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Zinc chlorophyll aggregates as hole transporters for biocompatible, natural-photosynthesis-inspired solar cells

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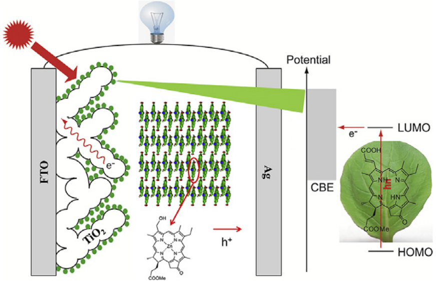
HIGHLIGHTS

- Two different chlorophyll-sensitized solar cells are fabricated and compared.
- Cost-effective ZnChl-1 is used as the hole transporter.
- The carrier mobility of ZnChl-1 is estimated and confirmed.
- We provided a new possibility of using bio-resources for electricity production.

GRAPHICAL ABSTRACT



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ABSTRACT

The intriguing properties of extremely efficient delocalization and migration of excitons in chlorophyll (Chl) J-type aggregates have inspired intense research activities toward their structural understanding, functional interpretation and mimicry synthesis. Herein, we demonstrated the J-aggregates of zinc methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide *a* (ZnChl-1) generated by spin-coating method for the application as a hole transporter in titania-based solar cells using methyl *trans*-3^2-carboxypyropheophorbide *a* (H_2Chl-2) or its zinc complex (ZnChl-2) as the sensitizer. The effective carrier mobility of the J-aggregates films was determined by the organic field-effect transistor to be 6.2×10^{-4} cm^2 V^{-1} s^{-1}. Solar cells sharing the architecture of FTO/H_2Chl-2 or ZnChl-2 on TiO_2/$(\text{ZnChl-1})_n$/Ag were fabricated and the factors that presumably determine their photovoltaic performances were discussed. The photovoltaic devices studied herein employing inexpensive and pollution-free biomaterials provide a unique solution of utilizing solar energy with a care of the important environmental issue.

1. Introduction

Chlorophylls (Chls) are the most abundant natural pigments

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playing key roles of light-harvesting as well as energy- and electron-transfer in natural photosynthetic apparatus [1–4]. The physicochemical property of Chls can be readily tailored through molecular engineering on their cyclic tetrapyrrole rings [5,6]. Such infinite natural resource and the structural feasibility of Chls have their applications to the molecules engaged in optoelectrical devices.

Over the last decade, a series of investigations has been carried out to explore the possibilities of employing Chls as the electron donor/acceptor materials for dye-sensitized solar cells (DSSCs) [7–18], and organic heterojunction solar cells (OSCs) [19–22]. Although these investigations demonstrated the large potential of Chls as functional materials for photovoltaic cells, there are still some remaining challenges for these Chls-based photovoltaic devices. (1) For both typical DSSCs and OSCs, they always utilize some harmful and/or expensive materials, which not only substantially reduced the biocompatibility but also increase the produce/recycle costs of the photovoltaic devices. (2) The Li^+ salt of the electrolyte solution in DSSCs can cause desorption of Chl dyes from TiO_2 nanoparticles resulting in a reduced solar cell durability [9]. (3) The small diffusion lengths of Chl donor/acceptor molecules in OSCs substantially limited the thickness of the active layer resulting in a reduction in light-harvesting efficiency [19]. In view of these problems, a plausible solution is to remain the Chl-sensitized TiO_2 photoelectrode for efficient light-harvesting and charge separation, meanwhile to replace the electrolyte solution with some inexpensive and biocompatible materials for hole transport.

Chlorosomes, the antenna systems of photosynthetic green bacteria, employ the self-aggregated Chls for light-harvesting followed by extremely efficient exciton delocalization and charge transport [23]. To mimic the chlorosomal antenna system in vitro, zinc chlorophyll (ZnChl) derivatives were semi-synthesized and found to form regular cylinder-shaped J-aggregates in nonpolar solvents through $\pi-\pi$ interaction [24]. The rod-shaped ZnChl aggregates prepared on a solid surface can exhibit a high charge carrier mobility of 0.28 $cm^2\ V^{-1}\ s^{-1}$ [25]. The high carrier mobility of the ZnChl aggregates strongly encourages the optoelectrical applications particular in solar cells.

