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Assessing Diphenyl Polyenes as pH-Sensitive Colorimetric Probes of Proton Gradients in Polymer Coatings

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Shesham, Vaishnavi, "Assessing Diphenyl Polyenes as pH-Sensitive Colorimetric Probes of Proton Gradients in Polymer Coatings" (2021). *Graduate Student Showcase*. 22.

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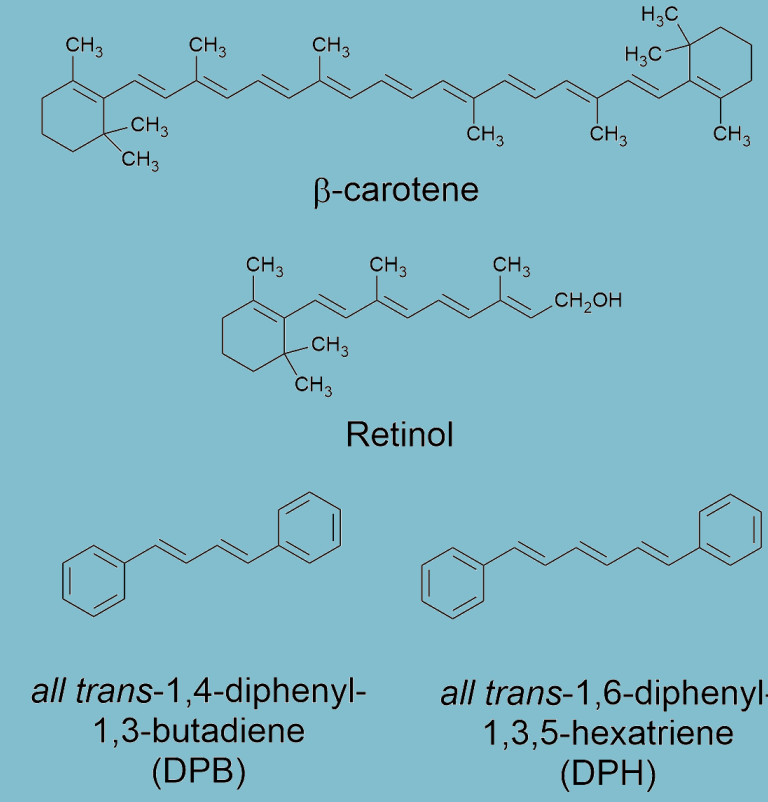
ASSESSING DIPHENYL POLYENES AS PH SENSITIVE COLORIMETRIC PROBES OF PROTON GRADIENTS IN POLYMER COATINGS



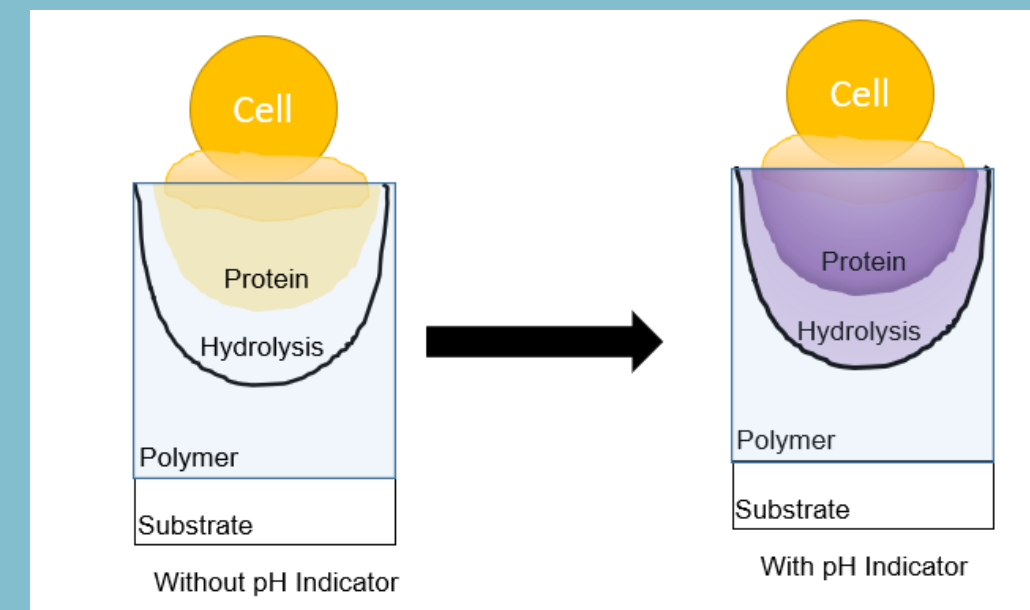
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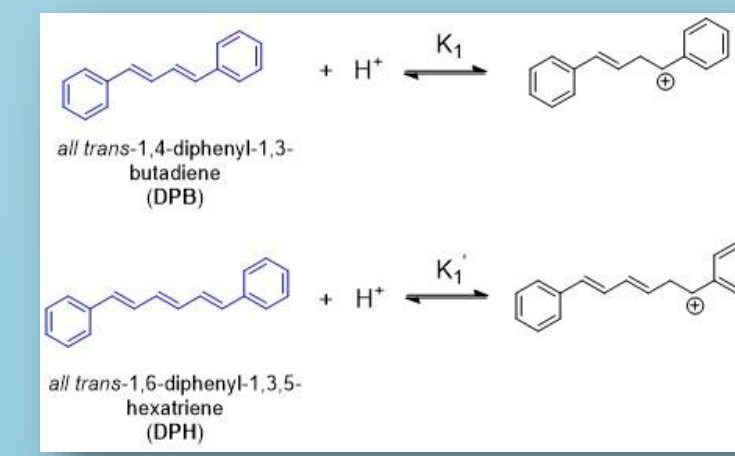
Objective: Blend pH indicators into polymer coatings that are suitable for imaging acidic regions



