

## Photophysical Efficiency Factors of Singlet Oxygen Generation from Core-modified Trithiasapphyrin Derivatives

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Received November 12, 2001

The photophysical properties and the singlet oxygen generation efficiencies of *meso*-tetraphenyl-trithiasapphyrin (S<sub>3</sub>TPS) and *meso*-tetrakis(*p*-methoxyphenyl)-trithiasapphyrin ((*p*-MeO)-S<sub>3</sub>TPS) have been investigated, utilizing steady-state and time-resolved spectroscopic methods to elucidate the possibility of their use as photosensitizers for photodynamic therapy (PDT). The observed photophysical properties were compared with those of other porphyrin-like photosensitizers in geometrical and electronic structural aspects, such as extended  $\pi$  conjugation, structural distortion, and internal heavy atoms. The steady-state electronic absorption and fluorescence spectra were both red-shifted due to the extended  $\pi$ -conjugation. The fluorescence quantum yields were measured as very small. Even though intersystem crossing rates were expected to increase due to the increment of spin orbital coupling, the triplet quantum yields were measured as less than 0.15. Such characteristics can be ascribed to the more enhanced internal conversion rates compared with the intersystem crossing rates. Furthermore, the triplet state lifetimes were shortened to  $\sim 1.0 \mu\text{s}$  as expected. Therefore, the singlet oxygen quantum yields were estimated to be near zero due to the fast triplet state decay rates and the inefficient energy transfer to the oxygen molecule as well as the low triplet quantum yields. The low efficiencies of energy transfer to the oxygen molecule can be attributed to the lower oxidation potential and/or the energetically low lying triplet state. Such photophysical factors should be carefully evaluated as potential photosensitizers that have extended  $\pi$ -conjugation and heavy core atoms synthesized for red-shifted absorption and high triplet state quantum yields.

**Keywords :** Trithiasapphyrins, Triplet state, Singlet oxygen, Photophysics, Photodynamic therapy.

### Introduction

Sapphyrins, extended  $\pi$ -conjugated porphyrins that have an overall aromatic 22  $\pi$ -electrons annulenes framework, have received considerable attentions due to their potential biomedical applications, such as MRI contrasting agents, macrocyclic receptors for transport, and photosensitizers of photodynamic therapy (PDT).<sup>1,2</sup> Recently, their heteroatom-substituted analogues in which one or more of the pyrrole rings are replaced by furan, thiophene, selenophene moieties have also been synthesized and their physical properties have been investigated.<sup>3,4</sup> The ring expansion and heavy atom substitution in these core-modified expanded porphyrins cause their chemical and physical properties to be different from those of common porphyrins, *i.e.*, the ring expansion and the core-modification affect the metal binding efficiency due to the size change of the macrocyclic cavity and alter the overall photophysical characteristics, such as quantum yields and lifetimes. Understanding the photophysical nature of this new class of sapphyrins is an important prerequisite to determining their potential suitability

in PDT applications in addition to their biological factors, such as specific binding efficiency to cancer cells and nontoxicity.<sup>5</sup> One of the most desirable photophysical properties for PDT application is red light absorption since red light penetrates the tissue more deeply with minimal light loss in biological media. The high singlet oxygen quantum yield is also one of the most important photophysical requirements because the singlet oxygen is considered to be the main mediator of photodynamic cytotoxicity. Since the singlet oxygen is mainly generated from the triplet state, the high triplet state quantum yield of PDT photosensitizer is desirable for generating singlet oxygen. Besides the triplet quantum yield, other photophysics of the lowest triplet state, such as triplet state lifetime and triplet state quenching rate by oxygen, profoundly affect the formation efficiency of the singlet oxygen. This formation efficiency of the singlet oxygen can be expressed by several photophysical parameters concerning the triplet state and the singlet oxygen.

In the present work, we have investigated the photophysics of *meso*-tetraphenyl-trithiasapphyrin (S<sub>3</sub>TPS) and *meso*-tetrakis(*p*-methoxyphenyl)-trithiasapphyrin ((*p*-MeO)-S<sub>3</sub>TPS) and measured the singlet oxygen generation efficiencies to provide information for determining the possibility of their usage as PDT photosensitizers by employing both steady-state and time-resolved spectroscopic methods.

