Synthesis, Characterisation and Nonlinear Optical Properties of Two-Dimensional Octupolar Systems Based on Phthalocyanine Compounds

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Four phthalocyanine-based compounds with pseudo D_{3h} symmetry have been synthesised and fully characterised. Palladium cross-coupling methodologies were employed in order to synthesise 1,3,5-tris[(phthalocyaninyl)ethenyl]benzene (Heck) and 1,3,5-tris[(phthalocyaninyl)ethynyl]benzene (Sonogashira) derivatives. Knoevenagel condensation conditions were then applied to the synthesis of 1,3,5-tris[cyano(phthalocyaninyl)ethenyl]benzene and 2,4,6-tris[(phthalocyaninyl)ethenyl]-1,3,5-triazine. Preliminary second-order nonlinear optical studies, by hyper-Rayleigh scattering measurements, revealed that the compounds containing ethenyl linkers induce a strong octupolar effect while the ethynyl-containing compound does not show any octupolar enhancement. The introduction of a triazine central core does not modify significantly the nonlinear optical behaviour of the compound.

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Introduction

There is continuous interest in the preparation of organic nonlinear optical (NLO) materials with potential applications for the construction of optoelectronic devices.[1] Push–pull molecules are among the most studied systems for such purpose; they are composed of a donor and an acceptor moiety linked by a highly polarizable π-conjugated bridge.[2] While many of these NLO chromophores have shown very efficient NLO responses in terms of β- and γ-hyperpolarizability values, short response times and chemical and photochemical stability, their ordering into non-centrosymmetric arrangements is still a challenge as a consequence of the natural tendency of dipoles to align in an antiparallel fashion.[3]

More recently, the realisation that the first-order hyperpolarizability tensor β could be reduced in a unique manner into dipolar $\beta^{J=1}$ and octupolar $\beta^{J=3}$ contributions paved the way for the synthesis of a wide variety of organic NLO chromophores that fulfil the octupolar symmetry requirements.[4] The main advantage of these chromophores lies in their ability to generate a second-order NLO response whatever their organisation in condensed phases. Among the possible octupolar geometries (tetrahedral, cubic, etc.), the D_{3h} symmetry has been shown to give very good results both in terms of raw NLO response and processability.[5] The most common organic building block for attaining such symmetry is the 1,3,5-trisubstituted benzene residue,[5c,6] and recently, 2,4,6-trisubstituted 1,3,5-triazine molecules have also been shown to be very promising candidates for such purposes.[5c,7]

As a consequence of their highly polarizable 18-π-electron aromatic core phthalocyanines (Pcs), when unsymmetrically substituted, possess very good second-order nonlinear optical properties.[8] Many strategies have been employed in order to break the inherent symmetry of these macrocycle[9] and to favour the electron flow within the plane of the molecule.[10] Thus, push–pull phthalocyanines, push–pull phthalocyanine dimers and conjugated non-centrosymmetrical dimers have been synthesised and their NLO properties studied. Although we and others have already reported examples of octupolar systems based on Pc analogues,[11] to the best of our knowledge there is only one previously described example of a Pc molecule incorporated within an octupolar three-dimensional framework, i.e. a tetrahedral phosphorus atom, that gave very good results when compared with the corresponding non-octupolar Pc.[12] In the same line of thought, we decided to take advantage of the planar π-conjugated system that characterises Pcs in order to incorporate them into planar octupoles. In this article we describe the synthesis and preliminary NLO studies of a series of pseudo-D_{3h} symmetrical[13] 1,3,5-tris(phthalocyaninyl)benzenes **1**–**3** and 2,4,6-tris(phthalocyaninyl)-1,3,5-triazine **4**.

