

Synthesis and Physicochemical Characterization of Bis(macrocycles) Involving a Porphyrin and a *meso*-Substituted Corrole – X-ray Crystal Structure of a [(Free-base porphyrin)–corrole]bis(pyridine)cobalt Complex

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A very efficient, simple synthesis of face-to-face porphyrin–corrole free-bases bearing substituents at the *meso* positions of the corrole ring is reported. Starting from the (porphyrin–aldehyde)zinc species **1Zn**, porphyrin–corrole free-bases (**3M**, **3C**) are obtained in two steps, in fairly good yields (40–43 %), compared to 11 steps for their corrole β -pyrrole-substituted counterparts. Moreover, the possibility to directly synthesize the free-base (porphyrin–corrole)cobalt complex (**5M** or **5C**) allows for the further preparation of heterodimetallic

derivatives. Crystals of the bis(pyridine) adduct of **5M** have been grown; the molecular structure clearly shows that the two pyridine molecules are coordinated to the cobalt ion in *endo* and *exo* positions, leading to an open-mouth geometry of the bis(macrocycle). The structure of **5M(py)**₂ also shows intermolecular π – π interactions along the [100] direction, leading to stacking of the complexes.

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Introduction

Enzyme mimics have always been of great interest. For example, considerable studies of heme/copper terminal oxidases have led to several models of the active site. In addition, several reviews have been published recently.^[1–3] Concurrently, cofacial bis(porphyrins) were proposed as synthetic models of the dioxygen reduction site and, particularly, face-to-face bis(porphyrin)bis(cobalt) complexes appeared to be very efficient catalysts for the four-electron reduction of O₂ to water in acidic media.^[1,2,4,5] Cofacial heterodimetallic bis(porphyrins) containing one cobalt atom were later reported, and also proved to be good catalysts for O₂ reduction.^[1,6–8] Numerous studies on the synthetic models indicate that the catalytic activity originates from intermetallic cooperation between the two metal atoms of the bis(porphyrin) complex, tuned by the nature of the spacer.^[1,5] Moreover, the Lewis acid character of one of the two metals in the bis(porphyrin) complex is a key factor in stabilizing the dioxygen adduct during catalysis.^[1]

Our research in this domain has focused on cofacialbis-(macrocycles) where a porphyrin and a corrole are held together by a rigid spacer.^[9,10] The originality of this approach lies in the difference in coordination properties

between the porphyrin and the corrole rings. Indeed, corroles can coordinate metal ions in higher oxidation states than porphyrins.^[11,12] Therefore, complexation of the bis-(macrocycle) by a cobalt ion could directly generate the active species in the O₂ four-electron catalytic cycle, i.e. cobalt(II) in the porphyrin and cobalt(III) in the corrole ring.^[13] We recently demonstrated that this mixed-valence species is a good catalyst for the 4e reduction of O₂ to water.^[14]

Most investigated porphyrin–corrole bis(macrocycles) were substituted at the β -pyrrole positions by electron-donating groups.^[9] However, recent syntheses of *meso*-substituted corroles allow significant variation of the substituents on the corrole ring, particularly at the *meso* positions.^[15–23] Electron-withdrawing substituents on the bis(macrocycle) corrole ring enhance the Lewis acid character of the complexed metal ion [namely cobalt(III)], the main parameter in stabilizing the dioxygen adduct. Therefore, the stability of the dioxygen adduct formed during the catalytic process increases with the Lewis acid character of the corrole-coordinated metal ion. By adapting the new procedures, involving the reaction of dipyrromethanes with an aromatic aldehyde, we could prepare new porphyrin–corrole derivatives with the corrole counterpart substituted at the *meso* positions with mesityl or 2,6-dichlorophenyl groups. Moreover, the corrole ring is formed in only two steps, allowing for the synthesis of gram quantities of these model catalysts.

Here we describe the synthesis of these new bis(macrocycles), and show the possibility of selectively metalating the corrole ring by cobalt (or another metal) to access heterodimetallic derivatives.

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Results and Discussion

Synthesis and Physicochemical Characterization

We recently reported a significant improvement in the syntheses of β -substituted porphyrin–corrole and bis(corrole) bis(macrocycles), allowing the yield in final free-bases to be almost tripled.^[10] However, even if one can introduce electron-withdrawing substituents (i.e. phenyl groups) at the β -pyrrole positions of the corrole ring, the synthetic pathway affording the final free-bases is somewhat long. As an example, Scheme 1 shows the synthesis of a β -phenyl-substituted porphyrin–corrole derivative.

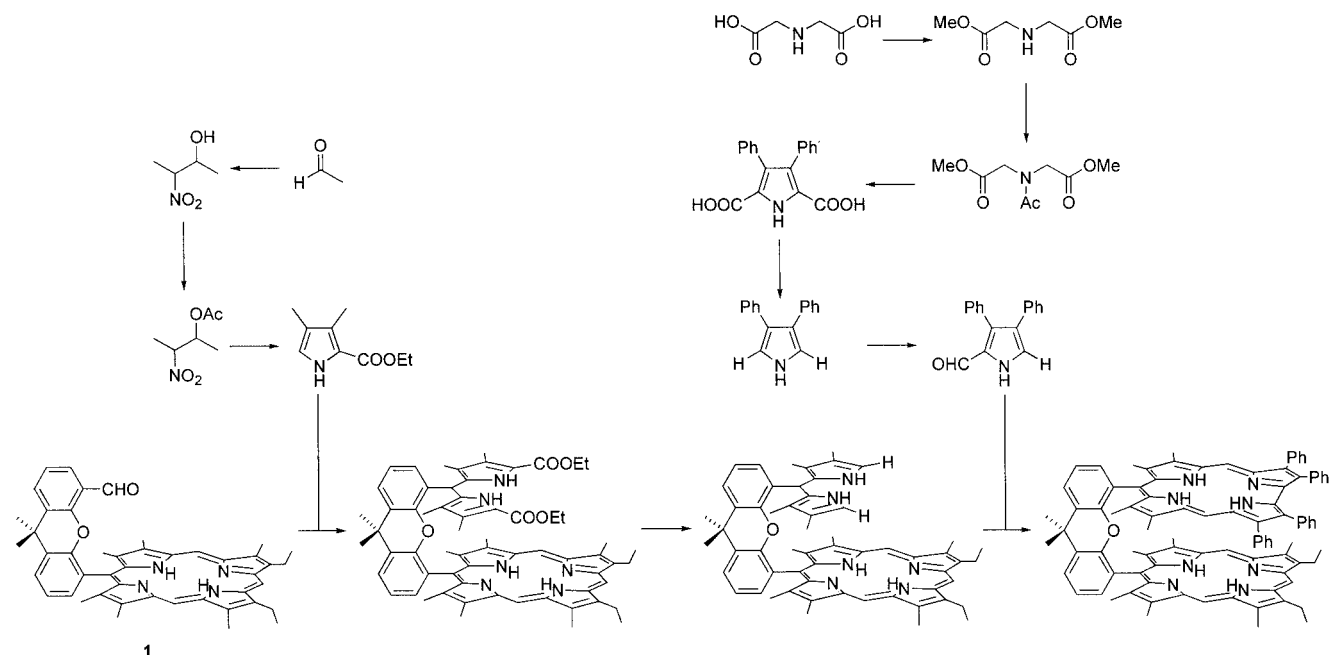
When starting from the porphyrin–aldehyde precursor (**1** in Scheme 1), the target compound is obtained in 11 steps due to the step-by-step nature of this approach, which firstly requires the formation of a dipyrromethane. This dipyrromethane is then coupled with a pyrrole–aldehyde to obtain the final corrole ring by formation of an *a,c*-biladiene. Each pyrrole precursor is obtained in three to five steps, depending upon the substitution at the β -pyrrole positions (Scheme 1). Notably, a symmetrical corrole ring is prepared in only eight steps since only one pyrrole derivative is needed. Another drawback of this multistep synthetic route is that any variation in the structure of the desired bis(macrocycle) requires the synthesis of a new pyrrole precursor (Scheme 1). Nevertheless, this is still the only method that allows the insertion of electron-donating substituents at the β -pyrrole positions of the corrole ring.^[9,10]

An alternative to these β -substituted derivatives would be the *meso*-substituted ones. Indeed, the new methods leading to *meso*-substituted corrole rings^[15–23] can be adapted to the synthesis of porphyrin–corrole derivatives. In the present case, starting from **1Zn**, the porphyrin–cor-

