Expanded Porphyrins

meso-Aryl-Substituted [26]Hexaphyrin(1.1.0.1.1.0) and [38]Nonaphyrin(1.1.0.1.1.0.1.1.0) from Oxidative Coupling of a Tripyrrane**

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In recent years, there has been a surge in the development of expanded porphyrins which has been boosted by their unique optical, electrochemical, and coordination properties, as well as their potential uses as receptors of anionic or neutral substrates.[1] Rubyrin, which represents a class of [26]hexaphyrin(1.1.0.1.1.0) macrocycles, was first synthesized and characterized by Sessler et al. as a dication of a β-dodeca-(alkyl)-substituted molecule.[2,3] A range of core-modified rubyrins that bear *meso*-aryl substituents have also been explored by Chandrashekar and co-workers.[4] The rubyrins prepared so far all exhibit a strong diatropic ring current in line with their 26-π-aromatic circuit. Furthermore, dicationic rubyrins have been shown to serve as a good receptor for anions,[2,4] but structural details of resultant complexes have been only poorly studied except for the case of the parent rubyrin. Herein we report the concise synthesis of *meso*-aryl-substituted rubyrin **2** and interesting anion-recognition behavior of its dication. To the best of our knowledge, an all-aza isomer of a *meso*-aryl-substituted rubyrin has not been reported, despite its importance in the chemistry of expanded porphyrins. Besides the rubyrin derivative, its higher homologue nonaphyrin(1.1.0.1.1.0.1.1.0) was also obtained, and its structural characterization is also described here.

Following the method reported by Chandrashekar and co-workers,[4b,c] a solution of *meso*-pentafluorophenyl-substituted tripyrrane **1**[5] in CH_2Cl_2 was treated with 0.5 equivalents of trifluoroacetic acid (TFA) in CH_2Cl_2 for 90 minutes at room temperature, then 3 equivalents of chloranil (tetrachloro-1,4-benzoquinone) was added, and the mixture was subsequently heated at reflux for 90 minutes. Sequential separations by column chromatography provided the rubyrin 5,10,19,24-tetrakis(pentafluorophenyl)-[26]hexaphyrin-(1.1.0.1.1.0) (**2**) as a stable violet solid in 24% yield, and 5,10,19,24,33,38-hexakis(pentafluorophenyl)-[38]nonaphyrin

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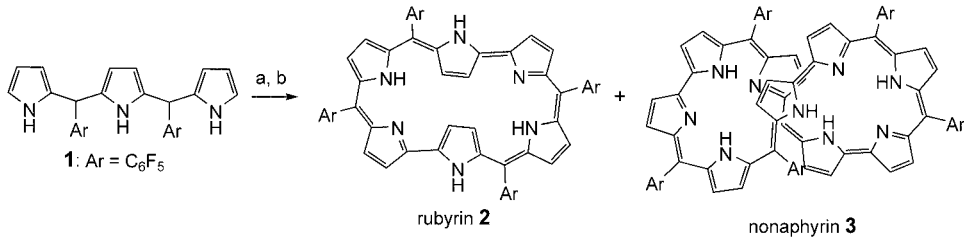


Scheme 1. Oxidative coupling reaction of *meso*-pentafluorophenyl-substituted tripyrrane **1** to form the rubyrin [26]hexaphyrin(1.1.0.1.1.0) (**2**) and [38]nonaphyrin(1.1.0.1.1.0.1.1.0) (**3**): a) TFA, CH_2Cl_2; b) chloranil, reflux.

(1.1.0.1.1.0.1.1.0) (**3**) as a green solid in 9% yield (Scheme 1).[6] Interestingly, MALDI-TOF-MS analysis of the reaction mixture revealed the formation of higher homologues such as dodecaphyrin and pentadecaphyrin, but macrocycles that may have formed through acidolysis of **1** were not detected.

