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Using Sugar-based Additives to Prolong the Lifetime of Air-Stable Radicals in Self-Assembled Perylene Bisimides

Ilze Lāce,^[a] Stephen Sproules^[a] and Emily R. Draper^{*[a]}

Sugar-based additives were introduced into self-assembled worm-like micelles of amino acid functionalized perylene bisimides. The solutions are then dried to form thin films and used as photoresponsive materials. The effects of the addition of dextran and sucrose on the properties of the perylene bisimide thin film are investigated using cross-polarized light optical microscopy, electron paramagnetic resonance (EPR) spectroscopy, rheology, UV-vis absorption spectroscopy and electrochemistry. The radical anion is stabilized by the presence of the additives in solution and in the thin films, resulting in a significantly increased lifetimes and persistent conductivity.

Perylene bisimides (PBIs) are known to be excellent materials in organic electronics in such applications as organic light emitting diodes (OLEDs), and bulk heterojunctions.^[1] In OLEDs in particular they are known to increase the operating lifetime of the device by 30 to 50 times.^[2] PBIs can act as the light emitting layer (LEL).^[2] They are thought to help as they reduce quenching in the luminescent material. In bulk heterojunctions, PBIs are useful n-type materials, accepting electrons from the p-type material, and also as useful n-type thin film transistors.^[3] PBIs have also been utilized in polymer-based solar cells as an additive to P3HT:PCBM to improve the p-n heterojunction.^[4] This improved the efficiency of the solar cell by 70%. They have also been used as electron transport layers and hole blocking layers in solar cells helping provide electrons from the cathodic materials into the active layer of the solar cell and preventing recombination, as well as in dye sensitized solar cells and perovskite solar cells.^[5] There are now examples of these multifunctional molecules being used in photocatalytic systems in reducing H₂.^[6] PBIs have also proved useful sensors and been used to detect oxygen and hydrazine.^[7]

The versatility of PBIs comes from their ability to be reduced to form a radical anion, and then further reduced to the dianion.^[8] These reduced states result in a change in color and sometimes make the material conductive.^[7a] For sensors, this radical anion can be induced or reduced depending on the molecule it is detecting. For the case of oxygen sensing, the non-fluorescent charged species is oxidized by oxygen and so the fluorescent ground state material is then detected.^[7b] In the case of hydrazine, this acts as a hole scavenger and so increases the amount of radical anion that is present, resulting in the distinctive purple color of the reduced species.^[7c] The radical anion has also been

seen to increase the mechanical properties of amino acid functionalized PBI hydrogels, as it is able to change the stacking between the molecules.^[9] In some examples, the radical anion can be quite stable in air,^[10] which is attractive for the use in organic electronics which would ideally not require an inert atmosphere to work. Therefore, there is interest in making these radical species more stable and increasing their lifetime.

We have recently shown a series of amino-acid functionalized PBIs that can self-assemble in water to worm-like micelles under specific conditions.^[10-11] These worm-like micelles are photoconductive when dried to form thin films. The ability to form the radical anion and the lifetime of it when irradiated with 365 nm light depended on which amino-acid with which the PBI was functionalized. Changing the amino-acid (and so changing the functional groups on the molecule) affects the bonding possibilities between molecules, the hydrophobicity, the size, the pK_a of the aggregates etc. resulting in changes in the self-assembly.^[11] We concluded that the stacking of the molecules into the fiber-like structures was affected by the amino-acid. As changing the amino acid has such a profound effect on the properties, we considered that perhaps using only one functional group and then using additives may be another possibility that is worth considering to reduce the complexity.

Here, we examine the effect of the addition of dextrans and sucrose to a valine-functionalized PBI (**PBI-V**, Figure 1a).

