Supporting Information for:

A Luminescent Charge Transfer Platinum(II) Metallacycle

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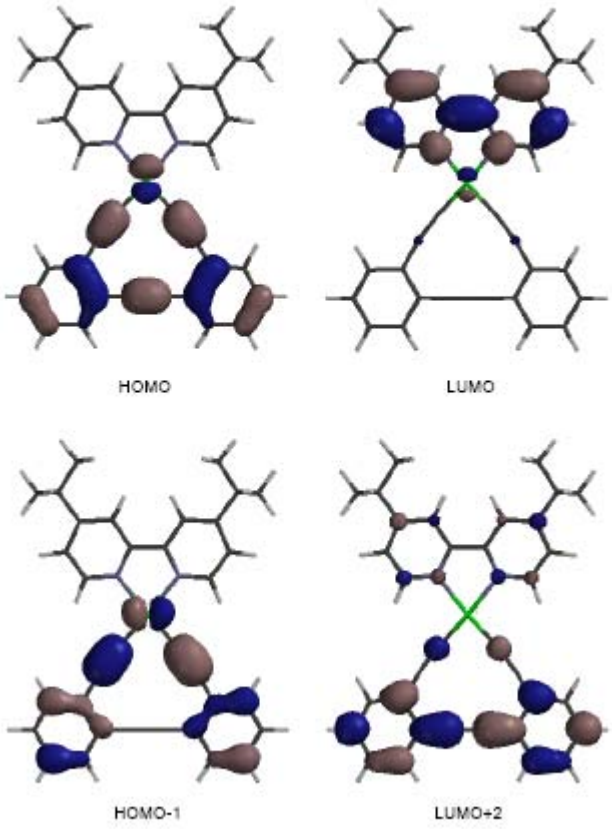
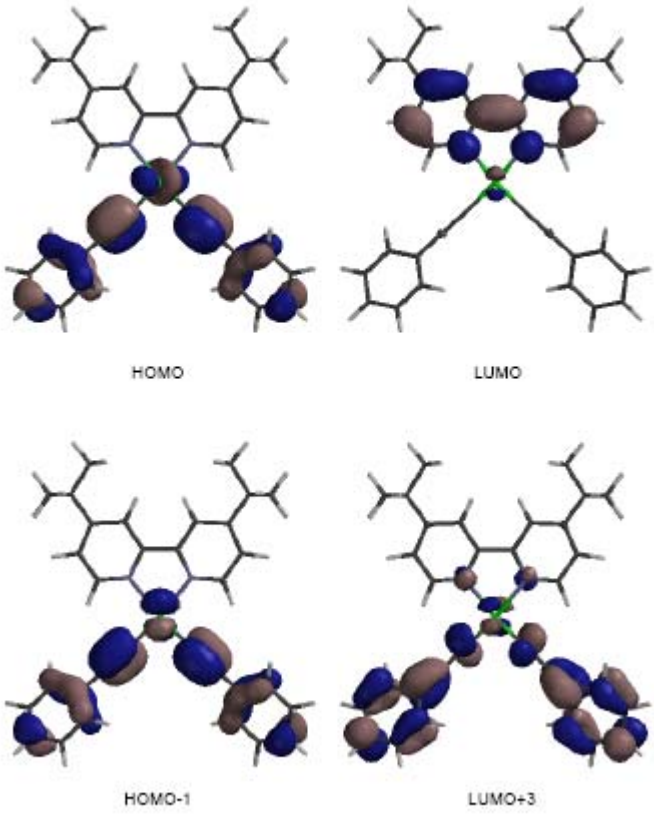
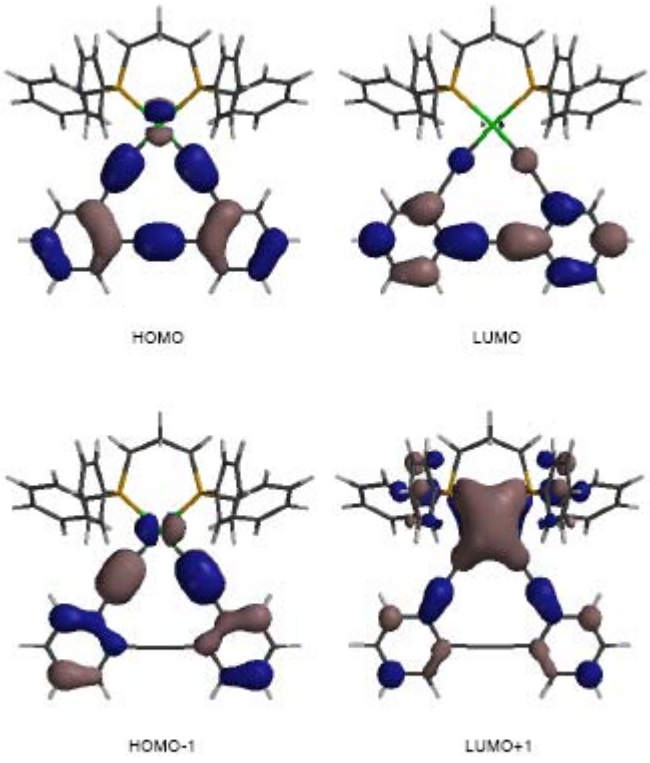
Representative Molecular Orbitals of 1



