

**LENGTH, TIME AND ENERGY SCALES IN PHOTOSYSTEMS AND
OXIDOREDUCTASES**

P. LESLIE DUTTON, CHRISTOPHER C. PAGE, DROR NOY, ARTUR
OSYCZKA and CHRISTOPHER C. MOSER

Departments of Biochemistry & Biophysics University of Pennsylvania,
Philadelphia, PA, 19104, USA

Here we reflect on the functional design, engineering, and construction of the proteins engaged in the harvesting of light energy and transforming it into membrane electrochemical gradients and the oxidants and reductants that provide energy and material substrates for the cell. We focus our attention on light harvesting (LH) proteins and on reaction center (RC) proteins of photosynthetic bacteria, cyanobacteria, algae, and higher plants. Useful perspective comes from comparing photosystem design and engineering with the analogous membrane redox proteins of respiration. And of particular interest among the respiratory type of oxidoreductases is the ubiquitous cytochrome *bc₁/b₆f* family. These cyts *bc₁/b₆f* perform the same transmembrane charge separation as the RCs and yet do it without the large amount of free energy available to the light-excited RC. The RC expends much of the absorbed energy to drive charge separation and thereby slow the reverse uphill charge returns that can lead to short-circuits. This highly energetically expensive yet successful engineering in the RC is not an option for the cyts *bc₁/b₆f* with its modest driving force provided by substrates quinone and cytochrome/plastocyanin. Moreover, as the membrane potential builds up, the free energy available to cyts *bc₁/b₆f* diminishes to zero with an increasing tendency to operate in reverse thereby presenting cyts *bc₁/b₆f* with added possibilities for short circuits. Only recently has the prevention of short circuits in cyts *bc₁/b₆f* been considered in mechanistic models (see Osyczka *et. al.* abstract this meeting).

We examine the structural kinetic and energetic relationships between the different functional domains that relay light energy, electron tunneling, redox linked proton exchange and transport and redox catalysis. We describe how the different energy forms are coupled and how energetic losses short circuits are minimized or suppressed. Although the proteins of photosynthetic and respiratory machinery are large and complex, it appears that the engineering that has been favored by blind natural selection is comparatively simple and resilient and does not require an atom-by-atom examination to appreciate its design and engineering. Instead we can begin by considering how nature has worked within the time constraints imposed by various decay processes by exploiting the distinctive length scales that are associated with each stage of the relay. We hypothesize that the membrane proteins of the relay evolved with a strong selection on the simple distance between the cofactors. We contend that distance selection is dominant in providing photosynthetic and respiratory energy

conversion with robust foundations that accommodate extensive structural and energetic tolerances. We further expect these tolerances within simple, robust frameworks have fostered the broad palette of evolutionary variety evident in the proteins of microorganisms, animals, and plants and have enabled them to generally operate well away from the boundaries of failure and pathogenesis. This relative simplicity and robustness also promises to be translatable to, and exploitable in, synthetic systems of energy conversion.