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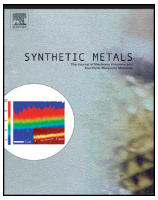

Light induced behavior of xanthene dyes with benzyl viologen

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ABSTRACT

The light induced processes of xanthene dyes with benzyl viologen have been studied by steady state and time resolved fluorescence spectroscopic measurements in aqueous medium. Steady state quenching is due to ground state complex formation and it is further verified by unaltered fluorescence lifetime. The strength of interaction between xanthene dyes and BV has been evaluated by Benesi–Hildebrand and Stern–Volmer methods. The role of halogen substitution on photophysics of xanthene dyes and with benzyl viologen has been studied. Non-halogenated dye molecule (fluorescein) is not interacting with benzyl viologen, on the other hand halogen loaded xanthene derivatives were interacting well with benzyl viologen through ground state complex formation. This fundamental work may be useful for energy harvesting devices towards the applications of solar cells.

1. Introduction

Photoinduced electron transfer (PET) is the subject of numerous investigations which have been intensively carried out in the last two decades and it contributes a significant role in solar energy conversion and storage devices [1–4]. On the other hand, it plays an important role in biological processes such as photosynthesis and oxidative processes which are involved in the degradation of biological material in living cells [5]. PET reaction evolves long-lived charge separated (CS) state leads to a crucial role in the power conversion efficiency of solar devices. For instance, Imahori et al. reported the photovoltaic investigation and ultrafast dynamics of mono phenyl (MP) and biphenyl spacer (BP) connected Zn-porphyrin sensitized TiO_2 electrodes. If electron transfer between the porphyrin core and semiconductor occurs through the connecting spacer, making spacer longer (BP) should slow down the electron transfer to the TiO_2 and it should result the high power conversion efficiency. Contrary to their expectation, the power conversion efficiency of BP ($\eta = 2\%$) is much lower than MP ($\eta = 4\%$). Time resolved absorption studies reveals that MP sensitizer has much higher amplitude of long-lived component than BP, moreover the lifetimes of the electron injection and recombination is faster for BP. This shows poor conversion efficiency of BP, since the number of long lived electrons in the conduction band or long range electron transport, will contribute to photocurrent and better solar cell efficiency. Based on these results it was suggested that the molecules with large amount of long lived electrons in the conduction band furnishes better solar cell power conversion efficiency or in other words minimizing fast recombination dye/TiO_2 electrodes is an important way to obtain high solar cell efficiency [6].

To date, various metal free organic dyes including coumarin, indoline, squaraine, polyene, cyanine, hemicyanine, oligothiophene, perylene, carbazole, benzothidizole and truexene have been developed for dye sensitized solar cells (DSSC) and have attained high efficiencies up to 10.3% [7,8]. Among them, xanthene dyes have attracted much attention in DSSC field. Due to their excellent light harvesting property, low cost, and often used as a fluorescent dye in biological research, has been used in DSSC and reached an efficiency of 2% [9–11]. Measuring the electron transfer kinetics between the sensitizer and inorganic semiconductor has been a subject of intense research, because understanding the interfacial injection process is essential for designing the interfaces that are favorable for charge injection and high solar cell efficiency. So, studying the photophysical processes of xanthene dyes is therefore becoming an interesting topic [12]. In order to imitate the ET process operating between excited dyes and a semiconducting electrode in a DSSC, one can monitor the correlation between the dye fluorescence quenching behaviors together with electron acceptor using fluorescence spectroscopy. In other words, photophysical characterization of the electron donor and electron acceptor in a homogenous system is a requirement for the better understanding of the effects occurring in DSSC.

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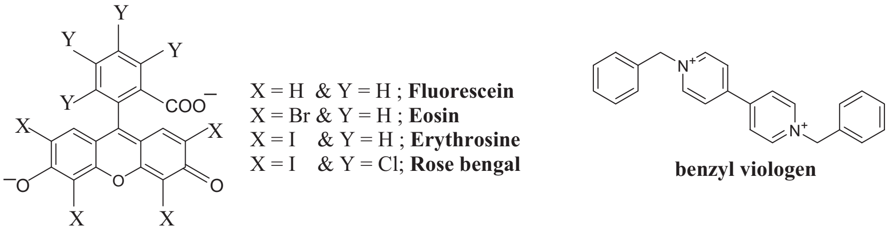

Scheme 1. Structure of xanthene dyes and benzyl viologen.

