

US EPA ARCHIVE DOCUMENT

# Dendritic Nanomaterials for Environmental Remediation

**Mamadou Diallo**

Materials and Process Simulation Center,  
Beckman Institute  
California Institute of Technology

And

Department of Civil Engineering  
Howard University

# Presentation Outline

## Synthesis and Characterization of Dendritic Nanomaterials

### Unique Properties Dendritic Nanomaterials

- (1) Nanoscale container and scaffolding properties
- (2) Amplification and functionalization of surface groups
- (3) Building blocks for mesoscale assemblies with well defined nanosized domains
- (4) Dendritic effect

### Applications to Environmental Remediation (Focus on Water Treatment and Soil Remediation)

- (1) High capacity and recyclable ligands for cations and anions
- (2) Recyclable unimolecular micelles for organic solutes
- (3) Redox and catalytically active dendritic nanoparticles
- (4) Bioactive dendritic nanoparticles

### Outlook on Dendritic Nanomaterials and Environmental Remediation

- (1) Dendritic nanomaterials for water treatment
- (2) Fate, transport and toxicity of dendrimers nanomaterials
- (2) Development of low cost dendritic nanomaterials

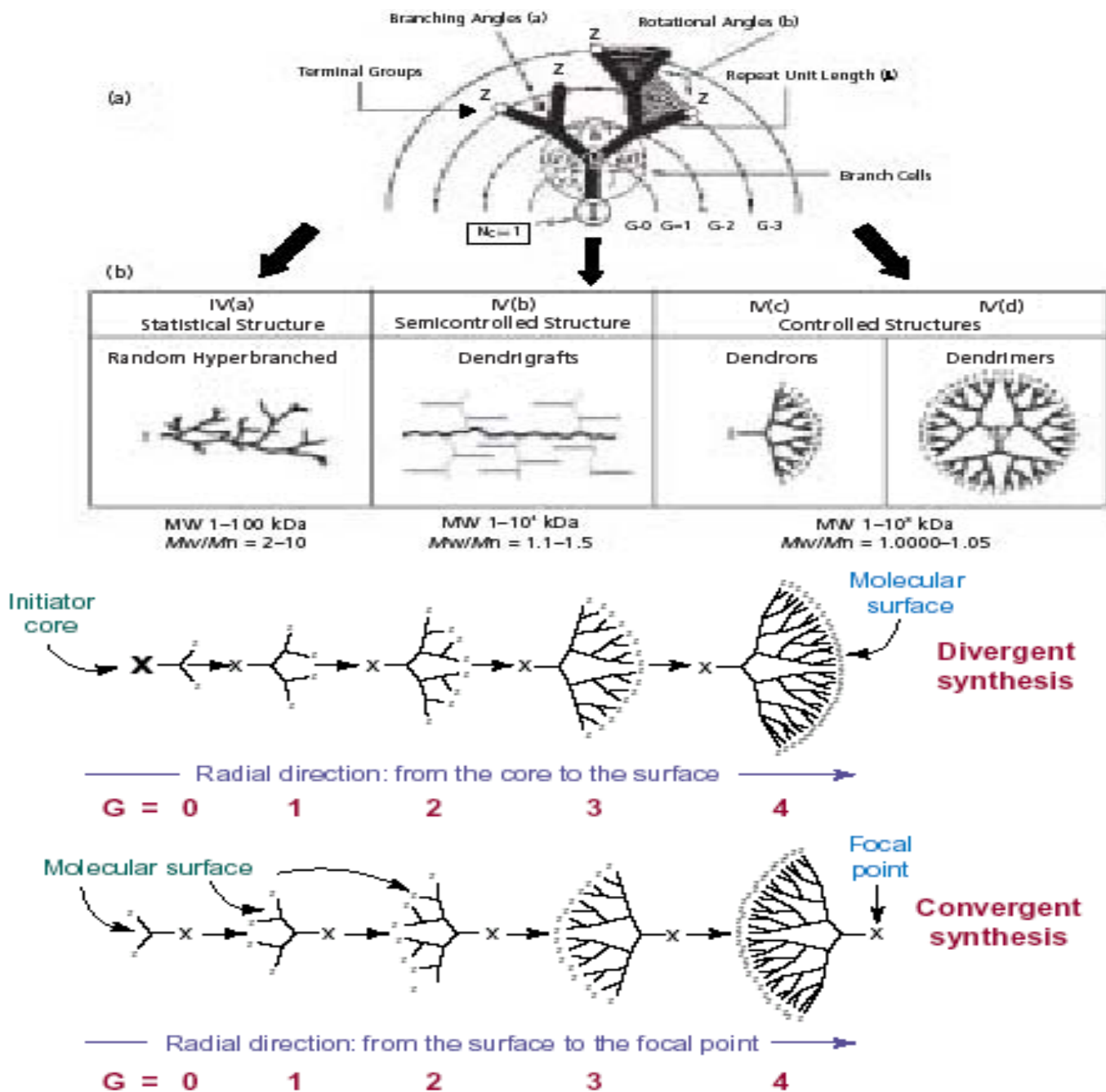
### Acknowledgments

# The Dendritic Macromolecular Architecture

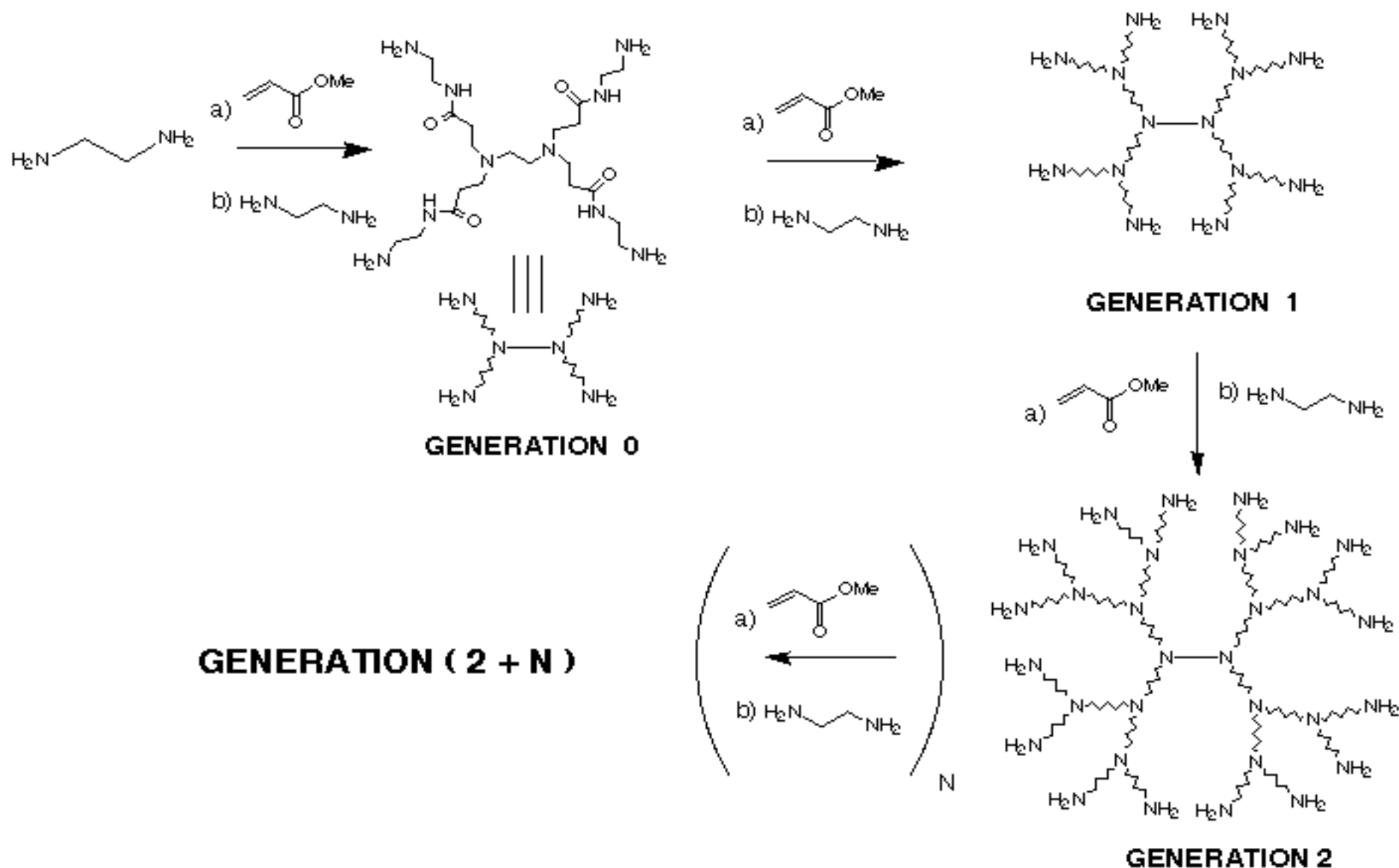
(Tomalia, D. A. Aldrichimica Acta. 2004, Vol 37, No 2, p. 39)

