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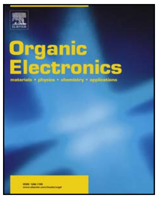

Exploring the properties of carbazole-based derivatives as hole transport materials from first principle and MD simulation

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ABSTRACT

Although the perovskite solar cell (PSC) without hole transport materials (HTM) has been developed, the power conversion efficiency (PCE) is still less than 15%. Exploring efficient and low cost HTMs is still the urgent requirement for the further development of efficient PSCs. Three new HTMs, **H5**, **H6**, and **H7**, are designed on the basis of **X25**, in which N-p-methoxyphenyl-1-naphthylamine, 9,9-dimethyl-acridine, and 9,9-dimethyl-10-phenyl-9,10-dihydroacridine are utilized as side groups, respectively, along with the 9-(4-methoxyphenyl)-9H-carbazole core. The performance of new designed molecules is evaluated from various aspects including frontier molecular orbital, absorption spectrum, and hole mobility. More importantly, the interfacial properties between HTM and $CH_3NH_3PbI_3$ (110) surface are explored. After adsorption, the band gap of $CH_3NH_3PbI_3$ (110) surface is almost kept but the energy levels of HTMs are varied indicating that it is necessary to study the adsorption properties rather than only the isolated HTM molecule. Actually, the side groups in **H5**, **H6**, and **H7** have been employed as side groups to constitute molecules applied in some relevant regions, which would provide an alternative pathway to develop new HTM rather than synthesis of new groups.

1. Introduction

Since the seminal report by Miyasaka [1], organic-inorganic metal halide perovskite solar cells (PSCs) are rapidly evolving into a promising photovoltaic technology owing to an unprecedented increase of power conversion efficiency (PCE) from less than 3.8% to over 20% in just seven years [2,3]. The extraordinary performance of PSCs is mainly attributed to the unique characteristics of perovskite including the direct band gap, broad absorption covering from UV region to near infrared region, and long carrier diffusion length [4]. Additionally, hole transporting material (HTM) plays a critical role in improving the PCE and enhancing the overall stability, which is attributed to the characteristic sandwich configuration of PSC [5]. Although the PCE of ~13% has been reported for the PSC deprived of HTM layer, it is still much less that those with HTM. Therefore, a great effort has been devoted to developing high-efficiency HTMs [6].

Organic small molecular HTMs have attracted extensive attentions with the easy tunable structure, convenient purification, and abundant raw materials [7]. Nevertheless, 2,2′7,7′-tetrakis(N,N-p-dimethoxyphenylamino)-9,9′-spirobifluorene (Spiro-OMeTAD) is the most state-of-the-art organic small molecular HTM in PSCs. However, its large scale applications have been greatly inhibited due to the tedious synthetic procedures and expensive price [8]. Attempts have been made to develop non-spiro type HTMs for viable commercial applications of PSCs including thiophene derivatives, carbazole, triphenylamine, and linear π-conjugated systems [9]. Among them, triphenylamine and carbazole are widely studied structural motif due to their low cost, convenient modification, and outstanding hole transport properties. Abate et al. reported a series of triphenylamine-based HTM with maximum PCE of 13.5% [10]. After that, a PCE of 16.3% is achieved on the basis of HTM with triphenylamine as core [11]. As early as 2014, Xu et al. have developed carbazole-based HTM resulting in a PCE of 9.8% [12]. After that, a promising efficiency of 15.24% was obtained by utilizing a simple carbazole-based HTM in PSCs by Petrikyte et al. [13]. Besides development of new groups, the combination of different existed groups is an alternative route to design high efficiency HTM [14]. Recently, carbazole-based HTM with N,N-di(4-methoxyphenyl)aniline substituted group is reported by Zhang et al. representing an impressive PCE of 17.4% that is the highest reported PCE for carbazole-based HTMs in PSCs [15]. Inspired by the successful example, three novel

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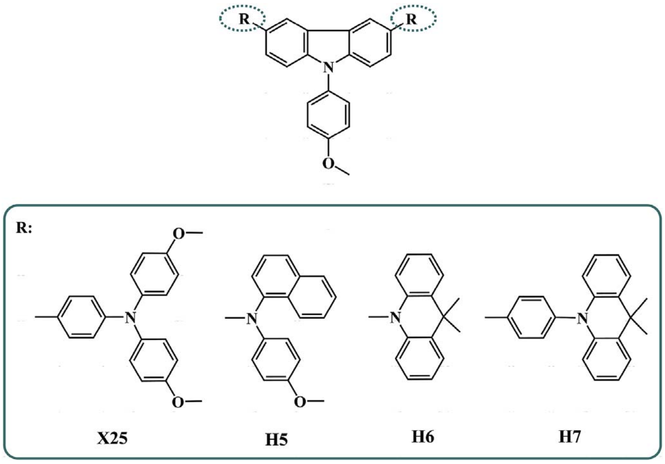

Scheme 1. Chemical structures of studied molecules.

carbazole-based HTMs, **H5**, **H6**, and **H7** (See Scheme 1), have been developed by employment of different side groups. To our best knowledge, they have never been synthesized and reported in previous literature. It is expected that three new designed carbazole-based molecules would be taken as the potential candidates for organic HTMs. Before the real application, their properties would be theoretically studied.

