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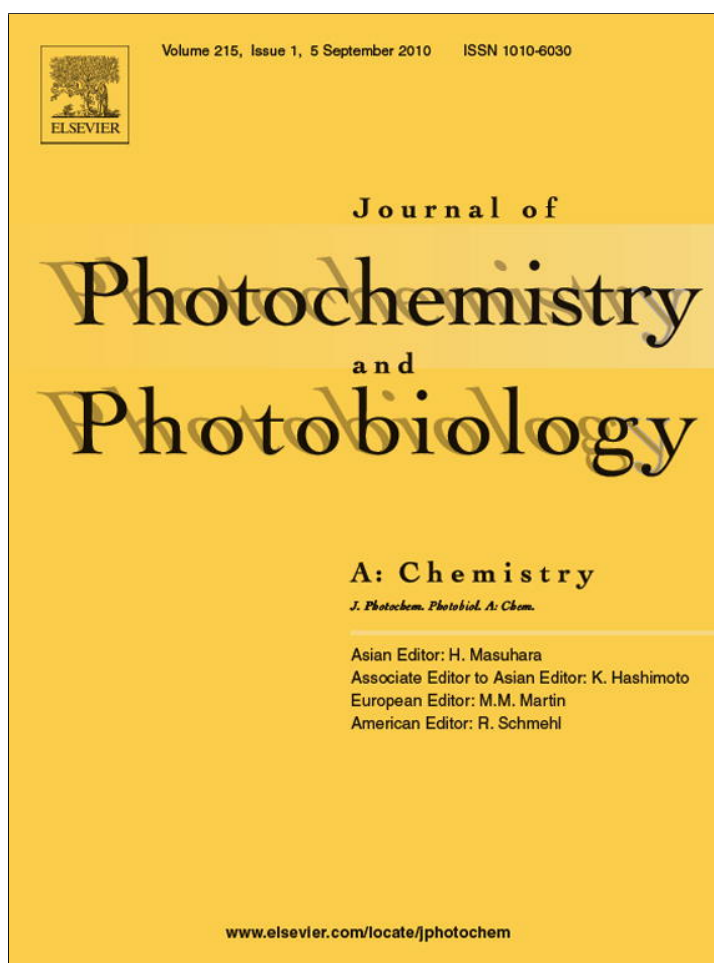


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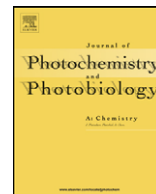
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Photophysical properties of nonperipherally and peripherally substituted triazatetrabenzcorrole phosphorous dihydroxy and singlet oxygen generation

Xian-Fu Zhang*, Jingyao Huang, Huizhi Zhao, Xuefang Zheng, Zhu Junzhong

Chemistry Department, Hebei Normal University of Science and Technology, Qinghuangdao 066004, Hebei Province, China

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ABSTRACT

Triazatetrabenzcorrole (TBC) is the nonplanar analogue of phthalocyanine (Pc), in which one *meso*-nitrogen is missing. A nonperipherally substituted TBC complex, i.e. tetra(α -phenoxy) TBC phosphorous dihydroxy (POTBC(α -OPh)₄) was synthesized and characterized for the first time together with a peripherally substituted POTBC(β -OPh)₄. The photophysical properties for each POTBC complex and its corresponding zinc Pc counterpart were measured by ground state absorption, steady state fluorescence, single photon counting technique and laser flash photolysis methods. These compounds possess long triplet lifetime, good triplet formation yield. They can effectively photosensitize the generation of singlet oxygen ¹O₂(¹ Δ_g). Their fluorescence yield and lifetime are comparable to the corresponding zinc Pcs. The nonperipheral α -OPh exhibits remarkably larger influence than the peripheral β -OPh on the photophysical properties, including: (1) the longer red shift for absorption, fluorescence spectra and T_1-T_n transient spectra and (2) the larger decrease of fluorescence lifetime and triplet lifetime. Although POTBC complexes are nonplanar in the structure, they still show the similar effect of nonperipheral substitution on the photophysical properties as that of the planar ZnPcs.

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1. Introduction

Triazatetrabenzcorrole (TBC) is a π -contracted phthalocyanine (Pc), as shown in Scheme 1, and was first obtained by Pc reduction in 1981 [1]. TBC is also considered as the π -expanded corrole derivative [2]. TBC and its derivatives, therefore, show the properties from both corroles and Pcs. TBCs show the ability to stabilize high-valent oxidation states, possess low oxidation potentials and high reduction potentials, and exhibit unique spectral characteristics in UV–vis region [2]. These properties make TBCs attract attentions recently because of the potential applications as excellent electron donors and sun light antennas in dye-sensitized solar cells, photo-medicine in photodynamic therapy of tumors (PDT) [3,4], and blue-laser dyes.

Phosphorous TBC (POTBC), in particular, is among the few TBC complexes (Si, Ge, Sn) synthesized so far [5]. The peripherally tetra-substituted POTBCs were later reported by Liu et al. [6–8], Li et al. [9,10], and the structures were also elucidated by them. Zhang et al. [11], Antunes and Nyokong [12], and Breusova et al. [13] recently also reported peripheral tetra-substituted POTBCs. Fox was the first to synthesize octa-substituted POTBCs [14]. Song and Huang have shown that sulfonated POTBC is effective for photodynamic therapy

of tumor (PDT) [3,4]. We also have been interested in the synthesis and photophysical properties of TBCs [11].

