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Intramolecular aggregation and optical limiting properties of

triazine-linked mono-, bis- and tris-phthalocyanines

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Abstract

A series of triazine-linked mono-, bis- and tris-phthalocyanines are synthesized, intramolecular aggregation is found in bis- and tris-phthalocyanines via π - π stacking interaction. Theoretical and experimental studies reveal the formation of the intramolecular aggregation. The spectrographic, photophysical and nonlinear optical properties of these compounds are adjusted for the formation of the intramolecular aggregation. The bis-phthalocyanine dimer presents smaller fluorescence quantum yield, lower triplet formation yield and the triplet-minus-ground state extinction coefficient, which causes poorer optical limiting performance. It is interesting that the tris-phthalocyanine is composed of a mono-phthalocyanine part and a bis-phthalocyanine part, the optical limiting property of the tris-phthalocyanine is similar to that of mono-phthalocyanine.

Keywords: phthalocyanine; triazine; optical limiting properties; intramolecular aggregation; photophysical properties.

1. Introduction

Phthalocyanines (Pcs) exhibit a remarkable photophysical properties that lead themselves to applications in optical limiters, solar cells, semiconductor, photodynamic therapy and so on [1]. Aggregation is a well-known phenomenon in Pc chemistry. Interactions can occur between adjacent phthalocyanine rings both in organic and aqueous phase, resulting in the coupling between the electronic states of two, or more, phthalocyanine units [2]. The outstanding optical and photosensitizing properties of Pcs with abroad absorption range and high excitons quantum yields are always restricted in an aggregated state. The suppression and control of aggregation properties of Pcs is a challenge in material science, especially for their applications in nonlinear optics [3]. In order to understand the electronic configuration between chromophores, the study on the photophysical processes of both monomeric and aggregated molecules is important in designing organic materials for applications in opticelectronic technologies.

Even though the intermolecular aggregation can be reduced by introduction of bulky substituents into peripheral or axial positions of Pc cores to enlarge the distance between molecules [4], only a few examples of investigations focus on the intramolecular aggregation of multi-nuclear phthalocyanine-based materials [5]. To get better insight into the relationship between aggregation and optical properties, especially the photophysical processes of excited states, it is necessary to design and synthesize new models with high fluorescence quantum yield and well-defined structures. Here we designed a series of triazine-linked compounds, connected with mono-, bis- and tris-phthalocyanines(Figure 1), to reveal the formation of the intramolecular dimers and the influence on the excited states and optical limiting behavior.

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2. Experimental

2.1 General

All organic solvents were commercially available, dried and distilled by appropriate methods before use [6]. 4*tert*-Butylphenoxyphthalonitrile and 4-hydroxylphenoxyphthalonitrile were prepared using similar methods as described in the literatures [7]. ¹H NMR spectra were performed on a DPX400 Bruker FT-NMR spectrometer with CDCl₃ 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. The fluorescence lifetimes were investigated with single-photon counting technique with Edinburgh FL900 spectrophotometer.

The triplet state formation yields were determined by flash photolysis at nanosecond time scale. The excitation light was the harmonic of Nd:YAG laser (Continuum Surelite II, 355nm and 7ns FWHM). A pulsed xenon arc lamp was used to provide the analyzing light. The configuration of the monitoring light with respect with the excitation laser pulse is right-angle geometry. The liquid samples (1.0cm quartz cell) were settled on the platform at the intersection of monitoring light and excitation pulse. All the samples are optically dilute at the laser excitation wavelength. The signals were detected by Edinburgh LP900 and recorded on Tektronix TDS 3012B oscilloscope and computer. The triplet-minus-ground state extinction coefficients ($\Delta \varepsilon_T$) were calculated by the method of total depletion or saturation [8]. The quantum yields of the triplet state (Φ_T) were determined by the comparative method [8], using unsubstituted ZnPc in 1-chloronaphthalene as reference standard (Φ_T =0.65). The optical limiting properties were measured by the standard

setup of previously reported method [8]. Theoretical molecular simulations were performed using the GROMACS simulation suite [9].

