

Femtosecond fluorescence dynamics of zinc biphenylporphine in nanocrystalline TiO₂ films: Evidence for interfacial electron transfer through space

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Abstract

The femtosecond fluorescence dynamics of zinc biphenylporphine (ZnBPP) were investigated in solution and in two solid-state environments – ZnBPP/glass and ZnBPP/TiO₂ – with S₂ excitation ($\lambda_{\text{ex}} = 410$ nm and $\lambda_{\text{em}} = 630$ nm). Our results indicate that the transient in solution involves a persistent component that becomes completely quenched in thin-film samples; for solid films at least three decay coefficients are required to fit the transients. For ZnBPP/TiO₂ films, the fluorescence was quenched significantly through J-type aggregation and interfacial electron transfer (IET) through space. Photocurrent measurements were also performed to confirm the existence of IET through space between ZnBPP molecules and TiO₂ nanoparticles.

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1. Introduction

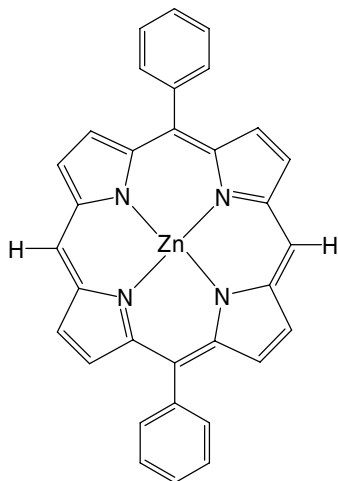
A dye-sensitized solar cell (DSSC) has attracted much attention as an alternative less expensive than a Si-based solar cell. Many organic molecules such as ruthenium complexes [1] and conjugated polymers [2] can serve as a sensitizer in a DSSC. The most efficient DSSC is the Grätzel cell, developed by Grätzel and co-workers in 1993 [1]. In this cell, a Ru–bipyridyl-based sensitizer served to sensitize nanocrystalline TiO₂ films; 10% conversion of light to electricity was achieved under AM 1.5 irradiation [1]. Because Ru²⁺ complexes are covalently adsorbed in nanocrystalline TiO₂ films via carboxylic groups in this Grätzel cell, much effort has been devoted to understand the dynamics of interfacial electron transfer (IET) through chemical bonds. Such IET has been extensively investigated [3–7]: the process occurs from fs to ns time scales, and the greatest injection time was determined to be 6 fs by Huber et al. [7].

Other candidates for a dye sensitizer are porphyrin and its derivatives, [8] of which the capacity to absorb visible light in regions 400–450 nm (Soret or B band) and 500–700 nm (Q bands) has proved useful in the design of artificial light-harvesting systems [9]. We reported the IET dynamics of a synthetic porphyrin, ZnCAPEBPP, adsorbed on glass and in TiO₂ nanocrystalline thin films using femtosecond fluorescence up-conversion with S₂ excitation ($\lambda_{\text{ex}} = 430$ nm) [10]. The results revealed that indirect IET through a phenylethynyl bridge occurred within 100–300 fs, but, as IET both through space and through bonds might occur on ZnCAPEBPP/TiO₂ films, distinguishing those two processes in our fluorescence decay measurements is impracticable.

If a phenylethynyl carboxyl group is lacking from a porphyrin sensitizer, no IET between the adsorbate (porphyrin) and the semiconductor (TiO₂) would occur through bonds. Here we report our femtosecond fluorescence results on a zinc biphenylporphine, ZnBPP (chemical structure shown in Scheme 1), physically adsorbed in TiO₂ thin films or spin-coated on a glass substrate. In the former samples, IET might occur through space at the interface

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Scheme 1. The chemical structure of ZnBPP.

between ZnBPP and TiO₂, but this process cannot occur in ZnBPP/glass samples. Photocurrent measurements of the ZnBPP/TiO₂ samples provide evidence for the existence of IET through space between ZnBPP molecules and TiO₂ nanoparticles.