Representative Molecular Orbitals of 2



Representative Molecular Orbitals of 3



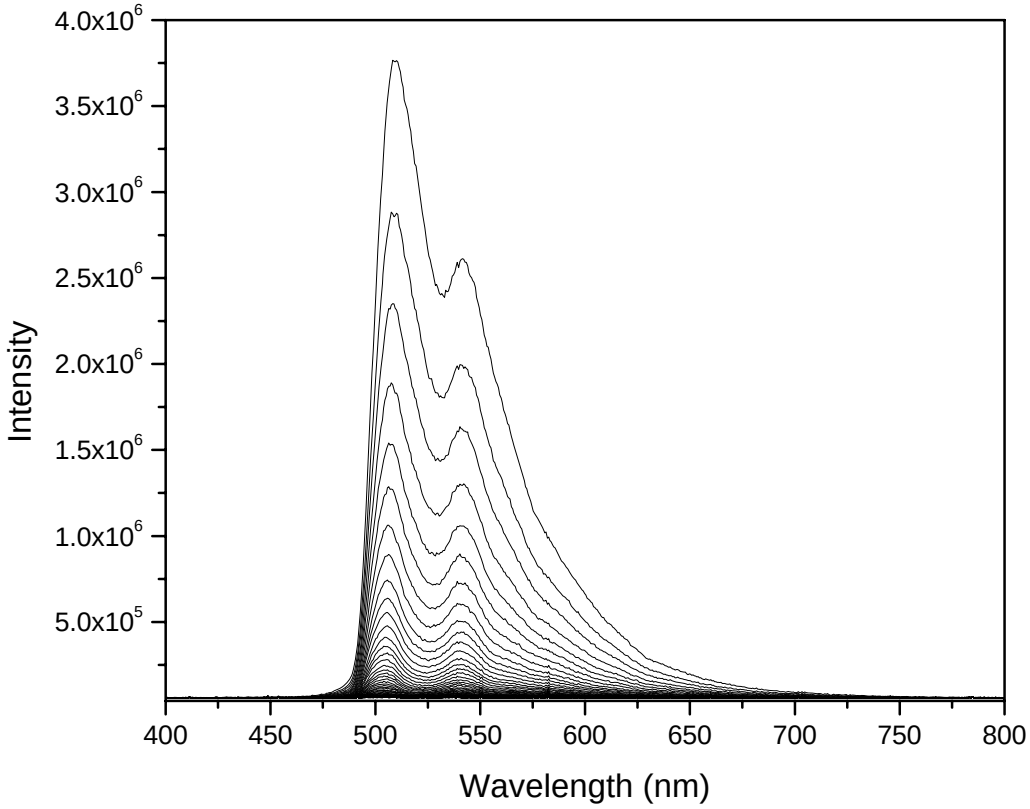


Figure S1. Time-resolved emission of **1** in EtOH:MeOH (4:1) at 77 K with λ_{ex} = 450 nm. The time delay between acquisitions is 3 μs with total elapsed time of 160 μs.

