FLAVIN PHOTOCHEMISTRY IN ELECTRON TRANSFER: PHOTOSENSITIZATION BEHAVIOR OF FLAVINS IN SPLITTING OF PYRIMIDINE CYCLOBUTANE DIMERS

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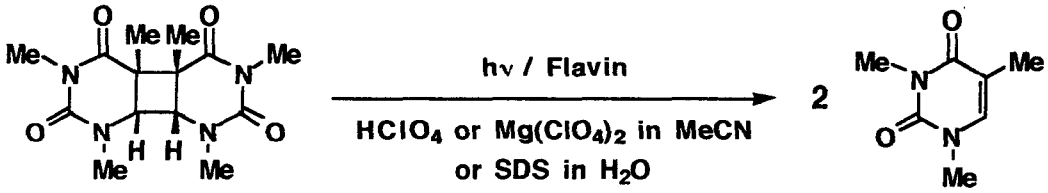
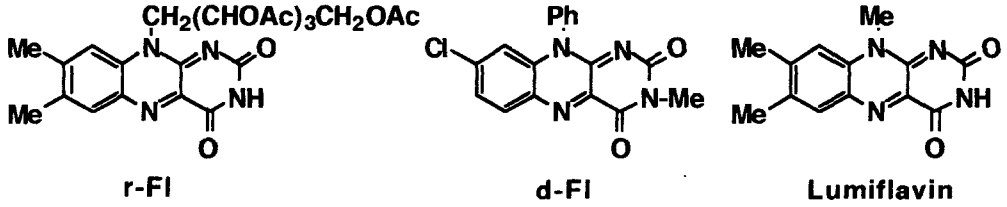
Flavins (FL's) are biologically important molecules that have versatile catalytic capabilities via either electron transfer (ET) or net hydride transfer. ET catalysis is particularly important in photochemistry of FL's, because an additional driving force by photoexcitation is available to allow ET with a variety of reactants. A unique photobiological phenomenon in FL-photocatalyzed ET reactions is the enzyme-dependent photorepair of UV-damaged DNA, an essential chemical process of which is the monomerization of pyrimidine cyclobutane dimers through photochemical ET with the FL chromophore of DNA photolyase. A chemical mimic of DNA photoreair is certainly an intriguing subject in ET photochemistry of FL's.

Early studies on model reactions of photorepair using nonbiological photosensitizers demonstrated that dimer models can be monomerized through photochemical electron transfer in various efficiencies depending upon photosensitizers used [1]. Attempts have been made to construct more realistic model reaction systems using FL's as photosensitizer. However, either the oxidized or reduced form of various FL's is ineffective in the photosensitized monomerization of dimer models in aqeous and polar organic solutions under neutral and weakly acidic or basic conditions [2]. The present lecture deals with our foundings that the oxidized form of some FL's can efficiently photocatalyze splitting of the cis,syn-dimethylthymine cyclobutane dimer in the presence of $HClO_4$ [3] or $Mg(ClO_4)_2$ [4] in MeCN or in the presence of SDS in aqueous solution under neutral conditions [5]. Mechanistic details will be discussed.





References

[1] A. A. Lamola, *Mol. Photochem.*, **1972**, *4*, 108; C. Pac and O. Ishitani, *Photochem. Photobiol.*, **1988**, *48*, 767.
[2] K. Mizuno and C. Pac in *CRC Handbook of Organic Photochem. and Photobiol.*, W. M. Horspool and P. -S. Song, Eds., CRC Press, Boca Raton, 358 (1995).
[3] C. Pac *et al.*, *Chem. Lett.*, **1992**, 319; *J. Am. Chem. Soc.*, **1992**, *114*, 10576.
[4] C. Pac *et al.*, *Photochem. Photobiol.*, **1993**, *58*, 631.
[5] C. Pac *et al.*, *Chem. Lett.*, **1995**, 563.