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The effect of the cobalt and manganese central metal ions on the nonlinear optical properties of tetra(4-propargyloxyphenoxy)phthalocyanines†

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The metal-free (H_2TPrOPhOPc), cobalt (CoTPrOPhOPc) and manganese (Mn(OAc)TPrOPhOPc) tetra propargyloxyphenoxy phthalocyanines were evaluated for their potential as optical limiting materials. The effect of the substituents and the central metal ions on the nonlinear optical properties was evaluated. The metal-free phthalocyanine exhibited better nonlinear optical properties when compared to the cobalt and manganese complexes owing to the metal ions quenching the excited state due to their half-filled d-orbitals. The nonlinear absorption coefficient (β_{eff}, $\times 10^{-5}$ m MW^{-1}) followed the trend of H_2TPrOPhOPc > CoTPrOPhOPc > Mn(OAc)TPrOPhOPc. The values β_{eff} ($\times 10^{-5}$ m MW^{-1}) using 532 nm Nd:YAG (560 nm monochromatic Ekspla) laser sources were 23.5 > 14.3 > 9.20 (14.4). The second-order nonlinear coefficient obtained using density functional theory calculations, the theoretical hyper-Rayleigh scattering (β_{HRS}, $\times 10^{-28}$ esu), showed the decreasing trend for H_2TPrOPhOPc (2.28) > CoTPrOPhOPc (2.10) > Mn(OAc)TPrOPhOPc (1.86). The 4-(propargyloxy)phenoxy substituents enhanced the optical limiting properties of the synthesized phthalocyanines.

Introduction

Metallophthalocyanines (MPcs), owing to their interesting physicochemical properties, have been investigated for various applications, such as liquid crystals[1] and molecular electronics,[2] and of importance to this study is their potential as optical limiting and nonlinear optical materials.[3–9] The wide ranging applications of phthalocyanines are universally dependent on their chemical composition. These include: (i) the type of central metal ion introduced in the Pc ring cavity, (ii) the type of functional groups as substituents on the Pc ring and (iii) the axial ligands on the metal ion. Amongst the different functional groups that can be used as substituents on the Pc ring is the terminal alkynyl ($C{\equiv}C$) group. The linearity and rigidity of this functional group has allowed for a number of synthetic organic materials to be constructed.[10–12] Acetylene-based scaffolding has been used widely for synthetic organic materials. Alkynyl-functionalized materials have been reported to exhibit excellent and remarkable nonlinear optical properties.[13,14] A few alkynyl-substituted MPcs have been synthesized mainly as building blocks or polymers in material synthesis and are also converted quickly to 1,2,3-triazole rings.[12,15–17] The terminal alkynyl ($C{\equiv}C$) substituted MPcs are difficult to synthesize, hence very few research groups have successfully managed to synthesize these interesting complexes. This work investigates the non-linear optical (NLO) properties of the recently synthesized tetra(4-propargyloxyphenoxy)phthalocyanines (**1–3**, in Fig. 1).[18] The majority of the MPcs that have been studied for their nonlinear optical properties are: (i) mononuclear Pcs, either metal free[19] or containing diamagnetic central metal ions, such as Zn, Ga, Al, Ge, In, V, Co, Cu, Cd, and Pb,[6,20–26] (ii) binuclear or dimer or ball-type or double-decker Pcs (Mg, Zn, Cu, Ni, Co, Eu, Lu)[26–30a] and (iii) trinuclear or triple decker Pcs (Yb, Lu, Nd, Ce, Eu).[30b–e] A few of the reported MPcs containing cobalt as the central metal ion have been investigated for their nonlinear optical properties and none have been reported that contain manganese as the central metal ion.

In this work, the metal-free (H_2TPrOPhOPc), cobalt (CoTPrOPhOPc) and manganese (Mn(OAc)TPrOPhOPc) tetra propargyloxyphenoxy phthalocyanines bearing terminal alkynyl ($C{\equiv}C$) groups are investigated as nonlinear optical materials. The use of the Z-scan to assess the nonlinear optical properties of the phthalocyanines in solution will be investigated at the conventional 532 nm irradiation wavelength. Owing to the potential interference of the metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge transfer band for the manganese

