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Rotational Libration of a Porphyrin/Phthalocyanine Double-decker Complex with Ce(IV) as Revealed by ^{1}H NMR and STM

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We provide evidence that a heteroleptic double-decker complex of Ce with phthalocyanine and porphyrin ligands undergoes rotational libration in solution for the first time on the basis of variable-temperature ^{1}H NMR. On the other hand, the Zr complex with the same set of ligands undergoes no rotational motion. These molecules deposited on graphite surfaces exhibited different shapes in STM images, revealing difference in the rotational motion at the molecular level.

Sandwich-type double-decker porphyrin/phthalocyanine complexes constitute an interesting class of compounds with potential applications as components of molecular machines,[1–3] making use of their inter-macrocycle rotational motion. The rotational motion should occur stepwise by 90° because the potential minima appear every 90° due to the antiprismatic coordination geometry (Figure 1).[4,5] Variable-temperature ^{1}H NMR and CD spectral studies showed that some double-decker porphyrin complexes undergo rotational motion with rates dependent on substituents on the macrocycle.[6–9] On the other hand, STM studies have revealed two-dimensional ordering of double-decker complexes on solid surfaces.[10–16] We previously reported that a double-decker porphyrin complex, [Ce(BPEPP)(C_{22}OPP)], and the corresponding free-base porphyrin, H_2C_{22}OPP, form an ordered, mixed array at 1-phenyloctane/HOPG interface {BPEPP: 5,15-bis[4-(phenylethynyl)phenyl]-porphyrin, C_{22}OPP: 5,10,15,20-tetrakis(4-docosyloxyphenyl)-porphyrin, HOPG: highly oriented pyrolytic graphite}.[14] In this array, the rotational motion was suggested on the basis of the observed shapes of the molecules. Recently, we successfully visualized the rotational libration on the surface for another double-decker porphyrin complex, [Ce(TPP-Fc)(C_{22}OPP)], which has a ferrocenyl substituent revealing the orientation of the macrocycle {TPP-Fc: 5-[4-(4-ferrocenylphenyl)ethynylphenyl]-10,15,20-triphenylporphyrin}.[16] While these previous studies, whether in solution or on surfaces, concerned double-decker *porphyrin* complexes, whether or not double-decker complexes involving a phthalocyanine ligand can rotate has not been addressed, except by a recent report by Miyake et al.[15] They suggested that a heteroleptic porphyrin/phthalocyanine double-decker complex has a mobility on the basis of blurred spots observed for the complex. However, it is difficult to draw a clear conclusion because their complex is of fourfold symmetry, for which expected orientation changes by 90° would not make any difference in the observed images.

To clarify the rotational behaviors of double-decker complexes containing a phthalocyanine ligand, we designed and prepared twofold symmetric complexes, [Ce(BPEPP)(C_8OPc)], which are displayed in Figure 1 [C_8OPc: 2,3,9,10,16,17,23,24-oktakis(octyloxy)phthalocyanine]. The twofold design enabled us to investigate the rotational behaviors with ^{1}H NMR. The Zr complex with the same set of ligands was also prepared for comparison purposes. These complexes deposited on the HOPG surfaces were studied with STM as well, affording images that reflected the difference in rotational motion on the surfaces.

