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Synthesis of Interlocked Basket Handle Porphyrins

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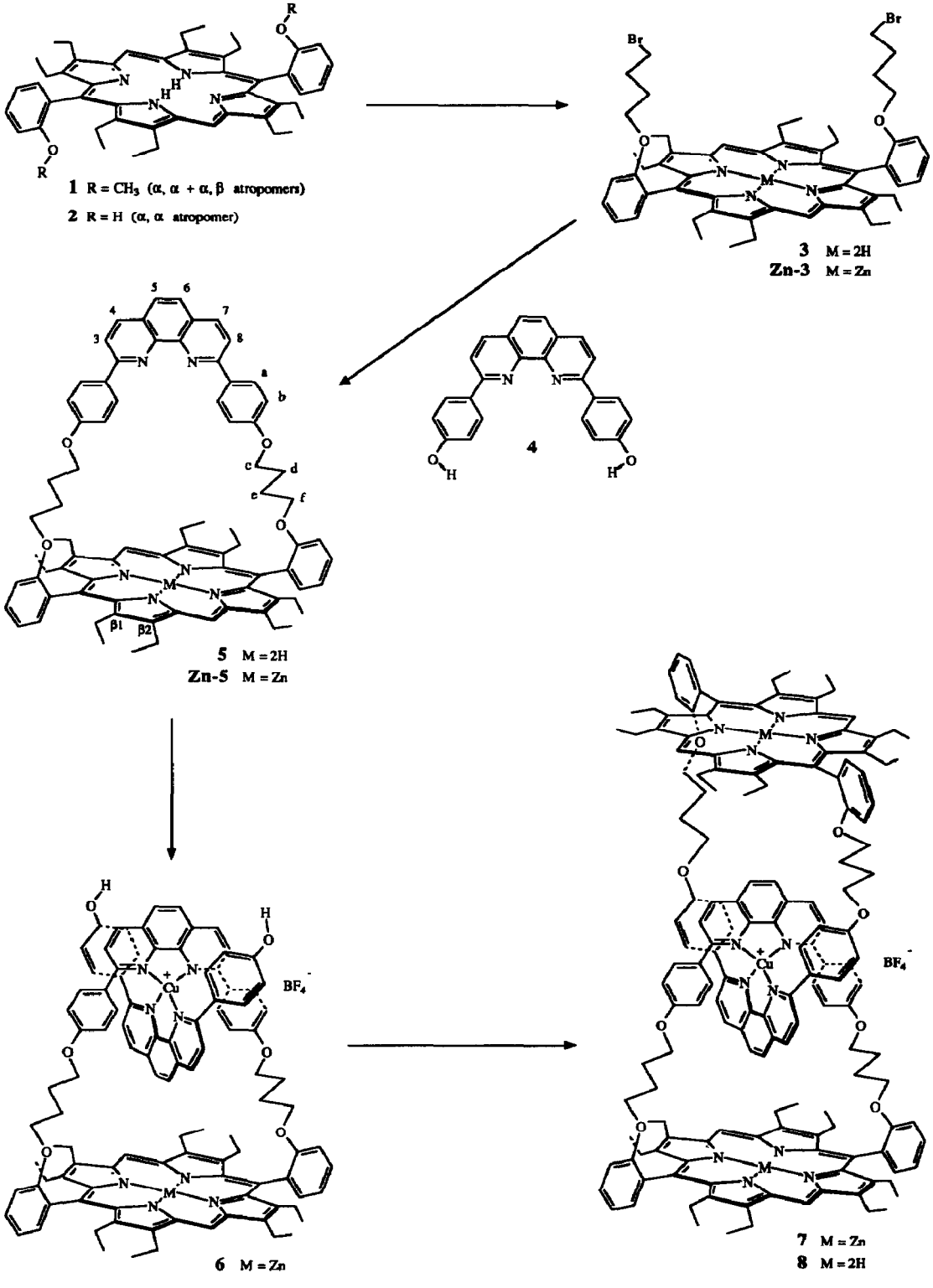
***Abstract** : The synthesis and the characterization by UV-visible and ^1H NMR spectroscopic analyses of interlocked basket handle porphyrins in which the two subunits are assembled by the Cu(I) complex of phenanthroline residues inserted into superstructures are reported.*

Development of molecular systems offering possibilities to study intermolecular interactions, cooperative phenomena, intramolecular energy and/or electron transfer processes has represented a growing interest in supramolecular chemistry[1]. Especially the synthesis of polyporphyrinic compounds to mimic hemoglobin, multiheme cytochromes and photochemical reaction centers has been a very active field of porphyrin chemistry.

