ARTICLES •



March 2017 Vol.60 No.3:423–430 doi: 10.1007/s11426-016-0393-5

# Efficient perovskite solar cells employing a solution-processable copper phthalocyanine as a hole-transporting material

Xiaoqing Jiang<sup>1</sup>, Ze Yu<sup>1\*</sup>, Jianbo Lai<sup>1</sup>, Yuchen Zhang<sup>1</sup>, Ning Lei<sup>2</sup>, Dongping Wang<sup>2\*</sup> & Licheng Sun<sup>1,3\*</sup>

<sup>1</sup>State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology, Dalian 116024, China

<sup>2</sup>College of Chemical Engineering, Shenyang University of Chemical Technology, Shenyang 110142, China

<sup>3</sup>Department of Chemistry, School of Chemical Science and Engineering, KTH Royal Institute of Technology, Stockholm 10044, Sweden

Received September 28, 2016; accepted November 9, 2016; published online February 14, 2017

The development of alternative low-cost and high-performing hole-transporting materials (HTMs) is of great significance for the potential large-scale application of perovskite solar cells (PSCs) in the future. Here, a facilely synthesized solution-processable copper tetra-(2,4-dimethyl-3-pentoxy) phthalocyanine (CuPc-DMP) via only two simple steps, has been incorporated as a hole-transporting material (HTM) in mesoscopic perovskite solar cells (PSCs). The optimized devices based on such a HTM afford a very competitive power conversion efficiency (PCE) of up to 17.1% measured at 100 mW cm<sup>-2</sup> AM 1.5G irradiation, which is on par with that of the well-known 2,2',7,7'-tetrakis(*N*,*N*'-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) (16.7%) under equivalent conditions. This is, to the best of our knowledge, the highest value reported so far for metal organic complex-based HTMs in PSCs. The advantages of this HTM observed, such as facile synthetic procedure, superior hole transport characteristic, high photovoltaic performance together with the feasibility of tailoring the molecular structure would make solution-processable copper phthalocyanines as a class of promising HTM that can be further explored in PSCs. The present finding highlights the potential application of solution processed metal organic complexes as HTMs for cost-effective and high-performing PSCs.

solution-processable copper phthalocyanine, metal organic complex, low-cost, hole-transporting material, perovskite solar cells

Citation: Jiang X, Yu Z, Lai J, Zhang Y, Lei N, Wang D, Sun L. Efficient perovskite solar cells employing a solution-processable copper phthalocyanine as a hole-transporting material. Sci China Chem, 2017, 60: 423–430, doi: 10.1007/s11426-016-0393-5

## **1** Introduction

Our society is facing a big technological challenge, developing abundant and renewable energy sources to meet the rapidly increasing energy demands and to replace traditional fossil fuels strongly correlated with climate and environmental concerns [1,2]. Among the various renewable alternatives, solar energy is unarguably the largest exploitable sources that potentially could be scaled up to meet the rising energy demands due to the world population growth and economic developments. A very promising approach to capture solar energy is utilizing photovoltaic (PV) cells, which directly convert solar energy to electrical energy. While the current PV market is still dominated by the silicon-based solar cells, next generation solar cell technologies fabricated through solution-processable techniques have emerged as cost-effective alternatives to replace conventional solar cells [3].

<sup>\*</sup>Corresponding authors (email: ze.yu@dlut.edu.cn; dpwang2015@163.com; lichengs@kth.se)

<sup>©</sup> Science China Press and Springer-Verlag Berlin Heidelberg 2017

Recently, solution-processable organic-inorganic halide perovskites with the composition ABX<sub>3</sub> (A=CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> (MA), NH=CHNH<sub>3</sub><sup>+</sup> (FA) or Cs<sup>+</sup>; B=Pb or Sn; X=Cl, Br, I) have received intense research attention as light absorbers in solid-state solar cells due to some of their excellent properties, such as broad spectral absorption range, large absorption coefficient, direct band gaps, high charge carrier mobility and diffusion length [4–9]. The power conversion efficiency (PCE) of perovskite solar cells (PSCs) has been rapidly increased from a mere 3.8% in 2009 [10] to the current record of 22.1% in April 2016 [11]. Considering the high efficiency and facile fabrication process, PSC has shown a great promise as a competitive low-cost solar cell to rival its conventional inorganic counterparts.

