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The position effect of electron-deficient quinoxaline moiety in porphyrin based sensitizers

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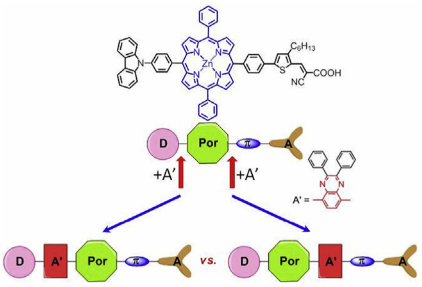
HIGHLIGHTS

- The novel porphyrin dyes containing 2,3-diphenylquinoxaline (DPQ) were synthesized.
- The position of DPQ unit in porphyrin based dyes influences the properties of the dyes.
- The structures, charge, and the frontier orbitals were studied by DFT calculations.
- The effect of DPQ position on the performance of quasi-solid-state DSSCs was systematically investigated.
- The position of DPQ near the acceptor was better than that near the donor towards higher efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

An electron-deficient group, 2,3-diphenylquinoxaline (**DPQ**), is incorporated as an auxiliary acceptor into the different positions of the porphyrin (Por) based donor-π bridge-acceptor (D-π-A) dye (**FNE57**) to construct D-A′-Por-π-A (**FNE58**) and D-Por-A′-π-A (**FNE59**) configurations. The incorporation of **DPQ** unit between the donor and porphyrin unit has negligible influence on the absorption property, whereas the **DPQ** unit located between the porphyrin unit and acceptor significantly increases the absorbance for the Soret band and the valley between the Soret and Q bands. Theoretical calculation reveals that incorporating the **DPQ** unit adjacent to the acceptor is more advantageous to delocalize the lowest unoccupied molecular orbital and enhance the electronic asymmetry, which facilitates the intramolecular charge transfer. The effect of **DPQ** unit and its linkage position on the performance of related quasi-solid-state dye-sensitized solar cells (DSSCs) is systematically investigated. The quasi-solid-state DSSC with sensitizer **FNE59** displays a power conversion efficiency of 6.02%, which is 23% and 51% higher than those for **FNE57** and **FNE58** based DSSCs. Our studies facilitate the understanding of the crucial importance of molecular engineering and pave a new path to design novel porphyrin based sensitizers for highly efficient DSSCs.

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1. Introduction

The increasing demand of renewable and sustainable energy sources has generated much interest in the development of next-generation photovoltaic devices. Dye-sensitized solar cells (DSSCs), regarded as the alternative to conventional inorganic photovoltaic devices, are currently attracting considerable attention because of their high light-to-electricity conversion efficiencies, ease of fabrication, and low cost of production [1]. The sensitizer [2–4], one of the key components in a DSSC, plays a crucial role in achieving high solar-to-electricity conversion efficiency and durability. Up to now, DSSCs employed ruthenium (II)-based dyes have reached more than 11% power conversion efficiency (PCE) under standard global air mass 1.5 (AM1.5G) solar conditions [3]. However, the ruthenium dye has poor harvesting of lower energy light, which can be enhanced with localized surface plasmon of noble metal nanostructures [5]. Thus, a lot of efforts have been devoted to the development of novel organic dyes for efficient and stable DSSCs due to their modest cost, ease of synthesis and modification, large molar extinction coefficients, and satisfactory stability [6–9]. However, the PCE of organic dye based DSSCs is either lower than or comparable to that of ruthenium dye based DSSCs [6–8].

Among the various noble-metal-free dyes, porphyrins and related derivatives have been considered to be promising candidates for DSSCs due to the following features: i) strong Soret bands (400–450 nm) and moderate Q bands (550–600 nm) [10,11], leading to efficient light-harvesting capability; ii) tunable spectral properties and energetics by functionalization at the *meso* and β positions of the porphyrins; iii) high thermal, chemical, and optical stability. However, porphyrin based dyes have been located in a deserted age as sensitizers for DSSCs because of their relatively low PCE values [12–16]. Great efforts have been devoted to modify the chemical structure of the dye molecules. Electron-rich systems, such as ethinyl [17], thiophene derivatives [18], and phenyl [19], were incorporated into the π-spacers to tune their photophysical properties and bulky substituents were introduced to weaken the intermolecular interactions. Until 2011, a PCE of 12.3% was achieved using $[Co(bpy)_3]^{2+/3+}$ based redox shuttle in conjunction with porphyrin-based D-π-A dyes **YD2-*o*-C8** with the organic co-sensitizer **Y123** [17], which results in a renaissance for D-π-A porphyrin dyes in developing high-efficiency DSSCs [20–23].

