DOI: 10.1002/anie.200804143

Black Porphyrins

"Blackening" Porphyrins by Conjugation with Quinones**

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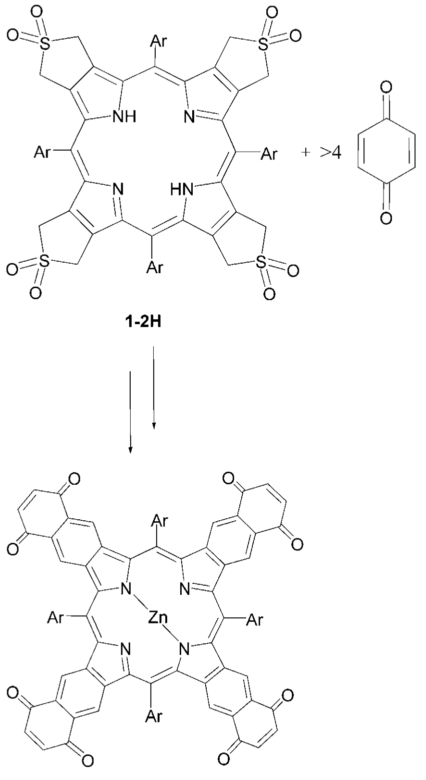
Dedicated to Professor Heinz Falk on the occasion of his 70th birthday

Heme and chlorophyll are fascinating porphyrinoid "pigments of life" in plants and in blood.[1,2] Their respective characteristic bright green and red colors are a consequence of the efficient absorption of narrow sections of visible light.[3,4] Heme and chlorophyll were targets of total syntheses[5–7] and have inspired the synthesis of artificial analogues that serve in the exploration of their properties as pigments.[8] Non-natural porphyrins are currently of interest as catalysts,[2,9] as redox systems,[10] as robust molecular components in optical[11] and other nanoscopic devices,[12–14] and in medical applications.[15]

Many of the applications of porphyrins rely on their characteristic bright colors and the associated properties.[16,17] Herein we describe "black" porphyrins, obtained by specific modification of the porphyrin chromophore with benzoquinones. The absorption spectra of these tetrapyrroles feature broad and intense electronic transitions covering all wavelengths of visible light. Pigments that absorb a large fraction of sunlight are in great demand.[18] Indeed, "black" leaves have been proposed to increase plants' capacity in collecting solar energy by biological photosynthesis.[19]

The symmetrical β,β′-tetrasulfolenoporphyrin (**1-2H**) was prepared earlier as a versatile reactive building block for further covalent attachment of functional units.[20] Its synthesis was first developed in conjunction with the attachment of C_{60}-fullerene units by [4+2] cycloaddition reactions.[21] Following a related strategy, but using a new "add & lock" methodology, covalent conjugates with quinones could be obtained systematically. Making use of the dienophilic and oxidative properties of quinones, we have achieved an effectively irreversible attachment of up to four electronically conjugated benzoquinone units, giving porphyrins with systematically extended π systems.

The "black" tetraquinonoporphyrin **2-Zn** was prepared by exhaustive thermolysis of a solution of **1-2H** in 1,2-dichlorobenzene at 140 °C and in the presence of a 24-fold excess of benzoquinone (Scheme 1). The crude reaction mixture was oxidized with dicyanodichlorobenzoquinone (DDQ) and then treated with zinc(II) acetate to give the zinc tetraquinonoporphyrin **2-Zn** in 86 % yield.



Scheme 1. Synthesis of the zinc tetraquinonoporphyrin **2-Zn**. Ar = 3,5-di-*tert*-butylphenyl.

Thermolysis of a solution of the porphyrin **1-2H** and a 19-fold excess of benzoquinone in 1,2-dichlorobenzene for only 45 minutes at 140 °C gave (at about 66 % conversion) a mixture of adducts, which was oxidized with DDQ. Subsequent treatment with zinc acetate furnished, after purification by chromatography, the five benzoquinone–porphyrin conjugates **2-Zn** to **6-Zn**. The products were isolated as dark microcrystalline solids, and they were identified as the adduct **3-Zn** (32.4 % yield), diagonal bis-adduct **4-Zn** (3 % yield), lateral bis-adduct **5-Zn** (7.9 % yield), tris-adduct **6-Zn** (6.4 % yield), and tetra-adduct **2-Zn** (0.7 % yield, see Scheme 2).

