MOLECULAR DEVICES: UNBOUNDING THE FUTURE USING NANOTECHNOLOGY

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> *"When nature finishes producing its own species, man begins, using natural things and in harmony with this very nature, to create an infinity of species."*
>
> *– Leonardo da Vinci*

The properties of compounds depend on how their atoms are arranged. Rearranging the atoms in coal we get diamonds. And since humans first made stone tools and flint knives, we have been manipulating atoms in great thundering statistical herds by casting, milling, grinding, and chipping materials. We rearrange the atoms in sand, for example, add a pinch of impurities, and we produce computer chips.

Even in our most precise work, we move atoms around in massive heaps and untidy piles—millions or billions of them at a time. Theoretical analyses make it clear, however, that we should be able to rearrange atoms and molecules one by one—with every atom in just the right place—much as we might arrange Lego blocks to create a model building or simple machine. This technology often called nanotechnology or molecular manufacturing.

Nanotechnology, by definition, is the craft of constructing devices smaller than a few hundred nanometers, or billionths of a meter. That equals the span of about a hundred atoms strung together.

There are a variety of chemical and physical methods for production of nanomaterials. They include nanolithgraphy, direct atomic & molecular manipulation with nanoscale probe, biotechnological selection and production of useful nanomaterials and chemical synthesis and self-assembly of functional molecules and molecular aggregates. Nanoscale structures and devices may be constructed synthetically from their atomic or molecular constituents (the synthetic or "bottom-up" approach, also referred to as nanochemistry), or by fabrication techniques that use methods to form small structures from larger ones (the reductive or "top-down" approach).

In our day to day life we come across a wide range of complex machines and devices like automobiles, fans, computers etc. which comprise of elementary components like motors, gears, bearings, brakes, turnstiles, wires, switches etc., each performing some specific assigned function. But can anyone imagine analogues of these macroscopic components working in the microscopic world. In this article we make a sincere effort to review some of these microscopic machine parts and devices, synthesised using nanotechnology.

The following are few of the molecular devices:

Photonic Molecular Devices

Conversion of absorbed light into emitted light of another frequency occurs in any luminescent species. One would like, however, to perform separately the various steps of the overall process by means of different components that may be optimised for a given process (frequency of absorbed or emitted light, lifetime of emission, etc.). This is the achieved by a light-conversion molecular device.

This device consists of two components, a light collector (or antenna) and an emitter, which allow separate optimisation of absorption and emission. In order to function, intercomponent energy transfer must occur as efficiently as possible. Such a device operates in 3 modes: absorption-energy transfer – emission (A-ET-E) Fig. 1.

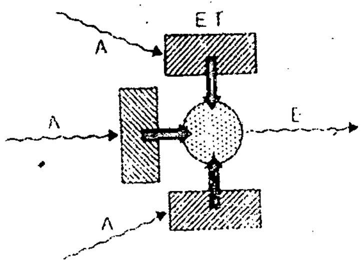


Fig. 1. Light Conversion Photo Molecular device, consisting of two components, a light collector (or antenna, light absorbing groups A) and a light emitter E

Such a device has been prepared using Europium(III) and terbium(III) cryptates of macrobicylic ligands that incorporate various heterobiaryl groups (2,2-bipyridine,phenanthroline, bisisoquinoline, etc.) serving as light collecting antenna components. These complexes have unique properties like :

(i) High thermodynamic stability (ii) Kinetic inertness (iii) Multiple absorbing groups suitable for ET (iv) Characteristic long wavelength (v) Long lifetime of emission.

Consider the complexes as shown in Fig. 2.

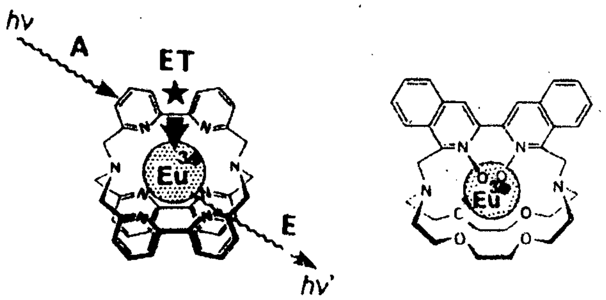


Fig. 2. Photoactive Cryptates

Here the organic groups absorb UV light and effectively transfer the energy to the included Lanthanide cation which then emits its characteristic visible radiation thereby displaying a bright luminescence. Hence these complexes act as light conversion molecular devices. Such photoactive cryptates are of interest as novel luminescent materials and as labels for biological applications subject to very stringent constraints.

