Free Radical Effect on the Quantum Yield of Silicon Nanoparticles

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PSU REU 2014
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August 18, 2014

Si NPs Background

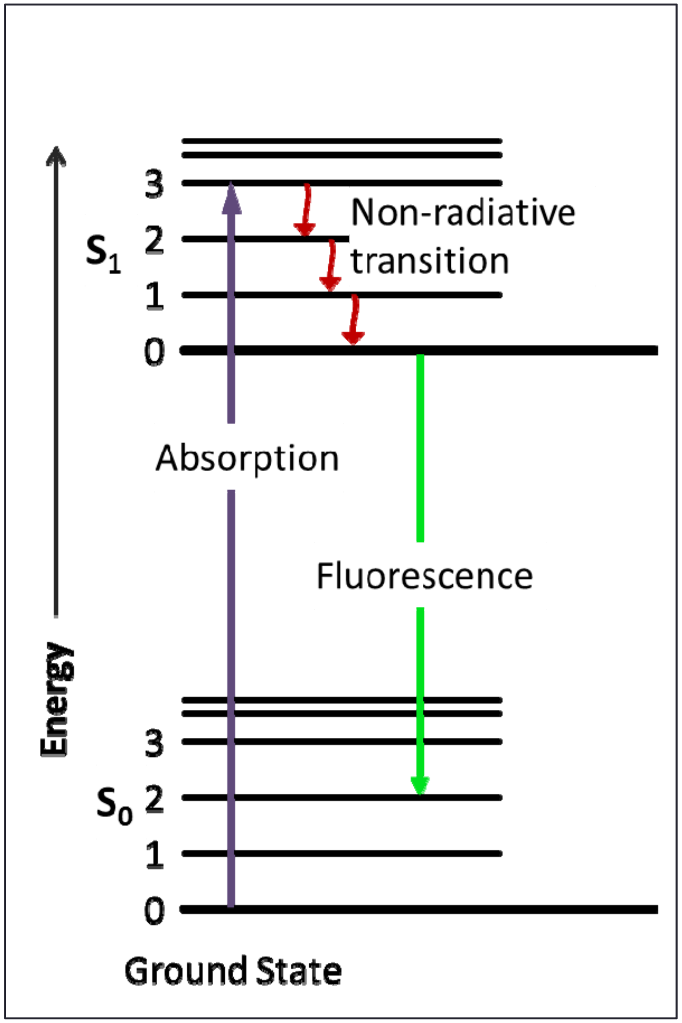
- Tunable light emission
- Applications
  - Light-emitting/harvesting devices
  - Biomedical imaging/tracking

Color tunabilitily by solvent switch (Christine Radlinger)

Quantum Yield

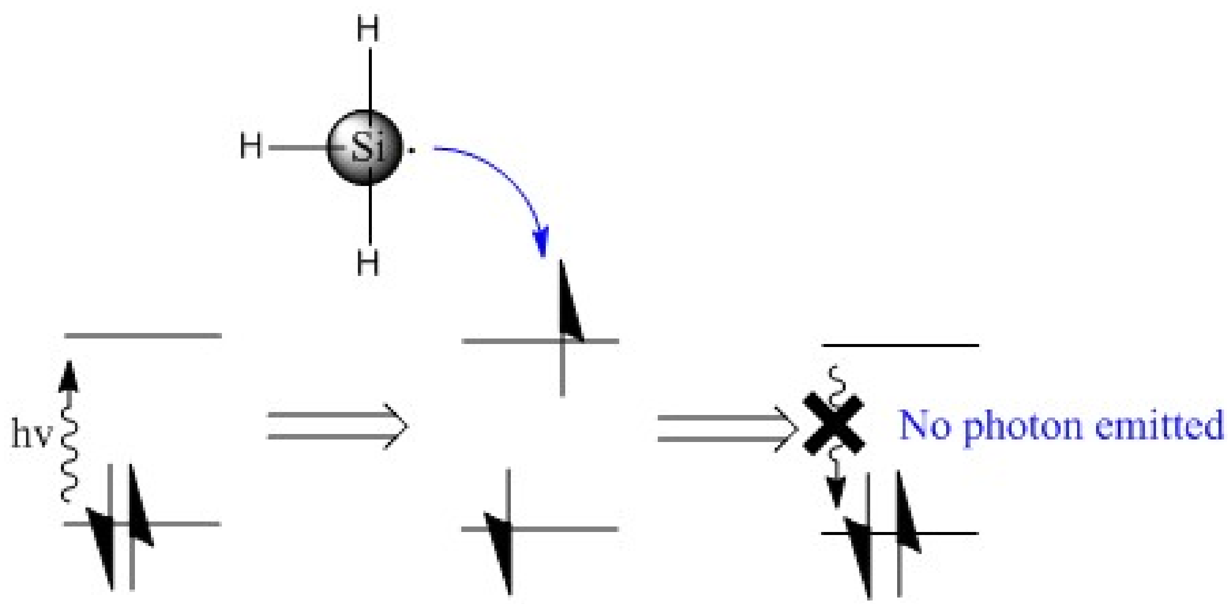
Ratio of excited molecules that deactivate through fluorescence rather than a non-radiative mechanism

$$\Phi = \frac{\#\ \text{photons emitted}}{\#\ \text{photons absorbed}}$$



Purpose

- Determine if free radicals are present on the outside of the Si NPs that are reducing the quantum yield.



