



## Computational model of hydrogen production by Coumarin-dye-sensitized water splitting to absorb the visible light in a local electric field

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### ABSTRACT

Visible light water splitting for hydrogen production using dye sensitized photo-electrode is one of the most promising method for future large-scale power production from renewable energy sources. A series of Coumarin dyes (C343, NKX-2311, NKX-2677 and NKX-2697) were applied as dye sensitizers for water splitting. The present study reports computational model of overall water splitting under visible light using a simple organic dye as a photosensitizer for H<sub>2</sub> production in combination with an electric field. This publication describes a method to calculate electrostatic properties of excited states of molecular systems using time-dependent density functional theory in a local electric field. The results show that field application, parallel to the dipole moment, can be very effective in order to achieve the enhancement of photo-electrochemical H<sub>2</sub> production under visible light irradiation. This research open the possibility of computationally screening the various predictions on the electronic structure, optical response and in consequence their influences on the efficiency, thus paving the way to an effective molecular engineering of further enhanced sensitizers for water splitting applications.

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### 1. Introduction

The photo-electrochemical water splitting, a promising process for producing H<sub>2</sub> from two plentiful renewable sources of water and solar light, is currently attracting widespread academic and commercial interest for the conversion of sunlight into hydrogen because of their low cost and reasonable efficiency [1–4]. Hydrogen is definitely one of the best fuels for the future since it has been recognized as an ideal energy carrier which can serve as a perfect energy source to be an appropriate alternative for limited and environmentally harmful fossil fuels. Whether hydrogen can be considered as a clean form of energy on a global scale depends on the primary energy that is used to split water [5–7]. In principle, as the difference between the potentials of the H<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>O/O<sub>2</sub> redox reactions is only 1.23 V, both visible and near-infrared light can be used for direct water splitting [8]. According to some in detail studies over the thermodynamics of photochemical water splitting, it is achievable to store about 12% of the incident solar energy in the form of hydrogen [9]. In practice, visible light photo-electrochemical water splitting have been reported very few, and the highest quantum yield reported so far is about 6.3% at 420 nm, implying that the best solar power conversion efficiency

is still under 0.5% [2,10–12]. Extensive efforts have been made in recent years to design visible-light-driven photocatalysts, which would pave the way of utilization of visible solar radiation for storable energy production. Presently, for well-organized water splitting there is a lack of an appropriate band gap position and suitable materials with sufficiently small band gap and the stability necessary for practical applications. In spite of the development of vast variety of photocatalysts working efficiently under ultraviolet irradiation, just a few visible light responsive photocatalysts have been reported for overall water splitting [10,11,13]. Tuning the band levels of inorganic, especially oxide, semiconductor can be regarded as the most prominent difficulty in achieving overall visible light water splitting. Since there is no sensitivity to visible light in large band gap semiconductors, such as those typically used in overall water splitting, a sensitizer (S), chemically bonded to the surface of the semiconductor, is required to accomplish visible light harvesting. After the absorption of the incident light by the sensitizer and getting excited (S\*), electrons are injected into the conduction band of the oxide semiconductor [14–17].

To further improve the performance of Dye Sensitized Water Splitting (DSWS), the sensitizers' response needs to be enhanced in all regions of the solar spectrum. However, a range of organic and organometallic dyes including Ru-complexes have been discovered to have both visible light absorption as well as a sufficiently negative energy level (LUMO) for H<sub>2</sub> production [18–20]. Furthermore, as it has been shown for dye-sensitized solar cells,

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easy molecular tailoring, facile dye synthesis, easily tunable absorption properties by suitable molecular design, compared to oxides, are among their numerous privileges [21]. In Dye Sensitized Water Splitting (DSWS), dye sensitizers are used to absorb the radiation from the sun and transform the photo excited electron into nanostructured semiconductor electrodes.

Moreover, to effectively promote the decomposition of water into  $H_2$  and  $O_2$ , suitable levels for the HOMO and the LUMO of the sensitizer matching the water redox potential and the conduction band edge level ( $E_{cb}$ ) of the photo-electrode are required. Therefore, to use organic and organometallic dyes in dye sensitized water splitting cells, strategically designing of the molecular structure of the photosensitizer is really vital.

