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Organic semiconductors with a charge carrier life time of over 2 hours at room temperature.

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Abstract: Recently, Gao et al. reported being able to measure significant quantities of photogenerated charge up to one hour after it had been generated in an organic semiconductor device. The aim of this paper is twofold; a) to provide conclusive experimental evidence to support the picture of device operation; and b) to understand and demonstrate how changes to the device structure and materials can be used to tune the charge carrier lifetime. By tuning both the materials used, and the device structure we are able to observe a charge carrier life time of over 2 hours and still extract significant amounts of charge from the device after 5 hours. This is achieved by engineering the band structure of the device to control the spatial overlap of the stored photoexcited electron and hole populations and thus the recombination rate. By performing lifetime measurements as a function of charge carrier density and applied voltage we find the recombination rate has a 0th order dependence on carrier density, and elucidate the mechanisms responsible for these long charge carrier life times. This work is of technological significance for the development of organic electronic high sensitivity photodetectors and memory elements.

Introduction: Since the emergence of the transistor in the late 1940s [1], silicon based components have been at the heart of all modern electronic devices. However, recently there has been considerable academic and industrial interest in developing a new class of electronic devices made from carbon based conducting organic molecules [2 - 4]. These new organic electronic devices have many advantages over their silicon counterparts; they have the potential to be fabricated from solution using traditional printing techniques [5]; the semiconductors can be produced from low energy wet chemistry [6]; and the final device can be flexible enabling building and product integration [7]. Despite these advantages, only organic light emitting diodes (OLEDs) [8,9] have as of yet reached the mass market [10-14]. The primary reason for this is the low performance of organic semiconductor devices, due to their low charge carrier mobilities [15] and high recombination rates [16]. In organic semiconductors charge is usually localized on individual semiconducting molecules and conduction occurs via thermally assisted hopping [17] between neighboring molecules. This hopping process is inherently slower [18] than the band like conduction process which occurs in silicon devices, resulting in charge carrier mobilities which are typically two orders of magnitude [15] lower than their silicon counterparts [19]. Furthermore, not all molecules in an organic electronic device are electrically well connected to their neighboring molecules, resulting in configurational and energetic dead ends [17], where charge carriers can become trapped and eventually become annihilated through recombination [16]. Thus recombination rates in organic materials are typically higher than in their inorganic counterparts [20], with charge carrier life times ranging from a few picoseconds for bound electron hole pairs [21] to a maximum of a second for charges confined to deep energetic traps [22]. The last decade has seen significant attention focused on understanding the mechanisms responsible for the low mobilities and high recombination rates in organic semiconductors [23-32]. Usually in

organic semiconductors, the recombination rate is defined as

$$R = k(n,p)np \quad (1)$$

where $k(n,p)$ is a carrier density dependent quantity, n is the electron density and p is the hole density.

In 2015, Gao et al. [33], reported a device design strategy to reduce the recombination rate in an organic semiconductor devices and as a result were able to extract significant quantities of charge up to one hour after photoexcitation. They proposed a sandwich structure of Glass/ITO/SiO₂/N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-1,1'-biphenyl-4,4'-diamine (NPB)/Al, where the organic semiconductor was doped (figure 1a). This doping resulted in a band structure resembling a potential hill (figure 1b). When the device was photoexcited by a short laser pulse, electrons drifted down hill towards the contact and were extracted (figure 1c), while holes drifted uphill towards the center of the device and became trapped in a potential well (figure 1d). At the center of the device, the doping pushed the HOMO edge very close to the equilibrium Fermi level (figure 1b,c,d) producing a hole rich/electron poor region. In this region, the recombination rate defined by $R=k(n,p)np$ was small because n was small. To assess how long charge carriers at the center of the device lived, a voltage ramp was applied at time t_{delay} after the laser pulse to extract any remaining photogenerated charge (see figure 2).

