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Direct and oxygen-mediated triplet–triplet annihilation of tetraphenylporphyrin in multilayers of decanol on the external surface of NaA zeolite

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Abstract

The kinetics of triplet state decay and concomitant delayed fluorescence (DF) of *meso*-tetraphenylporphyrin (TPP) adsorbed on the external surface of NaA zeolite covered by coadsorbed *n*-decanol (DEC) were studied by the laser flash photolysis. In deoxygenated solid samples of NaA with coadsorbed DEC, the diffusion-controlled bimolecular triplet–triplet annihilation (TTA) dominates in contrast to what is observed on the dry NaA surface. The TTA which results in DF can be described in terms of two reaction channels: (a) an energy transfer pathway with singlet excited state formation; (b) enhanced intersystem crossing in the triplet encounter complex. Whilst the TTA in multilayers occurs in DEC microphase, the reaction parameters change significantly when adsorbed ground-state molecules are involved. A fast TTA rate constant found at large TPP concentration in solid samples with DEC was attributed to triplet energy migration in TPP assemblies. Singlet oxygen works as an efficient mobile energy carrier between TPP triplets in both solid and liquid aerated samples. The parameters of this reaction may also be modified by changing the ratio [TPP]/[DEC] in multilayers, which in general act as microreactor systems with supramolecular organization of reactants. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Tetraphenylporphyrin; T–T annihilation; Delayed fluorescence; Singlet oxygen

1. Introduction

Bimolecular reactions of electronically excited states of organic molecules at the interfaces and, in particular, energy transfer processes of triplet excited states (T) have considerable importance in a number of scientific, biological and technological areas. Kinetic studies of triplet excitation energy transfer to the ground-state organic molecule have been performed with T adsorbed on porous surface and the acceptor in the gas phase [1], or with the coadsorbed organic acceptor [2–4] and with both T and acceptor trapped in zeolites [5]. These investigations could provide information concerning the strength of interaction between the surface and reactants, the molecular mobility at the interface, the interface dimensions, the nature of the medium separating the donor and the acceptor as well as other features of the organized systems.

The well-known reaction between two triplet excited states is the triplet–triplet annihilation (TTA), which often results in delayed fluorescence (DF) due to the formation of the fluorescent singlet excited state by triplet–triplet energy transfer (TTADF). This process needs considerable amounts of T and may be achieved using samples with high local concentration of reactants and strong laser pulse as an excitation source. The study of TTA kinetics for T adsorbed on the porous solid surfaces [6–8], on the surface of quantized colloidal semiconductor particles [9] and incorporated into membranes [10,11] was carried out in order to probe the effect of surface geometry, the diffusion and localization of adsorbates at the interface.

A specific particular case of triplet–triplet energy transfer is the quenching of T by molecular oxygen. Considerable attention has been given to the kinetics and mechanism of this reaction at gas/solid interfaces of porous surfaces and zeolites [1,2,4,5,12–18] in order to reveal the role of O_2 adsorption–desorption and the effect of T environment on the O_2 diffusion at the interface.

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Nomenclature

DEC	*n*-decanol
DF	delayed fluorescence
$k_{\mathrm{obs}}{}^{\mathrm{L}}$	apparent rate constant of triplet–triplet annihilation related to the decanol volume in the solid sample
$k_{\mathrm{obs}}{}^{\mathrm{S}}$	apparent rate constant of triplet–triplet annihilation related to the surface area
SOFDF	singlet oxygen feedback-induced delayed fluorescence
S_0	singlet ground state
S_1	first singlet excited state
T	triplet excited state
TPP	*meso*-tetraphenylporphyrin
TTA	triplet–triplet annihilation
TTADF	triplet–triplet annihilation-induced delayed fluorescence
Greeks	
φ_{FL}	fluorescence quantum yield
$\varphi_{\mathrm{FL}}{}^{\mathrm{SO}}$	apparent quantum yield of fluorescence from (S_1, $^3O_2$) couple
φ_{T}	triplet state quantum yield

The TTA requires translation molecular mobility of T which may be restricted by binding forces to the interface and by the reaction spatial geometry. In this case TTA can be mediated by some mobile energy carrier, e.g., by molecular oxygen. The $^3O_2$ quenching of T results in $^1O_2$ formation followed by singlet–triplet energy transfer from $^1O_2$ to other T (singlet oxygen feedback) generating the dye fluorescent state. Our recent laser flash photolysis investigation of $^1O_2$ feedback-induced DF (SOFDF) from porphyrins [15,16,18] and eosin [17] at gas/solid interface showed that SOFDF kinetics can provide dynamic parameters of the $^1O_2$ excitation migration in the dye–O_2 system at the interface.

