Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Ultrafast Förster Resonance Energy Transfer between Tyrosine and Tryptophan: Potential Contributions to Protein-Water Dynamics Measurements

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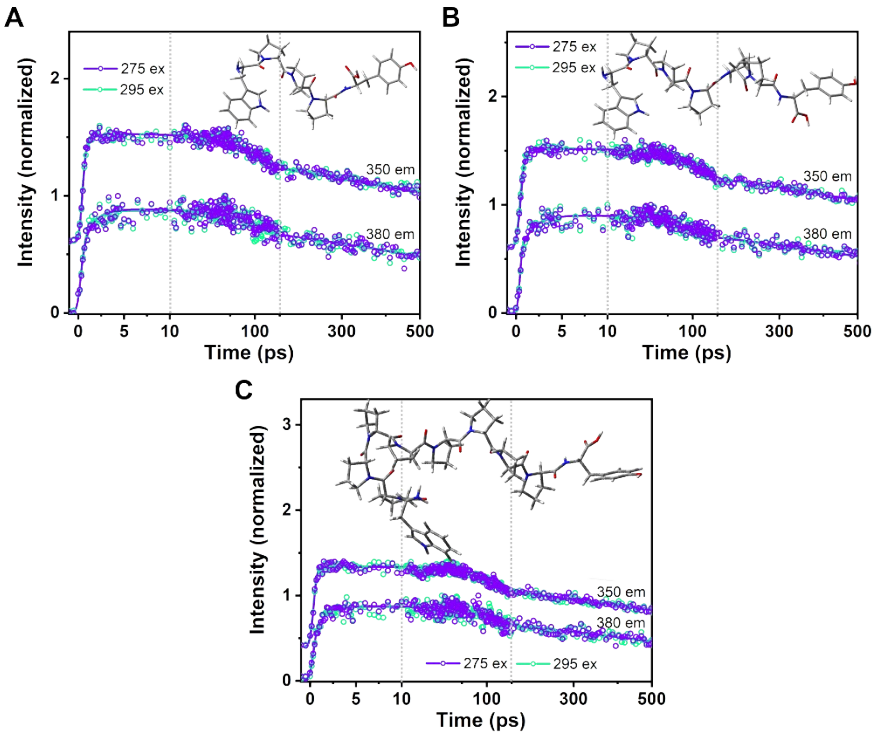


Figure S1. Normalized up-conversion fluorescence decay of WP3Y (A), WP5Y (B) and WP8Y (C) gated from typical emission wavelengths with excitation wavelength 275 nm and 295 nm.

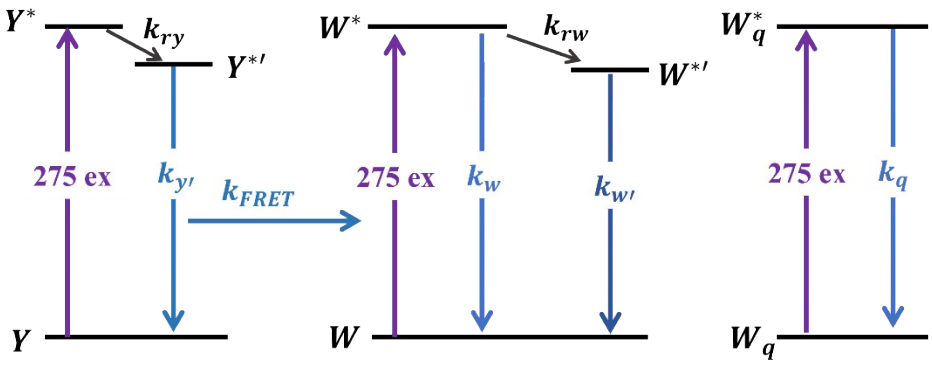


Figure S2. Simplified energy level structure diagrams of FRET, QSSQ and other components.

