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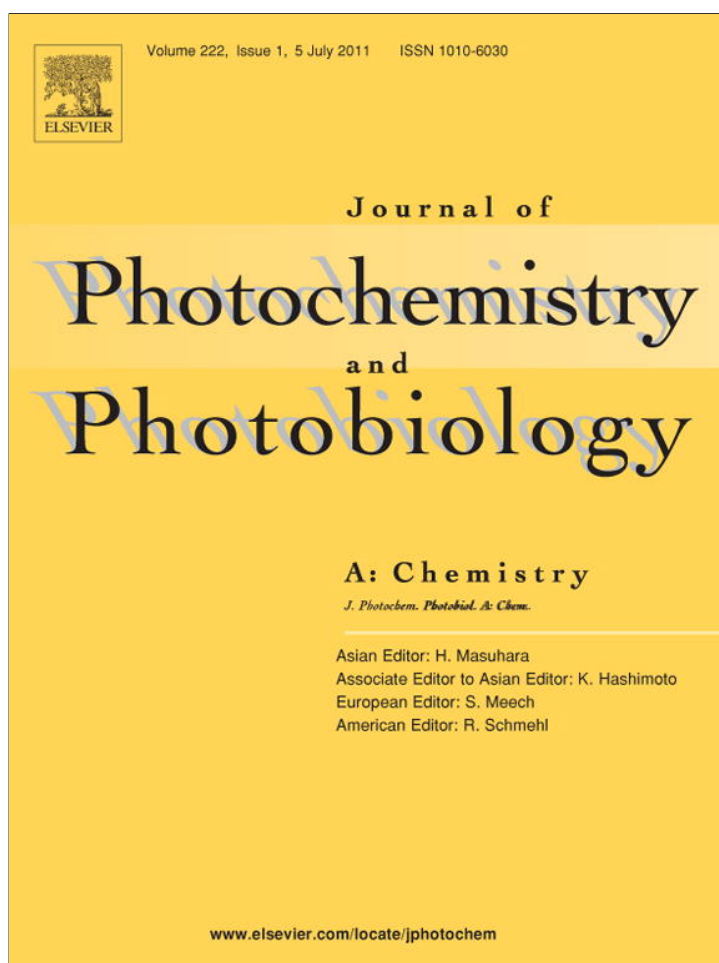


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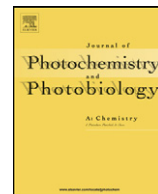
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Silicon tetrabenzotriaza corrole and silicon phthalocyanine: Synthesis, photophysics and singlet oxygen generation

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ABSTRACT

Synthesis, photophysical and photochemical measurements were carried out on silicon tetrabenzotriaza corrole. The results were compared with that of phosphorous tetrabenzotriaza corrole and silicon phthalocyanine. UV–vis absorption spectra, fluorescence emission spectra, fluorescence quantum yields and lifetimes, triplet–triplet absorption spectra, triplet formation quantum yields and lifetimes, and singlet delta oxygen quantum yields were measured in DMF. Silicon tetrabenzotriaza corrole exhibits quite different spectral and photophysical properties from both silicon phthalocyanine and phosphorous tetrabenzotriaza corrole. Silicon tetrabenzotriaza corrole features a longest fluorescence lifetime of 5.84 ns, but a lowest fluorescence quantum yield of 0.24. The quantum yields of the triplet state formation and sensitized generation of singlet delta oxygen by silicon tetrabenzotriaza are 0.72 and 0.61, respectively, which are significantly higher than those of silicon phthalocyanine and phosphorous tetrabenzotriaza corrole. Silicon tetrabenzotriaza corrole also showed a long triplet lifetime of 143 μ s. Silicon tetrabenzotriaza corrole is therefore a very efficient photosensitizer for singlet oxygen generation.

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1. Introduction

Tetrabenzotriaza corroles (TBCs) and phthalocyanines (Pcs) are large π -conjugated macrocyclic molecules with structures shown in Scheme 1. A TBC compound can be obtained by the elimination of one out of four bridging-nitrogen atoms in a Pc molecule [1–9]. Pcs have generated much interest over the last century and been applied in a number of fields including chemical sensors, non-linear optics, liquid crystals and as photosensitizers in photodynamic therapy [10]. TBCs are relatively much newer, only a few elements (such as P, Ge, and Si) have been inserted into the central cavity of TBC and isolated as pure stable complexes [1–9]. On the photophysical properties of TBCs, the studies are even rarer, only phosphorous TBCs have been explored [1,2,8,9,11]. Nevertheless, TBCs have shown some unique properties, such as the ability to stabilize high-valent oxidation states, low oxidation potentials and high reduction potentials [3,8,9,12]. Recently we also studied the effect of peripheral and non-peripheral substitution on the spectral, photophysical and photochemical properties of phosphorous TBCs [1,2]. We now extend the study to silicon TBC. SiPc is also included to show how the missing of a bridging N atom affects the

properties of TBCs, whereas POTBC is used to investigate the effect of the central element on the property of TBCs.

