Tetrahedron Vol. 47, No 28, pp 5123-5132, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

SYNTHESIS OF BIS-PORPHYRINS CONTAINING A 2,9-DIPHENYL-1,10-PHENANTHROLINE SPACER

Sylvie CHARDON-NOBLAT and Jean-Pierre SAUVAGE

Laboratoire de Chimie Organo-Minérale, UA 422 au CNRS, Institut de Chimie,
1, rue Blaise Pascal, 67008 STRASBOURG, France.

(*Received in Belgium* 25 *January* 1991)

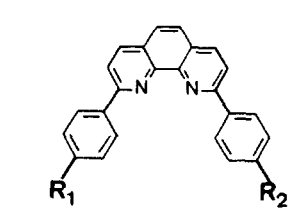
Abstract. The synthesis of bis-porphyrins disposed in an oblique fashion is described. The tetrapyrrole rings are linked via a 2,9-diphenyl-1,10-phenanthroline spacer. Two routes have been investigated : a stepwise procedure and a direct strategy involving a double cyclisation step. From the bis-free base porphyrin, synthesized with an overall yield of ~1% from 2,9-di(p-tolyl)-1,10-phenanthroline, an unsymmetrical zinc (II) porphyrin free base system was prepared and isolated in view of excited state energy and electron transfer.

The design and the construction of multifunctional molecular systems able to perform intramolecular electron or energy transport is of particular relevance for handling and carrying signals at the molecular level.[1-8] At the same time, this should contribute to the understanding of the factors which govern electron transfer processes between the various chromophores involved in natural photosynthetic systems.[9-14] In order to mimic the initial charge-separation step of photosynthesis, numerous bipartite compounds consisting of a porphyrin linked to an electron acceptor[7] have been synthesized and studied. A promissing extension is provided by tri- and tetra-partite systems.[8]

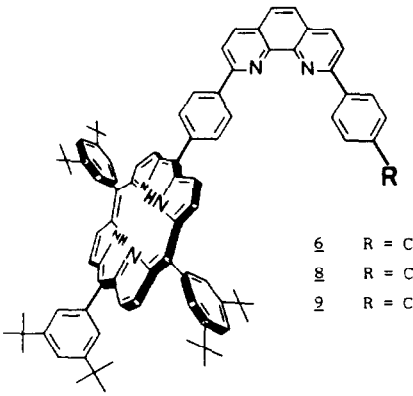
Electron transfer and energy migration are important processes involved in natural photosynthesis.[15] Since the X-ray study of the photosynthetic reaction centre from Rhodopseudomonas viridis in 1984,[16] several laboratories attempted to build multiporphyrin devices displaying geometrical analogy with the natural system. In particular, compounds in which two or several porphyrins are rigidly held in an oblique fashion are especially promissing and revelant to the modeling of the reaction centre. Among the molecular systems reported, the archetypical "gable" porphyrin described by Tabushi et al.[17] is of particular importance. Its basic framework has recently been used and generalized by Sessler et al. to build highly interesting multicomponent systems, aimed at photoinduced intramolecular electron transfer.[18] Another extension of Tabushi's molecule has recently been reported, allowing preparation of a bis-porphyrin systems[19] in which the two tetrapyrrole rings are likely to be disposed with an interplane angle of 60°. Porphyrin dimers

constructed on naphtalene or connected via a rigid spiro group[20] represent also a significant contribution. Some of their photophysical and electron transfer properties have been reported.[21]

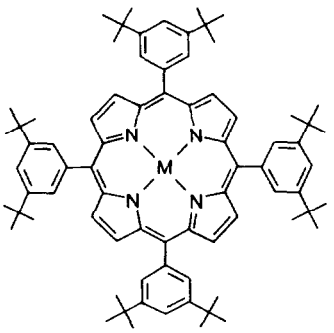
We have recently reported the preparation of several bis-porphyrin compounds containing a 1,10-phenanthroline spacer.[22,23] In such a system, an interplane angle of 60° between the tetrapyrrole rings seems to be probable, although rotation motions may lead to slightly different orientations. The centre-to-centre separation should be close to 13Å. This arrangement makes the molecule relatively similar to fragments of the photosynthetic reaction centre. The disymmetrical system (zinc porphyrin-free base porphyrin) has been shown to undergo fast and efficient intramolecular singlet energy transfer between the zinc containing part and the non-metallated ring.[23] We now report the full preparation of the various compounds synthesized, including a detailed experimental section.



