

Optimizing Interfacial Design in Emerging Photovoltaics for Advanced Tandem Application

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Declaration Form

DECLARATION

I hereby, declare that this manuscript, entitled “Optimizing Interfacial Design in Emerging Photovoltaics for Advanced Tandem Application”, is the result of my own work except for quotations and citations which have been duly acknowledged.

I also declare that, to the best of my knowledge and belief, it has not been previously or concurrently submitted, in whole or in part, for any other degree or diploma at Nazarbayev University or any other national or international institution.



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Abstract

In recent years, solar power has gained increasing attention as a sustainable energy alternative that can alleviate the burden on conventional fossil fuels. The third-generation photovoltaic (PV) technologies, including perovskite solar cells (PSCs) and organic photovoltaics (OPVs), have emerged as competitive technologies relative to commercial crystalline silicon solar cells due to their remarkable intrinsic optical and electronic characteristics and low manufacturing costs. A rapid increase in power conversion efficiency (PCE) has been reported for PSCs and OPVs in recent years. When single junction solar cells face a theoretical efficiency threshold of $\sim 33\%$, this ceiling can be broken by connecting two solar cells with varying bandgaps in series, extending the light utilization across visible and near-infrared regions. PSCs and OPVs are of specific interest due to their complementary absorption profiles.

While tandem solar cells (TSCs) offer a practical solution to surpass efficiency limits, optimizing the performance of individual sub cells is essential. In this manner, this work will focus on interfacial engineering of the perovskite and the upper hole transporting layer (HTL) interface through the incorporation of a thin film of a novel self-assembled monolayer (SAM). Consequently, the champion interfacially engineered PSC was able to obtain a PCE of 17.33% with an open circuit voltage (V_{OC}) of 1.03 V, short circuit current density (J_{SC}) of 22.73 mA cm⁻² and a fill factor (FF) of 73.85%. In comparison, the champion control device achieved the V_{OC} of 1.05 V, J_{SC} of 21.61 mA cm⁻², FF of 72.85%, and PCE of 16.48%. Increase in PCE and other photovoltaic parameters are attributed to more uniform perovskite film morphology, along with the ability of the SAM to passivate defects of the perovskite layer. Furthermore, unencapsulated interfacially engineered PSCs also deliver superior operational stability at ambient atmosphere compared to control devices.

To enhance the compatibility of the PSC within tandem architectures, conventional Spiro-OMeTAD HTL was replaced with common polymeric hole transporting materials, namely PTQ10, PTAA, Poly-TPD, PM6, and D18, by systematically investigating the photovoltaic parameters of PSCs within the new HTL systems. Among these, PSCs with the PM6 HTL delivered a V_{OC} of 1.11 V, J_{SC} of 21.54 mA cm⁻², FF of 64.25%, and PCE of 15.39%, demonstrating photovoltaic parameters comparable to Spiro-OMeTAD-based devices.

Finally, SAM-modified PSCs were integrated within the structure of perovskite-organic TSCs by optimizing the thickness of the silver within the interconnecting layer (ICL) and the band gap of the perovskite sub cell. The champion control and YY02-modified TSCs achieved a V_{OC} of 1.84 and 1.82 V, J_{SC} of 12.06 and 12.08 mA cm⁻², FF of 58.57 and 59.84%, and PCE of 13.25 and 13.67%, respectively, using a 1.5 nm thick Ag, a perovskite layer with a band gap of 1.86 eV, and PM6:Y6 OPV cell with an E_g of 1.33 eV.

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Chapter 1 - Introduction

1.1. Background

During the times where renewable energy has had an important role in alleviating the burden on fossil fuels, acting as an alternative source of energy, the search for a suitable eco-friendly energy harvesting system has never been more important. In this light, solar energy has been one of the main topics in research in the last decade, with rapid advancements highlighting novel materials for light absorption with record-breaking efficiencies. PSCs have caught a significant amount of attention in recent years because of their intrinsic photovoltaic characteristics, including tunable bandgap, high absorption, and low electron-hole recombination rates. Not only that, but their improvement in PCE, from 13% in 2013 and reaching to almost 27% in 2025, have solidified PSCs as a competitive technology for well-established silicon crystalline solar cells [1].

Despite these advancements, single junction solar cells remain limited by the Shockley-Queisser (SQ) limit, which is a theoretical maximum efficiency of around 33%. This limit can be addressed by connecting two or more solar cells with complementary band gaps in series, which is also called a TSC. TSCs provide a practical resolution to overcome the limitation of single junction devices by allowing a more efficient utilization of a solar spectrum, where wide band gap (WBG) sub cell absorbs high-energy photons, while narrow band gap (NBG) solar cells harvest photons in red and near infrared regions.

In this context, PSCs and OPVs have attracted a significant amount of attention within tandem architectures because of their remarkable optical and electronic properties, such as tunable band gaps, low rates of electron-hole recombination, and compatibility with low-temperature fabrication. The integration of perovskite and organic solar cells within tandem structures allows

for a thin film solution, which facilitate fabrication on flexible substrates and are well-suited for scalable roll-to-roll production methods.

However, the main problem for WBG PSCs is phase segregation and unwanted voltage losses, the latter of which arises from non-radiative recombination (NRR) at the device interfaces, defects at perovskite layer, or energy mismatch between perovskite photoactive layer and hole or electron transporting layers (HTL, ETL) [2]. In this context, the upper interface engineering between perovskite and HTL in n-i-p structured PSCs is essential, as this interface serves as a primary pathway for hole extraction [3].

In recent years, SAMs have been used extensively as HTL or at the HTL/perovskite interface in p-i-n structured (inverted) PSCs because of their ability to improve charge transfer of PSCs and passivate surface defects [4], [5]. For example, Lin *et al.* [6] have proposed a dual surface modification approach of nickel oxide (NiO_x)/perovskite interface by using ethanolamine combined with 2PACz SAM. He *et al.* [7] reported on the effects of co-SAMs on both the morphology and device performance of PSCs by investigating the use of mixed SAM, by co-dissolving MeO-4PACz and Me-2PACz SAMs in one solvent, as well as sequentially depositing them as HTLs.

Even though more research focuses on application of SAMs in inverted PSCs, there are also reports on its usage at the ETL/perovskite interface in conventional PSCs [8], [9], [10]. In one of these works, MPTMS SAM was used as an interlayer at the bottom interface of conventional PSCs by Shi *et al.*'s group [8]. Furthermore, p-type SAM HTLs have also been applied at the perovskite surface in conventionally structured PSCs as well. Mussakhanuly *et al.* [11] designed a passivation layer consisting of formamidinium bromide and a p-type SAM to treat surface defects of the

perovskite films and to target NRR pathways. Zhai *et. al.* [12] developed two p-type SAMs for perovskite modification and optimization of perovskite and HTL interface.

Though SAMs have emerged as a powerful nanomaterial to boost device performance of PSCs because of their abilities to alter chemical and physical interfacial properties, works on SAM molecules are mainly focused on inverted structures or at the ETL/perovskite interface of conventionally structured PSCs, while the perovskite/HTL interface of conventional PSCs still remains unexplored [13] [12]. Thus, this thesis will work on optimization of the top perovskite interface of conventional PSCs using novel SAM molecules. It is expected that the addition of SAM at the interface will provide a homogeneous charge distribution, improved energy alignment, and passivation of the perovskite surface. The optimized configuration of single junction PSCs is expected to provide better photovoltaic properties and increased operational stability. Furthermore, the interfacially engineered PSCs will be introduced as part of the perovskite-organic TSCs by coupling the PSC with NBG OPV based on PM6:Y6 bulk heterojunction.

1.2. Objectives

- To develop interfacial engineering techniques for metal halide perovskites in solar cell applications.
- To develop tandem compatible solar cells by investigating different HTL materials for single junction PSCs.
- To optimize the ICL stack for perovskite-organic tandem solar cells.

1.3. Research Questions and Hypotheses

— Novel SAM material systems can be successfully applied at the interfaces of PSC, improving energy band alignment between adjacent charge transport materials and passivating defects.

— High performing SAM-modified PSCs can be coupled with NBG OPVs for perovskite-organic tandem solar cell applications.

1.4. Outline

Chapter 2 describes the PSC, OPV, and TSC fundamentals concepts, beginning with an overview of the perovskite material, moving to the definition and recent highlights for SAMs, and concluding with working principles of PSCs, OPVs, and TSCs, as well as advances of TSCs through the means of optimizations of single junction devices and ICL. Chapter 3 outlines the methodology for device fabrication and information on material and device characterization techniques. Chapter 4 demonstrates the findings of interfacial interactions between the SAM and perovskite layers and the effects of the YY02 SAM on PV parameters of PSCs. Chapter 5 reports on the integration of single junction PSCs within the structure of perovskite-organic TSCs via device engineering. Final chapter concludes results discussed in the thesis work, along with the future plans on the improvement of the work.

Chapter 2 - Literature Review

2.1. Perovskite Crystal Structure

Perovskite material is a compound of formula ABX_3 and whose crystal structure follows the structure of a true perovskite material ($CaTiO_3$, Figure 2.1 a). In perovskite structures, ‘A’ (Cesium, Methylammonium, Rubidium, or Formamidinium) and ‘B’ (Lead, Tin) are differently sized cations, while ‘X’ (Iodine, Bromide, Chlorine) is an anion, which creates a bond with ‘A’ and ‘B’ cations [14]. The range of possible ionic combinations lead to optoelectronic tunability of the perovskite materials, illustrated in Figure 2.1 b. For example, tuning the ratio of Iodine/Bromide in lead-based perovskites alters the bandgap from 1.6 to 2.3 eV for $A = Cs^+$ [15].

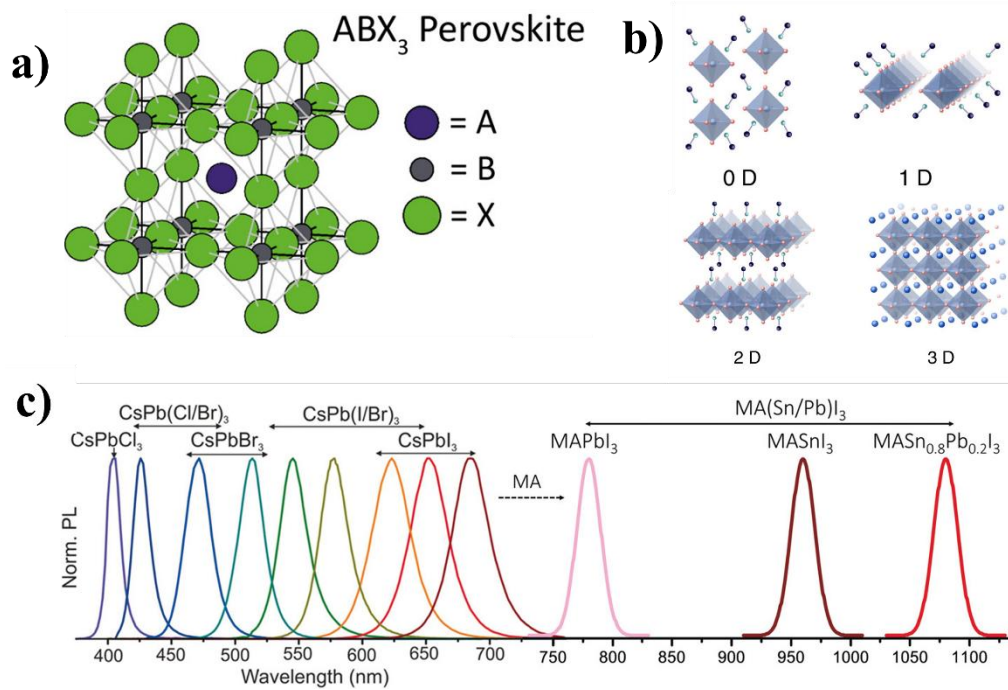


Figure 2.1. (a) Structure of a perovskite crystal [16]; (b) perovskite materials with different dimensionalities [17]; (c) PL spectra of different perovskite compositions [18]

Variants of the perovskite structure can also be engineered to form perovskite crystals of different dimensionality, such as perovskite nanocrystals (0D), 2D perovskites, 1D perovskites, and bulk perovskites (3D) by altering the stoichiometry (Figure 2.1 c) [19].

2.2. Self-Assembled Monolayers

SAMs are one molecule thick monolayers which can spontaneously form on any solid surface and usually have three functional groups: terminal, linker, and anchoring groups [20], [21], [22]. Figure 2.2 shows molecular structures of different SAMs.

The anchoring group establishes connection on the surface of a substrate. Modern SAMs for PSC applications are usually comprised of carboxylic acid (CA), siloxane, boric acid (BA), sulfonic acid (SA), and phosphoric acid (PA) anchoring groups [21]. Terminal groups usually consist of functional head groups, which are responsible for defect passivation of overlaying films/layers and bolstering the operational stability and PV parameters of the devices [23]. Linker groups are designed to connect terminal and anchoring groups. They can tune the interaction of the molecule with different solvents, intramolecular interaction between terminal group and the substrate, and intermolecular interaction. Common linker groups include aromatic conjugated moieties and alkyl chains. The length and direction of alkyl chains can be tuned to change the adsorbance strength between SAM and the substrate [24].

