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Excited-State Dynamics of Organic Dyes in Solar Cells

Ahmed M. El-Zohry

Abstract

Organic dyes are promising candidates for wide applications in solar cells, due to their controlled environmental impact, and low-cost. However, their performances in several solar cell architectures are not high enough to compete with the traditional semiconductor based solar cells. Therefore, several efforts should be gathered to improve the efficiency of these organic dyes. Herein, we discuss several deactivation processes recently found in several organic dyes using optical spectroscopic techniques. These processes are believed to be mostly detrimental for the performance of organic dyes in solar cells. These processes include deactivation phenomena such as isomerization, twisting, and chemical interactions with redox couple. Thus, based on similar studies, more optimized synthetic procedures for organic dyes could be implemented in the near future for high efficient solar cells based on organic dyes.

Keywords: charge dynamics, deactivation pathways, chemical interactions, spectroscopic tools

1. Introduction

1.1 DSSCs design

Dye Sensitized Solar Cells (DSSCs) have drawn the attention of renewable energy scientists, since the proof of concept done by O'Regan and Grätzel in 1991 [1]. In that concept, it was shown that an adsorbed photosensitizer on a low-cost low bandgap semiconductor can generate electricity with a reasonable efficiency from the incident sun light. Such a process was a breakthrough at the time, despite the low efficiency of the utilized sensitizer, as only highly crystalline semiconductor, such as Si, was believed to be the only way to capture the sunlight and convert it into electricity. In a typical Si solar cell, the light is absorbed by the crystalline Si atoms and the energetic charges are generated within the bandgap of the semiconductor, which later can be extracted by the external circuit [2]. However, in the DSSC, the light is absorbed by the photosensitizer "adsorbed dye" and then transfers its energetic charge to the low-cost semiconductor that is responsible for transferring the charge to the external circuit. The first utilized photosensitizer was based on metal complex, a Ru-complex, thus, many metal-based complexes were tested later on the best performances in DSSCs [3]. The main excited state charge dynamics for metal-based complexes for DSSCs are based on a MLCT (metal to ligand charge transfer process) state, in which the incident light moves an electron from the metal core to the surrounding ligands in the complex, then the charge hops from the ligand to the CB (conduction band of the semiconductor) via a triplet state. Thus, heavy metal ions

with low oxidation potentials were utilized such as Ru atoms [4]. Later on, plenty of attempts have been done to replace these costly metal photosensitizers by the metal-free photosensitizers, organic dyes, to further reduce the cost of the working cell [5].

2. Organic dyes and strategic designs

Several synthetic strategies have been implemented for optimizing the metal-free, pure organic photosensitizers for working conditions in DSSCs [6]. One of the successful approaches for building organic photosensitizers is based on **D-L-A** (Donor-Linker-Acceptor) approach [7]. In this approach, the D unit is an electron-rich moiety, the L unit is typically a single or several consecutive π -bonds, then the A unit is an electron-deficient moiety that is connected by an anchoring group, such as COOH (carboxylic acid), which binds to the low-band gap semiconductor, see **Figure 1** for a graphical illustration of the organic dye. The ultimate dye should absorb most of the incident solar spectrum especially in the visible and the infrared regions, with high oscillator strength [3]. One of the most successful organic photosensitizers in DSSCs is the indoline family, which is based on Indoline moiety as a D unit [9–11]. While other acceptor groups (A) have been utilized such as rhodanine and cyanoacrylic moieties [9–11].

3. DSSCs working mechanism

Different than Ru-complexes, the organic dyes in DSSCs inject the energetic electrons from the singlet states as the triplet state population has mostly a very low quantum yield [12]. As the spin state for both the excited and the ground state of the organic dyes is the same, various deactivation mechanisms can occur for the adsorbed dyes on semiconductor surfaces. These deactivation processes include large scale motions such as isomerization [13], twisting [14], and local chemical interactions such as interactions with electrolyte components surface species [15–17].

Figure 2 summarizes the main processes for exciting an adsorbed dye on low-band gap semiconductor such as TiO_2 . There processes are such as follow:

1. **Excitation:** The adsorbed dye absorbs part of the incident solar spectrum and an electron is transferred from the ground state to the excited state instantaneously.
2. **Decay:** The populated electron recombines back again to the ground state due to various excited state processes within the dye.

Figure 1. Schematic representation for the successful design of organic photosensitizers for utilization in DSSCs based on D-L-A strategy, readapted from reference [8].

Figure 2.