In this work we present the laser flash photolysis study of *meso*-tetraphenylporphyrin (TPP)–O_2–*n*-decanol (DEC)–NaA zeolite system supported by complementary ground-state absorption and steady-state emission techniques. A comparative study is presented on the transient absorption and emission of TPP adsorbed onto the dry external surface of NaA zeolite, in the presence of DEC multilayers covering the NaA external surface and in bulk of liquid DEC. While $^1O_2$-feedback is the only pathway of TTA on dry surface, it is demonstrated that both SOFDF and TTADF can be observed in DEC as well as on the zeolite surface covered by DEC multilayers. It will be shown that the efficiencies of SOFDF and TTADF are comparable and how $^1O_2$-mediated TTA competes with direct diffusion-controlled TTA. The dependence of the bimolecular rate constants extracted from the kinetic analysis of TTA, TTADF and SOFDF on the amount of TPP and coadsorbed DEC on NaA surface is obtained, showing that multilayers of DEC on external zeolite surface may be used as controlled size microreactors.

2. Experimental section

2.1. Materials

TPP (from Hambright, Washington, DC) was purified by recrystallization from methanol. The sodium form of zeolite A (NaA, Aldrich, Si/Al = 1.0, crystallite particle size 1–2 μm was controlled by electron microscopy, estimated external surface area 3 m^2/g [15,16]) was dried in a vacuum at ≈150°C for 48 h prior to use. Benzene (Aldrich, spectrophotometric grade) was dried over P_2O_5 and then used as solvent for the TPP and DEC. The purity of 1-decanol (Fluka, puriss., m.p. 6.4°C) was checked by zone melting.

2.2. Sample preparation

The solutions (3–5 ml) of TPP in benzene with various amounts of DEC were added to NaA samples (1 g). The suspensions were stirred during evaporation at 20°C. It was found that when 0.35 ml of DEC are loaded onto 1 g NaA the sample does not exhibit a distinguishable liquid macrophase, showing dry powder behavior. This DEC amount corresponds approximately to 300 monolayers (one monolayer is 1.2 μl/g, assuming 0.5 nm radius of DEC molecule) and is even larger than the internal NaA volume (0.3 cm^3/g). The large TPP and DEC molecules are both expected to be located at the crystallite external surface of NaA in which internal network is characterized by small windows of diameters 0.4 nm [4,19]. Samples were evacuated by freeze pump procedure up to 1×10^{-3} Torr. Selected amounts of air in the sample cell were obtained from a system of calibrated volumes. All measurements were carried out at 20°C.

2.3. Instrumentation and data analysis

The description of steady-state spectrophotometer, spectrofluorimeter and diffuse reflectance laser flash photolysis was given earlier [15–18].

Ground state and transient reflectance of solid samples were analyzed in terms of Kubelka–Munk theory using Eqs. (1) and (2), respectively, where R and R' are diffuse reflectance from the surface of the samples with and without TPP, respectively, and R_t is the reflectance observed at time t after the laser pulse [6–8]. The values of ΔF and ΔF_t,

$$\Delta F = \frac{(1-R)^2}{2R} - \frac{(1-R')^2}{2R'} \tag{1}$$

$$\Delta F_t = \frac{(1-R_t)^2}{2R_t} - \frac{(1-R)^2}{2R} \tag{2}$$

are proportional to the corresponding absorber concentration for optically thick samples with a homogeneous distribution of absorbers. The absorption of TPP at 532 nm in the solid samples was always smaller than 10%. Transient signal intensities were near saturation under experimental conditions and demonstrated almost total conversion of ground state into transient, implying the validity of Kubelka–Munk treatment for analysis of transient decays [6–8].

3. Results and discussion

3.1. Ground-state reflectance spectra of TPP on the NaA surface with n-decanol

The Soret band of TPP absorption on the surface of dry NaA at small loadings is much broader and blue shifted in comparison with that in DEC (half-width 30 and 11 nm, $\lambda_{\max} = 410$ and 416.5 nm, respectively, Fig. 1A, curves 1 and 4) [16]. The broadening of the absorption bands after adsorption onto the surface is a general observation which is likely due to the inhomogeneous environment of the adsorbed molecules [15,20]. The solvatochromic shift of TPP Soret band, from the gas to the condensed phase, is controlled by the dispersive forces and is proportional to $(n^2-1)/(2n^2+1)$ [21,22], where n is the medium refractive index. From the corresponding linear dependence $(1000/\lambda_{\max} = 2.535 - 0.6556(n^2-1)/(2n^2+1))$ [21] an apparent n value of 1.27 is extracted. Therefore, the n value for the medium where TPP is localized on gas/solid interface is smaller than that of solid support (NaA crystals are isotropic with $n = 1.385$ for dry zeolite [19]). It is worthwhile mentioning that one could expect even a smaller value of n on dry NaA surface since the specific interaction of TPP with the surface is able to induce a red shift in the Soret band (see below).

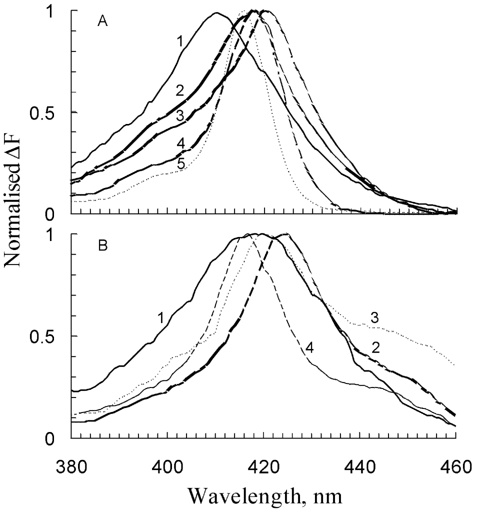


Fig. 1. Normalized reflectance spectra of NaA solid samples plotted using the differences in remission function ΔF: (A) 0.05 μmol/g TPP on dry surface (1), with coadsorbed 5 μl/g (2), 40 μl/g (3) and 300 μl/g (4) DEC and in liquid DEC (5) (in terms of optical density). (B) 2 μmol/g TPP on dry surface (1), with coadsorbed 5 μl/g (2), 40 μl/g (3) and 300 μl/g (4) DEC.

