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Synthesis of a Novel Chlorin-Quinone System for the Investigation of Light Induced Electron Transfer

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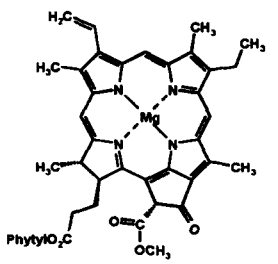
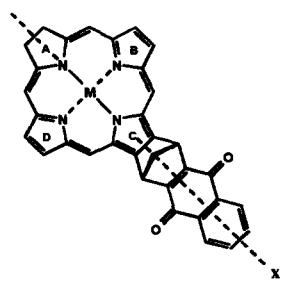
Abstract: In order to investigate the effect of the molecular symmetry on the light induced electron transfer in chlorin-quinone dyades we aimed at the synthesis of chlorin-quinone models **18a** and **18b** in which the quinone is situated at ring D adjacent to the reduced pyrrole ring A and thus orientated along the y-axis. © 1997 Elsevier Science Ltd. All rights reserved.

Covalently linked porphyrin-quinone dyades have been extensively investigated as model systems to understand the light induced electron transfer reaction of photosynthesis.[1] The investigations show that the efficiency of the light induced charge separation in these model systems depends on the geometry, with well-defined donor-acceptor distance. In contrast to these model systems, which make use of porphyrins, the natural photosynthetic systems contain chlorophylls which contain the chlorin chromophore with slightly different photophysical properties compared to the porphin system. Another point which has not been considered yet and can not be investigated with donor-acceptor systems based on the highly symmetric porphyrin chromophore is the symmetry of the arrangement of the donor and the quinone acceptor.[2] Due to the reduced symmetry of the chlorin chromophore in chlorine-quinone dyades there are two distinct orientations of the donor and acceptor. The quinone can either be orientated along the x-axis where the chlorin is intersected at the reduced A ring and the opposite C ring (chlorin I, **2**) or along the y-axis which intersects the chlorin along the B and D rings (chlorin II, **3**).



