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A theoretical design and investigation on Zn-porphyrin-polyoxometalate hybrids with different π-linkers for searching high performance sensitizers of p-type dye-sensitized solar cells

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ABSTRACT

Derived from an excellent sensitizer, Zn-porphyrin bearing phenylethynyl substituent, a series of Zn-porphyrin-polyoxometalate hybrids with different π-linkers were designed as sensitizers in p-type dye-sensitized solar cells. UV–vis spectra and charge transfer (CT) characters of studied hybrids were investigated by density functional theory (DFT) and time-dependent DFT methods to reveal the influence of π-linkers on sensitizers. The long π-linkers and high delocalization of systems **2**–**5** lead to the red shift and broadened absorption peak compared with system **1**. CT analysis on the amount of transferred electrons (q^{CT}), CT distance (d^{CT}) and t index assessing the charge separation extent indicate that system **3** reaches the maximum CT and spatial charge separation. Furthermore, it performs a balance on light harvesting efficiency (*LHE*), hole injecting efficiency (*HJE*), dye regeneration efficiency (*DRE*) and charge recombination efficiency (*CRE*). Meanwhile, its spectrum well overlaps with the solar spectra. Therefore, system **3** would be a promising p-type sensitizer.

1. Introduction

The current environment and energy crisis have stimulated our interest for searching the renewable energy sources, and solar power is outstanding in the promising "low-carbon level" future. Thus, the intensive research has focused on effectively harnessing solar energy by using photovoltaic (PV) cells. Particularly, dye-sensitized solar cells (DSSCs) have attracted continuous attention because of their advantages, such as low cost, efficiency, and simplified production processes [1]. Since the seminal work by Grätzel and co-workers in 1991, many researches have been focused on n-DSSCs [2–5]. Up to now, n-DSSCs exhibit promising efficiency exceeding 15% based on TiO_2, being a well-established technology [6,7]. More recently, another type of DSSCs that the cathode is photoactive (p-DSSC), has been studied intensively as a growing research area [8–11]. In 1999, Lindqvist and co-workers first applied NiO as semiconductor on p-DSSC [12]. Compared with traditional n-DSSCs, p-DSSCs possess some structural similarities, but have different charge transfer (CT) kinetics as the two types PV devices are the mirror images. The key step of n-DSSC is the electron injection from the photoexcited sensitizer into the conduction band (CB) of n-type semiconductor (n-SC), while p-DSSCs are based on the hole injection from the photoexcited sensitizer to the valence band (VB) of the p-SC. The potential utility of photocathodes provides an access to construct the "tandem" solar cells, which both the cathode and anode are active, and the overall efficiencies could surpass those of traditional n-DSSCs [13]. Though many attempts have been devoted to p-DSSCs, their efficiencies are relatively very low, which prohibits the fabrication of high-efficiency tandem pn-DSSCs. Therefore, it is of great importance to develop the efficient p-DSSCs.

Since the sensitizers are the key components in DSSCs, numerous efforts have been devoted to the design and optimization of different sensitizers to improve power conversion efficiency. The most extensively studied sensitizers share the donor-π-linker-acceptor (D–π–A) structural motif, which are able to effectively tailor the band gap energy for harvesting visible and near-infrared region light [2,14]. Polyoxometalates (POMs) are well-known electron-withdrawing groups and have been employed as

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inorganic building blocks for constructing organic-inorganic hybrid materials, which result in possible synergistic effects between POMs and organic components [15,16]. POMs have become a subject of general interest due to their superior redox properties, photochemical response and diversified structures, which have potential applications in catalysis, biology, medicine, and optics [17–19]. In addition, porphyrins and their derivatives are attractive components in materials due to their excellent chemical and optic properties, such as great conjugation of π electrons in macrocycles, long-lived excited states, intense visible absorption bands, and tunability by chemical derivatization [20–23]. Accordingly, porphyrins can be used as electron donors and POMs as electron accepters for organic-inorganic hybrids. Until now, many POMs-porphyrin hybrids have been synthesized and the Lindqvist-type POM-porphyrin derivatives were systematically studied using density functional theory (DFT) in our previous works [24–26]. These hybrids show intense and broad absorption in the visible region and have great potential for applications in DSSCs. With the initial interest of improving the light harvesting ability of sensitizers, it is necessary to apply appropriate modifications on the molecular structures to expand the coverage and intensity of absorption for sunlight. As the π-linkers in D–π–A sensitizers have significant influence on the overall performance, a series of POM conjugated Zn-porphyrin sensitizers with different π spacers were designed to examine the relationship between the expanded π-linkers and the performance of DSSCs.

The quantum chemical calculations can shed light on the relationships between structures and properties. In our previous works, DFT and time-dependent DFT (TDDFT) methods have been proved that are very useful for investigating the properties of POM-based organic-inorganic hybrids served as sensitizers [16,27–29]. The electronic structures, absorption spectra and CT characters of sensitizers were investigated using DFT and TDDFT methods for exploring their potential application in DSSCs [30–33]. In present work, we designed a series of POM-porphyrin hybrids to investigate the influence of π-linkers on the performance of the sensitizers and to give some theoretical guidance for further enhancing the efficiencies of POM-porphyrin sensitizers.

