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# Solar Energy Materials & Solar Cells

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## Renewed interest in metal phthalocyanine donors for small molecule organic solar cells

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## ARTICLE INFO

## Article history:

Received 19 December 2013

Received in revised form

6 February 2014

Accepted 8 February 2014

Available online 28 February 2014

## Keywords:

Organic solar cell

Phthalocyanine

Metal phthalocyanine

Bulk heterojunction

Schottky

## ABSTRACT

Alternative metal phthalocyanine (m-Pc) donors employed in mixed layer organic solar cells (OSCs) are shown to have impressive photovoltaic parameters when compared to the traditional and well-studied copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) donors. In this work, we employ a mixed layer OSC with substantially different donor-to-acceptor mixing ratios to study a wide set of m-Pc donors. The different m-Pc donors are thus studied in consideration of their intrinsic physical properties, such as the valency of their central moiety and their molecular energy levels. The non-traditional m-Pc donors are better suited when employed in Schottky OSCs with high acceptor content, allowing for improvements to all major photovoltaic parameters. In contrast, traditional m-Pc donors suffer from unavoidable charge accumulation and recombination effects in the Schottky device architecture, and are instead optimized with the standard 1-to-1 donor-to-acceptor bulk heterojunction architecture. External quantum efficiency measurements show that optimization of short circuit current density requires balancing photocurrent contributions from the m-Pc absorption and the fullerene aggregate absorption, which is accomplished by control of the donor-to-acceptor mixing ratio. Chloroindium phthalocyanine (ClInPc):C<sub>60</sub> OSCs are shown to be capable of near-IR absorption, promising power conversion efficiencies and open circuit voltages in excess of 1 V.

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### 1. Introduction

Metallo-phthalocyanines (m-phthalocyanines or m-Pcs) are historically some of the most studied donor materials in organic solar cells (OSCs). Their success stems from their long-established hole transport properties, and their well-known capability as a sensitizer by photo-induced electron transfer to quenchers/acceptors [1–3]. For OSCs, this photo-induced electron transfer was employed most effectively when the m-Pcs were coupled with the fullerenes C<sub>60</sub> and C<sub>70</sub>, as has been studied at depth in literature [4,5]. Copper phthalocyanine (CuPc) was employed as a donor in the first bilayer heterojunction OSC reported in literature over two decades ago by Tang [6]. CuPc was subsequently studied at depth for its use in OSCs [7–10]. Zinc phthalocyanine (ZnPc) may also be considered a traditional m-phthalocyanine, with its extensive use in OSCs by Gebeyehu et al. [11–14]. ZnPc was more recently chemically modified to F<sub>4</sub>-ZnPc, where it achieved 3.9% power conversion efficiency (PCE) in a bulk heterojunction (BHJ) single cell architecture [15]. Since 2005, with the rise in popularity of

solution-processable OSCs, the study of vacuum-deposited and thus phthalocyanine donor OSCs has been comparatively much less prevalent in literature. However, the development of alternative (non-traditional) m-Pc donors with high open circuit voltages (V<sub>oc</sub>) and impressive PCE values has triggered a resurgence of interest in m-Pc-based OSCs. To this end, subphthalocyanine chloride (SubPc) has shown promise as a donor material, granting 3.7% PCE when mixed with a C<sub>60</sub> acceptor and 5.4% PCE in an optimized graded-BHJ device with a C<sub>70</sub> acceptor [16,17]. OSCs with a chloroaluminum phthalocyanine (ClAlPc)-C<sub>60</sub> active layer have also been shown to grant good performance at 2 to 2.4% PCE, and ClAlPc has been further highlighted for its near-infrared sensitivity [18–20]. Recently, we showed that chloroindium phthalocyanine (ClInPc) donor can also be employed in simple BHJ OSCs to achieve reasonable device performance, providing 2.2% PCE when mixed with C<sub>60</sub> [21,22], and up to 3.9% PCE when mixed with C<sub>70</sub> [21,23]. When coupled with their relatively simple synthesis and straightforward purification (by train sublimation), these m-Pcs show their promise as cost-effective and highly capable donor materials for highly efficient organic photovoltaics.

