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Axial Halogen Ligand Effect on Photophysics and Optical Power Limiting of Some Indium Naphthalocyanines

Wenfang Sun,*,† Gang Wang,† Yunjing Li,† Mario J. F. Calvete,‡ Danilo Dini,‡ and Michael Hanack‡

Department of Chemistry, Biochemistry and Molecular Biology, North Dakota State University, Fargo, North Dakota 58105-5516, and Institute of Organic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

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Three axially substituted complexes, 2,3-octa(3,5-di-*tert*-butylphenoxy)-2,3-naphthalocyaninato indium chloride (**1a**), 2,3-octa(3,5-di-*tert*-butylphenoxy)-2,3-naphthalocyaninato indium bromide (**1b**), and 2,3-octa(3,5-di-*tert*-butylphenoxy)-2,3-naphthalocyaninato indium iodide (**1c**) have been synthesized and their photophysical properties have been investigated. Optical power limiting of nanosecond (ns) and picosecond (ps) laser pulses at 532 nm using these complexes has been demonstrated. All complexes display strong *Q*(0,0) absorption and measurable emission in the near-infrared region and exhibit strong excited-state absorption in the range of 470−700 nm upon ns laser excitation. The different axial ligands show negligible effect on the linear absorption, emission, and transient difference absorption spectra. However, the excited-state lifetime, triplet excited-state quantum yield, and efficiency to generate singlet oxygen are affected significantly by the heavier axial ligand. Brominated and iodinated complexes **1b** and **1c** show higher triplet excited-state quantum yield, while chlorinated complex **1a** has longer excited-state lifetime and is more efficient in generating singlet oxygen. The iodinated complex **1c** displayed the best optical limiting due to the higher ratio of excited-state absorption cross section to ground state absorption cross section (σ_{eff}/σ_0).

Introduction

Indium (III) phthalocyanines (Pcs)[1] and naphthalocyanines (Ncs)[2] have received particular attention in recent years due to their relatively higher efficiency as optical power limiting (OPL)[3] materials in the visible-NIR spectral range when compared to other metallic complexes.[4−6] For this type of application, the photoactive species undergoes a drastic and reversible reduction of its transmittance when intense optical fields (in the order of several MW/cm^2) are applied in order to protect light-sensitive optical sensors. Upon reduction of the field intensity the photoactive material recovers its state of high transparency and behaves as an intensity-dependent smart filter.[7] The general occurrence of such a nonlinear optical (NLO) effect[8] in metallophthalocyanines and analogues is based on a process of sequential multiphoton absorption (Figure 1), which involves the formation of highly absorbing excited states of Pcs.[9] OPL is achieved when the excited states of the Pc molecule have an absorption cross section (σ_{ex}) larger than that of the ground state (σ_0) at the irradiation wavelength. Such a phenomenon is called reverse saturable absorption (RSA)[4−6] through excited-state absorption (ESA). Occurrence of RSA via ESA also implies the fulfillment of two other conditions: first, a sufficiently long lifetime of the highly absorbing excited states and, second, a relatively rapid formation of these excited states[10] with respect to light pulse duration (usually within the range 10^{-15}-10^{-9} s in NLO regimes).[11] RSA based OPL possesses the main advantage of being passive, i.e., its activation does not require any additional feedback device.[3a,3c] Such a feature warrants the self-sustained activation of the RSA based filter with fast responses even to short luminous stimuli like those produced with pulsed lasers.[3a,3c]

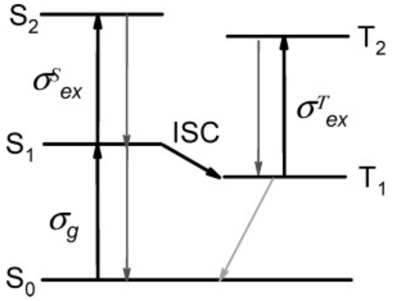

Figure 1. Jablonski diagram for the description of sequential multiphoton absorption upon irradiation of Pcs with intense light in the visible spectrum. S$_0$, S$_{1(2)}$, and T$_{1(2)}$ indicate the ground state, the first (second) singlet excited state, and the first (second) triplet excited state, respectively. Pc molecule absorbs the first photon through the transition [S$_0$ → S$_1$], and, depending on the dynamics of the irradiated system, can absorb sequentially a second photon through either the [S$_1$→S$_2$] or the [T$_1$ → T$_2$] transition. $\sigma^{S(T)}_{exc}$ and σ_g are the absorption cross sections from the excited singlet (triplet) state and the ground state, respectively. Skewed and straight shallow arrows indicate phosphorescence and fluorescence, respectively. ISC stands for intersystem crossing [S$_1$ → T$_1$]. For sake of clarity, only the fundamental vibrational level of the various electronic levels has been indicated.

The feasibility of indium phthalocyanines and naphthalocyanines for OPL application mostly relies on the heavy-atom effect[1b,12,13] of the central indium ion. The presence of an heavy atom like indium decreases the lifetime of the first singlet excited-state and increases the intersystem crossing rate and, thus, the triplet quantum yield (Figure 1) with respect to

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* Corresponding author. E-mail: Wenfang.Sun@ndsu.edu.
† North Dakota State University.
‡ University of Tübingen.

