Synthesis and Spectral and Structural Characterization of a New Series of Bis-Strapped Chiral Porphyrins Derived from L-Proline

Bernard Boitrel,*[a][‡] Valérie Baveux-Chambenoît,[a] and Philippe Richard[a]

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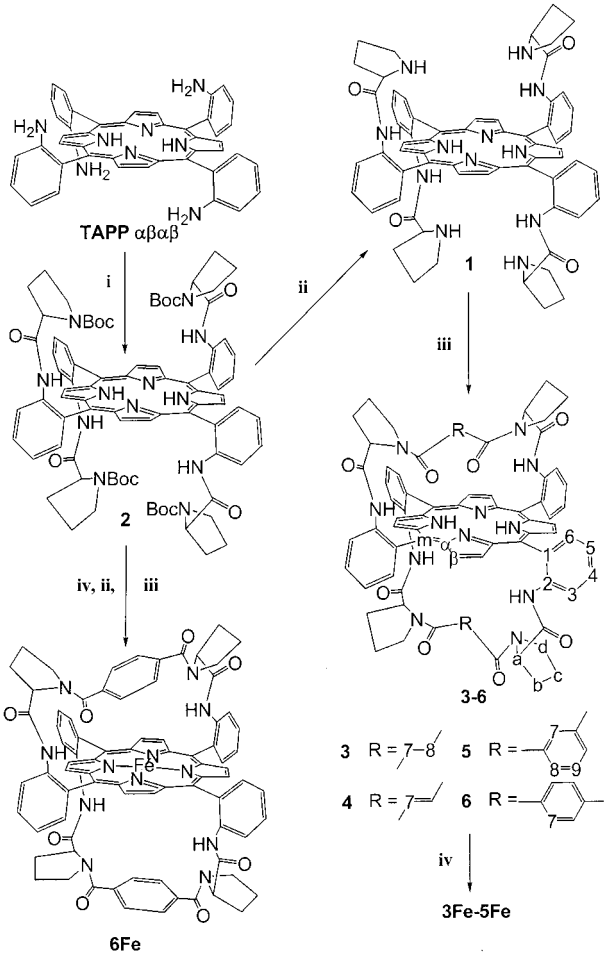
New chiral porphyrins were obtained in reasonable yields in three steps, starting from the αβαβ atropisomer of *meso*-tetrakis(*o*-aminophenyl)porphyrin (TAPP). These potential catalysts for the enantioselective epoxidation of alkenes were obtained by the reaction of different linkers on the same L-prolinoyl-picket porphyrin. Their ^{1}H NMR spectral characteristics, as well as the crystal structure of one of them, clearly indicate that the orientation of the proline cycle depends on the linker used to tether the two pickets on each side of the porphyrin. The same linker is employed for both sides of the porphyrin; hence the resulting D_2-symmetric superstructure.

Introduction

Since the initial report of possible oxidation reactions mediated by metalloporphyrins,[1] the preparation of this type of ligand, whether in a chiral environment or not, has been the subject of extensive investigations.[2−4] Accordingly, different families of chiral catalysts such as vaulted binaphthyl,[5] basket-handle,[6] glycoconjugated,[7] threitol-strapped,[8] twin-coronet,[9] binaphthyl-capped,[10] seat,[11] and chiroporphyrins[12] have been prepared. Nevertheless, most of these studies reported individual examples of chiral catalysts, for which it was very often difficult to account for the observed enantioselectivity a priori. Furthermore, few studies have tried to establish a structure-activity relationship.[13−16] In this context, we wanted to synthesise a new family of chiral porphyrins allowing convenient structural variation, to appraise the effect of steric hindrance on the enantioselectivity of asymmetric epoxidation. To do this, we chose to link an optically active amino acid onto a porphyrin. This idea of handling such a chiral linking moiety is not recent and has already been described, either for asymmetric reductions[17] and oxidations[18] or for other purposes.[19,20] On the other hand, the novelty of our work lies both in the choice of the amino acid and in the fact of the synthesis of not only one catalyst but a complete series, thus allowing direct comparison. Indeed, with the usual amino acid structure, the lateral chain can rotate around its bond with the chiral centre, thereby decreasing the steric hindrance close to the metal coordination site.

Results and Discussion

The synthetic strategy consists of using a very special chiral amino acid − L-proline, the only one with a cyclic lateral chain − and is achieved in three steps (Scheme 1).



Scheme 1. Synthetic pathway for the preparation of bis-strapped chiral porphyrins i) Boc-L-proline/Cl-CO_2*i*Bu/THF/*N*-Me-piperidine/−20 °C; ii) CH_2Cl_2/TFA; iii) R(COCl)$_2$/THF/Et_3N/high dilution conditions; iv) $FeBr_2$/2,6-lutidine/toluene/110 °C

[a] L. S. E. O. − UMR-CNRS 5632, Université de Bourgogne, 6, boulevard Gabriel, 21000 Dijon, France
[‡] New address: L. C. C. O. UMR CNRS 6509, Université Rennes 1, Campus de Beaulieu, Av. du Général Leclerc, 35042 Rennes Cedex;
Fax: (internat.) + 33-2/99281646;
E-mail: Bernard.Boitrel@univ-rennes1.fr
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Indeed, in comparison with Mansuy's catalyst[18] (which we have numbered **7** for convenience), we wanted to attach a much more rigid stereogenic centre with almost no flexibility. In addition, we designed our models so as to influence the orientation of the cycle of the proline in respect to the mean plane of the porphyrin itself.

Hence, porphyrin **2** was prepared starting from the αβαβ atropisomer of TAPP[20] by coupling of a *N*-protected optically active amino acid. *N*-*tert*-Butoxycarbonyl-L-proline (Boc-L-proline) was used in a typical coupling reaction, which was carried out using mixed anhydride activation, a classical procedure in peptide synthesis. The formation of the amide bond between the porphyrin and the *N*-Boc-L-proline was accomplished in dry tetrahydrofuran (THF) in the presence of *N*-methylpiperidine at room temperature, after activation of the carboxylic acid moiety of the amino acid with isobutylchloroformate at −20 °C in the same solvent. An excess of *N*-protected amino acid (100 equiv.) was required. The chiral integrity of the *N*-Boc-L-proline was retained during the coupling reaction. The protecting group was easily removed in CF_3CO_2H/CH_2Cl_2 (1:10) at room temperature, to form the porphyrin **1**. Compound **1** was used immediately, without neutralisation, because of its rapid degradation when the mixture was neutralised. Thus, no purification by flash chromatography was possible, the opposite of what had been observed in similar deprotection of L-phenylalanine residues. Compounds **3**−**6** were obtained by treatment of **1** with the desired diacyl chloride in anhydrous THF in the presence of triethylamine, under high dilution conditions [$8\cdot10^{-4}$ M] and slow addition of the reagents to minimise the formation of polymeric products. The expected bis-strapped porphyrins were obtained in a variable yield (10−70%), depending on the linker employed for the strapping reaction. It is worth noting that an unexpectedly high yield of 70% was obtained for **3** when R = $-CH_2-CH_2-$.

Insertion of iron into compounds **2**−**5** was carried out in a glovebox, with iron(II) bromide in refluxing toluene, in the presence of 2,6-lutidine. Completion of the reaction was monitored by UV/Vis spectroscopy. This logical procedure failed when applied to porphyrin **6**, presumably because of difficulty in access to the porphyrin core. It was therefore necessary to insert iron into the less hindered picket porphyrin **2** and then to perform the final strapping reaction. Chloro derivatives were generated by shaking a dichloromethane solution of the iron porphyrin with aqueous sodium chloride. These chloro iron(III) porphyrins were characterised by mass spectrometry and UV/Vis spectroscopy (Table 1). The mass spectra of the iron complexes exhibited peaks corresponding to the chloro ligand. These chloro iron(III) porphyrins are to be used as asymmetric epoxidation catalysts.