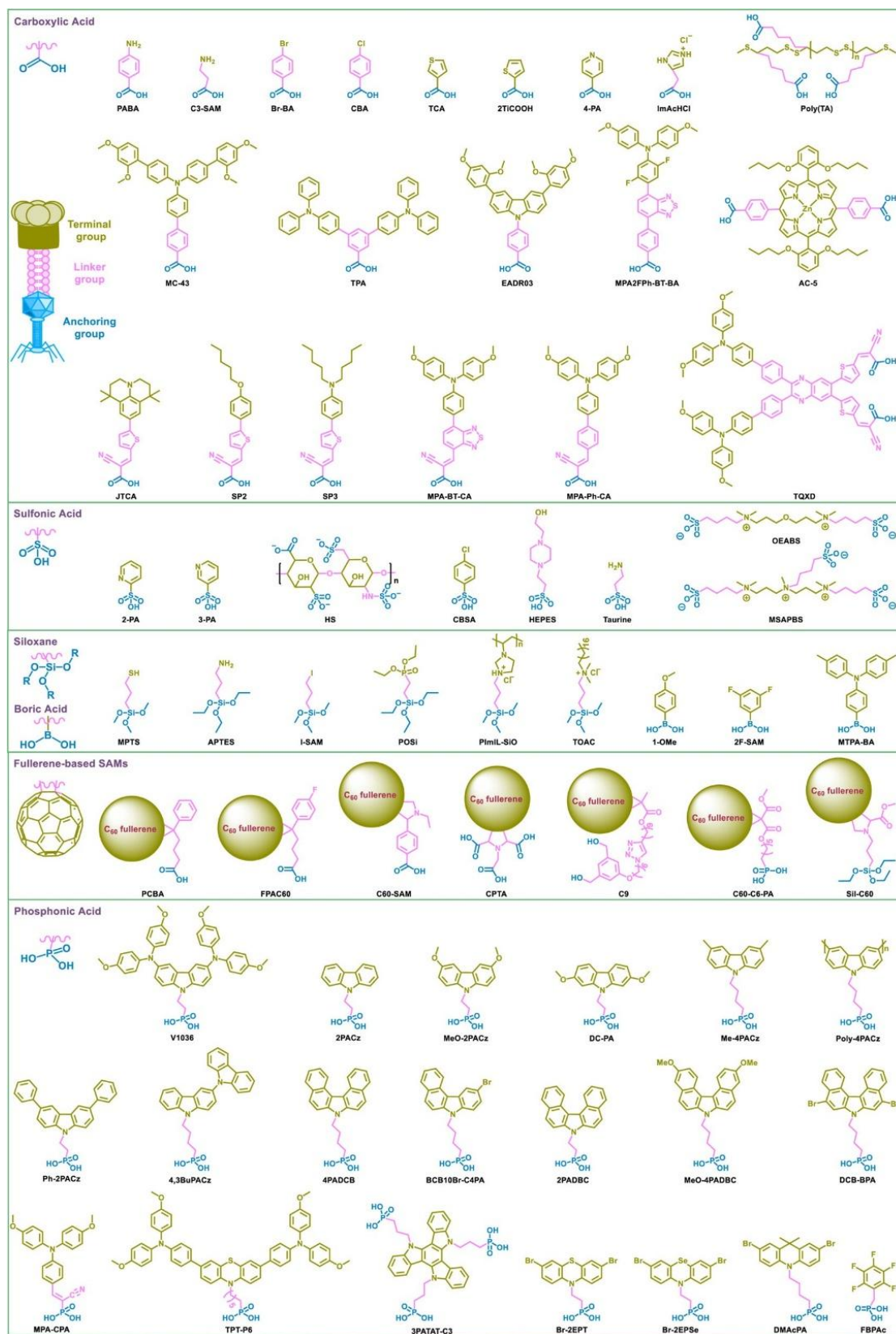


Figure 2.2. Molecular structure of different groups of SAMs [21]

SAMs have found application in different types of thin film electronics, most importantly, perovskite solar cells [24]. The emergence of SAMs as an HTL has reshaped the design principles of PSCs, mainly inverted ones, because of their intrinsic optical and molecular properties, eliminating parasitic absorption and overcoming optical losses [25]. Before the emergence of SAM molecules, most common HTLs for p-i-n PSCs were inorganic metal oxides such as NiO_x , or polymeric materials like PEDOT:PSS, Poly-TPD, and PTAA [26]. However, the mass deployment of inverted PSCs is hindered by the expensive cost and hydrophobic properties of polymeric HTLs and inferior photovoltaic properties of NiO_x based PSCs [27], [28]. Thus, research in inverted PSCs have shifted its attention to the use of SAMs as HTL or at the HTL/Perovskite interface. The latest advancements in inverted PSCs employing SAMs are presented in Table 2.1.

Table 2.1. Overview of photovoltaic performances for SAM-based inverted PSCs

Nº	SAM	Application	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	Ref
1	CbzNaph	HTL	1.17	24.69	83.39	24.1	[29]
2	Me-4PACz	NiO_x /PVK interface	1.33	18.06	84.2	20.2	[30]
3	2PACz	HTL	1.22	20.6	80.6	20.2	[31]
4	2PACz + PA	Co-SAM	1.19	26.25	84.85	26.55	[32]
5	Me-4PACz	HTL	1.15	26.13	84.6	25.49	[33]
6	I-2PACz	HTL	1.16	25.43	85.8	25.39	[34]
7	CBSA	NiO_x /PVK interface	1.11	23.72	80.18	21.1	[35]

8	MeO- 2PACz + PDADI	Co-SAM	1.17	25.54	85.17	25.49	[36]
9	MeO- 4PACz + Me-2PACz	Co-SAM	1.16	25.20	85.91	25.01	[7]
10	MeO- 2PACz and C60-SAM	HTL and ETL	0.92	18.8	48.0	8.32	[37]

2.3. Perovskite Solar Cells

PSC is an emerging PV technology with a perovskite material for light absorption, in which the perovskite is processed within two functional layers: ETL and HTL. The device structure of PSCs can follow both conventional (n-i-p) configuration or inverted (p-i-n) structures, illustrated in Figure 2.3. When sunlight is illuminated from the bottom of the substrate, the perovskite layer absorbs incident photons with energies ($h\nu$) greater than its bandgap (E_g), creating an electron-hole pair. Those photogenerated carriers are then driven apart by the built-in electric potential, which are subsequently moved to the anode and cathode via the HTL and ETL [38].

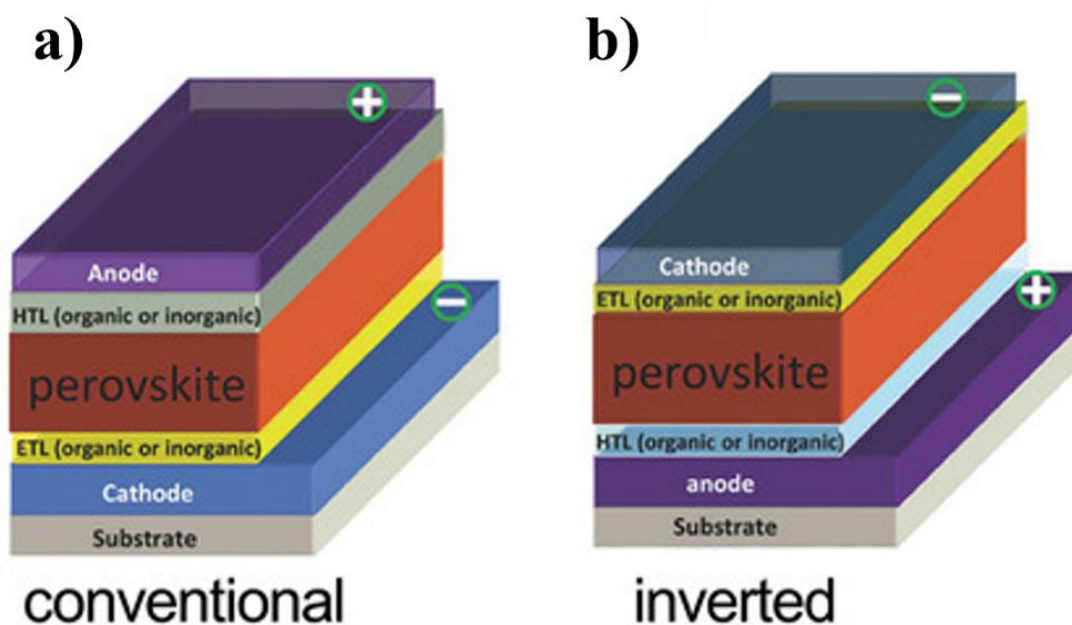


Figure 2.3. (a) Conventional and (b) inverted device configurations for PSCs. Adapted from [38].

2.4. Organic Photovoltaics

OPV is a solar cell where the active layer consists of organic semiconducting materials - semiconducting polymers or small molecules [39]. A typical structure of OPVs is similar to that of the PSCs, however, the light harvesting layer is composed of electron donor (D) and/or acceptor (A) materials. Upon illumination of the organic active layer, an exciton in the electron donating domain is created. Unlike typical solar cells, these excitons cannot be separated into electrons and holes by thermal energy alone, because of the presence of coulombic bound. Thus, a large driving force is required to separate the excitons into mobile charge carriers.

OPVs also can follow p-i-n (conventional) and n-i-p (inverted) structures like PSCs. Figure 2.4 depicts various device structures for OPVs, each of them having different morphologies for the

active layer: single component, bilayer, and bulk heterojunction (BHJ). Each structure offers its own advantages and disadvantages.

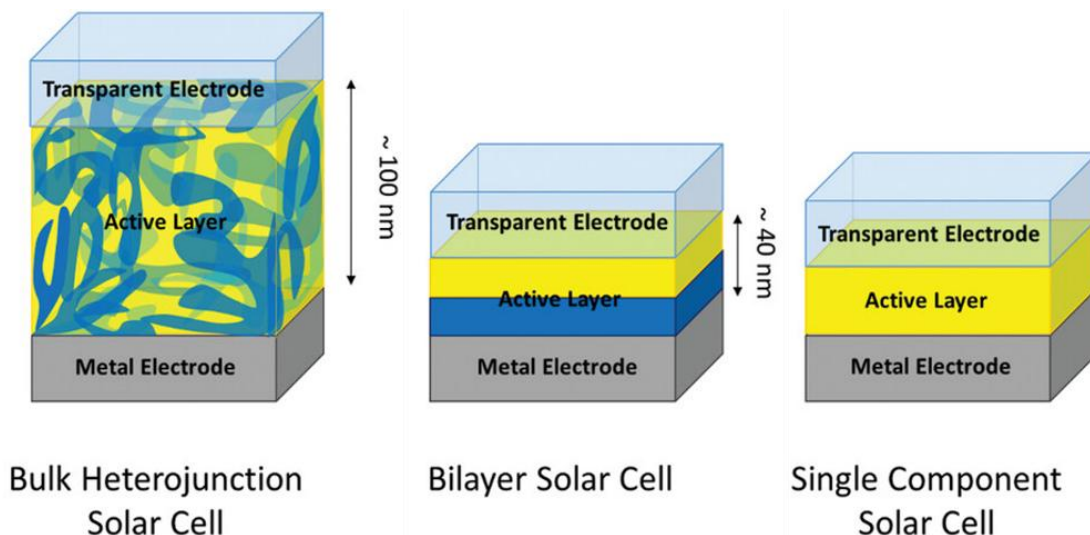


Figure 2.4. Schematic of various device structures for OPVs. Adapted from [40]

BHJ OPV involves the blend of D and A materials in varying concentrations, allowing for efficient charge separation and transportation [39]. Although BHJ OPVs can be used to fabricate efficient OPV devices, many factors should be considered when creating a donor and acceptor blends, which may severely impede the morphology of BHJ organic films, and in turn reduce efficiency. Furthermore, the network of D and A polymers in BHJ OPV films creates ‘islands’ of donors and acceptors, also negatively affecting the efficiency of the devices [41], [42].

Bilayer OPV is formed by sequentially growing organic electron donor and acceptor layers. The thickness and the morphology of the active layer can be precisely controlled with bilayer architecture, enabling OPVs with enhanced performance and reduced defects. Aside from the improved morphology for bilayer OPVs, this method of fabrication improves charge separation of excitons, creating independent transmission channels for the transportation of electrons and holes [41].

Single Component OPV uses a single semiconducting polymer with both electron donor and electron acceptor chemically bonded within one molecule of the polymer chain [43]. Although state-of-the-art single component OSCs lag behind BHJ and bilayer OPVs in terms of PCE, this structure enables a more straightforward device architecture, while also potentially reducing the production cost [39].

2.5. Tandem Solar Cells

The theoretical efficiency of solar cells was proposed in 1961 by William Shockley and Hans Queisser [44]. According to their model, the efficiency of a single junction solar cell is limited to ~33%, given the bandgap of a photovoltaic device is 1.34 eV. The limit exists because of fundamental loss mechanisms, which are present in a solar cell, such as transmission and thermalization of photons, recombination of charge carriers, and parasitic resistance losses [45]. To surpass the proposed limit, the research in photovoltaics has transitioned to the development of TSCs.

TSCs are comprised of two or more solar cells with varying bandgaps. This can be done either by growing an NBG solar cell on top of a WBG cell, creating a monolithic stack (2-terminal/2T TSC), or by mechanically connecting two individual cells together (4-terminal/4T TSC, Figure 2.5).

