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# The synthesis and characterization of zincphthalocyanines bearing functionalized bulky phenoxy substituents

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ABSTRACT

The synthesis and characterization of zincphthalocyanine derivatives bearing functionalised bulky phenoxy substituents are described. Target precursors were prepared using a nucleophilic aromatic substitution reaction between 4,5-dichloropthalonitrile and 2,6-di-*iso*-propylphenol containing either H, Br, CN or $NHCOCH_3$ at the *p*-position in an effort to tune both molecular and material properties. UV–vis and NMR analyses revealed that steric interactions between the bulky *iso*-propyl groups on adjacent phenoxy units effectively discouraged cofacial aggregation even in the solid state. This study explores the effectiveness of sterically hindered phenols situated at eight peripheral positions in improving some photo-physical properties.



## 1. Introduction

The synthesis, application and coordination chemistry of phthalocyanine (Pc) derivatives have been the subject of intensive studies over many decades [1]. In addition to their use as commercial dyes and coloring agents, Pcs are of increasing interest for different applications mainly in the field of nonlinear optics [2], xerography [3], solar energy conversion [4], liquid crystalline charge carriers [5], catalysis [6], colorants [7] and photodynamic therapy (PDT) [8]. For most of these applications, the organization of molecular components within the bulk material is required to enhance the photo-physical and opto(electronic) properties which can maximize their potential utility. For example, the self-association behavior of Pcs leads to excited state quenching and thus reducing both fluorescence and singlet oxygen formation which represent the primary role in PDT [9]. For NLO materials, such behavior usually brings up undesirable effects by reducing the effective nonlinear absorption. This has led to a growing interest in designing non-aggregated Pcs and controlling the nanoscale architecture of these macrocycles tailored to the intended applications in the field of PDT, NLO and other related applications. Many synthetic approaches have been attempted to prohibit the aggregation of Pc macrocycles but it involved more elaborate and laborious synthetic effort [10]. The most effective strategy to avoid cofacial self-association involves the use of bulky substituents, which can induce severe steric crowding adjacent to the phthalocyanine core [11]. Hence, we describe the synthesis of Pc derivatives 2,3,9,10,16,17,23,24-octa(2′,6′-di-*iso*-propylphenoxy)phthalocyanine which contain either H, Br, CN or $NHCOCH_3$ at the *p*-position of the phenoxy groups (Scheme 1; **Pc 1**; $M = Zn^{2+}$) to provide an alternative way to fine tune molecular and material properties. Recently we found that placing eight 2,6-di-*iso*-propylphenoxy substituents at the peripheral sites of **Pc** effectively prohibit cofacial association of Pc cores due to their orthogonal orientation relative to the plane of the macrocycle, which is rigidly enforced by the steric bulk of the *iso*-propyl groups [12]. This approach gave highly soluble and non-aggregated Pc derivatives in dilute solution as well as in the solid state. Zincphthalocyanine complexes have received greater attention since it shows beneficial properties in the PDT and some photo-physical applications due to their high molar absorption coefficient ($\varepsilon > 10^5\ M^{-1}\ cm^{-1}$) at the far red end of the visible spectrum, high triplet state quantum yields and long lifetimes [13].

## 2. Experimental

Dry DMF was purchased from Aldrich Co., and potassium carbonate was obtained locally. $^1H$ NMR spectra were recorded using a Bruker DPX 400 and Bruker Avance II 600; IR spectra were recorded on Perkin Elmer System 2000 FTIR. Absorption studies were undertaken on a Varian Cary 5 UV–vis spectrometer. Elemental analyses were carried out using LECO Elemental Analyzer CHNS 932. Mass analyses were obtained using a VG