2. Experiments

2.1. Sample preparation and photocurrent measurement

The target porphyrin, 10,20-biphenylporphyrinato zinc(II) (ZnBPP), was synthesized according to the literature method [11]; the procedure for synthesis of TiO₂ nanoparticles is likewise described elsewhere [10]. A transparent thin film of TiO₂ was obtained by spin coating a colloidal TiO₂ mixture on ITO conducting glass; the resulting film was annealed at 450 °C in air for 30 min. The ZnBPP/benzene solution was dropped onto TiO₂ nanocrystalline films and the solvent was evaporated in an exhaust hood. The ZnBPP/TiO₂ film served as an anode and a platinum thin-film plate as a cathode for solar-cell assemblies [12]; an iodine-based electrolyte solution filled between the two electrodes with a silica-gel membrane (thickness 1 mm) as a spacer. The electrolyte solution (iodine 0.05 M, lithium iodide 0.5 M) was formed in acetonitrile (all chemicals from Fluka Chemical). Photocurrents were measured using a picoampere ammeter (HP 4140B) coupled with a Xe lamp (Oriel, 1000 W) and a monochromator; the illumination intensity at 550 nm was 210 μW cm⁻².

2.2. Steady state measurement

UV/visible absorption spectra of ZnBPP in benzene solution and in solid thin films were recorded with a standard spectrophotometer (Cary 50, Varian). Emission spectra were obtained with a composite CCD spectrometer (USB2000FLG, Ocean Optics) via a Y-shape fiber (R600-UV, Ocean Optics) for front-face probes. The excitation source contains a pulsed diode-laser head (LDH-P-C-400,

PicoQuant) coupled with a laser-diode driver (PDL-800B, PicoQuant) that produces excitation pulses at 405 nm.

2.3. Femtosecond fluorescence measurement

To resolve the rapid rate of electron transfer, we employed a femtosecond laser system coupled with a time-resolved fluorescence spectrometer, described elsewhere [10]. The femtosecond pulse at 820 nm was doubled to provide an excitation pulse at 410 nm; its intensity was appropriately attenuated. The time-resolved measurements of fluorescence up-conversion involve two optical paths for excitation: for the transients of ZnBPP in benzene solution, we employed the transmission path and collected the fluorescence from the back side using two parabolic mirrors; for the transients of ZnBPP in solid films, we employed the reflectance path because the sample is not transparent. The polarization between pump and probe pulses was fixed at the magic-angle condition, 54.7°.

3. Results and Discussion

3.1. Steady-state measurements of ZnBPP in various environments

Fig. 1 shows the UV/visible spectra of ZnBPP in various environments. The absorption spectra of ZnBPP in benzene consist of two bands: the B band near 410 nm and the Q band near 540 nm. The B and Q bands are attributed to transitions S₀ → S₂ and S₀ → S₁, respectively [13]. When ZnBPP was adsorbed on solid films, the red-shifted and broadened spectral feature indicated the formation of J-type aggregates [10,14,15].

The inset of Fig. 1 shows the normalized emission spectra of ZnBPP in benzene and on a glass film. By comparison with the emission spectrum in solution, the emission spectrum for the glass film involves two notable features: the fluorescence was significantly quenched; beyond two

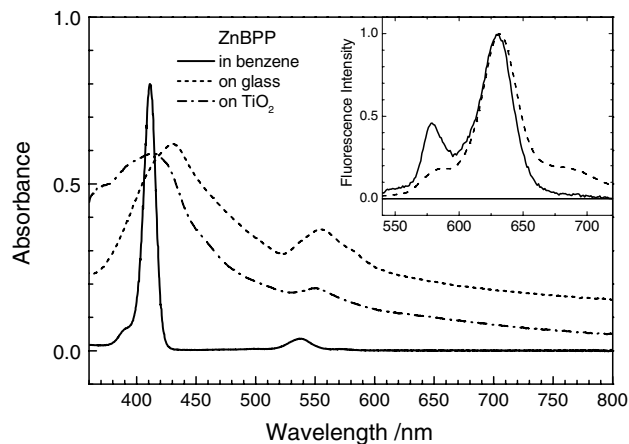


Fig. 1. Steady-state absorption spectra of ZnBPP in various environments as indicated. The emission spectra of ZnBPP in benzene and on a glass film are shown in inset. The excitation wavelength was fixed at 405 nm.

