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# The origin of slow electron injection rates for indoline dyes used in dye-sensitized solar cells

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ABSTRACT

This work highlights the direct impact of selecting acceptor moiety for organic dyes on the electron dynamics at faster time scales, in which overlooked photo-physical properties are present on semiconductor surfaces with specific acceptor moieties. Four top-performing dyes of indoline family (D131, D102, D149, and D205) sharing the same donor moiety, but through different acceptor groups, were selected and compared with respect of electron injection process, using ultrafast transient-infrared probe. The presence of rhodanine moiety at the acceptor unit in D102, D149 and D205, shows an additional slow electron injection process, of picosecond time-scale, on the low band-gap semiconductor, $TiO_2$. This slow process is expected to be present due to a twisted intramolecular charge transfer/isomerized state of the excited dye prior to electron injection. This isomerized state reduces as well the detrimental electron recombination process rates, and results of high performance in solar cells based on these rhodanine dyes. Replacing the rhodanine moiety by a cyano-acrylic group in D131 dye shows faster electron injection and recombination processes, due to the lower dipole moment present in the excited state, hindering the formation of an isomerized state. These findings will aid to enhance the organic dyes design used in dye sensitized solar cells, in which designed photo-physical processes on semiconductor surfaces can increase the efficiencies of the solar cells.

## 1. Introduction

The wide-accepted strategy for building metal-free organic dyes for solar cell applications is by far connecting a donor (D) electron-rich moiety, in the ground state, through a linker unit to an acceptor (A) moiety that is electron-deficient in the ground state, which is known as push-pull strategy [1–5]. Upon light excitation, an intramolecular charge transfer (ICT) process is induced from the D to A moiety, where the electron is further transferred to the conduction band (CB) of the semiconductor [1,6,7]. To absorb most of the incident sun light, the tune of optical and electronic properties of utilized dyes occurs via changing either the D or A moieties, as well as changing the length of the linker unit [8]. Several acceptor units have been used for this aspect such as cyanoacrylic and rhodanine moieties [1,8]. These two moieties have been heavily used in various organic dyes [1,9]. Each of these moieties has its cons and pros depending on the working conditions [10]. However, the influence of acceptor unit variation has been mainly to change the spectral response of the utilized dye and/or the thermodynamic driving force between the LUMO of the excited dye and the CB, which in turn affects the photocurrent density and the open circuit voltage values in solar cells [1,9,11,12]. Very few reports have discussed the variation of kinetic parameters, more specifically electron injection and recombination, upon changing either the D or A units [6]. Nevertheless, this paper illustrates the variation of electron injection dynamics for four well-performing, metal-free, indoline dyes sharing the same D unit but with four different acceptor units, known as D131, D102, D149 and D205 (see chemical structures in Fig. 1). As can be seen in Fig. 1, D131 has a cyanoacrylic group, D102 has one rhodanine moiety, D149 has two rhodanine moieties, and D205 has additional octyl chain in top of the two rhodanine moieties. Solar cells based on D131, D102, and D149 using ZnO have shown high efficiencies among other indoline dyes, reaching to ca. 5% [13]. On $TiO_2$ nanorods, solar cell based on D131 has higher efficiency (ca. 5.1%), than others based on D149 and D102, which has been attributed to the highest current produced due to strong electronic coupling between the cyanoacrylic group, wherein the LUMO is located, and the $TiO_2$ surface [14–16]. With a development of the structural design, the long octyl-chain in D205 has led to an improvement of efficiency, 7.1%, in comparison to D149 and D102 under the same conditions due to the retardation of electron recombination process [17]. With the aid of anti-aggregation agent, efficiencies of ca. 9.5% and 9.0%, on nanocrystalline-$TiO_2$, could be achieved by D205 and D149, respectively [18]. It is worth mentioning that the first breakthrough of indoline dyes, which attracts the intension towards these dyes, was achieved by D149, in which an

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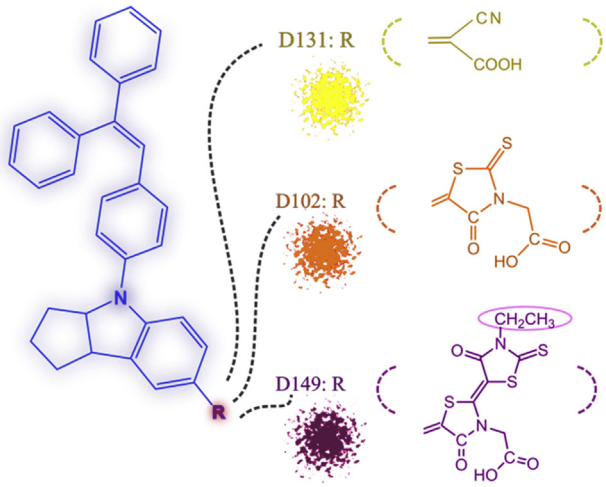


**Fig. 1.** Structures of indoline donor unit D (blue), and other emerging dyes D131, D102, and D149 (various colors of solid materials) with different acceptor units. The structure of D205 is similar to D149 except the presence of octyl chain instead of methyl group (surrounded by pink oval).

efficiency value of 8.2% could be obtained [19]. From the above information, one can see that efficiencies have been measured without deep understandings of the electron dynamics associated with the dye's structure. Thus, the relationship between the structure of these well-performing organic dyes and electron dynamics, mainly electron injection, will definitely improve our knowledge towards synthesizing robust dyes. To do so, the ultrafast transient absorption in the mid-infrared range (fs-IR) is used in this study to follow the electron dynamics of the selected adsorbed indoline dyes at the CB of $TiO_2$. The fs-IR probe has been utilized before for different systems for observing the electron injection [20–24]. The electron's transient absorption normally extends from 3333 to 11,111 nm with a broad featureless shape [25]. The fs-IR has recently shown more sensitivity towards injected electrons at the CB in semiconductors due to lack of electronic absorption from other species such as cationic organic dyes [26–28]. This unique advantage of mid-IR probe is utilized herein to follow the electron injection process for four dyes adsorbed on $TiO_2$, D131, D102, D149, and D205. The fs-IR dynamics show herein drastic changes in the electron dynamics upon changing the acceptor moiety for the studied dyes.

