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**Dynamics and pathway of electron tunneling in repair of damaged DNA by photolyase**[1] ZHEYUN LIU, XUNMIN GUO, CHUANG TAN, JIANG LI, YA-TING KAO, LIJUAN WANG, The Ohio State University, AZIZ SANCAR, University of North Carolina School of Medicine, DONGPING ZHONG, The Ohio State University — Through electron tunneling, photolyase, a photoenzyme, restores damaged DNA into normal bases. Here, we report our systematic characterization and analyses of three electron transfer processes in thymine dimer restoration by following the entire dynamical evolution during enzymatic repair with femtosecond resolution. Using (deoxy)uracil and thymine as dimer substrates, we unambiguously determined the electron tunneling pathways for the forward electron transfer to initiate repairing and for the final electron return to restore the active cofactor and complete the repair photocycle. Significantly, we found that the adenine moiety of the unusual bent cofactor is essential to mediating all electron-transfer dynamics through a super-exchange mechanism, leading to a delicate balance of time scales. The active-site structural integrity, unique electron tunneling pathways and the critical role of adenine assure these elementary dynamics in synergy in this complex photorepair machinery to achieve the maximum repair efficiency close to unity.

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