

Introduction to Supramolecular Polymers

Charles-André Fustin

**Institute of Condensed Matter and Nanosciences (IMCN)
Bio- and Soft Matter division (BSMA)
Université catholique de Louvain
Belgium**

Supramolecular chemistry

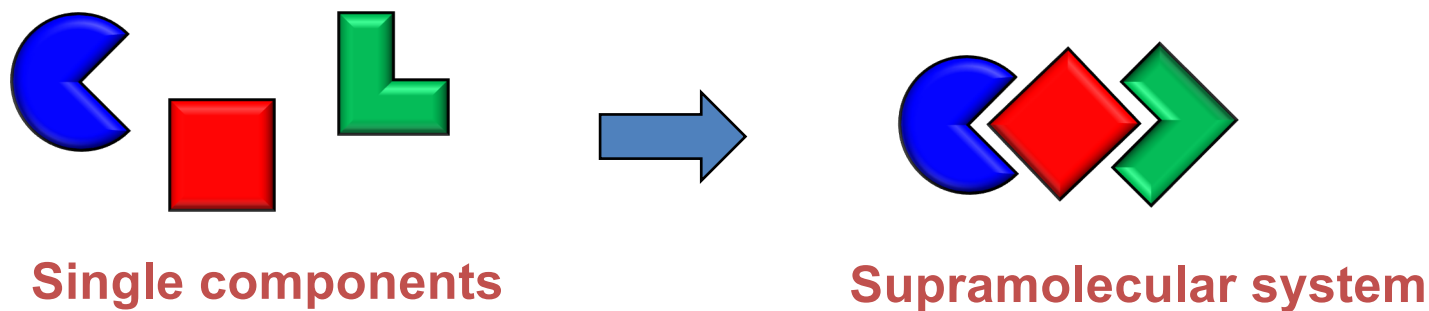
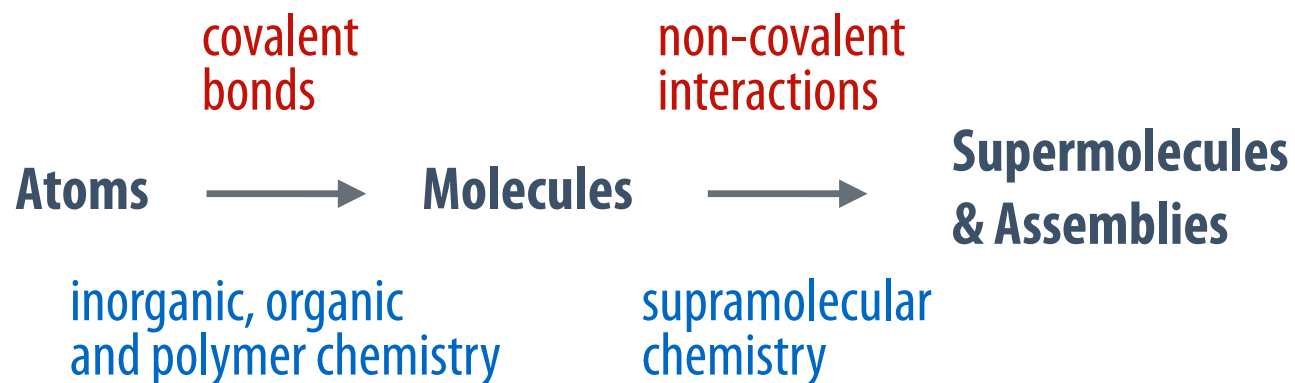
« Supramolecular chemistry is chemistry 'beyond the molecule', the science of non-covalent, intermolecular interactions »

« Just as there is a field of molecular chemistry based on the covalent bond, there is a field of supramolecular chemistry, the chemistry of molecular assemblies and of the intermolecular bond. »

1987

Nobel Prize for J.-M. Lehn, D. J. Cram, C. J. Pedersen

Supramolecular chemistry



Supramolecular systems display (new) additional properties

Two “sub-domains”

Supramolecules

- well-defined, discrete species formed from a defined, finite number of molecules
- the equivalent of low molecular weight organic molecules

host-guest chemistry

Supramolecular Assemblies

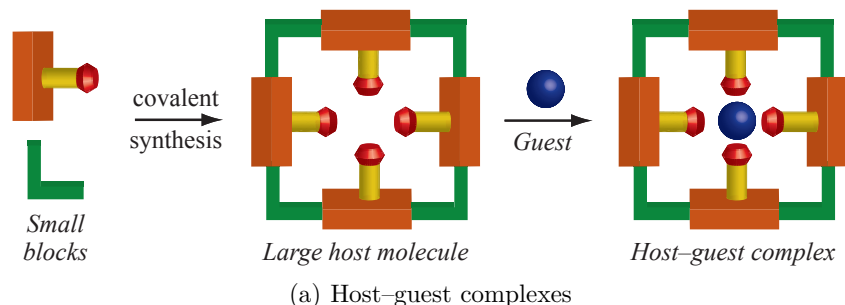
- polymolecular entities from spontaneous, but defined association of many molecules
- the equivalent of high molecular weight polymers and macromolecules

supramolecular self-assembly

Supramolecular chemistry

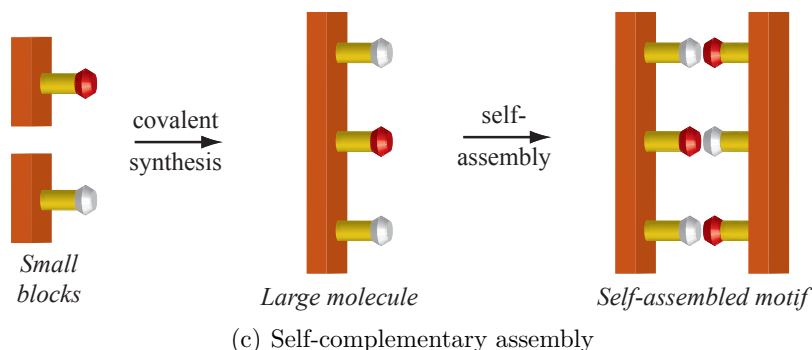
Supramolecules

Host-guest:
The study of large 'host' molecules that are capable of enclosing smaller 'guest' molecules via non-covalent interactions.



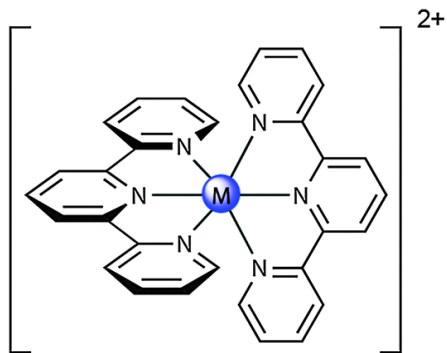
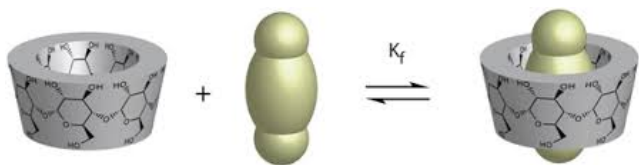
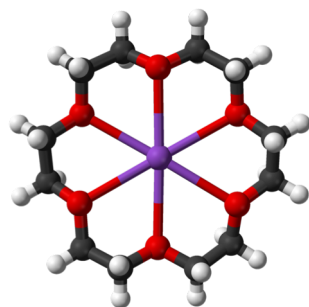
Supramolecular Assemblies

Self-assembly:
A dynamic equilibrium between two or more molecular species to produce a larger aggregate based on non covalent interactions

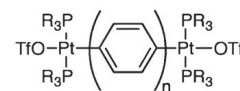
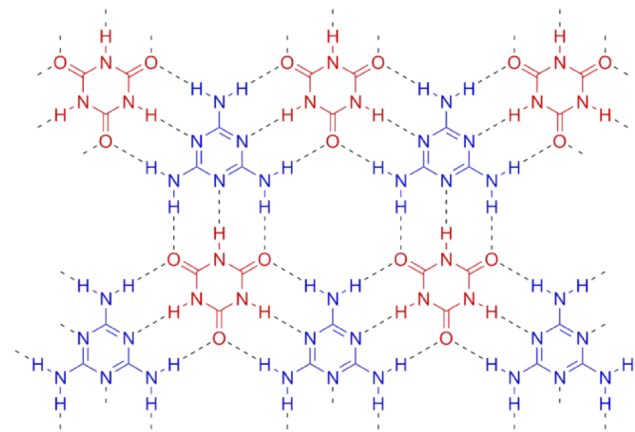


Supramolecular chemistry

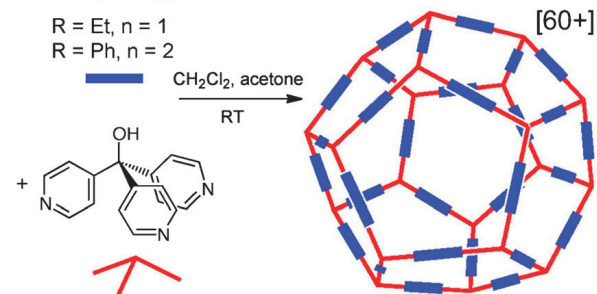
Supramolecules



Supramolecular Assemblies

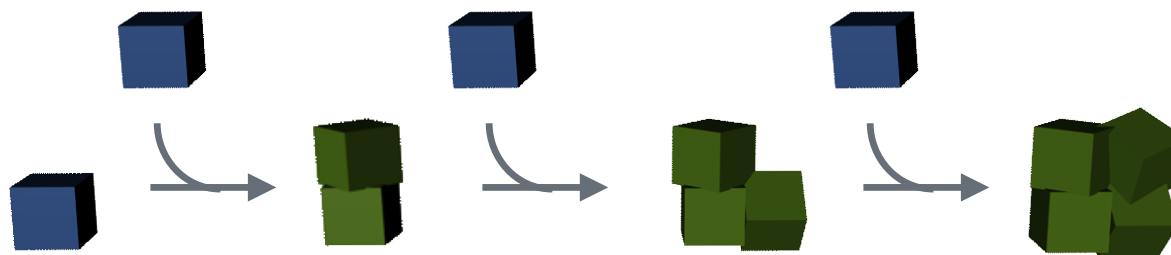


R = Et, n = 1
R = Ph, n = 2

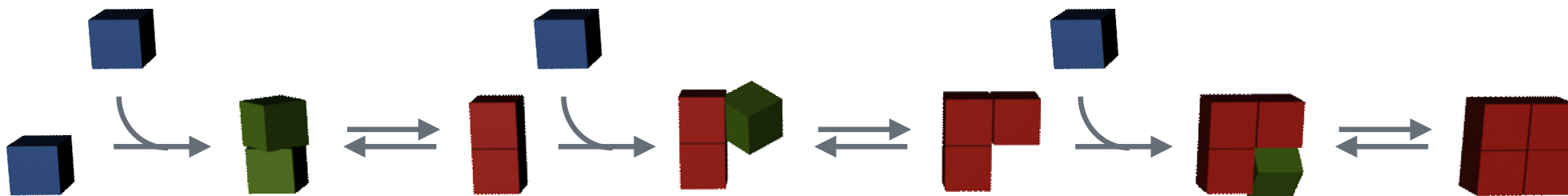


Supramolecular chemistry

Irreversibility leads to « glasses » (disorder)



Reversibility leads to « crystals » (ordered phases)



Individual non-covalent interactions may be weak, but many of them will still yield “stable” structures while allowing for “self-healing” (error correction)

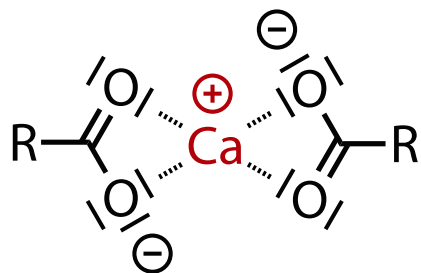
Supramolecular interactions

Interaction	Strength (kJ mol ⁻¹)
Ion-Ion	100-400
Ion-Dipole	50-200
Dipole-Dipole	10-50
Hydrogen bonding	2-120
Cation- π	5-80
π - π	5-50

