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Expanded Porphyrins

A Core-Modified Rubyrin with *meso*-Aryl Substituents and Phenanthrene-Fused Pyrrole Rings: A Highly Conjugated Near-Infrared Dye and Hg^{2+} Probe**

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Expanded porphyrins[1] with five or more heterocyclic rings, such as sapphyrins, rubyrins, and more extended structures, are large conjugated macrocycles that basically preserve key characteristics of porphyrins (e.g. Soret and Q-type absorption bands, photoactivity) yet often show various novel features that have led to applications in medical and pharmaceutical areas, nonlinear optics, and supramolecular photochemistry.[2] Expanded-porphyrin structures have been elaborated by macrocycle expansion, the introduction of heterocycles other than pyrrole (core modification), *meso* substitution, and heterocycle inversion ("confused" porphyrins).[1] Because such porphyrins are macrocycles, their interesting cation and anion coordination properties render them promising hosts in molecular recognition and chemical sensing.[3,4]

Of the large number of expanded porphyrins published in the past 20 years, only few have been employed in recognition and sensing studies, mainly all-pyrrole derivatives for anion signaling.[5] Core-modified expanded porphyrins have been employed even less frequently, for example, thiophene-modified sapphyrins and rubyrins in anion-binding studies.[6] Although the cation-coordination chemistry of expanded porphyrins has been investigated,[7,8] reports on the use of such compounds in metal-ion sensing are even scarcer.[9]

Based on our interest in the optical determination of heavy-metal ions, in particular of Hg^{2+},[10] and the development of new red/near-infrared (NIR) dyes,[11] we became intrigued by the possibility of equipping expanded porphyrins such as rubyrin, that is, [26]hexaphyrin(1.1.0.1.1.0), with various "soft" donor sites,[12–14] to shift metal-ion preferences from, for example, Zn^{2+}, Cu^{2+}, and Co^{2+} in all-pyrrole derivatives[7] to more thiophilic target ions. Moreover, since the strategy of core annelation has been successfully employed to shift the optical spectra of porphyrins into the NIR,[15,16] we synthesized rubyrin **1** and investigated its spectroscopic properties and Hg^{2+}-sensing features.

The synthesis of **1** started from the oxidative coupling of monolithiated thiophene[17] and commenced with the condensation of 5,5′-dilithiated **2** with 4-fluorobenzaldehyde to yield the novel bithiophene diol **3** (Scheme 1).[18] Condensation of **3** and phenanthrene-anellated pyrrole under modified Lindsey conditions and subsequent oxidation with DDQ yielded rubyrin **1** in 10% yield. In agreement with observations on **7**,[13] ^{1}H NMR measurements at −40 °C in $CDCl_3$ showed two multiplets at $\delta = 9.47$ and 9.16 ppm, corresponding to two types of magnetically nonequivalent bithiophene protons that presumably reflect a different degree of distortion from planarity for the two bithiophene units. Since the *ortho* and *meta* protons of the phenyl rings are directed toward the rubyrin macrocycle and are thus deshielded by the rubyrin and phenanthrene ring currents, multiplets are found at $\delta = 8.55$ (8H) and 7.95 ppm (8H). The remaining two multiplets at $\delta = 7.39$ (8H) and 7.09 ppm (8H) are assigned to the protons of the phenanthrene rings.

Figure 1 shows the X-ray crystal structure of **1**.[19] Average bond lengths of 1.354 and 1.395 Å for the $N{-}C_\alpha$ and $C_{meso}{-}C_\alpha$ bonds indicate π-electron delocalization in the macrocyclic core. Double-bond character is also found for the average $C_\alpha{-}C_\beta$ (1.397 Å) and $C_\beta{-}C_\beta$ (1.389 Å) bonds of the thiophene rings. In contrast, $C_\alpha{-}C_\beta$ and $C_\beta{-}C_\beta$ bond lengths of 1.504 and 1.374 Å indicate localized single and double bonds in the pyrrole rings. As a result of steric crowding, the phenanthrene units are largely bent away from the least-squares plane of the macrocyclic core (Figure 1) and the fluorophenyl rings are only tilted by $\theta = 8.5$–34.4° out of that plane; the average

