Chemical Systems and Reactivity

Fundamentals of supramolecular chemistry

Molecular Devices

Major accomplishments (Nobel Prize in Chemistry in 2016).

Jean-Pierre Sauvage successfully connected two ring shaped molecules together to form a catenane. This was considered the first step towards the construction of molecular machines.

J. Fraser Stoddart threaded a ring-shaped molecule on to a molecular axle through mechanical bonds and formed a supramolecular architecture named rotaxane.

Bernard L. Feringa developed a molecular motor, that rotates around an overcrowded alkene, to spin continually in one direction.

(Supra)Molecular machines

Shuttles, propellers (elevators), rotors, switches, ratchets and tweezers which are driven by light, electro(chemical) inputs, and temperature gradient effects.

Importance of molecular machines

1. Building of complex molecules more efficiently than via conventional synthetic routes.

2. Switching behaviours of molecular machines can be exploited to perform computation in parallel (molecular quantum computers).

3. Directed/oriented molecular motion, such as that seen in molecular rotors and shuttles, can be used to physically extract mechanical work, through synchronised or collective motion.

4. Biomimetic supramolecular devices for artificial photosynthesis and solar thermal energy storage.

Catenanes and rotaxanes

Catenanes are compounds defined by interlocking of two or more macro-cycles. [n]Catenanes (from Latin cadena) are defined by [n] interlocked macrocycles. The interlocked structures cannot be separated without breaking a chemical bond. The interlocked macrocycles can be seen as topological bonded structures. Rotaxanes are characterised as long, nearly linear molecule threaded through a macrocycle ring.
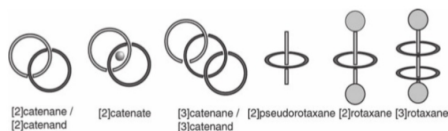

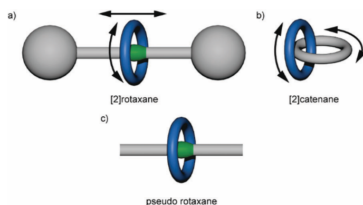Figure 1: Nomenclature for catenanes and rotaxanes(Adapted from Steed&Atwood

Figure 2: Illustration of the dynamics in catenanes and rotaxanes. Adapted from S. Kassem et al, Chem. Soc. Rev. (2017).
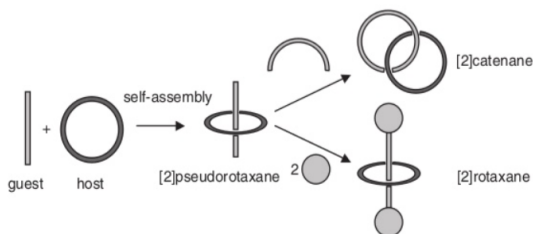

Figure 3: Synthesis of catenanes and rotaxanes via host-guest chemistry. Adapted from Steed&Atwood.

The synthesis of interlinked supramolecular structures (catenanes and rotaxanes) was driven by the analysis of the interactions in the paraquat-bisparaphenylene-[34]crown-10 complex (see next figure). This complex is stabilised by hydrogen bonding between the acidic aromatic hydrogens atom of the paraquat and the oxygen atoms of the crown ether and also by a charge-transfer $\pi - \pi$ interaction from the electron rich crown ether to the electron poor paraquat.
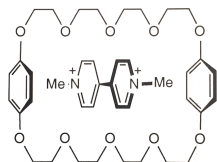

Figure 4: Paraquat-bisparaphenylene-[34]crown-10 complex

The figures below illustrate the synthesis of [2]catenane and rotaxane, where the crown ether macrocycle plays the role of a template.
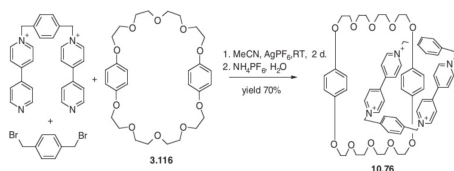

