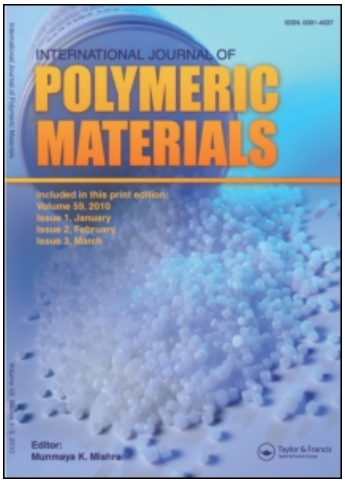


**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Molecular Electronics: Beyond the Limits of Conventional Electronics

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**To cite this Article** Pilkuhn, M. H.(1999) 'Molecular Electronics: Beyond the Limits of Conventional Electronics', International Journal of Polymeric Materials, 44: 3, 305 — 315
**To link to this Article: DOI:** 10.1080/00914039908009700
**URL:** http://dx.doi.org/10.1080/00914039908009700

*Intern. J. Polymeric Mater.*, 1999, Vol. 44, pp. 305–315
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# Molecular Electronics: Beyond the Limits of Conventional Electronics

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*(Received 15 April 1998)*



Future technologies in information science will rely on structures with decreasing size and on systems with increasing complexity. The physical and technological limits of semiconductor nanostructures point to the use of molecules and atoms in information science. In particular, organic molecules are very attractive because they can be engineered with very large complexity, and their electronic and optical properties can be controlled technologically. Already today many fundamental functions and devices relevant to information technology can be realized with systems of organic molecules: Switchable molecules lead to the development of memories with large capacity, transmission of information is possible through "molecular wires", and the flow of information can be interrupted by "switching molecules". Together with other logical elements this opens the possibility to develop future systems in information technology. However, this requires suitable supramolecular arrangements for complex interconnections of logical elements and memory molecules, as well as a suitable electrical or optical periphery.

*Keywords:* Molecular electronics; molecular photonics; conjugated $\pi$-systems information transport; super molecular arrangement

## 1. MOTIVATION, DEFINITION

Future information technology will require smaller and smaller sizes of devices together with increasing complexity of integrated systems. This trend was established over many decades in the past, and it is depicted in Figure 1.

Also over decades there has been a debate as to where the limits are for the smallest semiconductor device dimensions. Today in nano-

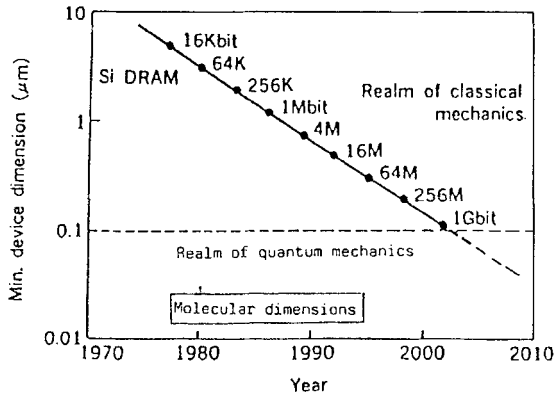


FIGURE 1 Decrease of device dimensions in the years 1970 to 2010.



technology we have reached dimensions of nanostructures which are in the order of 10 nm through which one can realize low dimensional structures like quantum wires and quantum boxes. New quantization effects can be observed which are at the same time of interest for specific applications. Technological problems like size fluctuations and interface effects, however, become dominant when one reaches these extremely small sizes which are not very different from the size of large molecules. In fact, the quantum box can be viewed as a large molecule rather than a semiconducting solid, and one could define this already as "molecular electronics". The continuation of this development points to the use of molecules or even atoms in information technology. Organic molecules are of particular interest because their structure and properties can be engineered in a controlable way leading to a seemingly endless variety of interesting possibilities. Moreover, all the functions necessary in information technology can be realized in these molecular systems, and this is the more generally accepted definition of "molecular electronics".

Besides electronics, optics will play an essential part because many of these molecules can be addressed easily by light. Figure 2 shows schematically that parallel to electronics, optical devices and components have also become smaller over the years which could also lead to the use of molecules or atoms.

