Dendritic Nanomaterials for Environmental Remediation

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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

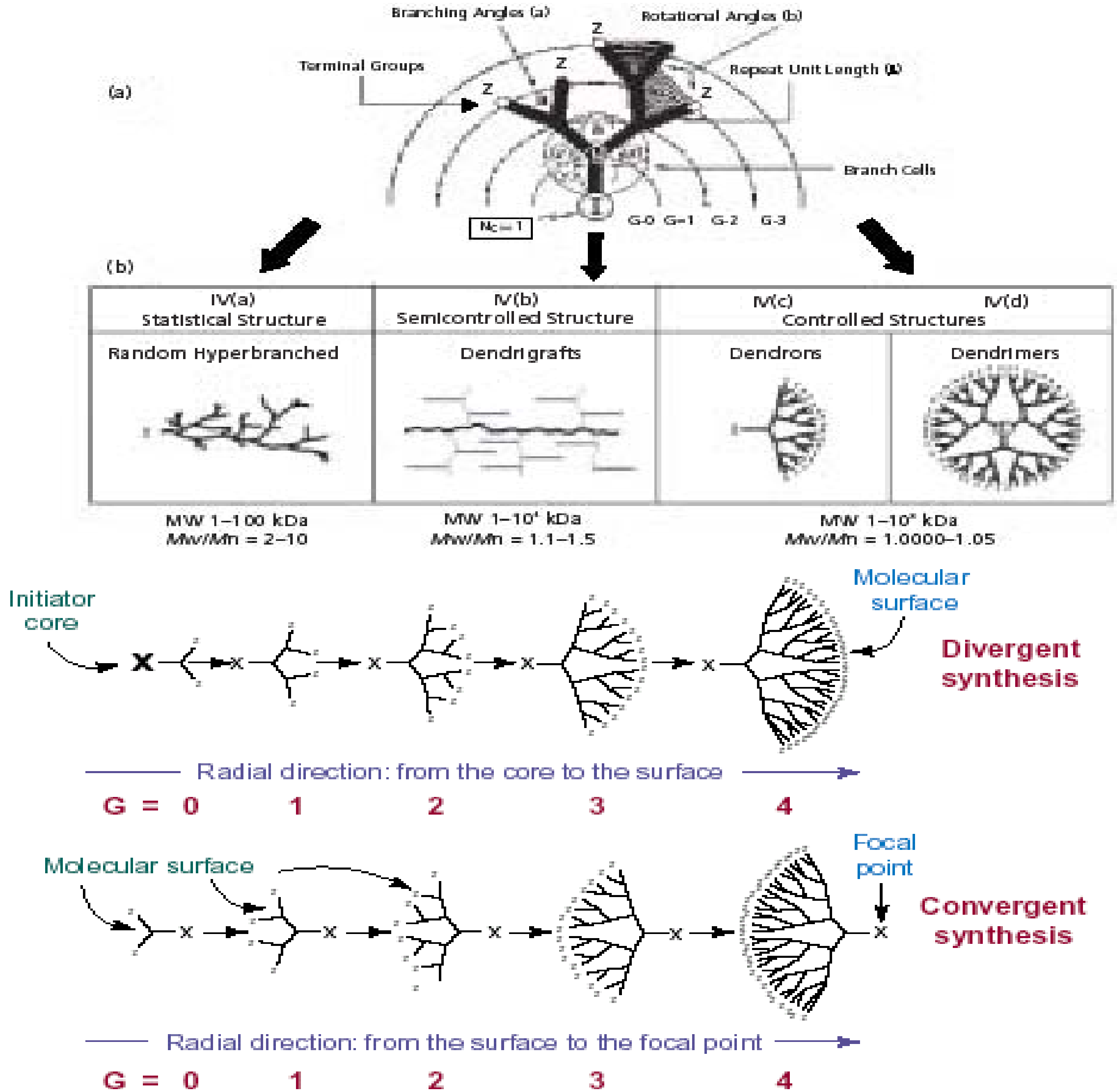
(2) Development of low cost dendritic nanomaterials

Acknowledgments

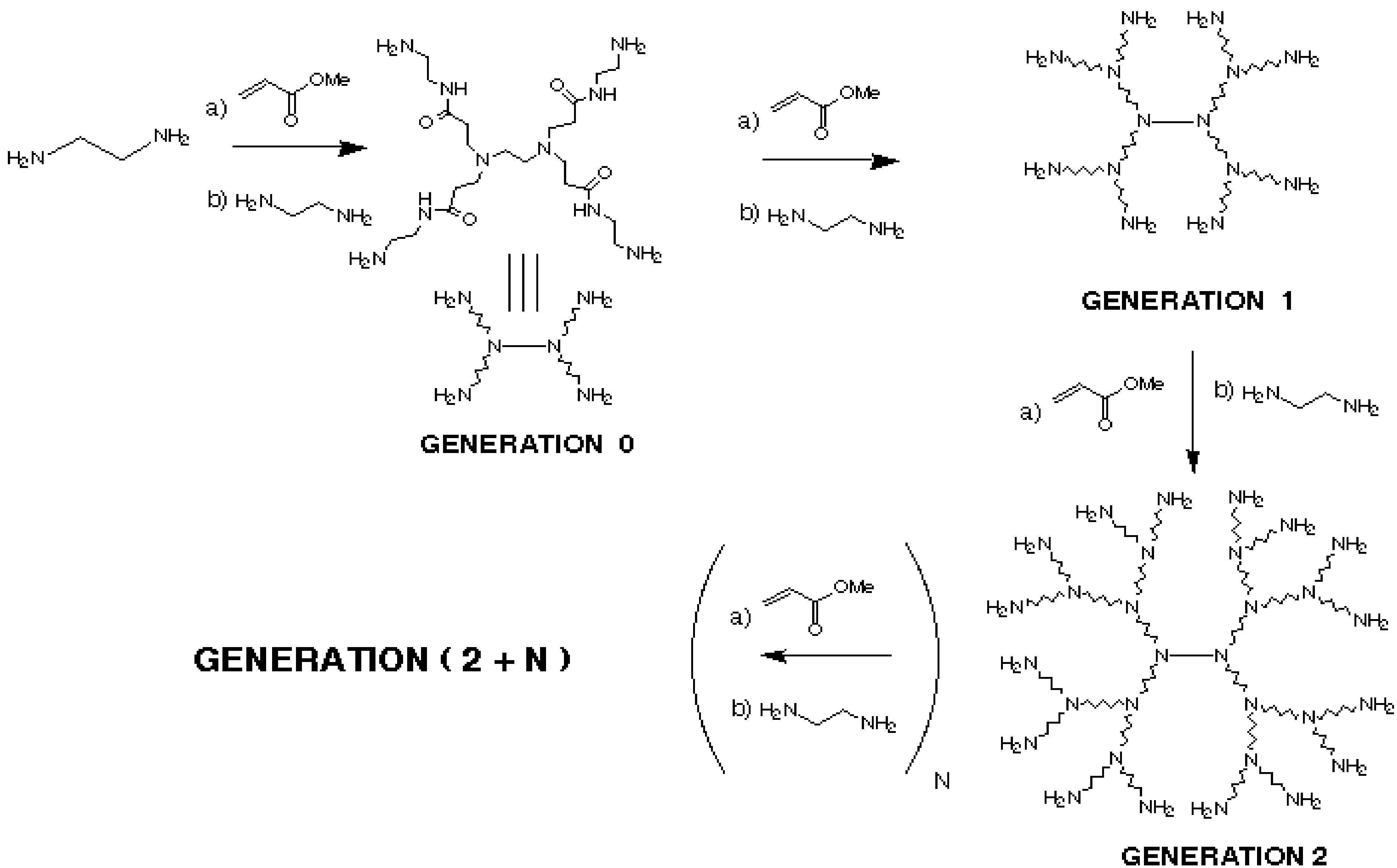
The Dendritic Macromolecular Architecture