Molecular motors

The conversion of energy into controlled motion plays an important role in both man-made devices and biological systems. The principles of operation of conventional motors are well established but the molecular processes used by biological motors, such as muscle fibres, flagella, cilia, sperms, etc. to convert chemical energy into co-ordinated movement, remain poorly understood.

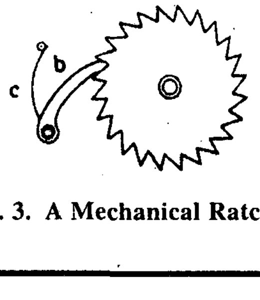
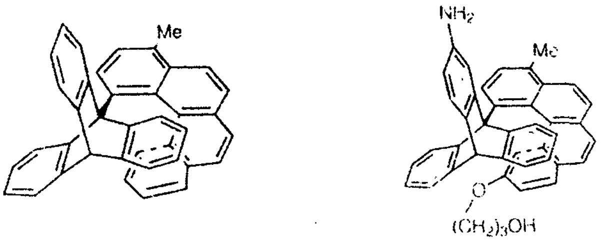


Fig. 3. A Mechanical Ratchet



(a) (b)

Fig. 4

The dynamics and control of rotational motion about the single bonds has engaged the attention of Chemists for decades. Dr. Kelley and his co-workers tried to design a molecular ratchet (motor providing unidirectional motion) containing a three-bladed triptycene as a wheel and a helicene unit functioning as a pawl and spring, joined together by a single bond. The triptycene wheel would spin randomly about the bond (1) {Fig. 4(a)}, but due to the presence of the helicene (pawl and spring arrangement) its motion in one direction will be hindered. Thus this molecular assembly should act as a ratchet. Such unidirectional motion, driven only by ambient thermal energy leads to a perpetual motion machine of the 2nd type thus violating the 2nd Law of Thermodynamics. Hence this design proved unsuccessful in acting as a molecular ratchet

However when this proposed molecular motor is driven chemically (and hence thermodynamically allowed) unidirectional motion is achieved. Molecule shown in Fig. 4b is activated by reaction with carbonyl dichloride to give the isocyanate 3 via carbamoyl chloride. Isocyanate 3 is chemically prepared to react with the OH group in the hydroxypropyl tether attached to the helicene, but in the rotational ground state 3, the isocyanate and the OH group are too far apart to interact. However, at those instants when a clockwise rotation of the triptycene (not possible with a comparable anti-clockwise rotation because an anti-clockwise rotation would bring the reactants further apart and prevent the essential urethane formation) brings the isocyanate and the OH group sufficiently close to react (4, urethane formation 5) can then result, irreversibly trapping the triptycene in a relatively high-energy (compared with 3) conformation around the triptycene/helicene axle. Ambient thermal energy then drives the exoergic unidirectional rotation from 5 to 6 (in contrast, but as expected, the control experiment involving treatment of 7 with $Cl_2C=O/Et_3N$ leads rapidly to 6, but 6 does not detectably convert to 5. Finally 6 is cleaved to give 7, thereby completing the chemically driven rotation 2 to 7.

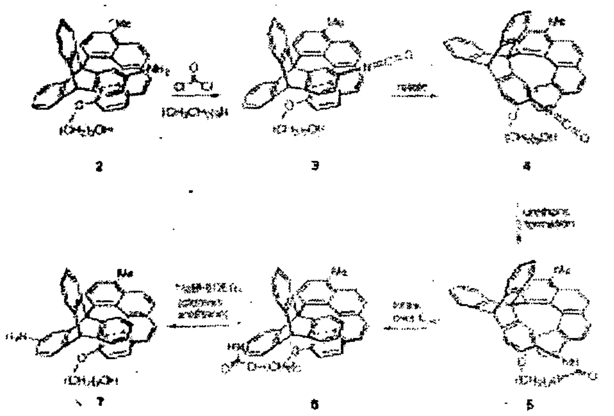


Fig. 5. The sequence of events in the chemically powered rotation of molecule 2 to molecule 7.

