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Original article

Modulation of photovoltaic behavior of dye-sensitized solar cells by electron donors of porphyrin dyes and cosensitization

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ABSTRACT

Porphyrin dyes have received great attention due to their excellent photovoltaic performance in dye-sensitized solar cells (DSSCs). In this work, dyes **XC1**–**XC3** were synthesized by introducing various numbers of bis(4-methoxyphenyl)amino and *p*-hexyloxyphenyl groups to porphyrin *meso*-positions. The **XC1** molecule contains two *p*-hexyloxyphenyl groups, and its DSSCs showed the power conversion efficiency of 4.81%. For **XC2** and **XC3**, the replacement of *p*-hexyloxyphenyl with diphenylamino groups can effectively enhance the light harvesting around 500 nm. However, the highest occupied molecular orbitals (HOMOs) were elevated too much, which suppressed the dye regeneration processes, leading to low cell efficiencies of 2.51% and 1.27% for **XC2**, and **XC3**, respectively. To further improve the cell performance, an anthracene derivative **C1** was used as the cosensitizer for **XC1**, which increased both the J_{sc} and V_{oc} values, with an improved efficiency of 5.75%.

1. Introduction

Since the first report by Grätzel [1], dye-sensitized solar cells (DSSCs) have attracted increasing attention in utilizing solar energy because of their relatively low cost, easy fabrication, and environmentally friendly character [2–6]. In recent years, many groups are devoted to the development of novel dyes to improve cell efficiencies. In this respect, porphyrins have been demonstrated to be promising, because of their high molar absorption coefficients, good photostability, beautiful color, as well as high cell efficiencies. In addition, the properties can be easily modulated by the peripheral substituents and inner coordinated metal ions [7]. Thus, D-π-A type porphyrins have been intensively investigated for developing efficient DSSC dyes. Especially, porphyrins containing *meso*-diphenylamine donor groups exhibited relatively high cell efficiencies [8,9]. For example, Grätzel and co-workers have reported the highest DSSC efficiency of 13.0% for porphyrin dyes containing diphenylamine donors and extended benzoic acid acceptors [10].

In addition to designing efficient porphyrin dyes, cosensitization with another organic dye is also effective in further improving the efficiencies of porphyrin-based DSSCs [11–13]. In this respect, our group recently reported porphyrin dyes with carbazole-based electron donors, in combination with the cosensitization approach, achieving the high cell efficiency of 10.75% [11,12].

Herein, we report the investigations on the effect of numbers and positions of the diphenylamine units on the DSSC efficiencies, with the purpose to further understand the efficiency–structure correlations. Thus, porphyrin dyes **XC1**–**XC3** were synthesized by introducing various numbers of bis(4-methoxyphenyl)amino and *p*-hexyloxyphenyl groups as the donors (Scheme 1), and the effect of dye structures on the efficiencies was investigated. To our delight, introduction of the bis(4-methoxyphenyl)amino unit can effectively enhance the light harvesting around 500 nm, and the cell efficiencies are highly dependent on the donors. By further application of the cosensitizer **C1** (Scheme 1), a cell efficiency of 5.75% was achieved.

2. Experimental

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. The transparent FTO conducting glass (fluorine-doped SnO_2, transmission > 90% in the visible range, sheet resistance 15 Ω/square) and the TiO_2 paste was purchased from Geao Science and Educational Co., Ltd. The FTO conducting glass was washed with a detergent solution, deionized water, acetone, and ethanol successively under ultrasonication for 20 min before use, respectively. The synthesis of **C1** has been communicated [12]. The synthetic

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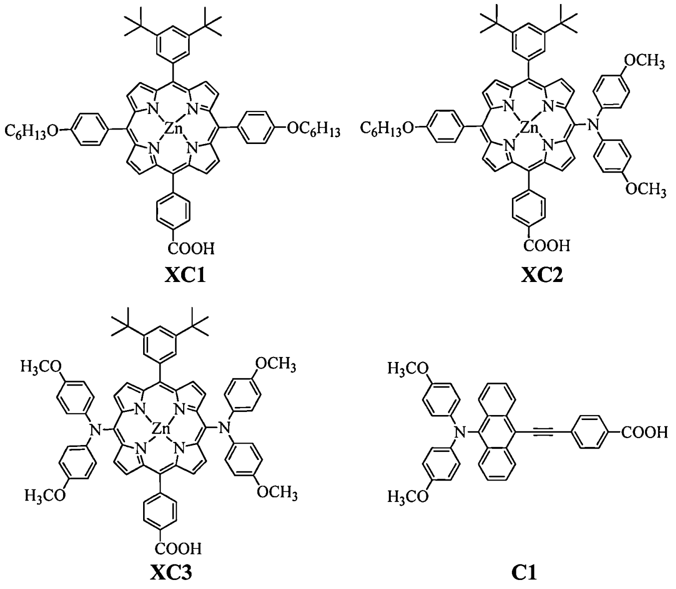

Scheme 1. Molecular structures of porphyrin dyes **XC1**–**XC3** and cosensitizer **C1**.

details, computational methods and photovoltaic measurements are described in the Supporting Information.

