DNAzymes as Sensors for Metal Ions and as Templates for Directed Assembly of Inorganic Nanomaterials

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Metal ion sensors have a wide range of applications in bioinorganic chemistry, from metalloneurochemistry, to environmental bioinorganic chemistry, developmental biology, and clinical toxicology. Despite recent progress, designing sensors based on a single class of molecules for a broad range of metal ions and different oxidation states of the same metal ions remains a significant challenge. In particular, few methods are general enough to allow for a) obtaining molecules for any specific target metal ion; b) improving selectivity of the molecule; c) transforming molecular recognition into physical detectable signals without compromising the binding affinity and selectivity; and d) fine-tuning the dynamic range. We have met the above challenges by using a combinatorial method called *in vitro* selection to obtain DNAzymes that can bind the metal ion of choice strongly and specifically (1,2). We have also used a “negative” selection strategy to improve the selectivity of the DNAzymes (3). By labeling the resulting DNAzymes with a fluorophore/quencher or gold nanoparticles, we have developed new classes of fluorescent and colorimetric sensors for metal ions (4-6). A fluorescent sensor for Pb(II) has a detection limit of 2 ppb, below the toxic level of 15 ppb for drinking water, and of 100 ppb in blood. A novel approach of using an inactive variant of DNAzymes to tune the detection range of the sensors is also demonstrated (6). Our methods are general enough so that sensors for other metal ions such as Zn(II), Hg(II), and U(VI) have been or are being obtained.

An extension of our colorimetric sensor work is the use of DNAzymes as templates for directed assembly of inorganic nanomaterials such as gold nanoparticles. The use of DNAzymes allows for genetic control of the synthesis and properties of materials in response to chemical stimuli under constant temperature, pressure and chemical equilibrium, a hallmark of biomaterials synthesis that has been difficult to reproduce in artificial systems until recently (6-8). The latest results in both areas will be presented.

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