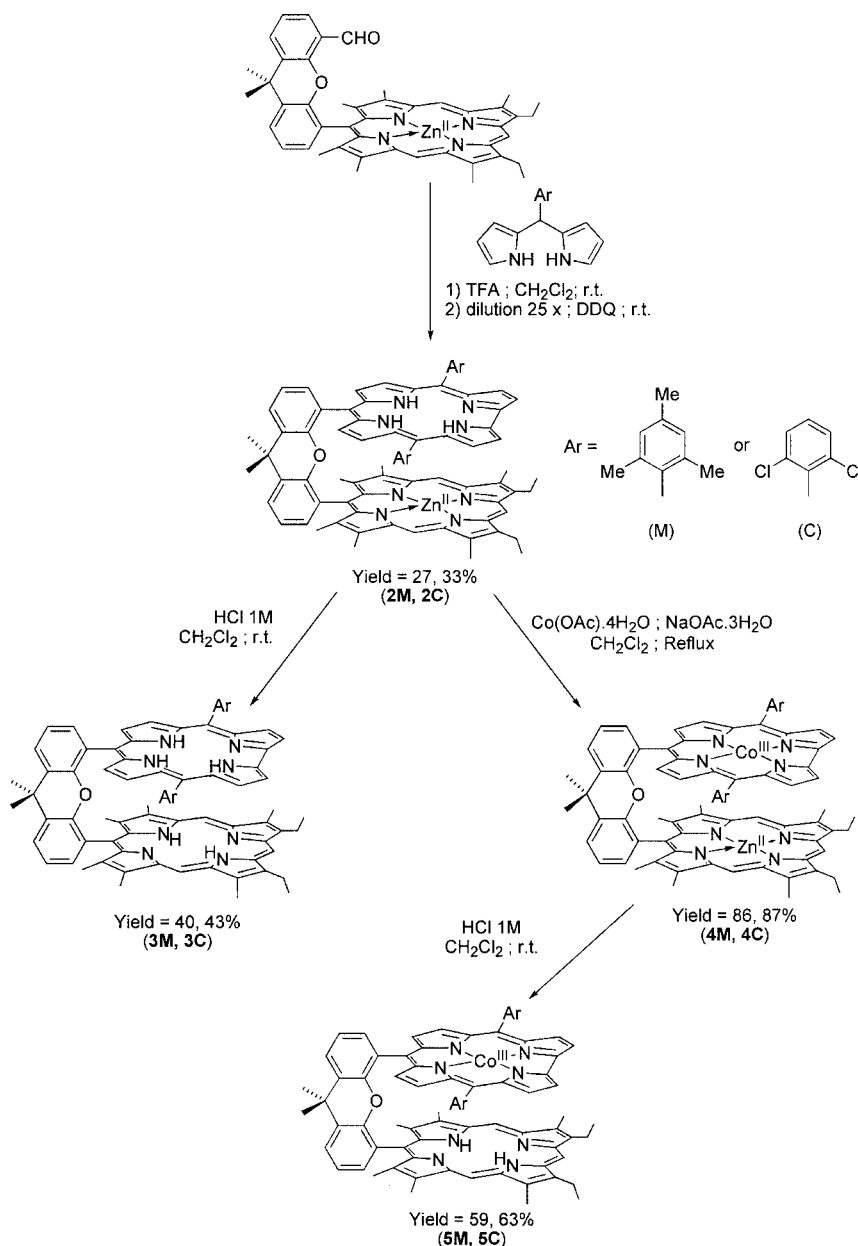
role bis(macrocycle) is obtained in only two steps. Scheme 2 gives the overall procedure.

5-Mesityldipyrromethane and 5-(2,6-dichlorophenyl)dipyrromethane were obtained from a previously described procedure^[24] and used for reaction with **1Zn**. **1Zn** was used in the condensation instead of **1** since the reaction requires the presence of trifluoroacetic acid (TFA), which can protonate the porphyrin moiety. For **1**, larger quantities of TFA must be used for the condensation reaction, and acidolysis of the reacting dipyrromethane can occur. Therefore, **1Zn** is a more appropriate precursor because no protonation of the porphyrin core can occur and the final derivatives **2M** and **2C** are much easier to purify by column chromatography than their non-metallated counterparts.

1Zn was obtained in 87% yield in classical conditions by simple metalation of **1** by zinc acetate dihydrate in chloroform/methanol (Scheme 2). The remaining aldehyde function of **1Zn** was treated further, with either 5-mesityldipyrromethane or 5-(2,6-dichlorophenyl)dipyrromethane, in dichloromethane in the presence of a catalytic amount of TFA (aldehyde/TFA = 17:1.3 mmol).^[19] Under the best experimental conditions, in which dipyrromethane was added in twice the stoichiometric amount (66 mmol, 4 equiv.) with respect to **1Zn**, both **2M** and **2C** were obtained in yields close to 30% compared to ca. 6% for stoichiometric amounts (33 mmol, 2 equiv.).^[19] To recover **2M** and **2C**, the final reoxidation process was performed using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) after a 25 $\times$ dilution in dichloromethane.^[21] **2M** and **2C** were isolated in 27 and 33% yield, respectively. Corrole ring formation is easily evidenced in MALDI/TOF by a distribution of peaks centered at 1253.92 (**2M**) and 1307.34 (**2C**), and by ¹H NMR resonance signals of the corrole (Table 1). Notably, no signal



Scheme 1.



Scheme 2.

could be attributed to the inner NH protons of the corrole ring.

Similarly, the corrole ring is evidenced in UV/Vis spectroscopy by two extra Q bands at 610 and 638 nm, and 617 and 636 nm for **2M** and **2C**, respectively. At the same time, the unique Soret band is slightly blue-shifted by 7 nm for both derivatives compared to that of **1Zn** (Table 2). This shift is generally interpreted in terms of the mutual influence of the porphyrin and corrole rings, thus increasing the HOMO–LUMO gap and therefore shifting the transition at lower wavelengths.^[25,26]

Corrole ring formation is further indicated by the disappearance of the C=O stretching band at 1680 cm⁻¹ of the aldehyde function of **1Zn** and the concomitant appearance of a new band around 3360 cm⁻¹ relative to the vibration

of the NH groups of the corrole ring of **2M** and **2C** (see Exp. Sect.).

2M and **2C** can be demetalated by washing with one molar hydrochloric acid solution to afford the free bases **3M** and **3C** in 43 and 40% yield, respectively (Scheme 2). UV/Vis spectroscopy reveals **3M** and **3C** formation by one extra Q band at ca. 510 nm when compared to **2M** and **2C** (Table 2). ¹H NMR spectra of **3M** and **3C** feature two signals corresponding to the NH protons of the porphyrin free-base at $\delta = -5.43$ and -4.69 ppm, and at $\delta = -5.63$ and -4.97 ppm, for **3M** and **3C**, respectively. Again, no signal is observed for the same protons in the corrole ring.

When treated with excess cobalt acetate tetrahydrate and sodium acetate in dichloromethane/methanol, **2M** and **2C** lead to **4M** and **4C** in ca. 85% yield, as confirmed by the

Table 1. ^1H NMR spectroscopic data of the investigated compounds.

Com- pound ^[a, b]	Solvent	Porphyrin ring ^[c]					Corrole ring ^[c]			
		NH	CH ₂ CH ₃	CH ₃	CH ₂ CH ₃	H _{meso}	CH _{3mesityl}	H _{mesityl}	H _β	
1	CDCl ₃	−3.24, −3.04	1.89	2.50, 3.50, 3.65	4.26	9.99, 10.16				
1Zn	CDCl ₃		1.88	2.48, 3.48, 3.63	4.08	10.02, 10.12				
2M ^[d]	C ₆ D ₆		1.83	2.60, 2.92, 3.19	3.86	9.07, 9.66	0.93, 1.48, 2.36	7.23	7.51, 7.81, 8.04, 8.28	
3M ^[d]	C ₆ D ₆	−5.43, −4.69	1.85	2.25, 2.56, 3.07	3.88	7.55, 9.44	0.84, 1.45, 2.20	6.97	7.55, 7.55, 8.11, 8.39	
4M	C ₅ D ₅ N		1.72	3.00, 3.36, 3.51	3.97	9.92, 10.00	0.80, 2.14, 2.65	7.35	8.22, 8.58, 8.69, 9.00	
5M	C ₅ D ₅ N	−3.72, −3.38	1.68	2.93, 3.33, 3.49	3.89	9.94, 9.94	0.71, 2.17, 2.29	7.33	8.23, 8.55, 8.73, 8.96	
							H _{dichlorophenyl}		H _β	
2C ^[d]	C ₆ D ₆		1.75	2.68, 3.16, 3.28	3.81	9.31, 9.56	6.87, 7.09, 7.43		7.49, 7.91, 7.93, 8.43	
3C ^[d]	C ₆ D ₆	−5.63, −4.97	1.88	2.31, 2.84, 3.12	3.89	8.66, 9.39	7.24, 7.41, 7.64		7.41, 7.64, 8.16, 8.37	
4C	C ₅ D ₅ N		1.70	2.97, 3.46, 3.50	3.94	9.89, 9.95	7.70, 7.86, 8.01		8.30, 8.59, 8.81, 9.12	
5C	C ₅ D ₅ N	−4.10, −3.49	1.67	2.88, 3.39, 3.47	3.88	9.90, 9.91	7.71, 7.86, 8.00		8.32, 8.64, 8.78, 9.09	

[a] Dimethylxanthene unit protons omitted. [b] See Schemes 1 and 2 for structures of the compounds. [c] Coupling constants given in the Exp. Sect. [d] Corrole NH protons not detected.

Table 2. UV/Vis data of the investigated compounds in CH₂Cl₂.

Compound		λ_{max} [nm] ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$)					
1		403 (141)	502 (11.2)	535 (6.1)	571 (5.2)		625 (2.)
1Zn	332 (23.6)	406 (346)		536 (16.9)	572 (16.0)		
2M		399 (252)		540 (14.6)	574 (18.1)	610 (5.9)	638(4.2)
3M		397 (238)	508 (12.7)	544 (11.9)	574 (17.4)	608 (8.3)	633 (5.2)
4M		393 (231)		538 (19.0)	575 (16.7)		
5M		389 (189)	507 (14.6)	541 (9.9)	576 (8.2)		628 (4.5)
2C		399 (296)		538 (16.1)	573 (20.7)	617 (5.8)	636 (3.8)
3C		396 (217)	509 (10.9)	543 (10.1)	574 (15.6)	616 (6.8)	
4C		389 (197)	501 (11.1)	539 (19.3)	575 (15.4)		
5C		389 (160)	506 (16.7)	540 (11.9)	573 (9.2)		627 (4.7)

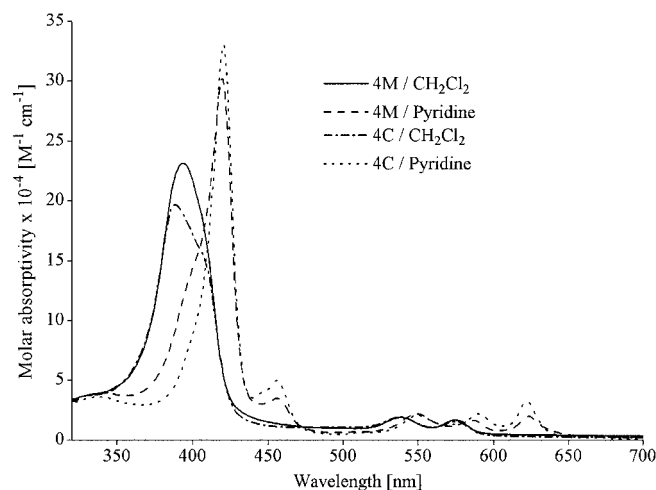


Figure 1. UV/Vis spectra of **4M** and **4C** recorded in CH₂Cl₂ and pyridine.