The rubyrin **2** exhibited its parent-ion peak at $m/z = 1105$ ($[M+H]^+$). Its ^{1}H NMR spectrum taken in $CDCl_3$ revealed the inner β-CH protons at $\delta = -2.11$ and -2.18 ppm as a pair of doublets ($J = 3.4$ Hz), the outer β-CH protons at $\delta = 9.16$ (2H, doublet, $J = 4.1$ Hz), 8.74 (4H), and 8.66 ppm (2H, doublet, $J = 4.1$ Hz), and the outer NH protons at $\delta =$ 11.5 ppm. The inner NH protons appeared at $\delta = 1.63$ ppm as a singlet. These data indicate a diatropic ring current for **2**. The structure of **2** was confirmed by X-ray crystallographic analysis[7] and adopts a parallelogram shape in which the pyrrole rings C and F of the bipyrrolic subunits are inverted and canted by 30° from the mean plane defined by the other pyrrole rings (Figure 1, type I conformation as shown in Scheme 2). This type of conformation was proposed for a dioxarubyrin macrocycle on the basis of the ^{1}H NMR spectroscopic data,[4e] but has now been revealed for the first time for a free-base *meso*-aryl-substituted rubyrin. In line with the 26-π-electron aromaticity, the bond lengths of bridging C–C bonds are rather similar. There are two intramolecular hydrogen-bonding interactions at the dipyrromethene moieties with a N–H···N distance of 1.99 Å and an angle of 125°. This shorter hydrogen-bonding distance accounts for the rather downfield shift of the inner NH protons that appear in a strongly shielding region.

The absorption spectrum of free-base **2** exhibited a sharp Soret-like band at 537 nm ($\varepsilon = 1.70 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$) and a weak broad Q-like band with peaks at 802, 832, and 919 nm (Figure 2), similar to the absorption spectra of other rubyrins.[2,4,8] Protonation of **2** upon addition of an excess amount of TFA in CH_2Cl_2 led to a red shift and intensification of the Soret-like band to 555 nm ($\varepsilon = 3.3 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$). Curiously, the protonation of **2** with HCl caused intensification of its Soret-like band ($\varepsilon = 3.4 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$) at 518 nm, which was distinctly blue-shifted relative to the free-base **2**. These results suggest that the resultant rubyrin dication salts **2**·2TFA and **2**·2HCl may have different conformations and thus different electronic structures.

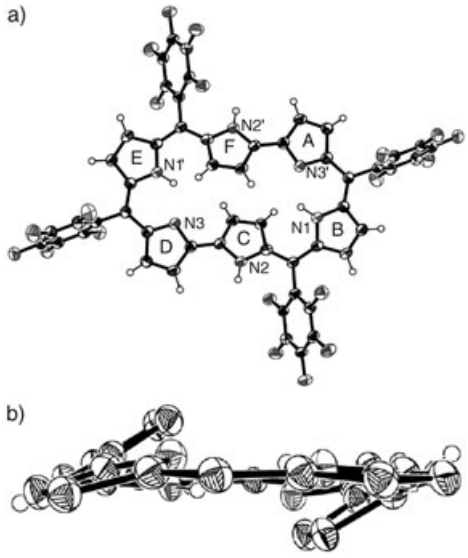
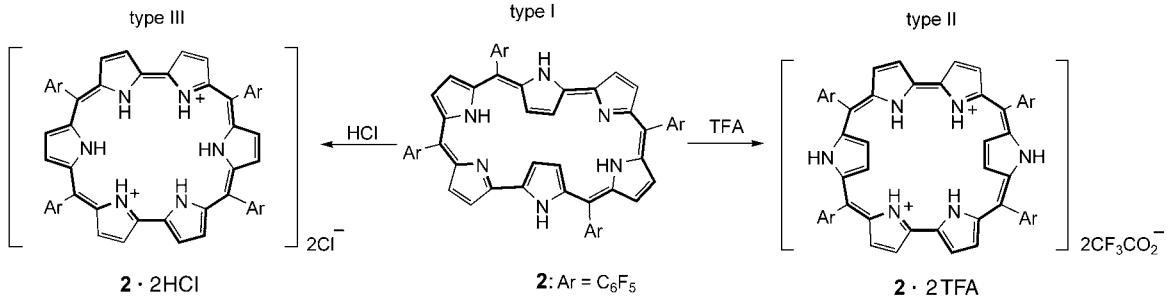


Figure 1. X-ray crystal structure of **2**: a) top view and b) side view. The thermal ellipsoids were scaled to the 50% probability level. The solvent molecule was omitted in the top view, and *meso*-pentafluorophenyl substituents and hydrogen atoms at the β position were omitted in the side view for clarity.



