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1997 J. Phys.: Condens. Matter 9 6467

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Interface phenomena in double-layer organic photoreceptors

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Received 27 February 1997, in final form 10 June 1997

Abstract. Single photogeneration layers of a phthalocyanine pigment dispersed in a polyvinyl butyral binder, and double layers consisting of the photogeneration layer coated with hole transport layers of TPTA, DEH and BD molecularly dispersed in polycarbonate were exposed to single-shot light excitation. The charge collected was measured as a function of temperature, electric field, exposure intensity and duration. The resulting mean transport level of TPTA was found to be 0.17 eV, and that of DEH 0.11 eV, below the valence band of the pigment, but that of BD was found to be 0.09 eV above it. The injection efficiencies were independent of field and amounted to 3×10^{-3} for TPTA and 0.02 for DEH, at room temperature, but that for BD was 0.1 independently of temperature. Models for the injection efficiencies in these cases are also discussed in this work for the first time.

1. Introduction

The organic photoreceptors most commonly used for xerography are double-layer structures. In these devices, charges are photogenerated in a layer of pigment dispersed in an electronically inert polymer (the photogeneration layer, PGL). The PGL is coated with a molecularly doped polymer transport layer (CTL) transparent to light. One species of the photogenerated charges, normally holes, is injected into the doped polymer, and traverses the CTL without trapping or recombination (Nemeth-Buhin and Juhasz 1997).

The photosensitivity of such photoreceptors is observed to be strongly dependent on the PGL/CTL combination. While this is common knowledge in xerography, there have been very few studies of the effect of the most likely cause for this, namely the PGL/CTL interface. Kakuta *et al* (1981) reported an exponential increase of photosensitivity with decreasing ionization energy of the transport molecule in the CTL on identical PGL. The increase of the photosensitivity amounted to two orders of magnitude for a change of ionization energy from 7 to 6 eV. Kitamura and Yokoyama (1990) compared the absorption current transients and their associated dielectric loss spectra for a series of PGL/CTL combinations. They also concluded that the efficiency of interfacial hole injection increased with decreasing ionization energy in the CTL, but only until the transport level matched the valence band energy in the PGL. Any further decrease in ionization energy left the efficiency unchanged. However, the residual charge which represents holes trapped at the interface exhibited a minimum when the above levels coincided. Kanemitsu and Imamura (1987) analysed the field dependence of the injection in terms of Richardson–Schottky emission, but the field-effect parameter β deduced was two orders of magnitude below a reasonable limit inferred from the dielectric permittivity. No acceptable theoretical description of the interface phenomena seems to have been given previously.

This dearth of information calls for a more detailed investigation of transport across the interface. Indeed, the injection efficiency must depend on the relative potential energies and populations of the states at the interface. In this paper we investigate the temperature and field dependence of the injection from a phthalocyanine PGL into various doped polymers and, drawing on results for the ionization energies (Sasvari and Juhasz 1997), we compare the measured efficiencies against simple models of the interface.

2. Experimental procedure

The structure of the transport molecules studied, namely p-diethylaminobenzylaldehyde diphenyl hydrazone (DEH), tri-p-tolylamine (TPTA), and 1,1-bis(p-diethylaminophenyl)-4,4-diphenyl-1,3-butadiene (BD), and the layers containing 40% of these molecules in polycarbonate were prepared by wire-bar coating. The PGL was based on the α -polymorph of metal-free phthalocyanine (Pc; Sharp and Lardon 1968) in microcrystalline powder form. This was dispersed in a binder of the saturated polymer polyvinyl butyral (PVB) in various pigment-to-polymer ratios. The solvent used was tetrahydrofuran.

The PGL was coated by the wire-bar technique onto aluminized polyethylene terephthalate foils over an area of about 10×20 cm. The dry thickness was checked by optical transmittance measurements. The thickness was between 0.5 and $1 \mu\text{m}$ with a uniformity of $0.1 \mu\text{m}$ over the parts of the layer used for the measurements. To form double-layer structures, the PGLs were coated with a transport polymer with a dry thickness of 5–6 μm . The composite thickness of the double layers was measured by an Elcometer 300 thicknessmeter, which offered a $0.1 \mu\text{m}$ accuracy.

Sandwich-type cells were formed from PGL layers alone as well as from double layers by vapour depositing Al contacts on the free surface. The transparency of the top electrodes was controlled by optical transmittance measurement during vacuum deposition and was between 15% and 20%.