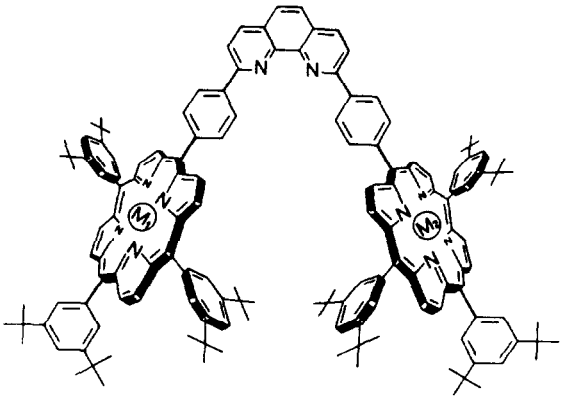
1 $R_1 = R_2 = CH_3$
2 $R_1 = R_2 = CH_2Br$
3 $R_1 = CH_2Br$ $R_2 = CHBr_2$
4 $R_1 = R_2 = CHBr_2$
5 $R_1 = CHO$ $R_2 = CH_2OCOC_2H_5$
11 $R_1 = R_2 = CHO$



6 $R = CH_2OCOC_2H_5$
8 $R = CH_2OH$
9 $R = CHO$



7 M = 2H
14 M = Zn



10 $M_1 = M_2 = 2H$
12 $M_1 = Zn$ $M_2 = 2H$
13 $M_1 = M_2 = Zn$

FIGURE 1

The bis-porphyrin systems described in the present article are shown in Figure 1 as well as their precursors. The corresponding monoporphyrins are also represented. They have been prepared and studied[23] in comparison to their dimer analogues.

The synthetic routes involve either two distinct reactions of porphyrin ring formation or a single double cyclization step. Both strategies are schematically represented in Figure 2.

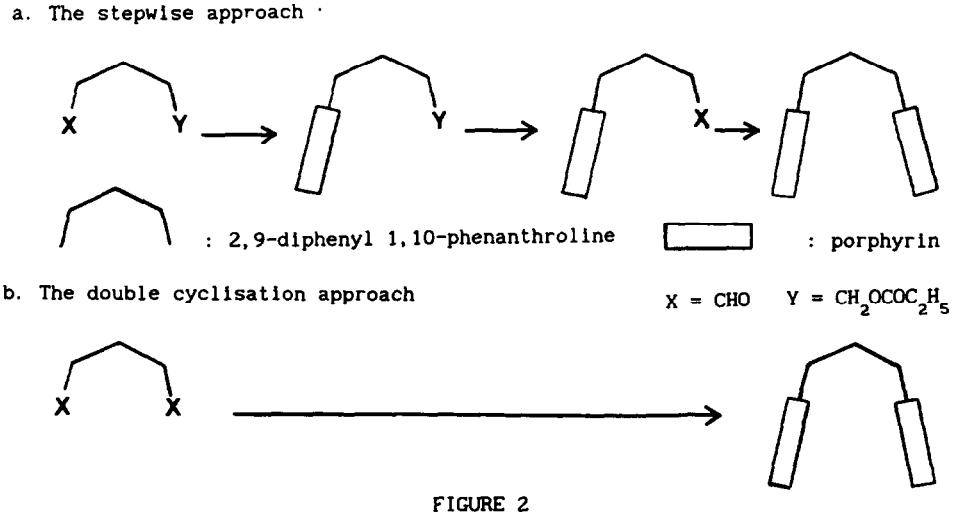


FIGURE 2

1. The stepwise approach

1 was obtained in 70% yield from 1,10-phenanthroline and 4-lithiotoluene, after hydrolysis and MnO_2 treatment, following a procedure earlier used to make various polyimine aromatic rings substituted by alkyl or aryl groups α to the nitrogen atoms.[24] Treatment of **1** with N-bromosuccinimide in refluxing benzene under light irradiation gave a mixture of **3** and **4**, plus a small amount of **2**, the proportion of which being dependent on the amount of N-bromosuccinimide used. The crude mixture was directly treated by CH_3CH_2COONa in propionic acid, leading to **5** and **11** which were obtained pure after chromatographic separation. In a typical preparation, the yields (calculated from **1**) of **5** and **11** were 37% and 20% respectively. Adler's reaction[25] applied to a 1 : 22 : 24 mixture of **5**, 3,5-di-t-butylbenzaldehyde and pyrrole in refluxing CH_3CH_2COOH led to **6** in 20% yield (calculated from **5**) in addition to the monomer porphyrin **7** (24% based on pyrrole in excess). Hydrolysis of the ester **6** gave the alcohol **8** (66% yield) which was quantitatively converted to the porphyrin-aldehyde **9** by activated MnO_2. The bis-porphyrin **10** was obtained in 21.6% yield from **9**, using Adler's condensation on a 1 : 27 : 28 mixture of **9**, 3,5-di-t-butylbenzaldehyde and pyrrole. Besides **10**, the monoporphyrin **7** was also isolated in 20% yield. Using the two-step cyclization approach, the final bis-porphyrin **10** could be synthesized with an overall yield of 1% from **1**. The preparation requires seven distinct steps from commercially available 1,10-phenanthroline (6 steps from **1**).

