

Optical nonlinearities and photophysicochemical behaviour of green and blue forms of lutetium bisphthalocyanines†

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A rare earth sandwich-type phthalocyanine: bis-{2,3,9,10,16,17,23,24-octa(4-*tert*-butylphenoxy) phthalocyaninato} lutetium(III) has been synthesized. The photophysical and nonlinear optical behavior of both the "green" and "blue" forms ($[\text{Lu}^{\text{III}}\text{Pc}_2]$ and $[\text{Lu}^{\text{III}}\text{Pc}_2]^-$, respectively) of the complex have been investigated. High triplet state and singlet oxygen quantum yield values were obtained for the neutral blue form which contains no unpaired electrons. Relatively high third order susceptibility and hyperpolarizability values of the order of 10^{-10} and 10^{-28} esu were obtained for both the green and blue forms, respectively. A very low threshold intensity of $0.00051 \text{ J cm}^{-2}$ was obtained for the blue form. Hence the complex shows promise for non-linear optical applications.

Introduction

Phthalocyanines (Pcs) have a wide range of applications including their use as molecular thermometers,¹ in light-emitting diodes,^{2,3} magnets,⁴ solar cells,^{5,6} photodynamic therapy⁷ and nonlinear optics (NLO).^{8,9} The NLO properties of Pcs have been shown to be based on reverse saturable absorption (RSA) mechanisms.^{10–12} Lanthanide bisphthalocyanines (LnPc_2) have attracted attention in this regard because of their intense colors, high thermal stability,^{13,14} electrochromic behaviour and high intrinsic conductivity.¹⁵ Neutral LnPc_2 complexes are known to exist as stable radicals¹⁶ with an unpaired electron on a π orbital delocalized over two phthalocyanine (Pc) rings.⁷ This is usually referred to as the "green" form, $\text{Pc}^1-\text{LnPc}^{2-}$. One-electron reduction leads to the formation of the so called blue form, $[\text{Pc}^{2-}\text{LnPc}^{2-}]^-$. LnPc_2 complexes have been found to exhibit NLO behaviour.^{17,18} It has been suggested that lanthanide bisphthalocyanines show improved optical nonlinearities due to their expanded electron π system and the presence of the heavy lanthanide central metal^{19–22} which enhances the rate of intersystem crossing (ISC) to the triplet state.²³ Thus, LnPc_2 complexes are expected to have higher excited state absorption (ESA) in the triplet state than in the singlet state due to enhanced ISC. To date, the studies on the NLO behavior of LnPc_2 have concentrated on the neutral green form, despite the paramagnetic nature, which shortens triplet state lifetimes. This work compares the NLO behavior of the neutral and reduced forms of Lu (bis-{2,3,9,10,16,17,23,24-octa(4-*tert*-

butylphenoxy) phthalocyaninato} lutetium(III), **2**) (Scheme 1). The phthalocyanine rings are substituted with *tert*-butyl phenoxy ligands at the peripheral positions to enhance the solubility. Herein, differences in the photophysical and nonlinear optical properties of the green (**2a**) and blue (**2b**) forms of LuPc_2 complexes are described.

Experimental

Materials

1-Pentanol, NaBH_4 and lutetium(III) chloride were purchased from Sigma-Aldrich. Dimethyl formamide (DMF) was purchased from Merck, tetrahydrofuran (THF) was obtained from MINEMA, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Fluka. The synthesis of 4,5-bis-{4-*tert*-butylphenoxy}-phthalonitrile (**1**), which was used as a precursor for **2** has been reported previously.²⁴

The details of the equipment, as well as equations used for photophysical and NLO parameters are found in the ESI.†

