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Synthesis, characterization and nonlinear optical properties of nonaggregating hexadeca-substituted phthalocyanines

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ABSTRACT

The microwave-assisted synthesis, characterization and photophysical properties of hexadeca-substituted phthalocyanine (Pc) complexes with bulky phenoxy substituents are reported. NMR and UV–Vis analyses confirm the ability of bulky groups to induce steric isolation of Pc cores even in the solid state. The Z-scan measurement indicates that the Zn-containing derivative has promising nonlinear optical properties (NLOs).

Phthalocyanine (Pc) and its derivatives are a class of organic functional materials that display interesting catalytic, electronic, and optical properties in addition to their widespread use as blue and green colorants.[1] Due to their fascinating properties, Pc-based materials find applications in nonlinear optics (including optical limitation).[2] optical data storage,[3] photodynamic cancer therapy,[4] sensors,[5] catalysis,[6] and solar energy conversion.[7] However, the use of these materials is limited by their low solubility in common solvents, which results in intermolecular aggregation in both solution and solid state, thus causing a drastic decay of their optical properties.[8] In particular, the aggregation behavior of Pcs can greatly affect the photodynamic activity and nonlinear optical properties through reducing the active absorbing excited-state lifetime.[9,10] Therefore, our current research has focused on modifying the phthalocyanine itself to tune both molecular and bulk properties for specific applications in the fields of optical limiting and photodynamic therapy (PDT).

The large architectural flexibility in the structure of phthalocyanines gives such materials attractive advantages to enhance their optical properties (color, aggregation, optical absorption, etc.) tailored to the required applications. Thus, many strategies have been investigated to prevent self-association of phthalocyanines in solution and in the condensed state.[11] Recently, we reported that bulky phenoxy substituents placed on the peripheral position of the phthalocyanine core perfectly prohibit close self-association of the macrocycle even within solid thin films and can result in the formation of remarkable cubic crystals containing massive solvent-filled voids.[12] In addition to the benefits arising from control over the molecular self-association (in modifying the photophysical and opto-electronic properties of phthalocyanine macrocycles), tuning the ground-state absorption (i.e., the position of the principle Q-band absorption and the molar absorption coefficient) is critical to the application of Pcs as photosensitizers and optical limitation systems. For example, the Q-band bathochromic shift in the visible spectrum into the near-IR region gives a wider transparent window in the spectrum. This is required for possible material applications of Pcs, which make them potentially suitable for PDT as photosensitizers and in nonlinear optics (e.g., human eye protector). Placing phenoxy groups at the nonperipheral positions (1, 4, 8, 11, 15, 18, 22 and 25) of the phthalocyanine ring results in a shift of the Q-band in the visible spectrum into the near-IR region so that the Pc does not display its characteristic blue or green color.[13] The aim of our work is to synthesize 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecakis(2,6-dimethylphenoxy)phthalocyanine (Pc; M = 2H, Zn, Co, Ni), which contains sterically hindered phenoxy substituents at each of the 16 peripheral and nonperipheral sites of the macrocycle. To the best of our knowledge, the synthesis, structural characterization and material properties of such interesting Pc-based materials are described for the first time.

Scheme 1 shows the synthetic route for the new phthalocyanines substituted with bulky dimethylphenoxy groups. The phthalonitrile precursor 2,3,4,5-tetrakis(2,6-dimethylphenoxy)phthalonitrile **1** was prepared in good yield (75%) from the aromatic nucleophilic substitution reaction between the anion of 2,6-dimethylphenol and commercially available tetrafluorophthalonitrile.[14] Spectroscopic characterizations of **1** were consistent with its expected structure, and the IR spectrum shows an intense band at 2220 cm^{-1} corresponding to the CN groups. Initial attempts at formation of Pc **2** using a mixture of lithium pentoxide/pentanol, the most common procedure, resulted in a very low yield and isolation of the pure product from other Pc by-products could not be achieved using various purification techniques (e.g., chromatography). This was expected due to the steric bulk exerted by the four substituents placed on the phthalonitrile ring **1**. Other common synthetic procedures were also used, but the outcome was the

