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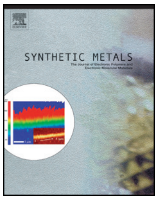

Effect of thiophene chain lengths on the optical and hole transport properties for perovskite solar cells

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ABSTRACT

We report the effect of the thiophene chain extension on optical property and hole mobility of a set of 3,4,5-tetra[4,4′-bis(methoxyphenyl)aminophen-4″-yl]-thiophene (H111) derivatives (H112, H113, H114, and H115) by using first-principles calculations combined with Marcus theory. Our results show that extension of the thiophene chain not only brings a red-shift on the absorption spectrum, but also enhances the intensity of the largest absorption. Moreover, with the increase of the thiophene number, the reorganization energy between the neutral and cation states gradually reduces, leading to a continuous decrease in exciton binding energy from H111 to H115. Importantly, we reveal that sulfur (S) atoms play dominant roles in hole transfer, and the corresponding S···S distances in stacked dimers are inversely proportional to hole mobility. Compared with H111 and H112, H114 and H115 exhibit evidently large hole mobility thus are recommended as potential hole transport materials for perovskite solar cells.

1. Introduction

Organic-inorganic perovskite solar cells (PSCs) based on organic hole transport materials (HTMs) have attracted much interest due to their excellent advantages such as large absorption coefficient, direct band gap, low cost, and high electron and hole carrier mobility, making them potential candidates for solid state solar cell devices [1–5]. Although HTM-free PSC were reported to exhibit impressive cell performance with over 10% efficiency [6,7], the existence of HTM layers is still advantageous to the inhibition of photo-generated carrier recombination and facilitating the hole transfer, especially for highly efficient PSCs [8]. To date, the most commonly used HTM is 2,2′,7,7′-tetrakis(*N*,*N*-*p*-dimethoxy-phenylamino)-9,9′-spirobifluorene (Spiro-OMeTAD), which demonstrates good pore filling of the TiO_2 layer and low recombination rate improving short-circuit density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) of solar cells. However the molecule requires an expensive multi-step synthesis and shows too low hole mobility ($3.67 \times 10^{-4}\,cm^2\,V^{-1}\,S^{-1}$) to carry all generated current [9–12]. Therefore, the development of new economical and efficient HTMs with ideal electronic properties remains an attractive and challenging goal. Recently, some researchers have pointed out that excellent HTMs for PSCs should meet three essential requirements: (1) good hole mobility, (2) compatible highest occupied molecular orbital (HOMO) energy level relative to organic-inorganic halide perovskites, and (3) low cost for commercialization [13]. In addition to the above three requirements, Grätzel found that HTMs with high light harvesting ability and the low energy gap can have additional contribution to the photocurrent generation of PSCs [14].

Of late years, to develop desired alternatives to Spiro-OMeTAD, different kinds of HTM have been developed involving poly-3-hexylthiophene (P3HT) poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT), poly [bis(4-phenyl)(2,4,6-trimethylphenyl) amine] (PTAA) [15] and poly[2,6-[4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′] dithiophene]-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT) [16], and so on. Compared to polymer HTM, the small organic molecules benefit from the fact that they are easy to purify and form crystalline films for the fabrication of desired efficiency PSCs [17,18]. As a very important class of small organic semiconducting materials, triphenylamine (TPA) derivatives have been investigated widely owing to their high carrier mobility. In 2014, Mhaisalkar and coworkers developed a thiophene-based HTM 3,4-ethylenedioxythioxythiophene (H101) as the core unit terminated with two TPAs [19]. When H101 is used as the HTM doping with *tris*(2-(1H-pyrazol-1-yl) pyridine) cobalt(III) tris(hexafluorphosphate) (FK102) in a PSC, the power conversion efficiency (PCE) reached13.8% under AM 1.5G solar simulation [19]. This is the

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first heterocycle-containing material achieving over 10% efficiency in PSC at that time. At the same time, anther novel swivel-cruciform 3,3′-bithiophene based HTM KTM3 was synthesized, and the with KTM3 PSC showed a higher V_{oc} and FF [20]. After that, the author reported three novel HTMs (named T101, T102, and T103) based on a triptycene core. The PSCs fabricated with T102 and T103 as HTMs showed a PCE of 12.24% and 12.38%, respectively, which are comparable to that obtained using the best performing HTM Spiro-OMeTAD (PCE = 12.87%) [21]. Recently, Mhaisalkar and coworkers synthetized two new electron-rich molecules, 3,4,5-tetra[4,4′-bis(methoxyphenyl) aminophen-4″-yl]-thiophene (H111) and 4,4′,5,5′-tetra[4,4′-bis(methoxyphenyl) aminophen-4″-yl]-2,2′-bithiophene (H112) [22]. When H111 and H112 were used as HTMs in PSCs, PCE of up to 15.4% under AM 1.5G solar simulation was obtained. This is the highest PCE achieved with HTM not composed of Spiro-OMeTAD. The H111 and H112 have great potential for application in PSCs. So it is necessary to further study H111, H112, and their derivatives to look for new HTMs. Recently, we have investigated the hole diffusion kinetics in PSCs by using density function theory and Marcus theory, and our results indicated that the small exciton binding energy and the large hole mobility of H112 contribute to the enhancement of the short-current density of PSCs [23]. Previous studies have shown that the longer the π-conjugated chain of organic semiconductor, the more favorable the charge carrier can transport due to the smaller reorganization energy [24]. As typical conjugation unit, thiophene is widely used as π-linker in organic sensitizers in dye sensitized solar cells (DSSCs), mainly because it can broaden the spectral region of the absorption [25–29]. To the best of our knowledge, no study on the charge carrier transfer properties has been reported when the number of thiophene ring attached to H111 skeleton increases.

