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Quantum Efficiencies of Photogeneration in Discotic Liquid Crystals. Part 2: Electric field and Temperature Dependence

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QUANTUM EFFICIENCIES OF PHOTOGENERATION IN DISCOTIC LIQUID CRYSTALS. PART 2: ELECTRIC FIELD AND TEMPERATURE DEPENDENCE

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DC photoconduction measurements are discussed in Part 1 of this paper as a viable method to deduce the quantum efficiencies of photocarrier production for various Discotic Liquid Crystals. However, high dark currents present in some materials prevent accurate measurement of the photocurrent. This paper describes how the time of flight (TOF) technique can be utilised to overcome this problem. Data for the quantum efficiencies of some DLC's are presented here. Also, a critique of Onsager's Theory of Geminate Recombination is given for the case of its use in DLC's.

Keywords: photogeneration; discotic liquid crystals; time of flight; quantum efficiencies; Onsager Theory

I. INTRODUCTION

Organic semiconductors continue to draw considerable interest due to their unique properties and the promise that they could one day be used to fabricate electronic devices on the molecular scale. There are numerous examples of these materials, for example: conducting polymers, carbon nanotubes and discotic liquid crystals. DLC's have the distinctive ability to self organise into stacks, with high carrier mobilities expected through the stacks due to the close proximity of neighbouring molecules and the corresponding electron wavefunction overlap of the conjugated system.

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Organic materials can be made to conduct continuously by the inclusion of dopants into the semiconducting material. Photons of sufficient energy can be used in lieu of dopants to excite electrons from the HOMO to the LUMO either continuously (DC light) or transiently (pulsed light). When a pulsed laser is used, transient photocurrents can be observed. If the incident laser pulse lasts for a time much less than the duration of the photo current, it can be assumed that charge is instantaneously created in the material and the resulting photocurrent will highlight the evolution of this mobile charge.

If there are $\boldsymbol{N}$ photons per unit area that are absorbed by a sample area $\boldsymbol{A}$, then the total number of photons absorbed by the sample as the result of a laser pulse would be $\boldsymbol{Nph} = \boldsymbol{NA}$ and therefore $\boldsymbol{Nph}$ chances of excitation. In practice however, only a fraction of these absorbed photons will cause excitations across the band gap. This fraction is the primary quantum efficiency for creating electron-hole pairs and is represented by the value η. Only a fraction of these electron-hole pairs will escape geminate recombination, as described by Onsager [1], denoted by the value ϕ, which varies as a function of electric field and temperature. Such behaviour has frequently been observed experimentally in organic materials. For example, Anthracene, which appears to fit the three dimensional, 3D, Onsager model [2].

The Onsager 3D model gives the probability of escape as

$$\phi = \left(\frac{1 + e\boldsymbol{E}r_{kT}}{2kT}\right) \exp\left(\frac{-r_{kT}}{b}\right) \tag{1}$$

where, $\boldsymbol{b}$ is the distance at which the electron-hole pair thermalise from each other, $\boldsymbol{E}$ is the applied electric field and $\boldsymbol{r_{kT}}$ is the Coulomb radius, given by:

$$r_{kT} = \frac{e^2}{4\pi\varepsilon\varepsilon_0 kT} \tag{2}$$

where ε is the material dielectric constant and ε_0 is the permitivity of free space.

The primary quantum efficiency and the geminate recombination rate cannot usually be deconvolved and are thus paired together as one entity written as $\{\eta\phi\}$, which will be referred to as the quantum efficiency.

DC photoconduction measurements can be used to deduce the quantum efficiencies of various materials. However, the dark currents that are sometimes present in such experiments saturate the measuring equipment and it is difficult to extract the photo component of the current from the dark component. In such situations, it is useful to employ transient photo conductivity measurements in order to overcome such difficulties. This technique is used in this work on the four discotic materials: **HAT6**,