Usually, UV/Vis spectroscopy is employed to evaluate the deviation of the porphyrin core from planarity. Indeed, if it is considered that a red shift is generally observed for a less planar porphyrin, the data indicate that the most distorted porphyrins are **4** (425 nm) and **7** (426 nm), even though the L-proline analogue of the latter compound, compound **6** (419 nm), seems to be quite planar. This apparent inconsistency might be explicable by the fact that a cyclic amino acid is supposed to induce more strength in the strap than a normal amino acid (with a typical lateral chain) does. On the other hand, the red shift observed for **4** (425 nm) in comparison with **3** (421 nm) is expected, as the fumaroyl linker is known to be shorter than the succinoyl one, and to be conjugated with the two adjacent carbonyl groups. Globally, and in contrast to what was assumed for such structures, these chiral bis-strapped compounds seem to be more planar than the chiroporphyrins described by Marchon et al.[15] In the case of the iron(III) chloride complexes, a red shift relative to the picket porphyrin **2Fe** appears to be general, with an average value of 8 nm.

Table 1. Wavelengths (nm) of absorption band maxima for iron porphyrins **2Fe**, **3Fe**−**6Fe**, **7Fe** (Mansuy's catalyst)

Compound	Soret	Q Band
(2Fe)	417	572
(3Fe)	426	583
(4Fe)	426	586
(5Fe)	422	584
(6Fe)	426	583
(7Fe)	424.5	510

In the case of these rigid bis-strapped porphyrins, ^{1}H NMR spectroscopy is a particularly useful technique to probe both the conformation of the straps and the symmetry of the porphyrin itself, as some types of protons are in a well known magnetic environment. For example, for reasons of symmetry and as has already been shown,[22] the β pyrrolic protons of the porphyrin can provide evidence as to the effective chirality of the asymmetric centres. The internal NH protons can also be an efficient probe with which to evaluate the macrocycle distortion, as illustrated with chiroporphyrins.[23] Nevertheless, in consideration of the very different influence that the aromatic ring of the strap, because of its apical position, may have on the NH internal protons, we decided not to take these into account. Obviously, the aromatic cycle can shield these two protons if in a parallel orientation, as in porphyrins **5**, but should have the opposite effect if perpendicular to the porphyrin as in **6**. The ^{1}H and ^{13}C chemical shifts for most of the protons of this new series are listed in Table 2 and Table 3, respectively. The usual aromatic pattern for such compounds is observed, appearing as two doublets and two triplets with a *J* value of around 7.5 Hz. This system of four signals presenting crossed peaks in 2D-correlated spectroscopy corresponds to the four *meso* aromatic protons in the porphyrin. The second observation to be made concerns the pattern of the β pyrrolic protons, as two singlets integrating as four protons each. This is direct proof of the effective chirality of the four stereogenic centres. This observation is true for all but one (**3Zn**) of the bis-strapped porphyrins described here. In that particular case, the β pyrrolic protons appear as eight doublets with a *J* value of 4.7 Hz, indicating that the porphyrin no longer has any symmetry element, a result

consistent with the crystal structure of **3Zn** as discussed later.

Table 2. Selected ^{1}H NMR spectroscopic data ($CDCl_3$, 300 K) for compounds **1−6**

	1	2	3	4	5	6
NH	−2.52	−2.58	−2.87	−3.00	−3.91	−3.15
a-H	3.16	3.56	3.74	3.71	4.25	4.62
b-H	1.51	1.28	1.13/ 2.32	1.04/ 2.33	1.57	1.50/ 1.67
c-H	0.01/ 0.73	0.35	1.47	1.49	1.37/ 1.57	1.40/ 1.67
d-H	0.47/ 1.12	0.35/ 1.53	1.13/ 1.76	1.49/ 1.83	1.57/ 2.22	1.88/ 2.35
7-H	−	−	−4.00/ −0.45	2.68	4.52	3.68
8-H	−	−	−4.00/ −0.45	−	5.22	−
9-H	−	−	−	−	5.14	−

Table 3. Selected ^{13}C NMR spectroscopic data ($CDCl_3$, 300 K) for porphyrins **1−6**

	1	2	3	4	5	6
CH-a	60.5	61.7	60.7	61.2	61.6	60.9
CH_2-b	30.5	30.7	26.6	26.2	27.4	30.1
CH_2-c	25.2	45.3	24.7	24.6	25.4	28.2
CH_2-d	45.6	46.4	46.1	46.4	49.3	49.6
C-7	−	−	24.5	126.8	122.7	124.2
C-8	−	−	−	−	125.1	−
C-9	−	−	−	−	127.8	−

For all compounds **3−6**, the protons of the linker experience a significant upfield shift, as expected for such protons above the porphyrinic macrocycle. In the case of **4**, for example, the chemical shift of the fumaryl protons is δ = 2.68, instead of 6.84 for diethyl fumarate, representing a variation of chemical shift (Δδ) of 4 ppm. The same comparison can be made between **7**,[24] **6**, and diethyl terephthalate, for which the chemical shifts are δ = 3.88, 3.68, and 8.10, respectively: hence a Δδ of 4.4 ppm for **6**. If one considers this Δδ as an efficient indicator of the distance between the considered protons and the porphyrin mean plane, its seems that the protons labelled 7-H are closer to the macrocycle in **6** than in **7**, and even than in **4**. These results seem to indicate that this particular amino acid, with its cyclic structure, might be able to induce specific changes in the strap.

For this reason, we studied the chemical shifts both of the protons and of the carbon atoms in the proline, to provide information about the orientation of the lateral chain. Indeed, it would be reasonable to expect a more pronounced enantioselectivity in the potential catalyst − on the basis of more significant steric hindrance − when the cycle of the proline is less perpendicular to the porphyrin. In other words, if the orientation of the proline residues is influenced by the type of linker used in the strapping reaction, this phenomenon should result in the signals for the methylene groups of the proline being shifted to a greater or lesser degree. In fact, the protons should appear more shielded as the heterocycle of the proline becomes more parallel, and hence closer, to the porphyrin. According to the ^{1}H NMR spectroscopic data (Table 2) and observing the signals labelled a-H, b-H, and c-H, two different groups can be seen: on one hand, **3** and **4**, on the other, **5** and **6**. This observation is particularly true for b-H. One proton of this methylene group is significantly shifted downfield (δ = 2.32 and 2.33, in comparison with δ = 1.13 and 1.04) in the case of the compounds with nonaromatic linkers. This shift is not observed for the compounds with aromatic linkers. It seems that, whatever the influence of the linker is, the protons of the amino acid are more influenced by the linker itself rather than by the anisotropy of the porphyrin, and so their employment as indicators for the orientation of the proline becomes questionable. Even the proton of the chiral centre, namely a-H, is shifted downfield in the case of the porphyrins bearing aromatic linkers, relative to porphyrins **3** and **4**. Again, this observation is logical if account is taken of the fact that this proton is located at the periphery of the aromatic cycle, whether connected in 1,3- or 1,4-fashion. The chemical shift of the latter proton is therefore not reliable for approximation of the position of the chiral centre relative to the porphyrin core.

Of the four bis-strapped porphyrins described in this work, the most intriguing compounds, from the points of view both of their very sharp NMR spectra and of the differences revealed by these spectra, are certainly **3** and its zinc(II) analogue **3Zn**, obtained with the succinoyl linker. The incorporation of zinc was achieved in refluxing DMF with zinc acetate and 2,6-lutidine. Difficulty of access to the core of the porphyrin and the deformation of the complex presumably explained the high temperature required for the metallation. Single crystals suitable for X-ray structural determination were obtained by slow evaporation of a solution of the porphyrin in a mixture of toluene/acetonitrile (1:1), at room temperature. Figure 1 and Figure 2 show the ^{1}H/^{13}C NMR spectra and a HMQC zoom view of **3**, respectively. The most striking observation concerns both the pattern and the chemical shifts of the methylenic protons of the succinyl moiety. The four methylenic protons appear as two multiplets at two chemicals shifts as different as −0.45 and −4.00 ppm (upper trace), whereas the two carbons bearing these protons appear as only one signal, at δ = 24.5, in the decoupled ^{13}C spectrum (lower trace).