Collected-photogenerated-charge measurements were carried out both on PGL layers alone and on double-layer structures. It should be noted that the advantage of charge measurements is that the mobility and its temperature and field dependence become irrelevant. The temperature range was from 188 K to 348 K limited by the minimal detectable signal at the lower end and the glass transition at the upper end of the range. Photoexcitation was by a filtered red (>680 nm) xenon flash which has an absorption coefficient $>32 \mu\text{m}^{-1}$ in the phthalocyanine PGL (Loutfy 1981). The exposure time, 1 μs long, was negligibly short compared to the transit times of carriers through the transport layers, which were in the ms region. The technique used in the collected-charge experiment is identical to the time-of-flight technique, but the time integral of the photogenerated current is measured. A Keithley electrometer was used in charge mode (the RC time constant of 10 s was long enough to accommodate the transit tail at all temperatures). To avoid space-charge perturbation, the measurements were carried out in the small-signal regime.

3. Results

The field dependence of the collected charge in the PGL alone, as well as in the composite layers, was always linear (figure 1), except possibly at the highest fields. The charge also increased linearly with exposure pulse intensity, or duration, up to values approaching the geometric charge ($Q = CV$) limit. At constant illumination intensity, the collected charge increased with increasing pigment concentration, and the double-layer compositions

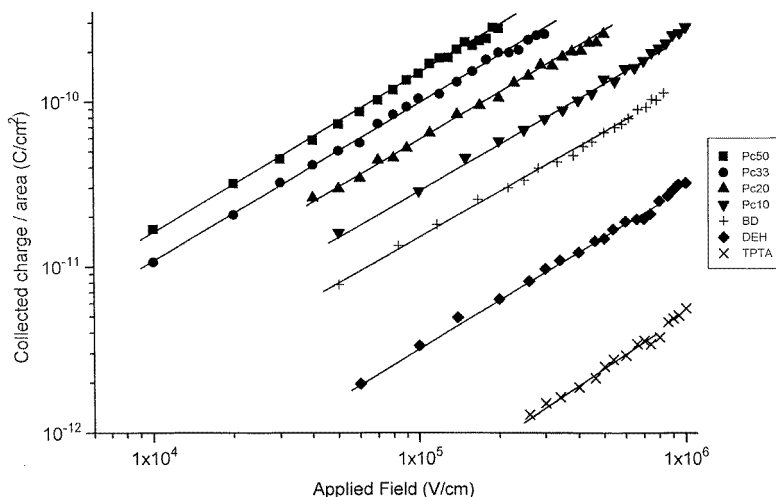


Figure 1. The field dependence of the collected charge for single- (CGL) and double-layer (CGL/CTL) samples at 298 K. Single layers: Pc50: 50% pigment; Pc33: 33% pigment; Pc20: 20% pigment; Pc10: 10% pigment; all in PVB. Double layers: the CGL was Pc50 throughout; CTL: DEH: 40% DEH; BD: 40% BD; TPTA: 40% TPTA; all in polycarbonate. The percentages are by weight.

produced at least an order of magnitude less charge than their PGL alone, at all fields and temperatures. Instead of the observed linear field dependence, an Onsager type S-shaped function with finite zero-field photogeneration might have been expected (Pai and Enck 1975, Noolandi and Hong 1979). The zero- and low-field photogenerated charges, however, could be trapped or could recombine at fast-recombination centres of the grain boundaries, resulting in an effective photogeneration monotonically decreasing to zero at low fields, in agreement with the results given by Popovic (1982).

Table 1. Collected-charge activation energies measured.

Structure	Collected-charge activation energy ΔE_Q (eV)
Double layer with DEH	0.15 ± 0.02
Double layer with TPTA	0.21 ± 0.02
Double layer with BD	0.04 ± 0.005
Single PGL	0.04 ± 0.005

The temperature dependence was observed to be of Arrhenius type (figure 2). The activation energies did not depend on field in either the single- or double-layer samples (figure 3), implying that the process of injection into the doped polymer is field independent. The charge activation energies were $\Delta E_Q^{\text{TPTA}} = 0.21 \pm 0.02$ eV for samples with TPTA and $\Delta E_Q^{\text{DEH}} = 0.15 \pm 0.02$ eV for samples with DEH as a transport molecule. However, the activation energy for samples containing BD as dopant (ΔE_Q^{BD}) was indistinguishable from that for the PGL itself, namely $\Delta E_Q^{\text{Pc}} = 0.04 \pm 0.005$ eV (see table 1). The activation energies in the monolayers were independent of the pigment concentration.