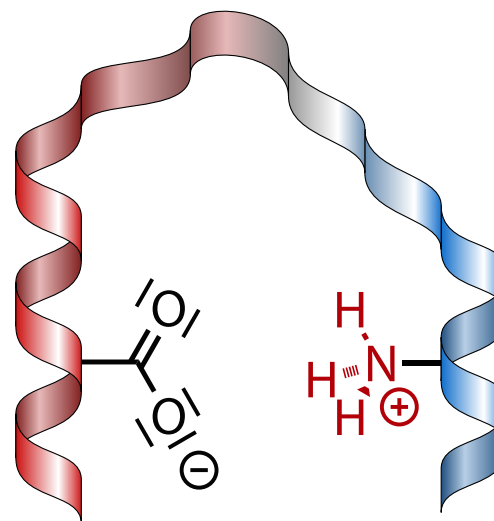
Supramolecular interactions

- **Coulomb Interactions (Ion-Ion Interactions)**

- strong (100–400 kJ/mol)
- long range ($\sim d^{-1}$)
- non directional



Salt bridges

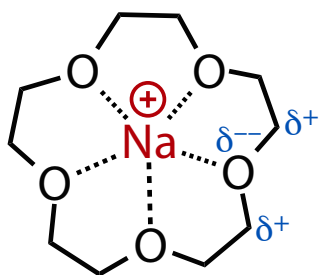


Acid-base pairs

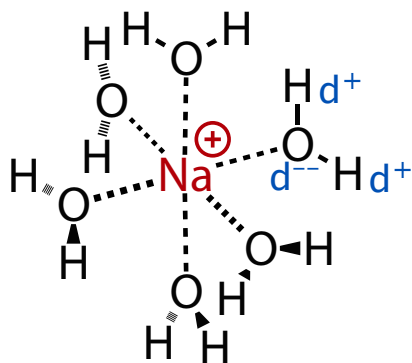
Supramolecular interactions

- **Ion-Dipole Interactions**

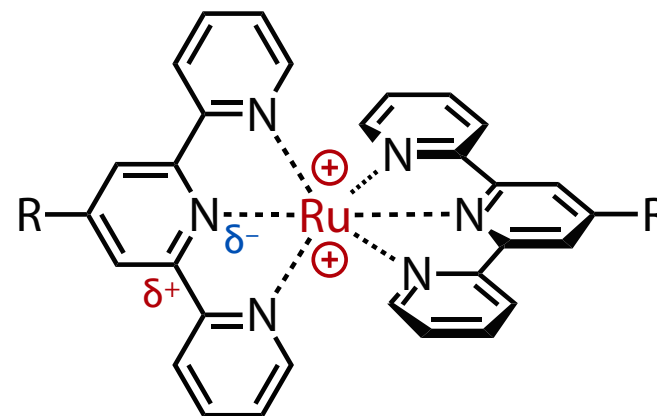
- moderately strong (50–200 kJ/mol)
- moderate range ($\sim d^{-2}$)



cation-binding hosts



solvation

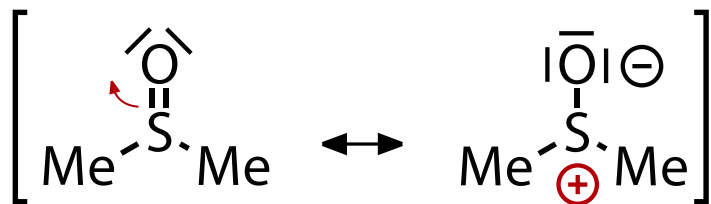
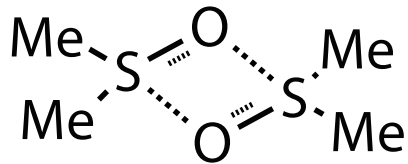


metal complexes (partially covalent)

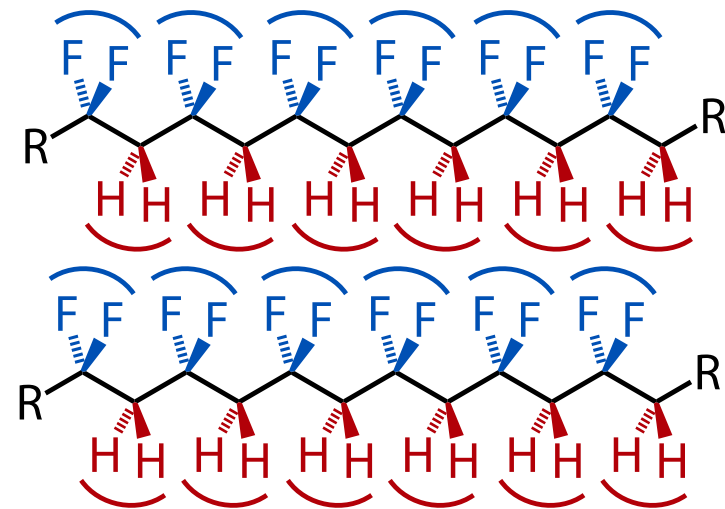
Supramolecular interactions

- **Dipole-Dipole Interactions (Keesom)**

- relatively weak (10–50 kJ/mol)
- short range ($\sim d^{-6}$)



Dimethylsulfoxide



Poly(vinylidene difluoride) PVDF

Supramolecular interactions

- Hydrogen Bonding

Occurs when a covalently bound hydrogen atom forms a second bond to another atom



H-bond

bond energy

D–H...A angle

H...A distance

bond character

weak

2–20 kJ mol

90–150°

2.2–3.2 Å

electrostatic

C–H...A

D–H... π

20–60 kJ mol

120–180°

1.5–2.2 Å

Alcohols

Amides

Biomolecules

moderately strong

60–120 kJ mol

$\approx 180^\circ$

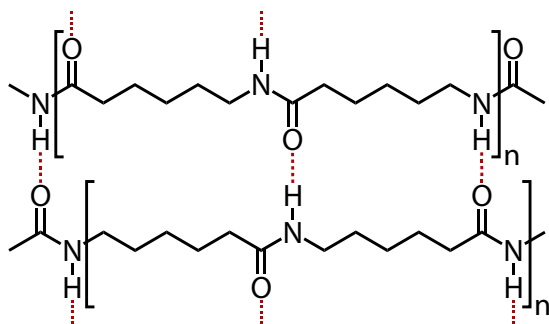
1.1–1.5 Å

covalent

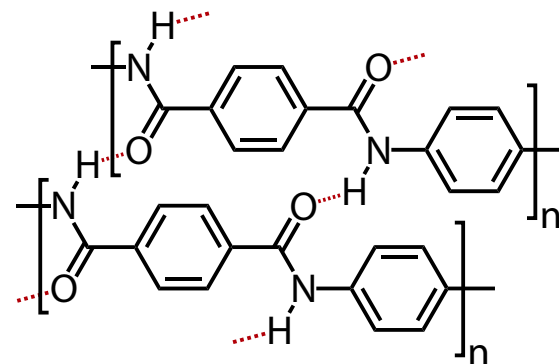
HF₂[–]

Supramolecular interactions

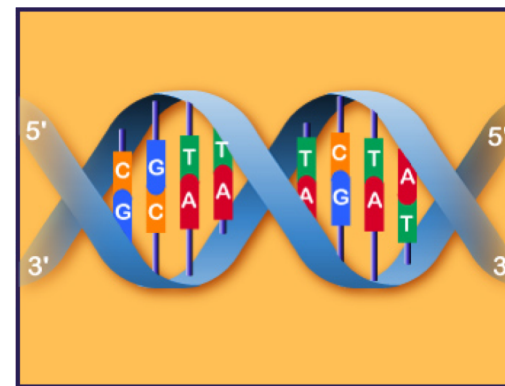
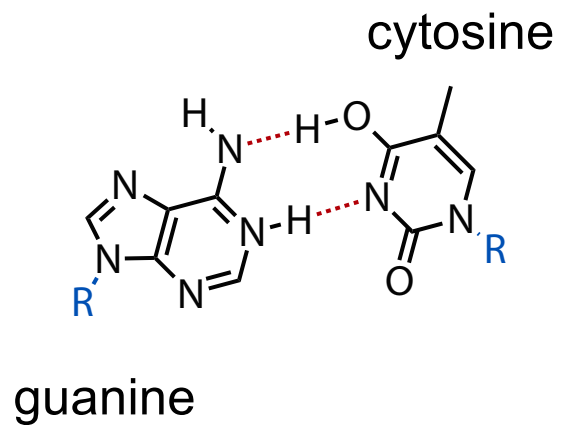
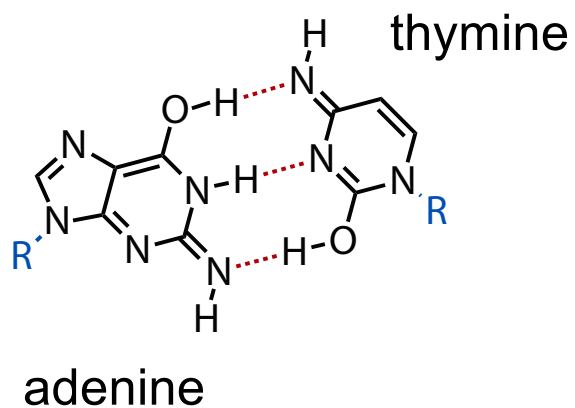
- Hydrogen Bonding



Nylon 6



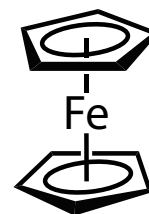
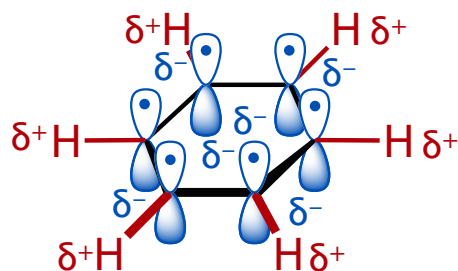
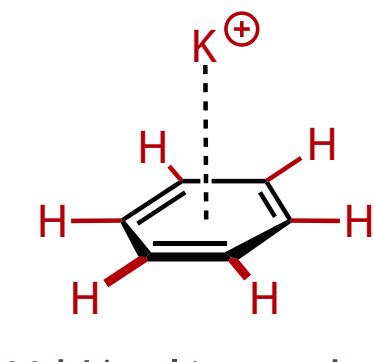
Kevlar



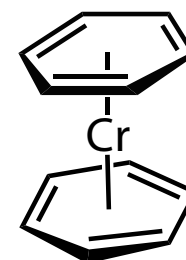
Supramolecular interactions

- **Cation- π Interactions**

- relatively weak (5–80 kJ/mol)
- relatively short range ($\sim d^{-4}$)



ferrocene
mainly covalent

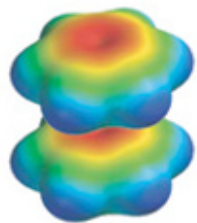
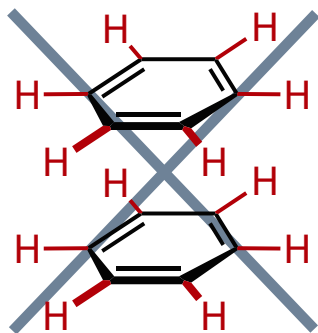


bis(benzene)chromium
covalent (no charges)

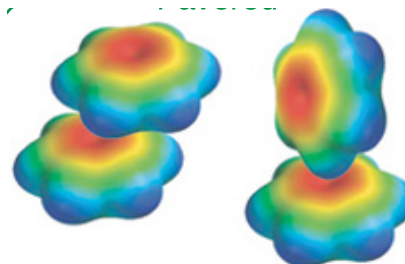
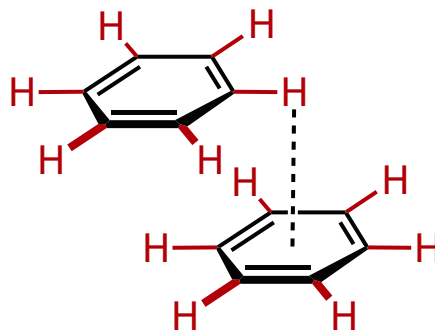
Supramolecular interactions

- **π - π Interactions (π - π stacking)**

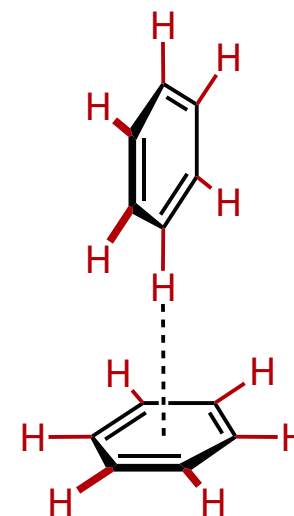
- weak (5–50 kJ/mol)
- short range ($\sim d^{-6}$)



Face-to-face



Parallel displaced

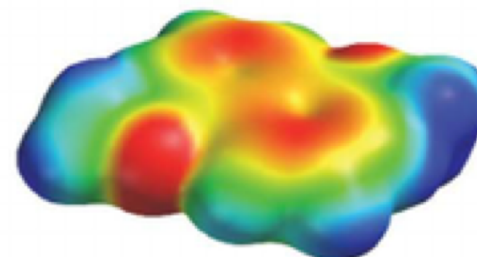
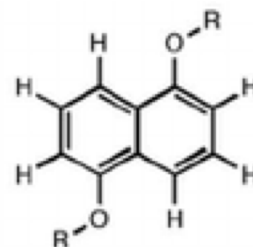
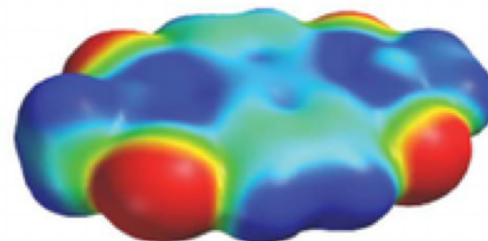
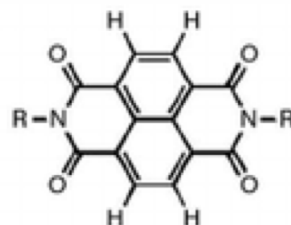
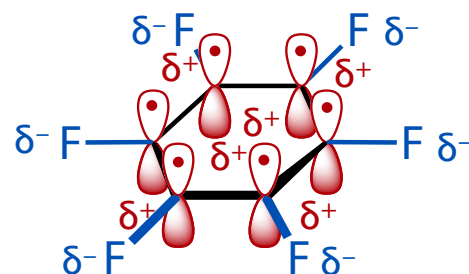
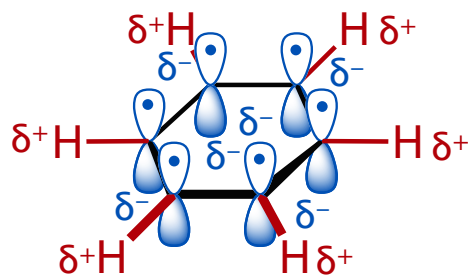


Edge-to-face

Supramolecular interactions

- π - π Interactions (π - π stacking)

- weak (5–50 kJ/mol)
- short range ($\sim d^{-6}$)



Supramolecular interactions

- **Other (very weak) interactions**

Dipole - induced dipole (Debye interactions)

Instantaneous dipole - induced dipole (Dispersion/London interactions)

- **What about Van der Waals interactions?**

They take into account all interactions excluding those involving a permanently charged species.

