Research progress and design strategy of hole transport materials for perovskite solar cells

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Abstract: In this paper, the hole transport layer in perovskite solar cells is divided into inorganic materials, organic small molecular materials and polymer materials, and their development in recent years is reviewed. After focusing on the factors affecting the transport ability of the hole transport layer, it was found that the thiophene structure and the triphenylamine group can significantly improve the hole transporting ability of the hole transporting material, thereby designing two novel hole transporting materials TTT and TST. According to the simulation calculation of density functional theory, the energy level prediction of TTT and TST shows that the HOMO energy level can reach -5.27eV and -5.33eV respectively, which can achieve better energy level matching.

1. Introduction

The photoelectric conversion efficiency of perovskite solar cells has been significantly improved in recent years, from 3.8% achieved by early Japanese scientists Kojima and others to more than 20% today. The perovskite material was used as a light absorbing layer for dye-sensitized solar cells in the early stage. Although the photoelectric conversion efficiency was improved, the metal halide in the perovskite was easily damaged by the battery electrolyte and its stability was not high. Later Sungkyunkwan University and Lausanne Institute of Technology used 2,2',7,7'-tetra[N,N-bis(4-methoxyphenyl)amino]-9,9'-spirobifluorene as The solid hole transport material is introduced into the perovskite solar cell. This improvement improves the stability of the battery and increases the battery efficiency to 9.7%, which is also beneficial to the packaging of the battery[1]. Subsequently, the introduction of mesoporous materials from the Snaith Group at the University of Oxford adopted the "mesoporous superstructure hybrid solar cell", which increased the efficiency of solid-state sensitized solar cells to 10.9%. Subsequently, they found that reducing the thickness of the mesoporous layer of the hybrid battery can further increase the photoelectric conversion efficiency to 15.4%, and based on this result they also proposed a planar heterojunction perovskite solar cell structure[1, 2]. 2018 Korea Institute of Chemical Technology KRICT Materials Scientist Sang Il Seok's group of nano-precipitation processes prepared perovskite solar cells with photoelectric conversion efficiency of up to 20.1%, an unprecedented rate of increase[1].

2. Perovskite solar cell overview

2.1. Crystal structure

The crystal structure of perovskite is ABX₃, which is usually cubic or octahedral. A is an organic cation which is usually methylamino, CH₃CH₂NH₃⁺, NH₂CH=NH₂⁺, etc. B is often a metal cation Pb²⁺,
Sn$^{2+}$; X is often halogen anion I, Br$^-$. 

![Figure 1. Schematic diagram of crystal structure of organometallic halide perovskite.](image)

2.2. Battery important parameters

$J_{SC}$: short circuit current; $V_{OC}$: open circuit voltage; FF: fill factor; PEC: photoelectric conversion efficiency; IPEC: energy conversion rate; t: tolerance factor.

The open circuit voltage ($V_{OC}$) is the voltage between the two poles when the external circuit is disconnected, which is the maximum output voltage. Hanna et al pointed out that for any photovoltaic material, the open circuit voltage $V_{OC}$ of the solar cell is related to the maximum difference between the electron quasi-Fermi level $E_{Fn}$ and the hole quasi-Fermi level $E_{Fp}$ under the ohmic contact assumption, see Equation 1.1 For perovskite solar cells, $V_{OC}$ is related to the maximum difference between the $E_{Fn}$ of titanium dioxide and the $E_{Fp}$ of the hole transport material (usually its HOMO level). It is not difficult to find from Equation 1.1 that the deeper the HOMO level of the hole transporting material, the theoretically greater open circuit voltage can be obtained. However, the too deep HOMO level will inevitably reduce the driving force of hole transport, which in turn affects all aspects of battery performance. Therefore, the ideal hole transport material HOMO level is close to the HOMO level of the active layer. In addition, the HOMO level is not only the factor affecting the open circuit voltage, but also related to the spectral absorption overlap of the hole transport material and the perovskite active layer, the specific force of the active layer and the perovskite, and the carrier mobility.

$$qV_{oc} = E_{Fn} - E_{Fp}$$  \hspace{1cm} (1.1)

Short circuit current ($I_{SC}$) is the current that passes through the solar cell when the external circuit is short-circuited. The short-circuit current density $J_{SC}$ is a short-circuit current per unit area, which is expressed as Equation 1.2.

$$J_{SC} = \frac{I_{SC}}{S}$$ \hspace{1cm} (1.2)

Fill factor (FF) is a parameter that reflects the performance of solar cells, generally between 0.5 and 0.8, expressed as Equation 1.3. It can be seen from Figure 2 that FF is the ratio of the rectangular area of the diagonal line ($P_{max} = V_{max} \times J_{max}$) and the area of the dotted rectangle ($V_{OC} \times J_{SC}$). Where $V_{max}$ and $J_{max}$ are the voltage and current at which the output power point is maximum.

