SI Text

Fluorescence from the Aggregates. The steady-state fluorescence spectrum obtained with 313-nm excitation showed a very weak new band at ≈350 nm (Fig. 4 and SI Fig. 10), which is red-shifted by ≈30 nm from the F_1 band due to monomer fluorescence. The peak wavelength (350 nm) of the new band is almost the same as that of the fluorescence from the dimer excited state before the proton transfer (the dimer fluorescence), which was reported in our previous time-resolved measurements (1). However, this 350-nm band in the steady-state spectrum is not assignable to the dimer fluorescence because of the following consideration of its intensity: The quantum yield of the dimer fluorescence was estimated to be more than a thousand times smaller than that of the tautomer fluorescence (F_2 band) (1), whereas the intensity of the 350-nm band relative to the F_2 band amounts to ≈2-3% in Fig. 4. The 350-nm band is highly likely attributed to the aggregate species, which absorbs more in the red in the concentrated solution (2). The dimer fluorescence (before the reaction) is negligibly weak in the steady-state spectra because of its very short lifetime, and it is only noticeable in femtosecond time-resolved measurements in the UV region. We note that the contribution of this aggregate fluorescence in the time-resolved measurement is negligibly small, as readily estimated from the fluorescence lifetime and small population of the aggregate.

Excitation Wavelength Dependence of the Fluorescence Dynamics at ≈440 nm. As seen in SI Fig. 11, when we shifted the excitation wavelength from 313 nm to 270 nm, an ultrafast decay appeared in the time-resolved fluorescence signal at ≈440 nm. The signal originated from the 0.2-ps component of the dimer fluorescence, which spectrally extends into the visible region. Importantly, however, even with the appearance of the 0.2-ps component, the fluorescence signal in SI Fig. 11*b* still shows a flat feature in the time region later than 1 ps, when the 0.2-ps component completely vanishes. This result means that the decay of the 1.1-ps dimer fluorescence exactly matches the rise of the tautomer fluorescence, regardless of the appearance of the 0.2-ps component. In other words, the correspondence between the dimer and tautomer dynamics is maintained, even when the

excitation wavelength is changed. These data support our conclusion that the 0.2-ps component has no relation to the proton transfer process.

Electronic Structure of the 7-Azaindole Dimer. Because the relative amplitude of the 0.2-ps component reflects the excitation efficiency to the S_2 state, the observed excitation wavelength dependence is correlated to the electronic structure of the 7-azaindole dimer. Here, we separate absorption spectra of the S_1 and S_2 states on the basis of the excitation wavelength dependence of time-resolved fluorescence and discuss the electronic structure of the excited dimer.

The initial population ratio between the S_1 and S_2 states can be written as $[S_2]:[S_1] = \gamma:1 - \gamma$ by using the following extinction-coefficient ratio (γ) of the two states at the excitation wavelength,

$$\gamma = \frac{\varepsilon_{S2}}{\varepsilon_{S1} + \varepsilon_{S2}}.$$

[1]

The population dynamics starting from this initial condition is readily obtained by solving rate equations for the following relaxation scheme in the dimer:

[2]

$$D \xrightarrow{h\nu} S_2 \longrightarrow S_1 \longrightarrow T^*$$

$$D \xrightarrow{h\nu} S_1 \longrightarrow T^*$$
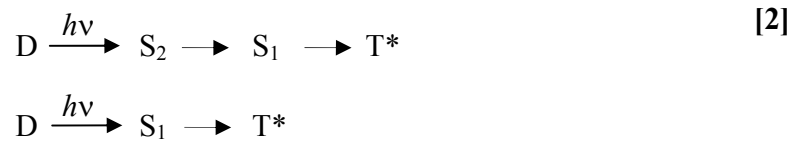
The obtained temporal behavior of the population of each excited state is expressed as

$$[S_2] = \gamma e^{-k_1 t}$$
$$[S_1] = \gamma \rho_{12} \left(e^{-k_2 t} - e^{-k_1 t} \right) + (1 - \gamma) e^{-k_2 t}$$

[3]

where $k_1 = \tau_1^{-1} = (0.2 \text{ ps})^{-1}$, $k_2 = \tau_2^{-1} = (1.1 \text{ ps})^{-1}$, and the ρ_{12} factor is defined as $\rho_{12} = k_1/(k_1 - k_2) = 1.22$. The time-resolved dimer fluorescence at 380 nm (Fig. 6) consists of the contributions from the S_2 and S_1 states, and it is expressed as

$$R(t) = a_1 [S_2] + a_2 [S_1]$$
$$= A_1 e^{-k_1 t} + A_2 e^{-k_2 t} \quad ,$$

[4]

where

$$A_1 = \gamma (a_1 - \rho_{12} a_2)$$
$$A_2 = [(\rho_{12} - 1)\gamma + 1] a_2 \quad .$$