In our studies directed towards the preparation of active site hemoprotein models, we have developed the so-called basket handle porphyrins in which the tetrapyrrolic macrocycle bears superstructures linked by means of ether or secondary amido groups[2]. In such an architectural design, a phenanthroline capped porphyrin has been recently described by Weiss[3]. From this kind of molecule where 2,9-disubstituted 1,10 phenanthroline is inserted into one handle we turned our attention to the design of free base or metallo-dimeric porphyrins based on a three dimensional template effect induced by a transition metal following the strategy introduced by Sauvage for the synthesis of interlocked macrocyclic ligands[4]. This strategy have been successfully applied to the construction of porphyrin-containing catenanes[5] or rotaxanes[6].

We report herein the preparation of an interlocked basket handle porphyrin system representing the first member of a new series of symmetrical and unsymmetrical polyporphyrinic compounds.

The starting di(2-methoxyphenyl)octaethylporphyrin **1** was easily prepared (70% yield) by a standard procedure[7]. After demethylation with BBr_3 in CH_2Cl_2, the α,α-atropomer **2** was separated by column chromatography on silica gel. **2** was then treated with a large excess of dibromobutane in DMF at 40°C in the presence of K_2CO_3 to give the disubstituted porphyrin **3** in 82 % yield. By treating this compound with 9-diphenol 1,10-phenanthroline **4**, obtained by previously reported methods[8], in the presence of a large excess of K_2CO_3 at 40°C for 40 h under argon a 33 % yield of the single face hindered porphyrin **5** was obtained after passage through a silica gel column (CH_2Cl_2/ ether, 100/5, v/v as eluent).


1 R = CH3 (α, α + α, β atropomers)
2 R = H (α, α atropomer)
3 M = 2H
Zn-3 M = Zn
4
5 M = 2H
Zn-5 M = Zn
6 M = Zn
7 M = Zn
8 M = 2H

In order to overcome the eventual insertion of copper in the porphyrin during the formation of unsymmetrical diphenanthroline complex **6**, porphyrin **5** was quantitatively converted to its zinc derivative using Zn $(OAc)_2$ $2H_2O$ in a refluxing CH_2Cl_2-methanol mixture. The copper (I) diphenanthroline compound **6** was produced by reaction of Zn-**5** with 1.1 equivalent of $[Cu(CH_3CN)_4]$ BF_4 [9] in a mixture of CH_2Cl_2-acetonitrile for 0.5 h at room temperature followed by addition of one equivalent of **4** in DMF. It was isolated after evaporation of solvents and chromatography on silica gel column (CH_2Cl_2/Acetone, 3/1 v/v). The cyclization procedure described for the preparation of compound **5** was applied to form **7**. Thus, a mixture of **6** and the zinc complex of porphyrin **3** in DMF/THF (4/1) was added dropwise (4 h) to a suspension of K_2CO_3 in DMF under argon. The reaction mixture was kept at 45°C overnight, then evaporated to dryness. The symmetrical diporphyrin compound **7** was purified by chromatography (silica gel, CH_2Cl_2/Acetone, 100/5, v/v as eluent) and isolated as its BF_4-salt after work up with KBF_4 in 31 % yield. The metal free diporphyrin copper (I) catenate **8** was obtained by treatment of **7** under acid conditions (HCl 1N), neutralization and subsequent anion exchange in 70 % yield.

The absorption spectra of compounds **7** and **8** exhibit an overall resemblance with those of monomeric diphenyloctaethylporphyrin derivatives indicating that the ground state interactions between porphyrins themselves, and/or between porphyrin and phenanthroline moieties are absent because their large separation[10].

^1H NMR spectroscopy was used for the characterization of compounds **7** and **8**[11]. Compared to the spectrum of the single face hindered porphyrin **5**, the protons of diphenylphenanthroline moiety are strongly shifted to high field. Such behaviors arise from the large ring current effect of the porphyrin rings. This is particularly marked for the two equivalent protons H5 and H6 which appeared as a singlet at 4.28 ppm and 3.6 ppm for compounds **7** and **8** respectively whereas the same protons appeared at 7.54 ppm for **5**. Ring current shift calculations from these shifts using the model of Abraham allowed an estimate of the distance of these protons with respect to the porphyrin cores[12]. A distance close to 4.5 Å is found. By contrast to the preceding observations, the pyrrolic NH protons of **8** appear at -1.68 ppm, slightly downfield shifted in comparison to those of the monomeric porphyrin **5** (-1.85 ppm). They are affected by a weak deshielding due to the ring current of the phenanthrolines. These results clearly demonstrate that the phenanthroline plane of each subunit of dimers is almost perpendicular to the porphyrine plane of the second subunit. The rigidity of the symmetrical dimeric systems is due to the presence of the copper (I) catenate.

The strategy presented here allowing the efficient preparation of free base and metallo dimeric porphyrins in an interlocked assembling might be extended to the construction of many other members of this new class of compounds in which the length and the chemical nature of spacers connecting phenanthroline residues to porphyrin rings should be systematically varied. Furthermore, such compounds in which mixed metalloporphyrins should be present, might allow new contributions to the study of through-space electron-transfer processes[13].