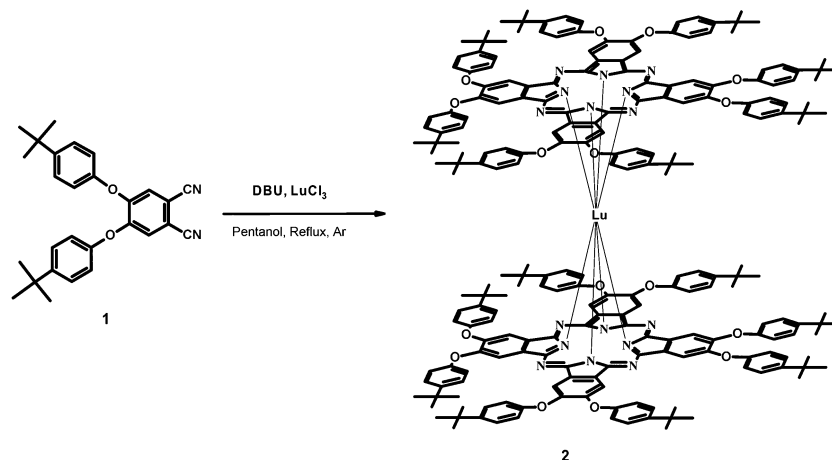
Synthesis of bis-{2,3,9,10,16,10,16,17,23,24-octa(4-*tert*-butylphenoxy) phthalocyaninato} lutetium(III) (**2**)

Complex **2** was synthesized according to methods employed for other LnPc_2 complexes.²⁵ Briefly, a mixture of compound (**1**) (300 mg, 0.71 mmol) and lutetium(III) chloride (24.9 mg, 0.088 mmol) was added to a round bottom flask and heated for 3 min. DBU (2 mL) and 1-pentanol (15 mL) were added to the reaction mixture, followed by heating under reflux for 21 h to obtain complex **2** as a green product. The crude product was purified by silica gel column chromatography using THF as an eluent.

Yield: 50%. IR: $[\text{KBr}, \nu, \text{cm}^{-1}]$ 830, 886, 985, 1013 (Pc skeleton), 1083, 1098, 1171, 1287, 1359, 1390, 1429, 1505 (C–O–C),

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Scheme 1 Synthesis of bis-(2,3,9,10,16,10,16,17,23,24-octa(4-*tert*-butylphenoxy) phthalocyaninato) lutetium(III) (2). The neutral green form is represented as **2a** and the reduced blue form as **2b**.

1601, 1728 (–C=N–), 2955 (C–H, aromatic). UV-Vis (DMSO): λ_{max} nm (log ϵ), 635 (4.40), 676 (4.77). Anal. calc. for $\text{C}_{224}\text{H}_{224}\text{N}_{16}\text{O}_{16}\text{Lu}\cdot 3\text{H}_2\text{O}$: C, 74.21; H, 6.41; N, 6.18. Found: C, 73.91; H, 6.92; N, 7.47%. ^1H NMR (DMSO- d_6): δ , ppm 8.42 (4H, s, Pc), 7.94–7.89 (4, m, Pc), 7.69–7.63 (8H, m, Pc), 7.45–7.41 (32H, m, Ar), 7.08–7.6.99 (32H, m, Ar), 1.31–1.25 (144H, m, *t*-butyl).

Results and discussion

Syntheses and characterization

A literature method²⁵ was employed to synthesize Lu bisphthalocyanines using compound **1** as a starting material. A reasonable but relatively low yield of 50% was obtained on purification *via* a column packed with silica and using THF as an eluent. The low yield is not surprising since mono phthalocyanines have been reported to form in the same reaction vessel during the preparation of LnPc_2 complexes.²⁶

The ^1H NMR data obtained were in agreement with the structure of complex **2**. The results obtained from the elemental analysis corresponded with the proposed structure of complex **2**. Pcs are often isolated as solvates,²⁷ hence the observed results. Complex **2** is soluble in organic solvents such as DMF, ethanol, toluene, THF, chloroform and dichloromethane.

The proton NMR spectra of **2** were broad due to the presence of the paramagnetic ions. However, the NMR data were resolved enough for the protons to be assigned.

