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INTERNAL ELECTRIC FIELD, ELECTRON-TRAPPING VOIDS, DEAD ELECTRONS, AND THE INCREASING OF THE EFFICIENCY OF POLYMER SOLAR CELLS WITH FLUORINATION

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We propose a model that allows an understanding of the nature of electron traps in π-conjugated polymers that are used in photovoltaic devices. It is assumed that the free-cavity voids in the polar π-conjugated polymer exhibit electron-accepting affinity and are filled with electrons, called herein as 'dead' electrons because they are hold by a static random internal electric field and are not driven to the cathode by external built-in voltage. As a result, the dead electrons into electron-trapping voids are unsuitable for use in the external circuit of organic solar cells. As justified here, the exciton dissociation on the surfaces of voids, the capture of drift electrons by voids, the emerging of the dead electrons and their non-geminate recombination are the main obstacles to create highly efficient polymer solar cells. The model of dead electrons allows explaining the increase in the power conversion efficiency of solar cells caused by the polymer fluorination, side-chain polymer manipulation, and dopant-controlled trap-filling. Some characteristics of hybrid P3HT:CdSe solar cells are also analyzed with the help of this model.

Keywords: polymer solar cells, internal electric field, electron-trapping voids, dead electrons, binding energy, polymer fluorination.

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ВНУТРЕННЕЕ ЭЛЕКТРИЧЕСКОЕ ПОЛЕ, ЗАХВАТЫВАЮЩИЕ ЭЛЕКТРОНЫ ПУСТОТЫ, МЕРТВЫЕ ЭЛЕКТРОНЫ И УВЕЛИЧЕНИЕ ЭФФЕКТИВНОСТИ ПОЛИМЕРНЫХ СОЛНЕЧНЫХ ЭЛЕМЕНТОВ ПРИ ФТОРИРОВАНИИ

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Предложена модель, позволяющая понять природу электронных ловушек в π-сопряженных полимерах, которые используются в фотоэлектрических устройствах. Предполагается, что пустоты со свободными полостями в полярном π-сопряженном полимере проявляют электроноакцепторные свойства и заполняются электронами, которые названы здесь «мертвыми» электронами, так как они удерживаются статическим случайным внутренним электрическим полем и не направляются к катоду с помощью внешнего напряжения. В результате, захваченные пустотами мертвые электроны непригодны для использования во внешней цепи органических солнечных элементов. Обосновано, что диссоциация экситонов на поверхности пустот, захват электронов пустотами при дрейфе к катоду, появление мертвых электронов и их негеминальная рекомбинация являются главными препятствиями при создании высокоэффективных полимерных солнечных элементов. Модель мертвых электронов позволяет объяснить увеличение эффективности преобразования энергии солнечных элементов, вызванное фторированием полимера, изменением боковых цепей полимера и наполнением ловушек добавками растворителей. Некоторые характеристики гибридных P3HT:CdSe солнечных элементов также анализируются с помощью этой модели.

Ключевые слова: полимерные солнечные элементы, внутреннее электрическое поле, захватывающие электрон пустоты, мертвые электроны, энергия связи, фторирование полимера.

Introduction. In the last 15 years a significant progress has been achieved on the improvement of the power conversion efficiency (PCE) of polymer solar cells (PSCs) operating on the principle of bulk heterojunction (BHJ) when the blends of electron-donating polymers and electron-accepting fullerene derivatives are employed as active layers [1]. Nevertheless the efficiency of PSCs is still greatly lower

than their inorganic counterparts – such as silicon, CdTe and CIGS – that slows down large-scale practical applications. Therefore, much attention is paid to the fluorination of π-conjugated polymer backbone, which provides a significant increase in PCE [2]. Recently Zhao et al. [3] described an environmentally friendly processing system of difluorinated polymer that yields single junction cells with PCE of up to 11.7 %. For acceptable morphology of blend their polymer:fullerene processing system incorporate the synergistic effects of the hydrocarbon solvent as additive, a suitable choice of side chains and aggregation temperature of difluorinated polymer.

