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Probing Charge Recombination in Organic Solar Cells

Abstract

Printable and flexible organic solar panels are promising sources of inexpensive, large-scale renewable energy, where panels can be manufactured by printing from polymer inks. There are some limitations to these types of solar cells, however. First, toxic halogenated solvents have historically been necessary to dissolve polymers to make the ink. In addition, organic solar cells typically have high rates of recombination, which limits their efficiency. Here, we use a transient photovoltage (TPV) technique to measure charge lifetimes in cells made from two different organic solvents. The first solvent is toxic, halogenated dichlorobenzene (DCB) which is typically used to make organic solar cells. The other is a less toxic, non-halogenated solvent, carbon disulfide (CS_2). By varying the processing methods in this way, we find that cells made from CS_2 have longer charge lifetimes and higher efficiencies than those made with DCB, as well as a different recombination rate order. Possible reasons for these differences are explored using simple analytic modeling. Our model indicates that while bimolecular recombination is dominant in both types of cells, those processed with DCB may have more trap-assisted recombination present than those processed with CS_2. Overall, this work demonstrates that we may be able to decrease the toxicity of organic solar cell manufacturing and simultaneously improve the efficiency of the devices, bringing this powerful method of capturing solar energy to the forefront of sustainable energy solutions.

Keywords

organic solar cells, recombination, transient photovoltage

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1 Introduction

As efforts increase to minimize carbon emissions and overall environmental impact from energy harvesting, solar power is a promising piece of the solution. In this light, organic solar cells are particularly cost-efficient sources of clean and renewable energy. Because they are printed from ink, OSCs are lightweight and can be mass-produced easily and printed on flexible substrates, allowing for a range of applications. While it is unlikely they will replace silicon cells on a wide scale, OSCs are a promising technology to be integrated into building windows, greenhouses, and vehicles, because they are semi-transparent, lightweight, and mechanically flexible. Organic solar cells are based on an electron donor and an electron acceptor. The focus of this research was polymer-fullerene organic solar cells, a common donor-acceptor pair, blended in a bulk active layer. Polymers are long, repeating molecular chains, and fullerenes are large spheroidal carbon-based molecules. The specific molecules used in this system are shown in Figures 1 and 2. These materials are first dissolved in an organic solvent, which is deposited as an ink to form the active layer.

Rather than generating free charges directly from incident photons as in inorganic semiconductors, organic solar cells operate by generating coulombically bound charge pairs called excitons. Excitons must diffuse to a donor-acceptor interface where the electron is drawn to the fullerene and the hole is drawn to the polymer domain. If there is enough energy to overcome their Coulombic binding, the charges will separate and travel to their respective electrodes through the donor or acceptor domains. The performance of organic solar cells is limited by several factors, notably the recombination of excitons and recombination of free charge carriers. Thus, charge recombination dynamics are an important field of study within organic solar cell research in an effort to reduce recombination and improve the solar cells' performance [9]. There are several relevant types of recombination in organic solar cells. In general, there are geminate recombination and nongeminate recombination. Geminate recombination occurs when an electron and hole generated from the same absorbed photon recombine. We will focus on nongeminate recombination, as this was the focus of our measurements. Nongeminate recombination consists of bimolecular recombination and trap-assisted, or Shockley-Read-Hall (SRH), recombination. Bimolecular recombination is the recombination of two free charges, while SRH involves a free charge recombining with a trapped charge [3]. In this project, we performed a charge lifetime measurement called transient photovoltage to quantify charge carrier lifetimes in cells processed with two different organic solvents, carbon disulfide and dichlorobenzene. Previous experiments in the lab where I conducted this research demonstrated that CS_2, a less toxic alternative solvent to DCB, yielded cells with higher power conversion efficiencies than its toxic, halogenated counterpart [1]. Additionally, some simple modeling was performed to attempt to distinguish between potential recombination mechanisms in cells processed with each solvent.

