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Fluorescence Based Sensing of Residues

Trace Detection of Explosives

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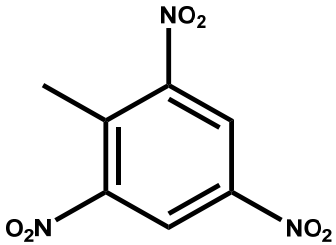
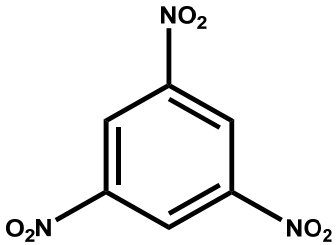
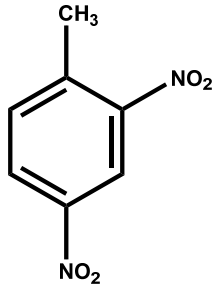
Explosives and related molecules of interest



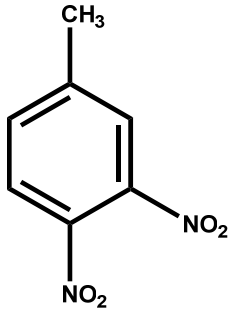
TNT



TNB



2,4-DNT



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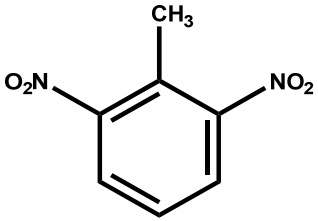
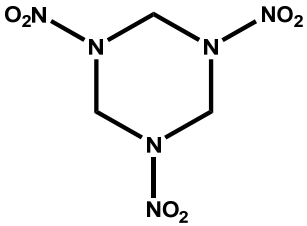
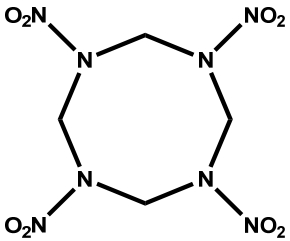


2,6-DNT



RDX



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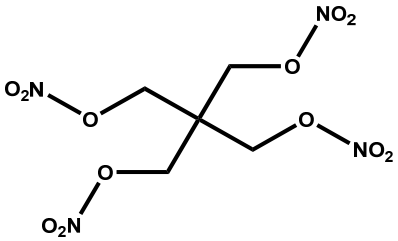
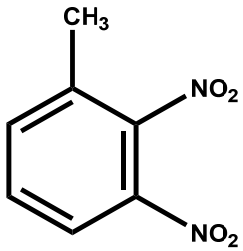
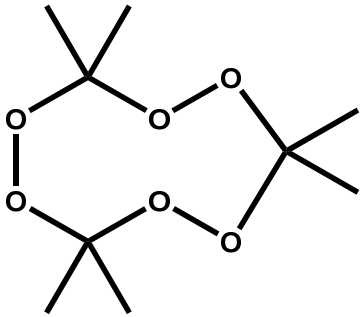


PETN



2,3-DNT

4-NT



TATP

Trace Detection of Explosives
Conjugated Polymers

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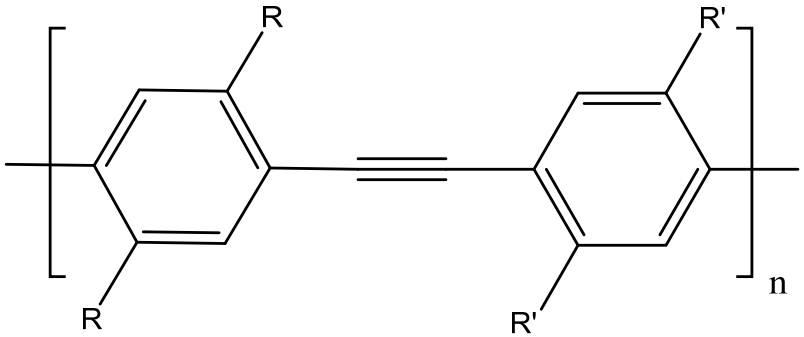
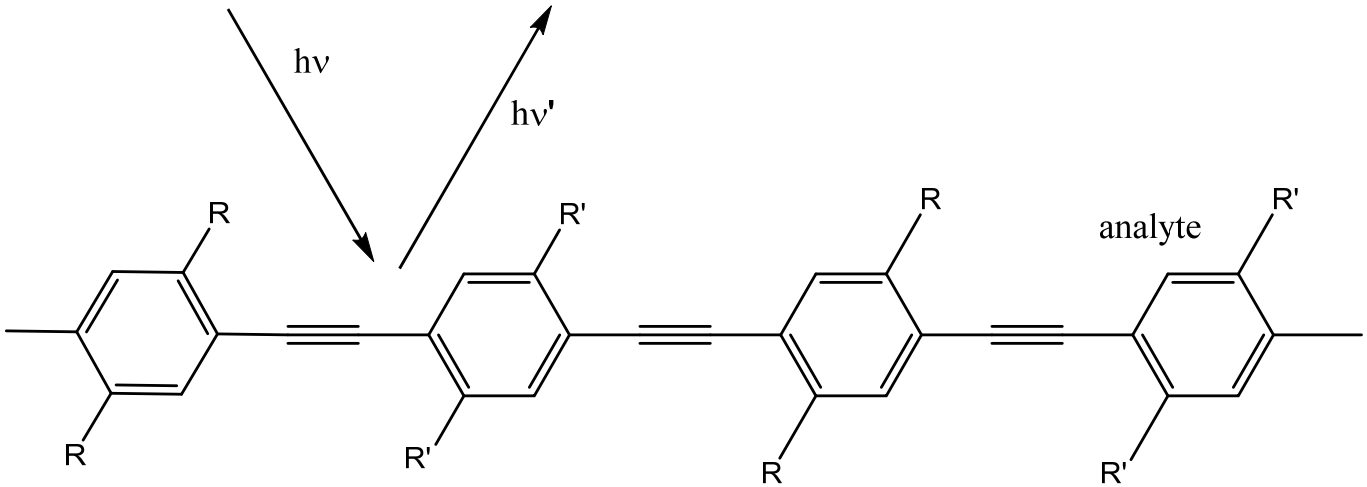
Swager, ca. 1995

Introduced the use of polyphenylenvinylenes as sensors



The conjugation amplifies the signal response because the analyte can cause quenching even if it is physically located a long distance from the excitation



Q. Zhou, T. M. Swager, *J. Am. Chem. Soc.*, **1995**, *115*, 7017 – 7018.

Trace Detection of Explosives
Xanthene Dyes

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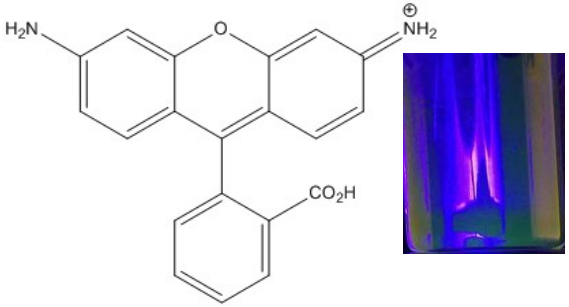
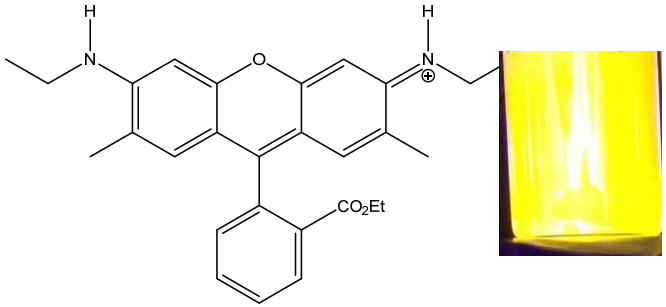
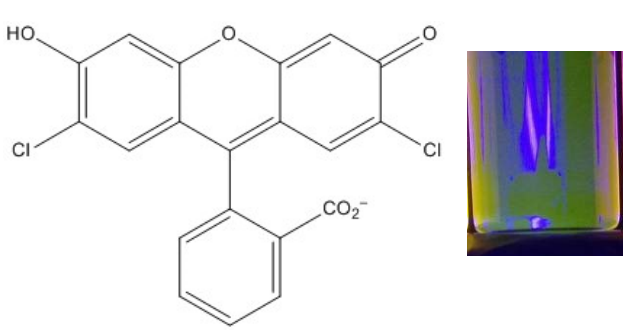


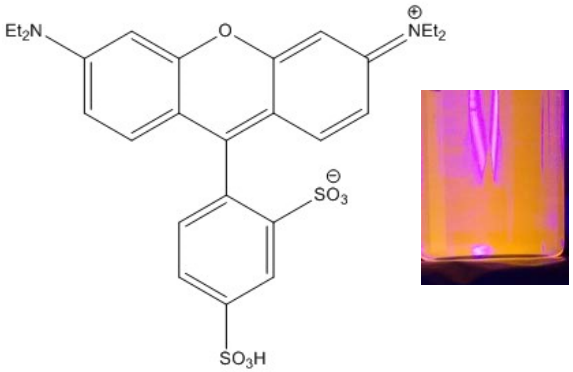
Rhodamine 560
(Rh560)