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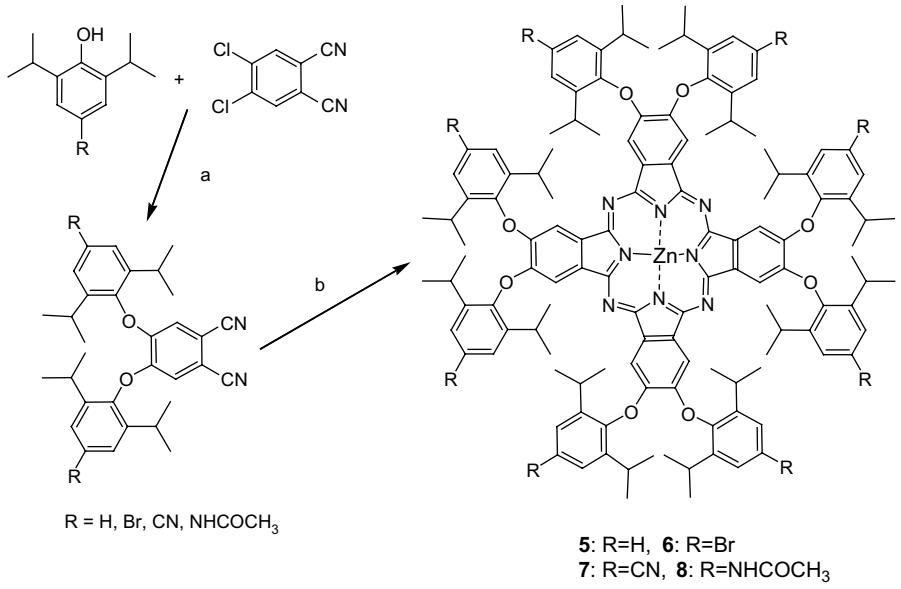


**Scheme 1.** The synthesis of ZnPcs (**5**–**8**). Reagents and conditions: (a) $K_2CO_3$, DMF, 80 °C, 24 h; (b) Metal acetate, quinoline, 180 °C, 6 h.

Autospec-Q. DSC analyses were carried out on Shimadzu DSC-50. MALDI mass spectra were obtained by using a Micro-Mass Tofspec 2E spectrometer. TLC was performed using Polygram sil G/UV 254 TLC plates and visualization was carried out by ultraviolet light at 254 nm and 350 nm. Column chromatography was performed using Merck silica gel 60 of mesh size 0.040–0.063 mm. All solvents were used as either supplied or dried as described in Perrin or Armarego [14].

### 2.1. Synthesis of phthalonitriles

#### 2.1.1. 4,5-Bis-(2,6-di-iso-propylphenoxy)-phthalonitrile (**1**)

To a stirred solution of 4,5-dichlorophthalonitrile (2.00 g, 10.15 mmol) and 2,6-di-*iso*-propylphenol (4.16 g, 23.35 mmol) in dry DMF (150 ml) finely grounded anhydrous potassium carbonate (9.67 g, 70 mmol) was added. The reaction mixture was heated at 80 °C under nitrogen for 24 h. On cooling, the reaction mixture was poured into acidified water. The resulting precipitate was collected by filtration and washed with distilled water, then air-dried. The crude product was then recrystallised from methanol to give a white crystalline solid (3.65 g, 75%). M.p. 181 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C) $\delta$ ppm: 1.18 (d, 12H), 1.26 (d, 12H), 2.96 (sept, 4H), 6.77 (s, 2H), 7.33 (d, 4H), 7.38 (t, 2H). IR (KBr) $\upsilon$/cm$^{-1}$: 2222 (CN); MS (EI): *m*/*z*: (%) 480 (100) $[M]^+$; Anal calc. (%) for $C_{32}H_{36}N_2O_2$: C 79.96, H 7.55, N 5.83; found C 79.30, H 7.80, N 5.94.

Compounds **2**–**4** were prepared from the corresponding phenols using a similar procedure adopted for **1**.

#### 2.1.2. 4,5-Bis-(4-bromo-2,6-di-iso-propylphenoxy)-phthalonitrile (**2**)

Yield 80%; M.p. 236 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C) $\delta$ ppm: 1.18 (d, 12H), 1.24 (d, 12H), 2.89 (sept, 4H), 6.78 (s, 4H), 7.42 (s, 2H). IR (KBr) $\upsilon$/cm$^{-1}$: 2230 (CN). MS (EI): *m*/*z*: (%) 638 (100) $[M]^+$, Anal calc. (%) for $C_{32}H_{34}Br_2N_2O_2$: C 60.20, H 5.37, N 4.39; found C 60.10, H 5.40, N 4.48.

