

# Molecular Interlayers in Hybrid Perovskite Solar Cells

Wentao Deng, Xinxing Liang, Peter S. Kubiak, and Petra J. Cameron\*

Organic–inorganic hybrid perovskite solar cells (PSC) are promising third-generation solar cells. They exhibit good power conversion efficiencies and in principle they can be fabricated with lower energy consumption than many more established technologies. To improve the efficiency and long-term stability of PSC, organic molecules are frequently used as “interlayers.” Interlayers are thin layers or monolayers of organic molecules that modify a specific interface in the solar cell. Here, the latest progress in the use of interlayers to optimize the performance of PSC is reviewed. Where appropriate interesting examples from the field of organic photovoltaics (OPV) are also presented as there are many similarities in the types of interlayers that are used in PSC and OPV. The review is organized into three parts. The first part focuses on why organic molecule interlayers improve the performance of the solar cells. The second section discusses commonly used molecular interlayers. In the last part, different approaches to make thin and uniform interlayers are discussed.

## 1. Introduction

From first generation single crystal silicon solar cells<sup>[1]</sup> to emerging third generation solar cells, such as dye sensitized solar cells,<sup>[2]</sup> quantum dot solar cells,<sup>[3]</sup> organic solar cells,<sup>[4]</sup> and organic–inorganic hybrid perovskite solar cells,<sup>[5,6]</sup> researchers have kept looking for devices that have high power conversion efficiencies (PCEs), are cheap to produce and can be manufactured and disposed of with minimal negative environmental impact. Among all these different types of solar cells, perovskite solar cells (PSC) and organic solar cells attract tremendous attention as they have the potential to be highly scalable and to be manufactured by low energy routes.<sup>[7]</sup>

Currently, there are two main pathways being investigated to improve the efficiency and sustainability of PSC (as shown in **Scheme 1**). First, there is a lot of research focusing on the search for better active materials. The perovskite absorber layer in PSC, has an ABX<sub>3</sub> structure, where A represents an organic cation or Cs, B is a metal such as Pb or Sn and C is a halide.<sup>[6,8]</sup> A range of (organo-) metal halide perovskites are being

investigated for different applications (e.g., CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>, CsPbI<sub>3</sub>, HC-(NH<sub>2</sub>)<sub>2</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>) and there is increasing interest in lead-free absorber layers.<sup>[9]</sup> The second approach is to work with existing materials to improve the architecture of the solar cells.<sup>[10,11]</sup> The architecture of the device is extremely important as the morphology of the different layers, as well as the nature of the interfaces between them, are critical to ensuring an efficient PCE.<sup>[11,12]</sup> In recent years, there has been a focus on interface engineering using small molecules as it is a relatively simple way to improve the performance of PSC.<sup>[13,14]</sup>

Interface engineering can significantly enhance the performance of solar cells in a number of ways. It can be used to modify band energy offsets at an interface and decrease interfacial loss processes

caused by surface recombination.<sup>[15]</sup> Interface engineering can also improve the morphology of the active absorber layer,<sup>[16]</sup> the work function of contact layers,<sup>[17]</sup> the intimacy of the contact at the interface,<sup>[18]</sup> and the long-term stability of the devices.<sup>[19]</sup> In PSC, which typically have a “n-i-p” (or “p-i-n”) structure, there are four locations where interlayers have been investigated (**Scheme 2**).<sup>[20]</sup>


Many different materials have been investigated as interlayers, including organic molecules,<sup>[21,22]</sup> metal oxides,<sup>[23]</sup> polymers,<sup>[24]</sup> and carbon based materials.<sup>[25]</sup> In particular, small organic molecules have attracted interest for their easy synthesis, purification, and reproducible properties.<sup>[26]</sup> Small chemical modifications of the organic molecules' structure allow for further fine-tuning of the interfacial properties according to the research requirements. Additionally, organic molecule interlayers can be deposited by solution-processing at low temperature, making interface engineering a low-energy and scalable technique.<sup>[27,28]</sup>

In this review, we give an overview of the range of organic molecule interlayers used in hybrid perovskite and (where relevant) organic solar cells.

## 2. The Role of Organic Molecule Interlayers in Solar Cells

A broad range of small molecules have been used as interlayers, including benzoic acid derivatives,<sup>[29,30]</sup> perylene diimide derivatives,<sup>[26]</sup> silanes,<sup>[31]</sup> and several families of aminofunctionalized molecules.<sup>[32]</sup> Interlayer materials need to be carefully selected to ensure an improvement in device performance.

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 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/aenm.201701544>.

DOI: 10.1002/aenm.201701544

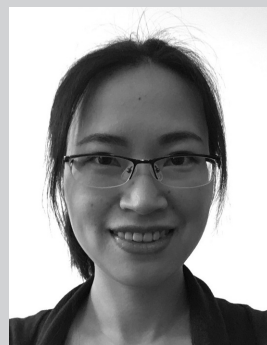
For example, an organic molecule with a dipole can be used as an interlayer to improve the  $V_{oc}$ . However the ordering of the molecule at the surface, and hence the direction of the dipole, needs to be controlled or it could cause a decrease in  $V_{oc}$ .<sup>[17]</sup> The use of a molecule with good conductivity can significantly improve the contact at the interface and decrease the series resistance ( $R_s$ ).<sup>[18]</sup>

## 2.1. Tuning the Morphology of the Absorber Layer

Morphological control of the perovskite absorber layer, e.g., by controlling the crystallinity, thickness, and roughness of the film, is critical in the production of high-efficiency PSC. A homogeneous perovskite layer with few defects and pin holes can significantly reduce recombination<sup>[33]</sup> and “shunting pathways.”<sup>[34]</sup> The morphology of the perovskite films has been controlled by tuning the composition of the precursor solution,<sup>[35]</sup> the annealing temperature,<sup>[36]</sup> solvent engineering,<sup>[37]</sup> and interface engineering.<sup>[17]</sup> In particular, interface engineering of the substrate on which the active layer is deposited is an easy and effective way to control the active layer morphology. The simplest interlayers influence active layer morphology by controlling the surface energy and the wetting properties of the substrate.<sup>[16]</sup> An interesting study into surface energy control of ZnO for organic solar cells was presented by Bulliard et al.<sup>[16]</sup> They used silane molecules with different terminal functional groups to modify the ZnO coated substrate in order to tune the surface energy ( $30\text{--}70\text{ mN m}^{-1}$ ) without changing the work function. The surface energy was effectively adjusted when different ratios of mixed molecules with hydrophilic ( $-\text{NH}_2$ ) and hydrophobic terminal groups ( $-\text{CH}_3$ ) were used. Accordingly, as shown in **Figure 1a,b**, the morphology of the active P3HT(poly(3-hexylthiophene)):PCBM([6,6]-p-phenyl-C61-butyrac acid methyl ester) blend varied with the substrate surface energy, leading to a variation in the cell performance. Zuo et al.<sup>[38]</sup> studied the effects of 3-aminopropanoic acid self-assembled monolayers (C3-SAM) as interlayers between  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite layers and a ZnO electron selective contact. It was revealed (**Figure 1c,d**) that extended plate-like perovskite grains grew on top of the C3-SAM and better coverage of the substrate (fewer “pin holes”) was achieved. As a result, the as-prepared cell showed a 31% enhancement in PCE from 9.8 to 14.2%. The research also found that the amino terminal of the molecule was involved in the crystallization of the perovskite and improved the morphology of the film. Yang et al. used 3-aminopropyltriethoxysilane to treat an  $\text{SnO}_2$  electron extracting layer in planar perovskite solar cells, and they also found that the subsequent  $\text{CH}_3\text{NH}_3\text{PbI}_3$  layer showed increased grain size and uniformity. The PCE of devices was improved from 14.7 to 17.0%.<sup>[39]</sup>

## 2.2. Work Function Adjustment

In addition to influencing the morphology, molecules with permanent dipole moments can change the work function at



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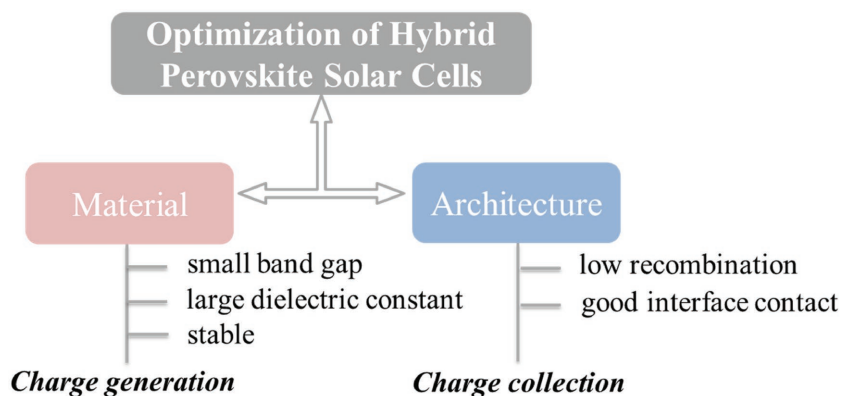
do her Ph.D. in perovskite solar cells. She is now working as a research assistant with Professor Laurie Peter on CZTS solar cells.



