



A quantitative structure-property relationship study of the photovoltaic performance of phenothiazine dyes



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ABSTRACT

Quantitative structure-property relationships (QSPR) are developed for a set of phenothiazine dyes used in dye sensitized solar cells (DSSCs). To this purpose, we have employed a number of structural descriptor variables ranging from representations based on the atom's environment to those that exploit semi-empirical molecular orbital information. We show that robust linear statistical regression models can be obtained for important photovoltaic parameters such as the power conversion efficiency (PCE), the open-circuit voltage (V_{oc}) and the short-circuit current (J_{sc}). Overall, models based on eigenvalue (EVA) descriptors derived from vibrational frequencies, demonstrated the best predictive ability for both the calibration and independent test sets. The high predictive power of these models accompanied by the ease of computation can pave the way for rapid screening of new potential dyes and computer-aided materials design.

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1. Introduction

Among the available technologies for converting solar energy into electricity, dye sensitized solar cells (DSSCs), also known as Grätzel cells are one of the most promising alternatives to conventional semiconductor photovoltaic devices. Owing to their use of abundant materials, ease of synthesis, lower manufacturing costs and tunable optical properties, they have received widespread attention. DSSCs consist primarily of a photosensitive dye that is anchored to a wide band gap semiconductor photoanode (typically TiO_2), a redox electrolyte (such as iodide/tri-iodide (I^-/I_3^-)) and a platinized photocathode. Upon illumination, the photoexcited dye injects electrons (charge separation leads to a photovoltage) into the nanoporous semiconductor and are further driven towards the back collecting electrode via diffusion, thereby producing a photocurrent. The ionized dye is regenerated by the redox mediator (electron donation from the electrolyte) while the resulting triiodide is reduced back to iodide ions at the counter-electrode [1,2]. The overall solar energy to power conversion efficiency (PCE) of the cell is determined by measuring the current–voltage (J–V) characteristic parameters that include the fill factor (FF), the short circuit current J_{sc} (measured in mA cm^{-2}), the open circuit voltage V_{oc} (measured in mV) and the intensity of the incident light

($P_{inc} = 100 \text{ W/cm}^2$ for the AM1.5 simulated solar illumination) and are related by the equation:

$$PCE(\%) = \frac{J_{sc} \cdot FF \cdot V_{oc}}{P_{inc}} \times 100 \quad (1)$$

Although the functioning of the DSSC involves multiple interacting components, particular attention is paid to the dye sensitizer, which is responsible for light harvesting and influences many of the key electron transfer processes that impact photovoltaic performance. Ideal photosensitizers are required to have desirable properties such as wide absorption in the visible region, high molar extinction coefficients, photochemical stability and oxide surface anchoring, to name a few [3,4]. A survey of recent literature [5–8] shows that judicious molecular design and device level modifications have lead to improved efficiencies. While zinc-porphyrin dyes exceeding 11% solar conversion efficiency [9] have been reported, there has been increased focus on the design of metal-free dyes, which offer greater flexibility in molecular design [4,5,7] as well as cost advantages. However, experimental verification of new materials can often be time-consuming and expensive and to this purpose, computational methods that provide timely and reliable estimates of the relevant properties are extremely valuable.

While *ab initio* approaches based on density functional theory (DFT) and time-dependent DFT (TD-DFT) [10,11] can reliably model some of the elementary mechanisms in DSSCs, they cannot, as yet, directly evaluate the PCE [12,13]. Furthermore, given the

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multifunctional nature of the DSSC, a fully combinatorial approach is computationally prohibitive and therefore unsuitable for screening a large number of compounds. On the other hand, quantitative structure–property relationship [14] (QSPR) models that relate descriptors derived from the molecular structure to known molecular/material properties, provide an efficient and relatively low-cost computational protocol for rapid screening of compounds prior to synthesis [15,16]. Such models have been recently applied in the area of organic photovoltaics as part of a virtual high-throughput screening framework [17,18].

QSPR models have also been reported for dyes used in photovoltaics with the primary focus being on the maximum absorption wavelength (λ_{max}) [19]. In an earlier work [20], we presented regression models for predicting structure–photovoltaic performance relationships for a set of coumarin dyes. These models were based on eigenvalue (EVA) descriptors derived from vibrational frequencies [21] and comparative molecular field analysis (CoMFA) [22]. More recently, regression methods have also been used to establish correlations between the properties of the dyes calculated using quantum chemistry approaches and the experimental solar cell efficiency [23]. Here, we further extend the study to include a broad set of phenothiazine-based [7] dyes that have been widely employed in the design of both organic and ruthenium-based [24] sensitizers. As with the coumarins, the phenothiazine molecule exhibits a high electron donating ability, but more importantly it adopts a nonplanar butterfly conformation that inhibits molecular aggregation [25]. In addition, compared to the coumarin dyes, there exists a larger (over 100 dyes reported in literature) and more structurally diverse set of experimentally validated phenothiazine dyes that have been tested under similar conditions, which allows for a robust statistical analysis. In our previous study [20], only three different descriptor types were investigated. Here, we explore a wider pool of molecular descriptors ranging from simple topological indices to quantum chemical descriptors that are analysed using both linear and non-linear regression approaches. Overall, we find that linear models based on EVA descriptors have good predictive ability for the important photovoltaic properties.