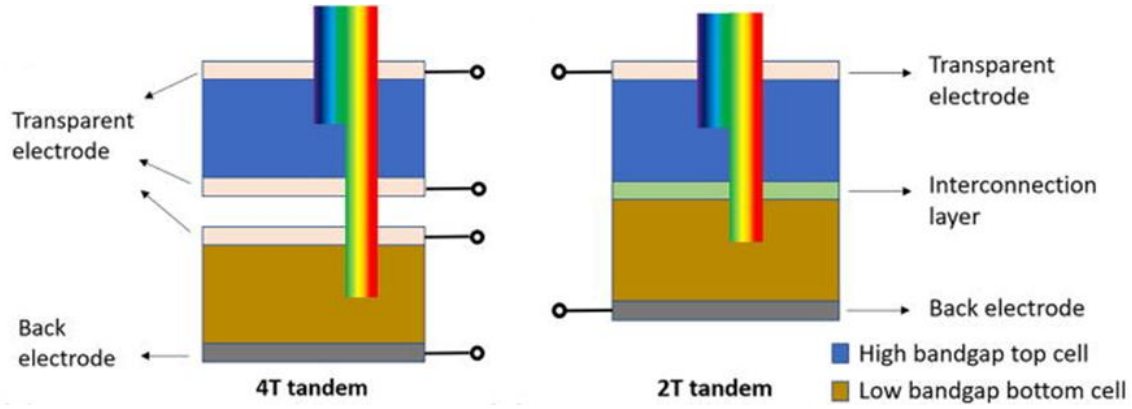


Figure 2.5. Schematics of 4-terminal (4T) and 2-terminal (2T) tandem solar cells [46]

Since in 2T TSCs NBG bottom cell is grown on top of WBG solar cell, the fabrication process for the bottom cell should be optimized as to not destroy or dissolve the layers of WBG bottom cell during the manufacturing. Furthermore, since ICL connects sub cells in series, it should possess certain characteristics to ensure adequate charge carrier transport and recombination, such as, high carrier mobility, work function alignment with adjacent layers, and low transverse conductivity [46], [47].

On the other hand, for 4T TSCs, since cells are mechanically connected together by an external circuit, there has to be an insulating layer between the two sub cells, to reduce refractive index mismatch and to minimize optical loss [46].

2T TSCs. In 2T TSCs, when light is illuminated to the rear cell, the active layer absorbs incident photons with energy greater than its bandgap, while transmitting remaining photons to the front cell through the ICL. During this process, the rear and front cells generate electron hole pairs; electrons from the bottom cell are collected by the bottom electrode (for n-i-p structure) and holes are transported to the ICL. Electrons generated in the front cell, on the other hand, are collected by the ICL where they recombine with holes from the rear cell, while holes are collected by the top electrode. In 2T TSCs both solar cells are connected in series, resulting in a voltage equal to the

combined voltages from two solar cells, whereas the photocurrent is constrained by the WBG solar cell.

4T TSCs. Since two solar cells in 4T tandem structures are connected independently, the working principle for this structure is the same as in single junction solar cells. Furthermore, total PCE in 4T TSCs is the sum of the PCEs acquired from both solar cells.

Since the performance of TSCs, regardless of the structure, is highly dependent on the performance of the individual cells, advances in perovskite-organic TSCs focus on interfacial engineering of individual cells to minimize charge recombination at the interfaces of the solar cell. Sun *et al.* [48] enhanced the ordering of SAM HTL for OPVs through a volatile solid additive strategy. They have incorporated 1,3,5-trichlorobenzene (TCB) into the 4PADCB SAM precursor. Their paper states that the electrostatic interactions between SAM and TCB have enhanced their interaction, which lead to improved face-on orientation of the SAM film, enhancing its hole transporting capabilities. Their optimized OPV devices show an increase in photovoltaic characteristics, achieving an V_{OC} of 0.86 V, J_{SC} of 28.83 mA cm⁻², FF of 80.64%, and PCE of 20.06% (Figure 2.6 b). The integration of the optimized OPV in perovskite-organic TSCs have resulted in the FF and PCE of 81.90 and 26.09%, respectively (Figure 2.6 c).

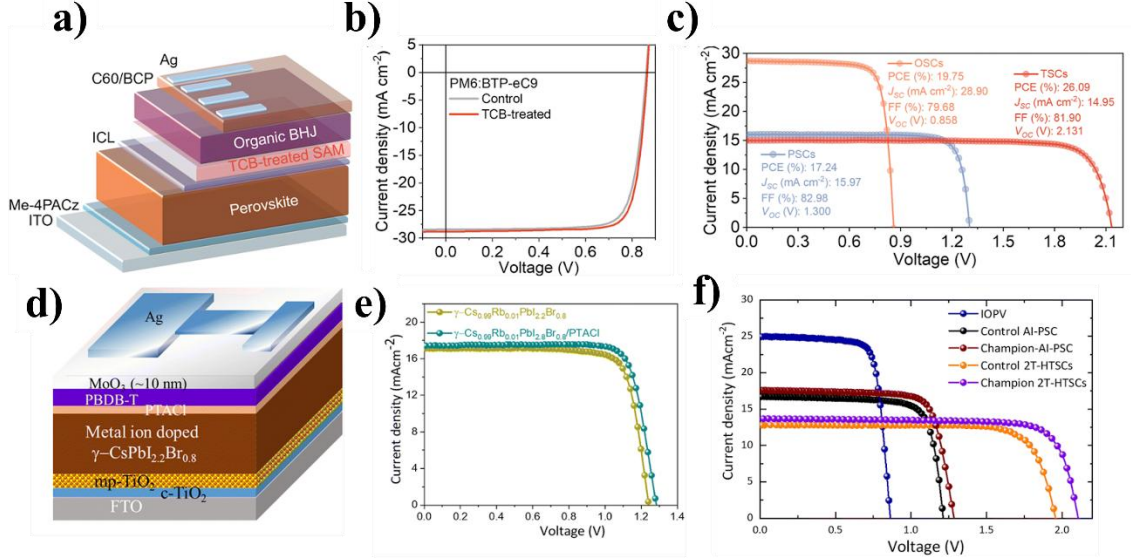


Figure 2.6. (a) Schematic of perovskite-organic 2T TSC device architecture; (b-c) J-V curves of (b) control and TCB-treated single junction OPV and (c) champion OPV, PSC, and perovskite-organic TSC [48]; (d) Schematic of all-inorganic PSC; (e-f) J-V curves of (e) metal ion doped PSC with and without PTACL-passivation and (f) champion OPV, PSC, and perovskite-organic TSC [49]

Mali *et al.* [49] reported on ambient air processed all-inorganic perovskite-organic TSCs through metal ion doping, surface passivation, and dynamic hot-air processing of the perovskite layer. They were able to improve phase stability of all-inorganic PSCs through metal ion doping by substituting metal ions in the composition of γ -CsPbI₂Br perovskite. Furthermore, perovskite surface passivation with PTACL increases photoluminescence (PL) intensities, hinting at reduced recombination in the perovskite thin films. PTACL surface passivation and metal ion doping not only improved photovoltaic performances of PSCs, but also passivated traps and provided smooth hydrophobic surface with enhanced the perovskite film stability against moisture in the ambient atmosphere. The device structure for metal ion doped and PTACL passivated PSCs is shown in Figure 2.6 d.

After optimization of the single junction all-inorganic PSCs, the authors implemented the strategy of metal ion doping and surface passivation to fabricate 2T perovskite-organic TSCs, where PM6:Y6:PCBM ternary BHJ acts as a top NBG OPV cell. Overall, passivation and compositional engineering of the perovskite lead to improved photocurrent and photovoltage of the TSCs.

Aside from interface modification, state-of-the-art TSCs also focus on ICL engineering, since it is crucial for TSC performance, as it electrically connects two sub cells together, creating a site for electron-hole recombination collected from the PSC and OPV. Thus, an ideal ICL should have an adequate transparency in the spectral range of underlying photoactive material [50].

To assess the role of the HTL in the ICL structure, Wang *et al.* [51] have investigated three different p-type polymers, PBDB-T-Si, D18, and Poly-TPD. The results state that among the three HTLs, Poly-TPD is ideal because of its minimal optical losses and adequate hole mobility. The authors also report that PBDB-T-Si and D18-only ICL stack possess J - V characteristics which resemble a diode, indicating injection barrier for electron and holes at the ICL. Poly-TPD, on the other hand, shows a linear J - V characteristic, indicating quasi-Ohmic contact within the ICL. Furthermore, their proposed charge carrier transport mechanism (Figure 2.6 a) , which explains the reason behind lower V_{OC} loss in TSC devices based on different PSC HTMs. They state that due to high hole mobility of PBDB-T-Si and D18, there is an excess of holes present at the ICL interface, forming a reverse electric field, leading to reduced FF and V_{OC} loss. Poly-TPD, on the other hand, has significantly lower hole mobility, slowing down hole accumulation at the ICL, which is beneficial for both FF and V_{OC} in the tandem structure.

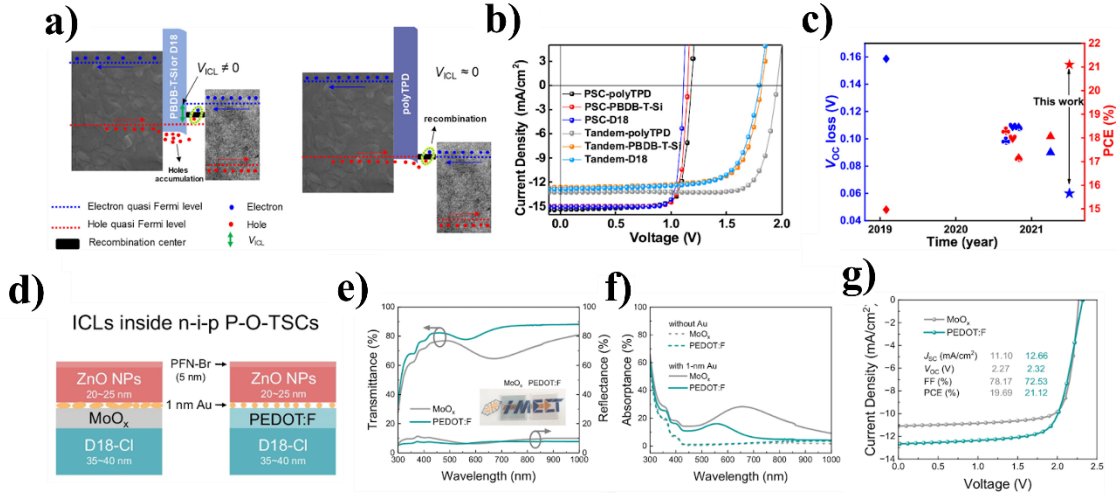


Figure 2.7. (a) Charge carrier transport mechanism for PBDB-T-Si, D18, and Poly-TPD based ICLs; (b) $J-V$ curves of champion OPV, PSC, and TSC; (c) Literature summary of V_{OC} loss and PCE of perovskite-organic TSCs [51]; (d) ICL structures in n-i-p perovskite-organic TSCs; (e-f) Optical characteristics of MoO_x and PEDOT:F-based ICLs; (g) $J-V$ curves of perovskite-organic TSCs with MoO_x and PEDOT:F-based ICLs [52]

Tian *et al.* [52] demonstrated a metal-free ICL structure which mitigates parasitic absorption commonly present in metal nanostructures, such as silver or gold. They supersede thermally evaporated MoO_x metal oxide with alcohol dispersed and solution processed PEDOT:F. By substituting the metal oxide with PEDOT:F solution, the authors report on the change in distribution size of Au because of different surface properties of PEDOT:F and MoO_x. The significant difference between the surface free energy of MoO_x ($\gamma_s = 28.32 \text{ mJ}/\text{m}^2$) and PEDOT:F ($\gamma_s = 6.93 \text{ mJ}/\text{m}^2$) implies that Au nanoparticles during thermal evaporation can adhere strongly to the surface of MoO_x. On the other hand, Au has an opposite migration behavior on the PEDOT:F surface. Taking all of this into account, the authors suggest that Au nanoparticles tend to massively adsorb on a substrate with higher surface free energy, forming irregular Au islands. On substrates

with lower surface energy, on the other hand, fewer Au atoms are adsorbed because of weak surface interaction, forming a more uniform nanostructures of gold.

PEDOT:F-based ICL stacks also exhibit better optical properties, compared to MoO_x-based ICL. PEDOT:F-based ICL shows better transmission in visible and NIR region (Figure 2.7 e). The absorbance of both MoO_x and PEDOT:F are similar, however, as 1 nm Au is introduced, both ICL stacks exhibit different, but significant parasitic absorption losses, which is assigned to LSPR effect of Au nanoparticles (Figure 2.7 f). The lower LSPR peak of PEDOT:F-based ICL (555 nm) is contributed to the formation of more uniform Au clusters, compared to MoO_x-based ICL (659 nm).

Aside from studying structural and optical differences between two ICL stacks, Tian *et al.* also compared device performance of TSCs based on MoO_x and PEDOT:F ICLs (Figure 2.7 g). Overall, tandems employing PEDOT:F/Au ICL deliver a superior J_{SC} with better current matching between perovskite and organic sub cells, compared to MoO_x/Au ICLs. In addition to reduced current mismatch, PEDOT:F-based TSCs were also able to achieve higher V_{OC} and PCE by improving the transmittance of ICL and reducing parasitic absorption of Au.

