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Exploratory synthesis and photovoltaic performance comparison of D–π–A structured Zn-porphyrins for dye-sensitized solar cells

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ABSTRACT

The design and synthesis of D–π–A structured Zn(II)–porphyrin sensitizers with extended π-conjugation, coded as **SGT-012, SGT-016, SGT-052** and **SGT-053**, were explored. The key schematic concept for the molecular design and synthesis of porphyrin sensitizers, with the target of modulation of donor groups by embedding an electron donor into the skeleton of two typical D-π-A porphyrin models, such as D–porphyrin-A sensitizers (**SGT-012** and **SGT-016**) and D-triple bond-porphyrin-triple bond-**BTD**-acceptor sensitizers (**SGT-052** and **SGT-053**), was proposed investigate the influence of the donor ability and the bulk of donor groups on the photophysical properties and cell performance of dye-sensitized solar cells (DSSCs). Also, based on the photophysical properties and cell performances, the co-sensitisation strategy was conducted to further enhance the cell performances. **SGT-012** and **SGT-052** porphyrins, containing a strong donor unit, exhibited similar S-band absorption and a slightly red-shifted Q-band absorption compared to **SGT-016** and **SGT-053** porphyrins containing a weak bulky donor unit, respectively. To further extend the π-conjugation and absorption to a longer wavelength range, the triple bond at two *meso*-positions of the porphyrin core and a benzothiadiazole (**BTD**) strong electron acceptor was introduced to yield **SGT-052** and **SGT-053**, resulting in a red-shift and broad visible region absorption ability. It was indicated that these modifications lead to the formation of a stronger intramolecular charge transfer complex, which is favourable for harvesting sunlight, than those of **SGT-012** and **SGT-016** porphyrins. To prevent undesirably reduced V_{oc} caused by charge recombination processes and dye aggregation from porphyrin-sensitized solar cells, **HC-Al** of co-adsorbent was adopted to fabricate **SGT-052-** and **SGT-053**-based solar cells. The DSSCs with **SGT-052** and **SGT-053** exhibit better light harvesting ability than the DSSCs with **SGT-012** and **SGT-016** porphyrins, due to the formation of the stronger intramolecular charge transfer complex. Thus, the incident photon-to-current conversion efficiency (**IPCE**) of **SGT-052** and **SGT-053**-based DSSCs was extremely red-shifted to a wavelength of 800 nm, resulting in higher J_{sc} values of 15.3 and 14.6 mA cm^{-2}, respectively. The DSSC utilising **SGT-052** and **HC-A1** exhibited a higher photovoltaic performance (η_{eff} ~ 9.6%) than did other sensitizers. On the basis of **SGT-052**-based DSSC, its DSSCs co-sensitized with **SGT-012** were prepared to improve the J_{sc}, V_{oc} and power conversion efficiency (10.2%).

1. Introduction

Research into renewable energy has become more and more important to solve the increasing energy crisis and environmental pollution. In this respect, dye-sensitized solar cells (DSSCs) have attracted much attention due to their high power-conversion efficiencies (PCEs), flexible device fabrication, and production of transparent colourful devices [1–3]. To enhance the power conversion efficiency (PCE) of DSSCs, the development of sensitizers plays an important role in the light-harvesting ability [4,5]. Among DSSCs, sensitizers can be categorised into three classes: (i) ruthenium (Ru)-based organometallic sensitizers [6,7], (ii) porphyrins [8–11], and (iii) metal-free organic sensitizers [12–14] composed of donor-π-bridge-acceptors (D-π-A). Among the various types of sensitizers [15–18], Zn(II)-porphyrin sensitizers have received considerable attention for DSSCs due to their good light-harvesting ability, easy chemical synthesis and high efficiency [19–22]. The highly efficient porphyrin sensitizers have a characteristic donor(D)-porphyrin-acceptor(A) structure. However, typical D-porphyrin-A structured sensitizers have strong light absorption in the B (400–450 nm) and Q (550–650) bands, along with weak absorption around 500–600 nm and beyond 700 nm [23–27]. For the development of panchromatic porphyrin sensitizers, considerable