2. Experimental

2.1. Materials and instruments

All experiments were carried out in redistilled DMF. Zinc phthalocyanine (ZnPc) was the product of Tokyo Kasei. Silicon phthalocyanine was purchased from Aldrich. The synthesis of POTBC used here has been reported by us previously [1,2]. All other reagents were analytical grade and used as received.

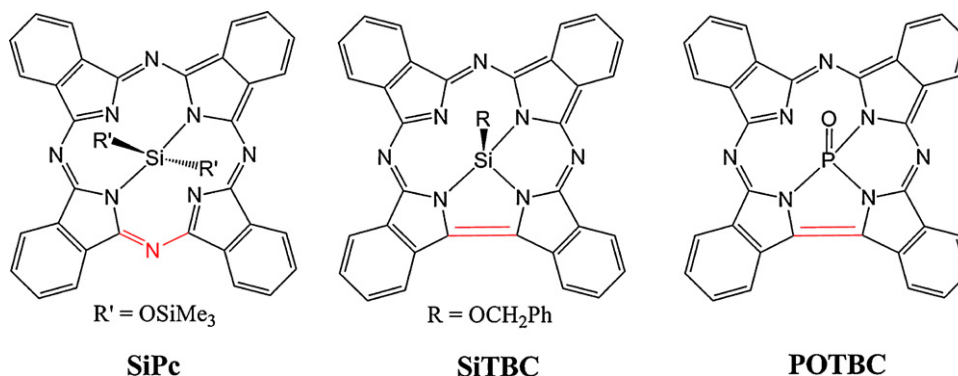
2.2. Spectroscopic studies

¹H NMR spectra were recorded at room temperature on a Bruker dmx 300 MHz NMR spectrometer. MS spectra were recorded either on a Bruker APEX II or Autoflex III Maldi-TOF spectrometer. IR spectra were recorded at room temperature on a Shimadzu FTIR-8900 spectrometer.

UV–vis spectra were recorded on a Shimadzu 4500 spectrophotometer using 1 cm matched quartz cuvettes. The molar absorptivity at the wavelength of maximum absorption was calculated from a least squares fit of absorbance against concentration, with an absorption spectrum of the reference solvent subtracted from the acquired data.

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Scheme 1. The chemical structure of SiPc, SiTBC and POTBC.

2.3. Synthesis of $\text{PcSi}(\text{OSiMe}_3)_2$

This was performed in dry pyridine (7 ml) according to Ref. [14]. In a sealed autoclave, 0.10 g dihydroxy silicon phthalocyanine and 1.0 ml $(\text{Me}_3\text{Si})_2\text{NH}$ were added and heated at 170°C for 7 h. The SiPc crystals formed were filtered, washed with methanol, recrystallized and dried in vacuum at 150°C . Yield: 0.090 g (71%). IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 1250 (Si–Me), 1030 (Me_3Si –O–SiPc). UV/vis (DMF) $\lambda_{\text{max}}/\text{nm}$: 355, 602, 634, 668. ^1H NMR (CDCl_3) δ/ppm 9.36–9.94 (8H, m, Pc–H), 8.06–8.61 (8H, m, Pc–H), –2.90 (18H, s, $\text{Si}(\text{CH}_3)_3$). Calc. for $\text{C}_{38}\text{H}_{34}\text{N}_8\text{O}_2\text{Si}_3$: %C 63.48, %H 4.77, %N 15.58; Found: %C 63.17, %H 5.02, %N 15.20. MS m/z (MALDI-TOF) 719.3 $[\text{M}+\text{H}]^+$.

