

Notes

## Enhancement of optical limiting response by embedding gallium phthalocyanine into polymer host

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### Abstract

The need for materials to protect optical sensors from intense laser has resulted in intense research into passive phthalocyanine (Pc)-based non-linear optical (NLO) materials. The majority of optical limiting research is mainly focused on solution based studies over the past several decades, with fewer reports investigating passive solid-state non-linear optical devices. In this study, gallium phthalocyanine monomer ( $t\text{Bu}_4\text{PcGaCl}$ ) and its  $\mu$ -oxo-bridged dimer ( $[t\text{Bu}_4\text{PcGa}]_2\text{O}$ ) were embedded into a commercially available polymer poly(methylmethacrylate) (PMMA) to produce composite films acting as passive solid-state optical limiters. The results show that Pc/PMMA composite display much larger non-linear absorption coefficient and lower saturable fluence for optical limiting when compared to the same Pc molecules in solution. No evidence of film fatigue or degradation was observed in the Pc/PMMA film after numerous scans at varying laser intensity.

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### 1. Introduction

It is well-known that intense laser beams can easily damage delicate optical instruments, especially the human eye, and consequently the field of optical limiting has invested much effort into the research of materials and processes in an attempt to afford some measure of protection from such beams. The need for materials to protect optical sensors from intense laser is not only limited to the military, but also is rather a growing societal problem that can only escalate [1]. Basically “optical limiters” are system that permit the transmission of ambient light levels but which strongly attenuate high intensity, potentially damaging light such as focused laser beams. The various non-linear optical mechanisms for optical limiting include non-linear absorption (reverse-saturable absorption (RSA), two-photon absorption and multi-photon absorption), non-linear refraction (electronics or thermal effects) and non-linear scattering [2].

Similar to  $\text{C}_{60}$  and its derivatives, phthalocyanines (Pc's) are materials that optically limit nanosecond light pulses in a fairly wide range of the UV/vis absorption spectrum *via* excited state absorption processes, and have been extensively investigated as one of the most promising NLO materials due to their architectural flexibility, which allows tailoring of their physical, optoelectronic and chemical parameters in a broad range, exceptional stability and processability features [3]. The non-linear optical absorption mechanism of Pc's in the optical region comprised between the Q- and B-bands involves the population of excited states which absorb more effectively than the ground state. This gives rise to the phenomenon of RSA as a consequence of multiphoton absorption. It has been shown that phthalocyanine compounds exhibit RSA because of the occurrence of intersystem crossing from the lowest excited singlet state ( $S_1$ ) to the lowest triplet state ( $T_1$ ) and the subsequent increase in the population of the strongly absorbing  $T_1$  state with nanosecond dynamics.

A practical optical limiter based on the non-linear optical response from phthalocyanines would almost inevitably require the casting of the optically active compounds in the solid state. Polymerizing the Pc's, or embedding them as inclusions in a polymer host to form a composite material, would allow

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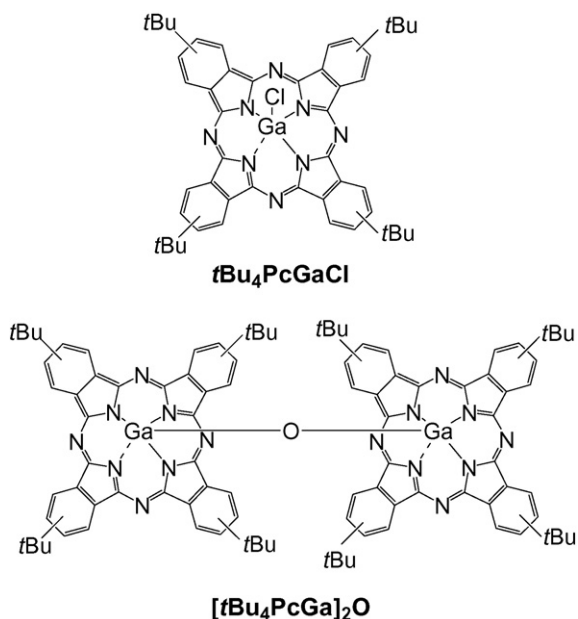


Fig. 1. Molecular structures of *t*Bu<sub>4</sub>PcGaCl and [tBu<sub>4</sub>PcGa]<sub>2</sub>O.

traditional methods such as spin casting to be employed to produce suitable films for these solid-state applications [4]. Previously, the majority of optical limiting research has focused on solution based studies [5], with fewer reports investigating passive solid-state non-linear optical devices. For this reason, gallium phthalocyanine monomer (*t*Bu<sub>4</sub>PcGaCl) and its  $\mu$ -oxo-bridged dimer ([tBu<sub>4</sub>PcGa]<sub>2</sub>O) (Fig. 1) were embedded into the commercially available polymer poly(methylmethacrylate) (PMMA), a clear plastic commonly used as a shatterproof replacement for glass, to produce composite films acting as passive solid-state optical limiters. As a result, the Pc/PMMA system shows much higher non-linear absorption than the solution system.

