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## Synthesis and Use of a Hyper-Connecting Cross-linking Agent in the Hole-transporting Layer of Perovskite Solar Cells

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## Synthesis and Use of a Hyper-Connecting Cross-linking Agent in the Hole-transporting Layer of Perovskite Solar Cells

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#### Abstract

Solution-processed organic semiconducting materials feature prominently in modern optoelectronic devices, especially where low-cost and flexibility are specific goals, such as perovskite solar cells. Their intrinsic solubility, poor cohesion and lack of adhesion to underlying substrates, however, curtail their scope of application and durability. To overcome this, a mechanically stiff, light-activated, tetra-azide cross-linking agent, 1,3,5,7-tetrakis-(pbenzylazide)-adamantane (TPBA), has been developed to transform solution processed organic of polymers into solvent-resistant and mechanically tough films. The use 3azidopropyltrimethoxysilane (AzPTMS) has been developed as a light-activated adhesion promotor, enabling testing of toughened, cross-linked polymers. Lithium bis(trifluoromethane)sulfonimide (LiTFSI) poly[bis(4-phenyl)(2,4,6doped trimethylphenyl)amine, poly(triaryl amine) (PTAA), a hole-transporting material used in perovskite solar cells, has been selected as a candidate system for demonstrating the utility of TPBA to transform a fragile, and highly-soluble hole-transporting organic semiconductor into a mechanically tough and solvent-resistant semiconducting composite. TPBA enables the solvent resistance and mechanical toughness of PTAA to be tuned without compromising the electronic functionality of the semiconducting material. While increasing the fracture toughness of PTAA by over 300%, TPBA cross-linking also enables fabrication of perovskite solar cells with increased photovoltaic efficiencies in n-i-p and p-i-n geometries, and promotes adhesion of the doped polymer to the perovskite layer, mitigating interfacial device failure.

#### Introduction

Solution processed semiconducting organic polymers are used in several promising electronic and optoelectronic technologies as charge-transporting layers<sup>1-4</sup>, light-absorbing photovoltaic materials<sup>5,6</sup> and as electroluminescent materials<sup>7-10</sup>. Moreover, solution-state deposition techniques compatible with roll-to-roll printing,<sup>11,12</sup> such as slot-die coating, shear coating<sup>13,14</sup>, and ink-jet printing<sup>15,16</sup> present the opportunity for low-cost, high-throughput fabrication of flexible electronic devices<sup>17</sup>.

A challenge limiting the scope of solution processed flexible electronic technologies is their inherent solubility once deposited, rendering them susceptible to etching or complete dissolution by the solvents of subsequent deposition steps<sup>18-20</sup>. Consequently, the fabrication of multilayer devices by solution processing is severely limited. The fabrication of solutionprocessed, p-i-n perovskite solar cells is a particular example of this limitation. In these devices, the ability of solution processed organic hole transporting layers to resist etching or complete dissolution during the deposition of the perovskite layer (which frequently require the use of aromatic anti-solvents) heavily influences the performance of the resulting devices.

Along with solvent resistance, the mechanical resilience of these layers is important for ensuring a high yield in fabrication, a strict requirement for low-cost devices, and reliability, ensuring performance lifetimes, which in the case of solar cells, may be 2-3 decades. The cohesion energy,  $G_c$ , of solution processed semiconducting polymer layers are often low, typically below ~ 5 J/m<sup>2 21,22</sup> as was the case of organic polymer photovoltaics, the predecessor to perovskite solar cells as a solution-processed, low-cost solar technology, which encountered significant reliability challenges and were generally regarded as being thermomechanically fragile <sup>23</sup>.

The fragility of solution processed semiconducting polymers stems from the low density of covalent bonding within these materials. When meaningful interactions between constituent polymer strands in these types of materials do not exist, such as  $\pi$ -orbital overlaps or hydrogen bonding for example, the degree to which energy-dissipating mechanism like plastic deformation ahead of an advancing crack tip may be engaged is restricted, lowering the barrier to critical fracture propagation. Increasing the MW of polymers, allowing for increased interactions and entanglements per strand, can effectively increase the cohesion of a layer<sup>24</sup>. This strategy for increasing polymer cohesion, however, requires that polymer solubility can be maintained during

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synthesis to achieve these higher molecular weights. Similarly, the absence of covalent chemical bonding and interactions at the interfaces of these organic semiconducting layers has resulted in some of the lowest values for adhesive fracture reported for electronic devices<sup>25</sup>.

A survey of the critical fracture energy,  $G_c$ , an essential indicator of thermomechanical reliability<sup>26</sup>, of perovskite solar cells highlights how their development within the academic research environment to increasingly higher efficiencies has occurred at the expense of the mechanical integrity of the devices<sup>22</sup>. In this work, we demonstrate that this need not be the case, and that increases in efficiency can be achieved in the pursuit of thermomechanical stability.

Imbuing solution-processed semiconducting polymers with increased resistance to fracture and dissolution following deposition, will enable fabrication of a new variety of robust, solution-processed polymer devices, increasing both their manufacturability and reliability. Generating covalent cross-links within polymers following solution-state deposition is a simple strategy to achieve this. In the case of semiconducting polymers, cross-linking can be achieved by redesigning the polymer to feature cross-linking chemical functionalities<sup>8,27</sup>, or more simply, by addition of a molecular cross-linking agent<sup>28-30</sup>. The latter approach has the advantage of using existing semiconducting polymers, avoiding the development of complex new polymer-specific syntheses and purification protocols.

To date, aromatic azide cross-linking agents, like the sterically hindered bis(fluorphenyl azide) (sFPA), bis(4-azido-2,3,-trifluor-6-isopropylbenzoate) shown in **Fig. 1a**, have been successfully used in organic polymer solar cells for creating semiconducting-polymer heterostructures<sup>28</sup>, nanotemplated polymer donor network films,<sup>31</sup> and for controlling the morphology of P3HT domains in bulk-heterojunctions<sup>32</sup>. The covalent cross-links of azide cross-linking agents are formed via thermal or deep UV activation of the azide group, forming singlet nitrene radicals which proceed to insert into C-H bonds present on the polymer<sup>28,30-32</sup>.

Singlet nitrene radicals formed on activation of aromatic and alkyl azides have been studied extensively in the solution state via photolysis experiments<sup>33-35</sup>. These complex experiments often require indirect detection of reaction products due to overlapping signals in the transient spectra<sup>33</sup>, and highlight the wide variety of reaction pathways along which singlet nitrene radicals may proceed in the solution state, most of which do not result in C-H insertion reactions required for effective cross-linking.

