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Editorial Essay

How to Tailor Molecular Electronics or Why is Nature Taking the 'Soft' Approach?**

By Dietrich Haarer*

Dedicated to Professor Wolfgang Hilger on the occasion of his 60th birthday

1. Introduction

The more we are able to understand the efficiency of biological systems, the more our mind is tempted to design *Molecular Devices* whose efficiency is comparable to the efficiency which nature has achieved during its evolutionary path. Here are three examples:

a) The **capacity of the human brain** is of the order of 10^{15} bits. To mimic this memory-capacity with magnetic disks (typically 60 MByte; 50 Watt power consumption) one would need about two million disks, consuming about 0.1 Gigawatts of electric power. Our human brain does this job for as little as a couple of Watts. Granted, a magnetic store of the above size would be more reliable than our brain; however, its energy consumption differs from the biological systems by some 7 orders of magnitude.
b) Highest performance can be achieved with **semiconductor devices,** but assuming a price of $10 for a 1 MBit chip, we would have to pay about 10 billion dollars to assemble a semiconductor memory of the capacity of the human brain.
c) The **sensitivity of the human eye** is comparable to that of a photomultiplier tube. On our retina we have in the order of 10^8 photon receptors of roughly the sensitivity of a photomultiplier tube. If we assume that a photomultiplier costs around $100 (including power supply), we would have to pay about 10 billion dollars in order to build, by conventional means, an optical device with the same performance as the human eye.

The above examples may be fortuitous, and it is certainly accidental that our 'multiplier eye' turns out to cost as much as our 'megabit brain'. The examples show, however, that nature must have some design secrets which we cannot yet handle.

Even more astounding than its price/performance is the accuracy with which nature is able to process molecular information. Consider that the rate of mutation per base pair per replication of DNA is of the order of 10^{-10} (drosophila; see[1]). Even the accuracy of the translation of the genetic information into amino acids with 10^{-5} to 10^{-4} errors per amino acid position is very impressive.[2] These numbers beat, by any means, what can be technically achieved by present magnetic, optical or chemical schemes.

With nature being able to perform the above 'miracles' and with the limits of the silicon based technologies becoming more and more visible, it was an obvious step to consider a synthesis of electronic schemes and molecular schemes, long before the word *'molecular electronics'* was coined. Starting with the possibility of creating quite accurate molecular assemblies it was shown in the early 70's[3] that by using monolayer techniques, molecules could be assembled at well defined distances and that energy transfer and tunneling processes could be investigated experimentally[3] as well as theoretically.[4]

The capability of achieving 'design' on a molecular level led to concepts like the *molecular rectifier*[5] and *molecular shift registers,*[6] where molecular and semiconductor terminologies were fused to give a new dimension, namely *'Molecular Electronics'.*

Speakers at two recent meetings, a workshop in Bangor (UK)[7] and a meeting in Strasbourg (France)[8] presented two aspects of molecular design. In Bangor, aspects of 'Molecular Metals' (*F. Garnier*), 'Monolayers and Thin-Films' (*D. Bloor*) and 'Spectroscopy on a Molecular Scale' (*D. Haarer*) were the center of attention, whereas in Strasbourg it was the chemistry of synthesizing molecules which are selective as to the size, shape and ionic state of other molecules (*Lehn,*[9] *Stoddart*[10]) as well as biological aspects which deal with very large molecules like bacteriorhodopsin (*G. H. Khorana*) and molecular schemes which fall into the category of 'Topobiology' (*G. Edelman*) which provided the central theme. All of these are topics which reflect the wide range of interests in the field of molecular design.

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The question which I would like to discuss briefly in this article is the following: Why does nature use such large units like phycobilisomes, bacteriorhodopsin and the photoreactive center of *Rps viridis*[11, 12] to perform electronic functions? (In the above mentioned examples, 'electronic functions' are functions which are triggered by photon absorption). Figure 1 shows the reaction center.[11] It is about 130 Å in length and has an elliptical cross section of 70 and 30 Å respectively.[12] The total molecular weight is about 125 000, about 250 times larger than the dye molecule phthalocyanine, and about 1000 times as large as a small organic donor molecule like naphthalene.