The structures of the five adducts were established by mass spectrometric analysis, and homo- and heteronuclear

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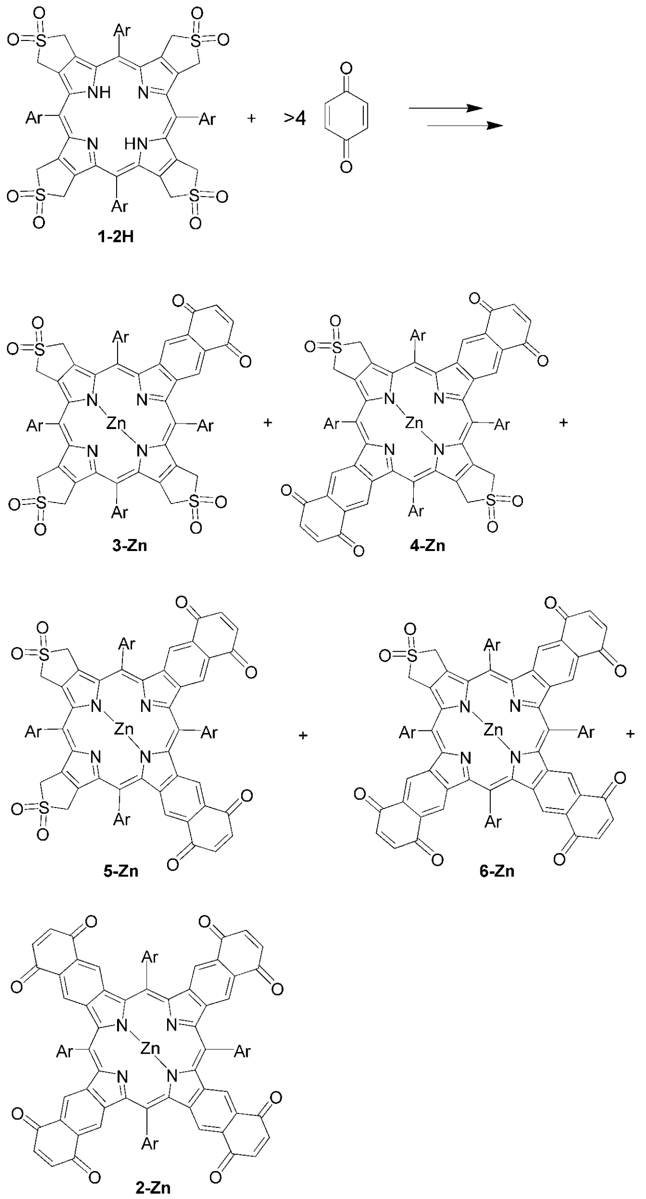
[**] The authors thank Thomas Müller, Simone Moser, and Prof. Ernst Ellmerer for mass and NMR spectra. The work in Innsbruck was supported by the Austrian National Science Foundation (FWF project no. P-17437) and the Tyrolean Science Foundation (project no. UNI 404/22).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804143.



Scheme 2. Synthesis of the zinc β,β′-quinonoporphyrins **2-Zn** to **6-Zn**. Ar = 3,5-di-*tert*-butylphenyl.

NMR spectroscopy. The NMR spectra are compatible with an effectively planar structure of the extended porphyrin-naphthoquinone moiety, and the specific addition pattern for the diagonal and lateral bis-adducts **4-Zn** and **5-Zn** could be determined (see the Experimental Section and the Supporting Information).

Both the tetra-adduct **2-Zn** and the lateral bis-adduct **5-Zn** gave monoclinic single crystals suitable for X-ray analysis. The crystal structures confirm the constitutional assignment (deduced from the NMR and mass spectra) and indicate largely planar porphyrin structures. They also reveal that the tetra-adduct **2-Zn** contains a hexacoordinate Zn center, to which two molecules of methanol are bound by means of long Zn–O bonds (2.308 Å) resulting in an unusual pseudo-octahedral coordination sphere at the zinc center (Figure 1).