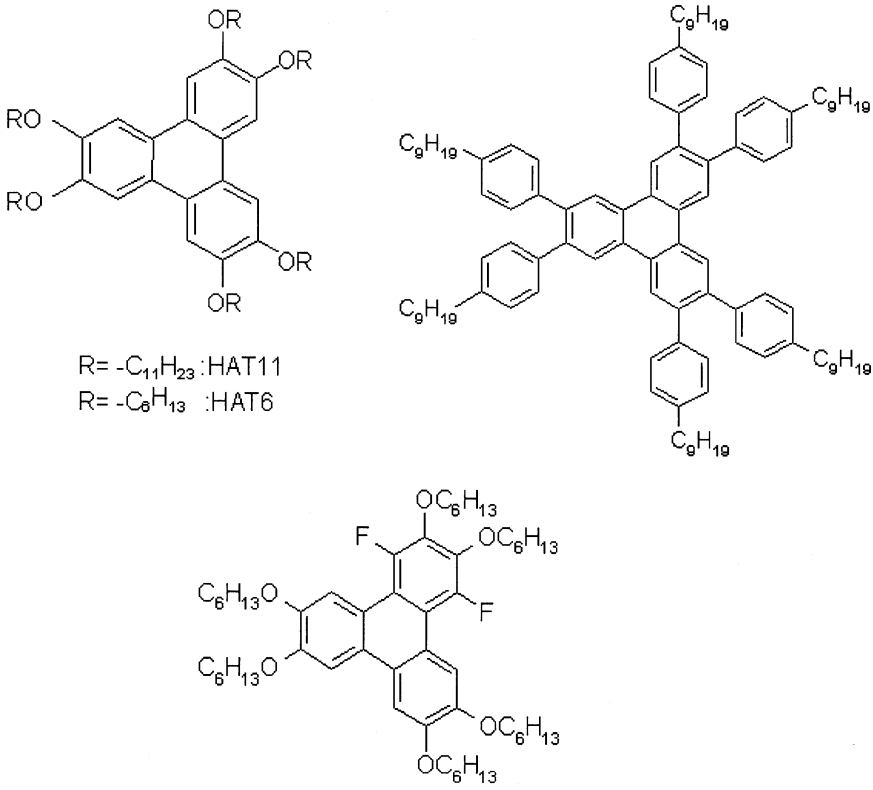

FIGURE 1 DLC's studied in this present work. The top left structure is the basic **HATn** molecule, the top right is the **PTP9** molecule and the bottom molecule is the **2FHAT6** DLC.

HAT6:PTP9, **HAT11:PTP9** and **2FHAT6.** These materials are depicted in Figure 1.

Techniques to measure the hole transits of DLC's via TOF are described in more detail elsewhere [3–7]. In this work, Onsagers' theory has been applied to different DLC's in an attempt to reconcile experimental results with theory.

II. EXPERIMENT

Evaporation of Aluminium onto two optically flat quartz slides formed semi-transparent electrodes. These were then separated by a dielectric spacer (PTFE) of known thickness. By placing a small amount of material at the

opening and then heating to the isotropic phase, capillary forces allow the liquid material to flow between the electrodes thus filling the gap. The material was then allowed to cool down to the discotic phase.

A Nitrogen laser with a pulse width of 6 ns and a wavelength of 337 nm was used to excite the material through the top semi-transparent electrode thus creating photocharge in a small skin depth of the DLC (≈0.1 μm). By applying an electric field across the sample (with the top electrode being positive), electrons created near this interface will immediately recombine at the top electrode leaving holes in the sample free to move in the DLC. This moving charge constitutes a current, which can be measured externally. By integration of this current, the total photocharge can be deduced.

$$Q = \int I(t)dt = \frac{e\{\eta\phi\}N_{PH}s}{d} \tag{3a}$$

Figure 2 demonstrates a typical photocurrent for the material **2FHAT6** in the discotic phase.

In Eq. (3a), ***s*** is the carrier distance and ***d*** is the electrode separation. In the materials studied, the holes are able to transit the sample and recombine with the bottom electrode (as demonstrated in Figure 2). The plateau seen is caused by the holes moving through the sample until they recombine at the counter electrode. The current is then observed to fall. The tail in the current decay is caused by a distribution of carrier velocities. As $s = d$, Eq. (3a) can be simplified to:

$$Q = e\{\eta\phi\}N_{PH} \tag{3b}$$

The intensity of the laser pulse is known by using a bolometric detector and so the number of photons ***Nph*** can be deduced. By rearrangement of

