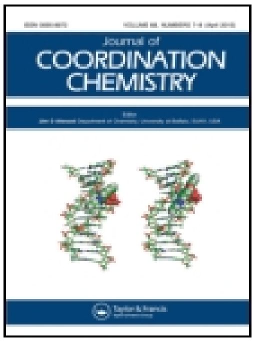

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Mercaptopyridine-substituted indium, zinc, and metal-free phthalocyanines: nonlinear optical studies in solution and on polymer matrices

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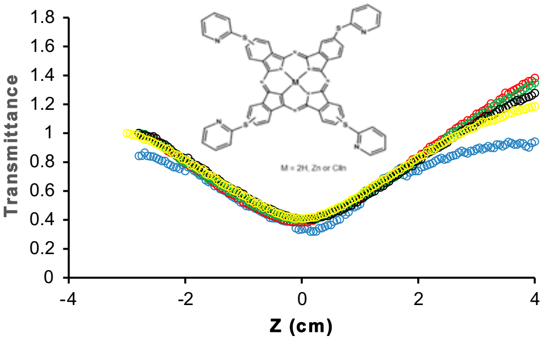

In this article, the nonlinear optical characterizations and optical limiting properties of metal-free (**2**), zinc (**3**), and indium (**4**) tetra 4-(2-mercaptopyridine) phthalocyanines are discussed. Nonlinear optical properties of the samples were evaluated using Z-scan at 532 nm and 10 ns pulse in $CHCl_3$, and doped on poly(bisphenol A carbonate) (PBC) thin films. Thin films for **2**, **3**, and **4** are represented as **2-PBC**, **3-PBC**, and **4-PBC**, respectively. We observed two-photon absorption (2PA) and strong reverse saturable absorption as the dominant mechanisms at nanosecond laser excitation in solution and thin films. By virtue of the magnitude of absorption coefficients and other nonlinear optical parameters estimated in this work, sample **4** was found to exhibit strongest nonlinear optical properties followed by **3**, while **2** is the weakest nonlinear absorber of the studied samples. Large third-order susceptibility (1.46×10^{-9} esu and 7.74×10^{-10} esu) and hyperpolarizability (2.13×10^{-28} and 8.37×10^{-29} esu) were estimated for **4-PBC** and **3-PBC**, respectively. Our studies show that these molecules are suitable candidates for practical passive optical limiters.

Keywords: Phthalocyanine; Poly(bisphenol A carbonate); Nonlinear optics; Reverse saturable absorption; Third-order susceptibility; Hyperpolarizability

1. Introduction

Nonlinear optics (NLO) is a branch of optics that has gained promising applications in biomedicine, photonics and photoelectronics [1–4]. Studies on nonlinear optics have been

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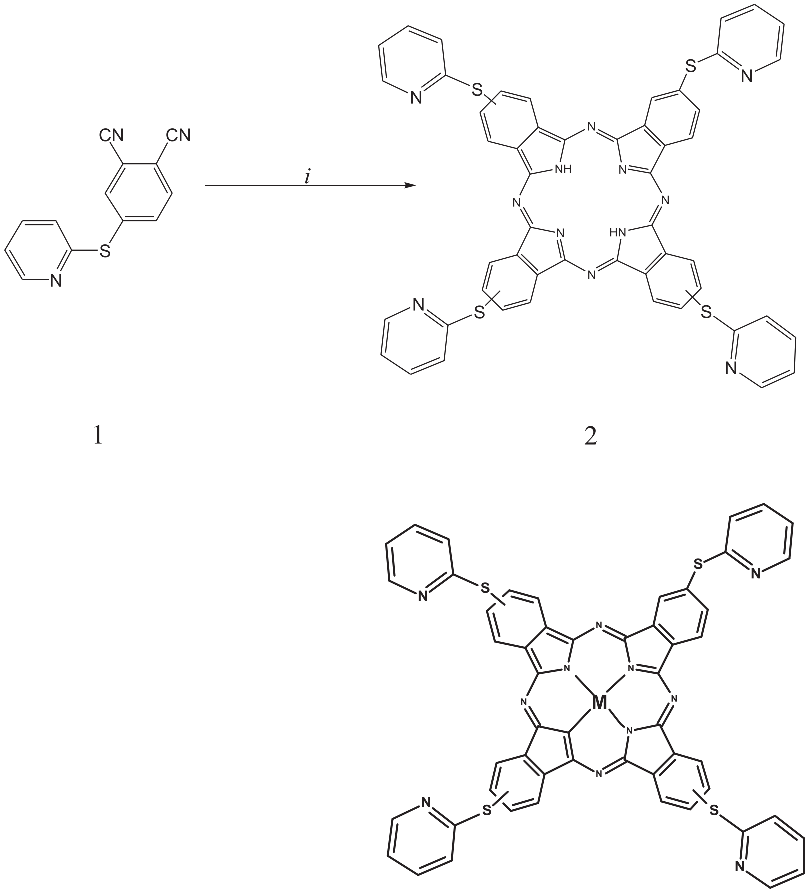
*Corresponding author. Email: t.nyokong@ru.ac.za useful in designing devices capable of decreasing transmission of light as the intensity is increased [5]. Nonlinear optical materials are important for protecting light sensitive materials like human eyes and optical sensors from intense laser beams [6, 7].