(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

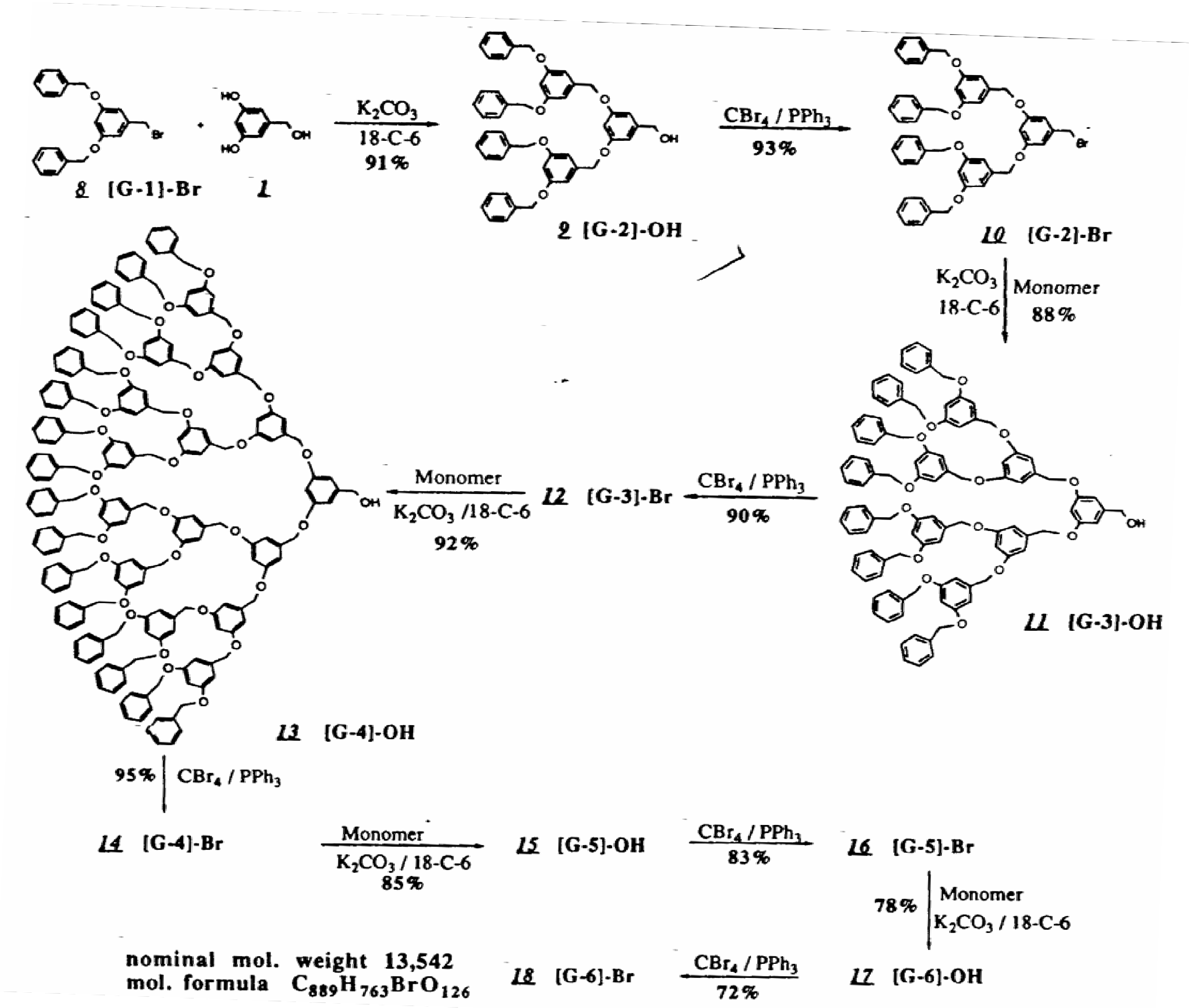


Divergent Synthesis of Poly(amidoamine) Dendrimers with Ethylene Diamine Core (EDA) and NH_2 Terminal Groups



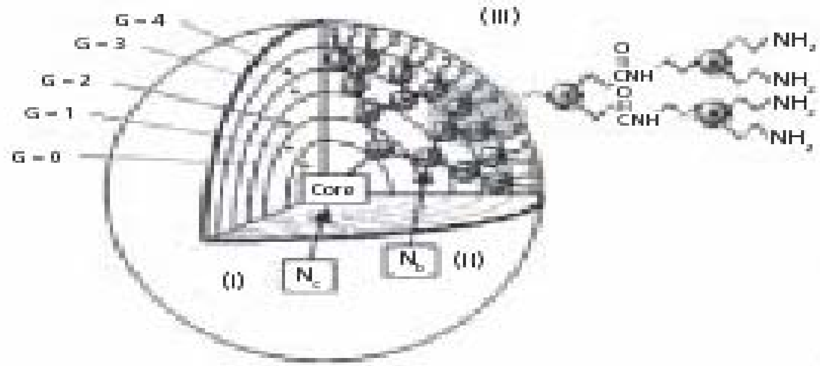
Convergent Synthesis of Poly(Benzyl Ether) Dendrimers

(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)



Number of Surface Groups	$Z = N_c N_b^G$	Surface Group Amplification per Generation
Number of Branch Cells	$BC = N_c \left[\frac{N_b^{G-1}}{N_b - 1} \right]$	Number of Covalent Bonds per Generation
Molecular Weights	$MW = M_c + N_c \left[M_{RU} \left(\frac{N_b^{G-1}}{N_b - 1} \right) + M N_b^G \right]$	

Gen	No. of NH_2 Surface Groups	Molecular Formula	MW	Hydrodynamic Diameter (nm)
0	4	$C_{24}H_{52}N_{10}O_4S_2$	609	1.5
1	8	$C_{64}H_{132}N_{26}O_{12}S_2$	1,522	2.2
2	16	$C_{144}H_{292}N_{58}O_{28}S_2$	3,348	2.9
3	32	$C_{304}H_{612}N_{122}O_{60}S_2$	7,001	3.6
4	64	$C_{624}H_{1252}N_{250}O_{124}S_2$	14,307	4.5
5	128	$C_{1264}H_{2532}N_{506}O_{252}S_2$	28,918	5.4
6	256	$C_{2544}H_{5092}N_{1018}O_{508}S_2$	58,140	6.7
7	512	$C_{5104}H_{10212}N_{2042}O_{1020}S_2$	116,585	8.1

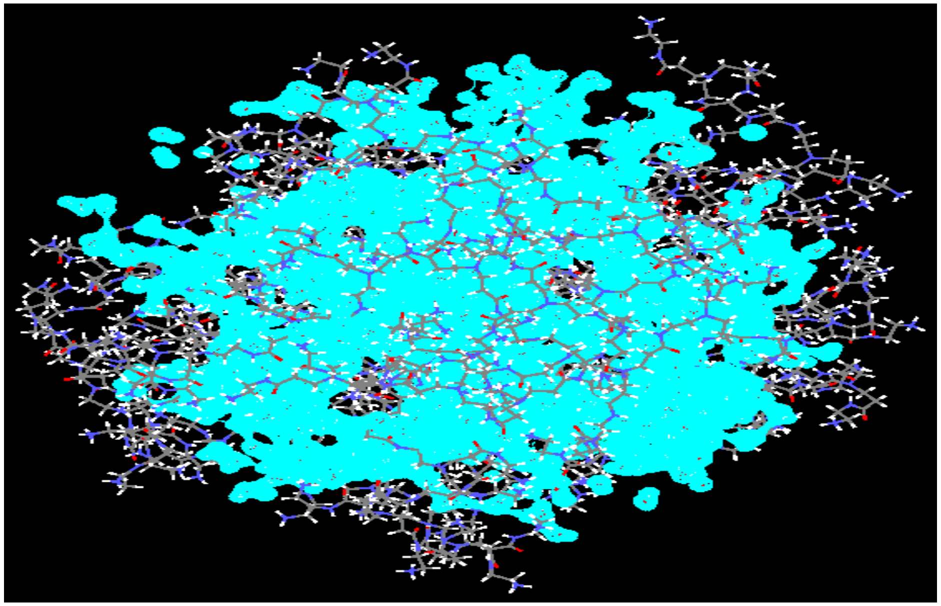
Z = monomer-shell-saturation level, N_c = core (cystamine) multiplicity, N_b = branch cell (BC) multiplicity, G = generation.