Scheme 2. Conformational changes in **2** upon protonation with HCl and trifluoroacetic acid (TFA).

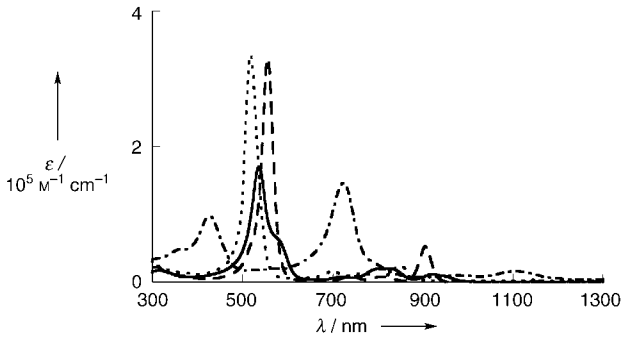


Figure 2. UV/Vis absorption spectra of **2** (——), **2**·2TFA (– – –), **2**·2HCl (·····), and **3** (–·–·) recorded in CH_2Cl_2.

The ^{1}H NMR spectrum of salt **2**·2TFA in [D_8]THF showed D_2O-exchangeable broad peaks at $\delta = -3.86$ and 16.5 ppm in a 2:1 ratio that have been assigned to the inner and outer NH protons. In [D_8]THF containing a small amount of D_2O, the spectrum showed a sharp singlet at $\delta = -3.30$ ppm and two signals at $\delta = 10.9$ and 10.2 ppm in a 1:1:1 ratio which have been assigned to the inner and outer β-CH protons, respectively. These data suggest a symmetric structure, with two bipyrrolic moieties pointing inward and two pyrroles pointing outward (type II conformation in Scheme 2). In contrast, the ^{1}H NMR spectrum of salt **2**·2HCl in $CDCl_3$ revealed the β-CH protons at $\delta = 10.6$, 9.75, and 8.95 ppm in a 1:1:1 ratio, and the NH protons at $\delta = -3.05$ and -3.26 ppm in a 1:2 ratio, which indicates a different symmetric structure with all the pyrrole rings pointing inward (type III conformation in Scheme 2).

Both the structures of **2**·2TFA and **2**·2HCl were explicitly determined by single-crystal X-ray diffraction analysis (Figure 3 and Figure 4, respectively).[9,10] The salt **2**·2TFA displays a rectangular conformation with the pyrrole rings B and E inverted and canted by 35° with respect to the mean plane defined by the other four pyrrolic rings (Figure 3).

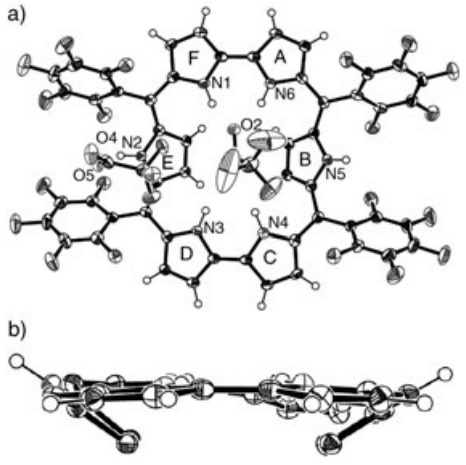


Figure 3. X-ray crystal structure of **2**·2TFA: a) top view and b) side view. The thermal ellipsoids were scaled to the 50% probability level. Solvent molecules were omitted in the top view, and *meso*-pentafluorophenyl substituents, hydrogen atoms at the β position, and counteranions were omitted in the side view for clarity.

meso-Pentafluorophenyl substituents are canted by about 50° in a V-shape to establish a channel above the molecular plane along which two trifluoroacetate anions, one molecule of TFA, and one solvent molecule (THF) are aligned. One trifluoroacetate anion lies just above the center of the macrocycle and is bound by the four bipyrrolic amine groups through hydrogen-bonding interactions, with N–H···O distances of about 1.9 Å, while the other trifluoroacetate anion resides at the edge of the macrocyclic ring, hydrogen-bonded with the amine group of the inverted pyrrole E (N–H···O: 1.94 Å, 140°). On the other hand, the salt **2**·2HCl exhibits a domelike ruffled structure in which all the pyrrole rings take inward orientation to interact with two chloride anions (Figure 4). One chloride anion is positioned

