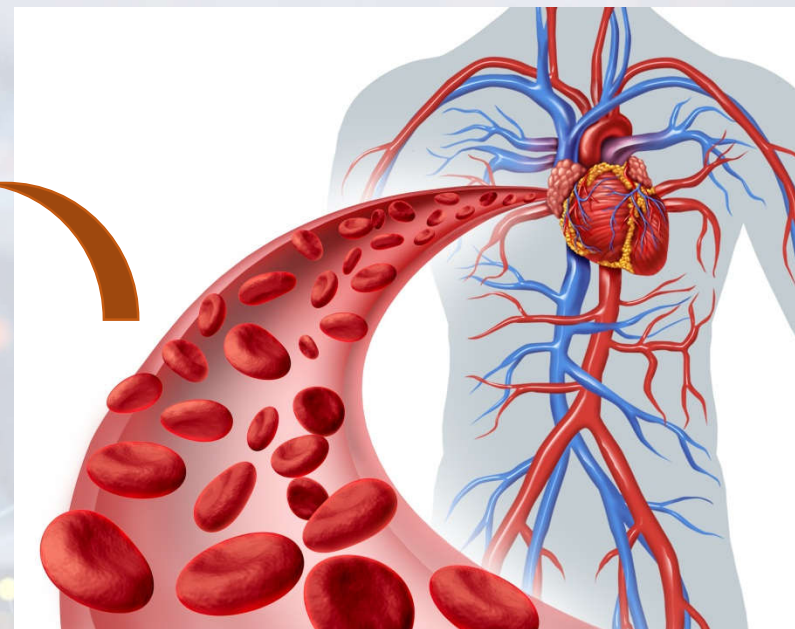




Supramolecular Chemistry



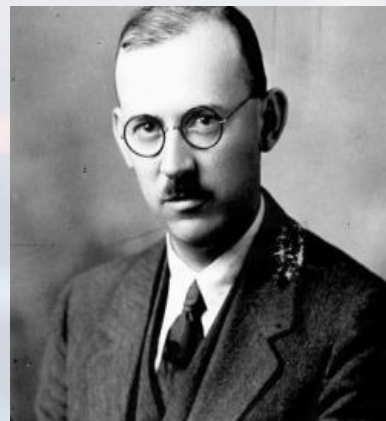
Beginning of Supramolecular Chemistry:



Van der Waals



H. E. Fischer



W. M. Latimer



W. H. Rodebush

The existence of intermolecular forces was first postulated by van der Waals in 1873. However, Nobel laureate H. E. Fischer developed supramolecular chemistry's philosophical roots. In 1894, Fischer suggested that enzyme–substrate interactions take the form of a "lock and key". In the early twentieth century non-covalent bonds were understood in gradually more detail, with the hydrogen bond being described by Latimer and Rodebush in 1920.



D. J. Cram



L. M. Lehn



C. J. Pedersen



F. Vögtle

The research developed by **Cram, Lehn and Pedersen** at the end of 1960s and beginning of 1970s established for the development of supramolecular chemistry as a recognized discipline. They were awarded **Nobel prize in Chemistry** in 1986 for their work in this realm.



J. F. Stoddart



I. Willner

In the 1990s J. F. Stoddart developed molecular machinery and highly complex self-assembled structures, and I. Willner developed sensors and methods of electronic and biological interfacing.

What is Supramolecular Chemistry?

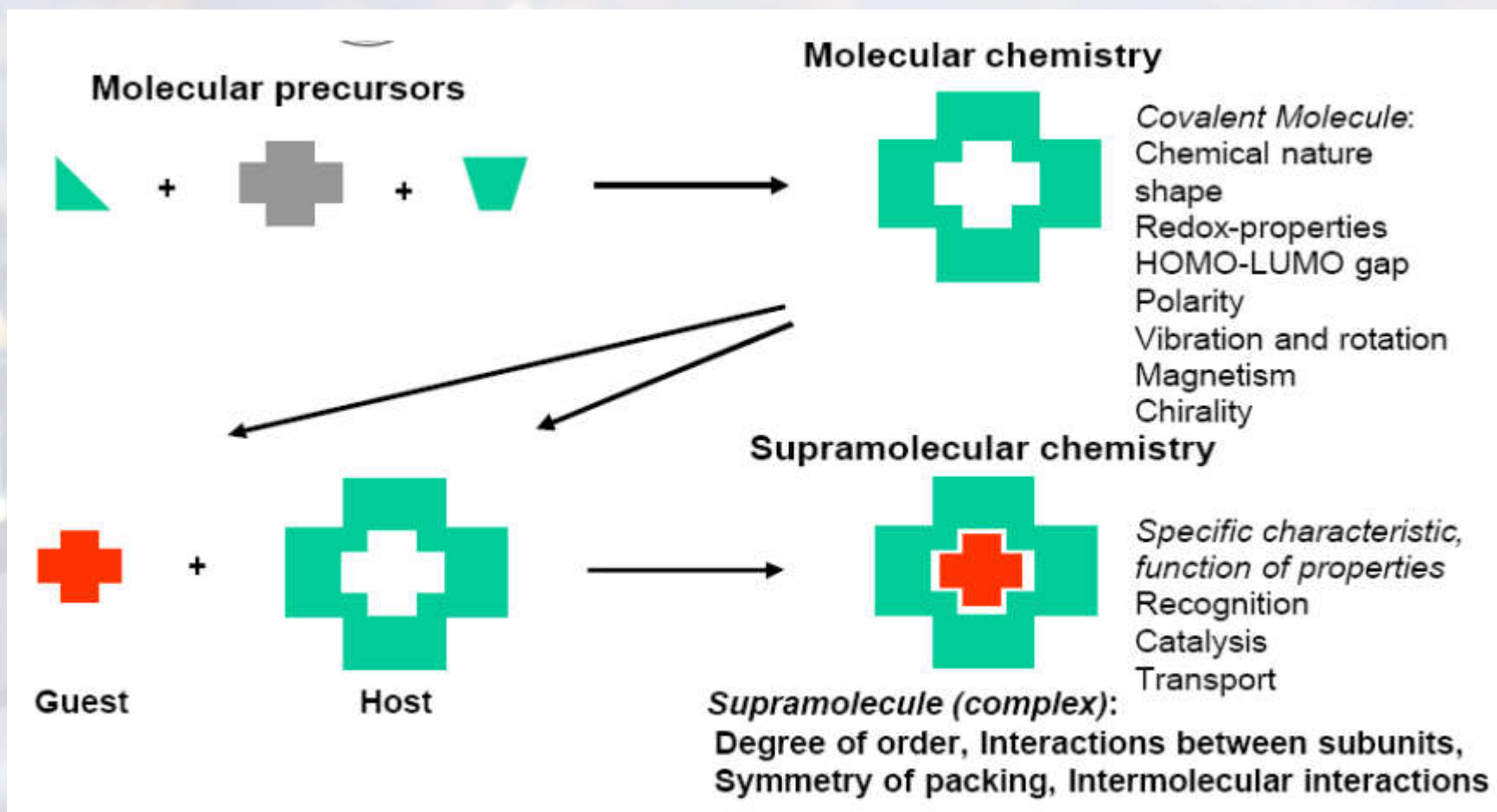
“Chemistry beyond the molecule”

“Chemistry of molecular assemblies and of the intermolecular bond.”

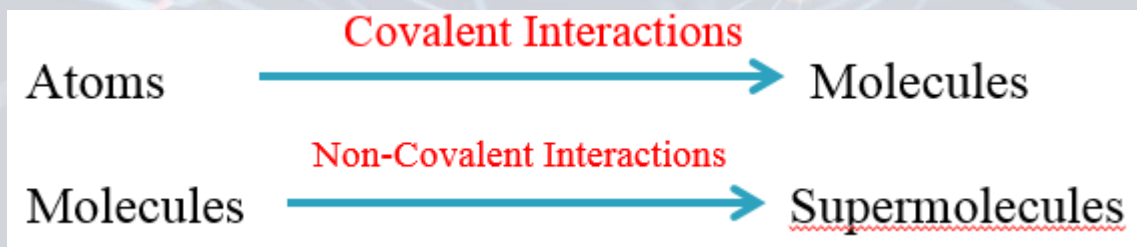
“The Chemistry of non-covalent bond.”

What is Supramolecular Chemistry?

- ❖ MOLECULAR CHEMISTRY – covalent bonds formation
- ❖ SUPRAMOLECULAR CHEMISTRY – “non-covalent bond” formation

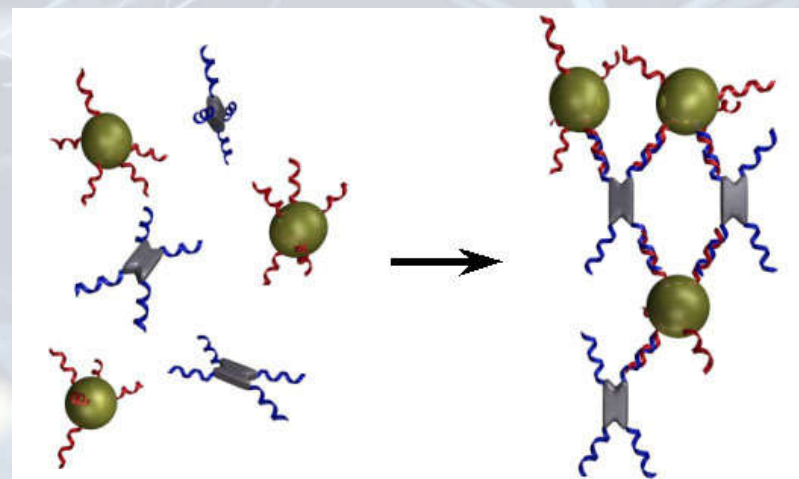
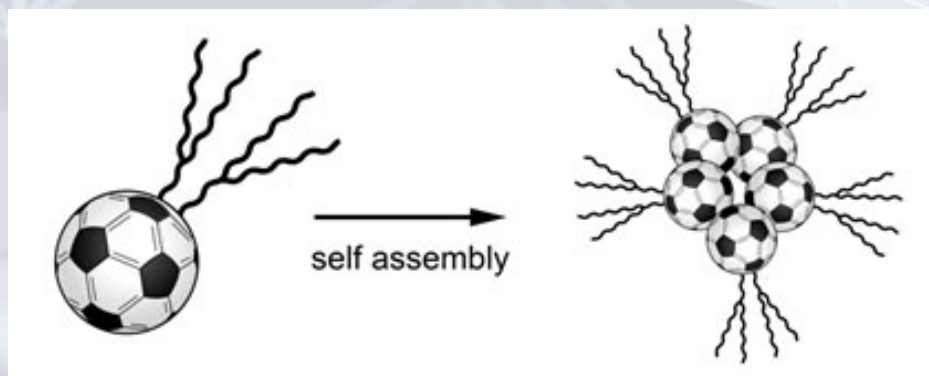


Supramolecular chemistry involves investigating molecular systems in which the most important feature is that components are held together by intermolecular forces, not by covalent bonds.