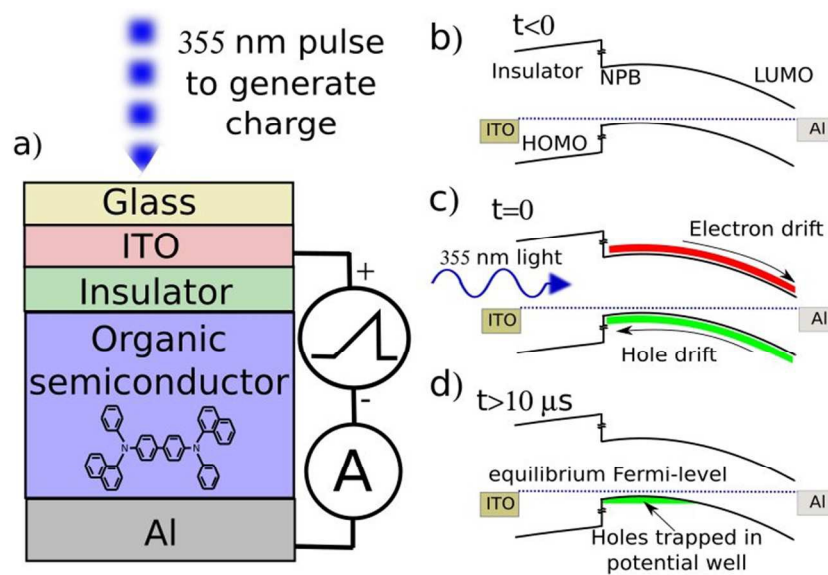


Figure 1: a) A picture of the device and the experimental setup. b) The curved band structure due to doping. c)

Photogeneration of electrons and holes, the holes drift towards the center of the device while electrons are extracted at the Al contact. d) A packet of holes being stored at the center of the device. Note the Fermi level is very close to the HOMO edge at the center of the device, meaning there will be very few electrons for the holes to recombine with. The doping is believed to come from by-products of the synthesis of NPB see SI of [33]. By solving Poisson's equation across the device in steady state, we found that the presence of doping was essential for the formation of the potential hill, and the closer the electron affinities of the contacts the more symmetric the potential hill would be.

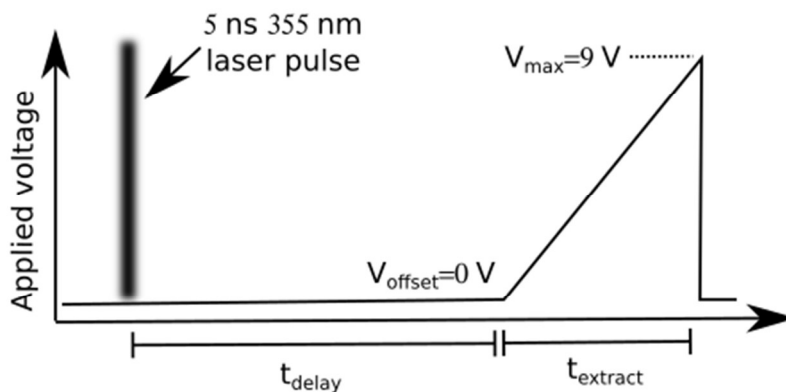


Figure 2: A timing diagram of the voltage applied to the device. At time t_{delay} after the laser pulse a voltage ramp is applied between the ITO and the Al contact to extract any remaining photogenerated carriers.

The aim of the present work is twofold; a) to provide conclusive experimental evidence to support the picture of device operation as presented by Gao et al.; and b) to understand and demonstrate how changes to the device structure and materials can be used to tune the charge carrier lifetime. To this end, we replace the spin coated SiO₂ insulator used previously, with a vapor deposited layer of Al₂O₃ and consequently observe a charge carrier life times of over 2 hours. We also investigate if the NPB molecule it's self played a special role in the previously reported long life times, by replacing it with a range of molecules of varying form factors but similar HOMO/LUMO energies. Finally, we perform life time measurements as a function of applied bias and light intensity to further elucidate and validate the mechanisms responsible for the ultra long life times.

Experimental: Devices with the structure Glass/ITO/Insulator/NPB(100nm)/Al were fabricated, where the insulator was chosen to be either Polystyrene (PS), Poly(methyl methacrylate) (PMMA), SiO₂ or Al₂O₃. Polystyrene, Poly(methyl methacrylate) and SiO₂ were spin coated from solution, while Al₂O₃ was deposited using a magnetron-assisted physical vapor deposition (PVD) system. The small molecule semiconductor NPB and a 30 nm thick Al capping electrode were then thermally deposited, at a speed less than 1Å/s under a vacuum of 5x10⁻⁴ Pa. After fabrication the charge carrier life time was measured using the photo-CELIV [34] technique. The devices were photoexcited using a 355 nm laser with a 5ns pulse width, after which the device was kept at short circuit, until at a desired delay time (t_{delay} see figure 2), a voltage ramp was applied to the device to extract the remaining photogenerated charge. Full experimental details are provided in the SI.

