Internal Dynamics of a Series of Pyrene-Labeled Dendrons Characterized by Fluorescence

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IPR Symposium
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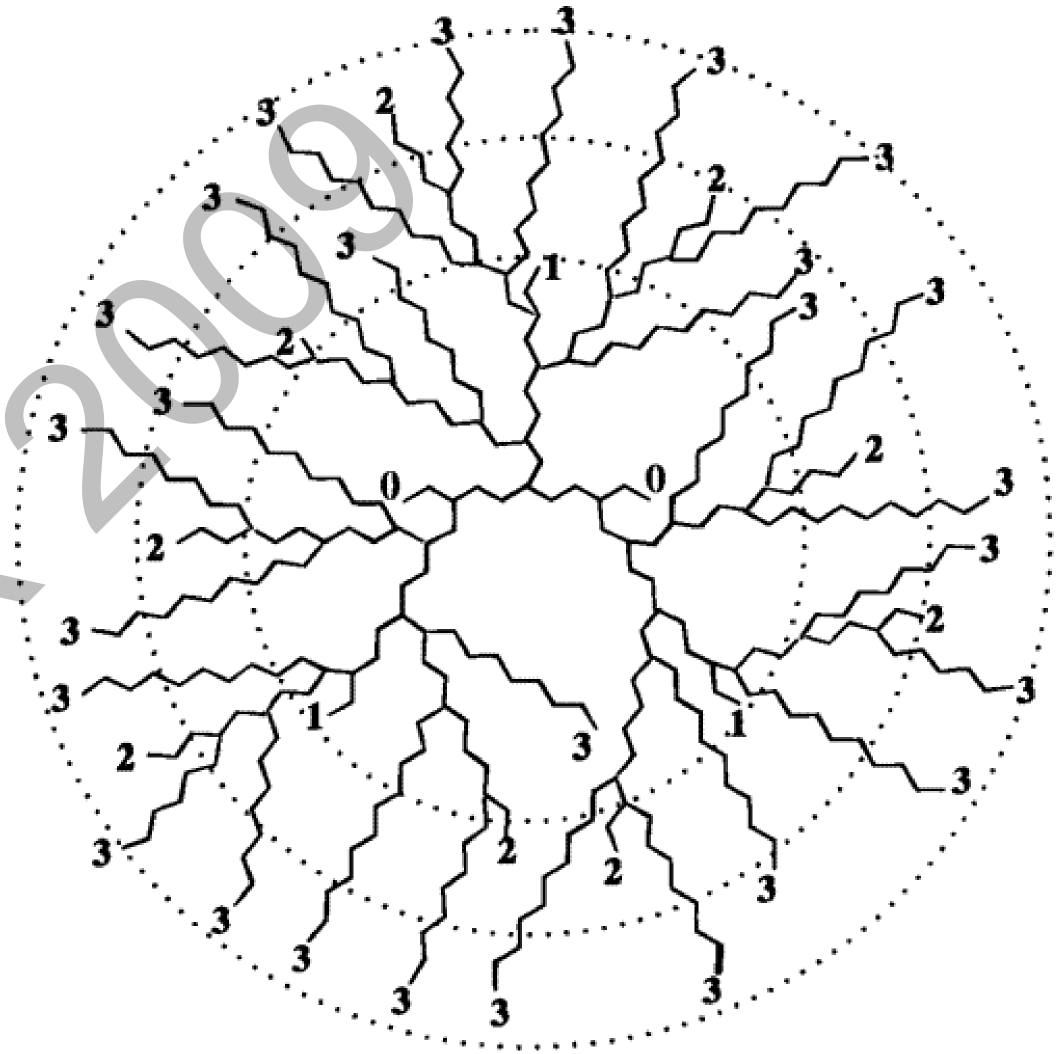
Outline

- Introduction
- Background
- Experimental Results
- Conclusions
- Acknowledgements

Sheiko, S. S.; Gauthier, M.; Moller, M. *Macromolecules.* 1997, *30*, 2343–2349.

Introduction

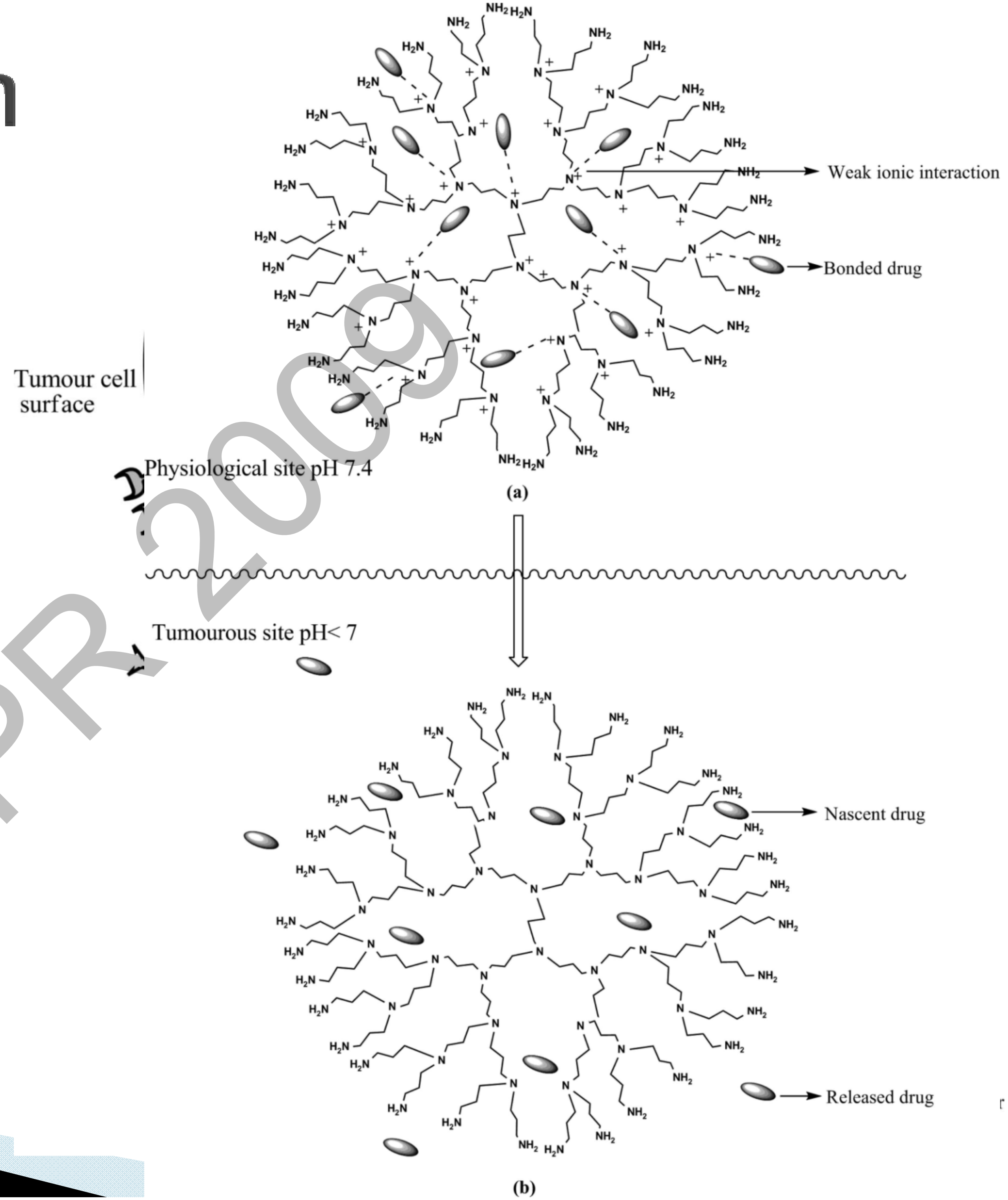
- What are dendrimers?
  - *Dendron* – tree
  - *Meros* – part
  - Molecules with a tree-like structure!



Tekade, R. K.; Kumar, V. P.; Jain, N. K. *Chem. Rev.* 2009, *109*, 49–87.

Introduction

- Why study dendrimers?
  - Molecular storehouse
    - Within internal cavities
    - **At end-groups**



Introduction

- How are we going to study dendrimers?
  - Fluorescence Dynamic Quenching (FDQ) experiments
    - Provides information concerning the flexibility of our molecules

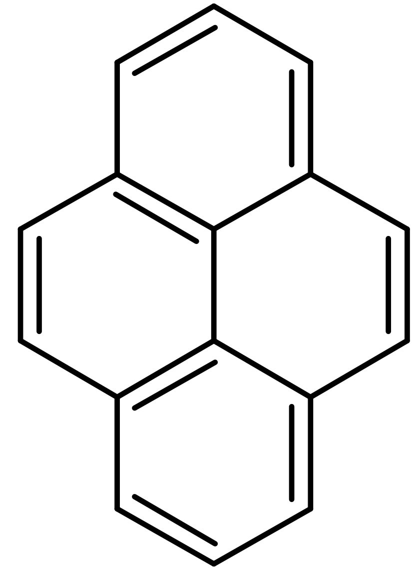
Background

- Fluorescence Dynamic Quenching (FDQ)
  - Involves monitoring quenching of a chromophore (M) by its quencher (Q)

