

Domain-like ultra-thin layers deposited electrochemically from carbazole-functionalized perylene bisimides for electron collection in inverted photovoltaic cells†

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Domain-like ultra-thin layers deposited electrochemically on an ITO electrode from perylene bisimide derivatives are found to improve the electron collection effectively in inverted photovoltaic cells.

The electrode modification thin layers in organic photovoltaics (OPVs) play an important role in the improvement of the power conversion efficiency (PCE) due to the proper energy level alignment for efficient charge collection, which have attracted more and more attention in the past years.^{1–3} Whilst during the multiple-layered device fabrication process the problem of the destructive effect from the subsequent solution procession to the electrode modification thin layer must be seriously considered, and usually this problem is solved either by creating an insoluble thin layer through *in situ* chemical cross-linking⁴ or by using solvent-selective insoluble surfactant polymers.^{3,5,6} However, these methods suffer from the accompanying penalty of either incomplete cross-linking reaction or poor morphological modulation. Electrochemical polymerization (ECP) of monomers bearing multiple electro-active groups has been proved to be an effective method to create insoluble films on the electrodes through electrochemical cross-linking reaction, which have the convenience of modulating the film thickness through controlling the total amount of charge passing through the cell.^{7,8} The morphology study of the thin layer electrochemically deposited on ITO showed that island-like domains were formed readily on ITO in the first stage of the polymerization, and further characterization results indicated that the cross-linking reaction was almost completed when carbazole groups were used as the electro coupling units, as investigated in our previous work.⁹

The domain-like surface of the modified electrode may increase the contact of the electrode and the active layers, which predicts that the ECP may be a nice method for the ITO electrode modification.

OPV devices having inverted architecture possess several advantages over their more common conventional counterparts, such as avoiding usage of a problematic ITO/PEDOT:PSS interface^{10,11} and applying air-stable, high-work-function metal electrodes *etc.*,^{12,13} which have been achieved by using n-type materials like ZnO^{14,15} to modify ITO and thus to collect the electrons. Perylene bisimides (PBIs) are attractive n-type organic semiconductors showing high electron affinity due to the electron withdrawing effect of four carbonyl groups in the molecule structure,^{16–18} which indicates the possibility of using these as electron collection materials in inverted OPV devices. In this communication, we report the perylene bisimide based domain-like ultra-thin layers cross-linked using the ECP method that are suitable for a further solution process to make multiple-layer organic electronic devices. This domain-like ultra-thin layer is applied as the electron collection layer in the inverted polymer photovoltaic cell and improved device performance has been achieved.

Perylene bisimide **1** bearing two bay-area 4-*t*-butyl-phenoxy substituents and four peripheral carbazole groups (Fig. 1a, left) was synthesized *via* two fold Suzuki coupling reaction as shown in Scheme S1 (ESI†),^{19–21} which was fully characterized by ¹H and ¹³C NMR, MS, and elemental analysis. One of the features of the molecular structure is that the perylene bisimide core is isolated with the peripheral carbazole units through long alkyl chains, which ensures their independent functions as revealed by the totally independent absorption spectra (Fig. S1, ESI†). The investigation of the redox properties of compound **1** showed that the onset and peak potentials of oxidation of carbazole units are 0.87 and 0.96 V (*vs.* Ag/Ag⁺), while the oxidation of the perylene bisimide core occurs at a more positive potential of 1.10 V (*vs.* Ag/Ag⁺), as shown in Fig. S2 (ESI†), demonstrating that the perylene bisimide core will not be affected during the ECP process within the potential range of –0.50 to +0.90 V as discussed below.