The impact of fluorination on the morphology of pure films and their blends with fullerenes arises mainly from the higher polymer planarity due to intramolecular non-covalent interactions, like hydrogen-bonding F$\cdots$H and electrostatics S$\cdots$F, F$\cdots$F [4; 5]. The higher molecule planarity of the fluorinated backbones induce stronger π-π stacking, polymer molecular ordering and higher crystallinity [5; 6]. As known today [7] a good blend should not only contain ordered regions to promote charge transport but also disordered ones to assist exciton dissociation. Nguyen et al. [5] demonstrated that (dialkoxyphenylene-benzothiadiazole)-based copolymers (PPDTBT, PPDTFBT PPDT2FBT) in the blend with PC70BM possess a semi-crystalline morphology and tight interchain packing. This gives well-balanced charge transport with h/e mobility ratio of 2, showing hole and electron mobility of $3.0 \cdot 10^{-3}$ and $1.5 \cdot 10^{-3}$ cm^2 V^{-1} s^{-1} for 2F-polymer PPDT2FBT, that ~1 order higher relative to F-polymer PPDTFBT and non-fluorinated polymer PPDTBT. The single junction cells based on PPDT2FBT exhibited 8–9 % PCE with a thick active layer of 290 nm. The PPDT2FBT:PC70BM film of 290 nm provided strong light absorption, yielding a high short-circuit current density (J_{SC}) of 15.7–16.3 mA cm^{-2} without the loss in open-circuit voltage (V_{OC} = 0.78–0.79 V) and in fill factor (FF = 0.71–0.73) [5]. It is particularly remarkable for mass-scale production, that only negligible changes are observed in the PPDT2FBT carrier mobility even at ~1 μm film thickness [5].

Many reasons have been suggested [2–6] to explain the positive effects of fluorination on the polymer photovoltaic properties. Nevertheless the fluorinated and non-fluorinated polymers exhibit in many relations the similar non-geminate recombination behaviour, so there is bound to be a common reason both of high and low device performance that remained to date a mystery. In our opinion, presented in this work, this common reason can be mainly attributed to the electron-trapping voids which exist always in all π-conjugated polymers, fluorinated or non-fluorinated. The free voids cavity are filled with electrons called herein as "dead" electrons because they are hold down by voids and are not driven to the cathode by a built-in voltage; in other words, the dead electrons are unusable for collection at the external circuit of solar cell.

The trap-limited electron transport in semiconducting disordered polymers is investigated by many authors [7; 8], but goal of our work is to understand the nature of traps and to get deeper insight into mechanism of electron capture by traps in fluorinated polymers.

Free spherical cavity in the polar solvent. As shown in Fig. 1, *a*, in a polar solvent chaotic reorientation of dipoles $\boldsymbol{\mu}_s$ gives rise a chance electric field $\mathbf{R}$ at the centre of a free spherical cavity (of spherical void) of radius a. The internal electric field $\mathbf{R}$ changes in both value and direction. Let $\mathbf{x}$ be an arbitrary fixed axis passing through the centre of free cavity. Inasmuch as field $\mathbf{R}$ originates from a high number of dipoles μ_s, the density probability $P(R_x)$ (R_x is a component $\mathbf{R}$ along $\mathbf{x}$) is Gaussian [9; 10] with the variance

$$\sigma^2 = \frac{2k_B T}{a^3} \Delta f. \tag{1}$$

The mean of internal chance electric field $\langle R \rangle$ at the free cavity is

$$\langle R \rangle = \langle |\mathbf{R}| \rangle = \sqrt{\frac{4k_B T}{\pi a^3} \Delta f}, \quad \Delta f = f(\varepsilon) + f(n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n - 1}{2n + 1}, \tag{2}$$

where k_B is Boltzmann constant, T is the temperature, Δf is Lippert–Mataga factor, ε and n are the dielectric constant and refractive index of medium. The results (1) and (2) have been originally obtained in [9; 10] using Onsager's approximation.
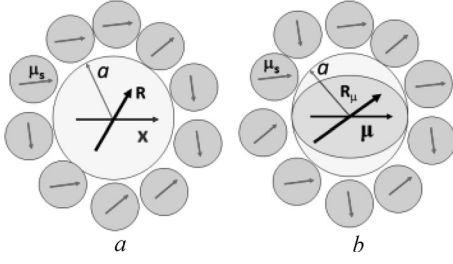
Fig. 1. Chance electric field **R** in a free spherical cavity (in a spherical void) of radius a for liquid solvent (*a*) and chance reaction electric field **R**$_\mu$ when solute molecule μ is placed at the centre of free spherical cavity for liquid solution (*b*)

