

**Excited state intramolecular
proton transfer reaction and
photochromism of the new family
of Schiff bases**

**Marcin Ziólek^a, Jacek Kubicki^a,
Andrzej Maciejewski^a, Ryszard Naskręcki^a
and Anna Grabowska^b**

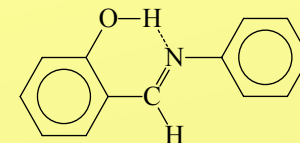
a Adam Mickiewicz University, Poznan, Poland

*b Institute of Physical Chemistry, Polish
Academy of Sciences, Warsaw, Poland*

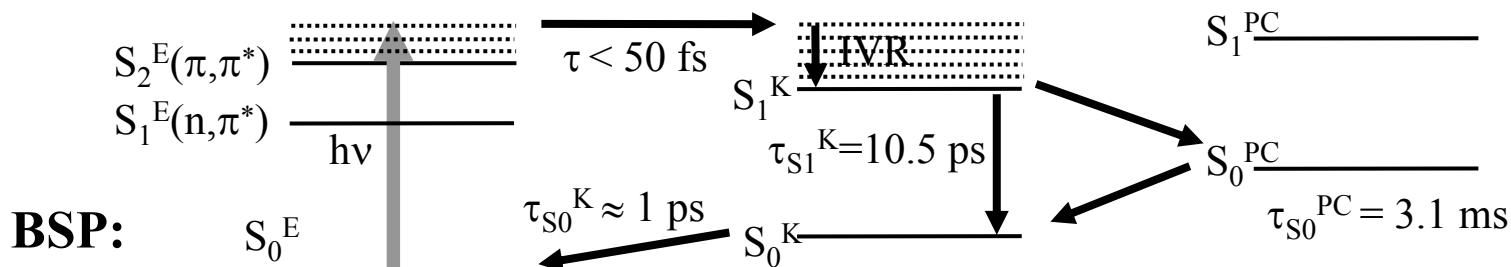
Our previous studies of Schiff bases

SA family: SA, SAA, BSP
in acetonitrile solution:

salicylideneaniline (SA):

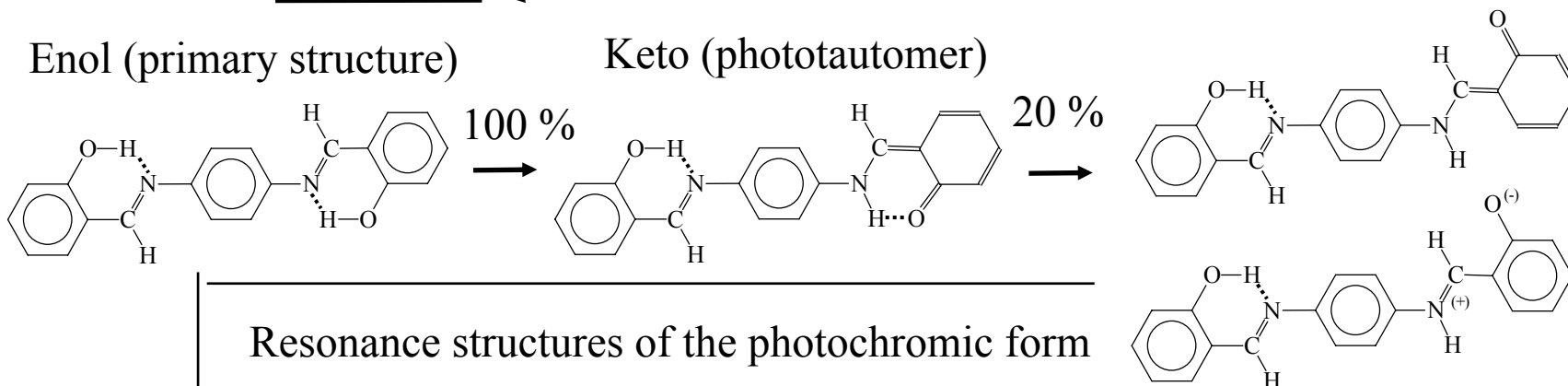


- M. Ziółek, J. Kubicki, A. Maciejewski, R. Naskręcki, A. Grabowska, *Chem. Phys. Lett.*, **369** (2003) 80
- M. Ziółek, J. Kubicki, A. Maciejewski, R. Naskręcki, A. Grabowska, *Phys. Chem. Chem. Phys.*, **6** (2004) 4682



