Computational investigation of low band gap dyes based on 2-styryl-5-phenylazo-pyrrole for dye-sensitized solar cells

Samaneh Bagheri Novir, Seyed Majid Hashemianzadeh[*]

Molecular Simulation Research Laboratory, Department of Chemistry, Iran University of Science & Technology, Tehran, Iran

A B S T R A C T

In this work, the geometry, electronic properties and absorption spectra of low band gap organic dyes based on 2-styryl-5-phenylazo-pyrrole, C1, C2 and S dyes were theoretically investigated via DFT and TD-DFT in the gas phase and in solution. Theoretical calculations have been also carried out on the adsorption of these dyes on the TiO$_2$ anatase (101) surface that show bidentate bridging is preferred adsorption mode in these dyes. Highest charge populated in the acceptor group, longest lifetime of the first excited state, highest electronic coupling constant ($|V_{RP}|$) of the S dye and the most negative shift of the conduction band of TiO$_2$ due to the adsorption of the S dye on TiO$_2$ (ΔE_{CB}) show that these parameters are favorable to increase V_{oc}. The calculated results of these dyes demonstrate that theoretical calculations are useful not only in the description of these properties, but also in the design of new sensitizers.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Solar energy is the most plenteous source of energy on earth, and its conversion into electricity, through photoelectrochemical solar cells, is generally regarded as the most appropriate method to solve the global energy crisis, owing to its massive reserves and pollution-free character. Although commercially available solar cells are currently based on inorganic silicon semiconductors, but their large-scale application has been limited due to the high cost of high-purity silicon. Among all the renewable energy technologies, the nanocrystalline dye-sensitized solar cells (DSSCs) which were presented by O'Regan and Grätzel in 1991, have attracted a lot of attention due to their potentially low fabrication costs, environmentally friendly components, relatively high conversion efficiencies and flexibility in their manufacture and employment [1–6]. In DSSCs process, light is absorbed by the dye anchored on the TiO$_2$ surface and then electrons from the excited dye inject into the conduction band of the TiO$_2$, generating an electric current. The oxidized dye is then reduced by electron transfer from the electrolyte, commonly based on the redox couple I$^-$/I$_3^-$ in an organic solvent [6–9]. Up to now, two kinds of dyes have been studied extensively as sensitizers, metal−organic complexes and metal-free organic dyes. Metal−organic complexes, mainly the noble metal ruthenium polypyridyl complexes, have provided the highest performances, with solar energy to electrical energy conversion efficiencies beyond 11% [6,8,10]. Recently, more attention has been directed to the use of metal-free organic dyes in DSSCs because of no noble metal resource limitation, their high molar absorption coefficient, relatively simple synthetic procedure, various structures, the tunable absorption spectral response from the visible to the near infrared (NIR) region, environmentally friendly and economical production techniques [7,11,12]. Organic dyes in DSSCs generally consist of an electron donor, an electron acceptor, a π-conjugated bridge between the donor and acceptor, and/or an anchoring group. Light absorption causes an intramolecular charge transfer from the donor group to the acceptor group, through the π-bridge [13,14]. Metal-free organic dyes used in DSSCs must have suitable levels for the HOMO and the LUMO of the sensitizer matching the iodine redox potential and the conduction band edge level of the TiO$_2$. The energy level of the LUMO of the dye must be higher (more negative) than the conduction band of the TiO$_2$ (−4.1 eV). On the other hand, the energy level of the HOMO of the dye must be lower (more positive) than the I$^-$/I$_3^-$ redox potential (−4.80 eV) [11,15,16].

The structure and physical properties of sensitizers are very important to improve the efficiencies of organic dye-based DSSCs. The conjugation across the donor and anchoring groups, and good electronic coupling between the LUMO of the dye and the conduction band of TiO$_2$ is useful for high electron-transfer rates.

---

* Corresponding author. Tel.: +98 21 77240287; fax: +98 21 77491204.
  E-mail addresses: hashemianzadeh@yahoo.com, hashemianzadeh@iust.ac.ir (S.M. Hashemianzadeh).

