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Photophysical And Nonlinear Optical Properties Of μ-Oxo-Bridged Indium And Gallium Phthalocyanines

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ABSTRACT

The photophysical and nonlinear optical properties of a μ-oxo-bridged phthalocyanine heterodimer, i.e., [$tBu_4PcGa\text{-}O\text{-}InPctBu_4$] **(5)**, where gallium is located in one macrocycle and indium is on the other macrocycle and the two metal atoms are connected through oxygen, have been described. Its photophysical properties are compared with the dimers: $[tBu_4PcGa]_2O$ **(3)** and $[tBu_4PcIn]_2O$ **(4)**. The very small shifts of Q- and B-bands for all μ-oxo Pc dimers 3-5 relative to the starting materials $tBu_4PcGaCl$ **(1)** and $tBu_4PcInCl$ **(2)** is indicative of a very weak interaction between two phthalocyanine rings in the ground state. The deactivation processes of the excited singlet state of **(5)** occur independently for tBu_4PcGa-O-moiety and tBu_4PcIn-O-moiety. Dimerization in the manner of **(5)** has no advantages over **(3)** and **(4)** from the point of view of optical limiting as it does not increase the ratio of the excited to ground state absorption cross sections nor does it reduce the saturation energy density (F_{Sat}). However if one were trying to fabricate a device with successive layers of increasing saturation energy density it may be useful as it does exhibit a different F_{Sat} to that found for the other compounds.

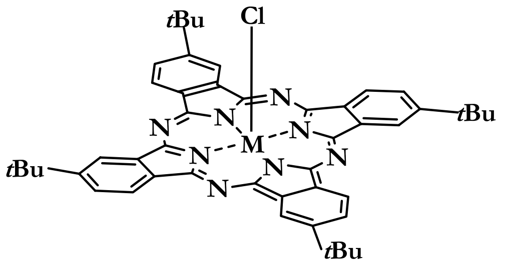
KEYWORDS

Ferrocene derivatives;
Bond length;
Bond angle;
Computational study;
Transition metal derivatives.

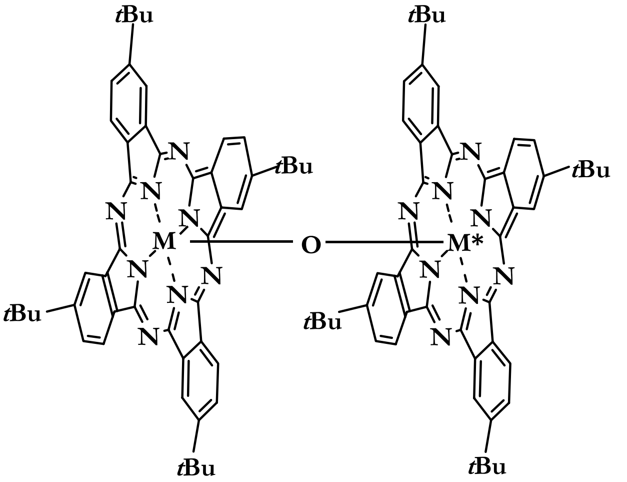
INTRODUCTION

The milestone invention of the first operating laser by Maiman[1] in 1960 has initiated a considerable strong and lasting interest in the fields of nonlinear optics and related materials chemistry[2-6]. The development of photonic and optoelectronic technologies, e.g. optical communications, high speed electro-optical information processing, short optical pulse generation and all-optical switching, significantly relies on the development of new nonlinear optical (NLO) materials. Among the large number of nonlinear optical absorbers that have been identified, phthalocyanines (Pc's) and their derivatives have recently emerged as promising materials due to their large optical nonlinearities, fast response times, and easy processability[7]. The first report on the third order NLO properties of Pc's appeared in 1987. Peripherally unsubstituted chlorogallium phthalocyanine (PcGaCl) and fluoroaluminium phthalocyanine (PcAlF) as the first Pc's were investigated for their third-order ($\chi^{(3)}$) nonlinear behavior[8], values of the order of 10^{-11} esu were found. The $\chi^{(3)}$ value for PcGaCl was half that of PcAlF at 1.064 μm. After this, the $\chi^{(3)}$ values of a various Pc's, including PcAlCl, PcInCl and PcTiO, were measured using THG techniques[7g,9a].