Background: Finding the suitable pH probe for imaging the spatial resolution of acidic regions will require low water solubility and mobility in the polymers



Theoretical Calculation of the Basicity of DPPs from Ground State Energies



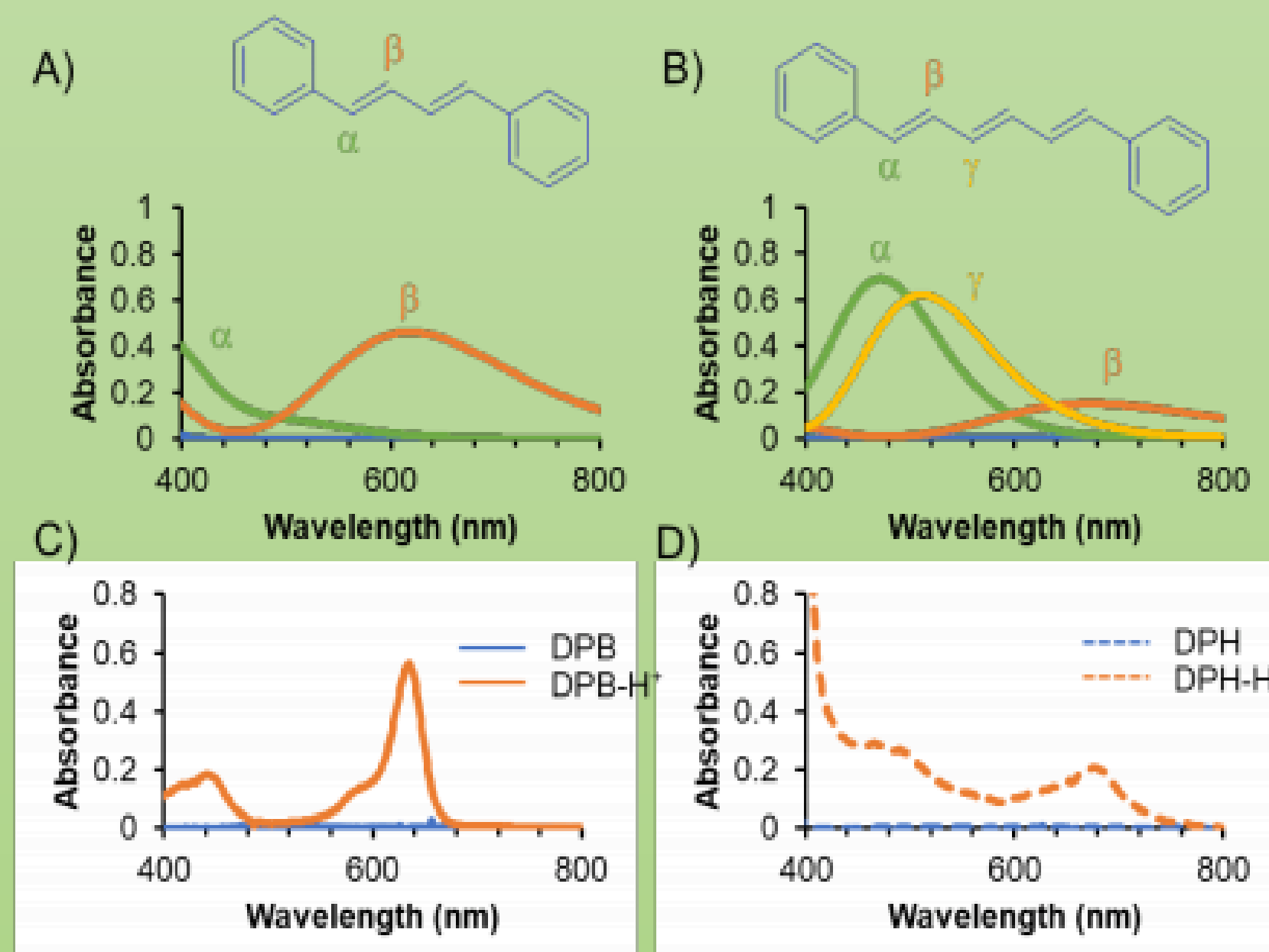
We calculated the ground state geometry optimized structures using PM6 calculations for protonated and unprotonated DPPs in *Gaussian09* to calculate the relative free energy change of the protonation of DPPs

