



Titanyl phthalocyanine and its soluble derivatives: Highly efficient photosensitizers for singlet oxygen production

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ABSTRACT

The photophysical properties of titanyl phthalocyanine (TiOPc), tetra(β -phenoxy) titanyl phthalocyanine (TiOPc(β -OPh)₄) and tetra(α -phenoxy) titanyl phthalocyanine (TiOPc(α -OPh)₄), were investigated in homogeneous solution. Absorption, fluorescence, triplet state and singlet oxygen [$O_2(^1\Delta_g)$] sensitization studies are reported. The phthalocyanines present high triplet quantum yields (Φ_T) of 0.81, 0.85 for TiOPc(β -OPh)₄ and TiOPc(α -OPh)₄, respectively, while they still maintain long triplet lifetime (τ_T) of 80 μ s and 69 μ s. This makes them produce $O_2(^1\Delta_g)$ very efficiently with quantum yields (Φ_Δ) of 0.79 (TiOPc), 0.76 (TiOPc(β -OPh)₄) and 0.86 (TiOPc(α -OPh)₄). The ground state of all the phthalocyanines shows a strong absorption band in the red region (690 nm for TiOPc, 698 nm for TiOPc(β -OPh)₄, and 718 nm for TiOPc(α -OPh)₄ with $\epsilon > 150,000 \text{ M}^{-1} \text{ cm}^{-1}$ in DMSO), which is located in the optimal optical window of photodynamic therapy of tumor (PDT). For the singlet excited state, the following data were determined in DMSO: energy levels, $E_s = 1.75 \pm 0.04 \text{ eV}$, lifetime, $\tau_f = 4.0 \pm 0.1 \text{ ns}$ and fluorescence quantum yield, $\Phi_f = 0.13\text{--}0.06$ in air-saturated solution. The high Φ_Δ , reasonable long τ_f and sufficiently good Φ_f make the phthalocyanines not only excellent for $O_2(^1\Delta_g)$ production as photosensitizers, but also good for fluorescent imaging of tumors and the biodistribution detection of the sensitizers themselves.

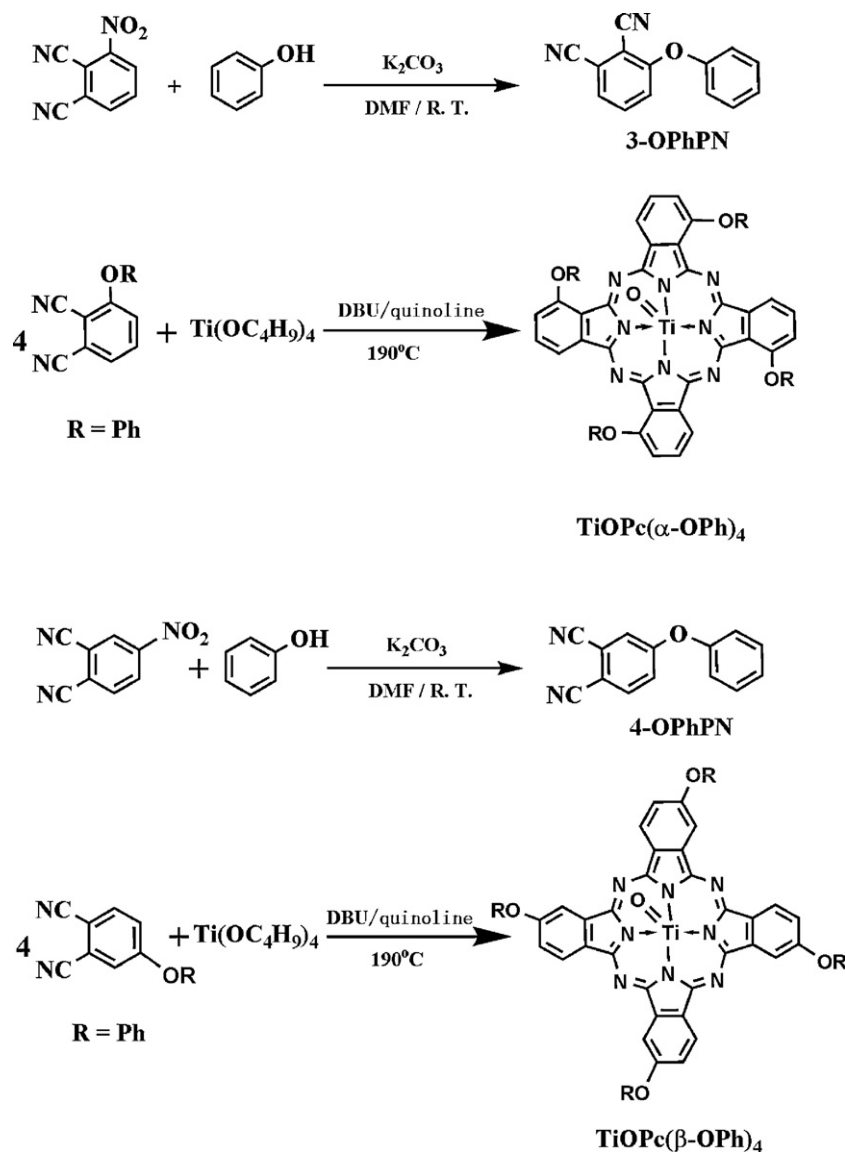
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1. Introduction