emission bands at 580 nm and 630 nm, a further emission band at ~ 690 nm appeared exclusively for the thin-film samples. Both spectral features support the formation of J-type ZnBPP aggregates on glass films. For the case of ZnBPP in a TiO_2 film, the fluorescence was further quenched, and no detectable signal was observed with our instrument. We expect that for the ZnBPP/ TiO_2 film the fluorescence was quenched not only by aggregation but also by the involvement of IET between ZnBPP and TiO_2 .

To demonstrate the existence of such IET, we performed photocurrent measurements for the ZnBPP/ TiO_2 film and the unsensitized TiO_2 film; the results are shown in Fig. 2. The excitation wavelength was fixed at 550 nm, which is near the absorption maximum of the Q band of ZnBPP. For ZnBPP absorbed in a TiO_2 film, the photocurrent measurements must be done promptly; otherwise the dye becomes gradually dissolved into the electrolyte solution because a linking group between ZnBPP and TiO_2 is lacking. Our results indicate a small but significant photocurrent ($J_{\text{SC}} \sim 50 \text{ nA cm}^{-2}$) to have been generated in the ZnBPP-sensitized TiO_2 film, whereas no photocurrent was observed for an unsensitized TiO_2 film. Taking into account the power density at 550 nm ($210 \mu\text{W cm}^{-2}$), we estimate the value for incident photon-to-current efficiency (IPCE) to be $5.3 \times 10^{-4}\%$.

This observed small IPCE value might arise from two conditions. First, because ZnBPP was not chemically bonded onto the TiO_2 surface, an excited molecule far from the dye/ TiO_2 interface injected no photoelectron into the conduction band of TiO_2 . Second, because ZnBPP physically adsorbed on TiO_2 surface might dissolve into the electrolyte solution, a photon absorbed by the ‘free’ dye molecule could not transfer a photoelectron into the surface of TiO_2 . Our photocurrent results nevertheless support the existence of IET through space in the ZnBPP/ TiO_2 film; further dynamical evidence of such process is provided and discussed in the Section 3.2.

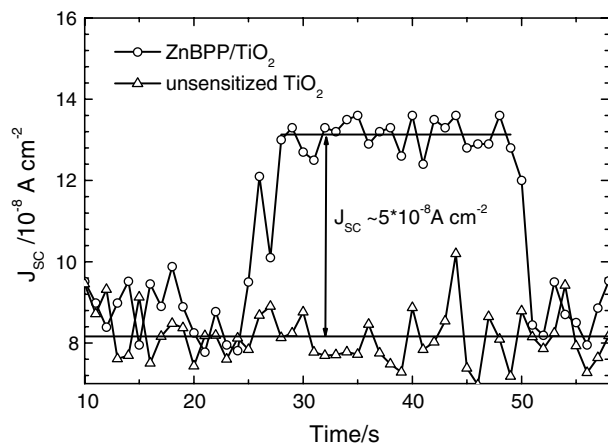


Fig. 2. Short-circuit photocurrent density (J_{SC}) of a ZnBPP-sensitized TiO_2 film (circles) and an unsensitized TiO_2 film (triangles). Both samples were excited at 550 nm with power density $210 \mu\text{W cm}^{-2}$.