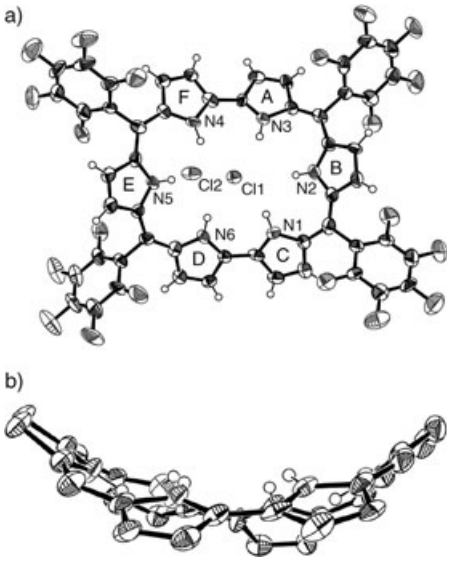


Figure 4. X-ray crystal structure of **2**·2HCl: a) top view and b) side view. The thermal ellipsoids were scaled to the 50% probability level. Solvent molecules were omitted in the top view, and *meso*-pentafluorophenyl substituents, hydrogen atoms at the β positions, and counteranions were omitted in the side view for clarity.

1.2 Å above the macrocycle mean plane and is bound by the four bipyrrolic NH protons with distances of 2.34, 2.33, 2.39, and 2.42 Å, while the other chloride ion lies near to the NH of pyrrole E through hydrogen-bonding interaction (N–H···Cl: 2.42 Å, 142°), thus lying slightly off-center. Furthermore, a molecule of acetic acid, which results from hydrolysis of ethyl acetate (the solvent used in crystallization), lies next to the second chloride anion and is held by the macrocycle through hydrogen-bonding interactions between the acid C=O moiety and the NH group of pyrrole B, and between the acid OH group and the chloride counteranion bound by the NH of pyrrole E (see Supporting Information).

The type III structure of **2**·2HCl is essentially the same as that of the β-dodeca(alkyl)-substituted-rubyrin–HCl salt reported by Sessler et al. which exhibited a blue-shifted Soret-like band at $\lambda = 505$ nm.[2] These results clearly indicate that the dication of rubyrin **2** can change its conformation in response to added acids, through interactions with counteranions.[11] This comes from conformational flexibility, partic-

ularly rotational freedom about the bipyrrolic bonds. Interestingly, the structural changes among types I, II, and III are linked, through changes in the conjugated electronic network, to the spectral changes, which can be detected easily. Preliminary measurements have shown that methanesulfonic acid behaves in essentially the same manner as TFA towards **2**, but the addition of H_2SO_4 or H_3PO_4 leads to two sharp Soret-like bands around 515 and 555 nm, which suggests the presence of both type II and type III structures. Conformational flexibility of **2** has been examined by variable-temperature ^{1}H NMR measurements. The spectrum did not change up to 60 °C, but became broader at 80 °C and converged to a signal at $\delta = 8.68$ ppm for the β protons and a broad signal at $\delta = -1.82$ ppm for the NH protons at 120 °C, probably indicating rapid flipping of the bipyrrolic moieties (see Supporting Information).