Chapter 3 - Methodology

3.1. Single Junction Perovskite Solar Cells

i) Perovskite Precursor

Perovskite layer was formed by two-step method. For the first step, the precursors were prepared by dissolving 1.3 mM of PbI_2 (600.6 mg) in 0.95 mL DMF with 0.5 vol% of CsI stock solution (prepared by dissolving 390 mg of CsI in 1 mL DMSO). The PbI_2 solution was left overnight on the hotplate at 70°C with a magnetic stirring rod inside a nitrogen filled glovebox. For the second step, 60 mg of FAI, 6 mg of MABr, and 6 mg of MACl (organic salt solution) were dissolved in 1 mL IPA.

ii) Device Fabrication

Before the start of fabrication, clean FTO substrates were UV-Ozone treated for 30 minutes. For ETL, the SnO_2 colloidal dispersion (15% in H_2O , Alfa Aesar) was mixed with DI water in 1:3 ratio. 65 μL of the ETL solution was dispensed at the substrate and spun at 4000 rpm for 30 seconds using a spin coater. SnO_2 coated samples were then annealed on a hotplate at 150°C for 30 minutes. This procedure was repeated once more.

Before perovskite deposition, SnO_2 coated samples on an FTO substrate were subject to UV-Ozone treatment for 10 minutes. 35 μL of PbI_2 solution was spin coated at 1500 rpm for 30 seconds and annealed at 70°C for 1 minutes. The samples were then coated with 41 μL of FAI:MABr:MACl solution at 1500 rpm for 30 seconds. The resulting film was then annealed on a hotplate at 150°C for 15 minutes to complete the conversion of the perovskite.

For interfacially engineered PSC devices, YY02 SAM (0.5 mg/mL in IPA) was applied on top of the perovskite by spin coating dynamically at 3000 rpm for 60 seconds without further annealing.

For HTL, 72.3 mg of Spiro-OMeTAD was dissolved in 1 mL CB with 35 μ L Li-TFSI (260 mg dissolved in 1 mL Acetonitrile) and 30 μ L 4-tbp additives. The solution was stirred on a vortex mixer for 15-20 minutes and spun coat on top of the perovskite film at 4000 rpm for 30 seconds. The samples were then left in an ambient atmosphere under dry conditions overnight.

10 nm of MoO₃ and 80 nm of Ag were thermally evaporated in a vacuum chamber with base pressure of 10⁻⁶ with a deposition rate of 0.2 Å/s and 0.5 Å/s, respectively. The active area of the solar cell is 0.06 cm².

3.2. Single Junction Organic Photovoltaics

Before the start of OPV fabrication, clean ITO substrates were treated with UV-Ozone for 15 minutes. Afterwards, 70 μ L of ZnO nanoparticle ink solution was spin coated on top of ITO substrates at 4000 rpm for 15 seconds and annealed on a hotplate at 130°C for 20 minutes. ZnO coated samples were then subject to UV-Ozone treatment for 15 minutes.

110 μ L of PM6:Y6 active layer (16 mg/mL in CF with 1:1.2 D/A mass ratio and 0.5 vol% 1-chloronaphthalene, stirred overnight at room temperature) was deposited by spin coating at 3000 rpm for 30 seconds and annealed on a hotplate for 10 min at 100°C.

Electrode deposition follows the same procedure as outlined for PSC fabrication.

3.3. Perovskite-Organic Tandem Solar Cells

For 2T TSCs, the bottom cell was prepared following the same methodology as for the single junction PSCs until the MoO₃ layer deposition. 1.5 nm thick Ag was employed as an ICL

and was thermally deposited in a vacuum chamber with base pressure of 10^{-6} with a deposition rate of 0.02 Å/s. After that, the ZnO/PM6:Y6/MoO₃/Ag OPV stack was prepared with the same procedure as for the single junction OPV fabrication.

3.4. Materials Characterization

i) Scanning Electron Microscopy (SEM)

To study the morphology of the perovskite film, top view of the layer was captured using SEM. SEM is an imaging tool used to obtain high-resolution microscopic images with a resolution varying from <1 nanometer up to several nanometers [53]. The SEM produces an image by directing a focused beam of high-energy electrons on a specimen, scanning it along a zig-zag pattern. The final image is obtained by signals produced due to electron beams interacting with the surface of the sample [54].

SEM uses three various detectors, which are positioned at an angle inside its vacuum chamber: back-scattered electron detector (BSE), secondary electron detector (SE), and X-ray detector [54]. BSE detector detects electrons, which are elastically scattered between the incident electrons and the sample. Though the resolution of a BSE image is worse compared to SE, it can give insight into phases with different compositions [53]. SE, unlike BSE, originates from the surface of the specimen material and comes from energy-loss interactions between the electron beam and the specimen surface. They are particularly effective in studying surface morphology of the sample [55].

The SEM equipment used in this work is Crossbeam 540 (Zeiss). The samples were prepared on an FTO substrate and were sputtered with 7 nm of carbon to avoid overcharging. Column mode was set to “Analytical”, scan speed is 3, EHT = 5 kV, WD = 4.3 mm, I Probe = 100 pA.

ii) Atomic Force Microscope (AFM)

AFM is an advanced imaging technique which employs a probe or a sharp tip mounted on a cantilever to scan the surface of the sample line by line [56]. When the tip lands on the sample surface, the cantilever bends, which is recorded by using a photodetector or a laser [57]. AFM can be used to analyze mechanical and electrical properties of the material by imaging the 2D topography, calculating the surface roughness and nanomechanical properties, such as adhesion, elasticity, and stiffness. The AFM equipment used in this methodology is SmartSPM 1000 Scanning Probe Microscope.

iii) X-ray Photoelectron Spectroscopy (XPS)

XPS is a common tool to study chemical and atomic composition within the samples. The measurement is performed by subjecting the specimen to a beam of incident X-ray radiation, while also measuring the kinetic energy of the emitted electrons within 1 to 10 nm of the surface of the material [58]. By analyzing chemical shifts, the information on chemical interactions between two materials can be analyzed. For the perovskite composition in this work, XPS core orbitals to be analyzed are Pb4f, I3d, C1s, N1s.

v) UV-Visible Spectroscopy (UV-Vis)

UV-Vis spectroscopy is tool for evaluating optical parameters of the sample, such as absorbance, reflectance, and transmittance. The instrument uses a light source, which passes light through a monochromator or a filter onto the sample, which is further transmitted to a detector. This detector is then used to transform the incoming light into an electrical output [59], [60].

The resultant absorption spectra of the sample can subsequently be analyzed to estimate the bandgap of the thin film by plotting the absorption coefficient ($\alpha h\nu$) vs photon energy ($h\nu/\lambda$).

3.5. Device Characterization

i) Current-Voltage Characteristics (I - V)

I - V characteristic of a solar cell determines the correlation between current and voltage of the cell under irradiance and temperature [61]. The I - V curve is a combination of the diode response of the solar cell measured in the dark together with the current produced. The illuminated light shifts the curve downward towards the fourth quadrant, as the device starts to generate power. The relationship describing the current of the solar cell both in dark conditions and under illumination can be expressed using the diode law [62]:

$$I = I_0 \left[\exp \left(\frac{qV}{nkT} \right) - 1 \right] - I_L \quad (3.1)$$

Plotting the above equation gives the I - V curve, where several parameters can be pinpointed, such as short circuit current (I_{SC}), V_{OC} , FF, and maximum power point (MPP).

I_{SC} is the current that passes through the electrodes of a solar cell when the device is under short-circuit conditions and it depends on the photon flux incident on the cell (AM1.5 spectrum for standard measurements of a solar cell) [63]. The value of I_{SC} is influenced by the area of the solar cell; therefore, to eliminate the impact of the active area of the cell, J_{SC} is used to represent the maximum current output of the device.

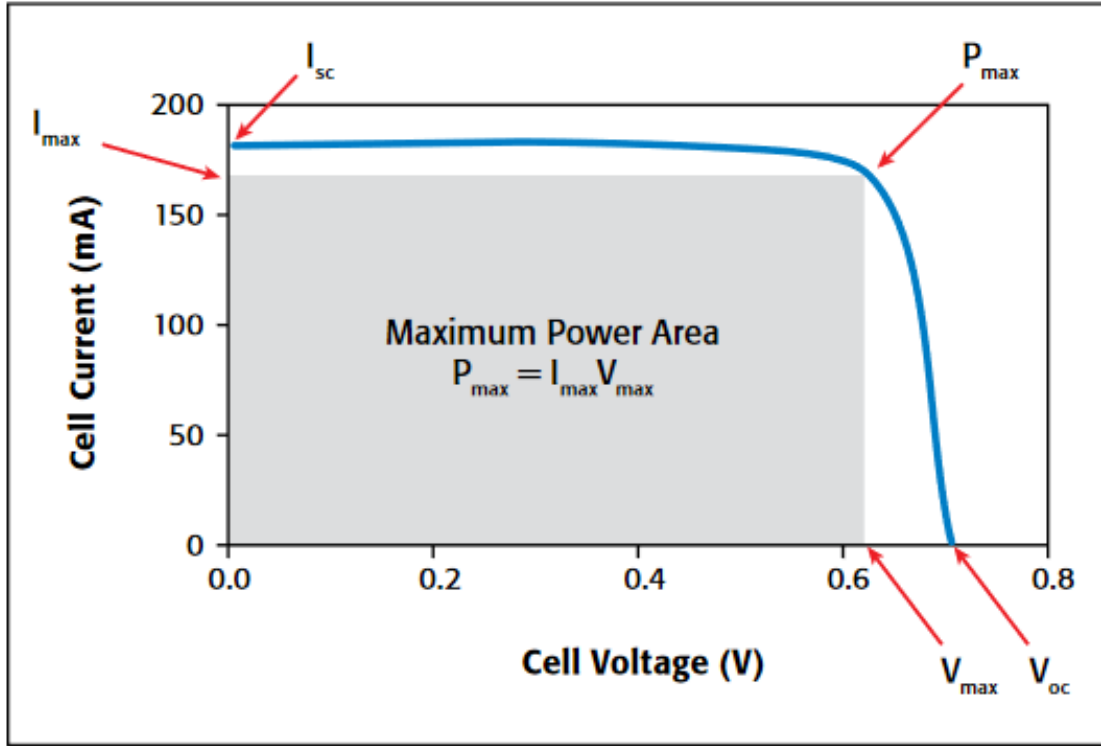


Figure 3.1. Typical I-V curve of a solar cell [64]

V_{OC} is the voltage where no current flows through the circuit of a solar cell and it is the maximum voltage that produced by the device [63]. V_{OC} is dependent on the photo-generated short circuit current density (J_{ph}) and the relationship can be modeled as follows [65]:

$$V_{OC} = \frac{nkT}{q} \ln \left(\frac{J_{ph}}{J_0} \right) \quad (3.2)$$

J - V measurement is used to evaluate the performance of the solar cell, as it provides parameters such as V_{OC} , J_{SC} , FF, and PCE. The measurements of solar cells for this thesis work were performed under the simulated illumination of 1 sun (100 mW/cm^2) from the AAA class solar simulator. The light intensity was adjusted by an AM1.5 filter and calibrated using a Si reference cell.

ii) Quantum Efficiency (QE)

QE represents the fraction of collected carriers generated by the device to the photons at a specific energy that reach the solar cell [66]. While the QE for an ideal solar cell has a perfect square shape, as shown in the figure below, for real devices this shape is reduced due to internal processes within the solar cell device, such as charge recombination.

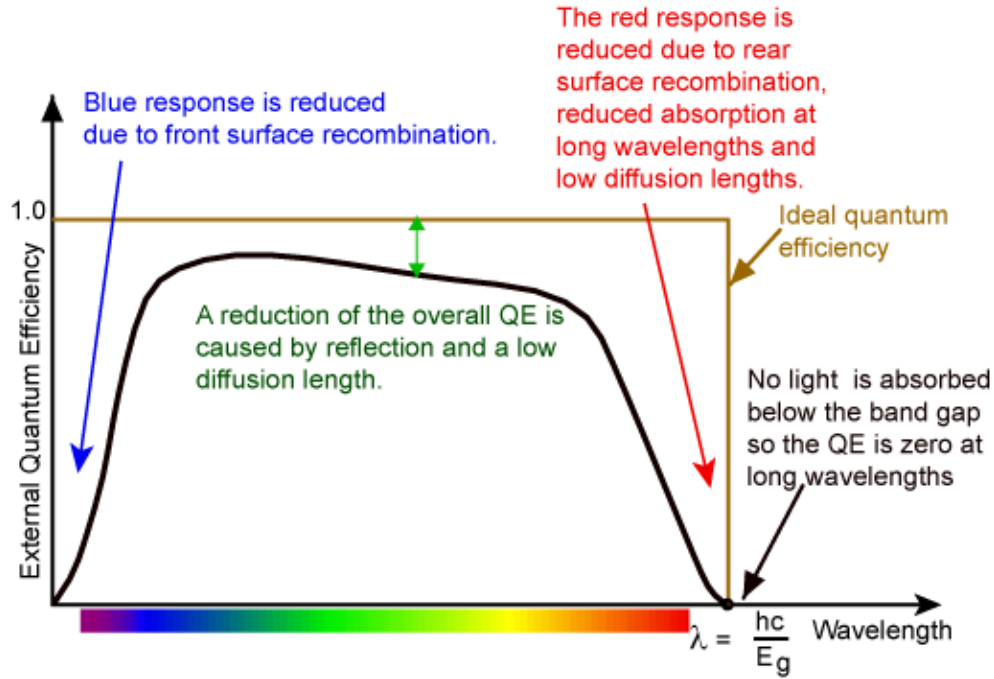


Figure 3.2. Quantum efficiency of a silicon solar cell [66]

External quantum efficiency (EQE) accounts for overall photon-to-electron conversion performance, including losses arising from reflection and transmission, whereas the internal quantum efficiency (IQE) is the fraction of photons that are absorbed within a device and contribute to generation of collectable charges. For EQE measurement, a monochromatic light source is used to illuminate the device across varying wavelengths.