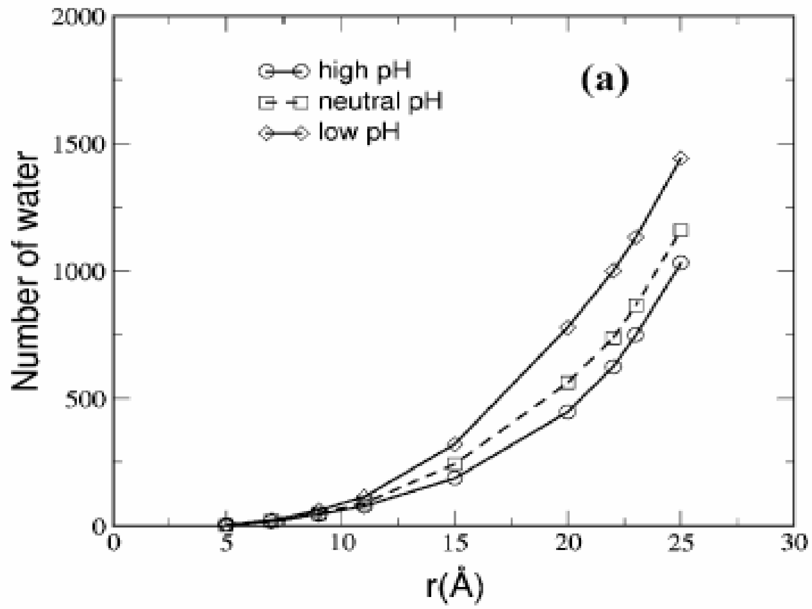
- **^{1}H and ^{13}C NMR Spectroscopy**
- **HPLC**
- **Size Exclusion Chromatography (SEC)**
- **Capillary Electrophoresis (CE)**
- **Polyacrylamide Gel Electrophoresis (PAGE)**
- **MALDI and ESI Mass Spectrometry**

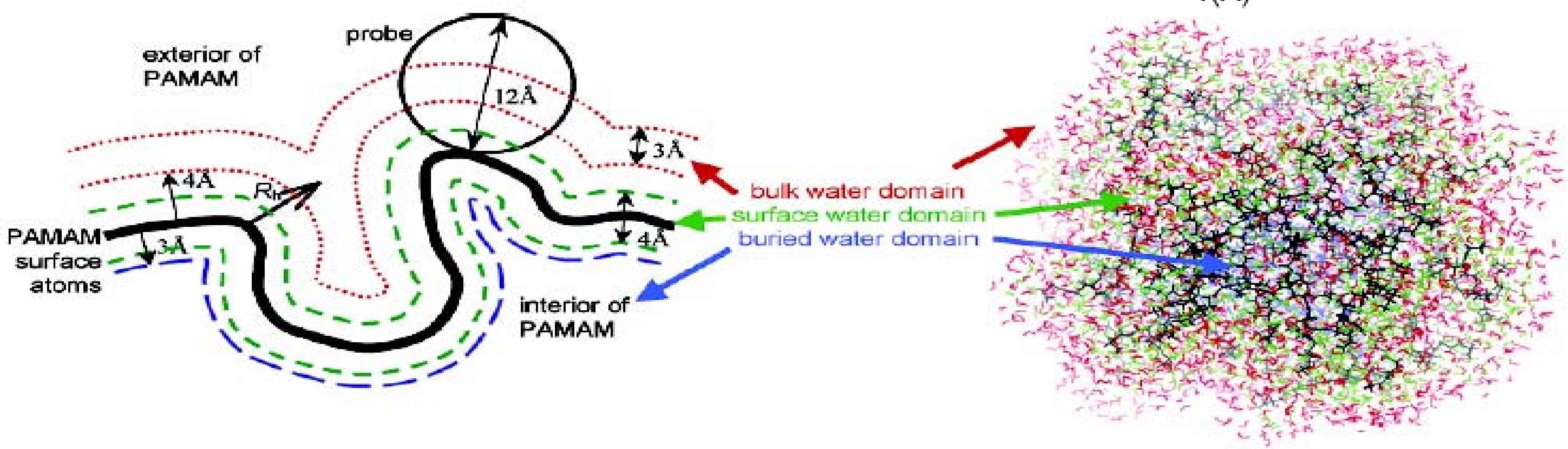
Characterization of the 3-D Structures of G5-NH_2 PAMAM Dendrimer by Molecular Dynamics Simulations in Water

