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OPTICAL MATERIALS RESEARCH GROUP

DEPARTMENT OF ENGINEERING PHYSICS

# ULTRAFAST DYNAMICS EXPLAINING PH PROBE MECHANISM IN BORONDIPYRROMETHENE BENZIMIDAZOLE COMPOUND

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# OUTLINE

- Motivation
- Optical Chemical Sensors
- Investigated Material
- Synthesis
- Experiments
- Results and Discussion

# MOTIVATION

## PH Sensors Applications

- Chemical Processing
- Pulp and Paper
- Food and Beverage
- Pharmaceutical
- Biomedical
- Industrial

## Requirements for Biomedical and Industrial Applications

- real time measurement
- continuous monitoring

A perfect solution → ***Optical Chemical pH Sensors***[1]

[1] *Anal. Chem.* 2014, 86, 15−29

# OPTICAL CHEMICAL SENSORS

SENSES OF ELECTRONICS[1]

EYES AND EARS CAPABLE OF SEEING AND HEARING BEYOND THE HUMAN PERCEPTION[1]

**Optical sensors** are based on reagents that change their optical properties on interaction with the analyte of interest.[2]

## The most commonly measured optical properties

- Absorption,
- Fluorescence intensity
- Decay time
- Reflectance
- Refractive index
- Light scattering
- Light polarization

**Fluorescent pH indicators offer better selectivity and sensitivity than absorption-based pH indicators.[2]**


[1]*Orellana, G. In Optical Chemical Sensors. Proceedings of the NATO Advanced Study Institute on Optical Chemical Sensors; Baldini, F., Chester, A. N., Homola, J., Martellucci, S., Eds.; Springer: Netherlands, 2006; pp 99−116.*

[2]*Dorota Wencel, Tobias Abel, and Colette McDonag, Anal. Chem. 2014, 86, 15−29*

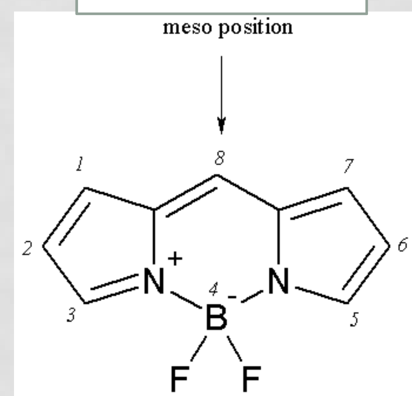
# MATERIAL

## Properties of Borondipyrromethene (BODIPY) dyes

- High fluorescence quantum yield[1]
- High extinction coefficient
- Narrow absorption and emission bands[2]
- Fine-tuned spectroscopic and physical properties
- Applications
  - Optical engineering
  - Fluorescence imaging
  - Fluorescent chemo sensors (such as pH probe)[3-5]
  - …..

[1]L. Gai, et al, Sens. Actuators B 182 (2013) 1–6.
[2]F.L.P. Arbeloa, et al, Int. Rev. Phys. Chem. 24 (2005) 339–374.
[3]Y. Ando, et al, Sens. Actuators B 121 (2007) 74–82.
[4]W. Qin, et al, ChemPhysChem 6 (2005) 2343–2351.
[5]T.Werner, et al, Fresenius J. Anal. Chem. 359 (1997) 150–154.

BODIPY scaffold



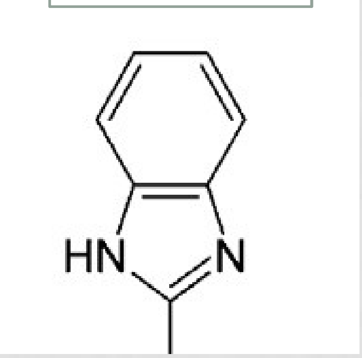
# MATERIAL

## Properties of Benzimidazole compound

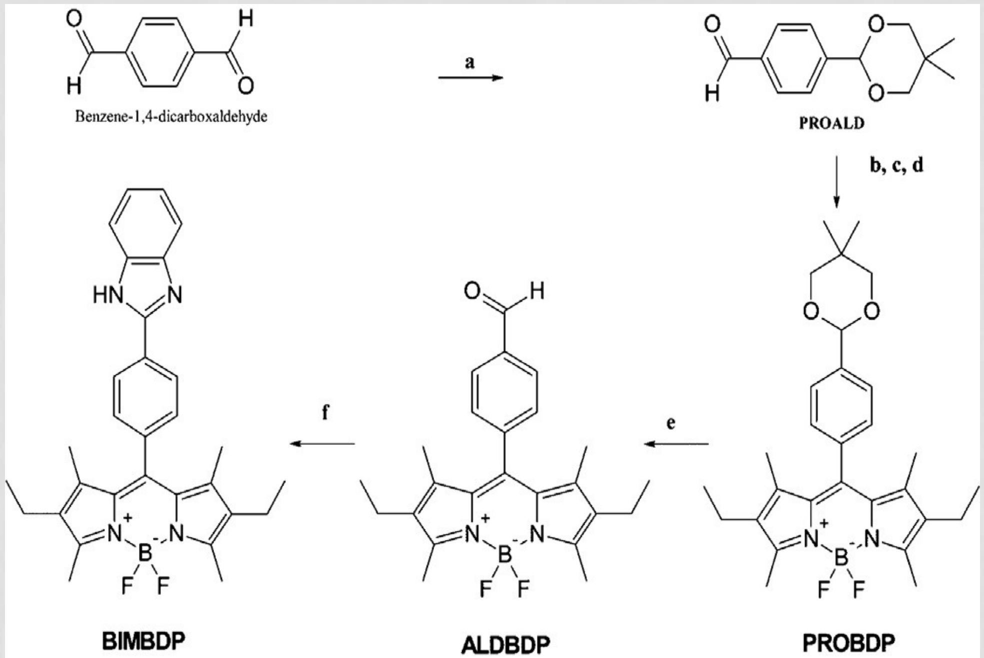
- A heterocyclic aromatic organic compound
- Consists of a fusion of benzene and imidazole
- Usually used as ligand for transition metal complexes
- Protonation property due to presence of pyridinic

