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Delayed Fluorescence Induced by Molecular Oxygen Quenching of Zinc Tetraphenylporphyrin Triplets at Gas/Solid Interfaces of Silica and Zeolite

Peter P. Levin[†] **and Silvia M. B. Costa***

Centro de Quimica Estrutural, Complexo 1, Instituto Superior Tecnico, 1096 Lisbon Codex, Portugal

L. F. Vieira Ferreira

Centro de Quimica Fisica Molecular, Complexo 1, Instituto Superior Tecnico, 1096 Lisbon Codex, Portugal

J. M. Lopes and F. Ramôa Ribeiro

Centro de Engenharia Biológica e Química, Departamento de Engenharia Química, Instituto Superior Tecnico, 1096 Lisbon Codex, Portugal

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The quenching of Zn(II) tetraphenylporphyrin (ZnTPP) triplets adsorbed onto porous silica or NaA zeolite by molecular oxygen in the gas phase was studied at different temperatures by the diffuse-reflectance laser flash photolysis technique. The quenching is enhanced with decrease in temperature (apparent activation energies are within the range −1.5 to −2.0 kcal/mol) and occurs with high rate constants (2.1×10^5 to 2.4×10^5 $Torr^{-1}$ s^{-1}). While the ZnTPP delayed fluorescence (DF) is undetectable in evacuated samples, it appears in the presence of O_2. The yield of this oxygen-induced DF of ZnTPP corresponds to 10−20% of the prompt fluorescence in a wide range of O_2 concentration (partial O_2 pressure from 0.001 up to 10 Torr). DF kinetics exhibits a distinct rise part at relatively high O_2 pressure. Experimental results are described in terms of a singlet oxygen feedback mechanism which includes the efficient triplet energy transfer from ^{3}ZnTPP to $^3O_2$ and formation of $^1O_2$ followed by a much more efficient energy transfer from $^1O_2$ to the neighbor ^{3}ZnTPP with formation of ZnTPP in the excited singlet state. A homogeneous kinetic treatment predicts some of the unique DF peculiarities (namely the apparent quadratic dependence of DF yield on initial amount of ^{3}ZnTPP, obtained by varying the laser pulse fluence, the growth of DF with a first-order rate constant 2 times greater than that of DF decay at high oxygen concentration, and DF decaying at the same rate as ^{3}ZnTPP at high O_2 content or faster at low O_2 content) except the lack of variation of DF efficiency with ZnTPP content on the surface, strongly suggesting the existence of a specific arrangement of ZnTPP molecules. The yield of ZnTPP triplets on the surface depends essentially on the oxygen amount in the narrow pressure range from 0.01 to 0.1 Torr which is ascribed to the specificity of ZnTPP adsorption sites on the surface based on oxygen vacancies type defects.

Introduction

Bimolecular reactions at gas/solid interfaces and, in particular, quenching of excited states of molecules on the surface by molecular oxygen in the gas phase have considerable practical and theoretical interest which triggered several experimental studies of reaction kinetics and mechanisms in the past decade.[1−6] Two basic reaction mechanisms have been defined. One is the Eley−Rideal (ER)[7] type for target annihilation between gas-phase molecule and a surface-bound excited molecule. The quenching efficiency of excited states on the surface by molecular oxygen in the gas phase may increase significantly when O_2 adsorption−desorption is involved and oxygen assimilation time on the surface influences the rate of reaction in the so-called modified ER regime.[3,4] At relatively low temperatures, the reaction may become substantially Langmuir−Hinshelwood (LH)[8] in nature and be controlled by the surface diffusion of O_2.[4]

An important aspect of gas/solid interface is that the adsorption of organic molecules onto the solid surfaces may provide spatially restricted environments and inhomogeneous distribution of reactants as well as specific surface reactive sites giving an opportunity to promote selectively some processes with participation of particular intermediates which do not occur in solution. For instance, it has been concluded that O_2-mediated electron and proton transfers occur on silica-based surfaces.[3f] The enhanced diffusion of oxygen molecules on the surface of porous glass with cobalt porphyrin has been recently observed.[9] Among the characteristic chemical functions of metalloporphyrins is the efficient oxygen carriage in biological systems.[10] Porphyrin triplet states are important in photodynamic therapy since singlet oxygen, which is formed via energy transfer, attacks tumours.[11] Both these processes are regulated not only by the reactivity of porphyrins and their excited states toward molecular oxygen but, in particular, by some specific organization of the reactional systems.

The purpose of this paper is to present the investigation of the surface effect of different widely used supports on the photophysics and photochemistry of the zinc(II) tetraphenylporphyrin (ZnTPP)−O_2 system. We describe the behavior of transient absorption and emission of ZnTPP adsorbed onto very different surfaces, namely, porous silica and the external surface of zeolite particles in the presence of molecular oxygen. The kinetics of ZnTPP delayed fluorescence (DF) resulting from the quenching of ZnTPP triplet state by O_2 at the gas/solid interface

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* To whom correspondence should be addressed.
† Permanent address: Institute of Biochemical Physics, Academy of Sciences of Russia, ul. Kosygina 4, 117334 Moscow, Russian Federation.

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is detected and ascribed to singlet oxygen-mediated energy transfer from one triplet molecule to the other one (a kind of singlet oxygen feedback mechanism which was supposed to be responsible for oxygen-enhanced fluorescence in polymer matrices[12]). It will be shown that this process, which should be inefficient in homogeneous systems due to relatively small accessible triplet concentrations, may have more than 10% efficiency on the gas/solid interface due to some specific arrangement within ensembles of ^{3}ZnTPP molecules on the surface. Spectroscopic support for the assumption of a structural arrangement of ZnTPP molecules on the surface was sought from ground state absorption and steady-state emission studies.

Experimental Section

Materials. The purity of ZnTPP (from Hambright, Washington, DC) was checked by UV−vis and fluorescence spectroscopies. Benzene (Aldrich, spectrophotometric grade) was dried over P_2O_5 and then used as solvent for the ZnTPP. Samples of silica with controlled pore size 14 nm (Si-14, Aldrich grade 62, 60−200 mesh, effective N_2 BET surface area 300 m^2/g) and sodium 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) were dried in a vacuum oven at $\approx$150 °C for at least 48 h prior to use. The NaA sample was characterized by X-ray diffraction in order to check the high crystallinity level of the structure.

Sample Preparation. Benzene solutions (1−3 mL) of ZnTPP (0.0005−0.1 μM) were added to Si-14 or NaA samples (0.5 g). The suspensions were stirred and allowed to evaporate slowly. All samples were evacuated up to 1×10^{-5} Torr for 5 h at 70−80 °C and then thermostated with the accuracy ±1 °C in an ethanol bath. Selected amounts of oxygen in the sample cell were obtained by a series of connect−disconnect manipulations at room temperature within a system of calibrated volumes connected to the vacuum line. The transient decay kinetics measured in the series of experiments with gradual decrease in the amounts of O_2 up to partial pressure 0.1 mTorr obtained by expansion of the cell volume to evacuated volumes were equal to those measured in the opposite series of experiments showing perfect reproducibility of experimental results.

