

REGULAR ARTICLE

Effects of functional group position on hole transporting properties of carbazole derivatives in perovskite solar cells

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Abstract: Several carbazole derivatives (V866, V867 and V868) as hole transporting materials (HTMs) in perovskite solar cells are designed to explore the functional group position effect on electrochemical properties. The material properties are studied on the first-principle calculations combined with the Marcus theory. The results illustrate that V866 (*ortho*-position) has the suitable HOMO energy level matched with the metal electrode (-5.1 eV) and the perovskite absorption layer (-5.4 eV). Moreover, the molecular planarity of HTMs with the *ortho*-position functional groups is improved, which enhances intermolecular face-to-face π - π stacking degree. Compared to V867 and V868, the largest hole mobility value ($0.007 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) of V866 is obtained due to its modified molecular planarity. Therefore, V866 (*ortho*-position) is indeed an excellent carbazole HTM. Our theoretical investigation of HTMs is helpful for understanding the hole transporting behaviors and developing higher performance HTMs.

Keyword: HTM; Carbazole derivatives; Hole mobility; PSC; Molecular planarity

1. Introduction

Hybrid lead halide perovskite solar cells (PSCs) have attracted wide interest in recent years,

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due to their high power conversion efficiency (PCE), facile processability, relatively cheap raw material and manufacturing cost [1-5]. Lately, it is reported that the highest PCE has reached 22%. The rapid development of PSCs attributes to the simultaneous development of device assembly technology, excellent perovskite absorption layers and suitable charge transporting layers. In the charge transporting layers, the hole transport layer is introduced to construct Ohmic contact and eliminate the Schottky contact between the perovskite absorbing layer and the metal electrode [6]. The construction of ohmic contact is an important way to improve charge transfer ability. Therefore, the hole transporting layer has been extensively explored due to its important role in PSCs.

As far as we know, most of PSCs have been assembled with spiro-OMeTAD as HTMs [7-14]. The PCE of the solar cells assembled with spiro-OMeTAD as HTMs has risen rapidly from 9.4% to 22% in recent years [15-18]. However, the synthesis of Spiro-OMeTAD is excessively expensive due to its complex synthesis steps and harsh synthesis conditions [19]. Thus, tremendous effort has been spared on synthesizing alternative molecules by many research groups [20-22]. However, the achieved PCE of PSCs using non spiral ring molecules as HTMs is very low. Most of these molecules fail to show performance similar to that of Spiro-OMeTAD. The only HTM without the spiro motif, known to date that demonstrated device efficiency close to 15% requires custom-made boronic acids as precursors for the final synthesis.

Recently, Gratia reported a new type of hole transporting twin molecule V866, based on methoxydiphenylamine-substituted carbarzole, with performance very similar to that of Spiro-OMeTAD [19]. The PSCs employing V886 as HTMs show the PCE up to 16.91%. Moreover, V866 does not require an extensive and expensive synthetic procedure. This is the highest PCE that can be achieved by using non spiral ring dopant-free molecules as HTMs at present. Furthermore, its simple two-step synthesis and the ready availability of the starting materials makes V866 very appealing for commercial prospects of PSCs [19]. Therefore, we choose V866 as our investigated subject.

Although the HTMs in PSCs have been extensively studied in experiment, few researchers have systematically studied the electrochemical properties of hole transporting materials in theory. Therefore, we plan to study the hole transporting properties based on the first-principle calculations combined with the Marcus theory [23]. Several experimental papers have pointed out that the introduction of a conjugated core into HTMs in PSCs can enhance the intermolecular hole mobility [15, 24]. However, little attention has been paid to the effect of the functional groups on the conjugated core, such as the benzene ring in HTMs. Based on this idea, V866 (*ortho*-position), V867 (*meta*-position) and V868 (*para*-position) are developed to study the effect on anisotropic hole mobility when the functional groups position changes in HTMs. Here, the functional group is methoxydiphenylamine-substituted

carbazole group (MSCG). The results show that the suitable HOMO level of V866 allows it to have enough hole injection driving force from the perovskite absorbing layer to the metal electrode when the MSCG is in the *ortho*-position,. Furthermore, compared with V867 (*meta*-position) and V868 (*para*-position), the hole mobility ability of V866 (*ortho*-position) is also effectively enhanced due to the improved molecular planarity. Therefore, V866 is indeed a promising HTM with excellent electrochemical properties. Our work may provide a theoretical exploration for designing high-performance HTMs.