2. The double cyclization approach

This strategy involves only three steps from **1**. Its low overall yield (0.5% from **1**) is amply compensated by its shortness which makes this approach more convenient than the two distinct cyclization steps procedure.

A 1 : 23 : 25 mixture of **11**, 3,5-di-t-butylbenzaldehyde and pyrrole was subjected to Adler's reaction (refluxing propionic acid for 16 hrs), leading to **10** in 2.6% yield (calculated from **11**) besides **7** (16% yield).

The difficulty of the preparation rests on the separation of the crude mixture obtained and the chromatographic purification of **10**. In a typical preparation, 70 mg of **10** was obtained from 500 mg of the dialdehyde **11**.

Noteworthy, the direct synthesis of bis-porphyrins from aromatic dialdehydes using two simultaneous Adler-Rothemund reactions seems to be very unusual. Bis-porphyrins attached to an aromatic nucleus have rather been prepared using the intermediate formation of bis-(dipyrrylmethane) derivatives from the corresponding bis-aldehyde, followed by cyclization to the bis-porphyrin using Mac Donald procedure.[26] Recently examples have been reported on the synthesis of two porphyrins linked to anthracene,[27] biphenylene,[28] phenyl[29,30] or naphtalene.[20]

3. Synthesis of the zinc complexes **12** and **13**

The disymmetrical system **12** was prepared by a statistical method : **10** was reacted with one equivalent of zinc acetate. A chromatographic separation of the expected statistical mixture afforded **12** (50% yield) and **13** (25% yield) in addition to unreacted **10**. **13** could be further purified by recrystallization.

4. Absorption electron spectroscopy of the bis-porphyrins **10**, **12** and **13**

The position, the shape and the width of the Soret band in bis-porphyrins has been used several times as a probe for estimating the size of the coupling interaction[17-20,30-40] between the two chromophores. For instance, in the original "gable" porphyrin of Tabushi, the Soret band is split into two well resolved peaks at 416 and 428 nm[17] whereas tetraphenyl porphyrin leads to a sharp single Soret band at 418 nm. This splitting reflects the relatively strong interaction between the two π-systems and it is still observed in the bis-zinc complex of Tabushi's gable porphyrin. Very different is the situation for the presently described oblique bis-porphyrin systems.

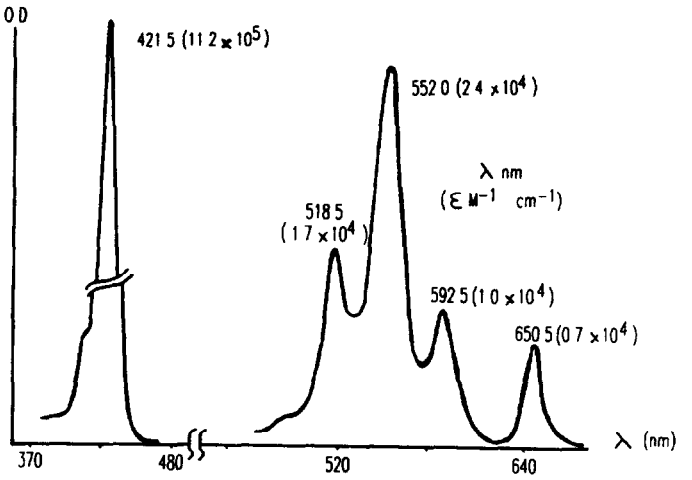


FIGURE 3

As shown in Figure 3, the absorption spectrum of the disymmetrical porphyrin **12** displays a single, relatively sharp Soret band (λ = 421.5 nm with ε = 1.1 x 10^6 cm^{-1} mol^{-1} l in CH_2Cl_2). The whole spectrum of **12** corresponds precisely to the addition of the spectra of **7** and **14**, with no modification either in the Soret band region nor for the Q bands (500 to 680 nm).