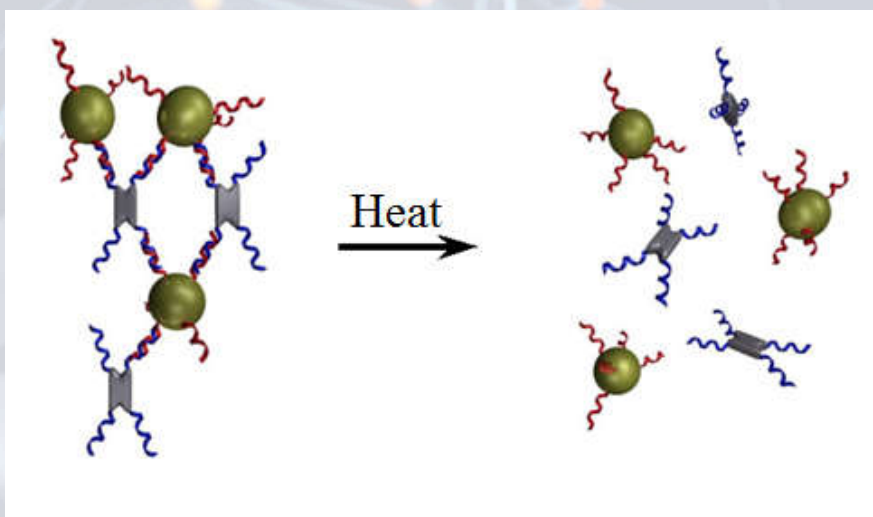
Molecular Self Assembly:

Molecular self-assembly is the construction of systems having many molecules by a non-covalent intermolecular interactions to form a large aggregate or supramolecule. The molecules are directed to assemble through noncovalent interactions. Molecular self-assembly also allows the construction of larger structures such as micelles, membranes, vesicles, and is important to crystal engineering.



Stability of Molecular Assembly:

Supramolecular chemistry deals with subtle interaction in the molecules. In particular, noncovalent bonds have low energies and often no activation energy for formation. Unlike in covalent bonding, the rate of bond formation is not increased at higher temperatures. In fact, chemical equilibrium equations show that the low bond energy results in a shift towards the breaking of supramolecular complexes at higher temperatures.

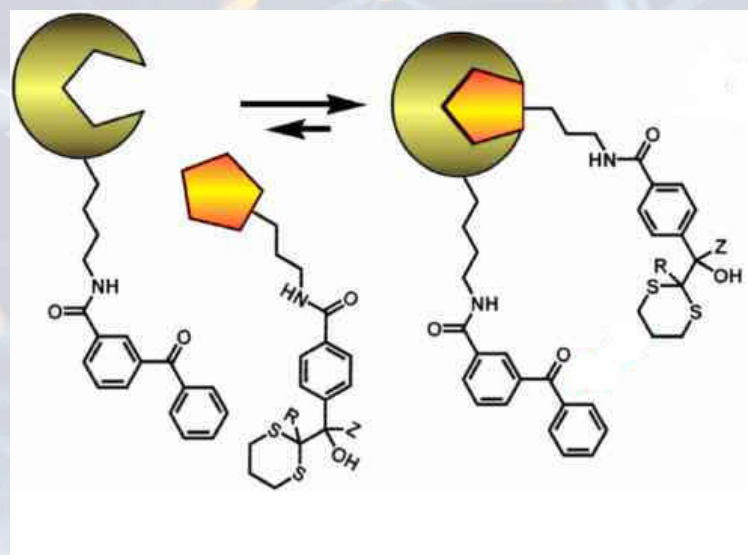


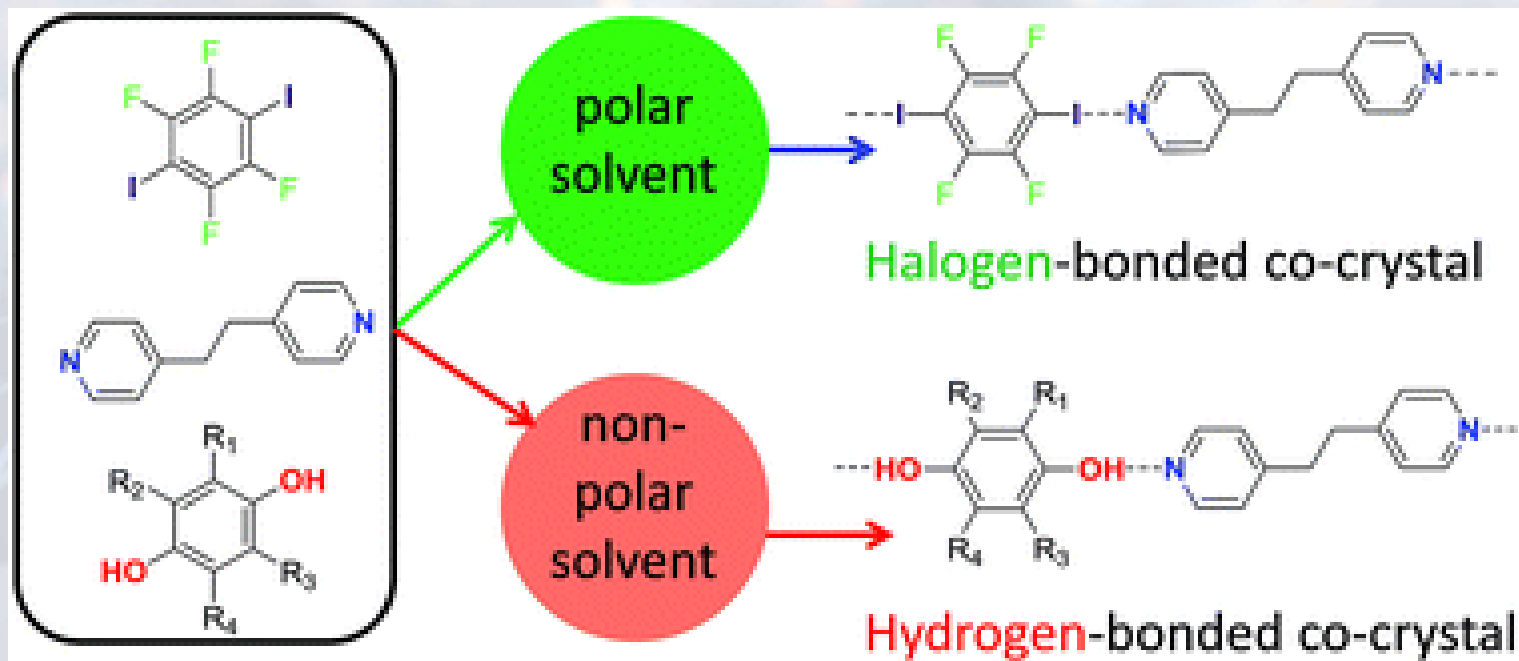
The thermal instability of a molecular assembly may be explained in terms of thermodynamics. The Free energy change for the formation of an aggregate is ...

$$\Delta G = \Delta H - T\Delta S$$

Molecular Recognition:

Molecular recognition is the specific binding of a guest molecule to a complementary host molecule through non-covalent interactions to form a host-guest complex. The interactions may be hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, π - π interactions, halogen bonding, electrostatic force etc.



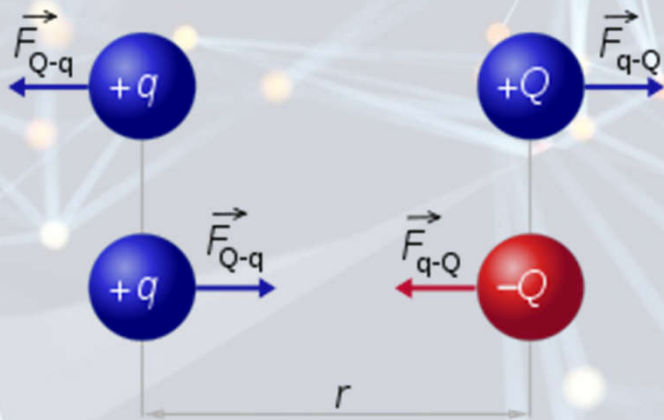


Supramolecular Interactions:

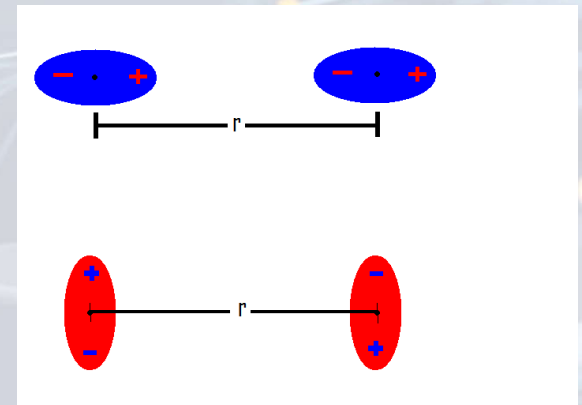
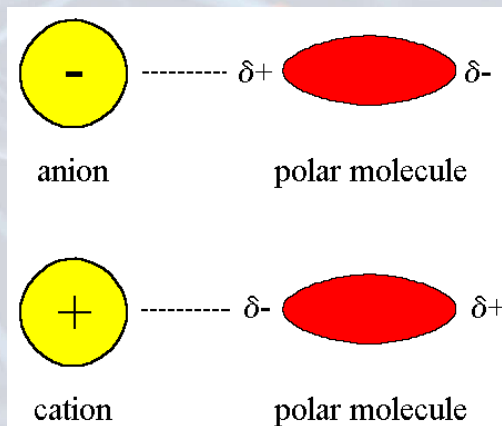
- ❖ **Electrostatic (Ion-ion, Ion-dipole and Dipole-dipole);**
- ❖ **Hydrogen bonding;**
- ❖ **π - π Stacking interaction;**
- ❖ **Cation- π interaction;**
- ❖ **Van der Waals Force;**
- ❖ **Hydrophobic Effect;**
- ❖ **Coordinate bonding;**

Electrostatic Interactions:

The attractive or repulsive interaction between objects having electric charges is called electrostatic interactions. The charges may be discrete or partial in the different parts of the same molecule.

