Synthesis and Optical Limiting Properties of Axially Bridged Phthalocyanines: [(tBu$_4$PcGa)$_2$O] and [(tBu$_4$PcIn)$_2$O]

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Abstract: Highly soluble [(tBu$_4$Pc-M)$_2$O] phthalocyanine dimers (M = Ga^{III} (**3**), In^{III} (**4**)) were prepared by the reaction of [tBu$_4$PcMCl] (M = Ga^{III} (**1**), In^{III} (**2**)) with excess of concentrated H$_2$SO$_4$ at $-20\,^{\circ}$C. The M–O–M linkages in **3** and **4** are not stable against concentrated H$_2$SO$_4$ at room temperature, 6 N HCl at reflux, or during isolation under column chromatographic conditions (e.g. silica gel/toluene). The stability of **3** in solution is considerably higher than that of **4**. The μ-oxo-bridged phthalocyanine dimers **3** and **4** have a more intense photoluminescence emission in the red region than the monomers **1** and **2**. The gallium phthalocyanines **1** and **3** have fluorescence lifetimes of a few nanoseconds, while those of the indium phthalocyanines **2** and **4** last for only several hundred picoseconds. Comparison of the fluorescence lifetimes of monomers **1** and **3** with dimers **2** and **4**, reveals that the dimers have longer lifetimes of the excited singlet states. The transient absorption spectrum is similar for all of the compounds, and the transient absorption band at about 520 nm, observed by nanosecond laser irradiation, can be assigned to the transition from the lowest triplet excited state to the upper triplet excited states (T–T absorption). The magnitude of the optical limiting exhibited by **1**, **3**, and **4** in toluene at 532 nm laser pulse irradiation is in the order: **3** > **4** > **1**. The values of the imaginary third-order nonlinear susceptibility Im{$\chi^{(3)}$} of the above compounds at 532 nm in toluene are also reported. These results demonstrate that these compounds are candidates for optical limiting applications.

Keywords: gallium · indium · nitrogen heterocycles · nonlinear optics · phthalocyanines

Introduction

Peripherally unsubstituted gallium phthalocyanines with an axial chloro, fluoro, or hydroxy ligand ([PcGaX], X = Cl, F, OH) were the first phthalocyanines (Pcs) to be investigated for their third-order ($\chi^{(3)}$) nonlinear behavior,[1] and nonlinear susceptibility values of the order of 10^{-11} esu were found. The μ-oxo-bridged dimer [(PcGa)$_2$O] has been described, and has been shown to exhibit good photoreceptor properties.[2] The next higher homologue of gallium, indium in its oxidation state of +3, can also be inserted easily into the Pc framework. As a result, chloroindium phthalocyanine ([PcInCl]) has found several applications in material science,[3] for nonlinear optical (NLO) materials, electrophotography, photovoltaic cells, or optical recording materials.

The disadvantage of peripherally unsubstituted Pcs is their poor solubility in organic solvents. To overcome this problem, a variety of substituents have been attached to the macrocycle in varying numbers and different substitution patterns.[4] Tetra(*tert*-butyl)-substituted Pc's and their metal complexes are the most frequently used when solubility is required.

While no peripherally substituted gallium phthalocyanines have been reported so far, we have recently synthesized a series of tetrasubstituted indium phthalocyanines, [R$_4$PcInX] (R = C$_5$H$_{11}$, tBu, X = Cl, Br, I, C$_6$H$_5$, C$_6$F$_5$, *m*- and *p*-CF$_3$C$_6$H$_4$, CH$_3$[5]), and others.[6] Octasubstituted indium phtahlocyanines, such as [R$_8$PcInX] with R = C$_5$H$_{11}$, X = Cl, C$_6$F$_5$, were also prepared.[5] As in the case of other substituted Pcs these indium phthalocyanines are also soluble in organic solvents of medium polarity.

Among the nonlinear optical applications of Pcs, optical limiting (OL) has been particularly promising.[7] Optical limiters are devices that strongly attenuate intense optical beams while exhibiting high transmittance for low-intensity ambient light levels. They are of significant interest for

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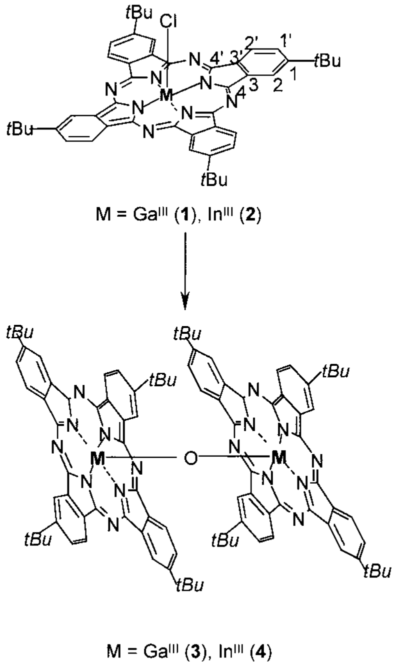
applications such as the protection of human eyes, optical elements, or optical sensors from intense laser pulses.[7, 8] Optical limiters usually rely on an effective third-order nonlinear response, such as nonlinear absorption or refraction. [Tetrakis(cumylphenoxy)phthalocyaninato]lead $[(CP)_4PcPb]$,[9] and tetra(*tert*-butyl)chloro(phthalocyaninato)indium(III) $[t\mathrm{Bu}_4\mathrm{PcInCl}]$,[8, 10] are very good materials for optical limiting. The systematic study of the effect of axial substitution on the optical properties of indium phthalocyanines[10] revealed that axially aryl-substituted $[t\mathrm{Bu}_4\mathrm{PcInX}]$ (e.g., $X = p\text{-}CF_3C_6H_4$) has a much lower threshold for optical limiting and a lower transmission at high fluences than $[t\mathrm{Bu}_4\mathrm{PcInCl}]$. Excitation of the (phthalocyaninato)indium complexes in the visible region initially gives an excited singlet state that crosses over into a triplet state with a quantum yield approaching unity and an intersystem crossing time of about 300 ps. The triplet state lifetime is much longer than 10 ns. This means that the nanosecond nonlinear absorption is dominated by the absorption from an orientationally averaged triplet state.[10]