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

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





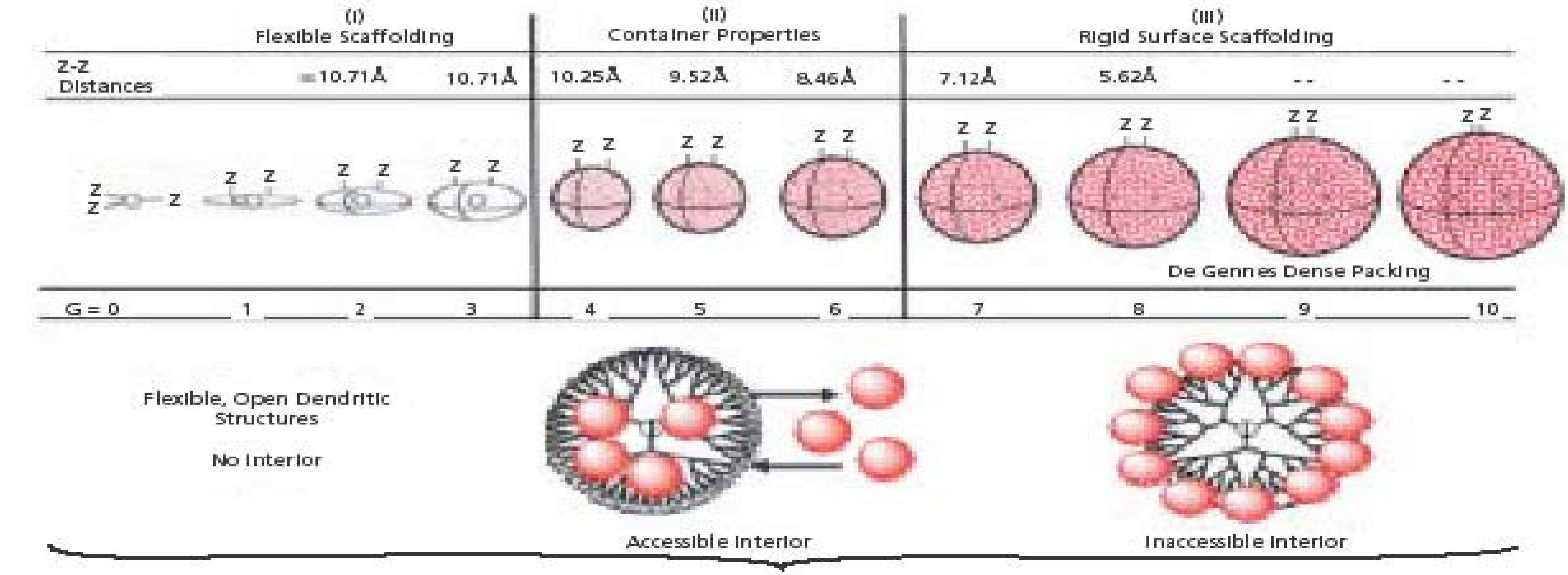


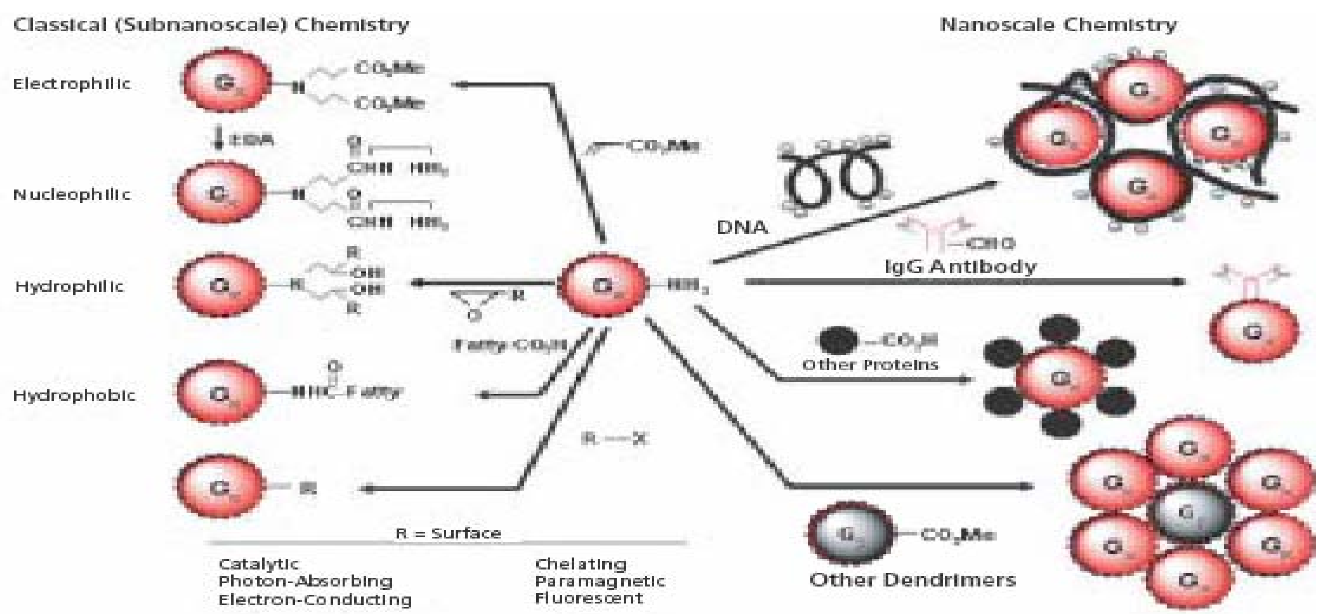
Schematic

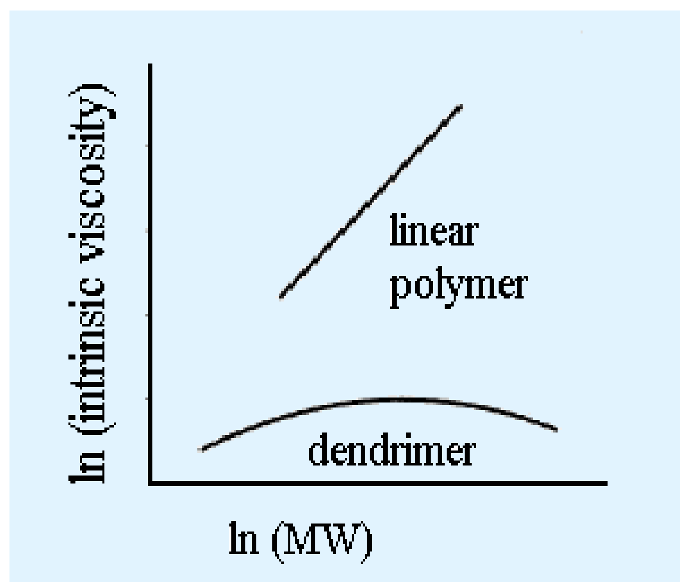
Atomistic

Unique Properties of Dendritic Macromolecules

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

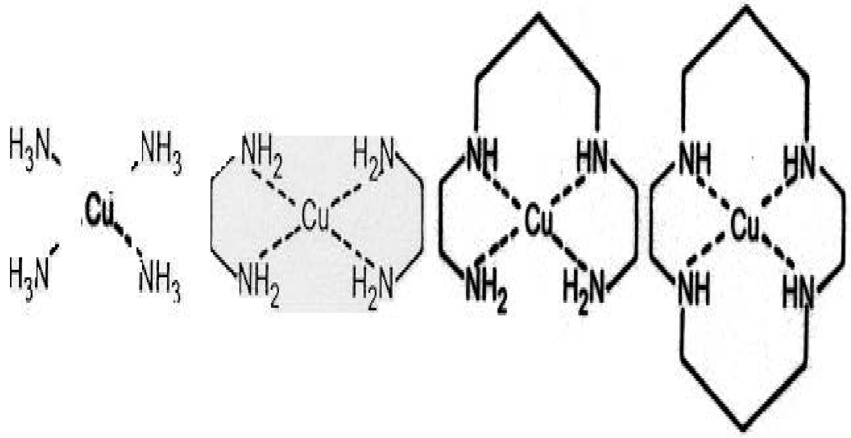


