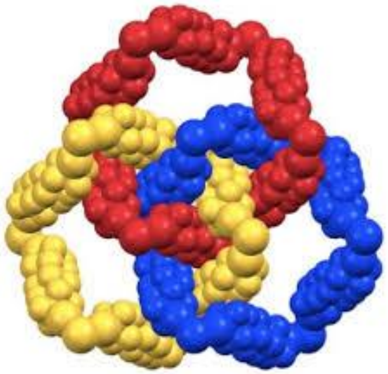


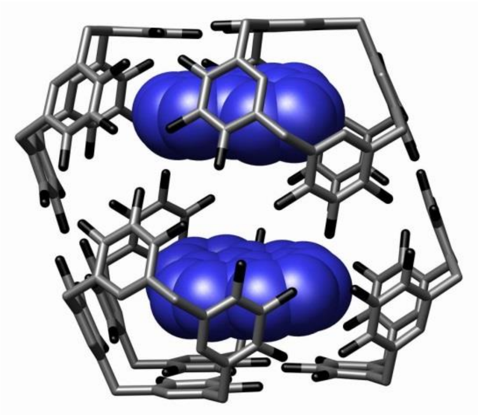
Corso di Chimica Supramolecolare

6 CFU

(LM in Chimica @Units)

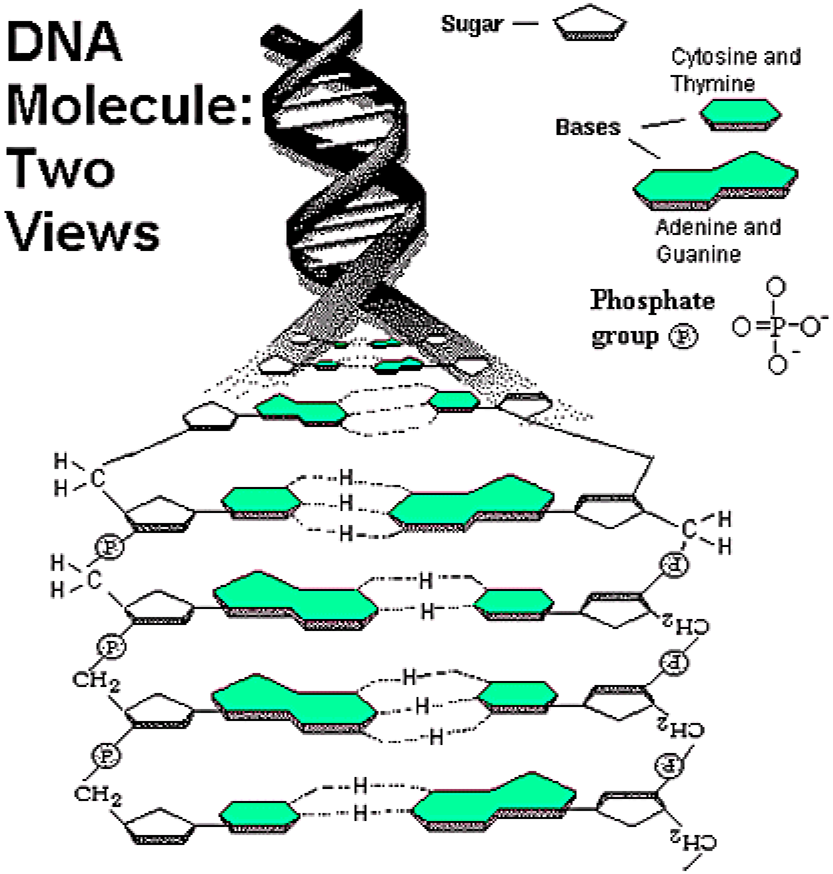
AA 2023/2024

Prof. E. Iengo
eiengo@units.it

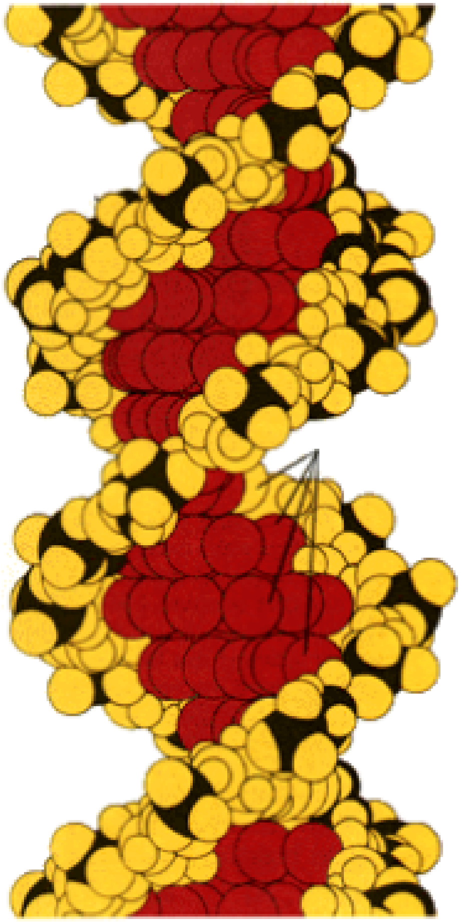


The original inspiration:
Supramolecular systems in Nature

DNA



Information Storage



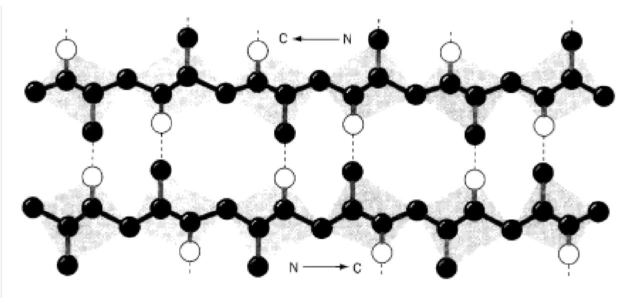
Watson & Crick 1953

The ultimate supramolecular material?

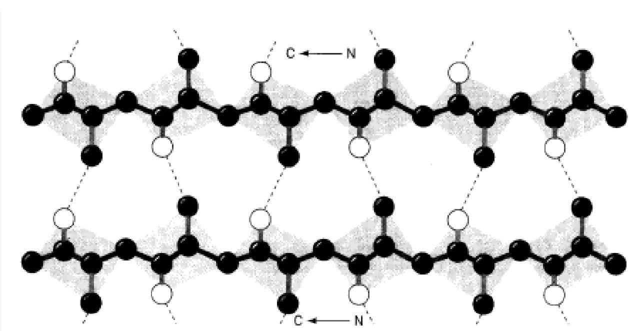
- Encodes gigabytes of data
- Can Self-Replicate
- Built-in Error Correction
- Is the basis of life

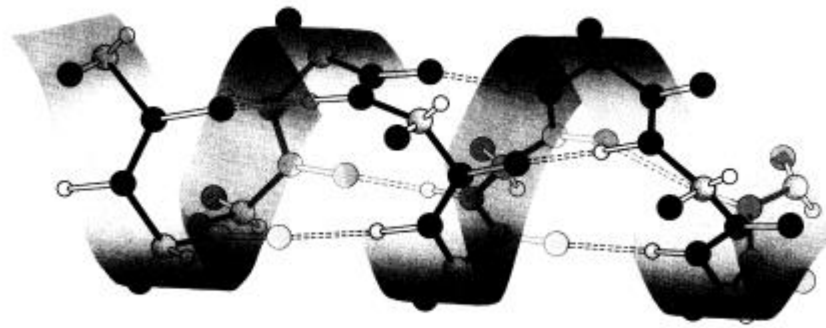
The original inspiration:
Supramolecular systems in Nature

PROTEINS



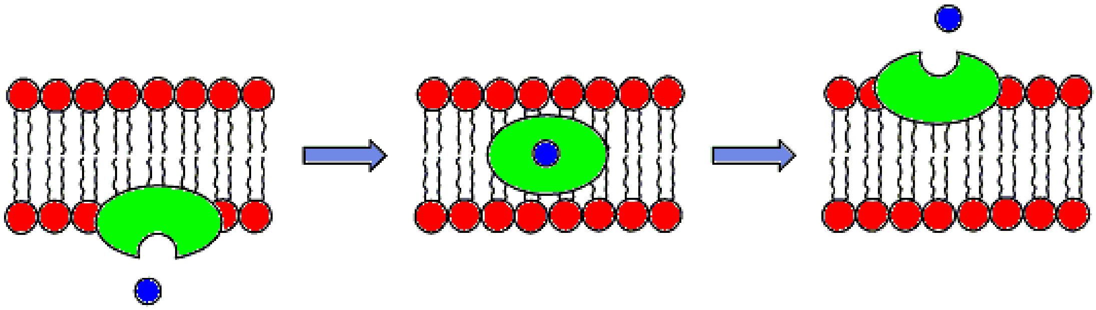
(a)

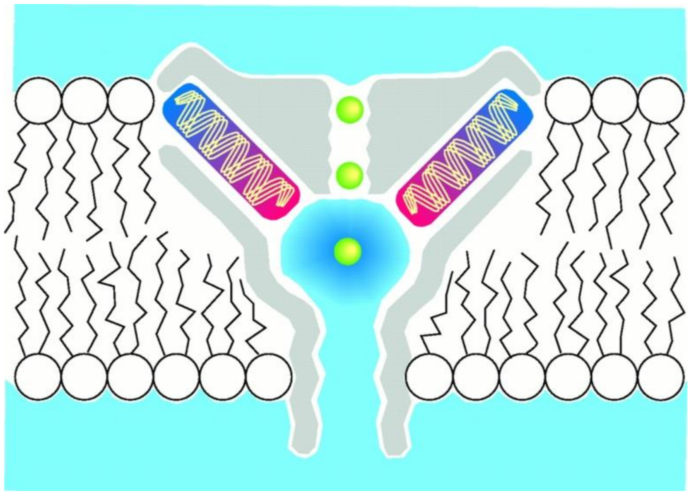




The original inspiration:
Supramolecular systems in Nature

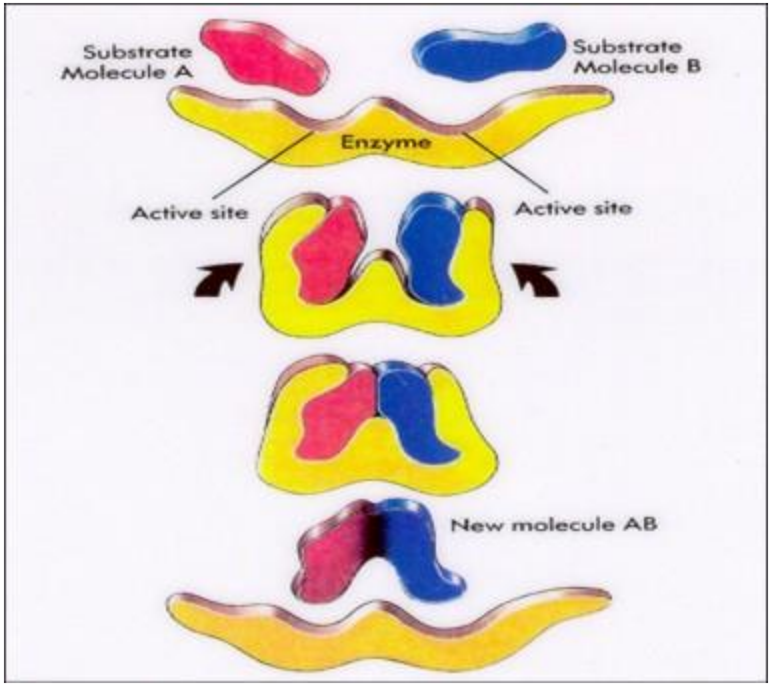
MEMBRANES and TRANSMEMBRANE CARRIERS





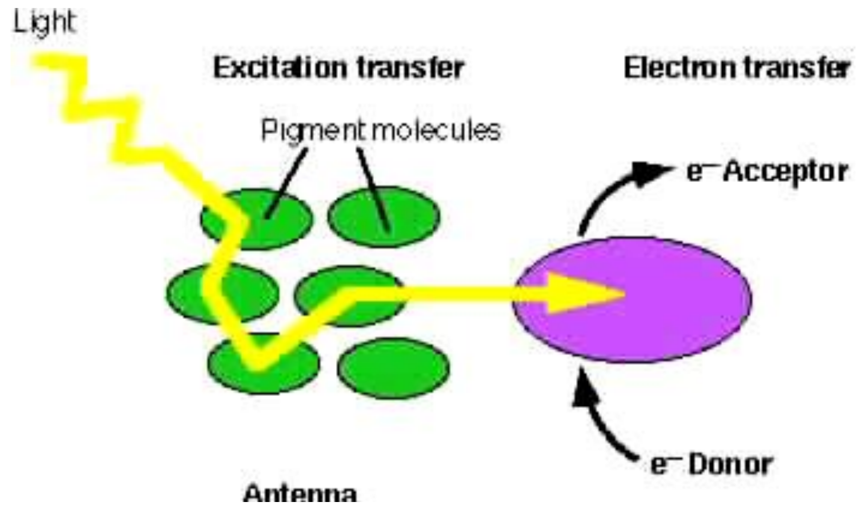
The original inspiration:
Supramolecular systems in Nature