Among the tetra-substituted TBCs reported, we notice that no nonperipheral modifications have been performed. Nonperipheral substitution, on the other hand, may exhibit quite different effects on the properties of TBC from peripheral substitutions, based on the knowledge from Pc chemistry.

Herein we report the synthesis of a nonperipherally substituted tetra(α -phenoxy) POTBC and the measurement of its excited singlet and triplet properties. The purpose is to compare the different effect of two types of substitution on photophysical properties of POTBC. ZnPc and its nonperipherally or peripherally substituted tetra(phenoxy) derivatives were also included to show the similarity and differences of the substitution effect between TBCs and Pcs.

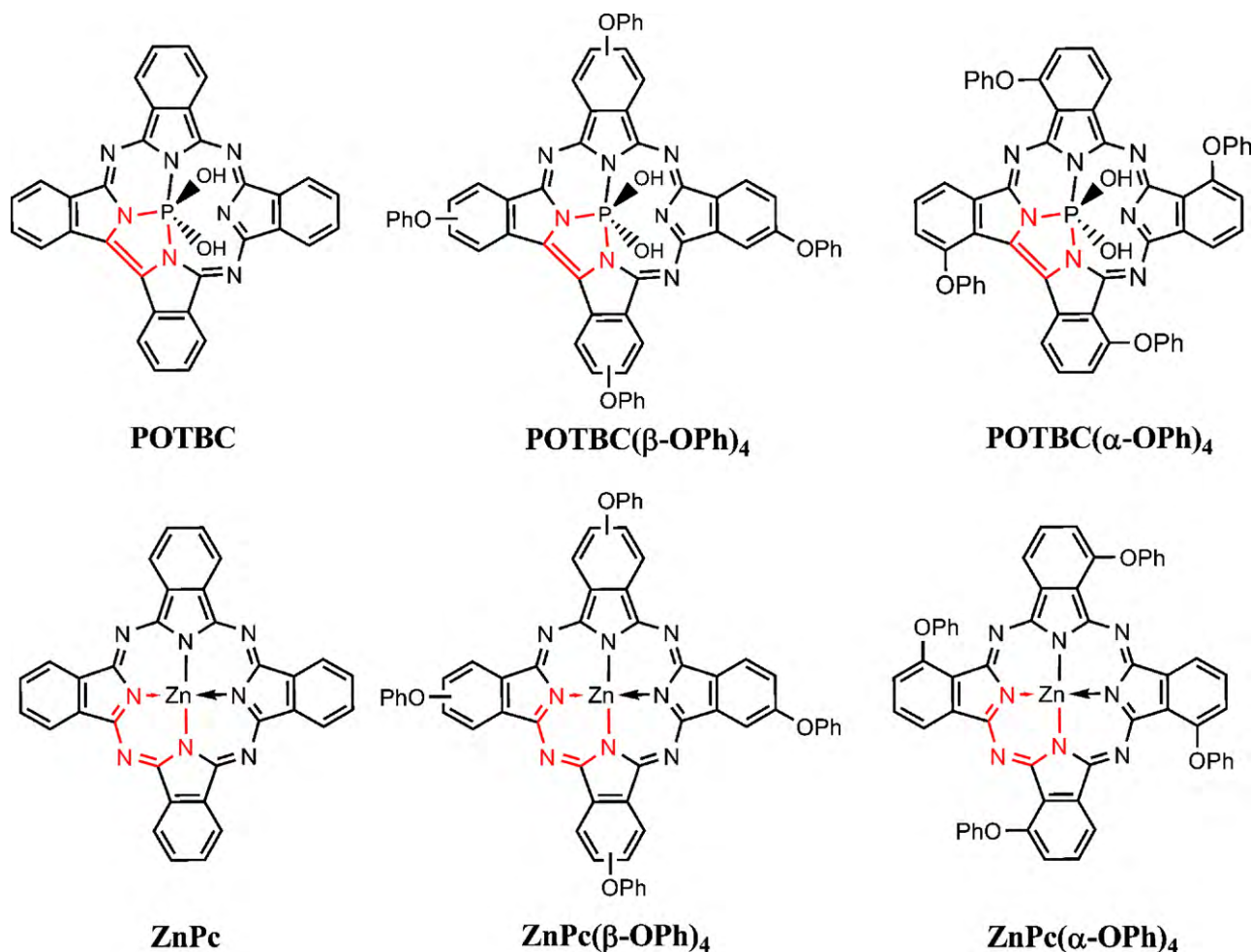
2. Experimental

2.1. Materials and instruments

Zinc phthalocyanine (ZnPc) was purchased from TCI. The synthesis of substituted phthalocyanines and POTBC used here has been reported by us previously [11,15,16]. All the other reagents were analytical grade and used as received. ¹H NMR spectra were recorded at room temperature on a Bruker dmX 300 MHz NMR spectrometer. MS spectra were recorded either on

* Corresponding author. Tel.: +86 3352039067; fax: +86 3352039067.

E-mail address: zhangxianfu@tsinghua.org.cn (X.-F. Zhang).



