Insights: Publications

Engineering Synthetic Electron Transfer Chains from Metallopeptide Membranes

Inorganic Chemistry

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The energetic and geometric features enabling redox chemistry across the copper cupredoxin fold contain key components of electron transfer chains (ETC), which have been extended here by templating the cross-β bilayer assembly of a synthetic nonapeptide, HHQALVFFA-NH2 (K16A), with copper ions. Similar to ETC cupredoxin plastocyanin, these assemblies contain copper sites with blue-shifted (λmax 573 nm) electronic transitions and strongly oxidizing reduction potentials. Electron spin echo envelope modulation and X-ray absorption spectroscopies define square planar Cu(II) sites containing a single His ligand. Restrained molecular dynamics of the cross-β peptide bilayer architecture support metal ion coordination stabilizing the leaflet interface and indicate that the relatively high reduction potential is not simply the result of distorted coordination geometry (entasis). Cyclic voltammetry (CV) supports a charge-hopping mechanism across multiple copper centers placed 10-12 Å apart within the assembled peptide leaflet interface. This metal-templated scaffold accordingly captures the electron shuttle and cupredoxin functionality in a peptide membrane-localized electron transport chain.