$$h\nu + M + Q \longrightarrow M^* + Q \xrightarrow{k_1[Q]_{loc} = k_q} M\,Q$$

$$M^* + Q \xrightarrow{1/\tau_M} \downarrow$$

Background

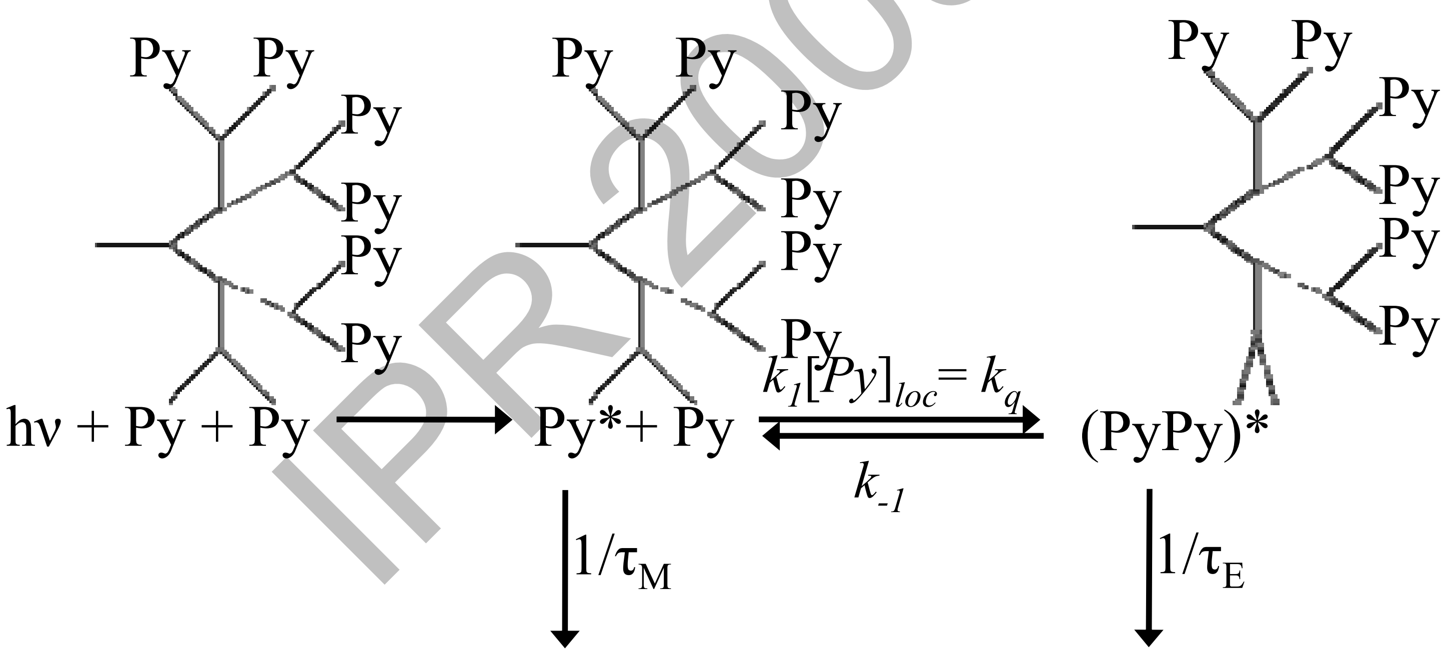


- Pyrene
  - High molar extinction coefficient
    - $\varepsilon = 43{,}000\ M^{-1}cm^{-1}$ for 1-pyrenebutanol in ethanol
  - High fluorescence quantum yield
    - $\Phi = 0.32$ in cyclohexane
  - Long natural lifetime
    - $\tau_M = 210$ ns for 1-pyrenebutyric acid in THF
  - Collisional quenching
    - Self-quenches upon encounter of an excited pyrene with a ground-state pyrene, forming excimer

Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; p 301–307.

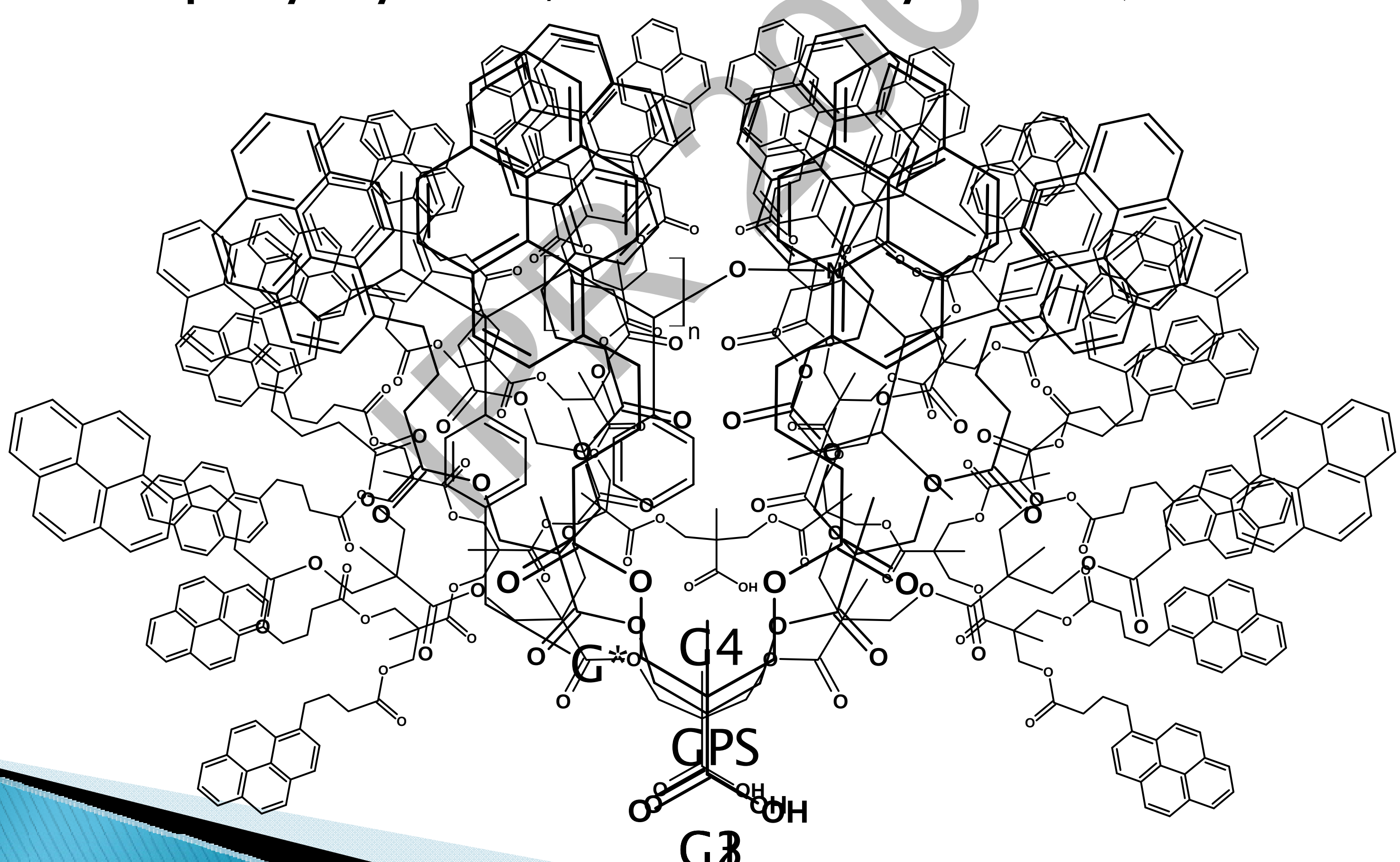
Background

- Pyrene
  - The Birks' Scheme



Background

- Dendrimer Structure
  - Four generations studied (G1–G4) as well as four linear polystyrene/dendron hybrids (G1PS–G4PS)



Background

- Experimental Techniques
  - UV-Visible Spectroscopy
  - Steady-State Fluorometry (SSF)
  - Time-Correlated Single Photon Counting (TC-SPC)
  - Gel Permeation Chromatography (GPC) with fluorescence detector

Background

- UV-Visible Spectroscopy
  - Absorbance measurements
  - Beer-Lambert Law:

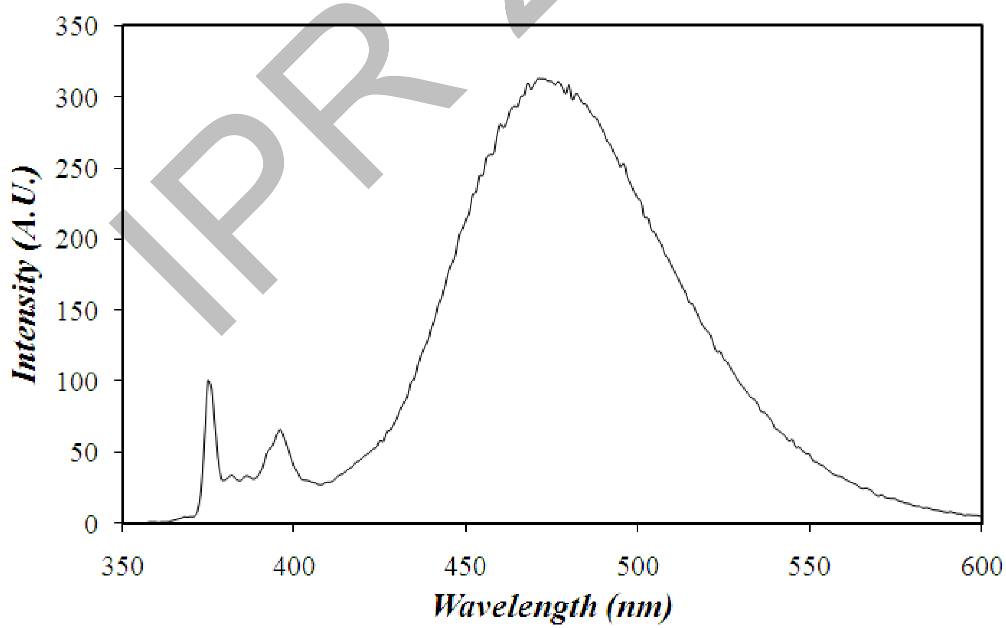
$$A = \varepsilon c l$$

    - A = absorbance
    - ε = molar extinction coefficient of pyrene ($M^{-1}cm^{-1}$)
    - c = concentration of absorbing species (M)
    - l = path length between incident and transmitted light (cm)

  - **Maintain a low pyrene concentration to ensure no intermolecular quenching is observed**

Background

- Steady-State Fluorometry
  - Provides steady-state emission spectra
    - Maintain constant excitation wavelength, monitor emission intensity over a range of wavelengths
  - **Can determine the I_E/I_M ratio**



G1 in THF
$[Py] = 2.5\ \mu M$
$\lambda_{ex} = 344$ nm

Cuniberti, C.; Perico, A. *Eur. Polym. J.* 1980, *16*, 887–893.

