

Self-Assembled Monolayer-Based Hole-Transporting Materials

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Ever since self-assembled monolayers (SAMs) were adopted as hole-transporting layers (HTL) for perovskite solar cells (PSCs), numerous SAMs for HTL have been synthesized and reported. SAMs offer several unique advantages including relatively simple synthesis, straightforward molecular engineering, effective surface modification using small amounts of molecules, and suitability for large-area device fabrication.

Keywords: self-assembled monolayers ; hole-transporting materials ; perovskite solar cells

1. Introduction

Perovskite crystals are one of the hottest materials for solution-processible electronic devices such as solar cells, photodetectors, transistors, and light-emitting diodes due to their high performance, which is comparable to that of existing silicon-based devices ^{[1][2][3][4][5][6][7][8][9][10][11][12][13][14]}. Among the various applications, perovskite solar cells (PSCs) have achieved remarkable progress, and the power conversion efficiency (PCE) of PSCs has dramatically increased over the past decade, now reaching a PCE value of 25.2%, which is comparable to that of commercialized silicon solar cells ^{[15][16][17][18][19][20][21][22][23][24]}. After the first report on PSCs in 2009 ^[25], there have been many attempts to improve the efficiency and long-term stability of PSCs, such as interface engineering, perovskite composition optimization and encapsulation techniques, and so on ^{[26][27][28][29][30]}. Among those attempts, modifying interfacial layers such as the hole-transporting layer (HTL) and the electron-transporting layer (ETL) has also been widely studied. These modifications enhance the charge transfer at the interface of the electrodes and directly affect the growth of perovskite crystals on the active layer ^{[31][32][33][34]}.

Both inorganic and organic materials have been developed as hole-transporting materials (HTMs) for inverted PSCs. In the case of inorganic HTMs, copper(I) iodide (CuI), copper(I) thiocyanate (CuSCN), copper oxides (Cu₂O and CuO), and nickel oxide (NiO) are currently being developed, with the great advantages of low production costs, high hole mobility, and chemical stability ^[35]. However, there are some limitations related to adjusting energy levels and solution processability ^[36]. In the case of organic HTMs, they require multiple synthetic steps from commercially available organic chemicals, but it is easy to diversify the molecular structures of materials, which allows for the fine-tuning of energy levels. In addition, they have the unique advantages of being light-weight, having a less-adverse environmental impact, and solution processability ^[37]. There are roughly two types of organic HTMs: (1) one comprises conventional polymer or small-molecule HTMs forming their own energy levels, and (2) the other includes small-molecule HTMs making self-assembled monolayers (SAM) capable of modifying the energy levels of electrodes. The well-known polymer-type HTMs are PTAA and PEDOT:PSS, which all possess excellent electrical conductivity with proper HOMO energy levels, facilitating hole transport from the perovskite layer to the electrode ^{[38][39][40][41]}. However, those HTMs should be deposited to a thickness of several tens of nanometers for film uniformity, and their HOMO levels and hole mobilities must be well controlled for the efficient transport of charge ^{[42][43][44]}. On the contrary, SAM-based HTMs are extremely thinly coated on the transparent conductive oxide (TCO) electrodes, forming a permanent dipole moment at the interfaces, which effectively modulates the work function (WF) of the electrode ^{[45][46][47][48]}.

2. SAM-Based HTMs

2.1. Structure and Characteristics of SAM-Based HTMs

The structure of the HTMs forming SAMs is categorized into three components, as shown in **Figure 1**. The first part is a head group in direct contact with the perovskite layer. Head groups are typically composed of hydrophobic conjugated molecules, such as triphenyl amine, carbazole, and phenothiazine, which improve contact with the perovskite layer compared to bare TCO ^[49]. The second part is an anchoring group that binds to the TCO electrodes, such as indium tin

oxide (ITO) or fluorine-doped tin oxide (FTO). The interaction between the anchoring group and the TCO creates an induced electric field at the interfaces, which down-shift the WF (increase the effective WF, ϕ_{eff}) of the TCO for efficient hole transport [34][50]. There are various anchoring groups, such as PA, CA, CAA, B(OH)₂, and -SO₃H.

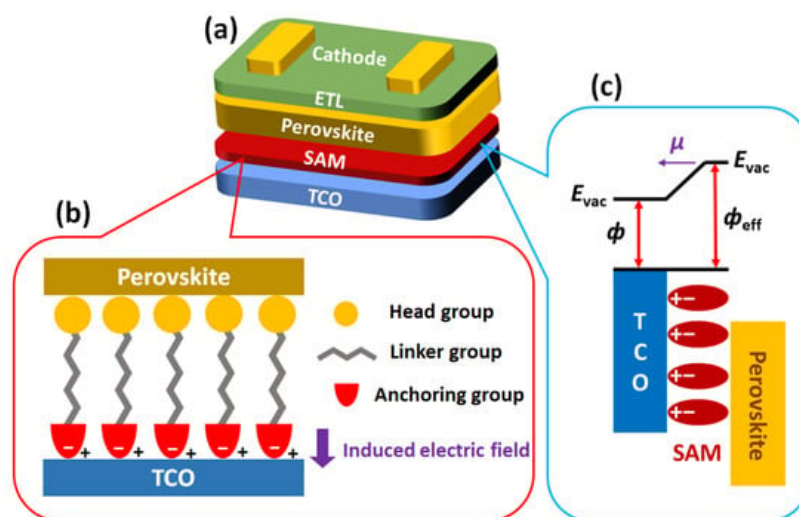


Figure 1. (a) The general device structure of inverted PSCs, (b) three components of HTMs forming SAM and their location in the PSCs, and (c) the modification of WF by SAM.

