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Photophysical Properties of Sulfonated Dihydroxy Phosphorus(V) Tetrabenzotriazacorrole

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The photosensitizing properties of a novel phthalocyanine analogue, sulfonated dihydroxy phosphorus(V) tetrabenzotriazacorrole [$P(OH)_2TBCS_n$] and a non-sulfonated one [$P(OH)_2TBC$] are reported in this paper. Different from other phthalocyanine derivatives, $P(OH)_2TBCS_n$ shows little aggregation in aqueous solution. The fluorescence quantum yield (Φ_F) of $P(OH)_2TBCS_n$ is lower than that of the non-sulfonated one. Studies of triplet state photophysics show that the presence of peripheral substituents on the macrocycle enhances the quantum yield of the triplet state. The sulfonated derivative, $P(OH)_2TBCS_n$, has a longer triplet lifetime ($\tau_T = 0.234$ ms) and higher singlet oxygen quantum yield ($\Phi_\Delta = 0.88$) than $P(OH)_2TBC$. Together with the ground-state absorption properties, the photosensitizing properties of the new compound suggest that it may be used as an excellent photosensitizer for photodynamic therapy (PDT).

Introduction

Metalloid phthalocyanines have recently attracted significant interest due to their potential applications in photodynamic therapy (PDT).[1−3] Phthalocyanine complexes of the group 14 and 15 elements, such as silicon and phosphorus, are of particular chemical and spectroscopic importance, because two different oxidation states are accessible to the center metalliod atom. When complexed with phosphorus, phthalocyanine may lose a bridging nitrogen atom. The phosphorus(V) complex has been proven to be a complex of the tetrabenzotriazacorrole (TBC).[4,5] The same ring-contractive reaction was reported for the complexes of the metalloids aluminum, silicon, gallium, and germanium.[5,6] Murakami et al. reported a chemical study which shows that the TBC macrocycle is useful for biological modeling,[7] and it has shown good biological dynamics in recent works.[8] In contrast to the silicon phthalocyanine, which has been widely studied, there are only a few reports of the phosphorus phthalocyanine until now.

Dihydroxy phosphorus has a lower molecular symmetry and shows an unusual electronic-transition spectrum, strong fluorescence, and high singlet oxygen formation yield.[4,9] Thus, the TBC complex provides a novel species to these macrocyclic compounds, with novel chemical and spectroscopic properties. Furthermore, the efficient sensitization of PDT agents needs a high triplet state quantum yield and long lifetime. New phthalocyanine analogues are expected to show improvements in both properties.

To understand and explain the behavior of these sensitizers in vivo, it is necessary to investigate them in a biologically compatible media. Singlet oxygen has been considered as responsible for the photosensitized tumor cell inactivation in PDT.[10] It is already known that the lifetimes and quantum yields of the excited triplet state of photosensitizers show significant dependence on the properties of solvents. This could be because of the relative shifts in the positions of the photosensitizer's

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singlet and triplet excited states.[11] In the present study, water-soluble phosphorus tetrabenzotriazacorrole was synthesized for being better absorbed by tumor tissue for the application in PDT. The effects of substituents and solvents on the photophysical properties of $P(OH)_2TBCS_n$ were studied. The photophysical property as well as singlet oxygen production of $P(OH)_2TBCS_n$ in Tris-HCl buffer, in addition to the photostability of these compounds in homogeneous solutions under Q-band excitation, was also investigated.