2. Computational methods

In this work, the hole transporting properties of all investigated molecules are based on a combination of first-principles quantum mechanic calculations and Marcus theory. The hopping mechanism is used to describe the hole transfer and the transfer rate (W) for all investigated molecules is expressed as [25, 26]:

$$W = \frac{V^2}{\hbar} \left(\frac{\pi}{\lambda k_B T} \right)^{1/2} \exp \left(-\frac{\lambda}{4k_B T} \right), \quad (1)$$

Herein, V denotes the intermolecular electronic coupling of a dimer [27]. k_B represents the Boltzmann constant, T is the temperature in Kelvin and $\hbar$ denotes the Planck constant. λ represents reorganization energy, which is calculated by using the adiabatic potential energy surface method [28, 29]. λ can be expressed in Eq. (2).

$$\lambda = (E_0^* - E_0) + (E_+^* - E_+), \quad (2)$$

E_0^* and E_+^* denote the energies of the neutral and cationic states with the geometries of the cationic and neutral species. E_0 and E_+ are the energies of the neutral and cationic species in their lowest-energy geometries [23].

$$V = \frac{J_{RP} - S_{RP}(H_{RR} + H_{PP})/2}{1 - S_{RP}^2}, \quad (3)$$

Where H_{RR} and H_{PP} represent the site energies. S_{RP} is the spatial overlap and J_{RP} is the charge transfer integrals for one dimer.

Hole mobility is used to evaluate hole transporting process, which is expressed as follows [23]:

$$\mu_\Phi = \frac{e}{2k_B T} \sum_i W_i r_i^2 P_i \cos^2 \gamma_i \cos^2 (\theta_i - \Phi), \quad (4)$$

γ_i denotes the dihedral angle between the hole transporting pathways and the chosen crystal plane [30]. In general, the plane where all the transmission paths lie is parallel to the chosen crystal plane, and at this point γ_i is 0. Φ denotes the orientation angle between the hole transporting channel and the chosen crystal axis [31]. This orientation angle is the

vector synthesis result of the hole mobility of all hole hopping paths [32]. θ represent the angle between the hole hopping pathway and the chosen crystal axis. r_i is the intermolecular centroid distance of the dimer. Herein, for a dimer, θ and r_i is directly measured by Materials Studio software (MS) [33-38]. P_i denotes the hopping probability of a pathway, which could be calculated by Eq. (5). W_i denotes the transfer rate of one dimer.

$$P_i = \frac{W_i}{\sum_i W_i}, \quad (5)$$

All the optimization of molecular structure are performed by Gaussian09 software package on the basis of the density functional theory (DFT) [39]. A series of functionals are tested for choosing suitable HOMO energy levels coinciding with experiment values [40, 41]. According to the comparison of different methods, only the HOMO energy levels (-5.326 eV) calculated by hybrid functional B3P86/6-311G(d) is the closest to the experimental value (-5.27 eV). Therefore, the hybrid functional B3P86/6-311G(d) applies to our research system. Due to the solvent effect, the polarized continuum model (PCM) equilibrium solvation is adopted in the ground state optimization. The required parameters (H_{RR} , H_{PP} , S_{RP} and J_{RP}) to calculate electronic coupling (V) for different dimers are implemented in Amsterdam density functional (ADF) program [42]. Here, the local density functional VWN in the conjunction with the PW91 gradient corrections with the TZ2P basis set in the energy calculation is chosen for all the invested molecules. Herein, the crystal data is predicted by Materials Studio software (MS) [43] based on common space groups $P2_1/c$, $P-1$, $P2_12_12_1$, $P2_1$, $C2/c$, P_{bca} , P_{na2_1} , P_{bcn} , $C2$ and C_c in Dreiding forcefield [44]. These space groups characterize most of all molecular crystals consisting of organic compounds [45, 46].