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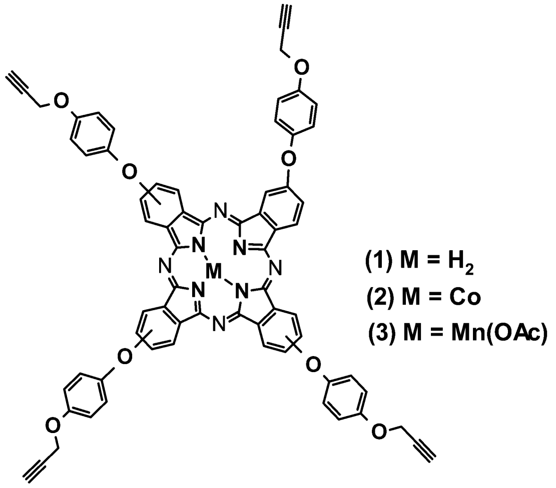

Fig. 1 Chemical structure of the tetra 4-(propargyloxy)phenoxy phthalocyanines (MTPrOPhOPc), with M = H_2 (**1**), Co(II) (**2**) and Mn(III)OAc (**3**).

complex at 532 nm, the use of the 560 nm irradiation wavelength using the monochromatic Ekspla as a laser source was investigated. To the best of our knowledge, the nonlinear optical properties of the metal-free, cobalt and manganese phthalocyanines bearing 4-(propargyloxy)phenoxy functional groups and an acetate axial ligand on the manganese complex have never been reported before. This is the novelty of the reported work and also to investigate the heavy atom effect of Co and Mn in promoting intersystem crossing of the populated single excited state to the triplet excited state.

Experimental

Materials

Tetrahydrofuran (THF) and dichloromethane (DCM) were purchased from Merck chemicals. The recently reported tetra 4-propargyloxyphenoxy substituted phthalocyanines (**1–3**)[18] were used in this study.

Equipment

A Shimadzu UV-2550 Spectrophotometer was utilized to record the electronic absorption spectra. Z-scan measurements were obtained using two laser systems. For the first analysis with the laser excitation at 532 nm (second harmonic) using the Nd:YAG, the experimental details were as previously reported.[19] The monochromatic laser light beams at 560 nm were provided by an Ekspla NT 342B-20-AW laser with 2.0 mJ/5 ns and 20 Hz. This allowed for Z-scan measurements as an optical parametric oscillator unit.

Density functional theory calculations

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations were performed using Gaussian 09 package[31] running on an Intel/Linux cluster. The modelled phthalocyanines (**1–3**) were optimized at the level of B3LYP geometry optimization with 6-31G(d) and SSD basis sets. Additional details of the theoretical calculations for DFT were as reported before[19] and were kept the same with only the phthalocyanines (**1–3**) used in this work. The B3LYP/6-31G(d) basis set as a formalism helped us to perform single-point energy calculations. This was useful in determining the second-order nonlinear optical (NLO) response coefficient, a beta hyper-Rayleigh scattering (β_{HRS}) of the synthesized phthalocyanines, following literature reports.[32] The DFT and TDDFT calculations of the optimized geometries were then used to study the second-order NLO response coefficient, a β_{HRS}, of the phthalocyanines (**1–3**). The use of an open aperture Z-scan technique and theoretical calculations have been reported before.[19] These have been employed in this study to investigate and evaluate the calculations of the nonlinear optical properties of the phthalocyanines (**1–3**).

Results and discussion

UV-vis characterization

Fig. 2 shows the electronic absorption spectra of phthalocyanines (**1–3**) measured in DCM. The metal-free phthalocyanine (H_2TPrOPhOPc, **1**) exhibited a split Q-band. The absorption maxima of the split Q-bands were observed at 666 nm and 705 nm. These were slightly shifted to lower values than the values reported in THF.[18] The shift in the Q-band maxima between the phthalocyanines in THF and in DCM is owing to the different solvents' dielectric constants. Both solvents (DCM and THF) are borderline polar aprotic solvents with different dielectric constants, which are 7.5 for THF and 9.1 for DCM; therefore, DCM is slightly more polar than THF.

