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Novel preparation of β,β′-connected porphyrin dimers†

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Porphyrin dimers were prepared from β,β′-dipyrrole derivatives *via* the double pyrrolylmethylation followed by double [2+2] MacDonald porphyrin synthesis.

Oligomeric porphyrins have attracted attention as biomimetic models for photosynthesis, opto-electric devices, and composites for supramolecular assemblies.[1] Porphyrin chromophores have been assembled in many ways. In some cases, they were connected directly with covalent bonds,[2] and spacers such as other π-systems,[3] hydrocarbon chains,[4] transition metal complexes[5] and hydrogen-bonding molecules[6] were employed in others. Oxidation of porphyrins with silver hexafluorophosphate or *via* an anode is one of the most versatile and reliable methods for connecting the porphyrin chromophore directly,[7] and this method was successfully applied for a gigantic 128-mer *meso-meso*-linked porphyrin array.[8] Other linkages such as *meso*-β, β–β, and fused fashions were observed in the oxidation of porphyrins under particular conditions.[9] Recently, *meso-meso*- and β–β-coupled porphyrins were prepared by nucleophilic dimerization initiated by addition of an alkyllithium[10] and by Suzuki coupling reaction,[2a] respectively. In this communication, we report a new method for the preparation of a β–β-connected porphyrin dimer based on the MacDonald [2 + 2] porphyrin synthesis.

In most cases of the preparation of directly connected porphyrin dimers, the key step is the coupling reaction of the porphyrin chromophores.[11] We thought that a β–β-connected porphyrin dimer could be constructed in the porphyrin ring construction step if a β–β-dimer of pyrrole would be employed. In the pyrrole dimer, the pyrrole rings must be nearly perpendicular each other, otherwise macrocyclic ring formation containing the dipyrrole moiety would occur.[12] For this purpose, we chose the known 4-formyl-3-methylpyrrole **1**[13] as a starting material (Scheme 1).†

The Knoevenagel reaction of the formylpyrrole **1** with nitroethane gave β-pyrrolyl nitro olefin **2** in 97% yield. Barton–Zard synthesis of the nitro olefin **2** with ethyl isocyanoacetate and DBU gave an unsymmetrical pyrrole dimer **3** in 46% yield. First, we attempted to apply the [3 + 1] porphyrin synthesis[14] for **3**. Thus, the ester groups of **3** were removed by heating with KOH in ethylene glycol, and symmetric 4,4′-dimethyl-3,3′-dipyrrole was obtained in quantitative yield. However, all our efforts concerning the derivatization of the dipyrrole by formylation and pyrrolylmethylation failed and intractable mixtures were obtained. This failure would be due to coplanarity of the pyrrole rings in the symmetrical dipyrrole. From the X-ray analysis of **3**,‡ the dihedral angle of the pyrrole rings is 68.6° and rotation around the pyrrole–pyrrole bond is sufficiently disturbed by the neighboring two methyl and one ethoxycarbonyl groups. We next examined the pyrrolylmethylation of the dipyrrole **3** with **4**. The reaction of **3** with **4** proceeded smoothly in the presence of acid to afford bis(dipyrromethane) tetra ester **5** in good yield. Removal of all four alkoxycarbonyl groups of **5** was easily accomplished under similar conditions to give crude acid- and oxygen-sensitive bis(dipyrromethane) **6**, which was directly subject to the next MacDonald [2 + 2] porphyrin synthesis. Condensation of **6** and dipyrromethane dicarbaldehyde **7** was achieved by slow addition of a solution of **6** and **7** in CH_2Cl_2–MeOH into a solution of pTSA in CH_2Cl_2–MeOH at rt, and the mixture was further treated with $Zn(OAc)_2$ under air. Chromatographic purification followed by recrystallization from EtOAc–hexane provided the targeted bisporphyrinato–zinc complex **8a** in 10% yield. Demetallation of **8a** with TFA gave porphyrin free base **8b** in quantitative yield.

The structure of **8a** was fully characterized by spectroscopic analyses.† Elemental analysis of **8a** gave the correct molecular composition as its *semi*-hydrate and the FAB MS spectrum displayed a typical pattern of the sum of molecular ion peaks and their protonated ones ($C_{68}H_{78}N_8Zn_2$: m/z = 1134.5–1144.5). In the ^{1}H NMR spectra of **8a** in $CDCl_3$, eight characteristic singlet signals due to *meso* protons were observed between 10.0 and 10.6 ppm, and this indicates no symmetric element existed in the dimer molecule. Signals of one each of butyl and ethyl group appeared at higher fields due to the anisotropic effect of the other part of the porphyrin ring, and were assigned to the butyl and ethyl groups at the 18′- and 18-positions, respectively. These methyl part absorptions of the butyl and ethyl groups were observed *ca.* 1.2 and 0.65–0.85 ppm higher than those of others, respectively. These facts suggest that the peripheral butyl group at the 18′-position cover one face of the other porphyrin core. The methylene protons of the butyl group appeared as AB signals, which clearly indicated the presence of axial chirality between the porphyrin rings. Fig. 1 shows the electronic absorption spectra of the porphyrin dimers **8a** and **8b**. Broad absorptions of the Soret and Q bands of **8a** have shoulders which are due to the exciton coupling of the porphyrin chromophores, and these absorption maxima and the shape are quite similar to those reported for the β,β′-linked porphyrin dimer.[2a] Similarly, one very broad Soret and four Q band absorptions are observed in the case of free base porphyrin dimer **8b**.