Phthalocyanine (Pc) complexes (Scheme 1) belong to a wide class of π -conjugated metallomacrocycles, which are of great interest due to their various important applications in modern science and technology [1,2]. Although all transition metals can coordinate to Pc ligands, only a few of them (Zn, Ti, Pd) can form highly photoactive complexes, such as titanyl phthalocyanine (TiOPc) and zinc phthalocyanine (ZnPc), owing to the closed shell nature of the electronic configuration of Ti^{4+} or Zn^{2+} , similar to that of main group metal ions. Other transition metal Pc complexes usually show very short lifetime for their S_1 , T_1 state and very low fluorescence emission efficiency [3]. Although TiOPc have found many more important applications in modern technologies than ZnPc and its derivatives, such as high sensitive photoconductors in laser printing and photo copying [4], the studies on synthesis and physical properties, however, are mainly placed on the latter [5]. Our understanding on the photophysical properties of TiOPc mainly stays on the various crystalline forms of its solid state

[6–9]. The related studies for the molecular state of TiOPc and its derivatives in solution are still rare [10,11], and the correlation of photophysical properties with their chemical structures is much less explored compared to the case of ZnPc. On the basis of our previous reports on the photosensitizing and other properties of molecular ZnPc and its derivatives [12–21], we now extend the studies to TiOPc and its derivatives. It was found in this study that its quantum yield of singlet oxygen ($O_2(^1\Delta_g)$) formation is among the highest for various PCs. $O_2(^1\Delta_g)$ is generally accepted to be a key intermediate in photodynamic therapy (PDT), and produced by energy transfer from an electronically excited triplet state of sensitizer molecule S to the ground state of molecular oxygen, $O_2(^3\Sigma_g^-)$ [22,23]. An active research area in PDT involves the search for and characterization of photosensitizers that improve upon the presently used hematoporphyrin derivative (HpD, Photofrin) [24]. Basic requirements for a PDT photosensitizer include optimal light absorbing properties in the therapeutic window, where HpD is very weakly absorbing [25]. Many researchers, include us, have synthesized quite some PCs meeting the conditions, but only a few of them have such a high efficiency of $O_2(^1\Delta_g)$ generation as TiOPc family. This shows that TiOPc and its derivatives have good potential for use in PDT, which leads us to synthesize well soluble TiOPc derivatives as shown in Scheme 1 and measure their photophysical and photosensitizing properties.

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Scheme 1. Synthesis of phenoxy substituted TiOPc.

The results should provide us with structure–property relationships.

2. Experimental

2.1. Materials and instruments

Dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), chloroform and dichloromethane quinoline were dried and redistilled before use. Titanyl Phthalocyanine was a product of Aldrich. Tetra(phenoxy) Titanyl Phthalocyanines and their precursors were synthesized as described below by modifying procedures in literature [26]. All other reagents were analytical grade and used as received. ^1H NMR spectra were recorded at room temperature on a Bruker dmx 300MHz 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 absorption measurements were made with either a HP 8451A or Shimadzu 4500 spectrophotometer in 10 mm quartz cuvettes.

