Expanded Porphyrins

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Siamese-Twin Porphyrin: A Pyrazole-Based Expanded Porphyrin Providing a Bimetallic Cavity**

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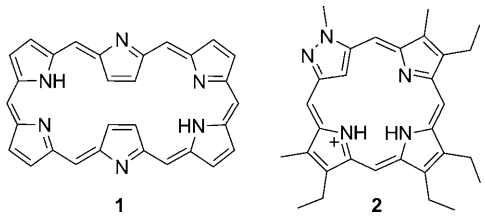
Dedicated to Professor Herbert W. Roesky on the occasion of his 75th birthday

Expanded porphyrins are synthetic analogues of porphyrins consisting of at least 17 atoms in a cyclic conjugated framework that contains at least three pyrrole or pyrrole-like heterocyclic subunits.[1] These macrocyclic systems have aroused great interest as near-IR-absorbing or -emitting chromophores and as two-photon dyes; their cavities are large enough to function as anion-recognition systems, and they may exhibit intriguing conformations.[2] Hexaphyrin **1** is a representative expanded porphyrin that exists in a number of conformations and oxidation states, capable of forming a variety of mono- and bimetallic complexes, including the formation of Möbius aromatic systems.[2d,3]



Naturally, the majority of expanded porphyrins employ pyrrolic building blocks but macrocycles incorporating, for instance, furan or thiophene building blocks are also known.[4] There are no expanded porphyrins containing pyrazole units. In fact, we are aware of only one porphyrin analogue incorporating a pyrazole unit, carbaporphyrin **2**, introduced in 2008 by Lash et al.[5]

We report here the synthesis of a pyrazole-based expanded porphyrin consisting of four pyrrole and two pyrazole units (Figure 1). This arrangement can be interpreted as the fusion of two $\{N_4\}$ porphyrin-like coordination sites. Thus, we like to dub it "Siamese-twin porphyrin". This naming is descriptive of the framework structure but does not imply the presence of porphyrinic conjugation pathways inherent to this system. We have previously shown pyrazoles with chelating side arms to be versatile bridging ligands in di- and multinuclear transition-metal complexes.[6] Consequently, one of the goals of the work was to bind two metals in close proximity in these highly preorganized binding pockets.[7]

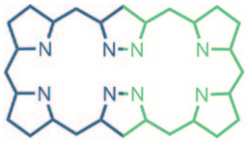


Figure 1. Framework of the Siamese-twin porphyrin highlighting the two fused constituent porphyrin-like macrocycles.

We are not the first to conceive the Siamese-twin porphyrin structure. Lind, in a 1987 dissertation, describes many innovative, but apparently unsuccessful, approaches toward this expanded porphyrin.[8] Recently we reported a bis(pyrrolylmethylene)pyrazole building block that was designed for the 3+3-type synthesis of the target macrocycle. Alas, this could not be achieved, though other interesting macrocycles were synthesized.[9] Three major problems became evident in our, as well as Lind's, work:[8,10] While MS evidence indicated that a macrocyclization of the appropriate building blocks was likely, the macrocycles could not be isolated. Moreover, the tremendous conformational flexibility and the large number of stereoisomers formed made it difficult to identify these intermediates by NMR spectroscopy. Lastly, our inability to reliably oxidize any of the methylene groups attached to the pyrazoles stymied progress.[11]

We thus decided to prepare the pyrrole–pyrazole hybrid **3** which is phenyl substituted in the *meso* positions as well as on the pyrazole (Scheme 1). Together with the β-ethyl substituents of the pyrrole, this was thought to enforce a conformation that places all substituents on the outside of the macrocyclic, nonconjugated precursor to the target structure.