As additional evidence, the two cross-peaks for the chemical shifts of the methylenic protons in Figure 2 are linked to the ^{13}C signal at 24.5. It is also clear that the other signal at δ = 24.7 is not correlated to these methylenic protons, but to a $-CH_2-$ residue in the proline, labelled c-H. The HMQC spectrum in Figure 3 actually shows that the two other methylenic signals, CH_2-b and CH_2-d, expected for the proline cycle are at 26.6 and δ = 46.1 and exhibit cross-peaks with the proton signals at δ = 1.13/2.32 and 1.13/1.76, respectively. The difference in the chemical shifts between the two methylenic proton signals is δ = 3.5; such a difference clearly demonstrates that two protons are directed towards the centre of the porphyrin where the two

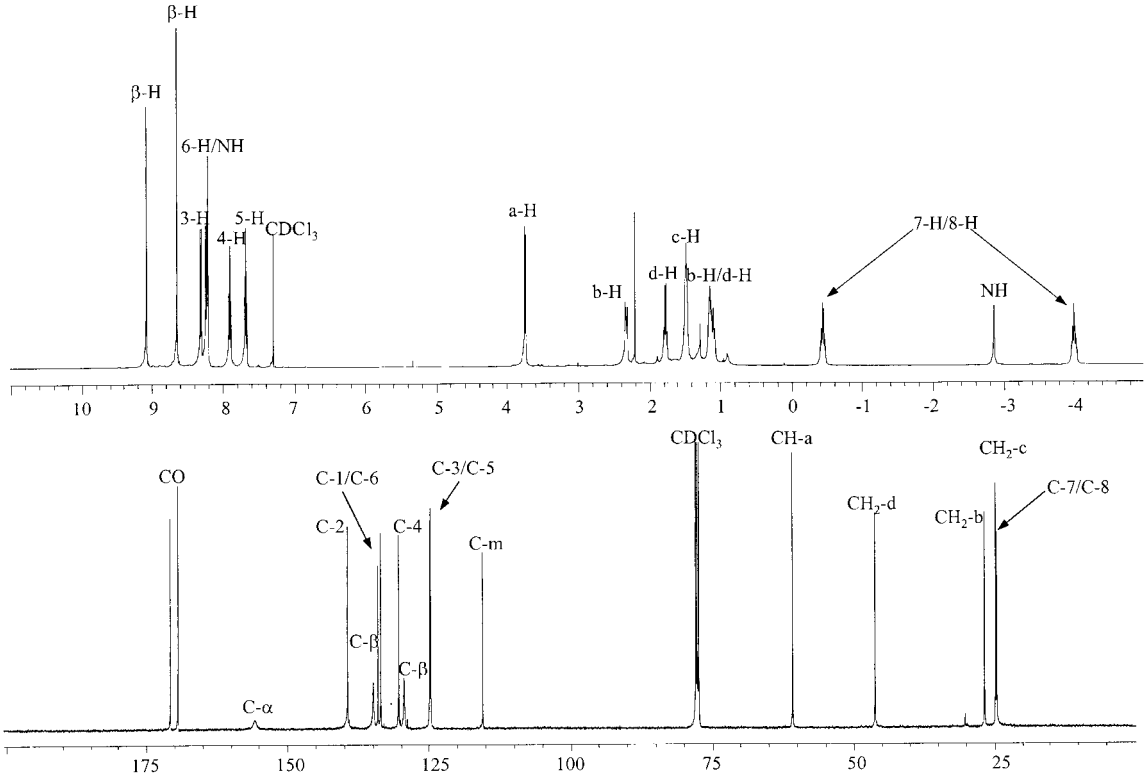

Figure 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra ($CDCl_3$, 300 K) of porphyrin **3**

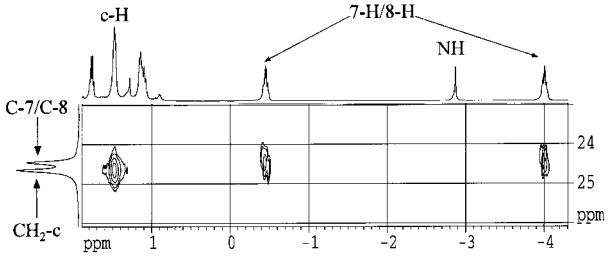

Figure 2. Heteronuclear Multiple Quantum Correlation (HMQC) zoom view on the methylene groups of the succinyl residues in **3**

other ones are turned outside the cavity. The 2D signature can be explained by the fact that each carbon atom bears the two types of proton; hence two cross-peaks for the single carbon signal. This situation is a perfect illustration of the conformational information that can be obtained through the study of this type of superstructure in solution.

The second important remark relates to comparison of the ^{1}H spectra of the free base and of the zinc(II) complex (Figure 4). For such spectra, one should usually expect quite similar signatures, with the absence of internal -NH signals as the only major difference. For a pair of compounds such as **3/3Zn**, not only are the two straps magnetically distinct in the zinc(II) porphyrin, but the symmetry group differs as well. In fact, as already mentioned above and as shown by the existence of a signal for each β-pyrrolic proton, **3Zn** has no symmetry at all! Moreover, we were able to obtain a crystal structure of this porphyrin (see Figure 6), and the structure appears to be the same both in solution and in the solid state. A complete description of this structure is detailed below.

Indeed, the ^{1}H NMR spectrum of **3Zn** shows that most of the signals are split, giving rise to a multitude of peaks. This phenomenon is particularly clear for the methylenic protons in the $\delta = 0$ to -4 domain, but also appears in the aromatic region. It is reasonable to distinguish between two different straps, as one is coordinated through a carbonyl group and the other is not, but this implies that there is no exchange between the two straps on NMR timescales at 300 K. The same conclusion can be reached for the exchange of the two carbonyl groups of the coordinated strap: the fact that the β-pyrrolic protons appear as eight different signals implies that there is no exchange between the coordinated CO and the other one on the same strap, and hence a loss of the principal C_2 axis.

A variable-temperature study was subsequently undertaken. If our explanation is correct, then the symmetry of the free-base should be recovered, with two magnetically equivalent straps, on increasing the temperature. For this purpose, proton NMR spectra of **3Zn** were recorded in [D_6]DMSO from 300 K to 410 K (Figure 5). Although the spectra were not as sharp as that in $CDCl_3$, it is obvious that as the temperature rises, the NMR fingerprint becomes simpler; at 410 K, a spectrum typical of a D_2-symmetric complex was obtained, with two singlets around $\delta = 9$ corresponding to the β-pyrrolic protons, two doublets and two triplets between $\delta = 7.5$ and 8.5 for the *meso* aromatic protons and, finally, two signals at high field ($\delta = -0.4$ and -2.2), consistent with the succinoyl motif in the strap.