2 Experimental Methods

To fabricate the cells, we start with a glass substrate with strips of indium tin oxide (ITO, a transparent conducting oxide). After cleaning the substrates, we deposit PEDOT:PSS, the electron blocking layer, using spin-coating. We then spin-coat the active layer from an ink prepared the previous day, and clean the portion of the substrate where the electrodes will be deposited for current extraction. Finally, we deposit layers of calcium and aluminum using thermal evaporation/physical vapor deposition. Once the cell is finished, we perform a basic characterization measurement to obtain a current-voltage curve. This identifies the short circuit current, open circuit voltage, fill factor, and power conversion efficiency, all important characteristics of the cell. We also perform

UV and visible absorbance spectroscopy on the cells to get a sense of the film thickness and ensure correct material absorbance profiles. The cells are kept in nitrogen glove boxes throughout all steps and measurements after the active layer is deposited since they are very sensitive to air and humidity.

The main goal of this project was to quantify the charge carrier lifetimes. We did so using a transient photovoltage measurement (TPV). TPV is a photovoltaic measurement technique performed at open circuit, in which the background steady state generation of the cell is perturbed by a laser pulse. The pulse temporarily increases the charge density, which then decays exponentially. The time constant of that exponential decay is taken to represent the "charge lifetime". Figure 4 shows this exponential decay for several different background voltages. In our setup, we used a 532 nm wavelength laser with a 3 nanosecond pulse every 10 milliseconds. We used variable-intensity LEDs to generate the background voltage so that we could perform the TPV measurement on each cell at various intensities, corresponding to different bias voltages in the cell. We performed this measurement on each cell after the J-V characterization measurement.

3 Experimental Results

Identical TPV measurements were performed on cells fabricated with CS_2 ink and with DCB ink. We varied the LED intensities and conducted the measurement at 7 intensities between 0 and 1 sun. We fit an exponential to the voltage decay and extracted the time constant. When we plot the time constants (lifetimes) versus intensity, we see a negative power law relationship. So, we can visualize the lifetime-intensity relationship on a log-log plot as seen in Figure 5. The slope of this plot, which is the exponent of the power law, is about -0.6 on average for the CS_2 devices. For devices processed with DCB, that slope is closer to -0.9 on average.

It is important to note that there was also a significant difference in the overall performance of the cells we averaged. Because of time constraints and cell degradation, we were unable to measure the high-performing CS_2 devices that we made. So, the CS_2 devices averaged in Figure 2 were unusually low-performing. This may contribute to the differences in lifetimes and lifetime dependence on intensity. However, the overall lifetimes measured at each intensity were quite similar between the two solvents. More noteworthy is the difference in slope on the log-log plot. This is potentially indicative of differences in recombination mechanisms due to the differences in processing solvents. This will be explored further in the modeling section.

4 Modeling

To further probe potential reasons for the recombination rate order differences in cells processed with CS_2 and DCB, we turn to a simple analytic model of charge recombination. The field of organic photovoltaic modeling is quite complicated, including drift-diffusion models, multiple trap states [5]. Here, we will focus on a very simple, phenomenological model limited to bimolecular and Shockley-Read-Hall recombination, with several simplifying assumptions. The goal is simply to probe the contributions of each of these recombination mechanisms in cells processed with each organic solvent by fitting the model to our experimental data above. In general, Equation 1 describes the rate of change of the charge carrier concentration [7].

$$\frac{dn}{dt} = G - k_b np - k_{SRH} n \tag{1}$$

We will first focus on the last term, the Shockley-Read-Hall (trap-assisted) recombination rate. Equation 2 defines this in terms of electron and hole concentrations and lifetimes.

$$k_{SRH}n = R = \frac{(np - n_i^2)}{\tau_n(n - n_i) + \tau_p(pi - p_i)} \tag{2}$$