The optical limiting (OL) properties of metallophthalocyanines (MPcs) have been reported to be based on reverse saturable absorption (RSA) mechanism due to their high absorption cross section ratio of excited triplet to ground states [8]. Phthalocyanines (Pcs) have been shown to be desirable candidates as NLO materials due to their extensive π–π conjugative system, excellent chemical and thermal stability, and ease of processability to OL components [9]. MPcs also possess large third-order susceptibilities, which translates into ultra-fast response needed to attenuate high-pulse laser radiation [10–12].

The tuning of NLO properties of Pcs can be achieved by varying the central metal in the cavity of the ring or by altering the peripheral functionalities [13, 14]. Reports have shown that phthalocyanines containing heavy metals, such as indium [12] and zinc [15], show



1

2

(3) M = Zn (II)

(4) M = ClIn(III)

Scheme 1. Synthetic route for the preparation of **2**: (i) Li metal, n-pentanol, glacial acetic acid, 140 °C, N_2. Structures of **3** and **4** are also provided.

increased intersystem crossing resulting in improved NLO behavior, compared to metal-free Pcs. However, metal-free Pcs are also known to possess good OL properties due to the structural deformation caused by the absence of central metals [12]. The phthalocyanine complexes containing substituents at the peripheral positions of the Pc have been reported to give better OL behavior than those that are nonperipherally substituted [15]. Hence, 4-(2-mercaptopyridine) peripherally substituted Pc complexes containing In, Zn, and metal-free analogs were employed in this work.

For practical applications, phthalocyanine complexes are embedded in thin films of polymers, such as poly (methyl methacrylate) (PMMA) [16, 17] or poly(bisphenol A carbonate) (PBC) [18], resulting in an improved OL behavior compared to solution [19, 20]. Recently, Mkhize *et al.* [21] reported improved NLO properties for cadmium and lead octakis butylphenoxyphthalocyanine, when doped in PBC compared to PMMA. They found that the enhanced NLO properties of PBC are due to their high mechanical strength, improved stability, and good refractive index with better light transmission than PMMA. Our aim, therefore, is to investigate the nonlinear optical properties of metal-free 4-(2-mercaptopyridine)phthalocyanines (**2**), 4-(2-mercaptopyridine)phthalocyaninato zinc(II) (**3**), and 4-(2-mercaptopyridine) phthalocyaninato indium chloride (**4**) in solution and in PBC, and compare the results with those previously reported. The synthesis and photophysical characterizations of **3** and **4** have been reported before [22, 23]. Our group recently reported the synthesis and photophysical characterizations of **2** [24]. This manuscript describes an alternative synthetic route for the preparation of **2** and the nonlinear optical characterizations in $CHCl_3$ for the first time (scheme 1). We employ mercaptopyridine substituted MPc complexes in this work since sulfur-substituted phthalocyanines have been shown to have improved OL properties [25].

2. Experimental

2.1. *Materials*

Chloroform ($CHCl_3$), n-pentanol, poly(bisphenol A carbonate) (PBC), and lithium metal were obtained from Sigma-Aldrich. Deuterated chloroform ($CDCl_3$), Glacial acetic acid, methanol, and DMSO were purchased from Merck. All solvents were of reagent grade and freshly distilled before use. The synthesis of 4-(2-mercaptopyridine)phthalonitrile (**1**) has been previously reported [26]. The purification process was carried out on silica gel 60 (0.063–0.200 mm) for column chromatography.

2.2. *Equipment and methods*

Infrared spectra were collected on a Perkin-Elmer Universal ATR Sampling accessory spectrum 100 FT-IR spectrometer. ^1H NMR spectra were obtained using a Bruker AVANCE 600 MHz NMR spectrometer in $CDCl_3$ solvent. Elemental analyses were done using a Vario-Elementar Microcube ELIII, while mass spectral data were collected on a Bruker AutoFLEX III Smart-beam TOF/TOF mass spectrometer using α-cyano-4-hydrocinnamic acid as the matrix in the positive ion mode. Ground state electronic absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer.

All Z-scan analyses were performed using a frequency-doubled Nd:YAG laser (Quanta-Ray, 1.5 J/10 ns fwhm pulse duration) as the excitation source. The laser was operated in a near-Gaussian transverse mode at 532 nm (second harmonic), with a pulse repetition rate of 10 Hz and energy range of 0.1 µJ–0.1 mJ, as limited by the energy detectors (Coherent J5-09). The low repetition rate of the laser prevents cumulative thermal nonlinearities. The beam was spatially filtered to remove the higher order modes and tightly focused with a 15 cm focal length lens. The Z-scan system size ($l \times w \times h$) used was 600 mm × 300 mm × 350 mm (excluding the computer, energy meter, translation stage driver, and laser system). The liquid samples were placed in a cuvette (internal dimensions: 2 mm × 10 mm × 55 mm, 0.7 mL) and a path length of 2 mm (Starna 21-G-2).

