Supplementary Information for:

Ionization Dynamics of a Phenylenediamine Derivative in Solutions as Revealed by Femtosecond Simultaneous and Stepwise Two-Photon Excitation

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Relative fluorescence quantum yield measurements

Relative fluorescence quantum yield, Φ_R, was obtained by eq.2.

$$\Phi_R = {n_{\text{flu}}}/{n_{\text{abs}}} \qquad (2)$$

Here, n_{flu} is the number of photons ejected as fluorescence and n_{abs} is the number of photons absorbed by the solute. Since n_{flu} is proportional to the fluorescence intensity, we measured the fluorescence excitation spectra by using a fluorescence spectrophotometer (Hitachi, F850). The excitation light intensity dependence as a function of the wavelength was collected by measuring the excitation spectrum of concentrated Rhodamine B in ethylene glycol. The collected excitation spectra, $E(\lambda)$, in *n*-hexane, ethanol, and acetonitrile normalized at 360 nm are displayed in figure S1a-c. On the other hand, the steady-state absorbance, $A(\lambda)$ is not proportional to the n_{abs} (= $I_0 - I$, where I_0 corresponds to the number of photons irradiated into the sample and I corresponds to the number of photons transmitted to the sample). Thus, steady-state absorption spectrum had to be collected to the values, $A'(\lambda)$, which is proportional to n_{abs}. Figure S2 shows the relative fluorescence intensity of TMPD in *n*-hexane (excited with 327 nm) as a function of absorbance at 327 nm. Since the fluorescence intensity is proportional to $I_0 - I$, we use the correlation function shown in figure S2 to convert from the observed absorbance to $A'(\lambda)$. The collected spectra normalized at 360 nm are displayed in figure S1a-c. Since $E(\lambda)$ is proportional to n_{flu} and $A'(\lambda)$ is proportional to n_{abs}, Φ_R is derived as shown in figure S1d by obtaining the ration between normalized $E(\lambda)$ and $A'(\lambda)$.

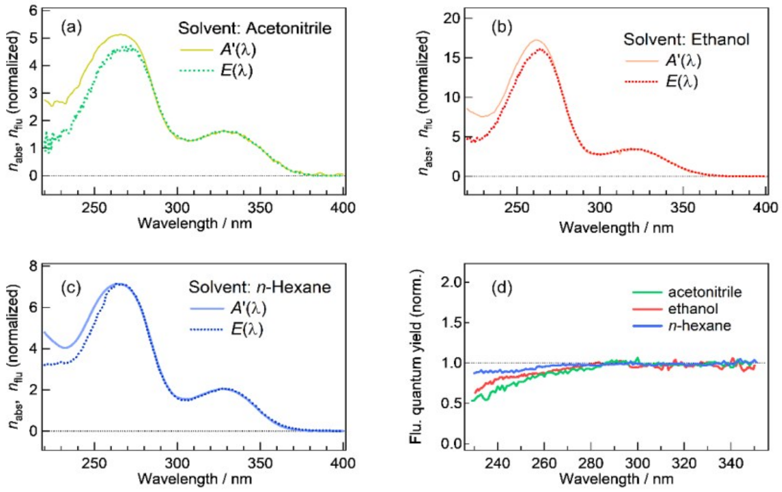

Figure S1 $A'(\lambda)$ and $E(\lambda)$ of TMPD in (a) acetonitrile, (b) ethanol, and (c) *n*-hexane normalized at 360 nm. (d) Relative fluorescence quantum yield of TMPD as a function of excitation wavelength in *n*-hexane (blue), ethanol (red), acetonitrile (green).

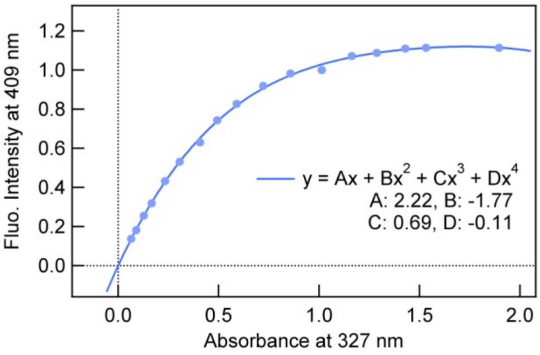

Figure S2 Relative fluorescence intensity of TMPD in *n*-hexane at 409 nm as a function of absorbance at 327 nm.

Transient absorption spectroscopy with the simultaneous two-photon excitation at 400 nm

Figure S3a shows transient absorption spectra of TMPD in ethanol solution excited with a 400-nm laser pulse. As is the case in the acetonitrile solution, the broad absorption band appears immediately after excitation, followed by the deactivation with a time constant of ≤100 fs. In the sub-ps to ps timescale, the spectra are gradually replaced with the new absorption band which can be assigned to the radical cation of TMPD and $S_n \leftarrow S_1$ absorption. Figure S3b shows the double logarithmic plot of the ΔAbsorbance at 615 nm with 4 ps after the excitation as a function of the pump intensity. The fittings to straight lines yield slopes ~1.8. These experimental results clearly indicate that the cation is generated immediately after the deactivation of the S_n state with 400-nm two-photon excitation.

