Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ultrafast Dynamics of a New Class of Highly Fluorescent Boron Difluoride Dyes

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Supporting Information

Instrumentation

Femtosecond pump-probe measurements were collected on an Ultrafast Systems HELIOS transient absorption spectrometer. A Spectra Physics Solstice system that contains a Mai Tai seed laser and Empower pump laser was employed to produce 3.5 W 800 nm pulses at a repetition rate of 1 kHz (~150 fs pulse width), which were used to generate the pump and probe beams for the transient absorption spectrometer. The pump beam wavelength was generated with a Light Conversion TOPAS-C. A portion (2.5%) of the 800 nm beam produced by the Solstice was utilized to excite a CaF_2 plate to generate a white light continuum (~330-650 nm) probe beam. The spectrum was integrated for 2 s for each measurement. Modulation of the laser power from ~0.3 mW to ~1 mW showed no evidence of non-linear or multi-photon effects. In a typical experiment, a sample solution was irradiated with an absorbance of ~0.2 AU at the excitation wavelength in a 2 mm path length cuvette. All transient absorption data was corrected by subtracting spectral background features that persisted from the previous pulse and appeared pre-pulse, as well as by applying chirp and t_0 corrections using Surface Xplorer Pro 1.1.5 software (Ultrafast Systems). Single-wavelength kinetics were fit using the Surface Xplorer Pro 1.1.5 software.

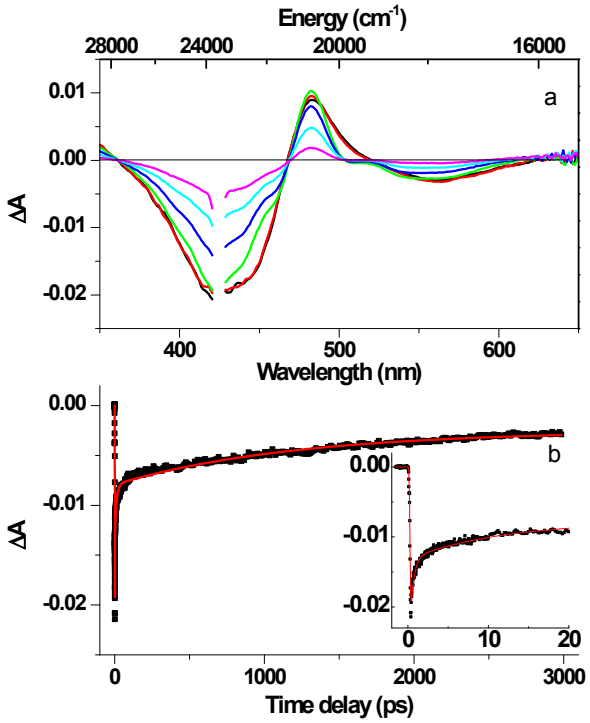

Figure S1. (a) Transient absorption spectra of compound **1** in DMF following 424 nm excitation with 573 μW. Spectra obtained at pump-probe delays of 0.75 (black), 1.0 (red), 10 (green), 100 (blue), 1010 (cyan), and 3000 ps (purple). The data points near the excitation wavelength have been removed for clarity. (b) Single wavelength (450 nm) kinetic trace (black) obtained from 424

nm excitation (573 μW) and tri-exponential fit (red). The fit yields three lifetimes of 0.43±0.05, 11.5±0.9, and 1193±134 ps. Inset: kinetic trace at fit from 0–20 ps.

