Novel Concept of Polymeric D-A Photocell: Optimization by Selective Doping

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To optimize the separation and collection of carriers by internal fields in D and A parts of D-A photocells, we propose a concept of a selective doping, which also supports collection and dissociation of excitons at D-A interfaces. Selective p_D dopants energy levels are matched to that of polymer in such a way that it can transfer holes only to D part, while n_A dopants provide electrons selectively only to A part of polymeric D-A network. It is shown that in D(p_D)-D-A-A(n_A) structures doped parts provide low serial resistance and create internal electric fields for collection of only proper sign charges. On the other hand in undoped parts light absorption creates excitons, which are not quenched by carriers and thus can reach the interface and effectively dissociate there creating primarily separated electrons in A and holes in D. Energetic selectivity allows to avoid special complicated geometries, and may optimise even randomly oriented interpenetrating D and A polymeric networks.

KEYWORDS : photocell, donor - acceptor photocell, D-A photocell, selective doping, polymerie photocell, interpenetrating network

ドナーーアクセプター型フォトセルの新概念:選択ドーピングによる最適化

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ドナー(D)－アクセプター(A)型フォトセルにおける内部電界によるキャリアの分離と集積を最適化するための選択ドーピングの概念を提案した。この選択ドーピングはD－A界面での励起子の解離を促進する。高分子D－Aネットワークのドナー(D)領域での選択ドーパント p_Dのエネルギー準位はD部の高分子のエネルギー準位に対してホールをD高分子に授与できるように、アクセプター(A)領域での選択的ドーパント n_Aのエネルギー準位はA高分子に電子を授与できるように選ばれる。D(p_D)-D-A-A(n_A)構造においてドープされた領域は直列抵抗の低減の寄与し、電荷の集積を促進する様な内部形成するのに役立つ。未ドープ領域では光吸収により励起子が形成され、界面で効率よく解離し電荷を形成する。

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1. Introduction

Conducting polymers with highly extended π electron system in main chains have attracted much attention , because they exhibits an insulator-metal transition upon dopings of small amount of either donors(D) or acceptors(A). With which charge transfer occurs between polymer main chains and dopants. This also means that conducting polymers itself can also behave as acceptors and also donors. Recently findings of various novel properties in conducting polymers - fullerene (C_{60}) composite system have stimulated developments of new fields of research[1-9].

Especially organic photocells based on interfacial D-A charge separation started to attract interest recently, which has been spured by successful models of conducting polymer/fullerene heterojunction devices[4-9], demonstrating high efficiency of primarily charges photoseparation.

It should be mentioned that D-A photocell need not always to be in the layered structure in which D-A interface is formed between D layer and the A layer, but also can be formed at the contacts between neighboring D and A polymer chains[8,9] and also between D and A polymer fibrils. In the latter case, the concept of condensed interface in bulk will be realized. This concepts stimulated studies of mixtures of different type of conducting polymers[10,11].

2. Donor - Acceptor Photocell

It has been recognized that contrary to conventional p/n junctions, (in which e-h pairs are primarily photogenerated and separated by the electric field of the junction built-in potential[12]), in D-A photocells, excitons are primarily photocreated in acceptor (A) polymer or donor (D) polymer, and diffuse to interface region, where they dissociate via electron tunneling across the interface. (as sketched in Fig. 1, a)[6-9]. At this stage the charge separation does not need any electric field. In earlier work[13], in which probably the first D-A organic photocell has been actually demonstrated experimentally, it was suggested that some electric field at interface, i.e. field of dipoles, induces the exciton (Ex) dissociation. How-

