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# Effect of core atom modification on photophysical properties and singlet oxygen generation efficiencies: tetraphenylporphyrin analogues core-modified by oxygen and/or sulfur

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## Abstract

Photophysical properties and singlet oxygen generation efficiencies of oxa- and/or thia-porphyrins have been investigated by time-resolved and steady-state spectroscopic methods. Introduction of sulfur atom into the porphyrin core induces a slight increment in the internal conversion rate and it also largely increases the intersystem crossing rate due to spin-orbit coupling enhancement, resulting the enhanced triplet state and singlet oxygen quantum yields. However, the quantum yields of mono oxygen-substituted porphyrin are reduced due to relatively more enhanced internal conversion. These suggest that sulfur modification in the core improves the photophysical efficiency of photosensitizers in the application respect of photodynamic therapy (PDT). © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Replacement of one or more of the porphyrin pyrrolic nitrogens with other heteroatoms, such as oxygen and/or sulfur, leads to a series of new heterocyclic molecules [1–3]. Since the first syntheses of oxa- and/or thia-porphyrin analogues were reported, various studies have revealed that the replacement of pyrrole rings by thiophene and/or

furan rings induces the different chemical and physical properties compared with the normal nitrogen porphyrins [4–7]. Although these heterocyclic porphyrins preserve the basic frame of porphyrin, the core modification affects the metal binding efficiency due to the size change of the macrocyclic cavity and also alters the overall photophysical characteristics, such as quantum yields and lifetimes. These properties of heterocyclic porphyrins stimulated the research for their potential usage as new complexing agents and photosensitizers for photodynamic therapy (PDT) [8,9]. In particular, some of 21-oxaporphyrins, 21-

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thiaporphyrins, and 21,23-dithiaporphyrins were revealed to be potent tumor photosensitizers in the environment of *in vitro* human cell and *in vivo* model animal [9,10].

Understanding the overall photophysical characteristics of the photosensitizer and the generated singlet oxygen is an essential prerequisite to determine the potential usage in PDT application since the photophysical information, such as intersystem crossing rate and quantum yield, are the determining factors for singlet oxygen generation and the high singlet oxygen quantum yield is one of the most important requirements as well as the biological factors, such as specific binding efficiency to cancer cell and non-toxicity. These photophysical factors are governed by the structural and electronic properties (aromaticity, degree of distortion, and spin-orbit coupling) of photosensitizer [11,12]. Therefore, the detailed study on the relationship between the photophysical parameters and the structural and electronic properties is necessary. However, for the sulfur and/or oxygen core-modified porphyrins, the photophysical properties of the triplet quantum yield and singlet oxygen generation quantum yield have not been fully investigated.

In this study, the overall excited state properties of 5,10,15,20-tetraphenyl-21-oxaporphyrin (OTPPH), 5,10,15,20-tetraphenyl-21-thiaporphyrin (STPPH), 5,10,15,20-tetraphenyl-21-oxa-22-thiaporphyrin (OSTPP) and the efficiency factors of singlet oxygen generation have been investigated to provide information on determining the possibility of their use as PDT photosensitizers. We have mainly examined the effect of oxygen and/or sulfur core atoms on the photophysical kinetics of triplet state population and singlet oxygen generation, such as the enhancement of intersystem crossing rate induced by the internal heavy atom effect and the structural distortion in the excited state.

## 2. Experimental details

### 2.1. Materials

All core-modified porphyrins (Fig. 1) were synthesized and characterized as previously re-

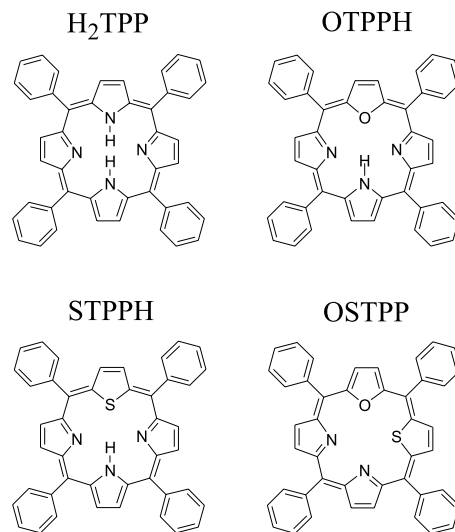


Fig. 1. Chemical structures of H<sub>2</sub>TPP and the core-modified porphyrins.

ported [13,14]. Toluene (Merk, HPLC grade) was used as received without further purification for the preparation of all solutions. The solutions were partially degassed by the thaw-freeze-pump cycle. Air-saturated solutions were prepared by bubbling with air gas (99.999%). All the conditions of degassing and air-saturation processes were consistent throughout the experiments. Concentrations of the samples were in the range of 10<sup>-5</sup> M.