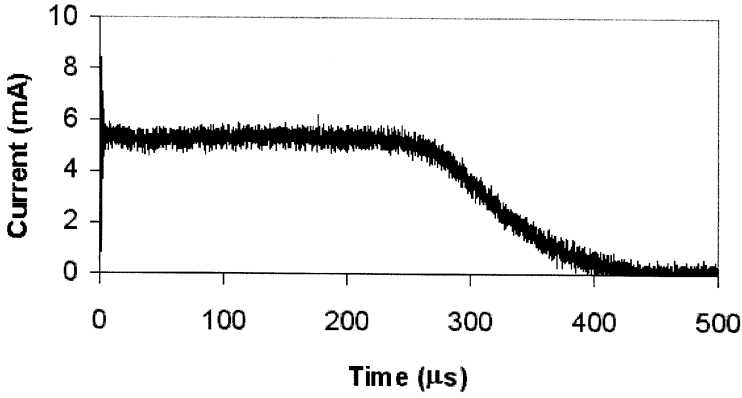

FIGURE 2 2FHAT6 Transient Photocurrent (**d** = 28 μm, **T** = 40°C, **E** = 2.0 MVm^{-1}, **Nph** = 4.07×10^{12}).

Eq. (3b), the quantum efficiencies can be calculated for a material at a given temperature and electric field.

III. RESULTS AND DISCUSSION

As was noted earlier, TOF measurements are useful when the DC dark currents become much higher than the photocurrent of interest. It is therefore necessary to prove that both methods used will yield the same quantum efficiencies. Figure 3 shows the experimental results of the **HAT6** DLC using both measurement techniques. As demonstrated, both approaches give comparable results.

The slope to intercept ratio of the data in Figure 3 is predicted by the Onsager theory of Eq. (1) as:

$$\frac{S}{I} = \frac{e^3}{8\pi\varepsilon\varepsilon_0(kT)^2} \tag{4}$$

The DC data gives an experimental ***S/I*** ratio of $3.47 \times 10^{-7}\,\mathrm{mV}^{-1}$ compared to the TOF experiment which gives $2.10 \times 10^{-7}\,\mathrm{mV}^{-1}$. Averaging these two results gives $2.78 \times 10^{-7}\ \mathrm{mV}^{-1}$. This is in good agreement with theory which at this temperature of 85°C and $\varepsilon = 3$, gives an ***S/I*** ratio of $2.51 \times 10^{-7}\,\mathrm{mV}^{-1}$. The experimental results for **HAT6** presented here are consistent with similar work carried out by Nakayama et al [8], who measured at 80°C an ***S/I*** ratio of $3.1 \times 10^{-5}\,\mathrm{cmV}^{-1}$.

Nakayama et al propose from this result that the Onsager model is applicable for describing the carrier generation process in the **HAT6**

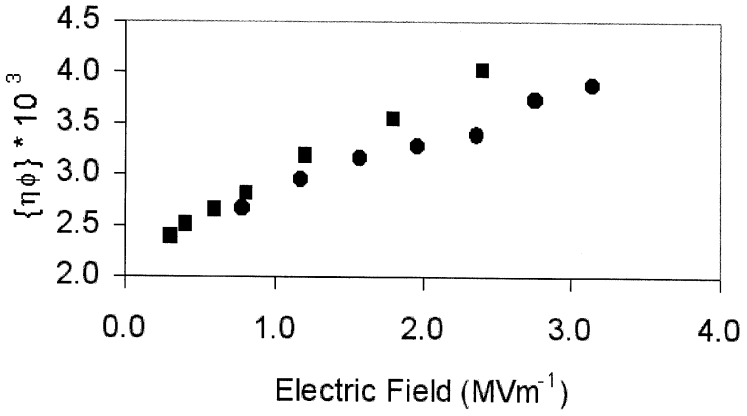

FIGURE 3 A comparison between the deduced $\{\eta\phi\}$ values for **HAT6** using both TOF • and DC ■ experimental methods (T = 85°C).

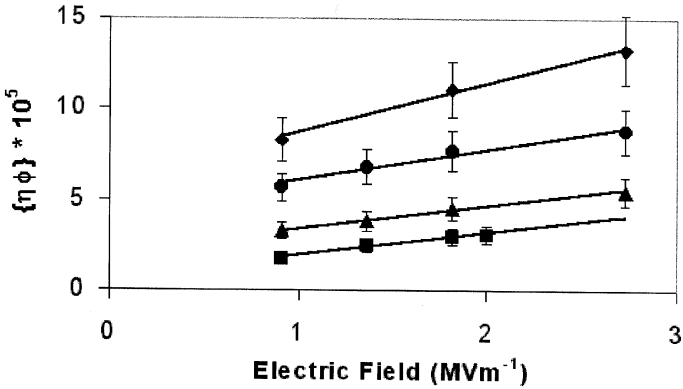

FIGURE 4 HAT6:PTP9 quantum efficiencies versus electric field at 50°C ◆, 70°C ●, 90°C ▲ and 130°C ■.

discotic liquid crystal. However, their results for the ***S/I*** theory were only given at one temperature and as seen in Eq. (4), the ***S/I*** ratio is proportional to $1/T^2$. In this present work, four DLC's are studied over a range of temperatures between room temperature up to 150°C in an effort to test the Onsager theory more rigorously.