nitrogen atom in benzimidazole

Benzimidazole



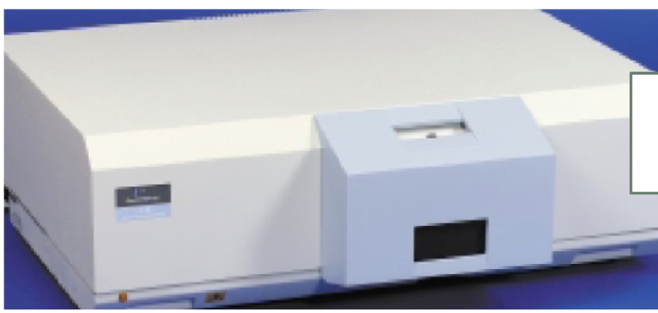
# SYNTHESIS




**a**: 2,2-dimethylpropane-1,3-diol, p-toluen sulfonic acid, toluen, Ar, refluks, 24h, %50;
**b**: 2,4-dimethyl-3-ethylpyrrole, trifluoroacetic acid, $CH_2Cl_2$, rt, 24 h.;
**c**: 2,3-dichloride-5,6-dicyano-1,4-benzoquinone (DDQ), 45min.;
**d**: Diisopropylethylamine (DIPEA, 5min) $BF_3.OEt_2$, 2h.(%20);
**e:** $CH_2Cl_2$:$H_2O$, trifluoroacetic acid, rt, 6h.(%90);
**f:** o-phenylenediamine, p-TsOH, DMF, 3h. Reflux (%60)

# EXPERIMENTAL TECHNIQUES

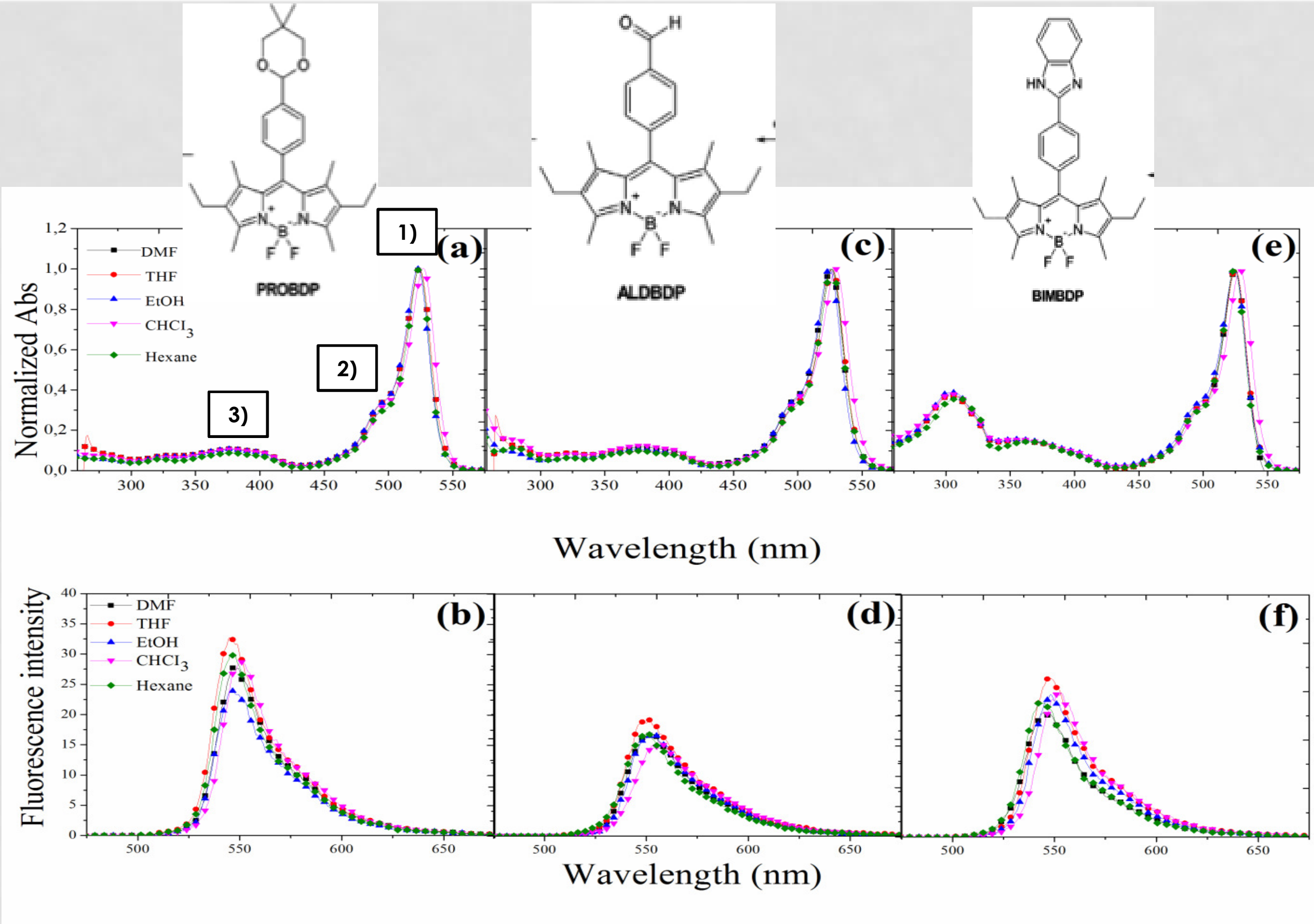
Linear absorption spectroscopy



Emission spectroscopy

Femtosecond transient absorption spectroscopy

# EXPERIMENTAL RESULTS

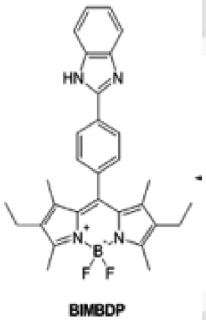



**1)** S0 → S1

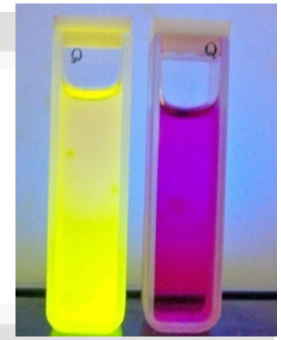
**2)** out of plane vibrations of the aromatic skeleton