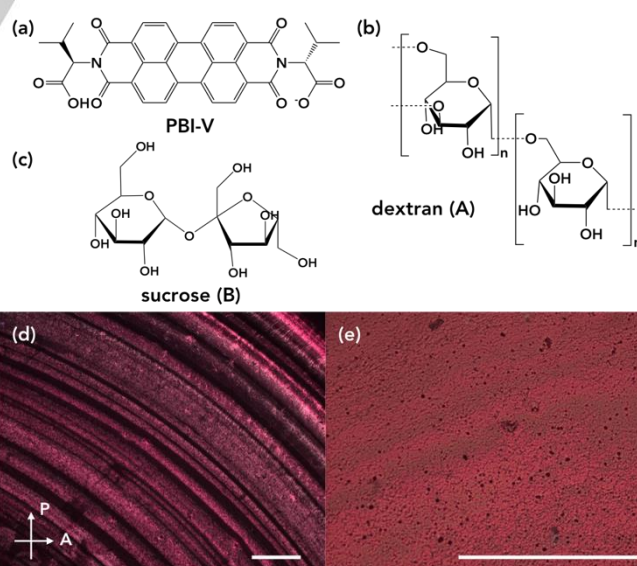


Figure 1. (a) Molecular structure of valine-functionalized PBI (**PBI-V**). (b) Generic structure of dextran and (c) structure of sucrose. Cross-polarised light microscopy images of dried films of (d) **PBI-V:A** and (e) **PBI-V:B**. Scale bar represents 250 μm.

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We assess the effect they have on the production and lifetime of the radical anion in solution and when dried into a thin film, and consequently the conductivity of the material. We also studied the effect on the alignment of the materials. We monitored the production and lifetime of the radical anion of **PBI-V** using a mixture of UV-vis absorption spectroscopy, electron paramagnetic resonance (EPR) spectroscopy and electrochemical techniques. Solutions of **PBI-V** with dextrans or sucrose were prepared at a 1:1 ratio unless otherwise stated, with each component at 5 mg mL⁻¹ in solution. Two different additives were used, dextran with an average molecular weight of 1,500,000 Da (Figure 1b; referred to as **A** in this study) and sucrose (referred to as **B**, Figure 1c). These were used to compare the long chains of sugar with effectively a sugar monomer.

First, the viscosities of the mixed samples were compared to that of the single component systems. The individual components of **PBI-V** and **A** show a shear thinning behavior which is indicative of these long fiber-like structures present in solution, with **A** showing the most shear thinning behavior and **B**, showing the least shear thinning behavior (Figure S1a, supporting information) as expected from the length of the polymer chains present in solution. For **PBI-V:A**, the viscosity increases to more than that of the single components (Figure S1b, supporting information). This indicates that the dextrans are interacting with the **PBI-V** worm-like micelles, increasing the viscosity of the sample. **PBI-V:B** viscosity is similar to that of the **PBI-V** alone, suggesting less interaction with one another. Each of these solutions was then dried in air to a thin film and examined under a cross-polarized light microscope. **PBI-V** shows some alignment as has been previously shown upon drying caused by the coffee ring effect (Figure S2, supporting information).^[12] Samples **A**, and **B** showed no alignment upon drying (Figure S3a-b, supporting information). The mixture of **PBI-V:A** showed no phase separation and showed an increased alignment in the images (Figure 1d). This again is suggesting there is some interaction between the additives and the **PBI-V** structures. **PBI-V:B** however shows a decreased coffee-ring effect, suggesting a disruption to the alignment due to interaction between sucrose and the micelles upon drying (Figure 1e).

To investigate this interaction further, FTIR spectra of the films was recorded of the individual components and compared to that of the mixtures (Figure S4 a and b, supporting information). In all of the mixtures, a shift in a peak's position was visible in the fingerprint region at 995 cm⁻¹ to 1010 cm⁻¹ (Figure S4d, supporting information) and a shift in peak's position from 2896 cm⁻¹ to 2930 cm⁻¹ (Figure S4c, supporting information). The first peak corresponds to a C-O alcohol stretch from the dextran and this latter peak corresponds to either a stretching alkane C-H bond or a stretching O-H bond on the PBI. Previously, examples in the literature from Miller et al. using PVA as an additive in similar systems have reported similar shifts in the FTIR and they suggest that the polymer chains hydrogen bond with the PBIs, protecting the radical anion from oxidation through this interaction.^[16] This could be happening here with the alcohol group on the dextran molecules or sucrose interacting with the PBIs.