The same observation is true for **10** and **13** whose visible spectra are almost superimposable to those of **7** and **14** respectively. Clearly, the dipole-dipole interaction existing in several bis-porphyrin systems (flat, twisted or gable) is no more found in our compounds. This different behaviour may originate from larger edge-to-edge and centre-to-centre separation of the porphyrin rings of **10**, **12** or **13** as compared to other bis-porphyrin systems. However, both chromophores do interact very strongly in the singlet excited state of **12**, as shown by emission spectroscopy.[22]

Acknowledgements

We thank the CNRS for financial support. The Ministère de la Recherche et de la Technologie is also acknowledged for its contribution. We also would like to thank Dr. C.O. Dietrich-Buchecker for fruitful discussions.

Experimental Section

General

Benzene was dried and purified by distillation (normal pressure) over Na. Pyrrole was purified by distillation (43 mmHg) over KOH. 3,5-diterbutyltoluene was prepared by the literature method.[41] All other chemicals were of the best commercially available grade and were used without further purification.

^{1}H-NMR spectra were recorded with a Bruker WP200SY or a AM400 spectrometer. All compounds based on diphenyl-1,10-phenanthroline showed a similar highly characteristic pattern : an AB pattern for H_3 or H_8 and H_4 or H_7 (coupling constant J ~ 8,5Hz) and an AA' XX' system (J ~ 8,1Hz) for H_o or $H_{o'}$ and H_m or $H_{m'}$.

Electronic spectra were performed with a Kontron Uvikon 860. Mass spectra were recorded on a Thomson T.H.N 208 (chemical ionization) or a ZAB-HF (F.A.B.). Melting points were measured with a Reichert Micro Melting Point apparatus or a Büchi SMP20.

Preparation of 2,9-di(p-tolyl)-1,10-phenanthroline **1**

p-tolyl-lithium was prepared by the direct interaction of freshly cut lithium with p-bromo-toluene in ether under argon at 35°.[42] The resulting organolithium solution was titrated by the double titration method described by Gillman et al.[43] In a typical run, 60 ml of a 1.1 M p-litho-toluene solution were obtained by reacting 3 g (432 mmols) lithium with 12.3 ml (100 mmols) of p-bromo-toluene in 120 ml of dry ether (66%). 60 ml of the latter solution was cannulated at room temperature in to a degassed suspension of 2.66 g (13.4 mmols) commercial 1,10-phenanthroline monohydrate in 30 ml toluene. After the resulting dark red solution was stirred for 45 mn under argon at room temperature, it was hydrolyzed at 0°C with water. The bright yellow toluene layer was decanted and the aqueous layer extracted three times with 100 ml portions of CH_2Cl_2. The combined organic layers were then rearomatized by successive additions of MnO_2 under effective magnetic stirring (MnO_2 Merck n° 805958, ~ 15 g for each batch).

This reoxidation, easily followed by TLC and the disappearance of the yellow colour, was complete after addition of 45 g MnO_2.

The mixture was dried over $MgSO_4$, the black slurry could be easily filtered off on a sintered glass and the filtrate evaporated to dryness to give crude **1**. After recrystallisation from hot benzene **1** was obtained in 55% yield (2.66 g, 7.38 mmols). A further 0.7 g (1.94 mmols) of **1** could be obtained by column chromatography of the filtrate on silica gel (toluene / 0.5% MeOH). Overall yield : 70%.

1. Colourless powder (mp : 197-199°C). ^{1}H-NMR ($CDCl_3$) : 8.40 (d, 4H, Ho) ; 8.29 (d, 2H, H_4 or H_7) ; 8.14 (d, 2H, H_3 or H_8) ; 7.77 (s, 2H, H_5 and H_6) ; 7.41 (d, 4H, Hm) ; 2.48 (s, 6H, CH_3). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 328 [4.45] ; 312 [4.54] ; 272 [4.76]; 237 [4.61]. Anal. calcd. for $C_{26}H_{20}N_2$: C, 86.64 ; H, 5.59 ; N, 7.77. Found : C, 86.59 ; H, 5.51 ; N, 7.69. MS : 360.46.

Preparation of **2**, **3** and **4** (Bromide derivative)

Bromination of **1** (408 mg, 1.1 mmols) to **2**,**3** and **4** by N-bromosuccinimide (621 mg, 3.5 mmols) was performed by light irradiation ($\lambda > 320$ nm) over 20 mn of a solution of **1** in 20 ml of refluxing benzene. The crude mixture was filtered on a sintered glass, and the filtrate was washed with water. After solvent evaporation, the crude product (550 mg) containing **2**, **3** and **4** was obtained. Although, these compounds (**2**, **3**, **4**) were difficult to separate, we have isolated small amounts of **2** and **4** and have characterized then by ^{1}H-NMR.

