SUPPLEMENTARY INFORMATION

for

"Spectroscopic and photophysical studies of hydroquinone family of photochromic Schiff bases analyzed over 17 orders of magnitude time scale."

by

Marcin Ziółek, Gotard Burdziński, Katarzyna Filipczak,
Jerzy Karolczak, Andrzej Maciejewski

General remark to the figures:
all stationary spectra are presented in the linear scale with respect to the wavenumbers, while the time resolved spectra are presented in the linear scale with respect to the wavelength.

Table S1.
Parameters of the solvents studied (ε and n denote the dielectric constant and the refractive index of the solvent, respectively; π^*, α, β denotes the parameters of Kamlet-Taft scale[1] and SPP, SA and SB – of Catalan scale[2])

solvent	ε	n	α	β	π^*	SA	SB	SPP
PEN	1.80	1.3575	0.00	0.00	-0.15	0.000	0.073	0.507
HEX	1.88	1.3723	0.00	0.00	-0.11	0.000	0.056	0.519
HEXD	2.05	1.4325	0.00	0.00	0.08	0.000	0.086	0.578
CCl4	2.24	1.4570	0.00	0.10	0.21	0.000	0.044	0.632
ClP	8.60	1.3880	0.00	0.00	0.40	0.001	0.138	0.837
DEE	4.20	1.3495	0.00	0.47	0.24	0.000	0.562	0.694
ClF	4.89	1.4420	0.20	0.10	0.58	0.047	0.071	0.786
ACN	35.94	1.3410	0.19	0.40	0.66	0.044	0.286	0.895
EtOH	24.55	1.3594	0.86	0.75	0.54	0.400	0.658	0.853
MeOH	32.66	1.3265	0.98	0.66	0.60	0.605	0.545	0.857
TFE	26.67	1.2907	1.51	0.00	0.73	0.894	0.107	0.908
DMSO	46.45	1.4770	0.00	0.76	1.00	0.072	0.647	1.000

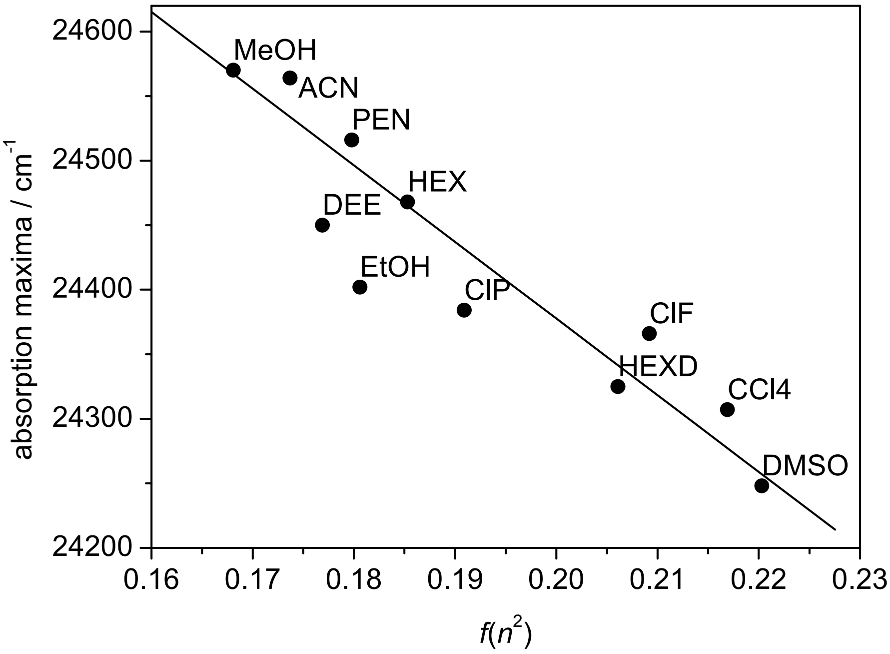


Fig. S1. Absorption maxima of $S_1 \leftarrow S_0$ (π,π^*) BPHMe enol state in different solvents versus the polarizability function. The solid line represents the linear fit (intercept=25570 cm^{-1}; slope=-6000 cm^{-1}; correlation coefficient r=-0.92).

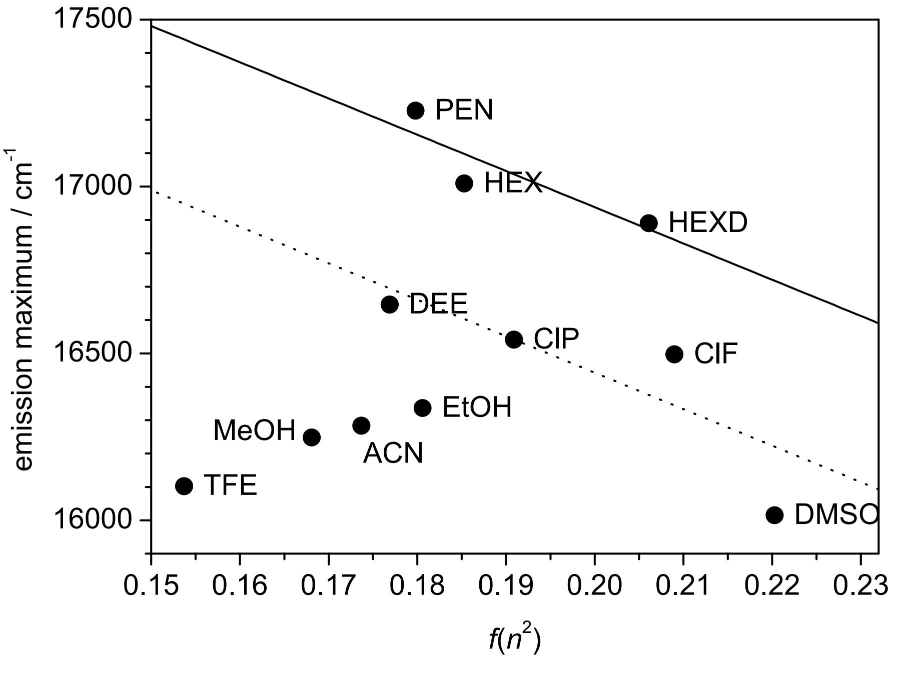


Fig. S2. Maxima of the BPHMe emission from keto S_1 (π,π^*) state in different solvents versus the polarizability function. The solid line represents the linear fit for hydrocarbons (slope= -11000 cm^{-1} intercept= 19100 cm^{-1}) and the dotted line the same slope for ClP.

Table S2.

