Synthesis, Characterization, and Optical-Limiting Properties of Axially Substituted Gallium(III) Naphthalocyanines

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The soluble axially substituted naphthalocyanine monomers, $tBu_4NcGaCl$ (**1**) and tBu_4-NcGa(p-TMP) (p-TMP = p-trifluoromethylphenyl) (**2**) and the μ-oxo-bridged naphthalocyanine dimer $[tBu_4NcGa]_2O$ (**3**) are synthesized under mild conditions. In comparison to the corresponding gallium phthalocyanine compounds, $tBu_4PcGaCl$, $tBu_4PcGa(p$-TMP), and $[tBu_4PcGa]_2O$, all gallium naphthalocyanines **1**–**3** are almost transparent in the yellow and red region of the UV/vis spectrum, suggesting that they are suitable for eye protection in a practical optical-limiting device. These compounds optically limit at sufficiently high intensity via a reverse saturable absorption mechanism into the excited T–T absorption band at 532-nm excitation. The substitution of the axially p-TMP ligand onto the central gallium atom results in a defocusing of the beam relative to the other gallium naphthalocyanine compounds. This added defocusing of the beam is important and desirable in practical optical limiters as it helps to spatially disperse the pulse, further reducing the energy density of incident laser pulses.

Introduction

Phthalocyanines offer a large architectural flexibility in a structure, which facilitates the tailoring of their physical, optoelectronic, and chemical parameters in a very broad range,[1–3] thus attracting the attention of chemists, physicists, biochemists, and material scientists. Utilizing the chemical reactivity of M–Cl [M = Ga^{3+}, In^{3+}] and M=O [M = Ti^{4+} etc.] bonds, a series of highly soluble axially substituted or bridged phthalocyanine complexes have been prepared by us under mild conditions.[4–6] The optical-limiting properties of these axially substituted phthalocyanines were surprisingly robust to structural changes in the axial position.[7,8] 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 example, for the protection of human eyes, optical elements, or optical sensors from intense laser pulses.[1,3,7,9]

The color of the optical-limiting materials is, however, of great importance in a practical device. The use of such a device will be in an environment in which it is necessary to see normal red light signals or displays; the strongly red-absorbing phthalocyanines would be unsuitable for eye protection, even though their performance in limiting high intensities would be good.[10,11] In contrast to phthalocyanines, naphthalocyanines (Ncs) are almost transparent in the red light region. Very recently, we synthesized highly soluble (naphthalocyaninato)indium(III) complexes with different axial ligands, developing a new unsymmetrical peripheral octasubstitution pattern with alkyl and alkoxy substituents in the 2- and 4-positions of the Ncs.[10] Among these indium-(III) naphthalocyanine compounds, $tBu_4(EHO)_4NcIn(p$-TMP) [EHO = 2-ethylhexyloxy, p-TMP = p-trifluoromethylphenyl] was the most promising as an optical limiter.[11,12] This material had a large excited-state cross

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section and an excited-state lifetime longer than 10 ns, which leads to large nonlinear absorption coefficients and effective optical limiting.[8,11,12]

In comparison, much less work has been done on the synthesis of gallium naphthalocy-anines. Only some peripherally unsubstituted gallium(III) naphthalocyanines, for example, NcGaCl, NcGa(OH), NcGaOSi(*n*-$C_6H_{13})_3$, and $(NcGaF)_n$, were reported so far.[13] The greatest disadvantage of these compounds is their poor solubility in organic solvents. We report here the synthesis and optical-limiting properties of the soluble axially substituted naphthalocyanine monomers: tBu$_4$-NcGaCl (**1**), tBu$_4$NcGa(*p*-TMP) (**2**), and the *μ*-oxo-bridged naphthalocyanine [tBu$_4$NcGa]$_2$O (**3**). Their spectral and optical-limiting properties are compared with the corresponding gallium(III) phthalocyanine compounds, tBu$_4$PcGaCl,[5] tBu$_4$PcGa(*p*-TMP),[5] and [tBu$_4$-PcGa]$_2$O,[14] reported by us earlier.

Experimental Section

General. The operations for synthesis 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 Analyzer 1104, 1106. Due to the possible decomposition of compounds **2** and **3** during the burning process, it is very difficult to obtain satisfactory elemental analysis values for these compounds. Here, only the EA result of compound **1** is given.

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-23FS), 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 mJ/pulse) of a Nd:YAG laser as an excitation source. Probe light from a pulsed Xe lamp was detected with a Si−PIN photodiode (400−1000 nm) equipped with a monochromator after passing through the sample in a quartz cell (1 × 1 cm).

