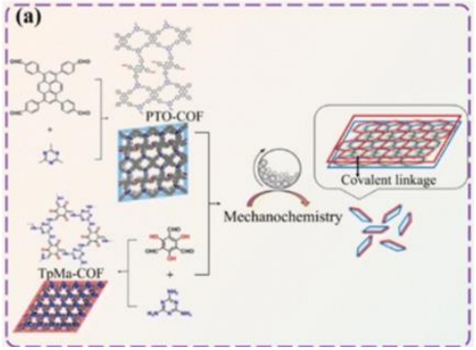
- Uses mechanical force to stimulate chemical reactions

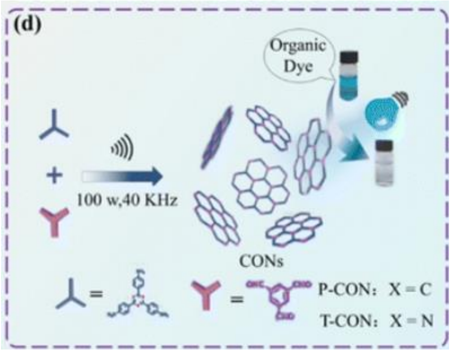
**Ultrasonic synthesis**

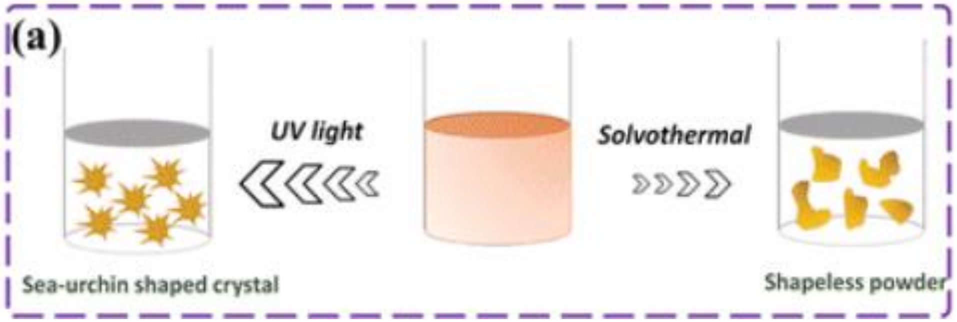
- Uses ultrasonic mechanical vibration

**Photochemical synthesis**

- Chemical reactions under light




[A comprehensive review of covalent organic frameworks (COFs) and their derivatives in environmental pollution control - Chemical Society Reviews (RSC Publishing)] (8th March, 2025)

# Evolution of COF synthesis

The synthesis of COFs is highly dependent on the desired application.

**Room temperature synthesis**

- chemical reactions at relatively low temperatures

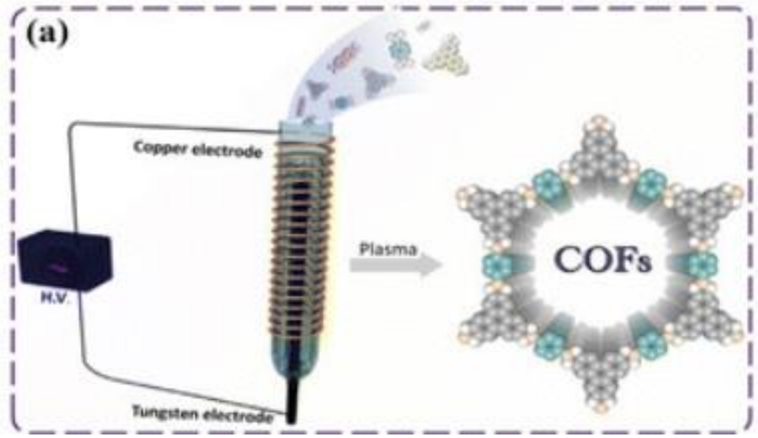
**Plasma-assisted synthesis**

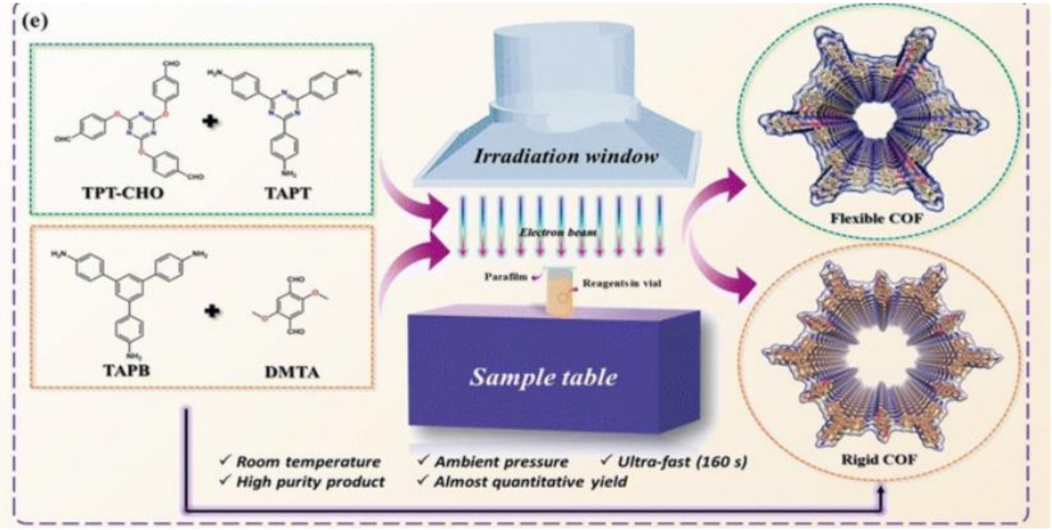
- using high-voltage plasma discharge

**Electric field-mediated synthesis**

- uses external electric fields to promote chemical reactions

Note: Every method has its advantages and disadvantages, ranging from yield, speed of reaction, energy consumption etc.!

