Synthesis and Properties of Metal Complexes of Ether-bonded Porphyrin–Chlorin Dimer

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A number of metal complexes of dimeric porphyrin–chlorin ether have been prepared; bis-zinc porphyrin–chlorin was shown to undergo photooxidation of the chlorin moiety, bis-zinc porphyrin–chlorin and porphyrin–porphyrin were also shown to form addition products with one oxygen molecule.

Porphyrin and chlorin dimers connected with an ether bond could be convenient models for the study of energy transfer and charge separation. We have some evidence of this derived from our earlier studies on the synthesis of similar compounds.[1] These dimers were found to exist as stable isomers with a certain fixed spatial arrangement of macrocycles. The oxygen bridge between the porphyrin rings was pretty stable in neutral, alkaline and slightly acidic media, and apparently could serve as an additional charge-transfer channel.

Based upon these observations we have decided to synthesise and study metal dimers of this type. For a starting compound we have taken porphyrin–chlorin dimer **1**, which was shown to exist in two stable configurations.[2] Each of these configurations is apparently a mixture of optical isomers $R_{Por}R_{Chl}$ + $S_{Por}S_{Chl}$ and $R_{Por}S_{Chl}$ + $S_{Por}R_{Chl}$, where R and S represent the porphyrin (Por) and chlorin (Chl) configuration, respectively. It has been shown that the structure with the lower chromatographic mobility was spatially more compact. Further investigation of the isomers by fluorescence spectroscopy confirmed the fact that the dimers had a different structural organisation, because on porphyrin macrocycle excitation we observed a response from the chlorin macrocycle, whereas the second form (more mobile on chromatography) did not react in this manner.[3]

Treatment of the less mobile form of dimer **1** with a saturated methanol solution of zinc acetate has shown that the metal ion first entered the porphyrin ring (during the first 5 min, structure **2**) and only afterwards entered the chlorin cycle. The reaction took 1 h to proceed to completion. The course of the reaction was monitored spectrophotometrically: the initial spectrum of the free-base porphyrin–chlorin with two main maxima at 500 and 640 nm subsequently began to exhibit three peaks at 537, 574 and 640 nm, the first two belonging to the zinc porphyrin. It finally transformed into a spectrum with maxima at 537, 574 and 614 nm, the last peak coming from the zinc-chlorin. This is consistent with a structure of bis-zinc complex **3**.[†]

An interesting feature of the metal complex is its ability to add an oxygen molecule on standing in the air. Evidence of this is the hypsochromic shift of the porphyrin bands (532 and 570 nm) and a bathochromic (617 nm) shift in the absorption spectrum of the chlorin moiety of the dimer (Fig. 1), and also the peak of m/z 1244 in the mass spectrum. $NaBH_4$ treatment of the compound **9** resulted in a reverse reaction leading to the starting bis-zinc complex **3**.

Treatment of the compound **3** with dilute HCl gave the initial dimer **1** not containing metal and exhibiting the initial structure.

Oxidation of compound **3** with simultaneous irradiation results in far deeper changes. The absorption spectrum exhibited a decrease of the peak at 614 nm intensity (the chlorin ring) up to its complete disappearance (Fig. 2). From the reaction mixture we have isolated a product with a mass two units smaller (m/z 1210) than the initial product **3**. Chromatographically and spectroscopically this product corresponded to a bis-zinc porphyrin–porphyrin **8**.[‡] Treatment of the oxidation product with HCl led to a known dimer **7**.[4] The structure of compound **8** was also confirmed by its cleavage with HBr/AcOH followed by methanol quenching to give two porphyrins: α-hydroxyethyl(heptaethyl)porphyrin and α-methoxyethyl(heptaethyl)-porphyrin.

