Supramolecular Chemistry

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Supramolecular Chemistry

Supramolecular chemistry may be defined as “**chemistry beyond the molecule**”, bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces.

In supramolecular chemistry, noncovalent interactions occur between molecular building blocks, which by molecular recognition and self-assembly form (functional) supramolecular entities.

It is also termed the “**chemistry of the non-covalent bond**.”

Basic Principles

Non-covalent Interactions

Bonding interaction that cannot be described in terms of classical "electron sharing between two atoms by the overlap of two atomic orbitals to form molecular orbitals." Noncovalent interactions are weak dispersion, dipole–dipole, cation–π interactions,or π–π stacking and quite strong electrostatic, coordinative interactions.

Molecular recognition

Molecular recognition is the specific interaction between two molecules, which are complementary in their geometric and electronic features (like two fitting pieces of a jigsaw puzzle).

Self assembly

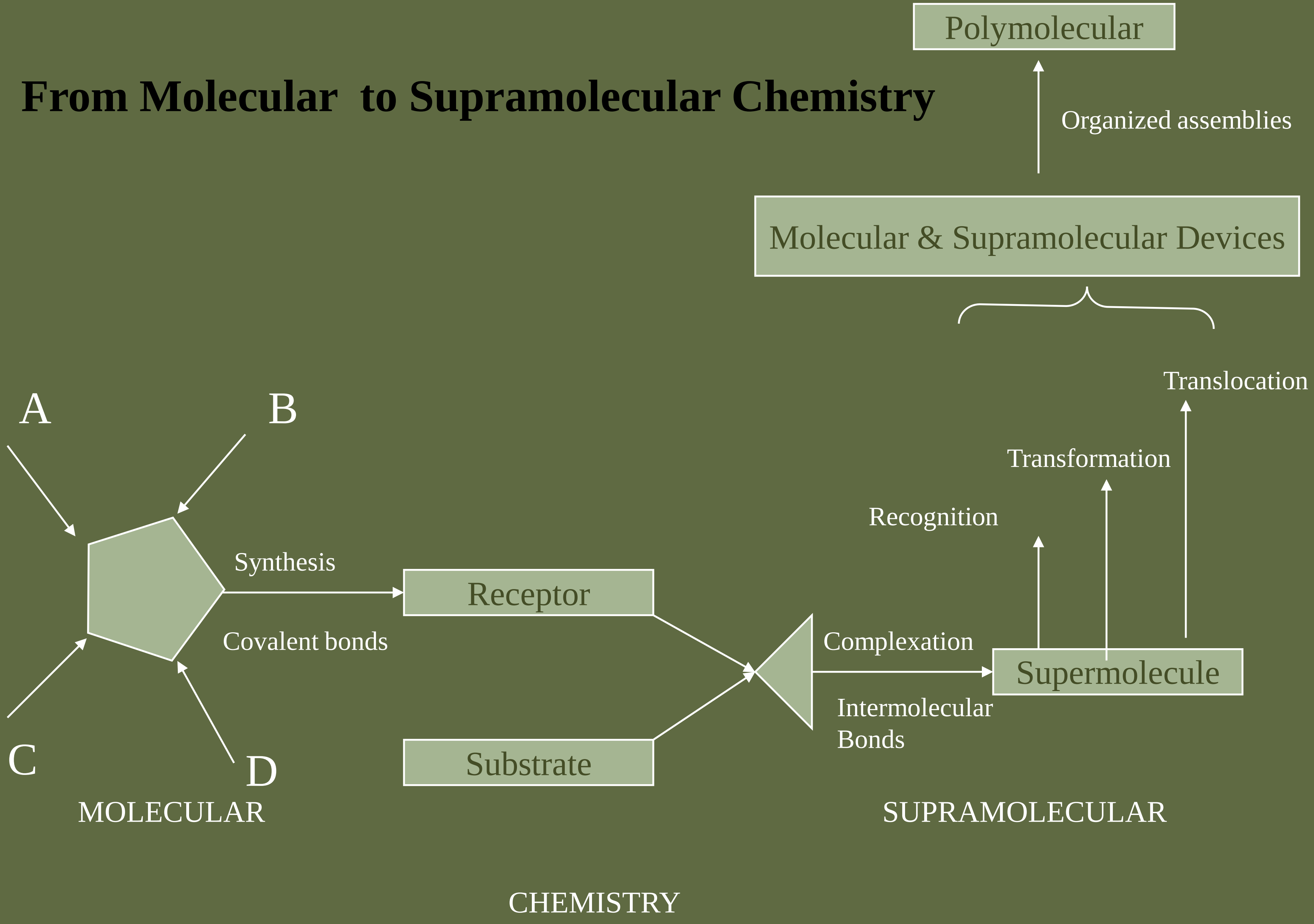
Recognition between molecules leads to an aggregation, which finally results in an ensemble that is composed of two or more discrete units which possess special properties or supramolecular functions, which are only found in the ensemble but not in the participating molecules.

