Organic salt semiconductor with high photoconductivity and long carrier lifetime

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Abstract

Intrinsic photo generation of charge carriers in organic semiconductors is generally attributed to high energy ionization or exciton dissociation by a strong electric field. Here we report on high bulk photoconductivity in pristine pentamethine cyanine films with photocurrent onset at the band-edge of the organic semiconductor. Single layer cyanine diodes with selective hole and electron contacts show linear dependence of photocurrent with reverse voltage and light intensity. Numerical drift-diffusion simulations reveal that the linear resistor behavior stems from low and unbalanced carrier mobilities giving rise to negative space charge. Slow bimolecular recombination kinetics of photoinduced charges obtained by time delayed charge extraction measurements show strongly reduced Langevin recombination with long carrier lifetime of the order of a millisecond. Such reduced charge carrier recombination puts forward a materials concept to be exploited in photodiodes and more generally in optoelectronic devices.

1. Introduction

Photoconductivity is a general term to denote an increase in conductivity upon irradiating a photoactive material by electromagnetic radiation and is commonly measured by applying two electrodes to the sample. Since the early studies on polyacenes, diverse generation mechanisms such as ionization by high energy radiation, thermal production of charge carriers, single and multi-photon processes, reactions between excitons as well as electric field induced exciton splitting have been identified and studied in various organic semiconductors.^[1] In crystalline materials, photoconductivity is usually investigated at relatively low electric fields and therefore field independent charge generation processes dominate.^[2] On the other hand, electric fields larger than 10^8 V/m can be readily applied in thin films. At such strong electric fields excitons can be split even in pure materials, overcoming the high exciton binding energy of ~ 0.5 eV.^[3] A clear signature of this process is given by luminescence quenching going along with current generation^[4] and by the fact that the photon energy at the photocurrent onset matches the bandgap of the semiconductor. There are however very few organic materials that are able to produce bulk photogenerated charges in the absence of an electric field^[5], except when doped with electron or hole acceptors. Recently, trap assisted current-injection from the electrodes with photo-multiplication factors of several hundred has been observed in thin films of conjugated polymer blends with fullerenes.^[6] In those devices, photo-induced current depends exponentially on applied voltage, since the effect is based on the tunneling injection from one of the electrodes. While many of above processes can be success-

fully implemented in applications such as xerographic photoreceptors ^[7] or photodetectors ^[8], the occurrence of photoconductivity in the bulk material may be detrimental to photovoltaic cells, since it leads to a photoshunt which lowers the fill factor. ^[9]

Since several years, cyanine dyes are becoming more attractive as organic semiconductors in organic solar cells ^[10], near infrared photodiodes ^[11] and light-emitting electrochemical cells. ^[12] Only few works have looked at charge transport and charge generation in bulk cyanine semiconductors. In pioneering early work, the photoconductivity of more than 50 different dyes was studied including a cyanine dye (pina-cyanol). ^[13] Later studies reported on the photoconductivity in pentamethine cyanine dye single crystals ^[14] and thin amorphous films. ^[15] It was established that charge generation upon photon absorption occurred in the bulk of the semiconductor, but a clear generation mechanism could not be identified.

Here we present the observation of remarkable photocurrent generation in thin pristine films of a common pentamethine cyanine dye salt in the absence of dopants. By using blocking contacts in reverse bias, a linear relationship of photocurrent with voltage up to an electric field of 10 MV/m is observed. Using a combination of experimental methods including spectral photosensitivity, photo-CELIV (Charge Extraction by Linearly Increasing Voltage), electric field induced fluorescence quenching as well as numerical simulation of drift and diffusion currents, we unravel the origin of photoconductivity in these cyanine films. In particular, we explain the ohmic resistor be-

havior of photocurrent with reverse bias and discuss the reasons for efficient photocurrent production in the bulk of these organic salt semiconductors.

