Characterizing the Dimensions and Dynamics of Pyrene Labeled Macromolecules in Solution

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UNIVERSITY OF WATERLOO

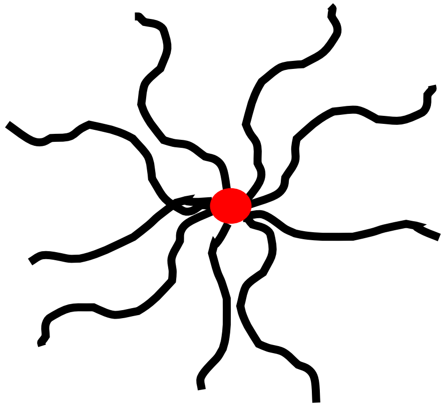
Outline

- Introduction
  - Dendrimers and their applications
  - Pyrene Excimer Fluorescence
- Dendritic Constructs
- Results
- Conclusions and Future Work
- Acknowledgments

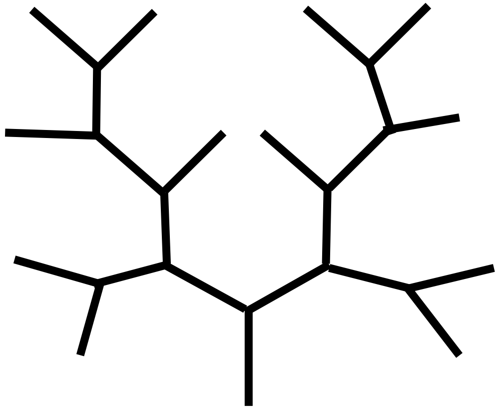
Introduction

- Polymers with complex architecture can be separated into 4 categories. These topologies include:

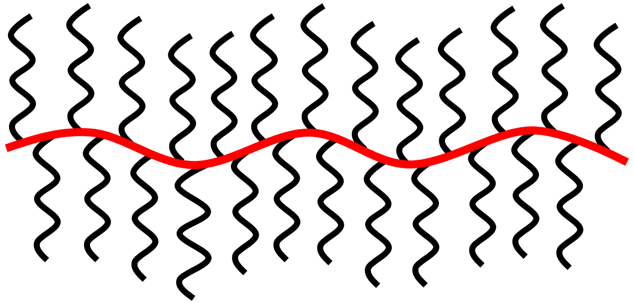
Star



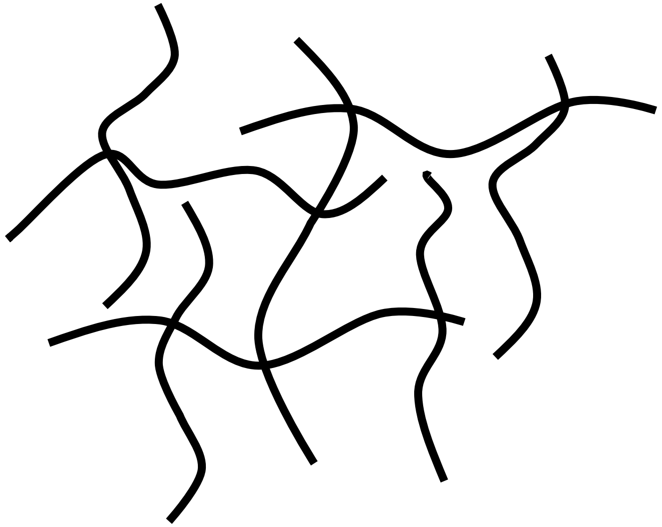
Hyperbranched/ Dendritic



Brush/ Comb

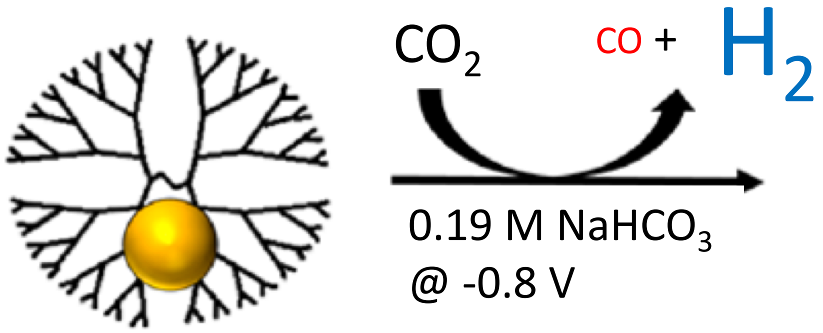


Networks/ Gels



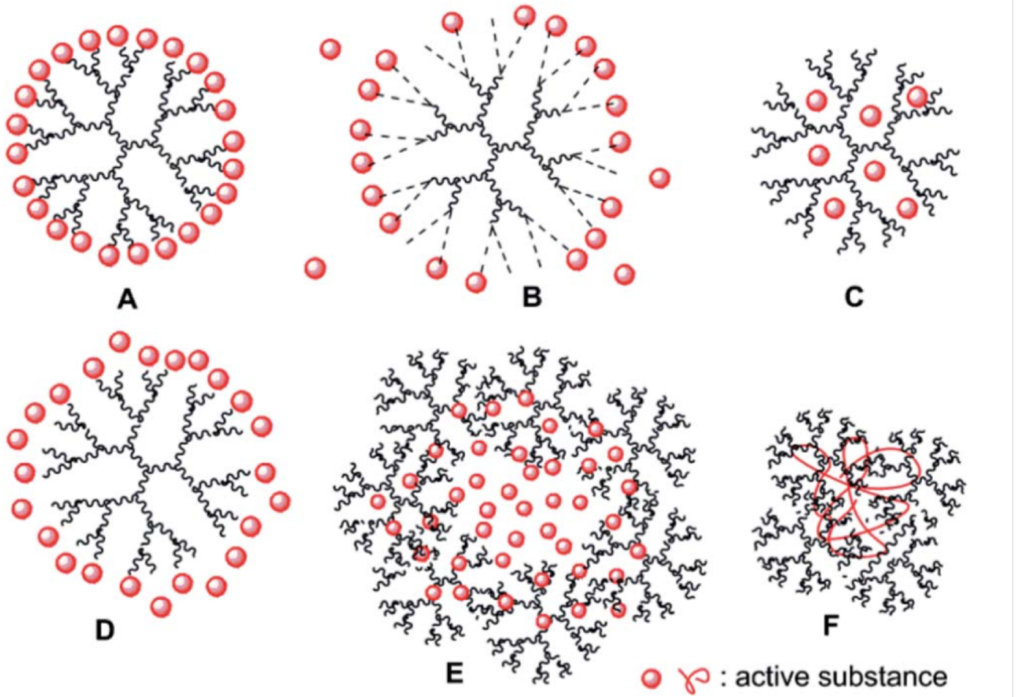
Dendrimer Applications

(1)



Encapsulation of metal nanoparticles for catalytic reactions

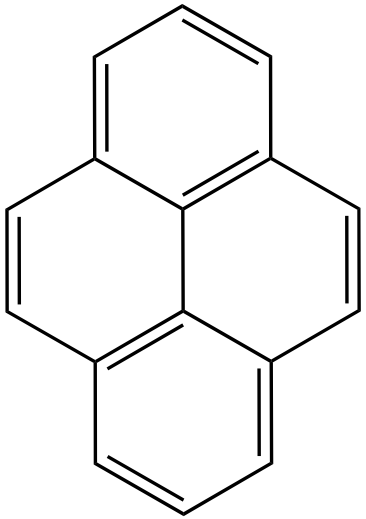
(2)

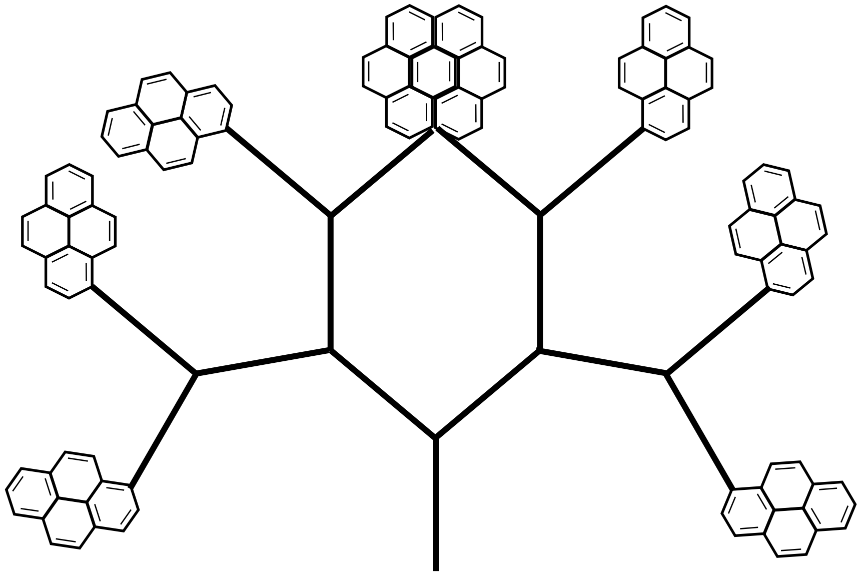


A- Covalent bond
B- Cleavable bond
C- Non-covalently internal
D)Non-covalently external
E) + F) Associated dendrimer

(1) Trindell, J. A.; Clausmeyer, J.; Crooks, R. M. Size Stability and H_2/CO Selectivity for Au Nanoparticles during Electrocatalytic CO2 Reduction. *J. Am. Chem. Soc.* **2017**, *139*, 16161-16167.
(2) Caminade, A.M.; Turrin, C.O.; Dendrimers for drug delivery. *J. Mater. Chem. B.* ***2014***, *2,* 4055-4066