Experimental stationary absorption and emission maxima (in cm^{-1}) of hydroquinone family of Schiff bases in the studied solvents. For BPHMe the short-wavelength maxima of the cis-keto emission are given (two Gaussian functions have been fitted in the spectrum range limited to about 2 500 cm^{-1} near the highest intensity of the emission profile).

solvent	BPHMe$_2$ absorption	BPHMe$_2$ emission	BPHMe absorption	BPHMe emission	BPH absorption
PEN	-	-	24 520	17 230	-
HEX	25 340	21 830	24 470	17 010	23 000
HEXD	25 290	22 230	24 330	16 890	22 950
CCl4	25 010	-	24 310	-	23 020
ClP	-	-	24 380	16 540	23 310
DEE	25 170	21 200	24 450	16 650	-
ClF	-	-	24 370	16 500	-
ACN	25 160	21 170	24 560	16 280	23 680
EtOH	25 030	21 200	24 400	16 340	-
MeOH	-	-	24 570	16 250	23 650
TFE	25 150	20 270	25 090	16 100	24 540
DMSO	24 730	20 860	24 250	16 020	-

The Onsager field theory application to BPHMe

The non-specific interactions of solute and solvent molecules cause a shift Δν of the emission/absorption maximum of the solute with respect to the gas phase. In terms of the Onsager field theory, the main contributions can be written in the following form for the absorption spectra (in CGS units):[3]

- dipole –dipole interactions:

$$\Delta\nu_{abs} = \frac{2\,\mu_0\,(\mu_0-\mu_1)}{h\,c\,a^3}\left[f(\varepsilon)-f(n^2)\right] \tag{S1}$$

- dipole of the solute – induced dipole of the solvent:

$$\Delta\nu_{abs} = \frac{(\mu_0^2-\mu_1^2)}{h\,c\,a^3}\,f(n^2) \tag{S2}$$

- induced dipole of the solute – induced dipole of the solvent (dispersion interactions):

$$\Delta\nu_{abs} = \frac{3\,(\alpha_1-\alpha_0)}{2\,h\,c\,a^3}\left(\frac{J_{solute}\,J_{solvent}}{J_{solute}+J_{solvent}}\right)\left(\frac{n^2-1}{n^2+2}\right) \tag{S3}$$

where: h is Planck constant, c – speed of light , a – Onsager cavity radius, J – ionization potential, μ_i and α_i – dipole moment and polarizability of the solute molecule in its ground (i=0) or first excited state (i=1) and the polarity function $f(\varepsilon)$ and polarizability function $f(n^2)$ are used in the following form:[4]

$$f(\varepsilon) = \frac{\varepsilon-1}{2\,\varepsilon+1}, \tag{S4}$$

$$f(n^2) = \frac{n^2-1}{2\,n^2+1}, \tag{S5}$$

where ε and n denote the dielectric constant and the refractive index of the solvent, respectively. In eq. (S3) the representation of the polarizability function different to eq. (S5) is used but note that $f(n^2) \approx 0.61\ (n^2\text{-}1)/\ (n^2+2)$ in the whole range of n of the solvents studied. For the emission maximum, the indexes for the dipole moments and polarizabilities have to be exchanged in eqs (S1) to (S3).

The absorption properties of the enol form of BPHMe will be discussed first. The lack of any correlation between Δν and $f(\varepsilon)$ or ($f(\varepsilon)$ - $f(n^2)$) indicates that the dipole moment in the ground state is close to zero,[4] μ_0=0 (or the dipole moments are similar enough in the S_0 and S_1 state). Good linear correlations between Δν and $f(n^2)$ (see Fig. S1) suggest that eq. (S2) or (S3) should hold (which means that main contribution to the solvatochromic shift comes from the induced dipole interaction and/or dispersion interaction). From the slope of the fitted linear function in Fig. S1 the dipole moment in the S_1 state can be estimated to be μ_1=12 D from eq. (S2) (when only induced dipole interactions are considered) or the increase in the polarizability in S_1 state is equal (α_1-α_0)=2.5 Å^3 from eq. (S3) (when only the dispersion interactions are assumed). Since such change in the dipole moment as 12 D, seams rather improbable for BPHMe (the charge distribution should be changed rather locally since the $S_1 \leftarrow S_0$ (π,π*) excitation of Schiff bases is of local character within the salicylideneamine chromophore), the main contribution should come from the dispersion interactions. For the calculations, two rough approximations have been made: the cavity radius for BPHMe was assumed (from similar systems) to be a=5 Å and the ionization potential was taken for both solute and solvent as J= 10 eV.

The absorption maxima of BPHMe can be also compared to the recently reported empirical solvent polarizability scale (SP).[5] In such a case the correlation coefficient is r=-0.81, which means that the correlation with SP scale is worse than with $f(n^2)$ given by eq. (S5).

The emission of the keto form of BPHMe exhibits the bathochromic shift with increasing both $f(\varepsilon)$ and $f(n^2)$ values. The slope of the plot of $\Delta\nu_{em}$ versus $f(n^2)$ for hydrocarbons with ($f(\varepsilon)$ - $f(n^2)$)=0 (see Fig. S2) shows the contribution of the induced dipole and/or dispersion interactions. Thus, eq. (S2) with the same approximations as the above, leads to the following expression:

$$\mu_1^2 - \mu_0^2 = x\,244\,[\mathrm{D}^2], \qquad \text{(S6)}$$

where x denotes the contribution of the induced dipole interactions (the rest (1-x) denotes the dispersion interaction). On the other hand, the maximum emission in ClP (with only non-specific interactions) is displaced in Fig S2 from the solid line for hydrocarbons by about 500 cm^{-1} which describes the contribution of dipole-dipole interactions for ($f(\varepsilon)$ - $f(n^2)$)=0.227 (for ClP). Therefore, from eq. (S1) a second expression involving dipole moments in excited and ground states of the keto form can be obtained:

$$\mu_1(\mu_1 - \mu_0) = 27\,[\mathrm{D}^2]. \qquad \text{(S7)}$$

Eq. (S6) and (S7) can be solved together only when x<0.2. Thus, in the dependence of emission maximum of BPHMe on the polarizability function the main contribution (80 % or more) comes from the dispersion interactions and eq. (S3) estimates the change in the polarizability of the keto tautomer equal $\Delta\alpha \geq 3$ Å^3.