The open aperture of a Z-scan experiment was used to measure the optical-limiting response of the samples. All experiments described in this study were performed using 6-ns pulses from a Q switched Nd:YAG laser. The beam was spatially filtered to remove the far field and was tightly focused using a 12-cm convex lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz. All samples were measured in quartz cells with a 1-mm optical path length and at concentrations of the order 10^{-4} M in chloroform.

Chlorogallium(III) 3,4-Tetra-(*tert*-butyl)-2,3-naphthalocyanine (1) [tBu$_4$NcGaCl]. A mixture of anhydrous gallium(III) chloride (315 mg, 1.79 mmol), 6-*tert*-butyl-2,3-

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dicyanonaphthalene (1.68 g, 7.17 mmol), quinoline, doubly distilled over CaH$_2$ (10 mL), and DBU (1.2 mL) was stirred at 180 °C for 20 h. After cooling, the mixture was poured into methanol (350 mL). The precipitate was filtered, washed with methanol, and subjected to Soxhlet extraction with methanol for 2 days. The dark green residue was chromatographed (silica gel/CHCl$_3$; $R_f \geq 0$) to remove the largest portion of polar impurities. The yellowish-green fraction was collected and the solvent evaporated. The solid product was stirred in methanol, collected by filtration, and vacuum-dried at 70 °C for 6 h. Yield: 862.3 mg (46%) of **1** as a dark green microcrystalline powder. FAB-MS (*m/z*): calcd for C$_{64}$H$_{56}$ClGaN$_8$ 1042.4; found 1041.8 (M$^+$), 1027, 1006 [tBu$_4$NcGa$^+$], 991, 947, 901, 875. EA: calcd C 73.75, H 5.41, N 10.75, Cl 3.40; found C 72.23, H 5.47, N 10.60, Cl 3.30. UV/vis (CHCl$_3$): λ_{max}(nm) = 807, 762, 721, 450, 422.5, 358, 336.5. FTIR (KBr, cm^{-1}): 3068 vw, 2953 ms, 2866 m, 1725w, 1619 w, 1500 w, 1478 w, 1461 w, 1368 ms, 1357 s, 1341 ms, 1318 m, 1270 m, 1257 m, 1206 w, 1164 w, 1142 m, 1101 vs, 1084 s, 1038 w, 1023 w, 945 m, 902 m, 891 m, 877 w, 865 w, 836 w, 810 m, 772 w, 742 ms, 724 m, 644 w, 471 ms, 338 w, 305 vw. ^{1}H NMR (CDCl$_3$): δ/ppm 1.74 (m, 36H, tBu), 7.91−8.03 (m, 4H, 5-H), 8.22 (m, 4H, 6-H), 8.64 (m, 4H, 6′-H), 8.78 (m, 8H, 2,2′-H). ^{13}C NMR (CDCl$_3$): δ/ppm 31.52 (tBuCH$_3$), 35.42 (CMe$_3$), 122.03 (C-1), 122.56 (C-1′), 124.82 (C-2′), 126.23 (C-2), 129.76 (C-6′), 132.24 (C-5), 134.03 (C-3,3′), 145.42 (C-6), 149.84 (C-5′), 151.38 (C-4,4′).

