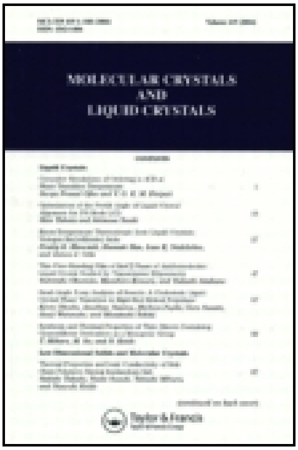

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Some Light-Sensitive Imide Molecular Systems with the Determined Functional Properties

Vladimir G Syromyatnikov [a], Valeriy N. Yashchuk [a], Tymish Yu. Ogulchansky [a], Irina A. Savchenko [a] & Alexey Yu. Kolendo [a]

[a] Kiev Taras Shevchenko University, 64, Volodymyrska St., 252033, Kiev, Ukraine

Version of record first published: 24 Sep 2006.

To cite this article: Vladimir G Syromyatnikov, Valeriy N. Yashchuk, Tymish Yu. Ogulchansky, Irina A. Savchenko & Alexey Yu. Kolendo (1996): Some Light-Sensitive Imide Molecular Systems with the Determined Functional Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 283:1, 293-298

To link to this article: http://dx.doi.org/10.1080/10587259608037902

Mol. Cryst. Liq. Cryst., 1996, Vol. 283, pp. 293–298
Reprints available directly from the publisher
Photocopying permitted by license only

SOME LIGHT-SENSITIVE IMIDE MOLECULAR SYSTEMS WITH THE DETERMINED FUNCTIONAL PROPERTIES

VLADIMIR G. SYROMYATNIKOV, VALERIY N. YASHCHUK, TYMISH YU. OGULCHANSKY, IRINA A. SAVCHENKO, ALEXEY YU. KOLENDO.
Kiev Taras Shevchenko University, 64, Volodymyrska St., 252033 Kiev, Ukraine

Abstract Some unconjugated molecular systems with different kinds of intramolecular energy transfer are proposed and discussed.

One of the main problems of molecular electronics is the construction and the synthesis of macromolecules possessing definite functional properties. The presence of different types of such systems (for example, functional acting macromolecules) would give the possibility to create essentially modern devices of technics.

It is known, that energy transfer in polymer macromolecules is realized by incoherent excitons randomly hopping to nearest neighboring units along the macromolecule[1-7]. In this paper on a base of previous investigations[8-12] the attempt has been done to design the macromolecule in which the excitons spread only in determined one-way direction. Such macromolecules may be used as the basic elements of molecular electronics.

The direct exciton current in the macromolecule is possible when there is the decreasing of levels energy values unit to unit along the macromolecular chain. In general case there are three variants of the suitable displacement of energy levels: a) Energy values of singlet levels decrease along the chain; b) Energy values of triplet levels decrease along the chain; c) Both energy values of singlet and triplet sites decrease from unit to unit. From our point of view the most interesting situation is that when c') the position of the first singlet excited state of the initial unit is lower than for the other units in the macromolecule but gradually lowering of triplet levels takes place along the chain. Only in this case the selective exciting of the first unit of macromolecule leads to direct one-way exciton propagation from initial to end unit along the macromolecule (Fig. 1).

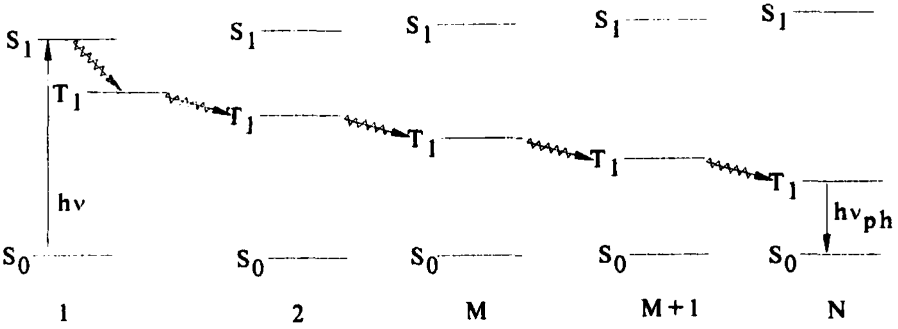

FIGURE 1 Scheme of energy transfer from unit to unit in macromolecular model c'.