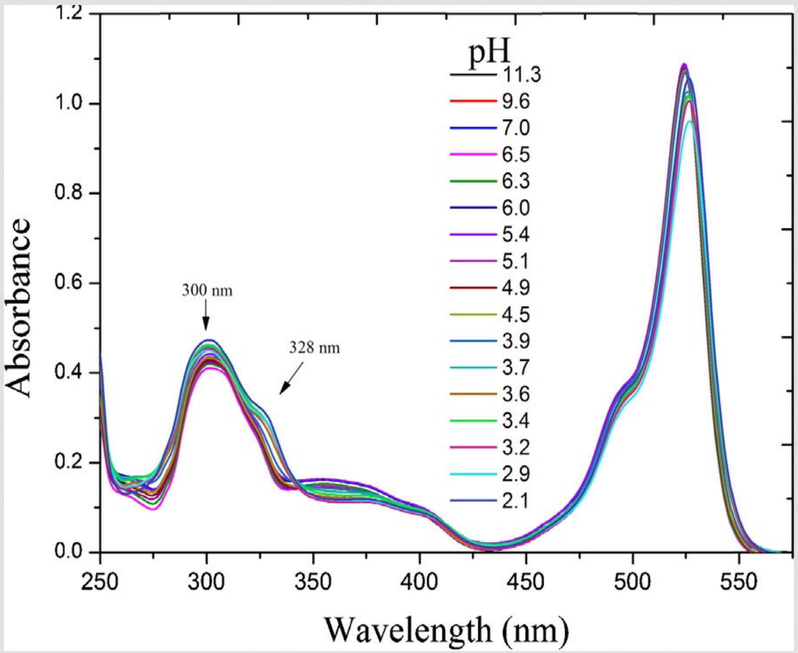
**3)** S0 → S2

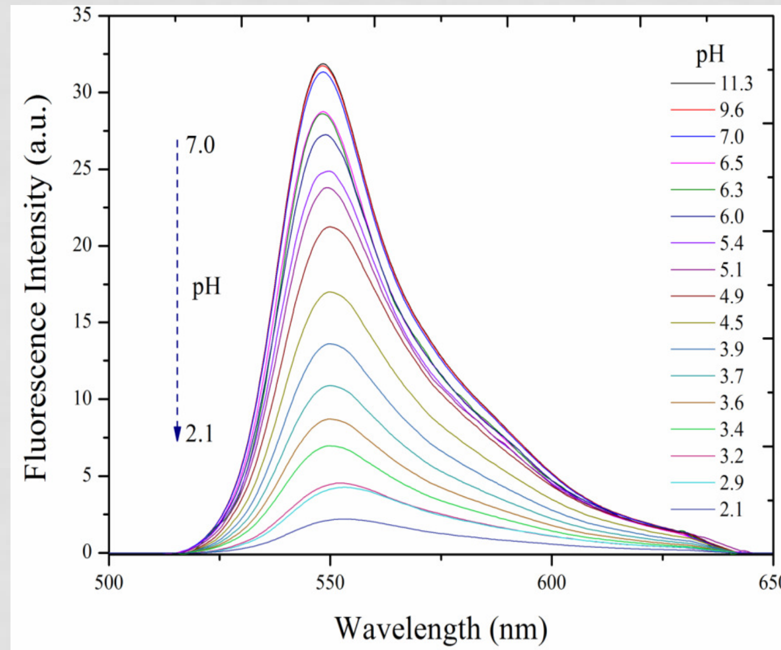
(a) Absorption spectra of PROBDP in different solvents. (b) Emission spectra of PROBDP. (c) Absorption spectra of ALDBDP. (d) Emission spectra of BIMBDP. (e) Absorption spectra of BIMBDP. (f) Emission spectra of BIMBDP.