Essential biological processes, e.g., reproduction, signal transduction, information storage, and processing are all based on supramolecular interactions between molecular components.

Enzymes, **viruses, membranes, and many other complicated structures with biologically relevant functions** are mainly built up by simple self-assembly processes.

The processes can be mimicked in small artificial supramolecular derivatives.

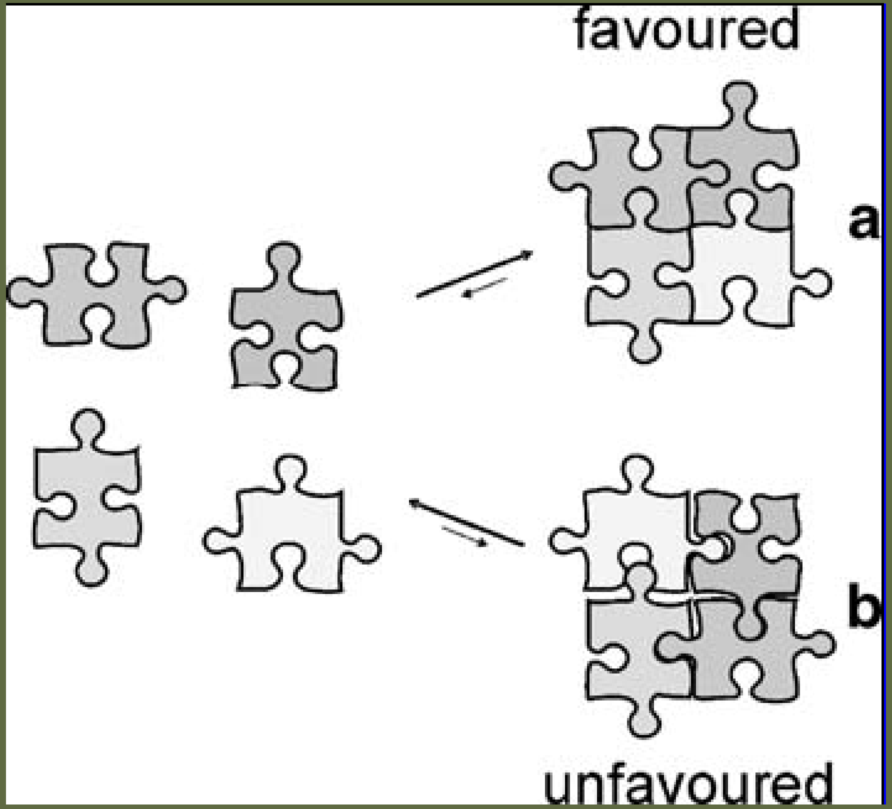
From Molecular to Supramolecular Chemistry



Molecular Recognition

- ✓ Molecules that interact physically and react chemically in specific and selective ways are the basic constituents of this living world. This is called the molecular recognition process and it controls the formation of multi molecular assemblies
- ✓ Molecular recognition is the specific interaction between two molecules, which are complementary in their geometric and electronic features (like two fitting pieces of a jigsaw puzzle).
- ✓ By the use of this principle we can construct large ensembles of molecules.

The most sophisticated and effective examples of self assembly occur in living systems.

