

7. Supramolecular structures

[Poole-Owens 11.5]

Supramolecular structures are large molecules formed by grouping or bonding smaller molecules together

It belongs to the realm of nanoscience since it is often possible to develop molecules of a desired shape or functionality.

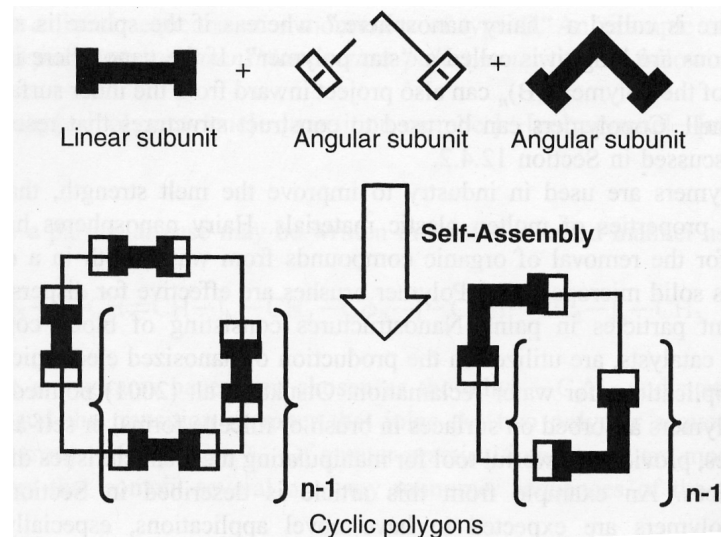
- This element of contrallability on the nanoscale fulfills the lecturers definition of nanoscience

7.1. Building geometric shapes from molecules

- Supramolecular structures can be used to develop numerous different shapes of molecules, including 2D triangles, squares, pentagons, hexagons and 3D octahedrons and cubes.

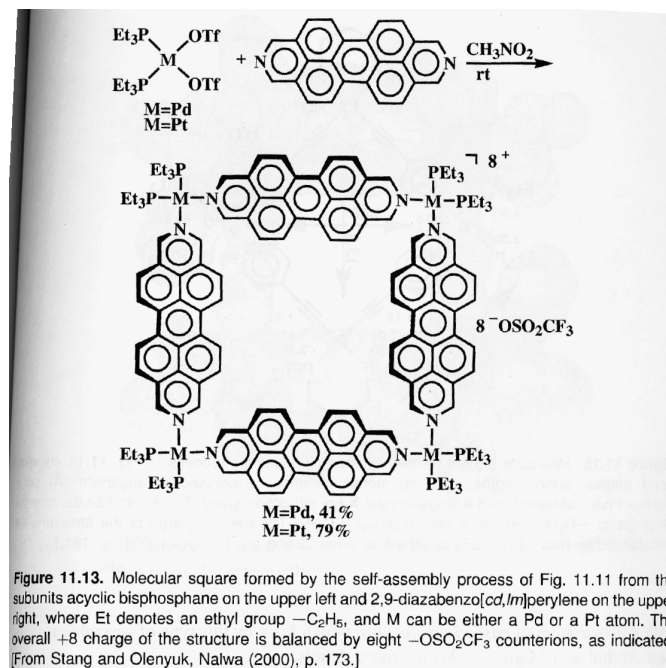
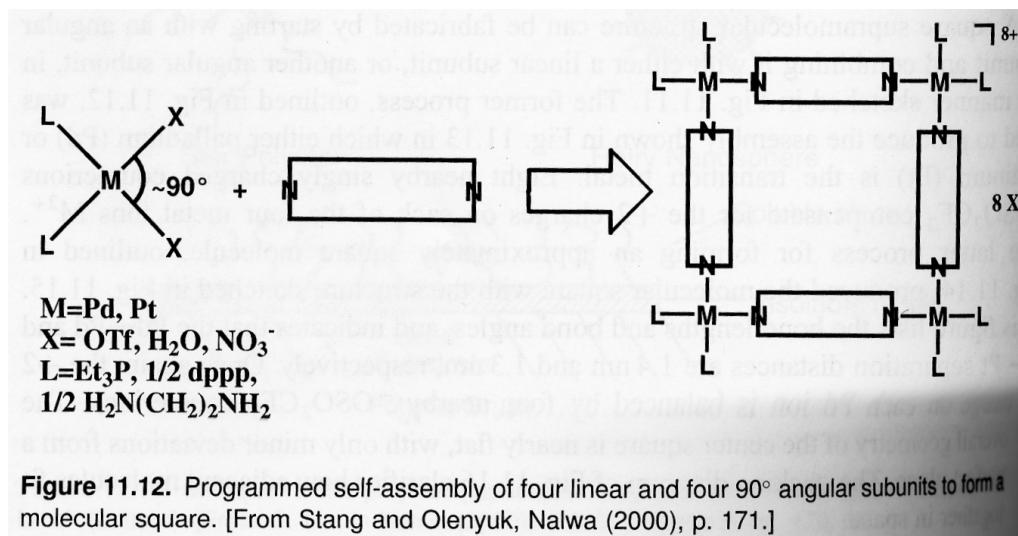
7.1.1. Example: supramolecular square