3. Results and discussion

All the geometries of material molecules investigated here are illustrated in **Figure 1**. As shown in **Table 1**, the HOMO energy levels of V866, V867 and V868 are -5.326 eV, -4.720 eV and 4.697 eV, respectively. In PSCs, the HOMO energy level is an important parameter to evaluate the hole injection driving forces. Generally, the HOMO energy levels of the perovskite absorbing layer and metal electrode are -5.4 eV and -5.1 eV from the schematic of PSC [47]. Although the higher HOMO energy level enables the material molecules to obtain stronger hole injection driving forces from the perovskite absorption layer to the hole transporting layer, it is not conducive to hole transfer process from hole transporting layer to the metal electrode. Therefore, only the HOMO energy level of V866 matches the perovskite absorption layer and the metal electrode perfectly. Furthermore, in order to hinder the electron transportation from perovskite absorbing layer to the metal electrodes, the LUMO energy level should be higher than the conduction band level of perovskite absorbing layer

such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ (-3.93 eV). The LUMO energy level of V866, V867 and V868 is -1.970 eV, -1.283 eV and -1.267 eV, respectively. Therefore, the LUMO energy levels of these three molecules are much higher than the conduction band level of the perovskite absorption layer, which can hinder the backflow of electrons effectively.

The optical bandgap (E_g) is the energy difference value between HOMO and LUMO energy levels. Some papers point out that smaller bandgap of a semiconductor is conducive to increase the intrinsic electrical conductivity by increasing the carrier concentration [48-51]. E_g values of V866, V867 and V868 is 3.390 eV, 3.437 eV and 3.430 eV, respectively. Therefore, the intrinsic electrical conductivity of V866 is larger than that of V867 and V868. The orbital spatial distribution and components of the HOMO and LUMO for these molecules are described in **Figure 2**. For these three molecules, the HOMO orbitals are almost populated over the benzene connected with methoxy and the carbazole. The LUMO orbitals are almost centered on the carbazole. However, the orbital overlap between the HOMOs and LUMOs remains slightly different. For V867 and V868, the orbital overlap between the HOMOs and LUMOs is larger than that of V866. The larger orbital overlap between the HOMOs and LUMOs suggests that fast formation of neutral excitons and hole may take place [52]. It can be seen that the hole transporting performance of V866 may be better than the performances of V867 and V868.

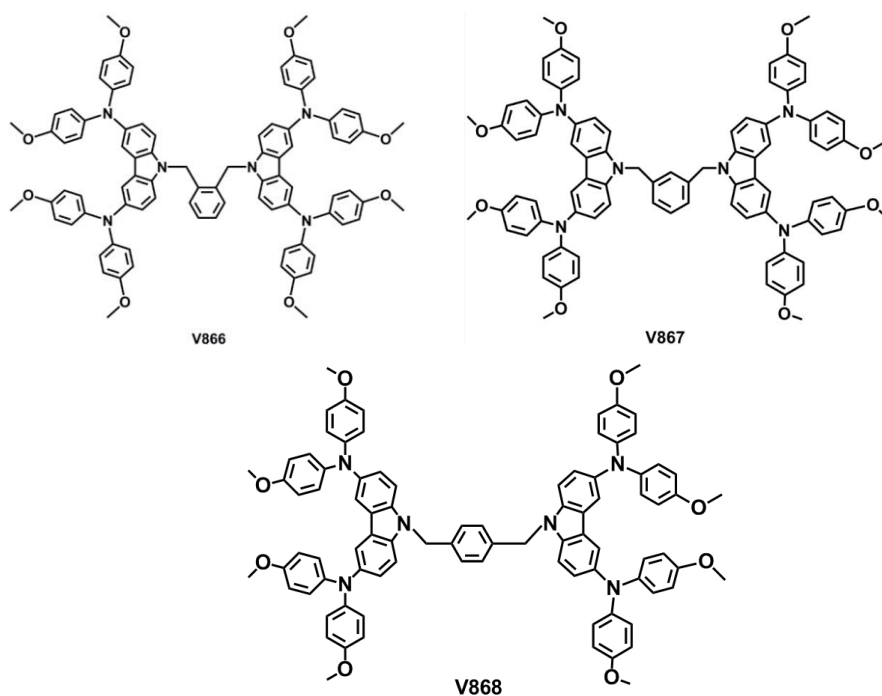


Figure 1: Molecular structures of V866, V867 and V868.