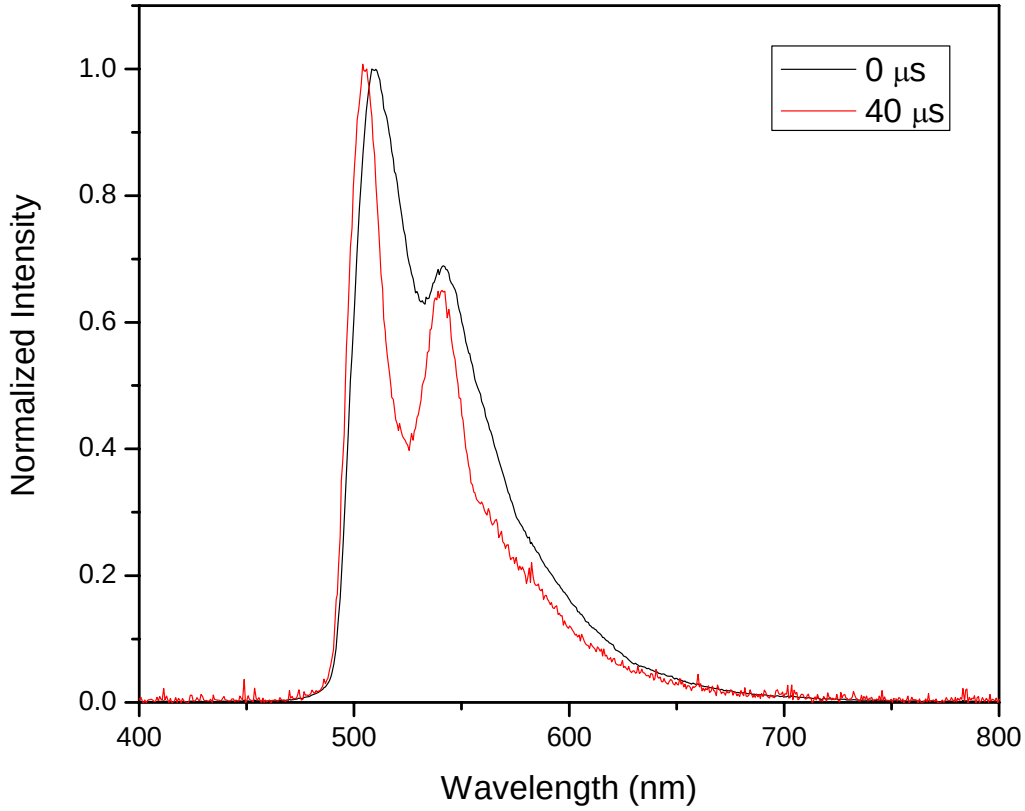


Figure S2. Normalized emission of **1** in EtOH:MeOH (4:1) at 77 K at 0 and 40 μs, data from Figure S1, highlighting the blue-shift and narrowing of the emission profile with time.

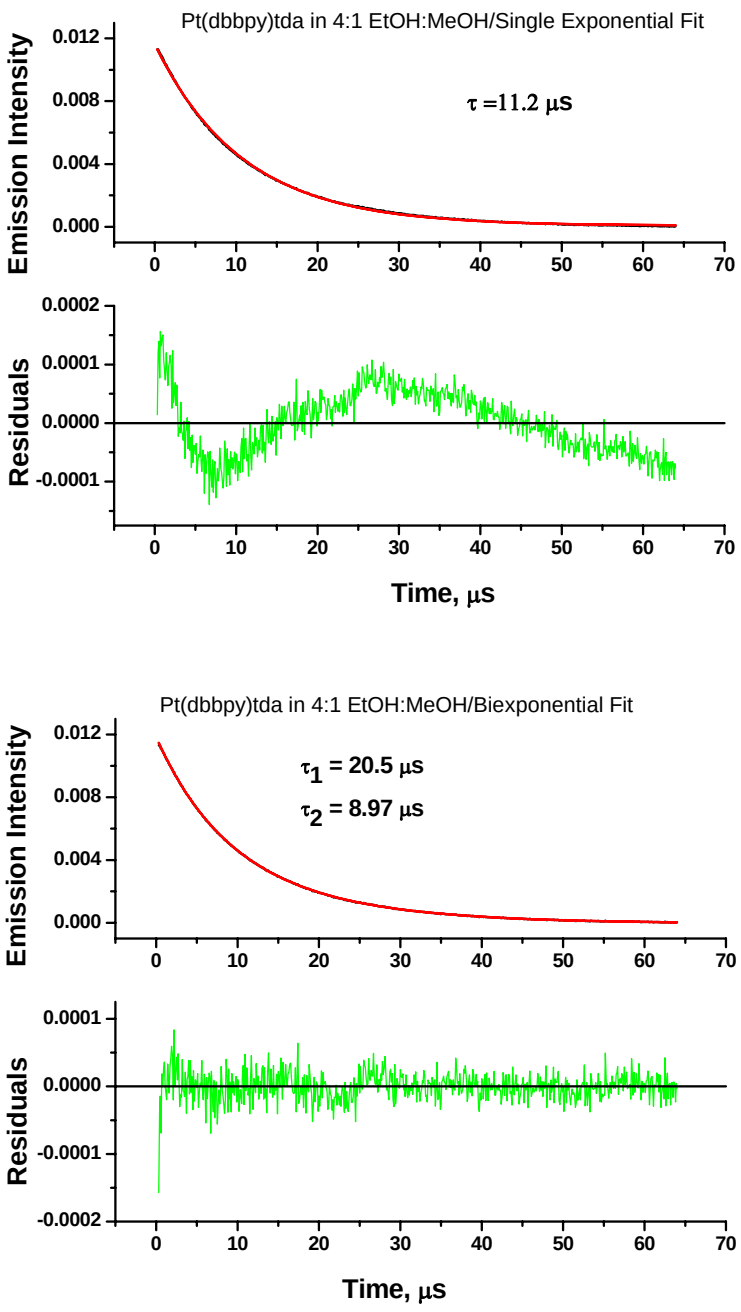


Figure S3. Luminescence intensity decay of **1** measured in 4:1 EtOH:MeOH at 77 K fit to a single exponential function (top two panels) and a biexponential function (lower two panels). Residuals illustrate the quality of the fits.

