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An Edge-Over-Edge Zn(II) Bacteriochlorin Dimer Having an Unshifted Q_y Band. The Importance of π-Overlap

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We report the structural and spectroscopic characterization of a Zn(II) bacteriochlorin dimer whose bacteriochlorin (BC) rings have a biologically relevant inter-ring separation but stack to *mimimize* overlap between their π-orbitals. This situation contrasts with the substantial π-overlap between BC molecules that are present as "special pairs" (SP) in bacterial photosynthetic reaction centers and as circular arrays in light-harvesting (LH) complexes. Although the contributions of BC orbital interactions to the unusual electronic spectroscopic features shown by these aggregates are of current interest,[1] we are not aware of any closely coupled BC dimers that have been characterized structurally, apart from the SP molecules themselves.

The BC subunits of the SP are laterally offset by ∼6 Å and oriented such that only their unsaturated acetyl-substituted pyrrole rings (ring I) overlap at a separation of ∼3.2 Å.[2] The resulting intradimer interactions serve to red-shift the lowest energy BC electronic absorption band (Q_y) and make the SP a better phototrap[3] for the LH complexes. Structural studies[1h,4,5] of two LH II complexes show that overlap within their cyclic arrays of BCs involves both unsaturated pyrroles (rings I and III). As a consequence of these interactions, the Q_y absorption of the monomeric BCs at ∼800 nm is successively red-shifted to ∼850 and then ∼875 nm for the cyclic arrays of BCs in LH complexes I and II, respectively. Since the SP spectra at higher energies than the Q_y band (other Q, Soret, and possible charge-resonance absorptions) are masked by overlapping absorptions having contributions from the accessory BC and bacteriopheophytin pigments,[1a,c] studies of model BC dimers are critical for revealing the effects of ring stacking on the *full* electronic spectra of the SPs.

Reduction of 5-(2-pyridyl)-10,15,20-tris(3,5-difluorophenyl)porphyrin (**1**)[6,7] with diimide generated *in situ*[8] gave the BC **2** [5-(2-pyridyl)-2,3,12,13-tetrahydro-10,15,20-tris(3,5-difluorophenyl)porphyrin], which was converted to Zn(II)·**2** by treatment with Zn(II) acetate in refluxing ethanolic 1,2-dichloroethane. That Zn(II)·**2** forms the self-coordinating dimer [Zn(II)·**2**]$_2$ in solution is indicated by the osmometric MW in $CHCl_3$ solution (MW 1354, 10.83 mg/10 mL, calcd for the dimer 1580) and by the strongly shielded and sharply defined pyridyl resonances in the ^1H NMR spectrum. As with the dimeric [Zn(II)·**1**]$_2$ porphyrin analogue,[6] dimerization-induced shifts ($\delta\Delta$ values) may be calculated with reference to the spectrum of the "monomer" Zn(II)·**2**·DMAP that is itself formed by treatment of a $CDCl_3$ solution of [Zn(II)·**2**]$_2$ with a 10-fold excess of 4-(*N*,*N*-dimethylamino)pyridine (DMAP). Comparison (see Supporting Information) of $\delta\Delta$ values of the BC dimer [Zn(II)·**2**]$_2$ and the porphyrin analogue [Zn(II)·**1**]$_2$ suggests that they are structurally analogous, although the magnitude of the shielding effect of the neighboring BC ring on the pyridyl protons and on H-7 and H-8 is somewhat less than in the porphyrin dimer. Slow evaporation (in the dark) of a solution of [Zn(II)·**2**]$_2$ in $CHCl_3$ and *p*-xylene afforded crystals suitable for an X-ray diffraction study.