Herein we report on the synthesis, structural characterization, and photophysical properties of the soluble μ-oxo dimers $[(t\mathrm{Bu}_4\mathrm{PcM})_2\mathrm{O}]$ (M = Ga (**3**) and In (**4**)). Compounds of this type may exhibit increased third-order nonlinearities in comparison with monomeric Pcs, owing to intramolecular interactions between the Pc rings.[11] Also, the optical limiting properties of **3** and **4** might be influenced by their dimeric structure. The μ-oxo axially bridged unsubstituted $[(PcGa)_2O]$[2] and [PcGa–O–AlPc][12] dimers have been briefly mentioned in the literature, however they have not been further characterized.



Scheme 1. Synthesis of μ-oxo-bridged gallium and indium phthalocyanine dimers: 1) 96% H_2SO_4, –20 °C, stirred for 2 h; 2) aqueous ammonia, reflux for 2 h, 3) wash with hot water, 68–72% yield.

Results and Discussion

The $[(t\mathrm{Bu}_4\mathrm{PcM})_2\mathrm{O}]$ dimers (M = Ga^{III} (**3**), In^{III} (**4**)) were prepared by the reaction of $[t\mathrm{Bu}_4\mathrm{PcMCl}]$[5, 6] (M = Ga^{III} (**1**), In^{III} (**2**), as mixtures of structural isomers) with an excess of concentrated H_2SO_4 at –20 °C (Scheme 1). Compounds **3** and **4** were found to be more soluble in many common organic solvents (even in methanol and acetone) than their starting compounds **1**[6] and **2**[5]. The enhanced solubility of **3** and **4**, compared with the chloro compounds **1** and **2**, shows that the tendency of phthalocyanines to form aggregates can be effectively suppressed by axial substitution.[5] Similar to the axially substituted indium(III) phthalocyanines,[5] the shape of the UV/Vis spectra of **3** and **4** is almost independent of the concentration of the solution. This is in contrast to $[t\mathrm{Bu}_4\mathrm{PcMCl}]$ (M = Ga^{III}, In^{III}) for which a concentration-dependent increase of the absorption on the red side of the Q-band indicates a larger degree of aggregation.[5, 6] Similar to the Al–O–Al linkage in $[(PcAl)_2O]$,[13] the M–O–M linkages in **3** and **4** can also be cleaved by concentrated H_2SO_4 at room temperature, by 6 N HCl at reflux, as well as under column chromatographic conditions (e.g. silica gel/toluene).

Figure 1 shows the FD-MS spectrum of $[(t\mathrm{Bu}_4\mathrm{PcGa})_2\mathrm{O}]$ (**3**), together with its simulated mass spectrum. The molecular peak appears at *m/z* 1628.1, with a pattern almost identical to that calculated for its respective isotopic composition. No fragmentation was detected. The molecular peak for $[(t\mathrm{Bu}_4\mathrm{PcIn})_2\mathrm{O}]$ (**4**) (*m/z* 1719) was only detected in the FAB-MS spectrum, accompanied by a number of fragment peaks centered at *m/z* 737.2 $[t\mathrm{Bu}_4\mathrm{PcH}^-]$, 849.9 $[t\mathrm{Bu}_4\mathrm{PcIn}^+]$, 1587.5 $[(t\mathrm{Bu}_4\mathrm{Pc})_2\mathrm{In}^+]$, and so on. The fragment peak at *m/z* 1587.5 appears in both the FAB-MS and FD-MS spectra of **4**, and can be attributed to $(t\mathrm{Bu}_4\mathrm{Pc})_2\mathrm{In}$ (*m/z* 1588.74).[14] These findings indicate that the In–O–In linkage in **4** is easily broken under the FAB and FD conditions to form $[t\mathrm{Bu}_4\mathrm{PcIn}]$ radical ions (*m/z* 849.9) and $t\mathrm{Bu}_4\mathrm{Pc}$ radical anions (*m/z* 737.2), which partially couple to give $[(t\mathrm{Bu}_4\mathrm{Pc})_2\mathrm{In}]$ (*m/z* 1587.5). The structural stability of **3** is evidently higher than that of **4**. This is also confirmed by the UV/Vis results (see below).

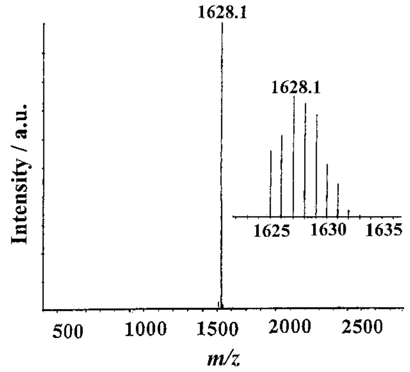


Figure 1. FD-MS spectrum of $[(t\mathrm{Bu}_4\mathrm{PcGa})_2\mathrm{O}]$ dimer. Simulated mass spectrum is shown in the inset.