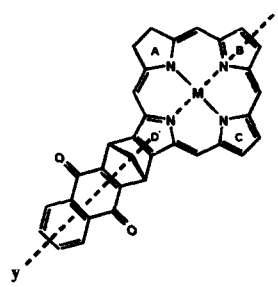
chlorophyll a

1



chlorin I

2

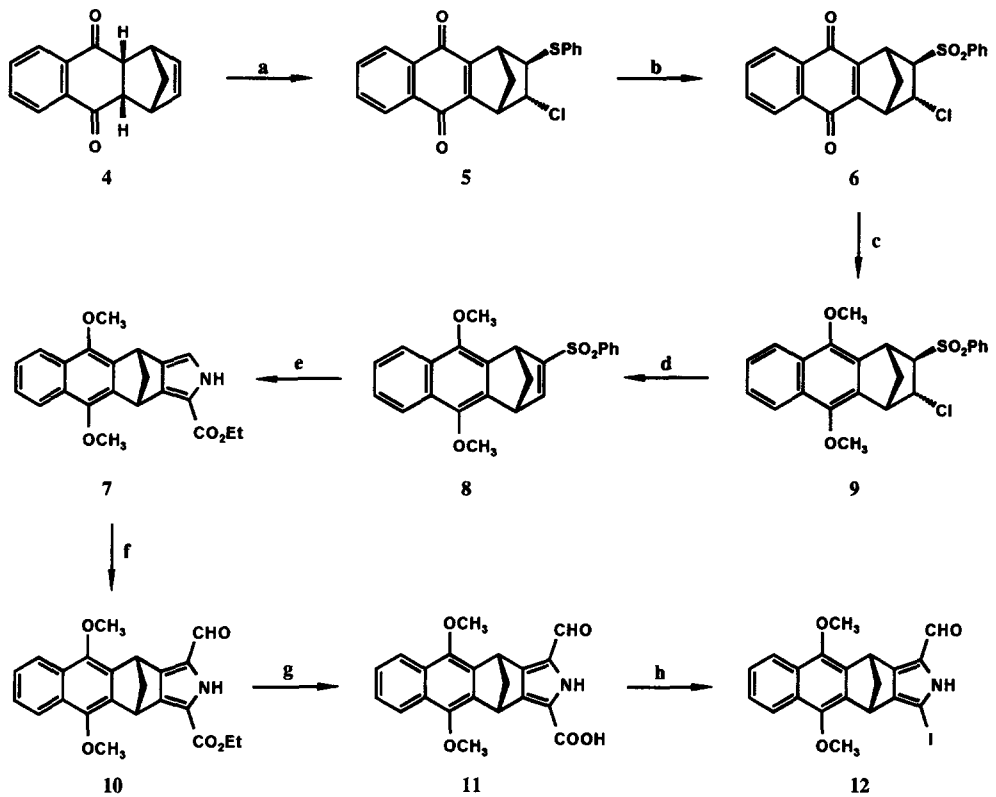


chlorin II

3

To obtain chlorin based dyades and in order to investigate the influence of symmetry on the light induced electron transfer we have aimed at the synthesis of appropriate chlorins.

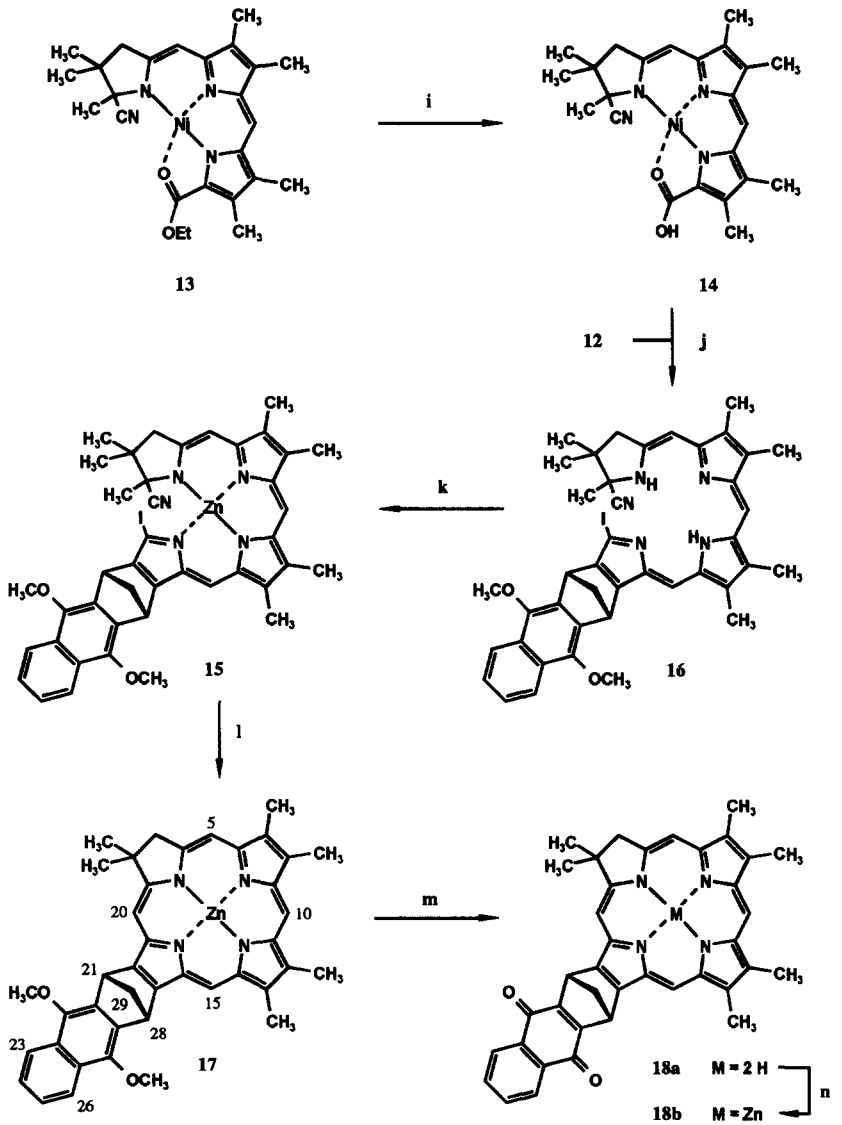
Here we report on the synthesis of a novel chlorin-quinone model in which the quinone is arranged at ring D adjacent to the reduced pyrrole ring A and thus orientated along the y-axis. The target chlorin **18** can be obtained according to an approach which was developed in our laboratory for the synthesis of chlorins and corrins.[3,4] A key intermediate in the previous synthesis is the nickel tricycle **13** which can also be used for the construction of the desired chlorin described here.[3]



