Synthesis and Functional Exploration of Nitrogen-containing Macrocyclic Tetramers In2Q2 and BIm2Q2

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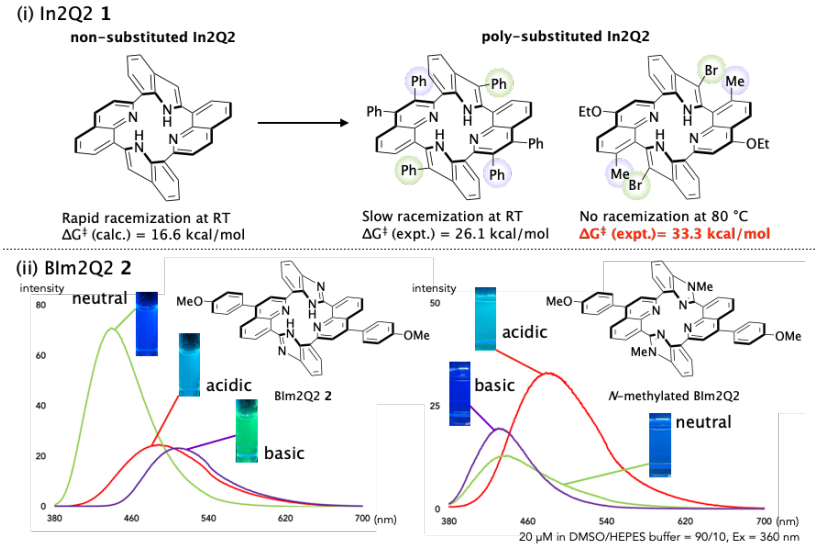
Porphyrin is an important nitrogen-containing macrocyclic compound with a wide range of applications, spanning its roles from essential functional units living organisms to dyes and ligands. Due to the planar structure of porphyrin, modification with chiral functional groups is essential for its further application in asymmetric catalysis. Therefore, it is highly desirable to design porphyrin analogs whose frameworks inherently possess chirality. Last year, our group developed In2Q2 **1**, a dianionic ligand with C_2-symmetry that is different from porphyrin[1]. However, its low flipping energy posed a challenge in achieving chiral resolution. In this study, we designed derivatives of In2Q2 by introducing multiple substituents on the indole (In) and quinoline (Q) rings to increase the flipping energy. Specifically, polysubstituted In2Q2 compounds with functional groups at the indole-3/quinoline-3 positions or indole-3/quinoline-7 positions were synthesized, which resulted in a significant enhancement of flipping energy, reaching up to 33.3 kcal/mol.

In addition, BIm2Q2 **2**, in which the indole units of In2Q2 were replaced with benzimidazole (BIm)**,** was synthesized. This new molecular entity exhibited pH-dependent fluorescence with different emission wavelength at 440−508 nm under acidic, neutral and basic conditions. In contrast, *N*-methylated BIm2Q2 showed similar fluorescence in neutral and basic conditions, highlighting the key role of free N-H of benzimidazole. The formation of metal complexes will be discussed.



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