Two Modes of Self-Coordinating Edge-over-Edge Zn(II) Porphyrin Dimerization: A Structural and Spectroscopic Comparison†

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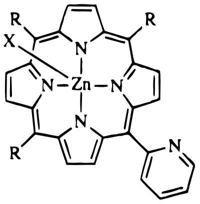
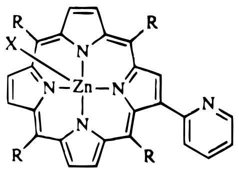
We report structural influences on the Soret and Q-band absorptions shown by self-coordinating Zn(II) porphyrin dimers (**1D**−**6D**) whose extent and direction of porphyrin ring overlap is controlled by positioning a Zn-ligating pyridine tether at a *meso*- or a *β*-position.



Compound	R	X
1D;**1M**	phenyl	N-5′;DMAP
2D;**2M**	4-(*n*-butoxy)phenyl	N-5′;DMAP
3D;**3M**	3,5-difluorophenyl	N-5′;DMAP
4D;**4M**	4-*tert*-butylphenyl	N-5′;DMAP
5D;**5M**	heptyl	N-5′;DMAP



Compound	R	X
6D;**6M**	heptyl	N-5′;DMAP
7M	phenyl	DMAP

Variations in the edge-over-edge overlap of porphyrin dimers have important electronic and photophysical consequences.[1] Bacterial photosynthetic reaction centers contain “special pairs” of bacteriochlorophyll (BC) molecules whose rings are laterally offset by ∼6 Å and oriented such that their edge-over-edge overlap involves only one pyrrole group of each ring interacting at ∼3.2 Å.[2] Intradimer electronic coupling splits the lowest energy BC absorption band Q_y and makes these special pairs better phototraps for the chlorophyll antenna pigments.[3] The unique orientation of BC pairs may be due to the ∼7 Å separation of their Mg(II) ions, which are positioned by ligation to histidyl imidazoles from the reaction center proteins. Unconstrained dimeric porphyrins exhibit a wide range of ring overlaps and orientations,[4] and duplication of the special pair geometry by self-assembly of BC monomers in the presence of imidazole may not be favored. Moreover, the special pair Soret and possible charge-resonance absorptions[1] are masked by the accessory BC and bacteriopheophytin pigments. Studies of model dimers are critical for revealing the effects of ring overlap and orientation on their full electronic structures. Other porphyrin dimers have been reported.[5]

Treatment of 5-(2-pyridyl)-10,15,20-trisubstituted-porphyrins[6] with zinc(II) gave *meso*-tethered dimeric complexes **1D**−**5D**, according to osmometric solution MW determination,[7] ^{1}H NMR analysis, electronic spectoscopy, and, for **1D** and **3D**, X-ray crystallography.[8] Each of the dimers **2D**−**5D** shows a single set of signals in $\mathrm{CDCl_3}$ solution wherein four *β*-pyrrole protons and all four pyridine protons are strongly shielded by the second porphyrin ring. In particular, the pyridine-H_6, which is pushed deep into the porphyrin ring current as a consequence of dimerization, is shielded in each dimer by 6.6 ± 0.1 ppm (a “dimerization-induced shift”[9]) relative to the corresponding monomers (**2M**−**5M**). The latter, which are formed by treating **2D**−**5D**, respectively, with 2−10 equiv of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) per Zn, show the expected ^{1}H NMR[10] and electronic spectra.[11]

For **3D** (Figure 1) and the analogue [**1D**[12]], the five-coordinate Zn(II) ions are displaced out of the porphyrin N_4 planes by 0.39 [0.40] Å toward the intermolecular pyridine N(5′) atom. Noteworthy are the unusual displacement of the Zn(II) from N(2) and N(3) toward N(1) and N(4) and the suboptimal overlap[8] with the pyridine N(5′) lone pair. These dimers possess fully developed $\pi-\pi$ stacking with mean plane separations of 2.92(1) [2.96(1)] Å for the N_4 planes and 3.30(1) [3.31(1)] Å for the full 24 atom porphyrin unit. The porphyrin subunits are laterally offset in the dimer by about 5.5Å, and the Zn···Zn separations are 5.955(2) [5.859(2)] Å.

