First synthesis of sterically hindered cofacial bis(corroles) and their bis(cobalt) complexes

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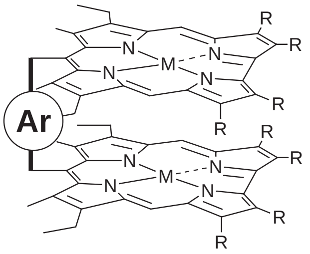
Syntheses of face-to-face bis(corroles) exhibiting electronic interactions between the two chromophores.

During the past few decades, numerous research has been devoted to the synthesis of dimeric and higher order porphyrins and, to a lesser extent, other macrocyclic tetrapyrroles covalently linked by rigid linkers.[1,2] Bis(porphyrins) with a gable or face-to-face spatial arrangement are effective catalysts for the four-electron reduction of dioxygen to water[3] and the oxidation of organic substrates.[4] A few years ago, 'Pacman' porphyrins achieved the microscopic reverse of dinitrogen fixation.[5] As a result of these significant data, many bisporphyrins and higher oligomers have been prepared with a wide variety of linking units.[6] Except for a few examples,[7] most of these rigidly linked dimeric and higher order oligomeric systems have consisted of porphyrin subunits. At the same time, corrole macrocycles were gaining considerable attention due, in part, to their very rich chemistry and to their ability, compared to porphyrins, to stabilize higher oxidation states of certain coordinated metals.[8] Very recently, symmetrical and unsymmetrical linear bis(corrole) and porphyrin–corrole dyads possessing *para*-phenyl linking units have been described.[7b] Herein, we wish to report the first synthesis of cofacial bis(corroles) **H_6BCA** and **H_6BCB**[9] as well as their bis(cobalt) complexes in order to study metal–metal interactions.