The UV/Vis spectra of **3** and **4** in $CHCl_3$ have the pattern typical of metal Pcs. As reported earlier,[5, 6, 8] the influence of different axial substituents on the electronic structure of the macrocycles of indium(III) or gallium(III) phthalocyanines is small. When compared with the UV/Vis spectra of

[tBu$_4$PcMCl] (M = Ga, In), formation of the μ-oxo metallophthalocyanine dimers **3** and **4** only leads to a weak (1–2 nm) blue shift of the Q-band, which is attributed to exciton splitting in the dimer,[11] and to a red shift (1.5 nm) of the B-band. The red shift of the B-band is related to the interaction of the oxygen atom with the central metal, gallium or indium. The shapes of the UV/Vis spectra are solvent-dependent.[15] An additional absorption at 738 nm was observed for **3** in n-hexane. Comparison of the UV/Vis spectra of a thin film and dilute solution of **3** and **4** in $CHCl_3$ reveals that the absorption spectra of thin films of **3** and **4** are apparently broader. By comparing the thin film and dilute solution UV/Vis spectra of **1** or **2**, we observed that the position of the Q-band maximum is shifted to the red by about 2.5 nm for the former, and 9 nm for the latter. In the case of **3** and **4**, the same comparison shows that the position of the Q-band maximum is almost unchanged, which is consistent with relatively weak aggregation of **3** and **4** in solutions.

In the UV/Vis spectra of **3**, the intensities of the Q- and B-bands decreased gradually with increased exposure to daylight, this was simultaneously followed by a red shift of the Q-band and a blue-shift of the B-band. After exposure to daylight for 54 days, the peak maxima of the Q- and B-bands move to the red by $\Delta\lambda = 2$ nm, and to the blue by $\Delta\lambda = 3.5$ nm, respectively. When solutions of **3** and **4** in chloroform are exposed to daylight for 24 h, the B- and Q-bands of **4** dramatically decrease in intensity (Figure 2), while the absorption spectra of **3** are almost unchanged under the same conditions. These results further indicate that **3** is more stable than **4** in solution.

Comparison of the IR spectra of **3** and **4** and their starting materials **1** and **2** reveals that they are almost identical, the only difference being the disappearance of the M–Cl stretching vibration bands ($\nu_{Ga-Cl} = 351$ cm^{-1}, $\nu_{In-Cl} = 336$ cm^{-1}) in the IR spectra of both **3** and **4**.

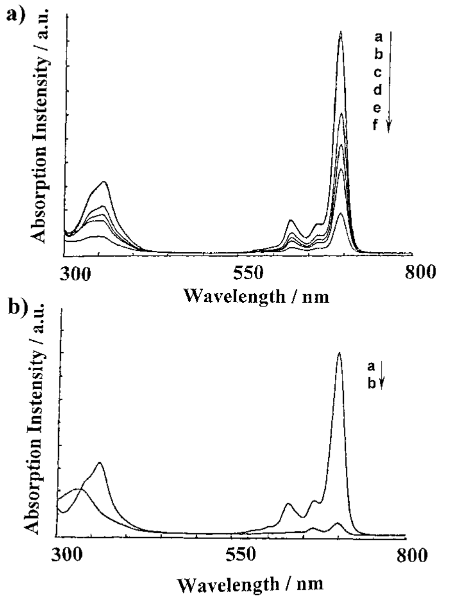


Figure 2. The changes of the UV-Vis absorption spectra of [(tBu$_4$PcGa)$_2$O] (**3**; A) and [(tBu$_4$PcIn)$_2$O] (**4**; B) in $CHCl_3$ before and after exposure to ambient light: a) before exposure, b) 24 h; c) 336 h, d) 720 h, e) 840 h, and f) 1296 *h*.

Because of the large diamagnetic ring current of the two macrocycles and the existence of structural isomers, the proton signals of **3** and **4** are broadened (the aromatic signals) and split (tBu signal) in the ^{1}H NMR spectra of **3** and **4.** In **3**, the aromatic protons (2,2′-H, see Scheme 1) appear at $\delta = 8.4–9.4$ ppm (multiplet), 1-H appears at $\delta = 7.8–8.3$ ppm (multiplet), and the tBu protons appear at $\delta = 1.7–1.9$ ppm. For **4**, the proton signals are very similar to those of **3**. The aromatic 2,2′-H protons give a multiplet between $\delta = 9.3–9.6$ ppm, 1-H protons appear at $\delta = 8.3$ ppm, and the protons of the tBu group are located at $\delta = 1.8–1.9$ ppm. The carbon signals of **3** and **4** in ^{13}C NMR spectra are rather similar to those of the corresponding starting materials[5, 6] and can easily be assigned to the appropriate carbon atoms in the macrocycle. Again, signals are broadened owing to the presence of structural isomers.

As described before, metallophthalocyanines are among the most effective optical limiters because they have low ground-state absorption in the spectral window between the intense B- and Q-bands, and strong excited-state absorption across the same region, as well as long excited-state lifetimes.[7, 10, 16] If the excited-state absorption cross-section exceeds that of the ground state, excited-state absorption from both singlet and triplet excited states will lead to reverse saturable absorption (RSA), which is the most important optical limiting mechanism.[16]

Photoluminescence (PL) is a powerful probe for the excited states of organic or polymeric compounds.[17–19] Fluorescence spectra and fluorescence lifetimes of peripherally unsubstituted chlorogallium(III) and chloroindium(III) phthalocyanines (i.e., [PcGaCl] and [PcInCl]) have previously been measured in 1-chloronaphthalene.[17] Figure 3 shows the fluorescence spectra of compounds **1**–**4** in toluene observed by excitation at 355 nm. It can be seen that the shape of the spectrum is similar for all species, and the maximum of the fluorecence bands of these compounds appears at 705, 710, 705, and 710 nm, respectively. The fluorescence bands of indium(III) phthalocyanines **2** and **4** are found to be shifted about 5 nm

