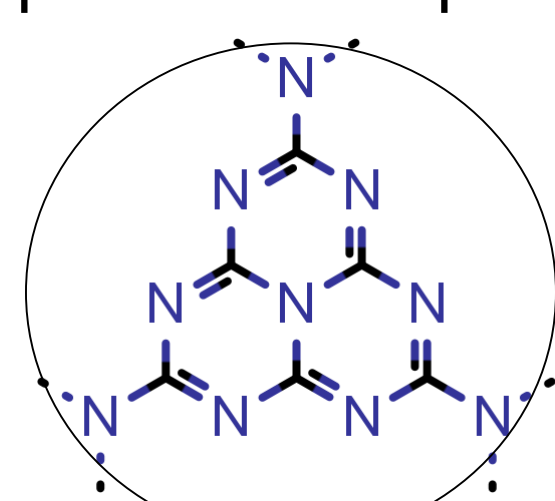


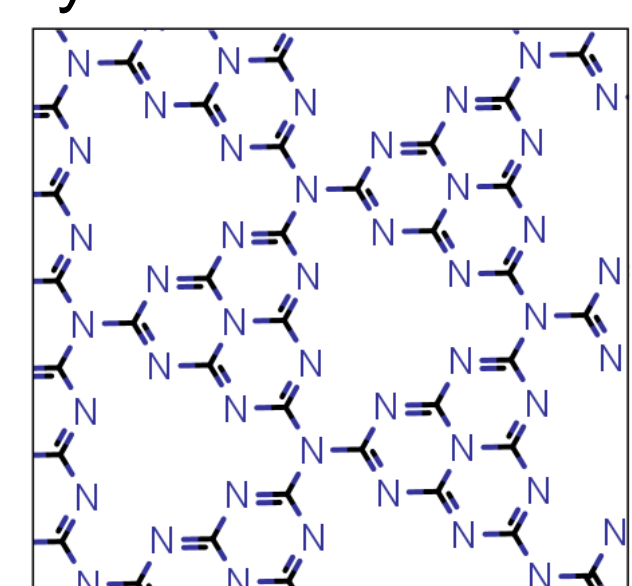
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## INTRODUCTION

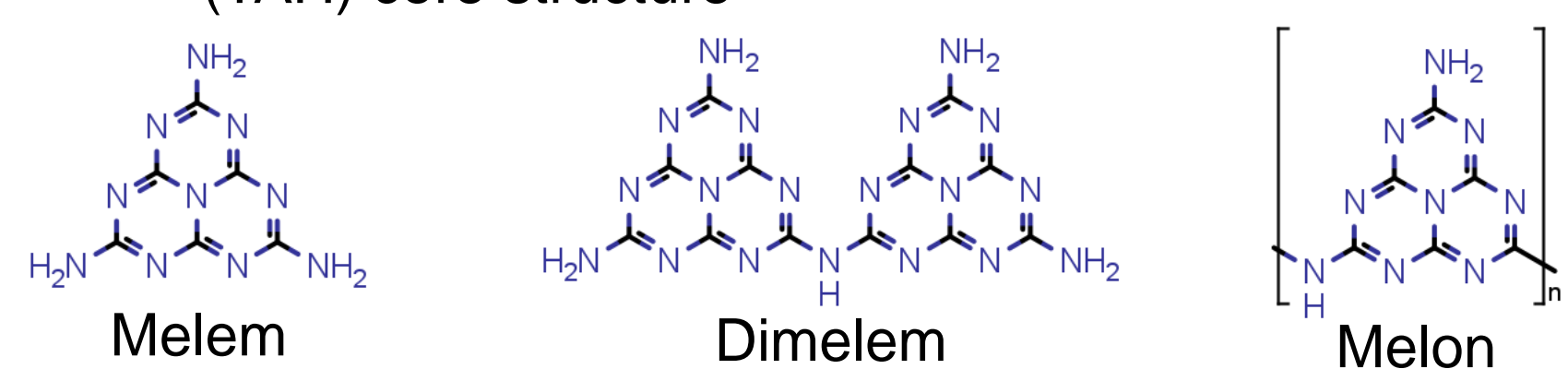
Triamino-heptazines (TAH's) comprise the fundamental building blocks of graphitic carbon nitride, an enticing material with promising applications in optoelectronics and catalysis.<sup>1</sup> Despite their straightforward synthesis,<sup>2</sup> characterization of electronic transitions remains difficult due to the existence of several polymeric forms,<sup>3</sup> as well as the inherent  $D_{3h}$  symmetric structure, which causes the lowest-energy excited states of the chromophore to be spectroscopically forbidden.<sup>4</sup>



