Nonlinear absorption properties of some 1,4,8,11,15,18,22,25-octaalkylphthalocyanines and their metallated derivatives

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The third-order nonlinear optical properties of a series of 15 unmetallated and metallated 1,4,8,11,15,18,22,25-octaalkylphthalocyanines have been investigated. The palladium-metallated compound is the strongest nonlinear absorber of the series, but, due to its comparatively high linear absorption coefficient, it exhibits a relatively low ratio of excited- to ground-state absorption cross-sections (k) when compared to the other compounds. The highest values for k were found for derivatives metallated with indium and lead. The nickel-metallated compounds are the weakest nonlinear absorbers, indicating that they are unsuitable as potential materials for practical passive optical limiters. Phenomenologically, the data for k and the saturation energy density (Fsat) were found to follow trends dependent upon the linear absorption coefficient. This may have some implications for the design of phthalocyanines for nonlinear optical applications.

1 Introduction

Optical limiters are materials that exhibit decreased transmission of light as incident light intensity is increased. Such a property, when applied to the attenuation of incident light intensity from laser pulses, for example, is recognised to have potential applications for the protection of human eyes and optically sensitive equipment. The phenomenon is a consequence of one or more nonlinear absorption processes, among which reverse saturable absorption (RSA) is recognised to be particularly important. During RSA, nonlinear absorption arises through further electronic excitation within a molecule already in an electronically excited state. Compounds exhibiting RSA as a result of $T_1 \rightarrow T_2$ excitation are most efficient as optical limiters when (i) there is efficient intersystem crossing from the $S_1$ excited state to $T_1$, (ii) the $T_1$ state is long lived and (iii) the $T_1 \rightarrow T_2$ transition has a large absorption cross-section. Phthalocyanines and their derivatives are attractive candidates for optical limiting because the ring system exhibits a number of the appropriate photophysical properties. Furthermore, there is potential to tune the desirable properties through the incorporation of different elements into the central cavity and/or substitution of the ring system. Metallated phthalocyanines shown to possess useful optical limiting behaviour include those containing aluminium, indium, silicon, vanadium, lead, titanium, nickel, gallium, tin and various lanthanides. In previous studies, compounds have generally been substituted to promote solubility. Ideally, substituents should also minimise cofacial aggregation, because this introduces further relaxation pathways which serve to shorten excited-state lifetimes. Thus derivatives bearing one or two axial ligands at the metal (or metalloid) centre, as in the majority of metallated phthalocyanines listed above, have received considerable attention. Previous work from one of our laboratories has demonstrated that eight straight alkyl chains located at the 1, 4, 8, 11, 15, 18, 22 and 25 sites of the phthalocyanine nucleus promote solubility in most aprotic organic solvents, particularly when the chains contain an even number of carbon atoms, they also have a beneficial effect in reducing aggregation. Iso-Pentyl groups in these sites cause distortion of the ring from planarity in the metal-free phthalocyanine and also show advantageous solubilising effects. The present paper reports a systematic study and comparison of the nonlinear absorption properties of a series of 15 octaalkyl-substituted compounds, covering a range of 7 metal centres, as well as the metal-free analogues. Measurements have been undertaken using the Z-scan method to investigate the nonlinear excited-state behaviour of the compounds and provide an insight into the effects of structural modification on the nonlinear optical response of phthalocyanine moieties.