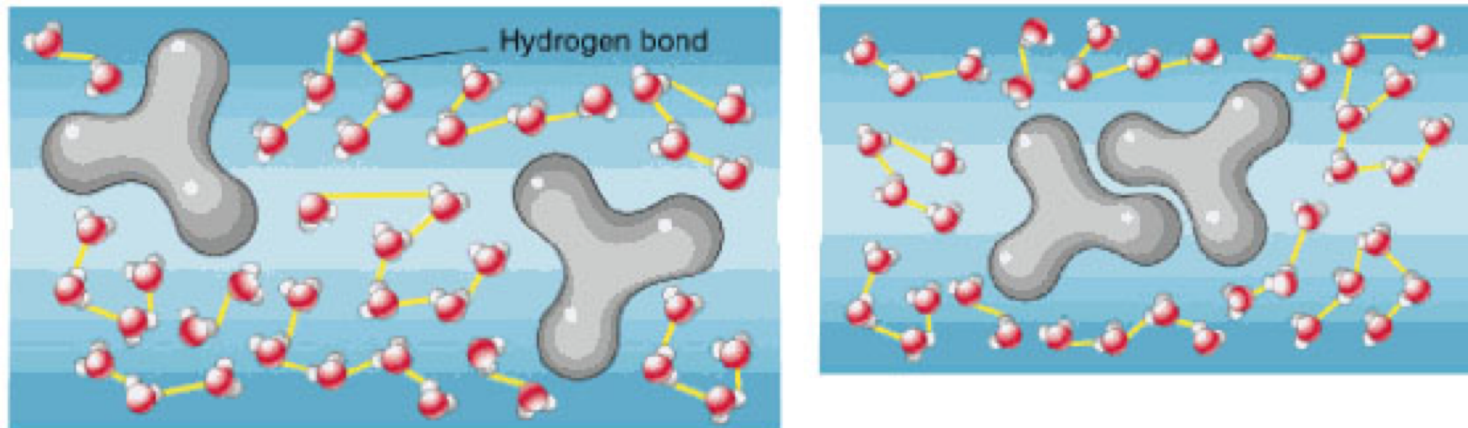
$$\text{VdW} = \text{Keesom} + \text{Debye} + \text{London}$$

Supramolecular interactions

- **Hydrophobic effects**

Hydrophobic effects are **entropy** driven.

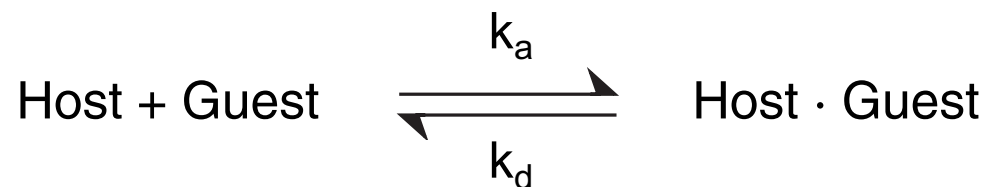
Water around a hydrophobic molecule is more ordered than in the bulk liquid. Aggregation releases water, which is entropically very favorable.



Examples: phospholipid bilayer cell wall, cyclodextrin inclusion complexes,...

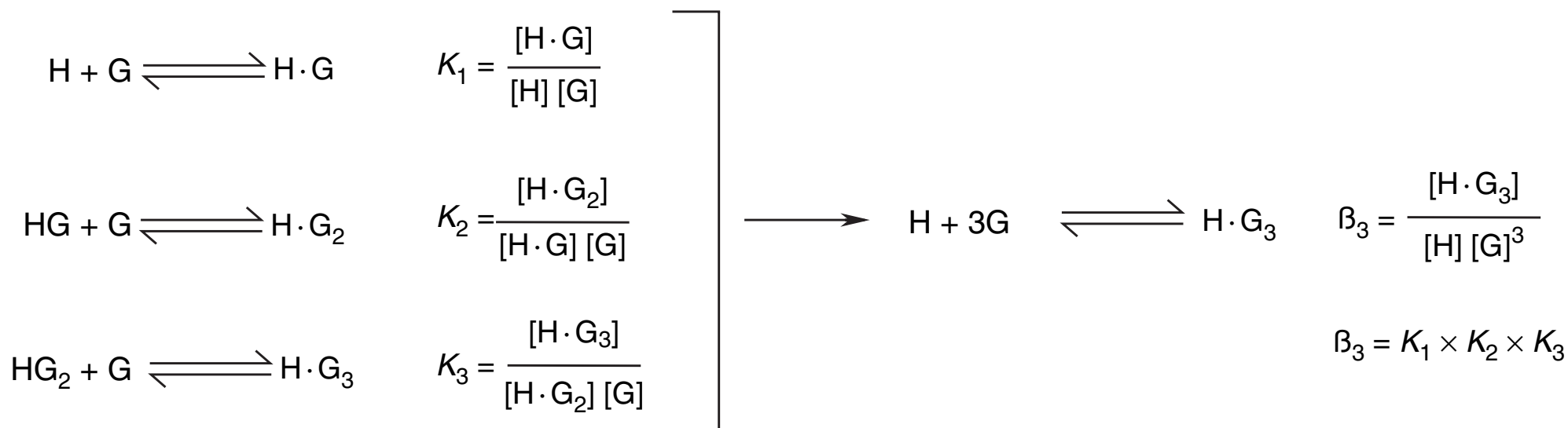
Supramolecular interactions

Binding constants



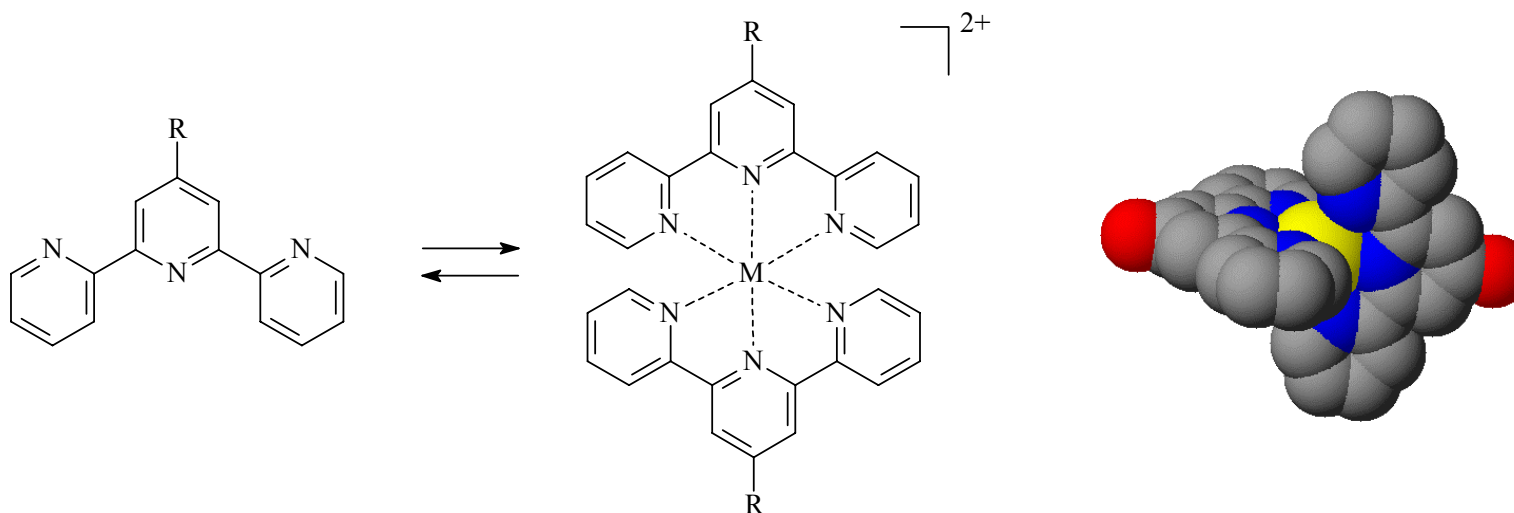
Binding constant:

$$K = \frac{[\text{H} \cdot \text{G}]}{[\text{H}][\text{G}]} = \frac{k_a}{k_d}$$



Supramolecular interactions

Binding constants



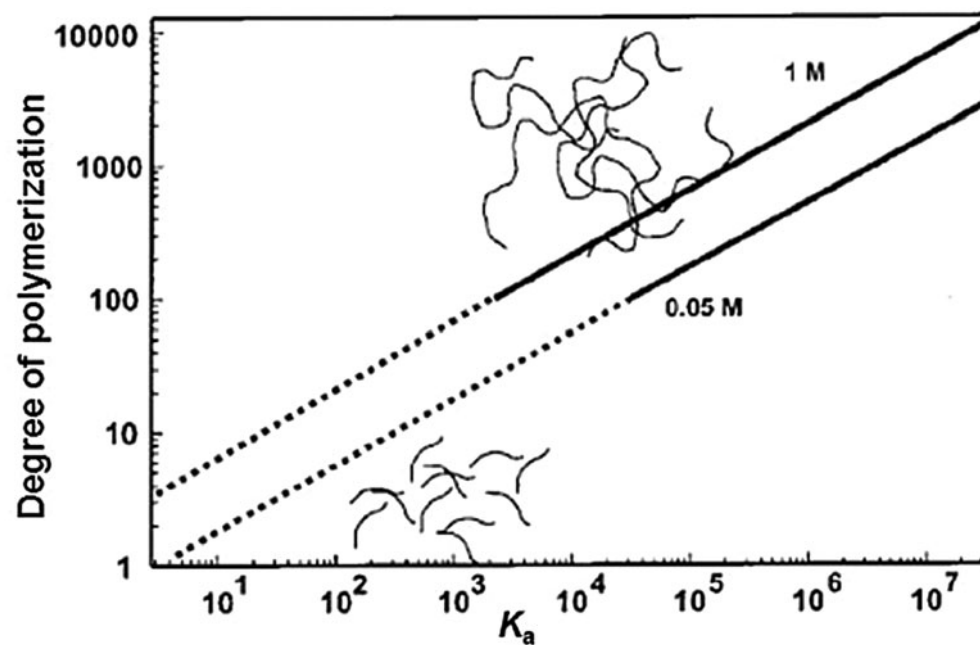
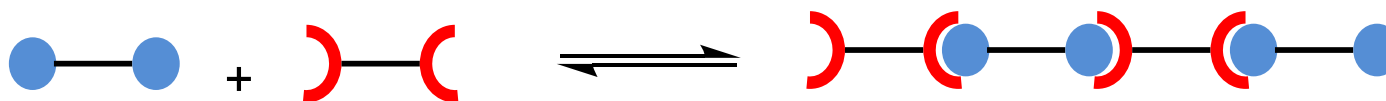
ion	Log K_1	Log K_2	Log β_2	k_{a1}	k_{d1}	k_{a2}	k_{d2}
Fe^{2+}	7.1	13.8	20.9	$10^{4.9}$	$10^{-2.2}$	$10^{7.0}$	$10^{-6.8}$
Ni^{2+}	10.7	11.1	21.8	$10^{3.1}$	$10^{-7.6}$	$10^{5.3}$	$10^{-5.8}$
Co^{2+}	8.4	9.9	18.3	$10^{4.4}$	$10^{-4.0}$	$10^{6.7}$	$10^{-3.2}$
Zn^{2+}	6.0	5.2	11.2	$10^{6.1}$	$10^{0.1}$	-	« fast »

