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Synthesis of 5,15-Diaryl-Substituted Oxochlorins from 5,15-Diaryloctaethylporphyrin

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Synopsis. 5,15-Diaryl-substituted oxochlorins were prepared from osmium tetraoxide oxidation of 5,15-diaryloctaethylporphyrin followed by acid-catalyzed pinacol rearrangement. Optical and electrochemical properties of this macrocyclic ring are studied by measuring the absorption and fluorescence spectra, fluorescence lifetimes, and one-electron oxidation and reduction potentials.

The appearance of the X-ray structure of bacterial photosynthetic reaction center (RC) has stimulated a wide range of synthetic modelling approaches towards this natural charge separation apparatus.[1] In the course of our research program aiming at construction of artificial photosynthetic reaction center,[2] we need conformationally restricted porphyrin-chlorin heterodimers as a rational extension of our porphyrin models.[3,4] Oxochlorin pigments, which was originally prepared by Fischer and Pfeiffer[5] and have recently been prepared by H_2O_2 or osmium tetraoxide (OsO_4) oxidation of porphyrin and subsequent acid-catalyzed rearrangement,[6] are of particular interest to us since its stability as well as high electron-accepting ability.[7] Functionally, the latter property leads to an expectation that intramolecular charge separation that is quite similar to the initial electron-transfer reactions in RC may be feasible in some covalently-linked porphyrin-oxochlorin hybrid dimers.[8] We therefore set out to prepare 5,15-diaryl-substituted oxochlorins to allow an incorporation of an oxochlorin moiety into our conformationally restricted oligomeric porphyrin models.

Results and Discussion

Treatment of 5,15-bis(4-methyl)phenyl-2,3,7,8,12,13,17,18-octaethylporphyrin (**1**)[9] with OsO_4 in CH_2Cl_2 at room temperature for 16 h in the dark under N_2 atmosphere followed by zinc ion insertion provided dihydroxychlorin **4** in 35% yield. Upon being refluxed with trifluoroacetic acid in $CHCl_3$, **4** rearranged to the oxochlorins **5** (54%) and **7** (38%), which were easily separated by flash column chromatography (silica gel, benzene/hexane) (Chart 1). Similar oxidation of zinc porphyrin **2** also gave dihydroxychlorin **4** in 20% yield. Zinc complexes **6** and **8** were prepared by the usual metalation procedure ($Zn(OAc)_2$, reflux) (Fig. 1). Assignment of the geometric isomers, **5** and **6**, and **7** and **8**, was based on their ^1H NMR data. In the ^1H NMR spectrum of **6**, the two meso-protons appear at 8.80 and 9.86

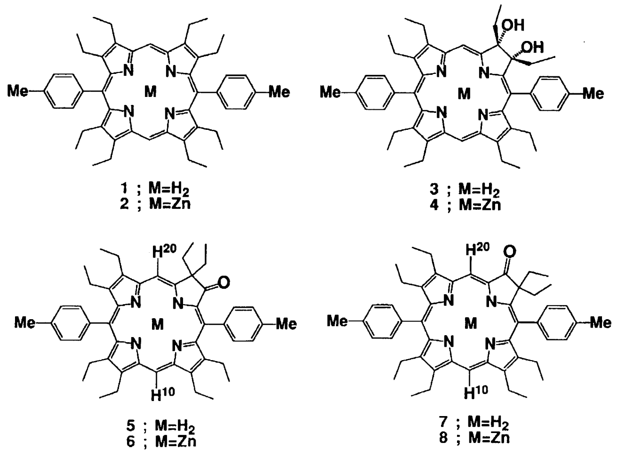

Chart 1.