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the surface of a given layer. Such molecules can be beneficial to charge collection when used to modify the charge transporting layer, the transparent conducting oxide or the metal electrodes (shown in **Scheme 3**) and can expand the choices of metal contacts that can be employed in solar cells.<sup>[18,40]</sup> When used to modify the anode of the device, molecules with a dipole moment that points away from the electrode bends the vacuum level and causes an effective reduction in the work function (see **Scheme 3a**). An Ohmic contact is then expected to form between the electrode and the active layer and better electron extraction can be obtained. In contrast, molecules with permanent dipole moments that point toward the cathode are expected to effectively increase the metal work function, where they can decrease the energy barrier for hole collection (**Scheme 3b**). It is worth mentioning that in some situations, the molecules are employed in combination with metal oxides to give a “synergistic effect” for electron or hole extraction.<sup>[16,38,41]</sup> For example, in a polymer solar cell, a layer of metal oxide is used as an electron blocking layer and a small molecule is used at the same time to tune the work function.<sup>[16]</sup>



**Scheme 1.** Approaches to improve the PCE of hybrid perovskite and organic solar cells.

Zhang et al. used two perylene diimide derivatives with good conductivity to tune the work function of the electrodes in polymer solar cells.<sup>[40]</sup> Perylene diimide interlayers can effectively reduce the work function of metal electrodes as can be seen in Table 1. Devices with PDINO (amino *N*-oxide functionalized perylene diimide) showed an efficiency of 8.24% which was higher than observed for devices without the interlayer (4.43%). PDINO has also been used in perovskite solar cells. Min et al.<sup>[42]</sup> showed that when PDINO was used as an interlayer, the perovskite solar cell showed a decreased series resistance and an increase in efficiency from 10.0 to 14.0%.

Generally, a molecule with dipole moment not only changes the work function but it also changes the surface energy of the substrate. In some cases, work function modifications come at the expense of morphological control which is highly dependent on the surface energy.<sup>[39]</sup>

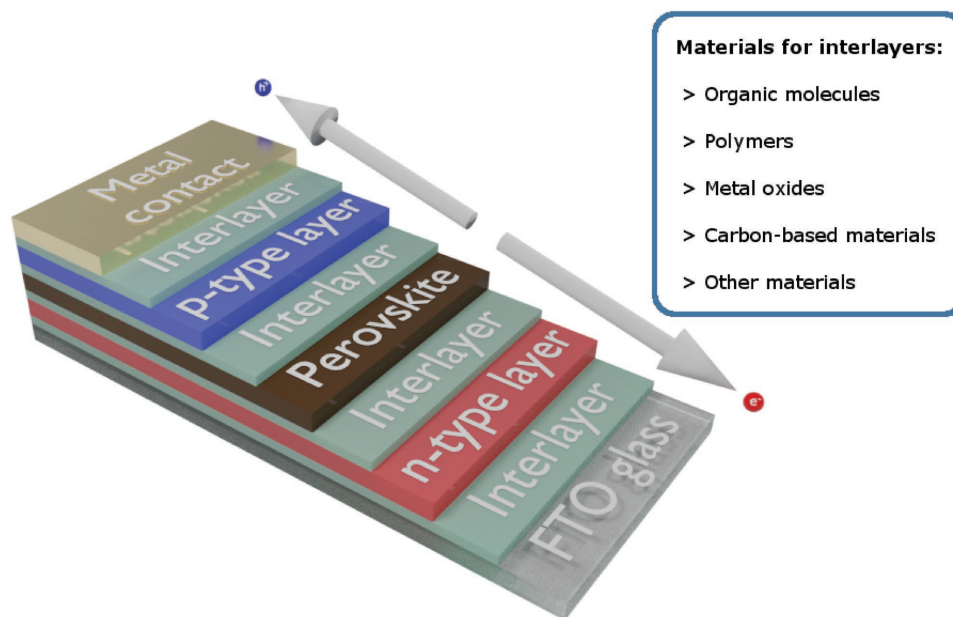
### 2.3. Passivation of the Surface (Reduction of Trap States)

In PSC and organic photovoltaics (OPV) organic molecules can be used to passivate surfaces in order to reduce trap states/defects (especially deep trap states) at the interface.<sup>[44–47]</sup> As displayed in Figure 2, imperfections in the crystal structure or chemical impurities can cause trap states which increase Shockley–Read–Hall (nonradiative) recombination.<sup>[48]</sup>

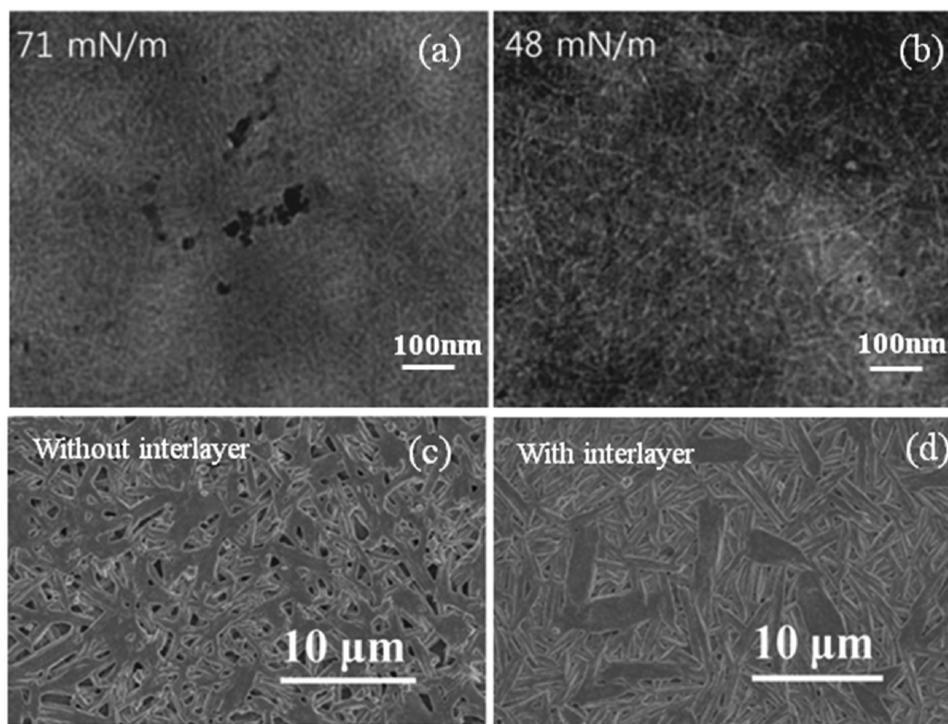
To reduce the effect of trap states, small molecules are used that can chemically react with surface nonbonded atoms or surface dangling bonds to reduce the number of surface defects.<sup>[46,47,49]</sup> The passivating

interlayer is usually sandwiched between the metal oxide electron extracting layer (e.g., TiO<sub>2</sub>, ZnO) and the photoactive layer. For example, molecules that can self-assemble such as thiols, C<sub>60</sub>-SAMs and some benzoic acid derivatives are widely used to modify the metal oxide layers.<sup>[47,50]</sup> They can form monolayers on metal oxides through self-assembly and change the surface energy at the same time. Consequently, the performance of the cells can be improved due to a reduction in surface recombination and an improvement in morphology.

In perovskite solar cells under-coordinated halogen (e.g., I<sup>-</sup>) and Pb<sup>2+</sup> sites on the crystallite surface are believed to form trap states which can act as recombination centers.<sup>[44,51]</sup> It has been suggested that the halogen anions act as hole traps and the lead cations as electron traps. It has been shown that Lewis acids can be employed to bond halogen anions and passivate the surface defects. In the same way, Lewis bases



**Scheme 2.** Possible positions of interlayers in hybrid perovskite solar cells.



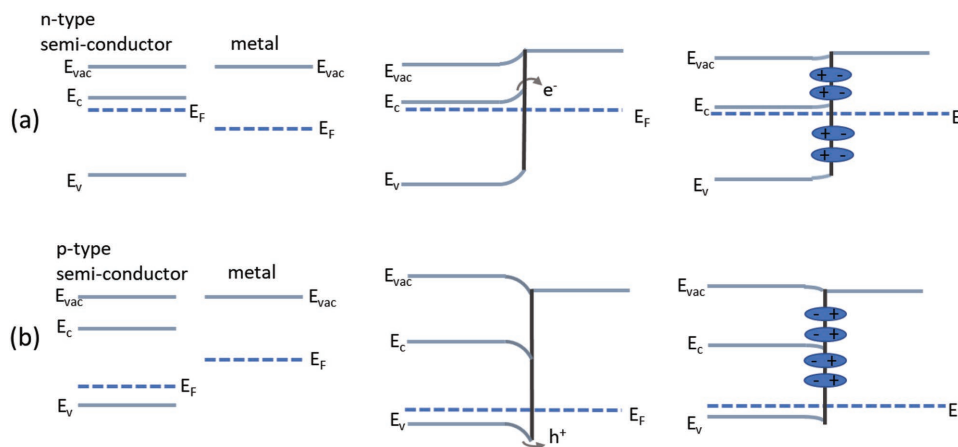
**Figure 1.** Scanning electron microscope images showing morphology changes introduced by interface engineering.<sup>[16,38]</sup> Panels a) and b) are images of a P3HT:PCBM heterojunction on substrates with different surface energies. Panels c) and d) are images of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite layers deposited on substrates with and without 3-aminopropanoic acid interlayers. Reproduced with permission.<sup>[16,38]</sup> Copyright 2015, American Chemical Society.

can be used to passivate nonbonded  $\text{Pb}^{2+}$  sites. For example, iodopentafluorobenzene (IPFB) shown in **Figure 3a**, is a Lewis acid that was used to reduce surface defects by coordinating to under coordinated iodide.<sup>[51]</sup> The IPFB treated cells reached an efficiency of over 15%, while the cells without IPFB treatment showed an efficiency of 13%. As typical Lewis bases, thiophenes (displayed in **Figure 3b**) and pyridines are good candidates to passivate surface lead cations.<sup>[44]</sup> In Noel's work, nonradiative recombination was significantly reduced, and photoluminescence lifetimes were increased by an order of magnitude. The efficiencies were consequently improved from

13 to 15.3 and 16.5% when the perovskite layer was treated by thiophene and pyridine.

