Readily synthesized dopant-free hole transport materials with phenol core for stabilized mixed perovskite solar cells

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HIGHLIGHTS

- A PCE of 16.97% was obtained with a dopant-free HTM in PVSC.
- A very low hole mobility and electron blocking will also ensure high PCE.
- Phenol and its derivatives show great potential as building block for HTMs.
- Device stability is enhanced with extremely cheap HTMs.

GRAPHICAL ABSTRACT
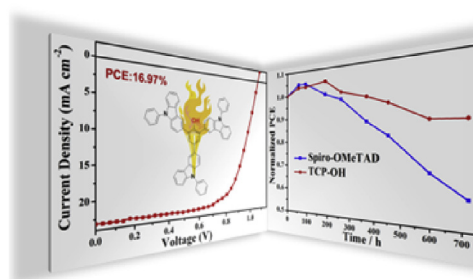
ABSTRACT

With the dramatic development of the power conversion efficiency (PCE) of perovskite solar cells (PVSCs), device lifetime has become one of the extensive research interests and concerns. To enhance the device durability, developing high performance dopant-free hole transport materials (HTMs) is a promising strategy. Herein, two new *C3*-symmetric HTMs with phenol core, **TCP-OH** and **TCP-OC$_8$** are readily prepared and show ultra-wide energy band-gap and excellent film-formation property. PCEs of 16.97% and 15.28% are achieved with pristine **TCP-OH** and **TCP-OC$_8$** film as HTMs, respectively, even though their hole mobilities are as low as 10^{-6} cm^2 V^{-1} s^{-1}. Phenol acts as hole trap in traditional concept, however, **TCP-OH** shows higher hole mobility than that of **TCP-OC$_8$**. Moreover, **TCP-OH** shows higher glass transition temperature and better matching band alignment than those of **TCP-OC$_8$**. Phenol shows great potential as building block for HTMs as it is beneficial to enhance hole mobility of HTMs. Moreover, our study demonstrates an interesting viewpoint to design HTMs with the balance of hole mobility and electron blocking effect.

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1. Introduction

Perovskite solar cells (PVSCs) has captured tremendous attention because of the special optical and electrical properties of perovskite material [1–3]. As a great light harvester, perovskite shows a wide light absorption over the whole visible solar emission spectrum [2h]. Moreover, perovskite materials also behave as efficient semiconductors with high charge mobility and a long carrier diffusion length. For example, methylammonium lead iodide, $CH_3NH_3PbI_3$ exhibits high carrier mobilities ranging from 7.5 cm^2 V^{-1} s^{-1} for electrons to 12.5 cm^2 V^{-1} s^{-1} - 66 cm^2 V^{-1} s^{-1} for holes, and the carrier diffusion length ranged between 100 nm

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and 1000 nm [2a]. Since the original research by Miyasaka in 2009 [1a], power conversion efficiency (PCE) of the record PVSCs has been boosted from 3.8% to over 20% in the last 7 years [1a,3f], making them as good candidates for the next generation solar cells. Considering the future practical application of PVSCs, low fabrication cost, high PCE and lifetime are critically important aspects that need to be considered.

Among the reported PVSC device structures, mesoporous PVSCs showed extremely high performance [2b]. Mesoporous PVSCs are composed of mesoporous layer of TiO₂, perovskite material and hole transport materials (HTMs). To achieve high power conversion efficiency and device stability of PVSCs, HTMs should be further developed [2,3]. HTMs play a central role to transport and extract holes at the anode interface [3–5]. The highest occupied molecular orbital (HOMO) energy level of HTMs must be well matched with the perovskite layer, meanwhile, the hole mobility in the HTM should be reasonably high, which are favorable to achieve high PCE. In general, chemical doping is indispensable to improve the hole mobility of HTMs due to the low hole mobility in their pristine films. As the most successful HTMs, 2,2′,7,7′-tetrakis(*N,N*-dis(*p*-methoxy-phenyl)amine)-9,9′-spirobifluorene (Spiro-OMeTAD) and polytriarylamine (PTAA) showed extremely high PCEs in PVSCs, after chemical doping with lithium bis(trifluoromethane-sulfonyl) imide (LiTFSI) and tert-butylpyridine (TBP) [4]. However, in spite of the dramatical enhancement of the PCE with doped HTMs, chemical dopants suffered a series of problems including fabrication cost and device stability [4b].

Recently, developing dopant-free HTM with high hole mobility has attracted wide interest of many researchers [5]. Nevertheless, progress on HTM is not smooth and the PCEs in PVSC devices are sparse over 16% based on dopant-free HTM. Meanwhile, most of them show a relatively high preparation cost owing to their complex synthesis and purification steps considering their large scale industrial production. Grätzel and co-workers designed a novel dopant-free HTM with an impressive PCE up to 16.3% based on a butterfly-shaped structure following a hole mobility of 8.49×10^{-4} cm² V⁻¹ s⁻¹ [5b]. Yang et al. reported a donor-acceptor (D-A) conjugation dopant-free HTM with a hole mobility of 1.0×10^{-4} cm² V⁻¹ s⁻¹ and it exhibited a PCE of 16.2% in PVSC [5c]. Park et al. presented a polymeric dopant free HTM with a PCE up to 17.3% and its hole mobility is 3.09×10^{-3} cm² V⁻¹ s⁻¹ [5d]. Chen et al. reported a remarkable PCE of 18.6% in an inverted-type PVSC based on a dopant-free HTM, which exhibited a hole mobility of 3.6×10^{-3} cm² V⁻¹ s⁻¹ [5e].

