Porphyrin Analogues

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Azacalixphyrin: The Hidden Porphyrin Cousin Brought to Light**

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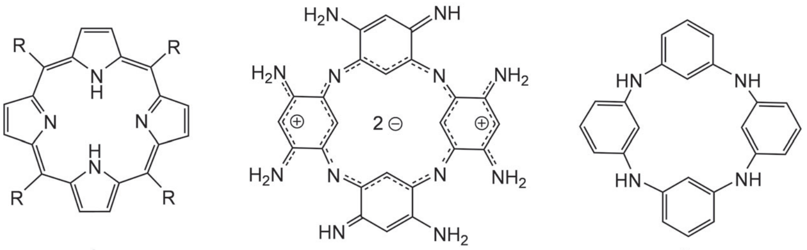
Porphyrins **1** are probably the most important and adaptable macrocycles since their research concerns areas ranging from chemistry to materials science, physics to biology, and engineering to medicine.[1,2] They are highly conjugated heterocyclic macrocycles composed of a 16-membered ring containing four nitrogen atoms and $4n+2$ cyclically delocalized π electrons ($4n+2=18$) implying aromaticity according to the Hückel's rule.

The exceptional versatility of porphyrins can be traced back, not only to their peculiar electronic and structural features but also to their synthetic accessibility.[1] Consequently, the access to a new isostructural (a 16-membered macrocycle bearing four nitrogen atoms separated by three carbon atoms) and isoelectronic analogue (an aromaticity generated by 18 delocalized π electrons) is of interest. Isomers of porphyrins and azaporphyrin derivatives, such as porphyrazines and phthalocyanines, have an impressive history.[2] Introduction of *meta*-phenylene subunits that are present in hemiporphyrazines, hemiphthalocyanines, or *m*-benziporphyrins have also found great interest, especially when the phenyl subunit can be converted to access aromatic conjugation.[3] However, beside all these pyrrol-based macrocycles, all attempts to isolate aza-analogue of porphyrins without a pyrrol subunit have been unsuccessful, and this therefore remains an extreme challenge for chemists. Indeed, no clear-cut synthetic route could be developed owing to the very limited strategies that allow the formation of an aromatic tetraazamacrocycle.

Herein, we report a new strategy affording a simple and efficient synthesis of a "pyrrol-free" porphyrin analogue, **2** (Figure 1). A salient feature of porphyrins **1** is the presence of nitrogen atoms in the ring at positions 1,5,9,13 (i.e. every three carbon atoms of the ring). Such a pattern is also present in azacalix[4]arenes **3**, an emerging class of macrocycles in calixarene chemistry for which the bridging atoms are always in *meta* position relative to each other with respect to the phenyl groups.[4] Compound **2** is an analogue to both azacalix[4]arenes **3** and porphyrins **1**. To underscore this analogy, we propose for **2** the term azacalixphyrin in order to denote this family of macrocycles.



1 **2** **3**

Figure 1. Tetraazamacrocycles: porphyrin **1**, azacalixphyrin **2**, azacalix[4]arene **3**.

The synthesis of **2** was inspired by Nietzki's work (1887)[5] who observed spontaneous oxidation in air of the electron-rich tetraaminobenzene **4** yielding the 2,5-diamino-1,4-benzoquinonediimine **5** (Scheme 1). In 1966, Dähne and Leupold reported theoretical studies which suggested, for this type of quinones, the so-called "coupling principle".[6] This concept explains that the overall 12π electron system in **5** should be best described as two 6π electron subunits connected through two C−C single bonds, thus providing a poor electronic conjugation (between the upper and lower parts of the molecule in Scheme 1). The coupling principle was finally

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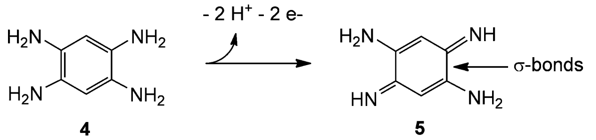
Supporting information for this article (experimental details, characterization data of the molecules, quantum mechanical calculations, spectroscopic, and thermodynamic data) is available on the WWW under http://dx.doi.org/10.1002/anie.201301217.