References:

1 R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 2886.
2 J. Catalán, in G. Wypych (Ed.), *Handbook of Solvents*, ChemTec Publishing, Toronto, 2001, p. 583.
3 P. Suppan and N. Ghoneim, *Solvatochromism*, The Royal Society of Chemistry, Cambridge, 1997.
4 A. S. Klymchenko and A. P. Demchenko, *Phys. Chem. Chem. Phys.*, 2003, **5**, 461.
5 J. Catalán and H. Hopf, *Eur. J. Org. Chem.*, 2004, 4694.

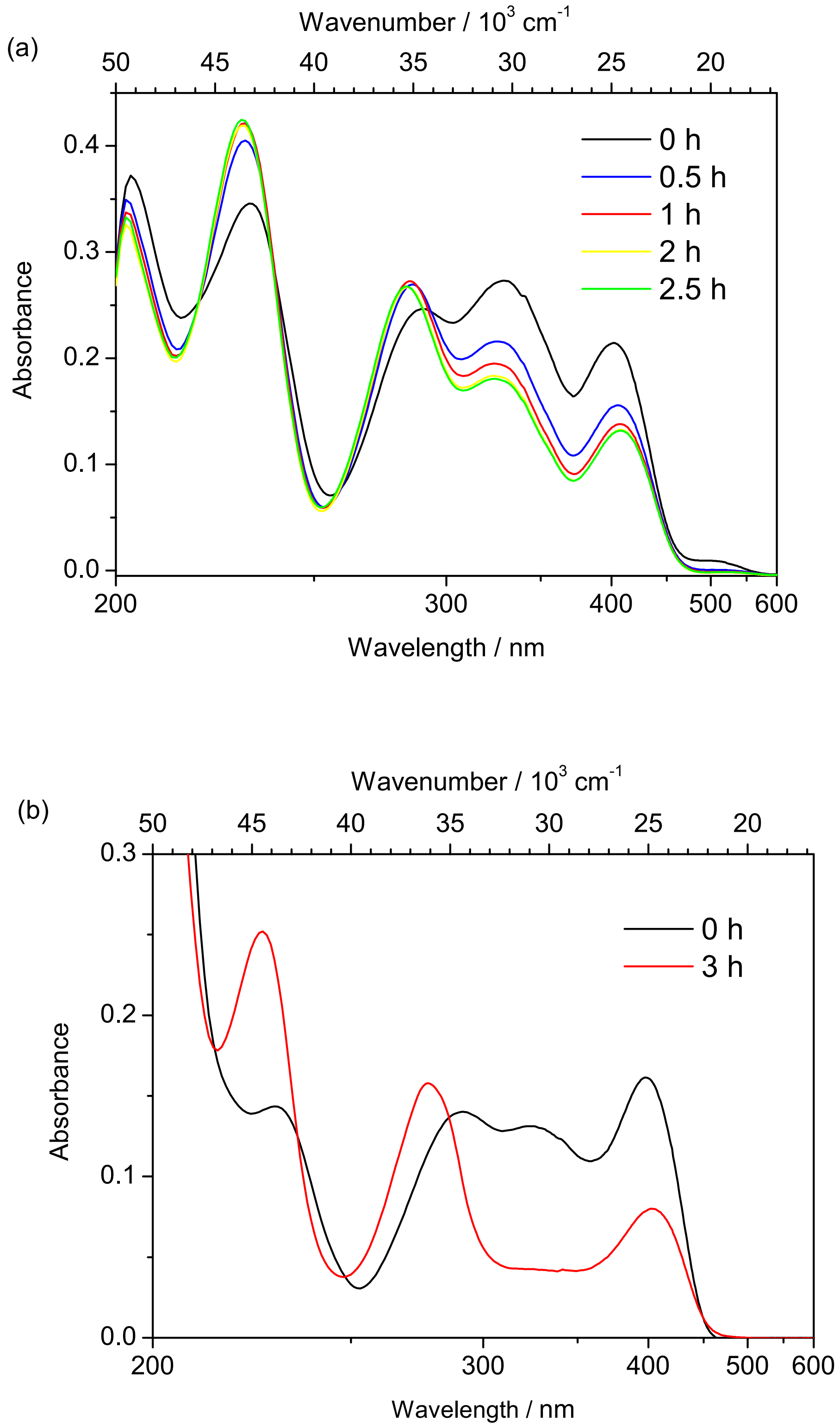


Fig. S3. Absorption changes (in hours) of BPHMe (a) and BPHMe$_2$ (b) in TFE.

