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# Ethene-bridged Diiron Porphyrin Dimer as Models of Diheme Cytochrome *c*: Structure-Function Correlation and Modulation of Heme Redox Potential

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## Abstract:

Multiheme cytochromes *c* are among the most fascinating molecular machineries evolved by Nature with essential functions in electron transfer and enzymatic catalysis. The multiheme architecture ensures fast intramolecular electron transfer over long distances. We explore here the structure–function relationship of the diheme cytochrome *c* (DHC2), the simplest member of such family, using a series of synthetic diheme analogs with a variety of imidazoles and pyridines as axial ligands which thereby enable structural and functional diversity. The molecules, both in the oxidized and reduced forms, have been synthesized and their structure and properties are scrutinized at the molecular level without any interference from large protein superstructure unlike in the native enzyme. The solid-state structure of such model diheme shows similar spatial orientation and heme-to-heme separation as also observed in the native DHC2 isolated from *Geobacter sulfurreducens* and *Haemophilus influenzae*. Also, the UV-visible spectra of the synthetic dihememes are similar to the DHC2 both in the oxidized and reduced forms. The solid-state X-ray structures of four such diheme analogs have been determined which show only a small structural change between the oxidized and reduced forms and hence smaller reorganization energy is required during electronic communications in dihememes. Spectroscopic characterizations through solid-state Mössbauer, EPR, and <sup>1</sup>H NMR studies confirm the presence of low-spin diiron centers in all the complexes. The Fe(III)/Fe(II) redox couple shows a linear relationship to the p*K*<sub>a</sub> of coordinated axial ligands and it is found to be dependent on the nature of the bridging group between two heme centers. These observations are further supported by DFT calculations.

**Keywords:** Diheme cytochrome *c*; coordination complex; porphyrin dimer; structure elucidations; redox potential; spectroscopic characterizations

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