$$FF = \frac{V_{max} \times J_{max}}{V_{OC} \times J_{SC}} = \frac{P_{max}}{V_{OC} \times J_{SC}}$$ \hspace{1cm} (1.3)
The power conversion efficiency (PCE) reflects the merits of the battery and is expressed as Equation 1.4. Pin is the solar radiation energy per unit area. In the experiment, the standard simulated sunlight AM 1.5 (100 mW/cm²) was used, and Pin = 100 mW/cm². In order to achieve a high PCE, the device should have a high V_{OC}, J_{SC}, FF.

\[ PCE = \frac{V_{OC} \times J_{SC} \times FF}{Pin} \]  

Incident photon-to-electron conversion efficiency (IPCE) indicates the effective utilization of sunlight. The mathematical expression is Equation 1.5. Among them, J_{SC}, \lambda, and Pin correspond to relevant parameters under monochromatic light illumination. Increasing the light absorption capacity and carrier transport capacity of the perovskite active layer contributes to the improvement of IPCE.

\[ IPCE = \frac{1240 \times J_{SC}}{\lambda \times Pin} \]  

It should be noted that energy conversion efficiency and photoelectric conversion efficiency are two different concepts. Energy conversion efficiency refers to the ratio of the energy available from an energy conversion device to its input energy, which refers to the ratio of electrical energy, and the research object is sunlight. The photoelectric conversion efficiency is the ratio of the number Ne of electrons generated in the external circuit per unit time to the number of incident monochromatic photons Np per unit time, and the research object is monochromatic light.

2.3. battery structure

As a light absorbing layer, perovskite material is the basic component that determines the photoelectric conversion efficiency of the battery. The absorption layer can fully absorb photons near the ultraviolet-visible-near infrared region produce electron-hole pairs, which are key steps in determining the subsequent process. The electron transport layer adopts a porous layer composed of titanium dioxide nanocrystals, and the dense layer structure plays a role in electricity, and functions as a hole blocking layer at the same time.

The efficiency of transporting holes in the hole transport layer is an important factor determining the energy conversion rate of the battery. It has the functions of optimizing the interface, adjusting the energy level matching, and has stable thermodynamic optical properties, which is helpful for obtaining higher energy conversion efficiency[3]. At first, the iodide-based liquid electrolyte has the problems of low energy conversion efficiency and poor stability, and the development of solid hole materials overcomes the original deficiencies, improves the energy level matching and hole transport rate, the efficiency and the stability of the battery has also been improved[1]. It can be seen from the calculation expression of PCE that a hole transport material with a lower HOMO level can obtain a larger PCE. However, studies by Portlander et al[4] show that the HOMO level of the hole transport
material is lower than \(-5.3\) eV, which lowers the PCE of battery. Table 1 shows that Jeon et al\[5\] synthesized three hole transporting materials prepared with derivatives of spiro-OMeTAD. The photoelectric properties of the materials were tuned by changing the relative positions of two substituted methoxy groups on four triphenylamine groups in spiroOMeTAD. It can be seen from the table that pm-spiroOMeTAD is the lowest HOMO level among the three derivative materials, and its PCE is also the lowest, so that the HOMO level of the hole transport layer is too low, which is not conducive to the improvement of PCE. In addition to this, it can be found that FF of different materials has a large influence on the PCE of the hole transport layer.

In this paper, the hole transport layer is divided into organic small molecule, polymer and inorganic, respectively, and its development in recent years is reviewed. According to the existing research results, several hole transport materials are designed. Performance and application prospects of these hole transport materials are predicted.

| spiro-OMeTAD | po | pm | pp |
|--------------|----|----|----|
| HOMO/eV      | -5.22 | -5.31 | -5.22 |
| LUMO/eV      | -2.18 | -2.31 | -2.28 |
| J_{sc}/(mA/cm^2) | 21.2 | 21.1 | 20.7 |
| V_{oc}/V     | 1.02 | 1.01 | 1 |
| FF           | 0.776 | 0.652 | 0.711 |
| PCE/%        | 16.7 | 13.9 | 14.9 |

### 3. Hole transport layer

#### 3.1. Inorganic hole transport material

The inorganic hole transporting material has many excellent characteristics such as wide band gap, high hole transport rate, high stability and low cost. Compared with the organic hole transporting material, the inorganic hole transporting material does not contain a carbon-carbon double bond, and the inorganic material is more stable because the carbon-carbon double bond is easily decomposed under light conditions. In addition, the inorganic material is not easily corroded by the influence of the electrolyte, the working process is resistant to high temperatures, and the processing performance in the production process is good.