2.2. Synthesis

2.2.1. 4-Phenoxyphthalonitrile

Phenol (1.87 g, 20 mmol) and 4-nitrophthalonitrile (3.46 g, 20 mmol) were added and stirred to dissolve in dry DMSO (30 ml) under argon. To this solution was added four equal portions of anhydrous K_2CO_3 (total 4.14 g, 30 mmol) every other 15 min during 1.0 h and the mixture was kept stirring at room temperature. After 24 h total reaction time, the mixture was poured into ice-water (50 ml), thus forming a precipitate that was filtered, washed by cold water to neutral and dried in air. Recrystallization twice from ethanol yielded a white product. Yield: 3.3 g (73%). m.p. 100–101 °C. IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3047 (Ar-H), 2233 (CN), 1600–1450 (C=C in Ph), 1235 (C–O–C). ^1H NMR (d^6 -DMSO, ppm): δ 7.75 (d, 1H, Ar-H), 7.44 (t, 2H, Ar-H), 7.21–7.33 (m, 3H, Ar'-H), 7.06 (d, 2H, Ar'-H). MS (m/z): 221 ($M+1$)⁺.

2.2.2. 3-Phenoxyphthalonitrile

The synthesis and purification procedures were the same as that described for 4-phenoxyphthalonitrile, using phenol (1.87 g, 20 mmol) and 3-nitrophthalonitrile (3.46 g, 20 mmol). Yield: 3.07 g (68%). m.p. 117–118 °C. IR [(KBr) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3082 (Ar-H), 2231

(CN), 1600–1450 (C=C in Ph), 1245 (C–O–C). $^1\text{H NMR}$ (d^6 -DMSO, ppm): δ 7.78–7.85 (m, 2H, Ar-H), 7.49–7.55 (t, 2H, Ar-H, Ar'-H), 7.25–7.34 (m, 4H, Ar'-H). MS (m/z): 221 ($M+1$) $^+$.

2.2.3. 2,9(10),16(17),23(24)-Tetra(β -phenoxy) titanyl phthalocyanine

4-Phenoxy-phthalonitrile (1.32 g, 6.0 mmol), two drops of DBU and urea (0.1 g) were dissolved in quinoline (10 ml) under dry argon. After the temperature was raised to 190 °C, $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (0.75 ml, 2.2 mmol) was then added with a syringe to the solution and the reaction mixture stirred at 190 °C for 6 h under argon. Most solvent was then removed by the vacuum distillation. After cooling, 30 ml hexane was added to the mixture and stirred. The resulting mixture was then filtered and washed with hexane and methanol. The dried crude product was chromatographed with CH_2Cl_2 -THF (v/v, 9:1) as eluent. Yield: 0.76 g (55%). UV/vis (DMSO): λ_{max} nm (log ϵ): 354 (4.73), 366 (4.72), 630 (4.50), 698 (5.20). IR [(KBr) $\lambda_{\text{max}}/\text{cm}^{-1}$]: 1234 (C–O–C), 970 (Ti=O). $^1\text{H NMR}$ (CDCl_3 , ppm): δ 8.62–8.90 (t, q, t; 4H; Pc-H), 8.34–8.51 (s, s, d; 4H; Pc-H), 7.64–7.78 (m, 4H, Pc-H), 7.54–7.61 (m, 8H, Phenyl-2,6-H), 7.42–7.50 (m, 8H, Phenyl-3,5-H), 7.30–7.41 (m, 4H, Phenyl-4-H). MALDI-TOF-MS (m/z): 945.4 ($M+1$) $^+$.