However, in reporting the use of sFPAs in heterojunction polymer solar cells, Png *et al.* observed that C-H insertion of nitrene radicals polymers is the dominant outcome of azide activation in the solid state and that the quantum yield of known triplet and ketenimine side reactions were suppressed to < 0.02, well below the solution state values that typically range from 0.5-0.8 in the solution state<sup>28</sup>. This work indicates that direct comparisons of solution state photolysis and photochemical cross-linking in the solid state may not be made with confidence and that further work is required specifically studying the solid-state reactivity of activated azides.

Derue *et al.* expanded on the use of azide cross-linking agents presenting a simpler design strategy, departing from the sFPA design using a bis-benzylazide cross-linking agent, 4,4'-bis(azidomethyl)-1-1'-biphenyl (BABP) (**Fig. 1a**) and demonstrating that in addition to C-H insertion reactions, azides cross-linking agents can be used to stabilize the morphology of polymer:fullerene blends through selective, thermally-activated addition reactions with fullerenes forming azafulleroids and closed [6.6]aziridinofullerenes. In this work, neither fluorination of the aromatic ring nor the presence of sterically inhibiting substituents defining the design of sFPAs were required for effective cross-linking. In addition to the simplified chemical make-up and corresponding ease of synthesis of BABP, Derue *et al.* reported that in contrast to sFPAs, which are liquid at RT, the solid form of BABP resulted in increased stability enabling storage at RT<sup>30</sup>.

While the solid-state reactivity of azides in the solid state do exhibit very different quantum yields in comparison to those characterized in solution, which in the case of benzyl azide in particular, has proven to be a controversial area of research<sup>36-38</sup>, even in the solid state limited side reactions can be expected that would reduce the cross-linking efficiency. Consequently, a cross-linking agent featuring only two azide groups is rendered ineffective if just one of the nitrene radicals formed proceeds along a reaction pathway that does not result in C-H insertion. The cross-linking efficiency of azide cross-linking agents can therefore be increased simply by increasing the number of azide groups present on an agent. When four azide groups are present on a cross-linking agent, failure to achieve cross-linking requires three of the azides to proceed along reaction pathways that do not result in nitrene insertion, which is far less probable than a two-azide agent that only requires one to render the agent ineffective. The presence of more azides significantly increases the opportunity for creating points of hyper-

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connectivity within polymeric materials where more than two independent polymer strands may be cross-linked (**Fig. 1b**).

In this work, focused on addressing the poor mechanical stability of semiconducting polymers and their intrinsic solubility through development of a cross-linking agent capable of creating these nodes of hyper-connectivity, we have selected to use the chemical simplicity of benzyl azide cross-linking agents like BABP<sup>30</sup> to create 1,3,5,7-tetrakis-(*p*-formylphenyl)-adamantane (TPBA) shown in **Fig. 1a**. TPBA features four reactive benzylazide groups positioned on a tetrahedral, sigma-bonded adamantane core. The selection of the rigid adamantane core is three-fold. Firstly, the rigid core prevents benzylazide groups from bending back upon one another, preventing self-reaction of the agent. Secondly, regardless of the orientation of TPBA in a polymer blend, at least one cross-linking arm is always subtended with a in each of the three dimensions of space, preventing isotropic toughening of polymers. Finally, the sigma-bonded adamantane core is three-final may interfere with electronic orbitals of semiconducting polymers.

In this work, we present the synthesis of TPBA and demonstrate its utility as a crosslinking agent for systematically transforming the hole-transporting polymer used in some of the most efficient perovskite solar cells fabricated to date<sup>39,40</sup>, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine, poly(triaryl amine) (PTAA), into mechanically tough films, increasing their fracture resistance by 345% and significantly increasing their resistance to solvent etching.

Through our work investigating the fracture behavior of solution processed perovskite solar cells, cells featuring the PTAA HTM doped with LiTFSI (HTM) fractured adhesively at the d-PTAA/perovskite interface at  $G_c$  values well below 0.5 J/m<sup>2</sup> <sup>22</sup>. This doped PTAA employs roughly one LiTFSI molecule to every eight PTAA mers <sup>39,40</sup>, a significant quantity, prompting an investigation of the influence of LiTFSI on PTAA adhesion and cohesion. We report that LiTFSI significantly compromises the adhesion of PTAA to substrates, that it reduces the cohesion of this PTAA as a whole, and that TPBA cross-linking can be used to overcome this decrease in fracture energy.

In addition, to address the poor adhesive properties of semiconducting polymers and to enable the fracture testing featured in this work, we have further leveraged azide chemistry and report the use of a light activated adhesion promoter, 3-(azidopropyl)triemthoxysilane (AzPTMS) for covalently bonding organic materials to oxide substrates that react readily with trimethoxy organosilanes, like glass and silicon (**Fig. 2b**), a significant advance for promoting adhesion of solution processed organic materials to substrates.

#### Results

The synthesis of TPBA was achieved from 1,3,5,7-tetrakis-(*p*-formylphenyl)-adamantane (1) in three, simple, high-yielding steps as shown in **Fig. 2a.** All steps in the synthesis can be accomplished quickly providing multi-gram quantities of pure TPBA. This synthesis involves reduction of 1 to produce 1,3,5,7-tetrakis-(*p*-benzylalcohol)-adamantane (2) in 96% yield using NaBH<sub>4</sub>. Introduction of the bromine leaving-groups of 1,3,5,7-tetrakis-(benzylbromide)-adamantane (3) is achieved by reaction of 2 with PBr<sub>3</sub>. Finally, the azide functionality of TPBA is introduced by substitution of the bromine atoms using NaN<sub>3</sub>, affording TPBA in 86 % yield.

In this work, we employed a known, two-step synthesis to obtain large quantities of the precursor 1,3,5,7-tetrakis-(*p*-formylphenyl)-adamantane (1) for the synthesis of TPBA. Specifically, 1,3,5,7-tetraphenyladamantane (TPA) was obtained using the literature method reported by Reichert *et al*<sup>41</sup> utilizing an AlCl<sub>3</sub> promoted Friedel-Crafts arylation of 1-bromoadamantane with benzene in the presence of *tert*-butyl bromide. This method<sup>41</sup> affords large (> 20g) quantities of the benzene-functionalized adamantane core, 1,3,5,7-tetrakis-(phenyl)adamantane (TPA). Synthesis of 1, was achieved by a TiCl<sub>4</sub> promoted Rieche formylation of TPA with  $\alpha,\alpha$ -dichlomethyl-methylether utilizing the modification to a patent procedure reported by Duncan *et al*<sup>42</sup>. TPBA dissolves readily in a wide variety of chlorinated and aromatic solvents and does not exhibit absorbance in the visible region of the electromagnetic spectrum or result in changes in the absorption spectrum of PTAA films cross-linked with TPBA (**Fig. S12**). The high ratio of carbon to azide in the molecule, 9:1, satisfies the "rule of six"<sup>43</sup> reducing concerns related to potential explosive hazards related to the azide group.