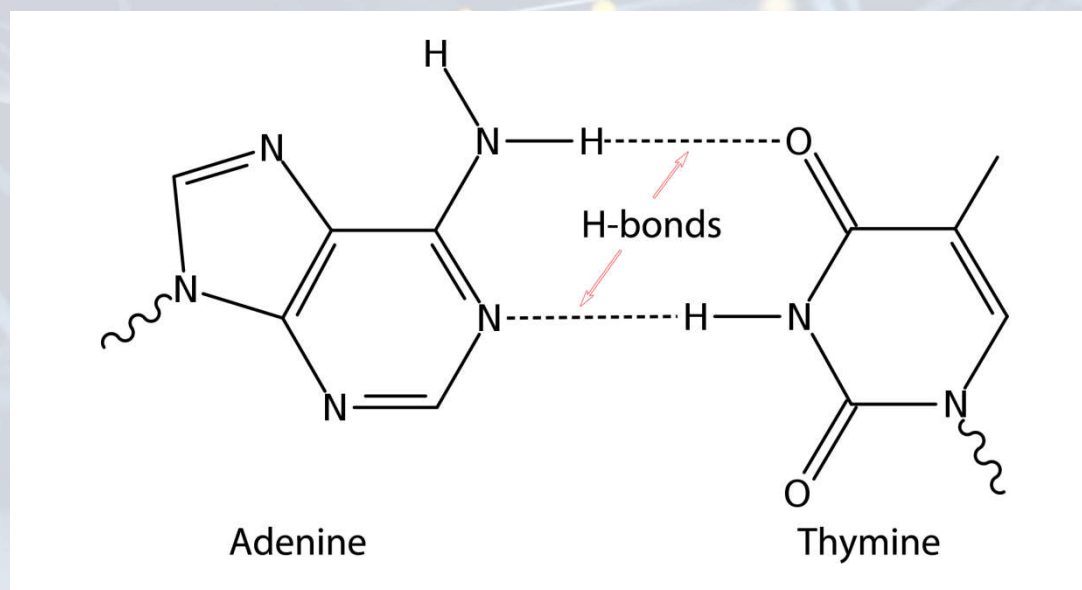
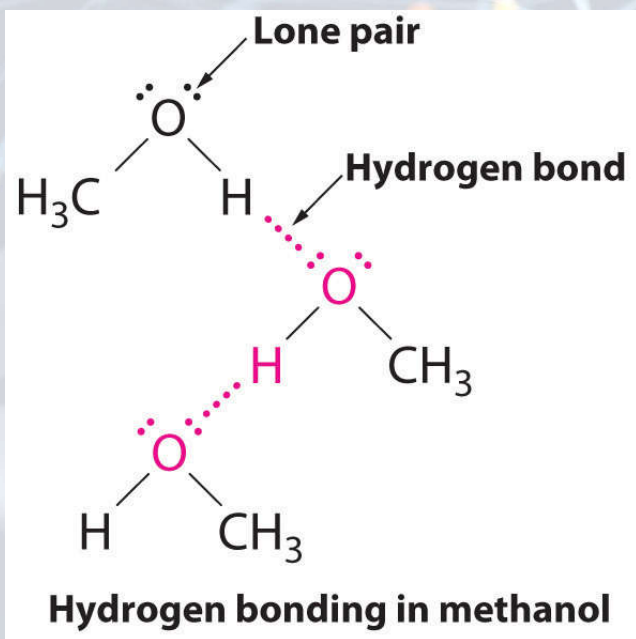


$$|\vec{F}_{Q-q}| = |\vec{F}_{q-Q}| = k \frac{|q \times Q|}{r^2}$$



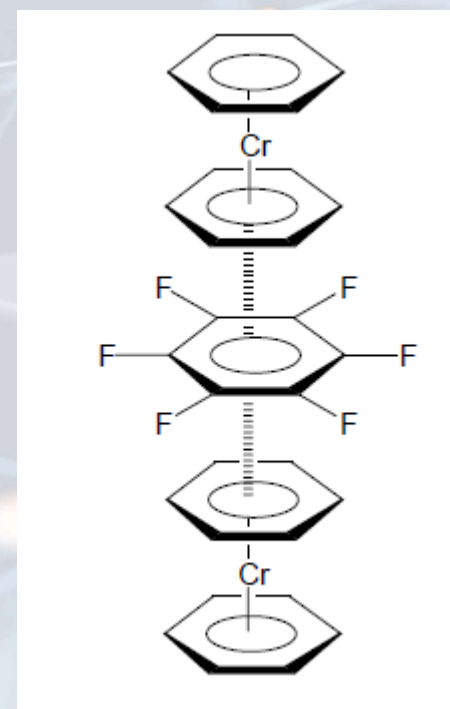
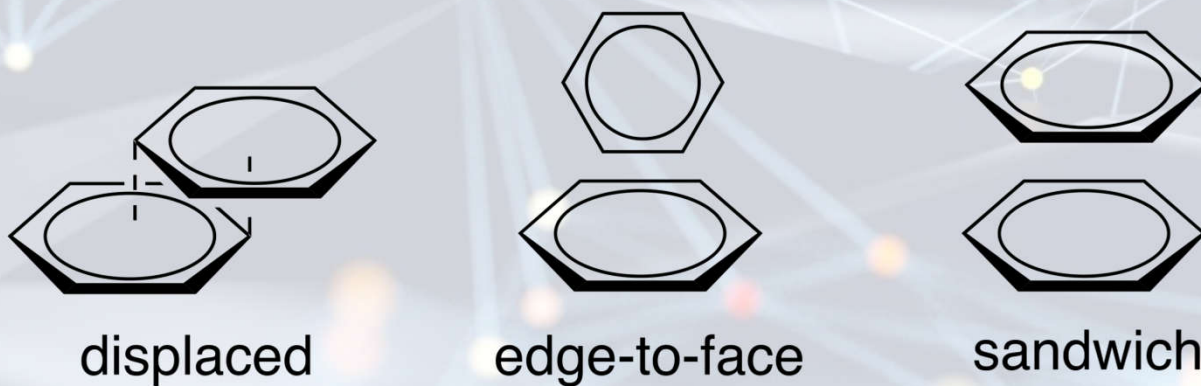
Hydrogen Bonding:

A **hydrogen bond** is the electrostatic attraction between two polar groups that occurs when a hydrogen (H) atom covalently bound to a highly electronegative atom such as nitrogen (N), oxygen (O), or fluorine (F) experiences the electrostatic field of another highly electronegative atom nearby.



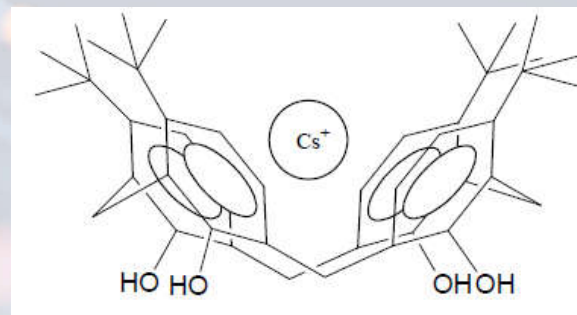
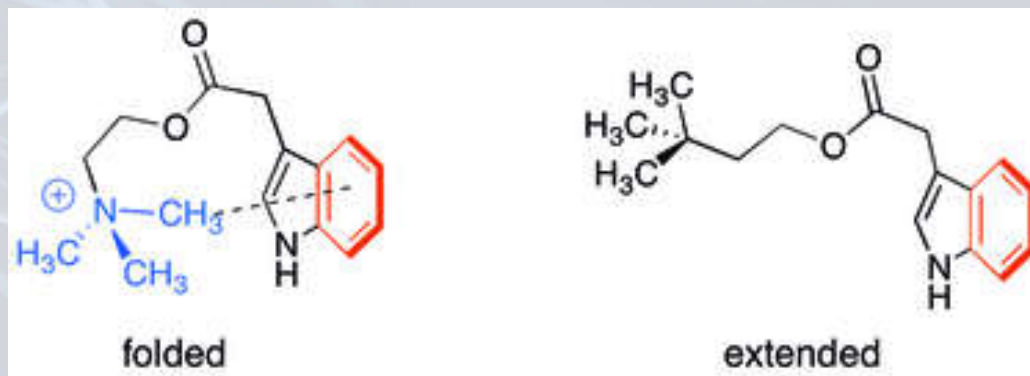
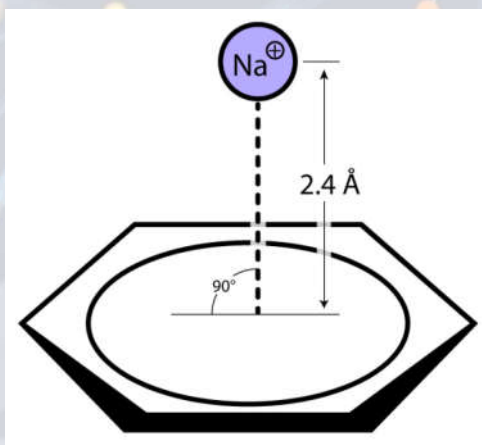
π — π Stacking Interaction:

π -Stacking or π - π stacking refers to attractive, non-covalent interactions between two layers of delocalized pi electrons specially in aromatic rings. These interactions are important in nucleobase stacking within DNA and RNA molecules, protein folding, template-directed synthesis, materials science and molecular recognition.



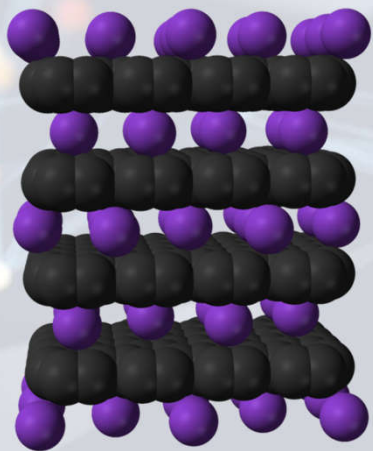
Cation— π Stacking Interaction:

Cation— π interaction is a non-covalent molecular interaction between the face of an electron-rich π system (e.g. benzene, ethylene, acetylene) and an adjacent cations (e.g. Li^+ , Na^+).



Intercalation:

Intercalation is the reversible inclusion or insertion of a molecule (or ion) into materials with layered structures. Examples are found in graphite and transition metal dichalcogenides.



