A Tethered Porphyrin Dimer with π Overlap of a Single Pyrrole Ring

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A "special pair" of π-interacting bacteriochlorophyll chromophores serves as the central electronic feature of the bacterial photosystem.[1] It is unique among its accompanying antenna and accessory pigments in that full π overlap is limited to the pyrrole 1-rings.[2] We report here the synthesis and spectroscopic characterization of **1**, a model system of the special pair (Figure 1). This amine-tethered zinc(II) porphyrin dimer exhibits mutual π overlap that is likewise limited to a single pyrrole ring.

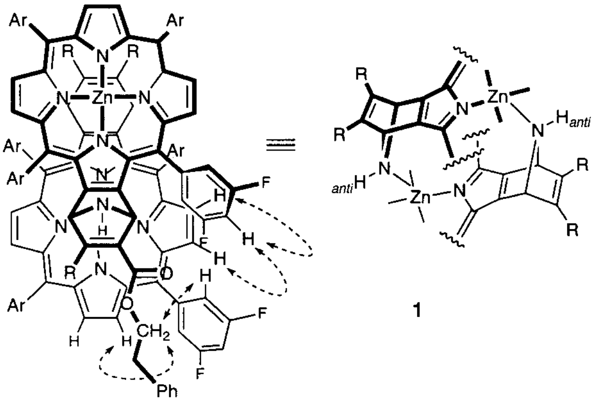
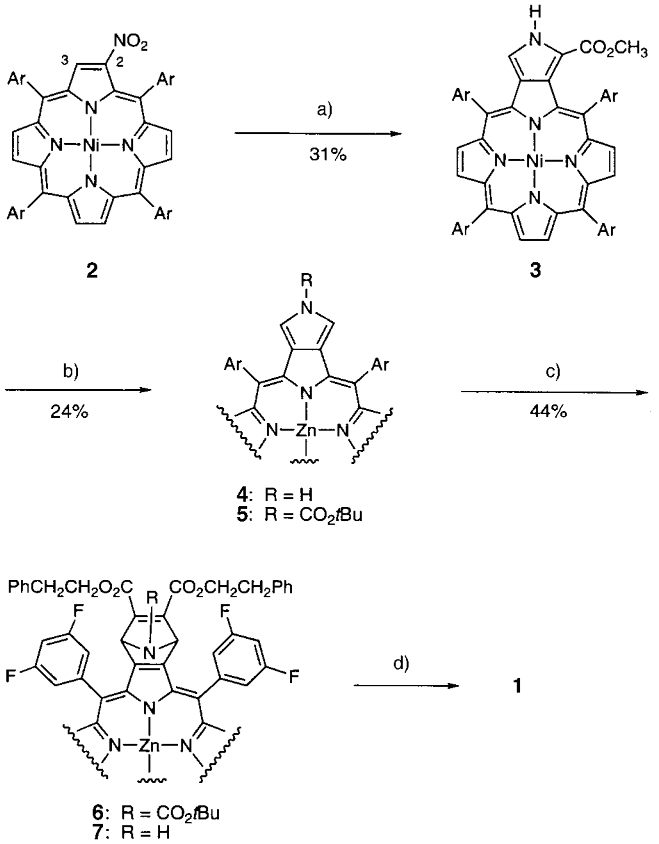


Figure 1. Top view of dimer **1** along with a side view of the partial structure. The inter-subunit contacts, as indicated by the 2D-ROESY NMR experiment for a solution of **1** in $CDCl_3$, are marked with dashed arrows. Ar = 3,5-difluorophenyl, R = 2-phenylethoxycarbonyl.

Dimers of zinc(II) porphyrin[3, 4] and bacteriochlorin[5] have been assembled by attaching a zinc-ligating heterocyclic substituent such as 2-pyridyl or 2-imidazolyl to a peripheral carbon atom of the chromophore. The natural tendency of porphyrinoids to π stack in parallel planes about 3.2 Å apart,[6] as well as the length, orientation, and point of attachment of the ligating tether, serve to position the π systems of the two rings in a stable dimeric arrangement that can be studied in solution. Overlapping component pigments in the bacterial photosystem possess spectroscopic and electronic characteristics critical for photosynthesis, such as red-shifted Q_y bands and perhaps unobserved features hidden by intense higher energy absorbances due to auxillary pigments.[7] There is therefore an impetus to construct and evaluate model dimers with similar π overlap of a single pyrrole ring.

