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Synthesis of porphyrazine-octaamine, hexamine and diamine derivatives

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Abstract—The syntheses of a variety of substituted diaminomaleonitriles, with variable nitrogen substituents, were undertaken. Linstead macrocyclization of the resulting diaminomaleonitriles gave access to a wide range of functionalized porphyrazine-octaamines and hexamines and norphthalocyaninediamines. Conversion of these macrocycles into metallic derivatives and studies of their electronic absorption, solubility and electrochemistry are described. These flexible tetraazaporphyrins show potential in a range of applications including biomedical agents, novel charge–transfer complexes, chemical sensors, novel electronic materials and non-linear optics.

1. Introduction

Tetraazaporphyrins (porphyrazines, pz) can be viewed as porphyrin analogues, with *meso* nitrogen atoms replacing the *meso* carbon atoms. This alteration results in significant structural and electronic changes within the macrocycle.[1] Porphyrazines, however, have received considerably less synthetic interest than the related porphyrins and phthalocyanines.[2,3] Peripheral heteroatom functionalization of the macrocycle results in significant modulation of their physical and electronic properties.[1] Barrett, Hoffman and co-workers have published extensively on the synthesis of porphyrazines bearing thiols, amines or alcohols as ring substituents, with the conversion of these polydentate ligands to a variety of coordination complexes.[1,4] Porphyrazines containing peripheral amino substituents constitute an important class of these flexible molecules. Since our original report on these electron-rich octaaminomacrocycles,[5] several structural analogues have been prepared, including *trans*-A_2B_2[6] and A_3B type porphyrazines[7–9] and porphyrazine–phthalocyanine hybrids.[10] We have explored the coordination chemistry of these novel ligands, preparing palladium(II) star-porphyrazines,[11] as well as a variety of solitaire-macrocycles.[8,12,13] The platinum(II) solitaire porphyrazines are potent photosensitizers and have the potential as dual-warhead anti-cancer agents.[14] In addition, we have prepared several charge-transfer complexes with C_{60}[15,16] and utilized amino-porphyrazine nitrogen donor pockets in metal sensing applications.[17] An important discovery was the oxidative scission of one of the pyrrole units to yield the *seco*-porphyrazines.[18] Detailed photophysical studies into these curious macrocycles unveiled their potent photosensitizing ability for the production of singlet oxygen.[19] We have utilized this feature in the dye catalyzed photooxygenation of dienes[20] and have prepared several novel *seco*-porphyrazines with variable solubility and photophysical profiles.[21,22] Ercolani and co-workers have prepared a variety of amino-porphyrazines with annulated heterocyclic rings.[23–27] We have exploited this 'protection' of the free amino functionality with selenium in the synthesis of Schiff Base porphyrazines, for application as molecular scaffolds.[28,29] Recently we have also disclosed a ROM-polymerization-capture-release strategy for the chromatographically-free synthesis of amino-porphyrazines.[30]

This report describes the syntheses of diverse amino-porphyrazines prepared in our laboratories with the aim to provide information on how the substituents bonded to the peripheral nitrogens intimately influence the physical,

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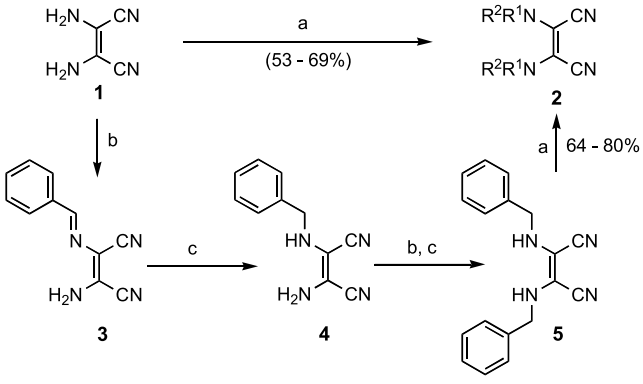
chemical and electronic properties of the porphyrazinic macrocycle.

2. Results and discussion

2.1. Dialkylamino functionalized porphyrazines

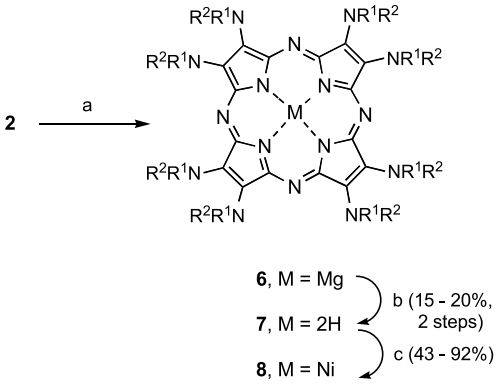
The peripheral nitrogen substituents of octaamino-porphyrazines have a profound influence on the physical and chemical properties of the macrocycle. This readily adaptable effect can be exploited for the synthesis of porphyrazines which display flexible solubility, variable electronic absorption spectra and tuneable redox properties. Following the method of Sheppard and co-workers,[31] tetra-functionalized maleonitriles were prepared in a controlled manner and subsequently cyclized to the desired porphyrazine products. Thus, commercially inexpensive diaminomaleonitrile (DAMN) was alkylated under strongly basic conditions to yield tetraalkylated maleonitriles **2a**–**2c** (53–69%) (Scheme 1). Alternatively, successive reductive alkylations with benzaldehyde yielded the dibenzyl derivative **5**,[31] which was subsequently converted into the fully substituted maleonitriles **2d**–**2e** (64–80%). Notably, derivative **5** has proved a robust derivative for the synthesis of various functionalized maleonitriles (vide infra).



In structure **2; a** $R^1 = R^2 =$ Me, **b** $R^1 = R^2 =$ Bn, **c** $R^1 = R^2 =$ allyl, **d** R^1 = Me, R^2 = Bn, **e** R^1 = allyl, R^2 = Bn

Scheme 1. Reagents and conditions: (a) Me_2SO_4 or BnBr or $CH_2{=}CHCH_2Br$, NaH, DME or THF, −30 to 20 °C. (b) C_6H_5CHO, MeOH, Δ. (c) $NaBH_4$, MeOH, THF.

Linstead macrocyclization[32] of dinitriles **2** gave access to the octaamino-porphyrazines **6** in reasonable yields (15–48%) (Scheme 2). The porphyrazines were isolated as blue-black solids with purple reflections. Acidic demetallation by short exposure to trifluoroacetic acid or prolonged contact with acetic acid gave access to the free base porphyrazines **7**. Remetallation with a variety of metal salts was then possible using the metal (II) acetate in DMF.[4] In particular, porphyrazines **7** were converted to the nickel(II) derivatives **8** in good yield (43–92%). All the octaamino-porphyrazines prepared were readily soluble in organic solvents, a feature of the heteroatom-substituted porphyrazines, which is more favorable than the structurally analogous phthalocyanines. Many of the derivatives were also crystalline. As a result, X-ray crystal structures have been solved for **6b** and **8e**.[5]



In structures **2, 6 - 8; a** $R^1 = R^2 =$ Me, **b** $R^1 = R^2 =$ Bn, **c** $R^1 = R^2 =$ allyl, **d** R^1 = Me, R^2 = Bn, **e** R^1 = allyl, R^2 = Bn

Scheme 2. Reagents and conditions: (a) $Mg(O^nBu)_2$, ^{n}BuOH, Δ, 24 h. (b) TFA or AcOH. (c) $Ni(OAc)_2$, PhCl, DMF, Δ.

The electronic absorption spectra for the amino-porphyrazines were consistent with previous observations[4] and can be rationalized using Gouterman's four orbital model.[33] Octaamino-porphyrazines have D_{4h} symmetry, with a doubly degenerate lowest unoccupied molecular orbital (LUMO) (e_g) and two highest occupied molecular orbitals (HOMOs) that complete the four Gouterman orbitals with a_{1u} and a_{2u} symmetry. The compounds therefore displayed two visible transitions, a long-wavelength Q band (~650 nm), corresponding to $a_{2u} \rightarrow e_g$ and a short wavelength B band (Soret) (~350 nm) corresponding to $a_{1u} \rightarrow e_g$. In addition, heteroatom-substituted porphyrazines display intense coupling between the non-bonding, lone pair electrons and the macrocyclic π-system. The resultant n–π* transitions were visible in the electronic absorption spectra (~550 nm). The strong coupling of the non-bonding electrons with the π-system also resulted in significant broadening due to vibrational fine structure. A representative UV–vis spectrum for porphyrazine **6a** is shown in Figure 1.

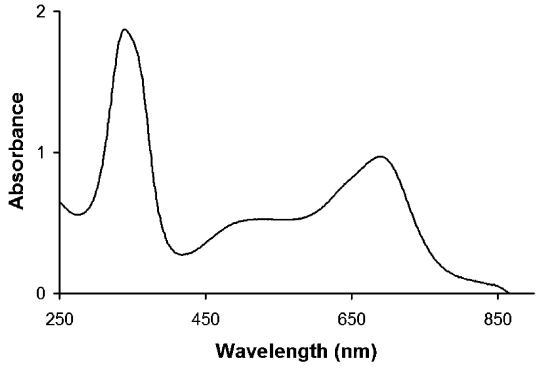


Figure 1. Electronic absorption spectra of **6a**.

The electronic absorption data for representative porphyrazines **6**–**8** are listed in Table 1.

As can be seen in Table 1, all the macrocycles prepared displayed qualitatively similar spectra with visible Soret and Q bands as well as an n–π* transition. However, it is difficult to glean any structure–absorption trends with

Table 1. Electronic absorption data for porphyrazines **6–8**

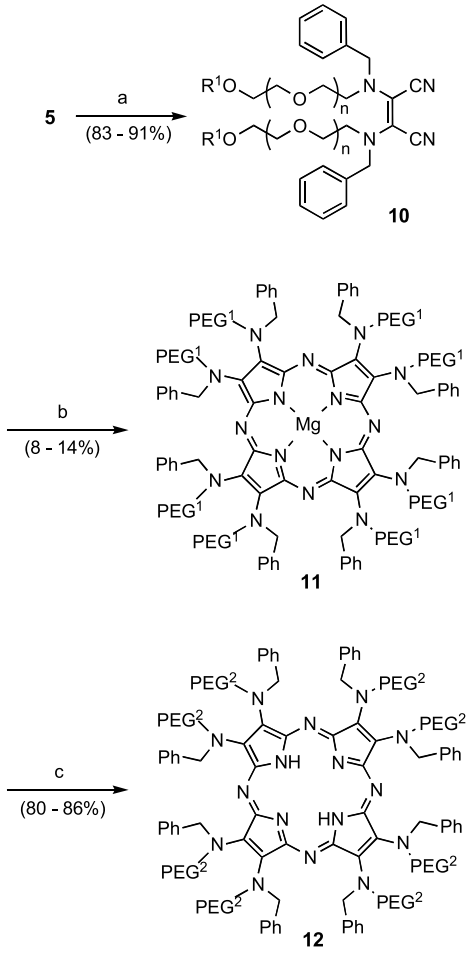
pz	R^1, R^2	Metal	λ_{max} (log ε)
6a[7]	Me, Me	Mg	335 (4.81), 599 (4.27), 752 (4.33)
6b	Bn, Bn	Mg	368 (4.75), 574 (4.45), 707 (4.51)
6d	Me, Bn	Mg	350 (4.56), 544 (4.10), 714 (4.38)
7a[7]	Me, Me	2H	334 (4.57), 531 (4.29), 709 (4.16)
7c	allyl, allyl	2H	333 (4.67), 526 (4.47), 730 (4.36)
7e	allyl, Bn	2H	330 (4.75), 536 (4.59), 734 (4.44)
8a	Me, Me	Ni	325 (4.92), 360 (4.50), 561 (4.42), 704 (4.52)
8b	Bn, Bn	Ni	322 (4.71), 536 (3.95), 654 (4.04), 674 (4.00)
8e	allyl, Bn	Ni	324 (4.72), 511 (4.53), 688 (4.49)

respect to either the amino substituents or the metal occupying the porphyrazine cavity. For example, on going from **6a** to **7a** to **8a** (M=Mg to 2H to Ni), the Soret band remained approximately stationary, whereas the Q band underwent a blue shift (~43 nm) on conversion to the free base, with no real change on remetallation with nickel. In addition, the n–π* transition also underwent a hypsochromic effect on demetallation (~68 nm), with a red shift on insertion of nickel (~30 nm). On changing the substituents from methyl ($R^1=R^2=$Me) to benzyl ($R^1=R^2=$Bn) for the magnesium derivatives (**6a** vs **6b**), the Soret underwent a red shift (~13 nm), whereas the Q band and n–π* transitions underwent a blue shift (~45 and ~25 nm, respectively). For the nickel macrocycles (**8a** vs **8b**), the Soret underwent no such shift and the Q band and n–π* transitions underwent a similar shift as observed for the magnesium derivative. Furthermore, the Soret was split for **8a**, whereas the Q band was split for **8b**. In general, the electronic absorptions of the macrocycles were sensitive to both the amino-substituents as well as the cavity metal, although it is hard to predict the differences these changes will produce.

2.2. Polyethyleneglycol-amino-functionalized porphyrazines

Polyetherol-appended thioporphyrazines have already shown promise as both chemical sensors[34] and biomedical imaging and therapeutic agents.[35,36] In particular, the polyethyleneglycol (PEG) chains confer enhanced aqueous solubility, which makes them ideal candidates for binding metal ions in water or for medical applications. Recently we have disclosed the synthesis of one such PEG-functionalized maleonitrile and its application to the synthesis of a novel *seco*-porphyrazine.[21] Alkylation of benzyl derivative **5**, with iodo-derivatives **9a**[37] or **9b** (formed on treatment of the mono-protected PEG[38] with iodine and triphenylphosphine), under the basic conditions gave the maleonitriles **10a** and **10b** with varying PEG chain lengths. In addition, reaction with iodide **9c**[39] yielded the methyl-capped derivative **9c** (Scheme 3). Macrocyclization furnished the PEG substituted amino porphyrazines **11** in low yield. In the case of THP-protected derivatives **11a** and **11b**, demetallation and concomitant deprotection using acidic conditions[21] gave access to the free base macrocycles **12a** and **12b**. For the methyl-capped product **11c**, simple acidic demetallation occurred on exposure to acetic acid (Scheme 3). Remetallation within the macrocyclic cavity was possible for the PEG-appended porphyrazines; for example **12c** was readily converted to its nickel(II) derivative (not shown).

