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# Diketopyrrolopyrrole based D-$\pi$-A-$\pi$-D type small organic molecules as hole transporting materials for perovskite solar cells

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ABSTRACT

Three novel diketopyrrolopyrrole (DPP) based small organic molecules were synthesized as hole transporting materials for perovskite solar cells. The effects of different donors and $\pi$ bridges on the performance of perovskite solar cells (PSCs) were discussed. The efficiency of TPADPP-1, TPADPP-2, PTZDPP-2 was 5.10%, 9.85% and 8.16% respectively. Compared to TPADPP-2, the voltage of PTZDPP-2 was higher. Because the electron-donating ability of phenothiazine based donor was larger than that of triphenylamine based donor, the HOMO level of PTZDPP-2 was lower than that of TPADPP-2. The results indicated that the diketopyrrolopyrrole based D-$\pi$-A-$\pi$-D type small organic molecule might be a promising hole transporting material in the perovskite solar cells.

## 1. Introduction

Organic-inorganic lead halide perovskite solar cells have attracted great attention since the invention by Miyasaka in 2009 [1]. The efficiency of perovskite solar cell has risen from 3.8% to 22.1% in recent years [2–5]. They exhibit many favorable properties, including a steep absorption onset with strong light absorption, high carrier mobility and long carrier lifetimes [6–8]. The fast increase in the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has motivated many groups to focus on the optimization of crystal formation and device architecture [9–14]. Many research results have indeed manifested that $MAPbI_3$ and $MAPbI_xCl_{3-x}$ are efficient light-harvesting materials with bipolar transport properties and they also function well in hole transporting layer (HTL) free PSCs [15]. However, the highest PCEs achieved by HTL-free PSCs are still much lower than those of the devices containing HTLs, indicating the necessity of interface modification for effective hole extraction from the perovskite layer to the hole contact. Among the materials used to fabricate perovskite solar cell devices, hole-transporting materials (HTMs) play a key role in enhancing the solar cell efficiency by inducing efficient hole transport and slowing electron-hole recombination. An appropriate energy level alignment and good hole-transporting properties of HTMs are important requirements to minimize losses in the electrical potential from the viewpoint of charge recombination [16].

Many organic molecules as HTM for perovskite solar cells were reported [17–27]. The most widely used HTM (spiro-OMeTAD (2,20,7,70-tetrakis[*N*,*N*-dip-methoxyphenylamine]-9,9-spirobifluorene)) reproducibly performs well, irrespective of the perovskite solar cell since it was developed as a HTM for use in solid-state dye-sensitized solar cells. Despite its promising properties, the high cost of spiro-OMeTAD impedes the practical applications of highly efficient perovskite solar cells in the photovoltaic market because spiro-OMeTAD requires complicated multi-step synthesis approaches [28–31]. The tedious synthesis of spiro-OMeTAD results in its high cost that limits its scale-up. Thus, the exploration of low-cost and high-efficiency HTMs is important [32–38]. As a very important class of organic semiconducting materials, diketopyrrolopyrrole (DPP) has been extensively investigated owing to its high charge-carrier mobility. DPP-based materials have shown great performance in organic photovoltaic

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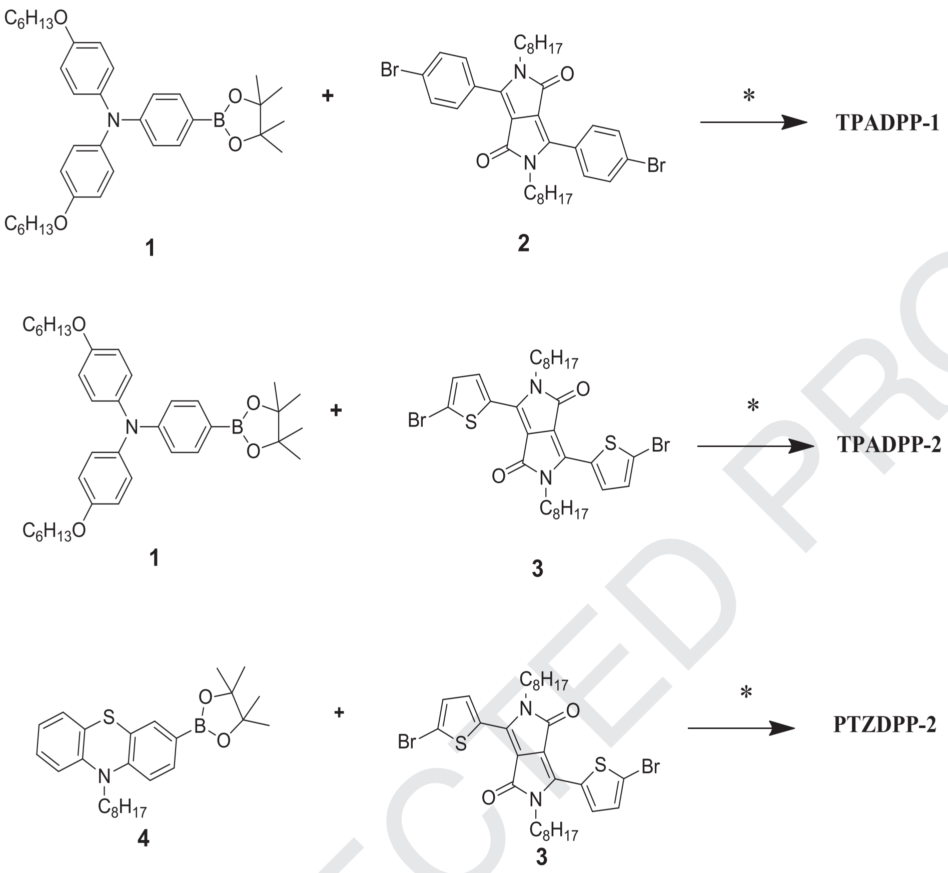