The state-of-the-art PSC devices routinely employed holetransporting materials (HTMs), which play key roles in extracting and transporting the photo-generated holes from the perovskites to the metal electrodes, and thus minimize undesired recombination losses at the interfaces. Hence, searching for an efficient HTM has been one of the hottest research topics in PSCs. A wide range of HTMs have been developed and incorporated into PSCs, including small molecular hole-conductors [12-16], conducting polymers [17-21] and inorganic p-type semiconductors [22-24]. Amongst these HTMs being developed, spiro-OMeTAD has been the most widely used HTM and has shown PCE of over 20% in conventional PSC structures [25]. However, the synthesis of spiro-OMeTAD is rather complicated, involving five reaction steps that require low temperature (-78 °C), and sensitive (n-butyllithium or Grignard reagents) and aggressive (Br<sub>2</sub>) reagents. Moreover, high-performing devices require high-purity sublimation-grade spiro-OMeTAD [26]. As a consequence, the price of spiro-OMeTAD is considerably expensive (more than 10 times that of gold) [22], which significantly impedes its largescale application in the future. It is therefore of great importance to explore alternative HTMs exhibiting comparable or even superior efficiencies relative to the widely used HTM spiro-OMeTAD, but with more easily synthetic processes and thus lower production costs.

With this regard, numerous novel small molecular holeconductors with facile synthesis routes have been developed in PSCs [15,27]. However, the overall efficiencies of these small molecular HTMs that can compete with the best efficiencies spiro-OMeTAD reached have been rare. Only few examples with two synthetic steps have shown efficiencies beyond 16%, which can rival the well-known spiro-OMeTAD [26,28–30].

It can be easily noticed that alternative high-performing HTMs with facile synthesis routes developed so far have been almost exclusively dominated by small molecular hole-conductors. Metal organic complex copper phthalocyanine (CuPc) has been widely used as a p-type semiconductor in organic thin film transistors and solar cells due to its flexibility, high hole mobility, excellent thermal and chemical stability [31,32]. More intriguingly, the synthesis of CuPc is quite simple, giving rise to rather low production cost. Pristine CuPc has been successfully applied into PSCs [33-35], showing excellent efficiencies of 16% together with excellent long-term durability [35]. CuPc possesses a large  $\pi$ -conjugated system which makes it difficult to dissolve in most commonly used organic solvents. Therefore, this complex has to be thermally evaporated under high vacuum in these PSC devices. The thermal evaporation method is by no means a desirable option, since it is highly energy-consuming, thus causing additional expenditure that counteracts the merit of low production cost for CuPc. The solubility of CuPc can be improved by introduction of substituents on the periphery, thus to some extent increasing the distance between the 18p electron conjugated system of CuPc and facilitating the solubility [36]. However, PSC devices employing solution-processable based CuPcs as HTMs have been rare up till now. Seok and co-workers [37] introduced soluble tert-butyl substituted CuPc as an efficient dopant for po-spiro-OMeTAD HTM, which resulted in a PCE of 19.4% for the spiro-OMeTAD based HTM (4.8 wt% doping amount). Very recently, Lianos et al. [38] reported n-butyl substituted CuPc as a solution-processable HTM in PSCs in combination with mixed-halides perovskites, which achieved a PCE of 8.5%.

Herein, solution-processable copper tetra-(2,4-dimethyl-3-pentoxy) phthalocyanine (CuPc-DMP, Figure 1) has been synthesized (Scheme 1) and incorporated as a HTM in mesoscopic PSCs based on a (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> light absorber. PSC device using CuPc-DMP affords a very competitive PCE of up to 17.1% at 100 mW cm<sup>-2</sup> illumination (AM 1.5G), which is on par with that of spiro-OMeTAD (16.7%) measured under the same conditions. It is worth emphasizing here that the synthesis of this new HTM only involves two simple steps from commercially available starting materials. This is the first example in PSCs employing a metal organic complex-based HTM yielding an efficiency reaching 17%.



Figure 1 Chemical structure of CuPc-DMP.



Scheme 1 Synthetic route of CuPc-DMP.

## 2 Experimental

#### 2.1 Materials

PbI<sub>2</sub> (>98%) was from TCI (Japan); PbBr<sub>2</sub> (99%), HI (48% in water), HBr (48% in water), CH<sub>3</sub>NH<sub>2</sub> (33 wt% in absolute ethanol), Formamidine acetate (99%), 4-tert-butylpyridine (TBP, 96%), Titanium diisopropoxide bis(acetylactonate) 75% in isopropanol (Tiacac) and Li-bis(trifluoromethanesulfonyl) imide (LiTFSI) were from Sigma-Aldrich (USA); and mesoporous-TiO<sub>2</sub> paste (18NR-T) were from Dyesol (Australia). All chemicals used as received unless otherwise stated. NH<sub>2</sub>CH=NH<sub>2</sub>I (FAI) was synthesized according to a reported procedure [39]. 30 mL hydroiodic acid (57% in water) and 15 g formamidine acetate were reacted at 0 °C for 2 h with stirring. The precipitates were recovered by evaporating the solutions at 50 °C for 1 h. The products were dissolved in ethanol, recrystallized using diethyl ether, and finally dried at 60 °C in a vacuum oven for 24 h. Similarly, CH<sub>3</sub>NH<sub>3</sub>Br (MABr) were prepared by reacting hydrobromic acid (48 wt% in water) with methylamine according to a reported procedure [25]. The mixed-cation perovskite precursor solution of  $(FAPbI_3)_{1-x}(MAPbBr_3)_x$  (x=0.15) was prepared in a glovebox, by dissolving the FAI (1 M), MABr (0.2 M), PbI<sub>2</sub> (1.1 M) and PbBr<sub>2</sub> (0.2 M) in a mixed solvent of dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) (4:1, v/v) [40].