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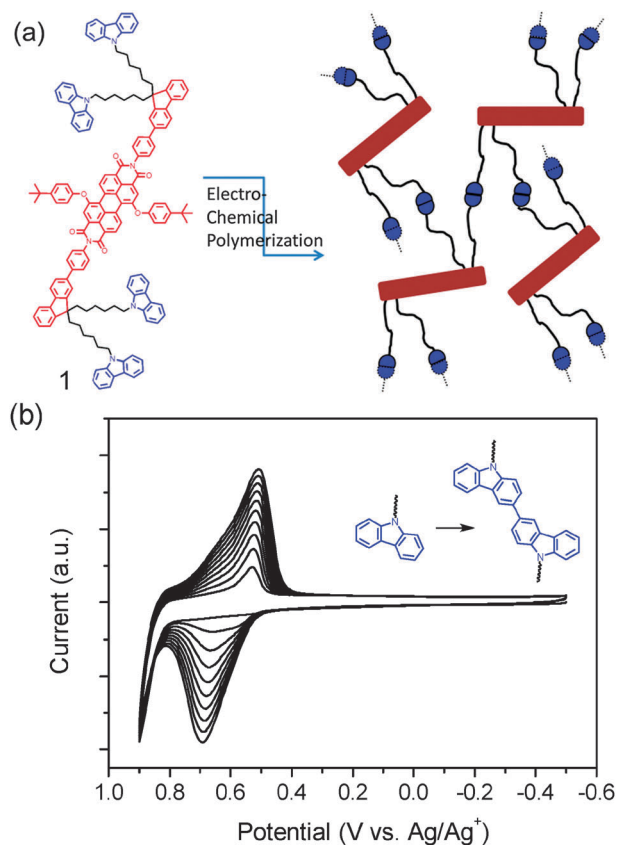


Fig. 1 (a) The chemical structure of perylene bisimide **1**, and the schematics of the ECP process. (b) Cyclic voltammogram for electrochemical polymerization under conditions such as: 0.8 mg mL^{-1} **1**, 0.1 M TBAPF_6 , scanning potential region -0.50 to $+0.90 \text{ V}$, mixed solvents $V_{\text{CH}_2\text{Cl}_2} : V_{\text{CH}_3\text{CN}} = 3:2$, scanning rate 200 mV s^{-1} . The inset shows the electrochemical coupling of carbazole.

ECP of perylene bisimide **1** was performed on the ITO electrode in the mixed solvent of dichloromethane and acetonitrile ($V_{\text{CH}_2\text{Cl}_2} : V_{\text{CH}_3\text{CN}} = 3:2$). The maximum of the potential was controlled to be $+0.90 \text{ V}$ that is high enough to form a carbazyl radical cation but still lower than the oxidation potential of the perylene bisimide core, in order to avoid the oxidation of the perylene bisimide unit during the polymerization process. As shown in Fig. 1b, there is a reductive signal at 0.53 V (vs. Ag/Ag^+) in the reverse scan from positive to negative potential, which is attributed to the reduction of dimeric carbazole cations to the neutral state as discussed in our previous publications.⁸ The dimeric carbazole is obtained from the coupling reaction between carbazyl radical cations and the resultant polymeric products are deposited on the electrode, which is confirmed by the appearance of a new oxidation signal at 0.66 V (vs. Ag/Ag^+) during the second cyclic voltammetry scanning. The peak current increased in the successive scanning cycles, indicating that more and more dimeric carbazole units are present on the surface of the electrode. Because there are four electroactive carbazole groups, a film with cross-linked structure of compound **1** formed through linkage of carbazole units (Fig. 1a).

The morphology evolution of the ultra-thin layers on ITO in initial several ECP cycles was monitored using atomic force microscopy (AFM) and the height images are shown in Fig. 2.

Firstly, domain-like particles with a size of $\sim 45 \text{ nm}$ and a height of $10\text{--}20 \text{ nm}$ were electrochemically deposited on the surface of the ITO electrode, which partially covered the ITO electrode (Fig. 2a and d). Upon increasing the scanning cycles, the amount of the domain-like products is increased obviously and they cover more and more of the ITO electrode surface gradually, but the size of each particle does not increase (Fig. 2b and c). Compared with the morphology of bare ITO (Fig. S3, ESI[†]), the domain-like particles resulted from the ECP of perylene bisimide **1**. The domain-like ultra-thin layer has rough surface morphology that may increase the interface contact between this layer and the active layer in the OPV devices, which will be favourable for the charge collection as discussed in the next section.

