Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: http://www.elsevier.com/locate/dyepig

Short communication

Molecular engineering of phenothiazine-based monomer and dimer hole transport materials and their photovoltaic performance

Mengde Zhai^a, Yawei Miao^{a,b}, Cheng Chen^{a,**}, Haoxin Wang^a, Xingdong Ding^{a,b}, Cheng Wu^a, Xichuan Yang^c, Ming Cheng^{a,*}

^a Institute for Energy Research, Jiangsu University, Zhenjiang 212013, China

^b School of Energy and Power Engineering, Jiangsu University, Zhenjiang 212013, China

^c State Key Laboratory of Fine Chemicals, Dalian University of Technology (DUT), Dalian 116024, China

ARTICLE INFO	A B S T R A C T
<i>Keywords:</i> Perovskite solar cell	Through molecular engineering, phenothiazine-based monomer hole transport material (HTM) PTZT and dimer
Hole transport material	the adjustment of the molecular structure. Applied in perovskite solar cells (PSCs), monomer HTM PTZT -based
Dimer Molecular engineering	device achieves the highest efficiency of 18.74% while only 15.45% for dimer HTM D-PTZT -based device under 100 mW cm ^{-2} AM 1.5G solar illumination.

1. Introduction

Perovskite solar cells (PSCs) have achieved an impressive power conversion efficiency (PCE) of 25.5% due to their excellent optoelectronic properties, and this remarkable PCE breakthrough makes them comparable to silicon solar cells [1–3]. Hole transport materials (HTMs), which are responsible for the hole extraction and transport, play a crucial role in acquiring highly efficient PSCs [4]. Apart from the typical HTMs such as 2,2',7,7'-tetrakis (N,N-bis(p-methoxyphenyl)amino)-9, 9'-spirobifluorene (Spiro-OMeTAD) and poly[bis(4-phenyl) (2,4,6-trimethylphenyl)amine (PTAA), various small molecular organic HTMs have been widely developed, due to their variable molecular structures, low synthesis cost and good batch-to-batch reproducibility [5-15]. Thereinto, phenothiazine (PTZ), which is an electron-rich heterocycle with a butterfly-like configuration, is widely employed as a core building block to construct HTMs, achieving excellent performance [16,17]. The reported PTZ-based HTMs are almost monomers, and the previous research work mainly focused on the optimization of peripheral substituents on the PTZ ring to tune the highest occupied molecular orbital (HOMO) energy levels. Moreover, the molecular geometries of HTMs have also proved to deeply influence their physicochemical and photoelectronic properties [18]. Nevertheless the in-depth impact of monomer and dimer configurations of PTZ-based HTMs on their properties and the photovoltaic performance have never been investigated.

2. Results and discussion

In this regard, we designed and synthesized a PTZ dimer 4,4',4'',4'''((9,9-dimethyl-9*H*-fluorene-2,7-diyl)bis(10*H*-phenothiazine-10,3,7triyl))tetrakis(*N*,*N*-bis(4-methoxyphenyl) aniline) and a PTZ monomer 4,4'-(10-(p-tolyl)-10H-phenothiazine-3,7-diyl)bis(*N*,*N*-bis(4-methoxyphenyl)aniline), termed **D-PTZT** and **PTZT** (see Scheme 1a), respectively, allowing us to study the effects of dimer and monomer configurations on their properties and the photovoltaic performance. The new HTMs were easily synthesized in 3-steps and the detailed synthetic routes were depicted in Scheme 1b and supporting information (SI). Both of the HTMs **D-PTZT** and **PTZT** were characterized by ¹H NMR and high-resolution mass spectrometry (HRMS) to verify their chemical structures. According to previous reported calculation model [19], the synthetic cost of HTMs **D-PTZT** and **PTZT** were evaluated to be 92.5 \$/g and 48.3 \$/g, respectively, which are much lower than that of Spiro-OMeTAD (200 \$/g), most notably **PTZT**, as shown in SI.