When polar solute molecules with dipole momentum μ are placed into a solution as it depicted in Fig. 1, *b*, to calculate the mean reaction electric field $\langle \mathbf{R}_\mu \rangle$, variance d^2, mean interaction energy between μ and solvent dipoles μ_s ($\langle W \rangle$), we also start from free-spherical-cavity model to obtain respectively [9; 10]:

$$\langle \mathbf{R}_\mu \rangle = -\frac{2\mu}{a^3}\Delta f,$$ (3)

$$d^2 = \frac{2\mu^2 k_B T}{a^3}\Delta f,$$ (4)

$$\langle W \rangle = -\frac{2\mu^2}{a^3}\Delta f.$$ (5)

Eqs (3)–(5) have been successfully employed to create a theory of solvent effect on the spectra and fluorescence nonradiative decay of dyes [10] and linear pigments, for instance, for peridinin in liquid solutions [11; 12]. Despite the complexity of problem, the theory of polarity-dependent fluorescence quenching turned out to be in a good agreement with experimental data [10; 11]. Consequently, it should be realized that the existence of full orientation disorder in the environment of free cavity must be taken as proved for liquids and likely for some glass-forming polymeric media, such as non-aggregated and low-aggregated π-conjugated polymers or amorphous regions in semi-crystalline π-conjugated polymers. Following this presupposition we are able to gain an insight into charge transport losses in the disordered polymer media through Eqs (1)–(5) with the proviso that $T = T_{polym}$, where T_{polym} is the temperature of polymerization. The reaction electric field $\langle \mathbf{R}_\mu \rangle$ in Eq (3) can be considered as a drive force, which is of prime importance for electrons and holes transport, when μ is ground-state dipole momentum of repeating backbone link of π-conjugated polymer, and a is effective radius of such link.

Electron-trapping voids, dead electrons and fluorination. For planar heterojunction SCs Petersen et al. [13] introduced an exciton dissociation model based on a field-dependent tunnel process and demonstrated its consistency with experimental observations. One can assume that when after percolation the excitons fall on the free-cavity border they dissociate just as it occurs at any donor/acceptor interface. In other words, in the polar π-conjugated polymer the voids are capable to exhibit electron-accepting affinity. The chance electric field $\langle R \rangle$ captures electrons at the voids of polymer and thus prevents their transport to cathode. In a like manner it takes place also when the drift electrons fall on the border with voids. As shown via Eg (2) a mean binding energy of trapped electrons in the voids is given by Eq (6) [14]:

$$W_{void}^- = -\sqrt{\frac{4\Delta f q^2 k_B T_{polym}}{\pi a_{void}}},$$ (6)

where q is the elementary charge, a_{void} is a mean radius of the voids.

In the deep traps, when binding energy meets the condition

$$\left| W_{void}^- \right| > k_B T,$$ (7)

the electrons are the dead ones, because they are not able to leave the voids and recombine (mainly nonradiative, or with photons emission) not reaching the cathode. As a result, a part of sunlight absorbed by PSC is converted into heat without avail. To shatter the electron-trapping voids and to reduce the losses on heating one can apparently use annealing of active-layer polymer under high pressure, but it is a time-consuming way. In our opinion the fluorination of π-conjugated polymer backbone is more readily available procedure that inhibits emergence of dead electrons because they are extruded out from voids due to repulsion from fluorine atoms.

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After fluorination the binding energy of trapped electrons in Eqs (6), (7) can be writing as $W_{\text{void}}^- + W_{\text{void}}^+$, where W_{void}^+ is repulsion energy of trapped electron. In the fluorinated polymer the dead electrons populate only the deepest traps with binding energy

$$\left| W_{\text{void}}^- + W_{\text{void}}^+ \right| > k_B T. \qquad (8)$$

As soon as in Eq (8) repulsion energy W_{void}^+ is greater than energy W_{void}^-, the chance electric field **R** is unable to capture electron into voids. Schematically, it is explained in Figs 2. As shown in Fig. 2, *a* in the case of ideal spherical voids the dead electrons move in circular orbits. Nevertheless, the voids of arbitrary shape with a

Fig. 2. Electron captured by chance electric field **R** for void of radius a_{void} in non-fluorinated disordered polymer (*a*) and free-of-electron void due to repulsion effect in fluorinated polymer when binding energy $W_{\text{void}}^- + W_{\text{void}}^+ \geq 0$ (*b*)

suitable electric field **R** are also able to capture electrons and no matter where they are located, in the disordered or semi-crystalline region of polymer active layer.

