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Reducing delamination of an electron-transporting polymer from a metal oxide for electrochemical applications

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Delamination of the electron-transporting polymer N2200 from indium tin oxide (ITO) in aqueous electrolytes is mitigated by modifying ITO with an azide-functionalized phosphonic acid (PA) which, upon UV irradiation, reacts with the polymer. The optical, electrochemical, and spectroelectrochemical properties of N2200 thin films are retained in aqueous and non-aqueous media.

Electroactive electron-transporting π-conjugated polymers, such as poly{[*N*,*N*′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5′-(2,2′-bithiophene)} (N2200 or P(NDIOD-T2), Fig. 1a) have been increasingly investigated as non-fullerene acceptors in blended heterojunction organic solar cells, as semiconductor active layers for photoelectrochemical generation of hydrogen, and as redox-active polymers for electrochemical energy storage.[1–3] Efficient energy generation and energy storage require that both electron-transporting and hole-transporting polymers form ohmic, energetically aligned, and chemically/mechanically robust interfaces with contacting electrodes – often metal oxides such as indium-tin oxide (ITO) – and/or electrolyte solutions, without introduction of mid-gap states that lead to recombination and/or loss of electric field gradients needed to drive charge separation and migration. Especially in cases when charge injection or harvesting is accompanied by uptake of counter ions needed to maintain electroneutrality from aqueous or non-aqueous electrolytes, there may be micro-structural changes within the polymer film that result in loss of mechanical and/or optoelectronic integrity and even delamination. Here we demonstrate an approach to reducing delamination via photochemical covalent tethering using a molecule (Azido PA, Fig. 1a) incorporating both the phosphonic acid functionality, which is known to bind strongly to metal oxides,[4] and the photoreactive azide group, which is known to photolyse to form a nitrene that inserts into C–H bonds.[5]

Fig. 1b illustrates a general challenge when interfacing a hydrophobic, low dielectric constant conductive polymer with a hydrophilic metal oxide support for the specific case of thin (100 nm) N2200 films on ITO. Fig. 1b shows voltammetric reduction in three different aqueous electrolytes (0.1 M KCl/HCl pH = 3; 0.1 M KCl pH = 7; 0.1 M KCl/NH_4OH pH = 11). The appearance of these voltammetric responses results from a combination of Faradaic (charge injection) events, and ion displacement associated with movement of counter ions into the thin film to retain electroneutrality, as well as the presence of two successive reductions expected for materials based on naphthalene diimides (NDIs). Importantly, reduction was accompanied by loss of film integrity and delamination (photographs in Fig. 1b; see †ESI for details).

The loss of mechanical properties/delamination during these voltammetric charge injection events (Fig. 1b) motivated us to examine approaches to stabilizing the ITO/N2200 interfacial region by modifying the ITO with phosphonic acids (PA), which are known to form strong covalent bonds to metal oxides (confirmed in the present cases by XPS, Fig. S8, ESI) and can be used to modify surface hydrophilicity/hydrophobicity and work function, and to add selective redox activities to the ITO surface.[4] Moreover (2-((4-azido-2,3,5,6-tetrafluorobenzoyl)oxy)ethyl)phosphonic acid (Azido PA, Fig. 1a) potentially enables covalent tethering of the polymer to the electrode; azide groups are known to be photolyzed to reactive nitrenes that can insert into polymer C–H bonds.[5] Benzylphosphonic acid (BPA) and azide PA modifiers allowed us to investigate the impact of different treatments on the physical properties of N2200/ITO interfaces and their resistance to both

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x delamination in aqueous electrolyte and dissolution in 1,2-dichlorobenzene (oDCB, from which the films were deposited). In each case N2200 was spin-coated onto the modified ITO; in the case of Azido PA-modified ITO, 254 nm UV was subsequently applied from the ITO side (shown schematically in Fig. 1c).