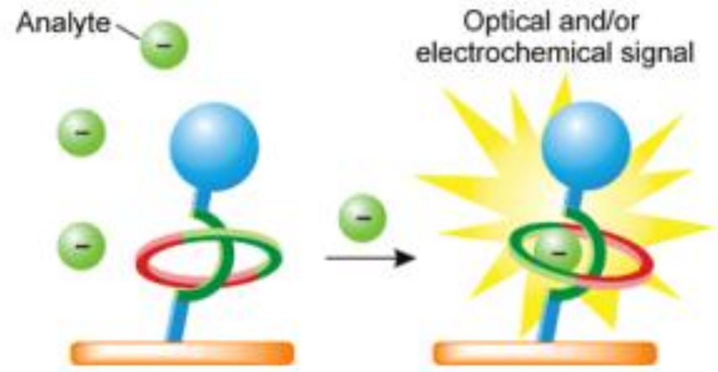


The pieces of the puzzle fit together, if they are complementary in shape (molecular recognition) and if this process is reversible (non-covalent interactions, the best-fitting result is favored. By connecting all the pieces of the jigsaw puzzle in the correct way (self assembly) the final object is obtained (a). Wrong connections lead to an unfavored and thus more unstable entity (b), which is eventually disconnected again to arrange the pieces correctly.

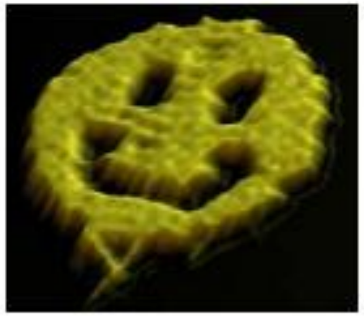
Schematic representation of self-assembly of a supramolecular aggregate by molecular recognition and non-covalent interactions (Jigsaw puzzle model)

Applications of Molecular recognition

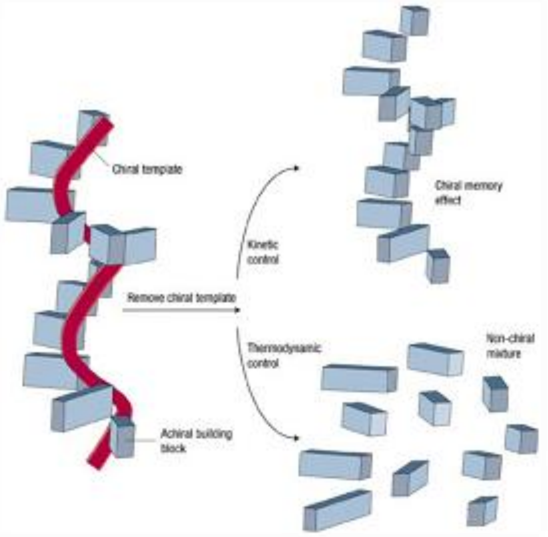
- ✓ **Sensor technology**
- ✓ **Molecular electronics- switches, transistors and molecular wires**
- ✓ **Molecular magnetic devices**
- ✓ **Photo-chemical molecular devices**
- ✓ **Catalysis**
- ✓ **Drug design**