In water at 25° C

Supramolecular interactions

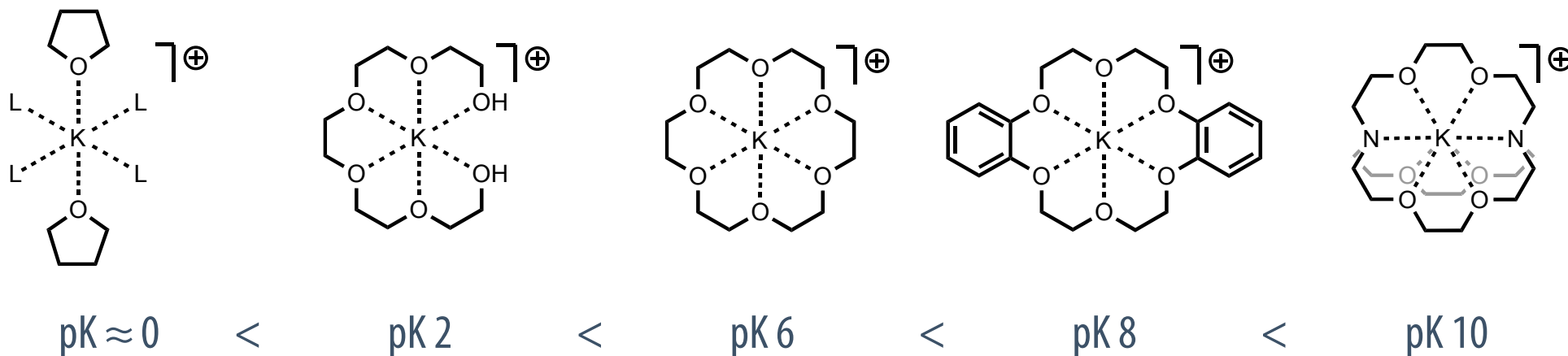
Importance for supramolecular polymers:

$$DP \sim (K[M])^{1/2}$$

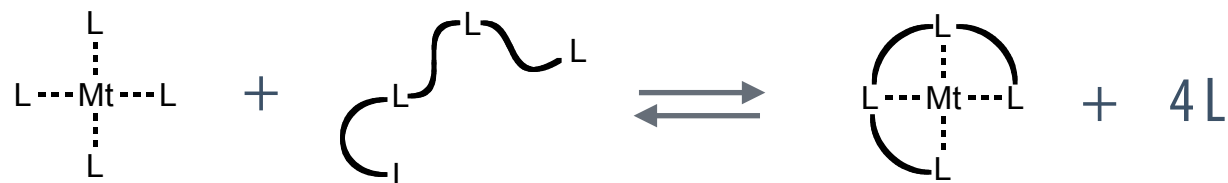


Supramolecular interactions

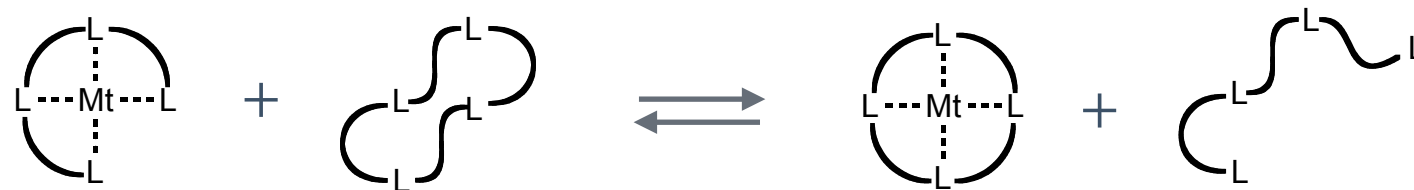
Pre-organization and chelate effects:



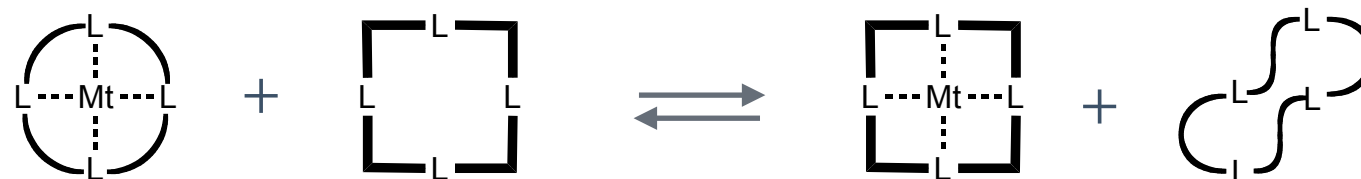
Chelate effect



Macrocyclic effect



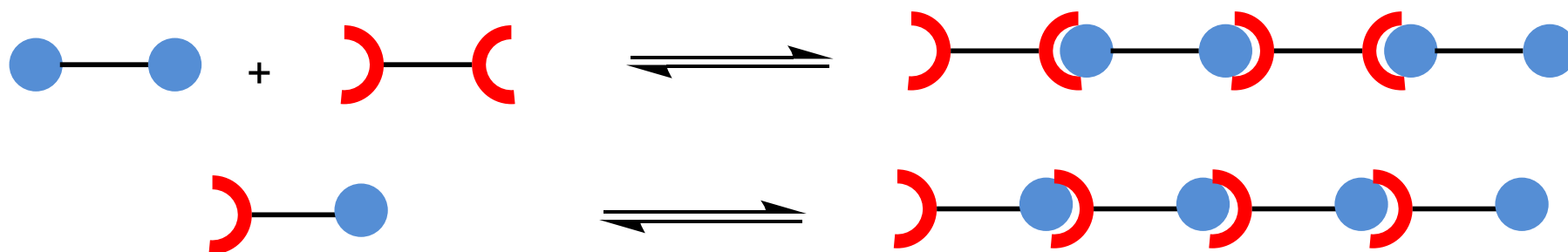
Preorganization



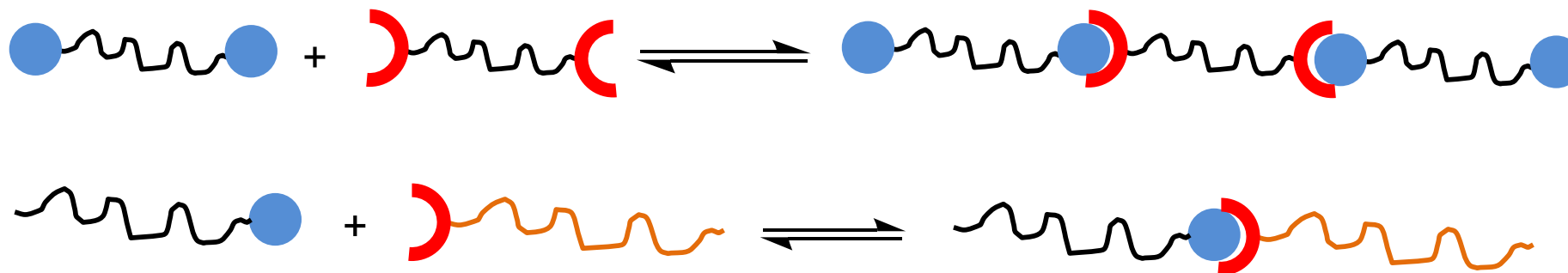
Supramolecular polymers

General strategies:

From small molecule building blocks

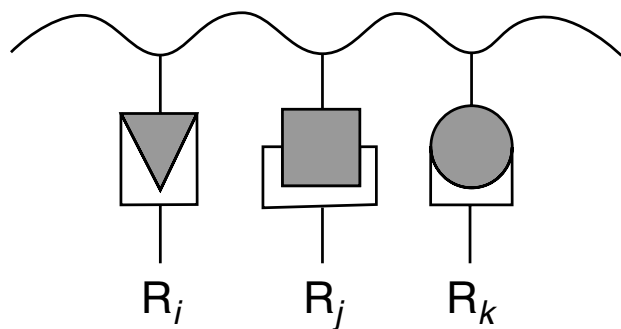


From polymeric building blocks

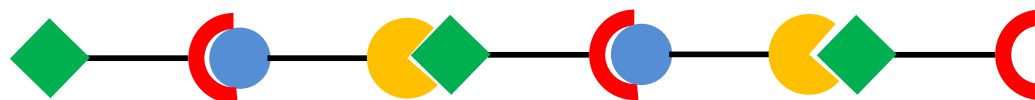


Supramolecular polymers

Side chains:



Combination of different (orthogonal) interaction types:

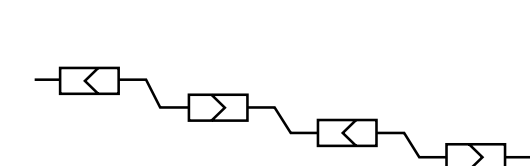


Supramolecular polymers

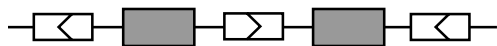
Different “dimensions”:

linear

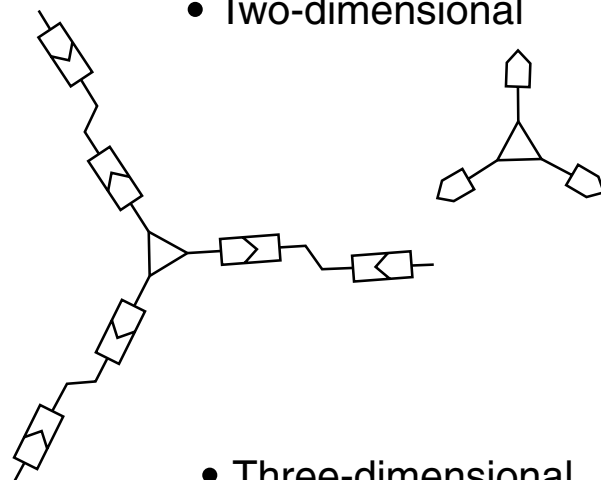
supramolecular cross-linking, self-assembled dendrimers,...



