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Nickel porphyrin nanotweezers†

Stéphanie Gazeau, Jacques Pécaut and Jean-Claude Marchon*

Laboratoire de Chimie Inorganique et Biologique (CEA, CNRS, UJF), Département de Recherche Fondamentale sur la Matière Condensée, CEA-Grenoble, 38054 Grenoble cedex 9, France.
E-mail: jcmarchon@cea.fr

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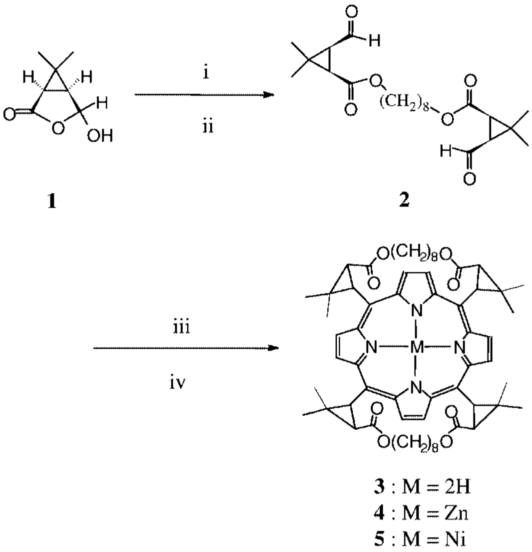
A strapped chiroporphyrin free base with two 8-methylene chains linking two adjacent meso-substituents was synthesized as the α^4 conformer; insertion of Ni(II) triggered a complete conversion to the αβαβ complex, and demetallation totally regenerated the strapped free base in the α^4 conformation.

Metalloporphyrin compounds which have a rigid concave shape can trap molecular guests by coordinative or non-covalent interactions; recognition of the guest is due to complementarity in size, shape and functional groups.[1] A 'Venus flytrap' zinc porphyrin that reversibly swings between an open and a closed form upon binding and dissociation of pyridine has also been reported.[2] We have now designed a strapped chiroporphyrin whose shape can be controlled at will by exploiting the specific coordination requirements of nickel(II). The forces which operate this molecular metamorphosis might be useful in the design of nanoscale tweezers.

Deprotonation of (1*R*)-cis-hemicaronaldehyde **1** by sodium hydride, followed by nucleophilic attack[3] on 1,8-diiodooctane, led to the diester-strapped dialdehyde **2** in 99% yield (Scheme. 1). The latter was reacted with pyrrole according to a literature method[4] to afford the bis-strapped chiroporphyrin **3** in 5% yield.‡ In contrast to the first-generation chiroporphyrins devoid of straps, which are always obtained as the αβαβ atropisomer,[5] **3** shows an α^4 conformation with the two 8-methylene straps linking adjacent *meso* substituents on the same face of the porphyrin. This unusual conformation is apparent in the C_2 symmetry of the NMR spectra of **3** [*e.g.* two AB systems for the pyrrole protons, Fig. 1(a)], and in the large upfield shifts of the methylene groups of the straps. The zinc complex **4** exhibits the same spectral symmetry [Fig. 1(b),§ and its α^4 conformation was confirmed by its X-ray structure shown in Fig. 2.[6]



Scheme 1 *Reagents and conditions:* i, NaH, THF, 10 °C, 30 min under Ar; ii, 1,8-diiodooctane in DMF, 25 °C, 24 h under Ar (99%); iii, pyrrole, TFA, CH_2Cl_2, 25 °C, 6 days; iv, DDQ, 4 h (5%).

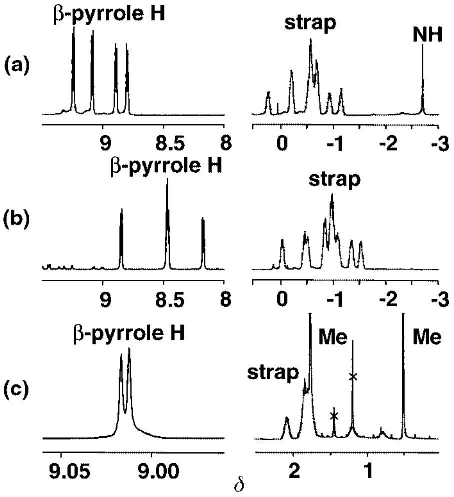


Fig. 1 ^1H NMR spectra (400 MHz, $CDCl_3$, 298 K) for (*a*) the free base chiroporphyrin **3** with two 8-methylene straps in the α^4 conformation; (*b*) its α^4 zinc(II) complex **4**; and (*c*) its αβαβ nickel(II) complex **5**; crossed peaks correspond to $CDCl_3$ solvent impurities.

