Χημεία & Τεχνολογία Υλικών

Materials Chemistry & Technology

Πολυμερή
Polymers

Καταλύτες
Catalysts

Κολλοειδή
Colloids

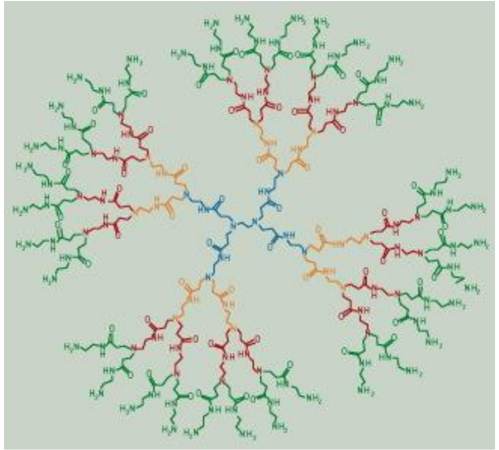
Νανοδομές Άνθρακα
Carbon Nanostructures

Σύνθετα Υλικά
Composites

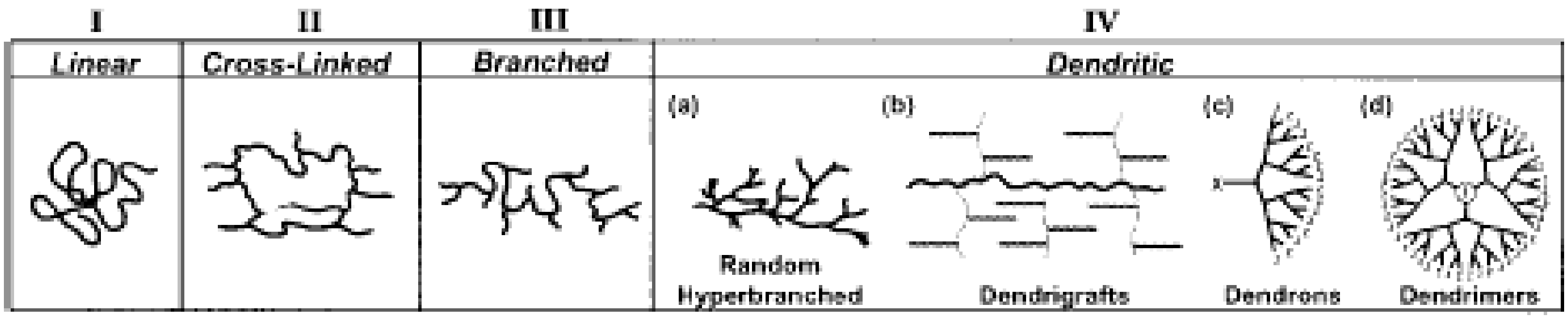
Κεραμικά
Ceramics

Δενδρομερή-
Δενδρόμορφα Πολυμερή

Dendrons - Dendrimers
&
Dendronized Polymers



Major Macromolecular Architectures



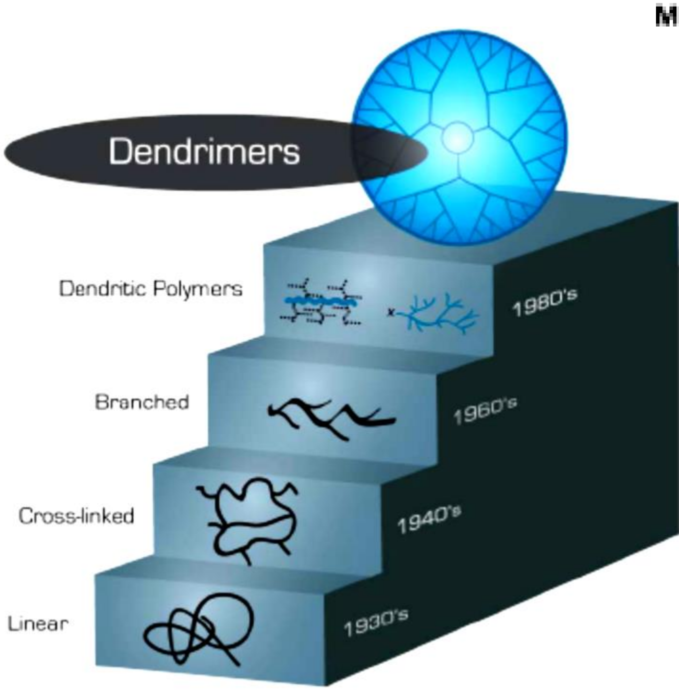
1930's	1940's	1960's	Present
Plexiglass, Nylon	Rubbers, Epoxies	Low Density Polyethylene Metallocene-Based Polyolefins	

Biomedical
- nano-drugs
- gene expression
- immuno diagnostics
- controlled delivery