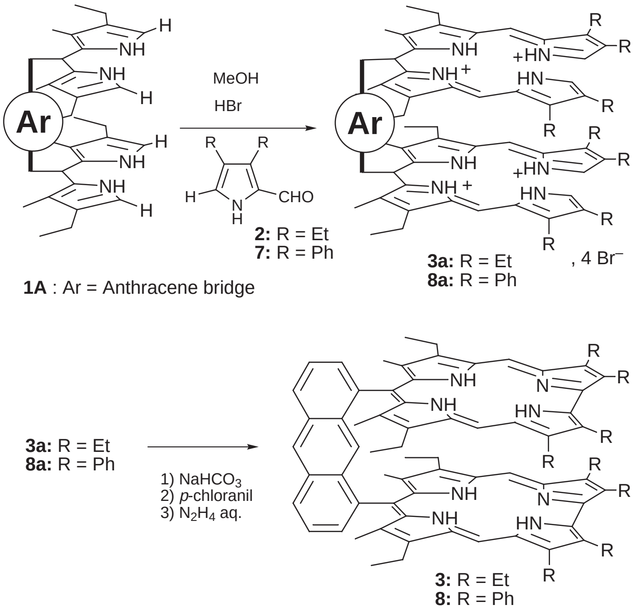


H_6BCA : Ar = Anthracene bridge

3: M = 3H, R = Et
8: M = 3H, R = Ph
10: M = Co(py), R = Ph
11: M = Co, R = Ph

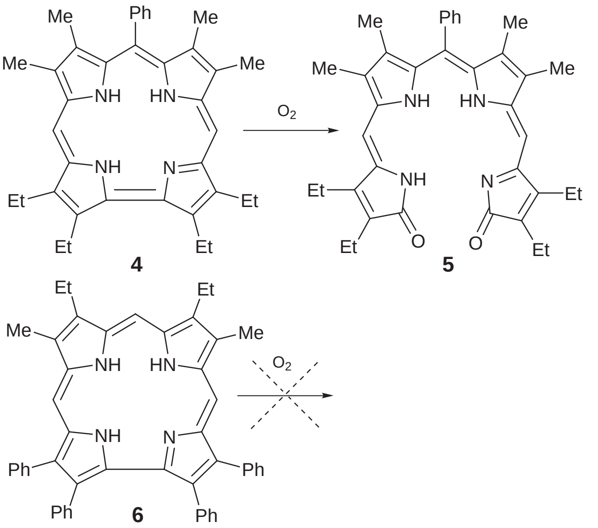
H_6BCB : Ar = Biphenylene bridge

9: M = 3H, R = Ph



Scheme 1

In the course of our work on the syntheses of cofacial bis(porphyrins),[10] it occurred to us that the conjugate addition of a 3,4-disubstituted-2-formylpyrrole to a face-to-face bis(dipyrromethane) followed by a cyclization step should represent a versatile method for new cofacial bis(corroles) formation. Indeed, reaction of compound **1A**[10] with 4 equivalents of **2** in methanol and in the presence of 30% hydrobromic acid in acetic acid led in a first step to the bis(*a,c*-biladiene) salt **3a** (Scheme 1), the progress of the reaction being monitored by UV–VIS spectroscopy. *In-situ* addition of sodium hydrogencarbonate and *p*-chloranil followed by addition of 50% hydrazine in water gave **3** as a crude compound after solvent removal. Final purification by chromatography on basic alumina afforded **3** in 5.5% yield. The proton NMR spectrum of the C_2 symmetric derivative **3** exhibits the characteristic patterns of two corrole units cofacially linked by an anthracenyl bridge.[11a] Compound **3** displays a pseudo-molecular peak at $m/z = 1163$ $[M + H]^+$, a Soret band at 402 nm and three Q bands at 510, 548 and 598 nm. Unfortunately, the free-base bis(corrole) **3** was found to be too unstable for a full characterization. Indeed, when left in solution in the presence of air and light, **3** readily decomposed over a period of a few minutes into a small amount of less-polar compounds, along with a large amount of base-line materials presumably due to the decomposition reaction with dioxygen of the free-base bis(corrole) which acts as a sensitizer. Such an instability has been pointed out for 10-monophenyl corrole **4** (Scheme 2).[11b] Indeed, compound **4** (as a free-base) was found to be air-sensitive when left in solution and one of its



Scheme 2

decomposition products was identified as an open chain tetrapyrrole structure **5**.[11b] To our knowledge, this is the first example of molecular oxygen oxidation of a corrole macrocycle to a biliverdin structure. Our data led to a possible reaction mechanism involving addition of dioxygen at the 1,19-double bond of the corrole derivative followed by bond cleavage giving two amide groups as terminal functions. In order to prevent oxidative attack of the corrole ring and cleavage of the 1,19-double bond, the four β-pyrrole positions (positions 2,3,17 and 18) were substituted by phenyl groups. As expected, free-base corrole **6**[11b,12] is far more stable than its alkyl-substituted counterpart **4** as the presence of the bulky phenyl groups prevent dioxygen oxidation of the 1,19-double-bond. Indeed, the decomposition of **6** in solution in the presence of air and light only occurred over a period of a few days.

According to these results, we were able to synthesize a stable free-base bis(corrole) **8** (Scheme 1) by reacting first **1A**[10] with **7**,[13] and then by cyclizing the bis(*a*,*c*-biladiene) intermediate **8a**, using *p*-chloranil as an oxidant. The free-base derivative **8**[14] was isolated in 12.5% yield. Starting from 1,8-diformylbiphenylene as a spacer and using the same experimental procedure, compound **9**[15] was obtained in 12% yield. LSIMS mass spectra confirms the dimeric structure of **8** and **9** (*m/z* 1549 $[M + H]^+$ and 1523 $[M + H]^+$, respectively). Cofacial bis(corroles) **8** and **9**, containing phenyl rings at eight β-pyrrole positions, are really more stable than the unprotected one **3**. Indeed, when **8** and **9** are exposed in solution to air and light, no major decomposition is observed after a period of 48 h. Interestingly, the UV–VIS absorptions of **8** and **9** show that the spectra are not simply superpositions of the absorptions of the two corrole chromophores. In particular, the Soret bands of **8** and **9** are red-shifted with respect to those of the simple corrole possessing the same substitution patterns due to the electronic interactions occurring between the two corrole units in **8** and **9**. It is also worthy to note that no electronic interaction has been observed in the recently published linear dimers.[7b]

Standard procedures were employed to metallate the corrole core with cobalt acetate.[16] Compound **8** was heated at 80 °C in pyridine with 2.5 equivalents of $Co(OAc)_2$, the metallation reaction being monitored by UV–VIS spectroscopy. Completion of the reaction occurring within 1–2 h was indicated by the complete disappearance of the absorption at 607 nm and the appearance of a Q band at 597 nm; the Soret band being simultaneously slightly red-shifted (λ_{max} 414 and 435 nm). After purification, the homobimetallic $BCA(Co)_2(py)_2$ derivative **10** was isolated in 23% yield. Interestingly, the two axial pyridine ligands can easily be removed under vacuum (20 mmHg, 50 °C) to yield quantitatively **11**. The electronic absorption spectra of **11** shows a 37 nm blue-shift of the Soret band [λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) = 377 (117 000), 398 (144 000), 529 (47 900) nm] compared to **10**. In LSIMS mode, the molecular peak for the **BCA** complex is observed at *m/z* = 1660 $[M + H]^+$ (100%). It is also worthy to note that **11** decomposes rapidly in the absence of coordinated axial ligands.

