than to cytochrome bc1 from the mitochondrial respiratory chain, and possess an additional cofactor (heme c1) in the quinone reducing site, with an unknown function. This supercomplex has been enriched by anion exchange chromatography and density gradient centrifugation. Here we present a first characterization by UV/VIS and EPR spectroscopy.

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2970-Pos Board B662
Enhancing Electron Transfer Form Photosynthetic Reaction Centers to Electrodes by Exposing Quinone Binding Pocket
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Due to their potential for bio-energy generation and as bio-sensors, photosynthetic reaction centers (RCs) have been characterized quite extensively for their light induced electroactivity on electrode surfaces. Most such studies have depended on the presence of redox mediators to achieve higher current densities. We are aiming to effect direct electron transfer from both the acceptor and donor sides of the RC to electrodes and to determine the distance and orientation dependence of this process. The RC from Rhodobacter sphaeroides is a model system for photosynthesis research and is generally more robust than its counterparts from plants, in vitro. It consists of three subunits, L, M and H. The H subunit is not involved in the scaffold for electron transfer cofactors and can be removed without compromising the light dependent reduction of the primary quinone. We have developed an improved protocol to remove the H subunit, rendering a LM dimer that behaves as previously report (Debus et al. 1985 Biochemistry 24, 2488). Preliminary data suggest that unlike the complete RC, reduced semiquinone in LM dimers can donate electrons to a gold electrode without any redox mediators present. We are now working to obtain direct linkage between electrode and RC, in various orientations, through covalent gold-thiol bonds to site-directed cysteines on the LM surface and by randomly generated and selected peptides that bind RCs in a very different manner. By comparing and modeling the light induced current, we hope to arrive at a quantitative description of the electron transfer events between the RC and electrode.

2971-Pos Board B663
Midpoint Potential of the Interpolypeptide [4Fe-4S] Cluster FX in Reaction Centers from Heliobacterium Modesticaldum
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Heliobacteria are members of a class of poorly characterized phototrophic bacteria that utilize a photosynthetic reaction center (RC) containing Fe/S clusters to convert light into chemical energy. The homodimeric RC of heliobacteria contains ~22 light harvesting bacteriochlorophyll g (BChl g) pigments, the primary donor P800 (a special pair of BChl g) and the electron transfer cofactors A0 (81-OH ChlaF) and FX (an interpolypeptide [4Fe-4S] cluster). This terminal Fe/S cluster has been characterized by electron paramagnetic resonance (EPR) and Mössbauer spectroscopies as being in the [4Fe-4S]1+ oxidation state with S = 3/2 in isolated RCs. To further characterize this cluster isolated RCs were titrated with sodium dithionite and FX (an interpolypeptide [4Fe-4S] cluster). This terminal Fe/S cluster has been characterized by electron paramagnetic resonance (EPR) and Mössbauer spectroscopies as being in the [4Fe-4S]1+ oxidation state with S = 3/2 in isolated RCs. To further characterize this cluster isolated RCs were titrated with sodium dithionite and analyzed by low temperature, transient, and field-modulated time-resolved EPR. Titration of the S = 3/2 signal with low temperature EPR revealed a midpoint potential of ~504 mV (v. SHE). These results were confirmed by analysis of the one-and-the same samples by both transient and field-modulated time-resolved EPR.

Altogether these three techniques reveal a midpoint potential of ~500 mV ± 5 mV (v. SHE) for the FX cluster at pH 11. In agreement with previously published work, the lifetime of the flash-induced field-modulated EPR signal of P800+ was ~2 ms. These experiments suggest that the midpoint potential of FX in heliobacteria is ~200 mV more positive than the counterpart FX cluster in Photosystem I, and show recombination kinetics with the primary donor that are faster at 90 K (~2 ms) than at room temperature (~15 ms). Funded by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy, under Grant DE-FG02-08ER15989.

2972-Pos Board B664
Electric Field Asymmetry in the Photosynthetic Reaction Center?
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The initial charge-separation steps of photosynthesis occur in the photosynthetic reaction center, which is a membrane-integral protein-pigment complex. The photosynthetic pigments comprise four bacteriochlorophylls, two bacterio-phaeopigments, two quinones, one carotenoid and one non-heme iron. Although these pigments are arranged in a pseudo C2-symmetry (L- and M-branch), electron transfer occurs almost exclusively along the L-branch. One possible explanation for this unidirectionality is based on the asymmetry of the protein electrostatic fields, which leads to a better stabilization of the charge-separated intermediates in the active L-branch. The vibrational Stark effect provides a way to measure electrostatic fields in proteins and we exploit this effect to compare electric fields between the L- and M-branch by using the carboxyl groups of the pigments involved in the electron transfer reaction.

2973-Pos Board B665
Cu-To-Cu Electron Tunneling in Copper Monoxygenases
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The copper enzymes x-hydroxylating monoxygenase (PHM), tyramine β-monoxygenase (TJM) and dopamine β-monoxygenase (DJM) catalyze critical physiological reactions that process hormones and neurotransmitters in higher eukaryotes. In these enzymes, a finely tuned long-range electron-transfer reaction between the enzyme’s copper sites is required for catalytic turnover. We conducted extensive electronic structure analysis of PHM, providing understanding of the mechanism of electron tunneling. Our focus has been on the long-range Cu-to-Cu electron coupling, mediated by protein and by water. Our results indicate that the Tyr79 residue plays an important role in shuttling electrons between the centers. We interpret these results in light of kinetic studies as well as prior theoretical results on related copper oxygenases. Ongoing studies are probing how ligands bound to the catalytic electron acceptor site influence charge transfer kinetics.

2974-Pos Board B666
Exponential Distance Decay of Electron Transfer Rates without Tunneling: A Flickering Resonance Model for Transport
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Biological electron transfer (ET) reactions are usually described in the framework of coherent two-state electron tunneling or multi-step hopping. Yet, many ET reactions involve multiple redox cofactors with vibronic broadenings on the same scale as the energy gaps among the states and the interstate electronic interactions. In this regime, excitations to electronic resonances among states are found to support coherent (ballistic) charge transfer through the structures. Importantly, ET rates arising from flickering resonance (FR) decay exponentially with distance: the probability of matching multiple energies is multiplicative. Transport arising from FR thus mimics the exponential distance decay that is well known for electron tunneling, but the rapid decay with distance is of an entirely different origin. Likely candidates for FR transport are multi-porphyrin systems with ET groups in van der Waals contact: DNA, bacterial nanowires, multimeric proteins, strongly coupled porphin arrays, and proteins with closely packed redox-active residues. I will develop the theory of FR transport and apply this model to problems in nucleic acid charge transfer.

2975-Pos Board B667
Squeezing or Stretching Molecules as a Possible Way to Facilitate Electron Transfer
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Mechanical energy from moving mica sheets is a possible renewable energy source for the origin of life.[1] Energy is needed for prebiotic molecular synthesis, among other things. The Reverse Tricarboxylic Acid Cycle is a reduction reaction cycle proposed for the prebiotic synthesis of amino acids, sugars, and other molecules before the existence living organisms with enzymes.[2] Can moving muscovite mica sheets lower the energy barriers for the chemical reduction of molecules such as succinate and citrate by deforming these molecules? A unit cell of mica - K Al2Si3O10(OH)2 has 2 de-localized hydrogens available for reducing molecules of the Reverse Tricarboxylic Acid Cycle, such as oxaloacetate or oxaloacetate. A precedent for this idea comes from