Scheme 1: a) **4**, CH_2Cl_2, -78 °C, 2.3 eq. $PhSCl/CH_2Cl_2$ → -50 °C, 4 h → room temp., 1 h, chromatogr. (93 %). b) **5**, CH_2Cl_2, 0 °C, 2.5 eq. MCPBA (50 %)/CH_2Cl_2, 1 h → room temp., 1 h, chromatogr. (99 %). c) 1. **6**, 2 eq. $Na_2S_2O_4$, 0.8 eq. Adogen 464®, CH_2Cl_2, H_2O, 15 min; 2. poor NaOH (10 eq.), 15 min, room temp.; 3. 10 eq. CH_3I, 4 h, room temp., chromatogr. (53 %). d) **9**, CH_2Cl_2, 1.8 eq. DBU, 1 h → room temp., 1 N HCl, chromatogr. (87 %), e) 3 eq. KO-*t*Bu/THF, 3 eq. isocyanoacetic acid ethylester, **8**, room temp., 1.5 h, chromatogr. (85 %). f) DMF, 6 eq. $POCl_3$, 5 °C, 15 min; **7**/$ClCH_2CH_2Cl$, rfl., 2 h, chromatogr. (71 %). g) **10**, 3.5 eq. LiOH x H_2O, H_2O, rfl., 1.5 h → room temp., 1 N HCl. h) **11**, 4 eq. $NaHCO_3$, H_2O, 70 °C, 10 min; 1.05 eq I_2, 3.5 eq KI, 70 °C, 20 min, chromatogr. (60 %).

A new pathway had to be developed for the ring D building block bearing the quinone moiety of the chlorin (Scheme 1). Naphthoquinone was therefore treated in a Diels-Alder reaction with cyclopentadiene to yield the known hydroquinoide adduct **4**,[5] which on treatment with PhSCl reacted at the olefinic double bond and was reoxidized to the quinone **5**. Oxidation of the sulfide to the sulfone **6** followed by reductive methylation afforded the hydroquinone ether **9**.[6] The protection of the quinone structure as its hydroquinone ether was necessary to avoid side reactions at the quinone moiety during the pyrrole formation. The pyrrole **7** was formed

by treatment of the α,β-unsaturated sulfone **8** with isocyanoacetic acid ethylester in the presence of base according to a method which was recently developed in our laboratory.[7] The α,β-unsaturated sulfone **8** can be derived easily from the chloro sulfone **9** by base-induced elimination reaction with DBU. The pyrrole aldehyde **10** was obtained by Vilsmeier formylation at the α-position of the pyrrole. Hydrolysis of the ester in **10** yielded the free carboxylic acid **11** which led to the desired ring D building block **12** on treatment with iodine through decarboxylation.



Scheme 2: i) **13**, 5 N KOH, THF, 70 °C, 45 min. j) **14**, 1.5 eq. **12**, 13 eq. 0.4 N *p*-TsOH, $CHCl_3$, rfl., 15 min. k) **16**, 5 eq. $Zn(OAc)_2$, 5 eq. NaOAc, MeOH, room temp., 20 min, chromatogr. (80 %). l) **15**, 180 eq. DBU, sulfolane, 80 °C, 2 h, chromatogr. (44 %). m) **17**, 15 eq. 1 N BBr_3/CH_2Cl_2, CH_2Cl_2, room temp., 16 h. H_2O, chromatogr. (67 %). n) 5 eq. $Zn(OAc)_2$, 5 eq. NaOAc, MeOH, room temp., 20 min, chromatogr. (71 %).

