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Clathrate Formation from Octaazaphthalocyanines Possessing Bulky Phenoxyl Substituents: A New Cubic Crystal Containing Solvent-Filled, Nanoscale Voids

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Abstract: The synthesis of octaazaphthalocyanine (AzaPc) derivatives, with bulky phenoxyl substituents placed at eight peripheral positions and containing either H^+, Ni^{2+} or Zn^{2+} ions in their central cavity, is described. The required precursors, derivatives of pyrazine-2,3-dicarbonitrile, were prepared using a nucleophilic aromatic substitution reaction between 2,6-diisopropylphenol or 2,6-diphenylphenol and 5,6-dichloropyrazine-2,3-dicarbonitrile. Analysis of the resulting AzaPcs by UV/Visible and ^{1}H NMR spectroscopy confirms that steric isolation of the AzaPc cores was enforced both in solution and in the solid state. X-ray diffraction studies of single crystals of the AzaPcs reveal that solvent inclusion takes place in each case. Of particular significance is the finding that the zinc derivative of 2,3,9,10,16,17,23,24-octa-(2,6-diisopropylphenoxy)octaazaphthalocyanine provides nanoporous cubic crystals, containing massive (8 nm^3) solvent-filled voids, similar to those of the analogous phthalocyanine derivative. Exchange of the included solvent within the voids can be readily achieved by using a number of alternative solvents including water. Based on the observed loading of included water, the internal volume of this nanoporous cubic crystal appears to be more hydrophilic than its phthalocyanine counterpart.

Keywords: clathrates · dyes/pigments · microporous materials · phthalocyanines

Introduction

Phthalocyanine (Pc) and its derivatives are one of the most studied class of organic molecular materials due to their outstanding optical and electronic properties combined with excellent thermal and chemical stability.[1] In addition to their widespread use as blue and green colourants, phthalocyanines are of increasing interest for applications in nonlinear optics (including optical limitation),[2] Xerography (as photoconductors),[3] hole- and electron-transport materials in organic electronic devices,[4] liquid-crystalline charge carriers[5]and exciton-transport materials,[6] optical data storage (as the laser absorption layer within recordable discs),[3] photodynamic cancer therapy,[7] solar energy conversion,[8] catalysis[9] and as the active component of gas sensors.[10] The extended planar shape, fourfold symmetry and synthetic diversity also makes phthalocyanine an excellent building block for use in supramolecular[11] and polymer chemistry.[12] Furthermore, the phthalocyanine macrocycle can be modified in order to tune molecular and materials properties, for example, by the replacement of carbon within the benzo units with nitrogen. In particular, 1,4,8,11,15,18,22,25-octaazaphthalocyanines (AzaPc), often termed tetrapyrazinoporphyrazines, possess significantly different physical properties to phthalocyanines that are beneficial for some applications.[13] For example, the main adsorption band in the visible spectrum (the Q-band) of AzaPc is shifted to shorter wavelength