The solvent effect was more pronounced on the metallo phthalocyanine complexes, that is CoTPrOPhOPc (**2**) and Mn(OAc)TPrOPhOPc (**3**). The Q-band absorption maxima were observed at 667 nm for CoTPrOPhOPc in THF and shifted to 674 nm in DCM. For the Mn(OAc)TPrOPhOPc the Q-band maxima shifted from 725 nm in THF to 735 nm in DCM. The ~10 nm shift in the Q-band absorption maxima was attributed to DCM having a higher dielectric constant of 9.1 when

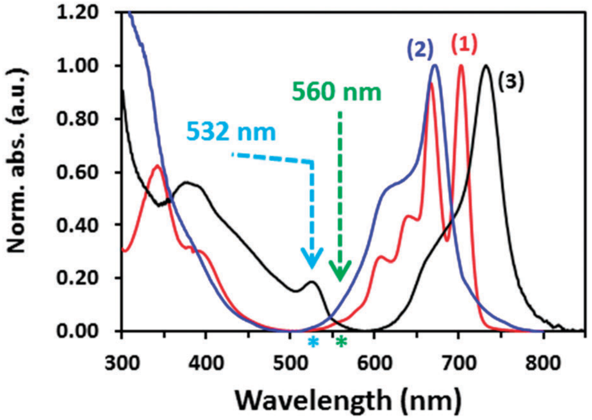

Fig. 2 Electronic absorption spectra of H_2TPrOPhOPc (**1**), CoTPrOPhOPc (**2**) and MnTPrOPhOPc (**3**) in DCM. Concentration ~1 × 10^{-5} M. The marked wavelengths (532 and 560 nm) are for irradiation during Z-scan measurements.

compared to 7.5 for THF. The absorption in phthalocyanines is due to electronic transitions from the HOMO (highest occupied molecular orbitals) to the LUMO (lowest unoccupied molecular orbitals).[33] The various electronic transitions observed for the phthalocyanines studied were discussed in our previous work.[18] The studied aprotic solvents THF (studied before) and DCM (in this work) yielded the same transitions with the shift of the Q-band maxima owing to the different dielectric constants of the two solvents (THF and DCM). Other than the Q-bands, the B-bands and the charge-transfer (metal-to-ligand and ligand-to-metal) were also observed and are as discussed in our previous report.[18]

Nonlinear absorption properties of phthalocyanines (1–3)

The nonlinear absorption properties of phthalocyanines (**1–3**) were investigated using the Z-scan technique and DFT theoretical calculations. The open aperture Z-scan technique was performed in DCM solution at 532 nm using the Nd:YAG laser source and at 560 nm using the monochromatic Ekspla NT 342B-20-AW laser source. Fig. 3 shows the schematic diagram for the Z-scan measurement using the irradiation wavelengths of both the laser sources highlighted in Fig. 2. The wavelengths were on the blue side of the Q-bands for all the studied phthalocyanines (Pcs). Pcs are known to exhibit an excited state absorption (ESA) cross section higher than the ground state absorption at wavelengths between the B and the Q bands.[34] ESA is a major mechanism of the nonlinear absorption of the optical limiters in solution. Other mechanisms that might contribute are two-photon absorption (TPA), free-carrier absorption (FCA), thermal defocusing/scattering, photo refraction, nonlinear refraction and induced scattering.[35,36]

Fig. 4 shows a typical open aperture Z-scan (a–d) and nonlinear fitted curves (a′–d′) ($Q_0(Z_S)$). Fig. 4(a–c) were measured using a 532 nm Nd:YAG laser source and Fig. 4(d) was measured using a 560 nm monochromatic Ekspla NT 342B-20-AW laser source. The open aperture Z-scan were for (a) H_2TPrOPhOPc (**1**), (b) CoTPrOPhOPc (**2**) and (c and d) Mn(OAc)TPrOPhOPc (**3**) measured at 1.0×10^{-5} M for each compound in DCM. Using the 532 nm Nd:YAG laser source, the curves for H_2TPrOPhOPc (**1**) and CoTPrOPhOPc (**2**) showed a decrease in transmission from −30/−40 mm towards focal point (Z_S = 0 mm). The reverse of absorption was observed when the sample position was moved gradually away from the focal point towards +30/+40 mm. This is a typical nonlinear absorption that strongly resembles the reverse saturable absorption (RSA) profiles for H_2TPrOPhOPc (**1**) and CoTPrOPhOPc (**2**). A close inspection of the curve of phthalocyanine (**1**), in Fig. 4(a), shows the initial broadening of the curve then the sudden narrowing as the sample approaches the focal point, and finally the broadening occurs as the sample moves away from the focal point. The observed decrease in transmittance close to the focal point suggests the formation of plasma owing to the presence of nonlinear scattering at high intensities. Nonlinear scattering occurs when the intensity inside the sample is high enough to form a localized plasma, which acts as a centre

