# Supramolecular Organization of Imidazolyl–Porphyrin to a Slipped Cofacial Dimer

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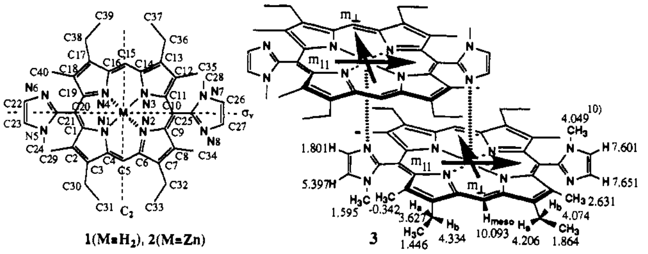
The photosynthetic reaction center contains a special pair of chlorophylls, which are separated at a distance of ca. 3.2 Å in a nearly parallel orientation with partial overlap of $\pi$-orbitals, i.e., a slipped cofacial orientation.[1] Such a specific arrangement of functional groups in space is crucial for the efficient operation not only of the photosynthetic system but also of many other biological catalysts as well. Therefore, a number of porphyrin dimers and oligomers have recently been synthesized for scrutinizing factors influencing intramolecular energy and/or electron-transfer reactions. In order to fix chromophores in a certain stereochemical environment, porphyrins have been connected by rigid aromatic spacers to avoid the ambiguity arising from conformational mobilities.[2] Here we report another approach for the construction of a rigid model based on self-organization via ligand-to-metal coordination.[3] The resulting supramolecule exhibited a large splitting of its Soret band through interactions between two porphyrins oriented in a slipped cofacial arrangement.

We introduced two *N*-methylimidazolyl substituents into the facing meso positions of tetraethyltetramethylporphyrin **1** (Figure 1), so that the metal porphyrin **2** is self-organized into a dimer by coordination from the imidazolyl ligand.[4]

Table 1 lists the absorption and fluorescence spectral data of **1** and **2** along with those of octaethylporphyrin, OEP, and its Zn complex, Zn(OEP), as the reference compounds with or without the axial coordination from *N*-methylimidazole, MeIm. Free base **1** gave a slightly red-shifted Soret and four Q bands with similar half-band widths relative to OEP. In contrast, the spectrum of Zn complex **2** showed a big difference from that of Zn(OEP); i.e., the Soret band was split by 18 nm, and the Q bands were shifted by more than 20 nm, with a significantly decreased $\epsilon_\alpha:\epsilon_\beta$ ratio. The split Soret bands strongly suggest the chromophoric interaction which can be brought about by the coordination of *N*-methylimidazole in one porphyrin to Zn in the other. The decreased $\epsilon_\alpha:\epsilon_\beta$ ratio is also compatible with *N*-methylimidazole coordination. However, the coordination of *N*-methylimidazole itself to Zn(OEP) was weak and required as much as 0.1 M MeIm for obtaining saturation. In contrast, the self-organizing coordination of the imidazolyl unit in one porphyrin to the other occurred at a highly dilute concentration as low as $10^{-6}$ M and was maintained down at the detection limit of the absorption ($10^{-7}$ M) or fluorescence ($10^{-9}$ M) spectrum. The concentration factor for the MeIm coordination is therefore as high as at least $10^8$, which must be a result of the presence of the porphyrin $\pi$-system next to the imidazolyl unit. Furthermore, an attempt at mixed dimer formation from **1** and **2** was unsuccessful even in the presence of a 9-fold excess of **1**, implying that cooperativity in the mutual imidazolyl–Zn coordination with $\pi$-stacking is too strong to be competed with appreciably by simple coordination of imidazolylporphyrin to Zn.



**1**(M=H$_2$), **2**(M=Zn)

**3**

**Figure 1.** Structure of compounds **1** and **2** along with the stacking model **3**. Numerical values in **3** show the assignment of the $^1$H NMR chemical shifts.