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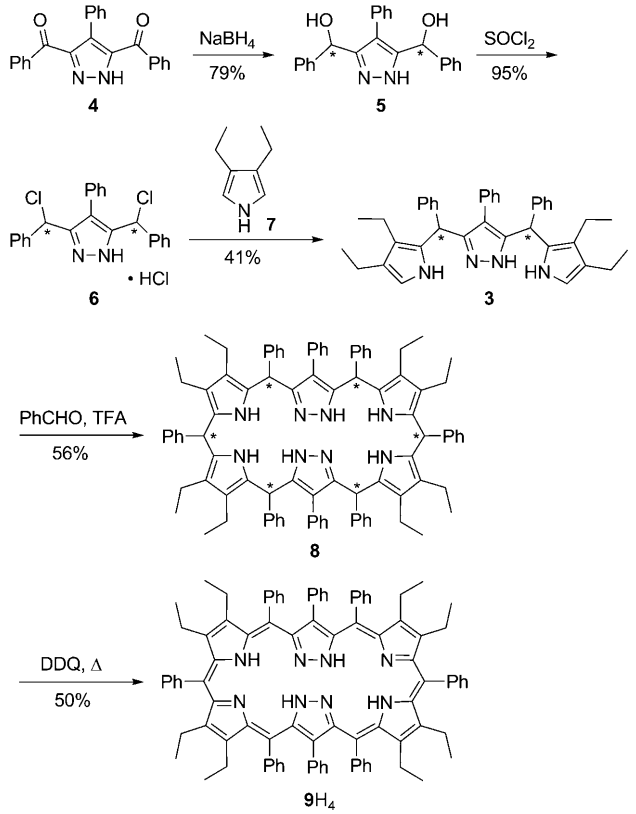


Scheme 1. Synthesis of the Siamese-twin porphyrin $\mathbf{9}H_4$ (see the Supporting Information for details). All stereocenters are marked with an asterisk.

We also reasoned that any oxidation in this electron-rich system ought to be facilitated. As we will demonstrate here, this strategy was crowned with success.

The preparation of the key building block **3** was made possible by our recent synthesis of 3,5-dibenzoyl-4-phenyl-1*H*-pyrazole (**4**),[12] and followed the general route (reduction to **5**, halogenation to **6**, followed by substitution with 3,4-diethylpyrrole (**7**)) as the synthesis of its non-phenyl-substituted analogue.[9] The modified pyrrole–pyrazole hybrid **3** was isolated as a mixture of stereoisomers.

The reaction of **3** with 1 equivalent of benzaldehyde and 1 equivalent of trifluoroacetic acid (TFA) in CH_2Cl_2 provided the "Siamese-twin porphyrinogen" **8**. The reaction time, the type of acid, and the concentrations of all components critically determine the outcome of this condensation reaction. The HR ESI(+) mass spectrum of **8** indicates the formation of this macrocycle (of composition $C_{92}H_{93}N_8$ for $[MH^+]$; Figures S2 and S3 in the Supporting Information). Its ^{1}H NMR spectrum is complex because of the presence of multiple stereoisomers (Figure S1). Light-yellow porphyrinogen **8** ($\varepsilon_{390\,nm} = 1250\,M^{-1}cm^{-1}$) is converted to a deep-green product using dichlorodicyano-*p*-quinone (DDQ; Figure 2).

The HR ESI(+) MS of this product indicates the composition $C_{92}H_{85}N_8$ (for $[MH^+]$). Both the mono- and diprotonated species ($C_{92}H_{86}N_8$ for $[MH_2^{2+}]$) are detectable (Figure S11). The UV/Vis spectrum of product $\mathbf{9}H_4$ is reminiscent of the spectra of bilindiones and related tetrapyrrolic pigments, including their minimal changes upon (de)protonation, and are distinctly nonporphyrinic (extinction coefficients at least one order of magnitude less than porphyrins, $\varepsilon_{398\,nm} = 15\,060\,M^{-1}cm^{-1}$, no Soret band, absence of multiple Q-bands; Figure 2).[13,14]