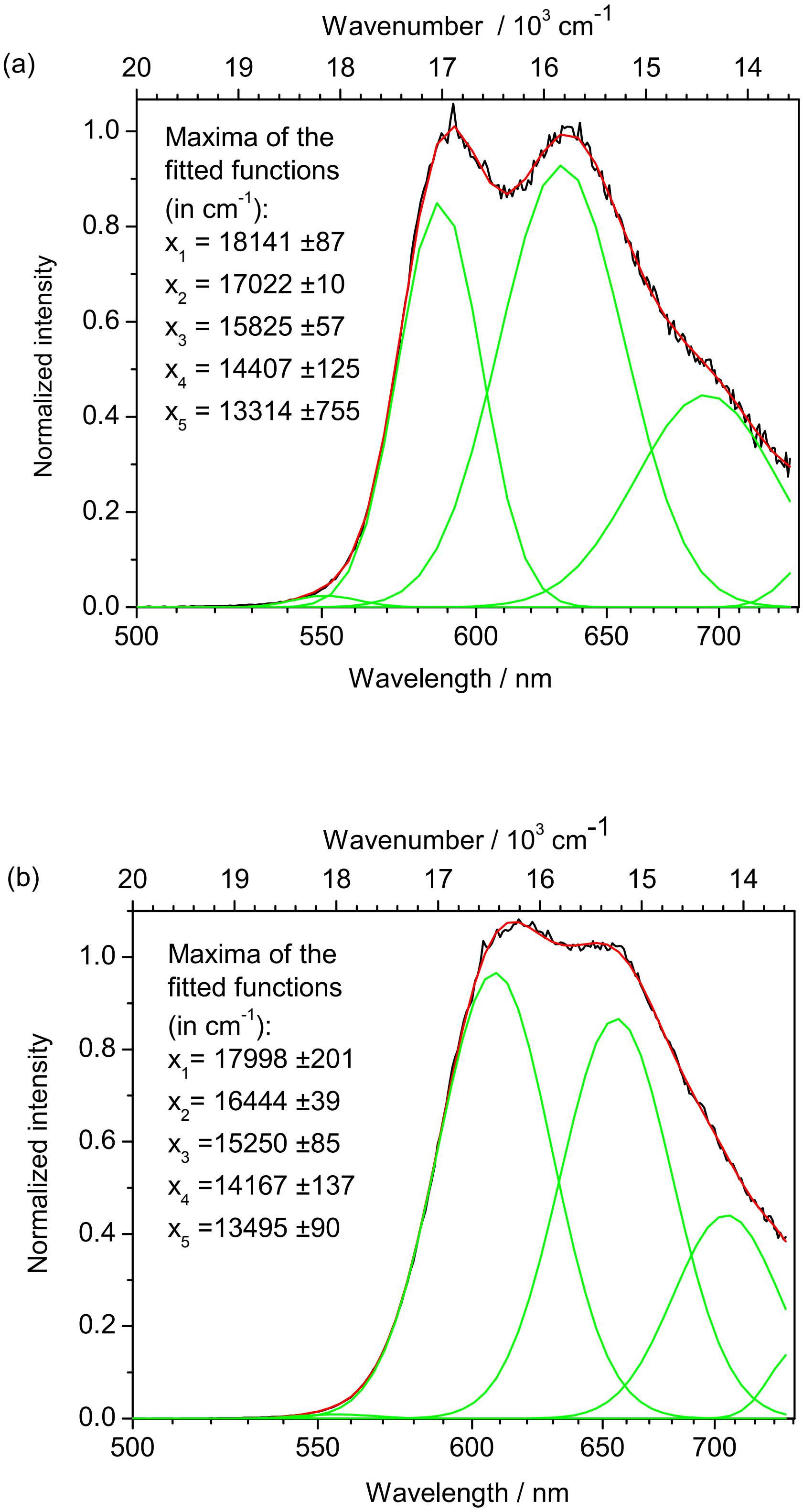


Fig. S4. Emission spectra of BPHMe in HEX (a) and ClP (b) fitted with the sum of 5 Gausian functions (with maxima indicated as insets). Black line – experimental data, green line – particular fitted functions, red line – sum of the fitted functions.

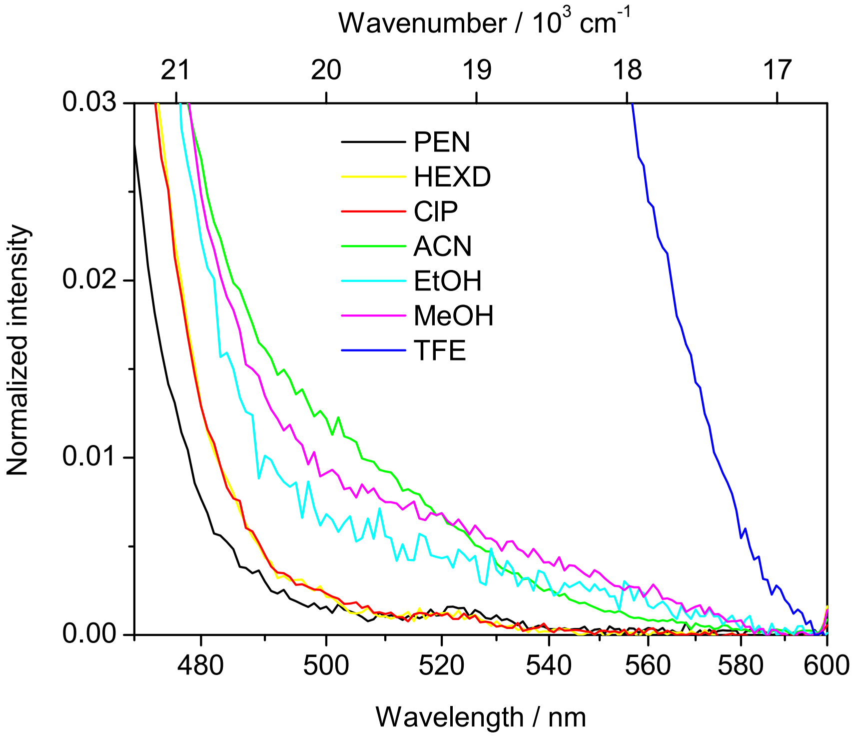


Fig. S5. Long-wavelength part of the fluorescence excitation spectra of BPHMe in different solvents (λ_{em}=620 nm).

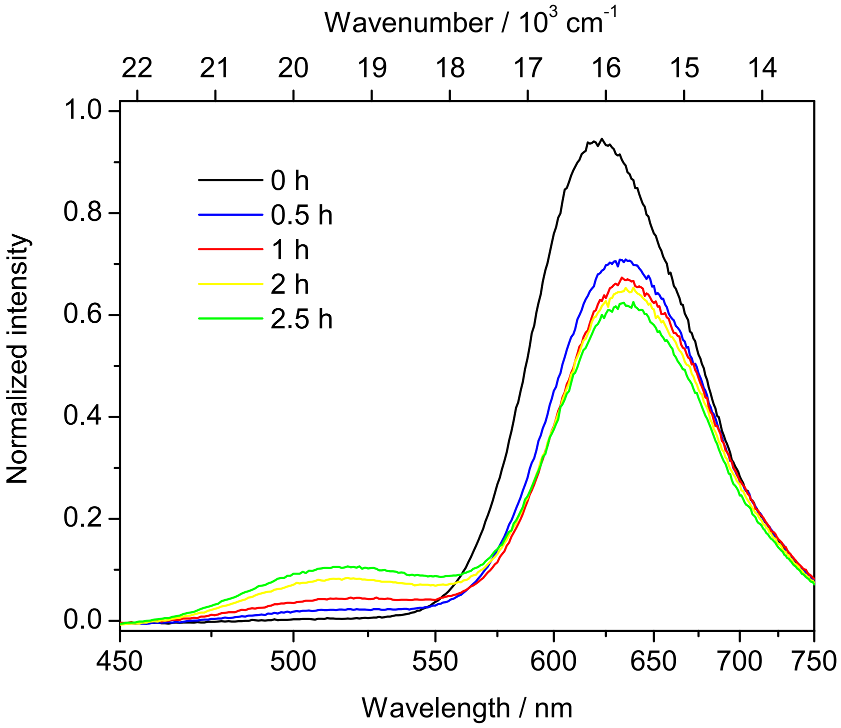


Fig. S6. Emission spectra changes (in hours) of BPHMe in TFE (excitation at 360 nm).