Cyclic voltammetry (CV) and UV–vis absorption spectroscopy were used to evaluate the energy of **D-PTZT** and **PTZT**. The results presented in Fig. 1a and b, and the corresponding optical and electrochemical data were summarized in Table 1. The detailed calculation method of energy levels was described in the SI. The HOMO energy levels of **D-PTZT** and **PTZT** were estimated to be -5.16 and -5.17 eV vs. vacuum, respectively, which were more negative than the valence band (VB) of

** Corresponding author.

https://doi.org/10.1016/j.dyepig.2021.109340

Received 27 February 2021; Received in revised form 22 March 2021; Accepted 22 March 2021 Available online 31 March 2021 0143-7208/© 2021 Elsevier Ltd. All rights reserved.





^{*} Corresponding author.

E-mail addresses: chencheng@ujs.edu.cn (C. Chen), mingcheng@ujs.edu.cn (M. Cheng).



(**I**) p-lodotoluene for the compound 1, Phenothiazine for the compound 3, Pd(OAc)₂/Tri-tert-butylphosphine, Tert-BuOK, toluene, 110°C, 12h; (**II**) NBS, THF, 0-5°C; (**III**) 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline, Pd(PPh₃)₄, K₂CO₃, THF, 80°C.

Scheme 1. (a) The chemical structure of HTMs D-PTZT and PTZT. (b) The detailed synthetic routes of HTMs PTZT and D-PTZT.

perovskite (-5.45 eV), facilitating the hole extraction and transport at the perovskite/HTM interface. Combining with the UV–vis absorption and photoluminescence test results, the lowest unoccupied molecular orbital (LUMO) energy levels of **D-PTZT** and **PTZT** were estimated to be -2.37 and -2.35 eV vs. vacuum, respectively, which is more positive than the conduction band (CB) of perovskite (-3.90 eV), effectively blocking the backward electron transfer from perovskite. It is found that there were no significant changes occurring in the HOMO and LUMO energy levels from PTZ monomer to dimer, considering the test error (see Fig. 3a).

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were also conducted to analyze the thermal stability of **D-PTZT** and **PTZT** (see Fig. S7 and Table S10). The decomposition temperature (T_d) of **D-PTZT** and **PTZT** were detected to be 443 °C and 424 °C, respectively, manifesting the good thermal stability of these two PTZ-based HTMs. Meanwhile, no glass transition temperatures (T_g) were found in the DSC measurement for **D-PTZT** and **PTZT**, demonstrating their intrinsic amorphous phase which is helpful for obtaining good film formation property.

To take deep insight of the molecular configuration and the charge distribution, the density functional theory (DFT) calculation was performed by using the Gaussian program at the B3LYP/6-31G* level. As shown in Fig. 2, both **D-PTZT** and **PTZT** exhibit a twisted butterfly configuration. Due to the orthorhombic insertion and steric hindrance of fluorene linker, **D-PTZT** shows weaker intramolecular force. For **PTZT**, HOMO is delocalized along the whole backbone, while LUMO shifts to

the PTZ core unit. The substantial overlap between HOMO and LUMO of **PTZT** testified the existence of a Coulomb interaction, which is favorable for the exciton formation and hole migration. Totally different from **PTZT**, the HOMO of **D-PTZT** is mainly distributed on either of the two PTZ units, the LUMO transfers to the fluorene core unit. The extreme variation in the charge delocalization between HOMO and LUMO of **D-PTZT** implies the poor hole extraction. As expected, the hole mobility and conductivity of the monomer HTM **PTZT** are measured to be 2.62×10^{-4} cm² V⁻¹ s⁻¹ and 3.00×10^{-4} S cm⁻¹, which are much higher than those of the dimer HTM **D-PTZT** (1.62×10^{-4} cm² V⁻¹ s⁻¹ and 1.52×10^{-4} S cm⁻¹), as shown in Fig. 1c and d and Table 1. Furthermore, it is detected that the S and O atoms on the PTZ unit have strong negative electrostatic potential from the electrostatic potential maps, indicating the HTMs may interact with uncoordinated Pb²⁺ thereby further passivating surface defects due to the Lewis base nature of S and O [20].