Enol (primary structure)

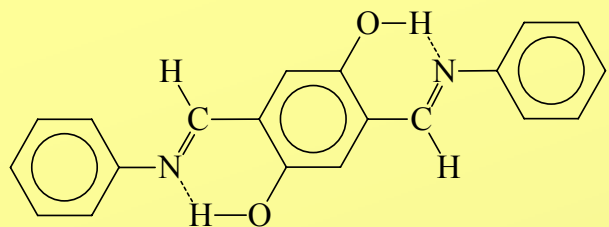
Keto (phototautomer)



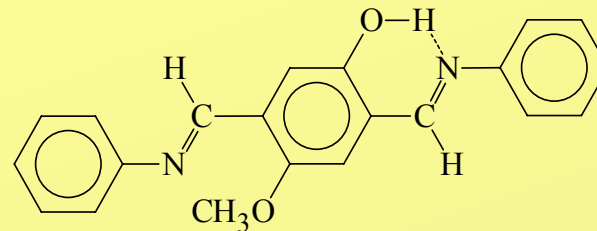
Resonance structures of the photochromic form

Present studies: new family of Schiff bases

New family of Schiff bases, introduced in: A. Grabowska, K. Kownacki, J. Karpiuk, S. Dobrin, Ł. Kaczmarek, Chem. Phys. Lett. **267** (1997) 132



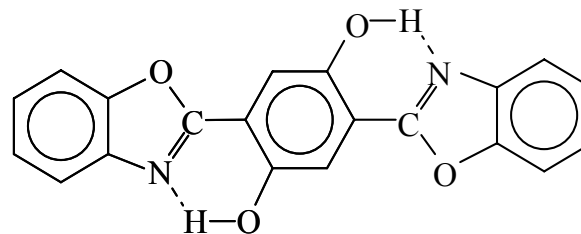
bis(phenyliminomethyl)hydroquinone
(BPH)



4-methoxy-2,5-bis(phenyliminomethyl)-phenol
(BPHMe)

In some respect BPH and BPHMe are structurally also similar to the widely studied system, 2,5-bis(benzoxazolyl)hydroquinone (BBHQ), also possessing in its framework a hydroquinone fragment:

- dual fluorescence was observed after cooling in supersonic jet and in non-polar solvents at room temperature;
- in non-polar solvents the exceptionally low rate of proton transfer (tens of ps) was measured.



BBHQ

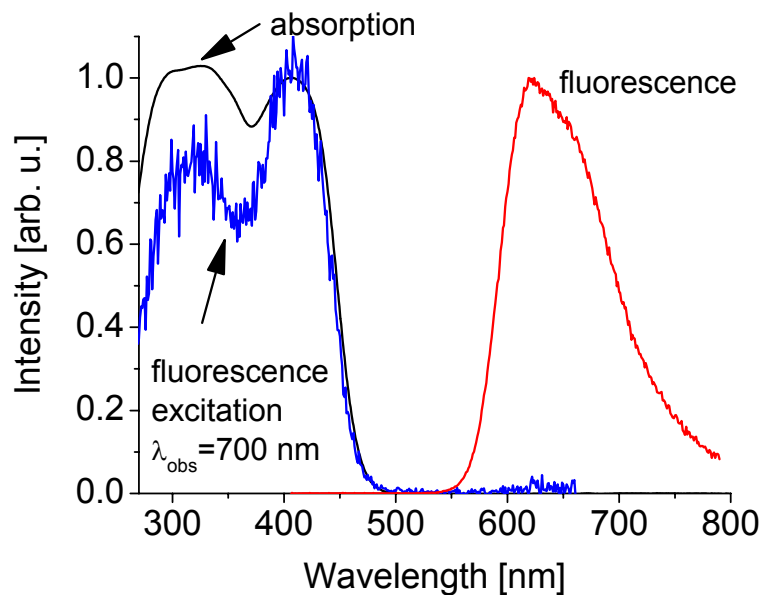
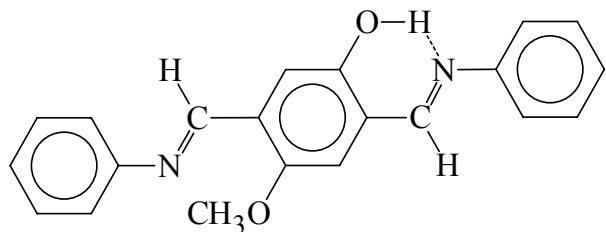
Ultrafast laser setups based on titanium-sapphire lasers

