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Studies on *seco*-porphyrazines: a case study on serendipity

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The conversion of porphyrazine-diamine derivatives into either *seco*-porphyrazines or porphyrazine palladium or platinum complexes has a profound effect on the photophysical and photochemical properties which has relevance to the design of switchable agents for photodynamic therapy and other applications.

Introduction

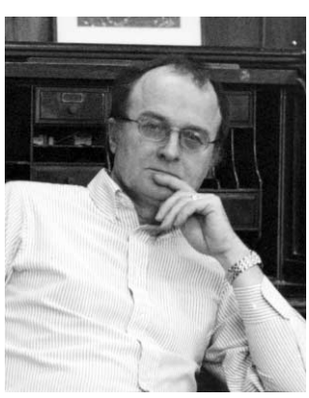
Porphyrins (P)[1] and their structural relatives—phthalocyanines (Pc)[2] and porphyrazines (Pz)[3]—constitute a distinct class of macrocyclic tetrapyrrolic systems with unique physico-chemical properties (Fig. 1). Due to their chemical diversity, these compounds, and in particular porphyrins and phthalocyanines, have been at the focus of multidisciplinary interest for many years. However, although the molecular structures of all three types of macrocycles are very similar, benzo- and especially aza-substitution have a strong impact on the overall chemical behavior of the corresponding tetrapyrrolic ligands.[2,3]

The Barrett and Hoffman team began work on the synthesis of porphyrazines in late 1987 at Northwestern University. The first graduate student on the project, Chris Velázquez, started work on the synthesis and characterisation of derivatives of the multidentate ligand porphyrazineoctathiol **3** (Scheme 1). This

Antonio Garrido Montalban studied Chemical Engineering at the University of Applied Sciences, Darmstadt and graduated in September 1991. He then went on to work with Professor Alexander McKillop at the University of East Anglia, Norwich and obtained his master and doctorate in Organic Chemistry in September 1992 and March 1995, respectively. He was immediately appointed as a research associate and soon thereafter co-Director of research within Professor Anthony Barrett's group at Imperial College, and in October 1998 Fixed Term Lecturer at the same University. He recently moved to San Diego, CA where he is currently working as a Research Scientist at Kemia, Inc.

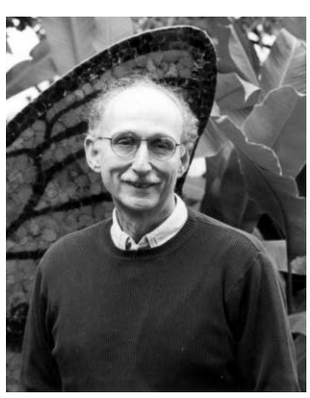
Sven Baum was born in Frankfurt a. M., Germany in 1968. He studied chemistry at the Technical University of Darmstadt (Germany) and the University of East Anglia, Norwich and obtained his diploma at the TU Darmstadt in 1996. He then moved to Imperial College of Science, Technology and Medicine, London, to carry out his Ph.D. under the supervision of Professor Anthony G. M. Barrett. In 1999 he spent six months at Northwestern University to work with Professor Brian Hoffman and received his Ph.D. in 2001 from Imperial College where he remained as a postdoctoral fellow. His research is currently focused on the synthesis of novel serial cyclopropanes.

Antonio Garrido Montalban



Tony Barrett

Sven Baum



Brian Hoffman

Tony Barrett obtained his Ph.D. (1975) with Professor Sir Derek H. R. Barton and was appointed as Lecturer (1975) and Senior Lecturer (1982) at Imperial College. At the age of 31 he was appointed a full Professor of Chemistry at Northwestern University, Evanston, IL (1983) and Colorado State University (1990). In 1993 he returned to his alma mater, IC as Glaxo Professor of Chemistry, Sir Derek Barton Professor of Synthesis, Director of the Wolfson Centre for Organic Chemistry in Medical Science and Head of Synthesis. His research interests include the total synthesis of bioactive natural products, porphyrazine chemistry, the design of methods for organic synthesis including novel catalysis, enantioselective transformations and supported reagents.

Brian Hoffman was born in Chicago, as an undergraduate went to the University of Chicago, then wandered to the west coast for a Ph.D. from Caltech under the direction of Harden McConnell, and thence to the east coast for a postdoctoral year with Alex Rich at MIT. From there he joined the faculty at Northwestern University, where he is Professor in the Chemistry and BMBCB departments. His research interests include: electron-nuclear double resonance (endor) of metallobiomolecules; electron transfer within protein complexes; as well as the preparation/characterization of porphyrazine macrocycles. He and his wife Janet are collectors of daughters (four total) and grandkids (4.4 current).

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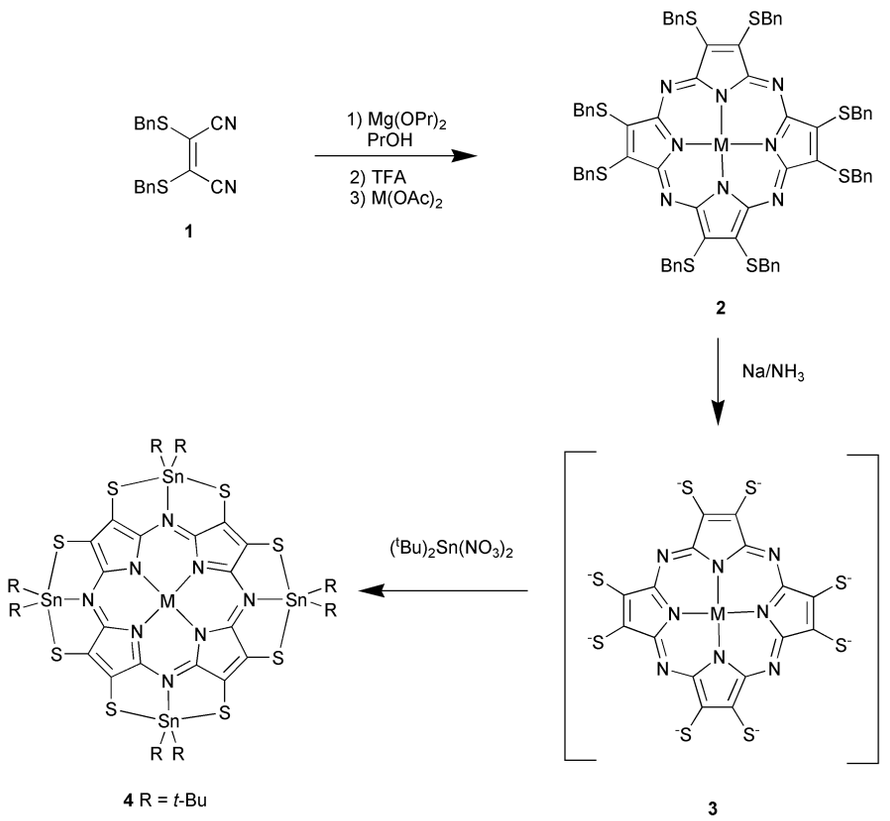


