

Alkynyl substituted phthalocyanine derivatives as targets for optical limiting

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One of the key issues in the development of efficient optical limiters is the search for appropriate materials with improved nonlinear absorption. Phthalocyanine materials are among the most promising nonlinear absorbers described in the literature. Ethynyl and butadiynyl-bridged bisphthalocyanines and related ethynyl-containing mononuclear compounds have been synthesized and experimentally studied using the z-scan technique with nanosecond pulses at 532 nm. We intend to ascertain the effect of the electronic interaction between macrocycles in the optical limiting performance of phthalocyanines.

Introduction

Optical limiters are materials that are fairly transparent at normal ambient light intensities but strongly attenuate intense optical beams. These are of great interest¹ since they can protect optical sensors and the human eye from intense light sources such as lasers. Passive optical limiting (OL) usually relies on two non-linear effects: non-linear absorption and/or refraction. Nonlinear refraction means that the refractive index of a material varies under the influence of the incident light. This index variation forms a lens that can defocus the beam and deflects a fraction of the light into the wings of the beam, where it is blocked by a properly located aperture. Materials with a positive nonlinear absorption coefficient are often said to exhibit *reverse saturable absorption* (RSA), where a decrease of transmittance is observed at high illumination levels. This is the most common effect that takes place in optical limiting processes. Mechanistically, RSA occurs when the incident light is intense enough to provide a significant population in the excited state and the excited state absorption cross-section (σ_{ex}) is larger than that of the ground state (σ_0). Thus, an ideal material would have both a weak ground-state absorption and a large excited-state absorption, in addition to a long excited state lifetime, over a wide spectral width.

Over the last decade, many scientists have been concerned with the search of materials with improved optical limiting capabilities.² Phthalocyanines³ (Pcs) have emerged as very promising materials for OL^{4–8} because of their unique electronic absorption features, allowing high linear transmission in the spectral window between the main two absorption Soret and Q bands, and their chemical, optical and thermal stability. They show strong excited-state absorption and long excited-state lifetimes, which can vary over orders of magnitude depending on the central atom. Another advantage this family offers is a tremendous architectural flexibility, which allows the tailoring of their electronic structure and physical properties over a wide range of structural modifications, such as attaching peripheral groups to the periphery of the macrocycle, incorporating many different metal ions into the ring and attaching axial substituents to this metal. Thus, for example, the role of the central metal atom has been widely

