Solar Energy 134 (2016) 1–8

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Design, computational screening and synthesis of novel non-peripherally tetra hexylthio-substituted phthalocyanines as bulk heterojunction solar cell materials

Meral Arı, Zeliha Kanat, Hatice Dinçer *

Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 11 November 2015
Received in revised form 21 April 2016
Accepted 26 April 2016
Available online 3 May 2016

Keywords:
Phthalocyanine
Bulk heterojunction solar cell
Time-dependent density functional theory (TDDFT)

ABSTRACT

New bulk heterojunction organic solar cell materials of phthalocyanines (Pcs) were designed, screened computationally and synthesized for the first time in a study with the aim of finding more efficient products. The electronic absorption spectrum and the molecular orbital properties of the novel non-peripherally tetrasubstituted Pcs were investigated by DFT/TDDFT calculations. The screened compounds were found to be promising for providing good performance on BHJ solar cells with their small band gaps, red-shifted absorption bands in near infrared region, deep HOMO energy levels and high electron mobilities. Furthermore, the model of Scharber et al. (2006) was used for open-circuit voltage (V_{oc}) prediction for the first time for Pcs as the donor moiety and calculated eV_{oc} values up to 0.56 was found with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the acceptor moiety. All studied Pcs except one were found to provide energetic driving force for Pc-PCBM cells computationally. Hence, the new precursor 3-hexylthio phthalonitrile (**3**) was obtained by the nucleophilic aromatic substitution of 3-nitrophthalonitrile (**1**) and 1-hexanethiol (**2**) and then cyclotetramerized in the presence of metal salts and/or DBU to achieve a series of non-peripherally tetrahexylthio substituted phthalocyanines (**4–12**). The phthalocyanines with lead, indium and manganese metal centres have red-shifted Q bands as well as non Q-band absorptions in the 450–600 nm region. The precursor and the targeted phthalocyanines were characterized comprehensively by ^{1}H NMR, ^{13}C NMR, FT-IR, UV–Vis, mass spectroscopies.

1. Introduction

Organic solar cells (OCS) have been the focus of increasing interest due to their potential as a low cost photovoltaic energy producing source. The performance of OSCs has been greatly improved by introduction of the bulk-heterojunction (BHJ) concept (Irwin et al., 2008; Itoh et al., 2013; Mihailetchi et al., 2005; Ren et al., 2012; Scharber et al., 2006; Yu et al., 1995) as an active layer where electron donor and acceptor materials are mixed in a solution and cast into a thin film sandwiched between two electrodes. In the last decade, large progress has been made in improving the power conversion efficiency (PCE) of organic BHJ solar cells. Today a single junction organic BHJ solar cell with an efficiency of 10% is listed in the efficiency table of the Journal of Progress in Photovoltaics (Green et al., 2015). Although this progress is impressive, the performance of these cells has to be improved for larger scale applications.

Materials innovation is one of the major forces driving the performance of OSCs. Some polymers were used as electron-donor in the history of solar cell research (Li et al., 2012). However, devices based on poly(3-hexylthiphene) (P3HT) remain at the forefront of solar cell technology in terms of industrialization (Cortina-Marrero et al., 2013; Geethu et al., 2015; Kaltenbrunner et al., 2012; Ranganathan et al., 2015; Thambidurai et al., 2014; Yang et al., 2015). Fullerene and its derivatives are broadly used as electron acceptor materials in organic photovoltaics. The C60 derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) is one of the most successful fullerene derivative, which exhibits excellent photovoltaic properties as an electron acceptor material (Choy, 2013). Phthalocyanines (Pcs) are good p-type semiconductors and present rich redox chemistry, which can be modulated as a function of the peripheral substitution and/or the central metal included in the aromatic cavity. Therefore, once photoexcited, Pcs are capable of acting either as electron-donors when they are connected to appropriate electron-acceptor moieties such as fullerene derivatives (Sánchez-Díaz et al., 2011), or as electron-acceptors when linked to donor systems such as polythiophenes (Abdullah