#### 2.2 Synthesis of CuPc-DMP

2.2.1 Synthesis of 3-(2,4-dimethyl-3-pentyloxy)phthalonitrile (1)

3-(2,4-Dimethyl-3-pentyloxy)phthalonitrile (1) was prepared as described previously with some modifications [41]. Sodium hydride (1.92 g, 48 mmol, 60% dispersion in mineral oil) was added portion-wise to a cooled DMF (30 mL, 0 °C) under argon, and then 2,4-dimethyl-3-pentanol (4.53 g, 39 mmol) was added drop-wise, followed by stirring for 1 h. A solution of 3-nitrophthalonitrile (5.19 g, 30 mmol) in DMF (10 mL) was added slowly to the above solution over 1 h. The resulting solution was warmed to room temperature, and stirred for 1 h. After the reaction, the reaction mixture was poured into water (500 mL) and stirred for 1 h. The solid formed was recovered by filtration and washed with water (50 mL×3). This crude product was purified by column chromatography on silica gel using CHCl<sub>3</sub> as eluent to give a white solid (4.83 g, 66% yield). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 0.95 (d, 6H), 1.01 (d, 6H), 2.13 (m, 2H), 4.05 (t, 1H), 7.26 (d, 1H), 7.28(d, 1H), 7.57 (t, 1H).

#### 2.2.2 Synthesis of CuPc-DMP

Following the literature [42], the mixture of **1** (3016.9 mg, 12.5 mmol), urea (1486.5 mg, 24.8 mmol), ammonium molybdate (58.8 mg, 0.3 mmol), and copper(I) chloride (297.0 mg, 3.0 mmol) in nitrobenzene (12 mL) was heated at 160 °C for 12 h. Solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using CHCl<sub>3</sub>/*n*-hexane (2:1, *v*/*v*) as eluent to afford a blue-green powder (2.11 g, 68% yield). Anal. Calcd. for ( $C_{60}H_{72}CuN_8O_4$ ) (%): C, 69.77; H, 7.03; N, 10.85. Found: C, 70.96; H, 7.24; N, 10.63.

#### 2.3 Device fabrication and characterization

Fluorine-doped tin oxide (FTO)-coated glass (NSG-Pilkington, 15  $\Omega$  per square, Japan) was firstly patterned by etching with Zn powder and 2 M HCl. The etched substrate was then sequentially cleaned by using detergent, de-ionized water and ethanol. Remaining organic residues were removed under oxygen plasma for 30 min. A compact TiO<sub>2</sub> blocking layer (BL) of roughly 30-40 nm was deposited on the cleaned FTO glasses by spray pyrolysis of titanium diisopropoxide bis(acetylacetonate) diluted in anhydrous ethanol at a volumetric ratio of 1:10 and then heated at 500 °C for 30 min. A mesoporous TiO<sub>2</sub> layer was deposited by spin-coating TiO<sub>2</sub> paste (Dyesol 18NR-T, Australia) diluted in anhydrous ethanol at ratio of 1:5 by weight at 5000 r min<sup>-1</sup> for 30 s. The layers were then sintered in air at 500 °C for 30 min. The mixed-cation perovskite films were deposited onto the mesoporous TiO<sub>2</sub>/BL TiO<sub>2</sub>/FTO substrate substrates

from the precursor solution by a two-step spin-coating procedure, at 1000 r min<sup>-1</sup> for 30 s and then 5000 r min<sup>-1</sup> for 20 s. During the second step, 200  $\mu$ L of chlorobenzene was dropped onto the substrates 10 s prior to the end of the program. Subsequently, the HTM layer was produced by spincoating the CuPc-DMP or spiro-OMeTAD solution on top of the perovskite layer with a spin speed of 3000 r min<sup>-1</sup> for 30 s. The CuPc-DMP or spiro-OMeTAD solutions were prepared by dissolving 80 mg HTM, 30  $\mu$ L 4-*tert*-butylpyridine (TBP) and 20  $\mu$ L lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) solution (520 mg LiTFSI in 1 mL acetonitrile) in 1 mL chlorobenzene. Finally, a layer of 100 nm Au was deposited on top of the HTM layer under high vacuum (<4×10<sup>-4</sup> Pa) by thermal evaporation.