**Dendritic Architecture:** predicated upon the covalent linkage of molecular connectors and branching points to a core with multiple branching sites

**High level of Synthetic Control:** makes possible the synthesis of nearly monodisperse nanoscale ligands with well defined molecular composition, size and shape

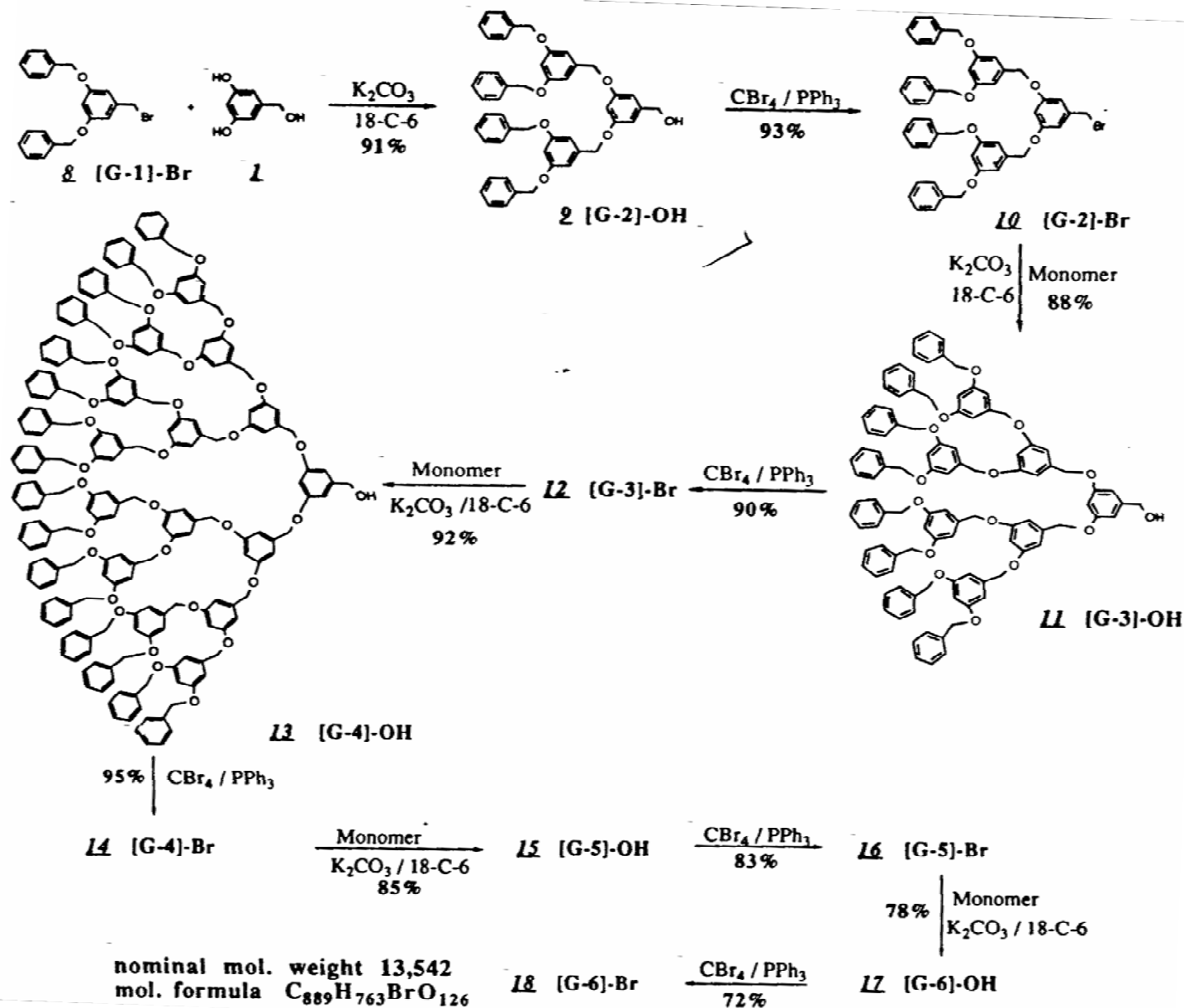


# Divergent Synthesis of Poly(amidoamine) Dendrimers with Ethylene Diamine Core (EDA) and $\text{NH}_2$ Terminal Groups



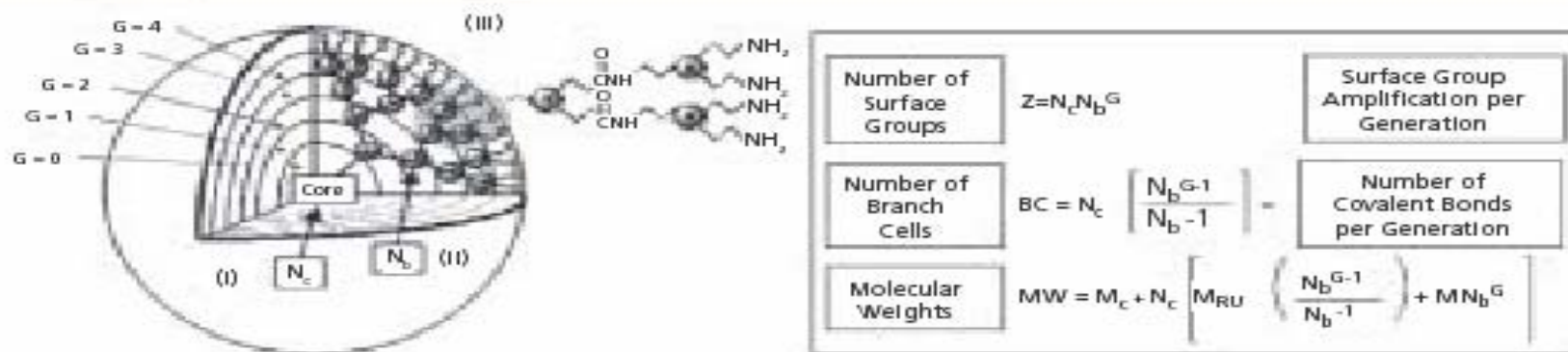
# Convergent Synthesis of Poly(Benzyl Ether) Dendrimers

(Hawker, C. and Frechet, J. M. J., JACS, 112, 7639, 1990)



# Chemical Characterization of Dendritic Macromolecules

(Tomalia, D. A. Aldrichimica Acta. 2004, Vol 37, No 2, p. 39)



Gen	No. of NH <sub>2</sub> Surface Groups	Molecular Formula	MW	Hydrodynamic Diameter (nm)
0	4	C <sub>24</sub> H <sub>52</sub> N <sub>10</sub> O <sub>4</sub> S <sub>2</sub>	609	1.5
1	8	C <sub>64</sub> H <sub>132</sub> N <sub>26</sub> O <sub>12</sub> S <sub>2</sub>	1,522	2.2
2	16	C <sub>144</sub> H <sub>292</sub> N <sub>58</sub> O <sub>28</sub> S <sub>2</sub>	3,348	2.9
3	32	C <sub>304</sub> H <sub>612</sub> N <sub>122</sub> O <sub>60</sub> S <sub>2</sub>	7,001	3.6
4	64	C <sub>624</sub> H <sub>1252</sub> N <sub>250</sub> O <sub>124</sub> S <sub>2</sub>	14,307	4.5
5	128	C <sub>1264</sub> H <sub>2532</sub> N <sub>506</sub> O <sub>252</sub> S <sub>2</sub>	28,918	5.4
6	256	C <sub>2544</sub> H <sub>5092</sub> N <sub>1018</sub> O <sub>508</sub> S <sub>2</sub>	58,140	6.7
7	512	C <sub>5104</sub> H <sub>10212</sub> N <sub>2042</sub> O <sub>1020</sub> S <sub>2</sub>	116,585	8.1

Z = monomer-shell-saturation level, N<sub>c</sub> = core (cystamine) multiplicity, N<sub>b</sub> = branch cell (BC) multiplicity, G = generation.