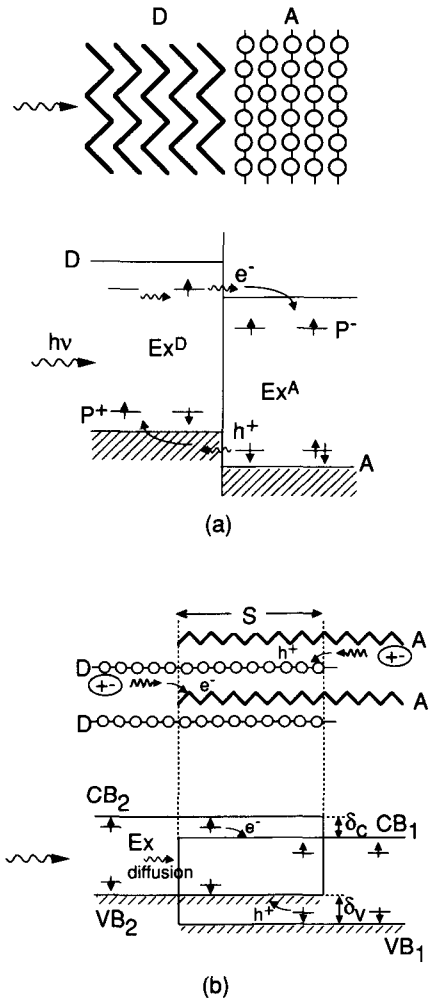

Fig.1: The primary "excitonic step" of interfacial charge separation by exciton dissociation at D-A interfaces: a) in planar interface geometry: Ex(D) → (e^-—CB) → $P_D^+ + P_A^-$, Ex(A) →(h^+—VB)—P_A^- + P_D^+, two excitons creating 4 charges separated by sign in different components + in D and - in A, b) interchain geometry, which has extended interface area S: the overlappingregion can be viewed as a composite solid with two conduction bands and two valence bands separated by δc and δv. Within S excitonic levels became resonating with states in lower conduction band (CB) or upper valence band (VB), and thus unstable with respect to dissociation.

ever what is really needed for such dissociation is the hybridization of the excitonic local level on one side of interface with a manifold of free band states on the other side, which causes electron tunneling across the interface. The probability of such dissociation has been calculated in a simple two-chain model of D-A polymeric photocell (Fig.1 b), and was found to be dependent only on the interchain π-π overlapping integral t and density of free band states[8,9]. The probability of this process, due to which an excitonic level (ω_0) possesses a decay width γ (ω_0), has been found as:

$$\gamma(\omega_0) \sim 2\pi / h \sum_k |\langle \phi_\rho^*(\omega_0) | t_\perp | \phi_c(k) \rangle|^2 \delta\left(\omega_0 - \sqrt{\Delta_1^2 + k^2}\right)$$

Exact analytic expressions for γ can be found for various cases of D-A energy matching in[8,9], but simple estimates e.g. for Ex in cis -polyacetylene decaying by electron tunneling into conduction band of trans- polyacetylene, give for the t=0.03～0.1 eV and δ_C=0.4 eV rather small tunneling decay time $\tau = 10^{-11}$ ～10^{-12}sec. that is much smaller than radiative life-time of Ex in conducting polymers.

This type of photoinduced charge transfer (CT) resembles the process in the natural photosynthetic systems, in which after first step of primary D-A separation in a reaction center, a sequence of following CT processes to a cascade of secondary D_2 and A_2 provide further separation of carriers[14,15].preventing them from back CT recombination.

For the collection of primarily separated charges in artificial D-A devices, one has no of course any secondary donors D_2 and acceptors A_2, (which usually have chemical composition different from D and A), and so, one needs some type of electrical field, to provide further separation and collection of carriers at electrodes. In reported D-A devices in CP/C_{60} heterojunctions[4-7] the asymmetrical ohmic contacts, (e.g. Au and Al, or ITO and Al) with different work functions ϕ_1 and $\phi_2$have been used to create an internal field as shown in Fig.2. In this case photovoltage Voc is determined by $\Phi = \phi_1 - \phi_2$ and the energy discontinuities δ_C and δ_V at the interface: Voc max≦ Φ-δ_C.