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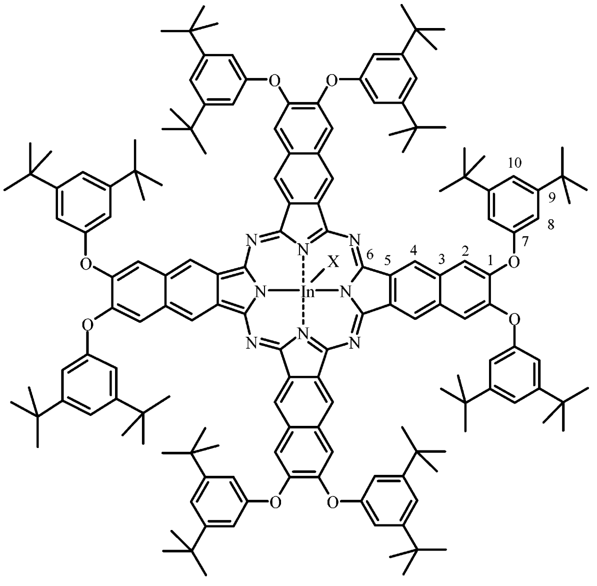
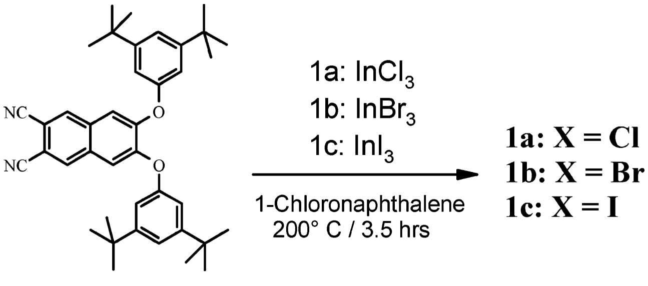
CHART 1: Structures of 1a−c



1a: X = Cl
1b: X = Br
1c: X = I

SCHEME 1



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analogous complexes with light central metals.[1b,12] Another important feature associated with the presence of indium central metal in Pc is the possibility of varying the nature of the axial ligand thus altering the OPL properties of the complexes.[1c] For PcInXs and NcInXs with axial aryl groups, it was found that these complexes displayed better OPL properties with respect to PcInCl and NcInCl[1b,1d] due to the lower extent of aggregation in concentrated solutions of these PcInXs. The reduced intermolecular interactions prevents excitation quenching and the excited-state becomes stabilized in comparison to that of PcInCl.[1c,1d] A further positive contribution from axial aryl substituents to OPL is rendered by the polarizability of the aryl groups and the axially oriented dipole moment associated with such a substituent.[1c,1d,14] Since axial substitution has proven to be a generally favorable approach for the improvement of the OPL effect in Pc and Nc based indium complexes, in this work we have synthesized a series of axially halogenated indium 2,3-naphthalocyanines with general formula R_8NcInX [R = 3,5-di-*tert*-butylphenoxy (*t*-Bu_2PhO); X = Cl(**1a**), Br(**1b**), I(**1c**)] (Chart 1) to evaluate the effect of axial halogen ligand on the photophysics and OPL properties of complexes **1a**−**c**. It is expected that the axial halogenation of the indium complexes would accelerate the kinetics and increase the yields of triplet excited-state formation in **1b** and **1c** with respect to **1a** due to the increasing mass of the axial halogen (heavy atom effect).[13] As a consequence, an enhancement of the OPL effect via ESA[3] is envisaged for complexes **1b** and **1c** in comparison to **1a**.

The selection of the naphthalocyanine ligand in **1a**−**c** is motivated by the larger optical window in naphthalocyanines in comparison to phthalocyanines due to the extended conjugation in naphthalocyanines, which significantly red-shifts the Q-band but shows a less marked effect on the B band.[15] As a result, the spectral range that exhibits low linear absorption is expanded. This is a useful feature for a clearer vision of the field if the OPL device is used to protect human eyes.[2b,16] In addition, Ncs offer a more extended range of nonlinear absorption against agile wavelength lasers, therefore showing a great potential for broadband OPL.[2g]

Experimental Section

Materials. $InCl_3$, $InBr_3$, and InI_3 were purchased from Aldrich. 1-chloronaphthalene was also obtained from Aldrich. The major precursor **2** was synthesized according to our previously reported procedure.[2h] All of the reagents were used as is without further purification. Solvents were purified and/or dried according to standard methods.

Characterizations. The structures of the synthesized compounds were characterized by UV−vis, ^1H− and ^{13}C NMR, and field desorption mass spectrometry. The UV−vis spectra were measured on a Shimadzu UV 2102 PC spectrophotometer. The path lengths were 1 cm. The NMR spectra were obtained using a Bruker AC250 spectrometer. Deuterated solvent was used as an internal standard. The mass spectra were measured on a Finnigan MAT 711A spectrometer with an ion source temperature of 30 °C.

Synthesis. All reactions for the preparation of Ncs **1a**−**c** were carried out in argon atmosphere, unless otherwise stated.

1a. **2**[2h] (2.93 g, 5 mmol) and $InCl_3$ (360.0 mg, 1.65 mmol) were mixed in 1-chloronaphthalene (1.5 mL) and heated to 200 °C for 3.5 h. After cooling, the reaction mixture was poured into methanol (100 mL) and stirred. The precipitates were collected and washed with hot methanol to give a dark yellowish green solid (1.5 g, 48%). MS−FD (*m/z*): 2497.6 (M^+). UV−vis (toluene): λ (ϵ/L mol^{-1} cm^{-1}): 806 (145731), 765 (20214), 716 (22164), 368 (41855), 338 (53888) nm. ^1H NMR (250.131 MHz, THF-d_8) δ: 1.33 (s, br, 144 H, CH_3), 7.03 (s), 7.23 (s), 7.44 (s) (br, 24 H, phenoxy), 7.89 (s, 8H on C-2), 9.55 (br, 8H on C-4) ppm. ^{13}C NMR (62.902 MHz, THF-d_8) δ: 30.9 (CH_3), 34.9 (C−CH_3), 113.8, 114.2 (br, C-8, C-10), 118.9, 121.7 (br, C-2, C-4), 131.3, 133.3 (br, C-3, C-5), 149.3 (br, C-6), 152.9 (br, C-7), 156.0 (br, C-1) ppm.

