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Application of phenonaphthazine derivatives as hole-transporting materials for perovskite solar cells

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ABSTRACT

Two electron-rich, solution-processable phenonaphthazine derivatives, 5,12-bis{*N*-[4,4′-bis-(phenyl) -aminophen-4′′-yl]}-phenonaphthazine (BPZTPA) and 5,12-bis{*N*-[4,4′-bis(methoxy-phenyl)aminophen-4′′-yl]} -phenonaphthazine (MeO-BPZTPA) have been designed and employed in the fabrication of perovskite solar cells. BPZTPA and MeO-BPZTPA exhibit excellent thermal stabilities, hole mobilities ($\sim 10^{-4}$ cm^2/(V s)) and suitable HOMO levels (−5.34 and −5.29 eV, respectively) relative to the valence band of the $CH_3NH_3PbI_3$ and Au work function, showing their potential as alternative hole-transporting materials (HTMs). Meanwhile, the corresponding mesoporous TiO_2/$CH_3NH_3PbI_3$/HTM/Au devices are investigated, and the best power conversion efficiency of 10.36% has been achieved for MeO-BPZTPA without using *p*-type dopant.

1. Introduction

Perovskite solar cells (PSCs) have shown tremendous advancement in power conversion efficiency (PCE) starting from 3.8% to 20.2%, comparable to conventional inorganic solar cells (i.e. CdTe, CIGS) [1–4]. In PSCs, hole-transporting layer plays a key role in facilitating hole transportation from perovskite to the electrode and inhibiting back electron transfer as well [5]. 2,2′,7,7′-Tetrakis(*N*,*N*′-di-*p*-methoxy-phenylamine)-9,9′ -spirobifluorene (*spiro*-OMeTAD) has been widely used as the hole-transporting materials (HTMs) for efficient PSCs, however, its expensive price and uncertain stability are challenges for the PSCs' future. Recently, different kinds of HTMs have been developed, including inorganic HTMs, polymeric HTMs and small molecular HTMs. Inorganic HTMs (CuI and CuSCN) have drawn much attention due to their high hole mobilities and low production cost [2]. Organic HTMs appear to be good candidates for PSCs. Polymeric HTMs, such as conjugated PTAA (polytriarylamine) [4], DR3TBDTT [6], have also shown the competitive performances in PSCs. However, small molecular HTMs have advantages of their convenient purification, controllable molecular structures and relatively high efficiency [7]. Such HTMs including DOR3T-TBDT [8], DMFA-FA [9] and PST1 [3] etc., have shown PCEs more than 13%. From a commercialization viewpoint, these compounds deserve extensive investigation to reduce the high cost of PSCs.

As an important type of organic HTMs, triphenylamine (TPA) derivatives not only have the advantages of high hole mobility and good thermal stability, but also their energy levels can be adjusted reasonably by changing the molecular structure. To date, many TPA-based HTMs for PSCs have been widely reported [10–13]. For example, Mhaisalkar and Grimsdale fabricated the PSCs with HTMs containing thiophene core with TPA side groups, presenting 15.4% PCE [14]. Li and Meng reported a series of HTMs containing TPA moiety for PSCs with PCEs over 11% [5,15–18].

Encouraged by these reports, we developed two alternative HTMs with phenonaphthazine core and TPA side groups, namely BPZTPA and MeO-BPZTPA, which were prepared using a simple C–N coupling reaction versus the widely used *spiro*-OMeTAD. The molecular structures and synthetic route for the HTMs are depicted in Scheme 1. The introduction of electron-rich phenonaphthazine unit is to adjust their HOMO levels to match well with that of perovskite and Au. On the other hand, the symmetrical structure is expected to enhance π–π stacking interactions, which could be beneficial for high hole mobility and enhancing the lifetime of a