2. Results

Pentamethine cyanine Cy5-P has so far been used as rather efficient electron donor component in bilayer solar cells in conjunction with fullerene C₆₀ as electron acceptor.^[10a] In the latter devices, the observed photovoltaic effect is due to charge generation at the organic heterojunction^[16] yielding a power conversion efficiency of nearly 3 % with a short circuit current and open circuit voltage of about 7 mA cm⁻² and 0.64 V, respectively.

Single layer devices with rectification ratios larger than three orders of magnitude between forward and reverse current density at ± 2 V could be readily fabricated using a MoO₃ anode buffer layer as well as a top aluminum contact including a thin Alq₃ interlayer (materials and energy levels are displayed in **Figure 1a** and **1b**). In spite of the missing donor-acceptor junction, an important photocurrent is observed at short circuit condition and in reverse bias. **Figure 1c** shows the current-voltage (*J-V*) characteristics of ITO/MoO₃ (10 nm)/Cy5-P (40 nm)/Alq₃ (2 nm)/Al (40 nm) devices for different white light irradiances from an AM 1.5 G solar simulator. Striking linear photoconductivity-voltage dependence is observed in reverse bias reaching more than 20 mA/cm² at an irradiance of 283 mW/cm² (corresponding to a solar irradiance of roughly 3 suns). Due to the asymmetric workfunctions of the selective electrodes, a built in field of roughly $E_{bi} = V_{oc}/d$ adds to the applied field, where V_{oc} and d are the

open circuit voltage and the Cy5-P layer thickness, respectively. Logarithmical open circuit voltage dependence on light intensity is obtained (Supporting Information, Figure S1) reaching 0.82 V at the maximum irradiance of 283 mW/cm².

Figure 1 (a) Chemical structure of Cy5-P and (b) energy level diagram of the materials used in the thin film diodes. (c) Current- voltage characteristics of single layer ITO/MoO₃(10 nm)/Cy5-P (40 nm)/Alq₃ (2 nm)/Al (40 nm) devices in the dark and under a simulated solar irradiance of 100 mW/cm² and 283 mW/cm².

When Ag is used as cathode metal, the diode showed reduced V_{oc} and higher forward current onset voltage as compared to Al (Figure S2a). Devices using PEDOT:PSS anode buffer layers and a silver cathode exhibited higher dark current in reverse bias and presented poorly rectifying J - V characteristics (Figure S2b). However the slope in the linear part of the current-voltage characteristics under light irradiation stayed unchanged.

In order to compare photoconductive behavior under various conditions, we use the linear part of the photocurrent in reverse bias direction and define the effective conductivity σ_{eff} as:

$$\sigma_{eff}(I, d) = \frac{dJ}{dE} \quad (1)$$

where I is the irradiance, J is the current-density in reverse bias and E is the average electric field through the device. The latter can be approximated by $(V_{ap}-V_{oc})/d$, where V_{ap} is the external applied voltage. Even though V_{oc} clearly changes according to the effective work function of the electrodes (Figure S2), the effective conductivity is not depending on the type of electrode or buffer layer used in the device. Furthermore σ_{eff} depends linearly on irradiance (**Figure 2a**). Both, the linear electric field and irradiance dependence over two orders of magnitude is a strong indication that the charge generation is intrinsic and can not be ascribed to electrode injection enhancement by trapped photogenerated charges, which would lead to exponential dependence. The absence of electrode workfunction sensitivity also supports the conclusion that electrode interface effects are not playing a dominant role.

Figure 2 (a) Effective conductivity σ_{eff} extracted from the linear slope of the current-voltage characteristics a ITO/MoO₃ (10 nm)/Cy5-P (40 nm)/Alq₃ (2 nm)/Al (40 nm) diode measured at different simulated solar irradiances (corresponding J-V curves are

shown in Figure S4). (b) IPCE spectra of the same device as in (a) at different biases. For comparison the calculated absorptance of the device is also indicated (dotted line).