#### 2.1.3. 4,5-Bis-(4-cyano-2,6-di-iso-propylphenoxy)-phthalonitrile (**3**)

Yield 78%; M.p. 265 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C) $\delta$ ppm: 1.23(d, 12H), 1.28 (d, 12H), 2.95 (sept, 4H), 6.74 (s, 4H), 7.64 (s, 2H). IR (KBr) $\upsilon$/cm$^{-1}$: 2232 (CN); MS (EI): *m*/*z*: (%) 530 (100) $[M]^+$, Anal calc. (%) for $C_{34}H_{34}N_4O_2$: C 76.95, H 6.46, N 10.56; found C 76.72, H 6.49, N 10.46.

#### 2.1.4. 4,5-Bis-(4-acetylamino-2,6-di-iso-propylphenoxy)-phthalonitrile (**4**)

Yield 75%; M.p. 245 °C; $^1$H NMR (DMSO, 400 MHz, 25 °C) $\delta$ ppm: 1.11(d, 12H), 1.24 (d, 12H), 2.07 (s, 6H), 2.85 (sept, 4H), 7.09 (s, 4H), 7.59 (s, 2H), 10.64 (s, 2H). IR (KBr) $\upsilon$/cm$^{-1}$: 3303 (NH), 2242 (CN) 1669 (CO), 1554 (NHCO); MS (EI): *m*/*z*: (%) 594 (100) $[M]^+$, Anal calc. (%) for $C_{36}H_{42}N_4O_4$: C 72.7, H 7.12, N 10.76; found C 69.02, H 6.975, N 9.21.

### 2.2. Synthesis of zincphthalocyanines (**5**–**8**)

#### 2.2.1. 2,3,9,10,16,17,23,24-Octa(2,6-di-iso-propylphenoxy) phthalocyaninatozinc(II) (**5**)

A mixture of **1** (1.00 g, 2.1 mmol) and excess of anhydrous zinc acetate (40 mg) in dry quinoline (10 ml) was stirred at 180 °C under nitrogen for 6 h. The reaction mixture was poured into stirred distilled water (200 ml) on cooling, and the solid product was collected by filtration, washed with water and methanol. The crude product was purified by column chromatography on silica (eluent: chloroform) to give a green powder. Yield 15%; M.p. >300 °C; $^1$H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta$ = 1.19 (d, 48H), 1.39 (d, 48H), 3.43 (sept, 16H), 7.48 (d, 16H), 7.59 (t, 8H) 8.16 (s, 8H). IR (KBr) $\upsilon$/cm$^{-1}$: 3063 (ArH); 1630 (C=N); UV–vis (THF); $\lambda_{max}$ nm ($\varepsilon$) = 678 (305000 M$^{-1}$ cm$^{-1}$); MALDI MS: isotropic cluster at *m*/*z*: 1988 $[M]^+$; Anal calc. (%) for $C_{128}H_{144}N_8O_8$ Zn: C 77.26, H 7.24, N 5.63; found C 76.93, H 7.44, N 5.56.

The following ZnPcs (**6**–**8**) were prepared from corresponding phthalonitriles using similar procedure adopted for **5**.

#### 2.2.2. 2,3,9,10,16,17,23,24-Octa(4-bromo-2,6-di-iso-propylphenoxy) phthalocyaninatozinc(II) (**6**)

Yield 20%; M.p. >300 °C; $^1$H NMR (600 MHz, $CDCl_3$, 25 °C) $\delta$ ppm: 1.28 (d, 48H) 1.32 (d, 48H) 3.44 (sept, 16H,), 7.69 (s, 16H), 8.28 (s, 8H); IR (KBr) $\upsilon$/cm$^{-1}$: 1652 (C=N); UV–vis (THF); $\lambda_{max}$ nm ($\varepsilon$) = 679 (315000 M$^{-1}$ cm$^{-1}$); MALDI MS: isotropic cluster at *m*/*z*: 2618 $[M]^+$; Anal calc. (%) for $C_{128}H_{136}Br_8N_8O_8$ Zn requires C 58.67, H 5.20, N 4.27; found C 58.71, H 5.93, N 4.23.

