Substitution effect of hydroxyl group on photophysical properties of tetraphenylporphyrin (H₂TPP) and germanium(IV) tetraphenylporphyrin dichloride (Ge(IV)TPPCl₂)

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Abstract

Photophysical properties of tetraphenylporphyrin (H₂TPP), tetra(p-hydroxyphenyl)porphyrin ((p-OH)₄TPPH₂), germanium(IV) tetraphenylporphyrin dichloride (GeTPPCl₂), and germanium(IV) tetra(p-hydroxyphenyl)porphyrin dichloride (Ge(p-OH)₄TPPCl₂) have been investigated to elucidate the effects of *para* OH substituents on the free-base and the metal-incorporated porphyrin π systems by steady-state and time-resolved spectroscopic methods. The observed photophysical properties were correlated with various molecular aspects, such as extended π-conjugation, nonplanar structural distortion, and central heavy atoms. Changes to steady-state absorption and fluorescence spectral characteristics of the OH-substituted porphyrin derivatives were attributed to the enhanced π-conjugation between phenyl ring and porphyrin π-electron system in the ground and the excited states. Such π-conjugation effects of the OH-substituted derivatives are greater when Ge(IV) is introduced into the core. The enhanced π-electron interaction of the OH-substituted derivatives in the excited state shortened the fluorescence lifetimes but increased the fluorescence quantum yields since the radiative rate was enhanced more than the fluorescence decay rate increased. The radiative decay rate of the OH-substituted Ge(IV) porphyrin is even greater due to more intensive π-conjugation of the metalloporphyrin in the excited state. The metal incorporation into the core also enhanced the nonradiative decay rates due to increased spin–orbit coupling and, consequently, reduced the fluorescence lifetimes and quantum yields. However, the spin–orbit coupling effect is not as large as expected. On the other hand, the OH group substitution enhanced only the nonradiative decay rate of the Ge(IV) metalloporphyrin and did not increase that of the free base porphyrin. This is ascribed to much more intensive π-conjugation of the Ge(IV) metalloporphyrin in the excited state which may induce excited state charge transfer and structural distortion. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Porphyrin derivatives play a central role in natural photosynthetic reactions [1] and artificial photochemical reactions [2]. Since photophysical properties of porphyrin are the essential prerequisites to understand these functionalities, they have been
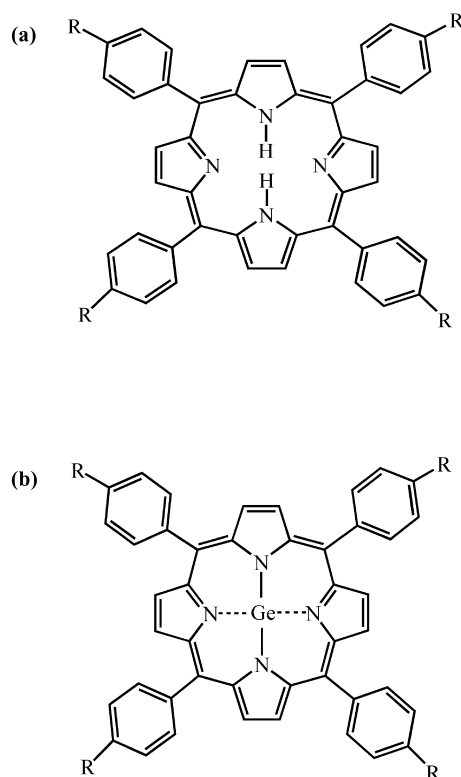
Fig. 1. Chemical structures (chloride ligands are not shown): (a) H₂TPP (R=H), (p-OH)₄TPPH₂ (R=OH), (b) GeTPPCl₂ (R=H), Ge(p-OH)₄TPPCl₂ (R=OH).

investigated extensively by various spectroscopic methods [3,4]. The photophysical properties of porphyrins are revealed to be affected by the molecular structural characteristics which depend on various substituents and central metals [5,6]. Therefore, porphyrins with different substituents and central metal atoms have been synthesized to elucidate the relationship between the excited state dynamics and the molecular structure. The tetraphenylporphyrin (TPP) series, investigated in this study, are typical synthetic porphyrins and are also important model compounds for the study of substituent effects on the central π system [7]. Although there is a large dihedral angle between the plane of the phenyl ring and the porphyrin π system of the TPP series, conjugation exists to some extent and is affected by the substituents on the phenyl ring [7]. Such properties induced by various substituents have also been precisely studied by the correlation with the structural

aspects of porphyrin ring, such as bond angles and bond strengths, obtained by X-ray crystallography, Raman spectroscopy, and computational chemistry [8–11].

