Self-assembly processes of imine-based [2+2] rings and [3+2] cages through imine exchanges

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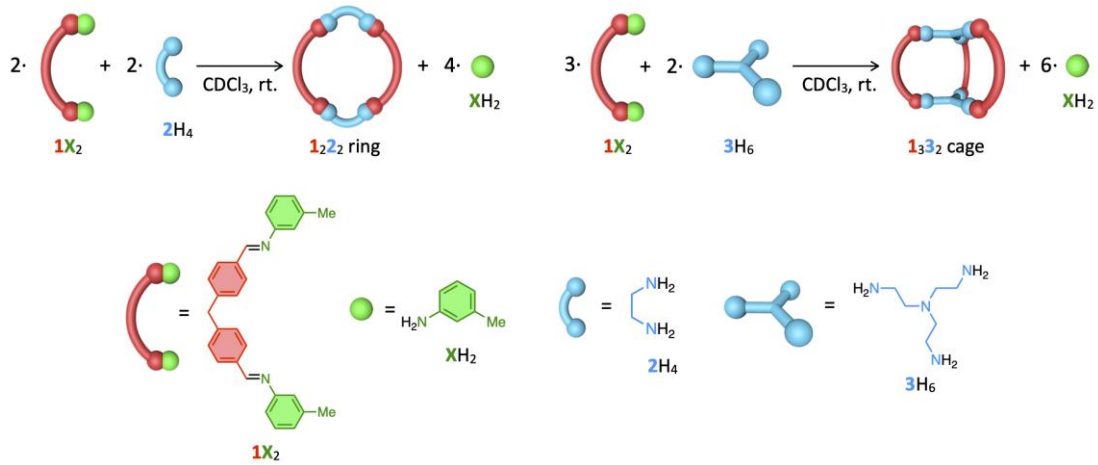
Imine-based assemblies have attracted much attention in materials science. Imine formation process by mixing aldehyde and amine in the presence of acid catalyst and/or dehydration reagent has often been applied in imine-based self-assembly to produce discrete assemblies by precipitation or under thermodynamic control. Here, we discuss the self-assembly process of [2+2] ring and [3+2] cage assemblies through imine exchange process by QASAP (quantitative analysis of self-assembly process)[1] and NASAP (numerical analysis of self-assembly process)[2], which have been used to reveal coordination self-assembly processes. *m*-toluidine (**X**H_2) was chosen as a leaving amine. It was found that the imine exchanges take place in $CDCl_3$ at room temperature without acid catalyst to produce a thermodynamically stable [2+2] ring, $\mathbf{1}_2\mathbf{2}_2$, and a [3+2] cage, $\mathbf{1}_3\mathbf{3}_2$. The information about average composition of all intermediates produced during the self-assembly was obtained by quantification of all substrates and products in the [2+2] and [3+2] assemblies and model reactions. Numerical fitting of the experimental data in each reaction network model gave a good data set of the rate constants, which enabled us to simulate the self-assembly with the rate constant in the reaction network to find the major self-assembly pathway and the rate-determining step.



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