In our previous studies of porphyrin absorption spectra on the surface it was argued that the broadening and blue shift of Soret band at gas/solid interface could reflect the exciton coupling in a stack face-to-face type organization of porphyrin molecules on the surface, possible even at very low surface loadings [15,16]. Similar conclusions based on the studies of adsorption isotherms and absorption spectra of methylene blue on the external surface of zeolite X were proposed [23]. Since the shape of the reflectance spectra does not change with surface loading, one may assume that in the course of adsorption, the surface is covered with growing islands of clustered molecules in which the environment of each adsorbed molecule is rather similar and independent of surface concentration. However, the effect of DEC coadsorption on TPP absorption spectra on NaA surface imply that the effects are more likely due to the low n value at the gas/solid interface rather than to the aggregation (see below).

The coadsorption of 1–10 monolayers of DEC on the NaA external surface results in narrowing and gradual red shift of the TPP Soret band maxima to $\lambda = 421$ nm which is larger than that in pure DEC (Fig. 1A, curves 2 and 3). These changes reflect the transition from the gas/solid to liquid/solid interface. Similar red-shifted Soret bands of phenylsubstituted porphyrins at other liquid/solid interfaces have been observed [9,24,25]. These surface-induced red shifts cannot be explained by polarizability effects. They may point to the fact that TPP specific interaction with the surface brings some structural variation, e.g., the decrease of the angle between the porphine and the phenyl rings followed by the increase of the effective π conjugated system [25].

Further increase of DEC amount in the samples with small TPP content leads to a significant narrowing and blue shift of TPP Soret band (Fig. 1A, curve 4). The TPP absorption spectra in multilayers of DEC on NaA surface becomes practically identical to that in DEC if the ratio of TPP/DEC in the sample is smaller than 0.1 mmol/l which corresponds to the solubility of TPP in DEC.

Spectral shape and peak position of TPP Soret band measured with dry NaA samples did not exhibit any variations and ΔF values showed a linear dependence on TPP concentration at the surface loadings in the range 0.005–0.1 μmol/g (0.1 μmol/g corresponds to 5.7% of a TPP monolayer on the surface if the size of TPP molecule is taken to be equal to TPP long axis, 1.9 nm [22]). Further increase of TPP concentration results in a red shift (up to 420 nm) and broadening of Soret band, indicating aggregation of TPP on the surface (Fig. 1B, curve 1) [15,16]. The addition of DEC to concentrated TPP solid samples results in further red shift of broad Soret band (up to 425 nm) and in the appearance of a broad shoulder at 440–450 nm (Fig. 1B, curves 2 and 3). This additional band, which is shifted to the red from the main Soret absorption, may correspond to TPP aggregates in the liquid microphase. The contribution from the narrow Soret band of the monomer TPP in the liquid microphase is distinguishable at large amount of DEC on the surface (Fig. 1B, curve 4).

3.2. Steady state and prompt fluorescence of TPP on the NaA surface with n-decanol

The emission spectrum of TPP on dry surface of NaA is noticeably broader than that in DEC (Fig. 2). The 0–0 and 0–1 vibronic bands are 5 nm shifted to the red and to the blue, respectively. The TPP steady-state fluorescence quantum yield ($\varphi_{\rm FL}$) and the lifetime of prompt fluorescence (PF) on dry NaA surface (0.076 and 8.6 ns, respectively) are smaller than those in solution (values 0.12 and 12.5 ns, respectively, were measured in the deoxygenated DEC), showing an insignificant surface quenching effect (inset in Fig. 2) related to the specific nature of the adsorption sites [16]. The coadsorption of DEC results in a gradual change of the TPP fluorescence spectrum and lifetimes as compared to those observed in neat DEC (see Fig. 2).

The rate constant of TPP fluorescence quenching by O_2 on dry NaA gas/solid interface was estimated as $2.4 \times 10^{10}\,{\rm l\,mol^{-1}\,s^{-1}}$. The quenching of singlet excited state of porphyrins on NaA and other surfaces by O_2 results in ^{3}TPP formation as a major pathway since the amount of ^{3}TPP generated by the laser pulse did not decrease in the presence of O_2 [15,16,18]. The rate constant of TPP fluorescence quenching by O_2 on NaA surface with coadsorbed monolayer of DEC is 20 times smaller than that on dry surface. A similar screening effect of coadsorption of long chain alcohols on fluorescence quenching with O_2 was reported also for other surfaces [12]. Further increase of DEC content in the sample results only in insignificant increase of TPP fluorescence lifetime in aerated solid samples to that observed in aerated DEC solution (11.3 ns). In DEC, the rate constant of TPP PF quenching by $^3O_2$ was estimated to be $5.4 \times 10^9\,{\rm l\,mol^{-1}\,s^{-1}}$ (the concentration of oxygen in air saturated DEC was taken as 1.6 mmol/l [26]).