For the zinc(II) porphyrin/bacteriochlorin dimer system, this reduces to attaching a zinc-ligating atom along an axis through the midpoint of the C2–C3 bond (see **2**), with its lone pair of electrons positioned several angstroms outside of and above the π perimeter to interact with the zinc atom of the partner chromophore. These requirements are met by a 7-azabicyclo[2.2.1]heptadiene framework fused at C2–C3 of the porphyrin ring.



Scheme 1. Synthesis of **1**. Ar = 3,5-difluorophenyl. a) $CNCH_2CO_2CH_3$, 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), THF, *t*BuOH, 15 min, reflux; b) 1. 1% H_2SO_4 in TFA, room temperature (RT), 1 h; 2. $Zn(OAc)_2$, MeOH, CH_2Cl_2, RT, 10 min; 3. LiCl, DMSO, 3 h, reflux; 4. $(BOC)_2O$, DMAP, CH_2Cl_2, 5 min; c) 1. bis(2-phenylethyl) acetylenedicarboxylate, toluene, 15 min, reflux; 2. 10% TFA in CH_2Cl_2, 0 °C, 4 h; 3. $Zn(OAc)_2$, MeOH, CH_2Cl_2, RT, 15 min; d) spontaneous dimerization in solution.

Nitration[8] of [5,10,15,20-tetrakis(3,5-difluorophenyl)porphyrinato]nickel(II) [3, 9] (81% yield, Scheme 1) gave the mononitro derivative **2**, which was subjected to a Barton–Zard procedure[10] to deliver the pyrroloporphyrin **3**. Replacement[11] of Ni^{II} with Zn^{II} and subsequent decarboxylation[12] led to **4**, which was further converted into the *N*-BOC derivative **5** (*N*-Boc = *tert*-butoxycarbonyl). Thereby activated,[13] this diene reacted with bis(2-phenylethyl) acetylenedicarboxylate[14] to give the Diels–Alder adduct **6** (the phenylethyl groups were chosen to improve the solubility of the dimer). Removal of the BOC group with trifluoroacetic acid (TFA) resulted in loss of Zn^{II} as well, but the metal was subsequently reintroduced to provide the required amino-tethered porphyrin **7**.

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Several lines of evidence indicate that **7** dimerizes in solution to afford the overlapped structure **1**. Osmometric molecular weight determination of a solution in $CHCl_3$ (13.13 mg in 3 mL) gave $M_r = 2304$ (calcd for $C_{132}H_{78}F_{16}N_{10}O_8Zn_2$: 2367). The UV/Vis spectrum (5.1 mg mL^{-1}, Figure 2) shows a Q-band region that matches that of typical five-coordinate zinc(II) poryphyrins, but also a strongly split Soret band, which is indicative of close π interaction between porphyrin units.[15] The 400-MHz ^{1}H NMR spectrum of a solution of **1** in $CDCl_3$ (2 mg in 0.5 mL) at 23 °C shows signals for a single species. Included are several resonances for strongly shielded centers, which are assignable to protons in the vicinity of the amino nitrogen atom: The signal for the amino protons appears at $\delta = -2.01$, that for the bridgehead H atoms at -0.05, and that for the ester α-methylene protons at 3.40. Upon addition of five equivalents of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) to the solution in $CDCl_3$ (DMAP disrupts zinc(II) porphyrin/amino ligation[3]), the corresponding resonances appear at positions expected for the DMAP-coordinated monomer (e.g., bridgehead protons at $\delta = 4.94$, α-methylene protons at $\delta = 4.22$).

