

Laser-Induced Optoacoustics Combined with Near-Infrared Emission. An Alternative Approach for the Determination of Intersystem Crossing Quantum Yields Applied to Porphycenes[†]

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An approach was developed to determine triplet quantum yields, Φ_T , which overcomes most of the difficulties usually encountered in flash photolysis studies of triplet states. The combined application of near-IR emission and optoacoustics yields Φ_T values which are independent of the absorption properties of the triplets. Thus, the triplet energies derived from near-IR phosphorescence spectra together with the values of the heat stored by the triplets determined from optoacoustic experiments afforded $\Phi_T = 0.3 \pm 0.1$ for porphycene (PO) and 0.4 ± 0.1 for its tetra-*n*-propyl derivative (TPrPO). Several calorimetric references for optoacoustic measurements in the red region were tested. The Φ_T values, combined with flash photolysis data, yielded accurate triplet- minus ground-state absorption coefficients. The quantum yields for singlet molecular oxygen production determined by time-resolved phosphorescence were $\Phi_\Delta = 0.34 \pm 0.05$ for PO and 0.36 ± 0.03 for TPrPO which implies an efficiency near unity for $O_2(^1\Delta_g)$ production upon collision of the triplet states of the porphycenes with ground-state O_2 .

Introduction

In this work we report an approach developed for the study of triplet-state properties that overcomes difficulties usually found in the complete conversion and sensitization procedures.¹ In particular, excitation with short laser pulses using the complete conversion method with flash photolysis leads to uncertainties for substances with relatively long fluorescence lifetimes.² With the sensitization method a usual problem is the overlapping of spectra of sensitizer and quencher which may introduce large uncertainties. An additional problem arising specially with triplets of low energy content is the determination of such values (E_T) due to (i) the up to recently low sensitivity of detectors in the near-IR region and (ii) the lack of sensitizers with known low E_T which could allow the energy evaluation from quenching experiments.³ The availability of germanium detectors makes possible the measurement of emission spectra in the near-IR region. The use of such detectors is now common practice in singlet molecular oxygen [$O_2(^1\Delta_g)$] research (e.g., ref 4).

Time-resolved photothermal methods (e.g., laser-induced thermal lensing or optoacoustics), on the other hand, yield accurate values of total heat stored by triplet states (or other short-lived species, like radicals, isomers, etc.) after pulsed excitation.⁵ These results, in conjunction with the E_T values, can be used to determine quantum yields of production of the triplets.⁵

The approach we present now is based on the derivation of the triplet energy content from the phosphorescence spectrum, the calculation of Φ_T from optoacoustic experiments, and finally the calculation of the triplet- minus ground-state molar absorption coefficient ($\Delta\epsilon_T$) from the comparative method with flash photolysis.

We have applied this procedure to benzene and toluene solutions of porphycene (PO) and its 2,7,12,17-tetra-*n*-propyl derivative (TPrPO), structural isomers of the porphyrins, which have been synthesized by Vogel and co-workers for the first time in 1986.^{6,7} Some photophysical properties of porphycenes have been reported in a previous publication from our laboratory⁸ and by other research groups.^{9,10} For the case of PO the first estimate of the intersystem crossing quantum yield, Φ_T ,⁸ was affected by one of the problems mentioned above since its long singlet lifetime (10

ns) could prevent complete conversion to the triplet within the 20-ns duration of the excitation ruby laser pulse. Should the conditions for the complete conversion not be fulfilled, the value of $\Delta\epsilon_T$ would be a lower limit¹¹ yielding, in turn, a too high Φ_T .

Since for highly fluorescent substances the optoacoustic results strongly depend on the value of the fluorescence quantum yield, Φ_f , this magnitude was redetermined by steady-state thermal lensing. This method is particularly appropriate for the determination of Φ_f in the red region of the spectrum where standards are not easily available.¹² In addition, the quantum yield for $O_2(^1\Delta_g)$ production, Φ_Δ , was determined for the two porphycenes in benzene, from the analysis of the time-resolved phosphorescence of $O_2(^1\Delta_g)$.