2.2.4. 1,5(8),9(12),13(16)-Tetra(α -phenoxy) titanyl phthalocyanine

The procedure for synthesis and purification was the same as that described for tetra(β -phenoxy) titanyl phthalocyanine, using 3-phenoxyphthalonitrile (1.32 g, 6.0 mmol) and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (0.75 ml, 2.2 mmol). Yield: 0.41 g (30%). λ_{max} nm (log ϵ): 324 (5.12), 360 (4.99), 644 (4.72), 718 (5.43). IR [(KBr) $\lambda_{\text{max}}/\text{cm}^{-1}$]: 1247 (C–O–C), 971 (Ti=O). $^1\text{H NMR}$ (CDCl_3 , ppm): δ 7.62–9.10 (m, 12H; Pc-H), 7.14–7.19 (m, 20H; Ar-H). MALDI-TOF-MS (m/z): 945.3 ($M+1$) $^+$.

2.3. Photophysical measurements

DMSO and other solvents were dried and freshly distilled before use. Measurements were carried out at room temperature of 22 °C. UV–vis absorption measurements were made in DMSO with 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 0.20–2.0. Fluorescence spectra up to 900 nm were monitored using a PerkinElmer LS 55, with 2.5 nm slits. 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 ($\Phi_f^0 = 0.20$) [27]. 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 FL-900 spectrophotometer) with excitation at 660 nm by a CdS diode laser (50 ps FWHM) and emission was monitored at 700 nm. Transient spectra were recorded in degassed DMSO (prepared by bubbling with Argon for 20 min) with an Edinburgh LP-920 laser flash photolysis system. A Nd:YAG laser (Continuum surelite II, 355 nm and 7 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 LP900 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 μM providing $A_{355} = 0.3$ in a 10 mm cuvette.

The triplet–triplet absorption coefficients (ϵ_T) of the samples were obtained using the singlet depletion method [28], and the following equation was used to calculate the ϵ_T :

$$\epsilon_T = \epsilon_S \frac{\Delta A_T}{\Delta A_S} \quad (1)$$

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 ($\Phi_T = 0.65 \pm 0.02$, $\epsilon_T(480) = 30,000 \pm 1000 \text{ M}^{-1} \text{ cm}^{-1}$) [29], using the equation:

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

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 [30]. Typically, a 2 ml portion of the respective TiOPc 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 (0.65 for ZnPc in DMSO) [31], k and k^{ref} are the DPBF photo bleaching 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. Synthesis

The reactions used to prepare the phenoxy substituted TiOPcs, are summarized in Scheme 1. Phenoxy substituted TiOPcs were selected for the study because the aromatic electrophilic reactions of phenol such as that used for 4-OPhPN and 3-OPhPN (Scheme 1) gave products in much better yield over that of alcohol under the condition at room temperature. It was found that the product yield

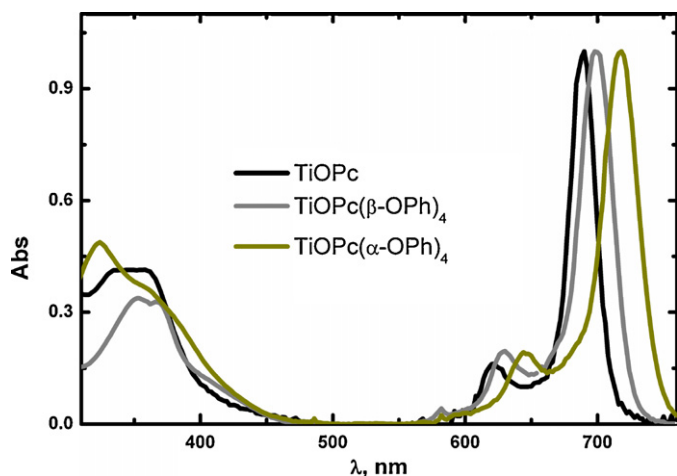


Fig. 1. Normalized UV-vis absorption spectra of TiOPc and its derivatives in DMSO.

was quite low when *n*-pentanol, a common solvent for Pc synthesis, was employed, and products are mixed with the metal free Pcs. This suggests that titanium is harder to form complex with Pc than zinc, copper, nickel etc. Raising reaction temperature by using high b.p. solvent quinoline solved the problem. The reaction time, however, needs to be controlled since the Pcs, especially α -phenoxy substituted TiOPc, could decompose slowly at the temperature. To remove quinoline by distillation after the reaction, vacuum is highly suggested to lower the b.p. and hence reduce the decomposition. Both substituted TiOPcs show excellent solubility ($\geq 0.55 \text{ mmol L}^{-1}$) in most organic solvents, which makes purification by column chromatography convenient. Maldi-TOF mass spectra, IR and ^1H NMR showed satisfied results that are agreed with their structures. UV-vis spectra were obtained as expected, as shown below.

