SUPPORTING INFORMATION

Effect of Substitution on the Ultrafast Deactivation of the Excited State of Benzo[*b*]thiophene-arylamines

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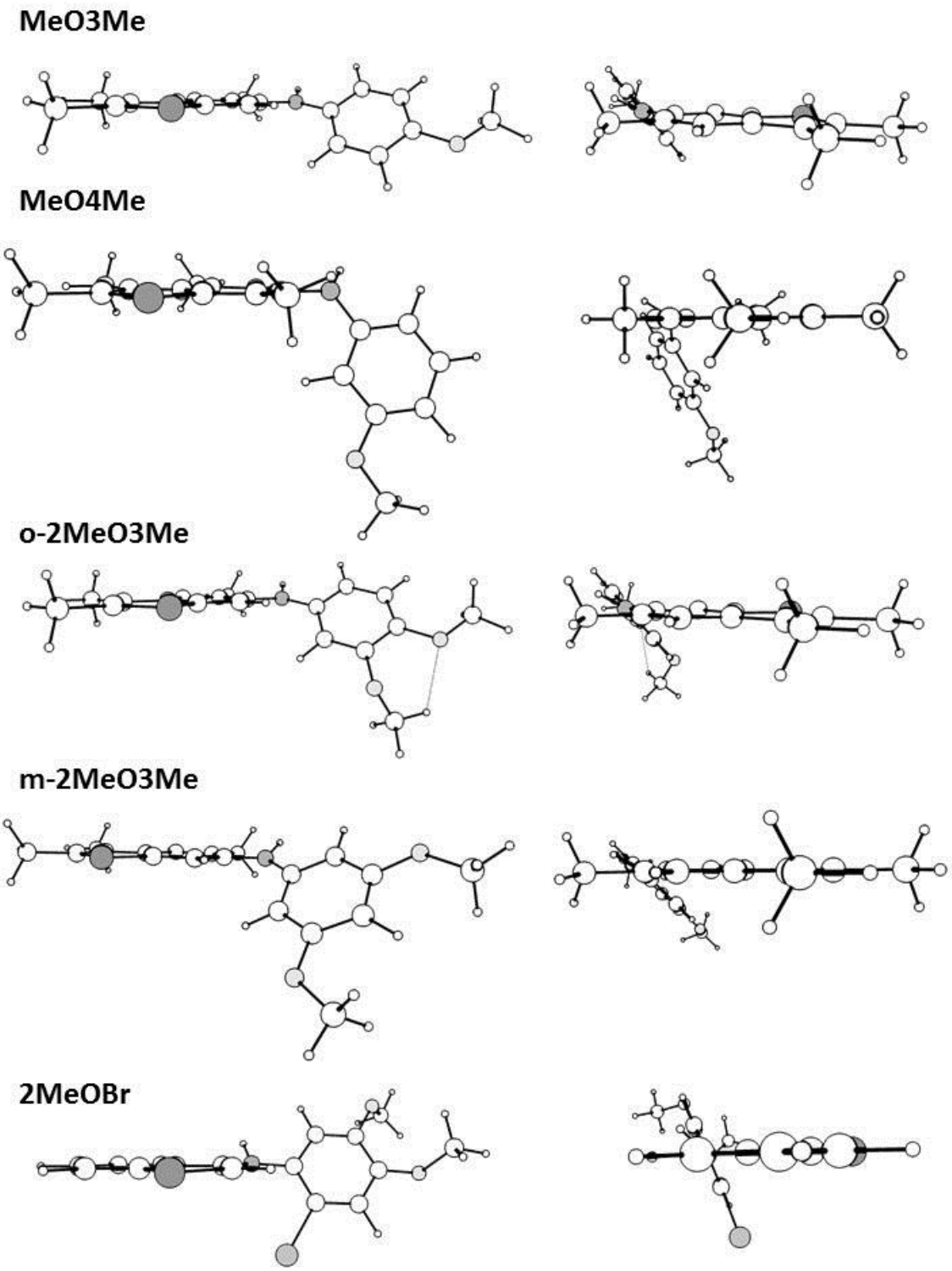

Figure S1- DFT//B3LYP/6-31G(d,p) optimized ground-state geometry for the investigated samples.

