HISTORY AND EMERGENCE OF SUPRAMOLECULAR CHEMISTRY

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In 1756, on heating the mineral stilbite in a flame, Cronstedt observed the release of vapor and named this material zeolite.

(Greek zein lithos: boil stone)

Axel Cronstedt
(Sweden, 1722-1756)

Zeolites are microporous, aluminosilicate minerals. An example mineral formula is: \( \text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot2\text{H}_2\text{O} \).

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves."
In 1778, Priestley discovered ‘anomalous ice’. This was the compound \((\text{SO}_2)\bullet(\text{H}_2\text{O})_x\), the first of the important clathrate hydrate family of materials.

In 1810, Davy reported the synthesis of a clathrate hydrate, that of chlorine. He observed that a solution of chlorine in water froze at a temperature higher than the ice melting point. Upon decomposition, this unique new material returned unchanged to the starting materials.
In 1774, Benjamin Franklin observed the spreading of oil on water.
The ‘birth’ of nanochemistry

In 1818, Richters correlated the color of colloidal gold to the particle size.

The dichroic effect is achieved by making the glass with tiny proportions of minutely ground gold and silver dust.

When viewed in reflected light the minute metallic particles are just coarse enough to reflect enough of the light without eliminating the transmission. In transmitted light the fine particles scatter the blue end of the spectrum more effectively than the red end, resulting in red transmission, and this is the colour observed.
1893 — Alfred Werner: coordination chemistry

In 1893, Werner was the first to propose correct structures for coordination compounds containing complex ions, in which a central transition metal atom is surrounded by neutral or anionic ligands.

The Nobel Prize in Chemistry 1913 was awarded to Alfred Werner "in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry".
1920 — Wendell Latimer and Worth Rodebush describe the hydrogen bond

‘Polarity and Ionization from the standpoint of the Lewis Theory of Valence’

A footnote in their paper credits "Mr. Huggins of this laboratory [who], in some work as yet unpublished, has used the idea of a hydrogen kernel held between two atoms as a theory in regard to certain organic compounds".

Prof. Stewart and Prof. Bray also discussed some of the unsolved problems of chemistry. These problems intrigued me. Could some of them be solved by the application of the Lewis theory, perhaps with modifications? (Notes from Maurice Huggins)

Latimer and Rodebush themselves do not actually use the terms "hydrogen bond" or "hydrogen bonding" in their paper. The closest they come is to describe it as "the hydrogen nucleus held between two octets constitutes a weak 'bond'."

The first use of the term in the literature was in Lewis' book, Valence and the Structure of Atoms and Molecules, in which the section headed "Bivalent Hydrogen" begins (4):

*It seems to me that the most important addition to my theory of valence lies in the suggestion of what has become known as the hydrogen bond.*
The recognition by Paul Ehrlich in 1906 that molecules do not act if they do not bind.

*Corpora non agunt nisi fixata;*

In this way, Ehrlich introduced the concept of a biological receptor.

The Nobel Prize in Physiology or Medicine 1908 was awarded jointly to Ilya Ilyich Mechnikov and Paul Ehrlich "*in recognition of their work on immunity*"
“Lock and key”: In 1894 Emil Fischer postulated that binding between proteins and their substrates resembled the image of a key in a lock. The guest has a size and shape complementary to the host (*molecular recognition*).

Emil Fischer (Germany, 1852-1919)

The Nobel Prize in Chemistry 1902 was awarded to Emil Fischer *"in recognition of the extraordinary services he has rendered by his work on sugar and purine syntheses"*.

In 1958 Koshland refined this idea by proposing an induced fit model. The protein assumes a complementary shape only when interaction with the substrate

*Figure 2*  
(a) Rigid lock and key and (b) induced fit models of enzyme–substrate (and hence host–guest) binding.
Linus Pauling
(USA, 1901-1994)

In 1951, based on the structures of amino acids and peptides and the planar nature of the peptide bond, Pauling, Robert Corey and Herman Branson correctly proposed the alpha helix and beta sheet as the primary structural motifs in protein secondary structure.

The Nobel Prize in Chemistry 1954 was awarded to Linus Pauling *"for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances".*
The molecule of life – self-assembly

The Nobel Prize in Physiology or Medicine 1962 was awarded jointly to Francis Harry Compton Crick, James Dewey Watson and Maurice Hugh Frederick Wilkins "for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material".

The origins of crown ethers are usually traced back to Charles Pedersen’s groundbreaking 1967 paper in which he describes the synthesis and metal binding properties of almost 50 macrocycles containing the –CH$_2$CH$_2$O– repeating structural motif.
On 5 July 1962, to his surprise, he isolated an unusual material that had unexpected solubilizing effects on alkali metal cations. Given that the material was isolated in less than 1% yield, most chemists would have ignored it and turned their attention to the major products. Fortunately, Pedersen was very inquisitive and, in his own words:

*Crown ethers were in no danger, because of my natural curiosity.*

Upon careful analysis, the product was found to be a macrocycle containing two benzene rings, six oxygen atoms, and ethylene spacers between the oxygens.
1969 — Jean-Marie Lehn: synthesis of the first cryptands

Cryptands (from Greek: cryptos = cave) are cage-like ligands

Figure 8 (a) Stick and (b) space-filling depictions of the X-ray structure of the [Na(2.2.2)]⁺ cryptate showing (b) how the metal ion completely fills the cavity of this cryptand (red, oxygen; blue, nitrogen; gray, carbon).56

Jean-Marie Lehn
(France, 1939)
Spherands are a category of macrocyclic receptors with **rigid** cavities whose donor sites (normally oxygen) are fixed in space in relation to each other and directed inward for complexation with a range of complementary guests, which often have a spherical shape.

Cram termed the enhanced stability compared to flexible analogues the “**preorganization effect**.”
Nobel Prize in Chemistry 1987

The Nobel Prize in Chemistry 1987 was awarded jointly to Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen "for their development and use of molecules with structure-specific interactions of high selectivity".
Where is supramolecular chemistry now?

Nearly everywhere!

self-assembly

catalysis

materials

sensing

nanotechnology
Books - 10 Volumes, 4014 pages

- Concepts
- Techniques
- Molecular recognition
- Supramolecular reactivity
- Supramolecular aspects of chemical biology
- Self processes
- Supramolecular devices
- Supramolecular materials chemistry
- Soft matter
- Nanotechnology
Conferences - international

The official website is now open.

Online registration and abstract submission is now open.

Prof. Ivan Aprahamian is selected as the CLP prize winner of this year.

**Important Dates**

**January 1, 2016**
Registration Open
Abstract Submission Open

**March 31, 2016**
Oral Abstract deadline

**Symposium Chairs**
Kim, Kimoon (POSTECH)
Kim, Jong Seung (Korea University)
Yoon, Jyuong(Ewha Womens University)

**General Secretary**
Park, Won-Bae
Suprachem 2013
XI Congresso Nazionale di Chimica Supramolecolare

Accommodation

General Information

Registration

Deadlines

Scientific Program

Padova 24-27 Settembre 2013
An inspirational book

Supramolecular chemistry

‘chemistry beyond the molecule’
The essence of chemical science finds its full expression in the words of **Leonardo da Vinci**:

‘...*dove la natura finisce di produrre le sue spezie, l’uomo quivi comincia con le cose naturali, con l’aiutorio di essa natura, a creare infinite spezie*...’

The **essence of chemistry** is not only to discover but to invent and, above all, *to create*.

The **book of chemistry** is not only to be read, but to be *written*!

The **score of chemistry** is not only to be played, but to be *composed*!

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J. M. Lehn