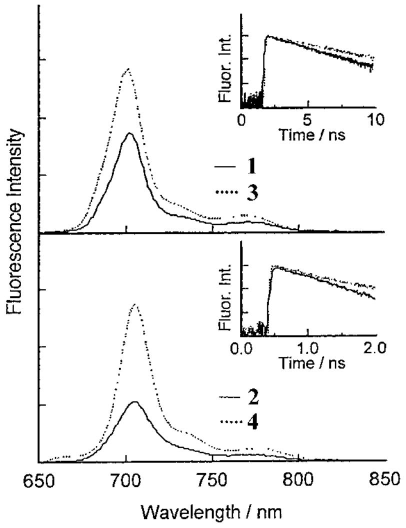


Figure 3. Fluorescence spectra of **1**–**4** in toluene. Absorption intensities were matched at the excitation wavelength (355 nm). Inset: Fluorescence decay profiles upon excitation with the 410 nm laser pulse.

towards longer wavelengths than those of gallium(III) phthalocyanines **1** and **3**, owing to the heavy atom effect. The μ-oxo-bridged phthalocyanines **3** and **4** have a more intense PL emission in the red region than the monomers **1** and **2**. The fluorescence decay characteristics were determined (Figure 3, inset), in which each time profile exhibits single exponential decay, from which the fluorescence lifetimes were determined. The fluorescence lifetimes (that is, the lowest excited single state lifetime, τ_F) of all samples are listed in Table 1. The gallium phthalocyanines **1** and **3** have lifetimes of a few nanoseconds (ns), while the lifetimes of the indium phthalocyanines **2** and **4** last for only several hundred picoseconds (ps). By comparing the fluorescence lifetimes of the monomers **1** and **2** with those of the dimers **3** and **4**, we found that the excited singlet states of the dimers have longer lifetimes.

Table 1. Properties of the excited states; fluorescence lifetimes (τ_f) and triplet-state lifetimes (τ_T), T–T annihilation rate constants (k_{TT}) and reaction rate constants with O_2 (k^T_{O2}) of gallium(III) and indium(III) phthalocyanine complexes **1**–**4**.[a]

Compounds	τ_f [ns] (λ_{fluo} [nm])	τ_T [μs] (λ_{TT} [nm])	k_{TT} [$mol^{-1} dm^3 s^{-1}$]	k^T_{O2} [$mol^{-1} dm^3 s^{-1}$]
1	2.57 (705)	159 (520)	4.5×10^8	2.2×10^9
3	3.57 (705)	270 (520)	3.3×10^8	2.0×10^9
2	0.47 (710)	46 (520)	6.5×10^8	2.2×10^9
4	0.64 (710)	42 (520)	5.0×10^8	2.1×10^9

[a] $\varepsilon = 10000\ mol^{-1} dm^3 cm^{-1}$.

To evaluate the contribution of the intersystem crossing process, nanosecond laser-flash photolysis studies[20–21] were carried out. Upon excitation with a nanosecond laser at 355 nm, transient absorption spectra of **1**–**4** in toluene were observed, and were similar for all samples. The transient absorption bands appear at about 520 nm, with the depletion of the ground state absorptions of phthalocyanine in the region 620–720 nm (Figure 4), and are easily quenched in the presence of a triplet energy quencher such as oxygen. The transient absorption band at about 520 nm can thus be assigned to the transition from the lowest triplet excited state to the upper triplet excited states (T–T absorption).[10, 20] The bimolecular quenching rates (k_{O_2}) of **1**–**4** were determined to be 2.2×10^9, 2.2×10^9, 2.0×10^9, and $2.1 \times 10^9\ dm^3 mol^{-1} s^{-1}$, respectively. From the laser power dependence of the decay rates of the T–T absorption, the intrinsic lifetimes of the triplet states (τ_T) were determined (Table 1).[20] The gallium phthalocyanine compounds **1** and **3** have a lifetime of a few hundred microseconds, while indium phthalocyanine compounds **2** and **4** exhibit shorter lifetimes. This trend is similar to that of the observed fluorescence lifetimes. The laser power dependence also gave the T–T annihilation rate constant (k_{TT}) as a ratio of the molar extinction coefficient (ε_T). On assuming the ε_T values as $10000\ mol^{-1} dm^3 cm^{-1}$, k_{TT} values on the order of $(3.3–6.5) \times 10^8 mol^{-1} dm^3 s^{-1}$ were calculated. Furthermore, interestingly for all samples, the triplet-state maximum occurs in the 400–610 nm region, which is located just inside the high-transmittance region between the intense Q- and B-bands in the UV/Vis spectra of all of the samples. This implies that this region is of particular interest for reverse-saturable absorption-based optical limiting[22–24] since it ensures that the absorption cross-section of the excited state always exceeds the ground-state absorption cross section.[25]

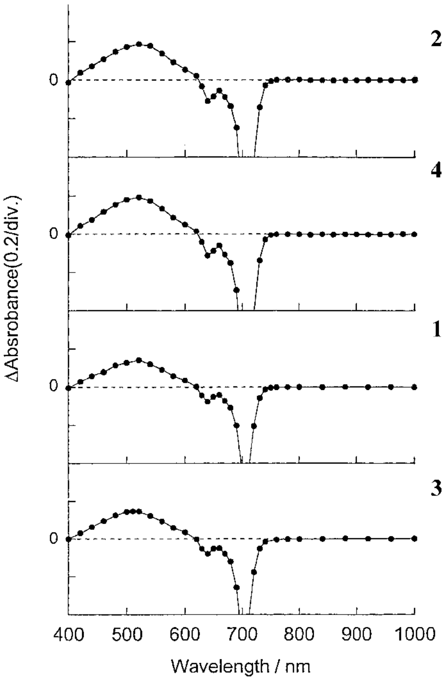


Figure 4. Transient absorption spectra of **1**–**4** in toluene 250 ns after the nanosecond laser irradiation at 355 nm laser light.