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attention has been paid to the tuning of the strong donor and acceptor structure of D-porphyrin-A structures through molecular engineering, resulting in improvements in photophysical and photovoltaic properties. As an example, **SM315** has remarkably improved absorption ability in the visible and NIR region by incorporation of the benzothiadiazole (**BTD**) strong acceptor between the porphyrin and anchoring group [28]. Despite the high PCE of 13% of **SM315**, it exhibits a low open-circuit voltage (V_{oc}) compared to that of **SM371**. In order to enhance the V_{oc} value, it is necessary to introduce the strong bulky donor group in place of a bulky diphenylamine donor of **SM315** to retain the slow charge recombination processes and enhance the light-harvesting ability. Among the a lot of available donor groups, the incorporation of a bulky fluorenyl moiety as the donor into the platform of a D-porphyrin-triple bond-**BTD**-acceptor sensitizer has previously been reported to result in slow charge recombination and enhancement of the light-harvesting properties, leading to a higher V_{oc} and power conversion efficiency compared to **SM315** [29].

In this work, the key schematic concept for the molecular design and synthesis of porphyrin sensitizers with the targeted modulation of donor groups by embedding an electron donor into the skeleton of two typical D-π-A porphyrin models, such as D–porphyrin-A sensitizers (**SGT-012** and **SGT-016**) and D-triple bond-porphyrin-triple bond-**BTD**-acceptor sensitizers (**SGT-052** and **SGT-053**), was proposed in order to investigate the strong influence of the donor ability and the bulk of donor groups on the photophysical properties and cell performance of dye-sensitized solar cells. Recently, Liu and co-workers reported that broad absorption bands and strong intramolecular charge separation can be achieved by introducing a cyanoacrylic acid acceptor group linked through a phenylene bridge to the porphyrin sensitizers, leading to an improvement of the cell performance of DSSCs [30]. However, porphyrin sensitizers containing frameworks of coexisting ethynylene and cyanoacrylic moieties exhibit low J_{sc} and V_{oc} values, related not only to the floppy structure of the cyanoacrylic group but also to the aggravated dye aggregation effect [31–34]. Thus, the key concept for the molecular design and synthesis of **SGT-012** and **SGT-016** porphyrin sensitizers by structurally integrating a HOP porphyrin sensitizer [19] with **SM315** through donor and alkoxy chain structural engineering was proposed in order to enhance the light-harvesting ability and to retard charge recombination in the platform of porphyrin sensitizers based on a cyanoacrylic acid acceptor group (D-porphyrin-A structure). Furthermore, to significantly extend the π-conjugation and absorption to a longer wavelength, a phenyl-ethynylene spacer between the donor group and the porphyrin core in the platform of the D-porphyrin-triple bond-**BTD**-acceptor sensitizer (**SM315**), coded as **SGT-052** and **SGT-053**, was introduced in order to enhance the light-harvesting ability. **SGT-052** and **SGT-053** resulted in red-shift and broad visible region absorption ability compared to **SGT-012** and **SGT-016**. Furthermore, to improve highly efficient DSSCs, the co-adsorbent from the CDCA to **HC-A1**, which broke up dye aggregates and improved the light-harvesting effect in the short wavelength region [11] was investigated. It was observed that the replacement of the co-adsorbent from CDCA to **HC-A1** in DSSCs with **SGT-052** and **SGT-053** porphyrins led to a significant enhancement in J_{sc} and V_{oc} by suppressing charge recombination and increasing electron lifetime. As a result, the DSSC utilising **SGT-052** and **HC-A1** exhibited higher photovoltaic performance (η_{eff} ~9.6%) than other sensitizers. On the basis of the **SGT-052**-based DSSC, DSSCs co-sensitized with **SGT-012** were prepared, to improve the J_{sc}, V_{oc} and power conversion efficiency (10.2%).

2. Results & discussion

We synthesised four new Zn(II)–porphyrin sensitizers: **SGT-012**, **SGT-016**, **SGT-052** and **SGT-053**, as shown in Fig. 1. The detailed synthetic procedure and characterisation are shown in the Supplementary Information.

