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Synthesis and characterization of non-aggregating octa-substituted azaphthalocyanines bearing bulky phenoxy substituents

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ABSTRACT

The synthesis and characterization of two novel series of octaazaphthalocyanines (AzaPc) bearing bulky phenoxy substituents are described. Target precursors to AzaPcs derivatives were prepared by using a nucleophilic aromatic substitution reaction between sterically hindered phenols (2,6-di-*iso*-propylphenol and 2,6-diphenylphenol) and 5,6-dichloropyrazine-2,3-dicarbonitrile. UV–vis and ^{1}H NMR analyses confirm that steric isolation of the AzaPcs cores enforced both in the solution and in the solid state. This study explores the effectiveness of the steric factor imposed by the applied bulky phenoxy substituents on the packing behaviour of azaphthalocyanines and thereby improving their solubility and photo-physical properties.

1. Introduction

Octaazaphthalocyanines (AzaPc), often termed tetrapyrazinoporphyrazine in the literature, are analogues of Pc in which eight nitrogen atoms occupying 1,4,8,11,15,18,22,25-positions of the four fused benzo-substituents of the phthalocyanine and possess significantly different physical properties including colour, oxidation and stability, which may be beneficial for the intended applications.[1] As a part of phthalocyanines analogous modification to tune molecular and materials properties, tetrapyrazinoporphyrazine was firstly reported by Linstead et al.[2] These macrocycles exhibit high chemical and thermal stabilities and their intense optical absorption properties (i.e., high extinction coefficient) have led to many applications in material science. For example, octaazaphthalocyanine (AzaPc) and its substituted derivatives have been investigated for potential use in photodynamic therapy,[3] nonlinear optics,[4] liquid crystals,[5] catalysis,[6] colourants[7] and as a red fluorophore.[8] Due to the large planar π-conjugated systems, AzaPc tends to form aggregates, which result in poor solubility and difficulties with purification and characterization. The aggregations result in broadening along with a bathochromic shift of the principal Q-band absorption in the visible region of the spectrum.[9] An additional consequence of self-association is the quenching of the photochemically excited state of AzaPc, thus reducing both fluorescence and singlet oxygen generation, which is considered as its primary role in photodynamic therapy (PDT).[10] Moreover, such behaviour reduces the life time of the excited state and hence may lead to negative non-linear optical and optical limiting responses.[11] Therefore, controlling the nanoscale architecture and ordering these macrocycles in the condensed state is crucial to incorporate the Pc analogues (e.g., AzaPc) into devices and represent an area of research with great potential applications in material science.[12] Inducing AzaPc units isolation in both solution and solid state is essentially required[13] in order to exploit the properties arising from both the extended conjugated system and the presence of the eight nitrogen heteroatoms, which may results in significant modulation of their physical and electronic properties.[14] Several synthetic approaches have been attempted for both phthalocyanine[15] and azaphthalocyanines[10,13] macromolecules to reduce aggregation phenomena in order to retrieve and enhance their optical properties (colour, aggregation, optical absorption, etc.) tailored to the required optical application. Recently, we found that one of the most effective strategy and less laborious synthetic effort is that the introduction of bulky phenoxy substituents on the peripheral position prohibit close self-association of the phthalocyanine macrocycle even within solid thin films and can result in the formation of a remarkable nanoporous cubic crystal.[16] Therefore, we applied this successful methodology to prepare novel substituted AzaPcs by using sterically hindered phenol substituents.

The aim of the present work was to investigate the synthesis and properties of a series of azaphthalocyanine derivatives functionalized with eight peripheral 2,6-di-*iso*-propylphenoxy or 2,6-diphenylphenoxy substituents. The steric factor effect exerted by the bulky substituents in reducing the self-association of AzaPc cores was explored by using ^{1}H NMR and UV–vis techniques. In addition, the surprisingly novel and fairly good yielding procedure of making metal-free phenoxy AzaPc derivatives without using strong base-catalyzed reaction (e.g., lithium pentoxide) is reported here.