- A square supramolecule can be fabricated using an angular subunit with a 90° angle as a starting point. This can be combined either with linear subunits or another angular subunit:



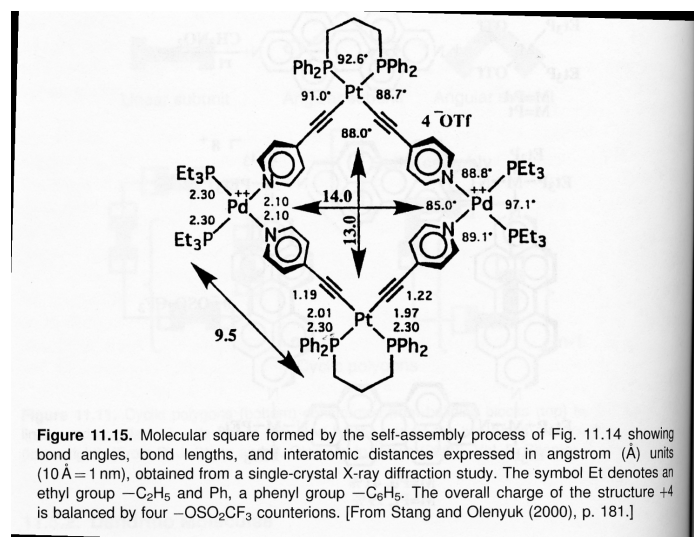
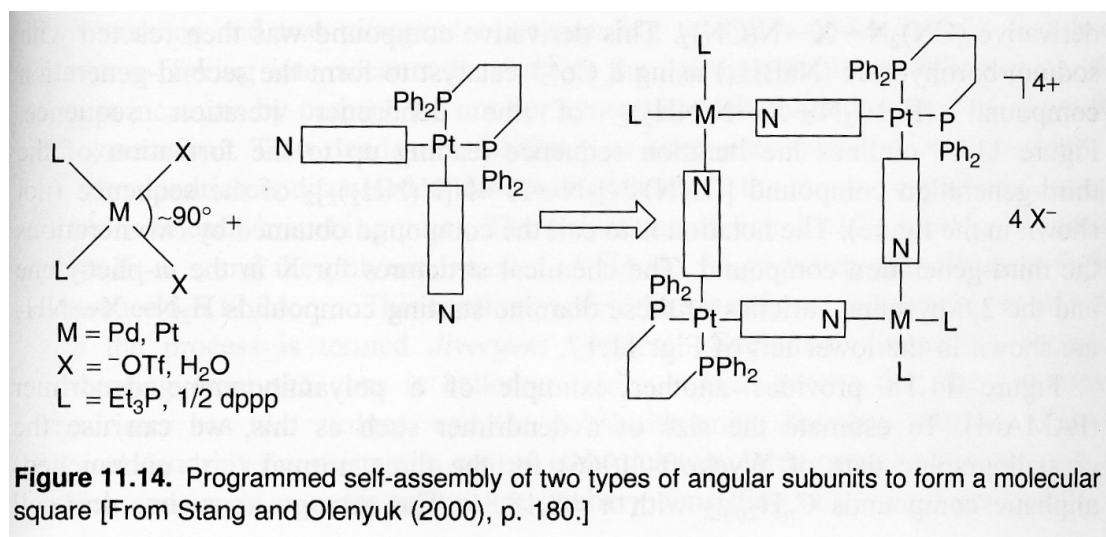
- Pt^{2+} and Pd^{2+} have a suitable tendency to form bonds with a right angle.