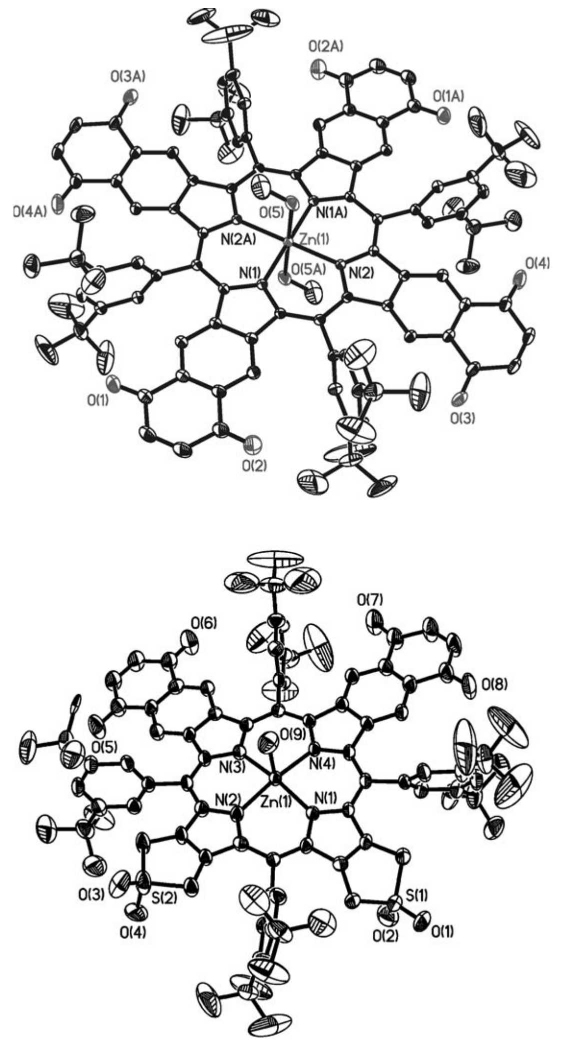


Figure 1. X-ray crystal structures of zinc tetraquinonoporphyrin **2-Zn** (top) and of the "lateral" zinc bisquinonoporphyrin **5-Zn** (bottom). (ORTEP plots; H atoms are omitted for clarity).

The conjugated quinone moieties have a remarkable and systematic effect on the UV/Vis spectra, intensifying the absorption bands at long wavelengths and shifting their maxima by 133 nm (in CH_2Cl_2; from 592 nm for **1-Zn**[20] to 725 nm for the tetra-adduct **2-Zn**). The position of the absorption maxima is also strongly solvent dependent: for example, in the UV/Vis spectra of **2-Zn** the maximum shifts from 710 nm in petroleum ether, to 725 nm in CH_2Cl_2, to 736 nm in MeOH. At the same time, the spectral features of typical metalloporphyrins disappear completely. Instead of the diagnostic strong Soret band near 400 nm and weaker Q bands near 550 nm (as in the spectrum of **1-Zn**),[3,20] a multiband structure covering the whole visible range is evident in the spectra of **6-Zn** and **2-Zn** (Table 1 and Figure 2). A gradual reduction of the characteristic band near 400 nm (Soret band of porphyrins, see Table 1) thus also occurs upon introduction of one to four conjugated benzoquinone units. However, integration of the absorption spectra of solutions in CH_2Cl_2 of the zinc porphyrinoids **2-Zn** to **6-Zn** (from about 380 to 800 nm) indicates a similar total (normal-

Table 1: UV/Vis spectral characteristics of the zinc porphyrin **1-Zn**[20] and of the zinc quinonoporphyrins **2-Zn** to **6-Zn** (in CH_2Cl_2).

Cmpd	λ_{max}[a,b] (lg ε)	λ_{max}[a,c] (lg ε)	Absorption[d] (lg ε)	
			400 nm	700 nm
1-Zn	590 (3.92)	424 (5.85)	4.19	< 2.0
3-Zn	614 (4.09)	418 (5.18)	4.61	2.6
4-Zn	648 (4.37)	408 (4.84)	4.65	3.1
5-Zn	642 (4.44)	425 (4.95)	4.58	2.7
6-Zn	680 (4.42)	425 (4.53)	4.35	4.1
2-Zn	725 (4.90)	418 (4.66)	4.49	4.5

[a] Wavelength in nm. [b] Band at longest wavelength. [c] Dominant band near 400 nm. [d] Absorptions at the boundaries of visible light.

ized) absorption cross section in the visible range for all five compounds.

Solutions of the porphyrins **1-Zn** to **6-Zn** (and of the deconjugated quinonoporphyrin **7-Zn**) are displayed in Figure 3. It is apparent that remarkable changes in color occur upon introduction of (up to four) conjugated benzoquinone units: The solution of **6-Zn** is dark brown, while that of the tetra-adduct **2-Zn** is black.