Chapter 4 – Interfacial Engineering of Single Junction Perovskite Solar Cells

4.1. Properties of the Self Assembled Monolayer

The novel SAM presented in this work (YY02) utilizes carboxylic acid-based anchoring groups. Since the adhesion of the SAM is governed by the type of anchoring group, the hydroxyl group (-OH) and an oxygen atom binding sites present in the carboxyl acid anchoring group can be anchored on a surface of a metal oxide *via* monodentate or bidentate bonding, and, in this case, it can be chemically attached to the perovskite active layer [67], [23], [68]. The SAM molecules also exhibit a carbazole terminal, as well as a I⁻ halogen atom. The carbazole terminal can form better interfacial coverage between the perovskite and HTL, while I halogen atom can strengthen the energy alignment of the interface, improve hole extraction, and form strong bonds with iodine ions in the perovskite and passivating its defects [68], [23].

Absorbance and transmittance spectra of YY02 (Figure 4.1 b) shows that the SAM layer has low absorbance on the low-energy side, appearing nearly opaque for the NIR photons. This transparency indicates that YY02 does not absorb photons of low-energy, which are utilized by the NBG OPV sub cell.

The proposed energy band diagram for an interfacially engineered PSCs is presented in Figure 4.1 c. It is evident that the YY02 interface is able to provide smoother energy gradient between the perovskite and HTL, which is beneficial for hole movement and overall device performance.

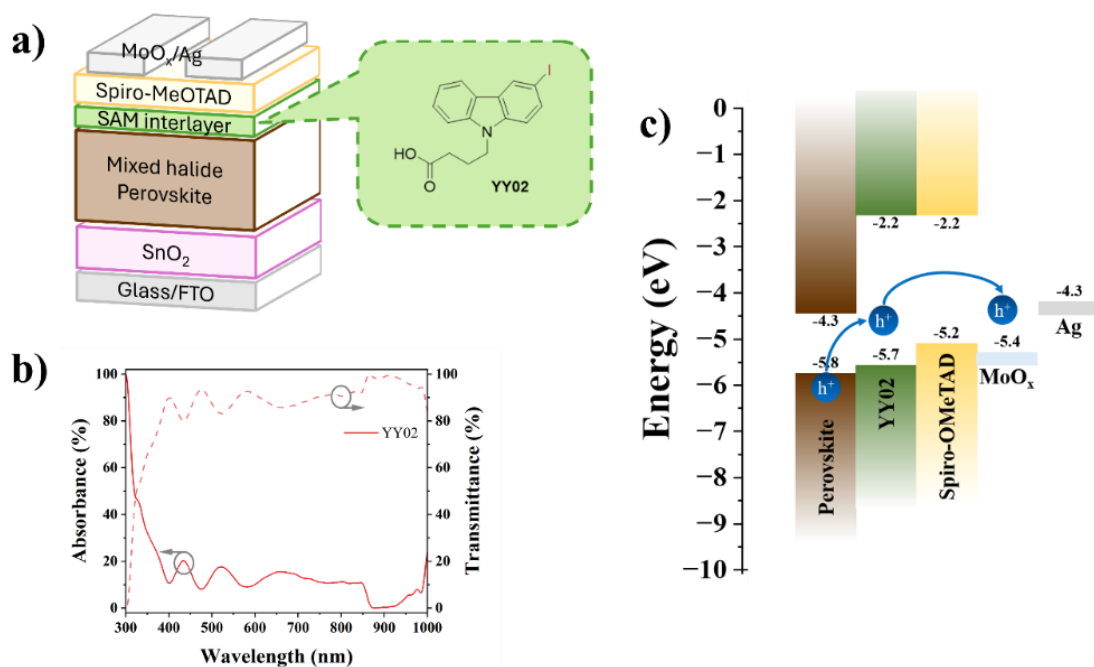


Figure 4.1. (a) Device architecture of the n-i-p perovskite solar cell and chemical structure of SAMs; (b) absorbance and transmittance spectra of YY01, YY02, and YY03 thin films; (c) Energy band diagram detailing the hole movement within the PSC.

4.2. Interfacial Interactions

To better understand how the YY02 film interacts with the perovskite film and influences its morphology, the SEM and AFM were performed on pristine perovskite (control) and YY02 coated samples.

Top-view SEM image of a pristine perovskite film (Figure 4.2 a) reveals a surface morphology with distinct and irregularly shaped grains, with sizes varying from ~500 nm to 1 μ m. Additionally, several secondary perovskite crystallites can also be clearly observed, which occupy the gaps between larger grains. The grain boundaries also appear very sharp, which can serve as traps or recombination sites for charge carriers. Upon introduction of YY02 (Figure 4.2 c), the film exhibits a more homogeneous surface morphology with more regular shaped perovskite grains and

less pronounced grain boundaries. Small perovskite crystallites are also less evident, suggesting that SAM modification contributes to a more uniform perovskite surface.

To further examine the surface morphology, AFM imaging was conducted on control and modified samples. The AFM topography images, shown in Figure 4.2 b and d, demonstrate the surface roughness of the perovskite surface, with control film exhibiting a root mean square (RMS) value of 29.61 nm, while the surface roughness of YY02-modified film is reduced to 26.10 nm. A smoother perovskite surface is less likely to create charge carrier recombination sites and provides more uniform interfacial coverage between perovskite and upper HTL.

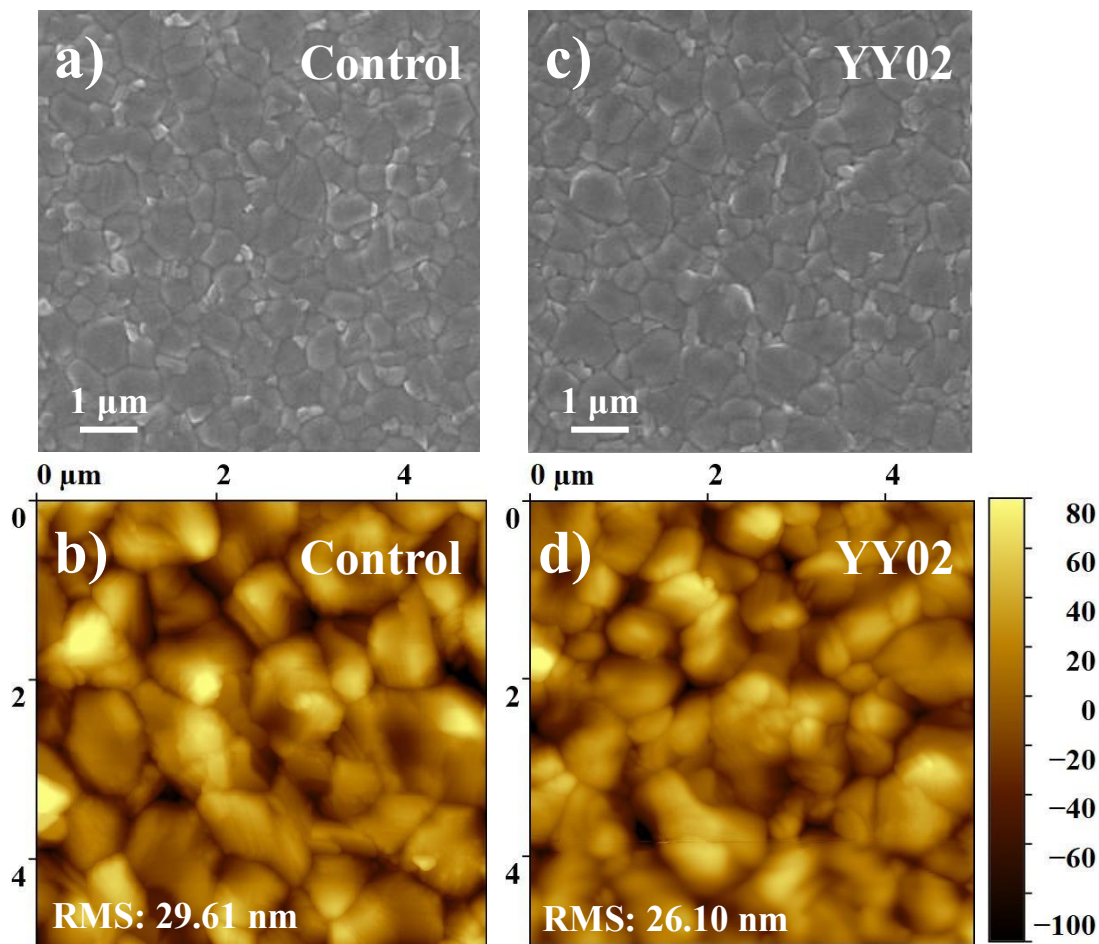


Figure 4.2. SEM images of (a) control and (c) YY02 coated perovskite films. AFM topography images of (b) control and (d) YY02 coated perovskite films.

To study the influence of SAM modification on the chemical state of the perovskite, XPS was used, with the corresponding results illustrated in Figure 4.3. The C 1s spectra of the pristine perovskite film showed 3 distinct peaks which relate to the C-C (284.9 eV), C-O-C (286.5 eV), and O-C=O (288.4 eV) bonds, respectively [69], [70]. These peaks are commonly associated with surface contaminants which originate from ambient. In contrast, the YY02-modified film exhibits the presence of a C-OH (~285.6 eV) peak. The emergence of this peak suggests the introduction of oxygen-containing functional group, which may be attributed to the anchoring group of YY02. Moreover, the presence of this peak may also suggest interfacial interactions, such as hydrogen bonding or coordination with uncoordinated Pb^{2+} sites, which are linked to defect passivation achieved from reduced density of surface state traps.

The Pb 4f XPS spectra are shown in the Figure 4.3 b with a set of double peaks at 143.2 and 138.4 eV for Pb 4f_{5/2} and Pb 4f_{7/2}, respectively, for the control sample, which are attributed to the Pb element in the composition of the perovskite [71]. The XPS spectra also does not possess any characteristic peaks for metallic lead, indicating stable chemical environment for the Pb element. After YY02 interlayer, there is a slight shift toward lower binding energy for the Pb 4f_{5/2} and Pb 4f_{7/2}, which is related to the increase in electron density of the Pb atom. Such increase in electron density is commonly attributed to the properties of a passivator. Additionally, the shift may have been caused by the electron donating C=O group of YY02. The lone pair electrons on the oxygen may coordinate with uncoordinated Pb^{2+} ions, forming an interaction which resembles a Lewis acid-base type [12], [72]. The interaction compensates for the electron deficiency of control Pb sites, facilitating chemical passivation.

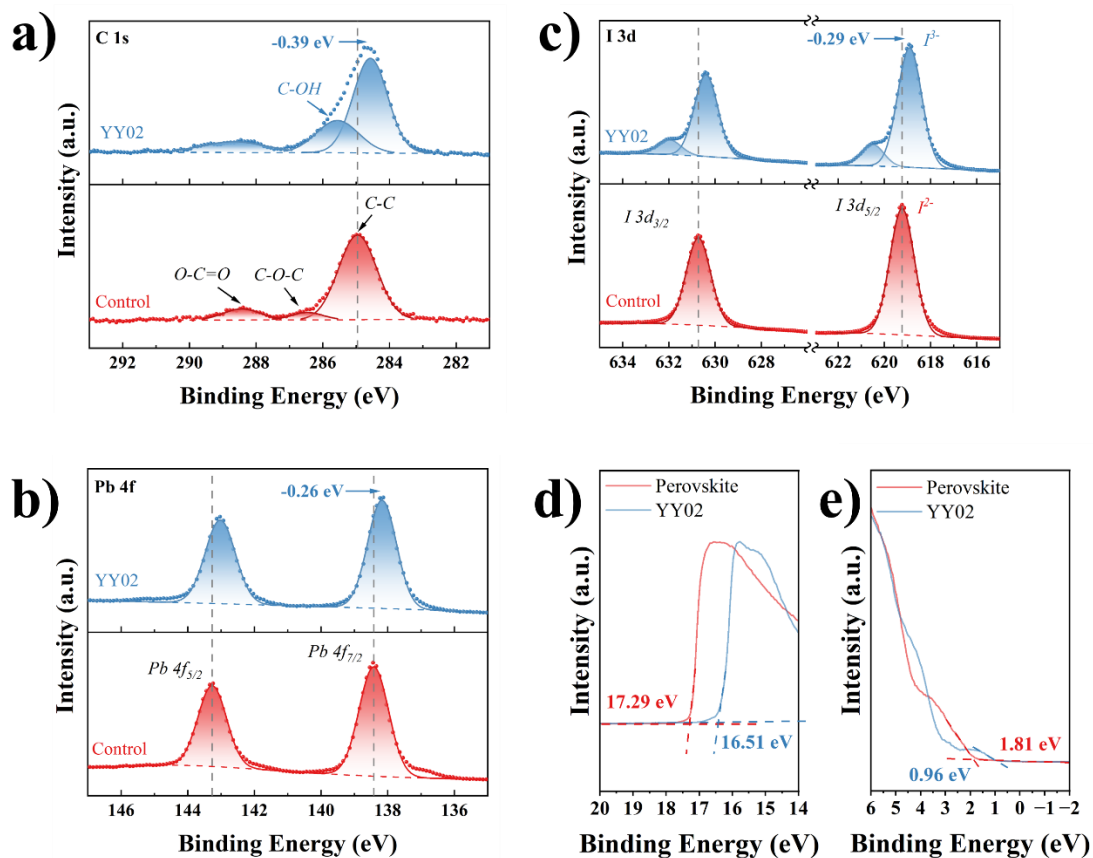


Figure 4.3. XPS results of (a) C 1s, (b) Pb 4f, and (c) I 3d for control and YY02-modified perovskite films; (d) E_{cut} off and (e) E_{on} set regions for perovskite and YY02 films.