2.4. Synthesis of SiTBC

This was performed by modifying the reported procedure [4]. Dichloro silicon phthalocyanine (0.10 g, 0.17 mmol) and NaBH_4 (0.020 g, 0.53 mmol) were added and stirred at 160°C in a mixture of benzyl alcohol (10 ml) and anisole (5 ml) for 2 h in an Ar gas atmosphere. The hot mixture was filtered under reduced pressure, and anisole in the filtrate was evaporated under reduced pressure at 100°C and the residue was successively washed with ether. The resulting solid was repeatedly extracted with hot xylene. The dark-green extract was evaporated under reduced pressure at 70°C . The residue was again washed with ether and dried in a vacuum for 5 h at 50°C . Yield: 0.084 g (69%). IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 1007 (SiOSi), 825 (SiO). UV/vis (DMF) $\lambda_{\text{max}}/\text{nm}$: 409, 440, 607, 659. ^1H NMR (CDCl_3) δ/ppm : 9.85–9.80 (m, 4H), 9.58–9.50 (m, 2H), 8.87–8.85 (m, 2H), 8.06–8.00 (m, 4H), 7.85–7.80 (m, 4H), 7.52–7.49 (m, 2H, Ph-H), 7.43–7.35 (m, 3H, Ph-H). Calc. for $\text{C}_{39}\text{H}_{23}\text{N}_7\text{OSi}$: %C 73.91, %H 3.66, %N 15.47; Found: %C 73.67, %H 4.02, %N 15.20. MS m/z (MALDI-TOF) 634.3 $[\text{M}+\text{H}]^+$.

2.5. Photophysics

The absorption and fluorescence spectra, fluorescence quantum yields and excited singlet-state lifetimes, as well as triplet properties were investigated at room temperature in DMF. Steady-state fluorescence spectra were acquired on a FLS 920 with 1 nm slit width for both excitation and emission monochromators. All spectra were corrected for the sensitivity of the photo-multiplier tube. The fluorescence quantum yield (Φ_f) was calculated by $\Phi_f = F_s A_0 \Phi_f^0 / (F_0 A_s)$, in which F is the integrated fluorescence intensity, A is the absorbance at excitation wavelength, the subscript 0 stands for a reference compound and s represents samples. Zinc phthalocyanine was used as the reference ($\Phi_f^0 = 0.30$) [13]. Excitation wavelengths of 610 nm corresponding to S_0 to S_1 transitions were employed. The sample and reference solutions were prepared

with the same absorbance (A_i) at the excitation wavelength (near 0.09 per cm). All solutions were air saturated.

Fluorescence lifetime of S_1 was measured by time-correlated single photon counting method (Edinburgh FLS920 spectrophotometer) with excitation at 672 nm diode laser (50 ps FWHM) and emission was monitored at 690 nm.

Transient absorption spectra were recorded in degassed DMF (prepared by bubbling with argon for 20 min) with an Edinburgh LP920 laser flash photolysis system. A Nd:YAG laser (Brio, 355 nm and 5 ns FWHM) was used as excitation source. The analyzing light was from a xenon lamp. The laser and analyzing light beams perpendicularly passed through a quartz cell with an optical path length of 1 cm. The signal was displayed and recorded on a Tektronix TDS 3012B oscilloscope and an Edinburgh LP920 R928B detector. The laser energy incident at the sample was attenuated to a few mJ per pulse. Time profiles at a series of wavelengths from which point-by-point spectra were assembled were recorded with the aid of a Pc controlled kinetic absorption spectrometer. The concentrations of the target compounds were typically $10\ \mu\text{M}$ providing $A_{355} = 0.25$ in a 10 mm cuvette.

2.6. Photochemistry

For the measurement of singlet oxygen, typically, a 2 ml portion of the respective sample solutions that contained diphenylisobenzofuran (DPBF) was irradiated at 660 nm in air saturated DMF. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the concentration of DPBF was lowered to $\sim 3 \times 10^{-5}\ \text{mol dm}^{-3}$. A solution of sensitizer (absorbance ~ 0.65 at the irradiation wavelength) that contained DPBF was prepared in the dark and irradiated in the Q-band region. DPBF degradation at 415 nm was monitored.

3. Results and discussion

3.1. Synthesis

The reaction of SiPc with NaBH_4 proceeds smoothly to yield SiTBC in a good yield. SiTBC is stable both as a solid and in solution of THF, ethanol, DMF, DMSO, etc. Another reported method [14], in which Mg and ClSiMe_3 act as reducing agents, was also tested but failed to produce isolated SiTBC.