As expected, the tuning of the amino substituent altered the solubility profile of the macrocycles. Although porphyrazines **12a** and **12c** showed a greatly enhanced solubility in polar, protic solvents such as methanol, unfortunately, they were not water soluble. However, to our delight porphyrazine **12b** was freely soluble in water, producing a homogeneous purple solution. Thus, one possibility for the synthesis of water soluble, neutral amino-porphyrazine analogues is the substitution of PEG chains of sufficient length, with free hydroxyl-functionality at the termini. We



In structures **9**, **10**; **a** n = 0, R^1 = THP, **b** n = 2, R^1 = THP, **c** n = 2, R^1 = Me; **11**; **a** $PEG^1 = CH_2CH_2OTHP$, **b** $PEG^1 = (CH_2CH_2O)_3THP$, **c** $PEG^1 = (CH_2CH_2O)_3Me$; **12**; **a** $PEG^2 = CH_2CH_2OH$, **b** $PEG^2 = (CH_2CH_2O)_3H$, **c** $PEG^2 = (CH_2CH_2O)_3Me$

Scheme 3. (a) $I(CH_2CH_2O)_{(n+1)}R^1$ (**9**), Cs_2CO_3, DMF, 50 °C. (b) $Mg(O^nBu)_2$, ^{n}BuOH, Δ, 24 h. (c) AcOH or AcOHHCl, $CHCl_3$, MeOH, 20 °C.

are currently looking to exploit this result in the context of porphyrazine biomedical agents.

In addition to the physical properties, PEG-appended aminoporphyrazines display intriguing electronic absorption spectra. We have previously noted this for the thioporphyrazine PEG derivatives.[4] For example, **12b** displays a complex spectrum with a split Soret band (327 and 356 nm) as well as a split Q band, which was further complicated by shoulders (667 and 741 nm). Furthermore, an intensive n–π* transition was visible at 556 nm.

2.3. Carboxymethylamino-functionalized porphyrazines

In order to extend the coordination chemistry of the aminoporphyrazines and moreover, provide new and varied macrocycles for application to chemical sensing of metal ions in solution, the synthesis of an acetic acid functionalized porphyrazine **6** ($R^1=R^2=CH_2CO_2H$) was examined. The linking of two acetic acid chains to each peripheral amino group would produce an analogue, which should mimic ethylenediaminetetracetic acid (EDTA). Previously reported macrocyclic analogues of EDTA have been reported to display much higher binding constants with metal ions.[40,41] Unfortunately, this challenging target has thus far eluded preparation. However, these failed attempts have led to several important observations, highlighting the limitations of both maleonitrile **5** as a difunctional starting material and the Linstead macrocyclization reaction.

Early in these synthetic studies, the direct tetra-functionalization of DAMN **1**, proved to be untenable. Attempted alkylation with methyl chloroacetate, the orthoester **13** (X=Cl, Br), the *ortho* ester precursor **14** or protected derivatives of chloroacetaldehyde (e.g., **15**) under basic conditions (NaH or Cs_2CO_3) all failed, resulting either in decomposition or no reaction (Fig. 2).

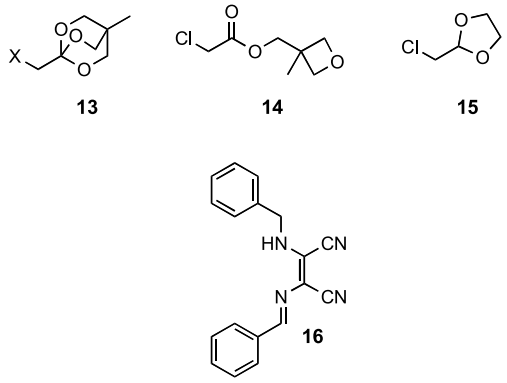
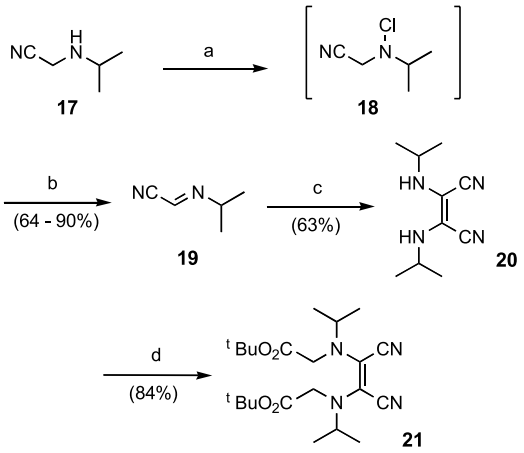


Figure 2.

The use of benzyl derivative **5** was therefore employed for the synthesis of acetic acid functionalized analogues. However, curiously, attempts to alkylate maleonitrile **5** with methyl chloroacetate in the presence of sodium hydride resulted in the formation of the imine **16** (Fig. 2) in 64% yield. Attempted alkylation with a range of functionally equivalent electrophiles provided the same result. Palladium catalyzed amination of **5** using methyl chloroacetate also provided imine **16** in 77% yield. Therefore, in the presence of certain electrophiles, benzyl maleonitrile **5** acts more like a hydride donor than a nucleophile. This is most probably due to the high acidity of the benzyl protons coupled with the low solubility of imine **16**, driving the reaction in an undesired direction.

It was anticipated that the introduction of aliphatic substituents would avoid this predominant side reaction and would serve as a better model for further investigations. Selective dialkylation of DAMN **1** with limited quantities of alkyl halides (for example methyl iodide) gave mixtures of substituted products. Likewise, aliphatic aldehydes proved troublesome in the reductive alkylation pathway (vide supra). An alternative strategy, which would allow the introduction of alkyl substituents prior to the formation of the maleonitrile, was therefore examined. The dimerization of imines has been previously demonstrated for this application.[42,43] *N*-(Isopropylamino)acetonitrile **17** was readily prepared following the procedure of Boyer et al.[43] The preparation of imine **19** was carried out by treatment with *tert*-butyl hypochlorite followed by dehydrochlorination with triethylamine[42,44] or using calcium hypochlorite as the chlorination agent followed by elimination with calcium hydroxide[43] (49%) (Scheme 4). Alternatively, the use of *N*-chlorosuccinimide (NCS) in carbon tetrachloride resulted in a quantitative conversion to the corresponding *N*-chloro derivative **18**, as judged by NMR, after 5 min. Subsequent elimination of intermediate **18** with calcium hydroxide provided imine **19** in an improved 90% yield. Dimerization of imine **19** was carried out by reaction with stannic chloride in dry benzene[43] and gave *N*,*N*′-diisopropyldiaminomaleonitrile **20** in 56% yield, along with 7% of the corresponding *trans*-isomer (as judged by ^{1}H NMR) (Scheme 4). Changing the solvent from benzene to carbon tetrachloride did not suppress dimerization and gave imine **19**, which was used directly without isolation to provide **20**. This provided multigram quantities of an alternative disubstituted aminomaleonitrile derivative **20**, a useful intermediate in our quest for other functionalized aminoporphyrazines.

Initially attempted alkylation of **20** with alkyl chlorides and



Scheme 4. Reagents and conditions: (a) $Ca(OCl)_2$, $CaCl_2$, CH_2Cl_2, 20 °C or NCS, CCl_4, 55 °C. (b) $Ca(OH)_2$, $CaCl_2$, CH_2Cl_2, Δ. (c) $SnCl_4$, PhH, 20 °C. (d) $BrCH_2CO_2$ ^{t}Bu, NaH, DMF, −10 to 20 °C.

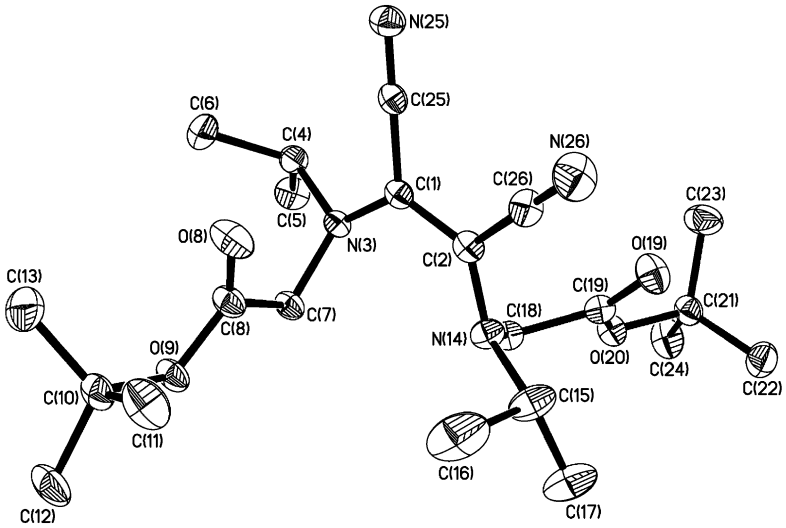
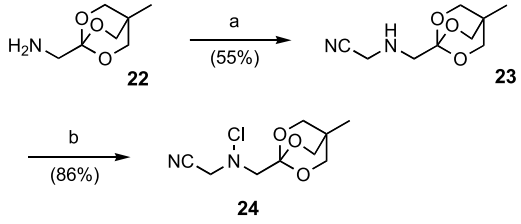


Figure 3. X-ray crystal structure of dinitrile **21**.

sodium hydride in THF was unsuccessful, with quantitative recovery of starting material. However, when DMF was used as the solvent, dinitrile **21** was obtained in an excellent 84% yield (Scheme 4). A single crystal X-ray analysis confirmed the structure of dinitrile **21** with the requisite *cis*-geometry of the double bond in place (Fig. 3).

Unfortunately, attempted macrocyclization of dinitrile **21** under Linstead conditions using either magnesium butoxide or propoxide failed to provide any of the corresponding porphyrazine and resulted in the decomposition of the starting material. It seems reasonable to assume that the failure of the reaction could be due to (a) the acidic protons adjacent to the carbonyl group or (b) steric hindrance of the *tert*-butyl ester. It was therefore considered that conversion of dinitrile **21** to its carboxylic acid counterpart would not only reduce the acidity of the α-protons, but also the steric hindrance. Thus, hydrolysis of the *tert*-butyl ester using neat TFA, produced a dark brown oil, the identity of which was established by spectroscopic analysis (NMR, IR, MS). Exposure of the crude material to magnesium butoxide resulted only in decomposition and none of the desired porphyrazine could be isolated.

In a final effort to utilize this methodology in the synthesis of an acetic acid functionalized porphyrazine, ortho-ester derivative **22** was converted into the *N*-alkylaminoacetonitrile derivative **23** (Scheme 5). Although *N*-chlorination was straightforward, dehydrohalogenation of the resultant derivative **24** gave only polymeric intractable products under a variety of conditions.



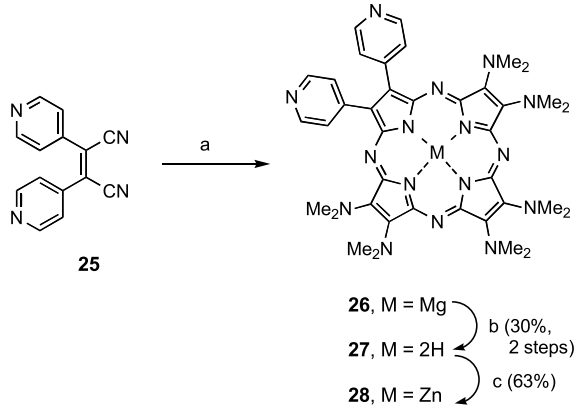
Scheme 5. Reagents and conditions: (a) $ClCH_2CN$, Et_3N, Et_2O, −10 to 20 °C. (b) $Ca(OCl)_2$, $CaCl_2$, CCl_4, 20 °C.

Despite these disappointing results, EDTA appended porphyrazines are still a valuable target in our studies on the aminoporphyrazines and alternate strategies for their production are currently being explored in our laboratories. The current synthetic efforts, however, highlight the problems associated with maleonitrile **5** as a functional intermediate and the incompatibility of certain substrates with Linstead macrocyclization.

2.4. Pyridyl functionalized porphyrazines

Following previous reports of cationic porphyrins as potential DNA-binding and cleavage agents,[45] as well as sensitizers for photodynamic therapy,[46] we first reported the synthesis of an octacationic pyridyl porphyrazine in 1999.[47] These novel systems were both freely soluble in water as the chloride salt and showed strong binding to calf thymus DNA.[48] Thus, in continuation of these studies, the synthesis of unsymmetrical pyridyl-substituted aminoporphyrazines was carried out. The resultant macrocycles should display rich and varied redox chemistry and could be of use in the application of non-linear optics due to the presence of both donor and acceptor functionality.

A statistical, mixed Linstead macrocyclization of pyridyl



Scheme 6. Reagents and conditions: (a) **2a**, $Mg(O^nBu)_2$, ^{n}BuOH, Δ, 24 h. (b) TFA. (c) $Zn(OAc)_2$, DMF, Δ.

maleonitrile **25**,[47] with aminomaleontrile **2a** furnished porphyrazine **26**, the desired (A_3B) hexamine, along with octaaminoporphyrazine **6a** (A_4) (Scheme 6). Traces of *cis* and *trans* A_2B_2 porphyrazines were also observable by mass spectrometry and were isolated as an inseparable mixture. Exposure of porphyrazine **26** to TFA gave the free base derivative **27** (30% overall) and subsequent remetallation under standard conditions gave the zinc(II) macrocycle **28** (63%).