Nonaphyrin **3** exhibited its parent-ion peak at $m/z = 1655$ (M^+) in its FAB mass spectrum. Its ^{1}H NMR spectrum displayed eighteen different signals for the peripheral β protons, among which seven β protons resonated in a slightly upfield region at $\delta = 6.30$, 6.08, 5.67, 5.54, 4.73, and 4.64 ppm relative to the others. Two D_2O-exchangeable singlets at $\delta =$ 11.3 and 11.0 ppm were assigned to two NH protons, while the rest of the NH proton signals were not detected probably on account of broadening of the peaks owing to hydrogen-bonding interactions. The structure of **3** has been also confirmed by X-ray crystallographic analysis (Figure 5),[12] which reveals a twisted figure-of-eight conformation without any planes of symmetry and is consistent with the ^{1}H and ^{19}F NMR spectroscopic data. The macrocyclic structure consists of two semihelical planes of four and five pyrrole rings aided by hydrogen-bonding interactions between amine NH groups and imine N atoms of the pyrrole rings (the N–H···N distances are 2.86 (A to B), 2.59 (B to C), 2.24 (C to D), 2.63 (D to E), 2.02 (F to G), 2.66 (G to H), and 2.02 Å (H to I), respectively). The dihedral angles between the neighboring pyrrole rings are 2.0, 21.2, 10.4, 7.5, 35.9, 14.3, 11.9, 10.0, and 26.9° clockwise from pyrrole A, and the pyrrole-linking C–C bond lengths are in the range of 1.38–1.41 Å and feature only modest bond-length alternation. The UV/Vis absorption spectrum of **3** exhibited two sharp Soret-like bands at $\lambda =$ 427 ($\varepsilon = 1.00 \times 10^5$) and 724 nm ($\varepsilon = 1.46 \times 10^5\,\text{M}^{-1}\text{cm}^{-1}$) and Q-like bands at $\lambda = 970$ and 1107 nm (Figure 1), which reflect a larger 38-π-conjugated electronic system.

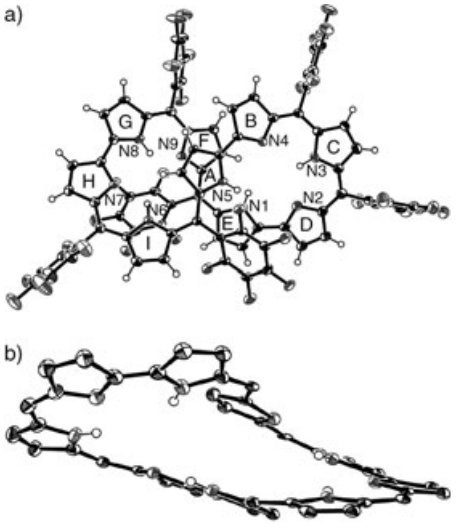


Figure 5. X-ray crystal structure of **3**: a) top view and b) side view. The thermal ellipsoids were scaled to the 50% probability level. Solvent molecules were omitted in the top view, and *meso*-pentafluorophenyl substituents and hydrogen atoms at the β positions were omitted in the side view for clarity.

In summary, rubyrin **2** and nonaphyrin **3** were simply prepared from the acid-catalyzed oxidative coupling reaction of the tripyrrane **1**. Rubyrin **2** is an aromatic macrocycle that exhibits a diatropic ring current and displays clear spectral changes upon the addition of acid, as a result of conformational changes through interaction with the counteranion, thus encouraging its dication as a potential anion-recognition reagent. The structural changes of expanded porphyrins induced by outer stimuli are being further investigated in our laboratory.

Experimental Section

Rubyrin **2** and nonaphyrin **3**: TFA (30.6 μL, 0.4 mmol) was added to a solution of **1** (450 mg, 0.81 mmol) in CH_2Cl_2 (90 mL), and the resulting solution was stirred for 90 min at RT under N_2. Then chloranil (594 mg, 2.63 mmol) was added, and the mixture was heated at reflux for a further 90 min. The reaction was quenched with an aqueous solution of $NaHCO_3$, and the organic layer was separated, washed once with water, and dried over anhydrous Na_2SO_4. After removal of solvent, the crude product was purified over a neutral-alumina column using a mixture of CH_2Cl_2/hexane as eluent. After elution of deeply colored fractions, a purple fraction was eluted with

Table 1: Selected physical data for **2**, **2**·2TFA, **2**·2HCl, and **3**.

2: ^{1}H NMR ($CDCl_3$, 600 MHz 298 K): $\delta = 11.49$ (s, 2H; NH), 9.16 (d, $J = 4.1$ Hz, 2H; β-CH), 8.74 (m, 4H; β-CH), 8.66 (d, $J = 4.1$ Hz, 2H; β-CH), 1.63 (s, 2H; NH), −2.11 (d, $J = 3.4$ Hz, 2H; β-CH), −2.18 ppm (d, $J = 3.4$ Hz, 2H; β-CH); UV/Vis (CH_2Cl_2): λ_{max} (ε): 537 (1.70), 802 (0.18), 832 (0.19), 919 nm ($0.11 \times 10^5\,\text{M}^{-1}\text{cm}^{-1}$); HRMS (ESI-TOF): m/z calcd for $C_{52}N_6F_{20}H_{17}$: 1105.1190; found: 1105.1186 (100%) $[M+H]^+$.