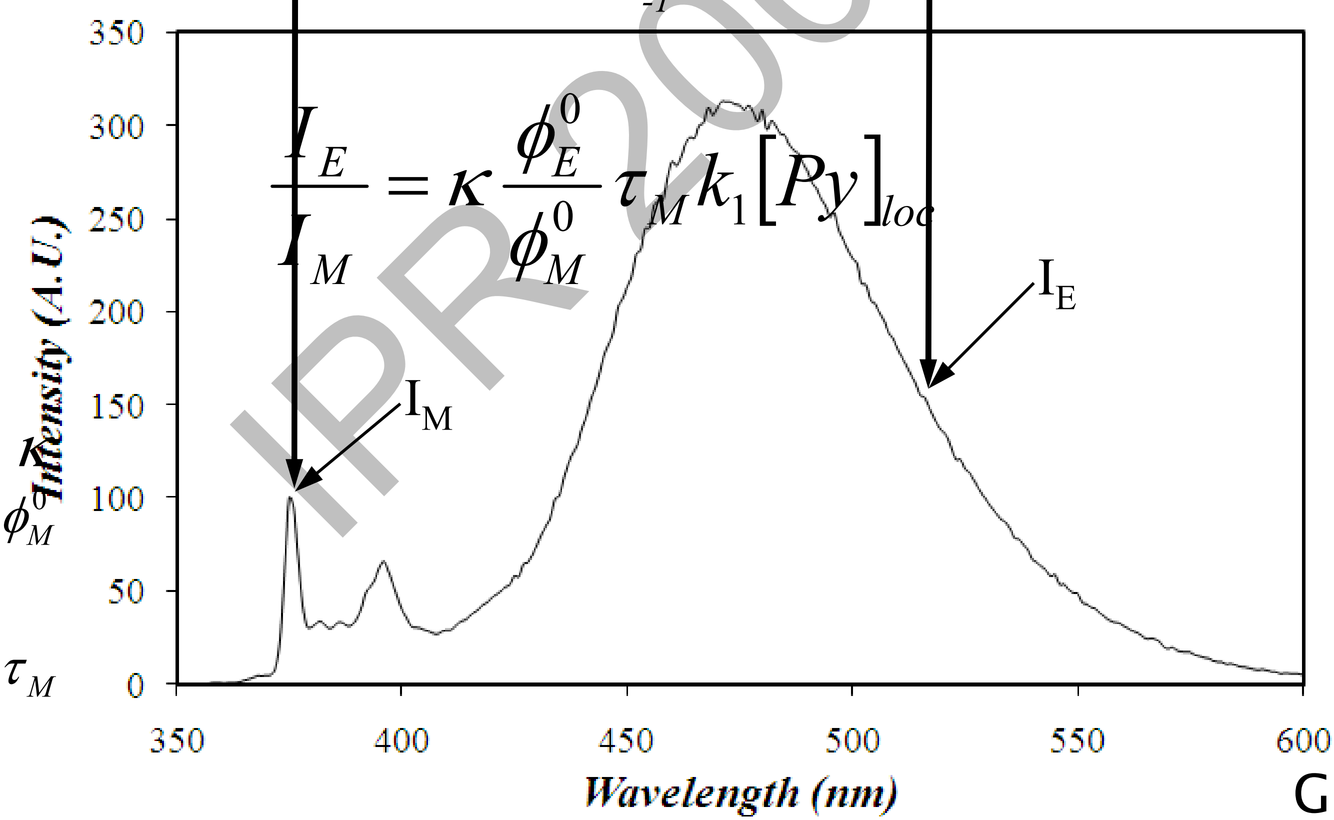
Background

- Steady-State Fluorometry

$$h\nu + Py + Py \longrightarrow Py^* + Py \underset{k_{-1}}{\overset{k_1[Py]_{loc} = k_q}{\rightleftharpoons}} (PyPy)^*$$

$$\frac{I_E}{I_M} = \kappa \frac{\phi_E^0}{\phi_M^0} \tau_M k_1 \left[Py\right]_{loc}$$

- κ
- ϕ_E^0, ϕ_M^0
- τ_M



G1 in THF
$[Py]$ = 2.5 μM
λ_{ex} = 344 nm

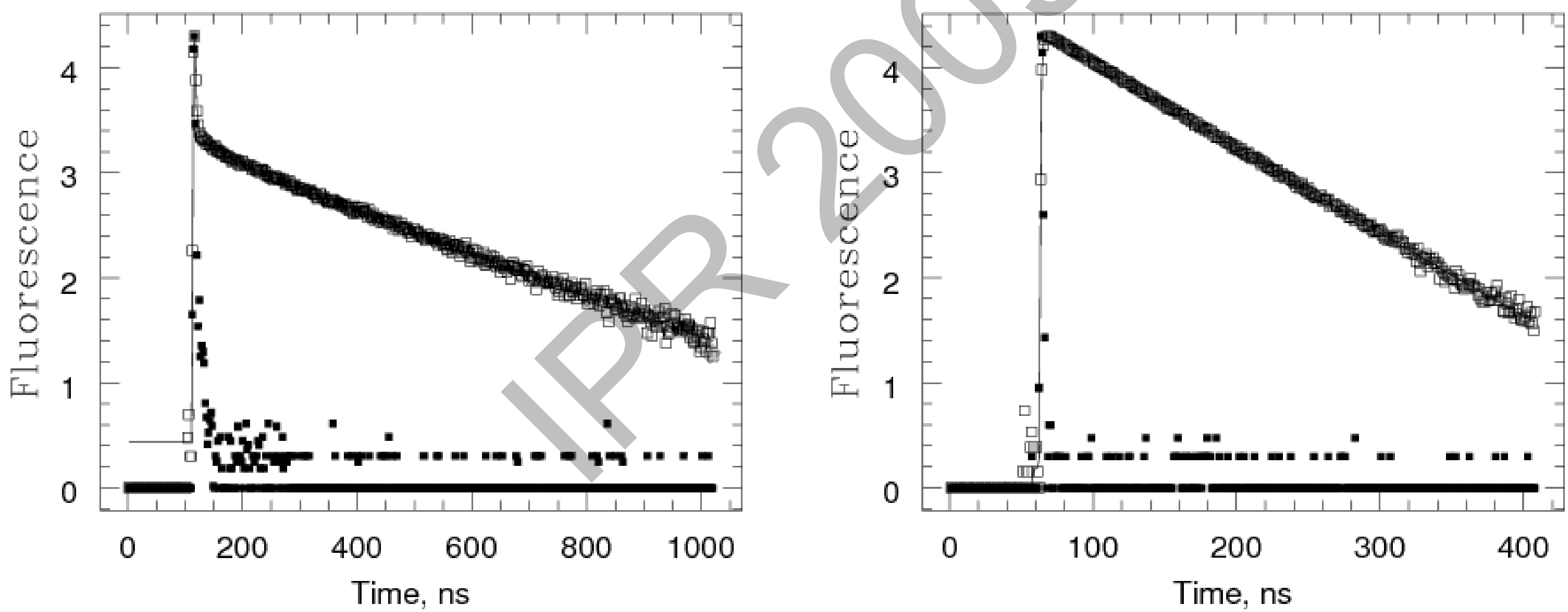
Background

- Time-Correlated Single Photon Counting
  - Allows acquisition of fluorescence decays at given excitation and emission wavelengths
  - Since pyrene monomer and excimer fluoresce at distinct wavelengths, monomer and excimer decays can be acquired separately
  - **Can determine k_q, the quenching rate constant**