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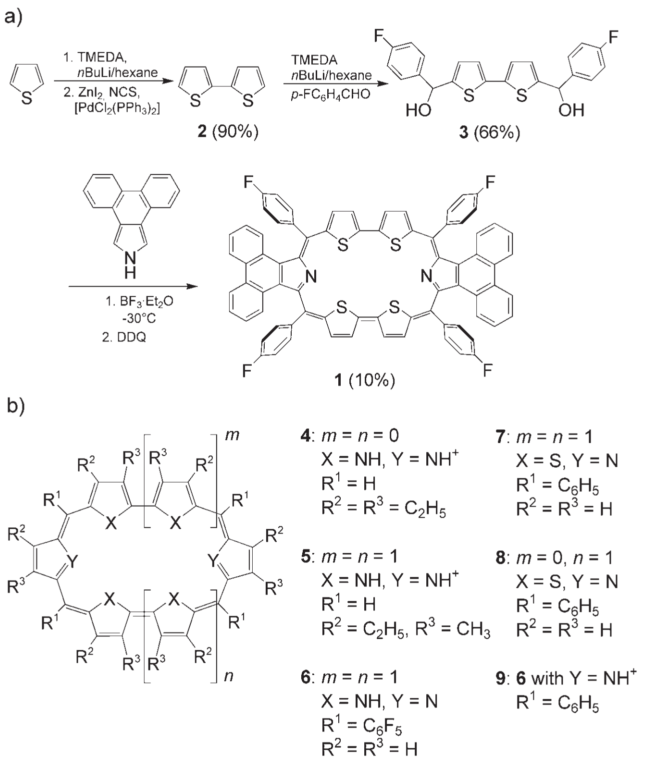


Scheme 1. a) Synthesis of phenanthrene-anellated rubyrin **1**. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, NCS = *N*-chlorosuccinimide, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. b) Known porphyrins discussed in the text.

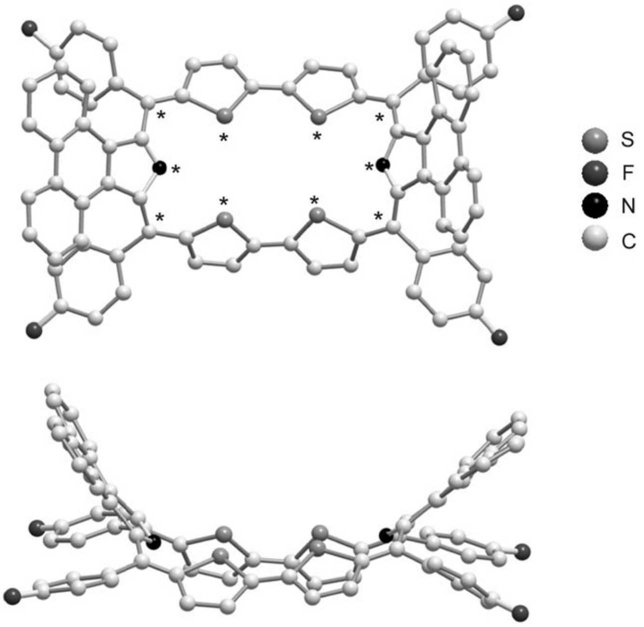


Figure 1. Top and side view of the X-ray crystal structure of **1**. Hydrogen atoms are omitted for clarity. Atoms marked with asterisks define the least-squares plane of the central macrocycle.

bond length between the C_{meso} atoms and the fluorophenyl rings is 1.4815 Å. The dominant structural features are thus the bowl-type distortion of the molecule and the existence of a 26-π-electron aromatic ring. Moreover, the fluorophenyl rings are much more in plane than those in related dyes such as a benzohexaphrin ($\theta = 49.3$–$76.3°$),[16c] the non-annelated sapphyrin **8** ($\theta = 57.9$–$68.6°$),[6] and the bowl-shaped hexaphyrin **9** ($\theta = 36.2$–$46.7°$).[20] If one considers porphyrin photochemistry this suggests that the exchange of the 4-substituent of the *meso*-phenyl rings could potentially be used to tune the spectroscopic properties of dyes such as **1**.[21]