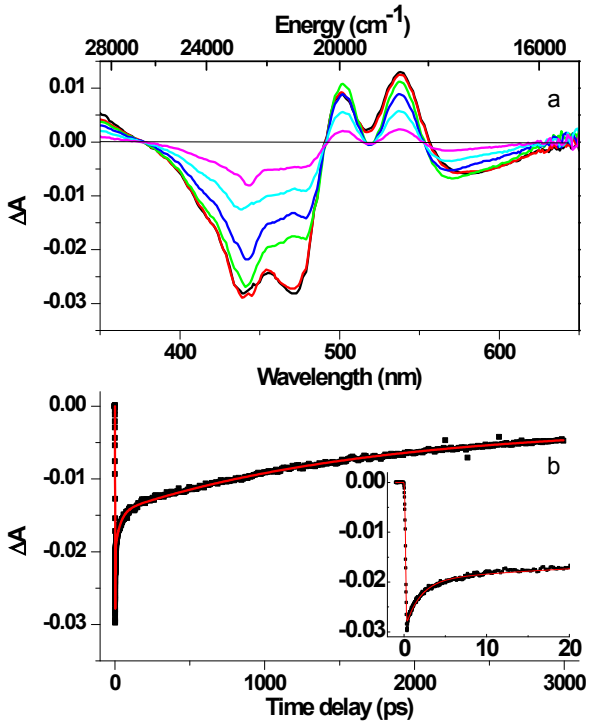

Figure S2. (a) Transient absorption spectra of compound **2** in DMF following 442 nm excitation with 583 μW. Spectra obtained at pump-probe delays of 0.75 (black), 1.0 (red), 10 (green), 101 (blue), 1006 (cyan), and 2996 ps (purple). The data points near the excitation wavelength have been removed for clarity. (b) Single wavelength (476 nm) kinetic trace (black) obtained from 442 nm excitation (583 μW) and tri-exponential fit (red). The fit yields three lifetimes of 1.82±0.10, 35.4±3.8, and 1665±137 ps. Inset: kinetic trace at fit from 0–20 ps.

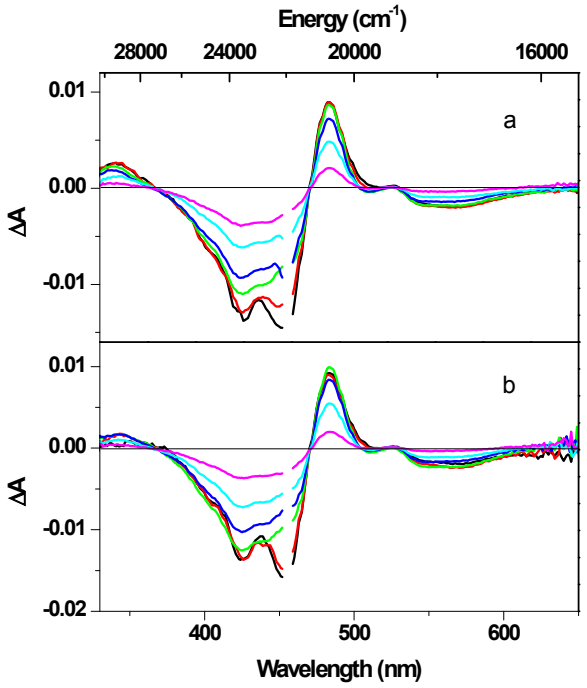

Figure S3. These plots compare pump intensity at the same excitation wavelength (455 nm). (a) Transient absorption spectra of compound **1** in DCM following 455 nm excitation with 264 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.1 (red), 10 (green), 101 (blue), 1010 (cyan), and 2990 ps (purple). The data points near the excitation wavelength have been removed for clarity. (b) Transient absorption spectra of compound **1** in DCM following 455 nm excitation with 575 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.0 (green), 101 (blue), 1010 (cyan), and 2990 ps (purple). The data points near the excitation wavelength have been removed for clarity.