In the present study, a zinc Chl derivative, namely zinc methyl 3-devinyl-3-hydroxymethyl-pyropheophorbide *a* (ZnChl-1) [26], and two carboxylated Chl derivatives, namely methyl *trans*-3^2-carboxypyropheophorbide *a* (H_2Chl-2) [13] and zinc methyl *trans*-3^2-carboxypyropheophorbide *a* (ZnChl-2) [27] were employed as the hole transporting layer and the active layers respectively in the natural-photosynthesis-inspired photovoltaic cells. The UV–visible absorption spectrum of the ZnChl-1 films prepared by simple spin coating on the porous TiO_2 suggests the formation of the J-aggregates. The hole mobility of the ZnChl-1 aggregates was estimated by organic field-effect transistor (OFET) measurements [28]. The fact that the power conversion efficiency of solar cell based on H_2Chl-2 is higher than that based on ZnChl-2 is attributed to the larger regeneration potential between ZnChl-1 and H_2Chl-2 than that between ZnChl-1 and ZnChl-2.

2. Experimental

2.1. Materials

Fluorine-doped SnO_2 glass (FTO, (8 $\Omega\ cm^{-2}$)) was purchased from Asahi Glass. TiO_2 nanoparticles were purchased from solaronix (solaronix T/SP). THF was purchased from Tianjin Fuyu Co. Chloroform was purchased from Aladdin Co.

2.2. Synthesis of chlorophyll derivatives

ZnChl-1, H_2Chl-2 and ZnChl-2 were synthesized as reported before [13,26,27] (see the Scheme S1 in the Supporting information for the synthetic route).

2.3. Fabrication of solar cells

The etched FTO substrates (etched by Zn powder and HCl) were pre-cleaned by detergent, tap water, deionized water, acetone, ethanol in sequence. The substrate was soaked in $TiCl_4$ aqueous solution (20 mM) at 70 °C for 30 min to form a compact TiO_2 layer. After being rinsed by deionized water and ethanol in sequence, the substrate was then spin-coated with TiO_2 nanoparticles ethanol solution (33 wt%). The thickness of TiO_2 nanoparticles was adjusted by controlling the spin-coating speed. The substrate was then sintered at 500 °C for 30 min in a furnace. This substrate was treated with the same $TiCl_4$ solution and sintering process at 500 °C again [29]. The substrate was then dipped in a H_2Chl-2 or ZnChl-2 ethanol solution (0.1 mg mL^{-1} in ethanol) overnight in dark. After dye loading, the substrate was rinsed with ethanol and dried in a glovebox. A ZnChl-1 solution (8 mg mL^{-1} in THF) was spin-coated onto the top of the H_2Chl-2/ZnChl-2-sensitized TiO_2 films (500 rpm for 6 s, and followed by 5000 rpm for 30 s). The film was then transferred into a high vacuum chamber (4×10^{-4} Pa) for evaporation of Ag (50 nm) onto the ZnChl-1 layer as a back electrode. Perovskite-based solar cells were fabricated with the same procedure, except for the absorber layer that employs $CH_3NH_3PbI_{3-x}Cl_x$ perovskite [30] instead of H_2Chl-2/ZnChl-2 sensitizer. The perovskite layer was prepared by spin coating of an N,N-dimethylformamide solution containing CH_3NH_3I (2.7 M) and $PbCl_2$ (0.9 M) followed by annealing at 100 °C for 90min.

2.4. Device characterization

The photocurrent–photovoltage (*J*–*V*) characteristics of the solar cells were measured by using a computer-controlled Keithley 2400 source meter measurement system with an AM1.5G filter at a calibrated intensity of 100 mW cm^{-2} illumination, as determined by a standard silicon reference cell (91150 V Oriel Instruments). The device area of 4 mm^2 was controlled by a metal mask. Incident photo-current conversion efficiency (IPCE) was measured in air under short-circuit conditions using Crowntech QTest Station 1000AD, which was equipped with a 100-W Xe arc lamp, filter wheel, and monochromator (light was chopped at 80 Hz, measured by a lock-in amplifier).

2.5. Thin film characterization

Highly doped n-type Si substrates as a gate were used for the development of the OFETs. A thermally grown 300-nm SiO_2 layer serves as the gate dielectric. ZnChl-1 films with a 100-nm thickness were prepared by spin coating from the THF solution. Gold electrodes were deposited using shadow mask with the channel length and width of 50 and 1000 μm, respectively. All the OFETs' characteristics were measured using a Keithley 4200-SCS semiconductor parameter analyzer under the ambient conditions. UV–Vis absorption spectra were recorded by a Shimadzu UV-3100 spectrophotometer. Photoluminescence (PL) intensities were measured by a Shimadzu RF-5301pc fluorescence spectrometer, with a 380 nm wavelength as the excitation source. The SEM image was acquired by a field emission scanning electron microscope (Hitachi SU 8020).