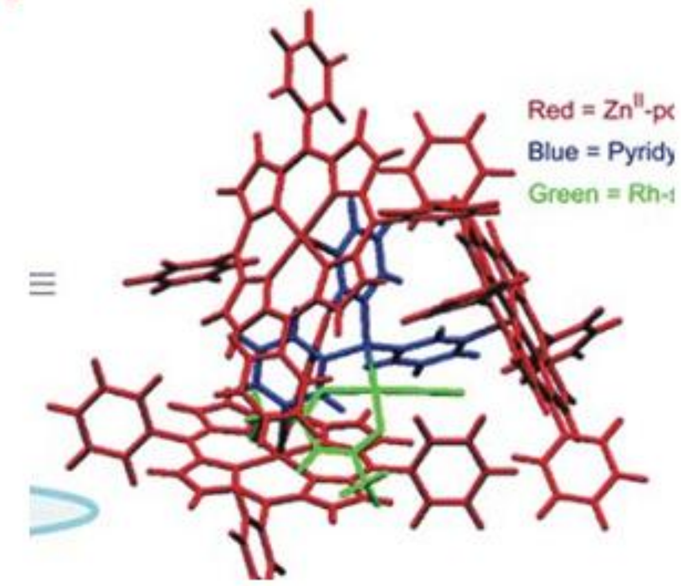
sensing



self-assembly



materials



catalysis

Synthetic Strategy

To construct supramolecules, the initial step involves the covalent synthesis (organic synthesis) to construct subunits which by non-covalent bonds can aggregate with themselves or other synthetic subunits to afford stable, structurally defined surface molecular assemblies. The lock and key principle describes the fit of a rigid substrate to a rigid receptor analogous to a key and a lock. Mechanically interlocked molecules like rotaxanes (a ring fixed on a terminally blocked axis), catenanes (two intertwined rings), and also molecular knots (e.g., trefoil knots) are considered as supramolecular species. The partners of a supramolecular species have been named *molecular receptor* and *substrate* , the substrate being usually the smaller component whose binding is being sought.

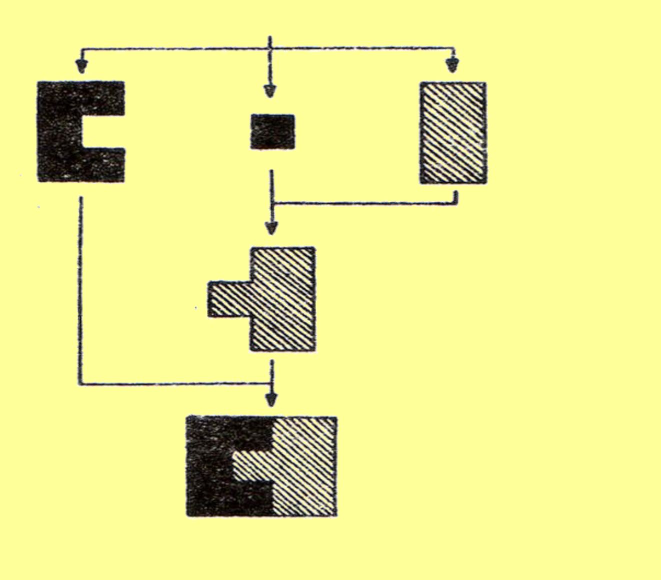


Figure 1. *Synthetic strategy based on self assembly: Conversion of simple building blocks, which can assemble into complex chemical entities*

An example of supramolecular assembly worth mentioning is the construction of rotaxane (a class of molecules in which a dumbbell shaped component is encircled by a macrocycle). The two components are linked by a non-covalent interaction. The complex formed between these two species can then be modified with blocking groups to produce the [2] rotaxane. The prefix [2] indicates the number of mechanically linked components within the molecule.

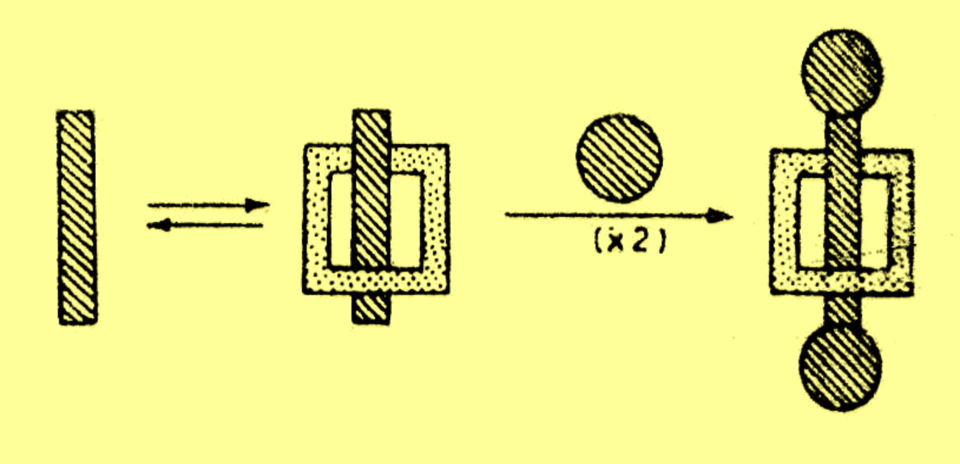


Figure 2. *Schematic representation of the synthesis of a [2] rotaxane by threading*

Ogino and coworkers, reacted diaminoalkanes with α-cyclodextrin (α- CD) or β CD which after the formation of inclusion complex further reacted with the cobalt complex $[CoCl_2(en)_2]$ (en = ethylenediamine) yielding [2] rotaxane.