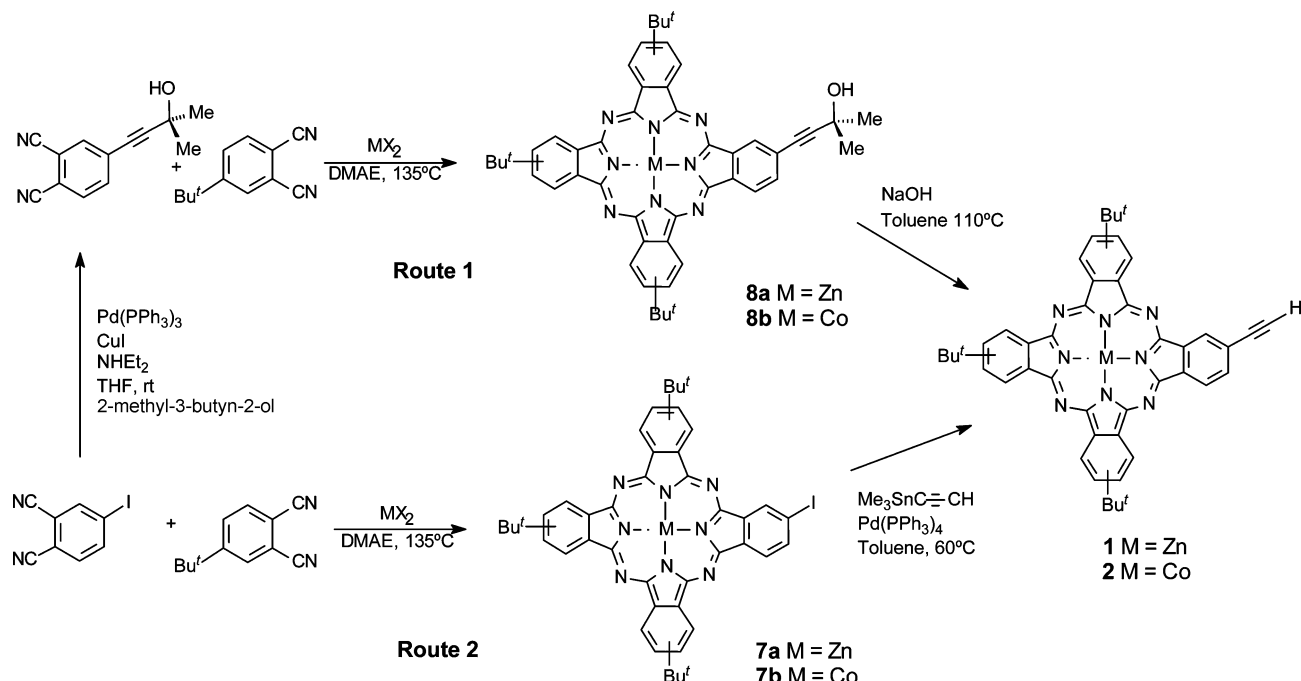
explored. It has been demonstrated that the insertion of heavy atoms into the phthalocyanine ring, such as indium^{9–11} and lead,¹² causes a significant improvement in the reverse saturable absorption behaviour, owing to an increased rate of inter-system crossing from the lowest excited singlet state to the strongly absorbing triplet state. Axial substitution over indium phthalocyanines has been shown to be effective in improving OL capabilities.^{10,11} On the other hand, the effect of the peripheral substituents is less clear.^{13–15}

Determining the rationale of the influence of the electronic interactions between macrocycles on the nonlinear absorption of Pc-based systems is also an appealing task that has not been addressed previously. Recently, we have prepared homo- and heterodimetallic ethynyl- and butadiynyl-bridged bisphthalocyaninato complexes using metal-mediated coupling methodologies.¹⁶ It has been recognized that ethyne and butadiyne linkages are ideal for enabling electronic interactions between chromophores. For this reason we have performed Z-scan measurements on a series of ethynyl-substituted mononuclear Pcs and ethynyl- and butadiynyl-bridged binuclear phthalocyanines **1–6** in order to ascertain the effect of the electronic communication between macrocycles on the nonlinear absorption properties of phthalocyanines, as well as the role of the substituents and central atoms in these molecular structures.