2.2 Synthesis

2,9,16-Tri-*tert*-butylphenoxy-23-hydroxylphenoxy-phthalocyanine (H₂Pc-OH)

A mixture of 4-*tert*-butylphenoxyphthalonitrile (0.236g, 1mmol) and 4-hydroxylphenoxyphthalonitrile (2.48g, 9mmol) was added to 50mL dry 1-pentanol with 1.5mL 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) as a catalyst. The mixture was stirred at 60°C for 1 hour under a nitrogen atmosphere. The mixture was slowly brought to boiling over 1 hour and then refluxed for 36h, after the reactant was cooled to room temperature, 50mL of methanol/water (1/1) mixture was added, the blue precipitated product was filtered, and washed with hydrochloric acid (5%, 50mL), then 50mL methanol, the crude product was purified by a silica-gel column chromatography with toluene as first eluent to remove the byproduct, and then using THF as eluent to give 0.78g (yield: 73%) of H₂Pc-OH (C₆₈H₅₈N₈O₅). MALDI-TOF: 1067.8(m/z) (calcd. 1066.45); ¹H NMR (DMSO-d6, 400MHz) δ = 7.78-8.11 (broad, 8H, Pc-H), 7.30-7.48 (dd, 6-H, Phenyl–H), 7.01-7.30 (m, 10H, Phenyl–H), 6.90-7.08 (broad, 4H, Pc-H), 5.30 (s, 1-H, OH), 5.12 (broad, N-H), 2.18 (broad, N-H), 1.26-1.37 (s, 27H, tBu-H) ppm; Anal. Calcd (%) for C₆₈H₅₈N₈O₅: C 76.53, H 5.48, N 10.50; found C 76.21, H 5.64, N 10.15.

1,3-Di-tert-butylphenoxy-5-phthalocyanine substituted triazine (Mono-phthalocyanine 1).

4-*tert*-Butylphenol (75mg, 0.5mmol) and 1,3,5-trichlorotriazine (46mg, 0.25mmol) were added to 5mL dry toluene with 6mg of sodium silk as catalyst. After stirring the reaction mixture at 60°C under argon for 3h, H₂Pc-OH(0.267g, 0.25mmol) was added and the mixture was stirred at 110°C for 4h, then the toluene was removed under reduced pressure. The crude product was washed with methanol and then purified by a silica-gel column chromatography with dichloromethane as first eluent and then THF to give 0.3g (yield: 83%) of the mono-phthalocyanine **1–H** (C₉₁H₈₃N₁₁O₇). MALDI-TOF: 1442.8(m/z) (calcd. 1442.65) (Figure 2); ¹H NMR (CDCl₃, 400MHz): δ =7.82-8.28 (broad, 8H, Pc-H), 7.53-7.60 (dd, 6H, Phenyl–H), 7.26-7.47 (dd, 12H, Phenyl–H), 7.15-7.25 (dd, 6H, Phenyl–H), 6.99-7.04 (m, 4H, Pc-H), 5.05 (broad, N-H), 2.10 (broad, N-H), 1.44-1.47 (s, 45-H, t-Bu-H) ppm; Anal. Calcd (%) for C₉₁H₈₃N₁₁O₇: C 75.76, H 5.80, N 10.68; found C 76.11, H 5.95, N 10.35.

1-H(144mg, 0.1mmol) and anhydrous $InCl_3(25mg, 0.11mmol)$ was added to 3mL 1-chloronaphthalene and the mixture was stirred at $140^{\circ}C$ for 2h, after the reactant was cooled to room temperature, 5mL of n-hexane was added, the blue precipitated product was filtered, and washed with 5mL methanol, the crude product was purified by a silicagel column chromatography with chloroform/THF (5:1) as eluent to obtain 135mg(yield: 85%) of **1-In** (C₉₁H₈₃N₁₁O₇InCl). MALDI-TOF: 1589.6(m/z) (calcd. 1589.5), 1554.1 (M⁺-Cl); ¹H NMR (CDCl₃, 400MHz): δ =9.09-9.12 (broad, 4H, Pc-H), 8.68-8.81 (broad, 4H, Pc-H), 7.76-7.83 (dd, 6H, Phenyl–H), 7.53-7.60 (m, 10H, Phenyl–H), 7.41-7,45 (dd, 2H, Phenyl–H), 7.29-7.37 (dd, 6H, Phenyl-H), 7.02-7.05 (m, 4H, Pc-H), 1.34-1.37 (s, 45H, tBu-H) ppm; Anal. Calcd (%) for C₉₁H₈₁N₁₁O₇InCl: C 68.70, H 5.13, N 9.68; found C 69.11, H 5.39, N 9.88.