Fluorescence





$$M + h\nu \longrightarrow M^* + M \xrightarrow{\langle k \rangle} (MM)^*$$

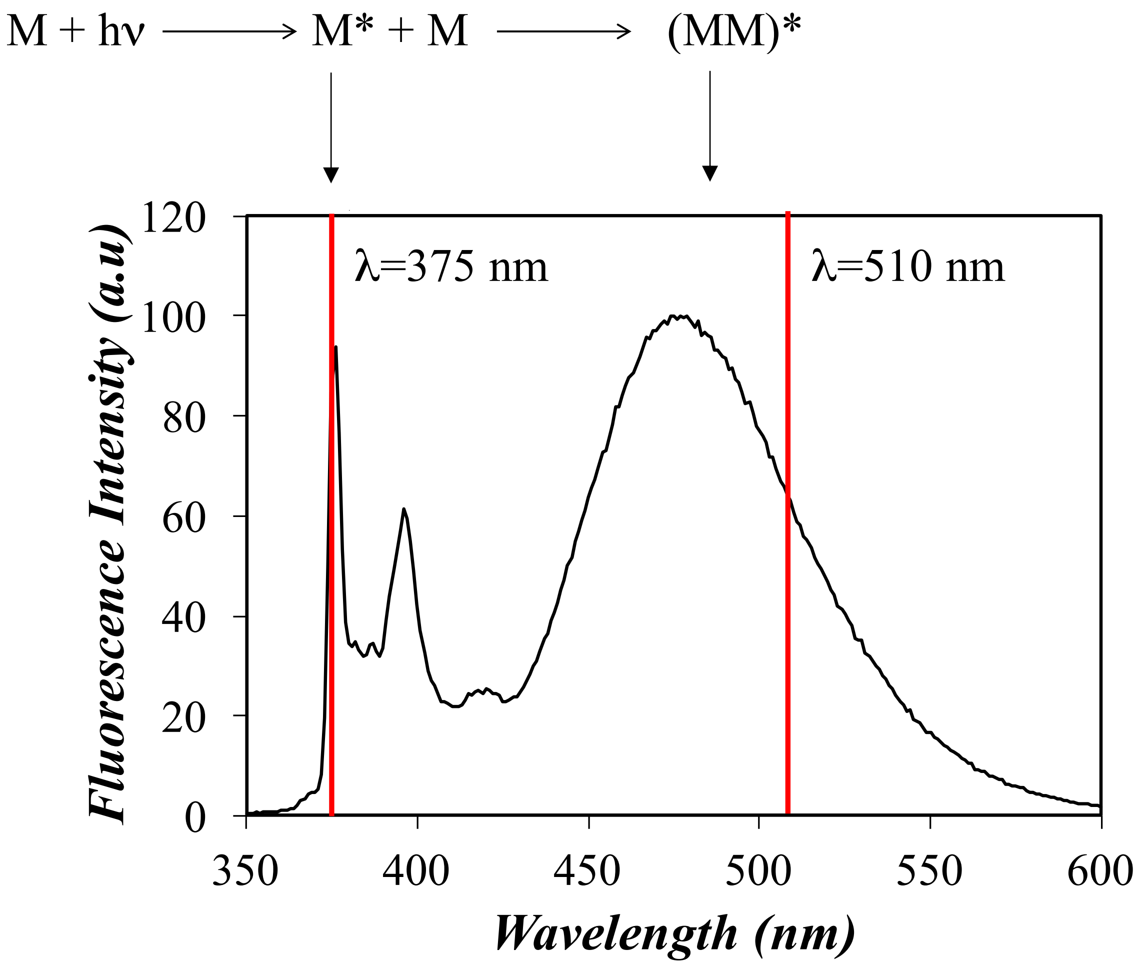
$$M^* \downarrow \tau_M^{-1} \qquad (MM)^* \downarrow \tau_E^{-1}$$

Pyrene was chosen because of its interesting characteristics:

- High molar extinction coefficient
- High quantum yield
- Excimer formation *

M* = Excited pyrene
M = Ground state pyrene monomer
(MM)* = Pyrene excimer
<*k*> = average rate constant of excimer formation

Steady-State (SS) Fluorescence

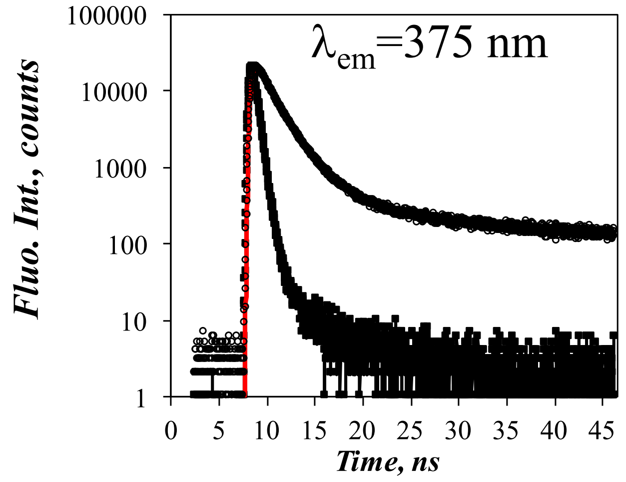


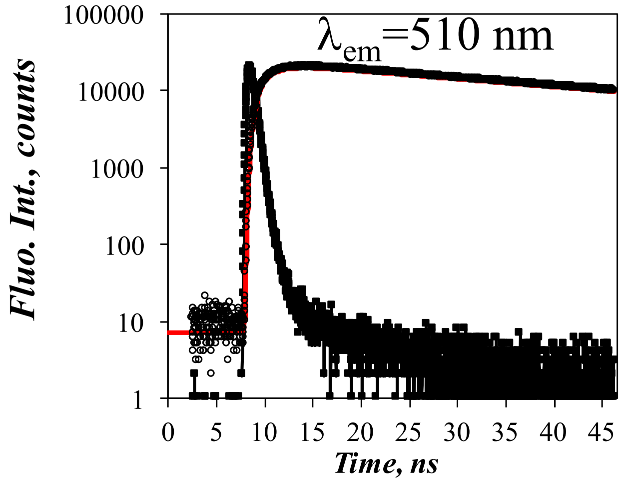
SS fluorescence measures the intensity of the monomer and excimer emission.

The monomer emission produces several fluorescence peaks between 375 nm and 410 nm.

Excimer emission produces a broad structureless emission which is centered around 480 nm.

Time Resolved (TR) Fluorescence





Monomer and excimer excited at 344 nm.

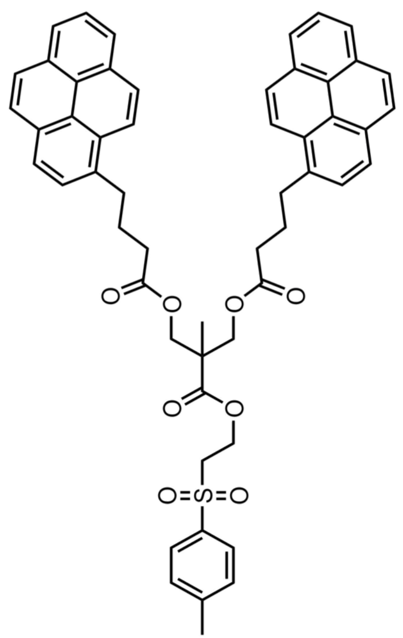
Fluorescence of monomer monitored as a function of time at 375 nm.
Immediate decay of the monomer is seen.

Fluorescence of excimer monitored as a function of time at 510 nm.
Rise time is seen because of the time required for an excited pyrene to encounter a ground state pyrene.

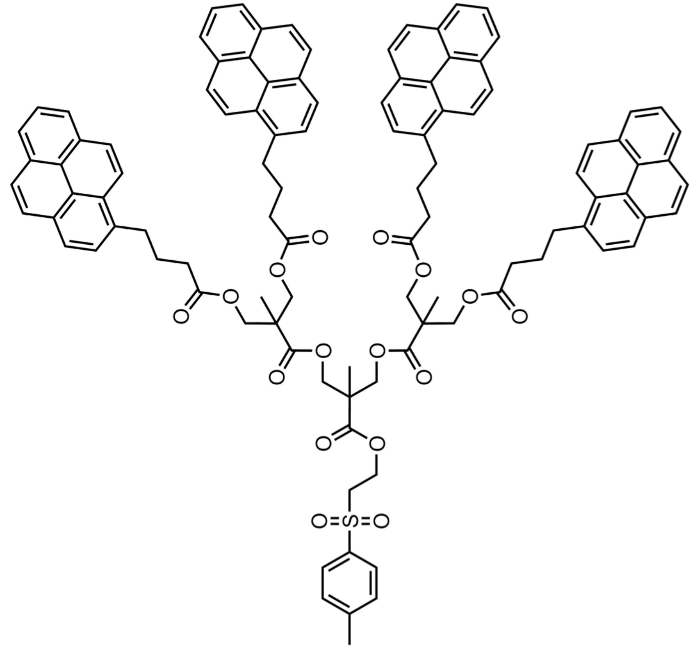
$$\langle k \rangle = k_{diff} \times [Py]_{loc}$$