An upper limit of 0.2 w.eq. was selected for the quantity of TPBA added to PTAA films in this work. 0.2 w.eg represents a larger that 10 % concentration. We regarded this a significantly large addition in a study focused on probing the efficacy of small additions of a potentially insulating agent to the semiconducting films. Films of PTAA containing increasing weight equivalents (0.01, 0.05, 0.1 and 0.2) of TPBA were deposited on silicon substrates by spin-coating and cross-linked by irradiation with UV-C (254 nm).ATR IR spectra revealed complete reaction of the azide groups within 10 min of irradiation (**Fig. S13**) with a hand-held UV lamp. To probe the influence of TPBA cross-linking on PTAA solvent resistance, films were dipped in toluene for 30 s. Films containing less than 0.1 weight equivalents of TPBA dissolved readily, while films containing 0.2 weight equivalents (PTAA- $X_{0.2}$ ) were significantly more resistant to dissolution by toluene (**Fig. S14**) with the presence of the film persisting on substrates tested.

#### Influence of LiTFSI doping on PTAA fracture

On increasing the concentration of LiTFSI in PTAA polymer films deposited on glass substrates from 0 to 0.15 molar equivalents (equivalent to PTAA monomeric units), we observed that the adhesion of PTAA to glass decreased by more than 90%, from 2.04 J/m<sup>2</sup> to only ~ 0.14 J/m<sup>2</sup> (**Fig. 3a**). We propose that with the increase of LiTFSI in the polymer film, interactions between the polymer and the substrate are increasingly inhibited by the presence of the TFSI anion and that the resulting decrease in contact of the polymer with the glass substrate reduces the adhesion at this interface.

Test structures of undoped PTAA deposited on perovskite exhibited failure within the perovskite layer at a  $G_c$  of ~ 0.5 J/m<sup>2</sup>, as shown in **Fig. 3b**. Again, addition of LiTFSI resulted in failure to occur at the interface of d-PTAA with a substrate, in this case, the perovskite. Here the two materials delaminated with a  $G_c$  of ~ 0.47 J/m<sup>2</sup>. By addition of 0.1 w.eq. and 0.2 w.eq. of TPBA to d-PTAA, this adhesive failure was inhibited, indicating that TPBA promotes adhesion of d-PTAA to the perovskite surface. A similar achievement has been reported<sup>44</sup> for perovskite cells using spiro-OMeTAD as the HTM through the use of polyethylenimine (PEI), but to date, has not been achieved for mitigating the delamination of d-PTAA from the perovskite surface. Advances required to mitigate the cohesive failure of the brittle perovskite layer further leverage TPBA and are reported elsewhere and which could not be achieved through the use of PEI.

If LiTFSI is found to decrease the cohesion of PTAA too, it would indicate that PTAA does not exhibit strong interactions with LiTFSI and so, enables a conclusion that the presence of

LiTFSI in PTAA and similar polymers would compromise their adhesion to other substrates regardless of the interaction between LiTFSI or the TFSI anion and a given substrate.

#### **AzPTMS adhesion promotion**

The poor adhesion of PTAA and d-PTAA to glass required a strategy for covalently bonding these films to the glass beams used in the double cantilever beam fracture test. This development would enable the cohesion of PTAA and the influences of LiTFSI doping and TPBA cross-linking on this cohesion to be measured. To date AzPTMS (**Fig. 2b**) has been used to functionalize a variety of substrates with azide groups to enable surface functionalization via "click chemistry" reactions<sup>45-47</sup>. To date, the use of AzPTMS functionalized substrates for promoting adhesion through solid state thermal or deep UV activation of the azide groups has not been investigated.

AzPTMS functionalized glass beams were prepared according to the scheme shown in **Fig. 2b**. Covalent bonding of films deposited on AzPTMS-functionalized substrates were activated by UV-C irradiation to generate reactive nitrene radicals, which readily insert into C-H bonds of material deposited upon the functionalized surface, in our case, PTAA, covalently bonding our PTAA films to the glass substrates. This novel use of AzPMTS enabled the cohesive fracture energy of PTAA and the influence of LiTFSI doping on the cohesion of PTAA to be determined (**Fig. 3a**). The cohesion of PTAA was measured to be 9.10 J/m<sup>2</sup>. Additions of LiTFSI to PTAA, as expected, decreased the cohesion of PTAA. Addition of 0.127 eq. of LiTFSI, the concentration used in perovskite solar cells, resulted in a 20 % decrease in the G<sub>c</sub> to 7.3 J/m<sup>2</sup>. This result indicates that the TFSI anion does not exhibit favorable interactions with PTAA and that its presence can be expected to compromise the adhesion of PTAA to a variety of substrates as previously discussed, increasing the risk of mechanical failure in devices.

#### Influence of TPBA cross-linking on PTAA cohesion

Using AzPTMS-functionalized glass beams, the cohesion of undoped PTAA films with increasing weight equivalents of TPBA (0.01, 0.05, 0.1 and 0.2) could be measured, exceeding energies of 40 J/m<sup>2</sup> without films delaminating. In this work, an upper limit of the adhesion provided by AzPMTS surface functionalization and bonding was not encountered. The cross-linking activity of the TPBA cross-linking agent resulted in a pronounced increase in the fracture

energy of PTAA cross-linked by TPBA as shown in **Fig. 3c**. With addition of 0.01 w.eq. of TPBA, the G<sub>c</sub> increased by 118 % from 9.1 J/m<sup>2</sup> to 19.9 J/m<sup>2</sup>. Addition of 0.05 w.eq. TPBA resulted in a 151 % increase, 0.1 w.eq., a 264 % increase and finally, 0.2 w.eq. a 345 % increase to 40.5 J/m<sup>2</sup> indicating that TPBA is a highly efficient cross-linking agent and that the hyperconnectivity introduced into the PTAA polymer results in sharp increases in PTAA fracture toughness.