Schematic representation for electron dynamics in DSSCs. Each process has its number that is mentioned in the main text. Red numbers are for deactivating processes and blue numbers are for favorable processes, readapted from reference [8].

3. **Electron Injection:** The excited electron is transferred from the dye to the CB of the semiconductor, leaving an oxidized adsorbed dye behind.
4. **Electron Diffusion:** The injected electron is diffused through the mesoporous semiconductor area reaching the conducting glass such as FTO (Fluorine doped Tin Oxide).
5. **Electron Regeneration:** The oxidized dye recovers its electron from the utilized electrolyte in the DSSCs, which has a low oxidation potential, such as (I^-/I_3^-) redox couple.
6. **Electron Recombination to Redox:** The injected electron in the CB diffuses backward to the adsorbed species on the semiconductor surfaces such as, the oxidized redox couple.
7. **Electron Recombination to dye:** The injected electron in the CB diffuses backward to the adsorbed species on the semiconductor surfaces such as, the oxidized dye.

All these processes contribute both positively and negatively to the overall performance of the DSSC. These processes are marked in different colors in **Figure 2**, depending on their role. However, due to the sake of this chapter, I will mainly be focusing on the excited state dynamics of organic dyes that improve or reduce the total performance of the DSSC. However, before presenting these dynamics, I will illustrate in the following section the main optical tools utilized for investigating these processes in DSSCs.

4. Optical spectroscopic tools

Several optical spectroscopic tools have been utilized to follow the charge dynamics for organic dyes in DSSCs. These common tools include TCSPC

(Time-correlated single photon counting), fs-TA (Femtosecond transient absorption), and fs-TE (Femtosecond transient Emission).

4.1 TCSPC

TCSPC helps to measure the emission decay of a molecule in a fast and an accurate way, due to the high repetition rate of the laser (ps or fs lasers). The accuracy of the measurements depends on the arrival of randomly emitted photons to the detector at different time channels. To initiate the measurements, a reference signal from the laser source is registered at the electronics, and the arrival time of the laser signal is measured by a constant function discriminator (CFD). Then, a linear increase in the voltage starts when the signal passes through time to amplitude converter (TAC). In the meanwhile, an electrical signal is registered from the emitted photon at the CFD, and another signal is sent to the TAC to stop the voltage increase. The time difference between the start and stop corresponds to the time delay after examining signal by the rest of the electronics. Repeating these measurements many times gives the histogram plot at the end. **Figure 3** presents the components of TCSPC [8, 12, 13].

4.2 fs-TA

As many ongoing processes of DSSCs are relatively fast ones, one needs a technique with high time-resolution to follow such processes in DSSCs. One of the most utilized techniques to follow such processes is the fs-TA setup [18–25]. Simply, in fs-TA, one needs a laser source of short pulses in the range of 100 fs per pulse, and by overlapping two laser pulses at the measuring sample (one to start the reaction ‘pump’, and another to probe it), the resulted spectrum at the detector provide exceptional information about both the ground state and the excited state of the reaction, **Figure 4** shows a simple scheme for utilizing fs-TA setup. The pump pulse is usually in the visible range to promote a charge transfer, and the probe pulse can be usually in the visible or in the infrared range [14, 26, 27]. The main advantages of fs-TA are the ability to detect dark states that are not observed by other time-resolved emission techniques such as charge transfer, energy transfer, intersystem crossing, and charge recombination [28–30].

Figure 3. Schematic representation for a typical TCSPC setup, readapted from reference [8].

Figure 4.
Illustration for the generation of TA signal by fs-laser pulses.

4.3 fs-TE

Time-resolved transient emission techniques are more versatile to follow the charge dynamics in general for the charge dynamics for dyes in DSSCs. To be able following the emission spectral information along with the emission lifetimes of the studied dyes, one commonly uses time-resolved emission streak camera, **Figure 5** shows the basic components for measuring emission using streak camera. The main advantage of using streak camera is the ease of utilizing it in comparison with other techniques such as fs-TA. Using emission streak camera, one needs only one laser source to excite the sample, then the emitted photons are collected and directed inside the streak camera, in which the photons can be spatially and temporally separated, resulting of a 2D-image that contain information about the time and energy of the emitted photons [12, 13].

Figure 5.
Typical design for a streak camera. Readapted from reference [8].