*2.2.3. 2,3,9,10,16,17,23,24-Octa(4-cyano-2,6-di-*iso*-propylphenoxy) phthalocyaninatozinc(II) (**7**)*

Yield 17%; M.p. >300 °C; $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ ppm: 1.25 (d, 48H), 1.39 (d, 48H), 3.42 (sept, 16H), 7.89 (s, 16H), 8.11 (s, 8H); IR (KBr) $\upsilon$/cm$^{-1}$: 1630 (C═N), 2232; (CN); UV–vis (THF); $\lambda_{max}$ nm ($\varepsilon$) = 679 (320000 M$^{-1}$ cm$^{-1}$); MALDI MS: isotropic cluster at *m*/*z*: 2188 [M]$^+$; Anal calc. (%) for $C_{136}H_{136}N_{16}O_8Zn$, requires C 74.66, H 6.27, N 10.24; found: C 74.07, H 6.34, N 10.43.

*2.2.4. 2,3,9,10,16,17,23,24-Octa(4-acetylamino-2,6-di-*iso*-propylphenoxy) phthalocyaninatozinc(II) (**8**)*

Yield 15%; M.p. >300; $^1$H NMR (400 MHz, Pyridine-$d_5$, 25 °C) $\delta$ ppm: 2.73 (d, 48H), 2.92 (d, 48H), 4.14 (s, 24H), 5.27 (sept, 16H), 9.70 (s, 16H) 10.32 (s, 8H), 12.52 (s, 8H). IR(KBr) $\upsilon$/cm$^{-1}$: 3437 (NH) 1667 (C═N), 1555 (NHCO). UV–vis (THF): $\lambda_{max}$ nm ($\varepsilon$) 678 (340000 M$^{-1}$ cm$^{-1}$); MALDI MS: Isotropic cluster at *m*/*z*: 2444 [M]$^{+\cdot}$ Anal calc. (%) for $C_{144}H_{168}N_{16}O_{16}Zn$: C 69.17, H 6.77, N 9.17; found C 68.96, H 7.08, N 9.49.

## 3. Results and discussion

### 3.1. Synthesis

The synthetic route for the target phthalocyanines is given in Scheme 1. The starting materials: 4-bromo, 4-cyano and 4-acetamide substituted phenols were synthesized from commercial available 2,6-di-*iso*-propylphenol in good yield according to the reported procedures [15]. The aromatic nucleophilic substitution reaction ($S_NAr$) between these materials and 4,5-dichlorophthalonitrile produces the required phthalonitriles precursors in 75–80% yield [16]. Zinc-containing Pc derivatives **5**–**8** were prepared readily by metal-ion mediated cyclotetramerisation reaction of corresponding phthalonitriles **1**–**4** in dry quinoline using anhydrous zinc acetate. Column chromatography was employed using chloroform as eluent to obtain the appropriate ZnPcs in good isolated yield (15–20%) from the reaction mixtures. The intense green colored complexes **5**–**7** are highly soluble in most organic solvents such as dichloromethane, chloroform, tetrahydrofuran, ethylacetate and toluene at room temperature, whereas **8** is only sparingly soluble. Furthermore, these complexes were found to be soluble in hot methanol and acetone. The structure and purities of ZnPc derivatives **5**–**8** were confirmed by $^1$H NMR spectroscopy, elemental analysis and UV–vis absorption spectroscopy. In addition, clusters of peaks, that correspond to the calculated isotope composition of the molecular ion were confirmed by matrix assisted laser desorption ionization mass spectroscopy (MALDI MS). A simple $^1$H NMR spectrum was obtained for each ZnPc complexes **5**–**7** under ordinary conditions ($CDCl_3$ and room temperature). They all exhibit well-resolved spectra with sharp peaks in both aromatic and aliphatic region implying that the aggregation behavior is totally absent. In addition, the high quality NMR spectrum was independent of concentration and remained unchanged with well-resolved peaks event at high concentration. Such behavior can be clearly attributed to steric hindrance imposed by the peripheral bulky phenoxy substituents that lie almost perpendicular to the plane of the Pc core and consequently prevent the efficient $\pi$–$\pi$ stacking of the macrocycle units [17]. This conformation of the phenoxy groups in the derived Pcs **5**–**8** has been clearly shown by the $^1$H NMR spectrum which shows two environment for the methyl hydrogens of the *iso*-propyl groups. For example, $^1$H NMR spectrum of **5** clearly shows two environments for the *iso*-propyl methyl groups [$\delta$ = 1.19 (d) and 1.39 (d) ppm], which can be ascribed to the frozen rotation about the aryl-oxygen bonds [18] on the NMR time-scale as shown in Fig. 1. Thermal stability of the products are confirmed by thermo gravimetric analysis where the decomposition occurs above 300 °C as well as these complexes show good stability under atmosphere and daylight either in solution or within solid state.