We define an injection efficiency $\eta = Q_{\text{coll}}/Q_{\text{gen}}$ where Q_{gen} is the time integral of the

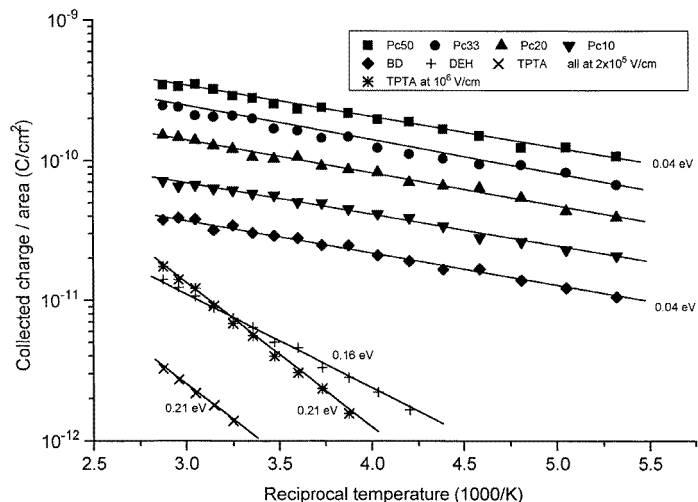


Figure 2. The temperature dependence of collected charge at $2 \times 10^5 \text{ V cm}^{-1}$ (unless otherwise stated) in single- (PGL) and double-layer (PGL/CTL) samples. The samples are as in figure 1.

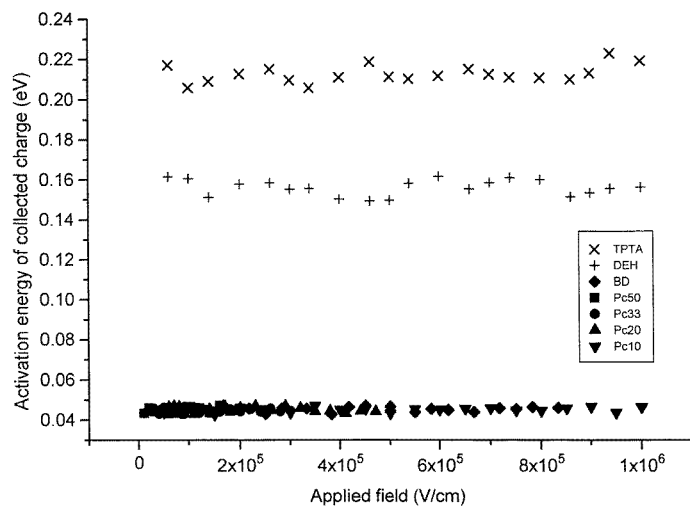


Figure 3. The field dependence of the activation energy of the collected charge in single and double layers. The samples are as in figure 1.

photoresponse current in the pigment dispersion alone, and Q_{coll} is the charge collected in transit through the corresponding double layer. For TPTA the efficiency was ~ 0.003 , for DEH ~ 0.02 , and for BD ~ 0.1 , independently of field (and, within limits, exposure intensity or duration).

4. Analysis of the results

The measured activation energy of the collected charge can be attributed to the charge generation and/or injection, as the mobility in CTL polymers plays no role. In figure 4(a), VB