- A combination of the angular subunit metal ions M^{2+} with linear building blocks can work as follows:

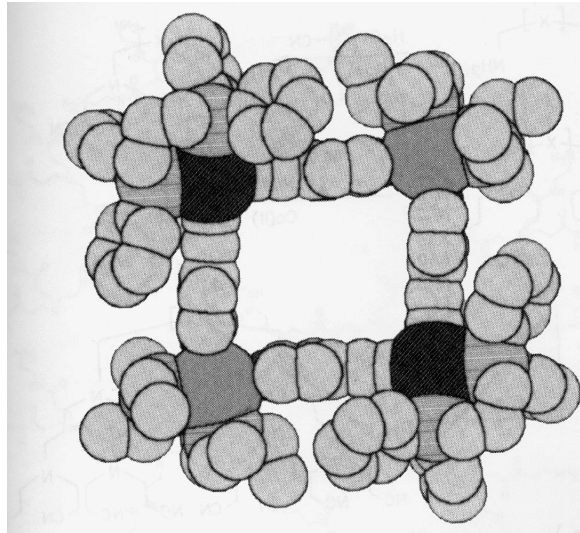


- The metals M stick to two nitrogens at the end of a largely linear molecule formed of a number of benzene rings
- The overall charge of the thing is +8, which is compensated by negatively charged OSO_2CF_3 groups.

- A combination of 2 angular subunit metal ions M^{2+} with 2 angular subunits can work as follows:



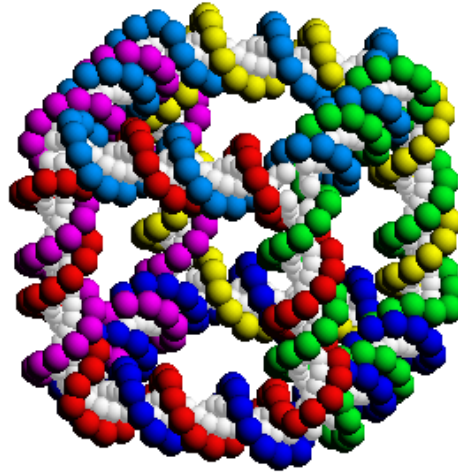
- The angular metal subunit is combined with another angular molecule which already contains a metal. Thus a less symmetric square is formed
- This structure is simpler than the previous (see right figure on top), but the angles are not exactly 90° .
- Here is an atomic picture of what the structure looks like:



7.1.2. Example: DNA cube

[<http://www.foresight.org/Conferences/MNT05/Papers/Seeman/>]

- Recently it has become popular to use DNA molecules to manufacture supramolecular structures.
- In addition to of course being the coding medium of genetic information, DNA has actually several advantages as a building block for nanostructures; we may return to these later on the course.)
- It is possible to manufacture 3D nanostructures of it. Without going into detail on how that works, here is an example: a cube made of DNA:



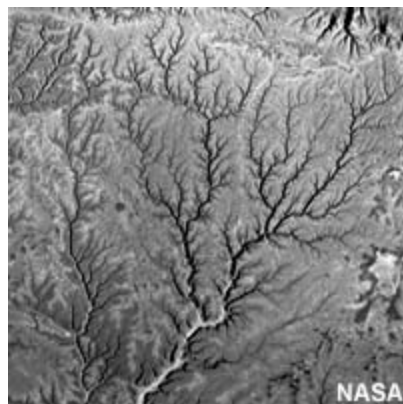
- Each nucleotide is represented by a single colored dot for the backbone and a single white dot representing the base

- Note that the backbones of the strands all go around one side of the cube (4 edges).