In this case the word "molecular photonics" might be more appropriate. The use of optical or electronic information processing

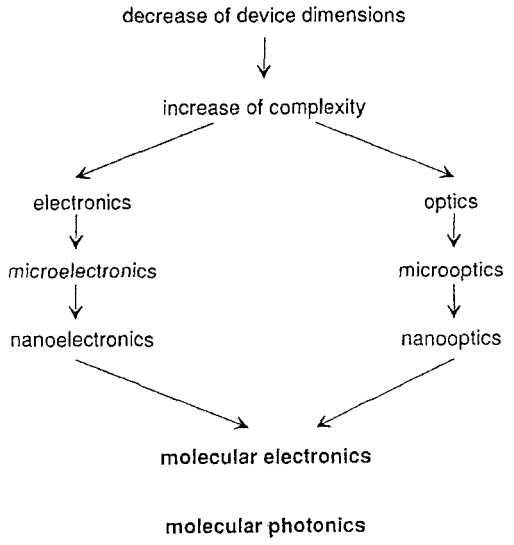


FIGURE 2 Development of molecular electronics/photonics from conventional electronics and optics.



functions in organic molecules has fascinated scientists for many years, and many proposals for molecular electronics have been made [1 – 6], leading to lively discussions and also controversy. Molecular functions can range from typical semiconductor functions like charge storage devices, diodes and transistors to complex systems like molecular shift registers [4, 7]. Other applications of molecules are optical memories [8] or non-linear optical devices [3, 6] as examples.

A strong support for the development of molecular electronics comes from our knowledge of biological systems. They are also based on organic molecular units where, by the way, many functions follow those in semiconductor devices like photo-induced electron-hole-separation. We all know that biological systems exceed our present technologies by many orders of magnitude. For this reason, the use of biological molecules in "bio-electronics" has been sometimes suggested. I think that the outstanding performance of biological systems should be viewed only as an "existence proof" that something similar might be possible in molecular electronics or bio-electronics. On the other hand, from studying biology we have so far not obtained much

technical knowhow in developing future practical systems in information technology.

Major problems in the past have been:

1. The manufacturing and control of complex systems, that is interconnections of logical elements and memory molecules in suitable supramolecular arrangements.
2. The development of a suitable periphery *i.e.*, electronic or optical addressing of molecular systems.
3. Stability problems of organic molecules and molecule arrangements.
4. High temperature operation ("$kT$-problem").

## 2. BASIC MOLECULAR UNITS



It has been pointed out very early [2] that basic molecular units can perform all the necessary functions one needs in information technology, and could be assembled to "idealized" molecular systems. For instance, molecular information storage is possible by using photochromic molecules which change their absorption spectrum with light irradiation. It is conceivable that a system of writeable and eraseable photochromic molecules leads to storage capacities of $10^{10}$ bit if arranged in a molecular associative matrix [7]. This can be increased even significantly if frequency selective memories are designed by employing, for instance, the effect of spectral hole buring [8]. Figure 3 shows as an example a phthalocyanine molecule with two potons which can be switched in a teutomeric geometry [8].

If this molecule interacts with an amorphous polymer matrix, the frequency of light which is needed for spectral hole burning will be slightly different for the various molecules because of molecular interactions with the surroundings. Laser light with a given frequency therefore addresses only particular molecules offering the possibility of a frequency selective memory system. In this type of molecular information storage systems, single molecules are used to store the information as a change in the electronic structure leading for instance to a change in absorption. Considering the size of a molecule (about $0.2\,\mathrm{nm}^3$) one can reach storage capacities which are easily 5 orders of magnitude larger than that of classical capacitor systems.

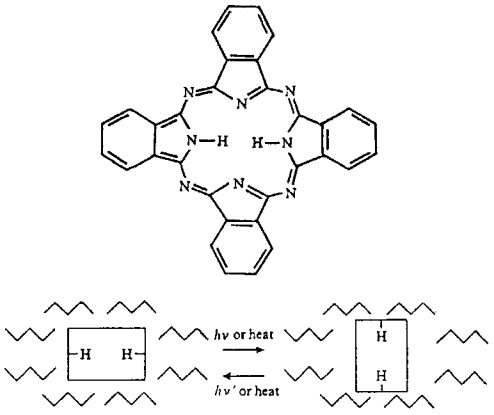


FIGURE 3 Proton switching process in a phthalocyanine molecule.



The fascinating possibilities of molecular memories are documented in the following comparison of bit densities:

| | |
|---|---|
| magnetic memories: | $10^8$ bit/cm$^2$ |
| optical/magneto-optical memories: | |
| (diffraction limited): | $10^8$ bit/cm$^2$ |
| photochemical hole burning | |
| (photon-gating): | $10^{11}$ bit/cm$^2$ |
| holographic memories: | $10^{13}$ bit/cm$^3$ |
| molecular memories: | $10^{15}$ to $10^{18}$ bit/cm$^3$ |

However, there are more complex possibilities for information retrieval and processing. Information can be also transferred in organic molecule chains in conjugated $\pi$-systems which can form one-dimensional conductors or "molecular wires". Examples are polyacetylene (PA), polyparaphenylene (PPP), polypyrole (Ppy) *etc.*, or more recently polythiophenes (PT) as key conductive polymers which are depicted in Figure 4 [9].

Endgroups can be added in order to functionalize the polythiophene, and by varying the nature of added functional groups, these "contacted" molecular wires can exhibit a wide range of interesting physical properties: Transfer switches, sensors, transducers, memories and logic operators.