### 2.2. Spectroscopic measurements

Steady-state absorption spectra were obtained by a UV-VIS spectrophotometer (Shimadzu, UV-160A). Steady-state fluorescence spectra were measured by a spectrofluorimeter (Hitach, F-4500). The excitation source for time-resolved fluorescence was a nitrogen laser (Laser Photonics, LN1000, 800 ps FWHM pulse). Fluorescence was collected at the perpendicular angle to the excitation beam and detected with a monochromator (Acton Research, spectrapro) and PMT (Hamamatsu, H5783-04) at the magic angle. The signals were processed by 500 MHz digital oscilloscope (Hewlett Packard, 54520A). Time-resolved T-T absorption was measured by using tungsten lamp (home-made) as a probe source. The probe light

from tungsten lamp was shaped by iris and then perpendicularly focused into the sample which was excited by the pump beam from Nd-YAG pumped optical parametric oscillator (OPO) laser (B.M. Industries, OP901-355, 5 ns FWHM pulse). The transmitted probe beam was collected by the same detection setup which was utilized for the fluorescence measurement. Triplet state quantum yields were determined by the power-dependent comparative method with various powers of excitation radiation. Singlet oxygen quantum yields were directly determined from the singlet oxygen phosphorescence signals. The signals were detected through cut-off (< 1000 nm, CVI) and interference filters (1270 nm, spectrogon) and by germanium photodiode (EG&G, Judson).

### 3. Results

#### 3.1. Steady-state spectra

Absorption spectra (Fig. 2) of H<sub>2</sub>TPP, OTPPH, STPPH show similarity in their electronic structures whereas OSTPP has rather different spectral shape. The peak wavelengths of  $Q_x(0,0)$  bands increase in the order of H<sub>2</sub>TPP < OTPPH < STPPH < OSTPP as shown in Table 1. Peak positions of  $Q_x^*(0,0)$  fluorescence bands are also red-shifted in the same sequence. The Stokes shifts (Table 1) of  $Q_x(0,0)$  are typical values compared with those of other porphyrins [15]. The fluorescence quantum yields (Table 2) in partially degassed condition were also measured by optical dilution method. The quantum yields of the sulfur-substituted porphyrins (STPPH and OSTPP) are much smaller than the others due to the enhanced non-radiative decay rates which are discussed in Section 3.5.

#### 3.2. Time-resolved spectroscopies

Time-resolved fluorescence decays were measured at the peaks of  $Q_x^*(0,0)$  emission bands in both partially degassed and air-saturated conditions (Fig. 3). Excitation wavelengths were in the range of 505–525 nm. Fluorescence decay signals were fitted by single exponentials with an iterative