The chemical modifications of phthalocyanines (Pc's) through axial substitution at the central metal atom, or through peripheral substitution on the phthalocyanine macrocycles, offer opportunities to tailor the nonlinear response and thus control the optoelectronic properties of these molecules. Hanack and Chen et al. [10] have synthesized a series of highly soluble axially substituted and bridged indium(III), gallium(III), and titanium(IV) phthalocyanine monomers and dimers, and systematically studied the effect of axial substitution on the NLO properties (including optical limiting properties) of phthalocyanines. The NLO properties of these materials were robust to structural changes in the axial position. The axially bridged Pc dimers exhibit increased NLO response in comparison with monomeric phthalocyannes. In this article, we report the photophysical and NLO properties of μ-oxo-bridged soluble phthalocyanine heterodimer [tBu_4PcGa-O-$InPctBu_4$] **(5)** (Figure 1). The photophysical data of $[tBu_4PcGa]_2O$ **(3)** and $[tBu_4PcIn]_2O$ **(4)**[10d] are also given in the present paper for comparison purposes. Although the μ-oxo axially bridged unsubstituted Pc heterodimer [PcGa-O-AlPc] has been briefly mentioned in the literature, this material is insoluble in some common



tBu_4PcMCl (mixture of structural isomers)
M = Ga^{3+} (1), In^{3+}(2)



tBu_4PcM-O-M^*PctBu_4
M = M* = Ga^{3+} (3)
M = M* = In^{3+} (4)
M = Ga^{3+}, M* = In^{3+} (5)

Figure 1: Molecular structures of μ-oxo-bridged gallium and indium phthalocyanine dimers and their starting materials

organic solvents[11].

EXPERIMENTAL

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 deaerated 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 exciting 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. The picosecond transient absorption spectra were measured by the pump and probe method using a Ti:sapphire regenerative amplifier seeded by SHG of Er-doped fiber laser (Clark-MXR CPA-2001 plus, 1 kHz, fwhm 150 fs). A white continuum pulse used as a monitoring light was generated by focusing the fundamental of the amplifier on a rotating H_2O cell. The samples were excited by SHG (388 nm) of fundamental or output of OPA (Clark-MXR vis-OPA, 560 nm). The monitoring light transmitted through the sample in a rotating cell was detected with a dual MOS detector (Hamamatsu Photonics, C6140) equipped with a polychromator.

A very convenient and fast experimental method to assess materials for NLO (including optical limiting) is the open aperture z-scan experiment. This measures the total transmittance through the sample as a function of incident laser intensity while the sample is gradually moved through the focus of a lens (along the z-axis). 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 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. All samples were measured in quartz cells with a 1 mm optical path length, and at concentrations of about 10^{-4} M in spectroscopic grade toluene.

RESULTS AND DISCUSSION

The $[tBu_4PcM]_2O$ dimers [M=Ga^{3+}(3), In^{3+}(4)] were prepared by the reaction of tBu_4PcMCl [M = Ga^{3+}(1), In^{3+}(2)][10a,10e] with excess of concentrated H_2SO_4 at –20°C[10d]. Compound **(5)** [tBu_4PcGa-O-$InPctBu_4$], a purplish blue colored product, was obtained in 73% yield using the similar method mentioned above. In order to ensure the uniformity of a mixture of $tBu_4PcGaCl$ **(1)** and $tBu_4PcInCl$ **(2)** (molar ratio: 1:1) as starting materials, before starting to prepare compound **(5)**, this mixture was previously soluble in CH_2Cl_2, followed by stirring for 1 hour in room temperature. And then solvent was removed under reduced pressure. The obtained mixture was dried at 80°C in vacuum for several hours, and then was used for the further reaction for the preparation of 5. The confirmation of the structure of 5 has been carried out by a variety of techniques such as UV/Vis, IR, EXAFS, ^{13}C NMR, ^1H NMR, FAB-MS and elemental analysis. The molecular ion peaks of 3 and 4 as possible byproducts were not apparently detected in the FAB-MS spectrum of 5. EXAFS measurements of this complex were carried out at both Ga K-edge and In K-edge. As a result, the distance between gallium atom and bridging oxygen atom is about 1.88 Å, while the In-O bond length is found to be 2.16 Å[9b].

