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Porphyrins with exocyclic rings. Part 20: Synthesis and spectroscopic characterization of porphyrins with fused 2,1,3-benzoxadiazole and 2,1,3-benzoselenadiazole moieties☆

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Abstract—Porphyrins with fused 2,1,3-benzoxadiazole and 2,1,3-benzoselenadiazole units were prepared by the '3+1' MacDonald-type methodology. 4-Nitro-2,1,3-benzoxadiazole, 6-chloro-4-nitro-2,1,3-benzoxadiazole and 4-nitro-2,1,3-benzoselenadiazole condensed with isocyanoacetates in the presence of the non-nucleophilic base DBU to give tricyclic pyrrole derivatives in excellent yields. Further cleavage of the ester moieties and decarboxylation afforded α-unsubstituted pyrroles and these were further condensed with 2 equiv of an acetoxymethylpyrrole *tert*-butyl ester to give crude preparations of tripyrranes. The *tert*-butyl ester protective groups were cleaved with TFA and following dilution with dichloromethane, '3+1' condensation with a pyrrole dialdehyde, and oxidation with ferric chloride, the heterocyclic ring fused porphyrins were obtained in moderate yields. The yields were lower than expected because of difficulties in preparing required tripyrranes due to the reduced reactivity of the pyrrolic intermediates. The UV–vis spectra of these new porphyrin systems were highly modified showing broadened split Soret bands. In addition, the nickel(II), copper(II) and zinc complexes gave unusual UV–vis spectra with weakened split Soret bands and strong Q-type absorptions above 600 nm. These modified structures show some potential for applications as photosensitizers in photodynamic therapy.

1. Introduction

Porphyrins with extended chromophores[1,2] have been investigated for applications that range from material science[3] to medicine.[4] Much of this work has concentrated on tetrabenzoporphyrins,[5] but other types of ring fused porphyrin systems have the potential to produce more diverse physical and spectroscopic properties.[1,2] In some cases, porphyrins with fused aromatic units show strongly red shifted absorptions,[1,2] a property that could result in the development of superior photosensitizers for photodynamic therapy (PDT).[4] In PDT, the porphyrin 'drug' is excited by visible light and transfers energy to generate singlet oxygen. As porphyrins commonly show an affinity for tumor cells over normal tissues, the highly toxic effects of singlet oxygen are localized to the malignant tissues. Bodily tissues strongly absorb light through most of the visible region, but red light in the region of 650–800 nm gives much better penetration while providing the necessary energy for singlet oxygen production.[4] Unfortunately, porphyrins usually only have weak absorptions above 600 nm, and for this reason modified chromophores are attracting considerable interest.[1,2] However, fusion of many benzenoid aromatic ring systems to the porphyrin nucleus produces only minor shifts to the UV–vis absorption spectra. Naphthoporphyrins **1a**[6,7] and the related quino- and isoquinoporphyrins **1b** and **1c**[8] produce shifts of less than 10 nm to the Soret and Q bands, and even phenanthro-(**2a**)[9] and phenanthrolinoporphyrins (**2b**)[10] give similar spectroscopic shifts (Chart 1).[11] However, acenaphthoporphyrins **3** have highly modified spectra with three Soret absorptions and a relatively strong Q band at 660 nm.[12–14] Di- and tetraacenaphthoporphyrins give even larger shifts, in some cases showing Soret bands above 600 nm.[13,14] Thiadiazolobenzoporphyrins **4a** also show intriguing UV–vis spectra with broadened split Soret bands and a highly modified Q band region.[13,15] The related nickel(II), copper(II) and zinc complexes also show two Soret bands that are atypically weakened, together with an intense Q-type band near 600 nm.[13] Although the absorptions fall short of the desired wavelength range from 650 to 800 nm, the relatively polar nature of these porphyrins and the presence of strong absorption bands at higher wavelengths makes the study of related chromophores a desirable goal. For this reason we targeted the synthesis of related porphyrins **4b–d** with fused 2,1,3-benzoxadiazole (benzofurazan) and 2,1,3-benzoselenadiazole units.[16]

☆ For part 19 in the series, see: Lash, T. D.; Lin, Y.; Novak, B. H.; Parikh, M. D. *Tetrahedron* **2005**, *61*, 11601–11614.

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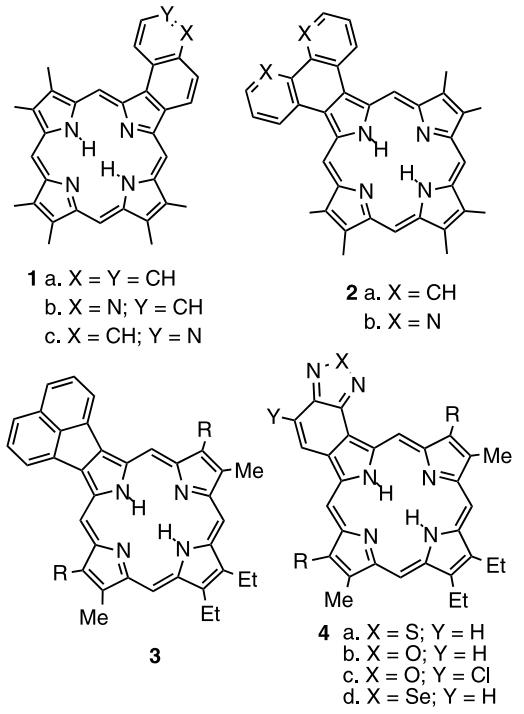


Chart 1. Porphyrins with fused aromatic subunits.

2. Results and discussion

The synthesis of porphyrins with fused heterocyclic rings required the availability of pyrrolic tricycles **5** (Scheme 1). Nitroaromatic compounds with a degree of nitroalkene character can react with isocyanoacetates in the presence of a non-nucleophilic base such as DBU to give *c*-annelated pyrroles.[8–20] This chemistry is in fact a variation on the Barton–Zard pyrrole condensation which was first reported in 1985,[21] and can be applied to the synthesis of diverse fused pyrrole and porphyrin products.[8–17] In previous work, 4-nitro-2,1,3-benzothiadiazole (**6a**) was reacted with ethyl isocyanoacetate (**7a**) in refluxing THF but only poor yields (15%) of the required pyrrole ethyl ester **8a** was

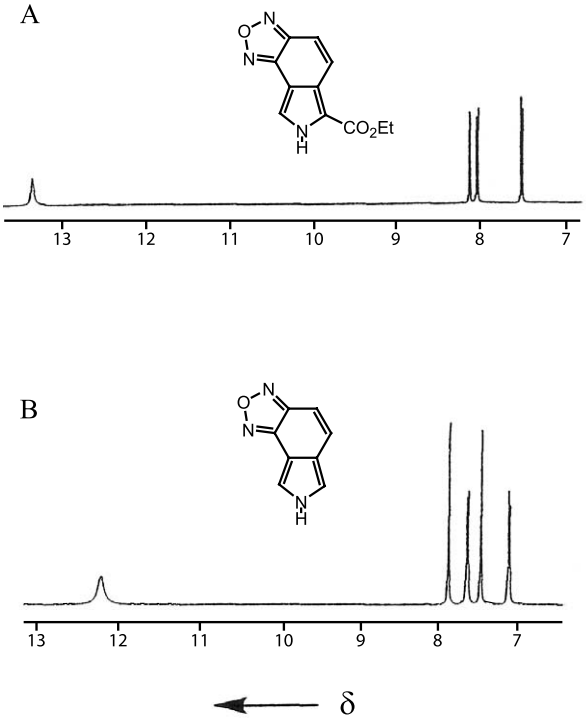
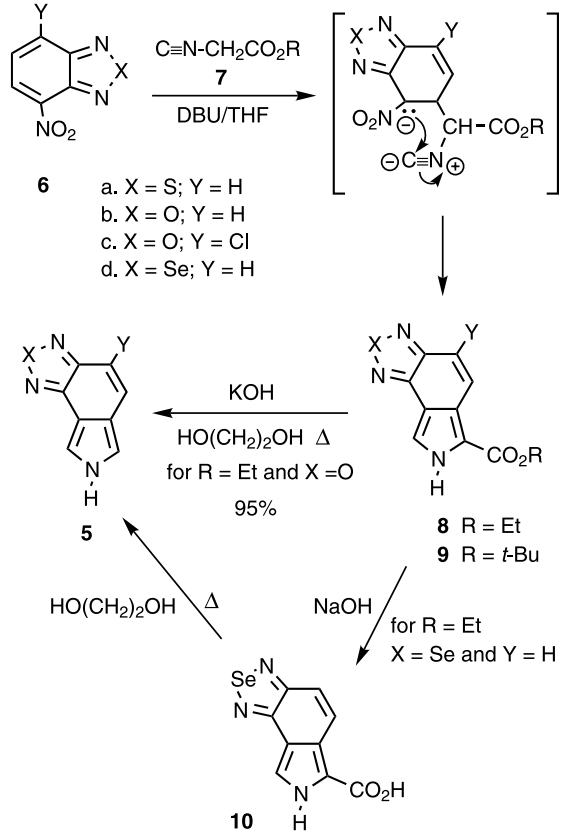
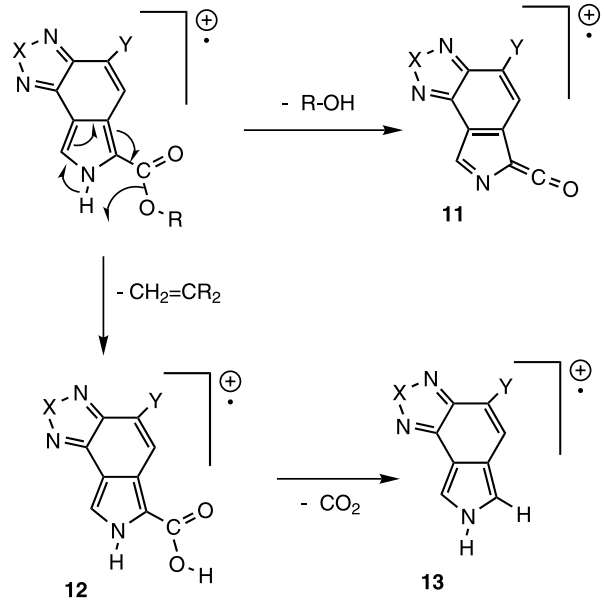