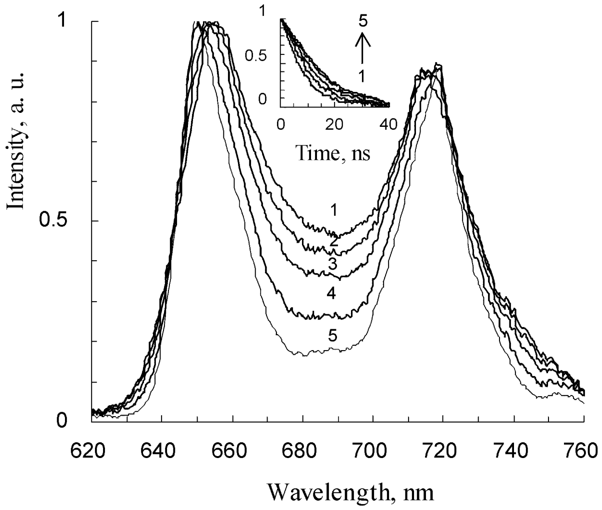


Fig. 2. Normalized steady-state corrected emission spectra of 0.05 μmol/g TPP adsorbed on dry NaA surface (1), with coadsorbed DEC 5 μl/g (2), 40 μl/g (3) and 300 μl/g (4) DEC and in pure DEC (5). Inset shows the corresponding normalized curves of PF decay measured at 720 nm.

3.3. Transient absorption and delayed fluorescence of TPP on the NaA surface with n-decanol

Photoexcitation of TPP on the surface [16,18] and in solution [27,28] produces the characteristic transient differential spectra of ^{3}TPP with strong bleaching at the wavelength of Soret band and maximum absorption near 440 nm. At large TPP concentration on NaA surface with DEC, the half-width of transient bleaching band was significantly smaller than that of the Soret absorption showing that the TPP monomers in liquid microphase are the source of ^{3}TPP. A comparison of differential triplet–triplet absorption (measured immediately after the laser pulse, $\Delta F_{t=0}$, at high laser fluence and small surface loading when transient signal intensities are in saturation) and initial TPP ground-state absorption at Soret band show, using literature values of corresponding extinction coefficients in solution [22,27,28] that the efficiency of ground-state conversion to the triplet state is larger than 50% [16]. The 80% value was measured for diluted solutions of TPP in DEC, which coincides with the ^{3}TPP quantum yield, $\varphi_{\rm T}$ ($\varphi_{\rm T}$ in the range 0.73–0.84 in different solvents has been reported [22,29]). It was assumed that $[{\rm T}]_0 = 0.8\,[{\rm TPP}]$ in solid samples at low TPP concentration and high laser fluence. For concentrated solid samples, the $[{\rm T}]_0$ values were estimated by comparison of $\Delta F_{t=0}$ and the PF yield ($Y_{\rm PF}$, an amount of light emitted during PF) with those measured for diluted solid samples with similar DEC content. In most experiments, the initial ^{3}TPP concentration, $[{\rm T}]_0$, was smaller than 0.01 μmol/g.

3.3.1. Triplet state and delayed fluorescence kinetics in the absence of oxygen

The mean lifetime of ^{3}TPP in evacuated samples of dry NaA is around 1 ms and depends neither on sample loading nor on the initial ^{3}TPP concentration [16]. The energy-dissipative pathway of ^{3}TPP in deoxygenated samples of dry NaA seems to be a unimolecular intersystem crossing slightly enhanced by the interaction with the surface (the measured rate constant of ^{3}TPP unimolecular decay in DEC is $500\,{\rm s^{-1}}$). In the presence of one or more DEC monolayers on the NaA surface in deoxygenated solid samples, the ^{3}TPP decay becomes much faster (lifetime as short as 0.5 μs has been observed at high ^{3}TPP concentration in the presence of one monolayer of DEC on the surface in solid samples with large surface loading) than in dry NaA samples and show the clear second-order behavior (Fig. 3). The TTA becomes the most important pathway of ^{3}TPP decay in the presence of DEC if the local ^{3}TPP concentration is large enough. The coadsorption of DEC onto the surface may increase the molecular mobility of TPP on the surface due to the shielding of strong adsorption sites [30,31]. However, this effect is not expected to be pronounced, e.g., a four