The photocurrent-voltage (J-V) characteristics of the solar cells were measured using a Keithley 2400 Source-measure unit (USA) under illumination of a simulated sunlight (AM 1.5G, 100 mW cm<sup>-2</sup>) provided by an Oriel Sol3A solar simulator (Model: 94023A; Newport, USA) with an AM 1.5 filter in ambient air. Light intensity was calibrated with a Newport calibrated standard Si reference cell (SER; No 506/0358; USA). A black mask with a circular aperture  $(0.09 \text{ cm}^2)$ smaller than the active area of the square solar cell  $(0.20 \text{ cm}^2)$ was applied on top of the cell. The J-V curves were obtained from forward bias to short-circuit at a scan rate of 10 mV  $S^{-1}$ . For the measurements of hysteresis, the *J*-*V* curves were obtained through forward scan (0-1.2 V) or reverse (1.2-0 V) at the rate of 10 mV S<sup>-1</sup>. The measurement of the incident photon-to-current conversion efficiency (IPCE) was obtained by a Hypermono-light (SM-25, Jasco Co. Ltd., Japan). Prior to measurement, a standard silicon solar cell was used as reference.

#### 2.4 Measurements

<sup>1</sup>H NMR spectrum was recorded on a Varian INOVA 500NMR apparatus (USA). Chemical shifts were calibrated against tetramethylsilane (TMS) as an internal standard. Cyclic voltammetry measurement was carried out with CHI 630 Electrochemistry Work station. Redox potentials of CuPc-DMP or Spiro-OMeTAD were conducted in dichloromethane solution with 0.1 M TBAPF<sub>6</sub> as the supporting electrolyte. A glassy carbon electrode with a surface area of 0.785 cm<sup>2</sup> was used as working electrode. The counter electrode consisted of a platinum wire and the reference electrode was an Ag/AgNO<sub>3</sub> electrode. The redox potential was calibrated against Fc/Fc<sup>+</sup> as an internal standard. The UV-Vis spectra were recorded an Agilent 8453 spectrophotometer (USA). Scanning electron microscopy (SEM) was performed with FEI (Field Emission Instruments: Nova Nano SEM 450, USA).

Hole mobility of HTMs was measured by using the spacecharge-limited current (SCLC) method with the device structure of FTO/PEDOT:PSS/CuPc-DMP/Ag, as reported previously [43]. For the hole-only devices, SCLC is described as  $J(V) = 9\varepsilon \varepsilon_0 \mu V V/8 d^3$ , where  $\varepsilon$  is the dielectric constant of the material (normally taken to approach 3 for organic semiconductors),  $\mu$  is the hole mobility, V is the applied bias, and d is the film thickness. Conductivity measurements were performed as follows [43]. Plain glass substrates were sequentially cleaned by detergent, de-ionized water and ethanol. Remaining organic residues were removed under oxygen plasma for 30 min. A thin layer of mesoporous TiO<sub>2</sub> was coated on the glass substrates by spin-coating with a diluted TiO<sub>2</sub> paste (Dyesol 18NR-T, Australia) with terpineol (1:3, mass ratio). The thickness of the film is ca. 500 nm, as measured with a DekTak profilometer. After sintering the TiO<sub>2</sub> film at 500 °C for 30 min, the film was cooled to room temperature. A solution of HTM in chlorobenzene was spin-coated onto the mesoporous TiO<sub>2</sub> substrate, whereas the concentration was the same as in case of the photovoltaic device. J-V characteristics were recorded on a Keithley 2400 Source-measure unit (USA).

## **3** Results and discussion

The synthesis of CuPc-DMP only involved two simple steps, as shown in Scheme 1. 3-(2,4-Dimethyl-3-pentyloxy)phthalonitrile was firstly prepared according to a previous procedure with some modifications [41] (<sup>1</sup>H NMR spectrum is shown in Figure S1, Supporting Information online). Then, 3-(2,4-dimethyl-3-pentyloxy)phthalonitrile was mixed with urea, ammonium molybdate and copper(I) chloride in nitrobenzene. After purification, blue-green powder of CuPc-DMP was finally obtained with a yield of 68%. More detailed information on the synthesis can be found in the Experimental Section.