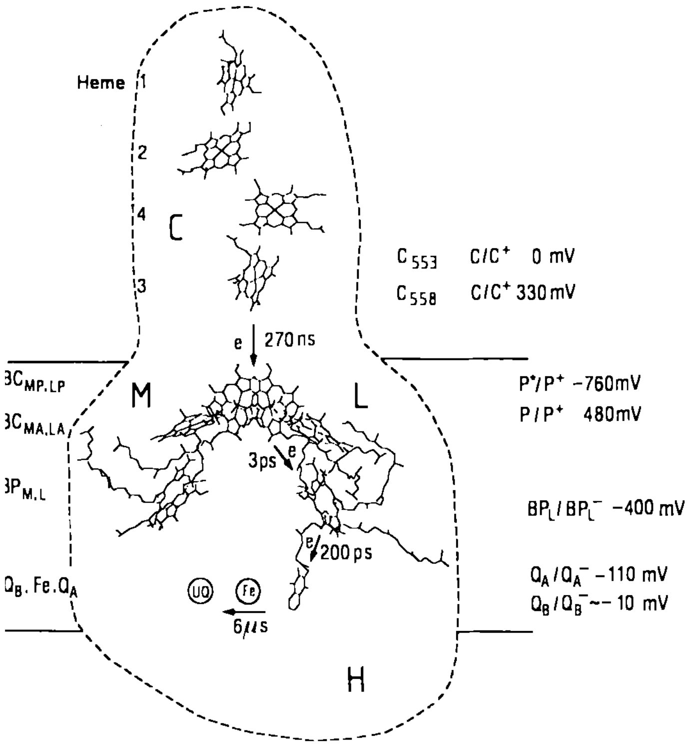

Fig. 1. Scheme of the structure of the reaction center of *Rps. viridis* showing the cofactor system, the outline of the protein subunits (C, M, L, H), the electron transfer half-times, and the redox potentials of defined intermediates [11].

Was nature wasteful with its valuable resources or does the large volume of 'biological machines' point towards a principle of *low densities of excited states* or *low charge carrier densities*, one of which may be the conditio sine qua non for the system to function? In typical configurations, as proposed for straightforward molecular electronics, one needs a high density of charge carriers where each charge carrier represents a bit of information and is, in general, confined to the space occupied by a small molecule. In other configurations one uses light to generate excited molecules at adjacent molecular sites (for instance donor-acceptor sites) in order to implement a clock which is able to shift molecular information along a molecular array. In other words, the charge density and the density of excited states tend to be of the order of one per small molecule. These situations are not easy to handle, as one knows from past experience with molecular crystals. Some of the following examples document what can happen if charges and excited states are brought into close proximity.

2. High Density of Excited States—Exciton Annihilation

Biological systems can be 'bleached' with low light levels and this seems to contradict the above statements about high densities. This contradiction, however, is not real, because nature has used certain construction principles:

- The dye-like molecules, absorbing in the visible spectral range, are present at a dilute concentration and surrounded by non-absorbing (and space filling) proteins.
- The systems are very complex, having subsystems with sub-picosecond electron transfer, nanosecond lifetimes, and microsecond to millisecond metastable states, which store chemical or electrical energy before allowing the systems to return to their ground state after the light has been switched off.

If one were to pack small molecules, similar to those which are often suggested for molecular electronics in close proximity to one another, and if one neglects long living interme-

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diates (which are undesirable in fast electronic systems because they would slow down molecular switches), one arrives at matrices resembling molecular crystals. Here we know that excited singlet states are delocalized (excitons, polarons) and annihilate i.e. transfer their valuable photon energy into heat if brought closer together than a typical distance of about 1000 Å.[13]

Having the above example in mind, nature has done two things to avoid annihilation: a) dye-like molecules with overlapping π-orbitals appear in dimers rather than in single crystal-like configurations and b) the dye molecules are surrounded by a large bulk of protein (solvent cage) which is transparent in the wavelength range of visible photons.

3. High Concentrations of Charge Carriers

3.1. The Electron-Hole Recombination Problem

Having made the point, that excited states do – in crystal-like media – not like to be packed closely, we have to discuss the same issue for charge carriers.

Light-induced charge carriers are always produced as electron-hole pairs, maintaining the total charge neutrality. Electron-hole pairs, however, have the tendency to annihilate unless they are created in a high electric field which is able to separate them. *Onsager* has calculated the probability of the geminate recombination of charge carriers performing a diffusionlike motion. Typical 'Onsager Radii', which define the distance at which the charge carriers thermalize, are of the order of 20 Å.[14,15] Following the model of *Onsager*, the quantum yields for electron-hole separation approach unity as the field strength increases beyond 10^6 V/cm. For external fields this field strength is close to the dielectric breakdown. Molecular fields in biological systems may even be higher than the above quoted numbers for external technical fields.