Considering the suitable energy levels, the excellent hole mobility and conductivity, and good thermal stability of **D-PTZT** and **PTZT**, they were further employed as HTMs to fabricate PSCs with the device structure of FTO/compact- TiO₂/mesoporous-TiO₂/perovskite/HTM/ Au (see Fig. 3a and b). The typical HTM Spiro-OMeTAD was chosen as the reference HTM and the light harvesting layer perovskite adopted in this work is (FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}. The detailed device fabrication process is described in SI. The thickness of HTM layer is measured to around 80 nm according to the cross-sectional SEM. From the top-view SEM images of **D-PTZT** and **PTZT** films coating on the perovskite (see Fig. S8), we can see that **D-PTZT** film exhibits more intensive pinholes,



Fig. 1. (a) Cyclic voltammograms of **D-PTZT** and **PTZT** in THF. (b) UV–vis absorption (solid line) and photoluminescence spectra (dashed line) of **D-PTZT** and **PTZT** in THF (1×10^{-5} M). (c) Hole mobility and (d) Conductivity of the doped **D-PTZT** and **PTZT**.

Table 1Optical and electrochemical properties of HTMs.

HTMs	$\lambda_{ab,max}$ (nm)	$\lambda_{ph,max}$ (nm)	E_{0-0} (eV)	HOMO (eV)	LUMO (eV)	Hole mobility (cm ² V ^{-1} S ^{-1})	Conductivity (S cm ⁻²)
D-PTZT PTZT	307 329	461 461	2.79 2.82	-5.16 -5.17	-2.37 -2.35	$\begin{array}{c} 1.62 \times 10^{-4} \\ 2.62 \times 10^{-4} \end{array}$	$\begin{array}{c} 1.52 \times 10^{-4} \\ 3.00 \times 10^{-4} \end{array}$



Fig. 2. DFT calculations of HTMs D-PTZT and PTZT.

which would become the charge recombination center and accelerate the non-radiative recombination at the interface. The electrochemical impedance spectroscopy (EIS) measurement further confirmed the conclusion. As shown in Fig. S9, the **D-PTZT** based PSC showed lower recombination resistance (59 k Ω) than that of **PTZT** based device (97 k Ω), suggesting the serious non-radiative recombination in **D-PTZT**



Fig. 3. (a) Energy level diagrams of PSCs. (b) Cross-section SEM image of PSC device containing HTM PTZT. (c) Current-Voltage (*J-V*) curves of PSC device based on HTMs D-PTZT, PTZT and Spiro-OMeTAD. (d) IPCE spectra of PSCs based on HTMs D-PTZT, PTZT and Spiro-OMeTAD.

Table 2				
Optimal photovoltaic performa	nce parameters of PSCs	applying	various H	TMs.

HTMs	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)	J_{sc}^{cal} (mA cm ⁻²)
D-PTZT	1.02	21.90	68.88	15.45	21.45
PTZT	1.06	22.78	77.69	18.74	23.05
Spiro- OMeTAD	1.05	23.82	73.57	18.57	22.99

based PSC. Therefore, a higher open-circuit voltage (V_{oc}) can be expected for **PTZT**-based PSC.

Fig. 3c presents the current density-voltage (J-V) curves of the optimized devices containing D-PTZT and PTZT as HTMs, and the specific photoelectric parameters are presented in Table 2. The device adopted PTZT as HTM achieved a power conversion efficiency (PCE) of 18.74%, with a short-circuit current density (J_{sc}) of 22.78 mA cm⁻², a V_{oc} of 1.06 V, and a fill factor (FF) of 0.78, which is much higher than that of D-PTZT (15.45%) and the reference Spiro-OMeTAD (18.57%). From the incident photo-to-electron conversion efficiency (IPCE) measurement shown in Fig. 3d, the IPCE values of PTZT were much higher than that of **D-PTZT**, and comparable with that of Spiro-OMeTAD. This is mainly attributed to the higher hole extraction and transport efficiency of PTZT because of higher hole mobility and conductivity of PTZT. The integrated J_{sc} of PTZT, D-PTZT and Spiro-OMeTAD were estimated to be 23.05, 21.45 and 22.99 mA cm⁻², matching well with the J-V test results. Moreover, 20 cells of each species were fabricated (see Tables S11–13) and the boxplots of J_{sc} , V_{oc} , FF and PCE values were depicted in Fig. S10. All devices exhibited good reproducibility.

photoluminescence (TRPL) spectroscopy were further conducted to characterize the charge transfer kinetics at perovskite/HTM interface (see Fig. 4a and b and Table S14). Significant PL quenching were detected for the cases of perovskite film coating with different HTMs. Furthermore, perovskite film coating with **PTZT** exhibited higher PL quenching efficiency than that of **D-PTZT**, indicating the more efficient hole extraction of **PTZT**. The PL decay lifetime (τ_{ave}) of **D-PTZT**, **PTZT** and Spiro-OMeTAD coated perovskite film were calculated to be 24.99, 9.72 ns and 12.35 ns, respectively, illustrating the faster hole extraction rate for **PTZT**. The results are consistent with the hole mobility and conductivity measurements mentioned above.