### 3.2. Absorption spectra and aggregation behavior

Tuning the photo-physical properties of Pcs by controlling the degree of molecular self-association is essential for many optical applications. The UV–vis spectroscopy is a very useful technique which can be used to study the aggregation phenomena of phthalocyanines in both solution and solid state. The extent and the nature of the molecular packing can also be deduced from the interpretation of UV–vis absorption spectra (Q-bands). As anticipated, the Zinc-containing derivatives **5**–**8** show no evidence of aggregation in solution as demonstrated by the sharp unperturbed single Q-band, typical of metallated phthalocyanine complexes with $D_{4h}$ symmetry (Table 1). For example, the absorption spectrum of **5** showed a single sharp Q-band at $\lambda_{max}$ = 676 nm which is typical of non-aggregated species as evaluated from its position and shape (Fig. 2). The concentration dependence of the UV–vis spectra of these derivatives was further assessed in order to prove the absence of aggregation (Fig. 3). It has been found that these complexes exhibited

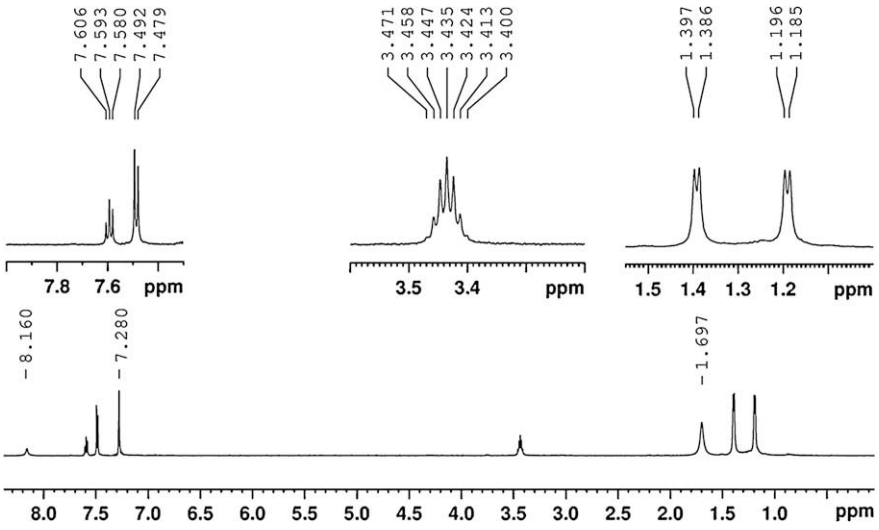


**Fig. 1.** $^1$H NMR spectrum of ZnPc (**5**) in $CDCl_3$, which shows two environments for the methyl hydrogens of the *iso*-propyl groups.

**Table 1**
A comparison of the Q-band position (nm) in the UV–vis absorption spectral data of ZnPcs in solution with that of the spin-coated film.

| Pc | $\lambda_{max,\ nm}$ (THF) | $\lambda_{max,\ nm}$ (film) | Q-band shift | $\varepsilon \times 10^5$ [1/M cm] (THF) |
|---|---|---|---|---|
| ZnPc-5 | 676 | 677 | 1 | 3.03 |
| ZnPc-6 | 676 | 677 | 1 | 3.05 |
| ZnPc-7 | 676 | 677 | 1 | 3.68 |
| ZnPc-8 | 676 | 678 | 2 | 3.66 |