1-tert-Butylphenoxy-3, 5-diphthalocyanine substituted triazine (Bis-phthalocyanine 2).

4-*tert*-Butylphenol (37.5mg, 0.25mmol) and 1,3,5-trichlorotriazine (46mg, 0.25mmol) were added to 5mL dry toluene with 6mg of sodium silk as catalyst. After stirring the reaction mixture at 60°C under argon for 3h, H₂Pc-OH(0.538g, 0.5mmol) was added and the mixture was stirred at 120°C for 12h, then the toluene was removed under reduced pressure. The crude product was washed with methanol and then purified by a silica-gel column chromatog-raphy with dichloromethane as first eluent and then THF to give 0.43g (yield: 72%) of the bis-phthalocyanine **2-H** (C₁₄₉H₁₂₇N₁₉O₁₁). MALDI-TOF: 2359.0(m/z) (calcd. 2359.0) (Figure 3); ¹H NMR (CDCl₃, 400MHz): δ =7.88-8.10 (broad, 16H, Pc-H), 7.50-7.51 (d, 12H, Phenyl–H), 7.29-7.44 (d, 14H, Phenyl–H), 7.10-7.26 (d, 10H, Phenyl–H), 6.97-7.03 (m, 8H,Pc-H), 5.0 (broad, N-H), 2.25 (broad, N-H), 1.34-1.43 (s, 63H, t-Bu-H) ppm; Anal. Calcd (%) for C₁₄₉H₁₂₇N₁₉O₁₁: C 75.84, H 5.42, N 11.28; found C 75.53, H 5.71, N 11.57.

2-H (236mg, 0.1mmol) and anhydrous InCl₃(50mg, 0.23mmol) was added to 3mL 1-chloronaphthalene and the mixture was stirred at 150°C for 2h, after the reactant was cooled to room temperature, 5mL of n-hexane was added, the blue precipitated product was filtered, and washed with 5mL methanol, the crude product was purified by a silicagel column chromatography with chloroform/THF (3:1) as eluent to obtain 205mg (yield: 77%) of **2-In** ($C_{149}H_{123}N_{19}O_{11}In_2Cl_2$). MALDI-TOF: 2655.7(m/z) (calcd. 2654.71), 2619.2 (M⁺-Cl); ¹H NMR (CDCl₃, 400MHz): δ =9.10 (broad, 8H, Pc-H), 8.69-8.82 (broad, 8H, Pc-H), 7.75-7.85 (dd, 6H, Phenyl–H), 7.57-7.58 (m, 12H, Phenyl–H), 7.41-7,45 (dd, 4H, Phenyl–H), 7.29-7.35 (m, 14H, Phenyl-H), 6.94-7.04 (m, 4H, Pc-H), 1.34-1.46 (s, 63H, t-Bu-H) ppm; Anal. Calcd (%) for C₁₄₉H₁₂₃N₁₉O₁₁In₂Cl₂: C 67.37, H 4.67, N 10.02; found C 67.76, H 4.95, N 9.92.

1,3,5-Triphthalocyanine substituted triazine (Tris-phthalocyanine 3).

1,3,5-trichlorotriazine (46mg, 0.25mmol) and H₂Pc-OH(0.805g, 0.75mmol) of was added to 15mL of toluene and the mixture was stirred at 120°C for 15h, then the toluene was removed under reduced pressure. The crude product was washed with methanol and then purified by a silica-gel column chromatography with dichloromethane as first eluent and then THF to give 0.64g (yield: 78%) of the tris-phthalocyanine **3-H** ($C_{207}H_{171}N_{27}O_{15}$). MALDI-TOF: 3276.5(m/z) (calcd. 3276.35) (Figure 4); ¹H NMR (CDCl₃, 400MHz): δ =7.85-8.10 (broad, 24H, Pc-H), 7.45-7.60 (d, 18H, Phenyl–H), 7.32-7.42 (dd, 18H, Phenyl–H), 7.12-7.26 (m, 12H, Phenyl–H), 6.88-7.04 (m, 12H, Pc-H), 5.15 (broad, N-H), 2.03 (broad, N-H), 1.25-1.43 (s, 81H, tBu-H) ppm; Anal. Calcd (%) for C₂₀₇H₁₇₁N₂₇O₁₅: C 75.87, H 5.26, N 11.54; found C 75.51, H 5.59, N 11.15.