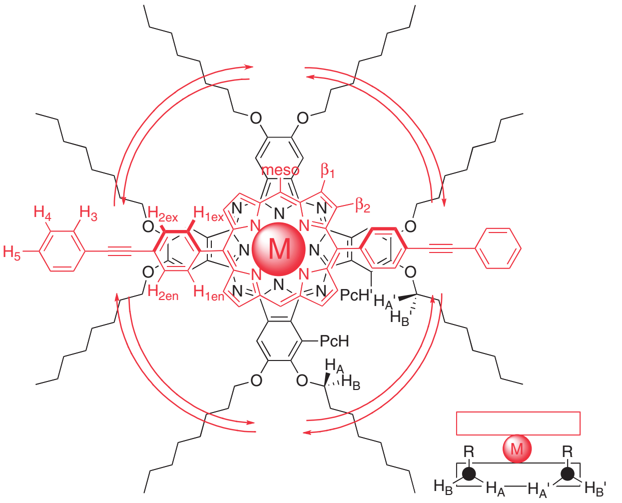

Figure 1. Double-decker complexes with a phthalocyanine ligand and a porphyrin ligand with a twofold symmetry, [M(BPEPP)(C_8OPc)], where M represents either Ce(IV) or Zr(IV) ion. Red arrows indicate possible rotational libration between equivalent antiprismatic geometries. The lower right cartoon illustrates that α-methylene protons H_A and H_B are diastereotopic.

The ^{1}H NMR spectrum for [Ce(BPEPP)(C_8OPc)] at 20 °C showed a single broad resonance for the aromatic protons (PcH) on the phthalocyanine moiety, a single multiplet signal for each of the diastereotopic α-methylene protons (OCH_2; Figure 1), and a single triplet signal for the terminal methyl protons, as shown in Figure 2. Upon cooling, each of these signals was initially broadened and then split into two sets of signals due to decreased rate of inter-ring rotational motion. Line-shape simulation[17] for PcH at each temperature and the resulting Arrhenius plot yielded a frequency factor, $\ln(A/\mathrm{s}^{-1}) = 15.1 \pm 1.7$, and an activation energy, $E = 22 \pm 4\,\mathrm{kJ\,mol^{-1}}$, for the rotational motion, that is, a flip by 90° from one antiprismatic coordination geometry to another.[4,5] We believe that this is the first unequivocal evidence for the rotational motion of a double-decker complex with a phthalocyanine ligand. The estimated

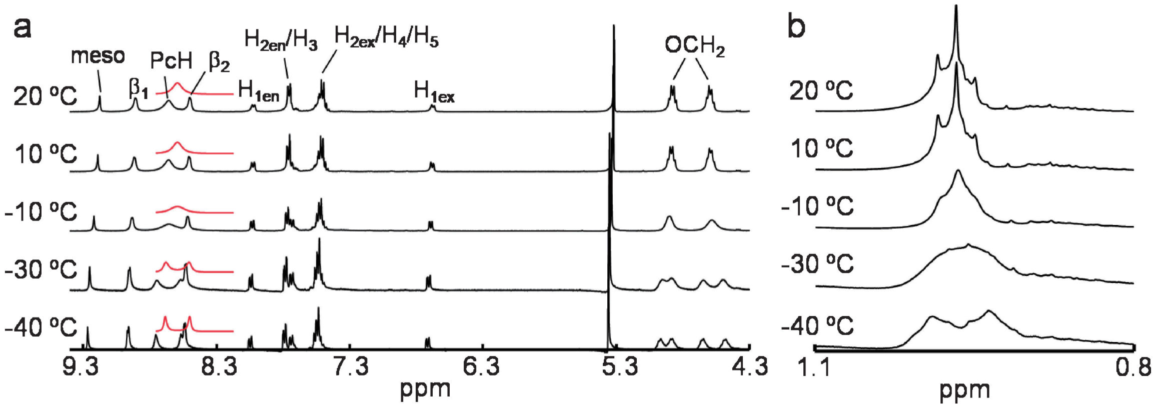

Figure 2. Variable-temperature ^{1}H NMR spectra for [Ce(BPEPP)(C_8OPc)] in CD_2Cl_2 in a low-field region (a) and in the methyl region (b). The red curves represent simulated resonances.