Bis(hydroxymethyl)propionic acid dendrimers

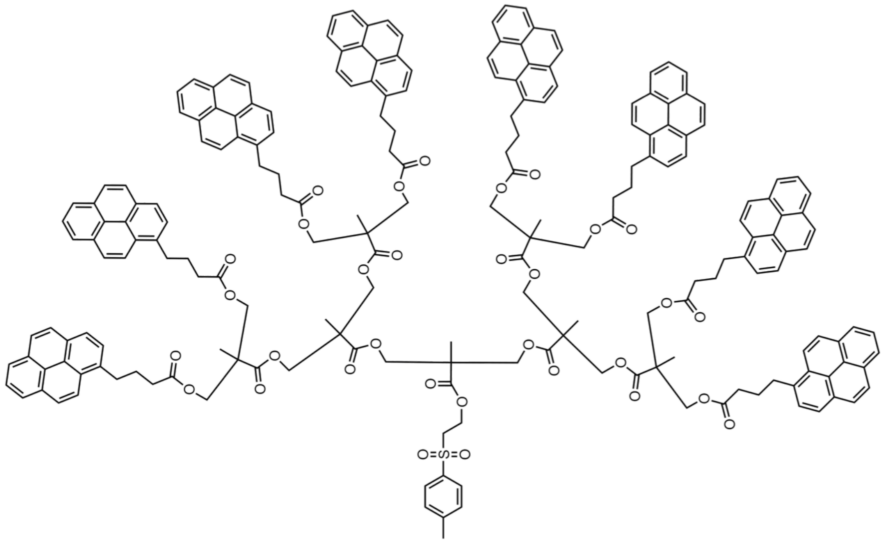
G1



G2



G3

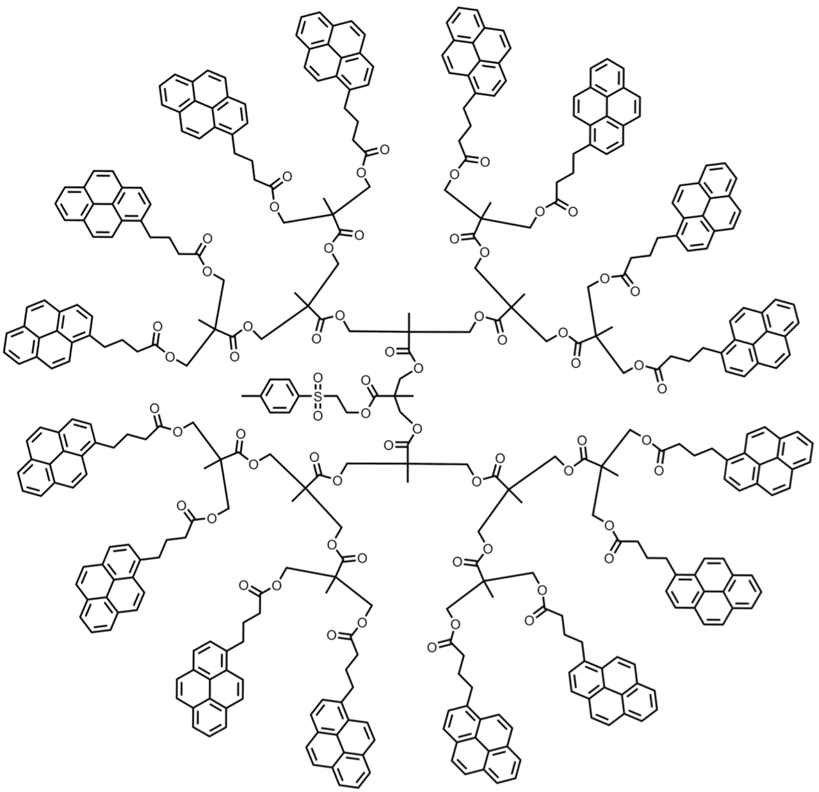


$Py_xG(N)$

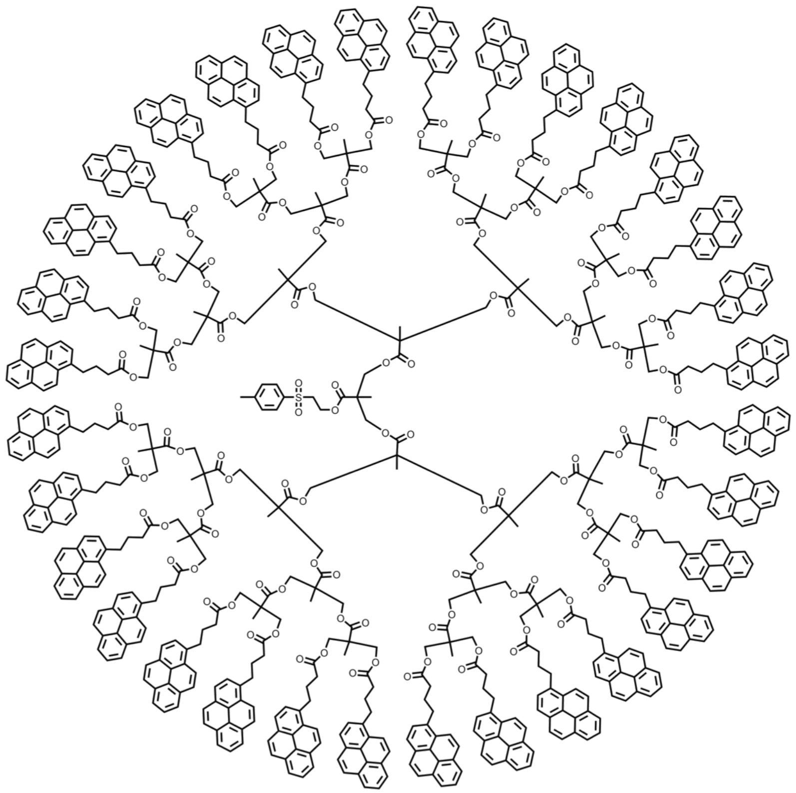
Synthesized by Prof. A. Adronov and S. A. McNelles from Department of Chemistry and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, Canada

Bis(hydroxymethyl)propionic acid dendrimers

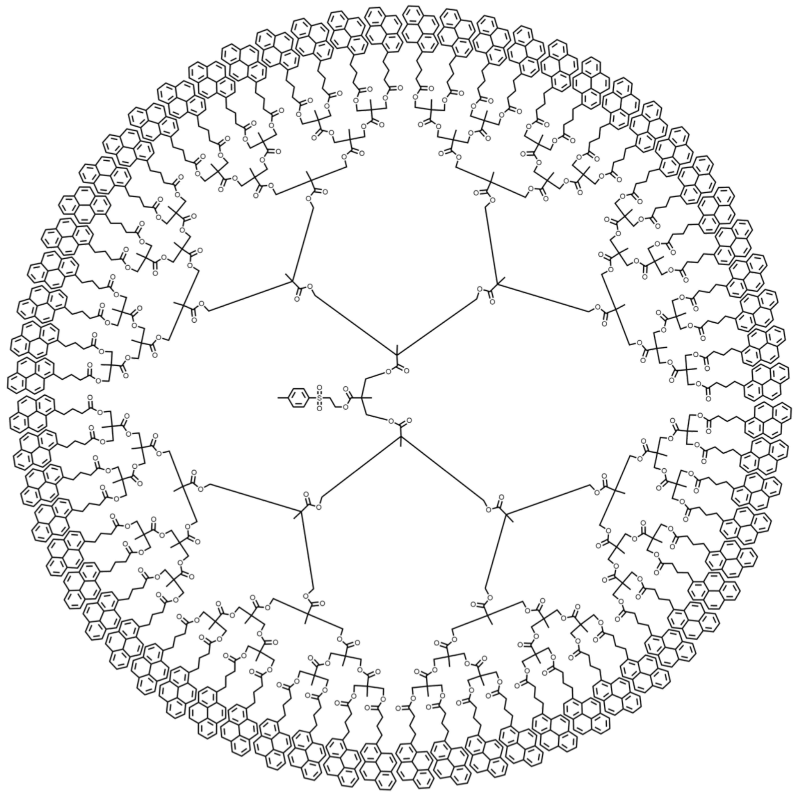
G4



G5



G6



$Py_xG(N)$

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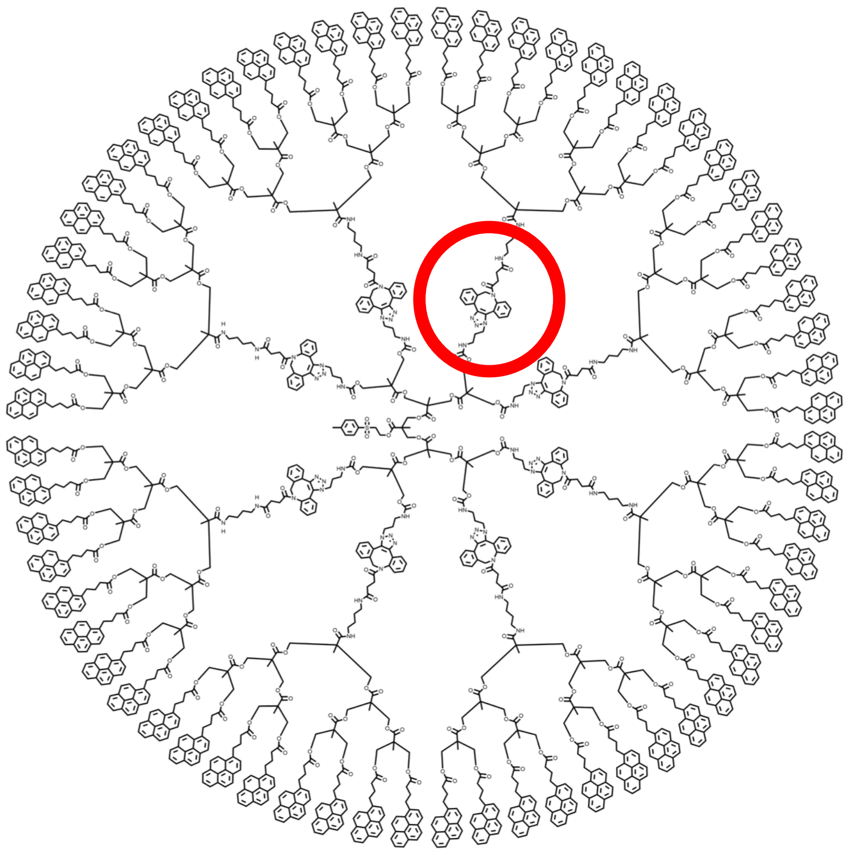
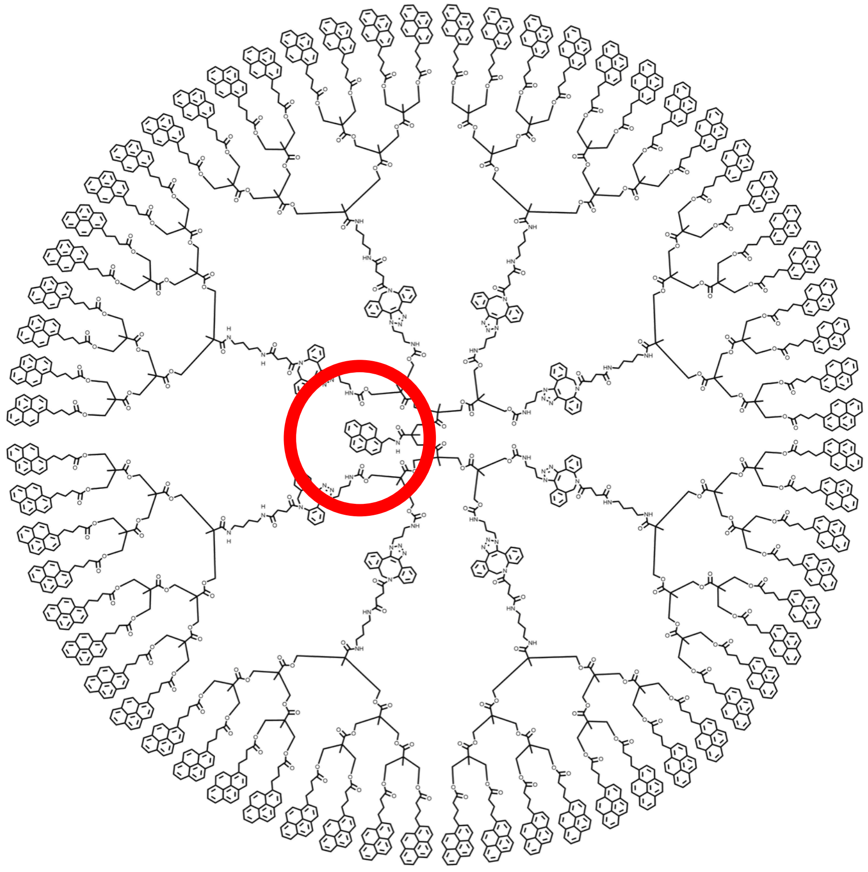
Bis(hydroxymethyl)propionic acid dendrons

$Py_{64}G(6)$-spacer



$Py_{64+1}G(6)$-spacer



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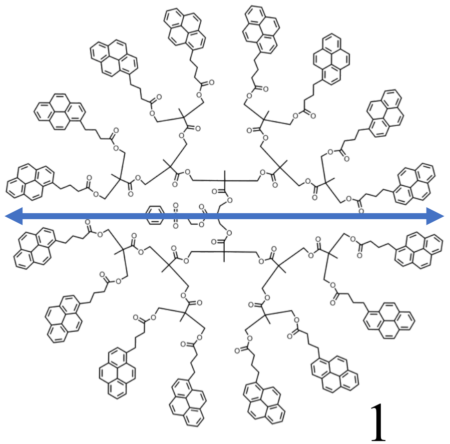
Determining <L_{Py}^2> - Average of the squared end-to-end distance separating every two pyrene labels

$$< k > = k_{diff} \times [Py]_{loc} = k_{diff} \times \frac{2^N - 1}{V_{dendron}}$$