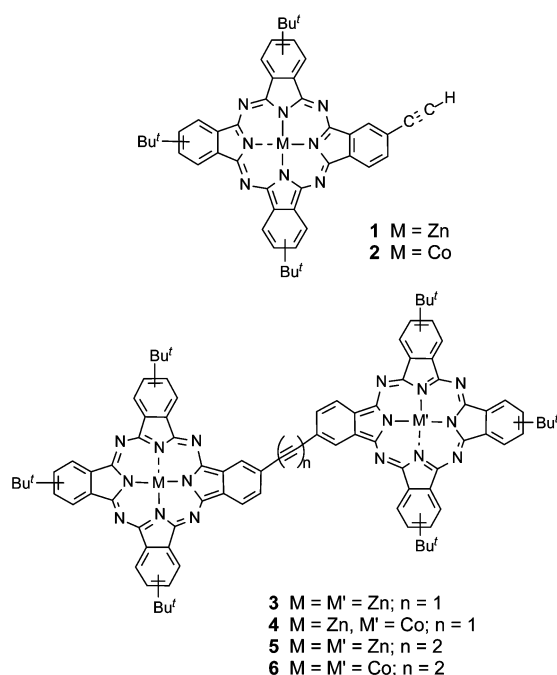
Results and discussion

Synthesis and characterization

The synthesis of ethynyl-containing phthalocyanines **1** and **2** was attempted by two different procedures. The first route involves mixed condensation of 4-(3-hydroxy-3-methyl-1-butynyl)phthalonitrile, prepared by Shonogashira coupling between the 4-iodophthalonitrile and 2-methyl-3-butyne-2-ol,¹⁷ with 3 equivalents of 4-*tert*-butylphthalonitrile in the presence of a metal(II) salt (Scheme 1, route 1), as previously described.¹⁶ After isolation of the desired phthalocyanine from the statistical mixture by column chromatography (24% yield for **8a** and 21% yield for **8b**), the protecting group of the ethynyl function was removed by treatment with sodium hydroxide in toluene to give **1** and **2** in 74 % yield.



Scheme 1 Synthesis of ethynyl-containing phthalocyanines **1** and **2** by two different routes.



The second approach involves the preparation of the iodophthalocyanines **7a–b** by mixed condensation of 4-iodophthalonitrile¹⁸ with 4-*tert*-butylphthalonitrile¹⁹ in the presence of the corresponding metallic salt (15% yield) (Scheme 1, route 2).¹⁶ The zinc(II) derivative **7a** yields the Stille coupling product **1** by reaction with tributyl(ethynyl)tin and a catalytic ratio of tetrakis(triphenylphosphine)palladium(0) in toluene (70 °C) in 92% yield. However, a Stille reaction with the cobalt(II) complex **7b** gives rise to a complex mixture of products (including homocoupling compounds of the starting iodophthalocyanine **7b** and demetallated derivatives), from which the desired phthalocyanine **2** could not be isolated.

Regarding the synthesis of the zinc(II) derivative **1**, one can compare the overall yield for the two experimental procedures starting from 4-iodophthalonitrile. Even though both routes

give rise to similar overall yields of the resulting phthalocyanine **1** (14%), the latter proceeds in only two steps and the intermediate iodophthalocyanine **7a** is also the starting compound for the synthesis of the butadiynyl-linked dimer **5** in high yields, as we will see below.

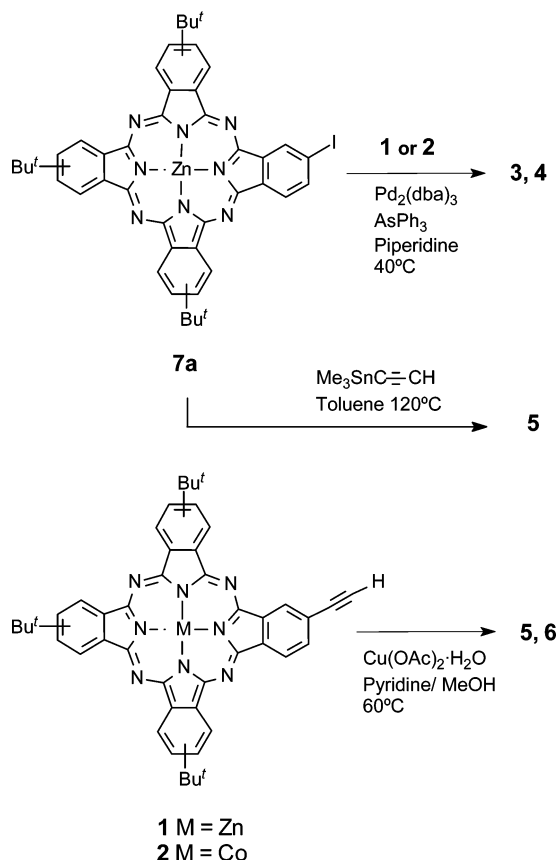
The preparation of ethynyl-bridged phthalocyanines **3** and **4**,¹⁶ has been previously reported. Metal mediated cross-coupling between the ethynyl-containing phthalocyanines **1** or **2** and the unsymmetrically substituted iodophthalocyanine **7a** affords the homo- and heterodimetallic ethynyl-bridged bisphthalocyanines **3** and **4** (Scheme 2).