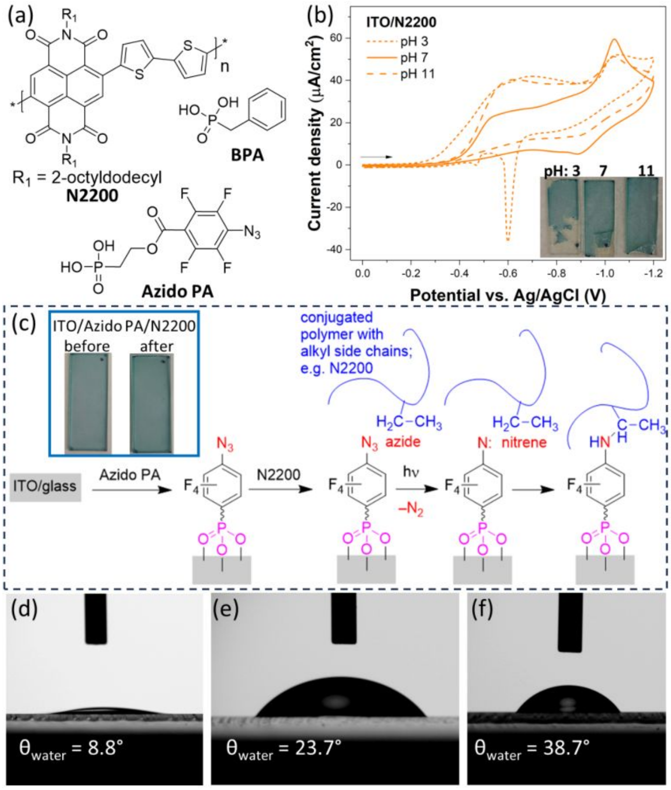

Fig. 1. (a) Chemical structures of the polymer and PA derivatives; (b) cyclic voltammograms of ITO/N2200 (100 nm) in different pH with scan rate of 25 mV/s (plotted using the American convention); inset are the photographs of N2200 films on UV-ozone treated ITO showing delamination of polymer after 1st cycle in different pH; (c) schematic showing the preparation of Azido PA modified ITO, and the subsequent surface photoinduced tethering of N2200, inset is the photograph of N2200 photo-tethered on Azido PA modified ITO showing no signs of delamination after aqueous electrochemistry at pH 3; water contact angles on (d) ITO (UV-ozone treated), (e) ITO/BPA and (f) ITO/Azido PA.

Importantly, BPA and Azido PA modification, both with without UV exposure, lead to reduced delamination of N2200 (shown in the inset of Fig. 1c for UV exposed films on Azido PA). We speculate that as the potential becomes increasingly negative, electrolyte cations (K^+ in our experiments) are drawn into the film, so that these ions, and associated water molecules and perhaps counterions, penetrate between the film and unmodified ITO, weakening the polymer:ITO interaction and ultimately resulting in delamination of the entire film in case of unmodified ITO. The water contact angles on the unmodified and PA-modified ITO surfaces (Fig. 1(d-f); see also Table S1 and Fig. S9, †ESI) indicate that BPA- or non-irradiated Azido PA-modified surfaces are less hydrophilic surfaces than the UV-ozone treated ITO and, thus, may inhibit the electrolyte ingress between the polymer and the ITO, while in the case of irradiated Azido PA the expected covalent tethering and reduced hydrophilicity presumably both play a role.

The surface modifications also have an impact on the dissolution of polymer films in a good solvent for N2200, specifically oDCB at 160 °C. Interestingly, N2200 deposited on UV-ozone treated ITO, even after dipping in hot oDCB, exhibited an absorbance in the visible spectrum, indicative of retention of ca. 20% of the N2200 on the surface (Table 1, Fig. S10a, †ESI). On the other hand, in the case of either PA without UV exposure, the N2200 was nearly completely removed from the surface under the same conditions, suggesting that N2200 interacts more strongly with bare ITO than the organic-modified (non-photoirradiated) surfaces, perhaps due to hydrogen bonding to surface hydroxyl groups. In contrast, a N2200 film on the azido functionalized surface after UV exposure and solvent washing exhibited about 2-3 times the absorbance of that of a washed polymer film on UV-ozone treated ITO (Fig. S10a, †ESI), indicating better N2200 retention, consistent with the expected covalent tethering chemistry. We extended this photo-tethering approach to another electron-transporting polymer, a side-chain polymer that we have previously reported[9] (Fig. S11a, †ESI), and also observed improved solvent resistance (Fig. S11(b,c), †ESI).

Table 1. Summary of observations from different studies on surface modified ITO.

Surface treatment	Delamination in aq. Electrolyte[a]	oDCB resistance[c] (% retention)	Electrochemical Activity[d]
ITO (UV-O_3)	Yes	19%	limited[e]
ITO/BPA	No[b]	<2%	Yes
ITO/Azido PA	No	<9%	Yes
ITO/Azido PA and UV light	No	52%	Yes

[a] Determined by visual inspection of the N2200 films and from UV-vis spectra on unmodified ITO and for surface modified electrodes in aqueous medium for pH 3, 7 and 11 before and after cyclic voltammetry (see main text). [b] For pH 3, ITO/BPA/N2200 films showed delamination during the reduction cycle (see main text). [c] Determined by comparing the absorbance change of N2200 films (10 nm) on the unmodified and PA modified substrates at 700 nm before and after the solvent wash. [d] The electrochemical activity of the N2200 films on unmodified and PA modified ITO upon cycling up to -1.2 V vs. Ag/AgCl in aqueous (pH 3, 7 and 11) and non-aqueous media (acetonitrile) with the film retained post-electrochemistry. [e] The ITO/N2200 films delaminated during the first cycle in all three of the pH values examined as shown in Fig. 1b.