K intercalated in Graphite

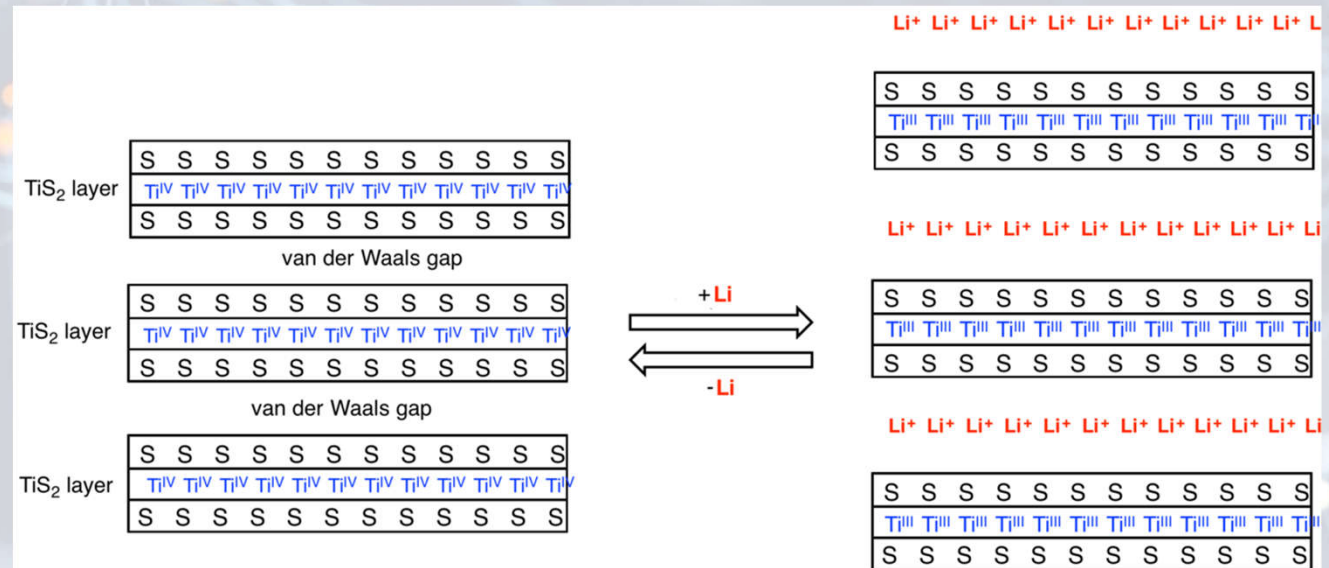
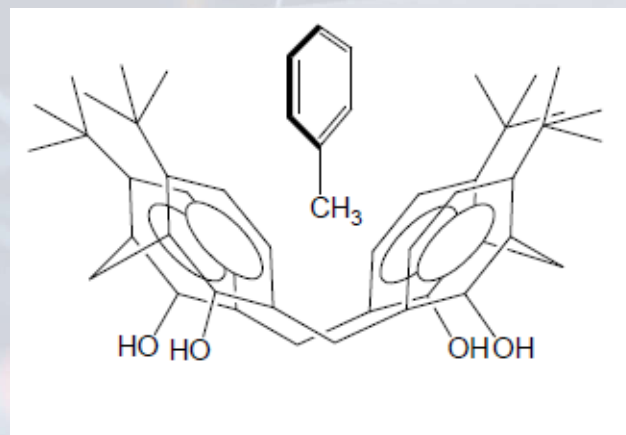
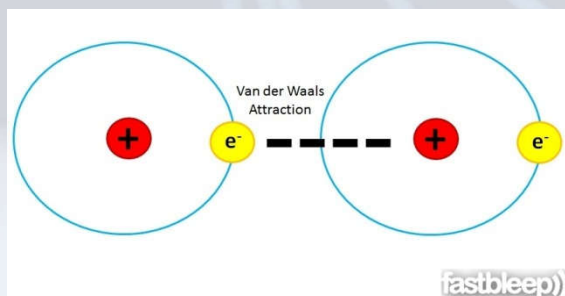
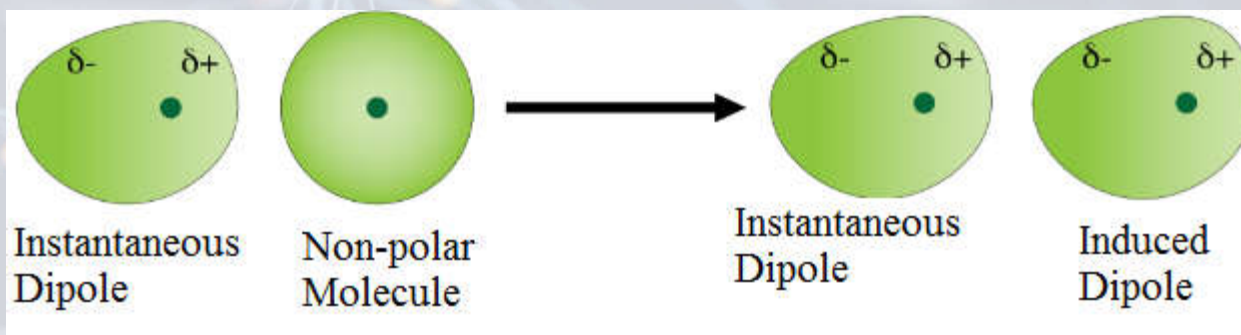


Diagram of intercalation of Li into a titanium disulfide cathode. One axis of the TiS₂ crystal swells, and charge transfers from Li to Ti.

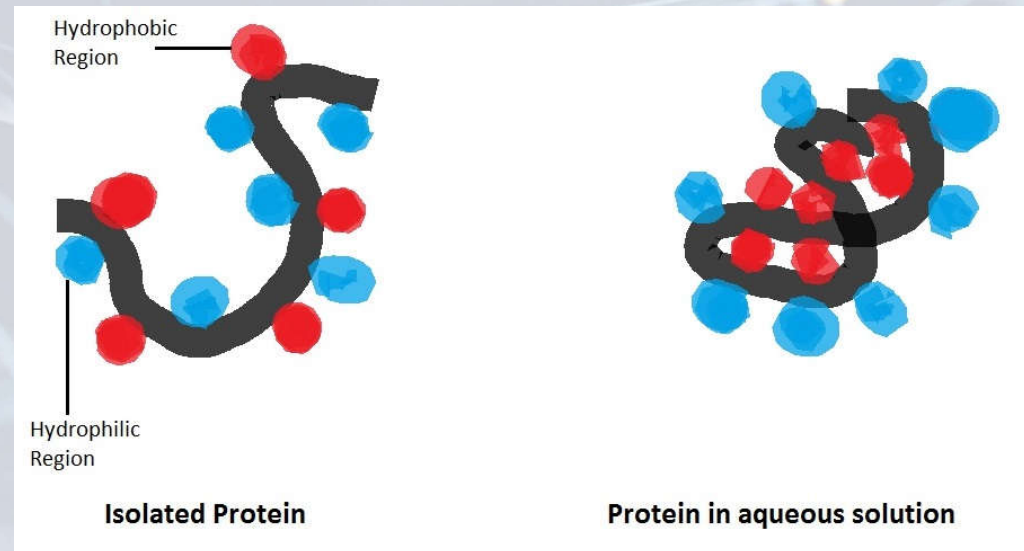
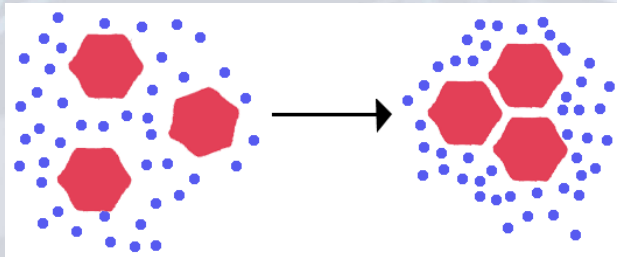
Van der Waal Force:

Van der Waals force is a weak attractive intermolecular force which is observed in non-polar compounds due to the polarisation of the electron cloud by the proximity of the adjacent nucleus.

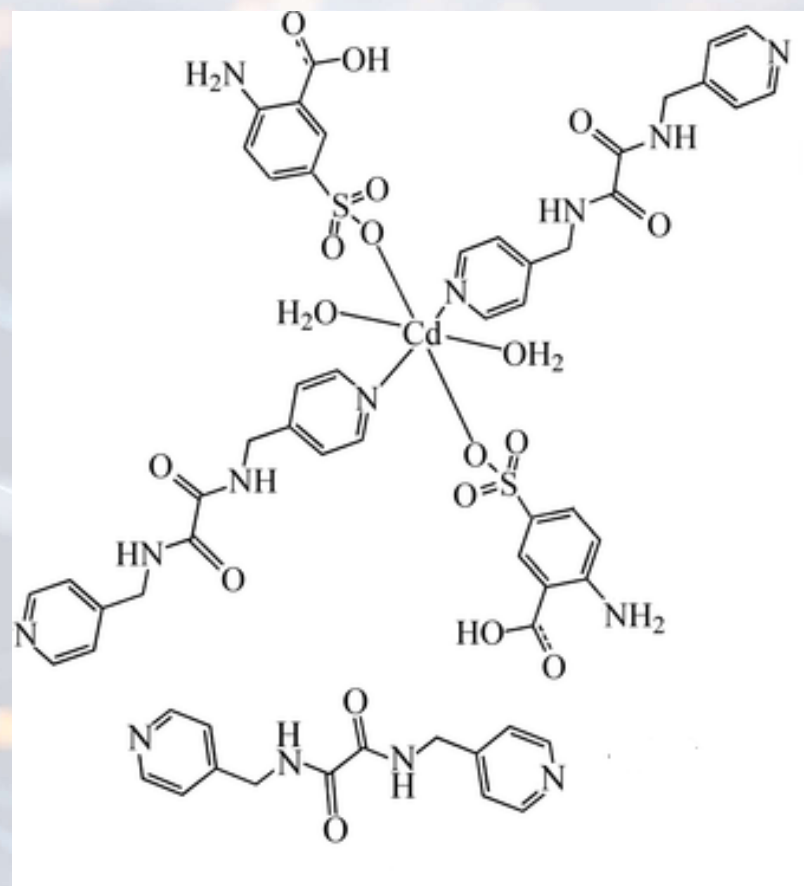
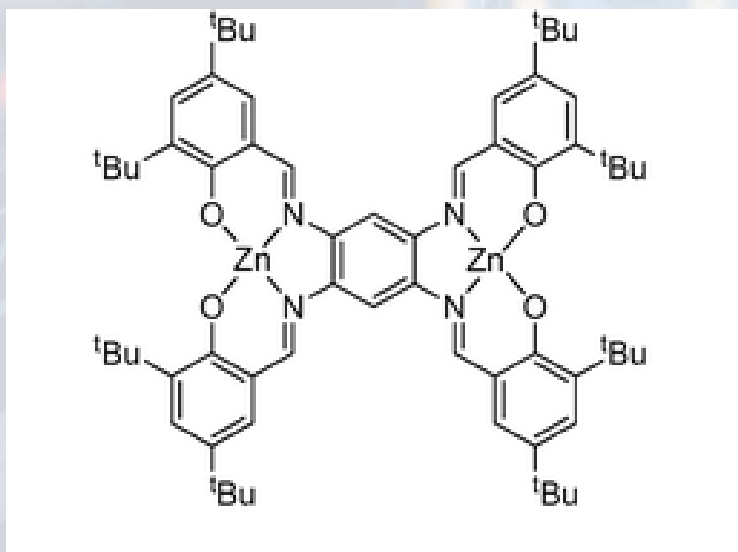


Hydrophobic Effect:

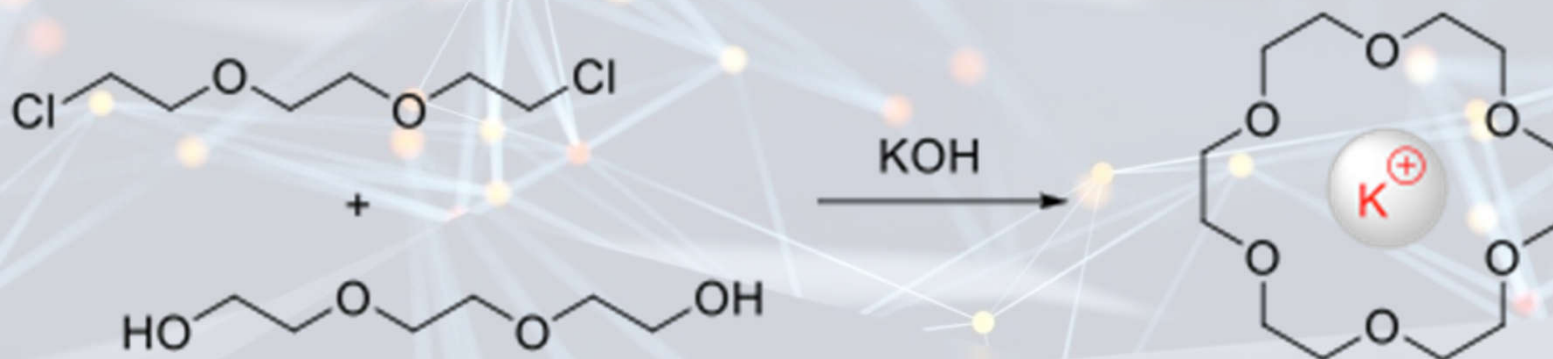
The **hydrophobic effect** is the desire for non-polar molecules to aggregate in aqueous solutions in order to separate from water. This phenomenon leads to minimum exposed surface area of non-polar molecules to the polar water molecules.