Experimental Section

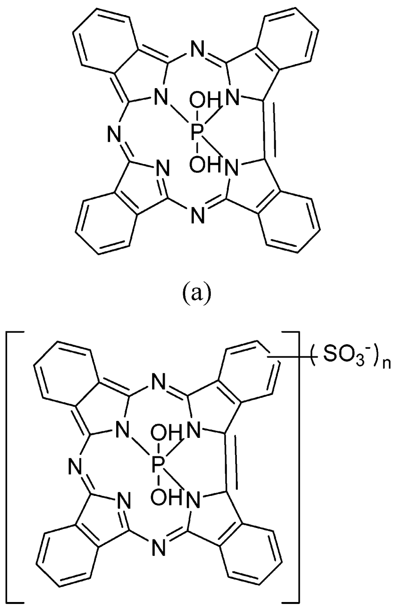
Synthesis. $P(OH)_2TBCS_n$ was synthesized from $P(OH)_2TBC$ which was prepared according to previous references.[12,13] $P(OH)_2TBC$ (0.1 g, 0.18 mmol) was dissolved in 3 mL of fuming sulfuric acid (30% SO_3) then heated at 80 °C with stirring. The mixture was kept at this temperature for 2 h and subsequently poured into crushed ice. The resulting green precipitate was filtered and washed with water/alcohol. The product was dried at 50 °C under vacuum. The crude product was then purified by column chromatography on neutral alumina with chloroform and methanol as the eluent. The light green fraction from methanol was the major product in the solution. The solution was dried at 50 °C under vacuum to give $P(OH)_2TBCS_n$ as a green solid (0.07 g, 47%). Experimental analytical data involved are as follows: IR (KBr, cm^{-1}): 3389 (P−OH), 1726 (C═C), 1677 (C═N), 1384, 1279, 1122 (SO_2), 1076, 749. UV−vis (pyridine, nm): 656 (log, 4.62), 640 (4.39), 626 (4.04), 446 (4.95), 416 (4.49). ^{31}P NMR (D_2O): −200 ppm; ^{31}P NMR ($(CD_3)_2SO$): −201.5 ppm. HRMS (MALDI-TOF) (*m*/*z*): 723.2 (calculated for $C_{32}H_{18}N_7O_8PS_2$, 723.04), 802.8 (calculated for $C_{32}H_{18}N_7O_{11}PS_3$, 803), 882.8 (calculated for $C_{32}H_{18}N_7O_{14}PS_4$, 882.95). EA ($C_{32}H_{18}N_7PO_{2+3n}S_n$): found (calcd) C, 45.67 (45.99); H, 2.11 (2.16); N, 11.96 (11.74); S, 12.85 (13.03).

All the solvents and reagents were of the purest grade available and purified by standard methods.

Instruments and Methods. UV−vis absorption spectra were recorded by an HP8452A diode-array spectrometer. Infrared (IR) absorption spectra were obtained using an AVATER 360 FT-IR spectrophotometer (Nicolet, American). MALDI-TOF mass spectra were measured by a BIFLEXIII MALDI-TOF Mass instrument. Fluorescence emission spectra were obtained by a PE LS55 luminescence spectrometer using a 1-cm path length cuvette with very dilute solutions of the compounds (absorbance < 0.05) at room temperature. The excitation wavelengths of 614 and 418 nm were used to obtain the first and the second excited excited singlet states (S_1, S_2). Fluorescence quantum yields were determined by a comparative calibration method using unsubstituted zinc phthalocyanine (ZnPc) in DMSO as a standard ($\Phi_F = 0.18$)[14] for S_1 and fluorescein disodium in THF ($\Phi_F = 0.92$)[15] as a standard for S_2.

Fluorescence lifetimes (τ_f) were measured by an Edinburgh Instruments FLS900 time-correlated single-photon-counting spectrofluorometer, employing an excitation wavelength of 660 nm from a CdSe diode laser.[16]

T_1-T_n absorption spectra were obtained using a nanosecond laser flash photolysis spectrometer (Edinburgh Analytical Instruments, LP920).[16] The samples were bubbled with N_2 for 20 min before measurement and then were excited using 7 ns laser pulses at 355 nm. Spectra were recorded in scanning mode over the wavelength range of 300−800 nm in 10 nm steps. The output signal of the LP920 was acquired and accumulated by a Tektronix TDS3012B oscilloscope and recorded by a computer. Triplet difference absorption coefficients ($\Delta\epsilon_T$) were measured by the complete conversion method[17] using a probe laser with wavelength of 460 nm. Each signal was averaged over 16 shots to reduce the noise. The absorbance was lower than 0.4 for the triplet state studies. Triplet state quantum yields (Φ_T) were determined by the comparative method using tetraphenylporphyrin (TPP) in benzene ($\Phi_T = 0.82$, ϵ_T (440 nm) $= 67000$ M^{-1} cm^{-1}).[18]



(a)

(b)

Figure 1. Structural formulas of (a) $P(OH)_2TBC$ and (b) $P(OH)_2TBCS_n$.