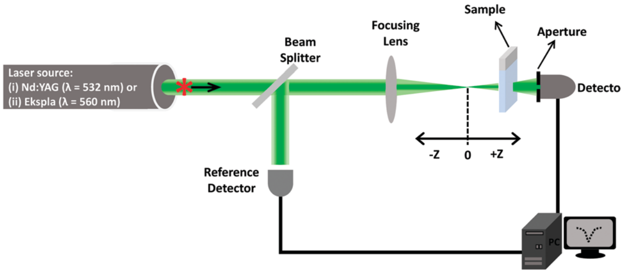

Fig. 3 Schematic diagram of the open aperture Z-scan measurements. The two laser sources (Nd:YAG) (λ = 532 nm) and monochromatic Ekspla (λ = 560 nm).

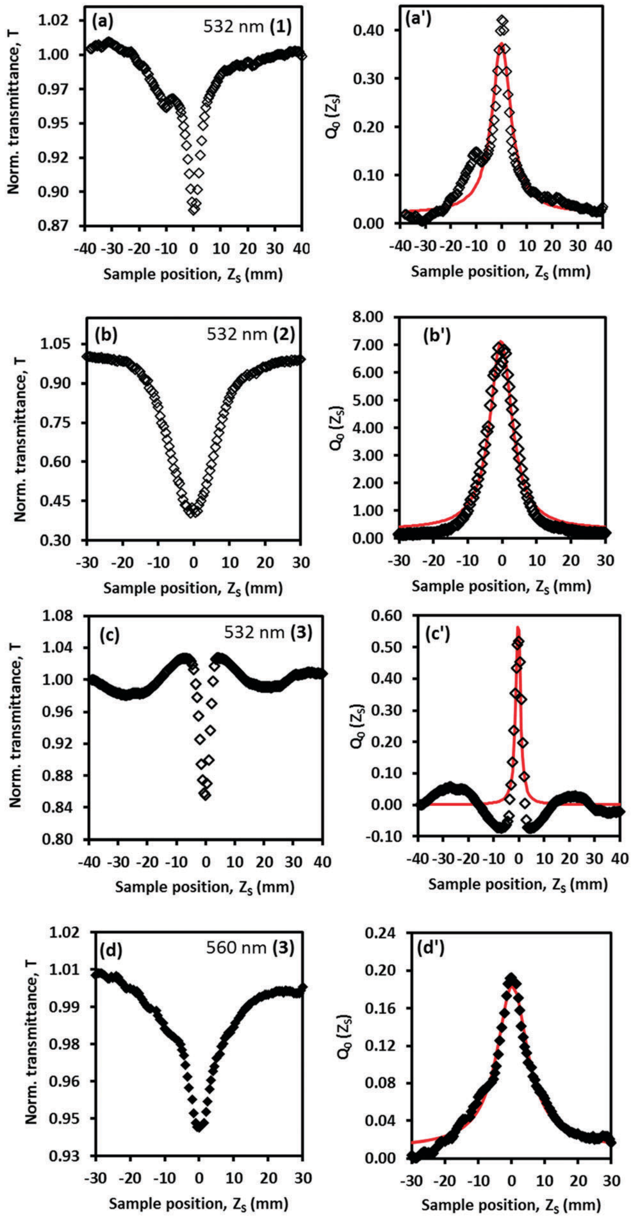

Fig. 4 Open aperture Z-scan (a–d) and nonlinear fit (a′–d′) curves ($Q_0(Z_S)$). (a–c) Measured using 532 nm Nd:YAG and (d) 560 nm monochromatic Ekspla laser sources. (a) H_2TPrOPhOPc (**1**), (b) CoTPrOPhOPc (**2**) and (c and d) Mn(OAc)TPrOPhOPc (**3**) for 1.0×10^{-5} M in DCM.