Scheme 1. Chemical structures of peripherally substituted $\text{ZnPc}(\beta\text{-OPh})_4$, $\text{POTBC}(\beta\text{-OPh})_4$ and nonperipherally substituted $\text{ZnPc}(\alpha\text{-OPh})_4$, $\text{POTBC}(\alpha\text{-OPh})_4$. The highlighted six-member ring in a ZnPc complex becomes five-member ring in a POTBC compound due to the loss of a *meso*-nitrogen.

a Bruker APEX II or Autoflex III Maldi-TOF spectrometer. IR spectra were recorded at room temperature on a Shimadzu FTIR-8900 spectrometer.

2.2. Synthesis

2.2.1. 1,8(11),15(18),22(25)-Tetraphenoxy-triazatetrazabenzcorrole phosphorous dihydroxy [$\text{POTBC}(\alpha\text{-OPh})_4$]

$\text{POTBC}(\alpha\text{-OPh})_4$ was prepared following the procedure in literature [8,9]. 1.81 g $\text{H}_2\text{Pc}(\alpha\text{-OPh})_4$ (2.05 mmol) in 20 mL of pyridine was added into a 50 mL three-necked round-bottomed flask, which was equipped with reflux condenser and a argon gas inlet tube. After 10 min argon-purged pyridine (10 mL) that contained 6.5 mL of PBr_3 (70.2 mmol) was then added and the resulting mixture was heated at 90–100 °C under stirring and argon atmosphere for 3.5 h. After cooling, the mixture was poured into water and filtered, the solid was washed thoroughly with water. The crude product was dissolved in THF and purified by column chromatography on silica gel using THF-dichloromethane (1:1) as eluent. Yield: 1.03 g (53%). IR(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3433 (PO–H), 1574, 1523(C=N), 1485, 1400, 1342, 1250, 1207, 1130, 1060, 1026, 991, 937(P–OH), 833, 746, 725. UV/Vis (DMF) $\lambda_{\text{max}}/\text{nm}$ 446, 461, 611, 640, 673. ^1H NMR (CDCl_3) δ/ppm 8.23–8.94 (4H, m, Pc–H), 7.61–7.97 (4H, m, Pc–H), 7.12–7.57 (24H, m, phenyl–H, Pc–H). ^{31}P NMR ($\text{D}^5\text{-pyridine}$) δ/ppm –201.30. MS m/z (MALDI-TOF) 932.3 [M^+], 914.5[$\text{M}-\text{H}_2\text{O}^+$].

2.2.2. 2,6(7),10(11),14(15)-Tetraphenoxy-triazatetrazabenzcorrole phosphorous dihydroxy [$\text{POTBC}(\beta\text{-OPh})_4$]

$\text{POTBC}(\beta\text{-OPh})_4$ was synthesized by the same procedure mentioned above from peripherally substituted unmetallated derivative $\text{H}_2\text{Pc}(\beta\text{-OPh})_4$. Yield: 0.52 g (27%). IR(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$ 3419(PO–H), 1577, 1527(C=N), 1482, 1403, 1341, 1253, 1203, 1131, 1058, 1023, 990, 939(P–OH), 835, 744, 721. UV/Vis (DMF) $\lambda_{\text{max}}/\text{nm}$ 416, 446, 600, 630, 656. ^1H NMR (CDCl_3): δ/ppm 8.75–8.93(4H, m, Pc–H), 8.37–8.60 (4H, m, Pc–H), 7.81–7.92 (4H, m, Pc–H), 7.65–7.74 (8H, d, phenyl–H), 7.51–7.59 (8H, t, phenyl–H), 7.38–7.46 (4H, t, phenyl–H). ^{31}P NMR ($\text{D}^5\text{-pyridine}$) δ/ppm –201.30. MS m/z (MALDI-TOF): 932.1 [M^+], 914.3[$\text{M}-\text{H}_2\text{O}^+$].

2.3. Photophysical measurements

Dimethylsulfoxide (DMSO) were dried and redistilled before use. The absorption and fluorescence spectra, fluorescence quantum yields and excited singlet-state lifetimes were investigated at room temperature in DMSO.

UV–vis absorption measurements were made with either a HP 8451A or Shimadzu 4500 spectrophotometer in 10 mm quartz cuvettes. Sample concentrations were adjusted so that the Q band absorption maxima were between 0.20 and 1.0 and their respective concentrations are given in the figures for various measurements. Fluorescence spectra up to 900 nm were monitored using EI FLS920 instrument, with 0.5 nm slits. All the 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 ($\Phi_f^0 = 0.30$) [17]. Excitation wavelengths of 610 nm corresponding to $S_0 \rightarrow S_1$ 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 the 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 DMSO (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 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 μ M providing $A_{355} = 0.25$ in a 10 mm cuvette.

The triplet–triplet absorption coefficients (ε_T) of the samples were obtained using the singlet depletion method [18], and the following equation was used to calculate the ε_T :

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

where ΔA_S and ΔA_T are the absorbance change of the triplet transient difference absorption spectrum at the minimum of the bleaching band and the maximum of the positive band, respectively, and ε_S is the ground state molar absorption coefficient at the UV–vis absorption band maximum. Both ΔA_S and ΔA_T were obtained from the triplet transient difference absorption spectra.

The triplet quantum yield Φ_T was obtained by comparing the ΔA_T of the optically matched sample solution at 355 nm in a 1 cm cuvette to that of the reference, ZnPc ($\Phi_T = 0.65 \pm 0.02$, $\varepsilon_T(470) = 47,000 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}$) [19], using the equation:

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

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.

Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the chemical trapping method [20]. Typically, a 2 mL portion of the respective sample solutions that contained diphenylisobenzofuran (DPBF) was irradiated at 670 nm in air saturated dimethylsulfoxide. 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 (0.67 for ZnPc in DMSO) [21], 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 of 670 nm by the samples and standard,

respectively. Their ratio can be obtained by Eq. (4):

$$\frac{I_a^{\text{ref}}}{I_a} = \frac{1 - 10^{-A_{670}^{\text{ref}}}}{1 - 10^{-A_{670}}} \quad (4)$$

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. The error in the determination of Φ_Δ was $\sim 10\%$ (determined from several Φ_Δ values).

3. Results and discussion

3.1. Ground state absorption spectra

The UV–vis ground state absorption spectra of the three POTBCs and the three ZnPcs (Scheme 1) in DMSO solution at room temperature are shown in Fig. 1. Both POTBCs and ZnPcs exhibit the typical spectra of their own kind, respectively. The spectrum of each compound, no matter it is a POTBC or a Pc complex, shows a near-UV Soret (B) band region (corresponding to $S_0 \rightarrow S_2$) and visible Q bands (corresponding to $S_0 \rightarrow S_1$). The B bands in POTBCs, however, become much stronger than its Q bands in contrast to that of Pcs. POTBCs also show more vibronic satellite, i.e. $Q(0,0)$, $Q(1,0)$, $Q(2,0)$ and $B(0,0)$, $B(1,0)$, $B(2,0)$ etc. The Q band absorption

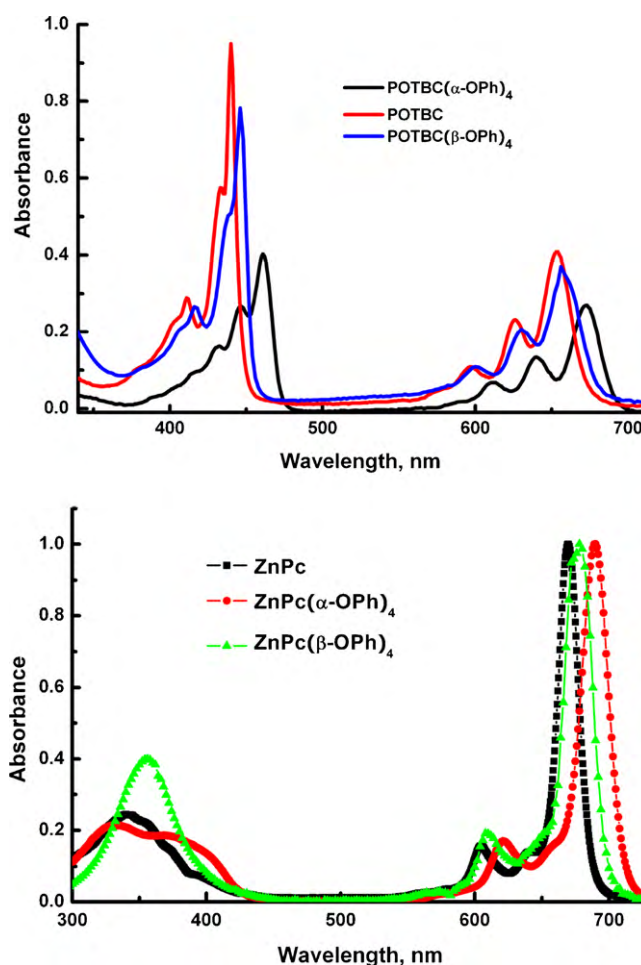


Fig. 1. UV–vis absorption spectra of the six compounds in DMSO at room temperature. Concentration is 3.6 μ M, 5.7 μ M, and 4.2 μ M for ZnPc, ZnPc(β -OPh) $_4$, and ZnPc(α -OPh) $_4$, respectively. Concentration is 27 μ M, 5.4 μ M, and 2.8 μ M for POTBC, POTBC(β -OPh) $_4$, and POTBC(α -OPh) $_4$, respectively.