2,5,8-triamino-heptazine (TAH) core structure



Graphitic Carbon Nitride



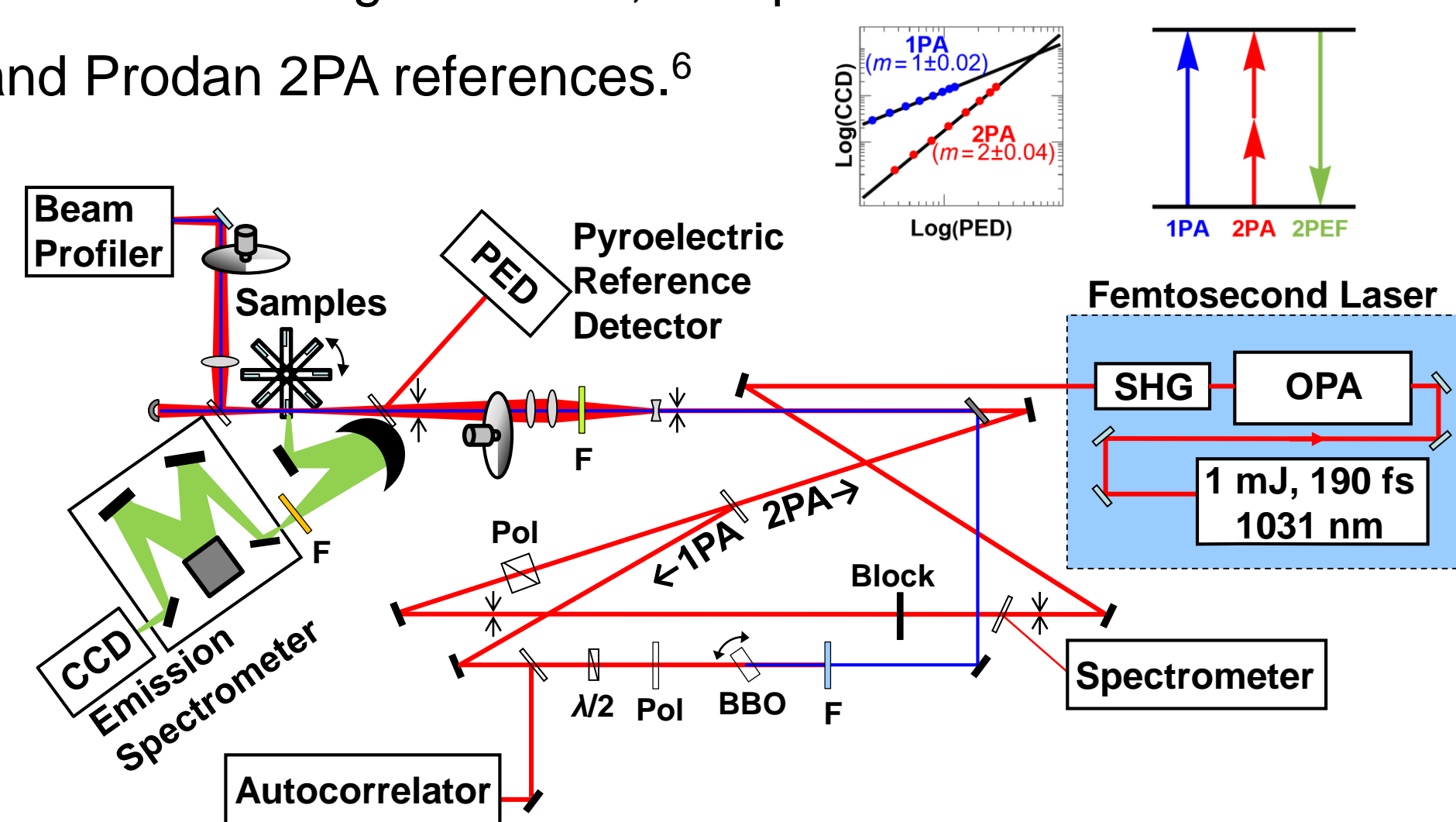
Molecular structures of 2,5,8-triamino-heptazine compounds.