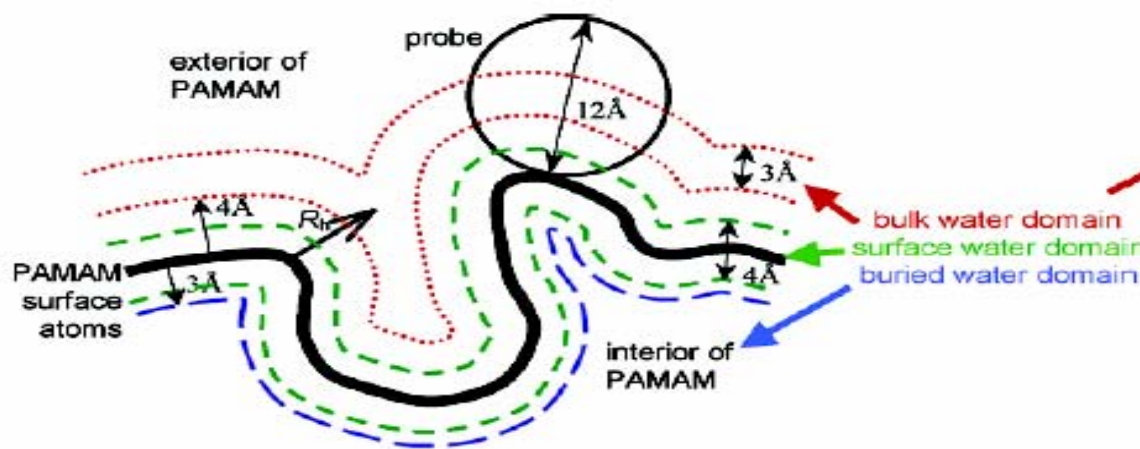
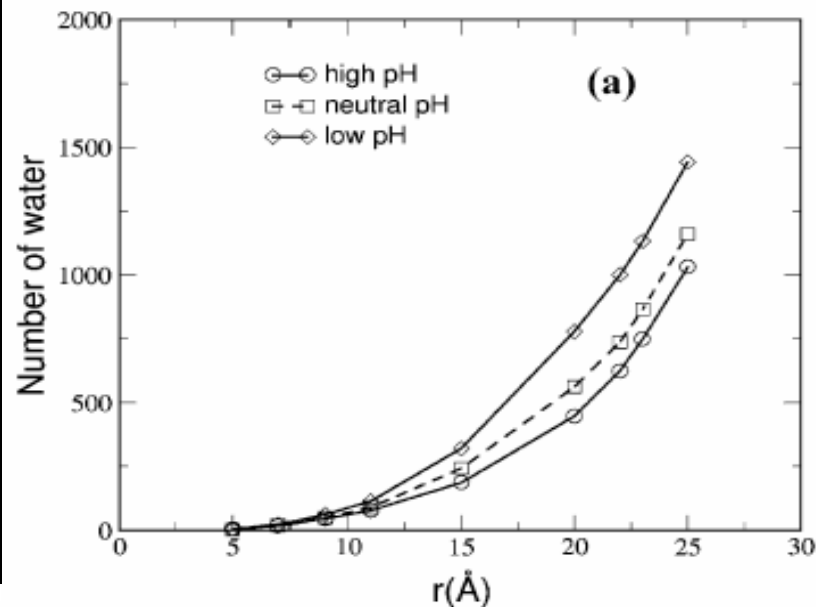
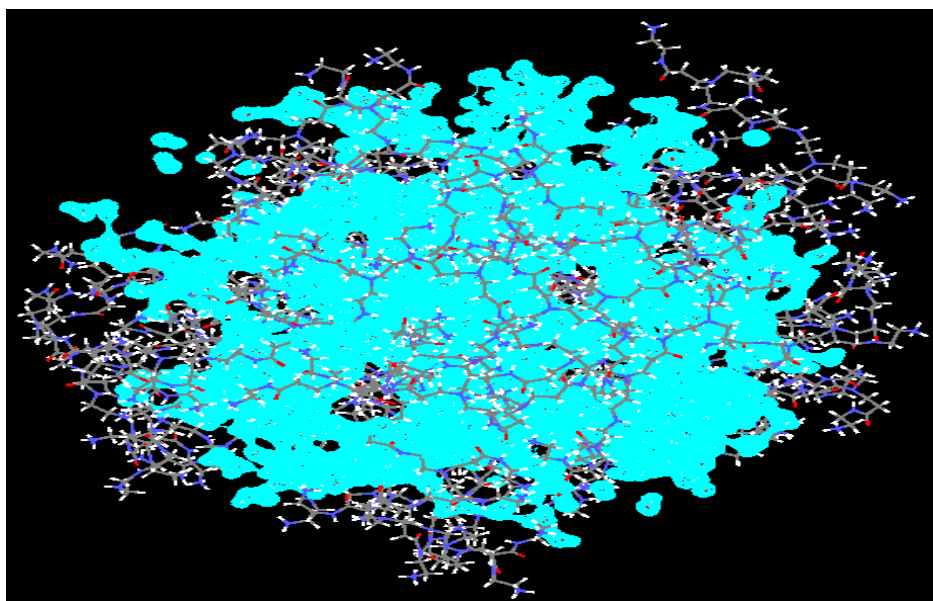
- <sup>1</sup>H and <sup>13</sup>C NMR Spectroscopy
- HPLC
- Size Exclusion Chromatography (SEC)
- Capillary Electrophoresis (CE)
- Polyacrylamide Gel Electrophoresis (PAGE)
- MALDI and ESI Mass Spectrometry



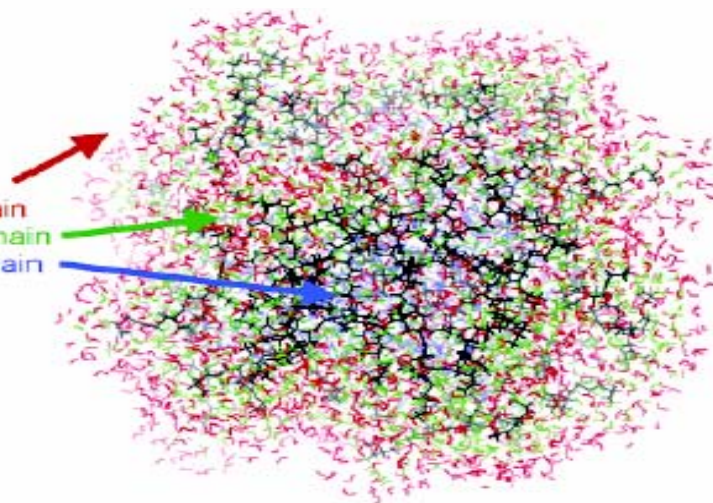
# Characterization of the 3-D Structures of G5-NH<sub>2</sub> PAMAM Dendrimer by Molecular Dynamics Simulations in Water

(Maiti et al. *Macromolecules*, 2005, 38, 979-991)

(Lin et al. *J. Phys. B.*, 2005, 109, 8663-8672 )



Schematic

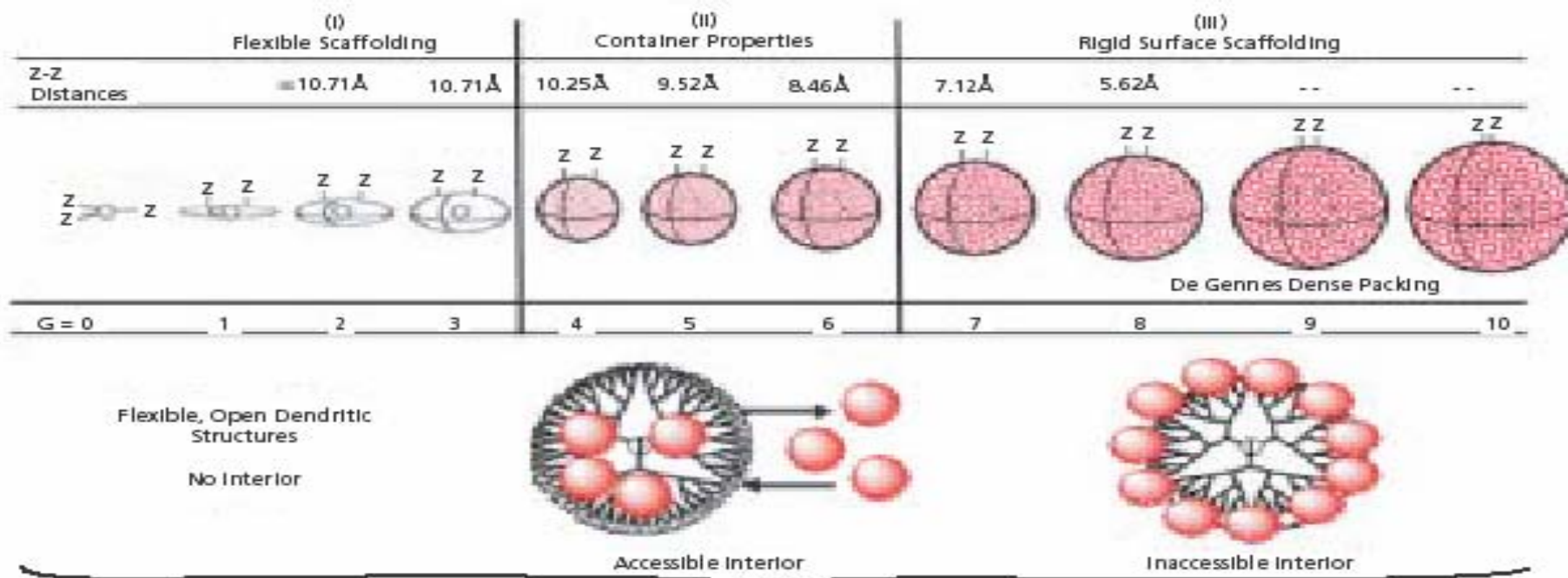


Atomistic



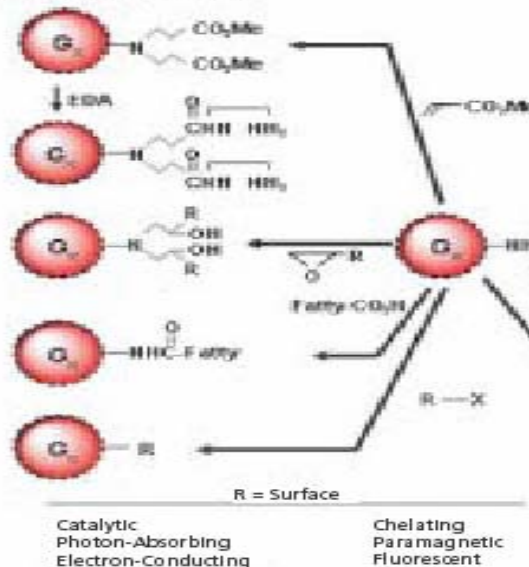
# Unique Properties of Dendritic Macromolecules