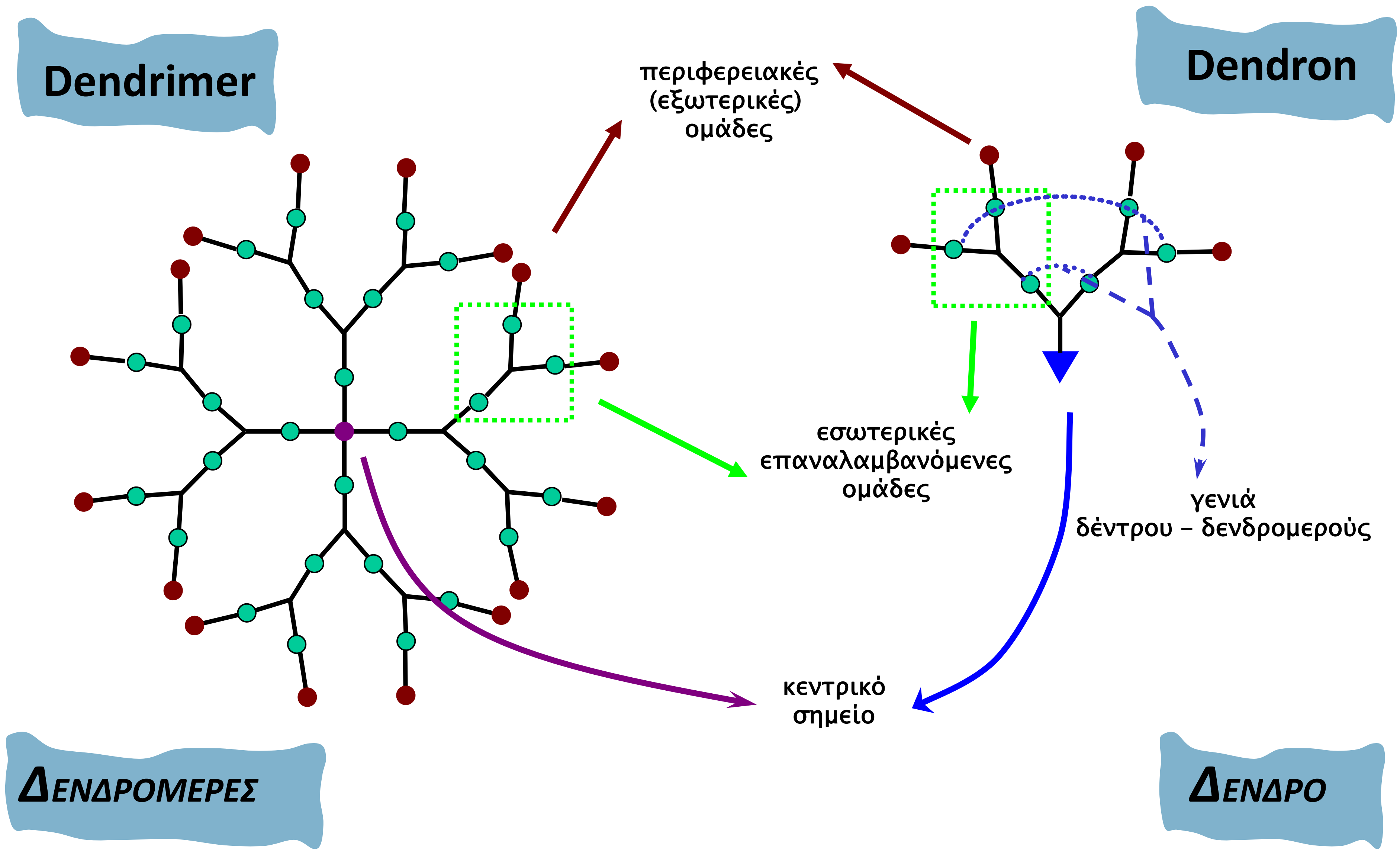
Electronics
- light harvesting
- 3-D conductivity
- quantum dots

