Transformable quadruply interpenetrated cage with multiple states of different reactivities

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Molecular self-assemblies with tunable multi-pockets are potentially functional molecules that generate multiple states. Pd_4L_8 interpenetrated cages (ICs), in which two Pd_2L_4 cages are quadruply interpenetrated, have three correlating, tunable pockets for anions. Here, we report that ICs binding three F^- or Cl^- ions, (F·F·F)- and (Cl·Cl·Cl)-ICs, were self-assembled from ditopic ligand L in high yields. The outer anions in the ICs were selectively exchanged with F^- or Cl^- under kinetic control, resulting in the quantitative formation of the thermodynamically most stable (Cl·F·Cl)-IC from the (F·F·F)-IC. The (F·Cl·F)-IC, which was produced from the (Cl·Cl·Cl)-IC with F^- by selective anion exchange, is a metastable transient species. The three thermodynamically stable ICs showed different reactivities in the presence of BF_3 and Ag^+. The addition of BF_3 to the (Cl·Cl·Cl)-IC afforded heteroleptic [2]-catenane via unusual ligand exchanges, whereas the outer F^- ions in the (F·F·F)-IC were removed by BF_3 to form a metastable (⊗·F·⊗)-IC. The heteroleptic [2]-catenane was converted into the (Cl·Cl·Cl)-IC by addition of Lewis base (F^- or Py*). The addition of Ag^+ to the (Cl·Cl·Cl)-IC caused dethreading to form the Pd_2L_4 cages, whereas the (F·F·F)-IC was intact against Ag^+. The thermodynamically most stable (Cl·F·Cl)-IC did not react with either BF_3 or Ag^+. As a result, a total of seven states were generated, affording a complicated network in response to halide ions, Lewis acids and bases, and Ag^+.[1]

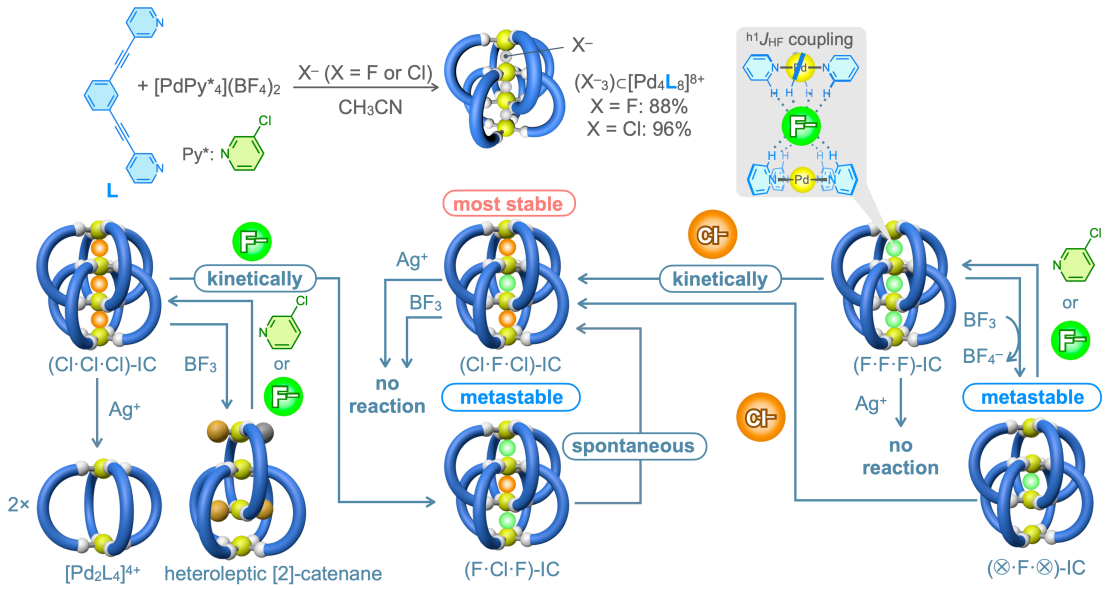

Figure Anion exchanges of quadruply interpenetrated cage (IC).

1) Tsukasa Abe, Yutong Zhang, Keisuke Takeuchi, and Shuichi Hiraoka, *Chem*, accepted.