Background

- Time-Correlated Single Photon Counting

Monomer, λ_{em} = 375 nm   Excimer, λ_{em} = 510 nm

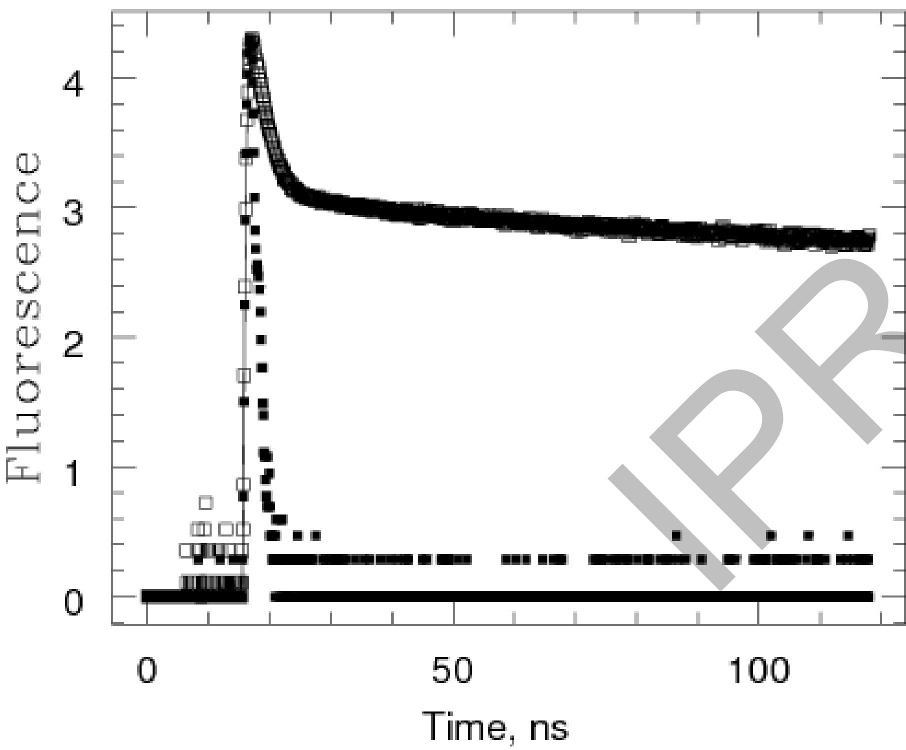


G4 in THF
[Py] = 2.5 μM
λ_{ex} = 344 nm

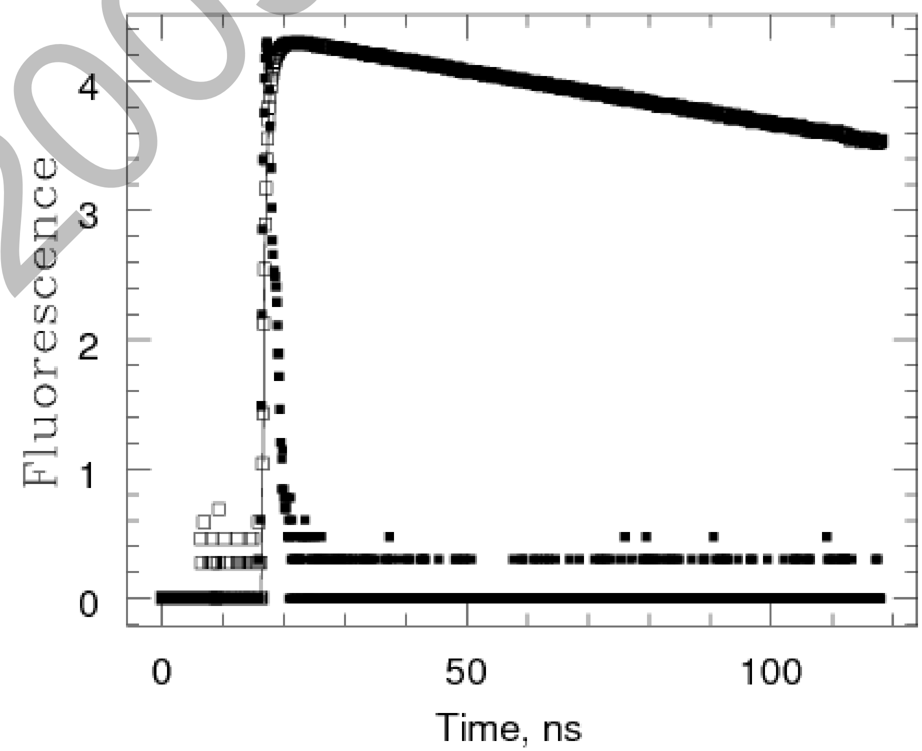
Background

- Time-Correlated Single Photon Counting

Monomer, λ_{em} = 375 nm



Excimer, λ_{em} = 510 nm



$$I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$$

G4 in THF
$[Py]$ = 2.5 μM
λ_{ex} = 344 nm

Winnik, M. A.; Egan, L. S.; Tencer, M. *Polymer*. **1987**, *28*, 1553–1560.

Background

- Time-Correlated Single Photon Counting
  - From global analysis:

τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_3 (ns)	A_3	χ^2	<τ> (ns)	<k> (10^7 s^{-1})
1.19	0.83	2.46	0.13	25.1	0.014	1.11	1.70	**58.2**

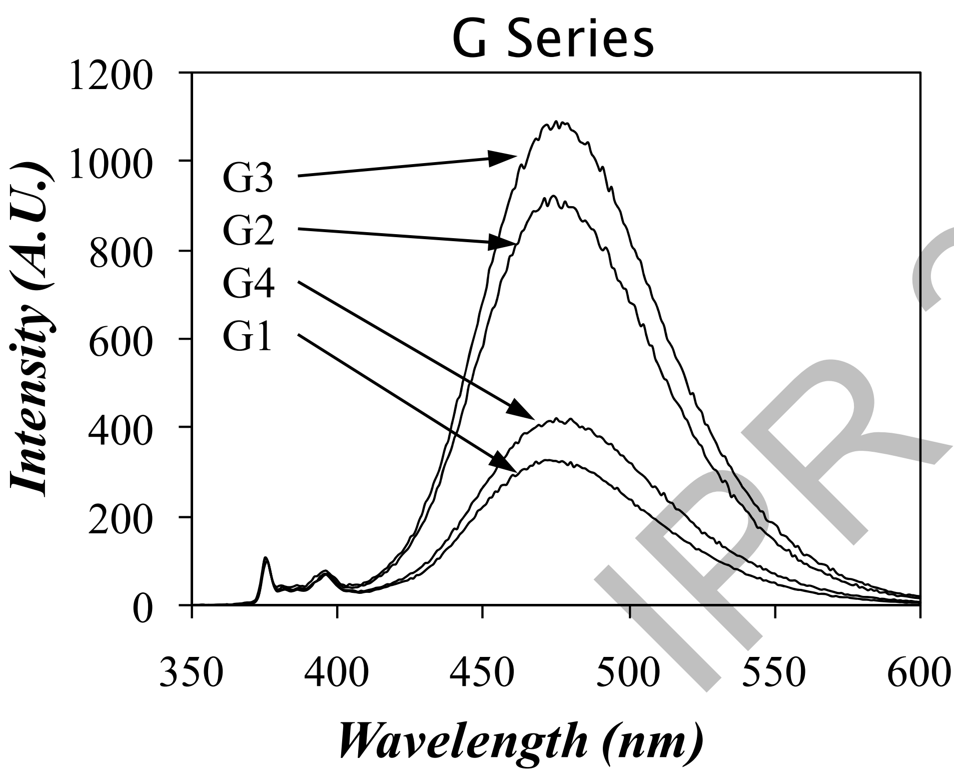
$$<\tau> = \frac{\sum_{i=1}^{n} A_i \tau_i}{\sum_{i=1}^{n} A_i}$$

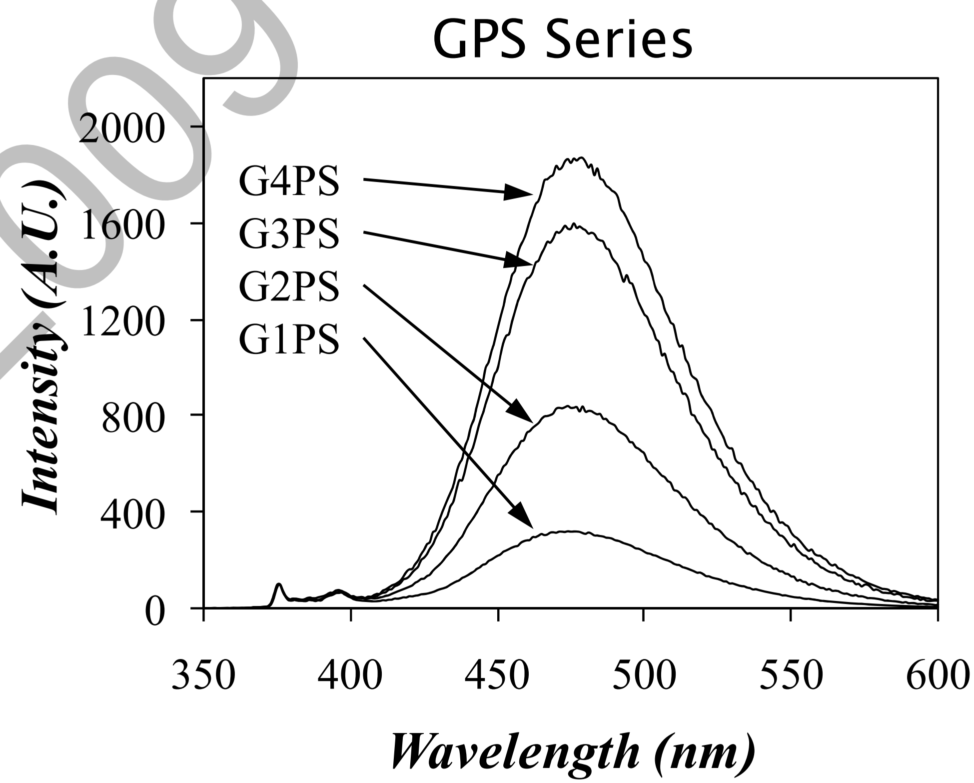
$$<k> = \frac{1}{<\tau>} - \frac{1}{\tau_M} = k_q = k_1 [Py]_{loc}$$

$$\tau_M = 210\, ns$$

Experimental Results

- Steady-State Fluorometry





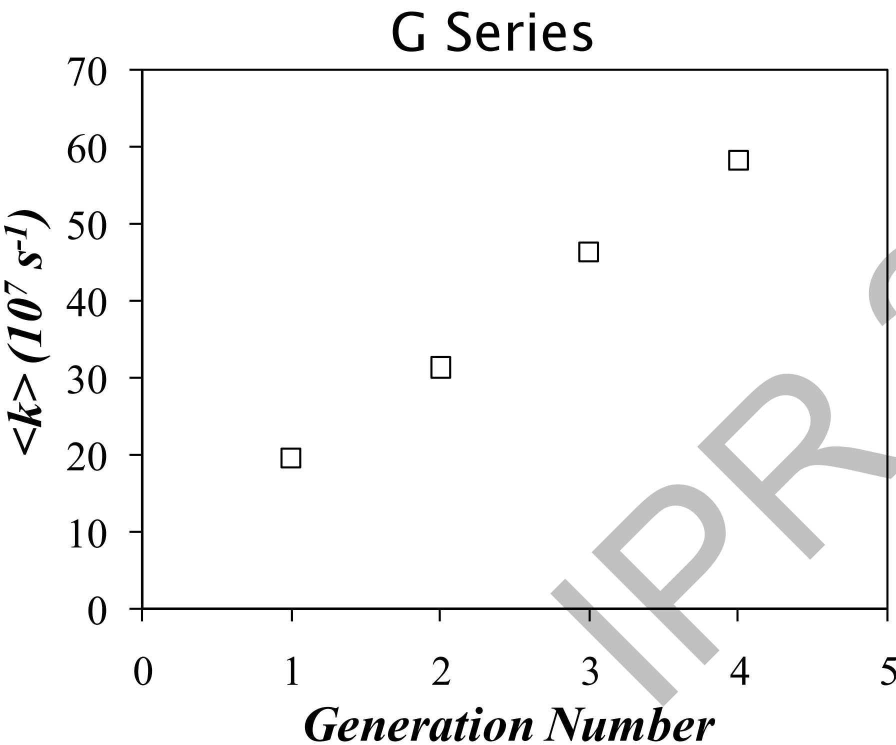
  - Is the decrease due to increased dendritic arm stiffness?