hypsochromic shift of the Soret band and by the presence of only two major Q bands (Scheme 2 and Table 2). The spectra of the two species recorded in pyridine are interesting (see Exp. Sect. for data). Figure 1 shows the UV/Vis spectra of both **4M** and **4C** in CH₂Cl₂ and pyridine. In dichloromethane, the data are close to those of pure zinc monoporphyrins, the only difference being the shoulder on the Soret band of the porphyrin corresponding to that of the corrole ring. In contrast, major differences arise when pyridine is used as a solvent. For example, all Q bands are red-shifted and a new absorption appears in the range 620–625 nm. Such a band is specific of the coordination of two pyridine molecules on the cobalt(III) ion of the corrole moiety.^[10,27–29] Therefore, the coordination of two pyridine molecules is expected on the cobalt atom in *endo* and *exo* positions. The spectra in pyridine exhibit another band, at 456 nm, for both **4M** and **4C** complexes, corresponding to the Soret band of the corrole ring. In ¹H NMR spectra recorded in deuterated pyridine all resonance signals appear

in the diamagnetic region ($\delta = 0$ –10 ppm) while in non-coordinating solvents (CDCl_3 or C_6D_6) broad signals appear over a wider range for the corrole counterpart. This behavior is attributed to the presence, in non-coordinating solvents, of a high-spin Co^{III} ($S = 1$) species while in coordinating solvents a low-spin Co^{III} ($S = 0$) is expected.^[11] A detailed study of these spectral characteristics will be published separately.^[30]

Demetalation of **4M** and **4C** using 1 M hydrochloric acid affords **5M** and **5C** in yields ranging from 59 to 63% (Scheme 2). No demetalation of the (corrole)cobalt moiety occurs, as demonstrated in MALDI/TOF mass spectrometry by single ionic patterns at $m/z = 1246.98$ and 1300.8 , which correspond to the **5M** and **5C** molecular ions, respectively. The relative “protective action” of the cobalt-containing corrole ring during metalation is interesting. Indeed, direct demetalation from **2M** and **2C** affords **3M** and **3C** in lower yields (around 40%). Other porphyrin–corrole and bis(corrole) bis(macrocycles) show such behavior; the free-bases exhibiting instability relative to the metalated derivatives.^[31,32] ^1H NMR spectra of **5M** and **5C**, recorded in $[\text{D}_5]$ -pyridine, do not differ significantly from those of **4M** and **4C**, apart from the NH proton resonances of the porphyrin pyrrole units, which are centered at $\delta = -3.72$ and -3.38 ppm for **5M**, and $\delta = -4.10$ and -3.49 ppm for **5C** (Table 1). The UV/Vis spectrum of **5M** recorded in CH_2Cl_2 closely resembles that of **5C** (Figure 2). Due to the lower molar absorptivity of the absorption bands on the corrole, both spectra exhibit characteristic features of free-base monoporphyrins, with four Q bands between 500 and 630 nm and a Soret band at 389 nm. This latter band is broadened slightly by overlap with the Soret band of the corrole ring. With pyridine as solvent, similar UV/Vis spectra are again obtained for **5M** and **5C** (Figure 2). The band close to 620–625 nm increases in intensity, in accordance with the coordination of two pyridine molecules on the cobalt atom in the corrole. As observed for **4M** and **4C**, **5M** and **5C** exhibit a band at 456 nm in pyridine corresponding to the Soret band of the corrole moiety. Finally, crystalli-

zation of **5M** in cyclohexane/pyridine furnished crystals of **5M(py)₂**.

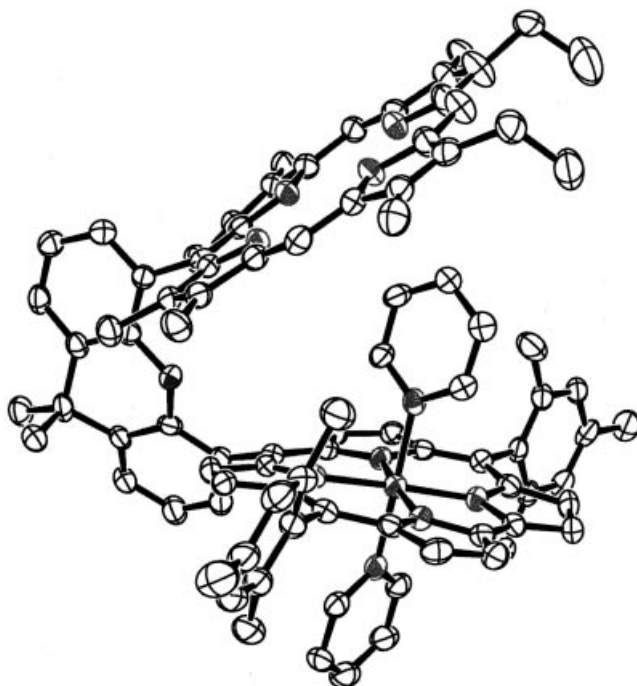


Figure 3. ORTEP view of the **5M(py)₂** complex. Ellipsoids drawn at 50% probability level; hydrogen atoms omitted for clarity.

Structural Study

A single-crystal X-ray diffraction analysis of **5M(py)₂** revealed the molecular structure of the monometallic cobalt(III) complex (Figure 3). The Co^{III} ion is coordinated to the four pyrrole nitrogen atoms ($4\text{N}_{\text{pyrrole}}$) in a planar conformation (the metal ion is only $0.011 \text{ \AA}$ out of the $4\text{N}_{\text{pyrrole}}$ mean plane), lying slightly out of the $4\text{N}_{\text{pyrrole}}$ centroid Ct_1 at $0.070 \text{ \AA}$. Two kinds of $\text{Co}-\text{N}_{\text{pyrrole}}$ distances are observed in the complex [$1.869(4)$ – $1.875(4)$ and $1.896(4)$ – $1.898(4) \text{ \AA}$, each group involving the nitrogen atoms in *trans* positions], indicating a slightly distorted $4\text{N}_{\text{pyrrole}}$ square coordination. In addition, two pyridine (py) nitrogen atoms (N_{py}) are in apical positions from the metal centre at $1.969(4)$ and $1.978(4) \text{ \AA}$, completing a close square-bipyramidal coordination geometry. These coordination distances and geometry are very similar to those reported for related complexes. Thus, for the [5,10,15-tris-(pentafluorophenyl)corrole]cobalt(III) complex,^[33] $\text{M}-\text{N}_{\text{pyrrole}}$ and $\text{M}-\text{N}_{\text{py}}$ distances are 1.873 – 1.900 and $1.994 \text{ \AA}$ for the monomer, and 1.868 – 1.899 and 1.989 – $2.000 \text{ \AA}$ for the dimer. In the face-to-face homodimetallic bis(corrole) complex $[(\text{BCA})\text{Co}_2(\text{py})_3]$,^[28] bearing three coordinated pyridine molecules (one inside and two out of the complex cavity), $\text{M}-\text{N}_{\text{pyrrole}}$ and $\text{M}-\text{N}_{\text{py}}$ distances are 1.879 – 1.905 and 1.976 – $1.979 \text{ \AA}$ for the hexacoordinate metal centre. In this latter structure, the coordination distances of the pentacoordinate metal centre, [$1.875(4)$ – $1.894(4)$ for $\text{N}_{\text{pyrrole}}$ and $1.946(5) \text{ \AA}$ for N_{py}], compare well with those of the mono-

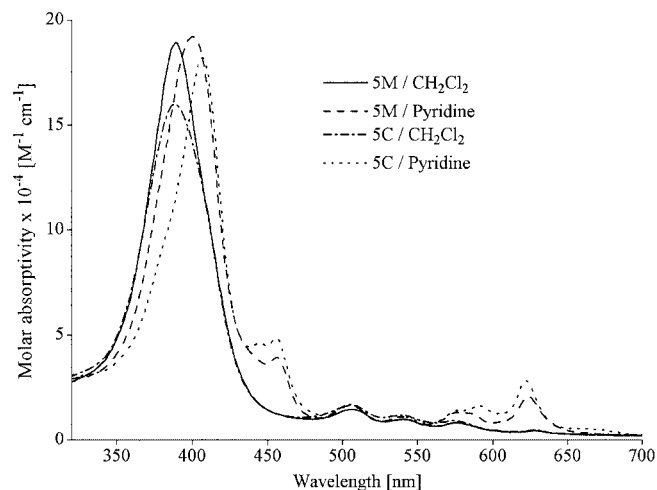


Figure 2. UV/Vis spectra of **5M** and **5C** recorded in CH_2Cl_2 and pyridine.

metallic (corrole–porphyrin)cobalt(III) complex, where the spacer is a biphenylenyl unit, [(PCB)H₂Co(py)],^[10] which binds one pyridine molecule out of the complex cavity. The corresponding distances were 1.882(3)–1.902(3) (N_{pyrrole}) and 1.945(4) Å (N_{py}). Thus, from penta- to hexacoordinate (corrole)cobalt(III) species having pyridine in apical positions, the most relevant difference in coordination geometry concerns: (i) elongation of M–N_{py} by about 0.03 Å and (ii) displacement of the metal centre towards the 4N_{pyrrole} mean plane ($\langle 4N_{pyrrole} \rangle$); the Co $\cdots\langle 4N_{pyrrole} \rangle$ distance being 0.202(1) and 0.252(1) Å for pentacoordinate cases in [(PCB)H₂Co(py)] and [(BCA)Co₂(py)₃] and 0.009(1) and 0.011(1) Å for hexacoordinate ones in [(BCA)Co₂(py)₃] and **5M(py)₂**.