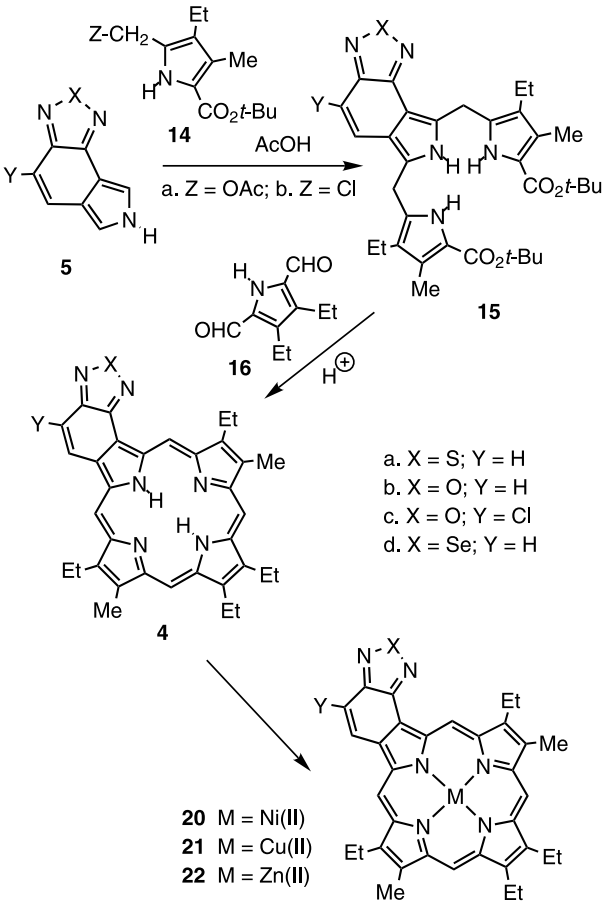
Figure 1. (a) Partial 400 MHz proton NMR spectrum of pyrrole ester **8b** in d_6-DMSO; (b) 400 MHz Proton NMR spectrum of oxadiazolobenzopyrrole **5b** in d_6-DMSO.



Scheme 1.

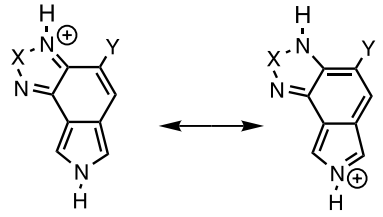


Scheme 2.

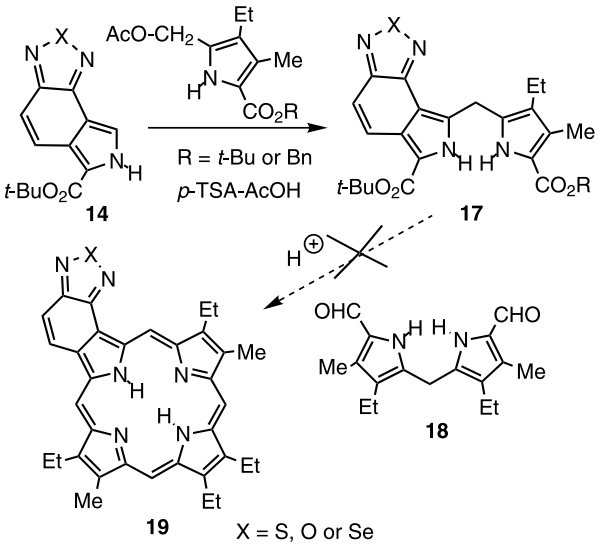


Scheme 3.

obtained.[13,15] However, under highly diluted conditions, where 400 mL of THF solvent was used for every 1 g of nitro compound, a 48% yield of the required tricycle **8a** was obtained, and the related *tert*-butyl ester **9a** was similarly prepared from **6a** and **7b** in 47% yield.[13,15] It was unclear why the dilute conditions were beneficial as better results were usually obtained at higher concentrations for other nitro compounds, but the low solubility of these heterocycles may be a factor.[13] The same approach was used to prepare the new heterocycles **8b–d** and **9b–d**. In all cases, dilute conditions gave superior results. 4-Nitrobenzofurazan **6b** (NBD) is not commercially available, and initial investigations were conducted using the available 7-chloro-derivative NBD chloride (**6c**). Reaction of **6c** with **7a** or **7b** gave the ethyl or *tert*-butyl esters **8c** and **9c**, respectively, in 65–72% yield. The very low solubilities of these products in organic solvents made purification by chromatography impractical, but impurities could be removed by heating the crude products with methanol and this gave the desired pyrroles in pure form. Nitration of



Scheme 4.



Scheme 5.

benzofurazan with concentrated nitric and sulfuric acids at 30 °C gave the nitro-derivative **6b** in 90% yield, and this similarly reacted with **7a** and **7b** in the presence of DBU in refluxing THF to give the pyrrole esters **8b** and **9b** in 65%

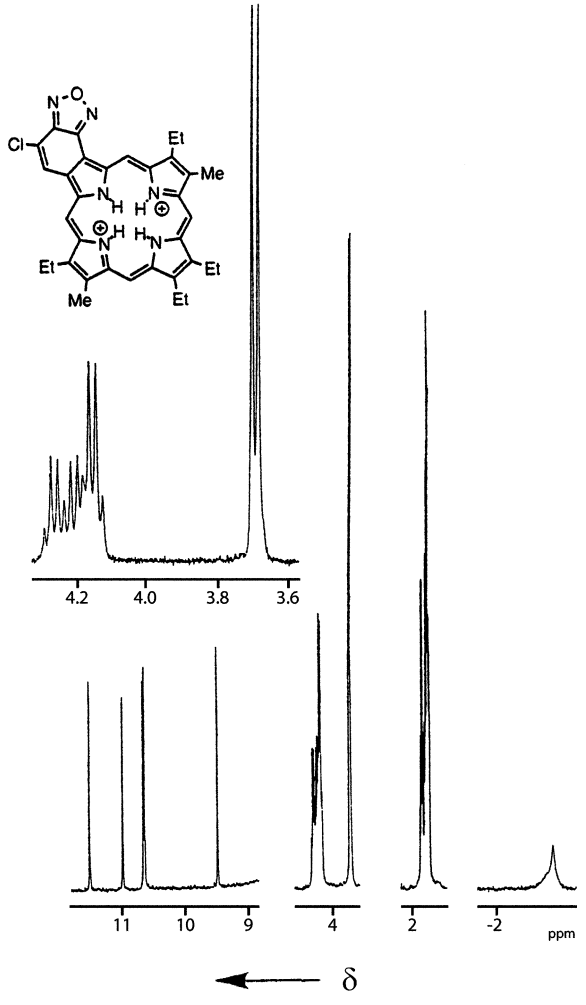


Figure 2. 400 MHz proton NMR spectrum of oxadiazolobenzoporphyrin **4c** in TFA–$CDCl_3$.

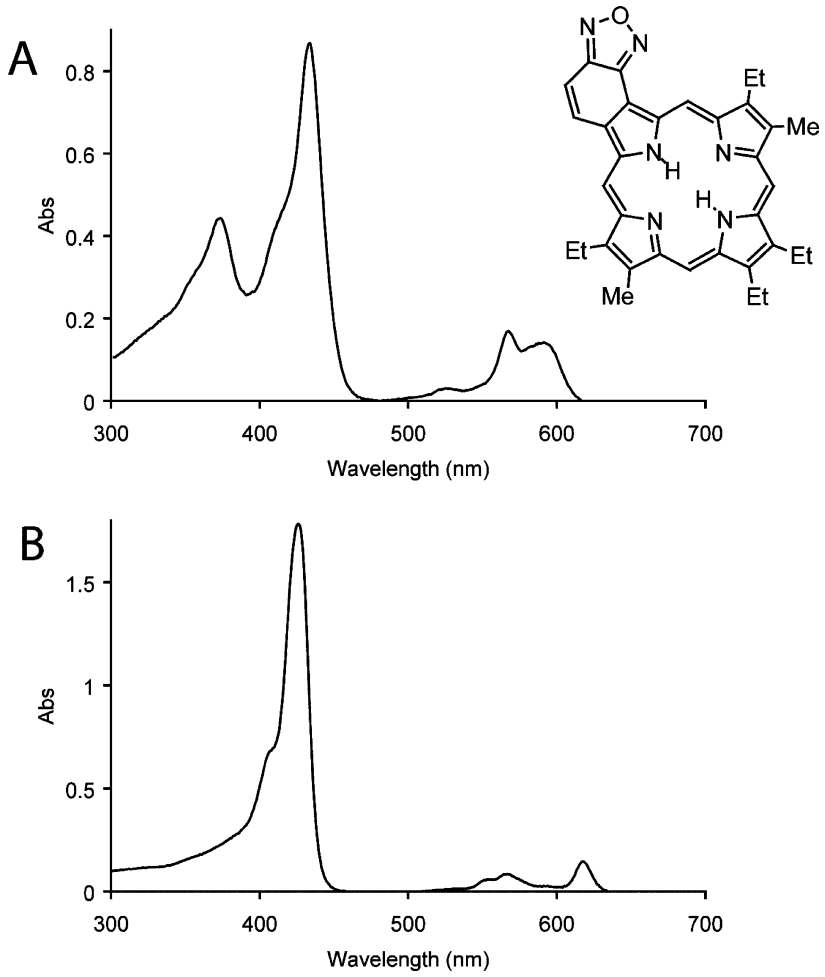


Figure 3. UV–vis spectra for oxadiazolobenzoporphyrin **4b**. (a) Free base in chloroform; (b) Protonated species in 1% TFA–chloroform.

yield. 4-Nitro-2,1,3-benzoselenadiazole (**6d**) similarly reacted with DBU and isocyanoacetates **7** in refluxing DBU to give the related pyrrole esters **8d** and **9d** in 86–89% yield. All of these pyrrole esters had very poor solubility characteristics, but NMR spectra could be obtained in d_6-DMSO. For instance, the proton NMR spectrum of oxadiazolobenzopyrrole **8b** (Fig. 1(a)) confirms the structure of this heterocycle showing the presence of two doublets at 7.5 and 8.0 ppm for the central benzo-unit and a singlet at 8.1 ppm for the pyrrolic CH. The NH is evident as a broad resonance at 13.4 ppm.