3.2. Non-radiative process in solution and solid films

We show a comparison of femtosecond fluorescence transients of ZnBPP in various environments in Fig. 3. All samples were excited at 410 nm (corresponding to the Soret band), and fluorescence was probed at 630 nm (corresponding to the Q band). For ZnBPP in benzene (Fig. 3a), the transient increases gradually and approaches an asymptotic level. The transient was fitted to include two components B and C according to a consecutive kinetic model, $A \xrightarrow{\tau_1} B \xrightarrow{\tau_2} C$, in which τ_1 and τ_2 were determined to be 1.4 and 8.1 ps, respectively. Similar results have been reported previously [10], for which the excited-state relaxation dynamics of a ZnBPP derivative (ZnCAPEBPP) in THF solution were investigated to yield 0.9 and 8.6 ps for τ_1 and τ_2 , respectively. Accordingly, for ZnBPP we attribute the first coefficient ($\tau_1 = 1.4$ ps) to $S_2 \rightarrow S_1$ internal conversion (IC) to produce a hot S_1 species (component B); the second coefficient ($\tau_2 = 8.1$ ps) is due to vibrational cooling of the hot S_1 molecules to produce cold S_1 species (component C) [10]. The cold S_1 species endure, but they

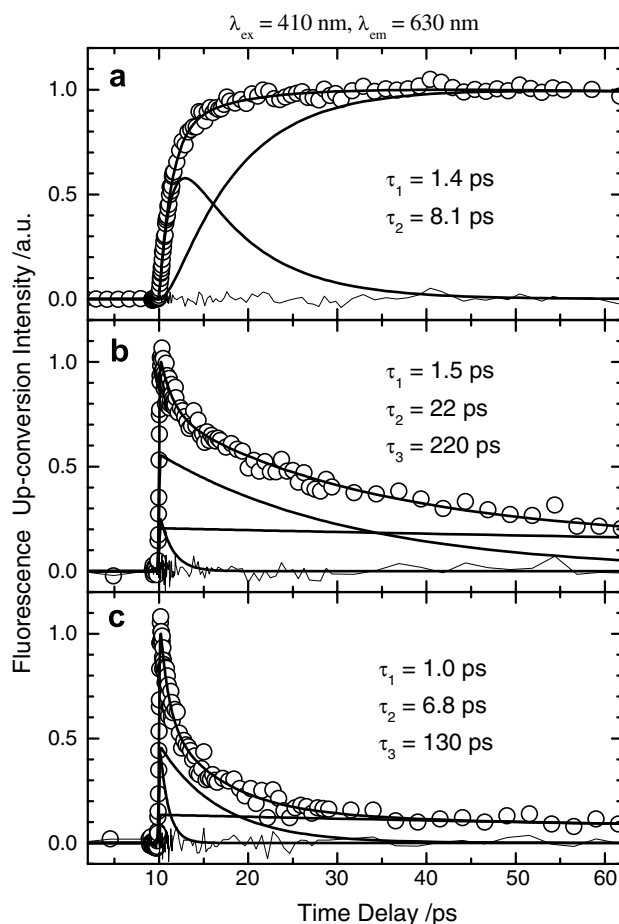


Fig. 3. Femtosecond fluorescence transients of ZnBPP in various environments: (a) solution; (b) spin-coated on a glass plate; (c) adsorbed on a TiO_2 thin film. The symbols are raw data; the solid curves represent theoretical fits of the transients whereas the curves under each transient represent deconvoluted components; the thin traces represent residuals of the fit.

might further relax via the $S_1 \rightarrow T_1$ intersystem crossing; its decay coefficient is on a nanosecond time scale [16]. Our real-time observation of the ZnBPP system is consistent with other femtosecond results for the zinc tetraphenylporphyrin (ZnTPP) system, for which the lifetime of the S_2 state of ZnTPP is reported in a range 1.45–2.35 ps, and vibrational cooling from the hot S_1 species occurs on a time scale ~ 10 ps [17–19].