Table S1- Experimental absorption maxima obtained in ethanol solution together with the relevant computed absorption properties (predicted vertical excitation energies and associated orbitals transitions major contributions together with oscillator strengths, f, and absorption band gap, E_g) for the investigated diarylamines obtained by TD-DFT at the B3LYP/6-31G(d,p) level of theory after ground-state geometry optimization using the same functional and basis set.

Compound	$\lambda_{máx}^{S_0 \rightarrow S_n}$ **(nm)**	$\lambda_{máx}^{S_0 \rightarrow S_n}$ **calc. (nm)**	**Transition and orbitals major contributions**	**Osc. Strength, f**	**E_g (eV)**
2MeOBr	309	302	S0→S1, HOMO→LUMO (91%)	0.0946	4.61
MeO3Me	303	305, 312	S0→S1, HOMO→LUMO (73%); HOMO→L+1 (22%) S0→S2, HOMO→LUMO (22%); HOMO→L+1 (74%)	0.2573, 0.2791	4.43
MeO4Me	307	303	S0→S1, HOMO→LUMO (95%)	0.2792	4.60
o-2MeO3Me	303	298, 313	S0→S1, HOMO→LUMO (89%); HOMO→L+1 (7%) S0→S2, HOMO→L+1 (86%); HOMO→LUMO (8%)	0.1679, 0.3996	4.41
m-2MeO3Me	303	307	S0→S1, HOMO→LUMO (95%)	0.4623	4.48

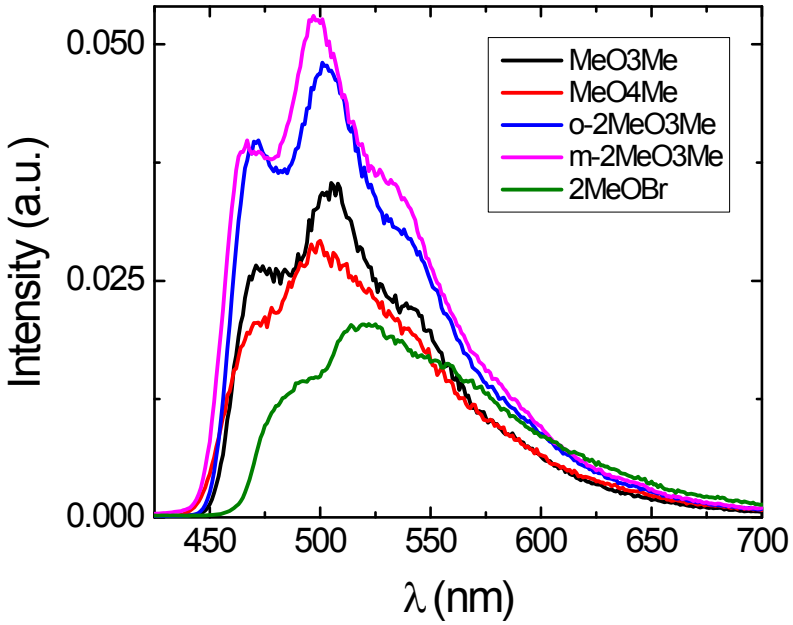

Figure S2- Phosphorescence emission spectra for the oligoanilines in ethanol solution at 77 K.