Figure 5: Template synthesis of [2]catenane. Adapted from Steed&Atwood
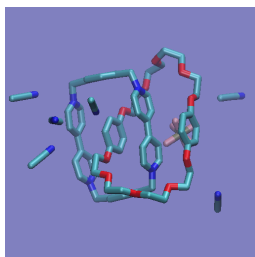

Figure 6: X-ray structure of [2]catenane. Adapted from Cambridge Crystallographic Data Center.
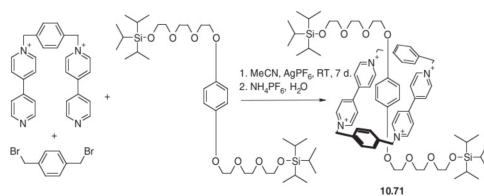
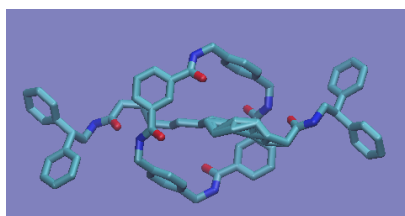Figure 7: Rotaxane synthesis. Adapted from Steed&Atwood

Figure 8: X-Ray structure of tetraoxo-tetra-
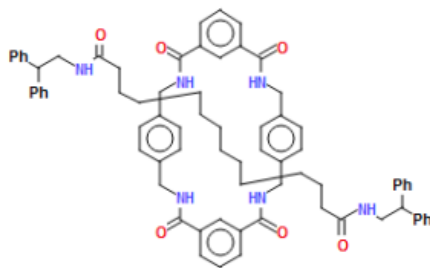aza-dibenzene-rotaxane.
BEMBOL(CCDC).

Figure 9: Molecular structure

Transition metal ions play a fundamental role in the synthesis of catenanes and rotaxanes. Metal-ligand bonds are energetically strong and also have different types of coordination thus providing specific structures for their coordination sphere. Metal-assisted and template effects are two major tools for the construction of complex topological supramolecular assemblies.
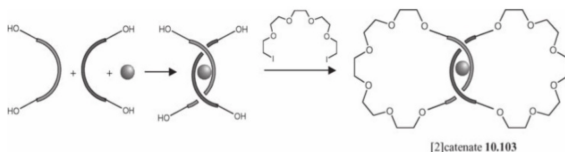

[2]catenate 10.103

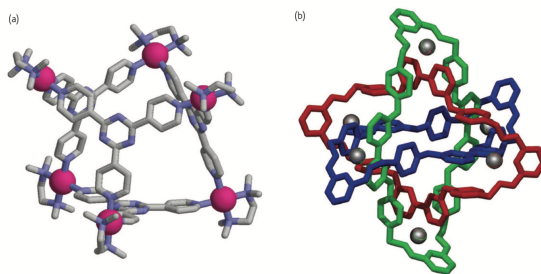Figure 10: Metal template synthesis of a catenate. Adapted from Steed&Atwood

Figure 11: Examples of artificial multicomponent molecules. (a) A coordination cage obtained by self-assembly of four triazine-based bridging ligands and six Pd(diamine) complexes. (b) Molecular rings, synthesized by using, in concert, coordination, supramolecular, and dynamic covalent chemistry. From V. Balzani et al, NanoToday (2007)

Shuttles and elevators

A chemically driven system exhibiting reversible switching is illustrated in the following figure. It is made of a dumbbell component containing an ammonium and an electron acceptor 4,4'-bipyridinium units that can establish hydrogen-bonding and charge-transfer interactions with the ring component (dibenzo-24-crown-8) a crown ether with electron donor properties. N^+-H$\cdots$O hydrogen-bonding interactions between the macrocyclic ring and the ammonium center are stronger and in this case, the crown ether is anchored at the NH_2^+ "station'. Deprotonation of the ammonium center with a base weakens the hydrogen bonding interaction. Now, the crown ether is attracted (shuttled) towards the bipyridinium unit and performs a Brownian motion to bipyridinium "station'. Reprotonation of NH$^\bullet$ with an acid pulls back the crown ether macrocycle to the ammonium center (station).