The splitting or shift of absorption bands of covalently linked porphyrin dimer or oligomer models[2] has been explained by exciton interactions.[5] When the theory is applied, the degenerated Soret transitions, $B_\parallel$ and $B_\perp$, in the monomeric unit are red- and blue-shifted depending on the head-to-tail and face-to-face orientations of the transition dipoles $m_\parallel$ and $m_\perp$,[6] respectively, in a slipped cofacial arrangement. The splitting energy $\Delta E$, being a function of distance and relative orientation of chromophores, corresponds to 1035 cm$^{-1}$, the largest class of splitting.[2a–c] A further unique feature of the present system is a significant red shift of Q bands suggesting a considerable perturbation even in their $S_1$ states.[7] In line with this observation, the fluorescence maxima of **2** are shifted to longer wavelengths compared to the monomeric reference, Zn(OEP)(MeIm).

All of the information is accommodated well by the idea of the formation of dimer **3**, since zinc metal allows only pentacoordination in the porphyrin system.[8] The NMR spectrum of **1** was simple and normal in all respects and assignable in a straightforward way.[9] Once Zn metal was introduced, however, a dramatic change occurred as a result of the loss of the $C_2$ symmetry element. All of the protons other than the meso ones appeared as a pair with *equal* intensities. In the COSY spectrum, among four sets of sextets at 3.627, 4.074, 4.206, and 4.334 ppm (2 H each) as AB pairs of C30-, C32-, C36-, and C38-H, the lowest

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(1) (a) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385–398. (b) Allen, J. P.; Feher, G.; Yeates, T. O.; Komiya, H.; Rees, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 5730–5734.

(2) For dimeric porphyrins connected by rigid aromatic spacers, see: (a) Osuka, A.; Maruyama, K. *J. Am. Chem. Soc.* **1988**, *110*, 4454–4456. (b) Osuka, A.; Maruyama, K. *Chem. Lett.* **1987**, 825–828. Osuka, A.; Ida, K.; Maruyama, K. *Ibid.* **1989**, 741–744. (c) Heiler, D.; McLendon, G.; Rogalsbj, P. *J. Am. Chem. Soc.* **1987**, *109*, 604–606. Nagata, T.; Osuka, A.; Maruyama, K. *Ibid.* **1990**, *112*, 3054–3059. Sessler, J. L.; Capuano, V. L.; Harriman, A. *Ibid.* **1993**, *115*, 4618–4628. (d) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388–5390. Osuka, A.; Kobayashi, F.; Maruyama, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1213–1225. (e) Tabushi, I.; Sasaki, T. *Tetrahedron Lett.* **1982**, *23*, 1913–1916. Sessler, J. L.; Hugdahl, J.; Johnson, M. R. *J. Org. Chem.* **1986**, *51*, 2838–2840. (f) Meier, H.; Kobuke, Y.; Kugimiya, S. *J. Chem. Soc., Chem. Commun.* **1989**, 923–924. Osuka, A.; Nakajima, S.; Maruyama, K. *J. Org. Chem.* **1992**, *57*, 7355–7359.

(3) For intermolecular complex models, see: (a) Aoyama, Y.; Kamohara, T.; Yamagishi, A.; Toi, H.; Ogoshi, H. *Tetrahedron Lett.* **1987**, *28*, 2143–2146. (b) Drain, C. M.; Fischer, R.; Nolen, R. G.; Lehn, J.-M. *J. Chem. Commun.* **1993**, 243–245.

(4) The 5,15-bis(methylimidazolyl)-substituted porphyrin **1** was prepared from alkylated dipyrrylmethane and *N*-methylimidazolecarboxaldehyde and isolated through a chromatography column packed with basic alumina (CHCl$_3$/EtOAc, yield = 4%). The product showed the presence of two spots on TLC in a nearly 1:1 ratio. The upper product, presumably the trans isomer as judged from the polarity on TLC and the NMR spectrum on dimer formation (see ref 10), was isolated pure (yield = 2%). The lower spot contained some of the upper. Both gave almost the same UV–visible, NMR, and mass spectra. The free base **1** and its Zn complex **2** gave FAB mass peaks at $m/z$ 639 and 701, each corresponding to M + 1, respectively.