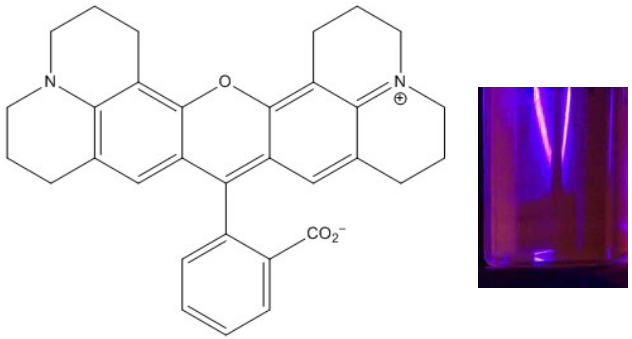
Rhodamine 6G
(Rh6G)



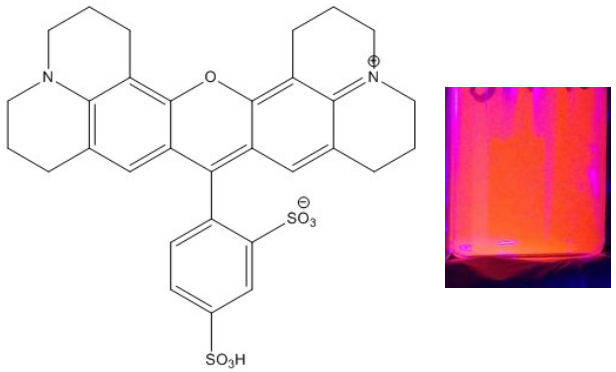
Fluorescein 548
(Fl548)



Sulforhodamine B
(SRhB)



Rhodamine 640
(Rh640)



Sulforhodamine 640
(SRh640)

Trace Detection of Explosives
Reaction of Xanthene Dyes in Solution

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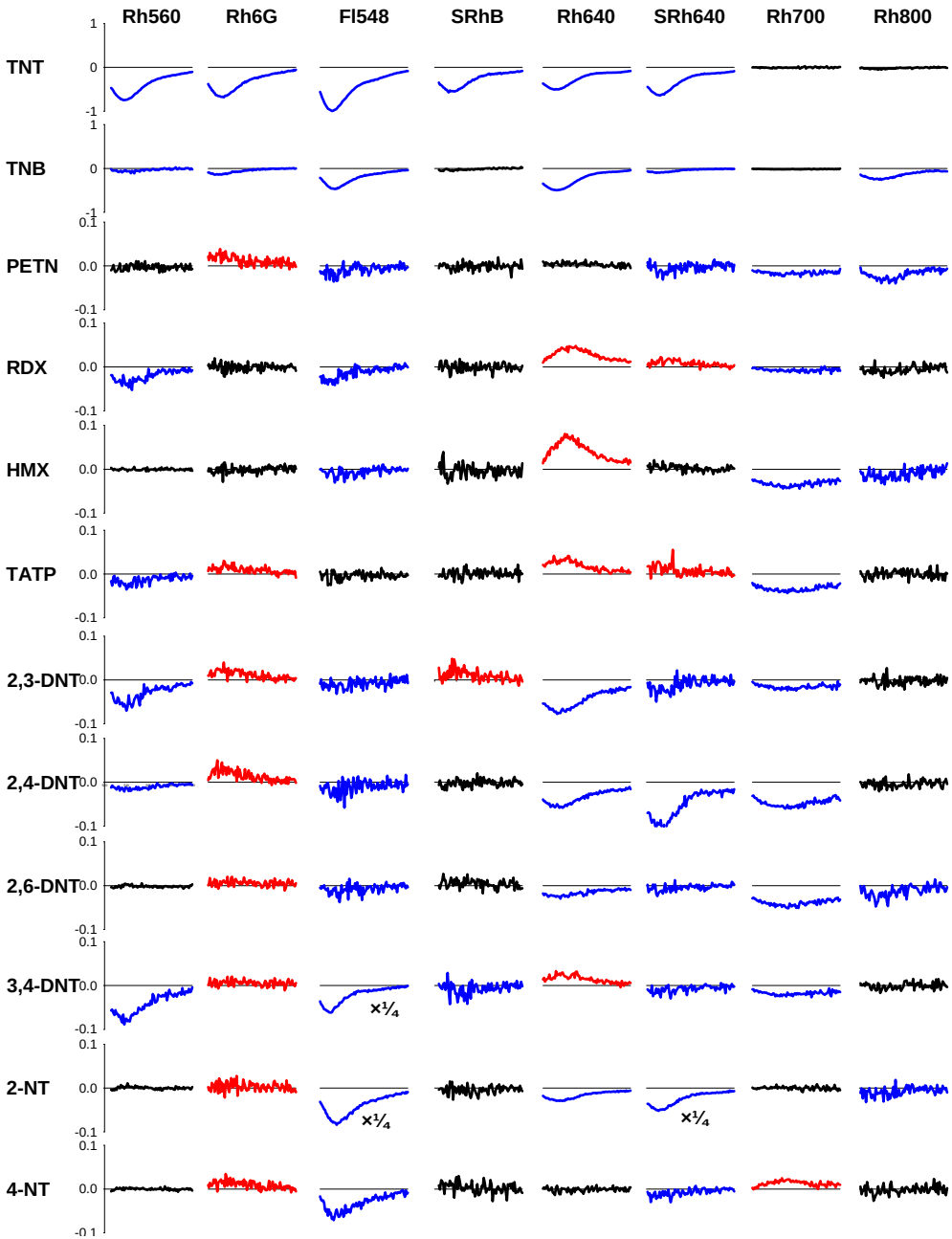

Difference spectra of each dye:

Dye + analyte → product

Blue: the analyte decreased the intensity (quenched) the spectrum

Red: the analyte increased the intensity (enhanced) the spectrum

Black: the analyte had no effect on the intensity of the spectrum

C. L. Latendresse, S. C. Fernandes, S. You, H. Q. Zhang, W. B. Euler, *Anal. Methods*, **2013**, *5*, 5457 – 5463.

Trace Detection of Explosives
Reaction of Xanthene Dyes in Solution

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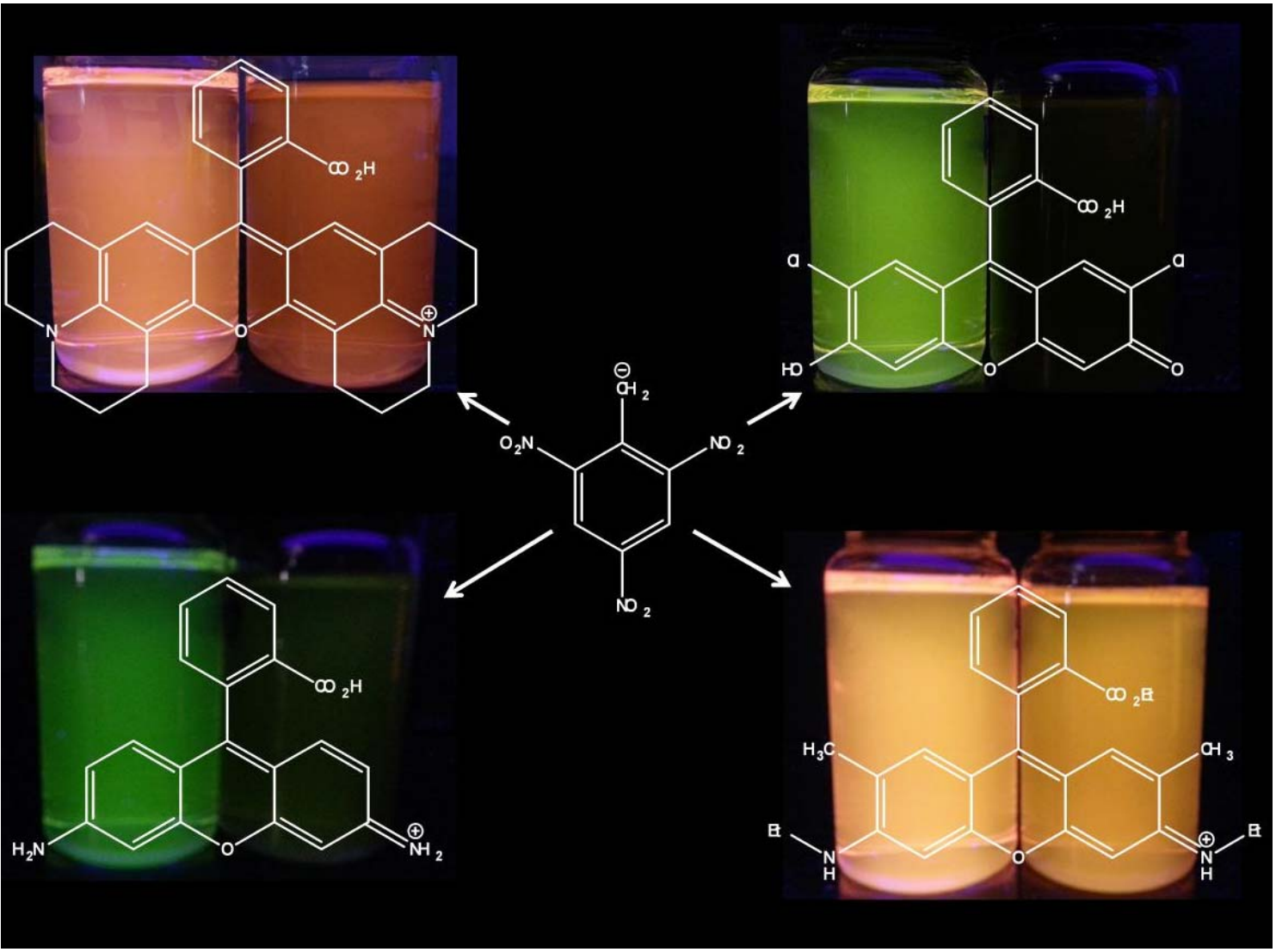