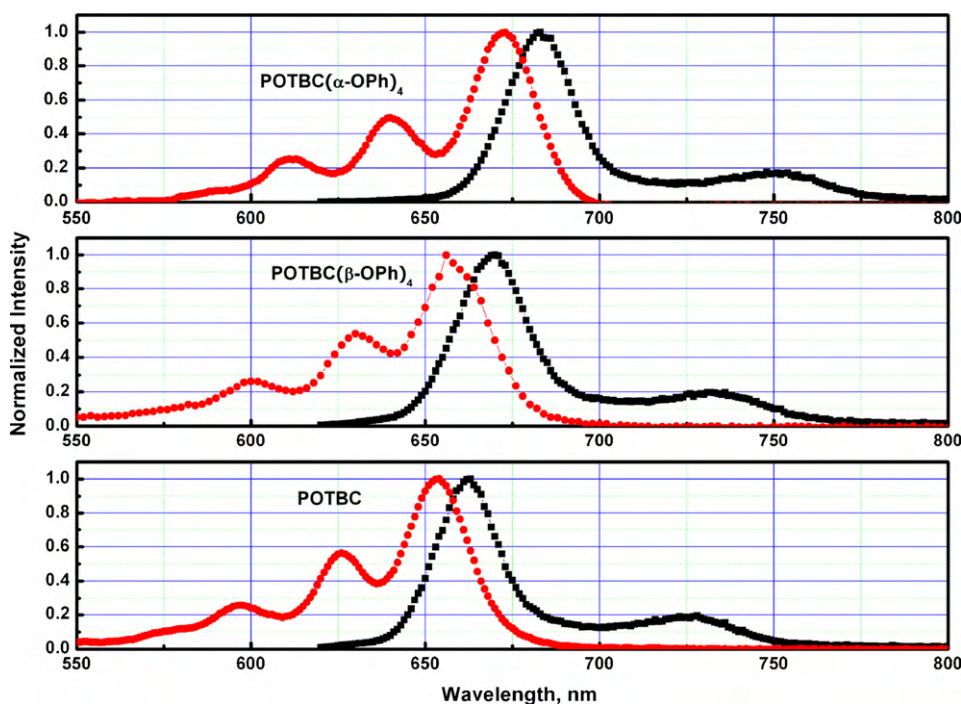


Fig. 2. Normalized emission and absorption spectra in DMSO. Emission spectra were measured with excitation at 610 nm (absorbance ~ 0.09).

maximum of POTBCs is blue shifted by ca. 15 nm relative to that of the corresponding ZnPcs, the B band absorption maximum of POTBCs, on the other hand, is red shifted significantly by ca. 100 nm. This band shift indicates that the energy gap between S_1 and S_2 in POTBCs is remarkably closer than the case in Pcs.

The substitutions in POTBCs with phenoxy, as that in Pcs, do not change the shape of the spectra but make the peak wavelength moved to the red direction. The nonperipheral substitution, however, causes a 19 nm red shift of Q band maximum which is much larger than a 2 nm red shift by the peripheral substitution. This trend is similar to the case in Pcs. The larger bathochromic shift of the nonperipheral substitution is due to the larger coefficients in linear combinations of atomic orbitals (LCAO) at the nonperipheral positions of the HOMO than those at the peripheral positions. As a result, the HOMO level is destabilized more at the nonperipheral position than that at the peripheral position. Essentially, the energy gap (ΔE) between the HOMO and LUMO becomes smaller, resulting in a bathochromic shift [22,23].

3.2. Fluorescence emission spectra

Fluorescence emission spectra for POTBCs in DMSO solutions at room temperature are shown in Fig. 2 with excitation at 610 nm, together with the Q band absorptions (left spectra). For all the POTBCs, the emission spectra are dominated by $S_1 \rightarrow S_0$ fluorescence, so are the case of Pcs (not shown). Even if POTBCs were excited at a B band wavelength, their $S_2 \rightarrow S_0$ fluorescence is still much weaker compared to that of $S_1 \rightarrow S_0$ fluorescence (not shown). For Pcs, the

shorter-wavelength feature is the Q(0,0) band and the longer wavelength one is the Q(0,1) vibronic satellite. The mirror symmetry exists in Pc compounds between the emission and corresponding absorption, which contrasts to the case of POTBCs. For POTBCs, two bands appear in the emission but three bands exist in the absorptions. The shorter-wavelength emission is the Q(0,0) band, while the longer one should be Q(2,0) band judging from its distance to the Q(0,0) band. The emission intensity ratio of Q(0,0) over Q(2,0) is 5.3 and not affected by the substitutions. In the absorption spectra of POTBCs, the absorbance ratio of Q(0,0) over Q(2,0) is 3.9 and also not varied by the substitutions. The absorbance ratio of Q(0,0) over Q(1,0), on the other hand, show the tendency of decrease from 2.00 for POTBC to 1.85 of POTBC(β -OPh)₄ and to 1.78 of POTBC(α -OPh)₄.

The α -substitution moves the emission maximum to a longer wavelength than the β -substitution, the same as that occurs in the absorption spectra.

3.3. Fluorescence yields and singlet excited state lifetimes

The fluorescence quantum yield (Φ_f) and the lifetime of the lowest singlet excited state (τ_f) for each of the six compounds in DMSO at 295 K are given in Table 1. The time profiles of fluorescence decay with excitation at 672 nm by a 50 ps laser pulse are displayed in Fig. 3. Fitting the data by single exponential function gave satisfactory results for these compounds, and the Chi squared (χ^2) for each fitting is also included in Table 1. The lifetimes are 3.20 ns, 3.00 ns and 2.58 ns for POTBC, POTBC(β -OPh)₄ and POTBC(α -OPh)₄ respectively. The α -substitution exerts a larger decrease in τ_f than

Table 1
Photophysical data for S_1 state.

	λ_{abs} , nm	$\log \epsilon$	λ_{em} , nm	Φ_f	τ_f , ns	χ^2
POTBC	654	4.18	663	0.36	3.20	1.23
POTBC(β -OPh) ₄	656	4.84	670	0.40	3.00	1.18
POTBC(α -OPh) ₄	673	4.98	683	0.33	2.58	1.00
ZnPc	670	5.44	680	0.30	3.41	1.11
ZnPc(β -OPh) ₄	678	5.25	690	0.29	3.23	1.03
ZnPc(α -OPh) ₄	690	5.38	708	0.26	3.04	1.00

