



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Exploring the effect of vibronic contributions on light harvesting efficiency of NKX-2587 derivatives through vibrationally resolved electronic spectra

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ARTICLE INFO

Article history:

Received 15 June 2016

Received in revised form 7 August 2016

Accepted 13 August 2016

Available online 15 August 2016

Keywords:

DSSCs

NKX-2587

Franck-Condon

Herzberg-Teller

Duschinsky

ABSTRACT

The vibrationally resolved electronic spectra of five metal-free NKX-2587 derivatives containing heteroatom with different atomic sizes and electronegativity, were simulated within the Franck-Condon approximation including the Herzberg-Teller and Duschinsky effects, aimed at exploring the correlation of vibronic structure associated with the spectrum and efficiency of dye sensitized solar cells (DSSCs). The parameters of short-circuit current density (J_{sc}) and open circuit voltage (V_{oc}) involving efficiency of DSSCs, such as total dipole moments (μ_{normal}), the light harvesting efficiency (LHE), injection driving force (ΔG_{inject}), and the number of electrons in the conduction band (n_c), were calculated and discussed in detail. Results showed that the heteroatoms in the same period with large size and weak electronegativity and the ones in the same main group with large size and weak electronegativity are beneficial to V_{oc} . The sizes and electronegativity of the heteroatoms have a weak effect on J_{sc} . The low-frequency modes play important roles in enhancing the intensities of the electronic spectra and structures can affect light harvesting efficiency (LHE). In this sense, our results provided guidance for understanding the sources of spectral intensities of dye molecules, and a valuable help for rational design of new molecules to improve the energy conversion efficiency (η) of DSSCs.

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1. Introduction

During the past two decades, dye sensitized solar cells (DSSCs) have attracted considerable attention as a promising candidate for the next generation of solar cells due to their low production cost, high conversion efficiency and ease of processing [1–4]. As one of the most important component in DSSCs, the photosensitizer fundamentally determines the light-absorption range and light-harvesting efficiency [2,5–8]. Up to now, ruthenium based compounds have exhibited a remarkable performance with more than 11–13% conversion efficiencies, which results from the broad absorption spectra and favorable photovoltaic properties [5,6,9–11]. However, their widespread application has been limited by the toxicity and high cost of Ru, problems associated with isomerization or decomposition during the purification process, as well as its low molar extinction coefficient [12,13]. Metal-free organic dyes possess a number of advantages over Ru-complex dyes and the above two organic dyes [14–16], such as a lower material cost, higher molar extinction coefficient, and greater ease of purification [6]. Furthermore, metal-free organic dyes with a donor- π -acceptor (D- π -A) configuration are typically easier to design through modifying the molecular structure and energy gap. The lowering of the energy gap

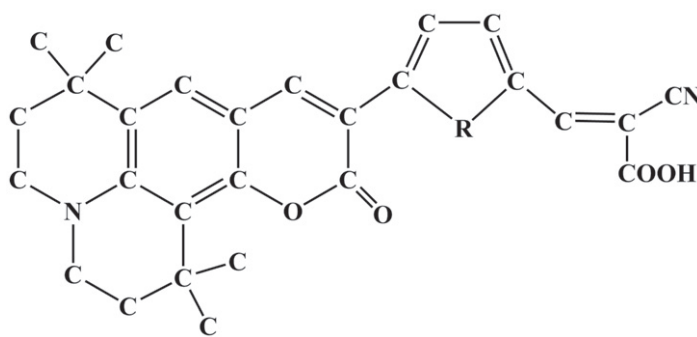
between HOMO and LUMO is used to accelerate the intramolecular charge transfer and results in the absorption spectrum red-shift with increasing the light-harvesting efficiency.

Coumarin 343 (C343) and its derivatives [17,18], have been successfully used in DSSCs due to their efficient and fast electron injection efficiency, but their performance is limited by the narrow photoresponse range in the whole visible region, unwelcomed π -stacked aggregation and undesirable charge recombination. For these reasons, generally the energy conversion efficiency (η) of DSSCs using coumarin sensitizers is lower than that of Ru-complex or Zn-complex dyes (recently, Kakiage and his coworkers reported that the DSSCs with the co-sensitization of two organic dyes reaches the 14.30% conversion efficiencies [19]). Hara et al. [20] expanded the π -conjugation by inserting more vinylene units ($-\text{CH}=\text{CH}-$) or π -conjugated rings (such as thiophene, benzene, furan or pyrrole and so on) into the π -spacers. It is helpful to broaden the absorption bands in long-wavelength region, but the relatively weak and narrow absorption bands in short-wavelength region are still unsolved. In order to solve these problems and further improve η of coumarins [21,22], computational tools have been extensively adopted to understand the spectroscopic and redox processes, rationalize the experimental data, and provide some guidelines and predictions [23].