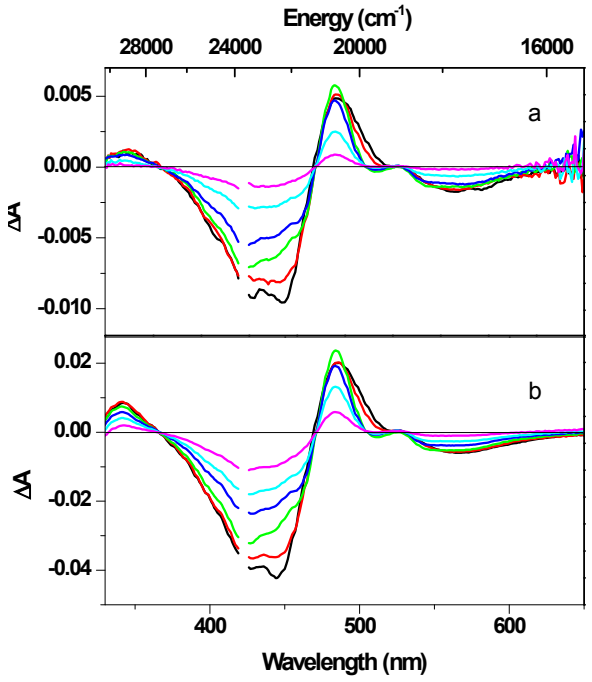

Figure S4. These plots compare pump intensity at the same excitation wavelength (424 nm). (a) Transient absorption spectra of compound **1** in DCM following 424 nm excitation with 278 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.0 (green), 100 (blue), 1010 (cyan), and 3000 ps (purple). The data points near the excitation wavelength have been removed for clarity. (b) Transient absorption spectra of compound **1** in DCM following 424 nm excitation with 578 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.0 (green), 100 (blue), 1010 (cyan), and 3000 ps (purple). The data points near the excitation wavelength have been removed for clarity.

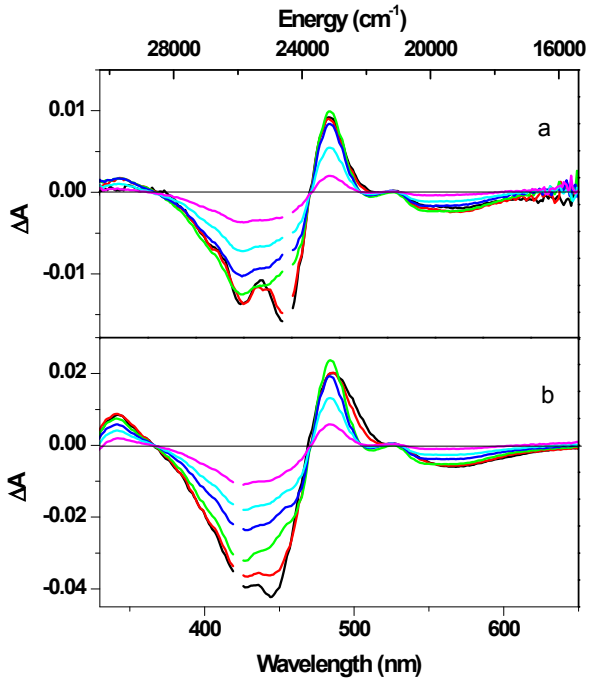

Figure S5. These plots compare excitation wavelength (455 vs. 424 nm) at similar pump intensity. (a) Transient absorption spectra of compound **1** in DCM following 455 nm excitation with 575 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.0 (green), 101 (blue), 1010 (cyan), and 2990 ps (purple). The data points near the excitation wavelength have been removed for clarity. (b) Transient absorption spectra of compound **1** in DCM following 424 nm excitation with 578 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.0 (green), 100 (blue), 1010 (cyan), and 3000 ps (purple). The data points near the excitation wavelength have been removed for clarity.

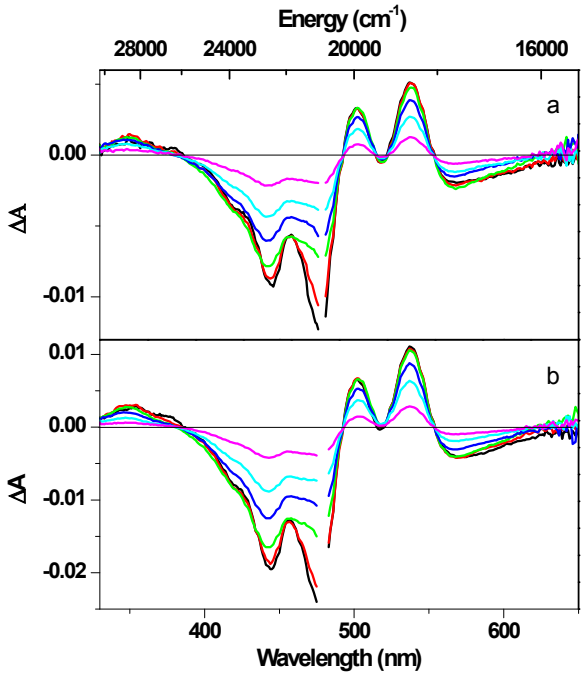

Figure S6. These plots compare pump intensity at the same excitation wavelength (480 nm). (a) Transient absorption spectra of compound **2** in DCM following 480 nm excitation with 259µW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.2 (green), 100 (blue), 1000 (cyan), and 3000 ps (purple). The data points near the excitation wavelength have been removed for clarity. (b) Transient absorption spectra of compound **2** in DCM following 480 nm excitation with 582 µW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.2 (green), 100 (blue), 1000 (cyan), and 3000 ps (purple). The data points near the excitation wavelength have been removed for clarity