## 2. Results and discussion

Fig. 2A shows the normalized absorption spectra for different indoline dyes including the D unit, D131, D102 and D149 in toluene. The nature of the D's excited state is a local excited state (LE), which is changed to an intramolecular charge transfer (ICT) state upon attaching the acceptor units in the emerging dyes [16,19,29,30]. As can be seen, with increasing the acceptor unit strength, connected to the D unit ($\lambda_{max}^{abs}\approx$ 375 nm), from cyanoacrylic (D131, $\lambda_{max}^{abs}\approx$ 460 nm) till rhodanine moieties (D102 $\lambda_{max}^{abs}\approx$ 500 nm, D149 $\lambda_{max}^{abs}\approx$ 535 nm, and D205 $\lambda_{max}^{abs}\approx$ 535 nm), bathochromic shifts can be observed. These acceptor strengths were illustrated before in the theoretical work of Tangui [16], in which the dipole moment is increased by ca. a factor of two upon going from cyanoacrylic group in D131 to two rhodanine moieties in D149. These absorption spectra are broadened upon adsorption of these dyes on $TiO_2$, probably due to the aggregation effect, which is shown in Fig. 2B for D149 on $TiO_2$. Similar broadenings have been reported previously for other dyes [31–34]. However, upon using the fs-IR probe in our measurements, the aggregation problem will not influence the observed kinetics as shown previously in the visible region [32], since the working spectral region is solely sensitive to the vibrating electrons in the CB of $TiO_2$ [26,27].

As can be shown in Fig. 3, the adsorbed dyes on $TiO_2$ were excited in the visible region by 410 nm, and probed in the mid-IR region at 4900 nm, where the signature of the electron dynamics in the CB in $TiO_2$ can be followed, different kinetic profiles can be observed depending on the dye structure. At time zero, the signal of injected electrons at 4900 nm is produced, representing the electron transfer process from the excited dye to the CB of $TiO_2$, see Fig. 3. Beyond time zero, slow injection time constants can be detected for D102, D149 and D205, except D131. Later on, the signal starts to decay due to the electron recombination process between electrons in the CB of $TiO_2$ to the nearby oxidized dyes on surface, however, the full recovery of electrons is beyond our time window of the current measurements, ca. 5 ns. Therefore, accurate analysis for electron recombination process has not been performed. Table 1 summarizes the time constants obtained from fitting the kinetic traces using multi-exponential components. To the best of current knowledge, the slow electron injection time constant, in the order of ps time scale, was rarely observed for organic dyes, and not fully understood [6]. Even for the D149 dye that has been heavily studied spectroscopically on semiconductors, only electron injection components of 100–250 fs were observed [35–37]. Most likely, the slow injection process was not observed due to the usage of visible probe to detect this crucial process, in which an overlap between signals of electron absorption, oxidized dye and excited state of non-injecting dyes on surfaces, making the data analysis quite challenging. Nevertheless, previously, the electron injection process of D149 in complete solar cell probed by mid-IR spectrum exhibited similar results to the ones in this work [23].

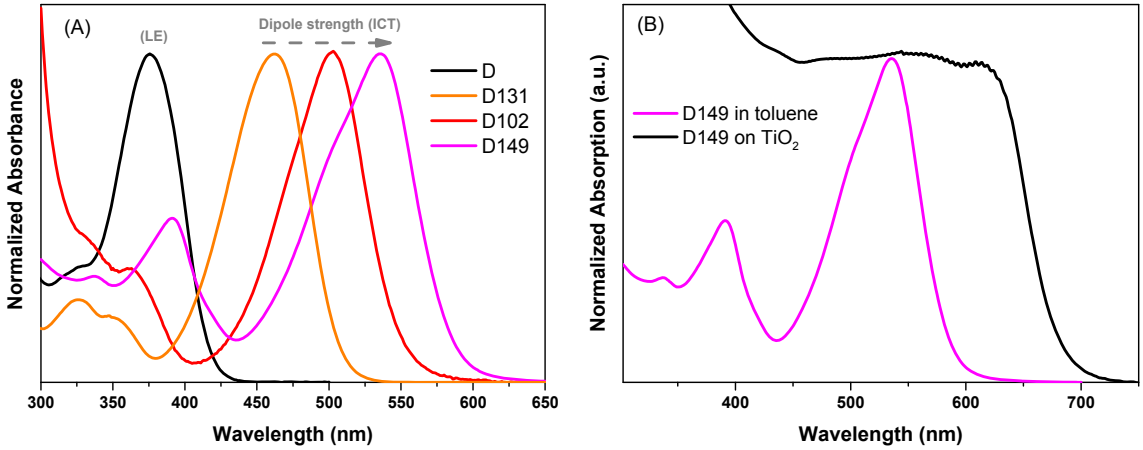


**Fig. 2.** (A) Normalized absorption spectra of the D unit and different dyes studied of the indoline family (D131, D102, and D149) in toluene. (B) Comparison between D149 in toluene and upon adsorption on TiO2. Check text for more information.

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