As a kind of P-type semiconductor material with good light transmission performance and wide band gap (3.1eV), CuI can be matched with HOMO of various active materials, and its valence band energy level is about -5.1eV. Since CuI is easily degraded under illumination and reacts with oxygen to form CuO, the stability of CuI is not good in inorganic materials, but its stability is still stronger than many organic hole transport materials. Christians et al\[6\] used CuI as a hole transporting material in a CH$_3$NH$_3$PbI$_3$ perovskite battery for the first time, and up to 6% of PCE was obtained. The CuI film prepared by them has large resistance, but it is found by impedance spectroscopy that the open circuit voltage and filling factor of the battery may be low due to the high CuI carrier recombination rate. The current hysteresis of the perovskite battery is serious, so the improvement of PCE is severely limited.

CuSCN is also a commonly used wide bandgap p-type semiconductor material\[7\], with conduction band and valence band energy levels of -1.5 eV and -5.3 eV, respectively. Because it can effectively block electrons during hole conduction, it does not degrade like CuI, and its stability is better than the former. Recently, Professor Grätzel etc\[8\], dissolved 35mg of CuSCN in 1ml of 98% diethyl sulfide, stirred at room temperature for 30min, and deposited CuSCN film by adding a perovskite film at a speed of 5000r/min within 2-3s. PCE reached 20.3% and has good stability.

#### 3.2. Organic small molecule hole transport material

Organic small molecules have good fluidity, good filling, poor stability and poor film formation.
Organic small molecule hole transport materials are usually designed into different molecular shapes according to requirements, and the spatial structure is used to increase the hole mobility. The most widely used small organic molecule is 2,2',7,7'-tetra[N,N-bis(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) and derivatives of triphenylamine.

3.2.1. Organic small molecule hole transporting material containing triphenylamine spiral structure

2,2',7,7'-tetra[N,N-bis(4-methoxyphenyl)amino]-9,9'-spirobifluorene in a perovskite cell (Spiro-OMeTAD Figure 3 (1)) is currently the most widely used hole transport material. This is because small molecules containing triphenylamines are suitable for their hole transport materials with high conductivity requirements due to their special structure. Firstly, the benzene ring-connected part of the molecular structure forms a relatively stable ππ conjugated structure, which is beneficial to the migration of carriers. Secondly, the unpaired electrons with unbonded N atoms participate in the electron transport and increase the current carrying current, which also forms a p-π-conjugated structure with the surrounding benzene ring. In addition, the methoxy group in the molecular structure is in close contact with the perovskite layer, which facilitates the transport of holes. In addition, it should be noted that such small molecular materials all adopt a helical structure, which can destroy the regularity of the molecule, and small molecules with poor regularity or symmetry are not easy to crystallize, because the crystal structure is not conducive to the transmission of electrons, thus the spiral structure ensures the rate of carrier transport within the material.

Eperon[9] et al, first reported the use of Spiro-OMeTAD, which achieved 11.4% PCE using a perovskite solar cell with FTO/TiO_2/CH_3NH_3PbI_3/Spiro-OMeTAD/Au. Saliba[10] et al, using CSX (MA_0.17FA_0.83)(100-x)Pb(I_0.83-Br_0.17) as the perovskite layer, and Spiro-OMeTAD as the hole transport layer to make the PCE of the perovskite solar cell reach 21.17%, and the introduction of CS increased the stability of the battery and prevented the generation of yellow impurities. Even if it was placed in the air for 250h, it could maintain 18% of PCE, which made the development of perovskite solar cells a new one Stage. In addition to the direct application of Spiro-OMeTAD, it is also possible to modify the Spiro-OMeTAD to synthesize new derivatives, so that the HOMO of the hole transport layer and the perovskite layer can achieve better energy level matching, optimize the conductivity of the battery, and improve PCE. Wang[11] et al, added a structure of aniline based on the structure of Spiro-OMeTAD, and realized the hole transport material SAF-OMe with higher hole transport rate (Figure 3 (2)). The PCE of perovskite solar cell is 12.39%. After doping and modification of SAF-OMe, the PCE of the battery can reach 16.73%, and the carrier transport rate and stability of the battery are also improved after doping. However, chemical dopants also promote the migration of ions in the electric field, which not only reduces the efficiency of the device, but also increases the manufacturing cost of the device. Bi[12] et al prepared a helical structure of X59 by a two-step synthesis method (Figure 3 (3)), and a perovskite solar cell PCE prepared by using X59 as a hole transport layer was 19.8%. At the same time, in the dark and dry environment, X59 as the material of HTM exhibits lower hysteresis, better plasticity and stability. The performance of X59 reflects the application of simplified spiral structure small molecules as HTM in PSCs, and further promotes the commercialization of PSCs. Xu[13] et al, also designed X60 (Figure 3 (4)) based on Spiro-OMeTAD through a two-step synthesis method. The battery with X60 as a hole transporting material was irradiated with light intensity of 100mWcm-2AM1.5G, Its PCE reached 19.84%. The synthesis method of X60 is relatively simple, and the yield is as high as 70%, so it is promising for mass production in industrialization.
3.2.2. Star-structured organic small molecule hole transport material containing triphenylamine structure