To determine whether the dextrans also protected the radical anion species from oxidation, we carried out conductivity measurements on the dried films. Based on earlier work,^[10] we

used a 365 nm LED to irradiate the samples and measured the photoresponse of the samples in the dark and after irradiation with the LED for 10 min. Samples **A** and **B** showed no conductivity and no response to the UV light (Figure S5, supporting information). **PBI-V**, **PBI-V:A**, and **PBI-V:B** showed response to the light, and little response in the dark (Figure 2a). **PBI-V** alone showed the largest response and **PBI-V:B** showed the smallest response. This decrease in overall conductivity could be due to the presence of the additives negatively affecting the formation of radical anion or could be due to phase separation and so the radical anion was being formed in isolated pockets rather than in a continuous pathway. It could also be that the samples with additives have different degrees of alignment than **PBI-V** and so are not as conductive due to a higher chance of recombination.

To investigate the possibility of the additives affecting the **PBI-V** and alignment issues, we aligned the samples using shear alignment as we have described previously.^[12]

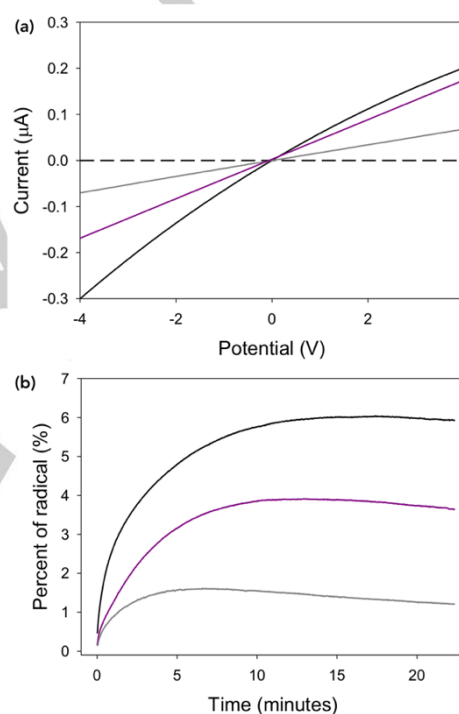


Figure 2. (a) I-V curves for **PBI-V** in the dark (dashed line) and **PBI-V** (black), **PBI-V:A** (purple) and **PBI-V:B** (gray) all after irradiation with a 365 nm LED for 10 min. (b) EPR data showing the growth of the radical anion during irradiation with 365 nm light for **PBI-V** (black), **PBI-V:A** (purple) and **PBI-V:B** (gray).

We expect that this alignment would remove any issues due to phase separation upon drying. The conductivity of these aligned samples was then measured with and against the direction of alignment. All samples showed significant directional dependence with the measurements against the direction of alignment being similar to those obtained in the dark (Figures S6 and S7, supporting information). All these samples also showed very similar currents when measured along the aligned direction, meaning that the additives did not have a negative effect on the radical anion formation, but the lower conductivity data collected

originally could have been due to a slight phase separation upon drying.

We then used EPR to quantify the amount of radical anion in the samples. EPR measurements take into account the whole sample, whereas the conductivity measurements are just utilizing the most conductive pathway, so the sample with the most radical anion content may not be the most conductive due to phase separation, or isolated areas of radical present on the sample. We compared the mixed samples after irradiation for 10 min with 365 nm light with a known standard (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) in water). The additives alone showed no presence of any radical species present in solution. The mixed samples did show the presence of a radical species at the same resonance position as **PBI-V** and so we assign this as the PBI radical anion. The EPR spectrum of **PBI-V** exhibited features attributed to weakly resolved hyperfine splitting, best visualized in the second derivative spectrum (Figure 3). The latter was simulated using an isotropic spin-Hamiltonian which gave $g = 2.0033$ and coupling to two sets of four equivalent protons of PBI of 1.4 and $0.6 \times 10^{-4} \text{ cm}^{-1}$. These parameters are consistent with similar EPR studies of the PBI radicals.^[13] The presence of additives reduce the intermolecular interaction between PBI radicals leading to more pronounced hyperfine definition. This separation of the radicals would lead to less recombination of charges and so would prolong the lifetime of the radical anion species. Their second derivative spectra of **PBI-V:A** and **PBI-V:B** have also been simulated with the same parameters as for **PBI-V**.