If in the first unit the I_0 excitons are generating per unit time, it can be shown that the value of the exciton current (this value we introduce as the quantity (N) of excitons which are passing through macromolecular cross-section per unit time) between unit m and unit m+1:

$$I_m \equiv dN_m/dt = I_0\beta^m(1-\beta e^{-\Delta E/kT})^m$$

where ΔE - difference between energy values of neighboring units sites, β - the probability of energy transfer between neighboring units without considering of the back transfer. The considering of the possibility of spontaneous deactivation (α) in every unit of macromolecule and processes of back transfer gives such dependence of the total exciton current on number of macromolecule's unit.

$$I_n = I_0\,[(1-\alpha)/(1+e^{-\Delta E/kT})]^n$$

For triplet excitons in aromatic-containing polymers $\alpha \sim 10^{-5}$. Then for $n=10^4$ and $\Delta E >> kT$ $I_n/I_0 \approx 0{,}9$. So, the losses of excitons in such model macromolecule are negligible. The initial steps in designing of the compounds with such properties are described in this paper.

As a part of this macromolecule it is proposed the compound which consists of almost independent several π-electrons systems with determined position of their energy levels. Two possible variants have been examined. 1) In the first of them the decreasing singlet as well as triplet energy levels values takes place from unit to unit and therefore the direct one-way S,T-energy transfer exists. Two compounds possessing such properties have been synthesized: a)oxyphenylnaphthalimide [based on naphthalimide (NAPHM) and aminophenol (APH)]; b) naphthalimidodiphenylbenzoate based on the NAPHM, aminooxydiphenyl (AODP) and benzoic acid (BA). The investigation of absorption, fluorescence and phosphorescence at 293 and 77 K indicates that T- and S-excitons do spread directly in these compounds (Fig.2,3).

Structure formulae of these compounds as well as the scheme of energy levels and some obtained spectra are shown at fig.2,3,4(a,b,c).

