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Synthesis and Coordination Chemistry of Unsymmetrical Tetraazaporphyrins Containing Single Oxathia- and Thiacrown Substituents

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Abstract—Singly crowned porphyrazines containing oxathia- and thiacrown ethers were prepared from a mixed condensation of 1,2-dicyanobenzene or its 3,4-dibutyl analog and the appropriate crowned maleonitrile precursor. Peripheral metal-binding to each porphyrazine was examined spectrophotometrically. The oxathiaether-crowned porphyrazines were found to coordinate Ag(I) and $HgCl_2$, though all complexes suffered from poor solubility and complexes with the latter were unstable in polar media. With an interest in the formation of comparatively more stable and soluble heavy and transition metal complexes, two new sets of thiaether-crowned porphyrazines were examined. In these cases, coordination of Hg(II), Ag(I), Cu(I) and Cu(II) was observed with no evidence for complexation of Tl(I), Pb(II) or $CdCl_2$.

Introduction

There is considerable interest in the design of ligand systems capable of binding multiple metal ions as their utility spans a wide range of applications including studies of electron transfer,[1] magnetic interactions,[2] and in biomimetic chemistry.[3,4] Much work in this area has been devoted to the synthesis of porphyrins and phthalocyanines that have been peripherally functionalized with appendages that can coordinate metal ions. Of these peripheral ligands, crown ethers are particularly noteworthy, as they allow for metal ion selectivity and complex stability to be enhanced through changing the numbers and/or types of crown donor atoms.[5] To date the most widely studied crowned porphyrinic molecules are those substituted with four oxacrown ethers,[6,7] with a recent report describing a triply crowned phthalocyanine.[8] Phthalocyanines with four aza-,[9–15] oxaaza-[16–19], thiaaza-[20] or thiacrowns[21] are known, although the very low solubility of the latter has limited their utility in the area of transition metal binding.

Our current interests lie in the peripheral chelation of transition and heavy metal ions. We have recently reported a tetrakis(oxathiaethercrown)porphyrazine that is capable of coordinating up to eight peripheral Ag(I) ions.[22] This type of crowned porphyrazine offers an advantage over phthalocyanine counterparts in that two donor atoms in each crown are in direct conjugation with the 18 π-electron core of the macrocycle. Indeed, the attachment of heteroatoms to these macrocyclic pyrrole positions has been shown to have a profound effect on the optical properties of the porphyrazine core,[23–26] and metal-binding to these heteroatoms results in further spectral changes.[22,24,27–29]

In contrast to their tetra-crowned analogs, unsymmetrical phthalocyanines bearing a single peripheral crown have received much less attention, due to, in part, the difficulty of isolating the desired compound from a mixed condensation of two different phthalonitrile derivatives, a problem which is enhanced by their low solubility in organic solvents.[30] One strategy that has been employed to synthesize singly oxa- and azacrown substituted phthalocyanines involves ring expansion of subphthalocyanine[31] by treatment with an appropriate crown substituted iminoisoindoline.[30,32] This method eliminates the need to separate different phthalocyanine products as only the singly substituted product is formed. However, this method requires the synthesis of functionalized iminoisoindolines, which are not always readily attainable.

We have recently developed a new method for the synthesis of related unsymmetrical porphyrazines in which one of the benzo rings of phthalocyanine is replaced by a protected dithiolato chelate.[33,34] This method utilizes the Linstead cyclization of phthalonitrile (present in 15–25 fold excess)

Keywords: maleonitrile; oxathia ether; thiacrown ether; porphyrazine; tetraazaporphyrin.

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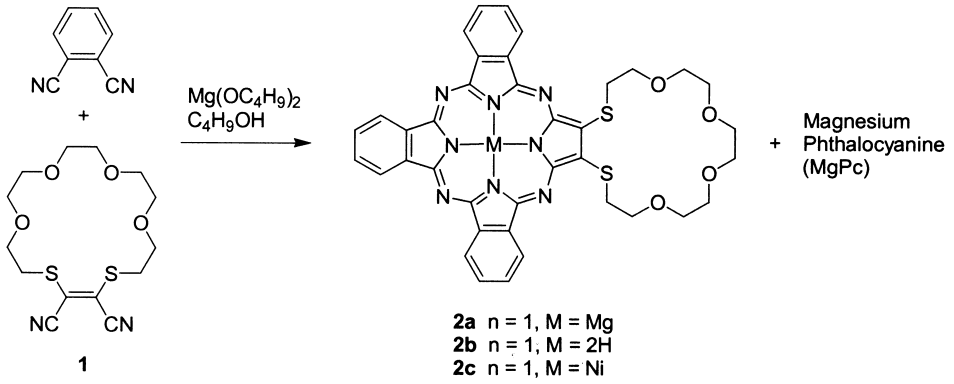