Results: Previously, Gao et al. [33], suggested that the higher the permittivity of the insulating layer, the smaller the potential drop over it would be and the more bent the bands would become over the semiconductor. He also suggested that this increased band bending would lead to longer charge carrier life times. However, in the previous work no high permittivity insulators were used (such as metal oxides) so it was not possible to determine if this trend would continue to hold as permittivity was increased and if even longer charge carrier lifetimes could be observed. Figure 3a, plots the triangular voltage waveform used to extract charge from a device which uses a high permittivity Al_2O_3 metal oxide insulating layer (the deep blue line). Also plotted in the same figure are the corresponding current transients, as function of increasing time from photoexcitation excitation (t_{delay}). Between 0 and 400 μs in the plot, a rectangle of current can be seen around 0.05 mA high. This is due to the application of the steadily increasing voltage, extracting capacitive charge from the contacts of the device. On top of this rectangle of current, a small hill of current is visible between 20 μs and 200 μs with a peak at around 120 μs . This small hill of current is the photogenerated charge extracted from the semiconductor layer itself. Between 400 μs and 800 μs a second voltage transient is applied to make sure all charge has been extracted from the device. No hill of charge can be seen in this pulse indicating that all photogenerated charge has been extracted. The red line, represents the case where the sample has been photoexcited and the charge extracted 100 μs later. The light blue line represents the case where charge was extracted 1 min after photoexcitation, it can be seen that there is only a small drop in charge extracted from the device between these two times. The purple line represents the charge extracted from the device 5 hours after photoexcitation.

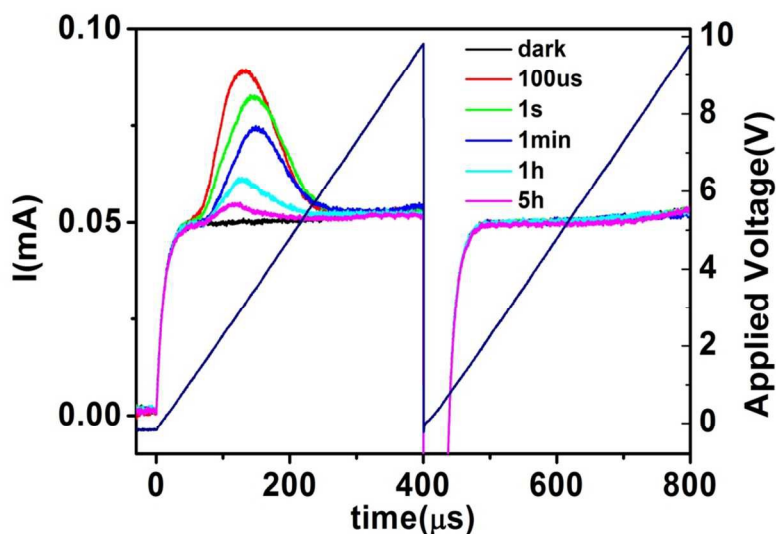


Figure 3: Charge extraction transients from a Glass/ITO/Al₂O₃/NPB/Al device. The black line represents the case where no laser pulse is used to photoexcite the sample. The right hand axis plots the voltage applied to the device to extract the remaining charge.

If one looks at Figure 3, it can be seen that the position of the maxima in the current transient shifts over time. If the band structure were flat and there were no traps in the device one could safely apply CELIV theory and interpret the shifting position of the peak as a change in mobility as a function of time. However, our device has a potential well which is not considered in Juska's work, and therefore it is not safe to interpret this as a change in mobility over time. Instead, we attribute the shifting the current maxima to the movement of the charge packet in the device during the measurement. The charge packet it's self will perturb the band structure, thus as it decays one would expect the band structure to also relax and

the charge to move in order to minimize energy.