3.2. Ground-state absorption spectra

The normalized UV-vis absorption spectra of the Pc compounds measured in DMSO solutions are displayed in Fig. 1, along with that of unsubstituted TiOPc. All showed similar spectral behavior, i.e., a strong but narrow Q-band centered around 700 nm and a B-band located at ca. 350 nm, which are typical for metallophthalocyanines in molecular state. As expected, the α substitution caused the larger red shift of Q-band than that of the β substitution. The detailed spectral data are collected in Table 1. The larger bathochromic shift of the α -substitution is due to linear combinations of the atomic orbital (LCAO) coefficients at the α positions of the HOMO being greater than those at the β positions. As a result, the HOMO level is destabilized more at the α position than it is at the β position. Essentially, the energy gap (ΔE) between the HOMO and LUMO becomes smaller, resulting in a bathochromic shift [32,33].

The Q-band absorption maxima of the TiOPcs are about 20 nm longer than other common metal Pcs, such as Mg, AlCl, Zn, and Ga, which are more suitable for PDT.

No indications for dimerization or aggregation in their ground states were found for the three Pcs in DMSO, which is evidenced by the absence of the typical broad dimeric band in their UV-vis spectra. Dimerization or aggregation occurs for many Pcs [12], but

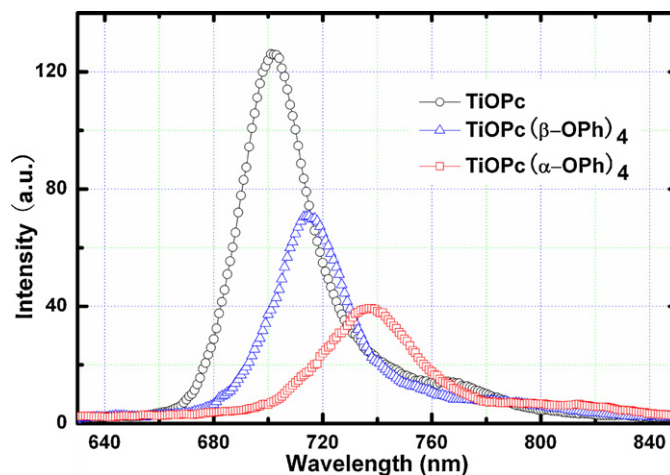


Fig. 2. The fluorescence spectra of three Pcs measured under same conditions, the excitation wavelength is 610 nm, absorbances at 610 nm were adjusted to be 0.090.

is not a desired feature for PDT since the H dimer or aggregate is non-photoactive. $\text{ZnPc}(\beta\text{-X})_4$ ($\text{X}=\text{I}, \text{Br}, \text{Cl}$), for example, forms H dimer in DMSO in significant amount [12]. TiOPcs are non-planar in which the Ti is out of the π plane structures, which is likely the reason of less aggregation than ZnPcs.

3.3. Fluorescence

The three Pcs showed different fluorescence behavior, as plotted in Fig. 2 in which three spectra were measured with the excitation at 610 nm. The fluorescence emission peak for TiOPc was observed at 701 nm, but the substitutions caused the red shift of the emission maximum and the significant reduction of their emission intensity. The bathochromic shift for $\text{TiOPc}(\alpha\text{-OPh})_4$ relative to TiOPc is 38 nm, which is larger than 14 nm for $\text{TiOPc}(\beta\text{-OPh})_4$. The fluorescence quantum yields were measured by reference to ZnPc and summarized in Table 1. Φ_f of TiOPc is 0.13 and the same magnitude as but smaller than that of ZnPc. The peripherally β -tetrasubstituted complex show larger Φ_f values, suggesting less quenching of the excited singlet state by peripheral β -tetrasubstitution compared to non-peripheral α -tetrasubstitution, which is generally true for all metallo Pcs [5].