The open aperture Z-scan method[26] has been used to study imaginary third-order nonlinear optical processes in molecular materials. By moving the sample along the z axis through the focus, the intensity-dependent absorption can be measured as a change of the transmission through the sample using a detector in the far field.[27, 28] On approaching the focus the intensity increases by several orders of magnitude relative to the intensity away from focus, thus inducing nonlinear absorption in the sample. The apparatus is shown in Figure 5.

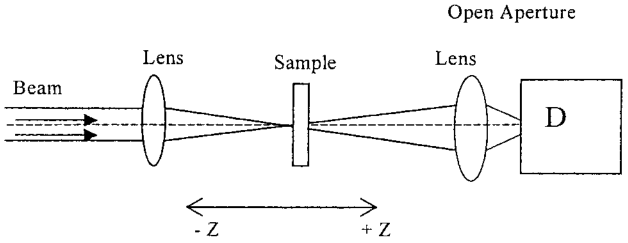


Figure 5. Schematic diagram of open aperture Z-scan experiment.

This allowed us to determine the magnitude of light energy dissipated in the sample. Absorption coefficients were calculated by fitting the following theory reported by Sheik-Bahae et al.[29] The normalized transmittance as a function of position z, $T_{Norm}(z)$ is given by Equation (1), where $q_0(z)$ is given by Equation (2), z_0 is the diffraction length of the beam,

$$T_{Norm}(z) = \sum_{i=0}^{\infty} \left(\frac{[-q_0(z,0)]^i}{(i+1)^{3/2}} \right) \quad (1)$$

$$q_0(z) = \frac{q_\infty}{1 + (z/z_0)^2} \quad (2)$$

and $q_{00} = \beta^{(3)} I_0 L_{\mathrm{eff}}$ where $L_{\mathrm{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$, $\beta^{(3)}$ is the third-order nonlinear absorption coefficient, I_0 is the intensity of the light at focus, and L_{eff} is known as the effective length of the sample, defined in terms of the linear absorption coefficient α_0, and the true optical path length through the sample, L.

The imaginary third-order susceptibility $\mathrm{Im}\{\chi^{(3)}\}$ and the second-order hyperpolarizability γ were used to quantify the nonlinear absorption.[7, 10, 30, 31] $\mathrm{Im}\{\chi^{(3)}\}$ is directly related to the third order absorption coefficient $\beta^{(3)}$ and is expressed as Equation (3), in which n_o is the linear refractive index, ε_o is the

$$\mathrm{Im}\{\chi^{(3)}\} = \frac{n_0^2 \varepsilon_0 c \lambda \beta^{(3)}}{2\pi} \tag{3}$$

permittivity of free space, c is the speed of light, and λ is the wavelength of the incident light. The relationship between $\mathrm{Im}\{\chi^{(3)}\}$ and γ is defined as Equation (4), where $f = (n_0{}^2 + 2)/3$ is the Lorentz local field factor, n_0 is the linear refractive index of the sample, c_{mol} is the molar concentration, and N_A is Avagados number.

$$\gamma = \frac{\mathrm{Im}\{\chi^{(3)}\}}{f^4 c_{\mathrm{mol}} N_A} \tag{4}$$

In the Z-scan experiments, a frequency-doubled Q-switched Nd-YAG laser was employed that produced 6 ns pulses at 532 nm wavelength. For each sample, a clear decrease of transmittance about the focus was observed, typical of an induced positive nonlinear absorption. Similar to **2**, reported previously,[5, 10] it can be seen that compounds **1**, **3**, and **4** also exhibit strong RSA on excitation at 532 nm.[5, 10, 27, 28]

The values of $\mathrm{Im}\{\chi^{(3)}\}$ at 532 nm for **1**, **2**, **3**, and **4** were determined to be about 1.00×10^{-11}, 1.56×10^{-11}, 1.27×10^{-11}, and 1.28×10^{-11} esu, respectively. The corresponding γ values for these compounds are approximately 0.71×10^{-32}, 1.15×10^{-32}, 1.72×10^{-32} and 1.83×10^{-32} esu, respectively. Comparison of **3** with **1** shows that the nonlinear response of **1** is clearly improved by dimerization (O-bridged).

The nonlinear transmission for **2** has recently been reported.[10] The onset of nonlinear absorption and optical limiting occurs at smaller incident fluences as the wavelength increases from 500 to 570 nm. The threshold for optical limiting, defined as the fluence at which the transmission falls to 0.5 of the initial transmission, varies by about an order of magnitude over this range of wavelengths. In the aryl-axially substituted (phthalocyaninato)indium complexes, such as [tBu$_4$PcIn(p-CF$_3$C$_6$H$_4$)] and [tBu$_4$PcIn(C$_6$F$_5$)], the nonlinear absorption begins at a lower fluence than for **1**. The normalized transmission as a function of pulse energy density was measured for **1**, **3**, and **4** at 532 nm in toluene. The results of these measurements are shown in Figure 6. The solid curves in Figure 6 are a theoretical fit, for which the energy density dependent absorption coefficient α is approximated using the phenomenological expression given in Equation (5) , where σ_0