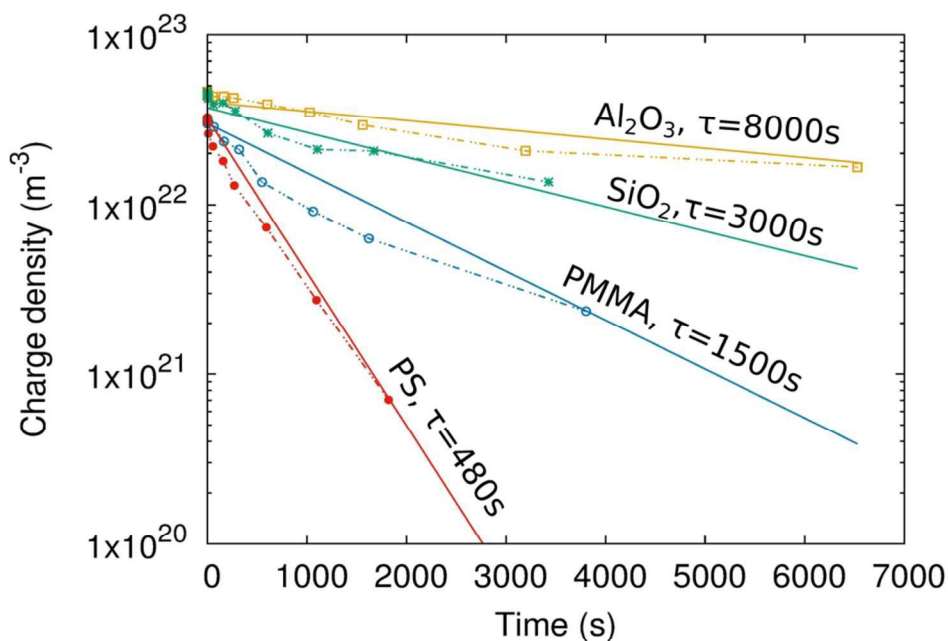


Figure 4: Extracted charge density as a function of time from a Glass/ITO/Insulator/NPB/Al device as a function of time, where the insulators PS, PMMA, SiO₂ and Al₂O₃ have been used. The points dashed lines with points represent the experimental data, while the solid lines represent the lines of best fit to extract τ , the charge carrier life time.

Figure 3, shows that by replacing the SiO₂ layer with a high permittivity metal oxide layer we are able to observe significant quantities of photogenerated charge over 4 hours longer than previously reported. To understand how the permittivity of the insulating layer affects charge carrier lifetime, three identical devices were fabricated with insulating layers of PS, PMMA,

and SiO₂. The experiment in figure 3 was then repeated for a wide range of delay times (t_{delay}), and the total charge extracted from the bulk of the device is plotted as a function of t_{delay} in figure 4. It can be seen that at 2000 seconds, the Al₂O₃ device retains the most photogenerated charge while the charge density in the PS device has dropped to $1 \times 10^{21} \text{ m}^{-3}$. The solid lines on the graph represent a fit to the carrier density decay of form $y(t) = Ae^{-t/\tau}$, where τ is defined as the charge carrier life time. It can be seen that the charge carrier life times range from just over two hours (8000 seconds) to 480 seconds. If one looks closely at all four curves, it can be seen that none of them perfectly follow the exponential, indeed they have a slight negative bias, possibly suggesting the presence of two different recombination mechanisms. We expect that the first, faster, regime corresponds to times when the electrons are still being swept out of the device, while the second, slower, regime occurs when most photogenerated electrons have left the device.”

Another limitation of previous work on this topic is that the actual permittivity of the insulators used was never measured so it was not possible to determine how charge carrier life time varied as a function of insulator permittivity or indeed if there was a maximum charge carrier life time. Therefore, we fabricated four capacitive Glass/ITO/Insulator/Al structures using PS, PMMA, SiO₂ and Al₂O₃ as the insulating layer. We then applied a voltage ramp to each of the structures and calculated the relative permittivity of the insulator by applying

$$i = \frac{\epsilon_0 \epsilon_r A}{d} \frac{dV}{dt} \quad (2)$$

where all symbols have their usual meaning. Figure 5, plots the relative permittivity of the insulating layer against the charge carrier life time τ . It can be seen that the relationship between τ and permittivity looks more or less linear on this log-linear graph, which indicates that charge carrier life time increases exponential as a function of permittivity. This opens up the possibility of yet longer lifetimes if higher dielectric materials were to be used.

