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Reductive fluorescence quenching of DMP with aniline

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ABSTRACT

The photoinduced electron transfer (PET) between 8-(4-methoxyphenyl)-3,5-di[(E)-1-(4-methoxyphenyl)methylidene]-1,2,3,5,6,7-hexahydrodicyclopenta[b,e]pyridine (DMP) and aniline is studied in acetonitrile medium by using steady state and time resolved absorption and fluorescence spectroscopic methods. Bimolecular quenching rate constants (k_q) were calculated from the obtained linear Stern–Volmer plots from both steady state and time resolved measurements. The rate constant (k_q) for PET between DMP and aniline is $1.4 \times 10^{10}\,M^{-1}\,s^{-1}$, which is in diffusion control limit. The free energy change (ΔG^0) has been evaluated by using Rehm–Weller equation for the evidence of electron transfer from aniline to DMP. Direct evidence for the electron transfer reaction in the present system has been obtained by characterizing the aniline cation radical using nanosecond time resolved absorption measurements in the visible region. Further, this quenching mechanism is attributed to be reductive in nature i.e. electron transfer occurs from ground state aniline to excited DMP. This is the first example of reductive fluorescence quenching of DMP with aniline in acetonitrile ever known.

1. Introduction

Natural photosynthesis applies photoinduced electron-transfer (PET) systems, where a relay of PET reactions evolves among chlorophyll (electron donor) and quinone (electron acceptor) moieties embedded in a transmembrane protein matrix, to attain a lifetime of the final charge separated (CS) state as long as seconds. The long-lived CS state leads to conversion of light into usable chemical energy [1]. Extensive efforts have so far been devoted being inspired from the natural photosynthetic systems to develop electron donor–acceptor (D–A) molecules that undergo PET reactions to afford CS states. So, the understanding of PET between D–A molecules has been a long-standing goal. In this context, the $Ru(bpy)_3^{2+}$ complexes represent an extremely popular choice for investigations of PET in combination with potent redox partners such as viologens and tertiary amines [2–6]. Such PET reaction between donor and acceptor molecules plays a significant role in solar energy conversion. A number of studies on PET fluorescence quenching have been performed using fluorophore and quencher, and it has been concluded that the quenching is due to partial ET (i.e. exciplex formation) in a non-polar or less polar solvent, and to complete ET (i.e. outer-sphere ET) in a highly polar solvent such as acetonitrile. This conclusion is based on the facts that exciplex fluorescence can be observed in non-polar or less polar solvent but not in acetonitrile [7], and that the quenching in acetonitrile occurs at a long distance (7 Å or greater) between the fluorophore and the quencher, yielding radical pairs [8,9]. Thus the electron transfer study in acetonitrile has been considered [10–12].

As we mentioned earlier, understanding PET between D–A molecules has been a long-standing goal, in this perspective, we focus our attention on PET reactions of distyrylpyrdine (A) with aniline (D). The PET reaction between many donor and acceptor moieties plays a significant role in solar energy conversion and storage devices [13–26]. Among the best known fluorescent molecules are xanthenes, coumarins, naphthalimides, cyanines, acridines, and phenoxazines [27]. However, to date there is no report available on PET reactions with distyrylpyridine. This system shows a high fluorescence quantum yield (0.45) and fluorescence lifetime in the range of 2–4 ns [28]. In addition, the dye sensitized solar cell (DSSC) community is actively seeking suitable acceptor and donor units to modify Porphyrin or Ru-complexes as efficient semiconductor sensitizers. Therefore, we have established a new acceptor moiety that can anchor to the TiO_2 surface through the pyridine ring as well. Of course it is well established that the carboxyl group (acceptor moiety) can anchor to the TiO_2 surface [29], however in recent reports show that the pyridine unit can also anchor to the TiO_2 surface [30]. So we think, this molecule may provide new insights in DSSC. Hence, understanding the dynamics of these molecules together with donor will provide new insights towards energy fields.