[3,(4)-Tetra-*tert*-butyl-2,3-naphthalocyaninato][*p*-(trifluoromethyl)phenyl]gallium(III) {tBu$_4$NcGa(*p*-TMP)} (2). A freshly prepared solution of R′MgBr (R′ = *p*-trifluoromethyl-phenyl) in THF (20 mL, 0.18 M R′MgBr) was added dropwise to a stirred solution of tBu$_4$NcGaCl [(**1**), 306 mg, 0.294 mmol) in dry THF (25 mL). The reaction was monitored by TLC and stopped when all of the chloro complex **1** had been consumed. The dark green mixture was poured on ice and was extracted several times with diethyl ether. The combined organic layers was washed with water and dried with MgSO$_4$. After evaporation of the solvent, the residue was rapidly subjected to column chromatography (silica gel/toluene). Light was strictly excluded during this step. Further purification of the complex was achieved by recrystallization from a mixture of CH$_2$Cl$_2$/MeOH(v/v 1:1) by slowly evaporating the more volatile dichloromethane in a rotary evaporator at 40−60 °C under slightly reduced pressure. To complete crystallization, the mixture was kept in a refrigerator overnight. The complex was collected by filtration, washed twice with methanol, and dried at 70 °C in a vacuum for 6 h. Yield: 194 mg (57%) of **2** as a yellow-green powder. FD-MS [(*m/z*(%)]: calcd for C$_{71}$H$_{60}$-GaN$_8$F$_3$ 1152; found 1152.8(100). UV/vis (CHCl$_3$): λ_{max}(nm) 808, 764, 719.5, 449, 351.5. FTIR (KBr, cm^{-1}): 3067 vw, 2962 ms, 2932m, 2853 w, 1619 w, 1529 vw, 1478 w, 1461 w, 1453 vw, 1412 w, 1359 ms, 1324 s (C−F), 1261 vs, 1204 w, 1164 m, 1100 vs, 1084 s, 1070 s, 1052 s, 1018 vs, 945 w, 902 m, 863 m, 803 vs, 742 ms, 723 m, 684 m, 665 vw, 470 m, 402 m, 390 m. ^{1}H NMR (CDCl$_3$): δ/ppm 1.82−1.86 (m, 36H, tBu), 3.78−3.85 (m, 2H, H−b,b′), 5.34 (d, ^3J = 7.5 Hz, 2H, H-c,c′), 8.05−8.12 (m, 4H, 5-H), 8.32−8.40 (m, 4H, 6-H), 8.52 (m, 4H, 6′-H), 8.72−8.79 (m, 8H, 2,2′-H). ^{13}C NMR (CDCl$_3$): δ/ppm 31.62−31.65 (tBuCH$_3$), 35.57 (CMe$_3$), 114.46 (CF$_3$), 117.75 (C-d), 121.45−121.51 (C-1), 122.25 (C-1′), 125.09 (C-2′), 126.43 (C-2), 127.28−127.37 (C-c,c′), 128.14−128.41 (C-b,b′), 129.95−130.06 (C-6′), 132.45 (C-5), 134.28 (C-6, 3,3′), 150.08 (C-5′,4,4′). ^{19}F NMR-(CDCl$_3$): δ/ppm −63 (CF$_3$-d).
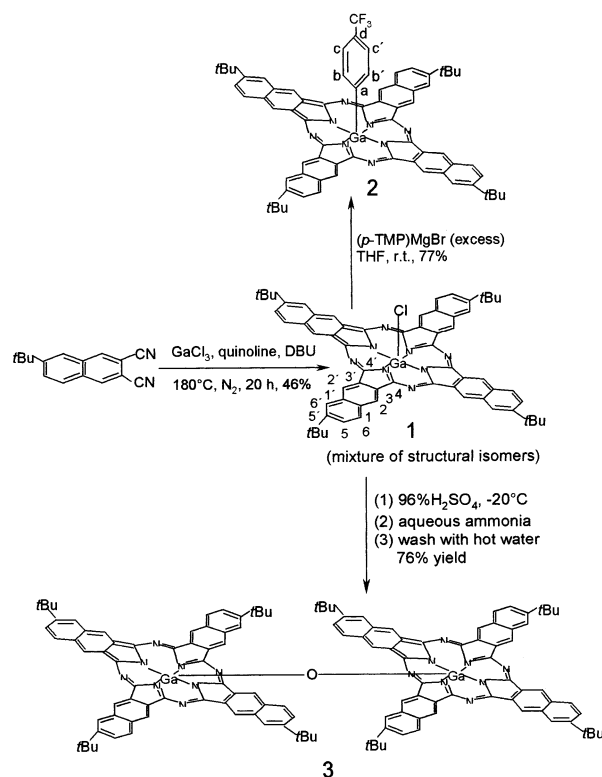
***μ*-Oxo-Axially Bridged Gallium(III)naphthalocyanine Dimer (3) ([tBu$_4$NcGa]$_2$O).** tBu$_4$NcGaCl (323 mg, 0.310 mmol) at −20 °C was mixed with 96% H$_2$SO$_4$ (35 mL). The brown solution obtained was stirred for 2 h at the same temperature. The mixture was quenched with ice water (100 mL). After 30 min, the temperature was allowed to rise slowly to room temperature and stirred for another 1 h. The crude product was filtered, washed with hot 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 in a vacuum. The dark blue colored product was obtained in 76% yield (240 mg). FD-MS [*m/z*(%)]: calcd for C$_{128}$H$_{112}$-Ga$_2$N$_{16}$O 2029.84; found 2030.2 (20, M$^+$), 1013.6 (100, M^{2+}),

Scheme 1

Figure 1. UV/vis absorption spectra of a 5.77×10^{-5} mol/L solution of (a) tBu$_4$NcGaCl, (b) tBu$_4$NcGa(*p*-TMP), and (c) [tBu$_4$NcGa]$_2$O in CHCl$_3$.