The presence of LiTFSI, was found to reduce the ability of TPBA to increase the fracture toughness of PTAA. Nonetheless, TPBA cross-linking was still found to increase the cohesive fracture energy of d-PTAA, as shown in **Fig. 3c**. Additions of TPBA to d-PTAA resulted in a linear increase in the fracture energy from 7.3 J/m<sup>2</sup> without TPBA, to 23.5 J/m<sup>2</sup> with 0.2 w.eq TPBA, a 221 % increase. TPBA is thus highly effective at increasing the fracture energy of a fragile semiconducting polymer, even one containing molecular dopants to values well beyond those observed for borosilicate glass, CIGS and c-Si solar cells, which are on the order of ~10 J/m<sup>2</sup>.

#### **DFT Energy Level Analysis**

An important design consideration of cross-linking agents for semiconducting polymers is to minimize the electronic hybridization of the cross-linker with the polymer to limit altering the energy and spatial distribution of the polymer's electronic orbitals. The cross-linking agent should feature sigma-bond connectivity between respective azide groups to decouple these groups from one another. This is a feature of sFPAs<sup>28</sup>. We use density functional theory (DFT) calculations performed using the Gaussian09 suite at the B3LYP/6-31G(d,p) level of theory to investigate the degree to which the sigma-bonded adamantane core of TPBA limits orbital hybridization across the cross-linking agent, resulting in reactions of TPBA with polymers being likened electronically to reactions of polymers with benzylazide. The frontier orbital energies of TPBA (**Fig. 4a**), the model compound benzyl azide (BA) (**Fig. 4b**), and corresponding reaction products of these two azides with a series of alkane and aromatic small molecules, (R groups) ranging from short chain alkanes, through benzene, to short acenes; naphthalene, anthracene and finally coronene were calculated (**Fig. 4**). This series of small molecules was selected for computational simplicity, distinct from computationally expensive polymers and provides insight to the trends in the hybridization of TPBA with molecules of decreasing HOMO-LUMO gaps.

In addition, the energies of 1,3,5,7-tetrakis-(p-benzylamine)-adamantane (TPBA-1) and benzylamine (BA-1) were calculated and are shown in **Fig. 4a** and **b**. While these two structures are not the products of nitrene insertion into C-H bonds, but rather, into diatomic hydrogen, the energies of the frontier orbitals of these two structures better resemble the energies of the states that will influence the orbital energies of the R-groups. Comparison of the results of **Fig. 4a** and **Fig. 4b** reveals a similarity in the influence of addition of TPBA and BA to the R groups, and the resulting TPBA-R and BA-R constructs.

The differences between calculated frontier orbital energies of BA-R and TPBA-R,  $\Delta E_{approx} = E_{BA-R} - E_{TPBA-R}$ , were calculated. The distribution of along  $\Delta E_{approx} = 0$  eV indicates the value of the benzylamine approximation, the degree to which cross-linking with TPBA is electronically analogous to benzylamine addition (**Fig. 4c**). In this light, addition of TPBA to an alkane group, results in frontier orbital energies characteristic of benzyl amine influenced by the alkane, whereas, addition of a TPBA to an increasingly  $\pi$  conjugated system with a smaller HOMO-LUMO gaps will exhibit orbital energies dominated by those of the  $\pi$  system, influenced by addition of benzylamine groups. In the context of mitigating the impact on semiconducting polymers, which typically exhibit HOMO-LUMO gaps smaller than those of TPBA-1, the latter result can be expected.

The difference in frontier orbital energies between R groups and the TPBA-R constructs, revealing how  $\Delta E$  (here  $\Delta E = E_R - E_{TPBA-R}$ ) tends to zero with increasing conjugation of the R group (**Fig. 4d**). These results suggest that when semiconducting polymers are cross-linked by reaction of TPBA with the aromatic back-bones of the polymers (reacting with alkyl side-chains are not expected to significantly influence the electronic properties of the polymers) the addition of TPBA will act to destabilize the orbitals slightly, again, being likened to addition of benzyl amine to the polymer.

The similarity of the first four HOMOs of TPBA further reveals the effective decoupling of the benzylazide groups by the adamantane core (**Fig. 5a**). This is even more pronounced in the reaction product of TPBA with benznene (TPBA-4), in which these first four HOMOs are largely degenerate and lie predominantly on the added benzene, as can be seen in **Fig. 5b**. The LUMO orbitals are less degenerate, yet do exhibit decoupling of the peripheral benzene moieties from one another. With addition of molecules and polymers with narrower HOMO-LUMO gaps, this further localization of the HOMO away from the TPBA core can be expected.

#### **PESA Ionization Potential Analysis**

Recently, Belisle *et al.* reported that the  $V_{OC}$  and associated performance of perovskite solar cells are quite forgiving to variations in the ionization potential (IP) of the HTM<sup>48</sup>. As such, for perovskite solar cells, changes in the IP that result from TPBA cross-linking may not have significant consequence on device performance if the changes are not too large, ca. 300 meV, while larger changes may influence the performance of these devices, not to mention other devices using TPBA cross-linked PTAA.

We investigated the influence and synergy of additions of LiTFSI, 4-*tert*-butyl pyridine (*t*BP) and TPBA along with UV-C irradiation to activate TPBA on the IP of PTAA using photo electron spectroscopy in air (PESA) (**Fig. 5c**). While PESA measurements produce values to the second decimal, which in some cases are informative, in general it is best practice to place confidence in only the first decimal, probing 100 meV or larger variances of materials under investigation. While it is known that LiTFSI oxidizes PTAA, our TPBA cross-linking agent results in addition of new secondary amines to the PTAA polymer which may either decrease the IP by adding electron rich groups to the periphery of the polymer, or increase it by facilitating more efficient oxidation of the resulting cross-linked polymer by LiTSFI. In addition, we suspected that the presence of *t*BP, which has been determined to enhance perovskite solar cell efficiency through direct interaction with the perovskite material<sup>49</sup>, may also alter the IP of LiTFSI doped PTAA through direct interaction with LiTFSI or though donation of electron density to the oxidized polymer, reducing the effective IP of LiTFSI-doped PTAA.

Addition of 0.2 w.eq. of TPBA to PTAA without UV-C irradiation results in an increase of the IP from 5.16 to 5.19 eV. Here, the observed IP is a function of PTAA and the presence of the deep lying HOMO of TPBA. UV-C irradiation of the PTAA-TPBA composite film to induce cross-linking lowers the ionization potential to 5.17 eV due to addition of the benzyl-azide groups of TPBA to the polymer, leaving the IP largely unaltered in comparison to PTAA. This result is consistent with the trends observed in the DFT calculations in which TPBA addition to increasingly conjugated molecules results in only a slight destabilization of the HOMO.