Instrumentation and Data Analysis. Ground-state absorption and steady-state fluorescence studies of solid samples were carried out with the spectrophotometer and fluorimeter previously described.[13] The fluorescence quantum yields of ZnTPP on the surfaces were measured using rhodamine 101 and 6G as standards by the method previously described in detail.[13]

The absorption spectra and decay kinetics of intermediates on the surface were recorded by laser photolysis in the diffuse reflectance setup described elsewhere[14] using the second harmonic (532 nm, $\leq$50 mJ cm^{-2}, 6 ns pulse width, 10 pps) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-3) as an excitation source. The analyzing source was a 300 W xenon arc lamp (XM 300-5HS, ORC Lighting Products), and detection used a F/3.4 monochromator (Applied Photophysics) and R446 photomultiplier (Hamamatsu), the output from which was digitized by an averaging system consisting of a Tektronix 2430A digital oscilloscope (up to 150 MHz) coupled to a PDP 11/73 microcomputer. The same sample geometry without analyzing light was used for monitoring delayed fluorescence kinetics.

Ground-state reflectance spectra of ZnTPP on the surface were analyzed in terms of a difference in remission functions of samples of NaA or Si-14 with and without ZnTPP, respectively

$$\Delta F(R) = (1 - R)^2/2R - (1 - R')^2/2R' = 2\epsilon C/S \quad (1)$$

where R and R' are diffuse reflectance from the surface of the samples with and without ZnTPP, respectively, ϵ is the molar Naperian absorption coefficient of ZnTPP, C is the ZnTPP concentration, and S is the scattering coefficient. The function $\Delta F(R)$ is proportional to the surface concentration of absorbers for optically thick samples with homogeneous distribution of absorbers throughout the sample.[15] Samples of very low concentrations of ZnTPP on the surface with absorption at 532 nm being less than 10% and high laser fluences were used in the present study in most systems. Transient signal intensities did not increase proportionally with increasing laser intensity and saturate in most systems, demonstrating that a saturated plug of ground state totally converted into transient is produced thereby supporting the validity of Kubelka−Munk treatment to analyze the decay of transients

$$\Delta F(R)_t = (1 - R_t)^2/2R_t - (1 - R)^2/2R = 2(\epsilon_t - \epsilon_g)C_t/S \quad (2)$$

where R and R_t are the reflectances observed before and at time t after lasing, respectively, ϵ_t and ϵ_g are the molar Naperian absorption coefficients of transient and ground state, respectively, and C_t is the transient concentration.[15]

Results and Discussion

1. Ground State Reflectance and Steady State Emission Spectra of ZnTPP on the Surfaces. The diffuse reflectance spectra of ZnTPP samples adsorbed on Si-14 and NaA (Figure 1A) show the well-known characteristic absorption of ZnTPP near 550 and 600 nm (Q-bands) and a very strong one near 420 nm (B or Soret band). An order of magnitude difference in $\Delta F(R)$ values found for Si-14 and NaA samples with the same sample loadings should be related to a difference in scattering coefficients.[15] The one corresponding to the very good reflector NaA is 10 times larger than that of Si-14 which exhibits relatively low reflectance. Spectral shapes and peak positions obtained using the difference in remission functions ($\Delta F(R)$, eq 1, is a linear function of ZnTPP concentration on both surfaces up to a loading of 0.1 μmol/g) resemble those of ZnTPP in solutions with the exception of blue shift (from 423 nm in benzene or 421 nm in methanol to 417 and 415 nm on the surfaces of NaA and Si-14, respectively) and broadening (half-width is near 11 nm in solvents and near 15 nm on both surfaces) of the most sensitive B-band. Similar broadening of B bands observed for ZnTPP and other porphyrins adsorbed on the surface of small semiconductor particles in aqueous solutions[16] in monolayers and covalently linked dimers and arrays of porphyrin molecules was explained in terms of exciton dipole−dipole coupling between transition moments of B-bands.[17]

The broadening and blue shift of the ZnTPP B-band on Si-14 and NaA surfaces may reflect the existence of some form of stack type organization even at very low sample loadings (0.1 μmol/g ZnTPP corresponds to 0.015% of Si-14 N_2 BET surface area and to 1.5% of estimated external surface area of NaA powder if the size of ZnTPP molecule is taken to be equal to 1 nm). It was shown that aromatic compounds begin to aggregate on the silica surface at concentrations much lower than a monolayer.[3,15] The ability of porphyrins to form aggregates is well-known.[18] Neither positions nor widths of B-bands exhibit any variations up to a loading of 0.1 μmol/g, showing that the structure of porphyrin aggregates is independent on ZnTPP content on the surface. However, further increase of sample loadings results in significant broadening
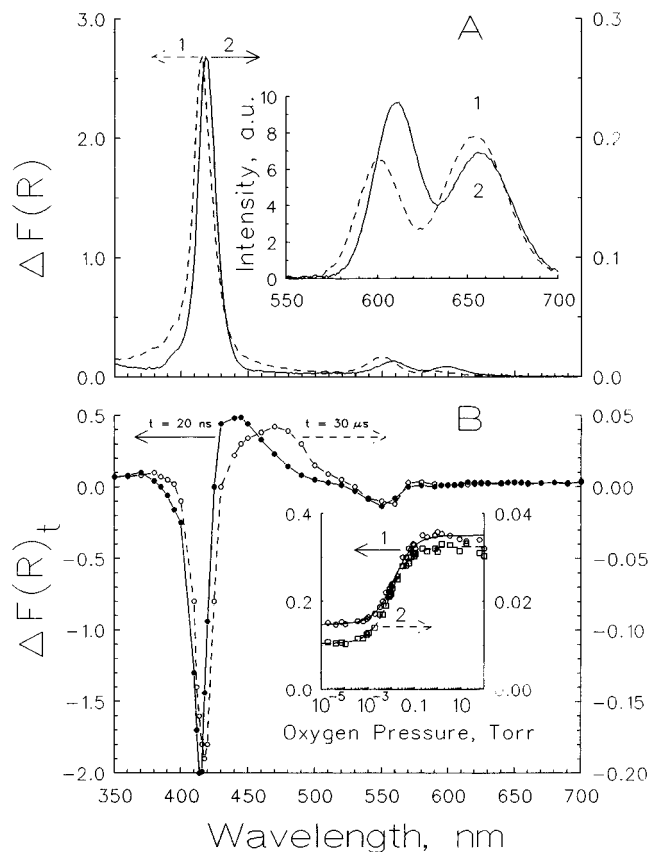
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Figure 1. (A) Reflectance spectra of Si-14 (1) and NaA (2) samples with 0.05 μmol/g ZnTPP plotted using differences in remission functions $\Delta F(R)$, eq 1. Inset shows the corresponding steady state corrected emission spectra. (B) Transient absorption spectra showing remission function change ($\Delta F(R)_t$, eq 2) of Si-14 with 0.05 μmol/g ZnTPP at oxygen partial pressure 1 Torr measured immediately ($t = 20$ ns) and 30 μs after the laser pulse. Inset shows the dependence of $\Delta F(R)_t$ measured at 460 nm 50 ns after the laser pulse (50 mJ/cm^2) on partial pressure of oxygen obtained for Si-14 (1) and NaA (2) samples with 0.05 μmol/g ZnTPP. Lines are obtained by fit to eq 3 (see text for details).