(5) (a) Kasha, M. *Radiat. Res.* **1963**, *20*, 55–71. (b) Pulton, R. L.; Gouterman, M. *J. Chem. Phys.* **1961**, *35*, 1059–1071; **1964**, *41*, 2280–2286. (c) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371–392.

(6) Transition dipoles along the 5,15- and the 10,20-axis were taken as $m_\perp$ and $m_\parallel$, respectively, considering the approximately $D_{2h}$ symmetry of the 10,20-disubstituted porphyrin ring.

(7) (a) Gouterman, M.; Holten, D.; Lieberman, E. *Chem. Phys.* **1977**, *25*, 139–153. (b) Selensky, R.; Holten, D.; Windsor, M. W.; Paine, J. B.; Dolphin, D.; Gouterman, M.; Thomas, J. *Chem. Phys.* **1981**, *60*, 33–46.

(8) Kirksey, C. H.; Hambright, P.; Storm, C. B. *Inorg. Chem.* **1969**, *8*, 2141–2144.

(9) −2.781 (br s, N1- and N3-NH), 1.806 (t, $J$ = 7.6 Hz, C31-, C33-, C37-, and C39-CH$_3$), 2.550 (s, C29-, C34-, C35-, and C40-H), 3.365 (s, C24- and C28-H), 4.056 (quartet, $J$ = 7.6 Hz, C30-, C32-, C36-, and C38-H), 7.470 (d, $J$ = 1.1 Hz, C23- and C26-H) and 7.642 (d, $J$ = 1.1 Hz, C22- and C27-H), and 10.266 (s, C5- and C20-H) ppm.

(10) A relatively large deshielding of C28-H suggests the trans configuration for the imidazole substituent here employed. See footnote 4.

(11) Too small a separation to discern the correlation.

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**Table 1.** Absorption and Fluorescence Spectral Data of the Free Base and the Zinc Complex of (*N*-Methylimidazolyl)porphyrin and Octaethylporphyrin in Chloroform

| porphyrin | absorption<br>Soret band (nm) | half-bandwidth (nm) | Q band (nm) | peak ratio $\epsilon_\alpha:\epsilon_\beta$ | fluorescence (nm) |
|---|---|---|---|---|---|
| OEP | 401 | 44 | 500, 533, 567, 619 | | 621, 685 |
| **1** | 405 | 41 | 507, 541, 577, 627 | | 628, 692 |
| Zn(OEP) | 403 | 15 | 533, 569 | 1.56 | 573, 623 |
| Zn(OEP)(MeIm)[a] | 417 | 13 | 546, 581 | 0.80 | 583, 634 |
| **2** | 408, 426 | ~39 | 556, 591 | 0.98 | 594, 647 |

[a] Zn(OEP) ($1.67 \times 10^{-6}$ M) in the presence of 0.1 M *N*-methylimidazole in chloroform.

and the highest peaks were correlated to each other and further to the triplet centered at 1.446 ppm (6 H). The middle two sets were correlated to each other and to the triplet at 1.864 ppm (6 H). Other correlations were observed between peaks at 1.801 and 5.397 ppm and between those at 7.601 and 7.651 ppm (1 H each).