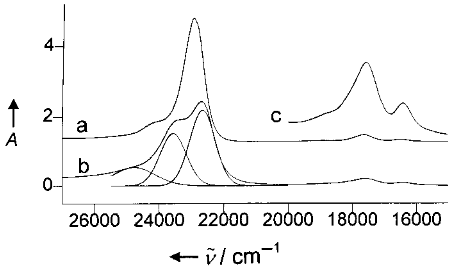

Figure 2. UV/Vis spectra ($CHCl_3$, 25 °C): a) **7** · DMAP (reference monomer; [**7**] = 5×10^{-4} M, [DMAP] = 5×10^{-3} M, path length 0.016 cm, offset A+1.3); b) **1** (4.3×10^{-3} M, path length 0.0027 cm) from the dimerization of **7**; c) Q-band absorptions of **1** as in b), enlarged ten times.

A 2D-ROESY NMR experiment[4, 16] performed at −10 °C allowed the unambiguous assignment of all resonances. The nature of the overlap of the subunits in **1** is indicated by the pattern of shielding in which signals for protons closer to the coordinating amine appear at significantly higher field than those for otherwise similar protons. Most conclusively, intersubunit crosspeaks (Figure 1) indicate the through-space proximity of the ester α-methylene protons of one subunit to the (otherwise) remote pyrrole protons and *endo-ortho*-protons of the aryl rings of the other subunit, and also the proximity in the dimer of the remaining pyrrole protons to the *para*-protons of the overlying aryl substituents of the partner subunit.

Gaussian deconvolution[17] of the electronic spectrum for a solution of **1** in $CHCl_3$ (Figure 2) reveals that the prominent Soret absorption seen for the reference monomer **7** · DMAP at 22 900 cm^{-1} is split (23 600, 22 700 cm^{-1}). The observed splitting of about 900 cm^{-1} is comparable to the range (890–1040 cm^{-1}) previously observed for self-coordinating porphyrin dimers whose overlapped region comprises an entire edge (the β-carbon atoms of two pyrrole rings and their connecting *meso*-carbon atom).[4]

In the region of the Q bands the spectra of **7** · DMAP and the dimer **1** are qualitatively similar.[17, 18] More concentrated solutions of **1** (5.1–12.9 mg mL^{-1}) show increased intensities for all absorbances according to Beer's Law, whereas stepwise dilution of **1** to 0.026 mg mL^{-1} caused the emergence of blue-shifted Q bands at 19 200, 18 200, and 17 200 cm^{-1}, which are diagnostic for the four-coordinate zinc(II) porphyrin monomer **7**.[19]

Attempts to grow crystals of **1** with a wide variety of solvents and solvent mixtures were unsuccessful. However, the cyclic zinc(II) porphyrin hexamer **8** (Figure 3) was obtained as red rhomboids by slow evaporation of a solution of dimer **1** in *p*-xylene/$CHCl_3$ (1/1).[20] Each zinc atom of the hexamer is apically coordinated to the secondary amino nitrogen atom of an adjoining monomer unit **7** to afford a square-pyramidal geometry similar to that in self-coordinating zinc(II) porphyrin and bacteriochlorin dimers.[4, 5] In contrast to the dimers, in which the porphyrin planes are approximately parallel and in π contact, the hexamer **8** features adjoining porphyrin ring π systems that are approximately orthogonal (Figure 4). This geometry is reminiscent of that in a polymeric oligomer of [10,15,20-triphenyl-5-(4-pyridyl)porphyrinato]zinc(II)[22] and in other metalloporphyr-

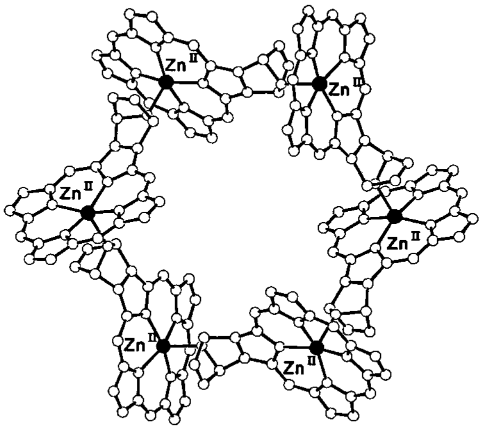

Figure 3. Ball-and-stick view of the hexameric units in crystals of **8** along the threefold inversion axis. Hydrogen atoms, ester groups, difluorophenyl groups, and solvate molecules have been omitted for clarity.

