論 文 内 容 の 要 旨

博士論文題目

Design and synthesis of molecular gear prototypes based on lanthanoid double-decker complexes

氏　　名　JEEVITHRA DEWI SUBRAMANIAM

（論文内容の要旨）

In this thesis, we focus on the design and synthesis of phthalocyanine double-decker complexes as molecular gear prototypes in solution and on surface.

In a first part, three highly sterically-hindered double-decker complexes have been prepared with phthalocyanines functionalized at the α-position despite their high steric hindrance. By finely tune the steric hindrance in these complex, we were able to fully block any rotation of a deck complex to the other. In a heteroleptic complex with unfunctionalized ligand, we demonstrated that rotation along the pseudo-C_4 symmetry axis can be switched on by heating the solution. The observed rotation is slow at room temperature, but as the temperature increases, some signals corresponding to the α- and β-protons of the unfunctionalized ligand appear as well-resolved signals.

In a second part, a heteroleptic cerium(IV)-based molecular gear composed of a thioether functionalized phthalocyanine anchoring ligand and a helical naphthalocyanine rotating cogwheel functionalized with four carbazoles was carefully designed to study the intermolecular gearing behavior on surface with STM. The design is composed of a prochiral 1,2-naphthalocyanine ligand as cogwheel with *tert*-butyl carbazole as gearing teeth, a phthalocyanine ligand with eight hexylthiol group as an anchor for the used Au(111) surface and Ce(IV) as ball bearing. The synthesis of this helicoidal ligand bearing bulky aromatic ligand was established after exploring different synthetic strategies. The naphthalocyanine ligand was obtained after eleven steps with an overall yield of 0.2%. Interestingly, this helicoidal ligand was obtained as a mixture of three geometrical isomers two of which being chiral and exhibit high steric hindrance as shown by DFT calculations. The third one with a C_{4h} symmetry is prochiral. This complexation with Ce(IV) and the anchoring thioether-functionalized phthalocyanine ligand gave the targeted heteroleptic complex, but its purification remains to be optimized. The major difficulty encountered during the purification is the limited solubility of the homoleptic complex obtained as a side product, preventing the purification of the targeted complex, by contaminating all fraction due to progressive solubilization. This limitation could be overcome by increasing the ratio of the anchoring ligand to strongly reduce the formation of the side-compound.

To conclude, it was shown phthalocyanine based double-decker complexes as new molecular gear prototypes have been achieved. Among them, the target helical double decker complex is a promising candidate to study intermolecular gearing rotation on surface with STM.

氏　名	JEEVITHRA DEWI SUBRAMANIAM

（論文審査結果の要旨）

In the field of molecular machines, molecular gears are highly desired to transfer powerstroke or information at the nanoscale. Double-decker complexes, in which lanthanoid ion is sandwiched between two porphyrinoid ligands such as phthalocyanine (Pc) or naphthalocyanine are attractive structural motifs for molecular gears since the ligands can rotate around metal ions. In order to study the influence of steric hindrance and chirality in the rotating motion, innovative double-decker complexes have been designed and synthesized.

In a first part, three highly sterically-hindered double-decker complexes have been prepared with phthalocyanines functionalized at the α-position despite their high steric hindrance. **$Ce^{IV}(Pc2)_2$** is a homoleptic complex of a tetrasubstituted Pc with carbazole and **$Ce^{IV}(Pc3)_2$** is a homoleptic complex of a desymmetrized Pc with three carbazole and one phenothiazine. Since the rotative motions were blocked even at high temperature in these homoleptic complexes, a heteroleptic **$Ce^{IV}(Pc)(Pc3)$** complex was also prepared with one unfunctionalized ligand to reduce the steric hindrance. The dynamic behavior of **$Ce^{IV}(Pc3)_2$** and **$Ce^{IV}(Pc)(Pc3)$** complexes were analyzed by VT-NMR. In the case of **$Ce^{IV}(Pc3)_2$**, no change in the spectrum was observed illustrating the too high steric hindrance preventing any rotation from occuring. In the case of **$Ce^{IV}(Pc)(Pc3)$**, we demonstrated that rotation along the pseudo-C_4 symmetry axis can be switched on by heating the solution. The observed rotation is slow at room temperature, but as the temperature increases, some signals corresponding to the α- and β- protons of the **Pc** ligands appear as well-resolved signals. Additionally, the carbazole substituents do not fully rotate even at higher temperatures, but their faster oscillation allows the unfunctionalized **Pc** fragment to rotate, which was not possible in the case of the homoleptic complexes.

In a second part, a heteroleptic cerium(IV)-based molecular gear composed of a thioether functionalized phthalocyanine anchoring ligand and a helical naphthalocyanine rotating cogwheel functionalized with four carbazoles was carefully designed to study the intermolecular gearing behavior on surface with STM. The design is composed of a pro-chiral 1,2-naphthalocyanine ligand as cogwheel with *tert*-butyl carbazole as gearing teeth, a phthalocyanine ligand with eight hexylthiol group as an anchor for the used Au(111) surface and Ce(IV) as ball bearing. The synthesis of this helicoidal ligand bearing bulky aromatic ligand was established after exploring different synthetic strategies. The naphthalocyanine ligand was obtained after eleven steps with an overall yield of 0.2%. Interestingly, this helicoidal ligand was obtained as a mixture of three geometrical isomers two of which being chiral and exhibit high steric hindrance as shown by DFT calculations. Three geometrical isomers were isolated namely C_{4h}, C_1 and C_2 in 17%, 8% and 3% yields respectively. Complexation of this ligand with Ce(IV) and the anchoring thioether-functionalized phthalocyanine ligand gave the targeted heteroleptic complex, but its purification remain to be optimized. The major difficulty encountered during the purification is the limited solubility of the homoleptic complex obtained as a side product, preventing the purification of the targeted complex, by contaminating all fraction due to progressive solubilization. This limitation could be overcome by increasing the ratio of the anchoring ligand to strongly reduce the formation of the side-compound. This complex is very promising as new molecular gear prototypes to study intermolecular gearing rotation on surface. Moreover, this complex will also allow us to clarify the significance of alternative right-handed and left-handed chiralities in intermolecular gearing rotation.

Therefore, all the reviewers recognized that this thesis has value as a doctoral thesis in science.