Now we will make two simplifying assumptions to aid in solving this system. First, we assume that the thermal generation rate is negligible compared to photogeneration. Thus, the electron and hole concentrations are each much larger than the intrinsic concentration n_i. Second, we will assume that the density of trap states is much lower than the carrier concentration, meaning we can set $n = p$. Then the SRH rate simplifies (Equation 3). We can see from this result that the SRH recombination rate is a constant - it does not depend on carrier concentration (Equation 4). This is a distinction from bimolecular recombination, which has a rate that is concentration-dependent and thus intensity-dependent. This leads to some simplifications:

$$k_{SRH}n = R = \frac{n}{\tau_n + \tau_p} \tag{3}$$

$$k_{SRH} = \frac{1}{\tau_n + \tau_p} \tag{4}$$

We can apply the assumptions we made above to equation 1 and it simplifies as follows:

$$\frac{dn}{dt} = G - k_b n^2 - k_{SRH}n = G - \frac{n}{\tau} \tag{5}$$

So, τ, the overall lifetime, is given as:

$$\tau = \frac{1}{k_b n - k_{SRH}} \tag{6}$$

We then solve Equation 5 for n in the steady state and we plug that expression into Equation 6. The resulting expression gives the overall lifetime in terms of known constants and G, the generation rate. G can be related to the absorbed light intensity, which is calculated from the LED spectrum and active layer absorbance profile [7]. Thus, as seen in Equation 7, we have a method of calculating the expected lifetime of charges at a given intensity, which we can fit to the experimental data in Figure 1. We performed this fit by manually adjusting k_b and k_{SRH} and evaluating the fit to data by eye. Initial estimates for the coefficients were found in the literature [2]. It's worth noting that for purely bimolecular recombination, without any trap-assistance, the lifetime would go as the generation to the power of -0.5 [8]. This is shown in Figure 6 by the solid black line.

$$\tau = \frac{\frac{1}{k_b}}{-\frac{3}{4}\frac{k_{SRH}}{k_b} + \frac{1}{2}\sqrt{\left(\frac{k_{SRH}}{k_b}\right)^2 + 4\frac{G}{k_b}}} \tag{7}$$

Upon performing this fit using Equation 7, we found that we were able to get fairly accurate fits, at least at higher intensities, for both solvent processing protocols. The fits and data can be seen together in Figure 2.

It is clear from the coefficients of recombination in Table 2 that the DCB data fits a higher coefficient of SRH recombination. Thus, an increase in SRH behavior could account for the steeper slope on the log-log plot for DCB devices. However, this model is simple, and the results are not conclusive that SRH recombination is the only explanation for the steeper slope. Instead it serves as a potential phenomenological explanation.

At intensities less than about 0.05 sun, the models each diverge from their respective data trends. The model seems to give artificially high lifetime values at these low intensities. The simplifying assumptions made as well as the overall simplicity of the model likely account for these differences. For the majority of the intensity range, the model fits well.

5 Discussion

The main takeaway from this work is the apparent difference in recombination rate order in cells processed with carbon disulfide compared to those processed with dichlorobenzene. Neither solvent is present in the final cell because they evaporate during deposition of the active layer. So the question arises: how do the solvents influence the cell's photoelectronic properties without being present during measurement? One plausible answer is that the rate of solvent evaporation affects the morphology of the active layer, including domain size and donor/acceptor interface morphology. Active layer morphology very likely impacts charge carrier dynamics and recombination [4]. CS_2 and DCB have quite different boiling points, which matches the hypothesis that rates of evaporation play a role in our results. The boiling point of CS_2 is 46℃ and DCB's is 174℃. Therefore, it's reasonable to assume that CS_2 evaporates more quickly during active layer deposition, leaving behind a different morphology which influences how charges move and recombine. Additionally, carbon disulfide active layers were considerably thicker when deposited at the same spin speed for the same time. A thicker active layer may mean charge extraction is slower, but interface effects are also suppressed [6]. Some combination of these effects may contribute to more bimolecular and less SRH recombination in thicker CS_2 devices compared to thinner DCB ones. To be certain of this would require further investigation of the morphology of the cells.

6 Limitations

There are several limitations to both the experimental and computational methods employed in this study. First, we encountered several barriers in fabricating high-performing devices and measuring them sufficiently before they degraded. As aforementioned, the devices are very sensitive to air and humidity, and typically degrade to unusable condition within a few days, even when kept in an inert environment. We also faced some strict time constraints in that all of the experimental work was during a summer internship. Our failure to conduct TPV measurements on high-performing CS_2 devices can be attributed to these constraints. The abbreviated time and limited performance of CS_2 devices were likely the biggest limitations of the research since they prevented us from obtaining lifetime data from equally high-performing devices with each solvent. Additionally, the transient photovoltage measurement has several shortcomings in itself. First, it probes non-geminate recombination, ignoring geminate recombination. Also, rather than precisely measuring the recombination dynamics, TPV more accurately measures charge redistribution in the bulk [2]. So, it's possible that the "lifetime" values we extracted are not exactly equivalent to the recombination rate as we have assumed.