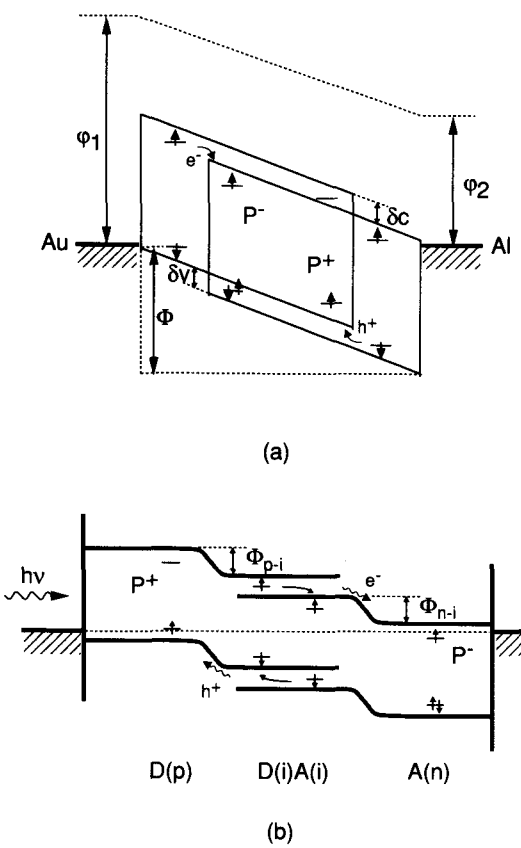

Fig.2: Secondary "electronic" step of charge separation and collection by internal electric fields: a) The field F created by asymmetry of ohmic electrodes, having differing work functions, as already realized in D-A photocell devices, b) the built in potentials of p-i and i-n intrachain junctions created by p doping of D and n doping of A.

The misadvantage of this approach, in which field drops in the depleted region, is the high serial resistance, due to low concentration of carriers in actually insulating D and A layers, which decreases the photocurrent, and makes solar cell application unfavorable, (although devices are effective photodetectors[4-7]).

We have suggested to create polarization double barriers at the D-A interfaces, appearing due to diverse polarization energies of D

and A, which create a potential profile, resembling secondary D_2 and A_2, and thus supports the photoseparation[16,17]. For better collection of photons the sensitizing molecular layer of "photon pump" molecules M in three layered D-M-A structures can be used[18].

Here we discuss the optimization of the both steps of primary and further separation and collection of carriers. It has been earlier suggested that doping of D and A parts by strong dopants, will create internal fields of p-i and n-i types supporting collection of charges (see Fig. 2,b), and increasing the conductivity of device[19], but excitonic processes in doped parts have not been taken into account. It should be noted that for optimization of D-A photocells one has to solve a new task to combine in a most effective way two physically different steps:

1. Excitonic photoabsorption, diffusion and dissociation at D-A interface.
2. Charge collection by some internal electric field, and possibly high concentration of charges for lower serial resistance.

This two steps require contradictory conditions, since charge carriers act as exciton quenchers, and moreover doping changes the optical absorption spectra of polymer, decreasing excitonic absorption. Interfacial dissociation of excitons in the presence of intragap states of polarons and bipolarons is also expected to become less efficient.

To separate excitonic and electronic steps it has been suggested to separate them spatially in different directions in highly oriented interpenetrating quasi-one-dimensional networks, by special geometry of assembling of D, A and other components[19].

In this paper we suggest another approach for optimization, which is based on the energetic selectivity of dopants, (rather than geometry of network) with the aim to provide correct fields in correct places for correct charges, and leaves a space for excitonic part of scenario, avoiding the bad influences of charges on excitons.

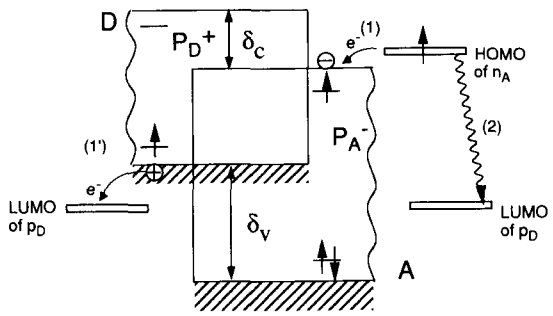

Fig.3: Energetics of selective doping: HOMO of n_A should be within δ_c while LUMO of p_D within δ_v. Processes 1-1' show selective charge transfer to chains of conducting polymer, (2) is for a compensation with formation of the dopant salt $n_A^+p_D^-$.

