

New hole transport materials with 1,2-dimethoxyphenyl as the terminal groups

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ABSTRACT

Two new compounds (J1 and J2) are synthesized and used as hole transport materials (HTMs) for perovskite solar cells (PSCs). In J1 and J2, 1,2-dimethoxyphenyl is used as the terminal group, with tetraphenyl ethylene and 9,9'-spiro[9H-fluorene] ring as the core structure, respectively. Compared to the commonly used methoxyl end group, there are two methoxyl units on 1,2-dimethoxyphenyl, which enhances the electron-donating ability of the end groups. Additionally, the introduced phenyl ring could extend π conjugation of the whole molecule, which is favorable for electron delocalization and charge transporting. Planar PSCs are fabricated, and J2-based device shows a power conversion efficiency (PCE) of 15.07%, with a short-circuit current density (J_{sc}) of 20.37 mA cm⁻², an open-circuit voltage (V_{oc}) of 1020 mV and a fill factor (FF) of 0.73.

1. Introduction

In recent years, perovskite solar cells (PSCs) have become one of the fastest growing topics in the field of solar cells, and the power conversion efficiency (PCE) increases dramatically from 3.8% to now exceeding 22% in less than a decade [1–3]. The rapid development of PSCs could be ascribed to its low cost and excellent performance, as well as the intrinsic merits of perovskite materials, such as direct bandgap, long charge diffusion lengths, and good light harvesting efficiency [4–10].

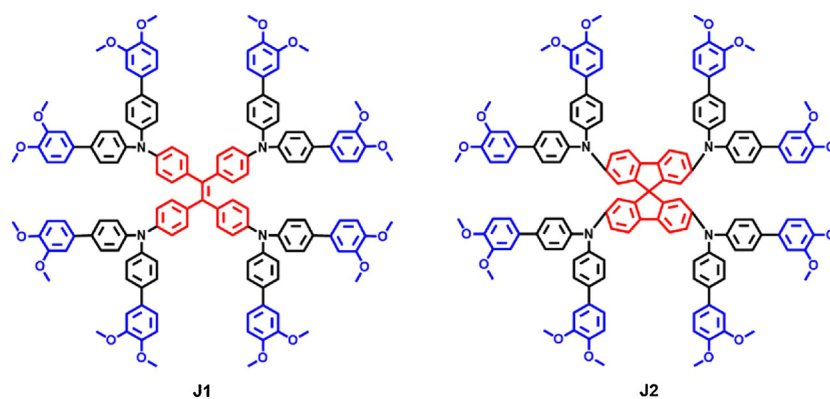
Hole transport material (HTM) is an important component in PSCs, it plays the role of extracting photogenerated holes from the perovskite layer and transporting them to the counter electrode [10–15]. Recently, HTMs based on organic small molecules have attracted great attention, because of its simple synthetic route, good reproducibility and tunable energy levels [16–21]. Based on these advantages, a large number of organic small molecules have been synthesized and applied as HTMs. Among them, the most studied HTM is Spiro-OMeTAD (2,2',7,7'-tetrakis (*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene). The efficiency of PSCs using Spiro-OMeTAD HTM has surpassed 22% recently [9,22,23]. However, the high cost of synthesis and the tedious purification processes hindered its commercialization [19,24,25]. In this regard, researchers made great efforts to develop new organic small molecules to replace Spiro-OMeTAD [26–31]. For instance, Grimsdale et al. synthesized a new small molecule using 3,4-ethylenedioxythiophene (EDOT) as the core structure exhibiting a PCE of 13.8%, and

this result is comparable with that obtained with Spiro-OMeTAD HTM (13.7%) [24]. Kim and co-workers reported three molecules with 1,4-phenyl, 4,4'-biphenyl, or 1,3,5-trisphenylbenzene as the core units respectively, and the 1,3,5-trisphenylbenzene core afforded the best PCE of 13%, which was close to that of Spiro-OMeTAD-based device (13.76%) [26].

According to literature reports, methoxyl groups are usually incorporated as the terminal groups in HTMs with three dimensional structures [12,16,32,33]. In addition, alkyl [34,35], dimethyl amino [36,37], methylsulfanyl [38,39] and dicyanovinylene [40,41] groups et al. can also be used as terminal group. Different terminal groups may have some influences on the electronic properties of the corresponding molecules. For example, Chen et al. synthesized TPP-SMeTAD with methylsulfanyl end groups. Compared to the analogue molecule TPP-OMeTAD with methoxyl end group, the methylsulfanyl group in TPP-SMeTAD provided a deeper HOMO level, and the S atoms were reported to be able to passivate the surface trap in perovskite film, making the PCE of TPP-SMeTAD (16.6%) outperform that of TPP-OMeTAD (14.6%) [38]. Our group replaced the methoxyl substituent of TPE-4DPA with *N,N*-dimethylamino and devised another tetraphenylethylene derivative TPE-NMe. By using the *N,N*-dimethylamino end group, the solubility of TPE-NMe (~40 mg/mL in chlorobenzene) was improved significantly in contrast to that of TPE-4DPA (~15 mg/mL), resulting in a better film quality of the HTM layer as well as a higher device performance [37]. On the other hand, the different substitution position of the end groups in HTMs may also lead to different performances of the

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Scheme 1. Chemical Structures of J1 and J2.

corresponding PSCs. Nam Joong Jeon et al. and our group separately designed HTMs with the methoxyl end groups at different positions (*pp*-, *pm*-, and *po*-), with 9,9'-spirobi[9H-fluorene]ring and tetraphenyl ethylene as the core structure, respectively. Experimental results showed that the position of the methoxyl end groups affected the HOMO energy levels of the HTMs, and the highest PCEs were obtained in *po*-Spiro-OMeTAD (16.7%) and *pm*-TPE-4DPA (15.44%) [42,43].

