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Properties of chromophores determining recombination at TiO₂-dye-electrolyte interface

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Abstract

Different classes of chromophores have been developed for the dye solar cell (DSC), including as the two main classes, organometallic dyes, with Ru-based complexes and Zn-porphyrin complexes, and metal-free dyes. They result in different behavior of recombination by electron transfer at titania/dye/electrolyte, where the dye molecule plays a pivotal role. We present an overview of the main factors that control recombination depending on dye structural and electronic properties: the substituent's nature, the size and nature of the π -bridge, type of absorption onto titania surface, the structure of donor electron moiety or anchoring group. Different recombination mechanisms arise, including direct recombination to redox electrolyte and through dye cation intermediate.

1. Introduction

Due to the need to find alternative energy sources, during the last decade high interest has been developed in the photovoltaic energy. The dye solar cells (DSC) research has been carried out all around the world and it has lead to the improvement of the device efficiency.¹ Amongst various strategies to improve the capacity of dye-sensitized solar cells to convert sunlight to electrical power, successful molecular engineering of photosensitizers has remarkably contributed to the progress of performance of this photovoltaic technology. Generally, an elaborately engineered photosensitizer is supposed to meet several requirements like long time and temperature stability, good anchoring capability,^{2, 3} good optical density,⁴ fast electron injection,⁵⁻⁷ strong absorption in the visible and near infrared spectra and good energy level orbital position respect to the redox electrolyte and semiconductor.³ All these parameters are extremely important and must be optimized at the same time in order to obtain good DSC performance. In this context, special care has to be taken to construct photosensitizers featuring desirable electronic and steric properties. A general problem that still remains is the detailed understanding of the titania/dye/electrolyte interface, because there are some controversial ideas about how the dye structure can interact with the rest of the components of the cell under illumination, like coadsorbents,⁸ redox shuttle⁹⁻¹¹ and electrolyte components, and how these interactions affect the cell performance.

In this feature article, we describe recent progress on the role that the dye structure plays in the recombination process that influences the overall conversion efficiency of the cells. We consider the correlation between dye structure (mainly focused on the donor and electron-rich conjugated bridging groups), and electron transfer rate, either to the redox electrolyte, to the oxidized dye molecule, or to an intermediate binding oxidized state of dye redox shuttle. We comment on the suggested mechanism to account for the kinetics of charge transfer, and how these electron transfer rates affect the value of the open-circuit voltage (V_{oc}) and the overall power conversion efficiency.

2. The structure and function of dyes in DSC

Dye molecules play a pivotal role in DSC, they are involved in light harvesting and

electron injection to the titania, therefore a large part of the final efficiency is associated to them. A classification of dyes could be summarized in two dominant blocks, (1) organometallic dyes, with Ru-based complexes,¹² Zn-porphyrin complexes^{1, 13-15} as the most representative sensitizers and (2) metal-free dyes¹⁶⁻¹⁸ where are included dyes without any transition metal in its structure (Figure 1).

The most extendedly used dyes have been ruthenium bypyridyl dyes that provide both large efficiency and good stability. In the present state of the DSC technology ruthenium dyes may find limitations for a large scale up and future devices commercialization, like sensitization time needed, associated to the low molar extinction coefficient and also the fact that Ru is not an abundant material, and the expensive purifications treatments that are necessary to process pure Ru-based dyes. Another important issue is that the structure of Ru based dyes is difficult to modify in order to increase the light harvesting to higher wavelength and better overlap with the sun spectra. Nonetheless well established Ru dyes like N719 (*cis*-diisothiocyanato-bis (2,2'bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) continue to be a benchmark for successful and stable operation of DSC devices.