3. Selective dopants

The existence of the energy bands offsets $\delta_c = A_A - A_D$, and $\delta_V = I_D - I_A$, (where A and I are corresponding electron affinity and ionization potential, respectively) at the interfaces, allows one to choose the dopants with their HOMO (and LUMO) levels within δ_C and δ_V, as shown in Fig.3. These dopants can be viewed as selective ones because electron from nA can be transferred favorably only to conduction band of A polymer (since the transfer to D requires energy, so that n_A is a weak dopant for D, which can transfer electron to it only upon photoexcitation[20]). We do not account here the possibility of direct electron tunneling from n_A to polaronic level ω_0 in A, which is below bottom of conduction band. This process will make a small decrease of the window for n_A, δ_C -Ep by polaronic binding energy Ep. Similarly p_D can favorably inject holes only into valence band of D, but only upon photoexcitation into A. Iodine I_2 is a clear example of a selective p_D dopant in a D-A composite of poly(3-alkylthiophene) (PAT) with C_{60}. We have shown experimentally that I_2 can only create positive polarons P^+ in a conducting polymer, but not in C_{60}, as proved by ESR [21]. Estimates for PAT/C_{60} system show that dopant windows are: $\delta_C = 1.8$ eV, while $\delta_V = 1.5$ eV, i.e. are very broad and

probably it would be easy to find an n_A dopant for this system as well. So probably even Al is a good n_A dopant for C_{60}, since Al injects charges into C_{60} but not neutral PAT. The dopant windows for pairs of D-A of conducting polymers are smaller, so for poly(3-hexylthiophene) (PAT6)/ poly(2,5-dioctyloxy-*p*-phnylenevinylene) (OO-PPV) D-A system we expect $\delta_C = 0.3$-0.4. eV. In this case selective doping can be done electrochemically, i.e. D will be doped p-type at lower electrochemical potential, than A. By addition of side groups which have large electron affinity, the conducting polymer may become more of A type, so CN groups added to PPV, make it better A[22], and thus increase the window δ_C.

If selective dopants are simultaneously introduced into the same place then compensation should occur, due to direct electron transfer from n_A to p_D, and the formation of a salt $(n_A)^+(p_D)^-$, like KI, or $LiClO_4$. In this case both D and A remain in a neutral, i.e. in insulating state A(i) and D(i), which have unchanged optical absorption spectrum, compared to doped parts in which intragap levels of P/BP are responsible for absorption and thus excitonic processes are suppressed. For p-n junctions in conducting polymer diodes, this type of compensation effect is known to take place at p/n interface due to easy interchain diffusion of counterions, and it normally decreases the performance of p/n diodes.

We will discuss below why in contrast excitonic processes may be more favorable in compensated parts compared to doped parts.

4. Advantages of selective doping of D-A network

Figure 4 shows the energetics of the interchain type D-A configuration, which is selectively doped from both sides. In p_D doped side only D fibrils will be doped, i.e. become conductive and thus change color (normally becoming nontransparent due to intragap polaronic absorption), while A fibrils are undoped,

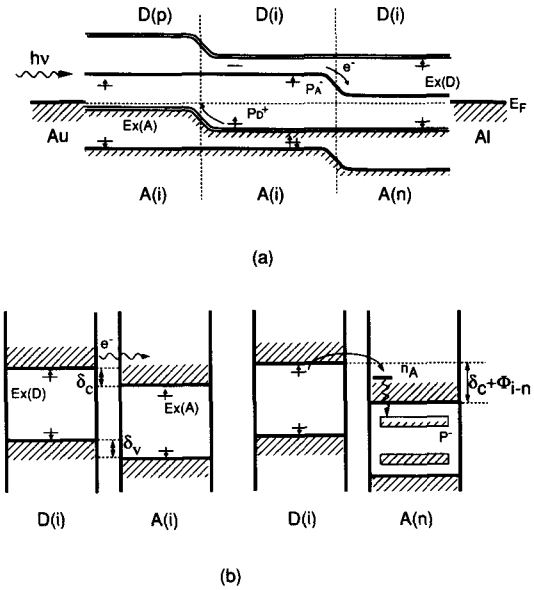

Fig. 4:a) Energetic diagram of interchain D-A photocell selectively doped from opposite sides: Collection of charges occur by electric fields in doped parts of D and A chains, while excitonic absorption is in undoped or compensated parts, the best dissociation is expected in undoped or compensated part as shown in b) cross sections of central and surface parts of photocell.