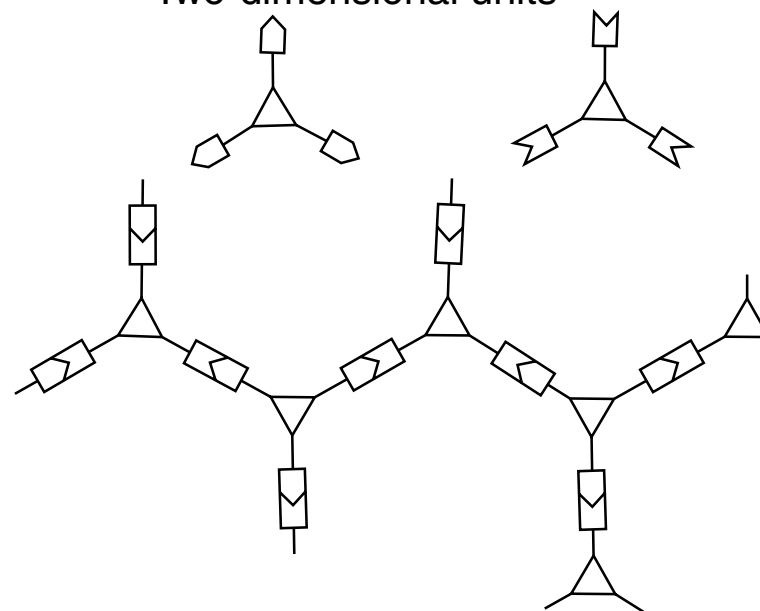
• Rigid rods



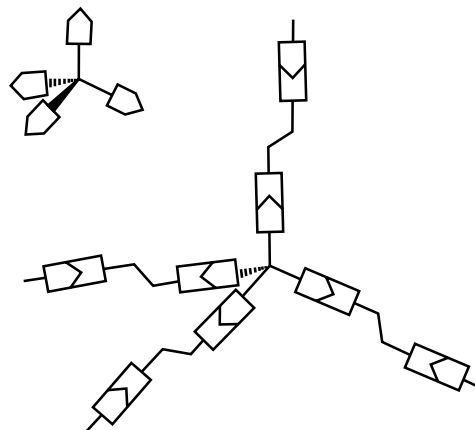
• Two-dimensional



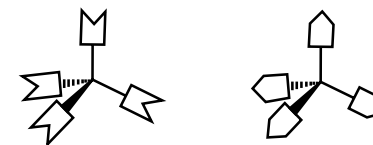
• Two-dimensional units



• Three-dimensional

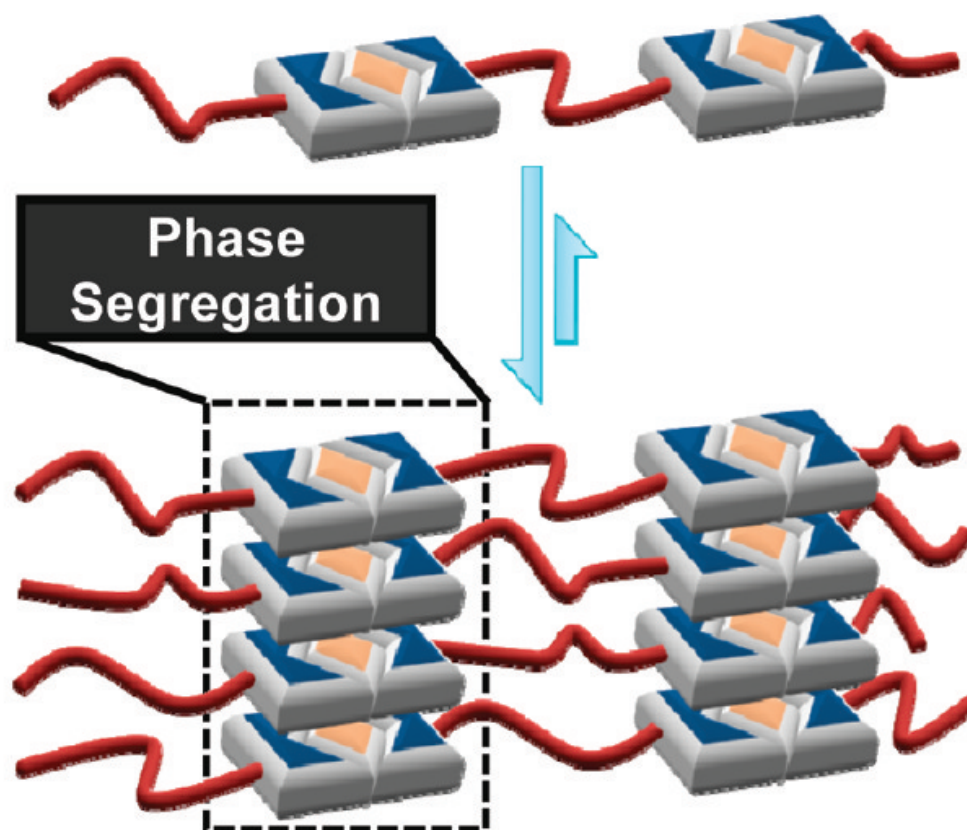


• Three-dimensional units



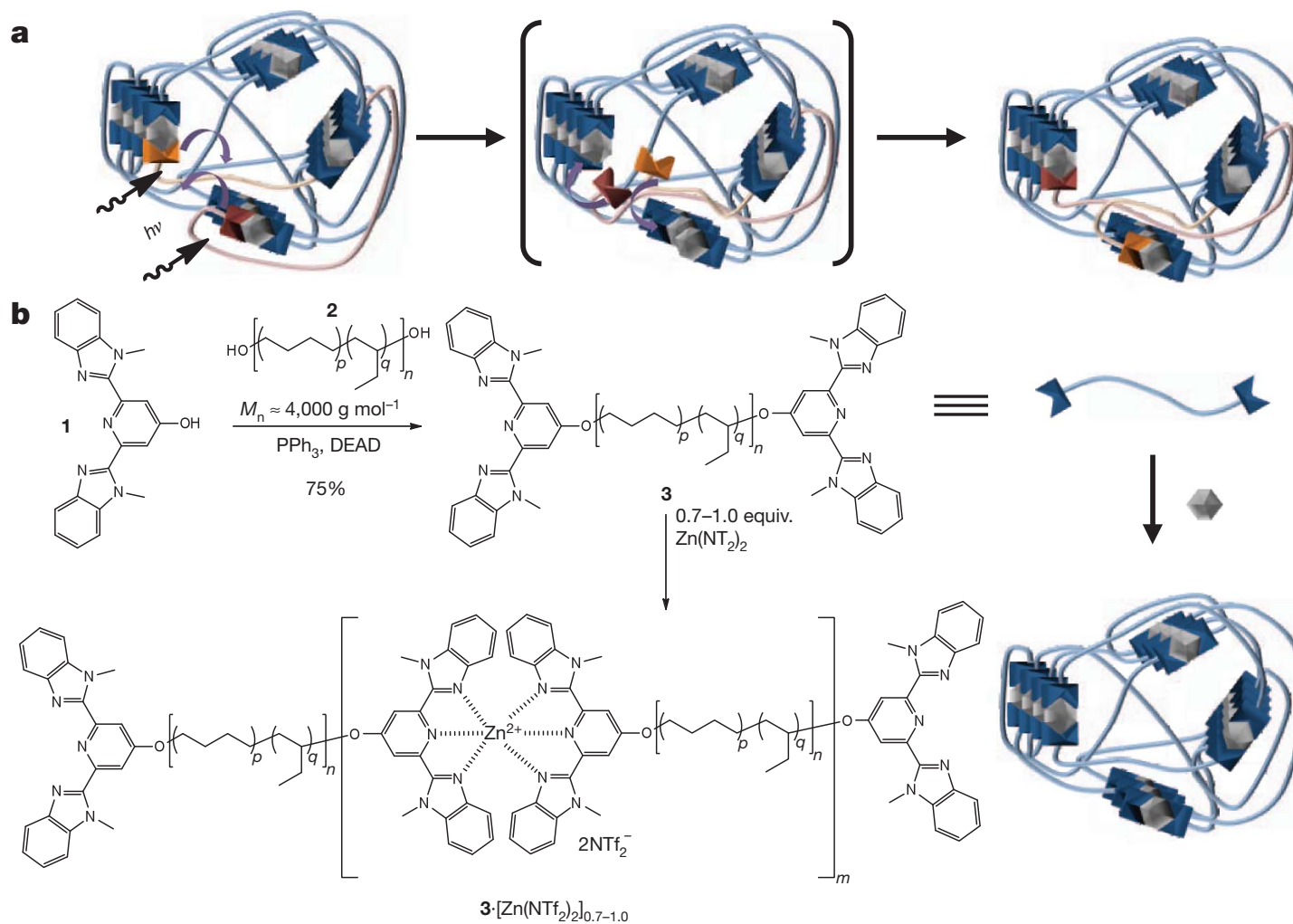
Supramolecular polymers

To keep in mind...



Supramolecular polymers

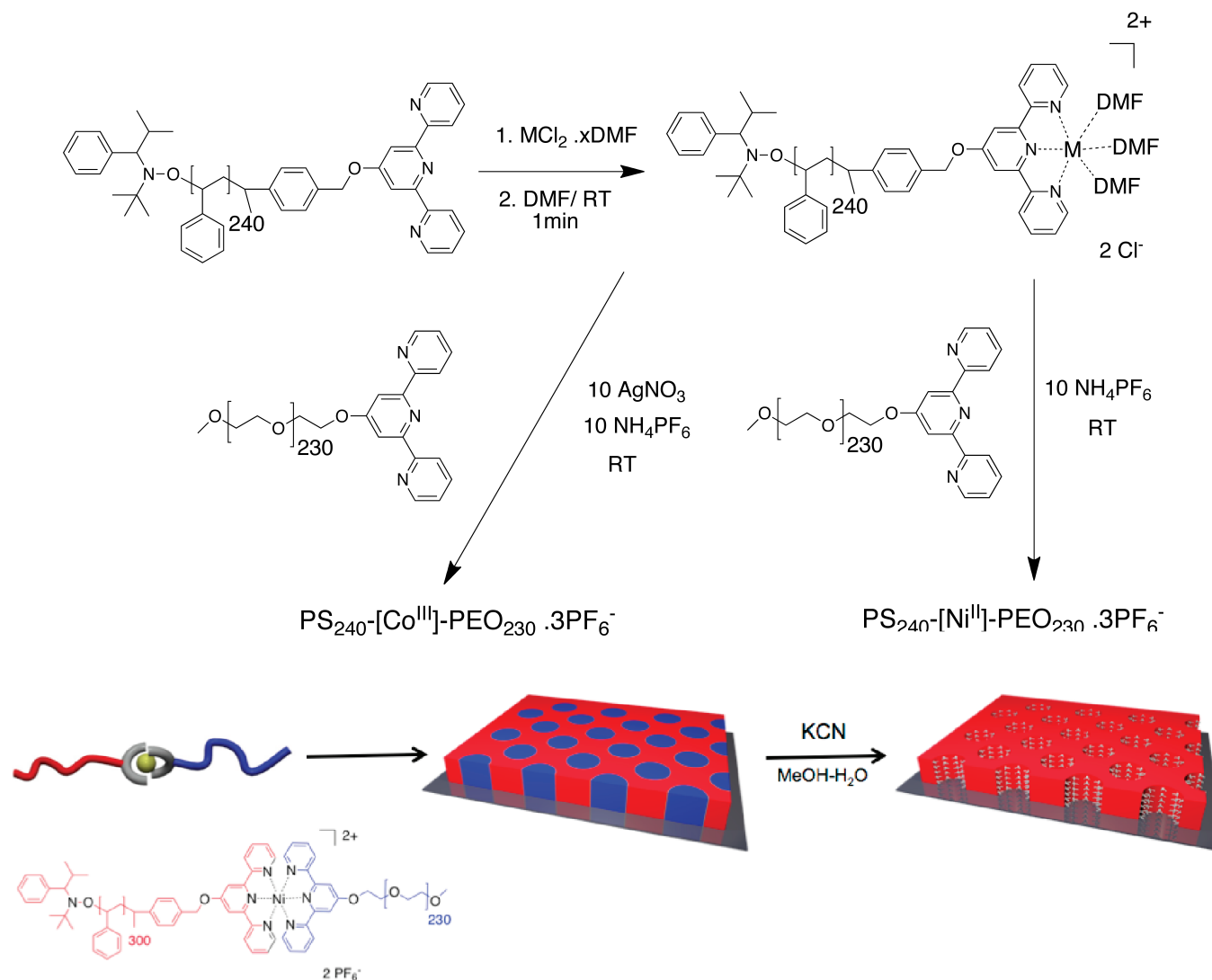
Metal-ligand coordination



Optically healable supramolecular polymers (UV: 320-390nm)

