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Regulation of dynamic structure of cyclophanes by their complexation with the porphyrin

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ABSTRACT

Dithia[3.3]metacyclophanes which consist of the pyridine unit connecting to the different positions of the parent cyclophane skeleton have been prepared. Conformational change has been observed for the cyclophane having a 4-substituted pyridine unit by binding to the porphyrin. In contrast the porphyrin binding has no influence on conformational behavior of the cyclophane having a 3-substituted pyridine unit.

Cyclophanes known as bridged aromatic compounds have been intensively investigated from various points of view because of their unique characteristics for the last few decades.[1] One of the most characteristic features of cyclophanes is their dynamic structure based on the conformational flexibility.[2] Thus, the conformational properties have been well studied in various cyclophane systems. Meanwhile we have been interested in the small-sized dithia[3.3]metacyclophane system because of their unique π systems owing to strong transannular π–electronic interactions between aromatic components in close proximity.[3] These dithia[3.3]metacyclophanes exhibit conformational features based on their ring inversion between the *syn* and *anti* conformations.[3i,4] Control of this conformational behavior is one of the attracting topics because some substantial characteristics of cyclophanes highly depend on their dynamic structures. On the other hand porphyrins are known to bind the pyridine derivatives.[5]

We have already reported the syntheses and properties of pyridinophanes that are the cyclophanes consisting of the pyridine component.[6] In this respect we describe here the conformational regulation of pyridinophanes by complexation with the porphyrins.

Starting with 5-hydroxyisophthalic acid, esterification and reaction with chloromethyl pyridines, followed by reduction, and chloromethylation gave the chloromethyl compounds **1a–c**. The sulfanylmethyl compounds **2a–c** were obtained from **1a–c** (see Fig. 1). The coupling reactions of **1a–c** and **2a–c** were carried out using Cs_2CO_3 as a base under a highly diluted condition to give the corresponding pyridinophanes **3a–c** and **3e** in the yields of 43–57% (see Fig. 2).

The ^{1}H NMR spectral titration has been carried out for **3a–c** with the zinc porphyrin **4a**. Figure 3 shows the profile of the ^{1}H NMR spectrum of **3a** on addition of **4a**.

The addition of **4a** induces the upfield shifts for the protons (H_A and H_B) neighboring the nitrogen atom, indicating that the binding of porphyryin against pyridinophane should occur. In over 1:3 ratio no remarkable shifts were observed. In accordance with this porphyrin binding the upfield shift of the inner proton (H_C) is observed as shown in Figure 3. It has been well known that an extensive upfield shift of the proton at the inner position in analogous [2.2]metacyclophanes is recognized due to the strong shielding effect of the opposite aromatic ring in the *anti* conformation.[7] It has also been reported that there exists a rapid inversion between a *syn* conformation and an *anti* conformation in the dithia[3.3]metacyclophane system at room temperature.[8] The addition of **4a** to the

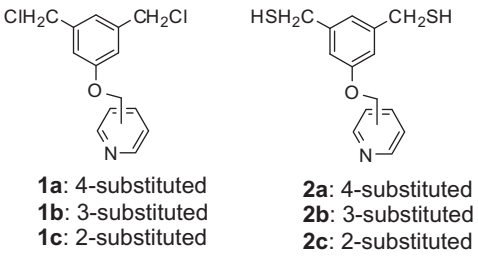

Figure 1. Chemical structures of **1** and **2**.

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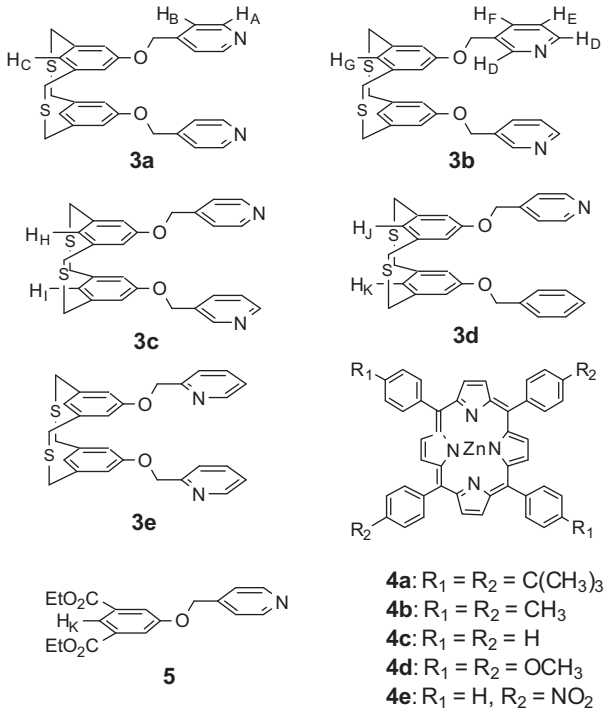

Figure 2. Chemical structures of **3**, **4**, and **5**.