As for modeling, our work was mostly phenomenological and qualitative. We made several simplifying assumptions, including that the light absorption, charge generation, and recombination were all spatially homogeneous. We also assumed just a single trap state and that only bimolecular and trap-assisted recombination were present. We fit the model to the data by eye rather than with a nonlinear curve fitting program, which may have yielded less than precise results for the recombination coefficients. However, for the scope of this project, our results are still qualitatively meaningful.

7 Conclusion

To summarize, we set out to compare charge carrier lifetimes and recombination in organic solar cells processed with two different solvents: carbon disulfide and dichlorobenzene. Our work aimed to determine if different recombination rates and mechanisms may be a reason for higher power conversion efficiencies in CS_2-processed devices. We fabricated devices with each solvent, measured typical electrical characteristics of the cells, and performed a transient photovoltage measurement at various background light intensities. From this measurement we extracted the exponential time constant from the voltage decay after a laser pulse, and took that to be the charge "lifetime", tau. When plotting these lifetimes versus the background intensity, we saw differences in the lifetime-intensity relationship between the two differently processed devices. With CS_2, the log-log plot of this data exhibited a slope of about -0.6, while DCB had a slope closer to -0.97. Based on simple modeling, we noted that a slope of -0.5 would indicate purely bimolecular recombination and steeper slopes could be fit by increasing the contribution of trap-assisted (SRH) recombination. Thus, we conclude that DCB processing likely yields active layer morphology conducive to more SRH recombination than CS_2. Bimolecular recombination dominates in both types of cells, but is not sufficient to describe the trends we observed.

This study was somewhat limited in its scope, leaving room for lots of future research directions. First, it would be interesting to connect our TPV results with other charge carrier measurements like time-delayed collection field (TDCF) and transient photoluminescence (TRPL). Our hypothesis that the solvent evaporation rate affects morphology could be confirmed with morphological characterizations like X-ray scattering and TEM. As for the model, we could expand it to account for spatial heterogeneity and space charge effects, as well as charge mobilities. We could also do more robust curve fitting to our data to obtain more concrete recombination coefficient values.

Based on both experimental characterization of solar cells and charge recombination modeling, we observe potential differences in the recombination mechanisms in OSCs processed with CS_2 and DCB. Both processing protocols yield cells dominated by bimolecular recombination, but the thinner layer deposited by DCB appears to also have a significant amount of trap-assisted recombination. These results indicate that carbon disulfide may be a better solvent choice in OSC processing moving forward.

References

[1] A. N. Alotaibi and B. A. Collins. *Accurate Measurement of Charge Generation at Interfaces of Organic Solar Cell Devices Printed from Non-Halogenated Solvents.* dissertation, 2022.

[2] M. Azzouzi, P. Calado, A. M. Telford, F. Eisner, X. Hou, T. Kirchartz, P. R. Barnes, and J. Nelson. Overcoming the limitations of transient photovoltage measurements for studying recombination in organic solar cells. *Solar RRL*, 4(5), 2020.

[3] S. R. Cowan, A. Roy, and A. J. Heeger. Recombination in polymer-fullerene bulk heterojunction solar cells. *Physical Review B*, 82(24), 2010.

[4] P. Dhakal, T. Ferron, A. Alotaibi, V. Murcia, O. Alqahtani, and B. A. Collins. Evidence for field-dependent charge separation caused by mixed phases in polymer–fullerene organic solar cells. *The Journal of Physical Chemistry Letters*, 12(7):1847–1853, 2021.

[5] A. Hofacker, K. Leo, and D. Neher. *Modelling Charge Carrier Dynamics in Organic Semiconductors.* dissertation, Dresden, 2021.

