Supporting Information

Photo-Induced Electron Transfer in Folic Acid Investigated by Ultrafast Infrared Spectroscopy

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1. Evidence of C=N Assignment (1667cm^{-1}) for Folic Acid at pH 6.2

Figure S1 (a) and (b) shows FTIR spectra of adenosine (AMP) in the phosphate buffer with pH 2.9 (a) and 6.2 (b). The peaks at 1625 and 1668 cm^{-1} in Fig. S1 (a) and (b) are assigned to unprotonated and protonated adenine group[1,2]. pKa of AMP is around 3.9 demonstrated by absorbance plot of 1625 and 1668 cm^{-1} as shown in Figure S2. This protonation on adenine ring (N1) increases the double-bond nature of the ring C=N, which induces strong sharp band at 1668 cm^{-1} [2]. For folic acid at pH 6.2, protonation on pterin ring (N5) is expected to have similar results as AMP. For comparison, FTIR spectrum of folic acid (c) is plotted in Figure S1. It is interesting to notice that sharp band appears at 1667 cm^{-1}, which is comparable to protonated peak 1668 cm^{-1}. Therefore, 1667 cm^{-1} in Fig. S1 (c) is attributed to C=N in pterin ring.

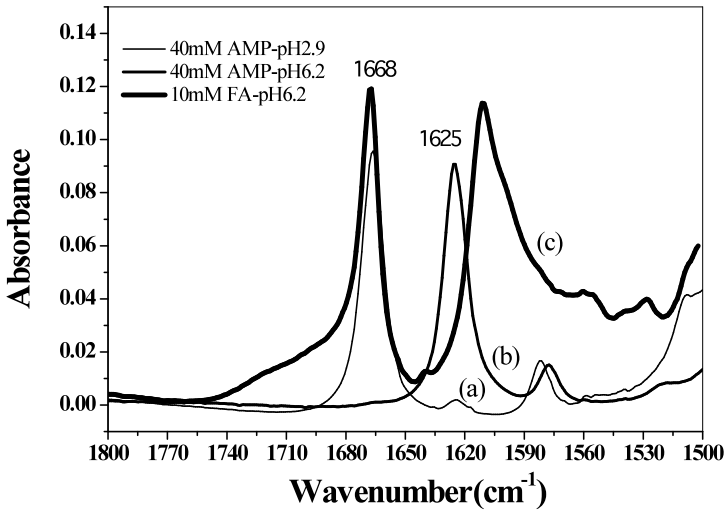

Figure S1 FTIR spectra of AMP at pH 2.9 (a) and 6.2 (b), and Folic Acid at pH6.2 (c)

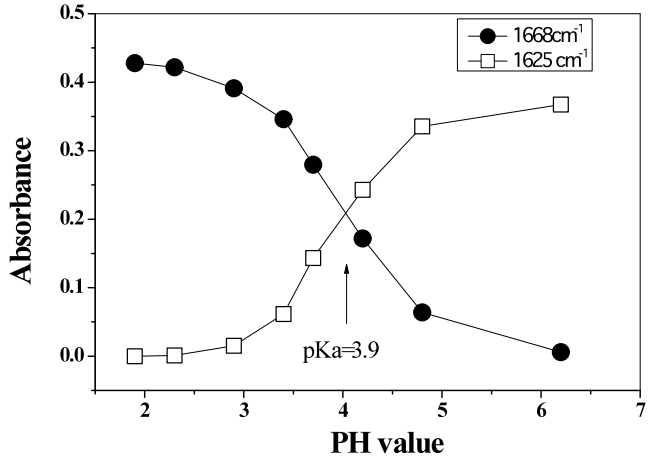

Figure S2 Absorbance of 1668 cm^{-1} (filled dot) and 1625cm^{-1} (open square) from AMP as function of pH value in phosphate buffer solution

2. pH Dependent Measurement of Folic Acid by UV-vis Spectroscopy

Figure S3 shows pH dependent UV-vis spectra of FA in buffer with different pH values (11.7, 9.0, 7.5 and 7.0) as indicated by various thick lines. As shown in the description of results and discussions, the broad band around 365 nm in FA (pH11.7) is assigned to the π–π* transition localized on the pterin ring in FA. The other peaks at 255 and 280 nm are also from π–π* transitions of the pterin ring[3,4]. With decrease of pH value, intensities of two peaks from 365 and 255nm become weak, and peak at 365nm is shift to low wavelength at pH 9.0. When the pH value is dropping to 7.5, the peak from 255nm completely disappears due to protonation (pKa=8.3), and the peak from 365nm continues to shift to 360nm. When the pH value is 7.0, we still can see the peak from 360nm keeps shifting to low wavelength. The arrow in Figure S3 shows wavelength shift of main peak at 365nm as decrease of pH value.