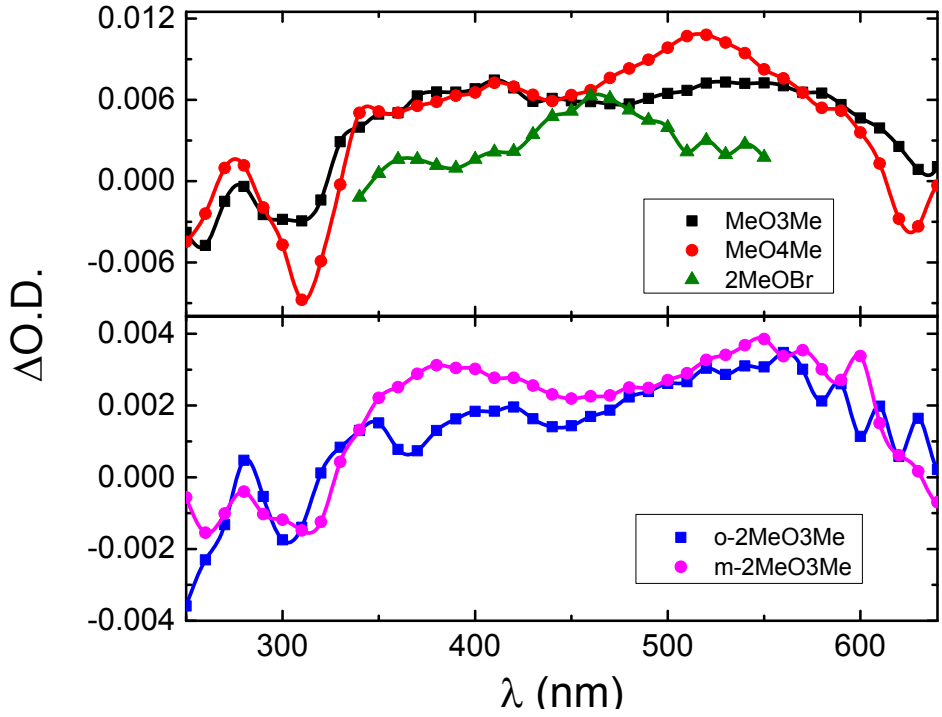

Figure S3- Room-temperature transient singlet-triplet difference absorption spectra for the oligoanilines in ethanol solution.