(Tomalia, D. A. Aldrichimica Acta. 2004, Vol 37, No 2, p. 39)

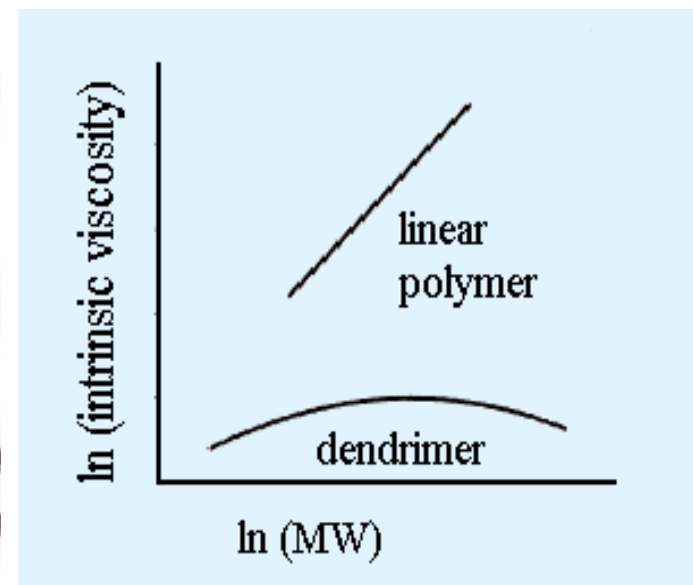
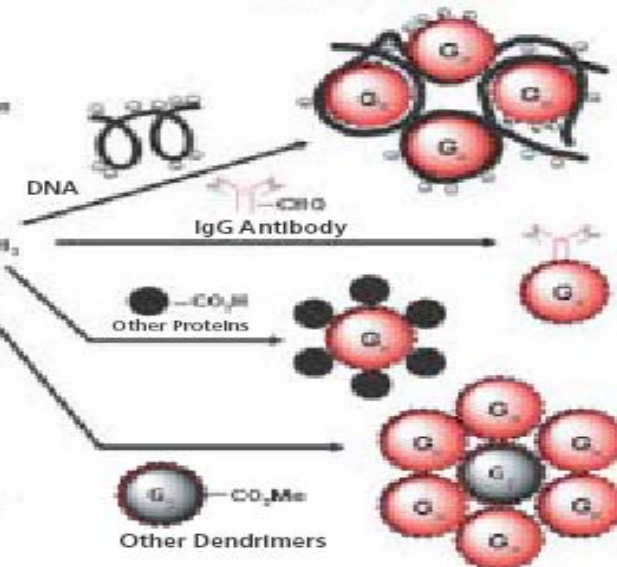


## Classical (Subnanoscale) Chemistry

- Electrophilic
- Nucleophilic
- Hydrophilic
- Hydrophobic

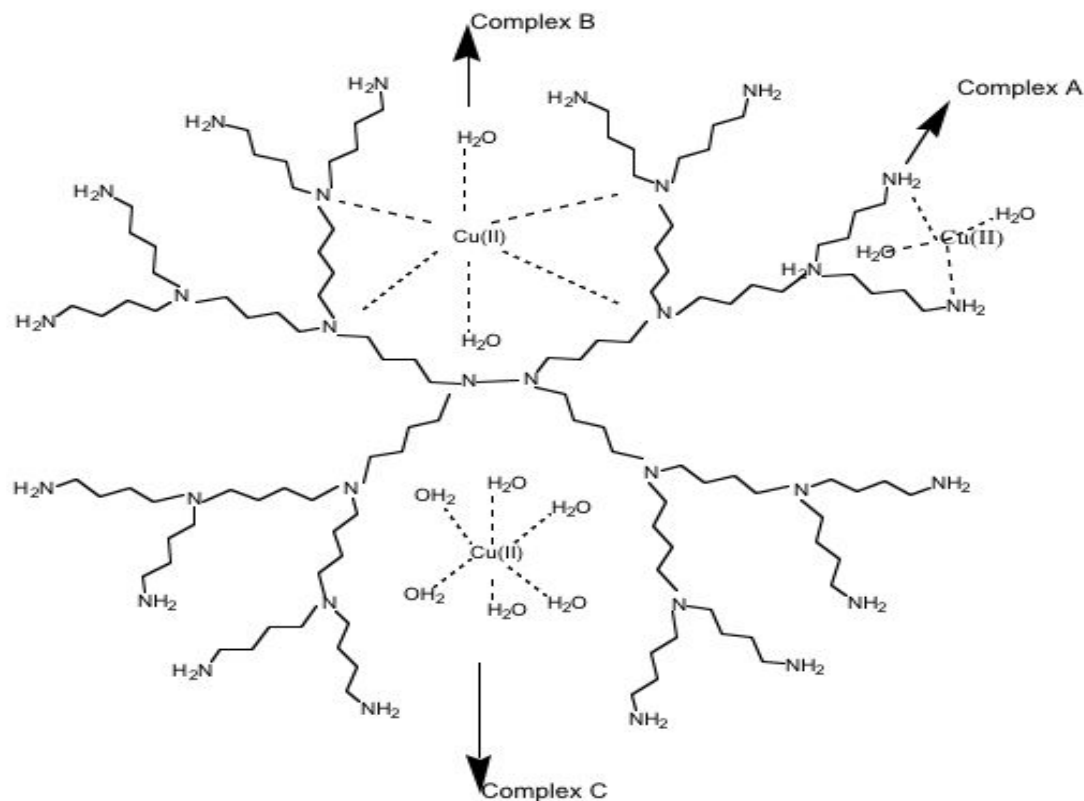
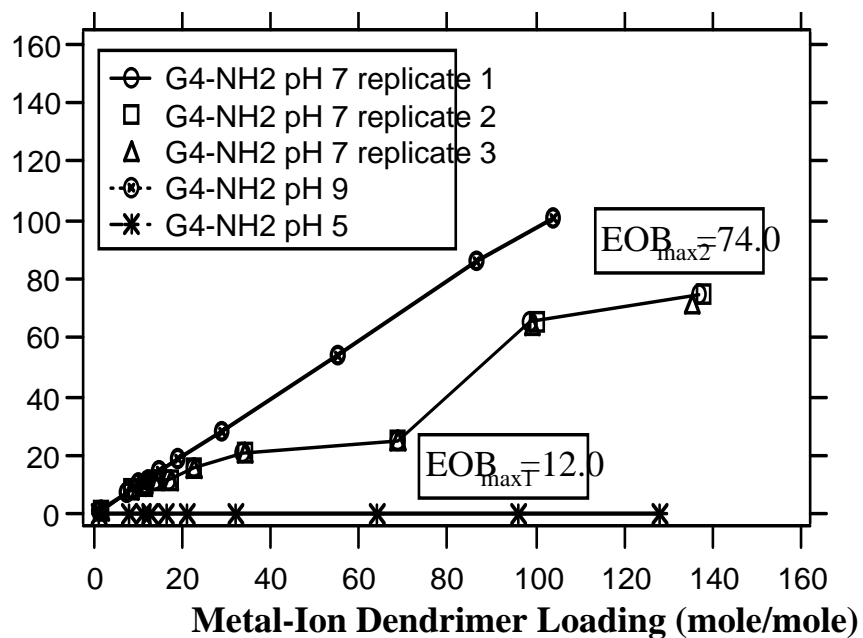
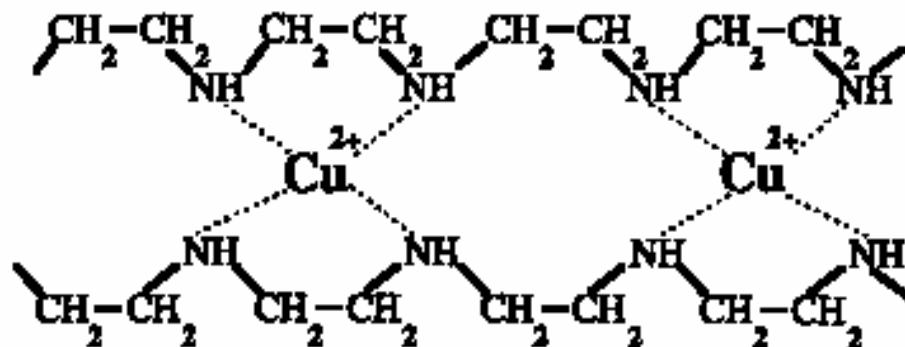
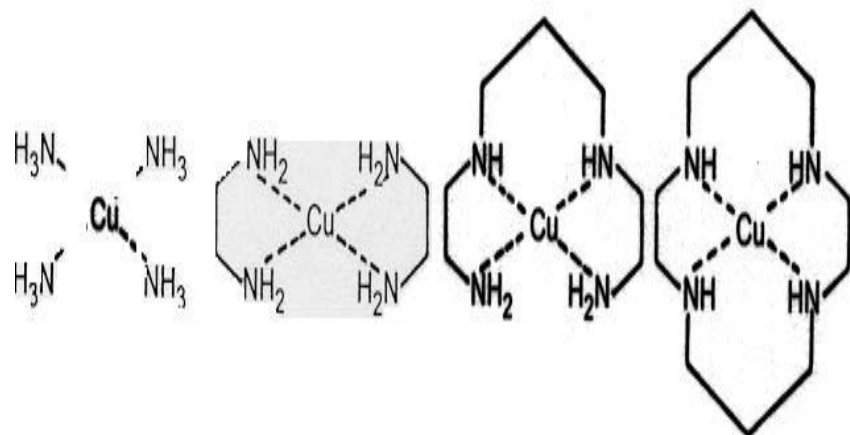