2. ^{1}H-NMR ($CDCl_3$) : 8.44 (d, 4H, Ho) ; 8.39 (d, 2H, H_4 or H_7) ; 8.18 (d, 2H, H_3 or H_8) ; 7.85 (s, 2H, H_5 and H_6) ; 7.64 (d, 4H, H_m) ; 4.63 (s, 4H, CH_2).

4. ^{1}H-NMR ($CDCl_3$) : 8.46 (d, 4H, H_o) ; 8.36 (d, 2H, H_4 or H_7) ; 8.16 (d, 2H, H_3 or H_8) ; 7.84 (s, 2H, H).

Preparation of **5**

The crude product (15.28 g) containing **3** was directly treated with a solution of 1.46 g ground soda (0.37 mmol) in 110 ml propionic acid. The mixture was heated under reflux for 2 hrs (128°C). After cooling to 20°C, the NaBr was filtered off and the propionic acid removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (200 ml) and neutralized by shaking with saturated $NaHCO_3$ solution (3 x 150 ml). The organic layer was washed with H_2O (3 x 150 ml) and dried over $MgSO_4$. Evaporation of the solvent gave 11 g of crude brown glassy product. Purification by column chromatography on silica gel (eluent CH_2Cl_2 containing 0 to 5% AcOEt) gave pure **5** (5.17 g, 37% yield from **1**).

5. Amorphous colourless powder (mp : 38-40°C).^{1}H-NMR ($CDCl_3$) : 10.16 (s, 1H, CHO) ; 8.64 (d, 2H, H_o) ; 8.46 (d, 2H, $H_{o'}$) ; 8.38 (d, 1H, H_4) ; 8.35 (d, 1H, H_7) ; 8.22 (d, 1H, H_3) ; 8.17 (d, 1H, H_8) ; 7.84 (dd, 2H, H_5 and H_6) ; 8.12 (d, 2H, H_m) ; 7.60 (d, 2H, $H_{m'}$) ; 5.26 (s, 2H, CH_2) ; 2.47 (q, 2H,

CH_2) ; 1.22 (t, 3H, CH_3).Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 315 [4.65] ; 274 [4.77] ; 231 [4.88]. Anal. calc. for $C_{29}H_{22}N_2O_3$: C, 78.01 ; H, 4.97 ; N, 6.27. Found : C, 77.78 ; H, 5.22 ; N, 6.08. MS : 446.

Preparation of monoporphyrin **6** and corresponding monomer **7**

One of the 2 aldehydes used for this reaction is 3,5-di-t-butylbenzaldehyde. The bromide derivative necessary for the Sommelet reaction[44] was obtained by bromination of 3,5-di-t-butyltoluene (10.05 g, 0.05 mol) by N-bromosuccinimide (13.08 g, 0.07 mol) in refluxing benzene (25 ml) under light irradiation (l > 320 nm) for 1 hr. After filtration and solvent evaporation, the crude product (12 g) was directly treated as described in reference[44] to obtain 3,5-diterbutylbenzaldehyde. The Adlers reaction[25] applied to a mixture of 5.79 g 3,5-diterbutylbenzaldehyde (26.51 mmols), 526 mg **5** (1.18 mmols) and 2 ml pyrrole (28.89 mmols) in 60 ml refluxing propionic acid for 16 hrs gave, after evaporation of the propionic acid, crude product. This mixture of porphyrins **6** and **7** was suspended in toluene (100 ml) and evaporated. This process was repeated twice more to remove the remaining propionic acid (toluene/propionic acid : bp 80°C). The resulting red-brown solid was dissolved in CH_2Cl_2 (100 ml), neutralized with 10% Na_2CO_3 solution (3 x 50 ml), stirred with silica gel and dried over $MgSO_4$.

Evaporation to dryness gave 7 g of red-brown solid. Column chromatography on silica gel (700 g) gave the crude monomer **7** (eluent toluene) and the crude mono-porphyrin **6** (eluent toluene / 6% AcOEt). Pure monomer **7** (1.49 g, 24% from pyrrole in excess) was obtained by recrystallization from benzene-ethanol (slow diffusion). A second flash chromatography on silica gel (eluent toluene) yielded 313 mg of **6** (20.6 % from **5**).