Coordinate bonding:

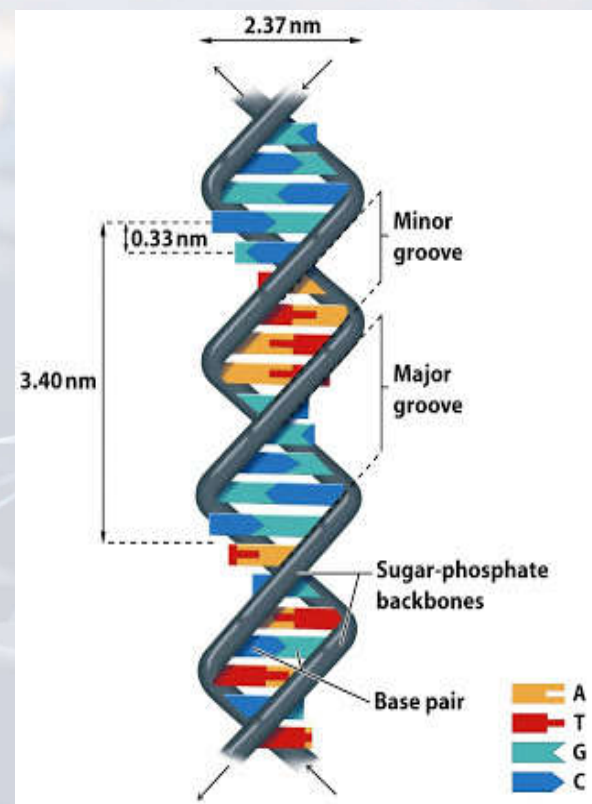
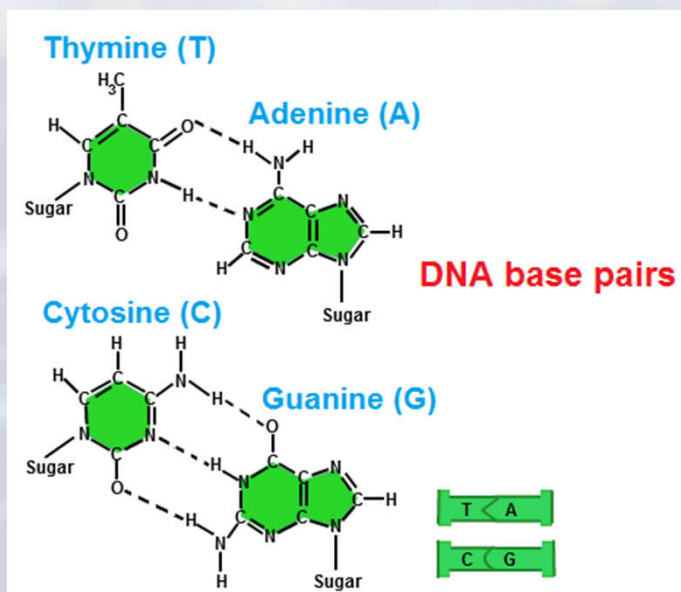


18-Crown-6 can be synthesized by the **Williamson ether synthesis** using potassium ion as the template cation.

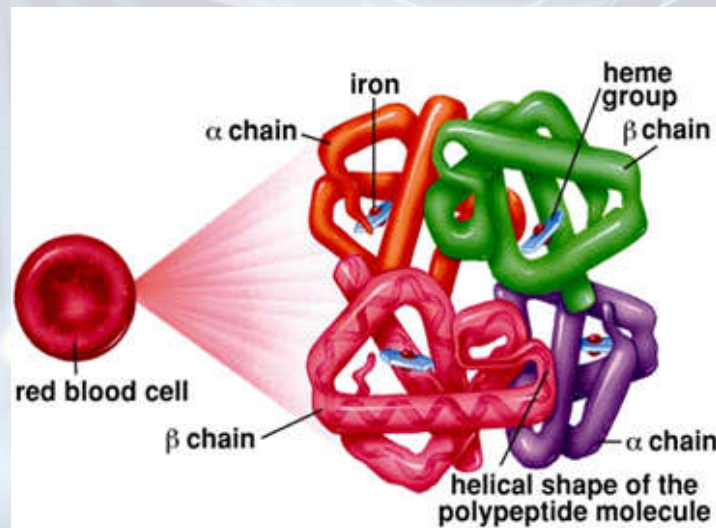
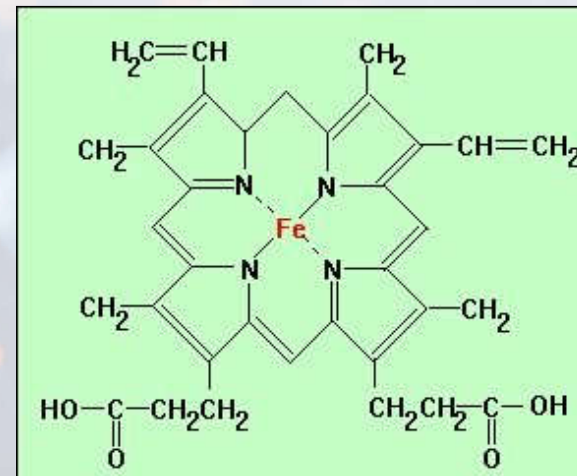
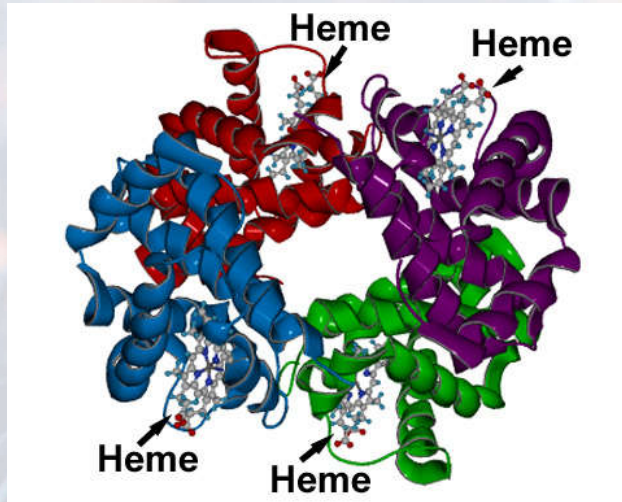


Supramolecular: Biology:

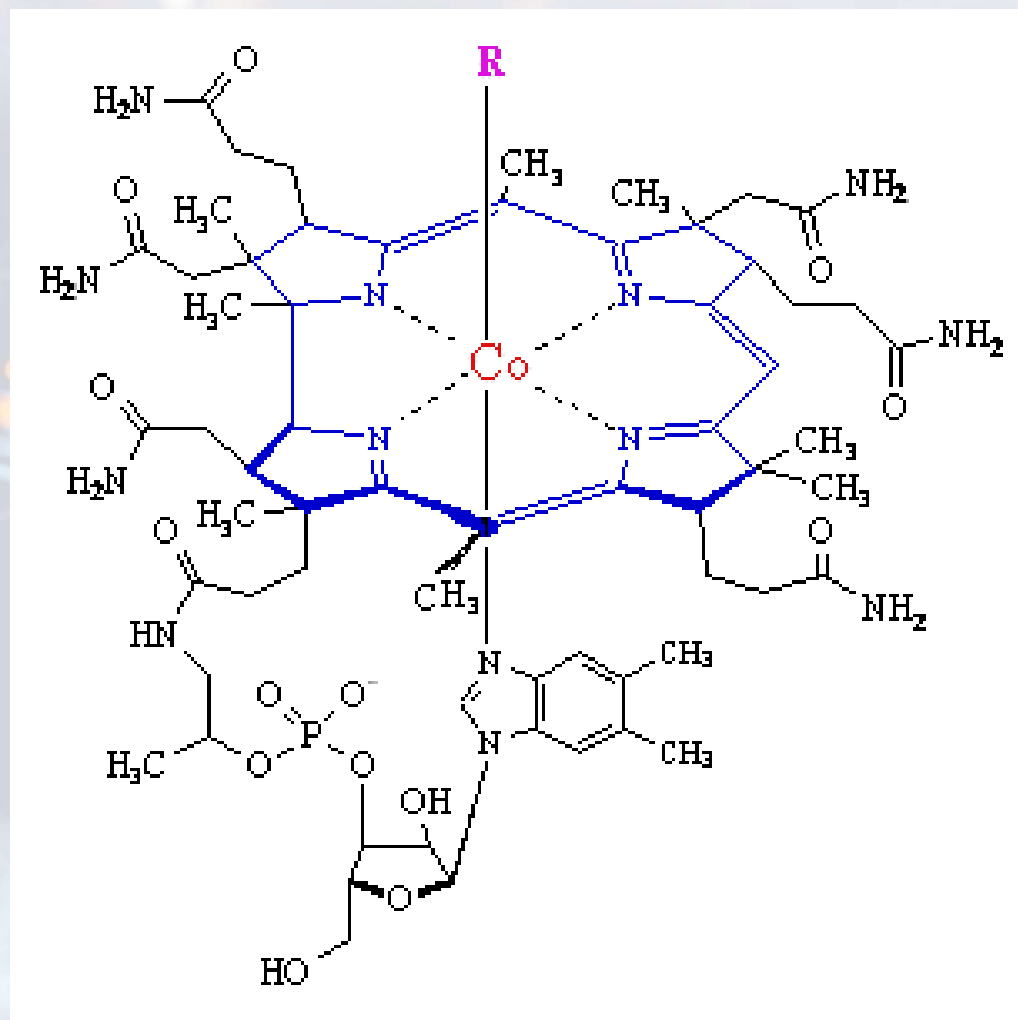
The study of non-covalent interactions is crucial to understanding many biological processes from cell structure to vision that rely on these forces for structure and function. Biological systems are often the inspiration for supramolecular research.