Here, we investigate a water-soluble TAH molecule by combining spectroscopic titration through one-photon absorption (1PA) together with two-photon absorption (2PA) spectral measurements. The observed 1PA and 2PA spectra reveal the lowest-energy excited state can be described according to symmetry-switching between  $C_{3h} \leftrightarrow D_{3h} \leftrightarrow C_s$  point groups of the chromophore structure.

## METHODS

Melem\* was purchased from Arctom Scientific, and the supernatant from its aqueous solution was extracted through a 0.1  $\mu\text{m}$  porous filter (MiniSart, Sartorius). Titration of this filtrate with either  $\text{H}_2\text{SO}_4$  or NaOH was monitored by pH (Ag/AgCl, LL-Biotrode, Metrohm), as well as 1PA spectra (UV 3600+, Shimadzu).

For 2PA measurements, samples were purged with Argon before the collection of two-photon excited fluorescence (2PEF) using a fs laser-based system<sup>5</sup> shown in the figure below, compared to Coumarin 153 and Prodan 2PA references.<sup>6</sup>

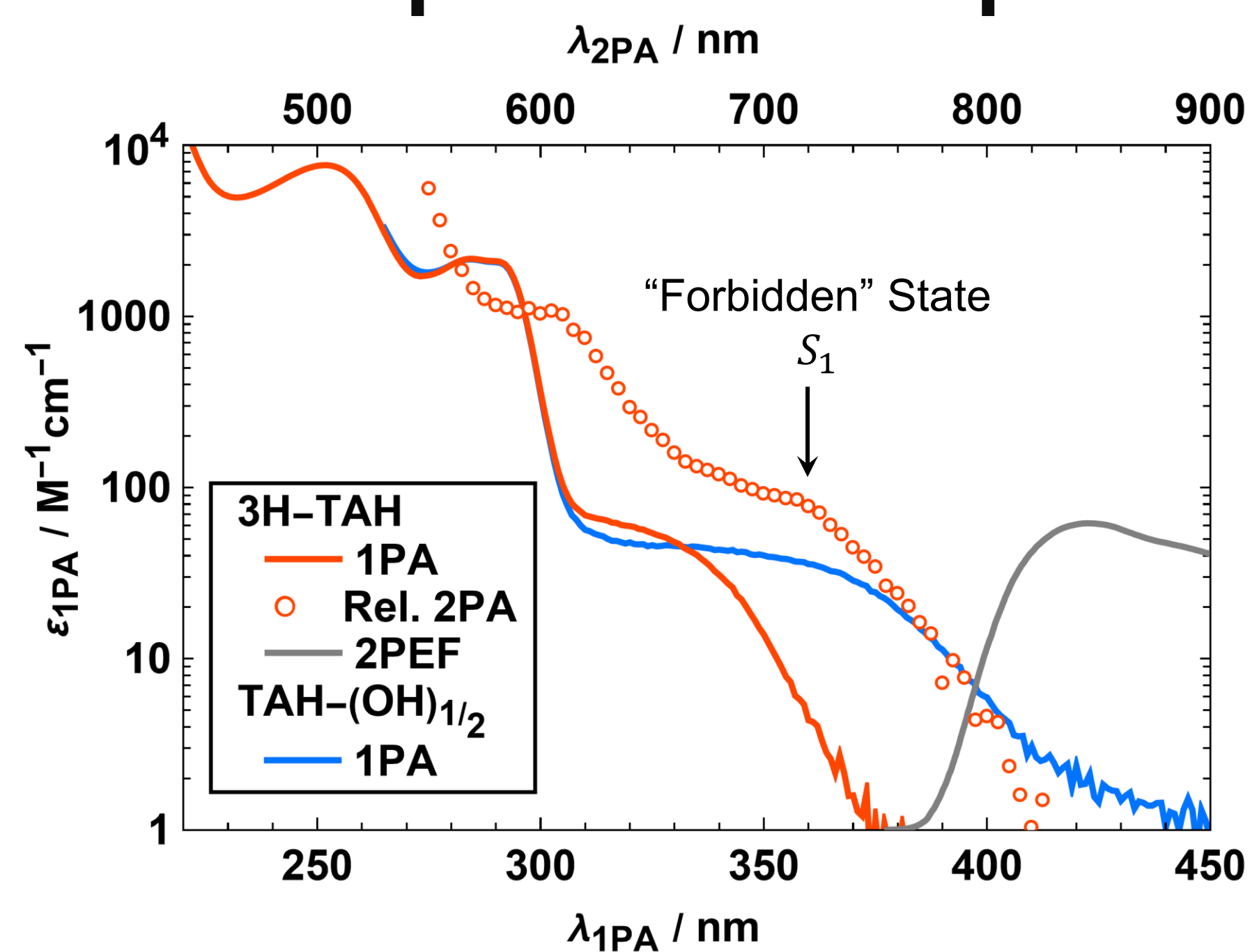


## ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education and Research, Republic of Estonia (grants PRG661 and PSG317). A.R. acknowledges support from NSF Award 210362. We thank Heiki Vija for the use of the pH probe.