3-H(327mg, 0.1mmol) and anhydrous InCl₃(75mg, 0.34mmol) was added to 5mL 1-chloronaphthalene and the mixture was stirred at 160°C for 2h, after the reactant was cooled to room temperature, 10mL of n-hexane was added, the blue precipitated product was filtered, and washed with 10mL methanol, the crude product was purified by a silicagel column chromatography with chloroform/THF (2:1) as eluent to obtain 320mg (yield: 86%) of **3-In** (C₂₀₇H₁₆₅N₂₇O₁₅In₃Cl₃). MALDI-TOF: 3720.8(m/z) (calcd. 3719.92), 3685.3 (M⁺-Cl); ¹H NMR (CDCl₃, 400MHz): δ =9.07 (broad, 12H, Pc-H), 8.60-8.80 (broad, 12H, Pc-H), 7.78-7.80 (dd, 6H, Phenyl–H), 7.51-7.59 (m, 18H, Phenyl–H), 7.41-7,45 (dd, 6H, Phenyl–H), 7.29-7.35 (m, 18H, Phenyl-H), 6.92-7.07 (m, 12H, Pc-H), 1.26-1.46 (s, 81H, tBu-H) ppm; Anal. Calcd (%) for C₁₄₉H₁₂₃N₁₉O₁₁In₂Cl₂:C 66.81, H 4.47, N 10.16; found C 66.30, H 4.88, N 9.88.

3 Results and disscussion

3.1 Synthesis and characterization

A series of triazine-linked compounds, connected with mono-, bis- and tris-phthalocyanines were synthesized (shown in Figure 1). 4-tert-Butylphenoxyphthalonitrile and 4-hydroxylphenoxyphthalonitrile were prepared using similar methods as described in the literatures [7]. After alkyloxylation of 3-Nitrophthalonitrile (**a**) by 4-tert-butylphenol and 4hydroxylphenol respectively, the precursor of substituted 4-tert butylphenoxyphthalonitrile (**b**) and 4hydroxylphenoxyphthalonitrile(**c**) were obtained. The cyclization of (**b**) with (**c**) in the molar ratio of 1/3 resulted in the asymmetrical single hydroxyl substituted phthalocyanine (**d**) (H₂Pc-OH) (Scheme 1) in 1-pentanol at 140°C using DBU as catalyst under N₂ atmosphere.

The target compounds, including monomer 1, dimer 2 and trimer 3, were prepared by mixing H_2Pc-OH with 1,3,5-trichlorotriazine in corresponding molar ratios. After alkyloxylation of 1,3,5-trichlorotriazine (e) by 1 equiv and 2 equiv of 4-*tert*-butylphenol respectively, the 1,3-di-(4-tert-butylphenol)-5-chloro-triazine (f) and 1-di-(4-tert-butylphenol)-3,5-chloro-triazine (g) were obtained. Compounds (f) and (g) were successively reacted with 1 equiv and 2 equiv of (H_2Pc-OH), to give the mono-phthalocyanine 1–H and bis-phthalocyanine 2-H, respectively. And the tris-phthalocyanine 3-H (Scheme 2) was obtained by the reactant of 1,3,5-trichlorotriazine with 3 equiv of (H_2Pc-OH). Then the mono-, bis- and tris-phthalocyanines (1-H, 2-H and 3-H) and InCl₃ were added to 1-chloronaphthalene respectively, reacting at 160°C to give the mono-, bis- and tris-metalophthalocyanines (1-In, 2-In and 3-In).

The mono-, bis- and tris-phthalocyanines(**1-H**, **2-H** and **3-H**) and metalophthalocyanines(**1-In**, **2-In** and **3-In**) were purified by silica-gel column and then sublimated under vacuum to remove all the residual impurities. All phthalocyanines 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 to point out that these phthalocyanines 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.

3.2 Simulated molecular conformation

For a deeper insight into the intramolecular interaction between the Pc macrocycles of the bis- and trisphthalocyanines, molecular dynamics simulations are performed, using the GROMACS simulation suite [9]. Figure 5 depicts the chain structures after conformation optimization and energy minimization. It can be seen that the two Pc rings in bis-phthalocyanine molecule face each other in a parallel fashion. This face-to-face conformation favors the formation of intramolecular dimer via π - π stacking interaction. While in tris-phthalocyanine molecule, two of Pc rings act as intramolecular dimer, leaving one Pc ring unpaired and stood alone as monomer.

