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Supporting Information

Investigation on a Dopant-free Hole Transport Material for Perovskite Solar Cells

Fei Wu,[a†] Baohua Wang,[b,c†] Rui Wang,[a] Yahan Shan,[a] Dingyu Liu,[a] King Young Wong,[c] Tao Chen[*b] and Linna Zhu[*a]

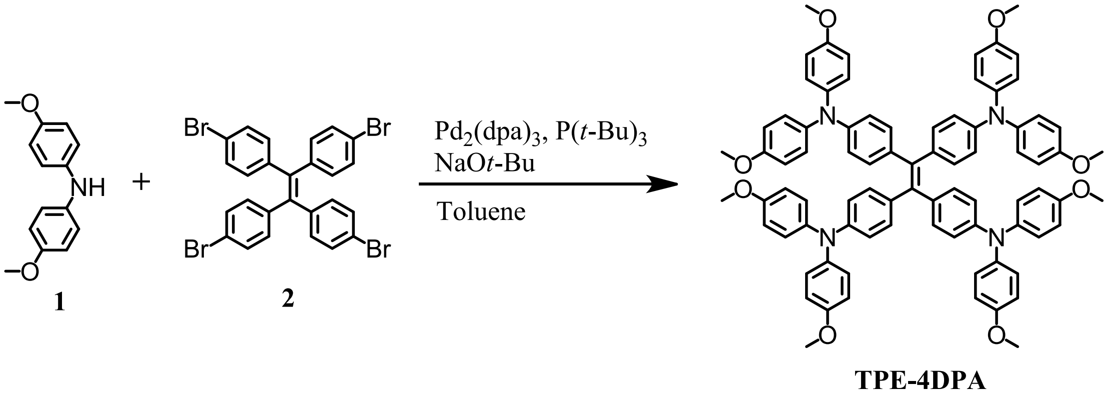
[a]*Chongqing Key Laboratory for Advanced Materials and Technologies of Clean Energy, Faculty of Materials & Energy, Southwest University, Chongqing 400715, P.R. China.*

[b]*Department of Materials Science and Engineering, University of Science and Technology of China, 96 Jinzhai Road, Hefei, 230026, Anhui, China*

[c]*Department of Physics, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China.*

Experimental Details

All starting materials were purchased from commercial suppliers (Sigma-Aldrich, J&K Scientific, and Energy Chemical) and used without further purification. Toluene for synthesis was freshly distilled over Na-K alloy under argon atmosphere prior to use. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a BRUKER AVANCE Ⅲ 600 MHz NMR Instrument in $CDCl_3$, using tetramethylsilane as an internal reference. The HRMS was measured on Thermo Scientific Q Exactive instrument. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. UV-Vis absorption spectra were recorded on a spectrophotometer (UV-2450, Shimadzu). Electrochemical experiments were performed using a CH Instruments electrochemical workstation (model 660A). The experiments were carried out under Ar atmosphere in CH_2Cl_2 solution containing 0.1 mol/L tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) as a supporting electrolyte at a scan rate of 50 mV s^{-1}. The potentials are quoted against the ferrocene internal standard.



Scheme S1. Synthetic routes for TPE-4DPA.

The general synthetic route for TPE-4DPA is depicted in Scheme S1. All of the intermediates were synthesized according to the methods reported in literature. The final compound TPE-4DPA was synthesized by the Buchwald−Hartwig amination reaction between bis(4-methoxyphenyl)amine (1) and 1,1,2,2-tetrakis(4-bromophenyl)ethane (2). The final compound has been fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, MALDI-TOF spectrometry, and Elemental Analysis as well.

Synthesis of 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetrakis(N,N-bis(4-methoxyphenyl)aniline) ***(TPE-4DPA)*** : A mixture of 1,1,2,2-tetrakis(4-bromophenyl)ethene (1.30 g, 2.00 mmol), bis(4-methoxyphenyl)amine (1.95 g, 8.50 mmol), sodium tert-butoxide (1.12 g, 11.6 mmol), tris(dibenzylideneacetone)dipalladium(0) (0.071 g, 0.078 mmol), tritert-butylphosphine (0.025 g, 0.12 mmol) and toluene (20 mL) was refluxed under argon for 18 h.. After cooling, the reaction mixture was extracted with brine and CH_2Cl_2, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using dichloromethane/petroleum (2:1 v/v) as the eluent to give a yellow powder. Yield: 73%. ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm): 7.01 (d, 16H), 6.87 (d, 8H), 6.79 (d, 16H), 6.69 (d, 8H), 3.77 (s, 24H). ^{13}C NMR (150 MHz, CDCl$_3$): δ (ppm): 155.58, 146.54, 141.19, 136.99, 132.19, 126.23, 119.96, 114.61, 55.47. HRMS-ESI *m*/*z*: calcd for 1241.5423, found 1241.5403. Anal. calcd for $C_{82}H_{72}N_4O_8$ (%): C, 79.33; H, 5.85; N, 4.51; Found: C, 79.52; H, 5.79; N, 4.67.

