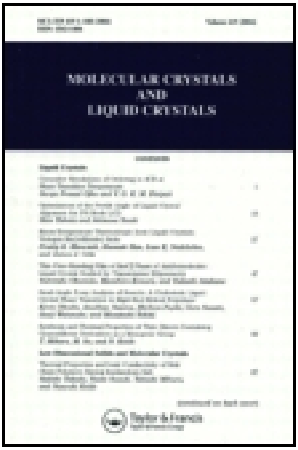

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Multifunctional Macromolecules and Structures as One-Way Exciton Conductors

Valeriy M.(N.) Yashchuk [a], Volodymir G. Syromyatnikov [a], Tymish Yu. Ogul'chansky [a], Alexey Yu. Kolendo [a], Tomasz Prot [b], Jerzy Błażejowski [c] & Vladislav Yu. Kudrya [a]

[a] Kyiv T. Shevchenko University, Department of Chemistry, Volodymir'ska 64, 252 033, Kyiv, Ukraine

[b] Pułaski Technical University, Department of Material Science and Footwear Technology, B. Chrobrego 27, 26-600, Radom, Poland

[c] University of Gdańsk, Department of Chemistry, J. Sobieskiego 18, 80-952, Gdańsk, Poland

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Multifunctional Macromolecules and Structures as One-Way Exciton Conductors

VALERIY M.(N.) YASHCHUK[a*],
VOLODYMIR G. SYROMYATNIKOV[a], TYMISH YU.
OGUL'CHANSKY[a], ALEXEY YU. KOLENDO[a], TOMASZ PROT[b],
JERZY BŁAŻEJOWSKI[c] and VLADISLAV YU. KUDRYA[a]

[a]*Kyiv T. Shevchenko University, Department of Chemistry, Volodymir'ska 64, 252 033 Kyiv, Ukraine,* [b]*Pułaski Technical University, Department of Material Science and Footwear Technology, B. Chrobrego 27, 26–600 Radom, Poland and* [c]*University of Gdańsk, Department of Chemistry, J. Sobieskiego 18, 80–952 Gdańsk, Poland*

The first steps in the design, investigations and possible applications of multifunctional macromolecules exhibiting one-way direct exciton conductivity are presented. Some problems that appeared during the formation of these systems are discussed.

Keywords: functional macromolecules; one-way excitation energy transfer

INTRODUCTION

Nowadays, the world of technology is striving to reduce the size of electronic devices. It seems, however, that with current technological approaches, electronic miniaturization has reached saturation. It is generally thought that a quality jump in the development of electronics can be achieved by the transition from the micro to the nano (or molecular) scale[1-6]. In this context, the search for functional macromolecules or macromolecular structures that could act as basic elements in electronics (such as molecular diodes or rectifiers, photodiodes, transistor lines of decay, generators) is very important. On the other hand, in a number of cases the

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* To whom correspondence should be addressed.

supply or drainage ('sucking off ') of energy to/from a given point in a system may be required to accelerate or stop reactions. Such goals can be also attained with the aid of special functional macromolecules.

This paper briefly reviews and discusses the results of the authors' work in creating and investigating one-way exciton conductors, as well as some applications of energy transfer to photochemistry.

MAIN IDEAS AND MODELS

It is known that excitation energy transfer in chromophore-containing nonconjugated macromolecules is realized by incoherent excitons[7-9]. Their spread along a macromolecule is of the nature of a random walk. This is why the resulting dislocation is considerably smaller than the total path they cover during their lifetime. The question arises whether it is possible to create a macromolecule in which energy transfer could be realized as direct one-way exciton motion (Fig. 1) in the following steps: (*i*) exclusive absorption of a photon by a first link, (*ii*) one-way direct excitation energy transfer, and (*iii*) exclusive location of excitation energy at the end link. Such a macromolecule could be applied as a one-way exciton conductor.

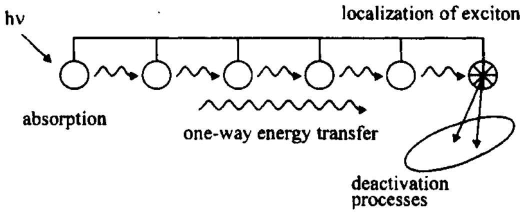
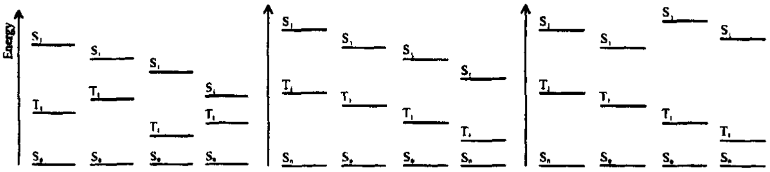


FIGURE 1 Macromolecule in which direct one-way exciton motion occurs.