Butadiynyl-bridged bisphthalocyanine **5** and **6** were prepared following procedures described earlier.¹⁶ They were synthesized by oxidative homocoupling of the terminal alkynes **1** or **2** in the presence of copper(II) acetate monohydrate in a mixture of dry pyridine and dry methanol (Scheme 2) in *ca.* 60% yield. Compound **5** was also prepared in 84% yield by reaction of iodophthalocyanine **7a** with tributyl(ethynyl)tin and catalytic amounts of tetrakis(triphenylphosphine)palladium(0) in refluxing toluene. One should note that the application of different temperatures to the same mixture of reactants can provide either the mononuclear ethynyl-containing phthalocyanine **1** or the butadiynyl-linked binuclear compound **5**. Once again, the application of Stille conditions to the cobalt derivative **7b** for the synthesis of compound **6** was unsuccessful.

The optical features of the binuclear chromophoric systems **3–6** differ from that of the corresponding unsymmetrically substituted parent alkynes **1**, **2** (Fig.1). In general, both the ethynyl- and the butadiynyl-bridged binuclear phthalocyanines show broad Q bands that are red-shifted with regard to their mononuclear counterparts. This shift to the red could be attributed to the enlargement of the π -conjugated system. The broadening and splitting of the Q band as a consequence of the splitting of the energetic levels must be due to electronic coupling between the two halves of the molecule more than to an intermolecular effect, since the spectra remain invariable when changing the concentration.

Z-scan measurements

The open-aperture Z-scan experiment²⁰ is a very convenient method to evaluate the optical limiting properties of materials.



Scheme 2 Synthesis of ethynyl- and butadiynyl-linked dimers **3–6**.

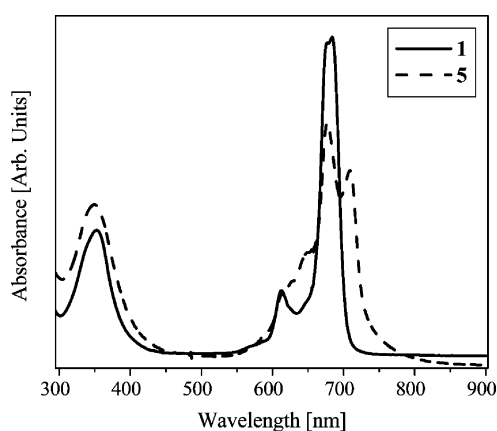


Fig. 1 UV-vis spectra in toluene of compounds **1** ($c = 5.5 \times 10^{-7}$ M) (solid line) and **5** ($c = 4.4 \times 10^{-6}$ M) (broken line).

This technique measures the total transmittance through the sample as a function of incident laser intensity while the sample is gradually moved along the optical axis of a convex lens. The set-up is shown schematically in Fig. 2. The normalized transmittance $T_{\text{norm}}(z)$ as a function of the position along the z axis is given by

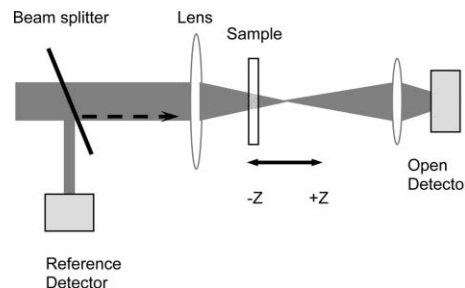


Fig. 2 Schematic diagram of the open aperture Z-scan apparatus.