Scheme 1

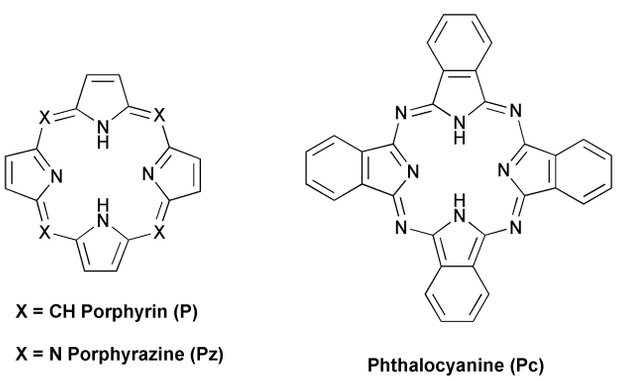


Fig. 1

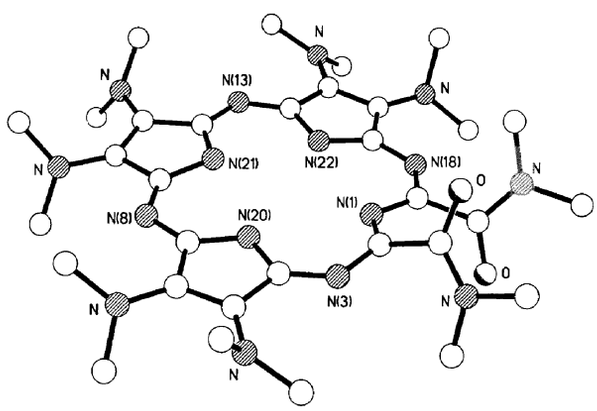


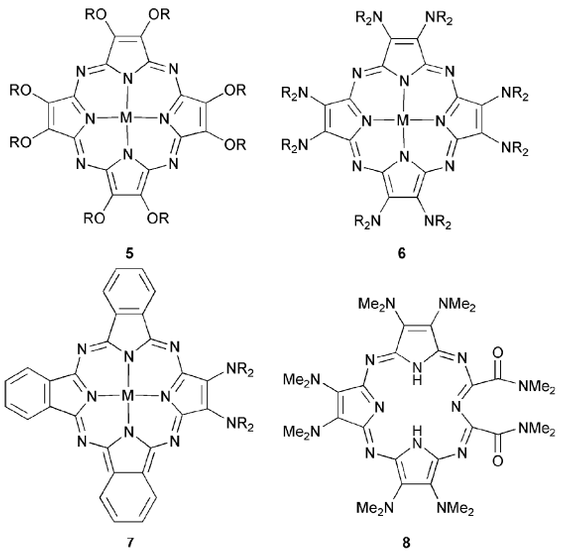
Fig. 2 The molecular structure of **8**.

was prepared by the Linstead macrocyclisation of the dinitrile **1**[4] followed by transmetallation and sodium in ammonia reduction of octasulfide **2** to provide the very air sensitive octathiolate **3**. Trapping with di-*tert*-butyltin dinitrate *in situ* gave the star porphyrazine **4**. This early success led the group to prepare a myriad of multimetallic complexes of porphyrazine bearing two, four or eight peripheral thiol residues.[5]

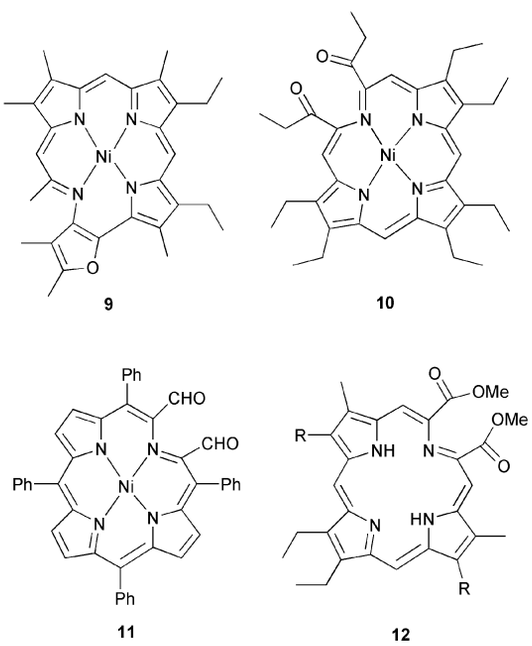
Further west in Fort Collins, CO some years later in 1991 and 1992, two postdoctoral research associates Todd Miller and Neelakandha S. Mani were seeking to prepare derivatives of porphyrazine-octaol **5** and octaamine **6**. At that stage the hydroxylated porphyrazine proved elusive but were prepared some years later due to the insight of Andrew Cook on matters of protecting groups.[6] Both Todd and Neelakandha were successful in preparing derivatives of porphyrazine-octaamine **6**[7] and porphyrazine-diamine **7**. At that stage the Colorado team sought to scale up the preparation of **6b** to send to Evanston, Illinois for the team led by Brian Hoffman to study peripheral metal ion binding. On significant scale up of the preparation of porphyrazine **6b** a catastrophe occurred. Whilst authentic **6b** has a simple NMR spectrum the spectroscopic signature of the purple dye isolated was most curious. Both the ^{1}H and ^{13}C NMR spectra showed that the compound lacked the expected D_{4h} symmetry. An X-ray crystallographic study (Fig. 2), however, unequivocally established the structure of this substance as that of *seco*-porphyrazine **8**.[8] †

The first cleaved porphyrin-type macrocycle (**9**) to be structurally characterised was isolated from an unexpected oxidative ring opening of a corrinato nickel(II) complex in 1992.[9] *Seco*-chlorin diketones[10] (**10**) and dialdehydes[11] (**11**) have also been obtained from an analogous oxidative cleavage of the corresponding nickel(II) chlorin diols with lead tetraacetate. However, the first non-metallated derivative (**12**) was only reported recently by Sessler *et al.*[12] as a result of a singlet oxygen mediated oxidative ring opening of dimethoxy-substituted porphyrins. In all cases the cleaved macrocycles exhibit enhanced

† A *seco*-porphyrazine is defined as a porphyrazine in which one of the pyrrole rings has been effectively cut and replaced by two acyclic substituents attached to the macrocyclic core. A di-*seco*-porphyrazine similarly has two pyrrole rings deleted. A solitaire porphyrazine is a porphyrazine with a single bidentate ligating site attached to the periphery of the macrocyclic core and bonded to a metallic entity at that peripheral site.



optical and/or photophysical properties, thus making them potential candidates for biomedical applications such as photodynamic therapy.