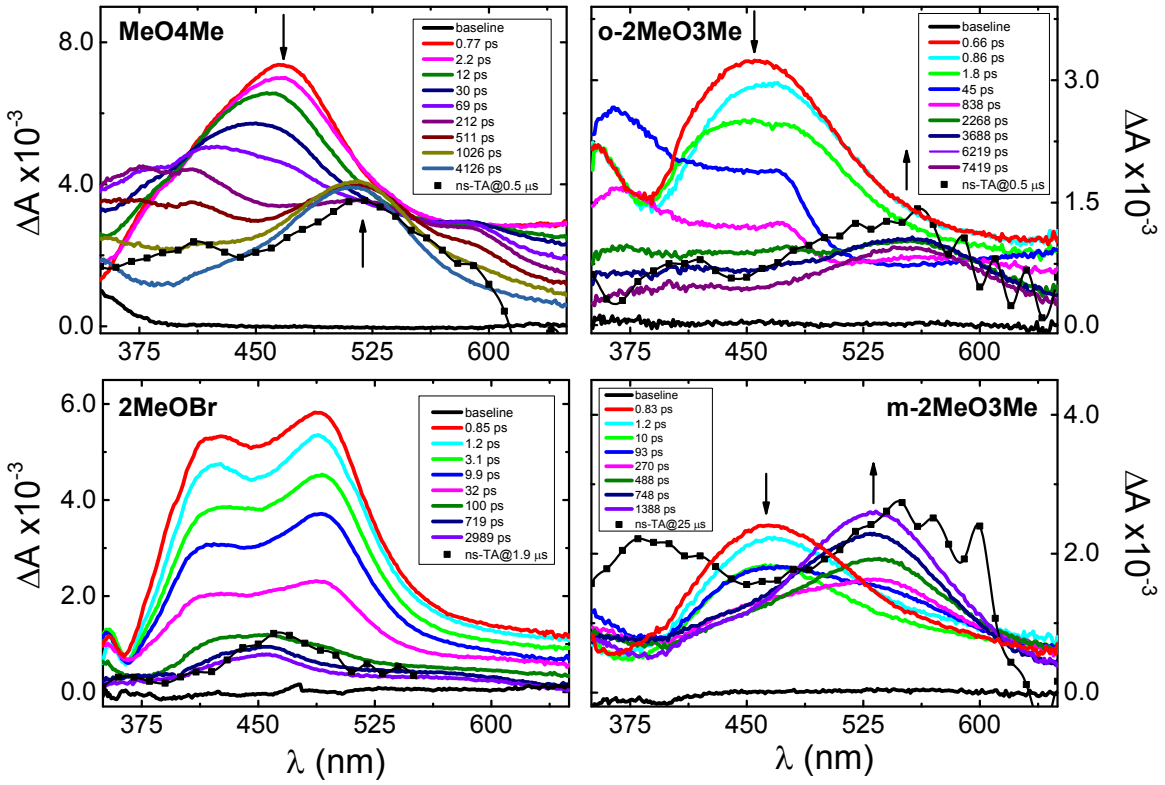

Figure S4- Time-resolved transient absorption data (collected in the fs-TA and in ns-TA spectrometers) for the investigated compounds in ethanol solution at room temperature. The vertical arrows indicate the direction of absorbance evolution.

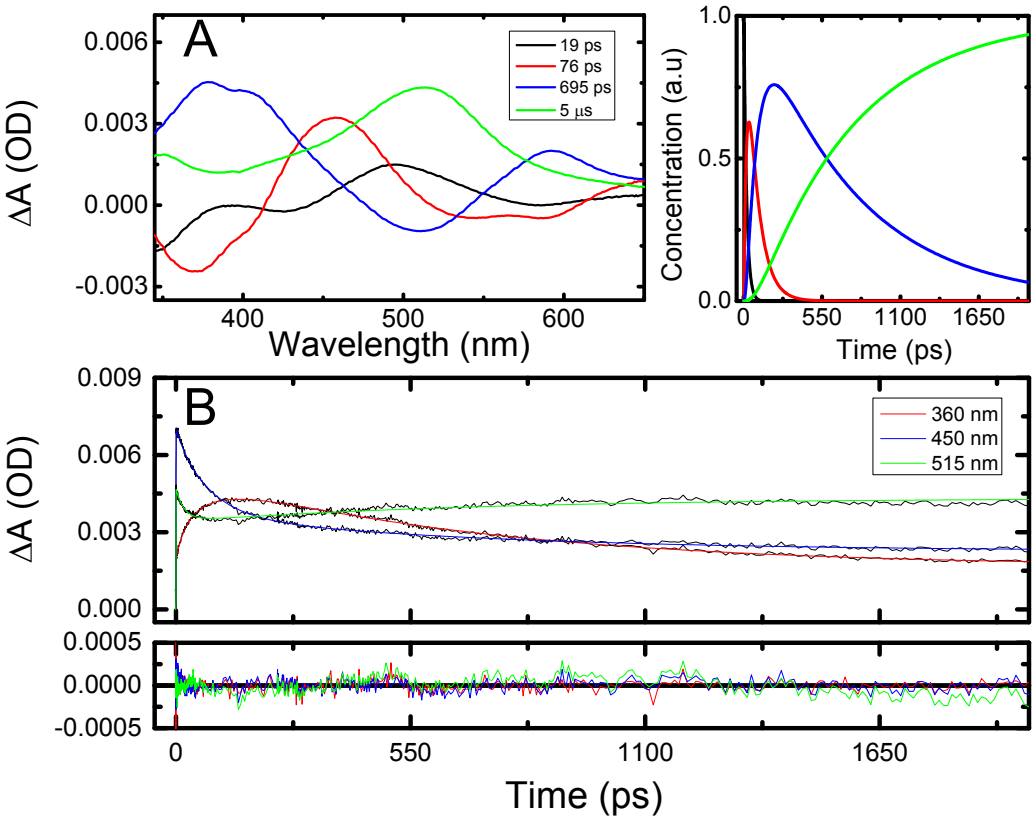

Figure S5-(A) Decay associated spectra (DAS) of the four time constants extracted from the time-resolved femtosecond transient absorption data (λ_{exc}= 310 nm) after SVD/global analysis together with the concentration profiles of the time constants for MeOMe in ethanol solution at 293 K; (B) representative kinetic traces with fits from the global analysis of the transient absorption data. The residuals are also presented for a better judgment of the quality of the fits.