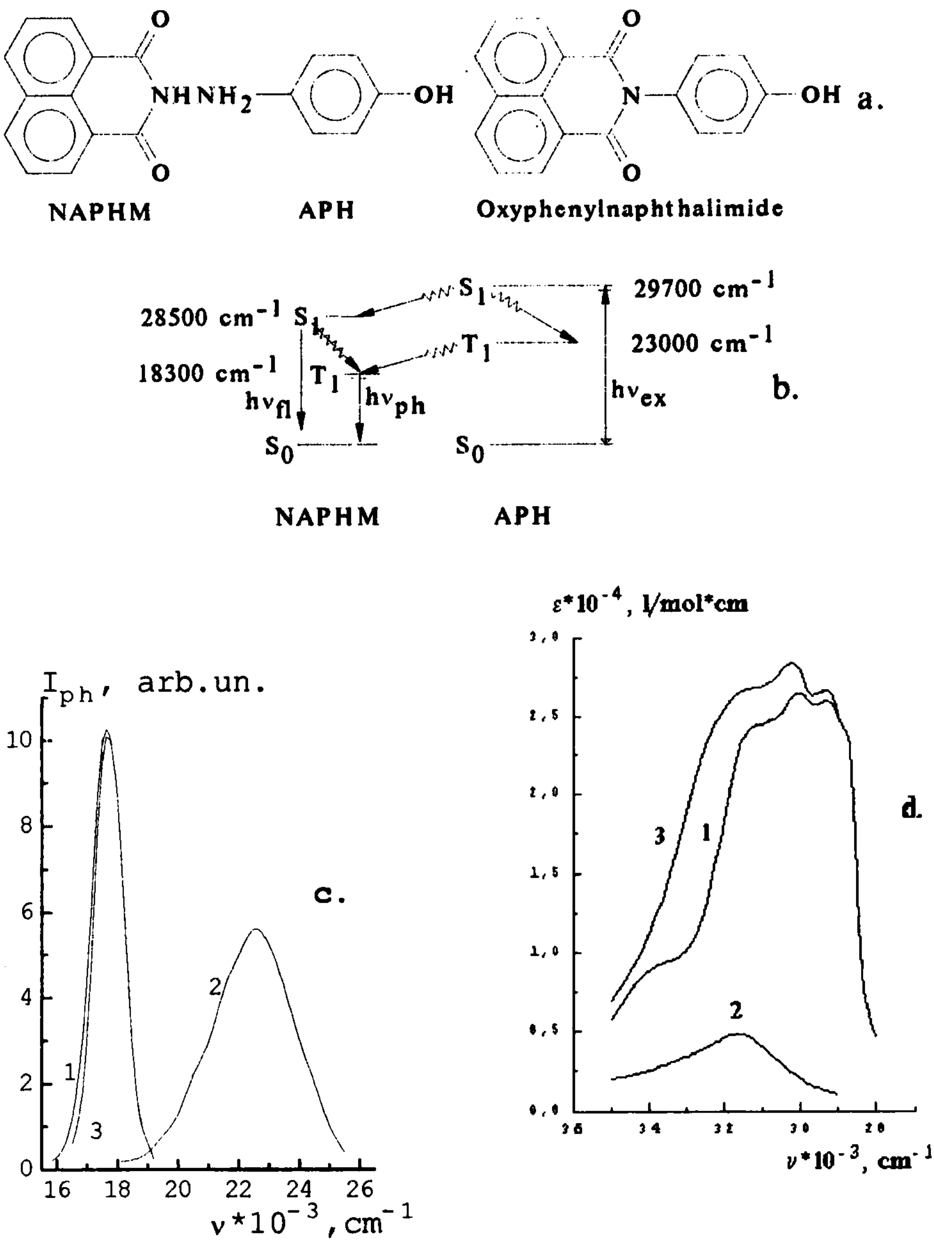

FIGURE 2 Energy transfer in oxyphenylnaphthalimide: a - formula and fragments; b - scheme of energy levels; c - phosphorescence spectra, d - corresponding absorption spectra: 1 - NAPHM, 2 - APH, 3 - oxyphenylnaphthalimide (dioxane, $C=10^{-4}$ mol/l, T=77K, λ_{ex}=337 nm).