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## Experimental Section

**Material.** Toluene, THF, and acetone (Aldrich, HPLC grade) were used as solvents for all samples without further purification. Partially degassed toluene solution was prepared by the thaw-freeze-pump cycle. Solutions of THF and acetone were partially degassed by bubbling with N<sub>2</sub> gas (high purity, 99.999%) for 60 minutes. All air saturated solutions were obtained by bubbling with air gas (high purity, 99.99%) for 40 minutes. All the conditions of degassing and air-saturation processes were consistent throughout the experiments. The chemical structures of S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS are depicted in Figure 1. The detailed processes of syntheses are reported in the reference.<sup>6</sup> Concentrations of all samples were less than 10<sup>-5</sup> M.

**Photophysical measurements.** Steady-state absorption and fluorescence spectra were obtained by a UV-VIS spectrophotometer (JASCO, V-530) and a spectrofluorimeter (Hitach, F-4500), respectively. Time-resolved T-T absorption was measured using a Tungsten lamp (home-made) as the probe source beam. The Tungsten lamp beam was shaped by an iris and then focused perpendicularly into the sample which was excited by an Nd-YAG pumped OPO (optical parametric oscillator) laser (B. M. Industries, OP901-355, 5 ns FWHM pulse). The transmitted beam was collected by focusing optics and then detected with a monochromator (Acton Research, spectrapro) and PMT (Hamamatsu, H5783-04). The signal was processed by a 500 MHz digital oscilloscope (Hewlett Packard, 54520A). Triplet state quantum yields were determined by the power-dependent comparative method, with various powers of excitation. The direct measurement of singlet oxygen quantum yields was per-

formed by the detection of singlet oxygen phosphorescence. The signals were detected through cut-off (< 1000 nm, CVI) and interference filter (1270 nm, spectrogon) and by germanium photodiode (EG&G, Judson) with a home-built amplification stage.

## Results

**Steady-state absorption and fluorescence.** As shown in Figure 2, S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS have typical porphyrin-like absorption spectra, which have intense Soret band around 500-515 nm, and several weak Q bands in the range of 550-900 nm. S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS have four Q bands of which the most red-shifted band lies in ~900 nm. The absorption spectra did not vary within the concentration range (10<sup>-5</sup>~10<sup>-7</sup> M), implying that the aggregation did not occur in our experimental condition.

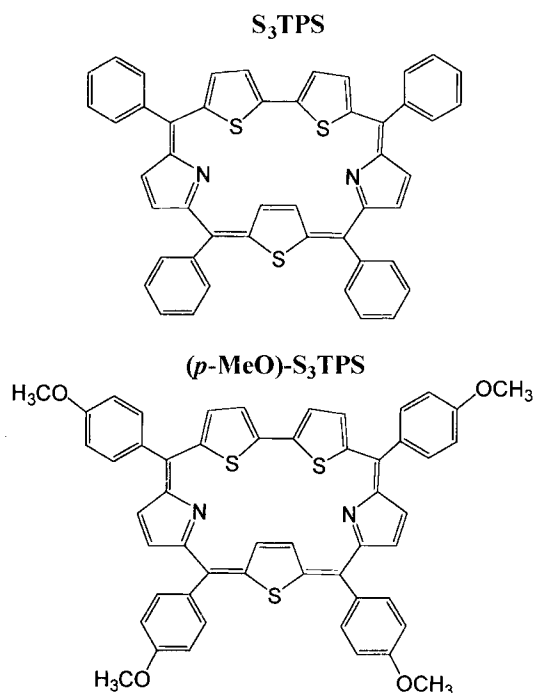
Steady-state fluorescence spectra of all samples were measured at the excitation of the Soret band, and very weak emission, which had two bands around 700 nm and 860 nm, was detected, as shown in Table 2. The fluorescence quantum yields were in the range of 10<sup>-5</sup>, with the reference being IR 144 in ethanol. The referenced value of IR 144 is estimated to be 0.08 by the equation of  $\Phi_f = k_r/k_f$ , where  $k_r$  and  $k_f$  are the radiative and fluorescence decay rates, respectively. In this equation,  $k_f$  is already known<sup>7</sup> ( $k_f = 1.7 \times 10^9 \text{ s}^{-1}$ ), and  $k_r$  is calculated by the strickler-berg equation.<sup>8</sup> ( $k_r = 1.3 \times 10^8 \text{ s}^{-1}$ )

**Time-resolved T-T absorption.** Time-resolved T-T absorptions were measured at around 420 nm under both partially degassed and air-saturated conditions. The signals were best fitted by single exponential decay from which the triplet lifetimes in both conditions were measured (Table 3).

