Ultrafast Spin Crossover in 4-Thiothymidine in an Ionic Liquid

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Electronic Supporting Information

I. Experimental Methods

1. *Chemicals and Methods*

4-Thiothymidine (4-thioThd, 99% purity) was obtained from Carbosynth Limited, Berkshire, UK and used as received. 1-butyl-1-methylpyrrolidium bis(trifluoromethylsulfonyl) imide, [BMPyrr][NTf_2], was obtained from Sigma-Aldrich (≥ 98.0% purity and ≤ 0.2% water content). Acetonitrile (99.9%) was bought from Fisher Scientific.

Steady-state absorption and emission spectra were measured at room temperature using a Cary 100 and Cary Eclipse spectrophotometers (Varian, Inc.), respectively. Background corrections were performed by subtracting a solvent-only scan under the same experimental conditions, as described elsewhere.[1] Fluorescence spectra were taken at medium PMT voltage with slit-widths of 5 nm and averaging times of 3.2 s. The absorption of the solutions for the emission experiments was 0.2 at the 340 nm excitation wavelength in a 1 cm^2 cell. The slit-widths were increased to 10 nm for the excitation spectra.

The pump-probe femtosecond transient absorption spectrometer and data analysis procedure have been described in detail elsewhere.[2] In short, a Quantronix *Integra-i/e 3.5* Laser generating 100 fs pulses at 800 nm with a repetition rate of 1 kHz is used to pump an optical parametric amplifier (OPA, TOPAS, Quantronix / Light Conversion). In this work, the OPA output is tuned to the excitation wavelengths of 340 or 360 nm. A reflective wavelength filter (λ-filter) and a Glan-Taylor prism are used to remove contributions from other wavelengths or polarizations to the excitation pulse. The excitation pulses are attenuated to the desired intensity using a neutral density optical filter in order to minimize multiphoton absorption and cross phase modulation effects.[3] The polarization of the excitation pulses is randomized by passing the beam through a depolarizing plate in the spectrometer to prevent rotational relaxation effects from contributing to the kinetics. A broadband spectrometer (Helios, Ultrafast Systems, LLC) is used for data collection. A continuously moving 2 mm CaF_2 crystal is used for white light continuum generation and the probe pulses are corrected for group velocity dispersion[4] using a home-made LabView (National Instruments, Inc.) program.[2]

Data analysis was performed using the Igor Pro 6.06 software (Wavemetrics, Inc.), as described elsewhere.[2] An instrument response function of 200 fs was used as determined from the coherent signal seen in solvent-only scans. In general, 27 representative kinetic traces were selected in the global fit analysis for each dataset covering the full range of probe wavelengths (350 to 650 nm). The kinetic traces were analyzed by globally fitting to a sum of two exponential terms and a constant offset convoluted with the instrument response function. All reported uncertainties are twice the standard deviation (2σ).

The absorbance of the solutions in the transient absorption measurements was typically 0.5 OD in [BMPyrr][NTf_2] and 1.0 OD in acetonitrile at the excitation wavelength, respectively. The sample in the excited volume was continuously refreshed by a magnetic stirrer to avoid re-excitation of the pumped volume by successive laser pulses. Degradation of 4-thioThd was monitored by UV absorption spectroscopy (see below) and solutions were replaced by fresh ones if the steady-state absorbance of 4-thioThd decreased by more than 10% during the course of the experiments. Importantly, no changes in the transient absorption spectra or decay signals of 4-thioThd were observed in solutions that showed 10% or less decrease in ground-state absorption at ~335 nm after the time-resolved experiments were completed.

