Synthesis of a 'face-to-face' porphyrin-corrole. A potential precursor of a catalyst for the four-electron reduction of dioxygen

François Jérôme, Claude P. Gros, Catherine Tardieux, Jean-Michel Barbe and Roger Guilard*

Laboratoire d'Ingénierie Moléculaire pour la Séparation et les Applications des Gaz (LIMSAG, CNRS UMR 5633), Faculté des Sciences 'Gabriel', 6 boulevard Gabriel, 21000 Dijon, France

L e t t e r

The synthesis of a cofacial porphyrin-corrole as well as a mixed valence $Co^{II}Co^{III}$ derivative is reported.

The development of efficient catalysts for the reversible multi-electron reduction of O_2 remains a daunting challenge for designers of superior fuel cells and batteries that utilize dioxygen as the reducible reactant. In this reseach area, dico-balt or heterobimetallic cofacial bisporphyrins are among the very few molecular electrocatalysts able to promote the direct reduction of dioxygen to water according to a four-electron process in an acidic medium.[1–6] The $(FTF4)Co_2$ complex described by Collman and coworkers was the first complex exhibiting activity as a four-electron catalyst and numerous research articles have been devoted to the elucidation of the key steps of the catalytic reaction.[3,5,7] An important result has revealed the unexpectedly high dioxygen affinity of a mixed-valence $Co^{II}Co^{III}$ cofacial porphyrin,[8] the key intermediate complex being a μ-superoxo derivative.[8] Dioxygen adducts of binuclear porphyrin complexes are also of high importance for mimicking the reaction mechanism of cytochrome c oxi-dases.[9,10]

Since very recently, some of our work has been devoted to developing a general methodology whereby a face-to-face porphyrin-corrole with an anthracenyl linkage can be pre-pared. Indeed, it is now well-known that the corrole macro-ring leads to the formation of highly stable Co^{III} complexes[11] whereas porphyrins stabilize cobalt in the II oxidation state. Thereby, the design of new face-to-face derivatives leading to mixed-valence $Co^{II}Co^{III}$ compounds represents an interesting challenge since such systems could be very useful in probing many currently unanswered questions in biochemistry and particularly should act as models for cytochrome c oxidases. Moreover, the bis-metallic derivatives of such cofacial porphyrin-corroles should be able to catalyse the four-electron reduction of dioxygen to water. Recently, linear porphyrin-corrole dyads possessing *para*-phenyl linking units have been reported but no electronic interaction was observed between the two chromophores.[12]
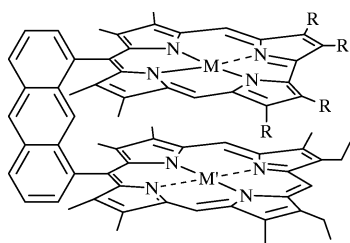
H_5PCA

8: M = 3H, M' = 2H, R = Et
9: M = 3H, M' = 2H, R = Ph
10: M = Co^{III}, M' = Co^{II}, R = Ph

* E-mail: Roger.Guilard@u-bourgogne.fr

In order to prepare the H_5PCA[13] porphyrin-corrole, the porphyrin-dipyrromethane **3**, bearing ethyl ester protecting groups, was prepared as the *key* intermediate (Scheme 1). The monoprotected monoaldehyde bridge [1-(1,3-dithiacyclohex-2-yl)-8-formylanthracene] recently described by Collman *et al.* was used as the starting derivative.[14] This monoprotected linker was cyclized with the desired a,c-biladiene using the classical Harris procedure.[15] *In situ* deprotection with BF_3 and DDQ gave the monoporphyrin monoaldehyde **1** in >25% yield (starting from the 1,8-diformylanthracene),[16] which was then condensed with 2 equiv. of ethyl 3,4-dimethylpyrrole-5-carboxylate **2** (Scheme 1) to give the porphyrin-dipyrromethane derivative **3**[17] in 81% yield. Saponification and decarboxylation according to the method of Abdalmuhdi and Chang[18] afforded the α-free porphyrin-dipyrromethane intermediate in 89% yield, which was then reacted with 2 equiv. of monoformyl pyrrole **4** to lead to the target porphyrin-a,c-biladiene **6**. *In situ* addition of sodium hydrogenocarbonate and *p*-chloranil, followed by addition of 50% hydrazine in water, gave the porphyrinyl corrolyl anthra-cene **8** as a crude compound after solvent removal. Final puri-fication by chromatography on basic alumina afforded **8** in 5% yield. Compound **8** displays the expected pseudo-molecular peak [LSIMS (liquid secondary ion mass spectrom-etry: m/z 1092 $[M + H]^+$ (100%)], a Soret band at 406 nm and four Q bands at 503, 536, 572 and 626 nm.