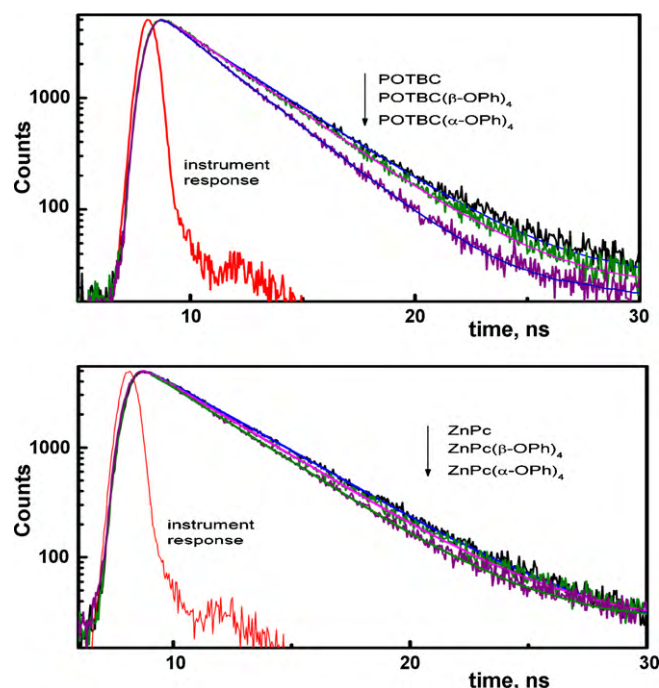


Fig. 3. Time profile of emission decay at 690 nm. The samples were excited at 672 nm (50 ps diode laser). The data were fit by mono exponential functions, Chi squared values are shown in Table 1.

the β -substitution for POTBC, so does the case for ZnPc. Φ_f change in ZnPcs matches their τ_f change, such that the radiation rate constant $k_f (= \Phi_f / \tau_f)$ remains constant $(0.88 \pm 0.02) \times 10^8 \text{ s}^{-1}$. k_f values of for POTBCs also show no significant change upon the substitutions $(1.24 \pm 0.11) \times 10^8 \text{ s}^{-1}$. It is therefore due to either internal conversion (IC) or intersystem crossing that decreases τ_f in these compounds.

3.4. Triplet state: nanosecond transient spectra and kinetics

Fig. 4 displays the transient spectra for the three POTBCs with laser excitation of 5 ns pulse at 355 nm. The samples were dissolved in DMSO and argon-purged for 20 min before measurement. The common features of the transient spectra are: (1) the minimum of negative absorptions in the B- and Q-band region showed peaks matching the maximum of the corresponding ground state absorption; (2) the positive absorption is broad, and the shape is similar to the T_1-T_n transient absorptions found previously for other POTBCs [11]; and (3) the positive bands are separated from the ground state bleaching with well defined isosbestic points, and the bleaching recovery kinetics are synchronous to the absorption decay kinetics (Fig. 5), indicating concomitant behavior, i.e. as the positive absorbing transient decays, the ground state is repopulated. It is very likely that the transient observable on the nanosecond and longer time scale has a broad continuous absorption between ca. 350 and ca. 800 nm, superimposed upon which is an intense ground state bleaching signal.

The positive absorption maximum is 463 nm, 470 nm and 505 nm for POTBC, POTBC(β -OPh) $_4$, and POTBC(α -OPh) $_4$, respectively. α -OPh is also more effective than β -OPh on the red shift of the transient spectra. The positive molar absorption coefficient (Table 2) is increased two- and three-folds by β -OPh and α -OPh modifications, respectively.

The typical transient decays at the wavelength of positive absorption maximum are given in Fig. 5. The concomitant bleaching recovery at ground state absorption minimum is also shown. These curves can all be well fit by the mono exponential func-