2.3. *Synthesis of 2, scheme 1*

Zinc (**3**) and indium (**4**) 2-mercaptopyridinephthalocyanines were synthesized and purified according to the reported procedures [22, 23]. The metal-free phthalocyanine (**2**) was synthesized as follows: 4-(2-mercaptopyridine)phthalonitrile **1** (2.0 g, 8.44 mmol) and lithium metal (3.80 g, 54.7 mmol) were suspended in 20 mL of dry n-pentanol and heated at 140 °C in a sealed glass tube for 5 h under a nitrogen atmosphere. The crude product was heated under reflux with glacial acetic acid (50 mL) at 100 °C for 2 h. On cooling to room temperature, the product was precipitated with methanol and washed several times with distilled water and dried under vacuum. The solid residue was purified on a silica gel column chromatography with chloroform/methanol (9 : 1) solvent system as eluent to afford metal-free phthalocyanines (**2**). Yield: 51%. UV/Vis ($CHCl_3$): λ_{max}/nm (log ε): 705 (4.97), 671 (4.96), 649 (4.70), 615 (4.52), 342 (4.81). MS (MALDI-TOF) *m/z*: Calcd: 950.2; Found: 950.5 $[M]^+$. FT-IR ν_{max}/cm^{-1}: 3286 (N–H, stretch), 3040 (Ar–H), 1602 (NH, bend), 1557 (C=N), 1571 (C=C), 1007, 695 (C–S–C). Anal. Calcd for $C_{52}H_{30}N_{12}S_4$: %C 65.66, %H 3.18, %N 17.67, %S 13.48; found: %C 65.40, %H 3.21, %N 17.20, %S 13.20. ^1H NMR (600 MHz, $CDCl_3$) δ, ppm: 9.20–7.92 (pyridyl-H, 16H, m), 8.64 (Pc-H, 4H, m), 7.78–7.50 (Pc-H, 8H, m).

2.4. *Fabrication of thin films*

Thin films for the studied phthalocyanine-polymer matrices were prepared according to the reported methods [18, 21]. Briefly, poly(bisphenol A carbonate) (110 mg) and 2.5 mg of **2** (5.3×10^{-4}), **3** (4.9×10^{-4}), or **4** (4.5×10^{-4}) were, respectively, dissolved in chloroform (5 mL) and sonicated for 30 min until a homogeneous mixture of Pc-polymer solutions were obtained. The Pc-polymer solutions were dropped on glass substrates placed in a Petri dish and the solvent was allowed to evaporate at room temperature. The prepared thin films from **2**, **3**, and **4** are represented as **2-PBC**, **3-PBC**, and **4-PBC**, respectively.

2.5. *Nonlinear optical parameters*

The nonlinear optical properties of phthalocyanines were evaluated using the Z-scan technique that has been previously described [27]. Z-scan technique relies on the total transmittance passing through the molecule as a result of the incident laser pulses. The intensity of the laser pulses are measured as the sample moves through the focus of a lens (along the

z-axis). The data collected from the Z-scan equipment were analyzed using the procedure described by Sheik-Bahae *et al.* [28], equation (1):

$$T(Z) = \frac{1}{1 + \beta_{\text{eff}} L_{\text{eff}} (I_{00}/(1 + (z/z_0)^2))} \tag{1}$$

where $T(Z)$ is the normalized transmittance of the sample, I_{00} is the intensity of the light on focus, β_{eff} is the two-photon absorption coefficient, z_0 is the diffraction length of the beam, z is the sample position with respect to input intensity, and L_{eff} is the effective length for two-photon absorption (2PA), equation (2):

$$L_{\text{eff}} = \frac{1 - e^{-\alpha \text{L}}}{\alpha} \tag{2}$$

where α is the linear absorption coefficient. The two-photon absorption cross section (σ_2, cm^4 s/photon) can be calculated from the known two-photon absorption coefficient (β_{eff}) using equation (3) [29]:

$$\sigma_2 = \frac{1000 h\upsilon \beta_{\text{eff}}}{N_{\text{A}} C} \tag{3}$$

where $h\upsilon$ is the incident photon measured in joules, N_{A} is the Avogadro constant, and C is the concentration of the sample.

The imaginary third-order susceptibility ($I_{\text{m}}[\chi^{(3)}]$) is directly proportional to the two-photon absorption coefficient, β_{eff} as shown in equation (4) [30]:

$$I_{\text{m}}[\chi^{(3)}] = n^2 \varepsilon_0 c \lambda \beta_{\text{eff}} / 4\pi \tag{4}$$

where n is the linear refractive index, c is the speed of light, ε_0 is the permittivity of free space, and λ is the wavelength of the laser.