3.2. Photophysics

The ground-state absorption spectra of SiPc, POTBC and SiTBC are shown in Fig. 1. SiPc shows the typical spectrum of phthalocyanines, which includes two distinct bands, a much weaker B band at 359 nm and a sharp Q-band in the near IR. The spectrum of SiTBC

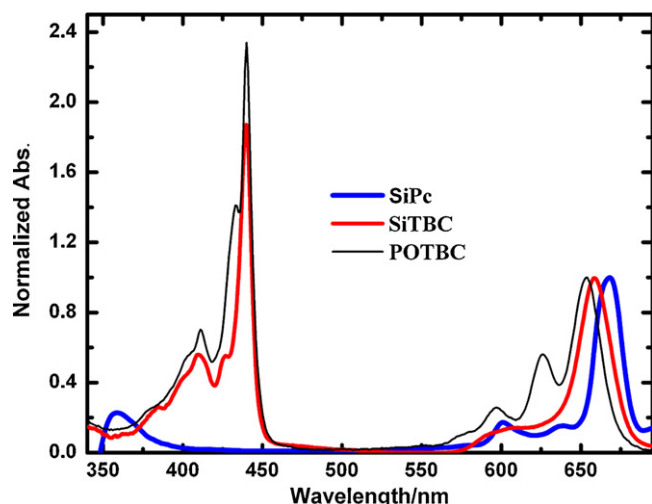


Fig. 1. Normalized UV-vis spectra of SiTBC, SiPc, and POTBC in DMF.

Table 1

The photophysical parameters^a of SiTBC, POTBC and SiPc.

	SiPc	SiTBC	POTBC
$\lambda_{\max, \text{abs}}$ [nm]	668	658	654
$\log \epsilon$	5.40	5.00	4.20
$\lambda_{\max, \text{em}}$ [nm]	677	671	663
Stoke's shift [nm]	9	13	9
Φ_f	0.42	0.24	0.36
τ_f [ns]	5.57	5.84	3.20
$\lambda_{\max, T-T}$ [nm]	490	470	458
$\epsilon_{\max, T-T}$ [$M^{-1} \text{cm}^{-1}$]	45,700	26,500	10,000
Φ_T	0.52	0.70	0.45
τ_T [μs]	115	142	173
Φ_Δ	0.48	0.61	0.43

^a $\lambda_{\max, \text{abs}}$: wavelength at absorption maximum; ϵ : molar absorption coefficient [$M^{-1} \text{cm}^{-1}$]; $\lambda_{\max, \text{em}}$: wavelength at emission maximum; Φ_f : fluorescence quantum yield; τ_f : fluorescence lifetime; $\lambda_{\max, T-T}$: T_1-T_n absorption maximum; $\epsilon_{\max, T-T}$: T_1-T_n molar absorption coefficient [$M^{-1} \text{cm}^{-1}$]; Φ_T : triplet formation quantum yield; τ_T : triplet lifetime; Φ_Δ : singlet oxygen quantum yield.

is also consisted of a B band and a Q-band. Contrary to that in SiPc, the B band absorbs much stronger than its Q band. The shape and absorption maximum of the B band of SiTBC is also quite different from that of SiPc. Compared to the spectrum of SiPc, the Q band of SiTBC is 10 nm blue shifted, the B band, on the other hand, is moved to longer wavelength by 81 nm. The structural change of SiTBC from SiPc is the missing of a bridge-nitrogen, as displayed in Scheme 1. This missing of the nitrogen atom reduces both the size and the planarity of the π -conjugated system in SiPc, which deeply affects the shape and position of the B band, and also reduces the molar absorptivity of the Q band (Table 1).

SiTBC has the very similar B band to that of POTBC, but exhibits variation in its Q-band absorption. Three peaks could be resolved in the Q-band of POTBC, while only two are observable in SiTBC, i.e. the 625 nm peak in POTBC nearly disappears in SiTBC (Fig. 1), this agrees with that in literature [4,14]. Fujiki et al. measured the UV-vis spectra for several other metallo TBCs [4], in which GeTBC Q band showed the same pattern as that of SiTBC reported here, while AlTBC and GaTBC exhibited another pattern. This shows that the central element of TBC can have remarkable effect on the absorption spectral properties, which is quite different from the case in Pc compounds. Also noted is the red shift of the Q-band of SiTBC from that of POTBC.

The Q band of SiTBC or SiPc is sharp and no observable new peaks, this indicates that little or no aggregation is occurring in solution.