The UV/Vis absorption and fluorescence data of compounds **(1-5)** are given in TABLE 1. As reported by Chen and Hanack et al.,[10] the influence of different axial substituents on the linear optical properties of indium or gallium phthalocyanine monomers is very small. In comparison with the UV/Vis absorption spectra of 1 and 2, the formation of 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,[12] and to a red-shift (1.5 nm) of the B-band[10d]. The red-shift of the B-band is related to

TABLE 1: Steady-state absorption and fluorescence data of compounds (1-5)

Samples	λ^{abs} / nm*					λ_{max}^{fluo},**	τ_f /ps**
	B(1.0)	B(0.0)	Q(2.0)	Q (1.0)	Q(0.0)	(nm)	(λ_{ex}= 410 nm)
1	338.0	357.0	625.5	664.0	695.0	702	2570
2	339.7	359.5	628.2	667.1	697.3	705	470
3	341.5	357.5	623.5	662.5	693.0	701	3570
4	343.0	360.0	628.0	665.5	697.0	705	638
5	340.0	358.0	626.0	664.5	695.5	703	610 (73 %) 3920 (27 %)

*measured in chloroform; ** obtained in deaerated anhydrous toluene

the interaction of the oxygen atom with the central gallium and indium atoms. In the case of 5, the Q-band maximum of 5 is located between the Q-band maxima of 3 and 4. While the UV/Vis spectrum of the mixture of 3 and 4 (molar ration: 1:1) is apparently broaden compared to that of 5 under the same concentration. The molar extinction coefficients (ε) of the absorption bands of 5 is apparently larger than that of 4, but less than that of 3. The very small shifts of Q- and B-bands for all μ-oxo Pc dimers 3-5 relative to the starting materials 1 and 2 suggest a very weak interaction between two phthalocyanine rings in the ground state.

The fluorescence decay time profile of 5 was curve-fitted with two single exponential functions, giving two fluorescence lifetimes (τ_{f1}=0.61 ns(73%) and τ_{f2}=3.92 ns (27%)). As can be seen from TABLE 1, the τ_{f1} value is similar to those of $tBu_4PcInCl$ and $[tBu_4PcIn]_2O$, while the τ_{f2} value is slightly larger than those of $tBu_4PcGaCl$ and $[tBu_4PcGa]_2O$. This suggests that the deactivation processes of the excited singlet state occur independently for tBu_4PcGa-O-moiety and tBu_4PcIn-O-moiety.

The nanosecond transient absorption spectrum observed by the excitation of 5 with 355 nm laser light in deaerated toluene shows a transient absorption band at 520, which is attributed to the triplet-triplet absorption of the Pc compounds[10d]. On addition of O_2, the decay of the 520 nm band was accelerated, indicating that the energy transfer takes place from the triplet excited states of the Pc compounds to O_2, yielding probably $^1O_2$. In the absence of O_2, compound **(5)** exhibits two exponential-decay processes, while homodimers (3,4) and monomers (1,2) show a single exponential decay. From the initial fast decay part of 5, the triplet excited state lifetime (τ_{T1}) was estimated to be 63 μs, longer than that of $[tBu_4PcIn]_2O$ (42 μs). From the slow decay part of 5, the triplet excited state lifetime (τ_{T2}) was found to be 100 μs, much shorter than that of $[tBu_4PcGa]_2O$ (357μs). These findings suggest a considerable interaction between tBu_4PcGa- and tBu_4PcIn-moiety.