2-(2-Pyridyl)-5,10,15,20-tetra-*n*-heptylporphyrin was prepared by Pd-promoted coupling[13] of 2-bromo-5,10,15,20-tetra-*n*-heptylporphyrin[14] with 2-(trimethylstannyl)pyridine. Its Zn complex **6D** is mostly dimeric in $\mathrm{CDCl_3}$ solution at room temperature (osmometric MW 1611; calcd 1687), but the broadened ^{1}H NMR spectrum suggests some exchange with a monomeric species. At −35 °C, the spectrum of **6D** sharpens to show a single set of signals with dimerization-induced shifts of the four pyridine protons that are identical within ±0.1 ppm to those observed for the *meso*-tethered dimer **5D**, strongly suggesting an analogous structure. The two possible ways in which the porphyrin rings of **6D** might be arranged are (a) “face-to-face” with a pyrrole ring of one porphyrin overlapping a pyrrole ring of the other and (b) “stacked” with a pyrrole/*meso* overlap (Figure 2). We assign the structure of **6D** as stacked on the basis of the lower (by 21 kcal/mol) calculated[15] energy and on the similarity of the dimerization-induced shifts of **6D**

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† This paper is dedicated to the memory of Professor Nobusama Kitajima, Tokyo Institute of Technology, deceased January 8, 1995.

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(7) Osmometric MW in $\mathrm{CHCl_3}$ solution: **2D**, 1785 (calcd for dimer 1791); **3D**, 1654 (calcd 1574); **5D**, 1403 (calcd 1491).

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(12) Crystal data for **1D**: $\mathrm{ZnN_5C_{43}H_{27}}$, $M = 679.07$, monoclinic, $P2_1/c$, $Z = 4$, $a = 16.272(2)$ Å, $b = 12.930(4)$ Å, $c = 17.478(4)$ Å, $\beta = 115.22(1)°$, $V = 3327(1)$ Å^3 at 292(2) K, $D_c = 1.356$ g cm^{-3}, Mo Kα ($\lambda = 0.71073$ Å), $R_F = 0.041$, $R_{wF}{}^2 = 0.092$ for 2291 $I_o > 2.0\sigma(I_o)$ and 442 variables, GOF (on all F^2) = 1.044. Crystal data for **3D**: $\mathrm{ZnN_5C_{43}H_{21}F_6N_5{\cdot}1.5\,CHCl_3}$, $M = 966.07$, triclinic, P_1, $Z = 2$, $a = 13.019(5)$ Å, $b = 13.065(3)$ Å, $c = 14.908(3)$ Å, $\alpha = 65.14(2)°$, $\beta = 64.17(2)°$, $\gamma = 71.36(2)°$, $V = 2041.9(10)$ Å^3 at 153(5) K, Mo Kα ($\lambda = 0.71073$ Å), $D_c = 1.571$ g cm^{-3}, $R_f = 0.039$, $R_{wF}{}^2 = 0.098$ for 4655 $I_o > 2.0\,\sigma(I_o)$, GOF (on all F^2) = 1.068. There are three disordered $\mathrm{CHCl_3}$ molecules with the total occupancy of Cl = 4.5.