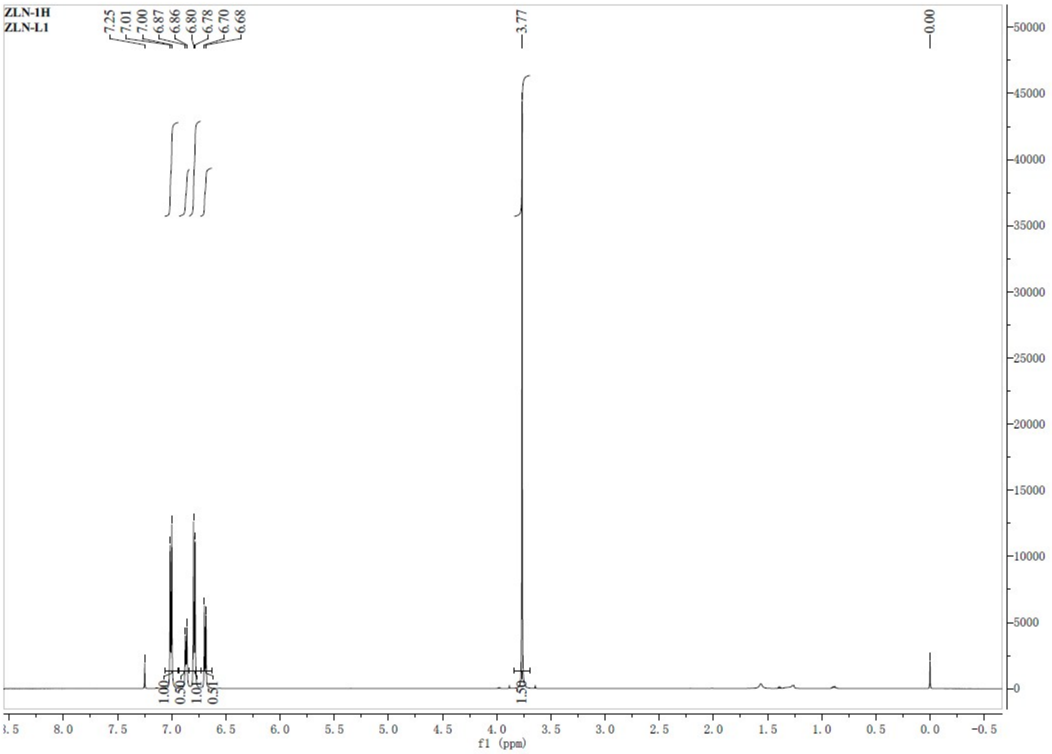


Figure S1. ^{1}H NMR spectrum of TPE-4DPA in CDCl$_3$.