In the last decade many efforts have been focused on different dye structures without transition metals in the molecule or in porphyrin structures with or without metals (being Zn the most common metal used), aiming at increased overlap with the solar spectra, as well as to reduce the cost of the dye and by extension the cost of the final product as an advantage over Ru dyes. Massive efforts were invested in designing push-pull dyes featuring various electron donors, including triarylamines,^{16, 19-21} carbazoles,²² indolines,²³⁻²⁸ heteroanthracenes (e.g. phenothiazine),^{29, 30} bis-dimethylfluoreneaniline like JK-1 and JK-2 dyes from Ko et al.¹⁶ and others. These developments achieved better overlap with the solar spectra, cheap fabrication routes, high extinction coefficient, low sensibilization time, etc. With optimization of other cell components such as redox shuttle, efficiencies up to 12.3% for laboratory devices under AM 1.5 conditions have been obtained.¹

The use of metal-free dye structures as sensitizers for DSC is related with new or different problems, like aggregation issues and specially the increase in the recombination processes,³¹ which is directly connected with the observed decrease in the value of the open circuit voltage.³²⁻³⁴ It is well known that within typical donor- π conjugated linker-acceptor chromophores (D- π -A) for DSCs, the electronic and steric

traits of the electron donor play a dominant role to determine the molecular energy levels. The dye features also affect the physicochemical interactions of multiple components at the titania/dye/electrolyte interface, which have profound effects on the ultimate power output of a DSC.³⁵ Such structural properties are intimately correlated with the light harvesting capacity of a photosensitizer and with the operation of some dynamic processes such as exciton dissociation and dye regeneration.

3. Photovoltaic performance of DSC

The DSC device is a complex system wherein three different components, the semiconductor, the chromophore and the electrolyte are brought together to generate electric power from light without suffering any permanent chemical transformation. Figure 2a³⁶ shows the operating principles of the DSC and all the processes that take place under illumination, that constitute a regenerative and stable photovoltaic energy conversion system. These processes can be expressed by means of the following reactions

$$S + hv \rightarrow S^* \tag{1}$$

$$S^* \rightarrow S^{\text{oxi}} + e^- \text{(injected)}$$
 (2)

$$I_3^- + 2e^- \text{(cathode)} \to 3I^- \text{(cathode)} \tag{3}$$

$$2S^{0X1} + 3I^- \rightarrow S + I_3^- \tag{4}$$

The first step is the absorption of a photon by the sensitizer *S* [Eq. (1)], leading to the photoexcited sensitizer S^* which injects an electron into the conduction band of the semiconductor, leaving the sensitizer in the oxidized state S^{oxi} [Eq. (2)]. The injected electron flows through the semiconductor network to arrive at the back contact and then through the external load to the counter electrode to reduce the redox mediator [Eq. (3)] which in turn regenerates the oxidized sensitizer [Eq. (4)] which process completes the electrochemical circuit.

Some undesirable reactions resulting in losses in the cell efficiency occur. They are the recombination of the injected electrons either with oxidized sensitizer [Eq. (5)] or with the oxidized redox couple at the TiO_2 surface [Eq. (6)].

$$S^{oxi} + e^{-}(titania) \rightarrow S$$
 (5)

$$I_3^- + 2e^-$$
 (titania) $\rightarrow 3I^-$ (anode) (6)

Understanding of the processes in a complete device has been achieved using a range of methodologies that have been reviewed recently.^{6,37, 38} The total efficiency of the dyesensitized solar cell depends on optimization and compatibility of each of these constituents, in particular on the semiconductor film along with the dye spectral responses. A very important factor is the high surface area and the thickness of the semiconductor film which leads to increased dye loading, thus optical density is increased resulting in efficient light harvesting.³⁹ Solar photon energy to electricity conversion efficiency is given by the expression.

$$\eta = \frac{j_{sc} \cdot V_{oc} \cdot FF}{\phi} \tag{7}$$

Here j_{sc} is the short circuit photocurrent density, FF the cell fill factor (Figure 2b) and Φ the power flux of the incident light; usually AM 1.5G illumination (100 mW cm⁻²) or 1 sun. The incident photon to current conversion efficiency (IPCE) is an important parameter of the solar cell which directly measures how efficiently the incident photons are converted to electrons.