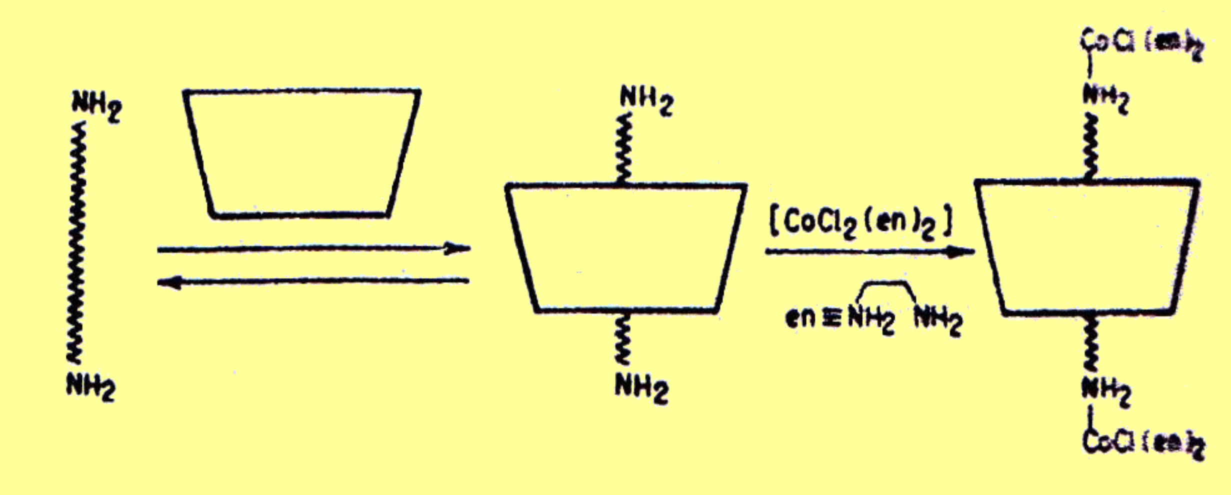


Figure . Cyclodextrin rotaxanes constructed from α,ω diaminoalkanes and cobalt based blocking groups

- ✓The supramolecular chemistry has its own terminology, like ligands in coordination compounds, the supramolecular compounds have been named as **receptor (ρ)** and **substrate (σ)** [being smaller component].

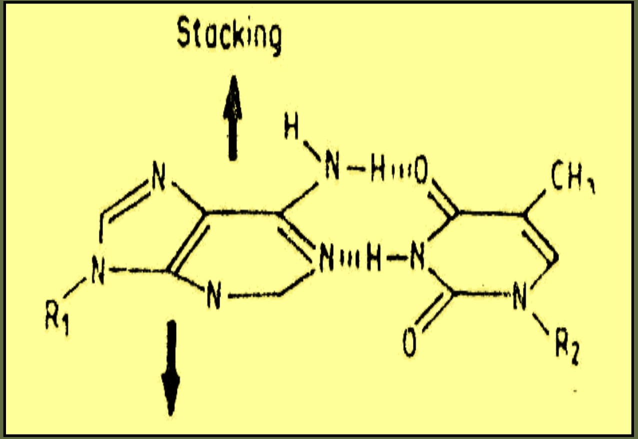
- ❖The selective binding of a specific substrate σ to its receptor ρ yields **supramolecule ρσ** and involves molecular recognition process. In addition to binding sites, if a receptor also bears reactive functions, it may affect a chemical transformation on the bound substrate thus behaving as a supramolecular reagent or catalyst.

- Naming of such compounds poses some specific problems. Receptors and substrates themselves are covalent structures whose naming is governed by rules approved in the Geneva conference.
- Conventions used for coordination compounds may be a starting point e.g; κ, kappa (indicating coordinating atom), hapto, η (for coordinated group) or μ (for bridging ligands).
- Spatial localization of bound substrate with respect to the receptor also requires some formalism. External addition complexes may be written as [A, B] or [A//B] , the mathematical symbols of inclusion € and intersection ∩ have been introduced.