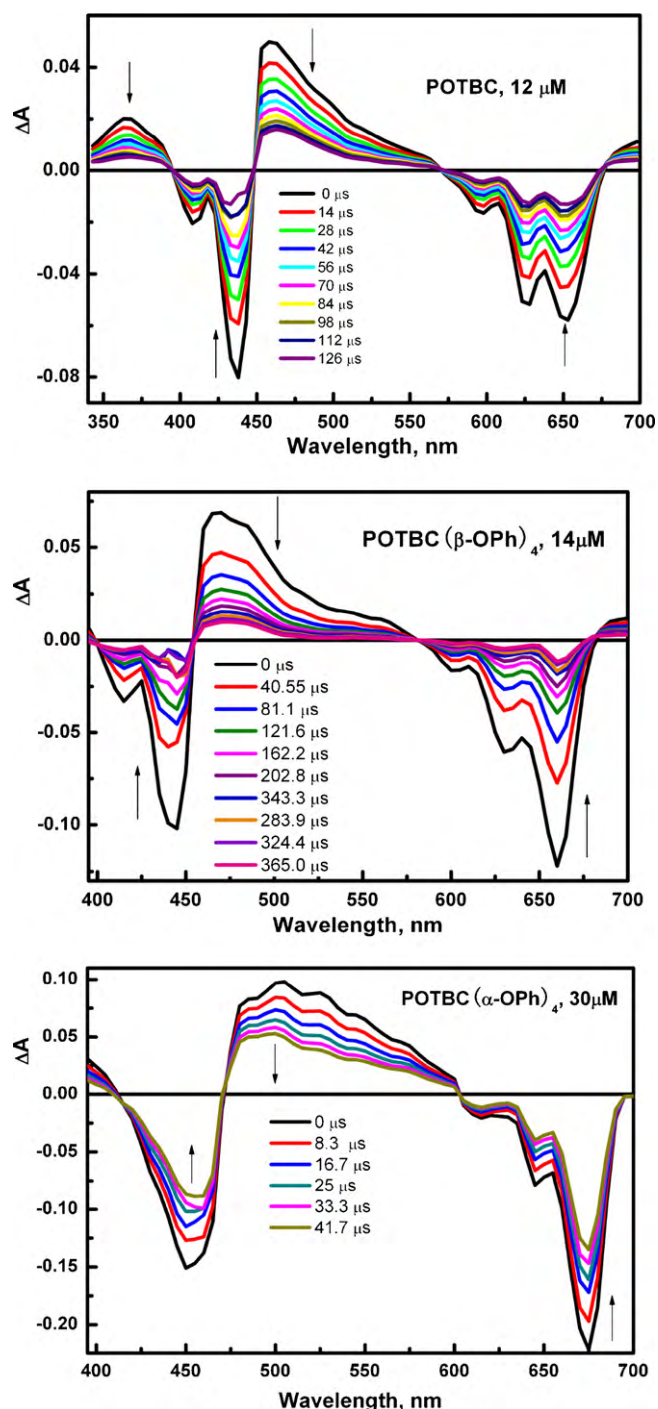


Fig. 4. POTBCs transient absorption spectra in argon saturated DMSO with laser excitation at 355 nm (absorbance was adjusted to ~ 0.25).

tion. The lifetimes thus obtained are collected in Table 2. The τ_T values are 173 μs , 179 μs and 118 μs for POTBC, POTBC(β -OPh) $_4$, and POTBC(α -OPh) $_4$ respectively. The lifetimes are comparable to those of Pcs [18], and are sufficiently long for photosensitizing the production of singlet oxygen.

The triplet lifetimes are shortened dramatically (Table 2) in air saturated DMSO solutions. The rate constant by oxygen quenching can be evaluated to be ranging from $0.92 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ to $1.50 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This effective oxygen quenching also indicates that the positive absorptions are due to T_1-T_n triplet absorptions.

The transient spectra for the three Pcs were also measured under the same conditions as that of POTBCs. The typical spectra are

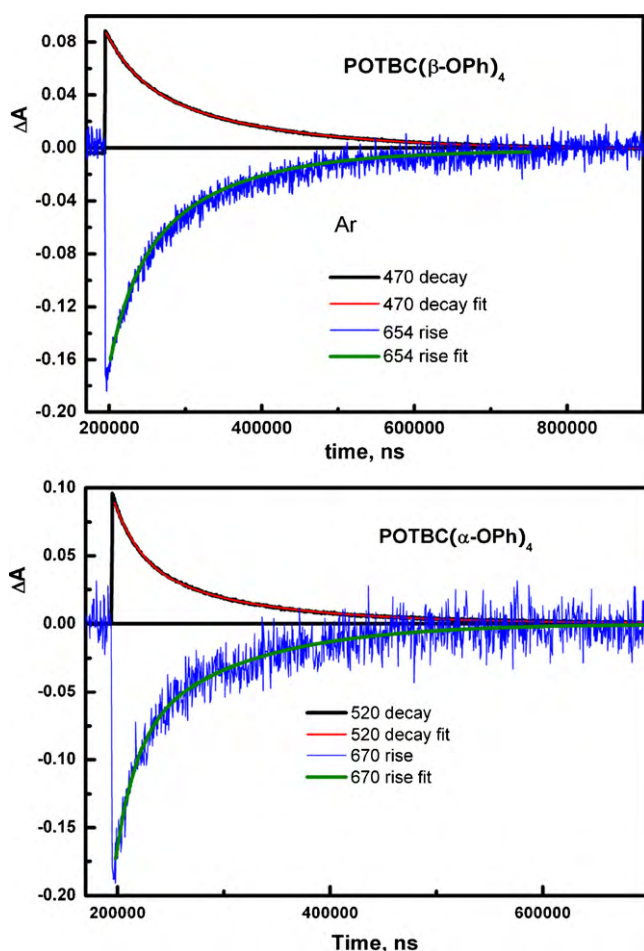


Fig. 5. Decay of positive transient signal and recovery of negative ground state absorption in argon saturated DMSO for POTBCs, excitation with 355 nm laser pulse.

shown in Fig. 6 together with the kinetic decay curves. By using the same analysis mentioned above, the positive signals are assigned to T_1 – T_n transient absorptions. The calculated properties for excited triplet states are listed in Table 2.

The T_1 – T_n transient absorptions of Pcs are similar to those of POTBCs, i.e. a broad band across the whole visible region and the wavelength of absorption maximum is close to 500 nm. The substitution effect between two types of complexes is also analogous, i.e. α -phenoxy has a larger influence on the red-shift of absorption maximum and the increase of absorptivities.