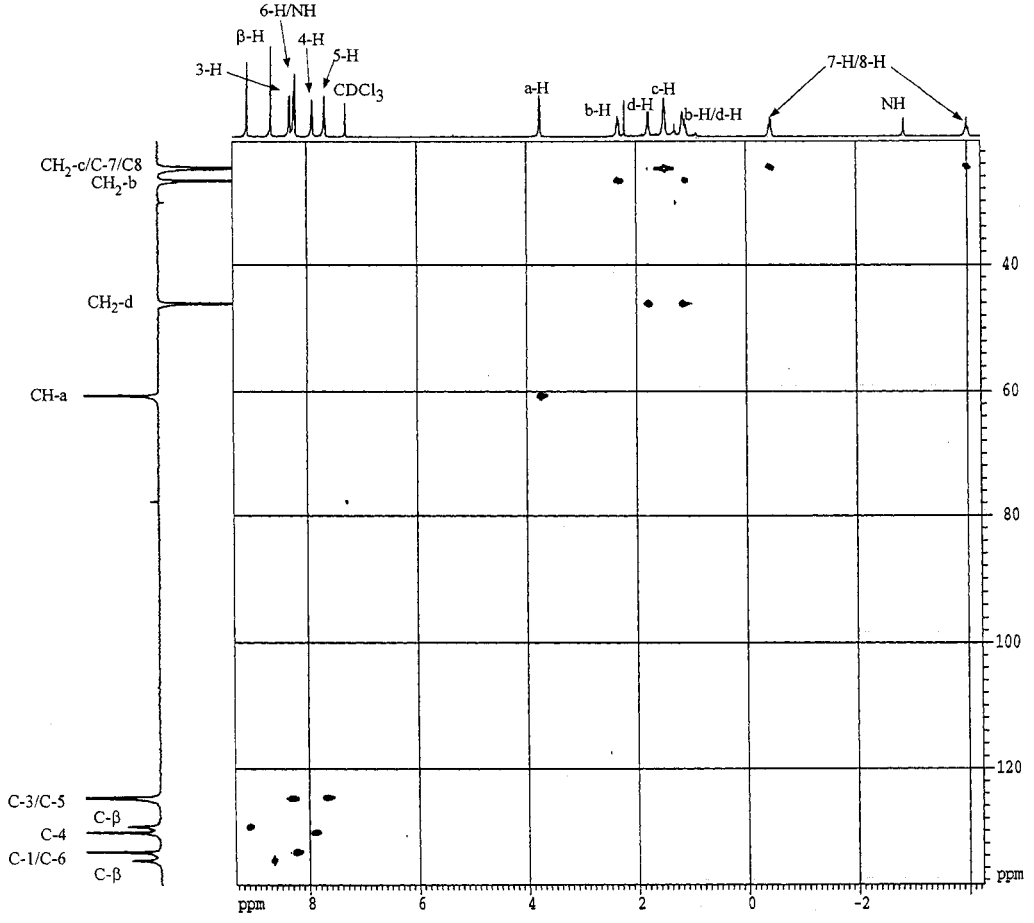

Figure 3. Entire HMQC spectrum of the porphyrin free base **3**

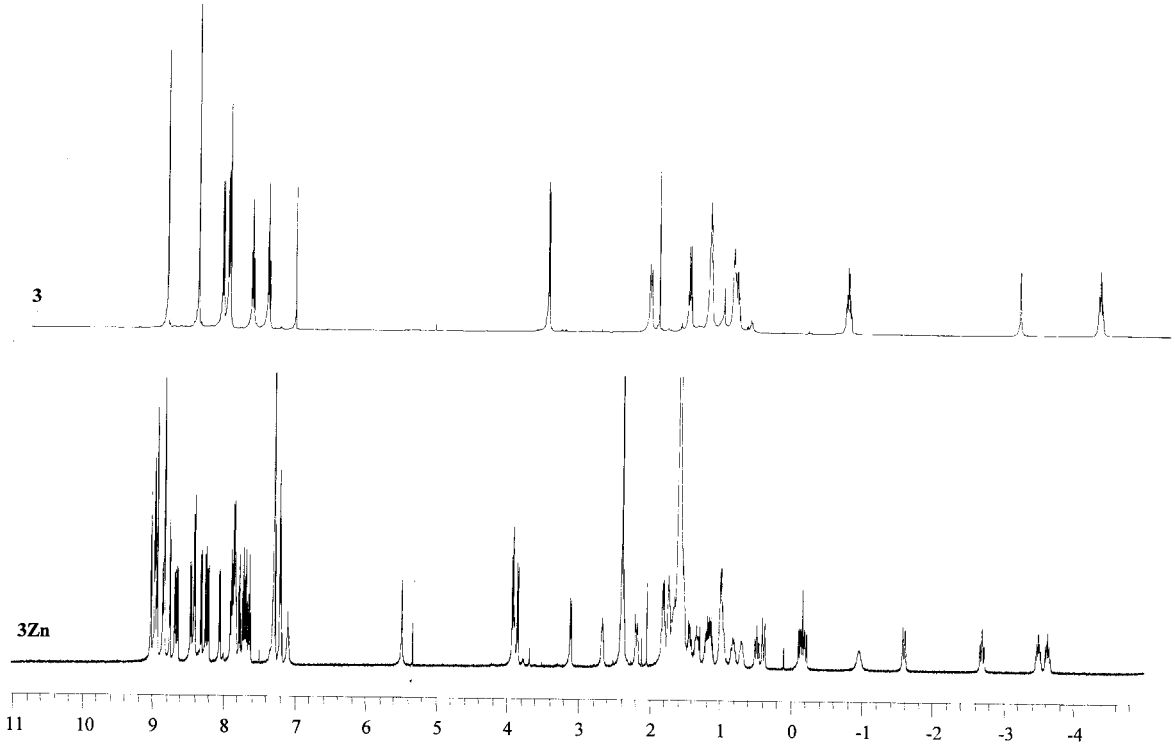

Figure 4. Comparison of the ^{1}H NMR spectra at 300 K in $CDCl_3$ of **3** (top) and **3Zn** (bottom)

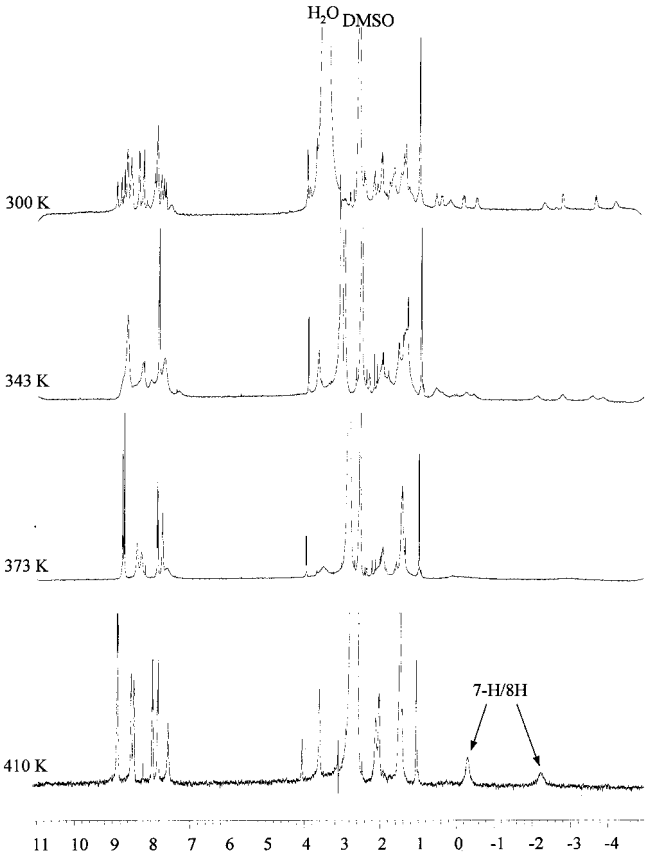

Figure 5. Variable temperature ^{1}H NMR spectra ([D$_6$]DMSO, from 300 K to 410 K) of **3Zn**

The Zn complex crystallised with three acetonitrile solvate molecules and one toluene one. The porphyrin molecule **3Zn**, shown in Figure 6, consists of a TAPP-based macrocycle with two straps anchored through an amide linkage to the *ortho* positions of two opposite phenyl groups in 5,10,15,20-tetrakis(*o*-aminophenyl)Zn porphyrin. Each strap is made up of a 2,2′-[*N*,*N*′-bis(1,4-dioxo-1,4-butanediyl)-L-prolinoyldiamido]diphenyl residue, but the two faces of the macrocycle are not equivalent: one proline carbonyl of one strap is bound to the Zn atom. As a consequence, the macrocycle has a dissymmetric ruffled conformation: the metal-bonded strap pulls more strongly than the non-bonded one on the *meso* carbon atoms.