Our intent was to prepare the targeted porphyrin systems by MacDonald-type '3+1' condensations using tripyrranes,[22,23] and the unsubstituted pyrroles **5** were required as precursors to these intermediates. Thiadiazolobenzopyrrole ethyl ester **8a** underwent saponification and decarboxylation with KOH in ethylene glycol under nitrogen at 180 °C for 30 min to give excellent yields of **5a**. When the oxygen analogues **8b** and **8c** were reacted under these conditions, very poor yields of the decarboxylation products were obtained. However, when a small amount of hydrazine was added to the reaction mixture, the required tricycles **5b** and **5c** were isolated in 50–76% yield. The hydrazine presumably protects the reactants from oxidative degradation due to the presence of trace amounts of oxygen. However, when the selenium heterocycle **8d** was treated with KOH under these conditions, complete decomposition occurred regardless of reaction time (5–30 min) or whether or not hydrazine was present. Following numerous attempts to modify these conditions, the best results were obtained in a two-step procedure. Ethyl ester **8d** was saponified under mild conditions to give the corresponding carboxylic acid. This underwent decarboxylation in ethylene glycol in the absence of any base at 180 °C to give the required α-unsubstituted pyrrole in 85% yield. However, attempts to convert *tert*-butyl esters **9** to α-unsubstituted pyrroles by treatment with TFA were unsuccessful. The NMR spectra for pyrroles **5** were again generally obtained in d_6-DMSO (e.g., Fig. 1(b)).

The electron impact mass spectra for the new heterocycles were also investigated. For pyrrole esters with fused phenanthrene, phenanthroline, quinoline, isoquinoline, fluoranthene or acenaphthylene rings,[8–11,13] the primary fragmentation pathway was loss of ROH to give species of type **11** (Scheme 2), although loss of an alkene fragment was more prominent for the *tert*-butyl esters resulting in carboxylic acid radical cations like **12**. Similar results were obtained for thiadiazolopyrrole ester **8a** and **9a**. The ethyl ester gave primarily loss of ethanol to give **11** and loss of alkene was a minor pathway, while both fragmentations

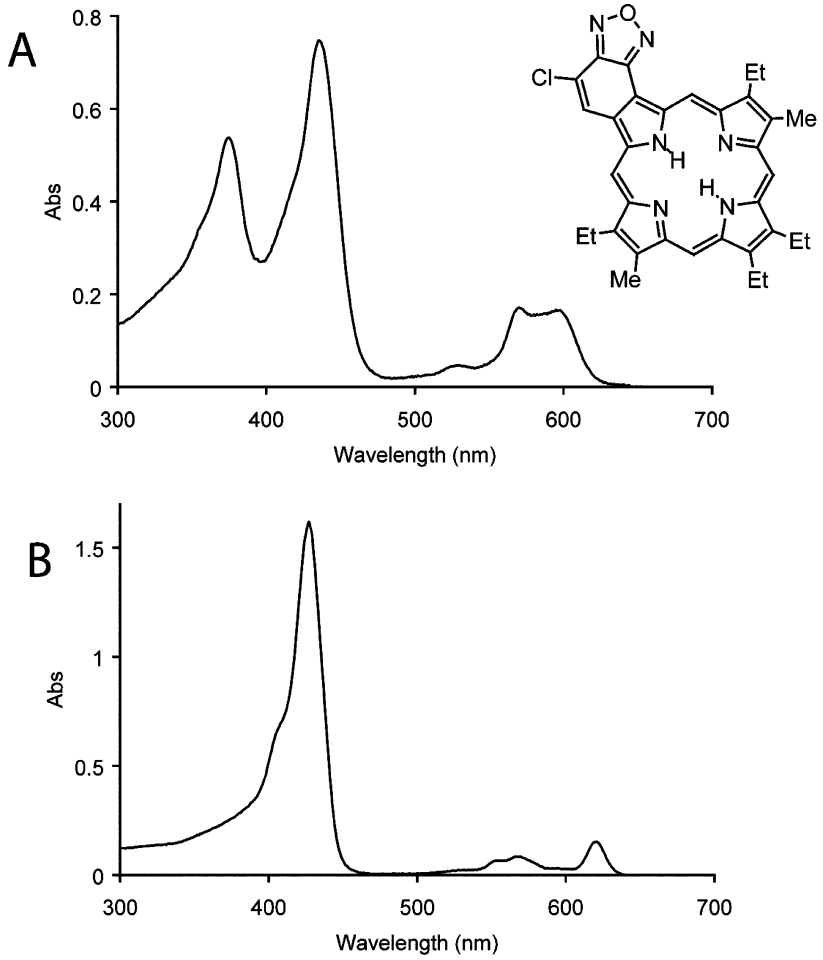


Figure 4. UV–vis spectra for chloro-oxadiazolobenzoporphyrin **4c**. (a) Free base in chloroform. (b) Protonated species in 1% TFA–chloroform.

were about equally favored for the *tert*-butyl ester **9a**.[13] Apart from the presence of multiple isotope peaks for selenium, esters **8d** and **9d** gave similar results. However, the oxadiazolopyrrole ethyl ester **8b** gave loss of EtOH to **11** as a minor fragmentation pathway, and the strongest fragment ion **13** corresponds to loss of ethylene and CO_2. The *tert*-butyl ester **9b** also gave strong fragment ions for **12** and **13**, although it slightly bucks the trend by showing a small increase in the loss of ROH to give **11**. The same types of fragmentation were observed for the chloro-derivatives **8b** and **8c**, although the spectra were not of as high a quality. The unsubstituted tricycle **5a** shows loss of HCN as the main fragmentation pathway.[13] As expected, the two oxadiazolobenzopyrroles **5b** and **5c** primarily gave loss of NO. Unfortunately, selenadiazolobenzopyrrole **5d** did not analyze well by EI MS and its behavior in mass spectrometry could not be determined.

Now that the heterocyclic building blocks **5** were available, the synthesis of the heterocyclic ring fused porphyrins could be investigated. The electron-withdrawing diazole units decrease the reactivity of the fused pyrrole moieties towards electrophilic substitution and this can lead to difficulties. This problem was previously encountered in the synthesis of phenanthrolinoporphyrins **2b** (Chart 1) where the fused pyridine rings exert a similar disruptive influence.[10] The best results for **2b** were obtained when the carbon–carbon bond forming steps were well removed from the fused heterocycle during macrocycle formation, thereby necessitating the use of tripyrrane intermediates.[10] In the earlier synthesis of thiadiazolobenzoporphyrin **4a**, tricycle **5a** was reacted with 2 equiv of an acetoxymethylpyrrole **14a** in refluxing acetic acid–ethanol[23,24] to give a crude preparation of tripyrrane **15a** (Scheme 3).[13,15] This intermediate was taken on without purification and treated with TFA to cleave the *tert*-butyl ester groups. In a one pot sequence, the mixture was diluted with dichloromethane, condensed with pyrrole dialdehyde **16**, and following neutralization with triethylamine the intermediary species were oxidized with DDQ to give **4a** in up to 40% yield. The same approach was used to prepare **4b–d**. Unfortunately, reaction of the oxadiazole derivatives **5b** or **5c** with **14a** in refluxing acetic acid–ethanol afforded virtually no tripyrrane product, and replacement of the alcohol solvent with 2-propanol gave no improvement to the yields. Weak acid is used to catalyze this chemistry but we recognized that protonation of the heterocycle would further decrease the reactivity of the pyrrole subunit (Scheme 4). The oxygen-containing heterocycles appear to have decreased reactivity compared to **5a**, and the major products in the reactions using **5b** and **5c** were ether derivatives of **14a** formed by solvolysis. Attempts to use other acid catalysts such as *p*-toluenesulfonic acid or Montmorillonite clay gave rise to no tripyrrane formation. The possibility of avoiding the use of an acid

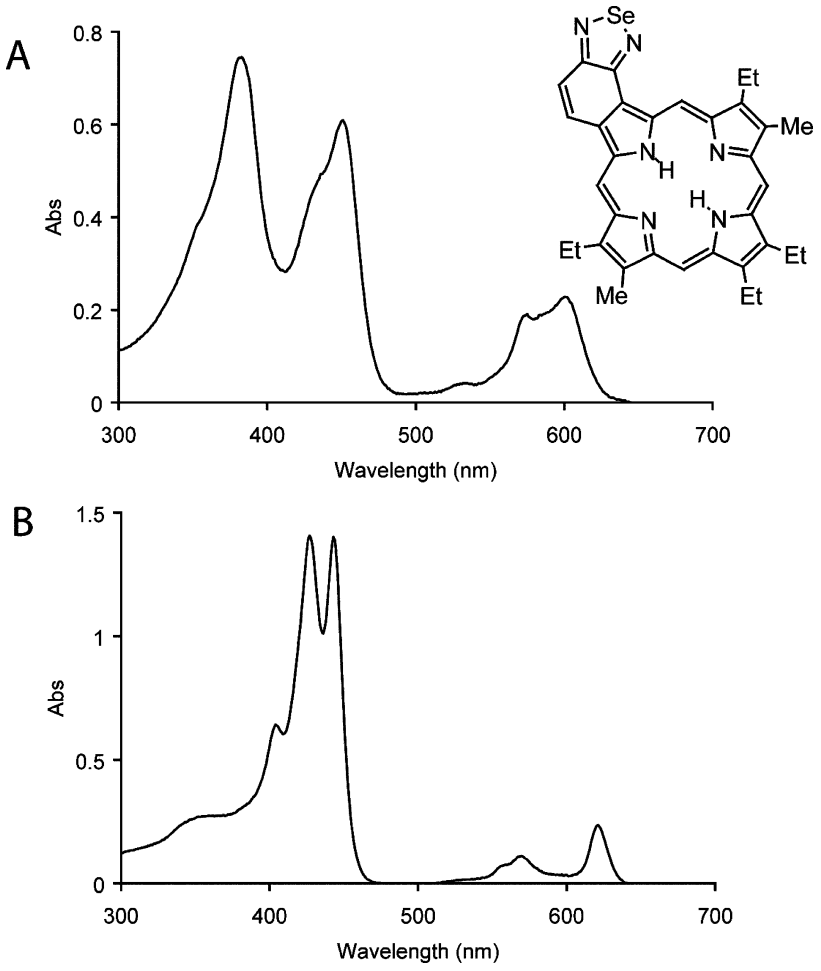


Figure 5. UV–vis spectra for selenadiazolobenzoporphyrin **4d**. (a) Free base in chloroform; (b) Protonated species in 1% TFA–chloroform.