of scattering[36,37] for the incoming intense laser. The localized plasma is believed to reduce transmission through the sample and hence increases the apparent absorption.[36] For CoTPrOPhOPc (**2**), the feature of a single valley signifies a reverse saturation absorption (RSA). This feature is prominent when the excited state of the molecule has strong absorption compared to the ground state. On the other hand, the open aperture Z-scan of CoTPrOPhOPc (**2**) exhibited a symmetrical 'W' shape near the focus, that is at Z_S = 0 mm. This suggests that complex (**2**) undergoes a transition state from RSA to saturable absorption (SA) at the excitation wavelength of 532 nm and in agreement with the literature.[19,38] The Z-scan curve of Mn(OAc)TPrOPhOPc (**3**) at 532 nm shows a broad 'W' shape with a sharp decrease near the focal point. This phenomenon suggests the presence of different processes when a sample is exposed to high intensity laser and is attributed to excited saturable absorption (ESA). The observed ESA phenomenon is due to the fact that the 532 nm laser excitation is in a region of the charge transfer band of the Mn(OAc)TPrOPhOPc (**3**), when DCM is used as the solvent, therefore indicating that Mn(OAc)TPrOPhOPc (**3**) undergoes a transitional state from ESA to RSA that might be attributed to the effect of the LMCT or MLCT bands. The nature of the charge transfer band is the combination of both as the theoretical study[18] could not distinctly separate the LMCT from the MLCT, or *vice versa*. Therefore the charge transfer was assigned as a combination of both MLCT and LMCT. To correct for the observed ESA from the Mn(OAc)TPrOPhOPc (**3**), the use of the 560 nm monochromatic Ekspla NT 342B-20-AW laser source was investigated and the effect of varying the excitation wavelength was evaluated for complex (**3**). It was interesting to observe a single valley for Mn(OAc)TPrOPhOPc (**3**) and reverse saturable absorption (RSA) when the 560 nm excitation laser was applied compared to 532 nm. This suggests that the Mn(OAc)TPrOPhPc (**3**) shows as a typical RSA curve at 560 nm. In addition, the H_2TPrOPhOPc (**1**) and CoTPrOPhOPc (**2**) both exhibited the RSA–SA transition state similar to when the 532 nm Nd:YAG laser source was used. The use of 560 nm was intended to move away from the MLCT and LMCT charge transfer bands at 532 nm for Mn(OAc)TPrOPhOPc (**3**) and this was accomplished by the disappearance of the broad 'W' shape Z-scan to a typical open aperture curve.

The nonlinear absorption coefficient (β), third-order optical susceptibility (Im[$\chi^{(3)}$]) and hyperpolarizability (γ) values were determined for all the phthalocyanines. The β_{eff} values were obtained from fitting of $Q_0(Z_S)$, a parameter that characterizes the strength of the nonlinearity in the curves depicted in Fig. 4 from different excitation laser sources, 532 nm and 560 nm. The difference in laser source has been discussed above and is due to the laser excitation wavelength at 532 nm coinciding with the MLCT or LMCT band at 531 nm for the Mn(OAc)TPrOPhOPc (**3**) complex. The measured β_{eff} values for the phthalocyanines displayed the following trend: for H_2TPrOPhOPc (23.5×10^{-5} m MW^{-1}) > CoTPrOPhOPc (14.3×10^{-5} m MW^{-1}) > Mn(OAc)–TPrOPhOPc (9.20×10^{-5} m MW^{-1}) with laser excitation at 532 nm. The measurements with excitation at 560 nm for the monochromatic Ekspla laser source for Mn(OAc)TPrOPhOPc gave 14.4×10^{-5} m MW^{-1}. The value for (**3**) was almost similar to that of (**2**) when the correct excitation was used. The decrease in the β_{eff} values was due to the paramagnetic nature of cobalt and manganese metal ions. For both excitation wavelengths, the β_{eff} values lie within the range for the previously studied phthalocyanines[19,39,40] and are higher than for those complexes studied in DCM. It was interesting to note that even the cobalt and manganese phthalocyanine complexes with half-filled d-orbitals exhibited good β_{eff} values. The use of full d-orbitals has been preferred for nonlinear optical properties of phthalocyanines with diamagnetic metal ion centres.[6,20–26] The reason for the higher values observed in this work is due to the combination of the terminal alkyne (propargyl) and phenoxy functional groups as substituents. The phthalocyanines with aliphatic alkynyl functional groups have been shown to give better nonlinear optical properties.[6] The values for the third order nonlinear susceptibility (Im[$\chi^{(3)}$]) and hyperpolarizability (γ) were also calculated. For phthalocyanines in solutions, the nonlinear hyperpolarizability values (γ) have been reported[41] to be between 10^{-29} and 10^{-34} esu. The γ values obtained in this study ranged from 1.30×10^{-31} to 4.63×10^{-31} esu and were within the range for the phthalocyanines. The values are summarized in Table 1.