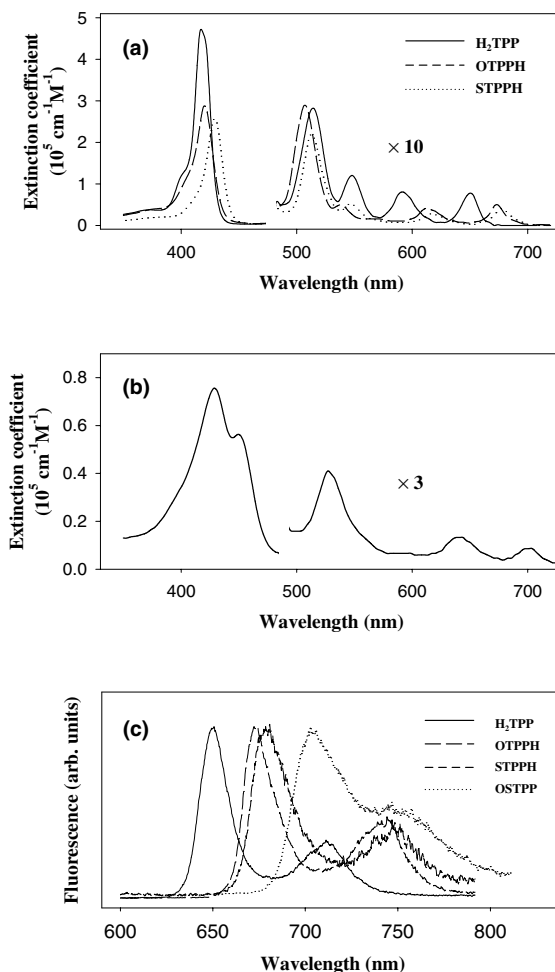


Fig. 2. (a) Steady-state absorption spectra of H<sub>2</sub>TPP, OTPPH, and STPPH. (b) Steady-state absorption spectrum of OSTPP. (c) Steady-state fluorescence spectra of all compounds.

Table 1  
Steady-state spectral properties

	$Q_x(0,0)$ (nm)	$Q_x^*(0,0)$ (nm)	Stokes shift (cm <sup>-1</sup> )
H <sub>2</sub> TPP	647	651	95
OTPPH	673	674	22
STPPH	677	679	43
OSTPP	701	703	40

non-linear deconvolution fitting method. Table 2 indicates that STPPH and OSTPP have much faster relaxation times of S<sub>1</sub> states than H<sub>2</sub>TPP and OTPPH as expected from the fluorescence

Table 2  
Photophysical parameters in partially degassed and air-saturated conditions<sup>a</sup>

	$k_f'^b$ ( $10^6 \text{ s}^{-1}$ )	$k_f''^b$ ( $10^6 \text{ s}^{-1}$ )	$\Phi_f'$	$k_T'$ ( $10^3 \text{ s}^{-1}$ )	$k_T''$ ( $10^6 \text{ s}^{-1}$ )	$\Phi_T'$
H <sub>2</sub> TPP	73.5	94.3	0.11	250	3.3	0.72 <sup>c</sup>
OTPPH	85.5	105	0.086	410	5.3	0.67
STPPH	570	590	0.016	410	4.7	0.92
OSTPP	930	960	0.0071	630	6.3	0.96

<sup>a</sup> Errors in all data are about  $\pm 5\%$ .

<sup>b</sup> Prime (') and double prime (") stand for partially degassed and air-saturated conditions, respectively. These notations are used throughout the manuscript.

<sup>c</sup>  $\Phi_T' = (k_f/k_f')\Phi_T + (k_q/k_f')[O_2]'$ : It includes the oxygen-assisted enhancement of intersystem crossing rate [16].  $\Phi_T = 0.72$  for H<sub>2</sub>TPP in completely degassed toluene [17].

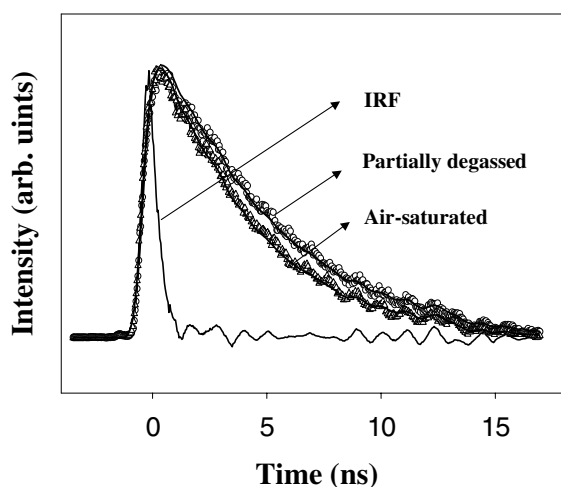


Fig. 3. Typical fluorescence decay signals and fitted lines of OTPPH. IRF indicates instrumental response function.

quantum yields. Time-resolved T–T absorptions were measured at 420–480 nm with the excitation of 510 nm. The measured triplet decay rates in partially degassed and air-saturated conditions are listed in Table 2.

