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The effects of central metals and peripheral substituents on the photophysical properties and optical limiting performance of phthalocyanines with axial chloride ligand

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A series of peripherally substituted phthalocyanines (Pcs) with different central metals (Al, Ga and In) and axial chloride ligand were synthesized and their photophysical and optical limiting properties were investigated. The Q band absorption of the Pc shifts to longer wavelength with the central metals changing from Al to In, and the fluorescence quantum yields of S_1 emission decrease remarkably from Al to In. Transient absorption spectra of the Pcs in THF were measured in determination of the photophysical parameters. The optical limiting properties were investigated by a nanosecond pulse laser at 532 nm. All of these compounds exhibit good optical limiting performance, and the optical limiting behaviors of solid solution in glass obtained by sol–gel technique are much better than that of liquid solution. Several factors which affect the optical limiting performance of the Pcs with different central metals and substituents are discussed.

1. Introduction

Nonlinear optical materials are continuously attracting attention for their potential applications in many fields such as optical storage, optical communications and optical limiting, etc. [1–3]. Among the large number of optical limiters, phthalocyanines (Pcs) are found to be outstanding optical limiting materials because of their special structures of two-dimensional highly conjugated delocalized π-electron system and metal-conjugant bond [4–7].

The optical limiting material can effectively attenuate glaring laser and dangerous optical beam, allowing only a reduced transmission to the target area. Therefore it may protect human eyes and optical sensors from being damaged [8–11]. For all favorable optical limiting materials, strong nonlinear absorption, nonlinear refraction or nonlinear dispersion are exhibited to reduce the input laser to suitable output intensity [12,13]. Pcs are typical compounds with suitable photophysical properties which result in excellent reverse saturable absorption for optical limiting and nonlinear transmittance application [14–17]. The occurrence of the reverse saturable absorption requires that the excited absorption cross section σ_{ex} is greater than that of the ground state σ_g [18–20]. For the practical applications of optical limiting and nonlinear transmittance effect, it is desirable to have reverse saturable absorbers, which allow high transmission of light at low optical fields over a large spectral window [21,22]. For the Pcs, the optical window of transient absorption occurs from 400 to 600 nm between the Q and B bands of the Pcs' ground state absorption. Introduction of central metals and peripherally substituted groups will effectively enlarge the optical window for optical limiting and nonlinear transmittance behaviors [23,24]. Among all investigation of the optical limiting materials, the essential condition of achieving preferable optical limiting properties is that the compounds in system could not be aggregated or only have little aggregation [25,26]. However, most of the Pcs are easy to be aggregated and have poor solubility in common solvents because of strong interactions between the Pc molecules. So reducing the aggregation and improving the solubility of the Pcs are important research works to achieve favorable optical limiting materials. Introduction of substituted groups is one of effective ways of improving the solubility of the Pcs, and also different substituents may cause different effects on the photophysical and optical limiting properties of the Pcs [27,28]. The axially substituted halogen atom which connect to the central metal could greatly influence the solubility and optical limiting behaviors of the Pcs [29,30]. Moreover, the central metals also play important roles in the properties of Pcs, and change the optical limiting behaviors [29,31]. The photophysical properties of Pcs can be modulated by altering the peripheral and axial substituents, central metals as well as the structures of the macrocyclic rings [32,33].

So far many researches have been focused on the effects of substituents or the central metals on the photophysical and optical

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limiting properties of the Pcs [5,34,35], and provided some useful guidelines. However, up to now, Pc-based materials are still being investigated to improve their optical limiting performance for the practical application. In order to meet this challenge, much more systemic and perspicuous studies on the relationships between the photophysical properties and the optical limiting behaviors with different central metals and substituents need to be paid more attention. Our group have investigated the optical properties of α-substituted Al Pc and peripherally α- and β-substituted In Pcs [36,37], respectively, and conclude that the α-substituted Pcs have better optical limiting behaviors. In this present paper the photophysical and optical limiting properties of α-substituted Al, Ga and In Pcs have been studied systemically and elaborately, and the relationship between them has been analyzed, in order to obtain more effective guidelines for the practical applications of optical limiting materials.

2. Experimental

2.1. Materials and methods

All organic solvents were commercially available, dried and distilled by appropriate methods before use. ^{1}H 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. 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 on a Hitachi F-4500 fluorescence spectrophotometer. Fluorescence quantum yield (Φ_F) of S_1 state were determined by the comparative method using zinc Pc in 1-chloronaphthalene ($\Phi_F = 0.30$) as reference standard [38,39]. The fluorescence lifetimes of these Pcs were investigated with single-photon counting technique with an Edinburgh FL900 spectrophotometer.

Transient absorption at nanosecond time scale was investigated in argon-saturated THF solution at the concentration of 2×10^{-5} 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 coefficient ($\Delta\varepsilon_T$) were calculated by the method of total depletion or saturation [40,41]. The quantum yields of the triplet state were determined by the comparative method [42], 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 [36,37]. All Pcs of **4**–**9** were dissolved in THF with the same linear transmittance T_{lin}, and 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 nanosecond Nd:YAG laser (Continuum Surelite II, 7 ns FWHM) was used as the laser source.