Due to the intermediate molecular weight of the compound, the NOESY spectrum gave information only on proton pairs that interchange environments on the transformation of dimer structure through slippage, rotation, or other mechanisms. Therefore, protons at −0.342 and 2.631 ppm (6 H), 1.446 and 1.864 ppm (6 H), 1.595 and 4.049 ppm (3 H), 3.627 and 4.206 ppm (2 H), 4.074 and 4.334 ppm (2 H), 1.801 and 7.651 ppm (1 H), and 5.397 and 7.601 ppm (1 H) are such pairs located in different local magnetic fields. The relative peak ratio of these pairs at lower to higher fields should provide information on the supramolecular structure, since the ratio is given by $1:(n-1)$ for an *n*-aggregate. Therefore, the equal intensity ratio observed proves the supramolecular structure as dimer **3**. Furthermore, the molecular weight was determined by vapor pressure osmometry to be 1340 ± 120 (calcd for dimer, 1400) in $CHCl_3$. Consideration of all of the above data and the shielding effect of the porphyrin ring leads to an unequivocal assignment of $^1H$ NMR chemical shift data as described in the structural model **3** in Figure 1. The chemical shift difference between **2** and **1** elucidates that all protons of the left half except C30-$H_b$ shifted to higher fields and those of the right half to lower fields, in complete agreement with the geometry of *N*-methylimidazole coordinated slipped cofacial porphyrin.[9]

These assignments were supported further by the PROESY spectrum shown in Figure 2. The NOE correlation is shown in the inset which depicts only correlated pairs arising from spacial proximity, pairs correlated through two or three direct chemical bonds were eliminated for the sake of simplicity. The correlation was observable between C29-H and only one of the methylene protons C30-$H_a$, while C34-H correlated to both C32-$H_a$ and -$H_b$ protons. This is explained in terms of conformational fixation of the C31-methyl group at the lower side to avoid steric interaction with the stacking porphyrin. This drives the C30-$H_b$ away from C29-H and leads to a downfield shift as described above. On the right half, no such conformational restriction is present and proximal positioning of both C32-$H_a$ and -$H_b$ to C34-H is allowed. The conformational fixation of the C30–C3 bond eliminates also the correlation between C30-$H_a$ and C5-$H_{meso}$ protons, while both C32-$H_a$ and -$H_b$ protons are correlated with C5-$H_{meso}$. All of the NMR data now establish firmly the stereochemical pictures of the slipped cofacial dimer **3**.

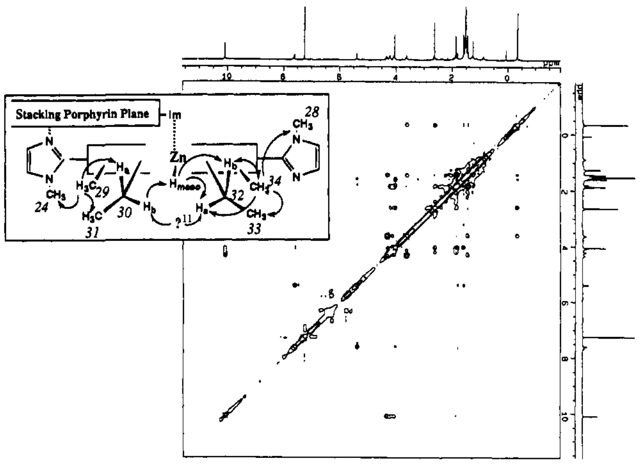

**Figure 2.** A phase sensitive ROESY spectrum of **2**, recorded at 500 MHz, 313 K, with a mixing time of 250 ms on a JEOL Alpha 500 spectrometer. The inset structure extracts correlation peaks arising from through-space interaction.

In conclusion, coordination of *N*-methylimidazole–Zn–porphyrin to another *N*-methylimidazole–Zn–porphyrin gave rise to dimer formation in a slipped cofacial orientation. Strong exciton coupling induced a remarkable split of the Soret band, a significant red shift of Q bands, and fluorescence maxima as well. Such a self-organization method may serve as an important tool to organize molecular systems with minimum synthetic effort and will open possibilities for designing more sophisticated molecular devices and other specialty materials.

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**Supplementary Material Available:** Normal and 2D NMR spectral (COSY, NOESY, and ROESY) data (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.