The synthesis and characterisation of *seco*-porphyrazines

Several years passed until we decided to further investigate the oxidation of porphyrazine **6b** to provide the *seco*-porphyrazine **8**. In 1996 one of the authors (A. G. M.) decided to examine alternative oxidants for the ring scission. Originally, *seco*-porphyrazine **8** was first isolated as a minor side product during the Linstead macrocyclisation of bis(dimethylamino)maleonitrile **13** (Scheme 2). Much to our surprise, the side reaction involved desymmetrisation and loss of the magnesium(II) cation. While compound **6a** showed a broad electronic absorption spectrum typical of aminoporphyrazines, with the Q band at 752 nm, an intense peak at 599 nm and a band in the Soret region at 335 nm, the UV-vis spectrum of **8** also showed a loss of symmetry with a concomitant red-shift of the Q band from 752 to 788 nm (Fig. 3). We assigned the peak at 599 nm to the n–π* transition of the lone-pair electrons on the peripheral nitrogen atoms into a π* ring orbital. Subsequently Neelakandha and Beall found that acid mediated demetallation

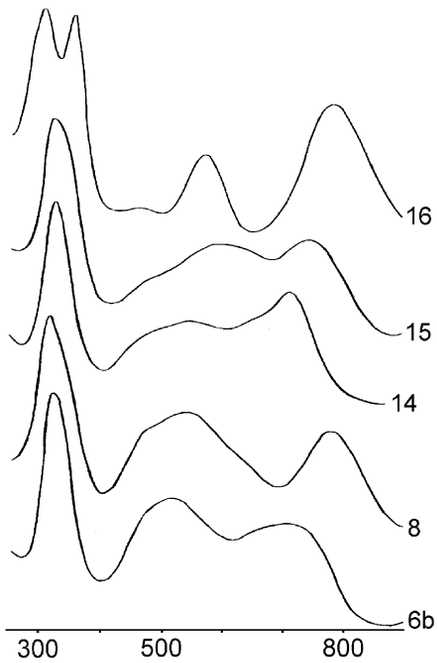
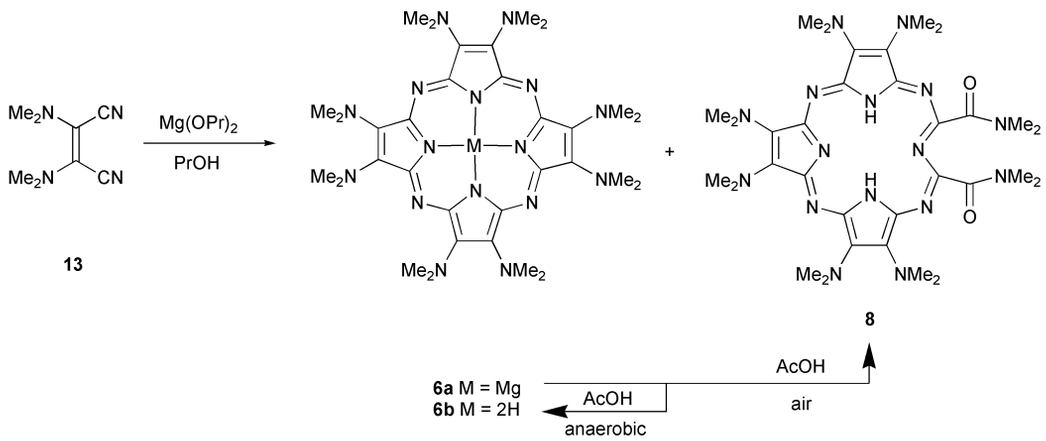


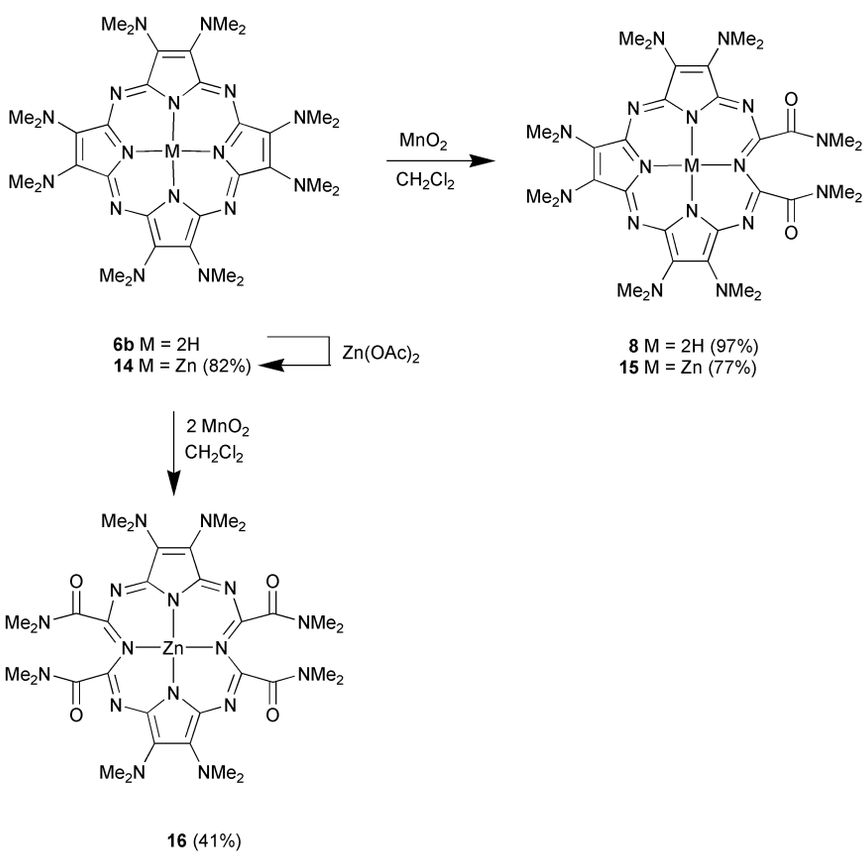
Fig. 3 UV-Vis spectra of porphyrazines **6b**, **8** and **14**–**16** in CH_2Cl_2.

of the magnesium porphyrazine **6a** in air also resulted in oxidative cleavage of one pyrrole ring to reveal the *seco*-porphyrazine **8**. In an attempt to explain the origin of this new compound a controlled experiment showed that dye **8** was formed exclusively in the presence of air (62%), while the same reaction under anaerobic conditions gave only the expected free base porphyrazine **6b** (69%).[8]

