Supplementary information for

"The methyl- and aza-substituent effects on nonradiative decay mechanisms of uracil in water: A transient absorption study in the UV region"

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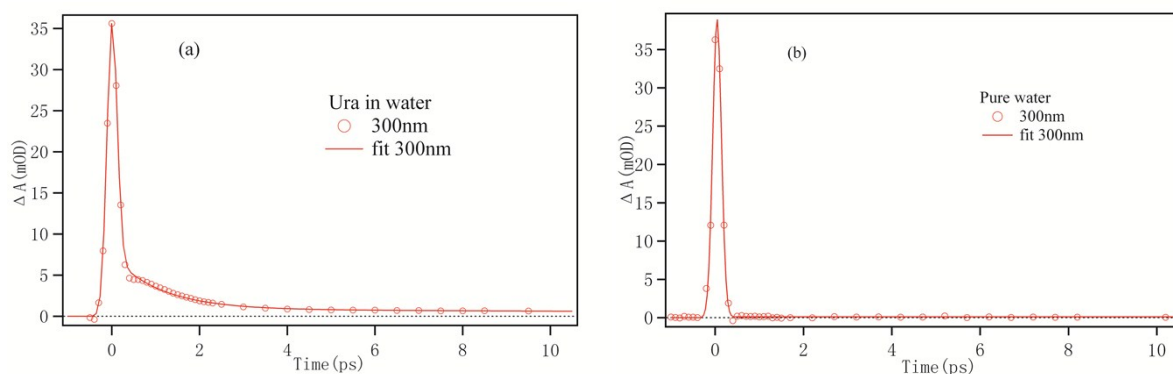* Author to whom correspondence should be addressed. *E-mail: xjliu@wipm.ac.cn*

Fig S1. The time dependent traces of Ura in water (a) and pure water (b) at 300 nm and their fitting curves

Fig S1.shows the transient absorption (TA) kinetics of Ura in water and pure water at probe wavelength 300nm. There is a prominent spike at time zero either for Ura in aqueous solution or for pure water. The spike exists at any other wavelength in our whole probe region. We assign this prominent spike at time zero to the two-photon absorption (TPA) artifact. The two-photon absorption signal is a typical artifact in transient absorption measurement.[1] It is induced by coherent absorption of the probe pulse with the pump pulse on the condition of the two laser pulses spatially overlap in the sample. Ultrashort laser pulse which results in extraordinary power density easily encourages the TPA artifact.[1]

For the TA measurement in aqueous solution, the TPA spike is much more prominent at UV probe than that in the visible probe. Take our experiment for example, the sum of the photon energy of 266 nm (4.66 ev) pump pulse and the UV probe pulse at wavelength less than 330 nm (3.76 ev) is more than 8.4 ev. This energy is larger than ionization potential of liquid water (~6.4 ev).[2] Thus, the water molecules can be easily ionized when the probe pulse and the pump pulse spatially overlap in the solution. Then, ionization product such as hydration electrons will appear.[2] Fortunately, the absorption spectrum of hydration electron covers mainly at the wavelength region above 400 nm. Accordingly, it should be no absorption of the hydration electron in our UV detection range. As Fig. S1(b) shows, there is almost no other TA signal for pure water except the TPA spike at time zero. Thus, for TA signals of sample solution, as Fig. S1(a) shows the signal of Ura solution at 300 nm, we believe, except the TPA spike at time zero, the TA signals represent the sample absorption at other delay times.

The TPA spike can be well fitted with a Gaussian function. The best fitting result for pure water at 300 nm is shown in Fig. S1(b) by the solid line. The FWHM of Gaussian function is obtained between 220 and 280 fs in our UV probe region. Therefore, the time resolution of our setup is determined to be ~250 fs.
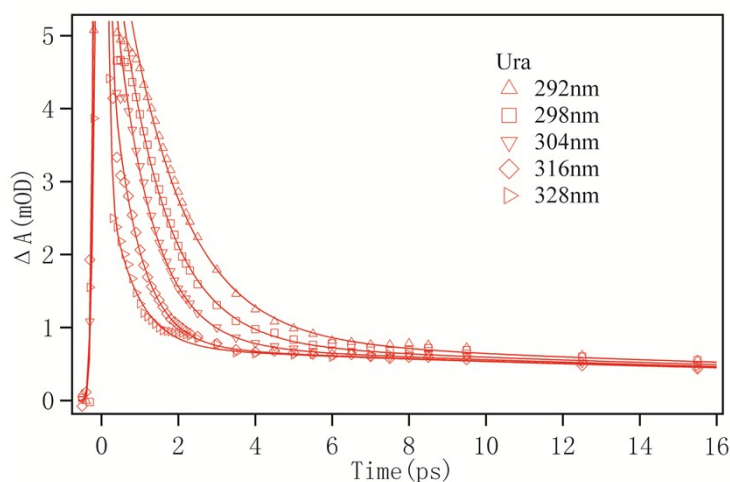