Sensors
- chemical
- biological

Coatings
- fast cure, low viscosities

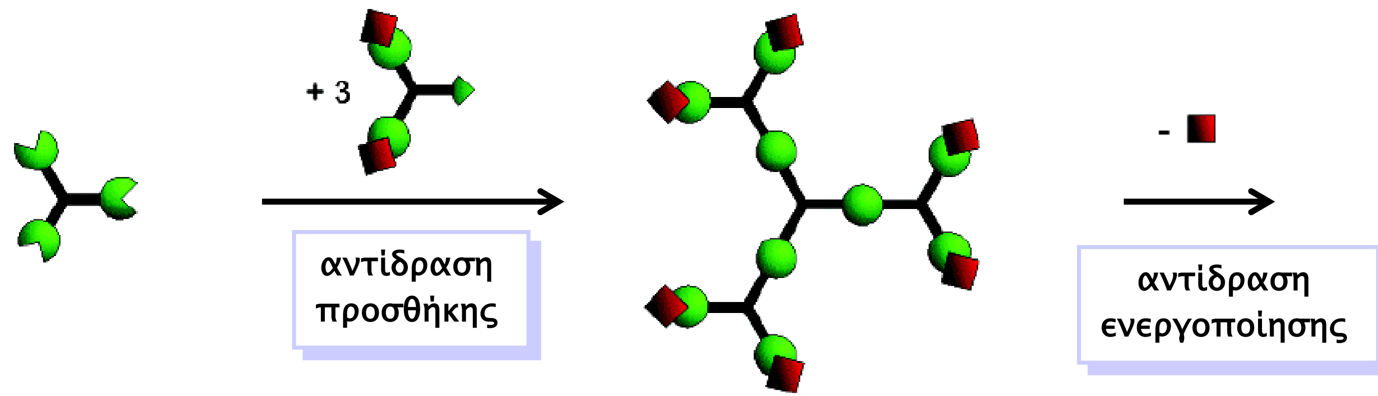


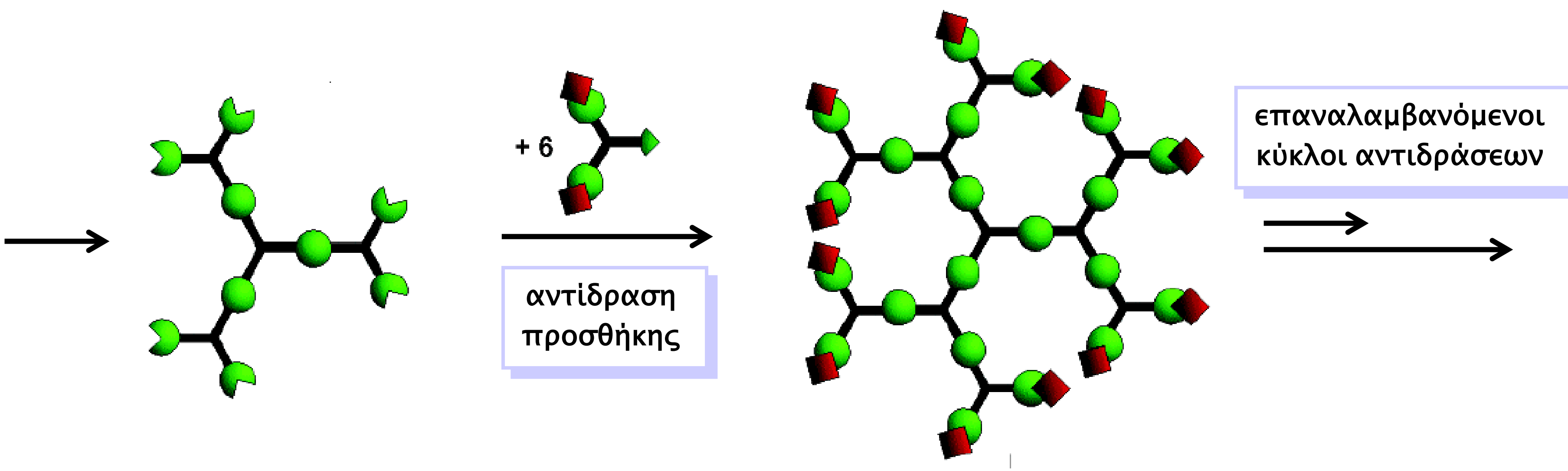
Dendrons & Dendrimers



“Divergent” approach:

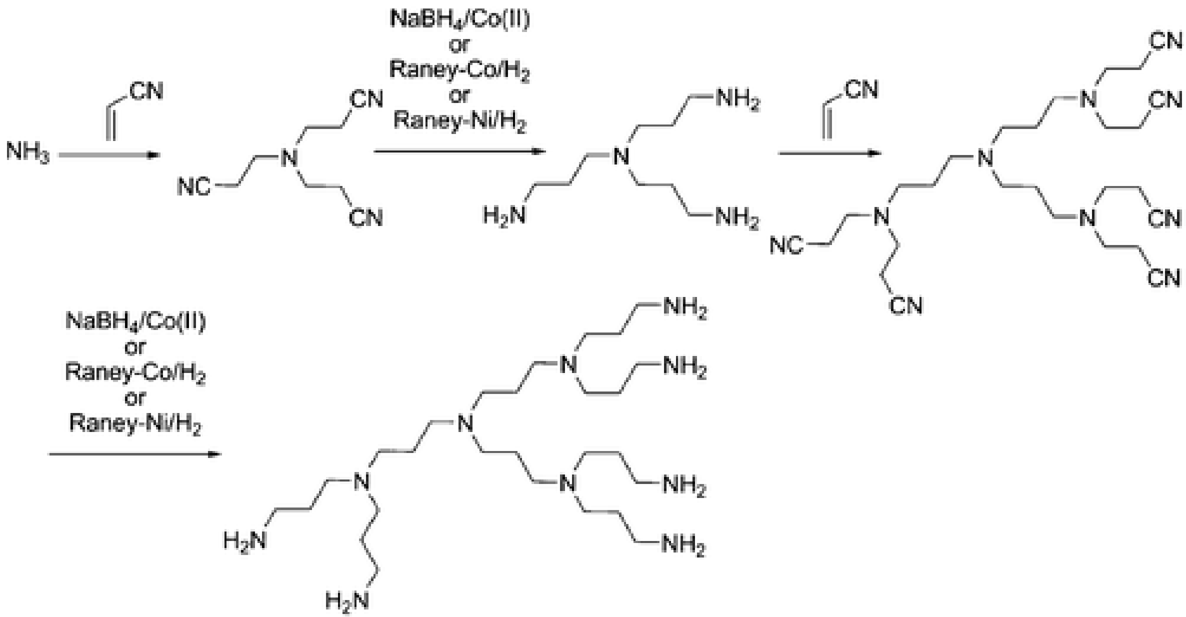
From the Central Point to the Outer Units