In the light of our model the fluorination of π-conjugated polymer improves dramatically PCE of solar cells inasmuch as the number of dead electrons in the voids is greatly reduced due to repulsion from non-shielded negatively charged fluorine atoms. Good points of fluorination depend on the number of fluorine atoms, their arrangement in the π-conjugated chain of polymer, their shielding by side groups as well as on the other factors.

Known experiments and model of dead electrons. We included a number of known results for discussion in this heading: 1) well-balanced transport of holes and electrons after fluorination [5; 6]; 2) dielectric constant side-chain polymer manipulation [15; 16]; 3) photovoltaic performance of films processed from different solvents [17]; 4) dopant controlled trap-filling induced by nanocrystals [18].

In view of the fact that dead electrons occupy voids up to recombination and do not take part in electron transport, their drift mobility is equal to zero. On the other hand, as may be inferred from Eqs (7), (8) using Boltzmann-like factors $1 - \exp(-\left| W_{\text{void}}^- \right| / kT)$ and $1 - \exp(-\left| W_{\text{void}}^- + W_{\text{void}}^+ \right| / kT)$, the concentration of dead electrons is lower for fluorinated polymers; consequently, they should exhibit higher electron mobility. Therefore, the model of electron-trapping voids and dead electrons must be invoked to account for balanced hole and electron transport with high h/e mobility ratio of 1–2 in the case of PPDT2FBT [5] (some details was already called in Introduction). If there is minor amount of dead electrons in polymer voids the h/e mobility ratio is come close to unity. When the electrons do not fall into the voids along their drift path to the cathode, the thickness-independent active layers become enable up to 300–1000 nm [5; 6]. It is also evident from our model that the larger open-circuit voltage of PPDT2FBT devices is correlated with slower non-geminate (bimolecular) recombination rate k_{rec} [5] which are strongly suppressed due to lack of dead electrons in active layer of fluorinated polymer PPDT2FBT.

Cho et al. [16] demonstrate that tailoring the dielectric constant can be used to control recombination dynamics in PSCs. They introduce polar nitrile side-chains tethered to the electron deficient diketo-pyrrolopyrrole (DPP) unit of an indacenodithiophene-based (IDT) copolymer (PIDT-DPP-CN) to control the dielectric properties of this active layers compared to an analogous polymer with alkyl side-chains (PIDT-DPP-Alkyl). Up to this, it has been shown [15] that PIDT-DPP-Alkyl and PIDT-DPP-CN have similar hole mobilities, orbital energy levels, and optical absorption. This suggests that the side-chain manipulation has a negligible impact on the called properties. Nevertheless, the transient photovoltage (TPV) measurements demonstrated that k_{rec} is substantially reduced in the PIDT-DPP-CN/C_{60} in contrast to the faster charge recombination rates k_{rec} observed for PIDT-DPP-Alkyl/C_{60}, with voltage decay times τ_1 and τ_2 of 73 and 15 μs respectively [16]. The bilayer heterojunctions made with the high dielectric polymer PIDT-DPP-CN show improvements in V_{OC}, *FF*, and J_{SC}. To understand these behaviours and TPV results the authors have used the Coulomb attraction between the electron and hole, and that the binding energy is inversely proportional to dielectric constant ε. They inferred that the improvements in device performance appear to be linked to suppressed non-geminate recombination [16].
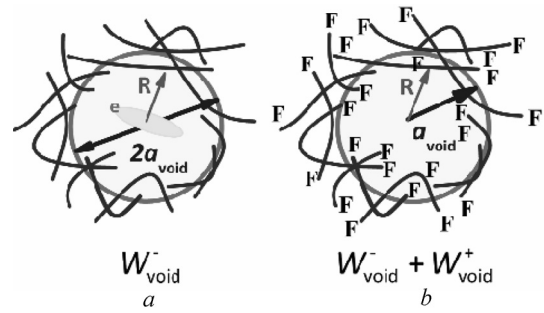
We think that the nitrile side-chains manipulation, as with fluorination, inhibit the emergence of dead electrons, because electrons are partly extruded out from voids due to repulsion from N atoms of CN-groups. A polaron pair interaction between hole in surrounding medium, on the one hand, and dead electron into void, on the other, is given by Eq (6) rather than the Coulomb attraction. The binding energy of trapped electrons is W_{void}^- (Eq (6)) for PIDT-DPP-Alkyl and $W_{\mathrm{void}}^- + W_{\mathrm{void}}^+$ for PIDT-DPP-CN. In the latter case W_{void}^+ is the repulsion energy between trapped electron and negatively charged nitrogen atoms of CN-groups. The non-geminate recombination rate k_{rec} (second order rate constant) is proportional to np and we can employ the Boltzmann-like factors for examination of rate constant k_{rec} affected by dead electrons with help of relations $1 - \exp(-\left|W_{\mathrm{void}}^-\right|/kT)$ and $1 - \exp(-\left|W_{\mathrm{void}}^- + W_{\mathrm{void}}^+\right|/kT)$ for PIDT-DPP-Alkyl and PIDT-DPP-CN respectively. Since $\left|W_{\mathrm{void}}^-\right| > \left|W_{\mathrm{void}}^- + W_{\mathrm{void}}^+\right|$ the population of the dead electrons into voids predominates for PIDT-DPP-Alkyl. Thus, the decay time of transient open-circuit voltage τ_1 for PIDT-DPP-CN/C_{60} will be considerably greater then τ_2 for PIDT-DPP-Alkyl, that have been observed by Cho et al. [16].