2 Experimental

2.1 Characterisation

$^1$H NMR spectra were recorded at 270 MHz using a JEOL EX 270 spectrometer, at 300 MHz on a Varian Gemini 2000 spectrometer or at 400 MHz on a Varian Unity plus spectrometer. $^{13}$C NMR spectra were measured on the same equipment at 67.5, 75 and 100 MHz, respectively. Tetramethylsilane was used as the internal standard and the positions of the peaks are reported in ppm. The splittings of the signals are described as singlets (s), doubles (d), triplets (t), quartets (q), quintets (qn), broad (br) or multiplets (m). The UV-Vis spectra were recorded using a Hitachi U-3000-X spectrophotometer. Low resolution matrix-assisted laser desorption ionisation (MALDI) mass spectra were obtained using a dithranol matrix at the University of Manchester, UK. Elemental analysis was carried out by the microanalytical service provided at the University of East Anglia by Mr A. W. Saunders. Solvents were HPLC grade or better. They were not specifically dried unless otherwise stated. Petrol refers to light petroleum (b.p. 40–60 °C). Silica gel (Merck grade 7734) was used in chromatographic separations. TLC was performed using Merck 5554 silica gel on aluminium sheets.
The imaginary third-order optical susceptibility, \( \text{Im}\{\chi^{(3)}\} \), is directly related to the intensity-dependent absorption coefficient, \( \beta_{\text{eff}} \), and is expressed as
\[
\text{Im}\{\chi^{(3)}\} = \frac{\text{Im}\{\chi^{(3)}\}}{f} = \frac{\text{Im}\{\chi^{(3)}\}}{f} = \frac{n_0^2 v_0 c^2 \beta_{\text{eff}}}{2 \pi} \tag{3}
\]
where \( n_0 \) is the linear refractive index, \( v_0 \) is the permittivity of free space, \( c \) is the speed of light and \( \lambda \) is the wavelength of the incident light. This expression is strictly only true for constant \( \beta_{\text{eff}} \) over incident intensities, corresponding to the physical situation where third-order effects are the only contribution to the nonlinear response. The relationship between \( \text{Im}\{\chi^{(3)}\} \) and the imaginary second-order molecular hyperpolarisability, \( \text{Im}\{\gamma\} \), is defined as
\[
\text{Im}\{\gamma\} = \frac{\text{Im}\{\chi^{(3)}\}}{f} = \frac{\text{Im}\{\gamma\}}{f} = \frac{\text{Im}\{\chi^{(3)}\}}{f} = \frac{n_0^2 v_0 c^2 \beta_{\text{eff}}}{2 \pi} \tag{4}
\]
where \( f = (n_0^2 + 2) / 3 \) is the Lorentz local field enhancement factor, \( n_0 \) is the linear refractive index of the sample, \( \text{cmol} \) is the molar concentration and \( \text{Avogadro’s number} \).

All experiments described in this study were performed using 6 ns pulses from a Q-switched Nd: YAG laser. The beam was spatially filtered to remove the higher order modes and tightly focused with a 9 cm focal length lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 6 ns pulses from a Q-switched Nd : YAG laser. The beam was operated with a 1 mm spatial filter to remove the higher order modes and tightly focused with a 9 cm focal length lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 6 ns pulses from a Q-switched Nd : YAG laser.
requires: C, 67.52; H, 7.55; N, 8.75%. δH (400 MHz, CDCl3) 7.83 (8H, s), 4.92 (8H, m), 4.63 (8H, m), 2.14 (16H, m), 2.0 (8H, m), 1.06 (48H, d). λmax (abs.) 744 nm (THF), ε = 1.6 × 10^4 M⁻¹ cm⁻¹.

Preparation of chloro[1,4,8,11,15,18,22,25-octakis(hexyl-phthalocyaninato)indium(ii)](13, 120 mg, 0.1 mmol) was dissolved in pentan-1-ol (7 ml) and heated to reflux. Excess indium(ii) chloride (80 mg) was added and reflux was continued for 2 h. The solvent was removed under reduced pressure and the resultant green residue chromatographed over silica gel, first eluting with petrol to remove a residual amount of the starting material and then with petrol–THF (19:1), collecting the first green fraction, which was recrystallised from THF–acetonitrile to give 13 (58 mg, 43%) as almost green needles. M.p. 110–112 °C. Found: C, 72.27; H, 8.32; N, 8.17; C_{60}H_{112}N_{16}Cl requires: C, 71.92; H, 8.45; N, 8.39%. δH (270 MHz, C6D6) 7.92 (8H, s), 4.84–4.62 (16H, m), 2.35–2.24 (16H, m), 1.84–1.70 (16H, m), 1.48–1.22 (32H, m), 0.82 (24H, t). δC (150 MHz, CDCl3) 153.3, 139.5, 134.9, 131.2, 132.1, 32.6, 32.1, 30.5, 28.9, 22.6, 14.0. MALDI-MS: isotopic cluster at 1336 M⁺, (100%). λmax (abs.) 729 nm (toluene), ε = 2.2 × 10^4 M⁻¹ cm⁻¹.