## Nanoscale Chemistry



# Dendritic Nanomaterials as High Capacity and Recyclable Ligands for Cations

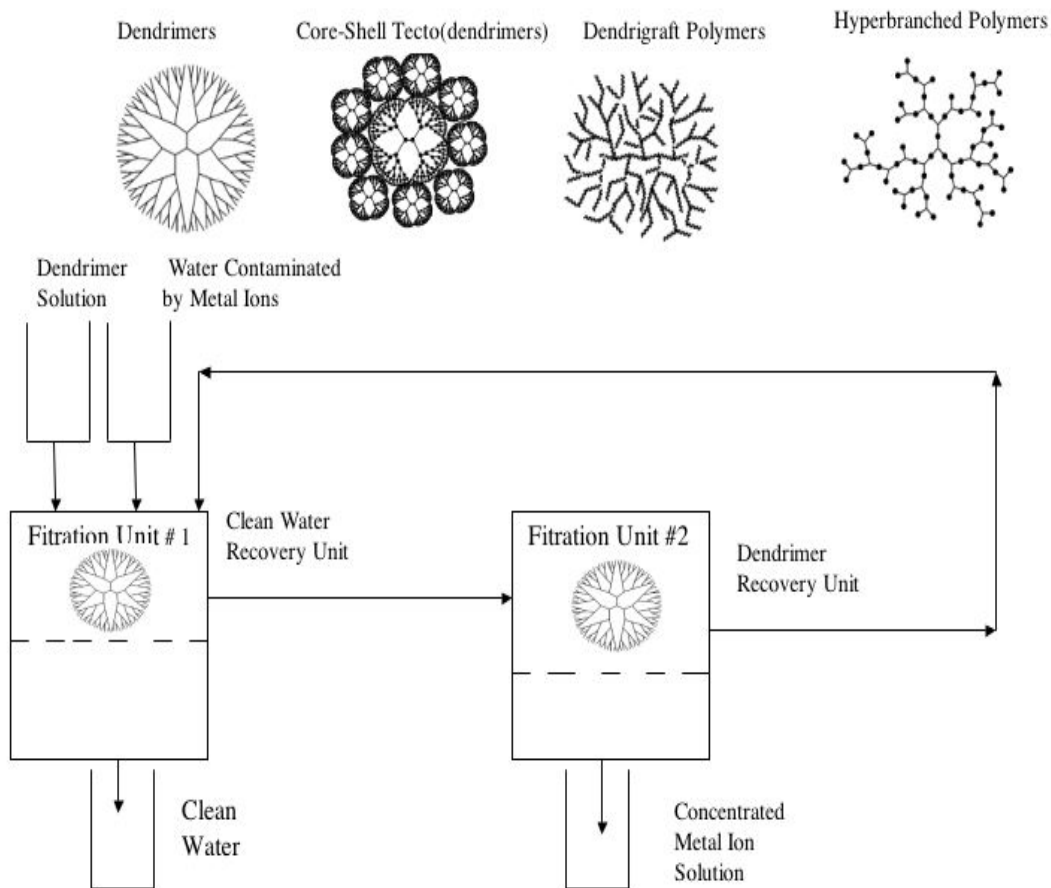
(Diallo et al. Langmuir. 2004, 20 (7): 2640-2651)



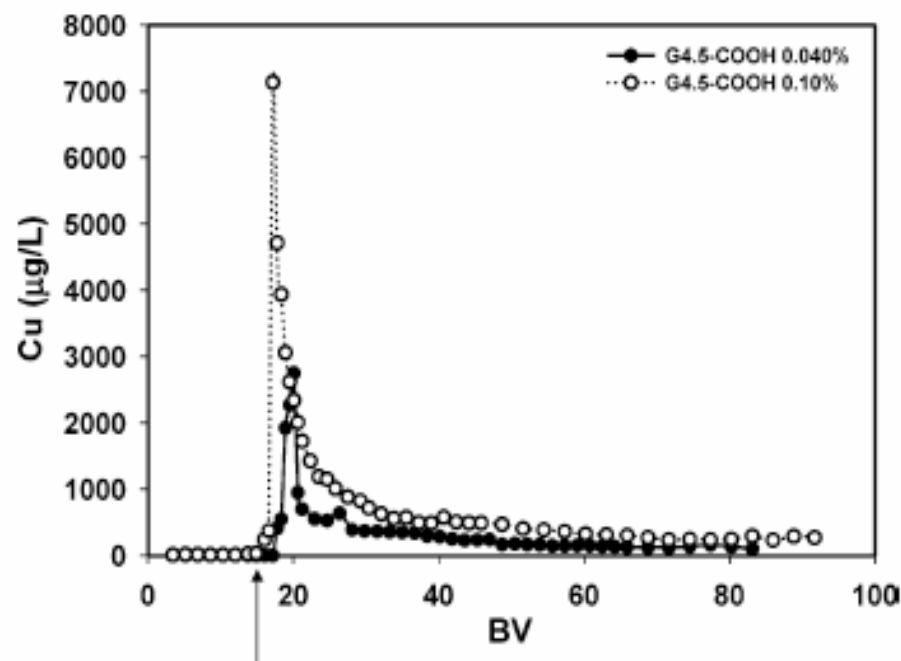
# Environmental Applications of Dendritic Nanoscale Chelating Agents

## Recovery of Metal Ions [e.g. Cu(II)] from Aqueous Solutions by Dendrimer Enhanced Ultrafiltration

Diallo et al. 2005, Environ. Sci. Technol. 39, 1366-1377 and Diallo, M. S. US Patent Pending)



## Removal of Cu(II) from Contaminated Soil Using PAMAM Dendrimers (Xu, Y. and Zhao, D. 2005, Environ. Sci. Technol. 39 2369-2375)