[5]

The coefficient a_i is proportional to the radiative transition probability of the corresponding excited state at 380 nm, whereas the A_i value is obtainable directly from the fitting analysis of the experimental data. By taking the ratio of these two equations, we obtain the following equation:

$$\frac{A_1}{A_2} = \frac{\gamma}{(\rho_{12} - 1)\gamma + 1} \left(\frac{a_1}{a_2} - \rho_{12} \right) ,$$

[6]

which relates the γ value to the experimentally accessible A_1/A_2 parameter.

A fitting procedure using Eq. **4** gave the amplitude of each component (A_i) and, hence, the A_1/A_2 factor in Eq. **6**. Another unknown factor is a_1/a_2. Because this a_i value is related to the oscillator strength intrinsic to the excited state, it does not change significantly by the shift of the excitation wavelength. Therefore, we used the a_i values that were determined in our previous study undertaken with 270-nm excitation (1), which gives the ratio of $a_1/a_2 = 1.82$. By combining this a_1/a_2 factor with the experimentally determined A_1/A_2 factor in Eq. **6**, we evaluated the γ value for all of the six excitation wavelengths (see SI Table 2).

From the γ value and the absorption spectrum of the dimer, which is equal to $\varepsilon_{S1} + \varepsilon_{S2}$, we determined the extinction coefficient of the S_1 and S_2 states separately at the six excitation wavelengths. The "separated" absorption spectra of the two excited states are shown in SI

Fig. 12. Although the S_1 and S_2 absorption bands considerably overlap with each other, the S_1 absorption is slightly red-shifted and extends more in the red beyond 315 nm. It is readily seen that a shoulder structure in the dimer absorption at $\approx$295 nm mainly comes from the corresponding structure of the S_2 absorption. This accords well with the assignment of S_2 (^1L_b) and S_1 (^1L_a), because it is typical for this class of molecules (3-5) that a broad absorption band due to the polar ^1L_a state is observed near a more structured band corresponding to the less polar ^1L_b state. The energy spacing between the intensity maxima of these two absorption bands is $\approx$1,600 cm^{-1}. It is very close to the energy spacing ($\approx$1,700 cm^{-1}) between the intensity maxima of the S_1 and S_2 fluorescence spectra, which was determined in our previous study (1). We also estimated the oscillator strengths of the S_1 and S_2 states as $\approx$0.06 and 0.1, respectively, by the spectral integration of the two absorption intensities over the 250- to 320-nm region. (These oscillator strengths are normalized for one 7-azaindole molecule in the dimer.) These values are in a fairly good agreement with the values obtained from the fluorescence data previously (0.048 for the S_1 state and 0.13 for the S_2 state) (1).

Recently, the excited-state electronic structure of the 7-azaindole dimer was studied by a high-level quantum chemical calculation, multistate CASPT2 (6). It was shown that the first and second lowest, optically allowed transitions occur at wavelengths of 317 nm (^1L_a-type state) and 273 nm (^1L_b-type state), respectively, at the geometry optimized for the ground state. The oscillator strengths of these ^1L_a and ^1L_b states were reported to be 0.143 and 0.237, respectively. (Note that these calculated oscillator strengths are the values for two 7-azaindole molecules in the dimer.) Although the calculated excitation energies of these two states and their energy gap show some deviations from the spectra shown in SI Fig. 12, it is remarkable that the relative ordering of the ^1L_a and ^1L_b states is consistent with the present results. Moreover, the calculated oscillator strengths of the two states agree quantitatively with the experimental values (0.143 $\sim$ 0.06 $\times$ 2 for the ^1L_a state and 0.237 $\sim$ 0.1 $\times$ 2 for the ^1L_b state).

The above argument further supports the concerted mechanism. Because the excited state corresponding to the 1.1-ps component has appreciable oscillator strength, it can be

populated by direct photoexcitation from the ground state. As is well known, the molecular structure (nuclear coordinate) is remained unchanged in the "instantaneous" photoexcitation process so that it is natural to consider that the molecular structure of the generated excited state is not drastically different from the ground-state structure. Therefore, the 1.1-ps component cannot be assigned to the intermediate species that has a largely different (one-proton transferred) structure from the ground-state.

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