Creating Enzymes with Chemically Programmed Active Site Functionality

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Biocatalysis is widely recognized as a sustainable technology for the production of high-value chemicals. At present, enzyme production and evolution strategies rely exclusively on Nature's standard amino acid alphabet of twenty canonical residues which contain limited functionality. Here we demonstrate that the incorporation of new 'chemically programmed' amino acids into existing laboratory evolutionary strategies *via* genetic code expansion provides a fruitful avenue to decipher complex biological mechanisms, and can be used to create enzymes with new functions that operate via catalytic mechanisms not accessible to Nature.

