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Singular Temperatures Connected to Charge Transport Mechanism Transitions in Perylene Bisimides from Steady-State Photocurrent Measurements

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ABSTRACT

Perylene bisimides (PBIs) are n-type semiconducting and photogenerating materials widely used in a variety of optoelectronic devices. Particularly interesting are PBIs that are simultaneously water-soluble and liquid-crystalline (PBI-W+LC), and thus attractive for the development of high-performing easy-processable applications in biology and "green" organic electronics. In this work, singular temperatures connected to charge transport mechanism transitions in a PBI-W+LC derivative are determined with high accuracy by means of temperature-dependent photocurrent studies. These singular temperatures include not only the ones observed at 60 ºC and 110 ºC, corresponding to phase transition temperatures from crystalline to liquid crystalline (LC) and from LC to the isotropic phase respectively, as confirmed by differential scanning calorimetry (DSC), but also a transition at 45 ºC, not observed by DSC. By analyzing the photocurrent dependence simultaneously on temperature and on light intensity, this transition is interpreted as a change from monomolecular to bimolecular recombination. These results might be useful for other semiconducting photogenerating materials, not necessarily PBIs or even organic semiconductors, which also show transport behavior changes at singular temperatures not connected with structural or phase transitions.

KEYWORDS: charge transport, photogeneration, perylene bisimides, photocurrent, recombination

INTRODUCTION

Among organic n-type semiconducting materials, some perylene bisimides (PBIs) present high electron affinity, and good chemical, photophysical and thermal stabilities. Thus, they have been used in the fabrication of many electronic and photonic devices, such as thin film transistors, solar cells, light emitting diodes and photodiodes.[1,2] In the last decade, some liquid crystalline (LC) PBIs with improved charge transport performance have been synthesized.[3-5] Recently, great efforts have also been dedicated to the production of water-soluble PBIs to be applied in the field of biology and pointing towards the possibility of their solution processing into "green" organic electronics using water as a nontoxic solvent.[6-8] A PBI that is simultaneously LC and water-soluble is the N,N'-Bis[1-(2,5,8,11-tetraoxadodec-1-yl)-3,6,9,12-tetraoxatridec-1-yl]-perylene-3,4,9,10-bis(dicarboximide) (PBI-W+LC, Figure 1). Recently, we have studied the temperature dependence of the time-of-flight charge mobility of this compound (denoted in that work as PBI-W).[9] From spectral studies, it was concluded that majority charge carriers are electrons. It was also found that the mobility follows an Arrhenius-type behavior up to its LC phase transition temperature, where it increases abruptly by one order of magnitude and becomes nearly temperature independent.

In the present study it is shown that the performance of steady-state photocurrent measurements allows determining with great accuracy singular temperatures at which changes in the dominating transport mechanism occur. In fact, this technique has been previously used by some of us to determine the glass transition temperature and other critical temperatures in photorefractive polymer composites.[10,11] When these temperatures are related with structural or phase transitions, they can be easily identified by differential scanning calorimetry (DSC). However, when they are not, an alternative technique involving an electrical parameter is

needed. In the case of PBI-W+LC, no singular temperatures, other than the ones related with phase transitions, could be detected from temperature dependent mobility studies.[9] Here it is shown that the steady-state photocurrent constitutes a very convenient parameter for such purpose. It is able to determine with accuracy temperatures undetectable by neither DSC, nor mobility. Moreover, it is demonstrated that the performance of temperature dependent photocurrent studies in combination with the analysis of the light-intensity dependence allows getting insights into the transport mechanisms taking place in PDI-W+LC, particularly the charge recombination processes arising in each temperature regime. Since recombination leads to a loss of photogenerated charge carriers, the identification of these processes is very useful for improving the performance of modern organic electronic devices.[12,13] The photocurrent and other derived magnitudes, such as the photocurrent density and the photoconductivity, have been previously used to study the electrical response to light of different photogenerating materials and devices.[14-17] Transient photocurrent experiments are also useful to obtain information about trapping and recombination on time scales of up to 1 μs after illumination.[18] In the present work we use the steady-state photocurrent, since experiments are simple and precise, and results under equilibrium conditions have the advantage of being widely applicable. Note that dark current is substracted from the current under illumination to determine a supposedly corrected photocurrent that is independent of carrier injection at the electrodes.[17]

The work performed with PBI-W+LC is presented and discussed as follows: Firstly, the photo-response at room temperature (RT = 22 ºC) is studied as a function of the applied electric field, in order to determine optimal conditions for subsequent measurements. Then, the photocurrent dependence on temperature is analyzed, with the aim of obtaining, from changes in the activation energy, singular temperatures delimiting different charge transport regimes. Finally, from

combined studies as a function of temperature and light intensity, charge recombination mechanisms are identified and their origin discussed.