Open aperture Z-scan spectra were collected for various pulse energies for each compound. The theory of Sheik-Bahae et al.[13] was fitted to the open aperture data and the imaginary third order susceptibilities, $\mathrm{Im}\{\chi^{(3)}\}$, and the second molecular hyperpolarizabilities, γ, were calculated from the fits. The waist radius (ω_0) of the beam was treated as a free parameter in the fitting algorithm and was found to be remarkably stable over all compounds 1-5 which exhibited on average $\omega_0 \approx 23.6$ μm in all cases. TABLE 2 gives the numerical values for $\mathrm{Im}\{\chi^{(3)}\}$ and γ. It is interesting that the indium phthalocyanine monomer (2) exhibited the largest value of $\mathrm{Im}\{\chi^{(3)}\}$ ($\approx(1.6 \pm 0.3) \times 10^{-11}$ esu) while the indium-gallium Pc dimer 5 exhibited the lowest with $\mathrm{Im}\{\chi^{(3)}\} \approx (1.1 \pm 0.2) \times 10^{-11}$ esu. However 1 exhibited the lowest molecular imaginary hyperpolarizability γ [$\approx (0.84 \pm 0.10) \times 10^{-32}$ esu] in the study while 4 exhibited the largest with $\gamma \approx (2.4 \pm 0.4) \times 10^{-32}$ esu. The molecular imaginary hyperpolarizability for 5 was found to be between these two extremes at γ $(1.5 \pm 0.3) \times 10^{-32}$ esu, the lowest γ for all the dimers **(3-5)**.

After manipulating the open aperture spectra, the normalized transmission (T_{norm}) was plotted against the incident energy density per pulse (F) to further investigate the optical limiting (Figure 2). The nonlinear absorption coefficient given by equation 1 was

TABLE 2: Summary of the nonlinear optical properties for compounds (1-5) in toluene

Samples	Conc. ($g.L^{-1}$)	α_0 (cm^{-1})	Im{$\chi^{(3)}$} ($\times 10^{-11}$ esu)	γ ($\times 10^{-32}$ esu)	κ σ_{ex}/σ_0	F_{Sat} ($J.cm^{-2}$)
$tBu_4PcGaCl$	0.5	1.10	1.2 ± 0.2	0.84 ± 0.1	13.5 ± 0.4	27.0 ± 1.0
$tBu_4PcInCl$	0.5	0.53	1.6 ± 0.3	1.30 ± 0.2	27.5 ± 0.6	24.2 ± 0.8
$[tBu_4PcGa]_2O$	0.5	1.60	1.3 ± 0.2	1.76 ± 0.3	11.3 ± 1.0	13.5 ± 1.0
$[tBu_4PcIn]_2O$	0.5	1.13	1.5 ± 0.3	2.40 ± 0.4	12.4 ± 0.3	7.6 ± 0.3
tBu_4PcGa-O-$InPctBu_4$	0.5	1.02	1.1 ± 0.2	1.50 ± 0.3	10.0 ± 0.2	14.6 ± 0.6

