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A systematic study of phenoxazine-based organic sensitizers for solar cells

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ABSTRACT

We perform a systematic theoretical and computational investigation of phenoxazine (POZ)-based organic dyes to rationalize the marked difference in the energy conversion efficiency. The geometries, electronic structures and absorption spectra of the dyes and their adsorbed dye-TiO_2 systems are carried out by means of density functional theory (DFT) and time-dependent DFT methods. The relevant physical parameters that dominate the performance of the cell, such as the light harvesting efficiency (Φ_{LHE}), exciton binding energy (E_b), the driving force for electron injection (ΔG_{inj}), the conduction band shift (ΔE_{CB}), and transferred charges (n_c) are assessed in detail to determine their contributions to either the short-circuit photocurrent density (J_{sc}) or the open-circuit photovoltage (V_{oc}), and establish the structure-property relationships. The calculated results elucidate that the extension of π-spacer, the introduction of di-anchoring group and auxiliary chromophores make significant influence on the PCE of the cells. The designed dyes with the introduction of elongated π-spacer, N-phenylcarbazole substitution at the 7-position of POZ and thiophene-linked di-anchoring group could be potential POZ-based candidates used in DSSCs. We hope that our calculations give a more in-depth physical insight on structure-property relationship for POZ-based dyes and provide a hint to design and screen novel high performance POZ-like dyes.

1. Introduction

Dye sensitized solar cells (DSSCs) have received widespread attentions since their first successful demonstration by O'Regan and Grätzel in 1991 [1–4]. Great efforts have been dedicated to the developments of efficient dyes for improving the power conversion efficiency (PCE) [5,6]. So far, the conversion efficiencies of ruthenium polypyridyl complexes have been reported over 11% [7–9]. Porphyrin-sensitized solar cells with cobalt-based redox electrolyte have exceeded 12% efficiency [10,11]. But the PCE of DSSC still lags far behind that of the traditional silicon-based solar cell. The development of novel high efficient dyes remains a challenging task. In comparison to typical metal complex dyes, organic dyes have been rapidly developing in recent years because of the advantages of high molar extinction coefficient, easily tunable optical properties, low-cost preparation processes and good flexibility in molecular tailoring. The impressive performance of the organic dye has yielded an efficiency over 12% [12], and it is believed that the high PCE of metal-free dyes can be achieved through molecular design and engineering.

The most efficient organic sensitizers are based on donor-π-acceptor (D-π-A) structures, in which the combinations of three components (D, π and A) provide the flexibility of molecular design [13–15]. The optimization of D-π-A structure could not only regulate the absorption spectra and molecular energy levels, thus determining the light harvesting ability and interfacial charge injection, but also affect the compatibility of multiple components at the titania/dye/electrolyte interface. Among many kinds of metal-free organic dyes, phenoxazine (POZ)-based D-π-A sensitizers exhibit promising photovoltaic properties [16–21]. POZ is a heterocyclic compound with electron-rich nitrogen and oxygen heteroatoms, and has a non-planar ring with a bent conformation in the ground state, which could avoid the molecular aggregation and the formation of intermolecular excimers. POZ dyes exhibit unique photophysical properties, good thermal and electrochemical stability [18], and have been explored for laser dyes [22], indicators [23] and hole-transporting materials [24]. Recently, a series of POZ-based dyes with different number of anchoring groups and miscellaneous substitutions at 7-position and N-terminal of POZ

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have been reported for their applications in DSSCs [16,17]. All compounds are shown in Fig. 1 with their available experimental PCEs. In contrast to 1a, the compound 1b shows an improved PCE (from 4.97% to 6.60%) by introducing a thiophene unit. Naturally, a straightforward question will be put forward on whether the efficiency can be improved by further elongating the π-spacer (e.g., two thiophene units). Compared to mono-anchoring sensitizers (1a and 3a), the di-anchoring sensitizers (1d and 3b) have not only more extended π-conjugations of the POZ moiety, but also more chances for adsorption on TiO_2 surface to achieve a higher dye coverage [25–27], which will benefit in light absorption and electron injection, thus leading to improved short-circuit current [28,29]. However, the additional anchoring group is not prominent for improving the PCE for the compounds 1d and 3b. The introduction of different chromophores at 7-position of POZ have successfully increased PCE of dyes (2a-c). On the basis of experimental findings, the question on why the subtle structural changes lead to significant effect on the PCE should be revealed at the microscopic level and a detailed understanding of the structure-performance relationship should be established for these POZ-based dyes.