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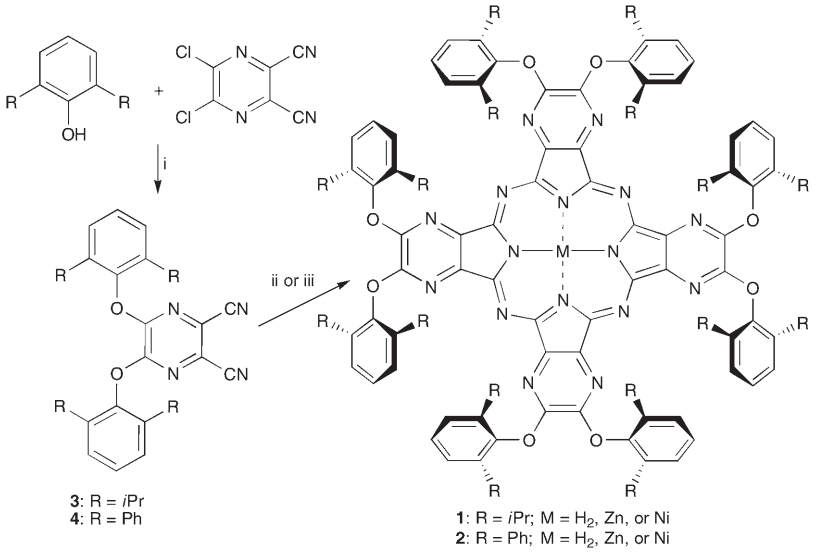
(e.g., $\lambda_{max} \approx 630$ nm) as compared to typical values for phthalocyanine (e.g., $\lambda_{max} \approx 680$ nm). Hence, substituted derivatives of AzaPcs have been studied for potential use in photodynamic therapy,[14,15] nonlinear optics,[16] liquid-crystal technology,[17] catalysis[18] and as a red fluorophore.[19] This last application is an example in which the properties of AzaPc provide a clear advantage as the main fluorescence band, corresponding to the Q-band of the absorption spectrum, provides an intense red fluorescence in dilute solution, whereas for phthalocyanines it falls outside of the visible region of the spectrum into the near IR. For many applications, it is necessary to control co-facial self-association of the disc-shaped macromolecules so as to avoid the effects of intermolecular processes (e.g., self-quenching of excited state, adsorption band broadening by exciton coupling or prevention of singlet-oxygen production). Although many strategies now exist for preventing self-association of phthalocyanines in solution and the solid state,[20,21] they are rarely adapted to bring about isolation of the AzaPc system.[22]

Recently, we reported that the bulky substituents of 2,3,9,10,16,17,23,24-octa(2,6-diisopropylphenoxy)-1,4,8,11,15,18,22,25-phthalocyanine (Pc**1**-H_2) prohibit close self-association of the macrocycle even within solid thin films and that the zinc derivative Pc**1**-Zn forms a remarkable cubic crystal containing massive solvent-filled voids.[23] Here, we describe the synthesis of the analogous AzaPcs, 2,3,9,10,16,17,23,24-octa(2,6-diisopropylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (AzaPc**1**-M; M = H_2, Ni, Zn) and also 2,3,9,10,16,17,23,24-octa(2,6-diphenylphenoxy)-1,4,8,11,15,18,22,25-octaazaphthalocyanine (AzaPc**2**-M; M = H_2, Ni, Zn) and present structures obtained by single-crystal X-ray diffraction studies to illustrate the prevention of cofacial self-association of the AzaPc cores and the inclusion of solvent molecules within these crystals.

Results and Discussion

Synthesis: Derivatives of AzaPc are generally prepared from substituted pyrazine-2,3-dicarbonitrile precursors through a metal-ion-mediated cyclotetramerisation reaction. Following the general methodology developed by Mørkved,[24,25] the aromatic nucleophilic substitution reaction between the appropriate phenol and 5,6-dichloropyrazine-2,3-dicarbonitrile[26] gave the precursors to AzaPc**1**-H_2 and AzaPc**2**-H_2, that is, 5,6-bis(2,6-diisopropylphenoxy)pyrazine-2,3-dicarbonitrile (**3**) and 5,6-bis(2,6-diphenylphenoxy)-pyrazine-2,3-dicarbonitrile (**4**), respectively, in good yield (Scheme 1). The metal-containing AzaPc**1**-M and AzaPc**2**-M (M = Ni, Zn) were prepared readily by the cyclotetramerisation of the precursor in quinoline using the appropriate metal acetate. Surprisingly, we found that the metal-free AzaPc**1**-H_2 and AzaPc**2**-H_2 could be prepared in reasonable yield simply by heating **3** or **4** in quinoline. This method avoids the problematic replacement of the phenoxy substituents through transetherification induced by the alkyloxide initiator,[15,25] which interferes with the synthesis of the metal-free AzaPcs by conventional methods.[27] This reaction is worth noting because metal-free phthalocyanines cannot usually be prepared by this method. It is well established that phthalonitriles containing electron-withdrawing substituents undergo cyclotetramerisation under relatively mild conditions[28] and it is likely that the electronic properties of the pyrazine ring favours macrocycle formation even without the introduction of an alkyloxide initiator or metal ion template.