of B-bands leaving Q-bands unchanged due to some other aggregation of ZnTPP on surfaces of both Si-14 and NaA. This aggregation effect becomes noticeable for Si-14 at a surface coverage 2 orders of magnitude smaller than that for NaA (the relatively large ZnTPP molecules are definitely located at external surface of crystallites of NaA zeolite, where the internal network is characterized by very small windows of 0.4 nm in diameter). Therefore, the concentration of ZnTPP adsorption sites on the external surface of zeolite is much higher than that on the surface of amorphous silica. It was already found that porphyrin molecules are able to adsorb onto the zeolite in monolayer quantities.[19]

On the other hand, some surface effects on ZnTPP absorption may be attributed to relatively strong interaction of ZnTPP with the surface and to the inhomogeneity of the surface adsorption sites, resulting in broadening of absorption bands of organic molecules and their transients.[14] The red shift of Q-bands and an increase of vibronic Q(0,0) relatively to the vibronic Q(0,1) band which is observed on going from Si-14 to NaA (Figure 1A) are similar to spectral changes characteristic of a binding of ZnTPP by e.g. pyridine derivatives[20] or ammonium salts[21] and may be an indication that the interaction of ZnTPP with NaA surface is stronger than with the surface of Si-14. Zeolite A presents the highest cation concentration and a considerable heterogeneous surface as far as electrical charges are concerned. Taking into account the chemical structure of ZnTPP, a strong

interaction of its highly polarizable π-electron clouds with the zeolite surface may be envisaged and, possibly, also the interaction of the Zn(II) species with the Lewis basic sites.

The emission spectra of ZnTPP on Si-14 and NaA (inset in Figure 1A) are similar to those observed in fluid solutions with the exception of small shifts and noticeable changes in relative intensities of two vibronic bands. These spectral variations are very similar to those observed for aggregated ZnTPP systems.[17] The fluorescence spectrum on NaA is noticeably shifted to the red relative to that on Si-14, and the 0−0/0−1 ratio increases from 0.85 up to 1.4, consistent with spectral changes characteristic of a complex formation of monomer and aggregated forms of ZnTPP with e.g. pyridine derivatives and ammonium salts.[20,21]

Neither yield nor spectra of ZnTPP fluorescence on the surface depend on the O$_2$ partial pressure in the range 0.1− 1000 mTorr. Fluorescence quenching by oxygen becomes noticeable at high pressures. Corresponding Stern−Volmer plots have slopes 3.6×10^{-3} and 4.4×10^{-3} Torr^{-1} for Si-14 and NaA, respectively. Fluorescence quantum yield values of ZnTPP on both surfaces (estimated as 0.025 ± 0.005) are similar to those in solution (values of ZnTPP fluorescence quantum yield in the range 0.03−0.04 have been reported for different solvents).[22] Therefore, one may assume that the fluorescence lifetime on the surface is similar to that in solution (approximately 2 ns[17,22]) and ZnTPP fluorescence quenching by oxygen occurs on the surface with a quenching rate constant $\approx 2 \times 10^6$ Torr^{-1} s^{-1}, nearly identical to those found for the modified ER quenching of aromatic singlets by oxygen on silica surfaces.[3]

2. Transient Absorption of ZnTPP on the Surfaces. Photoexcitation of ZnTPP on Si-14 and NaA with and without O$_2$ produces the transient difference spectra (Figure 1B) which resemble those of ^{3}ZnTPP in solutions[23] or on other surfaces[16] with the exception of the blue shift of the transient difference band near 440 nm observed at short times after the laser pulse (the absorption maximum has been reported at 460−470 nm in different solvents[23,24]). The complexation of ZnTPP or *p*-phenyl substitution with electron-withdrawing groups results also in a blue shift of ^{3}ZnTPP absorption band near 470 nm.[23d] The T−T absorption band of face-to-face porphyrin aggregates is blue-shifted relative to that observed in monomers.[17f]

In the presence of oxygen in the system there is a distinct dependence of the transient absorption spectra on the observation time (Figure 1B) showing the existence of two distinguishable different populations of ZnTPP molecules on the surface. Transients observed at long times have the same absorption maximum near 470 nm as reported for ^{3}ZnTPP in solution. In the absence of oxygen the time dependence of the transient absorption spectra is not observed.

The yield of ^{3}ZnTPP on both surfaces exhibits an unusual S-shaped dependence on O$_2$ content in reaction cell (inset in Figure 1B). The increase of partial oxygen pressure in the system from 1 to 100 mTorr results in a sharp increase of ^{3}ZnTPP amount (in 2.4 and 3.2 times on Si-14 and NaA, respectively). It is well-known that zeolites as well as silica surfaces provide a variety of active sites and defects which influence photophysical and photochemical reactions.[25] The defects or active sites which are able to either reduce the yield or lifetime of ^{3}ZnTPP appear only when O$_2$ is removed and have to be involved in the observed dependence of ^{3}ZnTPP yield on O$_2$ content. These centers should not affect the singlet excited state of ZnTPP on the surface, since the yield of ZnTPP fluorescence is independent of O$_2$ content at partial pressures smaller than 1 Torr. Defects originate on oxygen displacement
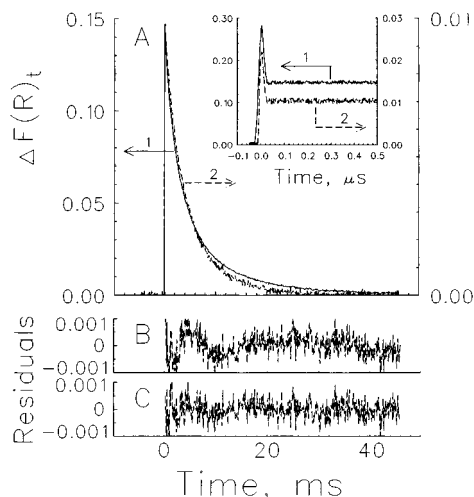
Figure 2. (A) Decays of the transient remission function change $\Delta F(R)_t$ measured at 460 nm with 0.05 μmol/g ZnTPP samples of Si-14 (1) and NaA (2) at partial pressure of oxygen $\leq$0.1 mTorr (see text for the respective parameters). Inset shows the earlier parts of corresponding decays. (B and C) Residuals from the fit of kinetic curve 1 to eq 4 and 5, respectively.

