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Molecular Tailoring of Phenothiazine-Based Hole-Transporting Materials for Highly Performing Perovskite Solar Cells

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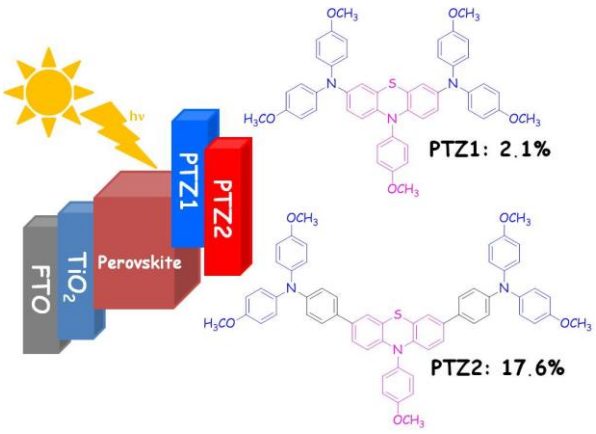
ABSTRACT. Phenothiazine-based compounds, **PTZ1** and **PTZ2,** were synthesized through straightforward Buchwald-Hartwig and Suzuki-Miyaura cross-couplings, respectively, by binding the suitable donor groups (diarylamine or triarylamine) to a phenothiazine core. Phenothiazine-based structures were proved for the first time as hole-transporting materials in solution-processed lead trihalide perovskite-based solar cells. A dramatic effect exerted by the presence of phenylene spacers was observed on the relevant photovoltaic performances. The power conversion efficiencies measured under AM 1.5 sun shoot up from 2.1% (**PTZ1**) to a remarkable 17.6% (**PTZ2**), a value rivaling those obtained with the state-of-the-art Spiro-OMeTAD (17.7%). These results point phenothiazine out as promising candidates to be used as readily available and cost-effective hole transporting materials in perovskite solar cells.

TOC GRAPHICS

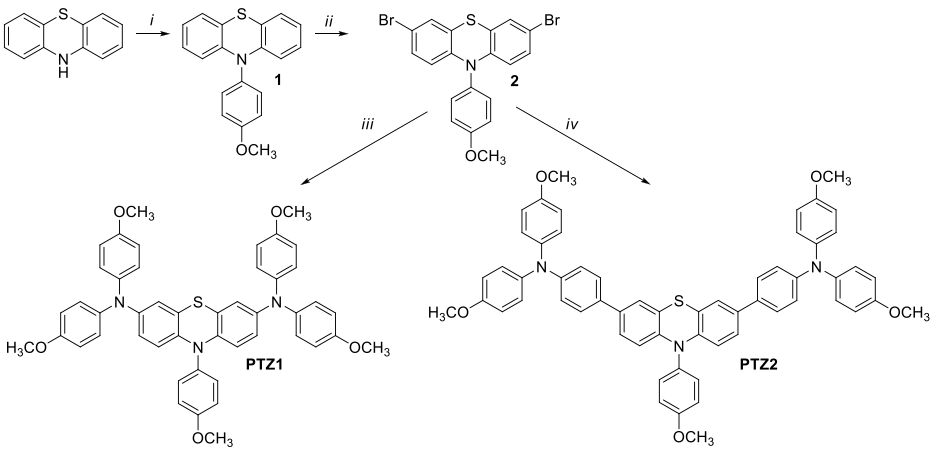


Since the pioneering report by Miyasaka *et al.* in 2009,[1] organic-inorganic perovskites have rapidly become the hottest topic in photovoltaics due to their excellent intrinsic properties, such as light-harvesting from visible to near-infrared wavelengths with high extinction coefficients and long electron-hole diffusion lengths.[2–5] The best performing device configuration for perovskite-based solar cells (PSCs) comprises a perovskite layer sandwiched in between an electron and hole transporting material (HTM).[6] While power conversion efficiencies (PCE) of ~10% have been reported for PSC deprived of the HTM layer, in the highest performance PSCs, the free photo-generated holes within the perovskite material need to be extracted and transported by efficient HTMs.