ENZYMES

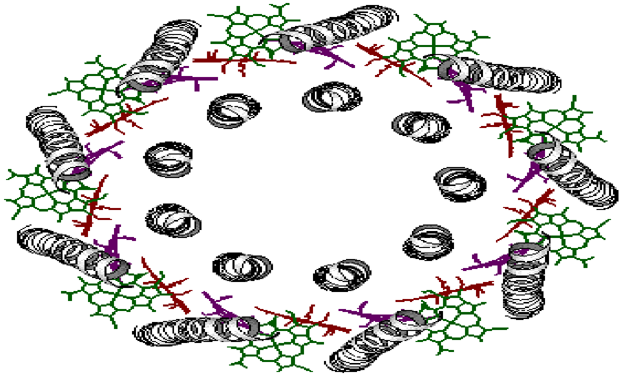


The original inspiration:
Supramolecular systems in Nature

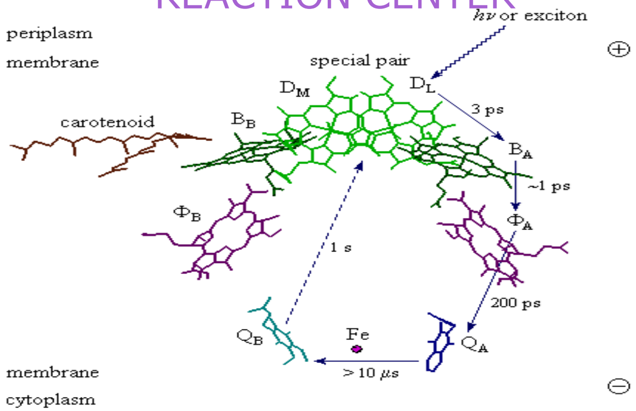
THE PHOTOSYNTHETIC APPARATUS



ANTENNA UNITS

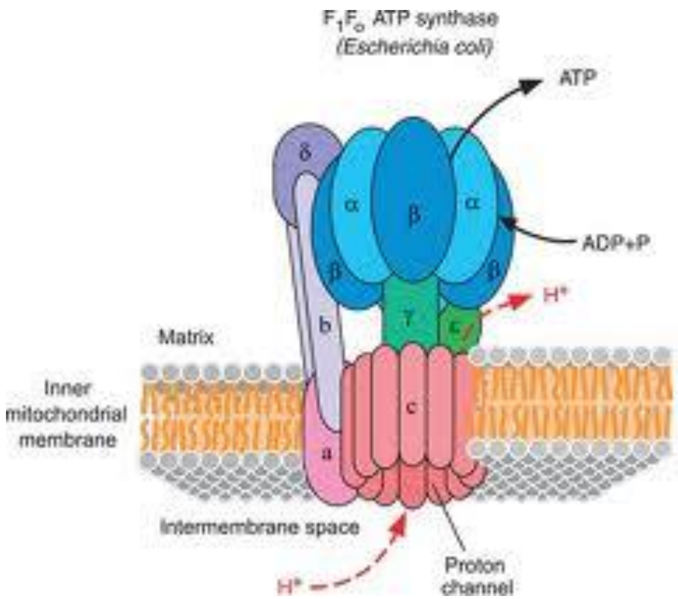


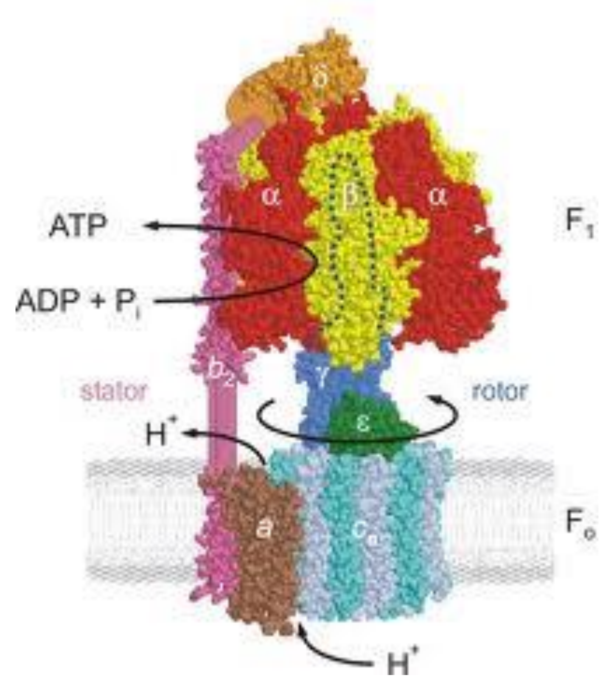
REACTION CENTER



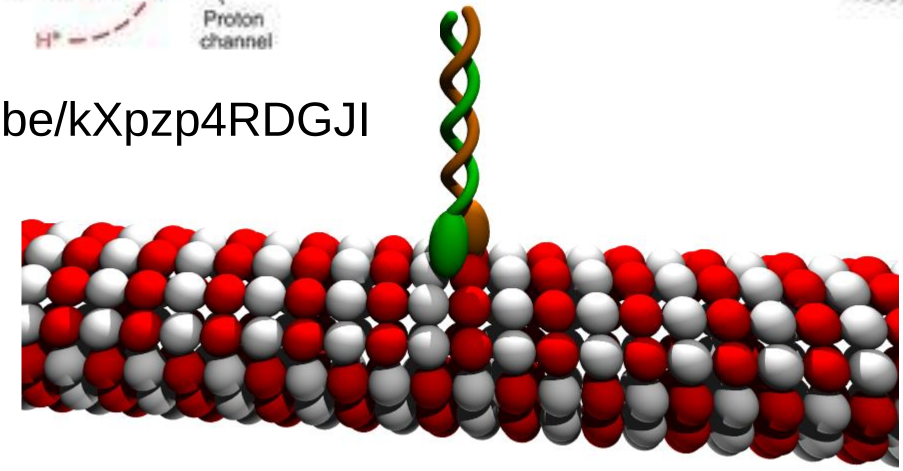
The original inspiration:
Supramolecular systems in Nature

ATP Synthase and KINESIN





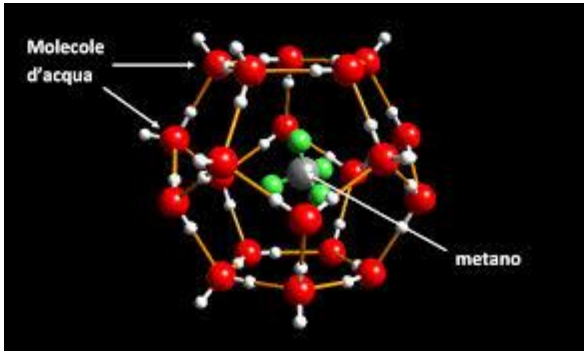
https://youtu.be/kXpzp4RDGJI



https://youtu.be/y-uuk4Pr2i8

The original inspiration: Supramolecular systems in Nature

METHANE CLATHRATE (Siberian craters)



Supramolecular Chemistry - definitions

- the chemistry beyond the molecules: molecules are already formed

- the chemistry of molecular assemblies and of the intermolecular bond: association of molecules

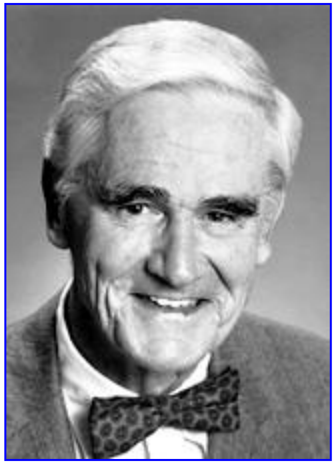
- the chemistry of the non covalent bond: weak interactions

Bottom-up approach

Nano objects

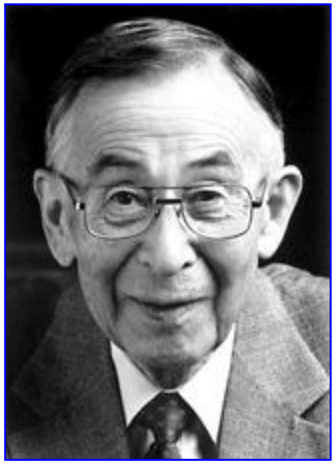
Smart and functional materials

Nobel Prize in Chemistry, 1987



Donald J. Cram

Jean-Marie Lehn



Charles J. Pedersen

«for their development and use of molecules with structure-specific interactions of high selectivity»

http://nobelprize.org/nobel_prizes/chemistry/laureates/1987/

The Nobel Prize in Chemistry, 2016

J-P. Sauvage

Sir J. F. Stoddart

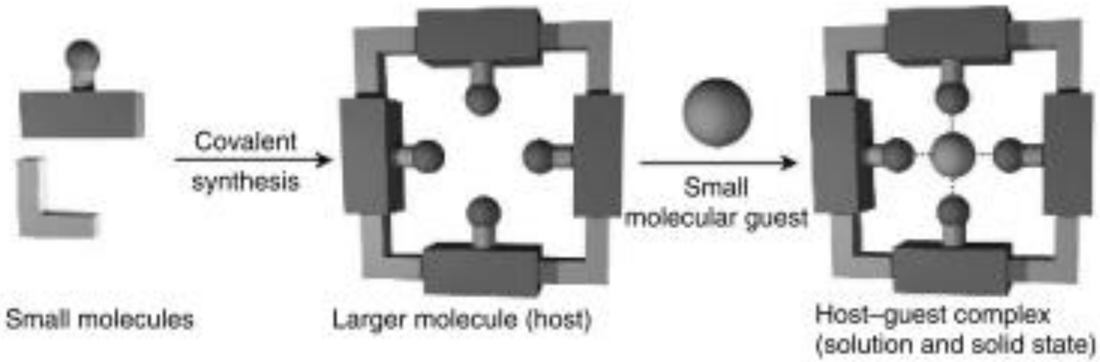
B. L. Feringa

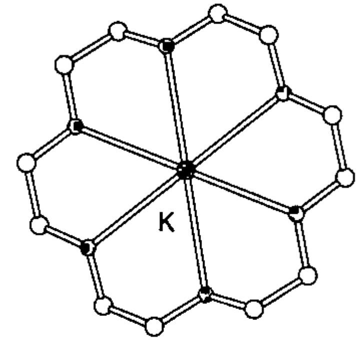
"for the design and synthesis of molecular machines"

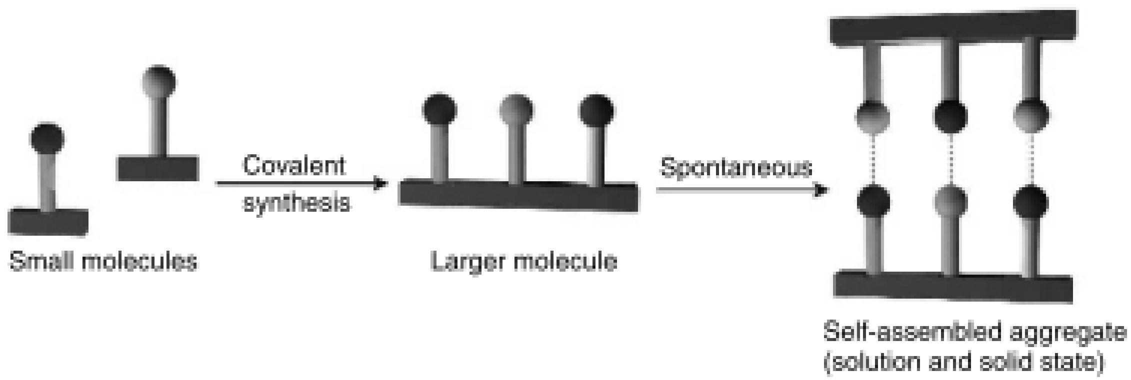
https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2016/

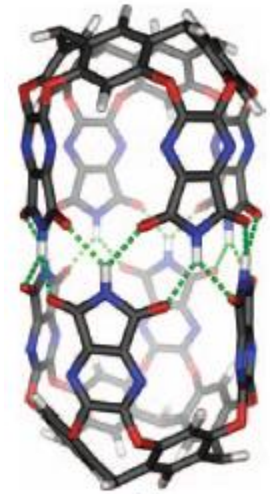
Chimica, il Nobel mancato

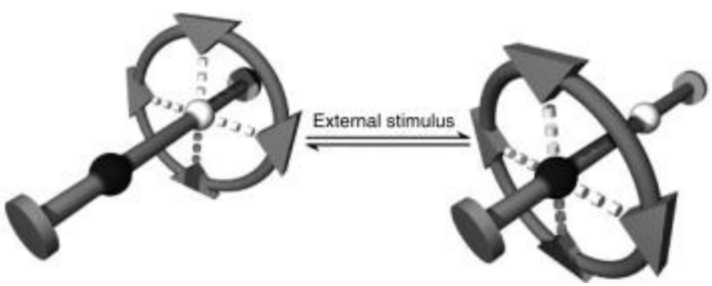
Prof. Vincenzo Balzani, docente emerito dell‘Università di Bologna



