



# The master factors influencing the efficiency of D–A– $\pi$ –A configured organic sensitizers in dye-sensitized solar cell via theoretically characterization: Design and verification



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## ABSTRACT

Series sensitizers of indoline and triphenylamine as the donor group, quinoxaline and its derivatives as the additional acceptor, different heteroaromatic rings (furan, benzene and selenophene) as the  $\pi$ -conjugated group, 2-cyanoacrylic acid as the acceptor/anchoring which featured on the D–A– $\pi$ –A architecture have been theoretically designed based on the reported dyes **IQ2** and **TQ2** used in dye-sensitized solar cells (DSSCs), to shed light on how the additional (auxiliary) acceptor and  $\pi$  spacer influence the performance of the dyes. These enable us to determine master factors influenced the efficiency of DSSCs, such as the light-harvesting efficiency, lifetime of excited state, exciton binding energy, total reorganization energy and electron injection driving force as well as the vertical dipole moment. The theoretical results revealed that compared with dye **IQ2**, our designed dyes **IQS2** and **IQS3** displayed much better light harvesting properties and longer first excited lifetime.

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## 1. Introduction

Since the sensational work reported by O'Regan and Grätzel in 1991 [1], the metal-free organic sensitizers have been widely investigated as a new generation solar cell of products in dye-sensitized solar cells (DSSCs), due to their high light-to-electricity conversion efficiencies, easy structural modifications and cost-effective [2,3] alternatives to conventional photovoltaic materials based on inorganic silicon or compound semiconductors [4,5]. As a key part of DSSCs, sensibilizers play a crucial role in high power conversion efficiencies (PCEs). Simultaneously, most efficient organic sensibilizers like coumarin [6,7], thiophene [8,9], indoline [10,11], triphenylamine [12,13] have been tested in this D– $\pi$ –A framework and show good performances. However, considerable progress has been made in the performance of DSSCs by experimental as well as theoretical methods, only a few DSSCs with

certified and recorded efficiencies of more than 10% have been reported based on metal-free organic sensitizers [14–18]. Generally, the critical factors leading to the low photo-to-current conversion efficiency are the formation of serious intermolecular aggregation on the TiO<sub>2</sub> films as well as the charge recombination between the internal and external circuit current.

In order to overcome the drawbacks of low efficiency of metal-free sensitizer based on DSSCs. Tian and Wang et al. [19–23] designed a series of novel dyes based on D–A– $\pi$ –A configuration which an auxiliary acceptor (such as the benzothiazole [24], benzotriazole [25], quinoxaline [26,27], phthalimide [28] etc.) is introduced between the donor and  $\pi$ -linker, during the last decades. These additional acceptor chromophores have been proved to exert a better charge delocalization ability, red-shift the charge-transfer absorption band to the low energy region, reduce reorganization energy and suppress charge recombination. Quite recently, Zhu et al. [22] synthesized and characterized a series of high performance D–A– $\pi$ –A featured sensitizers (**IQ1**, **IQ2**, **TQ1** and **TQ2**), these dyes consist of an indoline or triphenylamine unit acting as the electron donor, electron-withdrawing quinoxaline as the additional

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(auxiliary) acceptor, thiophene moiety as the  $\pi$ -conjugation bridge and 2-cyanoacrylic acid as the anchor group, respectively. The **IQ2** and **TQ2** based DSSCs can perform well without any co-adsorption, they successfully suppress the charge recombination and enhance the excited state electron lifetime. In particular, dye **IQ2** based DSSC exert the efficiency up to 8.50% under AM 1.5 illumination [22]. Moreover, with furan unit as the  $\pi$ -linker segment, dye displays an extraordinary high efficiency due to its high photovoltage, such as well-known WBS series of sensitizers (WBS-1F) developed by Zhu et al. [29].

In this work, we designed four new dyes **IQF**, **IQB**, **TQF** and **TQB** (see Fig. 1) with modification on the additional acceptor and  $\pi$ -spacer based on **IQ2** and **TQ2**. The electronic and optical properties, injection energy, orbital coupling and dipole moment could be influenced significantly by tuning these chromophores. Furthermore, to shed light on how the auxiliary acceptor influences the performance of dyes, attempts have been devoted to modify the quinoxaline (Fig. 5(a)). We hope our work could facilitate the future experimental studies to design and synthesize new efficient organic sensitizer.