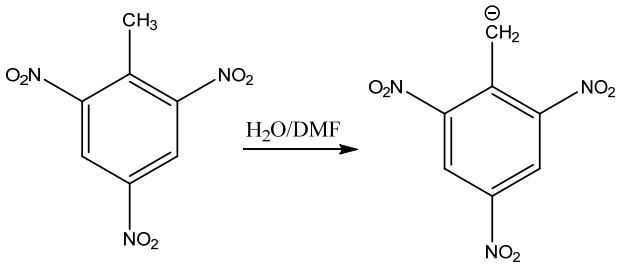

C. L. Latendresse, S. C. Fernandes, S. You, H. Q. Zhang, W. B. Euler, *Anal. Methods*, **2013**, *5*, 5457 – 5463.

Amplification of Fluorescence Emission

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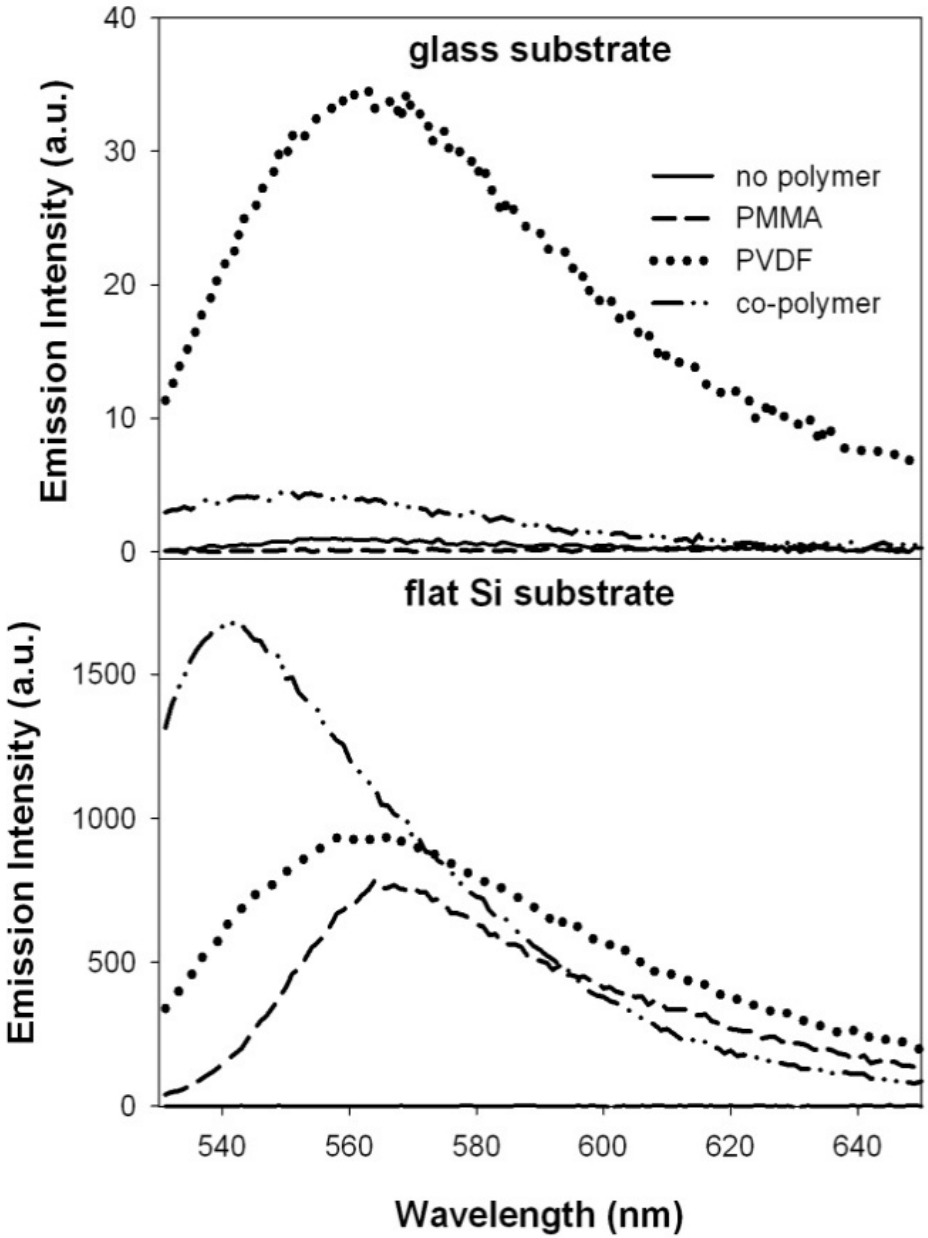

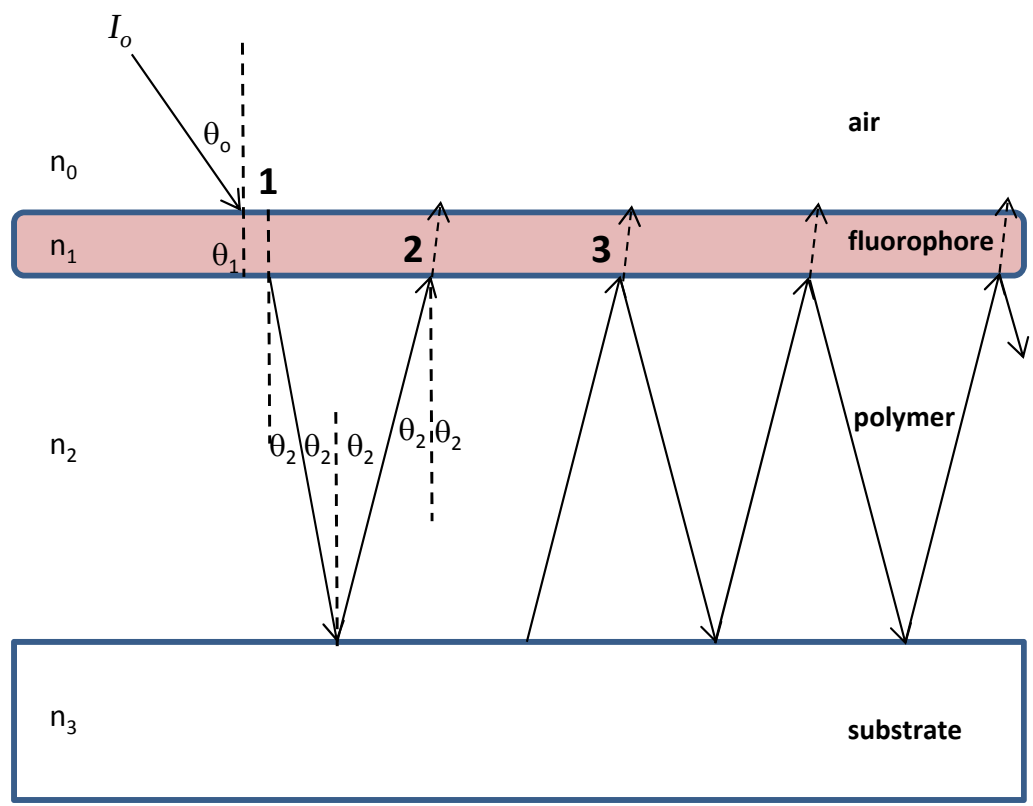

At least some portion of the fluorescent enhancement arises from internal reflections in the polymer layer.