The annulene-type cyclic, conjugated, 18 π-electron system in **6b** in conjunction with the dimethylamino groups acting as strong electron donors, results in the octakis(dimethylamino)-porphyrazine (ODMAPz) macrocycle having two opposed, quasi isolated and very electron rich double bonds. We speculated that as a result of these combined properties, *seco*-porphyrazine **8** was formed *via* a formal 2 + 2 cycloaddition of singlet oxygen to one of the activated pyrrole rings, followed by cleavage (retro 2 + 2) of the dioxetane intermediate (*vide infra*). We envisaged therefore, that high-valent metal oxides should cause a similar type of oxidative ring scission, resulting in the formation of the same product. Furthermore, a controlled second pyrrole cleavage could give access to *trans*-di-*seco*-porphyrazines.† In fact, *seco*-porphyrazine **8** was obtained in high yield after a very dilute solution of H_2ODMAPz **6b** (1.6×10^{-4} M) was treated with one equivalent of manganese dioxide at ambient temperature for 24 h (Scheme 3).[13] At higher concentrations, with an excess of manganese dioxide, or with the stronger oxidant potassium permanganate, however, only slow decomposition and no formation of any of the corresponding *seco*- or di-*seco*-porphyrazine was observed. However, oxidation of the core metallated ODMAPz derivative **14** provided not only the monocleaved product but also the desired di-*seco*-porphyrazine. ZnODMAPz **14** was prepared in high yield (82%) from reaction of H_2ODMAPz **6b** with zinc(II) acetate. Subsequent oxidation of the zinc complex **14** to *seco*-porphyrazine **15** occurred readily with one equivalent only of manganese dioxide in 4 h (Scheme 3). Prolonged reaction times, or the use of an excess of the oxidant, resulted in reduced yields of **15**, along with some of the expected second pyrrole cleavage and decomposition. If porphyrazine **14** was treated with two equivalents of manganese dioxide for 24 h, the rather unstable product of over-oxidation, di-*seco*-porphyrazine **16**, could be isolated in up to 41% yield (Scheme 3). While the electronic absorption spectra of porphyrazines **14** and **15** resembled those described earlier, the spectral changes for di-*seco*-porphyrazine



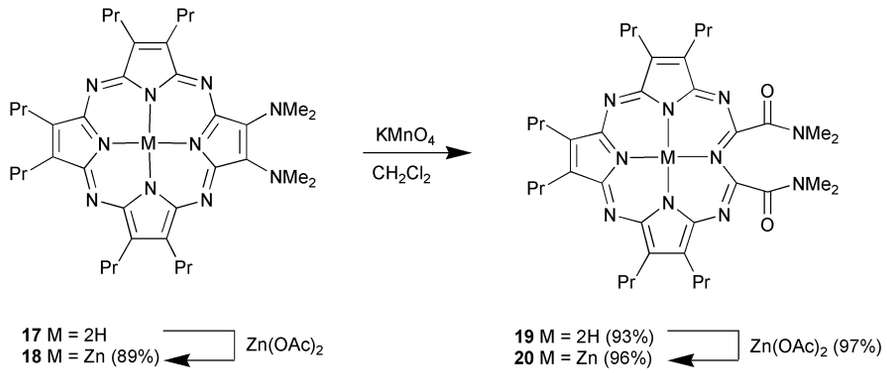
Scheme 2



Scheme 3

16 indicated a low degree of symmetry ($D_{4h} \longrightarrow D_{2h}$). We tentatively suggested that the peaks centered at 789 and 579 nm corresponded to the red-shifted split Q band, and that the n–π* peak was reduced to a small shoulder centered at 470 nm. In accordance with Gouterman's four orbital model,[14] the Soret region was also split into two absorbances which appeared at 363 and 314 nm (Fig. 3).

This convenient method was further extended to unsymmetrical porphyrazines. Thus, reaction of the free base porphyrazine **17**[15] with zinc(II) acetate resulted in selective metallation within the macrocyclic cavity to provide the corresponding zinc complex **18** in high yield (89%). Both, **17** and **18** were unreactive towards oxidation by manganese dioxide. However, reaction of compounds **17** and **18** with potassium permanganate gave the expected *seco*-porphyrazines **19** and **20**, respectively, in 93 and 96% yield (Scheme 4). In both cases, under optimised conditions, a ten-fold excess of the oxidant effected complete conversion in less than 3 h. Alternatively, zinc-*seco*-porphyrazine **20**, was obtained in high yield (97%) from the reaction of *seco*-porphyrazine **19** with zinc(II) acetate. Reversing the order of reactions (oxidation then metallation instead of metallation followed by oxidation), as in the above example, could prove useful for the synthesis of otherwise inaccessible core metallated *seco*-porphyrazines. In contrast to the electronic absorption spectra of the non-oxidised materials **17** and **18**, the electronic absorption spectra of *seco*-porphyrazines **19** and **20** display a split red-shifted Q band at 693 and 543 and at 649 and 565 nm, respectively (Fig. 4). In addition to the red-shifted Q band, the optical spectrum of the zinc-*seco*-porphyrazine **20** shows also a split band in the Soret region at 356 and 339 nm. The slow evaporation of a solution of compound **20** in CH_2Cl_2–hexanes (1 : 1) gave iridescent purple crystals suitable for an X-ray crystallographic study (Fig. 5). In contrast to *seco*-pophyrazine **8**, the molecules in crystals of **20**



Scheme 4

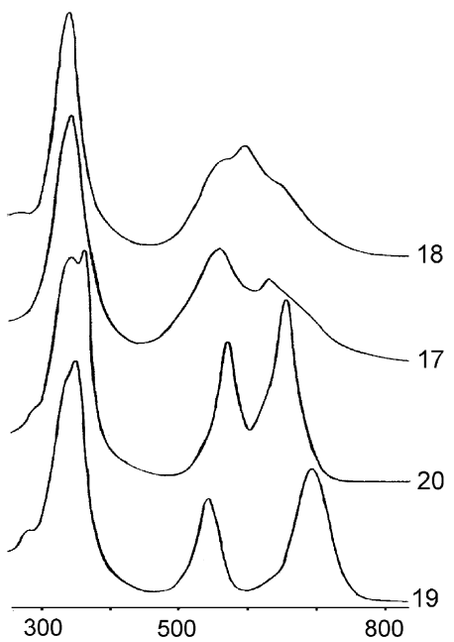


Fig. 4 UV-Vis spectra of porphyrazines **17**–**20** in CH_2Cl_2.

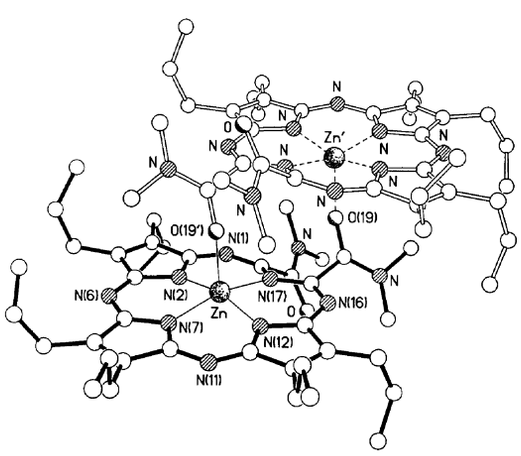


Fig. 5 The molecular structure of **20**.

