# Steady-State and Time-Resolved Photophysical Studies on a Series of Gallium Phthalocyanine Monomers and Dimers

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Intramolecular interaction between coplanar-stacked phthalocyanine (Pc) and porphyrin molecules plays an important role in the energy- and electron-transfer process. A series of results from different photophysical experiments on gallium phthalocyanine compounds are initially described. The PcGa dimer with a direct gallium–gallium bond, i.e. [$t$Bu$_4$PcGa]$_2$·2dioxane, may exist in two different conformations: one in which the two phthalocyanines are poorly interacting and the other in which they are very close and strongly interacting. In the former, the emission lifetime is quite close to that of the monomer model compounds; in the latter, it is much shorter probably due to different radiative and nonradiative deactivation constants from those of the monomers. Because no significant difference between the absorption spectra of the monomer and dimer was observed in the photophysical experiments, implying that no ground-state interaction can be assessed, the results regarding triplet excited state lifetimes of [$t$Bu$_4$PcGa]$_2$·2dioxane can be attributed to strong intramolecular interactions existing only in the excited state.


## Introduction

Phthalocyanines (Pcs) offer a high structural flexibility, which facilitates the tailoring of their physical, optoelectronic and chemical parameters over a very broad range. The exploitation of the chemical reactivity of the M–Cl (M = Ga, In) bond allows the preparation of a series of highly soluble, axially substituted and bridged phthalocyanine complexes.[1] Very recently, we have prepared a new dimeric gallium phthalocyanine complex with a direct gallium–gallium bond, i.e. [$t$Bu$_4$PcGa]$_2$·2dioxane.[2] The Extended X-ray Absorption Fine Structure (EXAFS)-determined gallium–gallium bond length of this compound was found to be 2.46 Å, which is in good agreement with the reported values in the literature.[3–6] The gallium center is located 0.45 Å out of the plane, which is quite close to the reported out-of-plane value of 0.439 Å in crystalline PcGaCl.[7] Z-scan experiments show that dimerization of $t$Bu$_4$PcGaCl is clearly a viable method of tuning saturation energy density ($F_{Sat}$) of the material. As a result, [$t$Bu$_4$PcGa]$_2$·2dioxane exhibits a significantly lower $F_{Sat}$ than that of $t$Bu$_4$PcGaCl,[8] by approximately a factor of 3. This reduction in $F_{Sat}$ is coupled with a slight increase in the non-linear absorption coefficient ($\beta_I$) at low incident intensity and with approximately equivalent $\beta_I$s at higher intensities. The ratio of the excited- and ground-state absorption cross sections ($\kappa$) is reduced by approximately 22% after dimerization of $t$Bu$_4$PcGaCl to [$t$Bu$_4$PcGa]$_2$·2dioxane. However, this can probably be mostly attributed to the increase in the linear absorption coefficient ($\alpha_0$) by approximately 18% over the same molecular modification.[2]

It has long been recognized that the intramolecular interaction between coplanar-stacked phthalocyanine and porphyrin molecules plays an important role in the energy- and electron-transfer process.[9] Studies on the facial interaction between the phthalocyanine macrocycles are thus very interesting. In the case of the μ-oxo-bridged silicon phthalocyanine dimer (PcSi–O–SiPc), strong intramolecular interaction between PcSi macrocycles was observed by us previously.[10] In contrast to this complex, μ-oxo-bridged gallium and indium phthalocyanine dimers ([$t$Bu$_4$PcGa]$_2$O and [$t$Bu$_4$PcIn]$_2$O)[11] exhibit no apparent intramolecular interaction. The inter-Pc distances in [$t$Bu$_4$PcGa]$_2$O and [$t$Bu$_4$PcIn]$_2$O are 3.72 and 4.32 Å, respectively.[1d] In this contribution, we report on the steady-state and time-resolved photophysical properties of [$t$Bu$_4$PcGa]$_2$·2dioxane (**5**). The photophysical data of the other four gallium phthalocyanine compounds, $t$Bu$_4$PcGaCl (**1**);[8] $t$Bu$_4$PcGa($p$-CPO) (**2**, $p$-CPO = $p$-chlorophenoxy);[12] {[$t$Bu$_4$Pc Ga]$_2$·SDPO}(**3**, SDPO = 4,4′-sulfonyl-diphenoxy)[12] and [$t$Bu$_4$PcGa]$_2$O (**4**),[11] are also given in this paper for comparison. Figure 1

