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Synthesis and characterization of thiophene-mediated hole transport materials for perovskite solar cells

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ABSTRACT

One of the most exciting fields in the search for renewable energy sources are perovskite solar cells (PSCs) whose power conversion efficiency (PCE) has increased from less than 5% to a certified value of over 22.0% in an incredibly short time. Hole transport materials (HTMs) are the vital part of PSCs, and a large number of HTMs have been developed until now. The design and development of molecular architecture that provides excellent transporting properties has become the most challenging issue for chemists. Among all HTMs, thiophene-based HTMs are found to be the most promising ones. This mini-review provides an adequate amount of information about the thiophene-based HTMs, *i.e.*, summarizes and discusses their synthetic routes and device parameters such as short-circuit current (*Jsc*), open-circuit voltage (*Voc*), and percent conversion efficiency (PCE). The results of this work will be helpful to further improve the technological performance of this process. Hopefully, this review will be supportive of new opinions in the quest for designs of more effective thiophene-based HTMs.

1. Introduction

One of the transformative technologies outcompeting the organic solar cells (OSCs) [1,2] and DSSCs [3] are rising organic-inorganic hybrid perovskite solar cells (PSCs), which potentially can be transited into light-weight, supple, and cost-effective power sources by high-throughput solution fabrication [4]. Hence, serious research endeavors from both scholarly community and industry are required for PSCs. The PCEs of PSCs have been swiftly ameliorated from 3.8% to 22.1% in a time span of just 7 years [5], demonstrating the competitiveness in efficiency to that of silicon solar cells. Despite the advances made for PSCs, there are still some challenges that range from fundamental to practical [6,7]. Although there are barriers to PSC advancement, encouraging discoveries have been made in the last 3–4 years for PSCs. It is doubtless that perovskites are essential for dealing with highly efficient and robust devices, as well as eco-friendly, yet challenging aspects of PSC research [8].

PSCs essentially benefit from the exceptional optoelectrical characteristics of semiconducting inorganic-organic hybrid perovskites, such as the high molar extinction coefficient, a direct band gap, diffusion length and long carrier life time [9–12], and high charge mobility in crystalline form [13,14]. More significantly, inorganic-organic lead halide perovskites facilitate the formation of free charge carriers within the perovskite by minimal cost of driving force due to the formation of loosely bound excitons with a small bonding energy [15,16].

The electrical, electronic, and mechanical contact between photoactive layer and counter electrode is as important as the quality of perovskite absorbers to evaluate the performance of solar cells [17–25]. In fact, an interfacial layer consists of electron transporting material (ETM) or hole transporting material (HTM). Photogenerated charge is selectively extracted by the interfacial layer from the photoactive perovskite layer and is transported to the corresponding electrode. To deal with organic-inorganic hybrid perovskite, interfacial materials can have additional properties as revealed by recent studies, such as template for perovskite crystal growth [26], passivation of trap states [27], and barrier for moisture [28]. In particular, proper interface engineering can solve the hysteresis problems identified previously in PSCs. All these features are keys that can enhance the performance and stability of the device and mitigate hysteresis [25].

Development of novel interfacial materials for PSCs is very important. The most frequently used HTM in mesoporous PSC that afford remarkable efficiency is spiro-OMeTAD. For efficient hole extraction and transport, pristine spiro-OMeTAD require the addition of doping agents due to the low conductivity and intrinsic hole mobility. However, this is the major drawback for current PSCs because doping leads to deteriorated device stability and complicated device processing [29,30]. Hence, dopant-free and easily fabricated HTMs are essential for PSCs [31–33]. To replace spiro-OMeTAD, Xu and co-workers developed a spiro-type-structured HTM X60, an analog of it by an easy synthetic route and achieved an efficiency of 19.84% [34] using cheap

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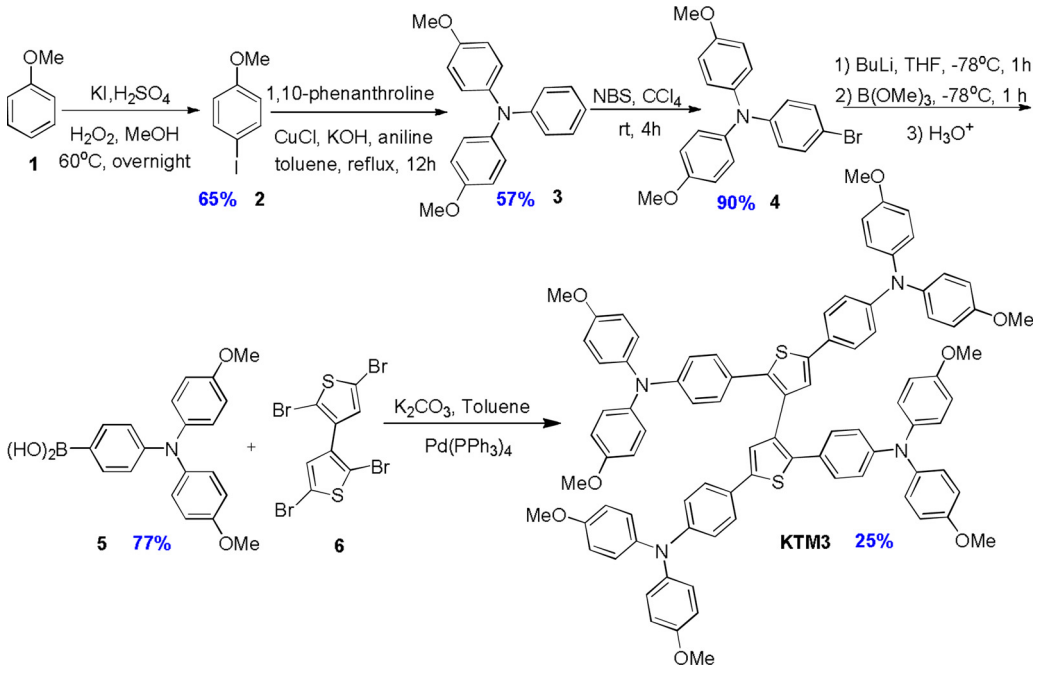