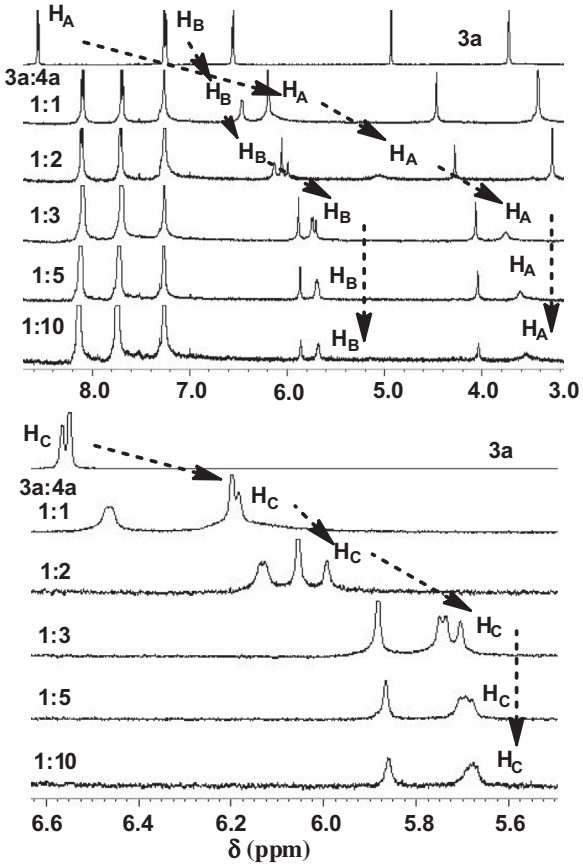

Figure 3. Partial NMR spectra of **3a** on addition of **4a**.

referential compound **5** under the same condition has little influence on the chemical shift of the inner proton (H_K) in **5**. Taking these results into account the upfield shift of the inner proton (H_C) seen in Figure 3 strongly suggests that the contribution of the *anti* conformation increases on the addition of porphyrin. This preference for the *anti* conformation can be considered as consequences of hindrance for formation of the *syn* conformation by means of the bulky aromatic cyclophane component binding the porphyrin ring as illustrated in Figure 4.

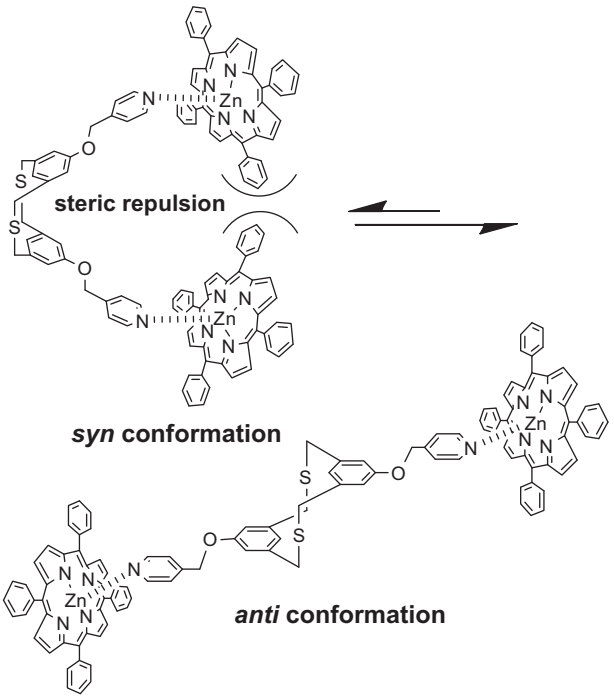

Figure 4. Preference for the *anti* conformation in the cyclophane–porphyrin system.

A similar ^{1}H NMR spectral titration was done for the pyridinophane **3b** and **4a** as shown in Figure 5.

The binding of porhyrin to **3b** can also be confirmed by the upfield shifts for the protons (H_D, H_E, and H_F) on addition of **4a**, however, the chemical shift of the inner proton (H_G) shows almost no change in contrast to **3a**. No chemical shift of the inner proton in the pyridinophane **3b** indicates that the binding of porphyrin to **3b** might have little effect on its conformational inversion, meaning that the ring inversion takes place without bumping between two bulky cyclophane components attached by the porphyrin rings. This should be due to the binding of porphyrin on the position of 3-substituted nitrogen in pyridinophane.

In order to confirm this assumption we have also examined the ^{1}H NMR spectral titration employing the pyridinophane **3c** and **3d** as shown in Figure 6. The inner protons (H_H and H_I) in **3c** exhibit about 0.45 ppm upfield shift on addition of the porphyrin **4a**. Under similar condition the upfield shifts for the inner protons (H_J and H_K) in **3d** are 0.33 ppm and 0.27 ppm, respectively. These values are smaller than the corresponding shift (0.88 ppm) recognized for **3a**, indicating that the *anti* conformation makes less contribution to the process of inversion between the *syn* and *anti* conformations compared with **3a**.

These results strongly suggest the bulky porphyrin ring on the position of 3-substituted nitrogen has a slight effect on the ring inversion in pyridinophanes. No apparent binding of **4a** against the pyridinophane **3e** was observed probably due to the steric hindrance.

Temperature should be considered for binding of porphyrin to pyridine derivatives. Thus, we have examined the conformational behavior of the porphyrin-bound pyridinophane **3a** depending on the temperature as shown in Figure 7.