The ^1H NMR spectrum is consistent with what would normally be anticipated for the structure of the synthesized complex, **2a**. The aromatic region exhibited peaks at 8.42 ppm, 7.94–7.89 ppm and 7.69–7.63 ppm. These were assigned to the protons on the Pc ring because of their close proximity to the deshielding region of the ring. The two other sets of signals in the region, 7.45–7.41 and 7.08–6.99 ppm (each representing 32 protons), were assigned to the protons on the benzyloxy substituent of the Pc. These were found at a slightly stronger field due to presence of the electron donating oxygen atoms as well as the *tert*-butyl groups. A peak at 1.26 ppm was assigned to the *tert*-butyl substituents. The presence of the unsymmetrical

spectral pattern as well as splitting of peaks suggests a degree of distortion of one of the Pc rings, with respect to the second Pc fragment, which is typical of bis(phthalocyaninato) lanthanides.^{28,29}

IR spectroscopy. The IR spectrum for **2**, the region of fundamental frequencies, is characteristic of the phthalocyanine ligand. Aromatic in-plane C–H bending vibrations are observed in the region of 1000–1300 cm^{-1} .³⁰ An aromatic C=C peak is observed at 1601 cm^{-1} . A weak band around 3090 cm^{-1} is due to the aromatic C–H stretches on the phthalocyanine rings.³⁰ The absorptions at 1505 cm^{-1} indicate the presence of C–O–C groups in the structure for **2**. The marker IR band for the phthalocyanine monoanion $\text{Pc}^{\cdot-}$ radical usually appears near 1300 to 1320 cm^{-1} (ref. 30) and was observed at 1287 cm^{-1} . The absence of the –CN bands that are observed in the IR spectrum of **1** confirmed the formation of **2**. The aromatic regions of the spectrum for **1** are maintained in the spectrum of **2**.

EPR spectroscopy. The spectra of LnPc_2 exhibit a relationship between the individual phthalocyanine macrocycles and the lanthanide central metal. The green bis phthalocyanine complexes can be regarded as single-hole complexes in which an unpaired electron is present in one of the macrocyclic ligands. The EPR spectrum for complex **2** (Fig. 1) was recorded

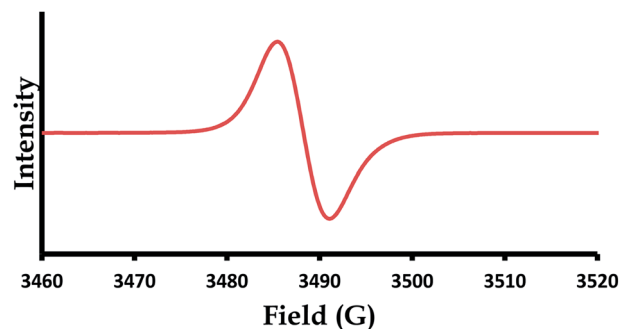


Fig. 1 EPR spectra of complex **2a** in the solid state.

at 298 K. The spectrum confirmed the presence of an unpaired electron in **2** ($g = 2.000$) with a band width around 4.88 G, confirming the presence of organic radicals in solution, as would be anticipated for $\text{Pc}^{1-}\text{LnPc}^{2-}$ (the green form).³¹ The spectra are comparable to those reported previously for LuPc_2 .³² On reduction with NaBH_4 and recrystallization, no EPR signal was observed for **2**. This provides direct spectroscopic evidence for the absence of an unpaired electron in the reduced neutral $[\text{Pc}^{2-}\text{LuPc}^{2-}]^-$ and confirms that the reduction was successful.

Electronic absorption and fluorescence spectroscopy. The ground state electronic absorption spectrum for complex **2a** in DMF is shown in Fig. 2(A). The Q band lies at 676 nm, Table 1. A split in the Q band into two components may be observed in LnPc_2 complexes depending on the solvent and the central metal. For example splitting has been observed in DMF but not in dichloromethane for some LnPc_2 derivatives.³³ We did not observe splitting in the Q band in this work.