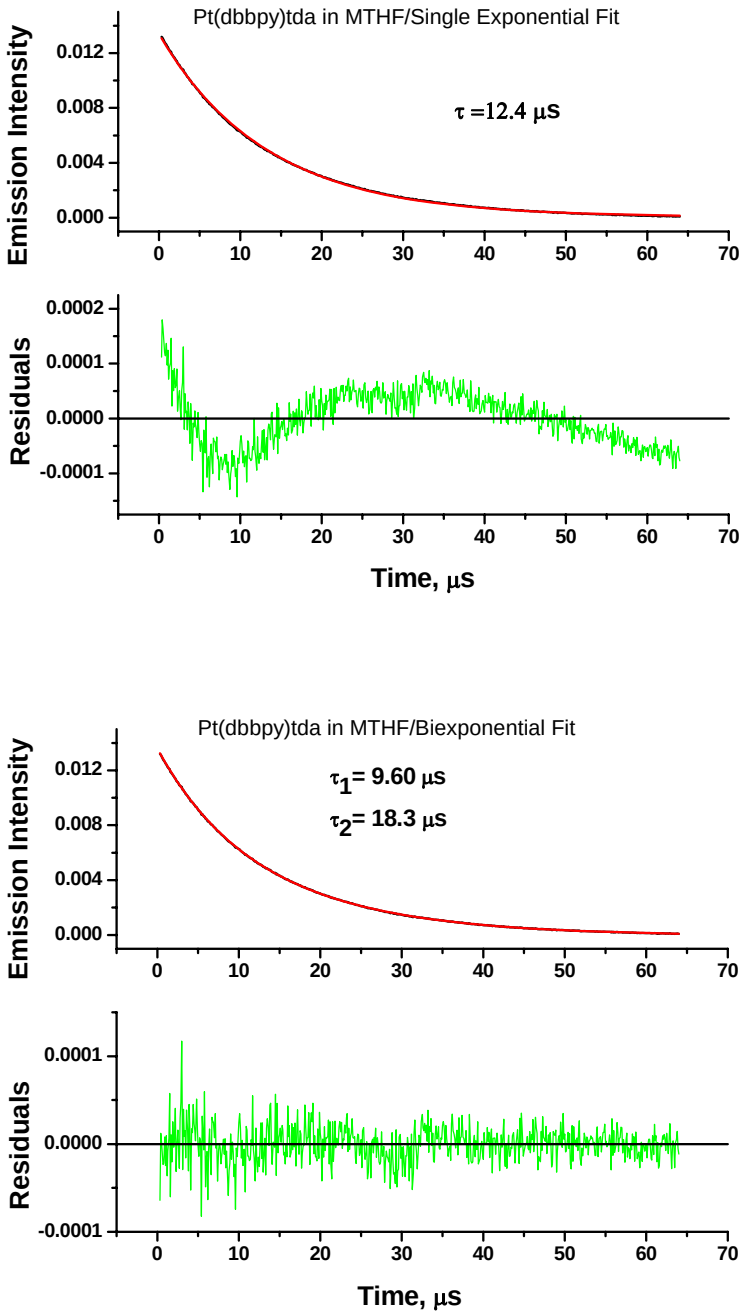


Figure S4. Luminescence intensity decay of **1** measured in MTHF at 77 K fit to a single exponential function (top two panels) and a biexponential function (lower two panels). Residuals illustrate the quality of the fits.