The absorption spectrum of **1** in its free-base form in $CHCl_3$ displays a Soret band at 596 nm ($\lg\varepsilon = 5.17$) and three weak and broad Q bands at 714 ($\lg\varepsilon = 4.24$), 784 (4.31), and 1076 nm (3.65), the latter well in the NIR region (Figures 2 and 3). These favorable features can be rationalized as follows: Extension of the π system of the parent porphyrin **4** (Scheme 1) by two pyrrole units yields rubyrin **5** and shifts the Soret and Q bands by roughly 100 and 270 nm, to 505 and 850 nm.[22] Further red-shifts can then result from *meso* substitution:[23] Rubyrin **6** displays bands at $\lambda_{Soret} = 543$ and $\lambda_Q = 926$ nm.[24] Modification of the rubyrin core by replacing the N atoms with other heteroatoms then alters the cavity size and electronic structure of the ring, leading to moderate hypsochromic shifts in the case of N-for-S exchange; for the tetrathiophenerubyrin **7**, $\lambda_{Soret} = 523$ nm.[13] Since our aim was to synthesize a dye that absorbs at distinctly longer wavelengths, the strategy of phenanthrene anellation at the β-pyrrole position that we recently employed for tetrapyrrole porphyrins[25] also proved very successful here: $\lambda_{Soret}{}^1$ and $\lambda_Q{}^1$ are red-shifted by approximately 70 and 120 nm relative to the bands of **7**.

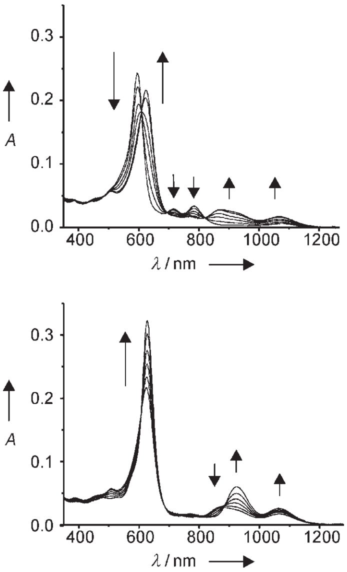


Figure 2. Titration spectra of **1** with TFA in $CHCl_3$. Top: no TFA and 2 μM ≦ c_{TFA} ≦ 0.32 mM; bottom: 0.32 mM ≦ c_{TFA} ≦ 19 mM.

Despite the wealth of information available on the absorption properties of extended porphyrins, only few studies of their emission features have been published.[8,9,24,26,27] This can be explained by the difficulty of measuring emission spectra of compounds with low fluorescence quantum yields—$\Phi_f \approx 10^{-4}$ have been reported[26,27]—at $\lambda_{em} > 900$ nm with conventional fluorometers. For the emission spectra shown in Figure 3, we used a different approach and employed an FTIR spectrometer equipped with a Nd:YAG laser and a photoluminescence detector operating in the conventional mode (see the Supporting Information for details). The fluorescence of **1** was observed between 1050 and 1350 nm with $\lambda_{max} = 1118$ nm, $\Phi_f = 3.3 \times 10^{-4}$, and a fluorescence lifetime $\tau_f = 90$ ps.[28] The Stokes shift of 355 cm^{-1} indicates that the conformational relaxation in the excited state is not very pronounced. However, the Stokes shift also suggests that the conformation of **1** deviates considerably from planarity because Stokes shifts of only 20–90 cm^{-1} have been reported for largely planar hexaphyrins.[8,26,27] This assumption is supported by the comparatively intense Q bands. When Q bands lose their ideal forbidden character, as in *meso*-substituted and anellated tetrapyrrole porphyrins that adopt a saddlelike conformation owing to internal steric strain, their intensity increases.[29]

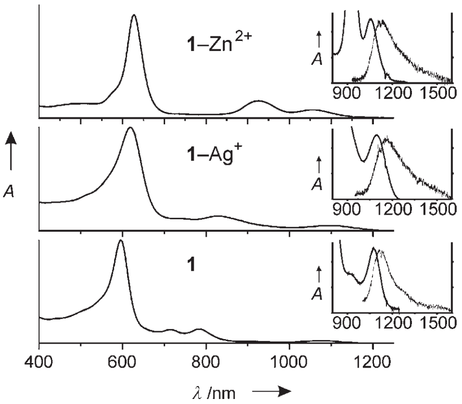


Figure 3. Absorption spectra of **1**, **1**-Ag^+, and **1**-Zn^{2+} in $CHCl_3$. Insets: normalized S_0–S_1 transitions in absorption and emission ($\lambda_{exc} = 532$ nm).