Normalized UV-Vis absorption spectrum of CuPc-DMP in dichloromethane solution is depicted in Figure 2(a). CuPc-DMP shows two intensive bands at 320 and 712 nm, corresponding to B-band (also called the Soret-band) and Q-band, respectively. The absorption spectrum of CuPc-DMP in the thin film state is also displayed, which exhibits a slight redshift (~10 nm) of the maximum absorption of Q-band (inset of Figure 2(a)). On the contrary, no significant absorption difference was observed for spiro-OMeTAD between the solution and thin films states. It implies that there might be certain amount of intermolecular  $\pi$ - $\pi$  stacking in the thin film state of CuPc-DMP, which is expected to facilitate a superior hole mobility as reported previously [44,45].

Cyclic voltammetric measurements were performed to evaluate the energy levels of this new HTM in comparison to spiro-OMeTAD. The cyclic voltammograms of both the HTMs were measured under the same conditions for a better comparison, as displayed in Figure 2(b) for CuPc-DMP and Figure S2 for spiro-OMeTAD. The HOMO (highest occupied molecular orbital) energy level is calculated from the oxidation onset potential referenced against ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) [28]. Accordingly, the HOMO and LUMO (lowest unoccupied molecular orbital) energy levels of CuPc-DMP were estimated to be -5.46 and -3.82 eV (Table 1), analogous to previously reported values [42]. The HOMO energy level of CuPc-DMP matches well the low lying valence band (VB) of perovskites (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> [40]. It indicates that CuPc-DMP should be capable of effectively extracting holes from the perovskites.

Hole transporting characteristics (mobility and conductivity) are very important parameters for HTM to effectively transport/collect the photo-generated holes from the perovskites. Hole mobility measurements were thus carried out for pristine CuPc-DMP and spiro-OMeTAD. The hole mobility of the HTM were estimated from a space-charge-



**Figure 2** (a) UV-Vis absorption spectra of CuPc-DMP and spiro-OMeTAD in dichloromethane solutions and in the forms of thin films on the glass substrates; (b) cyclic voltammetry (CV) of CuPc-DMP in dichloromethane solution, potential vs. Ag/AgNO<sub>3</sub> (color online).

limited currents (SCLC) method by using hole-only devices as reported previously [43]. By fitting the *J-V* curves (Figure 3(a)), the extracted hole mobility for pristine CuPc-DMP is  $9.8 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup>, which is considerably higher than that of spiro-OMeTAD ( $4.0 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup>).



**Figure 3** (a) *J-V* characteristics of pristine CuPc-DMP and spiro-OMeTAD based hole-only devices; (b) conductivity characteristics of doped CuPc-DMP and spiro-OMeTAD based devices; (c) thermal gravimetric analysis of CuPc-DMP (color online).

Table 1	Electrochemical	and optic	l parameters	of CuPc-DMP	and spiro-OMeTAD
---------	-----------------	-----------	--------------	-------------	------------------

HTM	$\lambda_{max}^{a}$ solution (nm)	$\lambda_{\max}^{b}$ film (nm)	$E_{\rm ox}^{\rm c)}$ (V)	$E_{\rm HOMO} ^{\rm d)}  ({\rm eV})$	$E_{\rm LUMO} e^{\rm e}$ (eV)	$E_{\rm g}$ f) (eV)
CuPc-DMP	712	722	0.66	-5.46	-3.82	1.64
spiro-OMeTAD	385	385	0.33	-5.13	-2.17	2.96

a) Absorption spectra were measured in dichloromethane solutions; b) thin films were prepared by spin-coating chlorobenzene solutions on glass substrates; c) cyclic voltammetry measurements were carried out in dichloromethane solutions with TBAPF<sub>6</sub>(0.1 M) as supporting electrolyte, referenced against Fc/Fc<sup>+</sup>; d) HOMO were determined by the equation  $E_{HOMO}=-5.1-(E_{ox}-E^{1/2}(Fc/Fc^+))$ ; e) LUMO=HOMO+ $E_g$ ; f) optical band gap was calculated by the onset of absorption. The conductivities of doped CuPc-DMP and spiro-OMeTAD (the same compositions as used in the PSC devices, doped with additives LiTFSI and TBP) were subsequently examined by using a two-contact electrical conductivity setup, the curves of which are displayed in Figure 3(b) [43]. CuPc-DMP also exhibits a much higher conductivity ( $6.62 \times 10^{-5}$  S cm<sup>-1</sup>), which is almost two times higher than that of spiro-OMeTAD ( $2.24 \times 10^{-5}$  S cm<sup>-1</sup>).

The thermal stability of CuPc-DMP was probed using thermal gravimetric analysis (TGA) as shown in Figure 3(c). The TGA shows that CuPc-DMP is quite stable and starts degrading only above 300 °C.