# EXPERIMENTAL RESULTS

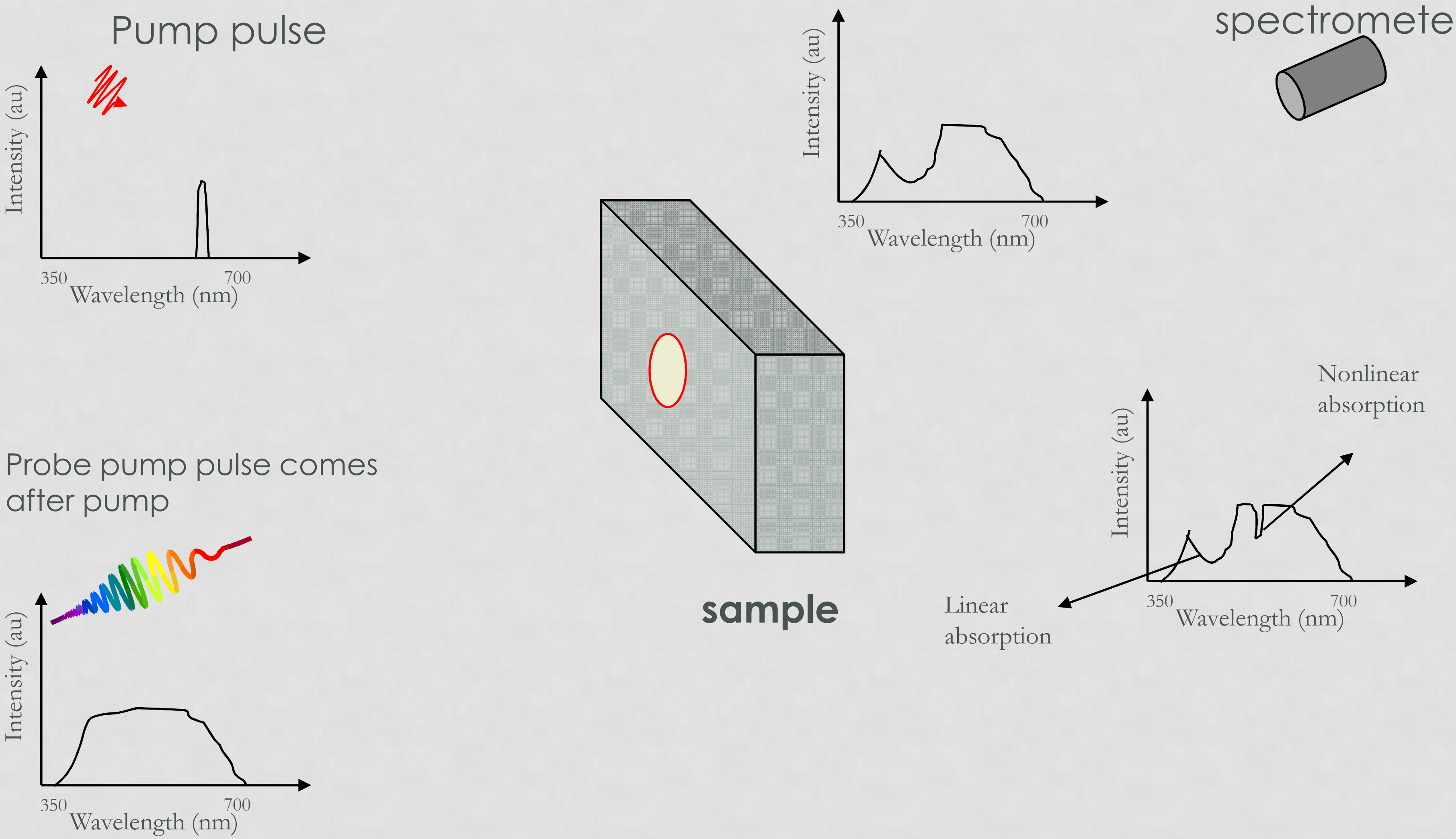




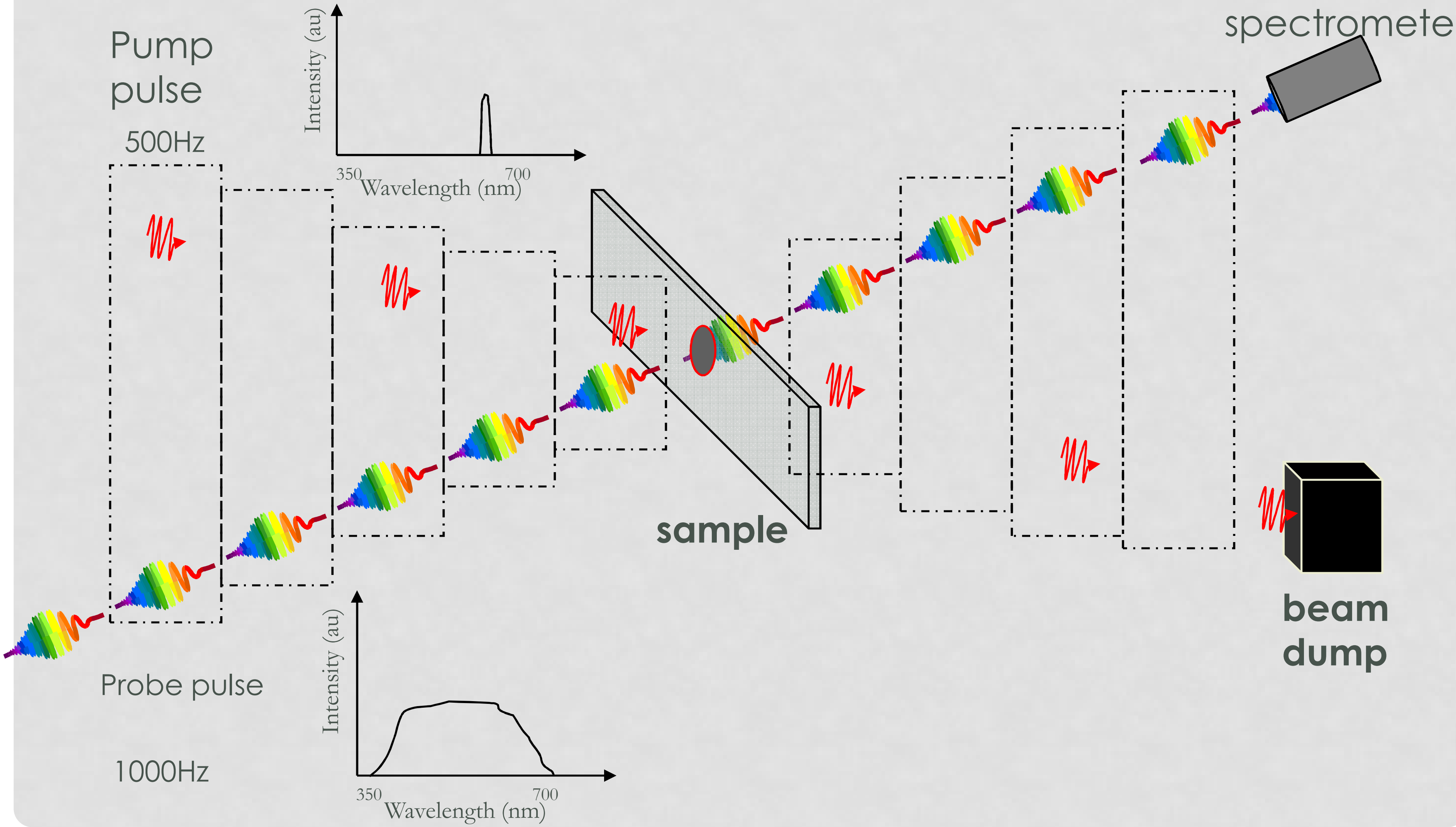



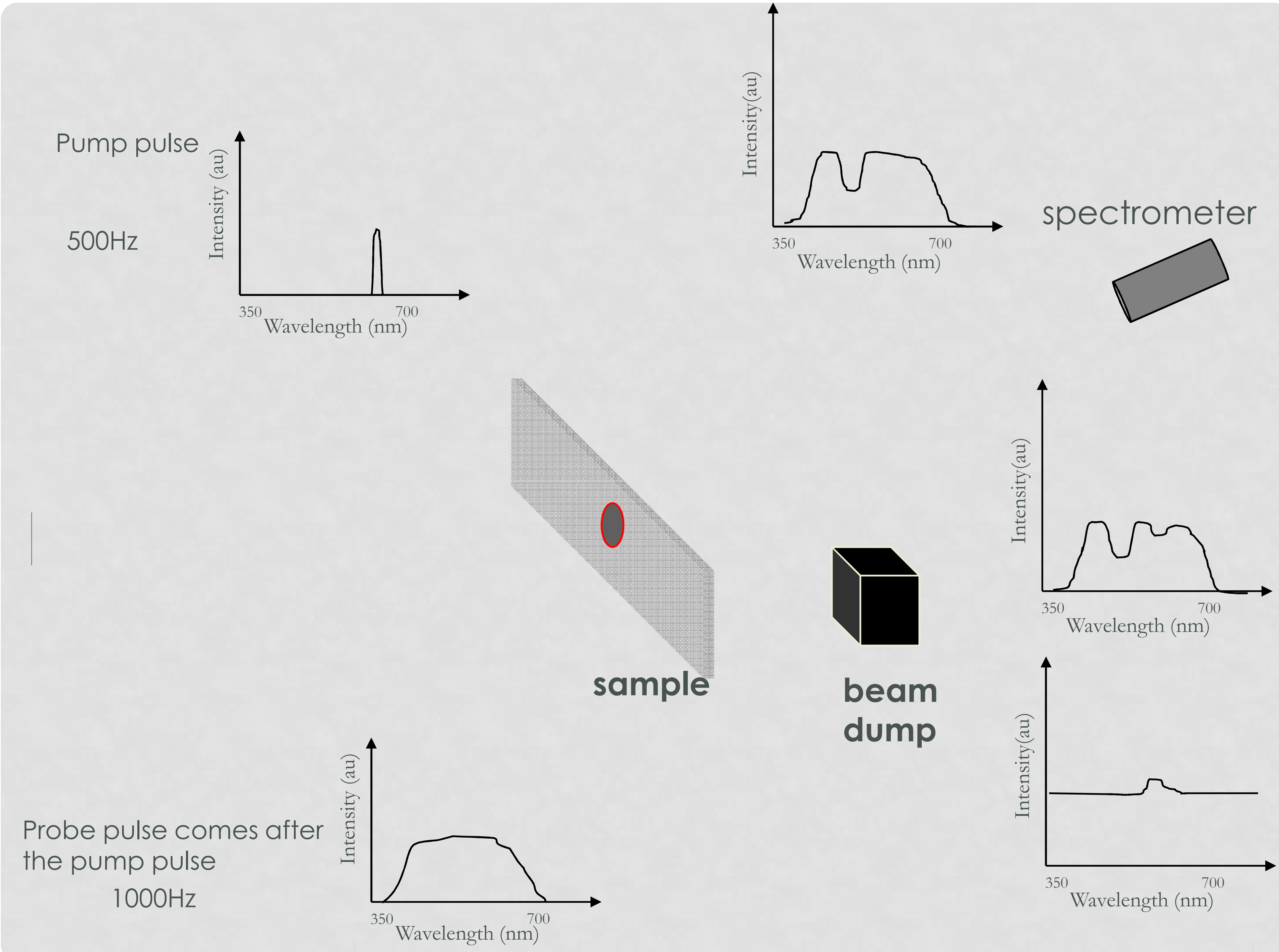

Absorption and emission spectra of **BIMBDP** in various pH intervals (dye concentration was $2\times10^{-5}$ molar in 5:1 methanol-water mixture at excitation wavelength of 525 nm).

# FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY EXPERIMENT

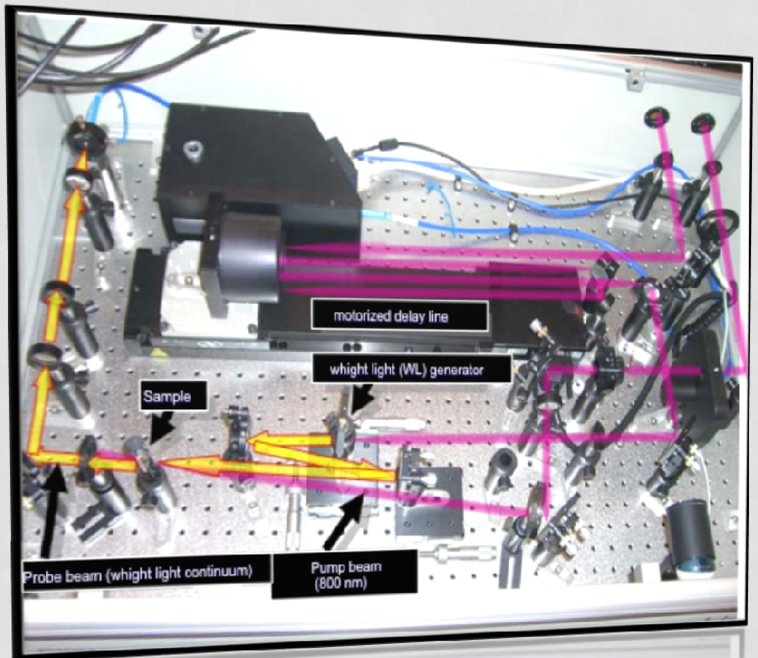


# FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY EXPERIMENT

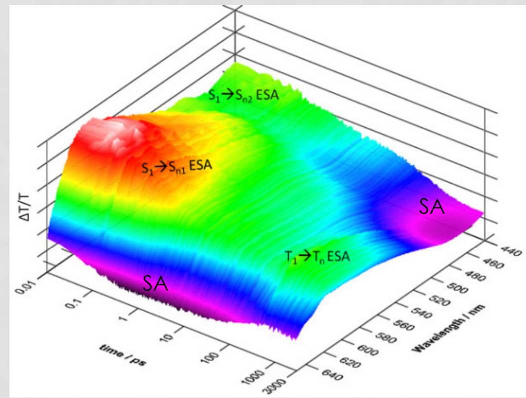


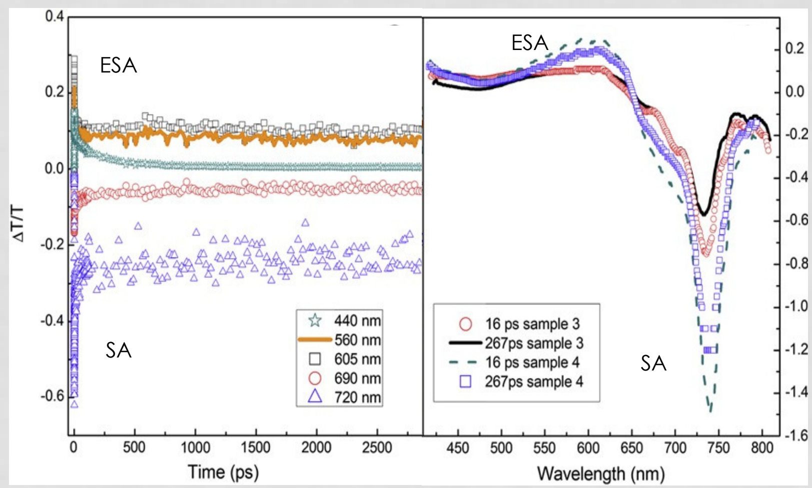

Pump pulse
500Hz
Intensity (au)
350
700
Wavelength (nm)
Intensity(au)
350
700
Wavelength (nm)
spectrometer
sample
beam
dump
Intensity(au)
350
700
Wavelength (nm)
Intensity(au)
350
700
Wavelength (nm)
Probe pulse comes after
the pump pulse
1000Hz
Intensity (au)
350
700
Wavelength (nm)

