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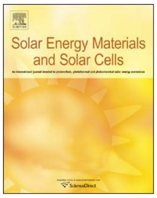

Molecular engineering of the organometallic perovskites/HTMs in the PSCs: Photovoltaic behavior and energy conversion

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ABSTRACT

In this work, a quantum chemistry study was performed on the organometallic perovskites/organic hole transfer materials (HTMs) in the perovskite solar cells (PSCs) from the molecular engineering viewpoint. Density functional theory (DFT)/time-dependent DFT (TD-DFT) was applied to investigate the electronic structures/excited state properties of a series of the perovskites, ABX_3 ($A = CH_3NH_3$, NH_4, $CH(NH_2)_2$, $B = Ge$, Sn, Pb, $X = Cl$, Br, I). On the basis of the energy level of the perovskites, HTMs and TiO_2, all perovskite compounds demonstrate a positive response to the hole/electron injection in the PSCs. A high occupied molecular orbital (HOMO) density of the HTMs, TPB, NPB, TPD, MDA1, MDA2, MDA3, TH101 and V950, are distributed over the whole molecule, homogeneously, which makes the hole transfer more proper. Investigation of the photovoltaic properties of the PSCs shows that they are strongly influenced by the chloride anion. The theoretical trend of the exciton binding energy is according to: F- < NH_4- < MA-based perovskites. Considering different analyses show that the rate of the electron injection rate constant and the light harvesting efficiency increase by an increase in the electron driving force and electronic chemical potential. The correlation of the band gaps and the chemical nature of the substitutions in the perovskites shows a collapse by an increase in the cation size. Finally, it is proposed that $ASnCl_3$ and $AGeCl_3$ perovskites are better candidates to be applied in the PSCs as photosensitizers due to an improved incident photon to current efficiency.

1. Introduction

Energy and environmental issues are the greatest challenges in the current century. The clean, inexpensive, and renewable energy sources are valuable discovery to deal with energy demands and global warming [1–3]. Solar energy is an alternative source of the traditional resources such as coal and fossil fuel, which can convert solar energy into the electricity based on the photovoltaic effect [4–6]. Reduced costs and higher conversion efficiencies are the main deterministic parameters in the competition of photovoltaic (PV)-based technologies [7,8].

Nowadays, solid state organometallic halide perovskite solar cells (PSCs) are promising photovoltaic technologies derived from the liquid state dye-sensitized solar cells (DSSCs) [9,10]. Hybrid organic-inorganic perovskite materials are proper to be used not only in photovoltaics, but also in light-emitting diodes, lasers, photodetectors and sensors [11–13]. Recently, PSCs have attracted considerable attention for their unique characteristics as direct band gap [14], low cost [15,16], high carrier mobility [17], long carrier life-time [18] and strong photovoltaic action [19].

PSCs consists of a perovskite as a light absorbing layer, electron transporting layer and hole transporting layer on each side [20]. In the most planar hetero-junction PSCs, the perovskite layer can be applied both as the light absorber and hole-electron transporter due to the relatively low optical gap and adequate lifetimes of the photoexcited carriers [21–23]. The perovskite can be sandwiched between a hole transport layer (HTL; p-type semiconductor) and an electron transport layer (ETL; n-type semiconductor) [24].

The work functions of the metal electrodes applied as the cathode (Al, Au and Pt) and anode (ITO; indium tin oxide) are such that charge collection sufficiently occurs [25]. Upon illumination, the perovskite layer creates excitons. Since the exciton binding energy (EBE) of the perovskites is sufficiently low, they are dissociated to free carriers, easily. Finally, the electronic charges flow efficiently to the electron/hole layers and respective electrodes [26,27]. Understanding the structural, physicochemical and optoelectronic properties of the perovskites is vital to develop the PSCs technology [28]. Therefore, a deep comprehension of the electronic and physicochemical properties of the perovskites and their relationship with the PSC performance seems essential. This purpose is realizable by new device architecture design,

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high-quality perovskite film formation and molecular engineering of the PSCs, etc.

Despite the outstanding photoactive properties of the liquid-DSSCs, the perovskites are unstable and degraded in the presence of liquid electrolytes (such as I^-/I_3^-) [29]. Nowadays, the worldwide attention has been surging to the new HTMs development to increase the power conversion efficiency (PCE) of the PSCs. In the configuration of PSCs, HTMs play a key role in suppressing the internal charge recombination, promoting hole extraction and migration, and improving the stability [30].

Generally, high performance HTMs must have some requirements to be applied in a photovoltaic device. These requisites include the compatible energy level to build a good regeneration process, good thermal/photochemical stability, excellent charge carrier mobility, low cost and environment-friendly [31]. Recently, various HTMs have been suggested for the PSCs such as newly designed organic materials (OMeTAD [32], TPA/pyrene/thiophene-based HTMs [33–35]) inorganic p-type semiconductors [36], small molecule hole conductors [37] and conductive polymers [38]. Competition between these charge-transporting hosts depends on the efficiency of charge injection and charge (hole) mobility.

Organic HTMs have outstanding advantages such as the good stability, great variety, low-cost, environment-friendly, easy fabrication and tuning the electronic properties in comparison to the inorganic HTMs [39]. Literature survey shows that the anions and cations of the perovskites play a key role in the stability of the perovskite-based photosensitizers, the charge separation and recombination process in the PSCs [40].

