CHEMISTRY LETTERS, pp. 2189-2192, 1989.

# Photochromic Systems Utilizing the Reversible Photoredox Reactions between a Flavin Analogue and Benzenethiol Derivatives

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Irradiation of a yellowish flavin analogue, riboflavin-2',3',4',5'-tetra-acetate (Fl) in a polymer matrix film as well as in acetonitrile containing benzenethiol derivatives and a base with visible light ($\lambda > 360$ nm) results in the decrease in absorbance due to Fl ($\lambda_{max}$ 442 nm). The color reverts to yellow by irradiation of the samples with ultraviolet light ($\lambda < 360$ nm).

Flavin coenzymes are known to act as catalysts for dehydrogenation reactions of various substrates by oxidants.[1)] Such flavin-catalyzed reactions consist of two half-reactions, i.e., reduction of flavins by substrates and oxidation of the reduced flavins by oxidants.[1,2)] Each half-reaction is reversible, and the transformation between the oxidized and reduced forms of flavins occurs in both directions.[1,2)] However, relatively little is known about oxidation of the reduced form of flavin analogues by oxidants except for dioxygen,[3)] although reduction of flavin analogues by various substrates has been studied extensively.[1,2)] Thus, there has so far been no report on the reversible transformation between the oxidized and reduced forms of flavin analogues in the same redox reactions. We report herein the reversible transformation between a flavin analogue, riboflavin-2',3',4',5'-tetra-acetate (Fl), and the reduced form ($FlH_2$) in the photoredox reactions between benzenethiol derivatives and the corresponding disulfides in a poly(methyl methacrylate) film as well as in acetonitrile under irradiation of visible or ultraviolet light. Such reversible transformation of Fl (yellow) and $FlH_2$

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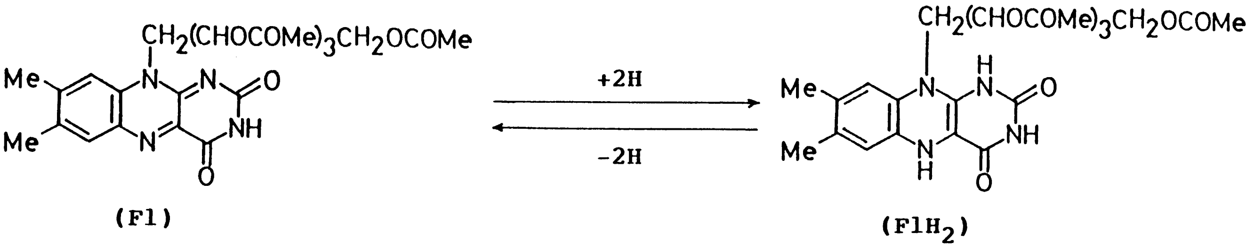

Scheme 1.

in Scheme 1 provides a unique example of intermolecular photochromic systems.[4,5]

When a deaerated acetonitrile solution containing Fl ($1.5 \times 10^{-4}$ mol dm$^{-3}$), *m*-toluenethiol ($7.5 \times 10^{-4}$ mol dm$^{-3}$) and tetrabutylammonium hydroxide ($5.0 \times 10^{-4}$ mol dm$^{-3}$)[6] is irradiated with the visible light ($\lambda > 360$ nm) from a Xenon lamp through a filter, which excites only the absorption band due to Fl ($\lambda_{max} = 442$ nm), the absorbance at 442 nm decreases with an increase in the irradiation time (Fig. 1a). Irradiation of the sample with ultraviolet light ($\lambda < 360$ nm) results in the reverse change, *i.e.*, an increase in the absorbance at 442 nm with an increase in the irradiation time (Fig. 1a). This cycle can be repeated more than 10 times.[7] Such a photochromic behavior may be ascribed to the photoreduction of Fl by *m*-toluenethiol, combined with the photooxidation of $FlH_2$ by the corresponding

