Scaling laws to probe the internal dynamics of macromolecules in solution by pyrene excimer formation

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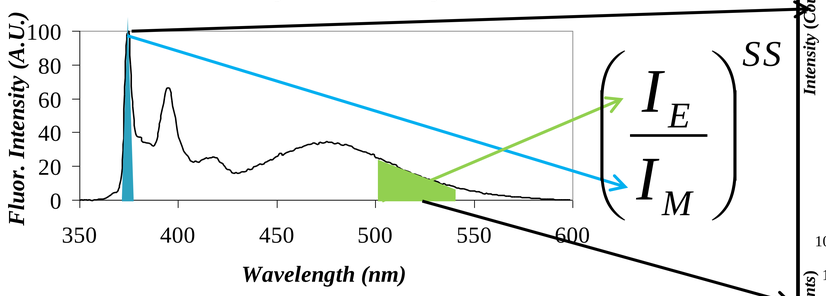
Problem:

I_E/I_M data from pyrene labeled macromolecules is extremely useful, but literature values cannot be compared due to variation in the methods used to calculate it.

I_E/I_M by Steady State Fluorescence:

Pros: Easy to acquire, internally consistent

Cons: Methods vary, externally inconsistent



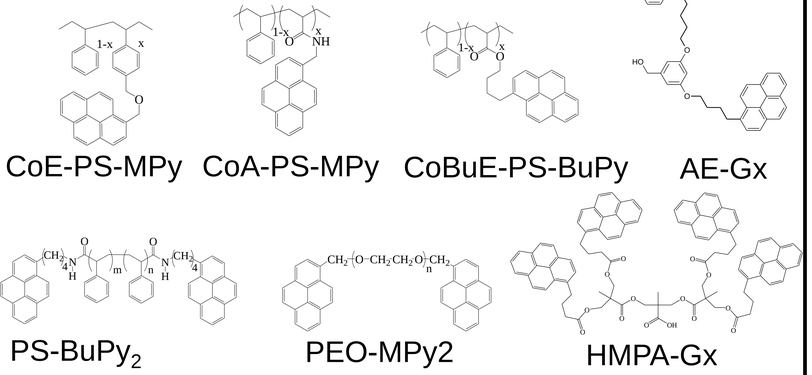
Factors Affecting $(I_E/I_M)^{SS}$:

- Wavelength ranges chosen for I_E or I_M
- Averaging vs Integration
- Slit widths
- Pyrene derivative used

Goal:

To develop a method of calculating I_E/I_M that yields the same value regardless of the pyrene derivative, instrument or lab involved.

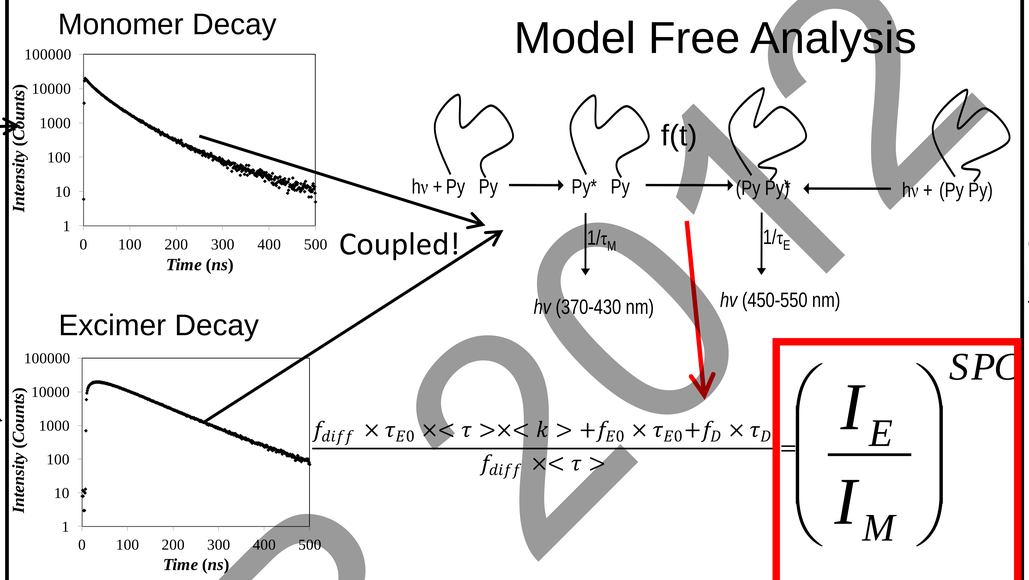
Samples:



