



## Review

## Interactions between molecules and perovskites in halide perovskite solar cells

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## ABSTRACT

Halide perovskite solar cells have been intensively researched in recent years, owing to their tremendous potentials to provide clean energy at low cost. To further improve their performances, molecular adsorption approach has been adopted to modify the halide perovskite surface/interface structures, with an aim to enhance the power conversion efficiency and stability of halide perovskite solar cells. In this article, we review recent progresses on the molecular adsorption approach, by surveying newly reported adsorbate molecules forming halogen bonds, hydrogen bonds, Lewis acid-base pairs and other interactions with the halide perovskite surface/interface. Representative examples of the molecular adsorption at three types of perovskite interfaces (perovskite/perovskite interface, perovskite/electron transporting layer, and perovskite/hole transporting layer) have been discussed, with a focus on their structural aspects. Recent progresses of molecular adsorption approaches in related optoelectronic materials and applications based on halide perovskites are also reviewed. It is hoped that this review will facilitate the rational design and development of novel molecular adsorption methods.

## 1. Introduction

The emergence of perovskite solar cells (PSCs) marks a revolution in the field of photovoltaics, promising the elusive combination of low cost and high efficiency. In conventional devices, the fabrication of the semiconductor absorber layer requires an energy intensive process. A great success of perovskite solar cells is the ability to fabricate highly efficient devices via solution processing. The high power-conversion efficiency (PCE) levels are a result of outstanding material properties, including strong and broad absorption, long carrier lifetimes and diffusion lengths, defect tolerance and photon recycling [1–4]. A further advantage is the tunability of the optoelectronic properties, in particular the band gap, which can be achieved by substitution and alloying. This opens up a large chemical space from which a plethora of material combinations are possible. With certified PCE values of over 22%, this new class of solar cell is set to contend with leading photovoltaic technologies, either as an enhancing tandem layer or as a standalone replacement [5–7].

Much effort continues to be spent on achieving higher PCE values; at the same time, there is a drive to enhance the stability of the

perovskite layer. The poor stability in air and moisture, especially when compared with traditional solar materials, is a major hurdle towards commercial adoption [8–18]. The solution processing to fabrication perovskite solar cells introduce a large amount of surfaces and interfaces. Among the many research strategies being explored [19–24], the use of molecules to passivate the perovskite surface and interfaces (molecular adsorption) has proven to be a particularly simple and effective approach [10,18,24–51].

This review provides a detailed look at the interactions between molecules and perovskites in perovskite solar cells and summarizes some of the major advancements in the area of molecular adsorption approach. Successful adsorption relies on the availability of functional groups in the molecular adsorbates that can interact with the perovskite surface/interface. In this review, the focus is on the nanoscopic structure of the molecule/perovskite system and how it relates to the perovskite properties. Rationalizing such structure-property relationships is key to the judicious design of improved devices.

The review begins with a general introduction to the types of molecules that can be successfully adsorbed onto the perovskite surface. This is followed by a discussion of bifunctional molecular adsorbates:

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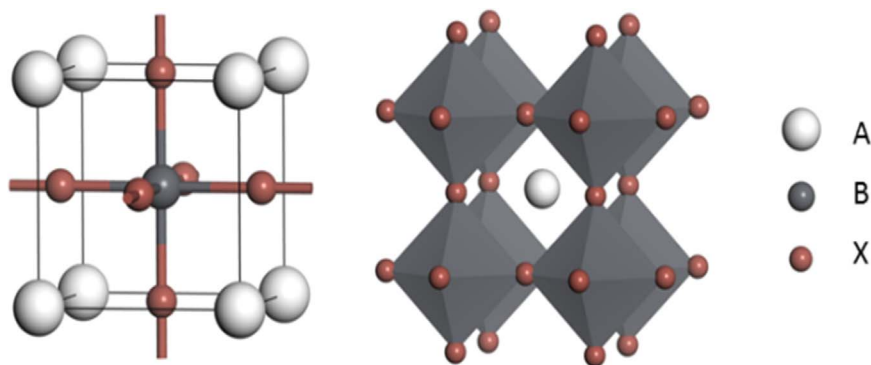


Fig. 1. The crystal structures of perovskite represented by the formula  $ABX_3$ : a unit cell view (left), and an octahedral view (right).

those that have one end-group interacting with the perovskite substrate, and the other end-group in contact with the electron transporting layer (ETL) or the hole transporting layer (HTL). The three interfaces (perovskite/perovskite, perovskite/ETL, and perovskite/HTL) that have been modified by molecules are considered. Unless otherwise specified, the term halide perovskite is simply used to refer to the compound  $CH_3NH_3PbI_3$ .