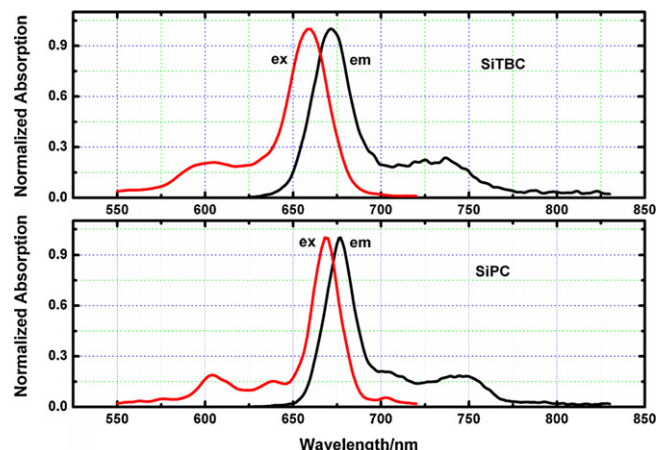


Fig. 2. Normalized fluorescence emission spectra with excitation at 610 nm (absorbance 0.090), Normalized fluorescence excitation spectra with emission at 750 nm.

The fluorescence excitation and emission spectra of SiTBC, POTBC and SiPc are shown in Fig. 2. The maximum emission of SiTBC occurs at 671 nm, which is 6 nm shorter than SiPc, but 8 nm longer than POTBC. The excitation spectrum is similar to the corresponding absorption and is the mirror image of the fluorescence emission for both compounds.

The UV/vis absorption and fluorescence emission data are summarized in Table 1. Fluorescence quantum yield (Φ_f) was determined using the comparative method. The standard used was ZnPc in DMF ($\Phi_f = 0.30$ [11]). The value of Φ_f obtained for SiPc is 0.42 and typical of peripherally substituted SiPcs. Both SiTBC and POTBC showed a smaller Φ_f , while that of SiTBC is only roughly half of SiPc.

The emission decay at 690 nm is shown in Fig. 3, by which the fluorescence lifetime (τ_f) was determined using time-correlated single photon counting with excitation at 672 nm by a 50 ps diode laser. The single exponential fitting gave satisfactory results for all compounds. τ_f is 5.57 ns ($\chi^2 = 1.04$) for SiPc, which is shorter than 5.84 ns ($\chi^2 = 1.19$) of SiTBC. τ_f of SiTBC is also significantly longer than 3.20 ns ($\chi^2 = 1.23$) of POTBC. The values obtained are summarized in Table 1.

The radiation rate constant of SiTBC ($k_f = \Phi_f/\tau_f = 0.41 \times 10^8 \text{ s}^{-1}$) is reduced to about 55% of that for SiPc ($0.75 \times 10^8 \text{ s}^{-1}$), due to the missing of the N atom. POTBC, however, has a larger k_f of $0.11 \times 10^9 \text{ s}^{-1}$.

The transient absorption spectra (TAS) are shown in Fig. 4. These spectra were recorded in argon saturated DMF with 5 ns pulsed laser excitation at 355 nm. TAS of SiPc is the typical of T_1-T_n absorptions for Pcs [2], which shows a broad peak with a maximum at 490 nm. TAS of SiTBC, on the other hand, exhibits very similar behavior to T_1-T_n absorption spectra of other TBCs [1,2]. In addition, the minimum of negative absorptions in the B- and Q-band region showed peaks matching the maximum of the corresponding ground state absorption; the positive bands are separated from the ground state bleaching with well defined isosbestic points, and the bleaching recovery are synchronous to the absorption decay (Fig. 4), indicating concomitant behavior, i.e., as the positive T_1-T_n absorption decays, the ground state is repopulated. TAS of SiTBC is similar to that of POTBC [1,2], but the absorption maximum shows a 12 nm red shift.

The transient decay at 480 nm is given in Fig. 5 for SiTBC, and inset of Fig. 4 for SiPc. The concomitant bleaching recovery at ground state absorption minimum is also shown in Fig. 5 for SiTBC. These curves can all be well fit by the mono exponential function. The triplet lifetime (τ_T) thus obtained is collected in Table 1. The