$$\alpha(\alpha_0, F, F_{\mathrm{Sat}}, \kappa) = \frac{\alpha_0}{1 + \frac{F}{F_{\mathrm{Sat}}}} \left(1 + \frac{\sigma_{\mathrm{ex}}}{\sigma_0} \frac{F}{F_{\mathrm{Sat}}} \right) \tag{5}$$

and σ_{ex} are the ground state and excited-state cross sections. F_{Pulse} and F_{Sat} are the pulse energy density and the saturation energy density respectively. F_{Pulse} is defined as $E_{\mathrm{Pulse}}/(\pi\omega(z)^2)$, where E_{Pulse} is the energy per pulse and $\omega(z)$ is the radius of the propagating focused gaussian pulse as a function of position z (Figure 6). It should be noted that σ_0, σ_{ex}, and F_{Pulse} were treated as free parameters in the fit. The magnitude of the optical limiting exhibited by **1**–**4** is in the order: **4** > **3** > **2** > **1**. A definite quantitative measure of how well a material responds as an optical limiter is the ratio of the excited and ground state absorption cross-sections. This will be called the 'merit coefficient', and given the symbol κ [Eq. (6)]. The merit coefficients for **1**, **2**, **3**, and **4** are $k \approx 13.5$, 27.5, 11.3, and 12.4, respectively.

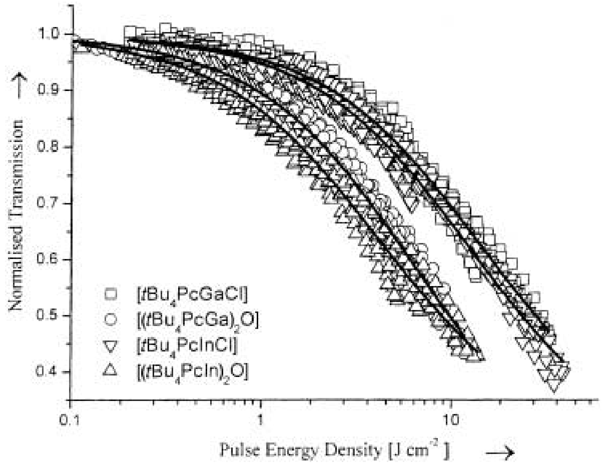


Figure 6. Normalized transmission of **1** (□), **2** (▽), **3** (○), and **4** (△) as a function of pulse energy density. Fitted with three-level model yielding results: 1) $k = 13.5$, 2) $k = 27.5$, 3) $k = 11.3$, and 4) $k = 12.4$, where k is the value of ration between the first absorption cross-section of the excited triplet state, and the ground state absorption cross-section.

$$\kappa = \frac{\sigma_{\mathrm{ex}}}{\sigma_0} \tag{6}$$

Conclusion

In conclusion, we have synthesized the highly soluble μ-oxo-bridged gallium(III) and indium(III) phthalocyanine dimers **3** and **4** by reaction of the corresponding phthalocyanine monomers with an excess of concentrated H$_2$SO$_4$ at −20°C, and we have determined their structures and photophysical properties, especially their optical limiting properties, and have also compared them with the starting materials [tBu$_4$PcGaCl] (**1**) and [tBu$_4$PcInCl] (**2**). Among the gallium(III) and indium(III) phthalocyanine monomers, **2** had been investigated earlier for its optical limiting properties.[5, 8, 10] The enhanced solubility of compounds [(tBu$_4$PcGa)$_2$O] (**3**) and [(tBu$_4$PcIn)$_2$O] (**4**), compared with the chloro compounds **1** and **2**, shows that the usual tendency of phthalocyanines to form aggregates can be effectively suppressed by axial substitution.[5] The stability of **3** in solution is considerably higher than that of **4**. The μ-oxo-bridged phthalocyanine dimers **3** and **4** have a more intense photoluminescence emission in the red region than monomers **1**, **2**. The gallium phthalocyanine compounds **1** and **3** have fluorescence lifetimes of a few nanoseconds, while indium phthalocyanine compounds **2** and **4** have lifetimes of only several hundred picoseconds. By comparing the fluorescence lifetimes of monomers **1** and **2** with those of dimers **3** and **4**, we found that the dimers have longer lifetimes of the excited singlet states. The transient absorption spectrum is similar for all species, and the transient absorption band at about 520 nm, observed by the nanosecond laser irradiation can be assigned to the transition from the lowest triplet excited state to the upper triplet excited states (T–T absorption). All compounds, including the starting materials, display strong positive nonlinear optical absorption at the excitation wavelength. The magnitude of the optical limiting exhibited by **1**, **2**, **3**, and **4** in toluene at 532 nm laser pulse is in the order: **4** > **3** > **2** > **1**. These results demonstrate that these compounds are candidates for use in optical limiting applications.

Experimental Section

General: The operations for synthesis prior to the termination reaction were carried out under purified dry nitrogen. Solvents were purified, dried, and distilled under dry nitrogen. FT-IR: Perkin-Elmer Spectrum 1000; UV/Vis: Shimadzu UV-365; MS: Varian Mat 711(FD, temperature of the ion source: 30 °C; FAB, temperature of the ion source: 50 °C); ^{1}H,^{13}C NMR: Bruker AC 250 (^{1}H: 250.131 MHz, ^{13}C: 62.902 MHz); Elemental analyses: Carlo-Erba Elemental Analyser 1104, 1106. Fluorescence spectra (excitation: 355 nm) were measured in toluene on a Shimadzu RF-5300PC spectrofluorophotometer. Fluorescence lifetimes were measured by a single-photon counting method using an argon ion laser, a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, fwhm 1.5 ps) 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 toluene with 410 nm laser light. Every decay can be fitted with a single exponential. Nanosecond transient absorption measurements were carried out in toluene using a third harmonic generation (THG, 355 nm, 24 J/pulse) of a Nd:YAG laser as an excitation source. Probe light from a pulsed Xe lamp was detected with a Si-PIN photodiode equipped with a monochromator, after passing through the sample in a quartz cell (1 cm × 1 cm).

