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Novel D–π–A structured porphyrin dyes containing various diarylamino moieties for dye-sensitized solar cells

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ABSTRACT

A series of novel zinc porphyrins which are featured with a donor–π–acceptor structure have been synthesized for use in the dye-sensitized solar cells. Various diarylamine moiety, such as diphenylamine, iminodibenzyl or iminostilbene, is introduced at porphyrin meso position as an electron donating group. The cell fabricated with the iminodibenzyl-substituted porphyrin sensitizer yields a short circuit photocurrent density of 9.68 mA/cm^2, an open-circuit voltage of 740 mV, and a fill factor of 73.48%, corresponding to an overall conversion efficiency (η) up to 5.26%, which is greater than those obtained by diphenylamine- and iminostilbene-substituted porphyrin-sensitized solar cells (η = 4.05% and 2.62%, respectively). The theoretical studies reveal that the iminodibenzyl donor has the strongest electron donating ability among all three diarylamine substituents employed, which is believed to play a significant role in influencing the photovoltaic properties of these sensitizer-based solar cells.

1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn intense attention since the pioneering work of Grätzel and coworkers in 1991 due to their low-cost fabrication and relatively high efficiency [1]. Polypyridyl ruthenium complexes had been regarded as the most efficient sensitizers and an overall solar-to-electric conversion efficiency (η) of up to 11% has been achieved for DSSCs containing Ru sensitizers under standard global AM 1.5 solar conditions [2]. However, in consideration of the cost and environmental issues arisen from the use of the ruthenium complex, a variety of organic dyes without metal or with cheap metals, such as Cu or Zn, have been developed as sensitizers for use in DSSCs [3–12]. Among those organic dyes developed, zinc porphyrins have proved to be one of the most popular sensitizers for DSSCs due to their vital roles in natural photosynthetic systems, and strong Soret (400–450 nm) and moderate Q bands (550–600 nm) absorptions, as well as readily tunable optical, photophysical and electrochemical properties by peripheral substitutions [13]. Typically, high conversion efficiencies could be achieved by using the "push–pull" porphyrin sensitizers featured with a donor–π–acceptor (D–π–A) structure [14], in which a diarylamine derivative is generally employed as an electron donating (or electron pushing) unit. For example, recently, Grätzel et al. [15] reported a new benchmark in porphyrin-sensitized solar cells, with an overall efficiency of 13%, by using a judiciously engineered porphyrin sensitizer (SM315) bearing a long alkoxyl chain-substituted diarylamine electron donor at the porphyrin meso position (Fig. 1a), along with a cobalt (II/III)-based redox electrolyte.

It is believed that the electron donating (or electron pushing) group attached to the porphyrin meso position can not only facilitate electron injection from porphyrin into the conduction band of TiO_2, but also stabilize the charged-separated state, thus increasing its lifetime [16,17]. However, to the best of our knowledge, few studies have reported on how the electron donating abilities of the diarylamine derivative influence the performance of the porphyrin-sensitized solar cells. It is known that different diarylamine substituent in a dye can have a significant influence on the efficiency of the dye-sensitized solar cells because of the different charge distribution in the dye molecule resulted from the electron-donating

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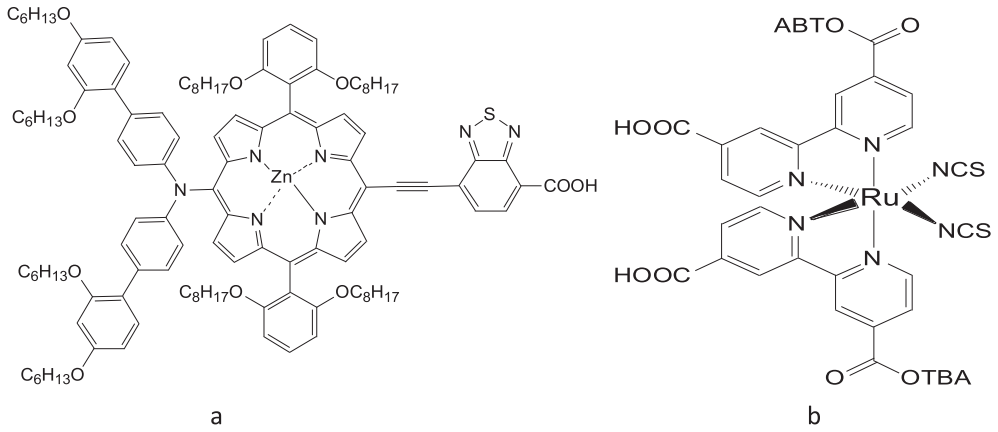


Fig. 1. The chemical structure of SM315 (a) and N719 (b).