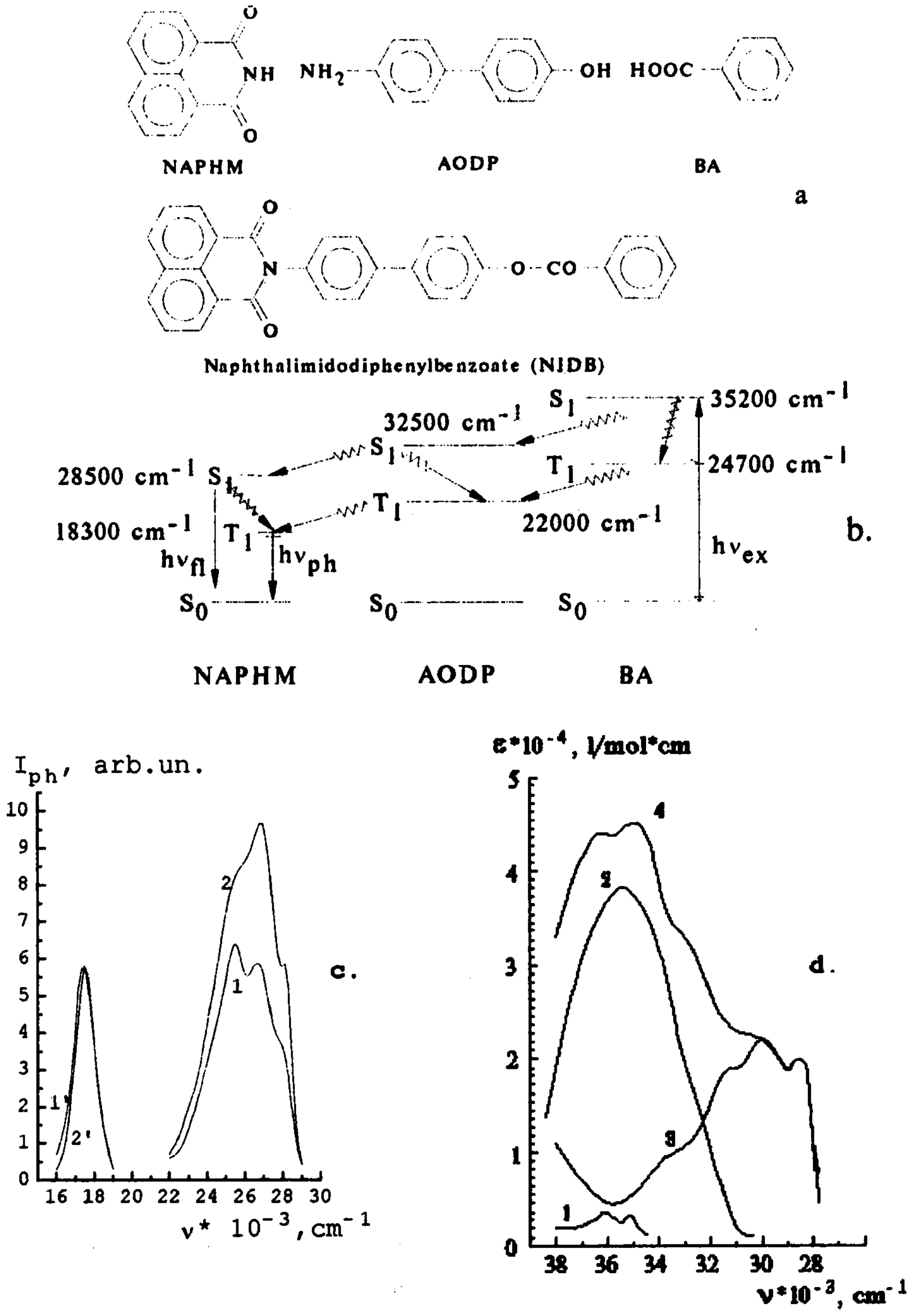

FIGURE 3 Energy transfer in naphthalimidodiphenylbenzoate (NIDB): a - formula and fragments; b - scheme of energy levels; c - spectra: 1',2' -phosphorescence of NAPHM and NIDB, 1,2 - fluorescence NAPHM and NIDB d - absorption spectra: 1-BA, 2-AODP, 3-NAPHM, 4-NIDB.