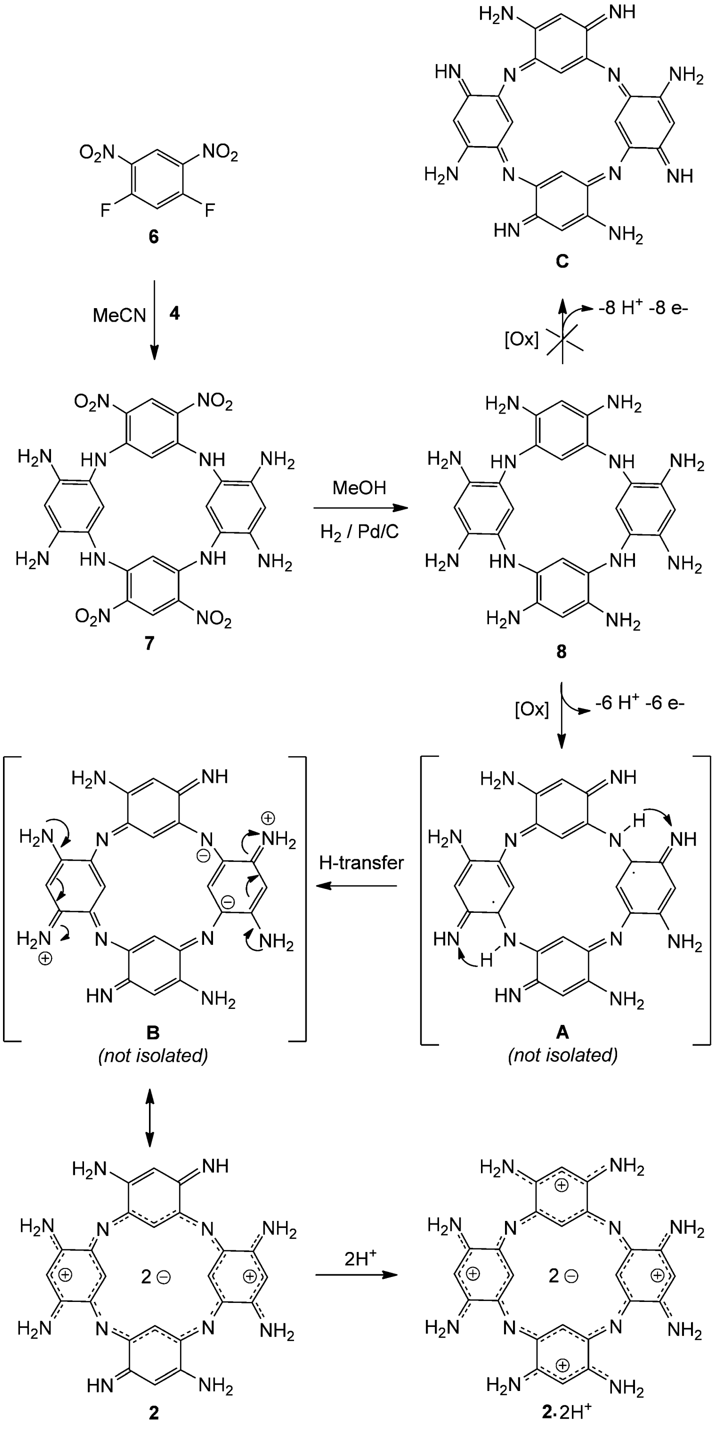
Scheme 1. Preparation and "coupling principle" in aminobenzoquinonediimines **5**.

confirmed experimentally in 2003 from X-ray diffraction studies.[7] Extrapolating this concept to the synthesis of π-conjugated cycles, we anticipated that a new family of aromatic tetraazamacrocycles could be accessible by the combination of four non-aromatic subunits of type **5**. To this end, the octoaminoazacalix[4]arene **8** was first synthesized because it can be regarded as an interconnected form of **4** that should undergo oxidation processes—by analogy with **4**—leading to a π-conjugated cycle (Scheme 2).