Not only side CN-group, but the others substituent are able to suppress the negative influence of dead electrons. It is only necessary that the substituent includes a negatively charged and slightly shielded atom. Uddin et al. [19] synthesized alkoxy-containing donor-acceptor copolymers with the high carrier mobility and PCE of 8.28 % for PPDT2FBT/PC70BM device. One can probably consider this success as finding of fine-drawn conjunction of repulsive forces on the side of negatively charged oxygen atom belonging to alkoxy-group as well as on the side of two non-shielded fluorine atoms. Such molecular design promotes the expulsion of dead electrons from PPDT2FBT voids.

The PSCs performance is closely related to surface and bulk morphologies of active layer [2–6; 17]. Guo et al. [17] investigated PBDTTT-C-T/PC71BM blend with high boiling points additives of solvents 1,8-octanedithiol (OT), 1,8-diiodooctane (DIO) and N-methyl pyrrolidone (NMP) to optimize the morphologies of active layer when o-dichlorobenzene have been used as host solvent. Four films processed without solvent and with solvents show low crystallinities, implying that the use of these additives has no impact on molecular packing structure in the PBDTTT-C-T/PC71BM films and the their material is largely amorphous and disordered. Nevertheless, the photovoltaic parameters of the PSCs changed greatly by using different solvent additives. For instance, the PCE amounted 5.43, 7.37, 7.44, 4.48 % for active layer materials, without solvent and with solvents DIO, NMP, OT respectively. The film possess the bad-balanced hole and electron transport with h/e mobility ratio of 104.9, 10.43, 41.22, 78.8, showing low electron mobility of $6.37 \cdot 10^{-5}$, $8.37 \cdot 10^{-4}$, $1.88 \cdot 10^{-4}$, and $8.08 \cdot 10^{-5}$ cm^2 V^{-1}s^{-1} respectively as in the above sequence. From our standpoint in the case of pure PBDTTT-C-T/PC71BM blend the low electron mobility of $6.37 \cdot 10^{-5}$ cm^2 V^{-1}s^{-1} and bad h/e mobility ratio of 104.9 exist owing the amorphous nature of material that have a lot of free electron-trapping voids. Following Eqs (6), (7) most of the voids with a small radius can be related to the deep traps which in active layer of PSC are populated by dead electrons. As noted above, this inevitably leads to a drop in electron mobility and a decrease in the PCE. The additives of solvents fill the void and prevent the appearance of the dead electrons to a greater or lesser extent. The most effective additive is DIO by reason of electron repulsion exerted by two non-shielded negatively charged iodine atoms. The protective effect of additives depends on their molecular structure, on sizes of voids, on the number of molecules which occupy voids as well as on the interaction of additive molecules with electrons, which are directed to the voids by reaction electric field $\langle \mathbf{R}_\mu \rangle$ and built-in voltage. This is a complex issue, which should not be attempted to be discussed now.

For further confirmation of our model we turn to the work of Gao et al. [18], which investigated P3HT:CdSe films with different CdSe nanocrystals (NCs) having average diameters of 3.3, 4.4, and 5.3 nm and constant shape. Employing the TPV measurements it was found that the photoinduced charge carrier lifetime τ includes slow component of 21, 10, and 1.8 ms respectively. After extensive research the authors have inferred that there are traps in all three P3HT:CdSe devices with charge trapping affecting the device performance regardless to the size of NCs. They have also drawn the important conclusion that the trap-mediated recombination is responsible for the loss of photogenerated charge carriers in such hybrid solar cells.

