

# Hybrid Orbital Deformation (HOD) Effect and Spectral Red-Shift Property of Nonplanar porphyrin

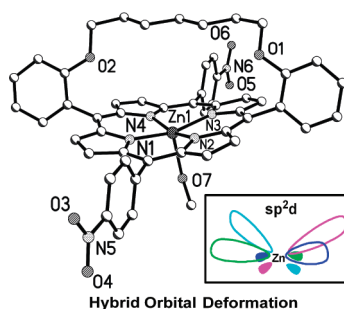
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## ABSTRACT



A series of 5,15-*meso,meso*-strapped nonplanar porphyrins with different degrees of ruffling distortion, as a model system, have been synthesized and characterized. The spectral red-shift of the nonplanar porphyrins was experimentally demonstrated to mainly originate from the hybrid orbital deformation (HOD) effect due to the distortion in the tetrapyrrole macrocycle, which confirmed previous explanations to the red-shift phenomenon.

Nonplanar heme distortion has been recognized to be a conserved structural feature of particular proteins, and significant attention has been paid to exploration of the distortion properties of porphyrins.<sup>1–3</sup> Distorted heme can stabilize the unligated Fe(II) oxidation state and also generate a high-valent iron(V)–oxo complex.<sup>4</sup> This potent oxidant is competent for hydroxylation chemistry of inactivated C–H bonds.<sup>5</sup> The out-of-plane heme distortions found in *Thermoanaerobacter tengcongensis* even show >2 Å deviations from planarity.<sup>6</sup>

Nonplanar porphyrins also show many specific properties, e.g., potent catalytic ability,<sup>7</sup> tunable coordination,<sup>8</sup> and an exceptional spectral red-shift.<sup>9</sup> This distortion is energetically unfavorable, suggesting that this distortion is crucial to the functions of heme or porphyrin.<sup>10,11</sup>

Distortions of porphyrin macrocycles are known to result in the spectral red-shift property.<sup>10</sup> Shelnutt<sup>12</sup> et al. carried

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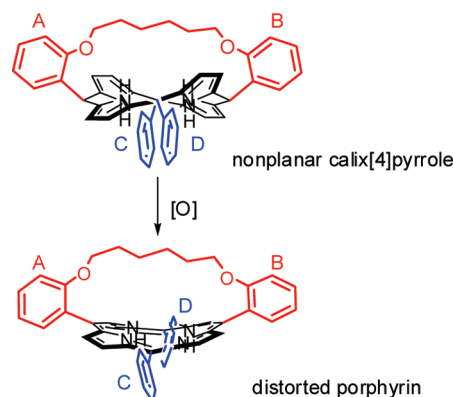
out numerous computational and experimental studies to explore the origins of the red shifts and demonstrated that the nonplanar deformation is the primary factor for the shift, rather than the early in-plane nuclear reorganization (IPNR).<sup>9</sup> Schweitzer-Stenner<sup>13</sup> et al. subsequently offered a clearer explanation using the static normal coordinate deformations (SNCDs) theory. Their results implied that the spectral shifts of the tetrapyrrole macrocycle are potentially useful indicators of the unique changes in the ring nonplanarity.

To clarify the relationship between the spectral shifts and the distortions to the porphyrin rings, we have (i) developed an efficient approach to synthesize a series of nonplanar porphyrins 5,15-*meso,meso*-strapped with different degrees of distortion as a model system (see the Supporting Information, S2) and (ii) augmented the previous “deformation” theories and experimentally demonstrated that the spectral red-shift of the nonplanar porphyrins is primarily due to the hybrid orbital deformation (HOD) effect of the distortion in the tetrapyrrole macrocycle.

The field of strapped-metalloporphyrin functional assembly has seen tremendous growth, with continuous emergence of exciting applications in selective guest inclusion,<sup>14</sup> photo-induced electron transfer,<sup>15</sup> molecular device,<sup>16,17</sup> and receptor model,<sup>18</sup> and so on. Strapped metalloporphyrins also show good potential in the fields of catalysis<sup>19,20</sup> and asymmetric catalysis.<sup>21</sup>

Porphyrin skeletons are known to originate from their corresponding porphyrinogen, a nonplanar calyx[4]pyrrole macrocycle,<sup>22</sup> by using the condensation of aldehyde and pyrrole, thus allowing the *meso* substituents A and B (or C and D) to approach each other (Figure 1). If the two substituents were bridged by a shorter strap (e.g., a 1,6-hexandiyl group or shorter) before formation of porphyrinogen, the resulting strapped porphyrin would exhibit a ruffling distortion<sup>10</sup> after its oxidation due to the competition between the binding of the alkyl strap and the coplanarity of the porphyrin  $\pi$ -system.<sup>23</sup>