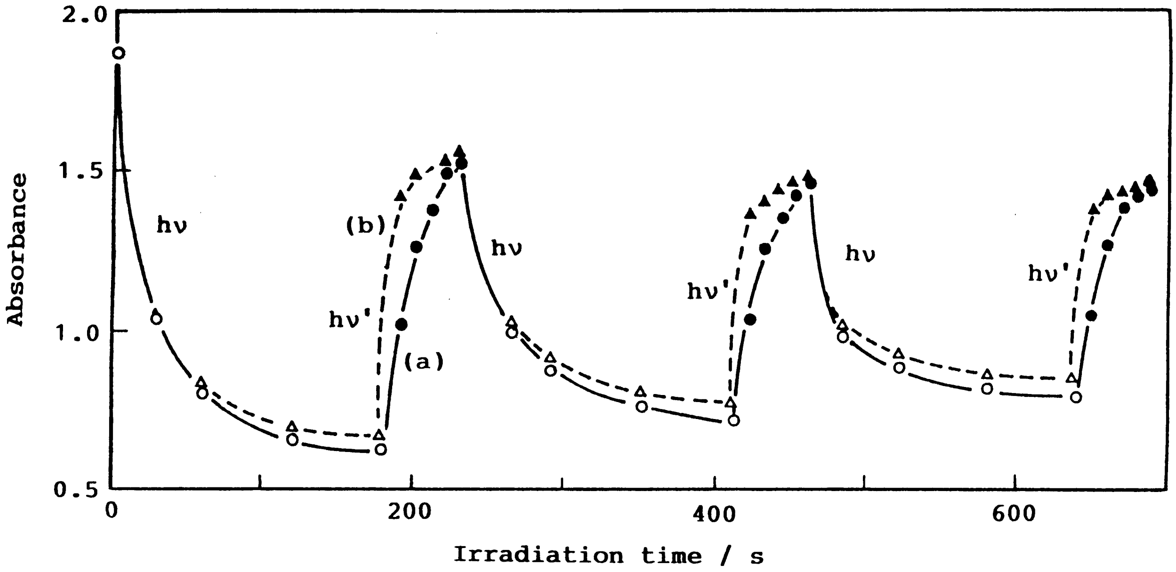

Fig. 1. Repeated cycles for the decrease and increase in absorbance due to Fl ($\lambda_{max}$ 442 nm) under irradiation of an acetonitrile solution containing Fl ($1.5 \times 10^{-4}$ mol dm$^{-3}$) by m-toluenethiol ($7.5 \times 10^{-4}$ mol dm$^{-3}$), and $Bu_4NOH$ ($5.0 \times 10^{-4}$ mol dm$^{-3}$) (a) in the absence (——) and (b) the presence (---) of diphenyl disulfide ($2.5 \times 10^{-4}$ mol dm$^{-3}$) with visible light (hν, $\lambda > 360$ nm) and ultraviolet light (hν', $\lambda < 360$ nm) at 298 K, respectively.

disulfide under irradiation of visible light ($\lambda > 360$ nm) and ultraviolet light ($\lambda < 360$ nm), respectively (Eq. 1), since the reduction of Fl by thiols is known to yield $FlH_2$ and the disulfide.[8)] The absorbance at 442 nm, which was decreased by the visible light irradiation, was readily recovered by introducing dioxygen to the sample, indicating that $FlH_2$ produced by the photoreduction of Fl by m-toluenethiol is oxidized by dioxygen to regenerate Fl.[3,9)] On the other hand, irradiation of aromatic disulfides with ultraviolet light is known to result in the cleavage of the sulfur-sulfur bonds to yield thiyl radicals (Eq. 2),[10)] which may be readily reduced by $FlH_2$ to regenerate thiols (Eq. 3).[11)] Thus, the reverse reaction under irradiation with ultraviolet light (Eq. 1) may occur via the photo-cleavage of the sulfur-sulfur bond of di-m-tolyl disulfide, followed by the dark reaction of thiyl radicals with $FlH_2$ to regenerate Fl. The reversible photochemical reaction (Eq. 1) can also be monitored by the fluorescence of Fl, since $FlH_2$ is non-fluorescent. The rate of the forward photochemical reaction (Eq. 1) increased with an increase in the thiol concentration. The rate of the reverse reaction to regenerate Fl can also be controlled by adding a disulfide to the starting sample as shown in Fig. 1b, where the rate in the presence of diphenyl

