## Responsive supramolecules incorporating luminescent dipyrrin complexes

- Oligomeric BODIPY hosts utilizing their B-F bonds as recognition units

BODIPYs, boron complexes of dipyrrins, exhibit strong fluorescence in the visible region. We focused on the fact that the B-F bond of the BODIPY is polarized and its fluorine atom possesses partial negative charges, and developed host molecules that utilizes BODIPYs as recognition units. A macrocyclic BODIPY trimer with $p$-phenylene linker had a cavity in which the fluorine atoms were accumulated, and it formed a pseudorotaxane by recognizing an axial ammonium guest via the electrostatic interactions and hydrogen bonds. Meanwhile, a linear BODIPY trimer changed its conformation to a helical form upon the interaction with the cations, and accordingly, its absorption and fluorescence were significantly shifted. It can be utilized as a sensor for alkali metal cations such as cesium.
(Chem. Commun. 2010, 46, 6732-6734; Chem. Commun. 2012, 48, 4818-4820)



- Molecular recognition by the aluminum complexes of the $\mathbf{N}_{2} \mathbf{O}_{2}$-type dipyrrin (ALDIPY).

The $\mathrm{N}_{2} \mathrm{O}_{2}$-type dipyrrin ligands were obtained by introducing 2-hydroxyphenyl groups to the $\alpha$-positions of the dipyrrins. Metal complexes and main group element complexes of the $\mathrm{N}_{2} \mathrm{O}_{2}$ dipyrrins exhibited interesting properties depending on the characters of the central elements. Aluminum complexes of the $\mathrm{N}_{2} \mathrm{O}_{2}$-type dipyrrins (ALDIPY) are stable to air and water, and showed strong red fluorescence. The aluminum center adopted octahedral geometry with the $\mathrm{N}_{2} \mathrm{O}_{2}$ ligand occupying four equatorial positions. This was in sharp contrast to the corresponding boron complex, whose boron center adopted tetrahedral geometry. The phenoxy oxygens of the $\mathrm{N}_{2} \mathrm{O}_{2}$ complex had partial negative charges. With this feature, the ALDIPY derivatives to which the oxygen atoms were appropriately incorporated worked as selective receptors toward alkaline earth metal ions.
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