We also evaluated the long-term stability of the unencapsulated PSCs containing **D-PTZT** and **PTZT** as HTMs in ambient atmosphere (60% humidity, room temperature) and the test results were shown in Fig. 4c. It is revealed that the **PTZT** based device exhibits much better stability than **D-PTZT** and Spiro-OMeTAD, maintaining over 62% of its initial efficiency after 1000 h storage. Considering the effect of moisture on the stability of the device, we carried out the contact angle (θ) measurement of **D-PTZT** and **PTZT** films coating on the perovskite (see Fig. 4c, illustration). The **PTZT** film showed larger water contact angle of 90.20° than **D-PTZT** (85.20°) and Spiro-OMeTAD (89.10°), suggesting the better hydrophobic property of **PTZT**. Furthermore, the **PTZT** film with less pinholes observed above also decreases the active site of the perovskite decomposition.

3. Conclusion

In conclusion, we synthesized PTZ-based dimer and monomer HTMs **D-PTZT** and **PTZT**, and further investigated the impact of the spatial

The steady-state photoluminescence (PL) and time-resolved



Fig. 4. (a) steady-state photoluminescence (PL) spectra; (b) the time-resolved photoluminescence (TRPL) curves of the bare perovskite film and with different HTMs. (c) Long-term stability of device in ambient environment. Inset, Contact angle measurement of the water droplet on the films of pristine perovskite and with different HTMs.

molecular structures of **D-PTZT** and **PTZT** on their physicochemical and photoelectrochemical properties. The results demonstrated the monomer structure is more favorable for hole extraction and transport. Applied in PSCs as HTMs, the monomer HTM **PTZT** based device achieved a higher PCE of 18.74% under 100 mW cm⁻² AM 1.5G solar illumination than that of **D-PTZT**-based one. The poor performance of **D-PTZT** may result from the more twisted molecular structure inducing by the non-linear π -linker. The dimer with linear π -linker, such as biphenyl and alkyne will be synthesized and investigated. This work is in progress.

Associated content

The Supporting Information is available free of charge on the Elsevier Publications website. Synthetic routes, synthesis cost calculation, device fabrication procedure, and other characterization data are supplied as Supporting Information.

Credit authorship contribution statement

Mengde Zhai: Investigation, Methodology, Writing-original draft. Yawei Miao: Investigation, Methodology, Writing-original draft. Cheng Chen: Project administration, Supervision, Writing-review & editing. Haoxin Wang: Methodology, Formal analysis. Xingdong Ding: Formal analysis. Cheng Wu: Formal analysis. Xichuan Yang: Software, Formal analysis. Ming Cheng: Conceptualization, Data curation, Resources, Writing-review & editing.

Declaration of competing interest

The authors declare no competing financial interest.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (grants 21905119 and 21805114), Natural Science Foundation of Jiangsu province (BK20180867 and BK20180869), China Postdoctoral Science Foundation (2019M651741), Six Talent Peaks Project in Jiangsu Province (XNY066), High-tech Research Key Laboratory of Zhenjiang (SS2018002), the State Key Laboratory of Fine Chemicals (KF1902).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109340.

References

 Chen Y, Tan S, Li N, Huang B, Niu X, Li L, et al. Self-elimination of intrinsic defects improves the low-temperature performance of perovskite photovoltaics. Joule 2020;4(9):1961–76.