Though the first artificial molecular motors are too slow and under powered, their successors will definitely enable a host of application in molecular robotics, manufacturing and medicine.

Molecular brakes

Both the arrest and creation of movement are fundamental aspects of dynamics of macroscopic as well as microscopic levels. Brakes are necessary for stopping the motion of a motor. Following is an example of a reversible molecular brake:

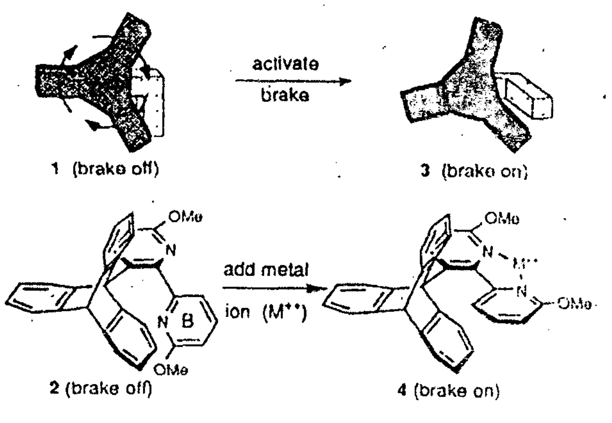


Figure 6. Conceptual and actual depiction of the operation of a molecular brake.

In this system the triptycene wheel performs unrestricted rotation, when the brake is disengaged. In this position, the unit constituting the brake is in the plane of the paper as shown in Fig. 6. But when a metal ion M^{2+} (eg. Hg^{2+}) is added to the system, we get N-M-N bond formation. This leads to a change in the geometry of the system by bringing the aromatic ring in the path of rotation of the triptycene ring. Thus the brake is activated remotely and reversibly.

Molecular gears

The torsional motions of two or more internal rotors in a molecule may be so strongly coupled that correlated rotation becomes energetically preferred over the independent rotation of the individual groups.

Imagine a pair of strongly coupled threefold rotors of the type XR_3 attached to a rigid frame. If the R's bound to X are likened to the teeth of a gear, a formal analogy can be drawn between the pair of chemical rotors and their mechanical counterparts, 3-toothed bevel gears.

Consider the molecular bevel gear consisting of two 9-triptycyl (Tp) groups joined by the bridge-head Carbons to a central atom X, where X= CH_2, CHOH or CO. There are 2 sets of independent molecules in the unit cells of Tp_2X. The molecules occupy general positions, with the Tp_2C and Tp_2O skeletons adopting approximate C_S symmetry. The co-existence of two independent structures in the unit cell, one of C_2 and the other of approximate Cs symmetry, implies that these conformations do not differ much in energy. All these molecules therefore undergo virtually unhindered dynamic gearing. The Tp rotor thus behaves as highly mobile (i.e. almost frictionless) and tightly meshed (i.e. securely interlocked) bevel gears; the cogs are benzene rings that fits snugly into the V-shaped notches formed by 2 rings in the other rotor.

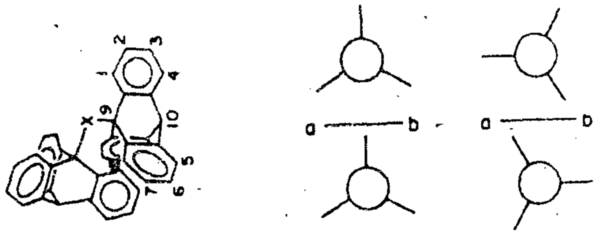


Fig. 7. Perspective view of the C_S conformation (left) and the enantiomeric C_2 form (right)

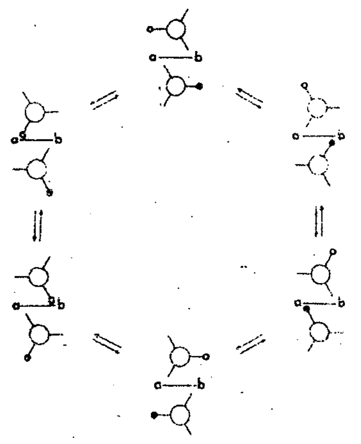


Fig. 8. Conformational gearing circuit for mesophase isomers of TP_2X

Molecular sensors

A sensor is a device that spontaneously responds to external and internal stimuli. A sensor consists of a receptor (host) and a signalling unit. When the substrate interacts with the specific receptor, the receptor stimulates the signalling unit to produce a signal, thus conveying to the operator that recognition has occurred.