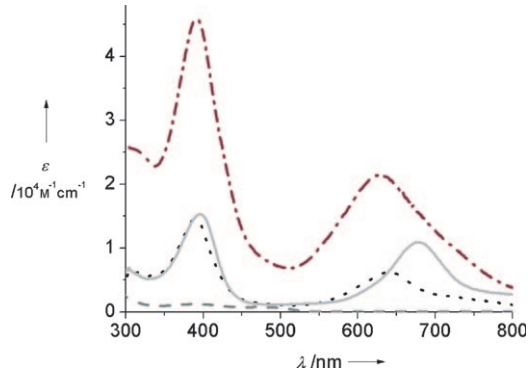


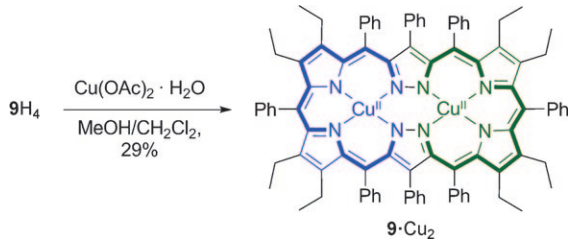
Figure 2. UV/Vis absorption spectra of **8** (-----), $\mathbf{9}\cdot Cu_2$ (–•–•) in CH_2Cl_2, $\mathbf{9}H_4$ (•••••) in $CH_2Cl_2 + 1\%$ NEt_3 and $\mathbf{9}H_4\cdot 2H^+$ (——) in $CH_2Cl_2 + 1\%$TFA.

The ^{1}H and ^{13}C NMR signals of $\mathbf{9}H_4$ are broadened beyond interpretation. The NMR spectra of the diprotonated form $\mathbf{9}H_4\cdot 2H^+\cdot 2(CF_3CO_2^-)$ are much simpler than those of the precursor **8** (or the free-base form), but still display some line broadening because of its conformational flexibility. Spectra recorded at −25 °C show a maximum sharpening of the signals (Figures S4 and S5). The presence of four distinct ethyl groups carrying diastereotopic CH_2 protons points toward a lower overall symmetry for $\mathbf{9}H_4\cdot 2H^+$ than anticipated for the target structure. A grossly twisted nonplanar geometry of $\mathbf{9}H_4\cdot 2H^+$ is also predicted by DFT calculations (BP86 functional, Figure S16). Two broad ^{1}H resonances at 11.4 and 13.3 ppm (2H each) were assigned to the pyrrole groups by ^{1}H,^{15}N HSQC spectroscopy, whereas a third broad peak at 15.4 ppm (2H) represents the protons on the pyrazole moieties (Figure S9). As expected, these protons undergo readily deuterium exchange with [D_4]methanol (Figure S7).

The low-field-shifted pyrrole/pyrazole NH signals show the absence of any diatropic ring current that would be indicative of a large aromatic π system (cf. the NH resonance around −2 ppm for a typical porphyrin). Alternatively, the positions of the NH signals may be attributable to the presentation of the NH groups toward the outside of the (aromatic) molecule. However, the computations show that the bulky phenyl and ethyl substituents prevent a complete inversion of the pyrrole/pyrazole units. In fact, NOESY spectra show a correlation of the NH signals, proving that they face each other. Thus, ligand $\mathbf{9}H_4\cdot 2H^+$ incorporates the nonaromatic π system shown, rather than the 26 π electron system that would be analogous to that of the hexaphyrins.[14]

Complexation of ligand $\mathbf{9}H_4$ with Cu^{II} resulted in the formation of a nonpolar (neutral), blue-green bimetallic complex with the composition $C_{92}H_{80}N_8Cu_2$ (for $[M^+]$), displaying a hyperchromic but otherwise only moderately shifted spectrum ($\varepsilon_{391\,nm} = 45\,000\,M^{-1}cm^{-1}$; Scheme 2, Figure 2).