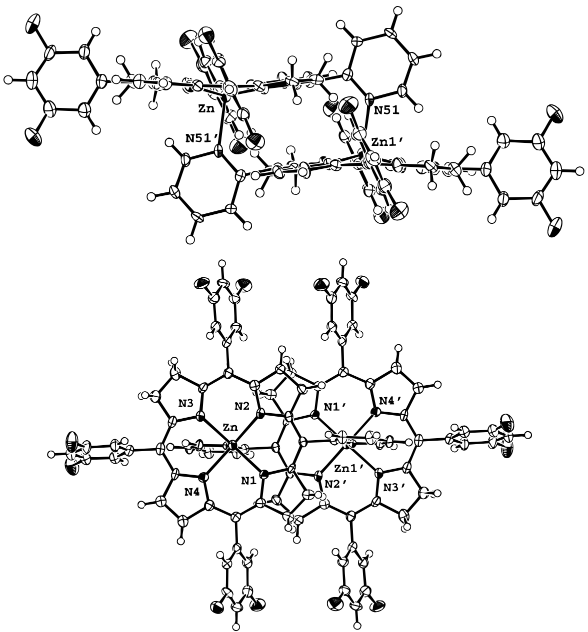

Figure 1. Molecular structure of [Zn(II)·**2**]$_2$·2 p-xylene. Selected distances (Å) and angles (deg) are the following: Zn−N(51′), 2.200(6); Zn−N(1), 2.085(6); Zn−N(2), 2.071(6); Zn−N(3), 2.123(6); Zn−N(4), 2.109(6); N(1)−Zn−N(51′), 103.9(2); N(3)−Zn−N(51′), 96.4(2). Primed atom labels indicate symmetry $1 - x, -y, 1 - z$.

[Zn(II)·**2**]$_2$ crystallizes as a bis(*p*-xylene) solvate (Figure 1) that is isomorphous with the porphyrin analogue [Zn(II)·**1**]$_2$; their three-dimensional molecular structures differ noticeably only in the rotation of the difluorophenyl group located *anti* to the pyridyl group. Intradimer Zn(II)−N(51′) pyridine ligation causes the five-coordinate Zn(II) ions to be displaced from the porphyrin N_4 planes by 0.38 Å [0.39 Å for the porphyrin analogue[6]], as well as away from N(1) and N(2) and toward N(3) and N(4) (see Figure 1). The mean separation of the monomer subunits is 2.98(1) [2.92] Å for their N_4 planes and 3.33(1) [3.30] Å for the full 24 atom BC units. These BC units are laterally offset in the dimer by 5.49(1) [5.51] Å, and the Zn···Zn separations are 5.942(1) [5.955] Å. Unfortunately, the X-ray results are ambiguous regarding the H atom positions and the associated C atom hybridization, which would indicate the nature of the overlap between the BC rings. The most prominent structural consequence of porphyrin reduction is the longer $C_\beta-C_\beta$ bond length shown by the reduced ring(s). The unsaturated $C_\beta-C_\beta$ bond distance for the four pyrrole units in porphyrins averages ∼1.36 Å. Reduction of porphyrins to chlorins, BCs, or iso-BCs generates reduced pyrrole rings having

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(9) Crystal data for [Zn(II)·**2**]$_2$·2(*p*-xylene):$ZnN_5F_6C_{43}H_{25}\cdot 2(C_8H_{10})$, MW = 1003.4, monoclinic, $P2_1/n$, $Z = 4$, $a = 20.742(7)$, $b = 10.977(3)$, and $c = 21.209(5)$ Å, $\beta = 103.88(3)°$, $V = 4688(2)$ Å^3 at 153(2) K, $D_c = 1.422$ g cm^{-3}, Mo Kα ($\lambda = 0.710\ 73$ Å), $R_F = 0.060$ for 2471 reflections having $I > 2\sigma(I)$.