Addition of LiTFSI to PTAA raises the ionization potential to 5.44 eV, typical of hole doping. Inclusion of *t*BP along with LiTFSI does alter the IP of LiTFSI doped PTAA, though far more than expected, largely nullifying the influence of LiTFSI on the IP, resulting in a film with

an IP of 5.17 eV. This indicates that the activity of *t*BP in the PTAA HTM may extend beyond modification of the HTM-perovskite interface. Addition of TPBA to a PTAA film containing both LiTFSI and *t*BP results in a 0.09 eV increase in the IP to 5.26 eV again with the observed IP being a function of the composite structure of d-PTAA and TPBA. Finally, UV-C activation of TPBA in this mixture, again, results in a marginal reduction of the IP to 5.25 eV indicating that TPBA cross-linking of PTAA may re-enable LiTFSI doping in the polymer typically inhibited by *t*BP. Altogether, the IP of d-PTAA and d-PTAA-X differ by only 0.08 eV which is certainly within the variation in IP tolerated by perovskites (valence band edge -5.39 eV) in perovskite solar cells.

#### Solar Cells using PTAA-X

Increases in fracture resistance and solvent resistance of d-PTAA through TPBA crosslinking do not come at the expense of solar cell performance. In fact, the use of TPBA crosslinked d-PTAA- $X_{0.2}$  results in appreciable increases in the PCE of perovskite solar cells using PTAA-X in both n-i-p and p-i-n architectures as shown in **Fig. 6** and **Table 1**, and verified by maximum power point tracking (**Fig. S19** and **S20**) The n-i-p cells utilized MAPbI<sub>3</sub> perovskite deposited by the acetate method<sup>50</sup>, and the p-i-n cells the  $C_{S0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(Br_{1.7}I_{.83})_3$ triple cation perovskite<sup>51</sup>. The perovskite used in each case was determined by the underlying layer on which perovskite deposition would occur. In the n-i-p architecture, the chlorobenzene anti-solvent used in the deposition of the triple cation perovskite etched the underlying fullerene layer, resulting in the formation of device-killing shunts. Similarly, in the case of the p-i-n architecture, the precursor solution of the acetate method did not suitably wet the underlying PTAA film preventing device fabrication. However, the added DMSO of the triple-cation enabled suitable wetting.

TPBA cross-linking resulted in systematic increases in the efficiencies of n-i-p cells (**Fig. 6a**) from 16.7 % for the d-PTAA control, to 16.8 % with addition of 0.1 w.eq of TPBA, and finally, to 17.2% for 0.2 w.eq. of TPBA. This increase is a product of improvements in the cells'  $V_{OC}$  and FF. Addition of 0.2 w.eq. of TPBA increases the FF from 0.78 to 0.81, and the  $V_{OC}$  from 1.00 V to 1.04 V. The  $J_{SC}$  of cells using d-PTAA-X<sub>0.2</sub> is lowered from 21.5 mA.cm<sup>-2</sup> to 20.0 mA.cm<sup>-2</sup>, but without reducing the overall efficiency. Maximum power point tracking of d-PTAA-X<sub>0.2</sub> cells showed sustained PCEs above that of control d-PTAA cells (**Fig. S19**).

Journal of Materials Chemistry A Accepted Manuscript

In the p-i-n cells studied cells (**Fig. 6b**), the use of TPBA to form a solvent resistant, mechanically robust film proved to be tremendously advantageous. Cells utilizing solvent resistant d-PTAA- $X_{0.2}$  dramatically outperformed cells using soluble d-PTAA as the HTM. The solvent resistance of d-PTAA- $X_{0.2}$  enabled the fabrication of a p-i-n solar cell exhibiting a PCE of 17.7 %, a marked 4.2 percentage-point efficiency increase in comparison to the d-PTAA control. The contrast in fill-factors of these two cells, 0.53 for d-PTAA and 0.78 for d-PTAA- $X_{0.2}$  highlights the benefits of TPBA induced solvent resistance which prevents etching by the chlorobenzene antisolvent used in the deposition of the triple-cation perovskite and the formation of FF-killing shunts in the control cell.

TPBA cross-linking in p-i-n cells also resulted in increases in the  $J_{SC}$ , from 21.1 to 22.4 mA.cm<sup>-2</sup> and produced cells that exhibited sustained PCEs during maximum power point tracking. (**Fig. S20**). These results show that increases in photovoltaic efficiency can be achieved by pursuing metrics related to reliability, which not only stands to enhance the yield of manufacture and reliability, but enables new device architectures to be created using solution state methods. This stands to be particularly advantageous for the field of tandem silicon-perovskite and perovskite-perovskite solar cells<sup>52</sup> that will benefit from the use of a room-temperature, cross-linkable HTM.

#### Methods

#### **General Experimental**

All anhydrous solvents were purchased from Acros Organics. NaBH<sub>4</sub>, PBr<sub>3</sub>, PbBr<sub>2</sub>, Pb(AcO)<sub>2</sub>, 4*tert* butylypyridine (*t*BP), formamadinium Iodide (FAI), and hypophosphorous acid (HPA) were purchased from Sigma Aldrich, PbI<sub>3</sub>, from Tokyo Chemical Industry Co., Methyl Ammonium Iodide (MAI) from Dyesol and NaN<sub>3</sub> from Acros Organics. PTAA was purchased from Solaris Chem. 10  $\Omega/\Box$  ITO coated 2 cm x 2 cm glass pieces were purchased from Xin Yan Technology. Deuterated NMR solvents were purchased from Acros Organics, Sigma Aldrich and Cambridge Isotope Laboratories.

NMR spectra were acquired at 25° C using a Varian VNMRS spectrometer fitted with a 4-nucleus (CP/HF) ASW probe, operating at a Larmor frequency of 399.7 MHZ for <sup>1</sup>H. MALDI-TOF mass spectra were acquired using a Bruker Daltronics spectrometer in positive or negative ion mode using 1,4-diphenylbuta-1,3-diene as the matrix. Waters GCT Premier was used in

electron ionization (EI) mode via direct insertion probe. Solid sample was applied to a quartz rod probe tip and the probe inserted into the source. Within the source, the probe was taken to 500°C to aid in volatilization of the samples. The EI source was set at 250°C and the electron energy was 70 V. PFTBA was used as internal calibration standard for AMM measurement. UV–vis spectra of MPMIC60 were acquired using an Agilent Carey 6000i UV–vis–NIR spectrometer. ATR IR spectra were acquired using a Nicolet iS50 FT/IR Spectrometer.