In previous work, Yuen et al. showed that a large set of m-Pcs, including both traditional m-Pcs (CuPc, ZnPc) as well as non-traditional (less-studied) m-Pcs, have some promise when used as

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donors in simple planar heterojunction OSCs and 1:1 BHJ OSCs [24]. This work focused on establishing a basic understanding of the donors at a 1:1 mixing ratio and with non-ideal device thicknesses—generally too thin to provide reasonable efficiencies. Recently, the Schottky device architecture has been highlighted in literature as a novel approach to grant high  $V_{oc}$  ( $> 1$  V) OSCs [25]. When employed for high performance OSCs, this device architecture relies on varied concentrations of the BHJ layer, usually with much higher  $C_{60}$  content than in the standard BHJ OSC [21,23,26–31]. The role of the Schottky architecture for the creation of high efficiency OSCs with traditional m-Pcs (CuPc, ZnPc) versus the more recently examined m-Pcs is currently unknown. To this end, a comprehensive study on the photovoltaic output characteristics of traditional versus non-traditional m-Pcs would be invaluable for the field of vacuum-deposited small molecule OSCs. Thus, we examine the untapped benefits of these non-traditional m-Pcs that have otherwise experienced success in other dye/pigment-related fields, such as xerography [32].

In the present work, we study OSCs comprising a m-Pc: $C_{60}$  mixed layer with substantially different mixing ratios, spanning the traditional BHJ architecture to the Schottky architecture. We further vary the central moiety in the m-Pc to gain a comprehensive understanding of the role of the m-Pc donor in the OSC photovoltaic output properties. The present work encompasses the following donors: metal free phthalocyanine ( $H_2Pc$ ), ZnPc, CuPc, ClAlPc, ClInPc, ClAlPc, TiOPc and SubPc. In this manner, we study impact of the m-Pc central moiety valency on achieving high efficiency OSCs primarily through mixed donor:acceptor ( $D:A$ ) active layer optimization. The results indicate that, while the traditional Pcs benefit most from a standard 1:1  $D:A$  BHJ architecture, all non-traditional Pcs show substantially enhanced performance with a high  $C_{60}$ -content Schottky architecture. In-depth analysis of photovoltaic output parameters and external quantum efficiency (EQE) measurements are used to explain these observations. ClInPc is highlighted as an especially promising small molecule donor, with very strong near-IR absorption and 2.5% PCE in a basic ClInPc: $C_{60}$  BHJ. Further device optimization allows for 2.8% PCE ClInPc: $C_{60}$  OSCs and open circuit voltages in excess of 1 V.

## 2. Materials and methods

### 2.1. Device fabrication

To fabricate the devices, patterned ITO slides were first cleaned by successive sonication in acetone, Micro-90 surfactant and isopropyl alcohol. The slides were scrubbed with a cotton swab after the acetone and Micro-90 sonication steps. The slides were then placed in an oven at 100 °C for at least one hour but no longer than one day before use. The substrates were then treated with  $O_2$  plasma in a Trion RIE/ICP system at 20 mTorr pressure and 100 W ICP power (flow rate of  $O_2$  kept at 20 sccm). 5 nm of  $MoO_3$  (Sigma Aldrich) was then deposited by thermal evaporation ( $< 5 \times 10^{-6}$  Torr base pressure) at a rate of 2 Å/s. The organic materials were subsequently deposited by thermal evaporation. The mixed layers were fabricated by the simultaneous co-deposition of  $C_{60}$  ( $> 99.9\%$ , M.E.R. Corporation) and the m-Pc donor material. Different mixing ratios were achieved by varying the deposition rates of the donor and  $C_{60}$ , and the sum total deposition rate of all materials was kept at 2 Å/s. All solar cells with the same materials system (i.e. having the same donor) were fabricated on the same substrate and in the same deposition run in order to minimize deposition-to-deposition variation. In this manner, m-Pc: $C_{60}$  OSCs with varying mixing ratios (1:0, 3:1, 1:1, 1:3, and 1:7) can be fabricated in duplicate with the