A comparison of the electrochemical data of the novel pyridyl-appended porphyrazine **27** and the related octa-amino-porphyrazine **6a** is presented in Table 2.

Table 2. Electrochemical data for porphyrazines **27** and **6a**

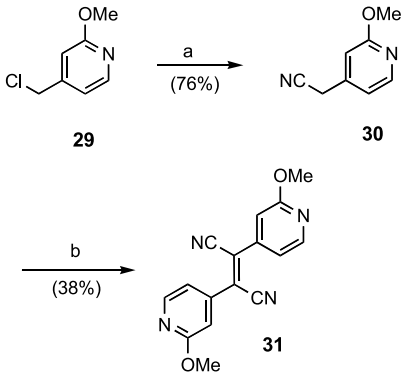
	pz^{2+}/pz^{+}	pz^{+}/pz	pz/pz^{1-}	pz^{1-}/pz^{2-}
27	+1.08	+0.95	−0.29	−0.49
6a	−0.06	−0.27	−1.61	—

Measured in dichloromethane, with 0.1 M Bu_4NPF_6 as electrolyte, Pt disk working electrode, at a scan rate of 110 mV s^{-1}.

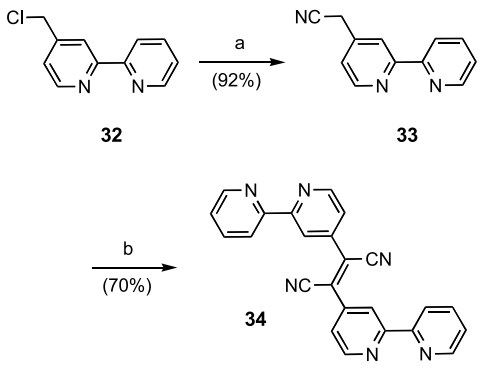
The presence of eight electron donating dimethylamino groups in ligand **6a** results in a system that is extremely easy to oxidize with a first reversible oxidation centered at $E_{1/2} = -0.27$ V with respect to Fc^{+}/Fc. Upon replacement of two NMe_2 units by the electron withdrawing pyridyl groups, the first oxidation potential is shifted to $E_{1/2} = +0.95$ V, thus, indicating that oxidation of the new system is, as expected, more difficult. Also as a consequence of the electron withdrawing pyridyl groups, the first reduction potential of compound **27** is found at −0.29. In contrast, the electron rich ligand **2a** is more difficult to reduce with the first reduction potential centered at −1.61 V. This result demonstrates how simple modification of the porphyrazine substituents can lead to profound differences in the redox potentials of the macrocycles.

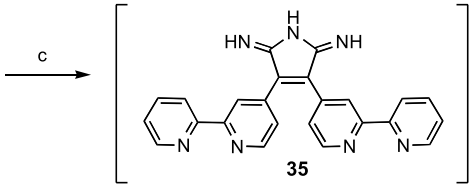
In addition to the potential biomedical applications of pyridyl-appended porphyrazines, we have demonstrated the synthesis of amino porphyrazines bearing pyridyl-based metal donor pockets **6** (R^1=Bn, R^2=2-pyridylmethyl).[17] Such systems show efficient binding of 4 equiv of a variety of metal cations including heavy metals such as cadmium(II) and therefore have potential in sensor applications. In a continuation of this work, the preparation of a bipyridyl porphyrazine **36** was initiated. Two strategies were envisaged, whereby the bipyridyl linkage could be constructed pre- or post-macrocyclization. Towards the latter goal, nitrile **30** was prepared by nucleophilic displacement of the corresponding chloride **29** (prepared from 2-methoxy-4-methylpyridine,[49] by chlorination of a transient silyl derivative synthesized following the method of Katrizky et al.[50]). Dimerization of **30** with sodium methoxide and iodine gave the requisite dinitrile **31** (Scheme 7). However, macrocyclization of dinitrile **31** was problematic, with low yields of a high polarity material, which could not be fully purified. Therefore, introduction of the bipyridyl residue before the Linstead macrocyclization reaction was investigated.

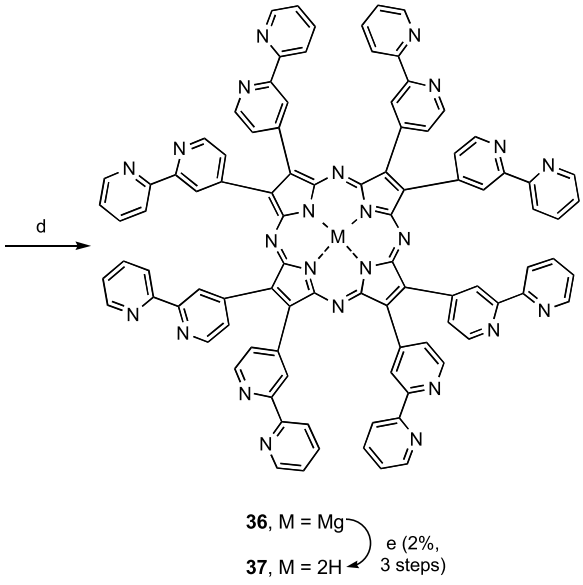
Similar cyanide displacement of acid sensitive chloride



Scheme 7. Reagents and conditions: (a) NaCN, DMSO. (b) I_2, NaOMe, MeOH, Δ.







Scheme 8. Reagents and conditions: (a) KCN, 18-crown-6, MeCN. (b) I_2, NaOMe, MeOH, Δ. (c) NH_3, cat Na, $HOCH_2CH_2OH$, Δ. (d) $Mg(O^nBu)_2$, ^{n}BuOH, Δ, 24 h. (e) TFA.

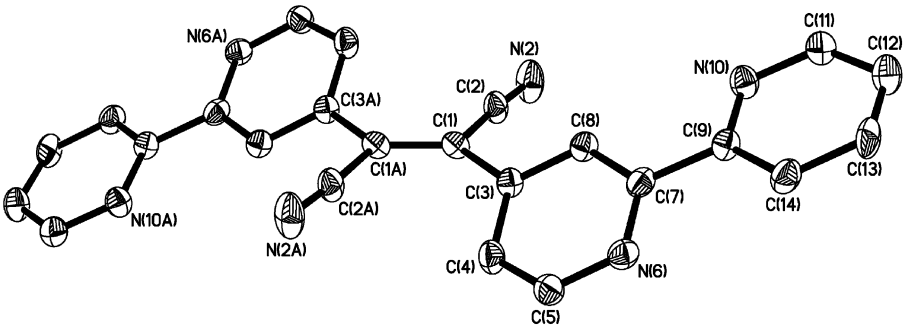


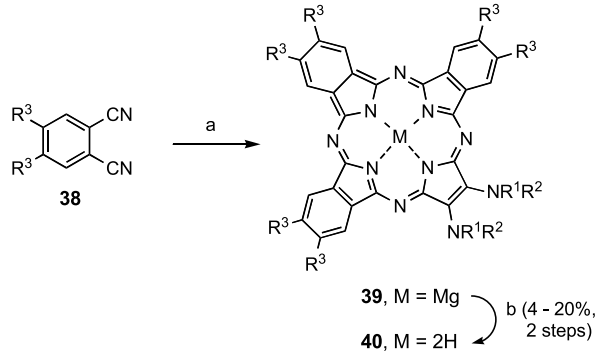
Figure 4. X-ray crystal structure of dinitrile **34**.

32,[51] yielded nitrile **33**, which was subsequently oxidatively dimerized in excellent yield (64% over 2 steps) (Scheme 8). The *trans* geometry of dinitrile **34** was elucidated by X-ray crystallography (Fig. 4). Unfortunately, attempted Linstead macrocyclization of dinitrile led to decomposition of the substrate. This was attributed to the slow thermal isomerization of dinitrile **34** and the general sensitive nature of the substrate. Instead, dinitrile **34** was first converted to the diiminopyrroline **35**, upon treatment with ammonia gas in ethylene glycol at reflux catalyzed by sodium 2-hydroxyethoxide.[52] The crude product **35** was immediately macrocyclized to yield the porphyrazine **36**, which was subsequently demetallated with trifluoroacetic acid, giving macrocycle **37**, albeit in low yield (ca. 2% from **34**) (Scheme 8).

The UV–vis spectra of the octabipyridyl porphyrazines **36** and **37** exhibited qualitatively similar spectra to the corresponding octapyridyl porphyrazines.[47] The magnesium derivative **36** displayed a Soret band at 337 nm and a Q band at 537 nm. In addition, there were also strong absorption bands at higher energy, 241 and 283 nm, which were assigned to the peripherally attached bipyridyl groups. The UV–vis spectrum of the demetallated ligand **37** displayed a Soret band at 362 nm and a split Q-band at 593 and 660 nm. Again, higher energy bands at 240 and 283 nm were assigned to the bipyridyl groups. The applications of these novel bipyridyl porphyrazines is currently being investigated with particular attention to their metal binding properties.

2.5. Amino functionalized norphthalocyanines

Norphthalocyanines are phthalocyanine–porphyrazine hybrids, consisting of three phthalonitrile units and one maleonitrile unit. Previously we reported the synthesis of norphthalocyanine dithiolates and coordination of these ligands to a variety of metals, yielding solitaire porphyrazines.[53,54] In addition, we have reported the preparation of pyridyl-appended systems as novel metal sensors[17] and a bis(dimethylamino)norphthalocyanine, which was characterized by X-ray crystallography.[10] We initiated the synthesis of several additional amino-appended norphthalocyanines to investigate how the benzo-substitution of these novel hybrids affects their physical properties and electronic absorption spectra. Commercially available phthalonitrile **38a** was utilized in a mixed Linstead macrocyclization with amino-maleonitriles **2b** and **2c**. This furnished magnesium norphthalocyanine derivatives **39a** and **39b** (Scheme 9). Chromatographic purification of these highly insoluble pigments proved impossible and therefore the macrocycles were demetallated to give free-bases **40a** and **40b**, which were sufficiently soluble to purify. However, the solubility of **40a** and **40b** precluded further manipulation and conversion to the nickel (II) derivatives lead to macrocycles with an even lower solubility profile. The poor solubility of the norphthalocyanines has been previously noted.[10]



In structures **38; a** R^3 = H, **b** R^3 = ^{n}Bu; **39**, **40**; **a** R^1 = R^2 = allyl, R^3 = H, **b** R^1 = R^2 = $PhCH_2$, R^3 = H, **c** R^1 = R^2 = allyl, R^3 = ^{n}Bu, **d** R^1 = R^2 = $PhCH_2$, R^3 = ^{n}Bu, **e** R^1 = $PhCH_2$, R^2 = allyl, R^3 = ^{n}Bu; **39f** R^1 = $PhCH_2$, R^2 = CH_2CH_2OTHP, R^3 = ^{n}Bu; **40f** R^1 = $PhCH_2$, R^2 = CH_2CH_2OH, R^3 = ^{n}Bu,

Scheme 9. Reagents and conditions: (a) **2**, $Mg(O^nBu)_2$, ^{n}BuOH, Δ, 24 h. (b) TFA.

The synthesis of more soluble derivatives was achieved by the modification of the norphthalocyanine cyclization partner. In particular, 4-*n*-butylphthalonitrile **38b**[55] was utilized in the Linstead macrocyclization to yield norphthalocyanines **39c–f**, with benzyl, allyl and tetrahydropyranoxylethyl substituents (Scheme 9). Demetallation was achieved to yield the free base macrocycles **40c** and **40d**, whereas demetallation and concomitant deprotection of norphthalocyanine **39f** was achieved, furnishing the di-(hydroxyethylamino)-porphyrazine **40f**. All the butyl-substituted norphthalocyanines were more soluble in organic solvents than their unsubstituted counterparts.

The electronic absorption data for porphyrazines **40a–d** are shown in Table 3.

As can be seen in Table 3, all the macrocycles prepared displayed qualitatively similar spectra containing Soret

Table 3. Electronic absorption data for porphyrazines **40a–d**

pz	R^1, R^2	R^3	λ_{max} (log ε)
40a	allyl, allyl	H	293 (4.46), 338 (4.83), 528sh, 577 (4.42), 649 (4.69), 688 (4.60), 723 (4.60)
40b	Bn, Bn	H	292 (4.45), 341 (4.83), 527sh, 583 (4.46), 644 (4.57), 691 (4.56), 727 (4.61)
40c	allyl, allyl	^{n}Bu	299 (4.56), 345 (4.89), 524 (4.25), 577sh, 656 (4.62), 691 (4.61), 733 (4.69)
40d	Bn, Bn	^{n}Bu	298 (4.58), 347 (4.90), 517 (4.24), 590sh, 655 (4.64), 691 (4.62), 734 (4.74)

transitions (~340 nm), as well as split Q bands (centered around 690 nm). In addition, n–π* transitions are observable (~570 nm) as well as high-energy bands at 290 nm. The splitting of the Q band is due to both the reduced symmetry of the norphthalocyanine (C_{2v}), combined with the reduced symmetry of the free base macrocycles. This reduction in symmetry destroys the degeneracy of the LUMO, resulting in two separate orbitals b_{2g} and b_{3g}.[33] In general, the substituents of norphthalocyanines **40a–d** have little effect on the position of the bands. Interestingly, the Q bands of the norphthalocyanines are only slightly blue shifted in comparison to the corresponding octaaminoporphyrazines **7** (see Table 1). Parent phthalocyanines display Q bands around 690 nm, whereas the Q band for unsubstituted porphyrazines is around 600 nm.[4] Benzo-substitution therefore results in approximately a 100 nm red shift. Heteroatom substitution of the porphyrazine macrocycle also results in approximately a 100 nm red shift. Therefore, norphthalocyanines containing three sites of benzo-substitution and one of amino-substitution result in a similar Q band shift than parent phthalocyanines or octaaminoporphyrazines, when compared to unsubstituted porphyrazines. This indicates that the benzo-substitution, present in the norphthalocyanines has approximately the same effect on the energetics of electronic transitions as amino-substitution does.