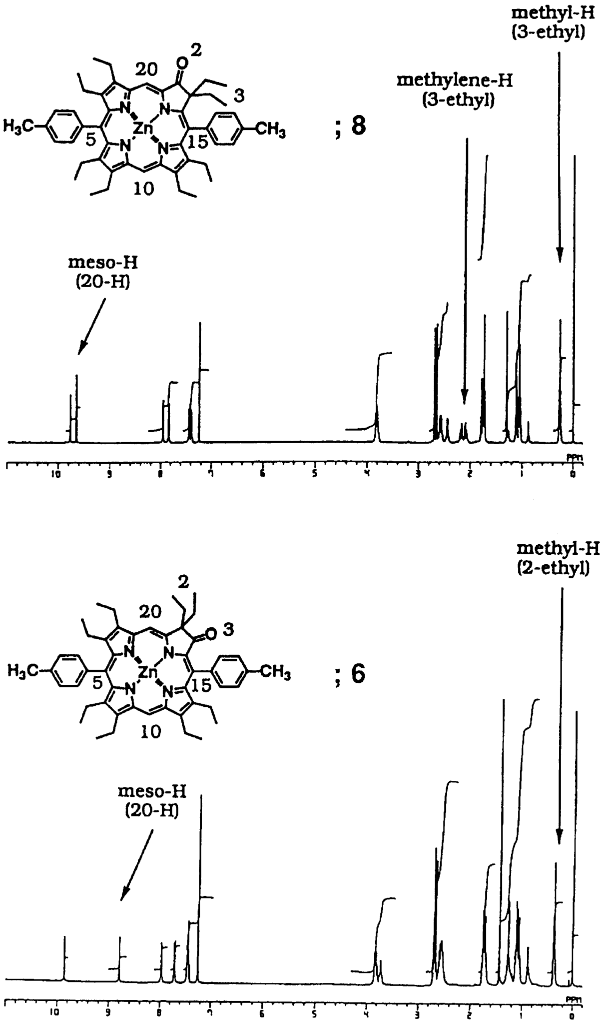

Fig. 1. Supplementary data for referring.

Table 1. Physical Properties of Oxochlorins

Compound	Absorption/nm (λ_{max})[a]	Fluorescence/nm (λ_{max})[a]	τ/ns[b]	S_1/eV[c]	E_{ox}/V[d]	E_{red}/V[d]
1	411, 509, 543, 576, 627	630, 698	12	1.97	+0.33	−1.88
5	414, 518, 557, 591, 648	648	5.2	1.91	+0.37	−1.68
7	415, 518, 557, 591, 645	650	5.9	1.92	+0.37	−1.67
2	412, 541, 576	584, 637	1.4	2.14	+0.14	<−2.00
6	421, 576, 623	628	0.50	1.98	+0.10	−1.77
8	426, 574, 625	637	0.57	1.97	+0.11	−1.80

a) Measured at room temperature in CH_2Cl_2. Concentrations are ca. 10^{-6} M (1 M=1 mol dm^{-3}). b) Fluorescence lifetime determined by single-photon counting technique at room temperature in THF. Concentrations are ca. 10^{-6} M. c) Excitation energy estimated on the basis of the absorption and fluorescence spectra in CH_2Cl_2. d) Redox potentials measured by cyclic voltammetry at Pt electrode at 20 °C in CH_2Cl_2 containing 0.1 M tetrabutylammonium perchlorate.

ppm. The high-field shifted signal can be assigned to the H^{20}-meso proton and that at 9.86 ppm, being similar to the normal porphyrin meso-proton, is assignable to the H^{10}-meso proton. On the other hand, the two meso-protons in **8** appear at 9.67 and 9.78 ppm, since the H^{20}-proton is adjacent to β-oxo functionality in a saturated pyrrole ring and its chemical shift is shifted to lower field in comparison to that in **6**. In consistent with this assignment, the geminal diethyl protons in **8** appear at higher field in comparision to those in **6** (see, Experimental section). The free base oxochlorins **5** and **7** exhibit virtually the same ^{1}H NMR specta as those of **6** and **8**. The absorption and fluorescence properties of these oxochlorins are listed in Table 1, together with the data for **1** and **2**. Strong absorptions characteristic of a chlorin chromophore are observed around 645—650 nm for **5** and **7** and at 623—625 nm for **6** and **8**. The excitation energy levels of these oxochlorins estimated on the basis of the absorption and fluorescence spectral data are lower than **1** and **2** by ca. 0.05 and 0.16 eV, respectively (Table 1). The fluorescence lifetimes of oxochlorins are shorter than those of the corresponding porphyrins. It is interesting to note that both in the free base forms and zinc complexes the fluorescence lifetimes of **5** and **6** are shorter than those of **7** and **8**, respectively. Redox potentials were measured by cyclic voltammetry in CH_2Cl_2. Noteworthy observations here are that the zinc complexes **6** and **8** are more easily oxidized than **2** and the free base forms **5** and **7** are more easily reduced than **1**. Accordingly, it may be concluded that these oxochlorin macrocycles are more redox active than related porphyrins[7] and thus will be useful for realization of intramolecular charge separation within tetrapyrrolic pigments.[8]