The star-shaped organic small molecule hole transporting material containing a triphenylamine structure is an organic small molecular material formed by bridging a triphenylamine-containing derivative by a double bond, a benzene, a thiophene or the like. The HOMO level of this type of small molecule material can also be matched with the perovskite material in a good energy level, and can maintain excellent stability during battery use, and some of the star-shaped small molecule hole transport materials containing triphenylamine can significantly enhance the PCE of perovskite solar cells. Compared with the organic small molecule hole transporting material containing triphenylamine spiral structure discussed above, the star organic small molecule hole transporting material containing triphenylamine structure also contains a large amount of ππ conjugated structure, effectively maintaining the stable structure of the battery. It also facilitates the migration of carriers in the material. Similarly, the methoxy group can be in close contact with the perovskite layer, and the presence of unbonded lone pairs of electrons on the N is beneficial to the transport of carriers. The main difference between such materials and the former is that the organic small molecule hole transporting material of the star structure does not have a helical structure, but a planar structure centered on the N atom or other bridging structure, such as OMeTPA-FA, FA-MeOPh et al, the small molecules have better regularity and are favorable for crystallization. This structural feature may limit the increase of carrier transport rate.

Do et al[14], reported the Triazine-th-ometpa (Figure 4 (1)), which was prepared by thiophene-bridge with 1,3,5-triazine as nucleus. The long chain alkoxy group of the polymer increases the solubility of the compound in chlorobenzene, thereby overcoming the deficiency of the small molecule compound and forming a small molecule film, which facilitates the preparation of the hole transport material spin coating onto the device. Thus, a higher carrier transport rate was achieved, and the PCE of the perovskite battery prepared as the hole transport layer was 12.51%. In addition, Triazine-Th-OMeTPA showed good stability within 250h, so it can be seen that HTM with better
carrier transport rate can be obtained by careful design of molecules. Nishimura et al.[15] synthesized Azulene 1, Azulene 2, Azulene 3, and biphenyl 4 using oxygen atom bridged triphenylamine. In particular, when Azulene 1 (Figure 4 (2)) was used as the hole transport layer, the PCE reached 16.5%. As can be seen from the above research progress, a slight change in the structure of the hole transport layer can cause a significant change in the performance of the battery. Rakstys et al.[16] synthesized KR131 (Figure 4 (3)) using a trimeric fluorene and a methoxy group, and adding it as a hole transport layer to the battery can achieve 17.7% of PCE, and this compound also exhibits a perovskite material. Good surface interaction, its HOMO level and LUMO level are in good agreement with perovskite materials, and can guarantee high transmission performance at low cost. Molinaontoria et al.[17] cross-linked different triphenylamine substrates with benzothiophene (BTT) as a core to synthesize three hole transporting materials BTT-1, BTT-2, and BTT-3 (Figure 4 (4)). The PCE of perovskite solar cells prepared by using them as hole transport layers reached 16.6%, 17.3%, and 18.2%, respectively. Among these three, since the HOMO level of BTT-3 achieves better energy level matching with the active layer, the PCE prepared by BTT-3 as HTM has the highest PCE among the three. Huang et al.[18] synthesized the compound Trux-OMeTAD (Figure 4 (5)) using three symmetric trimerizations containing an arylamine end and an ethyl side chain. The compound has good stability and high hole transport with the rate of 1.0x10^-3 cm^2 V^-1 S^-1, the hole transporting material PCE prepared by it reached 18.6%.

Figure 4. Star-structured organic small molecule hole transport material containing triphenylamine structure.

3.2.3. linear structure of small molecule hole transporting material containing triphenylamine

The linear small molecule hole transporting material is usually obtained by using a heterocyclic bridged triphenylamine such as thiophene or benzene, and the hole transporting ability of the compound can be improved by modifying the heterocyclic conjugated bridge or modifying the
triphenylamine substituted group. Higher PCE. Hua et al\[19\] designed long-chain organic small molecules AH1 and AH2, the FF of them can reach 0.76 and 0.78 respectively which is significantly higher than 0.69, the FF of spiro-OMeTAD. This linear small molecule is used as HTM for PSC. A higher PCE was achieved, with the PCE of AH1 (Figure 5 (1)) reaching 11.98%. Both PCE and FF are close to the parameters corresponding to the PSC prepared with Spiro-OMeTAD as HTM under the same conditions. In addition, the AH1 preparation process is more environmentally friendly, and the main component of AH1 is silver-based oxide, which can be synthesized and purified without using column chromatography, which simplifies the synthesis process. This result is based on the development of metal-organic complexes. Reduce costs and promote the application of PSC. Zhang et al\[20\] designed and synthesized three non-helical triphenylamine-based organic small molecules by adjusting the position and length of the alkyl chain perpendicular to the molecular framework. X21 (Figure 5 (2)) has the best energy level arrangement. This material has excellent carrier transport properties because it can prepare a film in which the constituents are arranged in a regular order. The PSC prepared by X21 for HTM can achieve 17.33% PCE. This work also shows that optimizing the alkyl side chains in organic molecules can significantly improve the planarity, electron delocalization and carrier transport properties of the structure, which are the key to the photovoltaic performance of hybrid perovskite solar cells. Zhao et al\[21\] synthesized a linear hygroscopic molecule, Z1011 (Figure 5 (3)), which has good energy level matching with perovskite and has strong hole transporting ability. Therefore, the HTM for batteries also achieved 16.3% PCE.