Despite these HTMs show an efficient performance in PVSCs, some of these HTMs show relatively weak electron blocking property due to the narrow energy band gap (E_g) [5c,5d,5h]. The relatively weak electron blocking capability might increase the chance of charge recombination. Hence, weak electron blocking capability of these HTMs are remedied by their high hole mobility. Therefore, the balance between hole mobility and band alignment is an important factor to be considered for the design of highly efficient dopant-free HTMs for PVSCs.

Will a low hole mobility HTM with excellent band alignment get high performance in perovskite cells? To our best knowledge, there was rare report based on this hypothesis, to date.

In this work, two novel phenol derivatives with the wide energy band-gap (**TCP-OH and TCP-OC₈**), have been readily synthesized. In spite of their hole mobility are as low as 10^{-6} cm² V⁻¹ s⁻¹, the best PCEs of these two HTMs, which are employed in PVSC by dopant-free process, are 16.97% and 15.28%, respectively. These two HTMs were carefully characterized to reveal their physical/optoelectronic properties and performance in PVSCs. The mechanism was investigated and discussed in detail.

2. Results and discussion

2.1. Structural design, preparation and characterization of TCP-OH and TCP-OC₈

#### 2.1.1. Structural design of TCP-OH and TCP-OC₈

The structural design of **TCP-OH and TCP-OC₈** was motivated by the traditional HTM in organic light-emitting diodes. 4,4′,4″-Tri(*N*-carbazolyl)-triphenylamine (TCTA) is a traditional HTM and has a wide energy band-gap (3.2 eV) with a hole mobility of 2×10^{-5} cm² V⁻¹ s⁻¹ [6]. However, the HOMO energy level of TCTA (−5.9 eV) is too deep to match the valence band of perovskite materials. To enhance the HOMO energy level of TCTA, phenol core is chosen to replace the nitrogen atom in the triphenylamine structure of TCTA, which is inspired by the recent work and concept on phenol-based organic electronic (PBOE) in our group [7d]. Our recent works show that non-conjugated phenol-based polymers and even weakly conjugated lignin were potential p-type transport materials [7].

2.1.2. Preparation of TCP-OH and TCP-OC₈

Two HTMs named 2,4,6-tris(9-phenyl-9H-carbazol-3-yl)phenol (**TCP-OH**) and 3,3′,3″-(2-(octyloxy)-benzene-1,3,5-triyl)tris(9-phenyl-9H-carbazole) (**TCP-OC₈**) were prepared (Scheme 1). The star-shaped and twisted structure is constructed by introducing 9-phenyl-9H-carbazole (CP) into the *o*-/*p*- positions of phenol via one-step Suzuki-Miyaura coupling reaction (Scheme 1). (9-phenyl-9H-carbazol-3-yl)boronic acid (PCBA) was purchased from Soo-chiral Chemical Science &Technology Co.,Ltd, China, and the price of this reagent is even lower than 1.5 $/g. 1,3,5-tribromo-2-(octyloxy)benzene was synthesized according to a previously reported procedure [8]. All the other materials were purchased from commercial sources and used as received. With the loading of excessive PCBA, the yields of **TCP-OH** and **TCP-OC₈** were as high as 87% and 93%, respectively, after the purification of silicon gel column chromatography. The simple synthesis of **TCP-OH** and **TCP-OC₈** based on commercially available and cheap starting materials, make these two HTMs very promising for their potential industrial production in the future. A detailed cost accounting was presented in supporting information (Fig. S17 and Tables S3–S5 in SI). **TCP-OH** and **TCP-OC₈** showed obvious advantages over the other high performance dopant-free HTMs applied in PVSCs.

2.1.3. Characterization of TCP-OH and TCP-OC₈

The chemical structures of HTMs were characterized by ¹H/¹³C NMR spectroscopy and high-resolution mass spectrometry (Figs. S1-S6). The two materials have good solubility in common organic solvents, including chloroform, toluene, chlorobenzene (>300 mg/mL), DMF and DMSO. It is noteworthy that **TCP-OH**
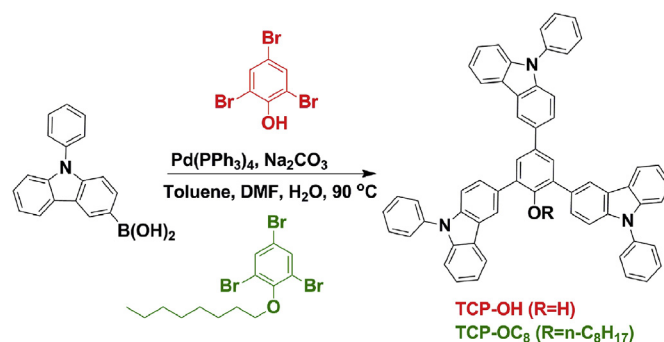
Scheme 1. The synthetic route of **TCP-OH** and **TCP-OC₈**.