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Bis(zinc porphyrin) Bridged by Benzo Orthocarbonates as a Conformational Switch under Regulation of DABCO and a Cu^+ Ion

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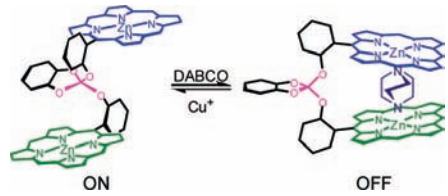
ABSTRACT



A tweezer-type bis(zinc porphyrin) bridged by benzo orthocarbonates was synthesized and applied as a molecular conformational switch under regulation of DABCO and a Cu^+ ion. The switch property has been confirmed by ^1H NMR, UV−vis spectral titration, and HR-MS spectra method.

Achieving specific or multifunctional properties is always one of the main goals in designing molecular devices.[1] The development of molecular systems that can change their state, both reversibly and irreversibly, is of interest because they conceptually provide a route for the development of molecular scale devices.[2,3] These devices are interesting because switching at the single-molecule (or complex) level[4,5] arouses the possibility of molecular-scale information processing. The practical issues, however, in terms of both positioning and interfacing the molecules are considerable.[6,7]

Many compounds are able to adapt their state (e.g., conformation, shape, luminescence, etc.) in response to external stimuli including pH,[8,9] temperature,[10] redox,[8,11] light,[12] ion-pairing,[13] etc. Many reports show that metal-

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loporphyrin dimers bridged by soft chains can fold and form stable sandwich complexes with bifunctional ligands,[14−16] but no report has shown that a bis(metalloporphyrin) linked to a rigid component can be distorted and form a 1:1 inclusion complex.

An inspection of the structure of 2,2-di(phenoxy)-benzo[1,3]dioxole **5** (Figure 1) reveals that the two phenoxy

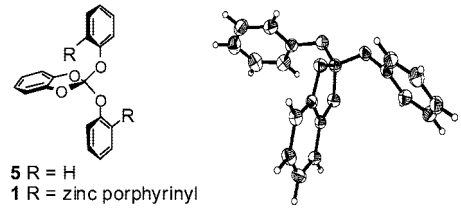


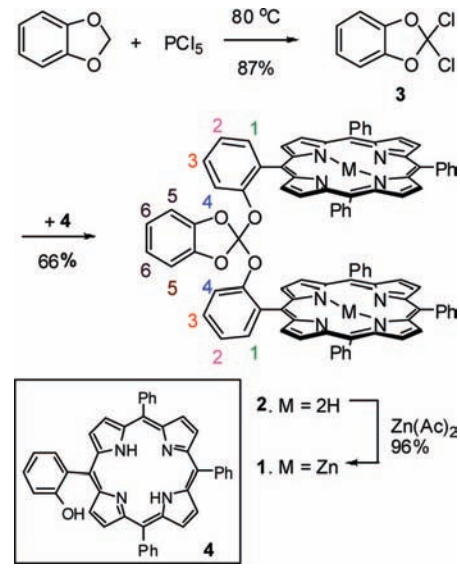
Figure 1. (Left) 2,2-Di(phenoxy)benzo[1,3]dioxole and its derivatives. (Right) X-ray structure of **5**.

groups are distributed on both sides of the benzodioxole plane. If two large-size substituents (e.g., zinc porphyrinyl) were linked at the *ortho*-position of the phenoxy groups, it is expected that they would adopt a reverse arrangement to the axis through the two O atoms of the phenoxy groups due to steric hindrance. If some driving force exists, the molecule would be folded such that its two substituents would be in a parallel arrangement, which implies the formation of a tweezer-type molecular conformational switch.

Here, we demonstrate that (i) the bis(zinc porphyrin) **1** linked to a rigid benzo orthocarbonate adopts an open tweezer like arrangement that can be quantitatively closed under regulation of 1,4-diazobicyclo[2,2,2]octane (DABCO) due to the formation of a stable, inclusive complex **1** ⊃ DABCO in chloroform solution; (ii) the closed tweezers can be reopened after removal of the complexed DABCO. Both of the above processes practically display a molecular conformational switch property. Direct measurement of the switch was achieved using ^{1}H NMR and UV−vis spectral titration methods and high-resolution mass spectrometry (HR-MS) technique. The experimental data fully prove that the molecule **1** takes on the well-defined "OFF" and "ON" reversible conformational switch behavior in response to the introduction and removal of DABCO.

Compound **1** was obtained by metallization of its precursor, free base porphyrin dimer **2**. Compound **2** was obtained from the condensation of 2,2-dichlorobenzo[1,3]dioxole **3** with 5-(*o*-hydroxyphenyl)-10,15,20-triphenylporphyrin **4** under a molar ratio of 1:2 (Scheme 1). Compounds **3** and **4**

Scheme 1. Synthesis of Bis(zinc porphyrin) **1**



were prepared according to the methods of Endo[17] and Lindsey,[18] respectively.