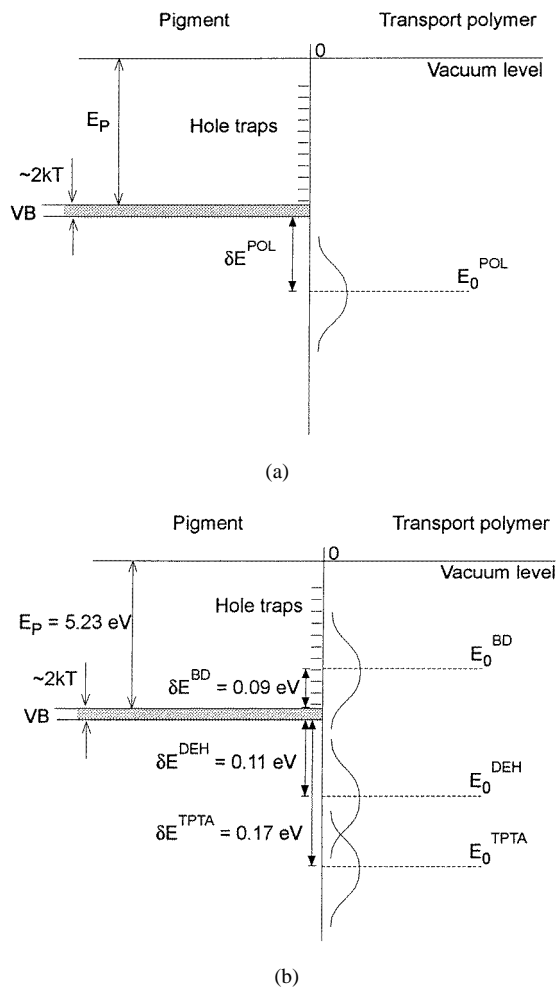


Figure 4. (a) The energy diagram of a PGL/CTL interface. E_0 : the mean transport level in doped polymer; E_p : the ionization potential of the pigment; VB: the narrow ($\sim 2kT$) valence band of the organic crystal (phthalocyanine); δE : the energy mismatch for hole injection. (b) A quantitative picture of interface energetics obtained for the systems investigated.

represents the band in which hole conduction occurs in the pigment, i.e. the highest occupied molecular level of the phthalocyanine. As is usual in molecular crystals, the width of this band is expected to be small, say $2kT$ (Chen 1969). The depth of the valence band below the vacuum level is called E_p . The ionization energies of the transport levels in the doped polymers are E_0 , and were determined by Sasvari and Juhasz (1997) as $E_0^{\text{DEH}} = 5.34$ eV, $E_0^{\text{TPTA}} = 5.40$ eV and $E_0^{\text{BD}} = 5.14$ eV. The critical quantity for hole injection from the pigment into the transport layer is the interfacial energy step $\delta E^{\text{POL}} = E_0^{\text{POL}} - E_p$ (POL = DEH, TPTA or BD). We associate δE^{POL} with the quantity $\Delta E_Q^{\text{POL}} - \Delta E_Q^{\text{PGL}}$, where ΔE_Q^{PGL} is the (small) activation energy associated with photogeneration in the phthalocyanine pigment, namely 0.04 eV (figure 2). To summarize,

$$\delta E^{\text{POL}} = \Delta E_Q^{\text{POL}} - \Delta E_Q^{\text{PGL}} \quad (1)$$

$$E_p = E_0^{\text{POL}} - \delta E^{\text{POL}}. \quad (2)$$

We calculate E_p from the results for TPTA and DEH:

(i) TPTA:

$$\delta E^{\text{TPTA}} = 0.21 - 0.04 = 0.17 \text{ eV}$$

$$E_p = 5.40 - 0.17 = 5.23 \text{ eV}.$$

(ii) DEH:

$$\delta E^{\text{DEH}} = 0.15 - 0.04 = 0.11 \text{ eV}$$

$$E_p = 5.34 - 0.11 = 5.23 \text{ eV}.$$

The agreement between the values of E_p allows us to conclude, with some confidence, that the valence band of the phthalocyanine lies 5.23 eV below the vacuum level. This value agrees well with that of 5.26 eV inferred from measurements by Kitamura and Chigono (1991). However, the situation in BD is different. Accepting the above value for E_p and an ionization energy for BD of 5.14 eV (Sasvari and Juhasz 1997), the transport level in BD lies 0.09 eV above the valence band of the pigment, while δE^{BD} is zero. For comparison, spectroscopic determination of the height of the transport level above the VB yields 0.11 eV (Kitamura and Chigono 1991). In the rest of the work we will choose the mean to be 0.1 eV. Figure 4(b) offers a quantitative picture of the PGL/CTL energetics as determined in this work.

5. Discussion

Hole injection occurs from pigment grains closest to the PGL/polymer interface by tunnelling through an unavoidable, thin, skin of PVB into the mean transport level of the polymer. When this level lies at an energy δE below the pigment valence band (VB), as in the case of DEH and TPTA, thermal excitation across δE is required prior to tunnelling. Our experiments suggest that the tunnelling rate is very fast (i.e. injection is not rate limited), and that a quasi-thermal (Mott) contact is established in a time short compared with the excitation pulse width (1 μs). The injection efficiency is then simply

$$\eta = (N_{\text{trans}}/N_{\text{VB}}) \exp(-\delta E/kT) \quad (3)$$

where N_{trans} is the concentration of transport states in an interval kT about the peak of the assumed Gaussian energy distribution of molecular states in the polymer, and N_{VB} the concentration of VB states in the pigment.