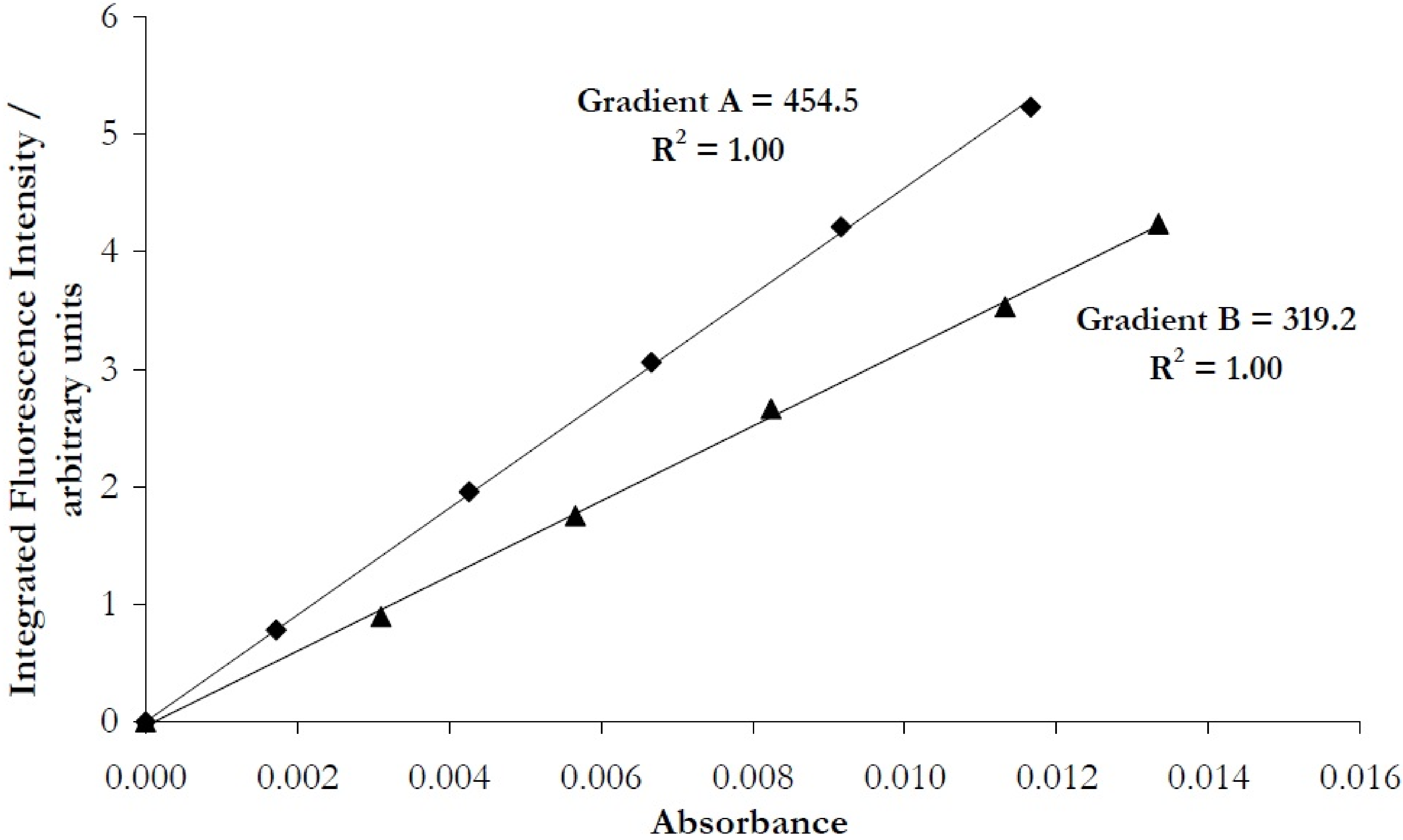
Determination of QY using Fluorescence

- Compare sample fluorescence to that of a fluorophore with a known quantum yield:

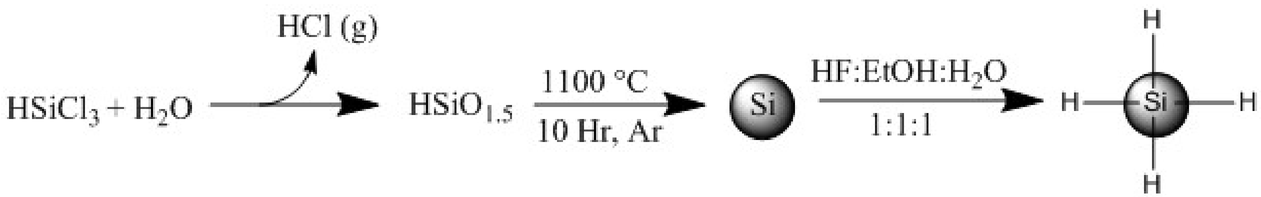
$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)$$

  - X indicates the test samples and ST indicates the standard
  - *Grad* is the Gradient, or slope from the plot of absorbance vs. integrated intensity
  - *η* is the refractive index of the solvents used