3. Results and discussion

As mentioned above, diphenylamino units may be introduced into the *meso*-positions of porphyrins as strong electron donors to synthesize efficient DSSC dyes. Meanwhile, *p*-hexyloxyphenyl groups not only can be used as weak electron donors, but also can be employed for suppressing the dye aggregation effect due to the presence of long alkyl chains [14]. Therefore, for the purpose of modulating molecular energy levels and suppressing dye aggregation, various numbers of bis(4-methoxyphenyl)amino and *p*-hexyloxyphenyl groups were introduced to afford the target porphyrin dyes **XC1**–**XC3** (Scheme 1, S1 and Figs. S1–S18 in Supporting information).

3.1. Spectral properties

Wide and strong absorption characteristics are favored for capturing the solar light. Dyes **XC1**–**XC3** exhibit the typical features of porphyrins, with an intense Soret band in the range of 400–450 nm, and less intense Q bands in a range of 500–750 nm (Fig. 1 and Table S1 in Supporting information). Compared with **XC1**, dyes **XC2** and **XC3** exhibit new absorption bands centered at *ca.* 485 nm with increasing intensities, which may be ascribed to the charge transfer associated with the strongly electron donating bis(4-methoxyphenyl)amino groups. Furthermore, the Q bands and emission wavelengths of **XC2** and **XC3** are successively red-shifted (Fig. 1), indicating that they may have stronger light harvesting ability in the long wavelength range, which is favorable for improving the cell efficiencies.

Compared with the corresponding solution spectra, absorption bands of the dyes loaded TiO_2 films are broadened (Fig. 2), which will result in increased light-harvesting ability. Dye **XC1** shows split Soret bands. The red-shifted one results from the *J*-aggregation of the dye molecules on the TiO_2 films [15], and the blue-shifted one can be ascribed to the deprotonation of the carboxylic acid group upon dye attachment to the TiO_2 surface [16,17], and/or the H-aggregation of the dyes [18,19].

In contrast to **XC1**, dye **XC2** shows a slightly blue-shifted Soret band when it is loaded onto the TiO_2 film, and no obvious change was observed for the Soret band of **XC3** upon loading onto TiO_2.

3.2. Electrochemical properties

To effectively realize the electron injection and dye regeneration processes in DSSCs, HOMO and LUMO orbitals of the dyes should be aligned at suitable energy levels. Thus, the cyclic voltammograms for **XC1**–**XC3** were recorded in CH_2Cl_2 (Fig. 3), and the corresponding data are summarized in Table S2 in Supporting information. It can be obtained from Fig. 3 that the first oxidation potentials for **XC1**–**XC3** are 0.70, 0.55, 0.49 V, respectively. The E_{0-0} energy gap values estimated from the absorption threshold of the dyes adsorbed on the TiO_2 films turn out to be 1.98, 1.76, 1.69 V for **XC1**–**XC3**, respectively. Thus, the LUMO levels of **XC1**–**XC3** can be calculated to be −1.28, −1.21, −1.18 V, respectively. These values are all significantly higher than the conduction band (CB) of the TiO_2 electrode, and thus enabling the electron injection processes. On the other hand, the HOMO level for **XC1** is obviously lower than the I^-/I_3^- energy level, which makes the dye regeneration process feasible. Hence, **XC1** is suitable for fabrication of efficient DSSCs in terms of the energy levels. In contrast, the HOMO levels for **XC2** and **XC3** are elevated too much by the strongly electron donating bis(4-methoxyphenyl) amino groups [5], and thus the dye regeneration process may be suppressed, which is unfavorable for the DSSC efficiencies.

3.3. Theoretical calculations

To gain further insight into the electron distribution of the frontier molecular orbitals, density functional theory (DFT)

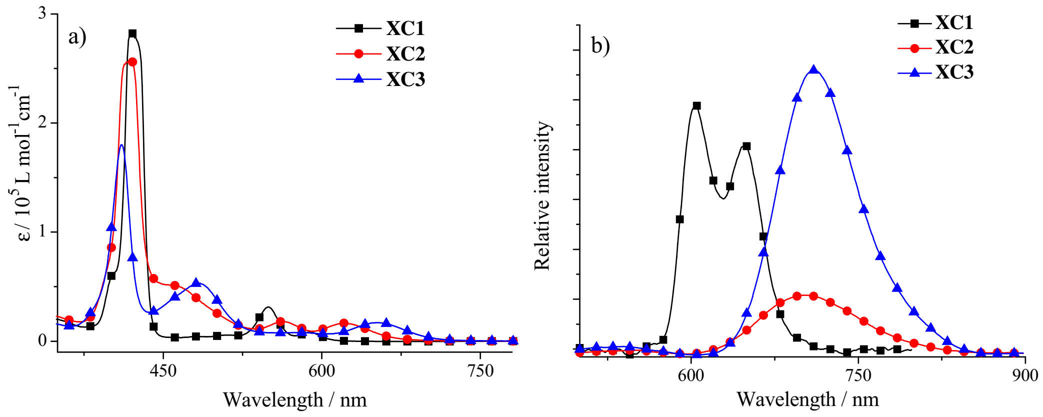

Fig. 1. (a) Absorption spectra and (b) emission spectra of porphyrin dyes **XC1**–**XC3** in $CHCl_3$–CH_3OH (v/v, 2/1).