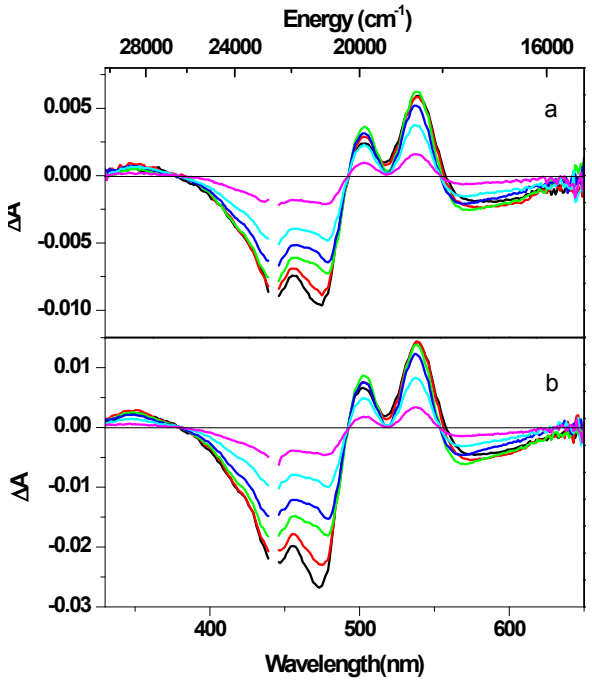

Figure S7. These plots compare pump intensity at the same excitation wavelength (442 nm). (a) Transient absorption spectra of compound **2** in DCM following 442 nm excitation with 258 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10 (green), 103 (blue), 1010 (cyan), and 2990 ps (purple). The data points near the excitation wavelength have been removed for clarity. (b) Transient absorption spectra of compound **2** in DCM following 442 nm excitation with 560 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.1 (green), 100 (blue), 1010 (cyan), and 2990 ps (purple). The data points near the excitation wavelength have been removed for clarity.

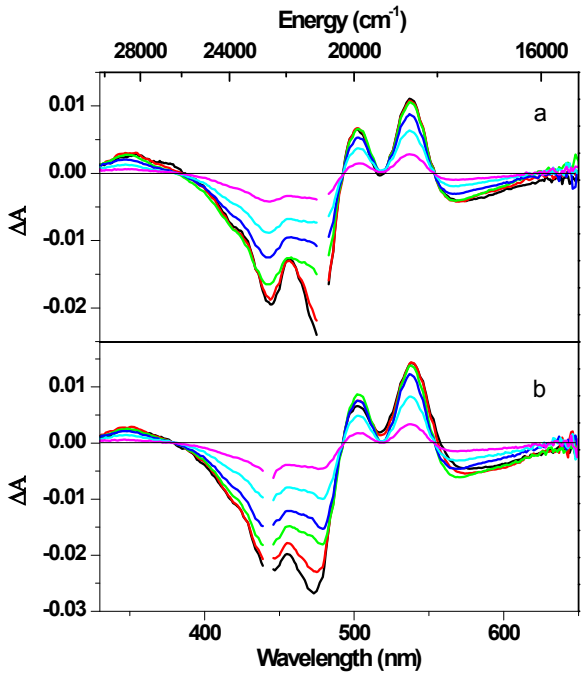

Figure S8. These plots compare excitation wavelength (480 vs. 442 nm) at similar pump intensity. (a) Transient absorption spectra of compound **2** in DCM following 480 nm excitation with 582 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.2 (green), 100 (blue), 1000 (cyan), and 3000 ps (purple). The data points near the excitation wavelength have been removed for clarity. (b) Transient absorption spectra of compound **2** in DCM following 442 nm excitation with 560 μW. Spectra obtained at pump-probe delays of 0.5 (black), 1.0 (red), 10.1 (green), 100 (blue), 1010 (cyan), and 2990 ps (purple). The data points near the excitation wavelength have been removed for clarity.