We characterized the effect of the PA modification and UV exposure on the adhesive and cohesive properties of N2200 on a sputtered ITO surrogate film on glass (with a higher than normal Sn:In ratio of ca. 1:1). We measured the fracture energy, G_c, using the double cantilever beam (DCB) method (Table S2, Fig. S13, †ESI). We measured pristine and UV-exposed specimens under various conditions and found that the G_c values were quite similar (~3 J m^{-2}) in all conditions. XPS measurements were conducted on opposing surfaces of each sample stack after fracture to identify the interface of fracture (Fig. S14,15, †ESI). In samples on bare oxide and BPA-treated oxide, Sn and In peaks could be identified on the "bottom" surface of the fractured sample. This was not the case for the samples on Azido PA where Sn and In peaks were much weaker or missing and, in contrast, a Si peak was observed; these observations may indicate a greater level of cohesive failure relative to adhesive failure consistent with the N2200 being covalently tethered to the surface, but more detailed studies are required to draw definitive conclusions.

While the above-mentioned experiments were based on visible absorption spectra, which clearly indicate that intact N2200 remains on the ITO following certain treatments, they do not indicate whether the polymer is still in electrical contact with the electrode itself nor how the electrochemical and optoelectronic properties of the N2200 films have been modified by the surface treatments. To examine this question, we performed (spectro)electrochemistry of N2200 films on modified substrates at pH 3, 7 and 11 using KCl as electrolyte. The cyclic voltammograms of the differently treated films resulted in a similar set of reduction peaks negative of -0.6 V albeit with different current densities for the different surface modifiers (Fig. 2a and Fig. S10b, c).

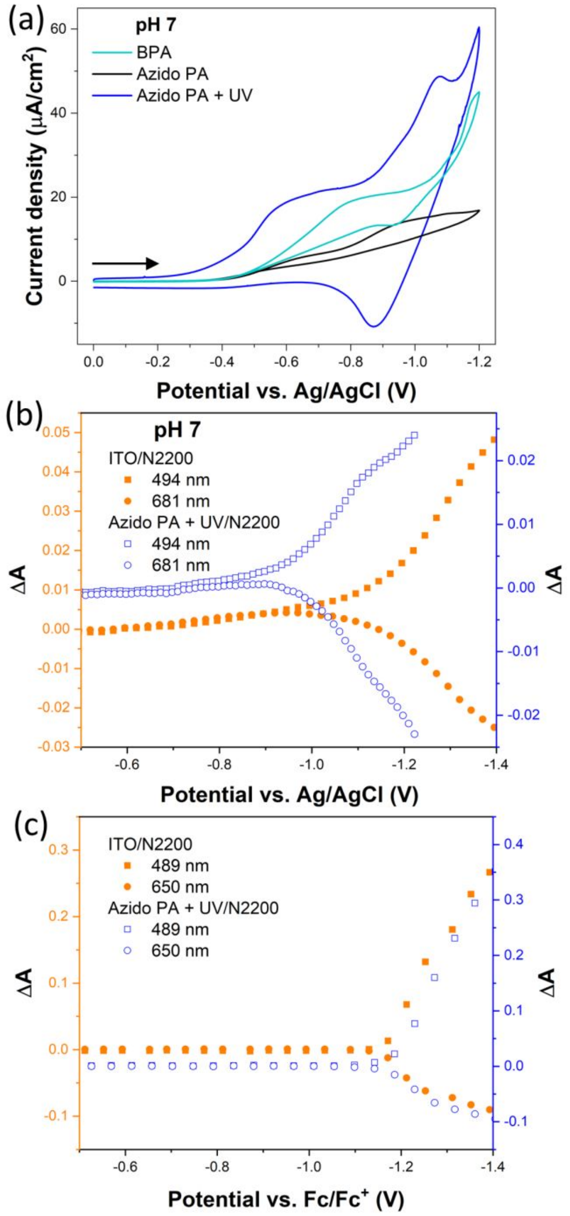

Fig. 2. (a) Cyclic voltammograms of 100 nm N2200 on BPA, Azido PA modified ITO, and Azido PA modified and photo-tethered in pH 7 0.1 M aq. KCl; (b) the evolution of polaronic peak of N2200 at 494 nm and ground state bleach at 681 nm with respect to applied potential obtained from spectroelectrochemical experiment in pH 7 0.1 M aq. KCl; (c) the evolution of polaronic peak of N2200 at 489 nm and ground state bleach at 650 nm with respect to applied potential obtained from spectroelectrochemical experiment in 0.1 M Bu_4NPF_6 in acetonitrile.

