

Rotational oscillation of two interlocked porphyrins in cerium bis(5,15-diarylporphyrinate) double-deckers

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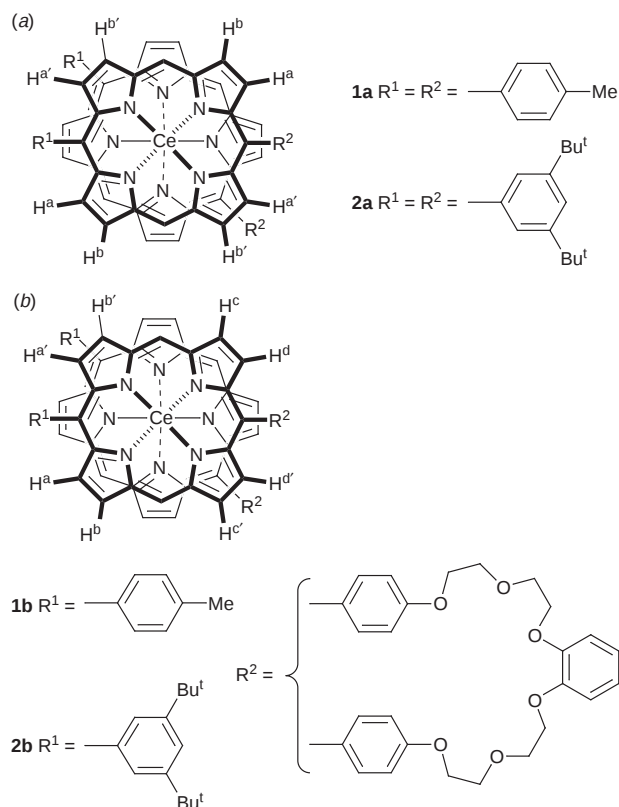
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Dynamic NMR coupled with racemization studies on chiral cerium bis(5,15-diarylporphyrinate) double-deckers demonstrate that the two interlocked porphyrin ligands oscillate rotationally around the metal center.

Oscillating molecules are interesting in their potential utilities for sensors, information transfer/storage devices and molecular machines, and several examples of molecular and supramolecular oscillating systems have been reported to date.^{1,2} Particularly interesting are oscillators consisting of chromophoric units because of a possible switching of their oscillation characteristics by light and/or redox. Metal bis(porphyrinate)s are double-decker complexes, in which a metal atom is sandwiched by two chromophoric porphyrin ligands.³ Recently, we have found that the porphyrin ligands in cerium bis(porphyrinate)s rotate thermally around the metal center, through studies on optical resolution and racemization behavior of a chiral cerium bis(tetraarylporphyrinate) with a symmetry group D_2 .⁴ The chirality of the complex originates from the staggered geometry of the two facing porphyrin ligands, where the relative rotation of the ligands leads to racemization. Herein we report that cerium bis(5,15-diarylporphyrinate)s are potential molecular oscillators, in which the two interlocked porphyrin ligands rotationally oscillate back and forth around the metal center.

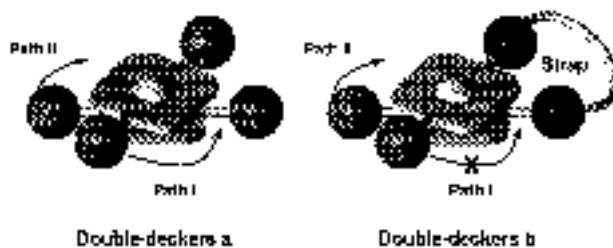
We have already reported that the D_2 -symmetric, chiral cerium complex **1a**, in contrast to a zirconium analogue of the same porphyrin ligands, shows no sign of optical resolution in chiral HPLC, as a result of racemization *via* a fast rotation of the porphyrin ligands.⁴ Our motivation to the present study arose from a preliminary observation that enantiomeric separation of **2a**† by chiral HPLC was also unsuccessful in spite of the presence of interferent bulky *meta*-substituents (Bu^t) on the *meso*-phenyl groups perpendicular to the porphyrin plane. In order to compare the rotatability of the porphyrin ligands in **2a** with that of **1a**, temperature-dependent NMR signal coalescence profile was investigated for exchangeable proton signals *via* ligand rotation. At a low temperature such as -20°C in CDCl_3 , **2a** showed four doublet signals at δ 8.48 (*a*), 8.58 (*a'*), 8.76 (*b*) and 8.84 (*b'*) [Scheme 1(a)] owing to nonequivalent pyrrole- β protons,[§] where the exchangeable pairs are signals *a/a'* and *b/b'*. Upon elevating the temperature, the paired signals *a* and *a'*, for example, coalesced completely at 0°C . From this coalescence profile, the rate constant for the rotation of the porphyrin ligands in **2a** was evaluated at 0°C to be $0.52 \times 10^2 \text{ s}^{-1}$,¶ which is almost comparable to that of **1a** ($0.63 \times 10^2 \text{ s}^{-1}$) at 1°C .⁴