The sidegroups of the basic triphenylene molecule can be chemically altered. This leads to many possible forms possessing different properties. It is possible to combine **HAT6** with **PTP9** resulting in a binary 50:50 stoichiometric **HAT6:PTP9** mixture, which is to be investigated.

$\{\eta\phi\}$ versus ***E*** for **HAT6:PTP9** shows a linear relationship (as demonstrated in Figure 4). Onsager theory predicts that as the temperature of the system is increased, the quantum efficiency also increases.

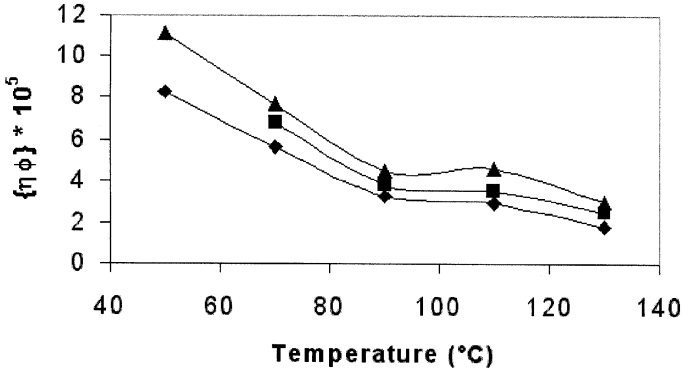

FIGURE 5 HAT6:PTP9 quantum efficiencies vs. temperature for different fields at 1.0 MVm^{-1} ◆, 1.5 MVm^{-1} ■ and 2.0 MVm^{-1} ▲.

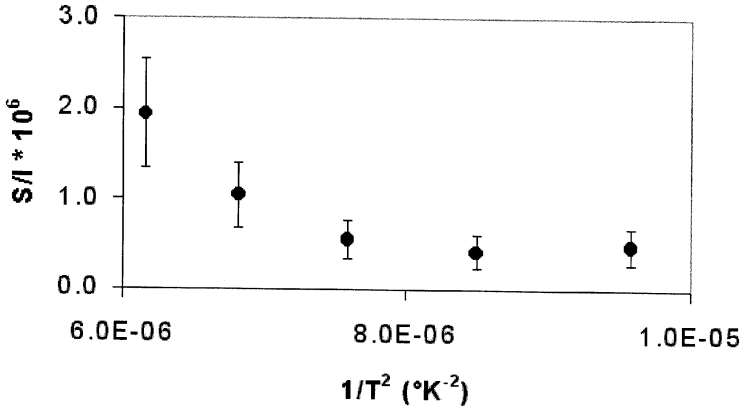

FIGURE 6 Experimental Slope to intercept ratios for **HAT6:PTP9** as **T** is varied. The Dielectric Constant of the material is assumed to be equal to 3.

It is obvious from Figure 4 that **HAT6:PTP9** does not obey the Onsager model as the quantum efficiency at any particular field reduces with increasing temperature. As shown in Figure 5, a downward trend is observed.

The slope to intercept ratios of the data in Figure 4 should be consistent with the theoretical values given by Eq. (4). A plot of S/I versus $1/T^2$ should, according to Eq. (4), give a straight line.

As shown in Figure 6, the S/I ratios for **HAT6:PTP9** are not in good agreement with theory as a linear relationship is not demonstrated. As such, Onsager is unsuitable for accurately describing the photogeneration mechanism within this material.