Additionally, the same trend can be observed in the I 3d XPS spectra (Figure 4.3 c). The pristine perovskite film shows two distinct peaks at 630.7 and 619.2 eV, corresponding to I 3d_{3/2} and I 3d_{5/2}, respectively [73]. The lower binding energy component I 3d_{5/2} at 619.2 eV is assigned to the I²⁻ anion from PbI₂ [74]. Following the introduction of YY02 SAM, there is a shift towards lower binding energies, with I 3d_{5/2} shifting to 618.95 eV. This shift may indicate a modification of the local chemical environment of iodide ions with possible redistribution of the perovskite lattice. Such redistribution may arise from halogen bonding between YY02 and the perovskite.

Furthermore, the observed shift of the lower energy binding component is assigned to the possible formation of a triiodide (I_3^-), as one iodide ion is likely donated through the I halogen atom from the structure of YY02 to the final perovskite composition [75]. Moreover, the iodine bands also exhibit the formation of a shoulder peak near 620 eV and 632 eV for YY02-modified perovskite films. The signal near 620 eV was considered as a C-I bonding by Cabibil *et al.* [76], further confirming the presence of the SAM layer on the surface of the perovskite.

To investigate the extents of energy level tuning of YY02 and to model the energy band diagram of the proposed PSC, UPS was conducted on perovskite and YY02 films. Using UPS data, binding energy (BE) cutoff (E_{cutoff}) and BE onset (E_{onset}) values can be calculated by linear extrapolation, as shown in Figure 4.3 d-e [77], [78]. Valence band maximum (VBM) is determined as follows [79]:

$$E_{VBM} = h\nu - (E_{cutoff} - E_{onset}) \quad (4.1)$$

where $h\nu$ is the energy of the He I gas source, which is equal to 21.2 eV. The conduction band minimum (CBM) is calculated by summing together E_{VBM} value and E_g of the material. From the energy band diagram presented in the Figure 4.1 c it can be noted that YY02 SAM exhibits a VBM value of -5.7 eV, providing a smooth energy gradient between the perovskite photoactive layer and the HTL. Typically, the ideal highest occupied molecular orbit (HOMO) level offset (that is, energy offset between the HOMO of the perovskite and the HTL) should be slightly higher than the exciton binding energy of the perovskite [80]. If the offset is too large, it can create an energy barrier, disrupting the flow of charge carriers across the junction and creating sites for recombination. The presence of YY02 interfacial layer can minimize this energy offset, resulting in an efficient hole carrier separation and reducing NRR within the perovskite [12].

4.3. Initial Device Characterization

Above discussions regarding properties of YY02 SAM as well as its interfacial interactions with the perovskite layer have confirmed positive impacts of the molecule on the perovskite film. To confirm these changes, PSCs were fabricated with the device architecture shown in Figure 4.1 a and the photovoltaic performances were evaluated using J-V measurements and EQE, as described in Chapter 3. Experimental details on solution preparation and single junction PSC fabrication can be found in - MethodologyChapter 3. Devices without YY02 interlayer are labeled as “Control”, and devices with YY02 inserted at the perovskite/HTL interface are labeled as “YY02” or “YY02-modified”.

The photovoltaic parameters are presented in Table 4.1, while the representative $J-V$ and EQE plots are shown in Figure 4.4 a and b. The champion control device with a V_{OC} of 1.05 V, J_{SC} of 21.61 mA cm⁻², FF of 72.85%, and PCE of 16.48% was achieved, meanwhile YY02-modified devices were able to achieve higher photovoltaic performances, with a V_{OC} of 1.03 V, J_{SC} of 22.73 mA cm⁻², FF of 73.85%, and PCE of 17.33%. The increase in J_{SC} is attributed to improved charge generation and collection, which is likely the effect of reduced defect states, reduced grain boundaries, and a more favorable energy band alignment, which are supported by SEM, AFM, XPS, and UPS results discussed in the previous chapter.

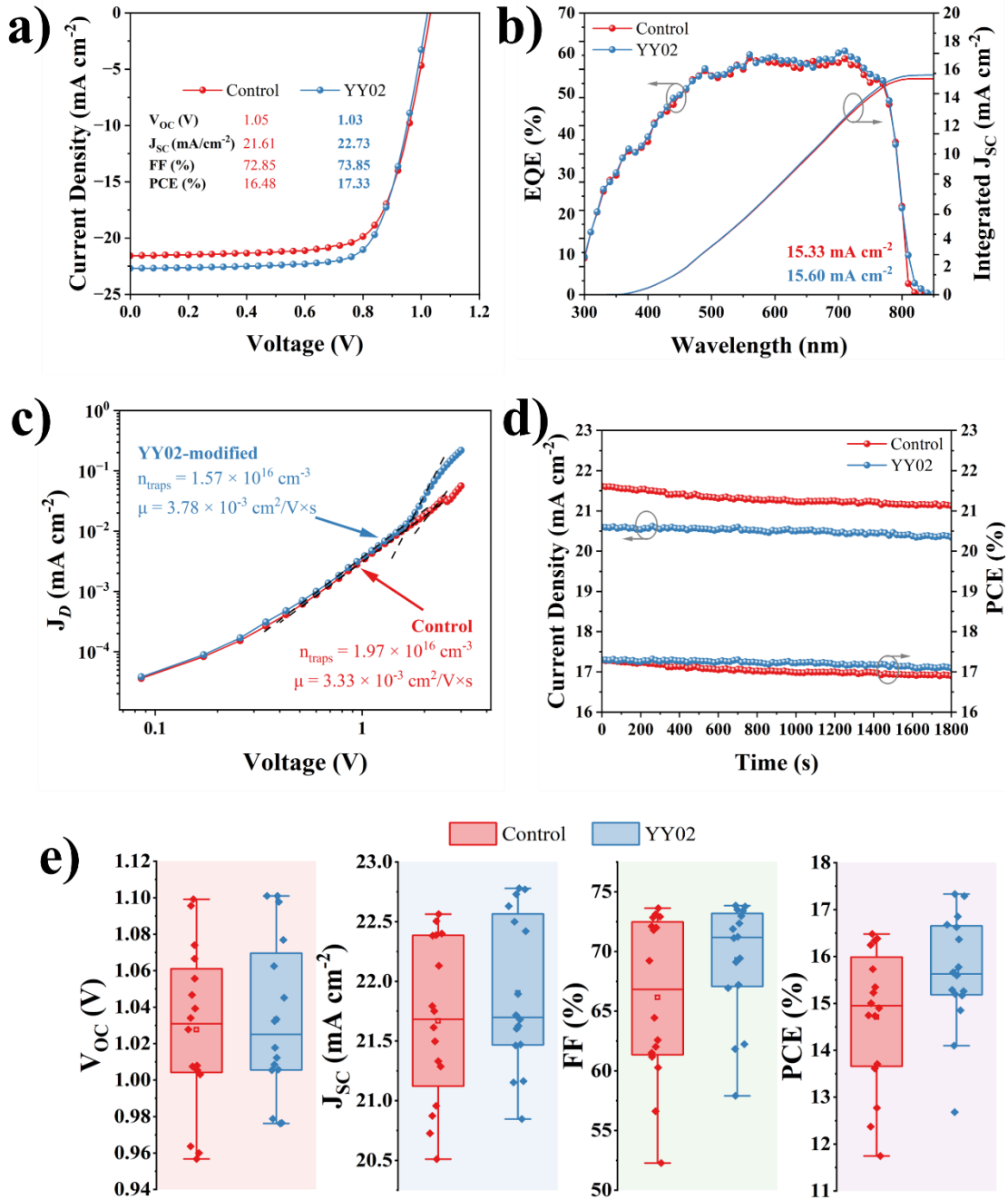


Figure 4.4. (a) J-V curves of champion control and SAM-modified PSC devices; (b) EQE plots (left) with integrated J_{sc} values obtained from EQE results (right) of control and YY02-modified devices; (c) J-V curves of hole-only devices of control and SAM-modified PSCs; (d) $I(t)$ scan of control and YY02-modified PSC devices; (e) Statistical box plots for photovoltaic parameters of control and SAM-modified devices

The statistical box plots (Figure 4.4 e) of control and interfacially engineered PSCs show similar values for V_{OC} , while J_{SC} values for YY02-modified devices are increased, which suggest that the YY02 interface suppresses interface traps and defects at the perovskite film, which are found to be the centers of recombination, limiting charge extraction [81], [82]. In addition to improvement in J_{SC} , the FF of YY02-modified devices not only show increase in average value, but a narrower spread. The improvement suggests uniform interfacial properties and better reproducibility of PSCs, compared to the control devices.

Table 4.1. Photovoltaic parameters of control and YY02-modified PSCs averaged over 4 devices

Device	Scan	V_{oc} (V, average)	J_{sc} (mA cm ⁻² , average)	FF (% , average)	PCE (% , average)	Champion PCE (%)	HI (%)
Control	For	1.02 ± 0.03	21.60 ± 0.48	71.70 ± 1.52	15.74 ± 0.49	15.96	3.04 ± 1.20
	Rev	1.03 ± 0.03	21.61 ± 0.49	72.84 ± 0.78	16.23 ± 0.34	16.48	
YY02	For	1.02 ± 0.01	22.15 ± 0.49	72.44 ± 1.01	16.36 ± 0.62	16.82	1.48 ± 1.00
	Rev	1.03 ± 0.01	22.18 ± 0.50	72.82 ± 1.16	16.61 ± 0.74	17.33	

Another reason for an improvement in J_{SC} may be the enhancement of EQE response from ~550 nm to ~750 nm for PSCs employing the YY02 interface layer, leading to more efficient conversion of incident photons to electron-hole pairs [83]. The integrated J_{SC} values calculated

from the EQE results for control and YY02-modified PSC devices are 15.33 mA cm^{-2} and 15.60 mA cm^{-2} , respectively, and were calculated using Eq. 4.2.

$$J_{SC,EQE} = \int_0^{\infty} qEQE(\lambda)S(\lambda)d\lambda, S = AM1.5 \quad (4.2)$$

Despite this improvement, it is noted that $J_{SC,EQE}$ values remain significantly lower compared to those obtained from $J-V$ measurements. The reason behind value mismatch is manifold. First, low-intensity monochromatic light is used for EQE measurements, which differ from standard operating conditions, limiting charge generation and collection. In contrast, $J-V$ measurements are performed under simulated AM1.5G illumination, which yields higher photon flux, thereby providing higher J_{SC} . Secondly, given the instability of the perovskite material against moisture and oxygen, the PSC devices may have degraded during the EQE measurement, which would decrease the $J_{SC,EQE}$ value. Additionally, since the EQE measurement is typically done after $J-V$ sweep under operational conditions, light induced phase segregation and ion migration, and the dependance of a dielectric constant on light intensity may all have an impact on mismatch between $J_{SC,JV}$ and $J_{SC,EQE}$ [84], [85], [86].

To investigate the impact of YY02 interface on hysteresis, which is a common phenomenon present in PSCs, hysteresis index (HI) of control and YY02-modified PSCs was determined using the Eq. 4.3. YY02 PSC devices exhibit a reduce in HI with 1.48% compared to 3.04% of the control devices. The origins of hysteresis in PSCs can be attributed to several factors, including ion migration, unbalanced transport of charge carriers, ferroelectric property of the perovskite layer, and trapping of charge carriers at the interfaces [87]. Reduced HI for PSC devices with YY02 interface signifies that the SAM can successfully suppress hysteretic behavior. In particular, YY02

is likely to reduce interfacial trap density and improve energy level alignment, facilitating balanced charge extraction, which correspond with XPS and UPS measurements.

$$HI = \frac{PCE_{rev} - PCE_{for}}{PCE_{rev}} * 100 \quad (4.3)$$

The trap density (n_{traps}) and hole mobility (μ) of control and YY02-modified PSCs were then evaluated *via* space charge limited current (SCLC). This method allows us to probe how easily the charge carriers (either hole or electron) can move freely within the junction and estimate the density of traps. For SCLS method, the perovskite layer is processed between two single carrier materials, in this case between two HTLs, and the response is measured in dark conditions to eliminate the influence of photogenerated carriers. The resultant J - V curve is then plotted in a log-log scale, as shown in Figure 4.4 c. From this plot, trap-filled limit voltage (V_{TFL}), which is a transition from a region of free charge carriers (Ohmic) to a trap dominant region (trap-filled), can be estimated by linearly extrapolating the mentioned transition regions. Once V_{TFL} is identified, n_{traps} can be calculated using the formula below [88]:

$$n_{traps} = \frac{2\varepsilon_r\varepsilon_0V_{TFL}}{(qA^2)} \quad (4.4)$$

where ε_r is the dielectric constant of the perovskite (~ 35) [89], ε_0 is the vacuum permittivity, and A is the thickness of the perovskite layer (650 nm). The calculated trap density for control and YY02-modified devices is $1.97 * 10^{16} \text{ cm}^{-3}$ and $1.57 * 10^{16} \text{ cm}^{-3}$, respectively, indicating reduced trap states for YY02 devices, suggesting effective defect passivation at the surface of the perovskite, which are commonly associated with undercoordinated ions. The presence of YY02 likely mitigates the defect sites through chemical interactions, as supported by XPS analysis discussed in Chapter 4.2.