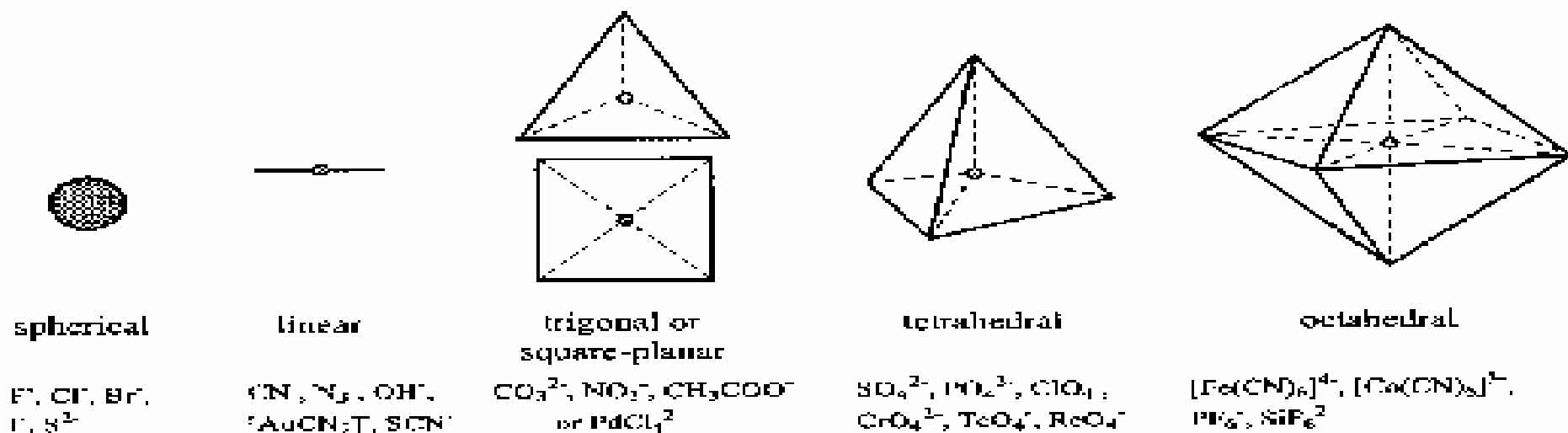


Dendrimer introduced here

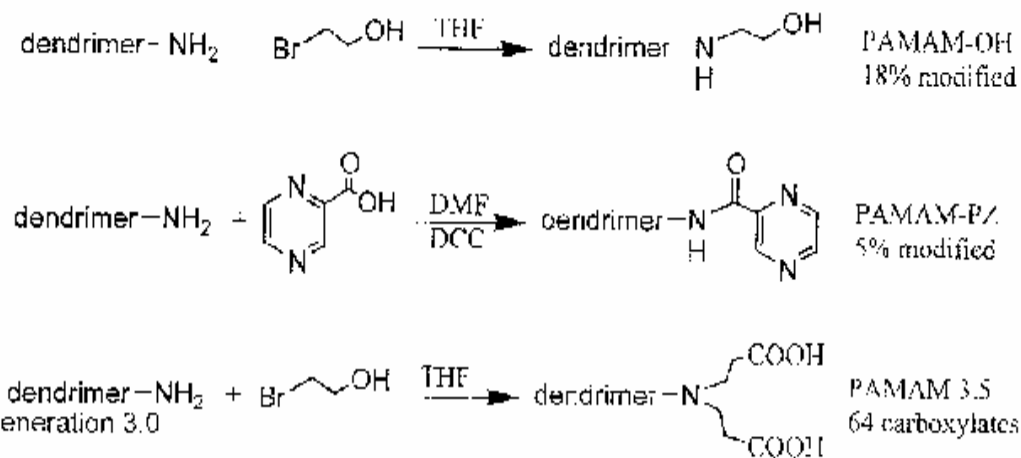
FIGURE 1. Copper elution histories during two separate column runs with 0.040% and 0.10% G4.5-COOH at pH 6.0.

# Dendritic Nanomaterials as High Capacity and Recyclable Ligands for Anions in Aqueous Solutions

Anions have a variety of shapes (Gloe et al. *Chem. Eng. Technol.* 2003, 26,1107-1117)



Birnbaum et al. *Sep. Sci. Technol.* 2003, 38, 389-404).



**Table 1.** Molar capacity of modified dendrimer complexes and polymers for oxyanions in single anion experiments.

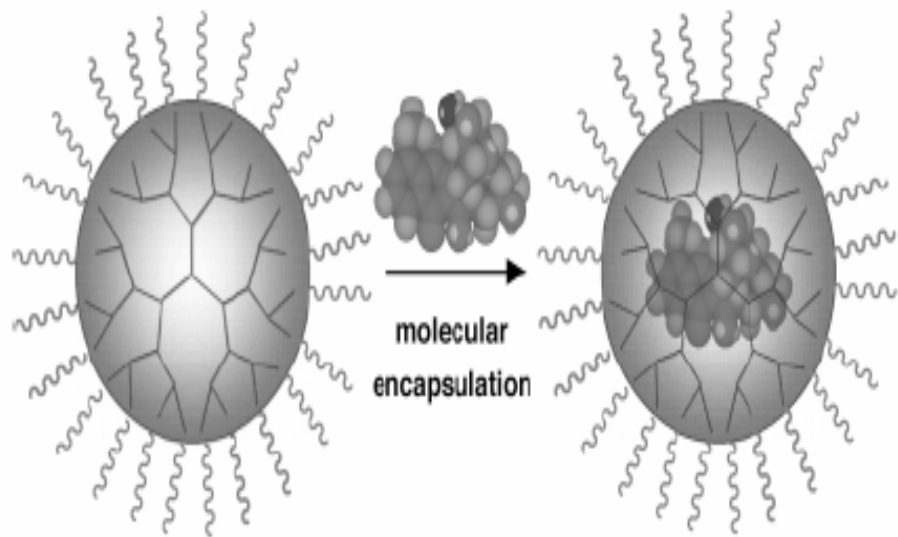
Single anion capacities polymer	Molar capacity (mmol ion/g dendrimer)		
	CrO <sub>4</sub>	AsO <sub>4</sub>	PO <sub>4</sub>
PAMAM 4.0	1.99	1.74	1.62
PAMAM-OH	2.39	1.28	2.07
PAMAM-PZ	1.17	1.08	0.40
PEI	4.13	4.91	6.25
PEI-OH	2.53	3.04	3.93
PEI-PZ	1.79	1.70	2.03

**Figure 1.** Synthetic scheme for the three modified dendrimers used for anion binding experiments. The polymers were prepared in an analogous fashion.

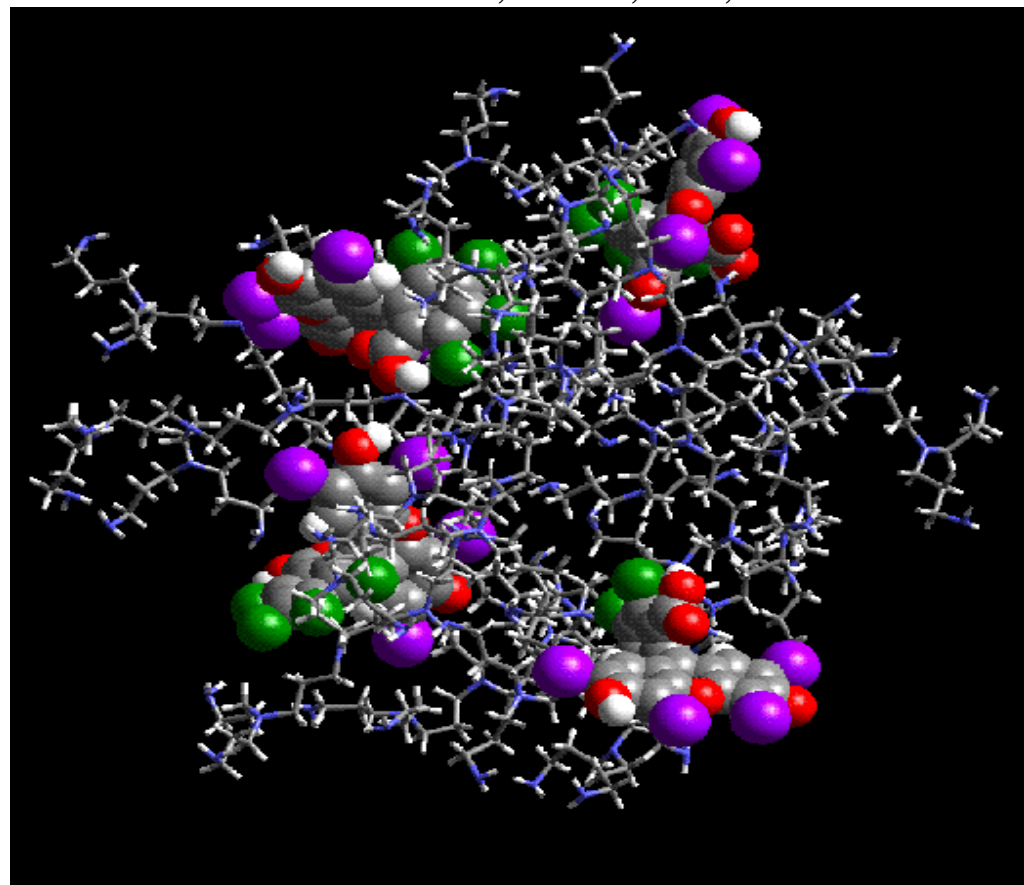


# Dendritic Macromolecules as Unimolecular Micelles for Organic Solutes

(Striba et al. 2002, Angew. Chem. Int. Ed., 41 (8), pp 1329-1324)