---

* Corresponding author.
E-mail addresses: dincerhat@itu.edu.tr, haticedincer@gmail.com (H. Dinçer).

http://dx.doi.org/10.1016/j.solener.2016.04.041

et al., 2012). Furthermore, it has been shown that the electron mobility in Pcs can be as high as the hole mobility (Kraus et al., 2011). All these features render these compounds valuable photoactive materials. P3HT absorb light with wavelengths ranging from 400 to 600 nm, the incorporation of Pc molecules absorbing from 600 to 700 nm to the active layer will cause a broadening of the absorption range. Recently, Torres et al. has demonstrated the clear contribution of the Pc around 700 nm to the photocurrent (Campo et al., 2011).

There are many studies on different types of solar cells and thin films including Pcs in their structure. The classical structure consists of superposed multilayer (Chen et al., 2014; Ke et al., 2015a, b; Tian et al., 2015; Zhang et al., 2015) or BHJ (Ichikawa et al., 2013; Jin et al., 2013; Raïssi et al., 2014; Xi et al., 2010) structures, based on the couple copper phthalocyanine (CuPc) as electron donor and fullerene as electron acceptor. The disadvantage of the multilayer solar cells is their low short circuit current density which limits the PCE (Dahou et al., 2010). BHJ OSCs utilizing phthalocyanine–tetrabenzoporphyrin hybrid macrocycles (Dao et al., 2015) and BHJ thin films made of 1,4,8,11,15,18,22,25-octahexylphthalocyanine ($C6PcH_2$) and PCBM via spin-casting (Dao et al., 2013a) are the ones to have the highest PCEs of 5.3% and 4.2% respectively for single junction cells. A non-peripherally alkyl-substituted phthalocyanine, $C6PcH_2$ exhibits not only excellent processability in the form of thin films but also appropriate electronic characteristics for OSCs, such as a deep highest occupied molecular orbital (HOMO) energy level, a relatively small band gap, strong optical absorption, and particularly high hole and electron drift mobilities in the crystalline phase exceeding 1.4 and 0.5 $cm^2/(V.s)$ respectively, which were evaluated by time-of-flight measurement (Hori et al., 2010; Miyake et al., 2011). Active layer thickness dependence, hole transport buffer layer dependence, application to a tandem structure (Hori et al., 2011), alkyl substituent length dependence of octaalkylphthalocyanine ($CnPcH_2$) (Dao et al., 2013b; Hori et al., 2012) and the doping effects of $CnPcH_2$ for BHJ solar cells (Masuda et al., 2012) were also reported. Dao et al. (2013b) stated that the PCEs of $CnPcH_2$-based BHJ OSCs were improved from 0.3% to 3.7% by changing the alky substituent length where maximum efficiency was achieved with $C6PcH_2$.

The red shifting for non-peripherally substituted derivatives is attributed to greater electron density enhancement caused by substitution at the non-peripheral substitution compared with that at the peripheral position. Among those containing nonperipheral substituents; the most highly red-shifted MPc complexes are the ones containing Mn, V or Ti as central metal and/or thio substituents (Jiang, 2010; Kadish et al., 2010).

