



Probing electron transfer dynamics of phenosafranine with iodide



Vadivel Ramanan, Arunkumar Kathiravan*, Perumal Ramamurthy*

National Centre for Ultrafast Processes, University of Madras, Taramani Campus, Chennai 600 113, Tamil Nadu, India

ARTICLE INFO

Article history:

Received 3 June 2015

Received in revised form

9 September 2015

Accepted 12 September 2015

Available online 25 September 2015

Keywords:

Phenosafranine

Electrolyte

Fluorescence quenching

DSCs

Laser flash photolysis

ABSTRACT

In dye sensitized solar cells (DSCs), the excited state deactivation of the dye typically occurs by either electron injection to the conduction band of the semiconductor or quenching by iodide ions present in the electrolyte. Complete understanding of latter process in DSCs is not encountered fully on small molecules (i.e. dyes). In this paper, we have employed time resolved techniques to probe the excited state deactivation of the dye by iodide ions. For this reason, we have chosen phenosafranine (PSF, electron acceptor in the excited state) and lithium iodide (electron donor) in acetonitrile medium. Results show that there is an efficient quenching between excited states of PSF with iodide ions. The obtained bimolecular quenching rate constants (k_q) were in diffusion controlled limit. Time resolved absorption studies reveals that the observed quenching is due to electron transfer from iodide to excited state of PSF, as evidenced by the observation of iodide anion radical at 440 nm. This fundamental work may provide hint to improve the power conversion efficiency of small molecules based devices.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Dye-sensitized solar cells (DSCs) have attracted considerable attention in recent years due to their high power conversion efficiency, low cost and facile fabrication [1–3]. DSCs based on ruthenium photosensitizers, such as N3, N719 and the black dye, have achieved outstanding conversion efficiency of up to 12% under AM 1.5G irradiation conditions [4–7]. However, the main drawbacks of the ruthenium sensitizers are highly expensive and hard to purify. In this context, metal-free organic dyes have gained increasing attention due to their unique advantages, such as high molar absorption coefficient, ease of structure modification and relatively low material cost. Specifically, Diau and Grätzel et al. reported [8] a push–pull porphyrin YD2, which exhibited a high η -value of 11%. They further utilized a cobalt(II/III) electrolyte [9] that can yield a higher open circuit voltage (V_{oc}), with a cocktail of a YD2 derivative, YD2-o-C8, and a complementary organic dye to achieve a record η -value of 12.3%. Very recently, DSC with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers [10].

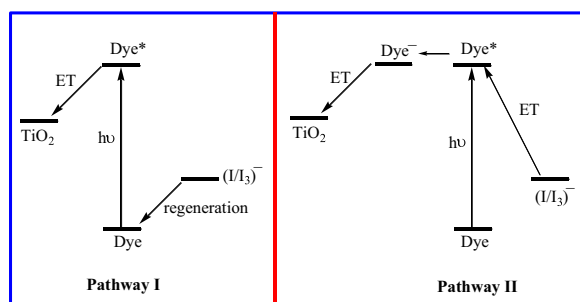
On the other hand, there are several key processes that controlling the power conversion efficiency of DSCs. In that, the most important process [11] is electron injection from the excited dye to conduction band of TiO_2 . Therefore, measuring the electron

injection kinetics between the excited dye and TiO_2 semiconductor has been a subject of intense research [12]. Experimentally, ultrafast spectroscopy has shown that excited state electron injection into TiO_2 often is characterized by non-exponential kinetics, a behavior attributed to the presence of a distribution of sensitizer-semiconductor binding geometries and distances [13]. Although different studies have reported very different time scales of electron injection, it is generally agreed that the high-energy conversion efficiency can be ascribed to fast-electron injection from the sensitizer to the semiconductor and much slow back electron transfer to the sensitizer [14]. In DSCs, two different pathways [15] of electron-transfer mechanisms have been documented (Scheme 1). First pathway is excited state dye can inject an electron into the semiconductor and then sensitizer ground state is regenerated by an electron donor (usually iodides). Second pathway [16] is electrolyte reductively quenches the excited state sensitizer and the reduced dye can either inject an electron into the conduction band of TiO_2 leading to photocurrent or it can be react with triiodide, which is a recombination reaction. The second pathway can be significant if the electron injection from the excited dye into the conduction band of the semiconductor is relatively slow time scale [17].

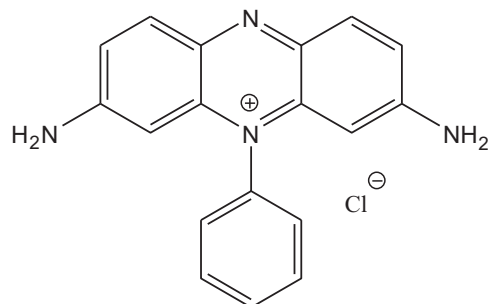
To date, organic solutions comprised of iodide and triiodide, (I/I_3^-), represent the only mediator that provides > 11% light-to-electrical power conversion efficiencies under one sun AM 1.5G illumination [18]. The application of a redox couple such as (I/I_3^-) is often useful for preventing back electron transfer as it quickly intercepts the oxidized sensitizer with electron transfer. However, it was reported that iodide present in the redox electrolyte can

* Corresponding authors.

E-mail addresses: akathir23@gmail.com (A. Kathiravan), prm60@hotmail.com (P. Ramamurthy).



Scheme 1. Pathways in dye sensitized solar cells.