Numerous organic small molecules have been investigated as HTM in PSCs. To date, the highest reported PCE values (over 20%) have been reached with molecules, such as Spiro-OMeTAD and FDT, sharing as common structural feature the spiro functionality.[7] However, the multi-step synthesis of the spiro *motif* is prohibitively expensive and challenging, since it requires low temperature and harsh acid and basic conditions. Moreover, high-purity sublimation-grade of commercial Spiro-OMeTAD is commonly required to obtain high-performance devices. For these reasons, alternative building blocks have been used as cores aiming at reaching state-of-the-art photovoltaic figures of merit in PSCs, such as thiophene derivatives,[8] triphenylamine,[9] bridged-triphenylamines,[10] pyrene,[11] 3,4-ethylenedioxythiophene,[12] linear π-conjugated systems,[13] triptycene,[14] silolothiophene,[15] tetraphenylethene[16] and triazines,[17] all of them suitably decorated with diarylamines, triarylamines and/or carbazole side groups. Furthermore, there are also examples of HTMs incorporating phenoxazine,[18] pentacene,[19] benzo-dithiophene derivatives[20] and *S,N*-

heteropentacene[21] as cores with absorption in the visible and near-infrared region, which have exhibited PCEs higher than 15%.

On the basis of the current interest towards carbazole- and fluorene-based cores in designing highly performing HTMs,[22-27] we deemed it worthwhile to investigate the use of the phenothiazine building block as a structural variant for the construction of molecularly engineered HTMs (**PTZ1** and **PTZ2**, Scheme 1). Phenothiazine is a low-cost and flexible electron-rich heteroaromatic unit, which provides access to a wide library of HTMs by relatively cheap synthetic procedures. The fundamental properties of the proposed phenothiazine-based HTMs were found to be strongly dependent on the presence of a π-bridge between the donor groups and the phenothiazine core, which literally boosts the **PTZ2** performance in PSCs *on par* with that of the Spiro-OMeTAD reference, providing solid ground for further investigations and potential improvements.



Scheme 1. Synthetic sequence for the obtainment of **PTZ1** and **PTZ2**: *i*) 4-bromoanisole, $Pd(AcO)_2$/dppf, *tert*-BuONa, toluene, 100 °C; *ii*) NBS, chloroform; *iii*) *p*-methoxy-diphenylamine, $Pd(AcO)_2$/dppf, *tert*-BuONa, toluene, 100 °C; *iv*) 4-methoxy-*N*-(4-

methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline, $Pd(PPh_3)_4$, 2M K_2CO_3, toluene, reflux.

The phenothiazine-based core was obtained in a two-step synthetic sequence starting from commercial sources (Scheme 1). A palladium-catalyzed cross-coupling reaction between phenothiazine and 4-bromoanisole was used to protect the nitrogen atom of the core affording the intermediate **1**, while the bromo-derivative **2** was obtained by reaction of **1** with *N*-bromo-succinimide. The target molecule **PTZ1** was prepared *via* a Buchwald-Hartwig C–N cross coupling between **2** and *p*-methoxy-diphenylamine in the presence of $Pd(AcO)_2$/dppf as the catalytic system, *tert*-BuONa as the base and toluene as the solvent in 71% yield. The variant **PTZ2** was synthesized *via* a Suzuki-Miyaura C–C cross coupling between **2** and 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline in the presence of $Pd(PPh_3)_4$ as the catalytic system, a 2M K_2CO_3 aqueous solution acting as the base and toluene as the solvent in 81% yield. The introduction of 4-methoxyphenyl group on the phenothiazine core was conceived to impart the necessary thermal stability to the corresponding material and warrant the formation of an amorphous thin film (*vide infra*). The synthetic details, primary characterization and estimate of the chemical costs[28] for **PTZ1** and **PTZ2** are reported in the Supporting Information. Noteworthy, the synthesis cost of **PTZ1** and **PTZ2** (111.90 $/g and 156.76 $/g respectively) were found to be remarkably lower with respect to that of Spiro-OMeTAD (~600 $/g).[29]