The absorption and fluorescence emission spectra are compared in Fig. 3. The fluorescence excitation spectra are quite similar to the absorption spectra and not shown. Each absorption spectrum is basically the mirror image of the corresponding fluorescence spectrum for all the complexes. The S_1 excitation energy (E_s) is then able to be calculated from each cross point and included in Table 1.

3.4. Fluorescence lifetime

The fluorescence decays in Fig. 4, were satisfactorily described by monoexponential functions. In all cases, the weighted residuals (such as that for $\text{TiOPc}(\beta\text{-OPh})_4$ on bottom of Fig. 4), their autocorrelation function and reduced chi-squared ($\chi^2 < 1.20$) were used to judge the quality of the fit. The decay lifetimes (τ_f) are given in Table 1. τ_f for α - and β -substituted TiOPcs is 4.0 and 4.1 ns, respectively, exhibited little difference from 4.0 ns of TiOPc itself. Ishii and

Table 1
Photophysical parameters for the Pcs in DMSO.

	λ_{abs} (nm)	Log ϵ	λ_{em} (nm)	Stoke shift (nm)	E_s (eV)	τ_f (ns)	λ_{T-T} (nm)	τ_T (μs)	$\Delta\epsilon_T$	Φ_T	Φ_f	Φ_Δ
$\text{TiOPc}(\alpha\text{-OPh})_4$	718	5.4	738	20	1.71	4.0	570	79	150,710	0.85	0.06	0.86
$\text{TiOPc}(\beta\text{-OPh})_4$	698	5.2	715	17	1.76	4.1	530	69	128,220	0.81	0.10	0.76
TiOPc	690	–	701	11	1.79	4.0	–	–	–	–	0.13	0.79

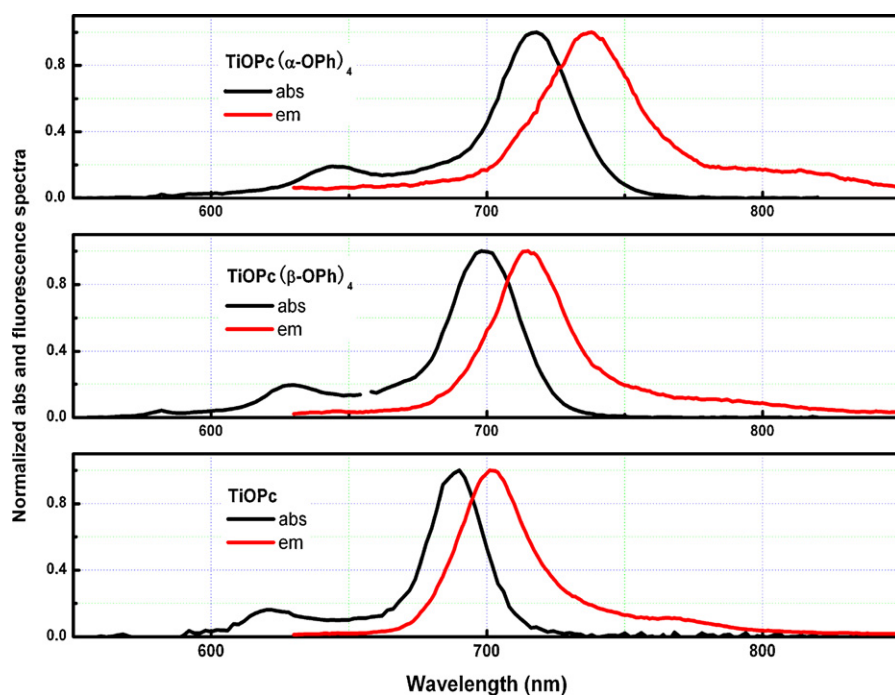


Fig. 3. Comparison of normalized absorption and fluorescence spectra of in DMSO. Excitation wavelength = 610 nm.

Kobayashi have given the most complete compilation for the τ_f values of various Pcs [3], but no data on TiOPc or its derivatives were included, probably because of lacking of such reports. The τ_f values measured in this study for TiOPcs are comparable to that of ZnPcs and other main group metal Pcs, typically in the range from 2 ns to 9 ns [3], while CoPc, NiPc, FePc, etc., transition metal Pcs show much shorter values which are usually only several ps [3]. This is apparently because of the closed shell nature of Ti^{4+} which reduces the spin–orbital interactions between the Ti^{4+} and the π system of the Pcs, so that the TiOPcs are highly photoactive.