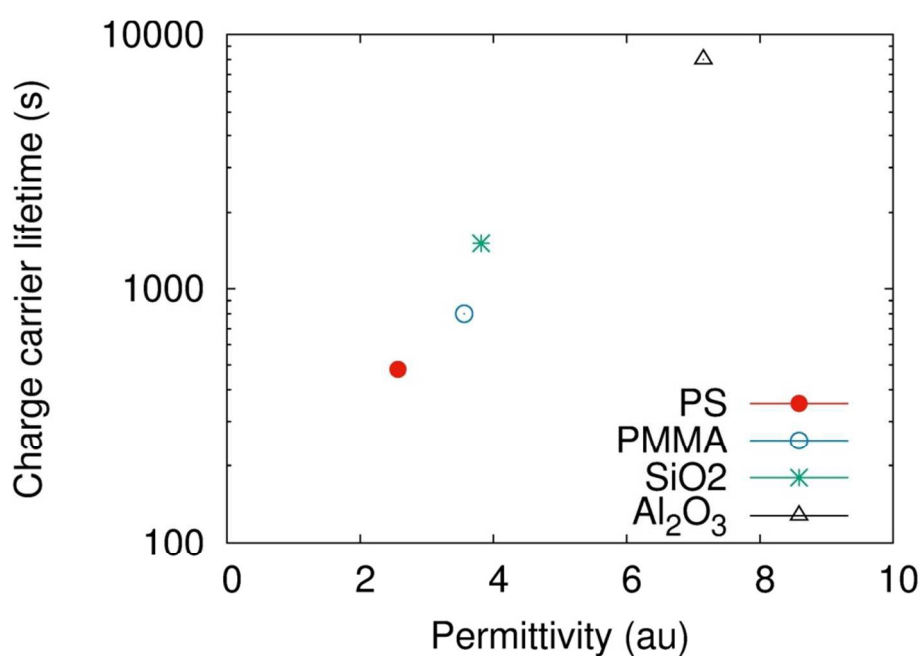


Figure 5: A plot of permittivity v.s the charge carrier life time.

Previously, the recombination mechanism in organic semiconductors has typically (and broadly speaking [37]) been described as bi-molecular [38], meaning that the recombination rate is proportional to the square of the carrier density ($R \sim n^2$). To determine if the recombination mechanism in the present device is also bi-molecular, we fabricated a Glass/ITO/SiO₂/NPB/Al structure, and photoexcited it with a range of light intensities over two

orders of magnitude. The charge left in the device as a function of time can be seen in figure 6, the points represent experimental data while the lines represent lines with slope, $\tau=1$ hour which act as a guide for the eyes. As in figure 4 it can be seen that there is a relatively fast phase to recombination just after photoexcitation, followed by a slower phase. We understand the initial faster recombination phase as electrons which did not get swept out the device annihilating the stored hole population. It can also be seen that the overall shape and slope of the curves do not change as a function of initial charge density, suggesting that recombination rate in the present device is not dependent upon the carrier density. This 0th order dependence of charge lifetime on carrier density, further supports the assertion of Gao [33], that a unipolar reservoir of charge is present at the center of the device and that very few photogenerated carriers stored in this reservoir are lost to electron-hole recombination.

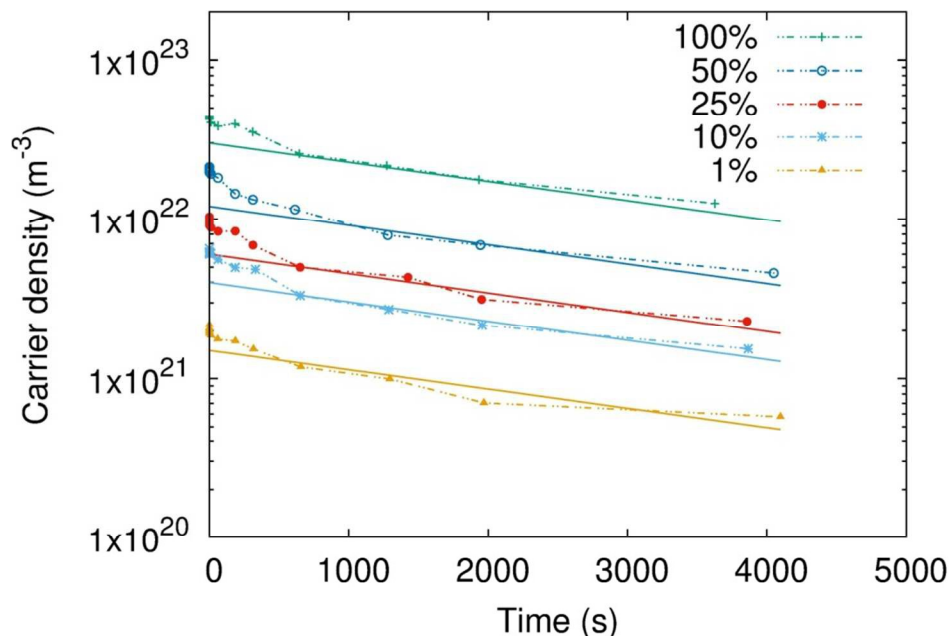


Figure 6: Extracted charge density as a function of laser energy for a Glass/ITO/SiO₂/NPB/Al device, where 100% laser power is 240 $\mu\text{J cm}^2$. It can be seen that the shape of the transient does not change as a function of laser power (charge density) indicating a 0th order recombination mechanism (not carrier density dependent).