676.8 (30, M^{3+}). UV/vis (CHCl$_3$): λ_{max}(nm) 803, 758, 717(sh), 420.5, 357, 335.5. FTIR (KBr, cm^{-1}): 3068 vw, 2956 ms, 2861 m, 1619 w, 1500 w, 1465 w, 1367 ms, 1358 s, 1341 ms, 1318 m, 1274 m, 1255 m, 1203 w, 1163 w, 1140 m, 1100 vs, 1080 s, 1037 w, 1020 w, 945 m, 902 m, 891 m, 877 w, 862 w, 807 m, 770 w, 740 ms, 723 m, 648 w, 470 m. ^{1}H NMR (CDCl$_3$): δ/ppm 2.14 (m, 72H, *t*Bu), 7.69–7.80 (m, br., 40H, H-2,2′,5,6,6′). ^{13}C NMR (CDCl$_3$): δ/ppm 31.03–31.41(tBuCH$_3$), 35.25 (CMe$_3$), 121.68 (C-1), 122.47 (C-1′), 124.76–124.90 (C-2′), 125.44–125.96 (C-2), 128.20 (C-6′), 129.55–129.88 (C-5), 131.98 (C-3,3′), 133.83 (C-6), 149.62 (C-5′), 151.40 (C-4,4′).

Results and Discussion

Scheme 1 gives the synthetic route of **1**–**3**, together with notation of the atoms of the macrocycles and the axial *p*-trifluoromethylphenyl (*p*-TMP) ligand. **1** was obtained (as a mixture of structural isomers) by the reaction of 6-*tert*-butyl-2,3-dicyanonaphthalene with anhydrous GaCl$_3$ in doubly distilled, deoxygenated quinoline at 180 °C in the presence of catalytic amounts of the nonnucleophilic base 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU). **2** was synthesized by the reaction of freshly prepared 10-fold excess *p*-TMP Grignard reagent with **1**. Dimer **3** was prepared by the reaction of **1** with an excess of concentrated H$_2$SO$_4$ at −20 °C. The solubilities of **2** and **3** in chloroform are much higher than that of **1**. In comparison with the corresponding tBu$_4$PcGa compounds mentioned above, all gallium naphthalocyanines **1**–**3**, especially compound **1**, showed a somewhat stronger tendency to form aggregation in solutions, especially at high concentration as observed from UV/vis spectra. Similar to the Ga−O−Ga linkage in [tBu$_4$PcGa]$_2$O,[14] the Ga−O−Ga linkages in **3** can also be cleaved by concentrated H$_2$SO$_4$ at room temperature, and by 6 N HCl at reflux, as well as under column chromatographic conditions (e.g., silica gel/toluene).
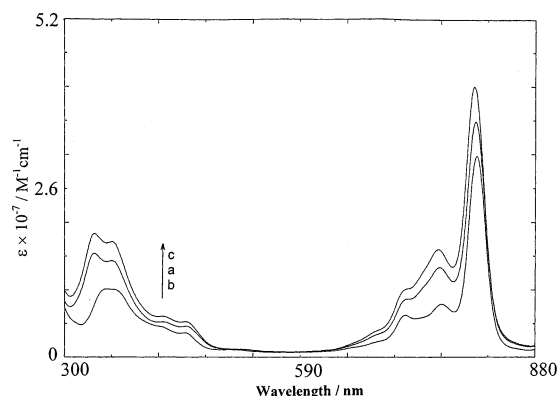
As shown in Figure 1, the UV/vis spectra of **1**–**3** in CHCl$_3$ are quite similar with almost identical Q and B bands. The axial *p*-TMP ligand has little influence on the position of the Q band around 800 nm in comparison with **1**. The observed red shift is only of the order of 1 nm. Similar results with tBu$_4$PcGaCl and tBu$_4$PcGa(*p*-TMP) have been reported by us earlier.[5] The formation of the μ-oxo naphthalocyanine dimer **3** only gives rise to a weak blue shift of the Q band of 4 nm attributed to exciton splitting in the dimer.[15] Because of extension of the phthalocyanine core by linear benzannellation, which affords the related group of 2,3-naphthalocyanines, all gallium naphthalocyanines (**1**–**3**) have their Q bands shifted about 100 nm toward the longer wavelength when compared to the corresponding gallium phthalocyanines.