The thermal behavior of **PTZ1** and **PTZ2** was assessed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements. A satisfactory thermal stability was evidenced by TGA: it was found that **PTZ1** exhibits a decomposition temperature at 359 °C,

while, in the case of **PTZ2**, it was observed at 416 °C (Figure 1A). This value is slightly lower than that of Spiro-OMeTAD (424 °C). The thermal transitions of **PTZ1** and **PTZ2** were studied by DSC and the obtained data were compared with those of Spiro-OMeTAD (Figure 1B).[27] During the first heating scan, glass transitions accompanied with enthalpic relaxation were observed for **PTZ1** and **PTZ2** and no melting processes were recorded, indicating that the materials exist in an amorphous state. No crystallization was observed during the cooling and second heating steps, only the glass transition at 74 °C and 135 °C for **PTZ1** and **PTZ2**, respectively. On these bases, it can be stated that **PTZ2** is more stable in the amorphous state with respect to that of Spiro-OMeTAD (glass transition temperature: 125 °C), making it particularly relevant for photovoltaic applications.[15,30]

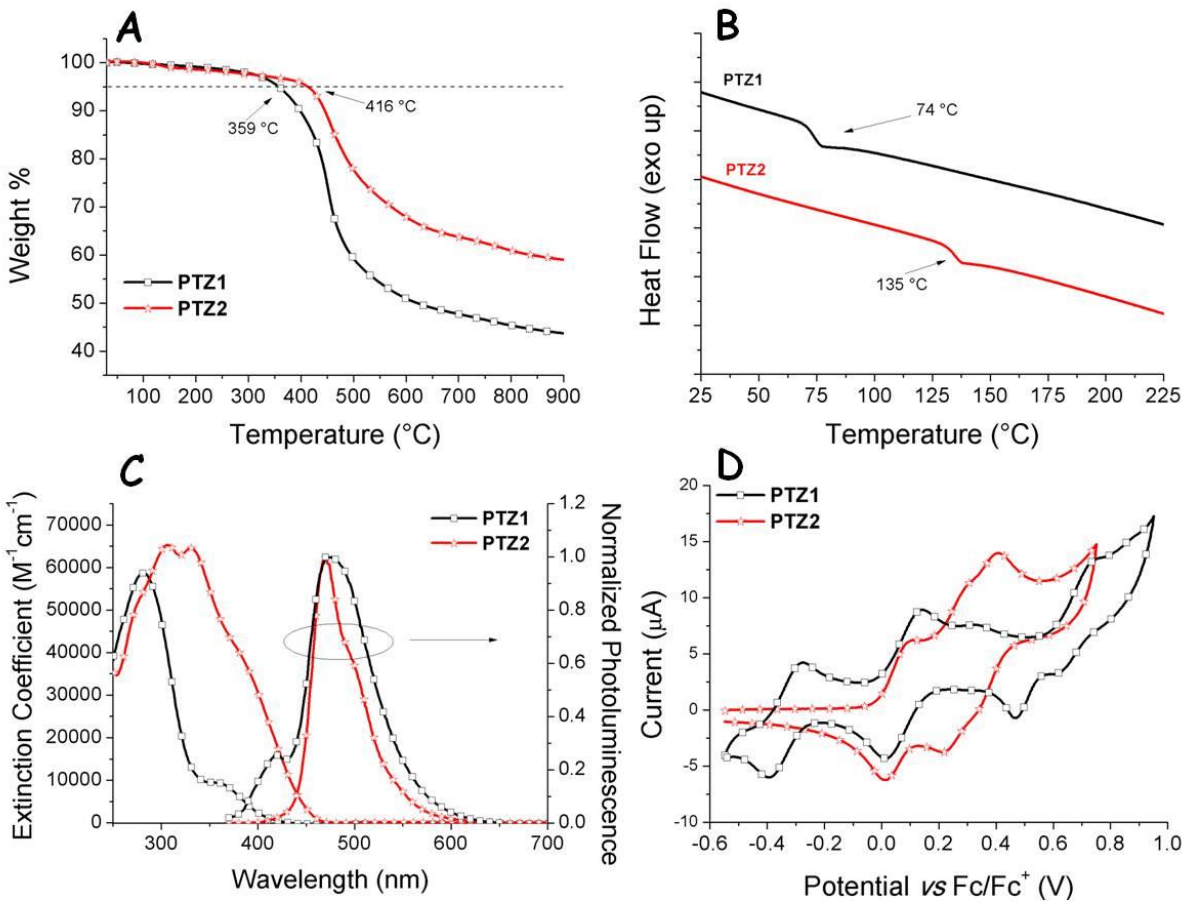


Figure 1. (A) Thermogravimetric analysis of **PTZ1** and **PTZ2** measured with a heating rate of 10 °C min^{-1}. (B) Second DSC heating traces of HTMs previously heating and cooling with a scan rate of 10 °C min^{-1} under nitrogen atmosphere. (C) Absorption spectra of **PTZ1** and **PTZ2** recorded in dichloromethane (3.0×10^{-5} M) and normalized photoluminescence spectra (λ_{ex} = 350 nm). (D) Cyclic voltammograms of HTMs in dichloromethane solutions (1.0×10^{-4} M) using Bu_4NBF_4 (0.1 M) as the supporting electrolyte.