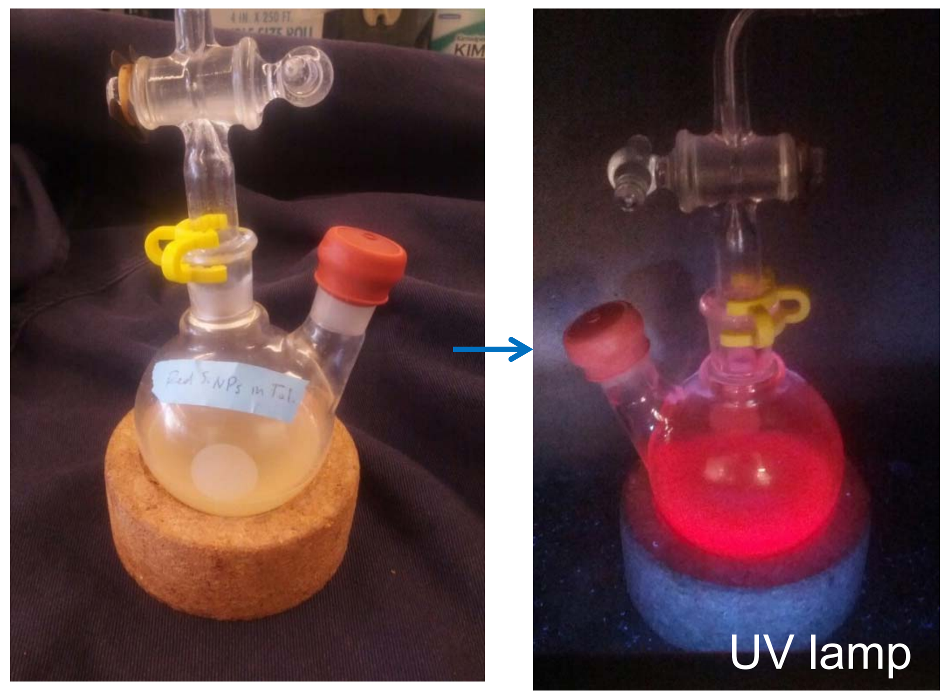
Sample Graph



Synthesis of Si NPs

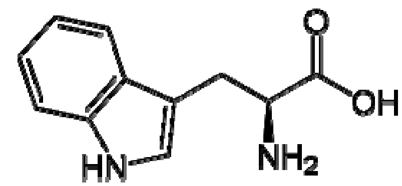


- Air free
- Hydrogen-terminated
- Red/orange-emitting
- Toluene solvent

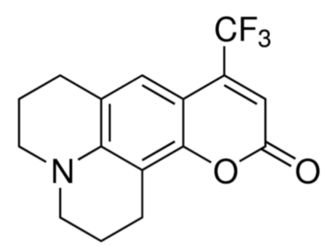


Standards

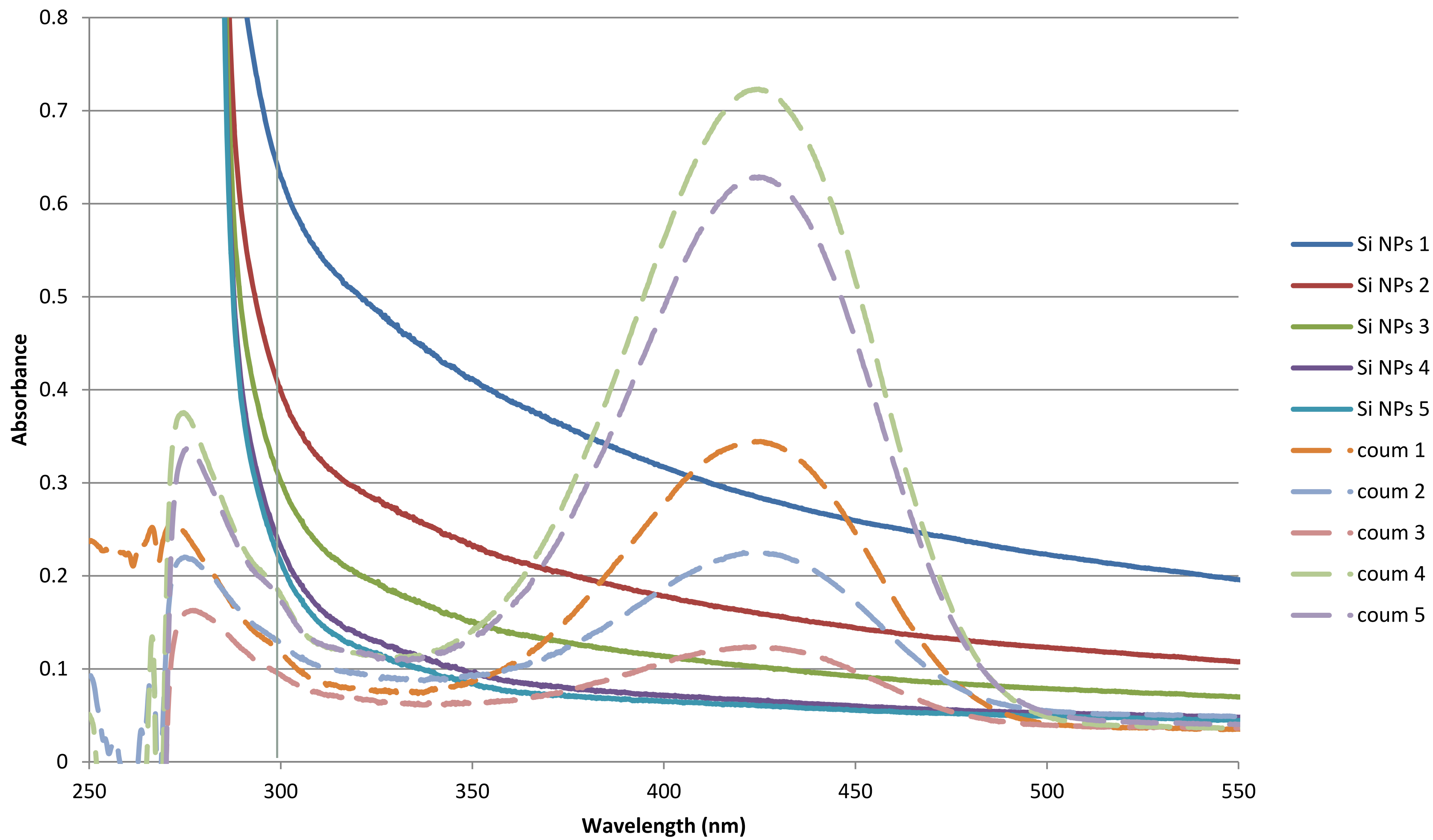
- Cresyl Violet
- Nile Blue
- **L-tryptophan**
  - Φ_F=0.12



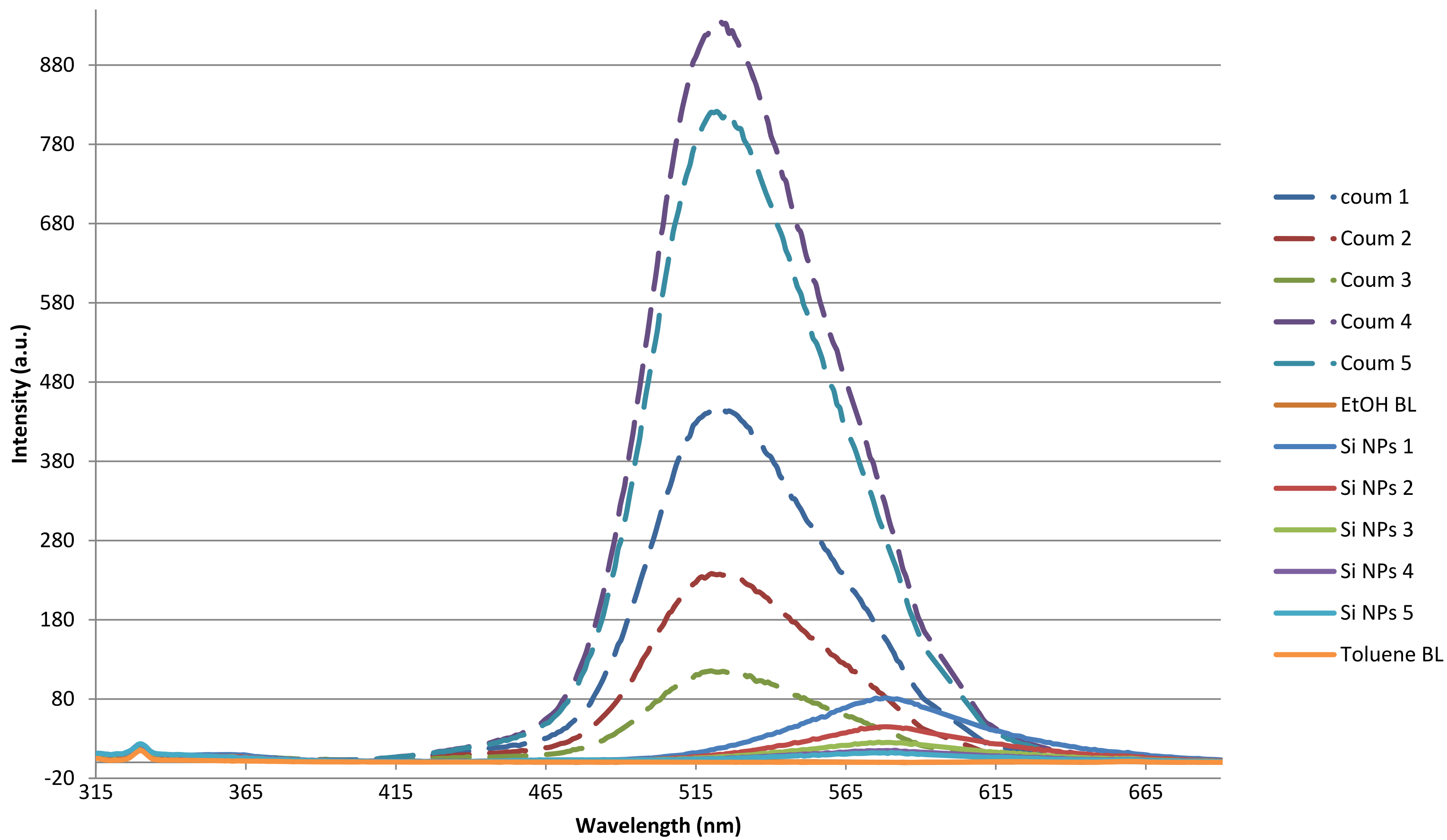
- Coumarin 153 in Cyclohexane
- **Coumarin 153 in EtOH**
  - Φ_F=0.38