In the IR spectrum of **1** many vibrations appear in the fingerprint range, which are due to both vibrations of the naphthalocyanine system and deformation modes of the *tert*-butyl groups. The C−H stretching frequencies of the *tert*-butyl group are in the 2853−2953-cm^{-1} region. For **2**, some new absorption bands, which do not appear in the spectrum of **1**, were observed (see Experimental Section). The C−F stretching band of *p*-trifluoromethyl was found at 1324 cm^{-1}. The new gallium−carbon bond stretching vibration, however, is not found in the IR spectrum of **2** because it is not always possible to assign the Ga−C stretching mode unambiguously due to coupling with C−C modes and vibrations of the naphthalocyanine moiety. Comparison of the IR spectra of **1** and **3** reveals that they are almost identical.

The molecular peak of **1** was only detected in the FAB-MS spectrum, accompanied by a number of fragment peaks centered at *m/z* 1041.8 (M$^+$), 1027, 1006[tBu$_4$-NcGa$^+$], 991, 947, 901, 875, and so forth. The field desorption (FD) mass spectrum of **2** shows a cluster of peaks centered at *m/z* (%) 1152.8 (100), which are almost identical in intensity to that calculated for its respective isotopic composition [*m/z* (%): 1148.6 (15), 1150.8 (90), 1151.9 (85), 1152.8 (100), 1153.8 (52), 1154.9 (40)]. In our previous paper,[14] we reported the FD-mass spectrum of [tBu$_4$PcGa]$_2$O. Its molecular peak appears at *m/z* (%) = 1628.1 (100). No fragmentation was detected. In the case of [tBu$_4$NcGa]$_2$O (**3**), its FD-mass spectrum

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shows three peaks centered at m/z (%) = 2030.2 (20, M^+), 1013.6 (100, M^{2+}), and 676.8 (30, M^{3+}), indicating that the stability of **3** is less than that of [tBu₄PcGa]₂O under FD mode.

The ¹H NMR spectra of **1−3** in CDCl₃ shows broad multiplets for the aromatic protons of the macrocycles. Also, the signals for the *tert*-butyl groups appear as multiplets (see Experimental Section). The numbering of the atoms of the macrocycle and the axial *p*-TMP ligand is shown in Scheme 1. For **2**, the proton signals of the *p*-TMP ligand are shifted upfield due to the diamagnetic ring current of the naphthalocyanine macrocycle. They appear at δ = 5.3 ppm (d, H-c,c′, 2H, ^3J = 7.5 Hz) and δ = 3.8−3.9 ppm (m, H−b,b′, 2H), respectively, whereas the proton signals of the pure *p*-trifluoromethylphenyl bromide (*p*-TMPBr) appear at δ = 7.5 (H-c,c′) and 7.6 (H-b,b′) ppm. Similar to the ¹H NMR spectrum of [tBu₄PcGa]₂O,[14] the aromatic proton signals of **3** are also significantly broadened.

The structurally related gallium naphthalocyanines **1** and **2** have similar ¹³C NMR spectra in terms of the periphery and core resonances. Their ¹³C NMR spectra are very similar to that of tBu₄NcInCl[16] and tBu₄NcIn-(*p*-TMP)[10,11] and can be easily assigned to the appropriate carbon atoms in the macrocycles. Only a part of the carbon signals of the *p*-TMP ligand in **2** are observed and appear at δ = 114.5 (CF₃), 117.8 (C-d), 127.3−127.4 (C-c,c′), and 128.1−128.4 (C-b,b′) ppm, respectively. These signals are split on account of C−F coupling. The ¹⁹F NMR signal of **2** appears at δ = −63 ppm for the axial ligand, which is rather close to that observed in tBu₄PcGa(*p*-TMP).[5] In comparison with **2**, the ¹⁹F signal of tBu₄NcIn(*p*-TMP) appears at δ = −64.5 ppm.[10] The difference in chemical shifts of the same fluorine atoms between tBu₄NcGa(*p*-TMP) and tBu₄NcIn(*p*-TMP) is due to the different electronic effects of In³⁺ and Ga³⁺. In the ¹³C NMR spectrum of **3**, it can be seen that the aromatic carbon signals are apparently broadened due to the structural and rotational isomers.

The fluorescence spectra were measured by the streak scope with relatively high sensitivity in the 700−900-nm region because the ordinal photomultiplier tube has quite low sensitivity in this region. The fluorescence spectra are shown in Figure 2. The fluorescence bands appear in the 800−900-nm region as the mirror images of the Q-absorption bands. A slight blue shift was observed from **1** to **2**. The fluorescence lifetimes were evaluated from the observed time profiles, which are curve-fitted with a single exponential. The data are listed in Table 1 in which the dimer **3** has a longer fluorescence lifetime than the monomers **1** and **2**. This tendency is in good agreement with that observed for the corresponding gallium phthalocyanine derivatives.