![Figure 5. linear structure of small molecule hole transporting material containing triphenylamine.](image)

3.2.4. Organic small molecule hole transporting material containing thiophene structure
It can be seen from the foregoing discussion that the thiophene structure is generally used for bridging other small molecules which have a conjugated structure such as triphenylamine. Different electron donors and electron withdrawing groups are bridged to obtain Donor-Acceptor type small molecule hole transport materials which can effectively extract the holes in the perovskite to the anode and increase the hole transport rate, and the application has broad prospects in the application field of the small molecule undoped HTM material.

Liu et al\[22\] found that the small molecules of the D-A structure have a good packing structure and thus have good carrier transport properties. Therefore, they first synthesized the A-D-A structured small molecule compound M1 (Figure 6 (1)) with benzodithiophene (BDT) as a donor and
phenyloxazolidone (POZ) as a receptor. It can be seen from the structural formula that M1 has a strong conjugation property, and its hole transport rate can thus achieve a hole transport rate of $2.71 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ to Spiro-OMeTAD of $1.32 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{S}^{-1}$ Doubled. A PSC with M1 as HTM can achieve 13.2% PCE. On this basis, the team also concluded that the key to improving undoped HTM is the energy level regulation of HTM. The relationship between HTM structure and properties is further explored at the molecular level by selecting different substituents. Liu et al. also synthesized the thiophene-containing small molecule material DRDTS-TBDT (Figure 6 (2)) and DORDTS-TBDT. The former uses 4,8-disubstituted benzodithiophene derivative (TBDT) as a receptor, ethylrodanine (DTER) and dithienothiazole (DTS) as donors; the latter consists of TBDT as a receptor. Diterpenoid derivatives (DFBT) and DTS are donor synthesis. Due to the HOMO energy level of DERDTS-TBDT is -0.509eV, the LUMO energy level of -2.92eV can achieve better energy level matching with perovskite, plus its higher hole transport rate ($1.0 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{S}^{-1}$), the PSC prepared with DRDTS-TBDT as HTM can reach 16.2% under the condition of illumination AM4.5G (100mV/cm²), and the DORDTS-TBDT can only reach 6.2% under the same conditions, otherwise the material also reflects the improvement of the stability of silicon-containing compounds.

Figure 6. Organic small molecule hole transporting material containing thiophene structure.

3.3. polymer hole transport material

The polymer hole transporting material is different from the small molecule discussed above. The molecular weight of the polymer is larger and the chain structure is more complicated, so the aggregated state exhibits different properties from the small molecule. Because of the higher molecular weight of these materials, the interaction between the molecular chains is more closely, so the polymer material is easier to form a film than the small molecule material, which facilitates the spin coating of the polymer onto the device. It is conducive to the improvement of carrier transport capacity, while the excessive molecular weight also brings the characteristics that the material is not easily dissolved. According to the current research progress, the polymer hole transporting material is mainly divided into two types: a thiophene-containing structure and a triphenylamine-containing structure. The former increases the conjugation of the hole transporting material by introducing a thiophene structure and increases the hole transport rate. Among them, poly 3,4 ethylenedioxythiophene: polystyrene sulfuric acid (PEDOT:PSS) and poly(3-hexylthiophene) (P3HT) are two kinds of polymers containing thiophene structure commonly used in perovskite solar cells hole transport material. Reasonable doping of these two batteries can improve the PCE of the battery, but the doped material is more likely to absorb water, making the electrode susceptible to corrosion, and the stability and service life of the battery are also reduced.

PEDOT: PSS (Figure 7 (1)) is a P-type organic semiconductor. As a hole transporting material, a planar heterojunction cell is often prepared by interfacing with an electron transport layer prepared by
PCBM. Liu et al[24] doped TiO$_2$/MoO$_3$ into PEDOT:PSS and used it as a hole transport layer to prepare a perovskite solar energy structure of ITO/PEDOT:PSS:TiO$_2$/MoO$_3$/CH$_3$NH$_3$PbI$_3$.Cl/C$_60$/Bphen/Ag. The battery, through testing different doping levels, found that the PCE reached 13.6% when the doping degree was 20%. The study also found that the battery can still maintain the original 92% in the dark condition at 400h, meaning the stability of battery is also higher, probably because the doping of TiO$_2$/MoO$_3$ increases the grain size and increases the stability of the battery.