The relationship between second-order hyperpolarizability (γ) and third-order susceptibility (($I_{\text{m}}[\chi^{(3)}]$)) of the material are expressed in equation (5) [30]:

$$\gamma = \frac{I_{\text{m}}[\chi^{(3)}]}{f^4 C_{\text{mol}} N_{\text{A}}} \tag{5}$$

where C_{mol} is the molar concentration of the active species in the triplet state, f is the Lorentz local field enhancement factor defined as $f = (n^2 + 2)/3$ (where n is the refractive index of the sample), and N_{A} is as defined above.

3. Results and discussion

3.1. *Synthesis and characterization of 2*

Scheme 1 represents the route for the synthesis of unmetallated phthalocyanines reported in this work. The precursor to the synthesis of metal-free phthalocyanine is 4-(2-mercaptopyridine)phthalonitrile (**1**) whose synthesis has been previously reported [26]. The cyclotetramerization of **1** with excess lithium metal in the presence of n-pentanol under nitrogen

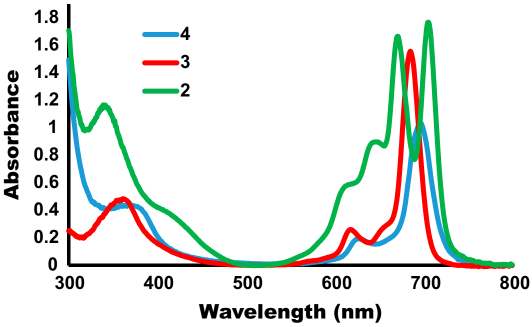


Figure 1. Electronic absorption spectra of **2** (green), **3** (red), and **4** (blue) in $CHCl_3$ (1×10^{-5} M) (see http://dx.doi.org/10.1080/00958972.2015.1077237 for color version).

results in the formation of lithium phthalocyanine (LiPc). Unmetallated phthalocyanine (**2**) was synthesized by refluxing LiPc in glacial acetic acid for 2 h to remove the loosely held lithium metal in the Pc cavity. The metal-free pthalocyanine was purified by column chromatography and characterized by FTIR, elemental analyses, ^{1}H NMR, electronic absorption, and MALDI-TOF mass spectroscopies. The obtained data were consistent with the predicted structure. FTIR investigations on the metal-free Pc confirmed the absence of the sharp C≡N vibration at 2230 cm^{-1}. The presence of single N–H (secondary amine) stretching vibration band at 3286 cm^{-1} of the inner core of the metal-free Pc further proved the successful conversion of mercaptopyridine phthalonitrile derivative to Pc. In the ^{1}H NMR spectra, the pyridyl-H of **2** was observed as a multiplet between 9.20 and 7.92 ppm, which on integrating gave 16 protons. The proton signals of the Pc ring were observed as multiplet between 8.64 and 7.50 ppm and integrated to 12 protons. The two inner core protons of the unmetallated Pc lie in the negative region of the spectrum and were not observed [31, 32]. The mass spectrum gave the expected value of the synthesized molecule at *m/z*: 950.5 $[M]^+$ and therefore confirmed the proposed structures. Elemental analysis of the compound was in agreement with the calculated values. The synthesized molecule showed good solubility in most organic solvents, such as chloroform, DMF, dichloromethane, and THF.

The electronic absorption spectrum of **2** in $CHCl_3$ is shown in figure 1, together with the spectra of **3** and **4**. For **2**, the Q-bands were observed at 705 and 671 nm with shoulders around 649 and 615 nm, while the B-band was observed at 342 nm. The Q-band absorptions of metal-free phthalocyanines possess D_{2h} symmetry, hence the splitting pattern was observed in the spectrum. The UV–vis measurements of **2**, **3**, and **4** at concentrations from 1.0×10^{-5} to 1.8×10^{-5} M did not show any sign of aggregation in $CHCl_3$. The Beer–Lambert law was obeyed at the studied concentrations.

3.2. *Characterization of thin films of Pcs with polymers*

The respective Pc molecules were mixed with PBC and sonicated in chloroform prior to immobilization on clean glass slides by drop-dry method. The concentrations of Pcs embedded in PCB polymer thin films are in the range of 4.5×10^{-4}–5.3×10^{-4} M.