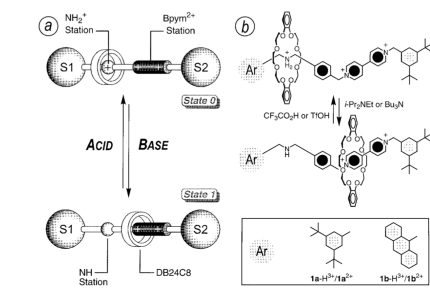
Figure 12: Acid-base controllable molecular shuttle. From P. R. Ashton et al, J. Am. Chem. Soc. (1998).
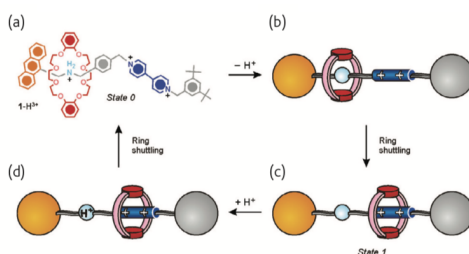

Figure 13: Schematic representation of the operation of a rotaxane as a reversible molecular shuttle controlled by acid-base chemical stimulation in CH$_3$CN solution. From V. Balzani et al, NanoToday (2007).

Elevators

The main chemical-architectural features of the previously discussed switchable rotaxane can be incorporated in a triply threaded two-component supramolecular device that can behaves as a nanoscale "elevator". This nanomachine, which is $\sim$ 2.5 nm high and has a diameter of $\sim$ 3.5 nm. Each pillar includes two different station - one ammonium center and one 4,4'-bipyridinium unit at different levels.
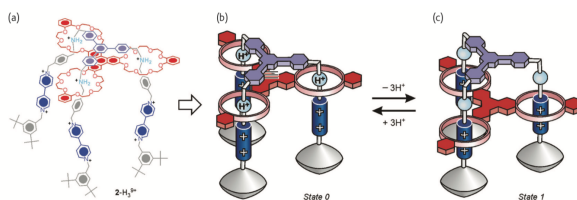

Figure 14: Chemical formula (a) and operation scheme in CH_3CN solution (b,c) of a molecular elevator According to molecular models, the elevator is approximately 2.5 nm high and 3.5 nm wide. From V. Balzani et al, NanoToday (2007).

Molecular shuttles (devices) powered by sunlight

The design and construction of molecular shuttles powered exclusively by light energy is a subject of fundamental interest. The following example is based on a rotaxane species (see V. Balzani et al, NanoToday (2007) for details).

The rotaxane type nanomachine incorporates one electron donor ring R (crown ether derivative) and the following units:

1. a ruthenium(II) polypyridine complex (P_2^+), which plays the dual role of a light fueled power station and stopper

2. a p-terphenyl-type rigid spacer (S)

3. a 3,3'-dimethyl-4,4'-bipyridinium unit (A_2^{2+}) and 4,4'-bipyridinium unit (A_1^{2+}) as electron accepting stations

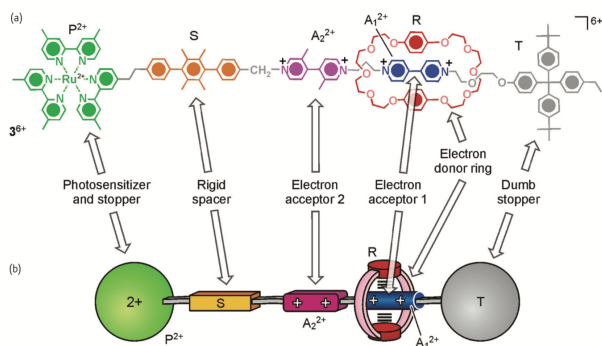4. a tetraarylmethane group as the second stopper (T)

Figure 15: Chemical formula (a) and schematic representation (b) of the rotaxane, showing its modular structure. From V. Balzani et al, NanoToday (2007).