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2. Results and discussion

2.1. Synthesis

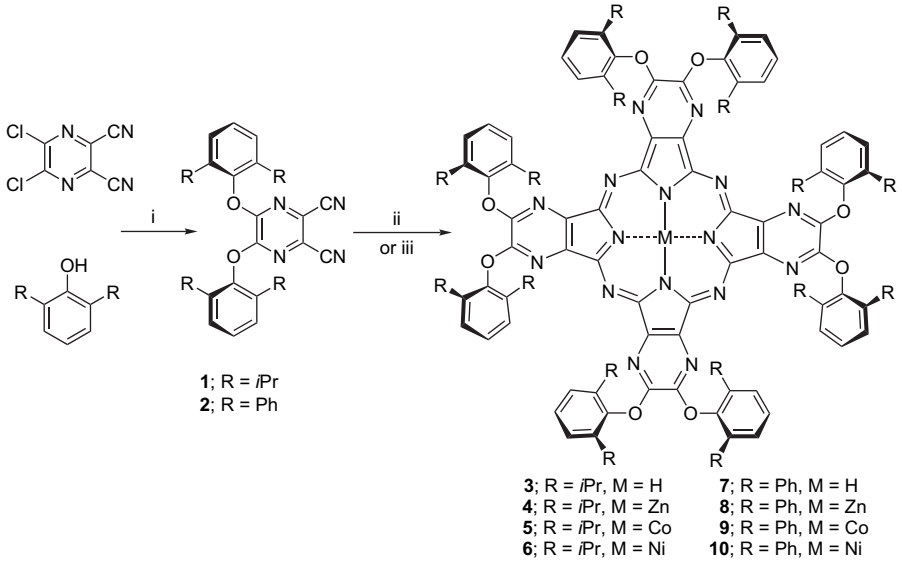
The starting material, 5,6-dichloro-pyrazine-2,3-dicarbonitrile, was synthesized from commercially available materials in a two-step reaction according to the reported procedure.[17] Our recent strategy[16] to avoid cofacial self-association seems to be a highly active route to prepare the newly targeted AzaPc derivatives. Scheme 1 shows the synthesis of octa-phenoxy substituted AzaPcs. The pyrazine-2,3-dicarbonitrile precursors **1** and **2** were prepared in good yield from the aromatic nucleophilic substitution reaction between 5,6-dichloro-pyrazine-2,3-dicarbonitrile and the anion of the sterically hindered phenols (2,6-di-*iso*-propylphenol or 2,6-diphenylphenol).[18] Spectroscopic analyses of **1** and **2** were consistent with their expected structure. Each compound gave a satisfactory elemental analysis and the IR spectrum shows an intense band at the range of 2246–2263 cm^{-1} corresponding to the CN groups.

All the attempted cyclotetramerisations of pyrazine-2,3-dicarbonitrile precursors **1** and **2** in pentanol with lithium pentoxide, the most widely used procedure,[19] failed to give the intended metal-free AzaPc derivatives **3** and, **7** due to the side chain displacement reactions (transetherifications) as reported in the literature.[20] ^{1}H NMR analysis of the crude reaction mixture clearly confirms the displacement of the phenoxy substituents by the alkyloxide anion initiator. The use of a hindered base such as 1,8-diazabicycloundec-7-ene (DBU) in conjunction with pentanol as a base-catalyzed reaction also gave undesired transetherification.[21] This problem, which was associated with the preparation of metal-free alkyloxy–AzaPc derivatives encountered by Mørkved[22] and still considered as an obstacle in preparation of many alkyloxy and phenoxy substituted AzaPc derivatives. With respect to the above-mentioned reports, the metal-free AzaPc derivatives **3** and **7** were surprisingly prepared in a fairly good yield (30–40%) by successful cyclotetramerisation of **1** and **2** precursors in quinoline at 160 °C prior to the addition of the metal salt (e.g., zinc acetate), a routinely used procedure to prepare the metallated derivative.[23] This could be attributed to the presence of the more electronegative nitrogen atoms in the pyrazine moieties, which successfully promote the macrocycle-forming reaction without using a base as an initiator.[24] Spectroscopic analyses of **3** and, **7** were consistent with their proposed structures and confirm a complete retention of the phenoxy substituents. The high solubility in most of the organic solvents (CH_2Cl_2, THF, hexane and partially in acetone) and the non-aggregating tendency of **3** and **7**, induced by the presence of bulky phenoxy substituents, facilitated an efficient chromatographic purification and this may explain the better yield in comparison with the reported corresponding AzaPc derivatives.

The synthesis of metal AzaPc derivatives **4**–**6**; **8**–**10** is successfully achieved by metal ion template cyclotetramerisation of pyrazine-2,3-dicarbonitrile precursors **1** and **2** in dry quinoline using anhydrous zinc acetate, cobalt acetate or nickel acetate. Column chromatography was employed using chloroform as eluent to obtain the appropriate metallated AzaPcs in good isolated yield (50–55%). All the metallated AzaPcs derivatives show simple ^{1}H NMR spectra due their high symmetry. Other characterization techniques such as UV–vis, IR, elemental analysis and MALDI gave results consistent with the proposed structures for all the prepared metallated derivatives. The thermal stability of all the prepared AzaPc products is confirmed by thermo gravimetric analysis where the decomposition occurs above 300 °C as well as these compounds show good stability under atmosphere and daylight either in solution or within solid state.

2.2. NMR investigations

Based on our previous work,[16] X-ray and ^{1}H NMR analyses of 4,5-di(2,6-di-*iso*-propylphenoxy)phthalonitrile and the corresponding zinc phthalocyanine (ZnPc) proved that the phenyl rings bearing two isopropyl groups are forced to lie out of the plane of the benzene-containing dicarbonitriles due to the steric hindrance exerted by the presence of two isopropyl groups. This conformation was clearly deduced by the ^{1}H NMR spectrum, which shows two environments for isopropyl methyl groups (δ=1.18 (d) and 1.26 (d) ppm), which can be ascribed to the frozen rotation about the aryl-oxygen bonds on the NMR time-scale as shown in Figure 1. However, the NMR spectrum of 5,6-bis(2,6-di-*iso*-propylphenoxy)-pyrazine-2,3-dicarbonitrile **1** shows only one doublet peak belonging to the methyl groups indicating that the NMR time-scale rotation around the ether linkage is allowed or fast enough to be detected at room temperature (Fig. 1). This may be attributed to the absence of a hydrogen atom (in case of pyrazine-2,3-dicarbonitrile **1**) in the non-peripheral benzo-positions, which clearly exert an



Scheme 1. Synthesis of azaphthalocyanine derivatives. Reagents and conditions: (i) anhydrous K_2CO_3, 50–70 °C; (ii) quinoline, 160 °C; (iii) appropriate anhydrous metal salt, quinoline, 160 °C.