Assume $V_{dendron}$ is a sphere

$$\left[Py \right]_{local} = \frac{(2^N - 1)}{\frac{4}{3}\pi r^3}$$

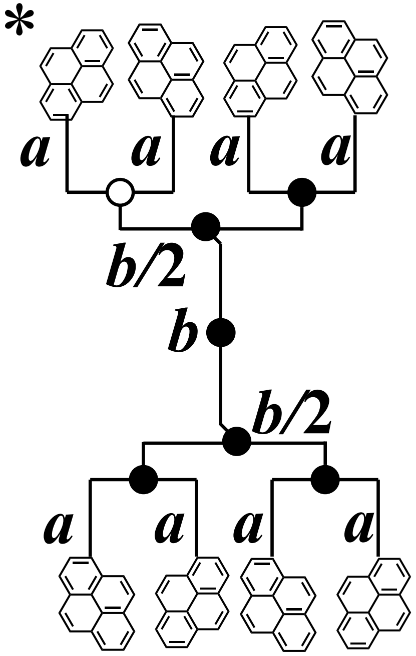


$$r = \left(\frac{\left\langle L_{Py}{}^2 \right\rangle}{2^2} \right)^{\frac{1}{2}}$$

$$\left\langle L_{Py}{}^2 \right\rangle^{\frac{1}{2}} = n^{\frac{1}{2}} \times l$$

$$\left\langle L_{Py}{}^2 \right\rangle^{\frac{1}{2}}$$

Example Calculation for G3



$$\frac{\langle L_{Py}{}^2 \rangle}{l^2} = \frac{(2a+1)+2(2a+1+b)+4(2a+1+2b)}{7}$$

$$\frac{\langle L_{Py}{}^2 \rangle}{l^2} = \frac{2a+1+4a+2+2b+8a+4+8b}{7}$$

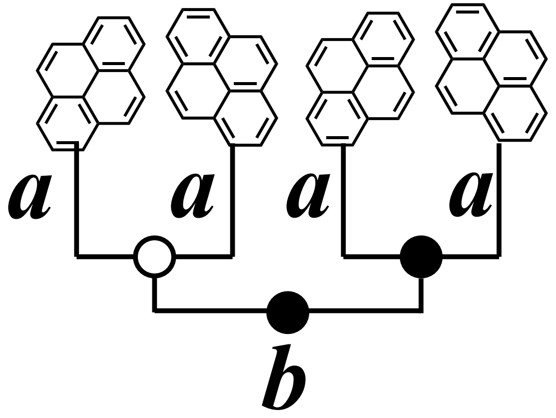
$$\langle L_{Py}{}^2 \rangle = n \times l^2$$

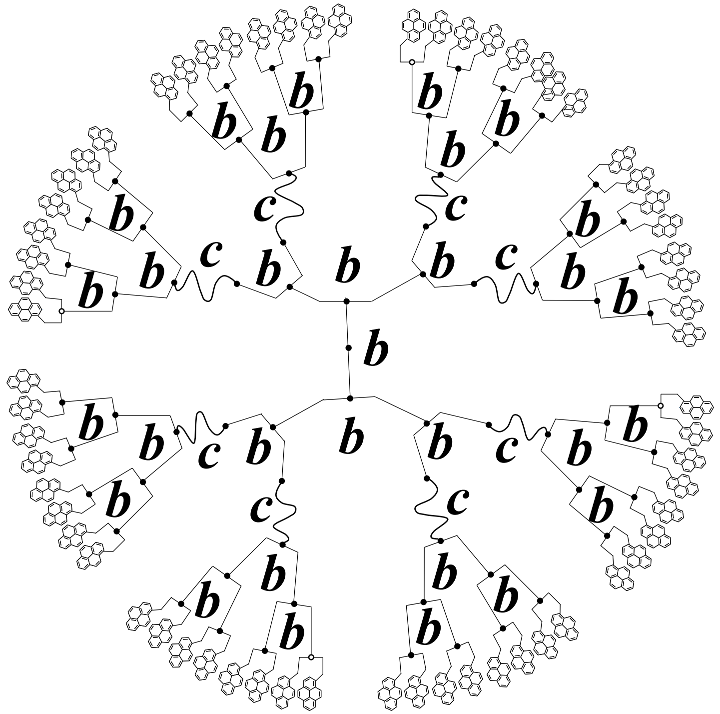
$$\frac{\langle L_{Py}{}^2 \rangle}{l^2} = n$$

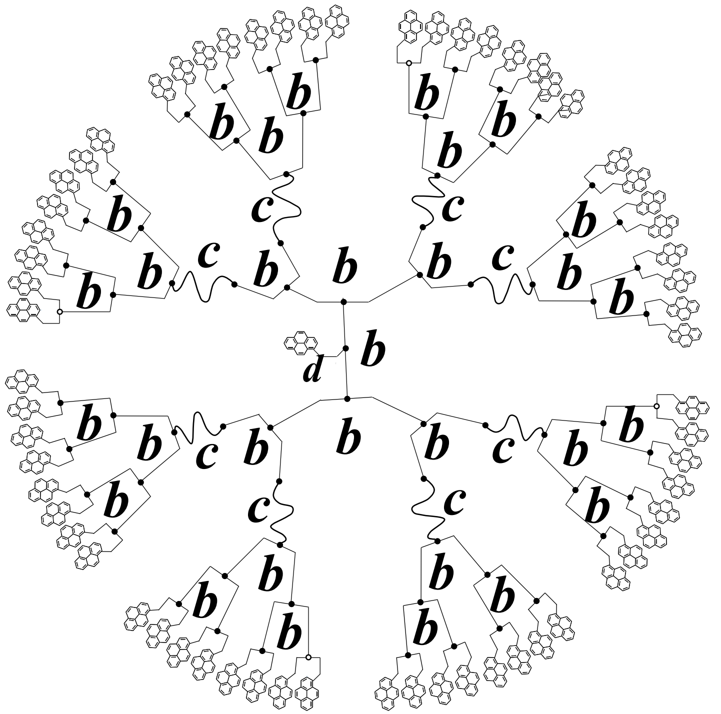
$$\frac{\langle L_{Py}{}^2 \rangle}{l^2} = \frac{14a+10b+7}{7} \longrightarrow \frac{\langle L_{Py}{}^2 \rangle}{l^2} = 1+2a+\frac{10b}{7}$$

$$\left\langle L_{Py}{}^{2} \right\rangle = n \times l^2$$

Determining $<L_{Py}{}^2>$







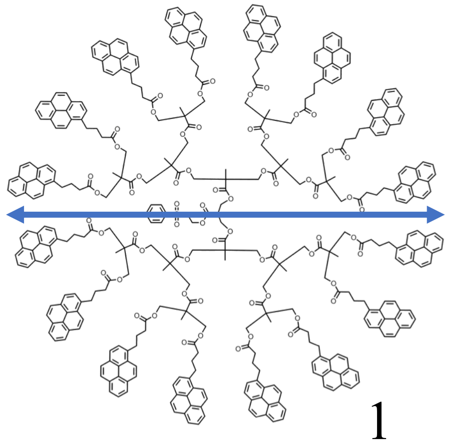
$$< L_{Py}^2 > = l^2 \left(1 + 2a + b \frac{N \times 2^N - 2^{N+1} + 2}{2^N - 1} \right)$$

$$< L_{Py}^2 > = l^2 \left(1 + 2a + b \frac{258}{63} + c \frac{112}{63} \right)$$

$$< L_{Py}^2 > = l^2 \left(1 + 2a + b \frac{258}{64} + c \frac{112}{64} + \frac{(a + 2.5b + c + d)}{64} \right)$$

Calculated $<L_{Py}{}^2>^{1/2}$

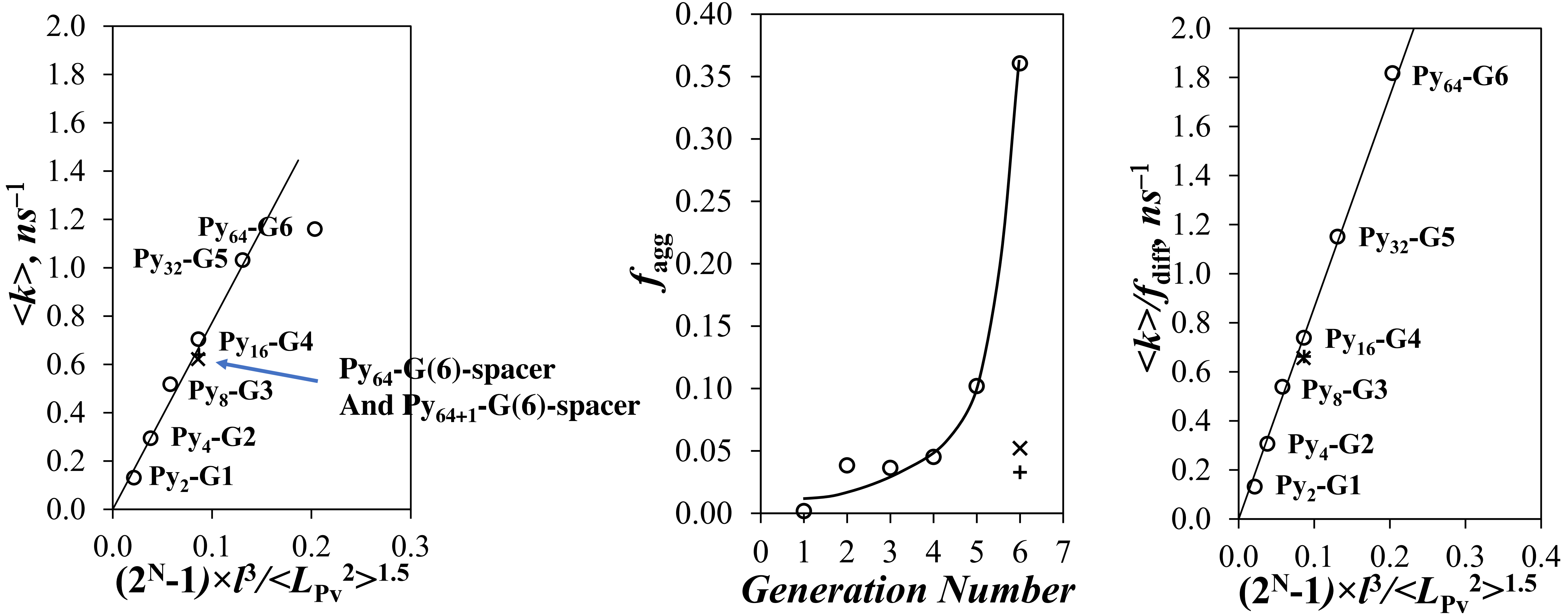
Generation	# of GS pyrenes	$<L_{Py}{}^2>^{1/2}$ (Å)
1	1	4.5
2	3	5.4
3	7	6.2
4	15	7.0
5	31	7.7
6	63	8.5
6-spacer	63	11.3
6-spacer	64	11.2



$$\left\langle {L_{Py}}^2 \right\rangle^{\frac{1}{2}}$$

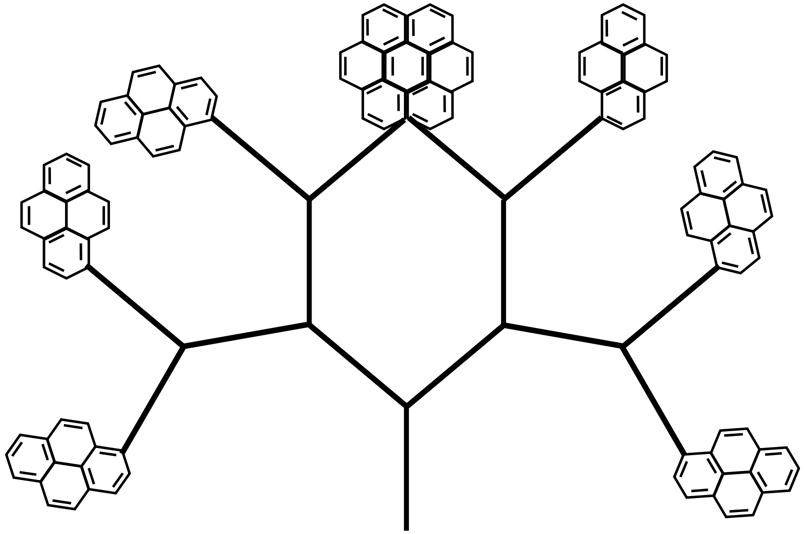
McNelles, S. A.; Thoma, J. L.; Adronov, A.; Duhamel, J. Quantitative Characterization of the Molecular Dimensions of Flexible Dendritic Macromolecules in Solution by Pyrene Excimer Fluorescence. *Macromolecules* **2018,** *51*, 1586- 1590.