Before moving on, we should discuss what in general limits the charge carrier lifetime and how in general this can be increased. Although, in the region under the potential hill, the quasi-Fermi level is very close to the LUMO edge, there will still be a small, but finite, number of electrons, the exact number of which will depend upon the distance between the LUMO level and the Fermi level (Maxwell Boltzmann statistics). The closer we can move the Fermi-level to the HOMO and the further one can move it from the LUMO, the fewer electrons will be present and the longer the charge carrier life time will be. Thus in general, we expect the electron density under the potential well to limit the charge carrier life time. We should

therefore expect longer lifetimes to be achieved with further optimization of the materials/device structure which push the Fermi-level closer to the HOMO.

Figure 7, plots the charge extracted from a Glass/ITO/SiO₂/NPB/Al device as a function of thickness of the NPB semiconductor. The first general trend that can be seen by looking at the early time charge densities is that the thinner the device, the less charge is generated; this is due to not all the photons being absorbed by the active layer. Also, the thicker the device, the steeper the decay of carrier density between 50 s and 1000 s. By changing the thickness of the device we are effectively tuning the curvature of the band structure. For the device to be charge neutral, a thin device will have a much more curved band structure than thick device. A steeper band structure (blue line Figure 7b) will make it energetically easier for electrons to escape the device and thus the charge carrier life time will be longer, this result further supports the picture of device operation as described by Gao et al.

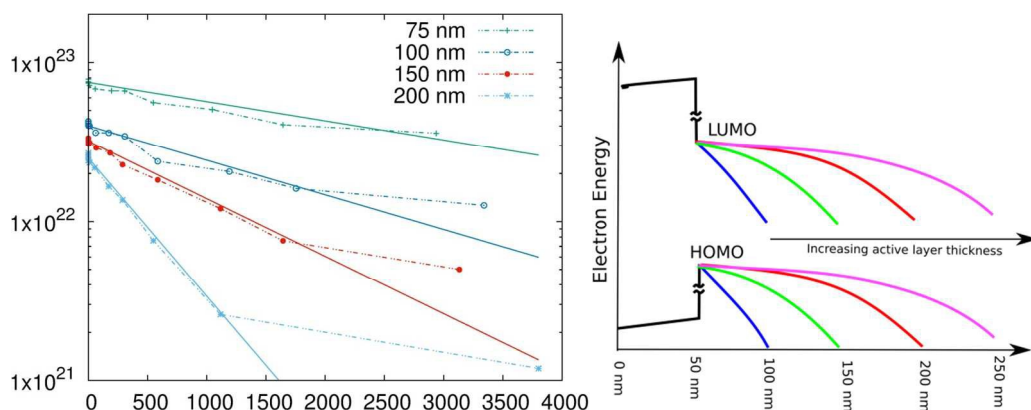


Figure 7: a) A thicker device results in a faster decay rate; b) a diagram based on simulations showing how the bands change as the active layer thickness is increased for a doping of $5 \times 10^{22} \text{ m}^{-3}$. It can be seen as the device thickness is reduced, the gradient of the bands becomes steeper. This will speed electron transport out of the device and increase carrier life time.

The above experiments run over a very long time period, we therefore thought that degradation of the device through the generation of oxygen/water defect states could be responsible for some of the decay dynamics we see. To ensure this was not the case, we encapsulated an NPB device and compared the extracted charge carrier life times to those of a non encapsulated device. We found that encapsulation did not significantly change the charge stored as a function of time, and therefore we do not think degradation is influencing our results (see SI for figure).

