

## 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  $\pi$ - $\pi$  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

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## 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 V866 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