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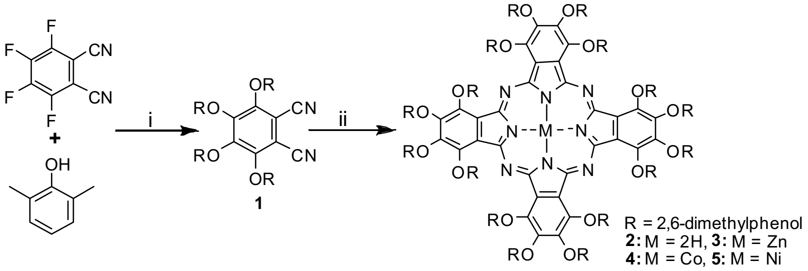

Scheme 1. Microwave-assisted synthesis of hexadeca-substituted phthalocynaine derivatives. Reagents and conditions: (i) anhydrous K_2CO_3, DMF, 120 °C, 72 h; (ii) microwave irradiation, 350 W, hydroquinone, appropriate metal salt, hexanol/DBU, 160 °C, 10 min.

same as in the first trial. Furthermore, metal ion template reactions in hexanol using zinc acetate, nickel acetate, or cobalt(II) acetate gave the same unpurifiable low yield products. Consequently, microwave-assisted synthesis was applied as an alternative approach in preparing the target phthalocyanines in good yield and high purity. The synthesis of metal-free phthalocyanine **2** was best achieved by the cyclotetramerisation of a phthalonitrile precursor **1** in the presence of hydroquinone in hexanol using a microwave-assisted method at 350 W for 10 min.[15] Following the same procedure, metal-containing Pcs (M = Zn, Ni, and Co) were prepared successfully in good yields using the appropriate metal acetate.[16–18] All the prepared phthalocyanines were purified easily by re-crystallization from ethanol/DCM (3:1) showing that the reaction proceeded efficiently with fewer by-products. As a result of placing bulky substituents around the Pc ring, all the prepared complexes are highly soluble in common organic solvents (e.g., THF, $CHCl_3$, DCM, and toluene) thereby facilitating spectroscopic characterization and also renders these compounds suitable for making high quality spin-coated films. Spectroscopic analyses of **2–5** were consistent with their expected structure. For example, fast atom bombardment (FAB) mass spectroscopy exhibited the parent ion for **Pc-2** with a cluster of peaks centered at 2433.8 corresponding to that calculated from the molecular formula (Fig. 1). The purity of each material was confirmed by elemental analysis and thin layer chromatography.

It is well known that disc-like macromolecules such as phthalocyanines tend to form aggregates, which can have different characteristics (e.g., optical properties) from the corresponding monomer. UV–Vis and NMR spectroscopic techniques were, therefore, used to investigate the aggregation behavior of the prepared complexes. The ^1H NMR spectrum of **1** displays two singlets for the methyl groups as there are two types of phenoxy groups (*ortho* and *meta* to each nitrile). In comparison to **1**, the Pc complexes surprisingly show four singlets related to the methyl hydrogens (Fig. 2).

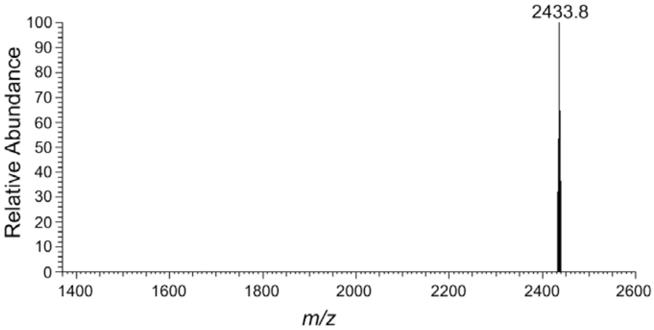

Figure 1. FAB mass spectrum of **Pc-2** with a cluster of peaks centered at 2433.8.