"Divergent" approach: From the Central Point to the Outer Units

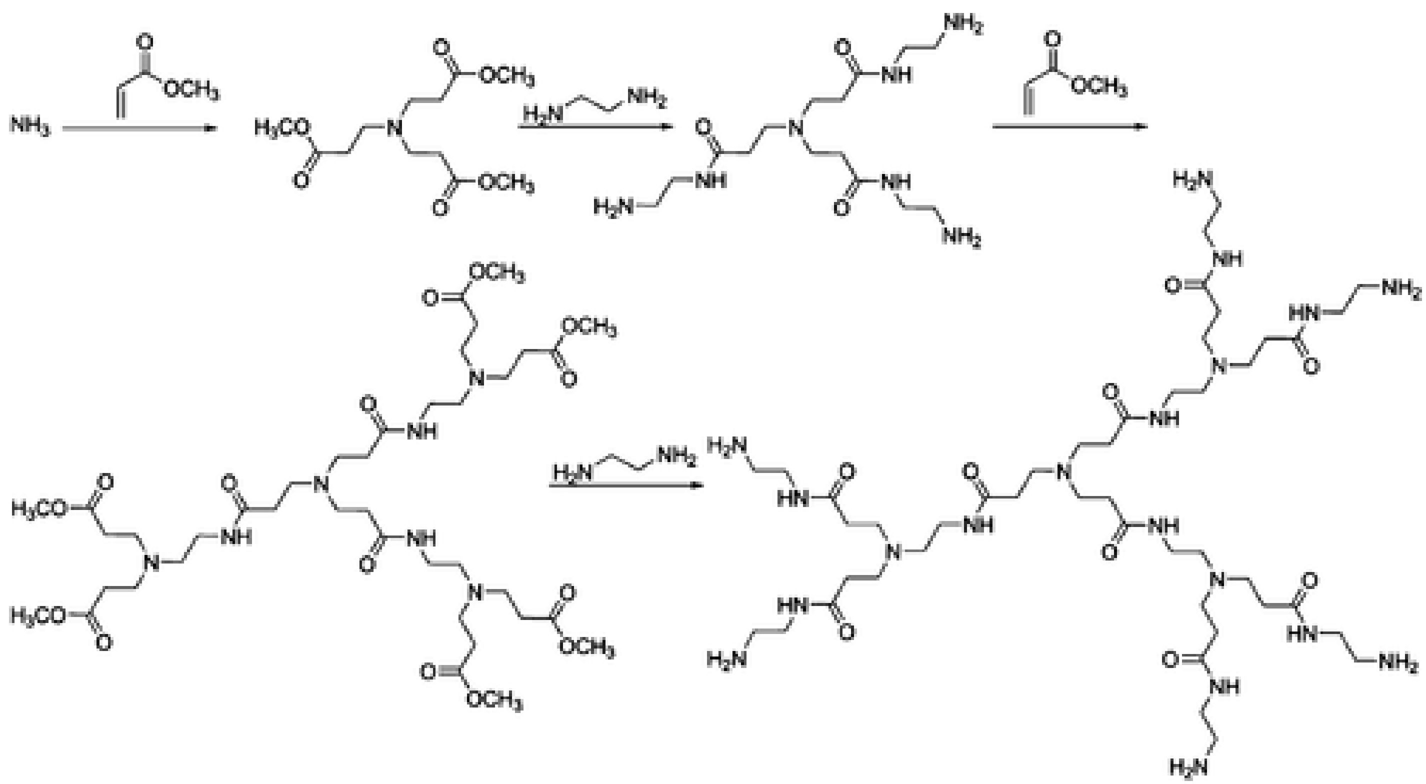
The **first low molecular weight dendritic molecules** branched G2-G3 **poly(propylene imine) (PPI)** dendrimers, were reported **by Vögtle in 1978**



Buhleier, E., Wehner, W., and Vögtle, F. Synthesis **1978**, 155

“Divergent” approach: From the Central Point to the Outer Units

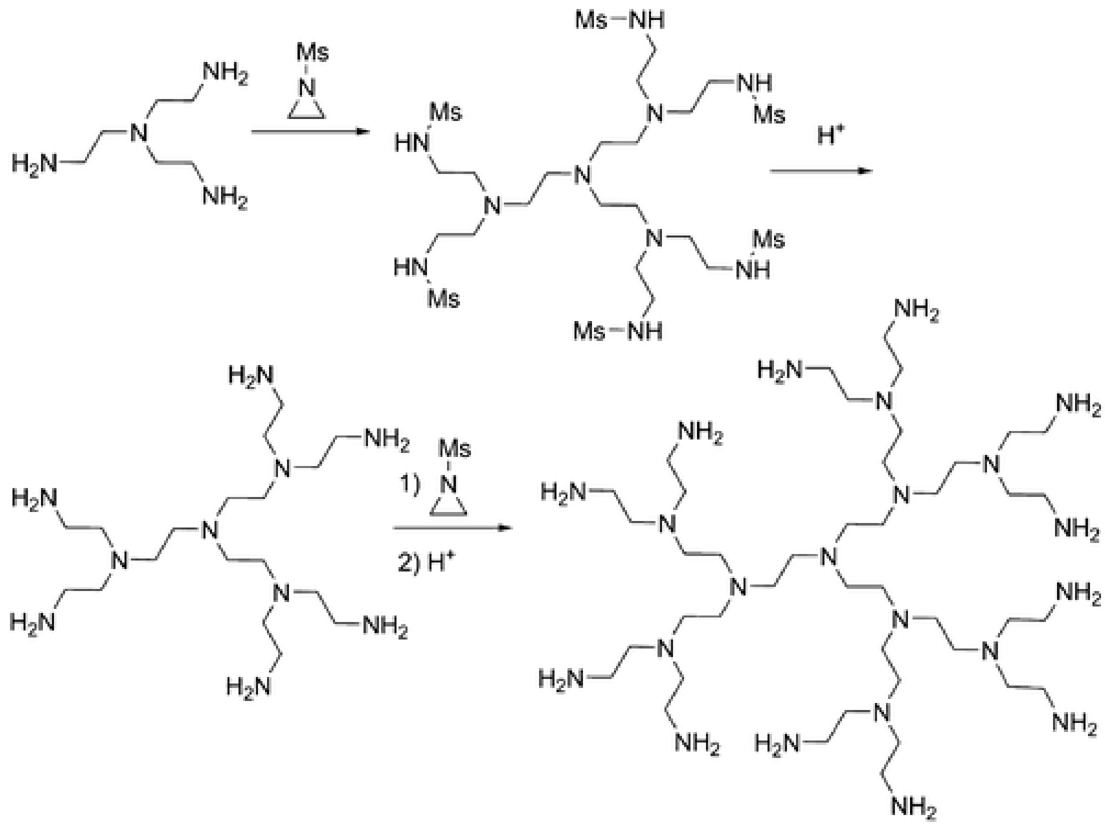
Synthesis of Tomalia-type poly(amidoamine) PAMAM Dendrimers in 1984



Tomalia, D. A.; Baker, .; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. Polym. J. **1985**, 17, 117.
Tomalia, D. A.; Baker, .; Dewald, J.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. Macromolecules **1986**, 19, 2466.