All Z-scan experiments described in this study were performed using 6 ns pulses from a frequency-doubled (532 nm), Q-switched Nd:YAG laser with a pulse repetition rate of 10 Hz. The beam was spatially filtered to remove the far field and tightly focused to a spot of about 20 µm. All samples were measured in quartz cells with a 1 mm path length, and at concentrations of about 10^{-4} M in spectroscopic grade toluene.

Chlorogallium(III) 2,(3)-tetra-(*tert*-butyl)phthalocyanine (1) [*t*Bu$_4$PcGaCl]: A mixture of anhydrous gallium(III) chloride (0.75 g, 4.26 mmol), 4-*tert*-butylphthalonitrile (3 g, 16.3 mmol), quinoline (doubly distilled over CaH$_2$, 15 mL), and 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU, 1 mL) was stirred at 180 °C for 7 h. The solvent was removed by distillation under reduced pressure to leave a dark green residue, which was chromatographed on silica gel using a gradient of toluene and chloroform to remove metal-free phthalocyanine and the largest portion of polar impurities. The blackish green fraction ($R_f \geq 0$) was collected, the solvent evaporated, and the crude compound recrystallized from a mixture of CH$_2$Cl$_2$/MeOH (v/v 4:3) by slowly evaporating the more volatile dichloromethane in a rotary evaporator at 40–60 °C under slightly reduced pressure. To complete the crystallization, the mixture was kept in a refrigerator overnight. The complex was collected by filtration, washed twice with methanol and dried under vacuum at 80 °C for 10 h, yielding **2** (2.35 g; 68.5 %) as a blackish green powder. ^{1}H NMR (CDCl$_3$): $\delta = 1.9$ (m, 36H; *t*Bu), 8.2–8.4 (m, 4H; H-1), 8.9–9.4 ppm (m, 8H; H-2, 2′); ^{13}C NMR (CDCl$_3$): $\delta = 31.1$–32.1 (*t*BuCH$_3$), 36.2 (CMe$_3$), 119.1–119.6 (C-2′), 122.6–122.9(C-2), 128.5–128.6 (C-1), 133.7–133.9 (C-3), 135.9–136.2 (C-3′), 150.4–151.1 (C-4, 4′), 154.2–154.6 ppm (C-1′); FTIR (KBr)): $\tilde{\nu} = 3068$ vw, 2958 s, 2866 m, 1734 w, 1682 w, 1615 m, 1507 m, 1483 m, 1406 m, 1394 m, 1364 m, 1334 vs, 1281 m, 1258 s, 1201 m, 1149 m, 1087 vs, 1052 m, 1024 w, 967 w, 929 s, 895 w, 831 m, 765 m, 750 s, 694 m, 670 m , 602 vw, 566 vw, 532 m, 444 vw, 350.5 cm^{-1} w (Ga–Cl); UV/Vis (CHCl$_3$): $\lambda_{\max} = 695$, 664.5 (sh), 625, 356 nm; FD-MS: calcd for C$_{48}$H$_{48}$ClGaN$_8$ 842.14, found 842.3(100); elemental analysis calcd (%) for C$_{48}$H$_{48}$ClGaN$_8$: C 68.46, H 5.74, N 13.31, Cl 4.21; found: C 66.50, H 5.63, N 12.36, Cl 4.15.

Chloroindium(III) 2,(3)-tetra-(*tert*-butyl)phthalocyanine (2) [*t*Bu$_4$PcInCl]: A mixture of InCl$_3$ (1.52 g, 6.88 mmol), 4-*tert*-butylphthalonitrile (5.07 g, 27.52 mmol), dry quinoline (12 mL), and DBU (1 mL) was stirred at 180 °C for 5 h. The solvent was removed by distillation under reduced pressure to leave a dark green residue, which was chromatographed on silica gel using chloroform as the eluent to remove large amounts of the impurities. The crude compound was then recrystallized from mixtures of CH$_2$Cl$_2$/MeOH (v/v 4:3) by slowly evaporating the more volatile chloromethanes in a rotary evaporator at 40–60 °C under slightly reduced pressure. To complete the crystallization, the mixture was kept in a refrigerator overnight. The complex was collected by filtration, washed twice with methanol, and dried at 80 °C in vacuum, yielding blue-green microcrystals (2.98 g; 49 %). ^{1}H NMR (CDCl$_3$): $\delta = 1.8$ (m, 36H; *t*Bu), 8.3 (m, 4H; 1-H), 9.3 (m, 4H; 2-H), 9.4–9.5 ppm (m, 4H; 2′-H); ^{13}C NMR (CDCl$_3$): $\delta = 32.0$ (CH$_3$), 36.2 (CMe$_3$), 119.7–119.8 (C-2′), 123.1–123.2 (C-2), 128.5–128.6 (C-1), 135.1–135.2 (C-3), 137.5–137.7 (C-3′), 152.7–153.5 (C-4,4′), 154.6–154.7 ppm (C-1′); FTIR (KBr): $\tilde{\nu} = 3075$ vw, 2975 vs, 2903 m, 2866 m, 1613 m, 1485 s, 1393 m, 1364 m, 1330 vs, 1280 m, 1256 s, 1199 w, 1147 w, 1087 vs, 1047 m, 922 s, 896 w, 831 m, 761 w, 746 m, 693 w, 671 w, 602 vw, 568 vw, 524 vw, 444 vw, 336 cm^{-1} w (In–Cl); UV/Vis (CHCl$_3$): $\lambda_{\max} = 697$, 667(sh), 628, 359.5 nm; FD-MS calcd for C$_{48}$H$_{48}$ClInN$_8$ 887.2, found 886.2(100); elemental analysis calcd (%) for C$_{48}$H$_{48}$ClInN$_8$: C 64.98, H 5.45, N 12.63, Cl 4.00; found: C 65.16, H 5.36, N 12.30, Cl 4.13.