In all the above experiments, the between time when the laser pulse was applied and the application of the charge extraction ramp, the device was kept at short circuit. If rather than keeping the device at short circuit we apply a small offset voltage (V_{offset}), we should be able to change how the bands are bent within the device and change the position of the point where the HOMO is at its maximum. This in turn will change the position where the photogenerated charge packet is kept within the device and its spatial overlap with any background charge (see figure 1d). We should therefore be able to adjust the charge carrier life time in this way, and if this works this will further support our picture of device operation presented above. Figure 8 plots the extracted charge in the device as a function of offset voltage applied to the Al contact. When a positive offset voltage is applied to the ITO contact, it can be seen that the charge carrier life time drops dramatically, this corresponds with the photogenerated charge packet being moved closer to the Al contact and making it easier for charge to escape. When a negative offset voltage is applied to the ITO contact it can be seen that charge carrier life time is extended, this corresponds to the photogenerated charge

packet being pushed away from the Al contact and back towards the SiO₂ insulating layer. It is also interesting to note that as the offset voltage becomes more negative, the total magnitude of extracted photogenerated charge increases. We suspect this is due to the potential accelerating the removal of electrons from the device after photogeneration and there being less time when the electron and hole populations spatially overlap. Conversely, when a positive voltage is applied this will hinder electron extraction from the device, and thus turn on recombination (note the almost vertical decay of the 1.0 V measurement).

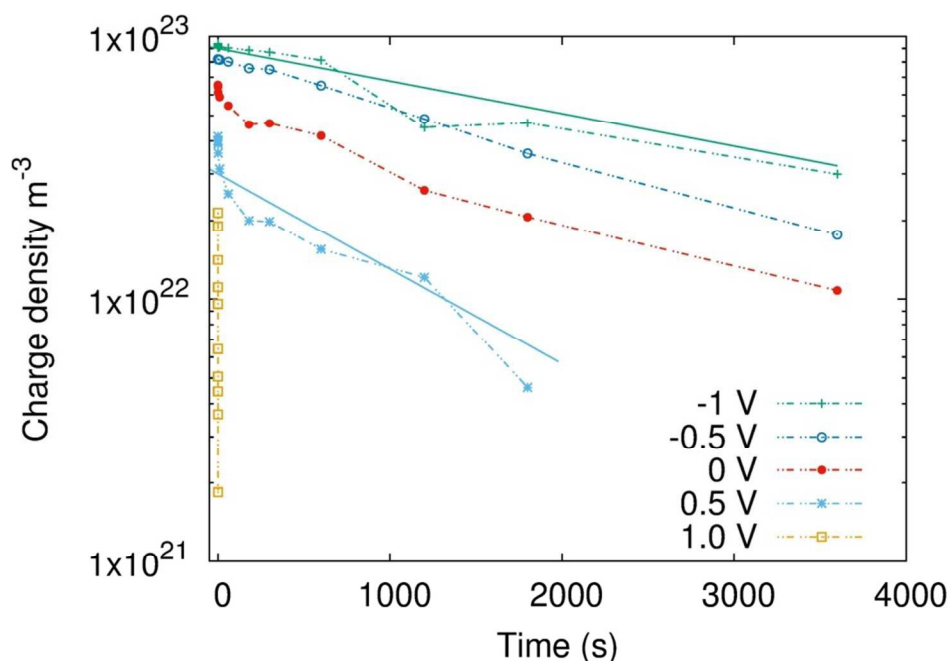


Figure 8: Charge carriers extracted as a function of offset voltage (V_{offset}). It can be seen that a negative offset voltage applied to the ITO contact helps extend charge carrier life time. This is probably due to holes charge carriers being drawn away from the Al extracting contact. When a positive voltage is applied to the ITO contact, the stored holes are shifted towards the Al contact and it becomes more likely they will leave the device.

Previously, ultra long charge carrier lifetimes have only been observed in devices based on the NPB small molecule semiconductor. We thought it possible that NPB had a special property (possibly well ordered) which enabled photogenerated charges to have a long life time. To understand if NPB was indeed special, or if other semiconductors could also exhibit long charge carrier life times, we fabricated ITO/Insulator/Semiconductor/Al structures in which we used Spiro, TAPC, TPD, Alq3 and C60 as the semiconductor. The results of the charge carrier life time measurements can be seen in figure 9. Note, in contrast to the rest of the results in this paper, figure 9 is plotted on a log-log scale enable comparison of materials with very short and long charge carrier lifetimes. As a consequence of this, the faster carrier decay phase between 1×10^{-4} seconds and 1×10^2 seconds is clearly visible. This fast phase gives way to a slower decay after 100 seconds. It can be seen that TAPC, NPB, Spiro and TPD all have similar decay characteristics. However, it is notable, that Alq3 and C₆₀ have much shorter charge carrier life times and very different decay characteristics.