Experimental

Dry pyridine (0.1 ml) was added to a solution of osmium tetraoxide (OsO_4) (92 mg, 0.36 mmol) in dry ether (4.0 ml) under N_2 atmosphere. The resultant yellow solution of OsO_4–pyridine complex was added to a solution of **1** or **2** (0.1 mmol) in dry CH_2Cl_2 (100 ml). The mixture was stirred for 16 h at room temperature in the dark under N_2 atmosphere. H_2S gas was passed through the mixture for 2 h, so as to induce the precipitation of osmium sulfide. The resultant solids were removed by filtration under reduced pressure, and the filtrate was neutralized with saturated aqueous Na_2CO_3. The organic layer was separated and dried over anhydrous Na_2SO_4. A saturated methanol solution of $Zn(OAc)_2$ (10 ml) was added to the solution and the resulting mixture was refluxed for 1 h. After usual work up, the products were separated with silica-gel flash column using CH_2Cl_2 as an eluent; **3** being eluted as a dark green band.

Trifluoroacetic acid (5 ml) was added to the solution of **4** (50 mg, 0.06 mmol) in $CHCl_3$ (25 ml). The mixture was refluxed for 5 h. After usual work up, two oxochlorins **5** and **7** were separated by flash column chromatography on silica-gel using benzene–hexane (4:6) as an eluent. Zinc complexes **6** and **8** were prepared by the usual metalation method ($Zn(OAc)_2$, reflux).

4; Mp 263—265 °C; ^{1}H NMR ($CDCl_3$) (Chemical shifts were found to be slightly dependent upon the concentation) δ=−0.42 (3H, t, J=5.0 Hz, $CH_2C\underline{H}_3$), 1.05 (9H, t, J=10.0 Hz, $CH_2C\underline{H}_3$), 1.37 (3H, m, J=5.0 Hz, $CH_2C\underline{H}_3$), 1.63 (3H, t, J=10.0 Hz, $CH_2C\underline{H}_3$), 1.70 (6H, t, J=10.0 Hz, $CH_2C\underline{H}_3$), 1.79 (1H, m, J=5.0 Hz, $C\underline{H}_2CH_3$), 1.94 (1H, m, J=5.0 Hz, $C\underline{H}_2CH_3$), 2.06 (1H, m, J=5.0 Hz, $C\underline{H}_2CH_3$), 2.42 (1H, m, J=5.0 Hz, $C\underline{H}_2CH_3$), 2.51 (4H, q, J=10.0 Hz, $C\underline{H}_2CH_3$), 2.61 (3H, s, Ar-CH_3), 2.68 (5H, s, J=10.0 Hz, Ar-CH_3, $C\underline{H}_2CH_3$), 2.87 (1H, m, J=5.0 Hz, $C\underline{H}_2CH_3$), 3.41 (1H, s, OH), 3.58 (2H, m, J=5.0 Hz, $C\underline{H}_2CH_3$), 3.71 (4H, q, J=10.0 Hz, $C\underline{H}_2CH_3$), 3.87 (1H, m, J=5.0 Hz, OH), 7.24 (1H, d, J=5.0 Hz, Ar-H), 7.30 (1H, d, J=5.0 Hz, Ar-H), 7.38 (1H, d, J=5.0 Hz, Ar-H), 7.44 (1H, d, J=5.0 Hz, Ar-H), 7.49 (1H, d, J=5.0 Hz, Ar-H), 7.82 (1H, d, J=5.0 Hz, Ar-H), 8.03 (1H, d, J=5.0 Hz, Ar-H), 8.28 (1H, d, J=5.0 Hz, Ar-H), 8.50 (1H, s, meso-H^{20}), and 9.55 (1H, s, meso-H^{10}); MS(FAB) m/z 811 (M^++1); UV-vis (CH_2Cl_2) λ_{max} (rel ε) 410 (1.00), 512 (0.03), 581 (0.03), and 623 (0.22) nm; IR (KBr) 3518 (OH) and 3440 (OH) cm^{-1}.