Recently viologen quenching of excited state dye molecules has become more interesting topic [13–16], in that way we have studied light induced behavior of xanthene dyes with benzyl viologen. Weiss et al. studied [13], ultrafast ET dynamics from colloidal CdS quantum dots (QDs) to alkylcarboxylate-functionalized viologen derivatives. If the ET process occurred via a through-bond pathway, then the rate of ET would decrease with increasing linker length i.e., in the alkyl linker extended the viologen away from the QD surface. However, their experimental data do not follow this trend, so they concluded that the ET pathway does not occur through the alkylcarboxylate group. So, the dominant ET pathway is "through space" pathway in CdS–viologen complexes. Moreover, the ET dynamics is independent of the number of methylene groups in the alkyl chain (n). The rate constant for ET is $(1.2 \pm 0.3) \times 10^{10}\,s^{-1}$ for all viologen derivatives. Ramamurthy et al. studied [14], supramolecular PET dynamics between coumarin 153 (C153) and 4,4′-dimethyl viologen dichloride (MV^{2+}). They have monitored forward ET and recombination process. The time constant of former is ~20 ps and latter is ~720 ps.

In this context, we have selected negatively charged xanthene dyes which enable these molecules to form ion-pair complexes with positively charged electron-acceptor molecule such as benzyl viologen (BV^{2+}, Scheme 1). Such complexes, when electronically excited, are known to generate charge transfer states that undergo fast electron-transfer reactions involving their singlet and/or triplet states [17–19]. Since we are interested in finding relationships between chemical constitution of xanthene dyes and acceptor molecules towards the use of solar cell applications, the present work is a fundamental approach of photoinduced interaction between xanthene dye molecules and benzyl viologen, a well known electron acceptor. This is mainly to understand how the non-halogenated and halogenated dye molecules are interacting with viologen molecule. This study is useful to understand the electron transfer nature of xanthene dye molecules in homogeneous solution of benzyl viologen which will give the basic idea of studying the interaction between visible light absorbing molecules with semiconductor nanoparticles in heterogeneous medium towards the applications of energy storing devices. For that, we have employed steady state and time resolved fluorescence techniques to investigate the ET dynamics between xanthene dyes and benzyl viologen.

2. Experimental

Xanthene dyes and benzyl viologen were purchased from Aldrich chemicals. The triple distilled water was used for preparing the solutions. The absorption spectra of the samples were recorded using an Agilent 8453 UV–visible diode array spectrophotometer. The fluorescence spectral measurements were carried out using Fluoromax-4 spectrophotometer (Horiba Jobin Yvon). The absorption and fluorescence maximum are listed in Table 1. Fluorescence measurements were made by taking fresh solution each time in rectangular quartz cell having an airtight stopper. All the solutions were excited at their absorption maximum. 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. Transient absorption experiments were carried out using nanosecond laser flash photolysis (Applied Photophysics, UK). The third harmonic (355 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 samples. The transients were probed using a 150 W pulsed xenon lamp, a Czerny-Turner monochromator, and Hamamatsu R-928 photomultiplier tube as detector. The transient signals were captured with an Agilent 500 MHz 1GSa/s Infiniium Oscilloscope, and the data were transferred to the computer for further analysis. For laser flash photolysis studies, samples were purged with argon gas for 45 min prior to the laser irradiation. Time-resolved fluorescence decays were obtained by the time correlated single-photon counting (TCSPC) technique exciting the sample at 410 nm. Data analysis was carried out by the software provided by IBH (DAS-6), which is based on deconvolution a technique using nonlinear least-squares method and the quality of fit is ascertained with the value of $\chi^2 < 1.1$. All the time resolved experiments were performed thrice and the average results were presented here.

3. Results and discussion

3.1. Photophysical properties of xanthene dyes

3.1.1. Absorption and emission characteristics

Fig. 1a and b shows the absorption and emission spectra of xanthene dyes respectively. The chromophore responsible for light absorption is xanthene ring which does not emit light radiation. While comparing xanthene and its derivatives, the latter shows light emitting nature. The fluorescence nature of xanthene dyes can be explained by molecular models, which shows that the benzoate group of xanthene dyes is sterically hindered and cannot lie in the plane of the xanthene group. So the combination of rigid structure of xanthene ring and steric hindrance impart by the benzoate group makes the xanthene derivatives as good fluorophores [20].

The shape of absorption spectra of all xanthene dye molecules look similar, which composed of sharp intense band (transition due to $S_0 \rightarrow S_1$) and broad weak shoulder (transition due to $S_0 \rightarrow S_2$). Absorption and emission wavelength of all dyes were shown in Table 1. It is observed that both absorption and emission maxima were shifted to higher wavelength (lower energy) from fluorescein to rose bengal as the degree of halogenation is increased.

Table 1
Photophysical properties of xanthene dyes in water.

Xanthene dyes	λ_{max} (nm)	λ_{emi} (nm)	τ_S (ns)	τ_T (μs)
Fluorescein	490	514	3.8	0.4
Eosin	511	534	1.2	100
Erythrosine	526	554	0.3	38
Rose bengal	546	574	0.5	42