1b. The same procedure for **1a** was used to synthesize **1b**, except that $InCl_3$ was replaced by $InBr_3$, and starting from 1.46 g of **2**. Yield: 0.9 g (56%). MS (MALDI-TOF): 2544.0. UV−vis (toluene): λ (ϵ/L mol^{-1} cm^{-1}): 809 (250394), 767 (41364), 717 (45452), 380 (71692), 361 (65153), 346 (70875) nm. ^1H NMR (250.131 MHz, THF-d_8) δ: 1.33 (s, br, 144 H, CH_3), 7.03 (s), 7.23 (s), 7.44 (s) (br, 24 H, phenoxy), 7.89 (s, 8 H on C-2), 9.53 (br, 8H on C-4) ppm. ^{13}C NMR (62.902 MHz, THF-d_8) δ: 30.9 (CH_3), 34.9 (C−CH_3), 113.8, 114.1 (br, C-8, C-10), 118.1, 121.6 (br, C-2, C-4), 131.1, 133.2 (br, C-3, C-5), 150.5 (br, C-6), 152.9 (br, C-7), 156.0 (br, C-1) ppm.

1c. The procedure was the same as for **1a**. InI_3 was used instead of $InCl_3$, starting from 1.46 g of **2**. Yield: 1.0 g (61%). MS (MALDI-TOF): 2591.0. UV−vis (toluene): λ (ϵ/L mol^{-1} cm^{-1}): 809 (279310), 767 (45660), 718 (49048), 381 (79013), 361 (70451), 346 (77319) nm. ^1H NMR (250.131 MHz, THF-d_8) δ: 1.42 (s, br, 144 H, CH_3), 7.04 (s), 7.23 (s), 7.43 (s) (br, 24 H, phenoxy), 7.89 (s, 8 H on C-2), 9.55 (br, 8H on C-4) ppm. ^{13}C NMR (62.902 MHz, THF-d_8) δ: 30.9 (CH_3), 34.9 (C−CH_3), 113.8, 114.3 (br, C-8, C-10), 118.9, 121.7 (br, C-2, C-4), 131.3, 133.3 (br, C-3, C-5), 150.6 (br, C-6), 152.7 (br, C-7), 156.0 (br, C-1) ppm.

Photophysical Measurements. The electronic absorption spectra were measured on a Shimadzu UV 2102 PC spectrophotometer. The samples were dissolved in toluene. The emission spectra and lifetimes, the triplet excited-state quantum yield, and the triplet transient difference absorption spectra were measured in benzene solutions on an Edinburgh LP920 laser flash photolysis spectrometer. The samples were excited by a 4.1 ns (fwhm) Quantel Brilliant Nd:YAG laser at its third-harmonic output (355 nm) with a repetition rate of 1 Hz. The emissions were collected using an ultrasensitive, fast speed germanium detector EI-P with a time resolution of 496 ns. The transient difference absorption spectra were recorded using a Hamamatsu R928 PMT detector. For both emission and transient difference absorption measurements at room temperature, the sample solutions were placed in a 1 cm quartz cell and the solutions were purged with argon for at least 20 min before each measurement. For emission measurement at 77 K, the samples were dissolved in dichloromethane.

Triplet−triplet extinction coefficients of NcInX **1a**−**c** in benzene were measured by the energy transfer method,[17] with zinc tetraphenylporphyrin (ZnTPP) taken as the donor (D) ($\Delta\epsilon = \epsilon_T - \epsilon_G = 73\,000$ M^{-1}cm^{-1} at 470 nm for ZnTPP).[18] The sample solutions were excited at 532 nm, where the ground state extinction coefficients of NcInXs is relatively low so that direct population of the triplet excited-state by laser excitation can be negligible. Because the probability for energy transfer from the donor (D) to the acceptor (A) is not always unity, the rate constant for the decay of the donor in the absence of acceptor (k_1) and in the presence of acceptor ($k_2 = k_1 + k_{et}$[A], where k_{et} is the energy transfer rate constant from the donor to the acceptor, [A] is the concentration of the acceptor added) need to be measured in order to calculate the probability of energy transfer ($P_{et} = k_2 - k_1/k_2$).[17a] k_1 and k_2 can be obtained by fitting the triplet decay profile of the donor (ZnTPP) at 470 nm in the absence and presence of the acceptor (NcInXs 1a−c), respectively. The triplet difference extinction coefficient can then be calculated using the following equation:[17a]

$$\Delta\epsilon_T^A = \Delta\epsilon_T^D(\Delta OD_A/\Delta OD_D)\frac{1}{P_{et}} \qquad (1)$$

where $\Delta\epsilon_T^A$ and $\Delta\epsilon_T^D$ are the triplet difference extinction coefficients of the acceptor and the donor, respectively, ΔOD_A is the maximum optical density of the donor triplet at 470 nm in the absence of the acceptor, and ΔOD_D is the maximum optical density of the acceptor triplet at 590 nm when both the donor and acceptor are present. Each sample was measured at least three times at different donor−acceptor concentrations (20 − 70 μM) and the results are averaged out.

Quantum yields of the triplet excited-state formation were determined by comparative method with excitation at 355 nm.[19] Commercially available SiNc (silicon 2,3-naphthalocyanine bis-(tri-hexylsilyloxide), whose triplet excited-state quantum yield (Φ_T) was reported to be 0.20 ± 0.03 in benzene[20] was used as a reference. The linear absorption of the sample and reference was adjusted to the same value to ensure the same singlet excited-state population. The following equation was then used for calculation of the triplet excited-state quantum yield:[19]

$$\phi_T^s = \phi_T^r \cdot \frac{\Delta OD_T^s}{\Delta DO_T^r} \cdot \frac{\Delta\epsilon_T^r}{\epsilon_T^s} \qquad (2)$$

