



Photoinduced electron transfer from zinc tetraphenylporphyrin to 2-nitrofluorene in polar solvent acetonitrile



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ABSTRACT

The possibility of intermolecular photoinduced ET (PET) is investigated in a novel donor–acceptor (D–A) system consisting of zinc tetraphenylporphyrin (ZnTPP) as donor and 2-nitrofluorene (2NF) as acceptor upon photoexcitation of the former moieties in polar solvent acetonitrile (ACN). The observed values ($7.23 \times 10^9 \text{ L}/(\text{mol s})$ and $7.04 \times 10^9 \text{ L}/(\text{mol s})$) of the fluorescence quenching rate constant from steady state and time-resolved data, respectively, are in good agreement with that ($5.65 \times 10^9 \text{ L}/(\text{mol s})$) obtained from Marcus theory. Excited state absorption (ESA) from the S_2 state of Soret excited ZnTPP to higher electronic states gives rise to broad transient absorption spectra in 560–700 nm region. Presence of 2NF leads to a faster decay (up to 100 ps time delay) of the ESA signal of ZnTPP at a probe wavelength of 620 nm. This indicates ultrafast ET from the S_2 state (zero vibrational level) as well as the higher vibrational levels of the S_1 state of ZnTPP to 2NF. Moreover, transient absorption kinetics at longer time delays (up to 7 ns) at a probe wavelength of 620 nm show the formation of a charge separated state due to ET from the S_1 state (zero vibrational level) of the Soret excited ZnTPP to 2NF.

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1. Introduction

Porphyrins play very important roles in biological electron transfer (ET) processes such as photosynthesis and respiration [1–7]. Chlorophylls, which are porphyrin derivatives, play a crucial role in natural photosynthesis for converting solar energy into chemical energy [1,8,9]. In order to develop artificial photosynthetic systems and organic photovoltaic cells, photoinduced ET (PET) and energy transfer processes have been studied extensively in porphyrin based donor–acceptor (D–A) systems [10–26]. The unique structural, photochemical and electrochemical properties of porphyrins make them useful for a variety of potential applications such as dye sensitized solar cells (DSSCs) [27–29], non-linear optics [30], telecommunication technologies [31], gas sensors [32], photochromic recording medium [33], catalysts in industrial processes [34,35], anticancer pharmaceutical drugs [36], photodynamic destruction of viruses [37,38], photodynamic therapy (PDT) [39,40], etc.

Porphyrins are cyclic molecules composed of four smaller 5-membered heterocycles, called pyrroles, each one containing one nitrogen and four carbon atoms. The electronic absorption spectra of a free base porphyrin consist of an intense band at about 400 nm, called Soret band (or B band) and four weaker bands in the visible region (about 500–700 nm), called Q bands. The Soret and Q bands are due to π – π^* transitions from the ground singlet state to the second excited singlet state ($S_0 \rightarrow S_2$) and from the ground singlet state to the first excited singlet state ($S_0 \rightarrow S_1$), respectively. Metalation of free base porphyrin increases the ring micro-symmetry from D_{2h} to D_{4h} accompanied by a decrease of the number of Q bands from four to two [1,41]. The internal conversion from S_2 to S_1 is rapid and hence fluorescence is usually observed from the S_1 state with a quantum yield $\sim 10^{-2}$ [42–44]. However, very weak fluorescence is observed from the S_2 state of porphyrins with a quantum yield $\sim 10^{-4}$ [19,20].

Among the various porphyrin derivatives, zinc tetraphenylporphyrin (ZnTPP) is one of the most extensively studied molecule so far mainly due to its good solubility in many commonly used organic solvents. Extensive studies on inter- and intramolecular PET have been carried out by many research groups in ZnTPP based D–A systems with various acceptors. Kuciauskas et al. [11] observed the transient absorption spectra of zinc porphyrin radical

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cation showing the formation with a time constant of 1.9 ps and decay with a lifetime of 50 ps in a covalently linked ZnTPP – fullerene (C_{60}) dyad. They concluded that the charge separated (CS) state lives for 50 ps in the dyad. Bell et al. [12] observed long-range PET in a dyad containing ZnTPP donor and C_{60} acceptor separated by a saturated norbornylogous bridge nine sigma bonds in benzonitrile (BN). They found that the CS state exhibits a long lifetime of 420 ns. Bahr et al. [13] investigated PET in a carotene(C)–ZnTPP– C_{60} molecular triad in 2-methyltetrahydrofuran (MTHF). They observed that excitation of ZnTPP leads to primary ET from ZnTPP to C_{60} and then secondary ET from carotene to ZnTPP⁺, thereby forming a final CS state of C^+ –ZnTPP– C_{60} – with a lifetime of 69 ns. Luo et al. [14] reported sequential PET in a ZnTPP–TPP– C_{60} triad in BN to form a final CS state of ZnTPP⁺–TPP– C_{60} – with a lifetime of 21 μ s. Also, they observed formation of a long-lived (580 ns) CS state in a ZnTPP– C_{60} reference dyad. Imahori et al. [15,16] studied photoinduced charge separation and recombination processes in various TPP and ZnTPP based dyads and triads. They observed broad transient absorption spectra of ZnTPP radical cation and a long-lived (16 μ s) CS state in ferrocene–ZnTPP– C_{60} triad [15]. Bell et al. [17] reported CS state in a giant ZnTPP–bridge– C_{60} system with a lifetime of 460 ns accompanied by the observation of a broad transient absorption spectra of ZnTPP radical cation in the 600–700 nm region. Boom et al. [18] prepared a large molecule in which four perylene-3,4:9,10-tetracarboxydiimide (PDI) molecules are attached to a central ZnTPP molecule. Photoexcitation of ZnTPP–PDI at the Soret band of ZnTPP results in the formation of a CS state with a time constant of 15 ps and decay lifetime of 5.3 ns. Yu et al. [19] reported ultrafast (<100 fs) ET from Soret band excited ZnTPP to dichloromethane solvent for a subset of excited ZnTPP molecules in favorably oriented contact with the solvent molecules. Hayes et al. [21] reported competitive ET from the S_2 and S_1 excited states of ZnTPP to a covalently bound pyromellitimide in MTHF and toluene solvents. Also, they observed broad transient absorption spectra of ZnTPP radical cation in 600–700 nm region. Zeyada et al. [23] investigated the transport mechanisms and photovoltaic properties of ZnTPP/n-type silicon heterojunction solar cells. Kanematsu et al. [24] studied the dynamics of intermolecular ET reactions of planar and nonplanar Al^{III} porphyrins with an axial ligand (PhCOO⁻) using a series of *p*-benzoquinone derivatives as electron acceptors in comparison with the corresponding Zn^{II} porphyrins (including ZnTPP). Robot-ham et al. [25] investigated PET in a covalently linked ZnTPP–amino naphthaline diimide (ANDI) dyad in BN and toluene solvents. They reported that upon Soret band excitation of ZnTPP, fast ET occurs from the S_2 state to ANDI followed by rapid charge recombination to form S_1 state of ZnTPP that subsequently undergoes a further slower ET to ANDI.