General cleaning procedure for glass and  $10 \ \Omega/\Box$  ITO coated 2 cm x 2 cm glass (Xin Yan Technology), used in this work was as follows: slides were cleaned by scrubbing with a toothbrush using a 1:10 Extran:DI water solution followed by sequential sonication and rinsing with DI water, acetone and IPA for 15 minute periods. Samples were exposed to UV-ozone for 15 minutes immediately before deposition of subsequent layers. Triple-cation perovskite films were deposited using the method reported by Saliba *et al.*<sup>4</sup> MAPbI<sub>3</sub> films were deposited using the acetate method described by Zhang *et al.*<sup>3</sup> C<sub>60</sub>, BCP and Al/Ag layers were deposited by thermal evaporation using an evaporator (Angstrom Åmod) contained within a N<sub>2</sub> glovebox.

#### Synthesis

The synthesis of 1,3,5,7-tetraphenyladamantane was achieved according the procedure reported by Reichert *et al*<sup>41</sup>. and 1,3,5,7-tetrakis-(*p*-formylphenyl)adamantane according to the procedure reported by Duncan *et al*<sup>42</sup>. AzPTMS was synthesized in accordance with the procedure reported by Paoprasert *et al*<sup>53</sup>.

**1,3,5,7-tetrakis-(***p***-phenylmethanol)-adamantane (2)** A dry, 1L 2-neck round bottom flask containing a magnetic stir bar was charged with 3.08 g (5.57 mmol) of 1,3,5,7-tetrakis-(4-formylphenyl)adamantane, 400 ml of dichloromethane and 150 ml of methanol. While stirring, 1.26 g (33.43 mmol) of NaBH<sub>4</sub> was added and allowed to stir at RT for 16 h. The solution was washed with 2M HCl and the organic layer filtered. The filtrate was added to an equivalent volume of hexanes, which caused precipitation of more of the product and further isolated by filtration. The isolated solids were combined and dried under air to yield 3.00 g (5.35 mmol, 96 % yield). ). ATR v/cm<sup>-1</sup>: 3261 (m), 2922 (m), 2848 (m) 1409 (m) 1047 (m), 1013 (m). MS (EI): *m/z* calcd for C<sub>38</sub>H<sub>40</sub>O<sub>4</sub>, 560.2927; found, 560.2905. <sup>1</sup>H NMR (400 MHz, DMSO-*d*6,  $\delta$ ): 7.50 (d, J = 8.4 Hz, 8H), 7.27 (d, J = 8.4 Hz, 8H), 5.08 (t, 5.6 Hz, 4H), 4.46 (d, 5.6 Hz, 8H), 2.06 (s, 12H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*6,  $\delta$ ): 148.15, 139.94, 126.39, 124.80, 62.71, 46.80, 38.70.

1,3,5,7-tetrakis-(p-benzylbromide)-adamantane (3) 3 g (5.35 mmol) of 1 and 100 ml of anhydrous THF were added to an oven dried 500 ml round-bottom flask containing a magnetic stir bar and cooled to 0 °C under N<sub>2</sub>. While stirring, 5.07 g (18.73 mmol) of PBr<sub>3</sub> was added dropwise. The vessel was allowed to warm to RT slowly and was left to stir for 16 h. 300 ml of saturated NaHCO<sub>3</sub> was added and allowed to stir for 5 minutes, causing precipitation of the white product. The precipitate was isolated by filtration, washed with 2 x 200 ml water and 2 x 200ml methanol and then dried in a vacuum tube at 50 °C for 1 day, yielding 4.03 g (4.96 mmol, 93 % yield). ATR v/cm<sup>-1</sup>: 3544 (sh, m), 3463 (sh, m), 3412 (s), 2930 (m), 2849 (m), 1206 (m), 606 (m). MS (EI): *m/z* calcd for C<sub>38</sub>H<sub>36</sub>Br<sub>4</sub>, 807.9550; found, 807.9557. The product was largely insoluble in all NMR solvents tested, which included CDCl<sub>3</sub>, Toluene- $d_8$ , Benzene- $d_6$ , 1,1,2,2-Tetrachloroethane- $d_2$ , DMSO- $d_6$  and trifluoroacetic acid- $d_1$ . A proton spectrum, however, could be acquired by heating a suspension in 1,1,2,2-tetrachloroethane- $d_2$  to 145°C. Residual aggregate/impurity peaks were present at  $\delta$  1.86 ppm which was the chief signal at 25 °C. With heating, this peak diminished in size as peaks for 3 grew in. <sup>1</sup>H NMR (400 MHz, 1,1,2,2tetrachloroethane- $d_2$ ,  $\delta$ ): 7.51 (d, J = 8.4 Hz, 8H), 7.57 (d, J = 8.4 Hz, 8H), 4.57 (s, 8H), 2.23 (s, 12H), 1.86 (s, signal of residual aggregate/impurity).

**1,3,5,7-tetrakis-(***p***-benzylazide)-adamantane (TPBA)** 60 ml of anhydrous DMF was added to a rubber septum-sealed, oven-dried 200 ml round-bottom flask and wrapped in aluminum foil containing 3.5 g (4.31 mmol) of **2**. The vessel was purged with nitrogen gas for 10 minutes, followed by the addition of 1.4 g (21.54 mmol) of NaN<sub>3</sub>. The flask was heated to 65 °C and allowed to react with stirring for 16 h, following which 60 ml of water was added. The white precipitate was isolated by filtration in the dark and washed with 2 x 50 ml water, 2 x 50 ml ethanol and dried in a vacuum tube overnight at 65 °C. The product was then recrystallized from CHCl<sub>3</sub>:MeOH to yield 2.45 g (3.71 mmol, 86 % yield). ATR v/cm<sup>-1</sup>: 2924 (m), 2851 (m), 2082 (s, N=N=N stretch), 1503 (m), 1241 (s), 769 (m). MS (EI): *m/z* calcd for C<sub>38</sub>H<sub>36</sub>N<sub>12</sub>, 660.3186; found, 660.3172. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.51 (d, J = 8.4 Hz, 8H), 7.32 (d, 8.4 Hz, 8H), 4.34 (s, 8H), 2.18 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 149.41, 133.51, 128.50, 125.67, 54.58, 47.30, 39.36.

Film Preparation and Cross-linking.