Much to our surprise, metallation of α^4-**3** by Ni(II) triggered a major conformational change. The nickel complex **5** shows a D_2-symmetric ^1H NMR spectrum [*e.g.* two singlets for the pyrrole proton resonances, Fig. 2(*c*) in which the chemical shifts of the methylene protons are in the normal alkyl range, unambiguously indicating an αβαβ conformation in which the straps now link the adjacent *meso* substituents on opposite faces of the porphyrin.¶ The conversion was complete, and no intermediate could be detected. This unprecedented conformation of a strapped porphyrin[4] was confirmed by the X-ray structure of **5** illustrated in Fig. 3.

Several experiments were carried out to try and remove the nickel(II) center from the porphyrin, in the view of examining

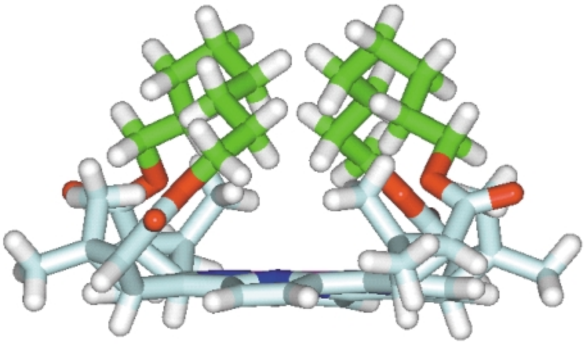


Fig. 2 Stick representation of the X-ray structure of the zinc(II) chiroporphyrin complex **4** showing the α^4 conformation and the two straps (green) linking adjacent *meso* substituents on the same face of the porphyrin (light blue).

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† Electronic supplementary information (ESI) available: spectroscopic data for **3**–**6**. See http://www.rsc.org/suppdata/cc/b1/b104715a/

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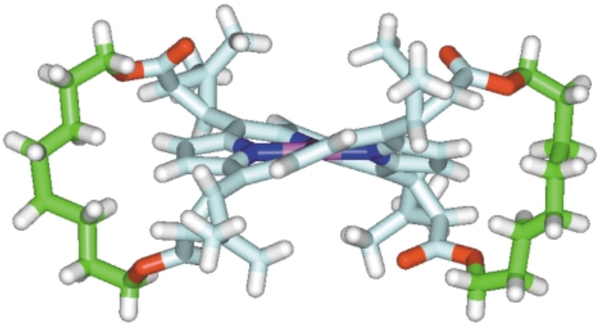

Fig. 3 Stick representation of the X-ray structure of the nickel(II) chiroporphyrin complex **5** showing the αβαβ conformation and the two straps (green) linking adjacent *meso* substituents on opposite faces of the porphyrin (light blue).

the conformation of the resulting free base. Among several acids which were tried, only trifluoromethanesulfonic acid was found strong enough to transfer protons to the very weakly basic nitrogen atoms of **5** and release the nickel(II) ion. Short reaction times (15 min, resulting in *ca*. 50% demetallation) were required with such a strong reagent, which also hydrolyzes the ester groups upon prolonged contact. The resulting free base exhibited α^1H NMR spectrum identical to that of the starting material **3**, indicating the same α^4 conformation. Thus the $\alpha^4 \longrightarrow$ αβαβ conformation change is entirely reversible upon nickel(II) insertion and extrusion (see Graphical Abstract).

Metal insertion in a porphyrin generally induces modest distortions of the core, such as the *sad*, *ruf*, *dom*, *wav* and *pro* types or combinations thereof,[7] but usually it does not affect the orientation of the macrocycle substituents. The intriguing $\alpha^4 \longrightarrow$ αβαβ conformation change which is observed upon Zn(II) $\longrightarrow$ Ni(II) substitution in the strapped chiroporphyrin may be related to the coordination requirements of the two metals and to the constraints induced by the short straps. While Zn(II) with its full d^{10} complement shows long Zn-N bonds (average 2.036(5) Å for the two independent molecules) compatible with the flat porphyrin core of α^4-**4**, square-planar d^8 Ni(II) with its vacant antibonding $d_{x^2-y^2}$ orbital requires short Ni–N bonds [average 1.916(5) Å for the two independent molecules] which are obtained by ruffling of the core of **3**. In this distorted core conformation, the 8-methylene straps apparently are too short to stride over their adjacent cyclopropyl substituent, which are forced to rotate toward the opposite face of the porphyrin. The low rotation barrier usually observed in ruffled nickel(II) porphyrins[8] may facilitate this motion, which results in the αβαβ complex **5**.