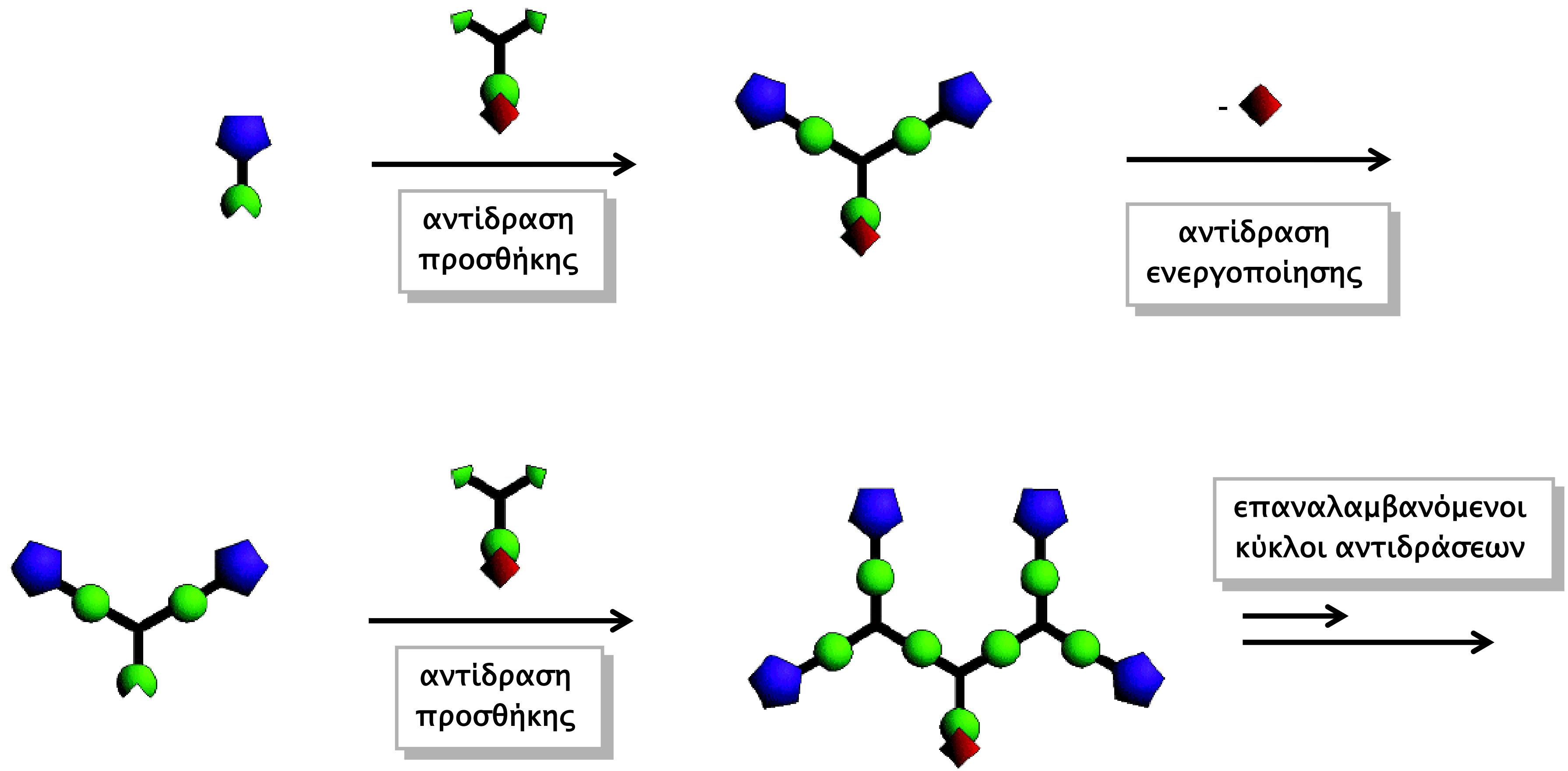
“Divergent” approach: From the Central Point to the Outer Units

Synthesis of Tomalia-type poly(ethylene imine) PEI Dendrimers



Tomalia, D. A., Naylor, A. M., and Goddard, W. A., III Angew. Chem., Int. Ed. Engl. **1990**, 29, 138
Tomalia, D. A. and Dewald, J. R. U.S. Patent 4,631,337, **1986**.