$$T_{\text{norm}}(z) = \frac{\text{Log}_e[1 + q_0(z)]}{q_0(z)}, \quad (1)$$

where $q_0(z)$ is given by

$$q_0(z) = \frac{q_{00}}{1 + \left(\frac{z}{z_0}\right)^2}, \quad (2)$$

z_0 is the is the diffraction length of the beam and $q_{00} = \beta_{\text{eff}} I_0 L_{\text{eff}}$, where $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$. β_{eff} is the effective intensity dependent nonlinear absorption coefficient, I_0 is the intensity of the light at focus. L_{eff} is known as the effective length of the sample, defined in terms of the linear absorption coefficient, α_0 , and the true optical path length through the sample, L . These equations were incorporated into a computer code and a least squares regression algorithm was used to fit this to the experimental data.

The imaginary third-order optical susceptibility $\text{Im}\{\chi^{(3)}\}$ is directly related to the intensity dependent absorption coefficient β_I and is expressed as

$$\text{Im}\{\chi^{(3)}\} = \frac{n_0^2 \epsilon_0 c \lambda \beta_I}{2\pi}, \quad (3)$$

where n_0 is the linear refractive index, ϵ_0 is the permittivity of free space, c is the speed of light and λ is the wavelength of the incident light. The relationship between $\text{Im}\{\chi^{(3)}\}$ and the second order molecular hyperpolarizability (γ) is defined as:

$$\gamma = \frac{\text{Im}\{\chi^{(3)}\}}{f^4 c_{\text{mol}} N_A}, \quad (4)$$

where $f = (n_0^2 + 2)/3$ is the Lorentz local field enhancement factor, n_0 is the linear refractive index of the sample, c_{mol} is the molar concentration and N_A is Avogadro's number.

The open aperture z-scan experiments were performed using 0.5 g L^{-1} solutions of phthalocyanines **1–6** in toluene, measuring the sample transmission at 532 nm. All the compounds exhibited a reduction in the transmission about the focus of the lens, which is indicative of positive nonlinear absorption attributed to reverse saturable absorption. Nonlinear absorption coefficients β_I (Table 1) were calculated from the data by least squares fitting of equations 1 and 2 with the waist radius of the beam treated as a free parameter. One should note that these nonlinear coefficients are not stationary with respect to the focus intensity since they reduce in magnitude with increasing focal intensity indicating that they

Table 1 Experimentally determined optical coefficients

Compound	α_0/cm^{-1}	$I_0/\text{GW cm}^{-2}$	$\beta_I/\text{cm W}^{-1}$	$\text{Im}\{\chi^{(3)}\}_{\text{eff}}/\text{ESU}$	$\gamma_{\text{eff}}/\text{ESU}$	$F_{\text{sat}}/\text{J cm}^{-2}$	$\kappa (\sigma_{\text{ex}}/\sigma_0)$
1	1.95	0.5	$(3.5 \pm 0.7)\text{e-}08$	$(1.3 \pm 0.2)\text{e-}11$	$(8.3 \pm 1.6)\text{e-}33$	14 ± 0.7	8.9 ± 0.3
2	1.76	2.0	$(1.4 \pm 0.3)\text{e-}09$	$(5.1 \pm 1.0)\text{e-}13$	$(3.2 \pm 0.6)\text{e-}34$	70 ± 30	3.3 ± 0.8
3	1.06	0.2	$(1.2 \pm 0.2)\text{e-}08$	$(4.6 \pm 0.8)\text{e-}12$	$(5.8 \pm 1.1)\text{e-}33$	1.9 ± 0.1	3.0 ± 0.1
4	1.22	0.5	$(5.6 \pm 1.1)\text{e-}09$	$(2.1 \pm 0.4)\text{e-}12$	$(2.6 \pm 0.5)\text{e-}33$	1.3 ± 0.1	1.8 ± 0.1
5	1.19	0.5	$(2.3 \pm 0.5)\text{e-}08$	$(8.7 \pm 1.6)\text{e-}12$	$(1.1 \pm 0.2)\text{e-}32$	3.9 ± 0.3	5.4 ± 0.2
6	1.60	0.5	$(3.5 \pm 0.7)\text{e-}08$	$(1.3 \pm 0.2)\text{e-}11$	$(1.7 \pm 0.3)\text{e-}32$	9.5 ± 0.2	11.0 ± 0.1