[6] D. Lübke, P. Hartnagel, M. Hülsbeck, and T. Kirchartz. Understanding the thickness and light-intensity dependent performance of green-solvent processed organic solar cells. *ACS Materials Au*, 3(3):215–230, 2023.

[7] J. Nelson. *The Physics of Solar Cells.* Imperial College Press, 2013.

[8] C. M. Proctor, M. Kuik, and T.-Q. Nguyen. Charge carrier recombination in organic solar cells. *Progress in Polymer Science*, 38(12):1941–1960, 2013.

[9] R. A. Street, M. Schoendorf, A. Roy, and J. H. Lee. Interface state recombination in organic solar cells. *Physical Review B*, 81(20), 2010.

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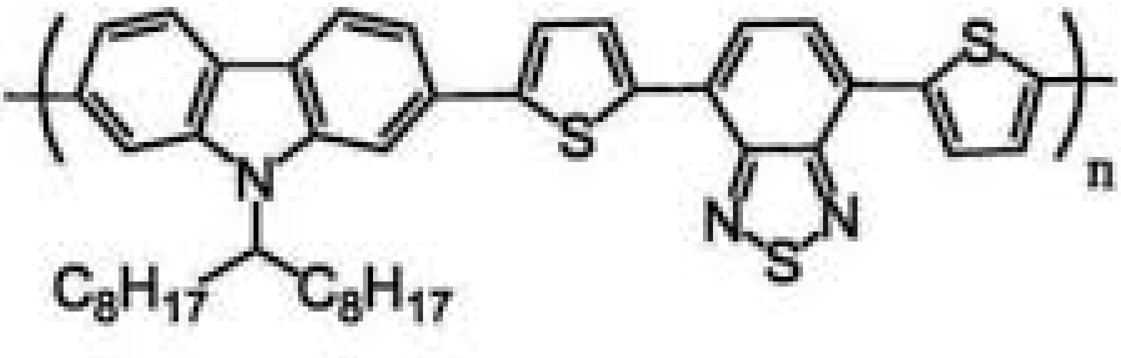


