Excited-State Dynamics of Phenothiazine Derivative Having a Quinoidal Structure

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Organic dyes that responses to the longer wavelength are important for dye-sensitized solar cells, triplet sensitizers, and photopharmacology because long-wavelength light is low phototoxicity, higher transmittance of matter, and higher selectivity for excitation. Organic molecules that have quinoidal structures are one of the efficient molecular frameworks to increase the absorptive properties in longer wavelength light. However, the lifetimes of the excited states of these compounds are generally extremely short due to nonradiative relaxations, which limit the potentials of their applications. In this study, we synthesized a phenothiazine derivative with quinoid structure **1** (Fig.1a) and investigated the excited-state dynamics.

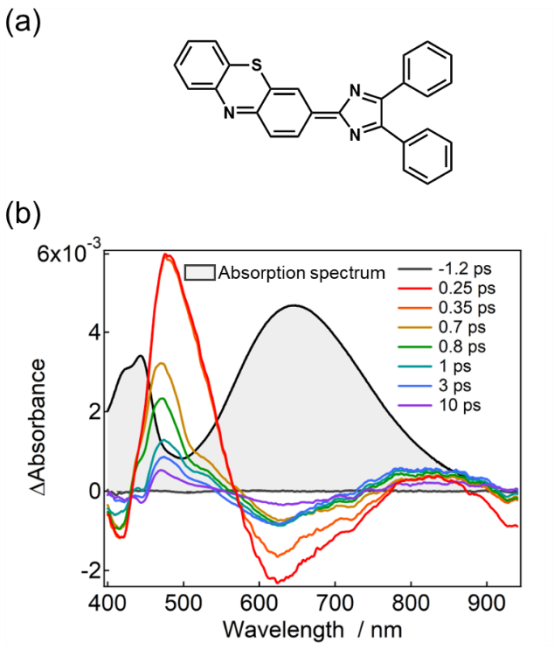

Fig.1 (a) Molecular structure, and (b) the steady-state and transient absorption spectra of **1** in acetonitrile (9.0×10^{-5} M) excited with a 650-nm femtosecond laser pulse (20 nJ/pulse) at room temperature.

Fig.1b shows the steady-state absorption spectrum and the transient absorption spectra of **1** in acetonitrile excited with a 650-nm femtosecond laser pulse. After the excitation of **1** in acetonitrile with a 650-nm laser pulse at 360 K (Fig.1b), ground-state bleach signals were observed at 410 nm and 620 nm, and an excited- state absorption signal was observed at 480 nm. Because **1** does not have any absorption at >900 nm, the negative signal at 950 nm is ascribed to the stimulated emission. The transient absorption signal at ~480 nm was blue-shifted, and the spectral shape also changed slightly. Subsequently, a component showing a broad absorption gradually appeared at 800 nm, and it decayed to the ground state with a time constant of 10 ps. These results suggest the deactivation process involves the conical intersection because the deactivation rate is extremely fast.