Supplementary Information:

Steady-state absorption

After the first absorption maximum (λ_{abs1}) a steep drop of absorption is observable towards higher wavelengths while a (approximately factor 200 weaker) absorption band around 420 nm remains in all solvents. Excitation of the weak absorption band does not differ in spectral structure and emits below excitation wavelength. This indicates a hot absorption at higher wavelengths than λ_{abs1} . This behavior is shown for PyA in DMSO exemplary in Figure S1.



Fig. S 1: Absorption and emission spectra ($\lambda_{exc.1}$ = 376 nm and $\lambda_{exc.2}$ = 421 nm) of PyA in DMSO to illustrate the existence of a hot absorption band in the ground state.



Fig. S 2: Excitation spectra of PyA in MeOH and DMSO. Normalized to the maximal intensity.



Fig. S 3: Time resolved measurements of PyA in protic (left side) and aprotic (ride side) solvents, sorted by permittivity for each solvent class (From high (top) to low ε_r (bottom)).



Figure S 4: Comparison of experimental PyA spectrum in DMSO and calculated lowest excited states. Calculated spectra have been shifted to fit the first experimental absorption peak.