2·2TFA: ^{1}H NMR ([D_8]THF, 600 MHz 298 K): $\delta = 16.47$ (br s, 2H; NH), 10.91 (br s, 4H; β-CH), 10.16 (br s, 4H; β-CH), −3.29 (s, 4H; β-CH), −3.86 ppm (s, 4H; NH); UV/Vis (CH_2Cl_2): λ_{max} (ε): 555 (3.30), 737 (0.10), 808 (0.08), 904 nm ($0.52 \times 10^5\,\text{M}^{-1}\text{cm}^{-1}$).

2·2HCl: ^{1}H NMR ($CDCl_3$, 600 MHz 298 K): $\delta = 10.57$ (d, $J = 3.5$ Hz, 4H; β-CH), 9.75 (d, $J = 3.4$ Hz, 4H; β-CH), 8.95 (s, 4H; β-CH), −3.05 (s, 2H; NH), −3.26 ppm (s, 4H; NH); UV/Vis (CH_2Cl_2): λ_{max} (ε): 518 (3.35), 700 (0.16), 764 (0.12), 848 nm ($0.24 \times 10^5\,\text{M}^{-1}\text{cm}^{-1}$).

3: ^{1}H NMR ($CDCl_3$, 600 MHz 298 K): $\delta = 11.28$ (br s, 1H; NH), 10.98 (br s, 1H; NH), 8.00 (d, $J = 4.8$ Hz, 1H; β-CH), 7.82 (d, $J = 4.8$ Hz, 1H; β-CH), 7.60 (d, $J = 4.8$ Hz, 1H; β-CH), 7.53 (d, $J = 4.1$ Hz, 1H; β-CH), 7.16 (d, $J = 4.8$ Hz, 1H; β-CH), 7.09 (d, $J = 4.8$ Hz, 1H; β-CH), 6.98 (d, $J = 4.9$ Hz, 1H; β-CH), 6.91 (d, $J = 4.8$ Hz, 1H; β-CH), 6.85 (d, $J = 4.8$ Hz, 1H; β-CH), 6.78 (2H; β-CH), 6.30 (m, 2H; β-CH), 6.08 (d, $J = 4.8$ Hz, 1H; β-CH), 5.67 (d, $J = 4.1$ Hz, 1H; β-CH), 5.54 (d, $J = 4.1$ Hz, 1H; β-CH), 4.73 (d, $J = 4.1$ Hz, 1H; β-CH), 4.64 ppm (d, $J = 4.8$ Hz, 1H; β-CH); UV/Vis (CH_2Cl_2): λ_{max} (ε): 427 (1.00), 724(1.46), 970 (0.10), 1107 nm ($0.16 \times 10^5\,\text{M}^{-1}\text{cm}^{-1}$); HRMS (ESI-TOF): m/z calcd for $C_{78}N_9F_{30}H_{24}$: 1656.1670; found: 1656.1699 (100%) $[M+H]^+$.

CH_2Cl_2 which contained **2** (107 mg, 24%). The first eluted fraction from the alumina column was further purified by column chromatography on silica gel using a mixture of CH_2Cl_2/hexane as eluent to give a green fraction of **3** (38 mg, 8.5%; see Table 1).

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[3] Sessler et al. noted that efforts to obtain the free-base form of β-dodeca(alkyl)-substituted rubyrin had so far been unsuccessful, but the free-base β-deca(alkyl)-substituted rubyrin, which may have some rotational freedom, was stable in contrast to fully β-dodeca(alkyl)-substituted rubyrin, which implies the importance of rotational freedom about the bipyrrolic bonds for the stability of free-base rubyrin.[2]

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[6] Similar acid-promoted oxidative coupling of pyrroles has been shown to be quite effective in the synthesis of expanded porphyrins. See: a) J. L. Sessler, D. Seidel, V. Lynch, *J. Am. Chem. Soc.* **1999**, *121*, 11257; b) D. Seidel, V. Lynch, J. L. Sessler, *Angew. Chem.* **2002**, *114*, 1480; *Angew. Chem. Int. Ed.* **2002**, *41*, 1422; c) T. Köhler, D. Seidel, V. Lynch, F. O. Arp, Z. Ou, K. M. Kadish, J. L. Sessler, *J. Am. Chem. Soc.* **2003**, *125*, 6872.