Scheme 1.

with a dithiomaleonitrile derivative to give only two porphyrinic products, insoluble MgPc and the soluble unsymmetrical compound. In this case the desired unsymmetrical product is easily separated from the MgPc by-product by a simple filtration. Here we use this methodology to synthesize porphyrazines in which one of the fused benzo rings of phthalocyanine is replaced by an oxathia- or thiaether crown. Because of the direct attachment of the crown to the π system in these porphyrazines, they should have wide ranging application as metal ion probes. Further, because they contain a single peripheral binding site, these porphyrazines can be viewed as model compounds for understanding the properties of peripheral metal complexes of the more common (and more complex) tetra-crowned porphyrazines. We report here the synthesis and metal binding properties of new singly oxathia- and thiacrowned porphyrazines.

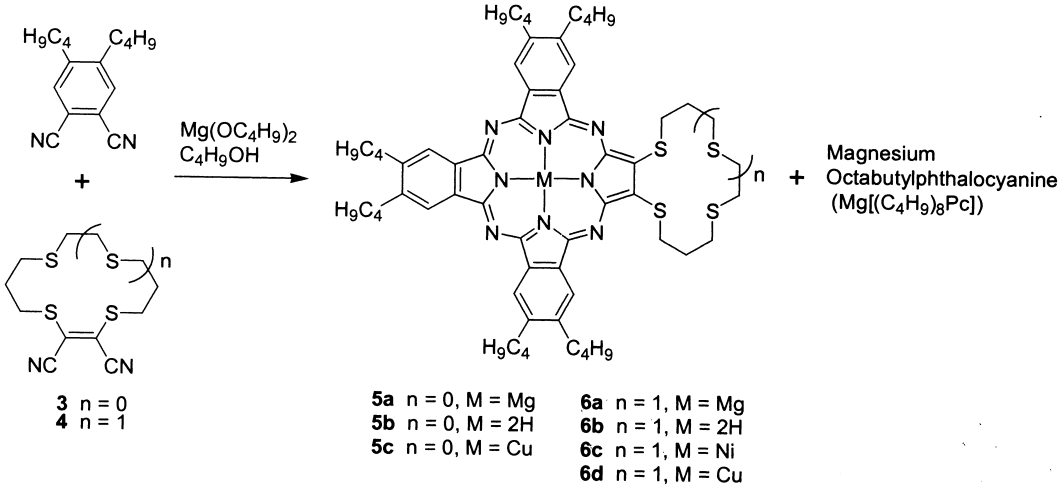
Results and Discussion

Synthesis of oxathiaether-crowned norphthalocyanines

Our initial attempts at developing a singly crowned porphyrazine involved a combination of our earlier work on *solitaire* porphyrazines[33,34] and *oxa*crowned dithiomaleonitrile derivatives.[35] As shown in Scheme 1, a mixed condensation of >15 equiv. of 1,2-dicyanobenzene and 1 equiv. of oxathiaether crown **1** under classic Linstead macrocyclization conditions (magnesium butoxide/*n*-butanol)[36] produced two porphyrinic products, the desired singly crowned Mg-norphthalocyanine **2a** and Mg-phthalocyanine. The largely insoluble Mg-phthalocyanine was simply filtered away. Normally a crossed cyclization of two different maleonitrile derivatives will result in the generation of all six possible porphyrazine products.[23] However, the synthetic method outlined here prevents the formation of mixed condensation products other than **2** without complicating the purification process through the use of a large excess of 1,2-dicyanobenzene. It is a general route to producing norphthalocyanines in yields of 16–18% provided they have significantly greater solubility than that of phthalocyanine. Demetallation of the Mg-norphthalocyanine **2a** using trifluoroacetic acid produced the free-base porphyrazines (**2b**) and remetallation with nickel(II) acetate yielded the centrally nickelated norphthalocyanine **2c**.

