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Synthesis of a Macrocyclic Porphyrin Hexamer with a Nanometer-Sized Cavity as a Model for the Light-Harvesting Arrays of Purple Bacteria

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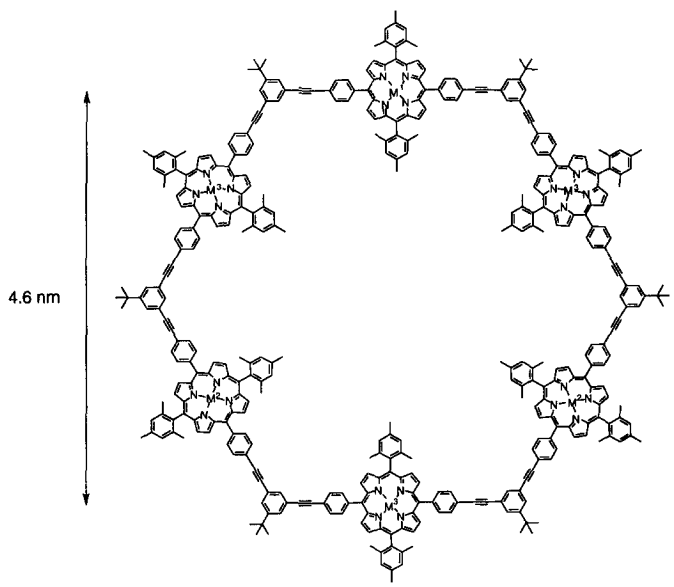
Abstract: The synthesis of a cyclic hexaporphyrin array with an integral acceptor chromophore, mimicking the light-harvesting complex of photosynthetic purple bacteria, is described. The cavity of this hexagonal macrocycle, which is circumscribed by five porphyrin rings, as Zn(II) chelates, and one porphyrin ring, as free base, has a diameter of about 4.6 nm. The quantum efficiency of intramolecular transfer of singlet excited-state energy determined by comparison with a solution of a mixture of the corresponding porphyrin monomers in a 5:1 ratio amounts to 40 %.

Since the discovery of the saturation of the rate of photosynthesis induced by increasing light intensity by *Robert Emerson* and *William Arnold* in 1932[1] it is well known that most of the chlorophyll molecules in a photosynthetic unit act just as antennas, whereas only a few (about one among 300 cholorophyll molecules in *Chlorella* cells) are able to transform excitation energy into chemical energy. More recently, the spacial arrangement of such light harvesting arrays in purple bacteria has been elucidated by X-ray diffraction studies. Thus, the antenna complexes of *Rhodopseudomonas acidophila* [2] and *Rhodospirillium molischianum* [3] consist of two concentric circular arrays of bacteriochlorophyll *a* molecules containing, both together, 27 and 24 chromophores, respectively, which are non-covalently bound to apoproteins.



1a : $M^1 = M^2 = M^3 = Zn$
1b : $M^1 = M^2 = 2\,H$, $M^3 = Zn$
1c : $M^1 = 2\,H$, $M^2 = M^3 = Zn$