Compared to methoxyl groups, the 1,2-dimethoxyphenyl is also potential to be applied as the terminal groups for HTMs: 1) the increased methoxyl groups could enhance the electron donating ability and tune the energy levels [44]; 2) the phenyl ring in 1,2-dimethoxyphenyl could extend the conjugation of the whole molecule, which is favorable for charge transporting [32,45,46]. Therefore, in this work, 1,2-dimethoxyphenyl is used as the end groups, and two new HTMs are synthesized, namely J1 and J2 (Scheme 1). Tetraphenyl ethylene and 9,9'-spirobi[9H-fluorene]ring are used as the core structure for J1 and J2, respectively. Planar PSCs are fabricated with conventional perovskite material ($\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$). It turned out that J2-based device achieves a V_{oc} of 1020 mV, J_{sc} of 20.37 mA cm^{-2} and a FF of 0.73, with the highest PCE of 15.07% among the HTMs studied. We note that the performance of J2 is close to the Spiro-OMeTAD-based solar cells under the same testing conditions, while J1 shows inferior performance. Because compared to J2, the HOMO energy level of J1 matching with perovskite is inferior and the hole mobility of J1 is slightly lower. In summary, 1,2-dimethoxyphenyl is potential to be used as the end groups to construct hole transport materials.

2. Results and discussion

Chemical structures of J1 and J2 are depicted in Scheme 1. Detailed synthetic procedures and characterizations are presented in Supporting Information. The structures of the new compounds were characterized through ^1H and ^{13}C NMR spectroscopy and the mass spectrometry. These results are also shown in the Supporting Information.

UV-vis absorption spectra of J1 and J2 in dichloromethane solution is shown in Fig. 1a. The main absorption bands for J1 and J2 both locate at 351 nm, and also a shoulder band at about 400 nm. The band at shorter wavelength could be related to the $\pi-\pi^*$ transitions, while the band around 400 nm is ascribed to the charge transfer bands. The absorption of J1 and J2 in the 400–900 nm range is weak, which has little effect on light utilization at the visible region. Cyclic voltammetry (CV) measurements for the two new compounds are shown in Fig. S9 using ferrocene as an internal standard, and CV of Spiro-OMeTAD is also tested for comparison. The highest occupied molecular orbital (HOMO) energy levels could be estimated from the first oxidation peak ($E_{\text{HOMO}} = -(4.74 + (E_{\text{onset, ox vs Fc}}^+ / \text{Fc}))$), and the HOMO levels for J1 and J2 are measured to be -5.27 eV and -5.38 eV , respectively. The conjugation of tetraphenyl ethylene is slightly better than 9,9'-Spirobi[9H-fluorene], leading to better electron delocalization in J1, resulting in a higher HOMO energy level of J1 than that of J2. According to the above data, the energy levels of J1 and J2 match well with that of the perovskite material, suggesting that hole transporting from perovskite to J1 or J2 is possible. Compared to J1, the HOMO level of J2 is closer to the valence band of perovskite, which is more favorable for hole transporting from perovskite to J2. The lowest unoccupied molecular orbital (LUMO) energy levels are calculated from the optical band gap (E_g , according to the onset of UV-vis absorption) and the HOMO levels ($E_g = 1240/\lambda_{\text{onset}}$ and $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$). Accordingly, the LUMO levels for J1 and J2 are calculated to be -2.54 eV and -2.41 eV , which are higher than the conduction band of perovskite, and is beneficial to prevent the electron transfer from perovskite to the metal electrode.

Thermal properties of the hole transport materials are measured by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the results are shown in Fig. S10. The decomposition temperature (T_d) for J1 and J2 are 477°C and 310°C , and the glass transition temperature (T_g) are 131°C for J1 and 110°C for J2, respectively. The results indicate that J1 and J2 have good thermal stability and are potential to be used in PSCs.

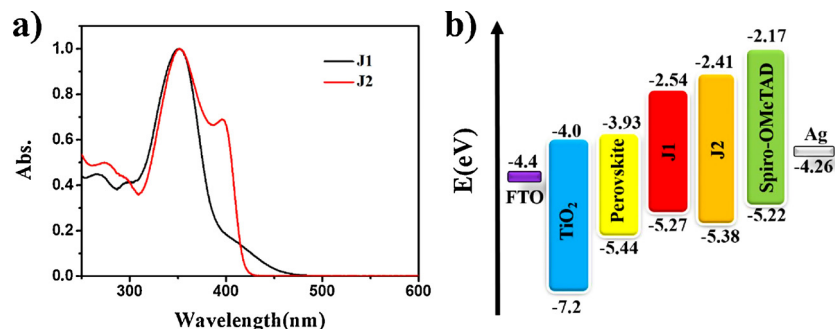


Fig. 1. a) UV-vis absorption of J1 and J2 measured in dichloromethane solution; b) Energy diagram of each layer in PSCs (energy level of Spiro-OMeTAD is shown for comparison).

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