M. Zhai et al.

Dyes and Pigments 191 (2021) 109340

- [2] https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20200104. pdf.
- [3] Shi D, Adinolfi V, Comin R, Yuan M, Alarousu E, Buin A, et al. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. Science 2015;347(6221):519–22.
- [4] Cheng M, Zuo C, Wu Y, Li Z, Xu B, Hua Y, et al. Charge-transport layer engineering in perovskite solar cells. Sci Bull 2020;65(15):1237–41.
- [5] Yin C, Lu J, Xu Y, Yun Y, Wang K, Li J, et al. Low-cost N,N'-Bicarbazole-Based dopant-free hole-transporting materials for large-area perovskite solar cells. Adv Energy Mater 2018;8(21):1800538.
- [6] Wang Y-K, Yuan Z-C, Shi G-Z, Li Y-X, Li Q, Hui F, et al. Dopant-free spirotriphenylamine/fluorene as hole-transporting material for perovskite solar cells with enhanced efficiency and stability. Adv Funct Mater 2016;26(9):1375–81.
- [7] Yin X, Zhou J, Song Z, Dong Z, Bao Q, Shrestha N, et al. Dithieno[3,2-b:2',3'-d] pyrrol-Cored hole transport material enabling over 21% efficiency dopant-free perovskite solar cells. Adv Funct Mater 2019;29(38):1904300.
- [8] Vaitukaityte D, Wang Z, Malinauskas T, Magomedov A, Bubniene G, Jankauskas V, et al. Efficient and stable perovskite solar cells using low-cost aniline-based enamine hole-transporting materials. Adv Mater 2018;30(45):e1803735.
- [9] Wang Y, Chen W, Wang L, Tu B, Chen T, Liu B, et al. Dopant-free small-molecule hole-transporting material for inverted perovskite solar cells with efficiency exceeding 21. Adv Mater 2019;31(35):e1902781.
- [10] Chen H, Fu W, Huang C, Zhang Z, Li S, Ding F, et al. Molecular engineered holeextraction materials to enable dopant-free, efficient p-i-n perovskite solar cells. Advanced Energy Materials 2017;7(18):1700012.
- [11] Wang J, Zhang H, Wu B, Wang Z, Sun Z, Xue S, et al. Indeno[1,2-b]carbazole as methoxy-free donor group: constructing efficient and stable hole-transporting materials for perovskite solar cells. Angew Chem Int Ed 2019;58(44):15721–5.

- [12] Wu C, Chen C, Tao L, Ding X, Zheng M, Li H, et al. Highly efficient perovskite solar cells based on symmetric hole transport material constructed with indaceno[1,2-b: 5,6-b']dithiophene core building block. J Energy Chem 2020;43:98–103.
- [13] Jeon NJ, Na H, Jung EH, Yang T-Y, Lee YG, Kim G, et al. A fluorene-terminated hole-transporting material for highly efficient and stable perovskite solar cells. Nature Energy 2018;3(8):682–9.
- [14] Shasti M, Volker SF, Collavini S, Valero S, Ruiperez F, Mortezaali A, et al. Perovskite solar cells based on oligotriarylamine hexaarylbenzene as holetransporting materials. Org Lett 2019;21(9):3261–4.
- [15] Jeong M, Choi IW, Go EM, Cho Y, Kim M, Lee B, et al. Stable perovskite solar cells with efficiency exceeding 24.8% and 0.3-V voltage loss. Science 2020;369(6511): 1615–20.
- [16] Grisorio R, Roose B, Colella S, Listorti A, Suranna GP, Abate A. Molecular tailoring of phenothiazine-based hole-transporting materials for high-performing perovskite solar cells. ACS Energy Lett 2017;2(5):1029–34.
- [17] Zhang F, Wang S, Zhu H, Liu X, Liu H, Li X, et al. Impact of peripheral groups on phenothiazine-based hole-transporting materials for perovskite solar cells. ACS Energy Lett 2018;3(5):1145–52.
- [18] Rodriguez-Seco C, Mendez M, Roldan-Carmona C, Pudi R, Nazeeruddin MK, Palomares EJ. Minimization of carrier losses for efficient perovskite solar cells through structural modification of triphenylamine derivatives. Angew Chem Int Ed 2020;59(13):5303–7.
- [19] Petrus ML, Bein T, Dingemans TJ, Docampo P. A low cost azomethine-based hole transporting material for perovskite photovoltaics. J Mater Chem 2015;3(23): 12159–62.
- [20] Jiang K, Wang J, Wu F, Xue Q, Yao Q, Zhang J, et al. Dopant-free organic holetransporting material for efficient and stable inverted all-inorganic and hybrid perovskite solar cells. Adv Mater 2020;32(16):e1908011.