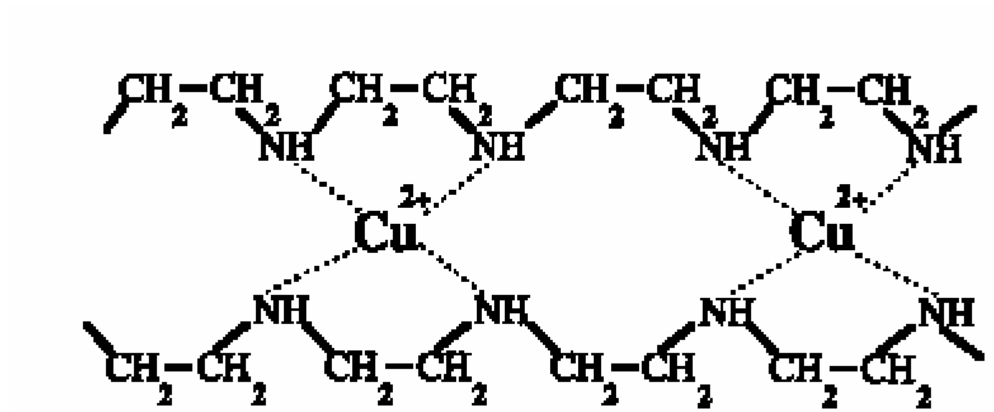


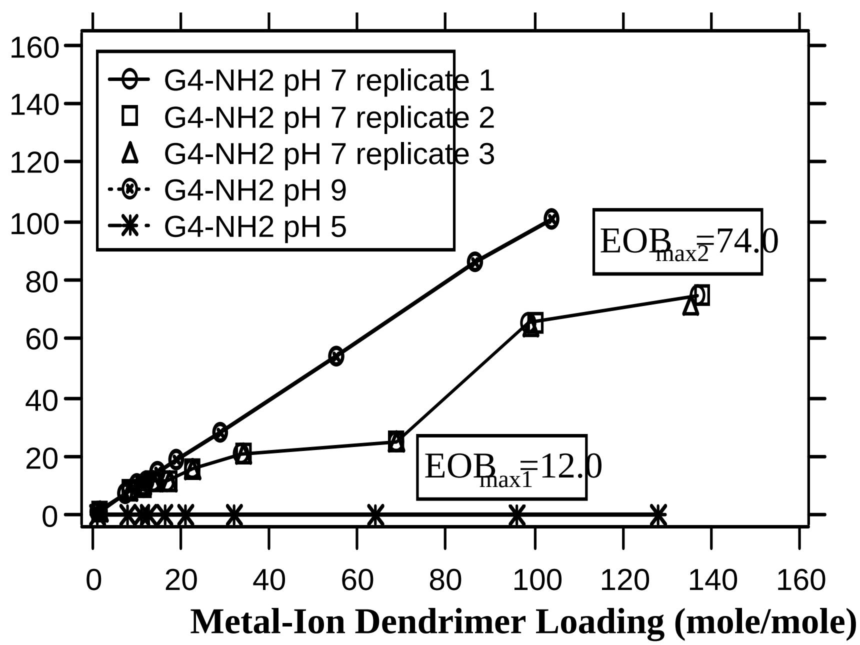


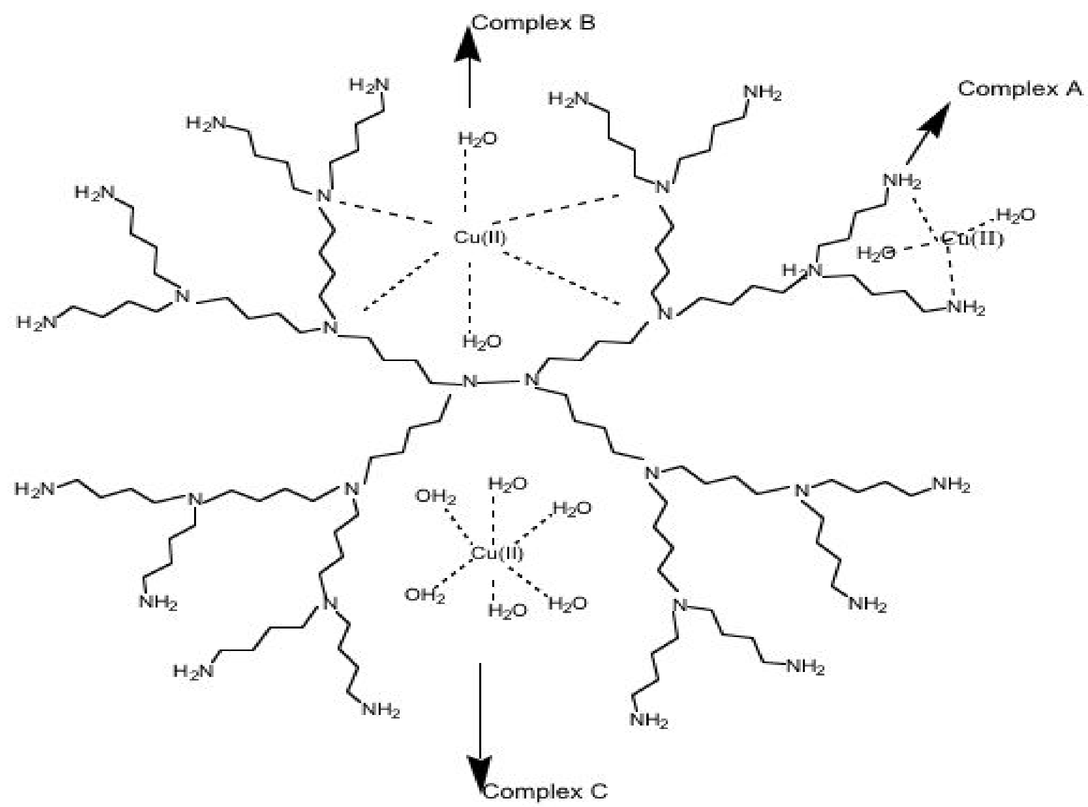
Dendritic Nanomaterials as High Capacity and Recyclable Ligands for Cations

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



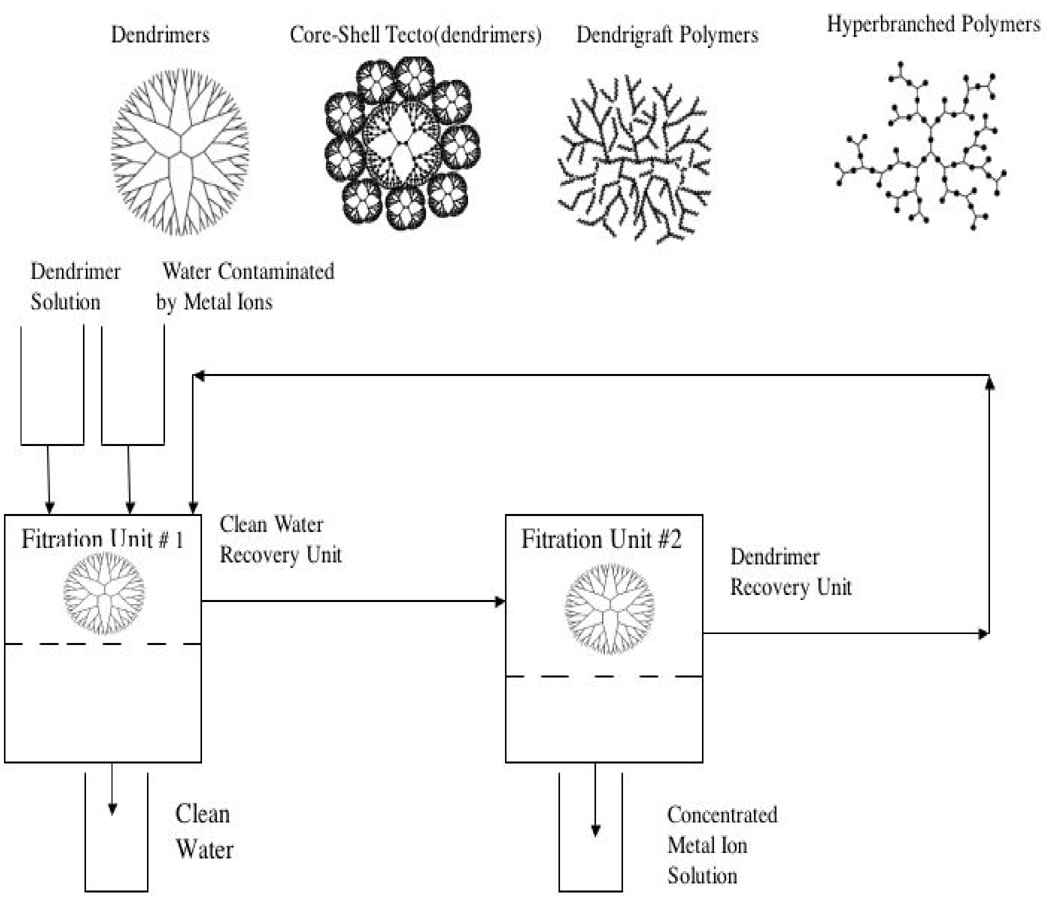






Environmental Applications of Dendritic Nanoscale Chelating Agents

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)