7.2. Dendritic structures

[Poole-Owens 11.52, <http://pubs.acs.org/hotartcl/cenear/960603/dend.html>]

- Dendritic structures are ones with lots of branches.
- Examples which everyone is familiar with: trees, snowflakes, lightning, riverbeds etc. etc.
- Here is an example which does **not** belong to nanoscience:

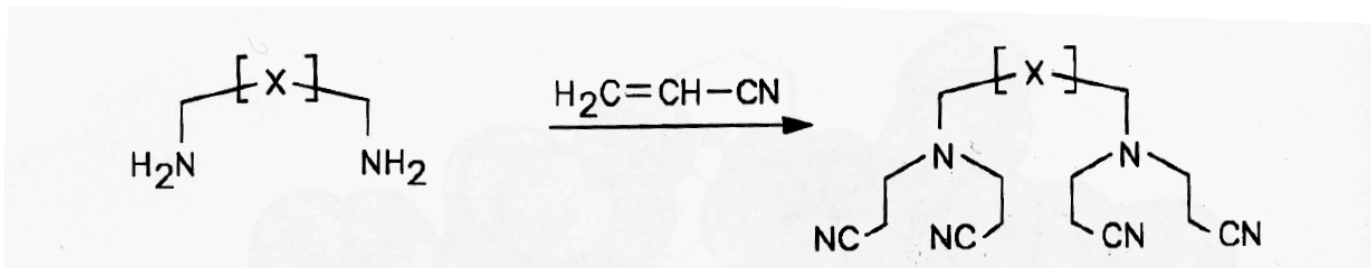


Dendritic supramolecules can be manufactured in a controlled manner.

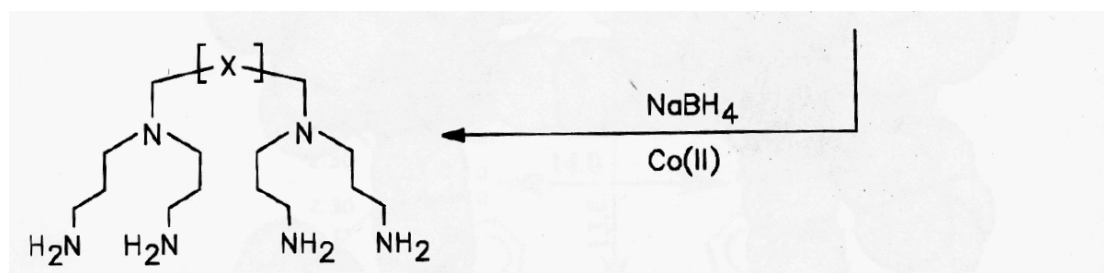
As an example we describe one of the first syntheses.

- The starting point is a diamine compound ($\text{H}_2\text{N-X-NH}_2$), which is a center molecule

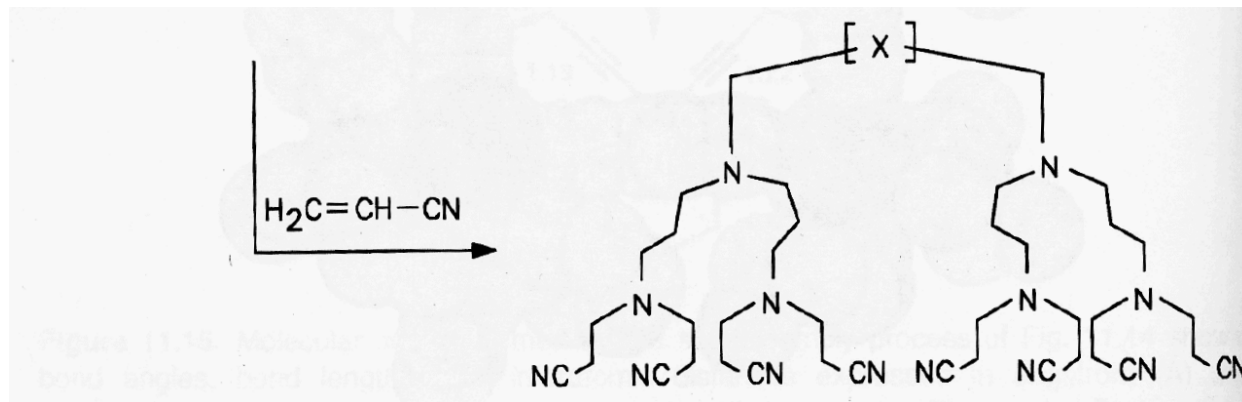
1. The H in the amino groups is replaced with CN by reaction with $\text{H}_2\text{C=CH-CN}$.