$$\Delta G_r^0 = (\Delta G^0_{\text{PolyeneH}^+}) - (\Delta G^0_{\text{Polyene}} + \Delta G^0_{\text{H}^+})$$

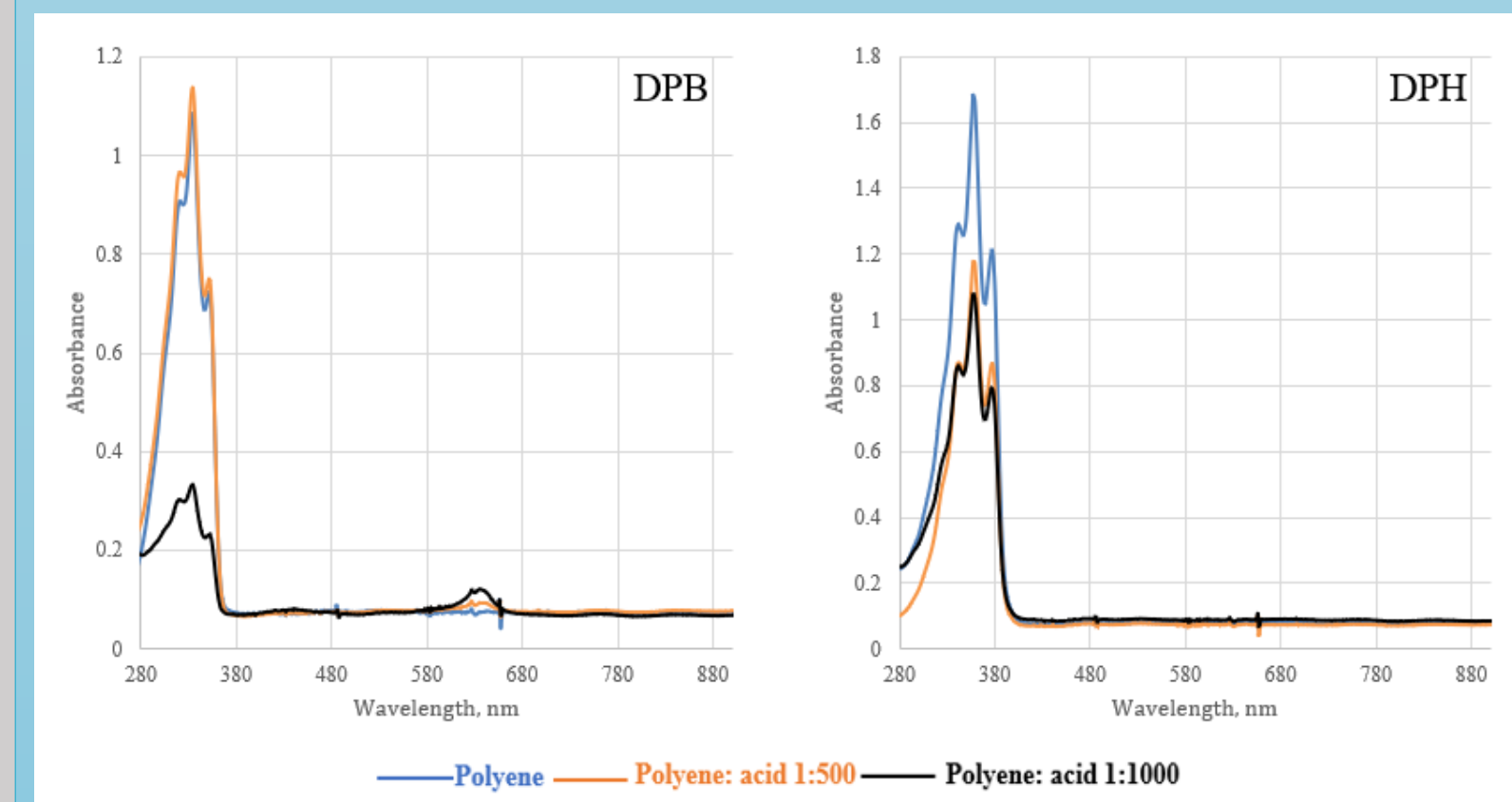
Polyene	ΔG^0 kJ/mol	Relative Kb (per condition)
DPB (gas phase)	737	1
DPH (gas phase)	766	7.32×10^{-6}
DPB (in Chloroform)	596	1
DPH (in Chloroform)	619	3×10^{-4}