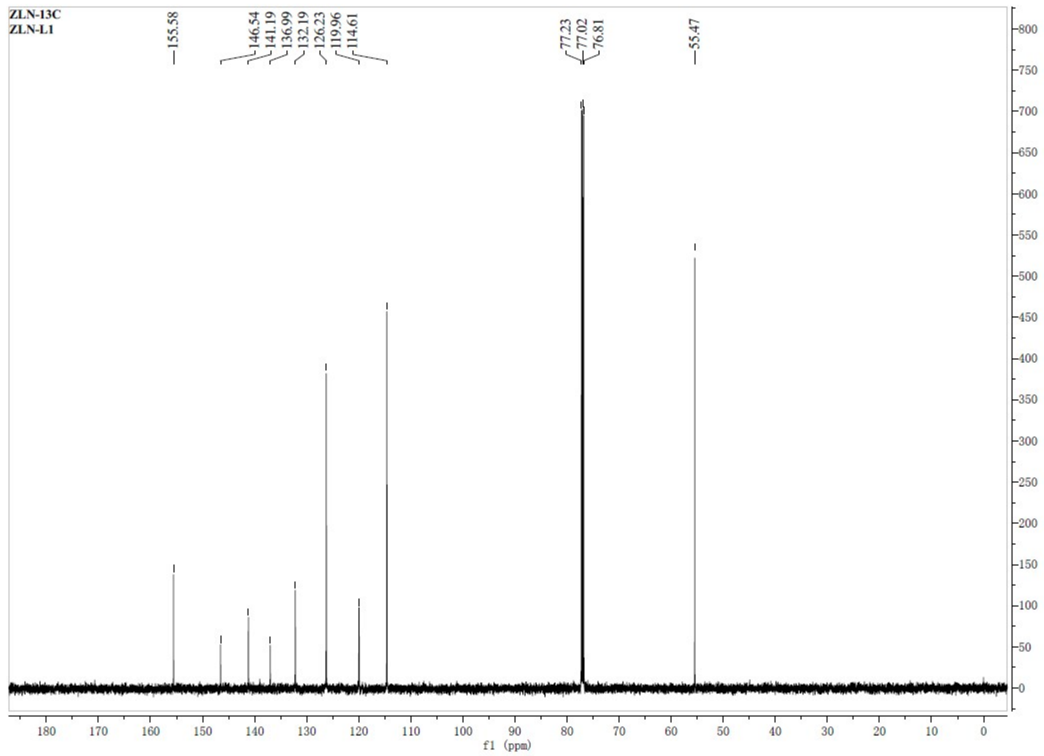


Figure S2. ^{13}C NMR of TPE-4DPA in CDCl$_3$.

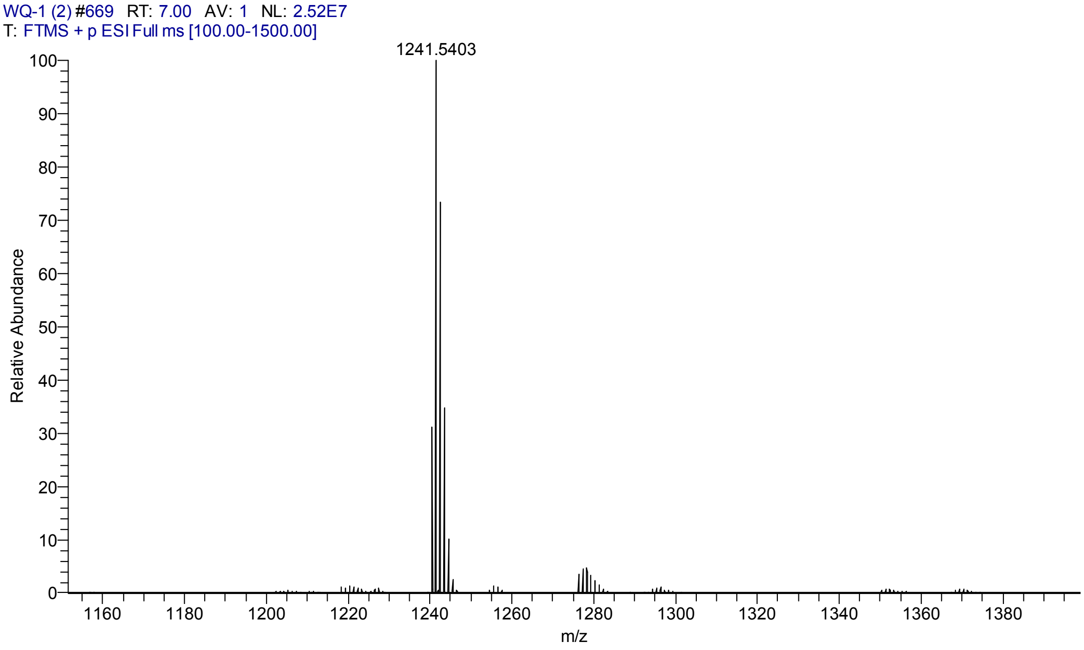


Figure S3. HRMS spectrum of TPE-4DPA.