I. Supporting Results

1. Steady-State Emission and Excitation Spectra of 4-thioThd in [BMPyrr][NTf$_2$] and in Acetonitrile

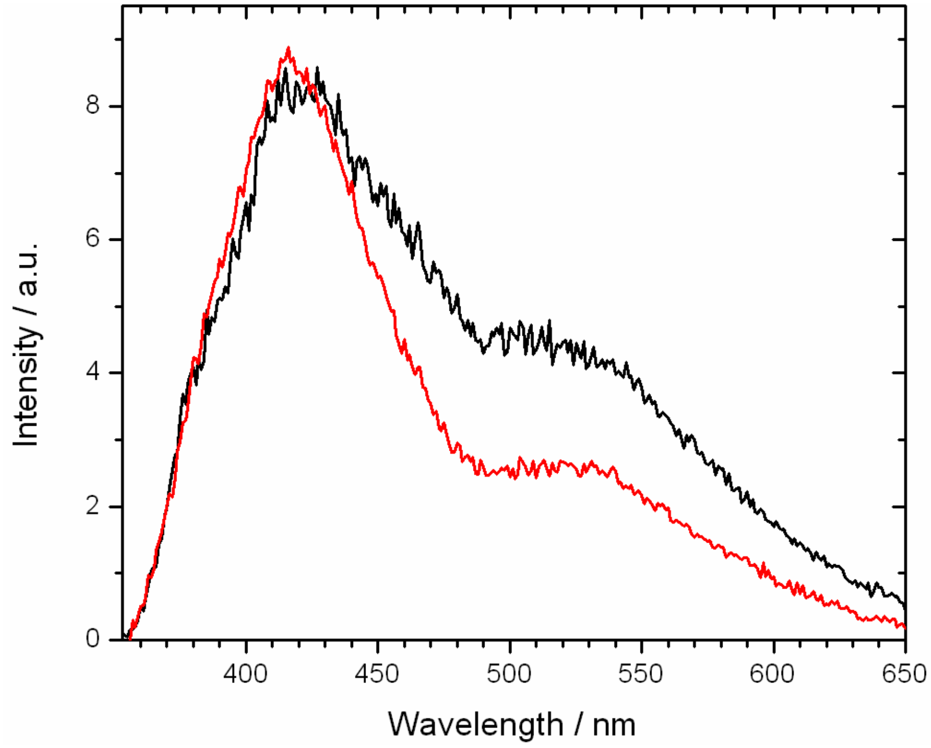

Fig. 1S Steady-state emission spectra of 4-thioThd in [BMPyrr][NTf$_2$] (black) and acetonitrile (red) solutions after excitation at 340 nm at room temperature.

Figure 1S shows the steady-state emission spectra of 4-thioThd in [BMPyrr][NTf$_2$] and acetonitrile solutions. Strikingly, dual emission is observed in each solvent in good agreement with the emission spectrum of 4-thioThd in aqueous buffer solutions at pH 7.4.[1] Potential complications from the formation of 4-thioThd aggregates were not observed under the experimental conditions used in this work. However, the blue edge of the emission spectra might be somewhat distorted by re-absorption from the 4-thioThd molecules. This is particularly true for the emission spectrum in acetonitrile where the absorption at the excitation wavelength was ~ 1. Clearly, more steady-state experiments are needed, which should include the temperature dependence of the emission spectra. We have recently shown that the high-energy emission band is due to fluorescence emission while the red-shifted emission band originates from phosphorescence emission in the triplet manifold.[1] The phosphorescence band is readily quenched by molecular oxygen while the fluorescence band is not.[1] The dual emission bands reported in this work in [BMPyrr][NTf$_2$] and acetonitrile strongly support the proposal that this is an intrinsic property of 4-thioThd. The differences in the relative intensity of the phosphorescence emission band in both solvents is likely due to the different fraction of triplet state population that is quenched by triplet-triplet annihilation (see main text) and the different concentration of dissolved molecular oxygen in each solvent.