The spectral shape of the IPCE curves do not vary notably with the electrical field be it in forward or reverse direction (**Figure 2b**) hinting at a field independent charge generation mechanism. Clearly, the line shapes of the IPCE spectra do not follow the absorptance spectrum obtained by SETFOS transfer matrix calculation for the full diode stack with a 40 nm thick cyanine film (Figure 2b and Figure S5). It is possible to estimate the highest achieved IPCE value since the latter is proportional to the photocurrent density. Taking the highest photocurrent density at $V_{ap} = -5$ V, which corresponds to the highest possible applied reverse field of $1.25 \cdot 10^8$ V/m before diode breakdown, a maximum IPCE of 28 % at 700 nm is obtained. This corresponds to an internal quantum efficiency (IQE) of 37 % given the absorptance of about 75 % at 700 nm for a cyanine thickness of 40 nm. Performing this calculation at different wavelengths where the film absorbs strongly gives the same order of magnitude but at wavelengths where the film absorbs weakly higher values with a maximum IQE of 80 % at 500 nm are observed.

Due to the high absorption coefficient of the cyanine film of about $3 \cdot 10^5$ cm⁻¹ at maximum, 90 % of the radiation in this wavelength range will be absorbed within 75 nm of the film. Therefore the fabrication of thick semitransparent diodes would allow probing whether photocurrent generation efficiency depends on front or backside irradiation and thus would allow assessing electrode sensitivity. For this purpose, diodes with 130 nm thick cyanine layers were fabricated using a semitransparent silver

top electrode with a thickness of 12 nm. Different from the IPCE spectra of thinner films, a dip appears in the wavelength range of strong Cy5-P absorption while an increased photosensitivity is observed at the band edges of the absorption spectrum (**Figures 3a** and **3b**). At an applied bias of 0 V, only a small IPCE difference in the region of maximum absorption is seen when comparing back and front irradiation. At higher reverse bias the difference in IPCE between band edge and the spectral region of maximum absorption diminishes (Figure 3b).

Figure 3 IPCE spectra of ITO/MoO₃ (10 nm)/Cy5-P (130 nm)/Alq₃ (2 nm)/Ag (12 nm)

semitransparent devices either from the ITO or Ag side (a) at short circuit condition and (b) biased at -3 V. Empty blue squares indicate irradiation from the ITO side, while empty red circles correspond to Ag side irradiation.

Another way to scrutinize electrode effects on charge generation is to modify the electrode interfaces. In organic salt semiconductors mobile ions can be displaced to-

wards the electrodes under an applied electric field, forming p- and n-doped zones at anode and cathode, respectively.^[12a] For 40 nm thick Cy5-P devices, weak light-emission set in after a few minutes and reached a maximum in about 10 minutes when poled at +3 V (Figure S6a). This process is faster than in similar devices using an analogue trimethine cyanine dye.^[12b] In such poled devices, the rectification ratio was twice as high as in unpoled devices, underlining non-injecting electrode behavior in the reverse bias range examined. Under white light irradiation, the slope of the linear current-voltage characteristics was very close to the one of unpoled devices (Figure S6b). Furthermore, V_{oc} increased to 0.94 V reflecting that the doped regions lead to ameliorated frontier orbital energy level matching with the electrode work functions. The loss of 0.7 eV between eV_{oc} and the optical bandgap (1.64 eV) is within the energy loss generally observed in efficient donor-acceptor organic photovoltaic devices.^[17] However, in single layer pristine Cy5-P films devoided of a heterogeneous donor -acceptor interface, some loss mechanisms must have different origin than in conventional solar cell devices, as will be explained below.