In general, direct energy transfer can be realized (as Kopelman pointed out in the 1970s) in a system in which energy levels fall gradually from one unit to the next. If we take this into account, we can consider the following variants in the arrangement of energy levels in macromolecules: (*a*) singlet levels of chromophores fall along a macromolecule and triplet levels are situated randomly, (*b*) singlet and triplet levels of chromophores both fall along a macromolecule, and (*c*) triplet levels (usually of π-electron systems) fall along a macromolecule, while singlet levels are situated randomly.



(*a*) (*b*) (*c*)

However, the peculiarities of electromagnetic radiation absorption by organic molecules are such that it is practically impossible to excite the upper S_1-level of one chromophore without exciting the lower S_1-level of another. For example, a photon in cases *a* and *b*, possessing sufficient energy to excite the S_1-level of the first chromophore (hereafter referred to as a cell), may also excite every other cell of a macromolecule. Only one variant of the energy level arrangement in macromolecules is appropriate for achieving one-way exciton motion, i.e. (*i*) when the S_1 level of cell number 1 is situated below the S_1 levels of the other chromophores, and (*ii*) when triplet level energies decrease gradually from cell to cell along a macromolecule. Only in this case is it possible to excite the first chromophore without exciting the others. If in addition the $S_1 \rightarrow T_1$ transition is efficient enough, the energy transfer is realized mostly in this way.

Let us define the quantity *exciton current* as the number of excitons that pass through a cross-section of a macromolecule per unit of time. If in the first cell I_0 excitons are generated per unit of time, one can show that the value of the exciton current I between cells n and $n+1$ is expressed by the formula: $I \approx I_0\,(1-\alpha)^n$

(where α is the probability of excitation deactivation). For triplet exciton-conducting aromatic polymers α is of the order of 10^{-5}. Then, for $n = 10000$ and $\Delta E >> kT$, $I / I_0 \approx 0.9$, where ΔE is the energy gap between neighboring cells, k is the Boltzmann constant and T the temperature. In such a case, the energy lost during exciton conduction is negligible and approximately 90% of the excitons are transferred between cells 1 and 10000. Taking into account the fact that the critical exciton hop distance is approximately 18-20 Å [10], one can evaluate the distance over which energy can be transferred (without significant losses): it is no less than 20μm. On the nanoscale, this is a very large distance.

Another proposed model is a nonlinear, branched macromolecule in which each branch has the same arrangement of energy levels, as shown in Fig. 2. At first sight this macromolecule looks like a dendrimer[11]. There is, however, an essential difference between a dendrimer branch and a branch of our macromolecule, which has been designed to achieve the required hierarchy of energy levels. In our case, photons are absorbed exclusively by the first cell and subsequently transported a long distance to the end cell in the form of a triplet exciton current.

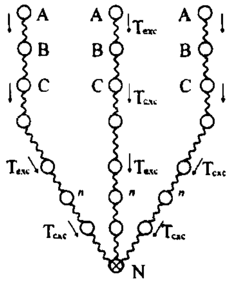


FIGURE 2 Branched functional macromolecule.

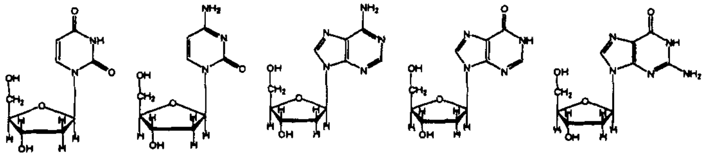
FIRST STEPS IN DESIGN AND SYNTHESIS

Design

We have selected a number of compounds (ordered in sequences) which have a hierarchy of energy levels suitable for the design and synthesis of functional macromolecules. The schemes below present these compounds and their energy (E) levels.

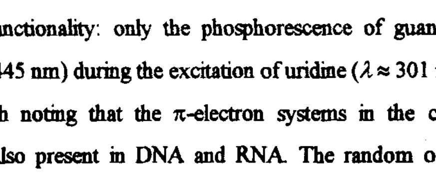
Sequence 1

Compounds



Uridine (UR) Cytidine (CY) Adenosine (AD) Inosine (IN) Guanosine (GU)

Energy levels

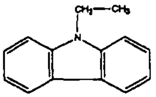


Test of functionality: only the phosphorescence of guanosine needs to be observed ($\lambda \approx 445$ nm) during the excitation of uridine ($\lambda \approx 301$ nm).