In light of the above mentioned information, in this study we have designed non-peripherally tetrahexylthio-substituted novel metal free ($SC6PcH_2$) (**4**) and metallo-Pcs (SC6PcM) (**5–12**) (M: Zn, Co, Pb, Cu, Ni, Mg, In, Mn) with the aim of adding the red lead effect of thio groups and investigating the effect of different metal centres on solar cell performance. Electronic characteristics of designed Pcs were screened computationally. A fast and reliable theoretical method that involves calculating the molecular orbital energy levels and describing the spatial orientations as well as the electronic absorption spectra is essential for screening the candidates of solar cell materials. For ground state properties, density functional theory (DFT) is clearly the method of choice. Ground state properties are accurately described in DFT, and the scaling of the computational cost with the number of atoms is very favorable compared to high-level quantum chemistry approaches (De Angelis et al., 2008). Concerning the calculation of the excited state properties, the time-dependent extension of density functional theory (TDDFT) (Stratmann et al., 1998) has been widely used in recent applications. DFT and TDDFT methods have been proven suitable for calculating the energy minimized structure, electronic distribution, molecular orbitals and electronic absorption spectra of a series of porphyrin and phthalocyanine derivatives (Keizer et al., 2003; Mack et al., 2005; Nemykin et al., 2007; Ricciardi et al., 2001; Yang et al., 2012; Zhang et al., 2005). Hence, the novel symmetrical Pcs were investigated by DFT and TDDFT calculations utilizing Perdew, Burke and Ernzerhof (PBE) with valence triple-zeta basis set (TZVP). Computationally screened compounds were found to be very promising for providing good performance on BHJ solar cells, thus, were synthesized. The new precursor (**3**) was obtained by nucleophilic aromatic substitution of 3-nitrophthalonitrile (**1**) and 1-hexanethiol (**2**) and then cyclotetramerized in the presence of metal salts and/or DBU to achieve non-peripherally tetrahexylthio substituted Pcs (**4–12**).

2. Experimental

2.1. Materials, instruments and method of computation

All the calculations have been performed by using TURBOMOLE V6.1 (Ahlrichs et al., 1989) quantum chemistry package. The geometries of the novel symmetrical Pcs in gas phase were optimized using DFT with the PBE functional and the TZVP basis set. Based on the optimized geometries of the molecules, TDDFT calculations at the level of PBE/TZVP were carried out to determine at least 100 vertical excitations to the excited state of the molecules and calculate the electronic absorption spectrum and the molecular orbital properties in gas phase.

Co, Cu and Mn atoms have open-shell configuration – in which the metal valence orbitals are not completely filled. The presence of single electrons in the frontier molecular orbitals of open-shell metal complexes presents additional challenges to the theoretical chemists, due to the possible involvement of higher multiplicity states (spin–orbit coupled states) such as doublet, triplet or quartet electronic states or, indeed, a mixture of these in the photochemistry of these complexes. State mixing causes problems even for the most successful computational methods.

There are two ways to describe the electron configurations in open-shell systems: restricted and unrestricted. Restricted configuration restricts both spins α and β to have the same spatial orbital. Unrestricted configuration allows each spin (α or β) to have a different spatial orbital. For a pair of α and β electrons in an orbital, and an unpaired electron in another orbital, the α and β electrons will respond differently to the unpaired electron (Langhoff, 1995). One of the problems which arise here is spin contamination. This increases with an increasing amount of spin polarization. Unrestricted configuration allows for modeling of spin polarization in open-shell molecules. Therefore, the electron configurations in open-shell metal complexes were described in unrestricted way.

The efficiency of BHJ solar cells is limited by the low open-circuit voltage (V_{oc}) (Schilinsky et al., 2002). A model was derived based on a simple relation between the energy level of HOMO of the donor and the V_{oc}, which is used to estimate the maximum efficiency of BHJ solar cells (Scharber et al., 2006). Based on the model, the V_{oc} of a donor–PCBM solar cell can be estimated by

$$V_{OC} = (1/e)(|E^{Donor}_{HOMO}| - |E^{PCBM}_{LUMO}|) - 0.3\ \text{V} \quad (1)$$

where e is the elementary charge and the value of 0.3 V is an empirical factor. The model states that the limiting efficiency of a BHJ solar cell can be predicted solely as a function of the band gap and the LUMO level of the donor and for PCEs exceeding 10%, the donor must have a band gap <1.74 eV and a LUMO level <−3.92 eV, assuming that fill factor and external quantum efficiency are set to 0.65. Recently, some BHJ solar cells which have pentacene (Pramanik et al., 2015) and some co-polymers (Balanay and Kim,