Scheme 1. The synthesis of AzaPcs-**1**-M and AzaPc**2**-M. Reagents and conditions: i) K_2CO_3, MeCN, 70 °C, 24 h; ii) quinoline, 160 °C, 24 h; iii) metal acetate, quinoline, 160 °C, 24 h.

Structural characterisation and self-association: All AzaPc products gave ^{1}H NMR and UV/Visible spectroscopic data consistent with their structures. In addition, clusters of peaks that correspond to the calculated isotope composition of the molecular ion were observed by matrix-assisted laser desorption ionisation mass spectroscopy (MALDI-MS). It was noted previously that the ^{1}H NMR spectrum of Pc**1**-Zn displays a doublet of doublets for the methyl groups at 298 K,[23] which can be ascribed to slow interchange between methyl groups in different environments due to restricted rotation.[21,29] In contrast, the ^{1}H NMR spectra of AzaPc**1**-Zn at 298 K displays a more typical doublet corresponding

to the methyl hydrogens of the isopropyl groups (Figure 1). Variable-temperature studies showed that the coalescence of the methyl peaks for AzaPc **1**-Zn and Pc **1**-Zn occurs at 268

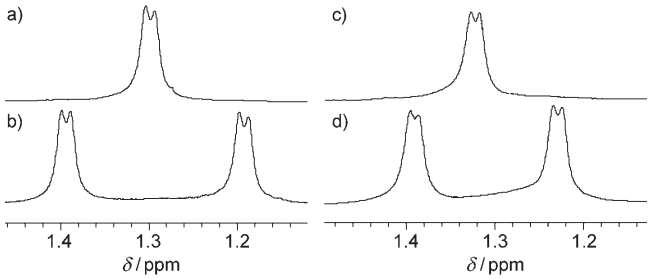


Figure 1. Details of the aliphatic region of the ^{1}H NMR spectrum of Pc **1**-Zn obtained at a) 333 K and b) 298 K compared to that of AzaPc **1**-Zn obtained at c) 298 K and d) 230 K illustrating the relative ease of methyl group positional interchange within AzaPc **1**-Zn.

and 303 K, respectively, corresponding to a free energy of activation of 54.7 and 62.3 kJ mol^{-1}, respectively. The difference can be attributed to the absence of the steric effect of the hydrogen atoms in the non-peripheral benzo-positions of AzaPc **1**-Zn, which provide greater freedom of movement for the conformational processes required for methyl interchange. Both UV/Vis absorption and NMR spectroscopy can be used to determine the degree of aggregation of phthalocyanines or azaphthalocyanines in solution or the solid phase. For example, ^{1}H NMR spectra of the AzaPc's show no broadening or peaks shifts over a broad concentration range, which indicates the absence of aggregation. Generally for UV/Vis adsorption spectroscopy, co-facial self-association of Pc's and AzaPc's results in broadening of the Q-band and a significant shift to a shorter wavelength due to exciton coupling. However, for the AzaPc's, the position and appearance of the Q-band is independent of concentration. Furthermore, no significant shift or broadening of the Q-band is observed from the visible spectrum of thin films cast from solution (Figure 2). For example, broadening of the Q-band from the spin-coated film of AzaPc **1**-Zn (λ_{max} = 634 nm) is only 0.2 nm at half peak height.

To investigate the effect of the bulky phenoxy substituents on the packing of the AzaPc's in the solid state, crystals were grown for analysis by X-ray diffraction (XRD). The AzaPc-**1**-M (M = H_2, Ni) complexes provide isomorphous orthorhombic crystals in which CH_2Cl_2 is included (Figure 3).