3. Conclusions

The synthesis of a wide range of amino-functionalized porphyrazines has been described in this report. It shows how the amino-groups, attached to the periphery of the macrocycle, can be tailored to alter the physical properties of the porphyrazine as well as its electronic absorption and reactivity. Some of the macrocycles prepared in this report are expected to find applications as diverse as biomedical agents, novel charge-transfer complexes, chemical sensors, novel electronic materials and non-linear optics. We are currently pursuing this direction and such work will be reported in due course.

4. Experimental

4.1. General procedures

All reactions were conducted in oven or flame dried glassware under N_2. Reaction temperatures reported refer to external bath temperatures. Solvents used in chromatography were BDH AnalR or GPR grade and were used without further purification. Hexanes refers to the alkane fraction boiling between 40 and 60 °C. Solvents used for reactions were distilled prior to use: THF, DME, and Et_2O (from K-Ph_2CO ketal); Et_3N, pyridine, CH_2Cl_2, and MeCN (from CaH_2); DMF (predried over BaO, distilled from neutral Al_2O_3 (activity I)); MeOH, *n*-PrOH, and *n*-BuOH (from Mg). All other reagents were purchased from commercial sources and were used without further purification. Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F-254 glass plates. Visualization was accomplished using the quenching of UV fluorescence (λ_{max} 254 nm), and by $KMnO_4$ (basic), ceric molybdate, anisaldehyde, and vanillin solutions, followed by heat. Flash chromatography utilized Merck Kieselgel 60 (230–400 mesh) or Aluminum oxide 90 active (activity I). Size exclusion chromatography was performed on Sephadex LH-20 or Bio-Beads S-X3 supports. All solvents were rotary evaporated at or below 50 °C under reduced pressure. Cyclic voltammetry data were recorded with a Cypress Systems 2000 computer-controlled potentiostat. A three electrode configuration was employed: a platinum disk working electrode, a silver wire counter electrode, and a silver–silver chloride reference electrode. Measurements were made in CH_2Cl_2, freshly distilled from CaH_2, with Bu_4NPF_6 as the supporting electrolyte. All measurements were calibrated by addition of ferrocene as an internal reference and $E_{1/2}$ values were calculated from $(E_{pa}+E_{pc})/2$ at a scan rate of 110 mV s^{-1}.

4.1.1. 2,3-*Bis*(dibenzylamino)-2(*Z*)-butene-1,4-dinitrile (2b). Diamine **1** (10.0 g, 92.6 mmol) in DME (60 mL) was added with rapid stirring to NaH (60% dispersion in mineral oil, 17.0 g, 425 mmol) in DME (100 mL) at −22 °C. After the addition was complete (0.5 h), the brown suspension was stirred at −22 °C for 0.5 h. $PhCH_2Br$ (69.1 g, 400 mmol) in DME (30 mL) was slowly added and stirring continued at −22 °C for 1 h, when the mixture was allowed to warm slowly up to room temperature. The suspension was filtered through Celite, rotary evaporated and crystallized from EtOAc–hexanes to give dinitrile **2b** (23 g, 53%) as a light brown solid: mp 129–130.5 °C (Et_2O/hexanes); TLC 0.71 (EtOAc/hexanes 1:1); IR ($CHCl_3$) 2400, 2186, 1591, 1579, 1454, 1215, 1152, 1028 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.2 (s, 8H), 7.05 (m, 8H), 7.28 (m, 12H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 55.9, 115.3, 118.0, 128.1, 128.6, 129.1, 136.4; MS (EI) *m/z* 468 ($M^{+\cdot}$), 377, 260, 181, 91, 65; HRMS (EI) *m/z* Calcd for $C_{32}H_{28}N_4$: ($M^{+\cdot}$), 468.2316; found: ($M^{+\cdot}$), 468.2324. Anal. Calcd for $C_{32}H_{28}N_4$: C, 82.01; H, 6.03; N, 11.96. Found: C, 82.15; H, 6.05; N, 11.96%.

4.1.2. 2,3-Bis(diallylamino)-2(*Z*)-butene-1,4-dinitrile (2c). Following the same procedure as for the preparation of dinitrile **2b**, diamine **1** and allyl bromide gave dinitrile **2c** (8.5 g, 69%) as an orange-yellow oil: TLC R_f 0.40 (EtOAc/hexanes 1:9); IR (film) ν_{max} 2186, 1643, 1585, 1443, 1403, 1244, 1178, 991, 928 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.71 (8H, d, J=6.3 Hz), 5.19–5.26 (8H, m), 5.66–5.81 (4H, m); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 54.7, 115.1, 117.1,

119.7, 132.9; MS (CI, NH_3) *m/z* 286 $(M+NH_4)^+$, 269 $(M+H)^+$, 227; HRMS (CI, NH_3) Calcd for $C_{16}H_{24}N_5$ $(M+NH_4)^+$, 286.2032; found: $(M+NH_4)^+$, 286.2035. Anal. Calcd for $C_{16}H_{20}N_4$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.51; H, 7.74; N, 20.84.

4.1.3. 2,3-Di(benzyl(methyl)amino)-2(*Z*)-butene-1,4-dinitrile (2d). Following the same procedure as for the preparation of dinitrile **2b**, diamine **5**[31] and dimethyl sulfate gave dinitrile **2d** (7.0 g, 64%) as a colorless solid: mp 86 °C (EtOAc/hexane); TLC 0.55 (EtOAc/hexanes 2:3); IR (film) 2184, 1593, 1450, 1429, 1284, 1233, 947, 881, 710, 675, 654 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.74 (s, 6H), 4.20 (s, 4H), 7.15 (m, 4H), 7.34 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.5, 58.7, 115.0, 117.5, 128.0, 128.4, 128.8, 136.1. Anal. Calcd for $C_{20}H_{20}N_4$: C, 75.91; H, 6.37; N, 17.71. Found: C, 75.99; H, 6.54; N, 17.89%.

4.1.4. 2,3-Di(allyl(benzyl)amino)-2(*Z*)-butene-1,4-dinitrile (2e).[5] Dinitrile **5** (10.0 g, 34.7 mmol) was added with rapid stirring to NaH (60% in mineral oil; 3.1 g, 76.4 mmol) in dry THF (350 mL) at −22 °C. After 30 min, allyl bromide (16.8 g, 139.0 mmol) was added and stirring continued at −22 °C for 2 h. The mixture was allowed to warm up to room temperature. After stirring for 2 h, distilled H_2O (40 mL) was added, the aqueous layer was extracted with Et_2O (3×200 mL), and the solvent evaporated. Chromatography (SiO_2, Et_2O/hexanes 9:1 to 1:1) gave dinitrile **2e** (10.3 g, 80%) as a viscous yellow oil: TLC R_f 0.16 (Et_2O/hexanes 9:1); IR (film) ν_{max} 2185, 1642, 1590, 1581, 1495, 1454, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.65 (4H, d, J=6.3 Hz), 4.25 (4H, s), 5.11–5.24 (4H, m), 5.56–5.68 (2H, m), 7.11–7.34 (10H, m); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 54.7, 55.4, 114.8, 117.1, 119.5, 127.9, 128.4, 128.8, 132.3, 136.1; MS (EI) *m/z* 368 $(M)^+$, 277; HRMS (EI) *m/z* Calcd for $C_{24}H_{24}N_4$: $(M^{+\cdot})$, 368.2001; found: $(M^{+\cdot})$, 368.2011. Anal. Calcd for $C_{24}H_{24}N_4$: C, 78.22; H, 6.57; N, 15.22. Found: C, 78.11; H, 6.76; N, 15.15.

4.1.5. (2,3,7,8,12,13,17,18-Octa(benzyl(methyl)amino)-porphyrazinato)-magnesium(II) (6d). PrOH (100 mL) and Mg turnings (550 mg, 22.6 mmol) were heated to reflux for 10 h and cooled to room temperature. Dinitrile **2d** (2.0 g, 6.3 mmol) was added and the mixture was heated to reflux for 48 h. The blue suspension was filtered off through celite and the solids leached with CH_2Cl_2 (150 mL). Rotary evaporation and chromatography (Al_2O_3 EtOAc/hexanes) gave **6d** (500 mg, 25%) as a dark blue amorphous solid: TLC 0.60 (EtOAc/hexanes 2:3); IR (nujol) 1567, 1450, 1394, 1065, 730, 696 cm^{-1}; UV–vis (PhCl) λ max (log ε) 350 (4.56), 544 (4.10), 714 (4.38) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 3.44 (s, 24H), 5.32 (s, 16H), 7.16 (m, 24H), 7.32 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.7, 60.8, 126.9, 128.4, 128.9, 139.5, 140.5, 152.8; HRMS (FAB) *m/z* Calcd for $C_{80}H_{80}MgN_{16}$: $(M^{+\cdot})$, 1288.6602; found: $(M^{+\cdot})$, 1288.6912.

4.1.6. 2,3,7,8,12,13,17,18-Octa(diallylamino)porphyrazine (7c). Dry *n*-PrOH (22 mL), Mg turnings (68 mg, 2.8 mmol) and I_2 (1 crystal) were heated to reflux for 24 h. After cooling to room temperature, dinitrile **2c** (2 g, 7.5 mmol) in dry *n*-PrOH (5 mL) was added and reflux continued for 24 h. After cooling, the deep purple mixture was diluted with $CHCl_3$, filtered through Celite and the filtrate evaporated. AcOH (15 mL) was added and, after 0.5 h in the dark, the mixture was added to ice and H_2O (100 mL) and the pH adjusted to 7.5 with 1 M NaOH. The dark precipitate was collected by filtration and washed with H_2O. Chromatography (SiO_2, EtOAc/hexanes 1:19) gave porphyrazine **7c** (300 mg, 15%) as a dark purple pasty solid: TLC R_f 0.73 (EtOAc/hexanes 1:9); IR ($CHCl_3$) ν_{max} 3301, 1848, 1639, 1573, 1551, 1415, 1190, 1121, 993, 921, 860, 562 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 333 (4.67), 526 (4.47), 730 (4.36) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ −1.01 (2H, s), 4.90 (24H, d, J=6.0 Hz), 5.17 (16H, d, J=10.0 Hz), 5.37 (16H, d, J=17.0 Hz), 6.10–6.23 (16H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.0, 116.7, 136.3, 148.5; FABMS *m/z* 1075 $(M^{+\cdot})$, 1034.

4.1.7. 2,3,7,8,12,13,17,18-Octakis(allyl(benzyl)amino)-porphyrazine (7e). Dry *n*-PrOH (375 mL), Mg turnings (2.6 g, 109 mmol) and I_2 (1 crystal) were heated at reflux for 24 h. After cooling to room temperature, dinitrile **2e** (10 g, 27.2 mmol) in *n*-PrOH (20 mL) was added and the mixture heated at reflux for 36 h. After cooling to room temperature, the deep purple mixture was diluted with CH_2Cl_2 (300 mL), filtered through Celite and the filtrate evaporated. Chromatography (Al_2O_3 EtOAc/hexanes 5:95) gave porphyrazine **7e** (M=Mg) (2.0 g, 20%) as a purple solid, which was used without further purification. AcOH (20 mL) was added to porphyrazine **7c** (M=Mg) (570 mg, 0.38 mmol) and the mixture stirred at room temperature for 3 h. The blue-purple solution was slowly added to ice and H_2O (300 mL) and the pH adjusted to 7.5 using aqueous 2.0 M NaOH. The dark precipitate was filtered off and washed repeatedly with H_2O. Chromatography (SiO_2, EtOAc/hexanes 1:19) gave porphyrazine **7e** (M=2H) (460 mg, 82%) as a purple solid: TLC R_f 0.6 (Et_2O/hexanes 1:4); IR (CH_2Cl_2) ν_{max} 3304, 1644, 1572, 1548, 1494, 1452, 1414, 1297, 924, 873 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max} (log ε) 330 (4.75), 536 (4.59), and 734 (4.44) nm; ^1H NMR ($CDCl_3$, 270 MHz) δ −0.93 (2H, s, N*H*), 4.70 (16H, d, J=6.4 Hz), 5.09 (8H, dd, J=2.0, 10.0 Hz) 5.23 (8H, dd, J=2.0, 17.0 Hz), 5.34 (16H, s), 5.97–6.07 (8H, m), 7.10–7.18 (24H, m), 7.30–7.34 (16H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 54.9, 55.2, 117.1, 126.7, 128.2, 128.7, 136.0, 136.5, 139.7, 148.5; FABMS *m/z* 1475 $(M^{+\cdot})$, 1435, 1385. Anal. Calcd for $C_{96}H_{98}N_{16}$: C, 78.11; H, 6.70; N, 15.19. Found: C, 78.12; H, 6.71; N, 14.96.

4.1.8. (2,3,7,8,12,13,17,18-Octakis(dimethylamino)porphyrazinato)nickel(II) (8a). Porphyrazine **7a**[7] (60 mg, 0.09 mmol), anhydrous $Ni(OAc)_2$ (160 mg, 0.9 mmol), PhCl (15 mL) and DMF (5 mL) were heated to reflux with stirring overnight. After cooling to room temperature, the mixture was filtered through celite and the solids leached with Et_2O and $CHCl_3$. The filtrate was evaporated, dissolved in heptanes, re-evaporated and chromatographed (SiO_2 Et_2O). The colored band remaining on the silica was eluted with MeOH and evaporated. Size exclusion chromatography (Sephadex LH20 $CHCl_3$) gave **8a** (28 mg, 43%) as a black amorphous solid: TLC 0.84 (EtOAc/hexanes 3:2); IR (nujol) 1599, 1385, 1092 cm^{-1}; UV–vis (CH_2Cl_2) λ max (log ε) 325 (4.92) 360 (4.90), 561 (4.42), 704 (4.52) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 3.63 (s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.3, 138.5, 144.1; HRMS (FAB) *m/z* Calcd for

$C_{32}H_{48}N_{16}Ni$: $(M+H^+)$, 715.3680, $(M^{+\cdot})$, 714.3601; found: $(M+H^+)$, 715.3726, $(M^{+\cdot})$, 714.3708.