Our route to β,β-connected porphyrin dimers is applicable for the preparation of a variety of porphyrin dimers with a non-symmetrical peripheral substitution pattern. Introduction of a

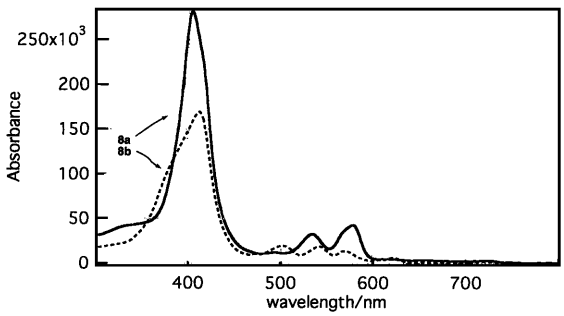

Fig. 1 UV/Vis spectra of bisporphyrins **8a** (—) and **8b** (. . . . .).

† Electronic supplementary information (ESI) available: experimental procedures employed in Scheme 1, ORTEP drawing of **3** and a ball and stick model of **3** showing hydrogen bonding. See http://www.rsc.org/suppdata/cc/b1/b108819j

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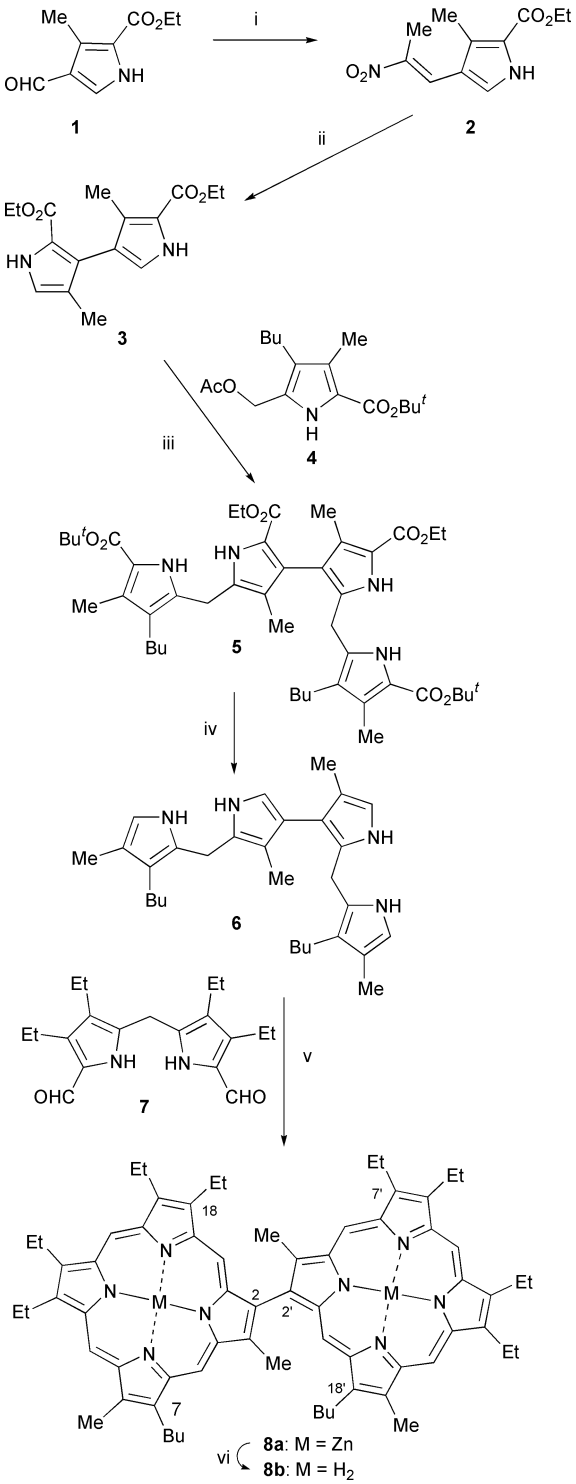

Scheme 1 *Reagents, conditions and yields*: (i) $EtNO_2$, NH_4OAc, reflux, overnight; 97%. (ii) ethyl isocyanoacetate, DBU, THF, rt, overnight; 46%. (iii) **4**, pTSA, AcOH, rt, 2 h; 68%. (iv) KOH, ethylene glycol, 180 °C, 2 h. (v) **7**, pTSA, CH_2Cl_2–MeOH, $Zn(OAc)_2$, air; 10% (2 steps). (vi) TFA, CH_2Cl_2, rt; quant.

ligating functional group in the 18- and 18′-substituents which cover over the other porphyrin chromophore will provide an easy access to a porphyrin dimer with different coordination state of metal centres.

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Notes and references

‡ *Crystallographic summary for* **3**: $C_{16}H_{20}O_4N_2$; FW = 304.35, colorless rods, 0.55 × 0.30 × 0.21 mm, monoclinic, $P2_1/c$ (#14), $Z = 4$ in a cell of dimensions $a = 11.134(2)$, $b = 7.626(2)$, $c = 19.564(2)$ Å, $\beta = 91.266(10)°$, $V = 1660.8(4)$ Å3, $D_{calc} = 1.217$ g cm^{-3}, Mo-Kα, $F(000) = 648.0$, 3814 unique reflections, 3811 with $I_o > -10\sigma(Io)$. The final $R = 0.081$ ($R_1 = 0.070$, 1733 with $I_o > 2\sigma(I_o)$), $R_w = 0.090$, goodness-of-fit = 1.66 for 240 parameters refined on F^2. CCDC 172085. See http://www.rsc.org/suppdata/cc/b1/b108819j/ for crystallographic files in .cif or other electronic format.

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