(Center for Ultrafast Laser Spectroscopy,
A. Mickiewicz University, Poznań, Poland):

- The time-resolved fluorescence measurements by the Time-Correlated Single Photon Counting technique with the temporal resolution up to 1 ps
- Femtosecond transient absorption measurements with the laser pulses of about 100 fs duration (second harmonic at 400 nm as an excitation pulses, generated supercontinuum as the probe pulses 330-700 nm)

Measurements conditions: room temperature, magic angle, acetonitrile solvent, 400 nm excitation – first (π, π^*) state of the enol form

BPHMe in acetonitrile



$$\epsilon_{\max} = 18\,500 \text{ M}^{-1} \text{ cm}^{-1} ;$$

quantum yield of fluorescence: 18×10^{-3} ;

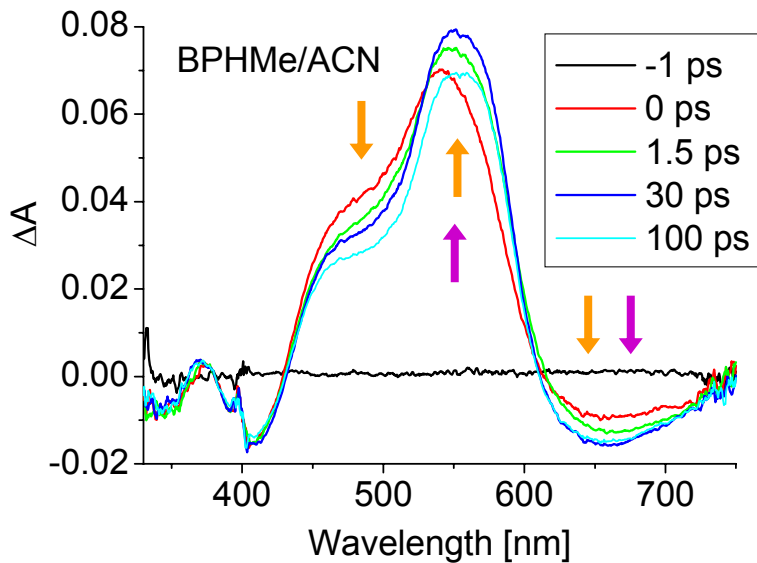
enol emission is 1700 times smaller
than keto emission

Parameters of time resolved fluorescence (decay amplitudes normalized)