The production of singlet oxygen was monitored by the near-infrared time-resolved singlet oxygen luminescence method. The laser irradiation system was the same as that used for the flash photolysis experiments. The samples were examined by detecting the luminescence in the near-infrared spectrum range at 1270 nm, where singlet oxygen phosphoresces, upon excitation by 7 ns pulses of a 355-nm laser. Relative quantum yields were determined using ZnPc in DMSO ($\Phi_\Delta = 0.67$) as a standard.[19]

Results and Discussion

Characterizing $P(OH)_2TBCS_n$. Figure 1 shows the chemical structures of the sulfonated and non-sulfonated dihydroxy phosphorus(V) tetrabenzotriazacorrole. There are many arguments about the structure of this molecule.[5,12,13,20] In recent research, the structure of the compound was considered to be $P(OH)_2TBC$ rather than $H[P^{III}(OH)TBC]$ as reported earlier,[21] and it is a six-coordinate compound. However, Fox et al.[22] reported the structure of octaalkoxy-substituted phosphorus(V) triazatetrabenzcorroles. They demonstrated that the structure should be five-coordinate phosphorus for the hydroxyphosphorus(V) 3,6,10,13,17,20,24,27-octabutoxytriazatetrabenzcorrole hydroxide, $[(BuO)_8(TBC)P(OH)]^+OH^-$, with resonances from −90 to −110 ppm and six-coordinate phosphorus for the dimethoxyphosphorus(V) 3,6,10,13,17,20,24,27-octabutoxytriazatetrabenzcorrole, $(BuO)_8(TBC)P(OCH_3)_2$, with resonances from −180 to −200 ppm. Since the chemical shifts of the phosphorus nuclei in ^{31}P NMR spectroscopy are sensitive to the coordination number of the phosphorus center,[23] the synthesized compound was identified by ^{31}P NMR. The ^{31}P NMR spectrum for $P(OH)_2TBCS_n$ reveals a peak at −200 ppm in H_2O and −201 ppm in DMSO, which indicate that this compound is six-coordinate with two OH− groups as ligands.

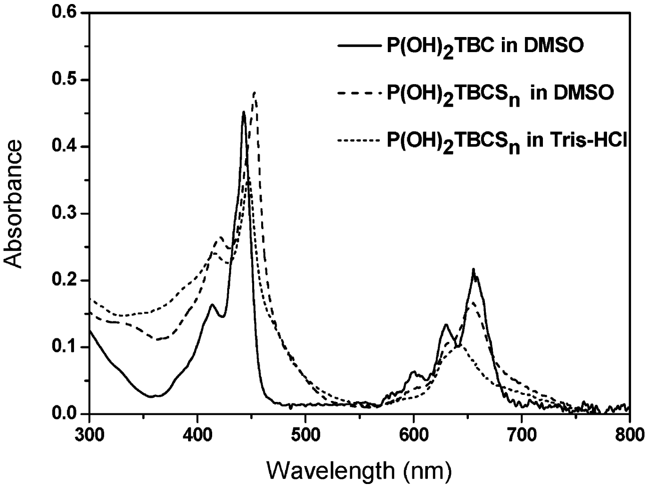


Figure 2. Absorption spectra of P(OH)$_2$TBC in DMSO solution (solid line), P(OH)$_2$TBCS$_n$ in DMSO solution (dotted line), and P(OH)$_2$TBCS$_n$ in Tris-HCl buffer at pH 7.4 (dashed line). All concentration are 10 μmol L^{-1}.

On the basis of the values of MALDI-TOF, the compounds are best formulated as P(OH)$_2$TBC and P(OH)$_2$TBCS$_n$.