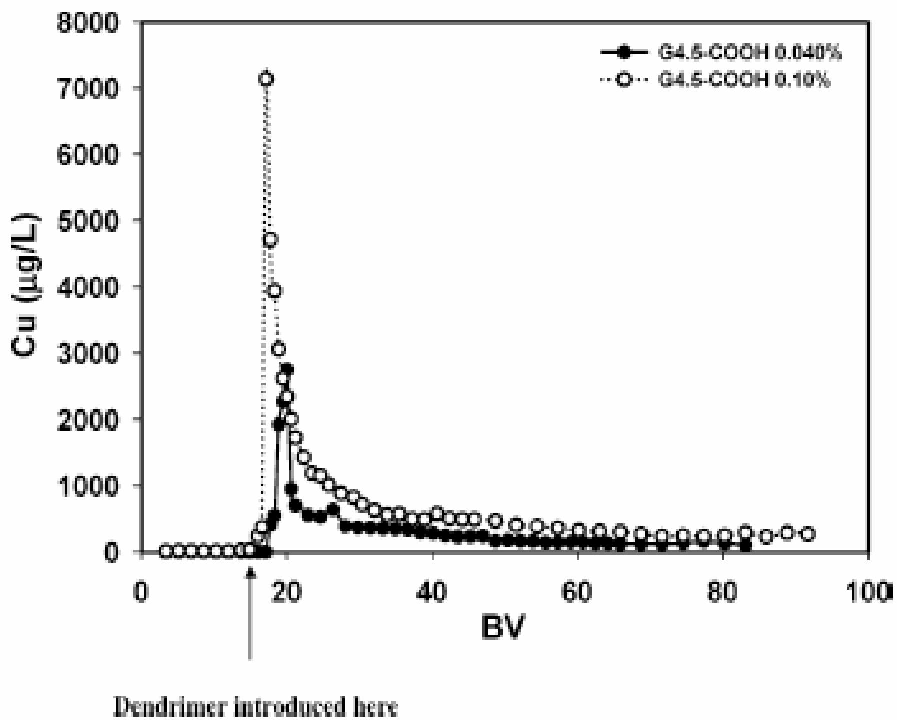
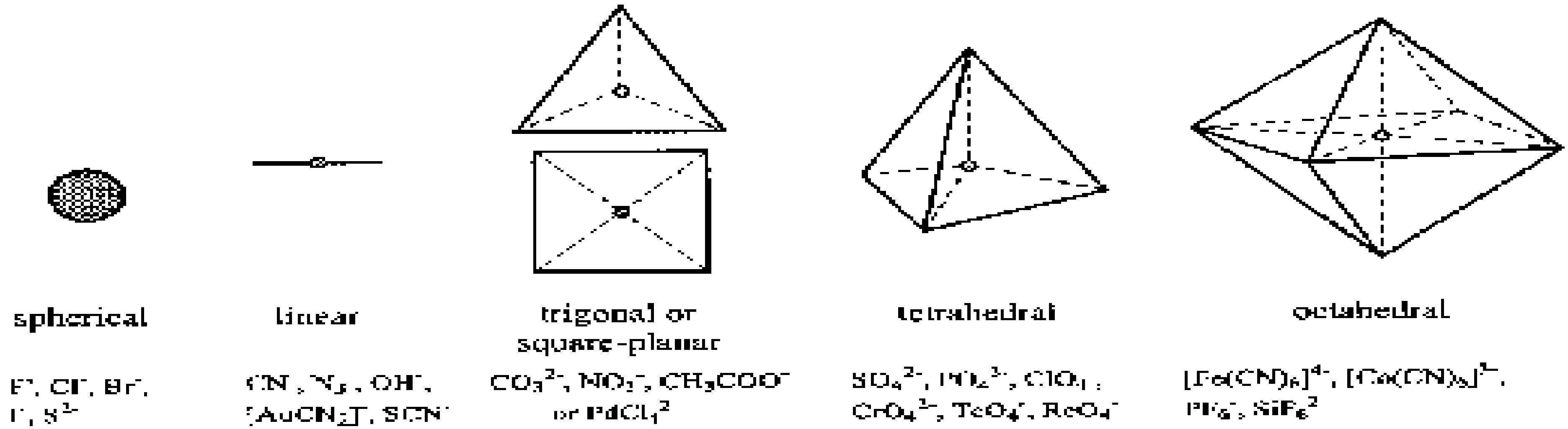


FIGURE 1. Copper elution histories during two separate column runs with 0.040% and 0.10% G4.5-COOH at pH 6.0.

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).

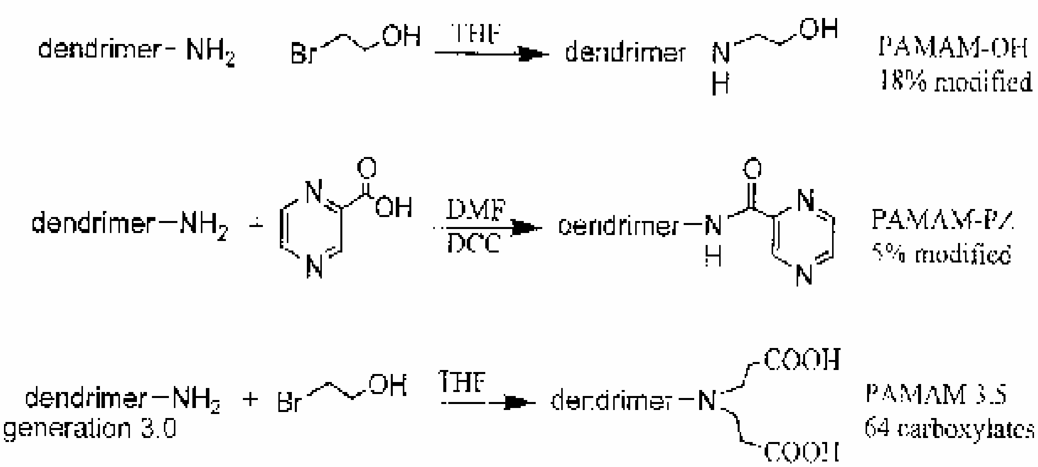


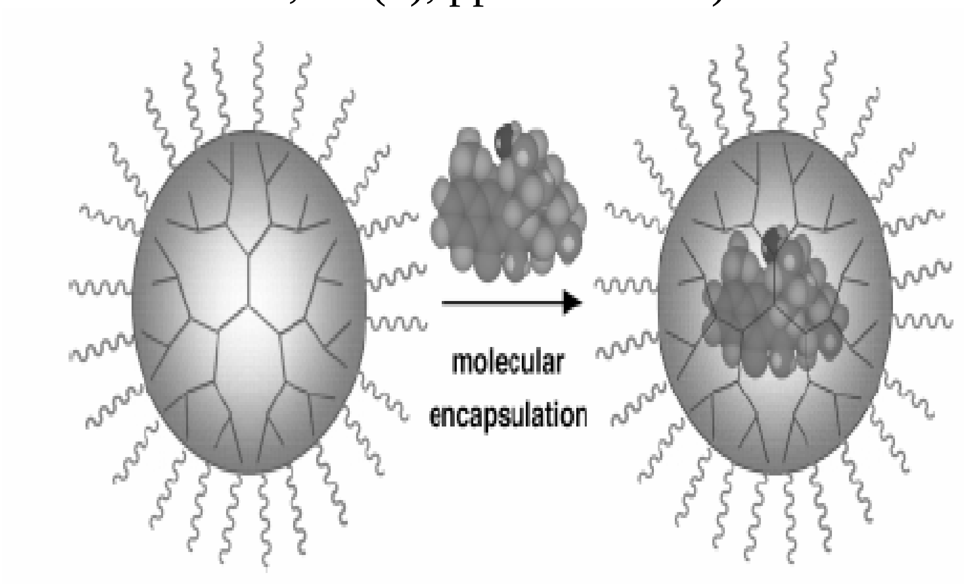
Figure 1. Synthetic scheme for the three modified dendrimers used for anion binding experiments. The polymers were prepared in an analogous fashion.

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

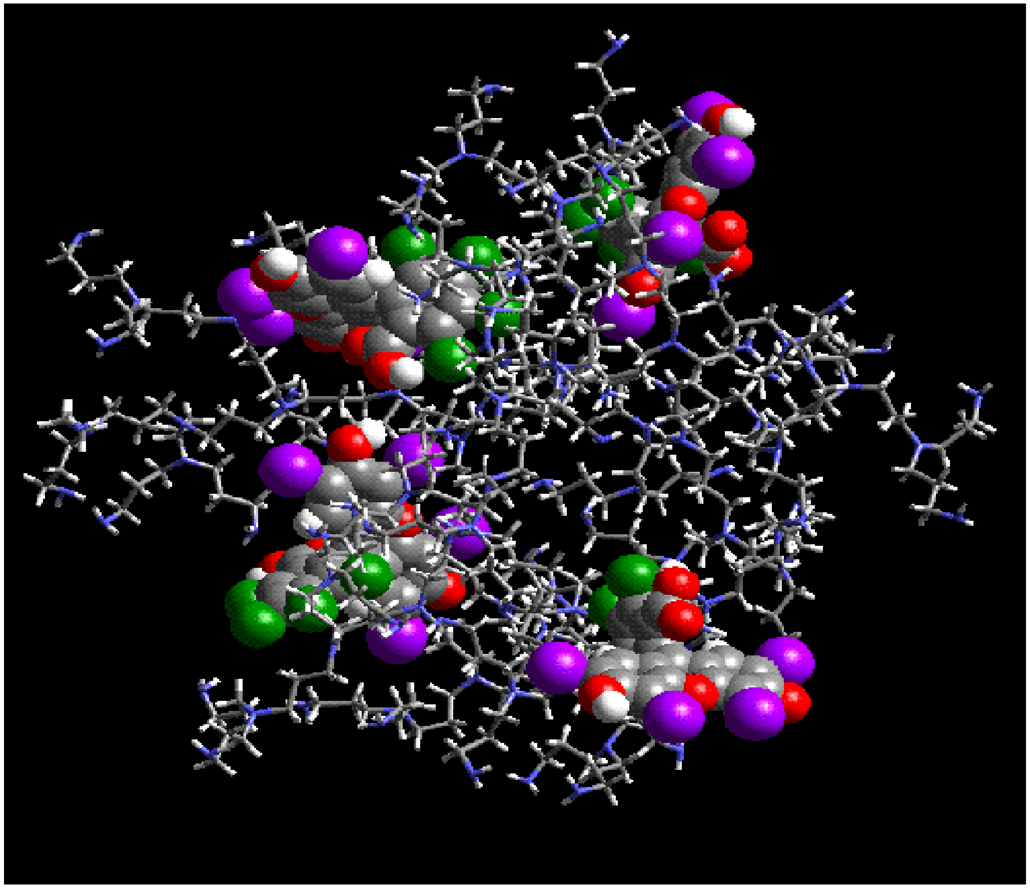
Single anion capacities	Molar capacity (mmol ion/g dendrimer)		
polymer	CrO_4	AsO_4	PO_4
PAMAM 4.0	1.99	1.74	1.62
PAMAM-OH	2.39	1.28	2.07
PAMAM-PZ	1.17	1.08	0.40
PEI	4.13	4.91	6.25
PEI-OH	2.53	3.04	3.93
PEI-PZ	1.79	1.70	2.03