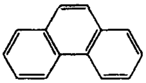
It is worth noting that the π-electron systems in the compounds of this sequence are also present in DNA and RNA. The random occurrence of these sequences in these latter important macromolecules must affect the electronic processes occurring in them, which are caused by ionizing radiation penetrating living matter. In such sequences triplet excitons most probably accumulate in guanosine groups. At the every points where these groups are located there exists a real possibility of nucleic acids being destroyed.

Sequence 2

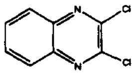
Compounds



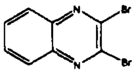
ethylcarbazole
(ECA)



phenantrene
(PHN)



2,3-dichloro-
quinoxaline
(DCQX)



2,3-dibromo-
quinoxaline
(DBQX)

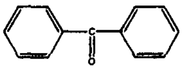
Energy levels (in cm^{-1})

$S_{1\,ECA}=28800$	$S_{1\,PHN}=29070$	$S_{1\,DCQX}=29600$	$S_{1\,DBQX}=29800$
$T_{1\,ECA}=24140$	$T_{1\,PHN}=22000$	$T_{1\,DCQX}=21570$	$T_{1\,DBQX}=21550$

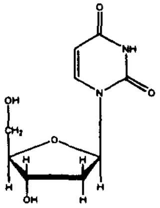
Test of functionality: only the phosphorescence of 2,3-dibromoquinoxaline needs to be observed ($\lambda \approx 464$ nm) during the excitation of ethylcarbazole ($\lambda \approx 347$ nm).

Sequence 3

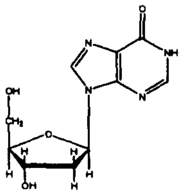
Compounds



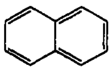
Benzophenone
(BPH)



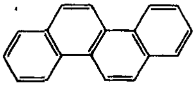
Uridine
(UR)



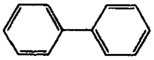
Inosine
(IN)



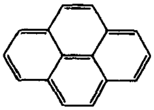
Naphtalene
(NAPH)



Chrysene
(CHR)



Biphenyl
(BPHL)



Pyrene
(PY)

Energy levels (in cm^{-1})

$S_{1\,BPH}=27000$ $S_{1\,UR}=33200$ $S_{1\,IN}=34500$
$T_{1\,BPH}=24300$ $T_{1\,UR}=23700$ $T_{1\,IN}=22730$

$S_{1\,CHR}=27640$ $S_{1\,NAPH}=31800$ $S_{1\,BPHL}=28100$ $S_{1\,PY}=29840$
$T_{1\,CHR}=20120$ $T_{1\,NAPH}=21300$ $T_{1\,BPHL}=18700$ $T_{1\,PY}=16800$

Test of functionality: only the phosphorescence of pyrene ($\lambda\approx$ 600 nm) needs to be observed during the excitation of benzophenone ($\lambda\approx$ 370 nm).

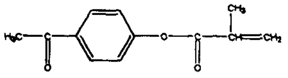
First Steps in Synthesis

Several functional molecular systems in which direct energy transfer occurs have already been obtained[4,12]. We synthesized two such systems, which are described below.

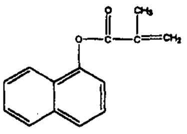
System 1

The basic units we used were 4-acetylphenylmethacrylate (APHMA) and 1-naphthylacrylate (NAPHA) (Fig. 3). These compounds were linked (1:1) in copolymer I. The absorption spectra of the substrates and copolymer demonstrate that the π-electron systems of APHMA and NAPHA interact with radiation independently. Fig. 3 shows the constitution of the substrates,

(*a*)



APHMA



NAPHA

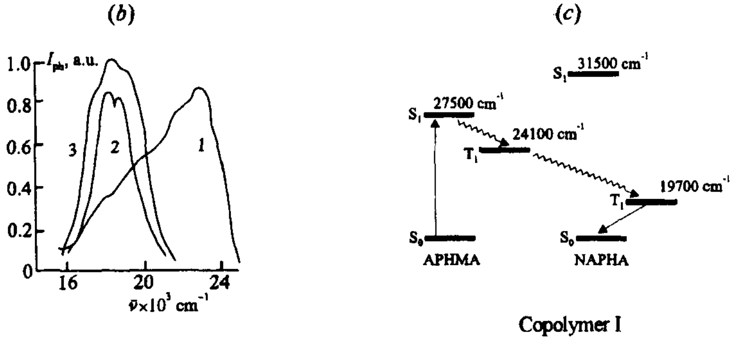


FIGURE 3 Constitution of substrates (*a*), phosphorescence spectra of APHMA (1), NAPHA (2) and copolymer I (3) (*b*), and diagram of the energy levels of copolymer I (*c*).