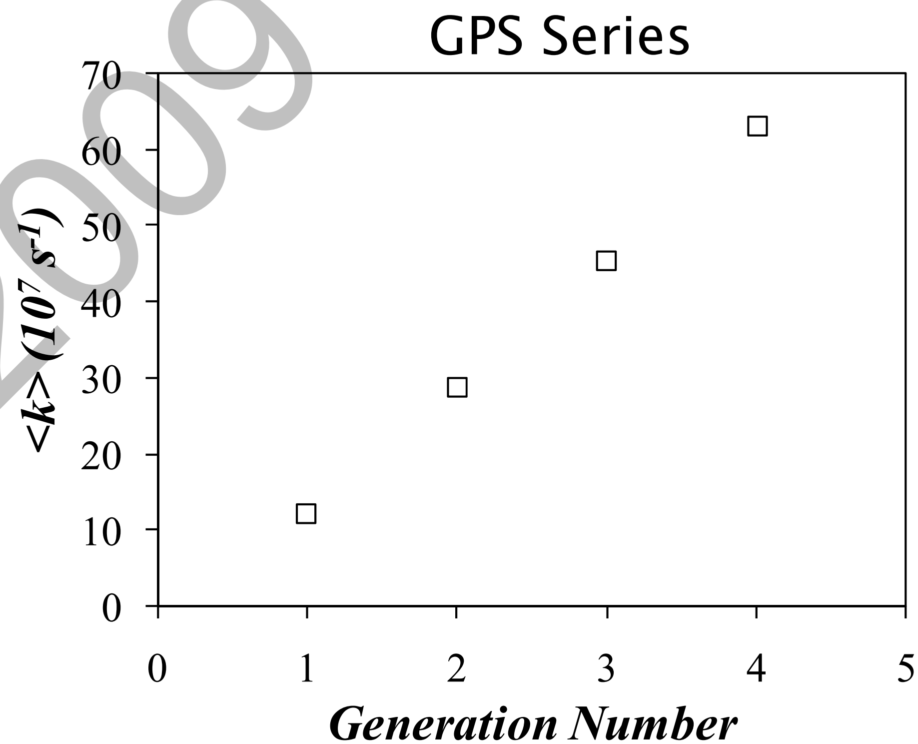
Solvent = THF
[*Py*] = 2.5 μM
λ_{ex} = 344 nm

Cuniberti, C.; Perico, A. *Eur. Polym. J.* 1980, *16*, 887–893.

Experimental Results

- Time-Resolved Fluorescence Decays



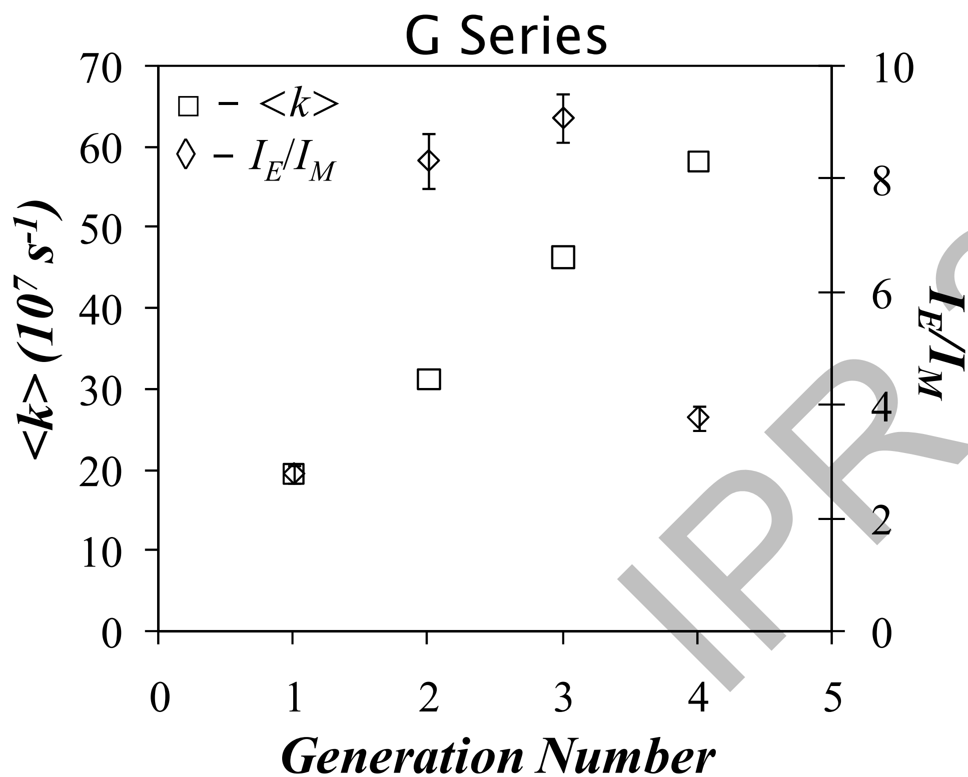


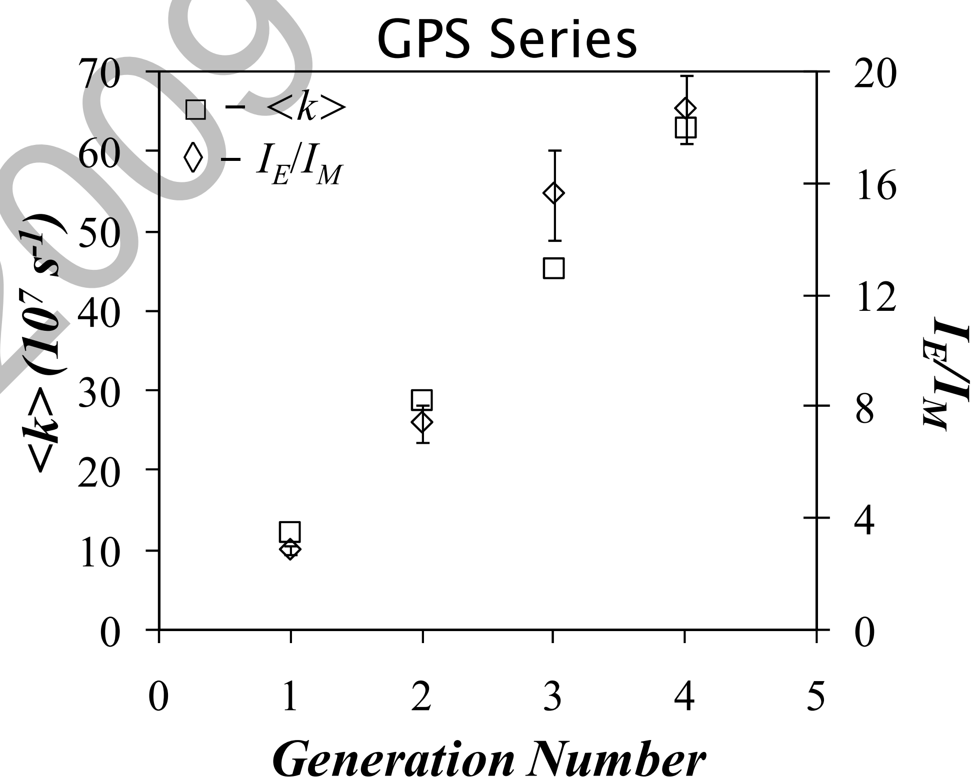
  - Recall: I_E/I_M should be proportional to $<k>$!

$$\frac{I_E}{I_M} = \kappa \frac{\phi_E^0}{\phi_M^0} \tau_M < k >$$

Experimental Results

- I_E/I_M and $<k>$

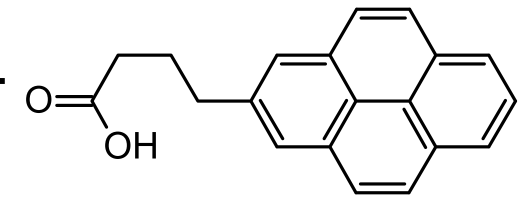




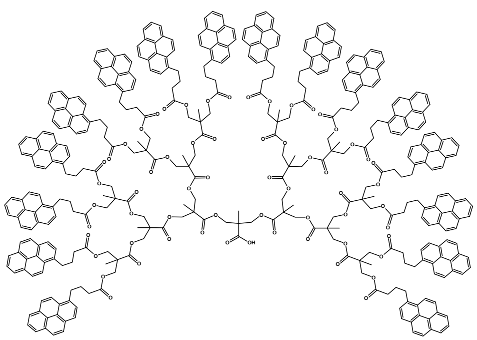
  - Why the decrease in I_E/I_M ratio for G4?