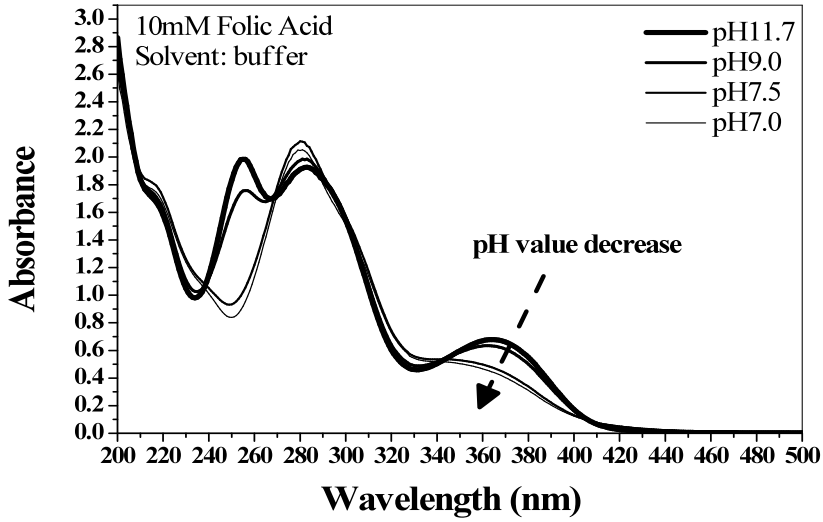

Figure S3 pH dependent UV-vis spectra of FA in buffer with different pH values (11.7, 9.0, 7.5 and 7.0) as indicated by various thick lines.

3. Solvent Dependent Measurement of Folic Acid

Figure S4 shows the TRIR transients at 1600 cm^{-1} for the DMSO:water ratios (v:v) as indicated, over the range from 8:2 to 0:10 (pH>9.0). The observed lifetimes of the bleach recovery depend strongly on the amount of DMSO in water, ranging from 131 ps in mostly DMSO to 5 ps in pure water. The rate of ET slows with added DMSO, despite having a constant FA concentration. The rate of inter-ET should not change with constant FA concentration, supporting intra-ET as the primary mechanism.

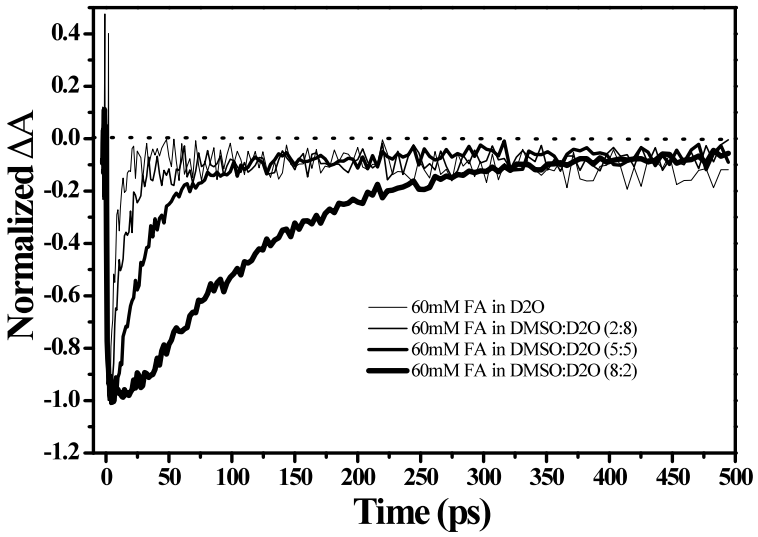

Figure S4 Normalized bleaching decays comparison of FA in phosphate buffer with different ratios of DMSO and water

References

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(3) Chen, X.; Xu, X.; Cao, Z. *J. Phys. Chem. A* **2007**, *111*, 9255.
(4) Seng, G.; Bolard, J. *Biochimie* **1983**, *65*, 169.