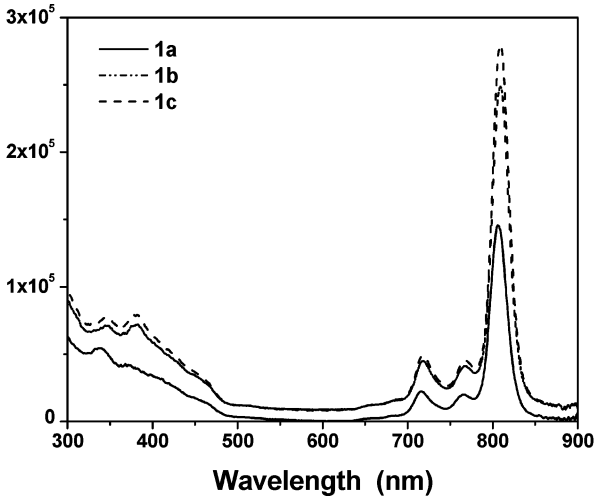

Figure 2. UV−vis absorption spectra of NcInXs **1a**−**c** in toluene.

where the subscripts s and r refer to the sample and reference solutions respectively, ϕ is the quantum yield of the triplet excited-state formation, ΔOD_T is the maximum optical density of the transient absorption, and $\Delta\epsilon_T$ is the triplet difference extinction coefficient at the wavelength of maximum absorption of the triplet excited state (590 nm).[20]

Singlet oxygen quantum yields (Φ_Δ) were determined by monitoring the emission of singlet oxygen at 1270 nm using an EI-P Ge detector. A silicon cutoff filter (>1100 nm) was used to reduce the scattered light from the YAG laser. SiNc was used as a reference. All samples and reference were dissolved in benzene. Excitation was at 355 nm. The linear absorption of the sample and reference solutions was adjusted to the same value of approximately 0.5 in a 1 cm thick cuvette. Both solutions were saturated with air. The emission intensity from NcInXs 1a−c was compared to that of SiNc ($\Phi_\Delta = 0.19 \pm 0.02$)[20] and Φ_Δ values were calculated using the following equation:

$$\phi_s = \phi_r(A_r/A_s)(n_s/n_r)^2(D_s/D_r) \qquad (3)$$

where the subscripts s and r refer to the sample and reference solutions, respectively, A is the absorbance at the excitation wavelength, n is the refractive index of the solvent, and D is the integrated emission intensity.

Optical Power Limiting Measurement. The optical power limiting measurements were carried out using a setup that has been described previously.[21] A Quantel Brilliant Nd:YAG laser was used as the light source and was operated at its second-harmonic output (532 nm) with a 10 Hz repetition rate. A 30 cm plano-convex lens was used to focus the laser beam to the center of a 2-mm thick quartz cell with the radius of the beam waist being approximately 75 μm.

Results and Discussion

UV−Vis Absorption. Figure 2 displays the UV−vis absorption spectra of NcInXs **1a**−**c** in toluene. Similar to the UV−vis absorption spectra of other metallonaphthalocyanines, these complexes exhibit an intense Q(0,0) band in the near-IR region (808 nm). Different axial halogen ligand exhibits no effect on the position of the Q- and B-bands, but the molar extinction coefficient is larger for the iodinated complex **1c** and smaller for the chlorinated complex **1a** in the whole spectrum (Figure 2). From 490 to 700 nm, the linear absorption of complexes **1a**−**c** is very low, thus providing a relatively broad optical

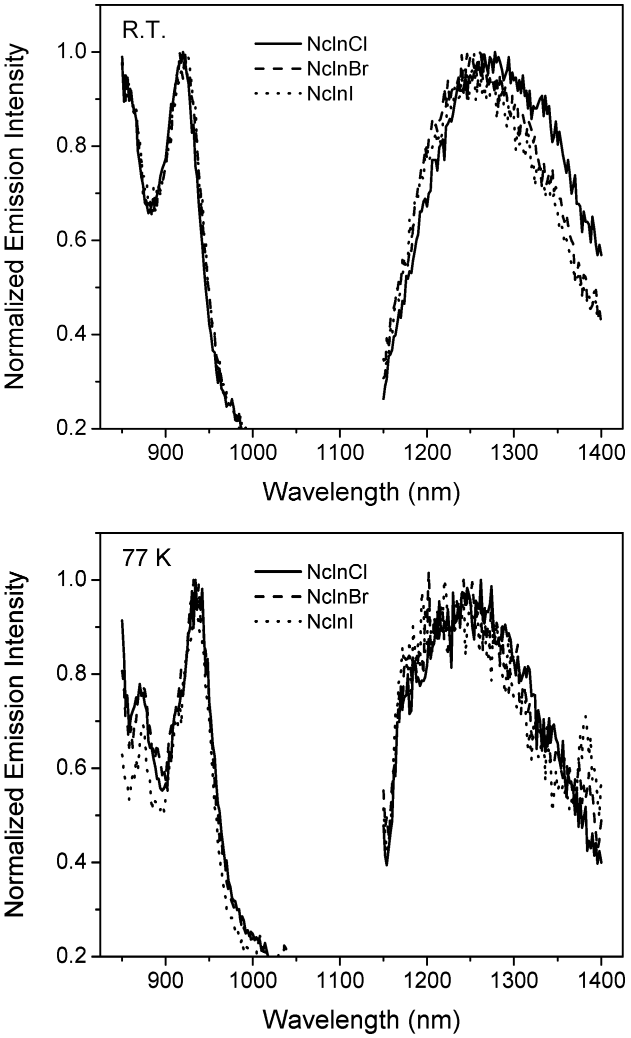

Figure 3. Normalized emission spectra of NcInXs **1a**−**c** at room temperature in benzene and at 77 K in CH_2Cl_2.

window for a clear view in the visible range when no high-intensity radiation interacts with the photoactive system.[3a,3c]

