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Communication

Binary hole transport materials blending to linearly tune HOMO level for high efficiency and stable perovskite solar cells

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ABSTRACT

To maximize the photovoltaic performance of perovskite solar cells (PVSCs) by developing new hole-transport layer (HTL) materials, the precise tuning of their energy levels especially the highest occupied molecular orbital (HOMO) is highly desirable. Here, a simple binary strategy for the first time is proposed to acquire ideal HOMO level by optimizing the composition of binary blend HTLs including CZ-TA (HOMO = −5.170 eV) and CZ-STA (HOMO = −5.333 eV). By adding 10 wt% CZ-STA, the binary HTM (HOMO = −5.199 eV) based perovskite solar cells achieve a maximum power conversion efficiency of 19.85% (18.32% for CZ-TA). The introducing of S atom in CZ-STA not only downshifts HOMO level but also forms stronger Pb-S interaction with perovskites than Pb-O in CZ-TA, leading to better device performance and reduced hysteresis. Importantly, the un-encapsulated PVSCs using CZ-TA:CZ-STA (90:10, w/w) binary HTL exhibit good environment stability in ambient air, maintaining over 82% of their initial efficiency after 60 days' storage with a relative humidity around 50%. Therefore, this strategy provides new insights on HTL development to push forward the progress of the emerging PVSCs

1. Introduction

In the past few years, organic-inorganic hybrid perovskite solar cells (PVSCs) have witnessed a rapid development due to their facile solution fabrication, strong light absorption over a broad spectrum, long carrier lifetime and diffusion length [1–5]. The certified power conversion efficiency (PCE) has reached 22.7% from the initial 3.8% [6–10]. In a typical PVSC device, electron transport layers (ETLs, *n*-type semiconductors) and hole transport layers (HTLs, *p*-type semiconductors) are usually required to assist charge separation and transport [11–14]. State-of-the-art high-performance PVSCs commonly use organic materials especially 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamino)-9,9′-spirobifluorene (spiro-OMeTAD) as HTL [15–18]. However, the complex multi-step synthesis and expensive sublimation process greatly limit its commercial application. Moreover, spiro-OMeTAD needs to be exposed to ambient environment for a long-time oxidation process to reach peak PCE. This is also a great drawback for industrial use.

Considering the disadvantages mentioned above, many efforts have been made by researchers all over the world to replace spiro-OMeTAD [9,19–24]. Malinauskas et al. [21] developed an effective HTL material named V862 through two-step reaction and the PCE can reach 19.96% with a total cost of only 23.11 \$ g^{-1} (~ 500 \$ g^{-1} for spiro-OMeTAD). By simply replacing spiro core with fluorene–dithiophene, Saliba et al. [25] synthesized FDT and PVSCs with this HTL showed an impressive PCE of 20.2%. Meanwhile, the lab synthesis costs of FDT is only one fifth of spiro-OMeTAD. Hou et al. [9] adopted Ta-WOx modified PDCBT to reduce V_{OC} losses and acquired a PCE as high as 21.2%. Recently, we reported a simple carbazole-based HTL, CZ-TA, synthesized through a facile one-step reaction with improved hole transport and reduced cost (1/80 of spiro-OMeTAD) [26,27]. PVSCs using CZ-TA as HTL showed a PCE of 18.32% with an impressive fill factor (FF) over 81% and good device stability. Additionally, CZ-TA does not require oxygen doping, eliminating the potential drop of PCE upon device encapsulation. The main drawback of CZ-TA is the relatively low V_{OC} (1.044 V), indicating the mismatch of energy level [28]. It is well known that appropriate energy-level alignment can facilitate charge extraction and transport, leading to improved V_{oc} J_{sc} and FF. However, in many cases, although careful theoretical simulation and calculation have been carried out