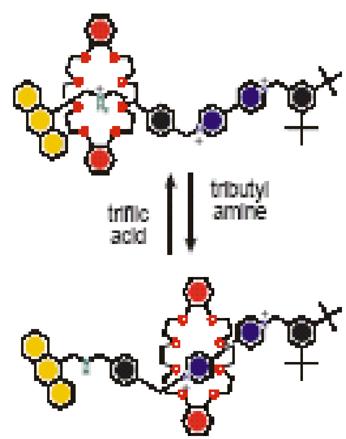




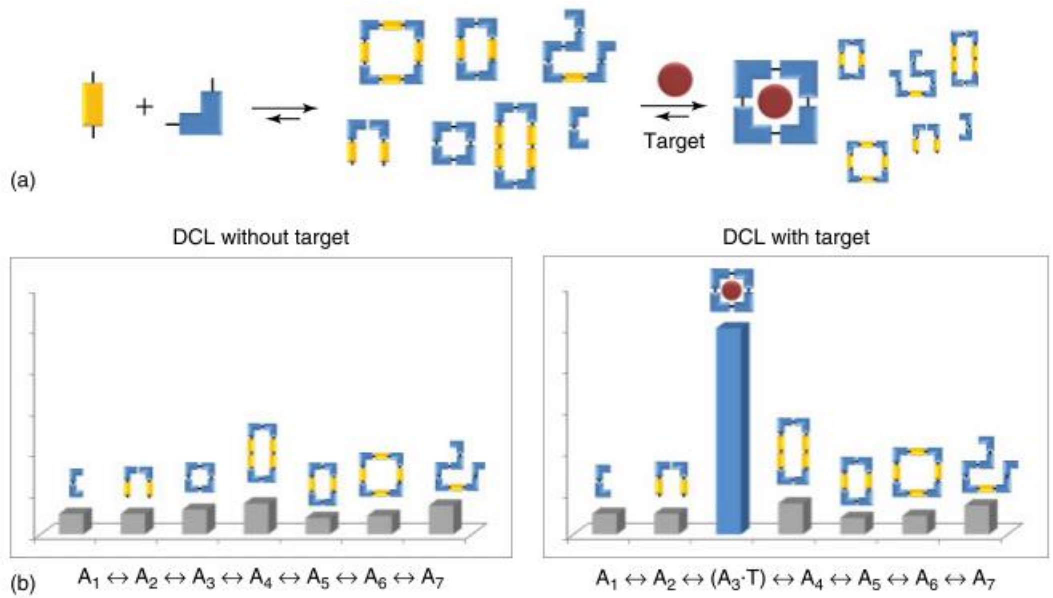




Rotaxanes and catenanes as molecular devices



DYNAMIC COMBINATORIAL LIBRARIES



nature nanotechnology

REVIEW ARTICLE

PUBLISHED ONLINE: 5 FEBRUARY 2015 | DOI: 10.1038/NNANO.2014.337

Supramolecular systems chemistry

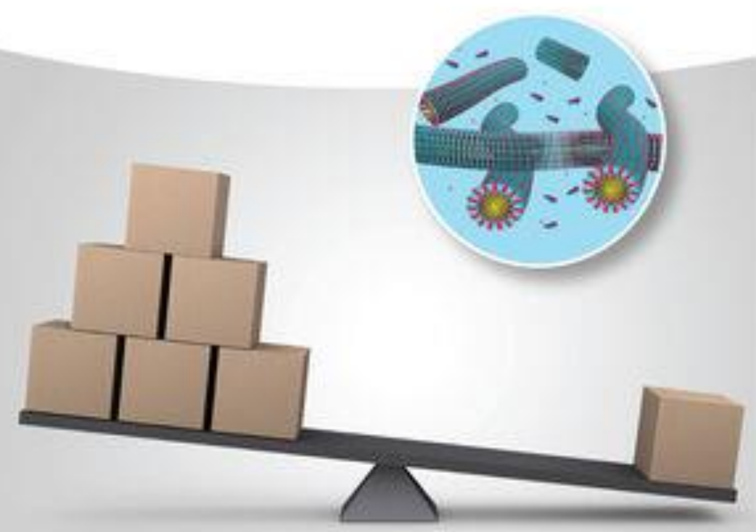
Elio Mattia and Sijbren Otto*

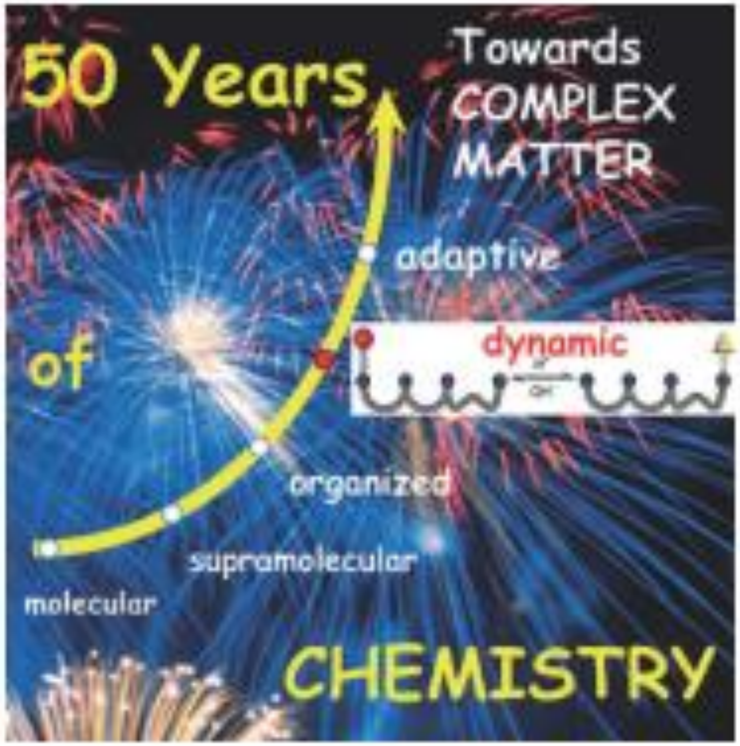
The field of supramolecular chemistry focuses on the non-covalent interactions between molecules that give rise to molecular recognition and self-assembly processes. Since most non-covalent interactions are relatively weak and form and break without significant activation barriers, many supramolecular systems are under thermodynamic control. Hence, traditionally, supramolecular chemistry has focused predominantly on systems at equilibrium. However, more recently, self-assembly processes that are governed by kinetics, where the outcome of the assembly process is dictated by the assembly pathway rather than the free energy of the final assembled state, are becoming topical. Within the kinetic regime it is possible to distinguish between systems that reside in a kinetic trap and systems that are far from equilibrium and require a continuous supply of energy to maintain a stationary state. In particular, the latter systems have vast functional potential, as they allow, in principle, for more elaborate structural and functional diversity of self-assembled systems — indeed, life is a prime example of a far-from-equilibrium system. In this Review, we compare the different thermodynamic regimes using some selected examples and discuss some of the challenges that need to be addressed when developing new functional supramolecular systems.

WILEY-VCH

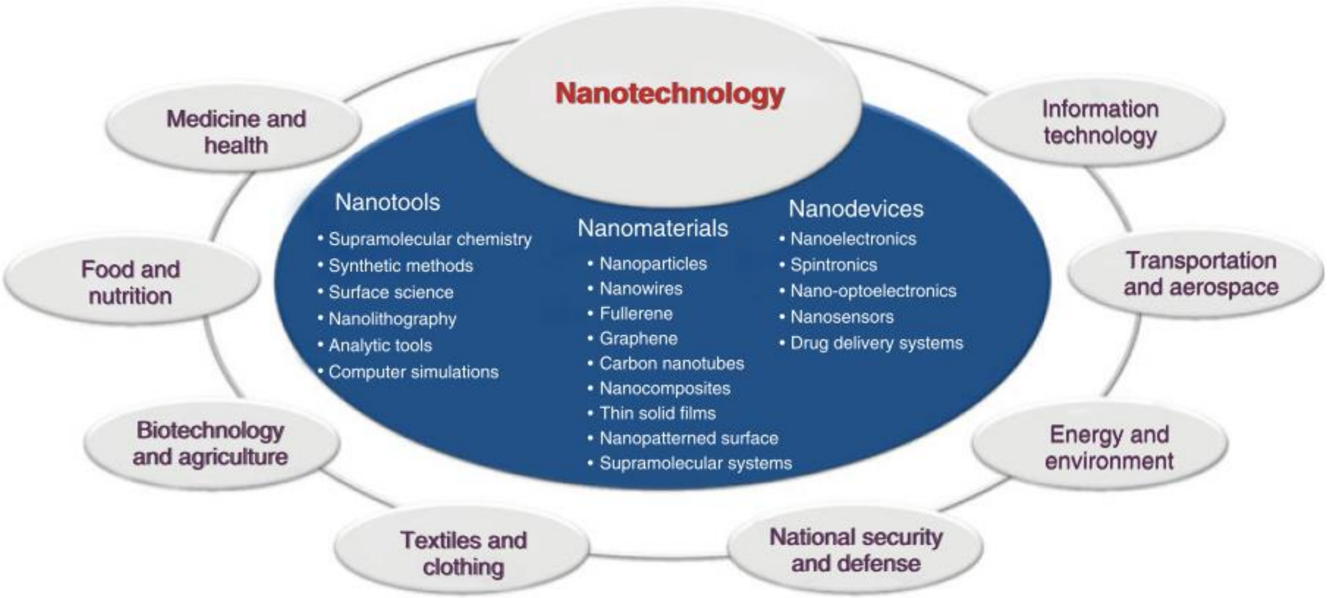
Edited by Nicolas Giuseppone
and Andreas Walther

Out-of-Equilibrium (Supra)molecular Systems and Materials




50 Years
Towards
COMPLEX
MATTER
adaptive
dynamic
of
organized
supramolecular
molecular
CHEMISTRY

From Supramolecular Chemistry to Nanotechnology



Bibliography

1. J.-M. Lehn *Supramolecular Chemistry: Concepts and Perspectives*, WCH, Weinheim (Germany), **1995**.

2. J. W. Steed, J. L. Atwood *Supramolecular Chemistry*, J. Wiley & Sons, UK, **2000**.

3. J. W. Steed, D. R. Turner, K. J. Wallace *Core Concepts in Chemistry and Nanochemistry*, Wiley, Chichester, **2007**.

4. H.-J. Schneider, A. Yatsimirsky *Principles and Methods in Supramolecular Chemistry*, J. Wiley & Sons, UK, **2000**.

5. L. F. Lindoy, I. M. Atkinson *Self-Assembly in Supramolecular Chemistry*, in *Monograms in Supramolecular Chemistry*, J. F. Stoddart ed., Royal Society of Chemistry, UK, **2000**.

6. V. Balzani, M. Venturi, A. Credi *Molecular Devices and Machines*, Wiley-VCH, Weinheim (Germany), **2003**.

7. P. J. Cragg *A Practical Guide to Supramolecular Chemistry*, J. Wiley & Sons, UK, **2005**.

8. C. A. Schalley (Ed.) *Analytical Methods in Supramolecular Chemistry*, Wiley VHC, Weinheim (Germany), **2007**.

9. P. W. N. M. Van Leeuwen *Supramolecular Catalysis*, Wiley-VCH, Weinheim (Germany), **2008**.

10. J.-P. Sauvage (Ed.) *Perspectives in Supramolecular Chemistry*, Wiley-VCH, Weinheim (Germany), **2007**.

Bibliography

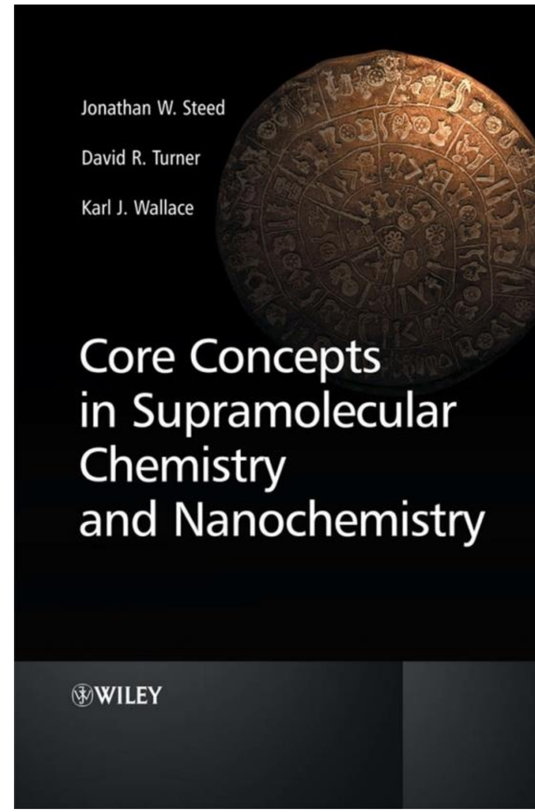
Core Concepts in Supramolecular Chemistry and Nanochemistry

Jonathan W. Steed,
Durham University, UK

David R. Turner,
Monash University, Australia

Karl J. Wallace,
University of Southern Mississippi, USA

John Wiley & Sons, Ltd



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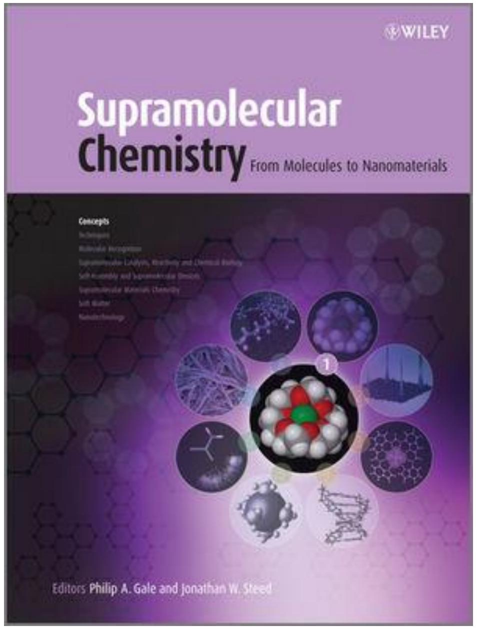
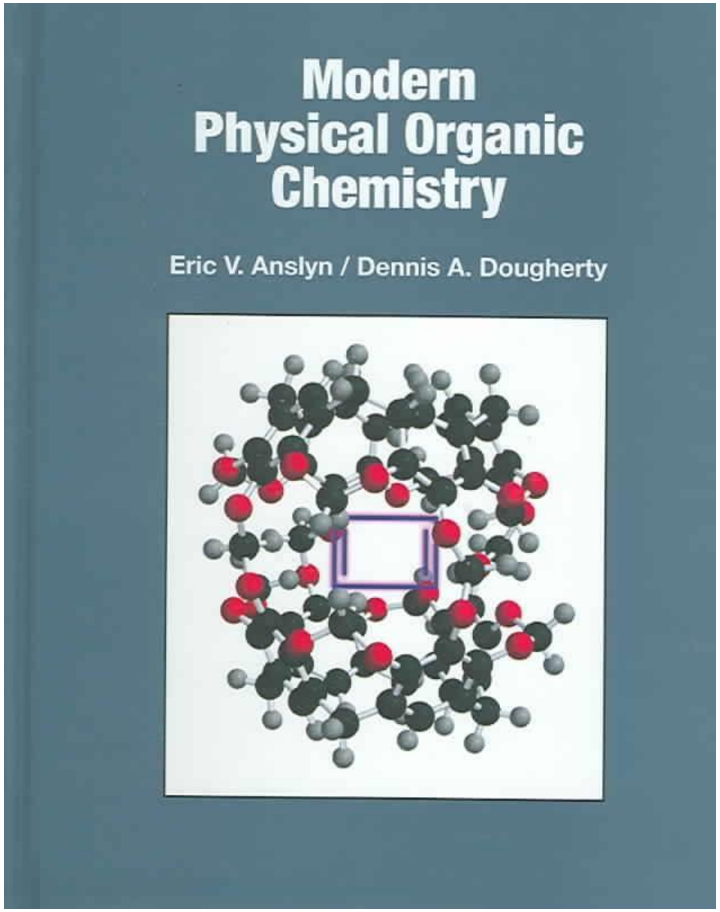


Supramolecular Chemistry: From Molecules to Nanomaterials, 8 Volume Set
Jonathan W. Steed (Editor-in-Chief), Philip A. Gale (Editor-in-Chief), Wiley.

