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Tetra(1,1,4,4-tetramethyl-6,7-tetralino)porphyrazine as a novel luminescence sensor of laser-induced singlet oxygen generation in solutions

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Abstract. Absorption and fluorescence spectra and quantum yields of fluorescence and singlet oxygen generation were studied in air-saturated solutions of a newly synthesised dye, tetra (1,1,4,4-tetramethyl-6,7-tetralino)porphyrazine (TMTP), in benzene. Photophysical properties of TMTP are similar to those of previously studied tetra(4-tert-butyl) phthalocyanine (TBPc). However, the TMTP absorption and fluorescence bands are shifted to the longer wavelengths compared with those of TBPc. The laser-induced generation of singlet molecular oxygen $^1O_2$ in TMTP solutions caused strong singlet oxygen-sensitised delayed fluorescence of the dye. The efficiency of singlet-oxygen-sensitised formation of excited TMTP molecules is two times higher than that of TBPc. It is shown that TMTP can serve as an efficient luminescence sensor of singlet oxygen.

1. Introduction

It is known that upon dye-photosensitised generation of the $^1\Delta_g$ singlet state of molecular oxygen $^1O_2$ in air-saturated solutions, the short-wavelength emission is observed in the 600 – 800 nm region along with the IR phosphorescence at $\lambda = 1270$ nm corresponding to the transition of O_2 molecules from the singlet to the ground state [1 – 5]. The decay kinetics of the short-wavelength emission and the dependence of its intensity on the excitation intensity suggest that two $^1O_2$ molecules are responsible for emission of one photon.

Spectral studies showed that the nature of the short-wavelength emission depends substantially on photophysical properties of dyes and oxygen. In dye solutions with the major fluorescence band located at $\lambda \leqslant 600$ nm, this emission is mainly related to dimers (dimols) $(^1O_2)_2$. In dye solutions with the major fluorescence band located at $\lambda \geqslant 700$ nm, the emission spectrum coincided with the fluorescence spectrum of the dye; i.e., singlet-oxygen-sensitised delayed fluorescence (SOSDF) of the dye was observed [1 – 5].

The SOSDF quantum efficiency varied within eight orders of magnitude, depending on the nature of the dye. The most intense SOSDF was observed in solutions of some phthalocyanines and naphthalocyanines [3 – 9]. Solutions of tetra(4-tert-butyl)phthalocyanine (TBPc) have been studied most thoroughly. The SOSDF quantum yield in TBPc solutions reached 0.2 – 0.4, which exceeds the quantum yields of the $^1O_2$ phosphorescence by 2 – 4 orders of magnitude [8, 9]. Therefore the detection of SOSDF can be considered a promising method for studying $^1O_2$ in chemical systems, and a search for novel dyes capable of efficient SOSDF becomes very important.

This work is a continuation of a series of previous publications devoted to the analysis of SOSDF of various dyes [3 – 6, 8 – 12]. The goal of this paper was to study a new compound, tetra(1,1,4,4-tetramethyl-6,7-tetralino)porphyrazine (TMTP), synthesised at the Research Institute of Organic Intermediates and Dyes. The structural formula of TMTP is shown in Fig. 1. This compound is a derivative of phthalocyanine containing symmetrical aliphatic 1,1,4,4-tetramethylcyclohexane moieties in benzene rings. The tertiary carbon atoms of these moieties, like the tert-butyl groups of previously studied TBPc increase the solubility of TMTP in organic solvents. In contrast to TBPc, representing a mixture of isomers with different arrangement of tert-butyl groups, which complicates the interpretation of the data obtained by using TBPc, TMTP is an individual compound that does not have isomers. In addition, the introduction of

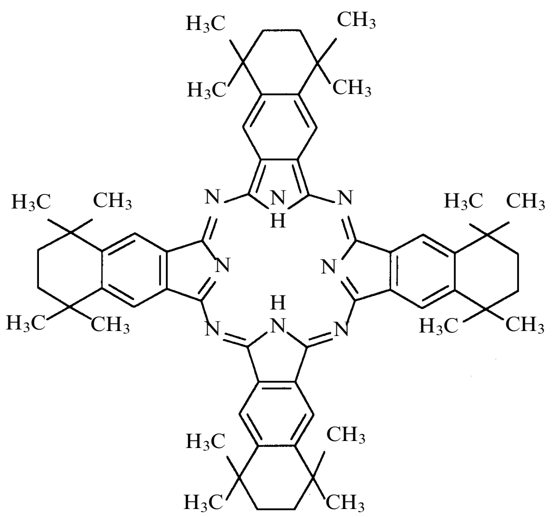

Figure 1. Structural formula of tetra(1,1,4,4-tetramethyl-6,7-tetralino)-porphyrazine.