Figure 3. (A) Decays of the transient remission function change $\Delta F(R)_t$ measured at 460 nm with 0.05 μmol/g ZnTPP samples of Si-14 (1) and NaA (2) at partial pressure of oxygen 1 Torr (see text for the respective parameters). Inset shows the transient decays measured at 385 and 425 nm with Si-14 sample. (B and C) Residuals from the fit of kinetic curve 1 to eq 4 and 5, respectively.

and are related to neutral oxygen vacancies, namely oxygen hole centers ($\equiv$Si$-$O) and peroxy radicals ($\equiv$Si$-$O$-$O)[26] which may effectively reduce the ^{3}ZnTPP lifetime on the surface by enhancement of intersystem crossing via spin exchange (see results on transient kinetics below). Aromatic hydrocarbon triplets with energies similar to that of ^{3}ZnTPP (1.6 eV[22,23]) are quenched by sterically shielded N$-$O radicals with relatively small rate constants,[27] whereas similar processes with peroxy radicals without steric hindrance in the reactive center occur at the diffusion-controlled limit.[28]

The dependence of ^{3}ZnTPP yield on O$_2$ pressure follows a Langmuir-type adsorption isotherm with saturation at partial oxygen pressure near 1 Torr and fit to the following Langmuir-type equation (see inset in Figure 1B)

$$([^3ZnTPP]_{O_2} - [^3ZnTPP]_0)/[^3ZnTPP]_\infty = K[O_2]f/(1 + K[O_2]) \quad (3)$$

where $[^3ZnTPP]_0$, $[^3ZnTPP]_\infty$, and $[^3ZnTPP]_{O_2}$ are the amounts of ^{3}ZnTPP observed in evacuated samples, at high oxygen content, and at a given pressure, respectively, K is the adsorption-like equilibrium constant, and f is the fraction of sites which give quenching centers after evacuation or the number of corresponding defects within a space occupied by the ZnTPP molecule. Values of K as high as 77 and 110 Torr^{-1} and f near 0.7 and 0.6 were obtained for NaA and Si-14, respectively. Values of f obtained correspond to defect densities approximately 2$-$5 times higher than those found in direct energy transfer interaction with singlet aromatic molecules on silica and silicalite.[25] This finding supports the hypothesis that ZnTPP molecules are localized on special surface sites which are characterized by a high density of defects. Very high observed K values seem to provide evidence that these centres are sites of chemisorbed molecular oxygen.

Triplet State Kinetics in the Absence of Oxygen. The lifetime of ^{3}ZnTPP in highly evacuated samples of NaA and Si-14 is around 5 ms (Figure 2A) which is shorter than that in solution (lifetime as long as 25 ms has been reported in solutions[22]). Neither sample loading nor laser fluence has any distinguishable effect on ^{3}ZnTPP decay kinetics. Temperature studies gave very small positive activation energies of 0.3$-$0.4 kcal/mol in the absence of O$_2$ in the reaction cell. These results suggest that
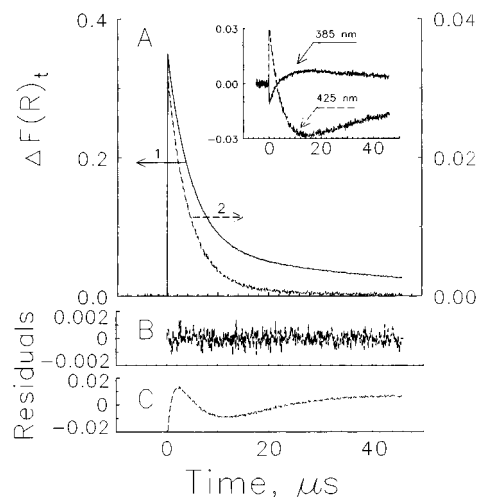
the energy-dissipative pathway of ^{3}ZnTPP on the surface is some unimolecular intrinsic intersystem crossing probably enhanced by some ZnTPP distortion due to adsorption on defective sites of the surface. The decay kinetics of ^{3}ZnTPP on the surface of evacuated samples is nonexponential and may be well fitted either to the biexponential function

$$\Delta F(R)_t = A_f \exp(-k_f t) + A_s \exp(-k_s t) \quad (4)$$

with k_f = 440 and 290 s^{-1}, k_s = 120 and 100 s^{-1}, and A_f/A_s = 1.3 and 3.6 for Si-14 and NaA, respectively, or to the dispersed kinetic Albery model with Gaussian distribution of the natural logarithm of first-order rate constant

$$\Delta F(R)_t/\Delta F(R)_t(t=0) = \pi^{-1/2} \int_{-\infty}^{+\infty} \exp(-x^2) \times \exp[-k_a t \exp(\gamma x)] \, dx \quad (5)$$

with mean rate constants k_a = 260 and 240 s^{-1} and width of the distribution γ = 1.1 and 0.67 for NaA and Si-14, respectively (Figure 2). The fitting to eq 5 may be even slightly better than that to eq 4 (see residuals in Figure 2) in spite of the smaller number of parameters in eq 5 than that in eq 4. Equation 5 described well the nonexponential kinetics of unimolecular decay of excited states of aromatic hydrocarbons and metallocomplexes on silica surface.[3,4] The inspection of the early parts of ^{3}ZnTPP decays in degassed samples showed the existence of some short-lived component with lifetime shorter than the resolution of the detection system (see inset in Figure 2A). This component disappears in the presence of 0.1 Torr of O$_2$ and seems to correspond to the fraction of ^{3}ZnTPP missing in degassed samples due to the quenching by surface radical centers (see above).

Kinetics of Triplet State Quenching by Oxygen. The ^{3}ZnTPP decay kinetics on the surface in the presence of O$_2$ becomes faster and also cannot be fitted to a single exponent (Figure 3). A two-exponential function (eq 4) describes better the ^{3}ZnTPP decay kinetics than the Albery one (eq 5) at relatively high oxygen pressures, when ^{3}ZnTPP reacts only with oxygen (see residuals in Figure 3). The decay kinetics shows a distinct dependence on the wavelength of observation and clearly demonstrates the existence of at least two distinguishable ^{3}ZnTPP populations with characteristic kinetic patterns observed
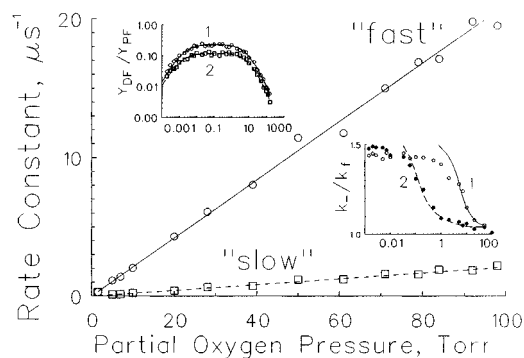
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Figure 4. Dependence of first-order decay rate constants for "fast" and "slow" populations of ^{3}ZnTPP on oxygen partial pressure extracted from fit to eq 4 of decays kinetics of the transient remission function change $\Delta F(R)_t$ measured at 460 nm on Si-14. Insets show the corresponding dependence of the yield of ZnTPP delayed fluorescence, Y_{DF}, related to that of prompt fluorescence, Y_{PF}, corrected for the variation of triplet yield with O_2 content (top) and ratio of first-order rate constants of delayed fluorescence decay, k_-, to that of decay of the "fast" population of ^{3}ZnTPP, k_f (bottom), measured for ZnTPP adsorbed (0.05 μmol/g) on Si-14 (1) and NaA (2). Lines on both insets are the results of the corresponding fits to kinetic Scheme 1 (see text for parameters and details).