The normalized UV/Vis absorption spectra **PTZ1** and **PTZ2** in CH_2Cl_2 are shown in Figure 1C. Noteworthy, the two absorption profiles are completely different, since **PTZ1** shows an absorption maximum at 282 nm with a shoulder at longer wavelengths, while **PTZ2** exhibits two distinct absorption maxima at 308 nm and 332 nm. The optical band gaps determined from the onset of absorption are 410 nm for **PTZ1** and 449 nm for **PTZ2** and are consistent with the different conjugation extension of the two molecules. Meanwhile, the emission spectra for **PTZ1** and **PTZ2** show fluorescence peaks at 475 nm and 470 nm, respectively.

The oxidation potentials of **PTZ1** and **PTZ2** should be suitable with respect to the perovskite energy levels in order to keep a high open-circuit voltage (V_{OC}) of the device and to warrant an efficient interfacial hole transfer kinetics. The HOMO levels of the new HTMs were determined by cyclic voltammograms (CVs), which are shown in Figure 1D. On the basis of the electrochemical data, the highest-occupied molecular orbitals (HOMOs) of the molecules have been estimated as –4.77 eV for **PTZ1** and –5.15 eV for **PTZ2** in solution, whereas, in the same conditions, Spiro-OMeTAD exhibited a value of –5.02 eV. The higher oxidation potential for **PTZ2** could be favorable for obtaining a high V_{OC} in PSCs, while the relatively lower oxidation potential of **PTZ1** could result in a faster hole transfer between the perovskite layer and the

HTM.[31] The oxidation potential trend is in good accordance with the results of the DFT calculations, corroborating the observation that the HOMO of **PTZ2** is substantially stabilized by the introduction of the phenylene spacers. It is worth noting that the lowest-unoccupied molecular orbitals (LUMOs) of **PTZ1** and **PTZ2** are mainly localized on the phenothiazine core, whereas the electron density of the relevant HOMOs differs significantly. While, in fact, the HOMO of **PTZ1** is mainly localized on the phenothiazine core and part of the two diarylamine groups, the HOMO of **PTZ2** is prevalently distributed (Figure 2) on the three arylamine groups of the structure, despite the dihedral distortion introduced by the presence of the phenylene moieties (Figure S5).