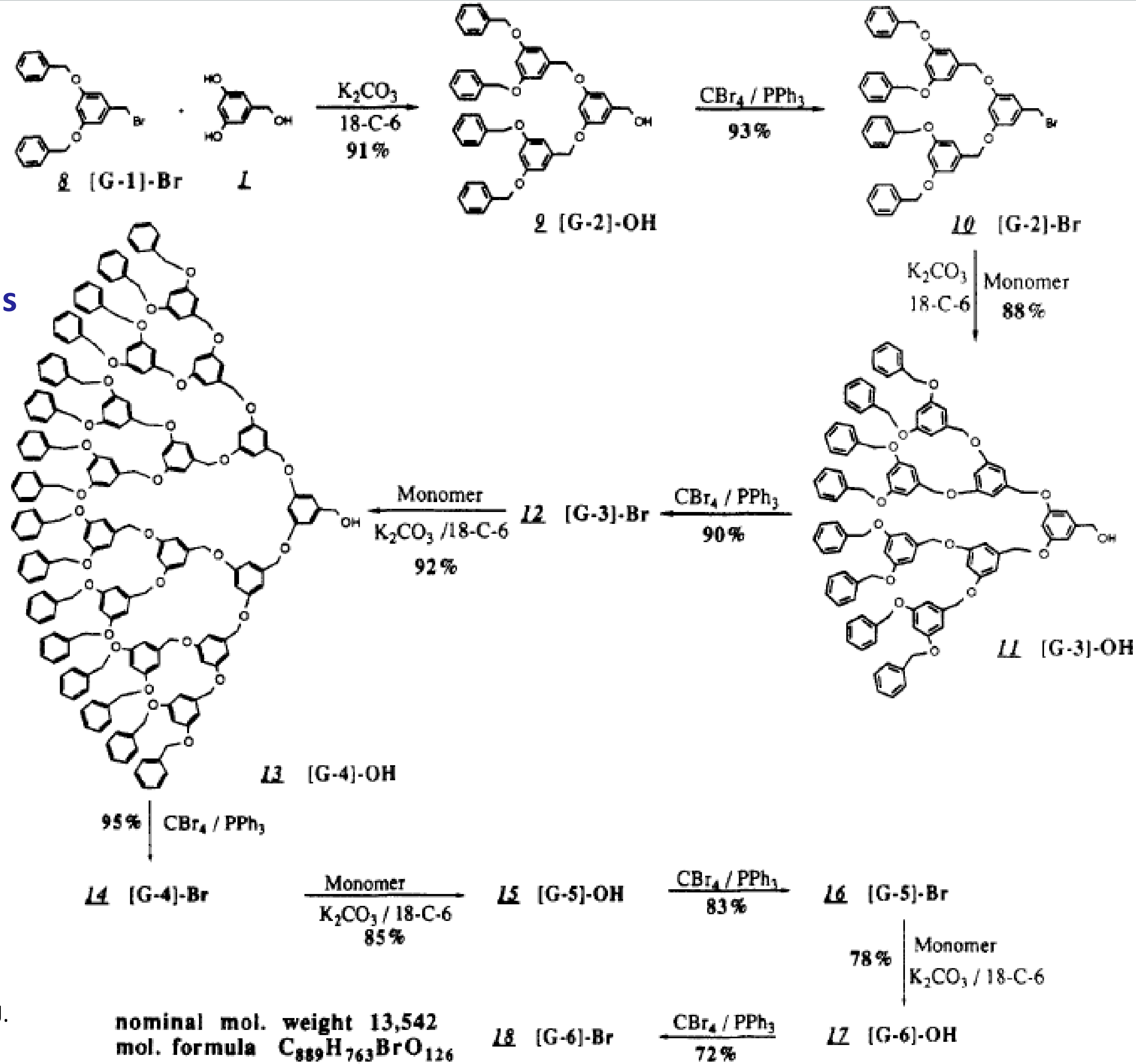
"Convergent" Approach:
From the Outer Units to the Central Point



“Convergent” Approach: From the Outer Units to the Central Point

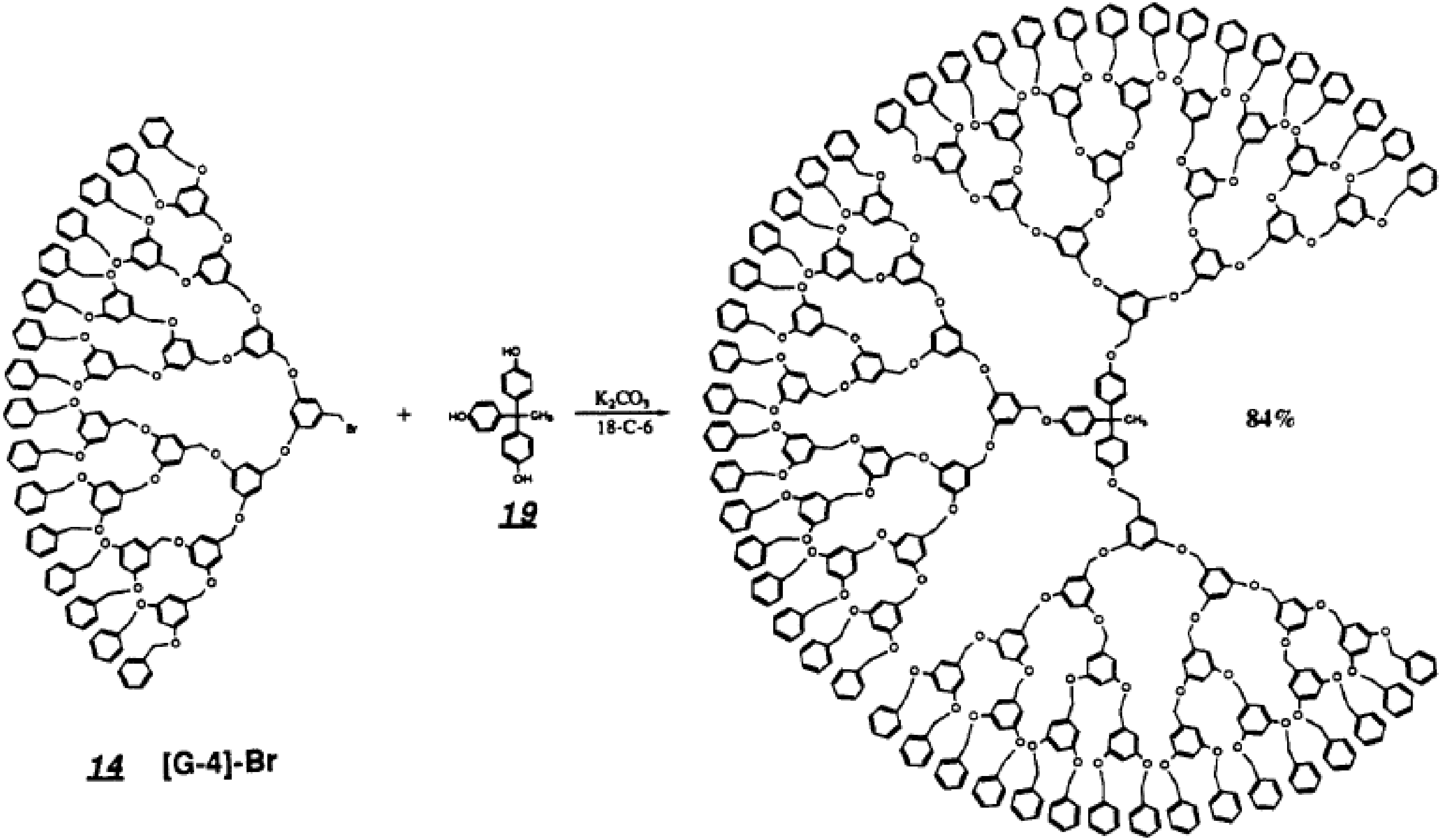
in 1990, Fréchet described the first truly convergent synthesis of dendrons based on