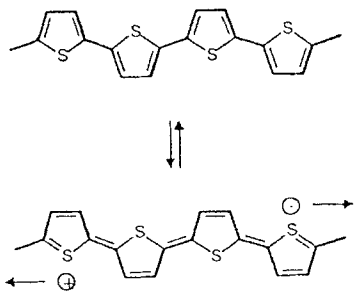

FIGURE 4 Conjugated pathway in polythiophene chains in their neutral (top) and oxidized, conducting state (bottom).

An example of a simple molecular storage unit is a donor-bridge-acceptor (DBA) molecule which can lead ultimately to the development of molecular cellular automata [7]. Figure 5 shows the picture of a basic storage molecule which is the building block for more complex cellular automata systems: A polaronic storage DBA molecule.

Information (*i.e.*, a charge) can flow from the donor molecule to an acceptor molecule by exciting the bridge molecule (see Fig. 6).

The bridge molecule can be viewed as a quasi one-dimensional conductor and it can have different length. In long conductors, the information flow can be interrupted by using switching molecules which can be switched optically like the thiophene fulgide molecules depicted in Figure 7.



## 3. SUPRAMOLECULAR ARRANGEMENTS

The construction of an elementary molecular functional unit is not sufficient for an application in molecular electronics. These units must

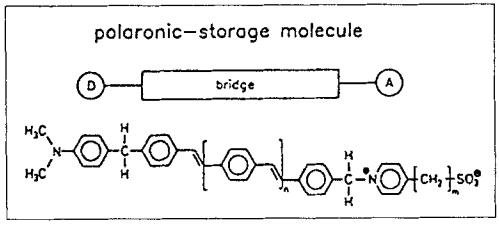


FIGURE 5 Basic layout of a bistable donor-bridge-acceptor (DBA) molecule which utilizes excitation of the bridge molecule.

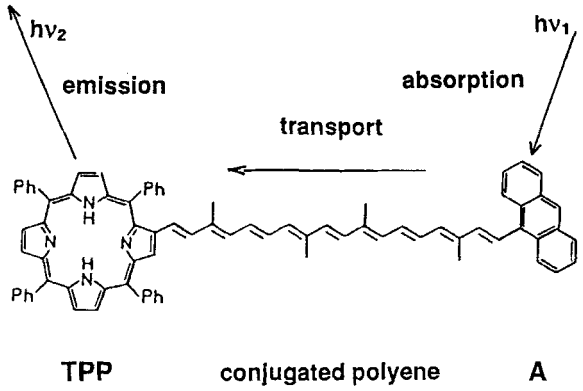


FIGURE 6 Information transport along conjugated polyenes

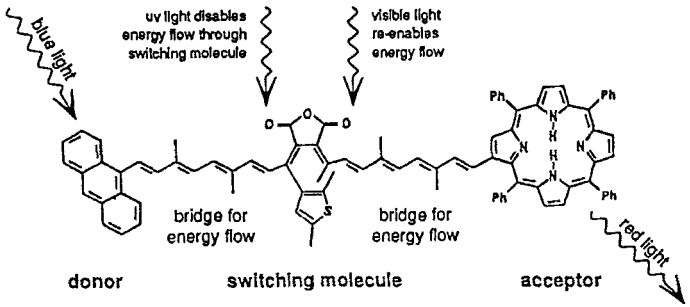


FIGURE 7 Donor and acceptor molecule connected through a bridge which can be interrupted by an optically switchable fulgide molecule

be connected to molecular systems, and this has been one of the very serious difficulties in the past impeding the development of a practical molecular electronics. Even the simplest supramolecular assemblies like simple parallel arrangements of molecular units have been a problem in the past. An old approach is the Langmuir-Blodgett technique where assemblies are controlled by amphiphilic molecules on aqueous surfaces. Modern methods for organized molecule arrays employ self-assembly techniques. For instance, end-capped oligothiophenes can be self-aligned on silicon surfaces. Figure 8 shows schematically the alignment of DBA molecular unit arrays.

Another example is the regular assembly of PTCDA molecules, as depicted in Figure 9 for the case of NaCl surfaces.

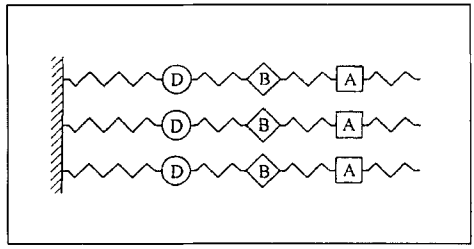


FIGURE 8 DBA (Donor-Bridge Acceptor) molecules connected in parallel to an electrode.