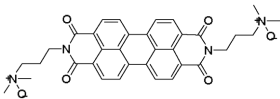
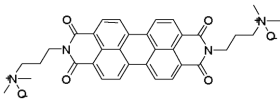
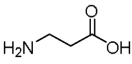
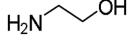
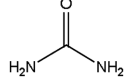
#### 2.4. Improvements in Long-Term Stability

Device stability during long-term operation is still a major challenge for hybrid perovskite solar cells.<sup>[52–54]</sup> Cells can achieve high energy conversion efficiencies but suffer from relatively low stability when they are subjected to high temperature, a humid atmosphere, UV light or even when a current



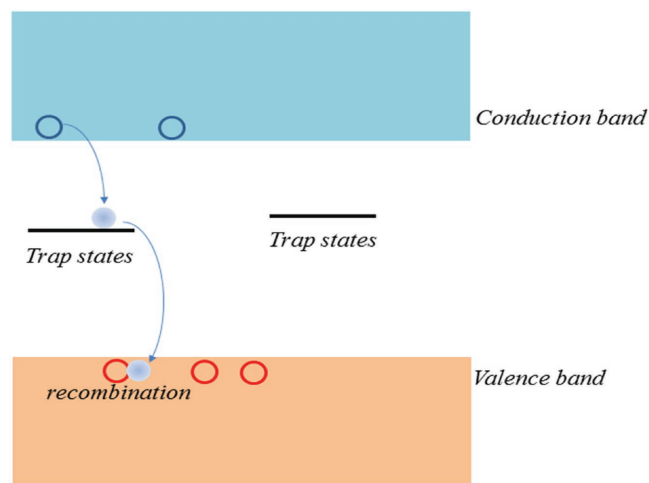
**Scheme 3.** Charge collection without (left) and with (right) molecular dipoles as interlayers in solar cells. a) Electron collection, and b) hole collection.

**Table 1.** Selected examples of tuning work function by molecular interface engineering.

Substrate	Interlayer	WF before modification [eV]	WF after modification [eV]
Al <sup>[40]</sup>		4.3	3.5
Ag <sup>[40]</sup>		4.3	3.6
ZnO/ITO <sup>[38]</sup>		4.2	3.5
TiO <sub>2</sub> <sup>[20]</sup>		4.0	3.7
P3HT:PCBM <sup>[43]</sup>		4.5	4.4

is drawn.<sup>[55,56]</sup> It has also been shown that in some cases the inorganic ZnO or SnO<sub>2</sub> electron extracting layer can decompose the perovskite.<sup>[57]</sup> The high sensitivity of perovskite solar cells to humidity in particular, has complicated commercialization of the technology. As reported by Leijtens et al.,<sup>[55]</sup> without additional protecting strategies, perovskite solar cells with a range of hole transporting materials degrade in hours at 80 °C in air. The loss of methylammonium iodide (MAI) made the dark-brown films turn yellow which indicated the formation of PbI<sub>2</sub>.

Mixed-cation perovskites<sup>[58]</sup> have been shown to be more stable than single cation perovskites. Recently, it has been shown that hybrid 2D–3D perovskite absorber layers can be used to dramatically increase the lifetime of the cells.<sup>[59]</sup> Other strategies have looked at encapsulation or the use of barrier layers.<sup>[60]</sup> Finally, there have been a number of studies investigating organic and inorganic interlayers to improve long-term



**Figure 2.** Recombination caused by trapping.

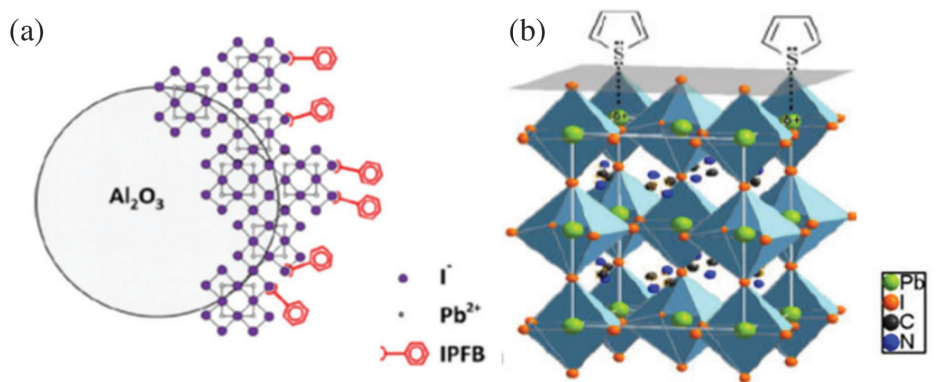
stability under ambient conditions.<sup>[61]</sup> One approach employs a hydrophobic hole transporting layer or a thin hydrophobic interlayer to protect the perovskite and reduce degradation due to moisture ingress.<sup>[54,62,63]</sup> When a hydrophobic hole conductor (DR3T-BDTP, benzo[1,2-b:4,5-b']dithiophene derivative) was used to replace the conventional spiro-OMeTAD (N<sup>2</sup>,N<sup>2</sup>,N<sup>2'</sup>,N<sup>2'</sup>,N<sup>7</sup>,N<sup>7</sup>,N<sup>7'</sup>,N<sup>7'</sup>-octakis(4-methoxyphenyl)-9,9'-spirobi[9H-fluorene]-2,2',7,7'-tetramine) hole transporting layer in a PSC, the device showed clear improvements in stability.<sup>[63]</sup> In practice, however, introducing a hydrophobic interlayer is often an easier way to achieve a similar effect. The hydrophobic layers are generally made from small molecules with alkyl groups and have been located both underneath and above the perovskite layer and the hole transporting layer. As shown in **Figure 4**, the organic interlayer dodecyl-trimethoxysilane was deposited on a perovskite

film (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) in a mesoporous perovskite solar cell and greatly improved the device stability as well as the PCE. The PCE of the device was monitored unsealed in ambient environment (humidity < 45%), and 85% of the initial PCE remained after 600 h.<sup>[31]</sup> In Yang's study, a range of alkyl ammonium salts with different functional groups were deposited on perovskite films as hydrophobic interlayers.<sup>[54]</sup> The substrate wetting properties were observed to change when the perovskite precursor solution was applied and tetraethyl ammonium iodide significantly improved the stability of the PSC. The device could be stored for over 30 d at around relative humidity (RH) 90%. As mentioned above hydrophobic interlayers have been investigated in all four interlayer positions indicated in Scheme 2, including immediately adjacent to the metal cathode.<sup>[64,65]</sup> For instance, Ciro et al. used Rhodamine 101 as a cathode interlayer to optimize the Ag/PCBM interface in a p-i-n structured perovskite solar cell.<sup>[64]</sup> They showed that device stability was significantly improved as the Rhodamine molecular interlayer appeared to act as a permeation barrier to slow the ingress of moisture from the atmosphere.

## 2.5. Other Roles

Interlayers can also serve many other roles such as blocking charge<sup>[66,67]</sup> and improving the intimacy of the contact between two layers.<sup>[43]</sup> For example, small molecules with low lying HOMO can be used to modify the electron extracting layer. The interlayer prevents the hole from moving to the contact, as shown in **Figure 5**. Increasing the selectivity for one charge carrier can result in less recombination and an increase in the efficiency of charge collection.

Organic molecule interlayers are also frequently used to increase the intimacy of the contact between different layers in the solar cells. In some cases the small molecules act to bind the two layers together, thereby reducing the

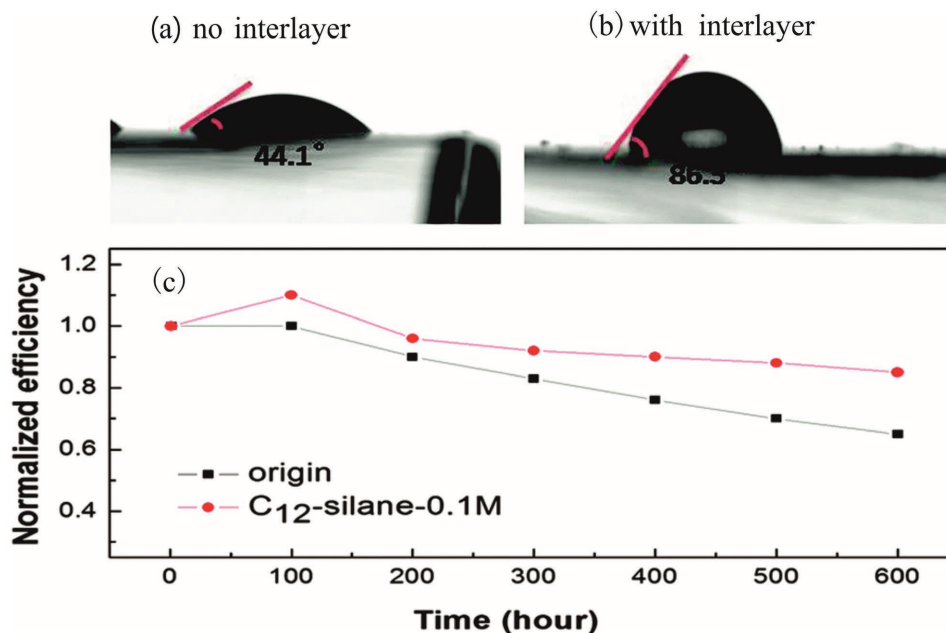


**Figure 3.** Surface passivation of perovskite layer through small molecules. a) Nonbonded I<sup>-</sup> was passivated by Lewis acid.<sup>[51]</sup> b) Nonbonded Pb<sup>2+</sup> was passivated by Lewis base.<sup>[44]</sup> Reproduced with permission.<sup>[44,51]</sup> Copyright 2014, American Chemical Society.