P3HT (Figure 7 (2)) is a P-type semiconductor with good performance. It is used in the preparation of HTM materials for PSCs due to its efficient hole transport efficiency, and is commonly used as a material for supplying electrons in batteries. Casaluci et al[25] filled single-walled carbon nanotubes (SWCNTs) and graphene sheets (GNPs) as nanofillers into P3HT as a hole transport layer. The doping of carbon nanotubes and graphene will introduce a large amount of π-π conjugated structure to enhance the transport rate of holes, and the scattering properties of graphene can enhance the absorption of long-band light by materials. By changing the density of the fillers and testing them separately, the authors found that SWCNT-PhOMe/P3HT has a density of 2%, and GNPs-PhOMe/P3HT has a high photoelectric conversion efficiency when the density is 4%. The PCE of these batteries after 3240h is shown in Table 2.

| HTM              | Average PCE(%) | Number of active cells |
|------------------|----------------|------------------------|
| P3HT             | Null           | Null                   |
| 1%GNPs-PhOMe/P3HT| 4.7            | 2                      |
| 2%GNPs-PhOMe/P3HT| 3.9            | 4                      |
| 4%GNPs-PhOMe/P3HT| 3.4            | 3                      |
| 1%SWCNT-PhOMe/P3HT| 5.7           | 4                      |
| 2%SWCNT-PhOMe/P3HT| 8.7           | 4                      |
| 3%SWCNT-PhOMe/P3HT| 3.6            | 4                      |

3.3.2. Polymer hole transport layer material containing aniline structure

The polymer hole transporting material containing an aniline structure is a polymer composed of aniline, triphenylamine, hydrazine or the like as a structural unit. This column of materials has a high hole transport efficiency and a good film formation property for carrier migration, and thus has attracted attention.

PTAA is a aniline-containing polymer (Figure 7 (3)) with a HOMO energy level of -5.14 eV, which can achieve better energy level matching with perovskite materials. Jeon et al[26] used PTAA as a hole transporting material to prepare a cell PCE with mesoporous TiO2 as an electron transport layer to reach 20.3%. Wang et al[27] prepared perovskite solar cells with polymer PDTSTTz (Figure 7 (4)) and PDTSTTz-4 (Figure 7 (5)) as hole materials, which were based on thiazole thiazole (TTz) and dithiazole thiazole (DTS) as basic unit, and the two form a rigid planar molecular skeleton due to the conjugation effect, so that the two polymers have a high hole transport rate of 3.6x10$^{-3}$cm$^2$V$^{-1}$S$^{-1}$ and 7.8x10$^{-2}$cm$^2$V$^{-1}$S$^{-1}$ respectively. Their HOMO levels are -5.1eV and -5.0eV, which achieve good energy level matching with perovskites, achieving 14.4% and 15.8% PCE.
4. Design section

4.1. Design Strategy
Factors affecting the performance of the hole transporting material are various, such as energy level matching, spectral absorption, carrier transport capability, open circuit voltage, fill factor, and the like. In molecular design, it is impossible to take into account each of the influencing factors, but should focus on the aspects that have the greatest impact on performance, while taking into account the feasibility of the design strategy. Therefore, the molecular design of this subject focuses on the energy level regulation and selection of appropriate functional groups and mother core, and the related calculations are carried out by means of Gauss 09 software.

4.1.1. HOMO level matches with perovskite
As shown in Figure 8, hole transport has sufficient driving force only when the HOMO level of HTM is higher than that of the perovskite active layer. Further studies have shown that the appropriate HOMO for HTM is above -5.3 eV\(^2\). If this threshold is exceeded, battery efficiency will be greatly lost. Therefore, a suitable HOMO level is the first factor to consider when designing a material. The most straightforward way to adjust the HOMO level is to change the access to the electron-donating group and the electron-withdrawing group. If the molecular HOMO level is too deep, the donor electron-donating group such as thiophene, EDOT, etc can be selected to raise the HOMO level; if the HOMO level is too shallow, an electron-withdrawing group such as a cyano group can be selected. Therefore, based on the simulation of density function theory, using Gauss 09 software, B3lyp/6-31G (d, p) unit can predict the energy level of the compound, which has an important guiding role in the design of new molecules. Note that there is a certain gap between the calculated value and the actual value. Therefore, the ideal range of the calculated value is first calculated based on the actual value. According to the literature, the actual HOMO value of Spiro (-5.22 eV\(^3\)) is at an appropriate level, while the actual HOMO value of T103 (-5.33 eV\(^3\)) is near the threshold. Therefore, the energy levels of the reported materials Spiro and T103 were first calculated and the results are listed in Table

![Figure 7. polymer hole transport material.](image-url)
4.1, thus determining the ideal range of HOMO energy level calculations: around -4.36 eV, and not lower than -4.51 eV.