With the ring D building block at hand, the synthesis of the target chlorin could be achieved (Scheme 2). Therefore, the nickel tricycle **13** was condensed with the iodopyrrole aldehyde **12**, after hydrolysis to the free carboxylic acid **14**, accompanied by decarboxylation to yield the tetrapyrrole **16**. To exercise a template effect in the cyclisation step to the chlorin, tetrapyrrole **16** was transformed into the zinc complex **15**. The cyclisation to the chlorin **17**[8] occurred after treatment with base which produced an enamine structure by HCN elimination at ring A. The enamine then attacked the iodo imine structure in ring D thus forming the 20 methine bridge of the chlorin. The synthesis of the target chlorin **18a**[8] was completed by cleavage of the hydroquinone ether with BBr_3 at room temperature which also removed the Zn(II) from the macrotetracycle. The resulting hydroquinone was readily oxidized in the presence of air which was not excluded during the reaction. Recomplexation of **18a** with $Zn(OAc)_2$ yielded the zinc chlorin **18b**.[8]

Whereas the zinc chlorin **17** with the attached hydroquinone ether moiety shows a very strong fluorescence, this could not be observed in the case of the chlorin **18a,b**. The missing flourescence for **18a,b** indicates that light induced electron transfer occurs from the chlorin chromophore to the naphthoquinone. Detailed photophysical investigations of chlorin **18a,b** will be reported elsewhere.

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References And Notes

Dedicated to Prof. Gerhard Quinkert on the occasion of his 70th birthday.

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2. We are grateful to Dr. S. N. Smirnow, Department of Chemistry, Dartmouth College, Hanover, New Hampshire, USA, who suggested to us the possible influence of symmetry of the arrangement of the donor chlorin and the quinone acceptor on the light induced electron transfer.
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8. All compounds show correct spectroscopic and analytic data. The represented formula pictures describe racemic mixtures. Selected spectroscopic data of **17** and **18a**: **17:** **^{1}H-NMR** (360 MHz, $CDCl_3$): δ = 1.86, 2.05 (2*s* 2 Me-C(2)); 3.17, 3.27, 3.32 (3*s*, 4 Me-C(7), C(8), C(12), C(13)); 3.30, 3.45 (2*m*, 2 H-C(29)); 4.03, 4.09 (2*s*, 2 *Me*O); 4.46 (*m*, 2 H-C(3)); 5.70, 6.79 (2*m*, 2H-C(21), C(28)); 7.25 (*m*, 2 H-C(24), C(25)); 7.76 (*m*, 2 H-C(23), C(26)); 8.53 (*s*, H-C(5)); 8.59 (*s*, H-C(20)); 9.30, 9.59 (2*s*, 2 H-C(10), C(15)). **UV/VIS** (THF): λ_{max}(lg ε) = 284 (4.25), 401 (5.21), 504 (3.73), 577 (3.85), 594 (3.83), 621 (4.84). **18a:** **^{1}H-NMR** (360 MHz, $CDCl_3$): -2.48, -2.30 (2br. *s*, 2 NH); 1.99, 2.08 (2*s*, 2 Me-C(2)); 3.34, 3.35, 3.39, 3.45 (4*s*, 4 Me-C(7), C(8), C(12), C(13); 3.63 (*m*, 2 H-C(29)); 4.47 (*m*, 2 H-C(3)); 5.56, 5.94 (2*m*, 2 H-C(21), C(28)); 7.56 (*m*, 2 H-C(24), C(25)); 7.99 (*m*, 2 H-C(23), C(26)); 8.79 (*s*, H-C(5)); 8.83 (*s*, H-C(20)); 9.48, 9.76 (2*s*, 2 H-C(10), C(15)). **UV/VIS** (THF): λ_{max}(lg ε) = 256 (4.19), 281 (4.31), 387 (5.04), 490 (3.97), 601 (3.53), 653 (4.37).

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