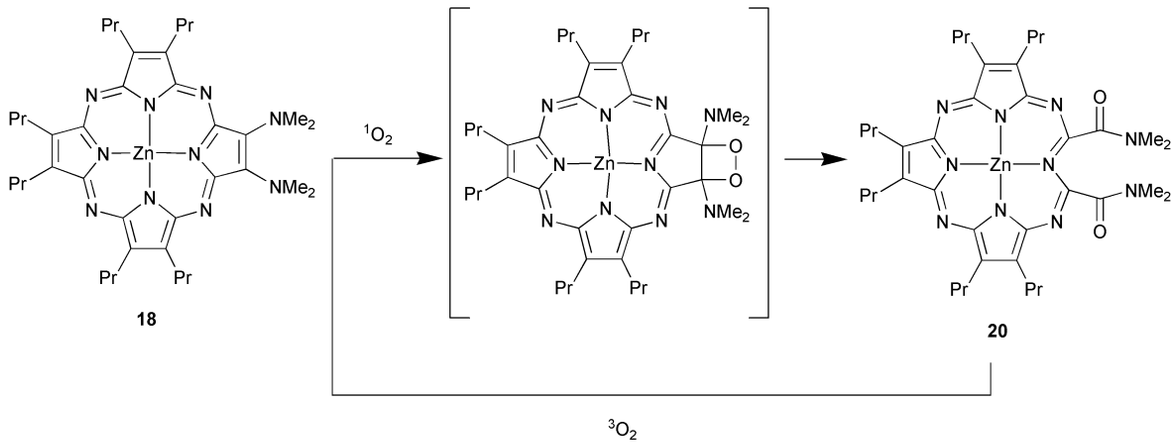
exist as face-to-face dimers linked *via* complexation of the zinc center in one molecule to one of the amide oxygen atoms in the other and *vice versa*.

We noticed that slow oxidation also occurred when solutions of the zinc complex **18** and related analogues were left standing in the presence of air for prolonged times. The reaction was found to be efficient in chlorinated solvents (CH_2Cl_2, $CHCl_3$) but not in coordinating solvents such as pyridine and DMF. At this stage we began a collaboration with Dr Garry Rumbles, Professor David Phillips and Hubert Meunier, an academic visitor from Assumption College, Worcester, MA, on the photophysics of *seco*-porphyrazine systems. Ironically, Dr. Rumbles moved west from Imperial College to Colorado during these studies although the collaboration continued unchanged. In our first article on photophysics[16] we reported the results from studies of the reactant, **18**, and product, **20**, and showed that the full reaction mechanism of the photoperoxidation involves attack on the reactant by singlet oxygen that has been sensitised by the triplet state of the product as we initially speculated (Scheme 5). As a consequence, the kinetics of the process were shown to be autocatalytic where the reactant is removed at a rate that increases with the amount of product formed. Thus, in contrast to the precursor macrocycle **18**, dye **20** exhibits fluorescence as well as intersystem crossing (ϕ_T = 0.64 ± 0.06) and is a superb photosensitiser for the formation of singlet oxygen with a quantum yield of ϕ_Δ = 0.54. In fact another co-worker, Dr Andrés Trabanco Suárez, observed that **20** catalyses the [4 + 2] cycloaddition of singlet oxygen to 1,3-dienes under mild conditions in a process superior to that of classical dye-mediated reactions.[17]

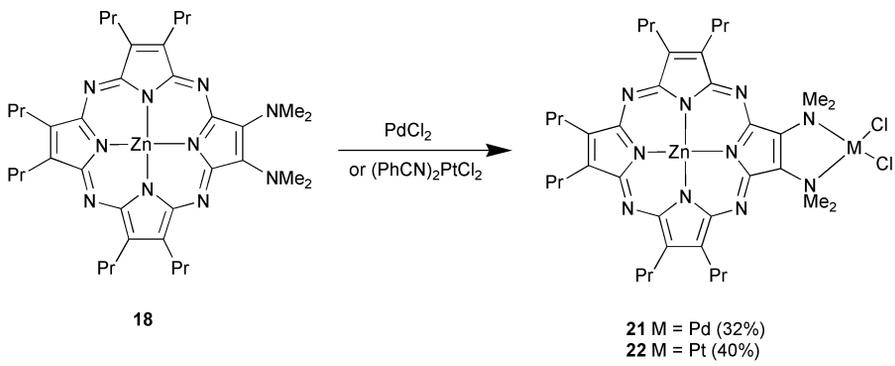
The high quantum yield of triplet state formation could be promoted by the two carbonyl groups of **20**, as this group is well known to promote intersystem crossing.[18] Thus, we assumed that the very different photophysical profiles of the bis(dimethylamino)porphyrazine **18** and its *seco*-derivative **20** were directly related to the decoupling of the non-bonding electron pairs of the peripheral nitrogen atoms from the macrocyclic core and amide formation. We therefore reasoned that similar changes in the photophysical properties of **18** should also be observed upon peripheral metallation.[19] Efstathia Sakellariou readily prepared the palladium solitaire† porphyrazine **21** through reaction of equimolar amounts of Zn-porphyrazine **18** with $PdCl_2$ in chloroform and acetonitrile (3 : 1) at reflux (Scheme 6). Similarly, treatment of the free ligand **18** with a stoichiometric amount of bis(benzonitrile)platinum(II) chloride in 1,2-dichloroethane at reflux gave the corresponding solitaire porphyrazine **22** in moderate yield (Scheme 6).

The electronic absorption spectrum of compound **18** has a distinct Q-band at 597 nm which is severely broadened. This broadening obscures the expected "split" of the Q-band which is normally observed for macrocycles of less than D_{4h} symmetry,[14] and is presumably due to overlap of underlying n–π* transitions that arise from the non-bonding electrons associated with the peripheral nitrogens. As previously observed (*vide supra*), removal of the broadening effect upon peripheral metallation lends credence to the assignment of the n–π* transition and indeed, both **21** and **22** exhibit a sharp, split Q-band having Q_x and Q_y absorbances at 605 and 578 nm respectively (see representative spectra in Fig. 6).

While the photophysical data for the free ligand **18** suggests that the dominant deactivation process for the first excited singlet state is non-radiative (neither fluorescence nor triplet



Scheme 5



Scheme 6

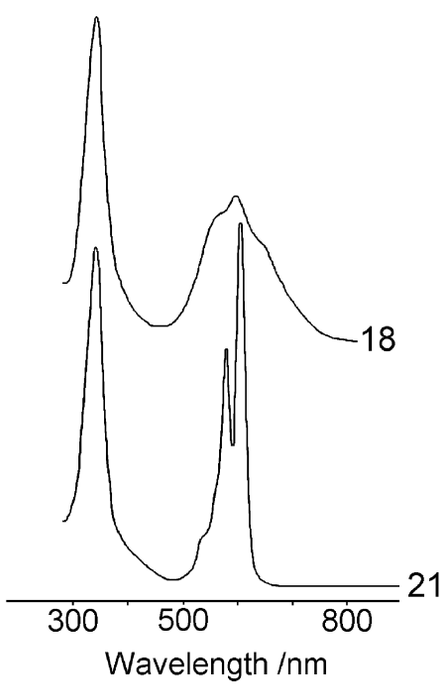


Fig. 6 Absorption spectra of porphyrazines **18** and **21** in CH_2Cl_2.