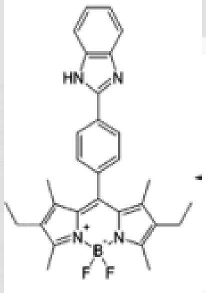
# FEMTOSECOND TRANSIENT ABSORPTION SPECTROSCOPY EXPERIMENT




Example Transient Absorption Data

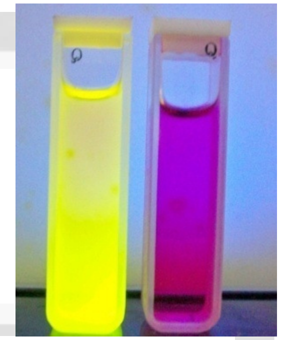


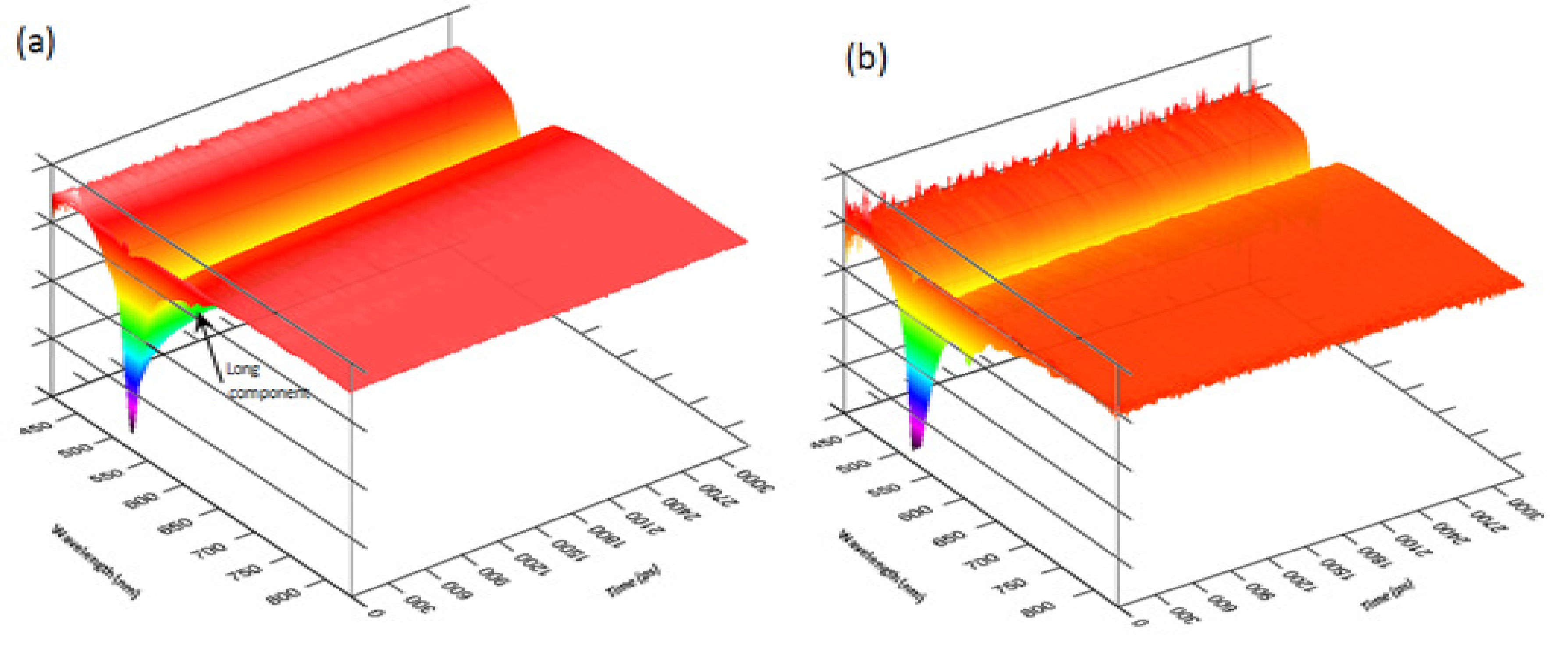





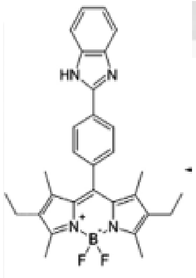
BIMBDP

# EXPERIMENTAL RESULTS



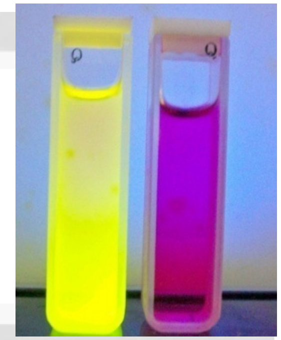


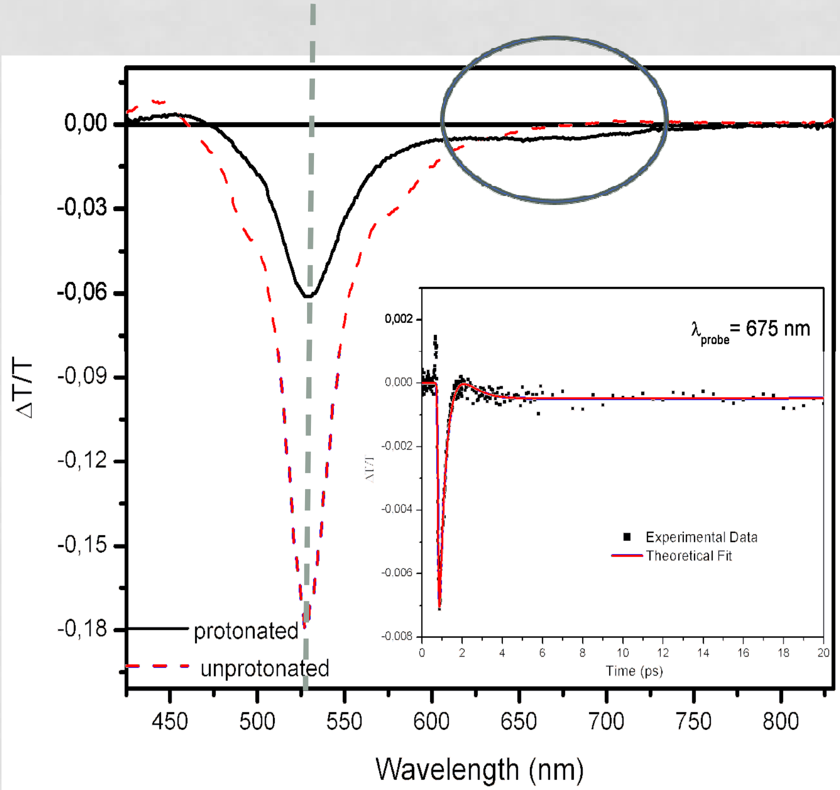

Femtosecond transient absorption spectra as a function of time for
(a) unprotonated and
(b) protonated compound of **BIMBDP**