Synthesis of thiaether-crowned norphthalocyanines

In an effort to increase the stability of transition and heavy metal ions, singly thiaether-crowned porphyrazines were also prepared. As shown in Scheme 2, the peripherally crown-appended porphyrazines **5a** and **6a** were synthesized by a crossed condensation of 4,5-dibutyl-1,2-dicyano-



Scheme 2.

benzene and thiaether crown dithiomaleonitrile derivatives **5** and **6**, respectively, under Linstead macrocyclization conditions,[36] followed by demetallation with trifluoroacetic acid. In both cases, the butyl groups were needed to enhance the solubility of the unsymmetrical product. As in the synthesis of **2**, the key feature of this macrocyclization was the use of an excess of the 1,2-dicyanobenzene component. In this case the two porphyrinic products of the reaction were magnesium octabutylphthalocyanine and the singly crown-appended porphyrazines. The limited solubility of octabutylphthalocyanine in dichloromethane allows for it to be separated from the soluble crown-appended porphyrazines by suction filtration through a pad of Celite. The crown porphyrazines are then easily purified by chromatography on silica gel. Remetalation of the porphyrazine core with Ni(II) or Cu(II) proceeds smoothly by treatment of the free base porphyrazines **5b** and **6b** with a small excess of the appropriate metal acetate.

UV/visible spectroscopy

The absorption spectra of **2**, **5** and **6** are very similar to each other and to those reported for other freebase and metalated 2,3-thioether-norphthalocyanines.[33] Two intense optical absorption bands are exhibited: one in the Soret region ($\lambda < 400$ nm) and a Q band at $\lambda > 600$ nm. Both the freebase and metalated compounds exhibit split Q-bands with the degree of splitting being greater for the freebase molecules. The splitting reflects the overall C_{2v} symmetry of the molecules and can be rationalized based on Gouterman's four-orbital model for the optical spectra of porphyrins.[37]

Metal binding studies of oxathiaether-crown norphthalocyanine 2

In contrast to purely S or O-containing crowns, a mixed set of S and O donor atoms imparts a preference for the coordination of heavy metal ions at the expense of transition and alkali metal ions.[35,38–47] Thus, our peripheral metal-binding studies with **2** focused initially on the complexation of $HgCl_2$, $AgBF_4$ and $Pb(OAc)_2$. We have shown previously that tetraazaporphyrins with heteroatoms fused directly to the periphery are optically sensitive to metal ions when the peripheral heteroatoms interact with the metals.[22,24] The room temperature addition of Ag(I) to solutions of porphyrazine **2** in 3:1 $CHCl_3/CH_3OH$ caused an immediate color change, from blue-green to green, suggesting complex formation. Unfortunately, this color change was followed by the rapid formation of an intractable blue solid which precluded its purification. FAB mass spectral analysis of the product indicated the formation of a 1:1 Ag(I) complex. The solubility of this putative Ag(I) complex could not be enhanced by changing counter anions. Surprisingly, there is essentially no change initially in the visible spectrum upon the addition of $HgCl_2$. This lack of change in the visible spectrum would be consistent with very weak or no coordination of the S atoms to the mercury ion. Thus leaving the $HgCl_2$ unit only loosely coordinated via the oxygen donors. This coordination mode was observed in the $HgCl_2$ complex of the dinitrile crown pz precursor, **1**, where linear $HgCl_2$ is coordinated endocyclically preferentially via the oxygen crown donors.[48] As in the reaction with Ag(I), a product that could not be purified was isolated. FAB mass spectral data indicates a 1:1 peripheral $HgCl_2$ adduct. However, this complex is essentially insoluble in nonpolar solvents and, unlike the Ag(I) product described above, decomposes upon the addition of polar solvents (methanol, acetonitrile, dimethylformamide, etc.) to give back the free ligand (**2**). No evidence for complexation with Pb(II) was observed.

Interestingly, in the FAB mass spectra of **2a–c** there are *m*/*e* peaks that correspond to peripheral 1:1 Na^+ complexes. Because we see no change in the visible spectrum upon addition of Na^+ ions and we have never isolated an Na^+ adduct, we infer that Na^+ ion complexation occurs weakly through the polyether portion of the peripheral crown alone. This is consistent with the preference of the hard Na^+ ion for O donor atoms vs. S donor atoms.