To examine the aggregation tendency of NcInXs **1a**−**c** in solution, linear absorption spectra at different concentrations have been studied. It is found that none of these complexes shows any evidence of aggregation up to a concentration of 1×10^{-3} mol/L. The actual concentration at which aggregation occurs for **1a**−**c** could not be evaluated because of the occurrence of saturation at concentrations higher than 1×10^{-3} mol/L with the thinnest cuvette available. The relatively low tendency of these complexes to aggregate is mainly due to the presence of the eight bulky peripheral di-*tert*-butylphenoxy substituents. In the case of **1b** and **1c** with bromide and iodide axial ligands respectively, the larger size of the halogen atoms also induces a more effective reduction of aggregation in comparison to the axially chlorinated complex **1a**.[1c,1d]

Emission. The emission spectra of **1a**−**c** in degassed benzene solution at room temperature and in degassed CH_2Cl_2 glass at 77 K are shown in Figure 3 and Table 1. All three complexes emit in the near-IR region with an intense band around 920 nm and one weak band around 1250 nm. Since the intensity of the emission band at 1250 nm is very weak, the widths of the entrance and exit slits of the instrument were adjusted much wider in order to increase the incoming signal. The observed emission at 1250 nm resembles the one from singlet oxygen at 1270 nm in analogous conditions of excitation.[17−20] In order to verify if this emission band is produced either by singlet oxygen or by complexes **1a**−**c**, the solutions of the samples **1a**−**c** and the reference complex SiNc have been thoroughly degassed. Although the emission at 1265 nm from SiNc disappears upon careful degasification, the emission around 1250 nm from NcInX solutions still stays on. This finding should exclude the presence of singlet oxygen in degassed **1a**−**c** solutions either as a solvated molecule or in a combined form with the NcInX complexes since the lifetime measurements of both emission bands at 920 and 1250 nm give a similar value of 14−16 μs. This implies that both emission bands could originate from the same excited states for the different complexes, with a triplet manifold if we consider the large Stokes shift of the emission band at 920 nm in comparison to the Q(0,0) band (i.e., a characteristic of phosphorescence), and the relatively long emission lifetime (the first singlet excited-state lifetime of an indium phthalocyaninato complex was reported to be only 0.3 ns).[12] Further support for this assignment comes from the fact that no substantial red shift has been found in the emission bands of these complexes at 77 K in comparison to that at room temperature. The difference in wavenumber ($\Delta\nu$) between the two emission bands in the NIR region is 3006 cm^{-1} for **1a**, 2849 cm^{-1} for **1b**, and 2869 cm^{-1} for **1c**. This value is comparable to what has been reported for benzophenone, which exhibits structured phosphorescence bands that originate from the vibronic structure of a single triplet state.[21] The fact that these two emission bands possess similar lifetimes should also exclude the possibility of these two bands originating from different triplet excited states. With reference to the phosphorescence bands of benzophenone,[21] the vibronic nature of these two bands can be tentatively assigned as (0,0) for 920 nm band and (0,2) for 1250 nm band. Since the emission features of this single triplet excited-state for Ncs **1a**−**c** are poorly dependent on the nature of the axial ligand (Table 1), we can attribute the $T_1(n,\pi^*)$ configuration, rather than $T_1\ (\pi,\pi^*)$ configuration, to the triplet emitting state of Ncs **1a**−**c**.[22]

Triplet−Triplet Transient Difference Absorption. As anticipated in the introductory part, occurrence of reverse saturable absorption (RSA) for effective optical limiting implies that the excited-state absorption cross section of the photoactive species is considerably larger than that of the ground-state absorption at the irradiation wavelength. Transient difference absorption measures the difference between excited-state absorption and the ground state absorption, and thus can provide information on the spectral range where RSA takes place. A positive band in the transient difference absorption spectrum indicates a larger excited-state absorption than that of the ground state absorption; while a negative band indicates the opposite situation. The decay profile of the transient difference absorption allows the evaluation of the triplet excited-state lifetime. In addition, using a comparative method,[19] quantum yields of the triplet excited-state can be determined. On this basis, the transient difference absorption spectra for NcInXs **1a**−**c** have been measured and the results are shown in Figure 4.

The shape of the spectra for these three complexes is quite similar, all featuring negative bands at 400−470 and 780 − 830 nm that are due to bleaching of the Soret and Q bands, and a broad, moderately intense positive band from 470 to 700 nm. Thus, from 470 to 700 nm, the excited-state absorption is stronger than that of the ground state absorption, indicating that RSA could occur at this wavelength region. Optical limiting is then expected in this spectral region. The triplet difference extinction coefficients ($\Delta\epsilon_T$) of the absorption band maximum at 590 nm were measured to be 53780 $L\cdot mol^{-1}\cdot cm^{-1}$ for NcInCl (**1a**), 57820 $L\cdot mol^{-1}\cdot cm^{-1}$ for NcInBr (**1b**), and 59650

TABLE 1: Photophysical Parameters of NcInXs 1a−c

samples	λ_{abs}, nm[a] (ϵ, L·mol^{-1}·cm^{-1})	λ_{em}, nm[b] (τ_{em}, μs) (R.T.)	λ_{em}, nm[c] (τ_{em}, μs) (77 K)	$\Delta\epsilon_T$, L·mol^{-1}·cm^{-1} [d]	τ_{TA}, μs (R.T.)[e]	Φ_T[f]	Φ_Δ[g]
InNcCl	338 (54640) 372 (42000) 716 (22420) 766 (20050) 806 (145670)	916 (14.17) 1264 (15.89)	872(50.15, 88%; 4.96, 12%) 934 (49.96, 88%; 4.95, 12%) 1262 (47.91, 88%; 4.49, 12%)	53780	14.43	0.225	0.100
InNcBr	345 (71090) 380 (71700) 717 (44820) 767 (41360) 808 (248720)	919 (14.87) 1245 (15.97)	872 (49.10, 88%; 4.84, 12%) 932 (48.95%, 88%; 4.82, 12%) 1250 (48.38, 88%; 4.50, 12%)	57820	1.70	0.287	0.046
InNcI	346 (77210) 382 (79270) 719 (49190) 768 (45270) 809 (279400)	919 (14.44) 1248 (14.28)	874 (49.31, 88%; 4.88, 12%) 934 (48.76, 88%; 4.74, 12%) 1234 (49.54, 88%; 4.72, 12%)	59650	1.61	0.273	0.049