6. Brown powder (mp > 280°C). ^{1}H-NMR ($CDCl_3$) : 9.010 (d, 2H, H_{py1}) ; 8.948 (d, 2H, Hpy_2) ; 8.926 (s, 4H, H_{py}) ; 8.846 (d, 2H, H_o) ; 8.484 (d, 2H, H_m) ; 8.533 (d, 2H, $H_{o'}$) ; 8.501 (d, 1H, H_4) ; 8.472 (d, 1H, H_3) ; 8.392 (d, 1H, H_7) ; 8.208 (d, 1H, H_8) ; 8.115 (d, 4H, H_{op}) ; 8.102 (d, 2H, $H_{op'}$) ; 7.906 (dd, 2H, H_5 and H_6) ; 7.808 (t, 3H, H_{pp}) ; 7.565 (d, 2H, $H_{m'}$) ; 5.181 (s, 2H, CH_2) ; 2.350 (q, 2H, CH_2) ; 1.568 (s, 18H, $CH_{3'}$) ; 1.540 (s, 36H, CH_3) ; 1.14 (t, 3H, CH_3) ; -2.770 (s, 2H, NH). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 649 [3.90] ; 593 [3.70] ; 553 [4.04] ; 518 [4.26] ; 415 [5.69].

7. Purple powder. ^{1}H-NMR ($CDCl_3$) : 8.90 (s, 8H, H_{py}) ; 8.10 (d, 8H, H_{op}) ; 7.79 (t, 4H, H_{pp}) ; 1.54 (s, 72H, CH_3) ; -2.67 (s, 2H, NH). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 648 [3.78] ; 592.5 [3.70] ; 553.5 [4.04] ; 518.0 [4.15] ; 421.0 [5.71]. MS : 1063.7.

Preparation of benzylic alcohol **8**

6 was hydrolyzed by aqueous NaOH 1.8 M in DMF ; 281 mg of ester **6** (0.22 mmol) was dissolved in 15 ml DMF at 60°C. This solution was purged with argon, then with stirring, 2.8 ml NaOH 1.8 M (5.04 mmols) was added dropwise. Stirring under argon was continued for 1 hr at ambiant temperature, followed by addition of 20 ml H_2O. Decantation, extraction with CH_2Cl_2 (3 x 100 ml), and washing with Na_2CO_3 10% (2 x 100 ml) and H_2O (100 ml) left, after drying over $MgSO_4$ and the removal of the DMF under high vacuum, 400 mg of crude product. This was adsorbed on alumina and purified by flash column chromatography on silica gel (eluent toluene containing 0 to 0.5% AcOEt) giving pure alcohol **8** (197 mg, 65.6%).

8. Purple powder (mp : 274-277°C). ^{1}H-NMR ($CDCl_3$) : 9.118 (d, 2H, H_{py1}) ; 8.955 (d, 2H, H_{py2}) ; 8.937 (s, 4H, H_{py}) ; 8.850 (d, 2H, H_o) ; 8.487 (d, 2H, H_m) ; 8.534 (d, 2H, $H_{o'}$) ; 8.464 (dd, 2H, H_4 and H_3) ; 8.346 (d, 1H, H_7) ; 8.186 (d, 1H, H_8) ; 8.125 (d, 2H, H_{op}) ; 8.113 (d, 2H, $H_{op'}$) ; 7.872 (dd, 2H, H_5 and H_6) ; 7.816 (t, 2H, H_{pp}) ; 7.813 (t, 1H, $H_{pp'}$) ; 7.572 (d, 2H, $H_{m'}$) ; 4.763 (s, 2H, CH_2) ; 1.543 (s, 54H, CH_3) ; -2.628 (s, 2H, NH). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 649 [4.11] ; 593 [3.85] ; 553 [4.26] ; 518 [4.45] ; 4.19 [5.59].

Preparation of the aldehyde **9**

3.9 g of MnO_2 (22.4 mmols) was added under efficient stirring to an argon purged solution of **8** (107 mg, 0.09 mmol) in CH_2Cl_2 (120 ml). The mixture was stirred for 1.5 hrs

under argon at room temperature, then $MgSO_4$ was added to dry the solution and to ease the removal of the MnO_2 by filtration. After 10 mn the mixture was filtered and the filtrate was evaporated to dryness to yield pure **9** in quantitative yield (109 mg, 0.09 mmol). **9** was used without further purification.

