Supplementary Information

Identification of Emitting Molecular Species by Time-Resolved Fluorescence Applied to Excited State Dynamics of Pigment Yellow 101

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Figure S1 shows the picosecond time-resolved fluorescence obtained by time correlated single photon counting method (TCSPC) method for the survey of fluorescence dynamics at long time scale. Time resolution was 60 ps (FWHM). The decay time constants at different wavelengths are practically the same on this time scale indicating that major dynamics are over in less than 10 ps.

Figure S2 shows the Fourier power spectra of the residuals of the exponential fits for the TRF signals of P.Y.101 dissolved in dichloromethane. TRF signals were fitted to a sum of exponentials and the residuals were Fourier transformed to give the power spectra at different probe wavelengths. Compared to the LPSVD method, the Fourier transform is model-independent and therefore robust. However, the LPSVD method gives the correct amplitudes. In addition, exponential fits and the oscillation may interfere at early times (<100 fs). To avoid any artifact caused by the exponential fitting, <100 fs data were discarded before the Fourier transformation. The Fourier power transforms are essentially the same as the LPSVD results.

Figure S3 shows the transient infrared absorption (IRTA) spectra of P.Y.101 dissolved in dichloromethane following the pump pulse at 400 nm. The data are the same as those in the

manuscript, but there are additional times.