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Results and Discussion

Synthesis

The tris(phthalocyaninyl)ethenyl compound **1** (Figure 1) was synthesised in 61% yield under standard Heck conditions by heating 1,3,5-trivinylbenzene[14] and tri-*tert*-butyl(iodo)phthalocyanine (**5**)[15] in DMF at 90 °C (Figure 2) in the presence of LiCl, tetrabutylammonium bromide, K_2CO_3 and catalytic amounts of $Pd(OAc)_2$ for 24 h. The tris(ethynyl) compound **2** was obtained in 70% yield under standard Sonogashira cross-coupling conditions by mixing 1,3,5-triethynylbenzene[16] and **5** in NEt_3 in the presence of catalytic amounts of both $[Pd(PPh_3)_4]$ and CuI at 80 °C for 65 h. The Knoevenagel condensation was applied to the synthesis of compounds **3** and **4**. Thus, reaction between tri-*tert*-butyl(formyl)phthalocyanine[2] (**6**; Figure 2) and 1,3,5-tris(cyanomethyl)benzene[17] in the presence of tetrabutylammonium hydroxide and potassium *tert*-butoxide as bases led to compound **3** in 59% yield. In the same manner, the synthesis of **4** was achieved in 24% yield by condensation of 2,4,6-trimethyl-1,3,5-triazine[18] with compound **6** in the presence of potassium hydroxide as a base. This reaction also gave a distyryl-Pc system as a side-product, as well as the products of the reduction and oxidation of **6**.

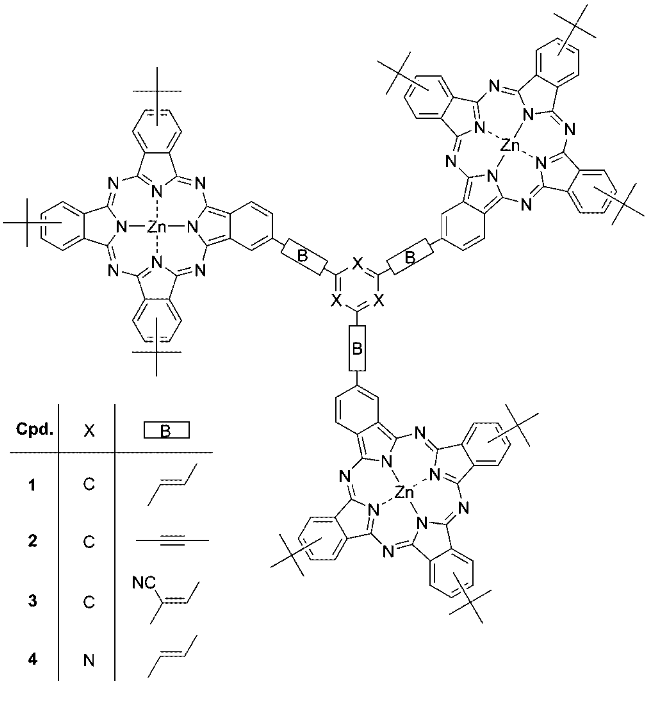


Figure 1. Phthalocyaninecompounds **1**–**4**.