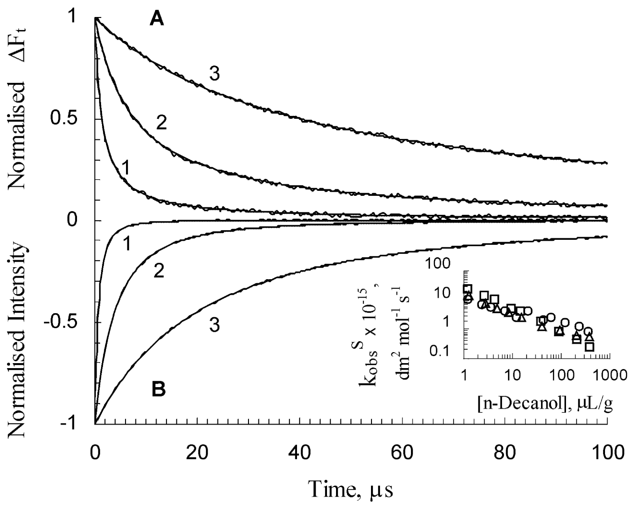
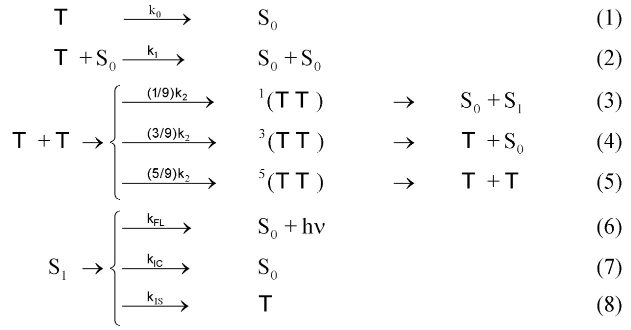


Fig. 3. (A) Normalized decays of the transient remission function change ΔF_t measured at 450 nm with 0.01 μmol/g TPP deoxygenated samples of NaA with coadsorbed 1 μl/g (1), 15 μl/g (2) and 100 μl/g (3) DEC. (B) Corresponding normalized decays of transient emission at 650 nm. Lines are the best fitting to Eq. (3) (A) and Eq. (4) (B). Inset shows the dependence of TTA rate constant related to the surface area, ${k_{\mathrm{obs}}}^{\mathrm{S}}$ (see text), on DEC concentration in the solid NaA samples with 0.01 μmol/g (□), 0.2 μmol/g (△) and 2 μmol/g (○) TPP.

times acceleration of the bimolecular rate was observed after addition of the DEC in submonolayer amounts onto the silica surface [30]. Moreover, the retardation of bimolecular fluorescence quenching on alumina surface in the presence of long chain alcohols was reported [12]. We suppose that the dramatic acceleration of ^{3}TPP mobility in the present system is related to the fast adsorption–desorption process and desorbed ^{3}TPP diffusion in the DEC microphase (see below). One could expect a fast desorption of photogenerated ^{3}TPP from the surface. For instance, adsorption–desorption relaxation times shorter than 1 μs of neutral molecules have been reported at alkylated silica/solution interfaces [32].

Little is still known about the TTA mechanism in porphyrins. For instance, it was found in some systems that, in the case of porphyrins, TTA results in electron transfer between triplets with formation of radical ions [10,33]. However, the formation of radical ions was not detected in the present system. The TTA does not lead to neat electron transfer, although this is energetically feasible, due to fast backward electron transfer with regeneration of corresponding excited states, unless there are specific reasons for charge separation [33,34]. In the present study, a strong TTADF was detected with a spectral pattern similar to those of PF and steady-state fluorescence. Therefore, the kinetic Scheme 1 was used [7,35] for quantification of ^{3}TPP decay kinetics. Scheme 1 takes into account the ^{3}TPP self-decay (reaction 1), the quenching by ground-state TPP (reaction 2), three possible channels of TTA via singlet (reaction 3), triplet (reaction 4) and quintet (reaction 5) intermediate complexes and three pathways of first excited singlet state decay: emission (reaction 6), internal conversion (reaction 7) and intersystem crossing (reaction 8). The integration of the system of equations corresponding to Scheme 1 in steady-state approximation ($d[S_1]/dt = 0$) gives Eq. (3) for ^{3}TPP concentration at time t, $[T]_t$,



Scheme 1.

$$\frac{[T]_t}{[T]_0} = \frac{k^1 \exp(-k^1 t)}{k^1 + k_{\mathrm{obs}}[T]_0(1 - \exp(-k^1 t))} \tag{3}$$

where $k^1 = k_0 + k_1[\mathrm{TPP}]$ ([TPP] is the analytical concentration of TPP) and $k_{\mathrm{obs}} = \frac{1}{9}k_2(5 - \varphi_{\mathrm{T}}) - k_1$. The time dependence of TTADF intensity, $I_{\mathrm{TTADF}}(t)$, is described by

$$I_{\mathrm{TTADF}}(t) = k_{\mathrm{FL}}[S_1] = \tfrac{1}{9}\varphi_{\mathrm{FL}} k_2 [T]^2 \tag{4}$$

and the relative yield of TTADF, $Y_{\mathrm{TTADF}}/Y_{\mathrm{PF}} = \varphi_{\mathrm{T}}/(5 - \varphi_{\mathrm{T}})$, where Y_{TTADF} is the total amount of light emitted in the course of TTADF.

A perfect fit of the ^{3}TPP and TTADF decay kinetics to Eqs. (3) and (4), respectively, was obtained for DEC solutions and for solid samples (Fig. 3). In multilayers of DEC on NaA external surface, the ^{3}TPP decay kinetics does not exhibit features of reactions in restricted geometries and a simple homogeneous model can be applied [11], supporting the idea that TTA takes place in relatively homogeneous DEC microphase.