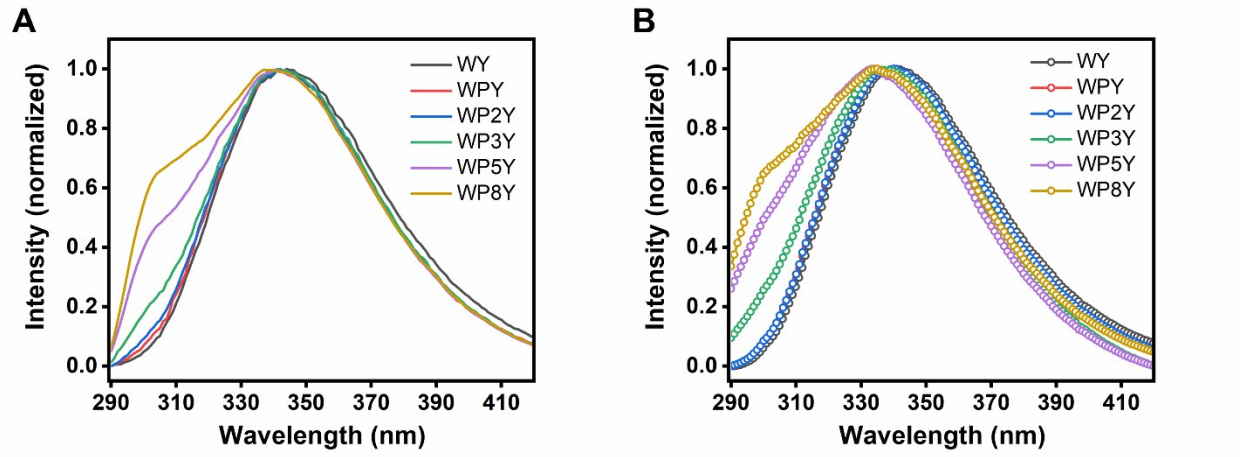
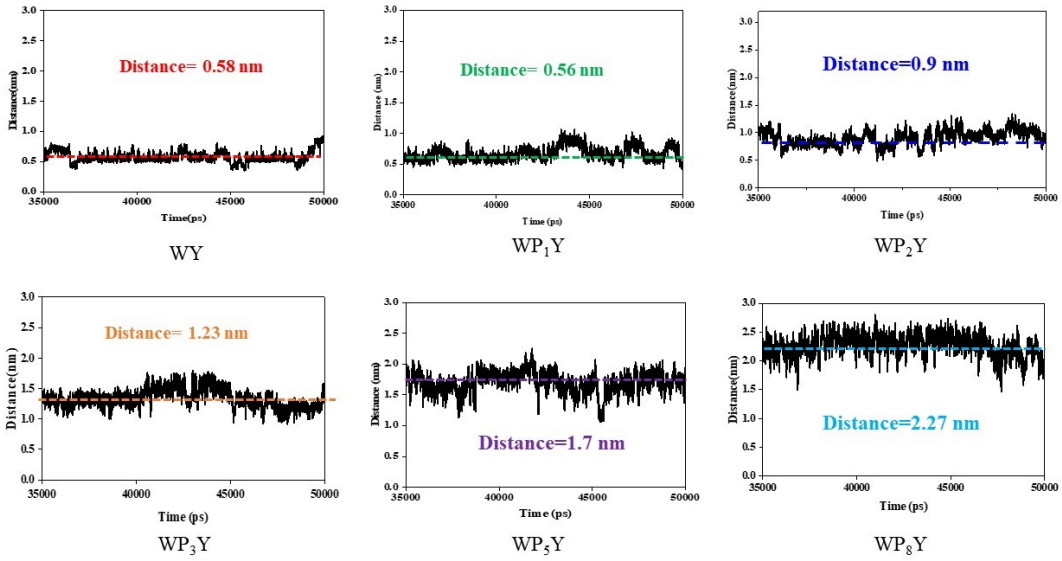


Figure S3. The fluorescence spectra (A) of all peptides excited at 275 nm and the spectra (B) calculated by the working model.



WY WP_1Y WP_2Y

WP_3Y WP_5Y WP_8Y

Figure S4. The counted centroid distance between fragments F1 and F3 for WPnY. Sampling was performed after the systems reach equilibrium. And trajectories of the last 15-ns were counted.