From **Table 1**, the reorganization energy of V866 is the smallest. The reorganization energy of V868 is slightly smaller than that of V867. According to Eq. (1), larger reorganization energy is not helpful for higher transfer rate W . Thus, V866 may possess higher transfer rate than V867 and V868.

As shown in **Figure 3**, the dihedral angle of two carbazole ring planes for V866, V867 and V868 is 7.29° , 60.2° and 10.31° , respectively. The dihedral angle for V866 is smaller than the other dihedral angles for V867 and V868. Herein, material molecules with smaller dihedral angle of two carbazole ring planes possess better molecular planarity. Good molecular planarity is beneficial to the formation of intermolecular face-to-face π - π stacking increasing the hole mobility between conjugated molecules. Therefore, compared with V867 and V868, V866 may have the largest hole mobility.

Table 1. HOMO and LUMO energy level, the optical bandgap (E_g) and the reorganization energy (λ) of all the molecules at level of B3P86/6-311G(d).

Molecules	HOMO (eV)	LUMO (eV)	E_g (eV)	λ (eV)
V866	-5.326	-1.936	3.390	9.897×10^{-2}
V867	-4.720	-1.283	3.437	1.262×10^{-1}
V868	-4.697	-1.267	3.430	1.069×10^{-1}

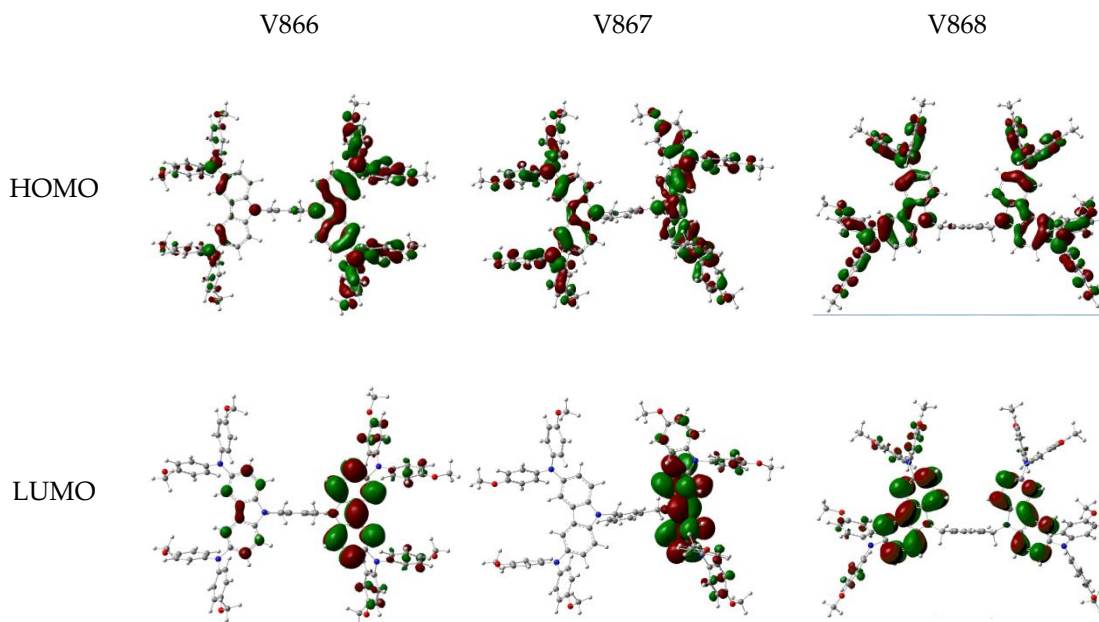


Figure 2: Frontier molecular orbitals of all the molecules at level of B3P86/6-311G(d).

Herein a first-principles-based simulation is used to predict intrinsic carrier transport behavior of organic crystals with crystal structures [23]. We cannot find the crystal structure data of V866, V867 and V868 in all databases. Thus, the crystal structures of invested molecules are predicted based on different space groups. Energy data from different crystal data are listed in **Figure 4**. It shown that three molecules have their respective lowest points in energy when the horizontal coordinate is $P2_1$. The crystal structure with the lowest energy is the most stable. The lattice parameters of three crystal structures are listed in **Table 2**.