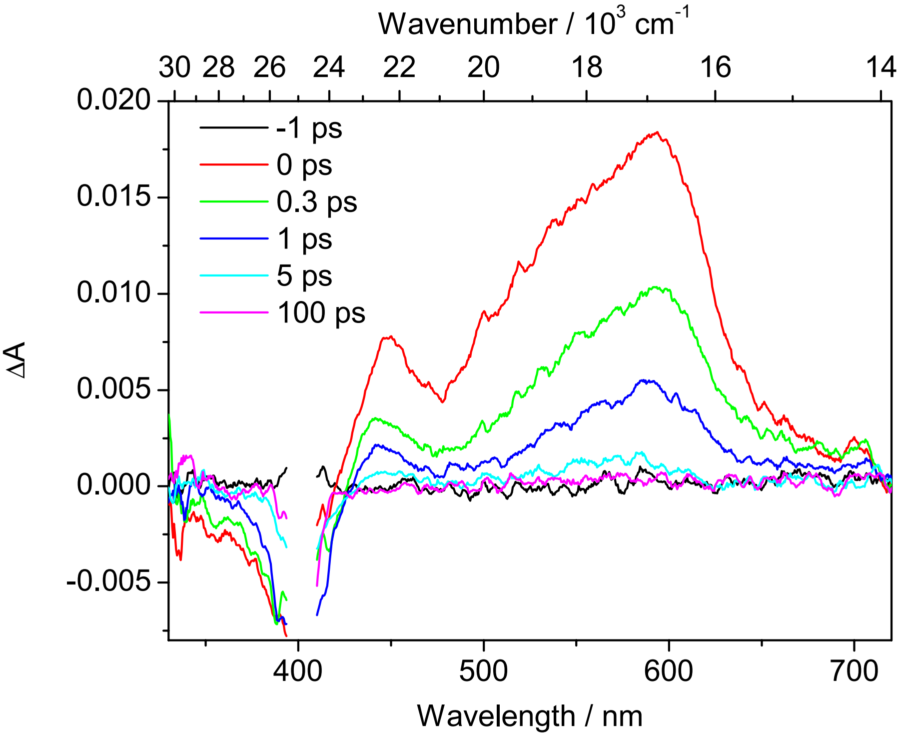


Fig. S7. Transient absorption spectra of $BPHMe_2$ in MeOH for selected pump-probe delay times (the spectral range near 400 nm is excluded due to the pumping beam scattered in the direction of detection).

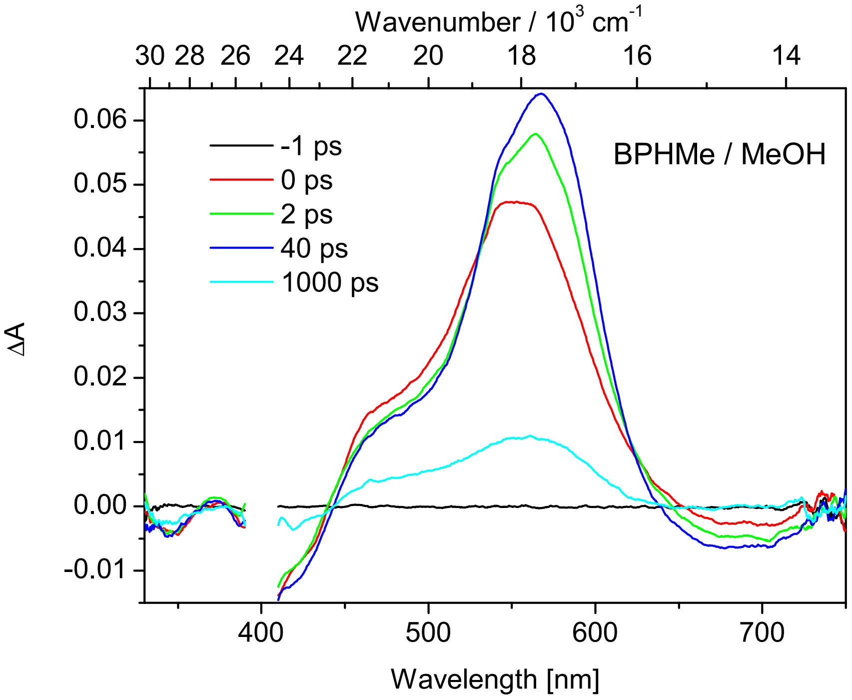


Fig. S8. Transient absorption spectra of BPHMe in MeOH for selected pump-probe delay times (the spectral range near 400 nm is excluded due to the pumping beam scattered in the direction of detection).

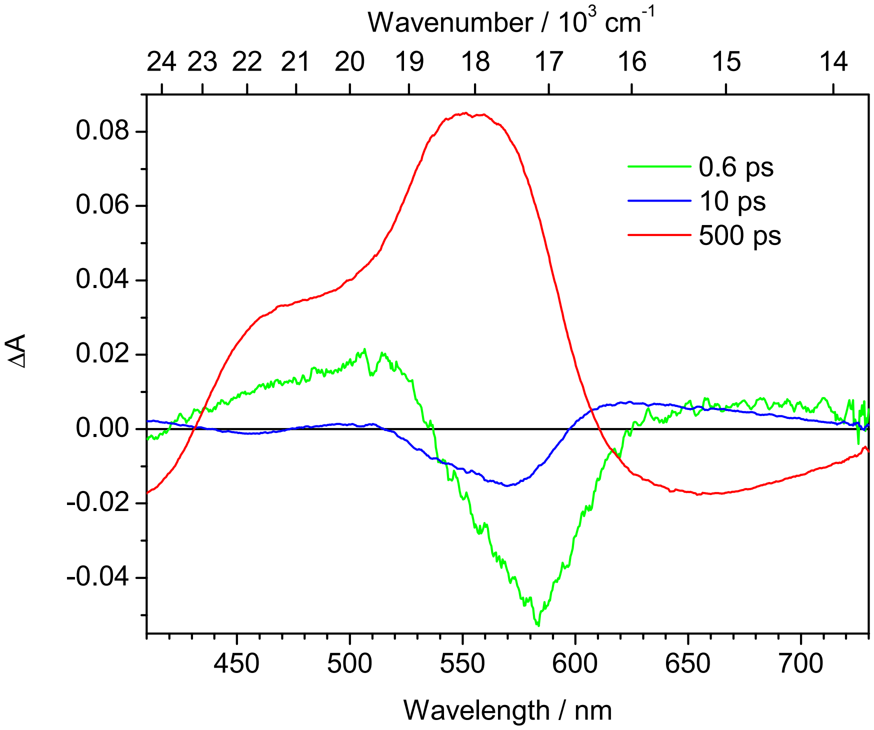


Fig. S9. Decay associated spectra of BPHMe in ACN (temporal range: 0.4-100 ps) obtained in the global analysis with 3 exponential fit (amplitudes of the time constants: 0.6 ps, 10 ps and 500 ps=const.). The positive values of the amplitude means a decay and the negative values – the rise of the transient absorption signal.