This compound was found to be very unstable when left in solution in the presence of air and light. This observation compares to our recent report on molecular oxygen oxidation of the corrole macrocycle, leading to an open-chain tetra-pyrrole (biliverdin) structure.[19] The substitution of the β-pyrrole positions (positions 2, 3, 17, 18) of cofacial biscorroles by phenyl groups prevents the oxidative attack of the ring and cleavage of the 1,19-double bond.[20] According to these preliminary results and in order to increase the stability of our aimed for porphyrin-corrole system, the porphyrin-dipyrromethane intermediate **3** was reacted with 2 equiv. of 2-formyl-3,4-diphenylpyrrole **5**[20] to yield **7**. Using the same experimental procedure as described for **8**, the porphyrin-corrole **9**[21] was obtained, after solvent removal, as a crude compound. Final purification was achieved by column chro-matography on basic alumina, using methylene chloride–heptane as eluent (70 : 30), and **9** was finally isolated in >10% yield. The LSIMS confirms the bis(tetrapyrrole) nature of **9** (m/z 1283 $[M + H]^+$). The electronic absorption spectrum of **9** shows a very slight red-shift of the Soret band and of the Q bands [λ_{max} = 398 (Soret band), 507, 541, 575 nm] compared to the well-known free-base 'Pacman' porphyrin H_4DPA[18] [λ_{max} = 395 (Soret band), 506, 539, 578 and 631 nm] (Fig. 1). Due to the presence of electronic interactions between the two macrocycles as already observed for 'Pacman' porphyrins, the

Scheme 1

Fig. 1 Absorption spectra of 9 and H$_4$DPA

UV/VIS absorption spectrum of **9** is not a simple super-position of the porphyrin and corrole chromophore spectra.[18]

In order to study further the potential catalytic properties for the electroreduction of dioxygen directly to water, the mixed-valence Co^{II}Co^{III} complex was prepared. The free-base porphyrin-corrole **9** was classically metalated with cobalt acetate in pyridine.[22] It is interesting to note that only the metalation of the corrole ring occurs at 60 °C. This is clearly evidenced by the electronic spectrum, which exhibits in the visible region the pattern of both the cobalt corrole (absorption at 600 nm in pyridine) and of the free base porphyrin (Q bands at 503 and 541 nm in pyridine). In the Soret region, only the strong absorption of the free base porphyrin at 406 nm is observed. This mono-metalation of the corrole moiety is also proven by the mass spectrum, which
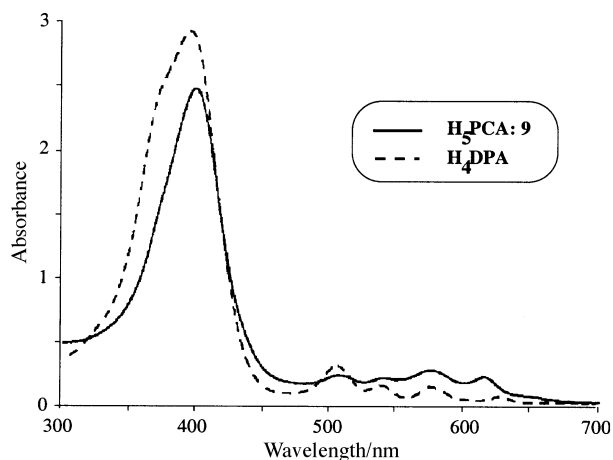
exhibits the pseudo-molecular ion $[CoH_2(PCA) + H]^+$ (m/z = 1340) as the parent peak. As the temperature is increased up to reflux, the metalation of the porphyrin ring leads to a bispyridine coordinated dicobalt complex. The decoordination of pyridine linked to the cobalt corrole moiety is readily done at room temperature under vacuum. In the UV/VIS spectrum in methylene chloride solution, the Soret band is observed at 427 nm for compound **10** $[\lambda_{max}/nm$ $(\varepsilon/mol^{-1}\ 1\ cm^{-1}) = 354$ (70 500), 384 (91 600), 427 (127 000)], as are two Q bands of increasing intensity at 538 (29 000) nm and 567 (22 800) nm. In LSIMS mode, the pseudo-molecular peak for the PCA complex was observed at $m/z = 1397$ $[M + H]^+$ (100%). The reactivity towards dioxygen as well as the electrochemical properties of this new mixed valence Co^{II}Co^{III} cofacial porphyrin-corrole will be detailed in a full paper.