Fig. 3b shows a fluorescence transient of ZnBPP coated on a glass plate. Of two dynamical features for the transient of ZnBPP on glass differing from the transient of ZnBPP in solution, first, the initial rise component that appears in solution became extremely rapid (<100 fs). This phenomenon indicates that the $S_2 \rightarrow S_1$ IC of ZnBPP was accelerated in a solid film through strong intermolecular interactions between porphyrin aggregates; thereby the hot S_1 species of ZnBPP were produced within 100 fs on a glass film, similar to the case of ZnCAPEBPP on glass [10]. Second, the fluorescence transient decays much more rapidly than for the solution. Fitting with three components yielded decay coefficients 1.5, 22 and 220 ps; the corresponding relative amplitudes are 0.27, 0.52 and 0.21, yielding a mean decay coefficient $\tau_{\text{ZnBPP}} = 58$ ps that satisfies the following expression:

$$(\tau_{\text{ZnBPP}})^{-1} = k_r + k_{nr} \quad (1)$$

where k_r and k_{nr} represent the radiative and non-radiative decay coefficients of ZnBPP, respectively. This transient result is consistent with the steady-state spectrum, for which the fluorescence intensity is significantly quenched through the formation of aggregates. We therefore assign the non-radiative process being mainly due to intermolecular energy transfer of the ZnBPP aggregates (decay coefficient k_{agg}), i.e.,

$$(\tau_{\text{ZnBPP}})^{-1} = k_r + k_{\text{ISC}} + k_{\text{agg}} \simeq k_{\text{agg}} \quad (2)$$

Maiti et al. [20] reported that the lifetimes of the J- and H-aggregates of ionic porphyrins are on the orders of 0.1 and 10 ns, respectively. Our result ($\tau_{\text{ZnBPP}} = 58$ ps) is consistent with that of Maiti et al. for the contribution of the non-radiative relaxation in ZnBPP aggregates is mainly of J-type.

In performing a similar experiment, Ogawa et al. [21] adsorbed a ruthenium complex, $\text{Ru}(\text{bpy})_3^{2+}$, on mesoporous silica and reported that the self-quenching dynamics of aggregated molecules depend on the proportion of adsorbed dye molecules. The decreased fluorescence lifetime from ns to <100 ps is thus attributed to the formation of aggregated molecules in solid films; the multi-exponential decay feature reflects the self-quenching of molecular aggregates to various extents. Note that the first two decay time coefficients of the ZnBPP/glass film are similar to those of the ZnCAPEBPP/glass films, but the third decay component (220 ps) became indiscernible for the latter [10]. These results indicate that porphyrin molecules in the latter system involve carboxylate group to form tighter

aggregates through hydrogen bonding so that no slow-decay component was observed for the latter.

3.3. Electron transfer through space between ZnBPP and TiO_2

Fig. 3c shows a fluorescence transient of ZnBPP adsorbed on a TiO_2 film. The transient decayed not only much more rapidly than for solution (Fig. 3a) but also significantly more rapidly than for the ZnBPP solid film (Fig. 3b). Three decay components are required to provide a satisfactory fit, yielding fitted coefficients $\tau_1 = 1.0$, $\tau_2 = 6.8$ and $\tau_3 = 130$ ps; the corresponding relative amplitudes are 0.47, 0.43 and 0.10. τ_1 of the ZnBPP/ TiO_2 film is notably smaller than that of the ZnBPP/glass film, and the relative amplitude of the former is larger than that of the latter, which yields a mean decay coefficient of the former ($\tau_{\text{ZnBPP}+\text{TiO}_2} = 16$ ps) almost a quarter of that of the latter ($\tau_{\text{ZnBPP}} = 58$ ps). The discrepancy of relaxation dynamics between the two solid samples reflects an additional non-radiative process that occurred only when TiO_2 nanoparticles were present. We therefore assign this non-radiative process to IET through space (decay coefficient k_{IET}) from the excited state of ZnBPP to the conducting band of TiO_2 . The inverse of the mean decay coefficient of the ZnBPP/ TiO_2 film can be formulated as follows:

$$(\tau_{\text{ZnBPP}+\text{TiO}_2})^{-1} = k_r + k_{\text{ISC}} + k'_{\text{agg}} + k_{\text{IET}} \simeq k'_{\text{agg}} + k_{\text{IET}} \quad (3)$$