Bibliography

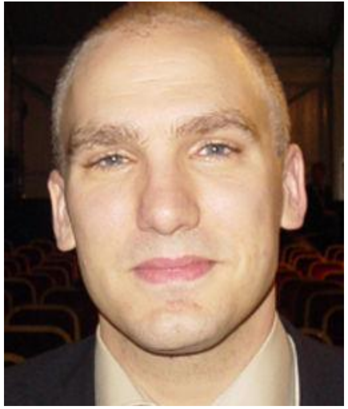


Eric V. Anslyn, Dennis A. Dougherty
University Science Books, 2006

Programma

Interazioni non covalenti
Recettori per cationi
Recettori per anioni
Esempi da articoli di letteratura
Discussione Articolo

Lezioni Prof. J. Nitschke (University of Cambridge, UK)
3a + 4a settimana di Ottobre (8h)
Metodi Analitici
Contenitori molecolari
Elicati/Catenani/Rotaxani/Nodi
Dispositivi e Macchine molecolari;
Discussione Articolo
(Problem Solving - Esercizi)



https://www.nitschkegroup-cambridge.com/

Programma

Cavitandi
Contenitori molecolari covalenti
Contenitori molecolari covalenti a legami H
Applicazioni
Discussione Articoli

Registrazione delle lezioni su *MsTeams*

Materiale su *Moddle*

Dispense e Capitolo su Metodi Analitici

Modifica

- Dispense — Modifica
- Capitolo Tecniche Analitiche — Modifica

Aggiungi un'attività o una risorsa

Diapositive Parte 1-2

Modifica

- Parte Prima — documento PDF — Modifica
- Parte Seconda — documento PDF — Modifica

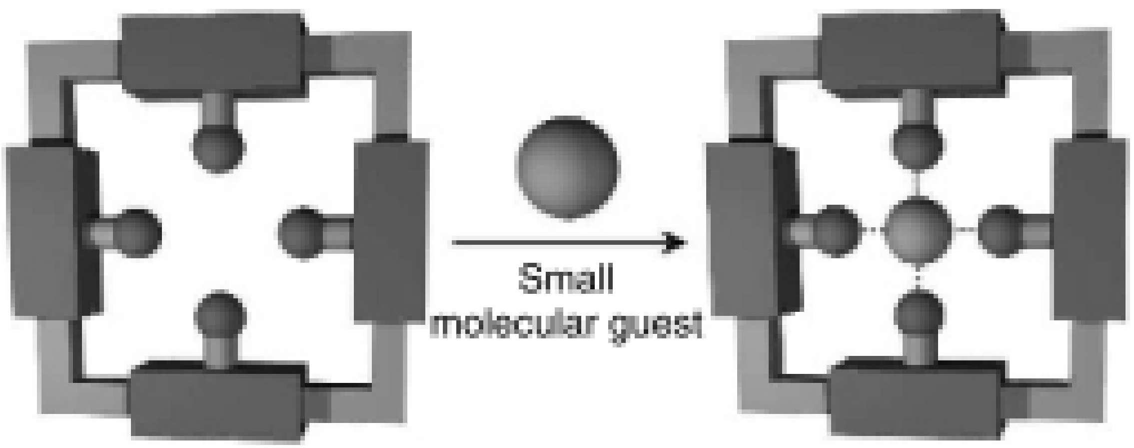
Aggiungi un'attività o una risorsa

Lezioni Prof. J. Nitschke

Modifica

- Materiale lezioni Nitschke — documento PDF — Modifica
- Articolo in discussione — documento PDF — Modifica

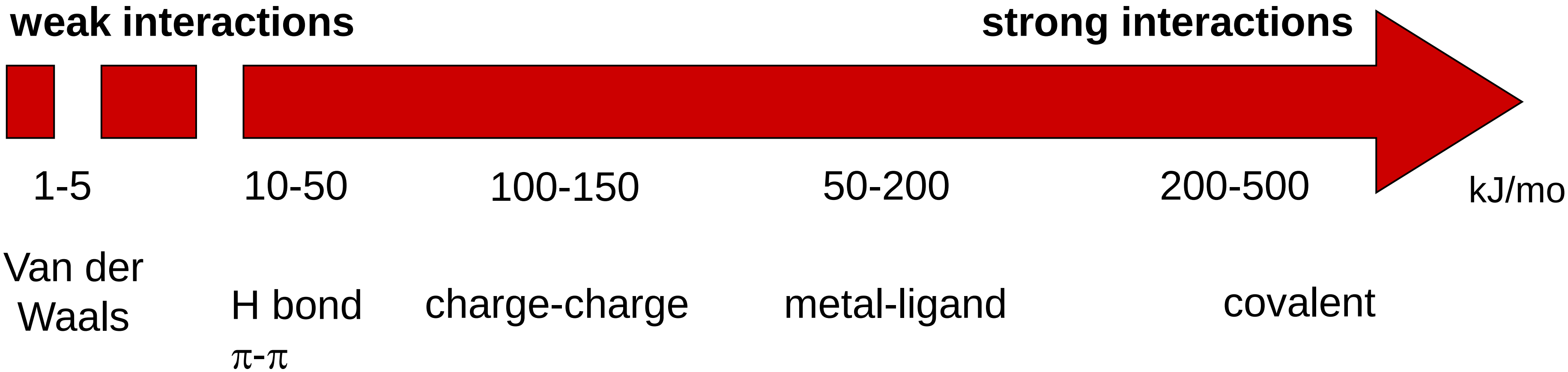
<u>Esame orale (discussione articolo)</u>


Small
molecular guest

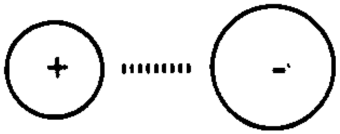
Weak (Reversible) Intermolecular Interactions

- Electrostatic
- π-π
- Cation-π/ Anion-π/CH-π
- H Bonding
- Halogen Bonding
- Metal-Ligand Coordination
- Reversible Covalent Bonding
- Chelate Effect
- Macrocyclic Effect
- Hydrophobic Effect

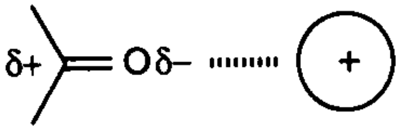
Weak Intermolecular Interactions



Electrostatic Interactions

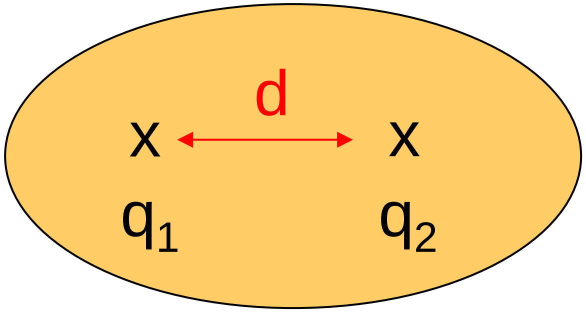


Charge-Charge Interactions 100-350 kJ/mol



Dipole-Charge Interactions 50-200 kJ/mol

Dipole-Dipole Interactions 5-50 kJ/mol



$$W = \frac{1}{4\pi\varepsilon_0}\,\frac{q_1 q_2}{\varepsilon\, d} \quad \text{(J)}$$

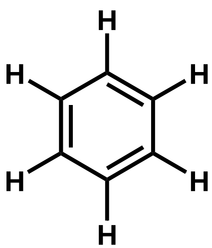
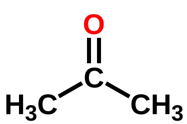
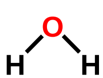
vacuum permittivity

dielectric constant (nature of solvant)

ε(vacuum) = 1

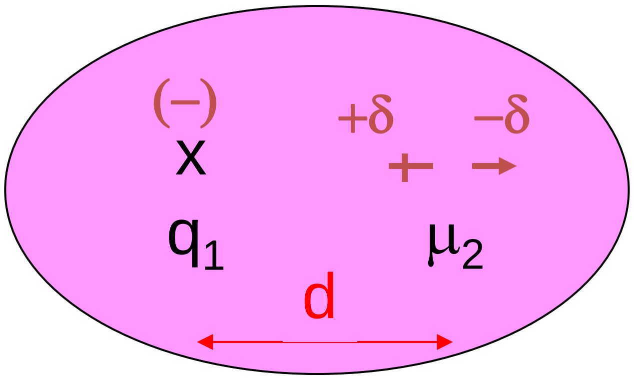
apolar medium ⇔ ε small (~ 2)
polar medium ⇔ ε big (H_2O ~ 80)

dielectric constant of the solvant

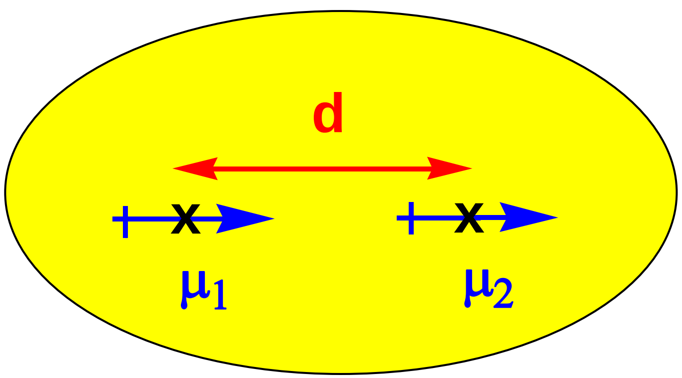
		ε
Benzene		2,3
Acetone		20,7
Ethanol	CH_3CH_2OH	24,3
water		78,5

apolar → polar

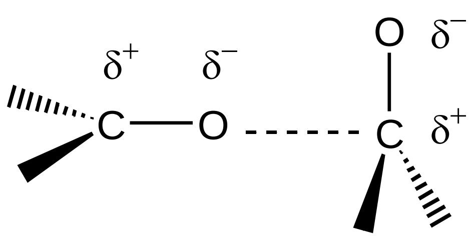
ε = 78.5 d = 0.5 nm => W = 3.75 kJ.mol^{-1}
ε = 2 d = 0.5 nm => W = 140 kJ.mol^{-1}

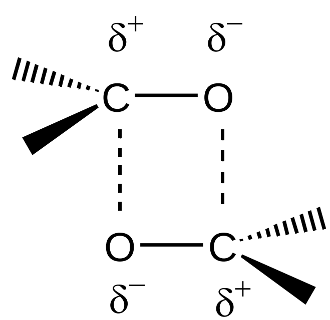


$$W = -\,C^{te} \times \frac{|q|\,\mu_2}{\varepsilon\, d^2}$$

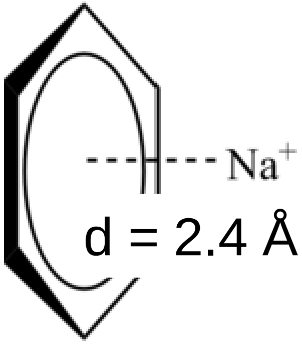


$$W = -\,C^{te}\,\frac{\mu_1\,\mu_2}{\varepsilon\, d^3}$$

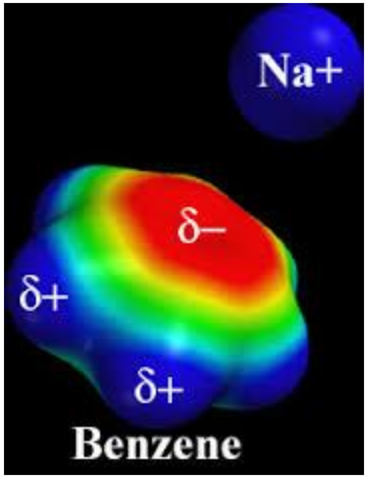


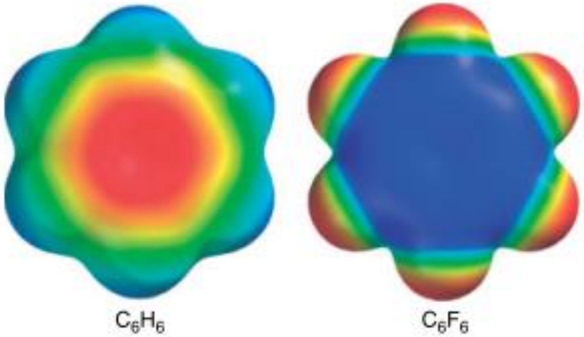


Cation-π Interactions



d = 2.4 Å





CHEMICAL REVIEWS

Review

pubs.acs.org/CR

dx.doi.org/10.1021/cr300222d | *Chem. Rev.* 2013, 113, 2100−2138

Cation−π Interaction: Its Role and Relevance in Chemistry, Biology, and Material Science