[a] Linear absorption band max. and molar extinction coefficient in toluene solutions. [b] Emission band max. and decay lifetime at room temperature in argon-degassed benzene solutions, $\lambda_{ex} = 355$ nm. [c] Emission band max. and decay lifetime at 77 K in argon-degassed CH_2Cl_2 glass, $\lambda_{ex} = 355$ nm. [d] Triplet transient difference absorption coefficient at 590 nm. [e] Transient absorption decay lifetime in benzene solutions at 590 nm, $\lambda_{ex} = 355$ nm. [f] Quantum yield of triplet excited-state formation in benzene solutions. [g] Quantum yield of singlet oxygen generation in air-saturated benzene solutions, $\lambda_{ex} = 355$ nm.

L·mol^{-1}·cm^{-1} for NcInI (**1c**), according to the energy transfer method.[17] The lifetimes extrapolated from the decay profile of the transient difference absorption are 14.43 μs for NcInCl (**1a**), 1.70 μs for NcInBr (**1b**), and 1.61 μs for NcInI (**1c**). The reduced lifetime for **1b** and **1c** is ascribed to the heavy-atom effect, which enhances the spin-orbital coupling, resulting in a faster intersystem crossing from S_1 to T_1, and a faster decay from T_1 to S_0.[23] As a result, the triplet excited-state lifetime becomes shorter in the order of **1c** ≈ **1b** < **1a**, while the quantum yield of the triplet excited-state increases in the opposite order. This is in line with our measured triplet excited-state quantum yield, which is 0.225 for NcInCl (**1a**), 0.287 for NcInBr (**1b**) and 0.273 for NcInI (**1c**). The larger excited-state absorption cross section in the visible region, the long triplet excited-state lifetime, and the relatively high triplet excited-state quantum yield all suggest that these complexes are appropriate candidate for optical limiting of nanosecond laser pulses in the visible region.

It is noted that the value of the triplet excited-state lifetime measured by the decay of the transient absorption and the kinetic emission is the same (~14 μs) for **1a**, but is different for **1b** and **1c**. This indicates that for **1a**, the transient absorbing species either originate from the same excited-state that emits, or the two excited states are in equilibrium. For **1b** and **1c**, the emitting state and the transient absorption state should be different due to the much different excited-state lifetimes. Similar to what has been recently demonstrated for a tetrabrominated naphthalocyaninato indium chloride,[2h] the inconsistence of the triplet excited-state lifetime measured by the kinetic absorption and kinetic emission for **1b** and **1c** can be explained by the population of an additional excited-state during the photoexcitation process. This additional excited-state would be responsible for the transient absorption and is distinct from the triplet excited-state that emits. The spin multiplicity of this highly absorbing excited-state is expected to be triplet since its lifetime is longer than 1 μs (Table 1), *i.e.* several order of magnitude larger than the lifetime of a singlet excited-state for this type of complexes.[1c] In the evolution of the excited states of **1b** and **1c**, the formation of charged species cannot be excluded a priori.[2h]

Singlet Oxygen Quantum Yields. In addition to optical power limiting, Pcs and Ncs have been extensively studied for their potential use as photosensitizers in photodynamic therapy (PDT).[24] For this application, one critical requirement for photosensitizers is the high efficiency of singlet oxygen generation, which is determined by the efficient energy transfer from the triplet excited-state of photosensitizer to the triplet ground state of molecular oxygen. Therefore, high quantum yield of triplet excited-state should favor the singlet oxygen generation. To verify if this is also the case for NcInXs **1a**−**c**, emission of the singlet oxygen at 1270 nm has been measured in air saturated benzene. Figure 5 displays a typical emission profile of these complexes measured by a germanium detector that collects all emissions above 1100 nm through a silicon cutoff filter. The emission profile consists of an intense spike due to the scattering of the fundamental YAG beam and a slow component. The least-square fit of the slow component leads to two exponential decays (one fast and one slower subcomponent) with a relatively short lifetime of 3−4 μs for the fast subcomponent and a longer lifetime of 37−42 μs for the slower one. The shorter-lifetime subcomponent could be attributed to the residue emission from NcInXs that spans to the 1250 nm as discussed in the previous section, while the much longer lifetime is close to the singlet oxygen lifetime in benzene (30.9 μs). However, this lifetime is several microseconds longer than the singlet oxygen lifetime produced by other photosensitizers in benzene, which is similar to what has been reported for SiNc in the literature and found to be caused by a reversible energy-transfer reaction.[20,24] With reference to these results, the longer lifetime of the singlet oxygen in benzene generated by NcInXs **1a**−**c** could be tentatively assigned to a reversible energy-transfer process. In addition, fitting of this much slower component with a monoexponential curve and extrapolating back to zero delay provides the magnitude of singlet oxygen signal. Comparing the singlet oxygen emission intensity produced by NcInXs **1a**−**c** to that produced by SiNC ($\phi_\Delta = 0.19 \pm 0.02$ in benzene)[20] gave rise to a singlet oxygen quantum yield (Φ_Δ) of 0.100 for NcInCl (**1a**), 0.046 for NcInBr (**1b**), and 0.049 for NcInI (**1c**). However, the trend of Φ_Δ does not appear to be consistent with the predictions based solely on heavy-atom effect considerations. In fact, heavy atoms (Br and I) do increase the triplet excited-state quantum yield, but they also decrease the lifetimes of the triplet excited-state due to heavy-atom enhanced intersystem