Recently, D-A′-π-A featured organic sensitizers [5–9,24–27], where an auxiliary acceptor (A′), such as benzothiadiazole [5,24], quinoxaline [7,25], and diketopyrrolopyrrole [26,27], is integrated into the traditional D-π-A framework, have been extensively investigated. Bathochromically shifted absorption band of the organic sensitizer can be achieved due to the enhanced donor–acceptor interactions, which results in an increased light harvesting efficiency. Most importantly, tunable lowest unoccupied molecular orbital (LUMO) levels along with enhanced photostability of the organic sensitizers can be achieved upon the incorporation of the auxiliary acceptor. Inspired by the success of the organic dyes with D-A′-π-A configuration, an auxiliary electron-deficient unit has also been implemented into porphyrin based sensitizers. Yeh and co-workers have introduced electron-deficient 2,1,3-benzothiadiazole (BTD) into the π-spacer between the anchoring group and the porphyrin chromophore and constructed dye **GY50** which has achieved a PCE of 12.75% without using a co-sensitizer [22]. The improved DSSC performance is stemmed from the broadening of the absorption spectrum, which partially fills the valley between the Soret and Q bands. Most recently, Grätzel and co-workers further utilized bulky bis(2′,4′-bis(hexyloxy)-[1,1′-biphenyl]-4-yl)amine instead of bis(4-hexylphenyl)amine donor in **GY50**, which afforded a panchromatic porphyrin sensitizer **SM315**. Impressively, the DSSC based on porphyrin sensitizer **SM315** have reaped a PCE record of 13.0% without the assistance of any co-sensitizer [21].

However, in the reported two examples, the auxiliary acceptor was implemented between the porphyrin and anchoring group. Questions may be raised on which is the best position for the auxiliary acceptor in the π-conjugated framework. To the best of our knowledge, the effect of the linkage position for the auxiliary acceptor in the porphyrin dyes on the DSSC performance has not been studied. As *N*-fused carbazole has demonstrated novel antenna function in amphiphilic Ru(II) sensitizers [28,29] and also has been introduced to organic dyes for efficient DSSC sensitizers [30,31], we employ carbazole as the donor of porphyrin dyes, which are rarely studied so far [32,33]. Herein, we have designed and synthesized three novel Zn(II)-porphyrin sensitizers containing the same electron donating moiety, carbazole, and the same electron-withdrawing moiety, cyanoacrylic acid. Based on the reference porphyrin dye **FNE57** with a typical D-π-A configuration, 2,3-diphenylquinoxaline (**DPQ**), a popular electron-deficient unit, was introduced between the electron donor and porphyrin unit for sensitizer **FNE58** (D-A′-Por-π-A) or between the porphyrin unit and the anchoring group for sensitizer **FNE59** (D-Por-A′-π-A) (Fig. 1). The effect of the position for the incorporated auxiliary acceptor on the sensitizer properties is systematically investigated. It can be found that by introducing the electron acceptor between the porphyrin unit and the anchoring group, the related absorption profile for sensitizer **FNE59** exhibits significant broadening of Soret absorbance features in comparison to that of **FNE57**, which results in improved light harvesting in 400–600 nm region of the spectrum with higher extinction coefficients. Therefore, the quasi-solid-

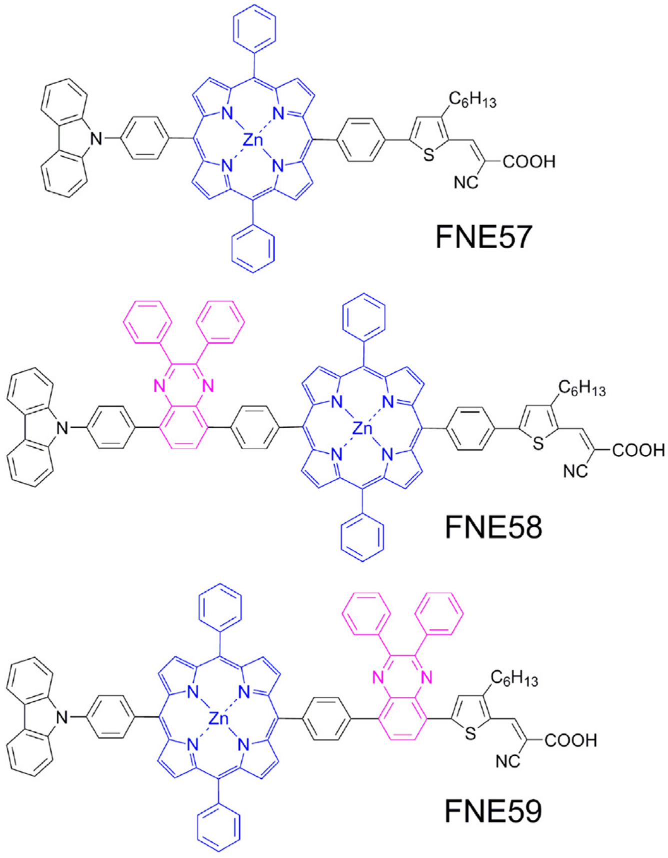

Fig. 1. Chemical structures of porphyrin based sensitizers **FNE57**, **FNE58**, and **FNE59**.