The increased π conjugation of **1** by fusion with phenanthrene rings is also evident from cyclic voltammetric studies. Two quasi-reversible reduction peaks were observed at −1.39 and −1.64 V (vs. Fc^+/Fc), while four quasi-reversible and one irreversible oxidation peaks appeared at −0.34, −0.26, 0.08, 0.23, and 0.50 V. The HOMO–LUMO gap for **1** is estimated to be 1.05 V, which is significantly smaller than those of, for example, **7**-H_2^{2+} (1.64 V) and meso-tetraphenylporphyrin (2.26 V), and reflects the pronounced red-shift of the absorption spectrum of **1**.[13]

In accordance with changes measured for other rubyrins upon protonation,[14,30] addition of an excess of trifluoroacetic acid (TFA) to **1** in $CHCl_3$ led to an additional bathochromic shift of the Soret band to 628 nm (Figure 2). Moreover, just as was observed for **7** and **7**-H_2^{2+},[14] the two high-energy Q bands at 716 and 785 nm disappear upon formation of **1**-H_2^{2+}, and the low-energy Q bands at 913 and 1068 nm strongly gain in intensity. Such behavior reflects a further distortion of the conformation from planarity. Titration of **1** with TFA revealed two well-separated protonation steps with apparent pK_a values of 4.62 ± 0.03 and 2.68 ± 0.02 (see the Supporting Information).

When divalent metal ions such as Cu^{2+}, Zn^{2+}, Pb^{2+}, or Hg^{2+} were added to an equimolar amount of **1** in $CHCl_3$, the observed effects were similar to those upon protonation (Figure 3). The Soret band is shifted to 627 nm and two Q bands are observed at 925 and 1056 nm (1058 nm for Hg^{2+}). In the case of Ag^+, the absorption maxima have a less pronounced shift, appearing at 616 (Soret band) and 828/1085 nm (Q bands), most probably because of the weaker interaction of the monovalent thiophilic ion with the pyrrole nitrogens. Fluorescence studies of **1**-Ag^+, **1**-Zn^{2+}, and **1**-Hg^{2+} revealed a 2.2- and 3.3-fold increase in emission upon complexation of the lighter diamagnetic metal ions Ag^+ and Zn^{2+}, and a 1.5-fold quenching for Hg^{2+} with band maxima at 1162, 1124, and 1190 nm. The comparatively weak influence of the heavy-atom effect of Hg^{2+} is tentatively ascribed to the short fluorescence lifetime τ_f of **1**, because intersystem crossing is much less probable than internal conversion for such red-emitting porphyrinoids.[27]

As mentioned above, **1** was designed as a Hg^{2+} probe. Although the public is alert to the dangers of mercury contamination,[31] there is still a need for new or improved sensing methods that are applicable on site and for screening purposes.[32] The development of Hg^{2+} indicators that can be principally employed in optical-sensing devices is thus an active research field.[10,33] Since **1** is not soluble in water, a common strategy was employed to work under realistic conditions: The probe was incorporated into a polymer membrane.[34] For most polymer-based Hg^{2+} sensors, PVC membranes are used.[34] However, the polyurethane hydrogel D4, which was recently identified as an excellent support for pH sensors,[35] gives a better performance with **1**. Figure 4 shows the titration spectra obtained after dipping D4–**1** into aqueous samples with increasing amounts of Hg^{2+}. In the absence of Hg^{2+}, the Soret band is found at 597 nm, virtually the same as for **1** in $CHCl_3$, indicating that the matrix does not influence the spectroscopic behavior properties of **1**. The response to Hg^{2+} is evident from a shift of the Soret band to 638 nm with a clear isosbestic point at 617 nm. By monitoring the intensity changes at 638 nm, a typical titration curve is obtained with a limit of detection of approximately 1 ppm. Quantitative analysis of several titration curves yielded