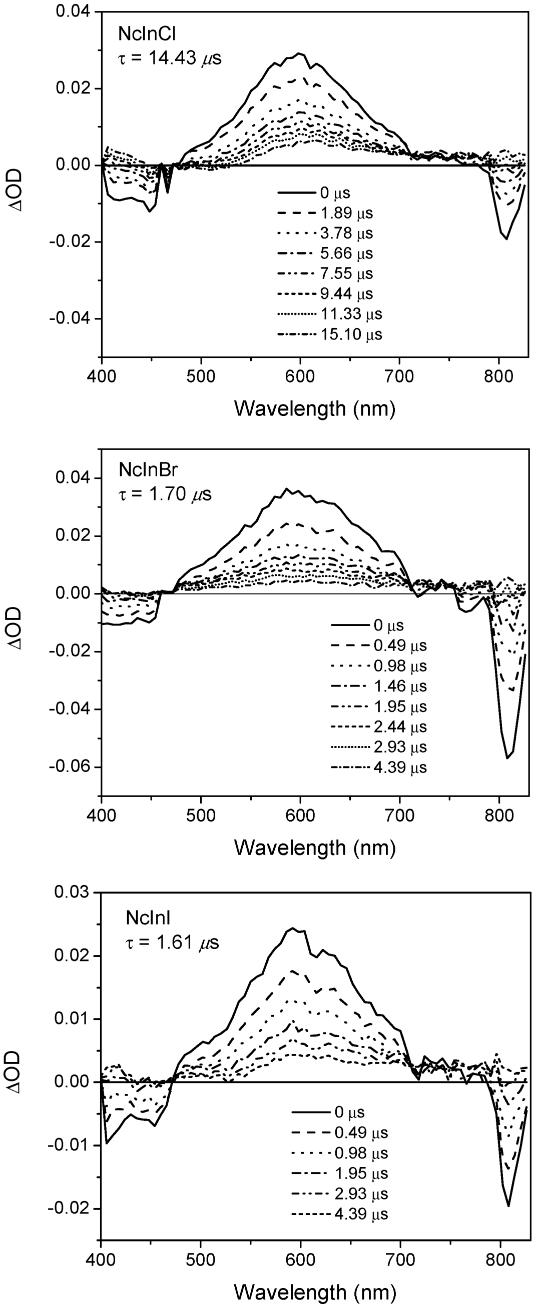

Figure 4. Triplet−triplet transient difference absorption spectra of NcInXs **1a**−**c** in benzene in a 1 cm cell. The linear absorption at the excitation wavelength (355 nm) is 0.37 for NcInCl and 0.44 for NcInBr and NcInI.

crossing decay from T_1 to S_0 (Figure 1). Therefore, the lower singlet oxygen quantum yields of **1b** and **1c** could be attributed to their reduced triplet excited-state lifetimes, especially considering the fact that the triplet lifetime of **1b** and **1c** is of the same order of the reversible energy-transfer reaction time from singlet oxygen to SiNc (reported to be ∼1.3 μs for SiNc).[20] Such a reversible energy-transfer reaction diminished the generation of singlet oxygen more in the case of NcInBr (**1b**) and NcInI (**1c**) than NcInCl (**1a**) simply due to the much shorter triplet lifetime of **1b** and **1c** with respect to **1a**.

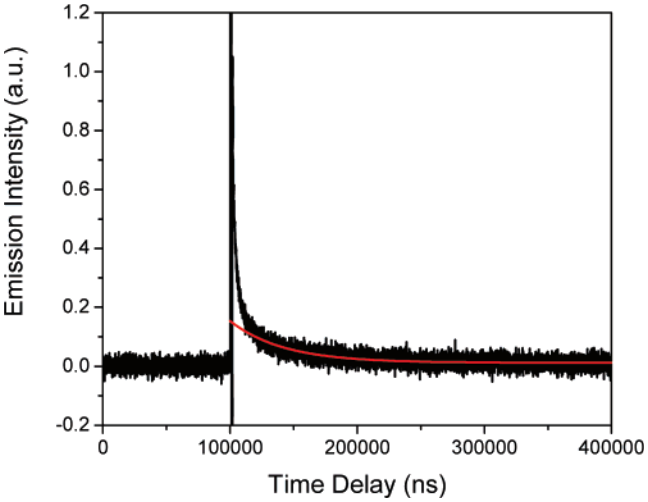

Figure 5. Time profile of singlet oxygen emission of NcInCl in benzene. The red line is the monoexponential fitting of the slow component with a time constant of 41.9 μs.

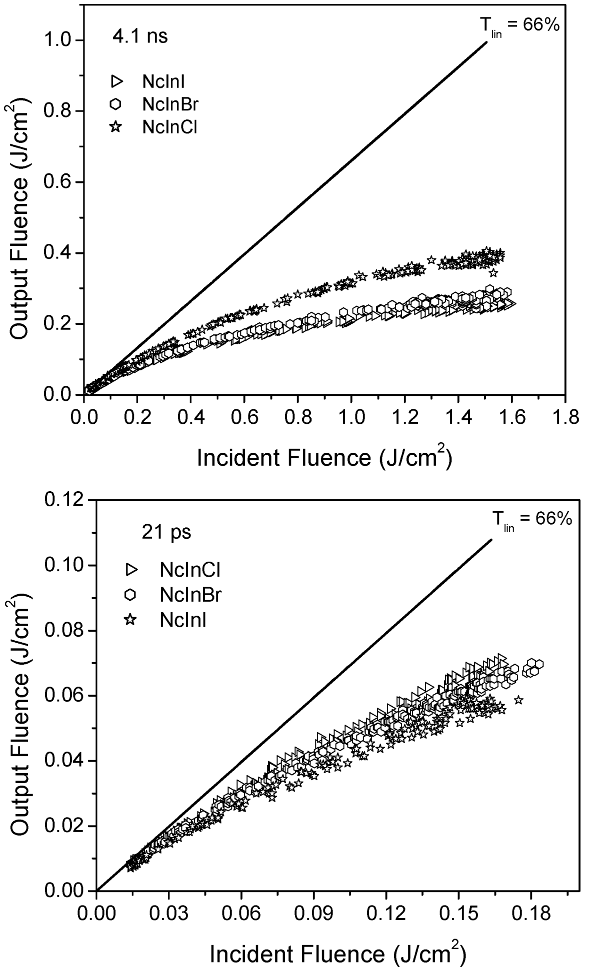

Figure 6. Optical power limiting curves of NcInXs **1a**−**c** in toluene for nanosecond and picosecond laser pulses. The laser wavelength is 532 nm, and the path length of the cuvette is 2 mm.

