Meso-meso Linked Diporphyrins from 5,10,15-Trisubstituted Porphyrins

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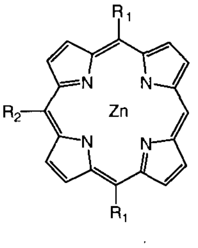
Meso-meso coupled diporphyrins were prepared from 5,10,15-trisubstituted zinc-porphyrins in high yields upon treatment with $AgPF_6$ alone or with $AgPF_6$ and I_2.

Constructing synthetic mimics of the natural antenna complexes and photosynthetic reaction centers has been a major objective of the field of artificial photosynthesis. Along this line, considerable attention has been devoted to the development of covalently linked porphyrin arrays.[1] Recently, several groups including us reported the synthesis of meso-meso coupled porphyrin arrays,[2-4] which are interesting and promising structural and functional motif exhibiting nearly orthogonal arrangement of porphyrins,[4] extensively large exciton coupling at Soret bands,[2-4] and large third non-linear optical properties.[5] Our method has several advantages, in that it gives oligomeric porphyrins in relatively high yields directly from 5,15-diaryl zinc-porphyrin and needs quite simple manipulation, just treating the zinc porphyrin with silver (I) ion in $CHCl_3$ followed by separation over size exclusion chromatography.[2] An interesting nature of this method lies in its easy extension to the synthesis of trimer, tetramer, and higher oligomers as demonstrated well in the precedent literature.[2] The product distribution that depends on the reaction time and the amount of silver (I) ion, however, is suffering from some difficulties in product separation. Thus we examined similar coupling reaction of 5,10,15-trisubstituted zinc porphyrins in which only a single meso-position is available for the meso-meso coupling.



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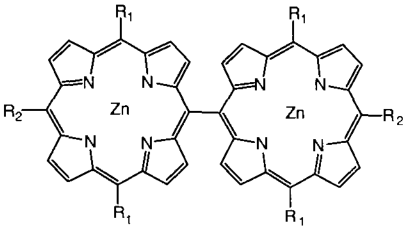

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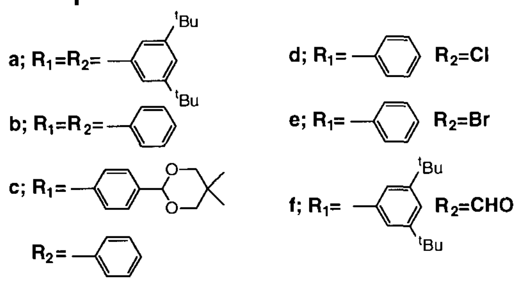
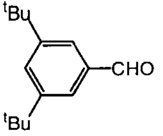


We first prepared 5,10,15-tris(3,5-di-tert-butylphenyl) zinc-porphyrin (**1a**)[6] by cross condensation of 3,5-di-terbutylbenzaldehyde (**3**), dipyrrylmethane (**4**),[7] and 3,5-di-terbutylphenyl substituted dipyrrylmethane (**5**)[8] followed by separation over a size exclusion column and zinc insertion in 16% overall yield. Treatment of a $CHCl_3$ solution of **1a** upon 0.5 equiv of $AgPF_6$ at room temperature for 5h gave dimer **2a** as a single product in 42% yield along with recovery of the starting material (57%). Use of an equiv amount of $AgPF_6$ enhanced the yield of **2a** to 75% with recovery of **1a** (22%). While an increase in the amount of $AgPF_6$ to 2 equiv did not improve the yield, a nearly quantitative yield (95%) of **2a** was attained upon the treatment with 1.0 equiv of $AgPF_6$ twice in a consecutive manner. The FAB mass spectrum indicated a parent ion peak at 1871 (Calcd for $C_{124}H_{142}N_8Zn_2$, 1871) and the ^1H NMR analysis revealed the presence of four β-protons, two of which are high-field shifted (8.15 and 8.70 ppm) compared with those in **1a**,[6] being characteristic of the β-protons adjacent to the meso-meso connection.[2-4] The absorption spectrum exhibits extensively split Soret bands at 420 and 457 nm with similar intensities, being quite analogous to the reported values.[2]