Metal binding studies of thiaether-crown norphthalocyanine 6

As thiaether crowns are known to coordinate both heavy and transition metal ions our metal binding studies of **6** have focused on the complexation of the heavy metal ions Ag(I), Hg(II), Cd(II), Tl(I) and Pb(II) and also Cu(II). We have employed UV/visible spectroscopy to monitor the ability of our porphyrazines to sense/coordinate transition metal ions. For these experiments, pronounced changes in the absorption spectrum of the ligand were observed upon addition of $AgBF_4$, $Hg(ClO_4)_2$, or $Cu(OTf)_2$ to room temperature solutions of **6**. These spectral changes are consistent with coordination of metal ions to the peripheral thiaether crown. Interestingly, no change in the absorption spectrum of **6** was observed with the addition of $HgCl_2$. This observation is consistent with exocyclic $HgCl_2$ coordination by the aliphatic crown S donor atoms. However with weakly coordinating ClO_4 anions, spectral changes were observed until approximately 2 equiv. of Hg were added (Fig. 1a).

Addition of Ag(I) to **6** caused a decrease in intensity of the 708 nm Q-band absorption during titration up to a metal–ligand ratio of ca. 1.0, thereafter a slightly red shifted band at 711 nm grew in until a Ag(I)–ligand ratio of ca. 1.3 was reached (Fig. 1b). Further addition of Ag(I) did not change the spectrum. The binding of Ag(I) also increased the splitting of the Q-band by approximately 14 nm over that observed for ligand **6**.

Titration with copper(II) triflate in chloroform-methanol solution resulted in a gradual decrease of the Q-band absorption that continued through a Cu(II)–ligand ratio of ca. 25 (Fig. 1c). Only with the addition of a large excess of Cu(II) (>100 equiv.) gave a visible spectrum that began to resemble the endpoint spectra of the Ag(I) and Hg(II) titrations. The relatively weak binding of Cu(II) exhibited by porphyrazine **6** in chloroform–methanol solutions was not unexpected as thiaether–Cu(II) complexes are known to have low stability constants in solvents that coordinate the Cu(II) ion reasonably well (i.e. aqueous or methanolic solutions).[49,50] The low stability constants are attributed to weak $Cu(II)–S_{thiaether}$ bonds,[51] and the tendency of uncomplexed cyclic polythiaethers to adopt the *exo* conformations in which the lone pairs of the S atoms are directed away from the macrocyclic cavity.[52,53] Rorabacher and coworkers