The bands that lie beyond 700 nm (Fig. 2(A), inset) are consistently observed in the spectra of the green forms of bisphthalocyanine complexes. These absorption bands are due to the presence of a 'hole' in the highest occupied molecular orbital (HOMO) of the green form of bisphthalocyanines.³⁴ A shoulder in the 400–500 nm region (circled for complex **2a**) of the absorption spectrum is characteristic of a radical phthalocyanine anion.^{35,36} Solutions of the blue form $[\text{Pc}^{2-}\text{LnPc}^{2-}]^-$ (complex **2b**) were obtained by reducing $\text{Pc}^{1-}\text{LuPc}^{2-}$ with

Table 1 Spectral and photophysical parameters of complexes **2a** and **2b** in DMF

Complex	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	Φ_{F}	Φ_{T}	$\tau_{\text{T}}/\mu\text{s}$	Φ_{Δ}
2a	676	684	693	0.029	— ^a	— ^a	— ^a
2b	674	675	693	0.10	0.68	375	0.32

^a Φ_{T} , Φ_{Δ} and τ_{T} values were not calculated for **2a** (green form) due to lack of decay curves.

NaBH_4 , Fig. 2(B). In Fig. 2(B), the bands near 900 nm disappeared, confirming reduction.

The absorption, excitation and emission spectra for **2a** and **2b** are shown in Fig. 3A and 3B, respectively. The emission signals for complexes are weak and broad and not comparable to the excitation spectrum. The splitting in the excitation spectra for **2b** suggests loss of symmetry on excitation. The poor fluorescence for both complexes may be due to the heavy atom effect of the central metal,³⁷ which encourages intersystem crossing to the triplet state at the expense of fluorescence.

Photophysical and photochemical parameters

Fluorescence quantum yields. The fluorescence quantum yields were low for both complexes at $\Phi_{\text{F}} = 0.10$ for **2b** and even lower for **2a** at $\Phi_{\text{F}} = 0.029$. For both complexes, the values are low due to the heavy atom effect of Lu which encourages

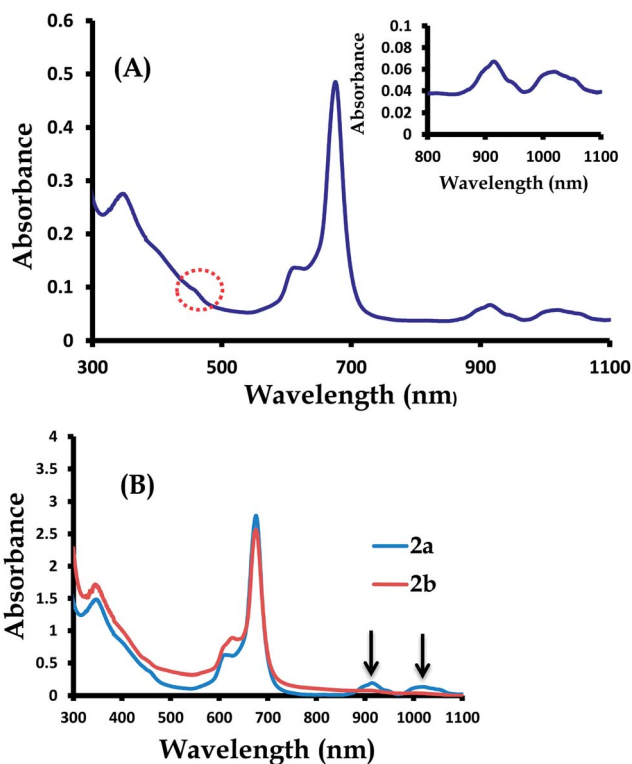


Fig. 2 Electronic absorption spectra of complexes (A) **2a** concentration = 8.0×10^{-6} M and (B) **2b** overlaid with **2a** in DMF. The inset in (A) is the expansion of the 900 to 1100 nm region. The arrows indicate the disappearance of peaks due to the presence of a radical.