The stable translational isomer of rotaxane is the one in which the crown ether macrocycle (R component) encircles the A_1^{2+} unit, in keeping with the fact that this station is a better electron acceptor than the other one.

Strategy to induce an abacus type displacement of R

(a) Destabilization of the translational isomer: light excitation of the photoactive unit P^{2+} (process 1) is followed by the transfer of an electron from the excited state to the A_1^{2+} station, which is encircled by the ring R (process 2), with a consequent "deactivation" of this station. Such a photoinduced electron-transfer competes with the deactivation of the P^{2+} excited state (process 3);

(b) Ring displacement: the ring moves (process 4) for 1.3 nm from the reduced station A_1^+ to A_2^{2+}, a step that has to compete with the back electron-transfer process from A_1^+ (still encircled by R) to the oxidized unit P^{3+} (process 5);

(c) Electronic reset: a back electron-transfer process from the reduced station A_1^+ to the oxidized unit P^{3+} (process 6) restores the electron acceptor power to the A_1^{2+} station;

(d) Nuclear reset: as a consequence of the electronic reset, back movement of the ring from A_2^{2+} to A_1^{2+} takes place (process 7).
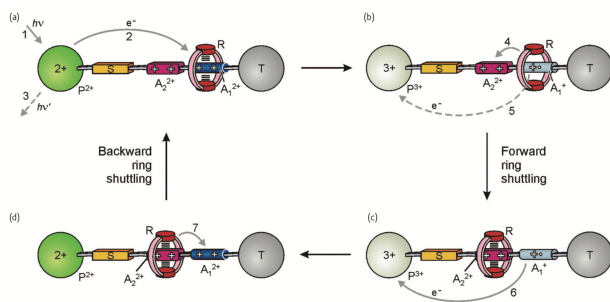

Figure 16: Operation scheme of rotaxane 6+] as a molecular shuttle powered by light. Notice the different competing processes. From V. Balzani et al, NanoToday (2007).

Molecular machines for artificial photosynthesis

Dye sensitised solar cells (DSSC).

The development of alternative energy sources to meet the increasing energetic demand without damaging environmental effects is of fundamental interest. In this scenario, the design of molecular systems for organic photovoltaics and solar thermal fuels plays a central role. Organic photovoltaics relies on biomimetic photosynthetic processes carried out in a dye-sensitised solar cell (DSSC) nanomachine or Grätzel cell.

A dye (sensitizer) is excited by solar radiation creating an exciton (electron-hole system) localized on the dye; the excited electron is transferred to the semiconducting TiO_2 layer, and diffuses through the porous TiO_2 matrix; after charge-separation, the electron is collected by a conductive SnO_2 layer on the glass surface; in the electrolyte, a mediator (I^-/I^{-3}) reduces the dye $(2I^- \rightarrow I_2^{-\bullet} + e^-)$, filling the hole; the mediator is then regenerated by the electron flowing through the load $(I_3^- + 2e^- = 3I^-)$ and a new cycle can be started. The full process is illustrated in the figure below.
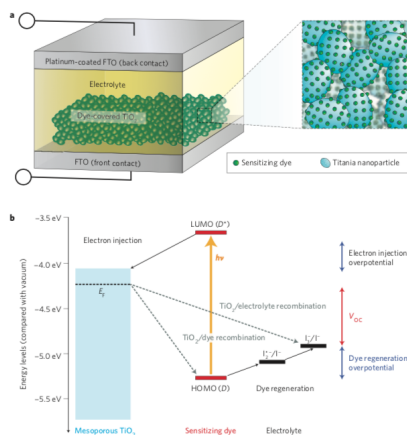