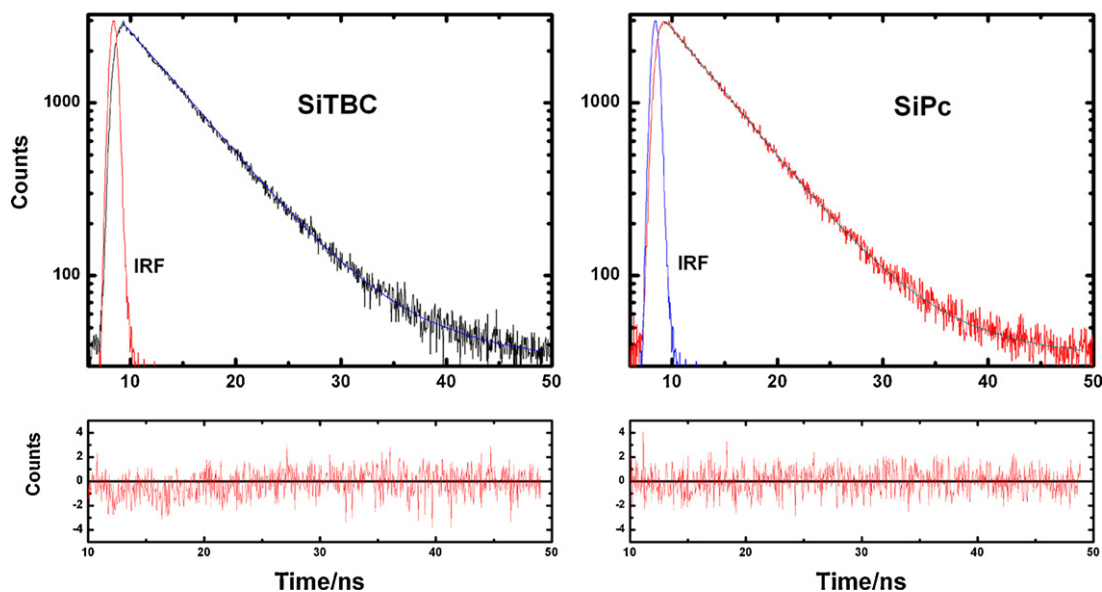


Fig. 3. Top: time profile of fluorescence decay with excitation at 672 nm diode laser (50 ps), the emission was monitored at 690 nm, the concentration of dyes is ca. 2.0 μM . Bottom: fitting residues.

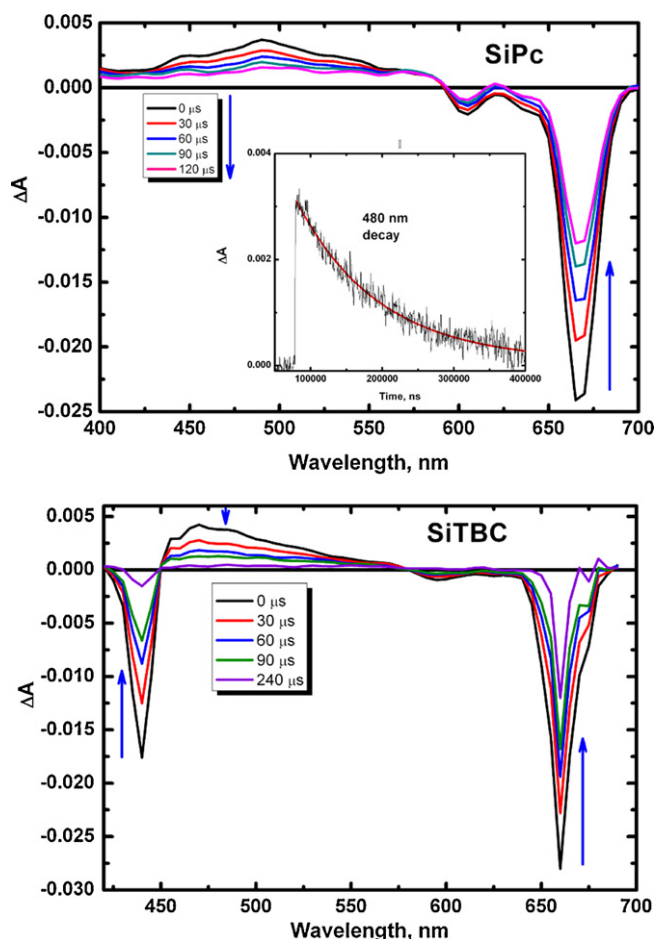


Fig. 4. Transient triplet-triplet absorption of SiPc and SiTBC in argon purged DMF, 10 μM , excitation wavelength 355 nm. Inset of SiPc shows the decay at 480 nm.

τ_T values are 142 μs for SiTBC, 173 μs for POTBC and 115 μs for SiPc, respectively. The lifetimes are comparable to those of TBCs or Pcs [1,2], and are all sufficiently long for photosensitizing the production of singlet oxygen.