$$\mathrm{Fl} + 2(\mathrm{m\text{-}MeC_6H_4SH}) \underset{h\nu'\ (\lambda\ <\ 360\ \mathrm{nm})}{\overset{h\nu\ (\lambda\ >\ 360\ \mathrm{nm})}{\rightleftharpoons}} \mathrm{FlH_2} + (\mathrm{m\text{-}MeC_6H_4S})_2 \qquad (1)$$

$$\mathrm{ArSSAr} \xrightarrow{h\nu'} 2\mathrm{ArS}\cdot \qquad (2)$$

$$\mathrm{FlH_2} + 2\mathrm{ArS}\cdot \longrightarrow \mathrm{Fl} + 2\mathrm{ArSH} \qquad (3)$$

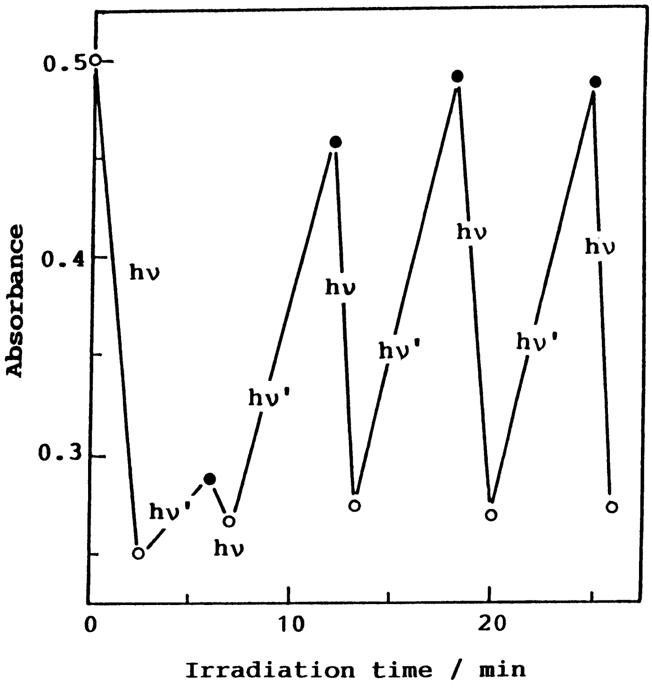

Fig. 2. Repeated cycles for the decrease ( o ) and increase ( ● ) in the absorbance at 442 nm due to Fl in a PMMA film containing Fl, p-toluenethiol, $Bu_4NOH$ under irradiation of visible light (hν) and ultraviolet light (hν') at 298 K, respectively.

disulfide ($2.5 \times 10^{-4}$ mol dm$^{-3}$) becomes faster than that in its absence (Fig. 1a).

In order to apply the photochromic behavior in an acetonitrile solution (Fig. 1) to that in a solid matrix film, which could be used as an optical memory device, Fl and p-toluenethiol were embedded in a poly(methyl methacrylate) (PMMA) film by casting a THF solution containing Fl ($1.5 \times 10^{-3}$ mol dm$^{-3}$), p-toluenethiol ($1.5 \times 10^{-2}$ mol dm$^{-3}$), $Bu_4NOH$ ($1.5 \times 10^{-2}$ mol dm$^{-3}$), and PMMA (10%) on the quartz cuvette, followed by drying under a stream of argon. The Fl-thiol system in a PMMA film also exhibits essentially the same photochromic behavior (Fig. 2) as observed in an acetonitrile solution (Fig. 1).12)

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(Received September 26, 1989)