3. Discussion

In thin film devices driven at strong electric fields, photoassisted tunneling injection of charges from the electrodes may occur. In the present study, we can discard the latter effect based on the following two reasons. First of all, electrode injection effects will sensitively depend on the injection barrier, which is affected both by the concentration of photoinduced trapped charge carriers^[18] and by the electrode workfunction.^[19] As a consequence the observed photocurrent generally depends non-linearly

on the applied voltage and on light-intensity.^[6, 18] In Cy5-P diodes we observe perfectly linear behavior in the reverse bias, both as a function of electric field and irradiation intensity. Also the alteration of cathode metal or anode buffer layer had no effect on the linear part of the photocurrent under reverse bias. A further argument against photo assisted charge injection comes from the reverse relationship of absorption and IPCE spectrum, which is particularly clear for the thicker cyanine layers. The fact that this behavior is symmetrical for both front and back illumination reveals that the photogeneration mechanism can not be related to a particular interface, in which case a strong difference of IPCE spectrum and intensity is expected.^[6b]

More insight into the charge carrier dynamics of Cy5-P films was obtained from photo-CELIV measurements. Steady state charge carrier densities n_{CELIV} of $6.3 \pm 0.8 \cdot 10^{16} \text{ cm}^{-3}$ and $7.5 \pm 0.5 \cdot 10^{16} \text{ cm}^{-3}$ were obtained for 40 nm and 130 nm thick cyanine films, respectively (transients are shown in Figure S7). For the thinner films, extraction of charge carriers did not vary when the sweep rate was changed from 10 to 100 V/ms. For the thick films, the low charge carrier mobility did not allow to extract all the charges when exceeding a rate of 10 V/ms. To confirm the extracted charge obtained by photo-CELIV, transient photocurrent was also analyzed (transients shown in Figure S8). Densities of $1.6 \cdot 10^{16} \text{ cm}^{-3}$ and $5.6 \cdot 10^{16} \text{ cm}^{-3}$ were obtained at 0 V bias for 40 nm and 130 nm thick films, respectively, which is of the same order of magnitude as obtained with CELIV. In order to analyze the recombination kinetics and to assess the carrier lifetime τ , charge extraction following the light pulse was delayed by different time periods up to 3 ms (**Figure 4a**). Since a constant bias at V_{oc} was applied during

the delay time we can not exclude that some charge injection occurred while the photogenerated charge carriers recombine.^[20] Current-densities preceding extraction of charge carriers were of the order of 0.02 - 0.05 mAcm⁻² and 0.001-0.005 mAcm⁻² for 40 nm and 130 nm thick devices, respectively. The effect of these small but non-zero injection currents were evaluated using dark CELIV measurements at various applied biases. The corresponding extracted charge densities were used to determine the error bars in Figure 4a. Since photo-CELIV data of thick devices have smaller error, they were used to analyze the recombination kinetics. A decent fit is obtained using the bimolecular recombination law for the time dependent charge density $n(t)=n(0)/(1+n(0)\cdot\beta_{exp}\cdot t)$ with fit parameters $\beta_{exp} = 2.7\cdot 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ and $n(0) = 7.5\cdot 10^{16} \text{ cm}^{-3}$. Here $n(0)$ is the initial charge density in the device and β_{exp} is the bimolecular coefficient such that $\tau=1/(n(0)\cdot\beta_{exp}) = 0.5 \text{ ms}$ is the carrier lifetime for the initial charge density $n(0)$. Such long carrier lifetimes have already been observed in polymer - full-erene blends with phase separated domains^[21] but are unusual in pristine small molecular materials. Since charge transfer states are much shorter lived, the recombination process can be attributed to nongeminate recombination. In previous work we indeed observed very long recombination times which we attributed to charge carrier trapping close to the anode interface induced by residual solvent.^[22] Since in this work low boiling point acetone was used as coating solvent, such effect can be discarded. Inhomogeneous charge carrier distribution may also be induced by surface recombination.^[23] Such effect, however, is more likely to occur in diodes with a thickness smaller than 100 nm and will give rise to reaction orders higher than two. Also,

given the low RC constant of 0.1 μs , a capacitive effect can not affect the measurement. It is known that care should be taken when interpreting recombination kinetics using photo-CELIV. Especially at high light intensity it is possible that recombination occurs already during the extraction pulse.^[24] In the present case, we do not expect a large impact of recombination during the extraction sweep, in particular at the long delay times used in the experiment. It has been proposed that if the charge stored at the electrodes is larger than the charge inside the active layer, then nongeminate recombination is essentially absent during charge extraction.^[25] This is indeed the case for the 40 nm thick device, where the extracted charge of $4.2 \cdot 10^{-8} \text{ C cm}^{-2}$ is smaller than the charge stored at the electrodes of $8.9 \cdot 10^{-8} \text{ C cm}^{-2}$. For the thicker device this condition is not satisfied. However, since the charge extracted from transient photocurrent is considerably higher than for the thinner devices, non-geminate recombination during extraction is assumed to be low in this case, too.