In conclusion, these cofacial bis(corroles) can be easily prepared in four steps (starting from the bridging unit) and on a large scale. Moreover, the synthesis of **8** and **9** described here integrate well for the development of coordination chemistry of cofacial bis(corroles) on a broad basis; work is currently underway in these directions.

Notes and References

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9 **H_6BC** for free-base biscorrole, **A** for anthracene bridge, **B** for biphenylene bridge.

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11 (*a*) ^1H NMR ($CDCl_3$) for **3**: δ 8.84 (s, 4 H, *meso* H), [10.27 (s, 1 H), 8.40 (s, 1 H), 7.65 (d, 2 H), 7.54 (d, 2 H), 6.94 (dd, 2 H) anthracene H], 3.91 (m, 24 H, CH_2CH_3), 2.15 (s, 12 H, Me), 1.44 (m, 36 H, CH_2CH_3), −2.61 (s br, 6 H, NH); (*b*) C. Tardieux, C. P. Gros and R. Guilard, *J. Heterocycl. Chem.*, 1998, in press.

12 Elemental analysis: Calc. for **6**, $C_{49}H_{42}N_4$: C, 85.68; H, 6.16; N, 8.16. Found: C, 85.77; H, 6.21; N 7.80%. ^1H NMR ($CDCl_3$): δ 9.76 (s, 2 H, *meso* H^5, H^{15}), 9.50 (s, 1 H, *meso* H^{10}), 7.88–6.96 (m, 20 H, Ph), 3.95 (q, 4 H, CH_2CH_3), 3.33 (s, 6 H, Me), 1.68 (t, 6 H, CH_2CH_3), −0.73 (s, NH), −1.47 (s, NH). IR : ν 3350 (NH), 2960 (CH), 2928 (CH), 2868 (CH) cm^{-1}. UV–VIS (CH_2Cl_2): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 400 (83 400), 413 (74 700), 564 (19 400), 599 nm (20 900); UV–VIS (after HCl bubbling): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 414 (95 900), 475 (15 000), 593 (39 500). MS (EI): *m/z* (%) 686 (100) $[M]^+$, 343 $[M]^{2+}$.

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14 Elemental analysis: Calc. for **8**, $C_{112}H_{90}N_8 \cdot 3H_2O$: C, 83.96; H, 6.04; N, 7.00. Found: C, 83.96; H, 6.00; N 6.78%. ^1H NMR (C_6D_6): δ 8.86 (s, 4 H, *meso* H), [8.79 (s, 1 H), 8.36 (d, $^3J_{H-H}$ = 6.5, 2 H), 7.98 (s, 1 H) anthracene H], 7.80 (m, 8 H, Ph), [7.65 (d, $^3J_{H-H}$ = 6.5, 2 H), 7.57 (dd, $^3J_{H-H}$ = 6.5, 2 H) anthracene H], 7.52 (m, 8 H, Ph), 7.29 (m, 24 H, Ph), 3.27 (qd, $^2J_{H-H}$ = 14.7, $^3J_{H-H}$ = 7.5, 4 H, $CH_AH_BCH_3$), 3.22 (qd, $^2J_{H-H}$ = 14.7 Hz, $^3J_{H-H}$ = 7.5 Hz, 4 H, $CH_AH_BCH_3$), 1.95 (s, 12 H, Me), 1.31 (t, $^3J_{H-H}$ = 7.5 Hz, 12 H, CH_2CH_3), −2.83 (s, 3 H, NH), −3.00 (s, 3 H, NH). IR : ν 3482 (NH), 3401 (NH), 2961 (CH), 2923 (CH), 2870 (CH) cm^{-1}. UV–VIS (CH_2Cl_2): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 406 (171 000), 578 (44 500), 607 nm (37 000). MS (LSIMS): *m/z* 1549 $[M + H]^+$.

15 Elemental analysis: Calc. for **9**, $C_{110}H_{88}N_8 \cdot 2H_2O$: C, 84.79; H, 5.96; N, 7.20. Found: C, 84.44; H, 5.98; N, 7.45%. ^1H NMR (C_6D_6): δ 9.59 (s, 4 H, *meso* H), [7.98 (d, 2 H), 7.61 (dd, 2 H), 7.47 (d, 2 H)] biphenylene H], 7.10 (m, 40 H, Ph), 3.54 (m, 8 H, Et), 3.07 (s, 12 H, Me), 1.52 (t, 12 H, Et), −2.80 (s, 3 H, NH), −3.00 (s, 3 H, NH). UV–VIS (CH_2Cl_2): λ_{max} (ε/dm^3 mol^{-1} cm^{-1}) 412 (142 000), 572 (34 000), 608 nm (33 000). MS (LSIMS): *m/z* 1523 $[M + H]^+$.

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