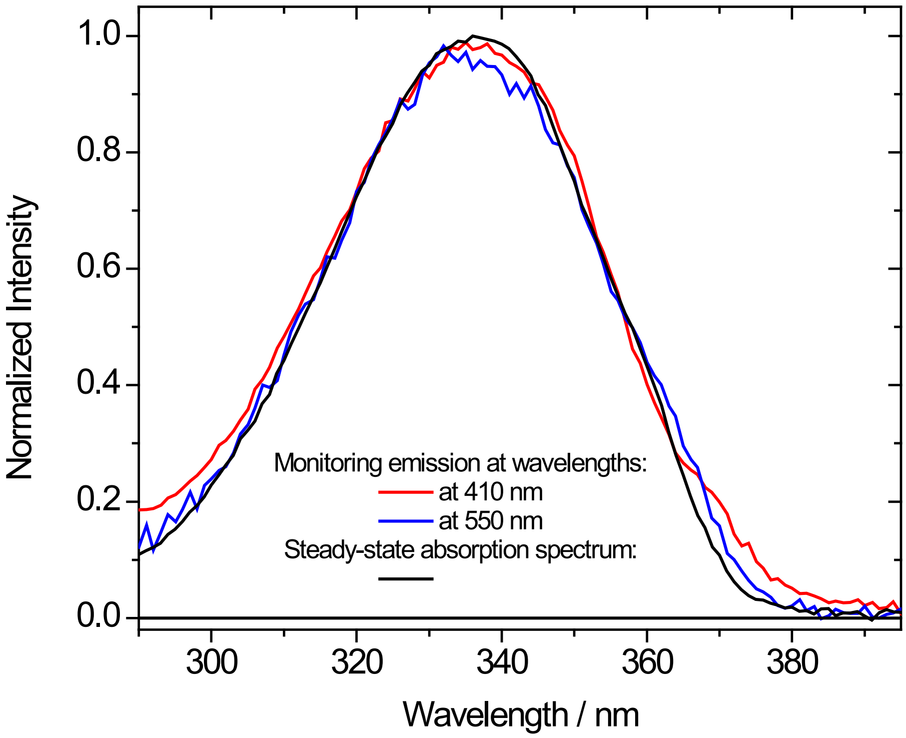

Fig. 2S Excitation spectra of 4-thioThd in acetonitrile solution recorded at 410 and 550 nm emission wavelengths. The steady-state absorption spectrum of 4-thioThd in the same solvent is also included for completeness.

The excitation spectra of 4-thioThd were also recorded in acetonitrile solutions at the emission wavelengths of 410 and 550 nm (Fig. 2S). The excitation spectra are reported from approximately 300 to 400 nm because of the small intensity of the emission bands and because of the known experimental difficulties in measuring excitation spectra in the spectral region below 300 nm.[5] As expected, the excitation spectra for both emission bands are identical (within experimental uncertainties) to each other and to the ground state absorption spectrum of 4-thioThd. These results unequivocally show that both emission bands originate from the 4-thioThd monomer and not from aggregates and/or impurities in the solution.

2. Determination of the Relative Triplet State Quantum Yield of 4-thioThd in [BMPyrr][NTf$_2$]

Harada and co-workers reported a triplet quantum yield of unity for 4-thioThd in acetonitrile.[6] We have recently used this information to estimate the triplet quantum yield of 4-thioThd in aqueous buffer solution at pH 7.4.[1] An important assumption was made in the estimation of the triplet yield. Namely, that the absorption cross sections of the triplet-triplet absorption band of 4-thioThd are the same in a given solvent.[1] Support for the applicability of this assumption came from the fact that excited-state calculations of 4-thioThd including explicit and implicit solvent effects do not show significant differences in the energy and order of the excited states when using water or acetonitrile as solvent.[1]

Thus, in analogy to our previous work,[1] the transient absorption spectra of 4-thioThd were recorded in a series of back-to-back measurements in acetonitrile and in [BMPyrr][NTf$_2$] solutions. Excitation was performed at 340 nm. Then, the transient absorption spectra at delay times from 5 to 12 ps were averaged in each solvent and used to estimate the triplet yield of 4-thioThd in [BMPyrr][NTf$_2$] relative to that reported in acetonitrile.[7] The triplet-state population was constant during that time delay period and thus quenching of the triplet state population by triplet-triplet annihilation (see main text) can be effectively minimized. Using this comparative procedure, we estimate a triplet quantum yield for 4-thioThd in [BMPyrr][NTf$_2$] solution of 110 ± 15 % relative to that reported in acetonitrile.[7] The higher than unity triplet quantum yield estimated by this comparative method can imply that the assumption above does not hold or that the recently determined value in acetonitrile[7] has considerable error. Work is underway to determine the triplet quantum yield of 4-thioThd in these and other solvents using well-known triplet yield standards.