3.5. Triplet state transient spectra and kinetics

Fig. 5 shows the transient spectrum changes for $TiOPc(\alpha-OPh)_4$ after laser excitation with 7 ns pulses at 355 nm. Both $TiOPc(\alpha-$

$OPh)_4$ and $TiOPc(\beta-OPh)_4$ showed similar spectral features, i.e., negative absorption in the Q- and B-band regions, a broad positive absorption maximum near 570 nm and 530 nm, respectively. 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, indicating concomitant behavior, i.e., as the positive absorbing transient decays, the ground state is repopulated. It is very likely that the transient

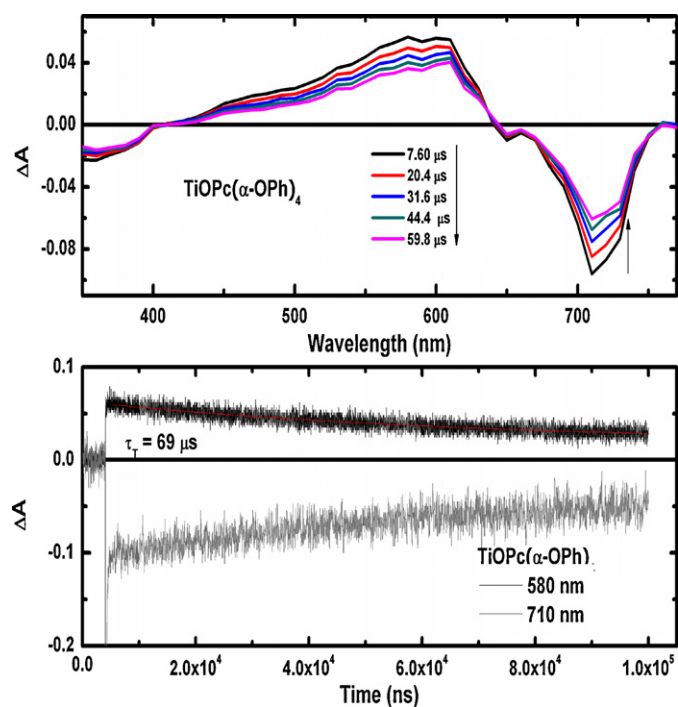


Fig. 5. The transient absorption spectra of $TiOPc(\alpha-OPh)_4$ in degassed DMSO with laser excitation at 355 nm (top). The bottom contains decays at 580 nm and rise at 710 nm. $[TiOPc(\alpha-OPh)_4] = 13 \mu M$.

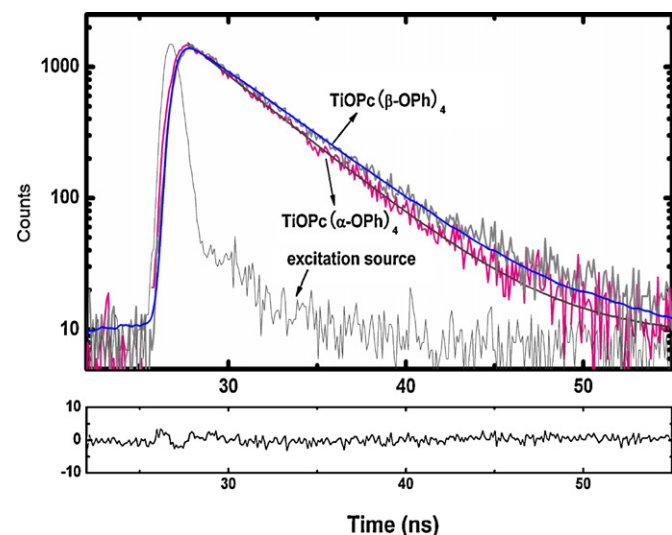


Fig. 4. Fluorescence decay curves of the Pcs at 700 nm in DMSO with excitation at 660 nm. The concentration of Pcs is controlled at $10 \mu M$.

observable on the nanosecond and longer time scale has a broad continuous absorption between ca. 400 and ca. 800 nm, superimposed upon which is an intense ground-state bleaching signal.