Within these crystals the AzaPc cores are planar and the aromatic planes of the phenoxy substituents lie almost perpendicular to the plane of the AzaPc core due to the mutual steric effects between the bulky isopropyl groups on adjacent phenoxy units. The resulting rigid, doughnut-shaped structure adopted by the substituents ensures that co-facial self-association of the AzaPc cores is prohibited and provides a cavity above and below the AzaPc macrocycle. The shape of the molecule also poses a challenge for the efficient packing of the molecules, which is solved by the adoption of a planar packing structure in which the AzaPc cores lie perpendicular to the plane in a herringbone structure so that two of the 2,6-diisopropylphenoxy groups of one molecule are placed within the cavity of its neighbour. Nevertheless, for AzaPc-**1**-H_2, this packing arrangement requires the inclusion of four solvent molecules of CH_2Cl_2 for each AzaPc molecule, two of which are weakly hydrogen bonded to the benzo nitrogen atoms of the AzaPc (N_{benzo}–$H_{CH_2Cl_2}$ = 0.2991 nm), and placed mid-way within the plane of the herringbone arrangement, whereas the other two CH_2Cl_2 molecules are highly disordered and lie in between these planes (Figure 3). Within the isomorphous crystal structure derived from AzaPc-**1**-Ni, these solvent molecules are made up of a disordered mixture of CH_2Cl_2, acetone and water.

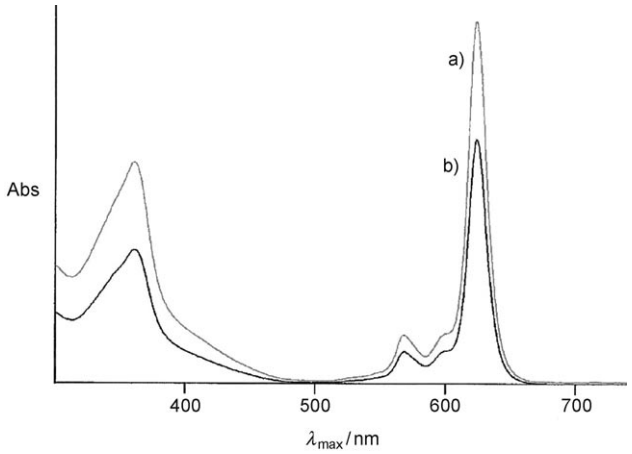


Figure 2. UV/Vis adsorption spectrum of AzaPc **1**-Zn a) in THF ($c = 1.2 \times 10^{-5}$ M) and b) from a solvent cast film.

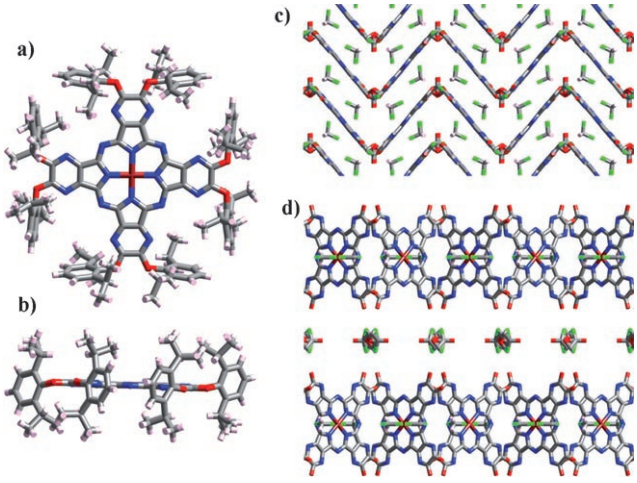


Figure 3. Results from the single-crystal XRD study of AzaPc **1**-Ni. a) Face-on and b) side views of the molecule showing the planarity of the macrocycle. c) A view of the herringbone arrangement of the macrocycles looking down the *x* axis of the crystal. d) A view along the *z* axis of the crystal showing the disordered solvent (CH_2Cl_2, acetone and H_2O) located between the layers of the herringbone structure. Note: to enhance clarity the 2,6-diisopropylphenoxyl groups are not shown in c) and d).