Preparation of 4-fluorophenylmagnesium bromide was added to a solution of 1,2-dibromoethane (4 drops) and iodine (1 crystal) in dry THF (10 ml) to a stirred mixture of magnesium turnings (200 mg, 8.2 mmol), triphenylphosphine (1.14 g, 6.5 mmol) in dry THF (10 ml) was added dropwise at 105 M under an atmosphere of argon. After 10 min, the solution was stirred for 4 h. TLC analysis (eluent: cyclohexane) was performed every 15 min before being allowed to cool to room temperature. A portion of the solution (3 ml) containing the Grignard reagent (200 mg, 0.17 mmol) and triphenylphosphine (1.14 g, 6.5 mmol) in dry THF (10 ml) was added via a plastic syringe directly into the solution. The dark green solution was stirred for 4 h. TLC analysis (eluent: cyclohexane–toluene 2:1 then 1:2). After removing the solvent under reduced pressure, 15 was obtained (180 mg, 87%) as a thick dark blue oil. Found: C, 76.94; H, 9.33; N, 8.43; C_{60}H_{112}N_{16}O_{5}Si requires: C, 76.99; H, 9.21; N, 8.98%. δH (400 MHz, C6D6) 7.91 (8H, s), 4.70 (16H, t), 2.30 (16H, qn), 1.75 (16H, qn), 1.38 (32H, m) 0.88 (24H, t), –5.74 (2H, br s). δC (75 MHz, C6D6) 147.96, 138.41, 133.44, 130.14, 31.88, 31.27, 29.80, 28.31, 21.78, 12.96. MALDI-MS: isotopic clusters at 1248 (20%, M⁺) and 1231 (100%, M – H2O). λmax (abs.) 703.5 nm (THF), ε = 2.4 × 10^4 M⁻¹ cm⁻¹.

3 Results and discussion

3.1 Preparation of materials

The synthesis and characterisation of 1–7 have been described elsewhere and the synthetic protocols devised earlier were applied within the syntheses of the novel compounds 8–15. Thus, octaalkylphthalocyanine derivatives were synthesised using the corresponding 3,6-dialkylphthalonitriles as precursors. The latter were cyclotetramerised under basic conditions to afford the metal-free phthalocyanines. Metalated derivatives were prepared either by direct cyclotetramerisation of the phthalonitriles in the presence of the appropriate metal salt, as in the case of 9, or by metal ion insertion into the metal-free analogue, which provided access to 8 and 10–12. The novel chloroindium derivative 13 was obtained by reacting the metal-free phthalocyanine with indium trichloride in pentanol. This was then converted into the 4-fluoropheny phthalocyanine derivative 14 using Grignard chemistry via procedures applied to related compounds by Hanack and Heckmann.

The dihydroxysilicon phthalocyanine 15 was prepared from the corresponding metal-free phthalocyanine using the general procedure developed by Kenney et al.

3.2 Optical limiting measurements

The linear absorption spectra of phthalocyanine compounds have two main features: a Q band in the region of 700 nm and a B band in the region of 350 nm. These materials have a window between these two absorption bands with high linear transmittance, making them attractive as limiters of visible light (λ ≈ 420–650 nm). The location (wavelength) of the peak of the Q band (lowest energy transition) is quoted for each of compounds 1–15 in Table 1.

All open-aperture Z-scan performed in this study exhibited a reduction in the transmission about the focus of the lens. This is typical of an induced positive nonlinear absorption of the incident light; in this case, attributed to reverse saturable excited-state absorption. All open-aperture Z-scan datasets were fitted using the method of least squares regression with eqn. 1 and eqn. 2. The beam waist radius 𝑤₀ and the nonlinear absorption coefficient 𝛽_L were treated as free parameters in the fit, and all fits typically converged with 𝑅^2 values in excess of 0.99. A sample of a typical open-aperture Z-scan spectrum with normalised transmission plotted as a function of sample position z is depicted in Fig. 2 for compound 10 under incident focal intensity of 0.36 GW cm⁻². It was noticed that the nonlinear absorption coefficient 𝛽_L in all cases, was not stationary with respect to the on-focus intensity. In Fig. 3, plots
Table 1  Linear optical properties, calculated nonlinear optical coefficients and optical limiting parameters for compounds 1–15, measured in toluene, except where otherwise indicated.