a monomeric form (i.e. no new blue-shifted band due to aggregation) as deduced from the recorded absorption spectra in different concentrations. In Fig. 3, the appearance of the Q-band absorption maxima (i.e. shape and position) of **8** at 676 nm remained unchanged as the concentration increases. Its apparent molar extinction coefficient remains almost constant indicating a pure monomeric form, which obeys the Beer–Lambert law in the outlined range of concentration. The molar extinction coefficients of the Pcs (**5**–**8**) are enlisted in Table 1. These values are higher than the literature value for the ZnPc in pyridine ($\varepsilon_{674\ nm} = 2.818 \times 10^5\ M^{-1}\ cm^{-1}$) [19]. The large molar extinction coefficient values can be effectively correlated with more efficient light penetration and subsequently more effective in therapeutic applications (PDT) [20]. Finally, it is worth noting that the introduction of a substituent at the *p*-position of the phenoxy groups, cannot cause any significant shift of the Q-band absorption maxima. However these substituents could be effectively used to enhance solubility in water by hydrolyzing carbonitrile into carboxylic group. In addition, some properties can also be modified or enhanced by extending the molecular architecture through coupling some interesting moieties (by Suzuki coupling).

### 3.3. Solid state properties

Thin films were prepared in order to investigate the molecular packing of the Pcs in the solid state. For that spin-coated films derived from ZnPc derivatives (**5**–**8**) were deposited onto untreated glass microscope slides from chloroform solution. The prepared spin-coated films gave a uniform appearance and optically clear films. The position and appearance of the Q-band absorption of spin-coated films derived from **5** to **8** were identical to those obtained from dilute solution indicating that the phthalocyanine units are present in the isolated form in the solid state. For example, the UV–vis absorption spectrum of the film derived from **5** is almost identical to its solution spectrum (Fig. 2) with only slight broadening of the Q-band (only 0.2 nm difference in the width at the half peak height). This also proves that the intrinsic conformation adapted by the eight peripheral bulky groups efficiently suppresses the cofacial interactions between the Pc cores. It can be

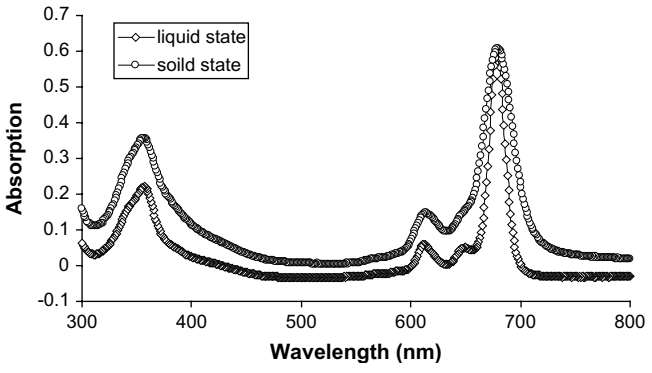


**Fig. 2.** UV–vis absorption spectrum of ZnPc (**7**) (–◇–) in Chloroform and (–○–) from a solvent cast film.

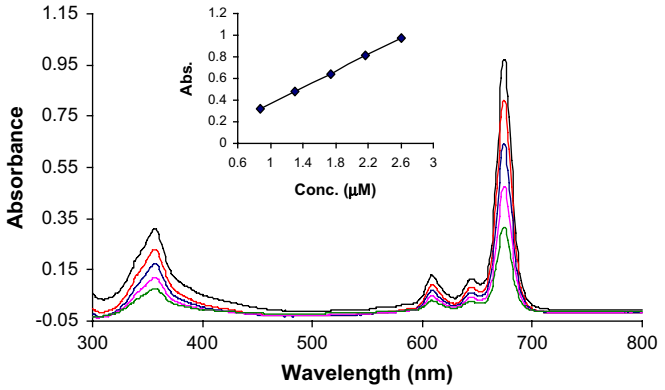


**Fig. 3.** UV–vis absorption spectrum of ZnPc (**8**) at different concentrations in THF solution.

considered as the most efficient strategy to induce the isolated arrangement of Pcs even in the solid state as revealed by UV–vis spectroscopy and NMR analyses.

## 4. Conclusion

We have successfully synthesized the zinc-containing phthalocyanines bearing peripheral bulky phenoxy groups decorated with different substituents at its *p*-position. The spectroscopic characterization results (UV–vis and NMR technique) have shown that the aggregation behavior can be greatly modified by placing bulky substituents at the Pc core which effectively enforce cofacial isolation and the attainment of intrinsically true solid solution. More over functionalisation of phenoxy substituents with different groups shows no significant changes in absorption and aggregation behavior of the ZnPcs. Studies to examine the nonlinear optical (NLO) and optical limiting properties of these materials are in progress.

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