In the molecular structure of the **5M(py)₂** complex both macrocycles exhibit a small distortion from planarity, the root mean square deviation of the 23 and 24 atoms from the corrole and porphyrin least-squares planes being 0.112 and 0.078 Å, respectively. While the corrole macrocycle shows a ruffled conformation, as indicated by the displacements of the alternated *meso*-carbon atoms above and below the corrole mean plane, the porphyrin moiety is closely planar. Thus, for the corrole ring, the *meso*-carbon atom C10 lies 0.210(4) Å above the mean plane, whereas C5 and C15 lie –0.159(4) and –0.175(4) Å below this plane. With the porphyrin, only five atoms lie more than 0.1 Å out of the mean plane [C55, C60, C61, C68, and C71 at 0.128(4), –0.108(4), –0.122(4), –0.105(4), and –0.207(4) Å, respectively]. [(BCA)Co₂(py)₃] and [(PCB)H₂Co(py)] complexes have similar macrocycle conformations.^[10,28]

Both H(–N) hydrogen atoms were found unambiguously in the porphyrin cavity, on N7 and N5, and are involved in hydrogen-bonding interactions with N6 and N8 pyrrole nitrogen atoms [$d(N-H) = 0.95(5)$ and $0.99(5)$ Å, $d(H\cdots N) = 2.23(5)$ and $2.11(5)$ Å and $\alpha(N-H\cdots N) = 120(4)$ and $127(4)^\circ$, respectively].

The coordination of one of the pyridine molecules within the complex cavity leads to a large open-mouth face-to-face geometry (the interplanar angle between the macrocycle mean planes β is 43.2°) due to the important steric effects with the porphyrin moiety. Nevertheless, the spacer is folded through the Csp³–O direction (the dihedral angle between both half parts is 28.9°), allowing for a short pyridine–porphyrin contact that balances the repulsive steric effect by the attractive (C_{py})H $\cdots\pi$ -system interaction (the 4N_{pyrrole} porphyrin centroid Ct₂ distance to the closest H_{py} atom is 2.22 Å, and the four H $\cdots$ Ct₂ $\cdots$ N_{pyrrole} angles range between 80 and 100°). The anchored sites of both macrocycles at the spacer and at the corrole–porphyrin moieties are 4.64 and 4.79 Å, respectively, apart. The small difference in distances (0.15 Å) suggests that, while steric repulsion mainly drives the corrole macrocycle orientation (leading to the large β angle), both the spacer folding and the attractive H $\cdots\pi$ -porphyrin interaction avoid a larger difference. Further support for both this attractive interaction and the role of the spacer follows from a comparison of the molecular structures of (BCA)Co₂(py)₃ and **5M(py)₂**, where the distances from the hexacoordinate metal centre to the

centroid of the other macrocycle are 7.23 and 6.86 Å, respectively. Thus, the latter complex exhibits a short “macrocycle-to-macrocycle” distance due to the folding of its spacer, which in the relaxed planar conformation corresponds to the distance observed for the anthracenyl moiety. Therefore, thanks to its flexibility, the dimethylxanthene spacer is of great interest for tuning potential metal $\cdots$ metal or metal $\cdots$ molecule $\cdots$ metal interactions in face-to-face macrocyclic complexes.

In **5M(py)₂**, the slip angle α , defined as the average angle between the vector joining Ct₁ $\cdots$ Ct₂ and the unit vectors normal to the two macrocyclic least-squares planes [$\alpha = (\alpha_1 + \alpha_2)/2$], is 24.0° and the lateral shift $L = \sin\alpha \cdot d(Ct_1\cdots Ct_2)$ is 2.80 Å [$d(Ct_1\cdots Ct_2) = 6.90$ Å]. These values are larger than those found in [(BCA)Co₂(py)₃] ($\alpha = 14.7^\circ$, $L = 1.84$ Å), even if α and L slightly differ in their definitions in the two complexes.^[28]

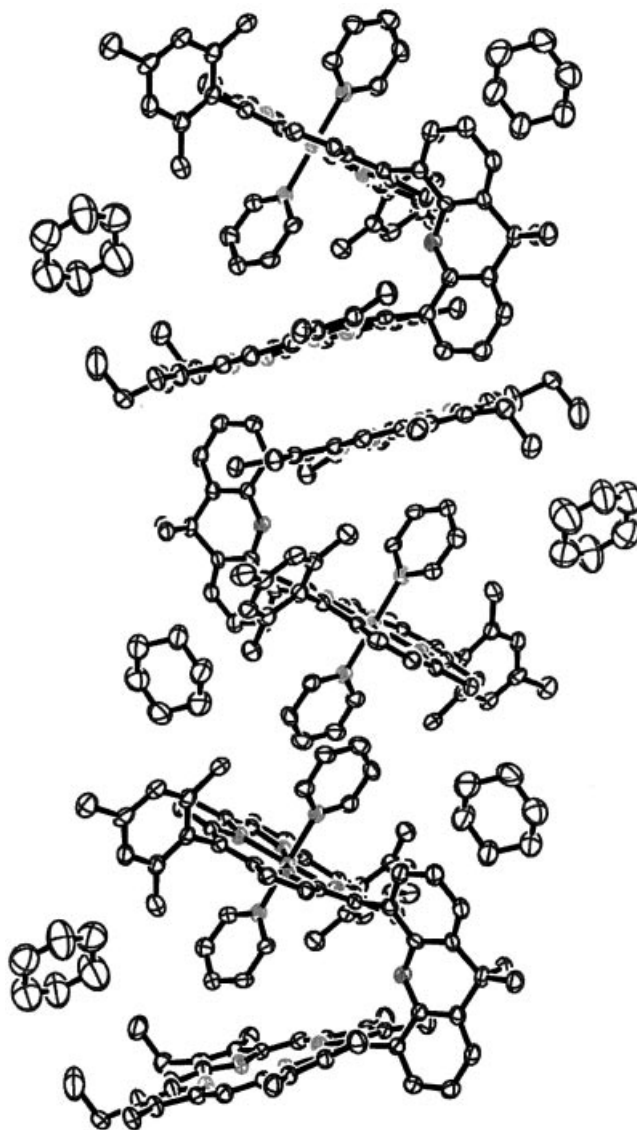


Figure 4. Stacking of **5M(py)₂** complexes along the [1 0 0] direction, including solvent molecules. Ellipsoids drawn at 50% probability level; hydrogen atoms omitted for clarity.

Moreover, the pyridine molecules are almost staggered around the metal centre; the dihedral angle between their mean planes being 87.9°. While this almost perpendicular orientation has also been observed in [(BCA)Co₂(py)₃] (88.2°)^[28] and [(Me₄Ph₅Cor)Co(py)₂] (83.7°),^[27] in the [5,10,15-tris(pentafluorophenyl)corrole]cobalt(III) complex a mutually parallel arrangement between both pyridine molecules is found for the monomer and dimer.^[33]

In the **5M(py)₂** crystal structure, the stacking of complexes is driven by two kinds of π – π interactions along the [100] direction (Figure 4). Hence, while the porphyrin ring interacts with the adjacent equivalent moiety of another molecule (the shortest distance is 3.57 Å for two equivalent *meso*-C atoms), at the other side of the complex the outer pyridine molecule makes a π – π interaction with an equivalent molecule of the closest complex (the shortest C–C distance being 3.33 Å). In the former case, the centroid–centroid distance is quite large (7.50 Å), indicating an important lateral shift between the macrocycles. In the second case, the centroid–centroid distance is 3.63 Å, reflecting significant overlap between the π -systems of both pyridine molecules.

The relative orientation of the inner pyridine in front of two methyl groups of the mesityl substituents (C_{methyl}...C_{tpy}...C_{methyl} = 160°) seems to indicate a further stabilisation by two quite weak C–H...aromatic ring interactions (H...C_{tpy} distances are 3.83 and 4.41 Å). A variable ¹H NMR analysis down to 220 K, to visualize tentatively any interaction involving a methyl proton of a mesityl group with a pyridine molecule, found no significant variation in signal shape or chemical shift for the protons concerned.

Summary and Conclusion

1Zn reacts with an aryldipyrrromethane to afford good yields of (free-base corrole–porphyrin)zinc complexes (**2M** and **2C**). Further metalation of the corrole ring by cobalt followed by demetalation of the porphyrin moiety gives the (free-base porphyrin–corrole)cobalt complex, which is a precursor of heterodimetallic derivatives. The “protective” effect of the zinc ion in the porphyrin ring is evidenced throughout the synthetic pathway and, especially, during the first step, leading to the formation of the corrole, where lower amounts of TFA are required than for the reaction carried out from **1**. Therefore, acidolysis of the dipyrrromethane reactant avoided, and reaction yields in bis(macrocycle) are obviously increased.

In the presence of pyridine, the bis(pyridine) adduct of **5M** crystallized. The structure of **5M(py)₂** was solved, exhibiting coordination of the two pyridine molecules on the cobalt atom of the corrole ring in *endo* and *exo* positions. Another interesting feature is that the complexes are stacked along the [100] direction through π – π interactions.

Work towards the preparation of heterodimetallic complexes and their use as catalysts for the reduction of dioxygen is being carried out.

Experimental Section

General Remarks: All analytical grade reagents, obtained from commercial suppliers, were used without further purification. 5-Mesityldipyrrromethane, 5-(2,6-dichlorophenyl)dipyrrromethane,^[24] 5-(13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-4-formyl-9,9-dimethylxanthene^[13,31,32] (**1**) were synthesized according to reported procedures. ¹H NMR spectra were recorded at 500 MHz with a Bruker DRX-500 Avance spectrometer of the “Centre de Spectrométrie Moléculaire de l’Université de Bourgogne” of the FR 2604. Chemical shifts are expressed in ppm relative to residual peaks of chloroform (δ = 7.26 ppm), pyridine (δ = 7.19, 7.55, 8.71 ppm) or benzene (δ = 7.16 ppm). UV/Vis spectra were collected with a Varian Cary 1 spectrophotometer in dichloromethane solution. Infrared spectra were measured in the attenuated total reflectance mode (ATR) with a Bruker Vector 22 Fourier transform spectrometer. MALDI/TOF mass spectra were obtained with a Bruker ProFLEX III spectrometer using dithranol as matrix. Microanalyses were performed with a Fisons EA 1108 CHNS instrument.