The average Cm deviations with respect to the 24-atom least-squares plane, then, are 0.221(7) and 0.162(5) Å, respectively, for the metal-bonded and the non-bonded straps. As previously observed for such "peptide-like" straps from X-ray or NMR spectroscopic data,[25] intramolecular hydrogen bonds give rise to a rigid conformation for these straps. In **3Zn**, two kinds of hydrogen bond are observed: NH···CO(proline) for the non-bonded strap and NH···N(proline) for the metal-bonded one. The Zn atom is pentacoordinated and lies 0.271(2) Å above the four-nitrogen plane. The mean Zn···N distance is 2.057(9) Å and the Zn···O distance is 2.132(2) Å [for this latter bond length, a compilation over 15 structures from CCDC in pentacoordinated Zn porphyrin systems results in a mean value of a 2.220(8) Å]. It is worth mentioning that the succinyl residues are not in a perfectly parallel position, as revealed by the two different distances between methylene carbons and the Zn atom (3.940 Å and 4.120 Å).

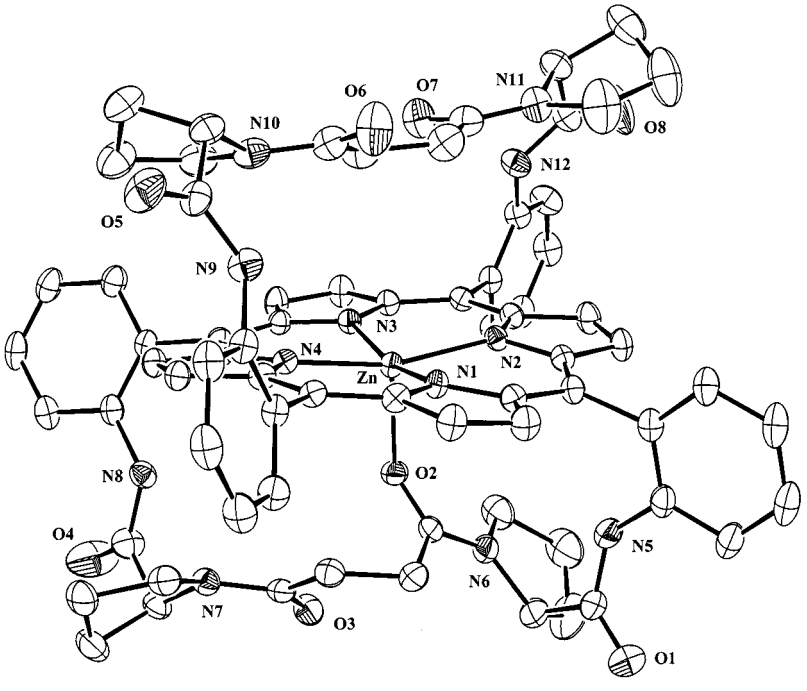

Figure 6. ORTEP view of the solid-state structure of **3Zn**. For the sake of clarity, the toluene and acetonitrile solvate molecules and also the hydrogen atoms are omitted

Conclusion

We have described the synthesis of a new family of chiral bis-strapped porphyrins. We wanted to obtain such a series of compounds, with the aim of establishing a structure-activity relationship between steric hindrance of the strap and the enantioselectivity in chiral oxidation reactions. To do so, we employed a specific amino acid, L-proline, because of its unique structural feature: a cyclic lateral chain. We were able to show that systematic variation of the linker is possible and that this should allow not only some changes in the proximity of the chiral motif from the centre of the porphyrin but also in the orientation of the chiral amino acid itself. Further information about the shape of these molecules in solution was obtained by an accurate study of the NMR spectroscopic chemical shifts. Moreover, the crystal structure of a zinc(II) analogue of these molecules clearly indicates that the solid-state structure is in full agreement with the conformation in solution. This structure shows that the lateral chain of the L-proline gives rise to permanent and rigid steric hindrance, which should favour a selective approach of the olefin during the oxidation process. Whether the influence of such a rigid structure is positive or negative, in terms of larger or smaller enantiomeric excesses, this new series of potential chiral catalysts should allow us to improve our understanding of enantioselective epoxidation, and is currently under investigation in regard to its catalytic activity.

Experimental Section

General Remarks: ^{1}H (500.13 MHz) and ^{13}C (125.05 MHz) NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer and are referenced to the residual protonated solvents. − Mass spectra were performed on a MS/MS ZABSpec TOF spectrometer at the University of Rennes I (C.R.M.P.O.). − UV/Vis spectra were recorded on a Varian Cary 1E spectrometer. − IR spectra were recorded on a Bruker IFS 66 spectrometer. All solvents (ACS for analysis) were purchased from Carlo Erba. − THF was distilled from potassium metal. CH_2Cl_2 was used as received. Triethylamine and *N*-methylpiperidine were distilled on CaH_2. The starting materials were generally used as received (Acros, Aldrich) without any further purification. All reactions were performed under an argon atmosphere and monitored by TLC (silica, CH_2Cl_2/MeOH). Column flash chromatography was performed on silica gel (Merck TLC Kieselgel 60 H, 15 μm).

α-5,15:β-10,20-Tetrakis{2-(L-prolinoylamido)phenyl}porphyrin (1): Compound **2** (0.16 g, 0.11 mmol) was dissolved in CH_2Cl_2 (10 mL) under argon, and TFA (1 mL) was added. After 30 minutes, the solvent was removed under vacuum. The yield was almost quantitative (0.11 g). − ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = −2.52 (s, 2 H, NH), 0.01 (m, 4 H, c-H), 0.3 (s, 4 H, NH), 0.47 (m, 4 H, d-H), 0.73 (m, 4 H, c-H), 1.12 (m, 4 H, d-H), 1.51 (m, 8 H, b-H), 3.16 (t, ^3J = 6.8 Hz, 4 H, a-H), 7.54 (td, ^3J = 7.6, ^4J = 1.2 Hz, 4 H, 5-H), 7.86 (td, ^3J = 7.5, ^4J = 1.5 Hz, 4 H, 4-H), 7.99 (dd, ^3J = 7.6, ^4J = 1.5 Hz, 4 H, 6-H), 8.76 (s, 4 H, β-H), 8.78 (dd, ^3J = 7.5, ^4J = 1.2 Hz, 4 H, 3-H), 8.83 (s, 4 H, β-H), 9.47 (s, 4 H, NH). − ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 25.2 (CH_2-c), 30.5 (CH_2-b), 45.6 (CH_2-d), 60.5 (CH-a), 120.9 (C-3), 123.3 (C-5), 130.3 (C-4), 134.7 (C-6). − MS (FAB): *m*/*z* = 1062.0 $[M]^+$.