4.1.9. (2,3,7,8,12,13,17,18-Octakis(dibenzylamino)porphyrazinato)nickel(II) (8b). CF_3CO_2H (10 mL) was added to porphyrazine **6b**[5] (200 mg, 0.29 mmol), the mixture stirred at room temperature for 12 h and added to ice and the pH adjusted to 7.5 using aqueous NaOH (1.0 M). The dark precipitate was filtered off and chromatographed (SiO_2 EtOAc/hexane) to provide **7b** (170 mg, 86%) as a black amorphous solid: TLC 0.85 (EtOAc/hexanes 3:2); HRMS (FAB) *m/z* Calcd for $C_{128}H_{114}N_{16}$: $(M+H^+)$, 1875.9490, found: $(M+H^+)$, 1875.9456. The crude porphyrazine **7b** was used directly without further purification. The crude porphyrazine **7b** (160 mg, 0.085 mmol), anhydrous $Ni(OAc)_2$ (300 mg, 1.7 mmol), PhCl (10 mL) and DMF (10 mL) were heated to reflux with stirring for 12 h. After evaporation, the residue was dissolved in CH_2Cl_2 and filtered through celite. The filtrate was evaporated and chromatographed (SiO_2 EtOAc/hexanes) to give porphyrazine **8b** (98 mg, 59%) as a purple-black amorphous solid: TLC 0.63 (EtOAc/hexanes 2:3); IR (nujol) 1576, 1493, 1448, 765, 689 cm^{-1}; UV–vis (PhCl) λ max (log ε) 322 (4.71), 536 (3.95), 654 (4.04), 674 (4.00) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 4.1 (s, 32H), 7.10 (m, 32H), 7.25 (m, 48H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 57.5, 114.3, 120.5, 128.2, 129.1, 136.2; MS (FAB) *m/z* 1932 $(M^{+\cdot})$, 1841, 1749, 1737.

4.1.10. (2,3,7,8,12,13,17,18-Octakis(allyl(benzyl)amino)-porphyrazinato)nickel(II) (8e). Porphyrazine **7e** (100 mg, 0.034 mmol), anhydrous $Ni(OAc)_2$ (84.0 mg, 0.34 mmol), PhCl (7 mL) and DMF (2.3 mL) were heated at reflux with stirring for 18 h. After cooling to room temperature, the mixture was filtered through Celite, the solids leached with $CHCl_3$ and the filtrate evaporated. Chromatography (SiO_2, Et_2O/hexanes 1:25) gave porphyrazine **8e** (96 mg, 92%) as a purple solid: mp 112–114 °C; TLC R_f 0.50 (Et_2O/hexanes 1:9); IR ($CHCl_3$) ν_{max} 1576, 1511, 1493, 1438, 1320, 1186, 1123, 918, 698 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max} (log ε) 324 (4.72), 511 (4.53), and 688 (4.49) nm; ^1H NMR ($CDCl_3$, 270 MHz) δ 4.62 (16H, d, $J=6.0$ Hz), 5.07 (8H, dd, $J=2.0$, 10.0 Hz) 5.20 (8H, dd, $J=2.0$, 17.0 Hz), 5.31 (16H, s), 5.94–6.04 (8H, m), 7.11–7.34 (40H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.3, 55.6, 117.2, 126.8, 128.3, 128.7, 136.1, 138.0, 140.0, 143.7; FABMS *m/z* 1532 $(M+H)^+$, 1491, 1441; HRFABMS *m/z* Calcd for $C_{96}H_{96}N_{16}Ni$: $(M^{+\cdot})$, 1530.7357; found: $(M^{+\cdot})$, 1530.7359. Anal. Calcd for $C_{96}H_{96}N_{16}Ni$: C, 75.23; H, 6.31; N, 14.62. Found: C, 75.13; H, 6.45; N, 14.43.

4.1.11. 1-Iodo-8-tetrahydropyranyloxy-3,6-dioxaoctane (9b). I_2 (15.5 g, 61 mmol) was slowly added rapidly with stirring to $THPO(CH_2CH_2O)_2CH_2CH_2OH$[38] (10 g, 43 mmol), Ph_3P (14.6 g, 55.5 mmol), and imidazole (4.0 g, 58.5 mmol) in MeCN (50 mL) and Et_2O (75 mL) at 0 °C. The brown-black slurry was stirred at 0 °C for 1.5 h, the mixture was diluted with Et_2O (900 mL), filtered, and washed with saturated aqueous $Na_2S_2O_3$ (3×250 mL), saturated aqueous $CuSO_4$ (3×250 mL), H_2O (3×250 mL), dried ($MgSO_4$: K_2CO_3 1:1), filtered, and rotary evaporated to give a white oily solid. Et_2O was added (100 mL), the suspension was filtered and the filtrate was rotary evaporated to give another white oily solid. This procedure was repeated with Et_2O (50 mL) to give a clear slightly yellow oil. Chromatography (SiO_2, EtOAc/hexanes 1:3) gave iodide **9b** (11.8 g, 80%) as a clear yellow oil: TLC R_f 0.35 (EtOAc/hexanes 1:3); IR (film) ν_{max} 1453, 1440, 1352, 1261, 1200, 1124, 1077, 1034, 988, 872, 814, 618 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.49–1.74 (6H, m), 3.24 (2H, t, $J=7$ Hz), 3.48–3.88 (14H, m), and 4.60–4.63 (1H, m); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 2.9, 19.4, 25.4, 30.5, 62.1, 66.6, 70.2, 71.9, 98.9; MS (CI, NH_3) *m/z* 362 $(M+NH_4)^+$, 345 $(M+H)^+$, 278, 261; HRMS (CI, NH_3) *m/z* Calcd for $C_{11}H_{22}O_4I$: $(M+H)^+$, 345.0563; found: $(M+H)^+$, 345.0559.

4.1.12. 2,3-Di(benzyl(2-tetrahydropyranyloxyethyl)-amino)-2-butene-1,4-dinitrile (10a). Dinitrile **5** (250 mg, 0.87 mmol) and $THPOCH_2CH_2I$ **9a**[37] (890 mg, 3.5 mmol) in dry DMF (2.5 mL) was added over 1 h to a rapidly stirring suspension of Cs_2CO_3 (620 mg, 1.9 mmol) in dry DMF (2.5 mL). After the addition was complete, the mixture was heated at 40 °C for 5 h and allowed to cool to room temperature. After 12 h, the mixture was poured into ice and H_2O (50 mL) and extracted with EtOAc (2× 20 mL). The combined organic layers were washed with H_2O (2×30 mL), brine (1×20 mL), dried ($MgSO_4$: K_2CO_3 1:1), and the solvent evaporated. Chromatography (SiO_2, EtOAc/hexanes 1:3) gave dinitrile **10a** (390 mg, 83%) as a mixture of E and Z isomers as a clear amber oil: TLC R_f 0.29, 0.42 (EtOAc/hexanes 1:3); IR (film) ν_{max} 2200, 1563, 1495, 1453, 1390, 1348, 1202, 1128, 1075, 1035, 976, 751, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.46–1.85 (12H, m), 3.25–3.53 (4H, m), 3.75–3.85 (4H, m), 4.30–4.66 (4H, m), 7.17–7.35 (10H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.4, 25.4, 30.6, 50.6, 55.9, 62.3, 65.0, 99.0, 115.2, 116.9, 127.8, 128.5, 128.8, 136.9; MS (CI, NH_3) *m/z* 545 $(M+H)^+$, 461 $(M\text{-}THP+H)^+$; HRMS (CI, NH_3) *m/z* Calcd for $C_{32}H_{41}N_4O_4$: $(M+H)^+$, 545.3128; found: $(M+H)^+$, 545.3102. Anal. Calcd for $C_{32}H_{40}N_4O_4$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.65; H, 7.26; N, 10.04.

4.1.13. 2,3-Di(benzyl(8-tetrahydropyranyloxy-3,6-dioxa-octyl)amino)-2-butene-1,4-dinitrile (10b). Following the same procedure as for the preparation of dinitrile **10a**, dinitrile **5** and $THPO(CH_2CH_2O)_2CH_2CH_2I$ **9b** gave dinitrile **10b** (6.98 g, 91%) as a mixture of E and Z isomers as a clear amber oil: TLC R_f 0.68 (EtOAc); IR (film) ν_{max} 2185, 1587, 1494, 1453, 1125, 1076, 1035, 988, 873, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.46–1.84 (12H, m), 3.19–3.27 (4H, m), 3.45–3.68 (16H, m), 3.81–3.90 (4H, m), 4.27, 4.38 (4H, 2 s), 4.59–4.62 (2H, m), 7.15–7.35 (10H, m); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 19.5, 25.4, 30.6, 50.6, 52.8, 55.9, 58.7, 62.20, 62.25, 66.6, 68.9, 69.3, 70.51, 70.55, 98.9, 114.1, 115.0, 116.7, 119.3, 127.8, 128.4, 128.6, 128.65, 128.72, 136.3, 136.9; MS (CI, NH_3) *m/z* 721 $(M+H)^+$, 634, 553; HRMS (CI, NH_3) *m/z* Calcd for $C_{40}H_{60}N_5O_8$: $(M+NH_4)^+$, 738.4442; found: $(M+NH_4)^+$, 738.4495. Anal. Calcd for $C_{40}H_{60}N_5O_8$: C, 66.64; H, 7.83; N, 7.77. Found: C, 66.57; H, 7.53; N, 7.66.

4.1.14. 2,3-Di(benzyl(3,6,9-trioxadecyl)amino)-2-butene-1,4-dinitrile (10c). Following the same procedure as for the preparation of dinitrile **10a**, dinitrile **5** and $Me(OCH_2CH_2)_3I$ **9c**[37] gave dinitrile **10c** (5.0 g, 83%) as a clear amber oil:

TLC R_f 0.11 (EtOAc/hexanes 1:1); IR (film) ν_{max} 2197, 1584, 1493, 1453, 1111, 747, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.27 (4H, t, $J=5.2$ Hz), 3.37 (6H, s), 3.49 (4H, t, $J=5.2$ Hz), 3.50–3.60 (16H, m), 4.40 (4H, s), 7.19 (6H, m), 7.29 (4H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 50.6, 56.0, 59.0, 69.0, 70.5, 70.58, 70.61, 72.0, 115.1, 116.8, 127.8, 128.4, 128.8, 137.0; MS (CI, NH_3) *m/z* 581 $(M+H)^+$, 491; HRMS (CI, NH_3) *m/z* Calcd for $C_{32}H_{45}N_4O_6$: $(M+H)^+$, 581.3339, found: $(M+H)^+$, 581.3366. Anal. Calcd for $C_{32}H_{44}N_4O_6$: C, 66.18; H, 7.64; N, 9.65. Found: C, 65.94; H, 7.34; N, 9.64.

4.1.15. 2,3,7,8,12,13,17,18-Octakis(benzyl(2-tetrahydropyranyloxyethyl)amino)-porphyrazinato)magnesium(II) (11a). Dry *n*-BuOH (2.5 mL), I_2 (1 crystal) and Mg turnings (0.11 g, 4.6 mmol) were heated at reflux for 24 h. After cooling to room temperature, dinitrile **10a** (250 mg, 0.46 mmol) in dry *n*-BuOH (2.5 mL) was added and the suspension heated at reflux for 24 h. After cooling to room temperature, the purple-black suspension was diluted with $CHCl_3$ (10 mL), filtered through Celite, and rotary evaporated. Chromatography (SiO_2, EtOAc/hexanes 1:3 to 2:3) gave porphyrazine **11a** (36 mg, 14%) as a purple oil: TLC R_f 0.30 (EtOAc/hexanes 1:2); IR ($CHCl_3$) ν_{max} 1601, 1556, 1493, 1452, 1285, 1122, 1070, 1032, 975, 733, 698 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 347sh, 359 (4.77), 516sh, 569 (4.38), 713 (4.58) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.88–1.56 (48H, m), 3.20–4.70 (56H, m), 5.45 (16H, m), 7.08–7.92 (40H, m); FABMS *m/z* 2201 $(M+H)^+$, 2110. Anal. Calcd for $C_{128}H_{158}MgN_{16}O_{16}$: C, 69.85; H, 7.24; N, 10.18. Found: C, 69.57; H, 7.00; N, 10.08.

4.1.16. (2,3,7,8,12,13,17,18-Octakis(benzyl(8-tetrahydropyranyloxy-3,6-dioxa-octyl)amino)porphyrazinato)magnesium(II) (11b). Mg turnings (1.35 g, 35.6 mmol) were heated to 300 °C under vacuum, allowed to cool to room temperature under dry N_2. Dry *n*-PrOH (250 mL) and I_2 (1 crystal) were added and the suspension heated at reflux for 24 h. After cooling to room temperature, dinitrile **10b** (4.0 g, 5.6 mmol) in dry *n*-PrOH (10 mL) was added and the suspension heated at reflux for 60 h. After cooling to room temperature, the purple-black suspension was diluted with $CHCl_3$ (200 mL), filtered through Celite, and rotary evaporated. The dark residue was dissolved in $CHCl_3$ (50 mL), filtered through Celite to remove the remaining particulates, and rotary evaporated. Chromatography (SiO_2, EtOAc/hexanes 1:2 to EtOAc/MeOH 9:1) gave porphyrazine **11b** (320 mg, 8%) as a purple oil: TLC R_f 0.32 (EtOAc/MeOH 95:5); IR (film) ν_{max} 1561, 1555, 1452, 1351, 1285, 1200, 1122, 1076, 1034, 987, 703 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max} (log ε) 333 (4.69), 365 (4.75), 574 (4.47), and 711 (4.57) nm; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.08–1.62 (48H, m), 2.77–2.85 (8H, m), 3.12–3.19 (8H, m), 3.21–3.50 (64H, m), 3.67–3.70 (16H, m), 3.89–3.91 (8H, m), 4.51–4.60 (16H, m), 5.38 (16H, br s,), 7.05–7.09 (24H, m), 7.40–7.43 (16H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.9, 24.9, 30.0, 51.2, 55.5, 61.4, 66.3, 70.0, 70.17, 70.23, 70.4, 98.2, 126.4, 128.0, 128.3, 137.1, 140.9, 151.5; FABMS *m/z* 2908 $(M+H)^+$, 2818. Anal. Calcd for $C_{160}H_{224}MgN_{16}O_{32}$: C, 66.09; H, 7.76; N, 7.71. Found: C, 65.79; H, 7.46; N, 7.56.