M. A. Matoian, R. Sweetman, E. C. Hall, S. Albanese, W. B. Euler, *J. Fluoresc.*, **2013**, *23*, 877 – 880.

Trace Detection of Explosives
Gas Phase Detection

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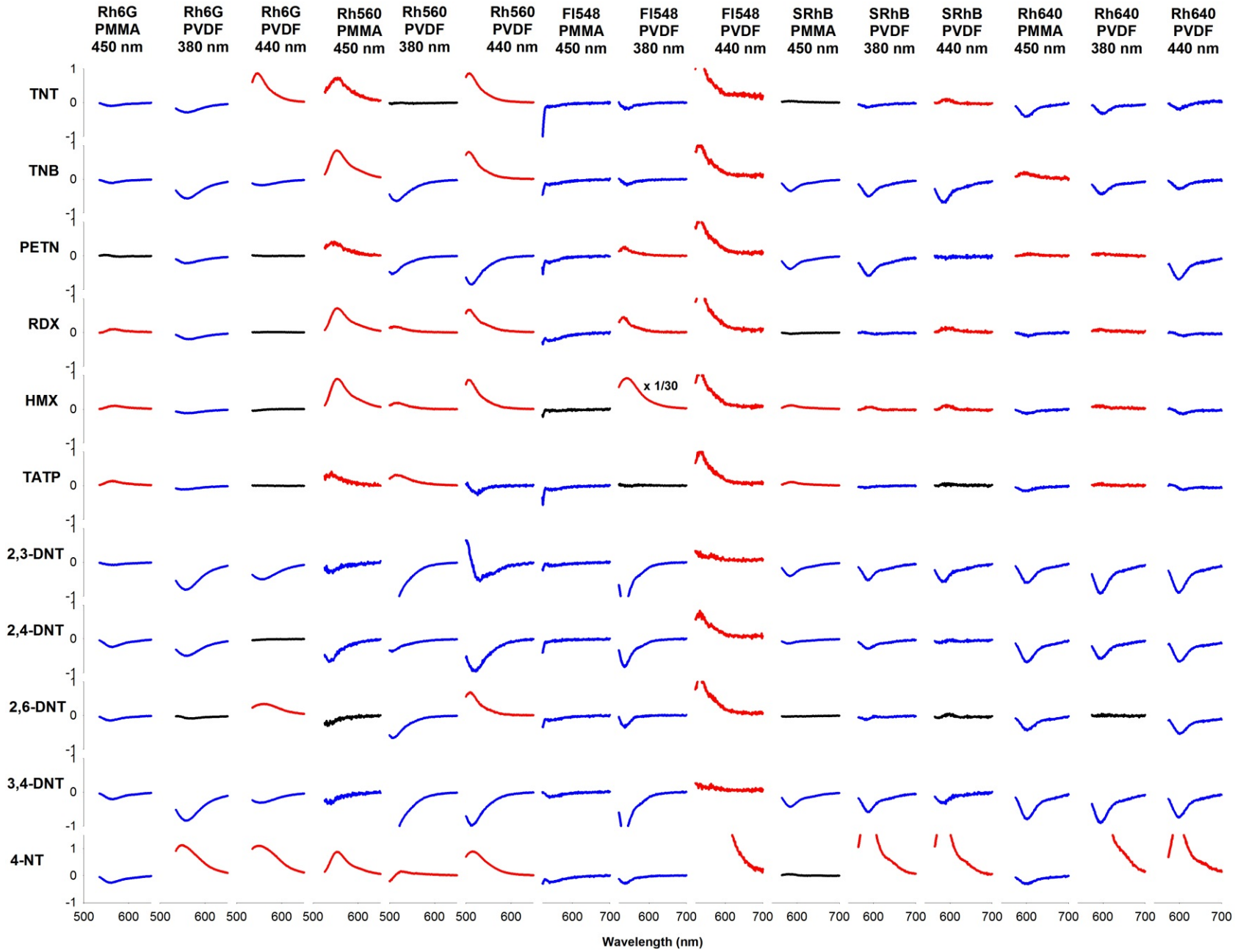

H. Q. Zhang, W. B. Euler, submitted to *Anal. Chem.*, **2015**.

Rh6G on a Glass Substrate

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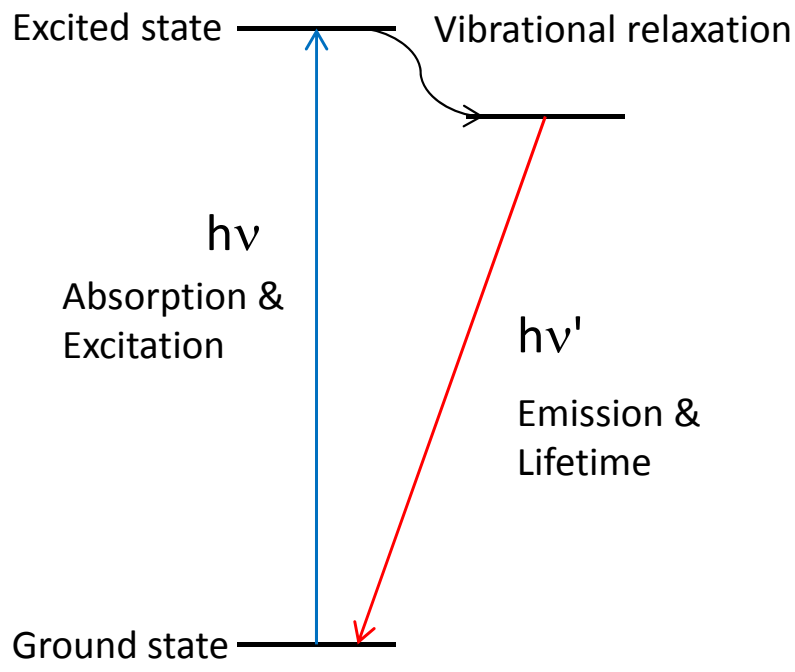
Investigate the fundamental photophysics of one fluorophore – Rh6G – thin film in detail

- Measure the absorption spectrum as a function of thickness
- Measure the excitation spectrum as a function of thickness
- Measure the emission spectrum as a function of thickness
- Measure the excited state lifetime as a function of thickness



Rh6G on a Glass Substrate
Molecular Dimensions

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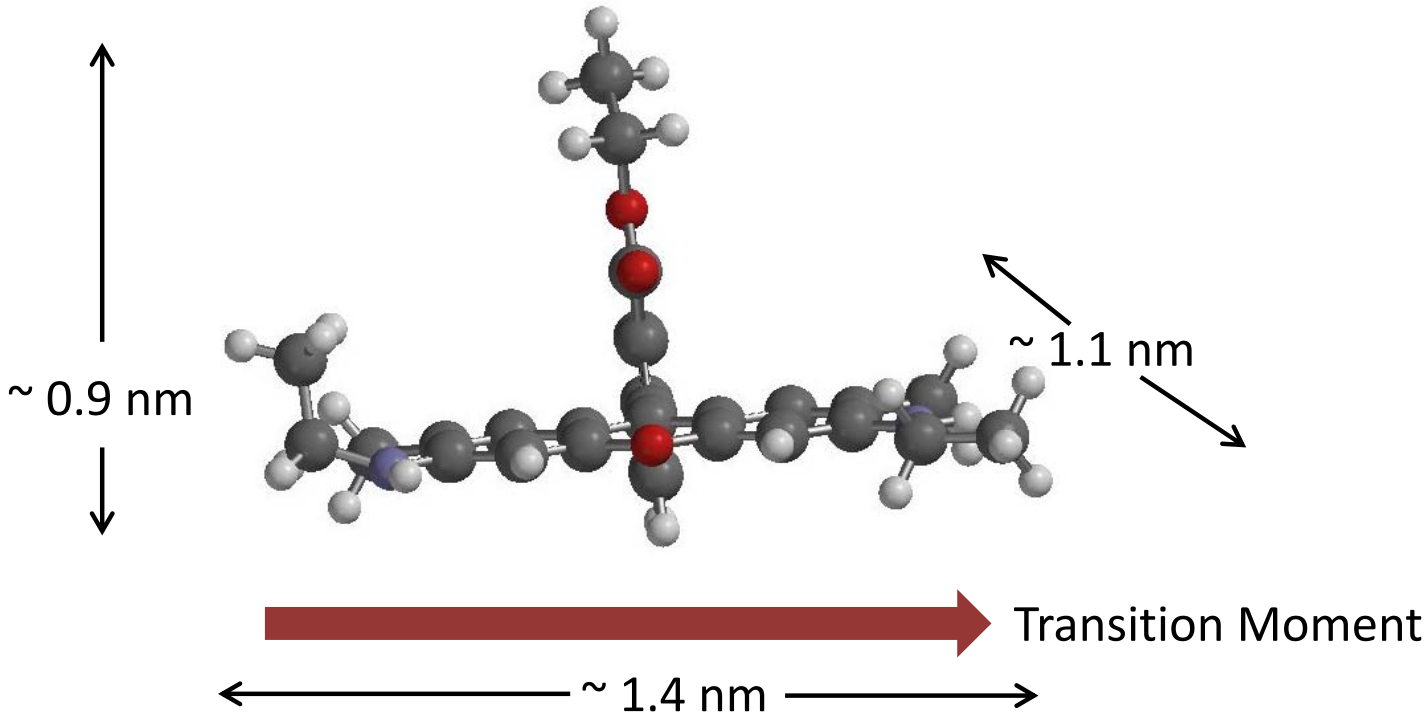
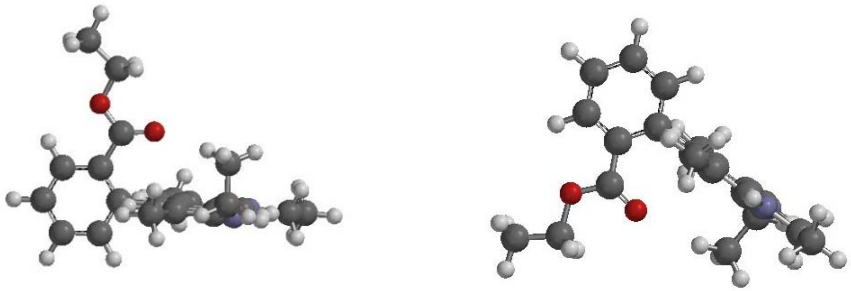
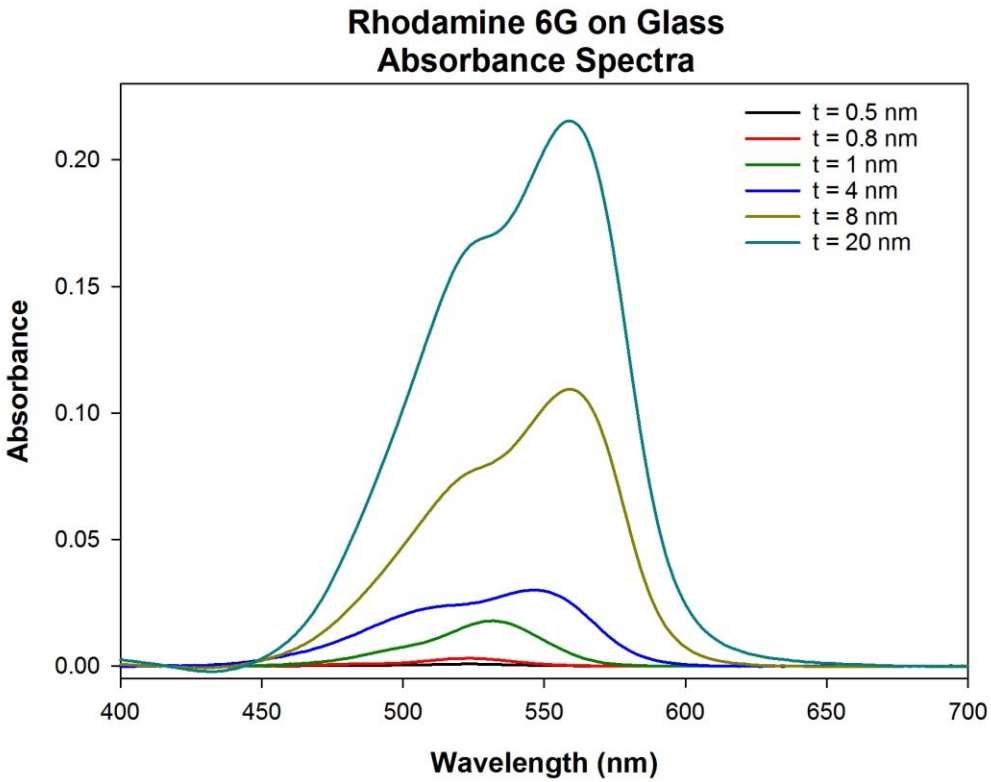
Rh6G