We can understand figure 9 by considering where the LUMO/HOMO levels of each material lie. The LUMO/HOMO level of NPB are 2.4 eV /5.5 eV respectively, if the LUMO and HOMO levels were lowered, this would bring the LUMO closer to the equilibrium Fermi-level, and the HOMO further away, which in turn would increase the electron population and decrease the hole population in the device; thus the recombination rate should be higher and life time should be shorter. The HOMO/LUMO level of Alq3, has both a deeper LUMO and HOMO than that of NPB (3.1eV /5.8 eV respectively), thus one would expect it to have a shorter charge carrier life time – which it indeed does (pink dots). The same argument can be used to explain why C60 also has a shorter life time (LUMO=4.5 eV, HOMO=6.2 eV). However, interestingly for pristine C60, we found that the charge recombined so quickly we were unable

to measure any charge density with our experimental setup. Only after aging were we able to extract charge from the device. The LUMO/LUMO levels of Spiro (LUMO=2.05 eV/ HOMO=5.11 eV), TPD (LUMO=2.3 eV/ HOMO=5.5 eV) and TAPC (LUMO=2.0 eV / HOMO=5.5 eV), are all comparable to those of NPB and thus we would expect the devices to have a similar band structure and hence recombination dynamics.

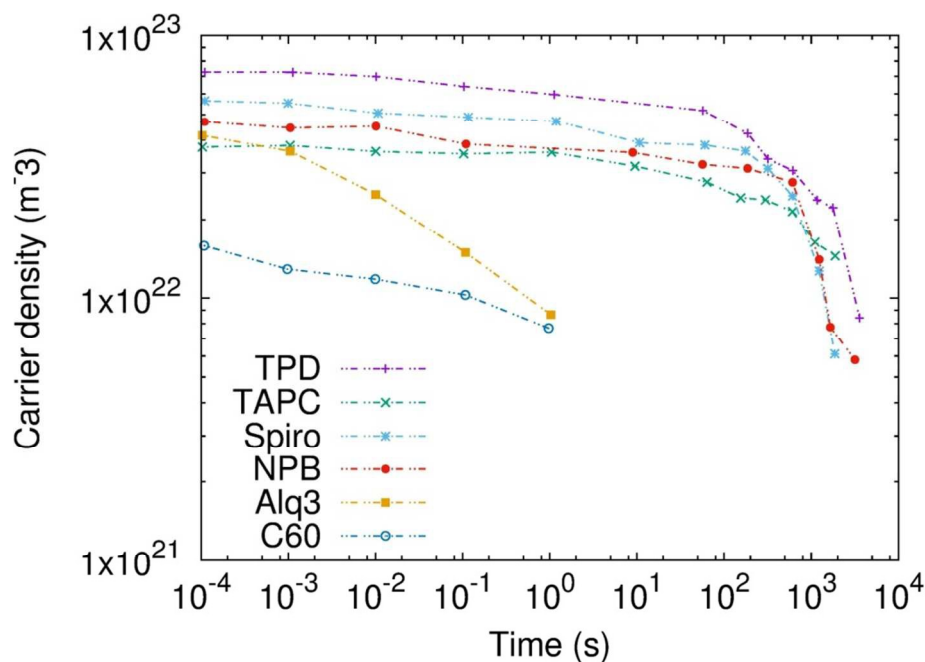


Figure 9: Extracted photogenerated charge density from a range of organic semiconductors in an ITO/SiO₂/Semiconductor/Al structure. It should be noted that TPD, TAPC, Spiro, Alq3 and C60, had purities of 99.6%, 99.6%, 99.9%, 99.6% and 99.8% respectively thus they can all be considered doped. See SI for further discussion of doping in organic semiconductors.

Conclusions: By altering both the device structure and measurement conditions we were able to tune the charge carrier lifetime in the device from a few hundred milliseconds to over two hours. We find charge carrier life time within the structure depends on the permittivity of the insulating layer, the applied bias, device thickness, and the LUMO/HOMO level of the

semiconductor used. By performing life time measurements as a function of laser intensity we were able to show that recombination is not bi-molecular in this device, in fact it is 0th order, i.e. not a function of charge carrier density all, further supporting the idea of a reservoir of one charge carrier species being present in the device. Very long charge carrier lifetimes could be find application in high sensitivity photodetectors and memory elements.

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