A series of 5,15-*meso,meso*-strapped porphyrins with different degrees of ruffling distortion have been synthesized



**Figure 1.** Strapped porphyrinogen (top) and strapped porphyrin (bottom). Take the 1,6-hexandiyl strap as the example.

and characterized according to the above mentality. Strapped materials **6–10** were obtained from the condensation of dialdehyde compounds **11–15** with a substituted dipyrromethane **16** under a molar ratio of 1:2<sup>24</sup> and then complexed with zinc(II) to afford compounds **1–5** (Scheme 1). The dialdehyde compounds **11–15** and the dipyrromethane **16** were prepared according to the methods of Whitlock<sup>25</sup> and Lindsey,<sup>26</sup> respectively. These types of strapped structures effectively avoid the disturbances due to substituent effects and the exchange of conformations in periphery crowded porphyrins that represent the most popular distorted porphyrin samples prepared.<sup>10,27</sup> Direct measurement of the compounds was achieved using NMR and UV–vis spectral methods and a high-resolution mass spectrometry (HR-MS) technique (see the Supporting Information).

Shorter alkyl straps induce a stronger degree of distortion to the porphyrin, and the length of the straps can be flexibly adjusted by their carbon atom number ( $n_C$ : from 7 to 3). The <sup>1</sup>H NMR spectra of compounds **1–5** indicated a distorted handbasket-type conformation (Scheme 1). All proton signals in the straps showed a distinct upfield shift resonating at <3.0 ppm (Figure 2). This observation is because the straps vertically locate to one side of the large  $\pi$ -system planarity<sup>28</sup> and their protons are shielded by the porphyrin  $\pi$ -system.<sup>29</sup>

The distortive degree of these porphyrins can be judged by the chemical shift of straps' protons, e.g., the chemical shift of ether methylene proton  $\alpha$  decrease as the alkyl straps shortened. For compound **5**, the signal  $\alpha$  appeared at 2.8

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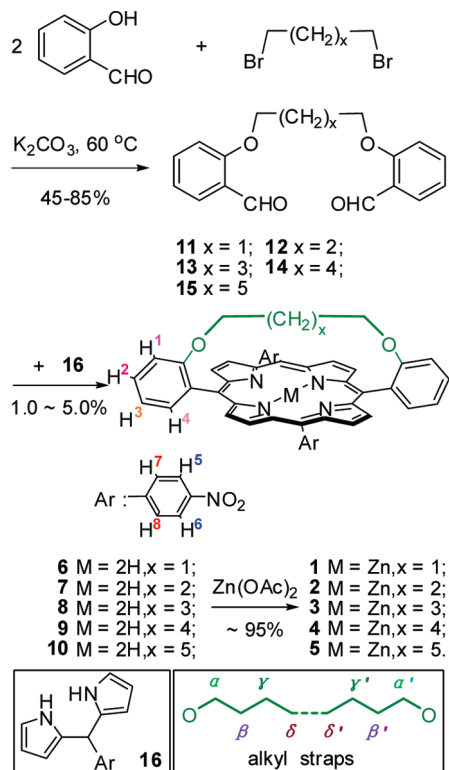
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**Scheme 1.** Synthesis of Strapped Free Base Porphyrins **6–10** and Their Corresponding Zinc Complexes **1–5**<sup>a</sup>

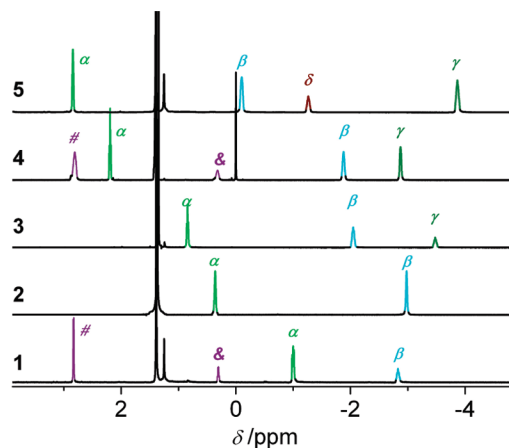


<sup>a</sup> Note: The protons labeled 5, 7 and the alkyl straps are at one side of porphyrin plane, and those labeled 6, 8 are at the other side of it.