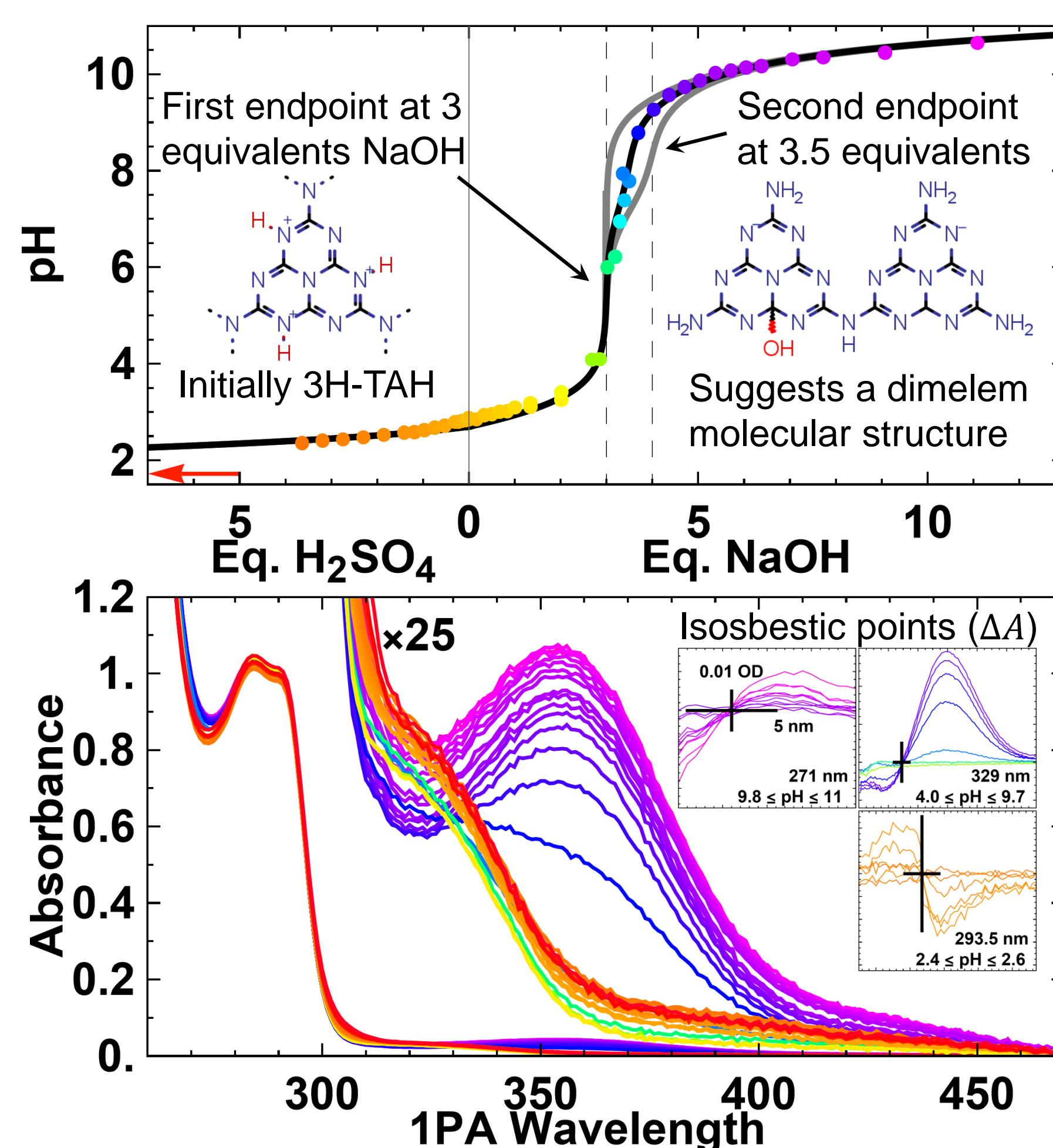
## RESULTS

## Two-photon absorption



The relative 2PA spectrum of 3H-TAH displays a low-energy band analogous to the TAH-(OH)<sub>1/2</sub> 1PA spectrum. This can be attributed to the lowest energy excited state ( $S_1$ ).