μ-Oxo-axially bridged gallium(III) phthalocyanine dimer (3) ([(*t*Bu$_4$PcGa)$_2$O]): [*t*Bu$_4$PcGaCl] (280 mg, 0.332 mmol) at −20 °C was mixed with 96 % H$_2$SO$_4$ (35 mL). The resulting red-brown solution was stirred for 2 h at the same temperature. The mixture was quenched with ice water (100 mL). After 30 min, the temperature was allowed to rise slowly to room temperature, and the mixture was stirred for another 1 h. The crude product was filtered, washed with water until neutral, and then refluxed with aqueous ammonia for 2 h, filtered hot, washed with hot water until neutral, and dried for 10 h at 80 °C under vacuum. The navy blue colored product was obtained in 72 % yield (196 mg). ^{1}H NMR (CDCl$_3$): $\delta = 1.7$–1.9 (m, 72H; *t*Bu), 7.8–8.3 (m, 8H; 1-H), 8.4–9.4 ppm (m, 16H; 2,2′-H); ^{13}C NMR (CDCl$_3$): $\delta = 30.5$–32.0 (*t*BuCH$_3$), 35.9–36.1 (CMe$_3$), 118.7–119.3 (C-2′), 122.2–122.6 (C-2), 128.2 (C-1), 133.1–133.6 (C-3), 135.9–136.4 (C-3′), 151.6–152.2(C-4,4′), 153.5–154.1 ppm (C-1′); FTIR (KBr): $\tilde{\nu} = 3068$ vw, 2958 s, 2863 m, 1736 w, 1615 m, 1506 m, 1484 m, 1456 m, 1394 m, 1364 m, 1335 s, 1282 m, 1258 s, 1200 m, 1155 m, 1088 vs, 1052 m, 1024 w, 967 w, 929 s, 895 w, 831 m, 767 m, 750 s, 695 m, 670 m , 633 w, 602 vw, 532 m, 446 cm^{-1} vw; UV/Vis (CHCl$_3$): $\lambda_{\max} = 693$, 662.5(sh), 623.5, 357.5 nm; FD-MS calcd for C$_{96}$H$_{96}$Ga$_2$N$_{16}$O 1629, found 1628.1(100); elemental analysis calcd (%)for C$_{96}$H$_{96}$Ga$_2$N$_{16}$O: C 70.77, H 5.94, N 13.75; found: C 69.03, H 5.79, N 12.88.

μ-Oxo-axially bridged indium(III) phthalocyanine dimer (4) ([(*t*Bu$_4$PcIn)$_2$O]): [*t*Bu$_4$PcInCl] (220 mg, 0.248 mmol) at −20 °C was mixed with 96 % H$_2$SO$_4$ (30 mL). The resulting red-brown solution was stirred for 2 h at the same temperature. The mixture was quenched with ice water (100 mL). After 30 min, the mixture was allowed to warm slowly to room temperature, and was stirred for another 1 h. The crude product was filtered, washed with water until neutral, and then refluxed with aqueous ammonia for 2 h, filtered hot, washed with hot water until neutral, and dried for 10 h at 80 °C under vacuum. The purplish blue colored product was obtained in 68.5 % yield (145.9 mg). ^{1}H NMR (CDCl$_3$): $\delta = 1.8$–1.9 (m, 72H; *t*Bu), 8.3 (m, 8H; 1-H), 9.3–9.6 ppm (m, 16H; 2,2′-H); ^{13}C NMR (CDCl$_3$): $\delta = 32.0$–32.1 (CH$_3$), 36.0–36.2 (CMe$_3$), 119.7 (C-2′), 123.1 (C-2), 127.5–128.6 (C-1), 135.1–135.3 (C-3), 137.5–137.8 (C-3′), 152.8–153.5 (C-4,4′), 154.3–154.7 ppm (C-1′); FTIR (KBr): $\tilde{\nu} = 2959$ s, 2900 m, 2862 m, 1735 w, 1715 w, 1682 w, 1614 m, 1487 s, 1394 m, 1364 m, 1330 vs, 1281 m, 1257 s, 1200 m, 1151 m, 1087 vs, 1047 m, 1019 w, 1004 w, 922 s, 896 w, 831 m, 761 w, 746 s, 694 m, 672 m, 599 w, 567 w, 525 w, 443 cm^{-1} w; UV-Vis (CHCl$_3$): $\lambda_{\max} = 696$, 665(sh), 627.5, 360 nm; FAB-MS: *m/z*: 1719 [M^+], 1587.5 [(*t*Bu$_4$Pc)$_2$In$^+$], 1473.7, 1052.3, 884.7, 849.9 [*t*Bu$_4$PcIn$^+$], 833.8, 793,9, 737.2 [*t*Bu$_4$PcH$^-$], 722.2, 681.2; FD-MS: *m/z*: 1587.5 [(*t*Bu$_4$Pc)$_2$In$^+$], 1220.9, 1016.2, 886.1, 851.1

[tBu$_4$PcIn$^+$]; elemental analysis calcd for $C_{96}H_{96}In_2N_{16}O$: C 67.06, H 5.63, N 13.03; found: C 66.24, H 5.63, N 11.76.

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