Experimental Results

- Contributions from τ_M from monomer decays



Sample	f_{Mfree} *(% of total contribution)*
G1	3.3
G2	0.62
G3	0.29
G4	**3.1**
G1PS	1.5
G2PS	0.61
G3PS	0.08
G4PS	0.23

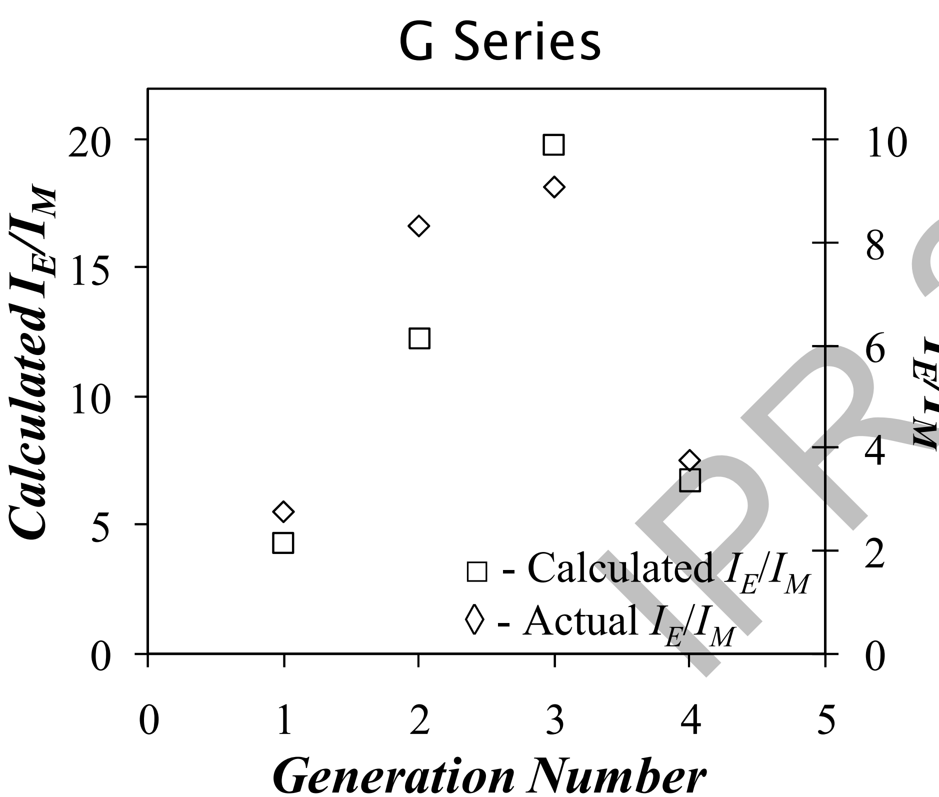


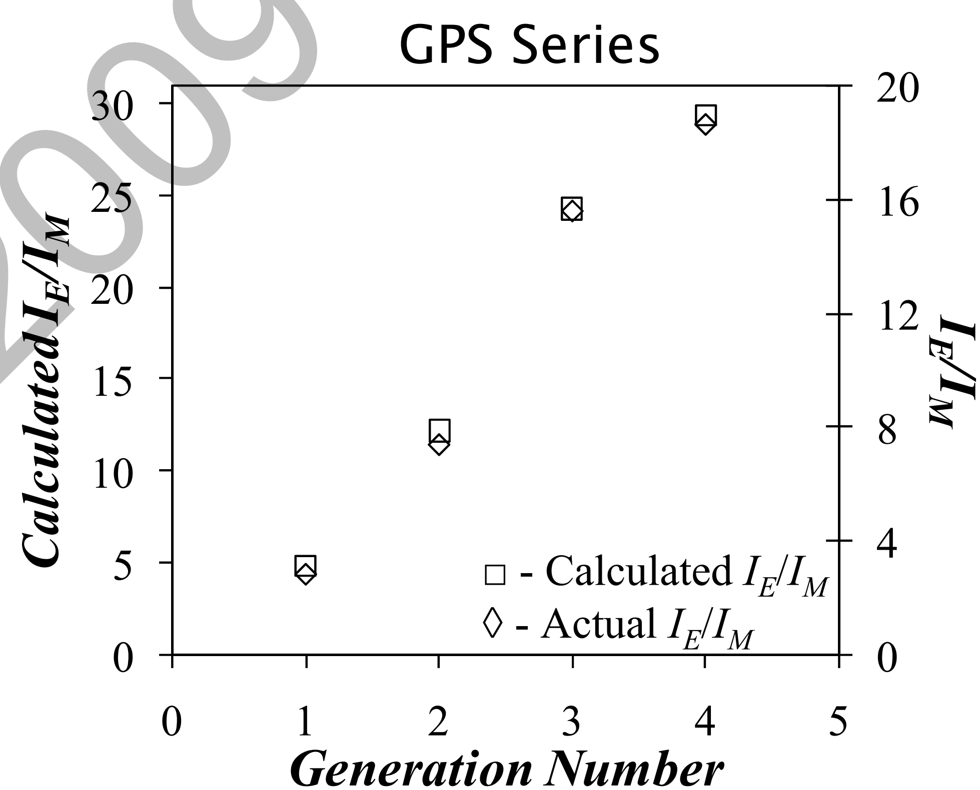
Experimental Results

- The new I_E/I_M equation
  - $<k>$ ignores contributions from free monomers in solution.
  - The new I_E/I_M equation takes into account all species in solution, as well as their relative contributions, *based on fluorescence decay data*.