same extraction layers/cathode on the same substrate. This greatly simplifies comparisons among devices and allows for easily identifying trends in performance with changes in mixing ratio, as will be discussed at depth throughout this work. The thicknesses of the deposited layers were monitored by quartz crystal microbalances in the deposition chamber, which were calibrated with a Veeco Dektak 8 Stylus Profiler. With the exception of SubPc, all m-Pcs were obtained from the Xerox Research Centre of Canada, where they were also purified by train sublimation. SubPc and BCP were obtained from Luminescence Technology Corp (both  $> 99\%$ , sublimed-grade). 8 nm of BCP was then deposited by thermal evaporation at 2 Å/s prior to the cathode. To finish the OSCs, 100 nm of Al was deposited by thermal evaporation at 3 Å/s. A final device area of 0.2 cm<sup>2</sup> was defined by the intersection of the Al electrode with the patterned ITO.

### 2.2. Device characterization

Photovoltaic parameters were measured with 1-sun AM1.5G radiation from an ABET Sun 3000 Class AAA Solar Simulator and a Keithley 2400 SourceMeter. Both illuminated and dark testing of the devices was done in an inert  $N_2$  atmosphere. UV/Visible absorption measurements were performed in air with a Shimadzu UV-2501PC UV/Vis Spectrophotometer. External quantum efficiency measurements were obtained in inert  $N_2$  atmosphere with a set-up employing a Newport 260 Cornerstone Monochromator and a Stanford Research 830 Lock-in Amplifier, as controlled by custom software.

## 3. Results and discussion

The m-Pcs in this work can be classified based on the valency of their central moiety in the molecule. To this end, we have examined monovalent ( $H_2-$  or metal-free), divalent (Cu, Zn), trivalent (ClIn, ClGa, ClAl) and tetravalent (TiO) phthalocyanines. We have also included boron subphthalocyanine chloride (SubPc) in this study, which differs from the other m-phthalocyanines in that it has three, instead of four, N-fused 1,3-diiminoisoindoline units around its central B-Cl moiety. The chemical structures of the standard m-Pcs as well as SubPc are shown in Fig. 1A and B. As noted previously, CuPc and ZnPc may be considered traditional phthalocyanines, as they have long been studied in literature for their application as donors in OSCs, while the other m-Pcs are considered non-traditional, as they have been comparatively much less studied for their use in organic photovoltaics. The energy levels for these m-Pc donors as well as the other species employed in the OSCs in this work are shown in Fig. 1C [8,11,16,25,33–38]. Note that energy level data for ClGaPc is not available in literature, so it is not included in this figure. It is also worth noting that the HOMO values taken from recent literature (Fig. 1C) align well with the ionization energies established historically [39,40], as well as with the orbital energy diagrams found computationally [41–43]. Interestingly, the latter studies show that for  $H_2Pc$ , CuPc, ZnPc and TiOPc (among others) the HOMO is exclusively formed by C-2p <sub>$\pi$</sub>  characteristics, so that changes in the central metal atom have very little effect on the HOMO. Given that the HOMO has been experimentally found to be deeper for many of the non-traditional m-Pcs, such as ClInPc, ClAlPc, ClGaPc and SubPc, it is likely that the HOMO for these species may include orbital contributions from their central moiety.

### 3.1. Optical properties of m-phthalocyanines

The absorption spectra of 50 nm films of the presently examined m-Pc donors, as well as fullerene ( $C_{60}$ ) acceptor, are presented in Fig. 2. All m-Pcs exhibit two strong peaks, one in the UV and one

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