Materials and Methods

A. Materials. Porphycenes (PO and TPrPO) were synthesized and purified as previously described.^{6,7} Cobalt(II)-*meso*-tetraphenylporphyrin (CoTPP) was purchased from Porphyrin Products (Logan, UT). Dodecaprene- β -carotene (DDC) was kindly provided by Dr. H. E. Kella (Hoffmann-La Roche A.G., Basel, Switzerland). *meso*-Tetraphenylporphyrin (H_2 TPP) and zinc(II)-tetraphenylporphyrin (ZnTPP) were synthesized and purified according to known procedures.¹³⁻¹⁵ Solvents were either ana-

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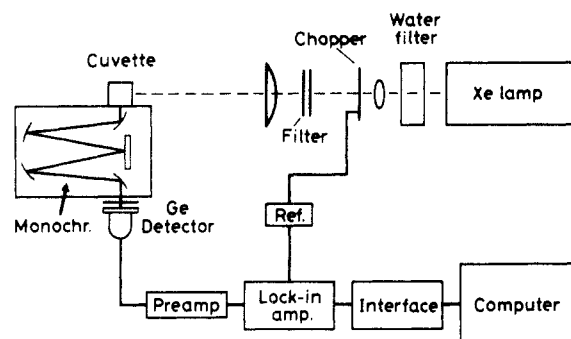


Figure 1. Scheme of the near-IR steady-state emission spectrometer.

lytical grade (Merck Uvasol) or Sintorgan (Argentina) freshly distilled.

B. Methods. 1. Steady-State Thermal Lensing. The apparatus was similar to the one described by Magde and co-workers.¹² Benzene solutions of the porphycenes and of H₂TPP (the reference) were excited with a 1-mW He-Ne laser (Melles-Griot) at 633 nm. The samples were deaerated by bubbling argon. Absorbances at 633 nm were measured on a Cary 2300 spectrophotometer with a precision of 0.0003 absorbance unit.

2. Near-IR Steady-State Luminescence. The home-built emission spectrophotometer is depicted in Figure 1. The excitation light from a 450-W Xe lamp was filtered by 3 cm of water, a KG5, and a 455-nm cutoff filter (Schott-Mainz) and focused on the sample. This was contained in a 1-cm² fluorescence quartz cuvette which was placed as close as possible to the entrance slit of a high-intensity monochromator (Applied Photophysics *f*/3.4, bandwidth 19 nm) provided with a 785-nm cutoff filter at the exit slit and an IR grating blazed at 1000 nm. The emitted light was detected by a Ge photodiode (Judson J16 8Sp, 5-mm diameter), thus allowing spectra measurements in the wavelength range 800–1800 nm. After preamplification (Judson 700 preamplifier), lock-in amplification (EG&G Princeton Applied Research 186A lock-in amplifier) with synchronized chopping (Chopper Bentham 218) of the excitation light at 40 Hz was used to improve the signal-to-noise ratio. The output signal of the lock-in amplifier was fed into a computer (Commodore CBM 4016), which also synchronously governed the stepper motor of the monochromator. The emission of O₂(¹Δ_g) with λ_{max} at 1270 nm and zinc(II)-phthalocyanine phosphorescence with λ_{max} at 1090 nm¹⁶ served for wavelength calibration. Emission spectra were recorded at room temperature.

3. Laser-Induced Optoacoustics (LIOAS). The experimental setup has been described previously.^{5,17} Argon-saturated benzene solutions of the porphycenes were excited at room temperature with the 15-ns pulse of either the second harmonic of a Nd:YAG (532 nm) or a dye laser (rhodamine 6G, λ = 558 nm) pumped by it. The beam was focused on the cuvette to a diameter corresponding to an effective acoustic transit time, i.e., the time required for the acoustic wave to traverse the laser beam diameter, of ca. 100 ns. The sound wave was detected with a ceramic Pb-Zr-Ti detector. Air-saturated solutions of I₂, CoTPP, and DDC and argon-saturated solutions of ZnTPP served as calorimetric references.