CuPc-DMP was further tested as a HTM in mesoscopic PSCs and its photovoltaic properties were evaluated in comparison to spiro-OMeTAD. The schematic illustration and cross-sectional SEM image of the device architecture are depicted in Figure 4. The solar cell devices were fabricated with a structure of FTO glass/compact TiO<sub>2</sub>/mesoporous TiO<sub>2</sub>/perovskite/HTM/Au. The mixed-cation perovskite light absorber (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> was prepared by using a solvent-engineering technique as reported previously [39,40]. The resulting perovskite films were coated with HTM CuPc-CMP via a solution process. More details of the solar cell fabrication procedures and component parameters are described in the Experimental Section.

Figure 5(a) displays the *J*-*V* characteristic of the champion cell using CuPc-DMP (doped with additives LiTFSI and TBP) as a HTM measured under at 100 mW cm<sup>-2</sup> illumination (AM 1.5G). A maximum PCE of 17.1% is achieved for CuPc-DMP based device, with an open-circuit voltage ( $V_{oc}$ ) of 1.04 V, a short-circuit current density ( $J_{sc}$ ) of 23.2 mA cm<sup>-2</sup> and a fill factor (FF) of 0.71. This PCE achieved by



**Figure 4** (a) Schematic device architecture of perovskite solar cells studied; (b) cross-sectional SEM image of the complete PSC device with CuPc-DMP as a HTM (color online).

CuPc-DMP rivals the state-of-the-art HTM spiro-OMeTAD with the same doping condition, which exhibits a maximum PCE of 16.7% with a  $V_{oc}$  of 1.05 V, a  $J_{sc}$  of 23.0 mA cm<sup>-2</sup> and a FF of 0.69, respectively, as presented in Figure S3. It is worth noting that the homo energy level of CuPc-DMP is 0.33 eV lower than that of spiro-OMeTAD from the cyclic voltammetry (CV) measurements as listed in Table 1. Deeper HOMO energy level is expected to result in a higher  $V_{oc}$ , as



**Figure 5** (a) *J-V* characteristic of the PSC device based on doped CuPc-DMP (inset: IPCE spectrum of the PSC device measured for (a)); (b) histogram of PCEs of 50 PSC devices using CuPc-DMP as HTMs; (c) PCE and current density as a function of time under illumination at a fixed voltage of 0.8 V for PSC devices based on CuPc-DMP (color online).

the photovoltage of a PSC device is determined by the difference between the quasi Fermi levels of both the electron and hole conducting materials. However, no significant difference of  $V_{oc}$  values was observed for these two HTMs. One likely reason should be mainly attributed to the lower lying LUMO level of CuPc-DMP, which results in poorer electron blocking ability as demonstrated by the previous report [37]. A slightly higher fill factor was found for the CuPc-DMP based device, which should be mainly originated from the much higher hole conductivity of this metal organic complex.

The IPCE spectrum (shown in the inset of Figure 5(a)) for the CuPc-DMP based device displays a wide spectra response to a long wavelength at around 840 nm, yielding a broad IPCE plateau of over 85% in the range of 400 to 700 nm. The integrated current density from the IPCE spectrum for the device based on CuPc-DMP is calculated to be 22.0 mA cm<sup>-2</sup>, which is basically in a good line with the measured value from the J-V curve. Figure 5(b) shows the histogram of 50 identical PSC devices employing CuPc-DMP, which exhibit good reproducibility, yielding an average PCE of 15.1%. The reproducibility of PSC devices based on spiro-OMeTAD (50 identical cells) was also investigated (Figure S3(b)), exhibiting an analogous average PCE of 14.9%. The J-V hysteresis effects for devices based on CuPc-DMP and spiro-OMeTAD were also evaluated and the results are summarized in Figure S4 and Table S1 (Supporting Information online). Small hysteresis effects were observed for both of these two HTMs. The hysteresis indexes are calculated to be 0.024 (CuPc-DMP) and 0.054 (spiro-OMeTAD), respectively, according to a previous literature [46]. It was reported that the stabilized power output is a reliable and scan-independent method to determine the efficiency of a PSC device [19]. Figure 5(c) displays the steady-state efficiency and current density of a representative PSC device based on CuPc-DMP measured at a constant bias of 0.8 V (close to maximum power point) over 180 s under 1 sun condition (AM 1.5G). CuPc-DMP based device exhibits a steady-state efficiency of 15.1% and current density of 18.9 mA cm<sup>-2</sup> during the testing period. Stabilized efficiency and current density for the spiro-OMeTAD based device were also recorded as shown in Figure S5.