<table>
<thead>
<tr>
<th>Central atom</th>
<th>Alkyl chain</th>
<th>c/g L⁻¹</th>
<th>ν₀ cm⁻¹</th>
<th>λmax/nm</th>
<th>I₀/GW cm⁻²</th>
<th>β₀/cm W⁻¹</th>
<th>Im{β₀}/esu</th>
<th>Im{β₀}/esu</th>
<th>F₁/fcm⁻²</th>
<th>κ (σₐ₀/σ₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 H₂,</td>
<td>Hexyl</td>
<td>1.0</td>
<td>0.94</td>
<td>733</td>
<td>0.5</td>
<td>(1.8 ± 0.3) × 10⁻⁸</td>
<td>(6.6 ± 1.3) × 10⁻¹²</td>
<td>(3.6 ± 0.7) × 10⁻¹²</td>
<td>16.8 ± 0.6</td>
<td>14.5 ± 0.3</td>
</tr>
<tr>
<td>2 H₂,</td>
<td>Decyl</td>
<td>1.0</td>
<td>0.83</td>
<td>730</td>
<td>0.5</td>
<td>(1.5 ± 0.3) × 10⁻⁸</td>
<td>(5.8 ± 1.1) × 10⁻¹²</td>
<td>(4.3 ± 0.8) × 10⁻¹²</td>
<td>20.2 ± 1.0</td>
<td>14.4 ± 0.5</td>
</tr>
<tr>
<td>3 H₃,</td>
<td>Hexyl</td>
<td>1.0</td>
<td>0.94</td>
<td>731</td>
<td>0.5</td>
<td>(1.8 ± 0.3) × 10⁻⁸</td>
<td>(6.6 ± 1.3) × 10⁻¹²</td>
<td>(3.6 ± 0.7) × 10⁻¹²</td>
<td>16.8 ± 0.6</td>
<td>14.5 ± 0.3</td>
</tr>
<tr>
<td>4 Ni,</td>
<td>Hexyl</td>
<td>1.0</td>
<td>1.05</td>
<td>702</td>
<td>0.5</td>
<td>(1.6 ± 0.3) × 10⁻⁸</td>
<td>(5.9 ± 1.1) × 10⁻¹²</td>
<td>(3.0 ± 0.6) × 10⁻¹²</td>
<td>14.4 ± 0.5</td>
<td>11.3 ± 0.3</td>
</tr>
<tr>
<td>5 Ni,</td>
<td>Decyl</td>
<td>1.0</td>
<td>0.94</td>
<td>702</td>
<td>0.5</td>
<td>(1.5 ± 0.3) × 10⁻⁸</td>
<td>(5.5 ± 1.1) × 10⁻¹²</td>
<td>(4.2 ± 0.8) × 10⁻¹²</td>
<td>13.3 ± 2.0</td>
<td>2.1 ± 0.1</td>
</tr>
<tr>
<td>6 Zn,</td>
<td>Hexyl</td>
<td>1.0</td>
<td>1.17</td>
<td>705</td>
<td>0.5</td>
<td>(4.0 ± 0.8) × 10⁻⁷</td>
<td>(8.6 ± 1.7) × 10⁻¹³</td>
<td>(7.1 ± 0.3) × 10⁻¹³</td>
<td>11.4 ± 0.3</td>
<td>11.3 ± 0.3</td>
</tr>
<tr>
<td>7 Zn,</td>
<td>Decyl</td>
<td>1.0</td>
<td>1.17</td>
<td>705</td>
<td>0.5</td>
<td>(2.4 ± 0.4) × 10⁻⁷</td>
<td>(6.9 ± 1.3) × 10⁻¹³</td>
<td>(13.6 ± 0.5) × 10⁻¹³</td>
<td>11.7 ± 0.3</td>
<td>11.7 ± 0.3</td>
</tr>