are comprised of contributions from third and higher order odd terms. Effective third order nonlinear absorption coefficients β_I were estimated using data interpolation at the focal intensities given in Table 1. $\text{Im}\{\chi^{(3)}\}$ and γ were also calculated and are quoted in Table 1. It can be seen that the effective nonlinear absorption coefficient β_I ranges from values of the order of 10^{-9} to 10^{-8} cm W $^{-1}$, which corresponds to effective second order molecular hyperpolarizabilities ranging from orders of 10^{-34} to 10^{-32} esu.

After manipulating the open aperture spectra, the normalised transmission (T_{norm}) was plotted against the incident energy density per pulse (F) to further investigate the optical limiting. The nonlinear absorption coefficient given by equation 5 was derived using laser rate equations²¹ and applied in a static state approximation, fitted using least squares regression. F_{sat} is the energy density at which the output reaches its saturated value. κ is the excited to ground state absorption cross-section ratio ($\sigma_{\text{ex}}/\sigma_0$). The parameters κ (realistically σ_{ex} as α_0 was measured) and F_{sat} were both treated as free constants in the fitting algorithm. The α_0 , κ and F_{sat} values for each compound are also presented in Table 1.

$$\alpha(F, F_{\text{sat}}, \kappa) = \frac{\alpha_0}{1 + \frac{F}{F_{\text{sat}}}} \left(1 + \kappa \frac{F}{F_{\text{sat}}} \right), \quad (5)$$

In Fig. 3 normalized transmission against incident pulse energy density is plotted for the mononuclear phthalocyanines **1** and **2**. The solid lines are the theoretical curve fits. The zinc centered Pc (**1**) is the strongest nonlinear absorber of the mononuclear compounds. It also exhibits the largest excited to singlet state absorption cross section ratio κ and the lowest saturation energy density F_{sat} .

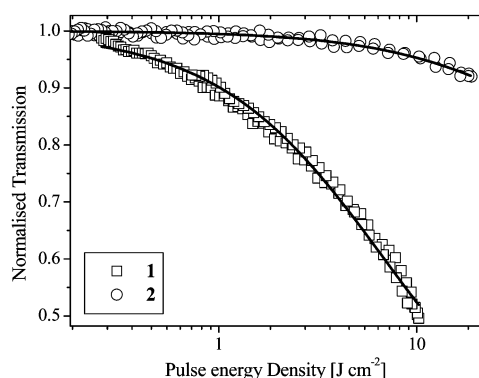


Fig. 3 Plots of normalized transmission against incident pulse energy density for mononuclear phthalocyanines **1** and **2**. The solid lines are theoretical curve fits.

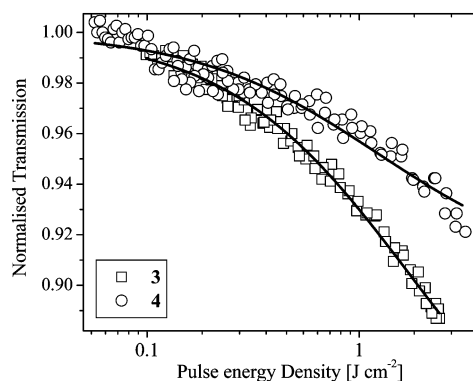


Fig. 4 Plots of normalized transmission against incident pulse energy density for ethynyl-bridged bisphthalocyanines **3** and **4**. The solid lines are theoretical curve fits.