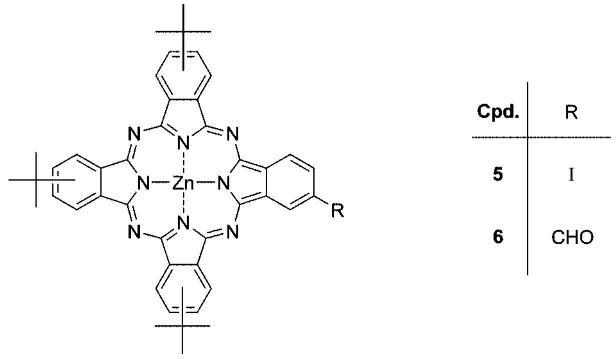


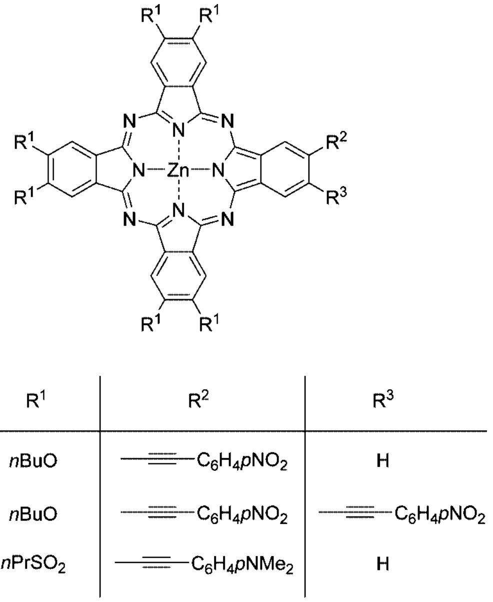
Figure 2. Phthalocyanine precursors **5** and **6**.

All four compounds were characterised by UV/Vis and ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis. As a consequence of the presence of many regioisomers (because of the peripheral *tert*-butyl groups) and of intermolecular stacking, the signals of the ^{1}H NMR spectra of **1**–**4** are very broad and uninformative. Nevertheless, the integration values of the various assignable signals are consistent with the expected values. The UV/Vis spectra of compounds **1**–**4** show, in all cases, the characteristic B-band at ca. 350 nm and a more intense Q-band at ca. 680–700 nm. In all cases, the Q-band is split as a consequence of the low symmetry of the phthalocyanine moieties and shifted to the red part of the spectrum with respect to the corresponding symmetrical tetra-*tert*-butylphthalocyanine in compounds **1**, **3**, and **5** due to the enlargement of the π-conjugated systems. Compound **2** does not show this red shift as a consequence of loss of conjugation coming from the probable orthogonal disposition of the three phthalocyanine planes with respect to the one defined by the central benzene ring, a phenomenon that cannot occur in the vinyl-containing compounds. Mass spectra for all four compounds show the corresponding molecular peak associated with the correct isotopic pattern. Moreover, in all compounds it was possible to observe very weak signals corresponding to the loss, by fragmentation within the spectrometer, of one phthalocyanine unit.

Nonlinear Optical Measurements

Before starting to analyse the experimental β_{HRS} values corresponding to compounds **1**–**4**, it is worth mentioning that phthalocyanines **7**–**9** (Figure 3) previously studied by us[10a] show values ranging from 11 to 53×10^{-30} esu (Table 1). These values were the best β_{HRS} values ever obtained in the case of (phthalocyanine)zinc compounds and were interpreted on the basis of their strong push–pull character, and, in principle, they could be considered as the best possible obtainable for a mononuclear (phthalocyanine)zinc compound.

The experimental β_{HRS} values (Table 1) for compounds **1**–**4** show very profound differences that may be interpreted in terms of both their octupolar character and π-conjugation. In a first instance it is clear from the comparison between pseudo D_{3h} symmetrical compound **1** and Pcs **7** and **9** that a strong octupolar effect is overruling the push–pull effect since β_{HRS}(**1**) is much more than three times β_{HRS}(**7**) or β_{HRS}(**9**), a magnitude that could be expected in the case of a molecule containing three phthalocyanine rings. The ratio β_{HRS}/M gives a first hyperpolarizability-related value independent of the number of phthalocyanine moieties that illustrates in a more quantitative way this analysis. In our case, we chose Pc **7** (β_{HRS}/M = 1) as a reference as it pos-



Cpd.	R^1	R^2	R^3
7	nBuO	$-\!\equiv\!-C_6H_4pNO_2$	H
8	nBuO	$-\!\equiv\!-C_6H_4pNO_2$	$-\!\equiv\!-C_6H_4pNO_2$
9	nPrSO$_2$	$-\!\equiv\!-C_6H_4pNMe_2$	H

Figure 3. Push–pull phthalocyanines **7**–**9**.

Table 1. Experimental β_{HRS} values for compounds **1**–**4** and **7**–**9**.