Nearly complete conversion to a paramagnetic piperidine adduct **6** was obtained by dissolution of **5** in neat $C_5D_{10}ND$, as judged from the UV–VIS spectrum.[9,10] The 500 MHz ^{1}H NMR spectrum of the resulting solution showed a broad peak near 40 ppm at room temperature for the pyrrole protons of the high-spin Ni(II) complex **6**, typical of a $d_{z^2}{}^1\,d_{x^2-y^2}{}^1$ configuration.[9,11] A pair of singlets was also observed at δ 7.44 and 7.61 for the pyrrole protons of the residual diamagnetic species **5**. The fact that **5** and **6** are not in fast exchange on the NMR time scale stands in contrast to the rapid equilibrium between Ni(TPP) and its high-spin piperidine adduct which has been observed earlier.[9] These observations suggest that **5** and **6** have quite different conformations, and they are consistent with the expected structural consequences of the singly occupied $d_{x^2-y^2}$ orbital in **6**. High-spin nickel(II) porphyrins usually exhibit an expanded core [average Ni–N bond length 2.04–2.07 Å] and reduced non planar distortion relative to their parent low-spin complex (average Ni–N bond length 1.89–1.93 Å).[12] The expanded porphyrin core of the piperidine adduct **6** is incompatible with the αβαβ conformation which imparts short Ni-N bonds. Thus this adduct is prone to undergo a structural change to the α^4 conformation which allows near planarity of the porphyrin core similar to that of the zinc complex **3**. The piperidine ligand located between the two straps is probably held by mechanical forces in addition to the coordination bond.

The strong effects of $d_{x^2-y^2}$ orbital occupancy on molecular shape and dynamics in this system could be exploited in the design of molecular machines such as motors and switches.

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Notes and references

‡ *Selected spectroscopic data* for **3**: MS (ES) *m/z* 979 (MH^+); UV–VIS (CH_2Cl_2) λ_{max}/nm 426, 526, 561, 605, 666; δ_H(200 MHz, $CDCl_3$) 8.52, 8.66, 8.81 and 9.02 (4d, 8H, *J* 4.9 Hz), 4.02 (2d, 4H, *J* 8.8 Hz), 3.37 (m, 4H), 2.89 (m, 4H), 2.73 (2d, 4H, *J* 8.8 Hz), 1.87 and 1.85 (2s, 12H), 1.28 and 1.18 (2s, 12 H), 0.13 (m, 2H), −0.3 (m, 4H), −0.7 (m, 14H), −1.1 (m, 2H), −1.32 (m, 2H), −3.07 (s, 2H).

§ *Selected spectroscopic data* for **4**: MS (ES) *m/z* 1040.5 ($M^{+\cdot}$); UV–VIS (CH_2Cl_2) λ_{max}/nm 429, 563, 613; δ_H(200 MHz, $CDCl_3$) δ 8.83, 8.44, and 8.14 (3d, 8H, J = 4.4 Hz), 3.77 (2d, 4H, *J* 9.3 Hz), 3.21 (m, 4H), 2.70 (2d, 6H, *J* 9.3 Hz), 2.50 (m, 2H), 1.92 and 1.88 (2s, 12H), 1.04 and 0.94 (2s, 12 H), −0.05 (m, 2H), −0.46 (m, 4H), −1.03 (m, 14H), −1.38 (m, 2H), −1.58 (m, 2H).

¶ *Selected spectroscopic data* for **5**: MS (ES) *m/z* 1034.2 ($M^{+\cdot}$); UV–VIS (CH_2Cl_2) λ_{max}/nm 427, 548, 583; δ_H(200 MHz, $CDCl_3$) 9.03 and 8.99 (2s, 8H), 4.59 (d, 4H, *J* 9.3 Hz), 4.06 (m, 4H), 3.75 (m, 4H), 2.66 (d, 4H, *J* 9.3 Hz), 2.14 and 1.88 (2s, 24H), 1.83 (s, 12 H), 0.67 (s, 12H).