In this study, *para*-OH substitution effects on the photophysical properties of tetraphenylporphyrin (H₂TPP), which is one of the TPP series, were investigated by steady-state and time-resolved spectroscopies. Also, the photophysical properties of germanium(IV) tetraphenylporphyrin dichloride (Ge(IV)TPPCl₂) and its hydroxyl derivative were studied to understand the OH-substituent effects in the presence of central Ge(IV) metal atom. These effects have rarely been studied.

2. Experimental

2.1. Materials

Ethanol (Merk, HPLC grade) was used as a solvent for all solutions without further purification. The studied *meso*-substituted porphyrins were tetraphenylporphyrin (H₂TPP), tetra(p-hydroxyphenyl)porphyrin ((p-OH)₄TPPH₂), germanium(IV) tetraphenylporphyrin dichloride (GeTPPCl₂), and germanium(IV) tetra(p-hydroxyphenyl)porphyrin dichloride (Ge(p-OH)₄ TPPCl₂), which were purchased from Midcentury (Illinois) and recrystallized. Their chemical structures are depicted in Fig. 1.

2.2. Spectroscopic measurements

Absorption spectra for dilute (~6.5 μM) solutions of all porphyrin derivatives were measured by a UV–VIS spectrophotometer (Shimadzu, UV-160A). All steady-state and time-resolved fluorescence experiments were performed at the excitation of the Q_{X10} bands for H₂TPP and (p-OH)₄TPPH₂ and of the Q(1,0) bands for GeTPPCl₂ and Ge(p-OH)₄TPPCl₂. The optical densities of all sample solutions at the excitation wavelengths were adjusted to be less than 0.1 for fluorescence measurements. Steady-state fluorescence spectra were obtained by using a fluorimeter (Hitach, F-4500). Wavelengths were calibrated by measuring the scattered intensity of the light source in the range 550–680 nm [12] and, also, by comparing the fluorescence spectrum of H₂TPP in benzene with the reported one in the wavelength region greater than
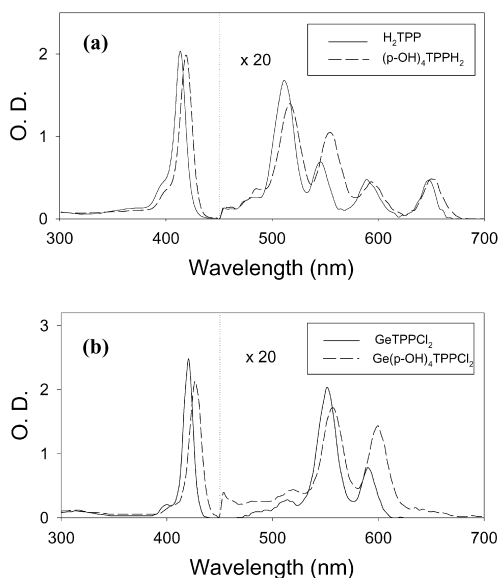
Fig. 2. Steady-state absorption spectra of (a) H_2TPP(—), (p-OH)$_4$TPPH$_2$(- - -), (b) GeTPPCl$_2$(—), Ge(p-OH)$_4$TPPCl$_2$(- - -).

680 nm [13]. Fluorescence quantum yields were calculated by integrating the corrected spectra and comparing them with the integrated spectral area of H_2TPP in ethanol. Fluorescence lifetimes were measured with a picosecond time-correlated single-photon counting (TCSPC) system. The picosecond dual-jet dye laser (Coherent 700) pumped by the mode-locked Ar ion laser (Coherent Innova 700) was used as a light source for the TCSPC system. Output beam power of the dye laser was 50 mW at a repetition rate of 3.8 MHz. The full width at half

maximum (FWHM) of the excitation pulse was 2 ps after cavity-dumping by the Coherent 7220 cavity dumper. The FWHM of the instrumental response function (IRF) was 72 ps. More detailed information on the TCSPC system was reported in a previous publication [14].