**Triplet quantum yields.** Triplet quantum yields were estimated by the power-dependent comparative method.<sup>9</sup> The excitation energy ( $E$ ) and the zero-time triplet transient  $\Delta\text{O.D.}$  have the following relationship<sup>10</sup>:

$$\Delta\text{O.D.} = a(1 - \exp(-b \cdot E)), \quad (1)$$

where  $a$  is a proportionality constant and  $b = k\Phi_T\varepsilon_g$  ( $\Phi_T$  is the triplet quantum yield,  $\varepsilon_g$  is the absorption coefficient of ground state, and  $k$  is the instrumental constant). With the measured values of zero-time triplet  $\Delta\text{O.D.}$  for both reference and sample, the triplet quantum yield is calculated



**Figure 1.** Chemical structures of S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS.

**Table 1.** Absorption peaks of Soret and Q bands of S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS\*

		Soret	Q <sub>1</sub>	Q <sub>2</sub>	Q <sub>3</sub>	Q <sub>4</sub>
S <sub>3</sub> TPS	Toluene	509	621	675	776	877
	THF	505	617	673	779	879
	Acetone	502	617	673	779	879
( <i>p</i> -MeO)-S <sub>3</sub> TPS	Toluene	515	635	690	786	891
	THF	512	632	687	789	894
	Acetone	508	630	685	790	893

\*All numbers have a unit of nm

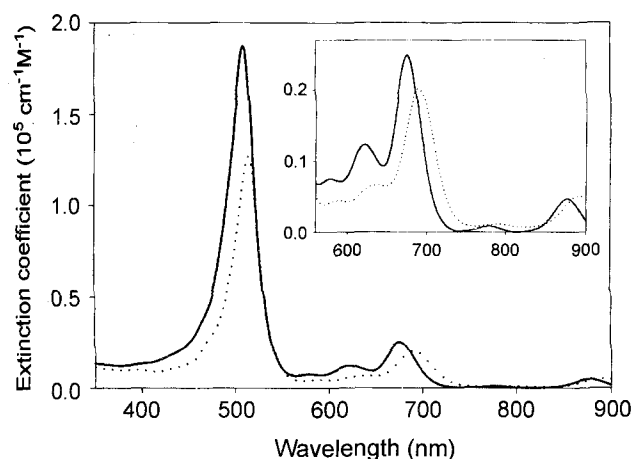


Figure 2. Steady-state absorption spectra of the toluene solutions of  $S_3$ TPS (solid line) and (*p*-MeO)- $S_3$ TPS (dotted line). Q-bands are enlarged in the inset.

Table 2. Fluorescence peaks of  $S_3$ TPS and (*p*-MeO)- $S_3$ TPS\*

		1 <sup>st</sup>	2 <sup>nd</sup>
$S_3$ TPS	Toluene	691	866
	THF	685	868
	Acetone	686	867
( <i>p</i> -MeO)- $S_3$ TPS	Toluene	707	875
	THF	702	877
	Acetone	692	871

\*All numbers have a unit of nm

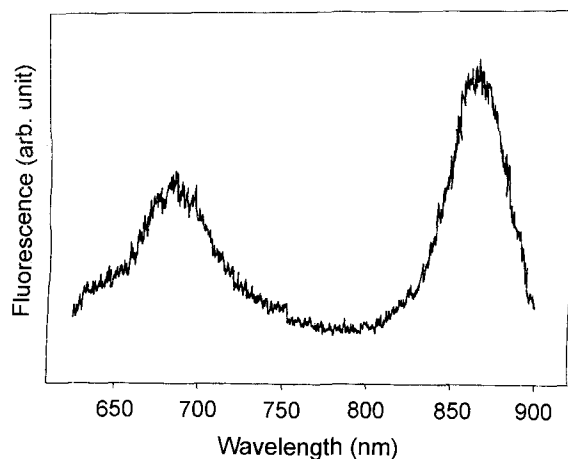


Figure 3. Steady-state fluorescence spectrum of the acetone solutions of  $S_3$ TPS.

as follows<sup>10</sup>:

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

where *S* and *R* are sample and reference, respectively. The triplet quantum yields ( $\Phi_T$ ) are estimated under partially degassed condition by using referencing tetraphenylporphyrin ( $H_2$ TPP) (Table 4). The triplet quantum yields are much

Table 3. Triplet lifetimes in partially degassed ( $\tau_T'$ ) and air-saturated conditions ( $\tau_T''$ )

		$\tau_T' / \mu s^a$	$\tau_T'' / \mu s^a$
$S_3$ TPS	Toluene	0.83	0.59
	THF	0.85	0.61
	Acetone	0.82	0.58
( <i>p</i> -MeO)- $S_3$ TPS	Toluene	0.68	0.48
	THF	0.65	0.47
	Acetone	0.62	0.39

<sup>a</sup>  $\tau_T = 1/k_T$ . Errors in all data are about  $\pm 5\%$ .