Here one should note two possible rotating paths, I and II, for the complex to racemize (Scheme 2), where path II is sterically more demanding than path I, since the former path must transiently involve an energetically disfavored ‘eclipsed conformation’ with respect to the two facing porphyrin ligands. In order to evaluate the rotating rate *via* path II, we synthesized two new chiral double-decker complexes **1b** and **2b**, which bear a flexible oligoether strap between the two porphyrin ligands.† Their CPK models suggested that path I is unlikely to occur even when the oligoether strap adopts the most extended



Scheme 1

conformation, thereby allowing selective evaluation of the rotating rate *via* path II. Prior to dynamic NMR studies, we investigated the possibility of optical resolution of these two strapped complexes by chiral HPLC,|| where **2b** was successfully separated into enantiomers. The enantiomers exhibited clear mirror-image circular dichroism (CD) spectra to each other (Fig. 1), but the spectral intensity at 10°C gradually decreased with time, where the rotating rate constant *via* path II was evaluated to be $0.39 \times 10^{-3} \text{ s}^{-1}$.¶ In sharp contrast,



Scheme 2

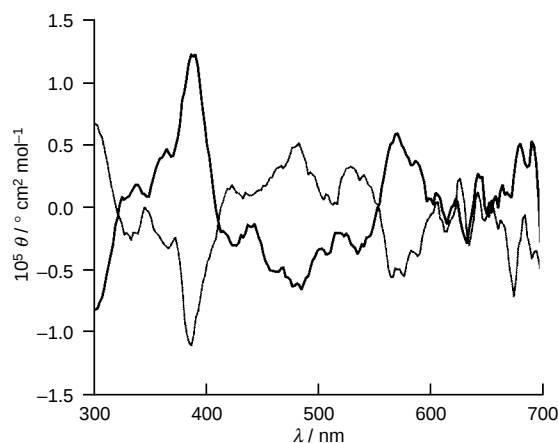


Fig. 1 Circular dichroism (CD) spectra of the enantiomers of **2b** in hexane–EtOH (1/1) at 10 °C

complex **1b** showed no sign of optical resolution, indicating that **1b** is more subject than **2b** to the ligand rotation *via* path II.

In order to evaluate the rotation rate of **1b**, we conducted ^1H NMR spectroscopy in CDCl_3 at varying temperatures. If the relative rotation of the porphyrin ligands is slower than the NMR chemical shift timescale, **1b** should display eight non-equivalent pyrrole- β signals because of the low symmetry of the molecular structure. In fact, we observed at 0 °C eight doublets at δ 8.30 (*a*), 8.38 (*d*), 8.54 (*d'*), 8.60 (*a'*), 8.68 (*b*), 8.72 (*c*), 8.81 (*b'*) and 8.82 (*c'*) [Scheme 1(b)] $\S$, where exchangeable pairs *via* ligand rotation are *a/a'*, *b/b'*, *c/c'* and *d/d'*, as determined from the cross-peaks in the EXSY spectra. However, even upon elevating the temperature to 55 °C, none of the paired signals coalesced, indicating that the site exchange in **1b** is much slower than that in the non-strapped analogue **1a**. Thus, the saturation transfer method 5,6 was applied, which is informative of exchange phenomena much slower than the NMR chemical shift timescale: When the pyrrole- β signal *d'* was irradiated at, e.g., 25 °C (δ 8.50), the paired signal *d* (δ 8.35) decreased to one-third in intensity. As the temperature was lowered, the saturation transfer was less pronounced, and virtually disappeared at 0 °C. From the degree of saturation transfer from the signals *d'* to *d* at 10 °C, the rate constant for the rotation of the porphyrin ligands (path II) in **1b** was evaluated to be 0.37 s^{-1} ,** which is almost three orders of magnitude larger than that of **2b**.

The observed rotation rates for the strapped complexes (**1b** and **2b**), compared with those for non-strapped **1a** and **2a**, allow us to estimate that the rotation *via* sterically more demanding path II takes place much less frequently at every 10^2 to 10^5 times the rotation *via* path I occurs. Therefore, cerium bis(5,15-diarylporphyrinate) double-deckers may be regarded as molecular oscillators, where the two facing porphyrin ligands rotationally oscillate around the metal center, because of the interlocking by the *meso*-aryl groups. Studies on stimuli-responsive oscillations of metal bis(porphyrinate) double-deckers are the subject worthy of further investigation.