Figure 5. Arrhenius temperature dependence for first-order decay rate constants of "fast" population of ^{3}ZnTPP (3 and 4, $E_a = -1.99$ and -1.45 kcal/mol, respectively) and those of delayed ZnTPP fluorescence (1 and 2, $E_a = -1.51$ and -1.88 kcal/mol, respectively) measured for ZnTPP adsorbed (0.05 μmol/g) on Si-14 (1 and 4) and NaA (2 and 3) at partial oxygen pressure 1 Torr. Insets show the dependence of first-order decay rate constant of "slow" population of ^{3}ZnTPP on Si-14 on square root of temperature (top) and Arrhenius temperature dependence of the yield of ZnTPP delayed fluorescence, Y_{DF}, related to that of prompt fluorescence, Y_{PF}, obtained for corresponding samples of Si-14 (1) and NaA (2) (bottom, $E_a = 0.21$ and 0.18 kcal/mol, respectively).

near the isosbestic points of B-band (see inset in Figure 3). The relatively long-lived populations are characterized by decay rate constants, k_s, which are approximately 5 and 10 times smaller than those for short-lived ones and by relative contributions $A_s/(A_s + A_f)$ (see eq 4) being equal to 0.05 and 0.2 at 460 nm for NaA and Si-14, respectively. A discrete biexponential behavior with wavelength-dependent decay kinetics has been recently found for excited states of aromatic molecules covalently bound to some selected small population of uniquely active silanols which are located in clusters.[25b] The dynamic behavior of ^{3}ZnTPP on the surface seems to exhibit similar features.

Figure 4 shows that a linear relationship exists between O_2 partial pressure and k_f or k_s obtained by fitting the ^{3}ZnTPP decay to eq 4 giving quenching rate constants k_q of the "fast" population of ^{3}ZnTPP equal to 2.1×10^5 and 2.4×10^5 Torr^{-1} s^{-1} at 20 °C and of the "slow" population approximately 10 and 5 times smaller for Si-14 and NaA samples, respectively. Similar linear dependence was observed for gas/solid reactions which obeyed a ER-type mechanism.[2,3] In the limit of a smooth surface the heterogeneous gas—target quenching can be described by eq 6

$$k_q^s = \pi \alpha \nu r^2 / 4kT \tag{6}$$

where α is the efficiency of the reaction ($\alpha \ll 1$), ν is the oxygen mean molecular velocity ($\nu = (8kT/\pi M)^{1/2}$, M is the mass of oxygen molecule), r is the interaction radius for the reactants ($r \cong 0.7$ nm for ^{3}ZnTPP—O_2 couple).[2c] Equation 6 gives k_q^s values equal to those measured experimentally for excited singlet and triplet ZnTPP quenching by O_2 on the surface with values of α being equal approximately to 0.5 and 0.05, respectively. The efficiency of excited singlet quenching by oxygen is expected to be near 1 in solution and that of triplet is reduced by a spin-statistic factor 1/9. However, a low efficiency should be expected for a gas phase reaction in the absence of mediating factors, such as a solvent cage which increases the encounter time and promotes the energy relaxation.[3d] The contribution of the LH mechanism may supply such mediating factors and results in an increase in the quenching efficiency.

The gas phase ER mechanism predicts the linear increase of k_q with the square root of temperature.[3d] Indeed such temper-
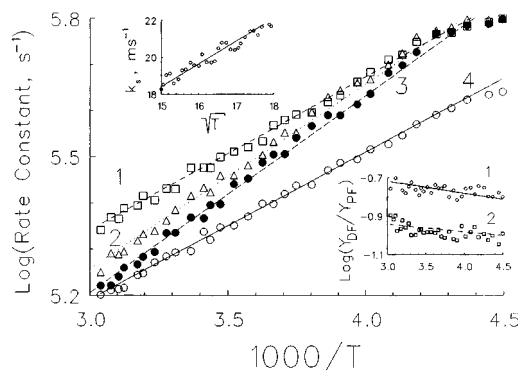
ature dependence is observed for "slow" population quenching on Si-14 (insets in Figure 5, apparent activation energy in Arrhenius terms is 0.3 kcal/mol). However, "fast" populations of ^{3}ZnTPP on both surfaces show decreasing oxygen quenching efficiencies with increasing temperature (Figure 5). Similar temperature dependence was found in the quenching of excited states of metallocomplexes and aromatic hydrocarbons on silica surfaces where conditions are such that the noticeable contribution of LH mechanism modifies the ER process.[3,4]

3. Transient Emission of ZnTPP on the Surfaces. Photoexcitation of ZnTPP on both surfaces results in the appearance of prompt ZnTPP fluorescence (PF) with time profile similar to that of the laser pulse. There is no detectable long-lived emission from highly evacuated samples showing that the yield of phosphorescence of ZnTPP on the surface is low and any processes which can give rise to delayed fluorescence (DF); i.e., triplet—triplet annihilation and thermally activated transition from ^{3}ZnTPP to the excited singlet state are not efficient in this system. Triplet—triplet annihilation on the surface is a consequence of molecular mobility.[15] This process and the accompanying DF were observed in several other systems on silica.[14,29] The lack of observation of any features of T—T annihilation and DF for samples of ZnTPP aggregated on surface defects seems to emphasize the low molecular mobility of ZnTPP on the surface.

Delayed Fluorescence of ZnTPP on the Surface in the Presence of Oxygen. The investigation of transient luminescence of ZnTPP on the surface under a variety of experimental conditions in order to detect any long-lived emission led to the unexpected result that while DF from highly evacuated samples is practically undetectable in our experimental setup it is observed for both surfaces in the presence of even small amounts of O_2 in reaction cell. The intensity (I_{DF}) and yield (the total amount of emitted light, Y_{DF}) of this O_2-induced DF is more than 1×10^{-5} and 0.2, respectively, compared to similar characteristics of PF (I_{PF} and Y_{PF}, respectively). The DF spectrum practically coincides with the one of ZnTPP PF for both surfaces.

The specific feature of oxygen induced DF kinetics is the existence of a distinct rising part which can be easily measured for Si-14 samples at relatively high oxygen partial pressures (Figure 6). The fitting of corresponding kinetic curves to the
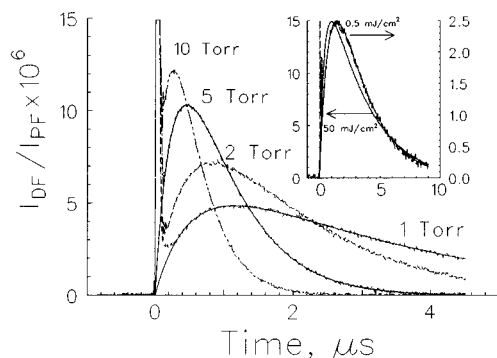
Figure 6. Decays of transient emission at 650 nm measured with 0.05 μmol/g ZnTPP on Si-14 at laser pulse energy 50 mJ/cm^2 and partial pressure of oxygen 10, 5, 2, and 1 Torr. Inset shows similar decays measured at laser pulse energies 0.5 and 50 mJ/cm^2 with Si-14 sample loading 0.1 μmol/g. Lines are the result of fit to eq 9.

simplest biexponential function, eq 7

$$I_{DF} = A_{DF}(\exp(-k_-t) - \exp(-k_+t)) \qquad (7)$$

is reasonable. At relatively high O_2 partial pressures the value of k_+ measured for Si-14 samples equals approximately 2 times that of k_-. The dependence of k_+ on O_2 partial pressure is not linear and shows a tendency to go on a limit estimated as 1.5 $\times$ 10^6 s^{-1} at low O_2 partial pressure. The rising part of DF on NaA was experimentally distinct at relatively high pressures but it was faster relative to that on Si-14 and not measurable quantitatively. The interesting unusual feature of DF kinetics on Si-14 is the 2 times decrease and 1.5 times increase of apparent values of k_+ and k_-, respectively, with the decrease of DF intensity by attenuation of laser pulse fluence (inset in Figure 6).