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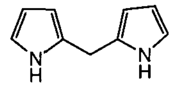

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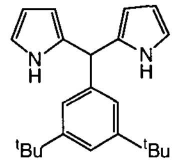

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5,10,15-Trisubstituted zinc-porphyrins **1b,c** were also prepared by Suzuki coupling of 10-bromo-5,15-diphenyl porphyrins **1e**[9,10] with phenylboronic acid in 80-90% yields.[9,10] Porphyrins **1b,c** were coupled under the same conditions to the corresponding dimers **2b,c** in 65-80% yields. It is worthy to note that only **2a-c** were formed in this oxidative coupling reaction and thus the product separation was much easier by the size-exclusion chromatography than in the reaction of 5,15-diaryl zinc-porphyrins.[2]

10-Chloro-substituted porphyrin **1d**[11] was converted into the dimer **2d** upon treatment with $AgPF_6$ under the same conditions in 57% yield. In contrast, 10-bromo-porphyrin **1e** was inert under the same conditions but was found to be smoothly converted into **2e** in 80% yield upon treatment with $AgPF_6$ and I_2.

Finally, the similar reaction of 10-formyl substrate **1f** with $AgPF_6$ and I_2 gave a relatively complicated reaction mixture from which we obtained dimer **2f** in 20% yield.

The meso-meso coupled diporphyrins displays the large exciton coupling in the Soret bands, ca. 1900 cm^{-1} for **2a-c** and ca. 1700 cm^{-1} for **2d-e**, and 1560 cm^{-1} for **2f**, respectively.[12] On the other hand, the dimers **2a-f** exhibit rather small electronic interactions in the S_1-state and there is virtually no attenuation in

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the fluorescence quantum yields upon dimerization.[2,3] This property may be favorable for antenna function.[3] The dimers **2c-f** have functional groups that may be usable in linking other groups to this diporphyrin moiety, thus encouraging an incorporation of this diporphyrin moiety into more elaborated photosynthetic models[13] capable of charge separation in an efficient manner. Work along this line is in progress.

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6 All the new compounds appeared in this paper were fully characterized by 500 MHz ^{1}H NMR and FAB mass spectra. Selected data are as follows: **1a** ^{1}H NMR ($CDCl_3$) 1.52 (s, 18H, t-Bu), 1.55 (s, 36H, t-Bu), 7.78 (t, J=1.8 Hz, 1H, Ar-H), 7.81 (t, J=1.8 Hz, H, Ar-H), 8.08 (d, J=1.8 Hz, 2H, Ar-H), 8.12 (d, J=1.8 Hz, 4H, Ar), 9.03 (d, J=4.9 Hz, 2H, Por-β), 9.06 (d, J=4.9 Hz, 2H, Por-β), 9.15 (d, J=4.9 Hz, 2H, Por-β), 9.41 (d, J=4.9 Hz, 2H, Por-β), and 10.27 (s, 1H, meso); FAB MS m/z 936, Calcd for $C_{62}H_{72}N_4Zn$, 936; **2a** ^{1}H NMR ($CDCl_3$) 1.43 (s, 72H, t-Bu), 1.57 (s, 36H, t-Bu), 7.70 (t, J=1.8 Hz, 4H), 7.82 (t, J=1.8Hz, 2H, Ar), 8.09 (d, J=1.8Hz, 8H, Ar), 8.15 (d, J=4.9 Hz, 4H, Por-β), 8.17 (d, J=1.8 Hz, 4H, Ar), 8.70 (d, J=4.9 Hz, 4H, Por-β), 9.03 (d, J=4.9 Hz, 4H, Por-β), and 9.07 (d, J=4.9 Hz, 4H, Por-β); FAB MS m/z 1871, Calcd for $C_{124}H_{142}N_8Zn_2$, 1871.

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11 Porphyrin **1d** was prepared by the chlorination of 5,15-diphenyl zinc-porphyrin with *N*-chlorosuccinimide.

12 Typically, split Soret bands were observed as follows: 423 and 455 nm for the meso-chlorinated dimer **2d**, and 430 and 461 nm for the meso-formyl substituted dimer **2f** in CH_2Cl_2.

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