## One-photon titration



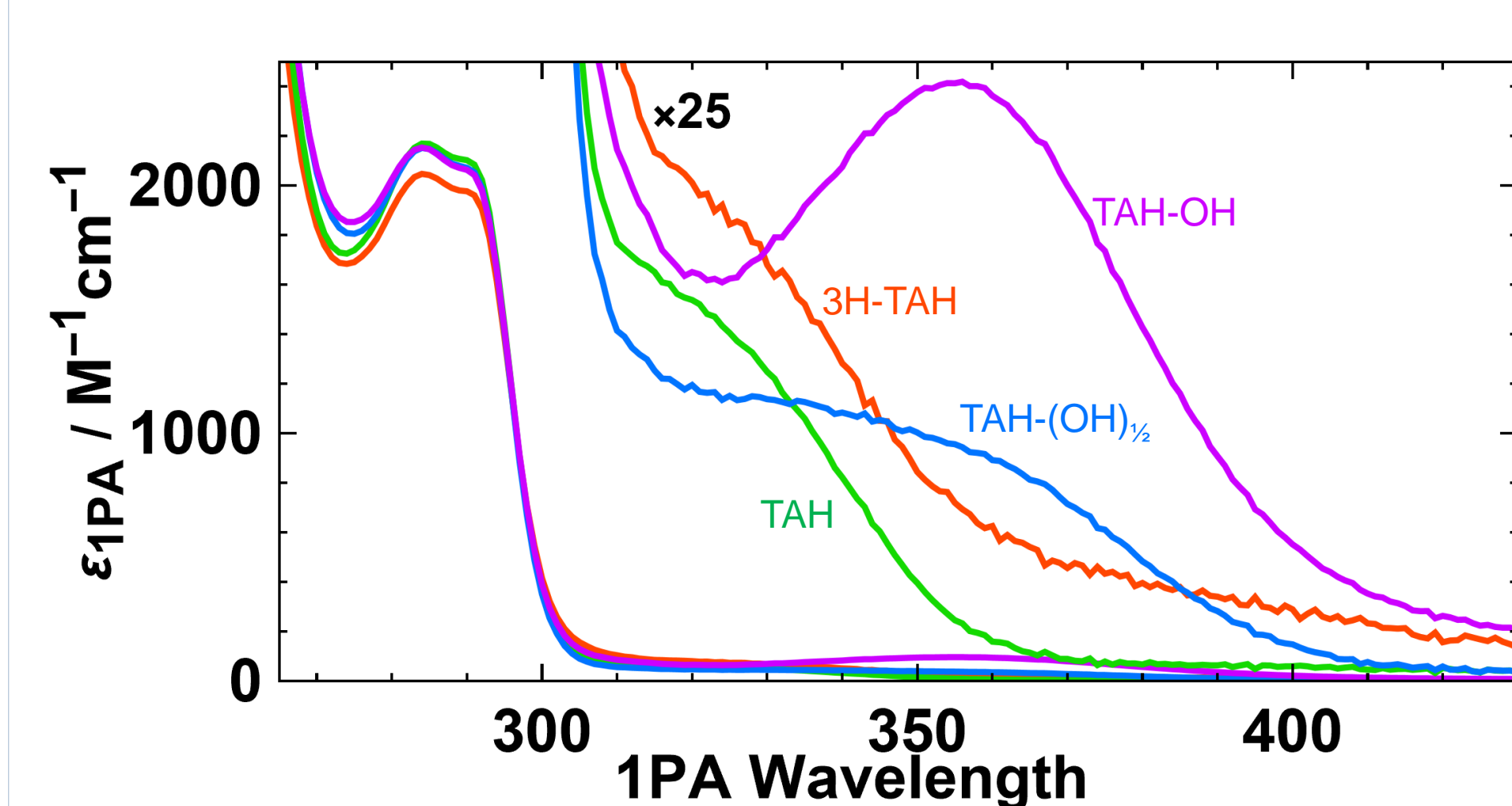
Titration of the triamino-heptazine compound using  $\text{H}_2\text{SO}_4$  and NaOH. Top: pH curve displays an endpoint at 3 equivalents of NaOH. Bottom: Major spectral changes occur after the endpoint, but also reveal three minor isosbestic points (inset).