EXPERIMENTAL SECTION

The synthesis of PBI-W+LC was firstly reported by Hansen et al.[19] Here we made some small modifications to the procedure for the isolation and purification of the final product as previously described.[9] PBI-W+LC shows a LC phase between 60 and 111 ºC and a crystalline-crystalline transition at 15 ºC, as determined from DSC. Its structure is characteristic for discotic packing in which the PBI building blocks assemble into columns arranged in a hexagonal unit cell. [9,19,20]

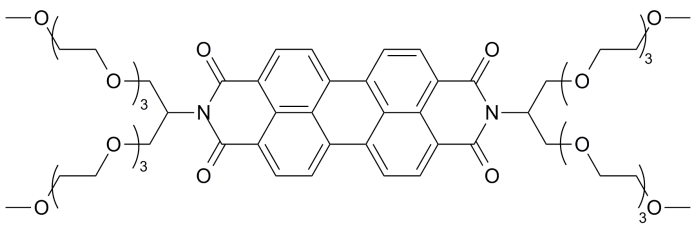


Figure 1.- Molecular structure of PBI-W+LC.

Samples for the photocurrent studies have been prepared by capillary-filling Linkam cells, consisting of two indium tin oxide (ITO)-coated parallel glass plates with a gap of 5.0 μm and effective area 0.81 cm^2, with the neat material in the isotropic phase (130 ºC). The cells were then cooled down to room temperature at a rate of about 1 ºC/min.[9] Conductivity measurements have been performed by a simple direct current (DC) technique using a picoammeter/voltage source HP 4140B to apply the voltage and to measure the current. A Melles-Griot He-Ne laser (633 nm) with a maximum light intensity of 25 mW/cm^2 was the light source selected to

illuminate the samples. Since absorption is low and the light distribution inside the material is quite uniform, the conductivity and photoconductivity values can be calculated without using correction factors.[21] Current densities in the absence of light, j_{dark}, and under illumination, j_{light}, were measured. Then, the corrected photocurrent density, j_{phot}, defined as j_{light} - j_{dark}, was calculated. No further corrections were needed,[22] since as described in the section below, results correspond to the injection-limited current regime. Transients were registered with an oscilloscope to study the temporal evolution of currents. As a consequence, the value in each measurement was taken after the current reached a quasi-steady state (≈ 60 s in the dark and ≈ 10 s more after illuminating the sample). Presumably, the viscosity of the material in the liquid crystal phase is very high (the filling of the cell at 130 ºC takes around 90 min). Besides, the material was highly purified.[9] So, even though neither viscosity nor impurities concentration were quantified, in our case ionic conduction processes, such as those observed in other liquid crystalline materials,[23] was not expected to contribute significantly to the conductivity. In the experiments for studying the temperature dependence of the photocurrent, samples were placed in a temperature-controlled set up regulated with an accuracy of ±0.5 ºC, and data were collected every 5 ºC, while the temperature varied at a rate of 0.5 ºC/min. Since each sample was used to make successive measurements of j_{dark} and j_{phot} from RT up to the transition temperature to the isotropic phase, it was important to work under moderate electric fields to prevent memory effects in the material.

RESULTS AND DISCUSSION

Dark current and photocurrent dependence on applied electric field

The PDI-W+LC dark current and photocurrent, measured at RT and at a moderate light intensity (10 mW/cm^2), as a function of the strength and polarity of the applied electric-field are shown in Figure 2. Since the device is symmetric (ITO/PBI-W+LC/ITO), the dark current is independent of the bias polarity. On the other hand, the photocurrent is dependent of the bias polarity on the illuminated electrode, but only weakly, because of the relatively low absorption at 633 nm. Photocurrent increases rapidly, reaching values acceptably high (10^{-10}-10^{-9} A/cm^2) to be measured with precision under fields lower than 1 V/μm. Thus, subsequent experiments as a function of temperature and light intensity were carried out under a negative bias (though this selection is not compulsory) of 0.4 V/μm and 10 mW/cm^2. According to the HOMO and LUMO values of PBI-W+LC,[20] the Shottky energy barrier of the device (see energy level diagram in the inset of Figure 2), is around 1 eV. Since this value is higher than 0.4 eV, which establishes the delimitation between regimes in which the current flow is space charge limited or injection limited,[24] it can be concluded than in our case the current is injection limited with a quite low injection efficiency. This means that currents are quite small, several orders of magnitude lower than those which would be obtained in a space-charge limited regime.