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shows the molecular structures of these five phthalocyanine compounds.

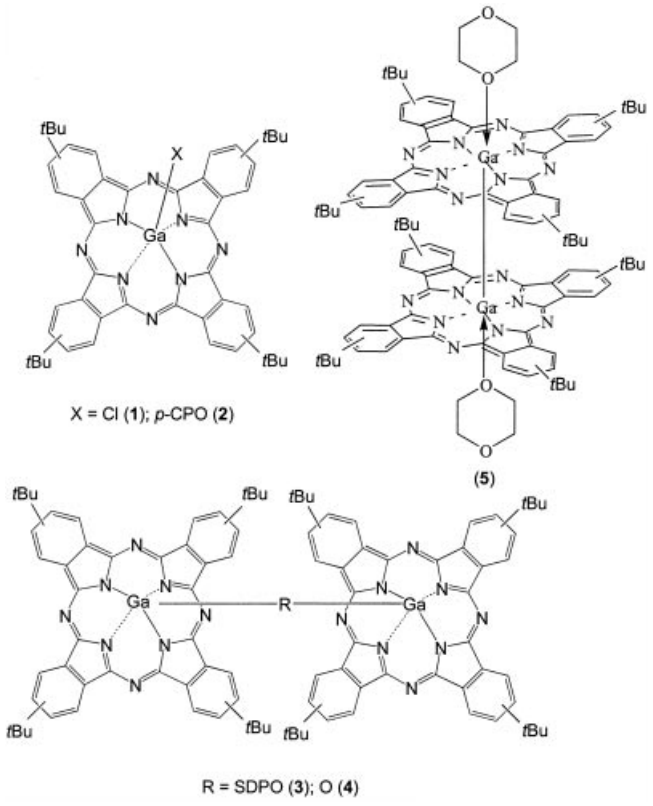


Figure 1. Molecular structures of **1**–**5**.

## Results and Discussion

Axial substitution in Pc complexes favorably influences non-linear optical absorption towards the presence of a dipole moment perpendicular to the macrocycle in the axially substituted phthalocyanines, but does not generally affect the linear optical properties of phthalocyanines; the Q- and B-bands in the UV/Vis absorption spectra are shifted only slightly by a few nanometers on exchanging the axial ligands on the metal.[1] Likewise, dimerization of $t$Bu$_4$PcGaCl does not considerably affect the spectral profile, as shown in Figure 2. The Q-band maxima of **1** and **5** are located at 695 and 693 nm, respectively. The extent of electronic conjugation in both compounds **1** and **5** is virtually identical, since compound **5** has a gallium–gallium single bond of σ-type lacking delocalized electrons. As expected, the main differences between the spectral features of these two complexes are related to the change in the extinction coefficient value because of the different number of absorbing Pc rings per molecular unit in the monomer relative to the gallium–gallium bridged dimer. Upon excitation with a laser light of 355 nm, both compounds display a Stokes shift of the emission peak with respect to the location of the Q-band absorption. Although dimerization affects both the UV/Visible and emission spectra differently, it influences the emission energy more strongly, since the extent of the Stokes shift is larger for the monomer than for the [$t$Bu$_4$PcGa]$_2$·2dioxane dimer. Maximum emission peaks for **1** and **5** are found at 713 and 700 nm, respectively. Such a difference could be assigned to the more rigid structure of the dimer than of the monomer. This means that the dimer relaxes radiatively from the electronic excited state π* in a higher vibrational level.[13–15] Similarly, the photoluminescence spectra of **2**–**4** also show the mirror images of the corresponding UV/Vis absorption spectra with small Stokes shift, suggesting that the structural change between the ground state and excited singlet state is small.

