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Short Communication

Study of π-conjugation effect of organic semiconductors on their optical parameters

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ABSTRACT

Metal free organic semiconductor "7,16-bis(3,3-dimethyl-3H-indol-2-yl)-5,14-dihydrodibenzo [*b*,*i*] [1,4,8,11] tetraazacyclotetradecine" and metal free with extended π-conjugation organic semiconductor "8,19-bis(3,3-dimethyl-3H-indol-2-yl)-6,17-dihydrodinaphthol [2,3-b:2′,3′-i][1,4,8,11] tetraazacyclotetradecine have been synthesized and the effect of conjugation on their photovoltaic parameters have been investigated. The photo-physical study reveals band gaps of 2.61 eV for metal free and 2.16 eV for extended material. The HOMO/LUMO levels of the materials are calculated using cyclic voltammetry (CV) study. The open circuit voltages of metal free and extended materials in single layer photovoltaic cells are observed to be 0.72 and 0.73 under simulated solar light illumination (air mass 1.5 G, 100 mW/cm^2), respectively. The short circuit current in the extended materials is found to be more than ~1.5 times higher the metal free material.

1. Introduction

Organic photovoltaic devices are envisaged to be enticing choice to fulfil the global energy demand in the near future by harnessing the solar power. The advantages which they offer, particularly low cost and excellent mechanical flexibility cannot be offered by their counterpart inorganic ones [1–5]. Furthermore, in contrast to inorganic semiconductors, which need elevated temperature and vacuum procedures for their deposition [6–8], organic materials can be simply deposited by solution-based techniques [9,10] such as spin coating, spray coating and inkjet printing. The power conversion efficiency (PCE) of the solar cells is substantially dependent upon the choice of photoactive material. Therefore, besides device engineering efforts, there exists a pressing need to develop new organic materials with significant light harvesting capability. Several organic photoactive materials have been successfully utilized ranging from small organic molecules to conjugated polymers [11–13]. The most extensively studied donor polymers are poly(p-phenylenevinylene) (PPV) derivatives [14,15], polythiophene derivatives [16] and phthalocyanines [17] whereas the fullerene derivative [6,6]-phenylC61-butyric acid-methylester (PCBM) is used as a electron acceptor material.

Researchers have also directed their efforts to randomly explore new donor materials with significant light harvesting e.g., Liang et al., proposed PTB1 to be used as donor material, which showed maximum absorption in 600–800 nm range [18]. Chen et al., reported PBDTTT as donor material which showed maximum absorption in 550–750 nm range [19]. Ashkanshafiee et al., used P3OT as donor material which shows absorption in the range of 470–620 nm [20]. However, the systematic approach to increase the absorption range requires lowering the energy band gap. One effective way to decrease the HOMO-LUMO energy level separation is to increase the conjugation length in the molecular structure [21]. The introduction of conjugated segments (benzene rings) on the backbone of metal free structure, effectively lowers the band gap and increases the absorption bandwidth. Nonetheless, the extension of conjugation lengths results in insolubility of the material [22]. In this study, we have investigated two photovolatic materials, namely, metal free (7,16-bis(3,3-dimethyl-3H-indol-2-yl)-5,14-dihydrodibenzo [*b*,*i*][1,4,8,11] tetraazacyclotetradecine) and extended (8,19-bis(3,3-dimethyl-3H-indol-2-yl)-6,17-dihydro dinaphthol[2,3-b:2′,3′-i][1,4,8,11] tetraazacyclotetradecine). The molecular structure of both materials is identical and involves only one structural modification. In the case of extended material π-conjugated benzene rings have been introduced on the side chain of metal free structure. We thereby aim to study the effect of conjugation length on the photovoltaic parameters of the materials.

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2. Experimental

Both materials, metal free "7,16-bis(3,3-dimethyl-3H-indol-2-yl)-5,14-dihydrodibenzo [*b*,*i*][1,4,8,11] tetraazacyclotetradecine" and extended material "8,19-bis(3,3-dimethyl-3H-indol-2-yl)-6,17-dihydrodinaphthol[2,3-b:2′,3′-i][1,4,8,11] tetraazacyclotetradecine" were synthesized in laboratory by using the protocol mentioned elsewhere. Molecular structures of metal free and extended materials are depicted in Fig. 1(a) and (b), respectively.

Indium tin oxide (ITO) coated glass slides (area ~25 mm × 25 mm), with sheet resistance ~10 Ω/sq served as substrates for our single layer solar cells. Primarily these substrates were well cleaned following the protocol, i.e., by sonication in deionized (DI) water, acetone, isopropyl alcohol and DI water sequentially. These substrates were later dried clean in a dust free environment by nitrogen blow. PEDOT:PSS layer was then spun cast on the ITO substrates at 3000 RPM for 60 s, resulting in 40 nm thin films. Later it was subjected to annealing at 120 °C for 30 min. Prior to photoactive layer deposition, 15 mg/ml concentrated solution of metal free material was prepared in chloroform. The metal free photoactive layer was then spun coated on the substrates. The spin speed was ~4000 rpm, which resulted in a film thickness of 80 nm. However, since the extended material is not solution process-able, therefore its thin films were deposited by means of physical vapor deposition process. Photoactive layer of extended material (film thickness ~80 nm) was achieved by evaporating it through home-made thermal evaporator. After photoactive layer deposition, the samples were thermally annealed at 120 °C for 30 min. Finally, to complete the device fabrication process, aluminum (Al) electrodes were deposited on the top of photoactive layers using thermal evaporation technique. Al electrodes were defined in round shapes utilizing a shadow mask. The diameter of each round shaped Al electrode was 2 mm. The post deposition annealing of the fabricated devices was performed at 120 °C for 30 min. The entire fabrication steps were carried out in the open air inside a clean room. Fig. 2(a) portrays the cross-sectional view of the single layer solar cell whereas Fig. 2(b) and (c) shows the energy level diagram of the metal free and extended organic material based devices, respectively. The HOMO/LUMO Energy levels were found using cyclic voltametry (CV) technique, which will be discussed in the results section below.