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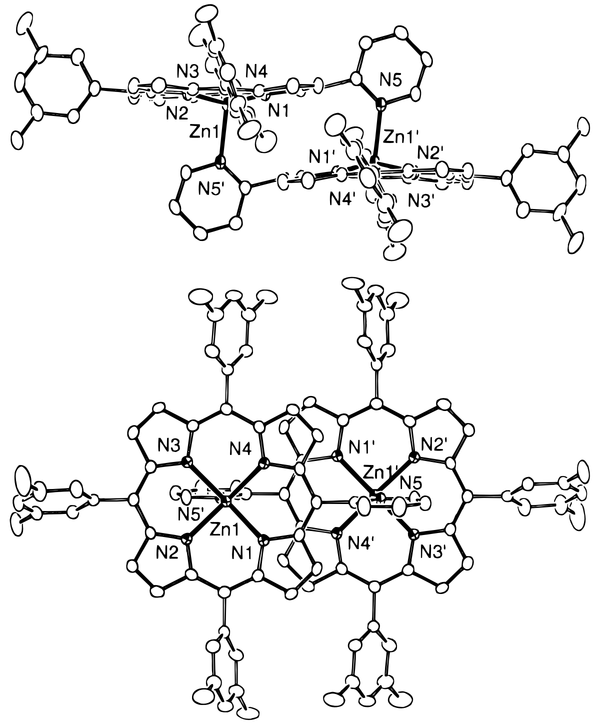

Figure 1. Molecular structure of **3D**. Selected distances and angles of **3D**, [**1D**] are as follows: Zn−N(5′), 2.193(3), [2.212(4)] Å; Zn−N(1), 2.065(3), [2.070(4)] Å; Zn−N(2), 2.081(3), [2.082(4)] Å; Zn−N(3), 2.109(3), [2.094(4)] Å; Zn−N(4), 2.055(3), [2.053(4)] Å; N(1)−Zn−N(5′), 107.6(1), [105.1(2)]°; N(4)−Zn−N(5′), 102.5(1), [108.0(1)]°.

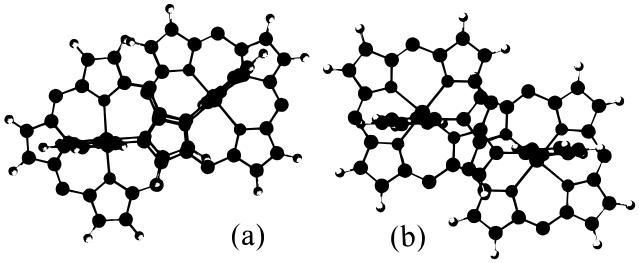

Figure 2. INDO/1-optimized[15] structures of **6D** having either (a) pyrrole/pyrrole or (b) pyrrole/*meso*-carbon inter-ring overlaps. *meso*-Ethyl groups were used instead of the *meso*-heptyl groups for calculational simplification and are omitted from the figure for clarity.

and **5D**. Destabilization of the face-to-face structure for **6D** may result from the short H_6(pyridine)−N(pyrrole) contact (calculated, 2.05 Å), compared to the H_6(pyridine)−C(*meso*) contact (calculated, 2.55 Å) for the stacked structure. For C−H distances fixed at 1.08 Å, the H_6(pyridine)−C(*meso*) contact is 2.58 Å for both **3D** and **1D**, where the pyridine planes are aligned with a *meso* carbon. 2-(2-Pyridyl)-5,10,15,20-tetraphenylporphyrin formed a complex that, probably because of intermolecular phenyl−phenyl contacts, is not dimeric, judging by the absence of shielded pyridyl signals in the ^{1}H NMR spectrum. Treatment of this zinc(II) porphyrin with DMAP led to the expected monomer **7M**.

The electronic spectra of **3M** and **3D** (Figure 3) reveal that dimerization causes the monomer Soret band (B_{00}, 23 340 cm^{-1}) to split (B'_{00}, 23 200 cm^{-1}; B''_{00}, 24 200 cm^{-1}) and the weak shoulder (B_{01}) to blue-shift from 24 500 to 25 100 cm^{-1}. Dimers **1D**−**5D** show similar spectra, with Soret band splittings spanning the range 890−1040 cm^{-1}. Comparable splittings have been reported for an imidazole-tethered Zn(OEP) dimer (1035 cm^{-1})[5f] thought to resemble **1D** and **3D** and for Zn(II) porphyrins linked by aromatic spacers.[5b,c] The band width of the B'_{00} absorption exceeds those of the companion B''_{00} and monomer B_{00} absorptions by 50−100%.