The ^{1}H NMR spectrum of compound **1** indicates an open conformation. The appearance of five protonic signals shifted downfield of the nonaromatic region (6.1−4.0 ppm, Figure 2a) is not in agreement with the theoretical positions of

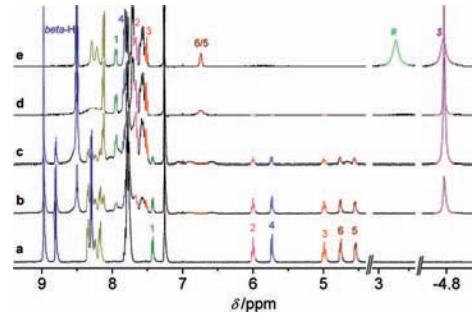


Figure 2. Signal changes of molecule **1** during a ^{1}H NMR titration with DABCO at 293 K; a, b, c, d, and e, respectively, represent the ^{1}H NMR spectra of the mixture of DABCO and molecule **1** in molar ratios of: 0, 0.3, 0.7, 1, and 2; $ and # denote the methylene signal of DABCO in the complexed and free states, respectively. The numbering colored is described in Scheme 1 and Figure 3.

aromatic protons not influenced by a magnetic shielding effect on the corresponding protons. A possible reason for this lies in the fact that one of the *meso*-phenyl groups linked to the benzo orthocarbonates is shielded by the other porphyrin π-system (Figure 3a). Four (two two-proton

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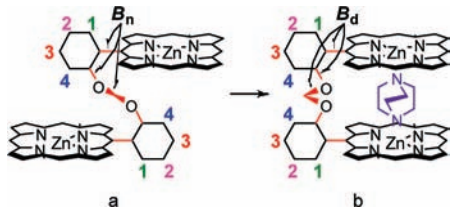

Figure 3. Relative position change of two porphyrin components after addition of DABCO, $\boldsymbol{B}_n$ are not distorted sigma bonds (a), $\boldsymbol{B}_d$ are distorted ones (b).

doublets and two two-proton triplets) of the diagnostic signals are derived from the four protons in the two *meso*-phenyl groups, and all four signals show a distinct upfield shift. A signal at ~4.1 ppm results from one of the protons in the benzo component located at the apex. The β-position signals of the porphyrin units are displayed at three isolated positions due to the π-system influence of the opposing porphyrin. Therefore, free molecule **1** can be considered to adopt an open tweezer like arrangement. That is, the molecule is in the "ON" state of the conformational switch.

The open conformation of compound **1** can be quantitatively closed following coordination of the bifunctional ligand, DABCO. The assembling behavior of compound **1** with DABCO was studied by ^{1}H NMR titration in $CDCl_3$ solution at 293 K (Figure 2). The diagnostic signals (1−4) in the *meso*-phenyl groups gradually disappear in the nonaromatic field and gradually increase in the aromatic field. Signals 5 and 6 approach each other and ultimately appear at the same position (δ 6.78) as the amount of DABCO was increased. The DABCO methylene unit is characterized by a sharp signal at δ −4.78.[19] Simultaneously, the other aromatic signals are also largely simplified. These facts suggest the formation of a sandwich complex in which the complex adopts a 1:1 host−guest assembly (Figure 3b).

Only the 1:1 inclusion complex is formed, and no other assembly modes, e.g. the 2:2 sandwich complex formed between compound **1** and DABCO exist in $CHCl_3$ solution. In general, ligand exchange in the zinc porphyrin-ligand systems readily takes place in the presence of the free ligand in solution because the zinc atom in the center of the porphyrin is a five-coordinated species,[15,19,20] which is usually embodied by the appearance of an averaged signal of the ligands. This phenomenon, however, was not observed in the spectrum of the ^{1}H NMR titration of **1** with DABCO when 2 equiv of the ligand were added. In this spectrum, the methylene proton appeared as two isolated peaks: one (δ 2.30) is attributed to the free ligands and the other (δ −4.78) is attributed to the complexed ligands (Figure 2e). This indicates that the sandwich complex **1** ⊃ DABCO cannot be opened by the excessive DABCO due to the difficulty of ligand axial exchange. The experiment showed that the open conformation of compound **1**, however, cannot be closed under coordination of the bifunctional 4,4′-bipyridyl (Bpy). The reason is probably that the distance between the two nitrogen atoms of Bpy is larger than that of DABCO and so there is no suitable size-matching between **1** and Bpy (see Supporting Information, S-14).

The inclusion behavior of compound **1** with DABCO was also studied by the HR MS technique. The formation of the stable 1:1 inclusion complex of **1** ⊃ DABCO was confirmed by the HR-MS spectral result (Figure 4). In contrast, the HR-MS spectral study of **1** ⊃ Bpy demonstrated that a stable 1:1 inclusion complex could not be formed under the same conditions.

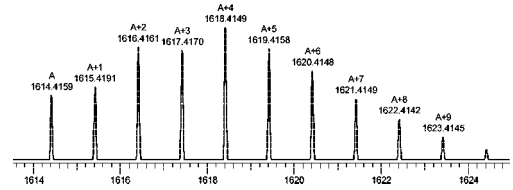

Figure 4. HR-MS spectrum of the inclusion complex **1** ⊃ DABCO, calcd for [**1** ⊃ DABCO]$^+$: 1614.4162, found: 1614.4159.

