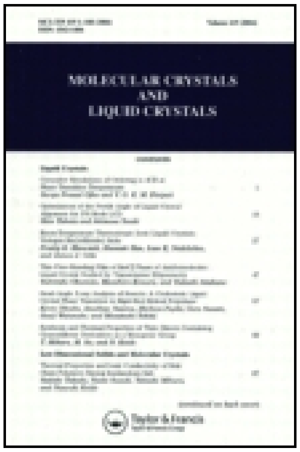

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Some Problems of Functional Macromolecule Design for Nanoelectronics

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Some Problems of Functional Macromolecule Design for Nanoelectronics

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Some models of macromolecular electronic systems, first steps in their creation and difficulties on the way of their design and synthesis were examined.

Keywords: molecular electronics, excitons, molecular design, exciton current

INTRODUCTION

The working out and designing of basic elements that could process, accumulate and transport information on molecular level are among the main problems of nanoelectronics. These elements can operate at the expense of intramolecular current flow that is connected with a stimulated electron or proton transfer in macromolecules or at the expense of intramolecular exciton processes. Polymers that contain π-electron groups in back chain belong to the most perspective ones for creating such elements from high molecular compounds. Just for such macromolecules, as our experience shows, it is succeeded in direct modifying of separate links at the same time having no influence on energetical structure of other links. This gives one the possibility to work out and synthesize macromolecules with set in advance hierarchy of energetical levels. That gives the definite functional properties to these macromolecules.

The problem of functional macromolecule creation, which can serve as basic elements for nanoelectronics, was the object of a number of papers [1-5]. In[2-5] the model of macromolecular exciton rectifier was suggested.

In the present work we examine some realistic models of molecular basic electronic systems (elements) first steps in their creation, and some difficulties on the way of their design and synthesis.

MACROMOLECULAR MODELS OF EXCITONIC RECTIFIER AND CONCENTRATOR

The excitation energy transfer in chromophore-containing macromolecules is realized by incoherent excitons randomly hoping to nearest neighbor link along the macromolecule. That is the reason that the resulting dislocation is considerably less than their total way during life-time.

The question arises: is there any possibility to create a macromolecule with direct one-way excitons motion in which energy transfer could be realized by the following steps: 1) the absorption of photon by initial (first) link; 2) one-way excitation energy transfer; 3) localization of excitation in the final link.

In the general case this situation (which is suitable for direct one-way energy transfer) can be realized in macromolecule in which there is a decrease in level energy values from unit to unit along a macromolecule.

There is a number of variants of suitable displacements of polymer cell energy levels:

a) Singlet levels of chromophores fall down along the macromolecule. The triplet levels are arbitrarily displaced.

b) Both singlet and triplet levels of chromophores fall down simultaneously.

c) Triplet levels of π-electron systems fall down along the macromolecule, but the singlet levels are displaced arbitrarily.

However, the peculiarities of organic molecule absorption are such that practically it is impossible to excite upper S_1-levels without exciting lower S_1-levels. For example, in scheme *b*) the photon with sufficient energy for exciting the S_1- level of first cell does excite all cells of a macromolecule.

Only one variant of suitable displacement of S- and T- levels of elementary cell π-electron systems satisfies the proposed scheme of energy transport. At least two conditions must be fulfilled to embody this model:

1) The position of the first excited singlet level of the initial link of macromolecule must be lower than the position of the first singlet levels of all links of macromolecule. The position of singlet levels of other links may be arbitrarily but all of them must be placed higher than S_1-level of the first link. The energy difference (ΔE_S) between S_1-levels of neighbour links must be essentially more than value kT ($\Delta E_S >> kT$).

2) The energies of the first triplet levels of macromolecule links must gradually decrease from link to link along the macromolecule and the value (ΔE_T) between T_1-levels of neighbour links must be essentially more than value kT ($\Delta E_T >> kT$).

Let us assume that the first macromolecular link absorbs I_0 photons per second (Fig.1). Then the exciton current between the link number **n** and the link number **n+1** (the quantity of excitons which pass through the cross-section of the macromolecule in a fixed direction per unit of time)

$$I_n \equiv \frac{dN_n}{dt} = I_o\beta^n - I_o\beta^{n+1} e^{-\frac{E}{kT}}$$

where ΔE is the difference between energy values of neighbouring unit sites; β is the probability of enérgy transfer between neighbouring units.

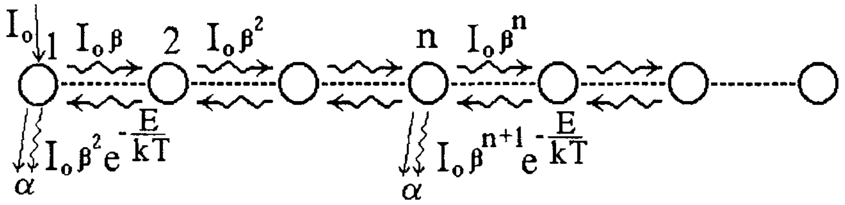

FIGURE 1 Energy transfer in a hypothetical macromolecule

It was shown [2,4] that

$$I_n = I_0 \cdot \left[\frac{1-\alpha}{1+e^{-\frac{\Delta E}{kT}}} \right]^n ,$$

α is the probability of spontaneous deactivation in every unit of a macromolecule.

For typical vinylaromatic polymer parameters the loss of excitons is negligible and reaches ~ 10 % for link number 10^4.

Another model proposed is a nonlinear branched macromolecule, each branch of which (A-B-C) has the same energy structure as in the model described above. Such macromolecule model could give one the possibility to create excited sites with high density population in C-type centres (Fig. 2).

There are two problems, which appear in designing and synthesizing of the model systems:

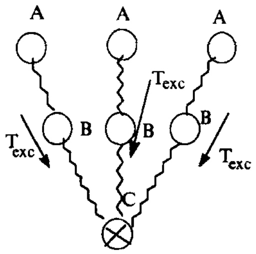

FIGURE 2

1) The dependence of singlet-triplet splitting on macromolecular side group structure. Up to now this problem has been solved empirically. But a principal solution is necessary.

2) Difficulties in synthesizing geterogenic multicell systems. The practical realization of such macromolecule is a very difficult task. Every link of this macromolecule must be different with a new position of singlet and triplet energy levels. Meanwhile during a chemical bond formation we observe changes in an electronic nature of unconjugated systems and in energy level distribution. There is no technological solution for step by step linking of new determined cells with a growing macromolecular chain.

We believe that photochemical methods are perspective for solving this problem.

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