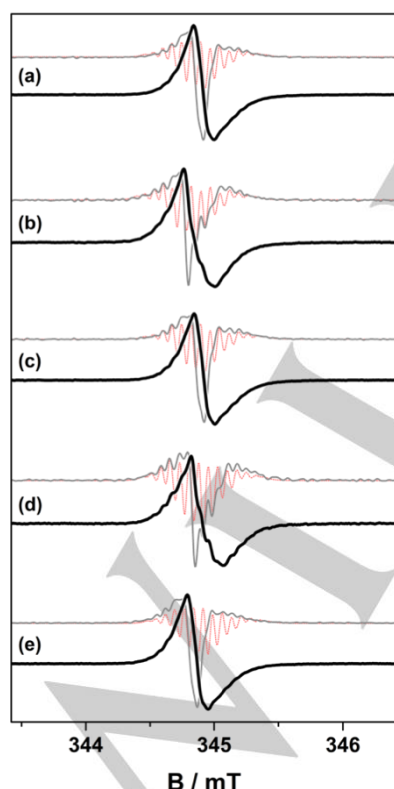


Figure 3. Comparison of the X-band EPR spectra (black line) recorded after 10 min irradiation ($\lambda = 365$) for aqueous solutions of (a) **PBI-V**, (b) 1:1 **PBI-V:A**, (c) 1:0.1 **PBI-V:A**, (d) 1:1 **PBI-V:B**, (e) 1:0.1 **PBI-V:B** (experimental parameters: frequency, 9.67 GHz; modulation, 0.05 mT; power, 0.63 mW; temperature, 293

K). Second derivative spectra are represented by the gray line superimposed with a simulation outlined by the dotted red trace. Simulations were achieved using the spin-Hamiltonian, $\hat{H} = g\mu_B B S + \sum a_i S_i$, for $g = 2.0033$; $a_{\text{H}} = 1.38 \times 10^{-4} \text{ cm}^{-1}$; $a_{\text{H}} = 0.59 \times 10^{-4} \text{ cm}^{-1}$.

There was a varying concentration of the radical anion in each of the samples (Figure 2b). **PBI-V** alone had 5.4% radical anion, **PBI-V:A** had 4.3% radical anion, and **PBI-V:B** had 2.5% radical anion. This data is entirely consistent with the conductivity data with the **PBI-V** alone being the most conductive and **PBI-V:B** being the least conductive. The UV-vis absorption spectra of the mixtures showed similar intensity peaks corresponding to the radical anion as for the spectra of **PBI-V** alone (Figure S8a-c, supporting information), and **A** and **B** alone showed no absorption (Figure S9, supporting information). However, the peaks due to the radical anion were more defined and there appears to be a higher concentration of the dianion present (assigned as the peak at $620 \text{ nm}^{[15]}$) in **PBI-V:B**, and in **PBI-V:A**. The highest concentration of the dianion was found in **PBI-V:B**, explaining the decreased conductivity and radical presence in the EPR (the dianion is EPR silent).

As Supur et al. had reported that incorporation of PVA enhanced the lifetime of the radical anions in air, we then evaluated the lifetime of the radicals in our systems.^[14] We used chronoamperometry to measure the conductivity, and UV-vis absorption spectroscopy to monitor the concentration of the radical anion. Again, the samples were irradiated in situ for 10 min with the 365 nm light. In the case of the UV-vis absorption spectra, a spectrum was recorded every 30 min after the LED was switched off until the radical peaks at 725, 810 and 985 nm had fully disappeared.^[10] (Figure 4a-b and S8d, supporting information). The lifetime of the radical for **PBI-V:A** and **PBI-V:B** are significantly increased from around 30 mins to over 8 h.

For the chronoamperometry, a constant voltage was applied and the current was monitored during irradiation and when the LED was switched off and returned to that of the dark measurements: All the samples increase in current when the LED is switched on. The current then drops even though the LED is still on. This is thought to be due to the production of the non-conductive dianion species and has been seen before (Figure S10, supporting information).^[11] When the LED is switched off, the current rapidly decreases, but at varying rates for each sample depending on how stable the radical anion is to the oxidation in air. The decrease in the conductivity can also be affected by the concentration of the dianion present; when this oxidizes, it first forms the radical anion and so the current can increase when this happens before further oxidation of the radical anion occurs. The **PBI-V:A** sample remained conductive for over 14 h, and **PBI-V:B** for 8 h, whereas, the **PBI-V** alone was conductive for around an hour. In both the chronoamperometry and the UV-vis absorption, the lifetimes of the radical anion were significantly increased as compared to **PBI-V** alone. The interaction with the additives must stabilize the radical anion and prevent oxidation or recombination in the films, making the lifetimes much longer than the **PBI-V** alone. These lifetimes could not be fitted due to the presence of dianion. The dianion decays at the same time as the radical anion and produces more anions (as seen in the chronoamperometry) and so the rate constants cannot easily be determined.