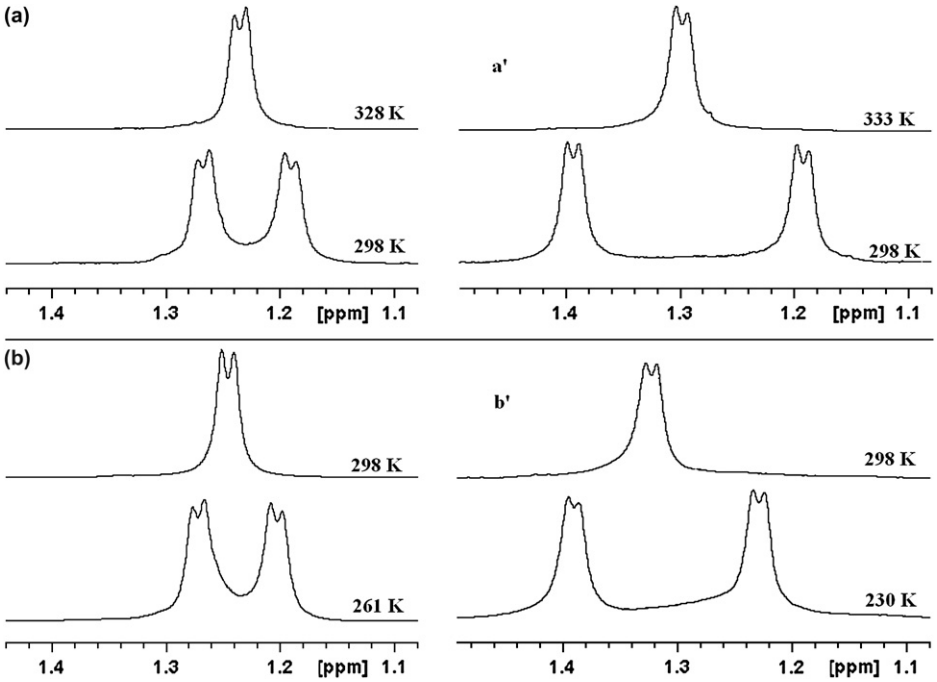


Figure 1. Aliphatic region (methyl groups of the diisopropyl units) of the ^{1}H NMR spectra of (a) 4,5-bis(2,6-di-*iso*-propylphenoxy)phthalonitrile, (a′) ZnPc; (b) 5,6-bis (2,6-di-*iso*-propylphenoxy)pyrazine-2,3-dicarbonitrile, (b′) AzaPc **4** at different temperatures in $CDCl_3$.

additional steric hindrance in case of the phthalonitrile and hence prevent rotation around the aryl ether. Therefore, tracing the energy barrier of rotation around the aryl ether linkage for both phthalonitrile and **1** was investigated using the NMR technique at different temperatures (Table 1). In case of the phthalonitrile, the two environmental doublet peaks merge into one doublet peak at 318 K indicating more freedom of rotation for the methyl groups interchange within the NMR time-scale. When the temperature is reduced up to 248 K, **1** shows two environmental doublets as a result of frozen rotation around the aryl ether linkage. In comparison to the starting precursor **1**, AzaPc **3** shows similarly one doublet peak related to the methyl hydrogens of the isopropyl groups and can be separated into two environmental doublet peaks by reducing the temperature up to 255 K (Fig. 1). However, the incorporation of the bulky phenoxy groups is still highly efficient to prevent self-association and produce highly soluble AzaPc-based materials.

Common features of the ^{1}H NMR spectra of Pcs and other disc-like molecules such as AzaPcs are proton peak broadening, an internal proton chemical shift for metal-free complexes and an upfield shift of the aromatic resonance due to the efficient cofacial stacks (π–π cofacial interaction) interaction.[25] Thus, getting a fairly good NMR spectrum can be obtained by running the NMR experiment either at high temperature (e.g., C_6D_6, 60 °C) or using deuterated pyridine solvent to overcome the aggregation as in case of metallated complexes. Subsequently, the NMR technique can be used as a sensitive probe for this phenomenon (a signature of aggregation) in this study to evaluate the self-association behaviour of the prepared complexes and support the results revealed by the UV–vis analysis.