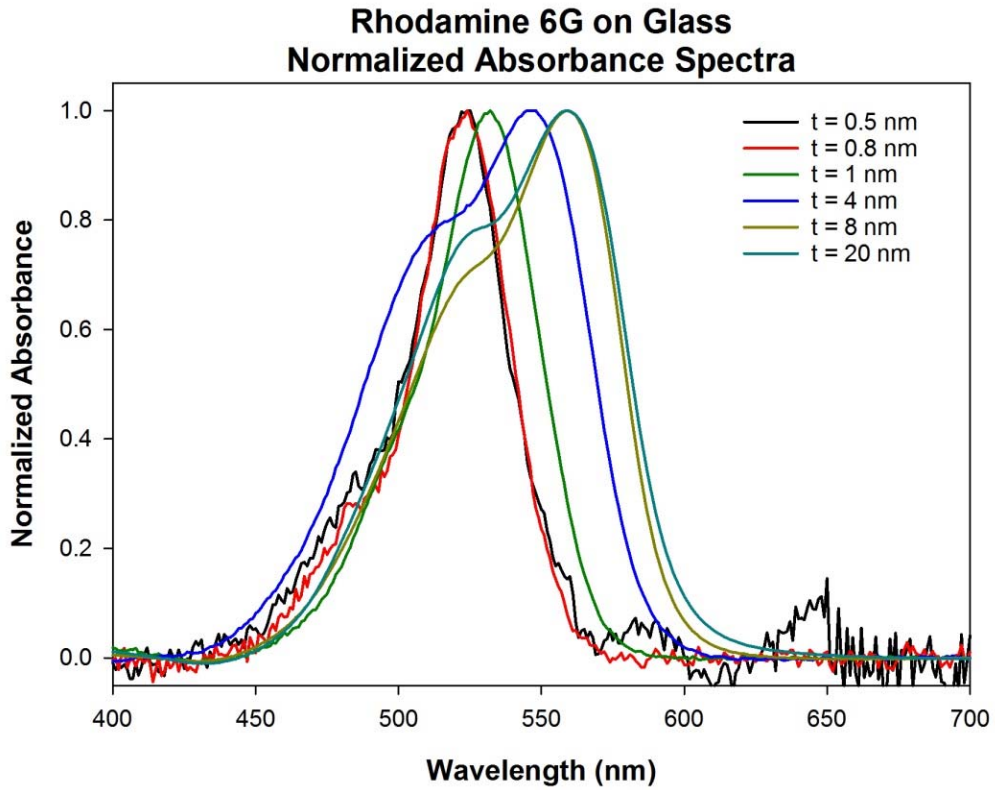




Rh6G on a Glass Substrate

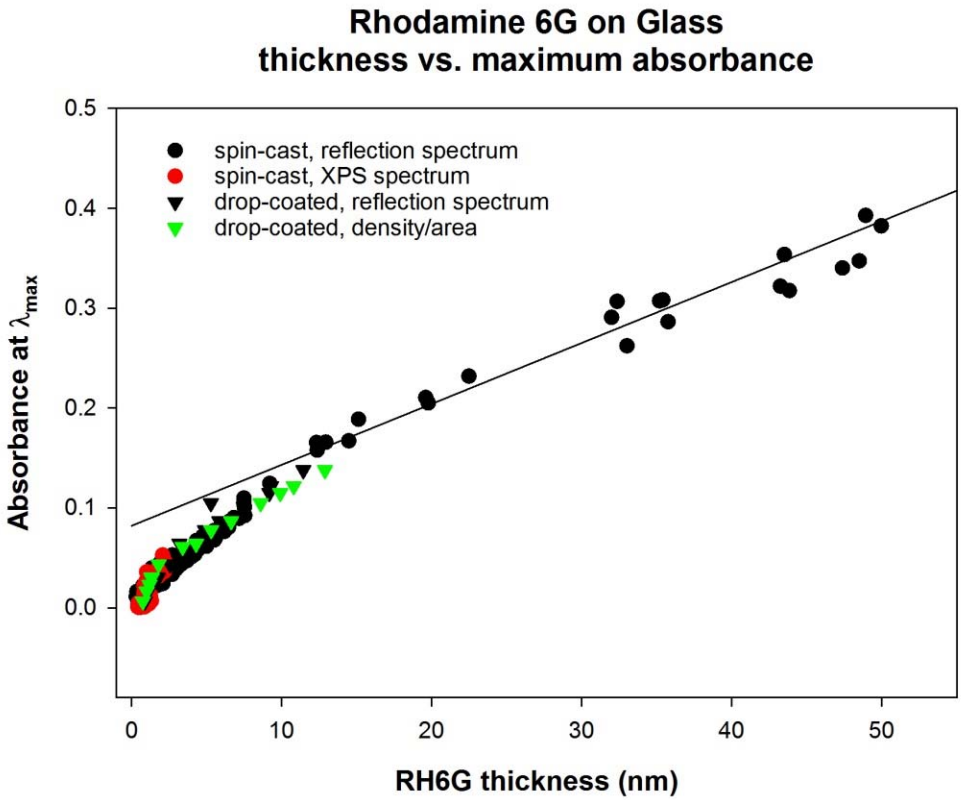
Absorption Spectra

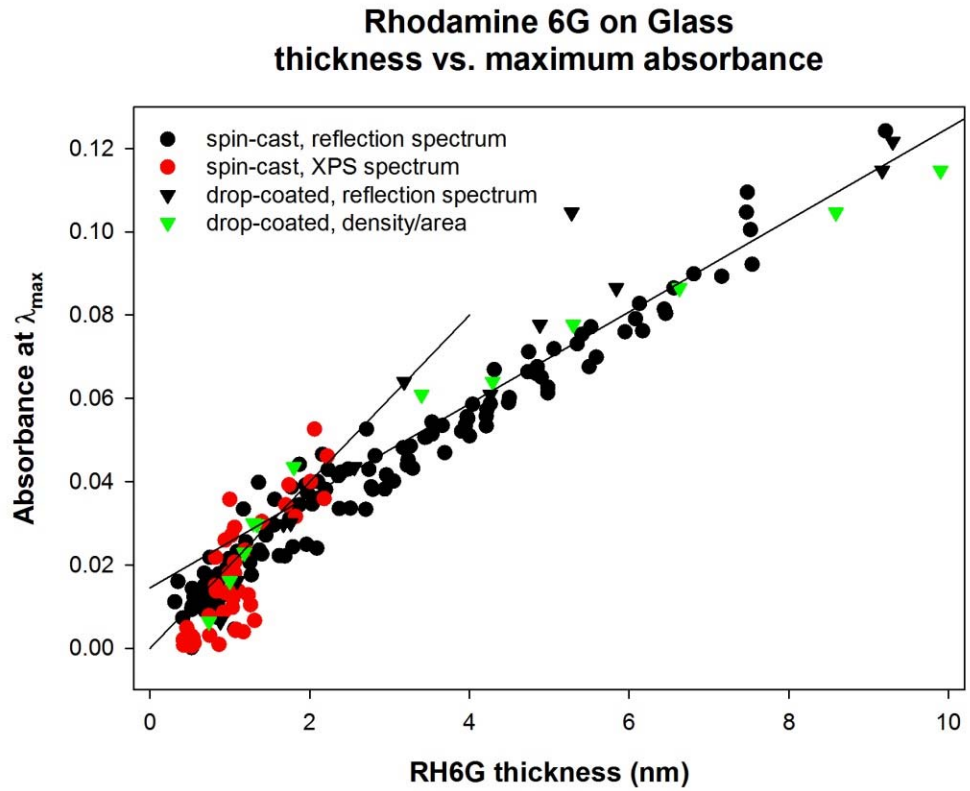




Rh6G on a Glass Substrate

Absorption Spectra





Rh6G on a Glass Substrate

