

Supporting Information for

Characterization in Aqueous Medium of an FMN Semiquinone Radical Stabilized by the
Enzyme-Like Microenvironment of a Modified Polyethyleneimine

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All UV-vis. measurements were performed with a Varian carry 300-bio ultraviolet-vis spectrophotometer in cuvettes equipped with septa for experiments under inert atmosphere. Fluorescence spectra were obtained with a Tecan infinite M200 pro-plate-reader. X-band EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer equipped with a Bruker ER 4116DM X band resonator, an Oxford Instrument continuous flow ESR 900 cryostat, and an Oxford ITC 503 temperature control system. Experimental conditions used were: Microwave frequency 9.63 GHz, microwave power 0.25 mW, modulation amplitude 8 Gauss, modulation frequency 100 KHz, gain 56 db, temperature 90 K.

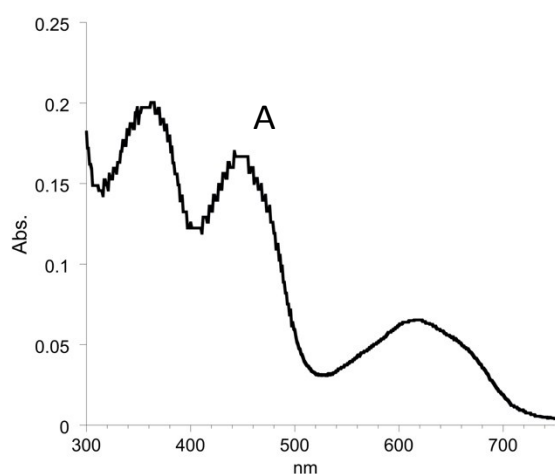


Figure 1. (A) Differential UV-Vis spectrum obtained by subtracting 32% of the original FMN spectrum (Fig. 1b, red line) to the spectrum of the intermediate measured in Fig.1b (thick black line) and (B) UV-Vis spectrum of an oxidized flavoprotein (solid line) and of the corresponding flavin semiquinone (dashed line) extracted from *Biochemistry* **1966**, 5, 10, 3181-3189.

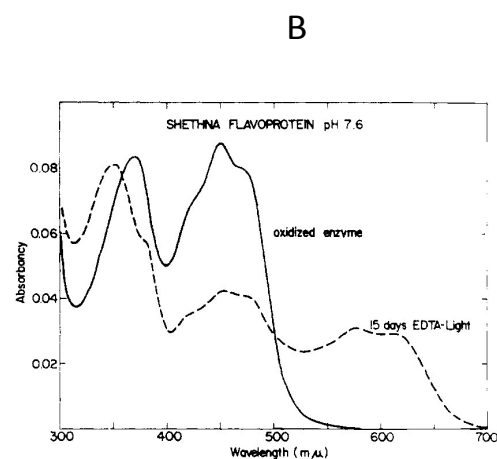


FIGURE 2: Effect of irradiation of *Azotobacter* flavoprotein for 15 days in the presence of 0.05 M phosphate and 0.05 M EDTA, pH 7.6. Approximately 90% conversion to the semiquinone was found on illumination for 5 days.