Experimental Results

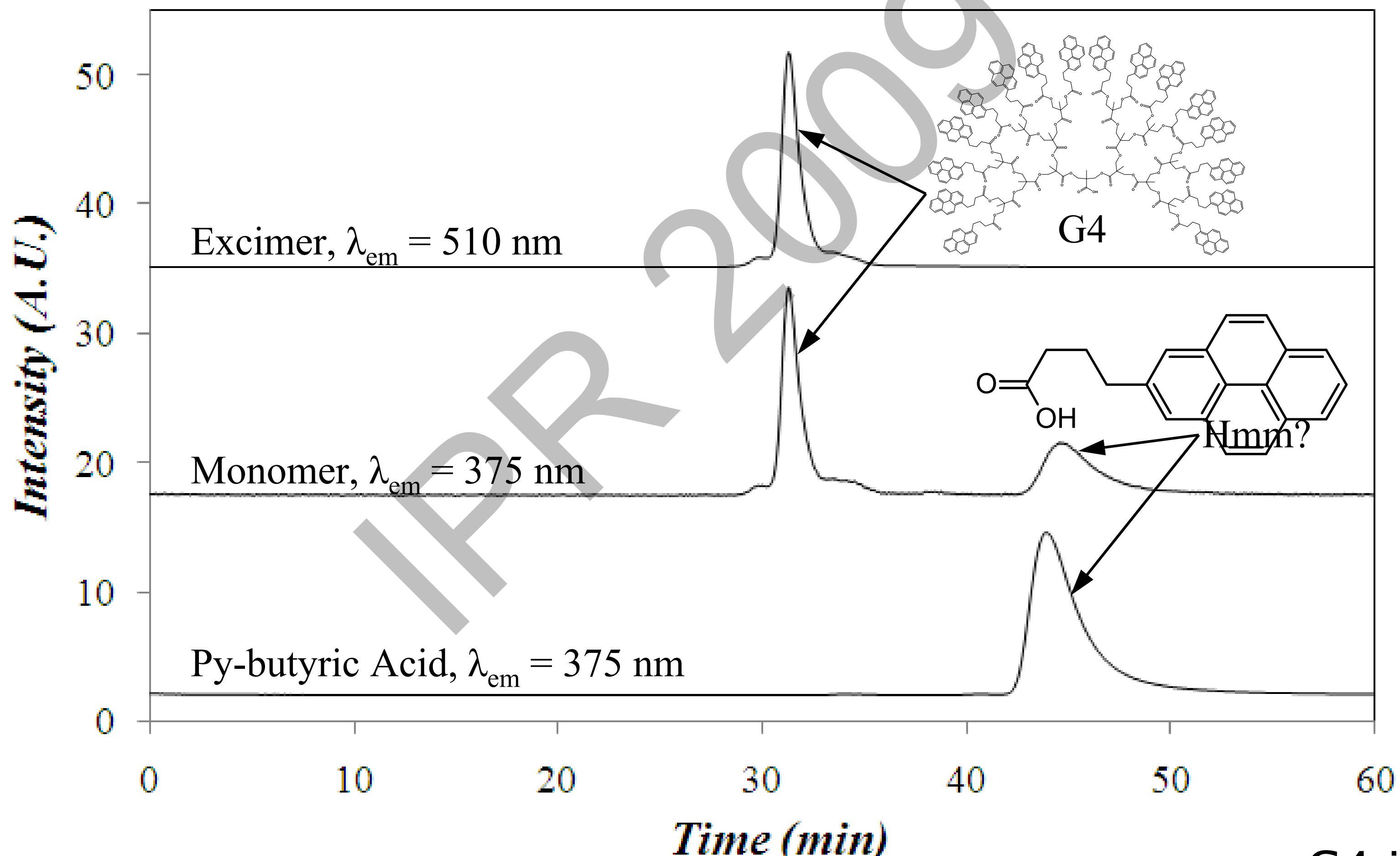
- The new I_E/I_M equation





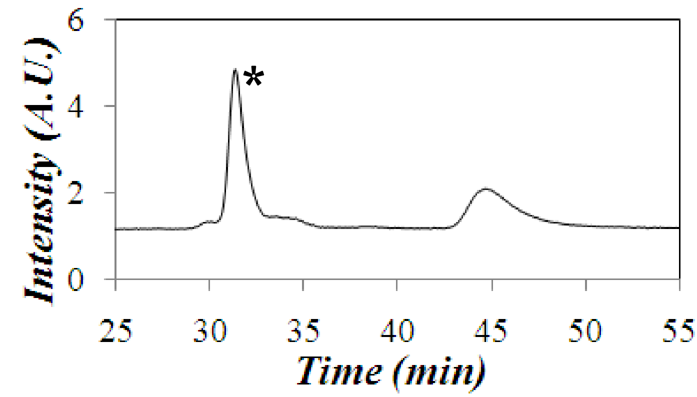
Experimental Results

- Gel Permeation Chromatography

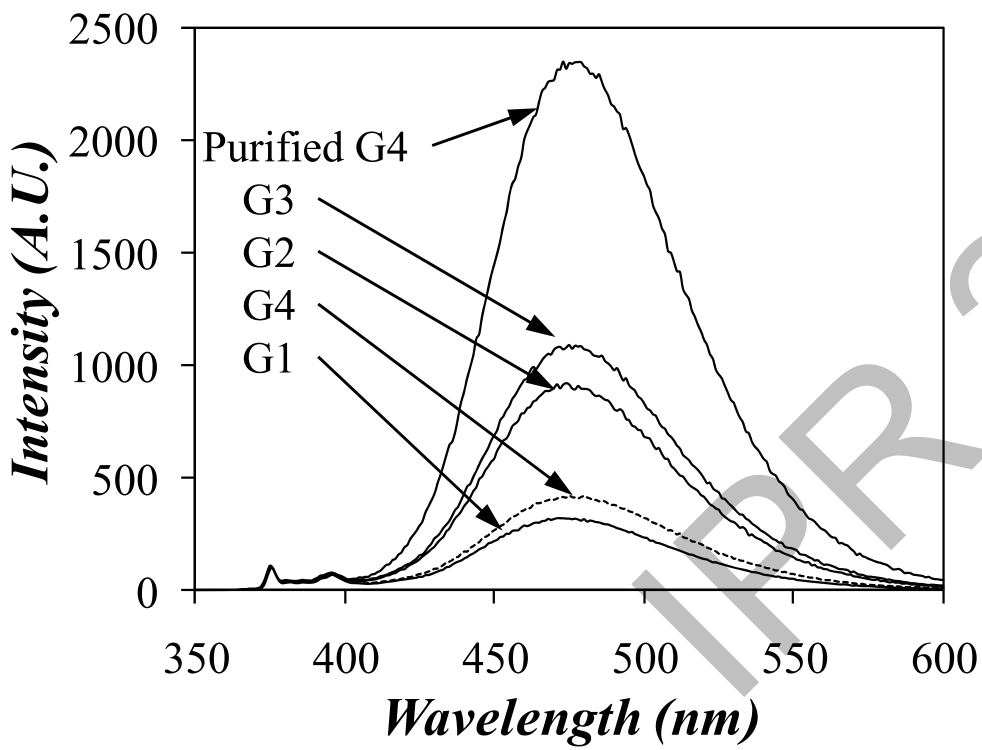


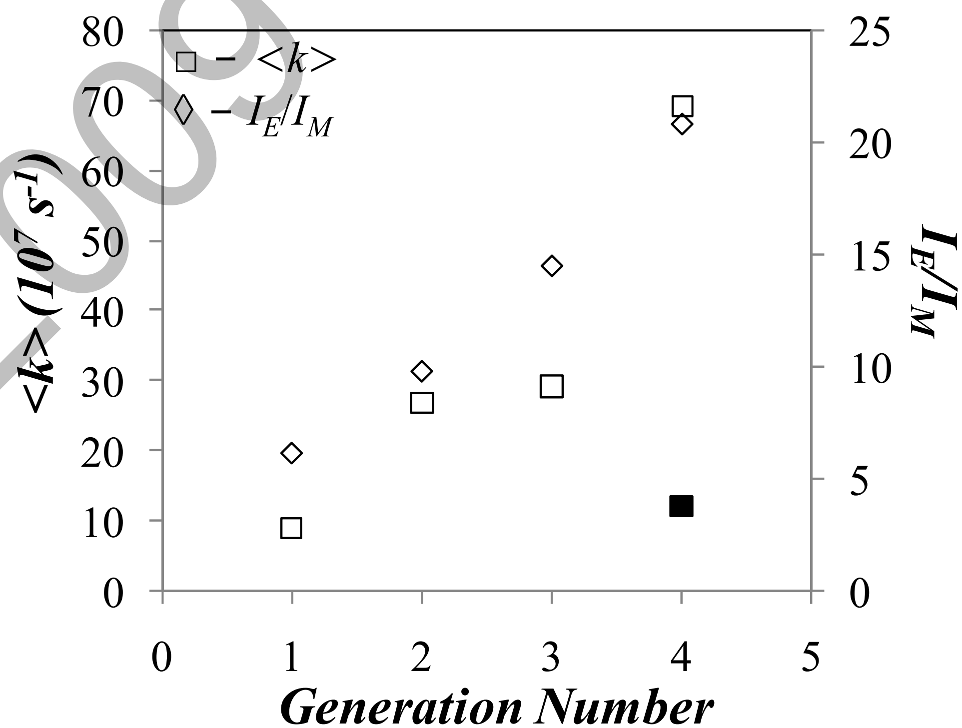
G4 in THF
$[Py]$ = 25 µM
λ_{ex} = 344 nm

Experimental Results



- G4 Purification





- The second peak fluoresced with a lifetime of 210 ns!

Meltzer et. al. *Macromolecules*. 1992, *25*, 4541–4548.

Experimental Results

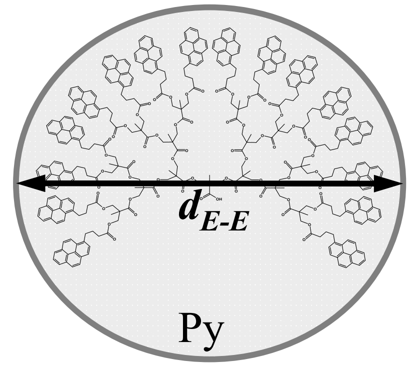
- Molecular Mechanics Optimizations
  - Recall:

$$<k> = k_1[Py]_{loc}$$

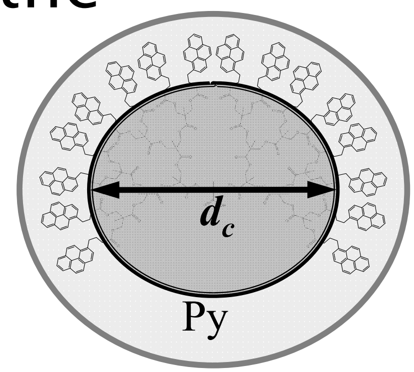
    - As generation number increases, $<k>$ increases.
    - Previous studies have shown that, at low generations, k_1 decreases slightly with increasing generation number.
    - Thus, $[Py]_{loc}$ must increase.
    - **Assuming k_1 constant, $[Py]_{loc}$ should show similar trends to $<k>$**