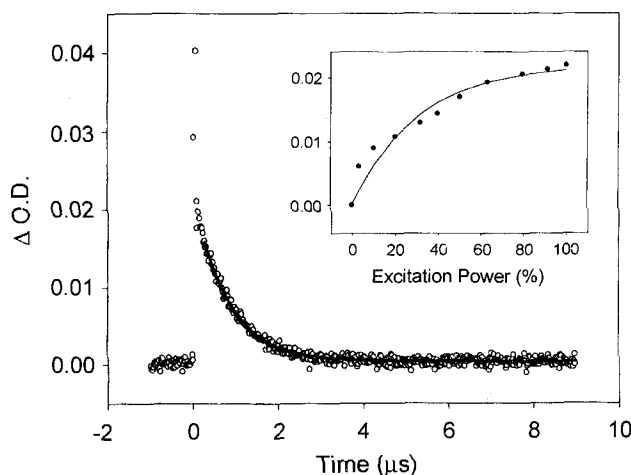


Figure 4. Triplet state decay signal of  $S_3$ TPS in partially degassed acetone solution. The inset represents the excitation power dependence of the zero time  $\Delta O.D.$

Table 4. Triplet state and singlet oxygen photophysical properties\*

		$\tau_T^0 / \mu s^a$	$k_q^{Tb} / 10^8 s^{-1} M^{-1}$	$\Phi_T^c$	$\Phi_\Delta$	$P_{O_2}^T$	$f_\Delta^T$
$S_3$ TPS	Toluene	0.86	2.6	0.11	<0.01	0.29	<0.3
	THF	0.98	2.9	0.05	<0.01	0.38	<0.5
	Acetone	1.1	3.3	0.08	<0.02	0.45	<0.6
( <i>p</i> -MeO)- $S_3$ TPS	Toluene	0.70	3.1	0.13	<0.01	0.32	<0.2
	THF	0.75	3.8	0.05	<0.01	0.37	<0.5
	Acetone	0.86	5.8	0.06	<0.02	0.54	<0.6

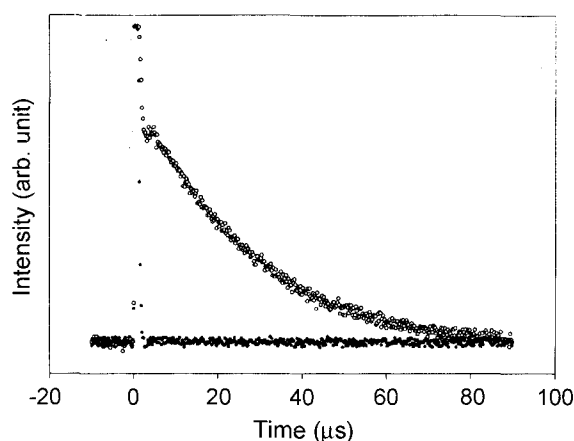
\*All data have the errors of <sup>a</sup>:  $\pm 8\%$ , <sup>b</sup>:  $\pm 20\%$ , and <sup>c</sup>:  $\pm 10\%$ .

smaller than other porphyrin-like photosensitizers.

**Singlet oxygen quantum yields.** Singlet oxygen quantum yields ( $\Phi_\Delta$ ) were obtained under air-saturated condition by the following equation with the reference to  $H_2$ TPP<sup>11</sup>:

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

where  $I_0$  is the phosphorescence signal at zero time and *A* is the absorbance at the excitation wavelength. *S* and *R* stand for sample and reference, respectively. A good linearity between the excitation energy and the phosphorescence intensity of the reference was obtained within experimental



**Figure 5.** Singlet oxygen phosphorescence signals of  $S_3$ TPS in THF (●) and tetraphenylporphyrin ( $H_2$ TPP), as a reference, in toluene (○).

errors and the signals were acquired at the same excitation energy. However, the singlet oxygen phosphorescence signals were not detected in any sample. This means that  $\Phi_{\Delta}$ 's for all samples were less than 0.02, which is the S/N sensitivity limit of our experimental apparatus. These values are much smaller than those of other photosensitizers, including another 26  $\pi$ -electrons core-modified porphyrin, tetrathiarubyrin ( $\Phi_{\Delta}=0.52$ ).<sup>12</sup> In Figure 5, the signal amplitude of  $S_3$ TPS is compared with that of  $H_2$ TPP.

