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A convenient synthesis of porphodimethenes and their conversion to *trans*-porphyrins with two functionalized *meso*-naphthyl substituents

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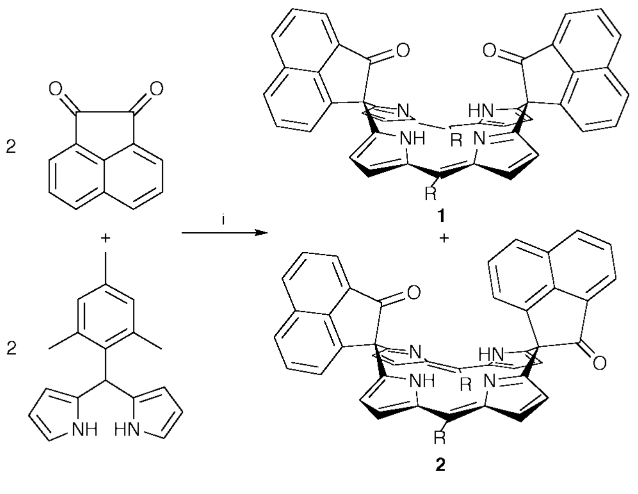
The Mac Donald-type 2 + 2 condensation of the readily available 5-mesityldipyrromethane with acenaphthenequinone leads to the *trans* (*syn* and *anti*) porphodimethenes, respectively, which, after treatment with KOH or NaOMe in THF and subsequent oxidation with air, yield the corresponding *trans*-8-carboxynaphthylporphyrins or their esters.

meso-Substituted porphyrins with rigid anthracene, biphenylene or naphthalene spacers have been widely used to determine the distance dependency of photo-induced electron transfer[1] as well as to prepare and examine cofacial diporphyrins[2] or other bridged porphyrins with well defined separations and varying relative arrangements of the porphyrin rings.[3] Porphyrins with a functionalized anthracene or naphthalene group have also found utility as building blocks for the synthesis of molecular receptors and for the design of dinuclear complexes.[4] Despite the numerous potential applications for these types of complexes, their development has been severely hampered by the inability to prepare large quantities of the porphyrin precursors. The syntheses, in general, require complex procedures for the preparation of the aromatic side arm and/or a multistep procedure for the porphyrin backbone. Chang *et al.*[5] and Therien and coworkers[6] have reported the preparation of porphyrins attached to the 1-position of an 8-functionalized naphthalene but to the best of our knowledge, a straightforward synthetic procedure for the synthesis of *trans* $\alpha\alpha/\alpha\beta$ porphyrins bearing two 8-functionalized naphthalene derivatives has yet to be reported.

As part of our building block approach towards the preparation of new di- and tri-nuclear porphyrin based complexes, a general two-step synthesis, starting from 5-mesityldipyrromethane, has been developed to provide convenient amounts of the desired porphyrins. Reaction of commercially available acenaphthenequinone with 5-mesityldipyrromethane in the presence of catalytic amounts of $BF_3{\cdot}OEt_2$[7] gives, after oxidation with DDQ and subsequent filtration through neutral alumina, a mixture of the corresponding porphodimethene isomers in 26% yield. Separation by column chromatography yields the two isomers [**1** (*syn*), **2** (*anti*)] in an almost 1:2 ratio.†



Scheme 1 *Reagents and conditions*: i, 1. $BF_3{\cdot}OEt_2$, CH_2Cl_2, room temp., 4 h, 2. DDQ, room temp., 1 h. R = mesityl.

The porphodimethenes **1** and **2** are air-stable, bright orange solids and they exhibit a characteristic absorption maxima in the visible region at λ_{max}/nm (log ε) 440(4.97) (**1**) and 438(4.93) (**2**), which when compared to previously described octaalkylporphodimethenes (414–426 nm) are bathochromically shifted.[8] The N–H and C=O stretch frequencies can be found, respectively, in the IR at 3345, 1732 cm^{-1} for **1** and 3279, 1720 cm^{-1} for **2**. The absolute configuration has been determined by ^1H NMR and by an X-ray structure analysis of the metallated (Zn^{2+}) porphodimethene **2b**. Although the X-ray structure analysis of **2** reveals a strong roof-like folded structure of the porphodimethene core,[9] only one type of acenaphtheneoyl can be identified in the ^1H NMR spectra of both **1** and **2**, suggesting a fast up and down motion of the acenaphtheneoyl groups together with a flexing of the two dipyrromethane units along a line joining the two saturated *meso* carbons. Even at 223 K, only minor changes were evident in the NMR spectra of **2**. Owing to the lack of aromaticity in the macrocycle, the signal of the N–H protons appears downfield at δ 13.92 (**1**) and 14.00 (**2**), respectively, characteristic of porphodimethenes.[8,10] Metal insertion has been demonstrated by reaction of **2** with $Zn(OAc)_2{\cdot}2H_2O$ in refluxing $CHCl_3$–MeOH. Complex formation can be easily monitored by UV–VIS-spectroscopy [Fig. 1, λ_{max} (log ε) 475 nm (5.17) (**2b**)]. As shown in Fig. 2, the Zn^{2+} in **2b** is complexed by a nearly planar, C_2 symmetric, tetrapyrrole macrocycle, although the metal is disordered over two positions in the solid-state structure. The