4.1.17. (2,3,7,8,12,13,17,18-Octakis(benzyl(3,6,9trioxadecyl)amino)-porphyrazinato)magnesium(II) (11c). Mg turnings (2.09 g, 86.2 mmol) were heated to 300 °C under vacuum, allowed to cool to room temperature under dry N_2. Dry *n*-PrOH (450 mL) and I_2 (1 crystal) were added and the suspension heated at reflux for 24 h. After cooling to room temperature, dinitrile **10c** (5.0 g, 8.6 mmol) in dry *n*-PrOH (10 mL) was added and the suspension heated at reflux for 60 h. After cooling to room temperature, the purple-black suspension was diluted with $CHCl_3$ (400 mL), filtered through Celite, and rotary evaporated. $CHCl_3$ (100 mL) was added, and the suspension was filtered to remove the remaining fine solids. Rotary evaporation and chromatography (SiO_2 EtOAc/hexanes 1:1 to EtOAc/MeOH 95:5) gave porphyrazine **11c** (400 mg, 8%) as a purple oil: TLC R_f 0.5 ($CHCl_3$: Me_2CO 7:3); IR (film) ν_{max} 1559, 1452, 1290, 1195, 1110, 1029, 850, 736, 701 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 330 (4.63), 365 (4.66), 577 (4.36), and 708 (4.51) nm; ^1H NMR ($CDCl_3$, 270 MHz) δ 2.92 (24H, s), 3.01–3.04 (16H, m), 3.13–3.17 (16H, m), 3.19–3.23 (16H, m), 3.31–3.35 (16H, m), 3.70–3.74 (16H, m), 4.51–4.54 (16H, m), 5.40 (16H, s), 7.08–7.11 (24H, m), 7.42–7.45 (16H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 51.1, 56.1, 58.4, 69.9, 70.2, 70.3, 70.4, 71.4, 126.4, 128.1, 128.5, 137.2, 140.9, 151.9; FABMS *m/z* 2347 $(M+H)^+$, and 2256. Anal. Calcd for $C_{128}H_{176}MgN_{16}O_{24}$: C, 65.50; H, 7.56; N, 9.55. Found: C, 65.28; H, 7.39; N, 9.32.

4.1.18. (2,3,7,8,12,13,17,18-Octakis(benzyl(2-hydroxyethyl)amino)porphyrazine) (12a). AcOH (4 drops) was added with stirring to porphyrazine **11a** (30 mg, 14 μmol) in $CHCl_3$ (2 mL) and MeOH (0.5 mL) at room temperature. After 1 h and 2.5 h respectively, concd HCl (1 drop) and 1 M NaOH (1.5 mL) were added and the layers separated. The aqueous layer was extracted with $CHCl_3$ (1×10 mL) and the combined organic extracts rotary evaporated. Chromatography (SiO_2, $CHCl_3$/MeOH 95:5 to 90:10) gave porphyrazine **12a** (17 mg, 80%) as a purple solid: TLC R_f 0.45 ($CHCl_3$/MeOH 90:10); IR ($CHCl_3$) ν_{max} 3336, 3297, 1568, 1548, 1494, 1453, 1378, 1310, 1174, 1135, 1060, 741, 699 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 335 (4.63), 556 (4.32), 725 (4.32) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.09 (2H, s), 3.65 (16H, br s), 3.73 (16H, br s), 5.33 (16H, s), 6.13 (8H, br s), 7.12–7.28 (40H, m); FABMS *m/z* 1508 $(M+H)^+$, 1417, 1326.

4.1.19. (2,3,7,8,12,13,17,18-Octakis(benzyl(8-hydroxy-3,6-dioxaoctyl)amino)-porphyrazine) (12b). AcOH (4 drops) was added with stirring to porphyrazine **11b** (30 mg, 10.3 μmol) in $CHCl_3$ (2 mL) and MeOH (0.5 mL). After 1 h, conc HCl (1 drop) was added and stirring continued for 1.5 h. 1 M NaOH (1.5 mL) was added, the layers were separated, the aqueous layer was extracted with $CHCl_3$ (1×10 mL) and the combined organic extracts rotary evaporated. Gel permeation chromatography (Sephadex LH20 $CHCl_3$) gave porphyrazine **12b** (18 mg, 80%) as a purple oil: TLC R_f 0.75 (MeOH/MeCN 1:1; Whatman $MKC_{18}F$ Reversed Phase TLC Plates); IR (film) ν_{max} 3412, 3303, 1551, 1492, 1449, 1130, 1074, 742, 701 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 328 (4.62), 348sh, 556 (4.53), 661sh, 740sh nm; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.94 (2H, s) 3.28–3.83 (80H, m), 4.42 (16H, br s), 5.33 (16H, s), 7.08–7.35 (40H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.8, 55.9, 61.5, 70.15, 70.23, 72.4, 126.7, 128.2, 128.5, 136.0, 140.0, 148.0; FABMS *m/z* 2212 $(M^{+\cdot})$, 2122, 1106

$(M)^{2+}$. Anal. Calcd for $C_{120}H_{162}N_{16}O_{24}\cdot CHCl_3$: C, 62.32; H, 7.04; N, 9.61. Found: C, 62.50; H, 6.90; N, 9.41.

4.1.20. 2,3,7,8,12,13,17,18-Octakis(benzyl(3,6,9-trioxadecyl)amino)porphyrazine (12c). AcOH (2.5 mL) was added to porphyrazine **11c** (M=Mg) (35 mg, 15 μmol) under N_2 in the dark. After 2 h, the purple solution was slowly added to ice and H_2O (100 mL) and neutralized with 1 M NaOH, extracted with $CHCl_3$ (3×20 mL), and dried ($MgSO_4$). Rotary evaporation and chromatography (SiO_2 $CHCl_3$: Me_2CO 4:1) gave porphyrazine **12c** (30 mg, 86%) as a viscous purple oil: TLC R_f 0.5 ($CHCl_3$: Me_2CO 7:3); IR ($CHCl_3$) ν_{max} 3301, 1571, 1550, 1495, 1452, 1292, 1248, 1105, 1029, 850, 715, 700 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 327 (4.60), 356 (4.60), 556 (4.60), 667sh, and 741sh nm; ^1H NMR ($CDCl_3$, 270 MHz) δ −1.05 (2H, s), 3.22 (24H, s), 3.24–3.34 (64H, m), 3.59–3.64 (16H, m), 4.34–4.40 (16H, m), 5.29 (16H, s), 7.04–7.11 (24H, m), 7.29–7.36 (16H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 50.9, 55.2, 58.8, 70.1, 70.2, 71.7, 126.6, 128.1, 128.5, 136.0, 140.2, 148.0; FABMS *m/z* 2323 $(M+H)^+$. Anal. Calcd for $C_{128}H_{178}N_{16}O_{24}$: C, 66.13; H, 7.72; N, 9.64. Found: C, 65.88; H, 7.63; N, 9.66.

4.1.21. (2,3,7,8,12,13,17,18-Octakis(benzyl(3,6,9-trioxadecyl)amino)-porphyrazinato)nickel(II). Porphyrazine **12c** (M=2H) (15 mg, 6.5 μmol) and $Ni(OAc)_2$ (15 mg, 65 μmol) in DMF (1 mL) and PhCl (2 mL) were heated at 100 °C for 4 h. After allowing to cool to room temperature, the dark purple solution was filtered through Celite, rotary evaporated and chromatographed (SiO_2 $CHCl_3$: Me_2CO 4:1) to yield the nickel(II) porphyrazine (13 mg, 84%) as a viscous purple oil: TLC R_f 0.40 ($CHCl_3$: Me_2CO 8:2); IR (film) ν_{max} 1578, 1513, 1494, 1449, 1351, 1322, 1250, 1195, 1111, 1030, 851, 745, 701 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 312 (4.68), 379sh, 532 (4.46), and 680 (4.38) nm; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.21 (24H, s), 3.26–3.28 (64H, m), 3.63 (16H, s), 7.09–7.17 (24H, m), 7.35–7.38 (16H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 51.0, 56.0, 58.9, 70.2, 70.26, 70.30, 70.7, 126.6, 128.2, 128.5, 137.3, 140.3, 143.3; FABMS *m/z* 2381 $(M^{+\cdot})$, 2290. Anal. Calcd for $C_{128}H_{176}N_{16}O_{24}Ni$: C, 64.55; H, 7.45; N, 9.41. Found: C, 64.73; H, 7.26; N, 9.18.

4.1.22. *N*-Isopropylformimidoyl cyanide (19).[43] Calcium hypochlorite (21.5 g, 0.09 mol, 60%) and anhydrous $CaCl_2$ (1.6 g, 0.015 mol) were added to (isopropylamino)acetonitrile **17**[43,56] (8.7 g, 0.09 mol) in CH_2Cl_2 (200 mL). The mixture was stirred for 2 days at ambient temperature, filtered, and the filtrate was heated to reflux for 2 days in the presence of powdered calcium hydroxide (13.0 g, 0.18 mol) and anhydrous $CaCl_2$ (1.6 g, 0.015 mol) until the *N*-chloro-*N*-isopropylaminoacetonitrile **18** was not detected by GC/MS. The mixture was filtered, rotary evaporated and distilled to give cyanide **19** (4.2 g, 64%) as a colorless oil (*Z*/*E* 64:36): bp 60 °C /20 mm; IR (film) ν_{max} 1620, 1465, 1384, 1366, 1143 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 1H, *E*), 7.28 (s, 1H, *Z*), 4.07 (heptet, *J*=6.3 Hz, 1H, *Z*), 3.60 (heptet, *J*=6.3 Hz, 1H, *E*), 1.25 (d, *J*=6.3 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.5 (*E*), 128.9 (*Z*), 115.0 (*Z*), 108.0 (CN, *E*), 63.4 (*C*HMe$_2$, *E*), 60.5 (*C*HMe$_2$, *Z*), 23.2; MS (EI) *m/z* 96 $(M^{+\cdot})$. Alternatively, to a preheated (55 °C) suspension of *N*-chlorosuccinimide (285 mg, 2.1 mmol) in CCl_4 (5 mL), *N*- isopropylaminoacetonitrile **17** (210 mg, 2.1 mmol) in CCl_4 (1 mL) was added dropwise. After 5 min the reaction mixture was allowed to cool to ambient temperature. The suspension was filtered, and the filtrate was heated to reflux for 6 h in the presence of powdered calcium hydroxide (316 mg, 4.3 mmol) and anhydrous $CaCl_2$ (40 mg, 0.4 mmol). Filtration, evaporation and distillation of the solvent gave cyanide **19** (184 mg, 90%) as a colorless oil.

4.1.23. *N*,*N*′-Diisopropyl-*N*,*N*′-di-((*tert*-butyloxycarbonyl)methyl)diamino-maleonitrile (21). $SnCl_4$ (12 mL, 26.6 g, 0.102 mol) in dry PhH (100 mL) was added over 1 h to *N*-isopropylformimidoyl cyanide **19** (8.2 g, 0.09 mol) in dry PhH (50 mL), at 0 °C.[43] The mixture was stirred overnight at 20 °C. H_2O (200 mL) and Et_2O (300 mL) were added and the organic layer separated. The organic phase was washed with aqueous $NaHCO_3$ (200 mL) and H_2O (200 mL), dried ($MgSO_4$) and rotary evaporated. Chromatography (Al_2O_3, hexanes/EtOAc 7:3) followed by sublimation (80 °C/20 mm) gave *N*,*N*′-diisopropyldiaminomaleonitrile **20** (5.2 g, 63%) as bright yellow crystals (2 isomers, *Z*/*E* 9:1): mp 74 °C; R_f 0.39 (hexanes/EtOAc 7:3); IR (film) ν_{max} 3361, 2205, 1603, 1465, 1366, 1178, 1126 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.20 (heptet, *J*=6.3 Hz, 2H, CH, *E*), 3.54 (heptet, *J*=6.3 Hz, 2H, CH, *Z*), 3.28 (bs, 2H), 1.36 (d, *J*=6.3 Hz, 12H, *E*), 1.18 (d, *J*=6.3 Hz, 12H, *Z*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 114.7, 113.0, 48.1, 23.5; MS (EI) *m/z* 192 $(M^{+\cdot})$. The dinitrile **20** was used directly without further purification. NaH (44 mg, 1.1 mmol, 60% dispersion in mineral oil, 10% excess) was added rapidly to dinitrile **20** (96 mg, 0.5 mmol) in DMF (10 mL) at −10 °C. After 2 h, *t*-butyl bromoacetate (0.29 mL, 2 mmol) in DMF (10 mL) was added to the dark green solution, which was stirred at −10 °C for 2 h, allowed to warm up to 20 °C, poured onto ice (50 mL) and extracted with Et_2O (3×50 mL). The combined extracts were dried ($MgSO_4$), rotary evaporated and chromatographed (SiO_2 hexanes/EtOAc 9:1) to give dinitrile **21** (177 mg, 84%) as yellow crystals: mp 78 °C (EtOAc); R_f 0.6 (hexanes/EtOAc 7:3); IR (film) ν_{max} 2203, 1740, 1561, 1461, 1370, 1226, 1154 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.82–3.79 (m, 6H, CH), 1.48 (s, 18H), 1.16 (d, *J*=6.6 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 117.4, 115.2, 82.1, 52.2, 46.7, 28.0, 20.6; MS (CI, NH_3) *m/z* 438 $(M+NH_4)^+$, 421 $(M+H)^+$, 420 $(M^{+\cdot})$. Anal. Calcd for $C_{22}H_{36}N_4O_4$: C, 62.83; H, 8.63; N, 13.32. Found: C, 63.10; H, 8.51; N 13.43.