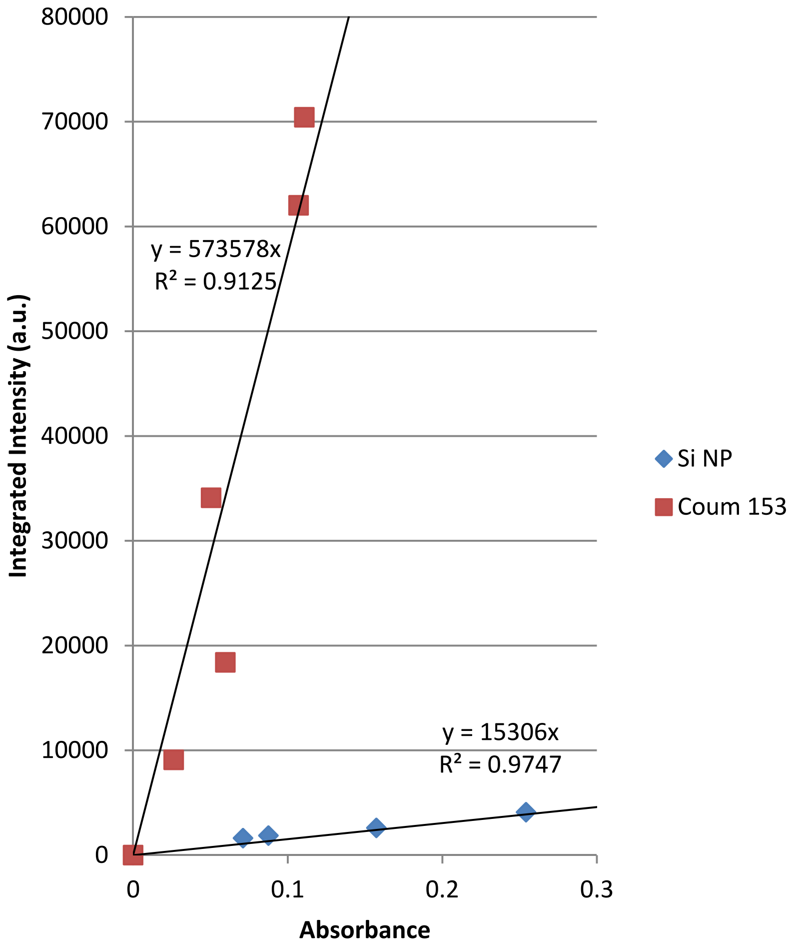
Coum 153 vs Si NPs – UV-Vis



Coum 153 vs Si NPs – PL 300



Si NPs Quantum Yield



Ex λ = 300 nm

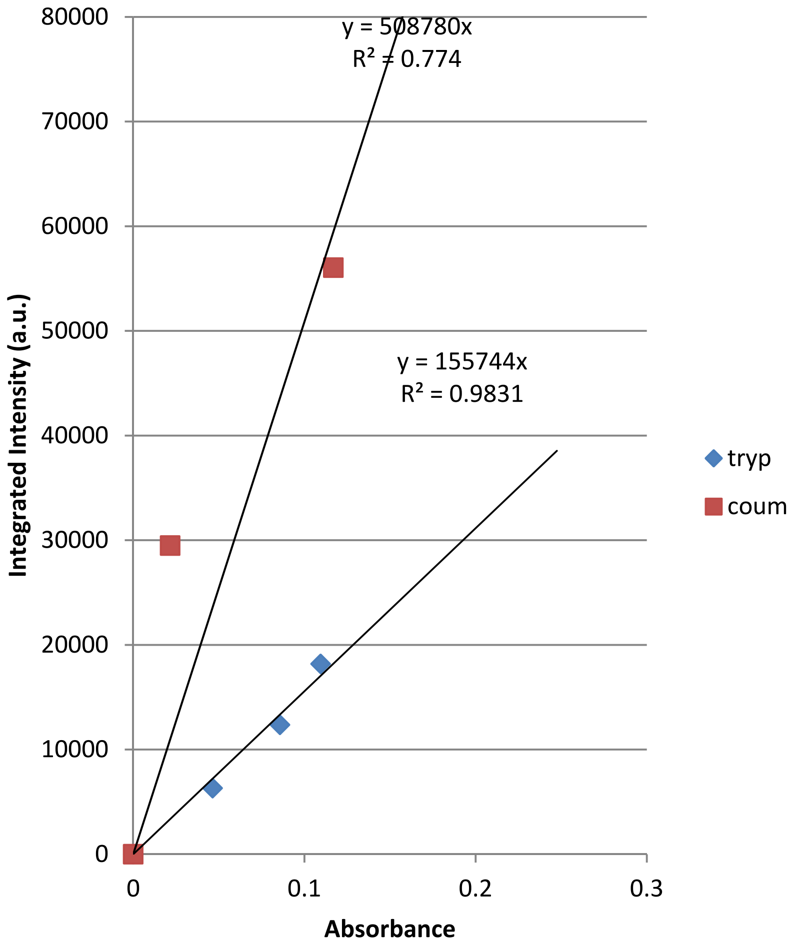
Standard = Coumarin 153 in EtOH

$$\Phi_X = \Phi_{ST}\left(\frac{Grad_X}{Grad_{ST}}\right)\left(\frac{{\eta_X}^2}{{\eta_{ST}}^2}\right)$$

$$\Phi_{NP} = (0.38)\left(\frac{15306}{573578}\right)\left(\frac{1.496^2}{1.361^2}\right)$$

$$\Phi_{NP} = 1.23\%$$

Standards QY Cross-Calculation



- Ex λ = 300 nm

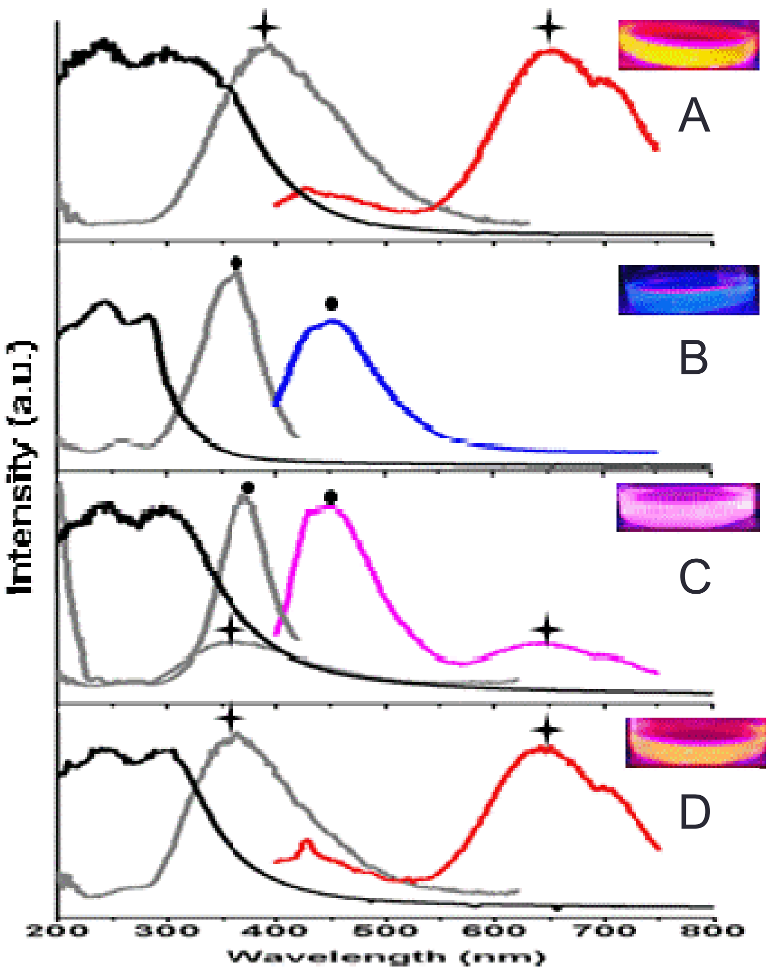
- Tryptophan:

Φ = 0.11 (0.12 actual)

- Coumarin 153:

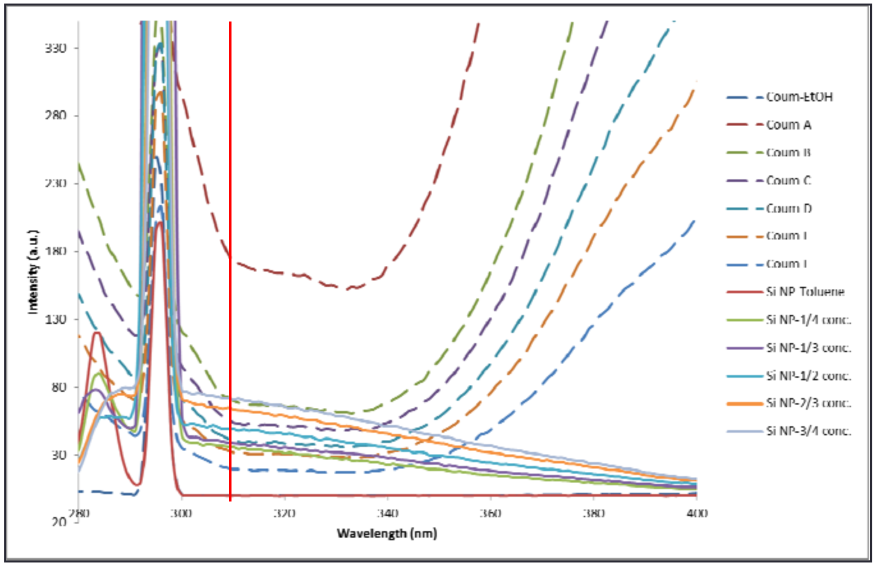
Φ = 0.40 (0.38 actual)

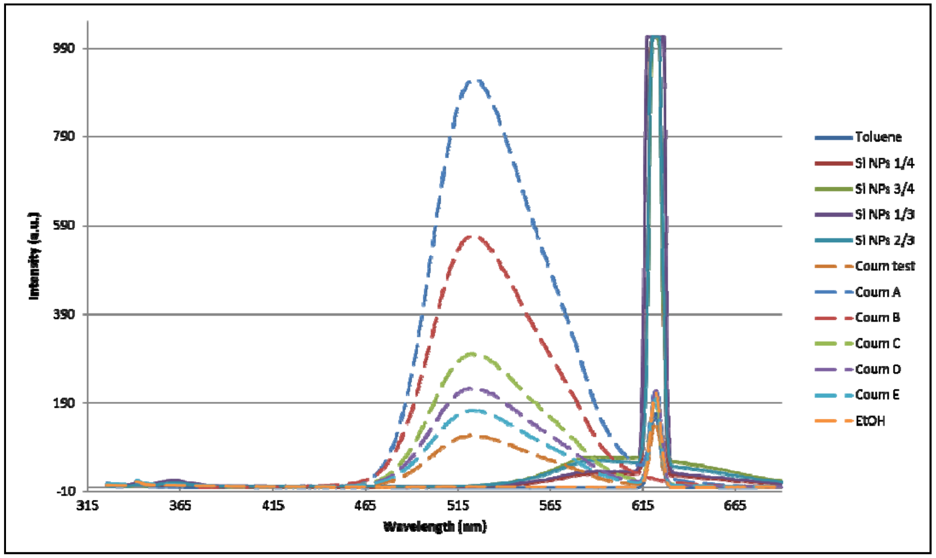
Difference in Absorption and PLE Spectra



Absorption (black lines), PLE (grey lines) and PL (red, blue, or pink lines) spectra of dec-Si NPs dispersed in (A) hexane, (B) ethanol, (C) butanol, and (D) decanol. (✚ and •) indicate corresponding PLE and PL spectra; that is the PLE is monitored at the correspondant PL λ_{max} (excitation at 370 nm). Arrows indicate the approximate onset of absorption. Insets, show the color of the Si NP colloids under 365 nm excitation.

Method 2: Using PLE



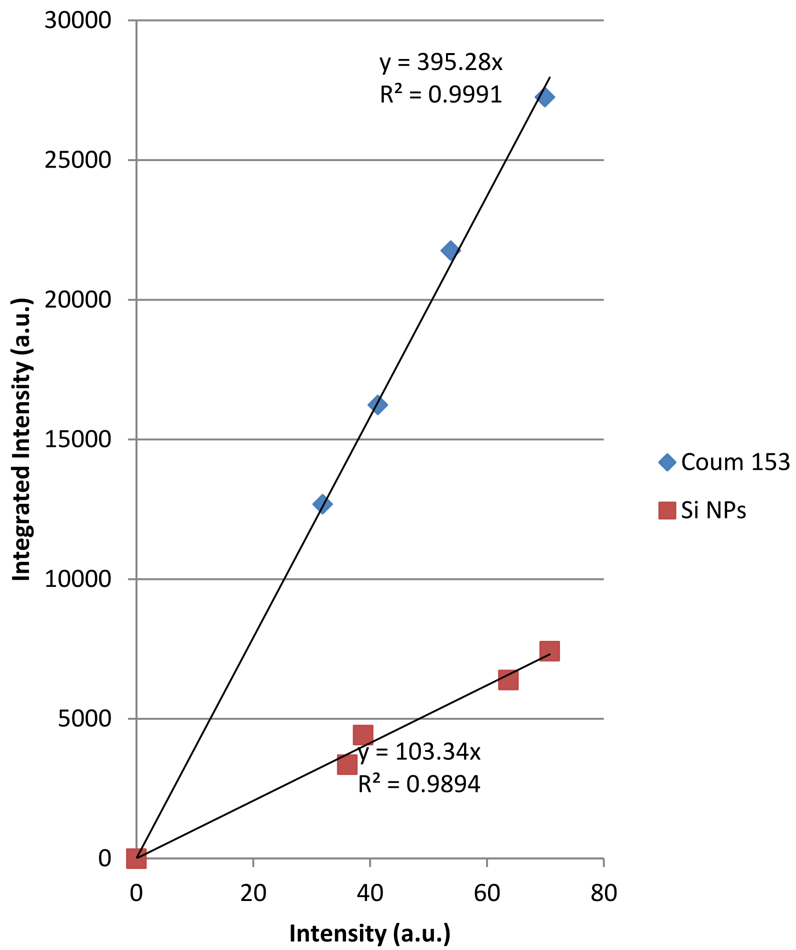


PLE 590: Measured intensity at 310 nm (x-axis of gradient).

PL 310: Integrate intensity of emission peaks (y-axis of gradient).

