

Correction to Probing the Reaction Mechanism of Spore Photoproduct Lyase (SPL) via Diastereoselectively Labeled Dinucleotide SP TpT Substrates

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Page 10443: After carefully calibrating the 5'-dA and SP repair products generated from the wild-type spore photoproduct lyase (SPL) reaction, it was found that 3 equiv of SAM support 5.4 turnovers upon a 3 h enzyme reaction, not the 12 turnovers reported in Figure 9A. The reported 5'-dA consumption in Figure 9B was due to an unknown contaminant enzyme but not the SPL activity to regenerate the S-adenosylmethionine. The corrected description of the reactivity of the wild-type SPL enzyme can be

found in the following paper: Yang, L.; Lin, G.; Nelson, R. S.; Jian, Y.; Telser, J.; Li, L. *Biochemistry*, **2012**, *51* (36), 7173–7188.

Page 10445: We are indebted to the cordial suggestion from Professor John-Stephen Taylor at Washington University, St. Louis, MO, that the stereoconfiguration of SP shown in Figure 10 is not correct. The corrected Figure 10 is shown.

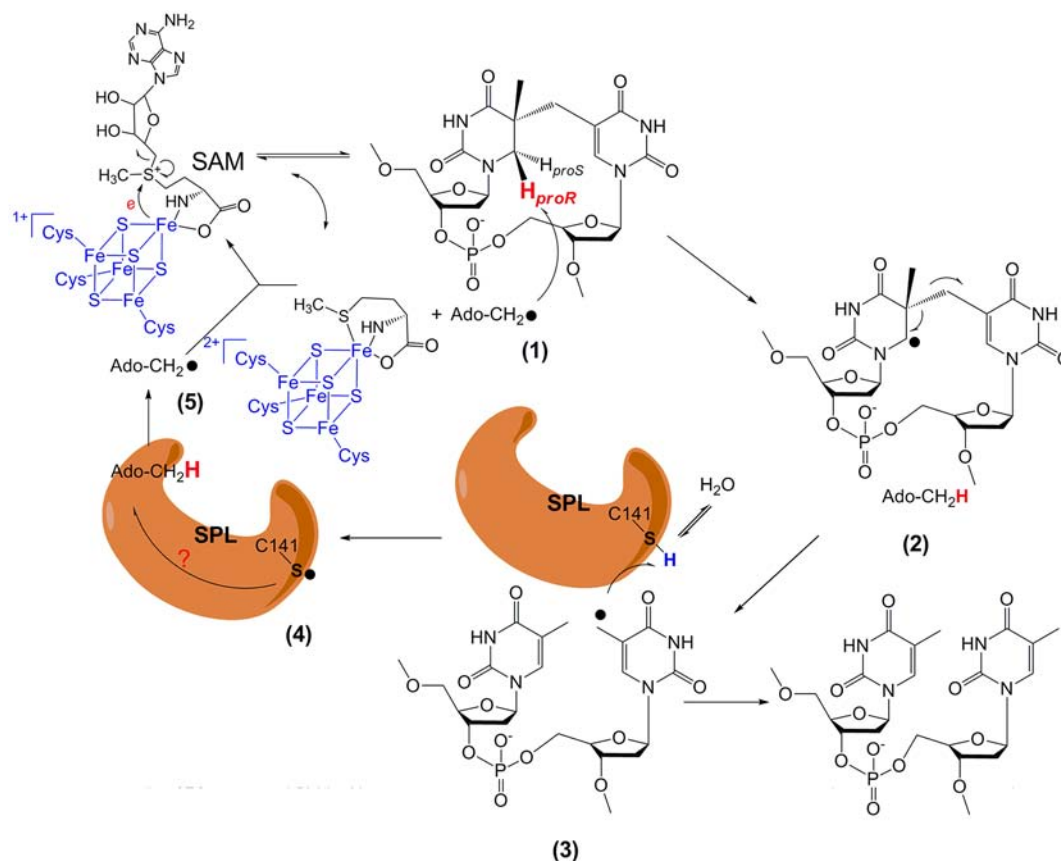


Figure 10. Newly proposed reaction mechanism for SPL-catalyzed SP dimer repair. The 5'-dA radical generated from SAM reductive cleavage reaction takes the 6-H_{proR} atom to yield a C6 radical on SP, and the SP methylene bridge subsequently undergoes a homolytic cleavage to give a thymine methyl radical. (Note: This allyl radical is likely to delocalize to the thymine aromatic ring; the current drawing as a methyl radical is a simplified model to facilitate discussion.) This radical abstracts an H atom back from an unknown protein residue, presumably C141, to generate a thiyl radical, releasing the repaired TpT. This thiyl radical either takes a H-atom back from the 5'-dA directly or reacts with other protein residues before the 5'-dA is reoxidized to the radical form again. The resulting 5'-dA radical recombines with methionine to regenerate SAM and finish one catalytic cycle.

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