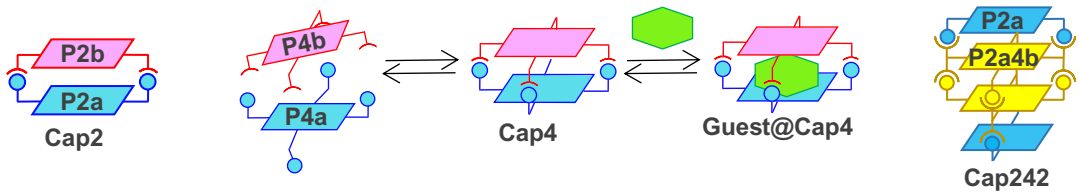
Building Heterodimer Porphyrin Capsules Bearing Different Number of Hydrogen Bond Function and Application to Aromatic Multi-Layer Structure

(*Graduate School of Engineering, University of Fukui*) ○Masahiro Ueda, Hayato Ban, Masaki Kimura, Shinobu Miyagawa, Masaya Naito, Yuji Tokunaga
Keywords: Porphyrin; Self-Assembled Capsule; Molecular Recognition; Hydrogen Bond; Thermodynamics

We have achieved construction of self-assembled porphyrin dimer and trimer capsules.[1,2] The capsules consisted of a pair of porphyrins bearing two or four benzoic acid or aminoquinoline units as H-bonding moieties at meso position, respectively, and could bind π-aromatic compounds, forming multi-layer π-aromatic structures. Here, we report kinetic and thermodynamic stabilities of two- and four- armed porphyrin dimers and their molecular recognition behaviors. Taking the results into account, we present construction of a higher order structure by using porphyrins featuring different numbers of the complementary H-bonding donor and acceptor pair.

Stabilities of porphyrin dimers: Two- and four- armed porphyrin dimers **Cap2** and **Cap4** quantitatively formed from the corresponding pairs of porphyrins in $CDCl_3$. In ^{1}H NMR spectra of an equimolar mixture of the pairs in a mixture of $CDCl_3$ and DMSO-d_6, the dimers and monomeric species were observed, respectively. **Cap4** is kinetically and thermodynamically more stable than **Cap2**. ^{1}H NMR titration experiments of the capsules and electron-deficient mono- and bicyclic aromatic guests revealed that recognition abilities of **Cap2** were ca. 10 times higher than those of **Cap4**.

Formation of porphyrin tetramer: We designed and synthesized porphyrin **P2a4b**, bearing two terephthalic acid and two aminoquinoline, for construction of porphyrin tetramer **Cap242**. Although **P2a4b** was not soluble in $CDCl_3$, the addition of an equimolar amount of the two-armed aminoquinolylporphyrin **P2a** and DMSO-d_6 solution of aromatic guest resulted in homogeneous solution. The ^{1}H NMR spectrum of the mixture featured complexes formed from **Cap242** and the guest molecule(s).



1) M. Kimura, J. Miyashita, S. Miyagawa, T. Kawasaki, H. Takaya, Y. Tokunaga, *Asian J. Org. Chem.* **2018**, *7*, 2087－2093. 2) M. Ueda, M. Kimura, S. Miyagawa, H. Takaya, M. Naito, Y. Tokunaga, *Chem. Asian J.* **2020**, *15*, 2212－2217.