

Doctoral thesis/dissertation Digest Form

Thesis/dissertation Title: Design and synthesis of molecular gear prototypes based on lanthanoid double-decker complexes
(ランタノイドダブルデッカー錯体をベースとした分子歯車プロトタイプ的设计と合成)

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Approved Digest

Artificial molecular machines are molecules capable to execute mechanical-like movements as an outcome of an appropriate external stimuli. Recently, this field drew a great attention since the pioneer works by Nobel Laureates Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa. There are now many examples like motors, shuttles, tweezers, nanocars and gears. Various kinds of molecular gears have been proposed among them, double-decker complexes, in which lanthanoid ion is sandwiched between two porphyrinoid ligands such as phthalocyanine or naphthalocyanine are attractive structural motifs for molecular gears since the ligands can rotate around metal ions.

In my thesis, I describe the synthesis of new phthalocyanine derivatives incorporating bulky aromatic substituents serving as prototypes for intermeshing gear-like molecules. Limited design and investigations on rotation of Pc sandwich complex particularly double-deckers are reported. Here, rational design of different types of cogwheels for the purpose of investigating their behavior in solution and on surface has been reported.

In Chapter 1, general background of artificial molecular machines, molecular gears in solution and on surface, phthalocyanine based molecular gears, NMR characterization techniques and the objectives of the research are described.

Chapter 2 is reported the design of sterically hindered homoleptic and heteroleptic double-decker complexes of symmetric and dissymmetric ligands and the observation of their behavior in solution using VT-NMR technique. It is revealed that the homoleptic bulky complexes did not show any visible behavior changes even at 140°C while the less bulky heteroleptic complex demonstrated some dynamic behavior in solution at higher temperature. The study on this complex disclosed that the observed rotation is slower at room temperature and as the temperature increased, some typical protons of the phthalocyanine ligands appeared as well-resolved signals. In addition, the substituents are

oscillating faster at higher temperature mimicking paddling motions like rowing but not rotating freely. This chapter concluded that optimizing the steric hindrance in a system is essential to observe stepwise rotation of phthalocyanine based double-decker complexes.

In Chapter 3 is presented a gear prototype designed to be deposited and studied on a surface with a helicoidal 1,2-naphthalocyanine as new pro-chiral cogwheel. The design is composed of a pro-chiral 1,2-naphthalocyanine ligand as cogwheel employed with *tert*-butyl carbazole as gearing teeth, a phthalocyanine ligand with eight hexylthiol group as anchor for Au(111) surface and a Ce(IV) as ball bearing to facilitate the rotation. The challenging 11 steps synthesis of helicoidal ligand bearing bulky aromatic ligand was established after many attempts. Three geometrical isomers were isolated namely C_{4h} (major compound), C_1 and C_2 in 17%, 8% and 3% yields respectively. I also found that formation of homoleptic complexes is more favorable than the targeted heteroleptic complex despite the steric hindrance which was revealed by MALDI-TOF-MS.

Overall, in this study, new sterically crowded phthalocyanine based double-decker complexes as new molecular gear prototypes have been constructed and investigated. In addition, the final target helical chiral complex is a promising molecular gear candidate to study intermolecular gearing rotation on surface with STM. The noteworthy of this design is that it will also allow us to clarify the role of the chirality (the complex can be right-handed and left-handed) in the intermolecular gearing rotation as no studies has been reported yet.