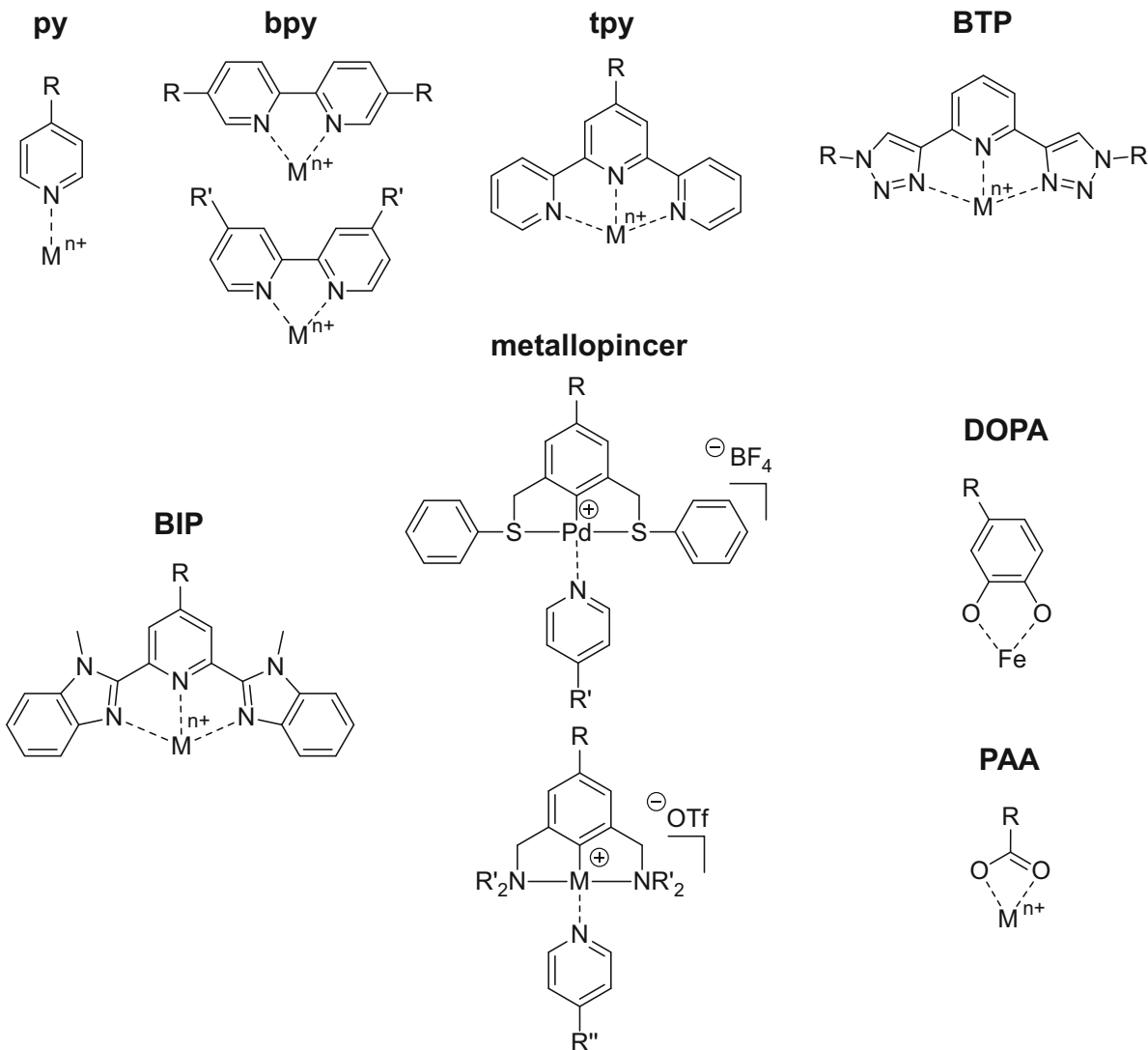
Supramolecular polymers

Metal-ligand coordination



Supramolecular polymers

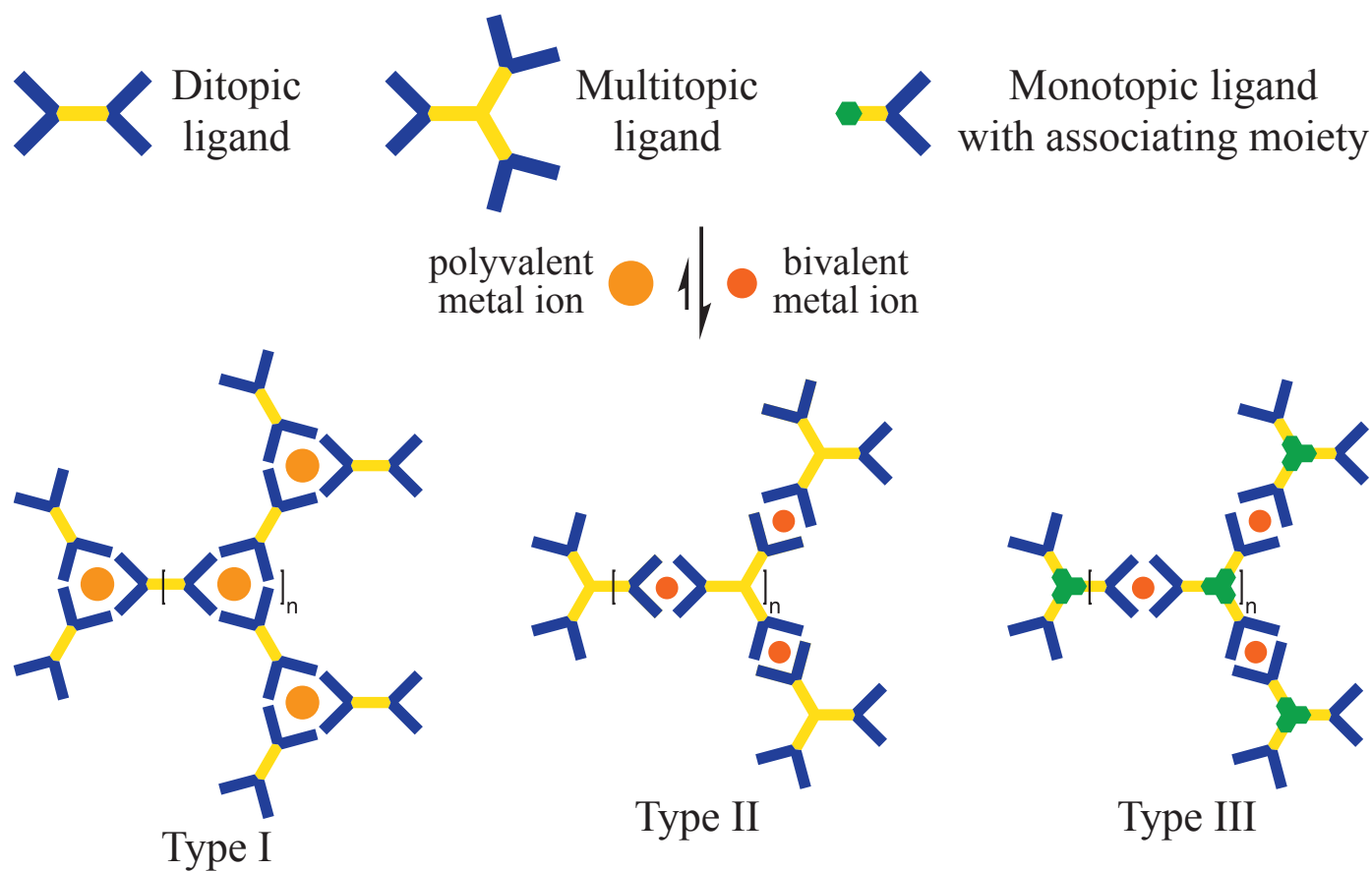
Metal-ligand coordination



Supramolecular polymers

Metal-ligand coordination

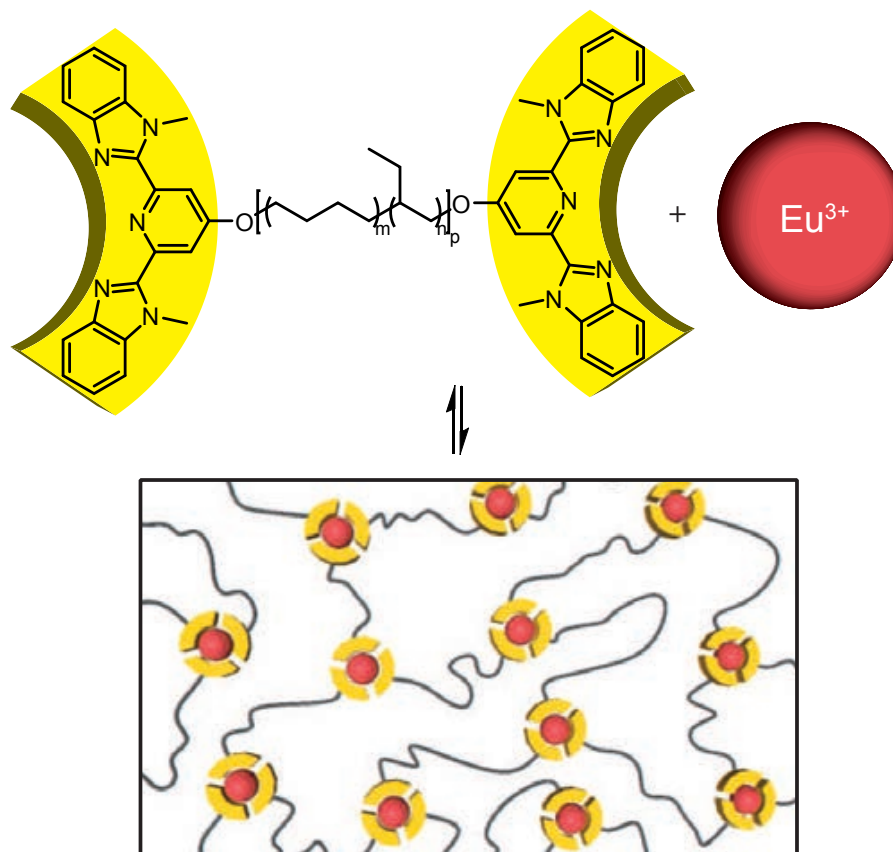
Polymer networks



Supramolecular polymers

Metal-ligand coordination

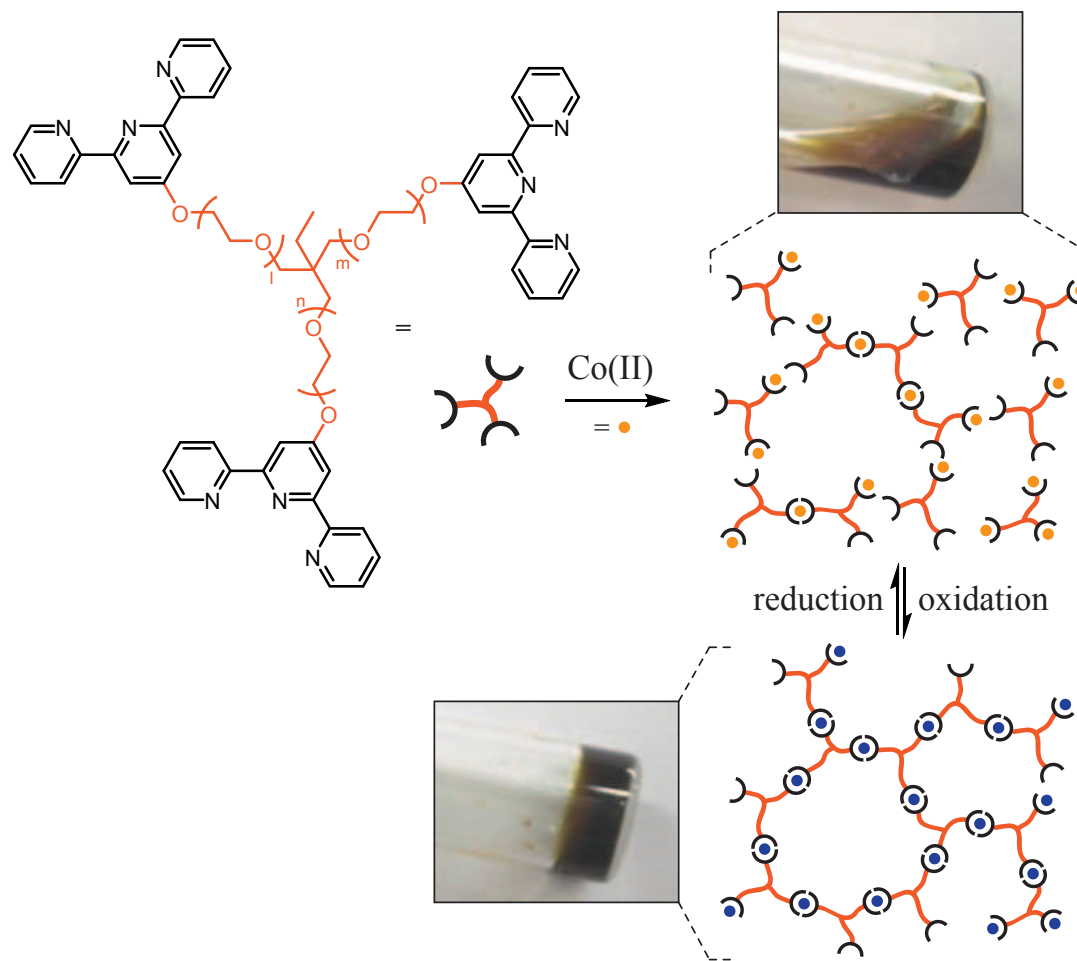
Type 1



Supramolecular polymers

Metal-ligand coordination

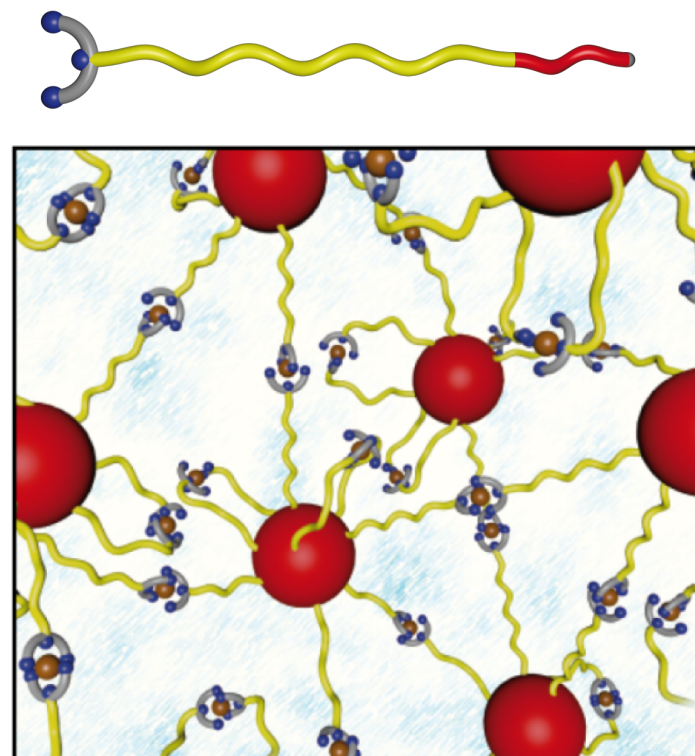
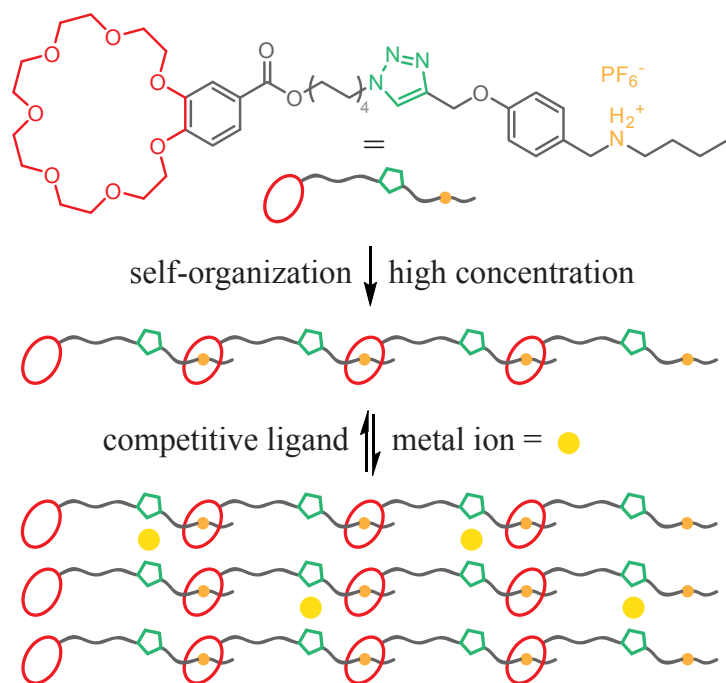
Type 2