The inclusion behavior of compound **1** is also reflected in the spectrophotometric titration experiments of compound **1** with DABCO. In the UV−vis titration of **1** with DABCO, the absorption spectra of **1** showed a distinct red-shift and clear isosbestic points at the Soret and Q bands as DABCO was introduced into the solution, but its absorption intensity and position showed almost no change when in the presence of more than 1 equiv of the ligand (Figure 5). Their association constants (K_{assoc}) evaluated by applying a nonlinear curve-fitting method[21] are up to 10^8 M^{-1}.

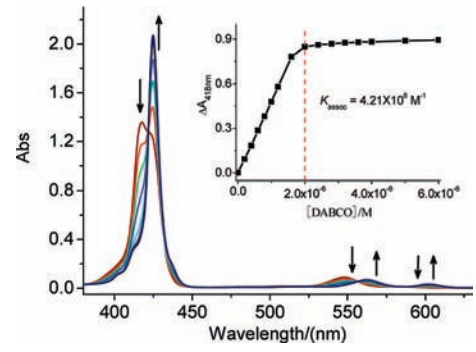

Figure 5. Absorption spectral change in the titration of **1** (2.0×10^{-6} M) with DABCO in $CHCl_3$ at 293 K. (Inset) ΔA_{418} vs [DABCO] plot, the association constant is up to 4.21×10^8 M^{-1}.

The high stability of the inclusion complex (K_{assoc} 10^8 M^{-1}) originates from the distortion of the relative sigma bonds (B_d; Figure 3) and the cooperative binding of the two nitrogen

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atoms inside the cavity.[15,19,22] It is thought that distortion of these bonds simultaneously takes place when the 1:1 inclusion complex was formed through rotation of the bonds. The distortion force of the bonds restricts the movement of the ligand in the localized microenvironment.

The open tweezer-type molecule **1** can be effectively closed by virtue of coordination of DABCO, while the close conformation cannot be completely destroyed by excessive DABCO. This is a unique property that distinguishes it from many similar switch systems.[2,15,19] Therefore, the complexed molecule **1** adopts a close tweezer like arrangement, which means that the molecule is converted to the "OFF" state, that is, another state of the conformational switch.

The conformation of the switch system is interconvertible between the "OFF" and "ON" states. The conformation of molecule **1** can be switched to the "OFF" position with adding DABCO, and switched to the "ON" position as the DABCO is removed (Figure 6 top). The reversible UV−vis

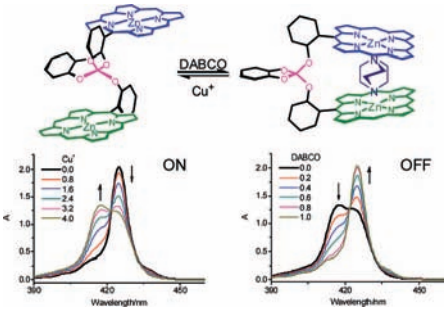

Figure 6. Conformational interconversions and consequent spectral shifts of **1** (2×10^{-6} M) in the reversible titration with DABCO and Cu^+ ions in $CHCl_3$ solution. The values beside the colored lines denote the molar ratio of DABCO (or Cu^+ ions) to **1**.

spectral changes of **1** via two processes result in a clear evidence for the conformational interconversion of molecule **1**, *close*-**1** and *open*-**1** (Figure 6 down). In "ON" process, it need 4 equiv of the Cu^+ ion (from $CuClO_4$•4MeCN) to remove the complexed DABCO and make the absorption spectrum of **1** fully recovered due to its competition for the central zinc atom of the porphyrin. The DABCO and Cu^+ ions readily form stable coordination polymers and expediently deposit from solution system,[23,24] which is a necessary condition to maintain the repeatable operation of the switch. Therefore, both of them mutually play the role as capture reagents in the two processes. The *close*-**1** can be returned to the *open*-**1** by adding a Cu^+ ion, which was also demonstrated by the ^1H NMR titration experiments of **1** ⊃ DABCO with Cu^+ ions (see Supporting Information, S-12).

No well-defined switch phenomena of compound **1** were observed under regulation of DABCO in the polar solvent DMSO (see Supporting Information, S-13).

In conclusion, we have reported a very efficient molecular conformational switch using the ordinal regulation of DABCO and a Cu^+ ion. The tweezer-type free molecule **1** being in the "ON" state can be quantitatively switched to the "OFF" state by coordination of DABCO, and the "OFF" state of molecule **1** can also be efficiently recovered to its open conformation by removing the DABCO with Cu^+. Furthermore, molecule **1** is a modifiable and potential stereostructure, which is of major significance since it provides more avenues for the construction of novel molecular scale devices and potential applications in the artificial molecular machines.

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Supporting Information Available: Experimental procedures, reference titration results, spectroscopic data and characterization, and HR-MS of compounds (or complexes), and crystallographic data of **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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