### 3.3. Triplet quantum yields

Triplet quantum yields were estimated by the power-dependent comparative method [18]. The excitation energy ( $E$ ) and the zero-time triplet transient  $\Delta OD$  have the following relationship [17] (Fig. 4).

$$\Delta OD = a(1 - \exp(-bE)), \quad (1)$$

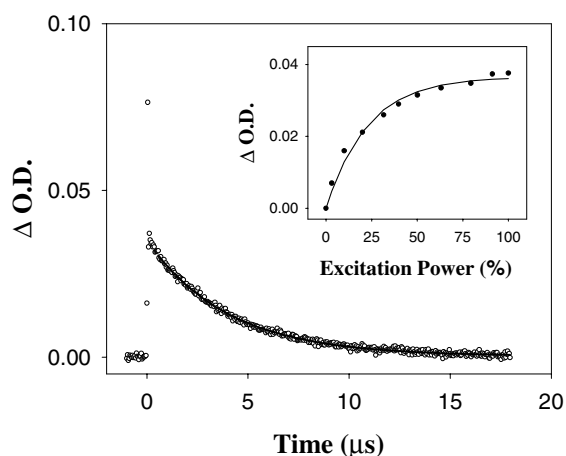


Fig. 4. Triplet state decay signal of H<sub>2</sub>TPP in partially degassed condition. The inset represents the excitation power-dependence of the zero-time  $\Delta OD$  for STPPH.

where  $a$  is a proportionality constant and  $b = k\Phi_T\varepsilon_g$  ( $\Phi_T$  is a triplet quantum yield,  $\varepsilon_g$  is an absorption coefficient of ground state, and  $k$  is an instrumental constant). With the measured values of the zero-time triplet  $\Delta OD$  for both reference and sample, triplet quantum yield is calculated as the following [17]

$$\Phi_T^S = \Phi_T^R \frac{b^S \varepsilon_g^R}{b^R \varepsilon_g^S}, \quad (2)$$

where S and R stand for sample and reference, respectively. The triplet quantum yields ( $\Phi_T'$ ) estimated by using the reference of H<sub>2</sub>TPP, are listed in Table 2. The  $\Phi_T'$  reference value of H<sub>2</sub>TPP is calculated by taking into account of the oxygen-

assisted enhancement of intersystem crossing rate (Table 2, footnote). The triplet quantum yields of the sulfur-substituted porphyrins are estimated to be higher than those of OTPPH and H<sub>2</sub>TPP, and OTPPH has lower  $\Phi_T'$  value than H<sub>2</sub>TPP.

### 3.4. Singlet oxygen quantum yields and lifetimes

The measured singlet oxygen phosphorescence signals (Fig. 5) were fitted to single exponentials,

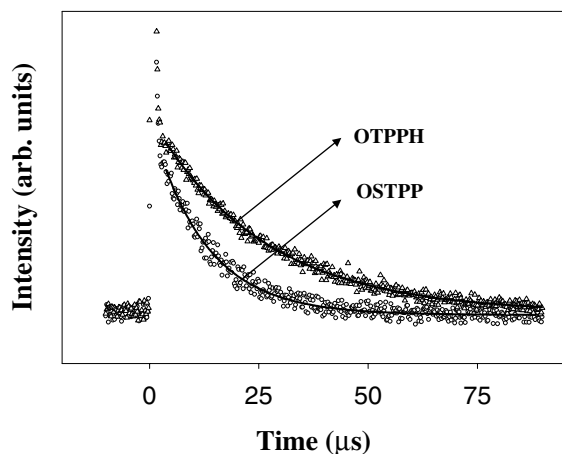


Fig. 5. Normalized time-resolved <sup>1</sup>O<sub>2</sub> phosphorescence signals and fitted lines of OTPPH and OSTPP solutions.