<tr>
<td>8 Zn,</td>
<td>Isopentyl</td>
<td>1.0</td>
<td>1.05</td>
<td>703</td>
<td>0.5</td>
<td>(4.0 ± 0.8) × 10⁻⁷</td>
<td>(7.9 ± 1.5) × 10⁻¹³</td>
<td>(7.9 ± 1.5) × 10⁻¹³</td>
<td>6.6 ± 0.2</td>
<td>12.2 ± 0.3</td>
</tr>
<tr>
<td>9 Cu,</td>
<td>Isopentyl</td>
<td>1.0</td>
<td>1.63</td>
<td>705</td>
<td>0.5</td>
<td>(6.4 ± 1.0) × 10⁻⁸</td>
<td>(2.4 ± 0.4) × 10⁻¹¹</td>
<td>(1.3 ± 0.2) × 10⁻¹¹</td>
<td>4.6 ± 0.1</td>
<td>8.8 ± 0.1</td>
</tr>
<tr>
<td>10 Pd,</td>
<td>Hexyl</td>
<td>1.0</td>
<td>2.60</td>
<td>687</td>
<td>0.5</td>
<td>(9.6 ± 1.9) × 10⁻⁸</td>
<td>(3.6 ± 0.7) × 10⁻¹¹</td>
<td>(2.1 ± 0.4) × 10⁻¹¹</td>
<td>2.1 ± 0.1</td>
<td>5.9 ± 0.1</td>
</tr>
<tr>
<td>11 Pb,</td>
<td>Hexyl</td>
<td>1.0</td>
<td>0.83</td>
<td>741</td>
<td>0.5</td>
<td>(2.9 ± 0.6) × 10⁻⁷</td>
<td>(1.1 ± 0.2) × 10⁻¹¹</td>
<td>(7.0 ± 1.4) × 10⁻¹¹</td>
<td>9.8 ± 0.3</td>
<td>16.1 ± 0.3</td>
</tr>
<tr>
<td>12 Pb,</td>
<td>Isopentyl</td>
<td>1.0</td>
<td>1.06</td>
<td>744</td>
<td>0.5</td>
<td>(4.6 ± 0.8) × 10⁻⁷</td>
<td>(1.7 ± 0.3) × 10⁻¹¹</td>
<td>(7.2 ± 1.6) × 10⁻¹¹</td>
<td>9.2 ± 0.2</td>
<td>16.1 ± 0.3</td>
</tr>
<tr>
<td>13 InCl,</td>
<td>Hexyl</td>
<td>1.0</td>
<td>0.93</td>
<td>730</td>
<td>0.5</td>
<td>(3.2 ± 0.6) × 10⁻⁷</td>
<td>(1.2 ± 0.2) × 10⁻¹¹</td>
<td>(7.3 ± 1.4) × 10⁻¹¹</td>
<td>10.1 ± 0.5</td>
<td>16.1 ± 0.3</td>
</tr>
<tr>
<td>14 InArF,</td>
<td>Hexyl</td>
<td>1.0</td>
<td>0.93</td>
<td>728</td>
<td>0.5</td>
<td>(3.5 ± 0.6) × 10⁻⁷</td>
<td>(1.3 ± 0.2) × 10⁻¹¹</td>
<td>(8.1 ± 1.6) × 10⁻¹¹</td>
<td>9.5 ± 0.2</td>
<td>16.2 ± 0.3</td>
</tr>
<tr>
<td>15 Si(OH)₂,</td>
<td>Hexyl (THF)</td>
<td>1.0</td>
<td>1.05</td>
<td>704</td>
<td>0.5</td>
<td>(2.7 ± 0.5) × 10⁻⁷</td>
<td>(1.0 ± 0.2) × 10⁻¹¹</td>
<td>(7.3 ± 1.4) × 10⁻¹¹</td>
<td>9.2 ± 0.3</td>
<td>12.4 ± 0.3</td>
</tr>
</tbody>
</table>