Hemoglobin

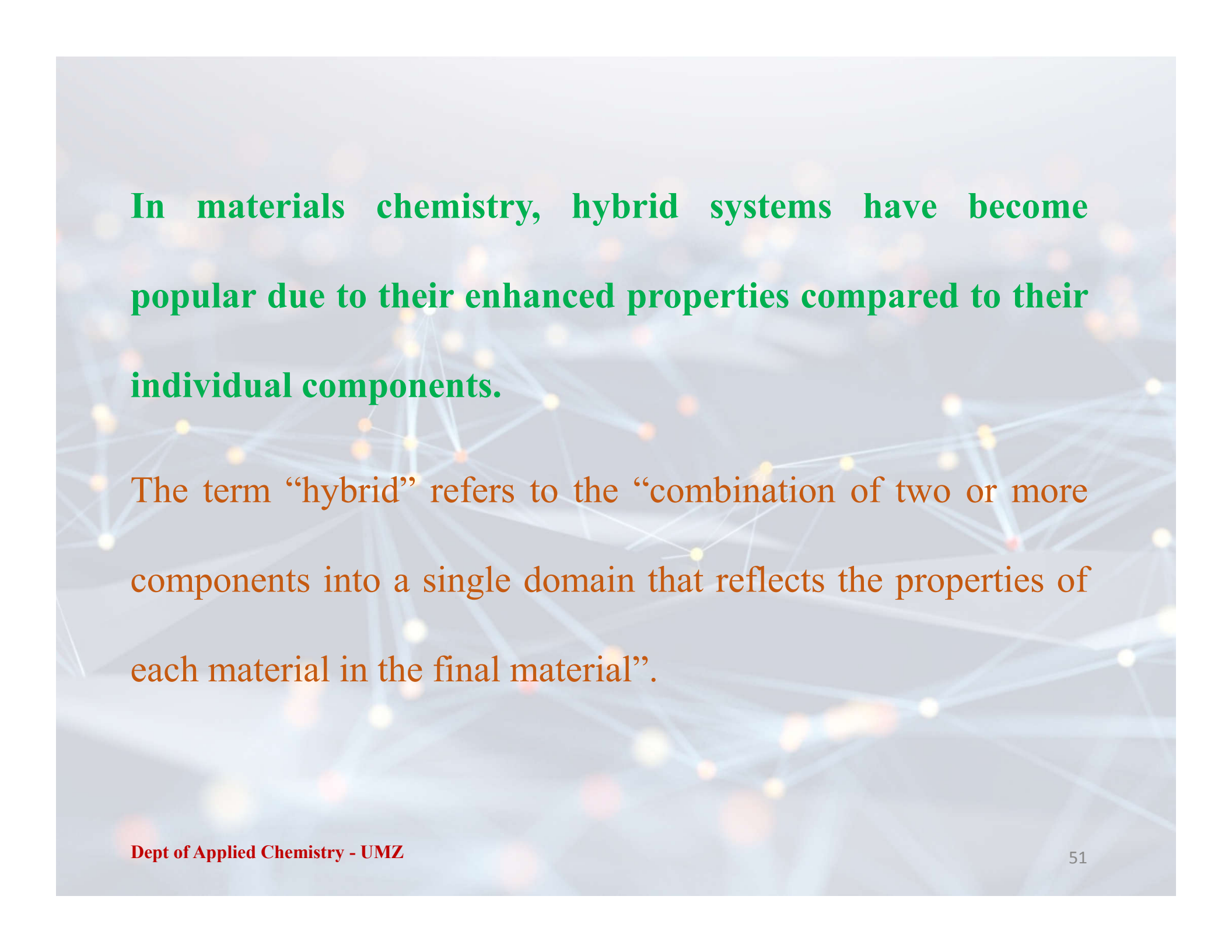


Vitamin B-12



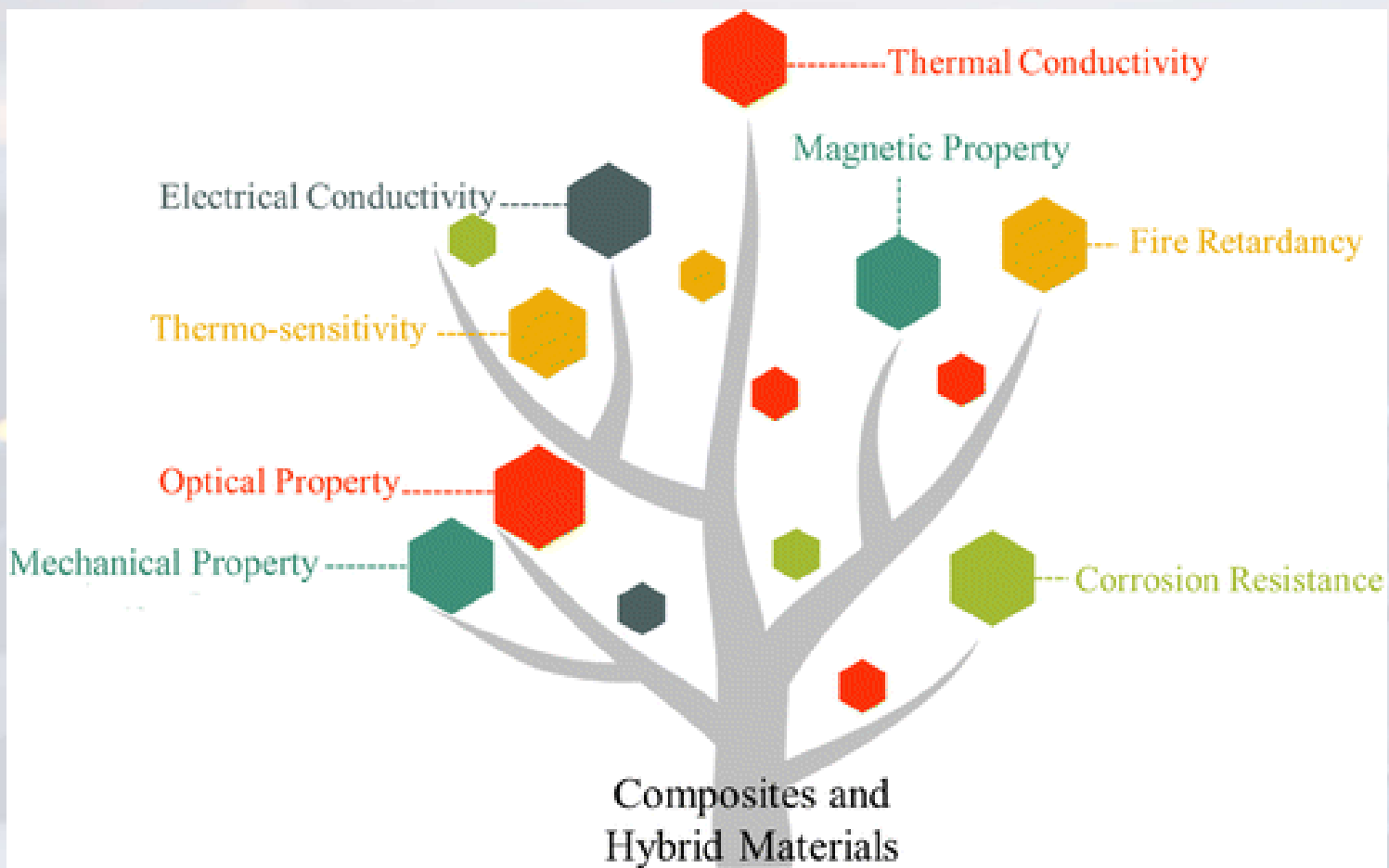


Hybrid Materials

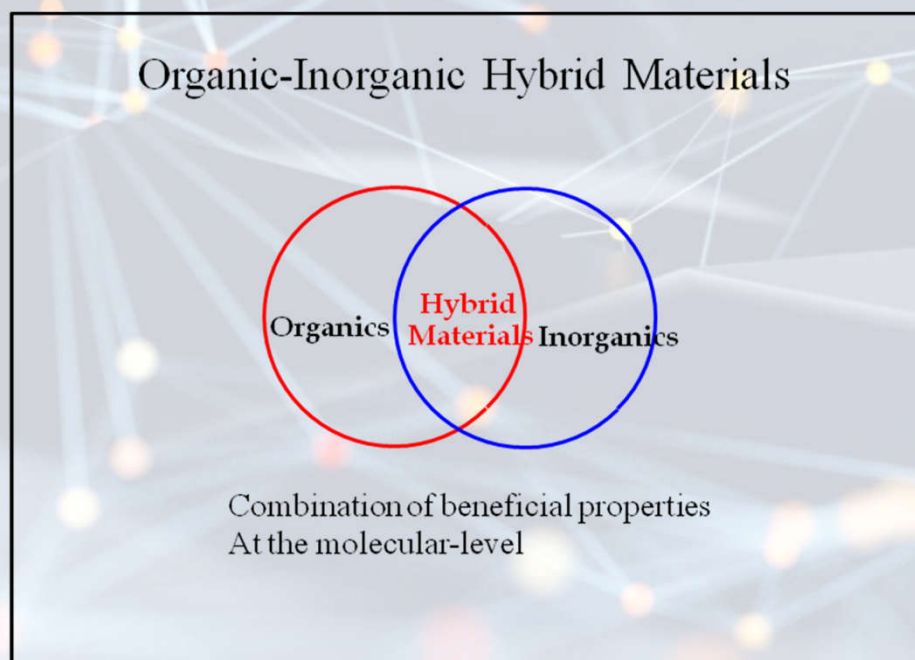


In materials chemistry, hybrid systems have become popular due to their enhanced properties compared to their individual components.

The term “hybrid” refers to the “combination of two or more components into a single domain that reflects the properties of each material in the final material”.



In general, hybrid materials consist of a minimum of two components, such as inorganic and organic materials, which are dispersed molecularly in the material.

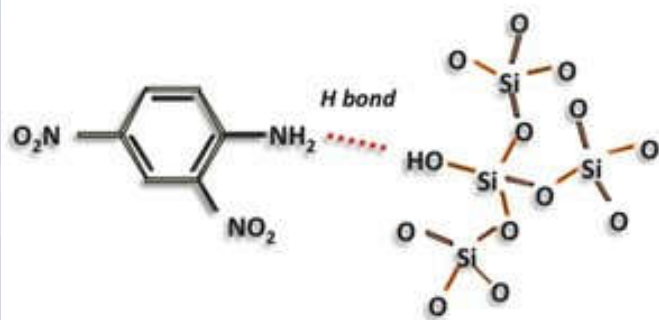


Hybrid materials are classified further into two classes on the basis of the **nature of the interface**. The interface of a material connected to the organic or inorganic components by **weak chemical bonds**, such as hydrogen, van der Waals, or ionic bonds, is classified as a **class I material**, whereas the interface of a material connected to organic or inorganic components by **strong chemical bonds**, such as covalent or ionic-covalent bonds, is classified as a **class II material**.