Table 1
Activation energy calculations of 5,6-bis(2,6-di-*iso*-propylphenoxy)pyrazine-2,3-dicarbonitrile [AzaPn (**1**)] and their corresponding metal and metal-free azaphthalocyanines [AzaPc (**3**–**6**)] in comparison with the 4,5-di(2,6-di-*iso*-propylphenoxy)phthalonitrile (Pn) and the zinc phthalocyanine (ZnPc)

Materials	T_c (K)	$\Delta\nu$ (Hz)	ΔG^* (kJ/mole)
Pn	318	45.9	68.04684
ZnPc	303	120.6	62.27790
AzaPn (**1**)	300	41.4	64.30733
AzaPc (**3**)	268	96.6	55.30536
AzaPc (**4**)	268	127.8	54.68077
AzaPc (**5**)	263	144.6	53.34889
AzaPc (**6**)	271	113.4	55.58775

The aggregation behaviour of the prepared complexes (**3**–**10**) in the concentration ranging from 10^{-2} to 10^{-3} M at room temperature was, therefore, investigated.[26] As expected, ^{1}H NMR spectra of **3**–**10** complexes gave well-resolved spectra with sharp peaks in both aromatic and aliphatic regions. The chemical shifts of both aromatic and aliphatic protons are essentially independent of concentrations and the quality of the spectra remained unchanged with well-resolved peaks even at high concentration. In addition, the spectra of both starting precursors **1** and **2** and their products **3**–**10** are almost identical and show exactly the same excellent quality spectra apart from the chemical shifts resulting from the ring current effect of the aromatic macrocycle, which causes the observed deshielding effects. As outlined in Figure 2, the ^{1}H NMR spectra of AzaPc **6** running at various concentrations show clearly the same quality with a well-resolved spectra in which the aromatic protons appear as a doublet at 7.44 ppm and triplet at 7.58 ppm and the aliphatic region as septet at 3.3 ppm and doublet at 1.31 ppm. Furthermore, the metal-free AzaPcs **3** and **7** show a well-resolved ^{1}H NMR spectrum in which the inner core protons exhibited no chemical shift at different concentrations.[26] Such behaviour can be attributed to steric hindrance imposed by the bulky phenoxy substituents that successfully prevent efficient π–π stacking of the macrocycle units.

2.3. Self-association study

It is well known that the self-association of phthalocyanines and their heteroaromatic analogues (e.g., AzPcs) is apparent even in dilute solution in which the macrocycle molecules tend to form dimers, trimers and higher oligomers.[22] These aggregates can be found in four different arrangements (cofacial, herringbone,

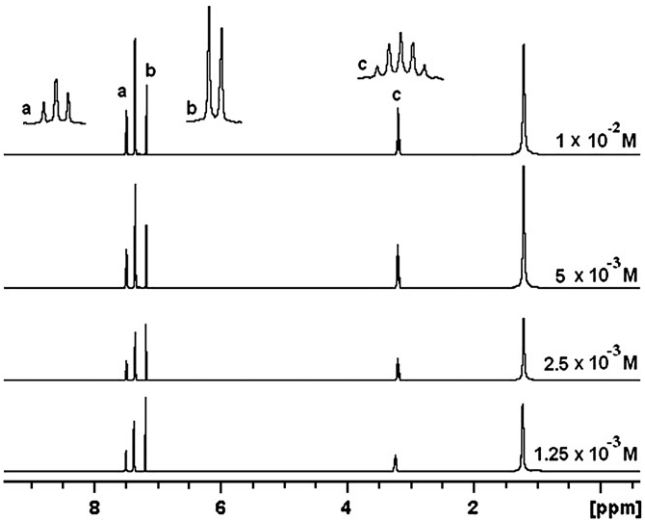


Figure 2. ^{1}H NMR spectrum of AzaPc **6** at different concentrations in $CDCl_3$.

edge-to-edge and isolated) each of which display a characteristic visible absorption spectrum determined by the nature and extent of the interaction exciton coupling between the aromatic cores of neighbouring macrocycle molecules.[27] This aggregation behaviour can considerably affect their properties and limit their uses in many optical and electronic applications.[28,29] UV–vis spectroscopy[30] is a very useful technique that has been used to study the aggregation phenomena in solutions or within the solid state as spin-coated films. The extent and the nature of molecular packing can be deduced from the interpretation of the UV–vis absorption spectra (Q-bands) because the aggregate species can have different optical properties from the monomer.[31] Here, the concentration dependence of the UV–vis spectra and the film forming properties of all the prepared materials will be assessed and reviewed to examine the aggregation behaviour.

The UV–vis absorption spectra of the metal-free azaphthalocyanines **3** and **7** (Table 2) exhibit the split Q-band with two peaks of comparable intensity accompanied by the typical vibrational satellite band on the blue side, suggesting a D_{2h} symmetry for the azaphthalocyanine core due to the consequent loss of degeneracy of LUMO orbital producing Q_y and Q_x states. The characteristic Q-band has been efficiently used as a probe in assessing the self-assembly features of azaphthalocyanine in solution. As expected, the spectra show no evidence of aggregation in solution using different organic solvents (CH_2Cl_2, $CHCl_3$, THF and DMF) as demonstrated by sharp unperturbed Q-band peaks at 606 nm and 645 nm for **3** and 611 nm and 651 nm for **7** (Table 2).[32] Similarly, all the metal ion containing AzaPc derivatives (**4**–**6** and **8**–**10**; M=Zn^{2+}, Co^{2+}, Ni^{2+}) show spectroscopic evidence that the self-associations between the AzaPc cores in solution are totally absent from the monomeric character of the exhibited single Q-band, which belong to D_{4h} symmetry (Table 2). For example, the absorption spectrum of