Analysis of the substitution of the X anion with hexafluorophosphate and tetrafluoroborate in the polyanion perovskites has shown that larger organic cations such as dimethylammonium are proper for maintaining a perovskite network with BF_4 and PF_6 anions [41]. The structural properties, defects and shift current for orthorhombic, tetragonal and cubic phase $CH_3NH_3PbI_3$ crystals have been theoretically studied. Moreover, the structures of different orientations of the cubic phases for $CH_3NH_3PbI_3$ have been investigated. Results show that the Van der Waals forces and hydrogen bonding play crucial roles in crystal packing as well as the structural defects in the perovskite lattice strongly affect the efficiency of the PSCs. Also, a large lattice distortion in the perovskite structure can shift the current response [42]. Also, the rotation of the MA cation deforms the surrounding inorganic lattice and disrupts Pb-I bond in the inorganic framework [40].

The use of less polar and less acidic cations such as formamide and cesium instead of methyl ammonium reduces the rate of the ion migration in the organohalide perovskites which makes the opotoelectronic devices more stable [43]. Also, the band gaps are depended on the halide ions and the interlayer distance of the perovskites. This correlation was predicted in a theoretical study on the modeling of a number of 2D layered perovskites A_2PbI_4 and $BPbI_4$, with A and B mono- and divalent ammonium and imidazolium cations [44,45]. On the basis of this study, an increase in the interlayer distance enlarges the band gap. Moreover, in the DFT + D2/HSE06 study of the tetragonal and orthorhombic $CH_3NH_3PbX_3$ (X = I and Br) it has been predicted that Br increases the band gap as much as 0.67 eV [46]. The electronic structure analysis has been indicated that an increase in the substituted cation size decreases the band gaps of the perovskites [46,47].

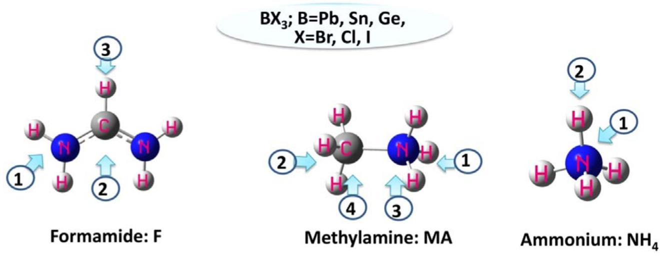

Fig. 1. Different probable configurations of the studied perovskites of $MAPbX_3$, FBX_3 and NH_4BX_3.

Research on the 2D materials such as phosphorene has also received an extensive attention due to a great potential for high electrochemical performance. They can apply for the photovoltaic devices, water splitting, photocatalytic hydrogenation and thermoelectric generators [48]. Phosphorene can play a key role in the PSCs, through an improvement in the charge transfer by suppressing the charge recombination [49]. For example, the planar ITO perovskite solar cells presented an increase of 18% in the energy efficiency, when phosphorene quantum dots were applied to bridge the PEDOT:PSS and perovskite layers [50]. Phosphorus quantum dots, as an HTM, can increase the extraction efficiency of holes, as well as improve the external quantum efficiencies and current density-voltage curves.

Since the structural, electronic and optical properties of the perovskites are sensitive to the processing conditions, rational design strategies are of great importance. Using the computational methods in the modeling of perovskite and HTM molecules would be helpful to have an improved PSC system [51].

The energy conversion efficiency of the PSCs is still low, even lower than that of the original electrochemical cells [52]. Therefore, the investigation of the optical and electrical characteristics of the solid-state perovskite solar cells is valuable [53]. To access the optimal organometallic halide perovskite solar cells, we have modified some of the designs and then investigated the molecular engineering of them. Here, we have used the organometallic halide perovskite compounds (ABX_3, A = CH_3NH_3, NH_4, $CH(NH_2)_2$, B=Ge, Sn, Pb, X = Cl, Br, I) as the light-harvesting active layer in the PSCs.

Although, the HTMs of 2,2,7,7-tetrakis(N,N-di-p-methoxyphenylamine)-9-9-spirobifluorene (Spiro-OMeTAD) and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) have represented the best efficiency in the PSCs, in spite of some drawbacks of high cost and hard synthesis procedure [54–57]. We have investigated the Methoxydiphenylamine-substituted fluorene and triphenylamine derivatives, MDA1, MDA2 and MDA3 which have a basis of two most effective HTMs. Also, the carbazole-based conjugated enamine, V950 employing 3-amino-9-ethylcarbazole and 2,2-bis(4-methoxyphenyl) acetaldehyde moieties was considered. The other set of the HTMs which have been applied in this research are tetraphenyl-benzidine, TPB, and its analogues of TPD and NPB. Also, they have a high hole mobility, their study is of interest in the PSCs. Since some photovoltaic properties of the triphenylamine-based HTMs with thiophene, TH101, are comparable with the well-known HTMs, their investigation of their molecular properties is of importance, too.

In this procedure, electronic and optical properties of the ground/excited states of the defined materials have been studied through the TD-DFT method and natural bond orbital (NBO) analysis. This strategy is helpful to design efficient solar cells on the basis of the molecular engineering of the chemicals.

2. Computational details

All calculations were performed by using the Gaussian 09 program [58]. DFT method [59] at the B3LYP/LANL2DZ for metals and halogens and 6-31G(d,p) for C, N, H atoms. Time-dependent DFT (TD-DFT) method [60] was applied to calculate the excited states of the molecules. For this purpose and NBO analysis [61], a more complete basis set of 6-311 + + G(d,p) was applied for C, N and H atoms. In this analysis, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) were characterized to calculate the DFT reactivity indices such as the chemical hardness, η, electronic chemical potential, μ, and the electrophilicity index, ω [62]. These quantum chemistry descriptors are important to understand comprehensively of the charge transfer dynamic in the PSCs.

Intra-/intermolecular electron transfer determines the incident