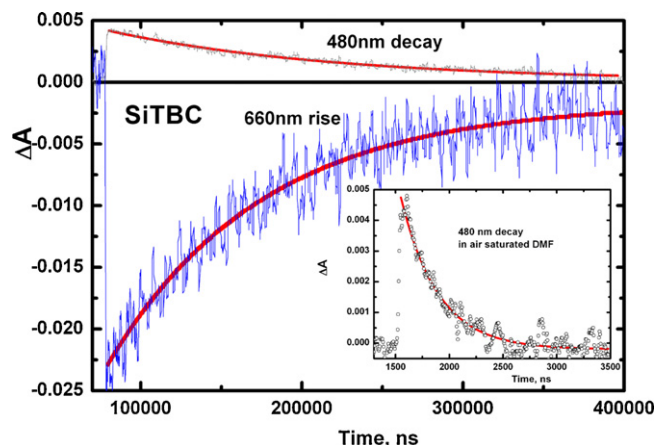


Fig. 5. Decay of positive transient signal and recovery of negative ground state absorption in argon saturated DMF for SiTBC, excitation with 355 nm laser pulse. Inset is the decay at 480 nm in air saturated DMF.

In air saturated DMF solution, the τ_T of SiTBC is shortened dramatically to 0.35 μs (inset of Fig. 5), while that of SiPc is reduced to 0.30 μs . The rate constant by oxygen quenching can be then evaluated to be $1.43 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for SiTBC and $1.66 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for SiPc, which are close to diffusion rate constant. This effective oxygen quenching also suggests that the positive absorptions are indeed due to T_1-T_n triplet absorptions.

The triplet extinction coefficients were determined using the expression,

$$\varepsilon_T = \varepsilon_S \frac{\Delta A_T}{\Delta A_S}, \quad (1)$$

where ΔA_T and ΔA_S were found by fitting exponential functions to the decay of signals at 470 nm for the triplet and 660 nm for the singlet in the case of SiTBC. Triplet absorption coefficient was determined to be $26,500 \text{ M}^{-1} \text{ cm}^{-1}$ for SiTBC, which is remarkably smaller than $45,700 \text{ M}^{-1} \text{ cm}^{-1}$ for SiPc. These values were then used to determine the triplet quantum yields (Φ_T) using the comparative

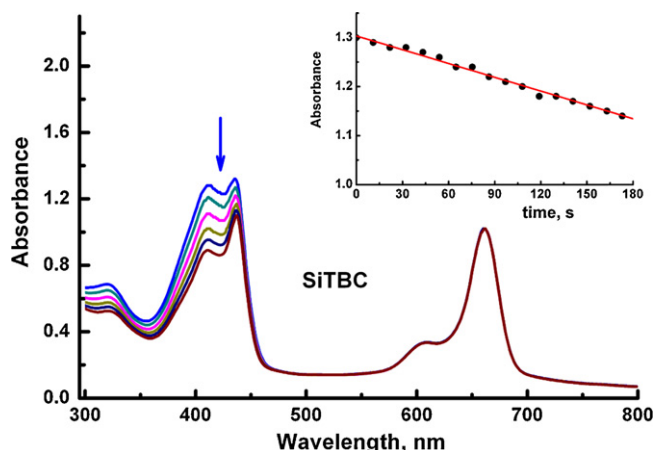


Fig. 6. The change of absorption spectrum upon irradiation time in air saturated DMF containing 5 μ M DPBF and 5 μ M photosensitizer with irradiation at 660 nm. Inset is the linear plot of absorbance at 415 nm against irradiation time.

method, for which details are given elsewhere:

$$\Phi_T = \Phi_{T}^{\text{ZnPc}} \frac{\Delta A_T}{\Delta A_T^{\text{ZnPc}}} \frac{\varepsilon_T^{\text{ZnPc}}}{\varepsilon_T}, \quad (2)$$

where the superscripts represent the reference, ΔA_T is the absorbance of the triplet transient difference absorption spectrum at the selected wavelength, and ε_T is the triplet state molar absorption coefficient. ZnPc was used as the standard ($\Phi_T = 0.65$, $\varepsilon_T(470) = 47,000 \text{ M}^{-1} \text{ cm}^{-1}$). The measured values are collected in Table 1.

SiTBC possesses a Φ_T value of 0.70, significantly higher than that of POTBC or SiPc. This is due to its higher rate constant of intersystem crossing (k_{isc}) calculated by $k_{\text{isc}} = \Phi_T/\tau_T = 0.49 \times 10 \text{ s}^{-1}$, comparing to the value of $0.26 \times 10 \text{ s}^{-1}$ for POTBC and $0.36 \times 10 \text{ s}^{-1}$ for SiPc.