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tetramethylcyclohexane moieties does not change the true D_{2h} symmetry of phthalocyanine, whereas in TBPc the symmetry is only inherent in its chromophore group, being distorted by the substituents.

2. Materials and methods

Absorption and luminescence measurements of samples were performed in a rectangular 4 mm × 10 mm quartz cell. The absorption spectra of dye solutions were recorded with a Uvikon 930 spectrofluorimeter (Kontron Instruments, Milan, Italy). The fluorescence and fluorescence excitation spectra were measured with a Perkin Elmer LS50 spectrofluorimeter (England).

Phosphorescence of singlet oxygen at $\lambda = 1270$ nm was detected with an Edinburgh Analytical Instruments setup (Edinburgh, Scotland). Phosphorescence was excited by the third harmonic (355 nm) of a Nd:YAG laser (Continuum Minilite, USA). The laser pulse energy was 0.9 mJ, the pulse repetition rate was 10 Hz, the pulse duration was 4 ns, the laser beam diameter was 3 mm and the energy density of laser radiation was 13 mJ cm^{-2}. Phosphorescence was detected with an EO-817 cryogenic germanium photodetector (North Coast Corporation, Santa Clara, California, USA) cooled by liquid nitrogen at an angle of 90° to a laser beam through a cut-off light filter transmitting light at $\lambda > 1100$ nm. The maximum transmission of the filter was 50%.

The delayed fluorescence was measured with the same setup through a cut-off filter transmitting at $\lambda > 630$ nm. The analogue signal of the photodetector was fed to a digital storage oscilloscope (Tektronix Tekscope) and then processed by a PC with software from the Edinburgh Analytical Instruments and also an Excel spread-sheet. The luminescence decays measured upon pulsed laser excitation were detected by accumulation and averaging signals over 20 – 100 laser pulses. The time resolution was a few microseconds.

The dyes TMTP and TBPc synthesised by the methods described in Refs [13, 14] were kindly provided by S A Mikhalenko and L I Solov'yova. Benzene, tetraphenylporphyrin and phenalenone were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin, USA).

3. Results and discussion

3.1 Absorption and fluorescence spectra

Absorption spectra of TBPc and TMTP in benzene are compared in Fig. 2. The strongest absorption bands are located at $\lambda = 699$ nm for TBPc and at $\lambda = 711$ nm for TMTP. These bands are known to correspond to Q_y transitions in dye molecules [15]. The molar extinction coefficients at the maxima of these bands are 1.7×10^5 mole litre^{-1} cm^{-1} for TBPc [13] and 2.5×10^5 mole litre^{-1} cm^{-1} for TMTP [14]. The Q_x bands at $\lambda = 663$ nm for TBPc and at $\lambda = 676$ nm for TMTP are weaker by ~20%.

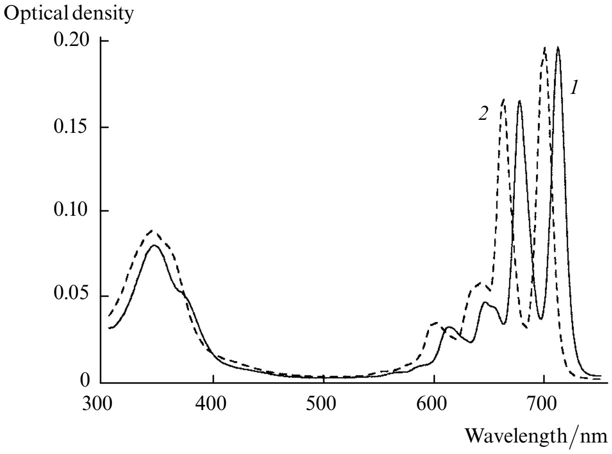

Figure 2. Absorption spectra of tetra(1,1,4,4-tetramethyl-6,7-tetralino)-porphyrazine (1) and tetra(4-tert-butyl)phthalocyanine (2) in benzene at room temperature.