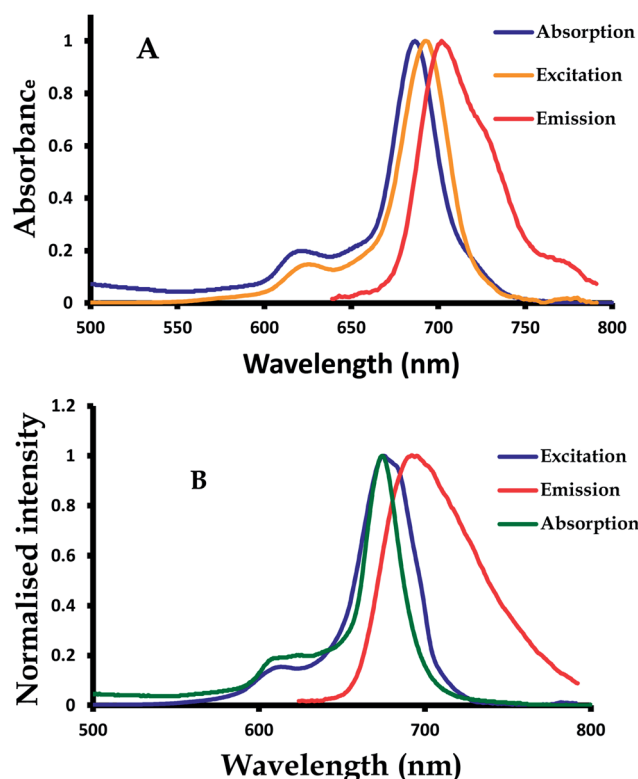


Fig. 3 Absorption, excitation and emission spectra of complex **2a** (A) and **2b** (B) in DMF.

intersystem crossing to the triplet state. For **2a**, the value is also affected by the paramagnetic nature of the complex, which also encourages intersystem crossing.²³

Triplet quantum yields (Φ_T) and lifetimes (τ_T). The triplet decay curve for complex **2b** is shown in Fig. 4. No signal was observed for the corresponding green form ($\text{Pc}^{1-}\text{LuPc}^{2-}$), due to the presence of a radical on one of the phthalocyanine rings. As stated above, paramagnetism results in enhanced intersystem crossing to the triplet state with increased triplet state quantum yields, but very short lifetimes,²³ hence there was no signal for **2a**. The triplet state lifetime of **2b** was 375 μs which is reasonable for phthalocyanines.²³ Triplet quantum yields are expected to be large due to the heavy atom effects. This is observed for **2b** with $\Phi_T = 0.68$.

Singlet oxygen quantum yields (Φ_Δ). The singlet oxygen decay curve for complex **2b** is shown in Fig. 5. High Φ_Δ values would normally be expected for complexes with high triplet

quantum yields (Φ_T) when there is efficient molecular oxygen energy transfer. The Φ_Δ value of 0.32 was observed for **2b** showing inefficient energy transfer from the excited triplet state. There was no signal for **2a** due to the reasons explained above for lack of the triplet state signal.

Optical nonlinearity studies

Table 2 summarizes the nonlinear optical properties of both the blue and green forms of **2**. Fig. 6 shows an open aperture Z-scan signal for **2**, see ESI.† The fit demonstrates that there is a decrease in the transmitted beam due to the RSA effect.