A. Subha Mahadevi and G. Narahari Sastry*

ACCOUNTS of chemical research

Vol. 46, No. 4 ■ 2013 ■ 885–893 ■ ACCOUNTS OF CHEMICAL RESEARCH

The Cation−π Interaction

DENNIS A. DOUGHERTY

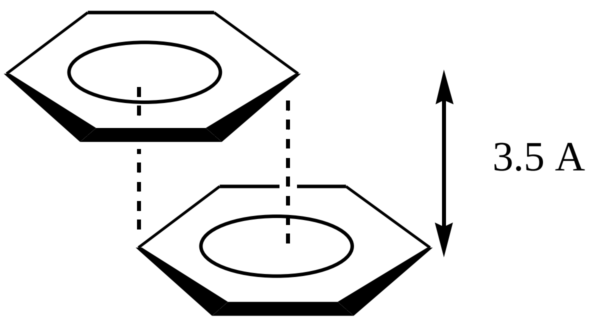
Chem. Rev. **1997,** *97,* 1303−1324

The Cation−π Interaction

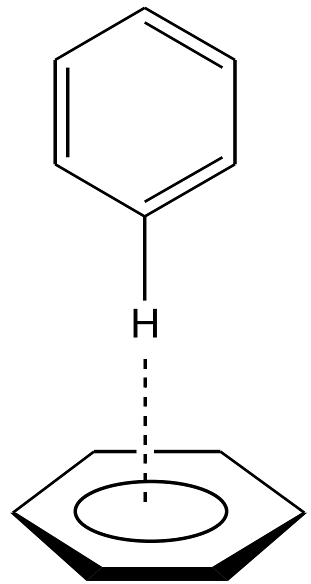
Jennifer C. Ma and Dennis A. Dougherty*

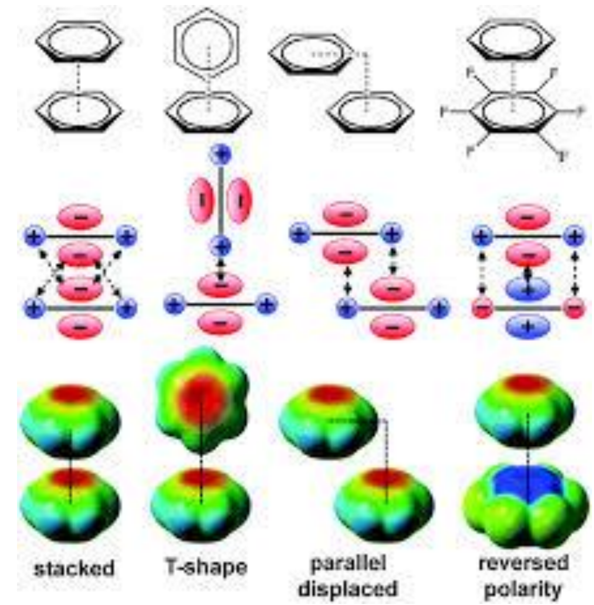
π-π Interactions up to 50 kJ/mol

edge to face



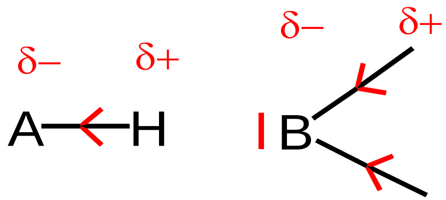
face to face



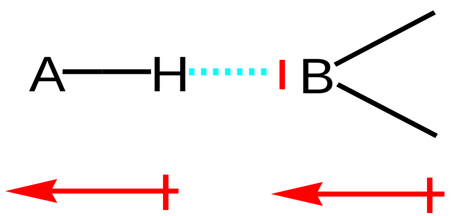


- C.A. Hunter and J.K.M. Sanders, ***The Nature of π - π interactions***, *J. Am. Chem. Soc.,* **1990**, *112*, 5525;
- E.-I. Kim, S. Paliwal and C.S. Wilcox, ***Measurements of molecular electrostatic field effects in edge-to-face aromatic interactions and CH- π interactions with implications for protein folding and molecular recognition***, *J. Am. Chem. Soc*., **1998**, *120*, 11192.

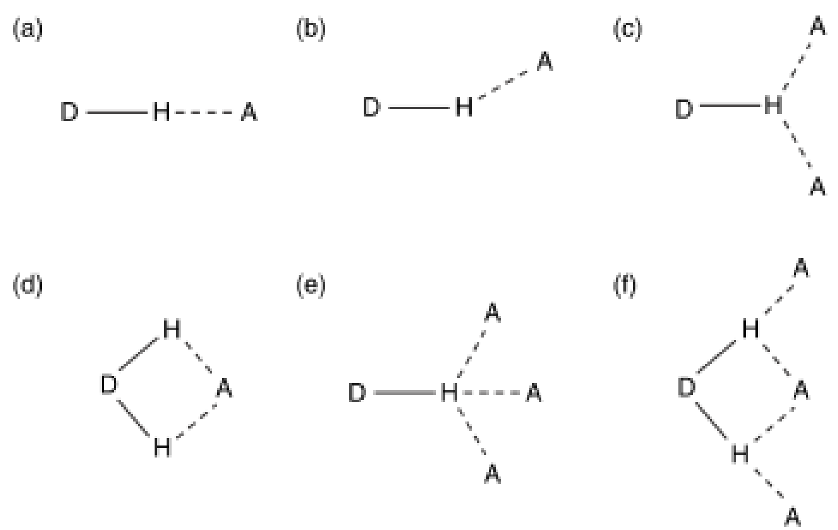
H Bond 4-120 kJ/mol

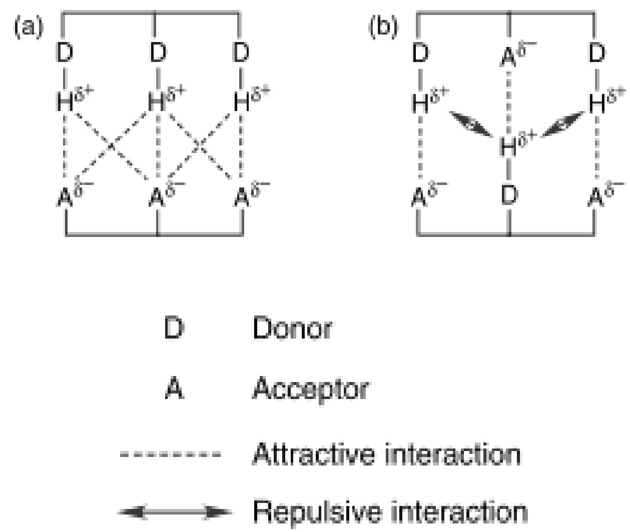


A, B electronegative or electrondeficient atoms

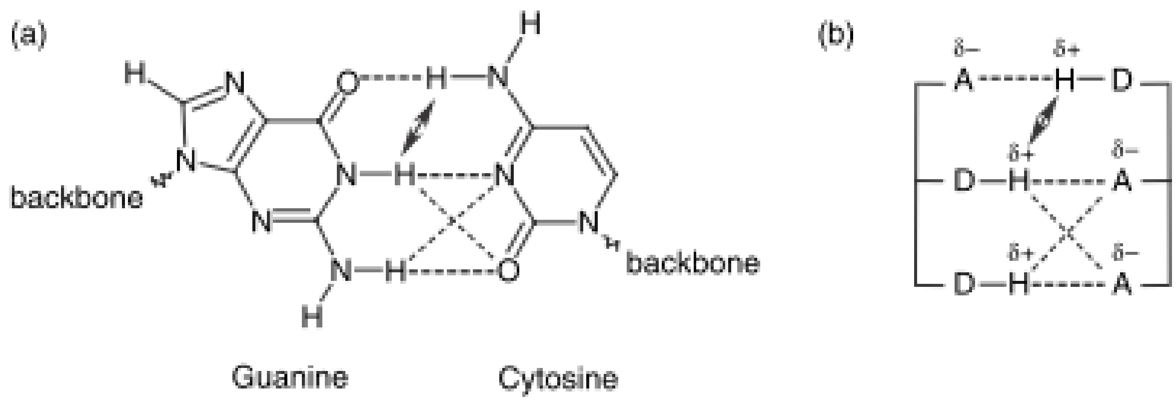


permanent dipoles





(a)
D
D
D
$H^{\delta+}$
$H^{\delta+}$
$H^{\delta+}$
$A^{\delta-}$
$A^{\delta-}$
$A^{\delta-}$
(b)
D
$A^{\delta-}$
D
$H^{\delta+}$
$H^{\delta+}$
$H^{\delta+}$
$A^{\delta-}$
D
$A^{\delta-}$
D Donor
A Acceptor
Attractive interaction
Repulsive interaction



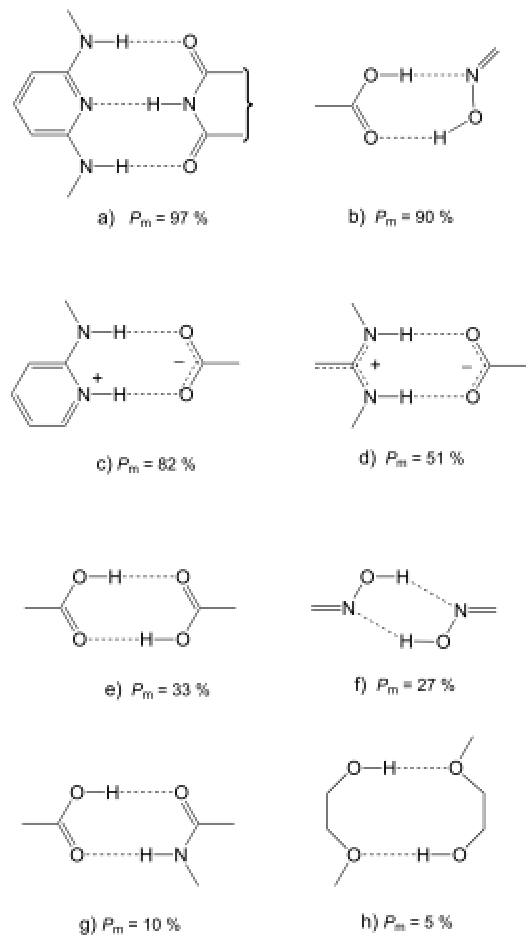
(a)
backbone
backbone
Guanine
Cytosine
(b)
δ−
δ+
A
H
D
δ+
δ−
D
H
A
δ+
δ−
D
H
A

	Strong	Moderate	Weak
interaction type	strongly covalent	mostly electrostatic	electrostat./ dispers.
bond lengths [Å]			
$H \cdots A$	1.2 – 1.5	1.5 – 2.2	> 2.2
lengthening of X–H [Å]	0.08 – 0.25	0.02 – 0.08	< 0.02
X–H versus $H \cdots A$	$X\text{–}H \approx H \cdots A$	$X\text{–}H < H \cdots A$	$X\text{–}H \ll H \cdots A$
$X \cdots A$ [Å]	2.2 – 2.5	2.5 – 3.2	> 3.2
directionality	strong	moderate	weak
bond angles [°]	170 – 180	> 130	> 90
bond energy [$kcal\,mol^{-1}$]	15 – 40	4 – 15	< 4
relat. IR shift $\Delta\tilde{\nu}_{XH}$ [cm^{-1}]	25 %	10 – 25 %	< 10 %
^{1}H downfield shift	14 – 22	< 14	

The Hydrogen Bond in the Solid State

Thomas Steiner*

Angew. Chem. Int. Ed. **2002**, *41*, 48–76



Scheme 17. Eight examples of intermolecular hydrogen bond motifs with their probability of formation (P_m) in crystals.[122] Notice that P_m of the carboxy–oxime heterodimer (b) is much higher than that of the carboxylic acid (e) and oxime homodimers (f).