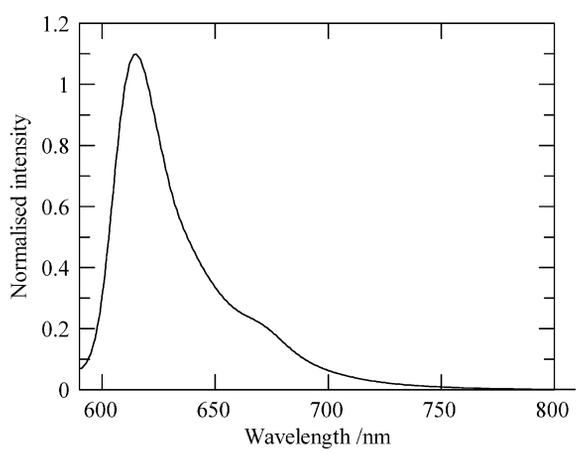
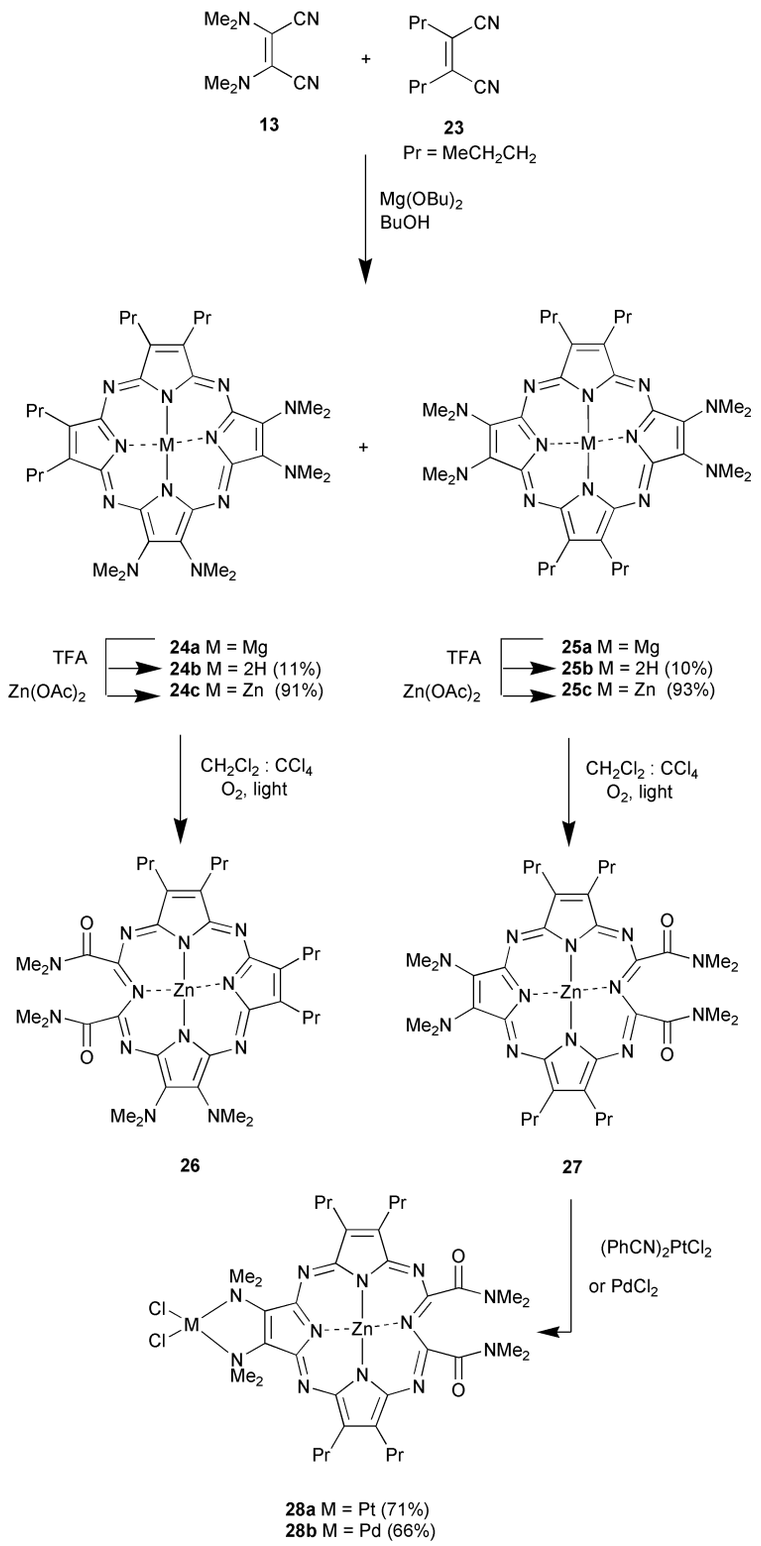


Fig. 7 Fluorescence emission spectrum of porphyrazine **21** in toluene. Excitation wavelength λ_{ex} = 582 nm.

absorption was detected although ground-state bleaching was observed),[16] both **21** and **22** exhibit fluorescence as well as intersystem crossing. The fluorescence quantum yields, ϕ_f, for the solitaire complexes **21** and **22** were determined to be 0.05 and 0.08 ± 0.01 respectively (a representative fluorescence spectrum of complex **21** is shown in Fig. 7) with lifetimes of 0.4 and 0.65 ± 0.05 ns. However, while ϕ_{ISC} is promoted, determination of the triplet state quantum yield, ϕ_T, proved difficult due to the dyes **21** and **22** undergoing photodegradation. These results, however, confirmed the above assumption that due to the lone pair electrons on the $(NMe_2)_2$ moiety being bonded datively to the metal ions and no longer interacting strongly with the porphyrazine π-system induces changes in the photophysical properties. This combined with the fixed geometry of the chelating unit may suppress internal conversion followed by vibrational relaxation as the only deactivation pathway of the first singlet excited state and we therefore observe fluorescence for the solitaire complexes **21** and **22** in contrast to the free ligand **18**. In addition, the heavy atom effect is expected to increase intersystem crossing ($S_1 \longrightarrow T_1$) and at the same time the decay rates for phosphorescence ($T_1 \longrightarrow S_0$) and non-radiative quenching ($T_1 \longrightarrow S_0$). Thus, although triplet state formation is observed, intersystem crossing back to the ground state followed by vibrational relaxation rather than phosphorescence seems to be the dominant deactivation process for the first excited triplet states of solitaire complexes **21** and **22**.



Scheme 7

In a continuation of our efforts in this field, the synthesis of the first macrocycles containing both an oxidatively cleaved pyrrole ring as well as a peripherally coordinated metal species was undertaken by Efstathia Sakellariou.[20] Thus, macrocyclisation using an equimolar ratio of dinitriles **13** and **23** gave the "*cis*" and "*trans*" Mg-porphyrazines **24a** and **25a** along with other porphyrazinic products (Scheme 7). The macrocyclisation mixture was further demetallated since the very similar polarities of the porphyrazines rendered their separation extremely difficult as the magnesium complexes. Thus, the free base porphyrazines **24b** (11%) and **25b** (10%) were obtained upon treatment with trifluoroacetic acid and subsequently separated by column chromatography. The novel free base porphyrazines **24b** and **25b** were separately allowed to react with zinc acetate in dry DMF to afford the corresponding porphyrazines **24c** and **25c**.