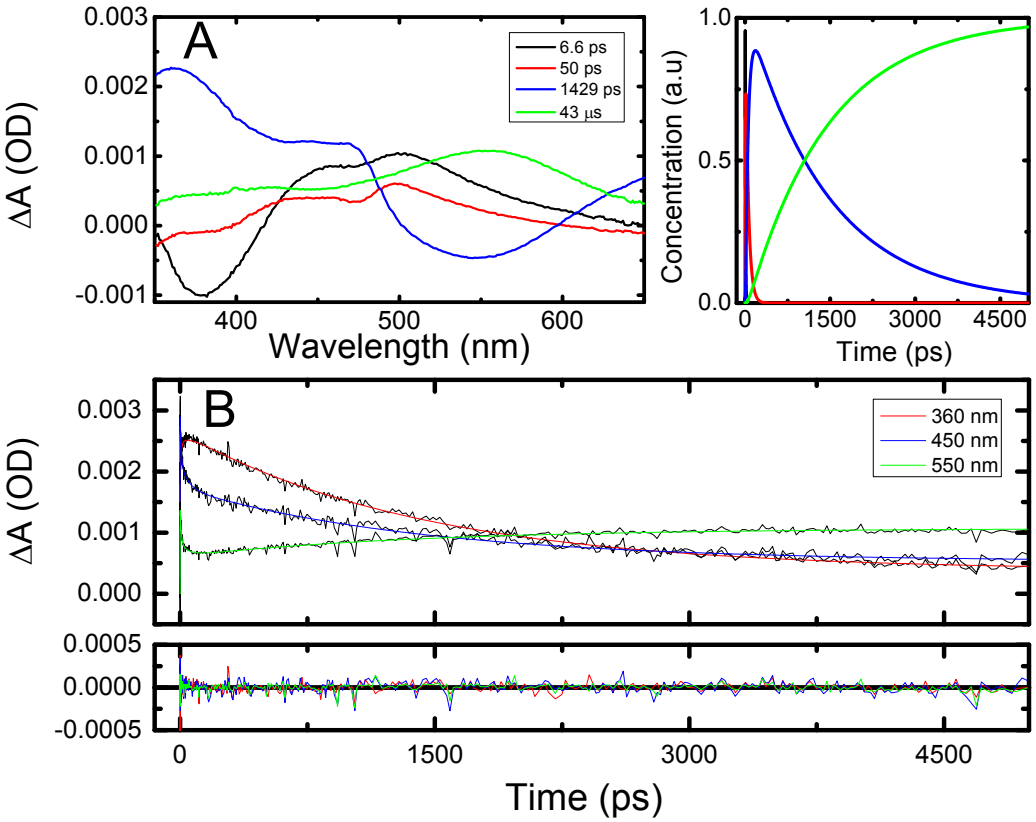

Figure S6- (A) Decay associated spectra (DAS) of the four time constants extracted from the time-resolved femtosecond transient absorption data (λ_{exc}= 310 nm) after SVD/global analysis together with the concentration profiles of the time constants for o-2MeO3Me in ethanol solution at 293 K; (B) representative kinetic traces with fits from the global analysis of the transient absorption data. The residuals are also presented for a better judgment of the quality of the fits.