4. Flash Photolysis. The apparatus has been already described.^{18,19} The comparative method was used to obtain the product Φ_TΔε_T for both porphycenes in degassed toluene solutions.² H₂TPP in toluene (Φ_T = 0.82,²⁰ Δε_T⁴⁵⁰ = 50 000 M⁻¹ cm⁻¹)²¹ was the reference for PO (λ_{exc} = 560 nm, λ_{obs} = 390 nm).⁸ ZnTPP

TABLE I: Photophysical Parameters for Porphycene (PO) and Its 2,7,12,17-Tetra-*n*-propyl Derivative (TPrPO) in Benzene

	this work		ref 8	
	PO	TPrPO	PO	TPrPO
Φ _f	0.44 ± 0.06	0.38 ± 0.06	0.36 ± 0.05	0.32 ± 0.05
E _T , kJ mol ⁻¹	121 ± 2	124 ± 2		
φ _T	0.3 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	
Δε _T ^{max,a} , M ⁻¹ s ⁻¹	(2.2 ± 0.6) × 10 ⁴	(2.1 ± 0.6) × 10 ⁴	≥ 1.6 × 10 ⁴	
k _{O₂} , M ⁻¹ s ⁻¹	(3.5 ± 0.4) × 10 ⁹	(2.9 ± 0.3) × 10 ⁹		

^a 390 and 395 nm for PO and TPrPO, respectively.

in toluene (Φ_T = 0.88,²¹ Δε_T⁴⁷⁰ = 73 000 M⁻¹ cm⁻¹) was the reference for TPrPO (λ_{exc} = 532 nm, λ_{obs} = 395 nm). Sample and reference had absorbances of ca. 0.1, matched within 0.002 absorbance unit at the excitation wavelength.

5. Near-Infrared Time-Resolved Phosphorescence (Time-Resolved Phosphorescence Detection, TRPD). A full description of the experimental setup has been given elsewhere.²² The solutions were excited either at 355 nm (Nd:YAG frequency tripled) or at 600 nm (rhodamine B pumped with the frequency-doubled Nd:YAG frequency at 532 nm). The phosphorescence from O₂(¹Δ_g) arising from aerated solutions of the sensitizers upon pulsed laser excitation was monitored at λ > 1050 nm (silicon cutoff filter, Glen Greston, 2 mm thick) and at 90° from the excitation. The detection was by a Ge diode similar to that described in a previous section but with a different home-built amplifier before the transient recorder Gould Biomation 4500. The Φ_A values were obtained by comparing the amplitudes of the phosphorescence, extrapolated to *t* = 0 (*I*₀) induced by the porphycenes, with those induced by reference compounds. For better accuracy the slopes of the linear plots of *I*₀ vs the energy of the laser pulse, *E*_l, were compared for sample and reference.

Results and Discussion

Determination of Φ_f by Steady-State Thermal Lensing. The steady-state thermal lensing method was used for the measurement of absolute values of Φ_f in benzene. The refractive index change caused by the heat evolved due to the radiationless processes after absorption of the incident CW laser beam turns the solution into a divergent lens which defocuses the beam. The method can be used to evaluate total (fluorescence plus phosphorescence) luminescence yields also for the case of substances producing triplet states. The radiationless decay of these states will be detected as heat due to the long time constant of the measurement. The thermal lensing signal, θ, was registered as the change of irradiation at the beam center relative to the stationary value. θ is proportional to the fraction of absorbed power dissipated as heat (P_{th}),²³ i.e.

$$\theta = kP_{th} \quad (1)$$

where *k* is a factor containing thermoelastic properties of the solvent and instrumental and geometrical parameters. The measurement of θ for the sample and for a nonfluorescent reference which transforms all the absorbed energy to heat allows the evaluation of the luminescence yield of the unknown, provided that the laser excitation power, the solvent, and geometrical arrangement are the same for sample and reference.²³ The fluorescence emission spectrum of the sample must also be known. Nevertheless, it is not essential that the reference is nonfluorescent. The energy balance can be carried out in the same way when both substances are fluorescent, and this leads to eq 2 which is derived

$$\Phi_p^s = (\nu_1 / \langle \nu_i^s \rangle) [1 - (1 - \Phi_f^r \langle \nu_i^r \rangle / \nu_1) (m^s / m^r)] \quad (2)$$

in the Appendix. The derivation assumes that the phosphorescence quantum yield, Φ_p << Φ_f (vide infra). In this equation the su-