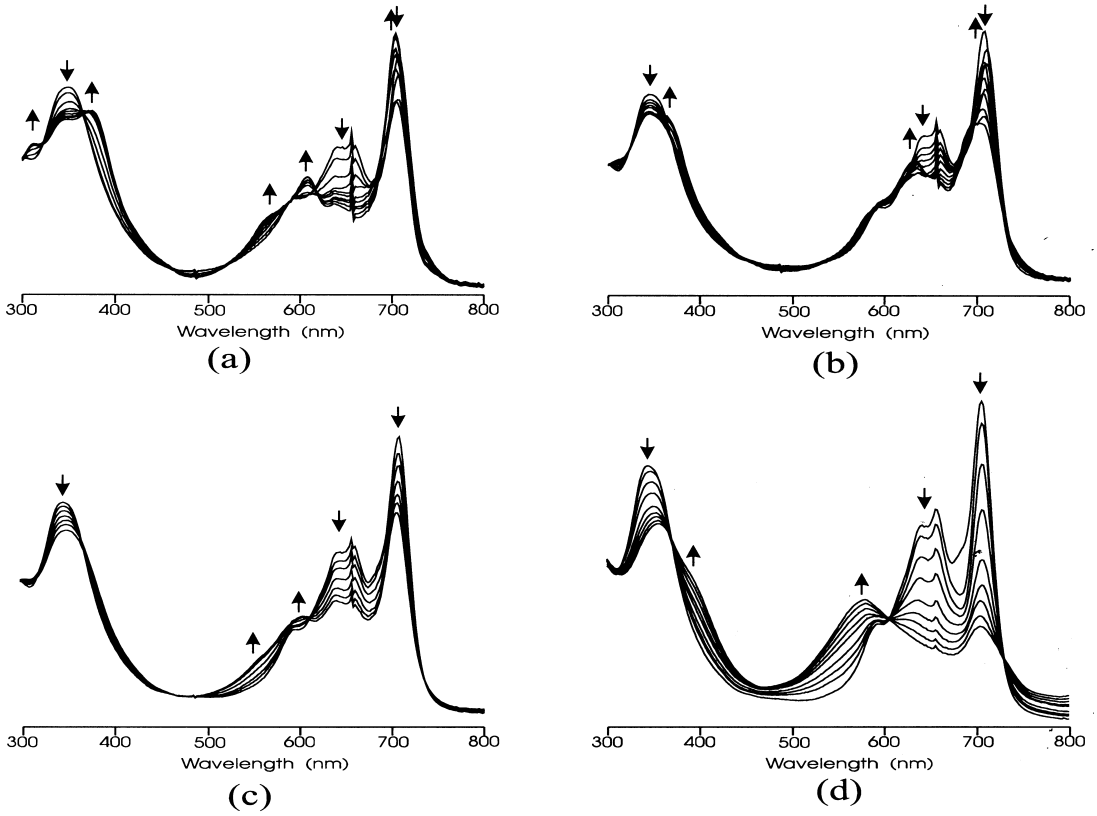


Figure 1. Titration of macrocycle **6** with: (a) 2 equiv. $Hg(ClO_4)_2$; (b) 1.3 equiv. $AgBF_4$; (c) 25 equiv. $Cu(OTf)_2$ in $CHCl_3$/MeOH (1:1); (d) 1 equiv. $Cu(OTf)_2$ in $CHCl_3$/CH_3CN (4:1).

have recently shown that replacement of one ethylene bridge for a phenyl bridge in [14]aneS_4 caused a *decrease* in the stability of Cu(II) complexes amounting to 3 orders of magnitude relative to the unsubstituted [14]aneS_4 macrocycle.[50] This decrease was attributed to the negative inductive effect of the benzene ring on the coordinating ability of the sulfur donors. These combined factors led to the incomplete complexation of Cu(II) exhibited by **6** in chloroform–methanol.

The formation of Cu(II)–thiacrown complexes is known to be enhanced in solvents that do not coordinate Cu(II) strongly (e.g. acetonitrile or nitromethane).[49,50] For this reason, we chose to examine the ability of porphyrazine **6** to coordinate Cu(II) in a mixture of chloroform and acetonitrile (4:1). In this solvent system, we observed changes related to Cu(II) binding up to a metal–ligand ratio of 1.0. Titration beyond 1 equiv. produced no further band shifting or relative absorbance band intensity changes, but did result in an overall decrease in intensity of all the peaks (Fig. 1d). This bleaching of the complex was nearly complete after the addition of 8 equiv. of Cu(II) ion and was also monitored as a function of time. A Cu(II)–ligand complex in the presence of 5 equiv. of Cu(II) was observed to bleach over a period of ca. 5 min. As Cu(II) is a moderately strong oxidant in acetonitrile,[54] it is likely that our complex bleached as a result of oxidation by uncomplexed Cu(II) ion present in excess. It is interesting to note that Rorabacher and co-workers also reported rapid bleaching of the Cu(II) complexes of their phenyl [14]aneS_4 derivatives in acetonitrile.[50]

Conclusions

We have prepared singly crowned porphyrazines and studied their peripheral metal binding properties spectrophotometrically. The porphyrazines were prepared by cocyclization of 1,2-dicyanobenzene or its 4,5-dibutyl derivative (present in excess) and the appropriate crown derivative of dithiomaleonitrile under Linstead conditions. Rapid complexation of Ag(I) was observed for porphyrazine **2**, with weaker complexation of $HgCl_2$ and Na^+ observed only by mass spectrometry. There was no evidence for complexation of Pb(II). However, due to either the insolubility or instability of the peripheral metal complexes of porphyrazine **2** and the general inability of the S_2O_4 crown to coordinate softer transition and heavy metal ions effectively, a new set of thiacrown-appended norphthalocyanines with solubilizing groups were prepared. Coordination by these porphyrazines of Hg(II), Ag(I), Cu(I) and Cu(II) was observed with no evidence for complexation of Tl(I), Pb(II) or $CdCl_2$.

Experimental

Materials and apparatus

Macrocycles **1**, **3**, and **4** were prepared as previously reported.[35,55] 4,5-Dibutyl-1,2-dicyanobenzene was prepared according to published procedures.[56,57] All other reagents and solvents were of reagent grade and used without further

purification. Chromatography was carried out on silica (eluants are given in parenthesis). Proton and carbon NMR spectra were recorded on a Varian Gemini-300 (300 MHz) spectrometer. UV/visible spectra were recorded on a HP 8453A spectrophotometer. EI and FAB mass spectra were recorded using a VG-70-250SE instrument. Elemental analyses were performed by Oneida Research Services.