3,5-dihydroxybenzyl alcohol



C. J. Hawker, J. M. J. Frechet
J. Am. Chem. Soc. **1990**, 112, 7638–7647
Grayson, S. M. and Fréchet, J. M. J. Chem. Rev. **2001**, 101, 3819

"Convergent" Approach: From the Outer Units to the Central Point



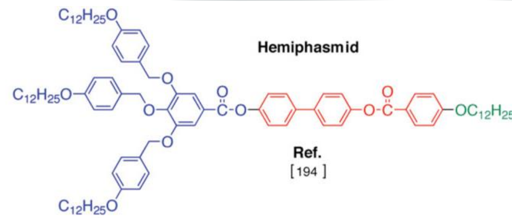
14 [G-4]-Br

20 $[G\text{-}4]_3\text{-}[C]$

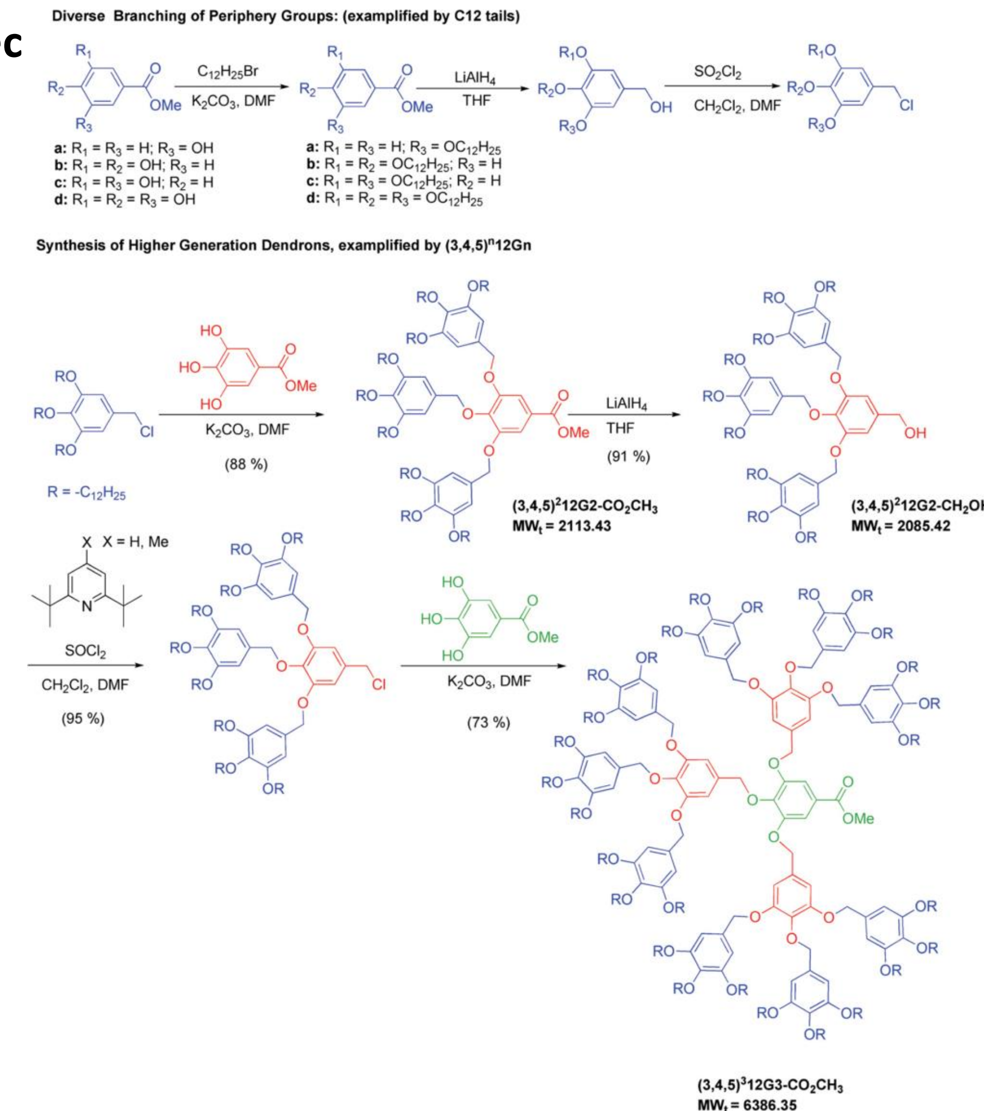
Grayson, S. M. and Fréchet, J. M. J.
Chem. Rev. **2001**, 101, 3819

