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Letter

Tin naphthalocyanine complexes for infrared absorption in organic photovoltaic cells



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ABSTRACT

In this work, we examine the optical properties of tin naphthalocyanine dichloride (SnNcCl₂), and its performance as an electron donor material in organic photovoltaic cells (OPVs). As an active material, SnNcCl₂ is attractive for its narrow energy gap which facilitates optical absorption past a wavelength of λ = 1100 nm. We demonstrate a power conversion efficiency of η_P = (1.2 ± 0.1)% under simulated AM1.5G solar illumination at 100 mW/cm² using the electron donor–acceptor pairing of SnNcCl₂ and C₆₀ in a bilayer device architecture. While some phthalocyanines have been previously used to improve infrared absorption, this is often realized through the formation of molecular dimers. In SnNcCl₂, the infrared absorption is intrinsic to the molecule, arising as a result of the extended conjugation. Consequently, it is expected that SnNcCl₂ could be utilized in bulk heterojunction OPVs without sacrificing infrared absorption.

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1. Introduction

Significant improvements in the design of organic photovoltaic cells (OPVs) have led to a rapid increase in device efficiency in recent years [1-5]. In addition to improvements in device design, the development of new materials has been equally important for recent observations of power conversion efficiencies approaching and exceeding 10% [6]. To date, the highest performing single-cell bulk heterojunction OPVs are limited in their optical absorption to a wavelength range extending from roughly $\lambda = 350$ – 750 nm [1], despite the fact that \sim 50% of the solar photon flux occurs at $\lambda > 750$ nm. This potential limitation highlights the need for the further development of materials that efficiently absorb light in the near infrared and infrared portions of the electromagnetic spectrum. In the past, low energy gap polymers [7–11], metal phthalocyanines [12-20], carbon nanotubes [21] and colloidal quantum dots [22] have been used to extend OPV absorption further

into the infrared. In this work, we investigate the use of tin naphthalocyanine dichloride (SnNcCl₂) as an electron donor material in OPVs (Fig. 1a). While SnNcCl₂ has not been previously reported in OPVs, it has been previously used in organic photodetectors [23,24]. Here, we compare the optical properties and photovoltaic performance of SnNcCl₂ with those of tin phthalocyanine (SnPc), a widely studied, narrow energy gap small molecule, electron donor [14,15,25]. Previous studies have demonstrated that SnPc owes its infrared absorption to the formation of physical dimers [14,15,25].

2. Materials and methods

Organic photovoltaic cells were fabricated on glass substrates pre-coated with a 150-nm-thick anode layer of indium-tin-oxide (ITO) having a sheet resistance of 15 Ω/\Box . Prior to thin film deposition, substrates were cleaned in tergitol solution and organic solvents and exposed to a UV-ozone treatment. For this study, SnNcCl₂ [26] was synthesized following a previously reported procedure [27] from 2,3-naphthalenedicarbonitrile and Tin (II) chloride,

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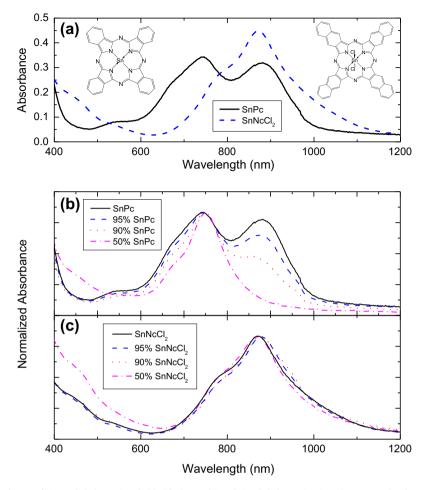


Fig. 1. (a) Thin film absorbance of tin naphthalocyanine dichloride $(SnNcCl_2)$ and tin phthalocyanine (SnPc). Inset: Molecular structures of $SnNcCl_2$ and SnPc. Normalized thin film absorbance spectra for neat and mixed films of (b) $SnPc:C_{60}$ and (c) $SnNcCl_2:C_{60}$ as a function of mixture composition.

while SnPc was obtained from Alfa Aesar [28]. Optimized bilayer devices based on each donor consisted of a 15-nm-thick donor layer and a 35-nm-thick acceptor layer of C_{60} . A 10-nm-thick exciton-blocking layer of bathocuproine (BCP) was grown on top of the active layers [29]. All devices were capped with a 65-nm-thick Al cathode that was deposited through a shadow mask with 1 mm diameter openings. All layers were deposited at room temperature. The organic layers were deposited at a growth rate of 0.2 nm/s, while Al was deposited at 0.3 nm/s.

Absorption spectra for organic thin films grown on glass substrates were collected using a OLIS Cary-14 spectrophotometer. Device characterization was performed in air immediately after fabrication in the dark and under simulated AM1.5G solar irradiance using a 150 W Oriel solar simulator. Current density–voltage characteristics were measured using an Agilent Technologies 4155C semiconductor parameter analyzer as a function of the optical illumination intensity. The optical power was measured during each testing session using a Newport 818P-010-12 high-power detector. The external quantum efficiency ($\eta_{\rm EQE}$) was measured under monochromatic light generated from a Xe lamp coupled to a monochromator. Photo-

current measurements at each wavelength were made using a lock-in amplifier.

3. Results and discussion

3.1. Optical characterization

Efficient OPVs often consist of a bulk heterojunction designed to maximize the area of the exciton dissociating donor-acceptor (D-A) interface [1,30-32]. As such, the optical properties of SnPc and SnNcCl₂ were compared to determine if efficient infrared absorption could be expected in a bulk heterojunction based on SnPc or SnNcCl₂. Fig. 1a shows the thin film absorbance of SnPc (30-nmthick) and SnNcCl₂ (32-nm-thick). The normalized absorption spectra of various 30-nm-thick mixed films of SnPc:C₆₀ is shown in Fig. 1b. The absorbance spectrum of SnPc has two prominent peaks centered at wavelengths of $\lambda = 745$ nm and 880 nm. Previous work on SnPc has identified these peaks as originating from monomer and dimer absorption, respectively [14,15,25]. Consequently, the peak at λ = 880 nm decreases in intensity with increasing C₆₀ concentration due to the suppression of dimer

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