The UV–vis spectra of phthalocyanines **2**–**4** when embedded in PBC polymer thin films are shown in figure 2. All the molecules exhibited aggregation with broadening of Q-bands and Soret bands in thin films. The presence of the common H aggregates in Pcs is judged

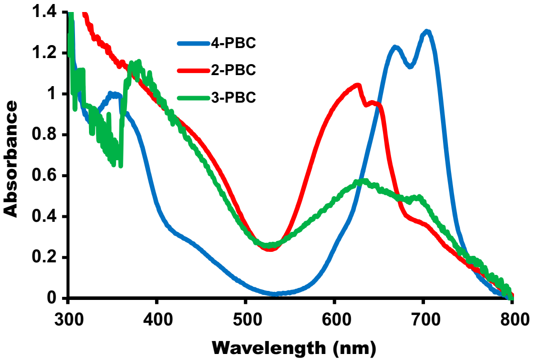


Figure 2. UV–vis spectra of phthalocyanines **2**–**4** in PBC thin films. Concentrations of Pcs in films ranged from 4.5×10^{-4} to 5.3×10^{-4} M.

by the presence of a blue shifted peak due to the aggregate and a monomer peak at lower energies [33]. For **4-PBC**, the monomer peak (lower energy) is more intense than the aggregate peak (higher energy). **2-PBC** and **3-PBC** are more aggregated in solid state than **4-PBC**, since for the former two, the high energy peak (due to the aggregate) is more intense than the peak due to the monomer. The spectra in thin films are broader compared to those in solution. The broadening of the spectra of Pcs in solid states can be attributed to the intermolecular interaction and molecular deformation [34, 35], which results in the slight modification of the energy level configurations of the Pcs [36].

3.3. *Nonlinear optical studies*

3.3.1. Z-scan measurements in solution. Figure 3 shows representative of open-aperture Z-scan signal for **2** obtained at 532 nm using 10 ns pulses under input intensity of 0.57 GW cm^{-2}. The concentration of the sample was maintained at 2×10^{-5} M in chloroform. Open circles (red) represent the experimental data while the solid line (black) represents the theoretical fit to the open aperture scan using equation (1). Figure 4(A)–(C) shows overlay of open aperture (OA) Z-scan spectra of **2**, **3**, and **4** in solution.

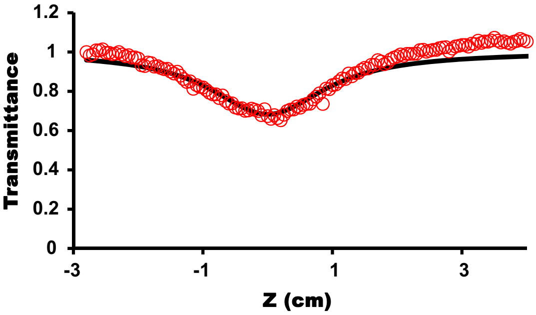


Figure 3. Representative open-aperture Z-scan with normalized transmission plotted as a function of sample position for **2**. Peak input intensity (I_{00}) ~0.57 GW cm^{-2}. Concentration 2.0×10^{-5} M in CHCl$_3$.

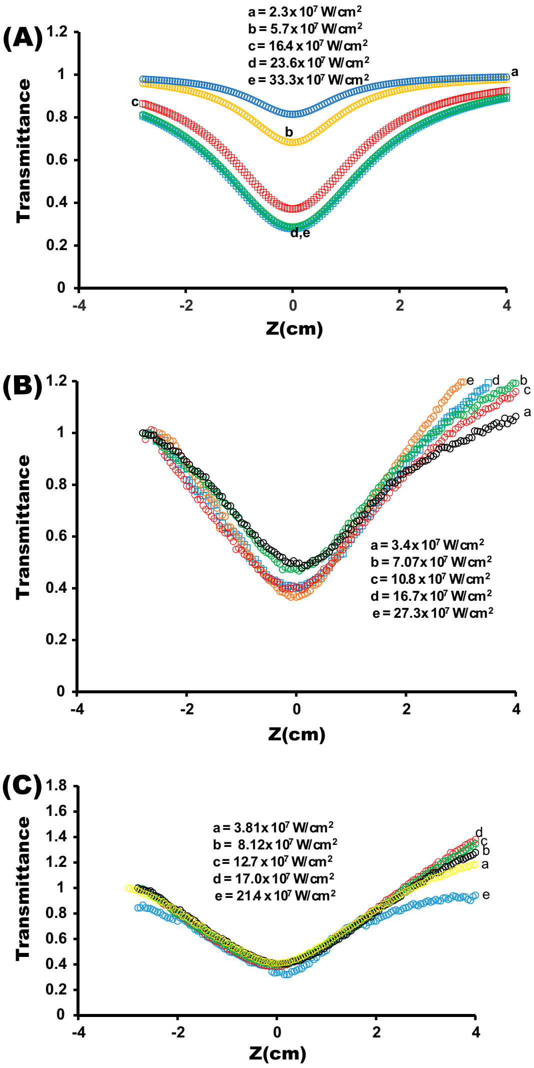


Figure 4. Plots showing OA Z-scan curves for evaluating β_{eff} for (A) **2**, (B) **3**, and (C) **4**. Concentrations = 1.0×10^{-4} in $CHCl_3$.