In air or oxygen saturated solutions the transient absorptions were effectively quenched. The shape of the broad positive absorption is similar to those found previously with other Pcs except the red shift of absorption maxima. By analogy the positive absorption band can be assigned to the triplet–triplet (T_1 – T_n) absorption. The red shift of absorption maxima from ca. 490 nm of other Pcs is reasonable, since the ground-state absorption spectrum of TiOPc(α -OPh)₄ and TiOPc(β -OPh)₄ is also red shifted about 50 nm and 30 nm from 670 nm of ZnPc, respectively. The appearance of the isosbestic point between positive absorption and ground-state bleaching indicated that the species near 570 nm or 530 nm is responsible for the ground-state repopulation. Therefore we can conclude that the positive peaks arise from a T_1 to T_n transition.

The values of the T_1 – T_n absorption coefficient and triplet state quantum yields for the Pcs were calculated and collected in Table 1. The time profiles (bottom of Fig. 5) at the maximum wavelengths were recorded from which kinetic parameters were extracted. The triplet state lifetime (τ_T) is 69 μ s and 79 μ s for them, and the triplet quantum yield (Φ_T) is 0.81 and 0.85, respectively. Φ_T and τ_T are the two major factors that govern the efficiency of singlet oxygen formation [12]. The Φ_T values for the TiOPcs are larger than that of other closed shell Pcs [3], which is an advantage for them to be singlet oxygen photosensitizers. The τ_T values, however, are somewhat smaller than, but still in the same order to that of other closed shell Pcs [3]. In cases studied in this report, triplet state decays were first order, indicating no triplet–triplet annihilation.

3.6. Singlet oxygen formation

Singlet oxygen quantum yields (Φ_Δ) were determined in DMSO using DPBF as a chemical quencher. The disappearance of DPBF was monitored using UV–vis spectrometer, the absorbance at 415 nm of DPBF absorption maximum was recorded and plotted against irradiation time for quantitative kinetic analysis (Section 2). The Φ_Δ values for three Pcs are 0.79, 0.76 and 0.86, all are very high compared to other Pcs.

The high Φ_Δ values can be attributed to their high Φ_T values, explained by Eq. (5) in which k_{et} is the rate constant for energy transfer from a triplet state to oxygen and η is the efficiency of the transfer that actually forms singlet oxygen (generally close to 1.0). k_{et} is in the order of $10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $[\text{O}_2]$ is $\sim 2.0 \times 10^{-3} \text{ mol dm}^{-3}$. Φ_Δ is mainly determined by Φ_T , τ_T , and k_{et} . Because the τ_T is sufficient long such that $(\tau_T)^{-1} \ll k_{et}[\text{O}_2] < k_{et}[\text{O}_2]/\eta$, hence $\Phi_\Delta \approx \Phi_T$:

$$\Phi_\Delta = \Phi_T \frac{k_{et}[\text{O}_2]}{\tau_T^{-1} + k_{et}[\text{O}_2]/\eta} \quad (5)$$

Note that the Φ_T of CuPc is also as high as 0.90 [3], but its Φ_Δ is much lower as of the short τ_T value of 0.035 μ s [3], so that $\Phi_\Delta \approx 0.065\Phi_T$. Generally $\Phi_\Delta \approx 0.5\Phi_T$, when $\tau_T = 0.5 \mu$ s.

4. Conclusion

In conclusion, we have measured and compared the photophysical and photosensitizing properties of β - and α -tetra-phenoxyl sub-

stituted titanyl phthalocyanines. These complexes are monomeric in DMSO solution. The phthalocyanines showed high singlet oxygen quantum yields ranging from 0.76 to 0.85 because of their large triplet quantum yields and sufficient long triplet lifetime. The Pcs still maintain long fluorescence lifetime and good fluorescence quantum yields. Together with their strong absorption in the red region around 700 nm, all these properties give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism), in particular as Type II photosensitizers for PDT.

Acknowledgement

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