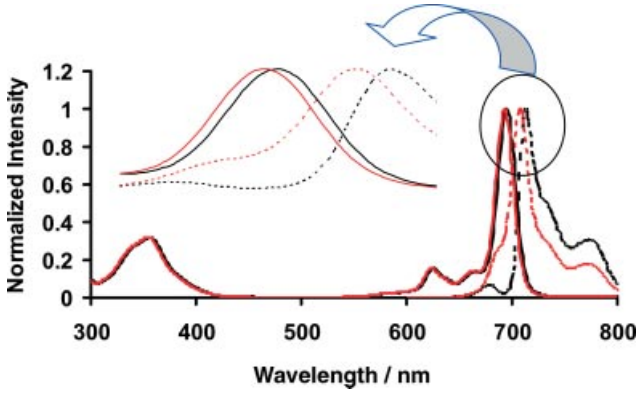


Figure 2. UV/Vis absorption spectra (solid line) and photoluminescence spectra (dashed line, $\lambda_{ex}$ = 355 nm) of **1** (black line) and **5** (red line) in dilute chloroform solutions.

The fluorescence-decay time profiles of **1**–**4** display a single exponential decay yielding long fluorescence lifetimes ($\tau_{fluo}$) in the range of 2570–3570 ps (see Table 1). On the contrary, the fluorescence-decay time profile of **5** was curve-fitted with two exponential functions, as shown in Figure 3, giving two fluorescence lifetimes [$\tau_{f1}$ = 180 ps (42%) and $\tau_{f2}$ = 2480 ps (58%)]. The $\tau_{f1}$ value is much shorter than those of **1**–**4**, while the $\tau_{f2}$ value is slightly smaller than those of the gallium phthalocyanine compounds mentioned above. This experimental finding suggests that the dimer may exist in two different conformations: one in which the two phthalocyanines are poorly interacting and the other in which they are very close and strongly interacting. In the former, the emission lifetime is quite close to that of the monomer model compounds; in the latter, it is much shorter probably due to different radiative and nonradiative deactivation constants from those of the monomer compounds.

Figure 4 shows that the nanosecond transient absorption spectra ($\lambda_{ex}$ = 355 nm) obtained in argon-saturated anhydrous toluene for all gallium phthalocyanine compounds studied here are very similar. After the laser pulse irradiation, the transient absorption band appeared at 520 nm, accompanying the depletion at about 700 nm due to the transient consumption of ground state of **5**. On addition of $O_2$, the decay of the 520 nm band, which is attributed to the triplet-triplet (T-T) absorption of the Pc compounds[11,12] was accelerated, indicating that quenching by $O_2$ takes place from the triplet excited state of **5** to $O_2$, probably yielding $^1O_2$. The decay of the 520 nm band in the presence

  

Table 1. The photophysical data of the gallium phthalocyanine complexes **1**–**5**. $a_0$: linear absorption coefficient; $\tau_{fluo}$: fluorescence lifetime at emission peak wavelength, $\lambda_{ex}$ = 410 nm; $\tau_T$: triplet excited state lifetime, $\lambda_{ex}$ = 355 nm; $k_{O2}$: second-order rate constant.