Compound	**1**	**2**	**3**	**4**	**7**[a]	**8**[a]	**9**[a]
β_{HRS}[b]	144	46	144	83	22	53	11
$(\beta_{HRS}/M)_{rel}$	3.1	1	3	1.8	1	2.1	0.4

[a] Values obtained from ref.[10a] [b] 10^{-30} esu at 1.06 µm.

sesses common features with the phthalocyanine components within the compounds. The octupolar effect is also observed in compound **3** even though the expected "help" from the cyano groups in **3** does not occur, β_{HRS}(**1**) being equal to β_{HRS}(**3**).

Not surprisingly, compound **2** does not show this octupolar enhancement [$(\beta_{HRS}/M)_{rel}$ = 1] as a consequence of the more favourable disposition of the phthalocyanine moieties in an orthogonal relationship with respect to the plane of the central benzene ring, as illustrated in Figure 4. In the case of the other compounds (**1**, **3** and **4**), the phthalocyanine residues are forced to adopt a coplanar conformation. The incorporation of a central 1,3,5-triazine unit as in the case of compound **4** is counterproductive both in terms of β_{HRS} values and synthetic efforts. Still, the triazine-containing compound shows a strong octupolar effect with a $(\beta_{HRS}/M)_{rel}$ value of 1.8.

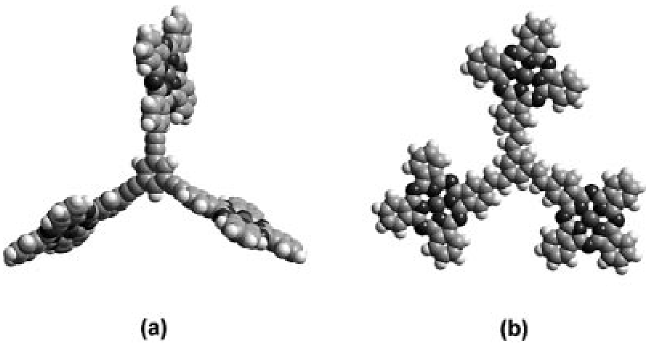


Figure 4. CPK representation of two (Pc)Zn compounds (PM3 calculations): (a) **1** and (b) **2** (*tert*-butyl groups have been omitted for clarity).

Conclusions and Outlook

Phthalocyanines are versatile nonlinear optical chromophores that have been incorporated within highly polarizable octupolar frameworks in **1**–**4**. Once more, the phthalocyanine backbone has been shown to be exceptionally robust to its chemical environment since it is able to sustain palladium cross-coupling reaction conditions and the strongly basic conditions of the Knoevenagel reaction. Depending on the relative orientation of the phthalocyanine moieties and the central aromatic ring, the octupolar character of the triads has been shown to be activated or not. The net effect of the octupolarity of the system (after removing the effect of the presence of three Pc rings instead of one) is a threefold enhancement with respect to other push–pull (phthalocyanine)zinc compounds. Once again, this study points out the relevance of designing Pc-based octupolar systems.

Experimental Section

General Remarks: UV/Vis spectra were recorded with a Hewlett–Packard 8453 and a Varian Cary 4E instrument. IR spectra were recorded with a Bruker Vector 22 spectrophotometer. L^{si}-MS and HR mass spectra were determined with a VG AutoSpec instrument. MALDI-TOF mass spectra were recorded with a Bruker Reflex III spectrometer. NMR spectra were acquired with a Bruker AC-300 instrument. Elemental analyses were performed with a Perkin–Elmer 2400 apparatus. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC on aluminium sheets precoated with silica gel 60 F_{254} (E. Merck). Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification. 1,3,5-Trivinylbenzene,[13] [tri-*tert*-butyl(iodo)-phthalocyaninato]zinc(II) (**5**),[14] 1,3,5-triethynylbenzene,[15] 1,3,5-tris(cyanomethyl)benzene[16] and [tri-*tert*-butyl(formyl)phthalocyaninato]zinc(II) (**6**)[14] were prepared according to published procedures.