The chemical structure of the P(OH)$_2$TBCS$_n$ is shown in Figure 1b. There are three main peaks in the mass spectrum at 723.2, 802.8, and 882.8, which correspond to the di-, tri-, and tetrasulfo-tetrabenzotriazacorroles, respectively. The average sulfonate degree is 3.4 according to an element analysis. In addition to the usual bands for TBC in the IR spectrum, the corresponding vibrational bands of P−OH and −SO$_3$H were also found. The UV−vis spectrum of P(OH)$_2$TBCS$_n$ in DMSO is very similar to that of P(OH)$_2$TBC but with a slight red-shift for the B-band. All the results mentioned above indicate that P(OH)$_2$TBC is sulfonated only at the peripheral positions.

P(OH)$_2$TBCS$_n$ is slightly or moderately soluble in solvents at room temperature, in the order of benzene < trichloromethane = dichloromethane < ethanol but highly soluble in pyridine, DMF, and DMSO.

Although many metallophthalocyanines can be demetalled with cold concentrated sulfuric acid, P(OH)$_2$TBCS$_n$ shows a unique stability. All these spectroscopic characteristics can be reversed when it is diluted with excess DMF and pyridine. The H$_2$SO$_4$ solution remains unchanged over several days in the dark.

Spectral Assignments for P(OH)$_2$TBCS$_n$. The UV−vis spectra of P(OH)$_2$TBCS$_n$ and P(OH)$_2$TBC are shown in Figure 2. TBC has two major absorption bands, namely, the Q-band in the visible light region and the B-band or Soret band in the violet or ultraviolet region. There are four peaks in the Q-bands between 548 and 680 nm for P(OH)$_2$TBC and P(OH)$_2$TBCS$_n$ in DMSO. Compared to the Q-band of P(OH)$_2$TBC, P(OH)$_2$TBCS$_n$ in DMSO exhibits a broad and slightly red-shifted absorption band even at a very low concentration. This red-shift is likely caused by the electron-attraction effect of the −SO$_3$H group. The P(OH)$_2$TBC has a higher extinction coefficient (25300 L mol^{-1} cm^{-1}) at 656 nm compared to the sulfonated derivative which has an extinction coefficient of 22000 L mol^{-1} cm^{-1} at 662 nm.

The B-bands of P(OH)$_2$TBCS$_n$ in DMSO and Tris-HCl buffer are also both red-shifted. There are two absorption peaks in the Soret region at 422 and 454 nm in DMSO and 416 and 446 nm in Tris-HCl buffer.

In DMSO solutions, the P(OH)$_2$TBC and P(OH)$_2$TBCS$_n$ complexes show a monomeric behavior at concentrations up to 10^{-5} mol L^{-1}. Beer's law is still obeyed up to 20 μmol L^{-1} for P(OH)$_2$TBC and P(OH)$_2$TBCS$_n$, which indicates that no significant aggregation occurs. This is probably due to the special structure of P(OH)$_2$TBC. It was found that the structure of P(OH)$_2$TBC is not planar due to the hydroxyl moiety on each side of the macrocycle. The axial ligands prevent close contact among the monomers. Aggregation often is a common behavior for sulfonated phthalocyanines,[24] which always reduces the photosensitivity. Thus, P(OH)$_2$TBCS is a better photosensitizer in this regard.

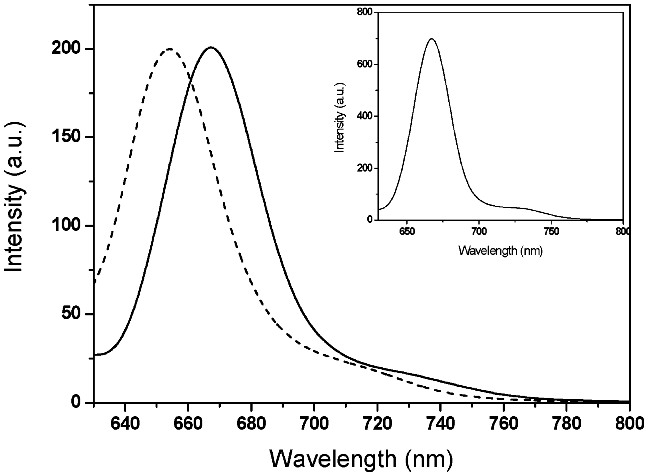


Figure 3. Fluorescence emission spectra of P(OH)$_2$TBCS$_n$ in DMSO solution (solid line) and in Tris-HCl buffer solution (dashed line) with an excitation wavelength of 614 nm. The inset shows fluorescence emission spectra of P(OH)$_2$TBC in DMSO solution.