Electron charge transfer processes in DSC can be analyzed by several approaches^{13, 32} and techniques,^{31, 40} such as Impedance Spectroscopy (IS), electron injection dynamics that allows monitoring of the rise of the oxidized dye formed after electron injection,⁴¹ and transients measurements that are carried out with tunable femtosecond laser pulses as a pump-probe technique for studying ultrafast electron transfer reactions.^{42, 43}

In recent years we have developed many studies of IS method^{13, 40, 44} which has the advantage to provide information of the physical processes determining the performance at each required single point of the current density-voltage (*jV*) curve of the DSC at specified illumination conditions. Using appropriate models developed for DSC analysis⁴⁰ it is possible to determine and isolate the recombination resistance (R_{rec}) from other resistive parameters in the cell. The R_{rec} relates to the recombination flux and it is a key performance-determining parameter in the photovoltaic device. Viewing R_{rec} with respect to the voltage (Fermi level in the TiO₂ film), a relation can be established between charge transfer resistance and the titania/dye/electrolyte interface to clarify the influence of the dye structure in recombination,^{13, 31} which enables improvement of the

dye design.

4. Recombination or electron charge transfer in DSC

The loss of electrons in the TiO_2 electron conductor to the hole carrier, i.e., recombination processes 8 and 9 of Figure 2c, that take place at the interface $TiO_2/dye/electrolyte$, is severely affected by properties of the materials and the surface conditions. It has been observed that some otherwise efficient dyes increase the recombination rate,⁴⁵ and recombination also produces a strong limitation for solid-state OMeTAD cells.²²

Early work indicated that the kinetics of the back-electron-transfer reaction from the conduction band to the oxidized sensitizer follow a multiexponential time law, occurring on a microsecond to millisecond time scale depending on electron concentration in the semiconductor and thus the light intensity.^{4, 6} Recombination of electrons in TiO₂ with acceptors in the electrolyte is normally quantified by the electron lifetime(τ_n)⁴⁶ and R_{rec} .⁴⁴ Lifetimes observed with Γ/I_3^- are very long (1-20 ms under one sun light intensity) compared with other redox systems used in DSC, explaining the success of this redox couple.

The electron travelling through the mesoporous TiO_2 film, normally formed by nanometer-sized anatase particles, remains within only a few nanometers distance of the semiconductor/electrolyte interface. Recombination of electrons with either oxidized dye molecules or acceptors in the electrolyte is therefore a major factor of electron dynamics in the DSC. With Ru-dyes, the dominant recombination pathway is recombination through the electrolyte because the electron charge transfer to the oxidized dye is negligible due to the molecule dye structure with good spatial separation between injected electrons and the oxidized dye.⁴⁷ This is achieved by the electron donating thiocyanate ligands which shift the distribution of the highest occupied molecular orbital (HOMO) on the oxidized dye away from the reacting TiO₂ surface and reducing the recombination rate accordingly.⁴⁸ However, when using metal-free dyes, it was observed that the overall recombination rate was higher and mainly attributed to the residual oxidized dye, because HOMO is delocalized along the structural backbone between the binding moiety and the remainder of the dye^{7, 21, 49, 50} as can be observed in Figure 3 for diverse dyes using DFT study. This common distribution of the HOMO level generates a stabilization of the intermediate in the dye regeneration process as has

been described in the literature, so the regeneration reaction may proceed via oxidized dye-iodide intermediate state,^{13, 31, 45, 51}creating a new path to the electron recombination. Such behavior produces typically a large decrease in the total charge transfer resistance in the case of some metal-free dyes versus ruthenium dyes. Those metal-free dyes generally are sensitizers without bulky substituents in the structure or with large expansion of the π -conjugated system that limits the packging. All of these processes that appear with the use of metal-free dyes without blocking effect create significant limitations in terms of recombination compared to organometallic dyes.^{52, 53}

The limitation, differences in the recombination, due to the molecular structure needs a deeper study to clarify the guidelines to design and synthesize the perfect dye or at least dyes that present good injection and low recombination. With this goal, the complete characterization of a DSC using IS and transient absorption measurements gives us information about the electronic processes that take place at the interfaces following photogenerated carrier injection and can be related with individual DSCs components for a future design optimization. Some examples are described below.

