



Enhanced optical limiting performance of substituted metallo-naphthalocyanines 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 ($\Delta\epsilon_T$) 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 organometallic 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 π – π 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- d_6 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 S_1 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 30 min to remove the dissolved O_2 . A 532 nm ns Nd:YAG laser (Continuum Surelite II, 7 ns FWHM) was used as the laser source.

2.2. Synthesis

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

Iodine (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 MgSO_4 and evaporated the solvent to obtain a semi-solid crude product. After recrystallization from alcohol, 61.5 g pure 4,5-dibromo-*o*-xylene **1** was obtained (yield, 62%). Mp: 85–88 °C; ^1H NMR (DMSO- d_6 , 400 Hz): 7.36 (s, 2H), 2.18 (s, 6H) ppm; MS-EI (m/z): 264 (M^+), 185 ($\text{M}^+ - \text{Br}$), 104 ($\text{M}^+ - 2\text{Br}$).

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 CCl_4 (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 a yellowish solid. The crude product was recrystallized from CCl_4 and dried at 45 °C under vacuum to obtain 53.0 g of **2** (yield, 91%). Mp: 122 °C; ^1H NMR (DMSO- d_6 , 400 Hz): 8.09 (s, 2H), 7.62 (s, 2H) ppm; MS-EI (m/z): 579 (M^+), 498 ($\text{M}^+ - \text{Br}$), 420 ($\text{M}^+ - 2\text{Br}$), 339 ($\text{M}^+ - 3\text{Br}$), 260 ($\text{M}^+ - 4\text{Br}$).

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 NaHSO_3 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 CH_2Cl_2 to obtain 12.0 g white powder of **3** (yield, 71%). Mp >250 °C; ^1H NMR (DMSO- d_6 , 400 Hz): 8.91 (s, 2H), 8.75 (s, 2H) ppm; MS-EI (m/z): 336 (M^+), 255 ($\text{M}^+ - \text{Br}$), 1780 ($\text{M}^+ - 2\text{Br}$).

2.2.4. 2,3-Dicyano-6,7-di(4-*tert*-butylphenoxy)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- d_6 , 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 ($\text{M}^+ - \text{CN}$), 389 ($\text{M}^+ - \text{C}_6\text{H}_{12}$), 326 ($\text{M}^+ - \text{tBuPhO}$).

2.2.5. Octa-(4-*tert*-butylphenoxy) 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 CH_2Cl_2 /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** ($\text{C}_{128}\text{H}_{120}\text{N}_8\text{O}_8\text{GaCl}$). Mp >250 °C; UV–vis (THF) λ_{max} : 799, 340 nm; ^1H NMR (DMSO- d_6 , 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 ($\text{M}^+ - \text{Cl}$), 1817.1 ($\text{M}^+ - \text{Cl} - \text{OR}$), 1669.0 ($\text{M}^+ - \text{Cl} - 2\text{OR}$); Elemental analysis (%), calculated for $\text{C}_{128}\text{H}_{120}\text{N}_8\text{O}_8\text{GaCl}$: 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*-butylphenoxy) indium naphthalocyanine (**6a**)

Compound **6a** was prepared by a similar method to compound **5a** in 58% yield ($\text{C}_{128}\text{H}_{120}\text{N}_8\text{O}_8\text{InCl}$). Mp >250 °C; UV–vis (THF) λ_{max} : 802, 339 nm; ^1H NMR (DMSO- d_6 , 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 ($\text{M}^+ - \text{Cl}$), 1861.5 ($\text{M}^+ - \text{Cl} - \text{OR}$); Elemental analysis (%) [14], calculated for $\text{C}_{128}\text{H}_{120}\text{N}_8\text{O}_8\text{InCl}$: C 75.04, H 5.90, N 5.47; found C 75.72, H 5.74, N 5.76.

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