Experimental Results

- Scenarios to consider:
  - Pyrene is free to diffuse throughout



  - Pyrene is confined to the outer shell of the dendrimer

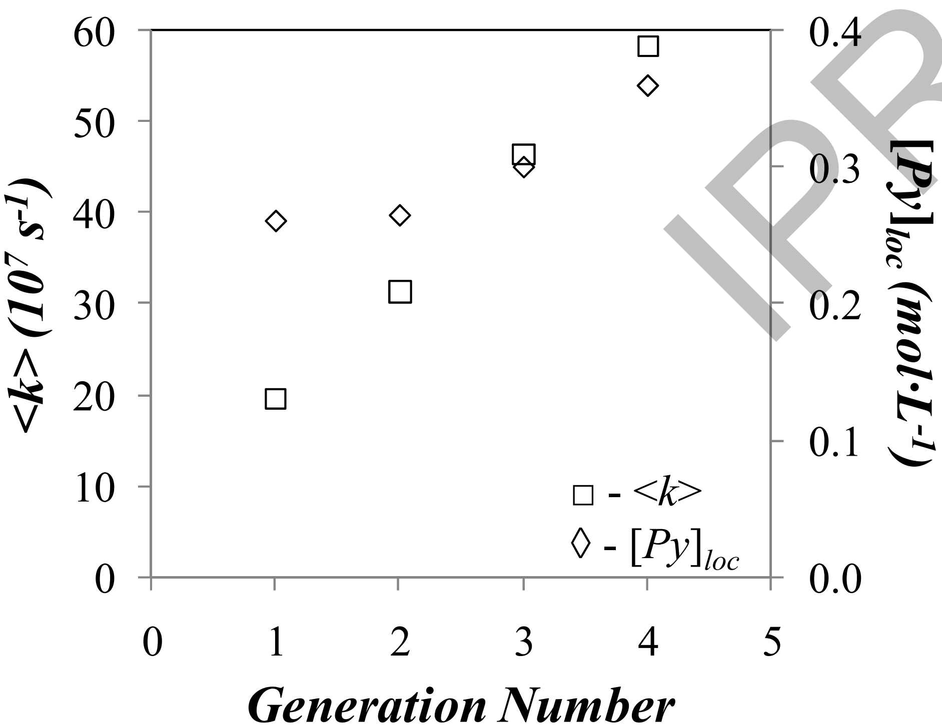


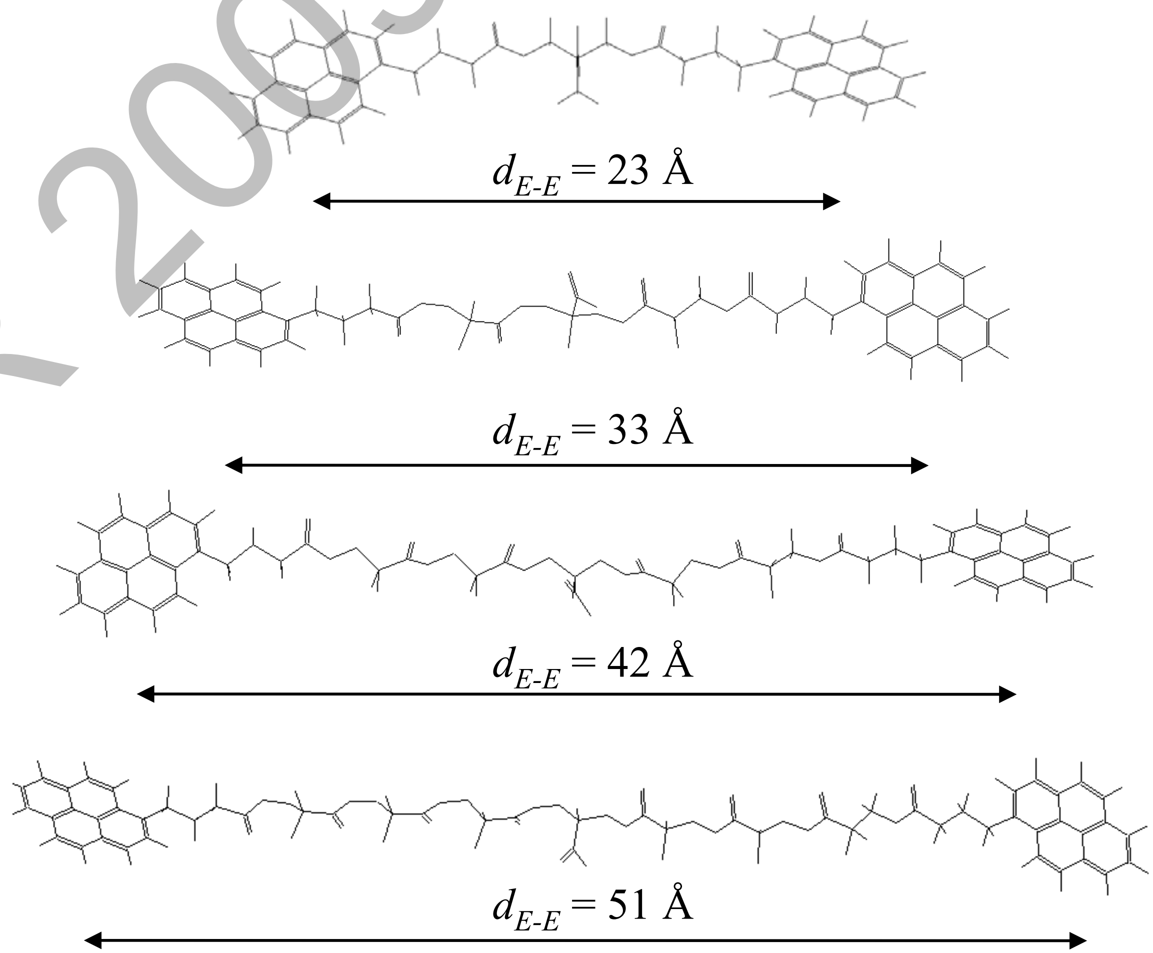
  - A combination of the two
- Need to determine the volume occupied by pyrene

Experimental Results

- Scenario 1:
  - Pyrene free to diffuse throughout

$$[Py]_{loc} = \frac{2^n - 1}{\frac{4}{3}\pi\, r_{E-E}^3}$$

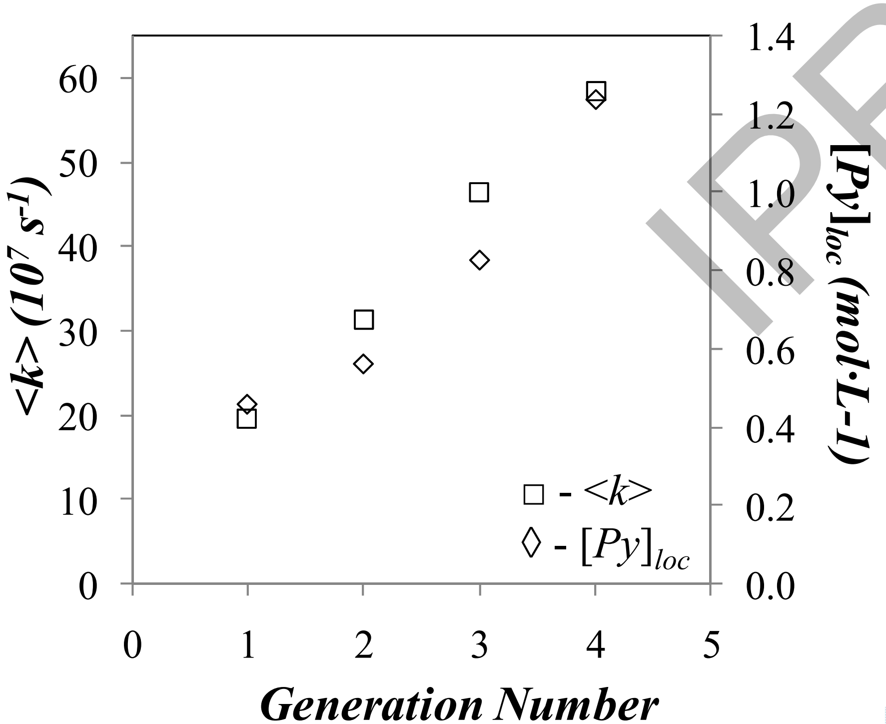


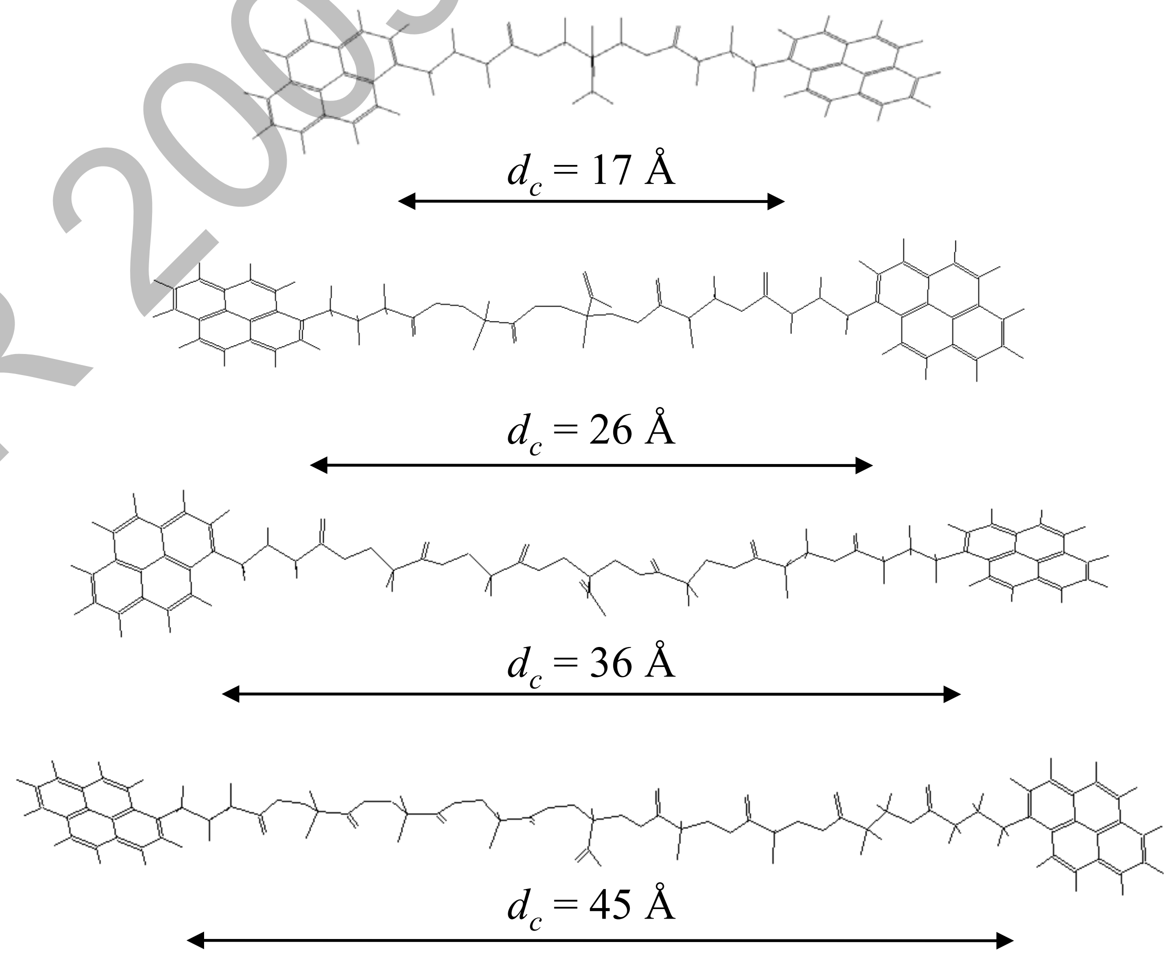


Experimental Results

- Scenario 2: Pyrene excluded to outer shell

$$[Py]_{loc} = \frac{2^n - 1}{\frac{4}{3}\pi\left(r_{E-E}^3 - r_c^3\right)}$$





Experimental Results

- Scenario 3:
  - G1 is free to diffuse throughout, higher generations are confined
  - Calculate k_1 for G1
  - Assume k_1 is constant for all generations
  - Calculate corresponding r_c

Experimental Results

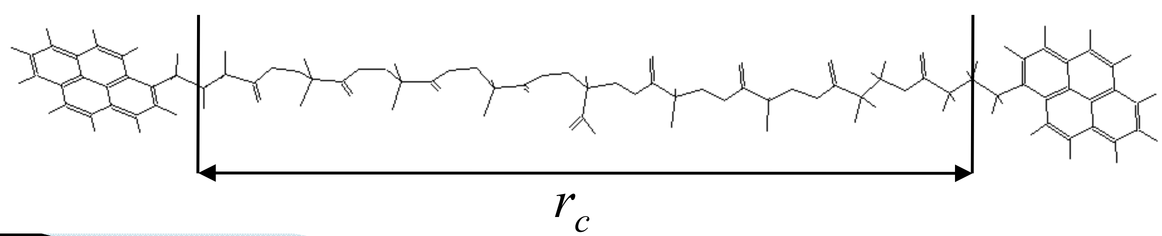
- Scenario 3
  - For G1:

$$k_1 = \frac{<k>}{[Py]_{loc}}$$

  - For G2-G4:

$$[Py]_{loc} = \frac{<k>}{k_1} \qquad r_c = \left(r_{E-E}^3 - \frac{2^n - 1}{\frac{4}{3}\pi [Py]_{loc}} \right)^{1/3}$$

  - **Result: For G2-G4, r_c corresponded to pyrene attachment point minus 1-2 carbons!**



Conclusions

- The decrease in I_E/I_M ratio is due to residual pyrenebutyric acid
- At generations > 1, internal steric hindrance may exclude pyrene to the outer spherical shell defined by the arms of the dendrimer molecules

Acknowledgements

- Dr. Jean Duhamel
- Dr. Alex Adronov
- Greg Bahun
- The Duhamel Group

Questions?