The molecular structure of $\mathbf{9}\cdot Cu_2$ was determined by single-crystal X-ray diffractometry (Figure 3).[15] The struc-



Scheme 2. Synthesis of the bimetallic Siamese-twin porphyrin copper complex **9**·Cu_2, highlighting the presence of two independent conjugation pathways (in bold).

ture confirms the spectroscopically determined Siamese-twin porphyrin connectivity of the macrocycle and the presence of the bimetallic copper complex. Immediately noticeable are the strongly saddled individual copper-binding pockets and the overall helical twist of the macrocycle (D_2 symmetry).

The absence of counterions to the Cu^{II}_2 complex confirms the dianionic nature of each copper-binding pocket. Each Cu^{II} ion coordinates in a severely distorted square-planar fashion (the N1-Cu1-N3 angle is 167°; the N1-Cu1-N2 and N3-Cu1-N4 planes are 49° off coplanarity). The Cu···N distances range from 1.96 to 2.01 Å, with the longer bonds to the pyrazole N3 and N4 atoms. Overall, each binding pocket is more distorted than in, for instance, [{ß-octaethyl-*meso*-tetraphenylporphyrinato}Cu^{II}].[16] The Cu···Cu distance of 3.88 Å is well within the range of metal–metal separations in pyrazolate-bridged binuclear systems (3.5–4.0 Å).[6,17]

In (aromatic) metalloporphyrins, the neighboring C_α–N and C_α–C_{meso} bonds are equal in length. The corresponding bond lengths in **9**·Cu_2 differ, however. The bonds show an alternating long–short pattern, characteristic of a conjugated, but not macrocyclic-aromatic π system (Figure S15).[14] This finding is consistent with the optical properties of the macrocycle.

Magnetic susceptibility measurements were carried out for **9**·Cu_2 (Figure 4). At room temperature, the effective magnetic moment of 2.73 μ_B is close to the spin-only value of two uncoupled $S = 1/2$ Cu^{II} ions (2.66 μ_B for $g = 2.17$). When the temperature is lowered, μ_{eff} gradually increases to reach a maximum of 3.06 μ_B at 8 K. Experimental data were modeled to the isotropic Heisenberg–Dirac–van Vleck spin Hamiltonian for exchange coupling and Zeeman splitting,[18,19] revealing a sizeable ferromagnetic coupling constant of $J = +16.3\ cm^{-1}$ ($g = 2.17$) between the Cu^{II} centers.

The possibility of ferromagnetic coupling in [Cu^{II}(μ-*N*,*N*′-pyrazolato)$_2$$Cu^{II}$] complexes was predicted to exist,[20a] but all complexes reported hitherto exhibit only antiferromagnetic exchange (typically in the range $-245 \le J \le -70\ cm^{-1}$).[20,21] The helical twist of the macrocycle **9**·Cu_2 can be quantified by considering the two Cu1-N^{pz}-N^{pz}-Cu1′ torsion angles τ of 78.7° and 80.0°; that is, the two magnetic $d_{x^2-y^2}$ metal orbitals are nearly orthogonal to each other.[22] The quasi-orthogonality results in a minimal overlap integral through the bridging ligand. Hence, a vanishing antiferromagnetic exchange contribution ($J_{antiferro}$) to the overall coupling term ($J = J_{ferro} + J_{antiferro}$) is observed, rendering the system ferromagnetically coupled. Although the torsion-angle-dependent change of the sign of the metal–metal interaction from antiferro- to ferromagnetic was observed for several bridging ligands,[23–26] the realization of ferromagnetic coupling is unprecedented for bridging pyrazolate units.