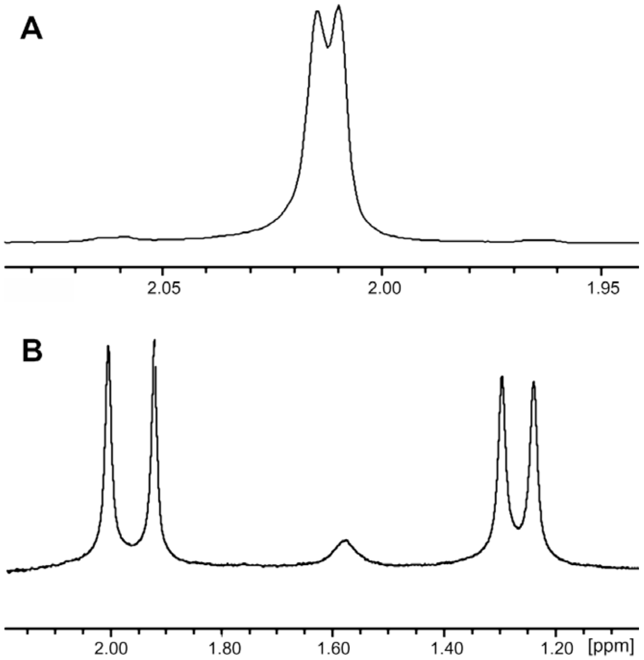

Figure 2. Aliphatic region (methyl groups) of the ^1H NMR spectra of (a) 3,4,5,6-tetrakis(2,6-dimethylphenoxy)phthalonitrile **1**; (b) **Pc-3**, in $CDCl_3$.

This difference can be attributed to greater steric hindrance and the ring current effect induced by Pc ring formation. This indicates that the phenoxy substituents are forced out of the plane of the macrocycle, where they adopt a configuration giving four different methyl hydrogen environments.[19] Due to the deshielding effect caused by the strong ring current of the Pc, the two upfield peaks (1.24 and 1.30 ppm) belong to the methyl aryloxy groups attached to the nonperipheral positions. In contrast, the downfield peaks (1.92 and 2.00 ppm) belong to the peripheral-positioned methyls. Thus, the resulting conformational arrangement adopted by the substituents ensures that cofacial self-association of the Pc cores is prohibited. This is clearly deduced from the ^1H NMR spectra, which show no broadening or resonance shifts over a broad concentration range as evidence of no aggregation.

The aggregation behavior was further assessed by UV–Vis spectroscopy in both solution and solid state as spin-coated films. Usually, aggregation of Pcs is indicated by a hypsochromic shift of the Q-band at 700 nm and its gradual broadening in a hypochromic fashion. As anticipated, the UV–Vis absorption spectra of metal-free Pc **2** along with the metal ion-containing derivatives **3–5** show no evidence of aggregation as shown by the position and the appearance of the intense Q-band. For example, the absorption spectrum of **3** showed a single sharp Q-band at λ_{max} 747 nm, which is typical of nonaggregated species (Fig. 3). In comparison to the

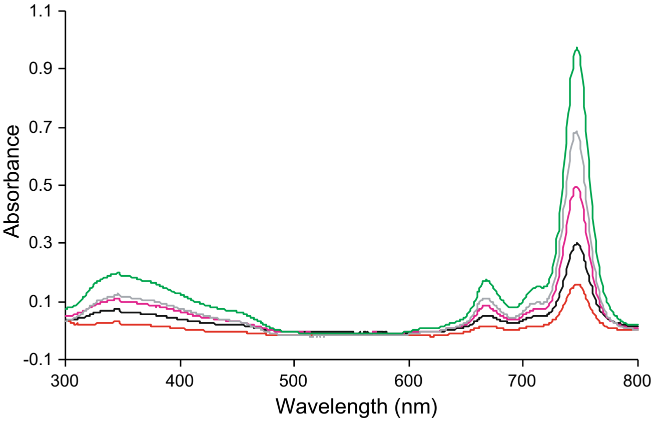

Figure 3. Absorption spectra of **Pc-3** at different concentrations in THF.

reported peripheral octaaryloxy-substituted phthalocyanine,[12] placing additional aryloxy substituents at the nonperipheral sites clearly produces a bathochromic shift of the Q-band absorption maxima of about 65 nm as in the case of **3**. In this study, the aggregation behavior of the complexes **2–5** was examined at different concentrations in THF. As depicted in Figure 3, the appearance of the Q-band absorption maxima remained unchanged as the concentration increases, and its apparent molar extinction coefficient remained almost constant indicating a purely monomeric form, which obeyed the Beer–Lambert Law in the studied concentration range. Thin films of Pcs **2–5** were prepared to further investigate the molecular packing of the Pc compounds in the solid state. Spin-coated films were deposited onto an untreated glass slide from chloroform solution. The UV–Vis spectra of spin-coated films of Pcs **2–5** were identical to those obtained from dilute solution indicating that the Pc chromophore is not perturbed by intermolecular exciton effects even in the solid state. Therefore, consistent with previous reports,[11] severe steric crowding at the Pc core is the most effective factor in reducing cofacial interactions between the Pc cores as was revealed by both UV–Vis and NMR spectroscopy.