Compound 1: A mixture of 1,3,5-trivinylbenzene (10.4 mg, 0.066 mmol), [tri-*tert*-butyl(iodo)phthalocyaninato]zinc(II) (174 mg, 0.2 mmol), LiCl (9.0 mg, 0.2 mmol), $Pd(OAc)_2$ (4.4 mg, 0.022 mmol), tetrabutylammonium bromide, (66 mg, 0.2 mmol) and K_2CO_3 (158 mg, 1.0 mmol) in DMF (10 mL) was heated under argon at 90 °C overnight. The solvent was then evaporated under reduced pressure and the resulting crude product was purified by flash column chromatography (SiO_2, dioxane/hexanes, 1:3 to 1:2) to yield **1** (96 mg, 61 %) as a green solid, m.p. > 300 °C. ^1H NMR ($CDCl_3$): δ = 9.0–7.1 (m, 45 H, arom. and olefinic H), 2.0–1.7 [m, 81 H, $C(CH_3)_3$] ppm. FT-IR (KBr): $\tilde{\nu}_{max}$ = 2953, 2885, 1613, 1486, 1392, 1253, 1148, 1085, 1048, 923, 745 cm^{-1}. UV/Vis (THF): λ_{max} (log ε) = 684 (5.18), 676 (5.10), 352 (4.94) nm. MS-MALDI-TOF: m/z = 2384–2396 [M$^+$]. $C_{144}H_{126}N_{24}Zn_3$ (2388.9): calcd. C 72.40, H 5.32, N 14.07; found C 71.87, H 5.18, N 13.63.

Compound 2: A mixture of [tri-*tert*-butyl(iodo)phthalocyaninato]-zinc(II) (156.9 mg, 0.18 mmol), 1,3,5-triethynylbenzene (9 mg 0.06 mmol), $[Pd(PPh_3)_4]$ (8.1 mg 0.0069 mmol) and CuI (3.9 mg

0.0204 mmol) in triethylamine (10 mL) was heated at 80 °C under argon for 65 h. The solvent was then removed under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, first dioxane/hexanes, 1:3 and finally THF) to yield **2** as a green solid (78 mg 70%); m.p. > 300 °C. ^1H NMR ($CDCl_3$): δ = 9.0–7.5 (39 H, arom), 2.0–1.7 [s, 81 H, $C(CH_3)_3$] ppm. FT-IR (KBr): $\tilde{\nu}_{max}$ = 2957, 2864, 1258, 1089, 896, 873 cm^{-1}. UV/Vis ($CHCl_3$) λ_{max} (log ε) = 643 (4.87), 341 (5.06) nm. MS-MALDI-TOF: *m/z* = 2376–2386 [M^+]. $C_{144}H_{120}N_{24}Zn_3$ (2382.8): calcd. C 72.59, H 5.08, N 14.11; found C 73.15, H 5.23, N 13.76.

Compound 3: Tetrabutylammomium hydroxide (10 µL, 10 µmol, from a 1 M solution in MeOH) was added to a well-stirred solution of (formylphthalocyaninato)zinc(II) (124 mg, 0.16 mmol), 1,3,5-tris(cyanomethyl)benzene (7.8 mg, 0.04 mmol) and potassium *tert*-butoxide (1.0 mg, 9.0 µmol) in dry THF (3.2 mL) and *tert*-butyl alcohol (0.8 mL) under argon and the mixture was heated at 50 °C for 3 h. The solvents were then evaporated under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, THF/hexanes, 1:2) to afford **3** (58 mg, 59%) as a green solid, m.p. > 300 °C. ^1H NMR ($CDCl_3$): δ = 9.0–7.3 (m, 42 H, arom. and olefinic H), 2.0–1.7 [m, 81 H, $C(CH_3)_3$] ppm. FT-IR (KBr): $\tilde{\nu}_{max}$ = 2955, 2844, 2210 ($C\equiv N$), 1618, 1480, 1388, 1250, 1148, 1090, 1045, 925, 743 cm^{-1}. UV/Vis (THF): λ_{max} (log ε) = 708 (5.18), 676 (5.10), 354 (4.94) nm. MS-MALDI-TOF: *m/z* = 2457–2468 [M^+]. $C_{147}H_{123}N_{27}Zn_3$ (2463.9): calcd. C 71.66, H 5.03, N 15.35; found C 72.12, H 4.90, N 14.93.