The synthesis of SAMs starts with the design of the core head group, which primarily employs electron-donating moieties. After that, the anchoring group is introduced into the head group with a proper space linker. The synthetic routes required to build SAM-based HTMs are mainly determined depending on the anchoring groups, and, thus, scholars categorized them by the anchoring groups, as follows. (1) PA anchoring group: First, the electron-donating core unit is brominated, and then it reacts with triethylphosphate to produce phosphonate. Then, a hydrolysis procedure is subsequently used to convert it to phosphonic acid. (2) CA anchoring group: CA anchoring groups can be incorporated into SAM-based HTMs in two different ways. The first way is introducing a benzoic acid group at the end of the HTMs. The head and linker are connected first, and then alkyl benzoate is reacted with by C-C coupling in the presence of a palladium catalyst. Subsequently, the resulting compound undergoes hydrolysis, followed by an acid treatment, to ultimately convert the ester group into a CA group. The second way consists of introducing an aliphatic CA to the HTMs. The aliphatic ester is alkylated to the electron-rich head group, usually including amine derivatives. The ester group is transformed into a CA group through a saponification reaction. (3) CAA anchoring group: Initially, an aromatic aldehyde is linked to the electron-rich head group via palladium-catalyzed C-C coupling. And then, a CAA group is easily introduced into the resulting compound through Knoevenagel condensation.

2.2. PA-Based SAMs

The PA group has been demonstrated to create strong and stable bindings on TCO surfaces, enabling efficient WF modifications [51][52]. This group contains two hydroxy groups and one phosphonic group, allowing for three different binding modes depending on the substrate surfaces and reaction conditions [36]. Among various anchoring groups, the PA group exhibited the highest bond energy, especially with TiO₂ surfaces [53]. These strong bonds contribute to an exceptional monolayer stability. Consequently, the PA group is considered to be one of the most powerful anchoring groups for SAMs, and numerous SAMs have been synthesized with this group in order to be used as HTMs for PSCs (Figure 2). The photovoltaic properties of PSCs are summarized in Table 1.

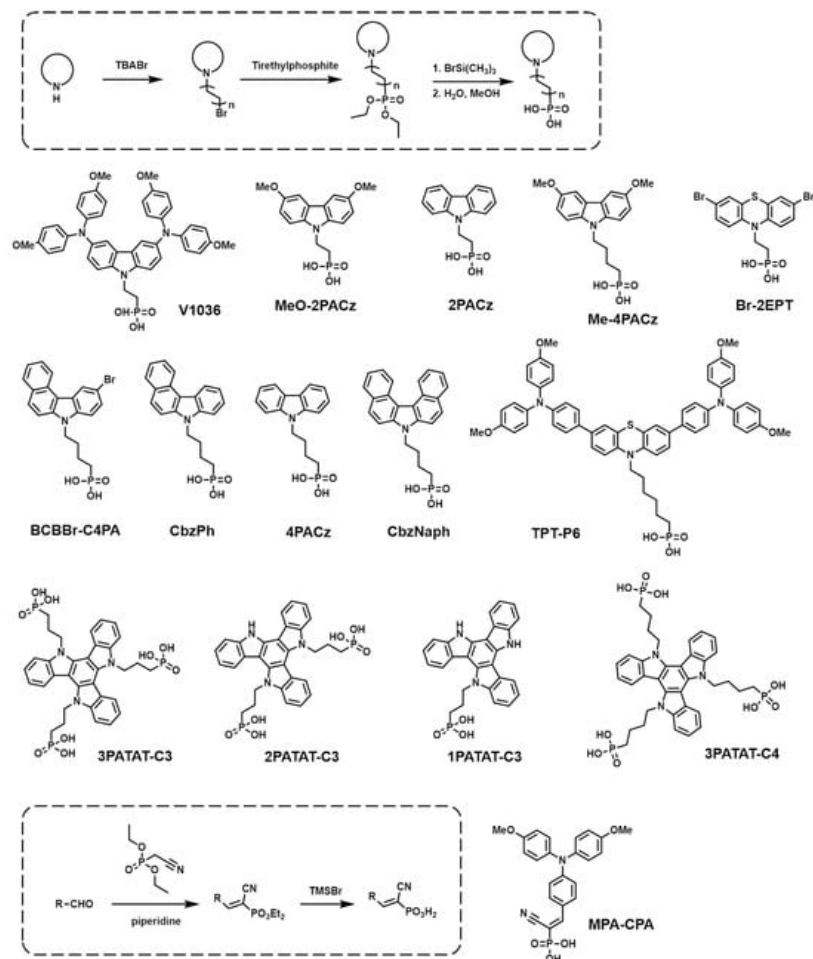


Figure 2. General synthetic routes and molecular structures of **PA** anchoring group-based SAMs.