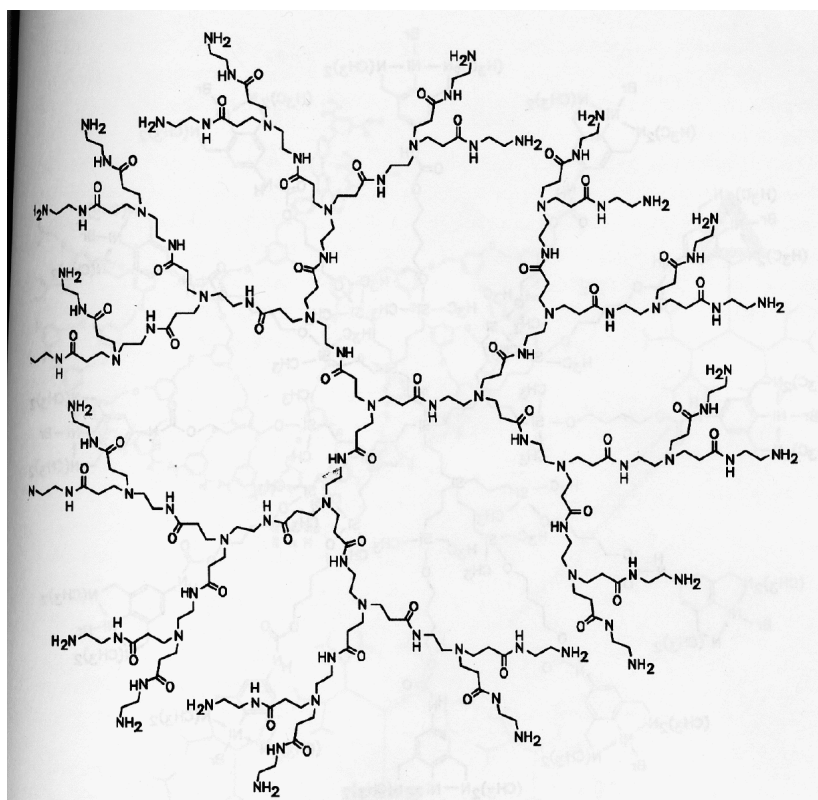
2. Then this thing is reacted with NaBH_4 in the presence of a Co^{2+} catalyst. This replaces the C with H_2 . I.e. the new molecule is now again ended with amino groups, but one layer of nitrogens has been added in between!



- Steps 1-2 can in principle be iterated arbitrarily far to form increasingly large molecules with dendritic shapes (Since the chemical bonds have desired angles, the molecule does not collapse into a dense sphere). Here is an illustration of the next step:



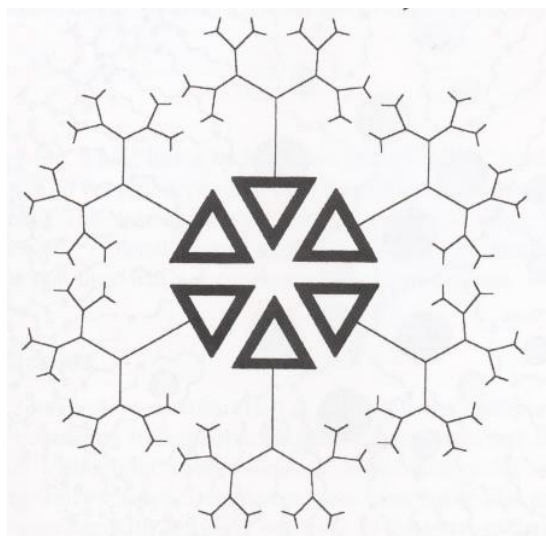
- Here is an example of an similarly formed larger dendritic molecule:



The previous examples are not supramolecules yet. But they can be combined with other dendrimers or molecules to form supramolecular dendrimers.