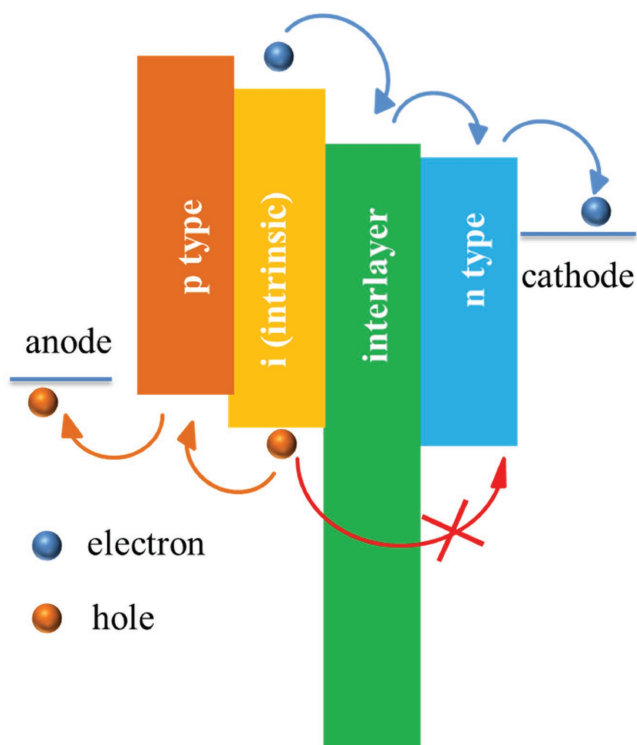
series resistance as well.<sup>[43,68]</sup> For example, when urea was used as the interlayer in polymer solar cells with PCBM and P3HT in the active layer,<sup>[43]</sup> the lone-pair electrons of the -NH<sub>2</sub> group were able to coordinate to the Al cathode, causing a "closer contact" at the interface as well as tuning the work function. In perovskite solar cells, links between perovskite layer and contact layer are improved when the interlayer molecules have terminal amino groups.<sup>[29,69]</sup> For instance, a group of molecules with generic structure HOOC-R-NH<sub>2</sub>I has been used to modify TiO<sub>2</sub> surfaces.<sup>[68]</sup> These molecules bind the TiO<sub>2</sub> surface through the carboxyl groups and participate in the crystallization process of the perovskite via the -NH<sub>2</sub>- terminus. The resulting perovskite device showed an improvement in PCE from around 7% to around 12%.

### 3. Classes of Small Molecules Used in Interlayers

There are a wide range of organic molecules that can be used as interlayers. Those most frequently used include perylene and its derivatives,<sup>[28,40,42,70,71]</sup> benzoic acid and its derivatives,<sup>[29,72]</sup> aminofunctionalized small molecules,<sup>[32,73]</sup> silanes,<sup>[31]</sup> dyes,<sup>[74]</sup> and fullerene derivatives.<sup>[75]</sup> As listed in Table 2, different molecules are employed depending on the aim of the research. For instance, to reduce the work function, a molecule with permanent dipole moment is required. In order to change the morphology of the active layer, a molecule with hydrophobic or hydrophilic functional groups is important. If the interlayer is deposited on metal oxides, such as indium tin oxide (ITO), fluorine doped tin oxide (FTO), TiO<sub>2</sub> or ZnO, small molecules with a "surface-active-head-groups" (anchoring group) can be



**Figure 4.** Long-term stability of solar cells with and without hydrophobic interlayers.<sup>[31]</sup> Panels a) and b) show the contact angle before and after the interlayer is added. Panel c) shows the change of normalized efficiency with time. Reproduced with permission.<sup>[31]</sup> Copyright 2015, The Royal Society of Chemistry.



**Figure 5.** Hole transportation blocked by low-lying HOMO of an interlayer.

considered, as they can be deposited by a simple immersion process to prepare a self-assembled interlayer (displayed in Figure 6a).

### 3.1. Benzoic Acid Derivatives

Benzoic acid derivatives are generally used in organic solar cells and perovskite solar cells to modify metal oxide layers like TiO<sub>2</sub>, ZnO or SnO<sub>2</sub>.<sup>[29,41,46,81]</sup> The carboxyl group binds strongly to the oxide making them robust interlayers and the wide range of dipole moments accessible through functional group modification can provide favorable conditions for charge extraction at a variety of interfaces. With an appropriate dipole moment, a benzoic acid derivative can be used to improve the  $V_{oc}$ , either as a cathode interlayer or an anode interlayer. **Table 3** displays the dipole moment of a range of benzoic acid derivatives that have been used in PSC and OPV.<sup>[69,82,83]</sup>

### 3.2. Aminofunctionalized Molecules

The most commonly used aminofunctionalized molecules can be classified into two groups: organic ammonium salts and neutral aminofunctionalized molecules.<sup>[86,84,85,88]</sup> Generally, ammonium salts are alcohol soluble and useful for tuning the work function of a surface.<sup>[84]</sup> Neutral amino-molecules are typically hydrophobic and can be used to tune the morphology of layers deposited on them. Some examples are listed in **Table 4**. Wang et al.<sup>[84]</sup> synthesized several molecules functionalized

with different amino groups as cathode interlayers for OPV. Depending on the aminofunctional groups chosen, the work function of the modified electrode could be varied allowing the formation of an Ohmic contact between the charge generating layer and the charge collecting layer.

### 3.3. Silanes

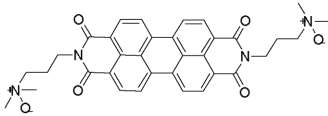
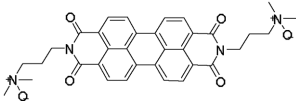
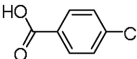
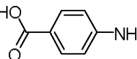
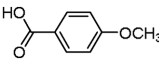
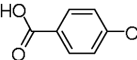
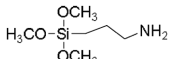
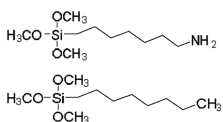
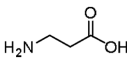


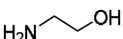
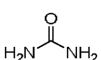

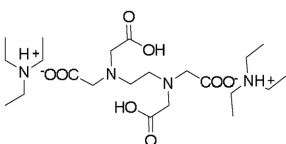
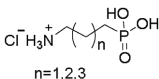
Silanes can form SAMs on a range of substrates. The self-assembly mechanism is shown in Figure 6b. Their interaction with surface –OH groups of the substrates is relatively straightforward. They react with transparent conductive oxides (TCO) to form a thin surface layer, while the nonreacting side functional groups are critical for the formation of surface dipoles.<sup>[89]</sup> They have been used to change the work function, surface wetting properties, and the stability of layers in solar cells. **Table 5** shows some examples of different silanes used in hybrid perovskite and organic solar cells. Song et al. synthesized a series of silanes with fluorinated head groups as interlayers and systematically studied the effects of different molecular dipoles and packing densities of layers on ITO.<sup>[90]</sup> After optimization of the structure and composition, the polymer solar cells with silanes exhibited a 54% increase of PCE and a 35% improvement of  $V_{oc}$ . A silane with a long alkyl chain (C12) was used in Zhang's work as an insulating layer for perovskite solar cells.<sup>[31]</sup> It was presumed that it acted as a spatial separator of electrons in the perovskite layer and holes in the hole transporting material (HTM) layer. As a result the shunt resistance ( $R_{shunt}$ ) increased and the series resistance  $R_s$  decreased. The PCE was enhanced by 40% from 9.8 to 13.7%, and device stability was also improved.

### 3.4. Perylene and Its Derivatives

Perylene and its derivatives (e.g., perylene diimides (PDIs) or perylene bisimides (PBIs)) are very typical n-type interlayers used in solar cells. The perylene core ensures good conductivity, and in addition their energy levels and solubility can easily be modified by changing the side functional groups or substitution in the bay positions of the conjugated core. As displayed in **Table 6**, several different perylenes (most of them are perylene diimides) have been investigated.<sup>[94]</sup> As briefly discussed above, a solution processable perylene diimide, PDINO was used as cathode modifier in inverted structure perovskite solar cells. It improved the contact between the ZnO and the Ag metal contact, significantly reducing  $R_s$  and increasing  $R_{sh}$ , the PCE of the device was enhanced from 11.3 to 14%.<sup>[42]</sup> Due to its good electric and electronic properties, PDINO has also been used in organic solar cells (as shown in Table 6),<sup>[40]</sup> and the device showed improved efficiency from 4.8 to 8.2%. To date there are limited examples of perylene derivatives used in perovskite solar cells, however, the success in OPV<sup>[95,96]</sup> (see Table 6) in organic solar cells suggests that this is an underexplored area in PSC.

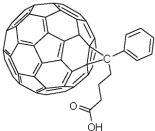
It is worth noting that the orientation in which PDIs pack or stack plays an important role in determining the electronic

**Table 2.** Relevant organic molecule interlayers that have been used in perovskite solar cells. Interesting examples of interlayers used in organic solar cells have also been included.