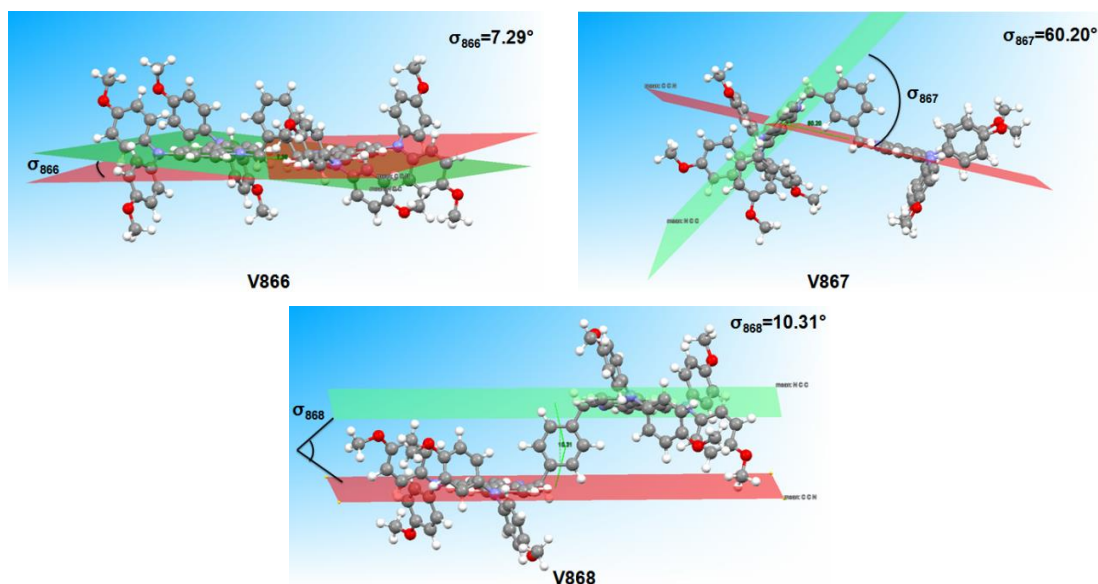


Figure 3: The dihedral angles of two carbazole ring planes for V866, V867 and V868.

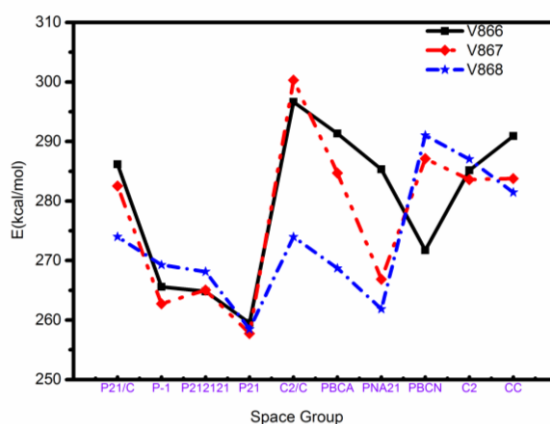


Figure 4: The energy distribution of crystal structures on different space groups for V866, V867 and V868.

All the dimers are characterized as transverse (T) dimer, parallel (P) dimer. For these three molecules, different dimers are found on crystal surface *bc* as shown in **Figure 5**. For V866, the centroid distance r of T1 dimer is equal to of the intermolecular centroid distance r of T3 dimer. However, the electronic coupling value V of T1 dimer is larger than that of T3 dimer. Thus, the centroid distance r may not be the only determinant of the electron coupling and hole mobility. The electronic coupling value V of T1 dimer for V867 and V868 is 0 eV. The intermolecular centroid distance r is so far away that the electronic coupling effect is very small. For V866, V867 and V868, the maximum values of electron coupling are -1.452×10^{-3} eV, 7.281×10^{-4} eV and -1.052×10^{-3} eV, respectively. Furthermore, at this time, the intermolecular centroid distances for V866, V867 and V868 are for 12.3 Å, 12.0 Å and 10.2 Å, respectively. Therefore, compared with V867 and V868, the strongest electron coupling effect of V866 is obtained due to the best molecular planarity.