The free-base porphyrin-corrole reported herein is the first cofacial porphyrin-corrole known up to now, to our knowledge. The peculiar propensity of this porphyrin-corrole system to be metalated first on the corrole ring is particularly interesting for developing a methodology for the preparation of heterobimetallic derivatives. We do hope that such a method will promote the synthesis of a wide variety of homo- and heterobimetallic complexes because the rigidity of the porphyrin cofacially linked to the corrole macroring should favour metal–metal interactions. Work is presently underway in these directions to prove the versatile chemical reactivity of the bimetallic complex towards small molecules such as O$_2$ or N$_2$.

Note added at proof. Preliminary electrochemistry of (PCA)Co$_2$ has been carried out in several non-aqueous solvents and indicates a behavior quite different than that of the simple monomeric Co^{II} porphyrin or Co^{III} corrole units under similar experimental conditions. The oxidation and reduction potentials of (PCA)Co$_2$ appear to be influenced in part by an interaction between the two electroactive metallomacrocycles and in part by an irreversibility of the electrode reactions due to the occurrance of coupled chemical processes, some of which may involve a gain or loss of axially coordinated ligands following electron transfer. Further electrochemical and spectroelectrochemical studies are now in progress to clarify the nature of these electron transfer steps and associated chemical processes.

References and Notes

1 Y. Le Mest, C. Inisan, A. Laouenan, M. L'Her, J. Talarmin, M. El Kalifa and J.-Y. Saillard, *J. Am. Chem. Soc.*, 1997, **119**, 6095.
2 H.-Y. Liu, I. Abdalmuhdi, C. K. Chang and F. C. Anson, *J. Phys. Chem.*, 1985, **89**, 665.

3 K. Kim, J. P. Collman and J. A. Ibers, *J. Am. Chem. Soc.*, 1988, **110**, 4242.

4 G. Park, S. Nakajima, A. Osuka and K. Kim, *Chem. Lett.*, 1995, 225.

5 J. P. Collman, P. Denisevich, Y. Konai, M. Marrocco, K. Koval and F. C. Anson, *J. Am. Chem. Soc.*, 1980, **102**, 6027.

6 R. Guilard, S. Brandès, C. Tardieux, A. Tabard, M. L'Her, C. Miry, P. Gouerec, Y. Knop and J. P. Collman, *J. Am. Chem. Soc.*, 1995, **117**, 11721.

7 J. P. Collman, F. C. Anson, C. E. Barnes, C. S. Bencosme, T. Geiger, E. R. Evitt, R. P. Kreh, K. Meier and R. B. Pettman, *J. Am. Chem. Soc.*, 1983, **105**, 2694.

8 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.

9 G. Malmström, *Chem. Rev.*, 1990, **90**, 1247.

10 S. I. Chan, S. N. Witt and D. F. Blair, *Chem. Scr.*, 1988, **28A**, 51.

11 S. Licoccia and R. Paolesse, in *Metal Complexes with Tetrapyrrole Ligands III*, ed. J. W. Buchler, Springer-Verlag, Berlin and Heidelberg, 1995, p. 71.

12 R. Paolesse, R. K. Pandey, T. P. Forsyth, L. Jaquinod, K. R. Gerzevske, D. J. Nurco, M. O. Senge, S. Licoccia, T. Boschi and K. M. Smith, *J. Am. Chem. Soc.*, 1996, **118**, 3869.