Table 2
A comparison of the Q-band position (nm) in the UV–vis absorption spectral data of AzaPcs **3**–**10** in THF with that of the spin-coated film

AzaPc	λ_{max} (Q_x, Q_y)	Colour	$(Q_x+Q_y)/2$	λ_{max} (film)	Q-band shift	ΔW (nm)
3	607, 645	Green	626	606, 644	−1	1
4	624	Green	—	624	0	0.2
5	606	Blue	—	605	−1	0.5
6	615	Blue	—	613	−2	1
7	611, 651	Green	631	611, 651	0	1
8	626	Green	—	625	−1	0
9	608	Blue	—	605	−3	0.1
10	619	Blue	—	617	−2	0.8

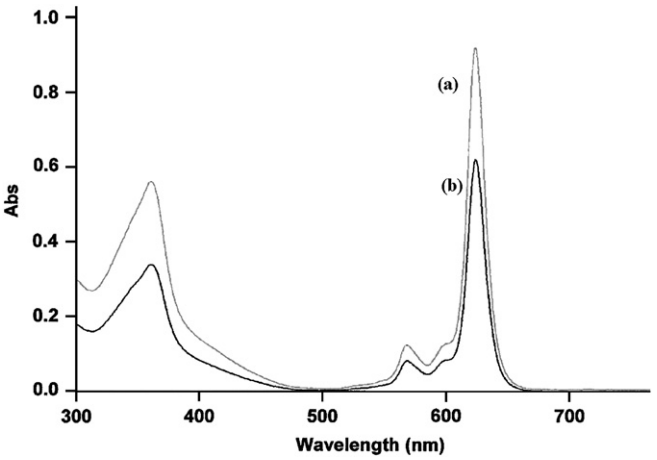


Figure 3. UV–vis absorption spectrum of AzaPc **4** in THF solution (c=1.2×10^{-5} M) and (b) from a solvent cast film.

4 showed a single sharp Q-band at λ_{max}=624 nm, which is typical of non-aggregated species as evaluated from its position and shape (Fig. 3).

Further assessment for all the prepared azaphthalocyanine compounds **3**–**10** has been done by recording the absorption spectra in different concentrations ranging from 10^{-6} to 10^{-5} M. It has been found that there were no spectral changes as the concentration increases and these complex species exhibited spectral of monomeric AzaPcs (i.e., no new blue-shifted band due to aggregation). All of these complexes obeyed the Beer–Lambert law in the outlined range of concentration as the concentration was directly proportional to the intensity of the Q-band. Moreover, the molar absorption coefficient of these complexes was measured within an even higher concentration range but was still independent of concentration and their coefficient values remained almost constant. As depicted in Figure 4, the appearance of the Q-band absorption maxima (i.e., shape and position) of **10** at 619 nm, for example, remained unchanged as the concentration increased. Furthermore, its apparent molar extinction coefficient remained almost constant indicating a purely monomeric form, which makes these materials having fascinating optical properties and might be beneficial for some applications (e.g., non-linear optics). The Ni-containing derivatives **6** and **10** show, in addition to the intense

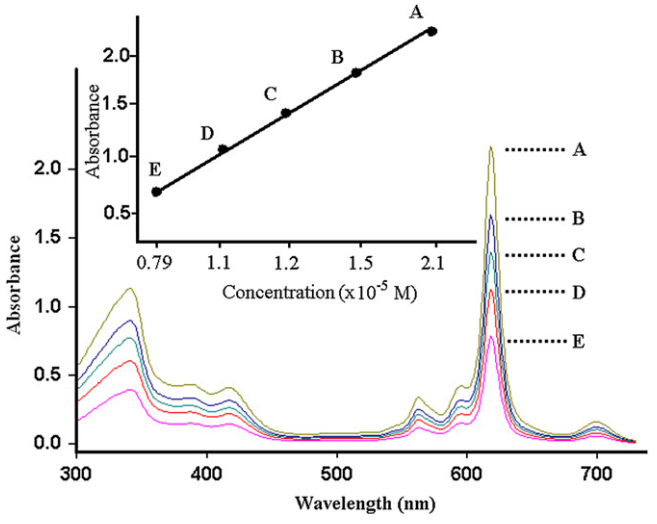


Figure 4. Absorption spectra of AzaPc **10** at different concentrations in THF solution: (A) 2.1×10^{-5}, (B) 1.5×10^{-5}, (C) 1.2×10^{-5}, (D) 1.1×10^{-5} and (E) 0.79×10^{-5} M.

Q-band absorption, a weak absorption peak in the NIR region which appears at 700 nm for **6** and 710 nm for **10**. Such NIR-transition peaks can be assigned to singlet–triplet transition (S–T) as confirmed by the fact that blue shifts are observed with increasing solvent polarity (in case of derivative **6**; DMF: λ_{NIR}=695 nm, in THF: λ_{NIR}=700 nm, in $CHCl_3$: λ_{NIR}=706 nm).[33] However, in the case of zinc-containing derivatives the metal d-orbitals are occupied and, therefore, no electron charge transfer transition was observed. Although the NIR-transition was not observed, the existence of such transition at lower energy and beyond our machine range (200–800 nm) is still possible due to the paramagnetic state of co-containing derivatives.

