

A Photosynthetic Variant of *Synechocystis* sp. PCC 6803 Sacrifices a Stress Response Pathway to Outcompete its Peers under Optimal Growth Conditions

David J. Vinyard¹, Brandon P. Russell¹, Vasily Kurashov², David F. Iwig³, Patrick Landry⁴, Wade Johnson⁵, Art van der Est^{6*}, John H. Golbeck^{2*}, and K. V. Lakshmi^{4*}

¹*Department of Biological Sciences, Louisiana State University, Baton Rouge, LA, 70803, USA. dvinyard@lsu.edu*

²*Department of Biochemistry and Molecular Biology, The Pennsylvania State University, University Park, PA, 16802, USA.*

³*Department of Chemistry and Howard Hughes Medical Institute, The Pennsylvania State University, University Park, PA, 16802, USA.*

⁴*Department of Chemistry and Chemical Biology and The Baruch '60 Center for Biochemical Solar Energy Research, Rensselaer Polytechnic Institute, Troy, NY, 12180, USA.*

⁵*Department of Chemistry, Susquehanna University, Selinsgrove, PA, 17870, USA.*

⁶*Department of Chemistry, Brock University, 500 Glenridge Avenue, St. Catharines, ON Canada L2S 3A1.*

Phylloquinone (PhQ) plays a unique role in photosynthesis as the A_{1A} and A_{1B} intermediates in light-driven electron transfer in Photosystem I (PSI). When PhQ biosynthesis is inhibited by deletion of the *menB* gene in the cyanobacterium *Synechocystis* sp. PCC 6803, previous studies have shown that plastoquinone-9 (PQ-9) occupies the A_{1A} and A_{1B} sites instead of PhQ.

However, a recent cryo-electron microscopy structure of a strain of $\Delta menB$ from the year 2023 revealed an unusual quinone electron acceptor in the A_{1A} and A_{1B} sites with a benzoquinone head group similar to PQ-9 and a phytyl tail similar to PhQ (Gisriel, et al. 2024 *Science Advances*, in press). Here, we use mass spectrometry to identify the quinone molecule as 2,3-dimethyl-5-phytyl-1,4-benzoquinone (DMPBQ). In contrast, only PQ-9 was found in PSI from the original $\Delta menB$ strain. Whole genome sequencing reveals that this difference is the result of a mutation in *slr1737* (tocopherol cyclase) that leads to the accumulation of DMPBQ, an intermediate in the tocopherol biosynthetic pathway. Transient optical and electron paramagnetic resonance spectroscopy studies show that when DMPBQ occupies the A₁ sites, it does not exchange with exogenously supplied PhQ in contrast to PQ-9 which exchanges readily. We propose that the $\Delta menB$ strain with the *slr1737* mutation has sacrificed a stress response pathway under low stress laboratory growth conditions, resulting in a strain that incorporates DMPBQ instead of PhQ in the A_{1A} and A_{1B} sites. The better quinone binding and function of DMPBQ allow this $\Delta menB$ strain to outcompete its peers under optimal growth conditions and dominate the population.