13 H_5PC for free-base porphyrin-corrole, A for anthracene bridge.

14 J. P. Collman, D. A. Tyvoll, L. L. Chng and H. T. Fish, *J. Org. Chem.*, 1995, **60**, 1926.

15 D. Harris, A. W. Johnson and R. Gaete-Holmes, *Bioorg. Chem.*, 1980, **9**, 63.

16 C. Tardieux, Ph.D. Thesis, Université de Bourgogne, Dijon, France, 1997.

17 Compound **3**: NMR (CDCl$_3$): δ = 10.17 (s, 2H, *meso*), 9.99 (s, 1H, *meso*), [8.76 (s, 1H), 8.45 (d, 1H), 8.04 (d, 1H), 7.96 (d, 1H), 7.93 (s, 1H), 7.83 (dd, 1H), 7.31 (dd, 1H), 6.67 (d, 1H) anthrac], 4.67 (s, 1H, CH), 4.09 (m, 4H, 2 × 2CH_2—CH$_3$), 3.98 (q, 4H, CH_2—CO$_2$Et), 3.66 (s, 6H, Me), 3.39 (s, 6H, Me), 1.93 (s, 6H, Me), 1.91 (t, 6H, CH_2—CH_3), 1.08 (t, 6H, CO_2CH_2—CH_3), 0.95 (t, 6H, CH_2—CH_3), −0.51 (s, 6H, Me), −2.94 (s, 1H, NH), −3.13 (s, 1H, NH); IR (KBr): ν = 3445 (NH), 3277 (NH), 2963 (CH), 2926 (CH), 2868 (CH), 1681 (C=O) cm^{-1}; UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm (ε/mol^{-1} l cm^{-1}) = 407 (150 500), 503 (14 600), 536 (7100), 572 (6400), 626 (3100); MS (EI): *m/z* 970 [M]$^{+\cdot}$ (100%).

18 I. Abdalmuhdi and C. K. Chang, *J. Org. Chem.*, 1985, **50**, 411.

19 C. Tardieux, C. P. Gros and R. Guilard, *J. Heterocycl. Chem.*, 1998, **35**, 965.

20 F. Jérôme, C. P. Gros, C. Tardieux, J.-M. Barbe and R. Guilard, *Chem. Commun.*, 1988, 207.

21 Compound **9**. Anal. calcd for $C_{91}H_{78}N_8 \cdot H_2O$: C 83.96, H 6.20, N 8.61; found: C 83.87, H 6.15, N 8.68; ^{1}H NMR (CDCl$_3$): δ = 9.97 (s, 2H, *meso* porph), 9.42 (s, 1H, *meso* porph), 8.89 (s, 2H, *meso* corr), [8.53 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 8.37 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 7.98 (s, 1H), 7.89 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 7.82 (dd, $^3J_{HH}$ = 9.1 Hz, 1H), 7.58 (dd, $^3J_{HH}$ = 6.4 Hz, 1H), anthrac], 7.64–7.44 (m, 5H, Ph), 7.39 (m, 5H, Ph), 7.32 (m, 5H, Ph), [7.30 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 7.09 (s, 1H) anthrac], 7.05–6.82 (m, 5H, Ph), 4.08 (dq, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 7.9 Hz, 2H, CH_AH_B—CH$_3$), 3.87 (dq, $^2J_{HH}$ = 15.2 Hz, $^3J_{HH}$ = 7.9 Hz, 2H, CH_AH_B—CH$_3$), 3.28 (s, 6H, Me), 2.98 (s, 6H, Me), 2.52 (s, 6H, Me), 1.87 (s, 6H, Me), 1.62 (t, $^3J_{HH}$ = 7.9 Hz, 3H, CH_2—CH$_3$), 1.41 (s, 6H, Me), 0.86 (t, $^3J_{HH}$ = 7.9 Hz, 3H, CH_2—CH_3), −5.22 (s, 1H, NH porph), −5.25 (s, 1H, NH porph); IR: ν = 3560 (NH), 3490 (NH), 3435 (NH), 2962 (CH), 2922 (CH), 2860 (CH) cm^{-1}; UV/VIS (CH$_2$Cl$_2$): λ_{max}/nm (ε/mol^{-1} l cm^{-1}) = 398 (200 200), 507 (21 060), 541 (19 900), 575 (25 400), 615 (21 750); MS (LSIMS): *m/z* 1283 [M + H]$^+$.

22 M. Conlon, A. W. Johnson, W. R. Overend, D. Rajapaksa and C. M. Elson, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2281.

Letter 8/05452E