[13,17-Diethyl-5-(5-formyl-9,9-dimethylxanthene-4-yl)-2,3,7,8,12,18-hexamethylporphyrin]zinc(II) (1Zn): A solution of porphyrin **1** (0.200 g, 0.291 mmol, 1 equiv.), zinc acetate dihydrate (0.128 g, 0.582 mmol, 2 equiv.), and sodium acetate trihydrate (0.396 g, 2.91 mmol, 10 equiv.) in a chloroform (35 mL)/methanol (15 mL) mixture was heated to reflux for 15 min. After cooling to room temperature, dichloromethane (50 mL) was added. The reaction mixture was then washed with water (3 × 100 mL), dried with magnesium sulfate, filtered and the solvents were evaporated. The resulting solid was chromatographed on silica gel using first toluene as eluent and then dichloromethane to collect a pink fraction. After concentration, the solid was recrystallized from dichloromethane/heptane. **1Zn** was obtained in 87% yield (0.190 g, 0.253 mmol). ¹H MNR (CDCl₃, 300 K): δ = 1.88 (t, ³J_{H,H} = 7.85 Hz, 6 H, CH₃CH₂–porphyrin), 1.92 (s, 6 H, CH₃–dimethylxanthene) 2.48 (s, 6 H, CH₃–porphyrin), 3.48 (s, 6 H, CH₃–porphyrin), 3.63 (s, 6 H, CH₃–porphyrin), 4.08 (m, 4 H, CH₃CH₂–porphyrin), 7.05 (t, ³J_{H,H} = 7.68 Hz, 1 H, H–dimethylxanthene), 7.30 (dd, ³J_{H,H} = 7.39, ⁴J_{H,H} = 1.19 Hz, 1 H, H–dimethylxanthene), 7.51 (s, 1 H, CHO), 7.60 (t, ³J_{H,H} = 7.71 Hz, 1 H, H–dimethylxanthene), 7.71 (dd, ³J_{H,H} = 7.90, ⁴J_{H,H} = 1.43 Hz, 1 H, H–dimethylxanthene), 7.87 (d, ³J_{H,H} = 6.40 Hz, 1 H, H–dimethylxanthene), 7.93 (dd, ³J_{H,H} = 7.95, ⁴J_{H,H} = 1.01 Hz, 1 H, H–dimethylxanthene), 10.02 (s, 1 H, H_{meso}–porphyrin), 10.12 (s, 2 H, H_{meso}–porphyrin). MS (MALDI/TOF): *m/z* = 747.30 [M – H]⁺; 748.28 calcd. for C₄₆H₄₄N₄O₂Zn. UV/Vis (CH₂Cl₂): $\lambda_{\max}$ ($\epsilon \times 10^{-3}$ L mol⁻¹ cm⁻¹) = 332.0 (23.6), 406.0 (346), 536.1 (16.9), 572.1 (16.0) nm. IR $\tilde{\nu}$ = 2959 (C–H), 2923 (C–H), 2861 (C–H), 1680 (C=O) cm⁻¹. C₄₆H₄₄N₄O₂Zn (750.27): calcd. C 73.64, H 5.91, N 7.47; found C 73.63, H 6.07, N 7.48.

{5-[5-(5,15-Dimesitylcorrole-10-yl)-9,9-dimethylxanthene-4-yl]-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin}zinc(II) (2M): (Porphyrin)zinc complex **1Zn** (0.20 g, 0.27 mmol, 1 equiv.) and mesityldipyrrromethane (0.28 g, 1.07 mmol, 4 equiv.) were dissolved in 16 mL of a solution of trifluoroacetic acid (0.02 mmol, 0.08 equiv.) in CH₂Cl₂ (10 μ L of TFA in 100 mL of CH₂Cl₂). The reaction mixture was then stirred for 5 h, diluted 25× with CH₂Cl₂ (400 mL) and a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 0.182 g, 0.80 mmol, 3 equiv.) in toluene (4 mL) was added with stirring. After a further 5 min, the reaction mixture was chromatographed on silica gel and eluted with CH₂Cl₂. The first collected, violet, fraction was concentrated, washed with pentane and dried under vacuum, yielding 0.091 g (27%, 0.07 mmol) of **2M**. ¹H MNR (C₆D₆, 330 K): δ = 0.93 (s, 6 H, CH₃–mesityl), 1.48 (s, 6 H,

CH₃-mesityl), 1.83 (t, ³J_{H,H} = 7.71 Hz, 6 H, CH₃CH₂-porphyrin), 2.11 (s, 6 H, CH₃-dimethylxanthene), 2.36 (s, 6 H, CH₃-mesityl), 2.60 (s, 6 H, CH₃-porphyrin), 2.92 (s, 6 H, CH₃-porphyrin), 3.19 (s, 6 H, CH₃-porphyrin), 3.86 (m, 4 H, CH₃CH₂-porphyrin), 6.81 (s, 2 H, H_{meta}-mesityl), 7.01 (dd, ³J_{H,H} = 7.18, ⁴J_{H,H} = 1.46 Hz, 1 H, H-dimethylxanthene), 7.15 (t, ³J_{H,H} = 7.50 Hz, 1 H, H-dimethylxanthene), 7.17 (t, ³J_{H,H} = 7.86 Hz, 1 H, H-dimethylxanthene), 7.23 (s, 2 H, H_{meta}-mesityl), 7.34 (dd, ³J_{H,H} = 7.28, ⁴J_{H,H} = 1.51 Hz, 1 H, H-dimethylxanthene), 7.51 (br. d, ³J_{H,H} = 3.06 Hz, 2 H, H_β-corrole), 7.72 (dd, ³J_{H,H} = 7.91, ⁴J_{H,H} = 1.53 Hz, 1 H, H-dimethylxanthene), 7.75 (dd, ³J_{H,H} = 7.97, ⁴J_{H,H} = 1.52 Hz, 1 H, H-dimethylxanthene), 7.81 (d, ³J_{H,H} = 4.38 Hz, 2 H, H_β-corrole), 8.04 (d, ³J_{H,H} = 3.88 Hz, 2 H, H_β-corrole), 8.28 (d, ³J_{H,H} = 4.58 Hz, 2 H, H_β-corrole), 9.07 (s, 2 H, H_{meso}-porphyrin), 9.66 (s, 1 H, H_{meso}-porphyrin). MS (MALDI/TOF): *m/z* = 1253.92 ([M]⁺); 1254.54 calcd. for C₈₂H₇₆N₈OZn. UV/Vis (CH₂Cl₂): λ_{max} (ε × 10⁻³ L mol⁻¹ cm⁻¹) = 399.0 (252), 540.0 (14.6), 574.0 (18.1), 610.0 (5.91), 638.0 (4.17) nm. IR ν̄ = 3366 (N–H), 2960 (C–H), 2918 (C–H), 2850 (C–H) cm⁻¹. C₈₂H₇₆N₈OZn (1254.95): calcd. C 78.48, H 6.10, N 8.93; found C 78.21, H 6.21, N 8.87.

(5-{5-[5,15-Bis(2,6-dichlorophenyl)corrol-10-yl]-9,9-dimethylxanthene-4-yl}-13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin)-zinc(II) (2C): This compound was synthesized as described above for **2M**, starting from **1Zn** (0.20 g, 0.27 mmol, 1 equiv.) and (2,6-dichlorophenyl)dipyrromethane (0.31 g, 1.07 mmol, 4 equiv.), in 33% yield (0.12 g, 0.09 mmol). ¹H NMR (C₆D₆, 330 K): δ = 1.75 (t, ³J_{H,H} = 7.74 Hz, 6 H, CH₃CH₂-porphyrin), 2.14 (s, 6 H, CH₃-dimethylxanthene), 2.68 (s, 6 H, CH₃-porphyrin), 3.16 (s, 6 H, CH₃-porphyrin), 3.28 (s, 6 H, CH₃-porphyrin), 3.81 (m, 4 H, CH₃CH₂-porphyrin), 6.87 (t, ³J_{H,H} = 8.31 Hz, 2 H, H_{para}-dichlorophenyl), 6.89 (dd, ³J_{H,H} = 7.19, ⁴J_{H,H} = 1.30 Hz, 1 H, H-dimethylxanthene), 7.09 (dd, ³J_{H,H} = 8.24, ⁴J_{H,H} = 1.15 Hz, 2 H, H_{meta}-dichlorophenyl), 7.11 (t, ³J_{H,H} = 7.63 Hz, 1 H, H-dimethylxanthene), 7.18 (t, ³J_{H,H} = 7.69 Hz, 1 H, H-dimethylxanthene), 7.28 (dd, ³J_{H,H} = 7.25, ⁴J_{H,H} = 1.54 Hz, 1 H, H-dimethylxanthene), 7.43 (dd, ³J_{H,H} = 8.38, ⁴J_{H,H} = 1.02 Hz, 2 H, H_{meta}-dichlorophenyl), 7.49 (br. d, ³J_{H,H} = 3.12 Hz, 2 H, H_β-corrole), 7.75 (m, 2 H, H-dimethylxanthene), 7.91 (br. d, ³J_{H,H} = 3.86 Hz, 2 H, H_β-corrole); 7.93 (d, ³J_{H,H} = 4.51 Hz, 2 H, H_β-corrole), 8.43 (d, ³J_{H,H} = 4.61 Hz, 2 H, H_β-corrole), 9.31 (s, 2 H, H_{meso}-porphyrin), 9.56 (s, 1 H, H_{meso}-porphyrin). MS (MALDI/TOF): *m/z* = 1307.34 ([M]⁺); 1308.29 calcd. for C₇₆H₆₀Cl₄N₈OZn. UV/Vis (CH₂Cl₂): λ_{max} (ε × 10⁻³ L mol⁻¹ cm⁻¹) = 399.0 (296), 538.0 (16.1), 573.0 (20.7), 616.9 (5.81), 636.1 (3.81) nm. IR ν̄ = 3357 (N–H), 2960 (C–H), 2918 (C–H), 2850 (C–H) cm⁻¹. C₇₆H₆₀Cl₄N₈OZn (1308.57): calcd. C 69.76, H 4.62, N 8.56; found C 69.97, H 4.82, N 8.32.