3. Representative Kinetic Traces in Acetonitrile

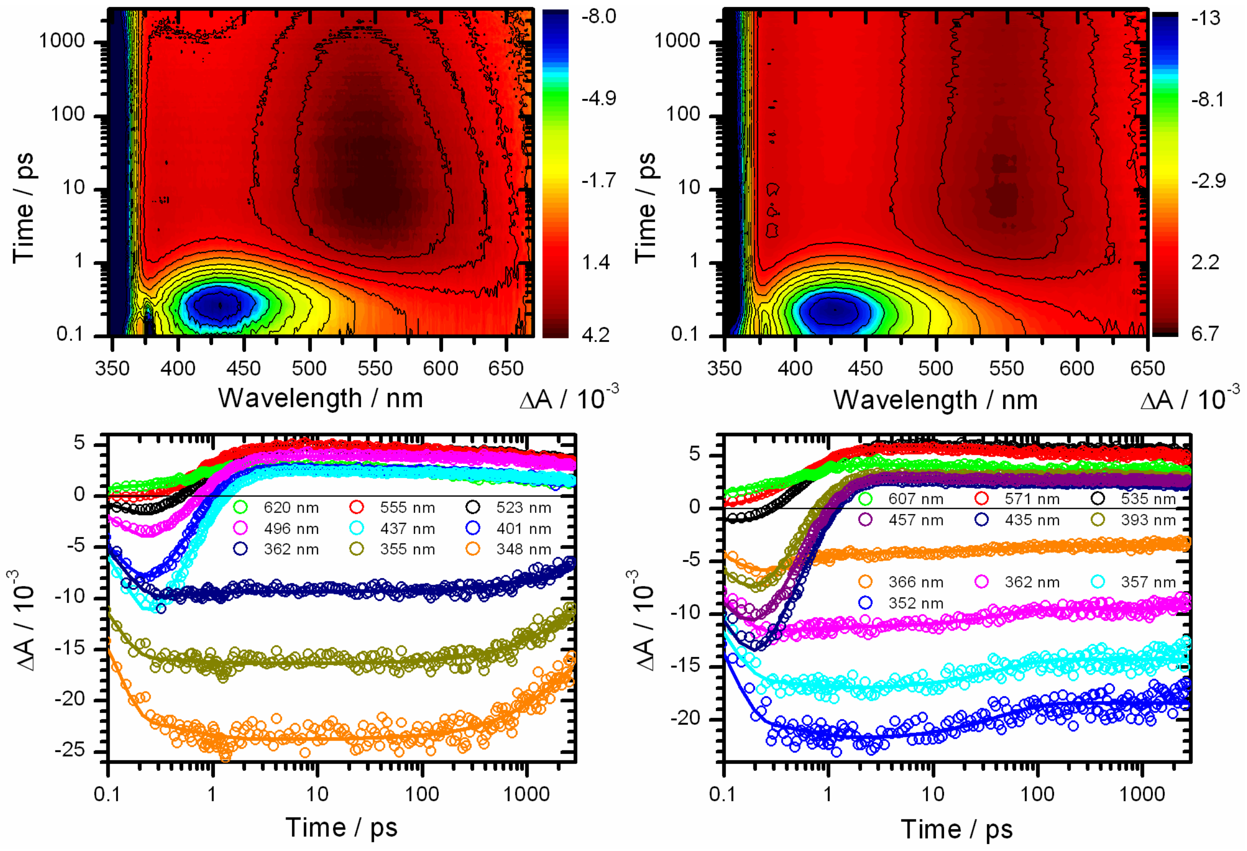

Fig. 3S Contour plots and representative kinetic traces for 4-thioThd in [BMPyrr][NTf$_2$] (left panels) and acetonitrile (right panels) solutions after 340 nm excitation. Best global-fit-curves are shown by solid lines.