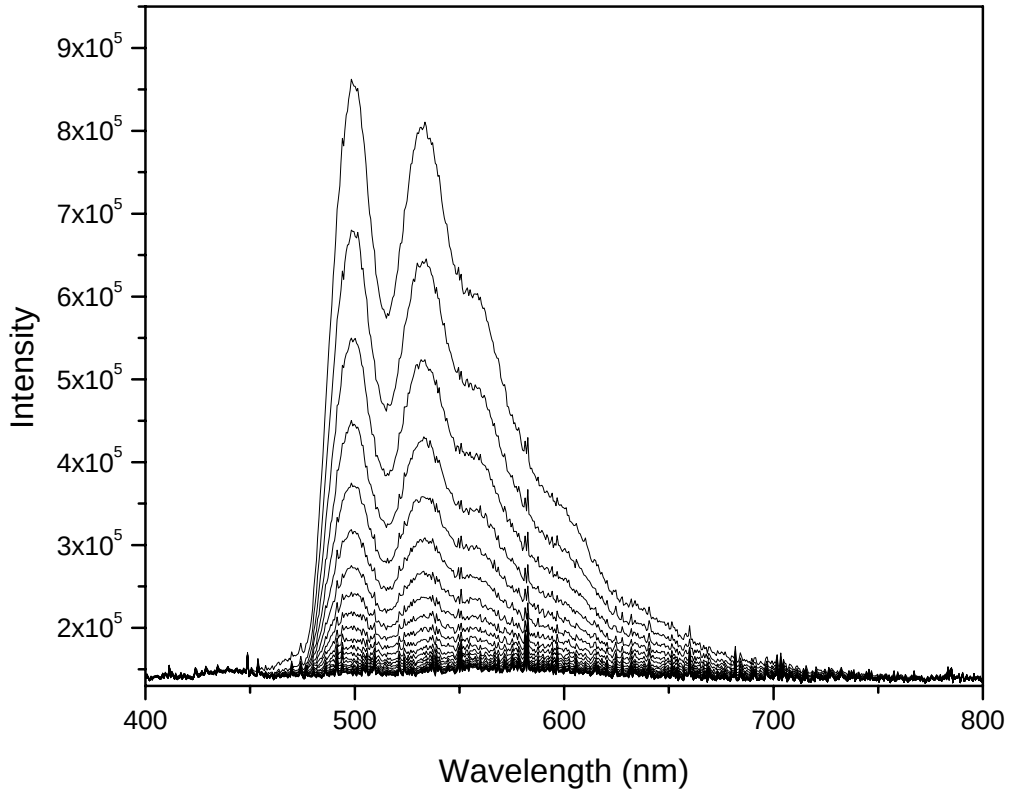


Figure S5. Time-resolved emission of **3** in EtOH:MeOH (4:1) at 77 K with λ_{ex} = 355 nm. The time delay between acquisitions is 20 μs with total elapsed time of 460 μs.

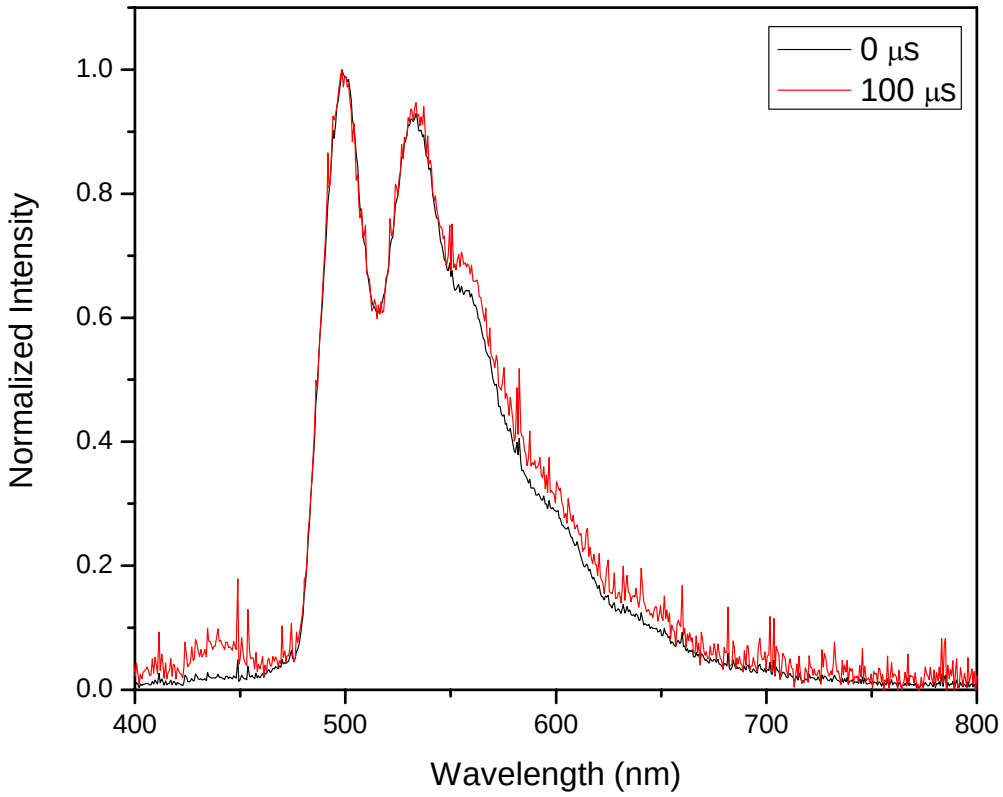


Figure S6. Normalized emission of **3** in EtOH:MeOH (4:1) at 77 K measured at 0 and 100 μs after the laser pulse, data from Figure S5, highlighting the constant spectral profile with time.