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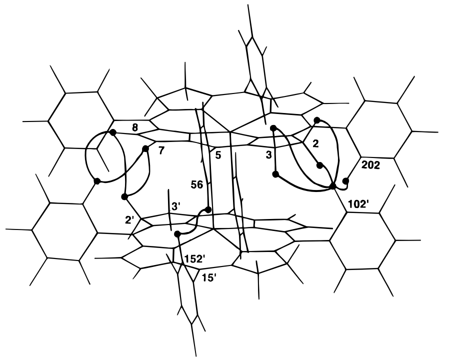

Figure 2. View of $[Zn(II)\cdot\mathbf{2}]_2$ showing one each of the ten pairs of close inter-BC contacts indicated by the ROESY experiment.

typical $C_\beta-C_\beta$ single bond distances of ~1.49 Å.[10] The $C_\beta-C_\beta$ bond distances for $[Zn(II)\cdot\mathbf{2}]_2$ [C(2)−C(3), C(7)−C(8), C(12)−C(13), C(17)−C18)] span the range of 1.417−1.462 Å and thus are likely averaged by a lattice disorder.

This ambiguity about the nature of the edge-over-edge stacking of the BC rings in $[Zn(II)\cdot\mathbf{2}]_2$ was resolved by performing a 2D-ROESY experiment[11] at 500 MHz on a $CDCl_3$ solution at 10 °C. Ten crosspeaks corresponding to inter-BC subunit proton−proton contacts are observed (Figure 2). In particular, both H(7) and H(8) of one BC ring show crosspeaks with $H(2)_{endo}$ of the other ring, a feature that can only be present if the BC units stack such that the pyrroline (i.e., reduced) portion of one BC overlaps the pyrrole (i.e., unreduced) portion of the other. This structural feature is also supported by crystallographic ($E^2 - 1$) statistics, which favor a centrosymmetric structure,[13] and by AM1 calculations that show the noncentrosymmetric alternative structure is disfavored (by 3.4 kcal/mol), a result in agreement with the additional destabilizing H−H contacts expected from overlap between two reduced pyrrole rings. The minor crystallographic disorder seems to originate in the packing of $[Zn(II)\cdot\mathbf{2}]_2$ rather than in the stacking of its BC subunits.

Preliminary electrochemical studies show that $[Zn(II)\cdot\mathbf{2}]_2$ and $[Zn(II)\cdot\mathbf{1}]_2$ undergo four reversible one-electron oxidations (Bu_4NBF_4, CH_2Cl_2, SCE) at 0.38, 0.82, 1.24, and 1.41 V and 0.56, 1.01, 1.21, and 1.55 V, respectively. Bubbling NH_3 through solutions of the dimers affords reference monomers $Zn(II)\cdot\mathbf{2}\cdot NH_3$ and $Zn(II)\cdot\mathbf{1}\cdot NH_3$ that exhibit two reversible one-electron oxidations at 0.60 and 0.96 V and 0.84 and 1.24 V, respectively.

Solution electronic spectra of $[Zn(II)\cdot\mathbf{2}]_2$ (at a concentration similar to that used for the MW study) and $Zn(II)\cdot\mathbf{2}\cdot DMAP$ are presented in Figure 3; cooling the solutions from 25 to −45 °C afforded no significant spectral changes. Some contamination by chlorin (~5% both by NMR integration and by assuming the ϵ of its Soret absorption at 23300 cm^{-1} is ~280 000, the value reported for Zn(II) tetraphenylchlorin[14]) is evident. Corrected for chlorin, the Q_y absorption for the $Zn(II)\cdot\mathbf{2}\cdot DMAP$ monomer is weaker ($\epsilon = 90\,000$) than that reported ($\epsilon = 130\,000$)[10,14a,b] for Zn(II) tetraphenylbacteriochlorin.

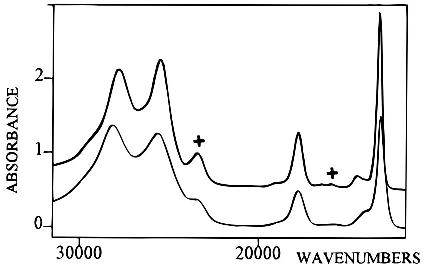

Figure 3. Electronic spectra at 25 °C of $Zn(II)\cdot\mathbf{2}\cdot DMAP$ (upper trace, offset 0.5 A) and $[Zn(II)\cdot\mathbf{2}]_2$ (lower) in $CHCl_3$, $[Zn(II)] = 1.43 \times 10^{-3}$ M with path length = 0.0196 cm for both; peaks due to chlorin impurity are identified by a plus sign (+).