## 2. Results and discussion

The synthesis and structural characterization of these two kinds of gallium phthalocyanines have been reported in details in our previous papers [6]. When compared with the UV/vis absorption spectrum of *t*Bu<sub>4</sub>PcGaCl in chloroform, whose main absorption bands are located at 695, 664.5(sh), 625 (Q-band) and 336 nm (B-band), respectively [6a], formation of the  $\mu$ -oxo-bridged [tBu<sub>4</sub>PcGa]<sub>2</sub>O dimer only leads to a weak (2 nm) blue shift of the Q-band and to a red shift ( $\sim$ 1 nm) of the B-band in the

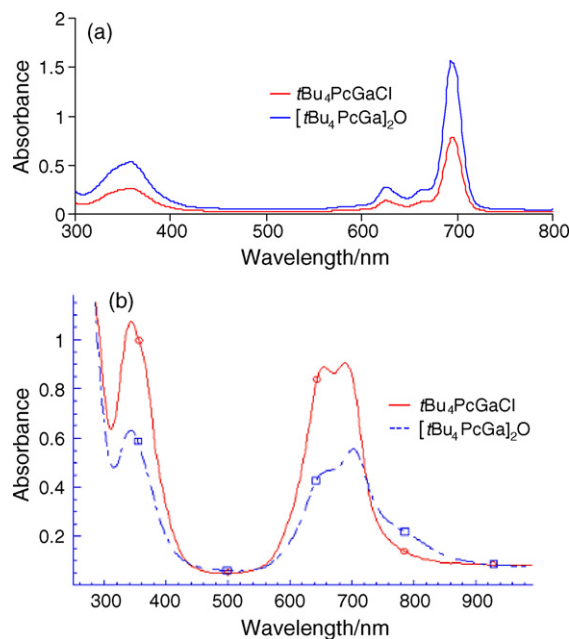


Fig. 2. UV/vis absorption spectra of gallium phthalocyanines (a) in dilute chloroform solutions and (b) in PMMA films.

same solvent (Fig. 2a) [6b]. Both PMMA solution and film are generally transparent over the visible wavelength region. In the solid state, the absorption spectra for both *t*Bu<sub>4</sub>PcGaCl/PMMA and [tBu<sub>4</sub>PcGa]<sub>2</sub>O/PMMA thin films (Fig. 2b) are very different from their solution spectra in which the Q-band looks like very sharp. In contrast to the dilute solutions, the absorption in the spectra of the films is apparently broader, including a wing beyond 800 nm on the red side of the Q-band, this being indicative of aggregated behavior, which is not unexpected due to the large partial concentration of about 10 g/L that was used in the film construction and the fact that the solid state is naturally more condensed. Although the spectral window comprised between the Q- and B-bands is slightly narrowed, it is still clearly evident, indicating that the composite films are still suitable for optical limiting of 532 nm light. The linear absorption coefficients ( $\alpha_0$ ) of both *t*Bu<sub>4</sub>PcGaCl and [tBu<sub>4</sub>PcGa]<sub>2</sub>O in the solid states are considerably larger than those in solutions, as listed in Table 1. The  $\alpha_0$ -value for the dimer in solution is just over double that for the monomer, however, in the solid-state case it is less than 50% of the value for the monomer. The absorption cross-section at 532 nm for the monomer phthalocyanine in PMMA is about a factor of 100 greater than that for the same molecule in solution

Table 1  
Linear optical properties and non-linear optical coefficients for Pc solutions (0.4 mM) and Pc/PMMA composites

	<i>t</i> Bu <sub>4</sub> PcGaCl in toluene	<i>t</i> Bu <sub>4</sub> PcGaCl/PMMA composite film	[tBu <sub>4</sub> PcGa] <sub>2</sub> O in toluene	[tBu <sub>4</sub> PcGa] <sub>2</sub> O/PMMA composite film
$\alpha_0$ (cm <sup>-1</sup> )	1.01	176.55	2.27	81.53
$I_0$ (GW cm <sup>-2</sup> )	0.33	0.35	0.28	0.29
$\beta$ ( $\times 10^{-8}$ cm W <sup>-1</sup> )	3.97	896.53	4.48	450.20
Im{ $\chi_{\text{eff}}^{(3)}$ } ( $\times 10^{-11}$ esu)	1.50	335.05	1.69	168.25
$\kappa = \sigma_{\text{ex}}/\sigma_0$	24.53 $\pm$ 0.36	3.68 $\pm$ 0.05	6.65 $\pm$ 0.36	5.05 $\pm$ 0.11
$F_{\text{sat}}$ (J cm <sup>-2</sup> )	10.39 $\pm$ 0.31	1.64 $\pm$ 0.05	8.50 $\pm$ 0.70	1.96 $\pm$ 0.08

under the conditions of the study. A possible explanation for this is that the concentration of absorbing molecules in the PMMA was significantly higher than in solution, or that the molecules had agglomerated in the PMMA to form dimers or higher associated clusters that absorbed more strongly than the monomers at 532 nm. It would thus be expected that the PMMA system shows higher non-linear absorption than the solution system.