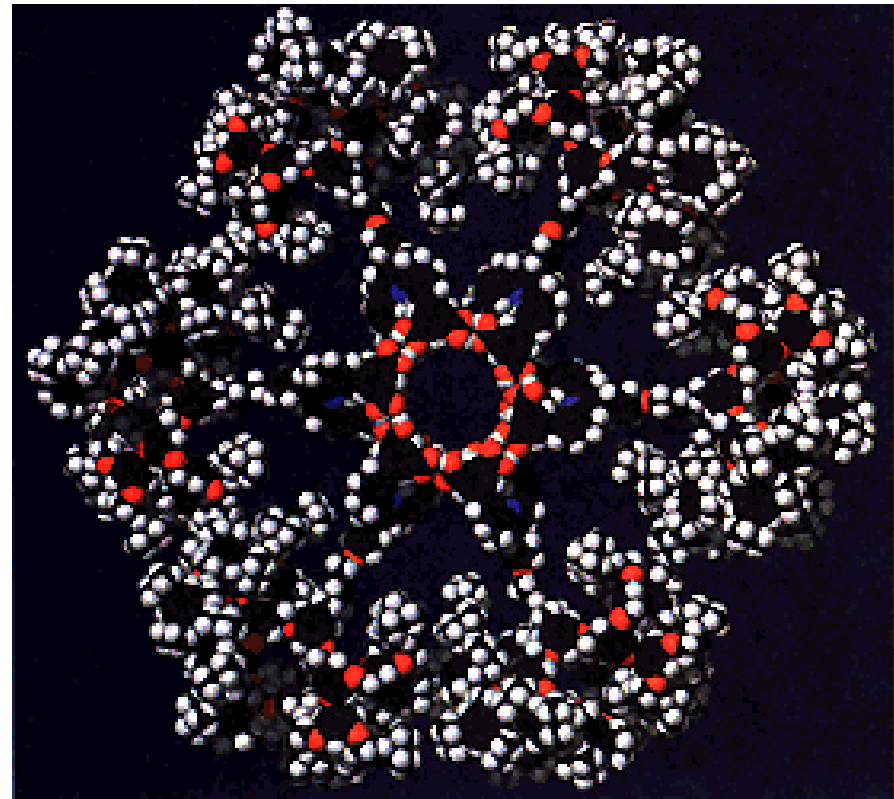
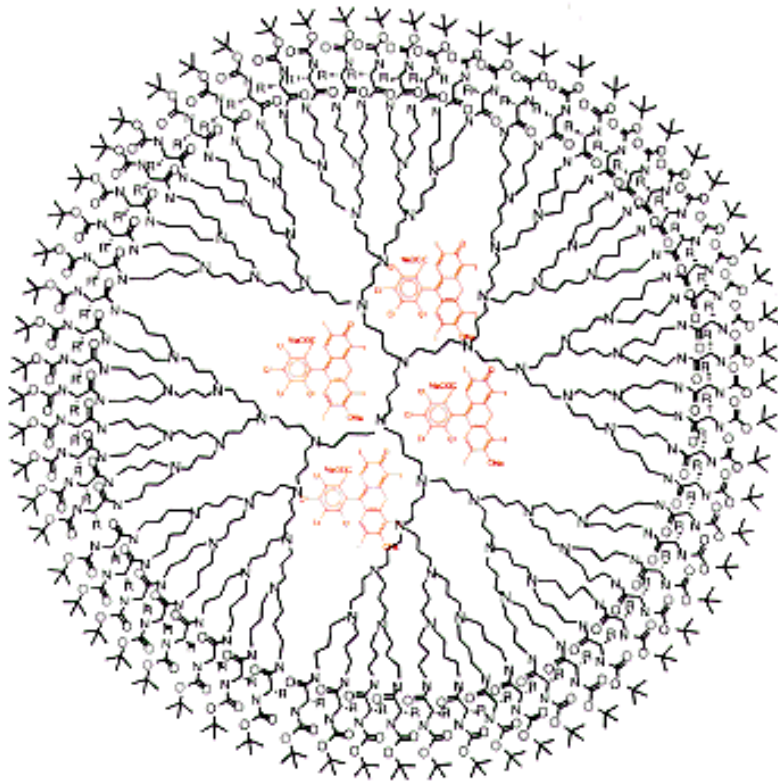
An example is given in the picture below: the shape of the complex molecule on the top left is

shown schematically with the thick triangle and thinner lines on the top right. Six of these things can be joint together to form a supramolecular dendritic complex.



- The black triangles are joint together with hydrogen bonds, which are weaker than the covalent bonds inside each molecules

Here is an image of an advanced globular dendritic molecule, which encapsulate 4 molecules of “Rose Bengal” (a dye molecule)



[Science [271,1095 (1996)],<http://pubs.acs.org/hotartcl/cenear/960603/dend.html>]

Dendritic molecules are interesting e.g. as

- Encapsulation tools for other molecules (e.g. to deliver medicines into cells)

- As catalysts (with metal atoms at the ends)
- Nanoscale reaction vessels
- High-spin organic molecules [<http://www.chem.unl.edu/rajca/structure.html>]