Figure 4 Photo-CELIV measurements of ITO/MoO₃ (10 nm)/Cy5-P/Alq₃ (2 nm)/Al (40 nm) devices for Cy5-P layer thicknesses of 40 nm (red) and 130 nm (black). (a) Recom-

ination kinetics measured by time delayed charge carrier extraction at a sweep rate of 10 V/ms. The dataset for the 130 nm thick devices was fit to the bimolecular rate equation using fit parameter $\beta_{exp} = 2.7 \cdot 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ (black curve), while the blue curve corresponds to recombination kinetics using the Langevin coefficient $\beta_L = 2.5 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. (b) Extracted charge carrier mobility at different sweep rates.

When measuring the photocurrent under steady state conditions, the balance between charge generation, drift and diffusion as well as recombination has to be taken into account to understand the current-voltage curves.^[26] With non-injecting contacts (in reverse bias) photocurrent saturation occurs when the drift length $L = \mu \cdot E \cdot \tau$ is larger than device thickness d . Prior to saturation, the photocurrent curve was found to follow either linear voltage dependence according to ohm's law^[27] or square root dependence^[28], if space charge is present.

Figure 4b displays extracted charge carrier mobilities obtained from photo-CELIV as a function of sweep rate and cyanine layer thickness. Without modifying device structure the current transient does not allow to distinguish between holes and electrons and usually the mobility of the faster carriers is detected (apparent mobility).^[29] Clear increase of the apparent mobility with the voltage sweep rate has already been predicted to occur in systems with trap states.^[30] The average mobility of about $5 \pm 1 \cdot 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ measured at higher extraction rates is still very low. Nevertheless due to the extremely long carrier lifetime $\tau = 0.5 \text{ ms}$, a drift length of $L = \mu \cdot E \cdot \tau = 1.3 \text{ }\mu\text{m}$ is obtained using $E = V/d = 1\text{V}/40 \text{ nm}$. Therefore at first sight it is not clear why current saturation in reverse bias is not observed. When irradiating the strongly absorbing

films, the charge generation profile is very inhomogeneous, in particular for the thicker films. Furthermore, there is evidence that hole and electron mobilities are unbalanced. In Figure 3a the IPCE measured in the centre of the absorption band is almost identical for front and back side irradiation at short circuit condition. This is surprising since the two electrodes have an important difference in reflectivity (transfer matrix optical modeling yielded absorptances of 30 % and 75 % for Ag and ITO side irradiation, respectively). Since most of the radiation at the maximum absorption wavelength is absorbed within 20 nm from the electrode interface, the current obtained is limited by those carriers traveling farthest. Even though twice as many electrons are produced by front side (ITO) irradiation as compared to back side irradiation, the two currents are comparable implying that electrons must have a smaller mobility than holes. With higher reverse bias the current generated in the high absorption region grows in a superlinear fashion revealing space charge limitation of the electron current. The IPCE peaks at the band edges of the Cy5-P absorption are attributed to the longer penetration depth of light and the more homogeneous charge distribution formed throughout the film. Hence, the greater transmission of the ITO vs. Ag electrode by about a factor of two becomes apparent.

To better understand the effect of mobility imbalance and inhomogeneous charge carrier generation in thin Cy5-P films, we simulated the J - V characteristics by varying the ratio μ_e/μ_h between electron and hole mobility. The simulation model implemented in SETFOS solves the coupled drift and diffusion equations for a given applied voltage. Langevin recombination with a reduction factor of $\beta_{exp}/\beta_L = 0.1$ was used.