Recombination to the electrolyte

From the point of view of the dye structure design, the charge recombination between the injected electrons in the conduction band (CB) of TiO_2 and the redox mediator (iodine or cobalt complexes electrolyte) can be effectively reduced by inhibiting the approaching of ions to the TiO_2 surface (Figure 4) using steric impediments in the dye molecule.^{9, 10, 35, 54}

The introduction of hydrophobic long alkyl and alkoxy chains on donor moiety or on π -bridges such as triphenylamine unit is effective to block the approach of hydrophilic redox ions to the TiO₂ surface and consequently to suppress the charge recombination, resulting an increase of the electron lifetime and V_{oc} value (Figure 4b), as demonstrated by Wang et al.⁵⁵ with C225-C226-C227 dyes from Figure 1, using cyclopentadithiophene moiety and two 3-hexylthiophene units on π -bridges (Figure 5). The transient absorption measurements and recombination resistance measured by IS indicate that the charge recombination between oxidized dye molecules and titania electrons is stepwise decelerated with the cyclopentadithiophene unit approaching the electron donor. Similar result has been demonstrated recently³⁵ in solid–state DSC with three new organic D- π -A sensitizing dyes, WN1, WN3 and WN3.1, where the alkyl

recombination lifetime and the number of hexyl chains.

chains on the electron-rich bridge of the dye and also in the electron donor part play a significant role in the suppression of recombination, with a relationship between

It has also been proposed that a compact dye sensitizer layer on TiO2 surface is important to reduce the charge recombination between TiO₂ and redox couple.⁵⁶⁻⁵⁸ Such layer can also prevent the recombination to the oxidized dye molecules as reported by Mori et al. for DSC based on coumarin dyes.⁵⁹ Recombination rate has been measured for zinc porphyrin complexes like those represented in Figure 1 named YD0 and YD2, where YD2 consists on a diarylamino group with two hexyl chains attached to the porphyrin ring acting as an electron donor, π -conjugated phenylethynyl group as a bridge, and the carboxylic acid moiety as an acceptor. The porphyrinchromophore itself constitutes the π bridge as a light-harvesting center in this particular D- π -A structure, and YD0 does not have the diarylamino substituent as a bulky donor and serves as a reference dye to test the effect of the electron donor in the recombination. It was observed that effectively the recombination resistance for YD2 is similar to a commercial Ru dye N719 (Figure 6) because the diarylamino group plays a key role to repel the triiodide ions from the titania surface and near oxidized dye. The charge recombination rate of YD2 is significantly less compared with that YD0, which impacts increasing the V_{oc} value.¹³ These results confirm that a good synthesis design, especially in the donor moiety, that can prevent the redox approach, is crucial to avoid the recombination process to the electrolyte.⁴⁵ For DSC based on D- π -A dye with starburst triarylamine and with D- π -A dye with the simple triarylamine²⁰ it has been reported that the starburst-shape dye sensitizers show better performances than rod-shape sensitizers by blocking charge recombination between TiO₂ and the triiodide ion.^{56, 58, 60}

The introduction of sterically hindered substituents often causes not only the twist between π -bridges but also the decrease in the amount of adsorbed dye on the TiO₂ surface, resulting in the reduction of the light harvesting efficiency and of the number of the injected electrons. Additionally, the expansion of π -conjugated system³¹ can no longer form a compact blocking layer (larger surface coverage),¹⁸ resulting in faster charge recombination and lower V_{oc} (Figure 7) as has been shown in our previous studies³¹ with oligithienylenevinylene dyes (FL*n*) and also demonstrated by Hagfeldt et al.¹⁸ (Figure 8) using the family of dyes shown in Figure 1 (L0, L2 and L3 dyes). It was Page 9 of 30

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shown that the recombination to the electrolyte is effectively controllable by the modification of dye molecular structure: the introduction of hydrophobic alkyl chains and bulky substituents to dye molecular structure discourages the recombination to the redox couple, leading to increased $V_{oc.}^{17, 28}$

It is also important to mention that the presence of deoxycholicacid (DCA) or chenodeoxycholic acid (CDCA) in organic based systems has been shown to improve the voltages,⁸ an effect often attributed to DCA/CDCA retarding recombination between injected electrons and electrolyte, through blocking effects.