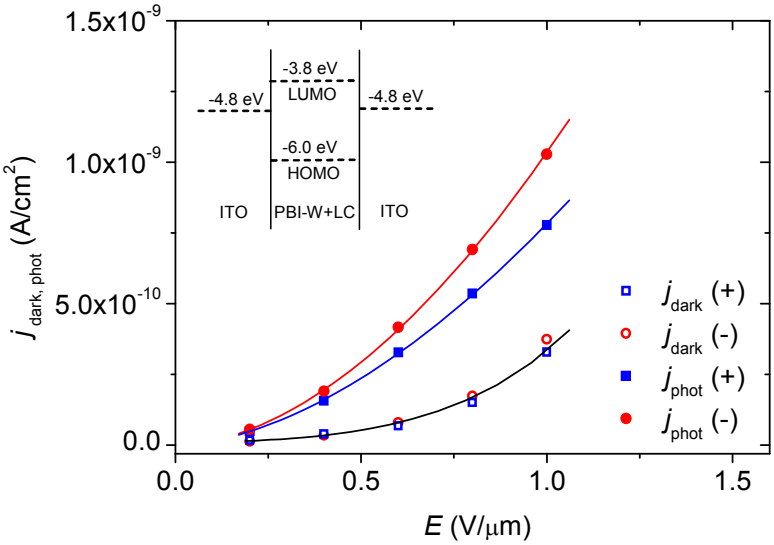


Figure 2.- Dark current, j_{dark}, and photocurrent, j_{phot}, densities for PBI-W+LC at room temperature (22°C) vs electric field, E, under positive and negative bias. The light intensity at 633 nm is 10 mW/cm^2. Full lines are guides to the eye. The inset shows the energy level diagram of the device ITO/PBI-W+LC/ITO.

Photocurrent dependence on temperature

The temperature dependence of dark current and photocurrent at a light intensity of 10 mW/cm^2 and at a negative bias of 0.4 V/μm are shown in Figure 3a. Since both, j_{dark} and j_{phot}, obey exponential laws of the form

$$j_{dark,phot} = j_{dark0,phot0} \exp\left(-\frac{\Delta E_{dark,phot}}{KT}\right) \quad (1)$$

where $j_{dark,phot}$ is a pre-exponential factor, $\Delta E_{dark,phot}$ is the activation energy and K is the Boltzmann constant, data are presented in Arrhenius diagrams (see Figure 3a). This expression is

used here empirically with the purpose of identifying with precision, from the changes in the photocurrent activation energy, the singular temperatures at which the photocurrent behavior changes. Note that understanding in depth the origin of the activation energy is not an obvious task, since it depends of many factors, such as the barriers between crystals, the amount and depth of traps, impurities, etc. It was established that from sample to sample the error in the currents is moderate, less than 10%. However the standard deviation in the transition temperatures is only ±1 ºC. For the whole temperature range explored, the photocurrent is higher than the dark current. Two appreciable changes can be observed at 60 ºC, where the activation energy decreases from 0.82 eV to 0.68 eV; and at 110 ºC, where the activation energy decreases again to 0.44 eV. These two temperatures coincide with those corresponding to the phase changes determined by DSC (see inset of Figure 3a), firstly from the crystalline (C) to the LC phase and then to the isotropic (I) phase. Highly remarkable is the observation of an abrupt change at 45 ºC, where the activation energy increases from 0.14 eV to 0.82 eV, which it is not observed in the DSC thermogram and therefore cannot be related to a structural or phase change of the material. We note that the three singular temperatures observed by considering the photocurrent are not appreciated in the dark current line, for which the activation energy, 0.59 eV, is constant in the whole range of temperatures explored. Also remarkable is the fact that the singular temperature observed at 45 ºC could not be detected in our previous mobility study of PBI-W+LC,[9] probably because errors are higher than 10%, due to the dispersive character of the transport process (for clarity, these mobility data have been included in Figure 3a).