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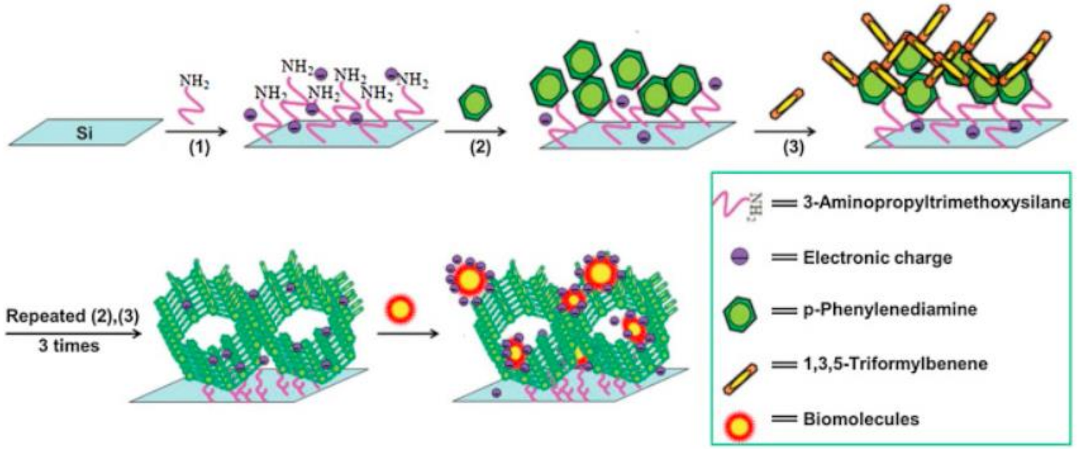
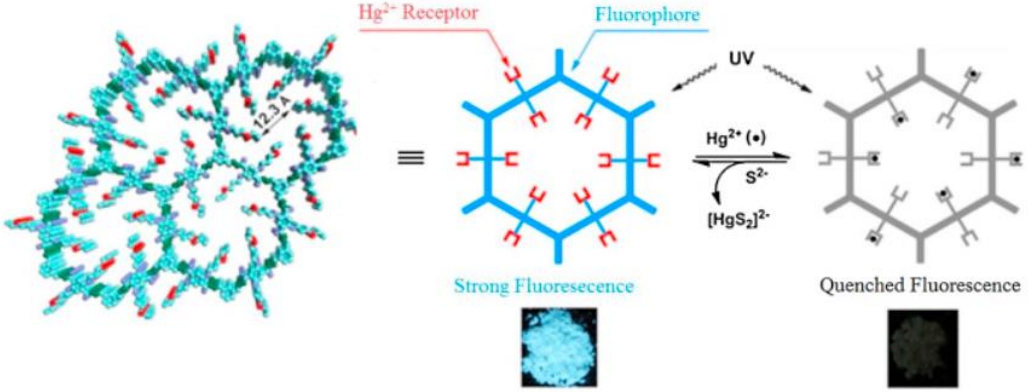
# Properties and Applications

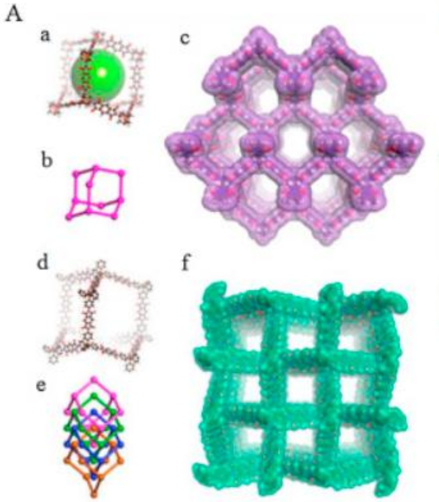
Due to their high structural versatility and therewith varying properties, COFs find use in various applications.

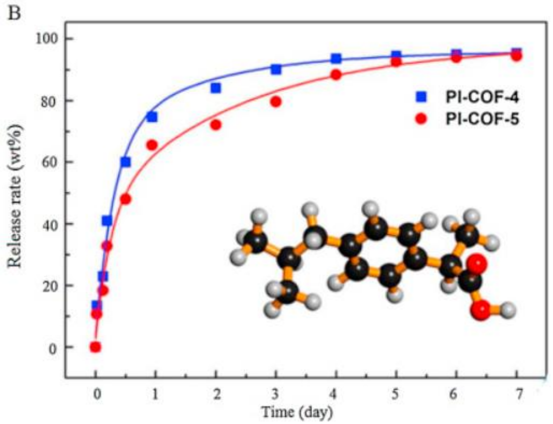



- Gas storage and separation
- Catalysis
- Semiconduction and photoconduction

- Energy storage
- Sensing
- Small molecule adsorption
- Drug delivery
- …




[Applications of covalent organic frameworks (COFs): From gas storage and separation to drug delivery – ScienceDirect](#) (9th March, 2025)

# Questions?