**Scheme 1.** Synthetic routes of TPADPP-1, TPADPP-2 and PTZDPP-2.
*Reaction conditions: $Pd(PPh_3)_4$, $Na_2CO_3$, $H_2O$, aliquat@366, $N_2$, toluene, reflux.

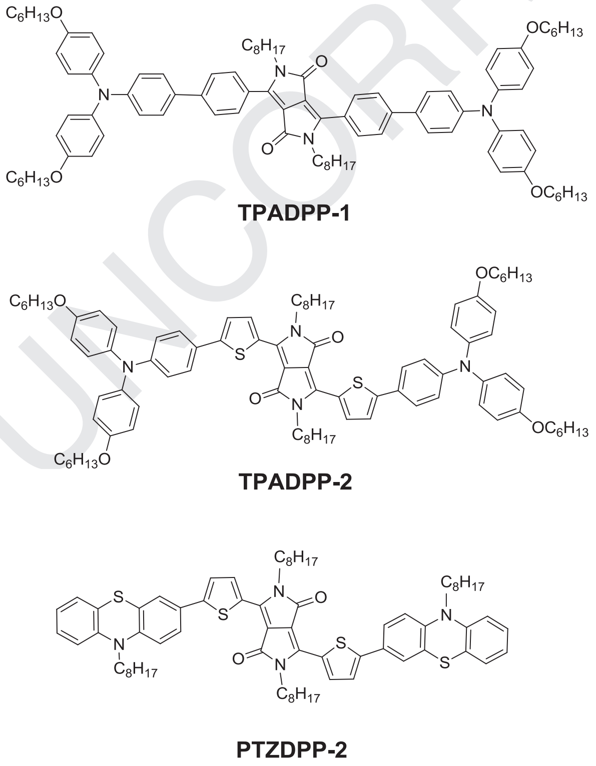

**Fig. 1.** Molecular structures of TPADPP-1, TPADPP-2 and PTZDPP-2.

devices as well as organic transistors [39–42]. However, the direct application of DPP-based hole transport layers to perovskite solar cells is still few [43,44].

In this paper, we designed and synthesized three DPP-based small organic molecules TPADPP-1, TPADPP-2 and PTZDPP-2. The effects of different donors and $\pi$ bridges on the performance of PSCs were studied and discussed (Fig. 1 and Scheme 1). Q2

## 2. Experimental

### 2.1. Materials

$PbI_2$ (>98%) was from TCI (Japan); HI (48% in water), HCl (57 wt% in water), Aldrich), $CH_3NH_2$ (33 wt% in absolute ethanol), formamidine acetate (99%), 4-*tert*-butylpyridine (TBP, 96%), titanium diisopropoxide bis(acetylactonate) in isopropanol (Tiacac, 75%) and Li-bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Sigma-Aldrich. Methylammonium iodide (MAI) and methylammonium chloride (MACl) were synthesized according to the literature. Compounds 1–4 were synthesized according to Refs. [39,45].

### 2.2. Measurements

$^1$H and $^{13}$C NMR spectra were measured on Bruker 400 MHz instruments in $CDCl_3$. The melting point was conducted on a SGW-X-4B microscopic melting point apparatus. HRMS spectra were recorded on an Agilent Technologies 1290 Infinity mass spectrophotometer. Scanning electron microscopy (SEM, Sirion200, Holland Fei) was performed to observe the film morphology. Time-resolved luminescence decays were recorded with time-correlated

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