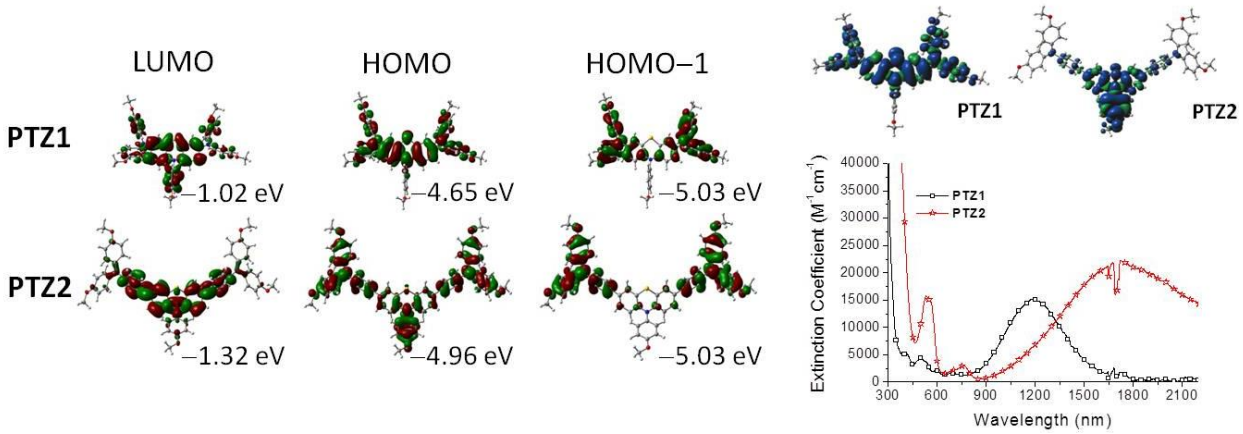


Figure 2. (Left) Isodensity plots of the LUMO, HOMO and HOMO–1 for **PTZ1** and **PTZ2** and the corresponding DFT-calculated energies of HOMO and HOMO–1 at the B3LYP/6-311G(d,p) level of the theory including solvent effects (CH_2Cl_2) using non-equilibrium implementation of the conductor-like polarizable continuum model. (Right) DFT-calculated electron spin density distributions of **PTZ1**$^{\bullet+}$ and **PTZ2**$^{\bullet+}$ (in the doublet state) at the UCAM-B3LYP/6-31G(d,p) level of theory (top) and UV–Vis–NIR spectra of **PTZ1** and **PTZ2** solutions (3.0×10^{-5} M in dichloromethane) upon equimolar addition of the FK209-dopant (bottom).

Although electrochemical measurements and theoretical calculations provide qualitative information about ground-state electron density distribution of the HTMs under investigation, information about hole delocalization within the molecular structure in its radical cation form (p-type doping) is crucial to represent a plausible scenario concerning hole hopping and, more generally, to draw the structure-property relationships needed for the molecular design of new HTMs. To test the response of **PTZ1** and **PTZ2** to the p-type doping, their absorption spectra were measured in the presence of an equimolar amount of the cobalt(III)-complex (FK209), which is used as dopant in the device construction. This experiment not only reveals the effective p-doping of potential HTMs by FK209 for increasing the positive charge carrier density, but also offers a tool to represent the charge distribution in the relevant radical cations. In the case of **PTZ1**, new absorption at 500 nm appears upon chemical oxidation and, more importantly, a relatively strong band crops up at 1194 nm (Figure 2). With the aid of TD-DFT calculations (Figure S6), this low-energy band was attributed to the amine→phenothiazine$^{\bullet+}$ charge transfer transition, suggesting the prevalent charge localization of **PTZ1**$^{\bullet+}$ on the phenothiazine core. In spite of its remarkably higher oxidation potential, also in the case of **PTZ2** the observed spectral changes upon chemical oxidation confirm the p-doping of the molecule by FK209, since two relatively intense bands appear at 539 nm and 1714 nm (Figure 2). The broad lower energy absorption can be reasonably ascribed to amine→amine$^{\bullet+}$ charge transfer transition in the case of **PTZ2**$^{\bullet+}$, as suggested by theoretical calculations (Figure S6), while its electron spin density distribution is prevalently localized on the *p*-anisyl-phenothiazine system (Figure 2). On these bases, we can anticipate that the strong charge localization in **PTZ1** (with respect to **PTZ2**) in its radical cation state may result in a rapid oxidative degradation of the molecule during the device working.