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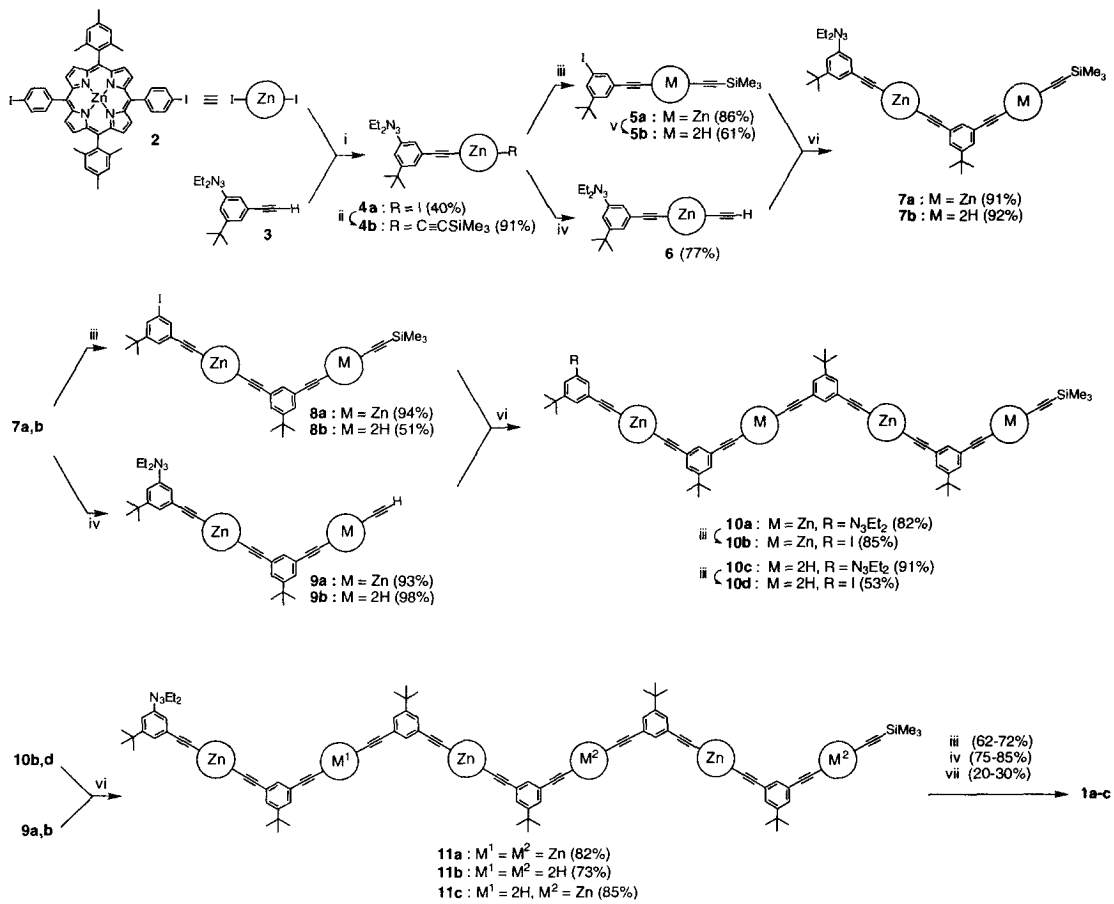
In the inner ring, which contains 2/3 of the chromophores, the planes of the bacteriochlorophyll *a* molecules are oriented perpendicularly to the plane of the thyllakoid membrane, whereas in the outer ring, which contains 1/3 of the chromophores, the planes of the latter are nearly parallel to the membrane plane. These spatial arrangements provide a most efficient energy transfer *via* Förster induced dipole-dipole resonance from the short- to the long-wavelength-absorbing pigments within the photosynthetic unit.

Although numerous oligomeric porphyrinic arrays have been synthesized with the goal of optimizing photophysical properties,[4-8] the construction of a cyclic array with an integral acceptor resembling the light-harvesting units of photosynthetic bacteria has not been described hitherto. In a recent modeling study of the quantum efficiency of energy transfer within the chromophores of different possible two-dimensional multiporphyrin arrays, the advantage of such a cyclic array *vs.* linear arrays has been emphasized.[9]

Thus, the present communication deals with the synthesis of hexagonal corral-shaped cyclic molecules **1a-c**, the cavity of which is circumscribed by six tetraphenyl porphyrin rings linked together by six *meta*-diethynylphenyl corner-stones. With an internal diameter of the cavity amounting to *ca.* 4.6 nm, they are, to the best of our knowledge, the largest *rigid macrocycles*, which have been synthesized so far.[10]



Scheme 1. Reagents and conditions: (i) Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 45 °C, 3 h; (ii) HC≡CSiMe_3, $Pd(PPh_3)_2Cl_2$, CuI, DMF/Et_3N, 35°C, 14h; (iii) CH_3I, 135 °C, 2 h; (iv) 1M NaOH, THF; (v) TFA, $CHCl_3$; (vi) $Pd(PPh_3)_4$, DMF/Et_3N, 40°C, 14h; (vii) substrate (2.5 x 10^{-4} M), $Pd(PPh_3)_4$ (1.25 x 10^{-3} M), DMF/Et_3N, 40°C, 14h.