2,3-[18]aneS$_2$O$_4$-norphthalocyanine, H$_2$([18]aneS$_2$O$_4$)-norpc, 2b. A suspension of magnesium turnings (700 mg, 29 mmol) in *n*-butanol (200 mL) was heated at reflux for 8–24 h using a small chip of iodine to initiate the reaction. To the resulting magnesium butoxide suspension was added solid **1** (1.02 g, 3.0 mmol) and 1,2-dicyanobenzene (9.46 g, 75 mmol). The solution rapidly turned yellow, then bright green, and finally settled as a deep blue/green color within 1–2 h. The reaction mixture was kept at reflux under a nitrogen atmosphere for 18 h. The butanol was removed by vacuum distillation, and the residue taken up in $CHCl_3$ and filtered to remove the insoluble Mg(pc) formed as a by-product. The filtrate was concentrated and chromatographed (1–2% $CH_3OH/CHCl_3$) to afford the Mg-porphyrazine **2a** which was used without further purification: UV/vis ($CHCl_3$) λ_{max} 356, 594, 634, 652, 694. FAB MS *m/e* 753 ($M+H^+$), 775 ($M+Na^+$); HR FAB MS *m/e* 753.1920 ($M+H^+$) (Calcd for $C_{38}H_{33}N_8MgO_4S_2$, *m/e* 753.1917).

The Mg-porphyrazine **2a** was dissolved in neat trifluoroacetic acid (10–15 mL) and stirred at room temperature for 1 h. The solution was poured over ice and neutralized with concentrated aqueous NH_3. The resulting precipitate was filtered and washed with water and MeOH. Chromatography (1–2% $CH_3OH/CHCl_3$) gave pure **2b** (16–18% yield based on **1**) as a blue solid: UV/vis ($CHCl_3$) λ_{max} 344, 567(sh), 614, 675, 707; ^{1}H NMR (CD_2Cl_2) δ −5.20 (2H, s, N*H*), 3.56–3.68 (12H, m, OCH_2, SCH_2), 3.82 (8H, m, OCH_2), 6.60 (2H, br, Ar), 6.77 (2H, br, Ar), 7.05 (2H, d, Ar), 7.14 (2H, t, Ar), 7.26 (2H, t, Ar), 7.66 (2H, d, Ar); ^{1}H NMR ($CDCl_3$) δ −3.98 (2H, s, N*H*), 3.57–3.75 (12H, m, OCH_2, SCH_2), 3.95 (4H, t, OCH_2), 4.07 (4H, t, OCH_2), 7.26 (2H, br, Ar), 7.42 (4H, m, Ar), 7.53 (2H, t, Ar), 7.65 (2H, d, Ar), 8.12 (2H, d, Ar); FAB MS *m/e* 731 ($M+H)^+$, 753 ($M+Na)^+$; HR FAB MS *m/e* 731.2196 (M+H+) (Calcd for $C_{38}H_{35}N_8O_4S_2$: *m/e* 731.2222), 753.2068 ($M+Na)^+$ (Calcd for $C_{38}H_{34}N_8NaO_4S_2$: *m/e* 753.2042). Anal. Calcd for $C_{38}H_{34}N_8O_4S_2$: C, 62.45; H, 4.69; N, 15.34. Found: C, 62.06; H, 4.71; N, 15.10.

(2,3-[18]aneS$_2$O$_4$-norphthalocyanato)nickel(II), Ni([18]aneS$_2$O$_4$)norpc, 2c. The 2H porphyrazine **2b** (100 mg) and a large excess of nickel(II) acetate were added to a mixture of chlorobenzene/DMF (3/1, 12 mL). The mixture was heated to 100°C under a nitrogen atmosphere and stirred for 18 h. The solvent was then removed by vacuum distillation, and the solid residue was washed with 1% HCl/MeOH and filtered. The resultant solid was washed with H_2O, MeOH and a small amount of Me_2CO. The product **2c** was isolated in near quantitative yield following chromatography (2% $CH_3OH/CHCl_3$): UV/vis ($CHCl_3$) λ_{max} 293, 333, 580, 641, 683; ^{1}H NMR ($CDCl_3$) δ 3.51–3.69 (12H, m, OCH_2, SCH_2), 3.92 (4H, t, OCH_2), 4.07 (4H, t, OCH_2), 7.42 (2H, br, Ar), 7.73 (2H, t, Ar), 7.80 (4H, m, Ar), 8.20 (2H, d, Ar), 8.52 (2H, d, Ar). FAB MS *m/e* 786 (M^+), 787 ($M+H)^+$, 809 ($M+Na)^+$; HR FAB MS *m/e* 786.1345 (M^+) (Calcd for $C_{38}H_{32}N_8NiO_4S_2$: *m/e* 786.1341), 787.1484 ($M+H)^+$ (Calcd for $C_{38}H_{33}N_8NiO_4S_2$: *m/e* 787.1420), 809.1374 ($M+Na^+$) (Calcd for $C_{38}H_{32}N_8NaNiO_4S_2$: *m/e* 809.1239). Anal Calcd for $C_{38}H_{32}N_8NiO_4S_2$: C, 57.96; H, 4.10; N, 14.23. Found: C, 57.28; H, 3.84; N, 13.72.