2.4. Solid state properties

As the case for phthalocyanine derivatives, controlling the molecular packing of AzaPc compounds within the solid state is necessary to utilize the electronic and optical properties (colours, molecular association and optical absorption) tailored to the requirement of the intended applications.[26,34] Therefore, it is crucial to fabricate AzaPcs as thin films in which the morphology and ordering can be reproducibly controlled. The higher solubility of these complexes in organic solvent renders these compounds suitable for deposition using a very simple technique such as spin-coated film.[35] Spin-coated films derived from AzaPc derivatives **3**–**10** were deposited onto untreated glass microscope slides from solution in chloroform. All of the spin-coated films gave a uniform appearance and optically clear films. Table 2 shows the Q-band parameters of the visible absorption spectra of these films. The position and appearance of the Q-band absorption of films derived from **3** to **10** are coincident with bands observed for those obtained from dilute solution thus suggesting that the azaphthalocyanine units are present in the isolated form within the solid state. For example, the UV–vis adsorption spectrum of film derived from **4** is almost identical to its solution spectrum (Fig. 3) with only slight broadening of the Q-band (for **4**; the difference in the width at half peak height ($\Delta W_{1/2}$)=0.2 nm).

Therefore, the isolated forms in either solution or solid state material of **3**–**10** complexes appear to be intrinsically related to the conformation adapted by the eight peripheral bulky groups, which efficiently suppress the cofacial interactions between the AzaPc cores as revealed by UV–vis spectroscopy and NMR techniques.

3. Conclusions

We have successfully synthesized and characterized the metal-free octaazaphthalocyanine derivatives using simple method without any noticeable transetherification side-reactions, which are considered up to date as an obstacle to prepare new phenoxy substituted AzaPc derivatives. Metal-containing derivatives (Zn^{2+}, Co^{2+}, Ni^{2+}) were also prepared in good yield using appropriate metal-template cyclotetramerisation reactions. Our results have shown that the solubility and the aggregation behaviour can be greatly modified by placing bulky phenoxy substituents at the eight peripheral sites of the AzaPc macrocycle. This attributed to the steric hindrance imposed by the bulky phenoxy substituents, which successfully prevent self-association of octaazaphthalocyanine cores, and thereby we obtained materials with intrinsically true solid solution properties as examined by UV–vis and NMR techniques. All the prepared derivatives can easily make high quality spin-coated films with uniform appearance and excellent optical quality. The combined interesting properties: non-aggregation behaviour, intense absorption in the red-region, high solubility, photostability and simple synthetic pathway make these new AzaPc materials of potential applications in PDT as photosensitizers, optoelectronic and near-IR devices.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded by using a Bruker DPX 400 MHz super-conducting NMR spectrometer. IR spectra were recorded on a Perkin Elmer system 2000 FTIR. Elemental analyses were obtained by using a LECO CHNS-932 Elemental Analyser. Mass spectra were measured on VG Autospec-Q (high resolution, high performance, tri-sector GC/MS/MS). MALDI mass spectra were obtained by using a Micro-Mass Tofspec 2E spectrometer. UV–vis spectra were recorded on Varian Cary 5 spectrometer. Melting points were recorded using Gallenkamp. Thin layer chromatography (TLC) was performed using Polygram sil G/UV 254 TLC plates and visualization was by an 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.[36]

4.2. 5,6-Bis(2,6-di-*iso*-propylphenoxy)pyrazine-2,3-dicarbonitrile (1)

To a stirred solution of 5,6-dichloropyrazine-2,3-dicarbonitrile (2 g, 10.10 mmol) and 2,6-di-*iso*-propylphenol (4.01 g, 23.23 mmol) in dry CH_3CN (150 mL) was added anhydrous potassium carbonate (8.01 g, 58.04 mmol). The reaction mixture was heated at 70 °C for 24 h under nitrogen. On cooling, the reaction mixture was poured into distilled water (500 ml) and neutralized with hydrochloric acid. The resulting precipitate was collected by filtration and washed with water, then air-dried. The crude product was recrystallized from *n*-hexane to give **3** as a white powder (3.8 g, 78.1%). Mp 253 °C; ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.25 (d, J=6.1 Hz, 24H), 2.81–2.87 (sept, 4H), 7.30 (d, J=7.4 Hz, 4H), 7.38 (t, J=7.5 Hz, 2H); IR ν (KBr)/cm^{-1} 2263 (CN); MS (EI): m/z (%): 482 (100) [M]$^+$; Anal. calcd (%) for $C_{30}H_{34}N_4O_2$: C 74.68, H 7.03, N 11.62; found: C 74.38, H 7.18, N 12.03.