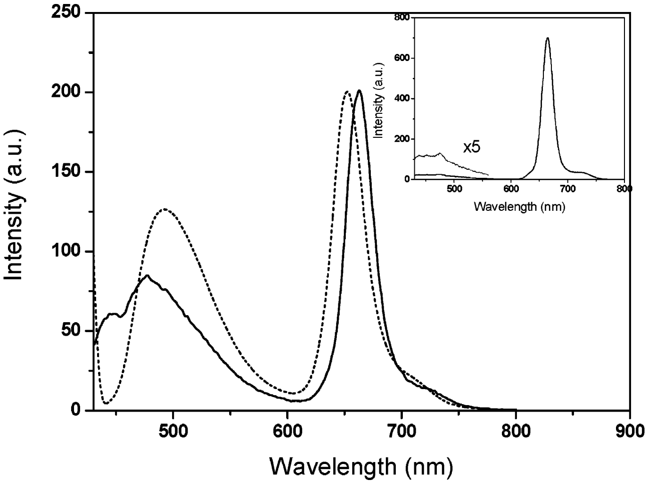


Figure 4. Fluorescence emission spectra of P(OH)$_2$TBCS$_n$ in DMSO solution (solid line) and in Tris-HCl buffer solution (dashed line) with an excitation wavelength of 418 nm. The inset shows fluorescence emission spectra of P(OH)$_2$TBC in DMSO solution.

The steady fluorescence spectra of P(OH)$_2$TBC and P(OH)$_2$TBCS$_n$ are shown in Figures 3 and 4, respectively. With excitation at 614 nm, the fluorescence maximum is at 664 nm for P(OH)$_2$TBC and at 662 nm for P(OH)$_2$TBCS$_n$ in DMSO, respectively. However, if P(OH)$_2$TBCS$_n$ is excited at 418 nm in DMSO, in addition to the fluorescence from the first excited singlet state (S$_1$ fluorescence), a new fluorescence peak appears at 477 nm, which is considered the fluorescence from the second excited singlet state (S$_2$ fluorescence). The two peaks at 493 and 652 nm for the fluorescence spectrum of P(OH)$_2$TBCS$_n$ in Tris-HCl buffer were ascribed to the fluorescence from the S$_2$- and S$_1$-states, respectively. A similar phenomenon has also been reported for phthalocyanines, but its S$_2$ fluorescence is much weaker than S$_1$. Table 1 shows the emission maxima and

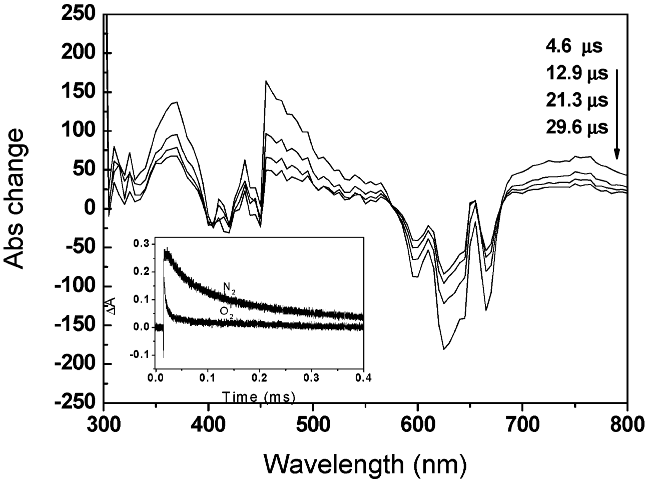


Figure 5. Transient absorption spectra recorded at different times (as shown) after irradiation with 7 ns pulses at 355 nm of $P(OH)_2TBC$ in DMSO. The inset shows the decay profile of the nitrogen-saturated $P(OH)_2TBC$ and the time profile of the $P(OH)_2TBC$ triplet in oxygen-saturated DMSO at 460 nm.

