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Synthesis and characterization of tetratriphenylamine Zn phthalocyanine as hole transporting material for perovskite solar cells

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ABSTRACT

A soluble Zn phthalocyanine has been synthesized by tetra-substitution with triphenyl amine. This substance is functional as hole transporting material combined with organometal halide perovskite solar cells. The efficiency was slightly increased compared with previously studied insoluble copper phthalocyanine indicating that it is possible to make fully solution processed perovskite solar cells based on phthalocyanine as hole transporter.

1. Introduction

Solution-processed hybrid perovskite solar cells (PSCs) have attracted considerable attention as alternative candidates for thin-film solar cells due to their excellent absorption in the visible and near-infrared region, charge transport properties, direct band gap and particularly their easy processability (Franckevicius et al., 2015; Liu et al., 2015; Singh and Nagarjuna, 2014; Burschka et al., 2013; Bi et al., 2013; Lee et al., 2012). Since the first report in 2009 with power conversion efficiencies (PCEs) of 3.1% for $CH_3NH_3PbBr_3$ and 3.81% for $CH_3NH_3PbI_3$, research on the use of perovskites as light absorbers in thin film solar cells has been intensified (Kojima et al., 2009; Im et al., 2011). Over the last 3–4 years, solid-state organo-lead halide thin film solar cells have been developed rapidly and an unexpected break-through has been achieved (Yang et al., 2015; Jeon et al., 2015; Liu and Kelly, 2014; Zhou et al., 2014; Liu et al., 2013). The efficiencies of PSCs are comparable with thin film solar cells (CdTe and GaAs). PSCs with and without hole-transporting materials (HTMs) have been reported in the literature. The PSCs without HTMs exhibit a PCE of over 10% (Shi et al., 2014). In contrast, the corresponding devices with HTMs can exhibit much higher efficiencies of over 20% (Yang et al., 2015). These high performances are due to the development of efficient processing and fabrication conditions of the perovskite layer.

In most of these devices, 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamino)-9,9′-spirobi-fluorene (spiro-OMeTAD) was used as the HTM due to its excellent performance in solid-state dye-sensitized solar cells. Even though, PSCs using spiro-OMeTAD as HTM showed excellent photon-to-current conversion efficiencies (PCE), they suffer from high cost and tedious synthetic protocols, low hole mobility and low conductivity, which limit large scale applications (Hsu et al., 2012; Docampo et al., 2014). In the meantime, several new molecular materials have been designed as alternative HTMs showing PCEs in the range of 12–17% (Choi et al., 2015; Gratia et al., 2015; Swetha and Singh, 2015; Cheng et al., 2015; Lv et al., 2014; Liu et al., 2014). First, a few polymer HTMs were successfully applied, such as poly(3-hexylthiophene) (P3HT), poly-triarylamine (PTAA) and poly-[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta-[2,1,-*b*:3,4-*b*′] (PCPDTBT) (Bi et al., 2013; Heo et al., 2013; Cai et al., 2013). For instance, PTAA showed the highest PCEs up to 12% in mesoscopic TiO_2-based devices and above 15% in planar heterojunction devices (Heo et al., 2013). In addition, low molecular weight amorphous HTMs are also good candidates due to their easy purification and

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good film forming properties, simply processed by coating techniques. These hole transporters resulted in high conversion efficiencies of 11–16%. Finally, in addition to organic HTMs, p-type inorganic semiconductors (i.e., CuI, CuSCN, and NiO) have also been studied (Li et al., 2015; Hossain et al., 2015).

We have recently reported Boron subphthalocyanine (SubPc) as HTM for perovskite solar cells and achieved a PCE of 6.6% with reasonably good stability due to the temporary protection of the SubPc layer on the underlying perovskite layer (Sfyri et al., 2015). The majority of HTMs do not show absorption in the visible and NIR region and some polymers, like P3HT absorb visible light and may participate in the sensitization process, even though, in the presence of organometal halide perovskites this type of sensitization is of minor importance. In this regard, phthalocyanines offer good alternatives as HTMs based on thermal, optical and electrochemical properties. Phthalocyanines are tetrapyrrolic cyclic organic molecules, which can find applications in several fields: artificial photosynthesis, photocatalysis for degradation of organic pollutants and as sensitizers for dye-sensitized solar cells, etc. (Thomas, 1990). Torres, Nazeeruddin and coworkers recently reported a non-aggregated Zn(II)octa(2,6-diphenylphenoxy) phthalocyanine (TT80) as HTM for solution processed perovskite solar cells with (bis(trifluoromethane)sulfonimide) lithium salt (LiTFSI) and *tert*-butyl pyridine additives and achieved a PCE of 6.7% (Ramos et al., 2015). Our group also used copper phthalocyanine as HTM by vacuum deposition technique and showed a PCE of around 5% (Kumar et al., 2015; Sfyri et al., 2016) using cells without efficiency optimization additives. In continuation of our efforts towards the design of phthalocyanine based HTMs, we propose a tetratriphenylamine substituted Zinc(II) phthalocyanine (**TPA-Pc**) for PSCs. This is a solution processed material, which simplifies cell assembly. In the present manuscript, we describe synthesis, characterization and device construction of PSCs based on TPA-Pc.

2. Experimental section

2.1. Materials

All materials were purchased from Aldrich, unless otherwise specified, and they were used as received. FTO glasses of 8 ohm/square were purchased from Pilkington.