4-(13,17-Diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-5-(5,15-dimethylcorrol-10-yl)-9,9-dimethylxanthene (3M): A solution of **2M** (0.06 g, 0.048 mmol) in dichloromethane (60 mL) was stirred vigorously in the presence of hydrochloric acid (1 M, 3 × 60 mL) in a separating funnel. The organic layer was washed with water (3 × 60 mL), dried with magnesium sulfate, filtered and the solvents were evaporated. The resultant solid residue was chromatographed on basic alumina and eluted with CH₂Cl₂. The first eluting fraction was concentrated and recrystallized from dichloromethane/methanol to yield **3M** as a violet solid (43%, 0.024 g, 0.02 mmol). ¹H NMR (CDCl₃, 300 K): δ = -5.43 (br. s, 1 H, NH-porphyrin), -4.69 (br. s, 1 H, NH-porphyrin), 0.84 (br. s, 6 H, CH₃-mesityl), 1.45 (br. s, 6 H, CH₃-mesityl), 1.85 (t, ³J_{H,H} = 7.76 Hz, 6 H, CH₃CH₂-porphyrin), 2.20 (s, 6 H, CH₃-dimethylxanthene), 2.25 (s, 6 H, CH₃-porphyrin), 2.43 (s, 6 H, CH₃-mesityl), 2.56 (br. s, 6 H, CH₃-porphyrin), 3.07 (br. s, 6 H, CH₃-porphyrin), 3.88 (m, 4 H, CH₃CH₂-porphyrin), 6.81 (br. s, 2 H, H_{meta}-mesityl), 6.97 (br. s, 2 H, H_{meta}-

mesityl), 7.09 (br. s, 1 H, H-dimethylxanthene), 7.33 (t, ³J_{H,H} = 7.62 Hz, 1 H, H-dimethylxanthene), 7.37 (t, ³J_{H,H} = 7.50 Hz, 1 H, H-dimethylxanthene), 7.42 (br. dd, ³J_{H,H} = 6.32 Hz, 1 H, H-dimethylxanthene), 7.55 (m, 6 H, H_β-corrole + H_{meso}-porphyrin), 7.91 (dd, ³J_{H,H} = 7.73, ⁴J_{H,H} = 1.74 Hz, 1 H, H-dimethylxanthene), 7.94 (br. dd, ³J_{H,H} = 8.03 Hz, 1 H, H-dimethylxanthene), 8.11 (br. s, 2 H, H_β-corrole), 8.39 (br. s, 2 H, H_β-corrole), 9.44 (s, 1 H, H_{meso}-porphyrin) ppm. MS (MALDI/TOF): *m/z* = 1191.06 [M]⁺; 1190.63 calcd. for C₈₂H₇₈N₈O. UV/Vis (CH₂Cl₂): λ_{max} (ε × 10⁻³ L mol⁻¹ cm⁻¹) = 397.0 (238), 508.0 (12.7), 544.0 (11.9), 574.0 (17.4), 608.1 (8.35), 633.0 (5.24) nm. IR ν̄ = 3388 (N–H), 3349 (N–H), 3278 (N–H), 2960 (C–H), 2921 (C–H), 2859 (C–H) cm⁻¹. C₈₂H₇₈N₈O·2MeOH (1255.66): calcd. C 80.35, H 6.90, N 8.92; found C 80.77, H 6.68, N 8.73.

4-[5,15-Bis(2,6-dichlorophenyl)corrol-10-yl]-5-(13,17-diethyl-2,3,7,8,12,18-hexamethyl porphyrin-5-yl)-9,9-dimethylxanthene (3C): This compound was obtained as described for **3M**, starting from **2C** (0.06 g, 0.046 mmol), in 40% yield (0.023 g, 0.018 mmol). ¹H NMR (CDCl₃, 300 K): δ = -5.63 (br. s, 1 H, NH-porphyrin), -4.97 (br. s, 1 H, NH-porphyrin), 1.88 (t, ³J_{H,H} = 7.77 Hz, 6 H, CH₃CH₂-porphyrin), 2.21 (s, 6 H, CH₃-dimethylxanthene), 2.31 (s, 6 H, CH₃-porphyrin), 2.84 (br. s, 6 H, CH₃-porphyrin), 3.12 (br. s, 6 H, CH₃-porphyrin), 3.89 (m, 4 H, CH₃CH₂-porphyrin), 7.17 (br. d, ³J_{H,H} = 7.07 Hz, 1 H, H-dimethylxanthene), 7.24 (m, 5 H, H-dimethylxanthene + H_{meta}-dichlorophenyl), 7.41 (m, 4 H, H_{para}-dichlorophenyl + H_β-corrole), 7.64 (br. s, 4 H, H_{meta}-dichlorophenyl + H_β-corrole), 7.90 (dd, ³J_{H,H} = 6.55, ⁴J_{H,H} = 2.96 Hz, 1 H, H-dimethylxanthene), 7.95 (dd, ³J_{H,H} = 8.06, ⁴J_{H,H} = 1.51 Hz, 1 H, H-dimethylxanthene), 8.16 (br. s, 2 H, H_β-corrole), 8.37 (br. s, 2 H, H_β-corrole), 8.66 (br. s, 2 H, H_{meso}-porphyrin), 9.39 (s, 1 H, H_{meso}-porphyrin) ppm. MS (MALDI/TOF): *m/z* = 1244.43 [M]⁺; 1244.38 calcd. for C₇₆H₆₂Cl₄N₈O. UV/Vis (CH₂Cl₂): λ_{max} (ε × 10⁻³ L mol⁻¹ cm⁻¹) = 395.9 (217), 509.0 (10.9), 543.0 (10.1), 574.0 (15.6), 616.0 (6.77) nm. IR ν̄ = 3359 (N–H), 3312 (N–H), 3280 (N–H), 2960 (C–H), 2922 (C–H), 2859 (C–H) cm⁻¹. C₇₆H₆₂Cl₄N₈O·CH₂Cl₂·H₂O (1348.14): calcd. C 68.60, H 4.93, N 8.31; found C 68.55, H 4.58, N 8.02.

Mixed Cobalt(III)–Zinc(II) Complex 4M: Two solutions, one of **3M** (0.050 g, 0.040 mmol, 1 equiv.) in dichloromethane (7 mL) and another of cobalt(II) acetate tetrahydrate (0.025 g, 0.1 mmol, 2.5 equiv) and sodium acetate trihydrate (0.027 g, 0.2 mmol, 5 equiv.) in methanol (3 mL), were combined and the mixture was heated to reflux for 15 min. After cooling, dichloromethane (50 mL) was added and the resulting solution was washed with water (3 × 50 mL), dried with magnesium sulfate, filtered and the solvents were evaporated under vacuum. The residue was then chromatographed on basic alumina and eluted with CH₂Cl₂/MeOH (98:2). The violet solid collected from concentration of the first fraction was recrystallized from CH₂Cl₂/MeOH, leading to **4M** in 86% yield (0.045 mg, 0.034 mmol). ¹H NMR (C₅D₅N, 330 K): δ = 0.80 (s, 6 H, CH₃-mesityl), 1.72 (t, ³J_{H,H} = 7.61 Hz, 6 H, CH₃CH₂-porphyrin), 2.14 (s, 6 H, CH₃-mesityl), 2.36 (s, 6 H, CH₃-dimethylxanthene), 2.65 (s, 6 H, CH₃-mesityl), 3.00 (s, 6 H, CH₃-porphyrin), 3.36 (s, 6 H, CH₃-porphyrin), 3.51 (s, 6 H, CH₃-porphyrin), 3.97 (m, 4 H, CH₃CH₂-porphyrin), 6.46 (dd, ³J_{H,H} = 7.25, ⁴J_{H,H} = 1.57 Hz, 1 H, H-dimethylxanthene), 6.77 (dd, ³J_{H,H} = 7.26, ⁴J_{H,H} = 1.58 Hz, 1 H, H-dimethylxanthene), 7.23 (m, 2 H, 2 H-dimethylxanthene), 7.31 (s, 2 H, H_{meta}-mesityl), 7.35 (s, 2 H, H_{meta}-mesityl), 7.97 (dd, ³J_{H,H} = 8.04, ⁴J_{H,H} = 1.42 Hz, 1 H, H-dimethylxanthene), 8.04 (dd, ³J_{H,H} = 7.89, ⁴J_{H,H} = 1.58 Hz, 1 H, H-dimethylxanthene), 8.22 (d, ³J_{H,H} = 3.96 Hz, 2 H, H_β-corrole), 5.58 (d, ³J_{H,H} = 4.61 Hz, 2 H, H_β-corrole), 8.69 (m, partially overlapped by a C₅D₄HN signal, H_β-corrole), 9.00 (d, ³J_{H,H} = 4.64 Hz, 2 H, H_β-

corrole), 9.92 (s, 2 H, H_{meso} -porphyrin), 10.00 (s, 1 H, H_{meso} -porphyrin). MS (MALDI/TOF): $m/z = 1309.84$ [M] $^{+}$; 1310.45 calcd. for $C_{82}H_{73}N_8OZnCo$. UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$) = 393.0 (231), 538.0 (19.0), 575.1 (16.7) nm. UV/Vis (pyridine): λ_{max} ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$) = 340.0 (39.4), 420.0 (302), 456.0 (34.7), 510.1 (6.96), 550.1 (21.8), 587.0 (16.3), 623.0 (19.8) nm. IR $\tilde{\nu}$ 2958 (C–H), 2920 (C–H), 2858 (C–H) cm^{-1} . $C_{82}H_{73}CoN_8OZn$ (1310.86): calcd. C 75.13, H 5.61, N 8.55; found C 75.40, H 5.70, N 8.80.