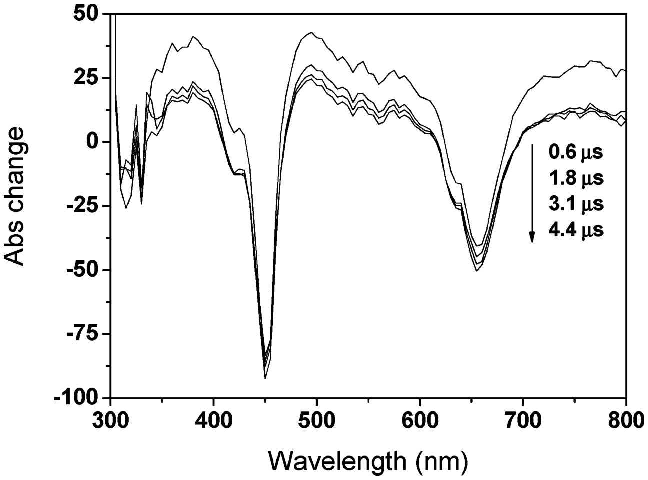


Figure 6. Transient absorption spectra recorded at different times after irradiation with 7 ns pulses at 355 nm of $P(OH)_2TBCS_n$ in DMSO.

fluorescence quantum yields of $P(OH)_2TBC$ and $P(OH)_2TBCS_n$. The intensity of the S_2 fluorescence is comparable to that of the S_1 fluorescence for $P(OH)_2TBCS_n$. The Φ_F value in DMSO is slightly higher than that in Tris-HCl buffer. The Φ_F value at 614 nm is significantly higher than the Φ_F value at 418 nm, which shows the effect of the excitation wavelength on Φ_F. This is similar to the observations for zinc phthalocyanine.[25]

As shown in Tables 1 and 2, the Stokes shift is small and almost independent of the solvent used in all the cases. For a molecule with a rigid skeleton, it is consistent with the structural point of view. This small Stokes shift leads to a high degree of spectral overlap. The fluorescence quantum yield of $P(OH)_2TBCS_n$ was found to be very low either in DMSO or in Tris-HCl buffer. Compared with $P(OH)_2TBC$, with excitation at 418 nm, $P(OH)_2TBCS_n$ in DMSO or in Tris-HCl buffer showed a slight decrease for the S_1 fluorescence quantum yield but a remarkable decrease for the S_2 fluorescence yield.

Triplet−Triplet Difference Spectra, Triplet Quantum Yields, and Lifetimes. The transient absorption spectra of $P(OH)_2TBC$ and $P(OH)_2TBCS_n$ were recorded in DMSO. The time-dependent transient absorption data for $P(OH)_2TBC$ is shown in Figure 5. The inset is a representative decay profile. The time-dependent transient absorption for $P(OH)_2TBCS_n$ is shown in Figure 6, which indicates similar absorption features for both $P(OH)_2TBCS_n$ in DMSO and in Tris-HCl buffer. It was found that they have negative absorptions (bleaching) in the Q-band and Soret band regions. A broad positive absorption feature centered near 490 nm and another positive absorption on the red side of the bleaching band were also seen. Under the prevailing conditions of nitrogen saturation, the negative and positive absorption features decay and approach the pre-pulse baseline exponentially.

The kinetic time profiles changed upon addition of oxygen to the solutions. For both compounds $P(OH)_2TBC$ and $P(OH)_2TBCS_n$, the addition of O_2 enhanced the absorption decay at 490 nm and bleaching recovery processes. The absorption decay rate was related to the oxygen concentration with a first-order kinetic pattern (Figure 5). This indicates that the peak at 490 nm of $P(OH)_2TBC$ in DMSO is caused by T_1-T_n absorption. For $P(OH)_2TBCS_n$, the O_2 quenching effect is similar to $P(OH)_2TBC$, except for the maximum peak at 505 nm.