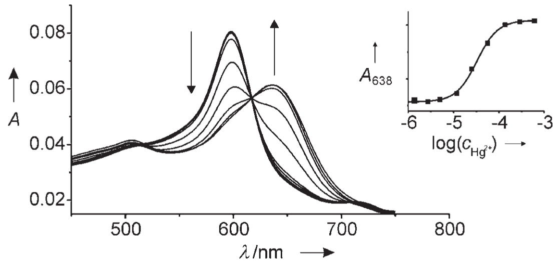
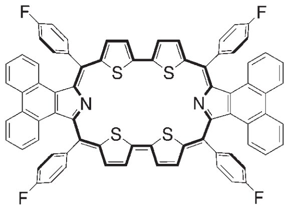


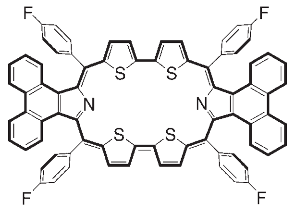
Figure 4. Changes in absorption (Soret-band region) of a glass slide coated with a 35-μm thick membrane of D4–**1** after it was dipped into water samples containing increasing amounts of Hg^{2+}. Inset: Titration curve of A_{638} vs. Hg^{2+} concentration.

acceptable fits for a 1:1 complex and a formation constant $K = (3.0\pm0.3)\times10^{4}\,\text{M}^{-1}$. Complexes with a ligand-to-metal ratio of 1:2[7a,8] have been found in neither H_2O nor $CHCl_3$, presumably because of the lack of preferred coordination sites for aminophilic cations like Cu^{2+} and Zn^{2+} and the rather large ionic radius in the case of Hg^{2+}. Competition studies with Zn^{2+}, Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Ag^{+}, Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} underscore the selective response of D4–**1**. Only at concentrations of $>100\ \mu\text{M}$ does the band at 638 nm increase 1.03- (for Ni^{2+}), 1.08- (for Cd^{2+} and Pb^{2+}), and 1.15-fold (for Cu^{2+}); the other ions have no effect. Moreover, as would be expected for free-base expanded porphyrins, different counterions do not influence the performance.[36]

In conclusion, we have synthesized a core-modified, expanded porphyrin with polycyclic aromatic units fused to the pyrrole rings and demonstrated its protonation and complexation features. Embedding **1** into a polyurethane membrane produced simple test strips for rapid Hg^{2+} screening. This is one of the very few examples—and the first one for cations—where expanded porphyrin probes can be used directly in aqueous samples without complications arising from aggregation.[37] Most examples so far use such indicator dyes in organic or mixed organic/aqueous solutions or in combination with solvent extraction and transport protocols.[5,6,9] Compound **1** shows exceptionally red-shifted absorption bands with the Soret band appearing at almost the same position (596 nm) as that of a 54-π-electron-containing dodecaphyrin (604 nm).[38] Although **1** formally represents a [26]hexaphyrin, the spectroscopic and redox properties suggest that ring fusion leads to a dye with cross-conjugated [26]- and [52]hexaphyrin chromophores.[39] This tremendous bathochromic shift results in an absorption spectrum that is is compatible with solar radiation in the respective wavelength range[40] and shows appreciable molar absorptivities of $\lg\varepsilon > 4.17$ at all common laser wavelengths between 322–780 nm, including HeNe, Ar^{+}, many diode lasers, and Nd:YAG laser harmonics. For example, in the case of D4–**1** and Hg^{2+}, the ratiometric response can be analyzed with a yellow (594 nm) and a red (633 nm) HeNe laser. Compounds such as **1** are thus promising candidates for photonic applications.[2–5] With the aid of FTIR–photoluminescence instrumentation, such dyes might make is possible to use the second optical window of telecommunication (O-band, 1260–1310 nm)[41] for fiber optical fluorometry and sensing.



[26]hexaphyrin



[52]hexaphyrin

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[19] Crystallographic data for **1**: $C_{76}H_{40}F_4S_4N_2{\cdot}4\,CHCl_3$, $M_r = 1662.938$, crystal dimensions: $0.10 > 0.08 > 0.07$ mm^3, monoclinic $C2/c$ (No. 15), $a = 26.880(5)$, $b = 25.710(5)$, $c = 20.240(5)$ Å, $\beta = 119.23(0)°$, $V = 12\,206(34)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.54$ g cm^{-3}, $T = 293(2)$ K, 23066 measured reflections, 6555 reflections with $[I > 2\sigma(I)]$. $R = 0.0550$, $R_W = 0.0972$, GOF $= 0.881$. CCDC 659352 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.

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