α-5,15:β-10,20-Tetrakis{2-(*N*-*tert*-butoxycarbonyl-L-prolinoylamido)phenyl}porphyrin (2): *N*-Boc-L-proline (19.46 g, 90.4 mmol, 100 equiv.) was dissolved in dry THF (120 mL) under an argon atmosphere at −20 °C. *N*-Methylpiperidine (16.5 mL, 135 mmol, 150 equiv.) and then isobutyl chloroformate (11.15 mL, 85.9 mmol, 95 equiv.) were added. A white precipitate appeared immediately. A solution of TAPP αβαβ (610 mg, 0.9 mmol) in THF (50 mL), maintained at −20 °C, was then added. The reaction mixture was stirred for 3 hours at this temperature and was then allowed to warm to room temperature. The mixture was filtered and the precipitate was washed with diethyl ether. The solution was evaporated under vacuum and the residue was chromatographed on silica gel [elution with a CH_2Cl_2/MeOH (98:2)]. Pure product (1.15 g, 85% yield) was obtained. − ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = −2.58 (s, 2 H, NH), 0.35 (m, 12 H, c-H + d-H), 0.95 (s, 36 H, Boc-H), 1.28 (s, 8 H, b-H), 1.53 (s, 4 H, d-H), 3.56 (s, 4 H, a-H), 7.57 (s, 8 H, 4-H + 5-H), 7.88 (s, 4 H, 6-H), 8.05 (s, 4 H, NH), 8.69 (s, 4 H, 3-H), 8.75 (s, 4 H, β-H), 8.78 (s, 4 H, β-H). − ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 28.2 (CH_3-Boc), 30.7 (CH_2-b), 45.3 (CH_2-c), 46.4 (CH_2-d), 61.7 (CH-a), 79.5 (C-Boc), 80.1 (C-Boc), 115.3 (C-m), 121.4 (C-3), 122.3 (C-β), 123.6 (C-4 + C-5), 130.4 (C-6), 131.9, 132.0, 134.8 (C-β), 138.7, 153.2, 154.6, 170.7 (CO), 171.3 (CO). − MS (FAB): *m*/*z* = 1463.0 $[M]^+$. − UV/Vis (CH_2Cl_2): λ, nm (10^{-3}·ε, M^{-1}·cm^{-1}) = 419 (357.1), 513 (22.3), 546 (5.2), 588 (6.3), 645 (1.8). − IR (KBr): ν̃, cm^{-1} = 3380 (NH), 1698 (CO).

Typical Procedure for the Synthesis of Porphyrins 3−6: A solution of **1**, freshly prepared in THF (10 mL), and a solution of the desired diacyl chloride (0.33 mmol, 3 equiv.) in THF (10 mL) were added over 5 hours, by syringe pump, to a solution of NEt_3 (1.37 mL, 9.8 mmol, 90 equiv.) in THF (120 mL) under an argon atmosphere, cooled with an ice bath. The solution was stirred for 10 hours. THF was removed under vacuum and the product was chromatographed on silica gel. A CH_2Cl_2/MeOH mixture (98:2) was used for the elution.

α-5,15:β-10,20-Bis[2,2′-{[*N*,*N*′-bis(1,4-dioxo-1,4-butanediyl)-L-prolinoyldiamido]diphenyl}]porphyrin (3): This compound was prepared from the succinic diacyl chloride and obtained in 70% (94 mg) yield. − ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = −4.00 (m, 4 H, 7-H + 8-H), −2.87 (s, 2 H, NH), −0.45 (m, 4 H, 7-H + 8-H), 1.13 (m, 8 H, b-H + d-H), 1.47 (m, 8 H, c-H), 1.76 (q, ^3J = 8.8 Hz, 4 H, d-H), 2.32 (d, ^3J = 8.8 Hz, 4 H, b-H), 3.74 (d, ^3J = 8.0 Hz, 4 H, a-H), 7.66 (td, ^3J = 7.5, ^4J = 1.1 Hz, 4 H, 5-H), 7.89 (td, ^3J = 7.9, ^4J = 1.2 Hz, 4 H, 4-H), 8.20 (s, 4 H, NH), 8.23 (dd, ^3J = 7.5, ^4J = 1.2 Hz, 4 H, 6-H), 8.30 (dd, ^3J = 7.9, ^4J = 1.1 Hz, 4 H, 3-H), 8.64 (s, 4 H, β-H), 9.07 (s, 4 H, β-H). − ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 24.5 (C-7 + C-8), 24.7 (CH_2-c), 26.6 (CH_2-b), 46.1 (CH_2-d), 60.7 (CH-a), 115.4 (C-m), 124.6 (C-5), 124.7 (C-3), 129.2 (C-β), 130.2 (C-4), 133.4 (C-6), 133.9 (C-1), 134.5 (C-β), 139.3 (C-2), 155.0 (C-α), 169.2 (CO), 170.6 (CO). − MS (FAB): *m*/*z* = 1226.9 $[M + H]^+$. − $C_{72}H_{66}N_{12}O_8$·CH_2Cl_2 (1312.3): calcd. C 66.81, H 5.22, N 12.81; found C 66.38, H 5.40, N 12.16. − UV/Vis (CH_2Cl_2): λ, nm (10^{-3}·ε, M^{-1}·cm^{-1}) = 421 (203.9), 516 (10.1), 548 (3.6), 588 (3.1), 644 (1.4). − IR (KBr): ν̃, cm^{-1} = 3484 (NH), 1691, 1625 (CO).

α-5,15:β-10,20-Bis[2,2′-{*N*,*N*′-bis[(*E*)-1,4-dioxobut-2-ene-1,4-diyl]-L-prolinoyldiamido}diphenyl]porphyrin (4): This compound was prepared from the fumaric diacyl chloride and obtained in 10% (14 mg) yield. − ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = −3.00

(s, 2 H, NH), 1.04 (m, 4 H, b-H), 1.48 (m, 4 H, c-H + d-H), 1.83 (d, ^3J = 6.8 Hz, 4 H, d-H), 2.33 (dd, ^3J = 12.3, ^4J = 4.5 Hz, 4 H, b-H), 2.68 (s, 4 H, 7-H + 8-H), 3.71 (d, ^3J = 7.3 Hz, 4 H, a-H), 7.64 (td, ^3J = 7.6, ^4J = 1.2 Hz, 4 H, 5-H), 7.89 (td, ^3J = 8.0, ^4J = 1.4 Hz, 4 H, 4-H), 8.18 (dd, ^3J = 7.6, ^4J = 1.4 Hz, 4 H, 6-H), 8.22 (dd, ^3J = 8.0, ^4J = 1.2 Hz, 4 H, 3-H), 8.53 (s, 4 H, β-H), 8.56 (s, 4 H, NH), 9.01 (s, 4 H, β-H). − ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 24.6 (CH_2-c), 26.2 (CH_2-b), 46.4 (CH_2-d), 61.2 (CH-a), 115.0 (C-m), 124.6 (C-5), 124.9 (C-3), 126.8 (C-7 + C-8), 128.7 (C-β), 130.0 (C-4), 132.7 (C-6), 134.2 (C-β), 135.0, 139.7, 162.2 (CO), 168.7 (CO). − MS (EI): *m/z* = 1222 $[M]^+$. − UV/Vis (CH_2Cl_2): λ, nm ($10^{-3}\cdot\varepsilon$, $M^{-1}\,cm^{-1}$) = 425 (172.3), 518 (7.2), 548 (1.4), 590 (2.7), 648 (1.6). − IR (KBr): ṽ, cm^{-1} = 3461 (NH), 1694, 1634 (CO).