In DEC solutions, the extracted value of k_{obs} near $1.9 \times 10^8\,\mathrm{l\,mol^{-1}\,s^{-1}}$ corresponds to $k_2 = 4.0 \times 10^8\,\mathrm{l\,mol^{-1}\,s^{-1}}$ if $\varphi_{\mathrm{T}} = 0.8$ (see above). The value of k_2 obtained is very close to the diffusion-controlled limit (the viscosity of DEC, $\eta = 13$ cP [36], gives $k_{\mathrm{dif}} = 8RT/3000\eta = 5 \times 10^8\,\mathrm{l\,mol^{-1}\,s^{-1}}$). The TTA of TPP in DEC seems to be a diffusion-controlled process with spin-statistical restrictions.

In order to compare the molecular mobility at different surfaces, it is convenient to relate the bimolecular rate constants to the surface concentration of reactants [1–3,6,7,30]. In diluted samples with DEC monolayer, the TTA rate constant expressed in units of surface concentration, ${k_{\mathrm{obs}}}^{\mathrm{S}}$, is $2.4 \times 10^{16}\,\mathrm{dm^2\,mol^{-1}\,s^{-1}}$ which is significantly larger than the rate constants reported for bimolecular reactions on the surfaces, in particular, in the presence of DEC submonolayer [1–3,6,7,30]. The value of ${k_{\mathrm{obs}}}^{\mathrm{S}}$ decreases dramatically with increase in DEC concentration (inset in Fig. 3) supporting the idea that the reaction volume of TTA is the total volume of DEC in the sample, rather than NaA surface.

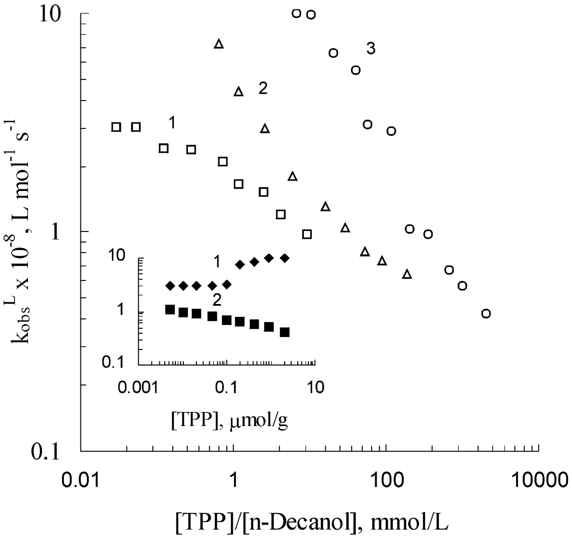


Fig. 4. Dependence of TTA rate constant related to the DEC volume, $k_{obs}{}^{L}$ (see text), on [TTA]/[DEC] varied by changing the DEC content in the solid NaA samples with 0.01 μmol/g (1), 0.2 μmol/g (2) and 2 μmol/g (3) TPP. Inset shows the dependence of $k_{obs}{}^{L}$ on surface loading in NaA samples with 300 μl/g (1) and 1 μl/g (2) of DEC.

In diluted samples with large amount of DEC when the ratio of [TPP]/[DEC] is smaller than 0.1 mmol/l (solubility of TPP in DEC), the value of the TTA rate constant, $k_{obs}{}^{L}$, calculated using the volume of DEC in the sample as a reaction space (3.0×10^8 l mol^{-1} s^{-1}), is similar to that in neat DEC and independent on DEC content and TPP concentration. The value of $k_{obs}{}^{L}$ decreases with the increase in [TPP]/[DEC] in the region where [TPP]/[DEC] (as well as [^{3}TPP]/[DEC]) is larger than 0.1 mmol/l (Fig. 4) showing the transition from the reaction in the bulk of DEC microphase to the process which involves adsorption–desorption equilibrium.

A very fast TTA was found in the presence of TPP aggregates in the samples with high TPP and DEC content (Fig. 4, plots 2 and 3, $[T]_0$ was in the range 0.01–0.1 μmol/g and always much smaller than TPP ground-state concentration). The value of $k_{obs}{}^{L}$ reaches a value one order of magnitude larger than that measured at small TPP concentration in the sample. Inset in Fig. 4 shows that the effect only appears in samples with large amount of DEC and large surface loading when new TPP aggregates were found from the absorption spectra analysis (see above). The triplet energy migration, within porphyrin aggregates in DEC microphase or within some appropriately organized aggregates on the surface can be responsible for the acceleration of triplet excitation mobility. One may suppose that the use of DEC multilayers on the surface as a reaction medium may facilitate the supramolecular organization of reactants which will induce fast triplet excitation migration neither available in homogeneous solution nor on dry surfaces.

It is worthwhile mentioning that the TTADF relative yield in DEC solution or in DEC multilayers when triplets are in DEC microphase and in the absence of TPP aggregates is 19% in accordance with that predicted by Scheme 1 if $\varphi_T = 0.8$. The Y_{TTADF}/Y_{PF} value decreases (down to 7%) for samples where triplets are adsorbed on the surface or TPP aggregates are involved. This finding implies some variation in TTA mechanism and/or quenching of TPP singlet excited state formed in reaction (3) (Scheme 1) at the liquid/solid interface and in TPP aggregates in comparison with those in the bulk of liquid phase.