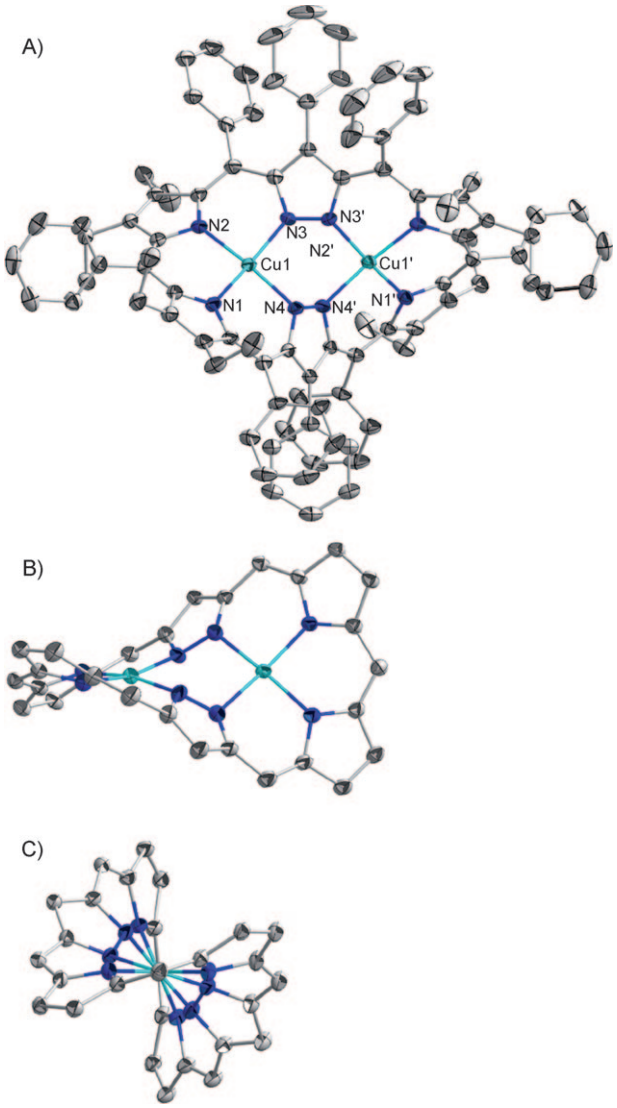


Figure 3. ORTEP plot (thermal ellipsoids set at 50% probability) of the molecular structure of **9**·Cu_2. A) Top view and numbering scheme used. B) Side view illustrating the near-orthogonal twist between the two (idealized) square-planar {N_4Cu} planes. C) View along the Cu1–Cu1′ axis. For clarity, all hydrogen atoms and solvent molecules (four toluene molecules per unit cell) are omitted. In addition, phenyl and ethyl groups are omitted for clarity in (B) and (C). For further details, see the Supporting Information.

In conclusion, we have synthesized a pyrazole-based expanded porphyrin **9**H_4 and its homobimetallic Cu^{II} complex **9**·Cu_2. This Siamese-twin porphyrin merges the architecture of two porphyrinoid {N_4} coordination sites, yet neither of the individual coordination sites, nor the entire macrocycle show porphyrinoid aromaticity. The formal replacement of a pyrrolic building block in a porphyrin by a pyrazole was previously shown to inhibit the aromatic conjugation pathways.[5a] This finding is mirrored in the

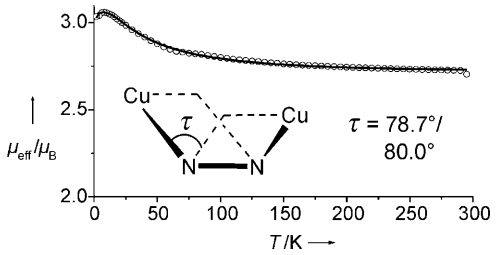


Figure 4. Plot of μ_{eff} versus T for **9**·Cu_2 (magnetic field of 0.5 T from 295 to 2.0 K); experimental data (○) and calculated curve fit (——). Inset: Illustration of the Cu-N^{pz}-N^{pz}-Cu dihedral angle.

pyrazole-based macrocycle **9**H_4. The large twist inherent to the macrocycle allowed the first preparation of a ferromagnetically coupled doubly pyrazolato-bridged dicopper(II) complex.

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