Table S1. Details of all parameters used in the working model.

	k_y (ns^{-1})	k_{FRET} (ns^{-1})	k_w (ns^{-1})	k_{rw} (ns^{-1})	$k_{w'}$ (ns^{-1})	k_Q (ns^{-1})	a	b
WY	0.3	50	0.25	500	0.5	6.2	0.6	0.4
WPY	0.3	200	0.25	500	0.5	10	0.5	0.5
WP2Y	0.3	20	0.25	500	0.5	5.8	0.5	0.5
WP3Y	0.3	2	0.25	500	0.5	8.0	0.7	0.3
WP5Y	0.3	0.5	0.25	500	0.5	8.0	0.5	0.5
WP8Y	0.3	0.02	0.25	500	0.5	8.0	0.5	0.5

Table S2. The fragment transition dipole moments of WP_nY(n=0,1,2,3) based on the optimized structure.

	vector	x	y	z
WY	μ_A (a.u.)	-0.4605	0.6145	-0.0916
	R_{DA} (a.u.)	9.5547	0.3255	0.2591
	μ_D (a.u.)	-0.0196	-0.0124	0.0007
WPY	μ_A (a.u.)	0.5172	0.0783	0.1591
	R_{DA} (a.u.)	9.1006	2.3978	-0.4921
	μ_D (a.u.)	0.0224	0.0007	0.0041
WP2Y	μ_A (a.u.)	0.5963	-0.2139	-0.6838
	R_{DA} (a.u.)	12.2504	-0.4265	0.0796
	μ_D (a.u.)	0.0075	0.0014	-0.0008
WP3Y	μ_A (a.u.)	-0.5711	0.2409	0.31
	R_{DA} (a.u.)	-15.9246	-2.722	0.048
	μ_D (a.u.)	-0.0095	-0.0012	-0.0034

Calculation details of R_0

The calculation formula is as follows,

$$\begin{cases} R_0^6 = \dfrac{9000(ln10)\kappa^2 Q_D}{128\pi^5 N n^4} J(\lambda) \\ J(\lambda) = \dfrac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda} \end{cases}$$

Q_D is the quantum yield of the PY. We calculated $Q_D = 0.14$ from the absorption and emission data (concentration gradient) of PY. N is Avogadro's number. n is the refractive index of the

medium and typically assumed to be 1.4 for biomolecules in aqueous solution. κ^2 is a factor describing the relative orientation in space of the transition dipoles of the donor and acceptor. It is usually assumed to be equal to 2/3. $F_D(\lambda)$ is the fluorescence emission of PY. $\varepsilon_A(\lambda)$ is the extinction coefficient of WP. According to this formula, we calculate $J(\lambda) = 6.86874 \times 10^{-16}\, cm^6$; $R_0 = 15.646$ Å.

In addition, we put the PY emission and WP absorption spectra on one graph below.

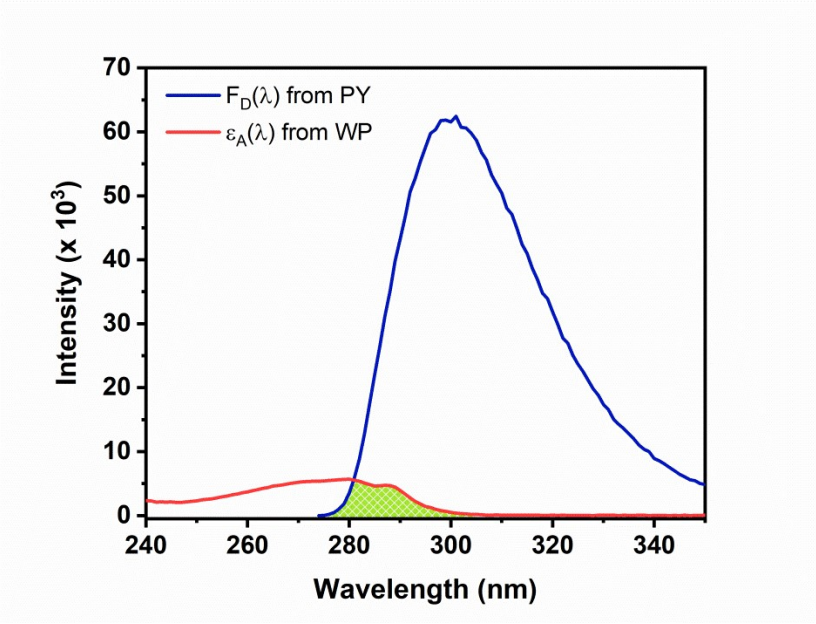


Figure S5. PY emission and WP absorption spectra overlap. Overlapping areas are marked in green.