4.3. 5,6-Bis(2,6-diphenylphenoxy)pyrazine-2,3-dicarbonitrile (2)

To a stirred solution of 5,6-diphenylphenol (5.71 g, 23.23 mmol) and 5,6-dichloropyrazine-2,3-dicarbonitrile (2 g, 10.10 mmol) in dry CH_3CN (150 mL) was added anhydrous potassium carbonate (15 g, 108.7 mmol). On cooling, the reaction mixture was poured into 500 mL of distilled water and neutralized with hydrochloric acid. The resulting precipitate was collected by filtration and washed with water (250 mL), then air-dried. The crude product was recrystallized from diisopropyl alcohol to yield **2** as yellow crystals (4.7 g, 75.3%). Mp 258 °C; ^{1}H NMR ($CDCl_3$, 25 °C): δ 7.12 (t, J=7.6 Hz, 8H), 7.21 (t, J=7.4 Hz, 4H), 7.34 (d, J=7.2 Hz, 8H), 7.48 (d, J=5.4 Hz, 4H), 7.52 (t, J=5.1 Hz, 2H); IR ν (KBr)/cm^{-1} 3118 (ArH), 2246 (CN); MS: m/z (%): 618 (100) [M]$^+$; Anal. calcd (%) for $C_{42}H_{26}N_4O_2$: C 81.05, H 4.21, N 9.16; found: C 81.13, H 4.26, N 9.16.

4.4. 2,3,9,10,16,17,23,24-Octa(2,6-di-*iso*-propylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (3)

A solution of 5,6-(2,6-di-*iso*-propylphenoxy)-pyrazine-2,3-dicarbonitrile **1** (1 g, 2.07 mmol) in dry quinoline (10 mL) was heated at 160 °C for 24 h under nitrogen. On cooling, the reaction mixture was poured into 200 mL distilled water. The resulting precipitate was collected and purified by means of column chromatography (eluent: $CHCl_3$) and recrystallized from acetone to give a green solid (0.45 g, 45%). Mp >300 °C; ^{1}H NMR ($CDCl_3$, 25 °C): δ −2.08 (s, 2H), 2.37 (d, J=6.2 Hz, 96H), 3.27–3.32 (sept, 16H), 8.55 (d, J=7.6 Hz, 16H), 8.63 (t, J=7.7 Hz, 8H); IR ν (KBr)/cm^{-1} 3205 (N–H)

3134 (ArH), 2963 (C–H) aliphatic, 1643 (C=N); UV–vis (THF): λ_{max} (ε)=645 nm (75,000 $mol^{-1}dm^3\,cm^{-1}$); MALDI MS: isotropic cluster at *m/z*: 1930 $[M]^+$; Anal. calcd (%) for $C_{120}H_{138}N_{16}O_8$: C 74.61, H 7.15, N 11.60; found: C 74.30, H 7.28, N 11.90.

4.5. 2,3,9,10,16,17,23,24-Octa(2,6-di-*iso*-propylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyaninatozinc(II) (4)

A solution of **1** (1 g, 2.07 mmol) and zinc(II) acetate (0.1 g, mmol) in dry quinoline (10 mL) was heated at 160 °C for 24 h under nitrogen. On cooling, the reaction mixture was poured into 200 mL distilled water. The resulting precipitate was collected and purified by means of column chromatography (eluent: $CHCl_3$) and recrystallization from acetone to give a purple reflective green solid (0.15 g, 15% yield). Mp >300 °C; ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.33 (d, *J*=6.5 Hz, 96H), 3.31–3.38 (sept, 16H), 7.46 (d, *J*=7.7 Hz, 16H), 7.59 (t, *J*=7.8 Hz, 8H); IR ν (KBr)/cm^{-1} 3048 (ArH), 1646 (C=N); UV–vis (THF): λ_{max} (ε)=624 nm (246,000 $mol^{-1}dm^3\,cm^{-1}$); MALDI MS: isotropic cluster centred at *m/z*: 1993 $[M]^+$; Anal. calcd (%) for $C_{120}H_{136}N_{16}O_8Zn$: C 72.25, H 6.82, N 11.24; found: C 72.13, H 6.9, N 10.87.

4.6. 2,3,9,10,16,17,23,24-Octa(2,6-di-*iso*-propylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyaninatocobalt(II) (5)

The product was prepared as for **4** using cobalt(II) acetate in 42% yield (0.46 g). Mp >300 °C; ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.37 (d, *J*=6.4 Hz, 96H), 5.16 (br s, 16H), 8.55 (d, *J*=7.4 Hz, 16H), 8.63 (t, *J*=7.8 Hz, 8H). MALDI MS: isotropic cluster at *m/z*: 1986 ($M^{+\bullet}$); IR ν (KBr)/cm^{-1} 3062 cm^{-1} (ArH), 1650 cm^{-1} (C=N); UV–vis (THF): λ_{max} (ε)=606 nm (64,000 $mol^{-1}dm^3\,cm^{-1}$); Anal. calcd (%) for $C_{120}H_{136}N_{16}O_8Co$: C 72.47, H 6.84, N 11.27; found: C 72.17, H 6.82, N 10.99.