2. Methods and materials

2.1. Data set

A set of 73 phenothiazine-based (see Fig. 1) dye sensitizers compiled from the literature have been analysed in this study [25–43]. These dyes are partitioned into a training and test set (TS-1) for assessing model performances. An additional test set (TS-2) of 23 dyes that was assembled at a later stage was further used as an independent external validation set. The relevant figures of merit, namely PCE , J_{sc} , V_{oc} and FF for all the dyes along with the 2D coordinates in SDF format are provided in the supporting information. Most dyes adopt a donor– π bridge–acceptor (D– π –A) configuration where the phenothiazine unit containing electron-

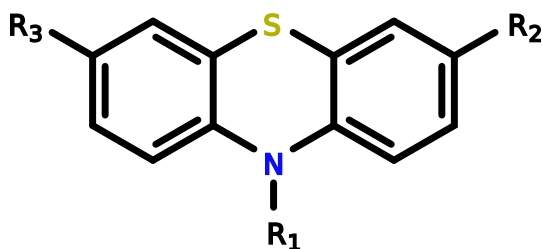


Fig. 1. Chemical structure of the phenothiazine scaffold with attachment points for functional groups denoted by "R_#". See the supporting information for details.

rich nitrogen and sulfur heteroatoms in the central ring acts as the electron donor and has further been shown to have a high propensity to form stable radical cations [44,45]. Some dyes consist of D–D– π –A architecture where triphenylethylene carbazole moieties are introduced as additional donors. While cyanoacrylic acid is used as the acceptor, the conjugated linker is based on different aromatic groups such as benzene, thiophene and furan.

Since the data have been obtained from different sources, we have imposed a few conditions in order to make the values reasonably comparable. Thus, for all selected dyes, the reported values are for the dye alone without the use of an anti-aggregation coadsorber (such as chenodeoxycholic acid) or cosensitizer and are experimentally tested (at room temperature) using a global standard AM 1.5 light source. It was additionally ensured that the measurements were made for DSSCs using TiO₂ as the semiconductor and I_3^-/I^- as the redox shuttle. Another, critical criterion regarding long-term stability has also been ignored owing to the fact that such data are not always available for all the dyes being studied. Although variations in the semiconductor thickness and cell fabrication can impact performances, further constraints based on these factors would leave very few structures and were therefore ignored.

In this article, we focus on the three main photovoltaic performance parameters, namely the PCE , J_{sc} and V_{oc} . The photocurrent (J_{sc}) is determined by the integral of the monochromatic incident photon-to-electron conversion efficiency (IPCE) which is a function of the light harvesting efficiency (LHE) at a given wavelength (λ), the charge injection efficiency ϕ_{inj} and charge collection efficiency (ϕ_{coll}). While both the LHE and ϕ_{inj} (collectively the charge generation contribution) are directly dependent on the properties of the dye, ϕ_{coll} is governed by the electron diffusion in the semiconductor and recombination losses. The V_{oc} is given by the difference between the conduction band (E_{CB}) potential of the semiconducting oxide electrode and the redox potential of the electrolyte and is only indirectly dependent on the dye [46]. The fill factor (FF) is strongly influenced by the total series resistance of the cell and other factors such as the electrolyte composition [47]. However, since the FF is difficult to map on to the properties of the dye [48], we focus on the product of the current and voltage $J_{sc} \times V_{oc}$ and assume FF to be constant for all molecules.

2.2. Molecule preparation

Molecules were drawn using Chemaxon MarvinSketch [49] followed by conformational search using *cxcalc* (based on the Dreiding force field [50]). The lowest energy conformer was then subjected to geometry optimization and normal mode calculations using the semi-empirical AM1 Hamiltonian in MOPAC [51]. Molecular descriptors were then calculated using the optimized geometries as described below.

2.3. Molecular descriptors

In order to establish the structure–property relationships, various types of descriptors were tested. In contrast to our previous study [20], we focus only on alignment-free descriptors that vary in origin and are derived from extended valence sequences [52], 2D-autocorrelations [53], vibrational frequencies [21], molecular orbital energies [54] and local electronic surface properties [55]:

2.3.1. Molecular signature

The molecular signature [52,56] consists of set of strings where each string is a canonical representation of the topological environment (up to pre-defined distance h) of every atom in the compound. The descriptor for a molecule is therefore an integer vector where each element corresponds to the occurrence count of the

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