The value of k_- coincides with that for "fast" population decay of ^{3}ZnTPP absorption on both surfaces at high oxygen pressures. The decrease of O_2 pressure results in acceleration of DF decay as compared to ^{3}ZnTPP. The dependence of the ratio of DF decay rate constant to that of "fast" ^{3}ZnTPP is S-shaped with a limiting k_- value which is approximately 1.5 times larger than that for "fast" ^{3}ZnTPP decay for both surfaces (inset in Figure 4). The temperature dependence of k_- is characterized by slopes equal to those measured for "fast" ^{3}ZnTPP decay (Figure 5). These results suggest that the quenching of "fast" ^{3}ZnTPP population by O_2 is responsible for the appearance of DF on both surfaces.

The inset in Figure 5 demonstrates that the yield ratio of DF/PF (Y_{DF}/Y_{PF}) is practically temperature independent since the increase of k_- with temperature decrease is compensated by the corresponding increase of DF intensity. This finding suggests that several parameters involved in the process of DF rise and decay are characterized by a different temperature dependence which cancel each other out.

The dependence of DF relative yield on oxygen partial pressure shows the plateau region in a wide range of oxygen content for both surfaces (inset in Figure 4) if the corresponding change of ^{3}ZnTPP yield on O_2 content is taken into account (inset in Figure 1B). The increase of Y_{DF} with O_2 content at low pressure coincides with the competition of two ^{3}ZnTPP decay pathways, namely a self one and one due to quenching by O_2. The abrupt Y_{DF} falloff with O_2 pressure increase at high oxygen content in the reaction cell suggests the existence of a competition between quenching of ^{3}ZnTPP by O_2 and reaction of ^{3}ZnTPP with some other species which gives the emitting singlet state of ZnTPP.

Figure 7 shows the dependence of the DF relative yield on PF yield which was varied by changing the laser pulse fluence
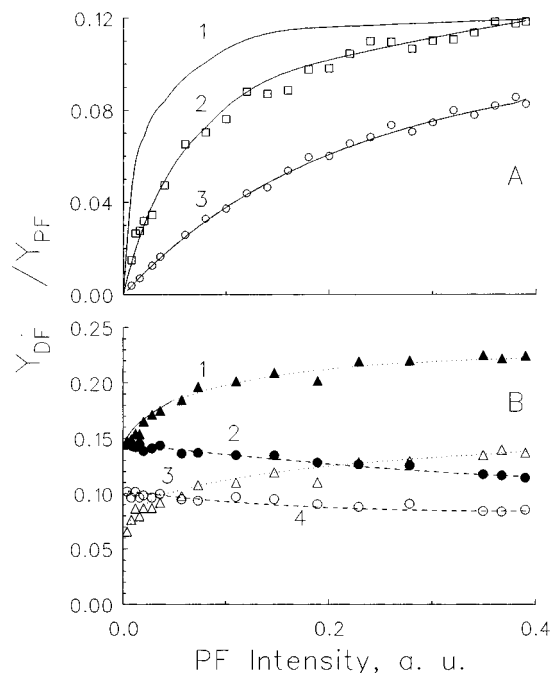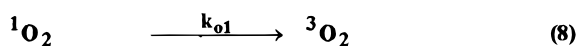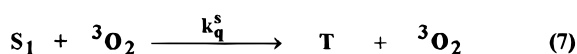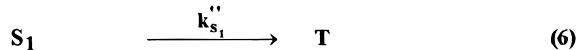

Figure 7. (A) Dependence of the yield of ZnTPP delayed fluorescence, Y_{DF}, related to that of prompt fluorescence, Y_{PF}, on peak intensity of prompt fluorescence at oxygen partial pressure 0.05 (2) and 5 Torr (3) obtained for NaA sample with 0.05 μmol/g ZnTPP by variation of laser pulse energy (0–50 mJ/cm^2). Lines 1, 2, and 3 are obtained from kinetic scheme 1 with $k_{o1} = 3 \times 10^4$ s^{-1} (1, 2, and 3) and $k_q^1[T_0]$ varied in the range (0–3.6) $\times$ 10^6 s^{-1} (1 and 3) and (0–4) 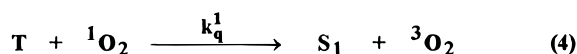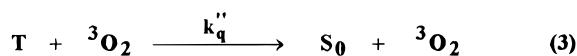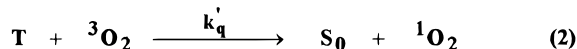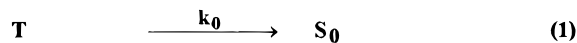$\times$ 10^5 s^{-1} (2) (see text for details). (B) A similar dependence obtained at oxygen partial pressure 0.05 (1 and 2) and 5 Torr (3 and 4) for Si-14 (1 and 3) and NaA samples (2 and 4) by variation of sample loading at laser pulse energy 50 mJ/cm^2.

(Figure 7A) or by changing the sample loading (Figure 7B). The correlations in Figure 7A are not linear but definitely show that the amount of light emitted in DF increases much faster than in PF (in other words the efficiency of DF increases with ^{3}ZnTPP amount), implying the existence of a quadratic dependence when two triplets are involved in generation of one quanta of light. On the other hand, Figure 7B shows that the DF relative yield is independent of ^{3}ZnTPP initial amount in a wide range if the initial concentration of ^{3}ZnTPP is varied by corresponding changes in sample loading. This inconsistency (the dependence of the result on the method of preparation of the reactional system) suggests that the DF generation takes place in ensembles of ^{3}ZnTPP molecules where the organization is independent of the sample loading.

4. Kinetic Scheme for Singlet Oxygen Feedback Mechanism of Delayed Fluorescence. The collection of results presented above shows that there is a mediator which appears in the process of ^{3}ZnTPP quenching by O_2 and then transfers the corresponding amount of energy to the other triplet state generating the excited singlet state of ZnTPP. Singlet oxygen may be such a mediator (singlet oxygen feedback mechanism) and agent responsible for the appearance of DF in the presence of molecular oxygen.[12]

The quenching of ^{3}ZnTPP by O_2 in solution results in $^1O_2$ formation with high efficiency (the value as high as 0.83 has been reported).[24d] The two lowest electronically excited singlet states of molecular oxygen lie approximately 0.98 and 1.64 eV, respectively, above the triplet ground state and may be generated by energy transfer from ^{3}ZnTPP (1.6 eV). The energy of a variety of transitions between lowest electronic states of molecular oxygen is sufficient to foresee the energy transfer to ^{3}ZnTPP with formation of the first excited singlet state of ZnTPP