All PTAA films featured in this work for mechanical testing or PESA analysis were deposited from 15 mg/ml solutions of PTAA (Solaris Chem) in anhydrous toluene (Acros Organics). The ratio of LiTFSI (Acros Ogranics) and tBP added were taken from the reports by Yang et  $al^{39}$ . and Jeon et al.<sup>54</sup>. Accordingly, 11.25 µl of a 170mg/ml solution of LiTFSI in acetonitrile and 6ul of distilled tBP were added to 1ml of 15mg/ml PTAA to create doped PTAA. To probe the influence of LiTFSI on PTAA cohesion, 6 ul of tBP was added to 15mg/ml PTAA solution along with varying quantities of the 170 mg/ml LiTFSI solution as required. Similarly, relevant weight equivalents (0.01, 0.05, 0.1 and 0.2) TPBA were added to films and heated to 80 °C prior to addition of dopants when relevant to ensure complete dissolution of TPBA. Films were deposited on glass beams, AzPTMS-functionalized glass or silicon beams (for testing solvent resistance) by spin coating (spun at 4000 rpm with a 2000 rpm/s ramp rate for 45 seconds) then heated on a hot-plate at 95 °C for 5 min in a dry air glovebox. Cross-linking was conducted in an N<sub>2</sub> glovebox by irradiation with 254 nm UV light for 5 minutes (~ 0.01 W/cm<sup>2</sup>). Control films containing no TPBA cross-linker were also irradiated. Solvent resistance was tested by dipping films deposited on silicon for 30 seconds in toluene, removing them and allowing to dry vertically in air.

#### **AzPTMS Surface Functionalization**

Glass beams for AzPTMS surface functionalization were cleaned with freshly-prepared pirhana, rinsed with DI water, sonicated in methanol, dried under a stream of  $N_2$  and dried in an oven at 100 °C for 10 min. AzPTMS surface-functionalization of glass substrates was accomplished in glass jars with screw-top Teflon lids containing 40 mM solutions of AzPTMS in anhydrous toluene. Jars were sealed and heated to 100 °C for 12 hours in the dark. Substrates were then sequentially rinsed and sonicated (5 min) in toluene (x 2) and *iso*-propyl alcohol and blown dry with  $N_2$  gas under low light conditions.

#### **Fracture Testing**

Double-cantilever mechanical test structures were fabricated by capping layers of interest deposited on glass or AzPTMS-treated glass beams with a 5 nm Ti, 200 nm Al metal adhesion and blocking layer deposited by e-beam evaporation in a Kurt J. Lesker evaporator after film deposition. Loctite E-20NS epoxy was then used to bond a second glass beam to this metal

Journal of Materials Chemistry A Accepted Manuscript

surface, completing the sandwiched DCB test structure. The epoxy resin was cured at room temperature in a drybox with <1 ppm O<sub>2</sub> for 24 hours under pressure to produce a thin, brittle layer before mechanical testing. Edges of the test structures were scraped clean of epoxy with a razor-blade prior to testing.

Fracture testing of double cantilever beams (DCBs) was performed in laboratory air (~25 °C and ~40 % R.H.) under displacement control in a thin-film cohesion testing system (Delaminator DTS, Menlo Park, CA) which measured the load, *P*, versus displacement,  $\Delta$ . The critical fracture energy,  $G_c$  (J. m<sup>-2</sup>), can then be calculated from equation 1:

$$G_c = \frac{12P_c^2 a^2}{b^2 E' h^3} \left(1 + 0.64 \frac{h}{a}\right)^2 \tag{1}$$

where  $P_c$  is the critical load at which crack-growth occurs, *a* is the crack length, *E'* is the planestrain elastic modulus, and *b* and *h* are the width and half-thickness of the substrates, respectively. The crack length, *a*, was estimated from the elastic compliance,  $d\Delta/dP$ , using the relationship in equation 2:

$$a = \left(\frac{d\Delta}{dP} \times \frac{bE'h^3}{8}\right)^{1/3} - 0.64h \tag{2}$$

After mechanical testing, a survey x-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe) scan (0 - 1000 eV) was made of each of the fractured specimens using monochromatic Al K<sub>a</sub> x-ray radiation at 1487 eV to locate the fracture path and thus the weakest layer or interface within the test structure.

#### **PESA Analysis**

Ionization potentials of thin films were acquired with a Riken Instruments AC-2 PESA spectrometer with a light intensity of 5-10 nW, depending on the samples.

#### **Computational Analysis**

Ground state optimizations of the lowest energy structures were calculated using Gaussian 09 software using density functional theory (DFT) employing the Becke, three-parameter, Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-31G (d, p) basis set, for which

there is precedent in evaluating semiconducting materials for use in perovskite solar cells and solid-state dye-sensitized solar cells <sup>55-58</sup>.

#### **Solar Cells**

Conventional (n-i-p) devices were prepared on cleaned ITO slides. Compact titania layers were formed by spin-coating an acidic solution of titanium iso-propoxide (Sigma Aldrich) in ethanol onto cleaned ITO-glass substrates at 4000 rpm for 30 seconds before drying at 150 °C for 60 minutes. A 15 nm layer of C<sub>60</sub> was deposited by thermal evaporation. The acetate perovskite layers featured were deposited using a method based on that reported by Zhang et al.<sup>3</sup> Accordingly, a 40 wt.% solution of 3:1 molar ratio methylammonium iodide to lead(ii) acetate in anhydrous N,N-dimethylformamide with 0.75% HPA/Pb(AcO)<sub>2</sub> hypophosphorous acid was passed through a 0.2 µm PTFE filter. The solution of MAI and Pb(AcO)<sub>2</sub> was spun at 2000 rpm, 2000 rpm/s ramp rate for 60 seconds. A constant stream of dry air was directed at the sample to aid solvent evaporation. Perovskite films were allowed to dry further at room temperature and then annealed at 100 °C for 5 minutes to complete the formation of the perovskite layer. d-PTAA-X<sub>0.2</sub> was prepared as described above with additives of 10 ul LiTFSI at 170 mg/mL in acetonitrile and 6 ul tBP and deposited on the perovskite by spin coating at 4000 rpm, 2000 rpm/s ramp rate for 45 seconds and dried at 75°C for 5 minutes. d-PTAA-X<sub>0.2</sub> were transferred to a dry N<sub>2</sub> glovebox and irradiated with UV-C light for 8 minutes. A top electrode of 100 nm Ag was then deposited by thermal evaporation. Inverted (p-i-n) cells were fabricated as follows: 5 mg/mL d-PTAA-X<sub>0.2</sub> were deposited on freshly cleaned ITO coated glass by spin coating at 4000 rpm, 2000 rpm/s ramp rate for 45 seconds and subsequently dried on a hot-plate at 95 °C for 15 minutes. d-PTAA-X<sub>0.2</sub> films requiring UV-C activation were transferred into a dry N<sub>2</sub> glovebox and irradiated with UV-C light for 8 minutes. Triple-cation perovskite layers were then deposited using the method reported by Saliba et al.<sup>4</sup> Finally, a 45 nm layer of C<sub>60</sub>, a 7 nm layer of BCP and a top electrode of 150 nm Al were deposited sequentially by thermal evaporation (Angstrom Engineering A-mod). Current-voltage measurements were performed using a Keithley model 2400 digital source meter and 300W xenon lamp (Oriel) solar simulator was used for irradiation. The lamp was calibrated with an NREL-calibrated KG5 filtered Si reference cell. J-V curves were taken from forward to reverse bias sampled at 0.05V intervals with a 0.5 second delay time at each voltage step before taking data. Cells were masked to expose a 0.12 cm<sup>2</sup> window.