Fig. 2  Typical open-aperture Z-scan spectrum with normalised transmittance plotted as a function of sample position, x. Sample curve depends on the effective nonlinear absorption coefficient β₁ against the focal beam intensity I₀ for compounds 6, 9, 10 and 15. Each open-aperture Z-scan spectrum is plotted as a function of sample position, x. The solid lines are modelled analytically to the open-aperture Z-scan data for compounds 6, 7, 8, 10 and 15 as a single envelope of the entire dataset. Each compound at the focus intensity of 0.5 GW cm⁻² (2.16 μJ μm⁻²) under a focused beam excitation for compounds 6, 7, 8, 10 and 15 as a single envelope of the entire dataset. Each compound at the focus intensity of 0.5 GW cm⁻² (2.16 μJ μm⁻²) under a focused beam excitation.
plots, the solid lines are theoretical curve fits used to determine $k_p$.

noting that the magnitude of $b$ is complex, with $b$.

$F$ density per pulse [$s$]

nonlinear absorption. The nonlinear absorption coefficient, $k$, is smallest for the Ni phthalocyanine 4 and largest for the Pb phthalocyanine 11; the $\kappa$ coefficient for the Pd phthalocyanine is approximately 2.7 times smaller than that for the lead complex and approximately 2.5 times larger than that for the nickel compound. Thus, the $\kappa$ coefficient of the Pd compound is relatively low, despite it having a larger nonlinear absorption coefficient than compounds 1, 4, and 6. This arises because of its relatively large linear absorption coefficient, $\chi_0 \approx 2.6 \text{ cm}^{-1}$.

It is clear then that substituting Ni into the central cavity has nothing but undesirable effects in terms of optical limiting, as the metal-free phthalocyanine 1 clearly has a much larger nonlinear response than the nickel compound. They have comparable $F_{\text{sat}}$ values, $(18 \pm 3) \text{ J cm}^{-2}$ for Ni and $(16.8 \pm 0.6) \text{ J cm}^{-2}$ for the metal-free case, but the $\kappa$ coefficient for the Ni compound is approximately 6 times smaller than that for the metal-free phthalocyanine. The decyl chain-substituted subset presented in Fig. 4(b) includes the metal-free (2), Ni (5) and Zn (7) compounds. Again, it can clearly be seen that the nickel compound (5) is far outperformed by its counterparts. Its $\kappa$ coefficient is approximately 5.5 times smaller than that for the zinc complex (7) and 7 times smaller than that for the metal-free compound (2). The two indium phthalocyanines, 13 and 14, both exhibit large values for their $\kappa$ coefficient (comparable to that for the lead compound 11) and provide further data which point to the potential of indium compounds in optical limiting.

General trends in the optical limiting data are investigated in Fig. 5. The ratio of excited- to ground-state absorption coefficients, $\kappa$, is plotted against the linear absorption coefficient, $\chi_0$ in Fig. 5(a), with data from all compounds included. The relationship between $\kappa$ and $\chi_0$ appears to exhibit a clear trend, with the exception of data from the nickel complexes. The solid line, merely intended as a guide for viewing the data, appears to span the data points in an approximate way, with the exception of data from 4 and 5. The Ni-centred phthalocyanines are poor optical limiters as they do not exhibit large nonlinear absorption coefficients relative to the other compounds. Thus, excluding the Ni compounds, this seems to suggest that the ratio of the effective excited- to ground-state absorption coefficients has a far closer link to the linear absorption coefficient than to the type of substituents in the central cavity or on the periphery of the phthalocyanine macrocycle. A similar plot of the saturation energy density, $F_{\text{sat}}$, against the linear absorption coefficient, $\chi_0$, is presented in Fig. 5(b). In this case, the approximate trend mapped out by the sketched solid line again appears to exhibit a general dependence on $\chi_0$. It is most interesting that the Ni compounds appear to be in approximate agreement with the trend line in this case. These data appear to suggest that phthalocyanine design for nonlinear optical applications may be inextricably linked to tuning the linear absorption coefficient due to ground to excited singlet-state transitions.

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as free constants in the fitting. The $\chi_0$, $k$ and $F_{\text{sat}}$ values for each compound are also presented in Table 1.