Consequently, decreasing the energy of the charge-transfer transition is necessary. Pyrrole group, as an electron-rich heteroaromatic ring, has been used as a conjugated bridge in organic dyes. On the other hand, azo dyes are a well-known class of compounds containing an N═N double bond and due to their ability to absorb visible light, they have been extensively used in organic photoactive materials due to their excellent optical switching properties, high solution process abilities and good chemical stabilities. Over the past decade, azo dyes based polymers and materials have drawn a considerable amount of attention. Among the known azo dyes, azopyrroles are important. They have obvious bathochromic absorptions compared to azobenzene dyes [11,17,18]. Recently, three new dyes C1, C2 and S based on 2-styryl-5-phenylazo-pyrrole (Fig. 1), have been synthesized by Mikroyannidis et al., that C1 and C2 dyes contain one and two carboxy anchoring groups, respectively, and S dye has one sulfonic acid anchoring group. In these dyes, substituted-phenylazo at one side and cyanovinylene 4-nitrophenyl at the other side of the pyrrole ring, extended the absorption band of the dyes into the near infrared region, which is a favorable feature for DSSCs. The hexyl chain in these dyes enhanced the solubility of the dyes [11]. Theoretical calculations are useful in the description of the physical properties and disclose the relationship among the performance, structures and the properties of dye sensitizers. They could also help in the design of new sensitizers with the better performance [19,20]. In this work, the geometries, electronic properties, electronic transition, oxidation potential, the free energy changes of electron injection and electronic absorption spectra of C1, C2 and S, were studied by using density functional theory (DFT) and time-dependent DFT (TD-DFT) methods. In order to calculate and compare the adsorption energies of different adsorption mode of the dyes and also studying TiO_2 conduction band energy shift upon the dyes adsorption, theoretical calculations have been carried out on the adsorbed dyes onto the TiO_2 anatase (101) surface. Because of the limitation of current computational capacity, the smallest possible TiO_2 anatase (101), the $(TiO_2)_{24}$, has been used in this work. The surface area of the $(TiO_2)_{24}$ is suitable for the anchoring groups of the dyes to anchor onto.

Finally, the computational results were compared and correlated with the available experimental information and allow us to describe qualitatively some effective factors in the efficiency of these dyes and theoretically explain why the S dye has the larger efficiency than C2 and C1 dyes.

2. Computational methods

All calculations on the free dyes in this work were performed by the Gaussian 03 program package [21]. The ground state geometries of C1, C2 and S were optimized at the DFT level of theory with Becke's [22] three parameters hybrid functional and Lee–Yang–Parr [23] correlation functional (B3LYP) [22] by using 6-311+G(d,p) basis set. Vibrational Frequency calculations were carried out on the optimized geometries at the same level to show that all optimized geometries reached a stationary point. Natural bond orbital (NBO) calculations also have been performed at the same level on optimized structures. Time-dependent DFT (TD-DFT) calculations for the lowest 30 singlet–singlet transitions at the optimized geometry in the ground state were performed with the hybrid functional B3LYP and 6-311+G(d,p) basis sets for calculation of excitation energies and oscillator strengths of these dyes. The free energy change (in eV) for electron injection from excited dyes to TiO_2 surface, can be calculated from Rehm Weller equation [16,24]:
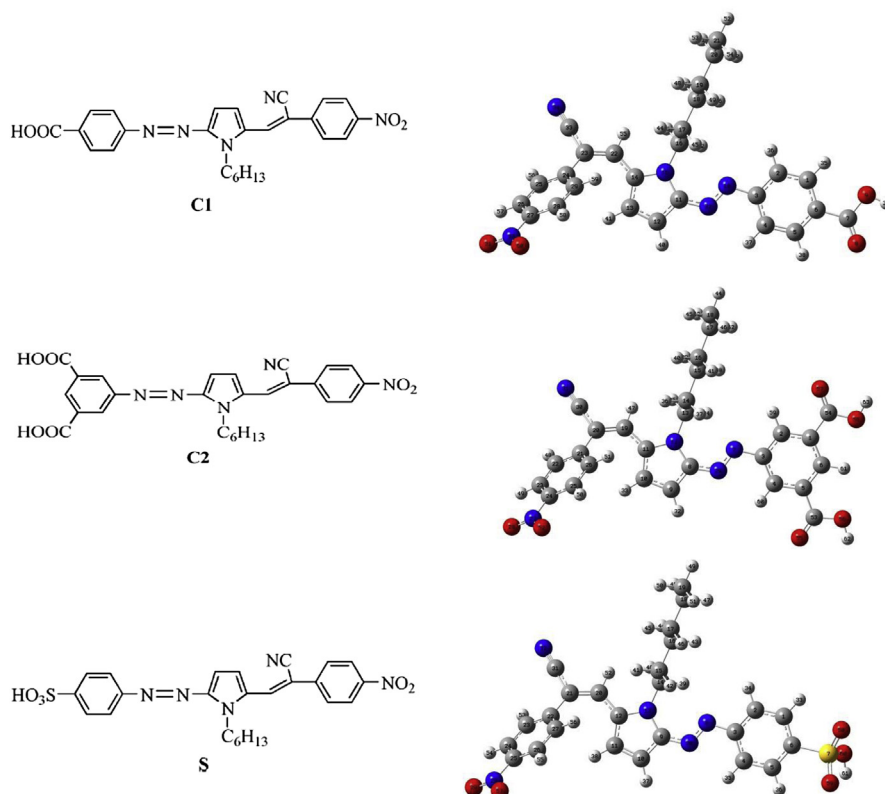

Fig. 1. Schematic and optimized geometrical structures of dyes C1, C2 and S with B3LYP/6-311+G(d,p).