

KEYNOTE: Mussel Adhesion – Prominence of Energy Dissipation Mechanisms

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In intertidal sessile organisms such as mussels, holdfasts provide secure attachment to hard surfaces in high flow environments and are imperative for survival. Holdfasts, however, are much more than an interface between living and nonliving materials. In mussel adhesion, for example, interfacial mussel foot protein 5 (mfp5) adheres to siliceous substrate surfaces with an adhesion energy comparable to streptavidin-biotin binding - often considered to be a high-end hallmark of noncovalent biological interactions; yet the mfp5 adhesion energy represents less than 1% of the average adhesion energy of a single plaque thus shattering the hypothesis that adhesive chemistry by itself enables adhesion [1]. On the contrary, although mfp5 may be adept at providing a critical wet adhesive toehold, an even greater adaptation may be how loads are distributed among other plaque proteins that in turn excel at dissipating energy. The most abundant known mussel foot proteins (mfp) in the plaque, mfp1, mfp2 and mfp4, all possess high-molecular weights, disordered structures, tandemly repeated peptide sequences, and a high metal ion binding capacity & affinity. Force-extension profiles of mfp-metal complexes exhibit prominent reversible cohesion and sawtooth patterns characteristic of toughness and energy dissipation by the “sacrificial bond and hidden length” mechanism [2] in which the sacrificial bonds are protein-metal ion complexes and hidden lengths are off-track sequence loops unraveled by bond rupture. The known metal-binding side-chains in mfps are primarily imidazoles from histidine and catechols from Dopa. Of these, Dopa-Fe³⁺ complexes are 10-fold stronger than His-Cu²⁺ and/or -Zn²⁺ complexes, but are prone to oxidation hence require redox maintenance. [3] Additional dissipation may be available if mfp2 and mfp4 are organized as double-network hydrogels reversibly cross-linked by Dopa-Fe and His-Cu complexes, respectively.

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[3] Wang, S.; Waite, J.H.. Catechol Redox Maintenance in Mussel Adhesion. *Nature Rev Chem* **2025**, *9*, 159-172.