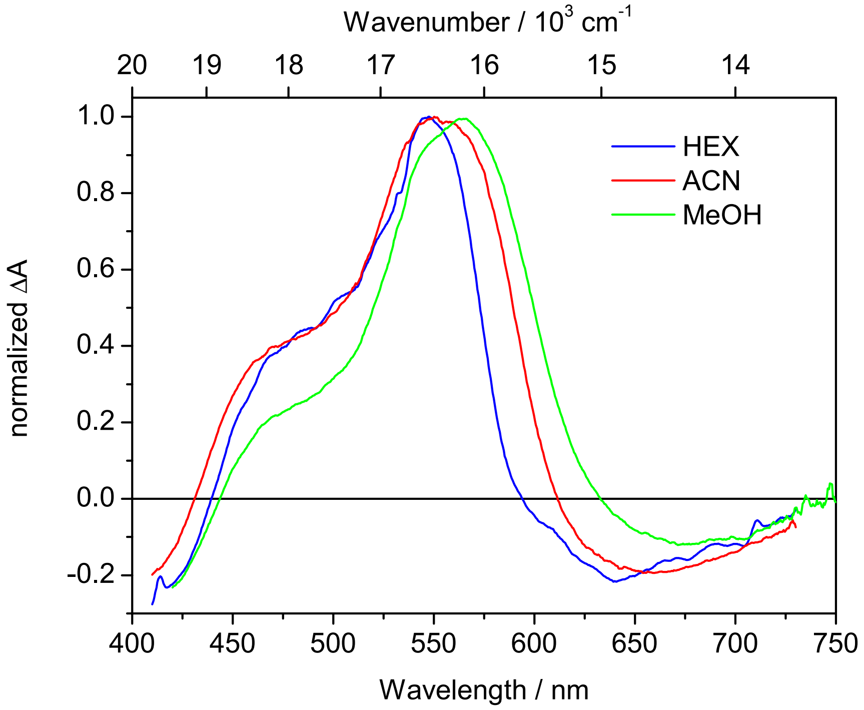


Fig. S10. Comparison of the transient absorption spectrum of the cis-keto tautomer of BPHMe (mean of the spectra measured for time delays between 15 and 40 ps) in different solvents.

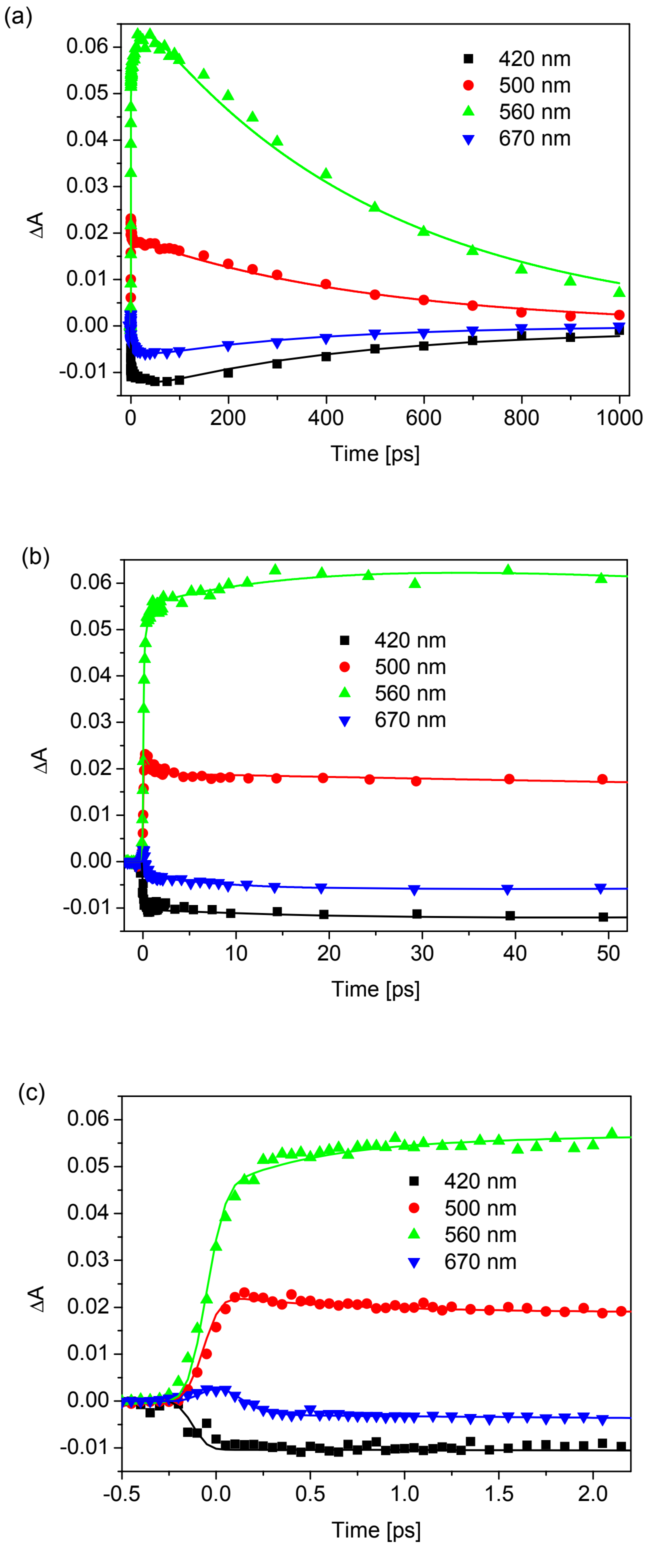


Fig. S11. Transient absorption kinetics of BPHMe in MeOH for selected wavelength (symbols) together with the fitted instrumental function convoluted with exponential functions (solid lines) with the following parameters: **420nm**: $A_1 = 0.004$; $\tau_1 = 30$ ps; $A_2 = -0.014$; $\tau_2 = 420$ ps; $A_0 = -0.002$; **500nm**: $A_1 = 0.003$; $\tau_1 = 700$ fs; $A_2 = 0.019$; $\tau_2 = 490$ ps; $A_0 = 0.001$; **560 nm**: $A_1 = -0.008$; $\tau_1 = 500$ fs; $A_2 = -0.014$; $\tau_2 = 20$ ps; $A_3 = 0.069$; $\tau_3 = 490$ ps; $A_0 = 0.002$; **670 nm**: $A_1 = 0.005$; $\tau_1 = 80$ fs; $A_2 = 0.001$; $\tau_2 = 500$ fs; $A_3 = 0.003$; $\tau_3 = 20$ ps; $A_4 = -0.006$; $\tau_4 = 350$ ps; $A_0 = 0.000$.