Compound 4: 20% KOH in methanol (0.48 mL) and [tri-*tert*-butyl(formyl)phthalocyaninato]zinc(II) (160 mg, 0.208 mmol), dissolved in dry toluene (20 mL), were added to a stirred solution of 2,4,6-trimethyl-1,3,5-triazine (6 mg, 0.048 mmol) in dry methanol (12 mL) under argon. The reaction mixture was stirred under reflux for 6 d. After removal of the solvents under reduced pressure, the crude product was washed with water and methanol, dried and purified by flash column chromatography (SiO_2, toluene/dioxane, 4:1) to give **4** (28 mg, yield: 24%) as a green solid, m.p. > 300 °C. ^1H NMR ($CDCl_3$): δ = 9.0–7.1 (m, 42 H, arom. and vinyl H), 2.0–1.7 [m, 81 H, $C(CH_3)_3$] ppm. FT-IR (KBr): $\tilde{\nu}_{max}$ = 2959, 2925, 2859, 1614, 1508, 1491, 1393, 1331, 1259, 1089, 1048, 922, 748 cm^{-1}. UV/Vis (THF): λ_{max} (log ε) = 671 (5.2), 349 (4.56) nm. MS-MALDI-TOF: *m/z* = 2388–2396 [M^+] with correct isotopic distribution. $C_{147}H_{123}N_{27}Zn_3$ (2391.8): calcd. C 70.80, H 5.18, N 15.81; found C 72.24, H 4.78, N 15.33.

Hyper-Rayleigh Scattering (HRS) or Harmonic Light Scattering (HLS) Measurements:[19] HRS or HLS experiments were performed in the earliest nonlinear optical studies (Maker and Terhune, see ref.[19a], but have somehow been superseded by EFISH in view of the dominance of the dipolar scheme. They have been revived in the current context to provide adequate and relatively easy measurement techniques of octupolar β values. Non-coherent HRS experiments performed in centrosymmetric solutions allow the retrieval of some basic tensorial features of the β tensor for multipolar molecules of interest. The nonlinear effect in HRS originates from orientational fluctuations of the scattering centres and leads to an NLO response proportional to the orientationally averaged $<\beta\otimes\beta>$ quantity. The experimental set-up is derived from that initially proposed by Terhune and Maker.[19a] In our configuration, the determination of the $<\beta\otimes\beta>$ quantity is inferred from the slope of the scattered second harmonic light plotted as a function of a "monitoring" SHG signal (emitted by a frequency doubling powder like NPP, for example). The incident fundamental laser beam can be varied continuously by rotating a half-wave plate between two crossed polarizers. The scattered harmonic signal is collected at 90° with respect to the incident beam using a set of converging lenses, and sent into a photomultiplier. As for EFISH measurements, HLS measurements were carried out on solutions of the investigated molecules at various concentrations, and compared to the HLS signal of a "reference" liquid, often the pure solvent. The HRS experiments were carried out by measuring the intensity of the scattered second-harmonic light generated when focusing the intense 1.064-µm laser beam on the centrosymmetric solution. Harmonic emission was registered in the perpendicular direction and no indication of multiphoton-induced fluorescence was obtained from our experiments, since any signal slightly out of the 2ω area was very weak, as checked with several narrow-band interferential filters. The following concentrations were employed: **1**: 0.77×10^{-4} M; **2**: 0.82×10^{-4} M; **3**: 0.77×10^{-4} M; **4**: 0.66×10^{-4} M.

Acknowledgments

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