| Samples | $a_0$ [$cm^{-1}$] | Stokes shift [$cm^{-1}$] | $\lambda_{max}{}^T$ [nm] | $\tau_{fluo}$ [ps] | $\tau_T$ [μs] | $k_{O2}$ [$M^{-1}s^{-1}$] |
|---|---|---|---|---|---|---|
| **1** | 1.10 | 185 | 520 | 2570 | 257 | $2.2\times10^9$ |
| **2** | 1.37 | 185 | 520 | 3110 | 324 | $2.0\times10^9$ |
| **3** | 3.13 | 406 | 520 | 3460 | 667 | $2.1\times10^9$ |
| **4** | 1.60 | 186 | 520 | 3570 | 357 | $2.0\times10^9$ |
| **5** | 1.30 | 144 | 520 | 180 (42%)<br>2480 (58%) | 2.1 (39%)<br>71 (61%) | $2.3\times10^9$ |

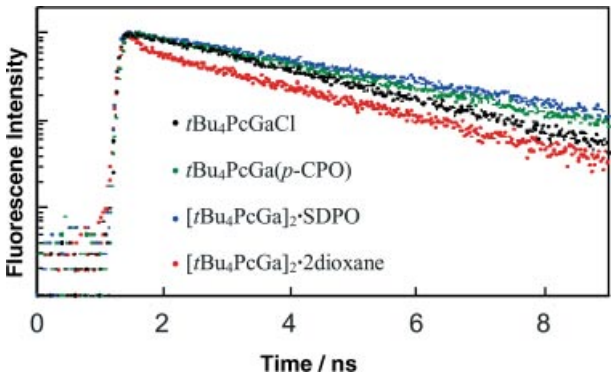


Figure 3. Time profiles of fluorescence intensities at 700–705 nm of **1**, **2**, **3** and **5** in deoxygenated anhydrous toluene by the excitation at 410 nm.

of $O_2$ obeys first-order kinetics, giving $k_{first\text{-}order}$, which increases with the concentration of added $O_2$; from the pseudo-first-order relation, the second-order rate constants for the reaction with $O_2$ ($k_{O2}$) were evaluated as listed in Table 1. Dimers and monomers have almost the same $k_{O2}$ values, but they are all less than the diffusion controlled limit ($k_{diff} = 1.1\times10^{10}$ $mol^{-1}dm^3s^{-1}$ in toluene).

In the absence of $O_2$, the decay rates depend on the laser power. Fast decay observed at high laser power is attributed to the T-T annihilation because of the collision between the highly concentrated triplet excited states. The time profile at 520 nm observed for $^3$(*t*Bu$_4$PcGa–X)* (X = Cl; *p*-CPO; O–*t*Bu$_4$PcGa; SDPO–*t*Bu$_4$PcGa) under the irradiation of low laser power reveals a single exponential decay giving the triplet excited state lifetimes ($\tau_T$) in the range of 257–667 μs. In contrast, two exponential-decay processes were observed for $^3$([*t*Bu$_4$PcGa]$_2$·2dioxane)* as shown in Figure 5. From the initial fast decay process, the triplet excited state lifetime ($\tau_{T1}$) of $^3$([*t*Bu$_4$PcGa]$_2$·2dioxane)* was evaluated to be 2.1 μs (39%), much shorter than the $\tau_T$ values of **1**–**4**. From the slow decay process of **5**, the second lifetime ($\tau_{T2}$) was found to be 71 μs (61%), which is still shorter than those of the other four gallium phthalocyanine compounds. It should be noted that in the photophysical characterization, no significant difference between the absorption spectra of the monomer and dimer was observed, suggesting that no ground-state interaction can be assessed. The results regarding triplet excited state lifetimes can thus be attributed to strong intramolecular interactions existing only in the excited state.