3. Results and discussion

3.1. Steady-state absorption

The absorption spectra of tetraphenylporphyrin derivatives are shown in Fig. 2. The wavelengths of the absorption peaks and their molar extinction coefficients are listed in Table 1. The number of Q bands in the absorption spectra of Ge(IV) porphyrins is less than those of free-base porphyrins. The absorption spectra of Ge(IV) porphyrins display a single Q band absorption which is a combination of the Q_X and Q_Y bands due to the D_{4h} symmetry of Ge(IV) porphyrins instead of the D_{2h} symmetry of free base porphyrins [15]. The absorption bands of (p-OH)$_4$TPPH$_2$ were red-shifted compared with those of H_2TPP. Ge(p-OH)$_4$TPPCl$_2$ also showed red-shifted absorption relative to GeTPPCl$_2$. Such red shifts originate from the reduction of the band gap energy, which is caused by a higher HOMO energy level. According to Gouterman's four orbital model [16], the substituents located in the *meso* position are known to affect the energy of the a_{2u} HOMO orbital and electron-donating substituents in the *para* position cause an increase in the a_{2u} orbital electron density, which

Table 1
Spectral properties of steady-state absorption spectra

Compound	Soret		Q_{Y10}		Q_{Y00}		Q_{X10}		Q_{X00}	
	λ[a]	ε[b]	λ	ε	λ	ε	λ	ε	λ	ε
H_2TPP	414	317,846	512	12,923	545	3,925	589	3,692	648	3538
(p-OH)$_4$TPPH$_2$	419	306,923	517	10,769	554	8154	594	3385	651	3692
			Q(2,0)		Q(1,0)		Q(0,0)			
	λ	ε	λ	ε	λ	ε	λ	ε		
GeTPPCl$_2$	422	379,846	514	2,154	553	15,538	593	6,000		
Ge(p-OH)$_4$TPPCl$_2$	427	324,462	520	3,385	557	13,385	600	10,923		

[a] Wavelength of absorption maxima is in nm.
[b] Molar extinction coefficient is in M^{-1} cm^{-1}.

Table 2
Ratio of molar absorption coefficients of Q bands

Compound	Q_{X00}/Q_{X10}	Q_{Y00}/Q_{Y10}
H_2TPP	0.96	0.42
$(p\text{-OH})_4TPPH_2$	1.1	0.76
	Q(0,0)/Q(1,0)	
$GeTPPCl_2$	0.39	
$Ge(p\text{-OH})_4TPPCl_2$	0.82	

Table 3
Steady-state fluorescence spectral properties

Compound	Q_{X00}^* λ [a]	Q_{X01}^* λ	Stokes shift $\Delta\nu$ [b]
H_2TPP	652	715	94.7
$(p\text{-OH})_4TPPH_2$	659	721	187
	$Q^*(0,0)$ λ	$Q^*(0,1)$ λ	$\Delta\nu$
$GeTPPCl_2$	599	653	169
$Ge(p\text{-OH})_4TPPCl_2$	613	664	353

[a] Fluorescence maxima is in nm.
[b] Stokes shift is in cm^{-1}.

consequently causes a_{2u} HOMO to shift to higher energy and induces a reduction of the band gap [7]. Such an interpretation can also be applied to the red-shifted absorptions of $(p\text{-OH})_4TPPH_2$ and $Ge(p\text{-OH})_4TPPCl_2$ relative to the parent molecules.

The absorption coefficient (ε) ratios of the Q band absorptions for the porphyrin derivatives are listed in Table 2. The ε ratios of Q_{X00}/Q_{X10} and Q_{Y00}/Q_{Y10} of $(p\text{-OH})_4TPPH_2$ showed larger values than those of H_2TPP. The ε ratio of Q(0,0)/Q(1,0) of $Ge(p\text{-OH})_4TPPCl_2$ is even larger than that of $GeTPPCl_2$. As the electron donating substituents in the *para*

Fig. 3. Steady-state fluorescence spectra of (a) H_2TPP(—), $(p\text{-OH})_4TPPH_2$(- - -), (b) $GeTPPCl_2$(—), $Ge(p\text{-OH})_4TPPCl_2$(- - -).