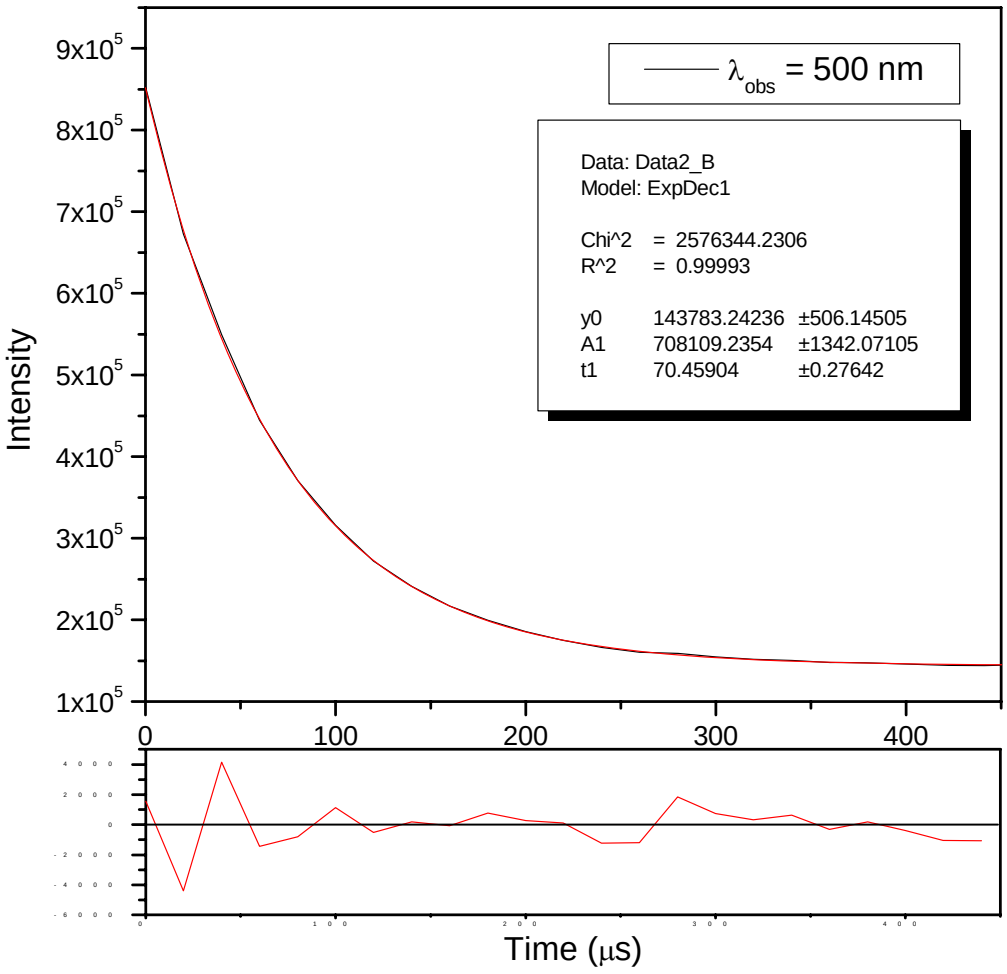
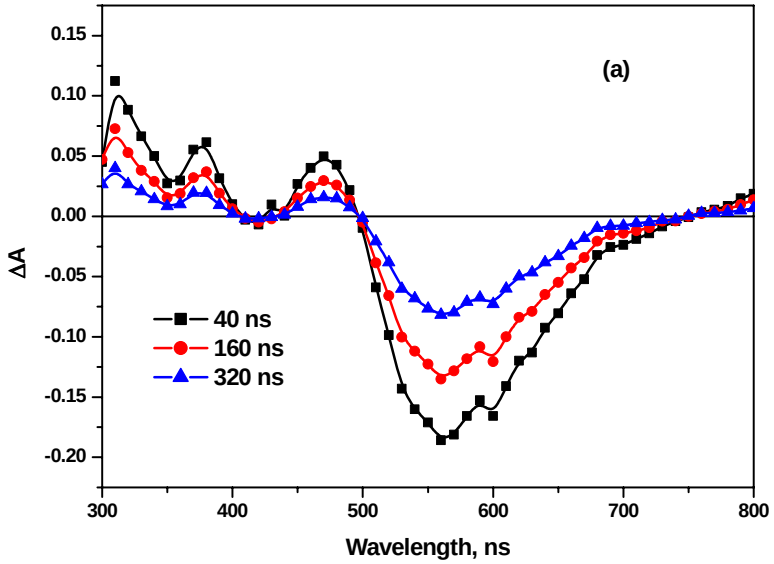
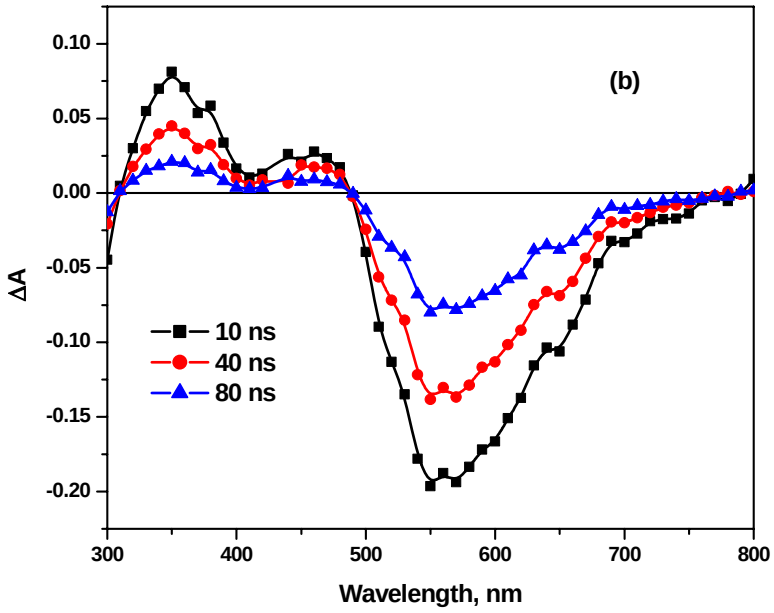