Table 1. Nonlinear optical properties of **2**, **3**, and **4** in $CHCl_3$ and thin films at 532 nm wavelength and 10 ns pulses.

Complex	β_{eff} (cm GW^{-1})	$(I_m[\chi^{(3)}])$ (esu)	γ (esu)	σ_2 (cm^4 s/photon)	I_{lim} (J cm^{-2})
2	300	7.04×10^{-11}	1.99×10^{-30}	5.59×10^{-44}	0.88
3	372	8.73×10^{-11}	2.47×10^{-30}	6.93×10^{-44}	0.57
4	432	1.97×10^{-10}	5.58×10^{-30}	1.56×10^{-43}	0.46
2-PBC	2455	1.07×10^{-10}	3.02×10^{-29}	8.46×10^{-43}	0.54
3-PBC	4555	7.74×10^{-10}	8.37×10^{-29}	4.55×10^{-43}	0.2
4-PBC	6213	1.46×10^{-9}	2.13×10^{-28}	1.16×10^{-42}	0.11

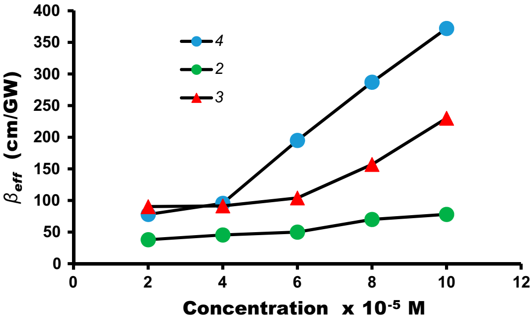


Figure 5. Plots showing the concentration dependence on β_{eff} for **2**, **3**, and **4**. $I_{00} \approx 0.21$ GW cm^{-2} for each independent measurement in CHCl$_3$.

All the Z-scan measurements carried out on the compounds at various input intensities showed reduction in the transmission about the focus of the lens. At input intensity >10^7 GW cm^{-2}, a positive nonlinear absorption (NLA) signature is induced in the sample [37], attributed to the RSA behavior [28, 38, 39]. The concentration of each sample was maintained at 1.0 × 10^{-4} M in CHCl$_3$, figure 4. At a constant concentration, it is expected that the dip around zero position remains constant in the presence of varying energies (input intensity). The Z-scan profile of **2** remained highly unstable (dip intensity changing) in the presence of different input intensities compared to **3** and **4**. As **2** remained unstable to the input intensity, so does the value of effective NLA coefficient (β_{eff}) measured for each sample. Using 2PA function, the best fit gave β_{eff} of 300 cm GW^{-1} for **2** at I_{00} of 23.6 × 10^7 W cm^{-2} [figure 4A(d)], 372 cm GW^{-1} for **3** at I_{00} of 27.3 × 10^7 W cm^{-2} [figure 4B(e)], and 432 cm GW^{-1} for **4** at I_{00} of 21.4 × 10^7 W cm^{-2} [figure 4C(e)], table 1. The estimated β_{eff} in solution for **2** is smallest followed by **3**, while the largest value was reported for **4**. This suggests better NLO behavior for **4** compared to **2** and **3**. The values were as expected, since inclusion of heavy metals in Pc leads to improved NLO and OL properties [40, 41]. The presence of indium is believed to have increased the triplet-state populations of **4** due to its heavier atom effect compared to zinc in **3** [5]. This explains the improved NLO properties of **4** compared to **3**, hence its larger β_{eff} value.

General trends for nonlinearity of the complexes in solution were also investigated at constant input intensity and varying concentrations. The measured β_{eff} values were plotted against the sample concentrations at I_{00} of ~0.21 GW cm^{-2} (figure 5). It can be clearly seen that β_{eff} increases in magnitude as the concentration of each sample increases; phthalocyanine **4** exhibits the largest effective NLA coefficient (β_{eff}) of 372 cm GW^{-1} at 1.0 × 10^{-4} M. The increase in magnitude of the β_{eff} as the concentration increases suggests direct relationship between the β_{eff} and the available sequential photon absorptions induced by RSA at the excited triplet states [42]. This confirms the 2PA-dependent RSA as the dominant mechanism responsible for the observed nonlinearity for the complexes in solution.