5; Mp 288—290 °C; ^{1}H NMR ($CDCl_3$) δ=−1.86 (2H, s(br), NH), 0.31 (6H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.08 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.17 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.20 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.75 (6H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.18 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 2.52—2.67 (4H, m, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.61 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.67 (3H, s, Ar-CH_3), 2.71 (3H, s, Ar-CH_3), 2.82 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.93 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.83 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.88 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.99 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 7.46 (2H, d, J=8.0 Hz, Ar-H), 7.48 (2H, d, J=8.0 Hz, Ar-H), 7.75 (2H, d, J=8.0 Hz, Ar-H), 7.99 (2H, d, J=8.0 Hz, Ar-H), 9.08 (1H, s, meso-H^{20}), and 10.07 (1H, s, meso-H^{10}); MS (FAB) m/z 731 (M$^+$+1); IR (KBr) 1716 (C=O) cm^{-1}.

6; Mp 87—89 °C; ^{1}H NMR (CDCl$_3$) δ=0.37 (6H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.05 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.09 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.11 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.17 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.73 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.75 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 2.51—2.65 (10H, m, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.67 (3H, s, Ar-CH_3), 2.70 (3H, s, Ar-CH_3), 3.72 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.81 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.83 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 7.44 (2H, d, J=8.0 Hz, Ar-H), 7.45 (2H, d, J=8.0 Hz, Ar-H), 7.71 (2H, d, J=8.0 Hz, Ar-H), 7.97 (2H, d, J=8.0 Hz, Ar-H), 8.80 (1H, s, meso-H^{20}), and 9.86 (1H, s, meso-H^{10}); MS (FAB) m/z 793 (M$^+$+1); IR (KBr) 1714 (C=O) cm^{-1}.

7; Mp 258—260 °C; ^{1}H NMR (CDCl$_3$) δ=−1.72 (2H, s(br), NH), 0.26 (6H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.10 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.15 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.19 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.76 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.79 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.85 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 2.08—2.30 (4H, m, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.64 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.68 (3H, s, Ar-CH_3), 2.70 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.71 (3H, s, Ar-CH_3), 2.83 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.83 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.98 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 4.00 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 7.44 (2H, d, J=8.0 Hz, Ar-H), 7.46 (2H, d, J=8.0 Hz, Ar-H), 7.89 (2H, d, J=8.0 Hz, Ar-H), 7.99 (2H, d, J=8.0 Hz, Ar-H), 9.95 (1H, s, meso-H^{20}), and 10.01 (1H, s, meso-H^{10}); MS (FAB) m/z 731 (M$^+$+1); IR (KBr) 1705 (C=O) cm^{-1}.

8; Blue solid; Mp 93—95 °C; ^{1}H NMR (CDCl$_3$) δ= 0.26 (6H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.05 (6H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.11 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.74 (6H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 1.78 (3H, t, J=8.0 Hz, $CH_2C\underline{H}_3$), 2.05—2.22 (4H, m, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.45 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.57 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.60 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 2.65 (3H, s, ArCH_3), 2.70 (3H, s, Ar-CH_3), 3.80 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.81 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 3.83 (2H, q, J=8.0 Hz, $C\underline{H}_2CH_3$), 7.39 (2H, d, J=8.0 Hz, Ar-H), 7.43 (2H, d, J=8.0 Hz, Ar-H), 7.84 (2H, d, J=8.0 Hz, Ar-H), 7.96 (2H, d, J=8.0 Hz, Ar-H), 9.67 (1H, s, meso-H^{20}), and 9.78 (1H, s, meso-H^{10}); MS (FAB) m/z 793 (M$^+$+1); IR (KBr) 1707 (C=O) cm^{-1}.

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