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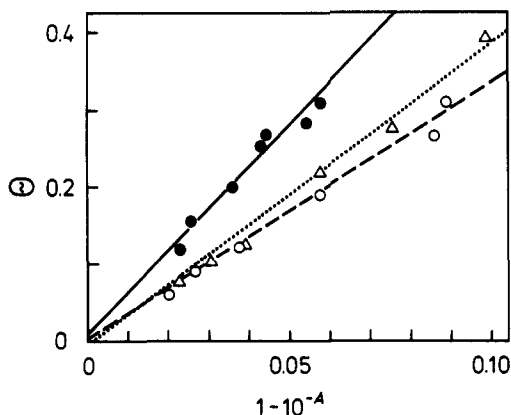


Figure 2. Thermal lensing signal vs the fraction of light absorbed by argon-saturated benzene solutions of (●) H₂TPP, (Δ) TPrPO, and (○) PO. $\lambda_{\text{exc}} = 633$ nm.

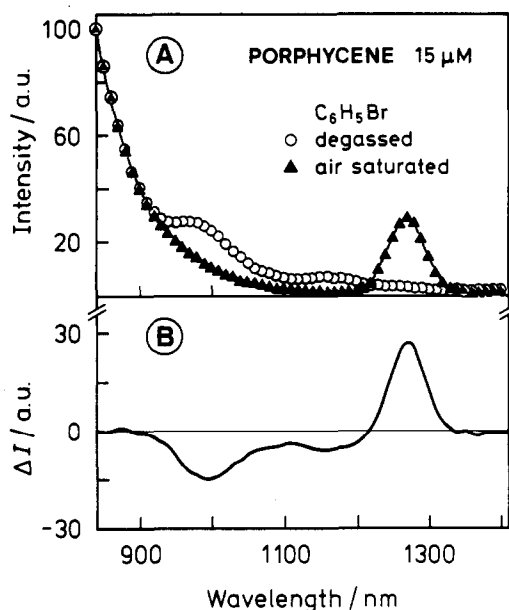


Figure 3. (A) Near-infrared steady-state emission spectra from a bromobenzene solution of PO as described, $\lambda_{\text{exc}} > 455$ nm. (B) Difference between both spectra in (A).

perscripts *s* and *r* refer to sample (porphycenes) and reference (H₂TPP), respectively, ν_l is the laser frequency (15 803 cm⁻¹), $\langle \nu_f^s \rangle$ are the respective mean fluorescence frequencies ($\langle \nu_f^r \rangle$ is 14 980 cm⁻¹ for H₂TPP²⁴ and 15 500 cm⁻¹ for PO and TPrPO), $\Phi_f^r = 0.04$ for H₂TPP,²⁰ and *m* is the slope of the graph of θ vs $i_a = 1 - 10^{-4}$. The results are plotted in Figure 2. At $\theta > 0.4$ deviations from the linear behavior were observed. Therefore, we restricted our measurements to the lower absorbance range. The slopes of the graphs in Figure 2 render, through eq 2, $\Phi_f^r = 0.44 \pm 0.06$ for PO and 0.38 ± 0.06 for TPrPO. Previously reported values, which are somewhat lower (0.36 and 0.32, respectively),⁸ are not significantly different. This implies that $\Phi_p \leq 0.1$ in both cases, and it is therefore valid to take the mean as the most likely value for Φ_f^r . This yields $\Phi_f^r = 0.40 \pm 0.06$ for PO and 0.35 ± 0.06 for TPrPO. These values are higher than those typically displayed by the related porphyrins (<ca. 0.15 in aromatic solvents²⁵⁻²⁷).

Determination of E_T by Near-IR Steady-State Emission. Figure 3 shows the emission spectra obtained for the same solution of porphycene in bromobenzene when it was either air saturated or freeze-pump-thaw degassed. Phosphorescence was observed in bromobenzene but not in benzene. The difference between the

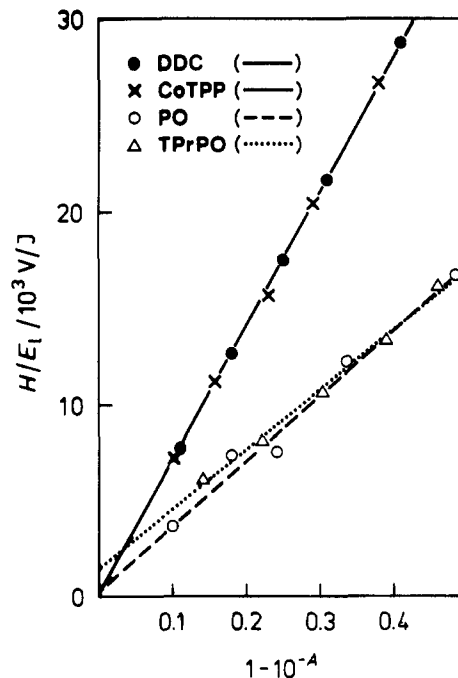


Figure 4. Energy-normalized optoacoustic signal maxima vs the fraction of light absorbed for the various argon-saturated benzene solutions of samples and references, as indicated. $\lambda_{\text{exc}} = 532$ nm.