Scheme 2. Structure of Phenosafranin.

quench the excited state of the sensitizer prior to electron injection into the semiconductor nanoparticles [19]. For Instance, Kamat and others reported the iodide quenching of ruthenium(II) polypyridyl complex in the solution phase [20]. The reaction between excited Ru(II) and I^- occurred with a rate constant of $1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. They observed electron-transfer products only at high concentrations of iodide. However, on a semiconductor surface such as SnO_2 the iodide quenching is not able to compete with the charge injection since the latter process is an ultrafast process that occurs in few femtoseconds–nanoseconds time scale. Later, Meyer et al. has demonstrated Ru(II) polypyridyl metal-to-ligand charge transfer (MLCT) excited states effectively oxidize iodide [21–23]. Ion-pairing interactions between I^- and ruthenium complex, greatly facilitated excited state iodide oxidation in dichloromethane and, to a lesser extent, in acetonitrile. They have also provided the experimental evidences for electron transfer products [24,25]. The absorption band observed at 530 nm was assigned to $\text{Ru}(\text{bpy})_2(\text{deeb}^-)^+$, and those at 410 and 750 nm are characteristic for $I_2^{\bullet-}$. Recently, Paige et al. reported the results of iodide quenching on an anionic porphyrin and a cationic porphyrin respectively [26,27]. They concluded that iodide quenching of the S_1 state of porphyrin can be a source of significant inefficiency in DSCs, but that iodide quenching of the S_2 state will be minimal except at extremely large iodide concentrations.

Till now the mechanism of quenching of small organic molecules by iodide is not studied enough. A recent review by Grätzel et al., says that a clear understanding of all mechanistic aspects and fundamental processes of iodine-based electrolytes in DSCs remain under debate [28]. Bringing about a challenging efficiency in DSCs considerably depends on the efficiency in blocking the excited state quenching of the sensitizer by iodide, thus facilitating the same by TiO_2 semiconductor. Hence it is important to explore the photophysics between the sensitizer and the iodide. Therefore, our interest is to investigate an alternative pathway II (i.e.) reductive electron-transfer study of phenosafranin with iodide in acetonitrile medium. The choice of phenosafranin (3,7-diamino-5-phenylphenazinium chloride, PSF), Scheme 2, is due to its strong absorption in the region of 500–550 nm with a high molar

absorption coefficient ($4.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). It has been extensively employed as a photosensitizer in electron transfer reactions in homogeneous media [29–33] and in semiconductor devices [34,35]. The use of PSF as a sensitizer in solar energy conversion was also discussed elsewhere [36–40]. Kamat et al. have reported the photoinduced electron injection from phenosafranin to TiO_2 semiconductor [pathway I] thereby he gave a hint that the phenosafranin can be used as a photosensitizer in DSCs [36]. Therefore, the detailed understanding of the electron transfer step in pathway II thus provides important information concerning a key performance characteristic of the small molecules based devices. Here, we have discussed about pathway II and provided experimental evidence for the efficient photoreductive quenching of phenosafranin by iodide.

2. Materials and methods

Phenosafranin (Sigma-Aldrich) was used without further purification. HPLC grade acetonitrile (Qualigens) was used as received. Lithium iodide (Sigma-Aldrich) stock solutions were prepared in spectroscopic grade acetonitrile and the reducing agent sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) from Merck was added to it to prevent the formation of triiodide. In the absence of such a reducing agent, lithium iodide is likely to be oxidized aerially and photochemically. Iodide oxidizes to iodine atom which combines with itself to form molecular iodine. The molecular iodine in turn combines with an iodide ion, producing triiodide species. The concentration range of lithium iodide solutions was 2–10 mM.

All UV–visible absorption spectra were recorded on a Varian Cary Bio UV 100 UV–visible spectrophotometer in a 1 cm^2 quartz cuvette at room temperature. The optical density of the samples was not exceeding 0.2 to prevent aggregation. All experiments were performed thrice and the average results were reported. The corrected fluorescence spectral measurements were carried out using a FluoroMax-4 spectrophotometer (Horiba Jobin Yvon) in a 1 cm^2 quartz cuvette at room temperature and at air saturated condition. Fluorescence measurements were made by taking fresh solution each time in rectangular quartz cell having an airtight stopper. The solute has maximum absorption at 517 nm. The solute was excited at 517 nm and the fluorescence spectra were recorded. The maximum fluorescence corresponds to 554 nm. First, the fluorescence intensity I_0 was measured without the quencher, and then the fluorescence intensity I was measured at different quencher concentrations at a fixed solute concentration. The experimental values are reproducible within 5% of the experimental error. Time-resolved fluorescence decay measurements were obtained by the time-correlated single-photon counting (TCSPC) technique with a micro-channel plate photomultiplier tube (Hamamatsu, R3809U) as a detector and the LED (495 nm) was used as the excitation source. The instrument response function for the TCSPC system is 1.4 ns. The data analysis was carried out by the software provided by IBH (DAS-6), which is based on a deconvolution technique using nonlinear least-square methods. All experiments were performed thrice and the average results are reported. Transient absorption spectra were obtained as described earlier [41]. Transient absorption experiments were carried out using nanosecond laser flash photolysis (Applied Photophysics, UK). The second harmonic (532 nm) of a Q-switched Nd:YAG laser (Quanta-Ray, LAB 150, Spectra Physics, USA) with 8 ns pulse width and 150 mJ pulse energy was used to excite the sample. The transients were probed using a 150 W pulsed xenon lamp, a Czerny–Turner monochromator, and a Hamamatsu R-928 photomultiplier tube as the detector. The transient signals were captured with an Agilent Infinium digital storage oscilloscope and the data were transferred to a computer for further analysis. For

Download English Version:

<https://daneshyari.com/en/article/5399239>

Download Persian Version:

<https://daneshyari.com/article/5399239>

[Daneshyari.com](https://daneshyari.com)