## 2. Methods

### 2.1. Theoretical background

As we have known, the overall efficiency ( $\eta$ ) of the DSSCs can be determined by the short-circuit current density ( $J_{sc}$ ), the open-circuit photovoltage ( $V_{oc}$ ) and the fill factor ( $ff$ ), it is an important parameter to evaluate the performance of DSSCs. This connection could be expressed by the following equation [30]:

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

where  $P_{in}$  is the total solar power incident on the cell. According to Eq. (1), improving  $J_{sc}$  and  $V_{oc}$  is an effective means to enhance  $\eta$ . As for  $J_{sc}$  in DSSCs, it can be expressed as [31]:

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

where  $LHE(\lambda)$  denotes the light harvesting efficiency at a given wavelength,  $\Phi_{inject}$  is the electron injection efficiency and  $\eta_{collect}$  is the charge collection efficiency. Based on Eq. (2), to obtain a high  $J_{sc}$ , the efficient organic dyes used in DSSCs should have a large  $LHE$ , which can be calculated with [32]:

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

where,  $f$  is the oscillator strength of the dye molecules, the larger  $f$  could fulfill a better light capturing. For a DSSCs to work properly, it is clear that both ground state oxidation potential energy ( $E^{dye}$ ) and the excited state oxidation potential energy ( $E^{dye*}$ ) of the dyes have to match the redox potential ( $-4.8$  eV vs. vacuum) of the iodine/iodide redox couple and the conduction band ( $-4.0$  eV vs. vacuum) of the  $TiO_2$  electrode, respectively. Which is roughly evaluated using the formula [33]:

$$E^{dye*} = E^{dye} - E_{00} \quad (4)$$

where  $E_{00}$  is the vertical transition energy. It is generally accepted that the electron injection from the photoinduced excited states of organic dyes to the semiconductor occurs before the vibrational relaxation. Hence, in this case,  $E^{dye*}$  is estimated using unrelax path. In DSSCs, the  $V_{oc}$  can be following [34]:

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

where  $E_{CB}$  is the conduction band edge of the semiconductor substrate,  $E_{redox}$  is the electrolyte Fermi level,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $q$  is the unit charge,  $n_c$  is the number of electron in the conduction band and  $N_{CB}$  is the accessible density of conduction band (CB) states.  $\Delta CB$  is the shift of  $E_{CB}$  when the dyes are adsorbed on the semiconductor surface and can be expressed as [35]:

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

where  $q$  is the electron charge,  $\mu_{normal}$  denotes the dipole moment of individual dye molecules perpendicular to the surface of the semiconductor substrate,  $\gamma$  is the dye's surface concentration,  $\epsilon_0$  and  $\epsilon$  are the permittivity of the vacuum and the dielectric constant of the organic monolayer. Moreover, the lifetime  $\tau$  of the excited state(s) is an important factor for considering the efficiency of charge transfer of dyes [36]. A dye with a longer lifetime in the excited state is expected to be more facile for charge transfer. In the present study, the  $\tau$  value was approximately set to the lifetime of spontaneous radiation, which is roughly evaluated using the formula [37]:

$$\tau = \frac{1}{A_{k,k'}} \quad (7)$$

$$A_{k,k'} = \frac{4e^2 \Delta E_{k,k'}^3}{3\hbar^4 c^3} |r_{k,k'}|^2 \quad (8)$$

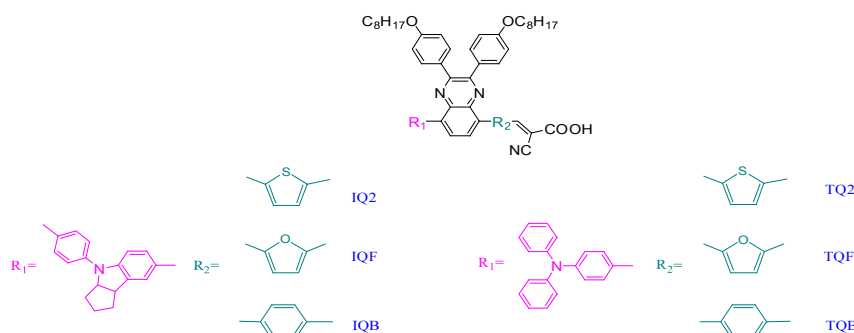


Fig. 1. Schematic representation of the simulated systems.

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