Scheme 1. Synthesis of globular shaped HTM namely KTM3.

spiro[fluorene-9,9'-xanthene] core. Malinauskas and co-workers prepared a new small-molecule HTM V826 mediated on OMeTAD-substituted fluorene moieties, obtaining a maximum efficiency of 20% [35]. Nishimura et al. developed azulene 1 HTM by using four quasi-planar arylamines and an azulene nucleus, giving a PCE of 16.5% [36]. A dopant-free HTM trux-OMeTAD based on truxene core was reported by Huang and coworkers. The symmetrical and planar truxene nucleus promotes ordered molecular packing in solid, which facilitates hole mobility as high as 10^{-3} cm^2/V s and enables an efficiency of 18.6% for the p-i-n planar PSCs [3]. As a brief conclusion, to largely enrich both the mesoporous and planar PSCs to over 18% PCE, as high as 22.1% PCE to date, many interfacial materials are designed and established with a series of functionalities. Nevertheless, to ensure excellent performances in mesoporous device, the abovementioned HTMs still require dopants to enhance their intrinsic mobility. For further exploration of new HTM and ETM for the perspectives, few controlling features would be required such as the capabilities to control perovskite crystal growth, to passivate the defects, and to save perovskite from moisture and UV-light degradation as well as classical considerations on energy level, charge mobility, and work-function tunabilities of interfacial layers [30].

Herein, we focus on the HTMs for PSCs based on thiophene, which may or may not require doping agents. Thiophene derivatives have been successfully used in many other areas of organic electronics such as in organic solar cells, OLEDs, electrochromic windows, and photochromic windows and as sensors. Because of the potential applications and various properties of thiophene derivatives, such as unique chemical stability, excellent electronic configuration, and incredible synthetic versatility, they have been employed as HTMs in PSCs [37]. In recent years, thiophene derivatives such as HTMs in PSCs have gained popularity attributed to their excellent results and low cost and reliability. Few of them outcompete the spiro-OMeTAD in terms of stability, solubility, and deep HOMO energy levels. Tuning of the materials further unveiled that thiophene has excellent ability to charge transport even under dopant-free circumstances. Thiophene-based HTMs in fact benefit due to their electron-rich thiophene cores that enhance the self-exchange rate of charges [37]. Thiophene-based HTMs are now under serious considerations. This review provides a complete detail about the synthesis, short-circuit current (*Jsc*), open-circuit voltage (Voc), percent conversion efficiency (PCE), optical properties, electrochemical properties, thermal properties, and fill factor (FF) of HTMs for PSCs based on thiophene derivatives. Different methods of synthesis of thiophene-based HTMs will provide reader to select the best and suitable method and provide ideas to design new synthetic approaches. We hope this timely special issue will encourage the research and development of valuable HTMs. Moreover, this review will serve to accelerate knowledge and lays the foundation for improved applications.

2. Globular shaped HTM based on swivel-cruciform 3,3'-bithiophene core

To explore the impact of geometry of HTM on device performance, **KTM3** was designed by T. Krishnamoorthy and co-workers with a globular shape based on swivel-cruciform 3,3'-bithiophene core [38]. The absorption spectrum of **KTM3** is very close to that of ultra-modern **Spiro-OMeTAD** with two absorption shoulders at 397 and 302 nm. A clear red shift in absorption onset with respect to **spiro-OMeTAD** results from the extended conjugation. The amorphous nature of the material can be demonstrated by its configuration minimizing the efficiency of molecular packing. It has a much lower value of T_g = 65 °C, and its HOMO energy is −5.29 eV. **KTM3** shows a *Voc* of 0.99 V and J_{sc} of 10.3 $mAcm^{-1}$ in dopant-free form, while **FK269**-doped **KTM3** shows a higher *Voc* of 1.08 V than the reference device made up of a similarly doped **spiro-OMeTAD** (1.06 V), but the *Jsc* is found to be quite low (13.0 *vs* 17.2 $mAcm^{-2}$). **KTM3**-based solid-state PSCs deliver an efficiency of 7.3% without doping and 11.0% when doped with **FK269** [38].

T. Krishnamoorthy et al. synthesized **KTM3** by a 5-step protocol. The synthetic strategy commenced with the known compound anisole **1**. Iodination of anisole **1** followed by coupling with 1,10-phenanthroline afforded **3** in 37% yield over two steps (Scheme 1). Halogenation of resultant **3** with NBS produced **4** in 90% yield. Boration of **4** generated boronic acid **5** in excellent yield (77%) [39]. Suzuki coupling reaction using tetrakis[triphenylphosphine]palladium(0) between tetrabromo 3,3'-bithiophene **6** and boronic acid **5** generated the material **KTM3** in 25% yield [38].