catalyst was also considered using pyridine as a solvent. The chloromethylpyrrole **14b** was reacted with **5b** or **5c** in refluxing pyridine. In principle, pyridine would initially generate a pyridinium salt[25] that could readily eliminate and further react with the pyrrole nucleus. However, only trace amounts of tripyrrane could be detected under these conditions as well. The best results for tripyrrane **15b** involved reacting **5b** with acetoxymethylpyrrole **14a** in refluxing acetic acid-toluene. However, the product was heavily contaminated with impurities and as these tripyrrolic compounds tend to decompose during chromatography this material was taken on through the '3+1' methodology (Scheme 3) in crude form and reacted with TFA and dialdehyde **16**. Subsequent oxidation with DDQ gave poor yields of the porphyrin product, but much better results were obtained using an aqueous ferric chloride solution for the oxidation step,[26,27] and following chromatography and recrystallization from chloroform–methanol the oxadiazolobenzoporphyrin **4b** was isolated as a green powder in 31% yield. The chloro-substituted tricycle **5c** gave the best results when reacted with **14a** in refluxing acetic acid-xylenes. The chloro-group may further decrease the reactivity of **5c** making the use of higher temperatures beneficial. Even so, the tripyrrane intermediate was obtained in very crude form. Following deprotection of the terminal ester groups with TFA, condensation with **16** and oxidation with DDQ, porphyrin **4c** was obtained as a very dark green powder in 17% yield. The selenium heterocycle **4d** was also unreactive toward tripyrrane formation, but the best solvent in this case was ethyl acetate. The poor solubility of **5d** may also exacerbate the problems due to diminished reactivity, and even under the best conditions when **5d** was sonicated for 20–30 min with ethyl acetate prior to the addition of acetic acid to maximize solubilization, the tripyrrane was generated in very crude form. This crude material was taken on through the '3+1' route as before, and selenadiazolobenzoporphyrin **4d** was isolated in 9% yield.

During the course of these studies, the use of dipyrrylmethane intermediates was briefly considered. The *tert*-butyl esters **9** were condensed with acetoxymethylpyrroles in the presence of *p*-toluenesulfonic acid in acetic acid to give moderate yields of dipyrrylmethanes **17** (Scheme 5). The di-*tert*-butyl esters were treated with TFA to cleave the protective groups and condensed with dipyrrylmethane dialdehyde **18** under MacDonald '2+2' reaction conditions[28–30] but no more than trace amounts of the desired porphyrin products **19** were observed. Again, the chemistry appears to be blocked by the reduced reactivity of the ring fused pyrrole unit.

The free base porphyrins **4b–d** were only sparingly soluble in organic solvents, but high quality NMR spectra were easily obtained for the protonated forms in TFA–$CDCl_3$.

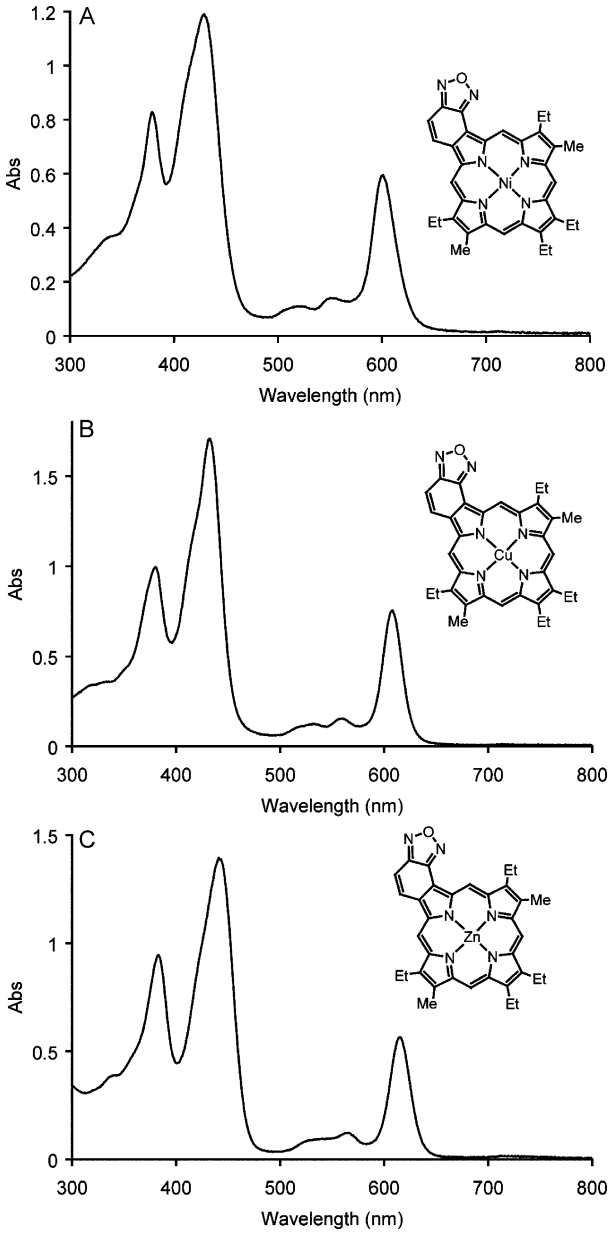


Figure 6. UV–vis spectra for metal complexes of porphyrin **4b** in chloroform. (a) Ni(II) complex **20b**; (b) Cu(II) complex **21b**; (c) Zn complex **22b**.

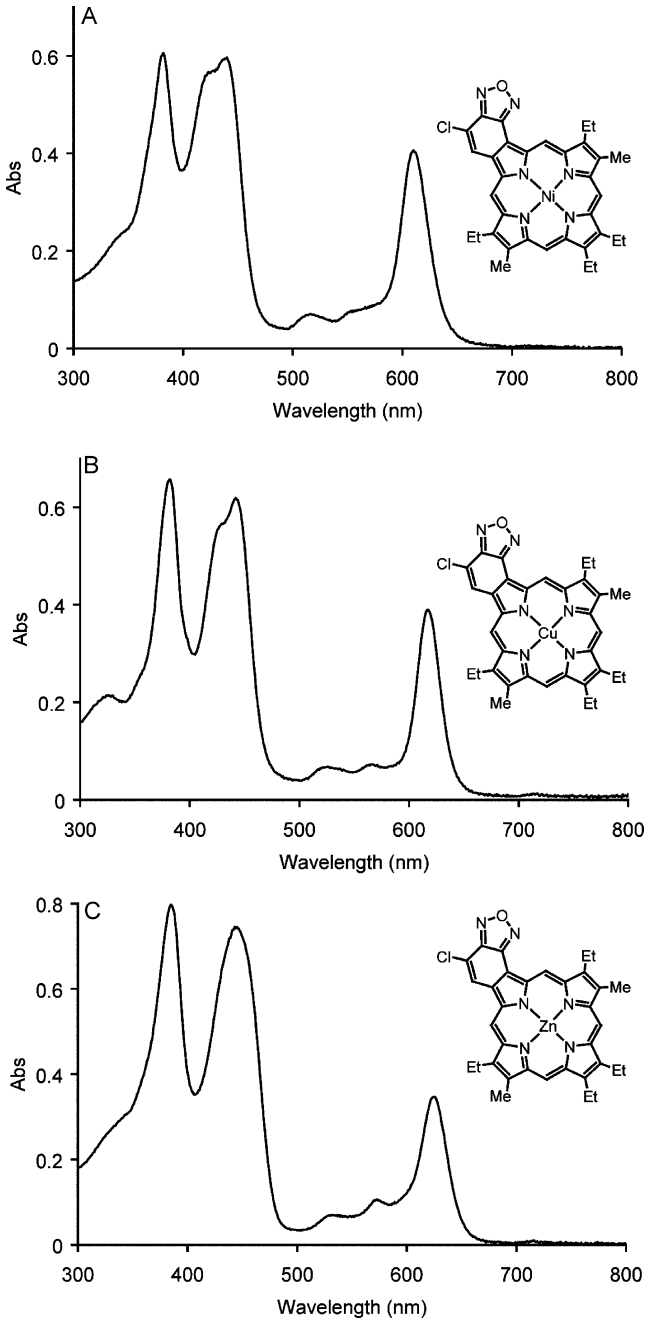


Figure 7. UV–vis spectra for metal complexes of porphyrin **4c** in chloroform. (a) Ni(II) complex **20c**; (b) Cu(II) complex **21c**; (c) Zn complex **22c**.

The proton NMR spectra showed typical diatropic ring currents for the porphyrin macrocycles. For instance, **4c** gives four singlets for the *meso*-protons downfield near 11 ppm, while the internal NHs resonate upfield near −3 ppm (Fig. 2).