Solar cell architecture	Small molecule	Role of small molecule	PCE modified cell versus not modified cell <sup>a)</sup>
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>x</sub> Cl <sub>1-x</sub> /PCBM/ZnO/PDINO/Ag <sup>[42]</sup>		Reduce R <sub>s</sub>	14.0% versus 11.3% (average)
ITO/PEDOT:PSS/PTB7:PCBM/PDINO/metal <sup>[40]</sup>		Reduce work function and R <sub>s</sub>	7.7% versus 4.4%
FTO/c-TiO <sub>2</sub> /m-TiO <sub>2</sub> /benzoic acid derivatives/FA <sub>x</sub> MA <sub>1-x</sub> PbI <sub>3-y</sub> Br <sub>y</sub> /spiro-OMeTAD/Au <sup>[69]</sup>		Enhance charge extraction speed	18.4% versus 17.5
FTO/c-TiO <sub>2</sub> /m-TiO <sub>2</sub> /benzoic acid derivatives/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-OMeTAD/Au <sup>[29]</sup>		Reduce surface defects	10.5% versus 7.5%
ITO/PEDOT:PSS/P3HT:PCBM/ZnO/benzoic acid derivatives/metal <sup>[41]</sup>		Reduce work function	3.2% versus 0.7%
ITO/benzoic acid derivatives/PTB7:PCBM/Al <sup>[30]</sup>		Increase work function/morphological control	8.2 versus 5.1%
FTO/TiO <sub>2</sub> /silanes/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> @ZrO <sub>2</sub> /C <sup>[21]</sup>		Morphological control	12.8% versus 9.7%
ITO/ZnO/mixed small molecules/P3HT:PCBM/MoO <sub>3</sub> /Ag <sup>[16]</sup>		Surface energy/morphological control	3.7% versus 3.3% (average)
ITO/ZnO/3-aminopropanoic acid/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-OMeTAD/MoO <sub>3</sub> /Ag <sup>[38]</sup>		Morphological control and reduce work function	15.7% versus 11.9%
FTO/TiO <sub>2</sub> /amino acids/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-OMeTAD/Au <sup>[76]</sup>		Enhance charge extraction speed	14.2% versus 10.8%
ITO/PEDOT:PSS/NH <sub>3</sub> /CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3-x</sub> Cl <sub>x</sub> /C60/BcP/Ag <sup>[77]</sup>		Morphological control	15.2% versus 14.3%
FTO/c-TiO <sub>2</sub> /EA/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3-x</sub> Cl <sub>x</sub> /spiro-OMeTAD/Au <sup>[20]</sup>		Reduce work function	16.3% versus 12.8%
ITO/PEDOT:PSS/P3HT:PCBM/urea/Al <sup>[43]</sup>		Reduce work function and R <sub>s</sub>	4.4% versus 3.4%
ITO/PEDOT:PSS/DMSO/P3HT:PCBM/BcP/Al <sup>[78]</sup>		Reduce R <sub>s</sub>	2.7% versus 0.1%
ITO/EDTA-N/PTB7:PCBM/MoO <sub>3</sub> /Al <sup>[79]</sup>		Reduce work function and R <sub>s</sub>	6.2% versus 0.7%
FTO/c-TiO <sub>2</sub> /mp-TiO <sub>2</sub> /butylphosphonic acid 4-ammonium chloride/perovskite/spiro-OMeTAD/Au <sup>[52]</sup>		Stability improvement	16.7% versus 8.8%



**Table 2.** Continued.

Solar cell architecture	Small molecule	Role of small molecule	PCE modified cell versus not modified cell <sup>a)</sup>
FTO/c-TiO <sub>2</sub> /PCBA/perovskite/spiro-OMeTAD/Au <sup>[80]</sup>		Reduce hysteresis	13.1% versus 10.1%

<sup>a)</sup>All the PCE data shown here are from the best performing cell and calculated from *J*-*V* scans except where otherwise mentioned.

properties of the interlayer.<sup>[26,98,99]</sup> **Figure 7** displays two different aggregation orientations of PDIs. It is reported that with different preparation methods, for example dipping or spin coating, the tilt angles of the molecular cores are different.<sup>[26]</sup> A phosphonic acid functionalized PDI film prepared using a dipping method showed a smaller tilt angle than the one made by spin coating<sup>[26]</sup> (**Figure 7a**). Zhang et al. investigated how the charge transfer process changed with variation in orientation at the interface.<sup>[99]</sup> The authors used different solvents to control intermolecular hydrogen bond formation which modified the PDI film morphology (**Figure 8**). Ultraviolet photoelectron spectroscopy (UPS) analysis was used to show that the solar cells with PBI-1 (5,6,12,13-tetrakis(*o*-tolylxy)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone) nanoparticles showed better charge transfer than those with PBI-1 nanofibers at the interface.

### 3.5. Other Molecules

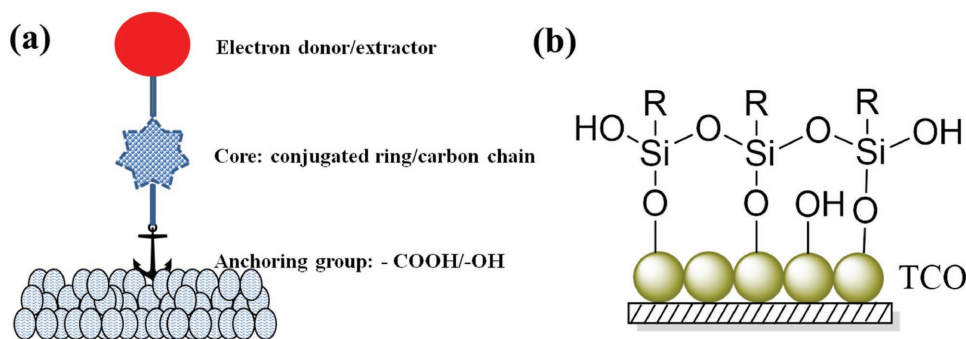
Other molecules including dyes,<sup>[70,100,101]</sup> phosphonic acids,<sup>[102,103]</sup> metal organo compounds,<sup>[73,104]</sup> alcohols,<sup>[105]</sup> and thiols<sup>[106–108]</sup> have also been used as interlayers, as shown in **Table 7**. Rhodamine 101 was found to increase the fill factor effectively when used as an interlayer between PCBM and the Ag contact in perovskite solar cells due to better aligned energy levels.<sup>[74]</sup> It was suggested that its introduction in the solar cell created an Ohmic contact at the interface, which resulted in an increase of PCE from 12.0 to 14.8%. Interestingly, molecular interlayers can also help build ITO free device architectures in

perovskite solar cells.<sup>[107]</sup> Chang et al. used two types of thiols and Ag was sandwiched between the two interlayers to form an ITO free electron collecting electrode.<sup>[107]</sup> Thiol interlayers adjusted the work function of the Ag and improved the stability of devices. Due to the low sheet resistance of the modified Ag electrode, it also partially overcame the problem of high sheet resistance introduced by TCOs in large area devices. The average PCE for devices with an active area of 0.12 cm<sup>2</sup> was 15% and 5 cm<sup>2</sup> active area devices showed an efficiency of 11.8%.

## 4. Methods Used to Prepare Organic Molecular Interlayers

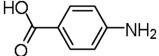
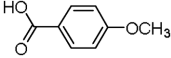
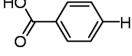
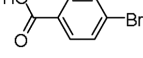
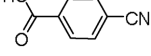
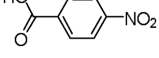
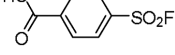
Due to the insulating nature of most small organic molecules, the interlayer in a device is generally less than 10 nm thick.<sup>[40,43,109]</sup> Interlayers are also required to be thin in order to avoid unwanted absorption of light before it can reach the active layer.<sup>[95]</sup> Although there are a few exceptions, especially when the molecule has good conductivity. As reported by Wang and co-workers, a perylene diimide based interlayer (conductivity  $\approx 10^{-5}$  S cm<sup>-1</sup>) gave a very good performance with thicknesses ranging from 6 to 25 nm.<sup>[40]</sup>

Several approaches can be employed to prepare thin interlayers. They can be made by solution processing or by vapor deposition. The method chosen depends on the properties of the material being deposited and the surface it is being deposited on. **Scheme 4** illustrates the three most common methods used to prepare thin layers, i.e., dip coating, spin



**Figure 6.** a) Organic molecule with dipole moment and anchoring group. b) Silane self-assembled on a transparent conductive oxide (TCO) surface.

**Table 3.** Dipole moments of some common benzoic acids.

Molecule	Dipole moment [Debye]
	-4.5
	-3.9
	-2.1
	1.4
	3.4
	3.8
	4.5

coating, and thermal evaporation. Notably, when using solution-processed approaches it is extremely important to account for the effects of the solvent on interlayer morphology. The stability of the interlayer in the presence of the solvent used to deposit subsequent layers is also important.