The $\text{Im}[\chi^{(3)}]$ and γ values shown in Table 2 decrease with the concentration of the complexes. The concentrations for **2a** and **2b** were of the order of 10^{-4} M and were weaker than the concentrations (order: 10^{-3} M) that were used for the bridged double-decker lutetium and indium phthalocyanines that were studied previously.³⁸

The $\text{Im}[\chi^{(3)}]$ values obtained for both **2a** and **2b** are higher than the range reported for monomeric In, Ga and Zn phthalocyanines in DMSO (ranging from $\text{Im}[\chi^{(3)}] \sim 10^{-12}$ to 10^{-11} esu (ref. 39)). The $\text{Im}[\chi^{(3)}]$ values reported in this work are also larger

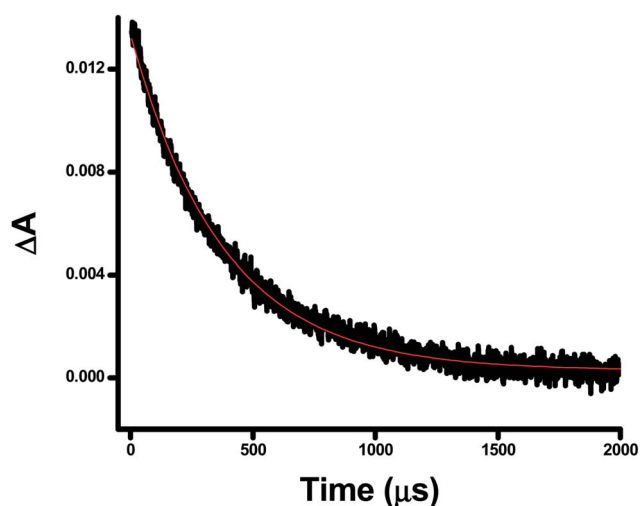


Fig. 4 Triplet lifetime decay curves for complex **2b** in DMF.

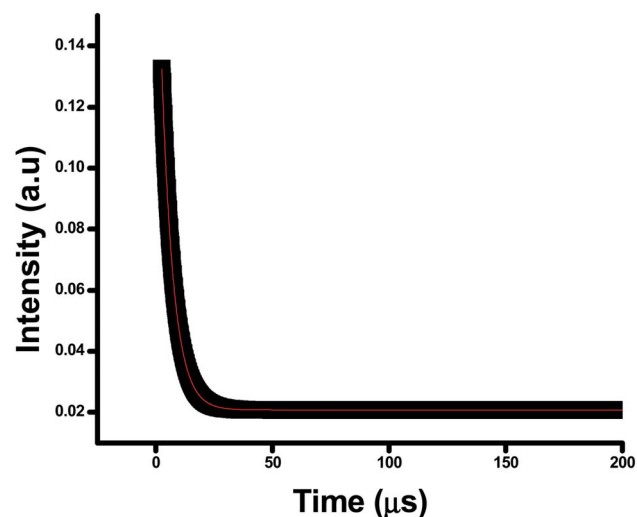


Fig. 5 Singlet oxygen decay curve for complex **2b** in DMF.

Table 2 Nonlinear optical properties of complexes **2a** and **2b** in DMF at various concentrations

Complex	C ($\times 10^{-4}$ M)	$\text{Im}[\chi^{(3)}]$ ($\times 10^{-10}$ esu)	γ ($\times 10^{-28}$ esu)	I_{lim} (J cm^{-2})
2a	3.3	2.07	4.50	— ^a
	3.1	1.03	2.37	— ^a
	2.9	0.46	1.14	— ^a
	2.7	0.27	0.71	— ^a
2b	3.3	2.44	5.33	0.00093
	3.1	1.68	3.91	0.00055
	2.9	0.92	2.30	0.00051
	2.7	0.12	0.33	0.00051

^a I_{lim} values of **2a** (green form) were not calculated due to lack of triplet decay curves (hence no triplet lifetimes).