Figure 17: Dye sensitised solar cell (DSSC) machinery. From Hardin et al, B. E. Hardin et al, Nature Photonics (2012).
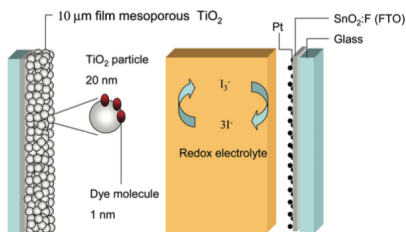
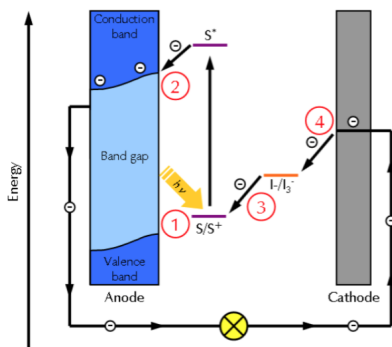Figure 18: Dye sensitised solar cell (DSSC) machinery. From Boschloo and Hagfeldt, Acc. Chem. Res. (2009).

Figure 19: Electron flow in a (DSSC. Adapted from the web.

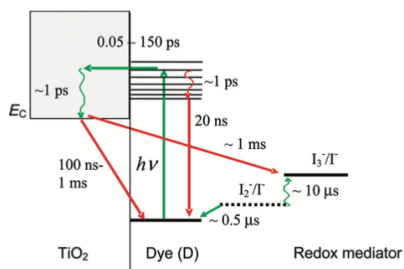
Figure 20: Time scales (kinetics) for the different processes in a DSSC. From Boschloo and Hagfeldt, Acc. Chem. Res. (2009).
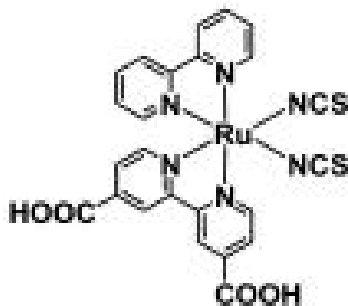
Figure 21: Structure of cis-bis(dithiocyanato)bis(2,2'-bipyridine-4,4'- di-carboxylato)ruthenium(II)or cis-Ru(dcbpy)$_2$(NCS)$_2$, a classical sensitizer in DSSC's.

It is important, to understand from a molecular point of view the energetics of the anchoring of the dye on the substrate well as the formation of a donor-acceptor charge-transfer configuration. The binding of a dye to the TiO_2 and the charge-transfer process are illustrated in the figure below. Notice that the HOMO is on the dye and the LUMO is on the matrix.
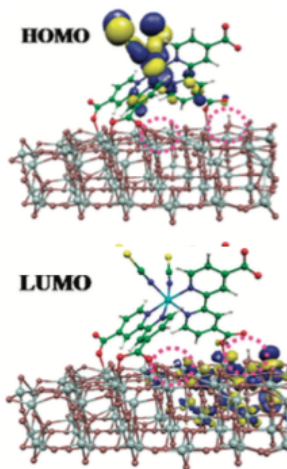

Figure 22: Charge-transfer process from a Ru(II) dye to a TiO_2 matrix. From De Angelis et al J. Phys. Chem. C (2010).
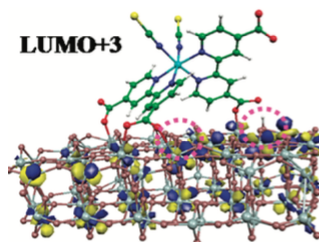

Figure 23: Charge-transfer process from a Ru(II) dye to a TiO_2 matrix. From De Angelis et al J. Phys. Chem. C (2010).

Important aspects concerning the DSSC performance

(1) The dye should have a strong light-harvesting ability/wide absorption spectrum. Therefore, an extension of the light-harvesting region into the near infra-red may improve the efficiency of DSSCs; the lowest unoccupied molecular orbital (LUMO) should be above the semiconductor conduction band thus providing a driving force for the electron transfer;

(2) The dye should have a high fundamental gap or the highest occupied molecular orbital (HOMO) should be low enough to allow a fast reduction by the redox electrolyte;

(3) The organic layer formed by the dyes should minimize aggregation that may inhibit exciton diffusion and charge transfer;