9. Purple powder (mp : 92-94°C). ^{1}H-NMR ($CDCl_3$) : 10.089 (s, 1H, CHO) ; 9.015 (d, 2H, H_{py1}) ; 8.959 (d, 2H, H_{py2}) ; 8.938 (s, 4H, H_{py}) ; 8.838 (d, 2H, H_o) ; 8.700 (d, 2H, $H_{o'}$) ; 8.500 (d, 2H, H_m) ; 8.483 (dd, 2H, H_4 and H_3) ; 8.408 (d, 1H, H_7) ; 8.238 (d, 1H, H_8) ; 8.125 (d, 4H, H_{op}) ; 8.112 (d, 2H, $H_{op'}$) ; 8.101 (d, 2H, $H_{m'}$) ; 7.817 (t, 3H, H_{pp}) ; 1.548 (s, 54H, CH_3) ; -2.626 (s, 2H, NH). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 648 [4.11] ; 592 [4.03] ; 554 [4.38] ; 518 [4.58] ; 416 [5.46]. Anal. calc. for $C_{87}H_{88}N_6O_1$: C, 84.70 ; H, 7.19 ; N, 6.81. Found : C, 84.57 ; H, 7.12 ; N, 6.74.

Preparation of bis-porphyrin **10** (stepwise approach)

An Adlers reaction was used to synthesize **10** from the aldehyde **9**. A mixture of 72 mg **9** (0.06 mmol), 362 mg 3,5-diterbutyl-benzaldehyde (1.66 mmols) and 0.12 ml pyrrole (1.72 mmols) in propionic acid (20 ml) was refluxed with stirring for 21 hrs.

After cooling the reaction solution was evaporated under high vacuum with successive portions of toluene (50 ml) (binary system at 80°C). The residue was taken up in CH_2Cl_2 and neutralized with 10% Na_2CO_3 solution (3 x 50 ml).

Evaporation of the CH_2Cl_2 gave the crude brown product which was purified by column chromatography on silica gel. Pure monomer **7** (319 mg, 20%) was obtained after two chromatography columns : the first on silica gel (eluent Hex/2% AcOEt) and the second on alumina (eluent Hexane/0.2% AcOEt). Three successive separations on chromatography column were necessary to obtain the pure symetrical bis-porphyrin **10** (27 mg, 21.6%) (first : SiO_2, toluene ; second : flash SiO_2, toluene ; third : Al_2O_3, Hex/5% AcOEt).

For further purification, recrystallization by slow diffusion was used (benzene / EtOH).

10. Purple powder (mp : 113-115°C). ^{1}H-NMR (CD_2Cl_2) : 9.003 (d, 4H, H_{py1}) ; 8.952 (d, 4H, H_o) ; 8.905 (m, 12H, H_{py2} and H_{py}) ; 8.600 (dd, 4H, $H_{3,4}$ and $H_{7,8}$) ; 8.483 (d, 4H, H_m) ; 8.075 (d, 4H, H_{opz}) ; 8.059 (s, 2H, H_5 and H_6) ; 8.032 (d, 8H, H_{opx}) ; 7.836 (t, 2H, H_{ppz}) ; 7.763 (t, 4H, H_{ppx}) ; 1.522 (s, 36H, $(CH_3)_z$) ; 1.426 (s, 72H, $(CH_3)_x$) ; -2.786 (s, 4H, NH). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 649 [4.08] ; 593 [4.00] ; 554 [4.32] ; 518 [4.52] ; 420.5 [5.95]. Anal. calc. for $C_{148}H_{160}N_{10}$: C, 85.50 ; H, 7.76 ; N, 6.74. Found : C, 85.49 ; H, 8.08 ; N, 6.46. MS : 2077.9.

Preparation of dialdehyde **11**

The dialdehyde **11** was a secondary product of the preparation of **5**. The crude product was separated by column chromatography on silica gel (eluent CH_2Cl_2 containing 10% AcOEt). 2.43 g of a beige powder (20% yield from **1**).

11. Beige powder (mp : 220-222°C). ^{1}H-NMR ($CDCl_3$) : 10.17 (s, 2H, CHO) ; 8.65 (d, 4H, H_o) ; 8.42 (d, 2H, H_4 and H_7) ; 8.25 (d, 2H, H_3 and H_8) ; 8.14 (d, 4H, H_m) ; 7.89 (s, 2H, H_5 and H_6). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 314 [4.65] ; 274 [4.81] ; 230 [4.81]. Anal. calc. for $C_{26}H_{16}N_2O_2$: C, 80.40 ; H, 4.15 ; N, 7.21. Found : C, 80.16 ; H, 4.44 ; N, 6.75. MS : 389.