Optical Power Limiting. To demonstrate the feasibility of NcInXs **1a**−**c** for optical power limiting (OPL) applications and to confirm the favorable effect of the axial heavy atoms for this purpose, nonlinear transmission measurement at 532 nm has been carried out using both ns and ps laser pulses. As shown in Figure 6 and Table 2, all three complexes exhibit a significant transmission loss with increased incident fluence. For ns laser pulses, the limiting threshold decreases from 0.27 J/cm^2 for NcInCl (**1a**) to 0.08 J/cm^2 to NcInI (**1c**). The transmittance drops to 26% at incident fluence of 1.5 J/cm^2 for **1a**, and 16% for **1c**. For ps laser pulses, the limiting threshold and limiting throughput also follow the same trend, with NcInI (**1c**) showing the lowest limiting threshold and limiting throughput. The enhanced

TABLE 2: Optical Power Limiting Parameters of NcInXs 1a−c in Toluene

		ns			ps		
complexes	$\sigma_0{}^a$ (cm^2)	F_{th} (J/cm^2)^b	$T_{nonlin}{}^c$	$\sigma_{eff}/\sigma_0{}^d$	F_{th} (J/cm^2)^b	$T_{nonlin}{}^e$	$\sigma_{eff}/\sigma_0{}^d$
NcInCl	3.30×10^{-18}	0.27	0.26	>3.24	0.100	0.41	>2.14
NcInBr	1.71×10^{-17}	0.11	0.19	>4.15	0.075	0.39	>2.27
NcInI	1.63×10^{-17}	0.08	0.16	>4.41	0.030	0.33	>2.67

[a] Ground state absorption cross section at 532 nm. [b] At $T/T_{lin} = 70\%$. [c] At incident fluence of 1.5 J/cm^2. [d] Ratio of effective excited-state absorption cross section to that of ground state absorption. [e] At incident fluence of 0.17 J/cm^2.

optical limiting performance of NcInI (**1c**) for ns laser pulses should be related to the higher triplet excited-state quantum yield, while for ps laser pulses, the better OPL performance is likely due to higher excited-state absorption cross section that needs to be confirmed from the singlet transient difference absorption measurement.

To quantitatively compare the optical limiting performance a figure of merit $\sigma_{eff}/\sigma_0 = \ln T_{sat}/\ln T_0$[12] could be used, in which σ_{eff} is the effective excited-state absorption cross section including the contributions from both the singlet and triplet excited states, σ_0 is the ground state absorption cross section, T_{sat} is the transmittance for which the slope of the transmittance versus the incident fluence curve approaches zero, and T_0 is the linear transmission. The condition for the validity of this equation is that the incident fluence exceeds the saturation fluence $F_{sat} = h\nu/\sigma_0\Phi_T$,[12] where σ_0 is the ground state absorption cross section and Φ_T is the quantum yield of the first triplet excited-state formation. This is because only when the incident fluence exceeds the saturation fluence, the ground state can be considered completely bleached and the resulting absorption can be mainly ascribed to the excited states. For NcInX complexes **1a**−**c** F_{sat} is approximately 0.08 − 0.50 J/cm^2. Therefore, at the maxinum fluence used in our experiment (1.5 J/cm^2), the ground state has been greatly bleached. Thus, the aforementioned equation can be used to estimate the σ_{eff}/σ_0 value. However, even at the highest incident fluence used in our experiment, the transmittance does not reach the saturation point. Nevertheless, the transmittance at 1.5 J/cm^2 can be used to calculate the lowest bound of the σ_{eff}/σ_0 value. The results are shown in Table 2. It is clear that this value increases from NcInCl (**1a**) to NcInI (**1c**), clearly demonstrating the heavier axial ligands effect.

Conclusion

This work has proven that heavier axial halogen ligand exhibit a pronounced effect on the photophysical properties and optical limiting performances of complexes 2,3-octa(3,5-di-*tert*-butylphenoxy)-2,3-naphthalocyaninato indium chloride (**1a**), 2,3-octa(3,5-di-*tert*-butylphenoxy)-2,3-naphthalocyaninato indium bromide (**1b**) and 2,3-octa(3,5-di-*tert*-butylphenoxy)-2,3-naphthalocyaninato indium iodide (**1c**). Heavier axial halogen ligands like Br and I in **1b** and **1c**, respectively, increase the quantum yield of the triplet excited-state formation but also decrease the triplet excited-state lifetime. However, as the consequence of overplay of these two effects, the optical limiting performances for both nanosecond and picosecond laser pulses are enhanced. In addition, all three complexes **1a**−**c** show near-IR emission at approximately 920 and 1250 nm. Neither heavier axial ligand nor temperature shows pronounced effect on the emission energy. The relatively long emission lifetime suggests that the emission could originate from a triplet excited state. However, for **1b** and **1c**, the difference between the lifetime obtained from kinetic emission measurement and that from the kinetic absorption measurement implies that the nature of the emitting state for **1b** and **1c** is different from the one that gives rise to the transient absorption. Nevertheless, all complexes exhibit similar transient difference absorption spectra, with two bleaching bands in the near UV and near-IR region that correspond to the B-band and Q-band positions of Ncs **1a**−**c**, and a broad, structureless positive band from 470 to 700 nm. Moreover, **1a** exhibits reasonably good quantum efficiency for the generation of singlet oxygen, suggesting that this complex could potentially be used as photosensitizer for photodynamic therapy besides its promising application in optical limiting.

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