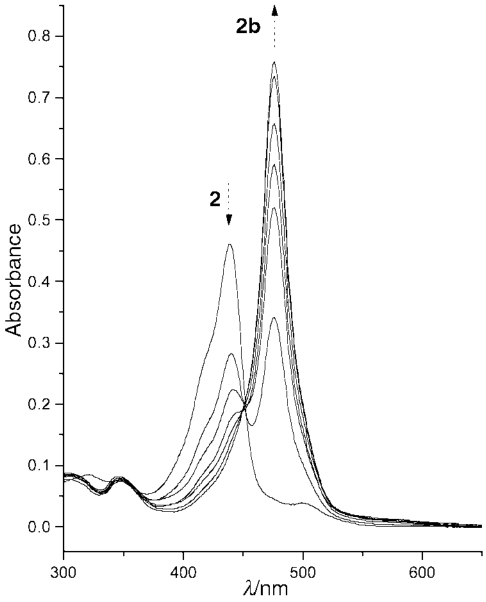


Fig. 1 UV-VIS spectra of **2** upon addition of $Zn(OAc)_2$ in boiling $CHCl_3$–MeOH. The arrows indicate the direction of change in peaks during metallation. Spectra were measured at 5 min intervals.

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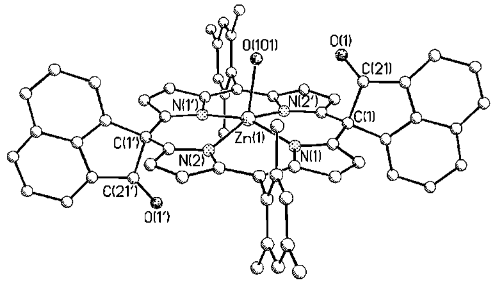

Fig. 2 Diagram of **2b**; the porphodimethene resides on inversion symmetry position, relating the prime and unprimed atoms. The zinc atom is disordered over two positions and the symmetry equivalent Zn(1′) and O(101′) atoms as well as all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.116(4), Zn(1)–N(2) 2.197(4), Zn(1)–N(1′) 2.038(4), Zn(1)–N(2′) 2.063(4), Zn(1)–O(101) 2.175(7), N(1)–Zn(1)–N(2) 85.2(1), N(1)–Zn(1)–N(2′) 88.6(1), N(1′)–Zn(1)–N(2) 87.0(1), N(1′)–Zn(1)–N(2′) 90.7(1), N(1)–Zn(1)–O(101) 97.9(2), N(2)–Zn(1)–O(101) 107.4(2), N(1′)–Zn(1)–O(101) 104.9(2), N(2′)–Zn(1)–O(101) 94.3(2).

largest out of plane displacements are observed for the saturated *meso* carbon atoms (0.11 Å) which are part of the five-membered rings of the two 1-acenaphthenone moieties aligned in an *anti* position. The Zn atom, coordinated by the four pyrrole nitrogens and an axial water molecule, resides 0.404 Å above the plane defined by the nitrogen donor set. The Zn–N bond lengths vary considerably from 2.038(4) to 2.197(4) Å, but the average distance of 2.10 Å is significantly larger than the corresponding linkage in tetra *meso*-aryl substituted porphyrins [mean: 2.036(6) Å; ZnTPP].[11]

Refluxing the porphodimethenes **1** and **2** in THF in the presence of 30% KOH results in ring opening and formation of the respective porphyrins without further oxidation by DDQ. Subsequent protonation with 6 M HCl gives the free acids (**3**, **4**) in high yields. While the αα isomer **3** is soluble in $CHCl_3$, the αβ atropisomer is virtually insoluble in most common organic solvents, possibly owing to strong intermolecular hydrogen-bonding interactions between the carboxylic acid groups. Accordingly, the αβ atropisomer has been fully characterized as the dipotassium salt.