A cyanoacrylic acid acceptor group linked through a phenylene bridge to the porphyrin sensitizers, coded as **SGT-021** and **SGT-016**, was introduced in order to achieve broad absorption bands and strong intramolecular charge separation [30]. The structure of **SGT-016** was designed with a bulky dihexyloxybiphenyl donor group in order effectively to prevent charge recombination and to reduce dye aggregation [15]. **SGT-012** porphyrin with a strong donor unit exhibited a similar S-band absorption and a slightly red-shifted Q-band absorption, compared to **SGT-016** porphyrin containing a bulky, weak donor unit. Compared to the two above-mentioned sensitizers, **SGT-052** and **SGT-053** were established by utilising the triple bond at two *meso*-positions of the porphyrin core and a benzothiadiazole (**BTD**) strong electron acceptor, leading to the formation of stronger intramolecular charge transfer (ICT) complex than **SGT-012** and **SGT-016** porphyrin sensitizers. **SGT-052** and **SGT-053** resulted in red-shift and broad visible region absorption ability compared to **SGT-012** and **SGT-016** [35,36]. These experimental absorption properties can be well reproduced by the simulated absorption spectra of time-dependent density functional theory (TD-DFT) calculations at M06/6-31G(d) (LANL2DZ for Zn atom) level in THF solvent using the Gaussian (see Fig. S2) [29].

The UV–vis absorption spectra of **SGT-012**, **SGT-016**, **SGT-052** and **SGT-053** porphyrins were measured in tetrahydrofuran (THF) (Fig. 2a) and their corresponding data are summarised in Table 1. As expected, all porphyrin sensitizers exhibited typically strong absorption bands within 400–500 nm and weak absorption bands in the range 550–750 nm, which correspond to the B- and Q-bands of porphyrin-based sensitizers, respectively. **SGT-012** and **SGT-052** porphyrins with a strong donor unit exhibited a similar S-band absorption and a slightly red-shifted Q-band absorption compared to **SGT-016** and **SGT-053** porphyrins with a weak bulky donor unit. Interestingly, **SGT-052** and **SGT-053** exhibited the red-shifted and broad B absorption peak in the range of 400–500 nm, compared to other two sensitizers, due to the formation of the strong ICT complex as well as the reinforcing light absorption and planarity by introduction of the triple bond at two *meso*-positions of the porphyrin core [37,38]. In addition, compared to **SGT-012** and **SGT-016**, the introduction of the strong electron acceptor benzothiadiazole (**BTD**) group in **SGT-052** and **SGT-053** resulted in remarkable further red-shifted and broad Q-band peaks in the UV–vis absorption range from 650 to 730 nm, which is favourable for harvesting sunlight, due to the formation of the strong ICT complex.

To evaluate the oxidation and reduction behaviours of all porphyrin sensitizers, cyclic voltammetry (CV) measurements was carried out (see Fig. S3) and their electrochemical data are collected in Table 1. From the J-V curves illustrated in Fig. S3, the ground-state oxidation potentials (S^+/S) of **SGT-012** and **SGT-052** with a bis(4-hexyloxyphenyl) amino donor group are similar to those of **SGT-016** and **SGT-053** with a bis(2′,4′-bis(hexyloxy)-[1,1′-biphenyl]-4-yl)amine donor unit. To discover the effects of donor groups on energy levels, the S^+/S of **SGT-012** and **SGT-052** were higher than those of the other two dyes, indicating that they were directly affected by alkoxy functional groups in the bis (4-hexyloxyphenyl)amino donor group, while **SGT-016** and **SGT-053** were weakly influenced by the bis(2′,4′-bis(hexyloxy)-[1,1′-biphenyl]-4-yl)amine donor unit owing to the torsion angle between the phenyl groups [10]. As the E_{ox} in solution is more positive than that of the cobalt electrolyte (+0.40 V vs. NHE), the E_{ox} of all porphyrins are all thermodynamically favourable for effective dye regeneration in a DSSC system (Fig. 2b).

Fig. 3 shows the photocurrent density–voltage (J–V) characteristics and the corresponding action spectra of incident photon-to-current conversion efficiency (IPCE) of DSSCs for all porphyrin sensitizers measured under standard photovoltaic conditions (global AM1.5 sunlight with irradiance of 100 mW cm^{-2} at 298 K), and their detailed photovoltaic parameters are summarised in Table 2. DSSCs with **SGT-052** and **SGT-053** exhibited much higher performance than did DSSCs with **SGT-012** and **SGT-016**. In the case of DSSCs with **SGT-052** and **SGT-053**, a remarkably broad IPCE action spectrum, absorbing the panchromatic visible region and part of the NIR region, was achieved