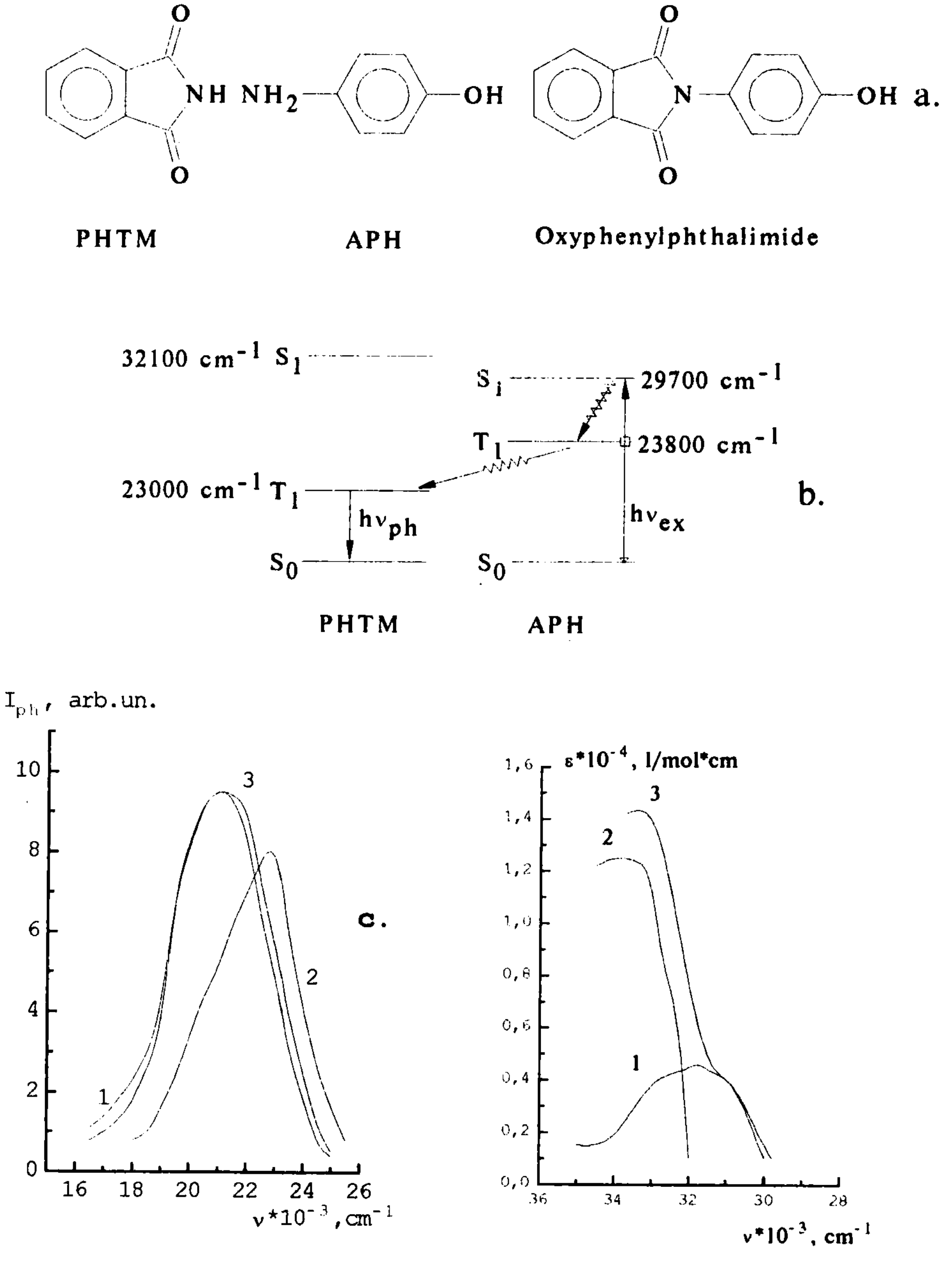

FIGURE 4 Energy transfer in oxyphenylphthalimide: a - formula and fragments; b - scheme of energy levels; c - phosphorescence spectra 1-PHTM, 2- APH, 3-oxyphenylphthalimide ; d-absorption spectra : 1 - APH, 2 -PHTM, 3 - oxyphenylphthalimide (dioxane, $C=10^{-4}$ mol/l, T=77K, $\lambda_{ex}=337$ nm).

2) Another variant of the unit's energy level positions has been realized in oxyphenylphthalimide (the compound which consists of APH and phthalimide (PHTM)) (Fig.4). The analysis of absorption and luminescence spectra gives for APH and PHTM's S,T-energy levels $S_{1APH} = 29700cm^{-1}$, $S_{1PHTM} = 32100cm^{-1}$, $T_{1APH} = 23800cm^{-1}$, $T_{1PHTM} = 23000cm^{-1}$. Such positions of levels except intramolecular S-S energy transfer in compound when S_1-level of APH-unit is excited. However only phosphorescence of PHTM-unit was observed, as a result of selective S_1-level exciting of APH-unit. The last proves that only T-T transfer energy takes place in this compound on scheme:

$$S_{0APH} + h\nu_{ex} \Rightarrow S_{1APH} \Rightarrow T_{1APH} \Rightarrow T_{1PHTM} \Rightarrow S_{0PHTM} + h\nu_{ph}$$

The macromolecules with great number of units may be design on this principle.

The research described in this publication was made possible in part by Grant N K2Q100 from the Joint Fund of the Government of Ukraine and International Science Foundation.

REFERENCES

1. W.Klopffer, J.Chem.Phys. 50, pp.1689-1692 (1969).
2. A.N.Faidysh, V.V.Slobodyanik, V.N.Yashchuk, J.Luminescence, 21, pp.85-90 (1979).
3. M.Pope, C.E.Swenberg, Electronic Processes in Organic Crystals, Clarendon Press: Oxford, 1982.
4. V.V.Slobodyanik, A.N.Faidysh, V.N.Yashchuk, L.N.Fedorova, J.Prikladnol Spectroskopii, 36, N2, pp.309-316 (1982).
5. V.V.Slobodyanik., V.N.Yashchuk, V.P.Naidyonov. et al., J.Luminescence, 29, pp.309-320 (1984).
6. J.Guillet. Polymer Photophysics and Photochemistry, Cambridge univ. Press. Cambridge, (1985).
7. W.Klopffer, in Photophysics of Polymers, edited by E.H.Charles and J.M.Torkelson (Amer.Chem.Soc., Washington, DC 1987), pp.284-285.
8. I.S.Gorban, Yu.P.Piryatinsky, V.N.Yashchuk, Mol.Mat. N1, pp.241-246 (1992).
9. J.S.Gorban', V.N.Yashchuk et al., Zh. Prikl. Spektr., 47, pp.96-102 (1987).
10. V.G.Syromyatnikov, E.V.Blazhko, V.V.Zagniy, V.P.Naidyonov, T.Prot., Proceedings of Intern. Conference on Electrography - Electrography - 91 (Moscow, 1991), 2, pp. 289- 292.
11. V.G.Syromyatnikov, V.N.Yashchuk, T.Yu.Ogul'chanski, J.A.Savchenko, A.Yu.Kolendo, Ukr.Fiz. Zh., 40, pp. 286 - 288 (1995).
12. V.G.Syromyatnikov, V.N.Yashchuk, T.Yu.Ogul'chanski, J.A.Savchenko, A.Yu.Kolendo, Ukr.Chem.Zh. , 61, pp.53-55 (1995).