4.7. 2,3,9,10,16,17,23,24-Octa(2,6-di-*iso*-propylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyaninatonickel(II) (6)

The product was prepared from the reaction between **1** and nickel(II) acetate using similar procedure as for **4**, the resulting crude product was purified by column chromatography (eluent: $CHCl_3$) to give a blue powder (0.56 g, 55% yield). Mp >300 °C; ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.31 (d, *J*=6.2 Hz, 96H), 3.26–3.33 (sept, 16H), 7.44 (d, *J*=7.7 Hz, 16H), 7.58 (t, *J*=7.8 Hz, 8H); IR ν (KBr)/cm^{-1} 3040 (ArH), 1648 (C=N); UV–vis (THF): λ_{max} (ε)=615 nm (170,000 $mol^{-1}dm^3\,cm^{-1}$); MALDI MS: isotropic cluster at *m/z*: 1986 $[M]^+$; Anal. calcd (%) for $C_{120}H_{136}N_{16}O_8Ni$: C 72.48, H 6.85, N 11.27; found: C 72.27, H 7.27, N 11.08.

The following AzaPcs were prepared from 5,6-di(2,6-diphenylphenoxy)-pyrazine-2,3-dicarbonitrile (**2**) using similar procedures adopted for AzaPcs: **3**–**6**

4.8. 2,3,9,10,16,17,23,24-Octa(2,6-diphenylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (7)

Yield 0.49 g, 39%. Mp >300 °C; ^{1}H NMR (pyridine-d_5, 25 °C): δ −2.8 (s, 2H), 8.57 (t, *J*=7.0 Hz, 16H), 8.61 (t, *J*=7.1 Hz, 32H), 9.46 (d, *J*=7.3 Hz, 16H), 9.53 (d, *J*=7.6 Hz, 32H), 9.58 (d, *J*=7.6 Hz, 8H); IR ν (KBr)/cm^{-1} 3215 (N–H), 3135 (ArH), 1645 (C=N); UV–vis (THF): λ_{max} (ε)=651 nm (106,000 $mol^{-1}dm^3\,cm^{-1}$); MALDI MS: isotropic cluster at *m/z*: 2474 $[M]^+$; Anal. calcd (%) for $C_{168}H_{106}N_{16}O_8$: C 81.48, H 4.28, N 9.05; found: C 81.05, H 4.36, N 9.07.

4.9. 2,3,9,10,16,17,23,24-Octa(2,6-diphenylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyaninatozinc(II) (8)

Yield 0.55 g, 42%. Mp >300 °C; ^{1}H NMR (pyridine-d_5, 25 °C): δ 8.46 (t, *J*=7.0 Hz, 16H), 8.52 (t, *J*=6.8 Hz, 32H), 9.43 (d, *J*=7.6 Hz, 16H), 9.51 (d, *J*=7.6 Hz, 32H), 9.56 (t, *J*=7.0 Hz, 8H); IR ν (KBr)/cm^{-1} 3128 (ArH) 1640 (C=N); UV–vis (THF): λ_{max} (ε)=626 nm (287,000 $mol^{-1}dm^3\,cm^{-1}$); MALDI MS: isotropic cluster at *m/z*: 2537 $[M]^+$; Anal. calcd (%) for $C_{168}H_{104}N_{16}O_8Zn$: C 79.46, H 4.09, N 8.82; found: C 79.7, H 4.33, N 8.93.

4.10. 2,3,9,10,16,17,23,24-Octa(2,6-diphenylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyaninatocobalt(II) (9)

Yield 0.50 g, 38.5%. Mp >300 °C; ^{1}H NMR (pyridine-d_5, 25 °C): δ 6.91(br s, 16H), 6.97 (br s, 32H), 7.84–7.87 (m, 16H), 7.66–7.99 (m, 40H). MALDI MS: isotropic cluster at *m/z*: 2530 ($M^{+\bullet}$); IR ν (KBr)/cm^{-1} 3093 (ArH), 1649 (C=N); UV–vis (THF): λ_{max} (ε)=608 nm (108,000 $mol^{-1}dm^3\,cm^{-1}$); Anal. calcd (%) for $C_{168}H_{104}N_{16}O_8Co$: C 79.65, H 4.11, N 8.85; found: C 79.79, H 4.34, N 9.17.

4.11. 2,3,9,10,16,17,23,24-Octa(2,6-diphenylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyaninatonickel(II) (10)

Yield 0.60 g, 46%. Mp >300 °C; ^{1}H NMR (pyridine-d_5, 25 °C): δ 8.63 (m, *J*=7.2 Hz, 56H), 9.43 (d, *J*=7.6 Hz, 16H), 9.51 (d, *J*=7.6 Hz, 32H), 9.56 (t, *J*=7.4 Hz, 8H); IR ν (KBr)/cm^{-1} 3069 (ArH), 1614 (C=N); UV–vis (THF): λ_{max} (ε)=619 nm (241,000 $mol^{-1}dm^3\,cm^{-1}$); MALDI MS: isotropic cluster at *m/z*: 2530 $[M]^+$; Anal. calcd (%) for $C_{168}H_{104}N_{16}O_8Ni$: C 79.66, H 4.11, N 8.85; found: C 79.95, H 4.51, N 8.84.

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