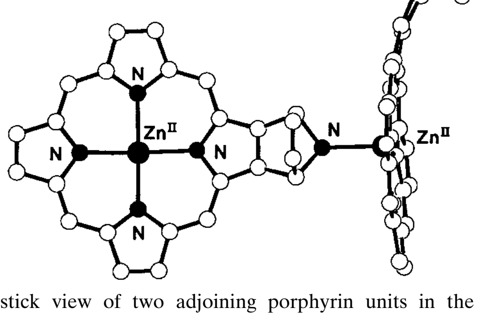

Figure 4. Ball-and-stick view of two adjoining porphyrin units in the hexameric crown in crystals of **8** approximately normal to one of the porphyrin planes.

ins.[23] Such orthogonal porphyrin systems do not show splitting of the Soret absorptions.[22, 23]

Dimer **1** and hexamer **8** also differ fundamentally in that the former features zinc coordination by the amino lone pair *syn* to the porphyrin ring (the N–H bond is *anti*), whereas the lone pair in the latter is coordinated in an *anti* position (the N–H bond is *syn*). As a consequence, hexamer **8** cannot arise directly from trimerization of dimer **1**, but instead both structures must come from monomer **7**. Crystals of **8** dissolve in $CDCl_3$ to reform **1**, according to the NMR spectrum. The degree of aggregation of **7** is thus phase-, concentration-, and additive-dependent.

Structural variations in partially π-overlapped porphyrin dimers now include the modes pyrrole-over-pyrrole (**1**), edge-over-edge,[3, 4] and pyrrole-over-edge.[4] The consequences for the electronic spectra for the first two modes are similar: split Soret absorptions and relatively unaffected Q bands. In contrast, the pyrrole-over-edge dimer[4] exhibits unusually broad Soret absorptions and a slightly split low-energy Q band. A detailed understanding of the origin of these structure-dependent effects is needed, but lacking at present. The structural dependences of other photophysical properties (e.g., fluorescence polarization, resonance Raman effects) of these dimers and their radical cations also remain to be determined.

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[20] Crystals of **8** were fragile and unstable in the absence of mother liquor. A crystal (0.64 × 0.64 × 0.18 mm) was mounted in a glass capillary along with mother liquor (separated from the crystal). Data were collected at 297 K (CAD-4 diffractometer, rotating Cu anode, $Cu_{K\alpha}$ radiation, $\lambda = 1.5418$ Å). Attempts to collect data at low temperature were unsuccessful owing to crystal fracture. Crystal data: $C_{66}H_{39}N_5O_4F_8Zn \cdot 2.5\,C_8H_{10} \cdot 0.2\,CHCl_3$; $M_r = 1472.67$, trigonal, space group $R\bar{3}$ (no. 148), $a = 42.183(4)$, $c = 21.849(2)$ Å, $V = 33670(5)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.307$ g cm^{-3}; of 10108 reflections ($2 < \theta < 42°$), 5120 were unique and 3211 with $I > 2\sigma(I)$. Data were corrected for Lorentz, polarization, and absorption (numerical, SHELX-76[21a]) effects. The structure was solved by the heavy-atom method SHELXS-86[21b] and refined on F^2 with all unique data. Disorder in the difluorophenyl and ester groups and the presence of loosely bound solvates necessitated use of distance and displacement parameter restraints. The restraints used do not appear severe, and the central zinc(II) porphyrin portion of the structure does not appear to be disordered. Refinement (SHELXL-97,[21c] 5120 data, 973 parameters, 820 restraints) gave $R_F = 0.062$ [$I > 2\sigma(I)$], $wR_{F^2} = 0.150$ (all data), GOF = 0.94. A final difference map showed excursions of −0.3 to 0.3 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100975. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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