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SCHEME 1

$$T \xrightarrow{\quad k_0 \quad} S_0 \qquad (1)$$

$$T + {}^3O_2 \xrightarrow{\quad k_q' \quad} S_0 + {}^1O_2 \qquad (2)$$

$$T + {}^3O_2 \xrightarrow{\quad k_q'' \quad} S_0 + {}^3O_2 \qquad (3)$$

$$T + {}^1O_2 \xrightarrow{\quad k_q^1 \quad} S_1 + {}^3O_2 \qquad (4)$$

$$S_1 \xrightarrow{\quad k_{S_1}' \quad} S_0 \qquad (5)$$

$$S_1 \xrightarrow{\quad k_{S_1}'' \quad} T \qquad (6)$$

$$S_1 + {}^3O_2 \xrightarrow{\quad k_q^s \quad} T + {}^3O_2 \qquad (7)$$

$${}^1O_2 \xrightarrow{\quad k_{o1} \quad} {}^3O_2 \qquad (8)$$
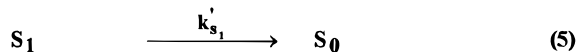
(2.1 eV[22,23]). This energy transfer process is a spin-allowed reaction and can be a diffusion-controlled one in condensed media. The singlet states of molecular oxygen have quite long lifetimes in the absence of collisions (values up to 45 min and 7 s, respectively, have been reported).[30] In condensed media the lifetime of ${}^1O_2$ decreases due to the electronic-to-vibrational energy transfer via a dipole−dipole interaction but is still in the range 1 μs to 100 ms depending on the solvent[31] making the singlet oxygen feedback mechanism a feasible one.[12]

Therefore, we propose that the simplified homogeneous kinetic model shown in Scheme 1 may be used to describe the kinetics of oxygen-induced DF of ZnTPP on the surface of Si-14 and NaA after the laser pulse. Here, it is assumed for simplicity that the quenching of singlet excited state of ZnTPP by O_2 (reaction 7) results in ^{3}ZnTPP formation as a major pathway since the amount of ^{3}ZnTPP generated during the laser pulse did not decrease with O_2 content in the range of oxygen partial pressures when the quenching of PF by O_2 is noticeable. The system of differential equations was numerically integrated and treated analytically. It is possible to make two approximations to solve the reaction Scheme 1 analytically. The first one is a steady state approximation, $d[S_1]/dt = 0$, which is valid since the rate constant of S_1 self-deactivation ($k_{S_1} = k_{S_1}' + k_{S_1}''$) is much larger than that of S_1 formation. The second is the assumption that $[{}^1O_2] \ll [{}^3O_2]$ is valid if $k_q^1 \gg k_q'$ (one has to suppose that the value of k_q^1 for the totally spin allowed reaction (4) is at least 9 times larger than that of k_q', which is limited by spin-statistical factor 1/9) or $[{}^3O_2] \gg [T]$). These two approximations give a single-exponential decay of T ($[T]/[T_0] = \exp(-k_T t)$, where $[T_0]$ is the initial concentration of T, $k_T = k_0 + k_q[O_2]$, $k_q = k_q' + k_q''$, and $[O_2]$ is the total concentration of oxygen in a system). Then if $k_{o1} = 0$ the following analytical solution, eq 8, may be easily derived (here we skip reactions 3,

$$\frac{[S]}{[T]} = \frac{k_q[O_2]}{k_{S_1}}\left(1 - \exp\left(\frac{k_q^1([T] - [T_0])}{k_T}\right)\right) \qquad (8)$$

5, and 7 and assume $k_q^1 \gg k_q$ in order to simplify the algebraic forms of parameters). If $k_{o1} > 0$ the analytical solution may be obtained in a form of series, eq 9. Both eqs 8 and 9 predict

$$\frac{[S]}{[T]} = \frac{k_q[O_2]k_q^1[T_0]}{k_{S_1}}\exp\left(\frac{k_q^1[T]}{k_T} - k_{o1}t\right) \times$$

$$\sum_{n=0}^{n=\infty}\left(-\frac{k_q^1[T_0]}{k_T}\right)^n \frac{\exp((k_{o1} - (n+1)k_T)t) - 1}{(k_{o1} - (n+1)k_T)n!} \qquad (9)$$

the kinetic behavior for $[S]/[T_0]$ (this parameter is close to the value of I_{DF}/I_{PF} measured experimentally) which is similar to that given by the biexponential eq 7 for each particular O_2 concentration.

Kinetics of Delayed Fluorescence of ZnTPP on the Surface in Terms of Singlet Oxygen Feedback Mechanism. In the limit of high $[O_2]$ ($k_T \gg k_q^1[T_0]$) both eqs 8 and 9 are reduced to eq 10 which is similar to eq 7 with the values of k_- and k_+ being

$$[S]/[T] = (k_q^1/k_{S_1})([T_0] - [T]) \qquad (10)$$

equal to k_T and $2k_T$, respectively. Such a kinetic behavior of DF was observed for Si-14 samples at high oxygen partial pressures. This limit can hardly be reached for NaA samples since the value of $k_q^1[T_0]$ for NaA samples seems to be significantly larger than that for Si-14 ones (see below).

Equation 8 gives the value k_- which is always very close to that of k_T. The 2 times increase of k_- with $[O_2]$ decrease is predicted by eq 9 which gives the S-shaped dependencies of k_-/k_T on O_2 similar to those observed experimentally (see inset in bottom of Figure 4) with the bending point at $[O_2]$ near that one where $k_T = k_{o1}$. In order to extract values of k_{o1} together with $k_q^1[T_0]$, a simultaneous fitting of several DF kinetic curves measured with Si-14 samples at different partial pressures of oxygen was performed using $k_q = 2.1 \times 10^5$ Torr^{-1} s^{-1}, $k_q^s = 2 \times 10^6$ Torr^{-1} s^{-1}, $k_q'/(k_q' + k_q'') = 0.83$, $k_s = 5 \times 10^8$ s^{-1}, and $k_s''/(k_s' + k_s'') = 0.88$. Variable parameters were k_{o1}, k_q^1-$[T_0]$, and I_{DF}. A good description of the experimental data has been obtained for the right half of S-shaped dependence of k_-/k_T on $[O_2]$ at high values of $[O_2]$ (see curve 1 in inset in bottom of Figure 4) with $k_{o1} = 8 \times 10^5$ s^{-1}, $k_q^1[T_0] = 7.5 \times 10^5$ s^{-1}, and adjusted value of I_{PF} which is 3 times larger than the peak intensity of PF emitted during the laser pulse. However, an inconsistency was observed at low $[O_2]$ where eq 9 predicts $k_- = 2k_T$ since the limit value of k_- observed experimentally is only 1.5k_T. A similar fitting of the NaA data gives $k_{o1} = 3 \times 10^4$ s^{-1}, $k_q^1[T_0] = 2 \times 10^6$ s^{-1}, and I_{PF} even smaller than the peak intensity of PF with the same deviations in the low $[O_2]$ part of k_-/k_T relation (see curve 2 in insert in bottom of Figure 4). The anomalous low value of adjusted I_{PF} may be explained if one assumes that only part of ^{3}ZnTPP on NaA surface participates in DF generation (see below).

In the limit of small $[O_2]$ ($k_T \ll k_q^1[T_0]$), eqs 8 and 9 predict a rise of DF with k_+ being equal approximately to $k_q^1[T_0]$ and $k_q^1[T_0] + k_{o1}$, respectively. Such a kinetic behavior of DF was observed for Si-14 samples (see above).

The essential achievement of the kinetic treatment derived from Scheme 1 is the perfect description of the DF kinetics dependence on laser pulse energy. The kinetic curves 1 and 2 presented in inset in Figure 6 both fit to eq 9 with a single value of $k_{o1} = 8 \times 10^5$ s^{-1} and those of $k_q^1[T_0]$ are equal to 1.5 $\times 10^5$ and 15×10^5 s^{-1}, respectively, in fair agreement with corresponding change in $[T_0]$ measured in T−T absorption or in Y_{PF}.