Even for the axially metallic chloride substituted Pcs, the intramolecular dimer is observed for 2 and 3. The distances between the two Pc planes of the dimers are calculated to be about 3.3 Å, which is much smaller than that of intermolecular distance (calcd. to be about 1300 Å at concentration of 4×10^{-6} M) between monomers in dilute solution. Despite of the high concentration of Pc solution or the solid powder Pc samples, the intermolecular distance of Pc units is about 35 Å [10], which is also more than 10 times larger than such intramolecular distance in dilute solution.

3.3 Ground state absorption and fluorescence emission

The UV-vis spectra of phthalocyanine species can provide a sensitive information for the presence or absence of interaction between phthalocyanine units. As shown in Figure 6, metal-free of monomer **1-H** shows two strong sharp bands in the 660-700nm region, and two weaker vibrational absorption bands in 610-640nm. A fully uncoupled species will display an electronic spectrum identical with that of mono-phthalocyanine unit, the spectroscopic profiles of bis- and tris-phthalocyanines are determined by the extent of coupling between the two Pc units. Apparently for **2-H** and **3-H**, the broad and intensity enhanced absorption in the 610-640nm region with weaker sharp peaks in the 660-700nm region are observed, the relative peak-intensity around 610nm and 640nm are increased and the peaks are almost reversed from that of monomer **1-H**. The peak-intensity change can be attributed to the strong π - π interaction of the face-to-face stacked Pc dimer. Moreover, the absorption spectrum of **2-H** is observed essentially unchanged in the range of 10⁻⁶-10⁻⁴M (Figure 7), suggesting that the change of peak-intensity around 610 and 640nm is not due to the intermolecular aggregation, but an intramolecular aggregation instead [11]. The aggregation peak is also observed in the spectra of **2-In** and **3-In**, which is located at about 650nm, especially for compound **2-In**. For indium substituted Pcs, the spectrum of **3-In** is almost identical to the sum of **1-In** and **2-In**, further suggesting that compound **3-In** is composed of a monomer part and a dimer part as expected.

The emission of monomer **1-In** is observed at 711nm, while the dimer **2-In** shows a little hypsochromic shift at 707nm with a much weaker intensity, and compound **3-In** exhibits its main emission band at 713nm with a bit smaller intensity compared with that of monomer **1-In** (Figure 8, excited at 610nm). Small Stokes shift for **2-In** relative to the monomer **1-In** and trimer **3-In** is probably due to the strong π - π interaction of intramolecular aggregation [12]. As compared to the monomer **1-In**, the relative fluorescence quantum yield has decreased to 37% and 80% for the dimer **2-In** and trimer **3-In**, respectively. The weaker intensity of the emission for the dimer **2-In** and trimer **3-In** is attributed to the fluorescence self-quenching of the two adjacent Pc units caused by intramolecular aggregation.

The monomer 1-In shows a fast decay process with a lifetime of τ_1 =0.37ns (98.8%), while two different decay processes are observed obviously for 2-In and 3-In. A fast process caused by the monomer and a slow one resulted from the dimer as shown in Figure 8 and Table 1. Apparently for the dimer 2-In, a short lifetime of τ_1 , about 0.36ns, with a decreased proportion (58.5%) and a long lifetime of τ_2 , about 5.39ns, with an increased proportion (41.5%) are

observed. The trimer **3-In** exhibits lifetimes of 0.36ns and 5.38ns with proportion of 81.8% and 18.2%, respectively. The shorter lifetime τ_1 belongs to monomer and the longer one τ_2 is attributed to the decay of the intramolecular dimer. Two decay modes of both τ_1 and τ_2 are observed although the two Pc planes act as dimer in **2-In**, which suggest that the excited state of the Pc dimer deactivate in the form of both monomer and dimer simultaneously, and that is why in compound **3** the value of A₁% is even much higher than A₂%.