In all the cases of N2200 films on PA modified ITO substrates, electrochemical behavior was consistent with the presence of electroactive N2200 addressable via the ITO. However, there are variations in the current densities and in the onset reduction potentials, the latter suggesting that the surface treatments affect the energetic landscape at the ITO:polymer interface, potentially in part via interface dipole effects (Table S1, †ESI), and suggesting the choice of surface treatment may affect the potentials at which the corresponding polymer films can be used in electrochemical applications. A feature unique to pH 3 (Fig. S10(b)) modified by BPA and non-irradiated Azido PA is the sharp oxidation peak at ca. -0.6 V which is one of the characteristic peaks of ITO degradation in acidic conditions.[6]

Spectroelectrochemistry of the N2200 films in aqueous electrolytes (Fig. 2b, Fig S16; full spectra shown in Fig. S17-19 †ESI) was further used to compare the different surface modifications, specifically by comparing the growth of a feature attributable to N2200 polarons (494 nm) and the bleach of the charge-transfer absorption band of the neutral polymer (681 nm) to indicate the onset of Faradic activity in the polymer films (the complete spectra are shown in Fig). At pH 7 (Fig. 2b) and 11 (Fig. S16b, †ESI) the UV-tethered N2200 on Azido PA is doped at a potential 100-200 mV less reducing potential than that needed for N2200 on unmodified ITO, but on the other hand at pH 3, the tethered film is doped at ca. 100 mV more reducing potential than the film on bare ITO (Fig. S16a). Importantly, N2200 on Azido PA modified with UV treatment shows no signs of delamination even after 50 cycles of cyclic voltammetry at pH 7 (Fig. S20a-c) indicating the photo-tethering approach to be the most viable of those examined here for preventing delamination of polymer films in aqueous media.

To further investigate the spectroelectrochemical behaviour of N2200 without conflation with changes specific to aqueous environments, we performed electrochemistry and spectroelectrochemistry in acetonitrile/0.1 M Bu_4NPF_6, which promotes considerably more swelling of the polymer as observed by the 5x increase in current density relative to samples examined in aqueous electrolytes. The N2200 film deposited on untreated ITO has sharp reduction and oxidation features (Fig. S21a, †ESI), consistent with previous reports.[7] The surface treatments modify these features to some extent, broadening both reduction and oxidation peaks for all films with treated ITO (Fig. S21(b-d)). These changes are also evident in the first cycle of the cyclic voltammogram, which is distinctly different from subsequent cycles for all four films, presumably due to irreversible changes from solvent and supporting electrolyte incorporation. Despite the broadening of N2200 electrochemical features in the treated films, the redox features are similar to those of the untreated film and onsets of doping are very similar potential (Fig. 2c). Furthermore, the absorbance and wavelengths of the optoelectronic signatures of reduced N2200, including both polaron ($NDI^{\bullet -}$) and bipolaron (NDI^{2-})

species,[8] are unchanged between untreated N2200 and N2200 with the introduction of a surface modifier (Fig. S22, †ESI).

In summary, we have found that treatment of ITO with either BPA or an azide-functionalized PAs inhibits delamination of N2200 in aqueous electrolytes, but neither, in the absence of UV irradiation, prevents dissolution of the polymer in oDCB. On the other hand, the use of the Azido PA with UV irradiation after deposition of the polymer film improves resistance to *both* organic solvent and aqueous electrolyte. These films are particularly resistant to delamination; we have demonstrated that these tethered N2200 films can be electrochemically cycled at least 50 times in a pH 7 aqueous electrolyte with no observable delamination, opening the door for further more application-related studies.

Other approaches to covalent tethering of electroactive polymers to electrodes for applications where polymers need to exhibit either/both resistance to delamination or/and solvent resistance (e.g., when depositing multiple polymer layers) have been reported. For example, both electropolymerization[9] and chemical polymerization[10] from surface bound-monomers or initiators have been widely used, but are not compatible with all polymerization chemistry and require different monomers or initiator molecules for different polymers. Similarly, grafting of polymers through, for example, “click” reactions with surface-bound functionalities[11] requires the synthesis of telechelic polymers. In an approach somewhat similar to ours a surface-bound epoxide is reported to react with the sulfonate groups of PEDOT:PSS, but is likely limited in scope to polymers bearing nucleophilic groups capable of reaction with epoxides.[12] In contrast to these previous approaches, the azido PA approach is anticipated to be rather general since C–H bonds are present in most electroactive polymers – indeed we have already demonstrated its application here for two very different electron-transport polymers – although conversely of course it will not be applicable to polymers with few or no C–H bonds. Additional studies to investigate the scope and limitations of both simple-PA modification and tethering via azido PA are in progress.

Author Contributions

Conceptualization – SRM; funding acquisition and supervision - ADP, MFT, ELR, NRA, ALG, SB, SRM; investigation - AAM, WKY, YZ, AAS, JT, CMD, DPM, ALG; writing - original draft - AAM, SB, SRM; writing - review and editing - all authors.

Conflicts of interest

There are no conflicts to declare.

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