The preparation of **8** required the synthesis of the dinitrodiamino derivative **7**, which was prepared by a condensation reaction between tetraaminobenzene **4** and an electron-deficient aryl **6** in MeCN in the presence of base (Scheme 2). Macrocycle **7** was obtained in 92% yield as a brown solid and fully characterized. Its reduction by catalytic hydrogenation on Pd/C (p_{H_2} =5 bar) in MeOH afforded the electron-rich macrocycle **8** which, under air, at room temperature, is oxidized into the bis-zwitterionic tetraazamacrocycle **2** as a green solid in 14% yield (Scheme 2).

The formation of **2** occurs most likely via a diradical semiquinoid intermediate **A** (not isolated) obtained through a net six-electron oxidation process. Intermediate **A** would then rearrange by : 1) proton migration from the N–H bridge to the more basic imine site, 2) coupling of the two radicals, 3) redistribution of the π electrons, affording **B**. Intermediate **B**—that can be viewed as a limit resonance form of **2**—is finally stabilized into **2** by intramolecular delocalization of the charges. Note that a complete oxidation of **A** that would have furnished **C**—by analogy with the full oxidation of **4** into **5**—is not observed because of the instability inherent to the anti-aromatic nature of **C** ($4n=16\pi$ electrons). Upon oxidation of **8** into **2**, the solution showed a marked color change from red to dark-green. No melting associated decomposition was observed for **2** up to 300 °C. Macrocycle **2** is soluble in DMF, MeOH (poorly), and DMSO at room temperature.

Azacalixphyrin **2** was experimentally characterized by NMR spectroscopy and high-resolution mass spectrometry (HRMS) as well as investigated with ab initio models. The HRMS spectrum of **2** shows a signal at m/z 479.2160 $[(M+H)^+]$ as expected for $C_{24}H_{22}N_{12}$ (error < 1 ppm). A well-resolved ^{1}H NMR spectrum of **2** shows four signals (Figure 2), indicating an average (symmetrical) structure that can be explained by a fast interconversion between tautomers under the experimental conditions, as observed in quinoid chemistry (see Supporting Information).[7,8] The most striking feature of this spectrum is the chemical shift of the internal CH protons, observed in an upfield region at $\delta=-2.1$ ppm, as a result of the presence of a diatropic ring current in **2** (Figure 2). This observation could be confirmed by theoretical calculations that demonstrate that only the presence of high electron density (located in the 16-membered ring and generating a dianionic cycle) allows such an upfield signature (see Supporting Information). To quantify the aromaticity of **2**, we



Scheme 2. Synthesis of azacalixphyrins.

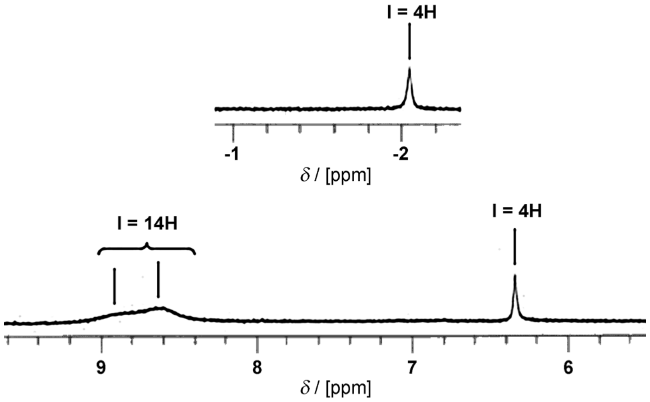


Figure 2. ^{1}H NMR spectrum of azacalixphyrin **2** in [D$_6$]DMSO at room temperature. The range $5.5 < \delta < -1$ ppm has been omitted because of the absence of signals (except those of solvents, see Supporting Information); I = integration.