Representative optical limiting plots are presented in Fig. 4. A subset of the hexyl-substituted compounds (1, 4, 6, 10 and 11) is case studied in Fig. 4(a) and a series of decyl-substituted compounds (2, 5 and 7) in Fig. 4(b). The optical limiting of the Pd phthalocyanine 10, which exhibits the largest $\beta_I$ at $(9.6 \pm 1.9) \times 10^{-8} \text{ cm W}^{-1}$, can be seen in Fig. 4(a). The other four compounds for which data are shown are the metal-free phthalocyanine (1) and the Ni (4), Zn (6) and Pb (11) complexes. In terms of the magnitude of the reduction in normalised transmission relative to incident energy density, the palladium compound 10 clearly outperforms the others. It also has a much lower saturation energy density, $F_{\text{sat}}$, than the other phthalocyanines on the plot. Interestingly, the ratio of the absorption cross-sections, $\kappa$, is smallest for the Ni phthalocyanine 4 and largest for the Pb phthalocyanine 11.

substituted to the macrocycle, the decyl-substituted compound 7 exhibits the lowest molecular imaginary hyperpolarisability, with Im$[\chi]$ $\approx (6.9 \pm 1.3) \times 10^{-33} \text{ esu}$. For the nickel compounds 4 and 5, the hexyl-substituted compound (4) also exhibits a lower Im$[\chi]$ than its decyl-substituted counterpart (5). The Pd-centred compound 10 exhibits the largest nonlinear absorption coefficient in this study, with $\beta_I \approx (9.6 \pm 1.9) \times 10^{-8} \text{ cm W}^{-1}$, while the lowest $\beta_I$ was found for 5, a Ni complex, with $\beta_I \approx (1.5 \pm 0.3) \times 10^{-9} \text{ cm W}^{-1}$. It is worth noting that the magnitude of $\beta_I$ for the nickel compounds (4 and 5) is an order of magnitude or more lower than the $\beta_I$ values exhibited by any other compound in the study.

The open-aperture spectra were manipulated and plotted as normalised transmission ($T_{\text{norm}}$) against the incident energy density per pulse [$F = \pi w_0^2$] to further investigate the nonlinear absorption. The nonlinear absorption coefficient, $\alpha(F, F_{\text{sat}}, \kappa)$, where $\alpha(F, F_{\text{sat}}, \kappa) \approx \chi_0(1 + F F_{\text{sat}})^{-1}(1 + \kappa F F_{\text{sat}})$, derived from laser rate equations in a static approximation, was used to fit the normalised transmission as a function of this energy density to a superposition of all open-aperture datasets for each compound. In this expression, $F$ represents the energy density, $F_{\text{sat}}$ the saturation energy density and $\kappa$ the ratio of the effective excited- to ground-state absorption cross-sections $\sigma_{\text{ex,eff}}$. The parameters $\kappa$ (realistically $\sigma_{\text{ex,eff}}$ as $\chi_0$ was measured) and $F_{\text{sat}}$ were treated


as free constants in the fitting. The $\chi_0$, $k$ and $F_{\text{sat}}$ values for each compound are also presented in Table 1.

Representative optical limiting plots are presented in Fig. 4. A subset of the hexyl-substituted compounds (1, 4, 6, 10 and 11) is case studied in Fig. 4(a) and a series of decyl-substituted compounds (2, 5 and 7) in Fig. 4(b). The optical limiting of the Pd phthalocyanine 10, which exhibits the largest $\beta_I$ at $(9.6 \pm 1.9) \times 10^{-8} \text{ cm W}^{-1}$, can be seen in Fig. 4(a). The other four compounds for which data are shown are the metal-free phthalocyanine (1) and the Ni (4), Zn (6) and Pb (11) complexes. In terms of the magnitude of the reduction in normalised transmission relative to incident energy density, the palladium compound 10 clearly outperforms the others. It also has a much lower saturation energy density, $F_{\text{sat}}$, than the other phthalocyanines on the plot. Interestingly, the ratio of the absorption cross-sections, $\kappa$, is smallest for the Ni phthalocyanine 4 and largest for the Pb phthalocyanine 11; the $\kappa$ coefficient for the Pd phthalocyanine is approximately 2.7 times smaller than that for the lead complex and approximately 2.5 times larger than that for the nickel compound. Thus, the $\kappa$ coefficient of the Pd compound is relatively low, despite it having a larger nonlinear absorption coefficient than compounds 1, 4 and 6. This arises because of its relatively large linear absorption coefficient, $\chi_0 \approx 2.6 \text{ cm}^{-1}$.