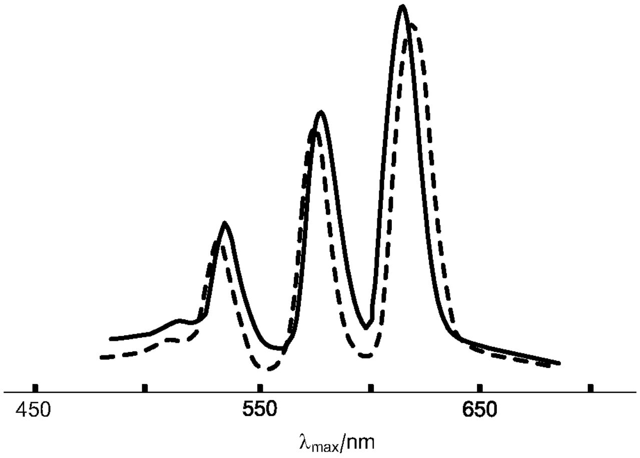

Fig. 1 Absorption spectra of bis-zinc porphyrin–chlorin **3** (solid line) and its addition product with oxygen **9** (dashed line).

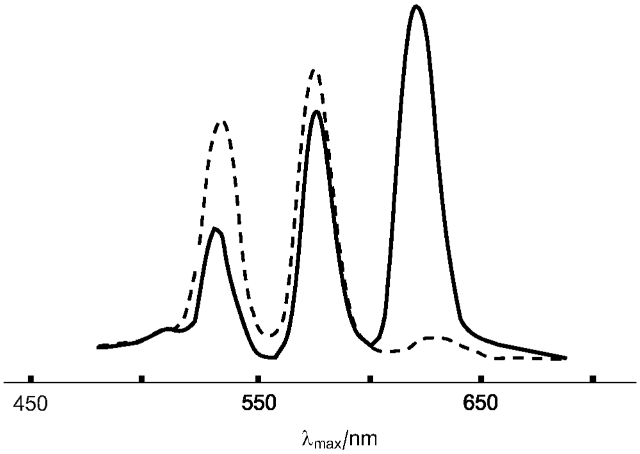

Fig. 2 Photoinduced oxidation of porphyrin-chlorin. Absorption spectra of bis-zinc porphyrin–chlorin **3** (solid line) and oxidation product **8** (dashed line).

Bis-zinc porphyrin–porphyrin **8**, similar to the dimer **3**, adds an oxygen molecule to give an additional product **10**, λ_{max} 533 and 569 nm, m/z 1241. Analogously to the