Solution:

I_E/I_M by Time Resolved Fluorescence:

Fluorescence lifetimes are only affected by quenching

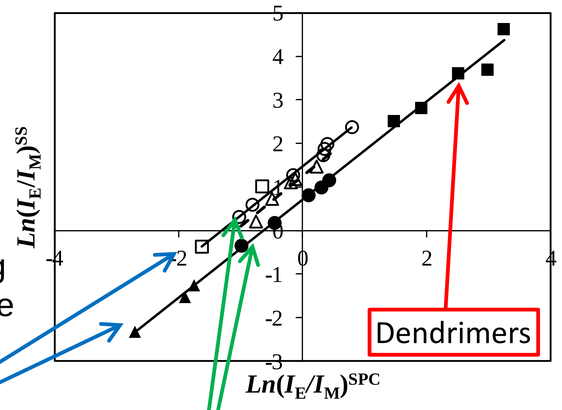


Results:

$(I_E/I_M)^{SPC}$ is a valid measure of IE/IM

- Each derivative forms a straight line, all lines have the same slope
- The lines have different intercepts due to the differing I_1 intensity for each derivative

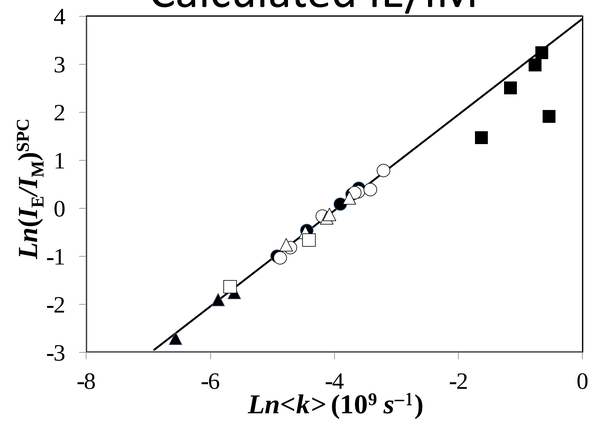
Calculation comparison



The data obtained from the model free analysis was used to calculate both I_E/I_M and <k>

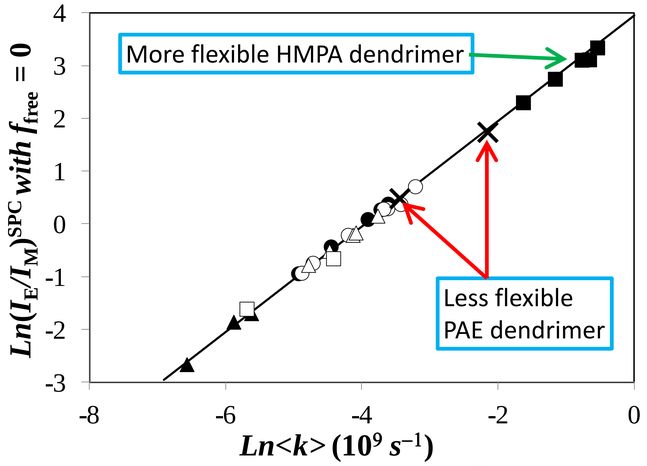
$$< k >= \frac{1}{< \tau >} - \frac{1}{\tau_M}$$

Calculated IE/IM



Dendrimers show the highest $(I_E/I_M)^{SPC}$ and<k> values, the end labeled polymers are lowest with randomly labeled being intermediate. These samples cover 2.6 orders of magnitude for each value.

Calculated IE/IM, f_{free}= 0



With f_{free} equal to zero, the new $(I_E/I_M)^{SPC}$ ignores any unattached pyrenes, bringing all points onto the line. This line can be used as a standard curve, to show the expected I_E/I_M for any system with a known <k>

Conclusions:

IE/IM calculated using time-resolved fluorescence yields an absolute parameter which may easily be compared between labs. Additionally, calculation of <k> allows the prediction of I_E/I_M for any pyrene labeled macromolecule