#### 4.1. Dip Coating/Immersion

Dip coating is a simple and low energy route to obtaining uniform thin films through molecular self-assembly. Small molecules deposited by dip coating usually have surface-active groups to anchor and self-assemble spontaneously on the solid surface. They can easily rearrange and form well-ordered and highly oriented ultrathin films through specific interactions such as formal chemical bonds, hydrogen bonds or  $\pi$ - $\pi$  stacking.<sup>[110]</sup> The molecules should be carefully chosen to match the surface properties of the substrates<sup>[111]</sup> in order to get uniform layers. As has already been mentioned, molecules with R-O-R', R-OH or R-COOH structures can form chemical bonds with TCO substrate surfaces. Other examples include thiols (R-SH) or dithiols which can self-assemble on metal surfaces<sup>[112]</sup> (e.g., Au, Ag, Cu, Pd, Pt, Ni, Fe, etc.) and phosphonic acids which can also form self-assembled monolayers on oxides such as silicon dioxide and aluminum oxide.<sup>[113]</sup>

**Table 8** lists the parameters that are important to achieve good dip coated film quality; e.g., the number of surface dangling functional groups (such as -OH on metal oxides) could significantly affect chemical adsorption on the surface. The temperature of the solution will influence the adsorption speed and the dipping time will have impact on the coverage. To make

a thin layer that is more strongly bound to the substrate a post annealing process after dipping can help convert physisorption into chemisorption. There are some studies mentioning that the high RH of the environment needs to be controlled as it can prevent molecules from forming chemical bonds with the substrates.<sup>[113]</sup>

Rather than getting a thin layer (monolayer or multilayer) through a self-assembly process, an exact monolayer can be obtained using the Langmuir-Blodgett technique (shown in **Scheme 5**). This technique relies on amphiphilic molecules forming a monolayer at the liquid/air interface. By slowly withdrawing a substrate from the liquid, a uniform monolayer can be obtained.<sup>[115]</sup>

#### 4.2. Spin Coating

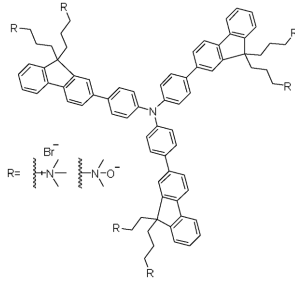
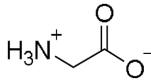
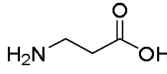
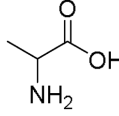
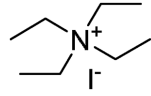
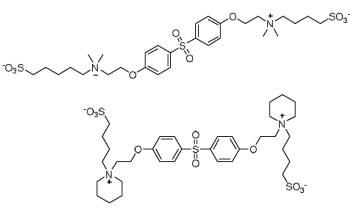
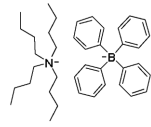
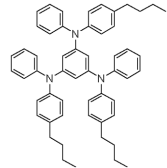
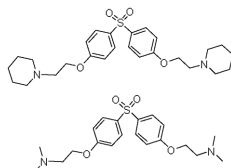
Spin coating is a highly controllable method for depositing thin films. It is very practical for small area substrates as long as the desired material is soluble or well dispersed in the selected solvent. Unlike dip coating, spin coating is a quicker process and has fewer substrate requirements. It typically only takes a few seconds to coat the film and usually a few minutes to anneal it. Spin coating can be used to deposit molecules that can physisorb or chemisorb onto the surface.

The thickness and the quality of spin coated films can be optimized by varying the spin speed, coating time or concentration of the precursor solution. In **Table 9**, a few parameters for commonly used spin coating processes are listed. To get good quality thin films, the solvent type, concentration of the solution, pH of the solution, spin coating parameters, and annealing procedures are all important factors that need to be considered.<sup>[95,99]</sup> As mentioned above Zhang et al.<sup>[99]</sup> used  $\text{CHCl}_3$  and THF as two different solvents to control the morphology of perylene diimide cathode interlayers by changing the intermolecular hydrogen bonding. In addition, the authors introduced acetic acid as an aggregation inhibitor to control the structure and dimensionality of the film.

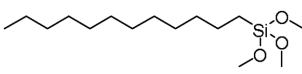
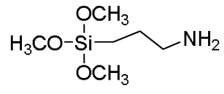
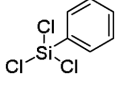
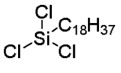
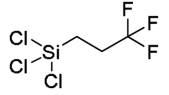
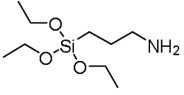
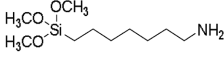
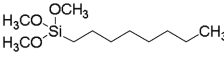
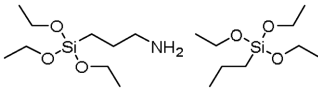
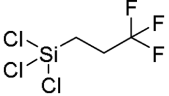
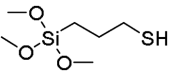
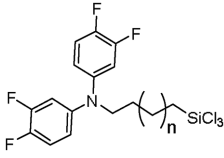
#### 4.3. Thermal Evaporation

Thermal evaporation is a simple physical vapor deposition process which is suitable for both inorganic and organic materials. The desired material is placed in a boat under vacuum and then heated to form vapor which will condense on nearby substrates. This is an effective approach to deposit multilayer films especially when the desired material has low solubility in common solvents. This method allows precise control of the film thickness (0.1 nm precision) and an easily controllable deposition rate. Despite the drawback that some organic materials easily decompose at high temperatures, it is a very popular method to deposit organic compounds for optoelectronic devices.<sup>[116]</sup> Huang et al. prepared a FPDI (fluorinated perylene diimide derivative) electron transporting layer using the vapor deposition method<sup>[117]</sup> for  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite solar cells. The thickness was precisely controlled from 25 to 75 nm, and the solar cell efficiency was effectively improved with the optimization of FPDI thickness.

**Table 4.** Aminofunctionalized small molecules as interlayers. Relevant interlayers used in organic solar cells have also been included.

Aminofunctionalized small molecules	Solar cell architecture	Molecule structure	References
Ammonium salts	ITO/ PEDOT:PSS/ PTB7:PC71BM/ammonium salt/Al		[84]
	FTO/c-TiO <sub>2</sub> /m-TiO <sub>2</sub> /glycine/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-OMeTAD/Au		[85]
	ITO/ZnO/3-aminopropanoic acid/ CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-OMeTAD/MoO <sub>3</sub> /Ag		[38]
	FTO/TiO <sub>2</sub> /amino acids/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /spiro-OMeTAD/Au		[76]
	FTO/TiO <sub>2</sub> /CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /ammonium salt/spiro-OMeTAD/Au		[54]
	ITO/ammonium salt/ PTB7:PC71BM/MoO <sub>3</sub> /Al		[86]
	ITO/PEDOT:PSS/PTB7:PC71BM/TBATPB/Al		[87]
Neutral amines	ITO/triarylamine/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/LiF/Ag		[13]
	ITO/ammonium interlayer/ PTB7:PC71BM/MoO <sub>3</sub> /Al		[86]

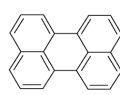
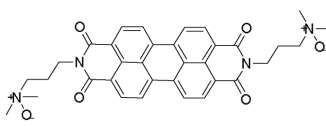
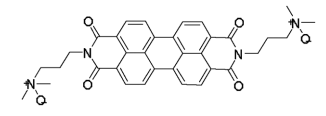

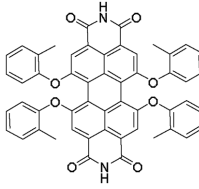
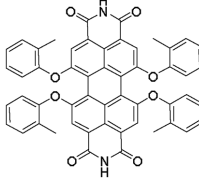
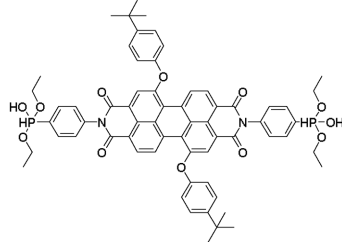
**Table 5.** Silanes in perovskite solar cells. Relevant interlayers used in organic solar cells have also been included.

Solar cell architecture	Silane structure	References
FTO/c-TiO <sub>2</sub> /m-TiO <sub>2</sub> / CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /silanes/ spiro-MeOTAD/Ag		[31]
FTO/TiO <sub>2</sub> /silane/ CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> @ZrO <sub>2</sub> /C <sup>[21]</sup>		[21]
ITO/PEDOT:PSS/ CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3-x</sub> Cl <sub>x</sub> /silanes/ PCBM/Ca/Al	 	[91]
ITO/PTAA/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> / C60-SAM/silanes/BCP/Cu		[92]
FTO/SnO <sub>2</sub> /silanes/ CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> / spiro-OMeTAD/Au		[39]
ITO/ZnO/mixed silanes/ P3HT:PCBM/MoO <sub>3</sub> /Ag <sup>[16]</sup>	 	[16]
ITO/silanes/P3HT:PCBM/ metal	 	[18]
ITO/P3HT:PCBM/silanes/ Au		[93]
ITO/silanes/PTB7:PCBM/ LiF/Al		[90]

#### 4.4. Other Methods

There are some other solution based methods to deposit thin films, such as drop-casting, solution printing techniques, and solvothermal methods.<sup>[118]</sup> For instance, Qu et al.<sup>[118]</sup> used a solvothermal method to prepare a thin carboxylic acid layer on a TiO<sub>2</sub> surface. The process was carried out in an autoclave at 100 °C for 24 h. The higher temperature and pressure conditions make the molecules chemically adsorb onto the TiO<sub>2</sub>

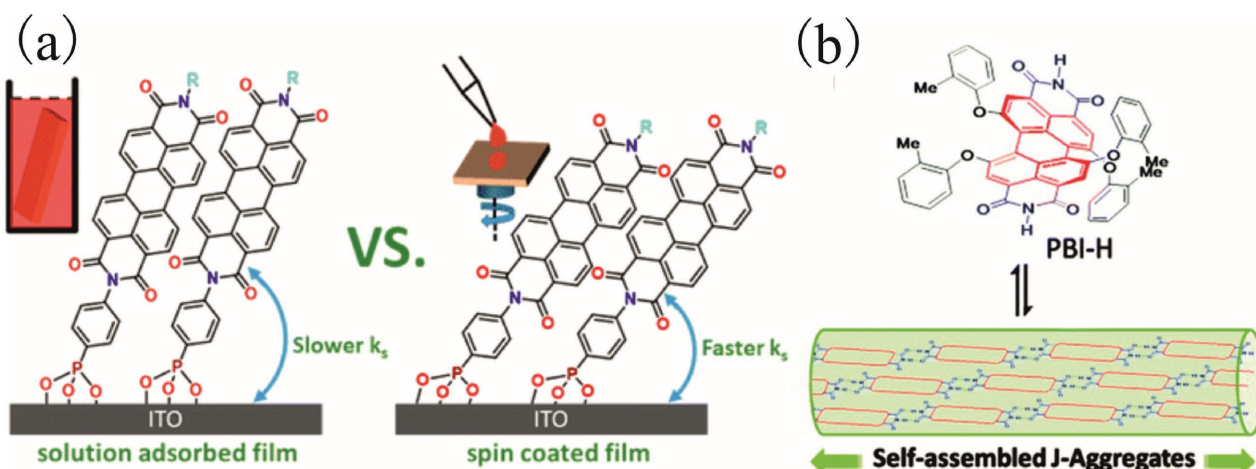
**Table 6.** Perylene and its derivatives used in perovskite and organic solar cells.