Polarized Absorption Spectra

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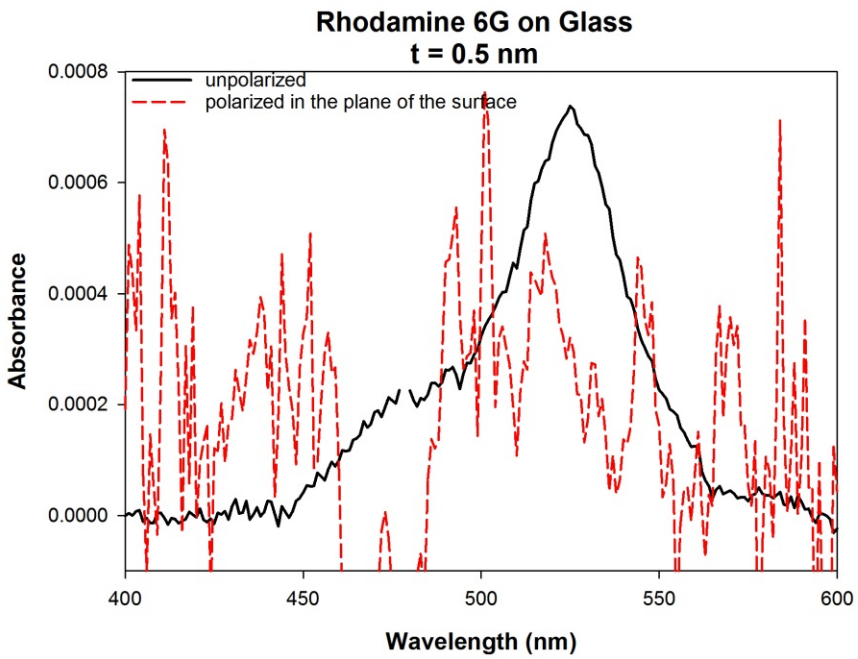
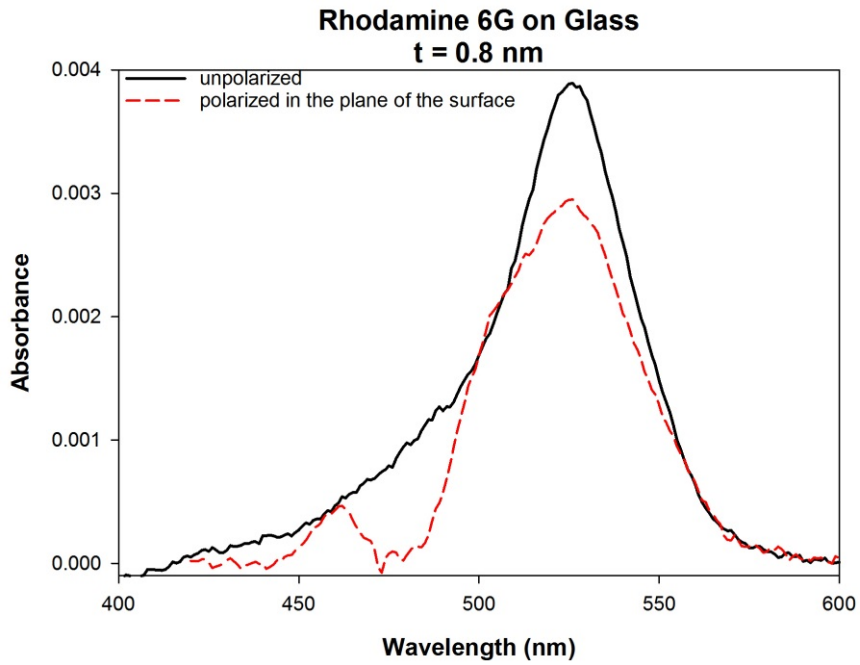
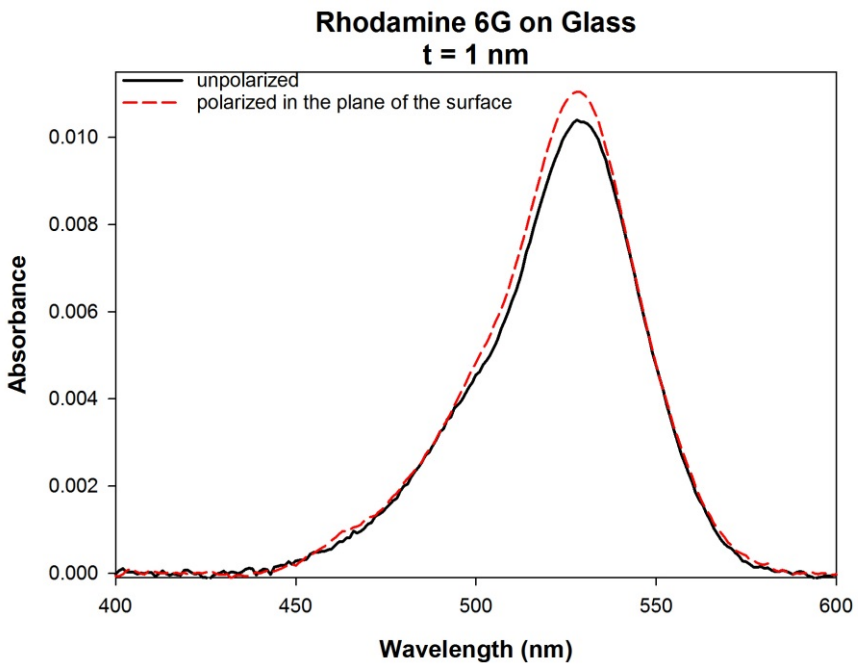
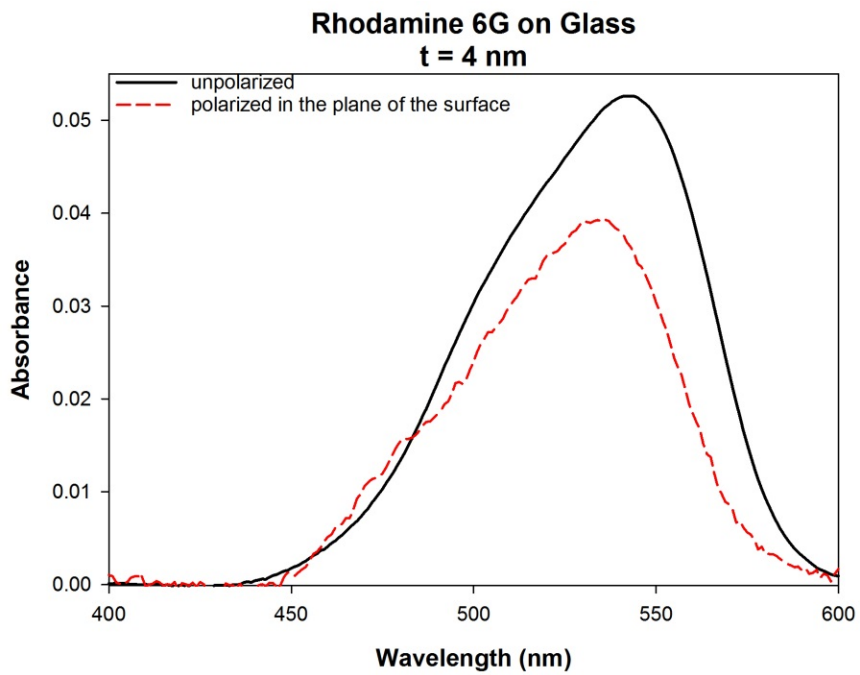