2. Methods

2.1. Theoretical background

The photoelectric conversion efficiency (η) is an important parameter to estimate the performance of DSSCs, which can be expressed by the following equation: [34]

$$\eta = J_{sc} V_{oc} FF / P_{\mathrm{in}} \tag{1}$$

where J_{sc} is the photocurrent density measured at short circuit, V_{oc} is the open circuit photovoltage, *FF* is the fill factor of the cell, and P_{in} is the intensity of the incident light.

With regard to J_{sc}, it can be expressed as follows: [35].

$$J_{sc} = \int LHE_{(\lambda)} \varphi_{inject} \eta_{collect} d\lambda \tag{2}$$

where $LHE_{(\lambda)}$ denotes the light harvesting efficiency at a specific wavelength, $\varphi_{\mathrm{inject}}$ is the electron injection efficiency, and η_{collect} is the charge collection efficiency. The η_{collect} can be regarded as a constant in the same DSSCs with sole different sensitizers, thus in order to improve J_{sc}, *LHE* and $\varphi_{\mathrm{inject}}$ should be as large as possible.

LHE is under the influence of oscillator strength (*f*) of the sensitizer corresponding to the maximum absorption $\lambda_{\max}$. It is given by: [36].

$$LHE = 1 - 10^{-f} \tag{3}$$

In Equation (3), the vital parameters $\lambda_{\max}$ and *f* are taken into account to assess the light absorption ability. The larger the *LHE* is, the stronger light harvesting ability of the compound has.

In addition, the η is also closely connected to the hole injecting efficiency (*HJE*), dye regeneration efficiency (*DRE*) and charge recombination efficiency (*CRE*). Their free energies (in eV) can be expressed as the following equations: [30,37].

$$\Delta G_{inj} = -\left[E_{\mathrm{V}} - E\left(\mathrm{S}/\mathrm{S}^{-}\right)\right] - E_{\mathrm{VB}} \tag{4}$$

$$\Delta G_{reg} = E\left(I_2/I_3^{-}\right) - E\left(S/S^{-}\right) \tag{5}$$

$$\Delta G_{CR} = E\left(\mathrm{S}/\mathrm{S}^{-}\right) - E_{\mathrm{VB}} \tag{6}$$

Here E_{VB} is the VB edge of NiO (−4.96 eV), E_{v} is the energy of excited state sensitizer, $E(\mathrm{S/S^-})$ is the reduction potential of sensitizer, $E(\mathrm{I_2/I_3^-})$ is the reduction potential of the redox mediator (−4.80 eV) [16].

The first step in p-type DSSC is the dye excitation by light absorption, then the hole injects from excited dye into the valence band of NiO, requiring the HOMO energy level of dye situates under the valence band edge of NiO. The negative ΔG_{inj} can guarantee the hole injection going on smoothly. Next, the dye is regenerated via electron transfer from reduced dye to $\mathrm{I_3^-}$, requiring the LUMO of dye is above the reduction potential of the redox mediator. ΔG_{reg} is closely related to this process, which the negative ΔG_{reg} promotes dye regeneration. However, if the regeneration reaction cannot carry out within the charge separated lifetime, the reduced dye may recombine with the hole in NiO. This process is judged by ΔG_{CR}, that is, the positive ΔG_{CR} implies that the charge recombination process is not spontaneous. Thus, the large *LHE*, negative ΔG_{inj}, ΔG_{reg} and positive ΔG_{CR} are favor of strong light harvesting ability, sufficient driving force to insure efficient hole injection and dye regeneration, and hinder the charge recombination process.

To evaluate the CT ability of the sensitizers, the CT parameters including the amount of CT (q^{CT}), the corresponding effective CT distance (d^{CT}) and the *t* index representing the degree of separation between $\rho^{+}(\mathrm{r})$ and $\rho^{-}(\mathrm{r})$ based on the total densities for the ground and excited states are computed [38–40]. $\rho_{\mathrm{GS}}(\mathrm{r})$ and $\rho_{\mathrm{ES}}(\mathrm{r})$ are defined as the electronic densities associated to the ground and excited states, and the difference of densities related to the electronic transition is described by:

$$\Delta\rho(r) = \rho_{\mathrm{ES}}(r) - \rho_{\mathrm{GS}}(r) \tag{7}$$

Two functions, $\rho^{+}(\mathrm{r})$ and $\rho^{-}(\mathrm{r})$ are proposed to represent the points in space where an enhancement or a reduction of the density upon absorption is produced. And q^{CT} can thus be defined:

$$q^{CT} = \int \rho^{+}(r) dr \tag{8}$$

The barycenters (r^{+} and r^{-}) of density distributions defined by $\rho^{+}(\mathrm{r})$ and $\rho^{-}(\mathrm{r})$ is given by:

$$\begin{aligned} r^{+} &= \left(x^{+}, y^{+}, z^{+}\right) = 1/q^{CT} \int r\rho^{+}(r) dr \\ r^{-} &= \left(x^{-}, y^{-}, z^{-}\right) = 1/q^{CT} \int r\rho^{-}(r) dr \end{aligned} \tag{9}$$

The distance separating these two barycenters is the CT distance: