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Enhanced optical limiting performance of substituted metallonaphthalocyanines with wide optical limiting window



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ABSTRACT

Octa-(4-*tert*-butylphenoxy) substituted naphthalocyanines coordinated with different central metals (Ga, In) were synthesized and their photophysical and optical limiting properties were investigated. The naphthalocyanines substituted peripherally with bulky groups have good solubility in organic solvents and the Q band absorption shows an obvious red shift to the near-IR region at about 800 nm. Studies on transient absorption spectra, photophysical parameters and optical limiting properties indicate that these compounds exhibit good optical limiting performance. The optical limiting thresholds of the naphthalocyanines are 0.26, 0.15 J cm⁻² for Gallium naphthalocyanines and Indium naphthalocyanines, respectively. The naphthalocyanines possess higher triplet state quantum yields (Φ_T) and triplet-minus-ground state extinction coefficients ($\Delta \varepsilon_T$) than other simple phthalocyanines, which results in better optical limiting behaviour.

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1. Introduction

Since the discovery of the laser in the 1960s, it has been extensively investigated and widely used as high-intensity light sources in many fields such as communication, image processing, optical storage and other applications [1]. Laser techniques brings enormous advantages for human society, while it also brings a potential hazard for human eyes and optical sensors. Therefore, there is a strong need to develop optical limiting materials for protection of optical sensors and human eyes from hostile or accidental intense laser pulses [2]. In the past years, some materials have been studied to meet this challenge, including fullerenes, porphyrins, phthalocyanines (Pcs) and other organicmetallic compounds [3]. Among them, the Pcs with two-dimensional highly conjugated delocalized π -electron system and metal-coordination bond are outstanding optical limiting materials because of their low linear absorption in the optical limiting wavelength window, strong reverse saturable absorption (RSA) as well as an ultrafast response time [4]. The occurrence of RSA requires that the excited state absorption cross-section σ_{ex} is greater than that of the ground state σ_g [5]. For practical applications of optical limiting effect, the reverse saturable absorbers are desirable, which allows high transmission of light at low optical fields over a large spectral window [6]. Introduction of substituent groups and central metals can effectively change the photophysical properties and improve optical limiting behaviour [7].

Up to now, phthalocyanine-based materials are still being investigated to improve their optical limiting performance and expand their optical limiting window from visible to near-IR range in order to meet the requirements of practical applications. Naphthalocyanines have larger π electron conjugation system than phthalocyanines, which will result in different photophysical properties and optical limiting behaviour and should be potential compounds to meet this challenge [8]. As a kind of potential optical limiting materials, different naphthalocyanines and metal naphthalocyanines have been studied in theoretical and experimental aspects by some research groups [3i,9]. The results showed that the optical limiting properties vary from different structures, even only different substituents might change the optical limiting properties dramatically. Our group had investigated the optical properties of a series of peripherally substituted phthalocyanines with different





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central metals [10]. The results indicated that the bulky substituted groups could enhance the solubility and decrease the molecular $\pi-\pi$ interaction, ultimately resulting in the improvement of the optical limiting performance. For the purpose of providing useful information for the practical applications in the field of optical limiting materials, we synthesized octa-(4-*tert*-butylphenoxy) substituted metallo-naphthalocyanines, extensively studied their photophysical and optical limiting properties, and analysed the difference of properties between naphthalocyanines and phthalocyanines.

2. Experimental

2.1. General

All organic solvents were commercially available, dried and distilled by appropriate methods before use. Phthalocyanines of **5b** and **6b** were synthesized by a method based on our published papers [10]. ¹H NMR spectra were performed on a DPX400 Bruker FT-NMR spectrometer with DMSO-d₆ as solvent and tetramethylsilane (TMS) as internal standard. The mass spectra were obtained on a Biflex MALDI-TOF or Micromass GCT-MS spectrometer. Elemental analyses were performed on a Carlo Erba-1106 elemental analyzer. UV–vis absorption spectra were recorded on a Hitachi U-3010 spectrophotometer.

Fluorescence spectra were recorded by a Hitachi F-4500 fluorescence spectrophotometer. Fluorescence quantum yields (Φ_F) of S₁ were determined by the comparative method using zinc phthalocyanine in 1-chloronaphthalene ($\Phi_F = 0.30$) as reference standard [11]. The fluorescence lifetimes of these phthalocyanines and naphthalocyanines were investigated with single-photon counting technique with Edinburgh FL900 spectrophotometer.

Transient absorptions at nanosecond time scale were investigated in argon-saturated THF solution at the concentration of 5×10^{-6} M. The excitation light was the harmonic of Nd:YAG laser (Continuum Surelite II, 355 nm and 7 ns FWHM). The signals were detected by Edinburgh LP900 and recorded on Tektronix TDS 3012B oscilloscope and computer. The triplet-minus-ground state extinction coefficients ($\Delta \epsilon_T$) were calculated by the method of total depletion or saturation [12]. The quantum yields of the triplet state were determined by the comparative method [13], using unsubstituted ZnPc in 1-chloronaphthalene as reference standard ($\Phi_T = 0.65$). The triplet lifetimes were obtained by kinetic analysis of the transient absorption.

The optical limiting properties were measured by the standard setup of our previously reported method [10]. All samples were dissolved in THF, placed in a 1.0 cm path length quartz cell and the solutions were bubbled with pure argon for about 30min to remove the dissolved O₂. A 532 nm ns Nd:YAG laser (Continuum Surelite II, 7ns FWHM) was used as the laser source.

2.2. Synthesis

2.2.1. 4,5-Dibromo-o-xylene (1)

lodine (1.6 g, 6.3 mmol) was added to *o*-xylene (40 g, 0.38 mol) and stirred under ice-water mixture, then bromine (124 g, 0.77 mol) was dropped slowly to keep the temperature at -5 to 0 °C. After stirring for 20 h, the mixture was dissolved in ether, washed with aqueous potassium hydroxide and fresh water for three times, dried with anhydrous MgSO₄ and evaporated the solvent to obtain a semi-solid crude product. After recrystallization from alcohol, 61.5 g pure 4,5-dibromo-oxylene **1** was obtained (yield, 62%). Mp: 85–88 °C; ¹H NMR (DMSO-d₆, 400 Hz): 7.36 (s, 2H), 2.18 (s, 6H) ppm; MS-EI (*m*/*z*): 264 (M⁺), 185 (M⁺–Br), 104 (M⁺–2Br).

2.2.2. 1,2-Dibromo-4,5-bis(dibromomethyl)benzene (2)

A mixture of **1** (26.4 g, 0.1 mol), NBS (90 g, 0.5 mol) and 2,2'azobisisobutyronitrile (AIBN, 0.1 g, 0.06 mmol) were added to CCl₄ (200 mL), after stirring for 15 h at 95 °C under a UV lamp irradiation, the mixture was filtered while hot and the filtrate was evaporated to obtain an yellowish solid. The crude product was recrystallized from CCl₄ and dried at 45 °C under vacuum to obtain 53.0 g of **2** (yield, 91%). Mp: 122 °C; ¹H NMR (DMSO-d₆, 400 Hz): 8.09 (s, 2H), 7.62 (s, 2H) ppm; MS-EI (*m/z*): 579 (M⁺), 498 (M⁺–Br), 420 (M⁺–2Br), 339 (M⁺–3Br), 260 (M⁺–4Br).

2.2.3. 2,3-Dicyano-6,7-dibromo-naphthalene (3)

A mixture of **2** (14.5 g, 0.025 mol), fumaronitrile (2.0 g, 0.03 mol) and NaI (6.0 g, 0.04 mol) in DMF were stirred for 13 h at 80 °C under a nitrogen atmosphere. After the reaction mixture was cooled overnight, it was poured into saturated NaHSO₃ solution (400 mL), the obtained yellowish precipitate was filtered, washed with water and dried under vacuum at 80 °C. The crude product was recrystallized from CH₂Cl₂ to obtain 12.0 g white powder of **3** (yield, 71%). Mp >250 °C;¹H NMR (DMSO-d₆, 400 Hz): 8.91 (s, 2H), 8.75 (s, 2H) ppm; MS-EI (*m/z*): 336 (M⁺), 255 (M⁺–Br), 1780 (M⁺–2Br).

2.2.4. 2,3-Dicyano-6,7-di(4-tert-butyl)phenoxyl naphthalene (4)

A mixture of **3** (3.4 g, 10 mmol), 4-*tert*-butylphenol (3.3 g, 22 mmol) and anhydrous potassium carbonate (11.0 g, 80 mmol) was added to dry DMF (30 mL) and stirred at 100 °C for 12 h under nitrogen condition. After the reaction mixture was cooled, it was poured into cold water (100 mL), the obtained white-yellowish precipitate was collected by suction filtration. The crude product was crystallized from alcohol to give 4.3 g of white crystals **4** (yield, 90%). Mp: 205–208 °C;¹H NMR (DMSO-d₆, 400 Hz): 8.29 (s, 2H), 8.07 (s, 2H), 7.48–7.51 (d, *J* = 7.6 Hz, 4H), 7.07–7.10 (d, *J* = 8.8 Hz, 4H), 1.38 (s, 18H) ppm; MS-EI (*m*/*z*): 474 (M⁺), 459 (M⁺–CN), 389 (M⁺–C₆H₁₂)), 326 (M⁺–tBuPhO-).

2.2.5. Octa-(4-tert-butylphenoxyl) gallium naphthalocyanine (5a)

Compound 4 (2.4 g, 5 mmol) was added to dry 1-pentanol (30 mL) containing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.5 mL) as a catalyst. The mixture was stirred for 1 h at 100 °C under a nitrogen atmosphere and then anhydrous $GaCl_3$ (0.26 g, 1.5 mmol) was added. The mixture was slowly brought to boiling over 1 h and then refluxed for 36 h, after the reactant was cooled to room temperature, methanol/water (1:1, 60 mL) mixture was added, the obtained yellow-green precipitate was filtered, washed with hydrochloric acid (5%, 50 mL) and methanol (50 mL), and then purified by a silica-gel column with CH₂Cl₂/ethanol (10:1) as eluent. The final product was dried at 50 °C under vacuum overnight to give 1.7 g (yield: 67%) of **5a** (C₁₂₈H₁₂₀N₈O8₄GaCl). Mp >250 °C; UV-vis $(THF) \lambda_{max}$: 799, 340 nm; ¹H NMR (DMSO-d₆, 400 Hz): 9.05 (s, 8H), 8.29 (s, 8H), 7.51–7.53 (d, J = 7.6 Hz, 16H), 7.36–7.39 (d, J = 7.2 Hz, 16H), 1.38 (s, 72H) ppm; MALDI-TOF-MS (m/z): 2001.1(M⁺), $1966.2(M^+-Cl),$ $1817.1(M^+-Cl-OR),$ $1669.0(M^+-Cl-2OR);$ Elemental analysis (%), calculated for C₁₂₈H₁₂₀N₈O8₄GaCl: C 76.73, H 6.04, N 5.59; found C 76.73, H 5.76, N 5.96.

2.2.6. Octa-(4-tert-butylphenoxyl) indium naphthalocyanine (6a)

Compound **6a** was prepared by a similar method to compound **5a** in 58% yield ($C_{128}H_{120}N_8O_8$ InCl). Mp >250 °C; UV–vis (THF) λ_{max} : 802, 339 nm; ¹H NMR (DMSO-d₆, 400 Hz): 9.17 (s, 8H), 8.41 (s, 8H), 7.56–7.67 (d, *J* = 8.8 Hz, 16H), 7.37–7.45(d, *J* = 8.8 Hz, 16H), 1.39 (s, 72H) ppm; MALDI-TOF-MS (*m*/*z*): 2046.2 (M⁺), 2010.6 (M⁺–Cl), 1861.5(M⁺–Cl–OR); Elemental analysis (%) [14], calculated for C₁₂₈H₁₂₀N₈O₈InCl: C 75.04, H 5.90, N 5.47; found C 75.72, H 5.74, N 5.76.

3. Results and discussion

3.1. Synthesis and characterization

Two different central metal (Ga and In) naphthalocyanines with peripheral substituents of 4-*tert*-butylphenoxy at two γ -positions were synthesized (shown in Scheme 1). o-Xylene was brominated to give 1.2-dibromo-4.5-dimethylbenzene **1** [15], **1** was successively brominated with NBS on the two methyl groups under UV irradiation using AIBN as catalyst in CCl₄ to obtain 2 [16], then cyclization of 2 with fumaronitrile to obtain dibrominated dinitriles 3 [17]. After alkyloxylation of **3** by 4-tert-butylphenol, the precursor of newly substituted dinitrile 4 was obtained. The cyclization of the dinitrile **4** with MCl_3 (M = Ga, In) resulted in the corresponding naphthalocyanines **5a** and **6a** in 1-pentanol at 140 °C using DBU as catalyst under N₂ atmosphere. This lower reaction temperature in cyclization of dinitriles resulted in good yields [18]. The naphthalocyanines were purified by silica-gel column and then sublimated under vacuum to remove all of the residual impurity. All naphthalocyanines were characterized by elemental analysis and spectroscopic methods including UV-vis, ¹H NMR and MALDI-TOF-MS, which were consistent with the proposed structures. It is worth pointing out that these naphthalocyanines exhibit excellent solubility in many organic solvents such as THF, chloroform, DMF and DMSO, which is suitable for the investigation of photophysical and optical limiting properties in solution.

3.2. Ground state absorption and fluorescence emission

Ground state absorptions of naphthalocyanines were investigated (shown in Fig. 1). Naphthalocyanines **5a** and **6a** display the Q bands at 799 and 802 nm, respectively. They are significantly red-shifted compared with the corresponding phthalocyanines with the same central metal **5b** (714 nm) and **6b** (722 nm), because of the larger π electron conjugation system of naphthalocyanine reducing the energy gap between the S₀ and S₁



Fig. 1. UV–vis absorption spectra of naphthalocyanines of **5a**, **6a** and phthalocyanines **5b**, **6b** at the concentration of 5.0×10^{-5} M (a) and the absorption spectra of **6a** in THF at different concentrations, the insert is the value of OD vs the concentration (b).

states. Meanwhile, the B bands of the naphthalocyanines only have slight red-shifts which results in wider optical limiting windows. According to the wavelength at the intersection points of the normalized absorption and fluorescence spectra, the energy



Scheme 1. Synthetic route of the naphthalocyanines 5a, 6a and the structures of the reference samples 5b and 6b. a) Br₂, I₂, -5 to 0 °C, 16 h; b) NBS, AIBN, UV irradiation, CCI₄, 8 h; c) fumaronitrile, NaI, DMF, 80 °C, 10 h; d) 4-tert-butylphenol, K₂CO₃, DMF, 100 °C, 8 h; e) MCI₃, DBU, 1-pentanol, 36 h.

 Table 1

 Photophysical parameters of naphthalocyanines and phthalocyanines.

	λ/nm (Q)	λ/nm (B)	$\epsilon(Q)/M^{-1} cm^{-1}$	Emission (Q)/nm	Emission (B)/nm	$\Phi_{\rm F}$ (S ₁)	$ au_{ m F}({ m S}_1)/$ ns	E (S ₁)/ ev
5a	799	340	2.1×10^5	809	411	0.066	2.51	1.55
6a	802	339	1.7×10^5	813	411	0.028	0.71	1.54
5b	714	331	1.5×10^{5}	723	406	0.429	3.66	1.73
6b	722	335	1.1×10^5	735	403	0.030	0.76	1.71

level of S₁ state is about 1.5ev for naphthalocyanines and about 1.7ev for phthalocyanines, respectively, and they are summarized in Table 1. UV–vis absorptions of 6a in THF at different concentrations were investigated (Fig. 1b), which follows the Beer's Law when the concentration is below 1.0×10^{-4} M. This result is in agreement with the assumption that the aggregation can be effectively suppressed by introducing the peripheral substituents and the axial chloride atom.

Fluorescence emission spectra were obtained as shown in Fig. 2. For naphthalocyanines **5a** and **6a**, the fluorescence emissions display shorter Stokes shifts (7 nm) than that of phthalocyanines **5b** and **6b** (15 nm). However, the lower energy gap between S₁ and S₀ states of naphthalocyanines **5a**, **6a** results in lower fluorescence quantum yields than phthalocyanines **5b** and **6b**, as summarized in Table 1.

3.3. Transient absorption

The transient absorption of naphthalocyanines **5a** and **6a** was investigated at the concentration of 5.0×10^{-5} M with excited wavelength at 355 nm (Fig. 3). All compounds exhibit strong and broad T_1-T_n absorption at about 600 nm with clear bleaching at Q and B bands. The λ_{max} of transient absorptions of 5a and 5b at 610 nm and 620 nm respectively, are red-shift compared with the

Table 2

Parameters of triplet state for naphthalocyanines 5a,	6a and phthalocyanines 5b, 6b.
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Compounds	λ _{max} / nm (T _n)	$\varepsilon_0/\mathrm{M}^{-1}~\mathrm{cm}^{-1}$	$\Delta \epsilon_{\rm T}/{\rm M}^{-1}~{\rm cm}^{-1}$	$ au_{\mathrm{T}}/\mathrm{\mu s}$	$k_{\rm ST}/{\rm s}^{-1}$	Φ_{T}
5a	610	$3.0 imes 10^3$	$12.8 imes 10^4$	71.4	4.2×10^9	0.70
6a	620	2.6×10^3	12.6×10^4	8.3	2.1×10^{10}	0.72
5b	580	1.2×10^3	6.4×10^4	114.2	3.5×10^8	0.51
6b	590	$6.1 imes 10^2$	7.2×10^4	24.1	$2.7 imes 10^9$	0.62

phthalocyanines of **5b** and **6b** at 580 nm and 590 nm, which should be caused by a smaller energy gap between T_1 and T_n states of the naphthalocyanines than that of phthalocyanines.

The triplet state quantum yields (Φ_T) and the rate of intersystem crossing (k_{ST}) were evaluated [10] and summarized in Table 2. The values of Φ_T are 0.70 and 0.72 for **5a** and **6a**, which are higher than that of 0.51 and 0.62 for **5b** and **6b**, respectively. The k_{ST} values of naphthalocyanines are one order of magnitude larger than corresponding phthalocyanines. The values of Φ_T and k_{ST} in Table 2 suggest that naphthalocyanines have lower energy gap between S₁ and T₁ states, leading to higher probability of intersystem crossing from S₁ to T₁ states. In addition, the triplet-minus-ground state extinction coefficient ($\Delta \epsilon_T$) [10] and the molar extinction coefficient of ground state absorption (ϵ_0) at 532 nm are evaluated and summarized in Table 2. The values of $\Delta \epsilon_T$ are higher for naphthalocyanines which would result in a stronger T₁-T_n absorption and finer optical limiting effect.

Decays of triplet state were investigated as shown in Fig. 4(b). The lifetimes of T_1 state, τ_T , are 71.4, 8.3 µs for **5a** and **6a**, and 114.2, 24.1 µs for **5b** and **6b**, respectively. Compared with the phthalocyanines, the naphthalocyanines possess shorter triplet state lifetimes. However, for the nanosecond pulse laser, the lifetimes are long enough to achieve the reverse saturable absorption (RSA) and optical limiting behaviour.



Fig. 2. a) Fluorescence emission spectra of naphthalocyanines 5a, 6a and phthalocyanines 5b, 6b. b) Decay profiles of naphthalocyanine 5a and phthalocyanine 5b.



Fig. 3. Transient absorption spectra of naphthalocyanines 5a and 6a (excited at 355 nm).



Fig. 4. (a) Transient absorption spectra of 5a, 6a and 5b, 6b at the time when ΔOD reached to highest value after excitation. (b) Decay profiles of triplet state for naphthalocyanines and phthalocyanines.

3.4. Optical limiting properties

Fig. 5 shows the optical limiting performance in 70% linear transmittances T_{Lin} at 532 nm of **5a** and **6a** in argon-saturated THF. It is obvious that naphthalocyanines 5a and 6a exhibit better optical limiting behaviour than corresponding phthalocyanines **5b** and **6b**. The optical limiting thresholds are 0.26, 0.15 J cm⁻² for naphthalocyanines 5a and 6a, and 0.46, 0.22 J cm⁻² for phthalocyanines 5b and 6b, respectively. In addition, the nonlinear attenuation factors (NAF) are 10.4, 16 for **5a** and **6a**, and 8.8, 14 for **5b** and **6b**, respectively. All of the parameters suggest that naphthalocyanines possess better optical limiting behaviour than the corresponding phthalocyanines. The Sun group has published a similar naphthalocyanine indium chloride (2,3-octa(3,5-di-tert-butylphenoxy)-2,3-naphthalocyaninato indium chloride) [9a], in nanosecond optical limiting studies in 70% linear transmittances T_{1in} at 532 nm, the optical limiting threshold is 0.27 J cm⁻². This optical limiting threshold value is comparable to those in our studies, but the optical limiting threshold of lead naphthalocyanine with bromo substituents (2,(3)-tetrabromo-3,(2)-tetra[(3,5-di-tert-butyl)pheny

loxy]-naphthalocyaninato lead) is as low as 0.10 J cm⁻² [3i], which maybe result from additional heavy atom effect. Dini and Hanack published the same naphthalocyanines indium chloride as the Sun group reported, and also resulted that the naphthalocyanines displayed good optical limiting properties [9b].

As previously discussed for the naphthalocyanine, the enlarged π electron conjugation system results in a lower energy of S₁ state and higher rate of intersystem crossing (k_{ST}), which leads to higher probability of intersystem crossing from S₁ to T₁ states. Correspondingly, higher values of Φ_T is observed for naphthalocyanines. Meanwhile, naphthalocyanines possess longer wavelength of T–T absorption and higher value of Δ_{ϵ_T} . Generally, high values of Φ_T and Δ_{ϵ_T} may result in good optical limiting properties for the reverse saturable absorption (RSA) mechanism, which has been discussed in some published papers [4,10]. All of these parameters indicate that the naphthalocyanines have stronger reverse saturable absorption (RSA) and better optical limiting behaviour, and which is capable to meet the challenge in practical applications for optical limiting materials, especially in wide wavelength range of optical limiting window.



Fig. 5. Optical limiting behaviour of naphthalocyanines 5a, 6a compared to phthalocyanines 5b and 6b.

4. Conclusions

Two soluble octa-(4-*tert*-butylphenoxy) substituted metallonaphthalocyanines were synthesized and the photophysical properties and optical limiting behaviour were evaluated and analysed. A wider and near-IR optical limiting window is observed for naphthalocyanine. The bulky substituents on naphthalocyanines not only effectively improve the solubility, but also reduce the molecular π - π interaction. The larger π electron conjugation system of naphthalocyanine results in a lower energy gap between S₁ and T₁ states, produces a higher intersystem crossing rate k_{ST} and triplet quantum yield Φ_T . Moreover, naphthalocyanines possess higher values of triplet-minus-ground state extinction coefficient (Δe_T) than corresponding phthalocyanines. All of these predominant photophysical and optical limiting properties suggest that the naphthalocyanines would be promising potential optical limiting materials for practical applications.

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