(4) The dye should be strongly adsorbed on the semiconductor matrix fostering electron transfer and charge separation. Moreover, the anchoring of the dye on the TiO_2 substrate is a dynamic process that is strongly dependent on the specific interactions between the dye and the substrate. After photoexcitation, the exciton, which is localized on the dye, can randomly diffuse through the organic layer before finding a favoring anchoring for charge transfer. Therefore, the exciton diffusion length $L = [D\tau]$, where D is the diffusion coefficient and τ is the lifetime of the exciton, should be comparable with the thickness of the organic layer. This aspect imposes a very delicate balance because thin layers favor fast exciton diffusion and thick layers favor efficient sunlight absorption;

(5) The lifetime of the DSSC device is very dependent on the photothermal stability of the dye skeleton/organic layer/TiO_2 matrix.

Photoactive molecules for solar thermal molecules

Molecular solar thermal systems (MOST) are promising materials with the capacity to store energy from the sun in the structural framework of photoactive molecules. In MOST materials light absorption leads to a reversible photo-isomerisation process, where a long-lived metastable isomer revert to the original conformation releasing part of the stored energy. These materials, mimic in a short-time scale, the long-time scale process of solar energy storage in fossil fuels. The development of MOST materials is still in its beginning. The increase in the performance of molecular nanomachines for the energy generation and storage is a major challenge in scientific research with a huge impact on the environment preservation and climate change.

A photochromic species (the parent species) is photoexcited and transformed into a higher energy metastable isomer. The metastable photoisomer can be converted back to the parent species by exposure to a catalyst or heating, and the stored energy is released in the form of heat. The stored thermal energy ΔH is defined by the energy difference between the metastable and parent molecules. The stability (half-life) of the metastable isomer depends on the thermal back reaction-barrier E_a, which is necessary to overcome for recovering the stored energy.
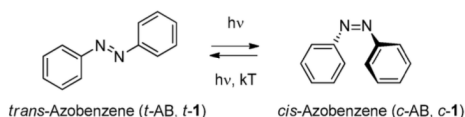

Figure 24: Azobenzene trans-cis isomerization. From M. H. Bandara and S. C. Burdette, Chem. Soc. Rev. (2012)
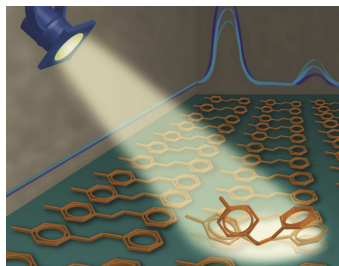

Figure 25: Azobenzene trans-cis isomerization. From M. H. Bandara and S. C. Burdette, Chem. Soc. Rev. (2012)
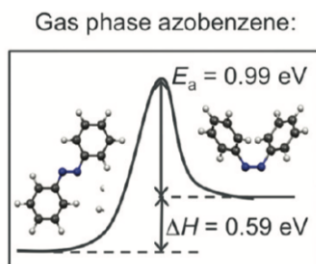
Figure 26: Energetics of azobenzene trans-cis isomerization. From A. M. Kolpak and J. C. Grossman, Nano Letters (2011).
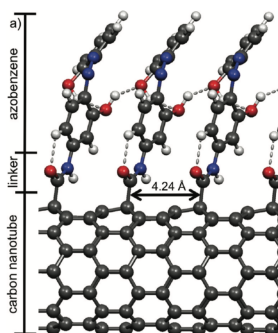
Nanostructured array of photoactive molecules

Figure 27: Array of functionalised azobenzene molecules in a carbon nanotube. From A. M. Kolpak and J. C. Grossman, Nano Letters (2011).
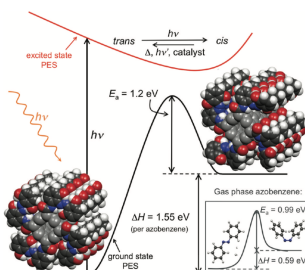

Figure 28: Energetics of trans-cis isomerisation of functionalised azobenzene in a carbon nanotube. From A. M. Kolpak and J. C. Grossman, Nano Letters (2011).