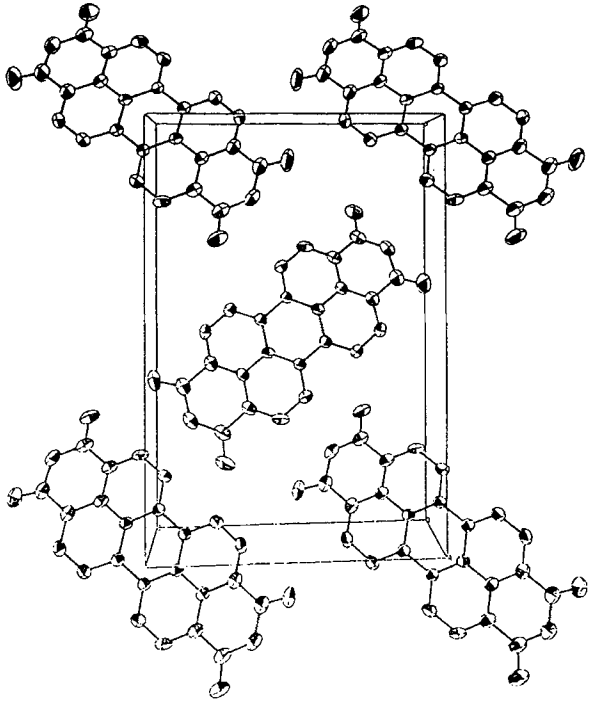

FIGURE 9 Regular assembly of PTCDA molecules on NaCl surface.

Recently, similar regular PTCDA arrangements could be obtained at Stuttgart on Si (111)/H surfaces and were studied by high resolution STM techniques.

However, all these developments are still in the area of basic chemistry and physics or fundamental interface studies, and far away

from any practical molecular electronic system. It is very easy to point out possibilities like developing molecular electronic shift registers or cellular automata on the basis of Figure 8. But the practical prospect for a utilization has not really improved over the last years.

An "external" manipulation of molecules is also possible by applying, for instance, electrical fields (poling techniques) or by employing an atomic force microscope (ATM)

## 4. ELECTRICAL AND OPTICAL PERIPHERY

Another basic problem of molecular electronics is the development of a suitable periphery, connecting molecular electronic systems with the outside (electronic) world. There are two approaches, an electrical periphery which connects molecular electronics with nano-electronics or an optical periphery connecting it with nano-optics. In the case of an electrical periphery, the study of self-assembly techniques on structured semiconductor surfaces is an approach which should be pursued. The chances of addressing one single molecular unit are very small, however. In principle it is possible by the use of STM which is not a very practical approach. The optical periphery seems to be more interesting by employing small and tuneable semiconductor lasers. For photochemical hole memories [8], only few suitable molecules are addressed by the laser light leading to a hole in the absorption spectrum. This is shown for example in Figure 10 which shows the absorption spectrum of phthalocyanene molecules embedded in a polymer matrix after a radiation of laser beams with various frequencies.

The development of very small semiconductor lasers (like tuneable DFB lasers or vertical cavity surface emitting lasers) for short wavelength would have a strong impact on solving the problem of optical addressing in molecular electronics.

## 5. CONCLUSIONS

Molecular electronics offers a huge number of extremely interesting possibilities in information technology. The dimensions of the

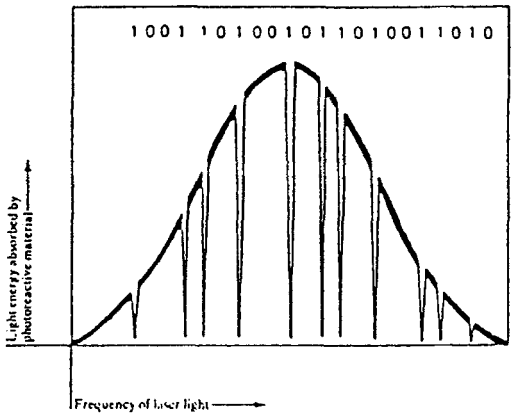


FIGURE 10 Photochemical hole burning memory: Bit pattern in frequency space. In addition, the laser spot can be $x, y$-scanned for storage in real space.



individual "molecular devices" seems to be an attractive continuation of the present trend to go to smaller and smaller sizes in electronic systems. The real attraction of molecular electronics comes from the observation of its apparent role in biology. In spite of these facts, molecular electronic has not developed significantly over the last years. It is not a big problem, to realize basic molecular units which can perform a large variety of interesting functions in information technology. The problem is to create supramolecular arrangements in order to connect these units to complex systems. The second problem is that of addressing molecules through a suitable electrical or optical periphery. Optical addressing seems to be more promising at present through the development of semiconductor lasers.

It is difficult to predict, if this "idealized" molecular electronics mentioned here can ever be realized for practical use. But it is likely that easier solutions and spin-offs (like optical memories, photorefractive and non-linear materials, liquid crystals, sensors or LEDs) will lead to a wide variety of applications.

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