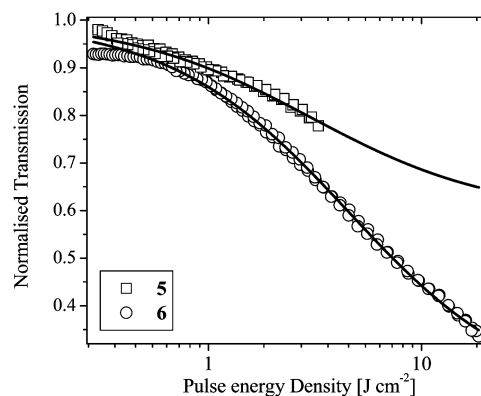


Fig. 5 Plots of normalized transmission against incident pulse energy density for butadiynyl-bridged bisphthalocyanines **5** and **6**. The solid lines are theoretical curve fits.

The optical limiting response of the ethynyl-bridged bisphthalocyanines **3** and **4** is presented in Fig. 4. The zinc dimer **3** exhibits a larger optical limiting response than that of the cobalt compound **4**. The κ coefficient exhibited by **4** is the lowest in the study at $\kappa \approx 1.8 \pm 0.1$ and it also exhibits the lowest saturation energy density at $F_{\text{sat}} \approx (1.3 \pm 0.1)$ J cm $^{-2}$. Compound **3** saturated at 1.9 J cm $^{-2}$ and exhibited a κ coefficient ~ 1.8 times that of **4** ($\kappa \approx 3.0 \pm 0.1$).

Plots of normalized transmission against incident pulse energy density for the butadiynyl-bridged bisphthalocyanines **5** and **6** are presented in Fig. 5, where again the solid lines are the theoretical curve fits. It is very interesting that in this case the cobalt dimer **6** exhibits a much larger nonlinear absorption than the zinc dimer **5**. This contradicts the trend in the associated mononuclear analogues **1** and **2**. The cobalt dimer **6** displayed the largest κ coefficient in the study at $\kappa \approx 11.0 \pm 0.1$, approximately twice that of **5**. It can also be noted that **6** exhibited a much higher saturation energy density, by a factor ~ 2.4 , than that of **5**.

In summary, the mononuclear cobalt derivative is a weaker nonlinear absorber than its zinc counterpart. In contrast, the cobalt dimer **6** exhibits the largest β_I response of all the binuclear derivatives. One can note that in the zinc series, the nonlinear absorption, the saturation energy density F_{sat} and also the κ coefficients decrease in the order $3 < 5 < 1$. One would expect that electronic interaction between the two chromophores would be maximum for **3** as the spatial separation of the macrocycles is less than that for **5**. The trends in the data therefore imply that the derivative with the highest degree of electronic interaction between the two chromophores (**3**) is the weakest nonlinear absorber. On the other hand, intermolecular interactions seem to positively affect the nonlinear response in the cobalt series since the cobalt dimer **6** has the largest β_I of all the compounds presented in this study. This is surprising since the cobalt(II) mononuclear derivative **2** is a poorer optical limiter as compared to the Zn^{II} compound (**1**). These results seem to indicate that there is an inseparable link between the peripheral structure and the central metal in this type of system. Thus, one cannot separately tune the nonlinear optical response by changing either the main structure or the central metal of the chromophore because both factors are inextricably intertwined. However, the knowledge of the fundamental photophysical properties (quantum yields and excited state lifetimes) of these derivatives could provide additional information for the understanding of these observable facts. All dimers exhibit lower F_{sat} than their mononuclear parent compounds, but the cobalt dimer **6** has the highest of the four bridged dimers. Notably this compound also exhibits the largest κ coefficient of the seven compounds studied, with $\kappa \approx (11.0 \pm 0.1)$.