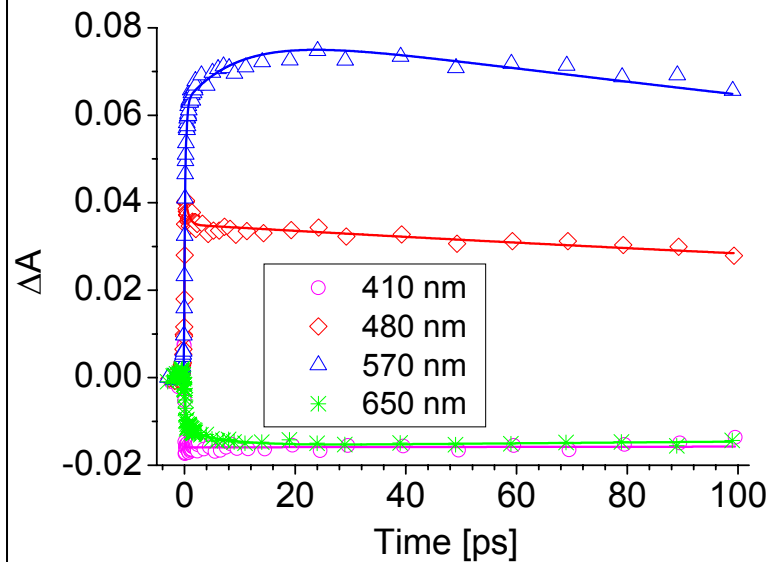
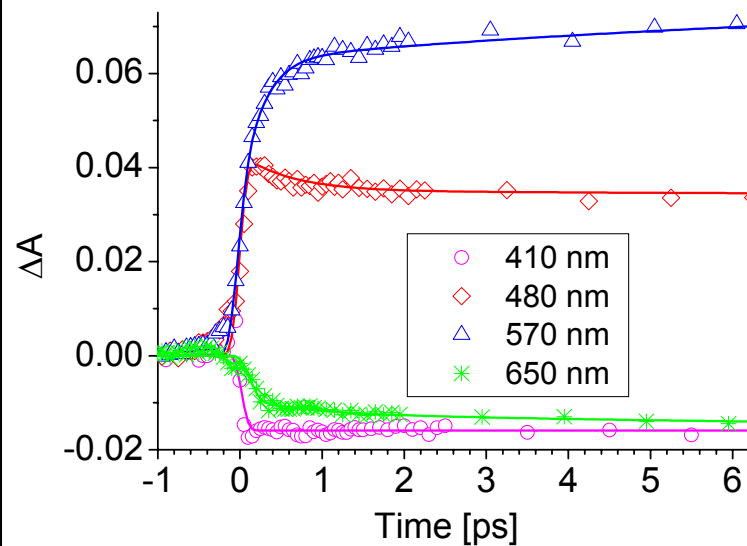
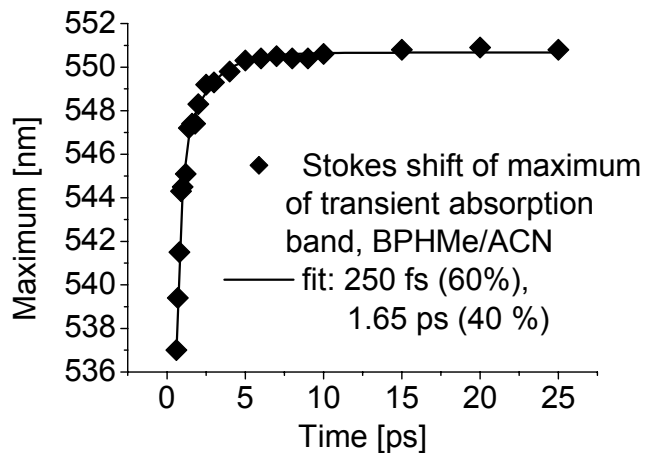
λ [nm]	a_1	t_1 [ps]	a_2	t_2 [ps]	a_3	t_3 [ps]	χ^2
464	1.00	<1	<0.01	900	-	-	0.95
500	1.00	4	<0.01	480	-	-	0.96
550	0.72	8	0.18	448	0.10	92	0.98
560	0.45	15	0.37	490	0.18	144	1.04
575	0.14	14	0.69	485	0.17	160	1.00
590	-0.34	11	0.81	483	0.19	126	1.05
600	-0.97	9	0.84	484	0.16	130	1.01
610	-0.36	11	0.87	482	0.13	104	1.06
615	-0.92	9	0.86	483	0.14	106	1.02
620	-0.22	11	0.89	484	0.11	122	1.01
630	-0.32	11	0.87	484	0.13	104	1.03
640	-0.96	6	0.87	485	0.13	128	0.98
650	-0.93	6	0.88	485	0.12	131	1.05
675	-0.94	7	0.86	484	0.14	114	1.02
700	-0.94	6	0.87	485	0.13	118	1.03
725	-0.93	7	0.86	485	0.14	113	1.08
750	-0.74	7	0.87	484	0.13	96	0.99

The amplitudes of rise time component
(yellow) are uncertain due to strong
correlation with the „time zero”.