The covalent attachment and conjugation of quinone units at the β positions of the porphyrins also has a dramatic effect on the luminescence properties. Whereas the zinc porphyrin **1-Zn** exhibits a typical bright red luminescence, the luminescence of all of the quinone conjugates is hardly detectable (see Figure S1 in the Supporting Information). Thus, these porphyrinoid compounds represent a class of zinc complexes that absorb light strongly throughout the whole visible range, and (not unexpectedly[22]) they hardly emit. The porphyrin and benzoquinone building blocks, simply linked and conjugated at the porphyrinoid β positions, result in remarkable, tunable photophysical properties.

As shown, porphyrins with conjugated quinone units at the β positions are easily obtained from the sulfolenoporphyrin **1-2H**.[20] Here, we have studied the quinonoporphyrins **2-Zn** to **6-Zn** more specifically. Their absorption bands were

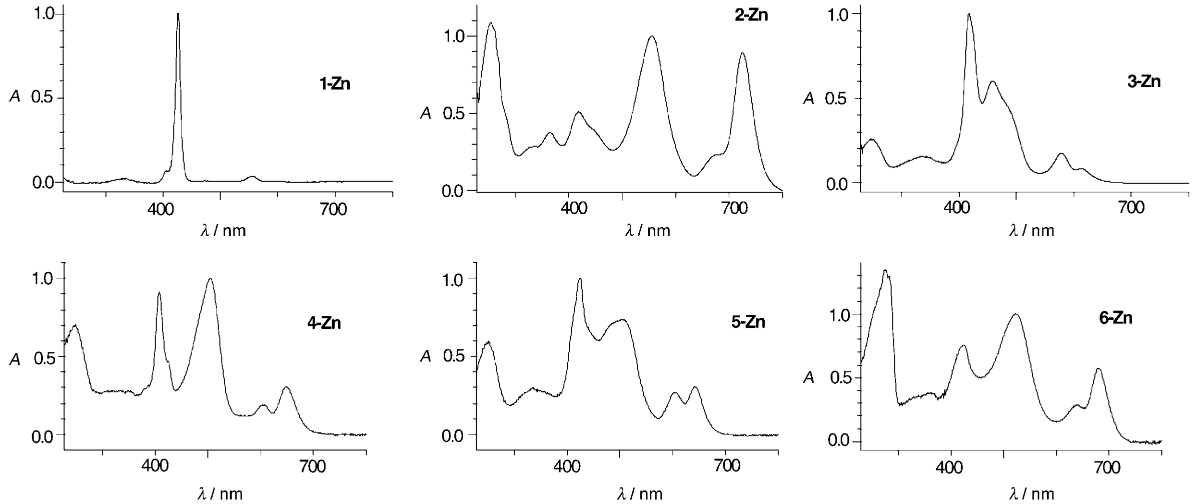


Figure 2. Effect of β,β′-bound quinone substituents. UV/Vis spectra of **1-Zn** and of **2-Zn** to **6-Zn** in CH_2Cl_2 (absorption not normalized; visible range (400–700 nm) highlighted).