In Figure 3b it is shown that the use of the photosensitivity, $S = j_{phot} / j_{dark}$, as an alternative parameter to the photocurrent, allows improving the accuracy in determining these singular temperatures at which the dominating charge transport mechanism changes. Although other

parameters such as the conductivity contrast, $M = j_{phot} / j_{light}$, could also be used for that purpose, S has the advantage respect to M that it stands out the relevant fact, as we show below, that the kink at 45 ºC takes place when dark current becomes of the order of the photocurrent ($S \sim 1$). At RT, S decreases with increasing temperature, while it remains relatively constant between the temperatures that limit the LC phase. It can also be seen that the singular temperatures are very well marked, especially the one at 45 ºC. This suggests that the activation energy transition at 45 ºC does not correspond to a pre-transitional change related to the phase transition observed in the DSC thermogram at 60 ºC, but to a change with a different origin.

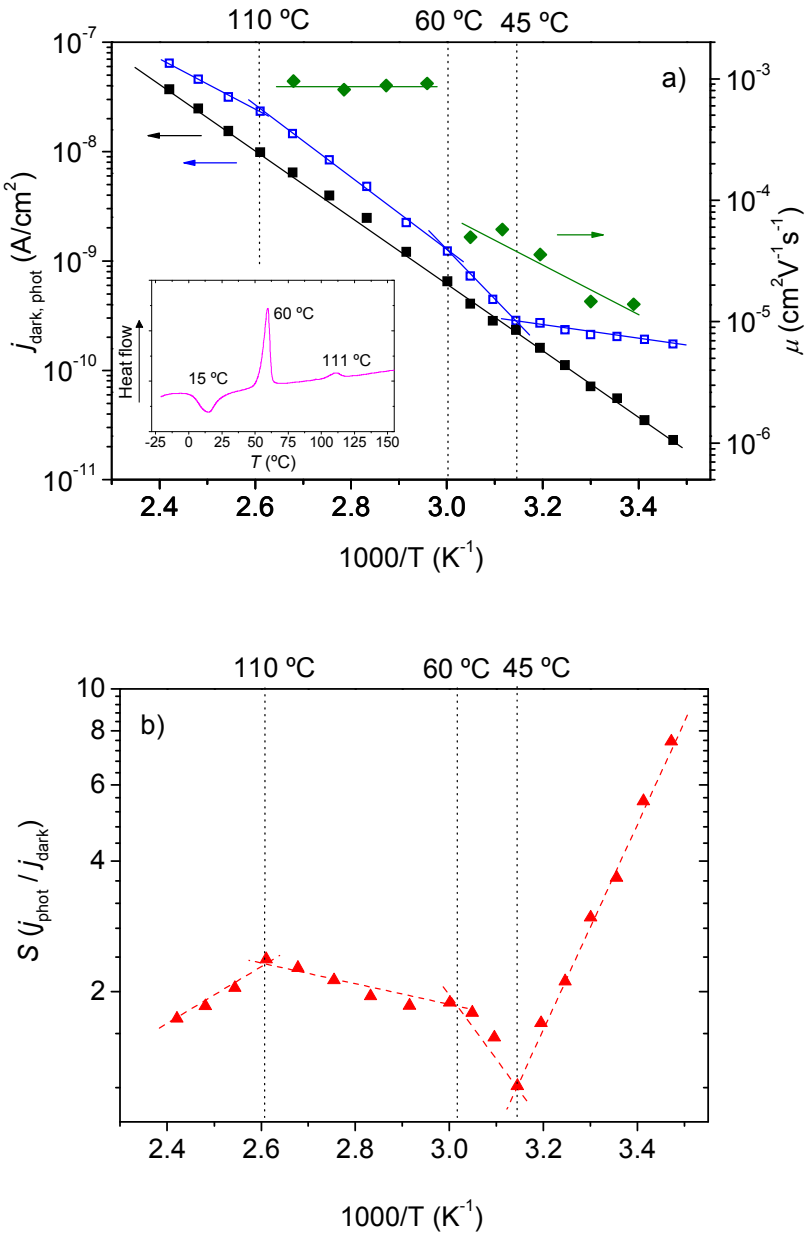


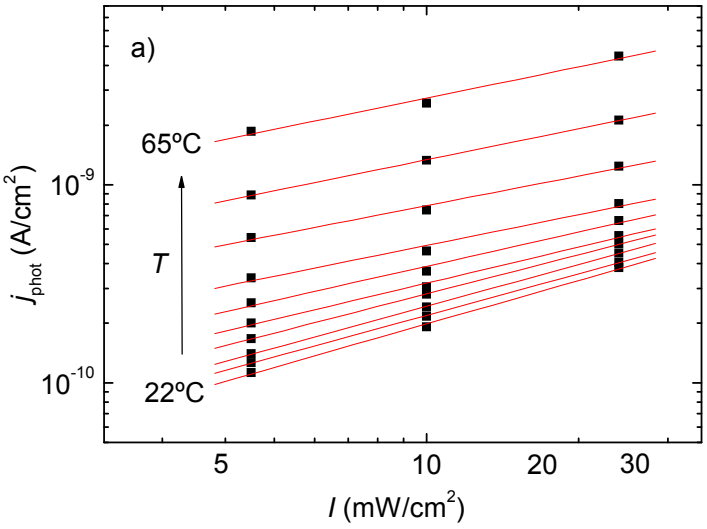
Figure 3.- Arrhenius plots of (a) dark current, j_{dark} (black full squares) and photocurrent j_{phot} (blue empty squares) and (b) photosensitivity $S = j_{phot} / j_{dark}$ (red full triangles) at an electric field of 0.4 V/μm, and a light intensity of 10 mW/cm^2 at 633 nm for PBI-W+LC. Solid lines are linear fits of experimental data to determine activation energies and dashed lines are guides to the eye. For comparison purposes, DSC (corresponding to the second heating cycle at a scanning rate of

10 K min^{-1}) and mobility data for PBI-W+LC, taken from Ref. 9, are included in (a), inset and green full diamonds plotted in right axis, respectively.

Photocurrent dependence on light intensity at various temperatures