3.4 Optical limiting performence

Pcs with heavy central metal show strong optical limiting performance because of strong reverse saturable absorption (RSA) [13]. To obtain a thorough understanding of the effect of intramolecular aggregation on nonlinear behaviour, optical limiting properties were investigated (Figure 9). It is clear that the monomer **1-In** shows the best optical limiting performance, and the trimer **3-In** displays almost equivalent optical limiting behaviour to **1-In**. While for the dimer **2-In**, the optical limiting behaviour is much worse than that of compound **1** and **3**, in which the samples have the same linear transmittance (T_{iin}) of 70%. The values of nonlinear attenuation factor (NAF) [8,14] for **1-In**, **2-In** and **3-In** are 20.3, 12.9 and 18.9, respectively, in which the NAF is the ratio of T_{iin} and T_{iim} is limiting saturated transmittance at high fluence. In addition, the optical limiting thresholds for **1-In**, **2-In** and **3-In** were 0.29, 0.49 and 0.32 (J·cm⁻²), the optical limiting threshold is defined as the input fluence at which the transmittance is 50% of the initial linear transmittance (T_{iin}). The ratios $\sigma^{T}_{es}/\sigma_{0}$ of **1-In**, **2-In** and **3-In** were estimated as summarized in Table 2 [15]. The dimer **2-In** shows the lowest value of $\sigma^{T}_{ex}/\sigma_{0}$, suggesting a higher cross section of ground state absorption (σ_{0}) and lower triplet absorption cross section (σ^{T}_{ex}) which result in lower probability of reverse saturable absorption (RSA) [16].

It's well known that optical limiting performance is mainly produced by reverse saturable absorption (RSA) resulted from excited state absorption in Pc compounds [17]. Thus, the triplet parameters such as k_{isc} , Φ_T and $\Delta \varepsilon_T$ are important parameters to affect the optical limiting performance [18]. Aggregation is undesirable in optical limiting material since strong intermolecular interactions usually increase relaxation pathways, shorten the excited state lifetime, and reduce formation of excited state and the effective nonlinear absorption. As listed in Table 2, monomer **1-In** have a high intersystem crossing rate (k_{isc}) and a high triplet quantum yield (Φ_T) [18].

As a result of intensive intramolecular aggregation, the linear transmittance of dimer 2-In and trimer 3-In are found to be lower than that of monomer 1-In. Then result in lower values of $\sigma^{T}_{ex}/\sigma_{0}$, even though all solutions have the same concentration. Moreover, aggregation and intermolecular interactions could also modify the geometry of the delocalized π -electron clouds and therefore reduce the electronic nonlinear optical response. So, as a result of intramolecular aggregation, the poorer optical limiting performance of 2-In can be attributed to a lower quantum yield for the intersystem crossing of Pc from its excited singlet to triplet state, lower linear transmittance as well as lower values of the triplet-minus-ground state extinction coefficients $\Delta \varepsilon_{T}$.

4 Conclusions

A series of triazine-linked mono-, bis- and tris-phthalocyanines were synthesized, two of the Pc rings in bis- and tris-phthalocyanine molecules face each other in a parallel fashion to form intramolecular dimer via π - π stacking interaction. Simulated conformations clearly depict the formation of the intramolecular aggregate, and both the ground state absorption and the decay mode of fluorescence emission support this fact. The bis-phthalocyanine dimer presents smaller fluorescence quantum yield, lower triplet formation yield and the triplet-minus-ground state extinction coefficient, which causes poorer optical limiting performance. The results will provide useful information for the design and application of phthalocyanine-based materials.

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Captions

Scheme 1. Synthetic route of the phthalocyanines $H_2Pc-OH(d)$

Scheme 2. Synthetic route of mono-, bis- and tris-phthalocyanines(1-H, 2-H and 3-H)

Figure 1. Structures of mono-, bis- and tris-phthalocyanines

Figure 2. MALDI-TOF spectra of 1-H

Figure 3. MALDI-TOF spectra of 2-H

Figure 4. MALDI-TOF spectra of 3-H

Figure 5. Simulated conformations of bis-phthalocyanine (2-In, left) and tris-phthalocyanine (3-In, right)

Figure 6. UV-vis absorption of metal-free and indium phthalocyanines monomer 1, dimer 2 and trimer 3 in THF with concentration of 4×10^{-6} M

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Figure 7. UV-Vis spectra of 2-H at different concentrations in THF

Figure 8. Fluorescence spectra (excited at 610nm) and decay profiles (excited at 370nm) of mono-phthalocyanine **1-In** $(6 \times 10^{-6} \text{M}, \text{detected at 711nm})$, bis-phthalocyanine **2-In** $(3 \times 10^{-6} \text{M}, \text{detected at 707nm})$, and tris-phthalocyanine **3-In**