In an attempt to obtain the corresponding mono-*seco*-porphyrazines, solutions of porphyrazines **24c** and **25c** in carbon tetrachloride and dichloromethane (1 : 1) were allowed to stand under ambient light in air (Scheme 7). Porphyrazine **25c** was found to undergo oxidation much faster than **24c**. On the other hand, four days were required for a significant amount (86%) of porphyrazine **26** to be isolated. In both cases, the newly formed *seco* derivatives were separated from the corresponding starting materials since both were unstable in

solution for prolonged times. Indeed, photolytic oxygenation of *seco*-porphyrazine **27** gave the over-oxidation product (di-*seco*) followed by decomposition. Unfortunately, the "*cis*"-*seco*-porphyrazine **26** was also found to be unstable in the solid state and under inert atmosphere for more than two days. Efforts were therefore concentrated to the synthetically more accessible "*trans*" analogue. Thus, upon treatment of porphyrazine **27** with $Pt(PhCN)_2Cl_2$ in 1,2-dichloroethane, the desired metallated product **28a** was isolated in a 71% yield. Similarly, reflux of **27** with palladium(II) chloride in acetonitrile and chloroform (4 : 1) gave the *seco*-solitaire-porphyrazine **28b** (66%). The lower yield of the palladium complex when compared to its platinum analogue correlates well with the previously reported yields for the solitaire complexes **21** and **22**.[19] The significantly higher yields of the platinum and the palladium *seco*-porphyrazines **28a** and **28b** when compared to dyes **21** and **22** indicate that the presence of the carboxamide units confers stability and favors the complexation reaction.

The UV-vis spectra of both solitaire complexes **28a** and **28b** display analogous bands in the Soret (B) and Q-regions. While no significant change is observed for the B band of these complexes with respect to the free ligand **27**, the Q band is clearly split and less broadened. As for **20**–**22** the removal of the broadening of the Q-band is directly associated with the peripheral metallation or *seco*-porphyrazine formation since the nitrogen lone pairs can no longer interact with the porphyrazine core. Thus, "sharpening" of the Q-band is clearly observed upon formation of dyes **28a** and **28b** both exhibiting Q_x and Q_y absorbances at 581, 619 and 581, 630 nm respectively (Fig. 8). Moreover, since the symmetry of both compound **27** and complexes **28a** and **28b** remains the same (C_{2v}), the sharp change in the UV-vis spectra can solely be attributed to the decoupling of the amine nitrogens by the platinum and palladium metals from the central ring.

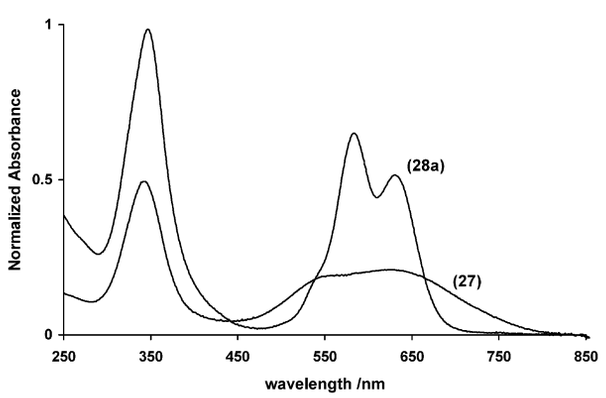


Fig. 8 UV-Vis absorption spectra of porphyrazines **27** and **28a** in CH_2Cl_2.

In contrast to the free ligand **18**, porphyrazine **27** was found to be very weakly fluorescent ($\phi_f = 1.1 \times 10^{-3}$) while, as previously observed with **21** and **22**, upon peripheral metallation the derived platinum and palladium complexes **28a** and **28b** exhibited fluorescence with quantum yields of 0.07 and 0.08 ± 0.01 respectively. The lifetimes were in the order of 0.54 ± 0.05 ns. More interestingly, for the photochemically more stable (compared to **21** and **22**) novel *seco*-solitaire porphyrazines **28a** and **28b** triplet states could be detected and the quantum yield for this process was determined to be 0.56 for complex **28a** (Fig. 9). Although determination of the quantum yield for the *seco*-palladium porphyrazine **28b** was not carried out, a similar result is expected as indicated from its singlet oxygen quantum yield. These new complexes proved to enhance not only intersystem crossing but also the photosensitisation of singlet oxygen formation. Thus, quantum yields of the singlet oxygen formation were determined to be 0.59 and 0.45 for compounds

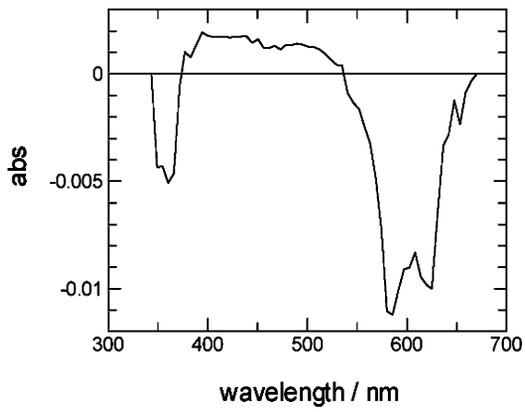
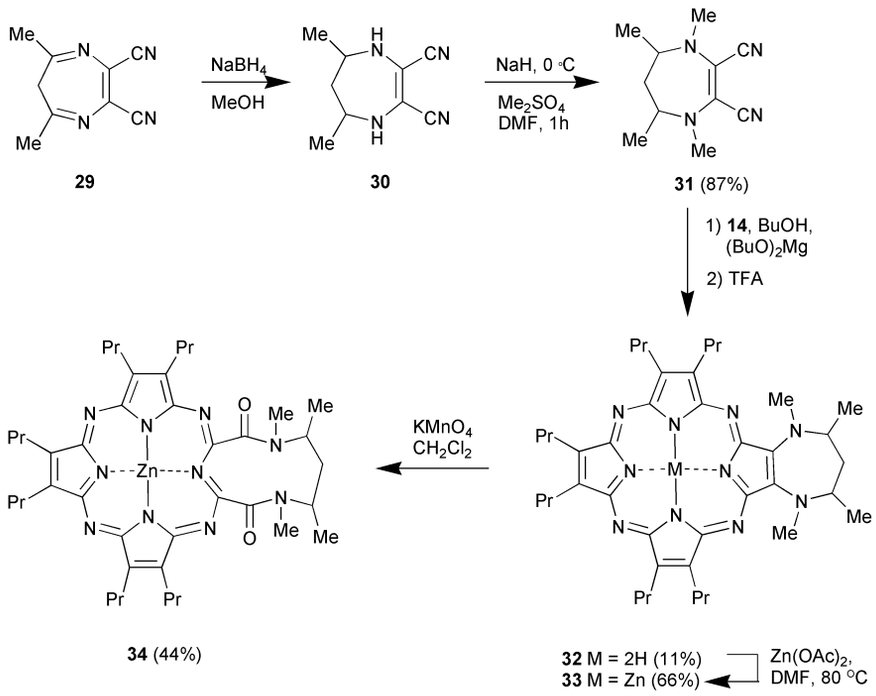


Fig. 9 Transient absorption spectrum of peripherally metallated *seco*-porphyrazine **28a**.