We scrutinized the charge extraction process at the perovskite/HTM interface performing steady-state and time-resolved photoluminescence analyses.[32] When a film of Spiro-OMeTAD, **PTZ1** or **PTZ2** was deposited on the perovskite layer, its steady-state radiative emission was severely quenched, suggesting that our phenothiazine-based compounds efficiently extract the photo-generated holes from the light-absorbing active layer (inset of Figure 3). The quantification of the hole extraction process was carried out by time-resolved analyses (Figure 3) and the radiative lifetimes retrieved with double exponential fitting of the curves are reported in Table S1. The photoluminescence quenching activity is stronger in the case of **PTZ1** in line with its lowest oxidation potential.

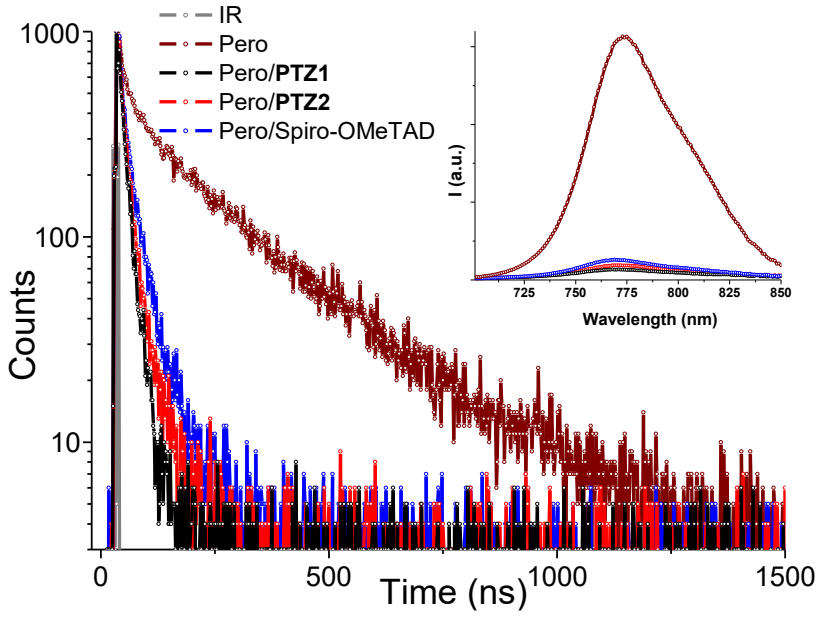


Figure 3. Time resolved photoluminescence measurements of glass/Pero/PMMA (wine line), glass/Pero/**PTZ1** (red line), glass/Pero/**PTZ2** (black line) and glass/Pero/Spiro-OMeTAD (blue line). The decays were collected at the maximum of the perovskite emission band (780 nm, excited at: 645 nm). Inset: photoluminescence spectra of glass/Pero/PMMA (wine line),

glass/Pero/**PTZ1** (red line), glass/Pero/**PTZ2** (black line) and glass/Pero/Spiro-OMeTAD (blue line).

On these bases, we fabricated state-of-the-art PSCs under inert atmosphere, using a lead-based mixed halide (bromine and iodine) and cation (methylammonium, formamidinium and cesium) perovskite, as reported in the most recent literature.[33] Figure 4 displays the current density-voltage (J-V) curves of the PSCs prepared with **PTZ1**, **PTZ2** and Spiro-OMeTAD as HTMs and their energy level diagram in comparison with the other solar cell components. The corresponding device performance parameters are listed in Table 1. It can be observed that **PTZ2** performs similarly to Spiro-OMeTAD device, with a power conversion efficiency (PCE) above 17.5%. The short circuit currents (J_{SC}) are quite similar, while the open circuit voltage (V_{OC}) and the fill factor (FF) are slightly higher for Spiro-OMeTAD and **PTZ2**, respectively. The higher FF of the **PTZ2** can be in part attributed to the higher conductivity of the HTM layer (Figure S7). Conversely, the PSC employing **PTZ1** as HTM showed rather poor performances (PCE = 2.1%), which we rationalized as the result of oxidative degradation due to the low oxidation potential of the molecule (see Supporting Information). It can be noted that J-V curves have been collected with a voltage scan rate of 10 mV/s, which has been proved as an optimum to currently estimate the efficiency of PSCs.[34]