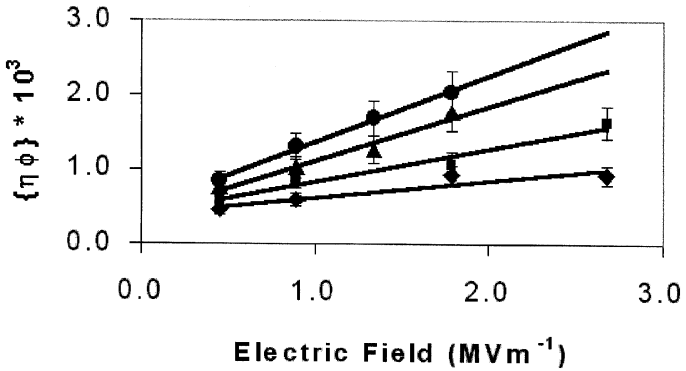

FIGURE 7 HAT11:PTP9 Quantum Efficiencies at 30°C ◆, 50°C ■, 70°C ▲ and 110°C ●.

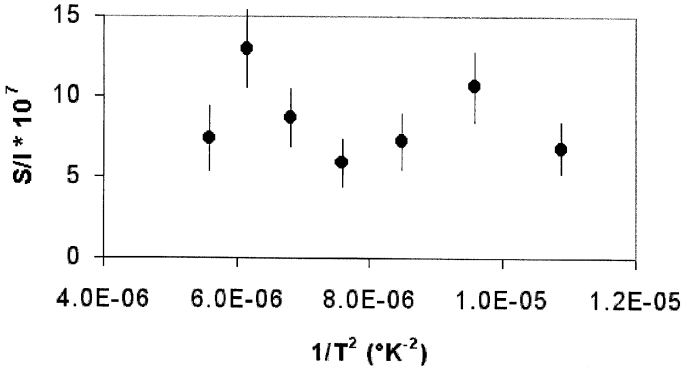

FIGURE 8 Experimental Slope to intercept ratios for **HAT11:PTP9** as **T** is varied. The Dielectric Constant of the material is assumed to be equal to 3.

The variation of $\{\eta\phi\}$ with temperature in **HAT11:PTP9** is shown in Figure 7. As a material, it would naively seem to obey the Onsager theory in its behaviour with temperature. Specifically, an increase in temperature leads to an increase in photocharge created at a given field. The measured slope to intercept ratios, however, are again not consistent with theory as they appear to be independent of temperature as shown in Figure 8.

The material which shows the closest agreement with the predictions of Eq. (4), is the DLC **2FHAT6**. The $\boldsymbol{S/I}$ ratios for this material differ from theory, being a factor of approximately 3 higher. However, the $1/\boldsymbol{T}^2$ behaviour is not clear from Figure 9, but one cannot preclude absolutely the possibility that hidden within the error bars such behaviour is exhibited.

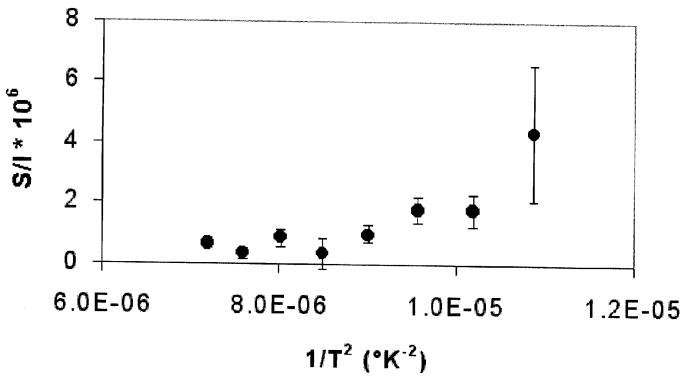

FIGURE 9 Experimental Slope to intercept ratios for **2FHAT6** as **T** is varied. The Dielectric Constant of the material is assumed to be equal to 3.

IV. CONCLUSIONS

$\{\eta\phi\}$ has been measured for a number of discotic materials using a transient photocurrent technique, where the current integrated under a transit signal gives the total charge created. This technique and its values are compared with values of $\{\eta\phi\}$ found from DC photoconduction measurements, and found to be comparable. We note that the current integration method works better than the DC photoconduction method when there are large dark currents to be accounted for.

Using this technique, we have thoroughly examined the field dependence of $\{\eta\phi\}$ in the context of Onsagers' theory of geminate recombination in three dimensions. In particular, we have measured the electric field dependence at a number of temperatures and shown that the $\boldsymbol{S/I}$ ratio does not follow the predicted form as temperature is varied. Thus, while studies of $\{\eta\phi\}$ against electric field made at one temperature may lead one to conclude that Onsagers' theory is operative in these materials: a more systematic approach shows this not to be the case.

The origin of the field dependence of the photocarrier production is still not clear and further detailed work needs to be done in order to understand the underlying factors determining the quantum efficiencies.

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