Figure S4 shows the effect of finite time resolution on the signal. The simulated TRF signals demonstrate that 30 fs dynamics can be readily resolved by the time-resolved fluorescence having instrument response function (IRF) of 50 fs (FWHM). Figure S4 (a) and (b) show for the decay and rise, respectively, that convolution of a Gaussian IRF with 30 fs exponential decay (and rise) are significantly different from the convolution with the instantaneous response. Figure S4 (c) is the simulation of the TRF signal with realistic parameters; convolution of the Gaussian IRF with 30 fs exponential rise and a small oscillation component. Experimental data are overlaid for comparison.
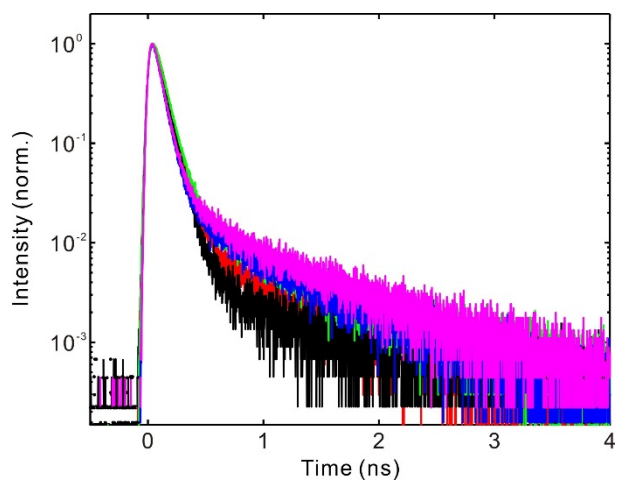
Figure S1.   Picosecond time-resolved fluorescence obtained by TCSPC detected at 470 (black), 500 (red), 530 (green), 550 (blue), and 580 nm (magenta).
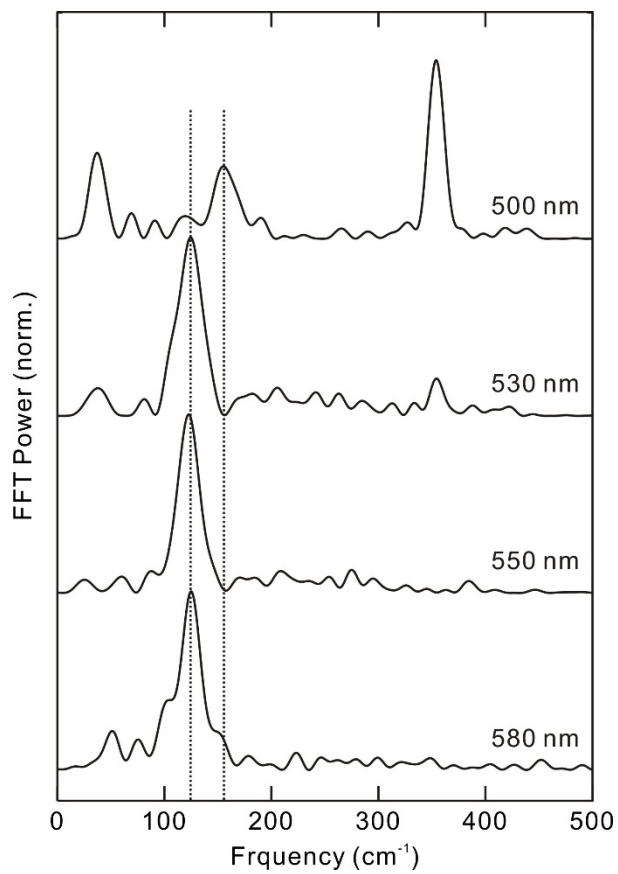
Figure S2. Fourier power spectra of the residuals of the exponential fits for the TRF signals of P.Y.1011 dissolved in DCM detected at several detection wavelengths.
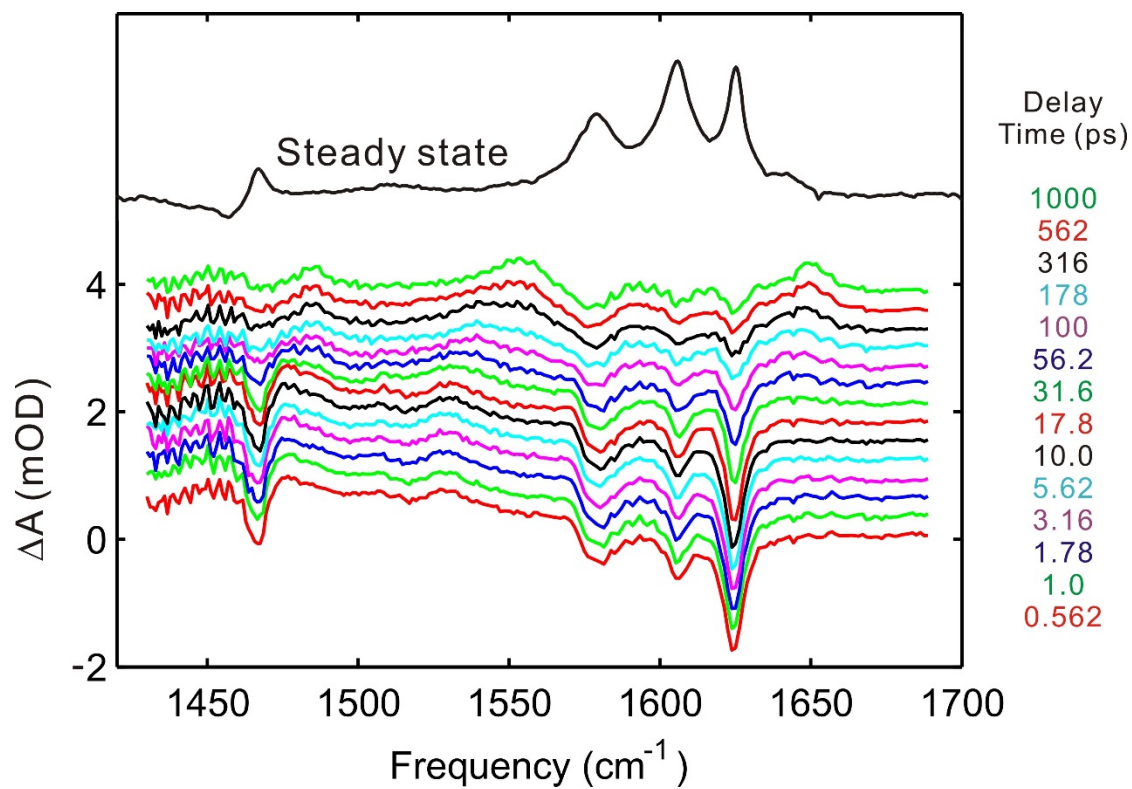
Figure S3. Infrared probe transient absorption (IRTA) spectra of P.Y.101 dissolved in dichloromethane following the pump pulses at 400 nm. Time increases from bottom to top. Each spectrum is displaced vertically by 0.3 from the previous spectrum. Steady state infrared absorption spectrum is also shown.
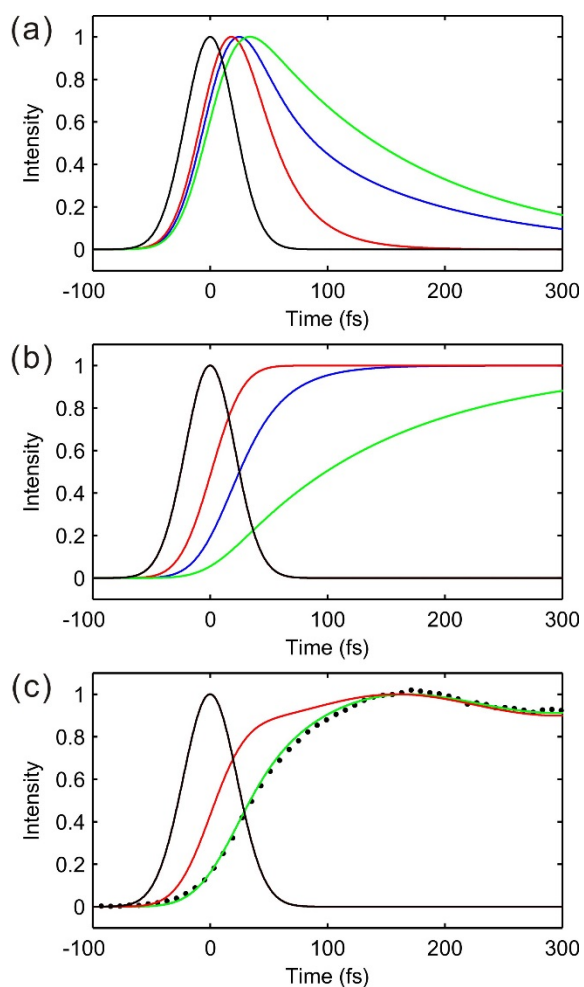
Figure S4.   Convolution of exponential functions with a Gaussian of 50 fs FWHM (black lines). (a) 30 fs decay (red); 30 (55%) and 140 (45%) fs biexponential decay (blue), and 140 fs decay (green). (b) instantaneous rise (red), 30 fs rise (blue), and 140 fs rise (green). (c) 30 fs rise with a 122 cm^{-1} (7.8%) oscillation (green), and instantaneous rise with a 122 cm^{-1} (7.8%) oscillation (red). Experimental time-resolved fluorescence at 550 nm (dotted line) is shown for comparison.