Porphyrin formation has also been accomplished by reaction of **1** or **2** with NaOMe in THF–MeOH at room temp. After bubbling air through the reaction mixture, the corresponding esters (**5**, **6**) were isolated in moderate yields.‡ All of the porphyrins exhibit a characteristic Soret band between 425 and 432 nm in the UV–VIS spectra and they have been characterized by IR, NMR and MS. In addition, the αβ atropisomer **6** has been characterized by an X-ray structural analysis (Fig. 3), and although most of the structural parameters of the porphyrin core are indistinguishable from other *meso*-aryl substituted porphyrins, a few particular details are worth noting. The two mesityl residues are oriented nearly perpendicular to the porphyrin plane (85.3°) while the naphthalene moieties exhibit a twist of 61.8° relative to the macrocyclic ring. Owing to the electronic repulsion of the ester group and the electron rich porphyrin plane, the functionalized naphthalene groups are slightly inclined back away from the porphyrin, lifting the two oxygen atoms above the plane of the macrocycle by 2.667 Å [O(2)] and 3.087 Å [O(1)], respectively.

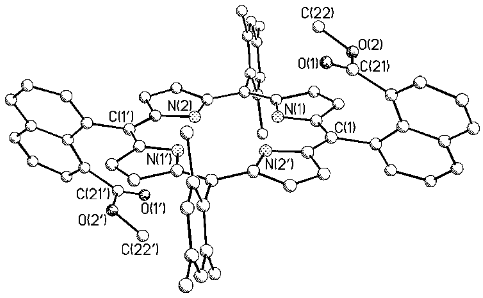

Fig. 3 Diagram of the structure of **6** outlining the atom numbering scheme. Primed and unprimed atoms are related by a center of inversion. The hydrogen atoms have been omitted for clarity.

In summary, we have demonstrated that acenaphthenone substituted porphodimethenes can be generated from 5-mesityldipyrromethane and acenaphthenequinone. Ring cleavage gives the desired porphyrins bearing two 8-functionalized naphthalene groups. Work is in progress to extend this reaction to other vicinale diketones. Other ring opening reactions are also under investigation.

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Notes and references

† 5-Mesityldipyrromethane was prepared as described before.[12] The formation of the porphodimethenes **1** and **2** and the porphyrins **5** and **6** were carried out under a nitrogen atmosphere in dried and degassed solvents. Satisfactory elemental analyses or HR-MS (MH^+) were obtained for new compounds. **1**: Yield: 8%. $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 440 (4.97). IR (KBr): 3345 (ν_{N-H}), 1732 cm^{-1} (ν_{CO}). **2**: Yield: 18%. $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 438(4.93). IR (KBr): 3279 (ν_{N-H}), 1720 cm^{-1} (ν_{CO}). **2b**: Yield: 91%. $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 475(5.17). IR (KBr): 1720 cm^{-1} (ν_{CO}) **3**: Yield: 92%. λ_{max} ($CHCl_3$) 432 nm. IR (KBr): 3327 (ν_{N-H}), 1708 cm^{-1} (ν_{CO}). **4** (potassium salt after recrystallization): Yield: 65%. λ_{max} (MeOH) 431 nm. IR (KBr): 1563 cm^{-1} (ν_{CO}). **5**: Yield: 69%. λ_{max} ($CHCl_3$) 425 nm. IR (KBr): 3315 (ν_{N-H}), 1727 cm^{-1} (ν_{CO}). **6**: Yield: 59%. $\lambda_{max}(CHCl_3)$ 425 nm. IR (KBr): 3315 (ν_{N-H}), 1725 cm^{-1} (ν_{CO}).

‡ *Crystal data*: **2b**·$CHCl_3$: $C_{61}H_{45}N_4O_3Cl_3Zn$, tetragonal, space group, $I4_1/a$, a = 29.539(2), c = 12.104(1) Å, V = 10561(1) Å^3, T = 173 K, Z = 8, D_c = 1.325 g cm^{-3}, μ(Mo-Kα) = 0.667 mm^{-1}, 27 497 reflections collected, 4520 unique, of which 2954 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined using full-matrix least squares refinement on F^2 and difference Fourier synthesis. Unless severely disordered, all non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at calculated positions. At convergence, R_1 = 0.0704 [$I > 2\sigma(I)$], wR_2 = 0.2010, GOF = 1.029 for 381 parameters.

6·CH_2Cl_2: $C_{63}H_{52}N_4O_4Cl_2$, monoclinic, space group $C2/c$, a = 25.800(1), b = 12.7094(7), c = 17.6758(9) Å, β = 115.168(1)°, V = 5245.6(5) Å^3, T = 173 K, Z = 4, D_c = 1.266 g cm^{-3}, μ(Mo-Kα) = 0.177 mm^{-1}, data collection, refinement and solution as above, 11 105 reflections collected, 3433 unique, of which 3006 with $I > 2\sigma(I)$ were used in all calculations. R_1 = 0.0611 [$I > 2\sigma(I)$], wR_2 = 0.1766, GOF = 1.047 for 357 parameters.

CCDC 182/1536. See http://www.rsc.org/suppdata/cc/a9/a907992k/ for crystallographic files in .cif format.

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