The aim of the present work is to investigate the possibilities and consequences of intermolecular PET in a novel D–A system consisting of ZnTPP as donor and 2-nitrofluorene (2NF) as acceptor in polar solvent acetonitrile (ACN, static dielectric constant $\epsilon_s = 37.5$) by using steady state and time-resolved spectroscopic measurements. 2NF is a well known electron acceptor [45–48]. It is a small organic molecule and quite cheaply available in the market. However, earlier ET studies of 2NF as an acceptor with various donors (dimethyl substituted phenols, tetrahydronaphthols, methylindoles etc.) showed concurrent occurrences of electron and energy transfer processes [45–48]. Such D–A systems are not suitable from application point of view as proper analysis of the fluorescence quenching data in terms of electron and energy transfer processes is often very difficult. In the present investigations, fluorescence (intensity as well as lifetime) quenching of ZnTPP is observed in presence of the quencher 2NF indicating the possibility of PET in this D–A system in polar solvent ACN by avoiding the competitive singlet–singlet energy transfer process.

The occurrence of PET in the presently used D–A system is further confirmed by the data obtained from femtosecond transient absorption measurements based on pump-probe technique.

2. Experimental

2.1. Chemicals

The samples ZnTPP (5,10,15,20-tetraphenyl-21H,23H-porphine zinc) and 2NF (Fig. 1) were used as supplied by Sigma–Aldrich. The solvent ACN of spectroscopic grade was purchased from Sigma–Aldrich and was tested before use to check any impurity emission in the wavelength region studied.

2.2. Instruments

The steady state electronic absorption spectra of the samples were recorded at the ambient temperature (300 K) by using 1 cm path length rectangular quartz cuvette by means of JASCO V-650 absorption spectrophotometer. Steady state fluorescence spectra of the samples were recorded by using JASCO FP-6500 fluorescence spectrometer at 300 K. Emission was detected at right angles to the direction of excitation light in order to avoid stray light.

The time-resolved fluorescence measurements were carried out by using a time correlated single photon counting (TCSPC) spectrometer from IBH (UK). The sample was excited with 560 nm light from a diode laser with 1 MHz repetition rate. A PMT based detector (TBX4, IBH) was used for detection of the emitted photons through a monochromator. The instrument response of the TCSPC set-up was measured by collecting the scattered light from a TiO₂ suspension in water. The instrument response function thus measured was ~ 200 ps. The decays were analyzed using IBH DAS-6 analysis software. The reduced χ^2 , Durbin–Watson (DW) parameter and residuals were used to judge the goodness of the fit.

For the pump-probe transient absorption measurements, a mode-locked automated broadband (tuning from 690 nm to 1040 nm) Ti:sapphire laser (Mai Tai HP, Spectra Physics), pumped by 14 W frequency doubled ND:YVO₄ (532 nm), was used as master oscillator. It produces laser pulses of <100 fs duration (full width at half-maximum, FWHM) and ~ 31 nJ (energy/pulse) centered at

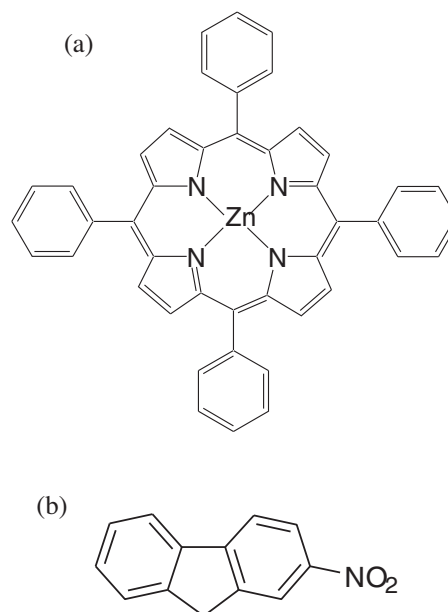


Fig. 1. Molecular structures of (a) ZnTPP and (b) 2NF.

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