What is immediately striking about Figure 3 is the near superimposibility of the dimer and monomer electronic spectra. The Q_y absorption of $[Zn(II)\cdot\mathbf{2}]_2$ at 13180 cm^{-1} shows no evidence of splitting and is only marginally red-shifted from that of $Zn(II)\cdot\mathbf{2}\cdot DMAP$ at 13250 cm^{-1}; the respective peak widths at half height are ~500 and ~320 cm^{-1}, respectively. In comparison, a red-shift of 1575 cm^{-1} has been calculated (ignoring protein-induced effects) for the Q_y absorption of the SP BCs.[1g] The origin of the red-shifted Q_y absorption is thought to reside in the combined excitonic and charge-transfer interactions present in the "supermolecule" that results from strong coupling of the monomers. Misalignment of the monomer π-systems in $[Zn(II)\cdot\mathbf{2}]_2$ apparently has attenuated the electronic coupling indicated for the above interactions.

Excitonic band splitting (ΔE) for the above dimers is given by the formula $\Delta E = 2|\mathbf{M}|^2(1 - 3\cos^2\theta)/r^3$ where the transition moments $\mathbf{M}$ are inclined by the angle θ to a line of length r (approximately the Zn−Zn vector) that connects the molecular centers.[15] Assuming the transition moments lie along the N−Zn−N directions, the moments make θ angles of 47.06 and 51.44° with the Zn···Zn vector ($r = 5.942$ Å) of $[Zn(II)\cdot\mathbf{2}]_2$ and 46.10 and 51.66° with the Zn···Zn vector ($r = 5.955$ Å) of $[Zn(II)\cdot\mathbf{1}]_2$. Excitonic coupling of the Q_y transition moment for crystalline $[Zn(II)\cdot\mathbf{2}]_2$ could be associated with either the 47.06 or 51.44° angle due to the minor crystallographic disorder noted above and likely averages to about 49° for the solution dimer. These angles are close to the "magic angle" of 54.7° at which excitonic coupling is predicted to vanish for these molecular dimers.

The intensities of the monomer absorptions are $\epsilon = 90\,000$ for the $Zn(II)\cdot\mathbf{2}\cdot DMAP$ Q_y band at 13250 cm^{-1} and $\epsilon = 580\,000$ for the Soret absorption[6] of the $Zn(II)\cdot\mathbf{1}\cdot DMAP$ at 23340 cm^{-1}. Since $|\mathbf{M}|^2$ is proportional to ϵ/ν where ν is the frequency of the absorption band,[16] this factor alone would limit the exciton splitting of the $[Zn(II)\cdot\mathbf{2}]_2$ Q_y absorption to ~27% of that shown by $[Zn(II)\cdot\mathbf{1}]_2$ Soret absorption. Thus, an upper limit for the exciton splitting of the Q_y absorption is estimated to be ~270 cm^{-1} assuming that the 1000 cm^{-1} splitting of the Soret band for $[Zn(II)\cdot\mathbf{1}]_2$ is completely exciton-derived.

The lack of either a significant red-shift or detectable splitting of the Q_y absorption for $[Zn(II)\cdot\mathbf{2}]_2$ suggests that the orientation of the stacked BC subunits in the SP has important spectroscopic consequences. Excitonic effects are thought[1] to be too small to account for the large red-shifts of the Q_y absorptions shown by the BCs in the SP and LH arrays; strong coupling of the BC π-molecular orbitals seems to be required.

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Supporting Information Available: Atom numbering scheme, tables of the X-ray crystallographic details, synthesis, characterization, and electrochemistry, dimerization-induced chemical shifts, and 500 MHz ^1H NMR data for $[Zn(II)\cdot\mathbf{2}]_2$ (24 pages). See any current masthead page for ordering and Internet access instructions.

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