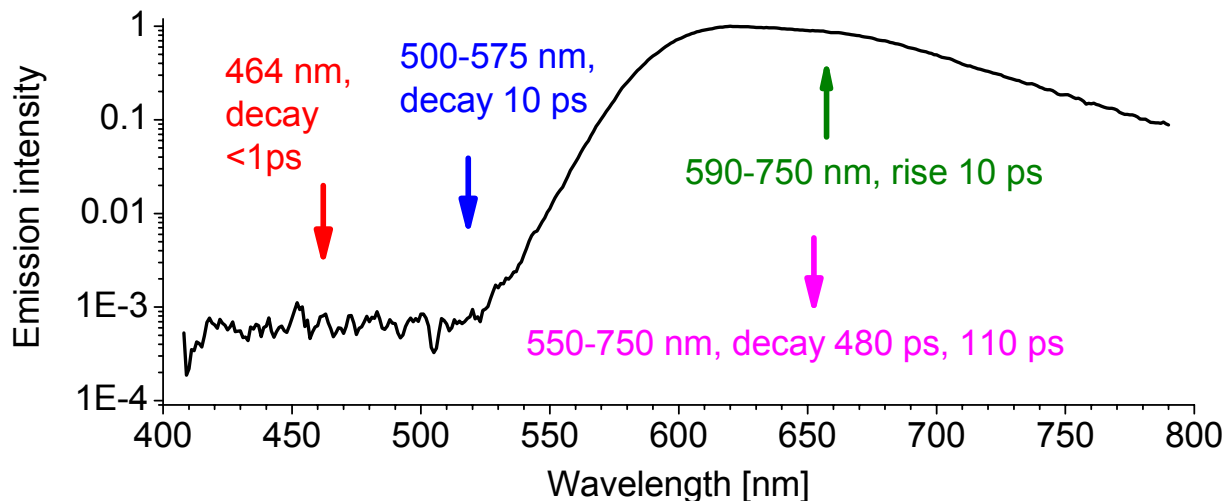
Transient absorption of BPHMe in acetonitrile



Spectral evolution: 500 fs →, 10 ps →



BPHMe in acetonitrile – two keto conformers



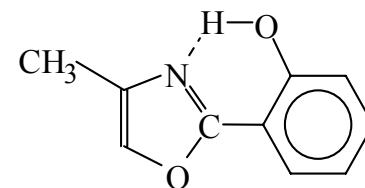
Similar results for 2-(2'-hydroxyphenyl)-4-methyloxazole (HMPO) in p-dioxane (D. Zhong, A. Douhal, A.H. Zewail, *Proc. Natl. Acad. Sci. US*, 2000, **97**, 14056)

Two proton transfer trajectories:

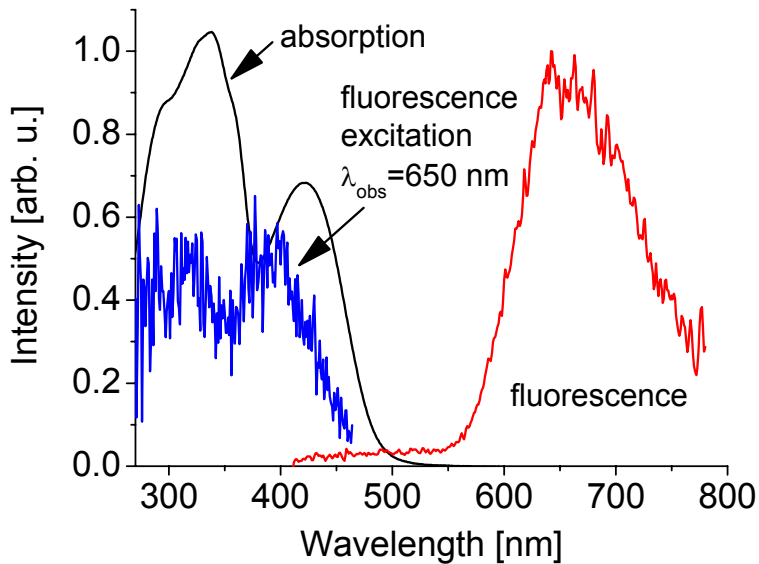
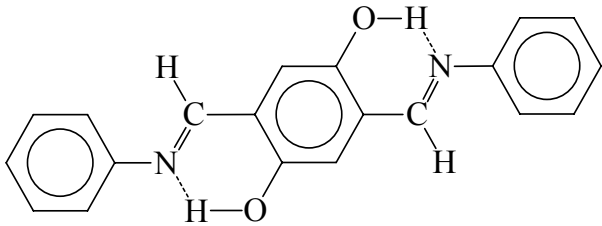
- the barrierless mechanism between the planar structures of enol and keto form occurring in ultrafast time scale of 50 fs;
- slower (10 ps) twisting motion of two fragments of the BPHMe molecule, usually involving energy barrier.