The domain-like ultra-thin layers electrochemically deposited on ITO have rough surface morphology and could not be dissolved in organic solvents (Fig. S4, ESI[†]), facilitating the subsequent solution process of the polymeric active layer. The work function of the ECP thin layer modified ITO was determined using ultraviolet photoelectron spectroscopy (UPS) (Fig. S5, ESI[†]) to be 4.0 eV , which is about 0.8 eV lower than that of bare ITO. Considering the very low work function and good light transmission properties (Fig. S6, ESI[†]), we fabricated inverted OPV cells using the modified ITO as the composite anode, in which the domain-like ultra-thin layers are used to collect electrons from the active layers. The device structure was an ITO/ECP thin layer (X cycles)/PCDTBT:PC₇₁BM (90 nm)/MoO₃ (10 nm)/Al (100 nm) (Fig. 3a), where PCDTBT was poly[*N*-9'-heptadecan-2,7-carbazole-*alt*-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] and PC₇₁BM was [6,6]-phenyl C₇₁ butyric acid methyl-ester, and MoO₃/Al was used as a hole collecting electrode. The density of the ECP domains on ITO was tuned by controlling the electrochemical scanning cycles, namely $X = 0, 3, 5, 7$ for different devices, and $X = 0$ means that there was no domain-like thin layer in the device, which was also fabricated as a reference. The energy level alignment in the inverted device is given in Fig. 3b.

Fig. 3c presents the J - V curves of the devices under 56 mW cm^{-2} air mass 1.5 global (AM 1.5 G) illumination, and detailed data for open-circuit voltage (V_{OC}), short-circuit current (J_{SC}),

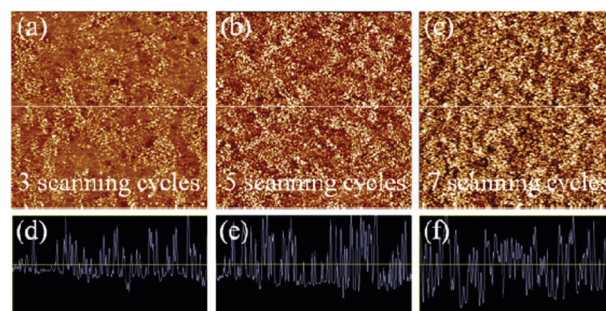


Fig. 2 (a-c) AFM height images of the ECP layers with different scanning cycles as indicated in the images. The size of the images is $5 \mu\text{m} \times 5 \mu\text{m}$, and the Z scale for all the three images is 30 nm . (d-f) The cross-section corresponding to the lines in a-c. The ultra-thin layers were prepared using the ECP method under conditions such as: 0.5 mg mL^{-1} **1**, 0.1 M TBAPF_6 , scanning potential region -0.50 to $+0.90 \text{ V}$, mixed solvents $V_{\text{CH}_2\text{Cl}_2} : V_{\text{CH}_3\text{CN}} = 3:2$, scanning rate 400 mV s^{-1} .