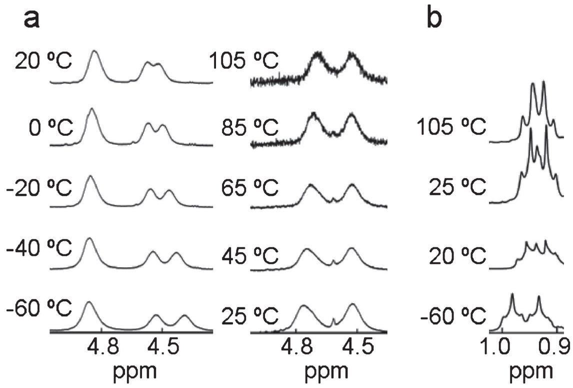

Figure 3. Variable-temperature ^{1}H NMR spectra for [Zr(BPEPP)(C_8OPc)] from −60 to 20 °C in CD_2Cl_2 and from 25 to 105 °C in $CDCl_2CDCl_2$ in the α-methylene region (a) and in the methyl region (b).

rate of the rotational exchange at 25 °C is ca. 500 s^{-1}, which is two orders of magnitude larger than that for [Ce(BPEPP)-(C_{22}OPP)].[14] The difference may be attributed to less steric hindrance for the present complex with the phthalocyanine ligand than that for [Ce(BPEPP)(C_{22}OPP)], in which two phenyl moieties in the BPEPP ring must go across the phenyl moieties of the C_{22}OPP ring when the 90°-flip takes place.

^{1}H NMR spectra for [Zr(BPEPP)(C_8OPc)] are somewhat solvent dependent. The spectrum in $CDCl_3$ at room temperature is shown in Supporting Information.[18] Appearance of the split peaks for a pair of the diastereotopic α-methylene protons (OCH_2) as well as for the phthalocyanine protons (PcH) clearly indicates that the rotational motion of [Zr(BPEPP)(C_8OPc)] is slower than the NMR time scale. In CD_2Cl_2, only a single peak and partly overlapping peaks appear for each of the diastereotopic α-methylene protons at 20 °C as shown in Figure 3a.[19] The latter peaks were shifted to separate into two distinct peaks with lowering temperature down to −60 °C without changes in the peak widths, which would be accompanied if the separation were due to changes in the rotational exchange. These observations indicate that the overlap is due to a mere coincidence and the rotational motion is slow in CD_2Cl_2 in the temperature range studied. This notion is corroborated by the appearance of two sets of triplet signals for the terminal methyl protons (Figure 3b) both at −60 and 20 °C. In $CDCl_2CDCl_2$, although the splitting of the α-methylene protons is not observed, the two sets of triplet signals for the terminal methyl protons indicate that the rotational motion is slow, even at a temperature as high as 105 °C.[19] Thus, we concluded that [Zr(BPEPP)(C_8OPc)] does not undergo rotational motion at least within the ^{1}H NMR time scale in any of these solvents.

Both [Ce(BPEPP)(C_8OPc)] and [Zr(BPEPP)(C_8OPc)] formed close-packed surface arrays at the interface of 1-phenyloctane and HOPG as shown by the STM images in Figure 4. These arrangements have common lattice parameters, $a = 2.6$ nm, $b = 2.6$ nm, and $\theta = 71°$, which are close to those of one of the polymorphic arrangements of H_2C_8OPc.[20,21] These results indicate that the double-decker complexes are immobilized on the HOPG surface with the C_8OPc macrocycle being adsorbed, presenting the BPEPP ring toward the solution. As for how alkyl chains fill the surface, we may borrow the model proposed for H_2C_8OPc,[20,21] which is depicted on the image in Figure 4b with each rectangle representing a C_8 chain.

While the lattice is identical for [Ce(BPEPP)(C_8OPc)] and [Zr(BPEPP)(C_8OPc)], a clear difference is recognized between them in terms of the shape of the spots. The spots for [Ce(BPEPP)(C_8OPc)] appear round (Figure 4a), which may be ascribed to the fast rotational libration of the BPEPP macrocycle with respect to the underlying C_8OPc ring. Although the rate of rotational libration could be quite different in solution and on a surface because of a conformational difference[22,23] among other factors, we may assume that the ring changes its orientation on the surface much faster than the STM time scale, considering the flip rate in solution as fast as 500 s^{-1} at an ambient temperature. Under the conditions used for the presented images, it took 6–8 s for completing each spot in the STM scanning.