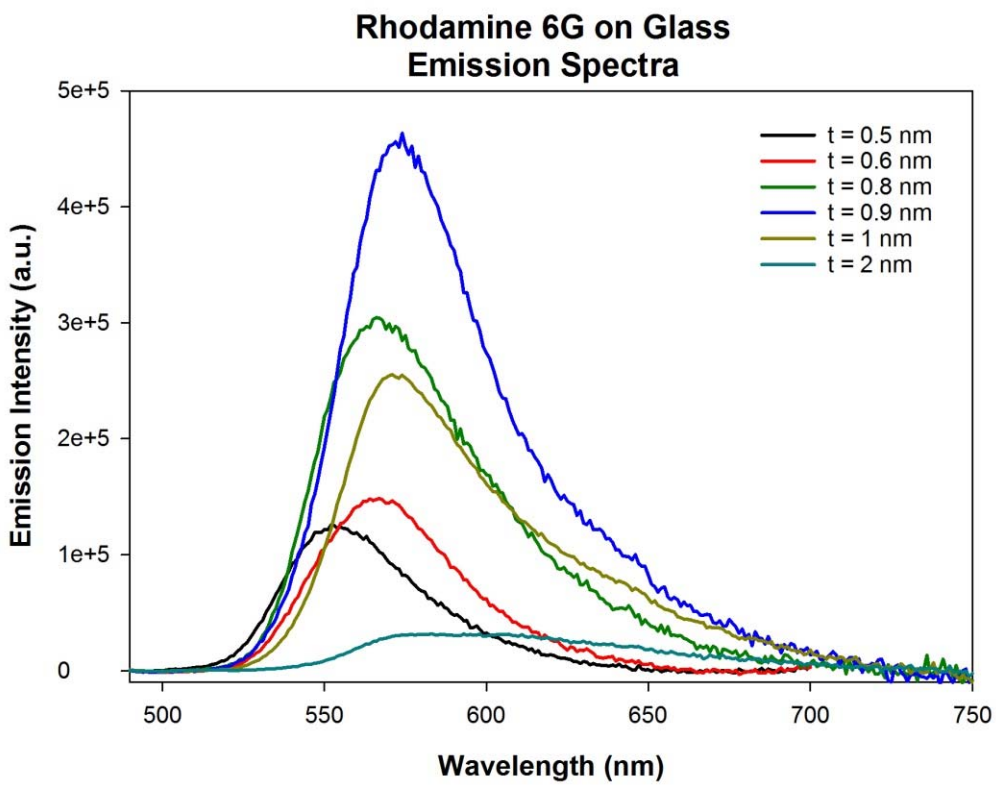


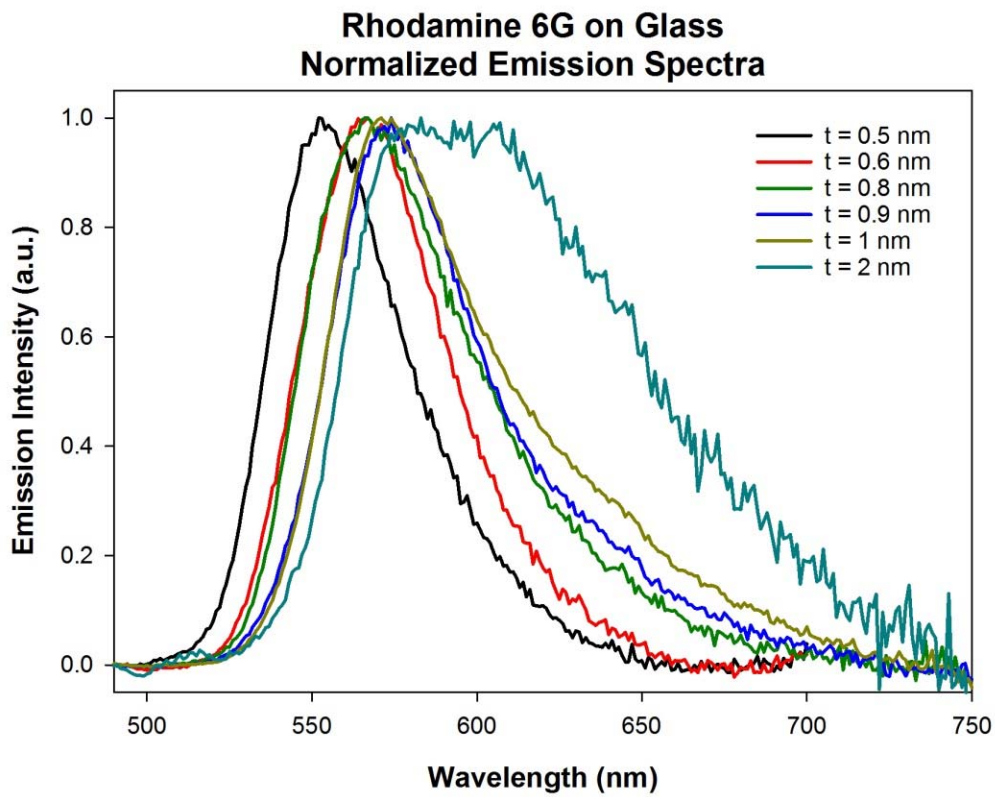




Rh6G on a Glass Substrate

Emission Spectra





Rh6G on a Glass Substrate

Normalized Absorption, Excitation, & Emission Spectra

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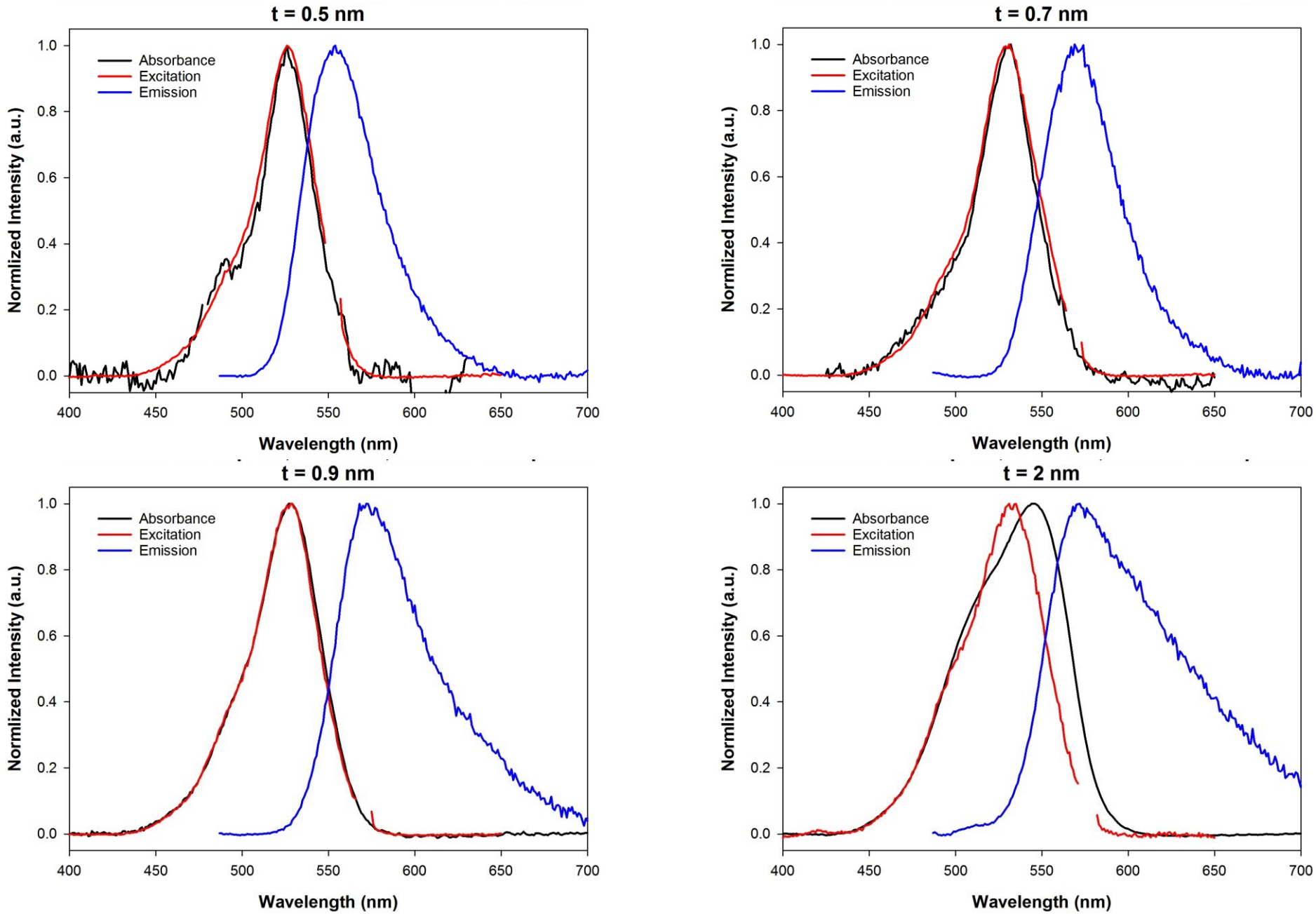

Rh6G on a Glass Substrate

Spectral Deconvolution

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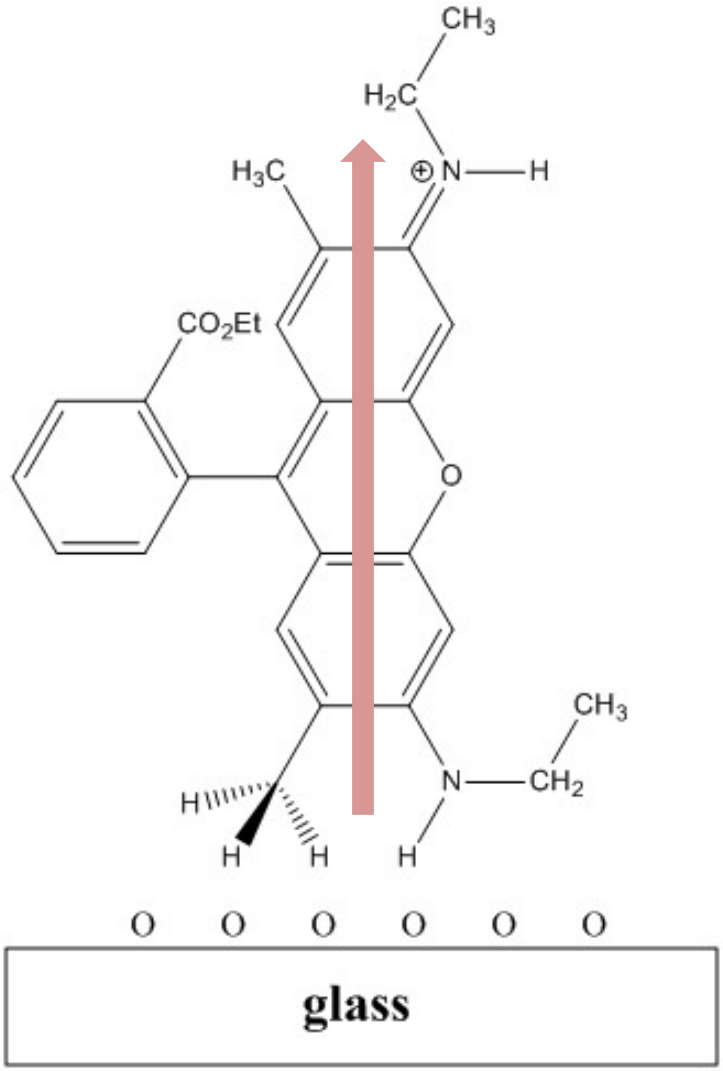
Peak	Absorbance (λ, Γ)	Thickness (nm)	Concentration (M)	Emission (λ, Γ)
1	(490, 18)	0.5 – 1.3	$6\times10^{-7} – 4\times10^{-5}$	(562, 18)
2	(510, 28)	1.2 – 60	$8\times10^{-6} – 1\times10^{-2}$	(562, 18)
3	(525, 18)	0.5 – 1.2	$6\times10^{-7} – 7\times10^{-6}$	(552, 18)
4	(533, 18)	1.2 – 60	$8\times10^{-6} – 1\times10^{-2}$	(580, 29)
5	(552, 18)	1.5 – 4.0	$4\times10^{-4} – 1.2\times10^{-3}$	(625, 38)
6	(564, 18)	4.0 – 60	$1.2\times10^{-3} – 1\times10^{-2}$	