Related with retarding recombination to the redox media, Diau et al.⁶¹ demonstrate that fluorine substituents on the donor part of the ruthenium complexes produce a slowing down of charge recombination. Similar results have been found with metal-free sensitizers.^{62, 63} In both cases, it is possible to argue that effect the surface of the TiO₂ can be protected from the electrolyte by the negatively charged of F increasing the V_{oc} due to an upward shift of potential and a retardation of charge recombination. The same effect is reported by Berlinguette et al.⁶⁴ using S in the donor part of metal-free dye instead of O with an increment in V_{oc}. That effect is similar to the function of NCS groups from the N719 protecting the closer proximity of the electrolyte species to the TiO₂.

When the redox shuttle is a Co (II)/Co (III) complex similar effects are observed. For N719, the efficiency decreases drastically due to a possible formation of ion-pairs between the negatively charged, TiO_2/dye and oxidized Co(III) electrolyte decreasing the photocurrent due to lower charge collection efficiency.¹⁰ Nevertheless, Ru dyes that contain long alkyl chain in the structure, like Z907, create a compact dye layer when absorbed on titania, that block the Co (III) redox species approach and a decrease of the photocurrent is not observed. The same effect is observed to metal-free dyes with bulky substituents on the donor part of the structure.^{9, 10, 55, 65}

For I₃⁻/ Γ redox shuttle the process of recombination through the electrolyte has been widely studied by transient absorption measurements^{11, 42, 66, 67,43, 53} in order to understand which are the predominant species in redox electrolyte that accelerate the recombination. Meyer et al.⁴² did not find a direct evidence for the reaction between injected electrons into TiO₂ and di-iodide, on DSC based on Ru- bipyridine sensitizers, being the data consistent with charge recombination with I₃⁻. However, later work¹¹ find the electron life time correlated with free-iodine (I₂) concentration and independent of

 I_3^- concentration, supporting that electron recombination to the electrolyte occurs by iodine reduction instead than reduction of triiodide in the case of N719 and Z907 and also for a squarine dye VG5⁶⁸ without any steric impediment.

In general an increase in the recombination with DSC based in metal-free dyes without steric impediments is observed, versus DSC based on Ru-dyes, due to a possible increment in the recombination to the oxidized dye molecule (reaction 8 in Figure 2c) that is added to the already established to the redox mediator.

Recombination to the oxidized dye molecule

The recombination through the oxidized dye can be interpreted in two different ways; (1) acceleration of recombination by dye molecule structure that induced electron transfer to the electrolyte due to poor titania surface blocking or (2) recombination via oxidized dye stabilization, then the recombination electrons regenerate the dye molecule. The extent to which these effects occur depends on the nature of the dye molecule, and usually metal-free dyes without bulky substituents show the largest influence of these effects.

As has been commented previously, if the dye molecule strongly influences the rate constant for recombination to electrolyte acceptor species, the recombination increment can be assigned to the influence of the dye on the local concentration of oxidized redox couple adjacent to the TiO_2 surface,^{13, 52} a possible dipole effect create by the dye molecule or changes in the polarizability^{69, 70} and even to a bound complex between redox and oxidized dye.^{49, 67, 71} In the second possibility, an electron-deficient substituent in the dye molecule could increase the charge recombination through the oxidized dye molecule due to the favorable electron affinity.

It has also been demonstrated that the electron affinity of the substituent in the dye structure has a strong influence on dye properties, especially if there are electron-deficient substituent or electron-rich substituent-like ethyl groups.⁵⁵ Although the modification of the substituent has a relatively small impact on the titania conduction band edge, it has a remarkably large effect in the charge transfer recombination process. There is a decrease in recombination reaction order for the cells made from electron-rich substituent chromophores versus their counterpart with electron-deficient substituent.