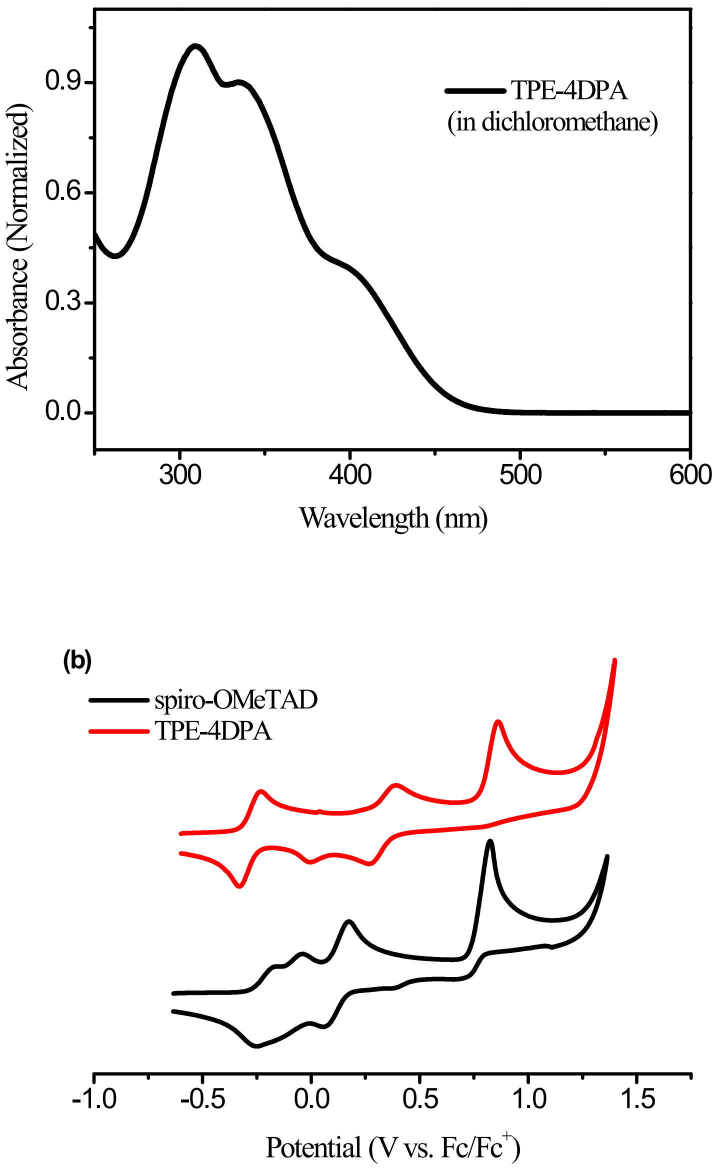


Figure S4. a) UV-vis absorption spectrum of TPE-4DPA in dichloromethane; b) CV curves of TPE-4DPA and Spiro-OMeTAD.

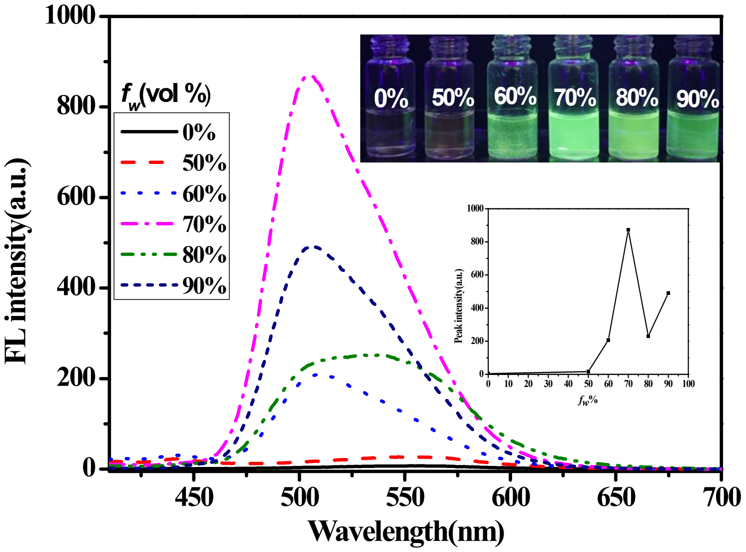


Figure S5. PL spectra of TPE-4DPA in THF/water mixtures. Inset shows plots of the maximum emission intensity versus water fractions. The photo indicates the emission color changes of TPE-4DPA in THF/H2O mixtures, and the photos are taken under the illumination of a 365 nm UV lamp.

The AIE characteristics of TPE-4DPA is studied. Water and THF are chosen as the solvent pair for their miscibility and the photoluminescence (PL) changes are recorded. The PL spectra of TPE-4DPA in THF/H_2O mixtures with different water fractions (f_w) are shown in Figure S5. Apparently, when TPE-4DPA is dissolved in pure THF solution, the PL curve is practically a flat line parallel to the abscissa. The PL intensity began to increase with more than 50 % water content, reflecting the typical features of AIE chromophores. From pure THF solution to THF/H_2O mixture with 70 % water content, the emission intensities increase over 140-fold, which could also be verified by visual observations. When illuminated under 365 nm UV lamp, the THF solution has almost no emission, while intense green emissions were clearly observed from THF/H_2O mixtures.