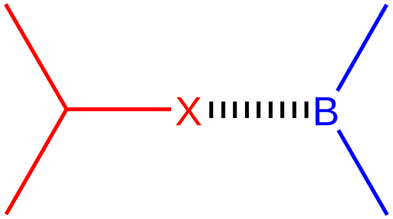
Halogen Bond

In 2009 the International Union of Pure and Applied Chemistry (IUPAC) started a project (project no. 2009-032-1-100) having the aim " to take a comprehensive look at intermolecular interactions involving halogens as electrophilic species and classify them"
http://www.halogenbonding.eu/
http://www.iupac.org/web/ins/2009-032-1-100

An IUPAC recommendation defining these interactions as halogen bonds was issued in 2013 when the project was concluded: This definition states that

" A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity. "

Halogen Bond



B : Lewis base (neutral or anionic)

X : electron-poor halogen atom

- Very directional (180°, but also other geometries)
- As strong as H-bond
- Often encountered in solid state, more rarely in solution

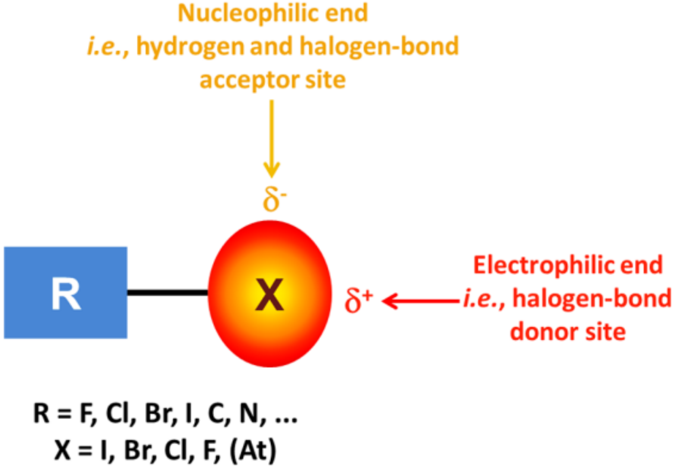
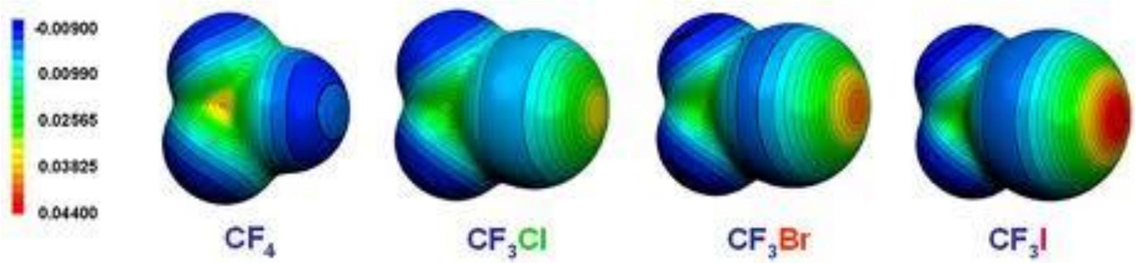


Figure 21. Schematic representation of the anisotropic distribution of the electron density around covalently bound halogen atoms and the pattern of the resulting interactions.



molecule	atom	bond producing a σ-hole
H_3C-F	F	C−F
H_3C-Cl	Cl	C−Cl
H_3C-Br	Br	C−Br
H_3C-I	I	C−I
F_3C-F	F	C−F
F_3C-Cl	Cl	C−Cl
F_3C-Br	Br	C−Br
F_3C-I	I	C−I
NC−F	F	C−F
NC−Cl	Cl	C−Cl
NC−Br	Br	C−Br
NC−I	I	C−I
		Dihalogens
F−F	F	F−F
Cl−Cl	Cl	Cl−Cl
Br−Br	Br	Br−Br
		Focus on Bromine
Br—C≡C—Br	Br	C−Br
H_3Si-Br	Br	C−Br
F_3Si-Br	Br	Si−Br
H_3Ge-Br	Br	Ge−Br
H_2N-Br	Br	N−Br
F_2N-Br	Br	N−Br
H_2P-Br	Br	P−Br
F_2P-Br	Br	P−Br
HO−Br	Br	O−Br
FO−Br	Br	O−Br
HS−Br	Br	S−Br
FS−Br	Br	S−Br
F−Br	Br	F−Br
Cl−Br	Br	Cl−Br

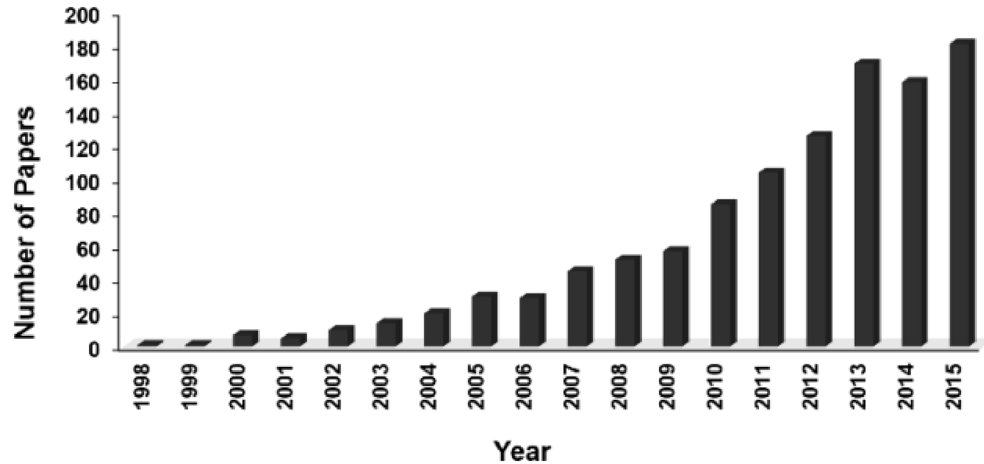
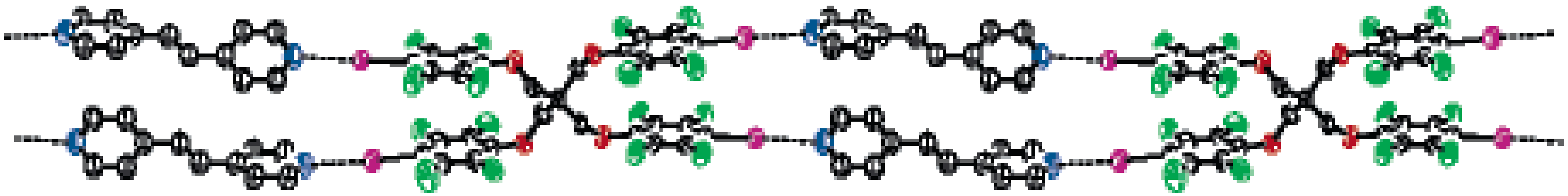
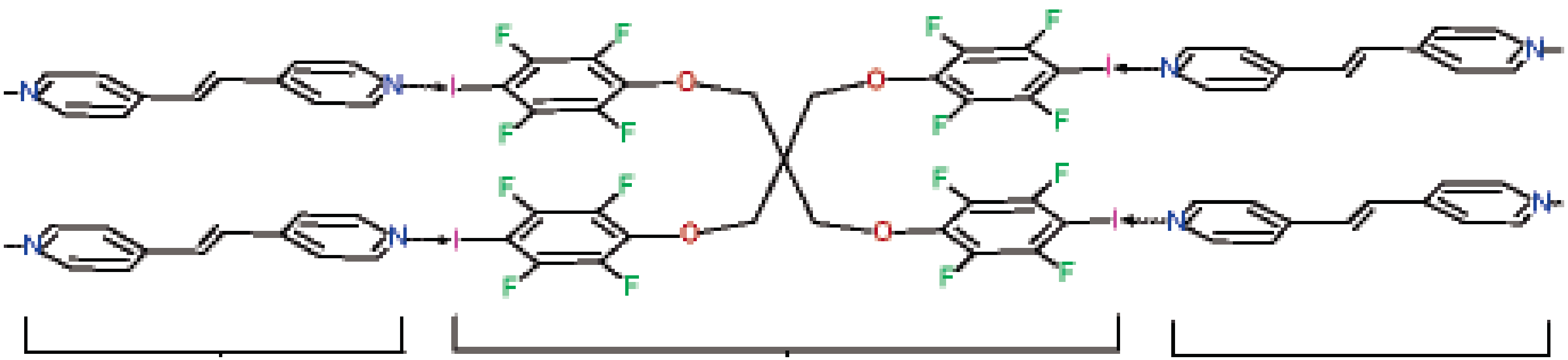
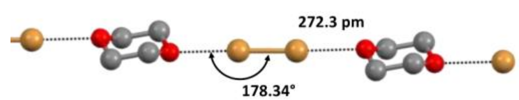


Figure 5. Number of papers per year having "halogen bonding" in the title and/or abstract (source SciFinder, search performed in November 2015).



14





Anion-π Interactions

Proposed by three research groups of theoreticians independently in 2002 based on their theoretical calculations, anion −π interactions are defined as attractive interactions between negatively charged species and electron-deficient aromatic rings.

Typical anion−π interaction indicates the attraction of an anion species to the centroid of an aromatic ring.

In comparison to a plethora of theoretical calculations of anion−π interactions, experimental studies on these intriguing noncovalent bond interactions are limited.

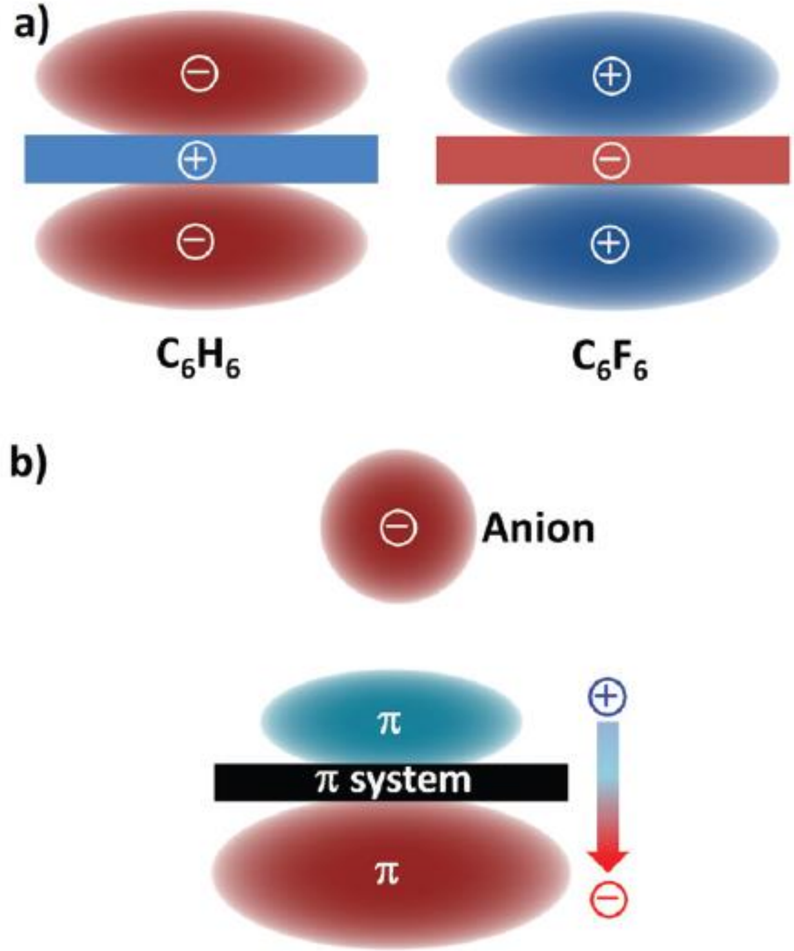


Fig. 1 (a) Schematic representation of the quadrupole moments of benzene (C_6H_6; Q_{zz} = −8.45 B) and hexafluorobenzene (C_6F_6; Q_{zz} = +9.50 B)[21] and (b) the ion-induced dipole[22] (the molecular polarizabilities parallel to the main symmetry axis are $\alpha_{\parallel}$ = 41.5 and 37.7 a.u (a.u. stands for atomic units), for benzene and hexafluorobenzene respectively).

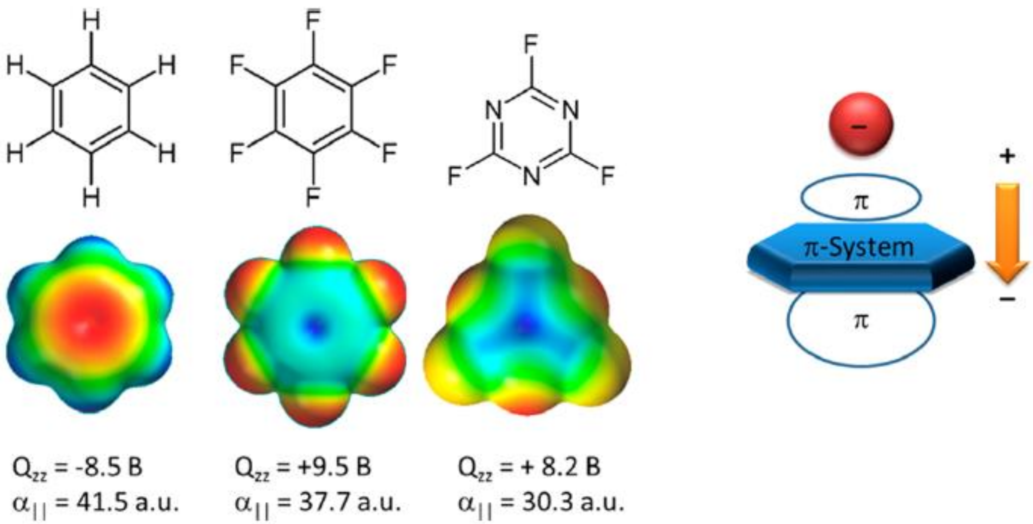


Figure 5. Structures and electron-density surfaces of selected arenes showing low electron density (blue region) in the aromatic core of C_6F_6 and $C_3N_3F_3$ (left). In addition the concept of "anion-induced dipole moment" is illustrated (right).[88]