CLASS I

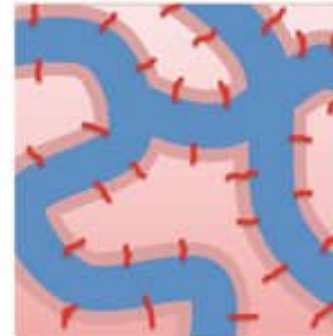


Hybrid Materials via
ENTRAPPING/ENCAPSULATION method

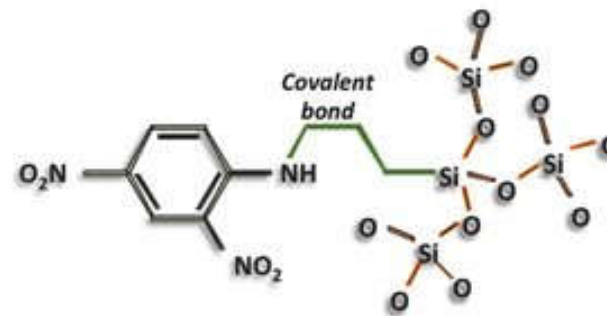


"Weak interactions" between the components
(van der Waals, hydrogen bonds, π - π , electrostatic
interactions).

CLASS II

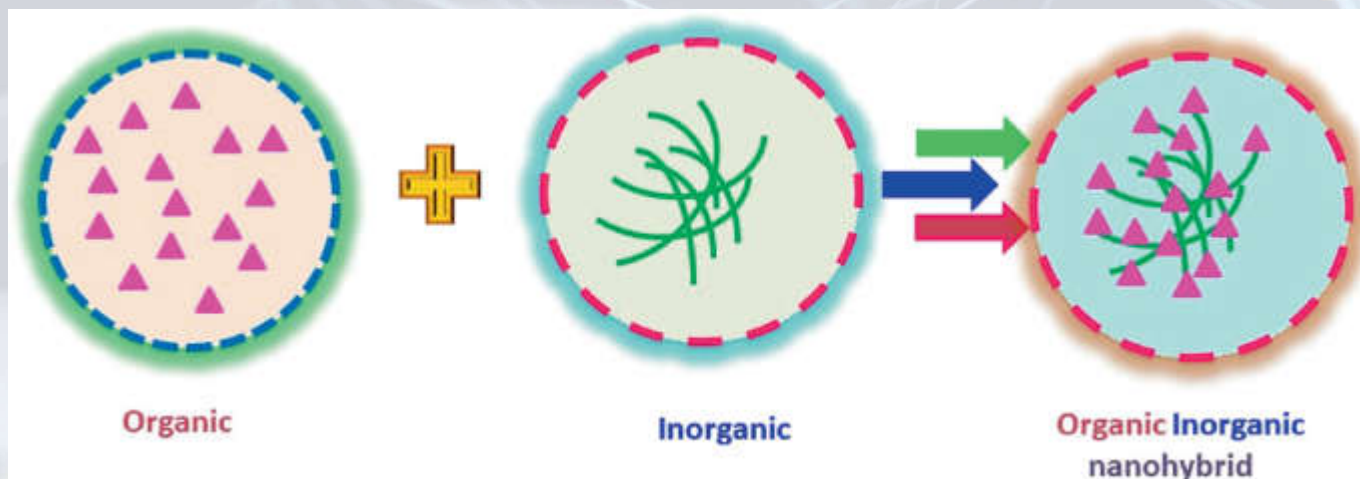


Hybrid Materials via
GRAFTING method

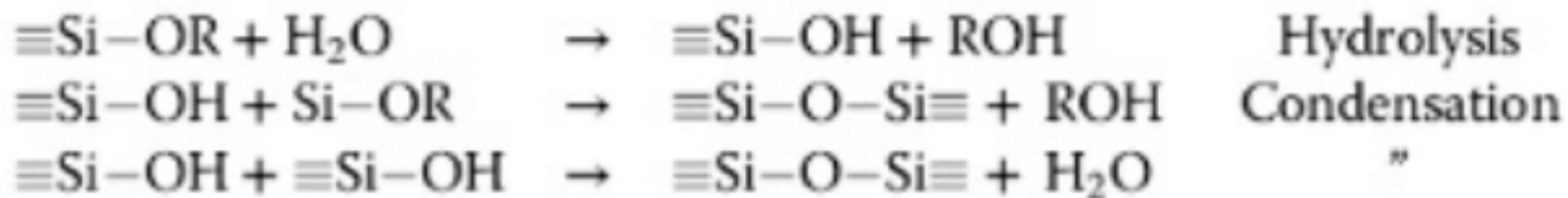


Chemical bonds (covalent or ionic-covalent)
between the components
"Strong interactions".

Organic-inorganic hybrid materials obtained from the addition of an inorganic source to the organic matrix show excellent properties, such as an improvement in the thermal, electrical, mechanical, optical, magnetic, electrochemical, and other physical properties.



Sol-gel technology is used widely for the synthesis of organocinorganic nanohybrid materials due to the versatile nature of the method. Several new types of organic-inorganic hybrid materials have been developed by the sol-gel method with a slight modification of the chemical nature of the materials.

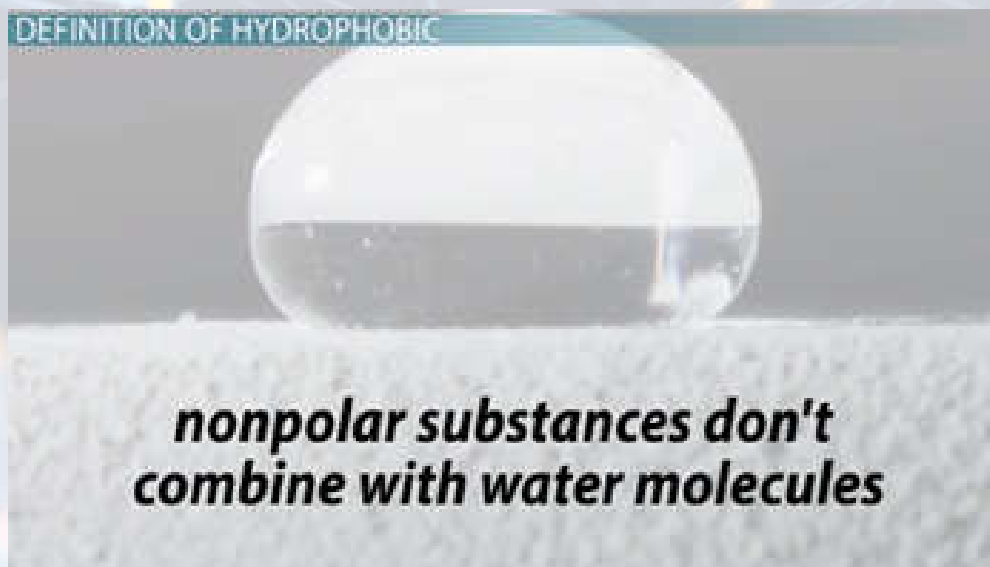


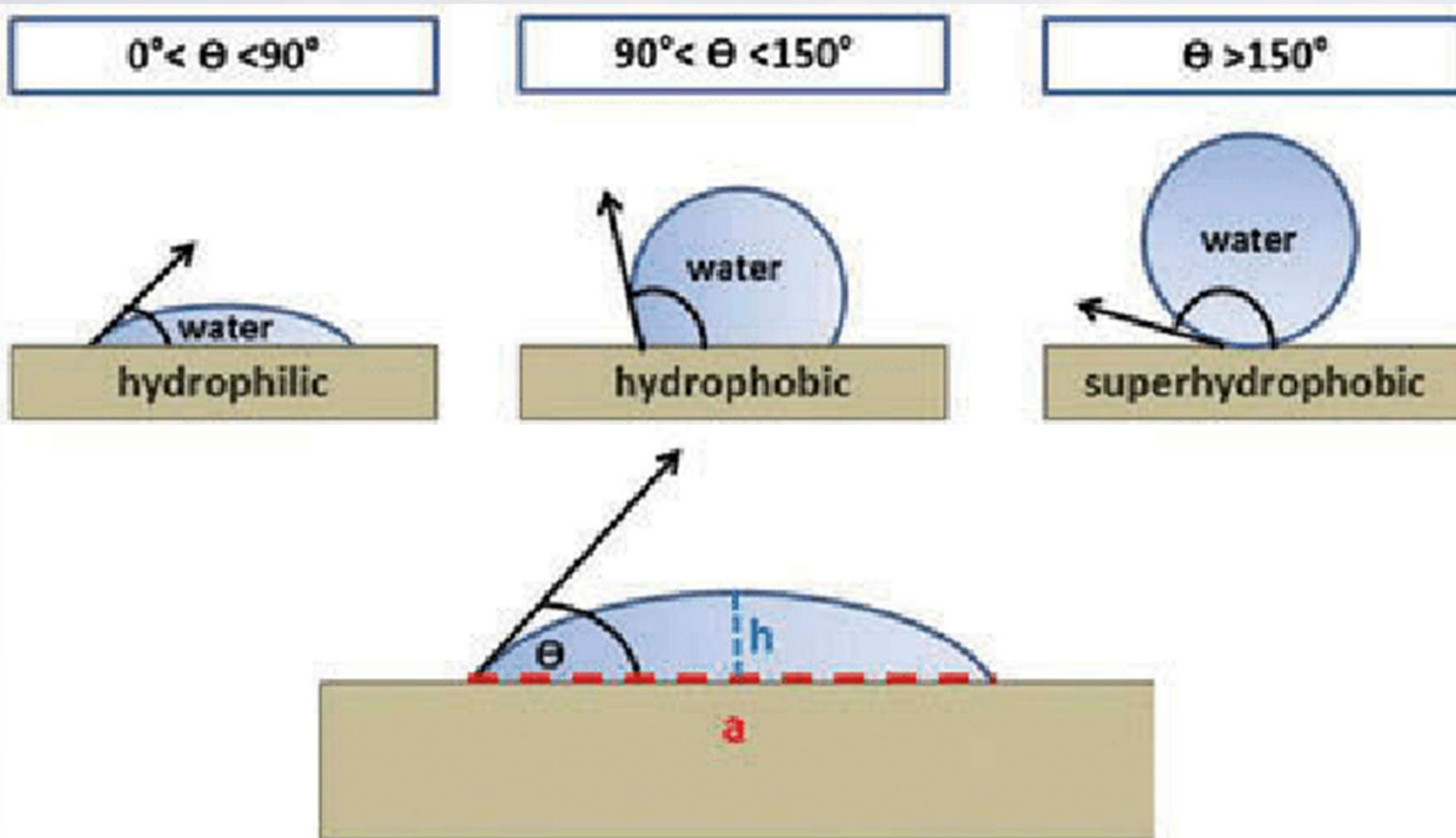
Hydrophobic Organic-Inorganic Nanohybrids:

Hydrophobicity is important in various coating applications to maintain or enhance the life cycle of the coating product. Hydrophobic materials can show strong hydrophobic interactions at the surface of a material.