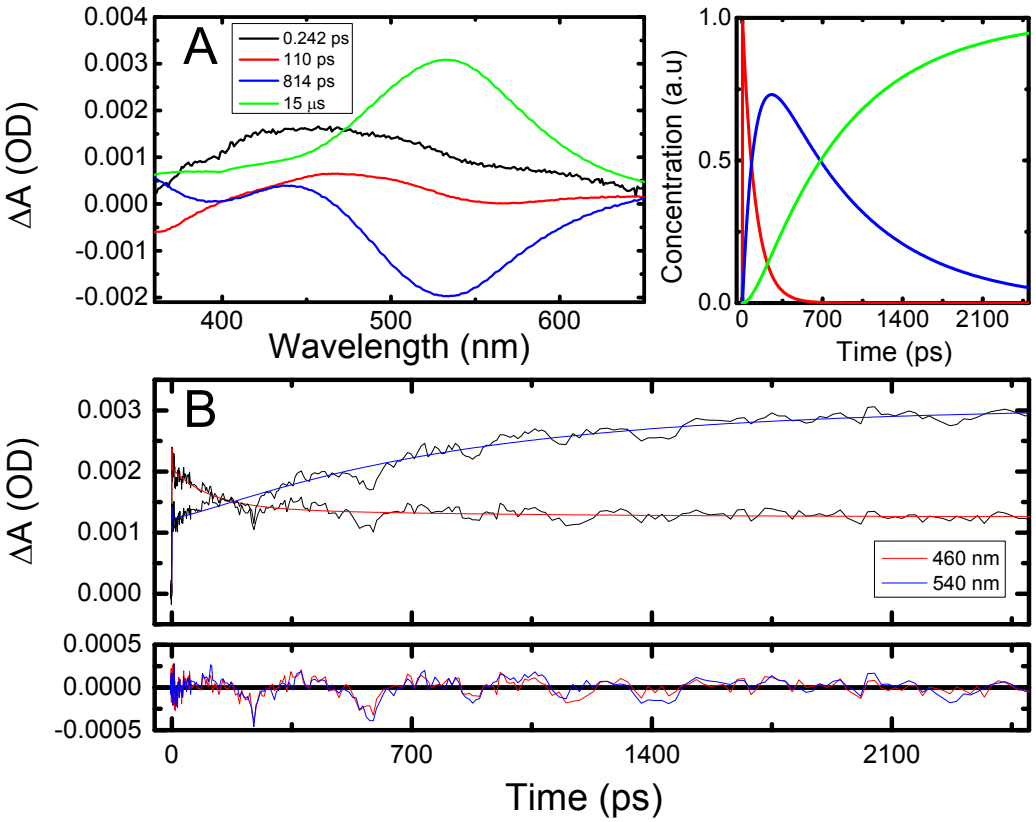

Figure S7- (A) Decay associated spectra (DAS) of the four time constants extracted from the time-resolved femtosecond transient absorption data (λ_{exc}= 310 nm) after SVD/global analysis together with the concentration profiles of the time constants for m-2MeO3Me in ethanol solution at 293 K; (B) representative kinetic traces with fits from the global analysis of the transient absorption data. The residuals are also presented for a better judgment of the quality of the fits.