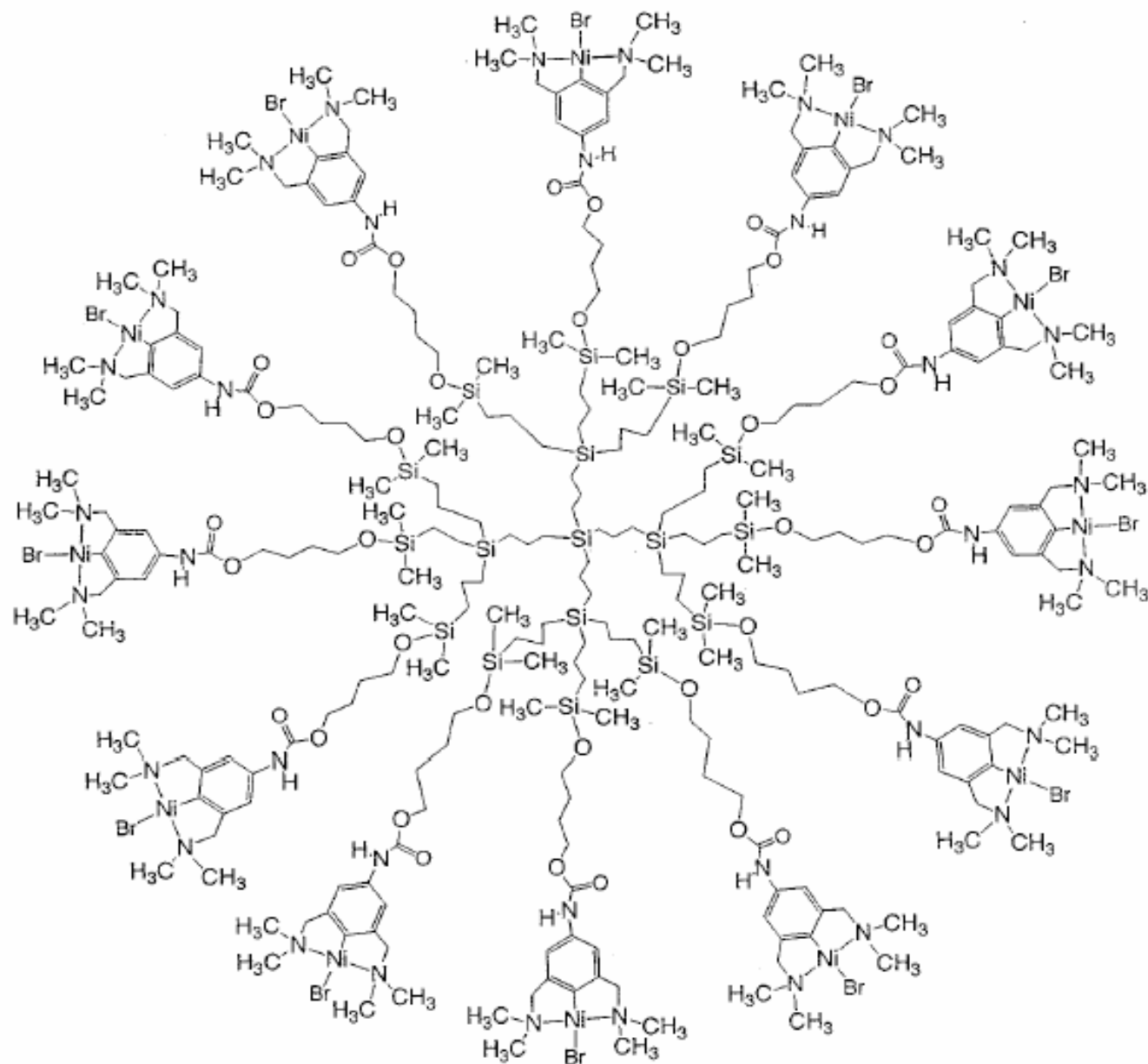


MD Simulations of the Meijer Dendrimer Box  
Miklis et al. 1997, JACS, 131, 7458



# Catalytic Dendritic Macromolecules

(Astruc D. and Chardac, F. Chem. Rev. 2001, 101, 2991-3023)



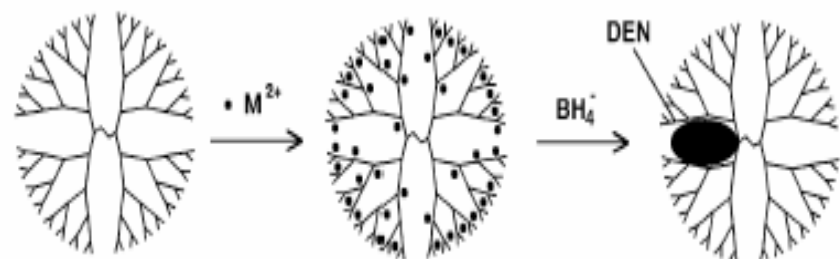
**Figure 1.** van Koten's metallodendrimer that catalyzes the Kharasch additions of polyhalogenoalkanes to C=C bonds



# Dendrimer-Encapsulated Zero Valent Metal Clusters

(Scott et al. *J. Phys. Chem. B.* 2005, 109, 692-704)

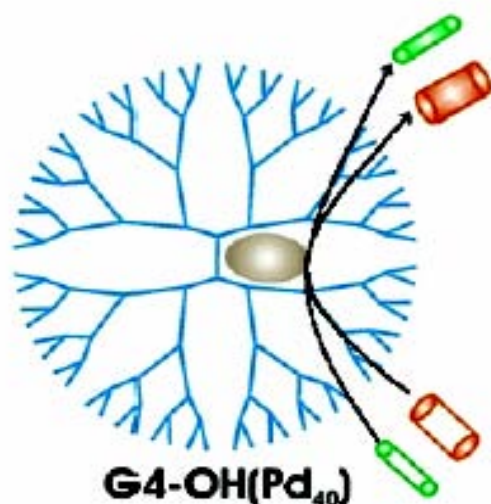
## SCHEME 1



G4-OH Dendrimer


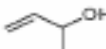


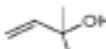
Reprinted with permission from *Chem. Mater.* 2003, 15, 3873–3878.  
Copyright 2003 American Chemical Society.

## SCHEME 2



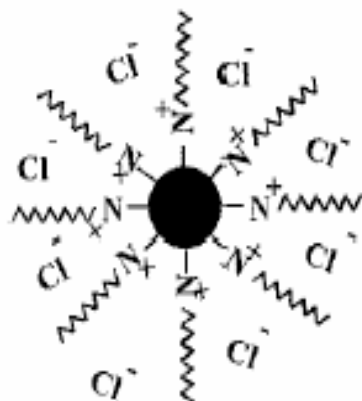
G4-OH(Pd<sub>40</sub>)

**TABLE 2: Hydrogenation Reaction Rates Using G<sub>x</sub>-OH(Pd<sub>40</sub>) Catalysts for Structurally Related Allylic Alcohols<sup>a</sup>**

Substrates	TOF [mol H <sub>2</sub> (mol Pd) <sup>-1</sup> h <sup>-1</sup> ]		
	G4-OH (Pd <sub>40</sub> )	G6-OH (Pd <sub>40</sub> )	G8-OH (Pd <sub>40</sub> )
	480/470 <sup>1</sup>	450/460 <sup>1</sup>	120
	450/460 <sup>1</sup>	380	93
	260	280	68
	150	75	62
	100	40	50

<sup>a</sup> Hydrogenation reactions were carried out at  $25 \pm 2$  °C using  $2 \times 10^{-4}$  M G<sub>x</sub>-OH(Pd<sub>40</sub>) catalysts in MeOH–H<sub>2</sub>O (4:1 v/v) mixtures. The turnover frequency (TOF) was calculated based on H<sub>2</sub> uptake. <sup>1</sup>Duplicate measurements were performed to illustrate the level of run-to-run reproducibility. Reprinted with permission from *J. Am. Chem. Soc.* 2001, 123, 6840–6846. Copyright 2001 American Chemical Society.

# Bioactive Dendritic Macromolecules

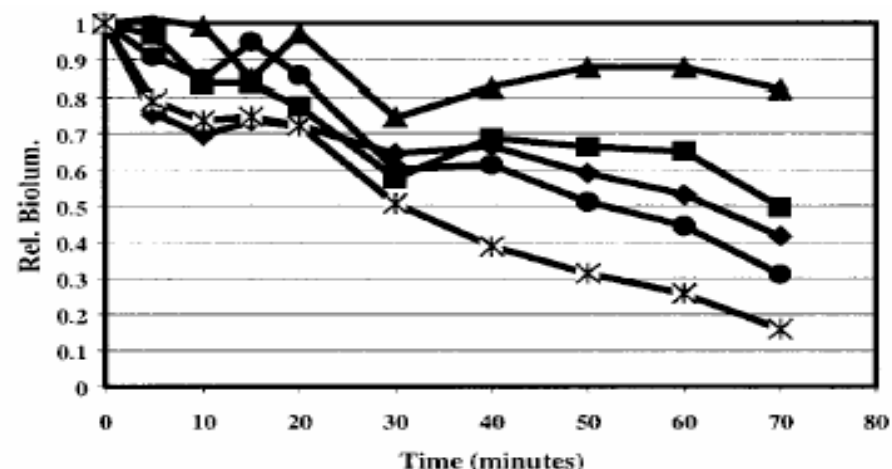


**Figure 2.** Scheme of generation 2 poly(propyleneimine) dendrimer quaternary ammonium biocides with 8 QAC groups on the surface.