## CONCLUSION

The TAH chromophore is tentatively assigned as the protonated form of dimelem, according to acid/base volumetric analysis and spectral properties. Notably, we observe a low-energy absorption feature (355 nm) which closely matches the computationally-predicted lowest excited state ( $S_1 = 356 \text{ nm}$ ).<sup>4</sup>

While the  $D_{3h}$  molecular symmetry of the neutral TAH chromophore forces the lowest excited state to be spectroscopically forbidden (for both 1PA and 2PA), we demonstrate that molecular symmetry-switching as a result of acidic- or basic-reactions reveals this forbidden state in either 2PA or 1PA, respectively.

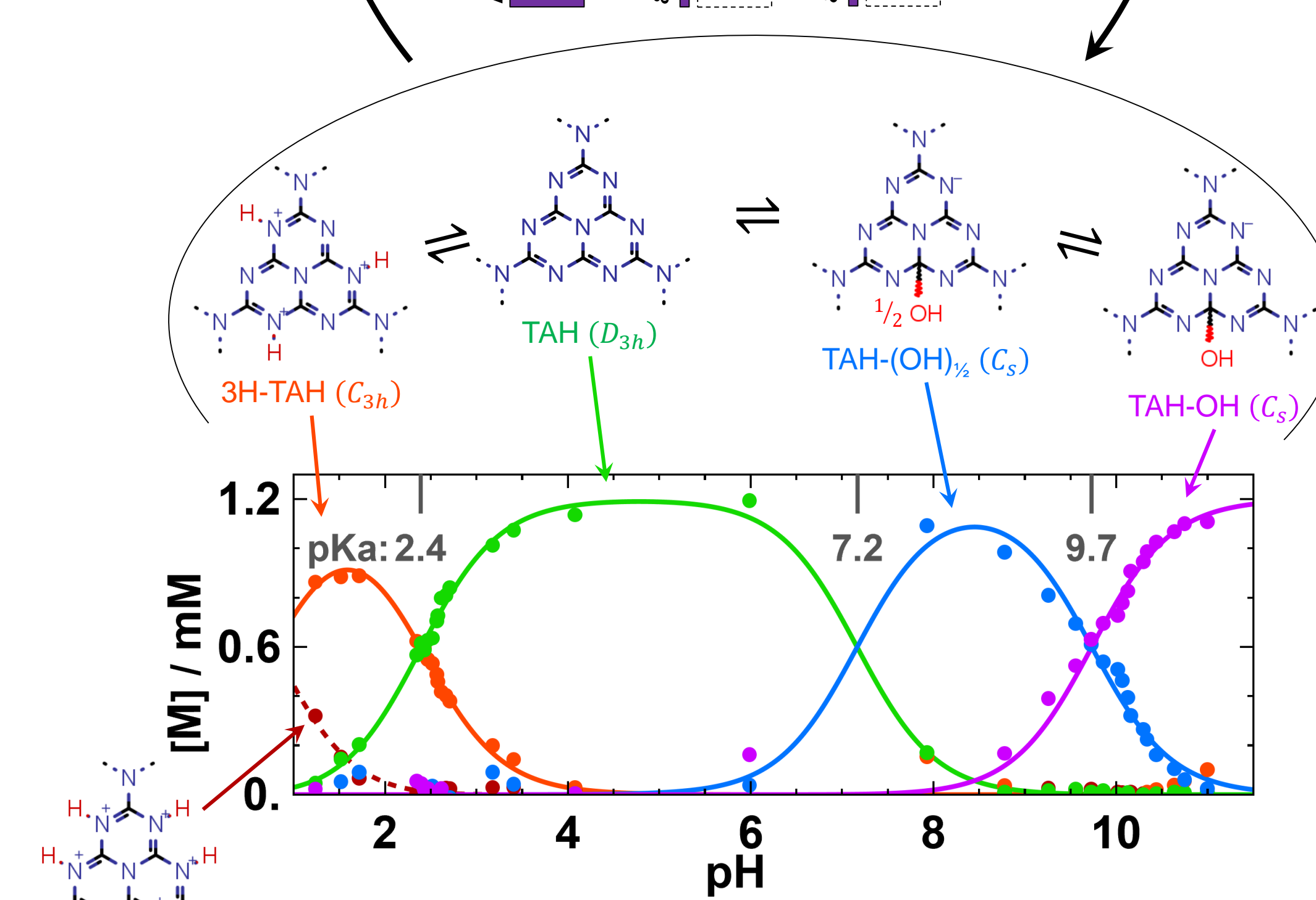
## Titration Model



Multivariate Curve Resolution Alternating Least Squares (MCR-ALS) optimization<sup>6-8</sup>

$$\epsilon^T = \frac{A}{d} \cdot C_m^T \cdot (C_m \cdot C_m^T)^{-1} \quad A = \epsilon^T \cdot C \cdot d \quad C = (\epsilon \cdot \epsilon^T)^{-1} \cdot \epsilon \cdot \frac{A}{d}$$

$$\text{Abs. pH} = \frac{[C_a]}{\epsilon_a(\lambda)} + \frac{[C_b]}{\epsilon_b(\lambda)} + \dots$$



Reaction model of 1PA absorption. Top: Molar absorbance spectra for four molecular species. Bottom: Corresponding titration curves.