The hole mobility is then calculated by fitting the Mott–Gurney equation [90]:

$$J = \frac{9}{8} \varepsilon \mu \frac{V^2}{A^3} \quad (4.5)$$

where J - current density and V - applied voltage. The calculated hole mobility is identified to be $3.33 * 10^3 \text{ cm}^2/\text{V*s}$ for control and $3.78 * 10^3 \text{ cm}^2/\text{V*s}$ for YY02 devices. The increase in hole mobility for YY02-modified devices indicates more efficient hole extraction, which is also contributed to reduced density of trap states. Furthermore, the increase in hole mobility is consistent with favorable energy alignment, which is obtained from UPS measurements (Chapter 4.2).

From SCLC measurement it was established that the introduction of YY02 reduces the trap density in the perovskite film, while also increasing the hole mobility within the PSC device. The simultaneous enhancement in trap density and hole mobility confirms the positive contribution of the SAM interlayer on overall photovoltaic performance of the interfacially engineered PSCs.

To evaluate the lifetime of the devices, stabilized current density and PCE at MPP were recorded by continuously measuring the PSC under continuous illumination at ambient and at the voltage at maximum power point (Figure 4.4 d). The results show that YY02 interlayer provides a stabilized performance output, while control devices exhibit continuous decay of photovoltaic parameters. This observation suggests significant operational stability for YY02-modified devices. The improved stability can be contributed to the ability of YY02 in minimizing charge recombination sites. Furthermore, SAM may act as an encapsulation layer for the perovskite, mitigating the effects of ambient atmosphere, as well as reducing ion migration and interfacial degradation under operational conditions. These effects contribute to enhanced charge extraction and reduced degradation pathways, resulting in more stable device operation.

Chapter 5 – Device Engineering for Perovskite-based Tandem

Photovoltaics

5.1. HTL Optimization of PSCs for Tandem Solar Cell Applications

Although Spiro-OMeTAD is widely used as HTL for regular structured PSCs due to its ability to produce efficient devices, the common additives, such as 4-tbp and LiTFSI significantly hinders the stability of the solar cells against atmospheric moisture and thermal stress [91].

An ideal HTL for PSCs should exhibit high hole mobility and excellent conductivity; however, pristine Spiro-OMeTAD does not possess these characteristics, hindering hole extraction to the top electrode and resulting in high series resistance and low device performance [92]. While additive engineering can address these limitations, their intrinsic hygroscopic and volatile nature leads to device instability against ambient atmosphere and thermal stress, the latter of which makes the HTL unsuitable for TSC application. Thus, this chapter will discuss the process and progress for HTL optimization by superseding the Spiro-OMeTAD layer with polymeric donors, such as PM6, D18, PTQ10, and Poly-TPD.

Table 5.1. Photovoltaic parameters of PSCs with different HTL systems averaged over 3 devices

Device	Scan	V_{oc} (V, average)	J_{sc} (mA cm ⁻² , average)	FF (% average)	PCE (% average)	Champion PCE (%)
Spiro-OMeTAD	For	1.03 ± 0.01	21.30 ± 0.70	70.83 ± 0.91	15.46 ± 0.50	15.96

		Rev	1.04 ± 0.01	21.31 ± 0.69	72.32 ± 0.46	16.02 ± 0.60	16.48
Poly-TPD		For	1.03 ± 0.01	15.75 ± 3.92	76.31 ± 17.69	11.88 ± 0.35	12.28
		Rev	1.01 ± 0.02	20.09 ± 0.74	60.39 ± 0.98	12.30 ± 0.31	12.56
PTQ10		For	1.04 ± 0.02	17.63 ± 4.05	64.54 ± 24.49	11.14 ± 1.68	12.77
		Rev	1.03 ± 0.02	20.01 ± 0.64	53.10 ± 5.01	10.97 ± 1.43	12.32
D18		For	1.06 ± 0.02	21.43 ± 0.07	61.65 ± 2.44	14.00 ± 0.27	14.31
		Rev	1.06 ± 0.02	21.41 ± 0.06	60.99 ± 2.63	13.82 ± 0.29	14.13
PM6, mg/mL	5	For	1.08 ± 0.03	21.65 ± 0.53	64.48 ± 0.57	15.03 ± 0.35	15.12
		Rev	1.08 ± 0.03	21.74 ± 0.51	63.99 ± 1.15	14.98 ± 0.65	15.39
PM6, mg/mL	7	For	1.06 ± 0.01	21.80 ± 0.23	65.22 ± 2.21	15.03 ± 0.61	15.52

	Rev	1.05 ± 0.01	21.87 ± 0.13	64.65 ± 1.73	14.90 ± 0.34	15.29
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Performance metrics and representative J - V curves for different HTMs are presented in Table 5.1 and Figure 5.1 e, respectively. The results indicate that Poly-TPD and PTQ10 show significant performance losses when compared to Spiro-OMeTAD reference HTL, with main constraints related to poor current generation (as indicated by J_{SC}) and unstable FF. D18 demonstrates improved performance with the J_{SC} comparable to Spiro-OMeTAD reference HTL; however, the overall efficiency remains limited by a low FF.

In contrast, PM6 exhibits the most favorable photovoltaic parameters among investigated polymeric HTMs. Although PM6 at 7 mg/mL exhibits higher PCE than PM6 at 5 mg/mL, the lower concentration was able to yield higher V_{OC} with minimal J_{SC} losses. Thus, perovskite-organic TSCs will be based on PM6 HTL at 5 mg/mL, as it is able to deliver consistently high performance with minimal material usage.

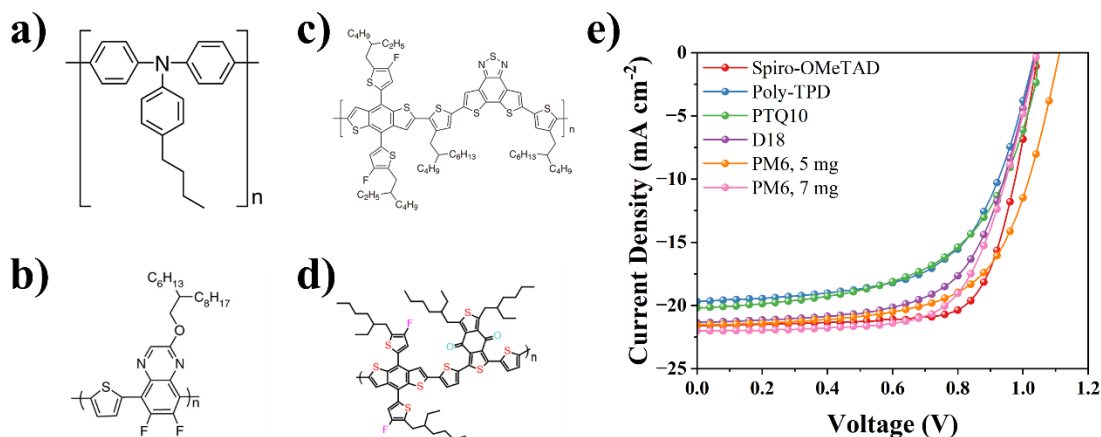


Figure 5.1. Chemical structure of (a) Poly-TPD [93], (b) PTQ10 [94], (c) D18 [95], and (d) PM6 [96] polymers; (e) J - V curves of champion PSCs based on different HTMs

Additionally, to observe the behavior of the YY02 SAM within the new PM6 HTL system, a series of batches with control and YY02-modified devices were fabricated. Representative J - V and statistical box plots are presented in Figure 5.2 a and d. The champion device for YY02 PSC exhibits a V_{OC} of 1.10 V, J_{SC} of 21.38 mA cm⁻², FF of 69.65%, and PCE of 16.39%, delivering superior performance compared to control champion devices (V_{OC} of 1.09 V, J_{SC} of 22.48 mA cm⁻², FF of 65.85%, and PCE of 16.10%). The improvement in FF is likely attributed to more efficient charge transport and reduced recombination at the interfaces. The YY02 can minimize the energy losses by promoting smoother movement of charges across the perovskite/HTL interface. As a result of increased FF, the overall PCE of the YY02-modified device also improves. However, interfacially engineered exhibit marginal decrease in J_{SC} , as indicated by the champion PSC device and the statistical box plot. This suggests that the SAM interacts differently with Spiro-OMeTAD and PM6 HTLs, as its interfacial dipole may weaken electronic coupling and alter interfacial morphology within the PM6-based PSCs [97].

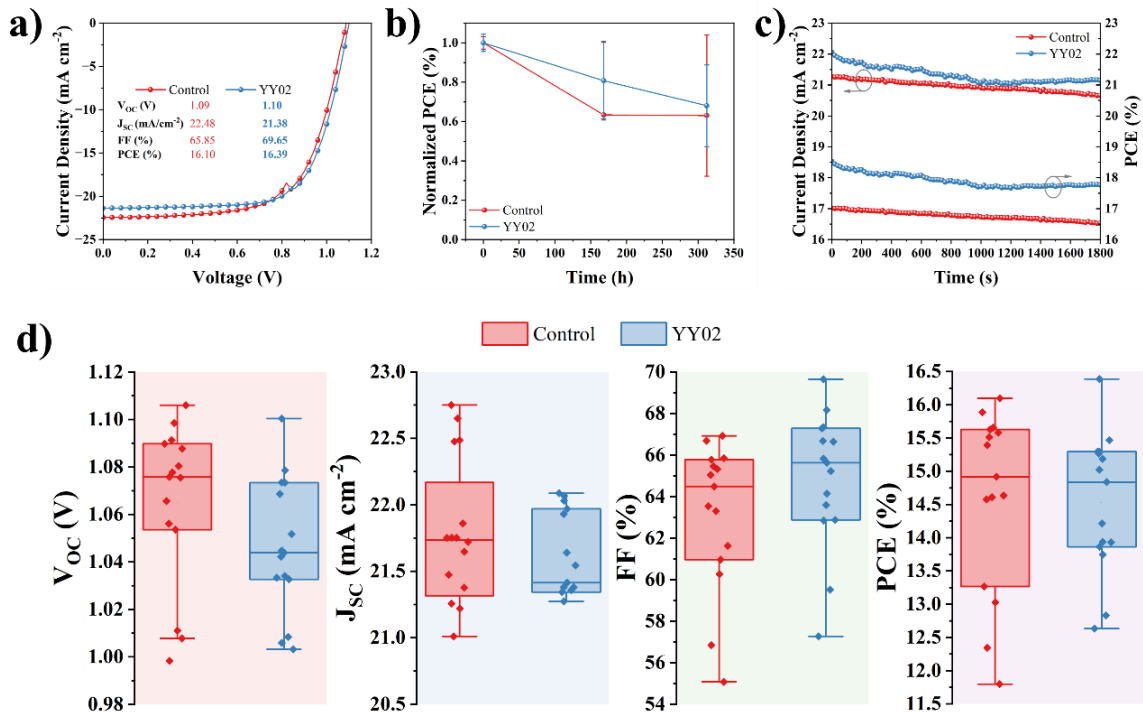


Figure 5.2. (a) J-V curves of champion control and SAM-modified PSC devices; (b) Shelf lifetime of control and YY02-modified devices; (c) I(t) scan of control and YY02-modified PSC devices; (d) Statistical box plots for photovoltaic parameters of control and SAM-modified devices

To evaluate the operational stability of control and YY02-modified PSC devices within the PM6 HTL system, shelf lifetime and stabilized current at maximum power point were recorded. The shelf lifetime (Figure 5.2 b) for control devices demonstrates a significant decline in PCE by almost 40% after 150 hours of storage in dry conditions, whereas interfacially engineered devices were able to retain almost 70% of their initial PCE even after 350 hours of storage in the same conditions.

The $I(t)$ scan, illustrated in Figure 5.2 c, further highlights superior operational stability of YY02-modified devices compared to control PSCs. This trend in operational stability align well with the performance of Spiro-OMeTAD-based PSC devices discussed in Chapter 4.2, suggesting that the SAM layer prolongs device lifetime.

5.2. Integration into Tandem Solar Cells

Since the introduction of YY02 at the perovskite/HTL interface has been thoroughly examined, with morphological, chemical, and device-level interactions described in previous chapters, this part will focus on the integration of the optimized perovskite sub cell into the structure of perovskite-organic TSCs. The methodology for OPV and TSC fabrication is described in Chapter 3. The energy band diagram for perovskite-organic TSCs and the complementary absorption spectra for OPV BHJ and perovskite layers are shown in Figure 5.3 a and b, respectively.