 $(2 \times 10^{-6} \text{M}, \text{ detected at 713nm})$ in THF

Figure 9. Optical limiting behaviours of 1-In, 2-In and 3-In with linear transmittance of 70% in THF

Table 1. Photophysical properties of monomer 1-In, dimer 2-In and trimer 3-In (excited at 370nm) in THF

Table 2. Parameters for optical limiting properties of 1-In, 2-In and 3-In in THF

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Figure 1. Structures of mono-, bis- and tris-phthalocyanines









6000 m/z



Figure 5. Simulated conformations of bis-phthalocyanine (2-In, left) and tris-phthalocyanine (3-In, right)



Figure 6. UV-vis absorption of metal-free and indium phthalocyanines monomer 1, dimer 2 and trimer 3 in THF with





of , and tris-ph Figure 8. Fluorescence spectra (excited at 610nm) and decay profiles (excited at 370nm) of mono-phthalocyanine 1-In $(6 \times 10^{-6} \text{M}, \text{detected at 711nm})$, bis-phthalocyanine **2-In** $(3 \times 10^{-6} \text{M}, \text{detected at 707nm})$, and tris-phthalocyanine **3-In** $(2 \times 10^{-6} \text{M}, \text{detected at 707nm})$ ⁶M, detected at 713nm) in THF

D CR P٦ PI Δ



Compds	$\lambda_{\rm F}/nm$	τ_1/ns	$A_1\%$	τ_2/ns	$A_2\%$	A_1/A_2	$\Phi_{\rm F}({\rm relative})$
1-In	711	0.37	98.8	5.00	1.20	82.3	1.0
2-In	707	0.36	58.5	5.39	41.5	1.41	0.37
3-In	713	0.36	81.8	5.38	18.2	4.49	0.80
Note: $\Phi_{\rm F}$ (re	lative) is d	etermined	as the rati	o of fluor	escence q	uantum yie	ld of 2 and 3 to 1 .
							0
						S	
					2		
				V.			
		*					
6							

Table 1. Photophysical properties of monomer 1-In, dimer 2-In and trimer 3-In (excited at 370nm) in THF

C/M	1-111	2-In	3-1n
	2.45×10 ⁻⁴	6.40×10 ⁻⁵	7.15×10 ⁻⁵
T_{Lin}	70.4%	69.7%	70.9%
T _{Lim}	3.47%	5.40%	3.75%
NAF	20.3	12.9	18.9
σ_0/cm^2	2.36×10 ⁻¹⁸	9.37×10 ⁻¹⁸	8.06×10 ⁻¹⁸
σ_{ex}^{T}/cm^{2}	2.27×10 ⁻¹⁷	7.58×10 ⁻¹⁷	7.68×10 ⁻¹⁷
$\sigma^{\rm T}_{\rm ex}/\sigma_0$	9.6	8.1	9.5
$k_{\rm isc}/10^8 {\rm \ s}^{-1}$	14.7	6.61	11.0
Φ_{T}	0.85	0.39	0.69
$\Delta \epsilon_T / M^{-1} cm^{-1}$	3.49×10 ⁴	3.27×10 ⁴	3.78×10 ⁴

Intramolecular aggregation and optical limiting properties of triazine-linked mono-, bis- and tris-phthalocyanines

Jun Chen, Tao Zhang, Shuangqing Wang, Rui Hu, Shayu Li, Jin Shi Ma, Guoqiang Yang



A series of triazine-linked mono-, bis- and tris-phthalocyanines are synthesized, intramolecular aggregation is found in bis- and tris-phthalocyanines via π - π stacking interaction. Theoretical and experimental studies reveal the formation of the intramolecular aggregation. The spectrographic, photophysical and nonlinear optical properties of these compounds are adjusted for the formation of the intramolecular aggregation. The bis-phthalocyanine dimer presents smaller fluorescence quantum yield, lower triplet formation yield and the triplet-minus-ground state extinction coefficient, which causes poorer optical limiting performance. It is interesting that the tris-phthalocyanine is composed of a monophthalocyanine part and a bis-phthalocyanine part, the optical limiting property of the trisphthalocyanine is similar to that of mono-phthalocyanine.

HIGHLIGHTS

- A series of triazine-linked mono-, bis- and tris-phthalocyanines are synthesized.
- Intramolecular aggregation is found in bis- and tris-phthalocyanines via π - π stacking interaction.
- r ar agre ► The dimers cause poorer optical limiting performance for the intramolecular aggregation.