3.2. The Space Charge Problem

One of the most severe problems if one wants to confine charge carriers to molecular-size boxes is the far reaching Coulomb force, which falls off slowly with $1/R$, where R is the distance between the charges. One problem, when dealing with molecular devices, will therefore be the difficulty of controlling charges using 'external fields', which are larger than the 'internal molecular fields' with which the charge carriers mutually interact. The simplest way of calculating the upper limit of how many charge carriers can be put into a molecular box, without exceeding the space charge conditions[16,17] is the following: one calculates the capacitance C_m of a molecular capacitor of the size of a 'molecular device'. The condition to be fulfilled is that the molecular charge q_m must be smaller than $C_m \times U$, where U is the applied voltage. For simplicity I assume a plane parallel capacitor geometry with two disks of diameter R_D separated by a distance d (see also Fig. 2). This capacitor is filled with a dielectric medium of dielectric constant ε ranging between 10 and 100. Now, the simple question to be answered will be the following: How many electrons can be packed into this device without running into space charge problems at a field of 10^6 V/cm (close to breakdown)? Doing this elementary calculation, one notes that the distance d does not enter into the figures, and one gets the result that it is only possible to pack 5×10^{-2} electrons into the box if ε is 10 and the diameter R_D is 10 Å.[18]

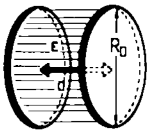

Fig. 2. Dimensions of a molecular capacitor – see text.

In spite of the crudeness of this estimate, I realize that it is quite difficult to control charges with external fields under conditions where the external field dominates (known from photoconduction experiments[15,16,19]). Since we cannot easily design a molecular deviced operating with 1/20 of an electronic charge, our recipe for avoiding space charge problems would be to take a capacitor diameter of 100 Å rather than 10 Å – and that's just what nature has done with biological devices, casting our mind back to the photoreactive center shown in Figure 1. A second comment should be made concerning the thickness d of the device. Since the thickness does not enter into the calculation (in our crude planar geometry model), it is always advantageous to deal with thin samples because here one can optimize the number of charges which can be controlled via external fields.

4. Conclusions

Admittedly, the above model assumptions are very crude, yet, they are based upon experiments with molecular crystals and polymer films and point to the fact that organic materials do not like high densities of excitated states. For instance, the molecular crystals, which were used for exciton annihilation experiments showed brown spots of carbonization after a few laser shots.[13] Organic materials also cannot accommodate many charges while still alowing us to control the charges individually. Certainly, one can make 'organic metals' like TTF-TCNQ and pack one electron and one hole into a charge transfer pair, but one is then dealing with metals, where the individual character of the charge carriers is lost in the Fermi-sea.

Taking into account all of the above 'hard restrictions' which must be satisfied in order to perform electronic processes on a molecular scale, we may not be so surprised that nature has chosen the 'soft' way in reaching its goals. It uses not so much the Coulombic approach with adjacent electrons and holes and not so much the excitonic approach with large single crystal-like structures and strongly coupling singlet excited states. More often, nature uses environments in which charges are screened, like *ionic* environments, *hydrogen bonded* environments and environments in which Van der Waals interactions dominate, and it also separates the active sites using bulky proteins. Fortunately, the fluid phase is an ideal medium for these interactions: geometries can be optimized, and defects which would be detrimental to a solid state device can heal in microseconds or milliseconds.

Not everybody will agree with this article, since it draws far reaching conclusions on the basis of simple model estimates. I hope, however, that the article is useful in the following sense: If some of the estimates turn out to be too skeptical, the article will stimulate experiments to prove that less severe conditions have to be fulfilled. Should the limitations be as severe as pointed out, we will have to proceed along the 'soft' path of molecular electronics. I believe that this can be done.

I will end the article with one example in a field of molecular electronics in which I have some knowledge and through this I would like to document that the soft approach can be realized. The example is photochemical hole burning.[20,21] In these experiments, optical saturation is achieved by using a three level scheme (idealized here; in a true model more levels are involved). After exciting dye-like molecules to their first singlet state (two level picture), the photochemical change occurs mostly in states which are subsequently populated and have longer lifetimes (for instance triplet states). From these states the system then relaxes into a photochemical state (being labelled as the third state), whose lifetime can be infinitely long (at least at sufficiently low temperatures). In this scheme the photon information is *accumulated photochemically* in a third state, whose lifetime can be varied over wide ranges (microseconds to years). This kind of photochemistry even occurs at the lowest light levels. The system accumulates the photon information and, if enough photons have been accumulated a bit of digital information can be stored. This can occur at integrated energies of as little as one picojoule and it only works in systems in which the molecules which store molecular information are very dilute (10^{-3}–10^{-5} M)[21] So, from my present viewpoint, the future of molecular electronics is a bright one if we follow realistic design principles.

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