## 2. General background

### 2.1. Crystal structures of halide perovskites

Perovskites are a class of material described by the formula  $ABX_3$ , where X is an anion and A and B are cations [52–68]. In the metal-halide perovskite variants used in solar cells, the larger cation at the A site is commonly chosen to be an organic molecule such as methylammonium (MA, or  $CH_3NH_3^+$ ). The metal cation at the B site and halogen anion at the X site are standardly chosen to be lead and iodine. In the halide-perovskite crystal structure (Fig. 1), the cation B has six nearest neighbor X anions, which form a surrounding octahedron, while the cation A, which sits in the void regions between corner sharing octahedra, has twelve.  $CH_3NH_3PbI_3$  is the archetypal organic-inorganic halide perovskite where A is MA, B is lead and X is iodine. Substitutions can be made at each of the three sites to engineer the material properties and the following approaches have been employed: (i) substituting the organic MA cation with FA ( $NH_2-CH^+-NH_2$ ),  $CH_3CH_2NH_3^+$ ,  $HN=CHNH_3^+$  or the inorganic  $Cs^+$  cation; (ii) changing  $Pb^{2+}$  to different cations such as  $Sn^{2+}$  and  $Ge^{2+}$ ; (iii) replacing the halide with  $BF_4^-$ ,  $PF_6^-$ , or  $SCN^-$  [69,70]. The halide perovskite crystals usually exhibit  $\alpha$ ,  $\beta$  and  $\gamma$  phases at different temperatures, although a non-perovskite  $\delta$  phase was also found in some perovskite examples. At higher temperature, phase transition occurs in the halide perovskites. For example, in the  $MAPbI_3$  perovskite, the  $\alpha$  to  $\beta$  to  $\gamma$  phase transitions happens at 330 K and 160 K, respectively [71].

The atomic structures of organic-inorganic perovskites are rather complicated to determine due to the disordered orientation of the organic cation molecule [71]. Band structure calculations reveal that the valence band maximum (VBM) has strong Pb-s and I-p antibonding character, whereas the conduction band minimum (CBM) is predominantly Pb-p character (Fig. 2), reflecting the unique dual ionic and covalent nature of halide perovskites [71–73].

In a traditional dye-sensitized solar cell (DSSC), the photoanode consists of a mesoporous  $TiO_2$  layer and molecular dyes are adsorbed onto the bare surface of the nanoparticles, acting as sensitizers for light harvesting [5,7]. This cell architecture enjoyed reasonable success with power-conversion efficiencies above 10%. In 2009, a nanocrystalline perovskite sensitizer was employed as a novel substitute for the standard molecular dye [74]. This seminal work sparked a rapid advancement and an evolution from the conventional dye-sensitized solar cell to the perovskite solar cell [5]. The new device design employs solid-state transport layers and has moved closer to traditional planar

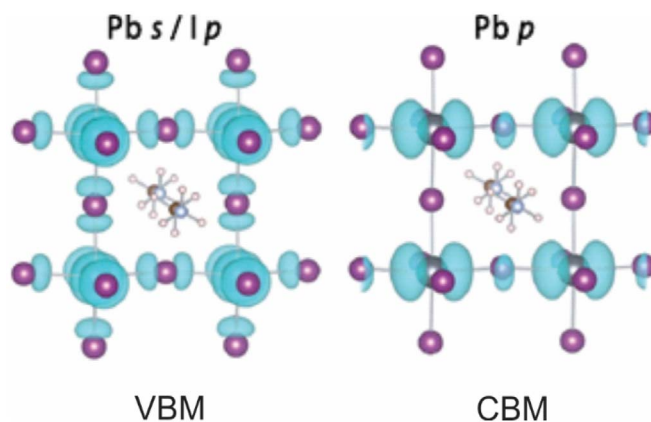


Fig. 2. Typical partial charge density of the perovskite VBM (left), and typical partial charge density of the perovskite CBM (right) [73]. Reproduced with permission from Ref. [73]. Copyright AIP (2013).

semiconductor devices. An interesting question now follows: can adsorbed molecules once again play a pivotal role by treating the perovskite interfaces to enhance the overall cell performance? Recent studies incorporating molecular adsorption have demonstrated that it is indeed a successful strategy, as it can passivate the large areas of perovskite surface/interface acting as charge traps and degradation sites [7,13,34].

### 2.2. Solar cell structure

The different halide perovskite solar cell architectures are summarized in Fig. 3 [75]. The structure evolved from a conventional DSSC-like design, to a meso superstructure, pillared structure and planar structure, which consists of a planar perovskite layer, electron transporting layer (ETL) and hole transporting layer (HTL). The perovskite layer is ambipolar and the electrons and holes have long diffusion lengths (greater than the depth required for complete solar capture) [68]. The ETL usually consists of a  $TiO_2$  (or metal oxides such as  $ZnO$  and  $Al_2O_3$ ) layer that extracts electrons and blocks holes while the HTL usually consists of spiro-OMeTAD and its derivatives which extract holes and block electrons [76].

### 2.3. Perovskite surfaces

A large number of lead halide perovskite surfaces exist in perovskite solar cells, and various thermodynamically stable perovskite surfaces along different crystallographic directions such as (110) and (001) surfaces have been investigated [77]. The (001) perovskite surface has been found very stable and thus it has been modelled extensively. The (001) perovskite surface is terminated by either the  $PbI_2$ -surface or the MAI-surface (Fig. 4) [32], although a defected vacant surface derived

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