the phosphorescence spectra of substrates and copolymer I, and a diagram of the energy levels of copolymer I (derived from absorption, fluorescence and phosphorescence spectra). The energy level arrangement shown in the diagram in the substrates and functional macromolecule is the same. Thus, one may expect similar electronic processes in the substrates and copolymer I during excitation. Actually, a photon having sufficient energy to excite APHMA to the S_1 level will not excite NAPHA to the S_1 level in neat substrates and copolymer I. Subsequent energy transfer processes will occur as shown in Fig. 3(*c*). Only the phosphorescence of NAPHA is observed in such a case. The spectra presented in Fig. 3(*b*) demonstrate this.

System 2

The basic units are aminophenol (APH) and phthalimide (PHTI), while p-hydroxyphenylphthalimide represents the product of their condensation. Fig. 4 shows the constitution of the substrates and the condensation product, their phosphorescence spectra and the diagram of energy levels in the p-hydroxyphenylphthalimide (obtained from absorption, fluorescence and phosphorescence spectra).

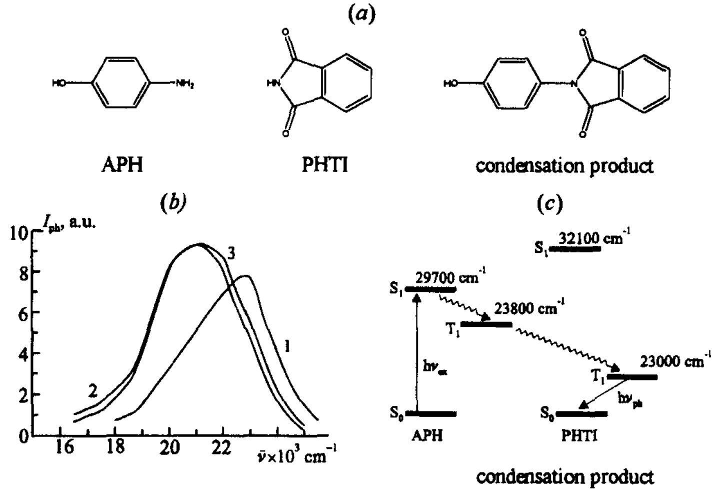


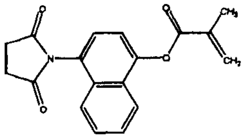
FIGURE 4 Constitution of the substrates and the condensation product (*a*), phosphorescence spectra of APH (1), PHTI (2) and p-hydroxyphenyl phthalimide (3) (*b*), and diagram of the energy levels in the condensation product (*c*).

PROBLEMS OF DESIGN AND SYNTHESIS

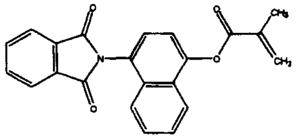
Initial Cell Selection

In the proposed model of a functional macromolecule the value of the T-exciton current depends mainly on the probability of the $S_1 \rightarrow T_1$ transition. For this reason the initial cell must contain a π-electron system where the probability of the $S_1 \rightarrow T_1$ transition is high. For example, chromophores based on benzophenone, sometimes with heavy atoms incorporated in them, may be used for these purposes. But there is another solution to the problem, as we have already shown [13]. We noted that the influence of one π-electron system on another, when they are linked together but not conjugated, leads to a substantial increase in the probability of the $S_1 \rightarrow T_1$ transition in one of them.

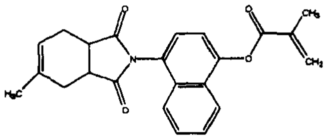
This indicates that a pair of π-electron systems in a functional macromolecule can be used as a T-exciton generator. This phenomenon was observed in the following compounds:



SINMA



PHTINMA



MTHINMA

In the PHTINMA molecule, the intensity of phosphorescence of the SINMA fragment increased markedly, while the intensity of fluorescence decreased almost to zero. This is quite different from the case of the unlinked SINMA. We explained this fact by assuming that the π-electron system of the phthalimide (PHTI) fragment of PHTINMA influences processes in the SINMA fragment and causes the probability of the $S_1 \rightarrow T_1$ transition to increase. This effect has also been observed in another model compound (MTHINMA) in which the breakdown of PHTI π-electron systems was imitated[14].

Influence of Singlet-Triplet Splitting on Macromolecular Chromophore Structure

Up to now this problem has mainly been solved empirically and we are still awaiting fundamental solutions of it.