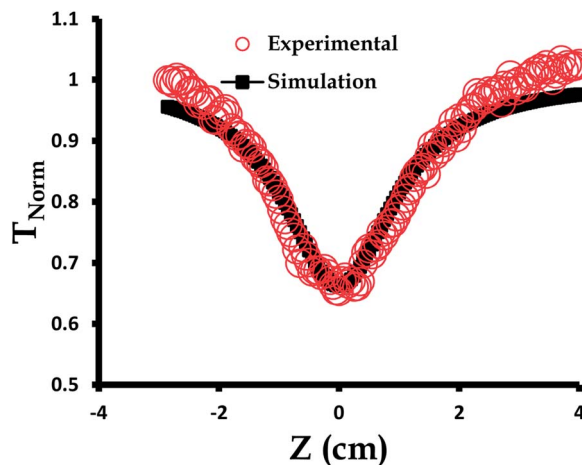


Fig. 6 Z-scan open aperture for complex **2b** in DMF.

than those reported for Yb, Gd and La polymeric phthalocyanines ($\sim 2.00 \times 10^{-13}$ to 2.52×10^{-13} esu) in DMF⁴⁰ but less than those obtained for scandium bisphthalocyanines.⁴¹ The γ values are higher than those reported for In, Ga or Zn phthalocyanines³⁹ ($\gamma \sim 10^{-31}$ – 10^{-30} esu). There has been an extensive exploration of non-linear optical properties of Pcs containing large diamagnetic central metals such as lead(II) or indium(III). Large central atoms are known to encourage intersystem crossing to the triplet state by the heavy atom effect.⁴² Lanthanide bisphthalocyanines show improved optical nonlinearities due to the presence of a large central metal and an expanded electron π system, as stated in the Introduction.

The higher values suggest better optical limiting for the LuPc₂ derivatives. At the same concentrations, the values of Im [$\chi^{(3)}$] and γ are larger for **2b** compared to **2a**, showing that the reduced blue form is a better optical limiter than the charged green form.

Optical limiting properties based on RSA in Pcs have been reported for both nanosecond and picosecond times at 532 nm.^{43–45} For phthalocyanines in general, two photon absorption occurs at 532 nm where there is negligible absorption and very strong triplet–triplet absorption. Varying the central metal atom in a Pc usually leads to considerable variation in the relevant NLO and OL properties.⁴⁶ In the case of complexes **2a** and **2b**, both the ligands and central metal are the same, hence similar optical limiting properties are expected. However, the two are different in that **2a** is paramagnetic while **2b** is not, resulting in improved photophysical behaviour for the latter. RSA depends on the differences in the excited state absorption (ESA) of the singlet and triplet states, where ESA in the triplet state has to be larger. **2b** is expected to exhibit better optical limiting properties due to the improved triplet state parameters.

The optical limiting (OL) effect of a NLO material is measured based on its response to intense incident beams of light in the form of a strong attenuation when the input intensity has passed a threshold value. Fig. 7 shows a plot of incident laser intensity (I_{in}) versus transmitted laser intensity (I_{out}) for **2b** at 2.9×10^{-4} M. It can clearly be observed that **2b** exhibits a deviation from linearity. A good OL should have a low I_{lim} value. The I_{lim} values obtained for complex **2b** are of the

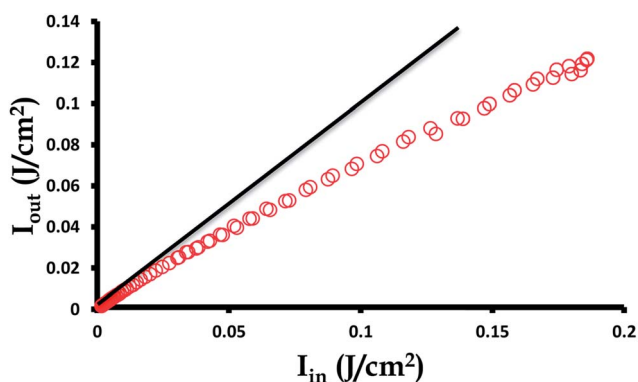


Fig. 7 Plot of I_{out} versus I_{in} for complex **2b** showing nonlinearity at a point of saturability. The black solid line represents a case of linear transmission. Concentration = 2.9×10^{-4} M.