The observation of singular temperatures at which the conductivity activation energy changes has been reported in the literature for various p-type organic materials: Nitta et al.[25] in amorphous carbon nitride at ≈ 400 K; Ilie et al.[14] in different amorphous carbon derivatives at ≈ 200 K; and Dulieu et al.[15] in polyparaphenylenevinylene (PPV) at ≈ 160 K. In this last case the activation energy change was assigned to a change from monomolecular to bimolecular recombination mechanism. This prompted us to investigate the light intensity dependence of the PBI-W+LC photocurrent at different temperatures (see Figure 4a) as to ascertain whether the change in the activation energy observed at 45 ºC (318 K) corresponds to a change in the recombination mechanism, as it occurs in PPV. In organic materials, photocurrent follows a potential law, $j_{phot} \propto I^{\gamma}$, similar to that of the electric field dependence, where the exponent γ, which can be obtained by fitting the experimental data to this power function, is related to the type of charge recombination mechanism. This parameter was used by other authors to identify the type of recombination mechanism in Phthalocyanine and C_{60}.[26,27] They found γ values between 1 and 0.5, corresponding to monomolecular and bimolecular recombination, respectively. As shown in Figure 4a, the PBI-W+LC photocurrent dependence on light intensity at RT shows a sublinear behavior. By fitting the data to the function $j_{phot} \propto I^{\gamma}$, a γ value of 0.7 was obtained. This means that part of electrons in the conduction band directly recombines with holes in the valence band, and other part recombines with holes through recombination centers in the gap. For higher temperatures, γ decreases with the increase of temperature, reaching a value

of 0.5 at temperatures higher than 45 ºC (see Figure 4b). Consequently, at RT, where $\gamma \approx 0.7$, the mechanism is a mixture of monomolecular and bimolecular recombination, while above 45 ºC it becomes a pure bimolecular mechanism. So in the range of temperatures explored, results coincide with those obtained with PPV at a lower temperature and under a similar applied electric field (0.2 V/μm).