Figure S7. Single-wavelength trace (top) of the 77 K emission of **3** in a 4:1 EtOH:MeOH glass. Excitation conditions noted above in Figure S5. The red line is the single exponential fit to the experimental data, τ = 70.5 μs. Residuals (bottom) illustrate the quality of the fit.


(a)
ΔA
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
300
400
500
600
700
800
Wavelength, ns
40 ns
160 ns
320 ns


(b)
ΔA
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
300
400
500
600
700
800
Wavelength, nm
10 ns
40 ns
80 ns

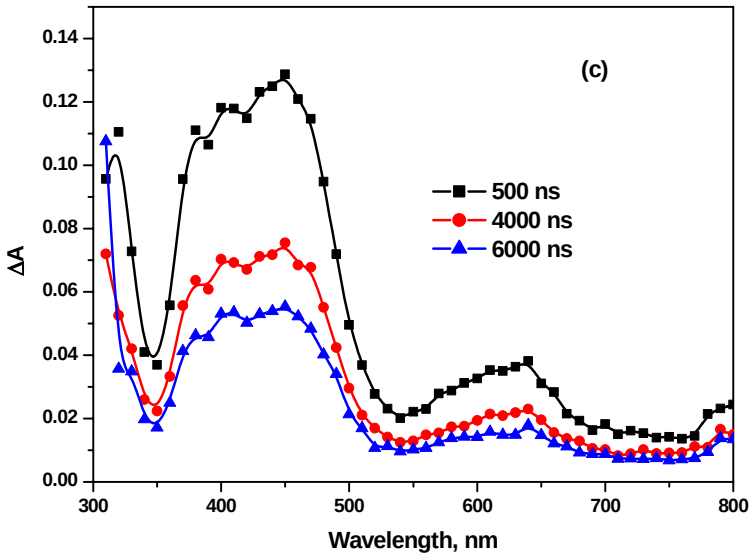


Figure S8. Nanosecond excited-state absorption spectra of **1** (a), **2** (b), and **3** (c) measured at the specified delay times in deaerated DMF. Spectra (a) and (b) were acquired following 430 nm excitation, while spectrum (c) was measured with 355 nm excitation. The apparent bleaching observed in (a) and (b) at long wavelengths are emission artifacts and do not represent transient absorption features in this region of the spectrum.

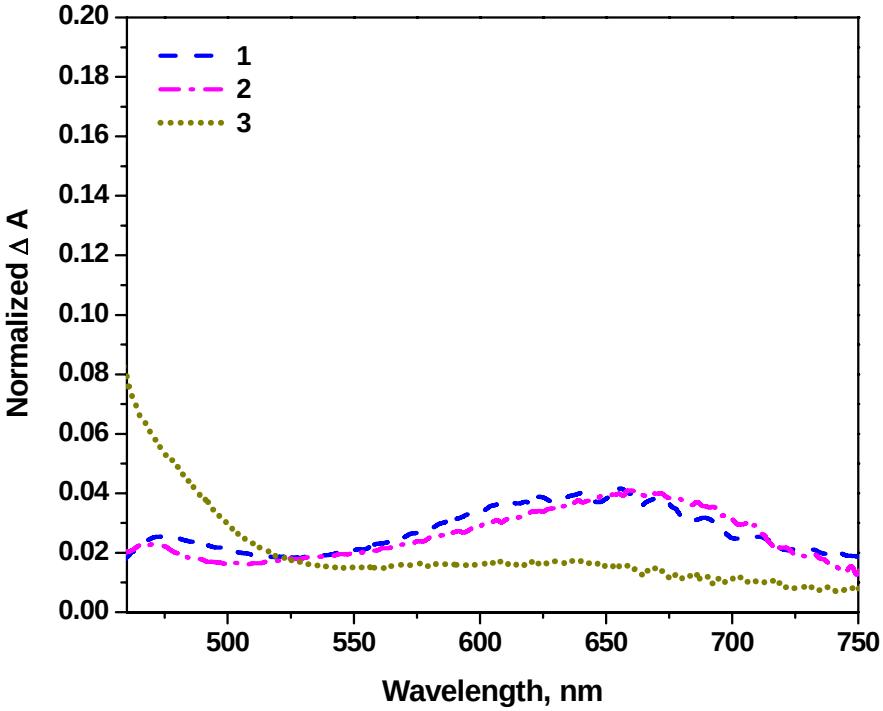


Figure S9. Normalized ultrafast transient absorption difference spectra of compounds **1** (delay time 923 ps), **2** (delay time 1129 ps), and **3** (delay time 958 ps) in DMF following a 150 fs, 340 nm excitation pulse.