Table 2 shows the values of the triplet quantum yield (Φ_T) and triplet lifetime (τ_T) for $P(OH)_2TBC$ and $P(OH)_2TBCS_n$. The triplet lifetime of $P(OH)_2TBCS_n$ is 234 μs, which is longer than that of $P(OH)_2TBC$ ($\tau_T = 91$ μs). Similar to the case of ZnPc, the τ_T of sulfonated ZnPc (530 μs) is longer than that of ZnPc ($\tau_T = 350$ μs).[10] The triplet quantum yield of $P(OH)_2TBCS_n$ (0.64) is moderately higher in DMSO than in Tris-HCl buffer (0.35). It is believed that the strong polar solvent affect on the photosensitizing ability by elevating the energy gap between the singlet and triplet excited states, which results in a low intersystem crossing rate from the excited singlet state to the excited triplet state.[26]

An increase in the Φ_T values is complemented by a slight decrease in the Φ_F values. However, it is still surprising that sulfonation produces a longer triplet lifetime.

$P(OH)_2TBCS_n$ is of current interest as PDT agent, which means that photophysical and photochemical studies in aqueous media are essential. Therefore, we also measured the values of Φ_T and τ_T in Tris-HCl buffer. However, no remarkable change for either parameter was found. All these results suggest that $P(OH)_2TBCS_n$ is a very good candidate for PDT.

Singlet Oxygen Quantum Yields. Singlet oxygen is most commonly produced by photosensitization from the triplet state of photosensitizers. The singlet oxygen quantum yield (Φ_D) is an indication of the photosensitizer's ability to generate singlet oxygen. As a result, the singlet oxygen quantum yield (Φ_D) depends upon a number of factors such as the triplet quantum yield, triplet lifetime, and triplet energy of the photosensitizer. It is also determined by the ability of substituents to quench singlet oxygen and the efficiency of energy transfer from the excited triplet state to the ground state molecular oxygen.[27]

The singlet oxygen quantum yield of $P(OH)_2TBC$ is 0.21 in DMSO, which is lower than that of ZnPc in DMSO ($\Phi_\Delta = 0.67$). The triplet quantum yield of $P(OH)_2TBC$ is 0.44 in DMSO, which is close to that of ZnPc ($\Phi_T = 0.50$).[24] In fact, it is expected that the trend in variation of Φ_Δ should be parallel to be consistent with variations in their Φ_T and τ_T values. In the current work, the trend observed for the Φ_Δ variation is almost the same as that observed for Φ_T. Table 2 shows that $P(OH)_2TBCS_n$ has larger Φ_T and Φ_Δ values in DMSO than those values of $P(OH)_2TBC$ in DMSO. This shows that the sulfonation of $P(OH)_2TBC$ remarkably improved both the triplet quantum yield and the singlet oxygen quantum yield, while these values are slightly lower for $P(OH)_2TBCS_n$ in Tris-HCl buffer than in DMSO. Compared to $ZnPcS_n$ in DMSO ($\Phi_\Delta = 0.72$), the singlet oxygen quantum yield of $P(OH)_2TBCS_n$ in DMSO ($\Phi_\Delta = 0.88$) is higher, which may result from the monomeric

TABLE 1: Comparison of Maximum Emission Wavelength (λ_{em}), Fluorescence Quantum Yield (Φ_F), and Fluorescence Lifetimes (τ_F) of the Dihydroxy Phosphorus Tetrabenzotriazacorroles

compound	solvent	λ_{max} (Q-band)/nm	λ_{em}	Φ_F (S2)	Φ_F (S1, 418 nm)	Φ_F (S1, 614 nm)	τ_F/ns
$P(OH)_2TBC$	DMSO	656	667	0.0027	0.058	0.134	2.85
$P(OH)_2TBCS_n$	DMSO	662	667	0.017	0.014	0.048	2.28
	Tris-HCl	658	654	0.0096	0.011	0.019	1.35