3.3.2. Z-scan measurements in thin films. The Z-scan profiles, figure 6(a)–(c), for the complexes in thin films were fitted to 2PA processes, revealing RSA. At input intensity of ~33 MW cm^{-2}, ~2455 cm GW^{-1}, ~4555 cm GW^{-1}, and ~6213 cm GW^{-1} β_{eff} values (table 1) were obtained for **2-PBC**, **3-PBC**, and **4-PBC**, respectively. Unmetallated **2** revealed fuzzy signals in both solution and on solid support, a characteristic of weaker

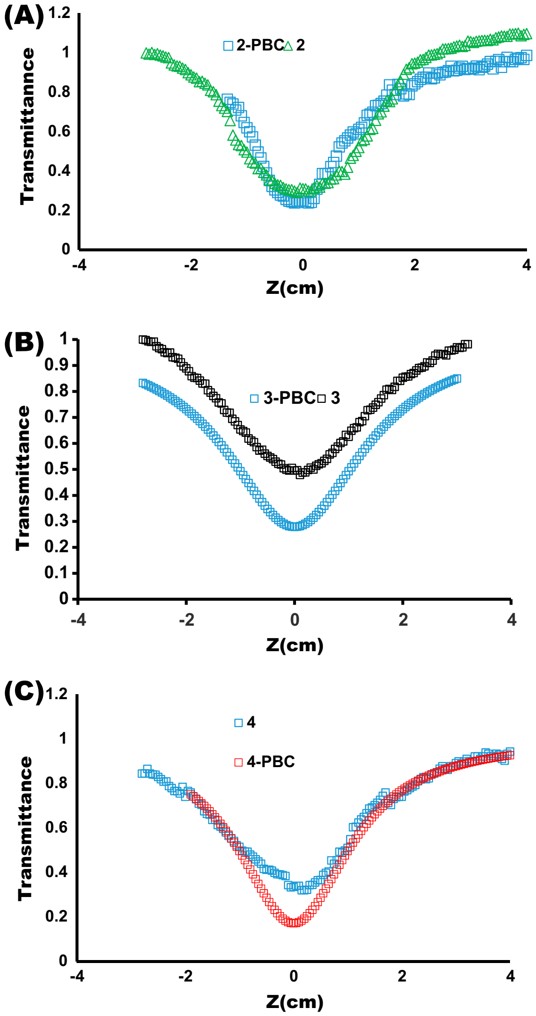


Figure 6. OA Z-scan curves for (A) **2** and **2-PBC**, (B) **3** and **3-PBC**, and (C) **4** and **4-PBC**. Peak input intensity (I_{00}) ~ 33 MW cm^{-2}, Concentration = 1.0 × 10^{-4} in CHCl$_3$ for all compounds.

nonlinear response. The distinct and sharp signals observed for **3** and **4** in both solution and solid state is an indication of stronger nonlinear responses. However, indium phthalocyanine **4** outperforms other molecules in terms of the magnitude of the reduction in the normalized transmittance relative to input intensity. The substantial increase in the magnitude of β_{eff} values in thin films compared to solutions for each sample revealed the importance of Pc-polymer composites for NLO applications.

3.3.3. Third-order nonlinear susceptibility ($I_{\mathrm{m}}[\chi^{(3)}]$) and second-order hyperpolarizability (γ). The imaginary third-order susceptibility, ($I_{\mathrm{m}}[\chi^{(3)}]$), is a measure of fast response time of a molecular material to the perturbation induced by the intense laser pulses. The second-order hyperpolarizability, γ, measures the interaction of the incident photon with the permanent dipole moments of the Pcs. Nonlinear optical materials protect light-sensitive materials by effectively limiting the energy output of an incident light. The third-order susceptibility ($(I_m[\chi^{(3)}])$) and hyperpolarizability (γ) (measured in esu) were evaluated in terms of 2PA coefficient (β_{eff}) using equations (4) and (5). The calculated ($I_m[\chi^{(3)}]$) and γ values for the samples, both in solution and in thin films, are presented in table 1. A good OL device must have high absorbency as the intensity of the incident light is increased. Hence, the higher the values of γ and/or ($I_m[\chi^{(3)}]$), the better the compounds as optical limiters. We expect the values of γ and ($I_m[\chi^{(3)}]$) to vary in the same trend as observed for β_{eff}. Generally, the ($I_m[\chi^{(3)}]$)and γ values in solution for the studied samples are lower than when embedded in thin films. Of the thin films, the ($I_m[\chi^{(3)}]$) value of 1.46×10^{-9} esu for **4-PBC** was the highest and the lowest value was obtained for metal-free phthalocyanine film (**2-PBC**, 1.07×10^{-10} esu). Since the substituents on the Pcs are all the same for the studied samples, it is safe to assume that the major factor responsible for the magnitude of ($I_m[\chi^{(3)}]$)in MPc is the influence of central metal. Similarly, the same trend was also observed for γ values in solution and in their thin films. The γ values in solution reported in this work are greater than those reported for ZnPc, CuPc ~10^{-31} esu in DMF [43], and LuTBPc 10^{-33} esu [44]. The estimated γ values for **2**, **3**, and **4** in $CHCl_3$ are comparable to the copper complexes (3.52×10^{-29}–7.6×10^{-30} esu) measured in DMF [45] and are much higher than tert-butyl-substituted ZnPc at ~4.3 10^{-31} esu, implying that the complexes in this work are good candidates as optical limiters.