The UV–vis spectra for the free base porphyrins **4b–d** (Figs. 3–5) were very different from typical porphyrin spectra, although they were similar to the results previously obtained for **4a**. Porphyrins usually give four Q bands but the longest wavelength band Q I appears to be very weak or absent in the spectra for **4a–d** and the shortest wavelength band (Q IV) is relatively weak. Two major Q bands, tentatively assigned as Q II and Q III, can be seen which are merging in to one another. The longer wavelength band Q II for **4a** shows up at 588 nm for **4a**, but the equivalent bands in the new porphyrins **4b**, **4c** and **4d** are comparatively red shifted and appear at 591, 595 and 600 nm, respectively. All four porphyrins also show split Soret bands, with λ_{max} values of 380 and 438 nm for **4a**, 374 and 434 nm for **4b**, 375 and 436 nm for **4c**, and 383 and 451 nm for **4d**. For both the Soret and Q absorptions, the largest shifts are seen for the selenium system **4d**, but the Soret bands are slightly blue shifted for the oxygen systems **4b** and **4c**. The presence of a chloro-substituent in **4c** induces small bathochromic shifts compared to **4b**. In TFA–chloroform, the protonated forms for the oxadiazolobenzoporphyrins **4b** and **4c** gave a single Soret band, while the sulfur and selenium containing

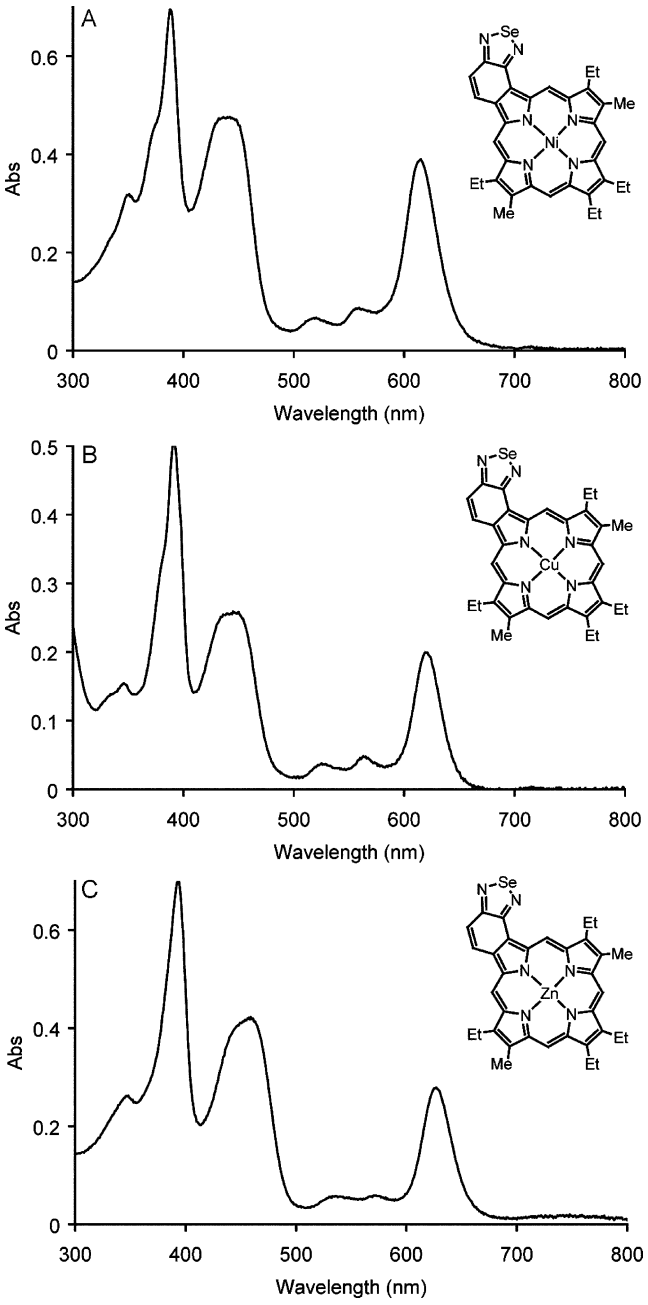


Figure 8. UV–vis spectra for metal complexes of porphyrin **4d** in chloroform. (a) Ni(II) complex **20d**; (b) Cu(II) complex **21d**; (c) Zn complex **22d**.

porphyrins **4a** and **4d** showed split Soret band regions (Figs. 3–5).

Reaction of porphyrins **4b–d** with copper(II), nickel(II) or zinc acetate in DMF or refluxing chloroform–methanol afforded the corresponding metalloporphyrins **20–22** (Scheme 3). These all showed very weak Soret bands and an intense Q band absorption above 600 nm (Figs. 6–8). The shifts for metallo-derivatives derived from **4a** and **4b** were similar, where the longest wavelength band for the 'b series' is red shifted by only 1–3 nm. The chloro-derivatives (or 'c series') showed larger bathochromic shifts with the major Q band having from 8 to 10 nm longer wavelengths than the 'b series'. The selenium chelates, or 'd series', consistently showed the largest effects with the longest wavelength band red shifted compared to the 'b series' by 11–14 nm. As is the case for most porphyrins,[31] the absorption bands for all four series are red shifted going across the period table from nickel(II) porphyrins **20** to copper(II) porphyrins **21** to zinc porphyrins **22**. Focusing on the zinc complexes **22**, the Soret absorptions were observed at 390 and 442 nm for **22a**, 383 and 441 nm for **22b**, 385 and 445 nm for **22c** and 393 and 458 nm for **22d**. The longer wavelength Q band was observed for this series at 612, 615, 625 and 627 nm, respectively, for **22a–d**. These unusually strong longer wavelength bands are approaching values that could be useful for PDT applications, and it is worth noting that the free base porphyrins **4a–d** have all been shown to be photosensitizers for singlet oxygen generation.[32]

3. Conclusions

Novel *c*-annelated pyrroles fused to 2,1,3-benzoxadiazole or 2,1,3-benzoselenadiazole have been synthesized in excellent yields by the Barton–Zard methodology. These pyrroles were taken on to tripyrrane intermediates that were used in crude form to give moderate yields of porphyrins with fused heterocyclic subunits. Oxa- and selenadiazolobenzoporphyrins and their metallo-derivatives have very unusual spectroscopic properties, and these studies may lead to the development of new photosensitizers for applications in PDT. The main limitation in the present study is the diminished reactivity of the ring fused pyrroles that inhibits tripyrrane formation. Further studies are in progress to both improve the yields of porphyrin products and further increase the bathochromic shifts to the intense Q bands for the nickel(II), copper(II) and zinc chelates by extending the fused heterocycles.[33]

4. Experimental

4.1. General

4-Nitro-2,1,3-benzoselenadiazole (**6d**), NBD chloride (**6c**), TFA, and DBU were purchased from Aldrich or Acros, and were used without further purification. THF was distilled from calcium hydride immediately prior to use. Chromatography was performed using Grade III neutral alumina or 70–230 mesh silica gel. Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. Due to the small quantities of porphyrin samples available, high resolution MS data were used in place of CHN analyses, and purity was established by NMR spectroscopy and TLC. UV–vis absorption spectra were run on a Varian Cary Spectrophotometer, and NMR data was obtained on a Varian Gemini 400 MHz FT NMR spectrometer. Mass spectral determinations were conducted at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, and elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

4.2. Synthetic procedures

4.2.1. Ethyl oxadiazolobenzo[4,5-*c*]pyrrole-1-carboxylate (8b). Benzofurazan[34] (1.00 g) was taken up in 4.0 mL of concentrated sulfuric acid and the solution cooled in an ice bath. Concentrated nitric acid (1.5 mL) was added dropwise, maintaining the temperature <30 °C, and the resulting mixture stirred at room temperature for a further 20 min. Water was added dropwise, and the resulting precipitate suction filtered to give 4-nitrobenzofurazan (**6b**; 1.25 g; 90%) as a pale yellow powder, mp 84–85 °C (lit. mp[35] 93 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (1H, dd, $J=7.6$, 8.8 Hz), 8.32 (1H, d, $J=8.8$ Hz), 8.52 (1H, d, $J=7.6$ Hz); ^{13}C NMR (d_6-DMSO): δ 124.7, 129.9, 130.1, 137.4, 142.8, 150.6. Ethyl isocyanoacetate[36] (0.63 g) and DBU (0.84 g) were dissolved in freshly distilled THF (300 mL) in a 1000 mL round bottom flask, a solution of **6b** (1.00 g) in THF (200 mL) was added, and the resulting dark mixture was allowed to stir under reflux overnight. The solution was diluted with dichloromethane, washed with water, dried over sodium sulfate, and the solvents evaporated under reduced pressure. Recrystallization from methanol gave **8b** (0.80 g, 57%) as a pale brown solid, mp 261 °C. An analytical sample was obtained by sublimation at 0.05 torr and 210 °C as pale yellow crystals, mp 263 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.36 (3H, t, $J=7$ Hz), 4.36 (2H, q, $J=7$ Hz), 7.51 (1H, d, $J=9.6$ Hz), 8.05 (1H, d, $J=10$ Hz), 8.14 (1H, s), 13.36 (1H, br s); ^{1}H NMR (400 MHz, $CDCl_3$, downfield region only): δ 7.43 (1H, d, $J=9.6$ Hz), 7.87 (1H, d, $J=3.6$ Hz), 8.07 (1H, d, $J=9.6$ Hz), 10.0 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 15.0, 61.1, 108.0, 112.1, 118.1, 121.5, 125.1, 129.2, 145.3, 149.4, 160.8; EI MS (70 eV): *m/z* (rel. int.) 232 (14), 231 (100, M^+), 203 (5, $[M^+-C_2H_4]$), 186 (13), 185 (17, $[M^+-$EtOH]), 159 (77, $[M^+-C_2H_4–CO_2]$), 158 (13), 157 (22), 156 (3), 155 (15); HRMS (EI): Calcd for $C_{11}H_9N_3O_3$: 231.0641. Found: 231.0644. Anal. Calcd for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17. Found: C, 57.01; H, 3.79; N, 17.76.