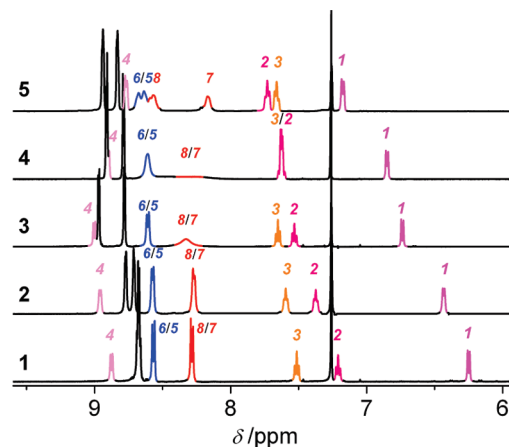
ppm (Figure 2e); for compound **1**, however, the signal  $\alpha$  shifted to  $-1.0$  ppm (Figure 2a) and the shift scope was up to 3.8 ppm between compound **5** and **1**; that is, proton  $\alpha$  of the former locate at the edge of porphyrin  $\pi$ -system and that of the latter is close to the center of the  $\pi$ -system. The shorter the alkyl strap is, the stronger the distortive degree of porphyrin is. This is a unique property that distinguishes it from many previous strapped systems.<sup>30–32</sup>

The structural deformation of the strapped porphyrins can also be reflected in the chemical shift of aromatic protons (Figure 3). In the phenyl linked to alkyl, the diagnostic signal (*I*) gradually extends shield field of porphyrin when the number of carbon atom decrease from 7 to 3; e.g., the diagnostic signal *I* of compound **5** and **1** appears at 7.18 and 6.24 ppm, respectively, and the latter is under the remarkable influence of the  $\pi$ -system. Furthermore, the <sup>1</sup>H NMR experiments also support that these porphyrins are a ruffling structure.

The series of nonplanar porphyrins **1–10** were selected as model compounds to investigate the HOD effect of the distorted porphyrins. These nonplanar porphyrins showed strongly red-shifted electronic spectra, which is in agreement



**Figure 2.** <sup>1</sup>H NMR signal changes of the alkyl chain in molecules **1–5** at 293 K. The symbols  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ , are described in Scheme 1, and the symbols # and & represent the ligands, methanol and water, respectively.



**Figure 3.** <sup>1</sup>H NMR signal changes of the aromatic protons in molecule **1–5** at 293 K. The numbering is described in Scheme 1.

with previous reports.<sup>3,9,10</sup> For zinc porphyrins **1–5**, as the degree of distortion increased the maxima were observed to red-shift further from 422.7 to 446.1 nm (**5**  $\rightarrow$  **1**) at the Soret band (Figure 4-top). For the corresponding free base compounds **6–10**, their spectra also show a similar red-shift trend (Figure 4-bottom, **10**  $\rightarrow$  **6**; 424.1 to 442.8 nm).

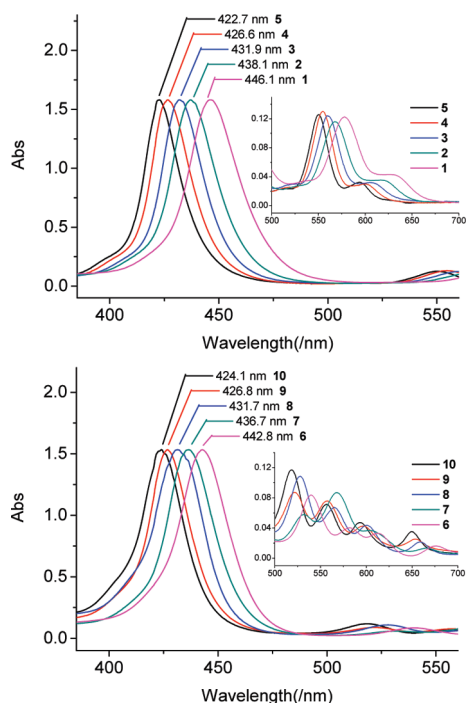
The spectral red-shift of the distorted porphyrin is believed to mainly originate from the HOD effect. The  $\text{sp}^2$  orbitals would be deformed following the distortion of the large  $\pi$  system. The relative  $\text{sp}^2$  orbital deformation of the C and N atoms results in an increase of the ground energy level and a consequent spectral red-shift. As far as each  $\text{sp}^2$  orbit is concerned; however, the change scope is noticeably weaker because there are 30  $\text{sp}^2$  orbitals involved in porphyrin. This implies that it is difficult to find the HOD effect in normal nonplanar systems (see the Supporting Information).