## 4 Conclusions

Solution-processable CuPc-DMP has been successfully incorporated as a HTM in mesoscopic PSCs. The optimized device based on this HTM exhibits an impressive PCE of 17.1% under 100 mW cm<sup>-2</sup> AM 1.5G illumination, which is on par with the well-known spiro-OMeTAD under equivalent conditions. However, by stark contrast to the complicated synthesis procedure for spiro-OMeTAD, the synthesis of CuPc-DMP is considerably easier, only involving two simple steps from commercially available raw materials. The advantages of this HTM observed, such as facile synthetic procedure, superior hole transport characteristic, high photovoltaic performance together with the feasibility of tailoring the molecular structure would make solution-processable copper phthalocyanines as a class of promising HTM that can be further explored in PSCs. The present finding will definitely open up a new avenue for developing cost-effective and highly efficient HTMs for large-area application of PSCs in the future.

Acknowledgments This work was supported by the National Natural Science Foundation of China (21606039, 21120102036, 91233201), the National Basic Research Program of China (2014CB239402), the Swedish Energy Agency, as well as the Knut and Alice Wallenberg Foundation.

**Conflict of interest** The authors declare that they have no conflict of interest.

**Supporting information** The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

- 1 Lewis NS, Nocera DG. Proc Natl Acad Sci USA, 2006, 103: 15729–15735
- 2 Service RF. Science, 2005, 309: 548-551
- 3 Yu Z, Li F, Sun L. Energy Environ Sci, 2015, 8: 760-775
- 4 Grätzel M. Nat Mater, 2014, 13: 838–842
- 5 Green MA, Ho-Baillie A, Snaith HJ. *Nat Photonics*, 2014, 8: 506–514
- 6 Chen W, Wu Y, Yue Y, Liu J, Zhang W, Yang X, Chen H, Bi E, Ashraful I, Grätzel M, Han L. Science, 2015, 350: 944–948
- 7 Liu J, Shirai Y, Yang X, Yue Y, Chen W, Wu Y, Islam A, Han L. Adv Mater, 2015, 27: 4918–4923
- 8 Kim HS, Lee CR, Im JH, Lee KB, Moehl T, Marchioro A, Moon SJ, Humphry-Baker R, Yum JH, Moser JE, Grätzel M, Park NG. *Sci Rep*, 2012, 2: 591
- 9 Lee MM, Teuscher J, Miyasaka T, Murakami TN, Snaith HJ. Science, 2012, 338: 643–647
- 10 Kojima A, Teshima K, Shirai Y, Miyasaka T. J Am Chem Soc, 2009, 131: 6050–6051
- 11 http://www.nrel.gov/ncpv/images/efficiencychart.jpg
- 12 Jeon NJ, Lee HG, Kim YC, Seo J, Noh JH, Lee J, Seok SI. J Am Chem Soc, 2014, 136: 7837–7840
- 13 Li H, Fu K, Hagfeldt A, Grätzel M, Mhaisalkar SG, Grimsdale AC. Angew Chem Int Ed, 2014, 53: 4085–4088
- 14 Abate A, Paek S, Giordano F, Correa-Baena JP, Saliba M, Gao P, Matsui T, Ko J, Zakeeruddin SM, Dahmen KH, Hagfeldt A, Grätzel M, Nazeeruddin MK. *Energy Environ Sci*, 2015, 8: 2946–2953
- 15 Yu Z, Sun L. Adv Energy Mater, 2015, 5: 1500213
- 16 Qin P, Kast H, Nazeeruddin MK, Zakeeruddin SM, Mishra A, Bäuerle P, Grätzel M. *Energy Environ Sci*, 2014, 7: 2981–2985
- 17 Heo JH, Im SH, Noh JH, Mandal TN, Lim CS, Chang JA, Lee YH, Kim H, Sarkar A, Nazeeruddin MK, Grätzel M, Seok SI. *Nat Photonics*, 2013, 7: 486–491
- 18 Zhu Z, Bai Y, Lee HKH, Mu C, Zhang T, Zhang L, Wang J, Yan H, So SK, Yang S. *Adv Funct Mater*, 2014, 24: 7357–7365
- 19 Habisreutinger SN, Leijtens T, Eperon GE, Stranks SD, Nicholas RJ, Snaith HJ. Nano Lett, 2014, 14: 5561–5568
- 20 Xiao J, Shi J, Liu H, Xu Y, Lv S, Luo Y, Li D, Meng Q, Li Y. *Adv* Energy Mater, 2015, 5: 1401943