Solar cell architecture	Perylene and derivatives structure	References
ITO/PEDOT:PSS/ perylene/ CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3-x</sub> Cl <sub>x</sub> / PCBM/Bphen/Al		[71]
ITO/PEDOT:PSS/ CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3-x</sub> Cl <sub>x</sub> / PCBM/ZnO/ PDINO/Ag		[42]
ITO/PEDOT:PSS/ PTB7:PCBM/ PDINO/metal		[40]
ITO/PDIs/ P3HT:PCBM/ V <sub>2</sub> O <sub>5</sub> /Al		[95]
ITO/ZnO:PDIs/ PTB <sub>7</sub> :Th:PCBM/ MoO <sub>3</sub> /Al		[94]
ITO/PDIs/ PTB <sub>7</sub> :PCBM/ MoO <sub>3</sub> /Al		[97]
ITO/PCDTBT:EP- PDI/PDIs/Al		[28]

surface (bidentate chelation). The coverage was optimized by changing the ratio of TiO<sub>2</sub> to the small molecules.

## 5. Conclusion and Outlook

In this review, we have surveyed recent progress in the interfacial engineering of PSC using organic molecules and have included some relevant and interesting examples from OPV.



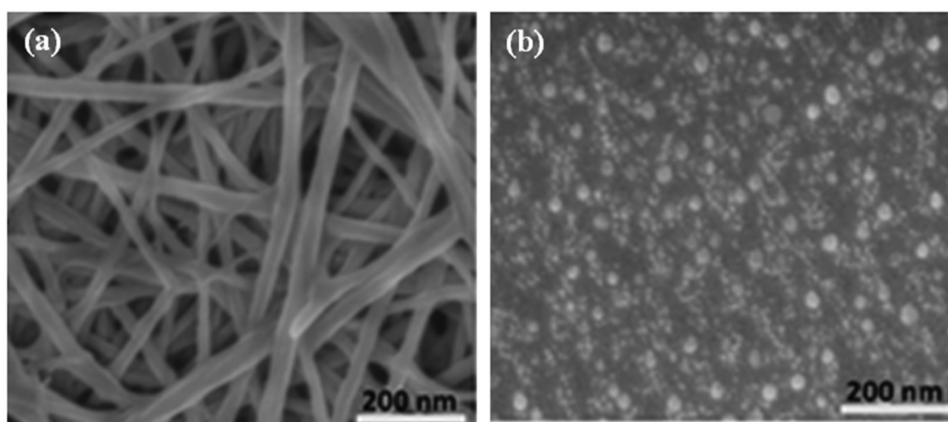
**Figure 7.** PDIs aggregating in different orientations. a) PDIs aggregates have different tilt angles depending on the preparation methods used. b) J-aggregation of PDIs. Reproduced with permission.<sup>[26,97]</sup> Copyright 2016, American Chemical Society.

There are many examples where organic molecule interlayers have increased the PCE and perhaps more importantly the long-term device stability of perovskite solar cells. The majority of research has focused on organic interlayers between the perovskite layer and the electron extracting contact; these interlayers help to improve charge extraction and can be critical in determining the morphology of the perovskite layer deposited on top of them. An interesting question is whether organic interlayers could also be used in this position to prevent degradation of the perovskite film that can be induced by the metal oxide (e.g., ZnO, TiO<sub>2</sub>) contact. Olthof and co-workers<sup>[119]</sup> showed that the perovskite degraded when PbI<sub>2</sub> is formed at the metal oxide/perovskite interface. Blend organic-inorganic interlayers have been investigated at this contact;<sup>[57]</sup> however given the widespread use of metal oxide layers in PSC a range of effective strategies are needed to suppress the degradation. A thin and stable molecular interlayer could be one relatively simple solution if it can suppress PbI<sub>2</sub> formation

but allow the beneficial properties of metal oxide layers to be retained.

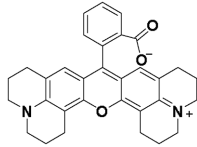
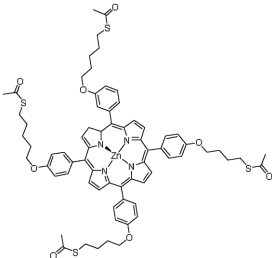
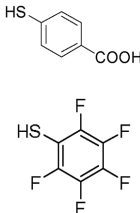
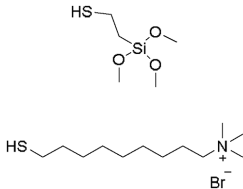
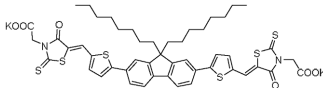
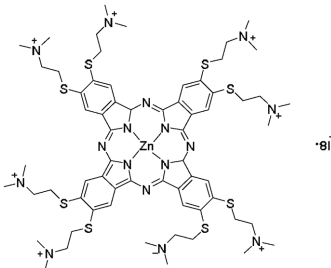

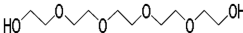
The second most investigated position for molecular interlayers is just above the perovskite film. In particular, we have described several studies where hydrophobic molecules are used to try and protect the perovskite film from ambient moisture. In our own experience these hydrophobic layers slow, but do not ultimately prevent, degradation in humid environments. It is likely that multiple strategies need to be adopted, combining 2D–3D hybrid perovskites with hydrophobic interlayers and also encapsulation to provide the longer term stability required.

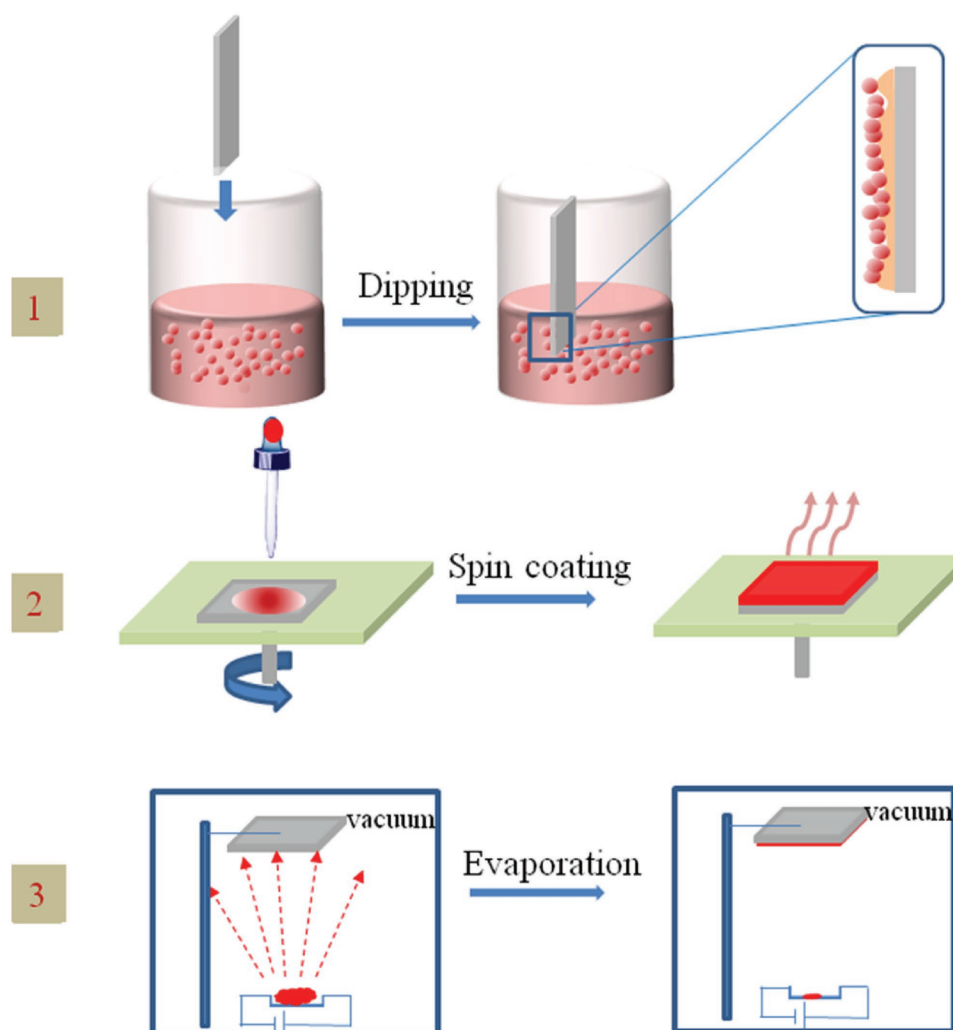
Less research has focused on interlayers directly adjacent to the transparent conducting oxide or the metal contact, but this is a growing area. Bifunctional molecules, for example, are a relatively simple way to better adhere the contacts to the rest of the device, reducing series resistances and improving charge extraction.