Preparation of bisporphyrin **10** (double cyclization approach)

499 mg of dialdehyde **11** (1.28 mmols), 6.6 g 3,5-diterbutyl-benzaldehyde (30.23 mmols) and 2.3 ml pyrrole (33.20 mmols) were dissolved in 135 ml propionic acid. The mixture was refluxed with stirring for 16 hrs, and after cooling to ambiant temperature, the solvent was evaporated under high vacuum with successive portions of toluene (3 x 100 ml). The crude residue was dissolved in CH_2Cl_2 (100 ml) and neutralized with 10% Na_2CO_3 solution (3 x 100 ml). The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness to give a mixture of **7** and **10** which, after purification by column chromatography, were obtained respectively in 16% yield (7,977 mg, Hex/0.5% AcOEt) and 2.6% yield (10.69 mg, toluene/25% hexane).

Preparation of mono- and bi-metallic complexes of bis-porphyrin **12** and **13**

57 mg of bis-porphyrin **10** (0.027 mmol) was dissolved in 22 ml $CHCl_3$ and the solution refluxed under argon. After stirring for 15 mn, a solution of 6.5 mg $Zn(AcO)_2$, $2H_2O$ (0.029 mmol) in 7 ml of MeOH was added dropwise with stirring over 10 mn. After the addition, the red color of the solution was more intense. Stirring and heating was continued for 1.5 hrs, the reaction being easily followed by TLC and absorption spectroscopy. The solution cooled to ambiant temperature, washed with water (3 x 40 ml), and the organic layers dried over $MgSO_4$. After filtration and evaporation the complexes were directly obtained. They were separated by column chromatography on alumina with eluent hexane containing 30 to 70% CH_2Cl_2. 29 mg of **12** (50%) and 15 mg of **13** (25%) were obtained. A further purification by recrystallization (slow diffusion) from CH_2Cl_2/Ethanol yielded red-purple crystals of **13**, which were suitable for an X ray structure determination.

12. Red purple powder (mp : 115-117°C). ^{1}H-NMR (CD_2Cl_2) : 9.090 (d, 4H, $H_{py1'}$ and $H_{py2'}$) ; 9.000 (-, 2H, H_{py1}) ; 8.950 (d, 4H, $H_{py'}$) ; 8.950 (-, 4H, H_o and $H_{o'}$) ; 8.900 (s, 6H, H_{py2} and H_{py}) ; 8.610 (dd, 4H, H_3 and H_4 and H_7 and H_8) ; 8.481 (d, 2H, H_m) ; 8.481 (d, 2H, $H_{m'}$) ; 8.080 (-, 2H, H_5 and H_6) ; 8.080 (dd, 4H, Hopz) ; 8.040 (dd, 8H, Hopx) ; 7.840 (tt, 2H, Hppz) ; 7.770 (tt, 4H, Hppx) ; 1.530 (s, 36H, $H(CH_3)_z$) ; 1.430 (s, 72H, $H(CH_3)_x$) ; -2.769 (s, 2H, NH). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 650.5 [3.85] ; 592.5 [4.00] ; 552.0 [4.38] ; 518.5 [4.23] ; 421.5 [6.05]. MS : 2141.8.

13. Red powder (mp : decomposition at 270°C). ^{1}H-NMR (CD_2Cl_2) : 9.084 (s, 4H, H_{py1}) ; 8.950 (-, 12H, H_{py2} and H_{py}) ; 8.950 (d, 4H, H_o) ; 8.605 (dd, 4H, H_3 and H_4 and H_7 and H_8) ; 8.472 (d, 4H, H_m) ; 8.070 (d, 4H, Hopz) ; 8.059 (s, 2H, H_5 and H_6) ; 8.029 (d, 8H, Hopx) ; 7.833 (t, 2H, Hppz) ; 7.769 (t, 4H, Hppx) ; 1.525 (s, 36H, $H(CH_3)_z$) ; 1.445 (s, 72H, $H(CH_3)_x$). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 591 [4.15] ; 551 [4.63] ; 421.5 [6.05]. MS : 2205.0.

Preparation of complex **14**

100 mg of **7** (0.09 mmol) was dissolved in $CHCl_3$ (20 ml) and refluxed with stirring under argon. 59 mg $Zn(AcO)_2$, $2H_2O$ (0.27 mmol) in MeOH (1 ml) was added dropwise. Stirring and heating were continued for 30 mn. Cooling, evaporation of the solvent and washing with H_2O gave complex **14** (95.8 mg) in quantitative yield.

14. Red purple powder. ^{1}H-NMR ($CDCl_3$) : 9.01 (s, 8H, Hpy) ; 8.11 (d, 8H, Hop) ; 7.80 (t, 4H, Hpp) ; 1.53 (s, 72H, CH_3). Absorption (CH_2Cl_2, λ_{max} (nm) [log ε]) : 589.5 [3.78] ; 550.5 [4.32] ; 422.5 [5.80]. MS : 1125.5.

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