In this work, the properties of new designed HTMs are investigated by joint of first principle and molecular dynamics (MD) simulation. Understanding the structural and electronic properties of HTM from an atomistic level is a prerequisite for the subsequent molecular engineering of new HTM with improved characteristics. Thus, theoretical study has become a powerful tool in the pathway to explore new HTMs, which is even incorporated in many experimental studies. However, the deviation between experimental and theoretical results is somewhat large. One possible reason is that only the isolated HTM is considered. The interfacial properties between HTM and perovskite is not included in almost all theoretical studies, thus, we systematically study not only the isolated HTM but also the interfacial properties between HTM and perovskite. Additionally, the hydrophoby, stability, and solubility of new designed HTMs are evaluated.

2. Computational details

All the structures in ground state were optimized by density functional theory (DFT) method with the Becke's three-parameter hybrid exchange functional combined with the Lee-Yang-Parr correlation functional (B3LYP) [16,17] and the 6-31G(d,p) basis set. Vibrational frequency was also calculated at the same level to ensure the accuracy of results. B3LYP could be regarded as one of the most classical and popular DFT functionals, which has been employed to perform the calculation for various molecules. Moreover, it presents excellent performance in calculation of small covalent systems. Therefore, it is also utilized in this work to perform the calculation for the ground-state structure. On the basis of the optimized geometries, the optical properties were calculated by time-dependent density functional theory (TD-DFT) with LC-BLYP method [18,19] at 6-31G(d,p) level in dichloromethane solvent with polarizable continuum model (PCM) [20]. The inclusion of long-rang correction (LC) scheme for exchange functional of DFT to TDDFT would remarkably refine the vertical excitation energy. It has been tested that the vertical excitation energy would be decreased by 1 eV for typical molecules [19]. All the abovementioned calculations were performed by the Gaussian 09 program [21].

Molecular dynamics (MD) simulations for dimer of all studied molecules were performed with the FORCITE module implemented in Materials Studio software package [22]. Dimer was initially randomly prepared in a box of approximate $50 \times 50 \times 50$ Å^3. Dreiding force field was employed to optimize the molecules and box, which was be helpful to predict the structure and dynamics of organic molecules [23]. Since the accuracy of Dreiding force field has been testified by comparison with crystal structures of some organic compounds, it is inferred that it could also be useful in predicting structures involving new combinations of elements.

After that, the MD trajectories ran under the isothermal and isochoric ensemble (NVT) for 30 ps with a time step of 1 fs at $T = 298$ K, where the Nose thermostat was employed. Subsequently, the coarse dimer of the lowest energy after MD simulation is chosen as the initial guess. Finally, the dimer was optimized at the M06-2X/6-31G(d,p) level [24] by Gaussian 09 program. To keep consistence, we also want to employ B3LYP method to optimize the dimer geometry. However, B3LYP is poor for the predictions of noncovalent bonding interactions, especially for the π-π interaction, with performance degrading dramatically as system sizes increase [25,26]. The M06-2X developed by Truhlar group is testified to be good candidate to apply in noncovalent interactions [24]. An ideal functional is expected to be suitable for all applications in chemistry and physics. However, such functionals are unknown and unlikely to be developed in the foreseeable future. Alternatively, different functionals are employed for the different goals.

To study the interfacial properties between the HTM and $CH_3NH_3PbI_{3,}$ HTM is adsorbed on the $3 \times 4 \times 4$ $CH_3NH_3PbI_3$ (110) facet in a box of $19 \times 36 \times 46$ Å^3. Ab initio MD simulation is carried out in NVT ensemble for 1 ps with the timestep of 1 fs to get an initial guess for the HTM-$CH_3NH_3PbI_3$ system. The bare $CH_3NH_3PbI_3$ (110), isolated HTM molecules, and HTM-$CH_3NH_3PbI_3$ were optimized by means of projector-augmented wave (PAW) potentials and the generalized gradient approximation (GGA) parametrized by Perdew-Burke-Ernzerhof (PBE) [27–29]. The PBE functional was employed to describe the exchange-correction potential. The PAW method was applied to describe the electron-ion interactions. Note that the bottom two layers of atoms were fixed during the structure optimization. The convergence threshold for self-consistent-field iteration was set at 10^{-3} eV. All other atoms were fully relaxed in three dimensions until the atomic forces were smaller than 0.1 eV/Å. The energy cutoff was set to be 400 eV. A $2 \times 2 \times 1$ centered k-point sampling of the Brillouin zone was used in the structural optimizations. Van der Waals interactions were considered by performing DFT-D3 calculations. Spin-orbit coupling (SOC) was also taken into account [30–32]. All the calculations were performed using the Vienna Ab Initio Simulation Package (VASP) [33,34].

3. Results and discussion

The chemical structures of all investigated HTM molecules are plotted in Scheme 1. It has been reported that the PSC with **X25** has achieved the highest PCE for the carbazole-based HTM. Perhaps the carbazole could be taken as a new choice to develop high efficient HTM except for spiro core. N-phenyl-1-naphthylamine has been taken as the substituted group to synthesize the HTM along with the spiro motif [35]. Here, it is still employed as side group with a small variation to combine with the carbazole core to form **H5**. 9,9-dimethyl-acridine has been employed as the side group along with the 9,9-dimethylthioxanthene-S,S-dioxide core group to constitute **DDMA-TXO2** that is utilized as thermally activated delayed fluorescence (TADF) emitter [36]. The commonly host material **CBP** in OLEDs has also shown good performance as the HTM in PSCs [37]. Inspired by it, organic molecules applied in other regions could also be an efficient HTMs in PSCs. **H6** and **H7** are designed by some modification, i.e., combination of 9,9-dimethyl-acridine group and carbazole core for **H6** and 9,9-dimethyl-10-phenyl-9,10-dihydroacridine group and carbazole core for **H7**. It is expected that they would be potential HTMs applied in PSCs.

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