Table 1. Photovoltaic properties of PSCs using **PA**-based SAMs.

HTM	Device Structure	V _{OC} [V]	J _{SC} [mA/cm ⁻²]	FF [%]	PCE [%]	Device Stability _a	Refs.
V1036	ITO/V1036/C4/Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /C ₆₀ /BCP/Cu	1.09	21.9	81.0	17.8	~94%, 180 d, RT ^{b,f}	[54]
MeO-2PACz	ITO/MeO-2PACz/Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /C ₆₀ /BCP/Cu	1.144	22.2	79.3	19.2	>97%, 11 h, -40 °C ^{c,f}	[55]
2PACz	ITO/2PACz/C4/Cs _{0.05} (MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ /C ₆₀ /BCP/Cu	1.188	21.9	80.2	20.9	~97%, 11 h, -40 °C ^{c,f}	
Me-4PACz	ITO/Me-4PACz/Cs _{0.05} (FA _{0.77} MA _{0.23}) _{0.95} Pb(I _{0.77} Br _{0.23}) ₃ /C ₆₀ /SnO ₂ /Ag	1.15	20.3	84	20.0	95.5%, 300 h, RT ^{c,d,g}	[56]
Br-2EPT	ITO/Br-2EPT/Cs _{0.05} (FA _{0.92} MA _{0.08}) _{0.95} Pb(I _{0.92} Br _{0.08}) ₃ /C ₆₀ /BCP/Cu	1.09	25.11	82.0	22.44	107.4%, 100 h, RT ^{c,e,g}	[57]
BCBBr-C4PA	ITO/BCBBr-C4PA/FA _{0.8} Cs _{0.2} Pb(I _{0.6} Br _{0.4}) ₃ /C ₆₀ /ALD-SnO ₂ /Cu	1.286	17.54	82.61	18.63	>90%, 250 h ^{c,f}	[58]
CbzPh	ITO/CbzPh/Cs _{0.05} MA _{0.15} FA _{0.80} PbI ₃ /C ₆₀ /BCP/Ag	1.17	23.43	73.06	19.2	91%, 120 h ^{c,f}	
CbzNaph	ITO/CbzNaph/Cs _{0.05} MA _{0.15} FA _{0.80} PbI ₃ /C ₆₀ /BCP/Ag	1.17	24.69	83.39	24.1	97%, 120 h ^{c,f}	[59]
4PACz	ITO/4PACz/Cs _{0.05} MA _{0.15} FA _{0.80} PbI ₃ /C ₆₀ /BCP/Ag	1.07	23.20	58.43	14.5	88%, 120 h ^{c,f}	

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Table 2. Photovoltaic properties of PSCs using **CA**-based SAMs

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120, 9835–9950.	HTM	Device Structure	Voc (V)	Jsc (mA/cm ²)	FF (%)	PCE (%)	Device Stability (h)	Refs.
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21.	Asmuntas, S.; Cui, J.; Ma, L.; Ren, P.; Li, B.; Wang, D.; PCBM/Ag	ITO/PC-43/Co ₂ (MA) ₄ Br ₂ /PCBM/Ag	1.07	20.3	80.0	17.3	90%, 20 d ^b	[67]
22.	Patil, P.; Sangale, S.; Kulkarni, A.; Phule, S.; Bhambhani, S.; PCBM/Ag	ITO/EA-40/MAPI ₃ /PCBM/Ag	1.06	17.18	89.36	18.9		
23.	Lye, Y.-E.; Chan, K.-Y.; Ng, Z.-N.	A Review on the Progress, Challenges, and Performances of Tin-Based Perovskite Solar Cells. Nanomaterials 2023, 13, 1886.						
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26.	Chi, W.; Banerjee, A.	Stability Improvement of Perovskite Solar Cells by Compositional and Interface Engineering. Chem. Mater. 2021, 33, 1540–1579.						
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2.4. CAA-Based SAMs

- Although, CAA includes the CAA group, it was classified separately because the synthesis of CAA-based SAMs is completely different from that of CA-based SAMs. The CAA group efficiently passivates the perovskite film because the Lewis base characteristics of CAA can trigger a coordination interaction with Pb²⁺ on defects [73]. Furthermore, the CAA group has a strong electron-withdrawing property than the CA group because it contains two electron-accepting moieties, -COOH and -CN. Thus, the combination with CAA and electron-donating head groups like carbazole and aryl amine forms a strong D-A structure, which is effective in enhancing hole extraction and reducing charge recombination in PSCs, making it suitable for HPM design. The photovoltaic properties of PSCs are summarized in Table 3.

Table 3. Photovoltaic properties of PSCs using CAA-based SAMs

- | Ref. | Device Structure | Voc [V] | Jsc [mA/cm ²] | FF [%] | PCE [%] | Device stability [h] | Refs |
|------|--|---------|---------------------------|--------|---------|----------------------|------|
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- 3. Conclusions and Outlook**
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