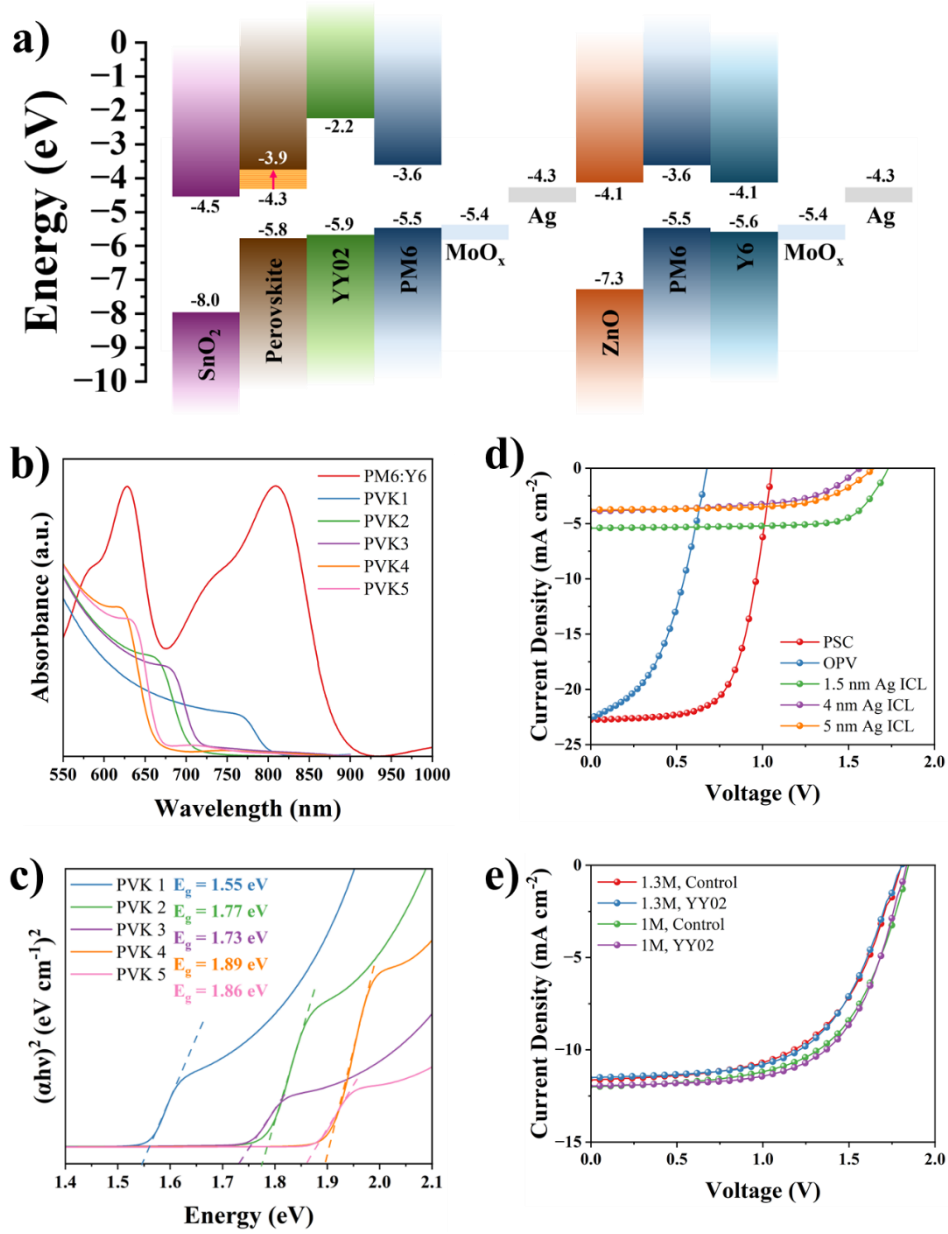


Figure 5.3. (a) Energy band diagram for perovskite-organic TSCs described in this work; (b) absorbance spectra for PM6:Y6 OPV active layer and perovskite films with varying compositions; (c) Tauc plot and calculated band gap values for perovskite layers with different compositions; (d) J-V curves of single junction PSC and OPV and TSCs with varying Ag thickness in the ICL; (e) J-V curves of control and YY02-modified TSCs with different perovskite molarities.

The thickness of Ag in the ICL structure must be carefully optimized, since it affects optical transmission and charge transport for TSCs, and strongly influences overall device performance. In addition, current matching is also one of the main aspects in TSCs. Adequate current matching can be achieved by engineering the band gap and the thickness of the back sub cell. Therefore, this section will firstly discuss the optimization process of the Ag-based ICL for TSC structures, followed by tuning the perovskite composition to enable efficient photon transmission from WBG perovskite rear cell to NBG OPV front cell.

The optimization of the Ag-based ICL involved thermal evaporation of a thin Ag between perovskite and OPV sub cells to systematically evaluate the effect of the ICL thickness on the electrical conductivity and optical transmission. Representative photovoltaic parameters and J - V curves of TSCs with varying Ag thicknesses are presented in Table 5.2 and Figure 5.3 d, respectively.

As shown in Table 5.2, the TSC with 1.5 nm Ag ICL exhibit the best PV performance, delivering a V_{OC} of 1.73 V, J_{SC} of 5.41 mA cm⁻², FF 73.63%, and PCE of 6.90%. This suggests that the Ag is continuous enough to provide efficient charge recombination, while remaining thin enough to maintain the transmittance required for photons to reach the OPV sub cell.

However, as the thickness of Ag increases to 4 nm, the J_{SC} and PCE decrease drastically to 3.89 mA cm⁻² and 3.47%, respectively. This is attributed to the increased parasitic absorption of the Ag as the film becomes thicker, limiting photon transmission to the OPV cell [98]. Additionally, the FF is also reduced from 73.63% to 57.09%, suggesting that the thick Ag may introduce increased series resistance or disrupts charge recombination. These effects are further confirmed 5 nm thick Ag is used, with J_{SC} and PCE decreasing to 3.76 mA cm⁻² and 3.91%, respectively. While

the FF for 5 nm Ag is partially recovered (63.03%) due to increased electrical conductivity, the optical losses still dominate the device performance.

Consequently, the optimal thickness for Ag-based ICL was determined as 1.5 nm, since it provides better optical transmittance, minimizing optical losses and ensuring efficient charge recombination.

Table 5.2. Photovoltaic parameters of champion single junction PSC and OPV, and perovskite-organic TSCs with varying Ag thickness in the ICL structure

Device	Scan	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
Single junction PSC	For	1.05	22.77	64.25	15.41
	Rev	1.05	22.75	65.32	15.66
Single junction OPV	For	0.68	22.62	45.14	6.95
	Rev	0.68	22.61	44.44	6.79
TSC with 1.5 nm Ag ICL	For	1.72	5.40	72.52	6.75
	Rev	1.73	5.41	73.63	6.90
TSC with 4 nm Ag ICL	For	1.55	3.88	56.77	3.42
	Rev	1.56	3.89	57.09	3.47
TSC with 5 nm Ag ICL	For	1.18	3.76	85.33	3.80
	Rev	1.65	3.76	63.03	3.91

Although tandem devices suffer from low J_{SC} , the functionality of the TSC is confirmed by the $V_{OC, tandem}$, since it is equal to the sum of V_{OC} obtained from single junction PSC and OPV

devices. The dramatic reduction in current density is related to the non-complimentary absorbance of the perovskite, with respect to the OPV BHJ layer, as shown in Figure 5.3 b, where PVK1 refers to the perovskite layer used in this TSC structure.

To improve current matching within the TSC, the E_g of the perovskite was adjusted by substituting parts of the iodide with bromide within the PbX ($X = I, Br$) precursor. The I:Br ratio was varied from 50:50 to 25:75 and the thickness of the perovskite layer was also adjusted by spin coating the PbX and organic cation solutions at 1500 and 4000 rpm. Absorption spectrum of PM6:Y6 BHJ and perovskite layers with different band gaps and their representative Tauc plots are presented in Figure 5.3 b and c, where PVK2 and PVK3 represent the 50:50 I:Br ratio spin coated at 1500 and 4000 rpm, respectively, and PVK4 and PVK5 represent the 25:75 I:Br ratio spin coated at 1500 and 4000 rpm, respectively.

Table 5.3. Photovoltaic parameters of control and YY02-modified TSCs with different perovskite molarities averaged over 3 devices

Device	Scan	V_{oc} (V, average)	J_{sc} (mA cm ⁻² , average)	FF (% average)	PCE (% average)	Champion PCE (%)
1.3M, Control	For	1.78 ± 0.01	11.06 ± 0.56	53.25 ± 1.83	10.47 ± 0.34	10.86
	Rev	1.80 ± 0.01	11.07 ± 0.58	57.72 ± 1.80	11.49 ± 0.48	12.04
1.3M, YY02	For	1.75 ± 0.03	11.45 ± 0.09	51.04 ± 3.30	10.22 ± 0.80	10.67

	Rev	1.79 ± 0.03	11.46 ± 0.09	56.64 ± 3.75	11.62 ± 1.03	12.26
1M, Control	For	1.84 ± 0.02	12.03 ± 0.06	51.75 ± 0.62	11.46 ± 0.22	11.67
	Rev	1.84 ± 0.01	12.06 ± 0.05	58.57 ± 1.47	13.00 ± 0.33	13.25
1M, YY02	For	1.79 ± 0.05	12.02 ± 0.12	51.63 ± 1.26	11.07 ± 0.12	11.20
	Rev	1.82 ± 0.04	12.08 ± 0.10	59.84 ± 2.56	13.15 ± 0.70	13.67

For optimized TSCs, PVK5 composition was chosen because of its suitable E_g and absorption relative to OPV BHJ layer. Moreover, the molarity of the perovskite precursors was also adjusted to reduce the final thickness of the perovskite film and to increase transmittance of photons to the OPV sub cell. The PV performance and representative J - V curves of control and YY02-modified perovskite-organic TSC are presented in Table 5.3 and Figure 5.3 e. 1.86 eV perovskite layer provides better current matching in final TSCs, whereas YY02 modification leads to improved photovoltaic parameters, namely J_{SC} and PCE, as for the single junction PSCs. The champion PSC devices are based on 1M perovskite composition, with interfacially engineered perovskite-organic TSCs were able to demonstrate increased device performance with V_{OC} of 1.85 V, J_{SC} of 11.96 mA cm⁻², FF of 62.29%, and PCE of 13.67%, meanwhile the champion control TSC demonstrates V_{OC} 1.85 V, J_{SC} of 11.99 mA cm⁻², FF of 59.81%, and PCE of 13.25%. Though PV parameters of TSC presented in this work are inferior to state-of-the-art perovskite-organic

TSCs, this may be due to the quality of the WBG perovskite film, which is subject to further optimization.

Chapter 6 – Conclusion

In conclusion, this work has addressed the challenges related to the interface within the PSCs, namely the interface between perovskite and HTL through the incorporation of a YY02 SAM layer, which is distinguished by an iodine halogen atom in its structure. The effects of SAM on the perovskite layer were studied by a series of morphological, chemical, and physical assessments, such as SEM, AFM, XPS characterization of the perovskite film and J - V , EQE measurements of final PSC devices.

SEM and AFM revealed the effects of the YY02 SAM layer on the morphology of the perovskite film. These tools confirmed the formation of uniform and smooth perovskite structure after the SAM modification, leading to better interfacial contact between the perovskite and HTL layers. Complementary XPS measurements were used to investigate the interaction of the SAM with the perovskite on a chemical level, confirming positive effects of the modification. XPS analysis revealed that the iodine atom and the electron donating C-OH group in the structure of the SAM can passivate the defects of the perovskite by interacting with uncoordinated Pb^{2+} sites. UPS was also used to draw an energy band diagram for the modified PSC system, which revealed that the SAM layer provides a smooth energy gradient between perovskite and HTL, resulting in an efficient hole carrier separation and reduced charge recombination.

The effects of SAM modification on complete PSC devices were then confirmed by fabricating a series of PSC devices, which showed improved photovoltaic parameters, with champion PSCs achieving a PCE of 16.48% and 17.33% for control and YY02-modified devices, respectively. Furthermore, the champion YY02-modified PSC was able to attain a V_{OC} of 1.03 V, J_{SC} of 22.73 mA cm^{-2} and an FF of 73.85% for Spiro-based devices.

To achieve compatibility within the structure of TSCs, Spiro-OMeTAD HTL was replaced by a dopant-free PM6 polymeric donor and device performance of YY02 SAM modification was also evaluated for a new HTL system. The champion interfacially engineered PSC device achieved a PCE of 16.39%, V_{OC} of 1.10 V, J_{SC} of 21.38 mA cm⁻² and FF of 69.65%. The operational stability of control and interfacially engineered PSCs was also assessed by stabilized current measurement at the voltage at maximum power point, which showed that SAM modified PSC devices exhibit superior operational stability, whereas control devices showed continuous decay of photovoltaic parameters. The results and observations discussed within the scope of this work establish the importance of interfacial engineering to alleviate issues regarding unbalanced charge extraction and energy band alignment for PSCs.

Interfacially engineered PSCs were then successfully introduced in the structure of TSCs by coupling them with NBG OPV and carefully optimizing processing parameters, such as the thickness of silver within the tandem ICL and the E_g and thickness of the perovskite layer. Although the final perovskite-organic TSCs show inferior PV parameters compared to state-of-the-art TSCs, the described results lay a foundation to further improve the tandem structure by carefully optimizing the final composition of the perovskite layer to complement the band gap and absorption spectra of the organic BHJ and the thickness of the perovskite film to allow the transmittance of photons to the OPV active layer, alleviating the issues related to current matching and final TSC PCE.

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