**Table 1.** Dendritic Biocides Synthesized in This Study<sup>a</sup>

	dendrimer/ HBP	gen	hydrophobic chain length	ctr	no. of QAC groups	theor MW
D1CINC12	dendrimer	1	12	Cl	4	1593
D2CINC12	dendrimer	2	12	Cl	8	3324
D3CINC12	dendrimer	3	12	Cl	16	6789
D4CINC12	dendrimer	4	12	Cl	32	13719
D5CINC12	dendrimer	5	12	Cl	64	27578
D2CINC16	dendrimer	2	16	Cl	8	3772
D3CINC16	dendrimer	3	16	Cl	16	7685
D4CINC16	dendrimer	4	16	Cl	32	15511
D3CINC8	dendrimer	3	8	Cl	16	5893
D3CNC10	dendrimer	3	10	Cl	16	6341
D3CINC14	dendrimer	3	14	Cl	16	7237
D3BrNC14	dendrimer	3	14	Br	16	7949
H3CINC12	HBP	3	12	Cl	32	13573

<sup>a</sup> Note: HBP refers to hyperbranched polymers. gen = generation. ctr = counteranion. theor = theoretical.



**Figure 4.** Effect of generation on biocidal activities on dendrimers with C<sub>12</sub> hydrophobes: triangle, D3CINC12; rectangle, D2CINC12; diamond, D1CINC12; filled circle, D4CINC12; star D5CINC12. The concentration was 4 μg/mL of dendrimer.

**Table 2.** Comparison among Small Molecule Biocides, Polymer Biocides, and Dendrimer Biocides Regarding Their Interactions with Bacteria

	small molecule biocides	polymer biocides	dendrimer biocides
initial adsorption	weak	strong	strong
diffusion to the cytoplasmic membrane	high	low	medium
binding to the membrane disruption and disintegration of the membrane	low	medium	high

## **Outlook: Dendritic Nanomaterials as Functional Materials for Water Purification**

- **The ability to design and synthesize water-soluble or solid supported high-molecular weight dendrimer based functional nanostructures with**
  - **Cation/anion binding functional groups,**
  - **redox active metal ions and clusters,**
  - **catalytically active metal ions and clusters**
  - **hydrophobic cavities**
  - **bioactive active agents**
- **provides new and unprecedented opportunities for developing a new generation of efficient, cost effective and environmentally acceptable functional materials for water treatment processes**

## **Outlook: Fate, Transport and Toxicity of Dendritic Nanomaterials**

- **Numerous dendrimer toxicity and biodistribution studies have carried out during the last 5 years**
  - **However, the effects of dendrimer core and terminal group chemistry, size, shape, hydrophobicity on dendrimer interactions with cell membranes and toxicity are still not well understood.**
- **Only a limited number of studies have been published on the fate and transport of dendrimers in the environment**
  - **Sorption of dendrimers onto mineral surfaces**

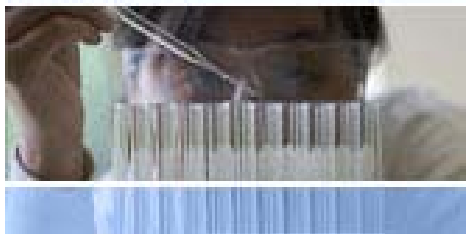
# The Price of Nanotechnology

(Slide Provided by Dendritic Nanotechnologies, INC)

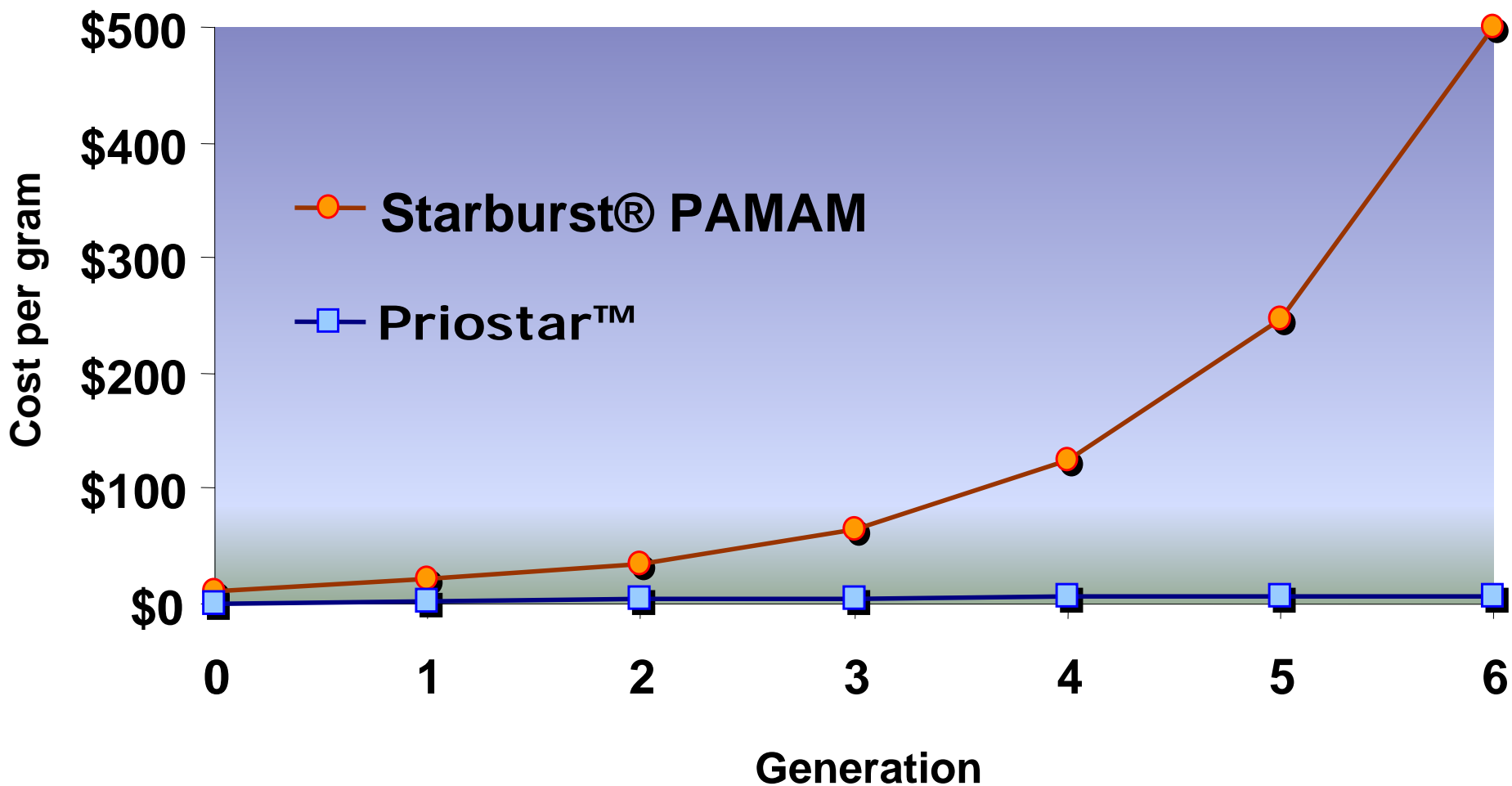
The retail price of the major classes of nanosized chemistries such as buckyballs, single wall nanotubes, dendrimers, and other nanoparticles are very expensive. Less expensive materials typically are impure, exhibit poor size control, and limited size range.

Nanotechnology	Retail Price (per gram)	
	Low (Less Pure)	High (Purified Product)
Buckyballs	\$ 30.00	\$ 120.00
Single Wall Carbon Nanotubes	\$ 50.00	\$ 2,000.00
Multi Wall Carbon Nanotubes	\$ 100.00	\$ 500.00
PAMAM G0 Amino Dendrimers	\$ 82.00	\$ 219.00
PAMAM G6 Amino Dendrimers	\$ 600.00	\$ 3,000.00
50 nm Silica Bead	\$ 100.00	\$ 100.00
50 nm Latex Bead	\$ 230.00	\$ 230.00
<b>Priostar™ Dendrimers</b>	<b>\$ 0.50</b>	<b>\$ 5.00</b>

Buckyball pricing from BuckyUSA,  
 SW & MWCNT pricing from BuckyUSA, CNI, and Carbon Solutions  
 Dendrimers pricing from Dendritech & DNT  
 Silica and Latex Beads from Polysciences



### Cost Profile: STARBURST® vs. Priostar™ Dendrimers





## Acknowledgments

- **National Science Foundation (Funding)**
- **Environmental Protection Agency (STAR Grant Funding)**
- **Department of Energy (Funding)**
- **National Water Research Institute (Funding)**
- **NSF Sponsored Cornell Nanobiotechnology Center (Funding)**
- **US Army High Performance Computing Research Center (Funding)**