In our present work, the photophysical study comprised of UV–Vis absorption measurement and photoluminescence (PL) measurement. UV–VIS spectroscopy was performed by using a UV–Vis–NIR spectrophotometer (Shimadzu UV-3101PC). The PL study was performed using RENISHAW inVia Raman Microscope using 325 nm wavelength laser source and laser intensity of 5%. The electrochemical study involved CV to determine the HOMO/LUMO levels of the organic materials. The CV study was performed by using Digi-Ivy potentiostat (DY 2311). The *I-V* response of the fabricated solar cells was investigated utilizing source measuring unit (computer interfaced Keithley SMU 2400) under the simulated solar illumination (air mass 1.5 G, 100 mW/cm^2) utilizing Abet Technology Sunlite Model 11002 solar simulator.

3. Results and discussion

X-ray diffraction (XRD) spectra of metal free and extended material thin film samples were recorded at room temperature using a PW 1830 diffractometer with 2θ (θ being Bragg angle) from 0° to 80°. The XRD spectra for both samples exhibit a broad hump known as amorphous hump at angle ~26°, which is the characteristic feature of the amorphous materials [23]. Furthermore, the absence of any characteristic Bragg peaks confirms the amorphous nature of the both materials under investigation (see Fig. 3).

The UV/Vis absorption spectra of metal free and extended material have been studied and have been portrayed in Fig. 4. The absorption spectrum of metal free thin film spreads from 300 to 470 nm, with a peak at 370 nm, whilst extended material shows its absorption in the 300–600 nm range with a peak at 370 nm. It is well established fact that longer chain lengths and enhancement in conjugation degree causes a decrease in the optical band gap [24,25]. The PL of metal free and extended materials have also been studied. Inset of Fig. 4 shows the PL spectra of metal free and extended material thin films, which were measured at room temperature and were obtained by an excitation wavelength of 325 nm in the range from 400 to 1000 nm. The PL of the metal free, with strong emission peak at 657.5 nm, lie near the red region. Our results of metal free are consistent with the results reported in the literature [26]. The strong PL signal can be ascribed to the first vibronic band whereas the shoulder may result due to the pure electronic transition. The PL emission peak at the longer wavelength indicates an ordering in the metal free [27,28]. The PL spectrum of extended material shows the emission in the green region (530–600 nm) with its broad peak at around 555 nm

HOMO and LUMO of organic compounds are basic parameters for the design and fabrication of an organic solar cell and are determined by electrochemical study (cyclic voltammetry). To determine the HOMO/LUMO level, the energy of the band gap (E_g) for each material has first been calculated by using optical absorption spectrum. Cyclic voltammetry was later used to estimate the oxidation potential and the HOMO level of the organic materials. The experiments were carried out in a three-electrode cell consisting of a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgCl reference electrode. Fig. 5(a) shows the

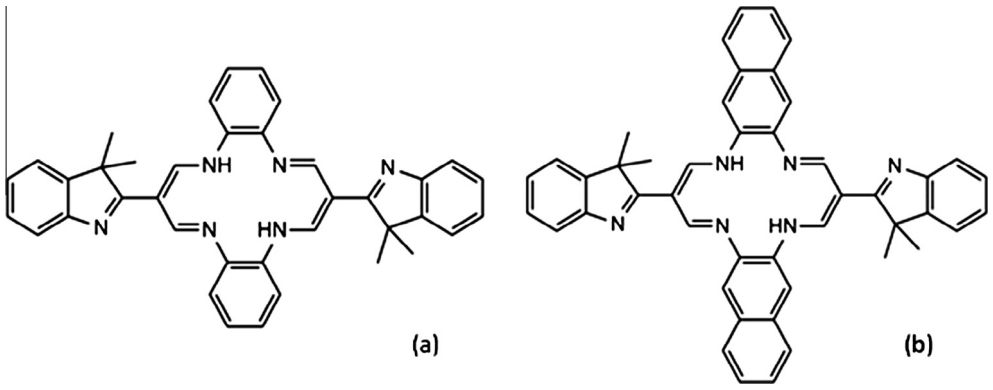

Fig. 1. The molecular structure of (a) metal free "7,16-bis(3,3-dimethyl-3H-indol-2-yl)-5,14-dihydrodibenzo [*b*,*i*][1,4,8,11] tetraazacyclotetradecine" (b) π-conjugation extended material "8,19-bis(3,3-dimethyl-3H-indol-2-yl)-6,17-dihydrodinaphthol[2,3-b:2′,3′-i][1,4,8,11] etraazacyclotetradecine".