two spectra shows the oxygen phosphorescence with a maximum at 1270 nm and the emission of porphycene triplet with two maxima at 990 ± 10 and 1160 ± 10 nm. This latter spectrum is totally quenched by oxygen. The O₂(¹Δ_g) phosphorescence quantum yield is smaller than 10⁻³ in solvents where its lifetime is relatively short²⁸ (<100 μs; e.g., bromobenzene⁴). The PO phosphorescence area is roughly of the same magnitude as the O₂(¹Δ_g) phosphorescence area which gives an upper limit value for the phosphorescence yield for PO of Φ_p ca. 10⁻³. This supports the assumption of a negligible Φ_p made on evaluation of the steady-state thermal lensing data for the determination of the fluorescence quantum yield.

The triplet energy (E_T) was taken from the maximum of the first vibrational band in the spectrum to be 121 ± 2 kJ mol⁻¹ for PO (Figure 3) and 124 ± 2 kJ mol⁻¹ for TPrPO (spectrum not shown). This choice is based on the similarity of triplet-, singlet-excited-, and singlet-ground-state configurations as supported by the identity of the vibrational spacing in the fluorescence and phosphorescence spectra, in conjunction with the mirror image and small Stokes shift in the fluorescence spectra.⁸ The energy difference between the maxima in the phosphorescence spectrum is 17 ± 2 kJ mol⁻¹ (ca. 1400 cm⁻¹), which compares well with the 16.3 kJ mol⁻¹ obtained for the vibrational spacing in the fluorescence emission spectrum.⁸ Thus, the 0'-0 band coincides practically with the position of the highest energy maximum. This criterion was also adopted by Herkstroeter et al. to assign triplet energies to a series of compounds.²⁹ The triplet energies of the porphycenes lie ca. 20 kJ mol⁻¹ below those of most free-base porphyrins.^{27,30}

Determination of Φ_T by LIOAS. Calorimetric References. Laser-induced optoacoustic spectroscopy was used to determine the heat stored by the triplet state ($\Phi_T E_T$, vide infra) produced in deaerated solutions.

The voltage amplitude of the first signal deflection *H* is related to the laser pulse energy E_1 and to *A* by the equation^{5,17,31}

$$H = K\alpha E_1(1 - 10^{-4}) \quad (3)$$

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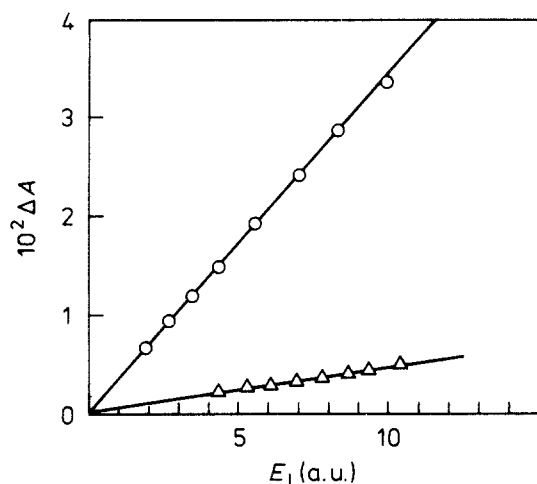


Figure 5. T-S absorbance difference immediately after the 15-ns laser pulse at 532 nm vs the pulse energy, E_1 , for argon-saturated toluene solutions of (O) ZnTPP ($\lambda_{\text{obs}} = 470$ nm) and (Δ) TPrPO ($\lambda_{\text{obs}} = 395$ nm).