The first attempt of overall water splitting under visible light using a simple organic dye as a photosensitizer for  $H_2$  production was reported by Abe et al. [1]. Organic Coumarin dyes are also promising for applications in DSWS in that they have much higher molar extinction coefficients than those for ruthenium polypyridine complexes. Coumarin dyes have several advantages as photosensitizers for DSWS: (1) they have larger absorption coefficients than metal-complex sensitizers, and these large coefficients lead to well-organized light-harvesting properties; (2) the variety in their structures provides possibilities for Molecular design, e.g., the introduction of substituents; (3) there are no worries about resource limitations because organic dyes do not contain noble metals such as ruthenium, and also Coumarin derivatives have been intensively studied, both experimentally and theoretically, and are one of the most promising dyes [43]. It was found that Coumarin dyes containing an oligo-thiophene moiety between the acceptor and donor parts show reversible oxidation–reduction cycles stable even in an aqueous solution. In order to improve photocatalytic activity, the effect of substitution in a series of Coumarin dyes was investigated. So, Abe et al. investigated a series of Coumarin dyes (C343, NKX-2311, NKX-2677 and NKX-2697) by inserting various numbers of thiophene or methine moieties as  $\pi$  bridge between Coumarin as electron donor and cyano carboxylic acid as electron acceptor. As the absorption area in the visible region is really narrow, wide absorption range in this region for the Coumarin dyes is required to achieve a high efficiency solar-energy to-power conversion. The introduction of electron-donating and withdrawing substituents into the dye framework and expansion of the  $\pi$  conjugation in the dyes can make the red shift of the absorption spectra possible.

Theoretical calculations are practical not only in the description of DSWS properties, but also in the design of new higher performance sensitizers manufactured by a change in their structure and/or physical properties such as solvent, temperature and external electric field [22,23]. Structural changes can be achieved by adding or substituting various substituents. Such design investigations have become possible only recently. Effective and accurate modeling of dyes' ground and excited state properties can take an important step toward their optimization. Large-scale quantum mechanical calculations, able to precisely predict the electronic and spectroscopic characteristics of the dyes, would be a really powerful and comparably low cost device in the earlier design of novel and greatly efficient sensitizers.

In this publication, the molecular structure and the electronic properties of the ground and lowest  $\pi$ – $\pi^*$  excited state for a series of Coumarin derivatives, C343, NKX-2311, NKX-2677, and NKX-2697, are studied. The reported Coumarin dyes absorb light weakly over 700 nm, and little success was achieved to extend photo response to the longer wavelength region. Therefore, it is still a challenge to efficiently harvest incident photons in the longer wavelength region.

Application of an external electric field is the strategy that we, in this research, suggest to overcome the challenge. Local electric

fields could simply lead to a change in the absorption spectrum due to the Stark effect. Such electric fields acting on ground-state dye molecules lower the energy gap between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) and, thus, red-shift the absorption peak of the dye. It can be strongly mentioned that the applied field led to a red-shift for DSWS, and, to our surprise, there was a striking increase in the absorption coefficient.

## 2. Computational methods

All sensitizer were optimized by the use of density-functional theory (DFT) calculations. The DFT was treated according to B3LYP and the standard 6-311G(d) basis set [24–27]. The excitation energies and oscillator strengths for the four dyes at the optimized geometry in the ground state were obtained in the framework of TD-DFT calculations with the hybrid functional B3LYP and the 6-311G(d) basis sets [28–32]. The solvent effects were evaluated using the non-equilibrium implementation of the conductor-like polarizable continuum model (CPCM) [33]. Solvent could affect the geometry, electronic structures and the related properties of molecule. In this work we also present the changes of the electronic structure and optical properties induced by an external electric field. Optimization calculations were carried out with and without an applied electric field. Seven different fields of 5, 10, 15, ..., 30 and  $40 \times 10^{-4}$  a.u., parallel to the dipole moment, were applied on the dyes and their geometry in each field was then optimized by DFT, B3LYP and the 6-311G(d) basis set. All chemical quantum calculations were carried out with the Gaussian03 program package [34].

Excitation energy calculations on the optimized sensitizer were later carries out in the corresponding electric fields at the same level of theory. The electric field term is included in the Hamiltonian and results in a change in the energy of both occupied and unoccupied levels which in situ results in a shift of transition energies.

To understand the nature and magnitude of the intermolecular resonance over the different parts of the dyes and to calculate the NBO conjugation stabilization energies, the natural bond orbital (NBO) theory was conducted on optimized geometries. NBO calculations were performed using the program packages of NBO5.0 [35].

## 3. Results and discussion

For a proper discussion and comparison of theoretical results, it is important to have a clear picture of our theoretical data. All of the calculations were conducted by B3LYP/6-311G(d) methods. In this section, we present results for C343, NKX-2311, NKX-2677 and NKX-2697, organized in the following manner. We first study, in detail, the electronic structure of these four dyes in gas phase and solvent. We then investigate the absorption spectra and electronic excitations between ground and excited states in the presence and absence of solvent effects. Following this, the electronic structure, absorption spectra and excitation energy between ground and excited states are analyzed in the presence of an applied electric field for C343, NKX-2311, NKX-2677 and NKX-2697. Finally, we interpret and analyze the resulted data.

### 3.1. Electronic structure

We analyzed the electronic structure of all of these organic sensitizers in vacuum and in water solution. A schematic representation of the molecular orbital energies and isodensity plots of the frontier molecular orbitals of C343, NKX-2311, NKX-2677 and NKX-2697 is reported in Fig. 1.

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