Equation (3) satisfies the general observation that η decreases with increasing ionization energy of the transport molecules, and agrees with the exponential form of this decrease reported by Kakuta *et al* (1981). We can make an order-of-magnitude estimate for η . If the concentration of transport molecules in the polymer is N_m , then

$$N_{\text{trans}} = (2\pi\sigma^2)^{-1/2} N_m kT \quad (4)$$

where σ is the half-width of the Gaussian distribution. For $\sigma = 0.1 \text{ eV}$, $N_m = 10^{21} \text{ cm}^{-3}$, and room temperature, we obtain $N_{\text{trans}} \simeq 10^{20} \text{ cm}^{-3}$. Substituting the value of N_{trans} and putting $N_{\text{VB}} = 10^{20} \text{ cm}^{-3}$, and $\delta E^{\text{DEH}} = 0.11 \text{ eV}$ in equation (3), we obtain $\eta^{\text{DEH}} \simeq 10^{-2}$, in good order-of-magnitude agreement with our experimental results (2×10^{-2}). For TPTA, $\delta E^{\text{TPTA}} = 0.17 \text{ eV}$. We then find $\eta^{\text{TPTA}} \simeq 10^{-3}$, also of the same order as our results (3×10^{-3}).

We cannot make a similar estimate for the injection efficiency into BD, but will nevertheless attempt to model this process. At the pigment grain boundaries, we expect the valence states to break up into a distribution of localized surface (Tamm) states. Those lying close to the VB act as hole traps, and those of higher energy as recombination centres, although recombination centres may also be formed out of conduction states. Let us assume the simplest possible form for the distribution of the traps, namely a uniform one extending from the VB upwards to a cut-off energy W . We further assume that the traps possess equal capture cross sections, and fast capture but slow release rates. Initially, therefore, the entire photogenerated charge Q_{gen} is uniformly distributed between these traps.

We envisage hole tunnelling from the pigment into the polymer transport level at δE above the VB to proceed via $N(\delta E)$ surface traps lying within an interval $\sim kT$ about δE . If the tunnelling rate is very fast, as we had to conclude for DEH and TPTA earlier, we may expect that the entire charge in the $N(\delta E)$ traps, namely $(kT/W)Q_{\text{gen}}$, is transferred from the traps to the CTL polymer. These assumptions lead to a simple, activation-free, expression for the injection efficiency:

$$\eta = kT/W. \quad (5)$$

This relation predicts an efficiency independent of δE for the CTL polymers whose transport level lies above the VB of the pigment, in agreement with the observations made by Kitamura and Yokoyama (1990). On the other hand, it predicts a linear increase in efficiency with temperature, which we did not observe. However, this effect may have escaped detection on account of the relatively narrow experimental temperature range. From the value of ~ 0.1 for the injection efficiency into the BD, we estimate ~ 0.25 eV for the cut-off energy W . Unfortunately, without further assumptions, the simple model considered above cannot account for all of the observations of Kitamura and Yokoyama (1990).

6. Summary

We have shown that collected-photogenerated-charge measurements have several advantages, as they are easy to carry out, and avoid complications due to any temperature or field dependence of the carrier mobility or to the interfacial tunnelling rates on the timescale of the experiment. Such measurements were conducted on layers of phthalocyanine pigment on their own, as well as on xerographic double layers incorporating the hole transport molecules TPTA, DEH and BD. From the values of the charge activation energy, and of the ionization energies found by Sasvari and Juhasz (1997), we were able to deduce the depth of the pigment valence band as 5.23 eV below the vacuum level, which is in agreement with the literature value. By direct measurement, the transport level in TPTA lies 0.17 eV and that in DEH 0.11 eV *below* the pigment valence band. In contrast, the transport level in BD lies 0.09 eV *above* the valence band. The injection efficiencies are independent of field (and exposure length as well as light intensity below the CV limit for the generated charge). Their values are 3×10^{-3} for TPTA and 0.02 for DEH, both at room temperature. However, the value of 0.1 for BD is *independent* of temperature. The temperature-dependent injection efficiencies can be accounted for a simple quasi-thermal-equilibrium model, which is shown to predict the experimental values quite well. The temperature-invariant efficiency for BD is discussed in terms of a crude non-equilibrium model of interfacial injection via a distribution of surface traps.

Acknowledgments

We acknowledge many useful suggestions and constructive discussions with Dr J Veres and Dr A Nemeth-Buhin, and support from GBL Ltd.

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