Figure S4a,b shows the time profile of the absorption signals integrated in the 430-630 nm range (a) and in the range of 650-950 (b). The rapid decays due to the deactivation of the S_n state with a time constant of 70 fs are observed in both time evolutions and are followed by very small decay with ~3 ps in the sub-ps and ps time region. These observations indicate that the ionization yield from the vibrationally excited S_1 state is negligibly small. In order to analyze the temporal behaviors more precisely, decay-associated spectra (DAS) obtained from the global analysis fitting on the basis of a double-exponential function. The broad DAS for the time constant of 70 fs could be attributed to the deactivation of the Franck-Condon S_n state. On the other hand, DAS for the time constants of 3.3 ps shows dip signals around the absorption peaks of the S_1 state and the radical cation on the broad positive band. It can be attributable to the vibrational cooling of the S_1 and the cation state. At and ca. 10 ps following the excitation, no remarkable evolution of the spectra was observed. By summarizing above results and discussion, it could be concluded that the radical cation is produced immediately after the excitation and is followed by the vibrational cooling. On the basis of the absorption coefficients of the cation radical and the S1 state, the formation yield of the radical cation and that of the S_1 state are estimated to be 0,45 and 0.55, respectively.

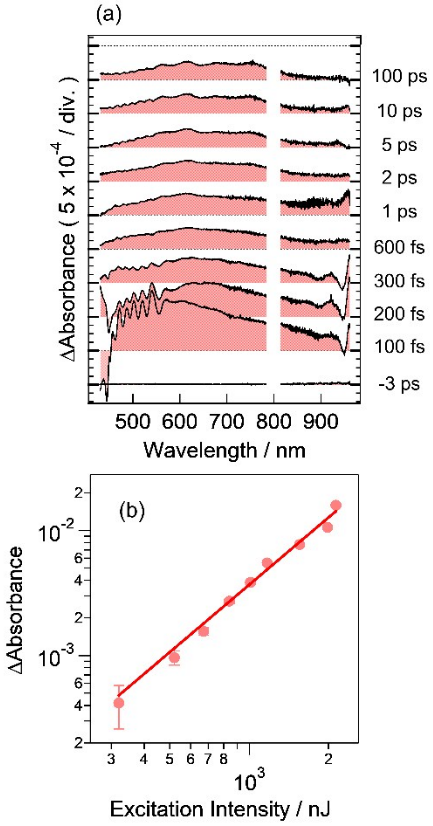

Figure S3 (a) Transient absorption spectra of TMPD in ethanol solution excited with 400-nm pulse (1.3 μJ / pulse). (b) Double logarithmic plot of the ΔAbsorbance at 615 nm, 4 ps as a function of the pump intensity. The slope of the excitation intensity dependence of the transient absorbance was 1.80

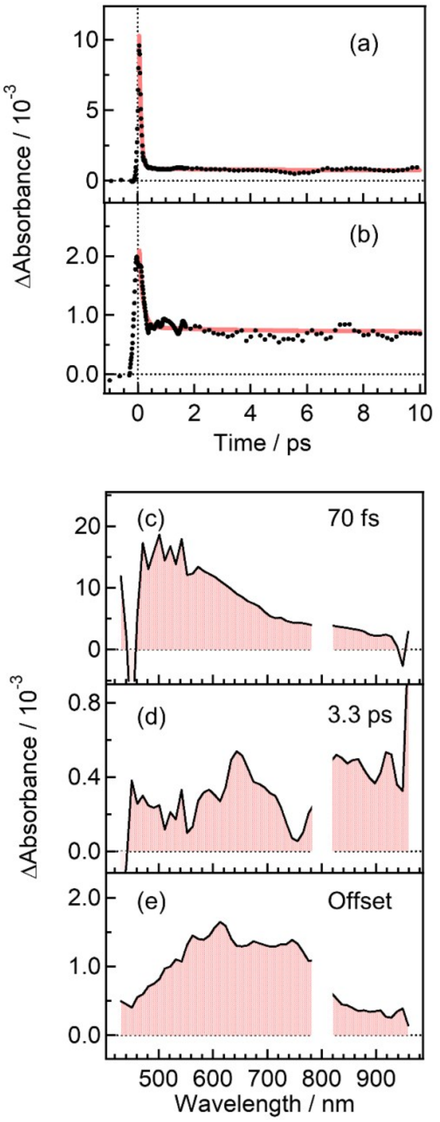

Figure S4. (a,b) Time profiles of the transient absorbance of TMPD in ethanol integrated in the range of 430-630 nm, (a), and in the range of 650-950 nm, (b). (c-e). DAS obtained from the global analysis of the transient absorption spectra of TMPD in ethanol,