**Triplet state and singlet oxygen photophysics.** The residual oxygen concentrations of partially degassed solutions,  $[O_2]'$ s were estimated by the triplet kinetic equations of  $H_2$ TPP in both partially degassed and air-saturated conditions.

$$k_T' = k_T^0 + k_q^T [O_2]' \quad (4a)$$

$$k_T'' = k_T^0 + k_q^T [O_2]'' \quad (4b)$$

where prime (') and double prime (") in  $k_T$  and  $[O_2]$  represent partially degassed and air-saturated conditions, respectively.  $k_T$ 's are the triplet state decay rates. The triplet quenching rate constant by oxygen,  $k_q^T$ , was assumed to be constant under our experimental oxygen concentration.<sup>13,14</sup> The oxygen concentrations of the air-saturated solutions,  $[O_2]''$ 's in toluene, THF, and acetone were reported to be  $2.1 \times 10^{-3}$  M,  $2.1 \times 10^{-3}$  M, and  $2.4 \times 10^{-3}$  M, respectively.<sup>15</sup> The intrinsic triplet decay rates,  $k_T^0$ 's of  $H_2$ TPP were considered to be much smaller than the oxygen quenching rates.<sup>15</sup> From these data,  $[O_2]'$ 's of toluene, THF, and acetone were estimated to be  $1.6 \times 10^{-4}$  M,  $5.4 \times 10^{-4}$  M, and  $8.0 \times 10^{-4}$  M, respectively.

Therefore, the intrinsic triplet state decay rates ( $k_T^0$ ) and the oxygen quenching rate constants of triplet state ( $k_q^T$ ) of all trithiasapphyrin solutions can be calculated from the equation (4a) and (4b) (Table 4). From these photophysical parameters, the fractions of the triplet state quenched by oxygen ( $P_{O_2}^T$ ) and the efficiencies of singlet oxygen generation ( $f_{\Delta}^T$ ) induced by energy transfer during the oxygen quenching of the triplet state are given by the following equations (Table 4).<sup>16,17</sup>

$$\Phi_{\Delta} = \Phi_T P_{O_2}^T f_{\Delta}^T \quad (5)$$

$$P_{O_2}^T = \frac{k_q^T [O_2]''}{k_T^0 + k_q^T [O_2]''} \quad (6)$$

The intrinsic triplet lifetimes of both  $S_3$ TPS and (*p*-MeO)- $S_3$ TPS are much faster than other photosensitizing porphyrins and their oxygen quenching rate constants of triplet state are rather low. These facts indicate that triplet states are not completely quenched by oxygen even under air-saturated conditions.

## Discussion

As shown in Figure 2, the Soret and Q bands of  $S_3$ TPS and (*p*-MeO)- $S_3$ TPS are shifted to longer wavelengths than those of common porphyrins, such as  $H_2$ TPP. Such red-shift occurs due to the 22  $\pi$ -electrons, leading to a large conjugation effect.

Steady-state fluorescences of  $S_3$ TPS and (*p*-MeO)- $S_3$ TPS are detected in the range of 700-900 nm as other sapphyrin derivatives,<sup>18,19</sup> which are also red-shifted compared with those of common porphyrins. The fluorescence quantum yields ( $\Phi$ ) are measured to be  $\sim 10^{-5}$ . Such low fluorescence quantum yields are considered to result from the more enhanced nonradiative decay rates, including the intersystem crossing and the internal conversion rates.