- 21 Kwon YS, Lim J, Yun HJ, Kim YH, Park T. *Energy Environ Sci*, 2014, 7: 1454–1460
- 22 Christians JA, Fung RCM, Kamat PV. J Am Chem Soc, 2014, 136: 758–764
- 23 Sepalage GA, Meyer S, Pascoe A, Scully AD, Huang F, Bach U, Cheng YB, Spiccia L. *Adv Funct Mater*, 2015, 25: 5650–5661
- 24 Qin P, Tanaka S, Ito S, Tetreault N, Manabe K, Nishino H, Nazeeruddin MK, Grätzel M. *Nat Commun*, 2014, 5: 3834
- 25 Bi D, Tress W, Dar MI, Gao P, Luo J, Renevier C, Schenk K, Abate A, Giordano F, Correa Baena JP, Decoppet JD, Zakeeruddin SM, Nazeeruddin MK, Gra tzel M, Hagfeldt A. *Sci Adv*, 2016, 2: e1501170–e1501170
- 26 Gratia P, Magomedov A, Malinauskas T, Daskeviciene M, Abate A, Ahmad S, Grätzel M, Getautis V, Nazeeruddin MK. *Angew Chem Int Ed*, 2015, 54: 11409–11413
- 27 Ameen S, Rub MA, Kosa SA, Alamry KA, Akhtar MS, Shin HS, Seo HK, Asiri AM, Nazeeruddin MK. *ChemSusChem*, 2016, 9: 10–27
- 28 Xu B, Bi D, Hua Y, Liu P, Cheng M, Grätzel M, Kloo L, Hagfeldt A, Sun L. Energy Environ Sci, 2016, 9: 873–877
- 29 Bi D, Xu B, Gao P, Sun L, Grätzel M, Hagfeldt A. Nano Energy, 2016, 23: 138–144
- 30 Hua Y, Zhang J, Xu B, Liu P, Cheng M, Kloo L, Johansson EMJ, Sveinbjörnsson K, Aitola K, Boschloo G, Sun L. *Nano Energy*, 2016, 26: 108–113
- 31 Zaumseil J, Sirringhaus H. Chem Rev, 2007, 107: 1296–1323
- 32 Xue J, Rand BP, Uchida S, Forrest SR. Adv Mater, 2005, 17: 66–71
- 33 Kumar CV, Sfyri G, Raptis D, Stathatos E, Lianos P. RSC Adv, 2015,

5: 3786-3791

- 34 Ke W, Zhao D, Grice CR, Cimaroli AJ, Fang G, Yan Y. *J Mater Chem A*, 2015, 3: 23888–23894
- 35 Zhang F, Yang X, Cheng M, Wang W, Sun L. *Nano Energy*, 2016, 20: 108–116
- 36 Ağirtaş MS, Bekaroğlu Ö. J Porphyr Phthalocya, 2001, 05: 717-720
- 37 Seo J, Jeon NJ, Yang WS, Shin HW, Ahn TK, Lee J, Noh JH, Seok SI. Adv Energy Mater, 2015, 5: 1501320
- 38 Sfyri G, Chen Q, Lin YW, Wang YL, Nouri E, Xu ZX, Lianos P. Electrochim Acta, 2016, 212: 929–933
- 39 Jeon NJ, Noh JH, Yang WS, Kim YC, Ryu S, Seo J, Seok SI. *Nature*, 2015, 517: 476–480
- 40 Correa Baena JP, Steier L, Tress W, Saliba M, Neutzner S, Matsui T, Giordano F, Jacobsson TJ, Srimath Kandada AR, Zakeeruddin SM, Petrozza A, Abate A, Nazeeruddin MK, Grätzel M, Hagfeldt A. *Energy Environ Sci*, 2015, 8: 2928–2934
- 41 Chen Z, Xia C, Wu Y, Zuo X, Song Y. *Inorgan Chem Commun*, 2006, 9: 187–191
- 42 Chen CH, Cheng WT, Tsai ML, Huang KT. *Ind Eng Chem Res*, 2012, 51: 3630–3638
- 43 Xu B, Sheibani E, Liu P, Zhang J, Tian H, Vlachopoulos N, Boschloo G, Kloo L, Hagfeldt A, Sun L. *Adv Mater*, 2014, 26: 6629–6634
- 44 Liu J, Wu Y, Qin C, Yang X, Yasuda T, Islam A, Zhang K, Peng W, Chen W, Han L. *Energy Environ Sci*, 2014, 7: 2963–2967
- 45 Cheng M, Xu B, Chen C, Yang X, Zhang F, Tan Q, Hua Y, Kloo L, Sun L. *Adv Energy Mater*, 2015, 5: 1401720
- 46 Kim HS, Park NG. J Phys Chem Lett, 2014, 5: 2927–2934