TABLE 2: Photophysical Parameters of Derivatives

compound	solvent	Φ_Δ	Φ_T	$\tau_T/\mu s$	$\Delta\epsilon_T$ ($\times 10^3$)
$P(OH)_2TBC$	DMSO	0.21	0.44	91	0.508
$P(OH)_2TBCS_n$	DMSO	0.88	0.64	234	0.115
	Tris-HCl	0.81	0.35	198	0.213

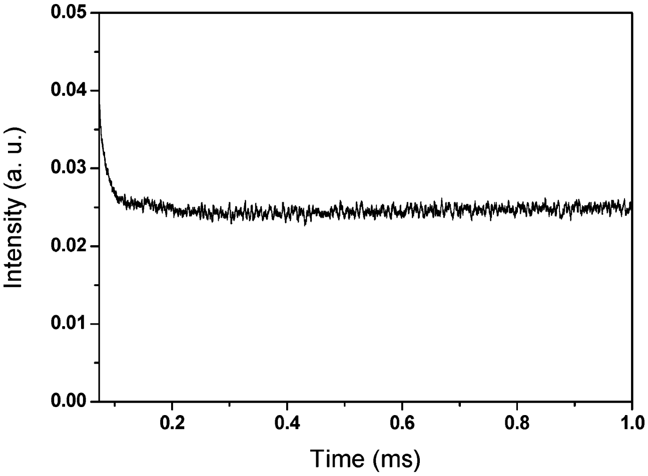


Figure 7. Typical singlet oxygen luminescence decay of $P(OH)_2TBCS_n$ in DMSO.

nature of the molecule. It is known that metal phthalocyanine complexes with a larger number of different substituted sulfonated derivatives are less aggregated than those containing fewer (or only one) isomers. This suggests that $P(OH)_2TBCS_n$ should be a better sensitizer than $P(OH)_2TBC$ in all applications involving singlet oxygen.

A typical singlet oxygen luminescence decay is shown in Figure 7. With the presence of an initial background signal, we found it difficult to measure the exact maximum emission intensity due to singlet oxygen luminescence. To minimize the measurement error, the experiment results were fitted with a monoexponential regression function. The fitted curve was then extrapolated to time = 0. The lifetime of singlet oxygen luminescence for $P(OH)_2TBCS_n$ in DMSO was found to be about 30 μs.

Conclusion

Sulfonated dihydroxy phosphorus(V) tetrabenzotriazacorrole was synthesized and characterized by MALDI-TOF, UV−vis, and IR, as well as its chemical reactivities. The photophysical properties of this novel macrocyclic compound were also investigated. $P(OH)_2TBCS_n$ was characterized by dual fluorescence. S_1-state fluorescence quantum yield in Tris-HCl buffer excited at 418 nm showed a slight decrease while the S_2 state showed a remarkable larger decrease.

Similar to ZnPc and $ZnPcS_n$, the triplet quantum yield of $P(OH)_2TBCS_n$ ($\Phi_T = 0.64$) is moderately high in DMSO and relatively low in Tris-HCl buffer ($\Phi_T = 0.35$).

Both Φ_T and τ_T values were found to increase after sulfonation. It is likely that the Type II photosensitization predominates in the DMSO solution.

One of the requirements in tumor phototherapy is to improve the comprehensive properties of the photosensitizers, in which the singlet oxygen photosensitizing efficiency is an important criterion. The comparative photophysical studies of $P(OH)_2TBCS_n$, $P(OH)_2TBC$, ZnPc, and $ZnPcS_n$ showed that $P(OH)_2TBCS_n$ is an efficient singlet oxygen-generating agent. The quantum yields are in the order of $P(OH)_2TBCS_n > ZnPcS_n > ZnPc > P(OH)_2TBC$. Further research on the $P(OH)_2TBCS_n$ photosensitizing properties in biological environment will provide in vivo data for PDT treatment.

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