The latter follows from the ratio between the experimentally determined coefficient $\beta_{exp} = 2.7 \cdot 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ and the Langevin coefficient $\beta_L \sim e \mu_h / (\varepsilon \varepsilon_0) = 2.5 \cdot 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. The hole mobility μ_h is assumed to be significantly larger than the electron mobility and was taken from the photo-CELIV measurement, $\varepsilon \varepsilon_0$ is the dielectric constant and e the elementary charge. MoO₃ was treated as a metal and in order to fit the full J - V curve, a cathode series resistance corresponding to $100 \text{ Ohm} \cdot \text{cm}^2$ was introduced. The light absorption profile was calculated based on the white LED source used for the measurement. All other model parameter values are listed in Table S1.

The simulation results in **Figure 5a** produce a good fit to the experimental data when the low carrier mobilities differ by one order of magnitude. Carrier density and potential calculated for various ratios μ_e/μ_h at an applied potential of -1V clearly show that negative space charge is accumulated close to the cathode, i.e. where only few carriers are generated. This leads to a band diagram with low and high electric field regions close to anode and cathode, respectively (**Figure 5b**). Charge carrier mobility was assumed to be field independent, which has indeed been observed in disordered organic materials.^[31] We also exclude exciton diffusion in our model, which we justify by the high energetic disorder expected in these films.

Figure 5 (a) Simulated current-voltage curves under AM 1.5 G solar irradiance using the parameter set described in Table S1. (b) Band diagram calculated from the charge carrier densities simulated for an applied voltage $V_{ap} = -1$ V. The different mobility ratios μ_e/μ_h are indicated in the graph.

Intrinsic charge generation in a pure organic semiconductor usually requires either strong electric fields or photon energies well above the optical bandgap of the semiconductor.^[32] In Cy5-P films the fluorescence quantum yield was below the detection limit of our apparatus ($<10^{-4}$) in the absence of electric field and therefore carrier generation due to field induced quenching of emissive excitons can only make a very minor contribution to the photocurrent. The weak emission has a small Stokes shift and narrow bandwidth (see Figure S9a) and therefore possibly originates from non relaxed excitonic states.^[33] This underlines that charge generation in the absence of electric field is strongly competing with radiative recombination. From the onset of field induced fluorescence quenching (see Figure S9b) an exciton binding energy of 0.4 eV is obtained which is comparable to the exciton binding energy of 0.2 eV determined for other cyanine dyes.^[34]

Further charge generation mechanisms could stem from exciton-exciton reactions such as exciton fusion ^[35] giving rise to a higher energy excited state which would be able to ionize. This process can clearly be discarded based on the linear dependence of photoconductivity with light intensity. It is also possible that charge transfer excitons or other non-radiative exciton precursors are formed, but given the very long lifetime observed using photo-CELIV this is unlikely. In addition, our previous pulsed laser spectroscopy study on the perchlorate salt of Cy5 ^[36] revealed fast generation of oxidized species within the 10 ns laser pulse in the absence of an applied electric field.

The necessary driving force for direct photogeneration of charge carriers can be caused by structural inhomogeneity creating energetic disorder in the film. Cyanine aggregates indeed give rise to important variations of orbital energy levels of up to 0.2-0.3 eV. ^[37] Inhomogeneous broadening is particularly prominent in Cy5-P films with spectral width at half maximum (FWHM) of ~0.7 eV and pronounced H-aggregate features. We indeed also observe similar photocurrents in reverse bias using other pentamethine cyanine salts with methanesulfonate and sulfoethyl methacrylate ions. The latter salts both show pronounced H-aggregate absorption features too and FWHM of 0.67 -0.72 eV (Figure S10). In single layer diodes composed of an analogous trimethine dye hexafluorophosphate salt (Cy3-P) having a less pronounced aggregation shoulder in the absorption spectrum with a FWHM of 0.5-0.52 eV (see Figure S11), photocurrent is also observed, though with a lower IPCE of less than 1 %. Energetic disorder is also favorable for charge carrier separation, since it considerably

reduces the charge escape radius^[38] with respect to the classical Coulomb radius of $r_C = e^2/(4\pi\epsilon\epsilon_0kT) = 14.2$ nm. We note that energetic disorder is also compatible with the low carrier mobility observed in pristine Cy5-P films.

