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Ferrocene as a rapid charge regenerator in dye-sensitized solar cells

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ABSTRACT

Using the reductive power of the ferrocene moiety (Fc), an ultrafast regeneration step via a covalent attachment of a Fc moiety to an organic triphenylamine-based dye (L1) when adsorbed on TiO_2 is highlighted. Two modified dyes with one and two Fc moieties attached (L1Fc, and L1Fc2), respectively, were synthesized by addition to the L1 dye. These dyes have been studied spectroscopically using ultrafast transient absorption spectroscopy in the visible and the infrared (IR) regions. In acetonitrile, the results show an ultrafast excited state quenching of the modified dyes due to an expected electron transfer process from the Fc(s) to L1. Adsorbed onto TiO_2, an electron transfer process is also detected from Fc to the oxidized dye ($L1^+$). Despite the occurrence of an ultrafast regeneration step, the solar cell performance does not improve by the attachment of Fc(s) to the dye L1. Transient absorption measurements in the IR region revealed a fast electron recombination process to the Fc^+ moiety on an average time scale of ca. 300 ps, outcompeting the >12 ns process to $L1^+$. The reasons for the observed considerably faster recombination rate to Fc^+ than to $L1^+$ are discussed in detail. This study provides deep spectroscopic insights for such organic dyes utilized to afford ultrafast regeneration step without showing high performance in photovoltaic devices. In addition, this study will improve our understandings for the triangular relationship between the molecular design, electron kinetics, and the performance in photovoltaic devices.

1. Introduction

Dye-sensitized solar cells (DSSCs) are anticipated to be one of the main alternatives for renewable solar energy in the future. In the early stages of the solar cell development, Shockley and Queisser predicted the maximum theoretical power conversion efficiency of a single junction to be ~32% [1]. However, the maximum reported efficiency using metal-free organic dyes in DSSCs is ~12.5% under standard conditions [2]. In order to fill the gap between the theoretical and experimental performance, a deeper understanding of the device electron dynamics is needed. Different reaction pathways exist in DSSCs; some of them contribute to the device efficiency, such as dye electron injection and dye regeneration, while others instead impede the performance, such as deactivation pathways of the sensitizing dye molecules and charge recombination processes (CR) [3]. Assuming an efficient charge injection from the excited dye to the conduction band (CB) of a semiconductor substrate, such as TiO_2, the electrons in the semiconductor material are exposed to many deactivation processes reducing the overall cell efficiency. In CR, the injected electrons are lost from the CB of TiO_2 back to oxidized species at the semiconductor/electrolyte interface. Therefore, the photovoltage (V_{oc}) and the photocurrent (J_{sc}) of the cell are lowered. The oxidized species can be the oxidized adsorbed dye molecules (D^+), or oxidized species in the electrolyte, such as the oxidized component of a liquid electrolyte redox system, viz. triiodide in the I^-/I_3^- system [4]. The recombination to D^+ is formally a second-order reaction, since it depends on the number of the D^+ species on the surface and on the number of electrons in the CB of the semiconductor substrate ($Rate_{CR} = kn_e[Dye^+]$), where k is the rate constant and n_e is the number of injected electrons [5]. While a high n_e leads to faster recombination, it is still needed to increase the J_{sc}, the electron lifetime in the CB, as well as the V_{oc} [4,6,7]. Experiments show that long electron lifetimes are correlated to both high photovoltage and high photocurrent [7]. A recent study showed that an increase in the reduced component concentration of the redox couple increases the electron lifetime due to the fast reduction of the adsorbed oxidized dye on the surface of the semiconductor, leaving

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only one pathway for CR to the oxidized components of the electrolyte [8]. Different regeneration rates by iodide- and cobalt (II)-based electrolytes have been reported for sensitizers based on Ru-complexes and organic dyes. These values range from ~1 to $37 \times 10^6\ M^{-1}\ s^{-1}$ [9,10]. The observed differences in regeneration rates can be caused by many factors ranging from differences in diffusion coefficients for the reducing agents used to the mechanism of charge regeneration dependent on the structure of the dye used. If slow enough, CR can compete with the process of charge regeneration leading to poor solar cell efficiencies.

