

Supporting Information

Photolytic Control and Infrared Probing of Amide I Mode in the Dipeptide Backbone-Caged with the 4,5-Dimethoxy-2-nitrobenzyl Group

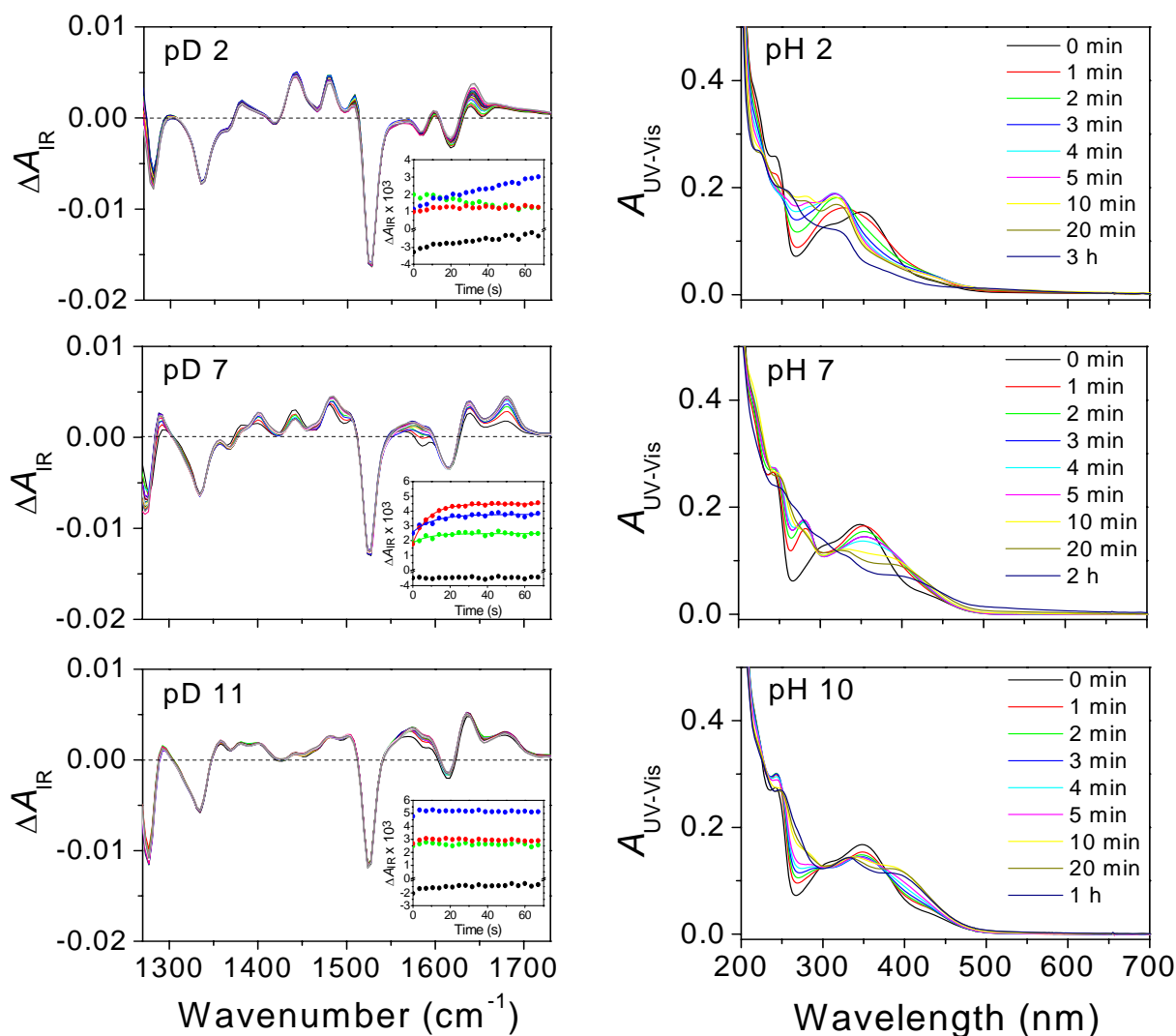


Figure S1. (Left) pD-dependence of the time-resolved IR spectra of **1** irradiated with a pulsed UV laser. The spectra were obtained under the same experimental conditions as those in Figure 4, with the exception of varying pD. Dashed lines correspond to $\Delta A = 0$. The insets show the kinetic traces of IR absorption change (ΔA) taken at four peak frequencies, 1505 (green), 1617 (black), 1635 (blue), and 1681 (red) cm^{-1} , from the time-resolved IR spectra. Experimental data (closed circles) at pD 7 are fitted to a single exponential function ($\Delta A = \Delta A_0 + a_1 \exp(-t/\tau_1)$, solid curves) with τ_1 , a_1 , and ΔA_0 values of Figure 4b. At pD 11, all four peaks show instantaneous changes, whereas slow rise components appear at pD 7 and 2. At pD 2, the extent of a slow component is more substantial and the band at 1635 cm^{-1} is even blue-shifted to 1643 cm^{-1} . (Right) pH-dependence of the steady-state UV-vis absorption spectra of **1** irradiated with a cw UV lamp. The spectra were recorded after **1** (ca. 30 μM , 1 cm path length) in H_2O (15 mM sodium phosphate, pH 2, 7, or 10) was exposed to varying irradiation time with a cw UV lamp (365 nm, 30 mW/cm^2 , Spectroline). The photolysis progress as irradiation time was monitored on an UV-vis spectrophotometer. No well-defined isosbestic point is shown at all the pH and the spectral changes are strongly pH dependent.