DPB more basic than DPH by 10^4 times

Comparing Experimental to Theoretical UV-vis spectra to Determine the Protonation Site on Diphenyl Polyenes (DPPs)

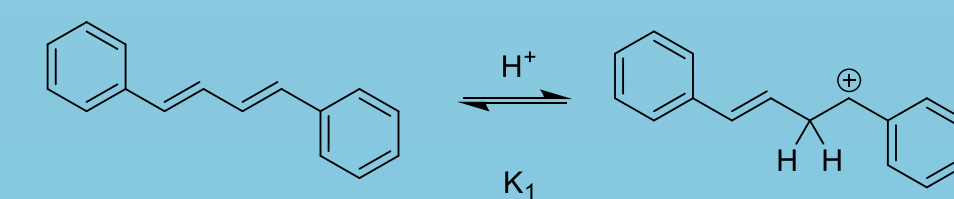


Calculation of the Experimental Basicity of DPPs in Chloroform

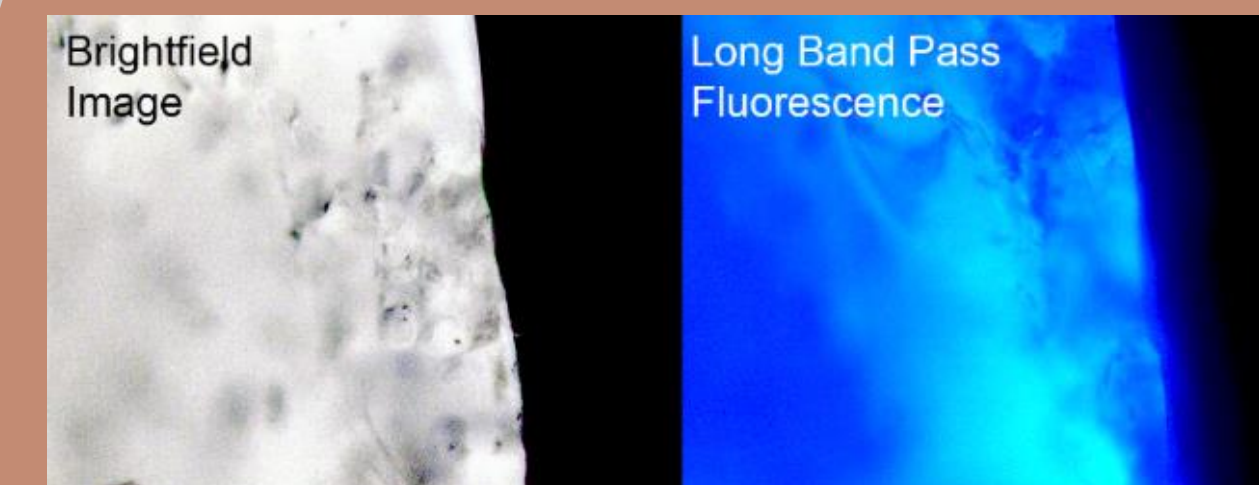


Spectroscopic Titration of DPPs in Chloroform with Trichloroacetic acid

The basicity of DPB was calculated to be **5 times** greater than DPH in chloroform using the systematic treatment of equilibria