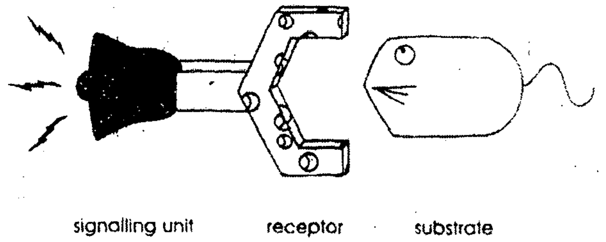


Fig. 9. Assembling a receptor and a signalling unit makes a sensor.

A specific sensor system is useless if it is not able to communicate immediately to the external operator. Fluorescence is a property detectable and measurable in real time using low cost instrument, even at very low concentration of the analyte ($\leq 10^{-7}$M). An anthracene based sensor for s-block metal ions is shown in Fig. 10.

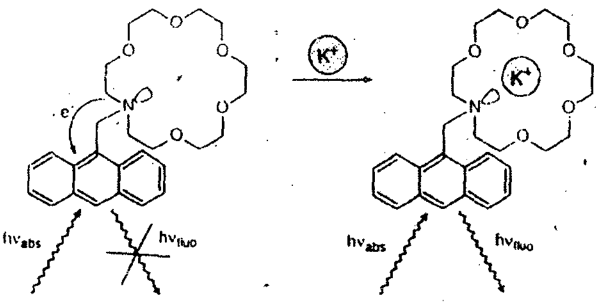


Fig. 10. A PET sensor for K$^+$. Metal coordination stops the electron transfer process from the tertiary amine group to the photo-excited anthracene fragment and restores fluorescence

The receptor is an 18-member macrocyclic containing 5 ethereal Oxygen atoms and an amine, Nitrogen atom as donors. Thus, by analogy with classical ligand 18-crowns-6, it is suitable for a selective interaction with K$^+$ ion. Before metal incorporation the supramolecular system is not fluorescent. In particular the typical anthracene fluorescence is quenched via an electron-transfer process from the fairly reducing tertiary amine group of macrocyclic ring (i.e. from amine lone pair) to the photo-excited fluorophore following metal co-ordination, the oxidation potential of the amine group is substantially lowered (as the lone pair is involved in co-ordination) and the electron transfer process is prevented on a purely thermodynamic basis. As a consequence, fluorescence is restored. Therefore. the interaction between the receptor and the K$^+$ ion is communicated to the outside by appearance of the intense emission of anthracene.

Molecular switches

A switch is a device which has two distinct states ON (1) OFF (0). A molecule which can act as a switch is as shown in Fig. 11.

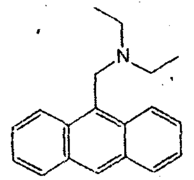


Fig. 11. A Molecular switch

One can switch on/off the fluorescence of the anthracene fragment linked through a –CH$_2$- bridge to a tertiary amine group, by varying the bulk parameter pH. In acidic solution, the intense fluorescence of anthracene is observed; subsequently, with pH approaching the pK$_A$ value of the anthrylammonium acid, fluorescence decreases and is completely quenched in definitely basic solution. In solutions of pH ^{3}(pK$_A$+1), the dominating species is the amine *form and an electron is spontaneously transferred from* the lone pair of amine nitrogen atom to the photo-excited to the fluorophore, quenching fluorescence. At pH £(pK$_A$-1), the amine group is protonated and the electron transfer is thermodynamically prevented. The pH switchable fluorescent system can be considered also as a sensor for H$^+$, receptor (the amine group) working as a switch. In a similar way, above sensor also can be considered as a switchable system which is operated through a variation of concentration of K$^+$

Molecular shuttles

Shuttles are devices which have to and fro motion between two stations. Molecular shuttles are chemical species in which the relative position of one of their component part can be altered between two positions by an external stimulus. Suitably designed chemical species like cantenanes, rotaxanes, and pseudo-rotaxanes act as novel molecular shuttles in which the relative displacement of their parts can be induced by chemical or electrical energies as well as by light. Their functioning can be monitored by a variety of techniques, such as NMR, absorption and emission spectroscopy, along with electrochemistry.