It is clear then that substituting Ni into the central cavity has nothing but undesirable effects in terms of optical limiting, as the metal-free phthalocyanine 1 clearly has a much larger nonlinear response than the nickel compound. They have comparable $F_{\text{sat}}$ values, $(18 \pm 3) \text{ J cm}^{-2}$ for Ni and $(16.8 \pm 0.6) \text{ J cm}^{-2}$ for the metal-free case, but the $\kappa$ coefficient for the Ni compound is approximately 6 times smaller than that for the metal-free phthalocyanine. The decyl chain-substituted subset presented in Fig. 4(b) includes the metal-free (2), Ni (5) and Zn (7) compounds. Again, it can clearly be seen that the nickel compound (5) is far outperformed by its counterparts. Its $\kappa$ coefficient is approximately 5.5 times smaller than that for the zinc complex (7) and 7 times smaller than that for the metal-free compound (2). The two indium phthalocyanines, 13 and 14, both exhibit large values for their $\kappa$ coefficient (comparable to that for the lead compound 11) and provide further data which point to the potential of indium compounds in optical limiting.

General trends in the optical limiting data are investigated in Fig. 5. The ratio of excited- to ground-state absorption coefficients, $\kappa$, is plotted against the linear absorption coefficient, $\chi_0$ in Fig. 5(a), with data from all compounds included. The relationship between $\kappa$ and $\chi_0$ appears to exhibit a clear trend, with the exception of data from the nickel complexes. The solid line, merely intended as a guide for viewing the data, appears to span the data points in an approximate way, with the exception of data from 4 and 5. The Ni-centred phthalocyanines are poor optical limiters as they do not exhibit large nonlinear absorption coefficients relative to the other compounds. Thus, excluding the Ni compounds, this seems to suggest that the ratio of the effective excited- to ground-state absorption coefficients has a far closer link to the linear absorption coefficient than to the type of substituents in the central cavity or on the periphery of the phthalocyanine macrocycle. A similar plot of the saturation energy density, $F_{\text{sat}}$, against the linear absorption coefficient, $\chi_0$, is presented in Fig. 5(b). In this case, the approximate trend mapped out by the sketched solid line again appears to exhibit a general dependence on $\chi_0$. It is most interesting that the Ni compounds appear to be in approximate agreement with the trend line in this case. These data appear to suggest that phthalocyanine design for nonlinear optical applications may be inextricably linked to tuning the linear absorption coefficient due to ground to excited singlet-state transitions.
Fig. 5 Investigation of general trends in the optical limiting data: (a) ratio of excited- to ground-state absorption coefficients, $\kappa$, plotted against the linear absorption coefficient, $\alpha_0$, for all compounds; (b) saturation energy density, $F_{sat}$, plotted against $\alpha_0$ for all compounds.

4 Conclusion

In summary, a series of 15 unmetallated and metallated octaalkylphthalocyanines have been synthesised and their third-order nonlinear optical properties characterised. The palladium-metallated compound is the strongest nonlinear absorber of the series, but, due to its comparatively high ratio of excited- to ground-state absorption cross-sections, $\kappa$, when compared to the other compounds. The highest values for $\kappa$ are exhibited by derivatives metallated with indium and lead. The nickel-metallated compounds are the weakest nonlinear absorbers, indicating their unsuitability as potential materials for practical passive optical limiters. This was interesting in that they were the only compounds to break the apparent trend observed in Fig. 5(a) between $\kappa$ and the linear absorption coefficient, $\alpha_0$. Phenomenologically, the data ($\kappa$ and $F_{sat}$) were found to follow trends dependent upon $\alpha_0$. This may have some implications for phthalocyanine design for nonlinear optical applications.

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References