In present work, we have theoretically studied the optical properties and the hole mobility of H111 and its four derivatives (H112, H113, H114 and H115, see Fig. 1 for the molecular structures), to investigate the thiophene chain extension effects. The obtained results are expected to throw lights on rational

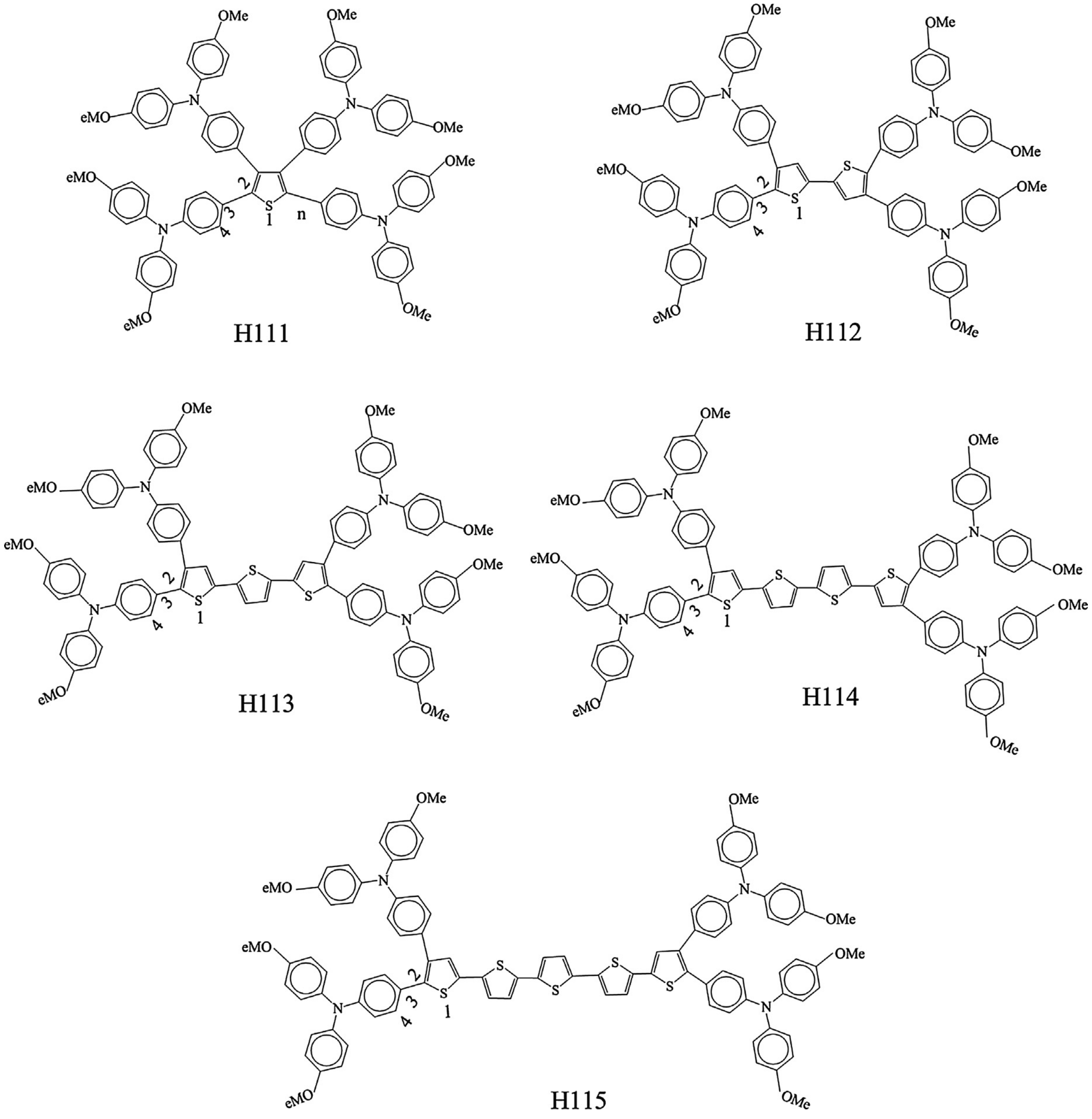

Fig. 1. Chemical structures of studied molecules H111, H112, H113, H114 and H115.