The multi-step synthesis of **1a-c** was carried out using a single building block (**4b**),† in which two reactive positions (a protected ethynyl group and a diethyltriazene-substituted phenyl C-atom) may be activated selectively (Scheme 1). The used divergent/convergent strategy has been described previously for the synthesis of oligomers of phenylacetylene.[11,12] Thus, in the presence of a Pd(0) catalyst, cross-coupling of **5a** with **6** - both readily accessible from **4b** by treatment with methyl iodide or NaOH, resp. - yielded the corner-stone **7a**, which contains the same functional groups as **4b**; corner-stone **7b**, containing a zinc chelate and a free-base porphyrin, was analogously prepared from **5b** (obtained by acidic treatment of **5a**) and **6**. The three-step sequence was then repeated to prepare the porphyrin tetramers **10a** and **10c**, which were transformed by reaction with methyl iodide into **10b** and **10d**, resp. Thereon, the linear porphyrin hexamers **11a-c** were obtained by reaction of tetramers **10b,d** with dimers **9a,b**. After subsequent activation of both their terminal functional groups, the three hexamers were finally cyclized in the presence of Pd(0) in high-diluted solution, to afford **1a-c**.‡ According to the D_{6h} symmetry of the molecule, the ^{1}H NMR spectrum of **1a** consists of only a few signals, whereas those of its linear precursors are much more complex.

The step-by-step method developed in this work enables the preparation of cyclic hexamers with different metallation states such as **1c**. A more straightforward synthesis of the Zn_6 porphyrin hexamer **1a** was attempted in that the ethynyl group of porphyrin dimer **8a** was deprotected, and the resulting compound was reacted under similar conditions to those used for the cyclization of the linear hexamers. In our hands, however, the desired trimerisation did not take place in appreciable extent, although the presence of **1a** in the obtained complex mixture of products could be detected by mass spectrometry.

The absorption spectra of the arrays **1a-c** in benzene is almost a composite of the spectra of the individual chromophores. However, the Soret band of **1a** at λ_{max} = 427 nm is red-shifted compared with λ_{max} = 423 nm of *meso*-tetraphenylporphinato zinc(II) (ZnTPP). The bands of the emission spectra are also red-shifted by 2 to 4 nm in the three arrays. The quantum yield of fluorescence of the Zn_6 hexamer **1a** (Φ_f = 4.4 %) is slightly higher than that of ZnTPP (Φ_f = 3.3%[13]). Singlet excited-state energy transfer from the Zn chelates to the free-base porphyrin (Fb) chromophores can be observed on both Zn_3Fb_3 (**1b**) and Zn_5Fb (**1c**) hexamers (Figure 1 and 2, resp.).

The overall yield of intramolecular energy transfer (Φ_{ET}) was estimated to be 91% for **1b**, a value which agrees with that observed in a starburst array of four porphyrin rings covalently bound to a central acceptor.[5] On the other hand, in hexamer **1c**, energy is transferred from five Zn(II)-porphyrin chromophores to a single free-base chromophore with an efficiency of 40%.

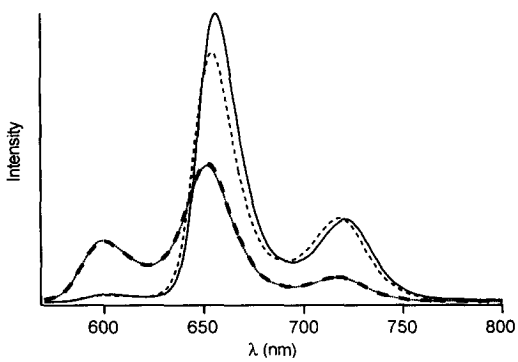


Figure 1 : Measured emission spectra of **1b** (——), and of a solution of the porphyrin monomers ZnTPP and TPP in a 3:3 ratio (— — —), in benzene at room temperature (λ_{ex} 550 nm, A_{550} = 0.036). Calculated curves for Φ_{ET} = 0% (·····) and for Φ_{ET} = 91% (- - - -).

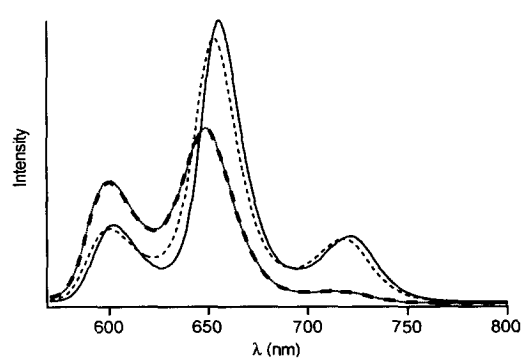


Figure 2 : Measured emission spectra of **1c** (——), and of a solution of the porphyrin monomers ZnTPP and TPP in a 5:1 ratio (— — —), in benzene at room temperature (λ_{ex} 550 nm, A_{550} = 0.036). Calculated curves for Φ_{ET} = 0% (·····) and for Φ_{ET} = 40% (- - - -).