calculated the nucleus-independent chemical shifts, NICS(0) and NICS(1), at the center of the ring. The result, −6 ppm for both values, suggests a strongly diatropic value in agreement with an aromatic compound (benzene and naphthalene ca. −8 and −10 ppm, respectively, and porphyrins ca. −16 ppm).[9]

An X-ray diffraction study on single crystals of the protonated form $\mathbf{2}\cdot 2\,\mathrm{HCl}$ confirmed the features deduced from the spectroscopic data (Figure 3).[10] The eight atoms constituting the diaminobenzoquinone–diimine moiety perfectly fit within a plane (the maximum deviation from planarity being equal to 0.034(7) Å).

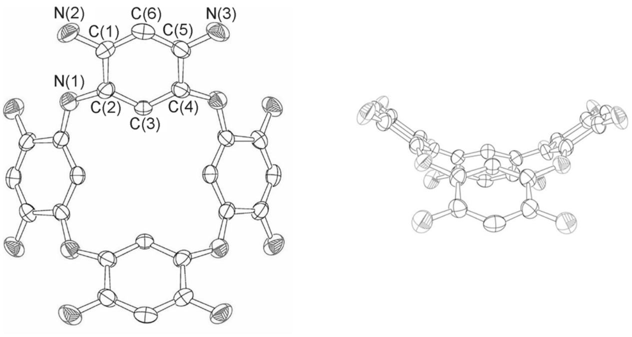


Figure 3. Structure of $\mathbf{2}\cdot 2\,\mathrm{HCl}$ (anisotropic displacement parameters set at 50%): top view and side view.[18] Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å]: N(1)–C(2) 1.337(10), C(2)–C(3) 1.374(10), C(3)–C(4) 1.374(10), C(4)–C(5) 1.455(11), C(2)–C(1) 1.459(11), N(2)–C(1) 1.311(9), C(1)–C(6) 1.362(11), C(6)–C(5) 1.365(11), C(5)–N(3) 1.314(10).

The dihedral angles around the nitrogen atoms connecting the cycles are close to 160° and the angle between planes of the neighboring diaminobenzoquinonediimine moieties is 75°. Hence, macrocycle **2** adopts a nonplanar saddle conformation (Figure 3) because of the repulsion of the internal C−H hydrogen atoms. Theoretical calculations on $\mathbf{2}\cdot 2\,\mathrm{H}^+$ confirmed that the D_{2d} structure is a true minimum on the potential energy surface. The presence of two hydrogen atoms on N(2) and N(3) could be confirmed experimentally (see Supporting Information). Examination of the bond lengths within the N(1)-C(2)-C(3)-C(4) and N(2)-C(1)-C(6)-C(5)-N(3) moieties in $\mathbf{2}\cdot 2\,\mathrm{HCl}$ (Figure 3) reveals a bond equalization because of the delocalization of the negative and positive charges, respectively . The C(1)-C(2) and C(4)-C(5) distances of 1.459(11) and 1.455(11) Å, respectively, indicate the relatively poor delocalization between the aromatic cycle and the external "cyanine-type" subunits in $\mathbf{2}\cdot 2\,\mathrm{HCl}$, as observed between the aromatic ring and the external C=C bonds in porphyrins **1** (R = Ph).[11] As a result, azacalixphyrin $\mathbf{2}\cdot 2\,\mathrm{HCl}$ is a diprotonated zwitterion that can be formally regarded as a combination of: 1) an aromatic ring in which the two negative charges are stabilized by intramolecular delocalization, and 2) four positively charged cyanine-like subunits which are mutually connected to the ring by two CC bonds.

Surprisingly, azacalixphyrin **2** is stable and could be exposed to air for months as a solid or for days in solution without detectable changes. This contrasts with other aromatic dianions which readily decompose as they are very reactive toward a broad range of compounds, such as oxidants and protic solvents (especially water).[12] The high stability of **2** is not only due to the aromatic behavior of the cycle but to the zwitterionic character of the molecule.