Fig S2. The time dependent traces of Ura in water at different probe wavelength and their fitting curves
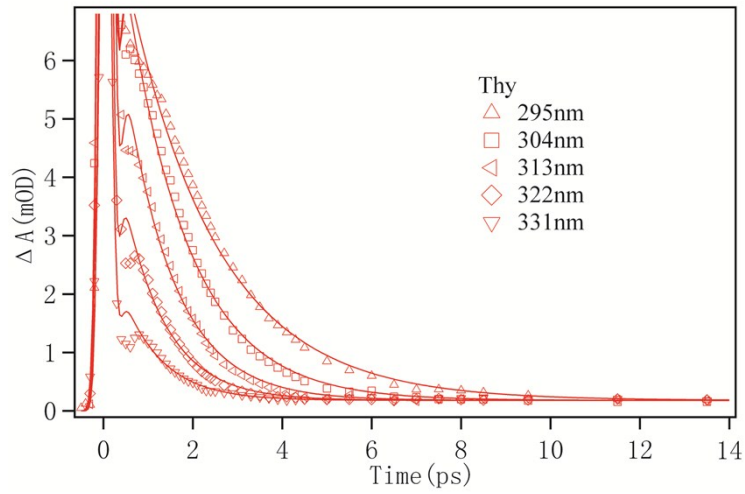
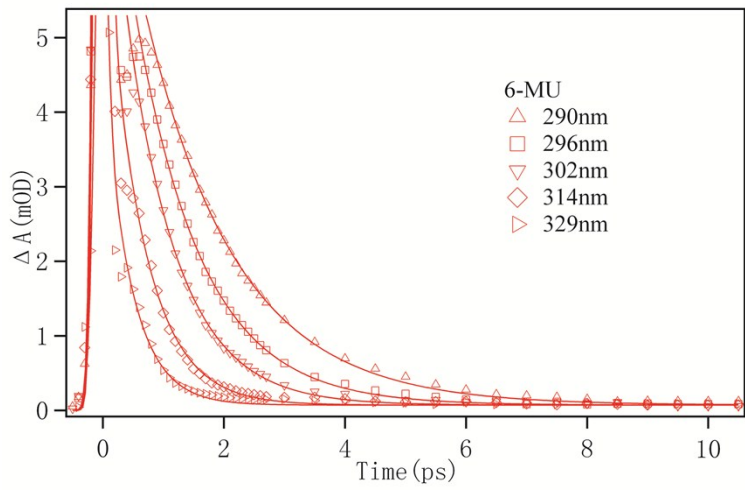Fig S3. The time dependent traces of Thy in water at different probe wavelength and their fitting curves

Fig S4. The time dependent traces of 6-MU in water at different probe wavelength and their fitting curves
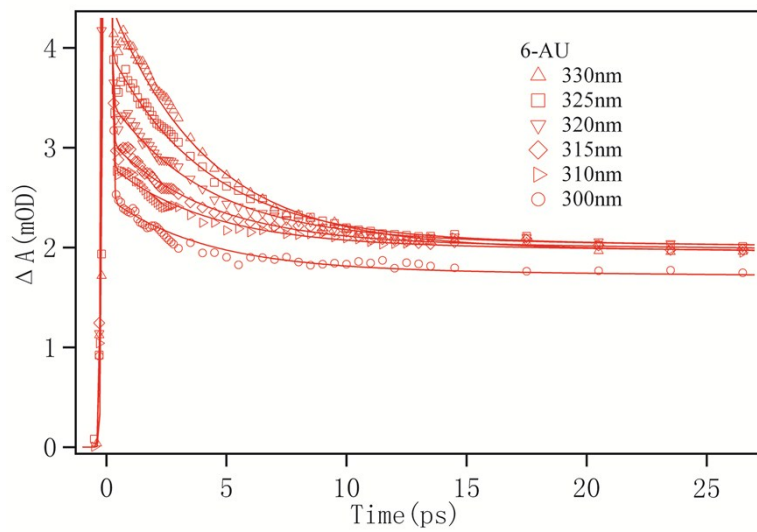
Fig S5. The time dependent traces of 6-AU in water at different probe wavelength and their fitting curves

The fitting method which we used for 6-AU is a simplified global fitting procedure. The decay scheme of 6-AU on the S_2 state is determined to be $^1\pi\pi^*(S_2)\rightarrow^1 n\pi^*(S_1)\rightarrow^3\pi\pi^*(T_1)\rightarrow S_0$. Due to the limitation of the time resolution of our setup and the high TPA artifact near time zero, the ultrafast IC process $^1\pi\pi^*\rightarrow^1 n\pi^*$ (<0.5 ps) is not analysed here. Thus, we globally fitted the obtained full spectra at each wavelength with two lifetime constants (The time constant of $^1 n\pi^*\rightarrow^3\pi\pi^*(T_1)$ decay is globally fitted as ~4.0 ps, while the decay of the last step, i.e., $^3\pi\pi^*(T_1)\rightarrow S_0$, cannot be observed in our observing window since the lifetime of the T_1 state is >1000 ps).

References

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2   A. Reuther, A. Laubereau and D. N. Nikogosyan, *J. Phys. Chem.*, 1996, **100**, 16794-16800.