4.1.24. 1-((*N*-Cyanomethyl)aminomethyl)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane (23). $ClCH_2CN$ (2.6 mL, 3.1 g, 0.40 mol) in Et_2O (20 mL) was added dropwise to 1-(aminomethyl)-4-methyl-2,6,7-trioxabicyclo[2,2,2]-octane **22**[57] (6.4 g, 0.40 mol) and Et_3N (6.2 mL, 4.5 g, 0.45 mol) in Et_2O (300 mL) at −10 °C. After stirring overnight at 20 °C, rotary evaporation and chromatography (Al_2O_3 hexanes/EtOAc 7:3) gave nitrile **23** (4.4 g, 55%) as a white solid: mp 31 °C; R_f 0.35 (hexanes/EtOAc 1:1); IR (film) ν_{max} 3347, 2235, 1723, 1472, 1405, 1356, 1286, 1193, 1148, 1115, 1052, 989, 935, 882, 749 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.93 (s, 6H), 3.68 (s, 2H), 2.89 (s, 2H), 1.71 (s, 1H), 0.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 117.9, 107.4, 72.5, 52.4, 37.1, 30.5, 14.3; MS (CI, NH_3) *m/z*

199 $(M+H)^+$. Anal. Calcd for $C_9H_{14}N_2O_3$: C, 54.53; H, 7.12; N, 14.13. Found: C, 54.83; H, 7.02; N, 13.92.

4.1.25. 1-(*N*-Chloro-(*N*-cyanomethyl)aminomethyl)-4-methyl-2,6,7-trioxabicyclo[2,2,2]octane (24). Amine **23** (0.6 g, 3 mmol) in CCl_4 (10 mL) was heated to reflux with calcium hypochlorite (0.72 g, 5.1 mmol, 60%) and anhydrous $CaCl_2$ (55 mg, 0.5 mmol) for 30 min. The suspension was filtered and the solvent evaporated to give chloramine **24** (0.6 g, 86%) as a white solid: mp 79 °C; IR (CCl_4) ν_{max} 1703, 1398, 1354, 1281, 1205, 1101, 1059, 1024, 993, 976, 933, 889 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.13 (s, 2H), 3.91 (s, 6H), 3.34 (s, 2H), 0.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.7, 107.0, 72.5, 65.1, 51.2, 30.6, 14.4; MS (CI, NH_3) *m/z* 233 $(M^{+\cdot})$.

4.1.26. 2,3-Dipyridyl-7,8,12,13,17,18-hexakis(dimethylamino)porphyrazine (27). Mg (19.5 mg, 0.8 mmol), *n*-BuOH (10 mL) and I_2 (3 small crystals) were heated to reflux under N_2 for 24 h. After cooling, dinitrile **2a** (180 mg, 1.09 mmol) and dipyridylmaleonitrile **25**[47] (36 mg, 0.15 mmol) were added, the mixture was heated at 110 °C for 12 h under N_2, filtered (Celite) and the solids washed with CH_2Cl_2. Rotary evaporation and chromatography (SiO_2 hexanes/EtOAc 9:1; $CHCl_3$/MeOH 9:1) gave the crude Mg-porphyrazine **26** as a blue solid: R_f 0.2 ($CHCl_3$/MeOH 9:1); MS (FAB) *m/z* 749 $(M^{+\cdot})$; HRMS (FAB) Calcd for $C_{38}H_{45}N_{16}Mg$: $(M+H)^+$, 749.3863; found: $(M+H)^+$, 749.3866. A small amount of a mixture of the *cis*- and *trans* tetrapyridyl-tetrakis(dimethylamino)porphyrazines were isolated by chromatography (SiO_2 hexanes/EtOAc 9:1; $CHCl_3$/MeOH 9:1; $CHCl_3$/MeOH 6:1) of the crude product obtained from the previous reaction, as confirmed by mass spectroscopy: MS (FAB) *m/z* 817 $(M^{+\cdot})$; HRMS (FAB) Calcd for $C_{44}H_{41}N_{16}Mg$: $(M+H)^+$, 817.3551; found: $(M+H)^+$, 817.3510. Porphyrazine **26** was demetallated without any further purification. CF_3CO_2H (7 mL) was added to the partially purified porphyrazine **26** (87 mg, 0.116 mmol), the mixture stirred at 20 °C for 30 min under N_2 and poured onto ice and H_2O (50 mL) and the suspension neutralized with 1 M NaOH. The solid was collected by filtration, redissolved in CH_2Cl_2, dried ($MgSO_4$), rotary evaporated and chromatographed (SiO_2 EtOAc/MeOH 9:1) to give porphyrazine **27** (25 mg, 30%) as a dark purple solid: mp >350 °C; R_f 0.4 (EtOAc/MeOH 9:1); IR (CH_2Cl_2) 3299, 1596, 1500, 1388, 1321, 1199, 1081, 1058, 869, 748 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max} (log ε) 339 (4.49), 539 (4.38) nm; ^1H NMR (300 MHz, $CDCl_3$) δ 3.48 (s, 12H), 3.72 (s, 12H), 3.9 (s, 12H), 7.89 (d, $J=5.8$ Hz), 8.72 (d, $J=5.8$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.6, 45.0, 45.7, 126.6, 127.1, 135.6, 138.9, 140.2, 143.9, 145.4, 149.7, 149.9, 151.0, 163.6; MS (FAB) *m/z* 727 $(M^{+\cdot})$; HRMS (FAB) calc for $C_{38}H_{47}N_{16}$: $(M+H)^+$, 727.4169; found: $(M+H)^+$, 727.4134. Anal. Calcd for $C_{38}H_{46}N_{16}$: C, 62.79; H, 6.38; N, 30.83. Found: C, 62.87; H, 6.38; N, 30.65.

4.1.27. (2,3-Dipyridyl-7,8,12,13,17,18-hexa(dimethylamino)porphyrazinato)-zinc(II) (28). Porphyrazine **27** (6.2 mg, 0.008 mmol) and anhydrous $Zn(OAc)_2$ (1.7 mg, 0.009 mmol) in dry DMF (10 mL) were heated at 100 °C for 16 h under N_2. The mixture was allowed to cool, filtered (Celite) and the solids washed with CH_2Cl_2. Rotary evaporation and chromatography (SiO_2 EtOAc/MeOH 9:1; EtOAc/MeOH 7:1) gave the zinc porphyrazine **28** (4 mg, 63%) as a dark blue solid: R_f 0.2 (EtOAc/MeOH 9:1); IR (CH_2Cl_2) 1650, 1608, 1380, 1313, 1097, 1018, 873 cm^{-1}; UV–vis (CH_2Cl_2) λ_{max} (log ε) 357 (4.77), 593 (4.46) nm; ^1H NMR (270 MHz, pyridine-d_5) δ 3.60 (s, 12H), 3.80 (s, 12H), 3.89 (s, 12H), 8.16 (d, $J=5.9$ Hz, 4H), 9.01 (d, $J=5.9$ Hz, 4H); ^{13}C NMR (67.5 MHz, pyridine-d_5) δ 43.4, 44.5, 45.5, 127.3, 129.0, 143.8, 146.8, 152.0, 160.0, 161.7; MS (FAB) *m/z* 789 $(M^{+\cdot})$; HRMS (FAB) calc for $C_{38}H_{45}N_{16}Zn$: $(M+H)^+$, 789.3304; found: $(M+H)^+$, 789.3275.

4.1.28. 2-Methoxy-4-pyridylacetonitrile (30). Finely powdered NaCN (0.46 g, 9.4 mmol) was added to 4-(chloromethyl)-2-methoxypyridine **29** (0.98 g, 6.2 mmol) in dry DMSO (50 mL), the mixture stirred for 8 h, diluted with H_2O (300 mL) and extracted with Et_2O (8×100 mL). The combined extracts were dried ($MgSO_4$), rotary evaporated and chromatographed (deactivated SiO_2 hexanes/EtOAc 7:3) to give nitrile **30** (0.74 g, 76%), as a white solid: mp 106 °C ($CHCl_3$); R_f 0.23 (deactivated silica, hexanes/EtOAc 7:3); IR (DRIFTS) ν_{max} 2248, 1939, 1614, 1563, 1486, 1455, 1401, 1324, 1221, 1184, 1152, 1040, 928, 813, 768 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, $J=5.3$ Hz, 1H), 6.85 (dd, $J=5.3$, 1.3 Hz, 1H), 6.74 (d, $J=1.3$ Hz, 1H), 3.95 (s, 3H), 3.71 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 147.8, 141.5, 116.3, 116.0, 110.1, 53.7, 23.1; MS (CI, NH_3) *m/z* 149 $(M+H)^+$. Anal. Calcd for $C_8H_8N_2O$: C, 64.85; H, 5.44; N, 18.91. Found: C, 64.90; H, 5.57; N, 19.02.

4.1.29. 2,3-Di-(4-(2-methoxy)pyridyl)fumaronitrile (31). I_2 (1.8 g, 7.15 mmol) was added to nitrile **30** (0.58 g, 3.9 mmol) in MeOH (10 mL), the mixture heated to reflux under N_2 for 1 h, cooled to room temperature and NaOMe, from Na (0.2 g, 8.6 mmol) in MeOH (5 mL) was added dropwise. The mixture was heated to reflux for 3 h, during which time a brown precipitate formed, allowed to cool, the solid filtered off and redissolved in $CHCl_3$. The solution was filtered, rotary evaporated and the residue recrystallized from $CHCl_3$ to give dinitrile **31** (0.22 g, 38%) as a light brown solid: mp 167 °C ($CHCl_3$); R_f 0.63 (deactivated silica, hexanes/EtOAc 1:1); IR (film) ν_{max} 2222, 1602, 1550, 1483, 1451, 1397, 1325, 1198, 1111, 1041, 867, 822, 787 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, $J=5.5$ Hz, 2H), 7.27 (dd, $J=5.5$, 1.5 Hz, 2H), 7.15 (d, $J=1.5$ Hz, 2H), 4.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 148.7, 140.9, 125.8, 114.9, 114.8, 110.5, 54.1; MS (CI, NH_3) *m/z* 293 $(M+H)^+$. Anal. Calcd for $C_{16}H_{12}N_4O_2$: C, 65.75; H, 4.14; N, 19.17. Found: C, 66.08; H, 4.36; N, 19.39.

4.1.30. 2,2′-Bipyridyl-4-acetonitrile (33). Finely powdered KCN (0.26 g, 4 mmol) was added to 4-chloromethyl-2,2′-bipyridine **32**[51] (0.1 g, 0.5 mmol) and 18-crown-6 (26 mg, 0.01 mmol) in CH_3CN (10 mL), the mixture stirred for 4 h, diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (4× 75 mL). The combined extracts were dried ($MgSO_4$), rotary evaporated, and rapidly chromatographed (deactivated SiO_2 hexanes/EtOAc 7:3) to give nitrile **33** (90 mg, 92%) as a white solid: mp 105 °C (EtOAc); R_f 0.9 (deactivated silica, hexanes/EtOAc 7:3); IR (DRIFTS) ν_{max} 2246, 1604, 1586, 1561, 1462, 1401, 1253, 1067, 992, 932, 853, 788, 751 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.74–8.71 (m, 2H), 8.50–8.47

(m, 2H), 7.92 (td, J=7.8, 1.8 Hz, 1H), 7.44–7.40 (m, 2H), 3.90 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 155.1, 150.0, 149.2, 140.0, 137.1, 124.2, 122.7, 121.3, 120.3, 116.5, 23.4; MS (CI, NH_3) m/z 212 $(M+NH_4)^+$, 196 $(M+H)^+$. Anal. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52. Found: C, 74.17; H, 4.79; N, 21.45.

4.1.31. 2,3-Di-(4-(2,2′-bipyridyl))fumaronitrile (34). Following the same procedure as for the preparation of dinitrile **31**, nitrile **33** gave dinitrile **34** (0.41 g, 70%) as a white solid: mp 241°C ($CHCl_3$); IR (DRIFTS) ν_{max} 2222, 1583, 1547, 1461, 1391, 1253, 1211, 1111, 1072, 993, 920, 846, 791 cm^{-1}; UV/vis λ_{max} (log ε) 286 (4.68); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.94 (d, J=5.0 Hz, 2H), 8.93 (s, 2H), 8.75 (d, J=5.1 Hz, 2H), 8.49 (d, J=7.8 Hz, 2H), 7.90 (td, J=7.8, 1.6 Hz, 2H), 7.74 (dd, J=5.1, 2.0 Hz, 2H), 7.41 (ddd, J=7.8, 5.0, 1.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 154.5, 150.5, 149.5, 139.7, 137.2, 126.5, 124.6, 121.6, 121.4, 119.9, 115.0; MS (CI, NH_3) m/z 387 $(M+H)^+$. Anal. Calcd for $C_{24}H_{14}N_6$: C, 74.60; H, 3.65; N, 21.75. Found: C, 74.61; H, 3.73; N, 21.85.