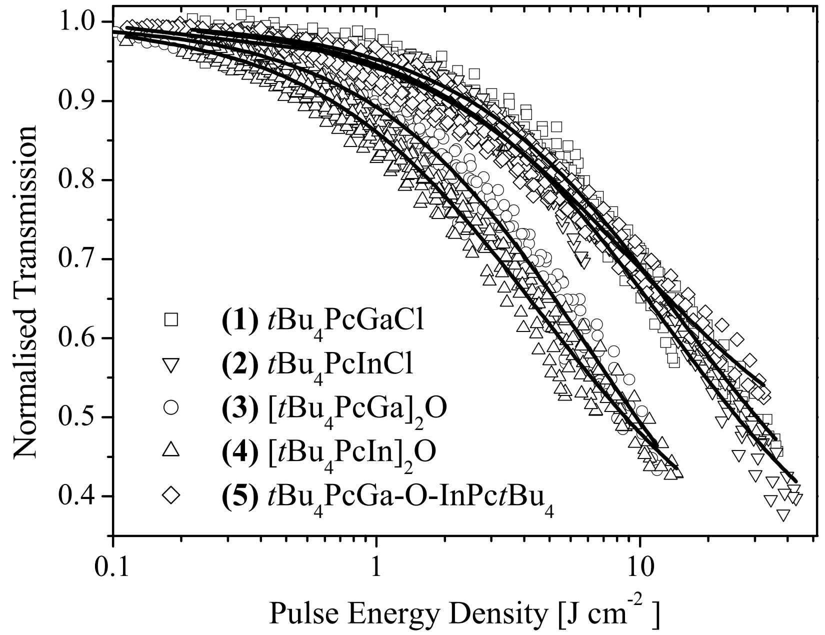


Figure 2: Plot of normalized transmission against pulse energy density for (1) $tBu_4PcInCl$, (2) $tBu_4PcGaCl$, (3) $[tBu_4PcGa]_2O$, (4) $[tBu_4PcIn]_2O$, and (5) tBu_4PcGa-O-$InPctBu_4$. The fitting parameters are given in TABLE 2.

derived using laser rate equations[13,14] and applied in a static state approximation, fitted using least squares regression. F_{sat} is the energy density at which the output reaches its saturated value. κ is the excited to ground state absorption cross-section ratio (σ_{ex}/σ_0). The parameters κ (realistically σ_{ex} as α_0 was measured) and F_{Sat} were both treated as free constants in the fitting algorithm. The α_0, κ and F_{Sat} values for each compound are also presented in TABLE 2.

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

As shown in figure 2, the gallium **(3)** and indium **(4)** dimers saturate at lower energy densities than their mononuclear analogues 1 and 2. The F_{Sat} values returned from fitting the transmission as a function of energy density using equation (1) as the nonlinear absorption coefficient reveal that 3 and 4 saturate at (13.5 ± 1.0) J cm^{-2} and (7.6 ± 0.3) J cm^{-2} respectively. In comparison their mononuclear analogues saturate at double the dimer value for the gallium case (1 and 3) and more than triple the dimer value for the indium case (2 and 4). Compound **(5)** exhibited an F_{Sat} value larger than that of the other dimers 3 and 4 but less than that of the monomers 1 and 2. Its F_{Sat} value at $F_{Sat} \approx$ (14.6 ± 0.3) J cm^{-2} is closest to that for the gallium dimer 3 which exhibited $F_{Sat} \approx$ (13.5 ± 1.0) J cm^{-2}. The ratio of the excited to ground state absorption cross sections, the κ coefficient, is largest for the indium monomer 2 and smallest for the tBu_4PcGa-O-$InPctBu_4$ dimer 5. In both the indium and gallium monomer and dimer cases 1-4 the monomer exhibited a larger κ coefficient than the corresponding dimer. The remarkably low linear absorption coefficient of 2 explains why its κ coefficient is at least two times greater than that exhibited by any of the other compounds.

Thus one can only conclude that dimerization in the manner of 5 has no advantages over 3 and 4 from the point of view of optical limiting as it does not increase the ratio of the excited to ground state absorption cross sections nor does it reduce the saturation energy density. However if one were trying to fabricate a device with successive layers of increasing saturation energy density it may be useful as it does exhibit a different F_{Sat} to that found for the other compounds.

SUMMARY

The very small shifts of Q- and B-bands for all μ-oxo Pc dimers 3-5 relative to the starting materials 1 and 2 is indicative of a very weak interaction between two phthalocyanine rings in the ground state. The fluorescence decay time profile of 5 was curve-fitted with two single exponential functions, implying that the deactivation processes of the excited singlet state occur independently for tBu_4PcGa-O-moiety and tBu_4PcIn-O-moiety. Upon excitation with nanosecond laser pulses at 355 nm, the observed transient absorption spectra for all compounds are almost similar. In the absence of O_2, compound **(5)** exhibits two exponential-decay processes, while homodimers (3,4) and monomers (1,2) show a single exponential decay. All compounds exhibit strong reverse saturable absorption at 532 nm excitation. In comparison with homodimers (3,4), dimerization in the manner of 5 has no advantages over 3 and 4 from the point of view of optical limiting as it does not increase the ratio of the excited to ground state absorption cross sections nor does it reduce the saturation energy density. However if one were trying to fabricate a device with successive layers of increasing saturation energy density it may be useful as it does exhibit a different F_{Sat} to that found for the other compounds.

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