α-5,15:β-10,20-Bis{2,2′-[*N,N′*-bis(isophthaloyl)-L-prolinoyldiamido]diphenyl}porphyrin (5): This compound was prepared from the isophthalic diacyl chloride and obtained in 40% (58 mg) yield. − ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = −3.91 (s, 2 H, NH), 1.37 (m, 4 H, c-H), 1.57 (m, 16 H, b-H + c-H + d-H), 2.22 (m, 4 H, d-H), 4.25 (m, 4 H, a-H), 4.52 (s, 2 H, 7-H), 5.14 (m, 2 H, 9-H), 5.22 (m, 4 H, 8-H), 7.57 (t, ^3J = 7.1 Hz, 4 H, 5-H), 7.87 (t, ^3J = 8.2 Hz, 4 H, 4-H), 8.08 (d, ^3J = 7.1 Hz, 4 H, 6-H), 8.17 (s, 4 H, NH), 8.57 (s, 4 H, β-H), 8.88 (d, ^3J = 8.2 Hz, 4 H, 3-H), 8.91 (s, 4 H, β-H). − ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 25.4 (CH_2-c), 27.4 (CH_2-b), 49.3 (CH_2-d), 61.6 (CH-a), 114.8 (C-m), 121.2 (C-3), 122.7 (C-7), 123.3 (C-5), 125.1 (C-8), 127.8 (C-9), 129.2 (C-β), 130.3 (C-4), 131.2, 131.4, 134.1 (C-β), 135.7 (C-6), 139.1, 167.1 (CO), 169.4 (CO). − HR-MS (LSI-MS): *m/z* ($C_{80}H_{66}N_{12}NaO_8$ $[M + Na]^+$): calcd. 1345.5024; found 1345.5079. − $C_{80}H_{66}N_{12}O_8\cdot CHCl_3\cdot CH_2Cl_2$ (1527.8): calcd. C 64.47, H 4.55, N 11.00; found C 64.71, H 4.45, N 11.13. − UV/Vis (CH_2Cl_2): λ, nm ($10^{-3}\cdot\varepsilon$, $M^{-1}\cdot cm^{-1}$) = 421 (388), 517 (22), 548 (6), 590 (7), 653 (6). − IR (KBr): ṽ, cm^{-1} = 3499 (NH), 1693, 1623 (CO).

α-5,15:β-10,20-Bis{2,2′-[*N,N′*-bis(terephthaloyl)-L-prolinoyldiamido]diphenyl}porphyrin (6): This compound was prepared from the terephthalic diacyl chloride and obtained in 40% (57 mg) yield. − ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = −3.15 (s, 2 H, NH), 1.40 (m, 4 H, c-H), 1.50 (m, 4 H, b-H), 1.67 (m, 8 H, b-H + c-H), 1.88 (m, 4 H, d-H), 2.35 (m, 4 H, d-H), 3.68 (s, 8 H, 7-H), 4.62 (m, 4 H, a-H), 7.48 (td, ^3J = 7.3, ^4J = 0.7 Hz, 4 H, 5-H), 7.69 (dd, ^3J = 7.3, ^4J = 0.9 Hz, 4 H, 6-H), 7.88 (td, ^3J = 8.3, ^4J = 0.9 Hz, 4 H, 4-H), 8.53 (s, 4 H, NH), 8.73 (s, 4 H, β-H), 8.85 (s, 4 H, β-H), 8.86 (dd, ^3J = 8.3, ^4J = 0.7 Hz, 4 H, 3-H). − ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 28.2 (CH_2-c), 30.1 (CH_2-b), 49.6 (CH_2-d), 60.9 (CH-a), 115.2 (C-m), 122.1 (C-3), 123.8 (C-5), 124.2 (C-7), 129.5 (C-β), 130.5 (C-4), 131.5, 134.3, 134.7 (C-β), 135.6 (C-6), 138.4, 169.6 (CO). − MS (FAB): *m/z* = 1323.9 $[M + H]^+$. − UV/Vis (CH_2Cl_2): λ, nm ($10^{-3}\cdot\varepsilon$, $M^{-1}\cdot cm^{-1}$) = 419 (150.7), 514 (7.5), 547 (1.6), 582 (2.6), 637 (1.4). − IR (KBr): ṽ, cm^{-1} = 3482 (NH), 1691, 1650 (CO).

[α-5,15:β-10,20-Bis{2,2′-[*N,N′*-bis(1,4-dioxo-1,4-butanediyl)-L-prolinoyldiamido]diphenyl}porphyrin]zinc(II) (3Zn): Compound **3** (50 mg) was dissolved in DMF (10 mL). 2,6-Lutidine and an excess of $Zn(OAc)_2$ were added to the mixture. The solution was heated for 24 hours, and the solvent was then removed under vacuum. The residue was dissolved in CH_2Cl_2 and washed with water. The product was chromatographed on silica gel. A CH_2Cl_2/MeOH mixture (95:5) was used for the elution. The yield was 95% (50 mg). − ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = −3.63 (m, 1 H, 7-H + 8-H), −3.48 (m, 1 H, 7-H + 8-H), −2.69 (td, ^3J = 14.3, ^4J = 3.9 Hz, 1 H, 7-H + 8-H), −1.60 (d, ^3J = 16.0 Hz, 1 H, 7-H + 8-H), −0.17 (m, 2 H, 7-H + 8-H), 0.38 (td, ^3J = 17.2, ^4J = 2.9 Hz, 1 H, 7-H + 8-H), 0.47 (td, ^3J = 14.1, ^3J = 3.9 Hz, 1 H, 7-H + 8-H), 0.99 (m, 2 H, Pro-H), 1.17 (m, 2 H, Pro-H), 1.34 (m, 1 H, Pro-H), 1.43 (m, 1 H, Pro-H), 1.58 (m, 8 H, Pro-H), 1.72 (m, 2 H, Pro-H), 1.81 (m, 2 H, Pro-H), 2.19 (m, 1 H, Pro-H), 2.39 (m, 4 H, Pro-H), 2.67 (m, 1 H, Pro-H), 3.13 (d, ^3J = 8.1 Hz, 1 H, a-H), 3.85 (d, ^3J = 7.9 Hz, 1 H, a-H), 3.91 (d, ^3J = 8.2 Hz, 2 H, a-H), 7.19 (s, 1 H), 7.27 (m, 2 H), 7.63 (t, ^3J = 7.5 Hz, 1 H), 7.68 (t, ^3J = 7.5 Hz, 1 H), 7.72 (t, ^3J = 7.5 Hz, 1 H), 7.77 (t, ^3J = 7.5 Hz, 1 H), 7.86 (m, 4 H), 8.05 (d, ^3J = 7.3 Hz, 1 H), 8.21 (d, ^3J = 7.3 Hz, 1 H), 8.25 (d, ^3J = 8.2 Hz, 1 H), 8.31 (d, ^3J = 8.2 Hz, 1 H), 8.40 (d, ^3J = 7.6 Hz, 1 H), 8.45 (d, ^3J = 8.5 Hz, 1 H), 8.64 (d, ^3J = 7.2 Hz, 1 H), 8.68 (d, ^3J = 7.2 Hz, 1 H), 8.75 (d, ^3J = 4.7 Hz, 1 H, β-H), 8.82 (d, ^3J = 4.9 Hz, 2 H, β-H), 8.85 (s, 1 H), 8.92 (d, ^3J = 4.5 Hz, 1 H, β-H), 8.93 (d, ^3J = 4.7 Hz, 1 H, β-H), 8.95 (d, ^3J = 4.6 Hz, 1 H, β-H), 8.96 (d, ^3J = 4.3 Hz, 1 H, β-H), 9.02 (d, ^3J = 4.8 Hz, 1 H, β-H). − ^{1}H NMR (500 MHz, [D$_6$]DMSO, 400 K): δ = −2.30 (s, 4 H, 7-H + 8-H), −0.40 (s, 4 H, 7-H + 8-H), 0.95 (d, ^3J = 6.5 Hz, 4 H, Pro-H), 1.39 (s, 12 H, Pro-H), 1.92 (s, 4 H, Pro-H), 2.02 (s, 4 H, Pro-H), 3.48 (s, 4 H, a-H), 7.45 (s, 4 H, NH), 7.69 (t, ^3J = 7.0 Hz, 4 H, 5-H), 7.83 (t, ^3J = 7.5 Hz, 4 H, 3-H), 8.30 (d, ^3J = 7.5 Hz, 4 H, 6-H), 8.37 (d, ^3J = 7.0 Hz, 4 H, 3-H), 8.72 (s, 4 H, β-H), 8.74 (s, 4 H, β-H). − ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 21.4 (C-7 + C-8), 24.2 (CH_2-Pro), 24.7 (CH_2-Pro), 24.9 (CH_2-Pro), 25.1 (CH_2-Pro), 26.1 (C-7 + C-8), 26.4 (CH_2-Pro), 26.7 (CH_2-Pro), 30.1 (CH_2-Pro), 30.6 (C-7 + C-8), 30.9 (C-7 + C-8), 43.7 (CH_2-Pro), 46.0 (CH_2-Pro), 47.2 (CH_2-Pro), 60.4 (CH-a), 60.5 (CH-a), 60.6 (CH-a), 61.6 (CH-a), 112.4, 115.0 (C-m), 116.4 (C-m), 117.2 (C-m), 118.9, 120.1 (C-β), 123.3, 123.9, 124.5, 124.7, 125.8, 129.6, 129.7, 130.2, 130.4, 130.8, 131.2 (C-β), 131.3 (C-β), 131.9, 132.4 (C-β), 132.7 (C-β), 133.5 (C-β), 133.6 (C-β), 134.1 (C-β), 134.4, 134.5, 134.8, 134.9, 135.1, 138.5, 138.7, 139.2, 148.6, 148.8, 149.9, 150.7, 150.8, 151.0, 151.9, 167.3, 169.5, 169.6, 169.9, 170.3, 170.5, 170.7. − HR-MS (LSI-MS): *m/z* ($C_{72}H_{64}N_{12}NaO_8Zn$ $[M + Na]^+$): calcd. 1311.4159 found 1311.4168. − $C_{72}H_{64}N_{12}O_8Zn\cdot CH_2Cl_2$ (1375.7): calcd. C 63.73, H 4.84, N 12.22; found C 63.78, H 5.25, N 11.79. − UV/Vis (CH_2Cl_2): λ, nm ($10^{-3}\cdot\varepsilon$, $M^{-1}\cdot cm^{-1}$) = 418 (144.9), 560 (5.9), 596 (1.2). − IR (KBr): ṽ, cm^{-1} = 3460 (NH), 1689, 1613 (CO).