However, when more water is added, the emissions of TPE-4DPA decrease, probably due to its relatively poor solubility caused by the rigid molecular structures.

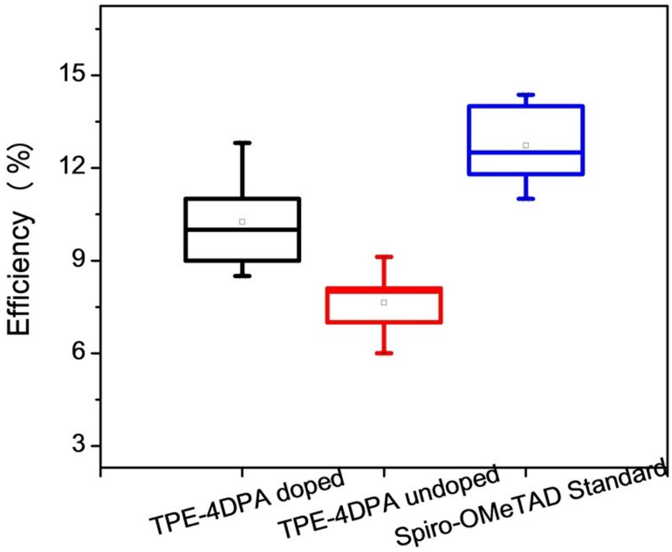


Figure S6. Statistics on the performance of perovskite solar cells using doped and undoped TPE-4DPA and standard spiro-OMeTAD as HTM

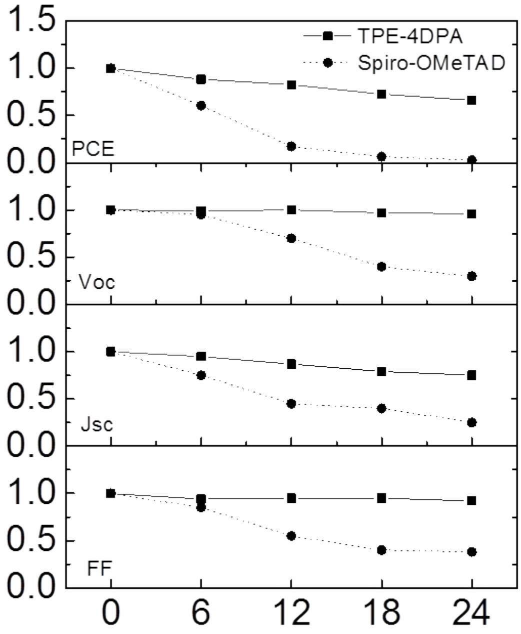


Figure S7 Normalized performance evolution of perovskite using TPE-4DPA and Spiro-OMeTAD as HTMs.

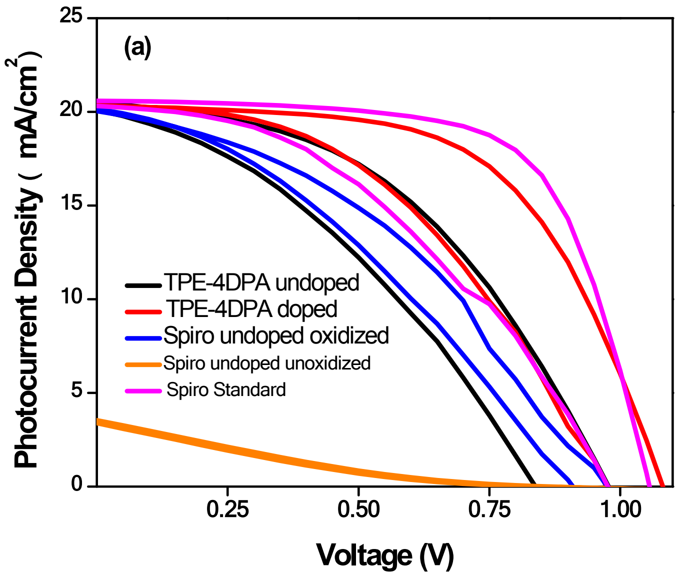


Figure S8. Current-voltage characteristics of the TPE-4DPA and Spiro-OMeTAD based perovskite solar cells in different conditions Current-voltage characteristics of the TPE-4DPA and Spiro-OMeTAD based perovskite solar cells under different conditions (in different scan directions).