Figure 1: PCDTBT Polymer

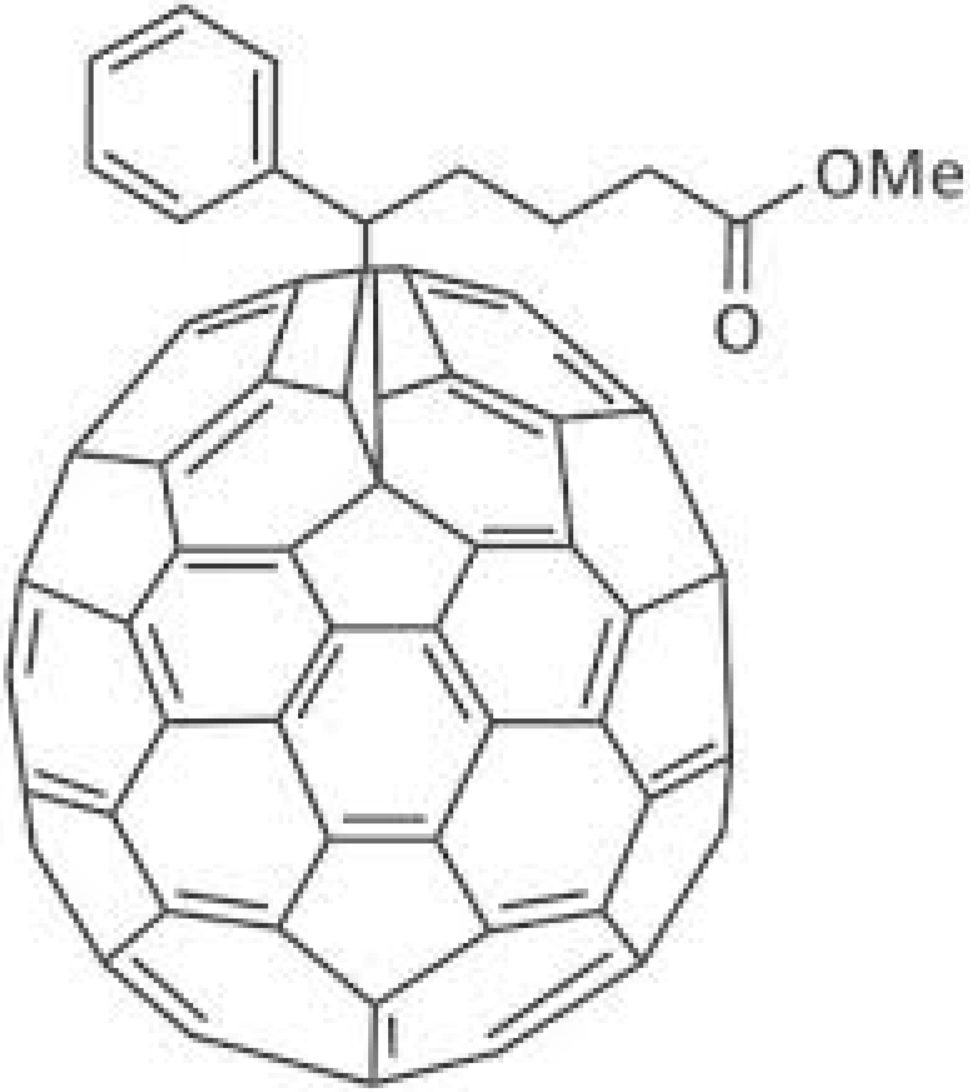


Figure 2: PC71BM Fullerene

