

主 論 文 要 旨

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論文題名

Fabrication of Multinuclear Metal Complexes Based on Acyclic Oligopyrrole Ligands

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主論文要旨

π -Conjugated dye moieties as building blocks enable the fabrication of novel supramolecular structures which have specific electrical and optical properties. Dipyrins (dipyrromethenes) known as half structures of porphyrins behave acyclic planar bidentate monoanionic ligands for metal cations. As well as these ligands can compensate positive charge of metal cations to form flexible neutral complexes. As candidate building subunits of helical assemblies, linear tetrapyrrole ligands *bidipyrins*, directly linked dimers of dipyrins, can fabricate metal complexes including [2 + 2]-type Zn^{II} -assisted double helices. Previous reports on bidipyrins and their metal complexes have focused on the primitive studies. Thus, we investigate the introduction of various substituents and the development of multinuclear metal complexes for exhibiting unique properties derived from acyclic π -conjugated ligands.

Covalently linked dipyrin dimers have afforded nanoscale [2 + 2]-type neutral coordination macrocycles with a diagonal of about 1.6 nm. Two moieties of the achiral dipyrin- Zn^{II} complex yield the chiral coordination macrocycles as minor species, as well as major *meso* stereoisomers by the covalent linkages. Tetrahedral Zn^{II} coordination by using acyclic ligands enables the dipyrin-metal complex units to readily rotate and pass through the cavity of the nanorings, showing the transitions between the chiral and achiral isomers.

On the other hand, bidipyrin-bridged macrocycles, prepared from Ni^{II} -bridged dipyrin-based nanorings by intramolecular oxidative biaryl coupling reactions, yielded [2 + 4]-type Zn^{II} -assisted stable twisted-ring dimers comprising two double helices. These [2 + 4]-type metal complexes can be optically resolved by chiral HPLC and exhibit tunable electronic and optical properties as a result of spring-like motions. The double helices behave as the glue to connect two macrocycles and also as the screws of hinges to form thermally responsive synchronized spring systems.