We close the discussion by addressing the strongly reduced Langevin recombination in pristine Cy5-P films. In organic solar cells based on bulk heterojunctions, Langevin theory very often fails to explain bimolecular recombination.^[39] Recently, reduced Langevin recombination rate as well as V_{oc} losses have been explained by the presence of an equilibrium between charge transfer (CT) states and free carriers.^[40] In Cy5-P films, we do not expect CT states, given the fact that cyanines are cationic dyes. Once reduced by an electron (**Figure 6a**) the chromophore becomes a neutral radical therefore degrading the electrostatic attraction between hole and electron. While the reduced chromophore site with its environment would still bear an additional negative charge, the local fields screen the negative charge carrier on the chromophore (**Figure 6b**). It can instead be assumed that the positive charge carrier would coulombically bind to a close-by counterion from where it is able to dissociate and become a free charge carrier without suffering recombination. This effect may contribute to a reduced Langevin recombination rate in addition to charge localization in the disordered films with random potential distribution.^[41]

Figure 6 (a) Proposed charge carrier generation mechanism present in aggregated Cy5-P films. A photon ($h\nu$) is absorbed in the amorphous region of the film (**1**) followed by electron (e^-) transfer to an aggregated cluster of molecules (**2**). In the following, the hole (h^+) is transferred from the photo-oxidized molecule to a neighboring site (**3**). (b) A free hole at a distant position (**5**) is experiencing the negative charge in the volume surrounding the free electron (**4**). As the positive charge approaches **4**, local fields by the anions surrounding **4** dominate and lower the probability of hitting the molecule, where recombination occurs.

4. Conclusions

We demonstrate efficient photoinduced charge carrier generation in the bulk of pristine pentamethine cyanine dye films with internal quantum efficiency exceeding 40 %. CELIV investigations reveal that free charges are created in the absence of an electric field with lifetimes of the order of milliseconds. Under reverse bias, charges generated under continuous irradiation lead to a linear dependence of the current-voltage curve, which we attribute to a space charge effect stemming from both inhomogeneous charge generation profile and mobility imbalance between holes and electrons.

This mechanism is confirmed by numerical simulation. We postulate that charges are generated within the bulk semiconductor by photoinduced charge transfer in the heterogeneous cyanine film since other mechanisms such as photo-enhanced electrode injection can be discarded. The reduced bimolecular Langevin recombination rate in these cyanine films with a typical millisecond half lifetime points towards a charge screening mechanism in these cationic dye salts. Our results put forward a materials concept with reduced charge carrier recombination to be exploited in photodiodes and more generally in optoelectronic devices.

5. Experimental Section

Device fabrication

Single layer cyanine diodes were fabricated and stored in a glove box under nitrogen ($\text{H}_2\text{O} < 1 \text{ ppm}$, $\text{O}_2 < 10 \text{ ppm}$). Indium tin oxide-coated glass substrates (ITO, Thin Film Devices, 140 nm, sheet resistance 20 Ohm/square) were sequentially cleaned in acetone, ethanol, detergent and de-ionized water. Anode buffer layers of MoO_3 (Sigma Aldrich, 99.99 %), cathode buffer layers of tris(8-hydroxyquinolino)aluminium (Alq_3 , Sigma-Aldrich, 99.995 %) and cathodes of Al (Kurt J. Lesker, 99.999 %) or Ag (Cerac, 99.99 %) were deposited by thermal evaporation under high vacuum ($< 5 \times 10^{-6} \text{ mbar}$). Semiconducting films consisting of pentamethine cyanine dye 2-[5-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-1,3-pentadien-1-yl]-1,3,3-trimethyl-3H-indolium hexafluorophosphate (Cy5-P, FEW Chemicals) were spin coated from filtered acetonitrile solutions. In some cases PEDOT:PSS (Clevios P VP Al 4083) was used as anode buffer layer instead of MoO_3 and was spin-coated from aqueous

solution. The top silver or aluminum electrode was evaporated through a shadow mask to define devices with active areas of 3.1 mm^2 or 7.1 mm^2 . The chemical structure of the dye and the energy levels of the materials used in this work are shown in Figure 1a and 1b, respectively.