Attempts to form suitable crystals from AzaPc **2**-M for XRD studies succeeded only for the Zn-containing deriva-

tive for which a tetragonal crystal, of $P\bar{4}2_1c$ space group, was obtained. Analysis of the molecular structure of this compound shows that the macrocycle is slightly twisted from planarity and that the phenyl groups of the eight 2,6-diphenylphenoxy substituents are forced out of the plane of the macrocycle so that they adopt a configuration that gives the whole molecule a square shape (Figure 4). The Zn cation is

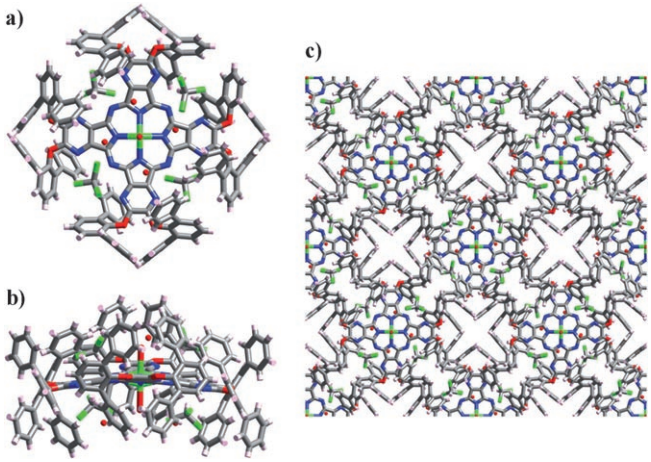


Figure 4. Results from the single-crystal XRD study of AzaPc**2**-Zn. a) Face-on and b) side views of the molecule. Molecules of $CHCl_3$ at 0.5 occupancy are bound through hydrogen bonding to the four *meso*-nitrogen atoms and molecules of H_2O at 0.25 occupancy are hydrogen bonded to the axial water molecule at four position. c) A view of the tetragonal arrangement of the macrocycles looking down the *z* axis of the crystal

disordered over two sites protruding from the macrocyclic plane. The cavities above and below the macrocycle produced by the bulky substituents are partially occupied by $CHCl_3$ (two per AzaPc) and H_2O (two per AzaPc) molecules, the former, at 0.5 occupancy, hydrogen bonded to the four meso-nitrogen atoms (N_{meso}–$H_{chloroform}$ = 0.2504 nm). One of the H_2O molecules is present as an axial ligand on the Zn cation (Zn–O = 0.2108 nm), which is disordered over two sites and the other is hydrogen bonded to the axial ligand (O_{axial}–O_{water} = 0.3240 nm) and is disordered over four equivalent sites. The square shape adopted by AzaPc**2**-Zn leads to tetrahedral packing of the molecules in columns within which the closest Zn–Zn distance is 1.0863 nm.

AzaPc**1**-Zn possesses striking crystal-forming properties. Very large, single blocks grow by diffusion of methanol into a concentrated solution of the compound in CH_2Cl_2 (Figure 5a). XRD analysis shows that these crystals are isomorphous with the nanoporous cubic crystals, of $Pn\bar{3}n$ space group, derived from Pc**1**-Zn. The molecular structure of AzaPc**1**-Zn within the crystal is conical with the oxygen of its axial water ligand at the apex of the cone. The solvent-filled voids, two per unit cell, are defined by six AzaPc molecules with each of the axial oxygen ligands pointing into the centre of the void. The distance between the Zn^{2+} ions across the void is 2.358 nm, which is slightly larger than the 2.331 nm found within the cubic crystal of Pc**1**-Zn, despite