2,3-[11]aneS$_3$-9,10,16,17,23,24-hexabutylnorphthalocyanine, H$_2$[Bu$_6$([11]aneS$_3$)]norpc, 5b. A suspension of magnesium butoxide was prepared by heating a mixture Mg (100 mg, 4.2 mmol) in butanol (30 mL) at reflux for 8–24 h and with the addition of a small chip of I_2 to initiate the reaction. To this solution (maintained at reflux) was added 4,5-dibutyl-1,2-dicyanobenzene[56,57] (2.8 g, 12 mmol) and **3** (0.50 g, 1.95 mmol) all at once. The color immediately turned green and after 30 min was deep blue. The solution was kept at reflux for a period of 12 h after which it was cooled to 80°C and the butanol removed by vacuum distillation. The solid residue was dissolved in CH_2Cl_2 (500 mL) and filtered through a pad of Celite. This filtration removed most of the magnesium octabutylphthalocyanine which has limited solubility in CH_2Cl_2. The filtrate was rotary evaporatorated and treated with trifluoroacetic acid (enough to dissolve all the solid) for 15 min and poured over crushed ice (250 g). The residue was rinsed with H_2O (200 mL) and the washings combined with the ice solution. The pH of the solution was raised to 10–12 by the addition of concentrated aqueous NH_3 and the precipitated solid collected by filtration. The solid was washed copiously with MeOH until the washings were clear. The pure product (0.305 g, 16%) was obtained following chromatography ($CHCl_3$): UV/vis ($CHCl_3$) λ_{max} 355, 575 (sh), 617, 675, 715; ^{1}H NMR ($CHCl_3$) δ −0.38 (2H, s, N*H*), 1.26 (18H, m, CH_2CH_3), 1.68 (16H, m, CH_2CH_3 and SCH_2CH_2), 1.95 (12H, m, $CH_2CH_2CH_2CH_3$), 2.61 (4H, t, CH_2SCH_2), 3.10 (12H, m, CCH_2CH_2), 3.87 (4H, t, $CSCH_2$), 8.45 (2H, Ar), 8.64 (2H, Ar), 8.66 (2H, Ar); HR FAB MS *m/e* 979.538 ($M+H)^+$ (Calcd for $C_{58}H_{75}N_8S_3$: 979.528).

[2,3-[11]aneS$_3$-9,10,16,17,23,24-hexabutylnorphthalocyanato]copper(II), Cu[Bu$_6$([11]aneS$_3$)]norpc, 5c. Freebase porphyrazine **5b** (105 mg, 0.11 mmol) and copper(II)acetate (0.290 g, 1.61 mmol) were dissolved in a mixture of PhCl (10 mL) and DMF (5 mL). The resulting solution was heated to 100°C for 3 h after which the solvent was removed by vacuum distillation. The blue residue was washed with copious amounts of MeOH and chromatographed ($CHCl_3$) to give the copper complex **5c** (0.065 g, 60%): UV/vis ($CHCl_3$) λ_{max} 356, 589, 638, 652, 707; HR FAB$^+$ MS *m/e* 1040.432 ($M+H)^+$ (Calcd for $C_{58}H_{73}CuN_8S_3$: 1040.442); Anal. Calcd for $C_{58}H_{72}CuN_8S_3$: C, 66.92; H, 6.97; N, 10.76. Found: C, 66.50; H, 6.90; N, 10.77.