The nanosecond laser flash photolysis of **1−3** in degassed toluene solution gave the transient absorption spectra as shown in Figure 3. The observed transient absorption bands in the 500−700-nm range with a peak maximum at 600 nm were attributed to the triplet−triplet (T−T) transition.[14,17] In comparison to gallium
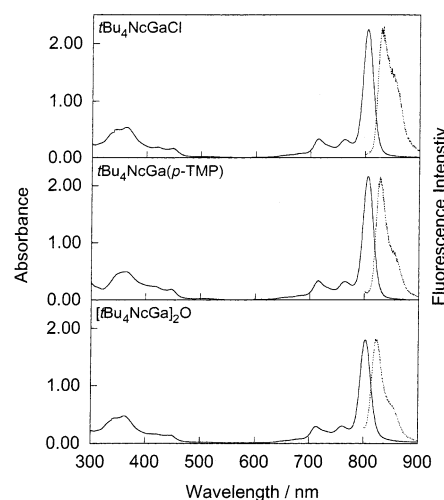
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Figure 2. Absorption and fluorescence spectra of (a) tBu₄-NcGaCl, (b) tBu₄NcGa(*p*-TMP), and (c) [tBu₄NcGa]₂O in toluene. Excitation wavelength for fluorescence spectra measurements was 410 nm.

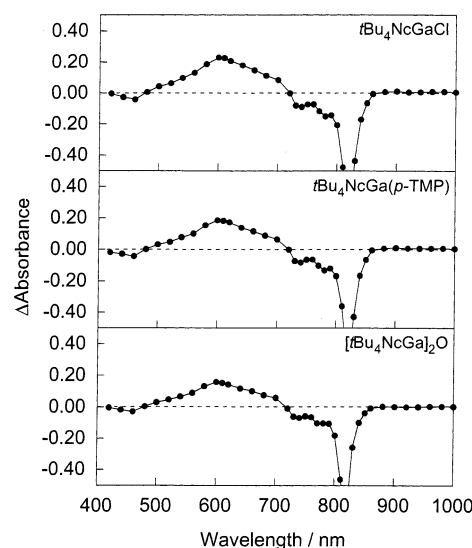**Figure 3.** Transient absorption spectra of tBu₄NcGaCl, (b) tBu₄NcGa(*p*-TMP), and (c) [tBu₄NcGa]₂O in toluene at 250 ns after the 355-nm laser excitation.

Table 1. Summary of Spectroscopic Data (λ_{max}^{abs} and λ_{max}^{fluo}), Fluorescence Lifetimes (τ_{fluo}), T−T Absorption Maxima (λ_{T-T}), and Intrinsic Triplet Lifetimes (τ_T^0) of Gallium Naphthalocyanines in Toluene

samples	λ_{max}^{abs} (nm)	λ_{max}^{fluo} (nm)	τ_{fluo} (ns)	λ_{T-T} (nm)	τ_T^0 (μs)
tBu₄NcGaCl	805	830	1.89	600	21.4
tBu₄NcGa(*p*-TMP)	806	828	1.79	600	18.2
[tBu₄NcGa]₂O	803	824	2.33	600	13.8

phthalocyanines,[5,14] gallium naphthalocyanines have their T−T bands red-shifted about 80 nm. It should be noted that these T−T absorption bands are located inside the high-transmittance region between the intense Q and B bands in the UV/vis spectra of all samples. After the laser exposure, the T−T absorption begins to decay for a hundred microseconds. The decay of the T−T absorption was curve-fitted with a single exponential when the laser power was employed. As can be seen from Table 1, the lifetimes of the triplet states are in the region of 13.8−21.4 μs, which are shorter than those of gallium phthalocyanine compounds,[5,14] but

Table 2. Summary of the Nonlinear Optical Properties for Gallium Naphthalocyanines and Gallium Phthalocyanines

