Construction of Molecular Gears based on Lanthanoid Double-decker Complexes for Intermolecular Gearing Motion Study

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Artificial molecular machines are molecules capable to execute mechanical-like movements as an outcome of an appropriate external stimuli. There are now many examples like motors, shuttles, tweezers, nanocars and gears.[1] Various kinds of molecular gears have been proposed,[2] among them, double-decker complexes, in which lanthanoid ion is sandwiched between two porphyrinoid ligands such as porphyrin, phthalocyanine or naphthalocyanine, are attractive structural motifs for molecular gears since the ligands can rotate around metal ions.[3]

In this study, we report the construction of double-decker complexes of cerium(IV) as new prototypes of molecular gears. Phthalocyanines substituted at the α-position with π-planar bulky substituents were used to synthesize two homoleptic and one heteroleptic double-decker complexes. It is expected that the upper and lower ligands tightly engage and work as gear due to these bulky and rigid substituents. A C_{4h} symmetric phthalocyanine H_2**Pc1** having 3,6-di-*tert*-butyl-carbazole at the α-position was employed and synthesized as a sub-unit of the gearing system.[4] Ce(**Pc1**)$_2$ was obtained in 40% yield through the complexation of H_2**Pc1** with Ce(acac)$_3$·nH_2O under microwave irradiation. The structure of Ce^{IV}(**Pc1**)$_2$ was confirmed by single crystal X-ray structure analysis (Fig. 1). Desymmetrised A3B-type phthalocyanine H_2**Pc2** bearing one phenothiazine and three 3,6-di-*tert*-butyl-carbazole at the α-position was also synthesized as the same manner as Ce(**Pc1**)$_2$. The formation of the complexes was confirmed with ^{1}H-NMR, 2D-NMR, and MALDI-TOF-MS. To study molecular gearing on surface with STM, our final target is constituted of a thioether-functionalized porphyrin as the anchoring ligand and a carbazole-functionalized naphthalocyanine as the cogwheel (Fig. 2). Thanks to the helical chirality of this double-decker complex, we hope to build a train of gears with consecutive molecules of opposite chirality.

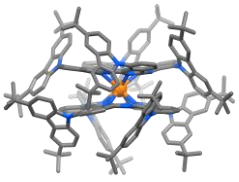

Fig. 1: X-ray structure of Ce^{IV}(**Pc1**)$_2$ (side view)

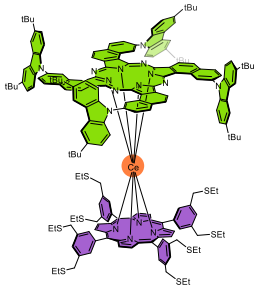

Fig. 2: Gear to study on surface with STM

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