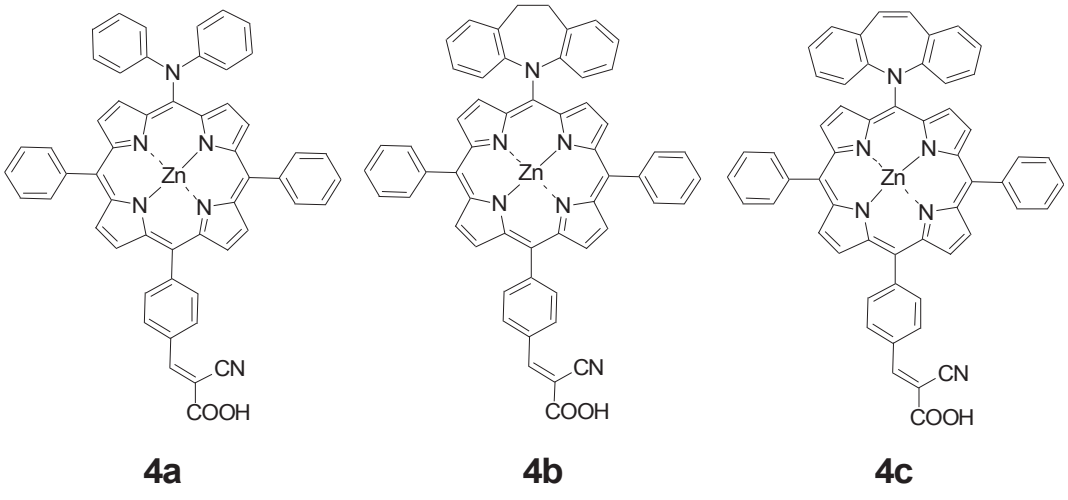
abilities of the diarylamine substituent [18]. 10,11-dihydro-5H-dibenzo[b,f]azepine (Iminodibenzyl, IDB) and 5H-dibenzo[b,f]azepine (iminostilbene, ISB) with two phenyl rings connected by alkyl and ethylene chains have been widely used in materials of organic light-emitting diodes (OLEDs) to achieve high luminescence quantum yield [19,20], and metal-free organic dyes for DSSCs to produce the high conversion efficiency [21–23]. The rotation of the phenyl rings in iminodibenzyl and iminostilbene substituents is limited due to their semi-rigid structure which could lead to the decreasing of energy loss [24,25] and different electron donating abilities of amine donor, compared to that of the diphenylamine (DPA) group. It is of interest to incorporate these substituents into the "push–pull" type porphyrin sensitizers as electron pushing groups to study how these semi-rigid diarylamine moieties influence the performance of porphyrin-sensitized solar cells.

Taking this into consideration, three new porphyrin molecules bearing diphenylamine, iminodibenzyl and iminostilbene as the electron donor, and benzo cyanoacrylic acid as π-spacer and the electron acceptor, shown in Scheme 1 were designed. The photophysical and electrochemical properties of the dyes were investigated by UV–Vis, fluorescence and cyclic voltammetry spectra. The further study has shown that the highest η of 5.26%, with a short circuit photocurrent density (J_{SC}) of 9.68 mA/cm^2, an open-circuit voltage (V_{OC}) of 740 mV, and a fill factor (FF) of 73.48%, was achieved for **4b**-sensitized solar cell in which the meso **IDB** moiety functions as an electron pushing group, and under the same conditions cis-diisothiocyanato-bis(2,2-bipyridyl-4,4′-dicarboxylato) ruthenium(II)bis(tetrabutylammonium) namely N719-based DSSC reached a η of 6.02%. This result is encouraging since the conversion efficiency of **4b**-sensitized DSSC has reached over 87% that of N719 based DSSC (Fig. 1b). The subsequent theoretical calculation has revealed that the **IDB** amino donor has the strongest electron donating ability among all three diarylamino substituents employed in the porphyrin sensitizers. The results provided a valuable direction for the future molecular design used in porphyrin-sensitized solar cell area.

2. Experimental

2.1. Materials

Starting materials were all commercially available and used as received if not specially mentioned without further purification. Solvents used for reaction and column chromatography such as THF, n-hexane, dichloromethane, methanol and granular neutral silica gel for column chromatography, were purchased from Aladding Institute, Tianjin, China. The FTO conducting glass was washed with a detergent solution, deionized water and ethanol successively under ultrasonication before use.



Scheme 1. Molecular structure of three porphyrin sensitizers.