Zinc phthalocyanine complexes have attracted much interest due to their high triplet quantum yield and long lifetimes, and hence display attractive properties in the field of nonlinear optical applications.[20] Hence, the nonlinear optical properties of **ZnPc-3** were studied using the Z-Scan technique with a continuous low energy laser regime. The preliminary study showed that the mechanism or the nature of the nonlinear absorption in **3** is dependent on the applied wavelength of the excitation beam. It was found that the complex **3** exhibits reverse saturable excited-state absorption (RSA) at 532 nm. Conversely, the nonlinear behavior changes to saturable absorption (SA) at 632.8 nm, which is close to the Q-band absorption at 747 nm and shows nonlinearity based on the refraction mechanism. The experimental results are shown in Table 1. As evaluated by open aperture Z-scan at 532 nm, the Zn-centered complex **3** exhibited a reduction in the transmission about the focus lens. This is typical of an induced positive nonlinear absorption of the incident laser beam, which is attributed to RSA. However, the negative nonlinear refraction sign from a closed aperture and SA type behavior from an open aperture by using continuous wave (cw) pumping at 632.8 nm confirm that **3** shows optical limiting properties, which are attributed mainly to nonlinear refraction. The large nonlinearity of this molecule probably results due to the strong linear absorption of the Q-band combined with a high thermo-optic coefficient.[21] The estimated values of n_2, β, and $\chi^{(3)}$ are among the highest reported values in the literature for nonlinear material with cw excitation.[22] Furthermore, the low threshold optical limiting (OL) at the two selected wavelengths (Table 1) clearly suggests that this robust complex **3** is characterized by large nonlinearity, and could be a potential candidate for optical limiting applications in the low cw region.

Table 1
Nonlinear parameters of **ZnPc-3** in toluene

Wavelength (nm)	$\Delta\Phi$ (rad)	β (cm/W)	Optical limiting threshold (kW/cm^2)
632.8	0.85	-2.8×10^{-2}	0.16
532	0.9	1.6×10^{-3}	0.90

To conclude, it is possible to prepare Pc derivatives derived from severely crowded phthalonitrile with four bulky phenoxyl susbtituents by microwave-mediated reaction. NMR and UV–Vis studies clearly show that the position adopted by the substituents relative to the Pc ring is the most important factor influencing the molecular packing of Pcs in the solid state and leading to materials with intrinsically true-solid solution properties. The nonaggregation behavior, high solubility and red-shifted Q-band make such new chromophore materials attractive candidates in applications such as PDT as photosensitizers, optoelectronic and near-IR devices. Furthermore, the large optical limiting parameter of **ZnPc-3** may lead to a nonlinear media for several optical applications, and further investigation is in progress to explore this phenomenon.

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14. *3,4,5,6-Tetrakis(2,6-dimethylphenoxy)phthalonitrile* (**1**): To a stirred solution of 3,4,5,6-tetrafluorophthalonitrile (1.0 g, 5 mmol) and 2,6-dimethylphenol (3.05 g, 25 mmol) in dry DMF (50 ml), anhydrous potassium carbonate (5.17 g, 37.4 mmol) was added. The mixture was heated for 72 h at 120 °C under a nitrogen atmosphere. After cooling, the mixture was poured into acidified water (200 ml). The resulting precipitate was collected and recrystallized from methanol to yield the product as yellow crystals (50%); mp 215 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.01 (s, 12H, CH_3); 2.02 (s, 12H, CH_3); 7.01 (d, 8H, J = 7.2 Hz); 7.07 (t, 4H, J = 6 Hz). MS (EI): m/z 608 [M$^+$]. Anal. Calcd for $C_{40}H_{36}N_2O_4$: C, 78.92; H, 5.96; N, 4.60. Found: C, 78.50; H, 5.83; N, 4.54.
15. *1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecakis(2,6-dimethylphenoxy)phthalocyanine* (**2**): 3,4,5,6-tetrakis(2,6-dimethylphenoxy)- phthalonitrile **1** (200 mg; 3.285×10^{-4} mol), hydroquinone (4 mg), and dry 1-hexanol (1 ml) were placed in a 10-ml microwave vessel and sealed. This mixture was irradiated at 350 W in a microwave (Single Mode Cavity Explorer Microwave Synthesizer-CEM Corporation, NC, USA) for 10 min at 160 °C with stirring. After cooling, the reaction mixture was precipitated from methanol. The crude product was collected, recrystallized from ethanol/dichloromethane (3:1), and dried under vacuum to yield **2** as a light green solid (9%); mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, 48H, CH_3), 1.97 (s, 48H, CH_3), 6.57 (d, 32H