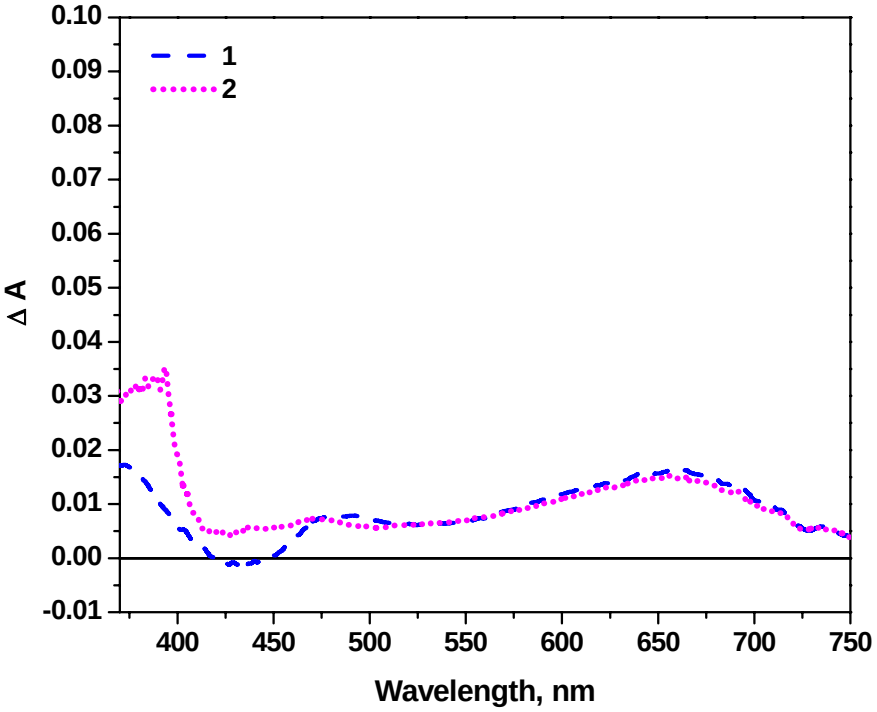


Figure S10. Normalized ultrafast transient absorption difference spectra of compounds **1** (delay time 935.5 ps) and **2** (delay time 1121 ps) in CH_2Cl_2 following a 150 fs 340 nm excitation pulse.

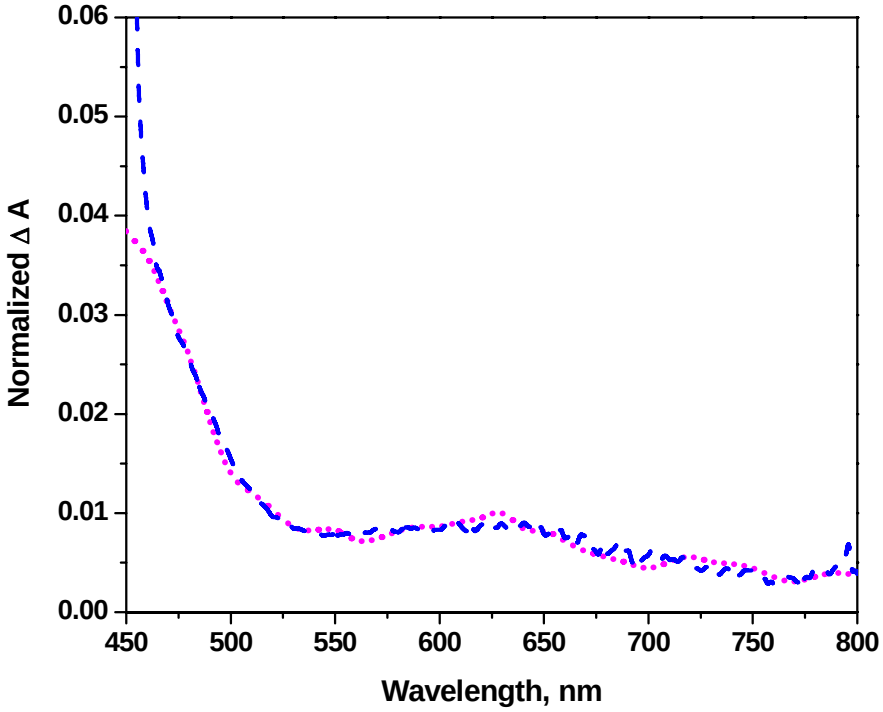


Figure S11. Normalized ultrafast and conventional transient absorption spectra of compound **3** in CH_2Cl_2 (dashed line = 837 ps delay time, 340 nm excitation pulse; short dot line = 200 ns delay time, 355 nm excitation pulse).