4.2.2. *tert*-Butyl oxadiazolobenzo[4,5-*c*]pyrrole-1-carboxylate (9b). *tert*-Butyl isocyanoacetate[9c] (0.86 g) and DBU (0.92 g) in THF (300 mL) were reacted with **6b** (1.00 g) in THF (200 mL) under the conditions described above. Recrystallization from methanol gave the title pyrrole (1.12 g, 71%) as a pale brown powder, mp 260 °C, dec. An analytical sample was obtained by sublimation at 0.05 torr and 210 °C as pale yellow crystals, mp 268–269 °C, dec. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.59 (9H, s), 7.49 (1H, d, $J=9.2$ Hz), 8.00 (1H, d, $J=8.8$ Hz), 8.10 (1H, s), 13.18 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 28.7, 82.3, 107.8, 111.9, 119.4, 121.0, 124.5, 129.3, 145.3, 149.4, 160.2; EI MS (70 eV): *m/z* (rel. int.) 259 (11, M^+), 203 (60, $[M^+-C_4H_8]$), 186 (13), 185 (24, $[M^+-t$-BuOH]), 160 (10), 159 (100, $[M^+-C_4H_8–CO_2]$), 158 (13), 157 (22), 156 (3), 155 (15); HRMS (EI): Calcd for $C_{13}H_{13}N_3O_3$: 259.0964. Found: 259.0957. Anal. Calcd for $C_{13}H_{13}N_3O_3$: C, 60.22; H, 5.05; N, 16.21. Found: C, 59.97; H, 4.86; N, 16.20.

4.2.3. Ethyl 7-chloro-oxadiazolobenzo[4,5-*c*]pyrrole-1-carboxylate (8c). Ethyl isocyanoacetate (0.56 g) and DBU (0.76 g) in THF (300 mL) were reacted with **6c** (1.00 g) in THF (200 mL) under the conditions described above. Recrystallization from methanol gave the title pyrrole (1.12 g, 83%) as a brown powder, mp 262 °C, dec. An analytical sample was obtained by sublimation at 0.05 torr and 175 °C as pale yellow crystals, mp 290 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.36 (3H, t, $J=7$ Hz), 4.36 (2H, q, $J=7$ Hz), 8.01 (1H, s), 8.13 (1H, s), 13.44 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 14.9, 61.4, 106.8, 116.5, 118.1, 122.0, 124.7, 127.8, 145.3, 148.7, 160.4; EI MS (70 eV): *m/z* (rel. int.) 267 (23), 265 (60, M^+), 237 (3.4, $[M^+-C_2H_4]$), 230 (7, $[M^+-$Cl]), 222 (5), 221 (6), 220 (8), 219 (18, $[M^+-$EtOH]), 205 (39), 203 (84), 195 (16), 194 (8), 193 (47, $[M^+-C_2H_4–CO_2]$); HRMS (EI): Calcd for $C_{11}H_8ClN_3O_3$: 265.0255. Found: 265.0254. Anal. Calcd for $C_{11}H_8ClN_3O_3$: C, 49.73; H, 3.03; N, 15.82. Found: C, 49.51; H, 2.79; N, 15.77.

4.2.4. *tert*-Butyl 7-chloro-oxadiazolobenzo[4,5-*c*]pyrrole-1-carboxylate (9c). *tert*-Butyl isocyanoacetate (0.71 g) and DBU (0.92 g) in THF (300 mL) were reacted with **6b** (1.00 g) in THF (200 mL) under the conditions described above. Recrystallization from methanol gave the title pyrrole (1.18 g, 80%) as a pale brown powder, mp 292 °C, dec. An analytical sample was obtained by sublimation at 0.05 torr and 210 °C as pale yellow crystals, mp 294 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (9H, s), 7.83 (1H, s), 8.05 (1H, s), 10.03 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 28.6, 82.5, 106.6, 116.2, 119.3, 121.5, 124.1, 127.9, 145.3, 148.7, 159.8; EI MS (70 eV): *m/z* (rel. int.) 295 (6), 293 (18, M^+), 239 (34), 238 (11), 237 (100, $[M^+-C_4H_8]$), 221 (17), 220 (18), 219 (50, $[M^+-t$-BuOH]), 203 (13), 202 (19), 195 (2), 193 (7.6, $[M^+-C_4H_8–CO_2]$), 192 (4), 191 (6.8); HRMS (EI): Calcd for $C_{13}H_{12}ClN_3O_3$: 293.0575. Found: 293.0567. Anal. Calcd for $C_{13}H_{12}ClN_3O_3\cdot\frac{1}{8}H_2O$: C, 52.76; H, 4.17; N, 14.20. Found: C, 52.58; H, 3.88; N, 14.19.

4.2.5. Ethyl selenadiazolobenzo[4,5-*c*]pyrrole-1-carboxylate (8d). Ethyl isocyanoacetate (0.63 g) and DBU (0.84 g) in THF (300 mL) were reacted with **6d** (1.00 g) in THF (200 mL) under the conditions described above. Recrystallization from methanol gave the title pyrrole (1.12 g, 85%) as a brown powder, mp 230 °C. An analytical sample was obtained by sublimation at 0.05 torr and 210 °C as pale orange crystals, mp 236 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.36 (3H, t, $J=7$ Hz), 4.36 (2H, q, $J=7$ Hz), 7.40 (1H, d, $J=9.6$ Hz), 7.98 (1H, s), 7.99 (1H, d, $J=9.6$ Hz), 13.12 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 15.1, 60.9, 116.0, 118.8, 120.8, 122.0, 125.6, 125.9, 155.8, 160.1, 161.2; EI MS (70 eV): *m/z* (rel. int.) 297 (18), 296 (13), 295 (100, M^+), 294 (8), 293 (50), 292 (18), 291 (17), 267 (5.0, $[M^+-C_2H_4]$), 265 (2.7), 259 (97.4), 252 (4.7), 251 (17), 250 (19), 249 (86, $[M^+-$EtOH]), 248 (17), 247 (44), 246 (16), 245 (15), 237 (20), 225 (2.2), 224 (2.7), 223 (8.0, $[M^+-C_2H_4–CO_2]$), 222 (8.1), 221 (15), 203 (41); HRMS (EI): Calcd for $C_{11}H_9N_3O_2Se$: 294.9866. Found: 294.9860. Anal. Calcd for $C_{11}H_9N_3O_2Se\cdot\frac{1}{5}H_2O$: C, 44.37; H, 3.18; N, 14.11. Found: C, 44.19; H, 2.98; N, 14.04.

4.2.6. *tert*-Butyl selenadiazolobenzo[4,5-*c*]pyrrole-1-carboxylate (9d). *tert*-Butyl isocyanoacetate (0.64 g) and DBU (0.87 g) in THF (300 mL) were reacted with **6d** (1.00 g) in THF (200 mL) under the conditions described above. Recrystallization from methanol gave the title pyrrole (1.30 g, 92%) as a pale brown powder, mp 210 °C. An analytical sample was obtained by sublimation at 0.05 torr and 210 °C as pale orange crystals, mp 212 °C. ^{1}H NMR

(400 MHz, d_6-DMSO): δ 1.60 (9H, s), 7.38 (1H, d, J=9.6 Hz), 7.95 (1H, s), 7.99 (1H, d, J=9.6 Hz), 12.94 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 28.8, 81.7, 117.2, 118.7, 120.3, 121.8, 125.0, 126.1, 155.9, 160.1 160.7; EI MS (70 eV): *m/z* (rel. int.) 325 (5.7), 324 (4.0), 323 (100, M^+), 322 (2.1), 321 (13), 320 (4.8), 319 (5.0), 270 (2.4), 269 (20), 268 (11), 267 (100, [$M^+-C_4H_8$]), 266 (62), 265 (48), 264 (17), 263 (18), 252 (4.6), 251 (17), 250 (19), 249 (86, [M^+-t-BuOH]), 248 (9), 247 (45), 246 (17), 245 (17), 224 (2.3), 223 (7.9, [$M^+-C_4H_8$–CO_2]), 222 (7.0), 221 (10), 220 (4.5), 219 (5.7), 218 (2.4); HRMS (EI): Calcd for $C_{13}H_{13}N_3O_2Se$: 323.0182. Found: 323.0172. Anal. Calcd for $C_{13}H_{13}N_3O_2Se$: C, 48.46; H, 4.07; N, 13.04. Found: C, 48.05; H, 3.92; N, 12.82.

4.2.7. Oxadiazolobenzo[4,5-*c*]pyrrole (5b). Nitrogen was bubbled through a mixture of ethyl ester **8b** (1.00 g), potassium hydroxide (2.35 g) and hydrazine (8 drops) in ethylene glycol (48 mL) for 10 min, and the resulting mixture stirred under nitrogen at 180 °C for 30 min. The mixture was poured into ice water, and the precipitate suction filtered and dried in vacuo to give the α-unsubstituted pyrrole (0.34–0.52 g, 50–76%) as a pale brown powder, mp 178–179 °C. An analytical sample was obtained by sublimation at 0.05 torr and 150 °C as pale yellow crystals, mp 180 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.11 (1H, d, J=9.6 Hz), 7.47 (1H, s), 7.64 (1H, d, J=9.2 Hz), 7.88 (1H, s), 12.32 (1H, br s); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.15 (1H, d, J=9.6 Hz), 7.26 (1H, s), 7.50 (1H, J=9.6 Hz), 7.74 (1H, s), 9.0 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 106.0, 107.2, 116.9, 117.4, 121.5, 130.6, 146.0, 150.0; EI MS (70 eV): *m/z* (rel. int.) 160 (11), 159 (100, M^+), 130 (8), 129 (39, [M^+-NO]), 128 (4.5); HRMS (EI): Calcd for $C_8H_5N_3O$: 159.0434. Found: 159.0433. Anal. Calcd for $C_8H_5N_3O$: C, 60.38; H, 3.17; N, 26.40. Found: C, 60.47; H, 3.00; N, 25.69.