3.3.2. Quenching of triplet state by molecular oxygen

A monoexponential ^{3}TPP decay kinetics was found in aerated solid samples of TPP on NaA with coadsorbed DEC when the contribution of TTA was small. The ^{3}TPP is quenched by $^3O_2$ in the presence of one DEC monolayer on the surface with $k_q = 2.4 \times 10^8$ l mol^{-1} s^{-1} which is 20 times slower than that measured for dry NaA samples (6.3×10^9 l mol^{-1} s^{-1} [16]). The increase of DEC content to three monolayers results in the insignificant decrease of k_q which becomes equal to the value found in neat DEC (1.7×10^8 l mol^{-1} s^{-1} using O_2 concentration in the gas phase). Further increase of DEC content has no effect on ^{3}TPP lifetime in aerated solid samples. Similar effects were observed for O_2 quenching of PF (see above). The contribution of gas phase oxygen diffusion to the quenching process is small even on the surface covered by very thin DEC film.

The rate constant of ^{3}TPP quenching by O_2 in neat DEC, calculated using the concentration of O_2 dissolved in DEC, is equal to 9.4×10^8 l mol^{-1} s^{-1} which is only 1.5–3 times smaller than k_q reported for nonviscous solvents [37,38]. Taking into account that this process is expected to be characterized by spin-statistical factor $\frac{1}{9}$ (quenching of ^{3}TPP by $^3O_2$ in solution results in $^1O_2$ formation with 80–90% efficiency [37,38]) one may conclude that the value of diffusion-controlled reaction with the participation of O_2 in DEC seems to be more than one order of magnitude larger than that estimated using $k_{dif} = 8RT/3000\eta = 5 \times 10^8$ l mol^{-1} s^{-1}. A nonlinear dependence on viscosity and large rate constants were reported for the oxygen quenching of chlorophyll fluorescence as well as other singlet and triplet excited states [26].

3.3.3. Delayed fluorescence in the presence of oxygen

The SOFDF can be readily detected in the presence of O_2 in both solid NaA samples [16] and in DEC. The corresponding DF kinetic curves contain the rising part followed by the decay with lifetime of the ^{3}TPP, making a difference for kinetics of direct TTADF (Fig. 5). The initial SOFDF rise originates from the participation of the mediator energy carrier. The relative yield of DF (Y_{SOFDF}/Y_{PF}, where Y_{SOFDF} is the total amount of light emitted in the course of SOFDF) from air saturated solid samples of TPP with DEC or in air saturated DEC solutions does not exceed 2%. (Y_{SOFDF}/Y_{PF} up to 15% is observed in dry NaA samples [16]). However, the peak intensity of this DF is larger than that from direct TTA.

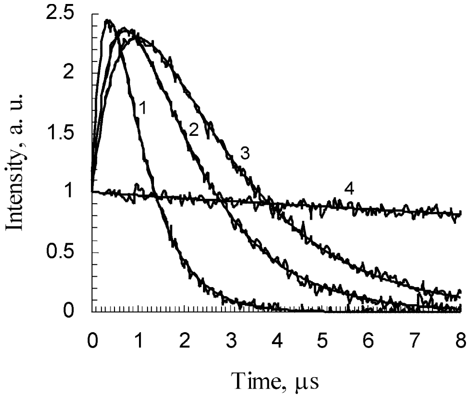


Fig. 5. Decays of the transient emission at 650 nm measured with 0.01 µmol/g TPP and 200 µl/g DEC in the solid NaA samples at air pressure 1 bar (1), 0.5 bar (2), 0.3 bar (3) and without air (4).

The analytical and numerical treatment of the singlet oxygen feedback kinetic Scheme 2 revealed that if the lifetime of the decay part of SOFDF is equal to that of triplet state, then the self-decay of $^1O_2$ is relatively slow [15–18]. The lifetime of $^1O_2$ in DEC is expected to be near 20 µs [39], therefore the self-decay of $^1O_2$ (reaction (7), Scheme 2) may be neglected at air pressures in the range 0.3–1 bar. In this case, Scheme 2 has a simple analytical solution in terms of steady-state approximation ($\mathrm{d}[(S_1, {}^3O_2)]/\mathrm{d}t = 0$) [15–18]. The expected contribution from TTADF may be taken into account if TTA is much slower than ^{3}TPP decay. The fitting of SOFDF kinetic curves gives the parameter $k_q{}^1[T]_0$ and the maximum value of $Y_{\mathrm{SOFDF}}/Y_{\mathrm{PF}}(\alpha = (\alpha_{\mathrm{FL}}{}^{\mathrm{SO}}/\alpha_{\mathrm{FL}})\varphi_{\mathrm{T}}$, where $\varphi_{\mathrm{FL}}{}^{\mathrm{SO}}$ is the quantum yield of fluorescence from the couple (S_1, $^3O_2$)) which can be observed at optimal $[O_2]$ and $[T]_0$.