position of phenyl ring increase the electron density of a_{2u} orbital through π conjugation and also raise the energy of a_{2u} orbital, the degeneracy of the a_{1u} and a_{2u} orbitals is removed [7]. It induces the intense Q band due to the enhanced transition probability of the forbidden Q band absorption and such an effect is larger for the Q(0,0) band, which results in the increased ε ratios of Q(0,0)/Q(1,0) [17]. Therefore, the enhanced ε ratios of $(p\text{-OH})_4TPPH_2$ and $Ge(p\text{-OH})_4TPPCl_2$ imply that the stronger π-interaction between the prophyrin π-system and the phenyl ring in the ground state is induced by the *para* hydroxyl substituent. The larger ε ratio of $Ge(p\text{-OH})_4TPPCl_2$ indicates more intensive π-conjugation in the Ge(IV) metalloporphyrin as previously reported with zinc tetraarylporphyrins [16].

3.2. Fluorescence spectra

The steady-state fluorescence spectra of H_2TPP, $(p\text{-OH})_4TPPH_2$, $GeTPPCl_2$, and $Ge(p\text{-OH})_4TPPCl_2$ were normalized at their Q^* maximum and presented in Fig. 3. All spectra show the typical Q^* emission bands of porphyrins. Fluorescence maxima wavelengths and Stokes shifts are listed in Table 3. The following characteristic spectral changes are observed when the hydroxyl groups are substituted in the *para* positions of the phenyl rings of H_2TPP and $GeTPPCl_2$: (1) both Q^* emission bands of $(p\text{-OH})_4TPPH_2$ and $Ge(p\text{-OH})_4TPPCl_2$ are shifted to longer wavelengths. (2) Band broadenings of both Q^* bands are observed in the fluorescence spectra of $(p\text{-OH})_4TPPH_2$ and $Ge(p\text{-OH})_4TPPCl_2$. (3) The Stokes shifts increase
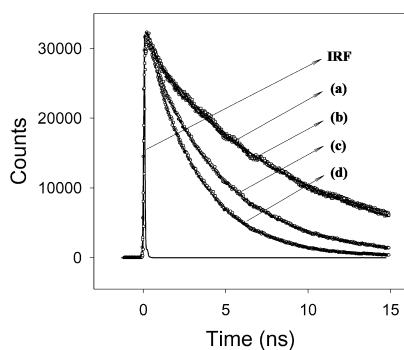
Fig. 4. Fluorescence decay signals and fitted lines of (a) H_2TPP, (b) $(p\text{-OH})_4$TPPH$_2$, (c) GeTPPCl$_2$, (d) Ge$(p\text{-OH})_4$TPPCl$_2$. The detection wavelengths are at the Q* (0,0) band maximum of the respective porphyrins. IRF indicates instrumental response function.

when the hydroxyl groups are substituted. Such spectral characteristics of these porphyrins are similar to those of porphyrins which have the approximate reverse mirror-image symmetry between the absorption and fluorescence spectra [13]. As suggested for such reverse mirror-image symmetry systems, the spectral changes of the *para* hydroxyl TPP derivatives can be attributed to the geometrical changes of the relaxed S$_1$ state, such as the reduction of the dihedral angles between the porphyrin ring system and the phenyl ring, which permits the greater π-conjugation in the excited state than in the ground state [13].

3.3. Photophysical properties

Fluorescence decay signals and fitted lines are presented in Fig. 4. The excited state lifetimes of all porphyrins were obtained by an iterative non-linear deconvolution fitting procedure and all decay data were well fitted with a single exponential. The fitted fluorescence lifetimes (τ_f) in Table 4 decrease in the order of H_2TPP $>$ $(p\text{-OH})_4$TPPH$_2$ $>$ GeTPPCl$_2$ $>$ Ge$(p\text{-OH})_4$TPPCl$_2$. The fluorescence quantum yields

Table 4
Photophysical properties of singlet excited state

Compound	τ_f (ns)	Φ_f	k_r (10^7 s^{-1})	k_{nr} (10^7 s^{-1})
H_2TPP	9.2	0.091	0.99	9.9
$(p\text{-OH})_4$TPPH$_2$	8.9	0.12	1.4	9.9
GeTPPCl$_2$	4.7	0.081	1.7	20
Ge$(p\text{-OH})_4$TPPCl$_2$	3.2	0.090	2.8	28