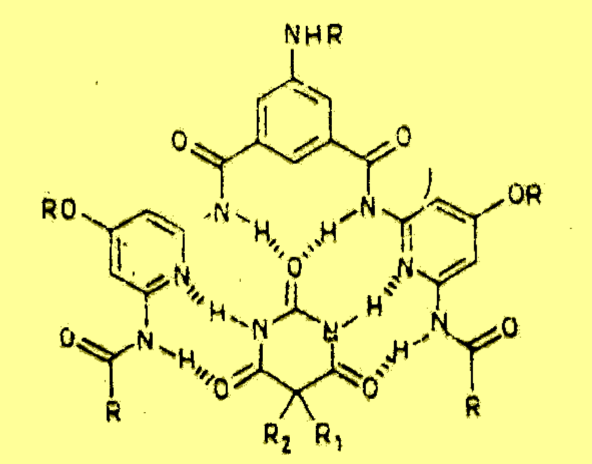
Requirements for the design of supramolecular system

- Steric factors (shape and size) presence of convex and concave domains in substrate and receptor molecules.
- Interactional complementarity (which depends on well-defined 3-D architecture with correct arrangement of binding sites),
- Large contact areas between receptor and substrate.
- Multiple interaction sites
- Strong overall binding
- medium also plays an important role through the interaction of solvent molecules with receptor and substrate as well as with each other.

Recognition implies the geometrical and interactional complementarity, i.e; presence of complementary binding sites (electrostatic such as positive/negative, charge/dipole, dipole/dipole, hydrogen-bond, donor/acceptor etc.) between the associating partners.



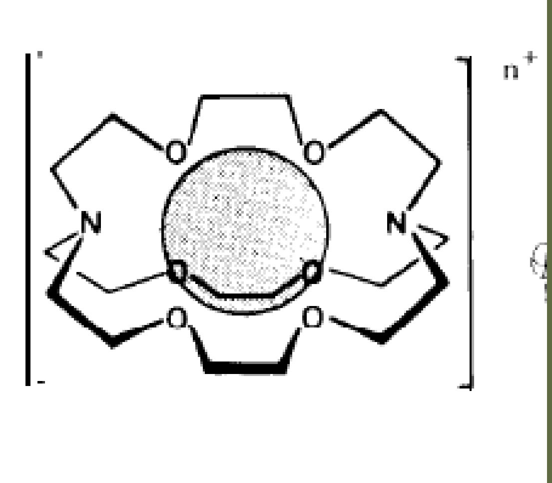
Base pairing Adenine and thymine(A-T)

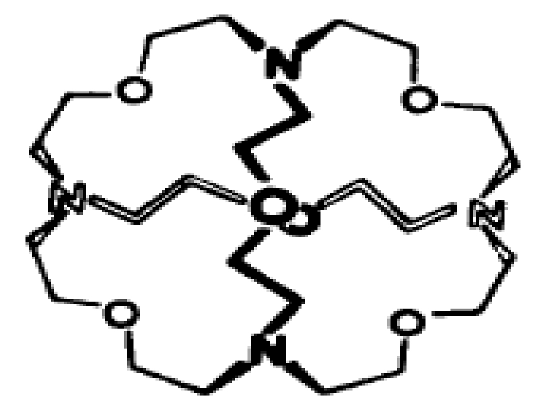


H-bonded barbiturate with 2,6-pyridine diamide groups

Different types of Molecular receptors

The simplest recognition process is that of spherical substrates; these are either positively charged metal cations (alkali, alkaline-earth, lanthanide ions) or the negative halide anions. cryptands as well as related compounds display *spherical recognition* of appropriate cations and anions. Their complexation properties result from their macropolycyclic nature and define a *cryptate effect* characterized by high stability and selectivity, slow exchange rates and efficient shielding of the bound substrate from the environment.





For further reading

- Supramolecular Chemistry-Scope and perspectives

-Jean-Marie Lehn, Noble lecture, December 8, 1987.

- Supramolecular chemistry—general principles and selected examples from anion recognition and metallo supramolecular chemistry.

- M. Albrecht, Naturwissenschaften (2007) 94:951–966