J = 4 Hz,), 6.64 (t, 16H *J* = 7.0). UV–Vis (THF): λ_{max} (ε): 757 (2.28×10^5 M^{-1} cm^{-1}) and 776.00 (2.59×10^5 M^{-1} cm^{-1}). MS (FAB) *m/z*: 2435. Anal. Calcd for $C_{160}H_{146}N_8O_{16}$: C, 78.88; H, 5.99; N, 4.60. Found: C, 78.50; H, 5.82; N, 4.76.

16. *1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecakis(2,6-dimethylphenoxy)phthalocyaninatozinc(II)* (**3**): 3,4,5,6-tetrakis(2,6-dimethylphenoxy)phthalonitrile **1** (200 mg; 3.285×10^{-4} mol) and anhydrous zinc(II) acetate (60 mg) were placed in a 10-ml microwave vessel. After the addition of dry 1-hexanol (1.0 mL) and DBU (10 drops), the vessel was sealed and irradiated in a microwave oven (350 W) for 10 min at 160 °C with stirring. After cooling, the reaction mixture was precipitated from methanol. The crude product was recrystallized from ethanol/dichloromethane (3:1) and dried under vacuum to yield the product as a light green solid (24%); mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (s, 24H, CH_3); 1.30 (s, 24H, CH_3); 1.92 (s, 24H, CH_3); 2.00 (s, 24H, CH_3); 6.54 (d, 32H, *J* = 7.2 Hz); 6.62 (t, 16H, *J* = 7.2 Hz). UV–Vis (THF): λ_{max} (ε): 747 (3.06×10^5 M^{-1} cm^{-1}). MS (FAB) *m/z*: 2497 [M$^+$]. Anal. Calcd for $C_{160}H_{144}N_8O_{16}Zn$: C, 76.88; H, 5.76; N, 4.48. Found: C, 77.22; H, 6.05; N, 4.59. The following **Pcs** (**4** and **5**) were prepared from **1** using a similar procedure to that adopted for **Pc 3**.
17. *1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecakis(2,6-dimethylphenoxy)phthalocyaninatocobalt(II)* (**4**): Yield 18%; mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 48H, CH_3), 1.34 (s, 48H, CH_3), 7.55 (s, 32H), 7.73 (s, 16H). UV–Vis (THF): λ_{max} (ε): 738 (1.32×10^5 M^{-1} cm^{-1}) MS (FAB): *m/z* 2492 [M$^+$]. Anal. Calcd for $C_{160}H_{144}N_8O_{16}Co$: C, 77.07; H, 5.78; N, 4.49. Found: C, 77.22; H, 6.04; N, 4.59.
18. *1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-Hexadecakis(2,6-dimethylphenoxy)phthalocyaninatonickel(II)* (**5**): Yield 19 %; mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (s, 48H, CH_3), 1.94 (s, 48H, CH_3), 6.54 (d, 32H, *J* = 7.0 Hz); 6.62 (t, 16H, *J* = 7.8 Hz). UV–Vis (THF): λ_{max} (ε): 749 (1.40×10^5 M^{-1} cm^{-1}) MS (FAB):*m/z* 2490 [M$^+$]. Anal. Calcd for $C_{160}H_{144}N_8O_{16}Ni$: C, 77.08; H, 5.78; N, 4.49. Found: C, 76.80; H, 5.76; N, 4.45.
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