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10. Compound **5**: λ max (nm) (ε 10^4.dm^3.$mole^{-1}$.cm^{-1}) CH_2Cl_2: 288 (66.2), 412 (211.7), 510 (16.8), 544 (5.2), 576.5 (6.9), 629 (1.5).

    Compound **Zn-5**: λ max (nm) (ε 10^4.dm^3.$mole^{-1}$.cm^{-1}) CH_2Cl_2: 288.5 (57.4), 413.5 (306), 541 (16.8 (16.8), 578.5 (8.4).

    Compound **7**: λ max (nm) (ε 10^4.dm^3.$mole^{-1}$.cm^{-1}) CH_2Cl_2: 414.5 (526.5), 542.5 (30.8), 577 (17.7).

    Compound **8**: λ max (nm) (ε 10^4.dm^3.$mole^{-1}$.cm^{-1}) CH_2Cl_2: 282 (67.7), 413.5 (354.8), 511 (25), 544 (13.2), 577 (13.8), 630 (2.8).
11. ^{1}H nmr of compound **5** ($CDCl_3$) δ ppm: 10.3 (s, 2H, H_{meso}), 8.22 (d, 4H, H_a), 8.03 (d, 2H, $H_{4,7}$), 7.88 (d, 2H, $H_{3,8}$), 7.83 and 7.30 (m, 8H, H_{phenyl}), 7.54 (s, 2H, $H_{5,6}$), 6.67 (d, 4H, H_b), 4.13 (m, 12H, β2 $\underline{CH_2}$-CH_3 and H_f), 3.46 (t, 4H, H_c), 3.12 and 2.94 (m, 8H, β1 $\underline{CH_2}$-CH_3), 1.93 (t, 12H, β2 CH_2-$\underline{CH_3}$), 1.41-1.22 (m, 8H, $H_{e,d}$), 1.26 (m, 12H, β1 CH_2-$\underline{CH_3}$), -1.85 (s, 2H, NH).

    ^{1}H nmr of compound **Zn-5** ($CDCl_3$) δ ppm: 10.19 (s, 2H, H_{meso}), 8.18 (d, 4H, H_a), 8.11 (d, 2H, $H_{4,7}$), 7.92 (d, 2H, $H_{3,8}$), 7.79 and 7.29 (m, 8H, H_{phenyl}), 7.54 (s, 2H, $H_{5,6}$), 6.62 (d, 4H, H_b), 4.0-4.11 (m, 12H, β2 $\underline{CH_2}$-CH_3 and H_f), 3.32 (t, 4H, H_c), 3.01 and 2.79 (m, 8H, β1 $\underline{CH_2}$-CH_3), 1.88 (t, 12H, β2 CH_2-$\underline{CH_3}$), 1.43-1.21 (m, 8H, $H_{e,d}$), 1.17 (m, 12H, β1 CH_2-$\underline{CH_3}$).

    ^{1}H nmr of compound **7** ($CDCl_3$) δ ppm: 10.09 (s, 4H, H_{meso}), 7.73 and 7.29 (m, 16H, H_{phenyl}), 7.09 (d, 4H, $H_{4,7}$), 6.78 (d, 8H, H_a), 6.68 (d, 4H, $H_{3,8}$), 5.32 (d, 8H, H_b), 4.28 (s, 4H, $H_{5,6}$), 4.11 (t, 8H, H_f), 3.97 (m, 16H, β2 $\underline{CH_2}$-CH_3), 2.90 (m, 16H, β1 $\underline{CH_2}$-CH_3), 2.70 (t, 8H, H_c), 1.77 (t, 24H, β2 CH_2-$\underline{CH_3}$), 1.40-1.00 (m, 16H, $H_{e,d}$), 1.07 (m, 24H, β1 CH_2-$\underline{CH_3}$).

    ^{1}H nmr of compound **8** ($CDCl_3$) δ ppm: 10.07 (s, 4H, H_{meso}), 7.73 and 7.31 (m, 16H, H_{phenyl}), 6.97 (d, 4H, $H_{4,7}$), 6.68 (d, 8H, H_a), 6.29 (d, 4H, $H_{3,8}$), 5.26 (d, 8H, H_b), 4.15 (t, 8H, H_f), 3.90 (m, 16H, β2 $\underline{CH_2}$-CH_3), 3.60 (s, 4H, $H_{5,6}$), 2.92 (m, 16H, β1 $\underline{CH_2}$-CH_3), 2.66 (t, 8H, H_c), 1.70 (t, 24H, β2 CH_2-$\underline{CH_3}$), 1.40-1.00 (m, 16H, $H_{e,d}$), 1.07 (m, 24H, β1 CH_2-$\underline{CH_3}$), -1.68 (s, 4H, NH).
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