To insight into the nature of these traps we can suggest, that NCs fall into the P3HT voids when preparing blends, and being polarized by the internal chance electric field $\langle R \rangle$, themselves are becoming the traps. The electron trapped by polarized NC is apparently localized in the surface layer of NC and for the idealized spherical nanodots it moves in a circular-like orbit in the surface layer of radius a_{NC}. For the disorder polymer the internal chance electric field $\mathbf{R}$ is the vector with the randomly oriented direction, moreover there are free voids of different size in polymer. Taken together these reasons lead to the fact that some part of the trapped electrons is dead electrons.

In approximation of spherical nanodots, in the case when $a_{NC} = a_{void}$, it can be shown that the mean binding energy $\left| W_{NC}^- \right|$ of electron, trapped by polarized NC, is given by Eq (9):

$$W_{NC}^- = -\sqrt{\frac{\Delta f q^2 k_B T_{polym}}{\pi \varepsilon_{NC}^2 a_{void}}},\qquad(9)$$

where ε_{NC} is the dielectric constant of NC. One can see that the trapped electrons have higher binding energy $\left| W_{NC}^- \right|$ in the case of small NCs. Accordingly with Eq (9), the lifetime τ decreases with increasing of particle size in sequence 21, 10, and 1.8 ms, since the non-geminate recombination rate k_{rec} is proportional to concentration of dead electrons with factor $1 - \exp(-\left| W_{NC}^- \right|/kT)$. Thus, the decrease of amount of dead electrons with the growth of NC size is also in consistent with the fact that the photocurrent generation in P3HT:CdSe films increase with increasing of NC size [18].

Employing Eq (2) one evaluates the internal chance electric field $\langle R \rangle$ of $6.51 \cdot 10^7$, $4.24 \cdot 10^7$, and $3.20 \cdot 10^7$ V/m for P3HT free voids with a diameter of 3.3, 4.4, and 5.3 nm respectively. Next data are used for these calculation: $T_{polym} = 423$ K, since the P3HT was annealed at 150 °C [18]; $\varepsilon \approx 3$; the second part of factor Δf was ignored i.e. $\Delta f = f(\varepsilon)$. With $V_{OC} = 0.2–0.6$ V for P3HT:CdSe thick films of 80 nm [18], the built-in electric field $R_{built-in}$ have to be of $2.5 \cdot 10^6$–$7.5 \cdot 10^6$ V/m. This example demonstrates the testing of Eq (2), and that the internal chance electric field $\langle R \rangle$ on the order of magnitude greater than the built-in electric field $R_{built-in}$ even for relatively large voids. But there are always free voids of smaller sizes in polymer and, as followed by reference to Eq (6) and factor $1 - \exp(-\left| W_{NC}^- \right|/kT)$ they are a major refuge for dead electrons in the active layer in hybrid P3HT:CdSe solar cells with large NCs. All presented evaluations are of importance for photovoltaic devices operating on the BHJ principle, but its detail discussion is beyond the framework of basic concept of this study.

Conclusions. Herein it is substantiated that the voids – not only spherical, but any other shape – are the most widespread kind of the electron traps in disordered or semi-crystalline polymer active layers of photovoltaic devices. The internal chance electric field in polymer captures and maintains the electrons after CT excitons dissociation on the surface of voids or when the electrons are driven to the cathode by a built-in voltage. So there appear dead electrons in the voids, and such expected to be the nature of the deep traps in π-conjugated polymer. Due to non-geminate recombination the dead electrons are unusable to be collected to external circuit of solar cell. For this reason the electron-trapping voids and non-geminate recombination of dead electrons are the main obstacles to create the highly efficient PSCs. Fluorination, side-chain manipulation in polymer backbone, and trap-filling additives in active layers prevent the appearance of dead electrons inside voids and partially eliminate these obstacles.

We come also to the conclusion that in P3HT:CdSe films the deep traps originate not only from free voids of smaller sizes but as well from polarization of CdSe NCs in the internal chance electric field of polymer, because after polarization the NCs become themselves the traps. Thus, the polarized NCs are able to capture electrons, some part of which are also classified here as dead electrons.

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