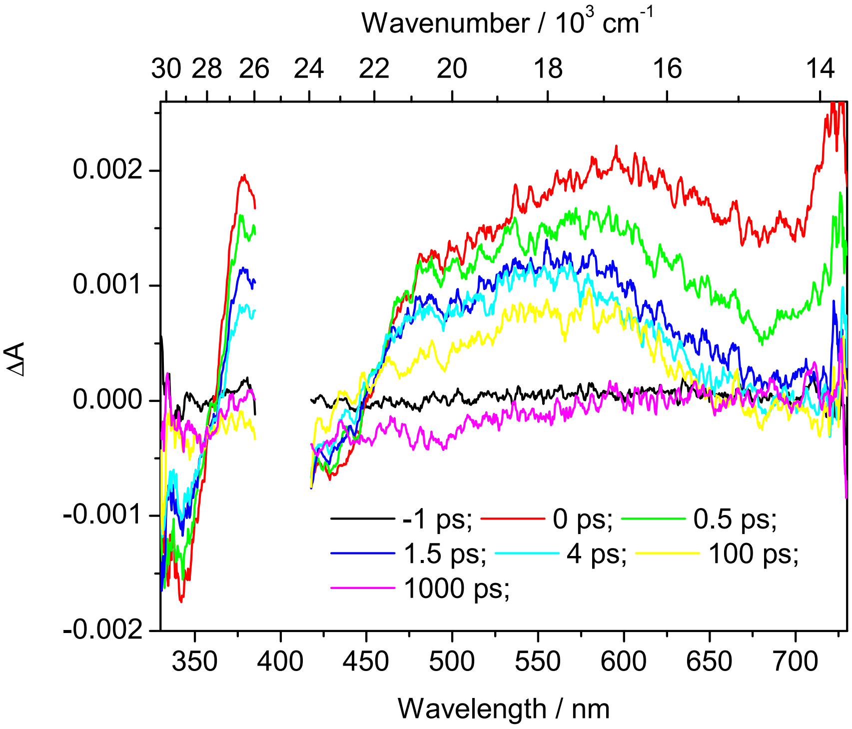


Fig. S12. Transient absorption spectra of BPH in MeOH for selected pump-probe delay times (the spectral range near 400 nm is excluded due to the pumping beam scattered in the direction of detection).

Table S3.

A summary of kinetic parameters obtained by TCSPC for the fluorescence of BPHMe in different solvents. The sum of the amplitudes of decay components (positive amplitudes) is normalized to 1.

HEX:

λ [nm]	a_1	τ_1 [ps]	a_2	τ_2 [ps]	a_3	τ_3 [ps]	χ^2
460	1.00	< 1	<0.01	190	<0.01	980	1.18
500	1.00	<1	<0.01	260	<0.01	930	1.02
550			0.70	293	0.30	67	1.18
586	-0.87	13	0.89	288	0.11	43	1.04
633	-0.92	13	0.93	288	0.07	54	1.05
700	-0.96	21	0.59	289	0.41	36	1.17
750	-0.89	18	0.82	293	0.18	69	1.19

MeOH:

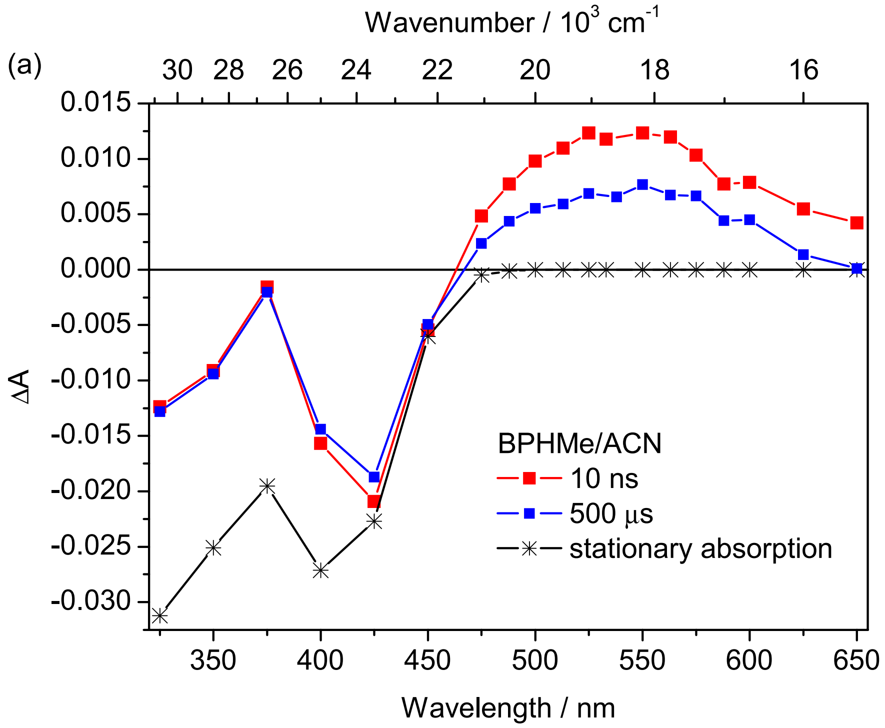
λ [nm]	a_1	τ_1 [ps]	a_2	τ_2 [ps]	a_3	τ_3 [ps]	χ^2
470	0.92	< 1			0.08	11	1.71
520	0.96	<1			0.04	15	1.77
570			0.62	352	0.38	46	1.03
620	-0.26	12	0.82	362	0.18	63	1.15
670	-0.83	9	0.81	360	0.19	54	1.05
720	-0.89	9	0.81	362	0.19	56	0.97
750	-1.00	13	0.65	360	0.35	35	1.09

ClP:

λ [nm]	a_1	τ_1 [ps]	a_2	τ_2 [ps]	a_3	τ_3 [ps]	χ^2
570	-1.0	5	0.72	468	0.28	62	0.97
600	-1.0	8	0.84	481	0.16	43	1.05
650	-1.0	9	0.82	482	0.18	44	1.05
700	-1.0	9	0.82	480	0.18	48	1.03

TFE:

λ [nm]	a_1	τ_1 [ps]	a_2	τ_2 [ps]	a_3	τ_3 [ps]	χ^2
570	-1.00	2	0.81	503	0.19	73	1.04
620	-0.88	8	0.90	518	0.10	67	0.96
670	-0.96	8	0.90	531	0.10	73	1.06
720	-1.00	9	0.89	540	0.11	62	1.02



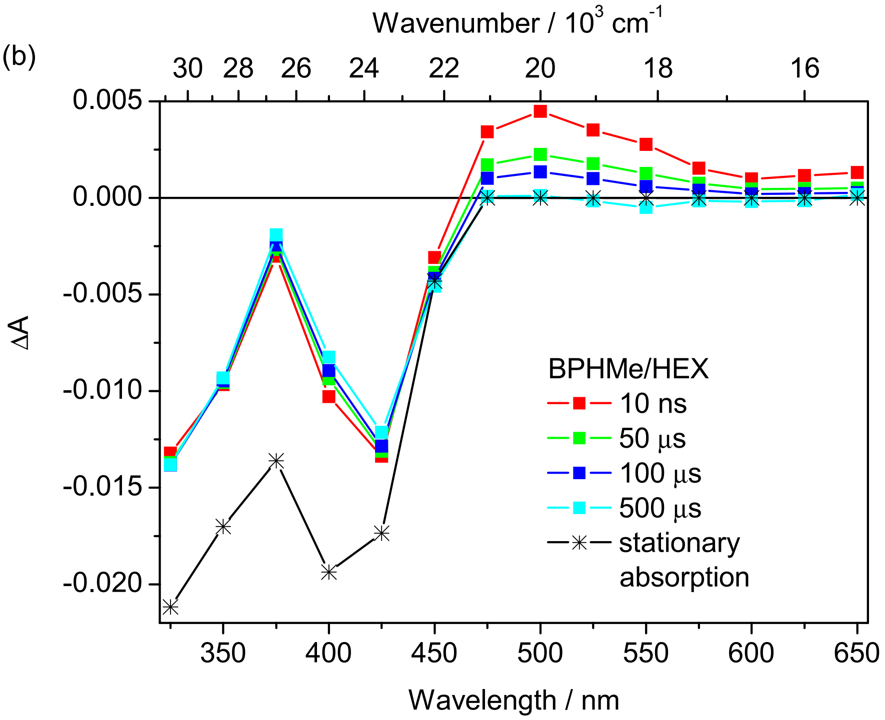


Fig. S13. Transient absorption spectra of BPHMe in ACN (a) and HEX(b) for selected pump-probe delay times.

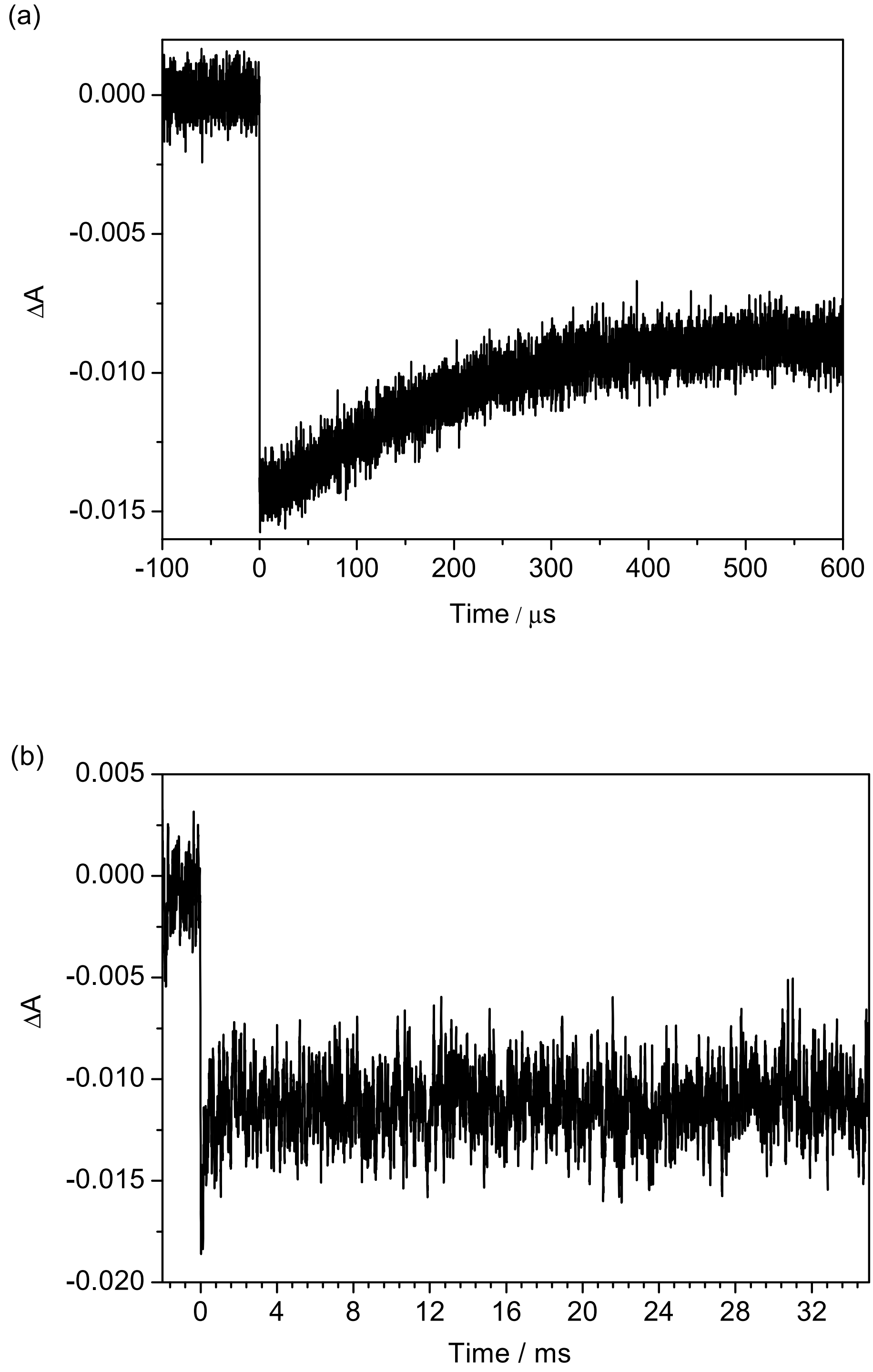


Fig. S13. Ground state depopulation kinetics (measured at 425 nm) of BPHMe in MeOH in shorter (a) and longer (b) time scale.