The influence of the substituents in the recombination to the oxidized dye has been also studied recently in a carbazole-type fluorescent dyes.⁷² In these dyes carboxyl

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groups on different positions on the chromophore skeleton induce not only electron injection from the excited state to the CB of TiO₂, but also the recombination process between the electrons injected to the CB of TiO₂ and the oxidized dye. The high energetic electron injection yield and the retardation of the charge recombination to the oxidized dye are lower for dyes which are functionally separated into an anchoring group for attachment on TiO₂ surface and an electron acceptor moiety. These features are responsible for the high j_{sc} comparable to that of the D- π -A dye sensitizer where carboxyl group acts both as the anchoring group for attachment on TiO₂ surface and as electron acceptor. The general idea applied here is that the conjugated part or linker between donor and acceptor groups is the critical moiety of the dye molecule. The linker must have the HOMO level distributed, to avoid the recombination increase due to a possible interaction between iodine and oxidized cation.^{1, 31, 48} and also must be separate from the acceptor unit, to be far enough from the titania surface. The addition of large groups that create steric impediment to redox electrolyte approach to the titania surface, in the donor or linker part of the structure, is also convenient. One critical point is the substituent in the linker, because if it is electron-deficient then the electron charge transfer rate from the injected electrons in the semiconductor through oxidized dye state increases, with a decrease in the V_{oc} of the cell and consequently lowering the DSC efficiency.

Conclusions

Recombination in DSCs presents different mechanisms depending of the dye nature and redox couple. It is generally observed that cells based on metal-free dyes reveal important differences of the interfacial factors determining recombination, with respect to the cells based on organometallic dyes. The rate of recombination is higher in metalfree dyes due to the extra recombination to the oxidized dye. Nevertheless, the observed increment could be compensated with optimized molecular engineering development, using bulky electron rich substituents that avoid the recombination through the oxidized dye and also block the redox shuttle from reaching the titania surface. It emerges from this survey that the recombination through the oxidized dye may not be disregarded in the metal-free dyes design and when Co is used as a redox shuttle, because it is a pivotal issue in the total rate of the DSC recombination, directly associated to the performance.

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Figure Captions

Figure 1. Structures of Zn-porphyrin complexes and metal-free dyes. Reproduced from Refs.^{1, 13, 16, 18, 20, 55} with permission.

Figure 2. (a) DSC structure, (b) The fill factor measures the squareness of the *I-V* curve and (c) schematic DSC where all the process that take place in the solar cell are described.

Figure 3. Optimized chemical structures and frontier molecular orbitals of two metalfree dyes, BG-1 (left) and BG-2 (right), based on thiophene units asymmetrically functionalized by *N*-aryl carbazole. HOMO distribution (lower) and LUMO distribution (upper).

Figure 4.Scheme of structures of D- π -A dyes.

Figure 5. (A) *j*-*V* characteristic of cells made with an iodine electrolyte and organic dyes named C225-C226-C227 with serially varied conjugation orders of a cyclopentadithiophene unit and two3-hexylthiophene segments. (B) Charge recombination resistance. The dye structures are shown in Figure 1b. Reproduced from Ref ⁵⁵ with permission.

Figure 6. Recombination resistance replotted with respect to equivalent common conduction band voltage so that distance between Fermi level and conduction band is the same in all cases

Figure 7. FL*n*dyesstructures; n is the number of thienylvinylene units. Current density-potential curves for DSCs at 1 sun with FL*n* as sensitizers

Figure 8. (A) Extracted charge as a function of V_{oc} and (B) electron lifetime as function of V_{oc} in dye-sensitized solar cells based onL0, L2 and L3 dyes, sensitized for 16 h using 6 µm TiO₂ and an electrolyte consisting of 0.6 M TBAI, 0.1 M LiI, 0.5 M 4-TBP, and 0.05 M I₂ in acetonitrile. Bare TiO₂ (circles), L0 (square), L2 (triangles), L3

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Figure 1





Figure 3





I₃-

donor

π linker

A

 I_3^-

 I_3^-

I₃-

I₃-

|₃-

Figure 5



Figure 6



Figure 7





FLn, n=1-5

Figure 8









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