i.e. still transparent for light with $h\omega < 2\Delta_A$ (as shown schematically by dark and bright fibrils at Fig.5). Opposite doping occurs at the n_A doped side of the network: doped A(n) coexist with undoped D(i) fibrils. In the central part due to compensation both A and D are in insulating state. This type of doping creates two separated built in potentials Φp-i and Φi-n, in spatially separated D and A segments of the network. What is important, the photogenerated P^+ which favorably are separated to D chains, will meet the electric field pulling them towards ohmic contacts into the doped segments D(p), which act like collecting wires due to their low resistivity, improving thus both collection by Φp-i and short circuit current by low serial resistance. Exactly similar behavior will be experienced by negative polarons P^- which are in A chains, and pulled by Φi-n into A(n) wires.

This part of scenario is quite similar to con-

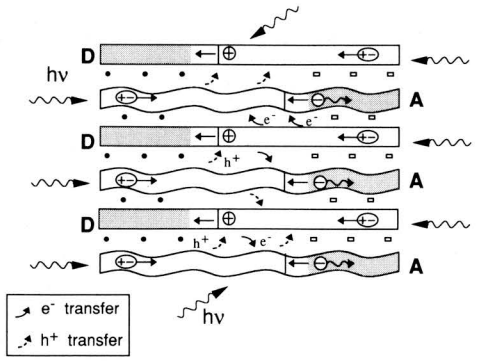

Fig.5:Scenario of photogeneration and photoinduced charge separation processes in selectively doped polymeric D-A network. Each D or A is a chain or a fibril (bundle of polymeric chains).
Undoped parts of A and D transmit light and provide excitonic absorption, Ex (A) and Ex (D) diffuse towards D-A interchain interface and dissociate there with e and h injection into depleted intrinsic (i) parts (i.e. undoped) of A(i) and D(i). Carriers diffuse within each D and A fibril, and meet the accelerating field of p^-i and i^-n intrafibrilar junction, which collects P^- in doped A(n) and P^+ in doped D(p) segments. The diffusive flows of excitons and charges are in opposite direction, but in spatially separated chains, which allows to avoid the strong intrachain decay of excitons on carriers.

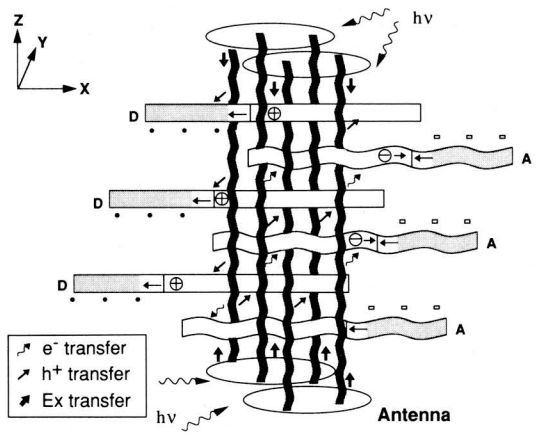

Fig.6:Highly oriented interchain network, with spatially separated excitonic and electronic processes. Excitons are diffusing along Z direction in transport chains, D-A separation occurs in Y direction by exciton decay, injecting holes into D and electrons into A, while doped parts have no interfaces and are composed of only D and A fibrils, in which internal fields are created.

ventional semiconductors, the only difference being the spatial separation of charges in D and A fibrils, which is important, since their recombination is significantly suppressed. Concerning the "excitonic" part of the scenario, advantages are also clear, as shown in Fig.5.

Undoped and compensated parts of D and A can transmit and absorb light creating excitons that will diffuse along the chains towards the central part, where they can have a highest probability of dissociation with injection of electrons from Ex(D) levels into band states of A, followed by relaxation into P^-, and hole injection from Ex(A) into D chains resulting in P^+.

Thus due to selective doping roughly half of fibrils remain undoped at the surface regions of the DA polymeric blend, providing light transmission into inner parts of the composite and serving as exciton transport chains, resembling excitonic transport chains of natural photosynthetic systems[14,15].

It should be pointed here that the dissociation of excitons at the interface with doped parts is expected to be suppressed since the density of band states there is decreased and is transferred to local intragap states of polarons/bipolarons, as well known. However even this Ex dissociation will be a useful one, still providing electrons to A(n) and holes to D(p), although probably not in a best correct place regarding the pulling electric fields.