3.5. Triplet and singlet oxygen formation yield

The formation yield of the lowest triplet excited state (Φ_T) for each of the six compounds in DMSO at 295 K is given in Table 2. Φ_T of POTBCs is generally lower than that of ZnPcs since their Φ_f is higher, as shown in Table 1. The rate constant of ISC (k_{isc}) calculated by

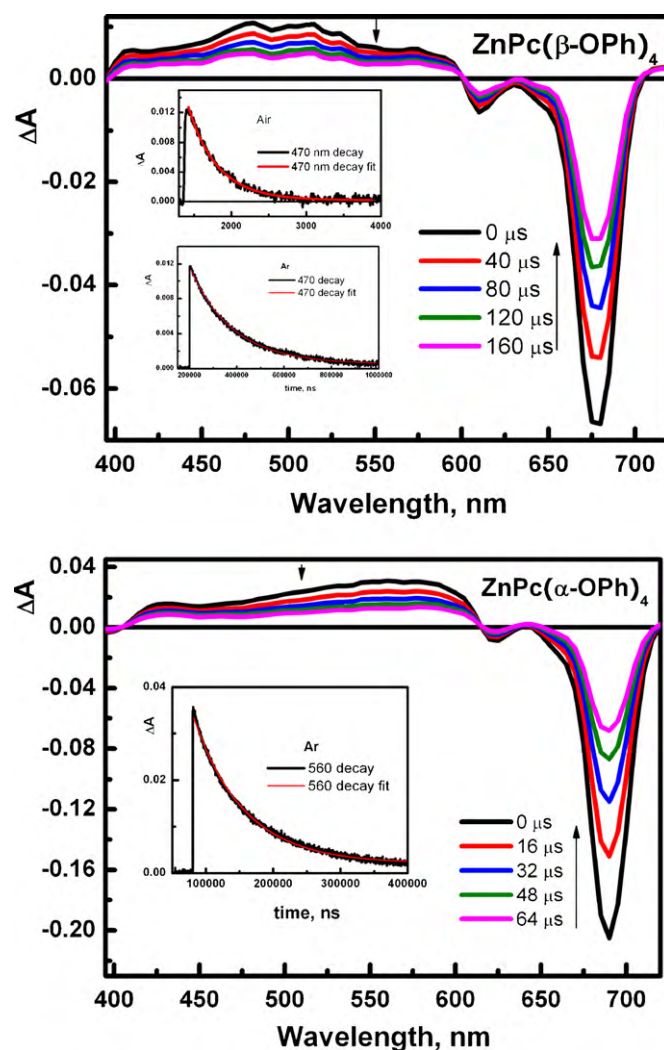


Fig. 6. Phthalocyanines transient absorption spectra in argon saturated DMSO with laser excitation at 355 nm (absorbance ~ 0.25).

Φ_T/τ_f , however, shows no big change upon substitution (Table 2). The summation of Φ_T and Φ_f in all the cases is less than 1, indicating the presence of internal conversion (IC). The substitutions, no matter α or β position, enhance IC in both types of compounds. The rate constant of IC (k_{ic}), evaluated by $(1 - \Phi_f - \Phi_T)/\tau_f$, is changed upon the substitutions.

The formation yield of singlet oxygen (Φ_Δ) is also included in Table 2. The value of Φ_Δ for a dye is very close to its Φ_T , suggesting a very high efficiency of energy transfer from a T_1 state to a molecular oxygen, $T_1(\text{PS}) + {}^3\text{O}_2 \rightarrow \text{S}_0(\text{PS}) + {}^1\text{O}_2$. The rate constant of this process by oxygen quenching (k_{et}) is listed in Table 2 for each compound. The k_{et} values obtained above are comparable to the rate constants obtained for O_2 quenching of the triplet excited states of a variety of porphyrins and phthalocyanines [21].

Table 2

Photophysical data related to triplet state.

	λ_{T-T} , nm	$\Delta\epsilon_T$, $10^4 \text{ M}^{-1} \text{ cm}^{-1}$	Φ_T	τ_T/Ar , μs	τ_T/air , μs	k_{et} , $10^9 \text{ M}^{-1} \text{ s}^{-1}$	k_{isc} , 10^9 s^{-1}	k_{ic} , 10^9 s^{-1}	Φ_Δ
POTBC	458	1.00	0.45	173	0.44	1.13	0.14	0.059	0.43
POTBC(β -OPh) $_4$	470	3.77	0.41	179	0.52	0.96	0.14	0.063	0.35
POTBC(α -OPh) $_4$	505	4.80	0.32	118	0.54	0.92	0.12	0.136	0.39
ZnPc	465	4.50	0.60	145	0.33	1.51	0.19	0.015	0.65
ZnPc(β -OPh) $_4$	480	2.82	0.47	181	0.39	1.27	0.15	0.074	0.50
ZnPc(α -OPh) $_4$	560	2.94	0.63	75	0.44	1.13	0.21	0.036	0.65

The values are close to one-ninth of the diffusion rate of O₂ in the solvent.

4. Conclusion

POTBC(α -OPh)₄ and POTBC(β -OPh)₄ were synthesized to compare the difference of the substitution effect. The photophysical properties for the POTBCs and ZnPcs were measured by ground state absorption, steady state fluorescence, single photon counting technique and laser flash photolysis. These compounds possess long triplet lifetime and good triplet formation yield. They can effectively photooxidize DPBF through singlet oxygen. POTBCs fluorescence yields and lifetimes are comparable to the corresponding ZnPcs. The nonperipheral α -OPh exhibits remarkably larger effect than the peripheral β -OPh on photophysics, including: (1) the longer red shift of absorption, fluorescence emission and T_1 – T_n transient spectra, (2) the larger decrease of fluorescence lifetime and triplet lifetime. Although POTBCs are nonplanar in structure, they showed the similar effect of nonperipheral substitution on photophysical properties as that of the planar ZnPcs.

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