MS44-1-1 Photoactivation in a Fluorescent Protein Proceeds via the Hula-Twist : Mechanism Revealed through TR-SFX
#MS44-1-1

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Abstract
The light-induced cis/trans isomerization of a chromophore double bond is a fundamental reaction in photochemistry and it has been shown to be the primary activation event for a variety of protein photoreceptors. A detailed understanding of the reaction pathway and of how it is steered by protein environment is key for the rational design of more effective photosystems.
In the 1980s, Liu & Asato coined and proposed a mechanism for chromophore photoisomerization in proteins: the hula twist. This was supposed to be volume conserving and therefore favorable inside a sterically-crowded binding pocket. By exploiting the time resolution available at XFELs and the insertion of a heavy atom to break the symmetry of the chromophore ring, we capture the ultrafast photoproduct of the trans-to-cis reaction in a fluorescent protein. This, to our knowledge, is the first direct experimental structural evidence that unequivocally supports hula-twist chromophore photoisomerization in a protein, more than 30 years after it was first hypothesized. By analyzing data from time points that span from 300 fs to 1 µs, we also resolve how photoisomerization leads to the sequential movement and relaxation of secondary structure elements. This data demonstrates the power of time-resolved crystallography for elucidating the ultrafast dynamical response in photoactivated systems.

References
Work so far unpublished.
Key relevant references :
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Graphical abstract