Method 2: Using PLE

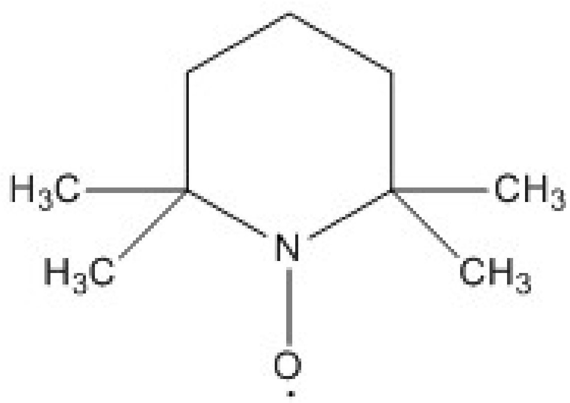
- Φ of Si NPs in Tol.
  - 310 nm: 0.16
  - 300 nm: 0.105



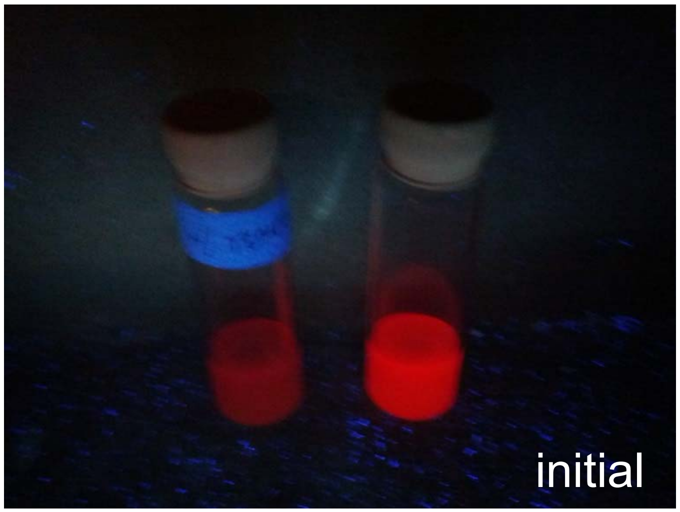
PLE/PL gradients at λ_{ex} = 310 nm

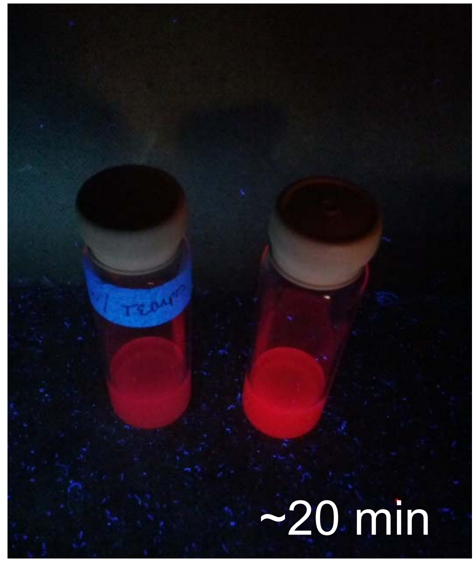
Radical Scavenger

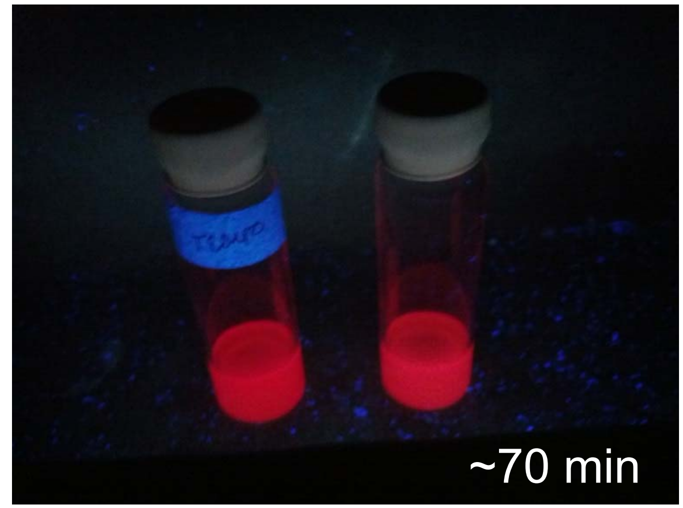
- TEMPO
  - (2,2,6,6-Tetramethylpiperidin-1-yl)oxy
  - Long-lived radical scavenger
  - Soluble in polar and nonpolar solvents

