DYNAMICS AND MECHANISM OF (6-4) PHOTOPRODUCT REPAIR IN DAMAGED DNA BY PHOTOLYASE

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(6-4) photoproduct, the second major DNA lesion induced by UV irradiation, is repaired by (6-4) photolyase using light energy. The molecular mechanism of enzymatic repair is poorly understood. Here we report the direct observation of catalytic processes by synchronizing the enzymatic dynamics with the repair function through femtosecond spectroscopy. We observed forward electron transfer from the excited flavin cofactor to damaged DNA at 225 ps, backward electron transfer from unrepaired DNA to flavin at 50 ps, and electron returns from repaired DNA to flavin at tens of nanoseconds. Strikingly, a 425-ps electron-induced proton transfer was observed for the first time, which is crucial for repair efficiency by competing with the non-repair backward electron transfer channel.