The changes in the degrees of distortion provided an interesting phenomenon, in which the change scope of the

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**Figure 4.** Comparison of absorption spectra of **1–5** (top) and **6–10** (bottom) in a  $\text{CHCl}_3$  solution ( $1.0\text{--}3.0 \times 10^{-6}$  M) at 293 K. Inset: absorption spectra at the Q-band.

red-shift is different after and prior to zinc complexation (Table 1). When  $n_C$  is 7, the spectral shift ( $\Delta\lambda_{\text{max}}$ ) between zinc porphyrin **5** and the corresponding free base porphyrin **10** is  $-1.37$  nm, and with decreasing  $n_C$ ,  $\Delta\lambda_{\text{max}}$  gradually increases until  $n_C$  is 3;  $\Delta\lambda_{\text{max}}$  between **1** and **6** is up to  $3.37$  nm.

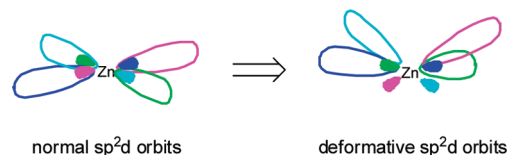
**Table 1.** Relationship between the Spectral Shift ( $\Delta\lambda_{\text{max}}$ ) and the Number of Carbon Atoms ( $n_C$ ) at 293 K

| compd                                    | <b>1</b> and <b>6</b> | <b>2</b> and <b>7</b> | <b>3</b> and <b>8</b> | <b>4</b> and <b>9</b> | <b>5</b> and <b>10</b> |
|------------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|------------------------|
| $n_C^a$                                  | 3                     | 4                     | 5                     | 6                     | 7                      |
| $\Delta\lambda_{\text{max}}/\text{nm}^b$ | 3.37                  | 1.49                  | 0.24                  | $-0.14$               | $-1.37$                |

<sup>a</sup>  $n_C$  is the number of carbon atoms in the alkyl straps. <sup>b</sup>  $\Delta\lambda_{\text{max}}$  is the spectral shift between the zinc porphyrin and the corresponding free base.

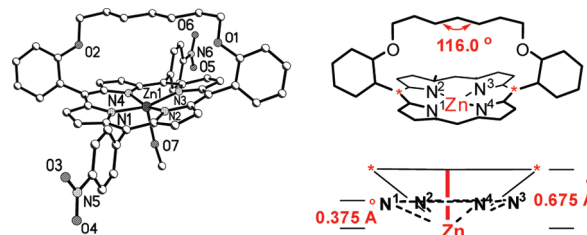
The HOD theory can also offer a satisfactory explanation to this phenomenon. For zinc(II) atoms of the third periodic elements, the hybrid orbits adopt an outer-orbital  $\text{sp}^2\text{d}$  hybrid mode due to its full 3d arrangement (Figure 5) and a smaller size than the 4-N cavity in planar porphyrin. Zincic 4  $\text{sp}^2\text{d}$  hybrid orbits are deformed due to the deviation of the zinc atom from the 4-N plane after distortion of the large  $\pi$  system. The determination of the crystal structure of **5** reveals that the  $\pi$ -system of the strapped porphyrin is distortive and the zinc atom is out of the 4-N plane ( $0.375$  Å deviation, Figure 6). As a result, the electrons in the deformed  $\text{sp}^2\text{d}$

hybrid orbits of the central zinc atom are also found at a relatively higher ground energy level than those in the normal coplanar system.



**Figure 5.** Graphic presentation of the hybrid orbital deformation of the central zinc(II) in the nonplanar porphyrin.

Stronger distortions lead to higher ground energy levels; therefore, the  $\Delta\lambda_{\text{max}}$  gradually increases as the length of the strap decreases (Table 1). However, the spectral change from the central zinc atom is much stronger than that from a  $\text{sp}^2$  hybrid orbit. The relative change in the molecular ground energy level ( $-R\Delta E_{\text{E,m}}$ : up to  $\sim 2.7$   $\text{kJ}\cdot\text{mol}^{-1}$ ) can be conveniently estimated according to their spectral red-shift (see the Supporting Information).



**Figure 6.** Crystal structure (left), strain behavior, and out-of-plane character (right) of the strapped porphyrin **5**.

In this study, the HOD model was used to interpret the spectral shifts of porphyrin and heme by influence from the degree of distortion in the porphyrin ring. That is, the distortion can be availably traced through a spectral shift in nonplanar porphyrin, which makes it feasible to investigate the biological functions of distorted heme molecules by applying this spectral technique. Moreover, the series of nonplanar porphyrins can be used as an ideal model system in exploring the characteristics of heme distortion and optimizing the biochemical functions of metalloporphyrins.

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**Supporting Information Available:** Explanation of the spectral shift, experimental procedures, spectroscopic data, and characterization of compounds and crystallographic data of **5** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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