from which the zero-time intensities and lifetimes were estimated. Singlet oxygen quantum yields ( $\Phi_{\Delta}$ ) were obtained by the following equation with the reference of H<sub>2</sub>TPP [19,20]

$$\Phi_{\Delta}^S = \Phi_{\Delta}^R \frac{I_0^S(1 - 10^{-A_R})}{I_0^R(1 - 10^{-A_S})}, \quad (3)$$

where  $I_0$  is the phosphorescence signal at zero-time and  $A$  is the absorbance at the excitation wavelength. The indexes S and R stand for sample and reference, respectively. A good linearity between the excitation energy and the phosphorescence intensity was obtained within experimental errors and the signals of all samples were acquired at the same excitation energy.  $I_0$  and  $(1 - 10^{-A})$  have also the linear relationship under our experimental conditions. The singlet oxygen quantum yields (Table 3) of the sulfur-substituted porphyrins are larger than that of H<sub>2</sub>TPP, and  $\Phi_{\Delta}$  of OTPPH is reduced compared with that of H<sub>2</sub>TPP. On the other hand, the singlet oxygen lifetimes in H<sub>2</sub>TPP, OTPPH, STPPH solutions are all measured to be  $\sim 29 \mu\text{s}$  which is the characteristic relaxation rate of singlet oxygen in toluene [21]. However, in OSTPP solution, the lifetime is reduced to be  $12.5 \mu\text{s}$ , which implies that some additional quenching processes occur in OSTPP solution. One of such additional quenching processes can be

Table 3  
Summary of photophysical properties

	$\Phi_T^{a,b}$	$k_T^c$ (10 <sup>6</sup> s <sup>-1</sup> )	$k_T^a$ (10 <sup>6</sup> s <sup>-1</sup> )	$k_{ic}^d$ (10 <sup>6</sup> s <sup>-1</sup> )	$k_{isc}^a$ (10 <sup>6</sup> s <sup>-1</sup> )	
H <sub>2</sub> TPP	0.11	71.8	7.9	12	52	
OTPPH	0.088	83.9	7.4	21	56	
STPPH	0.016	560	9.0	30	520	
OSTPP	0.0071	930	6.6	30	890	
	$\Phi_T^{c,e}$	$\Phi_T^{\prime a,f}$	$\Phi_{\Delta}^c$	$\tau_{\Delta}^c$ (μs)	$f_{\Delta}^{Ta}$	$P_{O_2}^T$
H <sub>2</sub> TPP	0.72	0.79	0.68 <sup>g</sup>	28.5	0.86	$\sim 1$
OTPPH	0.67	0.72	0.60	28.8	0.83	$\sim 1$
STPPH	0.92	0.92	0.80	28.5	0.87	$\sim 1$
OSTPP	0.96	0.96	0.85	12.5	0.89	$\sim 1$

<sup>a</sup>  $\pm 10\%$ .

<sup>b</sup>  $\Phi_T = (k_T'/k_T)\Phi_T'$ .

<sup>c</sup>  $\pm 5\%$ .

<sup>d</sup>  $\pm 15\%$ .

<sup>e</sup>  $\Phi_T = (k_T'/k_T)\Phi_T' - (k_a/k_T)[O_2]'$ .

<sup>f</sup>  $\Phi_T'' = (k_T'/k_T'')\Phi_T + (k_a/k_T'')[O_2]''$ .

<sup>g</sup> Ref. [23].

a physical quenching through exciplex formation of the electronic ground state ( $S_0$ ) of OSTPP with the singlet oxygen, as in the case of bacteriochlorophylls [22]. Such complexation can be favored by more polar electronic ground state of OSTPP which probably results in the increase of electron-donor ability [19] since the electronegativity difference between the core atoms (sulfur and oxygen) in OSTPP is larger than those in OTPPH and STPPH.

### 3.5. Kinetic rates

The residual oxygen concentration of partially degassed solution,  $[O_2]'$ , is estimated from the triplet kinetic equations of  $H_2TPP$  in both partially degassed and air-saturated conditions.

$$k'_T = k_T + k_q^T [O_2]', \quad (4a)$$

$$k''_T = k_T + k_q^T [O_2]'', \quad (4b)$$

where  $k'_T$  and  $k''_T$  are the triplet state decay rates in partially degassed and air-saturated conditions, respectively. The triplet quenching rate constant by oxygen,  $k_q^T$ , is assumed to be constant under our experimental range of oxygen concentration since a diffusion controlled process for triplet state quenching is generally considered to be dominant in the case of the free base porphyrin [24] and under our experimental oxygen concentration range [25]. The oxygen concentration of the air-saturated solution,  $[O_2]''$ , was reported to be  $2.1 \times 10^{-3}$  M [26] and the intrinsic triplet decay rate,  $k_T$ , was also reported to be  $1.0 \times 10^{-3}$  s $^{-1}$  in toluene [27]. From these data,  $[O_2]'$  can be estimated to be  $1.6 \times 10^{-4}$  M.