In conjunction with the linear optical investigation the morphology of the film surface was investigated using a Zygo White Light Interferometer. This technique allows for detailed three-dimensional rendering by probing the interference pattern created along a selected surface area. Film thickness measurements were made using the same technique. For each composite film prepared, apart from minor fluctuations on the film-air surface, it is extremely smooth in relation to the wavelength (532 nm), used later to probe the NLO properties. The surface roughness and average thickness of the PMMA-based thin films used in this study are 150 nm, 38  $\mu\text{m}$  (for *t*Bu<sub>4</sub>PcGaCl/PMMA); and 40 nm, 53  $\mu\text{m}$  (for [*t*Bu<sub>4</sub>PcGa]<sub>2</sub>O/PMMA), respectively.

The open aperture Z-scan method [7] has been used to study imaginary third-order non-linear 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. On approaching the focus the intensity increases by several orders of magnitude relative to the intensity away from focus, thus inducing non-linear absorption in the sample. From Fig. 3 it can be noted that all Z-scans performed exhibit a decrease in transmittance about the focus typical of an induced positive non-linear absorption of incident light. The absorption mechanism is due to population of excited states through a multi-step non-linear absorption. No evidence of film fatigue or degradation was noted in the PMMA/Pc films, after numerous scans at varying laser intensity. Although the *t*Bu<sub>4</sub>PcGaCl/PMMA film exhibits the smallest  $\kappa$  (the ratio of the excited to ground state absorption cross-sections) value in the entire study at  $\kappa = 3.68 \pm 0.05$ , its non-linear absorption coefficient ( $\beta = 8.99 \times 10^{-6}$ ) and effective third order susceptibility ( $\text{Im}\{\chi_{\text{eff}}^{(3)}\} = 3.35 \times 10^{-9}$  esu) are largest among all samples, almost double that of the [*t*Bu<sub>4</sub>PcGa]<sub>2</sub>O/PMMA film (Table 1). The Pc/PMMA composite device reduced the saturation energy density ( $F_{\text{sat}}$ ) (Fig. 4) by a factor of about 6.3 when compared to the monomer, 4.3 for the dimer, and reduced the  $\kappa$ -value by a factor of about 6.7 for the monomer, 1.3 for the dimer. The monomer/PMMA composite film saturates at  $(1.64 \pm 0.05)$  J cm<sup>-2</sup> while the dimer composite exhibits a saturation fluence of  $(1.96 \pm 0.08)$  J cm<sup>-2</sup>. It should be noted that in these composite systems the crystallization and morphology of the polymer can be affected by additions of phthalocyanines. The pure PMMA film exhibited no NLO (including optical limiting) responses of its own.

In summary, the passive optical limiting performance of the gallium phthalocyanine monomer and dimer-based polymer composite materials has been studied. Pc/PMMA composite devices displayed a larger non-linear absorption coefficient and a lower saturable fluence for optical limiting. Further improvements in the optical limiting efficiency of the Pc/polymer