The discrepancy between this figure and the estimated value (84%) for a monocyclic porphyrin decamer with internal receptor,[9] is justified by following reasons: a) the size of the macrocyclic arrays in the theoretical model and the synthetic molecule is different; b) the theoretical value has been calculated on the basis of the unrealistic assumption that the mean life time of the singlet excited state is the same in a cyclic array of ten porphyrin chromophores as in a linear polyporphyrin array containing the same number of chromophores. Actually, the rate of intramolecular energy transfer between the chromophores diminishes when the latter are bound to *meta* positions of the aromatic rings used as linkers;[8] c) under the experimental conditions used to determine the rate of intramolecular energy transfer presumably only one Zn(II)-porphyrin chromophore is excited in each polyporphyrin array, so that excitation energy may be lost by back and forth transfer between vicinal Zn(II)-porphyrin chromophores with a rate that is difficult to estimate in the theoretical model; d) in the synthetic macrocycle **1** the porphyrin chromophores can rotate around one of their symmetry axes, so that intramolecular energy transfer may take place in some conformers with less efficiency than in others.

In summary, the porphyrin hexamer, the synthesis of which is described in this work, provides a sound basis for the further study of energy transfer within chromophores which spacial arrangement mimicks the light-harvesting arrangement in purple bacteria and other photosynthetic organisms.[14]

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References and Notes

† The synthetic precursor (**4a**) of **4b** was synthesized from the known tetraarylporphyrin **2**[7] and from **3**, which was obtained in 87% yield by treatment of the corresponding trimethylsilyl derivative[11] with TBAF in THF.

‡ *Selected data for:* **1a**: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 1.49 (s, 54H), 1.84 (s, 72H), 2.64 (s, 36H), 7.29 (s, 24H), 7.75 (d, J = 1.4 Hz, 12H), 7.86 (t, J = 1.4 Hz, 6H), 7.97 and 8.27 (AA'XX', J_{AX} = 8.3 Hz, 48H), 8.81 and 8.92 (2 × d, J = 4.6 Hz, 48H); UV/vis (benzene) 289, 427, 551, 592; MALDI-MS (dithranol) *m/z* 5644.1 [M+1] (calcd avg mass for $C_{384}H_{300}N_{24}Zn_6$: 5643.03). **1b**: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ -2.61 (s, 6H), 1.49 (s, 54H), 1.84 and 1.85 (2 × s, 72H), 2.63 (s, 36H), 7.29 (s, 24H), 7.75 (d, J = 1.4 Hz, 12H), 7.86 (t, J = 1.4 Hz, 6H), 7.97 and 8.25 (AA'XX', J_{AX} = 8.1 Hz, 24H), 7.97 and 8.27 (AA'XX', J_{AX} = 8.1 Hz, 24H), 8.73 and 8.84 (2 × d, J = 4.4 Hz, 24H), 8.81 and 8.92 (2 × d, J = 4.8 Hz, 24H); UV/vis (benzene) 289, 425, 516, 551, 593, 650; MALDI-MS (dithranol) *m/z* 5453.9 [M+1] (calcd avg mass for $C_{384}H_{306}N_{24}Zn_3$: 5452.94); ES$^+$-MS (THF) *m/z* 2727.4 ([M+2H]$^{2+}$), 1818.6 ([M+3H]$^{3+}$). **1c**: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ -2.61 (s, 2H), 1.49 (s, 54H), 1.84 and 1.85 (2 × s, 72H), 2.64 (s, 36H), 7.29 (s, 24H), 7.75 (d, J = 1.4 Hz, 12H), 7.86 (t, J = 1.4 Hz, 6H), 7.97 and 8.25 (AA'XX', J_{AX} = 8.1 Hz, 8H), 7.97 and 8.27 (AA'XX', J_{AX} = 8.1 Hz, 40H), 8.73 and 8.83 (2 × d, J = 4.4 Hz, 8H), 8.81 and 8.93 (2 × d, J = 4.8 Hz, 40H); UV/vis (benzene) 289, 427, 516, 551, 592, 648; MALDI-MS (dithranol) *m/z* 5580.7 [M+1] (calcd avg mass for $C_{384}H_{302}N_{24}Zn_5$: 5579.67).

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