Titration isosbestic points confirm four molecular species; while a better fit<sup>6-8</sup> is found with a fifth-form (6H-TAH), its spectrum is not resolvable. Reactions can be realized as a triple-protonation in acid, as well as two-step hydroxylation in basic conditions. The spectral similarity and growth of the feature at 355 nm observed for TAH-(OH)<sub>1/2</sub> and TAH-OH conforms with OH<sup>-</sup> additions to each half of dimelem.

## Molecular Symmetry Switching

Assignments of 1PA/2PA transitions for x,y,z-molecular axes.

Activity	Function	$C_{3h}$	$D_{3h}$	$C_s$	$\lambda_{1PA}, \text{nm}$
2PA	$x^2 + y^2, z^2$	$A'$	$A'_1$	$A'$	355
1PA	$z$	$A''$	$A''_2$	$A'$	315
2PA	$(xz, yz)$	$E''$	$E''$	$A'$ $A''$	300
1PA & 2PA	$(x, y)$ $(x^2 - y^2, xy)$	$E'$	$E'$	$A'$ $A''$	283/293

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\* The purchased sample was listed as Melem, while 1PA-titration results and spectra suggest it is in fact the dimer. However, the appearance of isosbestic points, as well as the single emission profile found in the 2D-2PEF matrix, implies it is essentially pure.