Note also that, the selective dopants themselves may act in their ionic state as the intermediates for exciton dissociation, so n_A^+ may capture transiently the electron from Ex(D) and transfer it further into A(n) chains. The possibility of such type charged impurity assisted exciton dissociation, calls for more study, and shows that optimization of excitonic step of scenario may be beneficially helped by the residuals of the electronic scenario. Figure 4, b) shows energetics of exciton dissociation processes in D-A interfacial directions, indicating why dissociation into doped chains may be

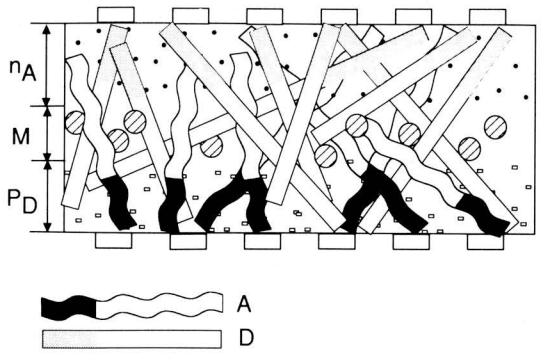

Fig.7:Selectively doped random D-A network, in which undoped fibrils serve for excitonic processes. In compensated part molecular sensitizer M is intercalated for better collection of photons.

suppressed and also showing the dopant-impurity mediated tunnelings.

It is important to point that selective doping do not require the orientation of D or A chains, as schematically shown at all previous Figs just for simplicity. Contrasting to a geometrical optimization, as earlier suggested[19] and shown in Fig.6, selective doping is rather robust and can work even for totally random orientation of fibrils. In Fig.6 the three steps of scenario are separated spatially in three different types of chains and act in three orthogonal directions: 1)excitonic absorption starts from antenna, then energy is transferred along exciton transport chains in, say Z direction, 2) excitons dissociate by electron injection into A and hole injection into D chains, providing D-A interfacial separation in Y direction, while the built in electric fields are formed in X direction and pull charges into p and n type doped wires and finally collected in ohmic contacts. This type of complicated stereospecific arrangement of fibrils or chains requires design by chemical engineering methods and actually has been suggested for molecular electronic mini-devices[19].

On the other hand energy selectivity of dopants proposed here is insensitive to geometry and can be applied for large area mixtures of two different D and A polymers which should have suitably wide δ_c and δ_v energy offsets for choice of selective dopants. Then role of excitonic chains is played by undoped chains of the same material at the account of spectral changes introduced by doping which are specific to conducting polymers.

Figure 7 shows a schematic diagram of thin film with random interpenetrating network which is selectively doped from both sides, and moreover for further optimization, contains in its compensated part a monomolecular sensitizer M molecules which are good light absorbers, and should have energy matching favorable for excitonic transfer. We do not discuss here the optimization of photons absorption i.e. the spectral selectivity (to use maximal part of solar spectrum), which can be done by manipulations of the band gaps and favorable geometries and thicknesses. But it worths to note that light absorbed in doped parts at lower photon energies (at intragap transitions) will also contribute to photoresponse, by volume e-h photogeneration in D(p) and A(n) fibrils.

5. Summary

One possible scheme is suggested for optimization of two controversial steps of charge separation in D-A interfacial photocells. Excitonic interface dissociation, requires good absorption by excitons, easy diffusion towards the D-A interface, and most importantly, high probability of tunneling decay. On the other hand at the electronic step, the charge carriers transport is in the opposite to excitonic flow direction and it needs good collection by electric fields of built-in potentials and high conductivity of collecting chains. Energetic selectivity of dopants provides such a possibility to optimize these two steps, separating them in undoped and doped chains. Two asymmetries are responsible for the photovoltaic effect: asymmetry of excitonic dissociation at D-A interface provides primary charge separation: electrons in A and holes in D chains, while asymmetry of selective doping, D(p) and A(n), gives correct electric fields. Naturally

opposite doping, D(n) and A(p), will be unfavorable for photocells, but contrary should be good for D-A type light emitting diodes (LED), which will be discussed separately. Experimental work is in progress to create such photocells in D-A networks.

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