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Notes and References

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$\ddagger$ According to the method reported in ref. 4, **2a** was obtained as brown powder in 11% yield. ^1H NMR (270 MHz, CDCl_3 , $-20\text{ }^\circ\text{C}$) δ 9.57 (s, 4 H, *o*-endo-H), 9.14 (s, 4 H, *meso*), 8.84, 8.76, 8.58, 8.48 (d $\times$ 4, *J* 4 Hz, 16 H, pyrrole- β), 7.78 (s, 4 H, *p*-H), 6.34 (s, 4 H, *o*-exo-H), 2.06 (s, 36 H, *endo*-Bu t), 1.14 (s, 36 H, *exo*-Bu t). FAB-HRMS (*m/z*); calc. for $\text{M} + \text{H}^+$ ($\text{C}_{96}\text{H}_{105}\text{CeN}_8$): 1509.7517, found: 1509.7510. For the synthesis of **1b** and **2b**, the ether linkages of 5-(4'-methoxyphenyl)-15-(4'-tolyl)porphine and 5-(4'-methoxyphenyl)-15-(3',5'-di-*tert*-butylphenyl)porphine were cleaved, respectively, by BR_3 and the products were reacted with the corresponding α,ω -tosylated oligoether in the presence of Cs_2CO_3 to give bridged free bases, which were metallated with $\text{Ce}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ in refluxing 1,2,4-trichlorobenzene for 3 h under Ar. The crude products were chromatographed on alumina and recrystallized from CH_2Cl_2 –hexane. The isolated yields were 5.6 (**1b**) and 17 (**2b**)%, respectively. **1b**: ^1H NMR (270 MHz, CDCl_3 , 0 °C) δ 9.68 (d $\times$ 2, 4 H, *o*-endo-H in $\text{C}_6\text{H}_4\text{Me}$ and $\text{C}_6\text{H}_4\text{O}$), 9.09, 9.08 (s $\times$ 2, 4 H, *meso*), 8.82, 8.81, 8.72, 8.68, 8.60, 8.54, 8.38, 8.30 (d $\times$ 8, *J* 4 Hz, 16 H, pyrrole- β), 8.12 (d, *J* 7 Hz, 2 H, *m*-endo-H in $\text{C}_6\text{H}_4\text{Me}$), 7.89 (br s, 2 H, *m*-endo-H in $\text{C}_6\text{H}_4\text{O}$), 7.17–7.08 (m, 6 H, *m*-exo-H in $\text{C}_6\text{H}_4\text{Me}$ and $\text{C}_6\text{H}_4\text{O}_2$), 6.98 (br s, 2 H, *m*-exo-H in $\text{C}_6\text{H}_4\text{O}$), 6.61 (br s, 2 H, *o*-exo-H in $\text{C}_6\text{H}_4\text{O}$), 6.35 (d, *J* 7 Hz, 2 H, *o*-exo-H in $\text{C}_6\text{H}_4\text{Me}$), 4.80–4.26 (m, 16 H, CH_2), 2.80 (s, 6 H, CH_3). FAB-HRMS calc. (*m/z*): for M^+ ($\text{C}_{80}\text{H}_{62}\text{CeN}_8\text{O}_6$): 1370.3847, found: 1370.3876. **2b**: ^1H NMR (270 MHz, CDCl_3 , 21 °C) δ 9.64 (br s, 2 H, *o*-endo-H in $\text{C}_6\text{H}_4\text{O}$), 9.52 (t, *J* 2 Hz, 2 H, *o*-endo-H in C_6H_3), 9.06, 9.02 (s $\times$ 2, 4 H, *meso*), 8.81, 8.80, 8.76, 8.65, 8.64, 8.56, 8.51, 8.28 (d $\times$ 8, *J* 4 Hz, 16 H, pyrrole- β), 7.85 (br s, 2 H, *m*-endo-H in $\text{C}_6\text{H}_4\text{O}$), 7.76 (t, *J* 2 Hz, 2 H, *p*-H in C_6H_3), 7.14–7.03 (m, 4 H, $\text{C}_6\text{H}_4\text{O}_2$), 6.95 (br s, 2 H, *m*-exo-H in $\text{C}_6\text{H}_4\text{O}$), 6.59 (br s, 2 H, *o*-exo-H in $\text{C}_6\text{H}_4\text{O}$), 6.31 (t, *J* 2 Hz, 2 H, *o*-exo-H in C_6H_3), 4.76–4.22 (m, 16 H, CH_2), 2.01 (s, 18 H, *endo*-Bu t), 1.11 (s, 18 H, *exo*-Bu t). FAB-HRMS (*m/z*): calc. for $\text{M} + \text{H}^+$ ($\text{C}_{94}\text{H}_{91}\text{CeN}_8\text{O}_6$): 1567.6117, found: 1567.6068.

$\S$ Assignments were made by ^1H – ^1H COSY and EXSY spectroscopies upon consideration of magnetic effects of proximate *meso*-aryl substituents.

$\P$ Calculated by the method reported in ref. 4.

$\parallel$ With a Chiralcel OD-H (Daicel) column using hexane–EtOH (1/1) as eluent at a flow rate of 0.5 ml min $^{-1}$; retention times: 35.9 and 85.8 min.

*** According to the method described in ref. 6, the rate constant of exchange (*k*) was calculated by the equation: $k = (I_0 - I_{\text{irrad}})/I_{\text{irrad}} T_1^{-1}$, where I_0 and I_{irrad} represent intensity of the pyrrole- β signal *d* and that upon irradiation to saturate the exchangeable proton singal *d'*, respectively, and T_1 represents the spin–lattice relaxation time for the signal *d'*.

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