Supramolecular polymers

Metal-ligand coordination

Type 3

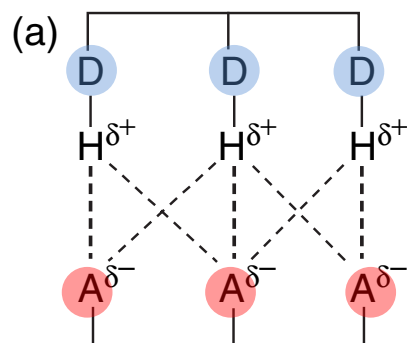


Metal-ligand coordination

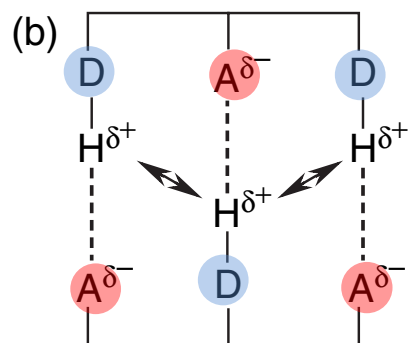
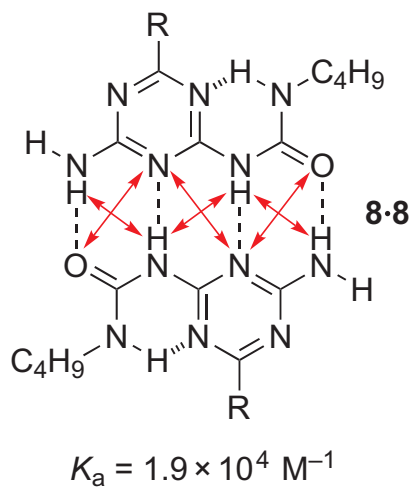
- ✓ Strength tunable in very broad range
Strength tuned simply by changing ions
Not sensitive to water (moisture)
Potential added properties of metal ions (catalytic, magnetic, redox...)
- ± Most complexes are charged → possible phase separation/aggregation
- ✗ Heterocomplementarity "difficult" to introduce
Potential toxicity of metal ions

Supramolecular polymers

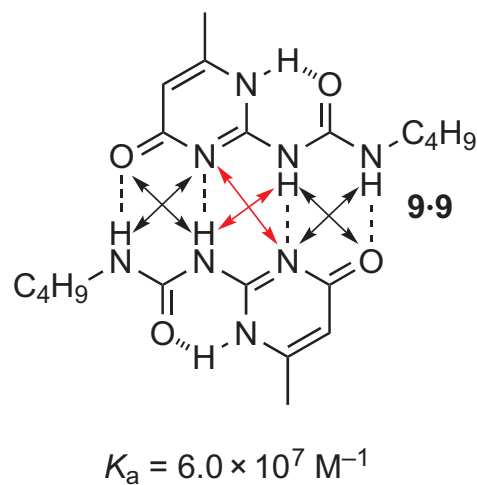
Hydrogen bonding



ADAD-DADA

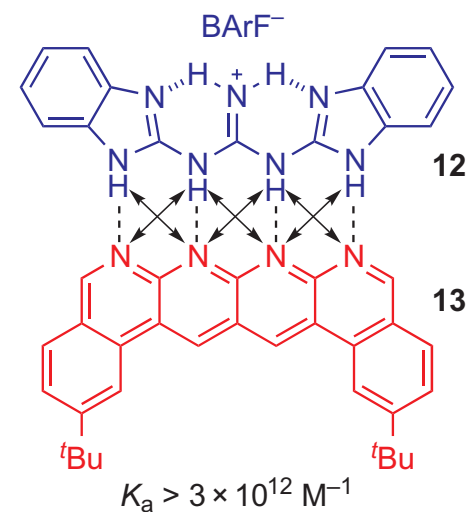


AADD-DDAA



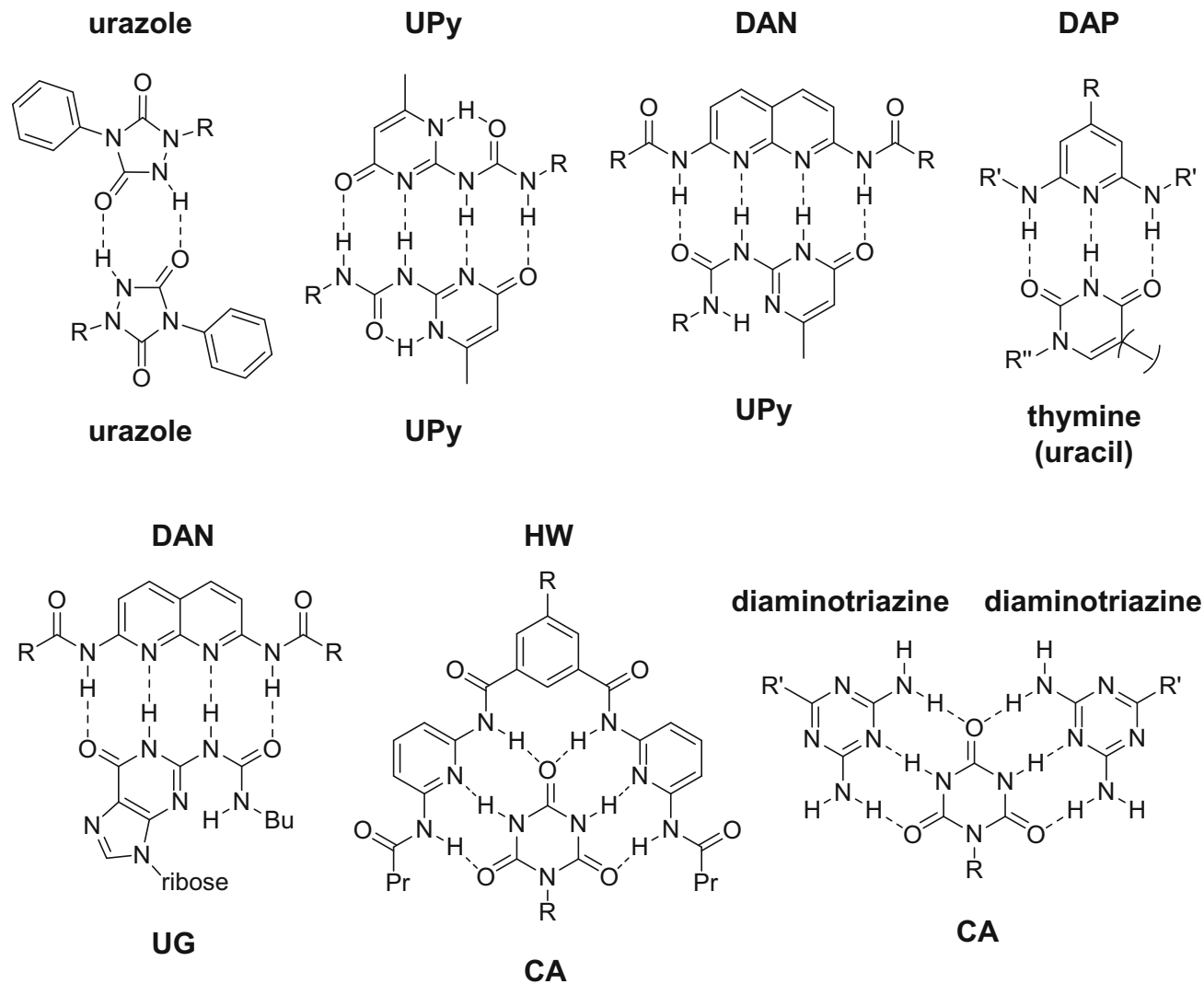
D Donor
A Acceptor
----- Attractive interaction
↔ Repulsive interaction

AAAA-DDDD⁺



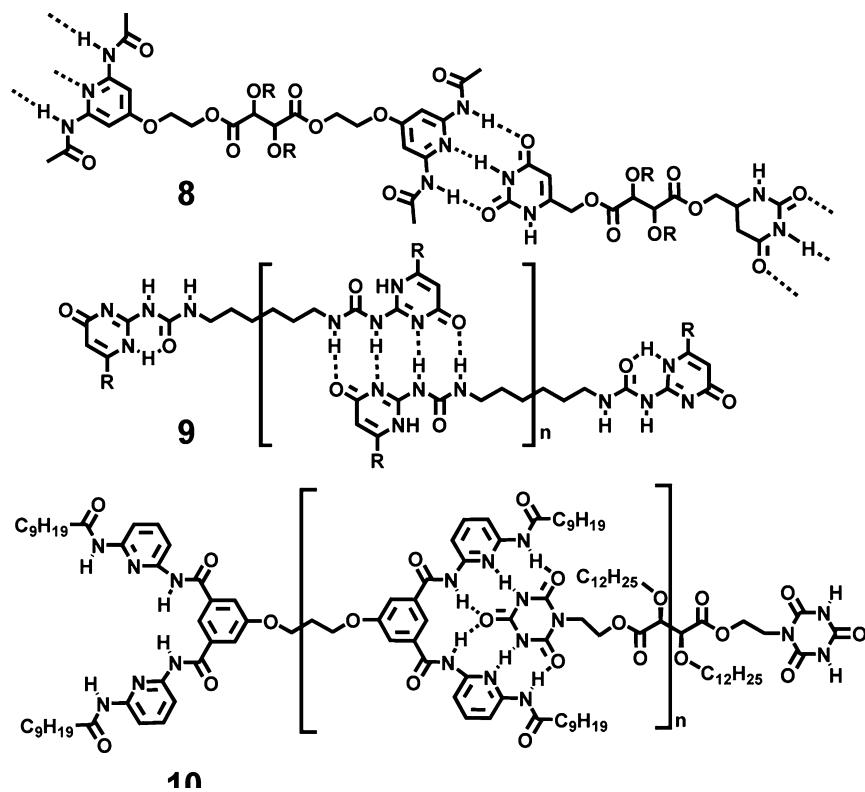
Supramolecular polymers

Hydrogen bonding



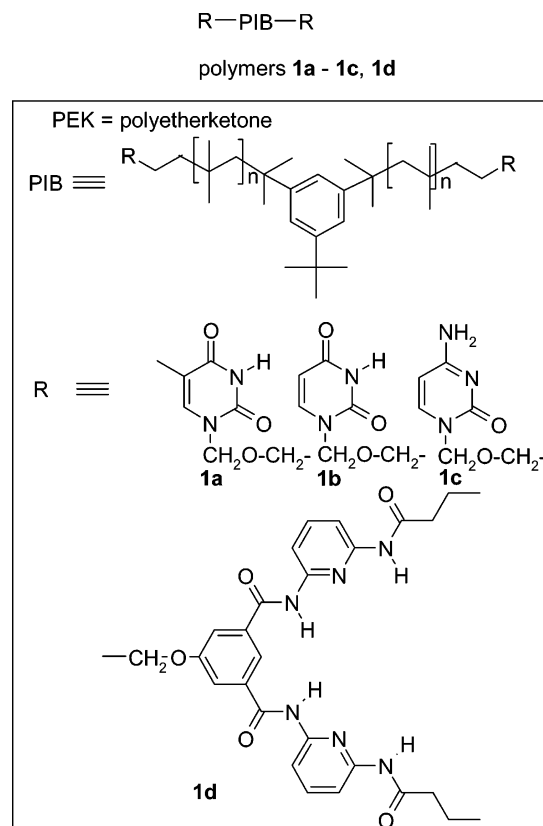
Supramolecular polymers

Hydrogen bonding

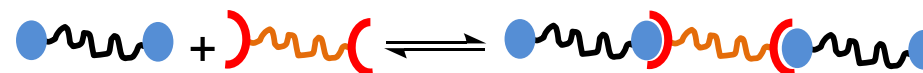
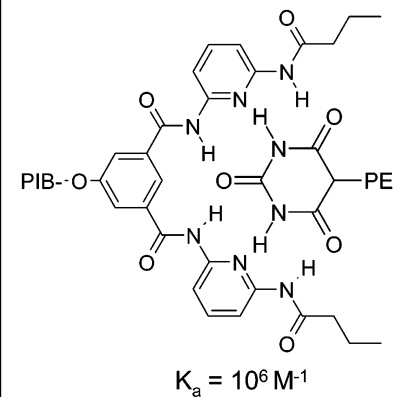
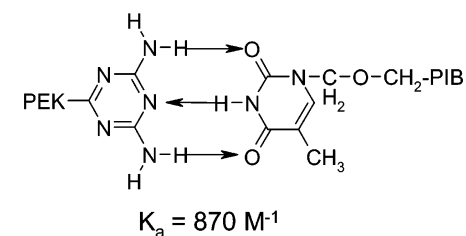