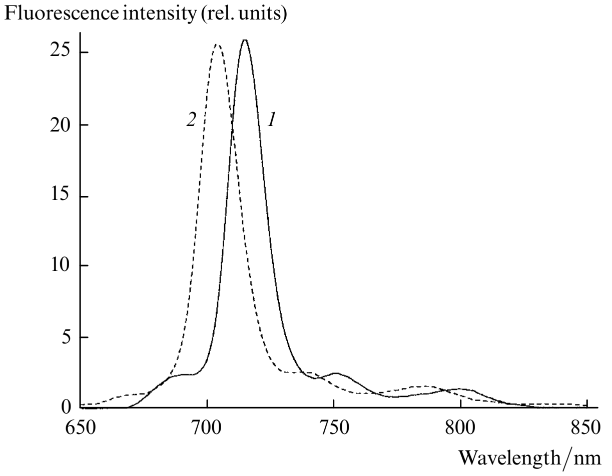

Figure 3. Fluorescence spectra of tetra(1,1,4,4-tetramethyl-6,7-tetralino)-porphyrazine (1) and tetra(4-tert-butyl)phthalocyanine (2) in benzene at room temperature.

The fluorescence spectra are shown in Fig. 3. To avoid reabsorption of fluorescence by dye molecules, the measurements were performed in solutions where the absobance in the maxima of the Q_y bands did not exceed 0.05. The most intense fluorescence bands are located at $\lambda = 703$ and $\lambda = 715$ nm for TBPc and TMTP, respectively. At longer wavelengths, vibrational peaks are observed at $\lambda = 740$ and $\lambda = 770$ nm for TBPc and at $\lambda = 755$ and 810 nm for TMTP. At shorter wavelengths, weak bands are observed at $\lambda \approx 670$ nm in TBPc solutions (see also Refs [3 – 5, 8]) and at $\lambda \approx 680$ nm in solutions of TMTP. Note that the short-wavelength band of the TMTP fluorescence is appreciably stronger (Fig. 3).

The excitation spectra of all fluorescence bands did not differ, within the experimental errors, from the absorption spectra of the dyes. Comparison of Figs 2 and 3 indicates that the most intense fluorescence band of TMTP is shifted by 4 nm to the red compared with its long-wavelength absorption band. No mirror symmetry between the fluorescence and absorption spectra is observed. These data show that fluorescence spectra of the dyes correspond to their electronic Q_y transitions, whereas the Q_x transitions do not participate in the fluorescence emission.

3.2 The fluorescence quantum yield γ_{f}

In these experiments, fluorescence was excited from the narrow side of a cell and detected at an angle of 90° to the excitation beam. Using Excel, we calculated the fluorescence intensity as an area under the fluorescence spectra corrected for the spectral sensitivity of the spectrofluorimeter. The relative values of γ_{f} were determined by exciting fluorescence into the dye absorption bands at

$\lambda = 600 - 700$ nm. To avoid reabsorption, we used dye solutions whose absorbance at the maxima of the Q_y bands did not exceed 0.08.

We found that the fluorescence quantum yield of TMTP coincided, within an accuracy of ±10%, with that of TBPc, which is 0.7 – 0.77 [16 – 18].

3.3 Quantum yields γ_Δ of singlet oxygen generation

We studied solutions of TBPc, TMTP, tetraphenylporphyrin (TPP), and phenalenone (PN). Phosphorescence was excited in a layer 4 mm in thickness. The absorbance of the solutions at the wavelength of laser radiation ($\lambda = 355$ nm) was 0.20 – 0.24. This corresponded to concentrations ~10, 7, 50, and 50 μmol litre^{-1} for TBPc, TMTP, TPP, and PN, respectively. The decay time of the $^1O_2$ phosphorescence excited by laser pulses was 30 μs (Fig. 4), which corresponds to the lifetime of singlet oxygen in benzene.

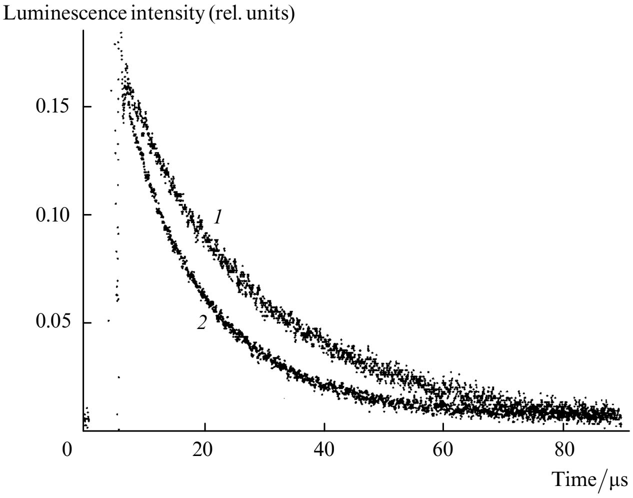

Figure 4. Decays of singlet oxygen phosphorescence photosensitised by tetra(1,1,4,4-tetramethyl-6,7-tetralino)porphyrazine in air-saturated benzene (1) and of singlet-oxygen-sensitised delayed fluorescence of this dye in the same solution (2) after laser pulse excitation. The decays are normalised to the initial luminescence intensity. Curves (1) and (2) are obtained by averaging over 50 and 10 laser pulses, respectively.