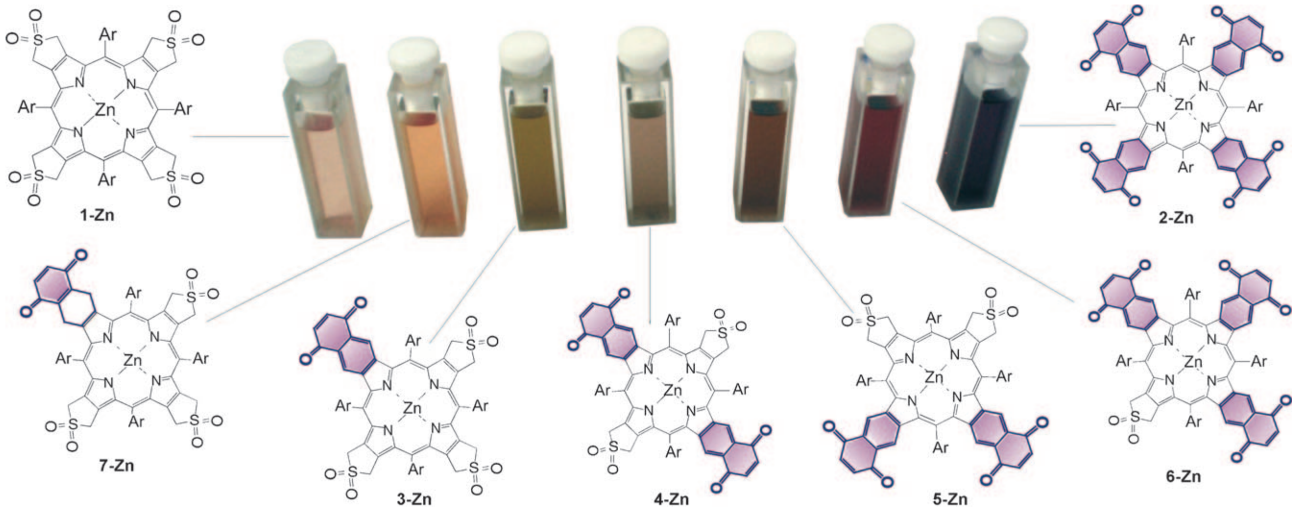


Figure 3. Colors of solutions of zinc porphyrins **1-Zn** to **7-Zn** (in MeOH, ca. 50 μm, 5–10% CH_2Cl_2).

found to broaden and shift gradually with the number of attached quinone units. The optical properties of **2-Zn** to **6-Zn** indicate electronic features that call for theoretical studies, as well as for better characterization in photophysical and electrochemical experiments. Indeed, the new quinonoporphyrins are expected to exhibit interesting electrochemical properties as a result of the directly conjugated porphyrin and benzoquinone moieties. Both types of basic chromophores are well-studied biological or artificial redox systems.[23,24] The zinc tetraquinonoporphyrin **2-Zn** is thus expected to accept a load of at least 10 electrons per molecule. Such quinonoporphyrins clearly promise to expand the range of redox properties of the "simple" porphyrins with a modified periphery.[10]

Solutions of **2-Zn** absorb light in all of the visible range (e.g. in CH_2Cl_2: $\varepsilon > 8800$) and do not decompose noticeably when exposed to daylight. They show negligible luminescence and the colors of the solutions range from gray to black, depending on the concentration. Thus, the porphyrinoid **2-Zn** is the first example of a (mononuclear) "black" porphyrin.[25] In this respect, on a molecular level its visual color properties are the same as those of nanoscopic carbon materials with extended π systems, such as graphene,[26] graphite, and nanotubes.[27] Similar to the porphyrin **1-2H**, the porphyrins **2-Zn** to **6-Zn** are also reactive building blocks, and they could be used for further modification of the porphyrin structure or for assembly of larger covalent porphyrin arrays.

"Black" porphyrins are presented here as new low-molecular-weight compounds of possible use in optoelectronic and redox systems. Their atypical optical and electronic properties are likely to be systematically tunable. These robust and structurally versatile β,β′-quinonoporphyrins appear to be of interest in solar-energy-converting devices,[18,28] and in other applications, such as photoprotection[29] and information storage.[11]

Experimental Section

Synthesis of **2-Zn**: A deoxygenated solution of **1-2H** (52 mg, 36.52 μmol) and *p*-benzoquinone (160 mg,1.48 mmol, 40 equiv) in 16 mL of 1,2-dichlorobenzene (DCB) was heated and stirred for 15 h at 140 °C. The solvent was removed from the mixture at 55 °C under high vacuum (ca. 0.03 mbar), and the residue was redissolved in 20 mL of CH_2Cl_2 and 1 mL of NEt_3. Then DDQ (200 mg, 0.88 mmol, 24 equiv) was added, and the mixture was heated to reflux for 6 h under argon. The cold reaction mixture was washed with aq. $NaHCO_3$ (3 × 25 mL), and the porphyrins were extracted with CH_2Cl_2 (4 × 50 mL). The organic extracts were filtered through a column of silica gel 60, which was washed with CH_2Cl_2/MeOH (99:1). The combined eluates were concentrated to dryness under reduced pressure and the dark residue was dissolved (in 25 mL of CH_2Cl_2 and 2.5 mL of MeOH). After addition of $Zn(OAc)_2 \cdot 2H_2O$ (100 mg, 456 μmol) the suspension was heated to reflux for 1.5 h. The cold mixture was washed with saturated aq. $NaHCO_3$ (3 × 40 mL), and porphyrins were extracted with CH_2Cl_2 (200 mL). The organic extract was filtered through a silica gel 60 column with CH_2Cl_2/MeOH (99:1), and the dark eluate was concentrated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 (2 mL), ethyl acetate (10 mL) and 10 mL of MeOH were added. The flask was left open in the dark for slow evaporation. Within 2 days black crystals separated out, which after drying gave 46.6 mg of **2-Zn**. A second crop of crystalline **2-Zn** (5.2 mg) of was obtained in a similar fashion. Thus a total of 51.8 mg (86.1 %) of black crystalline **2-Zn** was obtained (m.p. > 320 °C), which was characterized by mass spectrometry and by UV/Vis and ^{1}H NMR spectroscopy.