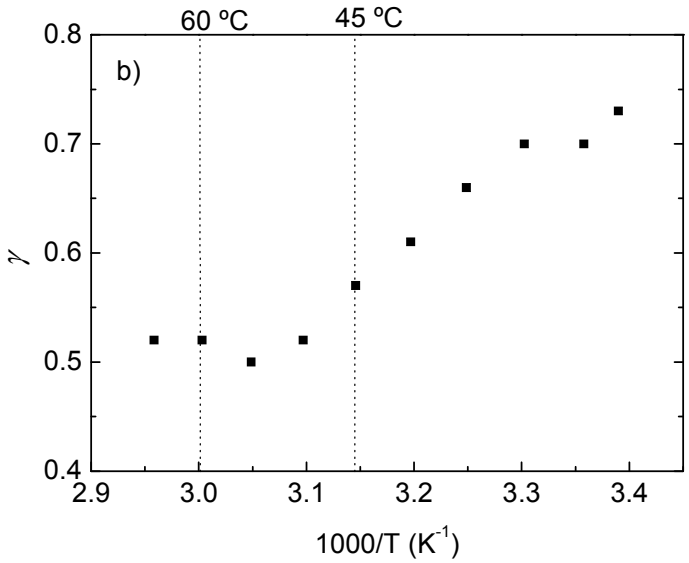


Figure 4.- (a) Log-log plot of the photocurrent density (j_{phot}) for PBI-W+LC vs light intensity (I) at 633 nm at RT (bottom line) and at higher temperatures up to 65 ºC (top line). Measurements were taken under negative electrode illumination, and the strength of the applied field was 1.0 V/μm. The solid lines are fits to data with the function $j_{phot} \propto I^{\gamma}$, from which the parameter γ is determined; (b) Temperature dependence of γ.

With regards to the cause of the recombination mechanism change, a possible explanation points to the influence of j_{dark} on j_{phot} when the temperature is increased. It can be observed in Figure 3 that the change in the activation energy in PBI-W+LC at 45 ºC occurs when the j_{dark} value becomes similar to j_{phot}, i.e. the total amount of charge carriers (not only the photocarriers computed to calculate j_{phot}), increases appreciably. This fact can also be observed in the Arrhenius plots of other organic,[14,25] inorganic[16,28] and photorefractive[10,11] materials in which j_{dark} and j_{phot} are presented simultaneously. For example, data in Figure 2 of Ref. 11 show the correlation between the transition temperatures and the abrupt increase of thermal carriers, although in that case the variable parameter is the frequency of the applied electric field. These activation energy changes can be interpreted by considering that the monomolecular recombination rate depends linearly with charge density and the bimolecular recombination rate is proportional to the square of the charge density.[29] In that case, in the presence of both mechanisms, bimolecular recombination will be more important at high charge density and monomolecular recombination will dominate at low charge density. The influence of the increased carrier density on the change from monomolecular to bimolecular recombination kinetics has been observed in polymer-fullerene bulk heterojunction solar cells where the charge density is very high.[13] In that case, the increase of the total number of carriers was due to a

decrease of the applied field, i.e. a decrease of the carrier sweep-out. It is also important to stress that according to the photocurrent definition, $j_{phot} = j_{light} - j_{dark}$, it seems that the effect of thermal carriers is subtracted. However, this is only true when the thermal carrier density is quite smaller than that of the photocarriers. When the amount of both densities becomes of the same magnitude, thermal carriers affect the recombination mechanism and, consequently, the photocarriers transport.

In order to explore how sensitive the transition temperature observed at 45ºC is to changes on the light intensity, we have performed additional temperature-dependent photocurrent experiments in the crystalline phase at light intensities of 4.5 and 20 mW/cm^2. These data, together with those obtained at 10 mW/cm^2, already included in Figure 3, are shown in Arrhenius-type plots in Figure 5. Results show that both, the transition temperature and the sensitivity *S*, increase with the illumination level from 43 ºC to 48 ºC, and from about 1 to 2, respectively. According to these results, the activation energy transition corresponds to a value of *S* of around 1, more specifically, to a value $S < 1$ for low light levels and $S > 1$ for high light levels. Remarkably, the activation energy values, below and above the transition temperature, are independent of light intensity, and the only change produced by the change in the total density of carriers (due to a change of illumination level) is the shift of the transition temperature at which the recombination mechanism changes. Such shifts of the transition temperature when the light intensity level varies, have also been observed by other authors in other types of materials.[25]