5. Excited state dynamics

5.1 Electron injection

Electron injection process is the transfer of a charge such as an electron from the excited dye to the CB of the semiconductor after light absorption, and it is considered the first beneficial process for high performance in DSSCs. The electron injection rate depends on the coupling strength between the adsorbed dye and the semiconductor, which includes the energy alignments of both the excited state of the dye and the fermi level of the semiconductor. For a long time, the electron injection time scale was trusted to be only in the range of 100 fs, however, this is not the case for all organic dyes as shown later by showing slower electron injections lifetimes [26, 27, 31]. The detection of slow electron injection in the picosecond time scale was mainly achieved by utilizing the IR (infrared) probe light in the fs-TA instead of the visible probe light [27, 29, 32, 33]. The advantage of using the IR versus the visible probe was mainly attributed the sole sensitivity of the IR to the vibrations of the electrons in the CB of the semiconductor, while the visible probe interacts with several species at the semiconductor surface such as the oxidized dye and the redox couple [8, 33, 34]. Famous organic indoline dyes were measured on TiO_2 mesoporous surfaces using fs-TA in the IR region centered at 5000 nm, and multi-exponential injection rates were detected including fast lifetimes of 100 fs and slow ones in the range of tens of ps [27, 33]. **Figure 6** shows the captured data for various indoline dyes, in which the D131 dye shows a fast injection lifetime of 100 fs, while other dyes (D102, D149, and D205) show additional slow injection lifetimes that can reach to 30 ps as in the case of D149 dye. These slow injection rates are connected to large scale motions on mesoporous surfaces as shown later on, such as isomerization. The presence of slow injection rates is thought to be beneficial to the overall efficiency of the DSSC, due to the expected minimized charge recombination afterwards [26, 31].

5.2 Deactivation processes

- Aggregation

Aggregation is a common problem for adsorption of organic dyes on mesoporous surfaces, in which the dyes are stacking in various ways very close to each other

Figure 6. Time resolved transient absorption for the electron injection process of indoline dyes adsorbed on TiO_2 . (A) Comparison between various dyes indicated in the legend. (B) Comparison between D205 on TiO_2 versus impeding the dye in PMMA, readapted from reference [27].

due to the high concentration utilized during the adsorption process, resulting of side deactivation pathways that hindered the charge transfer processes in DSSCs [13, 35, 36]. Reducing the dye aggregations can happen by utilizing co-adsorbent agents such as CDCA (cheno-deoxycholic acid) [37], or by impeding organic dyes in the MOF-ZIF8 structures, which increases the dye's emission lifetime by putting the dyes at far distances from each other [38]. **Figure 7** presents the appearance of fast emission lifetime components for the D149 dye upon the presence of aggregation. However, upon using low concentration of the D149 dye, the short lifetimes disappears due to the absence of aggregation. In DSSCs, the presence of aggregation reduces the amount of charges transferred to the CB of the semiconductor, and thus, reduces the overall efficiency of the cell.

- Isomerization

The local movement of adsorbed organic dyes was overlooked for a long time due to the expected well-packed order of adsorbed dyes, and many argued that isomerization is not a competing process with the electron injection as the latter is very fast. However, as electron injection process can be slow as well, the isomerization and the change of local arrangements of molecules on surfaces can reduce the DSSC efficiency due to uncontrolled deactivation processes [13, 39, 40]. **Figure 8** shows the absorption spectra changes of L0Br organic dye labeled by heavy bromine atom on the mesoporous ZrO_2 surfaces under photo-irradiation [40]. The changes in absorption spectra along the NMR measurements revealed the formation of *cis-trans* equilibrium on the mesoporous surfaces [13, 40].

- Twisting

Isomerization of organic dyes in DSSCs is not always spectroscopically detectable especially when the resulted isomers such as *cis* and *trans* isomers are chemically identical [14]. However, this is not the case for many organic molecules containing subunits such as phenyl groups that can rotate or twist without spectroscopic signatures. For instance, the parent molecule of the organic dye D149 dye has a diphenyl groups attached to a double bond. In solution, the lifetime of the parent molecule is very short of ca. 20 ps, and upon impeding this parent molecule in polymer matrix PMMA (Poly methyl methacrylate), the lifetime is extended to 2.5 ns, the time-resolved data for the parent molecule is shown in **Figure 9**. This ultrafast deactivation process is present in the derived dyes utilized in solar cells and it can

Figure 7. Time-resolved emission for D149 organic dye inside PMMA matrix showing the effect of concentration and the aggregation formation on the appearance of fast emission lifetime components (to the left), readapted from reference [13].

Figure 8.

Two organic dyes, LO, and LOBr were utilized to investigate the isomerization process on ZrO_2 surfaces under 400 nm photo-irradiation, readapted from reference [40].