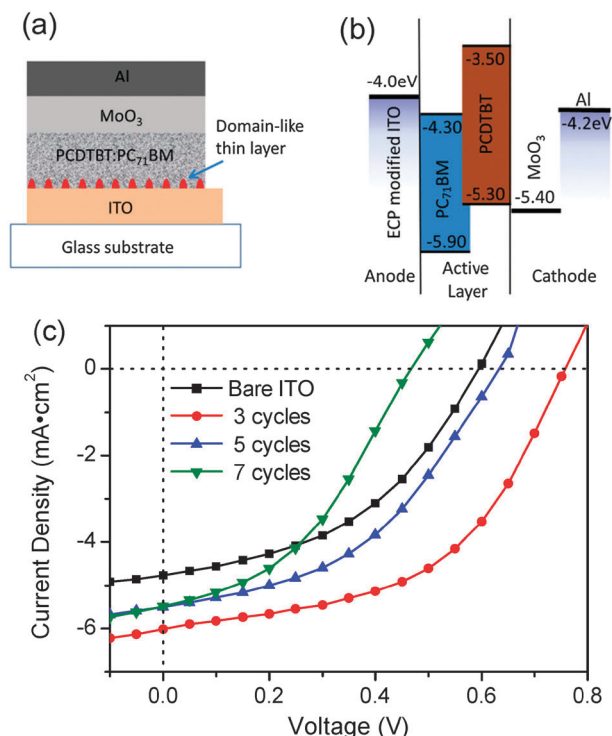


Fig. 3 (a) The inverted device structure of ITO/ECL/PCDTBT:PC₇₁BM (90 nm)/MoO₃ (10 nm)/Al (100 nm). As for the ECL, the density of the domains on ITO was tuned by controlling the electrochemical scanning cycles. (b) The HOMO–LUMO energy diagram of inverted OPV cells. (c) *J*–*V* characteristics of OPVs with different density of domains on ITO as ECLs (different scanning cycles). The data were recorded under 56 mW cm^{−2} air mass 1.5 global (AM 1.5 G) illumination.

Table 1 The device performance of inverted OPVs with the structure of ITO/ECL (X scanning cycles)/PCDTBT:PC₇₁BM (90 nm)/MoO₃ (10 nm)/Al (100 nm) (data were recorded under 56 mW cm^{−2} air mass 1.5 global (AM 1.5 G) illumination)

CV scanning cycles	<i>V</i> _{OC} (V)	<i>J</i> _{SC} (mA cm ^{−2})	FF (%)	PCE (%)
0	0.59	4.78	43.37	2.35
3	0.76	6.02	51.01	4.15
5	0.63	5.50	42.87	2.76
7	0.46	5.49	42.14	1.88

fill factor (FF) and power conversion efficiency (PCE) are included in Table 1. The best performance comes from the device that possesses domain-like ultra-thin layers of 3 scanning cycles as electron collection layers, with a PCE of 4.15%, an *V*_{OC} of 0.76 V, a *J*_{SC} of 6.02 mA cm^{−2} and a FF of 51.01% tested under 56 mW cm^{−2} illumination, which is much better than the device without the perylene bisimide domain-like ultra-thin layers (with a PCE of 2.35%).²² We also noted that with the increasing scanning cycles that is more domains on ITO, all three factors *V*_{OC}, *J*_{SC} and FF decreased in the OPV devices, resulting in an obvious drop in the PCE, which may be attributed to the lower conductivity of the chemically cross-linked domains according to the electrochemical impedance spectroscopy (EIS) measurement (Fig. S7, ESI†). Our primary device results indicate that the domain-like ultra-thin layer of n-type perylene bisimide can be used to modify the ITO electrode and act as an electron collection layer in the inverted OPV devices. Highly efficient inverted OPV cells are expected to be achieved by further device fabrication optimization.

In summary, domain-like ultra-thin layers were created on ITO by electrochemically cross-linking carbazole-functionalized perylene bisimides, which were successfully applied in the inverted organic photovoltaic cells to collect electrons from the active layers. The ECP method was proved to be a simple and effective method to prepare cross-linked insoluble ultra-thin layers that are suitable for further solution process of multiple layered devices; increased power conversion efficiency was achieved by using perylene bisimide derivative based domain-like ultra-thin layers as electron-collection layers in inverted polymer solar cells. Further investigation of the perylene bisimide based cross-linked layers on optoelectronic devices is still underway.

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