



Porphyrin sensitizers with acceptor structural engineering for dye-sensitized solar cells

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ARTICLE INFO

Keywords:

Porphyrin dye
 Acceptor design
 Aggregation
 Dye-loading amount
 High efficiency

ABSTRACT

Two porphyrin-based sensitizers, **SGT-028** and **SGT-029**, were designed and synthesized via acceptor engineering for application in dye-sensitized solar cells (DSSCs). Porphyrin **SGT-028** was designed by introducing a salicylic acid anchoring group instead of a conventional benzoic acid in the platform of donor-porphyrin-triple bond-BTD-phenyl-acceptor sensitizers (e.g., **SGT-021** and **SM315**). As for **SGT-029**, an additional alkylated benzothiadiazole (BTD) unit was substituted to the BTD of D- π -A porphyrin sensitizers. The impact of the anchoring group and long alkyl chains on the optical character, electrochemical property, and photovoltaic performance were studied and also compared with a reference dye of **SGT-021**, which had previously been synthesized by our group. As a result, both of these two porphyrin sensitizers obtained a similar absorption range and energy band gap to **SGT-021** dye. After performing optimization of DSSC devices, **SGT-029** achieved a comparatively high power conversion efficiency (PCE) of 10.5%, but was inferior to the benchmark porphyrin sensitizer **SGT-021** (12.7%), and a slightly lower PCE of 9.1% was exhibited by **SGT-028**, under the standard AM 1.5G light intensity. It is worth mentioning that the PCE of 12.7% is the highest efficiency for a **SGT-021**-based device up to now. The main reason was supposed to be the dye adsorption amount difference, maybe allowing for a serious dye aggregation, which often leads to an increased quenching of excited states and limits the charge injection into the TiO₂ semiconductor substrate, and lower light harvest efficiency (LHE), resulting in lower photocurrent, photovoltage, and PCE.

1. Introduction

Solar, hydropower, wind, and other renewable energy sources have been a worldwide energy demand. In particular, fast-growing photovoltaic systems are opening up a great number of opportunities in technology and research for using solar energy sources [1]. Since 1991, a relatively new type of photovoltaic device called dye-sensitized solar cells (DSSCs) was first introduced by Grätzel and O'Regan: sensitizers adsorbed to a nanocrystalline TiO₂ thin film as a photoanode to allow for low-cost solar electricity [2]. As a type of third-generation photovoltaic technology, a vast amount of research has been done on DSSCs due to good photostability, low cost, flexibility, colorfulness, and high efficiency in ambient light. Up to now, single sensitizer-based DSSCs have reached photon conversion efficiencies (PCEs) over 14% [3,4] under AM 1.5G standard illumination and 34% [5] under ambient light (103 mW/cm² at 1000 lux). Owing to sensitizers in DSSCs playing a crucial role in light absorption and photocurrent generation, the structural engineering of new dyes with high photovoltaic performance is

important [6].

Among various sensitizers, porphyrin dyes have attracted much attention due to their excellent light absorption ability in the visible light region, on account of a strong Soret band (450–500 nm) and moderate Q bands (550–600 nm), high molar extinction coefficients, tunable electronic structures, and easy structural modification. Up to now, porphyrin-based DSSCs have reached PCE higher than 13% on the laboratory scale [7], as well as extremely high efficiency by co-sensitizing with other organic dyes [3,8]. Nevertheless, there are still some drawbacks to most of the porphyrin sensitizers. For example, the deficient absorption in the NIR (near-infrared) wavelength range and the poor light harvest ability between the Q band and Soret band will be a barrier to reach high short-circuit current. Additionally, the extended π -conjugation in porphyrin molecules is liable to cause aggregation, with the unexpected aggregation in DSSC devices tending to quench the excited state of dye, leading to poor electron injection efficiency [9–11]. To overcome these problems, many effective structure engineering strategies have been reported to enhance the overall PCE. For example,

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<https://doi.org/10.1016/j.dyepig.2020.109082>

Received 6 October 2020; Received in revised form 8 December 2020; Accepted 9 December 2020

Available online 15 December 2020

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