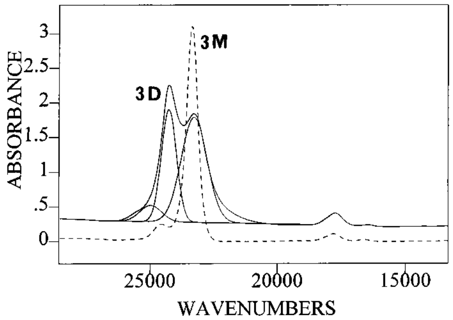

Figure 3. Electronic spectra at 25 °C of **3D** (0.2 cm cell) and **3M** (- - -, 0.1 cm cell): [Zn(II)] = 5.2 × 10^{-5} M in CH_2Cl_2 for both.

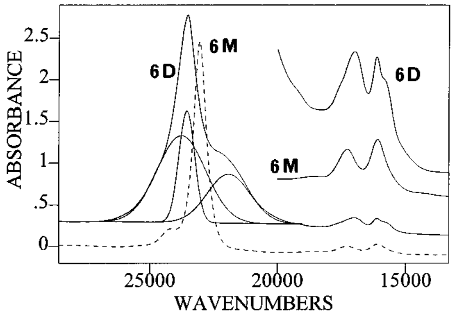

Figure 4. Electronic spectra of **6D** ([Zn] = 1.66 × 10^{-4} M, $CHCl_3$, 0.1 cm cell, −45 °C) **6D** inset ([Zn] = 1.38 × 10^{-4} M, 1.0 cm cell, −45 °C), **6M** (- - -, [Zn] = 5.46 × 10^{-5} M, CH_2Cl_2, 0.2 cm cell, 25 °C), and **6M** inset (cell = 1.0 cm).

Complete formation of **6D** (and **5D)** in dilute CH_2Cl_2 solution required cooling to approximately −40 °C, as its electron-donating *meso*-alkyl groups reduce the affinity of the Zn(II) for axial ligation compared to *meso*-aryls.[16] The monomer **6M** exhibits a typical Soret spectrum (Figure 4). However the β-(2-pyridyl)-tethered dimer **6D** shows puzzling spectra that, by analogy, have the appearance of proportionally broadened B'_{00} (21 900 cm^{-1}) and B''_{00} absorptions (23 500 cm^{-1}), now split by about 1600 cm^{-1} and flanked at higher energy by an absorption B_{01} (?) that has acquired considerable intensity. The Soret and Q-band (see below) solution spectra (−45 °C) of **6D** are the same in CH_2Cl_2, $CHCl_3$, toluene, and 1-nitropropane.

Dimerization has little consequence for the *Q*-bands of **1D**−**5D**, which generally red-shift by 100−150 cm^{-1} relative to those of the monomers. However, the Q_{00} absorption of **6M** at 16 000 cm^{-1} apparently is split in **6D**, which exhibits absorptions at 15 800 and 16 200 cm^{-1} that we attribute to the Q'_{00} and Q''_{00} bands. Some structure is apparent also on the Q_{01} absorption. Thus the variation in edge-over-edge overlap described here for Zn porphyrins has electronic−spectroscopic consequences that to our knowledge have not been observed previously. Further studies with bacteriochlorin dimers and other analogues are in progress.

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Supporting Information Available: Figures S1−4 and tables of the X-ray crystallographic details for **1D** and **3D** (S1−16), experimental details for the preparation of **1D**−**6D** and **1M**−**7M** (S-17), electronic spectra of **1D**−**6D** and **1M**−**7M** (S-18), and dimerization-induced chemical shifts for **2D**−**6D** (S-19) (19 pages); structure factors for **1D** and **3D** (50 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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