Rh6G on a Glass Substrate

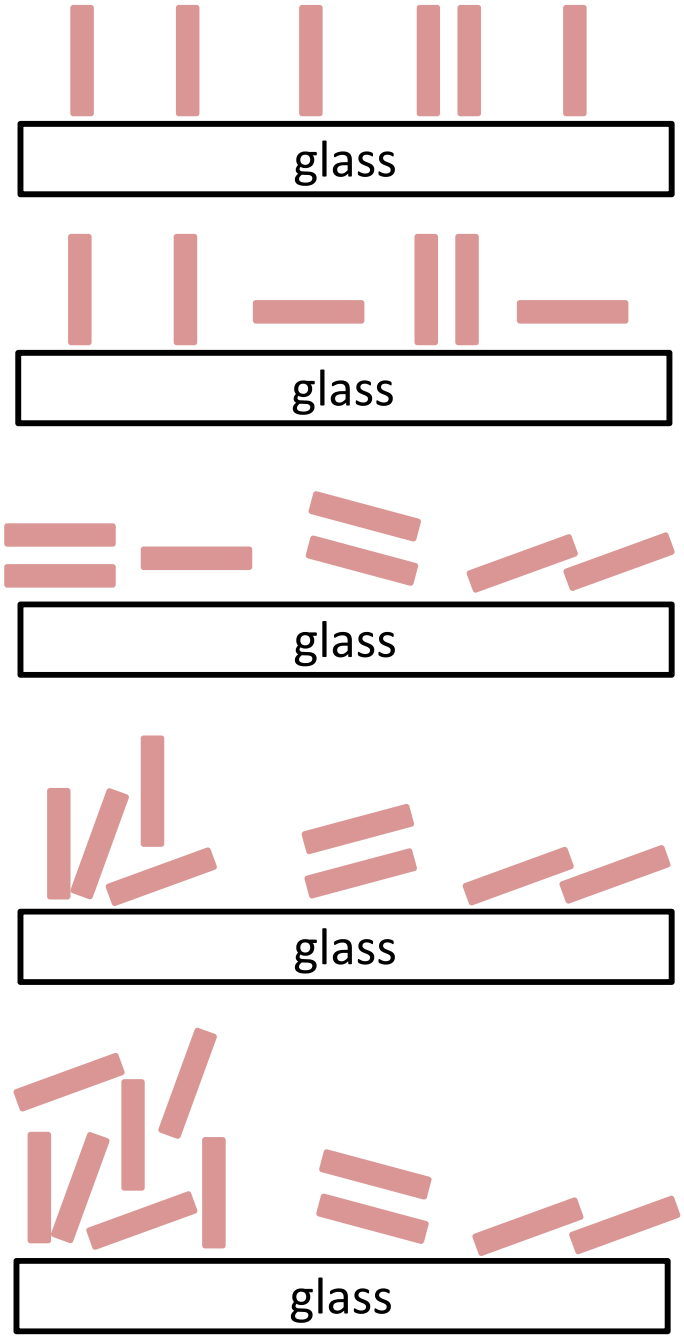
Structural Assignments



- Monomer
- Perpendicular to the surface at low coverage
- λ_{max} (absorption) = 525 nm
- λ_{max} (emission) = 552 nm

Rh6G on a Glass Substrate

Structural Assignments



Very low surface coverage < 0.5 nm
- perpendicular monomers λ_{max} = 525 nm
- perpendicular H-dimers λ_{max} = 490 nm

Low surface coverage ~0.5 – 1.1 nm
- perpendicular & parallel monomers λ_{max} = 525 nm
- perpendicular H-dimers λ_{max} = 490 nm

Approximately monolayer coverage ~1.2 – 1.5 nm
- parallel monomers λ_{max} = 525 nm
- perpendicular H-dimers λ_{max} = 490 nm
- tilted H-dimers λ_{max} = 510 nm
- tilted J-dimers λ_{max} = 533 nm

2- 3 layer coverage ~1.5 – 4 nm
- tilted H-dimers λ_{max} = 510 nm
- tilted J-dimers λ_{max} = 533 nm
- small aggregates λ_{max} = 552 nm

high coverage > 4 nm
- tilted H-dimers λ_{max} = 510 nm
- tilted J-dimers λ_{max} = 533 nm
- large aggregates λ_{max} = 564 nm

Lessons for Sensor Design and Optimization

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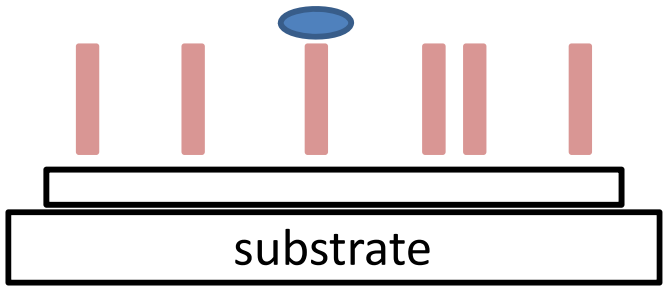
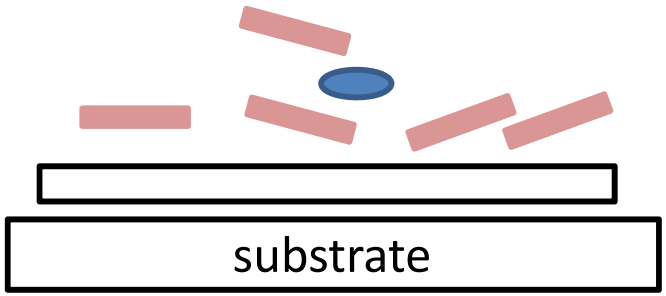
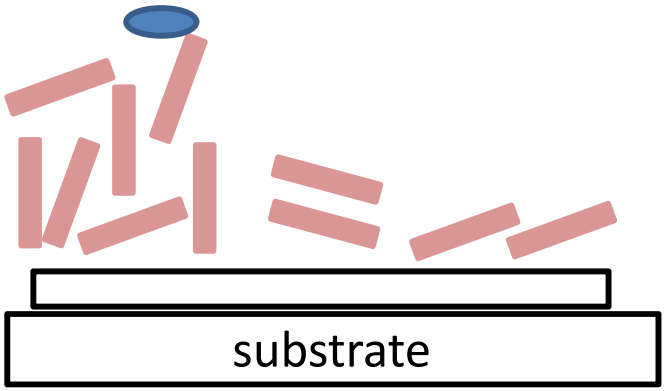


- Low coverage leads to a high emission signal
- Polymer layer provides signal amplification
- Analyte interacts with a high percentage of surface molecules, which leads to a large signal change



- Near monolayer coverage leads to an intermediate emission signal
- Polymer layer provides signal amplification
- Analyte interacts with a small percentage of surface molecules, which leads to a small signal change
- Analyte may break up dimers, which can lead to signal enhancement



- Thick coverage leads to a low emission signal
- Polymer layer provides signal amplification
- Analyte interacts with an insignificant percentage of surface molecules, which leads to no signal change

Conclusions

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- Xanthene dyes interact with explosive analytes to give measurable changes to their fluorescence spectrum
- The absence of a change in the absorption spectrum indicates that the dye/analyte interaction is with the excited state
- For Rhodamine 6G the thickness of a thin film has significant effects on the absorption and emission properties
- Thinner films of Rhodamine 6G have a higher emission intensity, which allows for more sensitive detection of analytes

Acknowledgments

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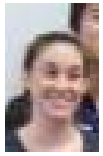
Students who did the work

Graduate Students

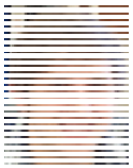
Chris Latendresse, PhD 2013

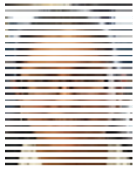
Meredith Matoian, MS 2013 

Emily Hall, MS 2013

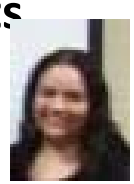
Mona Alhasani, current PhD student

Mingyu Liu, current PhD student

Matt Mullen, current PhD student 

Elsa Ortega, current PhD student 

Undergraduate Students

Syrena Fernandes, BS, Chemistry and Forensic Chemistry, 2013 

Sangmin (Jessie) You, BS, Chemistry, 2014

Hui Qi (Vicky) Zhang, BS Chemistry and Forensic Chemistry, 2014

Yoomin (Jamie) Chung, current PharmD student

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