Single layer devices with architecture ITO/MoO₃ (10 nm) or PEDOT:PSS (80 nm)/ Cy5-P (x nm)/ Alq₃ (2 nm)/Ag (80 nm) or Al (40nm) were fabricated by subsequent deposition steps on cleaned ITO substrates. The layer thicknesses x = 40 nm, 50 nm, 65 nm, 100 nm and 130 nm were achieved by varying the concentration and spin-coating speed from 16 mg/ml to 40 mg/ml and from 1000 rpm to 6000 rpm, respectively. Semitransparent devices were fabricated by replacing the thick metal electrode by a thin semitransparent film of Ag (12 nm).

Characterization

For photocurrent characterization, the substrates were sealed in a vacuum tight box with current feedthroughs and an optical window. Standard equipment was used to determine current-voltage (*J-V*) characteristics and incident photon-to-current conversion efficiency (*IPCE*) spectra (see Supplementary Information). During *J-V* and *IPCE* characterisation, possible ionic displacement of the salt-semiconductor had negligible influence on the measurement. In reverse bias, where photoconductivity was investigated, the *J-V* characteristics did not change when the scan rate was increased from 0.4 V/s to 40 V/s. Under forward bias at 3 V, however, the influence of ionic displacement on charge carrier injection is clearly visible within a dwell time of about 1 minute. Poling experiments were therefore performed by applying constant positive

bias of 3 V to the cell and monitoring the current density. Characteristic poling times of 30 minutes were determined at the maximum current density peak. *J-V* characteristics of poled devices were taken immediately after poling, thus avoiding the relaxation of ionic distribution in the device.

Photo-CELIV transients were measured using the PAIOS system ^[42] in a nitrogen-filled glovebox. Samples were illuminated by a 300 μ s white LED (Cree® XLamp® XP-G) pulse with a nominal intensity of 72 mW/cm². The diode source used in the CELIV experiments produced identical short circuit current to the solar simulator used in the other experiments. The method to determine charge carrier density, recombination kinetics and mobility are detailed in the Supplementary Information.

The simulations were performed using the SETFOS software that has previously been used to extract organic solar cell parameters by combining steady-state and transient techniques. ^[22, 43] The simulation provides steady state solutions of the coupled drift, diffusion and continuity partial differential equations taking charge migration and recombination into account.

Fluorescence measurements were performed in a vacuum tight chamber using the optical fibre accessory of a Fluorolog-3 spectrofluorometer (Jobin Yvon Horiba) for emission detection and excitation. For high intensity excitation, a 532 nm emission wavelength solid state laser (Thorlabs) with an intensity of 4.5 mW was employed. Fluorescence quantum yields were determined in an integrating sphere mounted into the sample compartment of the fluorimeter.

Absorption spectra were measured on a Varian Cary 50 UV-vis spectrophotometer. Film thicknesses were determined by profilometry (Ambios XP1). The absorptances of the films were determined with the optics simulation software SETFOS 4.3 which is based on the transfer matrix formalism for fast calculation of the photon flux across multilayer stacks. The absorptances of some films were double checked with the help of difference time domain (FDTD) simulations using the Lumerical FDTD Solution software (Lumerical Inc. Canada). Both calculations utilize the optical constants $n(\lambda)$ and $k(\lambda)$ shown in Figure S12 as obtained by variable angle spectral ellipsometry (M-2000, J.A. Woolam Co.).

Supporting information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Key Words

Organic salt semiconductor, heptamethine cyanine dye, photoconductivity, quantum efficiency, charge carrier recombination, aggregation

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