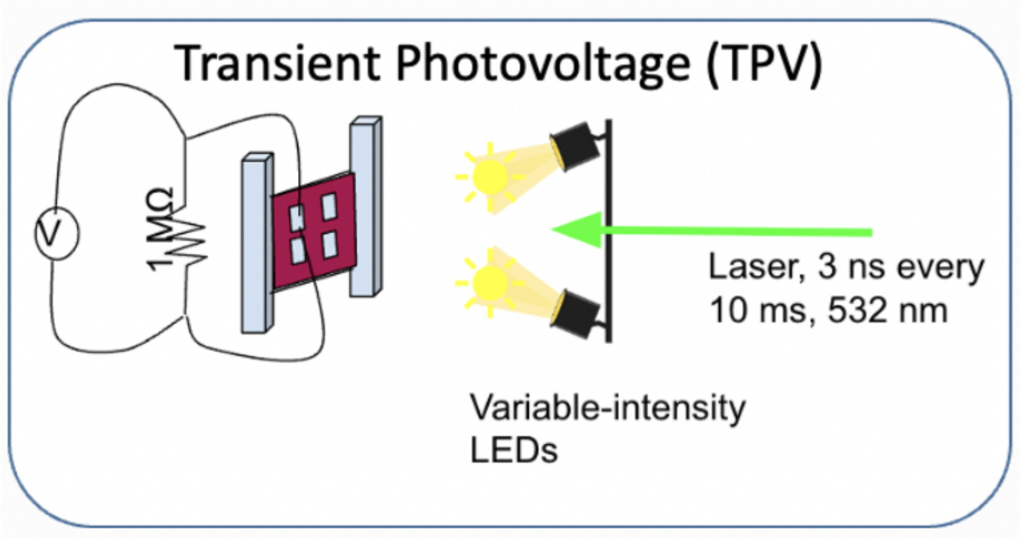
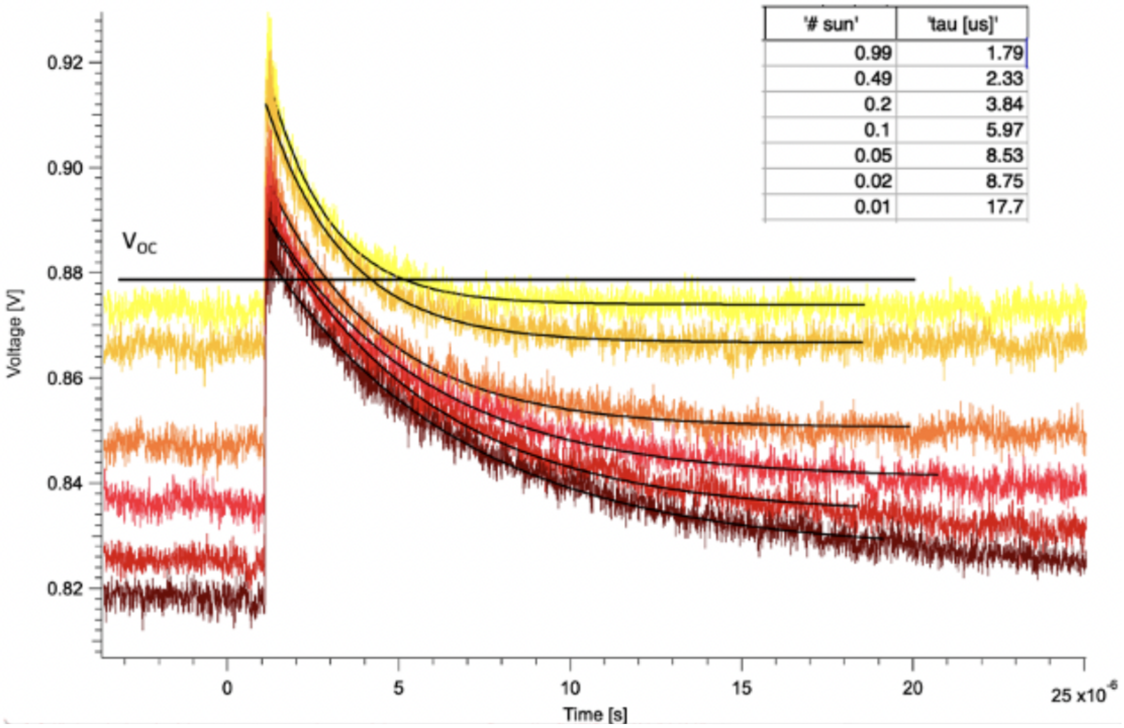