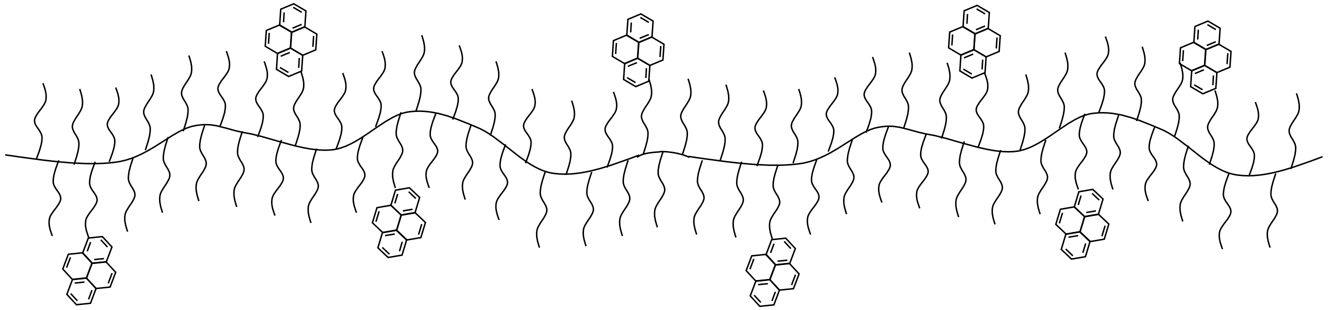
$$<k> = k_{diff} \times [Py]_{loc} = k_{diff} \times \frac{2^N - 1}{V_{dendron}} \qquad V_{dendron} = \frac{\pi}{6} \times \left\langle L_{Py}{}^2 \right\rangle^{\frac{3}{2}}$$



McNelles, S. A.; Thoma, J. L.; Adronov, A.; Duhamel, J. Quantitative Characterization of the Molecular Dimensions of Flexible Dendritic Macromolecules in Solution by Pyrene Excimer Fluorescence. *Macromolecules* **2018,** *51*, 1586- 1590.

Can this be applied to PBBs?

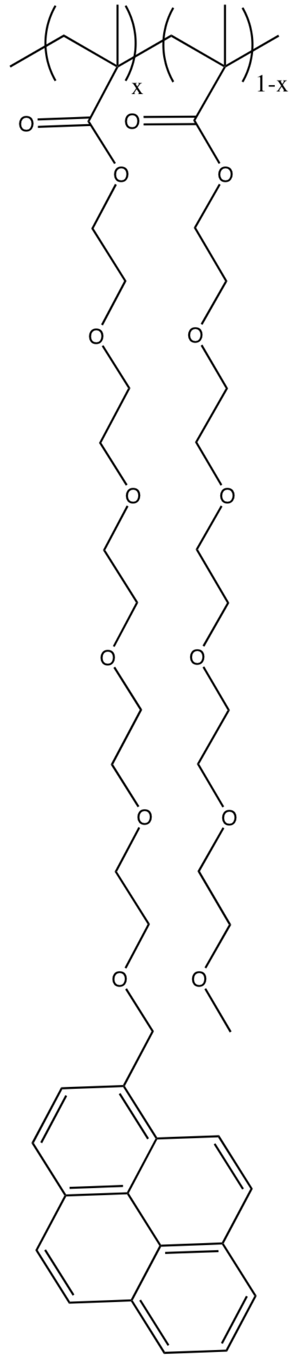




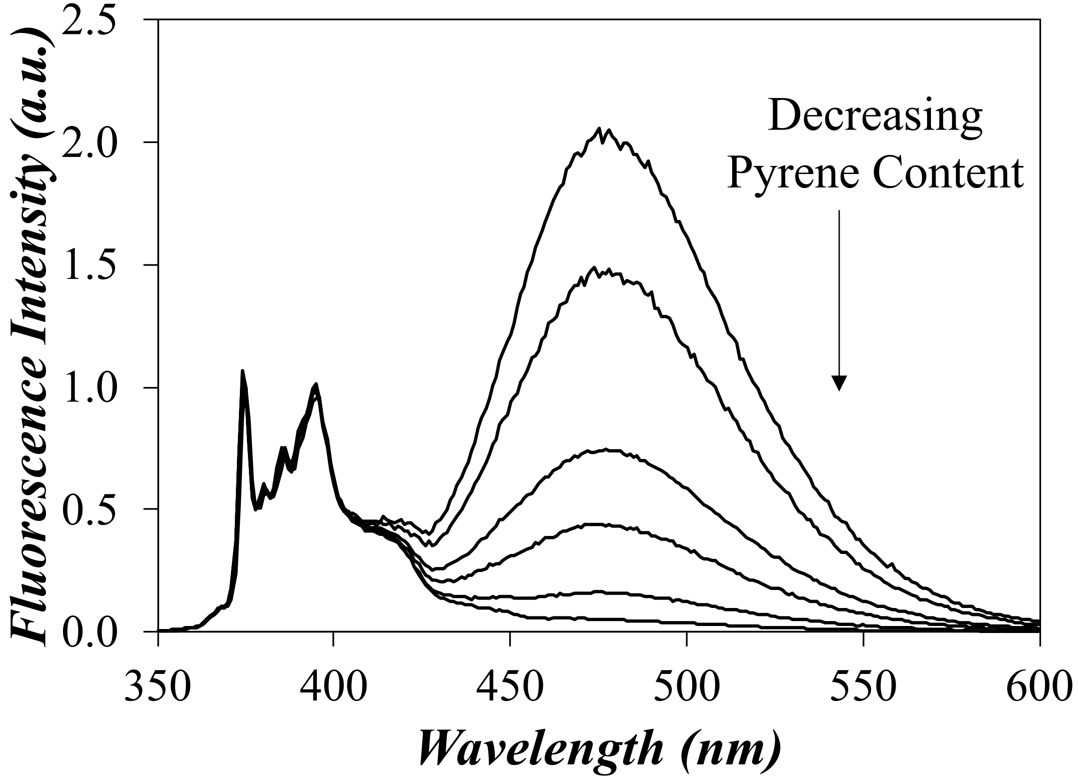
A polymeric bottle brush (PBB) is a highly branched macromolecule with a high degree of polymerization and high grafting density.

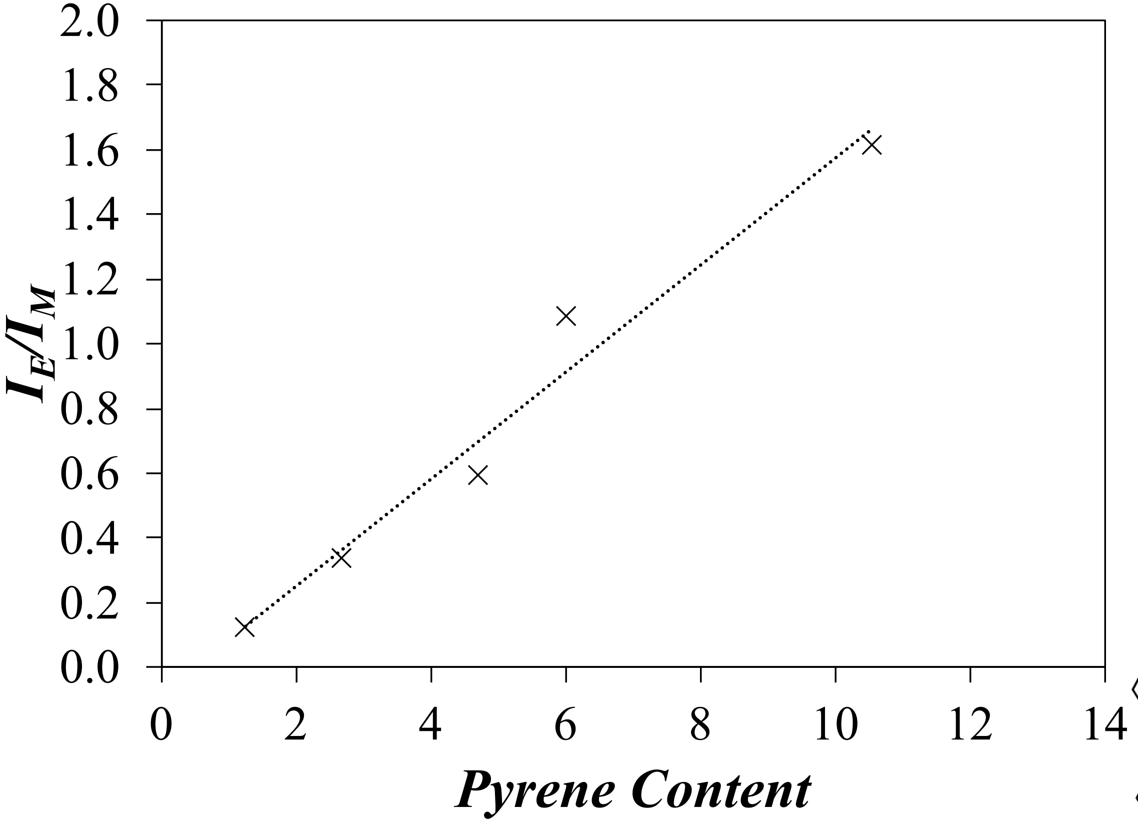
Pyrene labeled poly(EG_5MA)