Yield of Delayed Fluorescence of ZnTPP on the Surface in Terms of Singlet Oxygen Feedback Mechanism. The experimental value of Y_{DF}/Y_{PF} is a measure of the yield of S_1 (integrated amount of S_1 appeared during the overall reaction) related to $[T_0]$. This approximation seems to be a good one since the triplet yield is high. The numerical integration of Scheme 1 was used to describe the behavior of Y_{DF} on both surfaces. The dependence of the relative yield of DF on $[O_2]$ measured with Si-14 samples fits well (curve 1 in inset on top of Figure 4) to Scheme 1 with the same values of k_{o1} and k_q^1-$[T_0]$ as those used for the description of DF kinetics (see above)

and with $k_0 = 350$ s^{-1} which is slightly larger than the average rate constant of ^{3}ZnTPP decay measured in evacuated samples. It was not necessary to adjust the Y_{PF} value. On the other hand, data for NaA cannot be described in such a simple manner. Curve 2 (insert on top of Figure 4) is a result of fitting with $k_{o1} = 3 \times 10^4$ s^{-1} using $k_q^1[T_0]$, k_0, and Y_{PF} as variables. The fitting procedure gave $k_q^1[T_0] = 3.9 \times 10^6$ s^{-1} and $k_0 = 250$ s^{-1} (this value coincides with the corresponding experimental one), and Y_{DF} is 6 times smaller than that measured experimentally. These results are in agreement with those extracted from treatment of DF kinetics on NaA and suggest that only a part of the triplets participate in the process of DF generation but this process is more efficient than the one on Si-14 due to the small apparent rate constant of singlet oxygen self-decay.

Kinetic Scheme 1 with parameters extracted from DF treatment on Si-14 predicts the dependence of Y_{DF} on $[T_0]$ which is close to a quadratic one or in other words a linear dependence of Y_{DF}/Y_{PF} on Y_{PF} in agreement with experimental data obtained for Si-14 samples when $[T_0]$ was varied by changing the laser pulse energy (see above).

On the other hand, Scheme 1 predicts the transition from quadratic behavior at large $[O_2]$ to a linear one at small oxygen content with parameters extracted from DF behavior on NaA. This transition may be clearly demonstrated using the integrated form of eq 8 which gives $Y_{DF}/Y_{PF} = k_q^1[T_0]/2k_q[O_2]$ in a limit of $k_T \gg k_q^1[T_0]$ and $Y_{DF}/Y_{PF} = k_q[O_2]/k_T$ in a limit of $k_T \ll k_q^1[T_0]$. The corresponding experimental dependence obtained at oxygen pressure of 5 Torr for NaA samples ($[T_0]$ was varied with laser energy) fits Scheme 1 with parameters extracted above (see curve 3 in Figure 7A). However, the dependence observed at 0.05 Torr (dependence 2 in Figure 7A) differs significantly from that predicted by Scheme 1 with the same parameters (curve 1 in Figure 7A). A good fitting is obtained with much lower initial (maximum) value of $k_q^1[T_0] = 4 \times 10^5$ s^{-1} (curve 2 in Figure 7A).

Scheme 1 is not able to describe each dependence presented in Figure 7B which assumes the independence of parameter $k_q^1[T_0]$ on $[T_0]$. This deviation clearly demonstrates that the distribution of ^{3}ZnTPP on the surface is far from a homogeneous one and indeed the arrangement of ensembles of ZnTPP molecules on the surface should play a key role in the behavior of the oxygen induced DF.

5. Meaning of the Parameters Extracted from the Homogeneous Treatment of the Delayed Fluorescence of ZnTPP on the Surface in Terms of Singlet Oxygen Feedback Mechanism. The kinetic treatment presented above is essentially homogeneous, and therefore uses analytical concentrations of reactants. Fortunately, the important intrinsic property of Scheme 1 is that all bimolecular processes are reduced to pseudomonomolecular ones, giving equations which actually contain only first-order rate constants. The appearance of the first-order parameter $k_q^1[T_0]$ enables one to simplify the kinetic analysis, namely to isolate the ratio $[T_0]/[O_2]$. However, deviations obtained with the homogeneous treatment show that a detailed heterogeneous analysis is needed. The content of O_2 molecules on the surface is much lower than that of triplets at the temperatures used. Although the quenching of ^{3}ZnTPP by O_2 is not of pure ER nature, details of this process do not seem necessary for the understanding of DF kinetics and yield. On the other hand, a more rigorous treatment is quite important for the quenching of ^{3}ZnTPP by singlet oxygen, since extracted values of parameter $k_q^1[T_0]$ assume, in terms of bulk concentrations, that *the value of k_q^1 is several orders of magnitude larger than that of k_q*. This fact is the most important reason for the high efficiency of DF induced by singlet oxygen feedback. This

result may be ascribed to the very large resident time of ^{1}O$_2$ on the surface accompanied by a large diffusion coefficient. But this explanation is contradictory since large resident times assume slow diffusion. The extracted values of singlet oxygen self-decay rate constants seem to be apparent ones and reflect the resident time of singlet oxygen in some specific reaction volumes rather than on the whole surface or a real self decay.

The total collection of results presented above supports the idea that molecules of ^{3}ZnTPP on the surface are organized in some couples, aggregates, or clusters in such a way that changes dramatically the initial conditions of ^{3}ZnTPP quenching by ^{1}O$_2$. *The independence of DF kinetics and relative yield on sample loading is a crucial feature which shows that the aggregation is not random and the structure of aggregates or even couples is perfectly defined.*

6. Summary Remarks. At this stage of our investigation we are far from a detailed understanding of how the present system works. The observed dependence of ^{3}ZnTPP yield on the amount of oxygen in the system at relatively low oxygen pressure definitely shows that ZnTPP molecules are localized in adsorption sites which are chemically active toward the molecular oxygen. *Questions arise about the chemistry of triplet and singlet oxygen on the surface as well as on the role of this chemistry in singlet oxygen feedback.* We are not able to rule out totally a static-type mechanism which implies the formation of a chemically bound form of singlet oxygen followed by energy migration on the surface.

Preliminary investigations of the effect of water showed that the presence of water vapors in the reaction cell results in gradual quenching of DF and in dramatic decrease of ^{3}ZnTPP yield probably due to both quenching of singlet oxygen[31] and change in type of porphyrin aggregates. The deuteriation of Si-14 surface by proton exchange with D$_2$O did not result in any distinct changes in DF behavior. Attempts to quench singlet oxygen on Si-14 by the well-known quencher NaN$_3$[31] were not successful since the effect appears at concentrations of NaN$_3$ close to a monolayer and the yield of DF decreases simultaneously with the yield of ^{3}ZnTPP. The addition of decanol results in a dramatic decrease of the DF yield which, however, is still observable even in the presence of multilayer amounts of decanol.

The oxygen-induced delayed fluorescence of ZnTPP was observed also on surfaces of other zeolites and silicas showing that the effect may be a general one at least for SiO$_2$-based materials. Further investigations of the effects the nature of surfaces and of sensitizers on parameters which affect the oxygen-induced DF are in progress.

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