To rationalize the remarkable difference in the PCEs of these dyes, herein we have carried out the theoretical calculations to dwell on the structure-property relationships from the physical insights. The density functional theory (DFT) and time-dependent DFT (TD-DFT) methods are employed to investigate the molecular geometries, electronic structures and absorption spectra of the POZ-based dyes. Considering the real condition in the devices, the structures of dyes bounded to TiO_2 are also simulated. Based on the reliable quantum-chemical methods, novel POZ-based dyes with an elongated π-spacer (1c), a substitution of N-phenylcarbazole at 7-positon of POZ (2d), and thiophene-linked di-anchoring group (4a) are designed for the potential high PCE materials [30–33].

Theoretical calculation is becoming a powerful tool to study the electronic properties of dyes and predict their performances in various aspects of DSSC [34–47]. The conventional approach to developing novel dyes is based on the experimental trials and chemical intuition of chemists, but is ultimately time-consuming due to the structural diversities of promising candidate materials. Instead, the application of predictive computational design could be a rational and more efficient approach. The use of first-principles computational design to predict electronic properties beforehand offers the rational understanding of how different functional groups modulate electronic and spectroscopic properties. Hence, in this work, we will focus on the effect of structural changes on the electronic properties. By means of quantum chemical calculations, we aim to establish structure-property relationships of POZ-based dyes and shed light on the foundamental research and design of high PCE materials in DSSCs.

2. Method

2.1. Theoretical background of DSSCs

A schematic working principle in a typical TiO_2-DSSC is depicted in Fig. 2. The PCE (η) of the cell is determined by the short-circuit photocurrent density J_{sc}, the open-circuit photovoltage V_{oc}, the fill factor *FF*, and the incident solar power on the cell P_i [40].

$$\eta = \frac{J_{sc} V_{oc}}{P_i} FF \quad (1)$$

The *FF* is a non-dimensional cell parameter that reflects the extent of electrical (ohmic) and electrochemical (overvoltage) losses occurring during operation of the DSSC. In order to improve η,

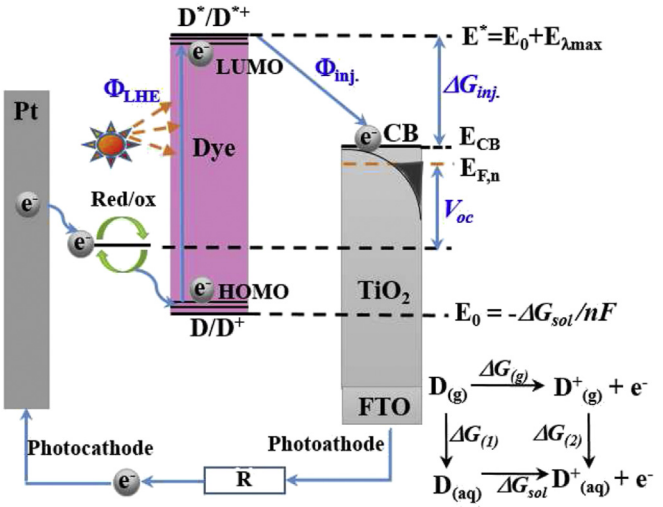

Fig. 2. Schematic working principle and energy levels of a conventional TiO_2-DSSC (D/D*: dye/excited dye; D^+: oxidized dye; CB: conduction band of TiO_2; V_{oc}: open circuit voltage; Red/ox: reduced/oxidized shuttle; HOMO/LUMO: highest occupied/lowest unoccupied molecular orbital; Φ_{inj}: efficiency for electron injection; ΔG_{ing}: driving-force for electron injection).

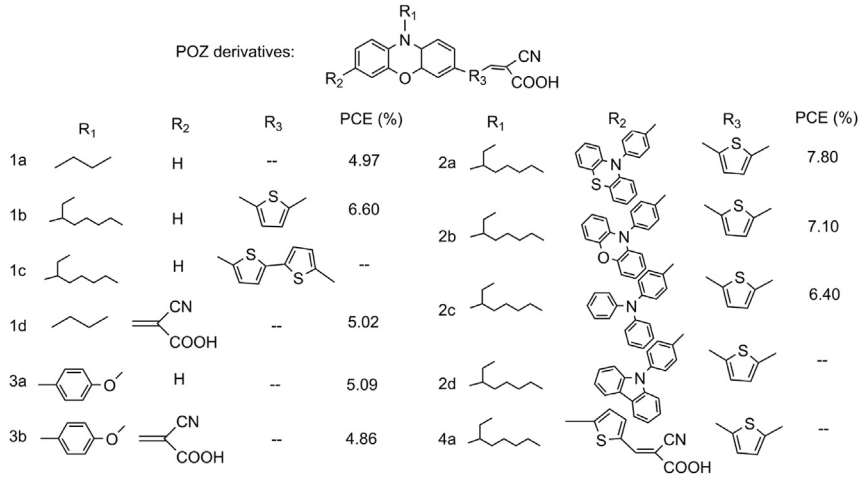

Fig. 1. The phenoxazine(POZ)-based sensitizers investigated in this work, together with available experimental PCE values.