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All slot-die coated organic solar cells using an amine processed cathode interlayer based upon an amino acid functionalised perylene bisimide†

Rebecca E. Ginesi, ^a Muhammad R. Niazi,^b
Gregory C. Welch ^{*b} and Emily R. Draper ^{*a}

Green solution-processable organic photovoltaic cells (OPVs) have the potential to provide low-cost, clean, and accessible electricity. However, there are few organic materials that are compatible with multi-layer film formatting from halogen-free solvents using scalable coating methods. Current research focuses on devices using tin oxide (SnO₂). However, SnO₂ has surface traps and requires a passivating layer to maximise performance. Therefore, it is crucial to develop electron deficient organic materials that can passivate metal oxides to achieve maximum device performance. Rendering these materials and films solvent resistance is thus a major goal. Herein, we show that SnO₂ modified with a tyrosine appended perylene bisimide (PBI-Y) can be applied as an electron transport interlayer in PM6/Y6C12-based organic photovoltaic cells using an amine-based ink formulation. The SnO₂/PBI-Y films are characterised by optical absorption spectroscopy and atomic force microscopy and exhibit solvent resistance. The electrical characterisation shows that a PBI modification improves the conductivity of the SnO₂. Spin-coated devices show a power conversion efficiency (PCE) of 13%, among the best for all air-processed SnO₂-based OPVs. Fully slot-die coated devices achieve PCEs of 10%, demonstrating the potential for scale-up. This work opens a viable and sustainable method to develop organic photovoltaic devices using more environmentally friendly processing conditions.

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Introduction

Solution-processed organic photovoltaic cells (OPVs) are considered one of the most promising next-generation, low-cost, clean energy technologies.^{1–4} Compared to the more traditional silicon-based solar cells, OPVs can be rendered lightweight, flexible, and stretchable, allowing them to be integrated onto large-area flat, curved, or flexible surfaces.^{5–8} Furthermore, lab-scale OPV devices with power conversion efficiencies (PCEs) of up to 18% have been reported, which paves the way for future commercialisation.^{9–11} However, further work to improve performance, lifetime, and processing is needed for this technology to become widespread in commercial applications.

Many high-performing OPVs currently are made using spin-coating methods inside gloveboxes,¹² and processing conditions and performance metrics are often not transferable

to industry-scale fabrication methods. The use of non-environmentally friendly halogenated solvents, such as chlorobenzene (most commonly used to cast photoactive layer films), also presents challenges due to the health and environmental impacts associated with such solvents.¹³ Therefore, a potential solution is to use large-scale coating techniques, such as slot-die coating,^{14–16} with green solvents (*i.e.*, solvents which are more environmentally friendly, are usually made from renewable resources, have a lower toxicity and are biodegradable)¹⁷ at the lab-scale to facilitate more rapid adoption of new innovations. Slot-die coating allows for highly reproducible uniform films, low material wastage, and can be compatible with roll-to-roll (R2R) processing technology, allowing for high throughput.^{18,19} Recently, all slot-die coated OPVs with a record PCE of 16.2% have been reported.²⁰

The electron transport layer (ETL) plays a crucial role in the PCE, stability and reliability of solar cells.²¹ OPVs with conducting transparent n-type metal oxides, such as tin oxide (SnO₂) and zinc oxide (ZnO), are commonly observed in consumer electronics, such as in touch screen panels, smart windows, and energy storage devices.^{22–25} However, ZnO can promote the photodegradation of bulk heterojunction (BHJ) materials, negatively impacting device performance.²⁶ Therefore, SnO₂ is the more viable choice owing to its higher

^a School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK.

E-mail: emily.draper@glasgow.ac.uk

^b Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N6, Canada† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3lf00183k>

cleaned glass/ITO/SnO₂-coated glass formed highly uniform thin films at room temperature. These films were thermally annealed at 100 °C for 10 minutes to accelerate the evaporation of residual butylamine.

PBI-Y film optical and surface characterisation

The optical properties of glass/ITO/SnO₂/PBI-Y films were studied *via* UV-visible absorption spectroscopy (Fig. 3a). The slot-die coated films showed an increased light absorption compared to the spin-coated films. This increase in intensity could be due to the butylamine evaporating more quickly during slot-die coating, as the printing head and bed were both heated, allowing more material to be deposited on the substrate. This was confirmed using profilometry, with spin-coated films having a thickness of 25 nm and slot-die coated films having a thickness of 32 nm (Fig. S3 and S4, ESI†). However, we note that it was not possible to resolve thickness data for films made at a PBI-Y concentration of 0.5 mg mL⁻¹. Therefore, the above data is for films made from a PBI-Y concentration of 5 mg mL⁻¹, but we would expect the same trend to be observed at lower concentrations. The peak ratios at 510 and 545 nm (attributed to the 0–0 and 0–1 vibronic bands of the S₀–S₁ transitions) can determine whether you have H-type of J-type aggregates present in the film.^{34,37,38} For both spin- and slot-die coated films, this peak ratio was very similar, suggesting a similar molecular packing of the PBIs regardless of coating method (Fig. 3a). AFM was used to investigate the surface of glass/ITO/SnO₂/PBI-Y film formation and, consequently, the surface modification of SnO₂ before and after deposition of PBI-Y (Fig. 3b). The root-mean-square (RMS) roughness values of SnO₂-only films are 1.4 and 1.1 nm for spin-coated and slot-die coated films, respectively. In both films, the presence of PBI-Y leads to a smoother surface, with an RMS value of 1 nm for spin-coated films and 0.9 nm for slot-die coated films.

PBI-Y film solvent resistance

As previously mentioned, solvent resistance is crucial when developing multi-layered devices. However, forming solvent resistant films of conjugated materials from green solvents is challenging. To test the films' solvent resistance, we exposed the glass/ITO/SnO₂/PBI-Y films to organic solvents commonly used in orthogonal processing (*o*-xylene, ethanol, and water) (Fig. 4). The films were inspected visually (Fig. 4a), and UV-visible spectra were collected to assess the film quality (Fig. 4b). All films showed no significant dissolution, swelling, cracking or dewetting. Only with water did we observe a slight decrease in the absorption of the film, with those dipped in *o*-xylene and ethanol giving identical spectra to the undipped film. Welch *et al.* have previously reported solvent resistant films from an N-annulated perylene bisimide (PDIN-H).³⁹ However, these films showed a change in absorption profile upon the addition of *o*-xylene, a common solvent used for processing photoactive layers.^{14,40,41} The solvent resistance of the PBI-Y films is likely due to the strong intermolecular hydrogen bonding between the amino acid carboxyl groups of adjacent molecules. Furthermore, the π–π stacking plays an important role in inducing more favourable aggregation and decreased solubility, allowing the films to be resistant in both polar and non-polar solvents. When designing solvent-resistant films, it is common for a post-treatment stage to be used postdeposition to generate this resistance.⁴² Such methods require either putting energy into the system using heat⁴³ or UV light⁴⁴ or by using chemical reagents.⁴⁵ However, here we present a way to make solvent resistant and uniform films without the need for such treatment.

Spin-coated organic solar cell devices

First, we optimised our OPV devices using spin-coating. A device architecture of glass/ITO/SnO₂/ETL/PM6:Y6C12/MoO_x/Ag was utilised to validate the film formation and performance of PBI-Y cathode interlayers in OPVs. We chose PM6/Y6C12 as our photoactive layer as we have previously

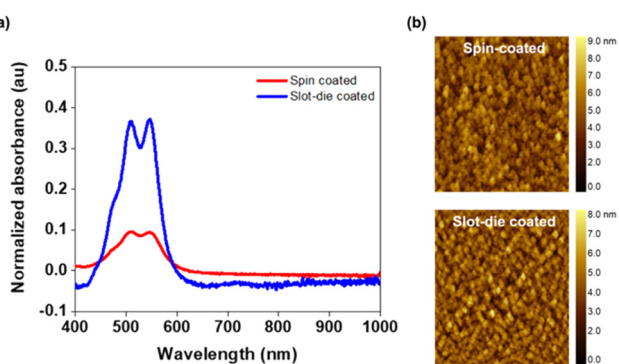


Fig. 3 (a) Absorption spectra of spin-coated and slot-die coated SnO₂/PBI-Y films. (b) AFM images of spin-coated (top) and slot-die coated (bottom) SnO₂/PBI-Y films. All films were cast at a concentration of 0.5 mg mL⁻¹, in air and at room temperature.

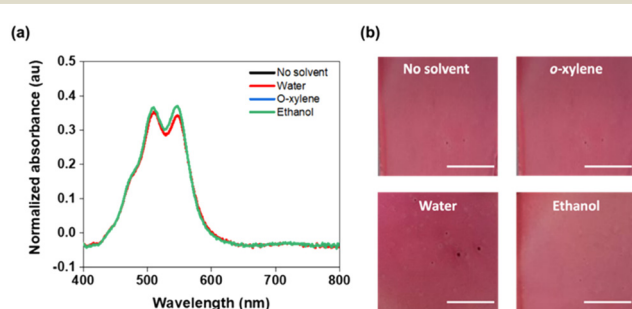


Fig. 4 (a) Optical absorption spectra and (b) photographs of 1.5 cm × 1.5 cm of glass/SnO₂/PBI-Y films with no solvent and films dipped in water, *o*-xylene and ethanol for 15 seconds and then removed and left to dry. All films were spin-coated at a concentration of 0.5 mg mL⁻¹, in air and at room temperature, onto glass substrates. The scale bar represents 1 cm.



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