The triplet quantum yields ( $\Phi_T$ ) were estimated to be  $\leq 0.1$ . These low triplet quantum yields of  $S_3$ TPS and (*p*-MeO)- $S_3$ TPS contrasted with our expectation that the enhanced intersystem crossing rates caused by the internal heavy atom effect may increase the triplet state quantum yields. However, although the intersystem crossing rates increase, the internal conversion rates appear to be much more enhanced, which result in the very low triplet quantum yields. Such enhancement of the internal conversion rates can be discussed in terms of the following three possible reasons: (1) the structural distortion in the excited state, (2) the formation of new low lying states, such as the intermediate charge transfer (CT) state induced by hetero atom substitution, and (3) the decrease in the energy of singlet excited state. Firstly, the internal conversion rates of  $S_3$ TPS and (*p*-MeO)- $S_3$ TPS can be enhanced by the structural distortion in the excited state as reported for the distorted porphyrin.<sup>20,21</sup> The structural distortion in the excited state is considered to enhance the Franck-Condon factor between the ground state and the excited state and to increase the nonradiative decay rates, especially of the internal conversion rather than the intersystem crossing.<sup>20,21</sup> Secondly, the introduction of hetero sulfur atoms into the quasi-aromatic sapphyrins can induce the low energy charge-transfer (CT) states.<sup>22</sup> The presence of such a CT state between  $S_1(\pi, \pi^*)$  and  $S_0$  has been reported to enhance the internal conversion rate.<sup>22</sup> Thirdly, as the singlet excited state energy falls, the Franck-Condon overlap between the singlet excited state and the ground state is generally known to be enhanced.<sup>23</sup>

The intrinsic triplet lifetimes of S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS are faster than those of other typical porphyrins. As mentioned previously, these compounds which have relatively heavy internal core atoms, are considered to promote the nonradiative T<sub>1</sub> relaxation rate through the enhanced inter-system crossing (T<sub>1</sub> → S<sub>0</sub>). On the other hand, the triplet quenching rate constants by oxygen are measured as 2.5 ~ 6 × 10<sup>8</sup>, which are somewhat lower than the values for other porphyrins. Owing to the relatively lower triplet state quenching rate and the faster triplet relaxation, the fractions of the triplet state quenched by oxygen, P<sub>O<sub>2</sub></sub><sup>T</sup>'s, are reduced to ~0.4 under the air-saturated condition. This indicates that the triplet states of S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS are quenched less by oxygen even under the air-saturated condition.

The efficiencies of singlet oxygen generation, f<sub>A</sub><sup>T</sup>'s, induced by energy transfer during the oxygen quenching are calculated to be approximately <0.5. Such low values mean that singlet oxygens are generated by the relatively small portion of the triplet states quenched by the oxygen molecules. However, f<sub>A</sub><sup>T</sup>'s of most common photosensitizers, including tetrathiarubyrin, are reported to be much larger (f<sub>A</sub><sup>T</sup> > 0.7).<sup>12</sup> Such a decrease of thiasapphyrin's f<sub>A</sub><sup>T</sup> values can be explained by the following factors: (1) the low oxidation potential and (2) the low lying triplet state compared with the singlet oxygen. As reported by Darmanyan *et al.*, the charge transfer exciplex formation with oxygen can promote the relaxation of its complex without singlet oxygen generation.<sup>24</sup> Trithiasapphyrin is reported to have the oxidation potential value of 0.8 V,<sup>3</sup> which is smaller than that of H<sub>2</sub>TPP. Therefore, there is a high possibility that the charge transfer exciplex with oxygen is formed and relaxes without singlet oxygen generation. On the other hand, S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS have overall 22 π-electronic system. In this 22 π-electronic system, the triplet state can lie below the energy state of singlet oxygen as other 22 π-photosensitizers,<sup>25</sup> which makes the energy transfer from the triplet state to oxygen molecule energetically unfavorable.<sup>26</sup>

### Conclusion

Lower triplet quantum yields of S<sub>3</sub>TPS and (*p*-MeO)-S<sub>3</sub>TPS are linked to enhanced internal conversion rates. In addition to the low triplet quantum yields, relatively faster triplet state relaxation and inefficient energy transfer to triplet oxygen result in very low singlet oxygen generation yields. Therefore, although these thiasapphyrin derivatives exhibit more red-shifted absorption characteristics, such evaluated photophysical properties hold their applications as photosensitizers for PDT.

**Acknowledgment.** We gratefully acknowledge the many contributions of professor Kyung-Hoon Jung to the field of physical chemistry. This study was financially supported by the Agricultural R&D Promotion Center and CRM-KOSEF

Grant (1998G0102) and K. S. thanks the financial support from the Nuclear R & D Program by MOST, Republic of Korea.

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