Typical Procedure for the Insertion of Iron into Porphyrins: Compound **2** or **3**−**6** was dissolved in toluene inside a glovebox maintained under 1 ppm of dioxygen. 2,6-Lutidine and an excess of $FeBr_2$ were added to the mixture. The solution was heated at reflux for 12 hours until the reaction was complete as indicated by UV/Vis spectroscopy. The product was oxidised by air for 1 hour. The solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2, and washed with water/saturated brine. The product was chromatographed on silica gel. A CH_2Cl_2/MeOH mixture (95:5) was used for the elution. The yield was almost quantitative (95%).

[α-5,15:β-10,20-Tetrakis{2-(*N*-*tert*-butoxycarbonyl-L-prolinoylamido)phenyl}porphyrin]iron(III) Chloride (2Fe): Compound **2Fe** was prepared from **2** − HR-MS (LSI-MS): *m/z* ($C_{64}H_{60}FeN_{12}O_4$ $[M - 4\,Boc - Cl + 4\,H]^+$): calcd. 1116.4212; found 1116.4212. − UV/Vis (CH_2Cl_2): λ, nm ($10^{-3}\cdot\varepsilon$, $M^{-1}\cdot cm^{-1}$) = 417 (66.1), 572 (3.7). − IR (KBr): ṽ, cm^{-1} = 3382 (NH), 1701 (CO).

[α-5,15:β-10,20-Bis-2,2′-{[*N,N′*-bis(1,4-dioxo-1,4-butanediyl)-L-prolinoyldiamido]diphenyl}porphyrin]iron(III) Chloride (3Fe): This compound was prepared from **3**. − HR-MS (LSI-MS): *m/z* ($C_{72}H_{63}FeN_{12}NaO_8$ $[M - HCl + Na]^+$): calcd. 1302.4139; found 1302.4224. − UV/Vis (CH_2Cl_2): λ, nm ($10^{-3}\cdot\varepsilon$, $M^{-1}\cdot cm^{-1}$) = 426 (92.9), 583 (7.0). − IR (KBr): ṽ = 3459 (NH), 1692, 1650 cm^{-1} (CO).

[α-5,15:β-10,20-Bis{2,2′-[*N,N′*-bis{(*E*)-1,4-dioxobut-2-ene-1,4-diyl}-L-prolinoyldiamido]diphenyl}porphyrin]iron(III) Chloride (4Fe): This compound was prepared from **4**. − HR-MS (LSI-MS): *m/z* ($C_{73}H_{63}FeN_{12}NaO_9$ [M − HCl + CH_3OH + Na]$^+$): calcd. 1330.4088; found 1330.4081. − UV/Vis (CH_2Cl_2): λ nm (10^{-3}·ε, M^{-1}·cm^{-1}) = 426 (69.9), 586 (4.8). − IR (KBr): $\tilde{\nu}$ = 3461 (NH), 1694, 1634 cm^{-1} (CO).

[α-5,15:β-10,20-Bis{2,2′-[*N,N′*-bis(isophthaloyl)-L-prolinoyldiamido]diphenyl}porphyrin]iron(III) Chloride (5Fe): This compound was prepared from **5**. − HR-MS (LSI-MS): *m/z* ($C_{80}H_{64}FeN_{12}O_8$ [M − Cl]$^+$): calcd. 1376.4319; found 1376.4318. − UV/Vis (CH_2Cl_2): λ, nm (10^{-3}·ε, M^{-1}·cm^{-1}) = 422 (77.3), 584 (6.4). − IR (KBr): $\tilde{\nu}$ = 3499 (NH), 1693, 1630 cm^{-1} (CO).

[α-5,15:β-10,20-Bis{-2,2′-[*N,N′*-bis(terephthaloyl)-L-prolinoyldiamido]diphenyl}porphyrin]iron(III) Chloride (6Fe): This compound was prepared from **2Fe**, following the typical procedure for the synthesis of porphyrin, with a 40% yield. − HR-MS (LSI-MS): *m/z* ($C_{81}H_{67}FeN_{12}NaO_9$ [M − HCl + CH_3OH + Na]$^+$): calcd. 1430.4404; found 1430.4477. − UV/Vis (CH_2Cl_2): λ, nm (10^{-3}·ε, M^{-1}·cm^{-1}) = 426 (48.9), 583 (5.8). − IR (KBr): $\tilde{\nu}$ = 3473 (NH), 1692, 1637 cm^{-1} (CO).

Crystal Structure Analysis of 3Zn: $C_{72}H_{64}N_{12}O_8Zn{\cdot}CH_3C_6H_5{\cdot}3CH_3CN$, M = 1506.02. Enraf−Nonius CAD4 diffractometer, Mo-K_α radiation (λ = 0.71073 Å), T = 293 K. Triclinic, $P\bar{1}$, a = 12.837(1), b = 13.136(1), c = 13.117 (1) Å, α = 62.281(8), β = 89.666(8), γ = 76.762(8)°, V = 1893.0(3) Å^3, Z = 1, D_x = 1.321 g·cm^{-3}, μ = 0.393 mm^{-1}. After data reduction,[26] the intensities were corrected for absorption (ψ-scan, Tmin.−Tmax. = 93−97%) and for a 28% linear decay. The structure was solved by direct methods and subsequent difference Fourier analysis.[27] The refinement was performed by full-matrix, least-squares on the 8028 unique intensities collected. All non-hydrogen atoms were anisotropically refined. Except for the hydrogen atoms bonded to the amide nitrogen atoms, which were located on a Fourier difference map and refined, hydrogen atoms were included in their calculated positions and refined with a riding model. A final refinement on F^2 (all data) and 950 parameters converged at $wR(F^2)$ = 0.0848, $R(F)$ = 0.0582, G.O.F = 1.037. For the 6900 intensities with $I > 2\sigma(I)$, the agreement indices were $wR(F^2)$ = 0.0779 and $R(F)$ = 0.0326. The Flack absolute structure parameter converged to 0.000(14) and the max. and min residual electron densities were 0.330 and −0.222 e·Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156093. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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