The ($I_m[\chi^{(3)}]$) values estimated for **2**, **3**, and **4** in solution are larger by two to four orders of magnitude than the values reported for naphthalocyanine and phthalocyanine derivatives at 532–604 nm in DMF [46–49]. Also, the measured ($I_m[\chi^{(3)}]$) value for **4** in solution is larger by one to two orders of magnitude than the values reported for InPc (3.49×10^{-12} and 1.89×10^{-11} esu) [50], cadmium(II) polymeric cluster in DMF (8.03×10^{-12} esu) [51] and tert-butyl-substituted ZnPc at ~4.3×10^{-14} esu. The ($I_m[\chi^{(3)}]$)values of ~10^{-10} esu in thin films reported in this work were the same order of magnitude for the trinuclear lanthanide phthalocyanines embedded in poly(bisphenol A carbonate) at 532 nm and in DMF, as reported by Sekhosana *et al.* [18]. Rao *et al.* [36] reported $\chi^{(3)}$ values of ~10^{-10} esu for five different Pcs doped in PMMA polymers; these are lower by one order of magnitude compared to **4-PBC** reported in this work. Reports [21] have shown that PMMA has poor mechanical strength and lower refractive index compared to PBC; hence, superior nonlinear transmittance is observed for our Pc-PBC composites.

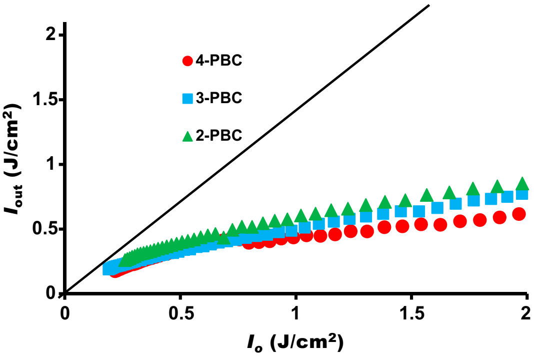


Figure 7. Output fluence (I_{out}) *vs.* input fluence (I_0) for **2-PBC**, **3-PBC**, and **4-PBC**. The black line represents a case of linear transmission. Peak intensity (I_{00}) ≈ 33 MW cm^{-2} for each sample.

The two-photon absorption cross sections (σ_2) reported in this work are very large and are within the class of organic-based nonlinear optical materials [52]. Again, the value for **4** is the highest, showing the potential of indium phthalocyanines in OL [53, 54].

3.3.4. OL threshold. Incident intensity threshold (I_{lim}) is an important parameter used for measuring OL performance of molecular materials when the input intensity is at 50% linear transmittance [9]. Molecular materials perform better as nonlinear optical device at I_{lim} value below 1.0. Therefore, the lower the I_{lim} value, the better the material as an optical limiter. Figure 7 shows a plot of incident laser intensity (I_{in}) against transmitted laser intensity (I_{out}) for **2-PBC**, **3-PBC**, and **4-PBC** at 532 nm, 10 ns, and $I_{00} \approx {\sim}33$ MW cm^{-2}. The black line on the plot represents the case of linearity from which the magnitude of the nonlinearity of the samples are estimated. The deviation of the samples from linearity is an indication of good NLO responses to the input intensity. From table 1, indium phthalocyanine **4-PBC** has the lowest I_{lim} value of 0.11 J cm^{-2}; this translates to excellent OL response compared to **2-PBC** and **3-PBC**, considering the same approximate concentration. The metal-free phthalocyanine is outperformed by other samples and showed the least OL properties in solution and in thin film. However, the I_{lim} values obtained for the samples are still within the acceptable limits for **2**.

4. Conclusion

We investigated the nonlinear optical and OL performances of indium (**4**), zinc (**3**), and metal-free (**2**) phthalocyanines tetrasubstituted at the peripheral positions with 2-mercaptopyridine in solution and in thin films. The open aperture Z-scan studies were carried out using 5 ns pulses at 532 nm. The profiles of the open aperture Z-scan for the compounds revealed reverse saturable excited state absorption in solution and in polymer mixture. Our findings showed that the phthalocyanines doped in thin films possess strong NLA coefficients and lower limiting thresholds than in solution. The highest value of $(I_m[\chi^{(3)}])$at 1.46×10^{-9} esu and y at 2.13×10^{-28} esu were recorded for **4-PBC**, making indium-centered phthalocyanine the strongest nonlinear absorber of the studied samples. The values of $(I_m[\chi^{(3)}])$ and γ recorded for metal-free Pc doped in PBC are 1.07×10^{-10} and 3.02×10^{-29} esu, respectively. This makes the metal-free Pc (**2**) the weakest nonlinear absorber of the studied samples. Our studies showed that these phthalocyanines can be used as protective devices for light-sensitive materials due to the high transmission to nondamaging light of PBC. Also, the ultra-fast response time of **3** and **4** in thin films, in terms of the magnitude of third-order susceptibility, make them suitable candidates for real-life applications, and for practical passive optical limiters.

Disclosure statement

No potential conflict of interest was reported by the authors.

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