Mixed Cobalt(III)–Zinc(II) Complex 4C:4C was prepared as described for **4M**, starting from **3C** (0.050 g, 0.038 mmol, 1 equiv.), cobalt(II) acetate tetrahydrate (0.024 g, 0.095 mmol, 2.5 equiv.) and sodium acetate trihydrate (0.026 g, 0.191 mmol, 5 equiv.). It was obtained as a violet solid in 87% yield (0.045 g, 0.033 mmol). ^1H NMR (C_5D_5N , 330 K): $\delta = 1.70$ (t, $^3J_{\text{H,H}} = 7.64$ Hz, 6 H, CH_3CH_2 -porphyrin), 2.34 (s, 6 H, CH_3 -dimethylxanthene), 2.97 (s, 6 H, CH_3 -porphyrin), 3.46 (s, 6 H, CH_3 -porphyrin), 3.50 (s, 6 H, CH_3 -porphyrin), 3.94 (m, 4 H, CH_3CH_2 -porphyrin), 6.12 (dd, $^3J_{\text{H,H}} = 7.30$, $^4J_{\text{H,H}} = 1.61$ Hz, 1 H, H-dimethylxanthene), 6.91 (dd, $^3J_{\text{H,H}} = 7.33$, $^4J_{\text{H,H}} = 1.62$ Hz, 1 H, H-dimethylxanthene), 7.11 (t, $^3J_{\text{H,H}} = 7.62$ Hz, 1 H, H-dimethylxanthene), 7.24 (t, $^3J_{\text{H,H}} = 7.66$ Hz, 1 H, H-dimethylxanthene), 7.70 (t, $^3J_{\text{H,H}} = 8.23$ Hz, 2 H, H_{meta} -dichlorophenyl), 7.86 (dd, $^3J_{\text{H,H}} = 8.22$, $^4J_{\text{H,H}} = 1.17$ Hz, 2 H, H_{meta} -dichlorophenyl), 7.96 (dd, $^3J_{\text{H,H}} = 7.93$, $^4J_{\text{H,H}} = 1.63$ Hz, 1 H, H-dimethylxanthene), 7.99 (dd, $^3J_{\text{H,H}} = 7.95$, $^4J_{\text{H,H}} = 1.73$ Hz, 1 H, H-dimethylxanthene), 8.01 (dd, $^3J_{\text{H,H}} = 8.17$, $^4J_{\text{H,H}} = 1.21$ Hz, 1 H, H_{meta} -dichlorophenyl), 8.30 (d, $^3J_{\text{H,H}} = 4.08$ Hz, 2 H, H_{β} -corrole), 8.59 (d, $^3J_{\text{H,H}} = 4.10$ Hz, 2 H, H_{β} -corrole), 8.81 (d, $^3J_{\text{H,H}} = 4.69$ Hz, 2 H, H_{β} -corrole), 9.12 (d, $^3J_{\text{H,H}} = 4.68$ Hz, 2 H, H_{β} -corrole), 9.89 (s, 2 H, H_{meso} -porphyrin), 9.95 (s, 1 H, H_{meso} -porphyrin). MS (MALDI/TOF): $m/z = 1364.16$, [M] $^{+}$; 1364.20 calcd. for $C_{76}H_{57}Cl_4N_8OZnCo$. UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$) = 389.0 (197), 501.0 (11.1), 538.9 (19.3), 575.1 (15.4) nm. UV/Vis (pyridine): λ_{max} ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$) = 337.9 (36.4), 420.0 (323), 456.0 (48.6), 515.1 (6.15), 550.1 (20.0), 590.0 (21.3), 621.9 (31.4) nm. IR $\tilde{\nu}$ 2961 (C–H), 2927 (C–H), 2862 (C–H) cm^{-1} . $C_{76}H_{57}Cl_4CoN_8OZn \cdot MeOH$ (1396.52): calcd. C 66.23, H 4.40, N 8.02; found C 66.48, H 4.38, N 8.38.

{10-[5-(13,17-Diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-9,9-dimethylxanthene-4-yl]-5,15-dimesitylcorrole}cobalt(III) (5M): A solution of **4M** (35 mg, 26.7 μmol) in dichloromethane (35 mL) was vigorously stirred with hydrochloric acid (1 M; 3×50 mL) in a separating funnel. The organic layer was then washed with distilled water (3×50 mL), dried with magnesium sulfate, filtered and the solvents were evaporated under vacuum. The resultant solid residue was chromatographed on basic alumina and eluted with dichloromethane/methanol (98:2). The first eluting fraction was concentrated and then recrystallized from dichloromethane/methanol, yielding **5M** (59%, 0.020 g, 0.016 mmol). ^1H NMR (C_5D_5N , 330 K): $\delta = -3.72$ (br. s, 1 H, NH-porphyrin), -3.38 (br. s, 1 H, NH-porphyrin), 0.71 (s, 6 H, CH_3 -mesityl), 1.68 (t, $^3J_{\text{H,H}} = 7.59$ Hz, 6 H, CH_3CH_2 -porphyrin), 2.17 (s, 6 H, CH_3 -mesityl), 2.29 (s, 6 H, CH_3 -dimethylxanthene), 2.65 (s, 6 H, CH_3 -mesityl), 2.93 (s, 6 H, CH_3 -porphyrin), 3.33 (s, 6 H, CH_3 -porphyrin), 3.49 (s, 6 H, CH_3 -porphyrin), 3.89 (m, 4 H, CH_3CH_2 -porphyrin), 6.62 (m, 2 H, H-dimethylxanthene), 7.29 (t, $^3J_{\text{H,H}} = 7.57$ Hz, 1 H, H-dimethylxanthene), 7.33 (m, 5 H, 4 H_{meta} -mesityl + 1 H-dimethylxanthene), 7.96 (dd, $^3J_{\text{H,H}} = 8.01$, $^4J_{\text{H,H}} = 1.53$ Hz, 1 H, H-dimethylxanthene), 8.08 (dd, $^3J_{\text{H,H}} = 7.53$, $^4J_{\text{H,H}} = 1.54$ Hz, 1 H, H-dimethylxanthene), 8.23 (d, $^3J_{\text{H,H}} = 3.88$ Hz, 2 H, H_{β} -corrole), 8.55 (d, $^3J_{\text{H,H}} = 4.64$ Hz, 2 H, H_{β} -corrole), 8.73 (d, $^3J_{\text{H,H}} = 4.01$ Hz, 2 H, H_{β} -corrole), 8.96 (d, $^3J_{\text{H,H}} = 4.56$ Hz, 2 H, H_{β} -corrole), 9.94 (s, 3 H, H_{meso} -porphyrin) ppm. MS (MALDI/TOF): $m/z = 1246.98$ [M] $^{+}$; 1246.54 calcd.

for $C_{82}H_{78}N_8O$. UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$) = 389.0 (189), 507.0 (14.6), 541.0 (9.91), 576.0 (8.20), 628.0 (4.50) nm. UV/Vis (pyridine): λ_{max} ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$) = 399.9 (192), 456.0 (39.2), 505.1 (16.4), 538.9 (11.1), 576.0 (br.) (13.1), 582.1 (br.) (12.9), 624.0 (20.5) nm. IR $\tilde{\nu}$ = 3276 (N–H), 2961 (C–H), 2918 (C–H), 2858 (C–H) cm^{-1} . $C_{82}H_{78}CoN_8O$ (1247.48): calcd. C 80.35, H 6.90, N 8.92; found C 80.77, H 6.68, N 8.73.

{5,15-Bis(2,6-dichlorophenyl)-10-[5-(13,17-diethyl-2,3,7,8,12,18-hexamethylporphyrin-5-yl)-9,9-dimethylxanthene-4-yl]corrole}cobalt(III) (5C):5C was obtained in 63% yield (0.021 g, 0.016 mmol) using the same procedure as described for **5M**, starting from **4C** (0.035 g, 0.026 mmol). ^1H NMR (C_5D_5N , 330 K): $\delta = -4.10$ (br. s, 1 H, NH-porphyrin), -3.49 (br. s, 1 H, NH-porphyrin), 1.67 (t, $^3J_{\text{H,H}} = 7.66$ Hz, 6 H, CH_3CH_2 -porphyrin), 2.33 (s, 6 H, CH_3 -dimethylxanthene), 2.88 (s, 6 H, CH_3 -porphyrin), 3.39 (s, 6 H, CH_3 -porphyrin), 3.47 (s, 6 H, CH_3 -porphyrin), 3.88 (m, 4 H, CH_3CH_2 -porphyrin), 6.27 (dd, $^3J_{\text{H,H}} = 7.28$, $^4J_{\text{H,H}} = 1.61$ Hz, 1 H, H-dimethylxanthene), 6.83 (dd, $^3J_{\text{H,H}} = 7.34$, $^4J_{\text{H,H}} = 1.62$ Hz, 1 H, H-dimethylxanthene), 7.14 (t, $^3J_{\text{H,H}} = 7.63$ Hz, 1 H, H-dimethylxanthene), 7.22 (t, $^3J_{\text{H,H}} = 7.63$ Hz, 1 H, H-dimethylxanthene), 7.71 (t, $^3J_{\text{H,H}} = 8.22$ Hz, 2 H, H_{meta} -dichlorophenyl), 7.86 (dd, $^3J_{\text{H,H}} = 8.16$, $^4J_{\text{H,H}} = 1.03$ Hz, 2 H, H_{meta} -dichlorophenyl), 8.00 (m, 4 H, 2 H-dimethylxanthene + 2 H_{meta} -dichlorophenyl), 8.32 (d, $^3J_{\text{H,H}} = 4.10$ Hz, 2 H, H_{β} -corrole), 8.64 (d, $^3J_{\text{H,H}} = 4.09$ Hz, 2 H, H_{β} -corrole), 8.78 (d, $^3J_{\text{H,H}} = 4.68$ Hz, 2 H, H_{β} -corrole), 9.09 (d, $^3J_{\text{H,H}} = 4.68$ Hz, 2 H, H_{β} -corrole), 9.90 (s, 1 H, H_{meso} -porphyrin), 9.91 (s, 2 H, H_{meso} -porphyrin) ppm. MS (MALDI/TOF): $m/z = 1300.80$ [M] $^{+}$; 1300.29 calcd. for $C_{76}H_{59}Cl_4N_8OCo$. UV/Vis (CH_2Cl_2): λ_{max} ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$) = 389.0 (160), 506.0 (16.7), 540.0 (11.9), 573.0 (9.22), 627.0 (4.70) nm. UV/Vis (pyridine): λ_{max} ($\epsilon \times 10^{-3} \text{ L mol}^{-1} \text{ cm}^{-1}$) = 406.0 (182), 444.0 (46.1), 456.0 (48.6), 506.0 (16.9), 541.0 (11.1), 577.0 (b.) (14.1), 591.0 (16.2), 621.9 (28.2) nm. IR $\tilde{\nu}$ = 3275 (N–H), 2960 (C–H), 2920 (C–H), 2860 (C–H) cm^{-1} . $C_{76}H_{59}Cl_4CoN_8O \cdot MeOH$ (1333.14): calcd. C 69.37, H 4.76, N 8.41; found C 69.11, H 5.11, N 8.04.