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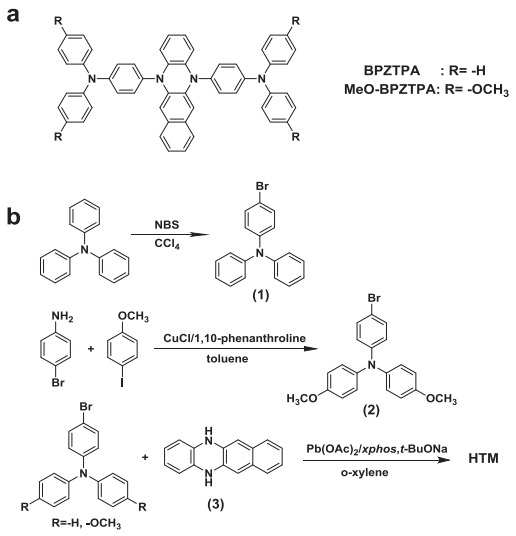

Scheme 1. (a) Molecular structures of BPZTPA and MeO-BPZTPA and (b) synthetic route for BPZTPA and MeO-BPZTPA.

charge-separated excited state [19]. In this work, 10.36% of PCE has been achieved for the device with MeO-BPZTPA.

2. Experimental

2.1. Materials

Starting materials were all available commercially and used without further purification if not mentioned specially. PbI_2 was obtained from Sigma-Aldrich. Hydroiodic acid (AR, 45 wt% in water) and methylamine (AR, 27% in methanol) were purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium *tert*-butoxide (*t*-BuONa) was supplied by Aladdin. *N,N′*-dimethylformamide (DMF) and chlorobenzene are got from Alfar Aesar. *Spiro*-OMeTAD was obtained from Luminescence Technology Corp. 2-dicyclohexylphosphino-2′,4′,6′-trisopro -pylbiphenyl (*xphos*) was purchased from Beijing HWRK Chem Co. Palladium acetate, *p*-bromoaniline, 4-methoxyiodobenzene, triphenylamine, 2,3-Dihydroxynaphthalene and *o*-phenylenediamine were got from Tianjin Xiensi Biochemical technology Co.LTD. Other reagents were supplied by Tianjin Guangfu Fine Chemical Research Institute, such as *N*-Bromosuccinimide (NBS), 1,10-phenanthroline, cuprous chloride and *o*-xylene. $CH_3NH_3I_3$ were synthesized according to literatures [20].

2.2. Measurements

^1H and ^{13}C NMR spectra were recorded with an INOVA 400 MHz spectrometer (Varian, USA) and AVANCE III 600 MHz spectrometer (Bruker, Switzerland). Mass spectra (MS) were performed on a Autoflex tof/tof III mass spectrometer (Bruker, Germany). UV–visible spectra of the HTMs in tetrahydrofuran (THF) solutions (1×10^{-5} mol/L) were recorded with Thermo Evolution 300 UV–vis spectrometer (Thermo Electron, USA) in the 200–800 nm wavelength range at room temperature. Thermo gravimetrical analyses (TGA) were recorded with TA Q500 thermo gravimetric apparatus (TA Instruments, USA) at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was conducted on TA Q20 Instrument (TA Instruments, USA) at a heating rate of 10 °C/min under nitrogen atmosphere. Photoemission yield spectroscopy (PYS) instrument was PYS-202 ionization energy test system (Sumitomo Heavy Industries, Japan) at the voltage of 100 V, waiting time of 1 s and energy range from 4.0 to 8.5 eV. The time-of-flight (TOF) measurements were performed on TOF401 (Sumitomo Heavy Industries. Ltd. Japan), for which the samples were prepared through spin coating using a structure ITO/HTM (about 1 μm)/Al (150 nm) with an active area of $3 \times 10\ mm^2$. Surface morphology of the $TiO_2/CH_3NH_3PbI_3$/HTM/Au film was obtained using a scanning electron microscope (SEM, XL30S-FEG, FEI, USA). The film thickness was performed on a surface profiler (P-6, KLA-Tencor, USA).

2.3. Synthesis of HTMs

N,N′-diphenyl-4-bromoaniline (1): Triphenylamine (7.41 g, 30.00 mmol) and NBS (5.61 g, 31.50 mmol) were dissolved in 80 mL CCl_4. The solution was heated to reflux for 5 h. The precipitated succinimide was filtered while hot, and the solvent was evaporated from the solution, getting light yellow oil. After recrystallization from dry ethanol, the desired product was obtained as a white powder, yielding 6.81 g (70%). Mp: 103–106 °C. ^1H NMR (600 MHz, $CDCl_3$) δ: 7.35–7.29 (m, 2H), 7.24 (d, $J = 7.6$ Hz, 4H), 7.06 (d, $J = 8.1$ Hz, 4H), 7.04–6.96 (m, 2H), 6.93 (dd, $J = 10.7$, 3.7 Hz, 2H).