Density functional theory calculations

The second order nonlinear optical property (β_{HRS}) values were theoretically evaluated (using DFT) in order to investigate the structure–property relationship for the phthalocyanines. All DFT calculations were carried out using SDD basis sets at

Table 1 Experimental and theoretical Z-scan results for nonlinear coefficients (β_{HRS} and β_{eff}) and the results for imaginary susceptibility, Im[$\chi^{(3)}$], and imaginary hyperpolarizability, Im(γ)

	Exp. β_{eff} (m MW^{-1}) $\times 10^{-5}$	Theor. β_{HRS} (esu) $\times 10^{-28}$	Q_0	Im[$\chi^{(3)}$] $\times 10^{-12}$	Z_R (mm)	Im(γ) (esu) $\times 10^{-31}$
532 nm using the Nd:YAG laser source						
(**1**)	23.5	2.28[a]	0.353	7.66	4.49	4.01
(**2**)	14.3	2.10[a]	0.808	11.2	4.51	4.60
(**3**)	9.20	1.86[a]	0.590	3.00	1.09	1.30
560 nm monochromatic Ekspla NT 342B-20-AW laser source						
(**3**)	14.4	1.86[a]	0.173	4.72	5.65	2.05

The results in Table 1 were obtained using two laser sources, a 532 nm Nd:YAG laser source and a monochromatic 560 nm Ekspla NT 342B-20-AW laser source for (**3**). [a] Values measured in vacuum for theoretical calculations. The DFT calculations were performed at the B3LYP level of theory with the 6-31G(d) basis set.

the B3LYP level of theory. The advantage of theoretically calculated β_{HRS} values is that the dipolar ($\Phi_{J=1}$) and octupolar ($\Phi_{J=3}$) contributions to the H_2TPrOPhOPc (**1**), CoTPrOPhOPc (**2**) and Mn(OAc)TPrOPhOPc (**3**) can be theoretically separated, which is not experimentally possible. In response to an applied electric field, dipolar/octupolar contributions are known to be characterised by their differences in spatial charge distribution. Different β_{HRS} values can result from the differences in π-electron instantaneous distribution, which is coupled with slower geometric relaxation. The instantaneous shift in π-electron density is responsible for the large and fast polarizabilities of π-electron networks.[42] The slow geometry relaxation is known to be related to third order NLO effects, which are related to the nonlinear absorption coefficient (β). However, theoretical β_{HRS} and Z-scan derived β values represent different nonlinear terms. Hence, they might not necessarily follow a similar trend or be directly comparable. However, the octupolar contribution has been known to affect the nonlinear absorption coefficient (β). Octupolar molecules have been found to exhibit large second-order hyperpolarizability values.[43] Hence, in this work the theoretical octupolar/dipolar contribution is correlated to the nonlinear absorption coefficient (β) as it is also associated to the third-order hyper-polarizability.

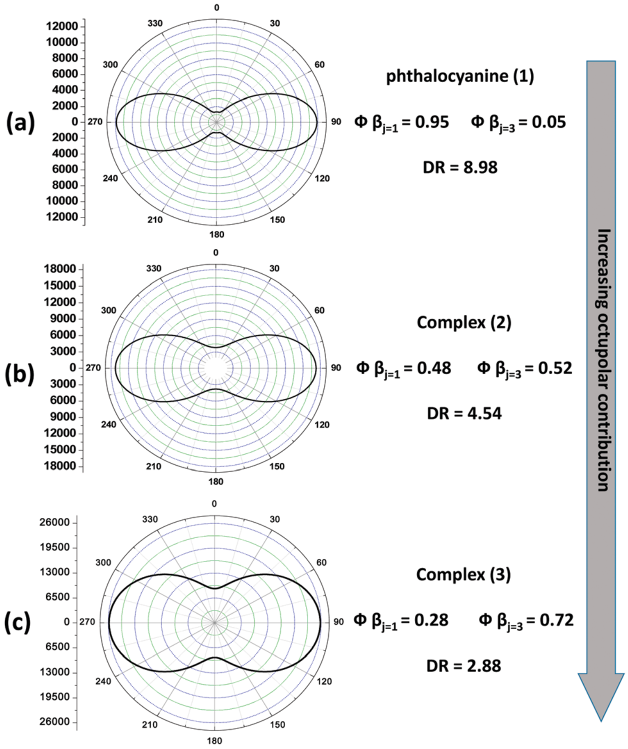

Fig. 5 Harmonic light intensity as a function of the polarization angle Ψ by polar representation for (a) H_2TPrOPhOPc (**1**), (b) CoTPrOPhOPc (**2**) and (c) Mn(OAc)TPrOPhOPc (**3**).