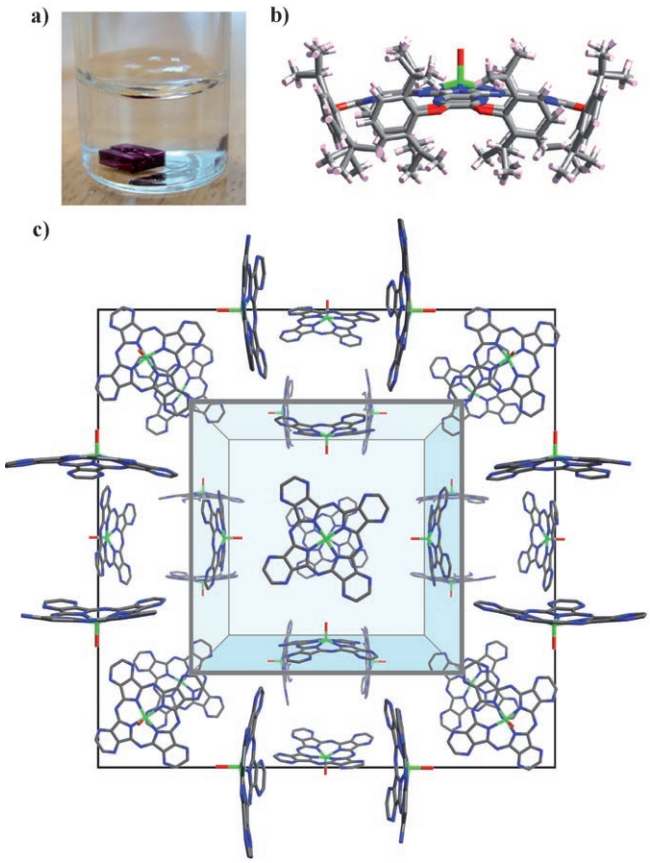


Figure 5. a) An example of the single-crystal growth of AzaPc**1**-Zn from the diffusion of MeOH into a solution of the sample in CH_2Cl_2. For scale, the diameter of the sample tube is 15 mm. Results from the single-crystal XRD study. b) The side view of the molecule showing the conical shape of the molecule and the oxygen atom of the axial ligand which is presumed to be H_2O and c) a perspective view of the unit cell (outer cube) with dimensions of 3.75 nm and which contains 12 molecules of AzaPc**1**-Zn. The shaded inner cube represents one of the two large (≈8 nm^3) solvent-filled voids found in each unit cell. In this view, the second nanovoid is distributed in ≈1 nm portions at each corner of the unit cell. MeOH molecules, with an occupancy of 0.5, are hydrogen bonded to each of the four *meso*-nitrogen atoms of the AzaPc. Note: to enhance clarity the 2,6-diisopropylphenoxyl groups are not shown in c).

the smaller unit cell of the AzaPc**1**-Zn crystal (a = 3.726 nm versus a = 3.770 nm), which reflects the shallower cone configuration adopted by the AzaPc macrocycle. Therefore, the large voids have a volume in excess of 8 nm^3, which accounts for most of the 19.6 nm^3 solvent accessible space estimated by the use of PLATON software.[30] ^{1}H NMR analysis of the composition of the crystals dissolved in $CDCl_3$ indicates that the ratio of MeOH:AzaPc**1**-Zn is 20:1 (i.e., 240 solvent molecules per unit cell). Two of these methanol atoms are localised, at 50% occupancy, by hydrogen-bonding to the four *meso*-nitrogen atoms of the AzaPc (N_{meso}–O_{MeOH} = 0.282 nm). Based upon an electron count, a further 81 solvent molecules are partially ordered within each unit cell suggesting that the remaining methanol molecules, deduced from NMR evidence, are wholly disordered. Simply by placing the crystals of AzaPc**1**-Zn in contact with other

solvents (e.g. hexane, acetone, H_2O), exchange of the included methanol can be achieved (Table 1).

Table 1. Composition of the included solvent within the cubic crystals of AzaPc **1**-Zn as compared to that for Pc **1**-Zn, showing the greater hydrophilicity of the AzaPc **1**-Zn system. The measurements were made by dissolving the crystals in dry $CDCl_3$ and comparing the integrated heights of the peaks due to the Pc with those of the solvent.