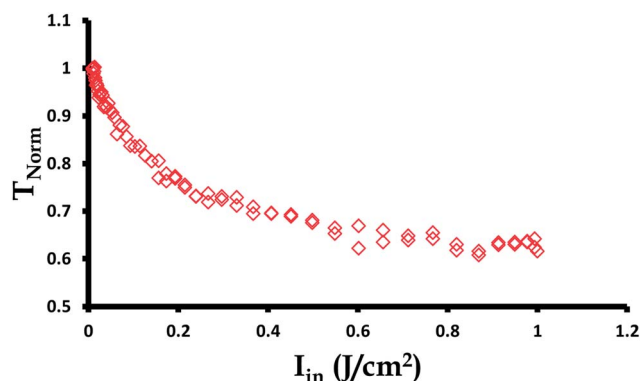


Fig. 8 Plot of normalized transmittance versus I_{in} for **2b**, concentration = 3.3×10^{-4} M.

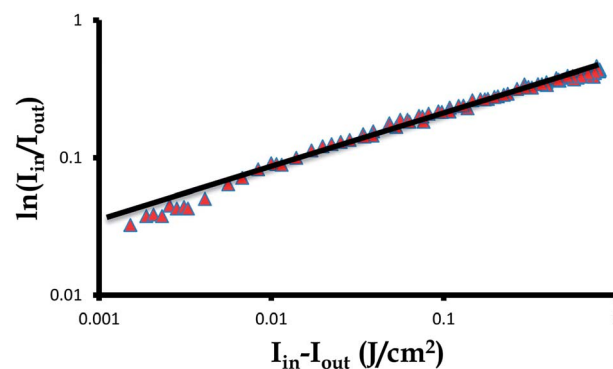


Fig. 9 Plot of $\ln(I_{in}/I_{out})$ versus $(I_{in} - I_{out})$ for **2b** concentration = 2.5×10^{-4} M indicating RSA as the main mechanism.

order of 10^{-4} J cm⁻² and are smaller than those reported for a series of mono phthalocyanines which were of the order of 10^{-2} J cm⁻².⁴⁷ Due to the lack of triplet–triplet absorption signals during laser flash photolysis measurements, I_{lim} values were not determined for complex **2a**.

To confirm the behavior of the NLO material in response to variations in laser intensity, normalized transmittance (T_{Norm}) values were plotted against the on-focus beam intensities, Fig. 8. It was observed that transmittance decreased with increase in the incident intensity as indicated in Fig. 8 for **2b**. The decrease in the transmittance of complexes **2a** and **2b** happens until a point where the excited molecules are saturated with the incident intensity and start giving almost the same transmittance of light. RSA was proven to be the main mechanism by fitting a plot of $\ln(I_{in}/I_{out})$ versus $(I_{in} - I_{out})$ see ESI,† and Fig. 9. As reported previously,⁴⁸ it can be demonstrated by curve fitting that RSA is the main mechanism, with the deviation at low $I_{in} - I_{out}$.

Conclusions

A novel lutetium bisphthalocyanine complex (Pc^1-LuPc^2- , **2a**, the green form) was synthesized and characterized using several techniques including elemental analysis and NMR

spectroscopy. The complex was reduced to form the blue form $[\text{Pc}^{2-}\text{LuPc}^{2-}]^-$ (**2b**). No triplet absorption signal was observed for the green form due to paramagnetism. The open-aperture Z-scan curves are consistent with reverse saturable absorption. The plots of normalized transmittance (T_{Norm}) values versus the transmitted on-focus beam intensities demonstrate that both the blue and green forms of complex **2** absorb the beam in a consistently nonlinear manner. The optical limiting thresholds could not be determined for the green form due to the absence of triplet decay signals.

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