Note that k'_{agg} might differ from k_{agg} because of the difference of surface morphology between TiO_2 and glass. Assuming that $k'_{\text{agg}} \simeq k_{\text{agg}}$, we determine the mean rate coefficient of the through-space IET process (k_{IET}) according to this expression:

$$k_{\text{IET}} = (\tau_{\text{ZnBPP}+\text{TiO}_2})^{-1} - (\tau_{\text{ZnBPP}})^{-1} \quad (4)$$

Using the lifetime values 16 ps and 58 ps for $\tau_{\text{ZnBPP}+\text{TiO}_2}$ and τ_{ZnBPP} , respectively, we obtain k_{IET} to be $\sim 5 \times 10^{10} \text{ s}^{-1}$.¹ IET thus occurs through space in the ZnBPP/ TiO_2 film on a time scale ~ 20 ps, which is substantially greater than that of IET through bonds occurring for the ZnCAPEBPP/ TiO_2 system [10].

Evidence for IET through space in other systems has been reported from both time-resolved [22] and photocurrent measurements [23]. Hashimoto et al. [22] stated that the luminescence decay of $\text{Ru}(\text{bpy})_3^{2+}$ on TiO_2 was fitted with four exponential components in total, with each decay component being attributed to a separate binding site in the TiO_2 films. Because the rate of electron transfer through space depends on the distance between donor

¹ In Fig. 1, it shows that the UV/visible spectrum of the ZnBPP/ TiO_2 sample is less red-shifted than that of the ZnBPP/glass sample, indicating that the contribution of the J-aggregate is less for the former than the latter. Because the energy relaxation of the J-aggregate is much more rapid than that of the H-aggregate, it follows that $k'_{\text{agg}} \leq k_{\text{agg}}$. In an extreme case for $k'_{\text{agg}} \ll k_{\text{agg}}$, k_{IET} is determined to be $(16 \text{ ps})^{-1} = 6.25 \times 10^{10} \text{ s}^{-1}$, which is an upper limit of k_{IET} .

and acceptor [24], the large range of the rate of electron transfer reflects the inhomogeneous nature of the TiO₂ surface. We thus conclude that the fluorescence of ZnBPP was quenched via electron transfer through space, and our observed multi-exponential decay is attributed to molecules with varied distances between donor and acceptor. Our fluorescence decay is the statistical mean for all dye molecules adsorbed on TiO₂ nanoparticles, causing the rate of electron transfer to have a broad distribution.

4. Conclusion

The effects of aggregation and IET through space for ZnBPP adsorbed on TiO₂ films have been investigated with femtosecond fluorescence up-conversion technique and S₂ excitation ($\lambda_{\text{ex}} = 410$ nm and $\lambda_{\text{em}} = 630$ nm). Our results indicate that when ZnBPP was coated on a glass plate, the fluorescence was significantly quenched due to the effect of J-type aggregation; the fluorescence transients feature three decay components with time coefficients 1.5, 22 and 220 ps. For TiO₂ films, the fluorescence of ZnBPP was further quenched because of not only aggregation but also IET through space; the three decay coefficients of the transients further decreased to 1, 6.8 and 130 ps. The multi-exponential decay feature reflects varied distances between ZnBPP molecules and TiO₂ nanoparticles that cause the rate of electron transfer to have a broad distribution. According to our data analysis, the mean time scale for IET through space in the ZnBPP/TiO₂ film was ~ 20 ps, which is substantially longer than that of IET through bonds occurring for the ZnCAPEBPP/TiO₂ system (100–300 fs) [10].

Acknowledgements

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