In order to obtain the reliable values of $k_q{}^1$, the simultaneous fitting of 5–10 kinetic curves of SOFDF measured with a given sample loading, but at different oxygen pressures (global kinetic analysis), was carried out using common values of α for all DF curves [16–18]. In DEC solutions or in diluted solid samples with large DEC amount (all ^{3}TPP assumed to be in the DEC microphase), this procedure gives the value of α equal to 8% and $k_q{}^1$ near $9 \times 10^9\,\mathrm{l\,mol^{-1}\,s^{-1}}$ (calculated using $[T]_0$ value related to DEC volume in the sample) which is, as one should expect, an order of magnitude larger than the k_q value. The value of α (the efficiency of singlet oxygen feedback) in DEC is only insignificantly smaller than the value of α obtained at gas/solid interface (α increases from 11 to 15% with surface loading), showing that the difference between the efficiencies of (S_1, $^3O_2$) primary couple separation in DEC and at gas/solid interface is not pronounced [17,18]. The rate constants of TPP PF quenching by O_2 are noticeably smaller than the expected value of $9k_q$ (see above) implying the incomplete singlet excited state quenching by O_2 during the lifetime of (S_1, $^3O_2$) encounter complex in both solid and liquid samples.

$$
\begin{array}{llll}
\mathrm{T} & \xrightarrow{k_0} & S_0 & (1)\\
\mathrm{T} + {}^3O_2 & \xrightarrow{k_q} & S_0 + {}^1O_2 & (2)\\
\mathrm{T} + {}^1O_2 & \xrightarrow{k_q^1} & (S_1, {}^3O_2) & (3)\\
 & \xrightarrow{k_{SO}^{FL}} & S_0 + {}^3O_2 + h\nu & (4)\\
(S_1, {}^3O_2) \rightarrow \Bigg\{ & \xrightarrow{k_{SO}^{IS}} & \mathrm{T} + {}^3O_2 & (5)\\
 & \xrightarrow{k_{SO}^{IC}} & S_0 + {}^3O_2 & (6)\\
{}^1O_2 & \xrightarrow{k_O^1} & {}^3O_2 & (7)
\end{array}
$$

Scheme 2.

It is worthwhile mentioning that a key step of SOFDF ($^1O_2$–T annihilation (3), Scheme 2) which produces fluorescence seems to be also the most likely source of fluorescent state in $^1O_2$-sensitized DF of phthalocyanines in liquid solutions [40,41]. The two-step mechanism of this oxygen induced DF involves the $^1O_2$ sensitizing of the ground-state dye to its triplet state followed by energy transfer from other $^1O_2$ molecule to T. The DF yield from phthalocyanines in solution is high [42] suggesting also the inefficient $^3O_2$ quenching of S_1 within (S_1, $^3O_2$) primary couple but no reason was put forward to explain it.

The estimation of the α values for SOFDF in concentrated solid samples with small amounts of DEC gave values three times smaller as compared with those found in neat DEC. This difference may reflect the changes in lifetime and mutual orientation of reactants within (S_1, $^3O_2$) primary couple at the interfaces, relative to these parameters in the bulk liquid. The rate constants $k_q{}^1$ extracted from concentrated solid samples with small amounts of DEC are approximately four times smaller than those in neat DEC which may be attributed to the trapping of singlet oxygen by TPP aggregates on the surface as it happened on gas/solid interface [17,18].

4. Conclusion

The kinetics of direct TTA and the same energy transfer between two organic triplets mediated by molecular oxygen are compared. The data recovered from both transient absorption and DF studies at gas/solid interface, at gas/liquid/solid system and in neat liquid showed that liquid multilayers covering a solid surface may be used as a specific microreactors for bimolecular processes. A very large local concentration of reactants may be obtained using small bulk amounts. A high molecular mobility and surface induced molecular ordering at liquid/solid interface may provide possibilities which can be hardly achieved in liquid media.

It is shown that the TTA of tetraphenylporphyrin in DEC is in complete agreement with the simplest model with two diffusion-controlled pathways characterized by spin-statistical factors $\frac{1}{9}$ and $\frac{1}{3}$ being proportionally involved. The relative contribution of different mechanisms and dynamics of the overall process may be modified significantly by using liquid multilayers on solid supports as the reaction media.

The TTA of tetraphenylporphyrin in aerated DEC can be mediated by molecular oxygen leading to DF (SOFDF). On the one hand, its relative yield is one order of magnitude smaller than that of DF induced by direct TTA (TTADF) in the absence of oxygen. On the other hand, the yield of SOFDF is several times larger than the yield of TTADF in aerated DEC. This is due to two factors: the fast diffusion of oxygen in a viscous solvent as compared with the diffusion of porphyrin and the relatively high yield of fluorescence originated from the encounter complex of singlet excited state with molecular oxygen. The efficiencies of SOFDF in liquid and at the gas/solid interface are comparable. However, the latter may be significantly amplified by energy migration in porphyrin aggregates on the dry surface. The parameters of singlet oxygen feedback in the liquid multilayers on solid surfaces are different from those observed either in dry surfaces or neat liquid solutions.

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