	AzaPc **1**-Zn/ Solvent[a]	AzaPc **1**-Zn/ H_2O	Pc **1**-Zn/ Solvent[a]	Pc **1**-Zn/ H_2O
H_2O	–	1:37	1:1[b]	1:30
MeOH	1:14	1:20	1:20	1:2
EtOH	1:16	1:14	1:21	–
acetone	1:13	1:14	1:11	1:3
isopropanol	1:14	1:10	1:14	1:2
hexane	1:5	1:8	1:9	1:1

[a] No attempt was made to dry the solvent or remove existing water from the crystals prior to exchange of the original solvent, which was MeOH for AzaPc **1**-Zn and acetone for Pc **1**-Zn. [b] Residual amount of acetone that remained included with the crystals of Pc **1**-Zn on exchange with water.

Conclusion

Placing eight bulky phenoxyl substituents at the periphery of AzaPc successfully prohibits self-association of the macrocycle even in the solid state, leading to unperturbed optical properties. Due to the shape of the resulting molecules efficient packing in the crystalline state is only achieved by the inclusion of solvent molecules. An extreme example of this is the formation of nanoporous crystals from AzaPc **1**-Zn, which contain large solvent-filled voids of 8 nm^3 volume. These voids are interconnected by narrow channels allowing the exchange of one type of solvent for another and providing access to the central metal ions. Work is in progress to determine whether the introduction of other metal cations within the central cavity of AzaPc **1**-H_2, especially those of more established catalytic activity, is compatible with the formation of this interesting crystal structure.

Experimental Section

Full experimental procedures for compounds **1**–**4** are provided in the Supporting Information along with crystallographic details. CCDC-670579 (AzaPc **1**-H_2), 670580 (AzaPc **1**-Ni), 670581 (AzaPc **2**-Zn) and 670582 (AzaPc **1**-Zn) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Example of typical procedures

*Synthesis of **3***: To a stirred solution of 5,6-dichloropyrazine-2,3-dicarbonitrile (2 g, 10.10 mmol) and 2,6-diisopropylphenol (4.01 g, 23.23 mmol) in dry CH_3CN (150 mL) anhydrous potassium carbonate (8.01 g, 58.04 mmol) was added. 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 neutralised with hydrochloric acid. The resulting precipitate was collected by filtration and washed with water, then air-dried. The crude product was recrystallised from *n*-hexane to give **3** as a white powder (3.8 g, 78.1 %). M.p. 253 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.25$ (d, $J = 6.1$ Hz, 24H), 2.84 (sept, $J = 6.7$ Hz, 4H), 7.30 (d, $J = 7.4$ Hz, 4H), 7.38 ppm (t, $J = 7.5$ Hz, 2H); IR (KBr): $\tilde{\nu} = 2263$ cm^{-1} (CN); MS (EI): *m/z* (%): 482 (100) $[M]^+$; elemental analysis 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.

*Synthesis of AzaPc **1**-Zn*: A solution of **3** (1 g, 2.07 mmol) and zinc(II) acetate (0.1 g) in dry quinoline (10 mL) was heated at 160 °C for 24 h under nitrogen. On cooling, the reaction mixture was poured into distilled water (200 mL). The resulting precipitate was collected and purified by means of column chromatography (eluent: $CHCl_3$) and recrystallisation from acetone to give a purple reflective, green solid (15 % yield). M.p. > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 1.33$ (d, $J = 6.5$ Hz, 96H), 3.34 (sept, $J = 6.7$ Hz, 16H), 7.46 (d, $J = 7.7$ Hz, 16H), 7.59 (t, $J = 7.8$ Hz, 8H); UV/Vis (THF): λ_{max} (ε) = 624 nm (246000 mol^{-1} dm^3cm^{-1}); MALDI MS: isotropic cluster centred at *m/z*: 1993 $[M]^+$; elemental analysis 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.

Acknowledgements

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