Dendritic Macromolecules as Unimolecular Micelles for Organic Solutes

(Striba et al. 2002, Angwate. Chemie. 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)

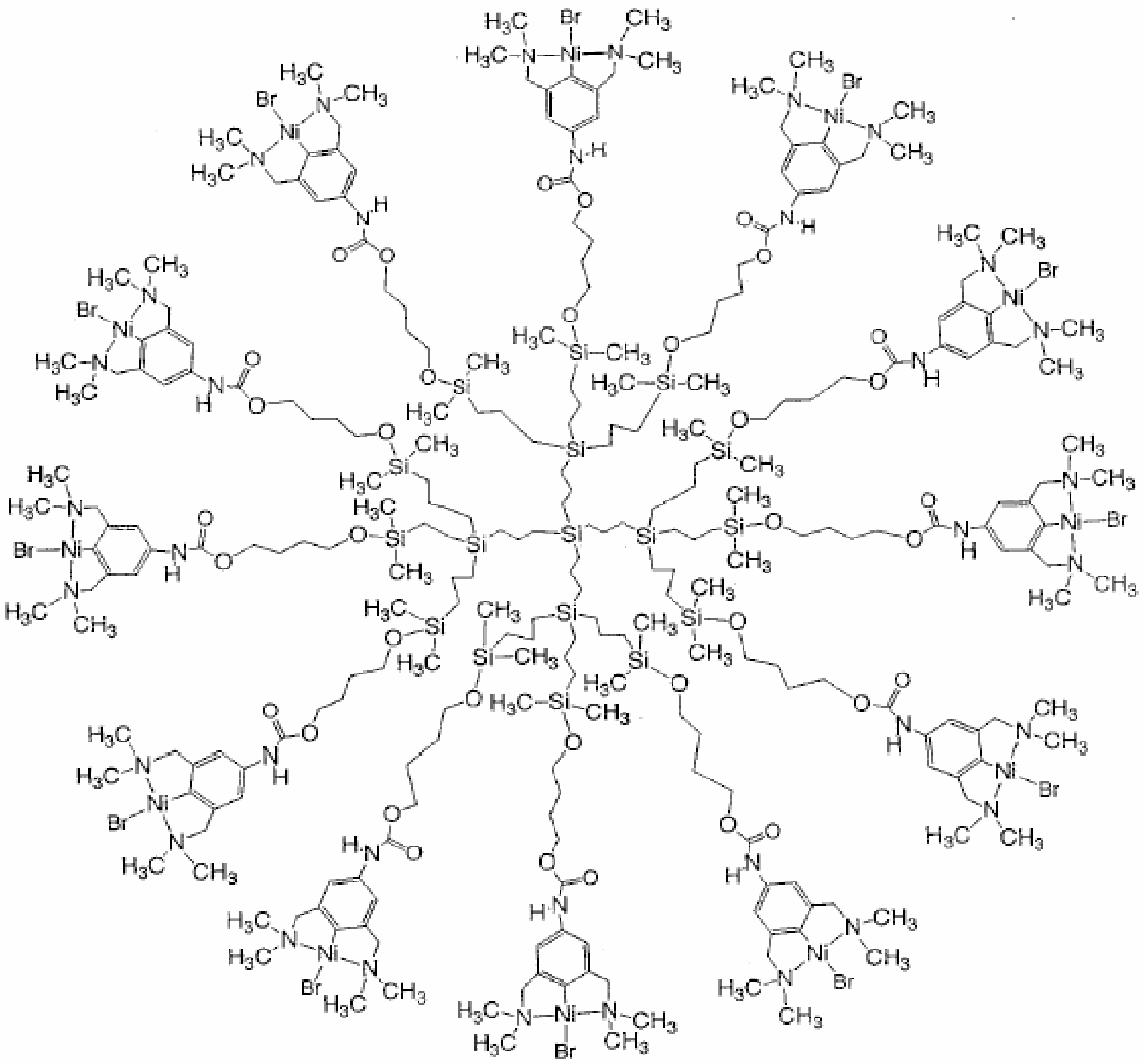
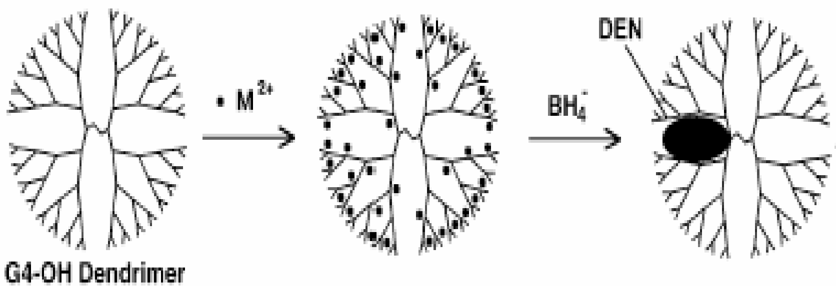


Figure 1. van Koten's metallodendrimer that catalyzes the Kharasch additions of polyhalogenoalkanes to C=C bonds

Dendrimer-Encapsulated Zero Valent Metal Clusters

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

SCHEME 1



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SCHEME 2

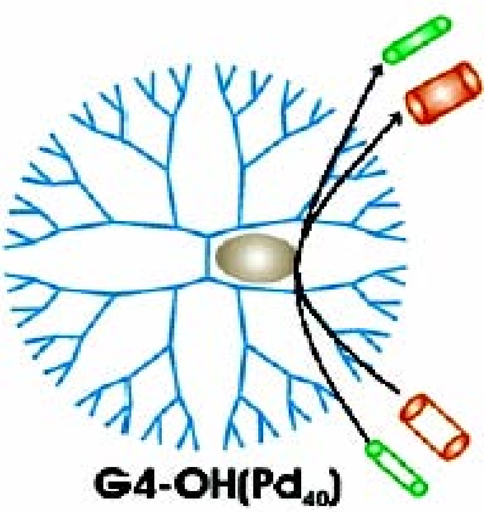
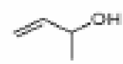
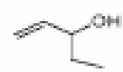


TABLE 2: Hydrogenation Reaction Rates Using Gx-OH(Pd_{40}) Catalysts for Structurally Related Allylic Alcohols[a]

Substrates	TOF[mol H_2(mol Pd)$^{-1}$ h^{-1}]		
	G4−OH(Pd_{40})	G6−OH(Pd_{40})	G8−OH(Pd_{40})
	480/470[1]	450/460[1]	120
	450/460[1]	380	93
	260	280	68
	150	75	62
	100	40	50

[a] Hydrogenation reactions were carried out at 25 ± 2 °C using 2 × 10^{-4} M Gx-OH(Pd_{40}) catalysts in MeOH−H_2O (4:1 v/v) mixtures. The turnover frequency (TOF) was calculated based on H_2 uptake. [1]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

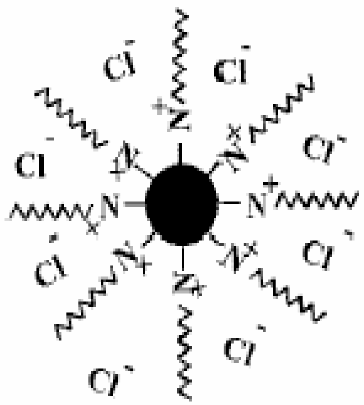


Figure 2. Scheme of generation 2 poly(propyleneimine) dendrimer quaternary ammonium biocides with 8 QAC groups on the surface.