Figure 8. Schematic diagram of energy level matching of hole transport materials.

4.1.2. **Functional groups form a special force with the perovskite active layer**

If the functional group in the molecule forms a special force with the active layer, it has a significant effect on the improvement of carrier transport performance. For example, a methoxy-substituted triphenylamine is a functional group commonly possessed by a hole transporting material, and has three main advantages: (1) a methoxy group in the functional group forms a strong interaction with a perovskite active layer. And mainly concentrated on the (001) and (110) interfaces[30] of the active layer to form channels for hole transport; (2) the nitrogen atom in the triphenylamine has excellent hole transporting ability[31]; (3) triphenylamine as a group that supply electron can conveniently adjust the HOMO level of the HTM to an appropriate level. Therefore, the introduction of triphenylamine groups is an important strategy for designing high performance HTM. However, the triphenylamine group also has its drawbacks, in which the N atom is hybridized with Sp3 and the molecular spacing is large, which results in poor conductivity[32]. In order to compensate for this disadvantage, a hole transporting material containing a triphenylamine group tends to be p-doped, such as adding trifluoromethane sulfonic imide lithium[33]. However, such dopants are prone to dehydration, shorten battery life, and increase battery cost. It can be seen that the introduction of functional groups also needs to consider a variety of factors, and only when the functional groups work synergistically and complement each other, the material properties can be optimized. In 2016, Michael et al[34] concluded that the methoxy group in the triphenylamine is attracted to the methylamino group of the active layer and mutually repelles with the iodide ion[35]; the thiophene group and the iodide ion can form a special force[36], as shown in Fig 4.2. Based on this, Michael improved the mainstream hole transport material Spiro, replacing the two benzene rings in the spirobifluorene with thiophene. The new molecule FDT forms a dual channel with the active layer, which greatly promotes hole transport and will be synthesized. The cost has fallen to 20% of Spiro, an improvement that complements the molecular design strategy and draws a blueprint for the highly promising high-efficiency, low-cost hole transport materials.
4.1.3. **mother core with fluffy structure**
Observing the structure of Spiro, it is not difficult to find that the mother snail has a twisted and fluffy structure, as shown in Figure 10 (a), which is beneficial to improve the way of molecular aggregation to reduce crystallization and promote film formation. Similarly, triptycene has a similar structure and is symmetrically stretched in three directions, facilitating lateral and longitudinal transport of holes, as shown in Figure 10 (b).

![Molecular structure of FDT and its interaction with the active layer of perovskite.](image)

4.2. **Molecular design**

4.2.1. **Introduction of benzodithiophene units**
The Benzodithiophene (BDT) unit has a large conjugate structure, good flatness, easy formation of π-π stacking, and excellent carrier mobility and battery performance when used in polymer solar cells[37]. The BDT unit was also used in the active layer of perovskite. Zheng et al[37] designed a new small molecule material of DR3TBDTT based on BDT as a hole transport layer preparation device, and harvested PCE 8.8% without doping.

Based on this, the BDT unit is first considered to be attached to triptycene, and a propylene dicyano group is formed at the tail to form a molecule T1, as shown in Figure 11. Propane cyanide forms a Donor-Acceptor structure as an electron-withdrawing group and an electron-donating BDT unit, and the D-A structure can adjust the bandwidth by push-pull electron effects. Based on the density function theory, the HOMO and LUMO energy levels of T1 were calculated. The results are shown in Table 3. Obviously, the calculated values of the HOMO levels of T1 and Spiro are far apart, meaning that the actual HOMO level of T1 will far exceed the threshold of -0.53 eV, so T1 is not an ideal molecule. In order to investigate the reason why the HOMO level is too deep, the electron-withdrawing cyano...
group and the bridging group thiophene are sequentially removed to obtain the molecule T2, and the energy levels are calculated. The results are shown in Table 3. Comparing the HOMO levels of T1 and T2, it is not difficult to conclude that the electron-withdrawing cyano group significantly lowers the HOMO level, but when this group is removed, the HOMO level of the T2 molecule is about 0.7 eV deeper than Spiro. This indicates that the BDT unit itself will lower the HOMO level, and there is no advantage in the molecular design with triptycene as the core.

![T1, T2 molecular structure](image)

Figure 11. T1, T2 molecular structure.