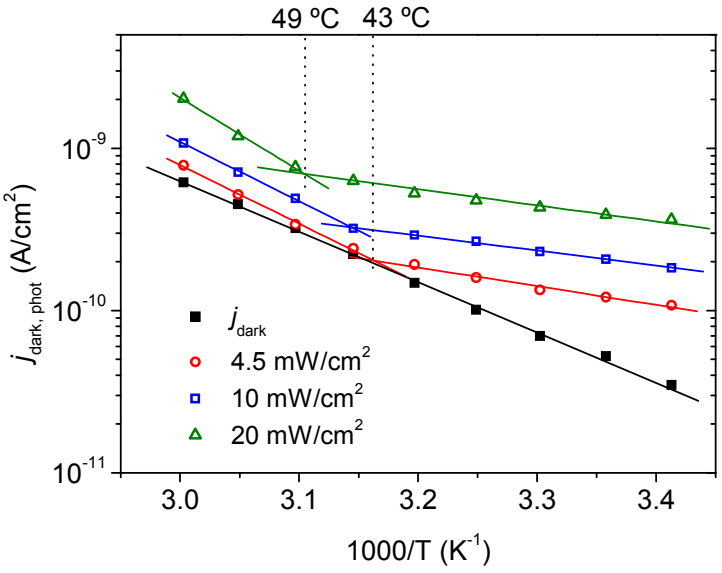


Figure 5. Arrhenius plots of dark current, j_{dark} (black full squares), and photocurrent j_{phot} for 4.5 mW/cm^2 (red empty circles), 10 mW/cm^2 (blue empty squares) and 20 mW/cm^2 (green empty triangles) at an electric field of 0.4 V/μm in PBI-W+CL.

The applicability of the methodology proposed in this work to other materials was studied by performing some photocurrent experiments with films of the PBI compound N,N′-Bis(1-hexylheptyl)-perylene-3,4:9,10-bis-(dicarboximide) (PBI-C6, chemical structure in Figure S1, Supporting Information) which is neither water soluble, nor LC. This material is crystalline in the whole temperature range from RT to the isotropic phase, so no phase transition temperatures are observed in its DSC diagram, except for the obvious C-I one, at 144 ºC.[9] Also in this case singular temperatures were observed in the Arrhenius plots of the photocurrent and the photosensitivity, particularly at 50 and 85 ºC (see Figure S2 in Supporting Information), which do not appear in the DSC thermogram. Unfortunately, a photocurrent study of PBI-C6 as a function of light intensity, such as the one performed with PB-W+LC, to get insights into the

origin of these transitions, could not be performed since the photosensitivity of this material is rather low (see SI for additional discussions). Despite the difficulties in some cases, such as in PDI-C6, of providing a precise explanation of the underlying transport mechanisms causing these singular temperatures, which are not connected with structural or phase transitions, but with the fact that thermal carriers get of the same order of magnitude than that of the photocarriers, the key point is that they appear in a wide variety of semiconducting photogenerating materials,[14-16,25,28] not necessarily PBIs, or even organic semiconductors. This suggests that the methodology proposed here might possibly be applied to study other materials, whenever they are both, charge transporters and photogenerators. Nevertheless, further studies to clarify aspects such as the origin of the dark current and the photocurrent, or the influence of working in charge injection regime, are still needed to reach such ambitious goal.

CONCLUSIONS

In summary, temperature-dependent steady-state photocurrent measurements have been performed in PBI-W+LC. Through the observed changes in the activation energy, the structural or phase transition temperatures and other singular temperatures at which variations in the transport mechanisms occur, have been determined with accuracy. Transport behavior changes were observed at 60 ºC and 110 ºC, related to phase changes from crystalline to LC and from LC to isotropic phases, respectively, as confirmed by DSC. In addition, a transition at 45 ºC has been observed, which cannot be detected by either DSC, or by mobility data. From the analysis of the light intensity dependent photocurrent at different temperatures, this singular temperature is interpreted as a change from monomolecular to bimolecular recombination, which occurs when the thermal carrier density becomes of the same magnitude than that of the photocarriers. The

fact that singular temperatures connected with this phenomenon haven been reported in the literature for other kind of semiconducting photogenerating materials, suggests that the proposed analysis methodology might be useful for other systems.

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ASSOCIATED CONTENT

Supporting Information Available

Additional Supporting Information about the molecular structure, and Arrhenius plots of dark current, photocurrent and phosensitivity of PBI-C6. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org

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