2,3-[14]aneS$_4$-9,10,16,17,23,24-hexabutylnorphthalocyanine, H$_2$[Bu$_6$([14]aneS$_4$)]norpc, 6b. 4,5-Dibutyl-1,2-dicyanobenzene (6 g, 0.025 mol) and **4** (0.527 g, 1.67 mmol) were allowed to react under the conditions described above for **5**. The pure product (0.311 g, 18%) was obtained following chromatography ($CHCl_3$): UV/vis ($CHCl_3$/MeOH, 4/1) λ_{max} ($\epsilon\times10^{-4}$ L mol^{-1} cm^{-1}) 354 (6.63), 578 (1.74), 623 (5.25), 680 (3.63), 718 (7.72); ^{1}H NMR ($CDCl_3$) δ −0.83 (2H, s, N*H*), 1.18 (18H, m,

CH_2CH_3), 1.72 (12H, m, $CH_2CH_2CH_3$), 1.98 (16H, m, $CH_2CH_2CH_2CH_3$ and $SCH_2CH_2CH_2S$), 2.31 (4H, s, SCH_2CH_2S), 2.65 (4H, t, $CH_2SCH_2CH_2SCH_2$), 3.05 (8H, t, $CCH_2CH_2CH_2CH_3$), 3.18 (4H, t, $CCH_2CH_2CH_2CH_3$), 4.40 (4H, t, $CSCH_2CH_2$), 8.44 (2H, s, Ar), 8.52 (2H, s, Ar), 8.82 (2H, s, Ar); FAB^+ MS *m/e* 1039 $(M+H)^+$; Anal. Calcd for $C_{60}H_{78}N_8S_4$: C, 69.32; H, 7.56; N, 10.78. Found: C, 69.28; H, 7.51; N, 10.74.

[2,3-[14]aneS$_4$-9,10,16,17,23,24-hexabutylnorphthalocyanato]nickel(II), Ni[Bu$_6$([14]aneS$_4$)]norpc, 6c. Free-base porphyrazine **6b** (0.311 g, 0.30 mmol) and nickel(II)acetate (35.5 mg, 0.30 mmol) were dissolved in a mixture of PhCl (30 mL) and DMF (10 mL). The resulting solution was heated to 90°C for a period of 18 h after which time the solvent was removed by vacuum distillation. The blue residue was dissolved in $CHCl_3$ (250 mL) and filtered. The volume was reduced to 20 mL by rotary evaporation and the product chromatographed ($CHCl_3$) (0.298 g, 91%): UV/vis ($CHCl_3$/MeOH, 4/1) λ_{max} ($\epsilon\times10^{-4}$ L mol^{-1} cm^{-1}) 338 (4.08), 380 (sh), 586 (2.05), 636 (4.80), 646 (4.71), 696 (6.03); ^{1}H NMR ($CDCl_3$) δ 1.18 (18H, m, CH_2CH_3), 1.70 (12H, m, $CH_2CH_2CH_3$), 1.95 (16H, m, $CH_2CH_2CH_2CH_3$ and $SCH_2CH_2CH_2S$), 2.35 (4H, s, SCH_2CH_2S), 2.65 (4H, t, $CH_2SCH_2CH_2SCH_2$), 3.01–3.18 (12H, m, $CCH_2CH_2CH_2CH_3$), 4.15 (4H, t, $CSCH_2CH_2$), 8.37 (2H, s, Ar), 8.44 (2H, s, Ar), 8.55 (2H, s, Ar); FAB MS *m/e* 1095 $(M+H)^+$; Anal. Calcd for $C_{60}H_{76}N_8NiS_4$: C, 65.74; H, 6.99; N, 10.22. Found: C, 65.14; H, 6.74; N, 10.06.

[2,3-[14]aneS$_4$-9,10,16,17,23,24-hexabutylnorphthalocyanato]copper(II), Cu[Bu$_6$([14]aneS$_4$)]norpc, 6d. Copper(II)acetate monohydrate (0.76 g, 3.81 mmol) and **6b** (0.420 g, 0.40 mmol) were allowed to react under the conditions described above for **5c**. The pure product (0.390 g, 88%) was obtained following chromatography (chloroform): UV/vis ($CHCl_3$/MeOH, 4/1) λ_{max} ($\epsilon\times10^{-4}$ L mol^{-1} cm^{-1}) 348 (4.98), 596 (2.15), 644 (3.80), 658 (3.90), 708 (6.10); UV/vis ($CHCl_3$/MeCN, 4/1) λ_{max} ($\epsilon\times10^{-4}$ L mol^{-1} cm^{-1}) 348 (5.64), 596 (2.18), 644 (4.52), 658 (4.95), 708 (7.42); FAB^+ MS *m/e* 1100 $(M+H^+)$; Anal. Calcd for $C_{60}H_{76}CuN_8S_4$: C, 65.45; H, 6.96; N, 10.18. Found: C, 65.00; H, 6.77; N, 9.98.

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