UV/Vis (CH_2Cl_2, $c = 9.712 \times 10^{-6}$ M): λ_{max} ($\lg\varepsilon$): 725 (4.90), 668 sh (4.29), 555 (4.95), 453.5 sh (4.52), 418 (4.66), 365 (4.53), 325 (4.39), 254 nm (4.99); λ_{min} ($\lg\varepsilon$): 690 (4.34), 634 (3.94), 482 (4.37), 387 (4.42), 341 (4.41), 306 nm (4.31). ^{1}H NMR (300 MHz, in $CDCl_3$): $\delta = 1.54$ (s, 72 H), 6.97 (s, 8 H), 7.97 (s, 8 H), 8.11 (br s, 8 H), 8.33 ppm (br s, 4 H). FAB MS ($C_{108}H_{100}N_4O_8Zn$; exact mass = 1644.683). *m*/*z* (%): 1651.8 (32), 1650.8 (48), 1649.8 (71), 1648.8 (86), 1647.8 (100) 1646.8 (95), 1645.8 (79, $[M+H]^+$), 1644.8 (61, M^+).

UV/Vis spectra (in CH_2Cl_2): **3-Zn** ($c = 1.18 \times 10^{-5}$ M): λ_{max} ($\lg\varepsilon$): 614 (4.09), 579 (4.42), 491 sh (4.79), 458 (4.96), 418 (5.18), 334 nm-(4.37). **4-Zn** ($c = 4.02 \times 10^{-5}$ M): λ_{max} ($\lg\varepsilon$): 648 (4.37), 604 (4.16), 505 (4.88), 408 nm (4.84). **5-Zn** ($c = 4.01 \times 10^{-5}$ M): λ_{max} ($\lg\varepsilon$):642 (4.44), 604 (4.38), 504 (4.82), 483 sh (4.80), 425 (4.95), 335 nm (4.43). **6-Zn** ($c = 3.42 \times 10^{-5}$ M): λ_{max} ($\lg\varepsilon$): 680 (4.42), 639 (4.11), 522 (4.66), 425 (4.53), 360 (4.24), 273 nm (4.79). **7-Zn** ($c = 2.94 \times 10^{-5}$ M): λ_{max} ($\lg\varepsilon$):589 sh (3.44), 551 (4.43), 423 (5.69), 402 sh (4.75), 327 nm (4.34).

X-ray structure analyses: Data collection on a Nonius Kappa CCD, equipped with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data for **2-Zn**: $C_{110}H_{108}N_4O_{10}Zn \cdot 2\,EtOAc$, $M_r = 1887.58$, monoclinic, $P2_1/c$, $a = 17.6879(4)$, $b = 18.9404(4)$, $c = 17.4055(3)$ Å, $\beta = 115.915(2)°$, $V = 5244.76(19)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.195$ g cm^{-3}, $T = 233$ K, $R1 = 0.0622$, $wR2 = 0.1753$ for 7328 reflections with $I > 2\sigma(I)$. Data for **5-Zn**: $C_{96}H_{102}N_4O_9S_2Zn \cdot 5\,CH_2Cl_2$, $M_r = 2009.94$, monoclinic, $P2_1/c$, $a = 27.9317(7)$, $b = 21.413(5)$, $c = 17.5983(3)$ Å, $\beta = 102.422(2)°$, $V = 10279(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.299$ g cm^{-3}, $T = 233$ K, $R1 = 0.0846$, $wR2 = 0.2194$ for 10100 reflections with $I > 2\sigma(I)$. CCDC 699276 and 699277 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.

Received: August 22, 2008

Keywords: cycloaddition · dyes/pigments · porphyrinoids · quinones · zinc

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