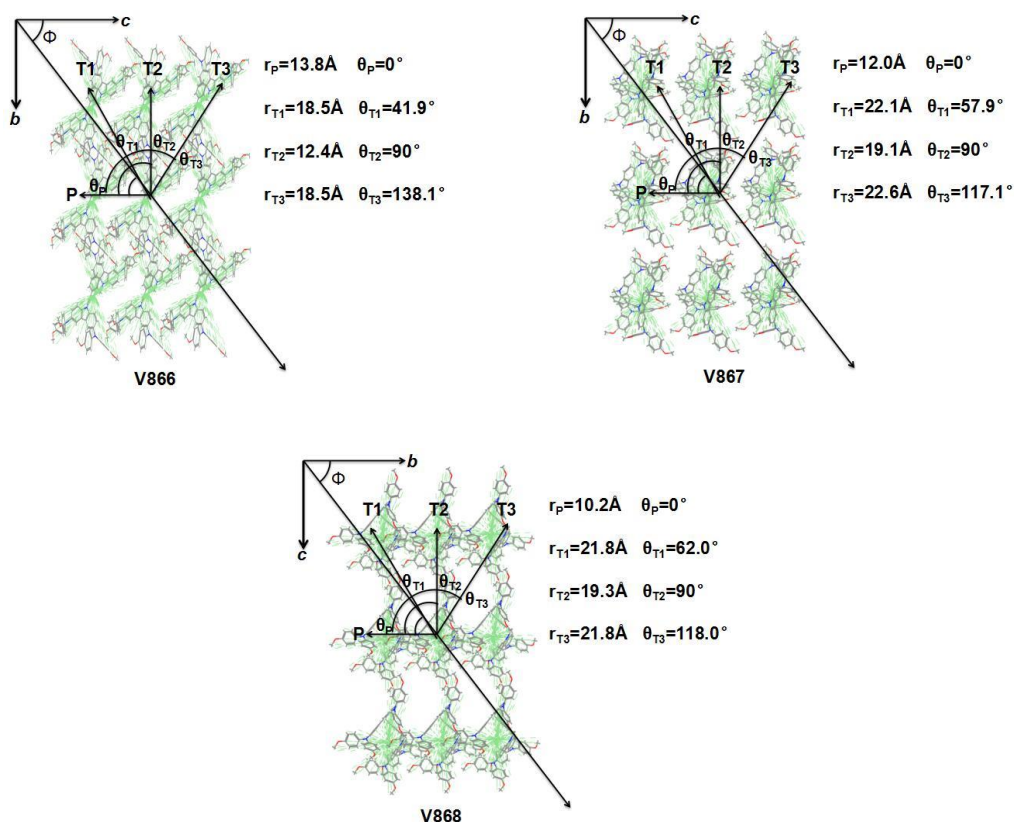


Figure 5: Comparison of molecular packings and charge hopping pathways in V866 (*bc*), V867 (*bc*) and V868 (*bc*) with the centroid distance r (Å) and the angle of the projected electronic coupling pathways relative to the reference axis. The long black arrow represents the transport channel.

From **Table 3**, it shows that the $\mu_{\max}$ of V866, V867 and V868 are $0.007 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $0.002 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.003 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Good molecular planarity is favorable for generating the face-to-face π - π packing. The face-to-face π - π packing with larger orbital overlap could contribute to stronger electronic coupling effect. Thus, the highest hole mobility of V866 (*ortho*-position) is obtained due to the face-to-face π - π packing. In conclusion, V866 is a promising hole transporting material indeed.

All the calculated hole mobility μ for V866, V867 and V868 are given in **Figure 6**. Understanding the anisotropic hole mobility can be helpful to control the orientation of charge transport channel relative to the reference axis of molecular crystal [32]. Angular-resolution anisotropic mobility curve of V866 is different from the curves of V867 and V868. The reason is that the hole mobility of P dimer is closed to the hole mobility of T2 dimer for V866. Here we choose the crystal axis c as the reference axis for V866. There is maximum hole mobility value ($0.007 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) along to the crystal axis b direction for V866 when Φ angle is $0^\circ/180^\circ$. However, the maximum hole mobility value along to the crystal axis b direction for V867 and V868 are near $90^\circ/270^\circ$ in the angle-resolution figure, which are $0.002 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $0.003 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

Table 2. The lattice parameters of the crystal structures for V866, V867 and V868.