The absorption spectrum of **2** in DMSO exhibits four main peaks in the visible light region [$\lambda_{\max} = 409$ ($\varepsilon^{409} = 19800\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$), 441 ($\varepsilon^{441} = 27700\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$), 492 ($\varepsilon^{492} = 18900\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) and 649 nm]($\varepsilon^{649} = 36300\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$)], and an additional broad and intense absorption in the NIR region ($\lambda_{\max} = 890$ nm, $\varepsilon^{890} = 17000\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$, see Figure 4).

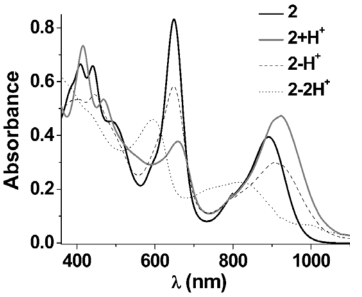


Figure 4. UV/Vis/NIR absorption spectra of **2** and the protonated/deportonated species of the azacalixphyrin **2** obtained by addition of HCl or NaOH. Solvent: DMSO/water (9:1 *v*/*v*); $T = 25.0(1)$°C; (**2**) $[\mathbf{2}]_0 = 2.38\times10^{-5}$ M; ($\mathbf{2}+\mathbf{H}^+$) $[\mathrm{H}^+]_0/[\mathbf{2}]_0 = 85565$; ($\mathbf{2}-\mathbf{H}^+$) $[\mathrm{OH}^-]_0/[\mathbf{2}]_0 = 21.8$; ($\mathbf{2}-\mathbf{2H}^+$) $[\mathrm{OH}^-]_0/[\mathbf{2}]_0 = 52.9$.

No significant emission radiation could be detected owing to the very low energy of the excited state as indicated by the energy gap law.[13] The acido-basic properties of **2** were examined in DMSO/water (9:1 *v*/*v*). Upon addition of HCl (Figure 4 and Supporting Information), the formation of the monoprotonated form ($\mathbf{2}+\mathbf{H}^+$) was characterized by a less intense absorption at 649 nm, a significantly faded color (i.e. the color of the solution turns from green to dark grey), while the NIR band experienced a joint bathochromic ($\Delta\lambda = +34$ nm) and hyperchromic shift. The diprotonated species ($\mathbf{2}+\mathbf{2H}^+$) was not accessible under our experimental conditions (see Supporting Information). The effects of base on the absorption properties of **2** could be also observed (Figure 4). The first deprotonation (i.e. formation of **2**–$\mathbf{H}^+$) induces a trifling bathochromic ($\Delta\lambda = +16$ nm) and hypochromic shift of the NIR absorption band, whereas the second deprotonation (i.e. formation of **2**–$2\mathbf{H}^+$) has a more significant impact ($\Delta\lambda = -70$ nm). These spectrophotometric data clearly confirmed that the electronic distribution is affected by the pH value. We underline that the protonation state of the peripheric nitrogen atoms does not affect significantly the zwitterionic aromatic macrocycle, as the NIR signature band remains present.

We also investigated the metal coordination properties of **2** by absorption spectrophotometric means. Figure 5 shows the UV/Vis/NIR absorption titration of **2** by $Co(acac)_2$, which clearly indicated the formation of two metal complexes with **2**. Coordination of the first "Co(acac)" unit induces hypochromic shifts of the two intense absorptions at 649 and 890 nm as well as variations in the 400–500 domain. Binding of a second "Co(acac)" unit leads to further spectral variations with the NIR band slightly increases with formation of a broad shoulder at lower energies. DFT calculations indicate that complexation might occur on two opposite binding cavities of **2** (see Supporting Information).