As the contribution of photochemical processes of the  $S_1$  state is considered to be negligible, the fluorescence kinetic rates in both conditions are the following:

$$k'_f = k_r + k_{ic} + k_{isc} + k_q [O_2]', \quad (5a)$$

$$k''_f = k_r + k_{ic} + k_{isc} + k_q [O_2]'', \quad (5b)$$

where  $k_r$ ,  $k_{ic}$ , and  $k_{isc}$  are radiative, internal conversion, and intersystem crossing rates of  $S_1$  state, respectively, and  $k_q$  is oxygen quenching rate constant of  $S_1$  state. As previously stated, prime (') and double prime (") represent partially degassed and air-saturated conditions, respectively.

From the equations, intrinsic fluorescence decay rate,  $k_f (= k_r + k_{ic} + k_{isc})$ , can be estimated and the radiative, internal conversion, and intersystem crossing rates can be calculated as follows [28]

$$\begin{aligned} k_r &= \Phi_f k_f, & k_{isc} &= \Phi_T k_f, \\ k_{ic} &= (1 - \Phi_f - \Phi_T) k_f. \end{aligned} \quad (6)$$

The results are listed in Table 3. The intrinsic quantum yields ( $\Phi_f, \Phi_T$ ) are obtained by the kinetic equations (Table 3, footnote) which remove the oxygen quenching effect in  $\Phi'_f$  and  $\Phi'_T$ . A notable feature is that  $k_f$  and  $k_{isc}$  increase in the order of  $H_2TPP < OTPPH < STPPH < OSTPP$  and the sulfur-substituted porphyrins show much higher values of  $k_f$  and  $k_{isc}$ .  $k_{ic}$  also increases in the same order with the small increment.

### 3.6. Singlet oxygen generation efficiencies

Since the singlet oxygen is produced dominantly from the triplet state, its generation efficiency can be expressed as follows [16,29,30]

$$\Phi_\Delta = \Phi''_T P_{O_2}^T f_\Delta^T, \quad (7a)$$

$$P_{O_2}^T = \frac{k_q^T [O_2]''}{k_T + k_q^T [O_2]''}, \quad (7b)$$

$$k_q^T = \frac{k''_T - k'_T}{[O_2]'' - [O_2]'}, \quad (7c)$$

where  $P_{O_2}^T$  is the fraction of the triplet state which is quenched by oxygen and  $f_\Delta^T$  is the generation efficiency of singlet oxygen induced by the energy transfer during the oxygen quenching of the triplet state.  $\Phi''_T$  is the triplet quantum yield in the air-saturated condition. This value was calculated from the kinetic equation including the oxygen-assisted intersystem crossing rate enhancement (Table 3, footnote). The intrinsic triplet decay rate ( $k_T$ ) can be obtained from the rate Eqs. (4a) and (4b) of the triplet states in both partially degassed and air-saturated conditions. However, the slight errors in the values of the residual oxygen concentration and the triplet decay rates may cause a great deviation in the estimation of the intrinsic

triplet decay rate. Therefore, from the Eqs. (4a) and (4b), the intrinsic triplet decay rate can not be calculated accurately and only the estimation of the oxygen quenching rate constant,  $k_q^T$ , is possible. When all these errors in the values of  $[O_2]'$ ,  $k_T$ 's, and  $k_q^T$  are considered in the calculation of  $P_{O_2}^T$ 's, even the minimum values of  $P_{O_2}^T$ 's are greater than 0.95. Consequently,  $P_{O_2}^T$ 's are reasonably assumed to be  $\sim 1$  for all compounds because the triplet decay rates of porphyrins are considered to be much smaller than the oxygen quenching rates in air-saturated condition [26].  $f_{\Delta}^T$  values (Table 3) of all modified porphyrins are  $\sim 0.9$ .