Molecules	Lattice parameters ($\text{\AA}$)	
V866	cubic $27.790 \times 12.359 \times 13.762 \text{ \AA}^3$	$\alpha=90.000^\circ$, $\beta=63.983^\circ$, $\gamma=90.000^\circ$
V867	cubic $19.745 \times 11.994 \times 19.098 \text{ \AA}^3$	$\alpha=90.000^\circ$, $\beta=100.804^\circ$, $\gamma=90.000^\circ$
V868	cubic $23.389 \times 10.247 \times 19.295 \text{ \AA}^3$	$\alpha=90.000^\circ$, $\beta=104.616^\circ$, $\gamma=90.000^\circ$

Table 3. The intermolecular centroid distance r ($\text{\AA}$), the electronic coupling value V (eV) and the $\mu_{\max}$ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for V866, V867 and V868.

pathway	V866		V867		V868	
	V	r	V	r	V	r
P	-1.311×10^{-3}	13.8	7.281×10^{-4}	12.0	-1.052×10^{-3}	10.2
T1	3.903×10^{-5}	18.5	0	22.6	0	21.8
T2	-1.452×10^{-3}	12.3	8.604×10^{-5}	19.1	4.271×10^{-4}	19.3
T3	-1.057×10^{-5}	18.5	1.000×10^{-5}	22.6	0	21.8
$\mu_{\max}$	0.007		0.002		0.003	

Compared with V867 (*meta*-position) and V868 (*para*-position), V866 (*ortho*-position) exhibits higher hole mobility in terms of anisotropy. The direction of the charge transporting channel is easy to be controlled so as to obtain a higher hole mobility. It is indicated that the charge transporting properties of V866 are better than that of V867 and V868. It also shows that the functional group position has a great influence on the intermolecular charge-transport properties. The difference can be derived from the relative magnitude of electronic coupling value. It also indicates that free charge in V866 crystal are much more intrinsically mobile than the charge in V867 and V868 crystal. The distribution of angular-resolution anisotropic mobility can help us understand the charge transporting property and design high-performance HTMs.

4. Conclusions

In conclusion, we have developed a series of carbazole derivatives (V866, V867 and V868) as HTMs to explore the functional group position effect on the electrochemical properties. The results illustrate that V866 (*ortho*-position) has the suitable HOMO energy level matched with the metal electrode and the perovskite absorption layer. Furthermore, compared with V867 (*meta*-position) and V868 (*para*-position), a higher hole mobility of V866 (*ortho*-position) is obtained due to the face-to-face π - π packing. We also find that the functional group position of material molecule plays an important role in determining the molecular stacking configurations and the Angular-resolution anisotropic hole mobility indeed. Our theoretical investigation of carbazole derivatives as HTMs in PSCs may be helpful for evaluating the charge transporting behaviors to realize better charge transfer efficiency and design higher performance HTMs.

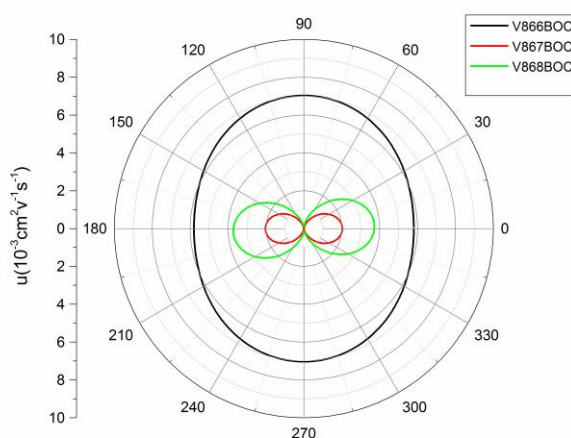


Figure 6: Angular-resolution anisotropic hole mobility curves of V866 ,V867 and V868.

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