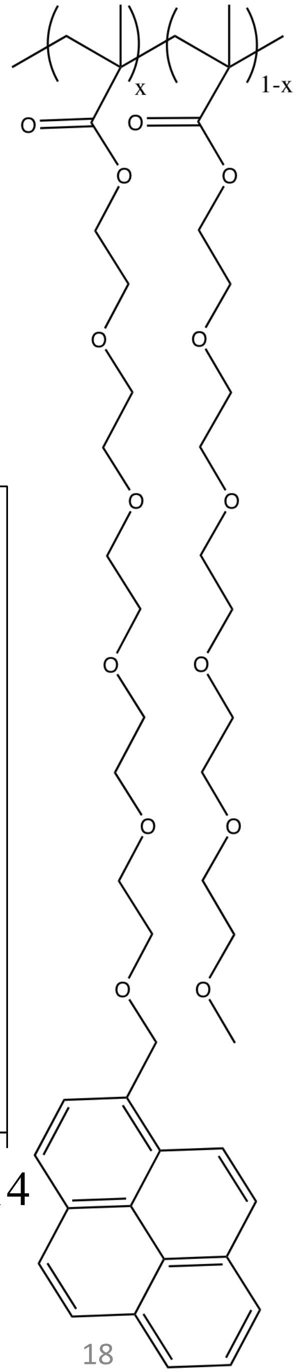
Pyrene Content (*x*)	M_n (g/mol)	M_w (g/mol)	PDI	DP
0.013	92000	140000	1.6	290
0.027	62000	93000	1.5	190
0.047	62500	96500	1.6	200
0.060	37000	55500	1.5	120
0.11	45000	75000	1.7	140