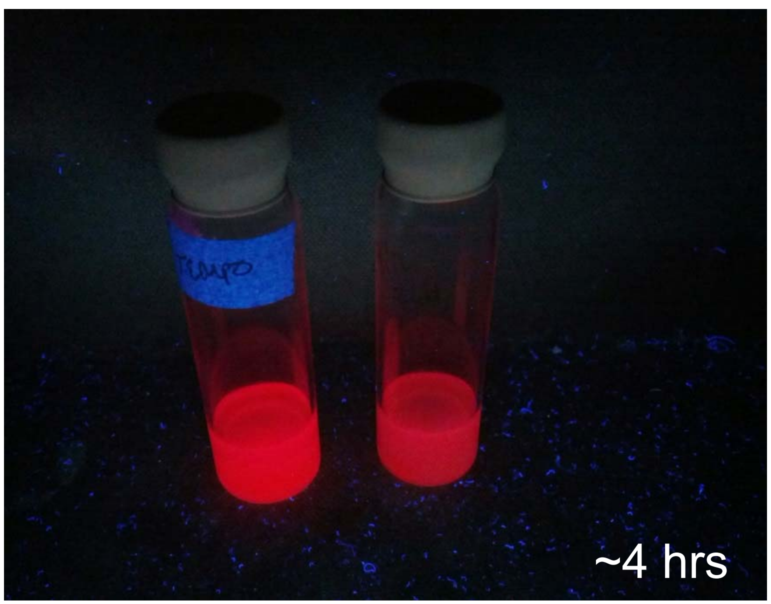


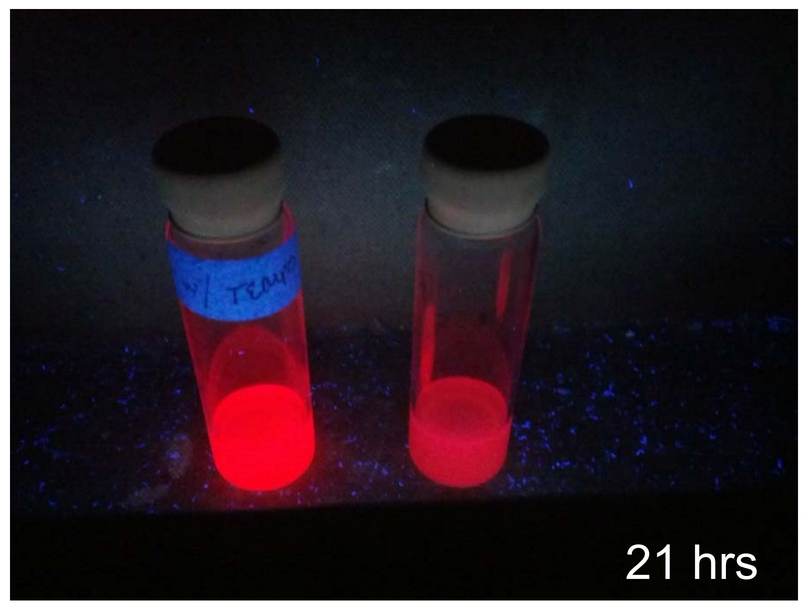
Red Si NPs w/ TEMPO Time Lapse



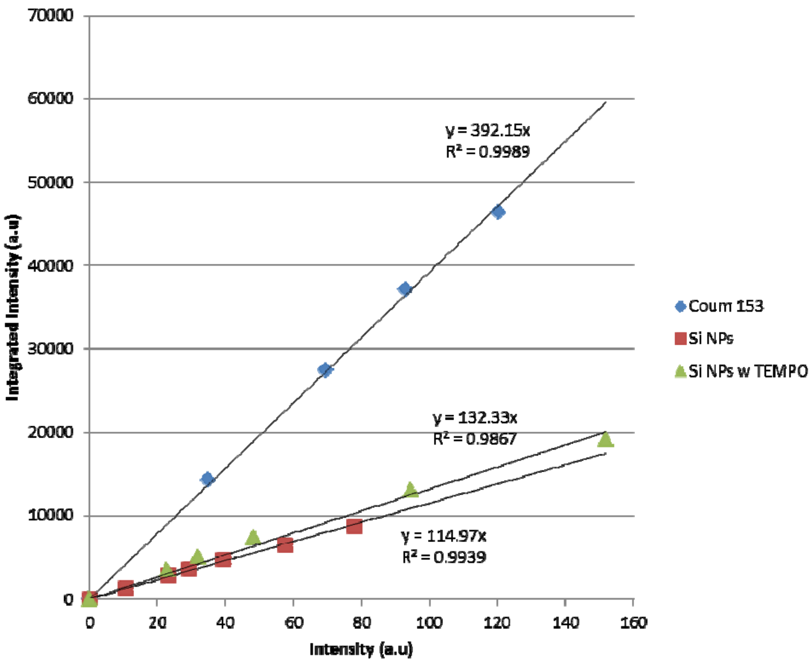




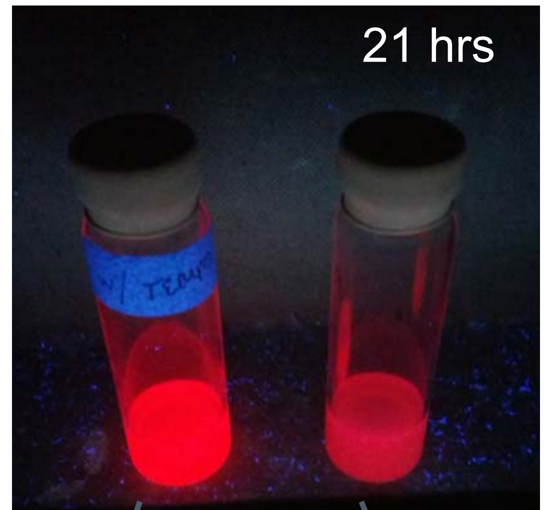




Quantum Yield Comparison



PLE/PL gradients at λ_{ex} = 300 nm

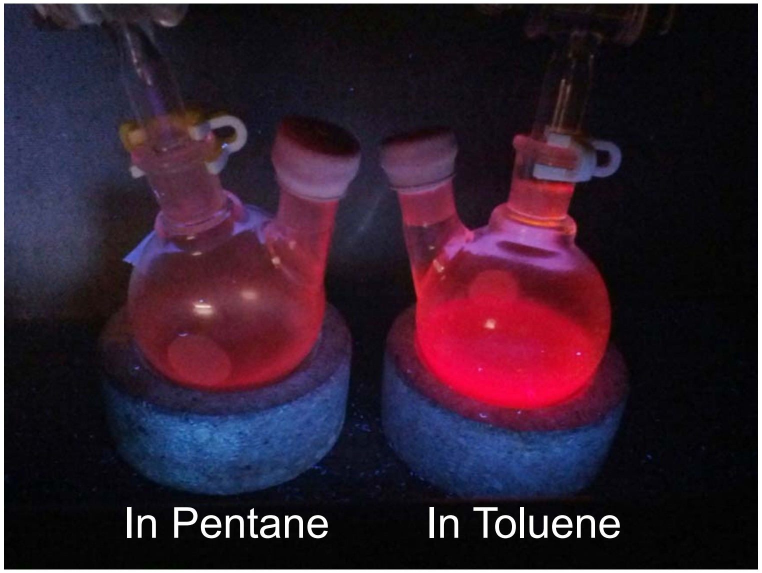


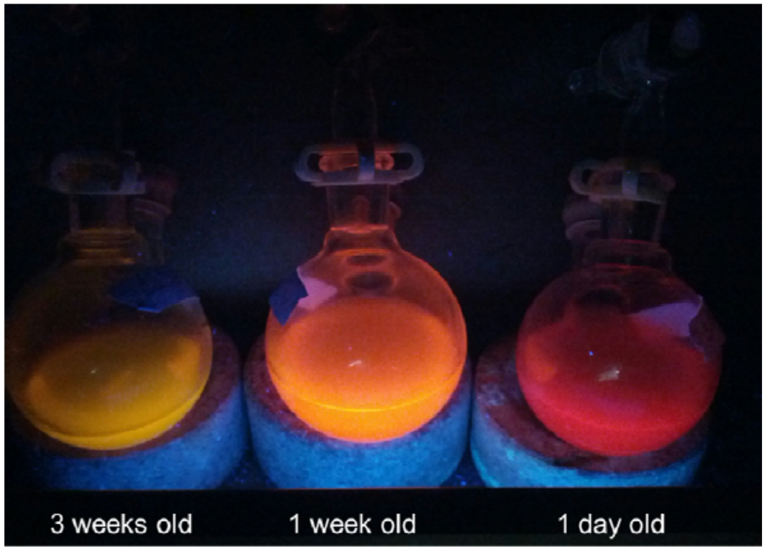
Si NPs w/ TEMPO: Φ =0.155

Si NPs: Φ = 0.135

Ways to Increase Quantum Yield

- Use toluene as a solvent (over pentane)
- Lower λ_{Ex}
- Oxidize Si NPs
- Add a radical scavenger (TEMPO)





Future Research

- Continue optimizing Quantum Yield Procedure for Si NPs
- Continue working with Radical Scavenger
- Quantum Yield of Si NPs
  - In different Solvents
  - Different times after etching
  - Different times after adding TEMPO
  - At different Excitation Wavelengths

Acknowledgements

- PSU REU Program
- Dr. Andrea Goforth
- Christine Radlinger
- Sheng, Victor, & Colin
- Candice Randall
- NSF