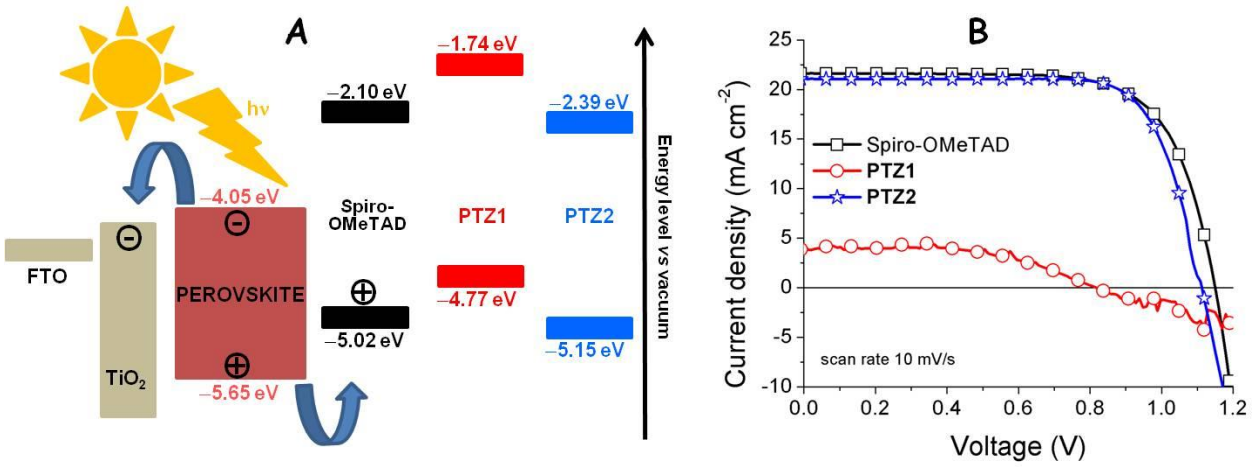


Figure 4. (A) Energy level diagram of the PSC components. (B) Current density-voltage (J-V) curves for a perovskite solar cells prepared with **PTZ1**, **PTZ2** and Spiro-OMeTAD as HTM. The J-V curves were measured at a scan rate of 10 mV/s from forward bias to short circuit condition under AM1.5 simulated solar light illumination. The devices were not preconditioned under light or voltage bias before each J-V scan. The active area was defined by a shadow mask with an aperture of 0.1 cm^2.

Table 1. Photovoltaic parameters extracted from the J-V curves in Figure 3: open-circuit voltage (V_{OC}), short circuit current (J_{SC}), fill factor (FF) and power conversion efficiency (PCE).

HTM	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
PTZ1	0.82	4.2	0.61	2.1
PTZ2	1.11	21.1	0.75	17.6
Spiro-OMeTAD	1.15	21.6	0.71	17.7

In conclusion, we demonstrated that the minor structural difference between **PTZ1** and **PTZ2** dramatically influenced molecular geometry and optoelectronic parameters of relevance for

HTMs in perovskite solar cells. We were able to deeply influence ground-state electron density and electron spin density distribution as well as potential ionization of these HTMs by spacing the dianisyl-amine donor groups from the phenothiazine core by phenylene units. The dramatic difference in photovoltaic performances exhibited by the two phenothiazine-based derivatives can be attributed to the modulation of electron density distribution, which controls the stability of molecules during the charge transfer dynamics at the perovskite/HTM interface. **PTZ2** is among the very few small molecule HTMs that can rival with Spiro-OMeTAD in PSCs. The present work reveals the potential versatility of the phenothiazine building block for the further development of inexpensive and efficient molecular HTMs for perovskite-based solar cells.

ASSOCIATED CONTENT

Supporting Information. Detailed synthetic procedures, characterization of all intermediates and calculations for chemical cost. Details of device construction and characterization.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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