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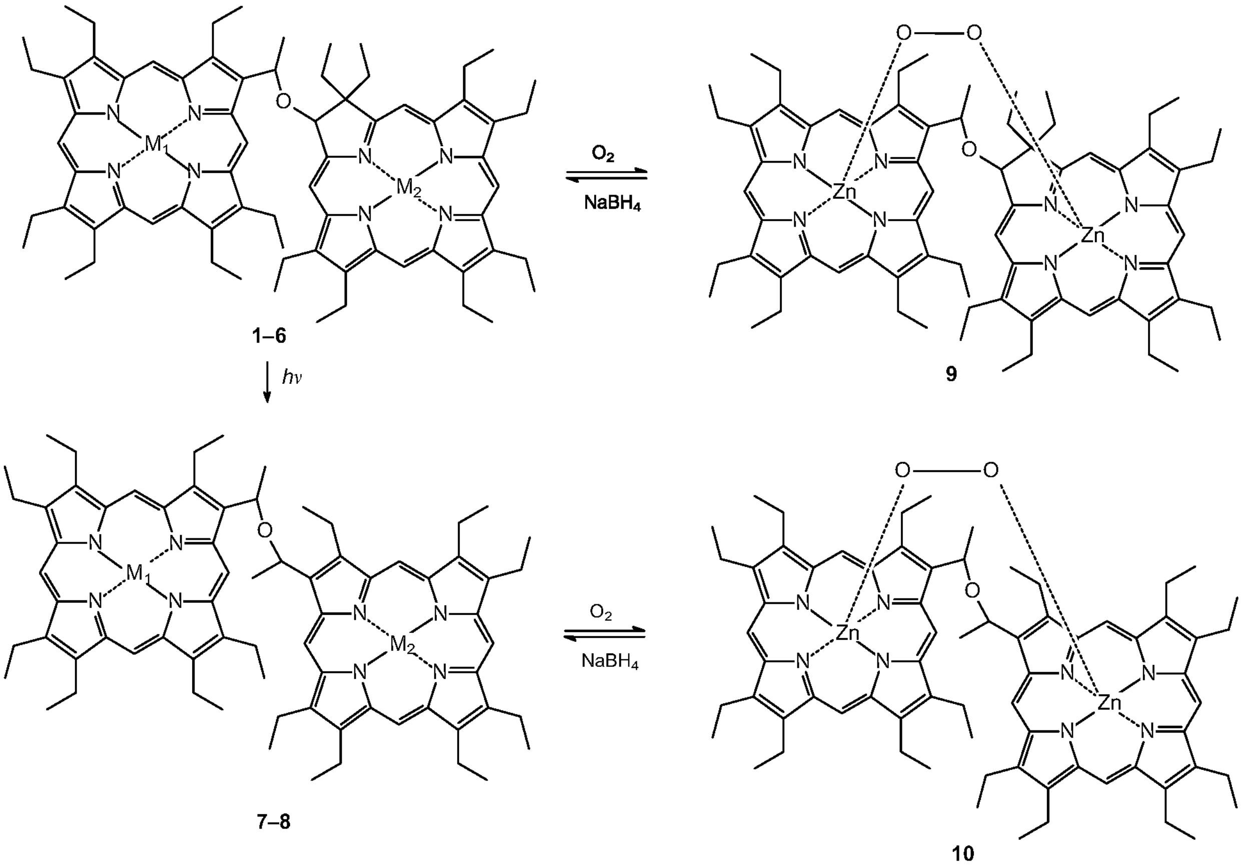
[†] Bis-zinc porphyrin–chlorin has been obtained in 96% yield. M.p. 264–268 °C (decomp.), λ_{max}/nm (Beckman DU 8): 393, 537, 574, 614 (7.3:0.6:0.8:1), m/z (Plasma Desorption Mass Spectrometry) 1212.6, Calc. for $C_{72}H_{90}N_8O_4Zn_2$ 1212 ; ^1H NMR δ_H (Bruker MSL 200, $CDCl_3$): 10.17 (s, H, 2 *meso*-H), 10.01, 9.30, 9.06, 8.88, 8.57, 7.50 (s, each 1H, *meso*-H), 6.64 (s, chlorin ring H), 6.50 [q, H, $OCH(CH_3)$], 1.8–4.3 (m, 30H, CH_2CH_3), 2.31 [d, 3H, $OCH(CH_3)$], 0.8–1.4 (m, 36H, CH_2CH_3), 0.75, 0.45, 0.19 (t, each 3H , CH_2CH_3).

[‡] Bis-zinc complex of the dimer **8** was obtained from bis-porphyrin **7**.[4] M.p. > 380 °C; λ_{max}/nm 537, 574; m/z 1210.2, Calc. for $C_{72}H_{88}N_8O_4Zn_2$, 1210.

Table 1 Spectral characteristics of the metal complexes of dimer **1**.

Metal ion	Reaction conditions		Absorption spectrum					m/z
	t/min	T/°C	λ_{max}/nm					
Cobalt	40	61	393	525	557	620	(7.4:0.3:0.7:1.0)	1199
Nickel	20	200	396	517	554	617	(5.5:0.3:1.2:1.0)	1198
Copper	5	20	394	528	566	618	(6.7:0.4:0.8:1.0)	1207



1–6

7–8

9

10

1 $M_1 = M_2 = 2H$
2 $M_1 = Zn$, $M_2 = 2H$
3 $M_1 = M_2 = Zn$
4 $M_1 = M_2 = Co$
5 $M_1 = M_2 = Ni$
6 $M_1 = M_2 = Cu$
7 $M_1 = M_2 = 2H$
8 $M_1 = M_2 = Zn$

porphyrin–chlorin complex, compound **10** is reduced by $NaBH_4$ to give the starting dimer **8**. Thus we can speak of zinc complexes of dimeric ether porphyrins as sharing the common property of giving addition products with oxygen. This could open up an interesting potential for the design of models for the mechanism of oxygen activation.

The tendency of the metal porphyrin–chlorin dimer **1** to undergo photooxidation was also observed for other metal complexes too. Copper, nickel and cobalt heterodimer complexes were obtained by treatment of dimer **1** with saturated methanol solutions of the corresponding metal acetates (Table 1). The susceptibility of the chlorin ring to photooxidation decreases in the series cobalt-nickel-copper.

References

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