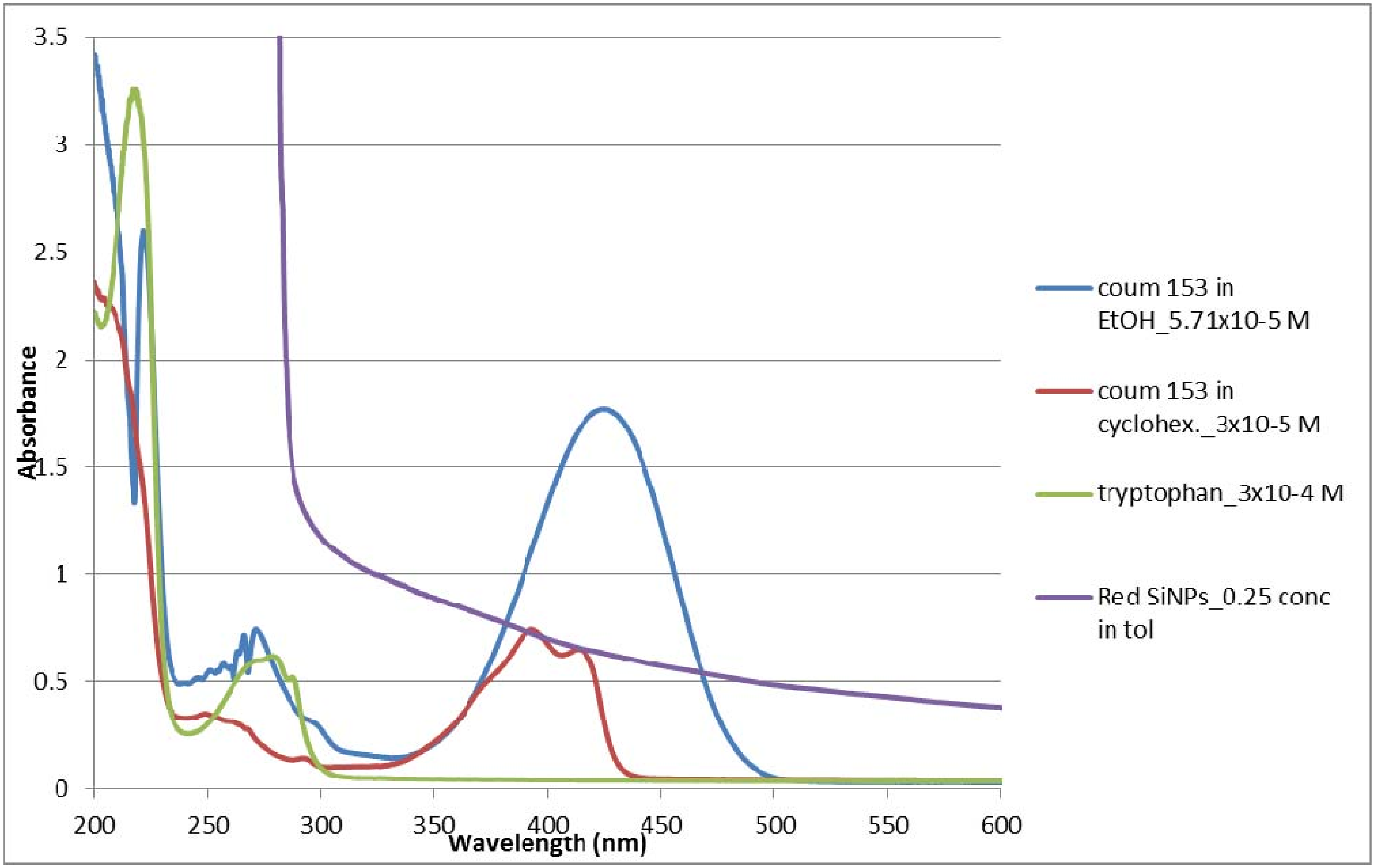
References

1. Brouwer, A. M. Standards for Photoluminescence Quantum Yield Measurements in Solution. *Pure Appl. Chem.* **2011**, *83*, 2213-2228.
2. Chiu, S. K.; Manhat, B. A.; DeBenedetti, W. J.; Brown, A. L. *J. Mater. Res.* **2013**, *28* (2), 216-230.
3. DeBenedetti, W. J. I.; Shi J.; Chiu S. K.; Manhat B. A.; Radlinger C. M. *J.Phys. Chem. C*. **2014** (submitted).
4. Fery-Fogues, S.; Lavabre, D. *J. Of Chem. Ed.* **1999**, *76*, 1260-1264.
5. Jobin Yvon Ltd. A Guide to Recording Fluorescence Quantum Yields.

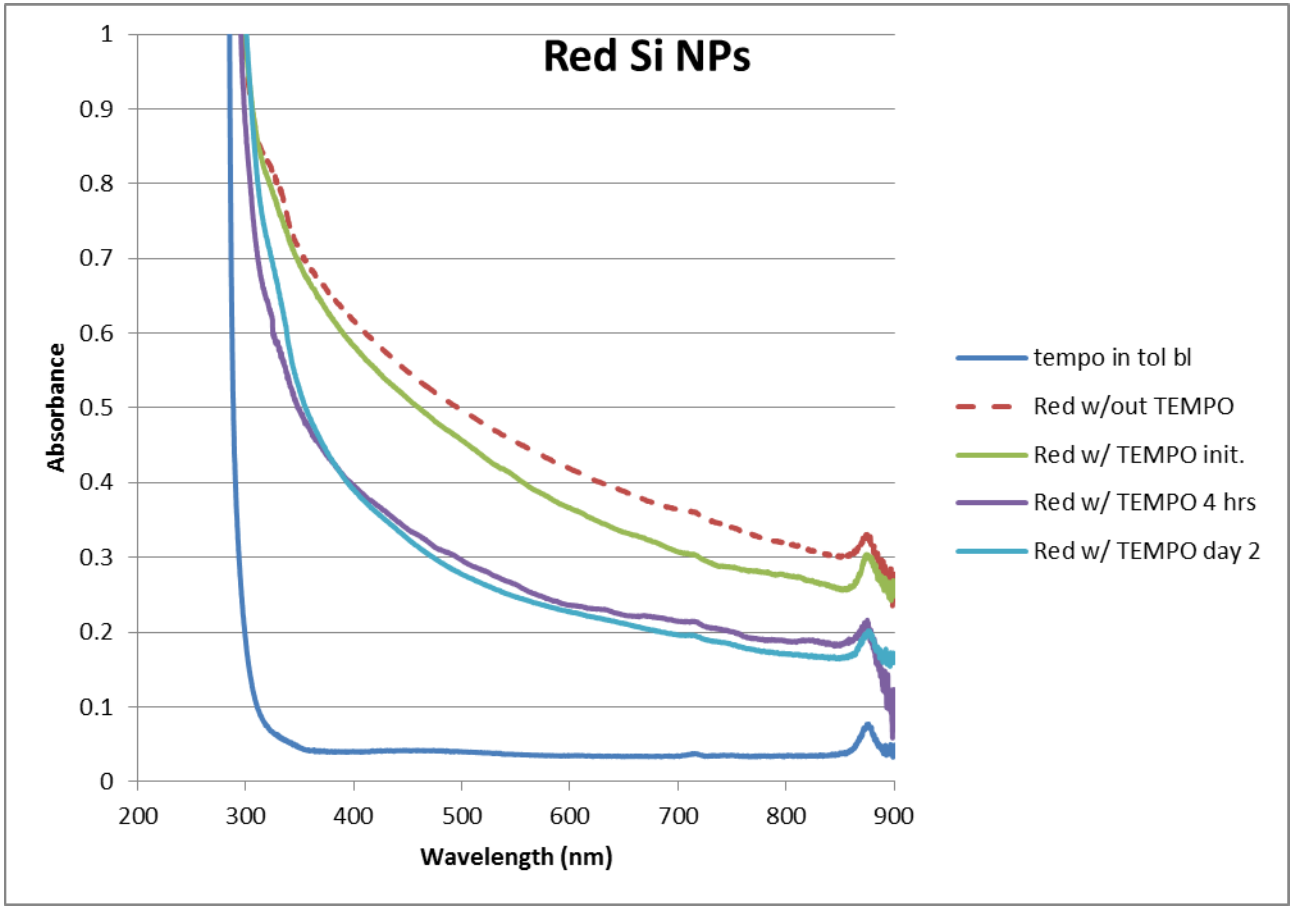
Image Citations

- http://en.wikipedia.org/wiki/Tryptophan#mediaviewer/File:L-Tryptophan_-_L-Tryptophan.svg
- http://www.sigmaaldrich.com/catalog/product/aldrich/546186?lang=en&region=US
- http://en.wikipedia.org/wiki/Fluorescence#mediaviewer/File:Jablonski_Diagram_of_Fluorescence_Only.png
- Jobin Yvon Ltd. A Guide to Recording Fluorescence Quantum Yields.
- DeBenedetti, W. J. I.; Shi J.; Chiu S. K.; Manhat B. A.; Radlinger C. M. *J.Phys. Chem. C*. **2014** (submitted).

Standards vs Si NPs – UV-Vis



Red Si NPs Absorbance Comparison



Red Si NPs Emission Comparisons