#### Conclusion

In summary, the synthesis of a novel, tetrahedral, azide-functionalized cross-linking agent featuring four reactive azide groups, TPBA, has been achieved. The use of 0.2 w.eq. of TPBA in PTAA and d-PTAA hole transporting materials enables their fracture toughness to be enhanced significantly by 345 % and 220 % respectively, significantly increasing the resistance to solvent etching and promoting adhesion of d-PTAA to organometal trihalide perovskite surfaces. LiTFSI was found to compromise the cohesion of PTAA and its adhesion to glass, which can be overcome through the use of AzPTMS light-activated adhesion promoter. The use of TPBA cross-linked PTAA in perovskite solar cells results in n-i-p and p-i-n perovskite solar cells with notable increases in efficiency. TBPA cross-linking will enable the fabricating entirely new device architectures through its ability to transform semiconducting organic films into robust, solvent-resistant layers without negatively impacting the performance of devices using them.

#### **Supporting Information**

Supporting information file contains ATR, NMR and Mass Spectral data of compounds synthesized, solvent resistance data, ATR spectra of PTAA-X films, UV-Vis spectra of PTAA-X films and TPBA in solution, XPS analysis of mating fracture surfaces, and maximum power point tracking of solar cells.

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**Table 1.** Solar cell performance data of p-i-n and n-i-p solar cells using d-PTAA and TPBAcross-linked d-PTAA-X hole-transport materials.

Architecture	НТМ	Voc	J <sub>SC</sub>	FF	РСЕ
		(V)	$(mA.cm^{-2})$		(%)
n-i-p	d-PTAA	1.00	21.5	0.78	16.7
	d-PTAA-X <sub>0.01</sub>	1.02	20.0	0.79	16.8
	d-PTAA-X <sub>0.2</sub>	1.04	20	0.81	17.2
p-i-n	d-PTAA	1.10	21.1	0.58	13.5
	d-PTAA-X <sub>0.2</sub>	1.08	22.4	0.73	17.7



**Fig. 1. a.** Azide cross-linking agents reported previously featuring reactive azide groups and the new tetrahedral azide cross-linking node of this work, TPBA featuring four reactive azide cross-linking groups. **b.** Schematic of cross-linking of polymer strands by the tetrahedral, four-site crosslinking agent, TPBA via C-H insertion of nitrene radicals generated by UV-C (254 nm) irradiation.



**Fig. 2. a**. Schematic of the synthesis of TBPA. **b**. Schematic of surface functionalization of an oxide substrate with AzPTMS and subsequent film deposition, UV-C activation of the azide groups in the solid-state resulting in covalent bonding of the film to the substrate through insertion of nitrene radicals into C-H bonds of the polymer film (dark blue).



**Fig 3. a.** Influence of LiTFSI concentration on fracture energy and pathway of PTAA deposited on glass beams with AzPTMS adhesion promotion, (red squares - cohesive fracture) and without AzPTMS adhesion promotion (black squares - adhesive fracture). The dashed blue line indicates the increase in fracture energy sustained by AzPTMS surface treatment. **b**. Influence of LiTFSI and TPBA concentration on the fracture behavior of d-PTAA (red squares) deposited on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite. When undoped PTAA (blue data point) is used, adhesive failure is not observed and fracture occurs within the perovskite layer. With addition of LiTFSI (red squares), adhesion at this interface is compromised resulting in adhesive failure. This adhesive fracture is mitigated with addition of TPBA, resulting in cohesive failure within the perovskite film. **c**. Influence of TPBA concentration on PTAA (black squares) and LiTFSI-doped PTAA (d-PTAA) (red squares) cohesive fracture. TPBA cross-linking significantly increases the fracture energy of both doped and undoped PTAA.



**Fig 4.** DFT B3LYP/6-31G(d,p)computational results of **a**, TPBA, R groups and products of nitrene insertion of TPBA with the R groups at the positions indicated by dashed bonds; **b**, TPBA, R groups and products of nitrene insertion of BA with the R groups at the positions indicated by dashed bonds. **c**. The difference in the HOMO and LUMO energy of the structures BA-R and TPBA-R showing the strength with which the influence of TPBA reactivity with various R groups may be likened simply to reactivity with BA. **d**. The difference in energy of the frontier orbitals of TPBA-R constructs and individual R groups, indicating the change in energy of these orbitals on reaction of differing R groups with TPBA. These computationally accessible calculations give insight to the influence of TPBA reactivity on the band energies of semiconducting polymers.



**Fig 5. a.** DFT-calculated orbital energies of TPBA and TPBA-4 showing how the four highest occupied molecular orbitals of TBA-4 are pinned by contributions from the benzene to all lie very close to -5.19 eV. **b**. DFT-calculated orbital energies and HOMO and LUMO diagrams TPBA-4 showing the absence of orbital density on the central adamantane core of TPBA-4 and that these four highest occupied molecular lie predominantly on the periphery of the molecule. The four lowest unoccupied molecular orbitals of TPBA-4 lie predominantly on the cross-linking agent while still decoupled by the adamantane core of the agent. **c**, Influence and synergy of additions of LiTFSI, *t*BP, TPBA and UV-C cross-linking on the ionization potential of PTAA.



**Fig 6. a**, JV-curves of conventional, n-i-p perovskite solar cells using d-PTAA and PTAA-X HTM. **b**, JV-curve of inverted, p-i-n perovskite solar cell using d-PTAA and d-PTAA-X as the hole-transporting materials. Use of TPBA to cross-link d-PTAA results in increases in the PCE of solar cells in both architectures.