Consider the [2] rotaxane, comprising of a dibenzo(24)crown-8 (DB24C8) macroring bound mechanically to a chemical "dumbbell" possessing two different recognition sites- viz. Secondary dialkylammonium (NH_2^+) and 4,4'-bipyridinium(Bpym^{2+}) units. It also bears a fluorescent and redox-active anthracene (Anth) stopper unit which is useful for (i) Monitoring the system's state and (ii) Propelling the macroring by photochemical and electrochemical stimulation.

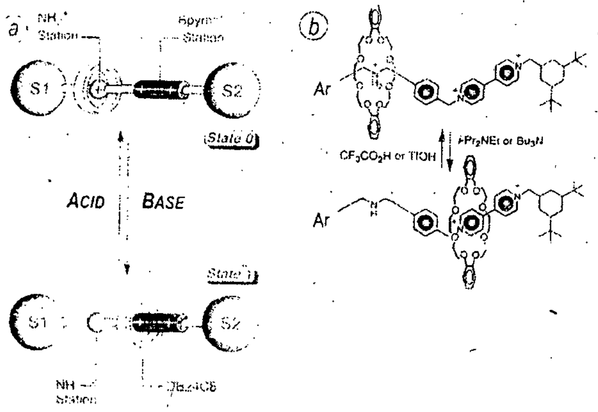


Fig. 12. An acid –base controlled molecular shuttle

The DB24C8 macroring exhibits complete selectively for the NH_2^+ recognition site (due to strong [N^+-H—O] hydrogen bond formation). Thus the [2]rotaxane exists as only one of two possible translational isomers. But deprotonation of the rotaxane's NH_2^+ centre causes a quantitative displacement of the DB24C8 macroring to the Bpym^{2+} recognition site, an outcome that can be reversed by acid treatment. Thus we see that in this shuttle action the macrocyclic ring resides initially only on the NH_2^+ station. After treatment with a non-nucleophilic base, deprotonation coerces the macroring to the Bpym^{2-} station. Addition of acid however regenerates the NH^{2+} center, moving the macrocyclic component back to bind its original station and rendering the switching cycle reversible.

Applications

The direct consequences of Molecular Nanotechnology (MNT) would be great. We could continue the revolution in computer hardware right down to molecular-sized switches and wires. The ability to build things molecule-by molecule makes a new class of structural materials that would be more than 50 times stronger than steel of the same weight: a Cadillac might weigh 100 pounds; a full-size sofa could be picked up with one hand..

Nanomachines, with their broad ability to rearrange atoms, will be able to recycle almost anything. Using nothing but sunlight and common materials, and with no by-products other than waste heat, they will produce a wide range of products. With production costs similar to those of plants, they will enable the clean, rapid production of an abundance of material goods.

Molecular nanotechnology could revolutionise medical sciences. The ability to build molecule by molecule could give us surgical instruments of such precision and deftness that they could operate on the cells and even molecules from which we are made Potential medical applications also show that small systems can have big effects. New molecular machines and computers of subcellular size could support the body's own mechanisms. Devices containing nanocomputers interfaced to molecular sensors and effectors could serve as an augmented autoimmune system, searching out and destroying viruses and cancer cells.

Conclusion

The ability to make nanoproducts probably lies a few decades away as MNT today is still in its infancy. But theoretical and computational models provide assurances that the molecular manufacturing systems needed for the task are possible—that they do not violate existing physical law. For people unfamiliar with the concept, the products of MNT and therefore MNT itself, seem like science fiction. There is no doubt the concept of space travel must have sounded equally strange around 1870 when even planes and automobiles did not yet exist. Molecular Nanotechnology is not contradictory with the present laws of physical science, but it does challenge the capabilities for imagining the enormous technical possibilities still within these constraints.

We would like to end by quoting Richard P. Feynman "THERE IS PLENTY OF ROOM AT THE BOTTOM"

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