where K is a proportionality constant involving geometrical parameters and thermoelastic properties of the solvent and α is the fraction of the absorbed energy released as heat within the effective acoustic transit time, 100 ns in our case. K is eliminated by measuring H under identical conditions for the sample and for a reference with known α (typically $\alpha = 1$ ³²). A more accurate procedure consists in measuring the energy dependence of H for sample and reference at various A . From the ratio of the slopes of H/E_1 vs $1 - 10^{-4}$ for sample and reference, the ratio $\alpha_{\text{sample}}/\alpha_{\text{ref}}$ is obtained (see Figure 4). We have used CoTPP ($\Phi_T = 1$, $\tau_T < 15$ ps³³), DDC (assumed to have a quantum yield of internal conversion of 1, and $\tau_S \ll 100$ ns, in accordance with the photophysical behavior of the parent β -carotene³⁴), I_2 ,³⁵ and ZnTPP ($\Phi_T = 0.88$, $E_T = 153.5$ kJ mol⁻¹, $\tau_T \gg 100$ ns, $\Phi_f = 0.04$, and $E_f = 198.8$ kJ mol⁻¹²⁷) as calorimetric references. CoTPP, DDC, and I_2 have $\alpha = 1$ at $\lambda_{\text{exc}} = 532$ nm due to their photophysical properties and to the short effective acoustic transit time used (100 ns, see Methods section). ZnTPP stores part of the absorbed energy in its triplet state ($=\Phi_T E_T$), and thus it should give $\alpha = 0.336$ at $\lambda_{\text{exc}} = 558$ nm, calculated from the energy balance equation (4), with $\langle E_f \rangle = h\nu_f$ and E_{exc} the molar exciting energy.

$$E_{\text{exc}} = E_{\text{exc}}\alpha + \Phi_f \langle E_f \rangle + \Phi_T E_T \quad (4)$$

Figure 4 shows the results obtained at $\lambda_{\text{exc}} = 532$ nm with CoTPP and DDC. Both references display the same slope, which supports the assumption that DDC has $\alpha = 1$ under our experimental conditions, and thus validates the use of DDC as a good calorimetric reference. With I_2 and ZnTPP the results (not shown) lie well within the experimental error of those with the other two references. The numbers given are the average of data obtained with all four calorimetric references for each porphycene.

Making use of eq 4 and the Φ_f and E_T values obtained as described in the previous sections, $\Phi_T = 0.3 \pm 0.1$ for PO and 0.4 ± 0.1 for TPrPO are derived. These yields are significantly lower than those of the free-base porphyrins (typically >0.8 ²⁷). The value for PO is slightly lower than the previous 0.4⁸ based, as already discussed, on a too low value for $\Delta\epsilon_T$ calculated from the application of the complete conversion method in flash photolysis using a 20-ns pulse which is too short compared with the fluorescence lifetime.¹¹ However, the newly determined Φ_T value is still within the relatively large experimental error of the previous measurements.

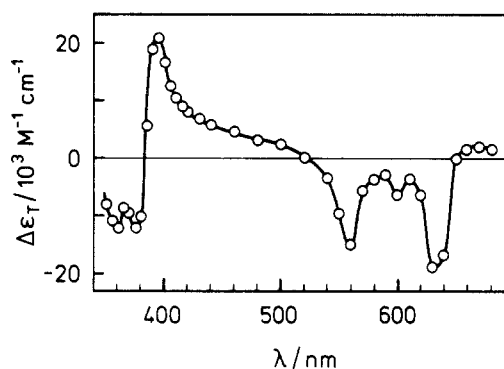


Figure 6. T-S absorbance difference spectrum for TPrPO in toluene. $\lambda_{\text{exc}} = 532$ nm.

Determination of $\Delta\epsilon_T$ by Laser Flash Photolysis. Only new data for TPrPO are reported here. For PO the values measured in ref 8 of the product $\Phi_T \Delta\epsilon_T$ at 390 nm are reinterpreted on the basis of the new Φ_T obtained in this work (see above).