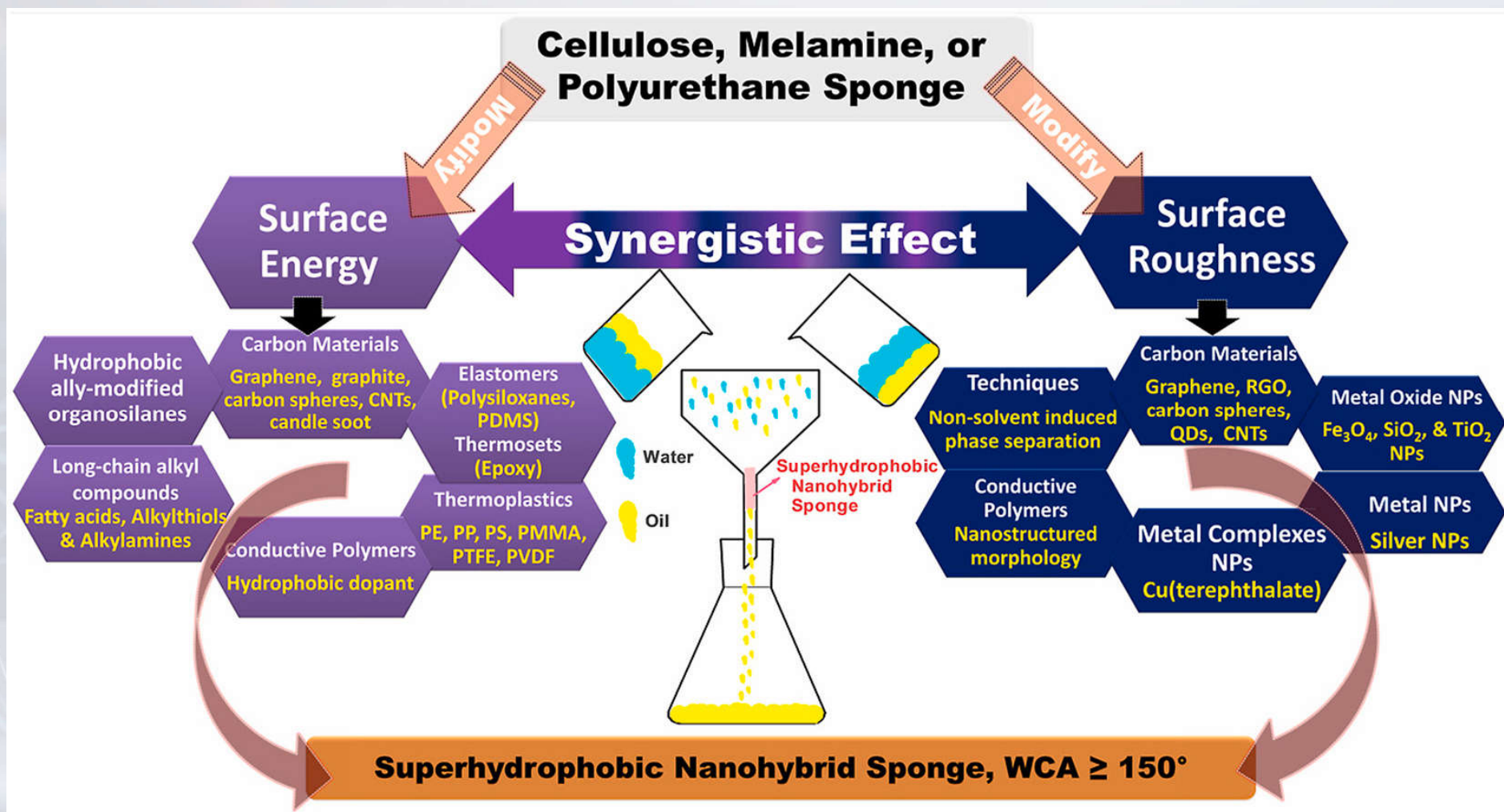
The hydrophobic organic-inorganic nanohybrids have been synthesized by changing the surface functional groups using several hydrophobic precursors.

Hydrophobicity (or lipophilicity) is a well-known and extensively studied phenomenon. It is commonly understood to be the tendency of non-polar molecules to form aggregates in order to reduce their surface of contact with polar molecules such as water.









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Original Article | Published: 30 November 2021

Thermo-driven self-healable organic/inorganic nanohybrid polyurethane film with excellent mechanical properties

[Haoliang Wang](#), [Hui Wang](#), [Junhuai Xu](#), [Xiaosheng Du](#), [Shiwen Yang](#)  & [Haibo Wang](#) 

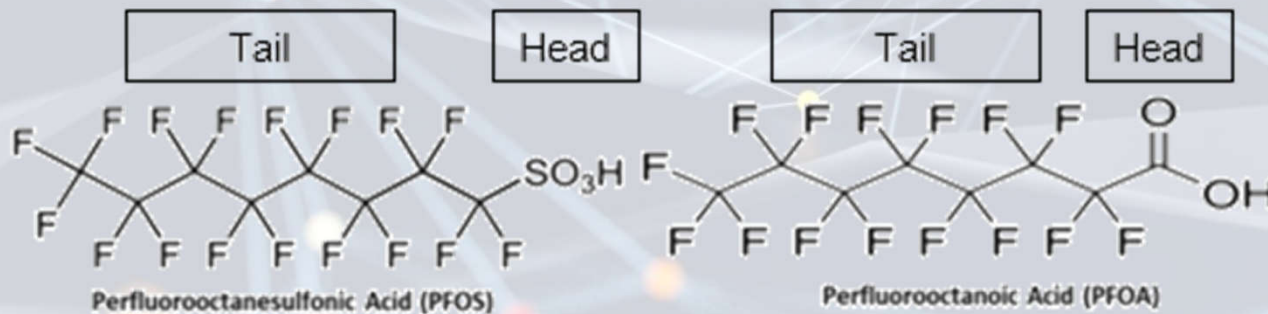
[Polymer Journal](#) **54**, 293–303 (2022) | [Cite this article](#)

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The strength of the hydrophobic interactions with water on a solid surface is determined by several factors:

- ✓ **Hydrophobic interactions depend on the number of hydrocarbons attached to the molecule. A molecule with a large number of hydrocarbons exhibits better hydrophobic interactions with water than a molecule with a lower number of hydrocarbons.**

✓ Hydrophobicity can be achieved easily by treating the solid surface with fluoro-compounds. This is due to the presence of low-surface-energy fluoro-compounds on the surface of the material. Fluoro-compounds also show fewer hydrophobic interactions with water on a solid surface.



✓ The shape of the hydrophobic molecule is an important parameter determining the hydrophobic interactions. In general, a molecule with aliphatic or linear chains shows stronger hydrophobic interactions than aromatic or branched molecules due to steric hindrance of the aromatic or branched molecules with each other, which reduces the interactions with water.

✓ **Hydrophobicity also depends on the temperature. The strength of the hydrophobic interaction increases with increasing temperature. This depends on some particular temperature beyond which the hydrophobic interaction is reduced to some level and the strength of the material is lost.**

Synthesis of Hydrophobic Organic-Inorganic Nanohybrids:

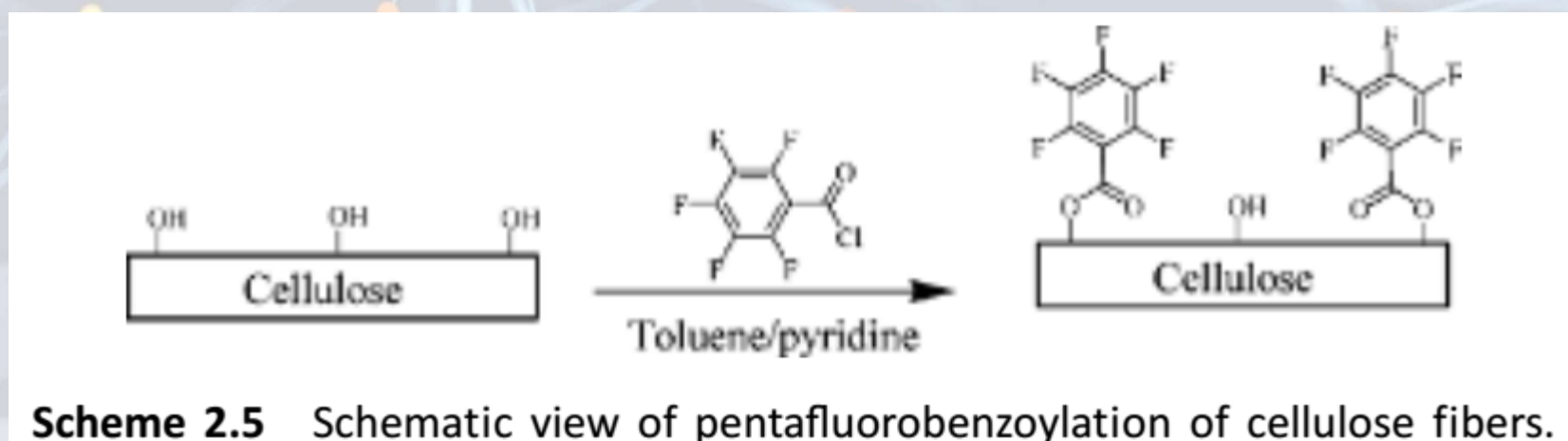
Hydrophobic organic-inorganic nanohybrid materials can be synthesized by a range of methods, such as sol-gel, emulsion, hydrothermal, self-assembly, surface grafting, and modification methods.

Surface Grafting and Modifications:

Surface grafting or modification is a simple method of modifying the surface property of a material using various grafting agents or crosslinkers. Surface grafting is used widely for the fabrication of hydrophobic organic-inorganic hybrid materials.

The main advantages of surface grafting are their simplicity and easy surface modification with various functional groups for the desired applications.

The organic-inorganic hybrid cotton substrate obtained by surface-treating the natural cellulose fibers with pentafluorobenzoyl chloride in the presence of toluene and pyridine as solvents showed stable hydrophobicity on the cellulose fiber surface.



The fluorine-treated cellulose fiber substrate also exhibited good oleophobicity, chemical inertness, and thermal and oxidative stability due to the presence of low surface energy of a fluorine-based material.



Spin Coating:

Spin coating is a type of coating method used to form a uniform thin film by spreading a hydrophilic or hydrophobic solution or suspension on a range of substrates by a physical force under a constant speed and pressure. The substrate is fixed in a pressure controlled disc and the solution or suspension is dropped on the substrate and rotated under fixed conditions to deposit a uniform thin film.