2.2. Synthetic procedures

2.2.1. 3-(4-tert-Butylphenoxyl)phthalonitrile (**2**)

Compound **2** was synthesized by a similar method in the published papers [36,37]. A mixture of 3-nitrophthalonitrile (6.9 g, 40 mmol), 4-tert-butylphenol (6.0 g, 40 mmol) and anhydrous potassium carbonate (22.0 g, 160 mmol) was added to 30 mL dry DMF and stirred at room temperature for 3 days under nitrogen condition. Then the reaction mixture was poured into 100 mL cold water, the precipitated crude product was collected by filtration and crystallized from toluene to give 7.2 g (yield: 71.8%) of 2. EI-MS: 276.3 (M^+); ^{1}H NMR ($CDCl_3$):δ (ppm) = 7.62 (t, 1H), 7.48 (d, 2H), 7.39 (d, 2H), 7.32 (d, 1H), 7.28 (d, 1H), 1.32 (s, 9H).

2.2.2. 3-(iso-Butoxyl)phthalonitrile (**3**)

Compound **3** was synthesized by a similar method in the published papers [36,37]. A mixture of 3-nitrophthalonitrile (6.9 g, 40 mmol), iso-butanol (5.9 mL, 48 mmol) and anhydrous potassium carbonate (22.0 g, 160 mmol) was added to 30 mL dry DMF and stirred at room temperature for 3 days under nitrogen condition, then the reaction mixture was poured into 100 mL cold water, the precipitated crude product was collected by suction filtration and crystallized with a little toluene to give 5.4 g (yield: 75.0%) of 3. EI-MS: 200.1 (M^+); ^{1}H NMR ($CDCl_3$, 400 Hz):δ (ppm) = 7.66 (t, 1H), 7.37 (d, 1H), 7.28 (d, 1H), 4.08 (d, 2H), 1.81-1.85 (m, 1H), 1.53 (d, 6H).

2.2.3. Tetra-α-(4-tert-butylphenoxy) aluminum phthalocyanine (**4**)

Compound **2** (2.8 g, 10 mmol) was added to 30 mL dry 1-pentanol with 1.5 mL 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) as a catalyst. The mixture was stirred at 60 °C for 1 h under a nitrogen atmosphere and then 0.4 g (3 mmol) of anhydrous $AlCl_3$ 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, 60 mL of methanol/water (1/1) mixture was added, the blue precipitated product was filtered, and washed with hydrochloric acid (5%, 50 mL), then 50 mL methanol, the crude product was purified by a silica-gel column chromatography with chloroform/ethanol (20:1) as eluent. Then the final product was dried at 50 °C under vacuum overnight to give 1.8 g (yield: 54.0%) of 4 ($C_{72}H_{64}N_8O_4AlCl$). UV–vis (THF) $\lambda_{\max}$: 705, 334 nm; MALDI-TOF: 1167.1 (M^+), 1132.0 ($M^+{-}Cl$); ^{1}H NMR (DMSO-d6, 400 Hz): δ (ppm) = 9.25–9.28 (m, 4H), 8.61–8.70 (m, 4H), 8.19–8.35 (m, 8H), 7.38–7.43 (m, 8H), 7.13–7.24 (m, 4H), 1.26–1.37 (d, 36H); Anal. Calcd. (%) for $C_{72}H_{64}N_8O_4AlCl$: C 74.06, H 5.48, N 9.60; found C 74.01, H 5.64, N 9.85.

2.2.4. Tetra-α-(4-tert-butylphenoxy) gallium phthalocyanine (**5**)

Compound **5** was prepared by a similar method to compound **4** in 71.8% yield ($C_{72}H_{64}N_8O_4GaCl$). UV–vis (THF) $\lambda_{\max}$: 712, 336 nm; MALDI-TOF: 1209.6 (M^+), 1173.5 ($M^+{-}Cl$); ^{1}H NMR (DMSO-d6, 400 Hz): δ (ppm) = 9.26–9.40 (m, 4H), 8.72–8.86 (m, 4H), 8.25–8.45 (m, 8H), 7.35–7.44 (m, 8H), 7.11–7.13 (m, 4H), 1.27–1.37 (d, 36H); Anal. Calcd. (%) for $C_{72}H_{64}N_8O_4GaCl$: C 71.43, H 5.29, N 9.26; found C 71.49, H 5.51, N 9.39.

2.2.5. Tetra-α-(4-tert-butylphenoxy) indium phthalocyanine (**6**)

Compound **6** was prepared by a similar method to compound **4** in 64.0% yield ($C_{72}H_{64}N_8O_4InCl$). UV–vis (THF) $\lambda_{\max}$: 720, 351 nm; MALDI-TOF: 1254.7 (M^+), 1219.7 ($M^+{-}Cl$); ^{1}H NMR (DMSO-d6, 400 Hz): δ (ppm) = 9.16–9.33 (m, 4H), 8.55–8.70 (m, 4H), 7.91–7.22 (m, 8H), 7.32–7.38 (m, 8H), 7.09–7.15 (m, 4H), 1.24–1.35 (d, 36H); Anal. Calcd. (%) for $C_{72}H_{64}N_8O_4InCl$: C 68.88, H 5.10, N 8.92; found C 68.96, H 5.45, N 8.53.

2.2.6. Tetra-α-(4-iso-butoxyl) aluminum phthalocyanine (**7**)

Compound **3** (1.7 g, 5 mmol) was added to 30 mL dry 1-pentanol with 1.5 mL 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) as a catalyst. The mixture was stirred at 60 °C for 1 h under a nitrogen atmosphere and then 0.27 g (2 mmol) of anhydrous $AlCl_3$ 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, 30 mL of methanol/water (1:1) mixture was added, the precipitated blue product was filtered, and washed with hydrochloric acid (5%, 50 mL), then 50 mL methanol, the crude product was purified by a silica-gel column with chloroform/ethanol (20:1) as eluent. Then