4.1.32. 2,3,7,8,12,13,17,18-Octakis((2-(2-pyridyl)-4-pyridyl)porphyrazine (37). Na (17 mg, 0.75 mmol) was added to dinitrile **34** (0.29 g, 0.75 mmol) in ethylene glycol (100 mL) and NH_3 bubbled through the suspension for 3 h, during which turned dark green. The solution was filtered hot and the filtrate was poured onto ice (200 mL) and extracted with $CHCl_3$ (4×100 mL). The combined extracts were dried ($MgSO_4$) and rotary evaporated to give crude 3,4-di-(4-(2,2′-bipyridyl))pyrroline-2,5-diimine **35** as a dark green oily residue that was used in the subsequent step without further purification. n-BuOH (100 mL), Mg (0.4 g) and I_2 (2 small crystals) were heated to reflux for 12 h under N_2. The suspension was cooled and the crude diimine **35** in n-BuOH (5 mL) added and the mixture further heated at reflux for 12 h. The dark green suspension was allowed to cool, filtered (Celite) and the solids washed with CH_2Cl_2. After rotary evaporation, the dark green residue was dissolved in TFA (10 mL). After 30 min at 20 °C under N_2, the mixture was poured onto ice and H_2O (50 mL), neutralized with 4 M NaOH, and filtered. The precipitate was filtered off and washed thoroughly with H_2O, dissolved in a minimum of CH_2Cl_2, dried (Na_2SO_4) and the solvent rotary evaporated. Double gel filtration (Sephadex LH20 $CHCl_3$; Biobeads SX3 $CHCl_3$), gave porphyrazine **37** (23 mg, 2% from **34**) as a dark green solid: mp 328 °C ($CHCl_3$); IR (film) ν_{max} 2191, 1583, 1249, 1093, 989, 793 cm^{-1}; UV–vis λ_{max} 240, 283, 362, 593, 660, CH_2Cl_2; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74–8.50 (m, 16H), 8.36–8.13 (m, 16H), 7.83–7.73 (m, 8H), 7.32–7.28 (m, 16H), –1.70 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 155.5, 150.4, 150.0, 149.1, 149.0, 148.8, 137.2, 136.9, 136.8, 125.1, 124.4, 124.3, 124.2, 123.9, 123.8, 122.6, 121.5, 121.4, 121.3, 121.1, 121.0, 120.4, 119.6, 119.2; MS (FAB) m/z 1549 $(M+H)^+$; HRMS (FAB) m/z Calcd for $C_{96}H_{59}N_{24}$ $(M+H)^+$, 1547.5355; found: $(M+H)^+$, 1547.5396.

4.1.33. 2,3-Bis(diallylamino)norphthalocyanine (40a). Dry n-BuOH (250 mL), Mg turnings (880 mg, 36 mmol) and I_2 (1 crystal) were heated at reflux for 24 h. After cooling to room temperature, phthalonitrile **38a** (12.0 g, 93.3 mmol) and dinitrile **2c** (1.0 g, 3.7 mmol) were added and heated at reflux was resumed for 24 h. After cooling, the deep purple mixture was diluted with $CHCl_3$, filtered through celite and the filtrate evaporated under reduced pressure. Chromatography (SiO_2, $CHCl_3$/MeOH 99:1 to 95:5) gave the crude norphthalocyanine **39a** as a greenish solid. CF_3CO_2H (20 mL) was added and the mixture allowed to stand in the dark for 1 h, added to ice and H_2O (200 mL) and the pH adjusted to 7.5 using aqueous 1.0 M NaOH. The dark precipitate was filtered off and washed repeatedly with H_2O. Chromatography (SiO_2, PhMe/hexanes 6:4 to 7:3) gave norphthalocyanine **40a** (175 mg, 7%) as a blue solid: mp 188–192 °C; TLC R_f 0.45 ($CHCl_3$); IR ($CHCl_3$) ν_{max} 3294, 1561, 1552, 1514, 1498, 1408, 1334, 1306, 1116, 1023, 996, 923, 706 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 293 (4.46), 338 (4.87), 528sh, 577 (4.42), 649 (4.59), 688 (4.60), 723 (4.60) nm; ^{1}H NMR ($CDCl_3$, 500 MHz) δ −3.40 (2H, s), 4.97 (8H, d, J=6.3 Hz), 5.34 (4H, d, J=10.1 Hz), 5.51 (4H, dd, J=1.6, 17.1 Hz), 6.38–6.44 (8H, m), 7.35 (2H, d, J=5.3 Hz), 7.62 (2H, t, J=6.9 Hz), 7.66 (2H, t, J=6.9 Hz), 7.91 (2H, d, J=6.9 Hz), 8.17 (2H, d, J=6.9 Hz), 8.45 (2H, d, J=6.9 Hz); ^{13}C ($CDCl_3$, 125 MHz) δ 55.6, 117.4, 122.0, 122.2, 122.6, 128.9, 129.0, 129.7, 133.0, 134.1, 136.2, 139.1, 139.9, 140.9, 141.5, 156.0, 158.4; FABMS m/z 1309 $(2\,M+H)^+$, 654 $(M^{+\cdot})$, 572; HRFABMS m/z Calcd for $C_{40}H_{35}N_{10}$: $(M+H)^+$, 655.3046; found: $(M+H)^+$, 655.3073. Anal. Calcd for $C_{40}H_{34}N_{10}$: C, 73.37; H, 5.23; N, 21.39. Found: C, 73.26; H, 5.39; N, 21.13.

4.1.34. 2,3-Bis(dibenzylamino)norphthalocyanine (40b). Following the same procedure as for the preparation of norphthalocyanine **40a**, dinitriles **2b** and **38a** gave norphthalocyanine **40b** (20 mg, 20%) as a blue solid: mp 243–245 °C; TLC R_f 0.55 ($CHCl_3$); IR ($CHCl_3$) ν_{max} 3294, 1549, 1513, 1495, 1453, 1334, 1320, 1116, 992, 875 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 292 (4.45), 341 (4.83), 527sh, 583 (4.46), 644 (4.57), 691 (4.56), 727 (4.61) nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −1.87 (2H, s), 5.78 (8H, s), 7.21–7.31 (12H, m), 7.49–7.53 (8H, m), 7.72 (2H, t, J=7.0 Hz), 7.80 (2H, t, J=7.0 Hz), 8.36–8.39 (2H, m), 8.57 (2H, d, J=7.0 Hz), 8.70 (2H, d, J=7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 56.1, 121.7, 121.9, 127.0, 128.5, 128.7, 128.8, 129.2, 132.2, 133.8, 138.7, 139.4, 139.6, 140.3, 141.2, 155.6, and 158.2; FABMS m/z 855 $(M+H)^+$, 763, 672, 581; HRFABMS m/z Calcd for $C_{56}H_{43}N_{10}$: $(M+H)^+$, 855.3672; found: $(M+H)^+$, 855.3689. Anal. Calcd for $C_{56}H_{42}N_{10}$: C, 78.67; H, 4.95; N, 16.38. Found: C, 78.43; H, 5.24; N, 16.02.

4.1.35. 2,3-Bis(diallylamino)-9,10,18,19,27,28-hexabutylnorphthalocyanine (40c). Following the same procedure as for the preparation of norphthalocyanine **40a**, dinitriles **2c** and **38b** gave norphthalocyanine **40c** (17 mg, 4%) as a dark blue solid: mp 183–185 °C; TLC R_f 0.46 ($CHCl_3$/hexanes 1:1); IR ($CHCl_3$) ν_{max} 3296, 1552, 1515, 1456, 1320, 1107, 996, 923, 720 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 299 (4.56), 345 (4.89), 524 (4.25), 577sh, 656 (4.62), 691 (4.61), 733 (4.69) nm; ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.89 (2H, br s), 1.15–1.19 (18H, m), 1.70–1.74 (12H, m), 1.95–2.02 (12H, m), 3.07–3.22 (12H, m), 5.00 (8H, d, J=5.8 Hz), 5.25 (4H, d, J=10.1 Hz), 5.46 (4H, d, J=16.9 Hz), 6.37–6.46 (2H, m), 8.71 (2H, s), 8.89 (2H, s), 9.20 (2H, s); ^{13}C NMR

($CDCl_3$, 100 MHz) δ 14.2, 23.1, 23.3, 33.3, 33.5, 33.6, 33.7, 33.9, 34.0, 55.6, 117.1, 122.1, 122.6, 123.1, 132.1, 133.7, 136.5, 137.3, 138.1, 140.4, 142.3, 142.4, 142.9, 144.2, 155.7, 158.9; FABMS *m/z* 991 $(M+H)$,$^+$950, 908, 868; HRFABMS Calcd for $C_{64}H_{83}N_{10}$: $(M+H)^+$, 991.6802; found: $(M+H)^+$, 991.6872. Anal. Calcd for $C_{64}H_{82}N_{10}$: C, 77.54; H, 8.34; N, 14.13. Found: C, 77.31; H, 8.24; N, 13.89.

4.1.36. 2,3-Bis(dibenzylamino)-9,10,18,19,27,28-hexabutylnorphthalocyanine (40d). Following the same procedure as for the preparation of norphthalocyanine **40a**, dinitriles **2b** and **38b** gave norphthalocyanine **40d** (100 mg, 10%) as a dark blue solid: mp 247–249 °C; TLC R_f 0.42 ($CHCl_3$/hexanes 1:1); IR ($CHCl_3$) ν_{max} 3292, 1566, 1514, 1495, 1451, 1320, 1108, 1027, 989, 746, 698 cm^{-1}; UV–vis ($CHCl_3$) λ_{max} (log ε) 298 (4.58), 347 (4.90), 517 (4.24), 590sh, 655 (4.64), 691 (4.62), 734 (4.74) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.40 (2H, br s), 1.12–1.20 (18H, m), 1.60–1.78 (12H, m), 1.88–2.05 (12H, m), 3.07–3.26 (12H, m), 5.68 (8H, s), 7.19–7.23 (12H, m), 7.38–7.41 (8H, m), 8.66 (2H, s), 9.07 (2H, s), 9.36 (2H, s); ^{13}C ($CDCl_3$, 125 MHz) δ 14.18, 14.21, 23.1, 23.2, 33.4, 33.6, 33.66, 33.74, 33.8, 34.0, 56.6, 122.4, 122.8, 123.3, 126.8, 128.3, 128.7, 132.3, 133.6, 137.3, 138.1, 139.5, 140.5, 142.56, 142.61, 143.6, and 144.3; FABMS *m/z* 1192 $(M+H)^+$, 1101, 1009; HRFABMS *m/z* Calcd for $C_{80}H_{91}N_{10}$: $(M+H)^+$, 1191.7428; found: $(M+H)^+$, 1191.7353. Anal. Calcd for $C_{80}H_{90}N_{10}$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.34; H, 7.38; N, 12.05.

4.1.37. 2,3-Bis(allyl(benzyl)amino)-9,10,18,19,27,28-hexabutylnorphthalocyanine (40e). Following the same procedure as for the preparation of norphthalocyanine **40a**, dinitriles **2e** and **38b** gave norphthalocyanine **40e** (25 mg, 6%) as a dark blue solid: mp 168–170 °C; TLC R_f 0.72 ($CHCl_3$/hexanes 1:1); IR ($CHCl_3$) ν_{max} 3297, 1549, 1514, 1496, 1452, 1321, 1106, 1033, 983, 767, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.74 (2H, br s), 1.17 (18H, t, J=7.1 Hz), 1.66–1.75 (12H, m), 1.88–2.00 (12H, m), 3.05–3.16 (12H, m), 5.00 (4H, d, J=5.8 Hz), 5.22 (2H, d, J=10.3 Hz), 5.39 (2H, d, J=16.7 Hz), 5.74 (4H, s), 6.26–6.32 (2H, m), 7.20–7.28 (6H, m), 7.51 (4H, d, J=6.5 Hz), 8.62 (2H, s), 8.97 (2H, s), 9.22 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2, 23.1, 23.2, 33.4, 33.6, 33.7, 33.9, 34.0, 56.0, 56.7, 117.3, 122.4, 122.8, 123.2, 126.8, 128.2, 128.8, 132.2, 133.9, 136.1, 137.4, 138.2, 139.7, 140.7, 142.5, 142.6, 143.4, 144.3, 155.8, 159.1; FABMS *m/z* 1091 $(M+H)$,$^+$1049, 999, 958; HRFABMS *m/z* Calcd for $C_{72}H_{87}N_{10}$: $(M+H)^+$, 1091.7115; found: $(M+H)^+$, 1091.7058. Anal. Calcd for $C_{72}H_{86}N_{10}$: C, 79.23; H, 7.94; N, 12.83. Found: C, 79.48; H, 7.75; N, 12.61.

4.1.38. 2,3-Bis(benzyl(2-hydroxyethyl)amino)-9,10,18,19,27,28-hexabutyl-norphthalocyanine (40f). Following the same procedure as for the preparation of norphthalocyanine **40a**, dinitriles **10a** and **38b** gave norphthalocyanine **40f** (33 mg, 7%) as a dark blue solid: mp 189–193 °C; TLC R_f 0.19 (EtOAc/hexanes 1:3); IR ($CHCl_3$) ν_{max} 3400, 3300, 1551, 1514, 1495, 1453, 1322, 1109, 1012, 970, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ −0.33 (2H, br s), 1.10–1.21 (18H, m), 1.63–1.76 (12H, m), 1.93–2.04 (12H, m), 2.68–2.72 (2H, m), 3.08–3.27 (12H, m), 3.99 (4H, br s), 4.39 (4H, br s), 5.64 (4H, s), 7.17–7.24 (6H, m), 7.51–7.59 (4H, m), 8.79 (2H, s), 9.05 (2H, s), 9.32 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.2, 23.1, 23.2, 33.5, 33.6, 33.7, 33.8, 33.9, 34.0, 56.0, 58.8, 61.3, 122.5, 123.0, 123.5, 127.1, 128.4, 128.6, 132.5, 135.1, 137.2, 137.6, 139.5, 140.8, 143.0, 143.2, 155.5, 159.4; FABMS *m/z* 1099 $(M+H)$,$^+$1008, 916; HRFABMS *m/z* Calcd for $C_{70}H_{87}N_{10}O_2$: $(M+H)^+$, 1099.7013; found: $(M+H)^+$, 1099.6948. Anal. Calcd for $C_{70}H_{86}N_{10}O_2$: C, 76.47; H, 7.88; N, 12.74. Found: C, 76.44; H, 7.72; N, 12.70.

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Supplementary data

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