1 Y. Le Mest, M. L'Her, J. Courtot-Coupez, J. P. Collman, E. R. Evitt and C. S. Bencosme, *J. Chem. Soc., Chem. Commun.*, 1983, 1286; M. J. Crossley, T. W. Hambley, L. G. Mackay, A. C. Try and R. Walton, *Chem. Commun.*, 1995, 1077; T. Hayashi, M. Nonoguchi, T. Aya and H. Ogoshi, *Tetrahedron Lett.*, 1997, **38**, 1603; A. Vidal-Ferran, N. Bampos and J. K. M. Sanders, *Inorg. Chem.*, 1997, **36**, 6117; M. Ikeda, S. Shinkai and A. Osuka, *Chem. Commun.*, 2000, 1047; M. Sirish and H.-J. Schneider, *J. Am. Chem. Soc.*, 2000, **122**, 5881; D. Sun, F. S. Tham, C. A. Reed, L. Chaker, M. Burgess and P. D. W. Boyd, *J. Am. Chem. Soc.*, 2000, **122**, 10 704; J. Brettar, J.- P. Gisselbrecht, M. Gross and N. Solladié, *Chem. Commun.*, 2001, 733.

2 M. Mazzanti, J.-C. Marchon, M. Shang, W. R. Scheidt, S. Jia and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1997, **119**, 12 400.

3 P. E. Pfeffer and L. S. Silbert, *J. Org. Chem.*, 1976, **41**, 1373.

4 R. W. Wagner, T. E. Johnson and J. N. Lindsey, *Tetrahedron*, 1997, **53**, 6755.

5 C. Pérollier, M. Mazzanti, J.- P. Simonato, F. Launay, R. Ramasseul and J.-C. Marchon, *Eur. J. Org. Chem.*, 2000, 583.

6 *Crystal data* for **4**: $C_{60}H_{72}N_4O_8Zn\cdot1.5CHCl3$, M = 1221.64, triclinic space group $P\bar{1}$, a = 14.1554(17), b = 14.795(3), c = 16.406(3) Å, α = 84.311(14), β= 77.063(10), γ = 65.296(10)°, V = 3042.2(8) Å^3, T = 193 K, Z = 2, μ(Mo-Kα) = 0.658 mm^{-1}, 11 286 independent reflections (R_{int} = 0.0297) which were used in all calculations. The final R was 0.0565, the final $wR(F^2)$ was 0.1425 [$I > 2\sigma(I)$]. For **5**: $C_{60}H_{72}N_4O_8Ni\cdot0.25CH_3CN\cdot H_2O$, M = 1064.21, monoclinic, space group $P2_1$, a = 16.8288(8), b = 19.5869(9), c = 20.0979(9) Å, β = 110.3270(10)°, V = 6212.2(5) Å^3, Z = 4, μ(Mo-Kα) = 0.366 mm^{-1}, 17 805 independent reflections (R_{int} = 0.0490) which were used in all calculations. The final R was 0.0637, the final $wR(F^2)$ was 0.1649 [$I > 2\sigma(I)$]. CCDC reference numbers 167256 and 167257. See http://www.rsc.org/suppdata/cc/b1/b104715a/ for crystallographic data in CIF or other electronic format.

7 W. R. Scheidt and Y. J. Lee, *Struct. Bonding (Berlin)*, 1987, **64**, 1; W. Jentzen, M. C. Simpson, J. D. Hobbs, X. Song, T. Ema, N. Y. Nelson, C. J. Medforth, K. M. Smith, M. Veyrat, M. Mazzanti, R. Ramasseul, J.-C. Marchon, T. Takeuchi, W. A. Goddard III and J. A. Shelnutt, *J. Am. Chem. Soc.*, 1995, **117**, 11 085.

8 M. Veyrat, R. Ramasseul, I. Turowska-Tyrk, W. R. Scheidt, M. Autret, K. M. Kadish and J.-C. Marchon, *Inorg. Chem.*, 1999, **38**, 1772.

9 G. N. La Mar and F. A. Walker, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol. 4, ch. 2, pp. 129–135.

10 S. L. Jia, W. Jentzen, M. Shang, X. Z. Song, J. G. Ma, W. R. Scheidt and J. A. Shelnutt, *Inorg. Chem.*, 1998, **37**, 4402.

11 T. La, R. A. Richards, R. S. Lu, R. Bau and G. M. Miskelly, *Inorg. Chem.*, 1995, **34**, 5632; K. Ozette, P. Leduc, M. Palacio, J. F. Bartoli, K. M. Barkigia, J. Fajer, P. Battioni and D. Mansuy, *J. Am. Chem. Soc.*, 1997, **119**, 6442.

12 H. Duval, V. Bulach, J. Fischer and R. Weiss, *Inorg. Chem.*, 1999, **38**, 5495; W. R. Scheidt, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. Smith, R. Guilard, Academic Press, San Diego, CA and Burlington, MA, 1999, vol. 3, ch. 16.