#### 4. Discussion

The red-shift in the absorption and emission spectra of oxa- and/or thia-porphyrins can be induced by the structural distortion of porphyrin  $\pi$ -systems and/or the electronic effect of heteroatoms [2]. According to X-ray crystallography data of similar compounds [2], the relatively small deviation from planarity is expected in the ground states of OTPPH and STPPH. The small Stokes shifts also imply that the excited states may have the similar structures to those of the nearly planar ground states [15,31]. Therefore, these red-shifted spectra of OTPPH and STPPH are more likely to be caused by the electronic effects of heteroatoms, which appear in the cases of furans and thiophenes as suggested by Latos-Grażyński [2]. On the other hand, OSTPP including no interior hydrogens/hydrogen bonds shows the different absorption spectrum compared with the others. This spectrum reflects that both the geometrical and electronic structures can be more significantly influenced by the heteroatoms.

The fluorescence quantum yields and lifetimes decrease in the order of  $H_2TPP > OTPPH > STPPH > OSTPP$ . However, the radiative lifetimes of them are not significantly changed. Therefore, the reduced fluorescence quantum yields and lifetimes are due to the enhanced non-radiative decay rates of the internal conversion and/or intersystem crossing. The  $k_{ic}$  can be a factor since their values increase in the order of  $H_2TPP < OTPPH < STPPH \approx OSTPP$ . Therefore, as sug-

gested by Gentemann et al. [15,31], this increment sequence implies that the structural distortion in the excited state may exist in the order of  $H_2TPP < OTPPH < STPPH \approx OSTPP$  as the case of nitrogen porphyrins. However, the changes in  $k_{ic}$  values are not large enough for the structural distortion to be a main factor for the enhanced non-radiative decay. On the other hand, STPPH and OSTPP show much larger (10 times)  $k_{isc}$  values than  $H_2TPP$  and OTPPH, implying that the enhanced intersystem crossing rates by the sulfur substitution is mainly responsible for the reduced  $\Phi_f$ . Such enhancement in  $k_{isc}$  seems to be induced by the effects of heavier nucleus of sulfur and its empty d-orbitals which have an appropriate symmetry for better coupling with the  $\pi$ -system of porphyrin [2], resulting in the high  $\Phi_T$ 's of STPPH and OSTPP. The  $k_{isc}$  value can also be enhanced by the structural distortion in the excited state as the case of the distorted nitrogen porphyrins [15,31,32]. From the comparison of the  $k_{isc}$  values of STPPH and OSTPP, OSTPP is considered to be structurally more distorted in its excited state than STPPH, which is also suggested by the significantly influenced electronic spectrum of OSTPP. In the case of OTPPH,  $\Phi_T$  of OTPPH is estimated to be less than that of  $H_2TPP$  due to relatively more enhanced  $k_{ic}$  and less increased  $k_{isc}$  as shown in Table 3.

The  $P_{O_2}^T$  values close to 1.0 of all core-modified porphyrins imply that the triplet states are completely quenched by triplet oxygen. Also, the triplet states undergo energy transfer process to the triplet molecular oxygen in the air-saturated condition with very high efficiencies ( $f_{\Delta}^T \sim 0.9$ ). As a result of the high triplet quantum yields and very large  $P_{O_2}^T$  and  $f_{\Delta}^T$ , the singlet oxygen quantum yields of STPPH and OSTPP become very high to be 0.80 and 0.85, respectively. Therefore, such sulfur modification can be suggested to improve, in respect of photophysical factors, the efficiency of PDT photosensitizers.