Chem. Rev. **2015**, *115*, 7196

Small molecule assembly



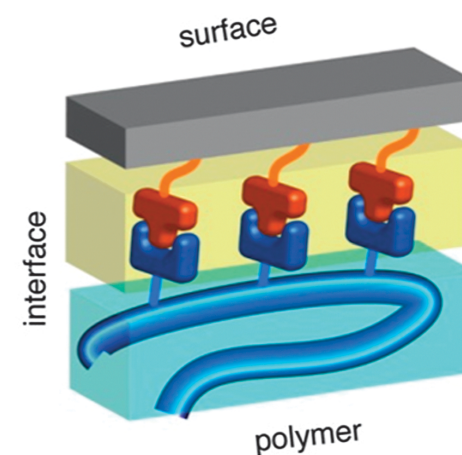
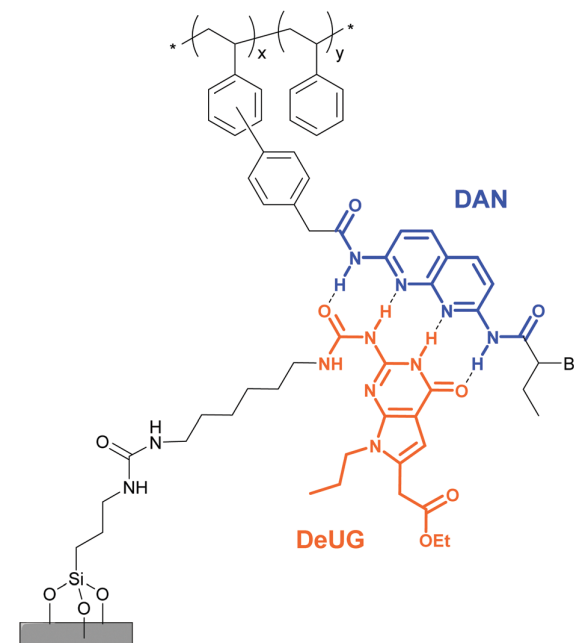
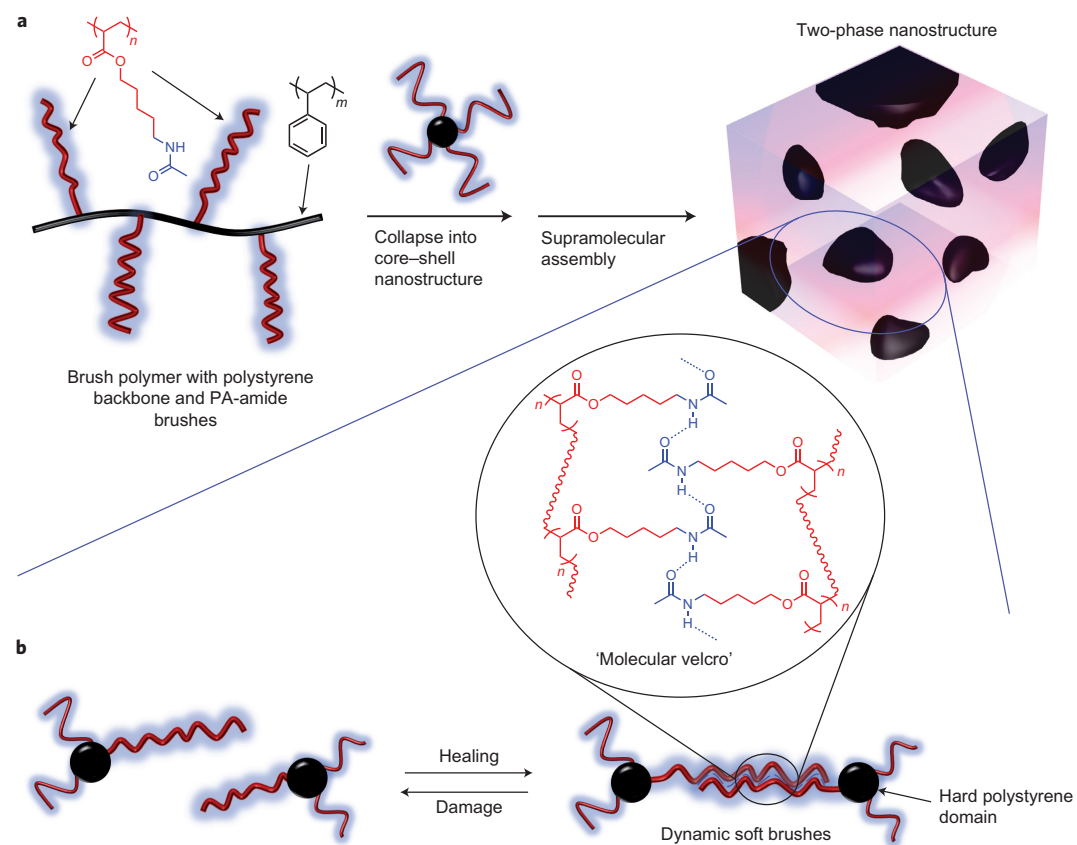
R-PIB-R
polymers **1a - 1c, 1d**



Macromolecules **2004**, *37*, 1749

Polymer assembly

Hydrogen bonding

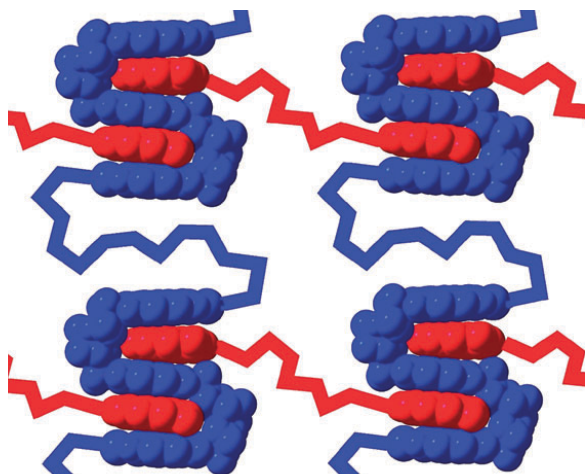
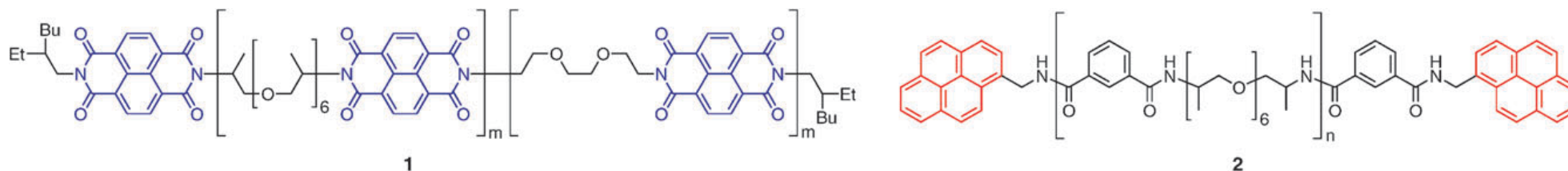


Hydrogen bonding

- ✓ Strength finely tunable
 - Heterocomplementarity easy to introduce
 - Full organic (no need to add metal ions)
 - Cooperative effect very important
- ± Highly polar groups → possible phase separation/aggregation
- ✗ Sensitive to solvents and water (moisture)
 - Tuning interaction strength requires changing binding motifs

Supramolecular polymers

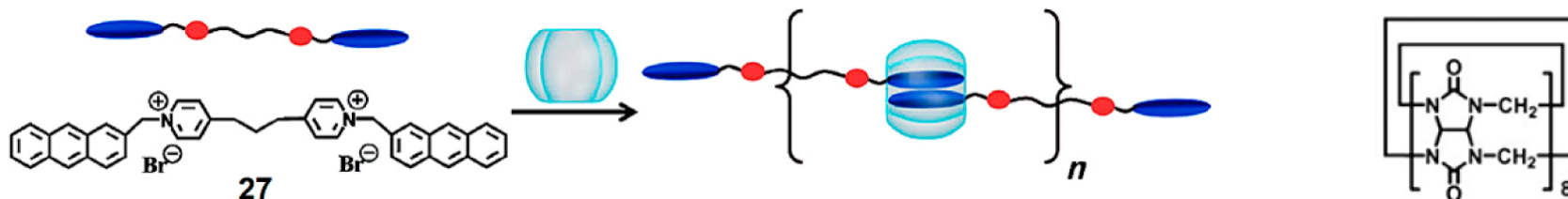
π interactions



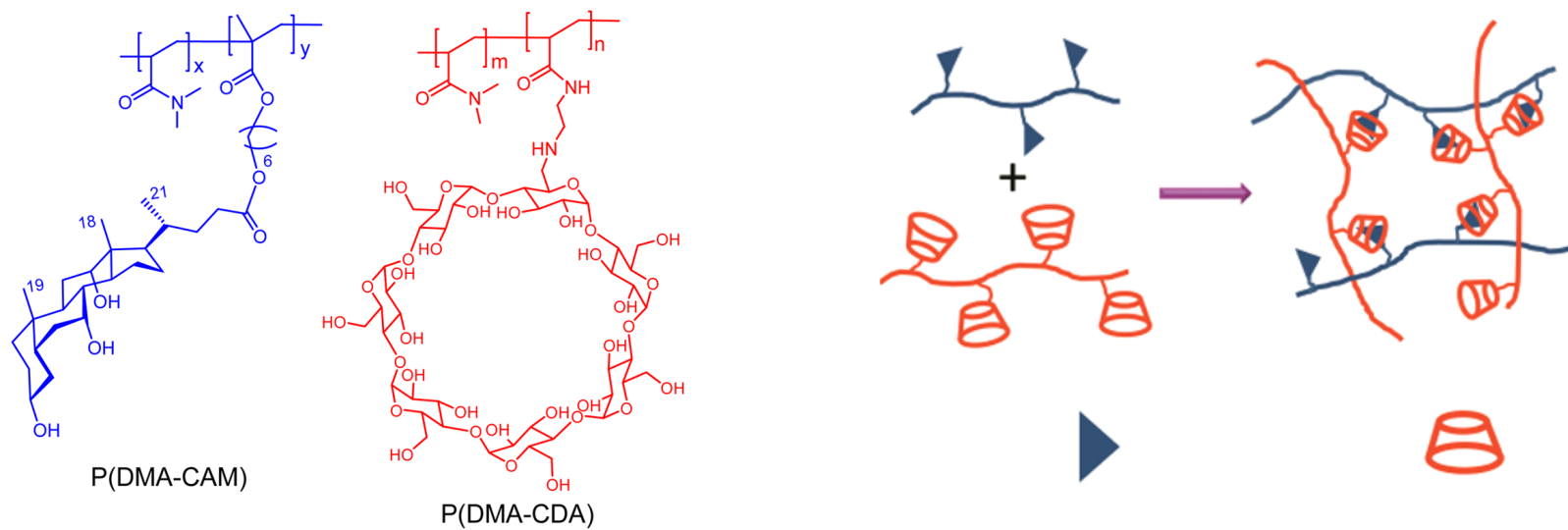
copolyimide 1 ($M_n = 16\,000$, $M_w = 27\,000$)
with
pyrenyl end-capped polyamide 2 ($M_n = 6\,000$, $M_w = 10\,000$).

Supramolecular polymers

Host-guest interactions



Chem. Eur. J. **2011**, 17, 9930



Chem. Mater. **2015**, 27, 387

To learn more

Chem. Rev. **2015**, 115, 7196

Chem. Soc. Rev. **2012**, 41, 5950

Chem. Soc. Rev. **2012**, 41, 5922

Chem. Rev. **2009**, 109, 5687

...