The relative quantum yields of singlet oxygen generation were determined by using the standard method of comparing the relative initial intensities of $^1O_2$ phosphorescence after the laser pulse, which were normalised to the number of photons that were absorbed during this pulse by dye molecules [19]. The data are presented in Table 1. As a reference compound, we used PN, which is known to generate singlet oxygen with the quantum yield close to unity [20]. One can see from Table 1 that the values of γ_Δ obtained for TPP and TBPc are in agreement with those measured earlier. For TMTP, the quantum yield of singlet generation has never been measured. Table 1 shows that it is close to γ_Δ for TBPc.

3.4 Singlet oxygen sensitised delayed fluorescence of dyes

As mentioned above, TBPc has a unique ability to emit SOSDF when singlet oxygen is generated in TBPc solutions. We found that TMTP showed the same ability. SOSDF was detected through the cut-off filter transmitting light at $\lambda > 630$ nm. Because SOSDF was much stronger than phosphorescence, an additional neutral filter that reduced delayed fluorescence by a factor of 50 was placed in front of the photodetector. In this case, the $^1O_2$ phosphorescence was not detected and only SOSDF was observed.

Table 1. Experimentally measured and given in the literature quantum yields of laser-induced generation of singlet oxygen by dyes.

Photosensitiser	Experimental data	Literature data
	γ_Δ (rel. units)	γ_Δ (absolute values)
PN	1.0	0.95 – 1.0 [20]
TPP	0.74	0.65 – 0.80 [17, 18, 20 – 24]
TBPc	0.20	0.17 – 0.27 [4, 5, 17, 18, 20, 25]
TMTP	0.18	–

The decay kinetics of SOSDF was exponential (Fig. 4) with the decay time being two times shorter than that of phosphorescence of singlet oxygen, in accordance with previous data [3 – 6]. This reflects the fact that SOSDF appears due to consecutive processes resulting in the accumulation of the energy of two singlet oxygen molecules by one dye molecule [6, 10]. A detailed analysis of the SOSDF mechanism is beyond the scope of this paper. Modern concepts of this mechanism are presented in Refs [7 – 12, 26] (see also referencies therein).

To compare efficiencies of singlet-oxygen sensitised excitation of dye molecules in TBPc and TMTP solutions, we used the previously proposed coefficient α [12]:

$$\alpha = \frac{(I^0_{\text{df}}/I^0_{\text{ph}})k_{\text{r}}}{\gamma_{\text{f}}[^1\text{O}_2]_0[\text{Dye}]},$$

where I^0_{df} and I^0_{ph} are initial intensities of SOSDF and phosphorescence of $^1O_2$ obtained by extrapolation of the luminescence decays to the zero time; k_{r} is the rate of $^1O_2$ radiative deactivation; $[^1O_2]_0$ is the singlet oxygen concentration just after a laser pulse and [Dye] is the dye concentration. Photosensitisers of the $^1O_2$ generation were the same dyes that emitted SOSDF or phenalenone. The absorbance of the photosensitisers in the solutions at the wavelength of laser radiation ($\lambda = 355$ nm) was 0.22 ± 0.02.

Because all the measurements were performed only in benzene, the values of k_{r} were the same in all experiments. The concentration of molecular oxygen, which, as was shown earlier, efficiently quenches delayed fluorescence [7, 12, 26], was also constant in all the experiments. As we noted above, γ_{f} is the same for solutions of TBPc and TMTP. Therefore, we ignored parameters k_{r} and γ_{f} and the oxygen concentration in calculations of relative values of α. Because it is known that $I^0_{\text{ph}} = k_{\text{r}}[^1\text{O}_2]_0$, we used relative values of I^0_{ph} instead of relative concentrations of $[^1\text{O}_2]_0$. The data obtained are presented in Table 2. One can see that, irrespective of the type of photosensitiser, the coefficient α is approximately two times higher in TMTP solutions than in solutions of TBPc.

4. Conclusions

Thus photophysical properties of TMTP are similar to those of TBPc. However, the absorption and fluorescence bands of TMTP that correspond to the Q_y transition are somewhat shifted to the red. TMTP exhibits intense fluorescence, generates singlet oxygen, and also emits intense SOSDF.