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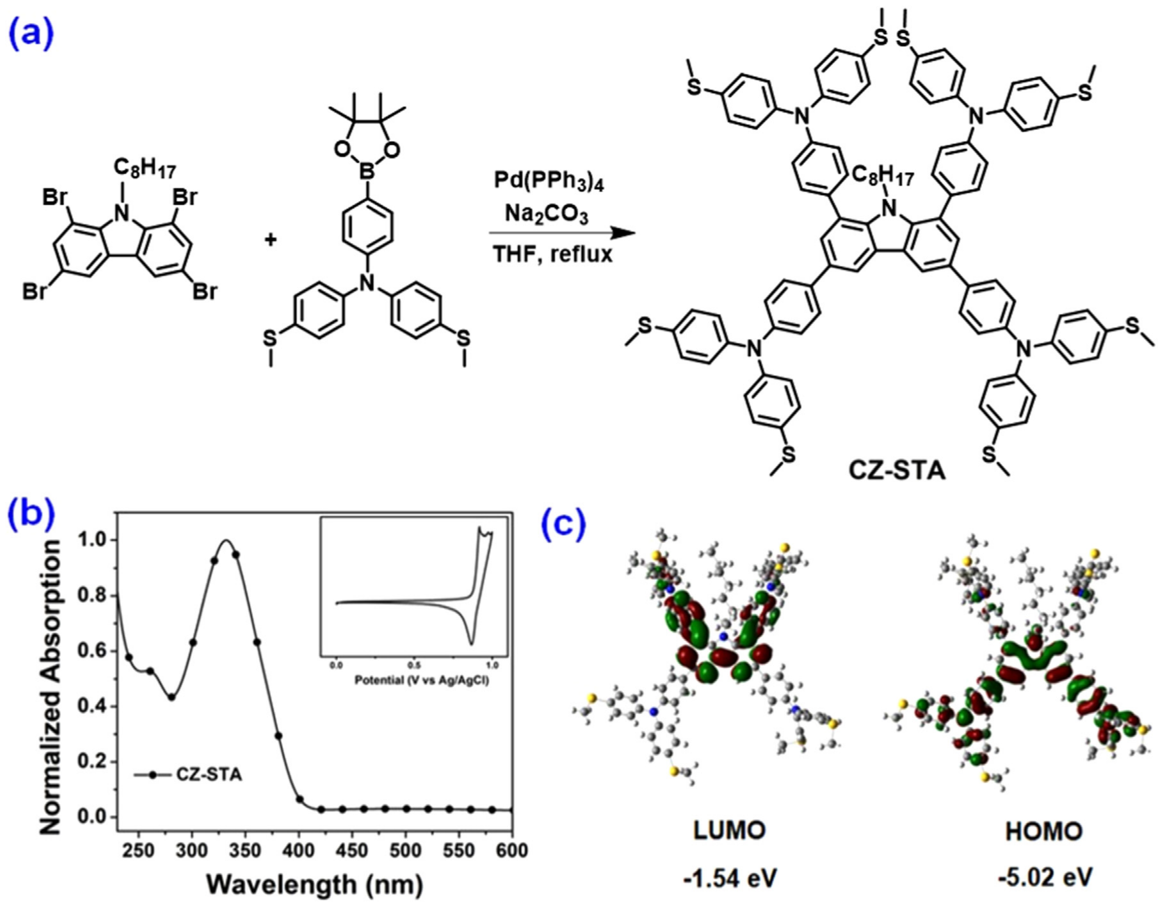

Fig. 1. (a) Synthetic route for CZ-STA. (b) Absorption spectra of CZ-STA film, the inset is cyclic voltagram of CZ-STA in 0.1 mol L^{-1} n-Bu_4NPF_6 solution in acetonitrile. (c) DFT-calculated HOMO and LUMO electronic structures of CZ-STA.

during HTL molecular design, the actual highest occupied molecular orbital (HOMO) level of HTL may still not be at ideal position resulting in V_{oc} loss [19]. Thus, simple, precise and efficient tuning of HOMO level is necessary for maximizing device performance when developing new HTL materials.

Herein, we report a new strategy for linearly tuning HOMO level of HTL materials to obtain maximum device performance. With CZ-TA as an example, firstly, we have designed and synthesized 4,4',4'',4'''-(9-octylcarbazole-1,3,6,8-tetrayl)tetrakis(*N*,*N*-bis(4-methylthiophenyl) aniline) (CZ-STA). By replacing methoxy group on CZ-TA with methylsulfanyl group, CZ-STA exhibits a deeper HOMO level due to the π-acceptor capability of sulfur atom. It can form $p\pi$(C)–$d\pi$(S) orbital overlap where divalent sulfur accepts π-electron from the π-orbital of C=C bonds into its empty 3*d*-orbitals [29,30]. Besides, stronger Pb-S interaction will also lead to more efficient charge extraction and surface traps passivation [31]. With CZ-STA in hand, HOMO levels can be easily tuned by changing ratios of CZ-TA and CZ-STA. Since these two molecules have almost the same conjugated structure, they are preferred to form very compatible blends [32,33]. Meanwhile, the S atoms of CZ-STA and O atoms of CZ-TA may form S…O non-covalent interactions in solid state to enhance their packing in HTL layers [34]. PVSCs using CZ-TA: CZ-STA (90:10, weight ratio) as HTL have reached a champion PCE of 19.85% (18.32% for CZ-TA) under reverse voltage scan and a steady-state efficiency of 19.55% (16.36% for CZ-TA). Compared with pure CZ-TA (V_{OC} = 1.044 V, J_{SC} = 21.66 mA cm^{-2}, FF = 81.0%), binary blend HTL system showed increased V_{OC} and J_{SC} without sacrificing FF (V_{OC} = 1.082 V, J_{SC} = 22.51 mA cm^{-2}, FF = 81.5%). Moreover, the cost for lab synthesis and purification of both CZ-TA (~ $25/g) and CZ-STA (~ $32/g) is much lower than that for spiro-OMeTAD (see cost calculation in Supporting information). It's worth noting that the CZ-TA:CZ-STA (90:10) blend HTL based devices can maintain over 82% of its initial PCE after storing for 60 days in air with a relative humidity around 50% without encapsulation. To the best of our knowledge, this is the first report of precisely tuning HTL energy level through a simple and cost-effective binary blend strategy.

2. Results and discussion

The synthetic route of CZ-STA is outlined in Fig. 1**a** and detailed synthesis can be found in Supporting information (SI). 1,3,6,8-Tetrabromo-9-octylcarbazole was obtained following the same procedure in our earlier report [26]. The details of synthesis of 4-methylthio-N-(4-methylthiophenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)aniline are outlined in SI [31,35]. After that, Pd-catalyzed Suzuki reaction was carried out to produce final CZ-STA with 78% yield. Simple column chromatography purification was adopted to acquire analytically pure CZ-STA for PVSC application, directly avoiding expensive sublimation process. The chemical structure of CZ-STA was