4.2.8. 7-Chloro-oxadiazolobenzo[4,5-*c*]pyrrole (5c). Ethyl ester **8c** (1.00 g), potassium hydroxide (2.35 g) and hydrazine (8 drops) in ethylene glycol (48 mL) was reacted as described for the previous procedure to give **5c** (0.38–0.48 g, 50–65%) as a khaki green powder, mp 274 °C. An analytical sample was obtained by sublimation at 0.05 torr and 150 °C as pale yellow crystals, mp 270 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.48 (1H, s), 7.83 (1H, s), 7.91 (1H, s), 12.51 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 104.9, 111.2, 117.6, 117.9, 121.2, 129.6, 145.9, 149.2; EI MS (70 eV): *m/z* (rel. int.) 196 (3.5), 195 (35), 194 (11), 193 (100, M^+), 165 (13), 164 (5.2), 163 (36, [M^+-NO]), 162 (3.8); HRMS (EI): Calcd for $C_8H_4ClN_3O$: 193.0043. Found: 193.0043. Anal. Calcd for $C_8H_4ClN_3O\cdot\frac{1}{2}H_2O$: C, 47.43; H, 2.48; N, 20.74. Found: C, 47.67; H, 2.08; N, 20.22.

4.2.9. Selenadiazolobenzo[4,5-*c*]pyrrole-1-carboxylic acid (10). Ethyl ester **8d** (0.80 g) was dissolved in DMSO (20 mL) on a preheated oil bath at 100 °C under a nitrogen atmosphere. A solution of sodium hydroxide (3.2 g) in water (10 ml) was added, and the mixture allowed to reflux under nitrogen for 2 h. The solution was diluted with water (60 mL) and cooled to 0 °C with the aid of a salt-ice bath. The solution was neutralized to litmus paper with acetic acid, maintaining the temperature <5 °C, the resulting mixture was stirred at room temperature for 20 min, and the deep green precipitate suction filtered and washed well with water. Following vacuum drying, the carboxylic acid (0.473 g, 69%) was obtained as a green powder, mp 218–219 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.36 (1H, d, J=9.6 Hz), 7.92 (1H, s), 8.03 (1H, d, J=9.6 Hz), 13.0 (2H, br); ^{13}C NMR (d_6-DMSO): δ 116.9, 118.7, 120.2, 121.6, 125.5, 126.3, 155.9, 160.2, 162.6; HRMS (EI): Calcd for $C_9H_5N_3O_2Se$: 264.9562. Found: 264.9554.

4.2.10. Selenadiazolobenzo[4,5-*c*]pyrrole (5d). Nitrogen was bubbled through a mixture of the foregoing carboxylic acid (1.00 g), and ethylene glycol (48 mL) for 10 min, and the resulting mixture stirred under nitrogen at 180 °C for 30 min. The mixture was poured into ice water, and the precipitate suction filtered and dried in vacuo to give the α-unsubstituted pyrrole (0.51 g, 60%) as a brown powder. An analytical sample was obtained by sublimation at 0.05 torr and 140 °C as pale orange crystals, mp 180 °C. ^{1}H NMR (400 MHz, d_6-DMSO): δ 7.03 (1H, d, J=9.6 Hz), 7.31 (1H, s), 7.55 (1H, d, J=9.6 Hz), 7.75 (1H, s), 12.07 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 114.9, 116.2, 117.7, 117.8, 121.8, 127.6, 146.7, 150.3. Anal. Calcd for $C_8H_5N_3Se\cdot\frac{1}{3}H_2O$: C, 42.12; H, 2.50; N, 18.42. Found: C, 42.28; H, 2.12; N, 18.04.

4.2.11. *tert*-Butyl 5-chloromethyl-4-ethyl-3-methylpyrrole-2-carboxylate (14b). *N*-Chlorosuccinimide (1.28 g) was added to a solution of *tert*-butyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate[37] (2.00 g) in carbon tetrachloride (200 mL) and the mixture stirred at room temperature overnight. The solution was washed with water (3× 200 mL) and evaporated under reduced pressure. Recrystallization of the residue from hexanes and subsequent removal of trace solvent in vacuo afforded the title pyrrole (1.60 g, 70%) as a pale brown powder, mp 96 °C, dec. Due to the instability of this compound, it was stored in the freezer. ^{1}H NMR ($CDCl_3$): δ 1.10 (3H, t, J=7.6 Hz), 1.57 (9H, s), 2.24 (3H, s), 2.45 (2H, q, J=7.6 Hz), 4.59 (2H, s), 8.66 (1H, br s); ^{13}C ($CDCl_3$): δ 10.5, 15.7, 17.4, 28.7, 37.0, 81.1, 121.1, 125.7, 126.7, 138.9, 161.2.

4.2.12. *tert*-Butyl 3(5-benzyloxycarbonyl-3-ethyl-4-methyl-2-pyrrolylmethyl)oxadiazolobenzo[4,5-*c*]pyrrole-1-carboxylate (17). A solution of benzyl 5-acetoxymethyl-4-ethyl-3-methylpyrrole-2-carboxylate[38] (185 mg) in acetic acid (15 mL) was added via a syringe pump over a 12 h period to a stirred solution of **9b** (150 mg) and *p*-toluenesulfonic acid (40 mg) in acetic acid under a nitrogen atmosphere. The resulting mixture was stirred for a further 12 h, poured into 200 mL of ice water, and the resulting precipitate suction filtered and dried in vacuo. The crude product was chromatographed on grade III alumina eluting with 5% ethyl acetate–toluene. Once the impurity fractions had been collected, the eluting solvent system was gradually increased in polarity to 10% ethyl acetate–toluene. A bright pink fraction was collected and recrystallized from methanol to afford the title dipyrrylmethane (140 mg, 48%) as pink crystals, mp 161–161.5 °C; ^{1}H NMR (400 MHz, d_6-DMSO): δ 0.65 (3H, t, J=7.2 Hz), 1.59 (9H, s), 2.10 (3H, s), 2.40 (2H, q, J=7.2 Hz), 4.37 (2H, s), 5.27 (2H, s), 7.37 (5H, m), 7.47 (1H, d, J=9.6 Hz), 7.92 (1H, d, J=9.6 Hz), 11.25 (1H, br s), 12.98 (1H, br s); ^{13}C NMR (d_6-DMSO): δ 10.9, 16.1, 17.1, 23.8, 28.7, 65.3, 82.3,

105.7, 112.1, 117.5, 118.5, 124.0, 124.5, 126.5, 128.4, 128.6, 129.1, 129.4, 129.9, 133.3, 137.5, 145.5, 149.6, 160.5, 161.4. Anal. Calcd for $C_{29}H_{30}N_4O_5 \cdot H_2O$: C, 65.40; H, 6.05; N, 10.52. Found: C, 65.26; H, 5.74; N, 10.71.

4.2.13. 8,12,13,17-Tetraethyl-7,18-dimethyloxadiazolobenzo[4,5-*b*]porphyrin (4b). Oxadiazolobenzopyrrole **5b** (100 mg) and acetoxymethylpyrrole **14a**[39] (352 mg) were stirred under reflux with acetic acid (0.75 mL) and toluene (8 mL) under nitrogen for 16 h. The solution was cooled, diluted with dichloromethane, washed with water and evaporated to dryness under reduced pressure to give the crude tripyrrane **15b** as a deep burgundy colored solid that was used without further purification. ^{1}H NMR (400 MHz, d_6-DMSO, downfield region only): δ 4.13 (2H, s), 4.29 (2H, s), 7.00 (1H, d, $J=9.6$ Hz), 7.49 (1H, d, $J=9.6$ Hz), 10.88 (1H, br s), 11.01 (1H, br s), 11.61 (1H, br s). Crude **15b** (100 mg) was dissolved in TFA (2.5 mL) and stirred for 5 min at room temperature under nitrogen. The mixture was diluted with dichloromethane (40 mL), followed by the immediate addition of dialdehyde **16**[23,40] (30 mg) and the mixture stirred under nitrogen for an additional 2 h. The dark solution was poured into a separatory funnel and shaken for 5 min with 0.1% aqueous ferric chloride solution. The organic layer was separated, the aqueous phase back extracted with dichloromethane, and the combined organic phases washed with water, 10% sodium bicarbonate solution, and water. The solvent was evaporated under reduced pressure and the residue chromatographed on grade III alumina eluting with 30% dichloromethane–toluene. A deep green colored fraction was collected, the solvent evaporated, and the residue recrystallized from chloroform–methanol to give porphyrin **4b** (29 mg, 31%) as green crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 373 (4.83), 393 (4.58), 434 (5.12), 567 (4.42), 592 nm (4.33); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 426 (5.39), 567 (4.06), 591 (3.56), 618 nm (4.30); ^{1}H NMR (400 MHz, TFA–$CDCl_3$): $\delta -3.37$ (4H, br), 1.73–1.88 (12H, m), 3.70 (3H, s), 3.72 (3H, s), 4.17–4.30 (8H, m), 8.74 (1H, d, $J=9.2$ Hz), 9.54 (1H, d, $J=9.6$ Hz), 10.71 (1H, s), 10.73 (1H, s), 11.11 (1H, s), 11.62 (1H, s); ^{13}C NMR (TFA–$CDCl_3$): δ 11.9, 16.3, 16.4, 17.2, 20.1, 20.3, 20.5, 99.0, 99.4, 99.9, 101.0, 119.5, 121.3, 126.5, 134.9, 136.4, 137.1, 138.8, 138.9, 142.3, 143.1, 143.5, 144.1, 144.4, 144.8, 145.1, 145.6, 146.3, 150.6; HRMS (ESI): Calcd for $C_{34}H_{34}N_6O+H$: 543.2872. Found: 543.2859.