The theoretical β_{HRS} values followed a similar trend to the (β_{eff}) values. The following trend was observed: H_2TPrOPhOPc (2.28×10^{-28} esu) > CoTPrOPhOPc (2.10×10^{-28} esu) > Mn(OAc)TPrOPhO Pc (1.89×10^{-28} esu). The DFT calculations show that the phthalocyanine (**1**) exhibits a higher β_{HRS} value than those of complexes (**2**) and (**3**). The β_{HRS} value of complex (**2**) is higher than that of complex (**3**). The above trend is attributed to variation in the centrosymmetricity of the molecules, with (**1**) being less centrosymmetric compared to (**2**) and (**3**). Complex (**3**) was expected to show a large β_{HRS} value compared to (**2**) owing to its increased octupolar character due to the axial ligand. It must be kept in mind that Co is slightly displaced above the Pc cavity and has an oxidation state of +2, while Mn is perfectly inserted in the Pc ring with an oxidation state of +3. Hence, the π-electrons in complex (**2**) are easily polarised compared to complex (**3**). Therefore, the larger β_{HRS} value determined for complex (**2**) compared to complex (**3**) is attributed to ease of polarizability.

DFT calculations were further employed to understand the contributions of the dipolar and octupolar symmetric nature of the phthalocyanines to the measured β values obtained in Table 1. The various theoretical calculations and equations involved are in the ESI.† The dipolar ($\Phi_{J=1}$) and octupolar ($\Phi_{J=3}$) contributions were calculated from β_{HRS} values following a literature method.[44] The study of dipolar/octupolar contributions to the second-order nonlinear response of phthalocyanines (**1–3**) was investigated by taking the harmonic light intensity as a function of the incident light, as depicted in the reported equations.[44] Polar plots of phthalocyanines (**1–3**) are shown in Fig. 5. From Fig. 5 it is discernible that phthalocyanine molecule (**1**) is purely dipolar in nature with the dipolar contribution of 95%, which is typical of C_{4h} and D_{2h} isomers.[44] There was an increase in the octupolar contribution upon metalation of the phthalocyanine (**1**) with cobalt to form complex (**2**) and with manganese to form complex (**3**). For complex (**2**), we observed an equal distribution of dipolar and octupolar nature with 52% dipolar and 48% octupolar. This equal contribution is attributed to the symmetrical and planar nature of complex (**2**) owing to the multidirectional charge transfer excitation. Manganese complex (**3**) exhibited a higher octupolar contribution of 72% and a lower dipolar contribution of 28%.

Manganese complex (**3**) has an axial ligand, which results in the distortion of the planarity of this complex upon interacting with the harmonic light intensity as a function of the incoming fundamental beam polarization angle. The slight inclination towards the octupolar contribution is attributed to the presence of the acetate axial ligand on the central metal ion for complex (**3**). Both the polar plots and the calculations of the dipolar/octupolar contributions show that Mn(OAc)TPrOPhOPc (**3**) exhibits higher octupolar contributions followed by CoTPrOPhOPc (**2**) and then lastly H_2TPrOPhOPc (**1**). The octupolar contribution trend did not correlate with the expected β values; the deviation is attributed to the differences in the oxidation states of the Co (+2) and Mn (+3) central metal ions.

The depolarisation ratios (DRs) are also sensitive to the structural properties of the phthalocyanines studied. The DR values ranging from 1.5 to 5 correspond to purely octupolar contributions to the NLO signal whilst DR values >5 correspond to the purely dipolar contribution.[45] DR values were obtained and increased from 2.88 for Mn(OAc)TPrOPhOPc (**3**)