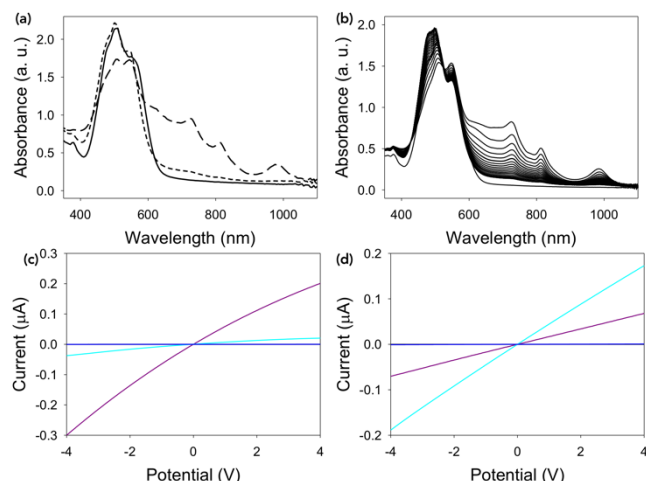


Figure 4. UV-vis absorption spectra of (a) **PBI-V** after irradiation with 365 nm LED for 10 min (dashed line) and the disappearance of the peaks after 30 min (dotted line) and 1 h (solid line) (b) **PBI-V:B** after irradiation with 365 nm LED for 10 min and the disappearance of the peaks after 8 h. I-V curves irradiating for 10 min using different wavelengths of light for (c) **PBI-V** and (d) **PBI-V:B**; the purple data is 365 nm, cyan is 400 nm and blue is 450 nm.

To further test this stabilization, we then performed the same I-V measurements but using different wavelengths of light. The more stable the radical is, the more easily it should be produced, so should require less energetic wavelength in order to be formed.^[17] **PBI-V** as previously shown, is the most least responsive to 365 nm light and shows a very small response to 400 nm and essentially none to 450 nm (Figure 4c). Both the mixed systems showed a preference to 400 nm light, meaning they both need less energy to form the radical anion (Figure 4d and S11, supporting information). The current produced under irradiation with 400 nm light for the mixed systems is similar to that of **PBI-V** with 365 nm. This could be again due to the enhanced stability of the radical anion from interaction with the additives.

In conclusion, the we have shown that dextran and sucrose interact with the **PBI-V** worm-like micelles in solution as shown by the increase in viscosity, but also when dried into a film. The dried films show by FTIR that there is increased O-H stretching and C-H stretching caused by the introduction of the additives, again indicating interaction between the two. Most interestingly, this interaction has led to the stabilization of the radical anion in the film and increases lifetime of this species in air dramatically. There is a decrease in the amount of radical produced at 365 nm with the mixed systems, which is not ideal. However, the stabilization of the radical anion leads to the mixed samples having a shift in preference towards the visible light, which is normally done by introducing a hole scavenger gas or the introduction of a p-type material into the system. The amount of radical produced at 400 nm for the mixed systems is comparable to that produced at 365 nm for the single component system. The shift in wavelength preference could be useful in solar cell application were visible light sensitivity is optimal. Compared to other systems where measurements are conducted under argon, or with the use of very strong dopants, our system works in air with the use of light to create the radical anion, giving it a major advantage in use in real life applications. This opens up the possibility of these PBI

materials being utilized in more devices just by the addition of sugar-based molecules.

Experimental Section

Full experimental procedures, viscosity, I-V measurements and UV-vis absorption spectroscopy and list of materials can be found in the supporting information.

Acknowledgements

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Keywords: radical anion • perylene bisimide • dextran • EPR • organic electronics

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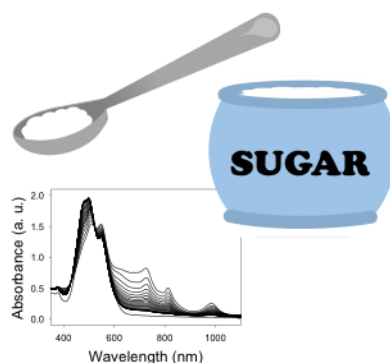
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Page No. – Page No.

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