(The initial steps of the slower proton transfer process should occur on the time scale of about several hundreds of femtoseconds, like for HMPO molecule, where it corresponds to the initial motion of the wave packet out of the repulsive potential surface)

HMPO
molecule:



BPH in acetonitrile

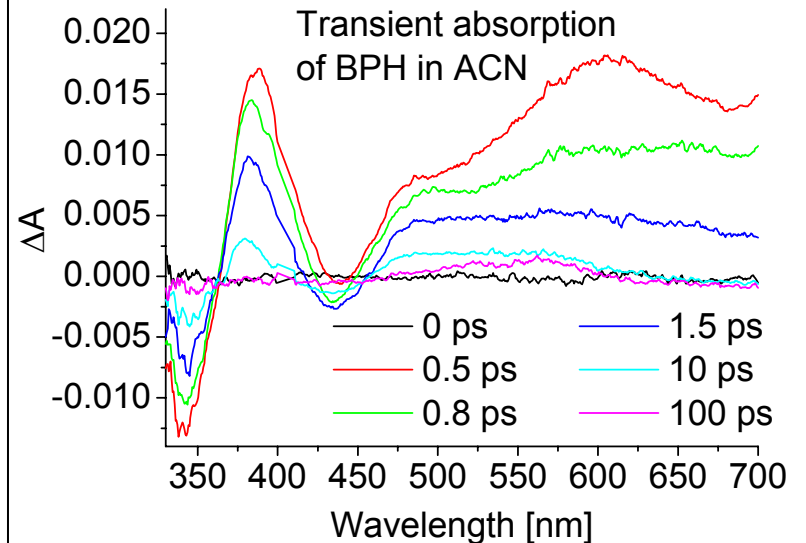


Fluorescence quantum yield:

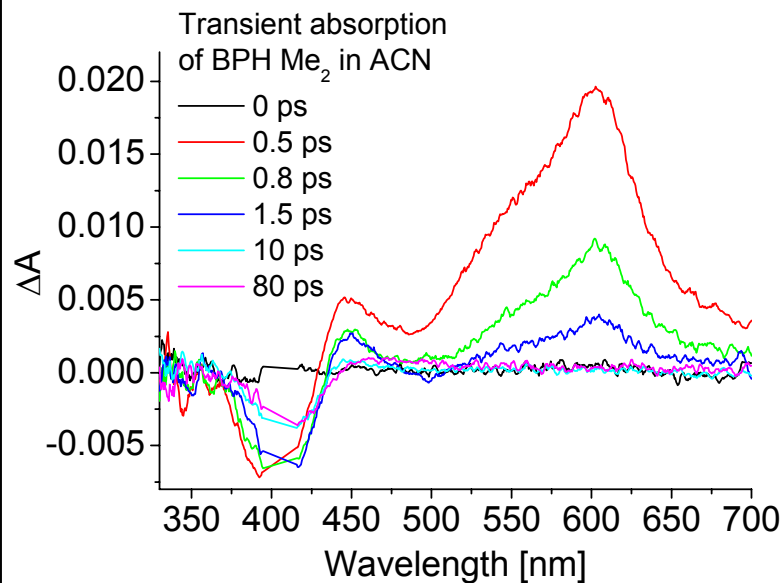
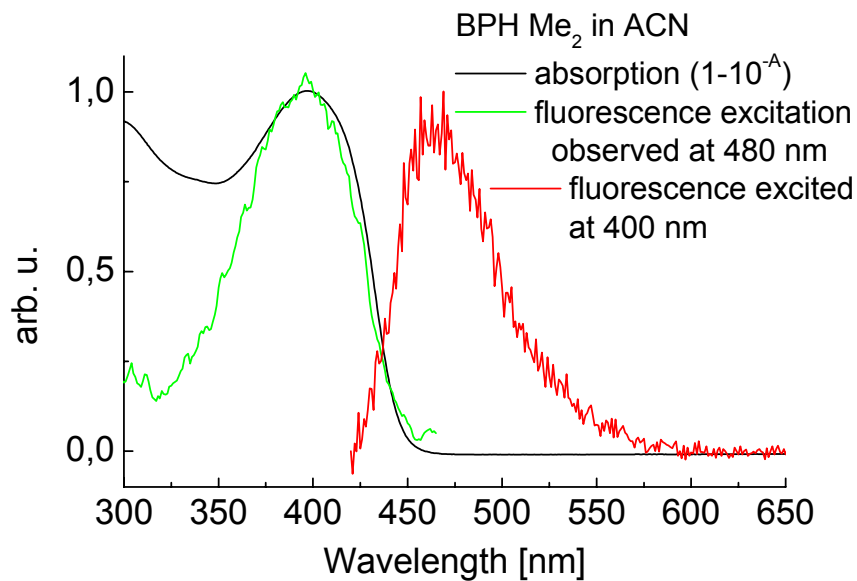
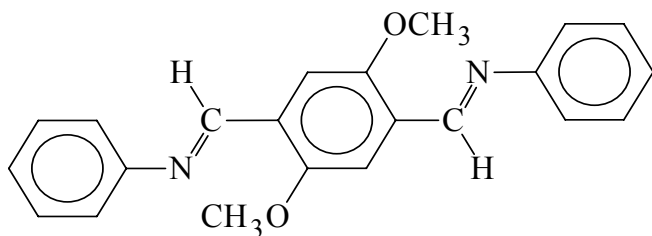
λ [nm]	400	415	450
$\Phi_\lambda [\times 10^{-4}]$	20	16	6