One can improve the efficiency of the solar cell by increasing the V_{OC}, which involves an increase of the gap between the quasi-Fermi level of the semiconductor and the Nernstian potential level of the electrolyte redox couple [7]. In order to increase the quasi-Fermi level, it would be necessary to increase the density of injected electrons by either increasing the electron injection efficiency or decreasing the CR (reducing the dark current) [7,11]. At least 200 mV can be gained from reducing the difference between the CB and the quasi-Fermi energy levels of the semiconductor [11]. On the other side, a higher V_{OC} can also be accomplished by reducing the energy gap between the redox couple and the ground state of the oxidized dye [11], different redox couples have been used to achieve that goal [12]. Aiming to reduce the unwanted CR process, by removing the positively charged hole in the oxidized dye further away from the semiconductor surface, two modified organic dyes were synthesized. The first modified dye molecule was covalently connected to one ferrocene (L1Fc), and the second modification involved two ferrocenes (L1Fc2) (see Fig. 1 and Fig. S1). Ferrocene is expected to reduce the oxidized dye following photo-excitation and charge injection processes. Such a process is expected to spatially generate a larger charge separation. Later on, the positive charge on Fc moiety will be reduced by the normal iodide electrolyte used. Previously, it has been shown that the CR rate can be suppressed by increasing the distance between the negatively charged electron in the semiconductor substrate and the positively charged hole in rigid molecules [13]. Connecting additional electron donor units to the main sensitizer has been investigated for metal complex dyes, mainly for Ru-based complexes [14,15]. The ferrocenium/ferrocene (Fc^+/Fc) as an electrolyte redox couple has been shown to be efficient involving a simple charge-regeneration process (no intermediates, and solely a one electron-transfer reaction), in contrast to the I^-/I_3^- redox system [12]. Although the Fc/Fc^+ system has shown efficient charge regeneration and higher V_{oc} than other systems [8], the CR rate is also larger unless surface passivation layers are used [16,17]. Recently, other dyes coupled to ferrocene units have been synthesized and investigated in DSSCs, showing quite high efficiencies as compared to cells containing non-modified N719 as sensitizer [18]. However, it was not clear if such high performance was due to an ultrafast regeneration or to the spectral response of those dyes [18]. Therefore, it is of interest to improve our understanding of the electron dynamics of dyes attached to ferrocene moieties in DSSC devices.

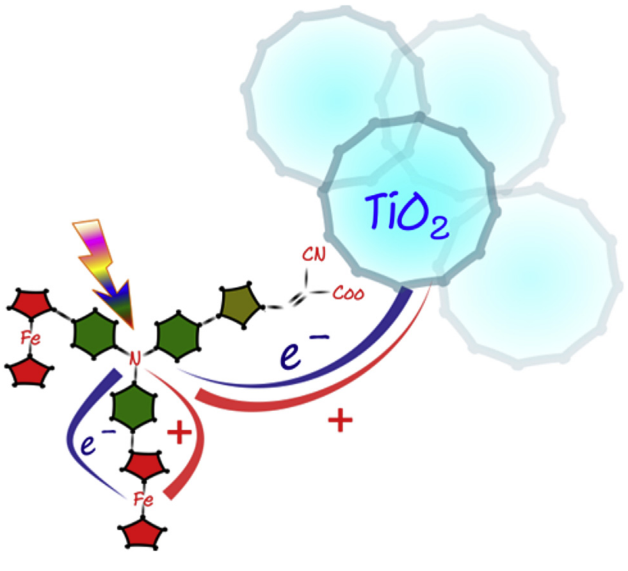

Fig. 1. Schematic representation of electron transfer processes for L1Fc2 dye adsorbed to TiO_2.

2. Experimental section

2.1. Electrochemistry

Cyclic voltammetry was performed in 0.1 M of $TBA.PF_6$ solution using an Autolab potentiostat with a GPES electrochemical software, glass carbon as the working electrode, an Ag/AgCl electrode (3 M KCl aqueous solution) as the reference electrode, and a Pt. rod as the counter electrode. All measurements were made in acetonitrile after purging with N_2 for 20 min.

2.2. Steady-state measurements

Absorption spectra were recorded using a Varian Cary 5000, and emission measurements were performed using a Horiba Jobin Yvon Fluorolog and the spectra were automatically corrected for wavelength dependent instrument sensitivity. Details about the instruments have been described before [19].

2.3. Chemicals

The synthesis procedures of the dyes (L1Fc and L1Fc2) are described in the supporting information. Acetonitrile was of spectroscopic grade purchased from Sigma-Aldrich.

2.4. Transient absorption (TA)

Two TA setups based on UV–Vis and IR probes were used in this study. The two systems are unique tools to follow electron dynamics at different interfaces and systems [20–23]. The detailed specifications of the instrumentation have been described earlier [24,25]. Briefly, with the UV–Vis probe, excitation wavelengths of 400 and 430 nm were used. Excitation wavelengths of 425 and 440 nm were employed using the IR probe. The average excitation power ranged from 200 to 350 μW. All the obtained data were chirp corrected.

2.5. Device fabrication and measurement

Device fabrication was done as follows. Fluorine-doped tin oxide (FTO) glass substrates (Pilkington, TEC15) were cleaned (in the order detergent water solution, and ethanol) using an ultrasonic bath. Subsequently, the substrate was treated with a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min to generate a thin blocking layer. A layer of 8 μm thick 18 nm size mesoporous TiO_2 (DSL 18NR-T, Dyesol) and a layer of 5 μm thick 150–250 nm size TiO_2 (WER2-O, Dyesol) were screenprinted on to the pre-treated FTO glass surface. The double-layer TiO_2 electrodes (area: $5 \times 5\ mm^2$) were heated in air at 480 °C for 30 min. The sintered films were treated with a 40 mM aqueous $TiCl_4$ solution again at 70 °C for 30 min, and then heated to 450 °C for 15 min. The resulting films were immersed into a 2×10^{-4} M solution of the different dyes in ethanol and