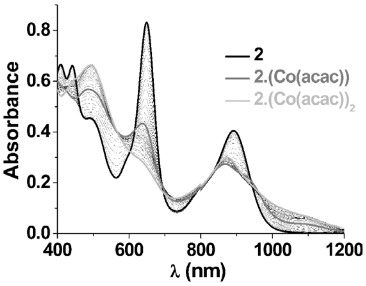


Figure 5. UV/Vis/NIR absorption titration of **2** with $Co(acac)_2$. Solvent: DMSO; $T = 25.0(1)$°C; $[\mathbf{2}]_0 = 2.38\times10^{-5}$ M; $[Co(acac)_2]_0/[\mathbf{2}]_0 = 0$; $[Co(acac)_2]_0/[\mathbf{2}]_0 = 10.6$; $[Co(acac)_2]_0/[\mathbf{2}]_0 = 37.3$.

Calculations on **2** carried out at the PCM-TD-PBE0/6-311++G(2d,2p) level were performed to gain insights into the nature of the two first low-energy bands (see Supporting Information). The first absorption is predicted at 887 nm and is significantly dipole-allowed (oscillator strength, f, of 0.2). This value is in remarkable agreement with experiments (ca. 890 nm). The electronic density reorganization corresponding to this transition is depicted in Figure 6. It is clearly a highly-delocalized excited-state, with a partial charge-transfer—occurring through the σ-like bond (a finding typical of alternating systems)—from the imine to the amine subregions. This enhanced delocalization accounts for its relatively small transition energy. The next significant band is computed at 588 nm ($f = 0.4$) and it corresponds to the strong 647 nm experimental band, the error being in the line of the TD-DFT accuracy.[14] Like the first absorption, this excitation implies a full electronic reorganization, but with no significant charge-transfer character.

The electronic properties of **2** were also examined by cyclic voltammetry (CV) at 10^{-3} M in DMSO/$TBAClO_4$ 0.1 M.

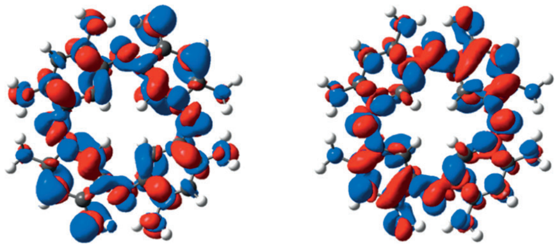


Figure 6. Electronic density difference (EDD) plots for the first two calculated absorption bands (left: 887 nm, right: 588 nm). Red/blue regions indicate gain/loss of electron densities resulting from absorption.

The CV exhibited a reversible redox wave at 0.543 V versus Ag/AgCl resulting from a two-electron oxidation process ($\Delta E_{1/2}(\text{ox}) = 0.521$ V). Interestingly, the macrocycle could also be reduced at −0.472 V ($\Delta E_{1/2}(\text{red}) = -0.435$ V), leading to an electrochemical HOMO–LUMO gap of 1.01 eV (E_g), also in the line of the DFT calculations.

In summary, the newly designed azacalixphyrin **2** a novel isostructural and isoelectronic "pyrrol-free" analogue of porphyrins[15] was easily prepared in two straightforward steps. The synthetic accessibility—based on a new strategy—is highly versatile because of the nature of the intermediates **7** and **8** for which substituents on the peripheral nitrogen atoms will be easily introduced and varied for tuning the properties of the macrocycles (solubility, geometry, donor/acceptor capability). Azacalixphyrin **2** revealed a high stability (even in the presence of water under air) owing to its unusual bis-zwitterionic character. As they are NIR-absorbing organic materials with a very low gap ($E_g = 1.01$ eV), the potential applications of these new macrocycles are diverse and extensive in many technological sectors.[16] With macrocycles such as **2**, we enter also the field of coordination chemistry[17] as macrocyclic ligands as indicated both by preliminary DFT calculations and coordination studies. We can thus envision for these new dyes exceptional versatility by analogy to porphyrins.[1]

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[18] CCDC 913387 ($\mathbf{2}\cdot 2\,\mathrm{HCl}$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.