Table 2. Relative coefficients α in air-saturated solutions of dyes in benzene for $^1O_2$ generation photosensitised by the same dyes or by phenalenone.

Photosensitiser	SOSDF emitter	I_{df}^0 (rel. units)*	I_{ph}^0 (rel. units)*	[Dye] (μmol litre^{-1})	α (rel. units)
TBPc	TBPc	0.24	0.21	97	1.0
TMTP	TMTP	0.24	0.17	62	2.3
PN	TBPc	0.85	0.96	16	1.0
PN	TMTP	1.4	0.98	11.8	2.3

*Measured through a neutral filter that reduced the SOSDF intensity by a factor of 50.

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References

1. Krasnovskiĭ A A Jr. Izv. Akad. Nauk SSSR, Ser. Fiz. **41** 343 (1978)
2. Krasnovsky A A Jr. Photochem. Photobiol. **29** 29 (1979)
3. Krasnovskiĭ A A Jr., Neverov K V Biofizika **23** 884 (1988)
4. Krasnovsky A A Jr., Neverov K V Chem. Phys. Lett. **167** 591 (1990)
5. Neverov K V, Krasnovskiĭ A A Jr. Opt. Spectrosc. **71** 691 (1991)
6. Krasnovsky A A Jr., Foote C S J. Am. Chem. Soc. **115** 6013 (1993)
7. Baigel D M, Gorman A A, Hamblett I, Hill T J J. Photochem. Photobiol. B.: Biology **43** 229 (1998)
8. Krasnovskiĭ A A Jr., Fu Y, Bashtanov M E, Murphy S, Foote C S Opt. Spectrosk. **83** 616 (1997) [Opt. Spectrosc. **83** 571 (1997)]
9. Krasnovsky A A Jr., Fu Y, Bashtanov M E, Murphy S, Foote C S Photochem. Photobiol. **67S** 77S (1998)
10. Fu Y, Krasnovsky A A, Jr., Foote C S J. Phys. Chem. A: Chemistry **101** 2552 (1997)
11. Bashtanov M E, Krasnovskiĭ A A Jr. Khim. Vys. Energ. **31** 375 (1997) [High Energy Chemistry **31** 338 (1997)]
12. Bashtanov M E, Krasnovskiĭ A A, Jr. Kvantovaya Electron. (Moscow) **26**, 163 1999 [Quantum Electron. **29** 163 1999)]
13. Mikhalenko S A, Barkanova S V, Lebedev O L, Luk'yanets E A Zh. Obshch. Khim. **41** 2735 (1971)
14. Mikhalenko S A, Solov'yova L I, Luk'yanets E A Zh. Obshch. Khim. **61** 996 (1991)
15. Kuzmitskiĭ V A, Solov'yov K N, Tsvirko M P Porphyrins: Spectroscopy, Electrochemistry, Applications (Moscow: Nauka, 1987), p. 7
16. Teuchner K, Pfarrherr A, Stiel H, Freyer W, Leupold D Photochem. Photobiol. **57** 465 (1993)
17. Darwent J R, Douglas P, Harriman A, Porter G, Richoux M-C Coord. Chem. Rev. **44** 83 (1982)
18. Lawrence D S, Whitten D G Photochem. Photobiol. **64** 923 (1996)
19. Gorman A A, Rodgers M A CRC Handbook of Organic Photochemistry (Boca Raton: CRC Press, USA, 1989, vol. 2, p. 229)
20. Schmidt R, Tanielian C, Dunsbach R, Wolf C J. Photochem. Photobiol. A: Chem., **79** 11 (1994)
21. Krasnovskiĭ A A, Jr., Egorov S Yu, Nazarova O V, Yartsev E I, Ponomarev G V Biofizika **32** 982 (1987)
22. Bonnett R, McGarvey D J, Harriman A, Land E J, Truscott T G, Winfield U-J Photochem. Photobiol. **48** 271 (1988)
23. Dzhagarov B A, Gurinovich G P, Novichenkov V E, Salokhiddinov K I, Shul'ga A M, Ganzha V A Khim. Fiz. **6** 1069 (1988)
24. Tanielian C, Wolff C J. Phys. Chem. **99** 9825 (1995)
25. Keir W E, Land E J, McLenan A H, McGarvey D J, Truscott T G Photochem. Photobiol. **46** 587 (1987)
26. Murphy S, Kondo K, Foote C S J. Am. Chem. Soc. **121** 3751 (1999)