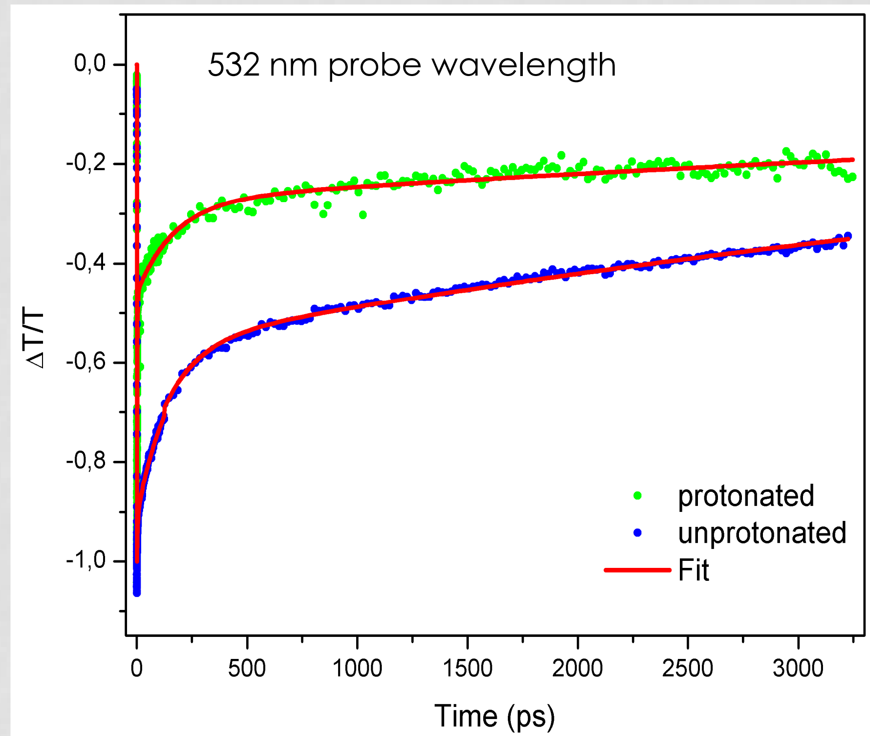


BIMBDP

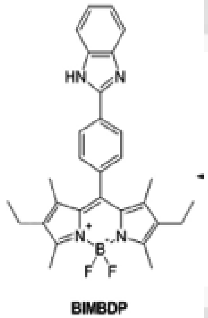
# EXPERIMENTAL RESULTS



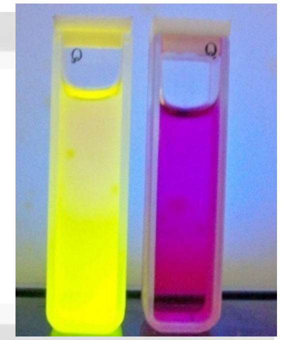


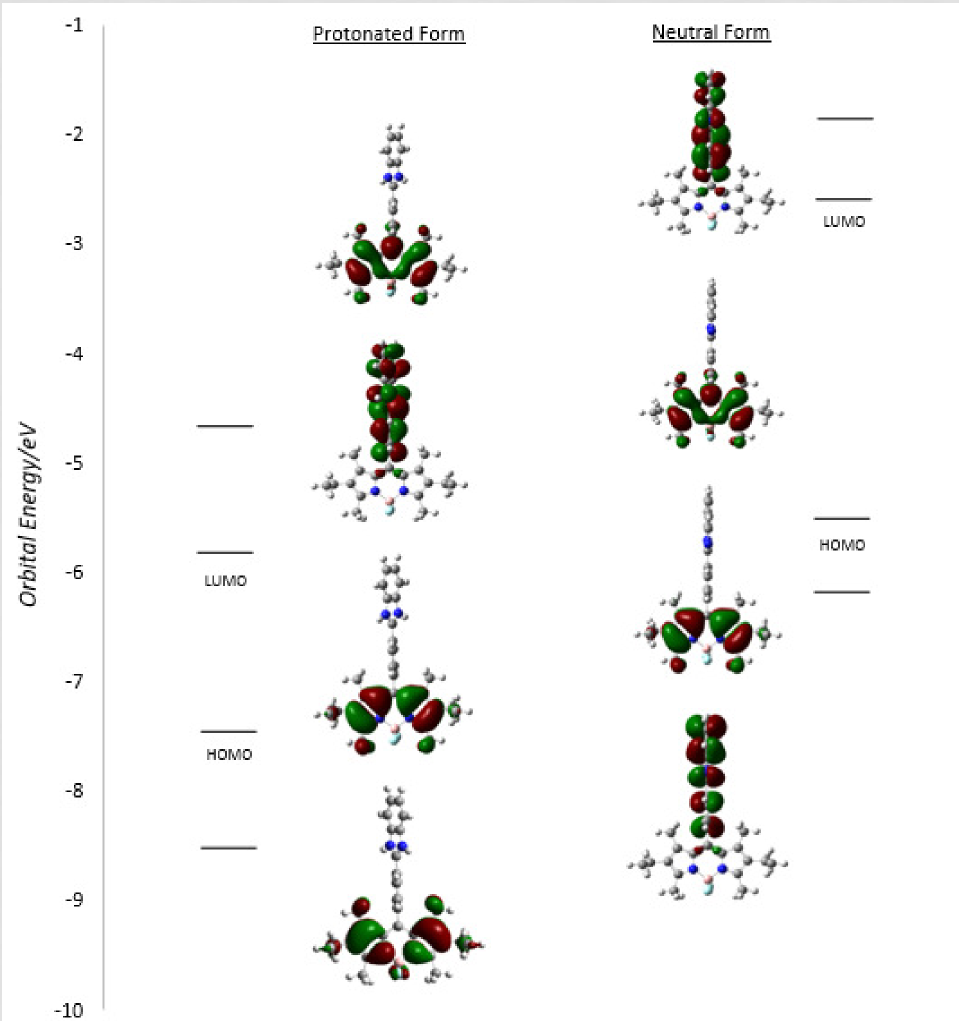




Femtosecond transient absorption spectra of **BIMBDP** compound in (5:1 MeOH-$H_2O$) with different pH value. The Fig. inset indicates fast decay of transient band corresponding to LUMO energy level of benzimidazole.

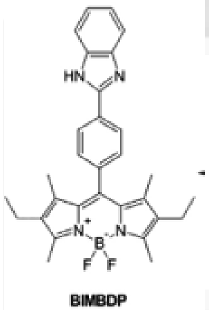



# DENSITY FUNCTIONAL THEORY CALCULATION

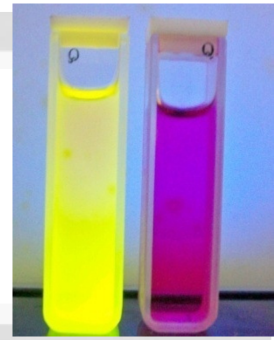


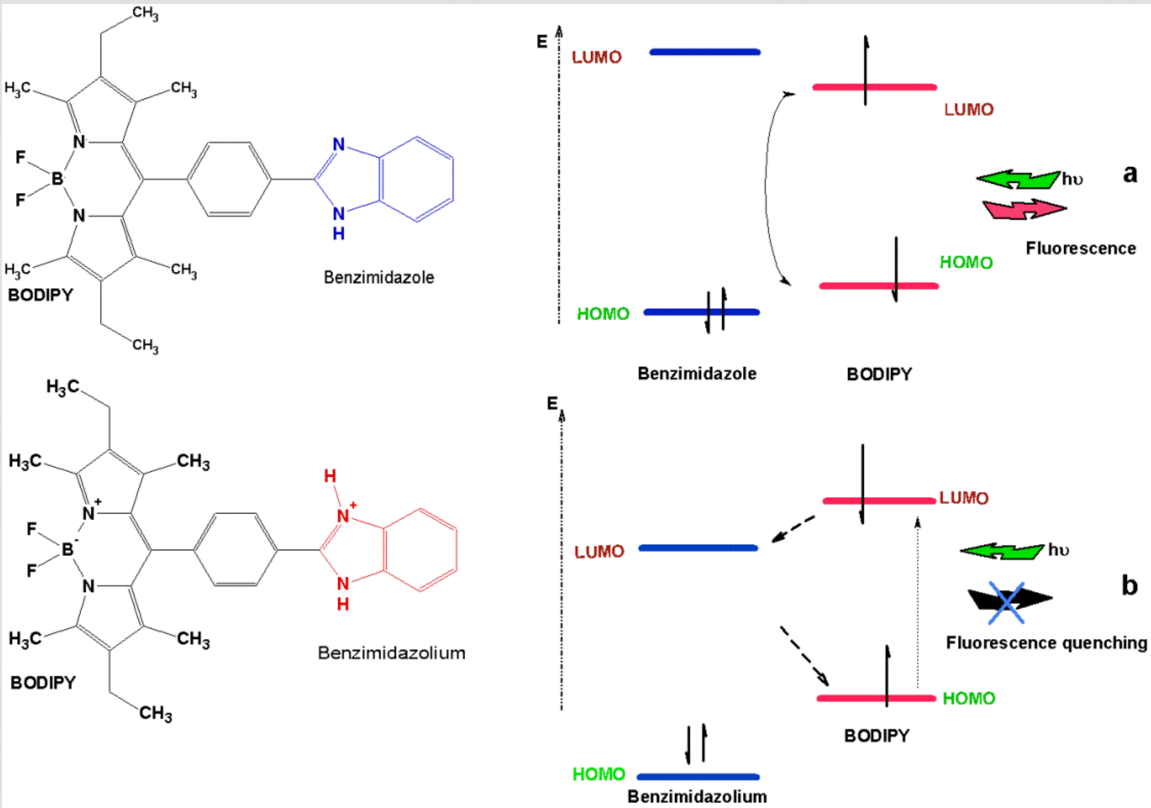



Energy levels and frontier molecular orbital distributions of the novel BODIPY compound in protonated and neutral states respectively



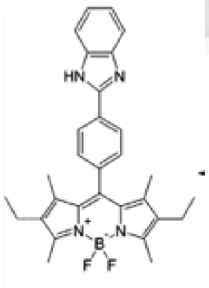

# PROPOSED MECHANISM





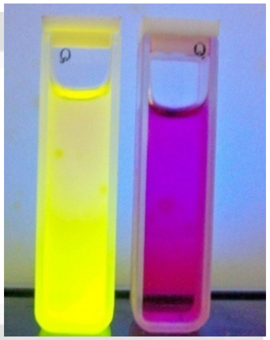

Proposed mechanism for fluorescence quenching of **BIMBDP** in acidic media attributed by d-PET

a) fluorescence mechanism
b) quenching mechanism



BIMBDP

# RESULT AND DISCUSSION



- We have designed and synthesized new BODIPY compounds
- Absorption and emission properties were investigated as a function of $H^+$ concentration
- Drastic fluorescence quenching was observed upon protonation
- Photo-induced electron transfer was proposed as an underlying mechanism
- Underlying mechanism was proved by DFT calculation and ultrafast transient absorption experiments

# THANK YOU FOR YOUR PATIENCE

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