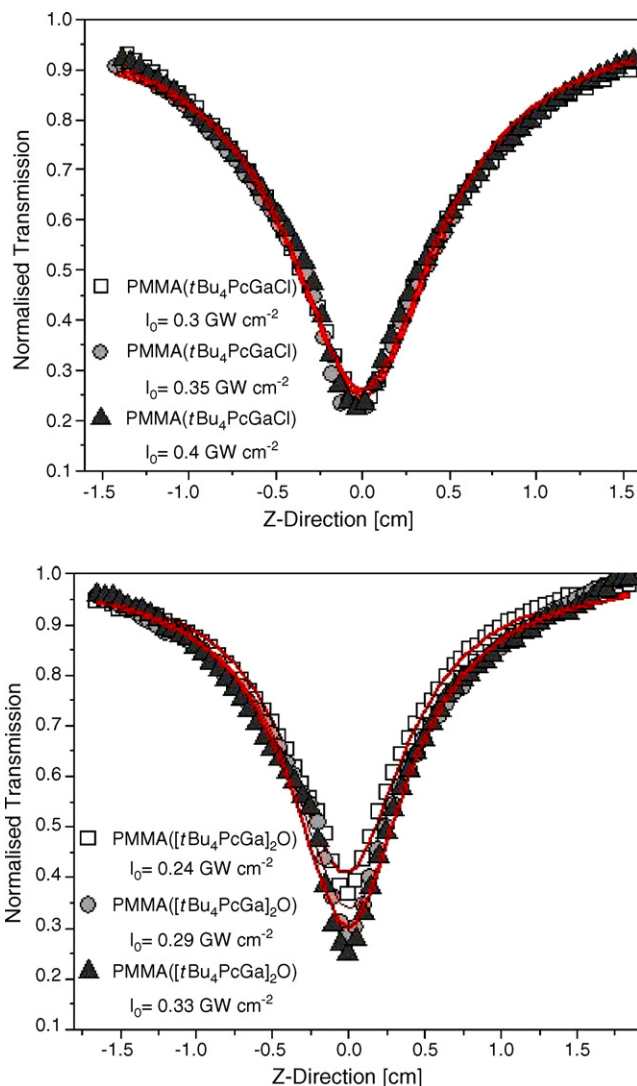


Fig. 3. Resulting open aperture curves with normalized transmission plotted as a function of sample position, Z for the *t*Bu<sub>4</sub>PcGaCl/PMMA film and [*t*Bu<sub>4</sub>PcGa]<sub>2</sub>O/PMMA film, at different focal intensities.

composites could be realized by variation of both phthalocyanine molecule and polymer host.

### 3. Experimental

*t*Bu<sub>4</sub>PcGaCl [6a] was obtained by the reaction of 4-*tert*-butylphthalonitrile with anhydrous GaCl<sub>3</sub> 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. The [*t*Bu<sub>4</sub>PcGa]<sub>2</sub>O dimer [6b] was prepared by the reaction of *t*Bu<sub>4</sub>PcGaCl with an excess of concentrated H<sub>2</sub>SO<sub>4</sub> at -20 °C. For the fabrication of the solid-state Pc/polymer films, a 100 g/L solution of PMMA in cyclohexanone was placed in a low power sonic bath for 48 h until completely dissolved. The gallium phthalocyanines were then added at a partial concentration of ~10 g/L, and were also sonically agitated until a completely dissolved, homogeneous solution was formed. Solid-state films samples of freshly dissolved Pc/polymer solutions were formed on quartz glass

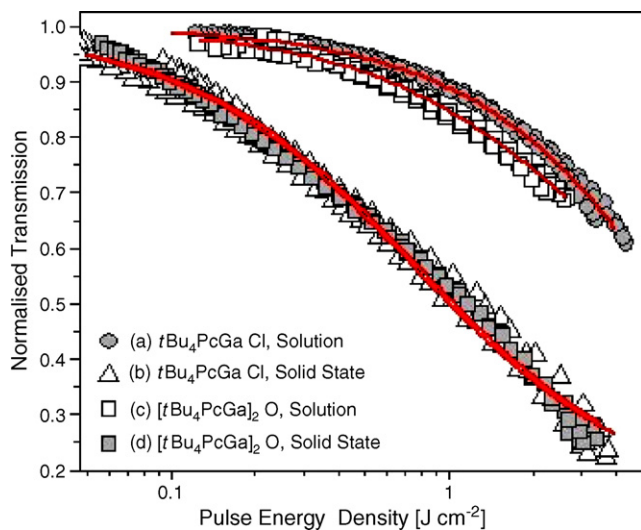


Fig. 4. Plot of normalized transmission against pulse energy density for compounds: (a)  $t\text{Bu}_4\text{PcGaCl}$  in toluene, (b)  $t\text{Bu}_4\text{PcGaCl/PMMA}$  film, (c)  $[\text{tBu}_4\text{PcGa}]_2\text{O}$  in toluene, and (d)  $[\text{tBu}_4\text{PcGa}]_2\text{O/PMMA}$  film, where the solid lines are theoretical fits to the experimental data.

substrates, using multi-layer conventional spin casting. These multi-layer Pc/polymer films were cast by sequentially spinning prepared composite solution with approximately 1 h of baking at  $60^\circ\text{C}$  between each layer to facilitate the removal of residual solvent. The linear optical properties of the materials in solutions and in the thin films were measured using a Shimadzu UV3100 UV–vis–NIR spectrometer.

All solution based NLO experiments were undertaken in quartz cuvettes with a path length of 1 mm. The concentration for each sample is about 0.4 mM. The solid-state non-linear optical investigation of the phthalocyanine–polymer composite system was conducted by depositing the composite onto quartz glass slides via conventional multi-layer spin coating techniques. The open aperture of the Z-scan experiment was used probing total transmittance through the samples. All optical limiting experiments described in this study were performed using  $\approx 6$  ns Gaussian pulses from a Q-switched Nd:YAG laser. The beam was spatially filtered to remove the higher order modes and tightly focused with a 9 cm focal length lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz.

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