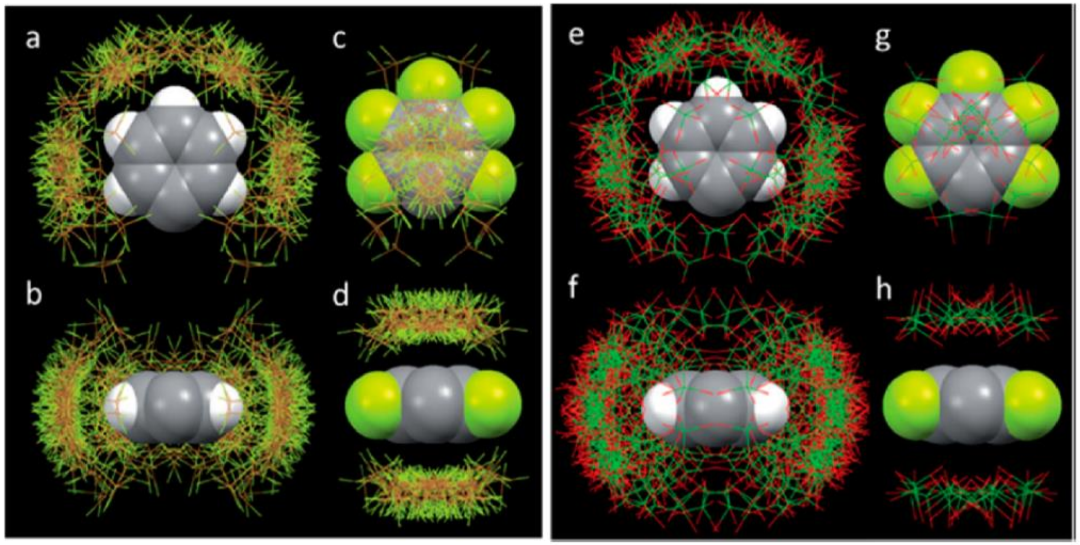
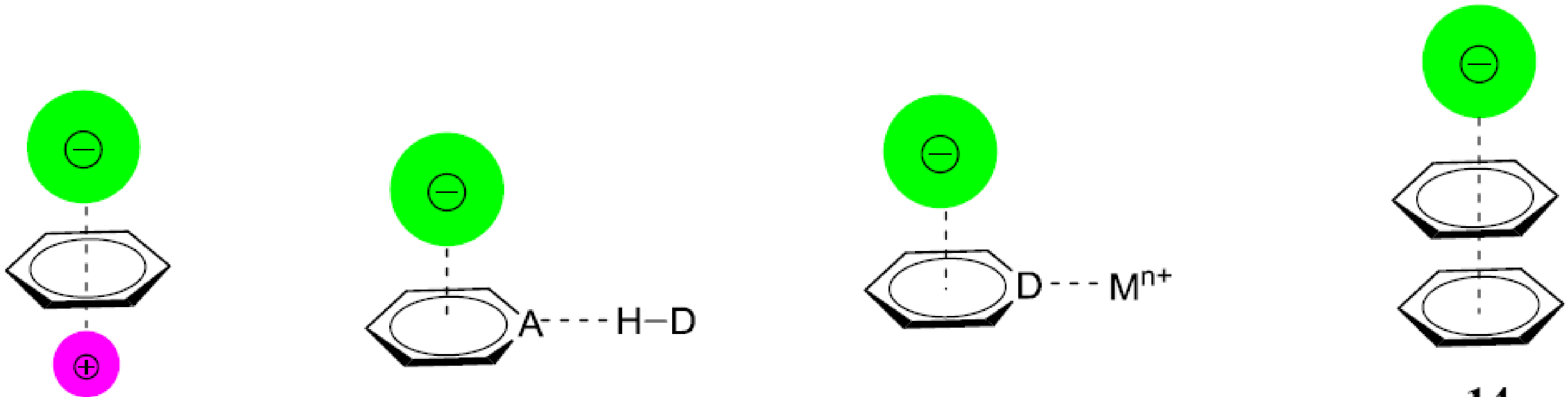


Figure 20. IsoStar plots showing anion contacts between C_6H_5 and BF_4^- (a and b) and ClO_4^- (e and f) as well as anion−π interactions between C_6F_5 and BF_4^- (c and d) and ClO_4^- (g and h). Reproduced and adapted with permission from ref 22. Copyright 2011 John Wiley and Sons.



11 Anion-π-cation

12 Hydrogen-bond donor

13 Metal atom coordination

14 Anion-π-π

Fig. 4. Illustration of diverse factors affecting the strength of anion-π interactions.

Review Coordination Chemistry Reviews 415 (2020) 213327

Emergence of anion-π interactions: The land of opportunity in supramolecular chemistry and beyond

Ishfaq Ahmad Rather, Shafieq Ahmad Wagay, Rashid Ali *

Anion−π Interactions with Fluoroarenes

Michael Giese,*,† Markus Albrecht,*,‡ and Kari Rissanen*,§

DOI: 10.1021/acs.chemrev.5b00156
Chem. Rev. 2015, 115, 8867−8895

Cite this: *Inorg. Chem. Front.*, 2014, **1**, 35

The anion–π interaction: naissance and establishment of a peculiar supramolecular bond

Patrick Gamez[a,b]

Supramolecular Chemistry

DOI: 10.1002/anie.201100208

Putting Anion–π Interactions Into Perspective

Antonio Frontera, Patrick Gamez,* Mark Mascal,* Tiddo J. Mooibroek,* and Jan Reedijk**

Angew. Chem. Int. Ed. **2011**, 50, 9564–9583

Metal-Ligand Interaction

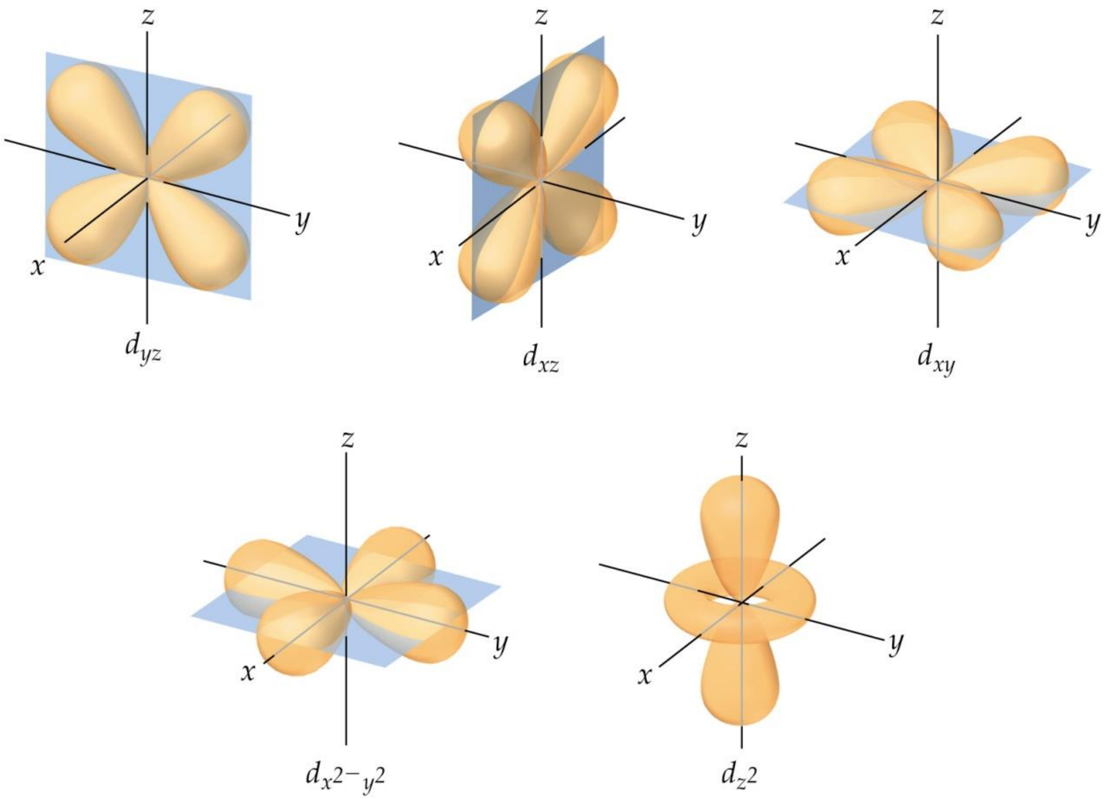
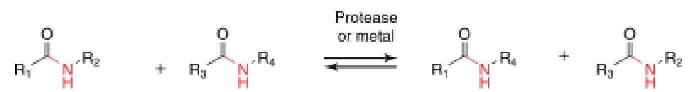
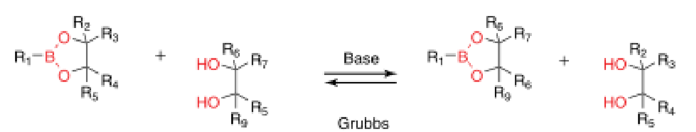
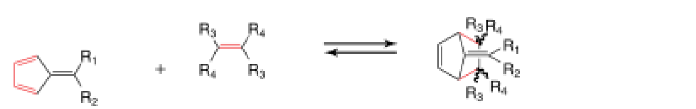
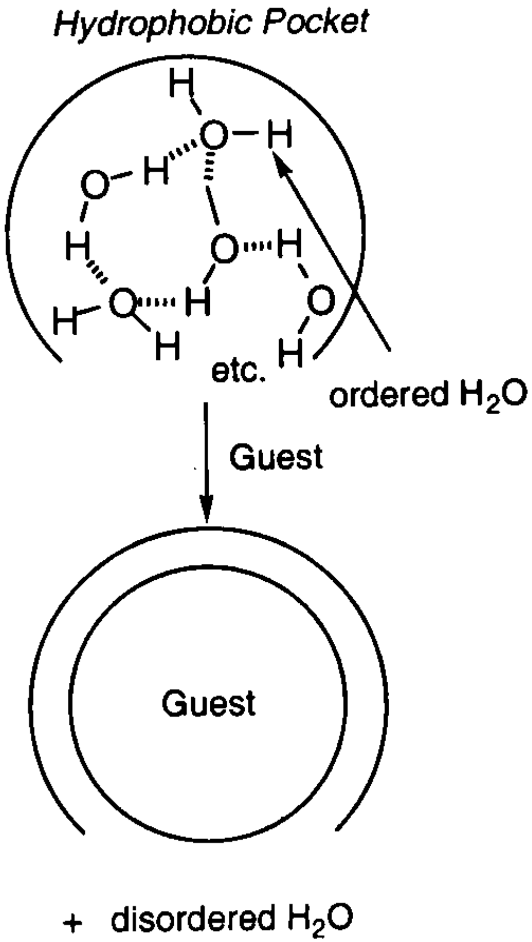
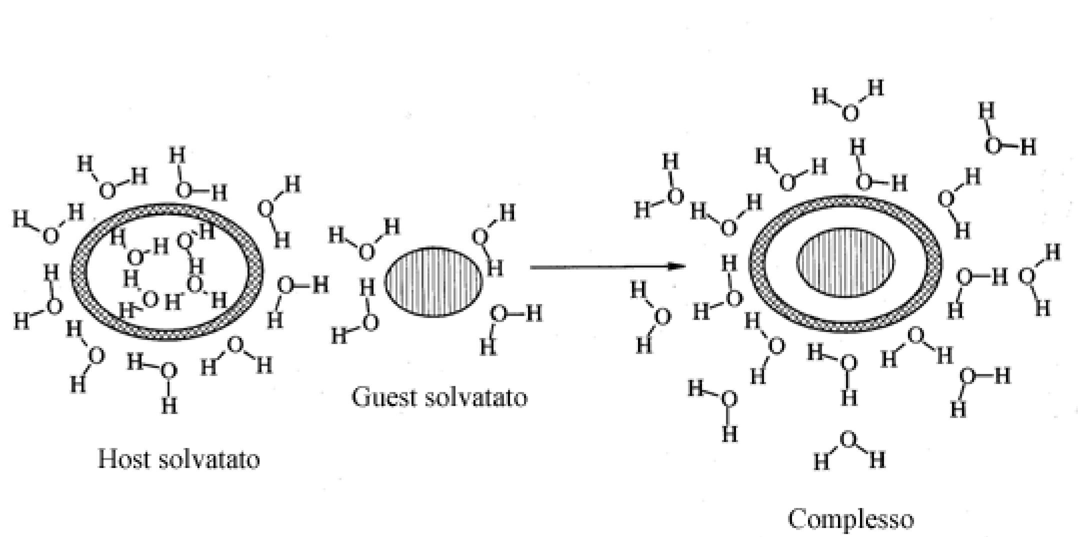


Table 1 Reversible covalent reactions.