Time resolved fluorescence (worse signal to noise ratio than for BPHMe):

- Enol emission ($\lambda_{em}=500$ nm): decay component < 1 ps
(+ minor decay components - several hundreds of ps and single ns – of less than 1% of the total amplitude)
- Keto emission ($\lambda_{em}=650$ nm): decay component about 300 ps



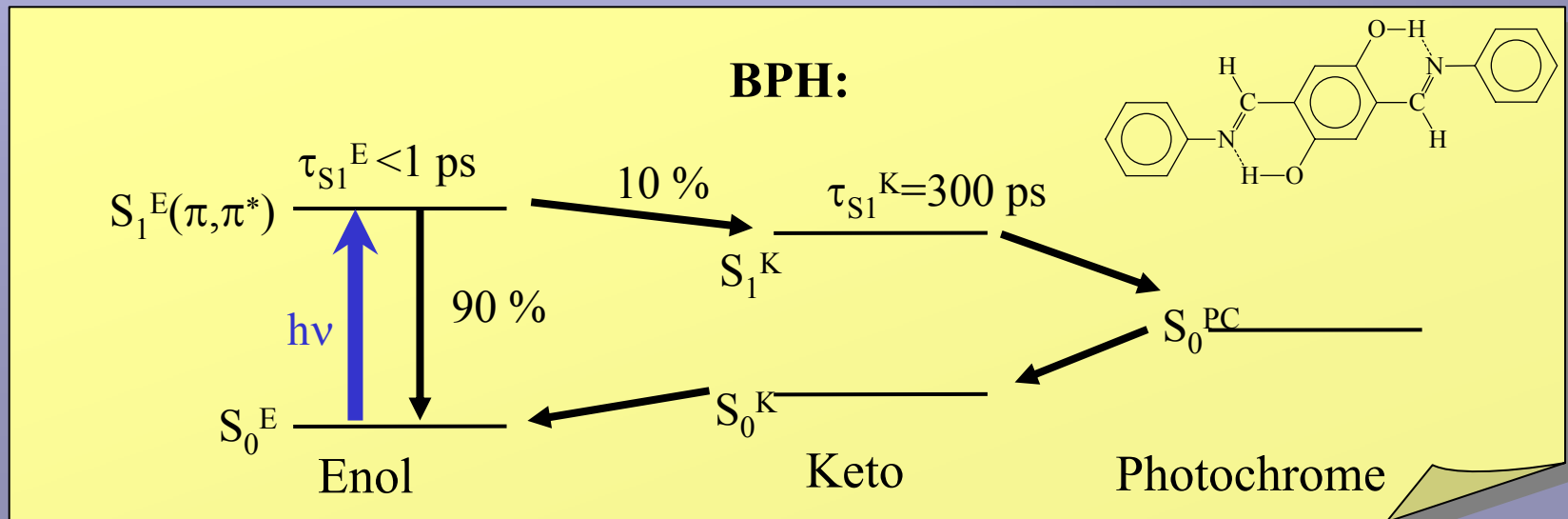
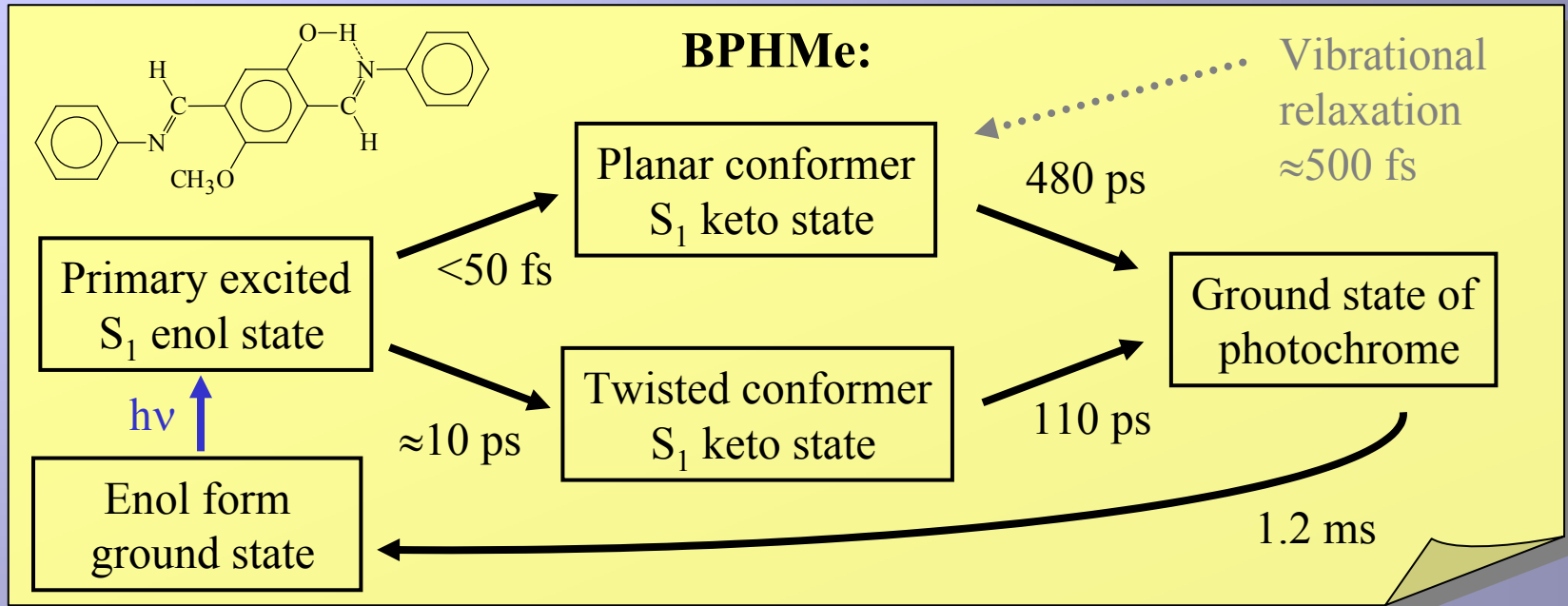
BPH Me₂ in acetonitrile



Low fluorescence quantum yield (0.2×10^{-3}), main component of the fluorescence lifetime is shorter than 1 ps.

Conclusion: internal conversion in the enol form takes place in the short time scale and it can be the competitive deactivation channel to the proton transfer process.

Conclusions – deactivation of BPH and BPHMe



Acknowledgements:

- the BPH, BPHMe and BPHME₂ compounds were synthesized by Dr. Wojciech Łuniewski (*Pharmaceutical Research Institute, Warsaw, Poland*)
- The work was done under financial support of the State Committee for Scientific Research (KBN) project
2 P03B 015 24