3.3. Photochemistry

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the chemical trapping method [15] with irradiation at 660 nm in air saturated DMF. Φ_Δ values were obtained by the relative method using ZnPc as the reference (Eq. (3)):

$$\Phi_\Delta = \Phi_\Delta^{\text{ref}} \frac{k}{k^{\text{ref}}} \frac{I_a^{\text{ref}}}{I_a}, \quad (3)$$

where Φ_Δ^{ref} is the singlet oxygen quantum yield for the standard (0.65 for ZnPc in DMF) [16], k and k^{ref} are the DPBF photobleaching rate constants in the presence of the respective samples and standard, respectively; I_a and I_a^{ref} are the rates of light absorption at the irradiation wavelength by the samples and standard, respec-

tively. DPBF degradation at 415 nm was monitored. Fig. 6 displays the decrease of [DPBF] upon irradiation time, for which the first order kinetics was observed.

Φ_Δ is also included in Table 1. The value of Φ_Δ for a dye is smaller but close to its Φ_T , suggesting a good efficiency of energy transfer from T_1 state to molecular oxygen, $T_1(\text{PS}) + {}^3\text{O}_2 \rightarrow \text{S}_0(\text{PS}) + {}^1\text{O}_2$. The rate constant of energy transfer (k_{et}) calculated previously are comparable to the rate constants obtained for O_2 quenching of the triplet excited states of a variety of porphyrins and phthalocyanines [16]. The values are close to one-ninth of the diffusion rate of O_2 in the solvent, and much higher than other radiative or nonradiative decay of T_1 state.

4. Conclusion

The absorption properties, lowest excited singlet properties, lowest lying triplet properties and singlet oxygen quantum yields of SiTBC, POTBC and SiPc have been measured. The results show that the missing of a bridging-nitrogen in SiPc caused a remarkable decrease in both fluorescence quantum yield, but the triplet quantum yield and fluorescence lifetime is increased significantly. The replacement of the central Si element in TBC by P, however, increases the triplet lifetime and fluorescence quantum yield but lowers the fluorescence lifetime. SiTBC shows the best photophysical and photochemical properties in terms of the triplet properties and singlet delta oxygen quantum yield for application as photosensitizers for photodynamic therapy.

Acknowledgements

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References

- [1] X.-F. Zhang, Y. Chang, Y. Peng, F. Zhang, *Aust. J. Chem.* 62 (2009) 434–440.
- [2] X.F. Zhang, J. Huang, H. Zhao, X. Zheng, Z. Junzhong, *J. Photochem. Photobiol. A: Chem.* 215 (2010) 96–102.
- [3] J.P. Fox, D.P. Goldberg, *Inorg. Chem.* 42 (2003) 8181–8191.
- [4] M. Fujiki, H. Tabei, K. Isas, *J. Am. Chem. Soc.* 108 (1986) 1532–1536.
- [5] J. Li, L.R. Subramanian, M. Hanack, *Chem. Commun.* (1997) 679–680.
- [6] J. Li, L.R. Subramanian, M. Hanack, *Eur. J. Org. Chem.* 1998 (1998) 2759–2767.
- [7] J. Liu, F. Zhang, F. Zhao, Y. Tang, X. Song, *J. Photochem. Photobiol. A: Chem.* 124 (1999) 165.
- [8] J. Liu, F. Zhang, F. Zhao, Y. Tang, X. Song, G. Yao, *J. Photochem. Photobiol. A: Chem.* 91 (1995) 99–104.
- [9] J. Liu, Y. Zhao, F. Zhao, F. Zhang, X. Song, F.T. Chau, *J. Photochem. Photobiol. A: Chem.* 99 (1996) 115–119.
- [10] C.G. Claessens, U. Hahn, T. Torres, *Chem. Rec.* 8 (2008) 75–97.
- [11] E.M. Antunes, T. Nyokong, *Met. Based Drugs* 2008 (2008) 1–9.
- [12] G. Golubkov, Z. Gross, *Angew. Chem. Int. Ed.* 42 (2003) 4507–4510.
- [13] P.G. Seybold, M. Gouterman, *J. Mol. Spectrosc.* 31 (1969) 1–6.
- [14] V.N. Myakov, Y.A. Kurskii, V.N. Sedel'nikova, T.V. Makhrova, M.A. Lopatin, *Russ. J. Coord. Chem.* 34 (2008) 522–526.
- [15] M.G. Lagorio, L.E. Dicio, E.A.S. Roman, S.E. Braslavsky, *J. Photochem. Photobiol. B* 3 (1989) 615–624.
- [16] W.R. Redmond, J.N. Gamlin, *Photochem. Photobiol.* 70 (1999) 391–475.