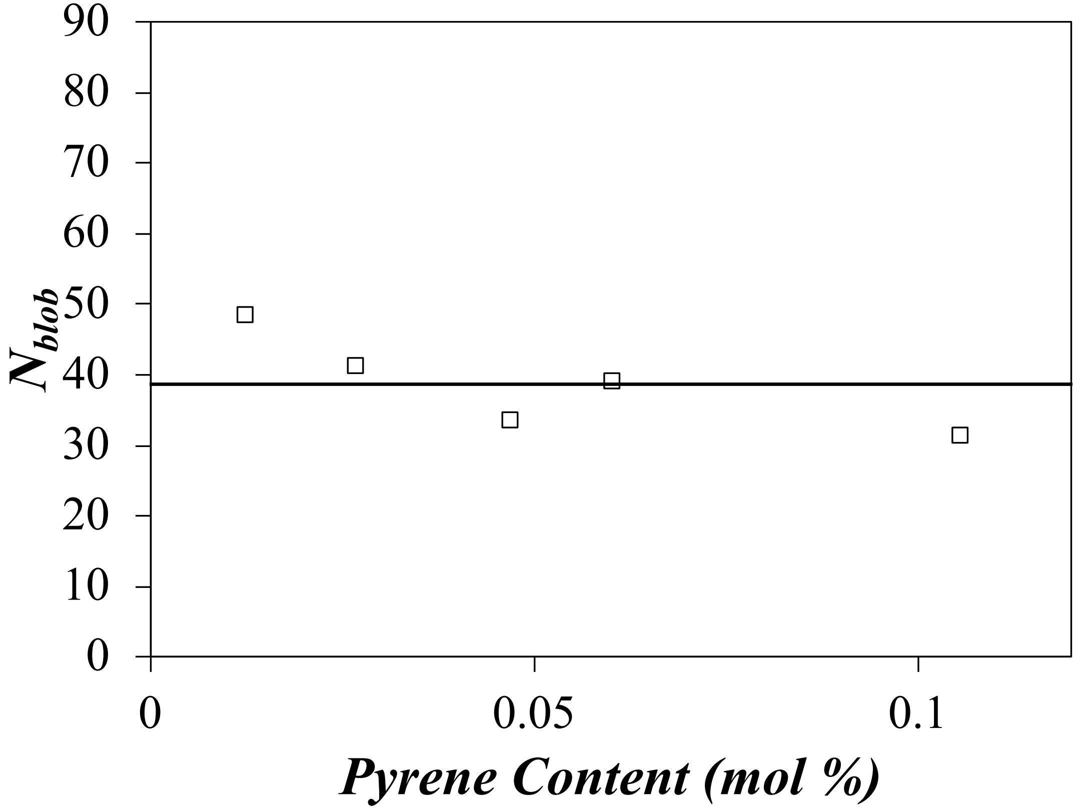
Steady State Fluorescence Results THF

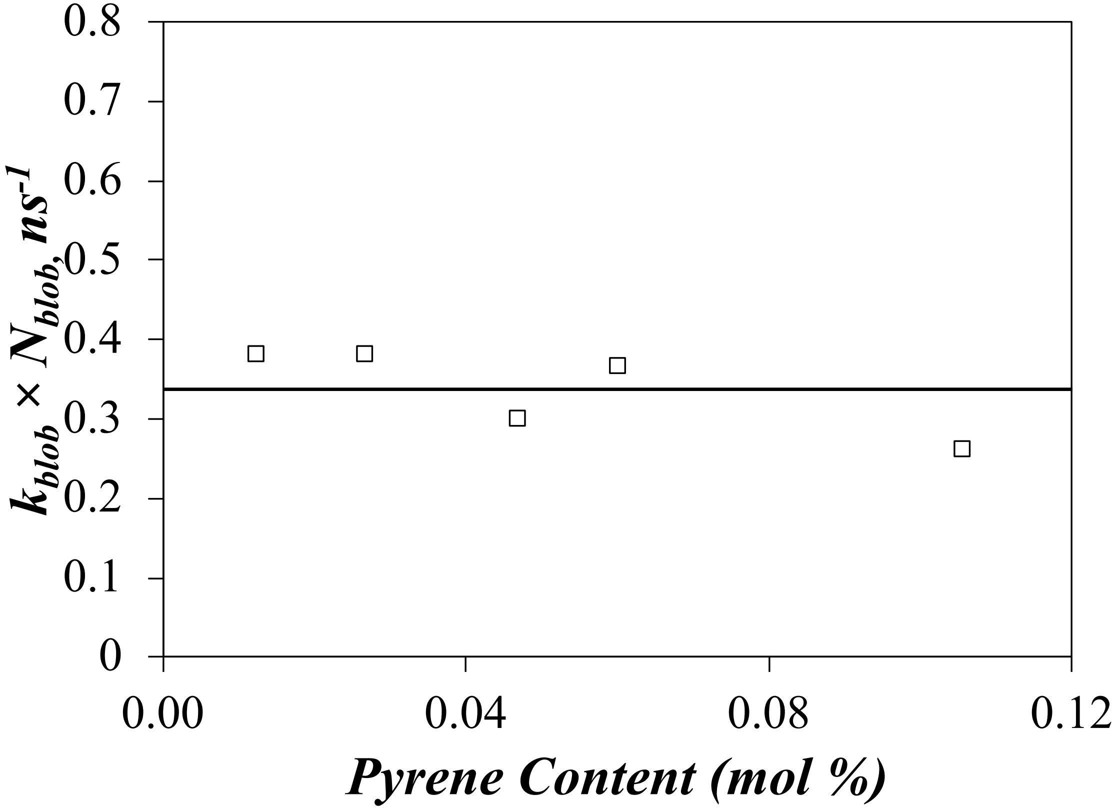






Time Resolved Fluorescence Results in THF





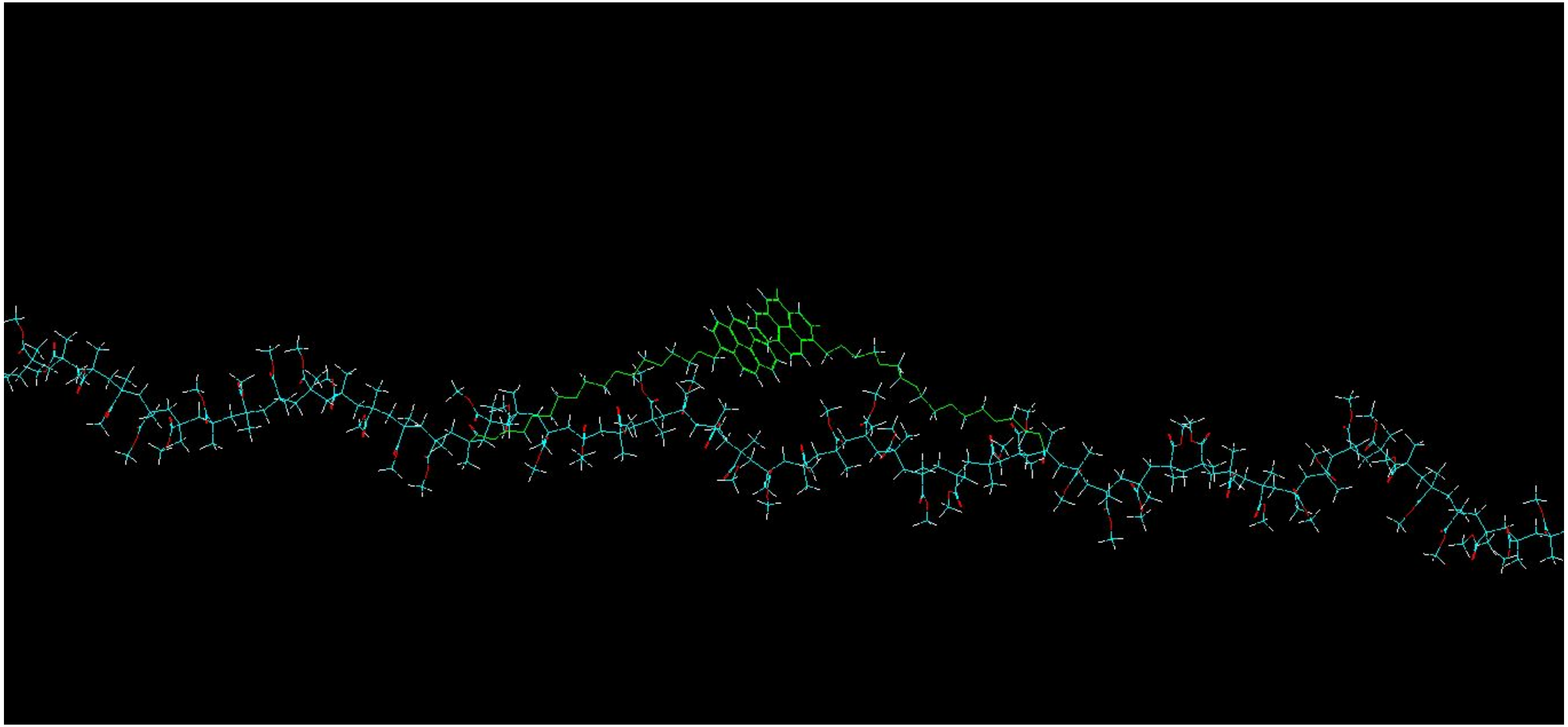
$N_{blob} = 39 \pm 7$

N_{blob}- The number of monomer units within a blob

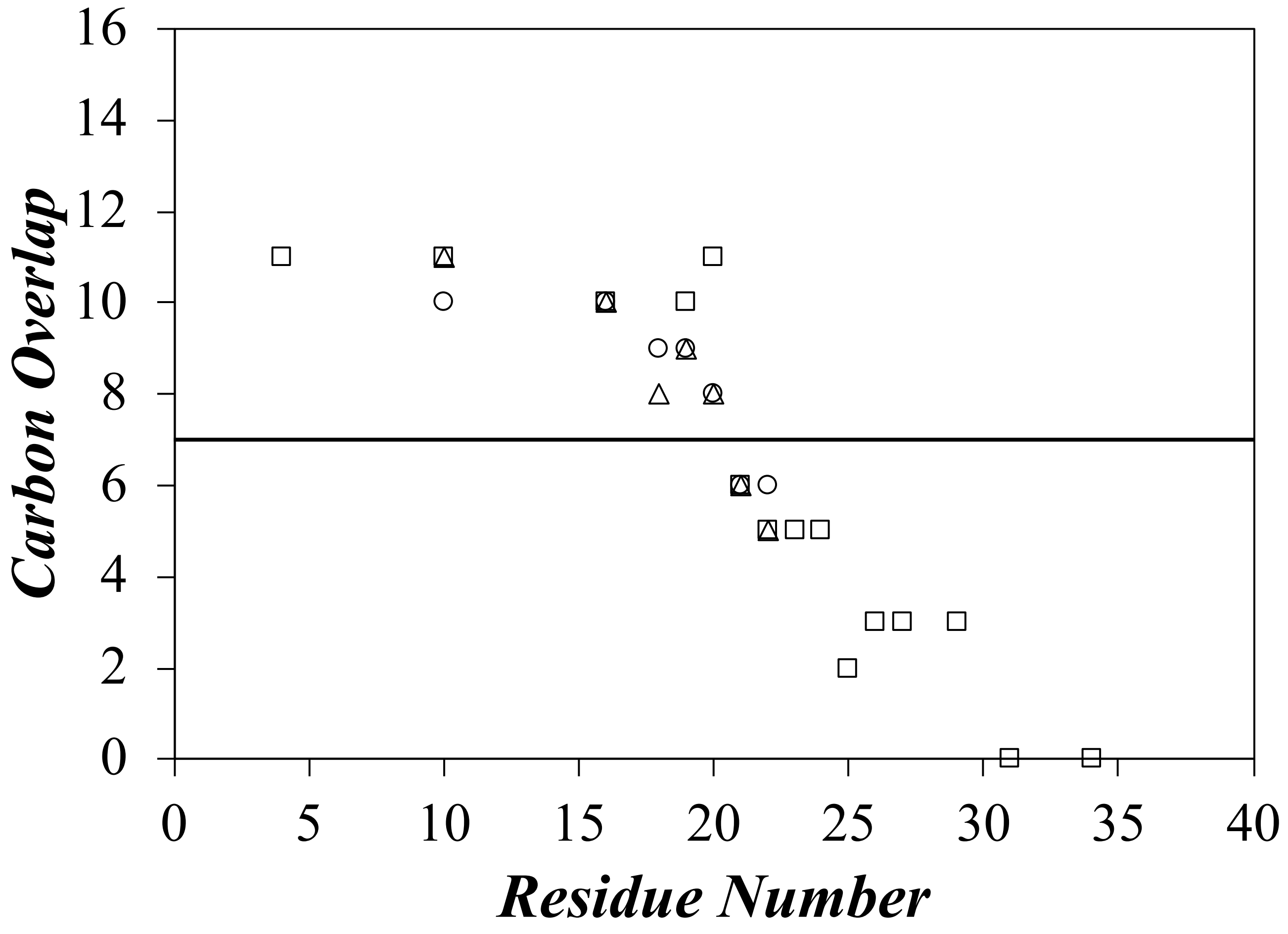
$k_{blob} \times N_{blob} = 0.34 \pm 0.05\ ns^{-1}$

$k_{blob} \times N_{blob}$- provides a quantitative measure of the rate constant of pyrene excimer formation