samples	concn ($\times 10^{-4}$ mol·L^{-1})	α_0 (cm^{-1})	Im{$\chi^{(3)}$} ($\times 10^{-11}$ esu)	γ ($\times 10^{-32}$ esu)	κ σ_{ex}/σ_0	F_{Sat} (J·cm^{-2})
tBu$_4$NcGaCl[a]	9.59	4.4	3.0 ± 0.6	1.52 ± 0.3	4.8 ± 0.2	5.6 ± 0.2
tBu$_4$NcGa(*p*-TMP)[a]	8.68	2.3	2.0 ± 0.4	1.12 ± 0.2	9.2 ± 0.8	8.5 ± 0.9
[tBu$_4$NcGa]$_2$O[a]	4.93	5.0	3.9 ± 0.7	3.84 ± 0.7	4.1 ± 0.1	3.9 ± 0.2
tBu$_4$PcGaCl[b]	5.90	1.1	1.2 ± 0.2	0.84 ± 0.1	13.5 ± 0.4	27.0 ± 1.0
tBu$_4$PcGa(*p*-TMP)[b]	5.26	0.91	1.1 ± 0.2	0.86 ± 0.2	13.6 ± 0.4	8.4 ± 0.4
[tBu$_4$PcGa]$_2$O[b]	3.07	1.6	1.3 ± 0.2	1.76 ± 0.3	11.3 ± 1.0	13.5 ± 1.0

[a] In chloroform. [b] In toluene.

longer than the nanosecond laser employed in the optical-limiting measurements. In addition, these observations of the T−T absorption in the microsecond region suggests that the fluorescence decay is mainly attributed to the intersystem crossing from the lowest singlet excited state to the lowest triplet state.

A 1 g/L of chloroform solution of each naphthalocyanine compound (**1**, **2**, and **3**) was prepared for nonlinear optical characterization from the point of view of optical limiting. Open aperture Z-scan spectra were collected with pulses of various energies for each sample. All Z scans performed exhibit a decrease of transmittance about the focus typical of an induced positive nonlinear absorption of incident light. These compounds optically limit at sufficiently high intensity via a reverse saturable absorption mechanism into the excited T−T absorption band[14,17] at 532-nm excitation. The theory presented by Sheik-Bahae et al.[18] was fitted to the open aperture spectra and the imaginary third-order susceptibilities (Im{$\chi^{(3)}$}), and the second molecular hyperpolarizabilities (γ) were calculated from the fits. In all cases the waist radius (ω_0) of the beam was treated as a free parameter in the fit. It was found, averaging over successive scans with increasing energy per pulse, that the magnitude of ω_0 for compounds **1** and **3** was ≈22.5 μm. Interestingly, the average value of ω_0 for compound **2** was found to be ≈27.9 μm. It is clear that the substitution of the axially *p*-TMP ligand onto the central metal gallium atom results in a defocusing of the beam relative to the other compounds. This added defocusing of the beam is important and desirable in practical optical limiters as it helps to spatially disperse the pulse, further reducing the energy density of incident laser pulses. Physically, this can help keep the incident energy density below the damage threshold of the limiting material. The numerical values of Im{$\chi^{(3)}$} and γ are quoted in Table 2.

Typical optical-limiting plots are presented in Figure 4, where the normalized transmission is plotted as a function of excitation pulse energy density. The solid curves in Figure 4 are a least-squares regression curve fit to the data, where the energy density dependent absorption coefficient $\alpha(\alpha_0, F, F_{Sat}, \kappa)$ has been derived from laser rate equations and applied in a static case approximation (i.e., where all time derivatives were set to zero).

$$\alpha(\alpha_0, F, F_{Sat}, \kappa) = \frac{\alpha_0}{1 + \dfrac{F}{F_{Sat}}} \left(1 + \kappa \frac{F}{F_{Sat}}\right) \qquad (1)$$

(18) Sheik-Bahae, M.; Said, A. A.; Wei, T.-H.; Hagan, D. J.; Van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760.

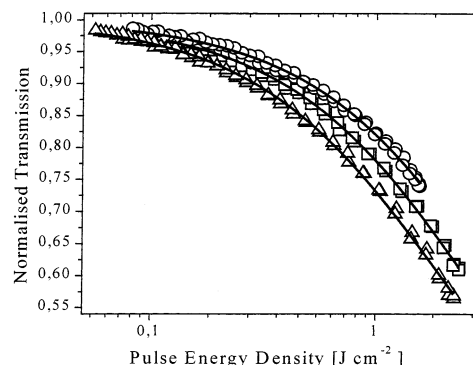**Figure 4.** Plot of normalized transmission against pulse energy density for tBu$_4$NcGaCl (□), tBu$_4$NcGa(*p*-TMP) (○), and [tBu$_4$NcGa]$_2$O (△) at 1 g/L in CHCl$_3$. The fitting parameters are given in Table 2.

where F is the pulse energy density, F_{Sat} is the saturation energy density, κ is termed the merit coefficient and is defined as $\kappa = \sigma_{ex}/\sigma_0$, where σ_{ex} and σ_0 represent the excited and ground state absorption cross sections, respectively, and α_0 is the linear absorption coefficient.