(Φ_f) in Table 4 are enhanced when the electron-donating hydroxyl groups are added. Other electron-donating groups, such as CH$_3$ and OCH$_3$ were also reported to decrease the fluorescence lifetimes and increase the fluorescence quantum yields when they were substituted at the *para* position of the phenyl ring [18]. When the Ge(IV) metal ion is incorporated into the core, both the fluorescence lifetime and quantum yield are reduced. These changes of photophysical properties can be explained in terms of the radiative (k_r) and the nonradiative (k_{nr}) decay rates of the S$_1$ state. The values of k_r and k_{nr} were estimated by the following equations [19]:

$$k_r = \Phi_f/\tau_f \qquad (1)$$

$$k_{nr} = k_f - k_r \qquad (2)$$

where $k_f (= 1/\tau_f)$ is the fluorescence decay rate. The values of k_r and k_{nr} in Table 4 indicate that the hydroxyl group substitution enhances the k_r values and the extent of enhancement is greater for the Ge(IV) porphyrin. Ge(IV) metal incorporation into the core also enhances the nonradiative decay rates of both H_2TPP and $(p\text{-OH})_4$TPPH$_2$. On the other hand, the k_{nr} value of the free-base porphyrin is not affected by the OH group substitution. However, the k_{nr} value of Ge$(p\text{-OH})_4$TPPCl$_2$ is somewhat increased compared with that of GeTPPCl$_2$. When the OH groups are substituted, the fluorescence lifetimes are decreased and, however, the fluorescence quantum yields are increased due to the larger enhancement of the radiative decay rate than the enhancement of the fluorescence decay rate. On the other hand, when the metal atom is incorporated, both the fluorescence lifetimes and quantum yields are reduced due to the more enhanced nonradiative decay rates.

The increased radiative decay rates caused by the OH group substitution appear to correlate with the more enhanced extent of π conjugation in the excited state than in the ground state, and such a correlation with the k_r value agrees with the suggestions by Fonda et al. [13]. Also, the even more enhanced k_r value of the OH-substituted Ge(IV) porphyrin in the presence of central Ge(IV) metal implies that the phenyl rings are more intensively conjugated with the porphyrin π system due to the effect of the central metal [16]. The nonradiative decay rates increase in the order of H_2TPP $\approx$ $(p\text{-OH})_4$TPPH$_2$ $<$ GeTPPCl$_2$ $<$ Ge$(p\text{-OH})_4$TPPCl$_2$. Such increase of k_{nr}

value can be governed by the following factors: (1) spin–orbit coupling enhancement caused by the heavy atom effect, (2) charge transfer in the excited state, and (3) structural distortion in the excited state compared with the ground state. Firstly, the nonradiative decays of Ge(IV) porphyrins are enhanced due to the larger spin–orbit coupling caused by the heavy atoms when the Ge(IV) ion is incorporated into the core and the chloride ions are ligated. In order to observe the effect of the central heavy atom on the nonradiative decay rate, we compared the k_r and k_{nr} values of GeTPPCl$_2$ (in this study) with those of ZnTPP (in cyclohexane) since Zn(II) ion also has the same d^{10} electronic configuration as the Ge(IV) ion. For ZnTPP, k_r is $1.7 \times 10^7 \text{ s}^{-1}$ and k_{nr} is $5.2 \times 10^8 \text{ s}^{-1}$ [20]. The k_r value of ZnTPP is same as that of GeTPPCl$_2$. On the other hand, the k_{nr} value of GeTPPCl$_2$ was expected to be larger than that of ZnTPP since the spin–orbit coupling constant of Ge ($\zeta_{l,Ge} = 800 \text{ cm}^{-1}$) [21] is greater than that of Zn ($\zeta_{l,Zn} = 390 \text{ cm}^{-1}$) [21] and, also, some additional spin–orbit coupling enhancement was reported to be caused by the ligand chloride ions [15]. However, the k_{nr} value of ZnTPP is much greater than that of GeTPPCl$_2$. The larger k_{nr} value of ZnTPP is considered to be due to the structural distortion of the porphyrin macrocycle induced by the larger size of the Zn^{2+} ion (ionic radii; Zn^{2+}: 74 pm, Ge^{4+}: 53 pm) [22–25]. Secondly, charge transfer in the excited state of the porphyrin OH derivatives may affect the nonradiative decay rate. If excited state charge transfer occurs in the investigated TPP derivatives, the k_{nr} value is expected to increase as suggested by Harriman et al. [18]. However, the k_{nr} values of both H$_2$TPP and (p-OH)$_4$TPPH$_2$ are nearly same. It indicates that the excited state charge transfer between the porphyrin π system and the phenyl ring of (p-OH)$_4$TPPH$_2$ is less probable. On the other hand, for Ge(p-OH)$_4$TPPCl$_2$, the k_{nr} value was somewhat increased. This increment may be partly caused by the excited state charge transfer since the reduced dihedral angle between porphyrin π^* system and phenyl ring in the excited state of Ge(p-OH)$_4$TPPCl$_2$ causes more favorable electronic conjugation which may enhance the excited state charge separation by the resulting orbital overlap [26]. Thirdly, structural changes of the porphyrin ring in the excited state have been reported to enhance the k_{nr} values due to the