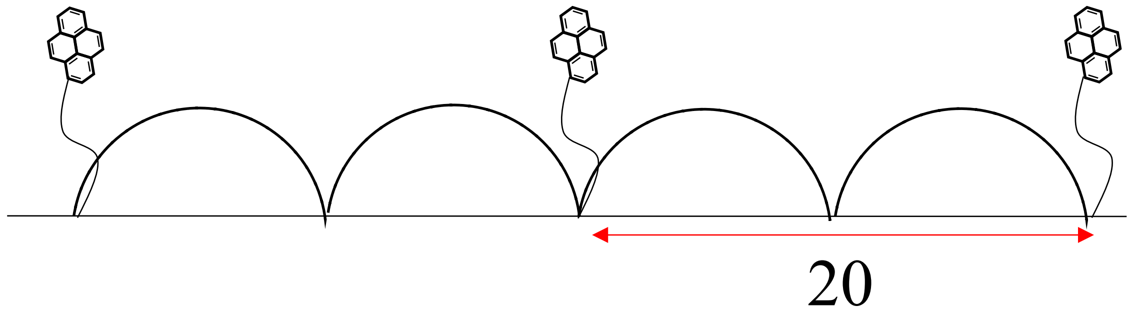
Hyperchem



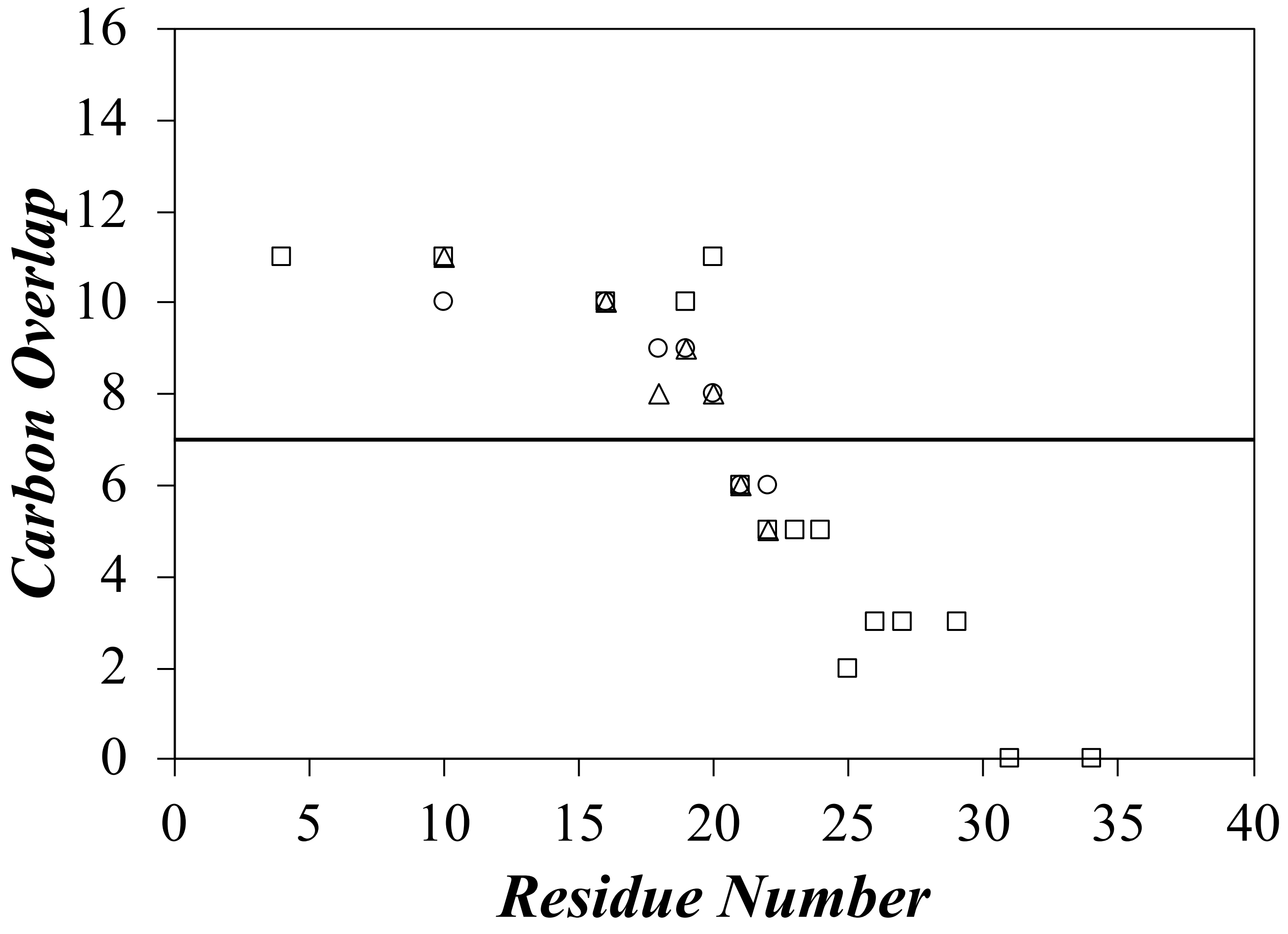
Hyperchem Results



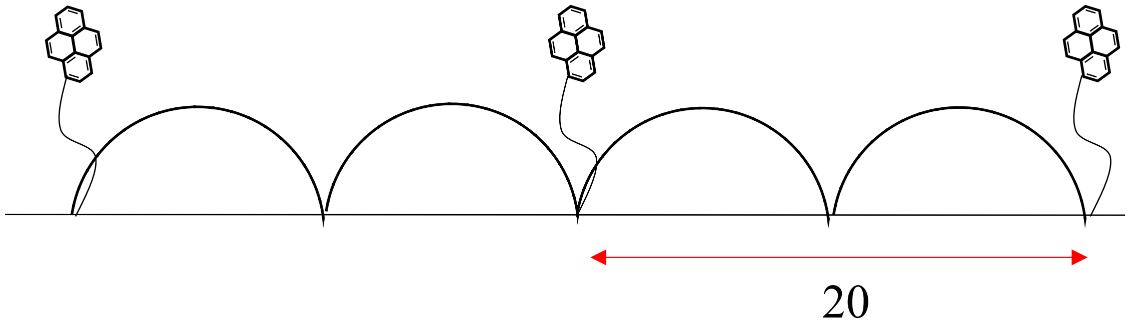
Hyperchem blob- $20 \times 2 + 1 = 41$



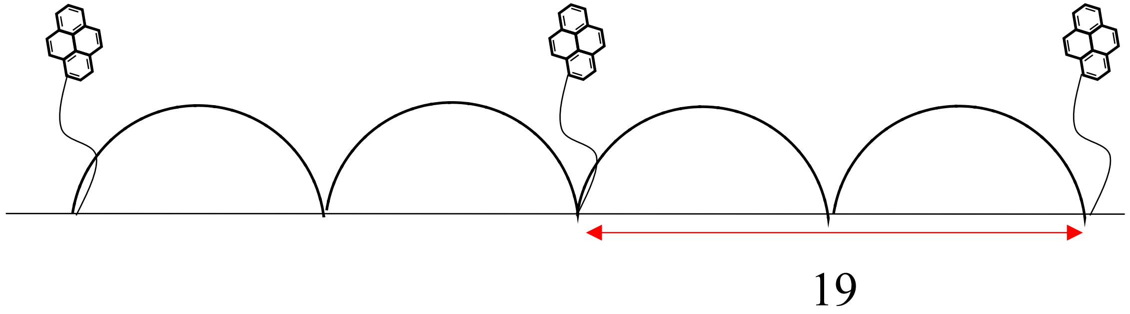
Hyperchem Results



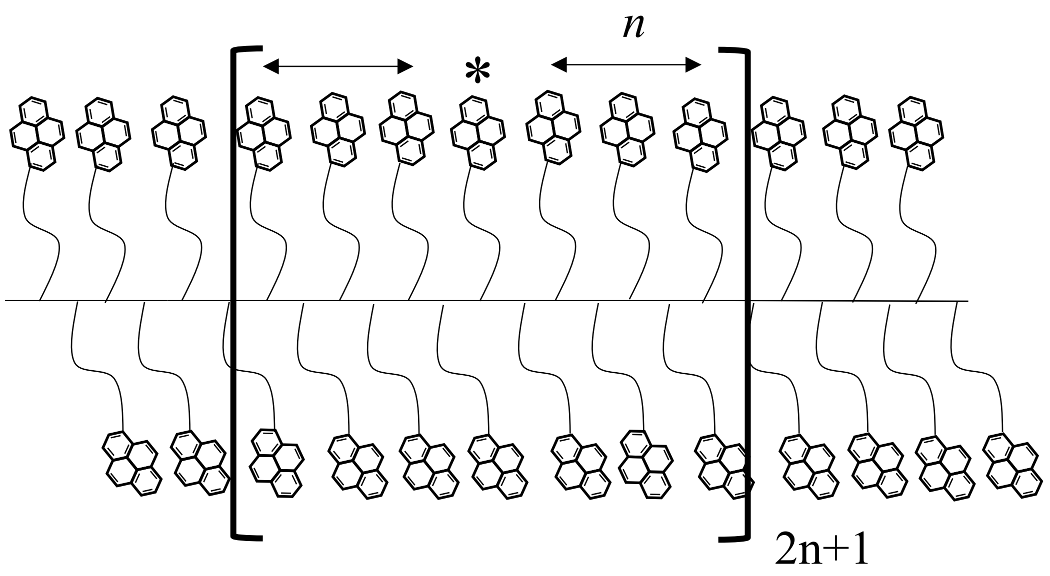
Hyperchem blob- $20 \times 2 + 1 = 41$



FBM = 39 ± 7



What is $\langle L_{Py}^2 \rangle^{1/2}$ for a blob?

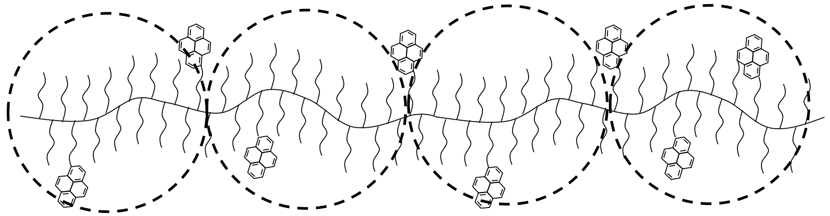


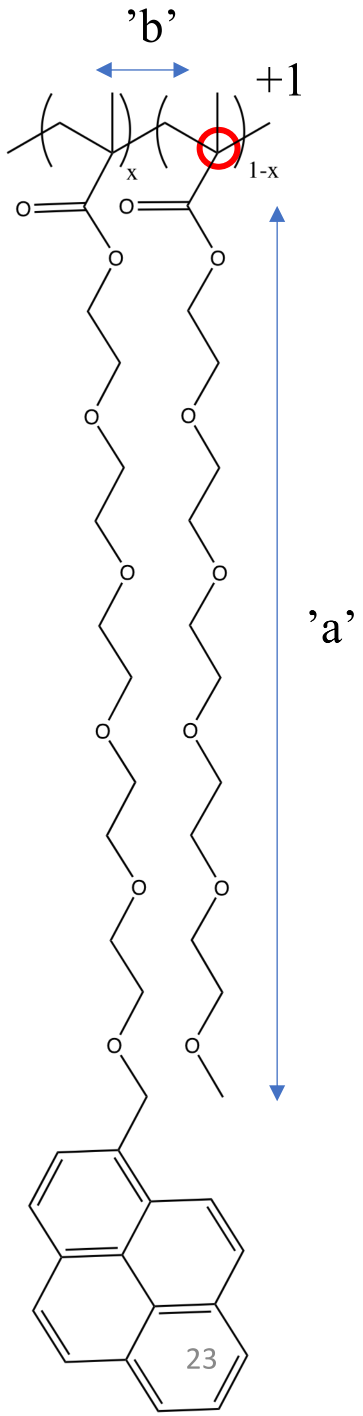
$$\left\langle L_{Py}^{\;2} \right\rangle = l^2 \times (2a + 1 + b(\tfrac{n+1}{2}))$$

Let a = 18 and b=2

From N_{blob} = 39 we know n = 19

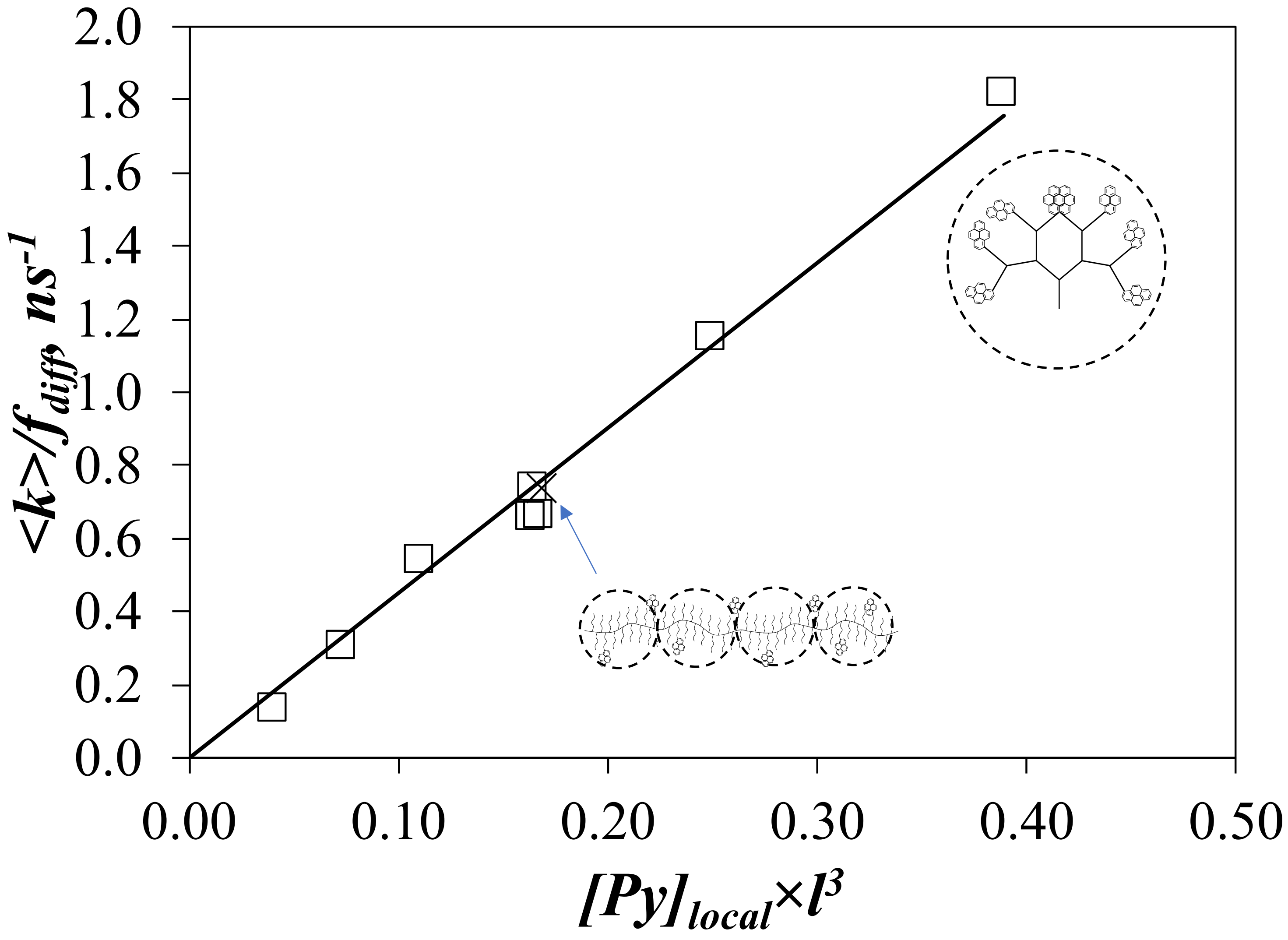
$$\left\langle L_{Py}^{\;2} \right\rangle^{\frac{1}{2}} = 9.4\ \text{Å}$$





Results in THF

$$<k> = k_{diff} \times [Py]_{loc}$$

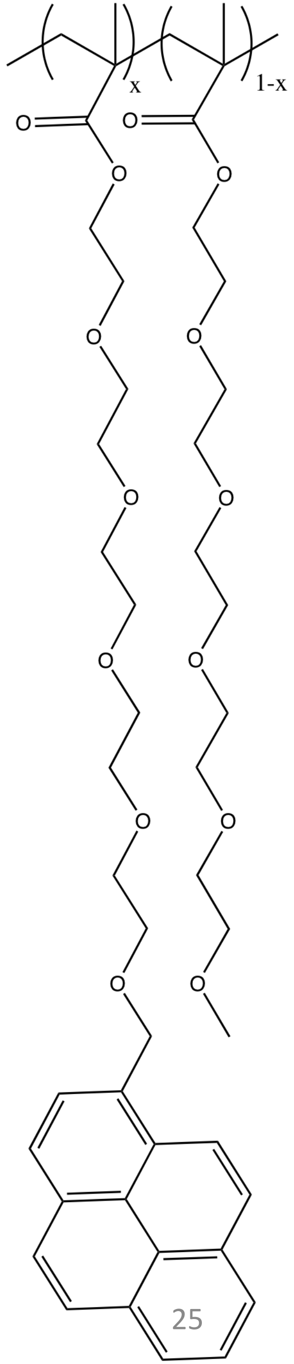


Conclusions

- $\langle L_{Py}^{2} \rangle^{1/2}$ was calculated for a series of dendrimers.
- Addition of a spacer reduces the fraction of aggregated pyrene.
- A calibration curve was constructed which relates the dimensions of a dendrimer with the dynamics of its terminal ends.
- Poly(EG_5MA) has a rigid backbone in solution.

Future Work

- Synthesize a pyrene labeled poly(MMA) using the EG_5 as the pyrene linker.
- Synthesize copolymers with 3, 8, and 12 EG units in the side chain



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- Stuart McNelles and Alex Adronov
- Everyone in the Duhamel lab
- NSERC

NSERC CRSNG

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