**Figure 8.** PDIs film morphology changes with different solvents (both films obtained by spin coating).<sup>[99]</sup> a) CHCl<sub>3</sub> as solvent. b) Oxolane (THF) as solvent. Reproduced with permission.<sup>[99]</sup> Copyright 2015, The Royal Society of Chemistry.

**Table 7.** Other organic molecule interlayer examples in perovskite solar cells. Relevant interlayers used in organic solar cells have also been included.

Solar cell architecture	Molecule structure	References	Classification
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3-x</sub> Cl <sub>x</sub> /PCBM/rodamine101/Ag		[74]	Dye
ITO/ PEDOT:PSS/porphyrin/ CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/BCP/Al		[67]	Dye
FTO/c-TiO <sub>2</sub> /m-TiO <sub>2</sub> /thiols/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /thiols/spiro-OMeTAD/Au		[106]	Thiol
Glass/thiols/Ag/thiols/PCBM/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PTAA/Ag		[107]	Thiol
ITO/NiO <sub>x</sub> / CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3-x</sub> Cl <sub>x</sub> /PCBM/metal organo compound/Ag		[104]	Metal organo compound
ITO/PEDOT:PSS/ PCDTBT:PC71BM/ metallophthalocyanine/Al		[100]	Dye
ITO/phosphonic acids/P3HT:PCBM/Al		[103]	Phosphonic acid
ITO/glycol/PTB <sub>71</sub> :PC <sub>71</sub> BM/Al		[105]	Glycol



**Scheme 4.** Thin interlayer preparation methods. (1) Dipping method, (2) spin coating method, and (3) thermal evaporation.

In summary, we believe that the use of molecular interlayers is a promising approach to improve the efficiency and stability of PSC. We have highlighted a number of interlayers used in OPV throughout this review, especially where there is the potential OPV-interlayers to be used directly in perovskite solar cells. There has been a lot of research into

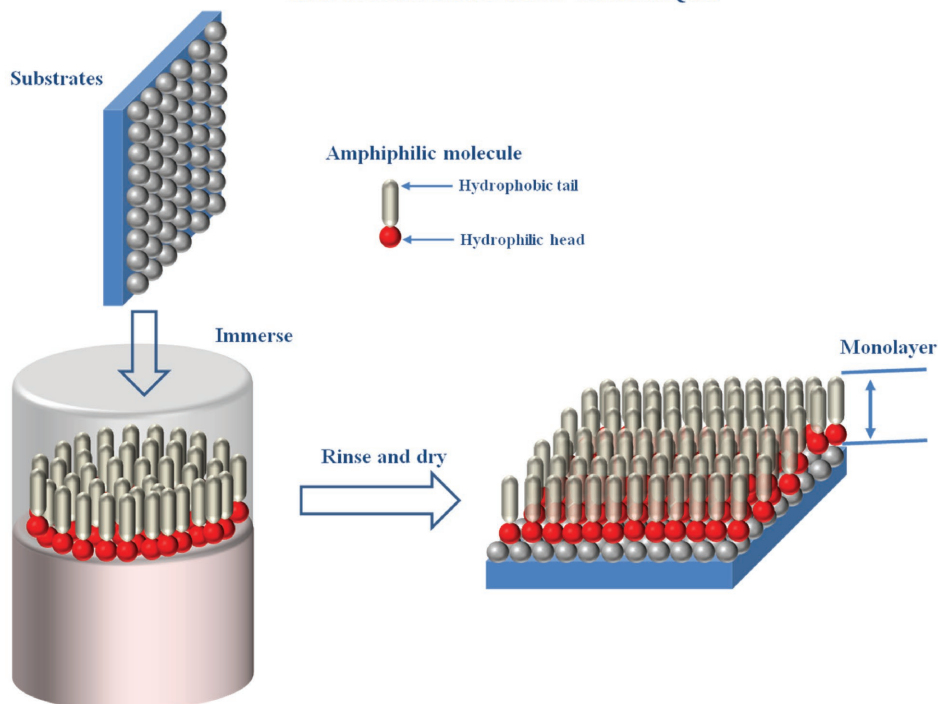
the morphology of interlayers used for OPV and it has been shown that the molecular stacking can influence both charge transfer and (very importantly) the morphology of subsequent layers. Some of these findings are very relevant to PSC where similar molecular interlayers are just starting to be investigated.

**Table 8.** Dip coating process parameters for making molecular interlayers.

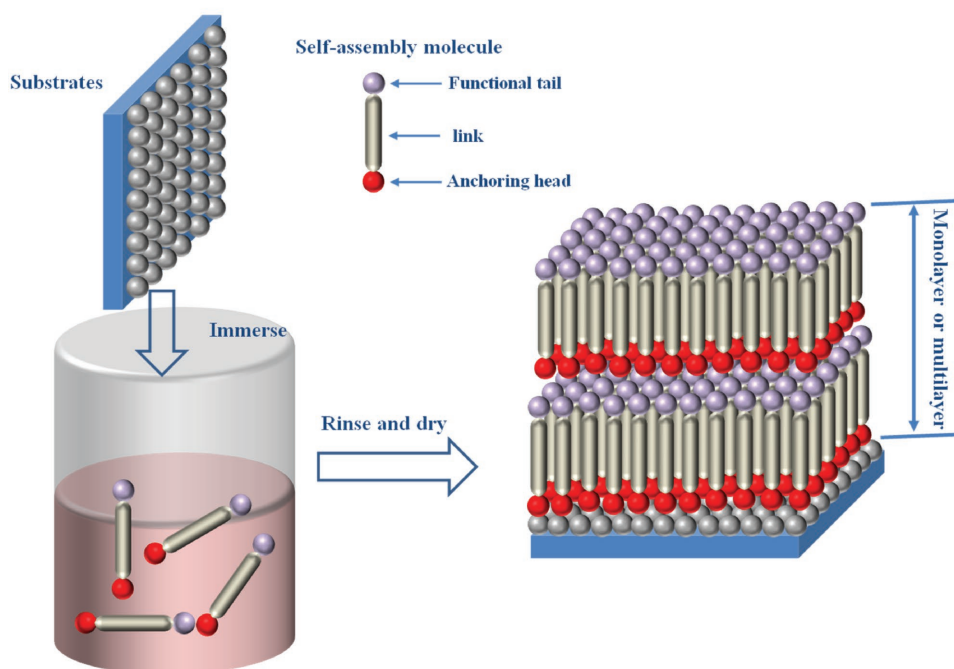
Substrates	Material	Solvent	Concentration	Dipping time	Dipping temperature	References
SiO <sub>2</sub>	ODPA	THF	$1 \times 10^{-3}$ M	3 h	60°	[113]
TiO <sub>2</sub>	Benzoic acid derivatives	THF:EtOH (1:1)	$0.1 \times 10^{-3}$ M	overnight	— <sup>a)</sup>	[46]
TiO <sub>2</sub>	Benzoic acid derivatives	MeCN	$1 \times 10^{-3}$ M	≈2 h	—	[82]
TiO <sub>2</sub>	Carboxylic/phosphonic acids	EtOH	$0.5 \times 10^{-3}$ M	18 h	—	[114]
TiO <sub>2</sub>	Glycine	H <sub>2</sub> O	$1 \times 10^{-3}$ M	overnight	—	[85]
ITO	Perylene diimide derivatives	DMF/CHCl <sub>3</sub>	$20 \times 10^{-6}$ M	1 h	Room temperature	[26]

<sup>a)</sup>Where a value has not been entered it was not mentioned in the reference.

### LANGMUIR-BLODGETT TECHNIQUE



### SELF-ASSEMBLY PROCESS



**Scheme 5.** Self-assembly process and Langmuir–Blodgett technique.

The low cost, easy design, modification, and purification of small molecules make them ideal candidates to carry out interface engineering. The fact that they can be deposited by scalable solution based techniques is an added advantage.

The molecules need to be carefully chosen to make sure that they are stable over long periods and in operating devices; but where this stability can be achieved molecular interlayers have the potential to be an important part of the



**Table 9.** Spin coating process parameters for making molecular interlayers.

Underlayer	Molecule	Solvent	Concentration	Spin coating speed	References
PCBM	PDINO	MeOH	1 mg mL <sup>-1</sup>	1 krpm	[42]
TiO <sub>2</sub>	Ethanolamine	2-methoxyethanol	0.35 wt%	3 krpm	[20]
PCBM:P3HT heterojunction	Urea	Methanol	1 mg mL <sup>-1</sup>	3 krpm	[43]
ITO	Perylene diimide derivatives	CHCl <sub>3</sub>	0.5 × 10 <sup>-3</sup> M	1 krpm	[26]
F-DTS:R-PDI heterojunction	Perylene diimide derivatives	Methanol with 0.2% acetic acid	1.5 mg mL <sup>-1</sup>	3 krpm	[98]

toolkit required to scale-up and commercialize perovskite solar cells.

## Acknowledgements

The authors thank the University of Bath 50th Anniversary Excellence Studentship scheme for funding and the Great Britain China Education Trust for support. Scheme 3 was replaced and the text in section 2.2. describing Scheme 3 was corrected on January 5, 2018 after initial online publication.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

interface, interlayer, perovskite, photovoltaics, solar cells

Received: June 6, 2017

Revised: July 16, 2017

Published online: September 18, 2017

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