[7] Crystallographic data for *meso*-pentafluorophenyl-substituted rubyrin **2**: $C_{60}H_{32}F_{20}N_6O_4$, $M_W = 1280.92$, monoclinic, space group $P2_1/a$ (no. 14), $a = 10.422(5)$, $b = 15.731(7)$, $c = 17.097(8)$ Å, $\beta = 103.03(4)°$, $V = 2730(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.558\ g\,cm^{-3}$, $T = -150\,°C$, 19549 measured reflections, 6201 unique reflections ($R_{int} = 0.073$), 2932 with $I \geq 3\sigma(I)$ used in refinement, $R = 0.062$, $R_w = 0.067$, GOF = 1.275.

[8] A stable β-deca(alkyl)rubyrin was reported to exhibit its Soret-like band at $\lambda = 513$ nm in its free-base form.[2]

[9] Crystallographic data for rubyrin–TFA complex **2**·2TFA: $C_{62}H_{26}F_{29}N_6O_7$, $M_W = 1517.88$, monoclinic, space group $P2_1/a$ (no. 14), $a = 17.51(1)$, $b = 18.18(1)$ $c = 18.87(1)$ Å, $\beta = 90.47(6)°$, $V = 6006(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.678\ g\,cm^{-3}$, $T = -150\,°C$, 105844 measured reflections, 13695 unique reflections ($R_{int} = 0.057$), 7364 with $I \geq 3\sigma(I)$ used in refinement, $R = 0.071$, $R_w = 0.087$, GOF = 1.266.

[10] Crystallographic data of rubyrin–HCl complex **2**·2HCl: $C_{62}H_{30}F_{20}N_6O_6Cl_2$, $M_W = 1405.83$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.62(1)$, $b = 15.07(1)$ $c = 15.87(1)$ Å, $\alpha = 82.74(7)$, $\beta = 73.73(6)$, $\gamma = 74.35(6)°$, $V = 3227(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.446\ g\,cm^{-3}$, $T = -150\,°C$, 29837 measured reflections, 29837 unique reflections ($R_{int} = 0.100$), 8804 with $I \geq 3\sigma(I)$ used in refinement, $R = 0.097$, $R_w = 0.125$, GOF = 1.045.

[11] Anion-binding behavior with conformational changes through interactions with anions are one of well-known and promising properties in the area of pyrrole-based macrocycles, such as calixpyrroles. See: P. A. Gale, J. L. Sessler, V. Kral, *Chem. Commun.* **1998**, 1. In the case of expanded porphyrins, sapphyrins are the first example of anion-binding agents, see: J. L. Sessler, J. M. Davis, *Acc. Chem. Res.* **2001**, *34*, 989. Similar counteranion-dependent spectral changes were reported for a dication of dithiarubyrin.[4a]

[12] Crystallographic data for *meso*-pentafluorophenyl-substituted [38]nonaphyrin(1.1.0.1.1.0.1.1.0) **3**: $C_{79}H_{23}F_{30}N_9O_2Cl_2$, $M_W = 1770.96$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.9440(19)$, $b = 17.319(3)$, $c = 17.915(3)$ Å, $\alpha = 82.739(4)$, $\beta = 71.418(3)$, $\gamma = 77.792(3)°$, $V = 3426.4(10)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.717\ g\,cm^{-3}$, $T = -153\,°C$, 12100 measured reflections, 9720 unique reflections ($R_{int} = 0.0241$). $R = 0.0847$, R_w (all data) = 0.2538, GOF = 1.041. CCDC 258963 (**2**), 258964 (**2**·2TFA), 258965 (**2**·2HCl), and 258966 (**3**) contain 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.