In the present work, a series of coumarin dyes (Fig. 1) were designed by introducing heteroatoms with different atomic sizes and electronegativity

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R=C, O, S, Si, Se

Fig. 1. Molecular structures of NKX-2587-based molecules (the hydrogen on the carbon atom is hidden).

into the five membered ring of the experimental molecule NKX-2587. The short-circuit current density (J_{sc}) and open circuit voltage (V_{oc}) of the dyes absorbed on TiO_2 surface, including total dipole moments (μ_{normal}), the light harvesting efficiency (LHE), the number of electrons in the conduction band (n_c) and injection driving force (ΔG_{inject}) were investigated. Results showed that the introduction of heteroatoms with different sizes and electronegativity would cause significant changes in the energy conversion efficiency (η) of the DSSCs is closely connected with photoexcitation, recombination, injection, and regeneration, especially the light harvesting efficiency (LHE). Since key properties to optimize the light harvesting are the intensities, the positions and the widths of the absorption spectra of the dye molecules, in previous reports [24–29] the absorption process in DSSCs has been evaluated in detail by computing the excitation energies of dye molecules. However, only a few computational studies have addressed the role of vibronic contribution on the light harvesting efficiency. As a step toward this goal, the vibrationally resolved electronic spectra of the five dye molecules were simulated within the Franck-Condon approximation including the Herzberg-Teller (HT) and Duschinsky effects, aimed at exploring the correlation of vibronic structure associated with the spectrum and efficiency of dye sensitized solar cells (DSSCs).

2. Computational methods

2.1. General theory

The energy conversion efficiency (η) of the DSSCs can be determined by the short-circuit current density (J_{sc}), open-circuit photovoltage (V_{oc}), and the fill factor (ff) [30].

$$\eta = \frac{ff V_{oc} J_{sc}}{P_{\text{inc}}} \quad (1)$$

where P_{inc} is the incident solar power on the cell. J_{sc} in DSSCs is determined as: [31]

$$J_{sc} = \int_{\lambda} LHE \Phi_{\text{inject}} \eta_{\text{collect}} I_s(\lambda) d\lambda \quad (2)$$

LHE is the light harvesting efficiency at the specific wavelength, Φ_{inject} is the electron injection efficiency, η_{collect} is the charge collection efficiency, I_s represents the total solar power incident on the cell. The LHE can be described by:

$$LHE = 1 - 10^{-f} \quad (3)$$

f is the oscillator strength corresponding to λ_{max} . The ΔG_{inject} can be expressed as: [32]

$$\Delta G_{\text{inject}} = E_{\text{dye}}^* - E_{\text{CB}} = E_{\text{dye}} - \Delta E - E_{\text{CB}} \quad (4)$$

where E_{dye}^* and E_{dye} are the excited and ground oxidation potential energy of the dye, respectively, E_{CB} is the conduction band edge of the semiconductor, and the ΔE is the adiabatic excitation energy corresponding to the λ_{max} . The V_{oc} can be described by: [33]

$$V_{oc} = \frac{E_{\text{CB}} + \Delta E_{\text{CB}}}{q} + \frac{\kappa_b T}{q} \ln \left(\frac{n_c}{N_{\text{CB}}} \right) - \frac{E_{\text{redox}}}{q} \quad (5)$$

where q is the unit charge, $\kappa_b T$ is the thermal energy, n_c is the number of electrons in the conduction band, N_{CB} is the density of accessible states in the conduction band, and E_{redox} is the electrolyte Fermi level. ΔE_{CB} is the shift of E_{CB} when the dyes are adsorbed on substrate and can be expressed as: [31]

$$\Delta E_{\text{CB}} = - \frac{q \mu_{\text{normal}} \gamma}{\epsilon_0 \epsilon} \quad (6)$$

Here, μ_{normal} is the dipole moment of individual dye perpendicular to the surface of semiconductor substrate. γ is the surface concentration of the dye. ϵ_0 and ϵ represent the vacuum permittivity and the dielectric permittivity, respectively.

We define two functions $\rho_+(r)$ and $\rho_-(r)$ to represent the increase and decrease of the charge density owing to electronic transition. The

Table 1

The calculated HOMO level (eV) of the experimental molecule NKX-2587. The asterisks in the table represent the polarization functions, the single is the polarization of the other atom in addition to the hydrogen atom, the double asterisk is polarization of hydrogen atoms.

	6-31G*	6-31G**	6-31 + G*	6-31 + G**	6-31 + +G**	6-311G*	6-311 + G*	6-311 + G**
B3LYP	−5.42	−5.42	−5.70	−5.70	−5.70	−5.63	−5.73	−5.73
PBE0	−5.51	−5.51	−5.64	−5.64	−5.64	−5.61	−5.67	−5.67
CAM-B3LYP	−6.38	−6.37	−6.59	−6.59	−6.59	−6.57	−6.63	−6.63
LC-BLYP	−7.59	−7.58	−7.71	−7.79	−7.79	−7.79	−7.82	−7.82
M062X	−6.33	−6.31	−6.49	−6.48	−6.48	−6.48	−6.52	−6.52
Exp. ^a	−5.46(NHE) ^b							

^a Experimental value is taken from Ref. 36.

^b NHE is the abbreviation of Normal Hydrogen Electrode.

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