4. Steady-State Difference Absorption Spectra and Photoproduct Formation

Figure 4S shows characteristic absorption spectra of 4-thioThd before and after the laser measurements in acetonitrile solutions. Also included in this plot is the difference spectrum obtained after normalizing the absorption spectra of 4-thioThd at 337 nm before and after the laser measurements. This difference spectrum should resemblance the absorption spectrum of the primary photoproduct(s). Similar results were observed when using the IL as a solvent. It is possible that small residual absorption band (i.e., a residual absorption of ~ 0.05 units) is present at wavelengths above 300 nm and below 400 nm but its contribution to the total absorption is insignificant. Chromatographic separation of the product(s) is needed to determine the number of photoproducts formed. Regardless, the difference spectrum shows that the main absorption bands of the primary photoproducts formed after laser irradiation at 340 nm lie below 300 nm. It is likely that these are analogous to the products observed previously in the photochemistry of the thymidine monomers.[8]

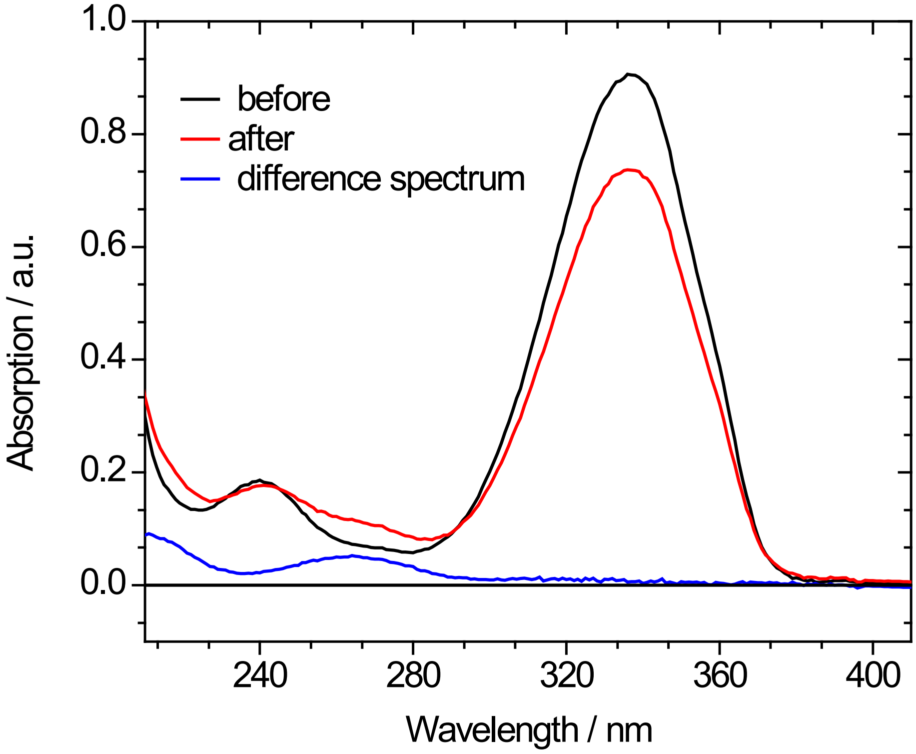

Fig. 4S Characteristic absorption spectra of 4-thioThd before and after a laser experiment in acetonitrile. Also include in this plot is the resulting difference spectrum after normalizing the before and after spectra at 337 nm. The difference spectrum should resemble the absorption spectrum of the primary product(s).

III. References to Electronic Supporting Information

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