The fitting of the normalized transmission using the energy density dependent absorption coefficient (eq 1) was realized with F_{Sat} and κ treated as free parameters. α_0 was calculated from the linear transmission of the sample. Mathematically, all fits have R^2 values in excess of 0.99, and the results for all parameters are quoted in Table 2.

The nonlinear optical response of all of gallium naphthalocyanines, whose solubilities in toluene are not so good, is measured in chloroform. The solvents used for optical-limiting measurements should not effect the magnitude of the optical absorption significantly. The F_{Sat} values of the monomer **1** and dimer **3** follow the same trend as their Pc analogues: tBu$_4$PcGaCl and [tBu$_4$PcGa]$_2$O (see Table 2), with the dimer having a lower value than that of the monomer. In the case for naphthalocyanines, the numerical values of F_{Sat} are much closer than those in the tBu$_4$PcGa case. The magnitude of F_{Sat} is also changed significantly from the tBu$_4$PcGa case where tBu$_4$PcGaCl and [tBu$_4$PcGa]$_2$O have F_{Sat} values of ≈27 and 13.5 J cm^{-2}, respectively, while the corresponding naphthalocyanines have F_{Sat} ~ 5.6 and 3.9 J cm^{-2}, respectively. In contrast to the tBu$_4$PcGa case the saturation density F_{Sat} for the axially *p*-TMP substituted tBu$_4$NcGa does not follow the same trend. The saturation density of **2** is larger than that of **1** and **3**, while in the case of tBu$_4$PcGa compounds the saturation density of tBu$_4$PcGa(*p*-TMP) is smaller than that of tBu$_4$PcGaCl and [tBu$_4$PcGa]$_2$O.

The merit coefficients κ for **1** and **3** follow the same trend as their tBu$_4$PcGa analogues, with the monomer being larger than the dimer. The *p*-TMP axially sub-

stituted Nc (**2**) and its Pc analogue exhibits a different trend in their response again with the Nc κ value being larger than the κ value of other Nc compounds by a factor of $\approx$2. This is in contrast to the *p*-TMP axially substituted tBu$_4$PcGa compound where its κ value was smaller than tBu$_4$PcGaCl and [tBu$_4$PcGa]$_2$O.

It is clear from Figure 4 that the magnitude of the nonlinear absorption is not hugely different for the three different compounds **1**, **2**, and **3**. The differences in the magnitude of the merit coefficient κ for these compounds are therefore dominated by the differences in their linear absorption coefficients α_0. This explains why **2** has a κ value larger than the other two compounds (**1** and **3**) by a factor of $\approx$2, despite it exhibiting the weaker nonlinear response, in terms of transmission versus pulse energy density, of the three compounds. Its linear absorption coefficient is significantly smaller than that for the other compounds, approximately by a factor of 2.

Conclusions

To combine all the requirements for a good optical limiter with properties such as high solubility and stability in a yellow-colored indium naphthalocyanine, we synthesized the soluble axially monosubstituted gallium naphthalocyanines, tBu$_4$NcGaCl (**1**) and tBu$_4$-NcGa(*p*-TMP) (**2**), and the μ-oxo-bridged gallium naphthalocyanine dimer [tBu$_4$NcGa]$_2$O (**3**) under mild conditions. They were structurally characterized by IR, UV/vis, FAB-MS, FD-MS, and NMR spectroscopy. In comparison with the corresponding gallium phthalocyanine compounds, tBu$_4$PcGaCl, tBu$_4$PcGa(*p*-TMP), and [tBu$_4$PcGa]$_2$O, all gallium naphthalocyanines **1**−**3**,

especially compound **1**, showed a somewhat stronger tendency to form aggregation in solutions, especially at high concentration. The Ga−O−Ga linkages in **3** can be cleaved by concentrated H$_2$SO$_4$ at room temperature, and by 6 N HCl at reflux, as well as under column chromatographic conditions (e.g., silica gel/toluene). Fluorescence lifetimes, the position of T−T absorption bands, and the triplet lifetimes suggest that these naphthalocyanines are capable of exhibiting optical limiting. All Z scans of gallium naphthalocyanines exhibit a decrease of transmittance about the focus typical of an induced positive nonlinear absorption of incident light. These compounds optically limit at sufficiently high intensity via a reverse saturable absorption mechanism into the excited T−T absorption band at 532-nm excitation. The substitution of the axially *p*-TMP ligand onto the central metal gallium atom results in a defocusing of the beam relative to the other gallium naphthalocyanine compounds. This added defocusing of the beam is important and desirable in practical optical limiters as it helps to spatially disperse the pulse, further reducing the energy density of incident laser pulses.