As a preliminary step, here we report on the electron transfer quenching of 8-(4-methoxyphenyl)-3,5-di[(E)-1-(4-methoxyphenyl)

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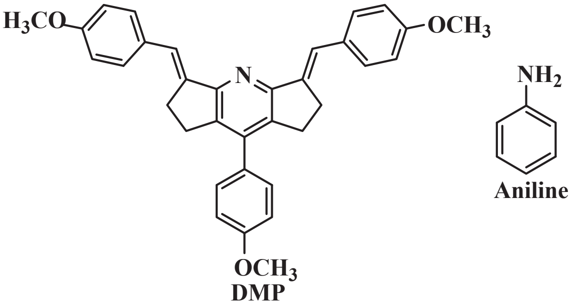
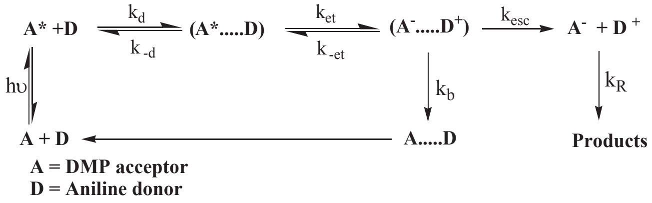


Scheme 1. Chemical structure of DMP and aniline.



Scheme 2. A general scheme for PET reactions of donor to acceptor, where, k_d and k_{-d} are the rate constants of diffusion and dissociation of the encounter complex, respectively. k_{et} and k_{-et} is the activation controlled rate constants of electron transfer, and k_{esc} is rate constant for the separation of radicals. k_b is rate constant for the recombination of radical pair. k_R is the rate constant for the decay of D radical.

methylidene]-1,2,3,5,6,7-hexahydrodicyclopenta[b,e]pyridine (DMP) excited singlet and triplet states by aniline in acetonitrile medium. The chemical structures of the DMP (acceptor) and aniline (donor) used in this study are given in Scheme 1. To the best of our knowledge, this is the first ever reported in the literature on PET reactions of DMP with aniline. Quenching rate constants were determined from both steady-state and time-resolved fluorescence spectroscopy. Quenching is due to electron transfer, it is further confirmed by detecting the cation radical of aniline using nanosecond time resolved absorption measurements. Scheme 2 represents a general idea showing the many stages involved in PET from excited DMP to aniline in solution.

2. Experimental

2.1. Materials

The synthesis and characterization of DMP has been described in literature [28]. Aniline was purchased from Merck, which was further purified by distillation before use. The spectroscopic grade solvent, acetonitrile was used for preparing the solutions. All measurements were performed at ambient temperature.

2.2. Methods

The absorption spectra of 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). 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 infiniium digital storage 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 405 nm. Data analysis was carried out by the software provided by IBH (DAS-6), which is based on deconvolution techniques using nonlinear least-squares method and the quality of the fit is ascertained with the value of $\chi^2 < 1.2$.

3. Results and discussion

3.1. Photophysics of DMP in acetonitrile

Fig. 1 shows the steady state and time resolved absorption and fluorescence spectrum of DMP in acetonitrile. Absorption and fluorescence maxima are found at 410 nm and 440 nm respectively. Fluorescence of DMP is due to ICT excited state charge recombination from the side aromatic rings π* to the central pyridine ring radical cation. The fluorescence decay of DMP (Fig. 1b) is obtained from the time correlated single photon counting (TCSPC) technique is fitted with single exponential function ($F(t) = A\exp(-t/\tau)$) and the fitted value of DMP is 3.24 ns which is assigned to singlet lifetime of DMP. Further, time resolved absorption measurements were carried out to record the triplet absorption spectrum of DMP using third harmonic output from the Nd–YAG laser. The transient absorption spectrum of DMP in acetonitrile solution is measured at 1 μs after excitation at 355 nm which is shown in Fig. 1c. According to Eq. (1) [31], the transient absorption spectrum has contributions from the ground state bleaching (GSB), stimulated emission (SE), excited state absorption (ESA) and triplet state absorption (TSA).

$$\Delta A = \Delta A_{ESA} + \Delta A_{TSA} - \Delta A_{GSB} - \Delta A_{SE} \quad (1)$$

However, measured transient absorption spectrum has strong contribution from TSA and GSB. Moreover at this time scale there is no more contribution from stimulated emission since the singlet lifetime of DMP is 3.24 ns. The transient absorption spectrum has pronounced band at 540 nm is assigned to the triplet state absorption. The triplet lifetime of DMP is 172 μs obtained from the kinetic trace at 540 nm (Fig. 1d).