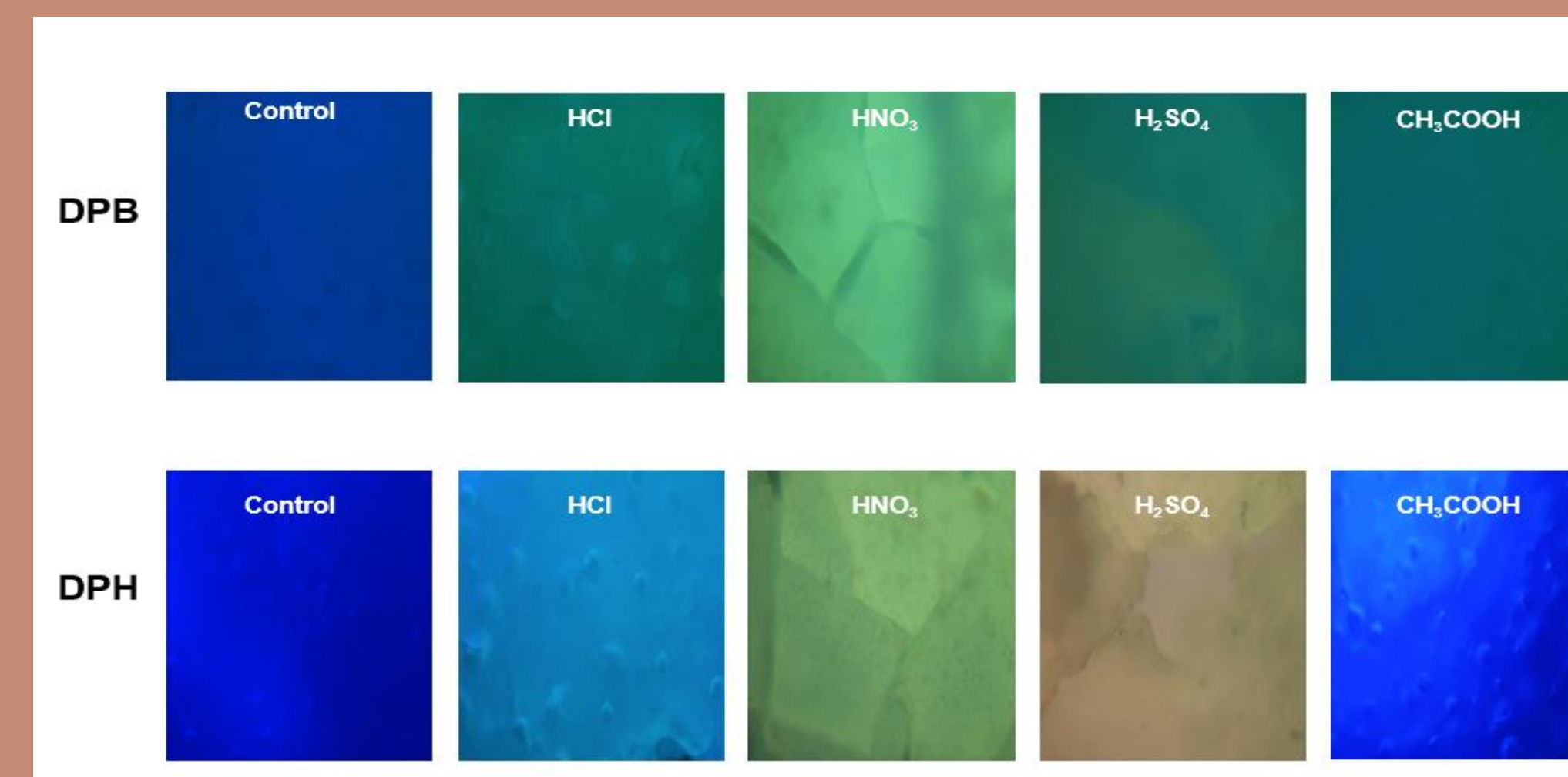
Polyene blended polymer coatings



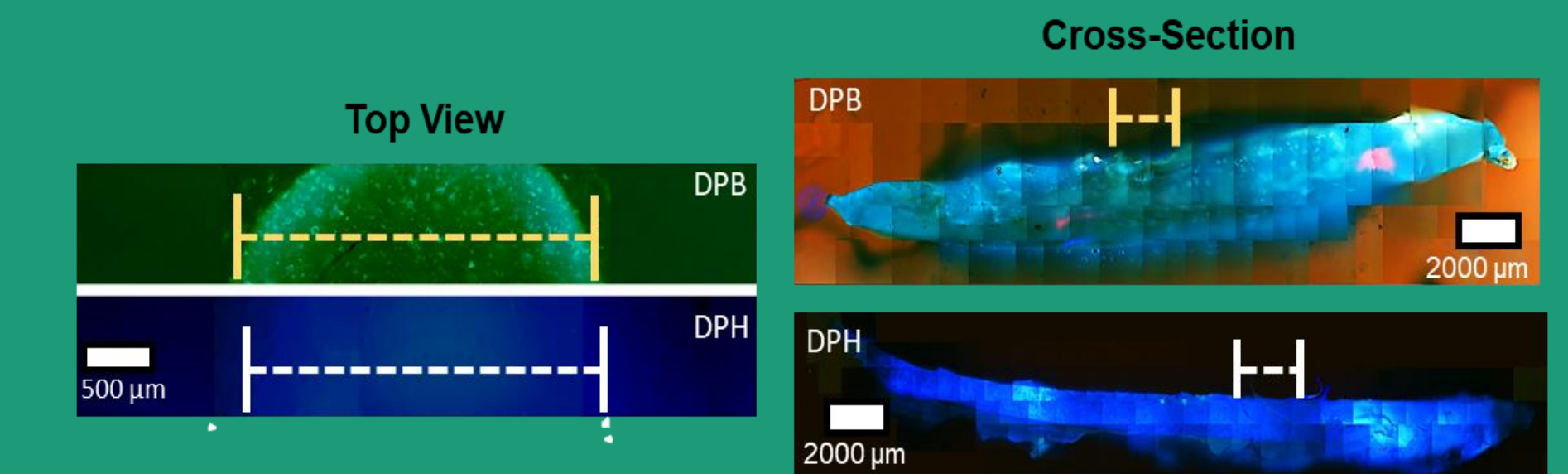
Fluorescence and Brightfield Microscopy Image of DPH coatings (0.1% w/w) melt cast with a polyester polyurethane coating

Exposure of DPP Coatings to Acids and Bases

The figure shows the fluorescence images of polyene blended polymer coatings exposed to various acids. $1 \mu\text{L}$ of each acid was drop cast on the coatings and the fluorescence images were taken after 48 hours of exposure to acid. Control shows the image of without any acid exposure. For diphenyl butadiene (DPB), HNO_3 was most reactive followed by H_2SO_4 and HCl , there is very slight decrease in the intensity with the acetic acid. For diphenyl hexatriene (DPH), H_2SO_4 completely quenched the fluorescence and HNO_3 also reacted, but there was no reaction with acetic acid, which shows that DPB is a better base compared to DPH as it reacted with the weak acid. From these images DPB and DPH can be used as potential pH sensitive probes for polymer coatings.



Preliminary Results: Biodegradation (using hydrolytic supernatants) of DPP containing polyester polyurethane coatings after 72 hours



Conclusions:

- DPPs are likely to be protonated at β -position.
- DPB is a stronger base than DPH.
- DPPs can be potential acid sensitive probes to differentiate the biological and chemical hydrolysis in polyurethane degradation process

Acknowledgements:

Funding: SERDP WP-1381

Department of Chemistry, University of Dayton.

Dr. Mark Masthay
Dr. Justin Biffinger



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