2.2. Synthesis of 4,4′-diphenylamino-biphenyl-3,4-dicarbonitrile

This ligand was synthesized according to the literature reported procedure (Giribabu et al., 2011) (see Scheme 1).

2.3. Synthesis of TPA-Pc

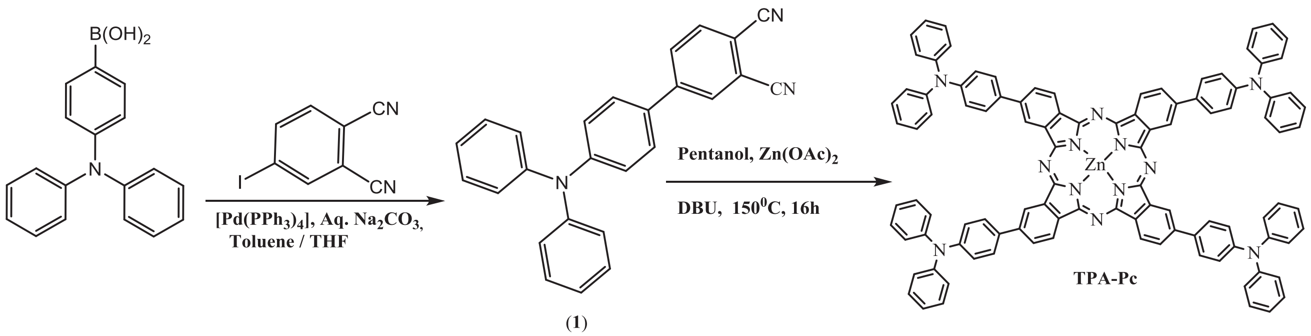
A mixture of anhydrous zinc acetate (1.90 g, 10 mmol), 4,4′-di phenylamino-biphenyl-3,4-dicarbonitrile (1.70 g, 5 mmol), 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, catalytic amount) and dry 1-pentanol (5 ml) was refluxed at 150 °C for 16 h under a nitrogen atmosphere. After cooling, the solution was precipitated by addition of methanol, filtered and dried. The obtained solid material was subjected to silica gel column chromatography and eluted with dichloromethane. The green coloured band was collected and recrystallized from methanol, to get the desired compound in 70% yield. Elemental analysis of Anal. Calcd. For $C_{104}H_{68}N_{12}Zn$ % (1551.11): C, 80.53; H, 4.42; N, 10.84. Found: C, 80/50; H, 4.43; N, 10.80. MALDI-TOF: ($C_{104}H_{68}N_{12}Zn$) m/z: 1550 (calcd. for $[M]^+$). ^1H NMR (500 MHz, $CDCl_3$): δ 7.68–7.63 (m, 4H), 7.55–7.54 (d, $J = 8.3$ Hz, 8H), 7.45 (s, 8H), 7.43 (d, $J = 1.7$ Hz, 8H), 7.35–7.29 (m, 40H). FT-IR (KBr) ν_{max} 3030, 2922, 1278 and 1099 cm^{-1}.

2.4. Synthesis of methyl ammonium iodide

Methylammonium iodide was synthesized by the previously reported procedure (Sfyri et al., 2015) by reacting 27.8 ml of methylamine (40 wt% in H_2O) and 30 ml of hydroiodic acid (57 wt% in water) at 0 °C for 2 h. Solid residue was obtained in a rotary evaporator by carefully removing the solvents at 40 °C. The yellow crude product methyl ammonium iodide (CH_3NH_3I) was washed with diethyl ether several times, and then finally recrystallized from a mixed solvent of diethyl ether and ethanol. After filtration, the pure solid was collected and dried at 70 °C in a vacuum oven overnight.

2.5. Fabrication of perovskite solar cells

FTO-coated glass substrates were cut in the dimensions of 1 × 3 cm. One third of the conductive layer was removed using zinc powder and hydrochloric acid. Then they were washed with detergent, rinsed several times with distilled water and subsequently with ethanol in an ultrasonic bath, finally dried under air stream. A compact thin layer of TiO_2 was first deposited by aerosol spray pyrolysis using a solution of 0.2 M Diisopropoxytitanium bis (acetylacetonate) in EtOH. After spraying, the sample was heated for 1 h at 500 °C. Subsequently, a mesoporous TiO_2 layer composed of titania paste made of P25 nanoparticles was spin coated at 4000 rpm for 30 s and then heated for 15 min at 500 °C. The thickness of this layer is approximately 500 nm. Mesoporous TiO_2 layer was then treated with $TiCl_4$ by dipping into a solution made of 0.04 M $TiCl_4$ in H_2O for 30 min, then copiously rinsing and finally calcining at 500 °C. Active perovskite layer was deposited on the thus prepared titania film by modifying published procedures (Etgar et al., 2012). A precursor solution was made by mixing 230 mg $PbCl_2$ with 394 mg methyl ammonium iodide in 1 ml of DMF. The atomic ratio Pb:Cl:I in the precursor solution was thus 1:2:3. The solution was kept under stirring for about half an hour and then it was deposited by spin coating at 3000 rpm for 60 s in a dry box where relative humidity was 15–20%. Heating at 80 °C



Scheme 1. Synthesis of TPA-Pc.