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**References**

- [1] L. Latos-Grażyński, E. Pachoska, P. Chmielewski, M.M. Olmstead, A.L. Balch, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2252.
- [2] L. Latos-Grażyński, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), *The Porphyrin Handbook*, vol. 2, Academic Press, New York, 2000, p. 361.
- [3] S.K. Pushpan, J.S. Narayanan, A. Srinivasan, S. Mahajan, T.K. Chandrashekar, R. Roy, *Tetrahedron Lett.* 39 (1998) 9249.
- [4] L. Latos-Grażyński, M.M. Olmstead, A.L. Balch, *Inorg. Chem.* 28 (1989) 4065.
- [5] L. Latos-Grażyński, J. Lisowski, M.M. Olmstead, A.L. Balch, *Inorg. Chem.* 28 (1989) 1183.
- [6] A. Gebauer, J.A.R. Schmidt, J. Arnold, *Inorg. Chem.* 39 (2000) 3424.
- [7] A.W. Johnson, in: K.M. Smith (Ed.), *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam, 1975, p. 729.
- [8] L. Latos-Grażyński, J. Lisowski, M.M. Olmstead, A.L. Balch, *J. Am. Chem. Soc.* 109 (1987) 4428.
- [9] P. Ziółkowski, K. Symonowicz, P. Chmielewski, L. Latos-Grażyński, G. Streckyte, R. Rotomskis, J. Rabczyński, *J. Cancer Res. Clin. Oncol.* 125 (1999) 563.
- [10] E. Marcinkowska, P. Ziółkowski, E. Pacholska, L. Latos-Grażyński, P. Chmielewski, C. Radzikowski, *Anticancer Res.* 17 (1997) 3313.
- [11] R.L. Hill, M. Gouterman, A. Ulman, *Inorg. Chem.* 21 (1982) 1450.
- [12] R.P. Pandian, T.K. Chandrashekar, G.S.S. Saini, A.L. Verma, *J. Chem. Soc. Faraday Trans.* 89 (1993) 677.
- [13] P.Y. Heo, K. Shin, C.H. Lee, *Tetrahedron Lett.* 37 (1996) 197.
- [14] C.H. Lee, W.S. Cho, *Tetrahedron Lett.* 40 (1999) 8879.
- [15] S. Gentemann, C.J. Medforth, T.P. Forsyth, D.J. Nurco, K.M. Smith, J. Fajer, D. Holten, *J. Am. Chem. Soc.* 116 (1994) 7363.
- [16] C. Grewer, H.D. Brauer, *J. Phys. Chem.* 97 (1993) 5001.
- [17] N.G. Angeli, M.G. Lagorio, E.A.S. Román, L.E. Dicalio, *Photochem. Photobiol.* 72 (2000) 49.
- [18] U. Lachish, P.P. Infelta, M. Grätzel, *Chem. Phys. Lett.* 62 (1979) 317.
- [19] A.P. Darmanyan, J.W. Arbogast, C.S. Foote, *J. Phys. Chem.* 95 (1991) 7308.
- [20] A.P. Darmanyan, C.S. Foote, *J. Phys. Chem.* 97 (1993) 5032.
- [21] R.D. Scurlock, P.R. Ogilby, *J. Phys. Chem.* 93 (1989) 5493.
- [22] A.A. Krasnovsky Jr., P. Cheng, R.E. Blankenship, T.A. Moore, D. Gust, *Photochem. Photobiol.* 57 (1993) 324.
- [23] E. Zenkevich, E. Sagun, V. Knyukshto, A. Shulga, A. Mironov, O. Efremova, R. Bonnett, S.P. Songca, M. Kassem, *J. Photochem. Photobiol. B: Biol.* 33 (1996) 171.
- [24] K.-K. Iu, P.R. Ogilby, *J. Phys. Chem.* 92 (1988) 4662.
- [25] K.-K. Iu, P.R. Ogilby, *J. Phys. Chem.* 91 (1987) 1611.
- [26] S.L. Murov, I. Carmichael, G.L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 1993.
- [27] V. Knyukshto, E. Zenkevich, E. Sagun, A. Shulga, S. Bachilo, *Chem. Phys. Lett.* 297 (1998) 97.
- [28] N.J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA, 1978.
- [29] A.A. Abdel-Shafi, P.D. Beer, R.J. Mortimer, F. Wilkinson, *J. Phys. Chem. A* 104 (2000) 192.
- [30] F. Wilkinson, A.A. Abdel-Shafi, *J. Phys. Chem. A* 103 (1999) 5425.
- [31] S. Gentemann, C.J. Medforth, T. Ema, N.Y. Nelson, K.M. Smith, J. Fajer, D. Holten, *Chem. Phys. Lett.* 245 (1995) 441.
- [32] M.K. Bowman, *Chem. Phys. Lett.* 48 (1977) 17.