(4-Bromo-phenyl)-di-p-methoxyaniline (2): In a 500 mL four-necked flask equipped with a mechanical stirrer, thermometer and water segregator, all under an argon atmosphere, 4-methoxyiodobenzene (29.30 g, 125.00 mmol), *p*-bromoaniline (8.60 g, 50.00 mmol) and 1,10-phenanthroline (1.80 g, 10.00 mmol) were added. 300 mL toluene was added and the reaction mixture was then heated to 100 °C, at which point potassium hydroxide flake (22.40 g, 400.00 mmol) and cuprous chloride (1.00 g, 10.00 mmol) were added. Then the mixture was heated to reflux for 12 h. The mixture was cooled to room temperature and extracted with ethyl acetate. The organic phase was combined and dried by $MgSO_4$. After filtrating the $MgSO_4$ and removing the solvent by reduced pressure distillation, the residue was purified by column chromatography on silicagel eluting with petroleum ether to give white product 11.41 g (59%). ^1H NMR (400 MHz, $CDCl_3$) δ: 7.27–7.17 (m, 2H), 7.03 (d, $J = 8.7$ Hz, 4H), 6.80 (dd, $J = 12.2$, 8.8 Hz, 6H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.08, 147.94, 140.58, 131.78, 126.59, 122.00, 114.81, 112.38, 55.50.

Phenonaphthazine (3): 2,3-dihydroxynapthalene (10.00 g, 62.50 mmol) and 1,2-phenylenediamine (6.75 g, 62.50 mmol) were placed into a round bottom flask under nitrogen atmosphere. 60 mL *N,N′*-dimethylaniline was added and mixture was heated to reflux for 4 h. After cooling to room temperature, suitable toluene was added and solid was collected by vacuum filtration. After washing with ethanol (100 mL) and hexane (50 mL) repeatedly, the product was dried under vacuum to yield 9.20 g (64%) of light yellow lamellar crystal. ^1H NMR (400 MHz, DMSO) δ: 8.11 (s, 2H), 7.16 (dd, $J = 5.9$, 3.3 Hz, 2H), 6.90 (s, 2H), 6.34 (s, 2H), 6.23 (s, 2H), 6.17 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ: 134.95, 132.88, 131.25, 125.23, 123.26, 120.64, 112.13, 104.72.

BPZTPA: Phenonaphthazine (0.93 g, 4.00 mmol), *N,N′*-diphenyl-4-bromoaniline (2.85 g, 8.80 mmol), *t*-BuONa (0.96 g, 10.00 mmol), *xphos* (0.26 g, 0.50 mmol) and *o*-xylene (120 mL) were all placed into a round bottom flask under a nitrogen atmosphere. After the mixture was dissolved, palladium acetate (0.03 g, 0.14 mmol) was added into flask quickly. Then mixture was heated to reflux for 6 h. When cooled to room temperature and added 200 mL water, the reaction liquid was extracted ethyl acetate. The organic phase was combined and dried by $MgSO_4$, leaving brown sticky liquid. After removing the solvent by reduced pressure distillation, the residue was purified by column chromatography on silicagel eluting with CH_2Cl_2:petroleum ether (1:6) to give yellow product 1.40 g (49%). ^1H NMR (400 MHz, DMSO) δ 7.59 (s, 2H), 7.39 (d, $J = 6.7$ Hz, 6H), 7.32 (s, 4H), 7.21 (d, $J = 7.0$ Hz, 6H), 7.13 (d, $J = 7.2$ Hz, 6H), 7.06 (s, 4H), 7.00 (s, 2H), 6.85 (s, 2H), 6.42 (s, 2H), 5.76 (s, 4H). MS (MALDI-TOF): *m/z* calcd for $C_{52}H_{38}N_4$: 718.31 [M^-]; found [M^-] 718.29.

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