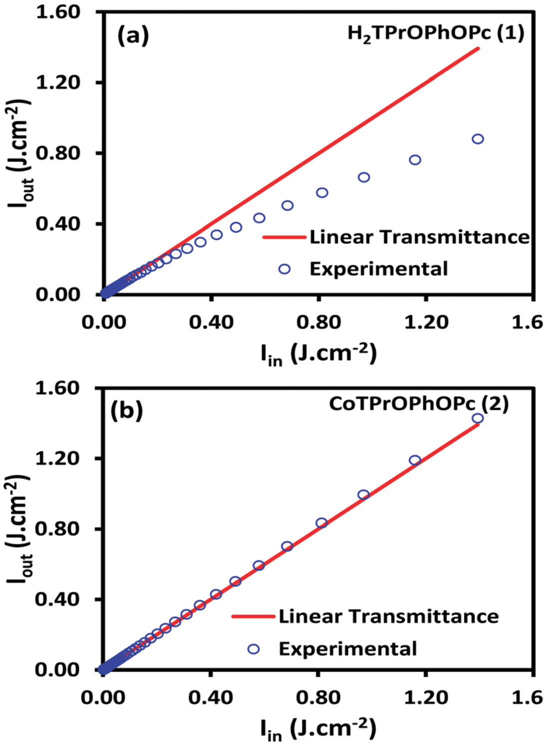

Fig. 6 The input intensity (I_{in}, J cm^{-2}) against the output intensity (I_{out}, J cm^{-2}) plot for (a) H_2TPrOPhOPc (**1**) and (b) CoTPrOPhOPc (**2**) at 532 nm Nd:YAG (similar to Mn(OAc)TPrOPhOPc (**3**) at 560 nm monochromatic Ekspla) laser excitation.

to 4.54 for CoTPrOPhOPc (**2**) and to 8.98 H_2TPrOPhOPc (**1**). The DR values for Mn(OAc)TPrOPhOPc and CoTPrOPhOPc are within the range of 1.5–5 DR for octupolar contributions. The DR value for the H_2TPrOPhOPc was 8.98 and above 5 for a purely dipolar contribution. Values above 5 have been reported before.[46] The values also confirmed the decreasing trend in the octupolar contribution. The nonlinear molecular anisotropy (ρ) was calculated from the ratio of octupolar ($\beta_{J=3}$) to dipolar ($\beta_{J=1}$) from the reported equation.[47] The ρ values were found to be 0.05 for H_2TPrOPhOPc (**1**) for a pure dipolar molecule, 1.08 for CoTPrOPhOPc (**2**) as an intermediate complex and 2.57 for Mn(OAc)TPrOPhOPc (**3**) for a pure octupolar complex.

The phthalocyanines were further investigated for optical limiting properties. The evaluation of the critical point at which the optical limiting material will display limiting properties is important and the threshold limiting intensity or fluence (I_{lim}) is a good measure. This limiting intensity is referred to as the input fluence at which the output fluence is 50% of the linear transmission.[48,49] This is a very important parameter to measure for optical limiting materials. The lower the value, the better the optical limiting material. Therefore, the attenuation of the input intensity (I_{in}) is strong if it is below 50% of the transmittance and is a good response to the intense beams. Such a response is typical of the optical limiting (OL) effect that an optical limiter can exhibit.[50] As opposed to the literature I_{lim} values greater than 1 J cm^{-2},[51,52] phthalocyanine (**1**) in Fig. 6(a) exhibited about 0.50 J cm^{-2} at 532 nm. This observation is in agreement with the transmittance shown in Fig. 4 for phthalocyanine (**1**) at 532 nm. Such I_{lim} values for phthalocyanine (**1**) therefore describe a good optical limiter. The opposite was observed for complex (**2**) at 532 nm and complex (**3**) at 560 nm, which exhibited a very weak RSA effect. This resulted in the lack of attenuation of the input intensity, as shown in Fig. 6(b) for complex (**2**) at 532 nm laser excitation. The same behaviour was observed at 560 nm for complex (**3**) (results not shown). In this case, complexes (**2**) and (**3**) are not reliable optical limiters and this could be attributed to the paramagnetic nature of the cobalt and manganese as metal ions quenching the excited state. The quenching of the excited state was observed previously for the cobalt complex (**2**), showing no fluorescence properties, and the manganese complex (**3**), showing appreciable fluorescence but not as good as for phthalocyanine (**1**).[18] The quenching of the excited state is the reason for the lack of attenuation of the input intensity for complexes (**2**) and (**3**).

Conclusions

The metal-free (unmetallated), cobalt and manganese tetra(4-propargyloxyphenoxy)phthalocyanines have been evaluated for their potential as optical limiters. The assessment clearly shows that the unmetallated phthalocyanine (**1**) is a superior optical limiter to complexes (**2**) and (**3**). The phthalocyanines (**1–3**) all possess optical limiting properties as judged by the Z-scan open aperture decrease in transmittance closer to the focus. However, due to the paramagnetic nature of the central metal ions in complexes (**2**) and (**3**) quenching the excited state, there was a lack of attenuation of the input intensity, thus making these complexes poor optical limiters. The unmetallated phthalocyanine (**1**) gave a good limiting threshold of 0.50 J cm^{-2}.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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