The absorbance difference at a particular wavelength after the laser pulse is represented as a function of the pulse energy in Figure 5 for TPrPO and for ZnTPP used as reference for the comparative method.² From the ratio of the slopes and with the values for ZnTPP given in the Materials and Methods section, a value $\Delta\epsilon_T^{395} = (2.1 \pm 0.6) \times 10^4$ M⁻¹ cm⁻¹ for TPrPO is obtained. The value for PO turns to be $\Delta\epsilon_T^{390} = (2.2 \pm 0.6) \times 10^4$ M⁻¹ cm⁻¹, somewhat higher than our previous $\Delta\epsilon_T^{390} = 1.6 \times 10^4$ M⁻¹ cm⁻¹.⁸ Both values correspond to the maximum in the T-S difference absorption spectrum which is quantitatively shown for TPrPO in Figure 6. The spectrum in toluene is identical with the one reported in ref 10 in benzene on a relative scale. This justifies the combination of fluorescence and optoacoustic data obtained in benzene with T-T absorption data obtained in toluene.

The position of the maximum in the T-S difference absorption spectra is slightly red-shifted from the blue absorption band. This feature is similar to the observation with porphyrins. The decays of triplet PO and TPrPO were strictly monoexponential with lifetimes $\tau_T = 200$ and 270 μ s, respectively. Oxygen quenched these species. Upon air saturation of the solutions the lifetimes observed were $\tau_{\text{obs}} = 150$ and 190 ns for PO and TPrPO, respectively. By use of the value 1.91×10^{-3} M for the oxygen concentration,³⁶ the rate constant for oxygen quenching of the triplet states results $k_{O_2} = 3.5 \times 10^9$ M⁻¹ s⁻¹ for PO and 2.9×10^9 M⁻¹ s⁻¹ for TPrPO. These values are close to 1/9 of the diffusional value (3×10^{10} M⁻¹ s⁻¹ in benzene³⁷). Similar values have been reported for k_q for porphyrin triplets³⁸⁻⁴⁴ and for $\pi-\pi^*$ low-energy aromatic triplet states.⁴⁵⁻⁵⁰ In such cases the efficiency of $O_2(^1\Delta_g)$ production resulting from the collision event between

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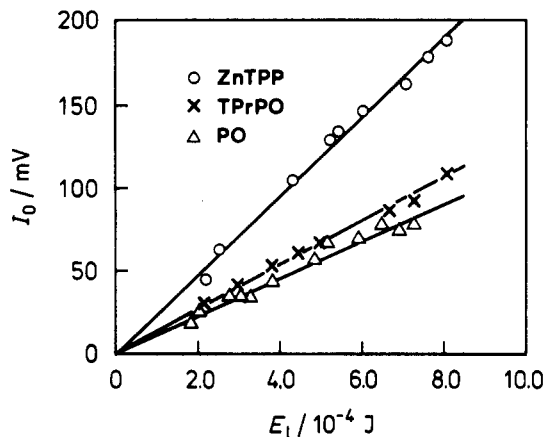


Figure 7. Dependence of the $O_2(^1\Delta_g)$ emission signal extrapolated to $t = 0$, I_0 , on the pulse energy, E_1 , for air-saturated benzene solutions of samples and references as indicated. $\lambda_{exc} = 600$ nm.

$O_2(^3\Sigma_g^-)$ and the triplet state ($S_\Delta = \Phi_\Delta/\Phi_T$) is usually close to unity.⁴⁵

Determination of Φ_Δ by TRPD. Time-resolved $O_2(^1\Delta_g)$ phosphorescence detection at $\lambda > 1050$ nm was used to determine Φ_Δ in benzene for both porphycenes.

Oxygen-saturated solutions containing sensitizer concentration in the range 1–10 μ M were irradiated either at 354 or at 600 nm. Anthracene ($\Phi_\Delta = 0.68$ at 354 nm⁴⁵) and ZnTPP ($\Phi_\Delta = 0.73$ ⁵¹) at 600 nm were used as standards. The lifetime of the emission, $\tau = 31 \pm 3$ μ s, in benzene corresponded to the value of the lifetime of $O_2(^1\Delta_g)$ in this solvent, as reported in the literature.⁴ The energy dependence of the emission intensity at $t = 0$, I_0 , is shown in Figure 7 for PO, TPrPO, and ZnTPP. The values of Φ_Δ (0.34 ± 0.05 for PO and 0.36 ± 0.03 for TPrPO) were independent of the excitation wavelength, and no difference was found between benzene and toluene. The $S_\Delta = \Phi_\Delta/\Phi_T$ values for the porphycenes are thus calculated to be 1.1 ± 0.1 for PO and 1.0 ± 0.1 for TPrPO, in line with the values obtained for π - π^* low-energy aromatic triplets.⁴⁵ Formation of $O_2(^1\Sigma_g^+)$ can be ruled out in the case of the porphycenes since its energy (157 kJ mol⁻¹⁵²) is higher than their triplet energies. Formation of $O_2(^1\Delta_g)$ via the porphycene singlet state can also be excluded since the energy gap between the first excited singlet and the triplet state is lower than 94.2 kJ mol⁻¹, the $O_2(^1\Delta_g)$ energy content.