Figure 9.

The time-resolved emission data for the parent molecule of D149 in solution and in PMMA matrix (left). fs-TA data for the parent molecule in toluene (right), readapted from reference [14].

potentially compete with the electron injection process, minimizing the amount of charges extracted through the DSSC.

• TICT (Twisted Intramolecular Charge Transfer)

Although the previous large scale motions of organic dyes apparently compete with the electron injection process, the TICT process of some studied organic dyes seems to help boosting the DSSC efficiency through an indirect pathway [31, 41]. Upon comparing organic dyes with the twisting ability on mesoporous semiconductor surfaces with the corresponding ones that do not show such a process, both the electron dynamics and the DSSC efficiency have been correlated [26, 31]. An organic dye named L1 dye shows the TICT process in solution as depicted in **Figure 10**. This dye shows a high performance in DSSCs of ca. 5.5% [26]. While the modified dye L1Fc that do not show any TICT state, instead shows a LCT (local charge transfer state), its efficiency in DSSCs was lower L1 of ca. 1.1% [26, 31].

Using fs-TA in the infrared region to investigate the electron dynamics in the CB of TiO_2 revealed that the presence of TICT state allows for slower electron injection from the L1 dye to the TiO_2 , and due the structural rearrangements of the L1 dye on the mesoporous surfaces, the back electron recombination is hindered allowing for

Figure 10. Chemical structures of L1 and L1Fc dyes along with their absorption and emission data in acetonitrile, readapted from reference [31].

Figure 11. (A) False 2D plot for the electron injection of the L1 dye to the CB of TiO₂ in the infrared. (B) Normalized kinetic traces for L1, L1Fc, and L1/PMMA on TiO₂, readapted from reference [31].

high performance in DSSCs. However, for the L1Fc case along with the L1/PMMA case, the TICT state is blocked and thus the electron injection was faster from the LCT state, but the electron recombination was order of magnitudes faster than in the L1 dye case, resulting of poor efficiency in DSSCs. **Figure 11** shows the time resolved data for electron injection for the discussed three cases. Thus, although the presence of TICT process can consume some energy to populate the TICT state, the benefit of reducing the charge recombination process is much larger on the DSSC efficiency.

- Chemical Interactions with the Redox Couple

Traditionally, the utilized electrolyte in DSSCs is solely assumed to regenerate the adsorbed oxidized dye on the mesoporous surface after the electron injection. This regeneration process is typically in the pico- to nano- second time scale [42–44]. However, just recently, it has been shown that the utilized electrolyte can form ground state interactions with the adsorbed dye on the surface that both affect the electron injection and recombination processes [15]. These effects will have detrimental effects on the performance of organic dyes in DSSCs. The formation of ground state complexes have been confirmed by using steady state absorption and emission measurements. **Figure 12** shows the kinetic traces for the electron dynamics of adsorbed organic dye D149 on TiO₂ in contact with different components of the

Figure 12.

Effect of chemical interactions between the D149 organic dye and the redox couple electrolyte (Iodide, iodine, tri-iodide) on the electron dynamics of D149 dye on mesoporous TiO_2 , the rise of the signal is due to electron injection, while the signal decay is due to the electron recombination, readapted from reference [15]. (A) Comparison between D149 and complexes of D149 with tri-iodide, and iodine. (B) Comparison between D149 and complexes of D149 with iodide, and full electrolyte.

traditional iodide electrolyte used in various DSSC sets [45]. For the case of D149/ TiO_2 , slower electron injection and recombination processes have been observed. However, upon adding I_3^- , I^- , or I_2 , the electron injection process was much faster of ca. 100 fs, and more importantly the electron recombination was increased dramatically, due to the adsorbed complexes species on the surface [15]. Thus, the chemical interactions between the chemical substances should be considered upon optimizing the DSSC efficiency.

6. Conclusion

Although the DSSC shows promising results with respect to low-cost and moderate efficiency in comparison with inorganic semiconductor solar cells, the ongoing processes in DSSC are quite complex and lots of studies are required to increase the output efficiency. In this chapter, we highlighted the fact that organic dyes have many excited state processes that have been overlooked in the past. Most of these processes showed detrimental effects on the overall performance of the DSSC. However, other excited state processes, such as the formation of TICT state, illustrated that high efficiency can also be attained through the excited state dynamics of the adsorbed dye. Understanding the dye's excited state processes will allow for fine tuning of such processes, via the chemical synthesis of organic dyes, correlating with the output efficiency of the DSSC.

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