Figure 3: Schematic of TPV setup



'# sun'	'tau [us]'
0.99	1.79
0.49	2.33
0.2	3.84
0.1	5.97
0.05	8.53
0.02	8.75
0.01	17.7

Figure 4: Raw data from TPV measurements at six background voltages.

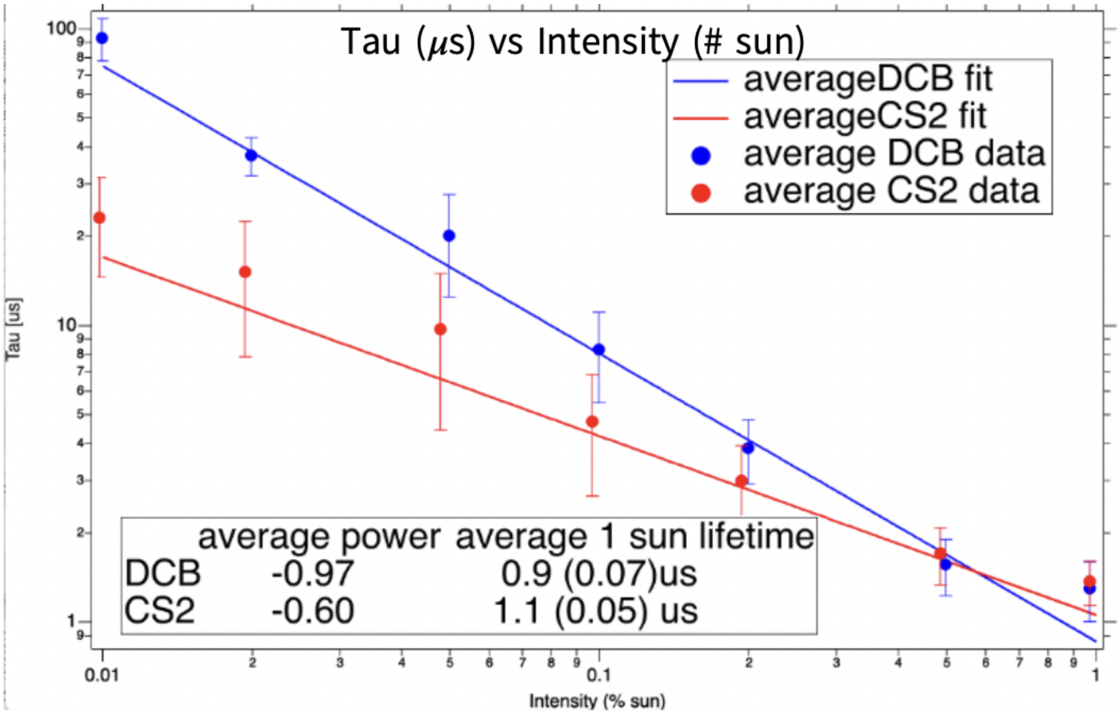


Figure 5: Lifetime [μs] versus Intensity [number of sun] plot for averages of CS_2 devices and DCB devices

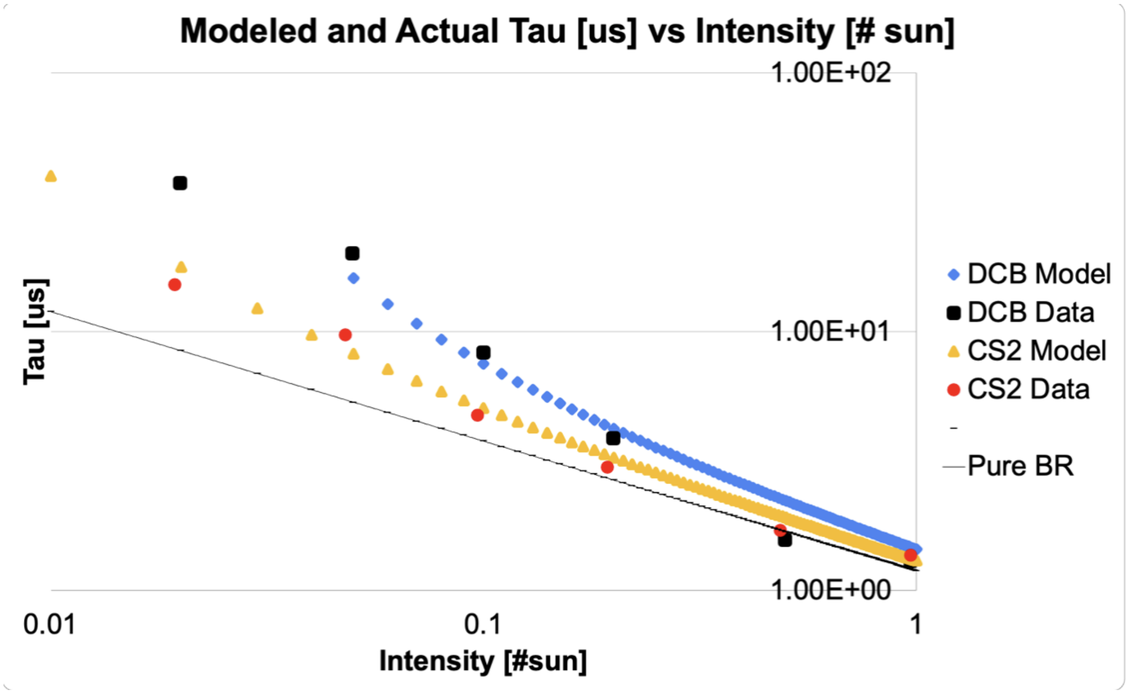


Figure 6: Modeled and experimental lifetime vs intensity plot

List of Tables

	CS_2	DCB
Model Slope	-0.6	-0.7
Data Slope	-0.6	-0.9

Table 1: Modeled and experimental log-log plot slopes for CS_2 and DCB

	CS2	DCB
k_{SRH} $[1/\mu\ \mathrm{s}]$	$9.5e4$	$2.0e5$
k_b $[cm^3/\mu\ \mathrm{s}]$	$7.0e-11$	$7.0e-11$

Table 2: Coefficients of bimolecular (k_b) and SRH (k_{SRH}) recombination from model fit to data for CS_2- and DCB-processed devices