Table 3. Crystal data and structure refinement details for **5M(py)**₂

Formula	$C_{92}H_{85}CoN_{10}O \cdot 2C_6H_{12}$
M_w	1573.94
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	13.6160(4)
b [Å]	15.8720(5)
c [Å]	20.1957(7)
α [°]	83.092(1)
β [°]	79.587(1)
γ [°]	81.574(1)
V [Å ³]	4226.6(2)
Z	2
$d_{\text{calcd.}}$ [g cm ^{−3}]	1.237
T [K]	115(2)
μ (Mo- K_{α}) [mm ^{−1}]	0.260
θ range [°]	$1.74 < \theta < 24.02$
Index ranges	$-15 \leq h \leq 15$ $-18 \leq k \leq 12$ $-23 \leq l \leq 20$
Collected reflns	17425
Unique reflns	11702 ($R_{\text{int}} = 0.0524$)
Data/parameters	11702/1088
R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0700$; $wR_2 = 0.1523$
(all data)	$R_1 = 0.1385$; $wR_2 = 0.1853$
GOF	1.024
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ [e·Å ^{−3}]	0.373/−0.454

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]\}^{1/2}$. [b] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

X-ray Crystallography: X-ray diffraction experiment and data processing: Dark green single-crystals of prismatic morphology were grown in a mixture of pyridine and cyclohexane. A specimen of good quality was selected for low-temperature [$T = 115(2)$ K] X-ray diffraction. The X-ray source was graphite-monochromatized Mo- K_α radiation ($\lambda = 0.71073$ Å) from a sealed tube. Data were collected with a Nonius KappaCCD diffractometer, equipped with a nitrogen jet-stream low-temperature system (Oxford Cryosystems).^[34] Lattice parameters were obtained by a least-squares fit to the optimised setting angles of all collected reflections observed up to the maximum diffraction angle $2\theta_{\max} = 48^\circ$. Intensity data were recorded as φ and ω scans with κ offsets. Data reduction was performed using the DENZO program.^[35] Table 3 shows crystal data and some experimental details. Structure solution and refinement: The structure was solved by direct methods using the SIR97 program.^[36] Refinements were carried out by full-matrix least squares on F^2 using the SHELXL97 program^[37] and the complete set of reflections. The applied weighting scheme was $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$ where $P = (F_o^2 + 2F_c^2)/3$, A and B being updated parameters (at convergence, $A = 0.0715$ and $B = 4.8787$). Anisotropic thermal parameters were used for non-H atoms. Most hydrogen atoms were observed from Fourier synthesis. Hydrogen atoms were placed at calculated positions using a riding model [except both H(-N_{pyrrole}) atoms belonging to the free porphyrin moiety, for which the structural parameters were refined]. All H atoms were refined with a global isotropic thermal factor. One ethyl group belonging to the porphyrin moiety was disordered over two positions, showing sites occupation factors of 0.58(2)/0.42(2). Two cyclohexane solvent molecules co-crystallized with the complex. CCDC-240510 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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- J. P. Collman, R. Boulatov, C. J. Sunderland, *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2003**, vol. 11, p. 1–49.
- J. P. Collman, R. Boulatov, C. J. Sunderland, L. Fu, *Chem. Rev.* **2004**, *104*, 561–588.
- E. Kim, E. E. Chufan, K. Kamaraj, K. D. Karlin, *Chem. Rev.* **2004**, *104*, 1077–1133.
- J. M. Barbe, R. Guilard, *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, vol. 3, p. 211–244.
- J. P. Collman, P. S. Wagenknecht, J. E. Hutchison, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1537–1554.
- R. Guilard, M. A. Lopez, A. Tabard, P. Richard, C. Lecomte, S. Brandès, J. E. Hutchison, J. P. Collman, *J. Am. Chem. Soc.* **1992**, *114*, 9877–9889.
- R. Guilard, S. Brandès, A. Tabard, N. Bouhaida, C. Lecomte, P. Richard, J. M. Latour, *J. Am. Chem. Soc.* **1994**, *116*, 10202–10211.
- R. Guilard, S. Brandès, C. Tardieux, A. Tabard, M. L'Her, C. Miry, P. Gouerec, Y. Knop, J. P. Collman, *J. Am. Chem. Soc.* **1995**, *117*, 11721–11729.
- R. Guilard, J. M. Barbe, C. Stern, K. M. Kadish, *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2003**, vol. 18, p. 303–349.
- J. M. Barbe, F. Burdet, E. Espinosa, C. P. Gros, R. Guilard, *J. Porphyrins Phthalocyanines* **2003**, *7*, 365–374.
- C. Erben, S. Will, K. M. Kadish, *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, vol. 2, p. 233–300.
- R. Paolesse, *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, vol. 2, 201–232.
- R. Guilard, F. Jérôme, C. P. Gros, J. M. Barbe, Z. P. Ou, J. G. Shao, K. M. Kadish, *C. R. Acad. Sci. Ser. IIC* **2001**, *4*, 245–254.
- K. M. Kadish, L. Frémond, Z. P. Ou, J. Shao, C. Shi, F. C. Anson, F. Burdet, C. P. Gros, J. M. Barbe, R. Guilard, *J. Am. Chem. Soc.*, submitted.
- Z. Gross, N. Galili, I. Saltsman, *Angew. Chem. Int. Ed.* **1999**, *38*, 1427–1429.
- L. Simkhovich, N. Galili, I. Saltsman, I. Goldberg, Z. Gross, *Inorg. Chem.* **2000**, *39*, 2704.
- R. Paolesse, S. Nardis, F. Sagone, R. G. Khoury, *J. Org. Chem.* **2001**, *66*, 550–556.
- D. T. Gryko, *Chem. Commun.* **2000**, 2243–2244.
- D. T. Gryko, K. Jadach, *J. Org. Chem.* **2001**, *66*, 4267–4275.
- C. V. Asokan, S. Smeets, W. Dehaen, *Tetrahedron Lett.* **2001**, *42*, 4483–4485.
- D. T. Gryko, K. E. Piechota, *J. Porphyrins Phthalocyanines* **2002**, *6*, 81–97.
- D. T. Gryko, B. Koszarna, *Org. Biomol. Chem.* **2003**, *1*, 350–357.
- R. Guilard, D. T. Gryko, G. Canard, J.-M. Barbe, B. Koszarna, S. Brandès, M. Tasior, *Org. Lett.* **2002**, *4*, 4491–4494.
- B. J. Littler, M. A. Miller, C. H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle, J. S. Lindsey, *J. Org. Chem.* **1999**, *64*, 1391–1396.
- J. W. Buchler, D. P. K. Ng, *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, vol. 3, p. 245–294.
- K. M. Kadish, G. Moninot, Y. Hu, D. Dubois, A. Ibnlfassi, J. M. Barbe, R. Guilard, *J. Am. Chem. Soc.* **1993**, *115*, 8153–8166.
- R. Guilard, C. P. Gros, F. Bolze, F. Jérôme, Z. P. Ou, J. G. Shao, J. Fischer, R. Weiss, K. M. Kadish, *Inorg. Chem.* **2001**, *40*, 4845–4855.
- R. Guilard, F. Jérôme, J. M. Barbe, C. P. Gros, Z. P. Ou, J. Shao, J. Fischer, R. Weiss, K. M. Kadish, *Inorg. Chem.* **2001**, *40*, 4856–4865.
- K. M. Kadish, Z. P. Ou, J. G. Shao, C. P. Gros, J. M. Barbe, F. Jérôme, F. Bolze, F. Burdet, R. Guilard, *Inorg. Chem.* **2002**, *41*, 3990–4005.
- F. Burdet, J.-M. Barbe, Z. P. Ou, J. Shao, K. M. Kadish, E. Espinosa, C. P. Gros, R. Guilard, manuscript in preparation.
- F. Jérôme, C. P. Gros, C. Tardieux, J. M. Barbe, R. Guilard, *New J. Chem.* **1998**, *22*, 1327–1329.
- F. Jérôme, C. P. Gros, C. Tardieux, J. M. Barbe, R. Guilard, *Chem. Commun.* **1998**, 2007–2008.
- A. Mahammed, I. Giladi, I. Goldberg, Z. Gross, *Chem. Eur. J.* **2001**, *7*, 4259–4265.
- COLLECT Program, Data Collection Software, Nonius, Delft, The Netherlands, **1998**.
- Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307–326.
- A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.
- SHELXL97 Program, Program for the Refinement of the Crystal Structures, University of Göttingen, Germany, **1997**.

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