Conclusions

In conclusion, these compounds do not exhibit, in general, high magnitude nonlinear absorption. It was found that putting cobalt into the central cavity of mononuclear phthalocyanines produces undesirable effects from the point of view of optical limiting as it reduces the magnitude of the nonlinear absorption. However, the cobalt(II) phthalocyaninate-based dimer **6** shows good nonlinear absorption coefficients and κ values, thus indicating that the presence of cobalt could be desirable in structures which can give rise to intermolecular electronic interactions. The other remarkable feature is that the other bridged binuclear derivatives **3–5** are promising when one would require low F_{sat} properties for practical optical limiters.

Experimental section

Melting points were determined on a Büchi apparatus and are uncorrected. ^1H -NMR spectra were recorded on a Bruker AC-300 (300 MHz). UV-vis spectra were recorded on a Perkin-Elmer 8453 spectrophotometer. Mass spectra were determined on a VG AutoSpec spectrometer. The starting 4-iodophthalonitrile¹⁸ and 4-*tert*-butylphthalonitrile¹⁹ were prepared following described procedures.

All z-scan experiments were performed using 6 ns pulses from a Q-switched Nd:YAG laser. The beam was spatially filtered to remove higher order modes and tightly focused with a 9 cm focal length lens. The laser was operated as its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz. Samples were prepared by dissolving the compound in toluene at 0.5 g L⁻¹ followed by gentle agitation for approximately 30 min in a low-power (60 W) sonic bath. All measurements were performed in quartz cells with a 1 mm through path length.

2-Ethynyl-9,16,23-tri-*tert*-butylphthalocyaninate zinc(II) (**1**)

A mixture of tri-*tert*-butyliodophthalocyaninate zinc(II) **7a**¹⁶ (22 mg, 0.025 mmol), Pd(PPh₃)₄ (1.3 mg, 0.001 mmol) and tributyl(ethynyl)tin (0.025 mmol) in dry toluene was heated at 60 °C for 4 h under an argon atmosphere. After the solvent had been removed, the crude was extracted with CH₂Cl₂ and washed with water. The blue solid was purified by column chromatography on silica gel, using a mixture of hexane–dioxane (4 : 1) as eluent. Yield: 92%. Mp > 250 °C. IR (KBr): $\nu(\text{C}\equiv\text{CH})$ 3495, $\nu(\text{C}\equiv\text{C})$ 2103 cm⁻¹. ^1H NMR (CDCl₃, 300 MHz) δ 9.0–7.5 (m, 12H, ar.), 3.40 (s, 1H, C $\equiv$ CH), 1.6 (bs, 27H, C(CH₃)₃). UV-vis (CHCl₃), λ_{max} (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 684 (5.4), 612 (4.7), 350 (5.1) nm. MS (FAB, NOBA), m/z (%): 769 (100) [M + H]⁺, 753 (26) [M – CH₃]⁺.

Bis[(tri-*tert*-butylphthalocyaninate)cobalt(II)]butadiyne (**5**)

A mixture of tri-*tert*-butyliodophthalocyaninate zinc(II) **7a**¹⁶ (63 mg, 0.072 mmol), Pd(PPh₃)₄ (15 mg, 0.013 mmol) and tributyl(ethynyl)tin (0.083 mmol) in dry toluene was refluxed for 9 h under an argon atmosphere. After the solvent had been removed, the crude was extracted with CH₂Cl₂ and washed

with water. The green solid was purified by column chromatography on silica gel, using a mixture of hexane–dioxane (2 : 1) as eluent. Yield: 84%. Mp > 250 °C. IR (KBr): $\nu(\text{C}\equiv\text{CH})$ 3428, $\nu(\text{C}\equiv\text{C})$ 2556 cm⁻¹. ^1H NMR (CDCl₃, 300 MHz) δ 9.5–7.2 (m, 24H, ar.), 1.6 (bs, 54H, C(CH₃)₃). UV-vis (CHCl₃), λ_{max} (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 709 (4.7), 675 (4.7), 350 (4.6) nm. MS (MALDI-TOF, dithranol), m/z (%): 1539–1535 (isotopic pattern) (100) [M + H]⁺.

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