enhanced Franck–Condon factor for internal conversion [24]. According to the prediction by Fonda et al. [13], the S$_0$ states of the investigated TPP derivatives are considered to be nearly planar as are other *meso*-substituted tetraarylporphyrins because of their similar spectral characteristics with the molecules having approximate reverse mirror-image symmetry between the absorption and fluorescence spectra. However, in the excited state, the structural change, such as a structural distortion, can be induced by the *p*-OH substitution to the TPP derivatives. To illustrate the possibility of a structural distortion in the excited state induced by the *p*-OH substitution, the k_{nr} values of H$_2$TPP and (p-OH)$_4$TPPH$_2$ were compared. As shown in Table 4, there are no significant changes in the k_{nr} values, which implies that there is no structural difference between H$_2$TPP and (p-OH)$_4$TPPH$_2$ in the excited state. However, the k_{nr} value of Ge(p-OH)$_4$TPPCl$_2$ is larger than that of GeTPPCl$_2$. For this Ge(IV) porphyrin, more intensively extended π-conjugation in the excited state is considered to occur when the hydroxyl group is substituted. Such intensively extended π-conjugation was reported to cause the reduction of the dihedral angle between the TPP porphyrin π system and the phenyl ring [13]. Such a smaller dihedral angle was predicted to accompany the structural distortion from the ring planarity of porphyrin and this was attributed to more free rotation of the substituents on the periphery of the porphyrin macrocycle when the porphyrin ring is nonplanar [13]. Therefore, it can be suggested that the structural distortion in the excited state caused by the intensively extended π-conjugation induces the larger k_{nr} value for this Ge(IV) porphyrin system.

4. Conclusion

The *para* OH substituent effects on the photophysical properties of H$_2$TPP and Ge(IV)TPPCl$_2$ were investigated by steady-state and time-resolved spectroscopic methods. The steady-state absorption is red shifted and the ε ratios of Q(0,0)/Q(0,1) are enhanced for the OH-substituted porphyrin derivatives. This indicates that the electron-donating *para* OH group increases the efficiency of π-conjugation between phenyl ring and porphyrin π-system in the ground state. The *para*-OH substitutions also induce

characteristic changes in fluorescence, such as a red shift, band broadening, and a larger Stokes shift. Such changes imply that the π-conjugation is more enhanced in the excited state, accompanying the reduced dihedral angle between porphyrin π system and phenyl ring for the *para*-OH substituted porphyrins. Such extent of π-conjugation becomes even greater in both the ground and the excited states as the Ge(IV) metal is incorporated into the core.

Although the fluorescence lifetimes decrease, the fluorescence quantum yields increase due to the enhanced radiative decay rates caused by the π-electron conjugation in the excited state when the OH groups are substituted. The radiative decay rate of the OH-substituted porphyrin is more largely enhanced by the metal introduction. However, when the Ge(IV) metal atom is incorporated into the core, both the fluorescence lifetimes and quantum yields are reduced due to the enhanced nonradiative decay rates. Such changes in the nonradiative decay rates are explained by the possible factors of heavy atom effect, excited state charge transfer, and structural distortion in the excited state. The metal incorporation enhances the nonradiative decay rates due to the increase in spin−orbit coupling. However, this effect is not great as expected. The OH group substitution also increases the k_{nr} value of the Ge(IV) metalloporphyrin but does not enhance that of the free base porphyrin. This is attributed to more intensive π-conjugation of the Ge(IV) metalloporphyrin in the excited state, which may induce the excited state charge transfer and the structural distortion more efficiently.

Acknowledgements

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