For PO and TPrPO the sum $\Phi_f + \Phi_T$ is 0.7 ± 0.2 and 0.8 ± 0.2 , respectively, which leaves 0.3 for PO and 0.2 for TPrPO as internal conversion yields. These values are similar to those calculated for free-base porphyrins after addition of the fluorescence and triplet quantum yields.²⁵ Thus, in free-base porphycenes, relative to free-base porphyrins, the lower Φ_T is compensated for by a higher Φ_f rather than by a higher internal conversion yield. The slightly lower internal conversion yield for TPrPO can be rationalized in terms of the steric hindrance introduced by the substituents on the possible rapid cis-trans isomerization of the exocyclic double bond acting as acceptor mode for the internal conversion.

Conclusions

The approach developed in this work combining room-temperature fluorescence and phosphorescence data with a photoacoustic method, i.e., laser-induced optoacoustics (LIOAS), is of wide application, specially for substances for which high absorption in the 320–400-nm range, low triplet energy, and long

fluorescence lifetime prevent the use of other techniques to obtain triplet parameters. Several of the substances studied as possible sensitizers in the photodynamic treatment of malignant tissues exhibit such properties. The approach we present is thus specially suited for these substances. Furthermore, the combination of methods is quite straightforward and the results are precise.

The near-IR steady-state phosphorescence spectrophotometer built on the basis of the Ge detection and lock-in amplification proved to be very sensitive, allowing the determination of triplet spectra of low-energy triplet states at room temperature.

For the case of porphycenes the present approach has not brought major differences with respect to the results obtained with other methods.⁸ This just confirms the general validity of our approach.

As far as the porphycenes, when compared to the porphyrins, they display larger absorption bands in the red region, higher fluorescence yields, lower Φ_T , and consequently lower Φ_Δ .

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Appendix

The energy balance equation used by Magde and co-workers^{12,23} to obtain Φ_f from steady-state thermal lens signal may be extended by a simple procedure to the case in which the reference is fluorescent.

The global energy conservation equation is

$$P_l = P_t + P_f + P_{th} + P_p \quad (A1)$$

where l, t, f, th, and p subscripts designate incident laser, transmitted, fluorescence, thermal power, and phosphorescence. Assuming the phosphorescence component to be of minor importance, the fluorescence quantum yield Φ_f can be expressed as follows

$$\Phi_f = \frac{P_f/\langle\nu_f\rangle}{(P_l - P_t)/\nu_l} \quad (A2)$$

where $\langle\nu_f\rangle$ and ν_l are mean fluorescence and laser frequency, respectively. The fraction of light absorbed is

$$i_a = 1 - 10^{-A} = \frac{P_l - P_t}{P_l} = \frac{P_f + P_{th}}{P_l} \quad (A3)$$

Replacing eq A3 in eq A2 and solving for P_{th} in eq 1, eq A4 results:

$$P_{th} = i_a P_l (1 - \Phi_f \langle\nu_f\rangle / \nu_l) \quad (A4)$$

The ratio of eq A4 applied to sample (s) and reference (r) is equal to the ratio of θ for sample and reference measured in the same solvent, at identical temperature and geometry.

$$\frac{\theta^r}{\theta^s} = \frac{i_a^r P_l^r (1 - \Phi_f^r \langle\nu_f^r\rangle / \nu_l)}{i_a^s P_l^s (1 - \Phi_f^s \langle\nu_f^s\rangle / \nu_l)} \quad (A5)$$

Taking into account that under our conditions the laser power is identical for sample and reference, and introducing the magnitude $m = \theta/i_a$ (the slope of the linear relation between θ and i_a), eq 2 of the text is obtained for Φ_f .

Registry No. PO, 100572-96-1; TPrPO, 106562-37-2.

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