4.2.14. Nickel(II) complex 20b. Porphyrin **4b** (12 mg) and nickel(II) acetate tetrahydrate (42 mg) were stirred with DMF (10 mL) in the dark under reflux overnight. The solution was cooled to room temperature, diluted with chloroform, and washed with water (3×200 mL). The organic layer was evaporated under reduced pressure and the residue recrystallized from chloroform–methanol to give the nickel complex (7.5 mg, 63%) as green sheets, mp >300 °C. UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 379 (4.66), 428 (4.82), 553 (3.92), 601 nm (4.52); HRMS (FAB): Calcd for $C_{34}H_{32}N_6ONi$: 598.1991. Found: 598.1992.

4.2.15. Copper(II) complex 21b. A saturated solution of copper(II) acetate in methanol (10 mL) was added to a solution of porphyrin **4b** (10 mg) in chloroform (10 mL), and the mixture stirred under reflux in the dark overnight. The solution was cooled to room temperature, diluted with chloroform, and washed with water (3×200 mL). The organic layer was evaporated under reduced pressure and the residue recrystallized from chloroform–methanol to give the copper complex (6 mg, 57%) as a deep green powder, mp >300 °C. UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 380 (4.75), 432 (4.98), 559 (3.93), 608 nm (4.63); HRMS (FAB): Calcd for $C_{34}H_{32}N_6OCu$: 603.1933. Found: 603.1932.

4.2.16. Zinc complex 22b. A saturated solution of zinc(II) acetate in methanol (10 mL) was added to a solution of porphyrin **4b** (10 mg) in chloroform (10 mL), and the mixture stirred under reflux in the dark overnight. The solution was cooled to room temperature, diluted with chloroform, and washed with water (3×200 mL). The organic layer was evaporated under reduced pressure and the residue recrystallized from chloroform–methanol to give the zinc complex (9.5 mg, 87%) as a green powder, mp >300 °C. UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 384 (4.71), 443 (4.84), 566 (3.86), 617 nm (4.48); HRMS (FAB): Calcd for $C_{34}H_{32}N_6OZn$: 604.1929. Found: 604.1929.

4.2.17. 3^2-Chloro-8,12,13,17-tetraethyl-7,18-dimethyloxadiazolobenzo[4,5-*b*]porphyrin (4c). Pyrrole **5c** (100 mg) and acetoxymethylpyrrole **14a** (288 mg) were stirred under reflux with acetic acid (0.75 mL) and xylene (8 mL) under nitrogen for 16 h. The solution was cooled, diluted with dichloromethane, washed with water and evaporated to dryness under reduced pressure to give the crude tripyrrane **15c** as a reddish brown solid that was used without further purification. ^{1}H NMR (400 MHz, d_6-DMSO, downfield region only): δ 4.16 (2H, s), 4.26 (2H, s), 7.77 (1H, s), 10.75 (1H, br s), 11.03 (1H, br s), 11.72 (1H, br s). Crude **15c** (100 mg) deprotected with TFA (2.5 mL) and reacted with dialdehyde **16** (30 mg) under the conditions described for **4b**. The crude product was chromatographed on grade III alumina eluting with 30% dichloromethane–toluene and recrystallized from chloroform–methanol to give porphyrin **4c** (16 mg, 17%) as dark green crystals, mp >300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 374 (4.86), 436 (5.00), 570 (4.36), 596 nm (4.35); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 427 (5.33), 568 (4.05), 620 nm (4.30); ^{1}H NMR (400 MHz, TFA–$CDCl_3$): $\delta -2.96$ (4H, br), 1.72–1.86 (12H, m), 3.67 (3H, s), 3.68 (3H, s), 4.13–4.26 (8H, m), 9.50 (1H, s), 10.63 (1H, s), 10.65 (1H, s), 10.97 (1H, s), 11.49 (1H, s); ^{13}C NMR (TFA–$CDCl_3$): δ 11.7, 16.2, 16.3, 17.2, 20.1, 20.3, 20.4, 99.1, 99.5, 100.1, 100.7, 119.5, 121.2, 125.6, 135.2, 135.9, 136.0, 136.2, 139.4, 139.4, 142.1, 142.2, 143.0, 143.1, 143.6, 144.2, 144.6, 145.3, 145.6, 150.2; HRMS (ESI): Calcd for $C_{34}H_{33}ClN_6O+H$: 577.2483. Found: 577.2506.

4.2.18. Nickel(II) complex 20c. Porphyrin **4c** (10 mg) and nickel(II) acetate tetrahydrate (40 mg) were reacted in DMF (10 mL) under the conditions described for **20b**. Recrystallization from chloroform–methanol gave the nickel complex (4.8 mg, 32%) as green sheets, mp >300 °C. UV–vis (1% Et_3N–HCl_3): λ_{max} ($\log_{10}\varepsilon$) 381 (4.40), 440 (4.39), 610 nm (4.23); HRMS (FAB): Calcd for $C_{34}H_{31}ClN_6ONi$: 632.1601. Found: 632.1603.

4.2.19. Copper(II) complex 21c. Porphyrin **4c** (8 mg) and copper(II) acetate monohydrate (48 mg) were reacted in DMF (10 mL) under the conditions described for **20b**. Recrystallization from chloroform–methanol gave the copper complex (6.2 mg, 77%) as a blue-green powder, mp > 300 °C. UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 325 (4.12), 382 (4.61), 442 (4.59), 618 nm (4.39); FD MS: *m/z* (rel. int.) 642 (7), 641 (20), 640 (30), 639 (89), 638 (42), 637 (100) (M^+).

4.2.20. Zinc complex 22c. Porphyrin **4c** (7 mg) and zinc acetate dihydrate (50 mg) were reacted in DMF (10 mL) under the conditions described for **20b**. Recrystallization from chloroform–methanol gave the zinc complex (6.3 mg, 86%) as a green powder, mp > 300 °C. UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 387 (4.67), 445 (4.65), 573 (3.83), 627 nm (4.32); FD MS: *m/z* (rel. int.) 645 (7), 644 (16), 643 (25), 642 (55), 641 (33), 640 (95), 639 (36), 638 (100) (M^+).

4.2.21. 8,12,13,17-Tetraethyl-7,18-dimethylselenadiazolobenzo[4,5-*b*]porphyrin (4d). Selenadiazolobenzopyrrole **5d** (100 mg) was taken up in ethyl acetate (20 mL) and sonicated for 20 min. Acetic acid (92 mL) and acetoxymethylpyrrole **14a** (254 mg) were added, and the resulting mixture was refluxed with stirring under nitrogen for 16 h. The solution was cooled, diluted with dichloromethane, washed with water and sodium bicarbonate solution, and evaporated to dryness under reduced pressure to give the crude tripyrrane **15d** as a dark red solid that was used without further purification. Crude **15d** (100 mg) deprotected with TFA (2.5 mL) and reacted with dialdehyde **16** (29 mg) under the conditions described for **4b**. The crude product was chromatographed on grade III alumina eluting with 30% dichloromethane–toluene and recrystallized from chloroform–methanol to give porphyrin **4d** (9 mg, 9%) as green crystals, mp > 300 °C; UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 382 (4.78), 450 (4.69), 574 (4.19), 600 nm (4.27); UV–vis (1% TFA–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 369 (4.33), 404 (4.70), 427 (5.04), 569 (3.94), 597 (3.44), 621 nm (4.27); ^{1}H NMR (400 MHz, TFA–$CDCl_3$): δ −3.62 (2H, br), −2.96 (2H, br), 1.73–1.88 (12H, m), 3.66 (3H, s), 3.69 (3H, s), 4.14–4.29 (8H, m), 8.74 (1H, d, J=9.2 Hz), 9.57 (1H, d, J=9.6 Hz), 10.62 (1H, s), 10.64 (1H, s), 11.04 (1H, s), 12.05 (1H, s); ^{13}C NMR (TFA–$CDCl_3$): δ 12.0, 16.6, 16.7, 17.5, 20.2, 20.3, 20.4, 20.5, 98.1, 99.2, 99.5, 102.1, 124.4, 126.7, 126.8, 134.5, 137.3, 137.6, 138.1, 138.3, 141.6, 142.3, 142.6, 143.4, 143.5, 143.9, 144.1, 144.4, 145.2, 156.3, 161.9; HRMS (ESI): Calcd for $C_{34}H_{34}N_6Se$ + H: 607.2088. Found: 607.2075.

4.2.22. Nickel(II) complex 20d. Porphyrin **4d** (5 mg) and nickel(II) acetate tetrahydrate (40 mg) were reacted in DMF (10 mL) under the conditions described for **20b**. Recrystallization from chloroform–methanol gave the nickel complex (3.2 mg, 58%) as dark green sheets, mp > 300 °C. UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 350 (4.15), 389 (4.49), 438 (4.33), 445 (4.33), 614 nm (4.24); HRMS (FAB): Calcd for $C_{34}H_{32}N_6SeNi$: 662.1207. Found: 662.1207.

4.2.23. Copper(II) complex 21d. Porphyrin **4d** (8 mg) and copper(II) acetate monohydrate (48 mg) were reacted in DMF (10 mL) for 3 h under the conditions described for **20b**. Recrystallization from chloroform–methanol gave the copper complex (8 mg, 85%) as a green powder, mp > 300 °C. UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 347 (4.00), 392 (4.51), 441 (4.23), 447 (4.22), 620 nm (4.11); HRMS (FAB): Calcd for $C_{34}H_{32}N_6SeCu$: 667.1150. Found: 667.1151.

4.2.24. Zinc complex 22d. Porphyrin **4d** (7 mg) and zinc acetate dihydrate (50 mg) were reacted in DMF (10 mL) for 3 h under the conditions described for **20b**. Recrystallization from chloroform–methanol gave the zinc complex (5.3 mg, 60%) as a green powder, mp > 300 °C. UV–vis (1% Et_3N–$CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 348 (4.22), 393 (4.64), 458 (4.40), 627 nm (4.25); HRMS (FAB): Calc for $C_{34}H_{32}N_6SeZn$: 668.1145. Found: 668.1146.

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