Molecular rectification behavior of the pyranopterin ligand of molybdoenzymes

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Molybdenum plays an indispensable role in human metabolism, global nitrogen and sulfur cycles, greenhouse gas formation, bacterial detoxification pathways, and anaerobic respiration. These processes are critical for maintaining human health and ecological balance. To become catalytically active, the Mo ion must be incorporated into a molecular scaffold by complexation with a singular ligand known as the pyranopterin, an arrangement commonly referred to as Moco, the nearly ubiquitous molybdenum cofactor found in molybdoenzymes. Molybdoenzymes typically catalyze the two-electron oxidation or reduction of a substrates coupled to formal oxygen atom transfer. The pyranopterin dithiolene (PDT) can adopt several distinct geometries that may correspond to different oxidation and tautomeric states, which we hypothesize will contribute to its suspected role as an electron transfer conduit during the redox reactions catalyzed by molybdoenzymes. Interestingly, the fully reduced tetrahydro PDT exemplifies the Van Dyke/Ratner design rules for synthetic molecular rectifiers, indicating that nature may utilize molecular rectification in catalytic processes involving vectorial electron transfer. The rectification ratio (RR) is the ratio of the amount of current that can flow at forward and reverse biases. This RR is an indicator of the efficiency of vectorial electron transfer. The RR can be modulated when the amine terminus of the tetrahydro PDT, which serves as an anchoring group to a gold electrode in the electron transport calculations, is replaced by a thiol or a nitrile group. We rationalize these findings by analyzing the nature of the current carrying molecular orbitals that derive from our computational results. This provides a basis for understanding how electron transfer processes occur in molybdoenzymes as well as informing further design criteria for novel biologically inspired synthetic molecular rectifiers.

Keywords: molybdoenzymes, electron transfer, pyranopterin, rectifier