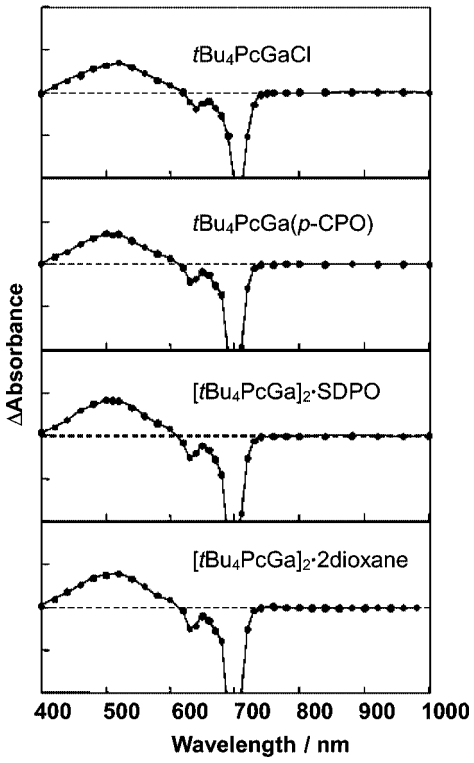


Figure 4. Nanosecond transient absorption spectra of **1**, **2**, **3** and **5** in deoxygenated anhydrous toluene by the excitation at 355 nm.

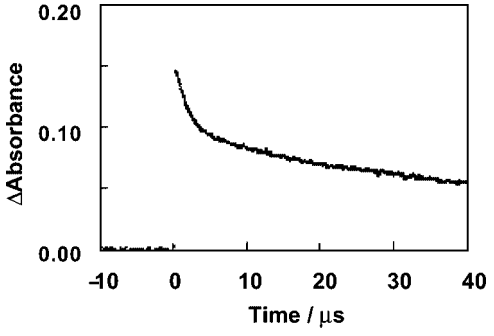


Figure 5. Absorption-time profile of 520 nm band of **5** in deoxygenated anhydrous toluene.

## Experimental Section

**Materials:** *t*Bu$_4$PcGaCl was obtained by the reaction of 4-*tert*-butylphthalonitrile with anhydrous $GaCl_3$ in doubly distilled, deoxygenated quinoline at 180 °C in the presence of catalytic amounts

  

of the non-nucleophilic base 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU).[8] $t$Bu$_4$PcGa($p$-CPO) was prepared by the reaction of $t$Bu$_4$PcGaCl with $p$-chlorophenol in anhydrous DMSO at 110 °C in the presence of $K_2CO_3$.[12] The [$t$Bu$_4$PcGa]$_2$O dimer was synthesized by the reaction of $t$Bu$_4$PcGaCl with excess concentrated $H_2SO_4$ at –20 °C.[11] The 4,4′-sulfonyldiphenoxy (SDPO)-axially bridged gallium phthalocyanine dimer {[$t$Bu$_4$PcGa]$_2$.SDPO} was synthesized by the reaction of $t$Bu$_4$PcGaCl with bis(4-hydroxyphenyl)sulfone in anhydrous DMSO at 110 °C in the presence of $K_2CO_3$.[12] [$t$Bu$_4$PcGa]$_2$.2dioxane was obtained in 83% yield by the reaction of soluble $t$Bu$_4$PcGaCl with activated magnesium in freshly dried THF, in the presence of 1,4-dioxane.[2]

**Photophysical Measurements:** UV/Vis absorption spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence spectra and lifetimes were measured by a single-photon counting method using an argon ion laser, a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3960, fwhm 150 fs) with a pulse selector (Spectra-Physics, 3980), a second harmonic generator (Spectra-Physics, GWU-23PS), and a streakscope (Hamamatsu Photonics, C4334–01). Each sample was excited in deoxygenated anhydrous toluene with 410 nm laser light. Nanosecond-transient absorption measurements were carried out using third harmonic generation (THG, 355 nm) of an Nd:YAG laser (Spectra-Physics, Quanta-Ray GCR-130, 6 ns FWHM) as an excitation source. For transient absorption spectra in the near-IR region (600–1400 nm), monitoring light from a pulsed Xe-lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834). For the visible region (400–1000 nm), a Si–PIN photodiode (Hamamatsu Phonics, S1722–02) was employed as a detector.

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