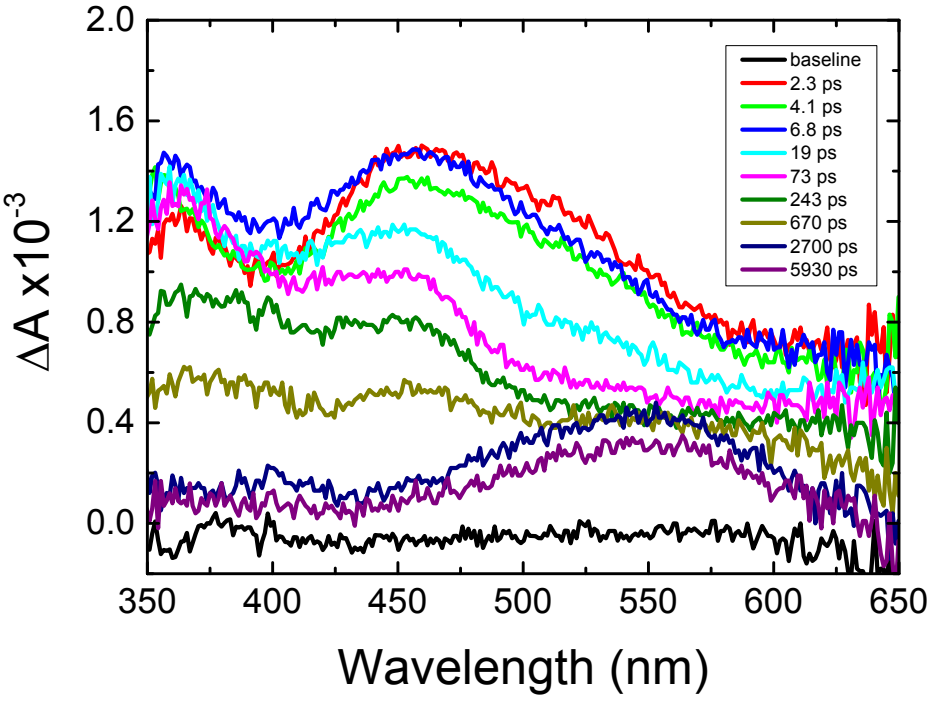

Figure S8- Room temperature time-resolved transient absorption data for MeO3Me collected with λ_{exc}= 315 nm in methanol:glycerol (50:50 v/v) mixture.

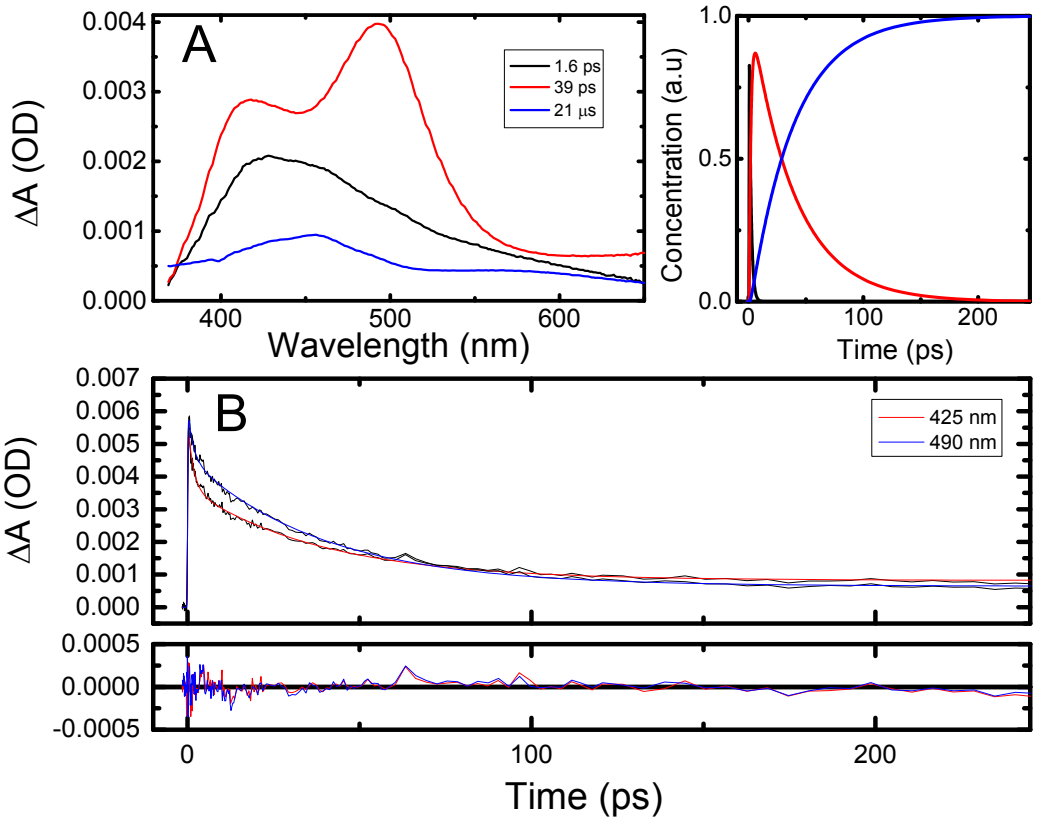

Figure S9- (A) Decay associated spectra (DAS) of the three time constants extracted from the time-resolved femtosecond transient absorption data (λ_{exc}= 310 nm) after SVD/global analysis together with the concentration profiles of the time constants for 2MeOBr in ethanol solution at 293 K; (B) representative kinetic traces with fits from the global analysis of the transient absorption data. The residuals are also presented for a better judgment of the quality of the fits.