Reaction	Scheme
C=N exchange	
Transmination	
Hydrazone exchange	
Oxime exchange	
Acyl exchange	
Transesterification	
Transthioesterification	
Transamidation	
Michael-addition	
Miscellaneous	
Disulfide exchange	
Boronic ester exchange	
Olefin metathesis	
Acetal exchange	
Diels–Alder	

Hydrophobic Effect





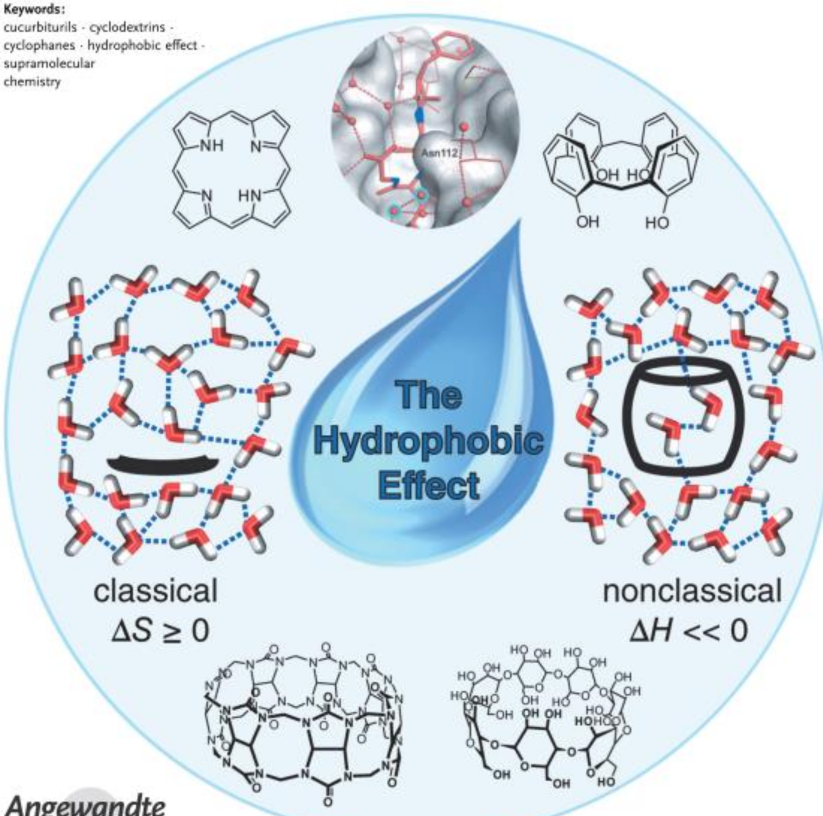
Hydrophobic Effect

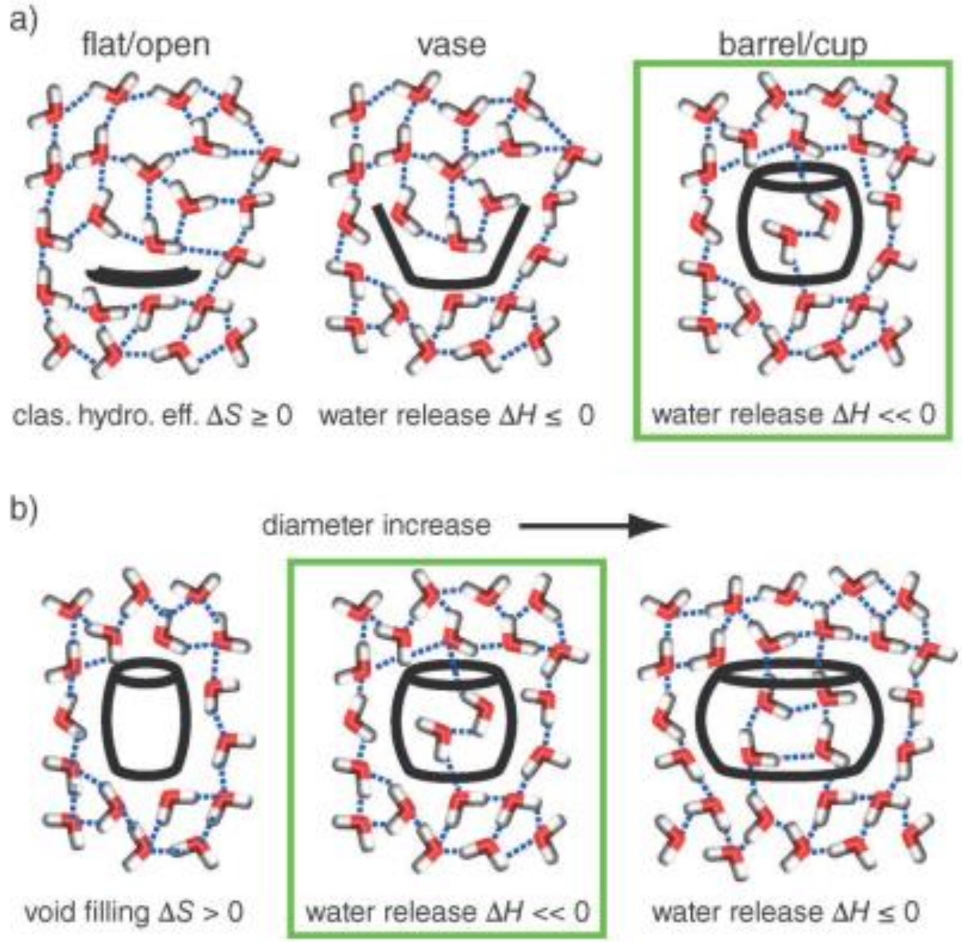
DOI: 10.1002/anie.201310958

The Hydrophobic Effect Revisited—Studies with Supramolecular Complexes Imply High-Energy Water as a Noncovalent Driving Force

Frank Biedermann, Werner M. Nau,* and Hans-Jörg Schneider**

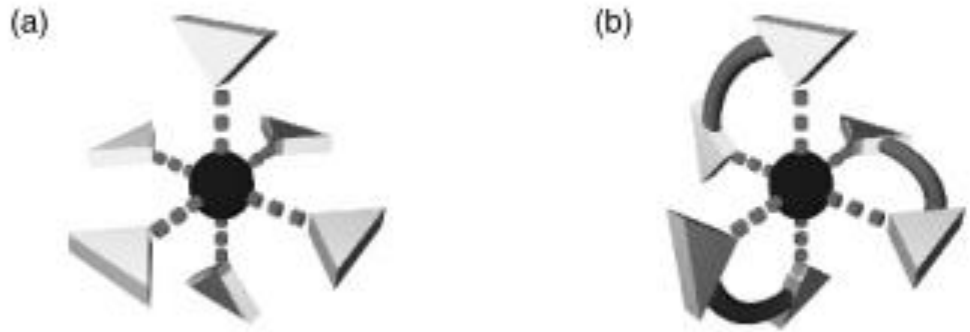
Keywords:
cucurbiturils · cyclodextrins · cyclophanes · hydrophobic effect · supramolecular chemistry





a)
flat/open
vase
barrel/cup
clas. hydro. eff. ΔS ≥ 0
water release ΔH ≤ 0
water release ΔH << 0
b)
diameter increase
void filling ΔS > 0
water release ΔH << 0
water release ΔH ≤ 0

Chelate Effect



$$[Ni(NH_3)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \underset{}{\overset{\log K = 8.76}{\rightleftharpoons}} [Ni(NH_2CH_2CH_2NH_2)_3]^{2+} + 6NH_3$$

$$[Ni(H_2O)_6]^{2+} + 6NH_3 = [Ni(NH_3)_6]^{2+} + 6H_2O$$

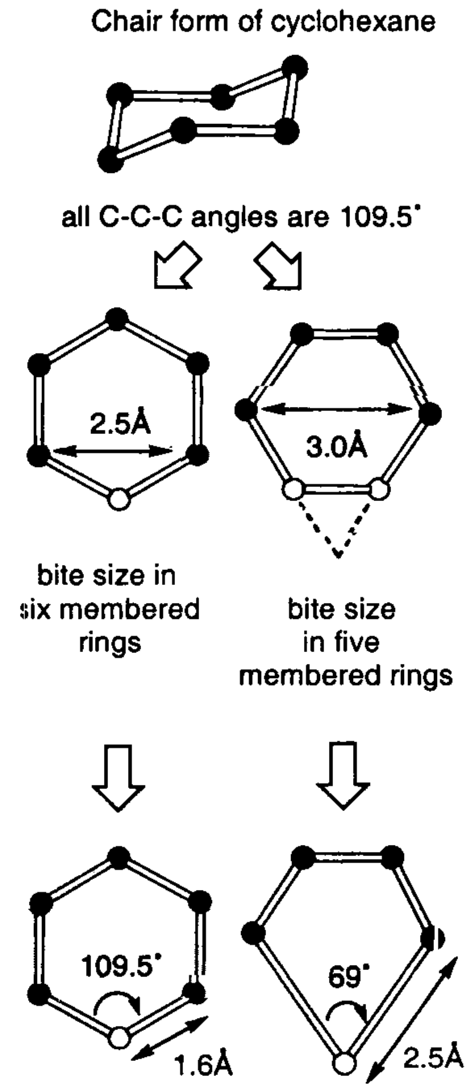
$$\beta \sim 10^9, \Delta G = -51.8 \text{ kJ mol}^{-1},$$

$$\Delta H = -100 \text{ kJ mol}^{-1}, \Delta S = -163 \text{ J mol}^{-1}\text{K}^{-1}$$

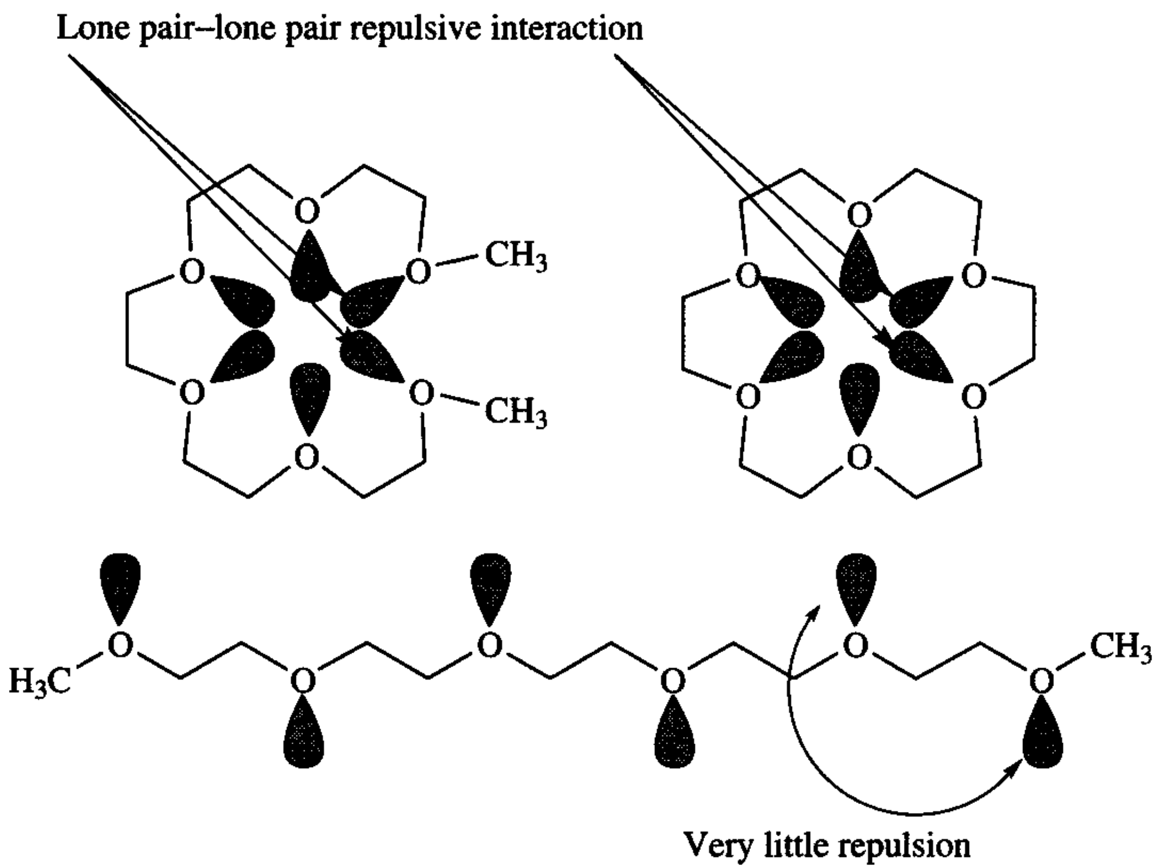
$$[Ni(H_2O)_6]^{2+} + 3en = [Ni(en)_3]^{2+} + 6H_2O$$

$$\beta \sim 10^{18}, \Delta G = -101.8 \text{ kJ mol}^{-1},$$

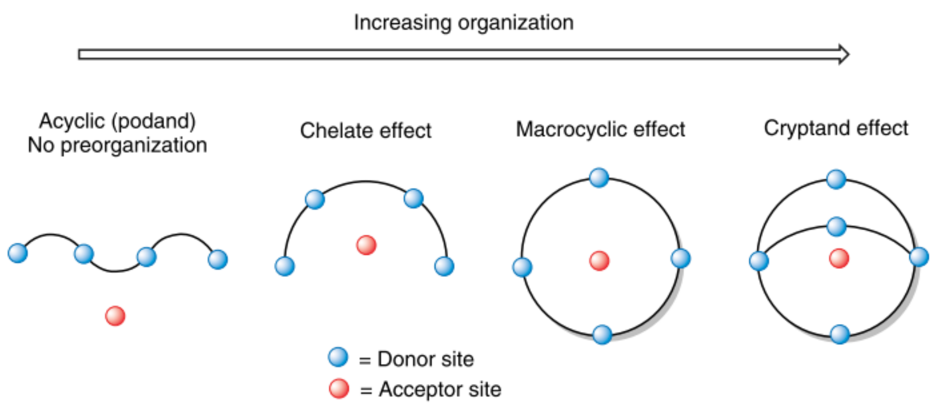
$$\Delta H = -117 \text{ kJ mol}^{-1}, \Delta S = -42 \text{ J mol}^{-1}\text{K}^{-1}$$

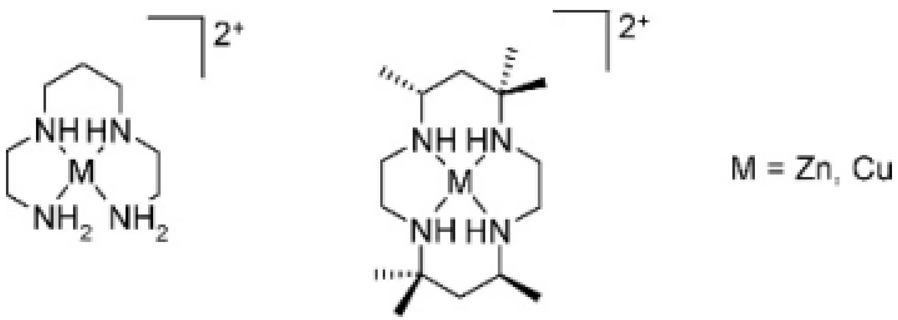


Macrocyclic Effect



Macrocyclic Effect





Stabilià: Sistema Ciclico 10^4 superiore Sistema Aciclico

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Cite this: *Chem. Soc. Rev.*, 2017, **46**, 2622

Assessing cooperativity in supramolecular systems†

Larissa K. S. von Krbek,‡[a] Christoph A. Schalley *[a] and Pall Thordarson *[b]