DOCTORAL THESIS

Utilization of molecular switching in rotaxane for manipulating organocatalysis and macromolecular size

Kwan, Chak Shing

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Abstract

Rotaxane organocatalysis is a new direction towards controlled catalytic reactions in one pot. By combining molecular shuttling and catalysis, a fluorescence and pH-responsive switchable rotaxane dual organocatalyst with exclusive selectivity of catalytic reactions in two or three-component system are demonstrated. The new design of a [2]rotaxane catalyst containing an anthracene group was to visualize the process of the catalytic reaction upon switching of macrocycle. Two catalytic moieties, secondary amine and thiourea, are chosen in this work. Both moieties act as organocatalysts and the binding sites for the crown ether macrocycle. Four sets of catalytic reaction of acetylacetone or dibenzoylmethane with *trans*-β-nitrostyrene and crotonaldehyde were catalysed by the rotaxane with high selectivity. *In situ* ON-OFF switching of the [2]rotaxane catalyst has also been demonstrated.

Type III-B rotaxane dendrimers (T3B-RDs) are hyperbranched macromolecules with mechanical bonds on every branching unit. First to third (G1–G3), and up to the fourth (G4) generation (*MW*>22,000 Da) of pure organic T3B-RDs and dendrons were successfully synthesized through the copper catalyzed alkyne–azide cycloaddition (CuAAC) reaction. By utilizing multiple molecular shuttling of the mechanical bonds within the sphere-like macromolecule, a collective three-dimensional contract-extend molecular motion was demonstrated by diffusion

ordered spectroscopy (DOSY). The discrete T3B-RDs were further observed and characterized by atomic force microscopy (AFM), dynamic light scattering (DLS), and mass spectrometry (MS). The binding of chlorambucil and pH-triggered switching of the T3B-RDs were also characterized by ^{1}H NMR spectroscopy.

Type III-C rotaxane dendrimer is a new type of rotaxane dendrimer where in the mechanical bonds are in between and constituing the branchning point to form the macromolecules. First and second (G1–G2) type III-C rotaxane dendrimers were synthesized successfully as a prototypical example. Two different shuttling processes have been deomostrated by the non-methylated and methylated type III-C rotaxane dendrimers, and characterized by ^{1}H NMR spectroscopy.

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