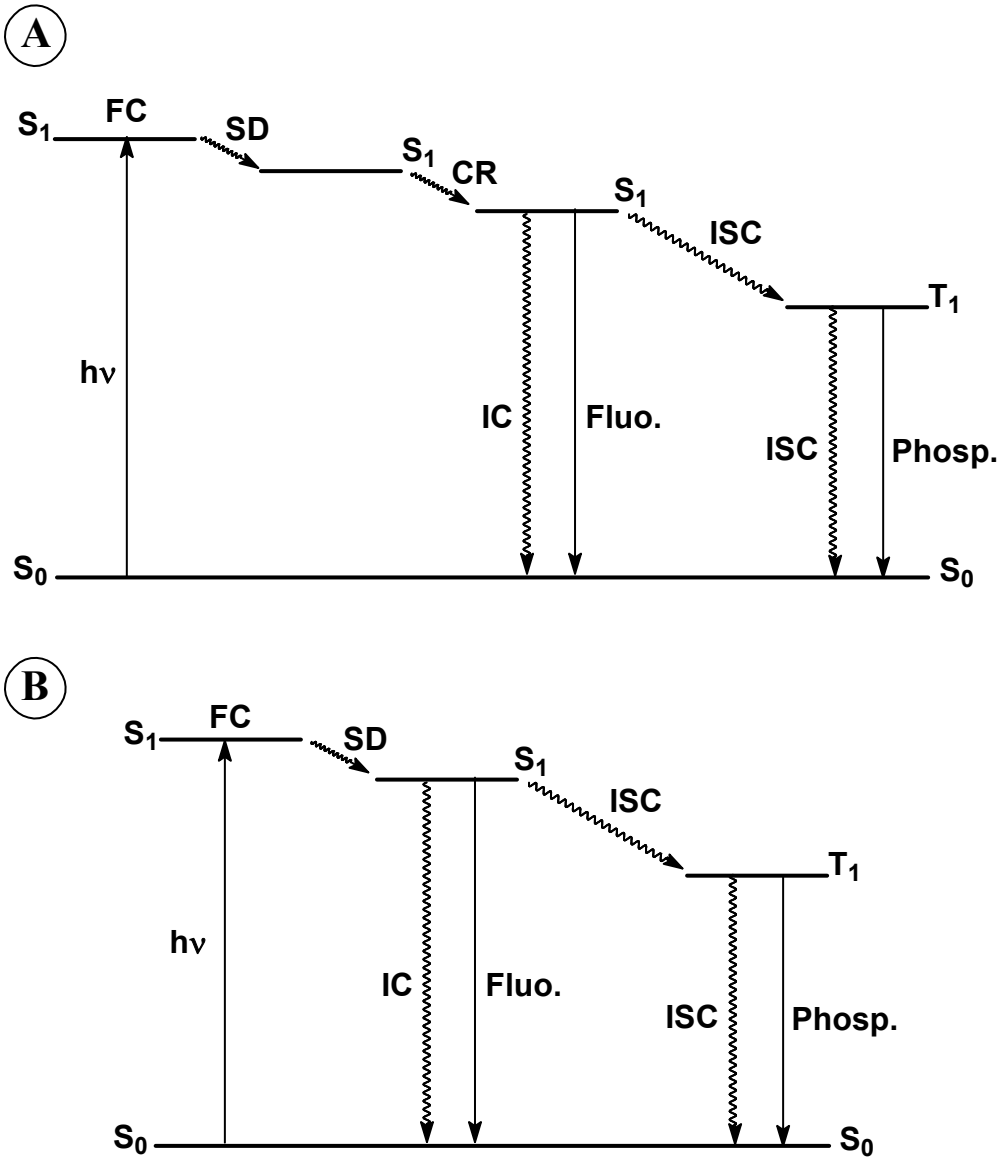

Figure S10- Scheme of the excited-state dynamics found for compounds (A) MeO3Me, MeO4Me, o-2MeO3Me, m-2MeO3Me and (B) 2MeOBr. FC- Franck−Condon state; SD- solvation dynamics, CR- conformational relaxation; ISC- intersystem-crossing; IC- internal conversion; Fluo.- fluorescence; Phosph.- phosphorescence