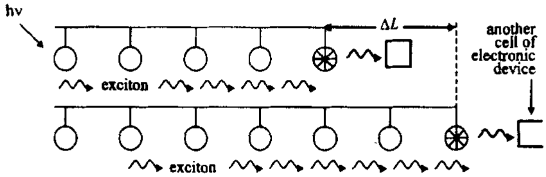
Optimal Distance Between Neighboring Chromophores in a Functional Macromolecule

In a number of cases neighboring chromophores tend to create charge-transfer complexes or exciplexes. Formation of the latter substantially influences the structure and arrangement of energy levels in macromolecules. To avoid this it is necessary to separate the chromophores in a macromolecule to distances longer than a certain critical one. On the other hand, this distance must be shorter than the critical one for an exciton jump ($h_{S,T}$). According to our data, $h_{S,T} \approx 18$ Å[15].

APPLIED PROBLEMS

Possible Uses of Functional Macromolecules in Nanoelectronics

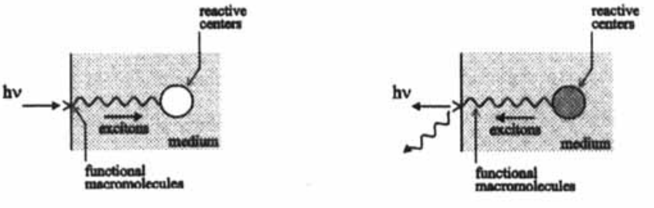
Some possible uses of functional macromolecules in nanoelectronics are indicated in Fig. 1. They can be applied as *one-way exciton conductors* or exciton rectifiers for information transfer from one cell of a nanoelectronic device to another. Moreover, a set of such macromolecules can be used as *lines of delay*, as shown below (the delay time is $\Delta L/V_{ex}$, where V_{ex} is the velocity of exciton propagation).



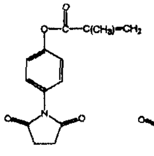
Branched functional macromolecules (Fig.2) can be used to populate sites of high energy density. Such systems can be used in the construction of *macromolecular lasers*.

Photochemical Applications

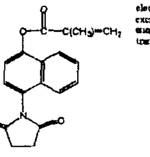
One can imagine a situation when the energy required to initiate a chemical reaction must be transferred to a given point in a medium. In other cases, energy has to be drained ('sucked off ') to prevent undesirable reactions. Such problems can be solved with the aid of macromolecules in which one-way electronic excitation energy transfer occurs.



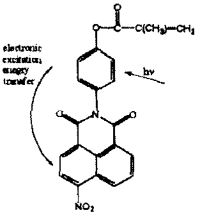
We have investigated the possibility of applying direct electronic excitation energy supply or drainage to initiate or terminate photochemical reactions in which the Fries photorearrangement takes place (Fig. 5)[15]. It was found that, as a result of energy supply, the rate of the latter process in the case of ANTRINMA increases substantially in comparison with that for SINMA. On the other hand, a decrease in the rate of the Fries photorearrangement in NNAPHTIPHMA in comparison with that in SIPHMA is observed under the same conditions. In the compound ABAB the Fries photorearrangement does not occur, since efficient energy drainage from the expected reaction site takes place. This is in contrast to the compound AOBA in which the process does occur.



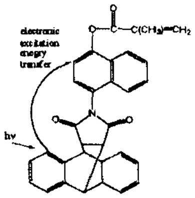
SIPHMA



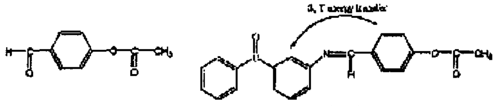
SINMA



NNAPHTIPHMA



ANTRINMA

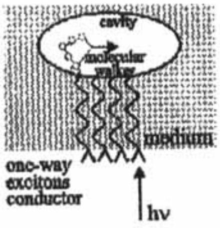


AOBA ABAB

FIGURE 5 Compounds in which the Fries photorearrangement was investigated.

Molecular Walkers

It was pointed out by Nunzi in his lecture at the 5th ICFPAM Conference that the photoinduced translatory motion of molecules can take place on the surface of solids[16]. Tamulis et al.[17] put forward a model of a molecular system - the so-called random walker - according to which molecules can move along chosen directions on the surface of a solid due to photoinduced intramolecular charge transfer. Clearly, these motions could be realized if energy were supplied to certain sections of a molecular system in the form of excitons. In situations where the motions of molecular walkers are impossible to initiate on the surface or in a cavity of a medium directly by photons, we suggest the use of functional macromolecules (one-way exciton condustors) which supply them with energy. The model of such a system is given below.



This system of energy supply provides the additional possibility of controlling the motion of the molecular walkers.

Acknowledgements

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