In contrast, the spots for [Zr(BPEPP)(C_8OPc)] appear oval as shown in Figure 4b. To quantify the elliptic appearance, we measured the full width at half maximum values for the cross sections along the ⟨11⟩ direction for each spot. While the histogram can be fitted by a single Gaussian distribution for [Ce(BPEPP)(C_8OPc)] (Figure 4a), reflecting its round shape, two peaks were found at 1.9 and 2.3 nm in the histogram for [Zr(BPEPP)(C_8OPc)] (Figure 4b).

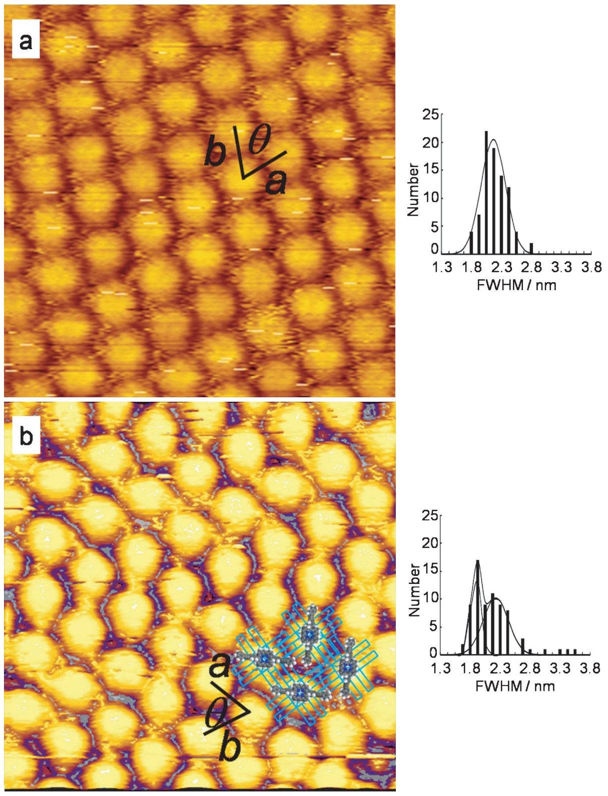

Figure 4. STM images (20 × 20 nm^2), histograms of full width at half maximum of spots along the ⟨11⟩ direction, and the Gaussian fit. (a) [Ce(BPEPP)(C_8OPc)], $I = 10$ pA, $V_{\text{sample}} = -1.0$ V. (b) [Zr(BPEPP)(C_8OPc)], $I = 4$ pA, $V_{\text{sample}} = -1.1$ V.

The molecular model (MM2) indicates that the length of the BPEPP fragment, i.e., distance between the para hydrogens on the phenyl groups, is 3.1 nm. This value is roughly consistent with the length of the long axis of the oval spot. There are two orientations of the long axes of the spots for [Zr(BPEPP)(C_8OPc)], i.e., one nearly parallel to the ⟨11⟩ direction and one nearly perpendicular to it. As these directions bisect the angle made by the alkyl chains of the C_8OPc ring, the two orientations are consistent with the antiprismatic coordination geometry for the central Zr metal ion, which lends further support for the correspondence of the shapes of the STM spot and the BPEPP ring. These considerations in turn indicate that the ring does not change its orientation during the scanning over the molecule at least until one spot is completed for each molecule (6–8 s).

In conclusion, we have proved that [Ce(BPEPP)(C_8OPc)] undergoes rotational libration both in solution and at liquid/solid interface. This is the first demonstration of the rotational libration for a double-decker complex involving a phthalocyanine macrocycle. On the other hand, [Zr(BPEPP)(C_8OPc)] does not exhibit rotational motion in solution within the ^{1}H NMR time scale or at the liquid/solid interface within the STM time scale. It is interesting to note that the length of the upper BPEPP ring, 3.1 nm, is longer than the intermolecular separation, 2.6 nm, in the array of [Ce(BPEPP)(C_8OPc)] on the surface. This means that some sort of cooperativity in the rotational motion might exist among neighboring molecules on the surface like mutually meshing gears. This and other aspects of rotating molecules on surfaces are targets of our ongoing research.

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