28a and **28b** respectively. These values are in good agreement with the value for singlet oxygen generation by the *seco*-porphyrazine **20**. In addition, peripheral metallation induces higher fluorescence in compounds **28a** and **28b** when compared to **20**, for which a quantum yield could not be determined due to the weak intensity of the process.

A most significant result was the singlet oxygen generation yield recorded for precursor **27** contrasted with complexes **28a** and **28b**. The process was of weak intensity and measured at the limit of detection to give a value of 0.03. This final result correlates well with our assumption that the nitrogen lone pair of the dimethylamino groups enhances non-radiative decay through electronic coupling with the macrocycle. On the other hand, if the amino groups were locked in a cyclic structure internal conversion followed by vibrational relaxation may be suppressed as the major deactivation pathway. This hypothesis was tested by one of the authors (S. M. B.). Commercially available diaminomaleonitrile was readily converted into the 2,3-dicyano-1,4-diazepine **30** which was obtained as an inseparable mixture of *cis*- and *trans*-stereoisomers *via* the corresponding diimine **29** (Scheme 8).[21] Although 5,7-diphenyl-2,3-dicyano-6*H*-1,4-diazepine has been reported to undergo macrocyclisation,[22] the analogue **29** failed to provide any porphyrazinic products. On the other hand, Linstead macrocyclisation of diazepine **30** gave the expected dark blue dyes, unfortunately, all attempts to isolate the presumed macrocycle resulted in decomposition. Thus, diazepine **30** was dimethylated and the product **31** was macrocyclised with a seven-fold excess of dipropylmaleonitrile **23** to give, after demetallation, the stable free base porphyrazine **32** in an 11% overall yield. An X-ray single crystal study of **32** reveals the crystals to contain a mixture of *cis*- and *trans*-stereoisomers (Fig. 10). Reaction of the free base porphyrazine **32** with zinc(II) acetate resulted in selective metallation within the macrocyclic cavity to provide the corresponding zinc complex **33** (66%). All attempts to oxidise the free base porphyrazine **32** to its corresponding *seco*-derivative failed. On the other hand, treatment of the zinc-complex **33** with one equivalent of potassium permanganate gave the requisite novel *seco*-porphyrazine **34** in 44% yield (Scheme 8).

Representative UV-vis spectra of compounds **33** and **34** are shown in Fig. 11. While porphyrazine **33** displays a broad Q-band in its UV-vis spectrum, *seco*-porphyrazine **34** exhibits a distinct split Soret- and Q-band with absorbances at 335 and 352 and 559 and 644 nm respectively. As before, the broadening of the Q-band region is presumably due to overlap of underlying n–π* transitions that arise from the non-bonding electrons associated with the peripheral nitrogens. In *seco*-porphyrazine **34** the peripheral nitrogen lone pairs do not strongly interact with the central ring and the broadening effect is removed. In addition, the cyclic structure of the amino groups has the expected effect on the photophysical properties



Scheme 8

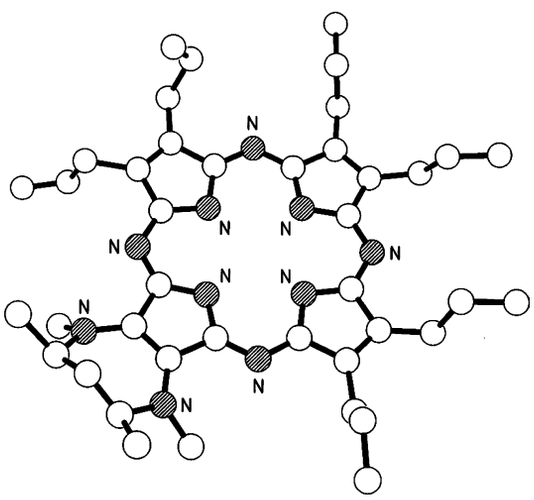


Fig. 10 The molecular structure of one of the pair of independent molecules present in the crystals of **32** [with the rel(*S*,*R*) configuration in the diazepine ring].

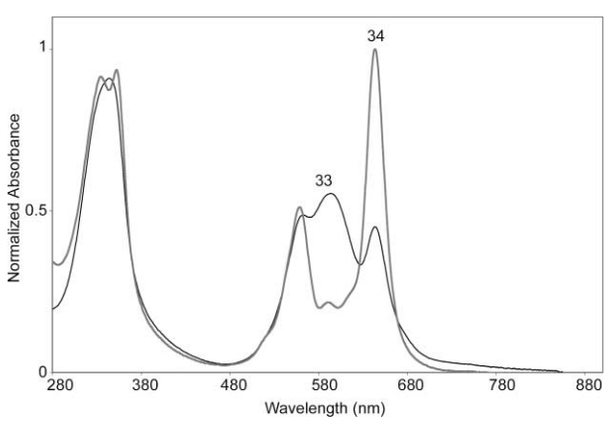


Fig. 11 UV-Vis spectra of porphyrazines **33** and **34** in CH_2Cl_2.

of the macrocycle. While the analogous bis(dimethylamino)-porphyrazine **18** shows neither fluorescence nor intersystem crossing, **33** exhibits fluorescence with $\phi_f = 0.06 \pm 0.01$. The fixed geometry of the cyclic amino-unit does indeed suppress internal conversion followed by vibrational relaxation as the only deactivation pathway for the first singlet excited state and we therefore observe fluorescence for compound **33**. Similarly, the fluorescence quantum yield, ϕ_f, for *seco*-porphyrazine **34** was determined to be 0.07 ± 0.01 with a lifetime of 1.35 ± 0.02 ns. More importantly, **34** turns out to be the *seco*-porphyrazine with the best singlet oxygen photosensitising ability reported so far. The quantum yield, ϕ_Δ, of the singlet oxygen formation was determined to be 0.74. This final result correlates well with the assumption (*vide supra*) that due to the rigid cyclic amide-unit the major deactivation pathways for the first singlet and triplet excited states of *seco*-pz **34** are intersystem crossing and quenching of the triplet state by ground state oxygen with a minor contribution of fluorescence.

It is clear from these results that the conversion of porphyrazine-diamine derivatives into either *seco*-porphyrazines or porphyrazine palladium or platinum complexes has a profound effect on the photophysical and photochemical properties. These results are relevant to the design of switchable agents for photodynamic therapy and other applications. The accidental discovery of *seco*-porphyrazines in Colorado has proven fortuitous.

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