4.2.2. Introduction of dendritic trithiophene

Studies have shown that thiophene has obvious hole transport advantages, and thiophene as an electron donating unit helps to raise the HOMO level. Based on this, the dendritic trithiophene was attached to the triptycene core, the molecular T3 was designed, and its energy level was calculated, as shown in Figure 12. The results are shown in Table 3. Interestingly, the HOMO level of T3 did not fall within the proper range as expected, but it was 0.8 eV deeper than Spiro. The specific reasons need further analysis. It can be seen that T3 is not dominant as a hole transporting material.
4.2.3. Introduction of triphenylamine groups

From the design strategy of the previous section, it can be seen that the triphenylamine group has its unique advantages. Based on this, two new molecules are designed and named as TTT and TST respectively, as shown in Figure 13. Thiophene, 3,4-ethylenedioxythiophene and selenophene all have excellent hole transport properties. They act as bridging functional groups, and connect triptycene and triphenylamine to expand a large conjugated structure.
Subsequently, we performed energy level simulation calculations on TTT and TST, and the results are listed in Table 3. The HOMO level of TTT (-4.41 eV) is close to Spiro (-4.36 eV) and significantly lower than T103 (-4.51 eV), which indicates that TTT may have stronger hole driving force.

Table 3. Molecular Simulation Calculation.

| Hole transport material | HOMO (eV) | LUMO (eV) |
|-------------------------|----------|-----------|
| Spiro                   | -4.36    | -0.80     |
| T103                    | -4.51    | -1.22     |
| T1                      | -5.44    | -3.20     |
| T2                      | -5.09    | -2.05     |
| T3                      | -5.17    | -1.56     |
| TTT                     | -4.41    | -1.14     |
| TST                     | -4.51    | -1.28     |

4.3. Design Strategy Application Example

The molecular TTT designed based on molecular simulation calculations has a calculated HOMO level of -4.41 eV. If it can be successfully prepared, the actual value is about -5.27 eV. By comparing the HOMO energy levels, it was found that the molecular M1 (Fig. 4(1)) prepared by Liu et al.[24] has a HOMO energy level of -5.29 eV, which is very close to the HOMO energy level of TTT. Therefore, the properties of M1 molecules can be designed according to TTT analogy. The M1 molecule is synthesized by BDT and POZ, and the molecular structure is highly conjugated, which provides favorable conditions for carrier transport. Similarly, the TTT molecule utilizes a thiophene structure to link the triadene and the N-containing compound with a conjugated structure and N. The role of atomic lone pairs of electrons also creates favorable conditions for the transport of carriers. It can be concluded from the experiment of Liu et al that the hole transport rate of the M1 molecule can thus be achieved by 2.71×10⁻⁴ cm²V⁻¹S⁻¹ higher than the hole transport rate of 1.32×10⁻⁴ cm²V⁻¹S⁻¹ of Spiro-OMeTAD, the PSC with M1 as HTM can achieve 13.2% of PCE, so the preparation and application of TTT has certain prospects. Krishnamoorthy et al.[38] synthesized KTM3 (Figure14. (7)), The key step for its synthesis is the Suzuki coupling reaction using [Pd(PPh3)4] between boronic acid and tetrabromo-3,30 bithiophene. HOMO energy of this polymer shows -5.29 eV. KTM3 has a swivel 3,30-bithiophene as the central unit, which exhibits a higher open circuit voltage of 0.99 V than spiro-OMeTAD, while based on the special structure of swivel-cruiciform thiophenes, KTM3 also has strong stability, and the HTM solid phase recombination rate prepared by it is low. KTM3 has a FF of 70.9% and a PCE of 7.3%, but PCE can reach 11.0% when used with FK269. The good application prospect of KTM3 can indirectly reflect the preparation and application prospect of TTT.
Figure 14. application examples

The calculated value of the HOMO level of TST is the same as that of T103, and the actual value of the HOMO level of the TST molecule should be -5.33 eV, and the hole transporting ability of the two can also be analogized. Krishna et al[29] prepared a yellow solid T103 (Figure14. (8)) with good thermal stability high level of Tg and good solubility with triadene as the precursor. It has a very similar molecular structure to TST. This type of molecule is distorted in space, and the triadene bridges large volume side groups, so the regularity of the molecule is poor and the crystallinity is low. This amorphous state can exhibit a high Tg, so when it is in working condition, the thermal stability is very good. In addition, its long conjugate structure and large steric hindrance provide a good structural basis for the stability of the material, thereby promoting the transport of carriers between molecules. The FF of the molecule is 61.9%, and as a HTM, it can show 12.38% of PCE, which is very close to the PCE 12.87% of spiro-OMeTAD. Therefore, it can reflect the similar properties of TST designed in this paper, and has good design and application prospects.

5. Conclusion

Based on the excellent hole transport properties of thiophene structure and triphenylamine group, thiophene and selenophene bridged triptycene and triphenylamine can extend a large conjugated structure respectively, thereby designing novel hole transport materials TTT and TST. The density functional theory simulation calculation predicts that the HOMO energy levels are -5.27eV and -5.33eV respectively, which can achieve better energy level matching with the perovskite active layer, and have a good application prospect.

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