Table 1. Dendritic Biocides Synthesized in This Study[a]

	dendrimer/ HBP	gen	hydrophobic chain length	ctr	no. of QAC groups	theor MW
D1ClNC12	dendrimer	1	12	Cl	4	1593
D2ClNC12	dendrimer	2	12	Cl	8	3324
D3ClNC12	dendrimer	3	12	Cl	16	6789
D4ClNC12	dendrimer	4	12	Cl	32	13719
D5ClNC12	dendrimer	5	12	Cl	64	27578
D2ClNC16	dendrimer	2	16	Cl	8	3772
D3ClNC16	dendrimer	3	16	Cl	16	7685
D4ClNC16	dendrimer	4	16	Cl	32	15511
D3ClNC8	dendrimer	3	8	Cl	16	5893
D3CNC10	dendrimer	3	10	Cl	16	6341
D3ClNC14	dendrimer	3	14	Cl	16	7237
D3BrNC14	dendrimer	3	14	Br	16	7949
H3ClNC12	HBP	3	12	Cl	32	13573

[a] Note: HBP refers to hyperbranched polymers. gen = generation. ctr = counteranion. theor = theoretical.

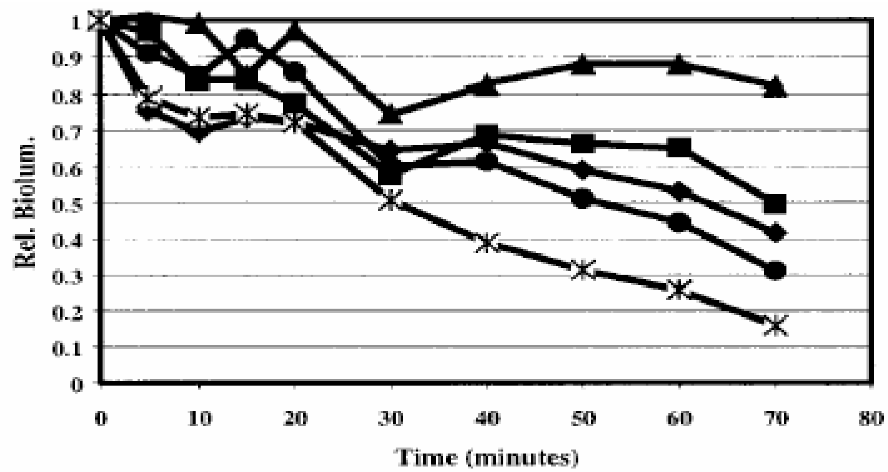


Figure 4. Effect of generation on biocidal activities on dendrimers with C_{12} hydrophobes: triangle, D3ClNC12; rectangle, D2ClNC12; diamond, D1ClNC12; filled circle, D4ClNC12; star D5ClNC12. The concentration was 4 μg/mL of dendrimer.

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	low	medium	high
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 tranport of dendrimers in the environment**
  - **Sorption of dendrimers onto mineral surfaces**

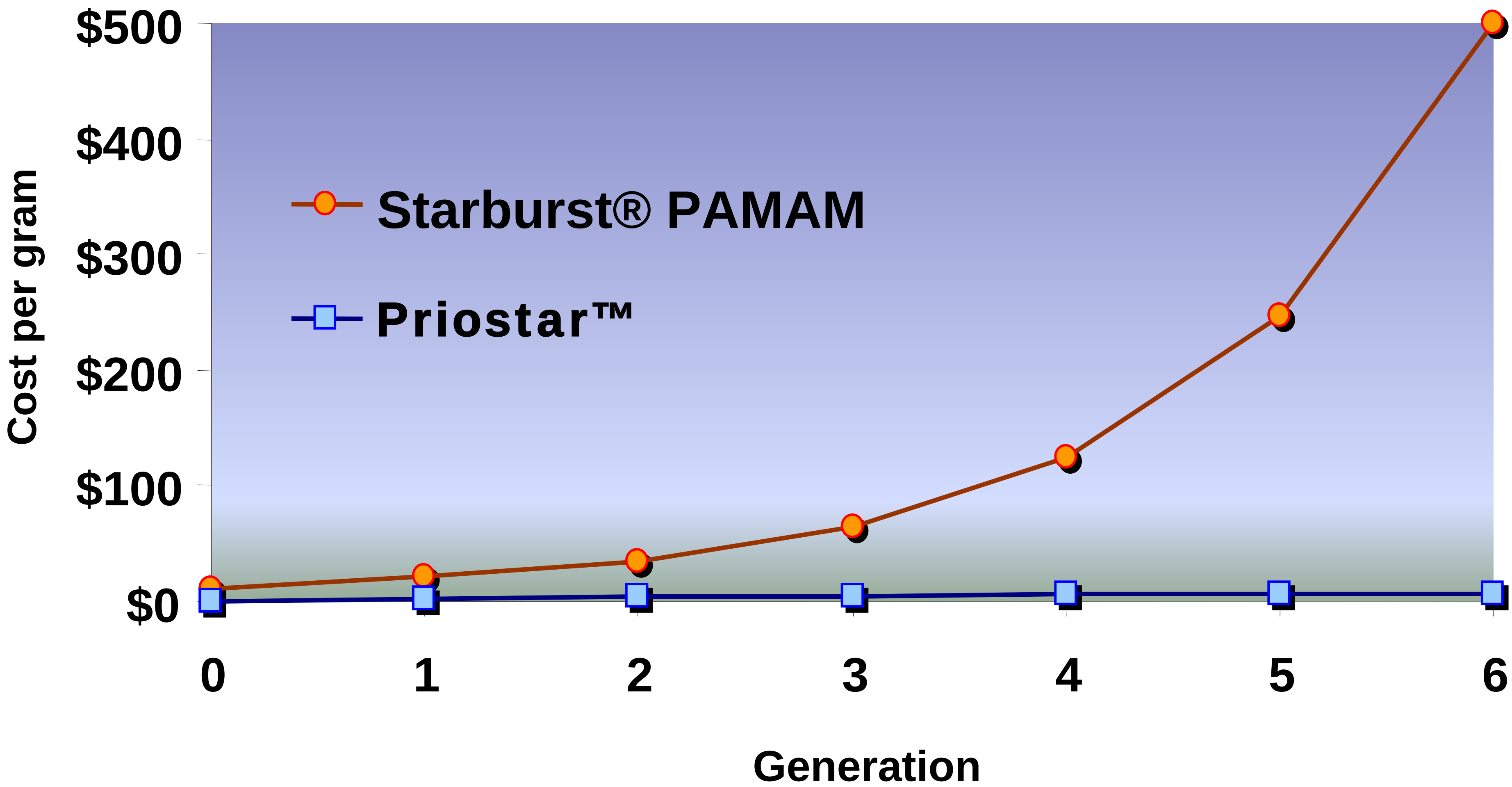
The Price of Nanotechnology
(Slide Provided by Dendritic Nanotechnologies, INC)

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
Priostar™ Dendrimers	**$ 0.50**	**$ 5.00**

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



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