"Convergent" Approach: From the Outer Units to the Central Point

by **Malthête**



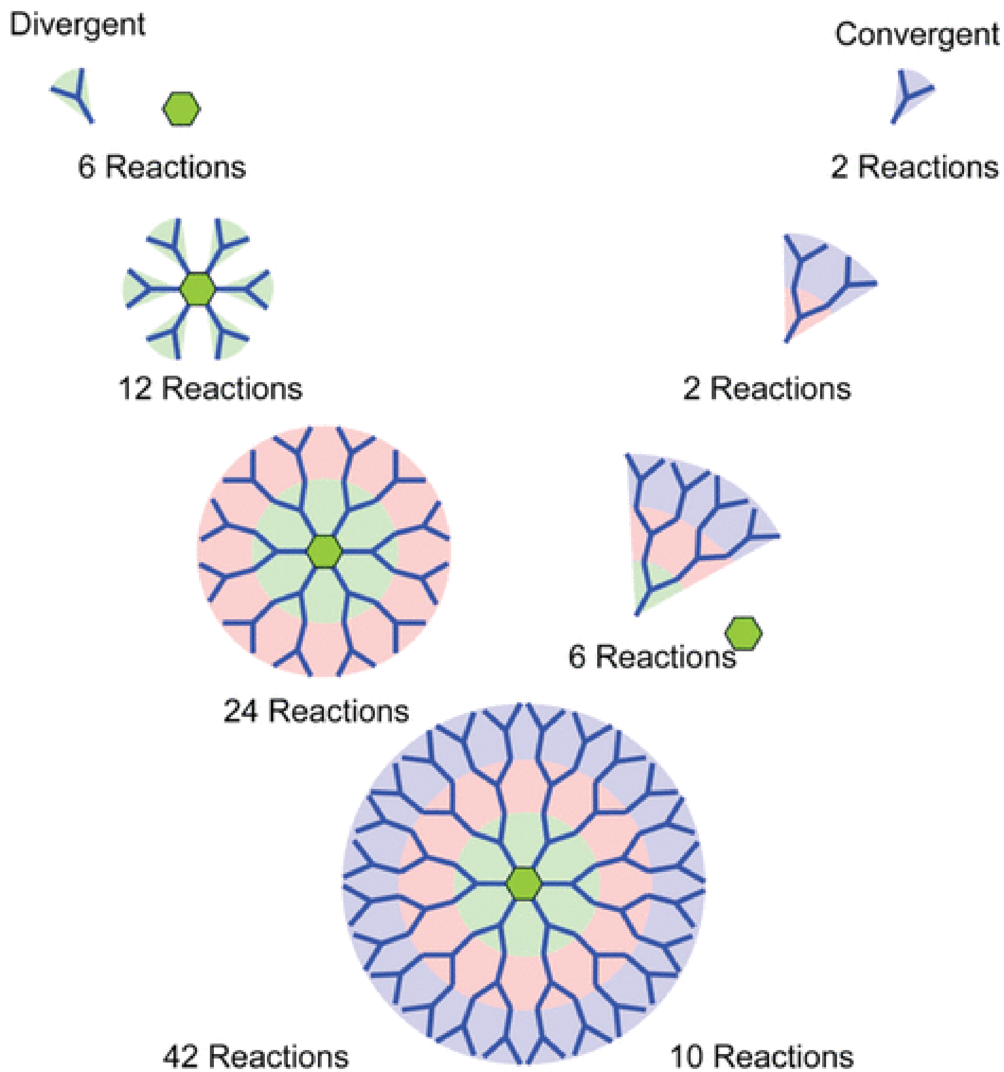
by **Percec**



Inspired by the hemiphasmid molecule **Malthête** in **1986**, and **in 1989 Percec** reported the synthesis of libraries of dendritic macromonomers based on (4-3,4,5)12G1, the **first examples of self-organizable dendronized polymers and the first self-assembling dendrons**

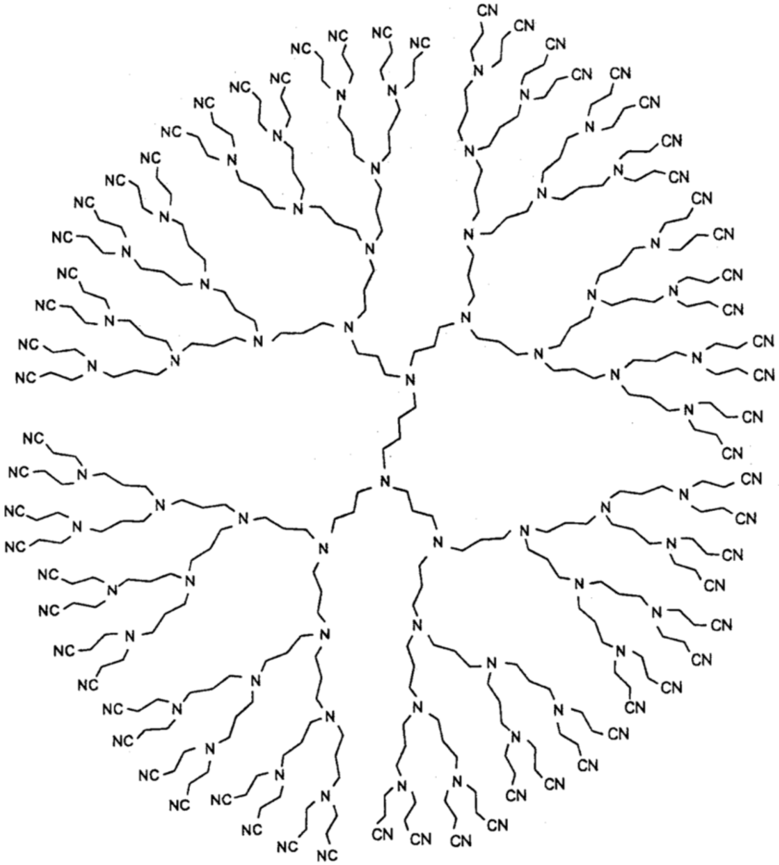
B.M. Rosen, C.J. Wilson, D.A. Wilson, M. Peterca, M.R. Imam, V. Percec
Chem. Rev. **2009**, 109, 11, 6275-6540

Convergent and divergent synthesis of dendrimers and dendrons



Dendrimers

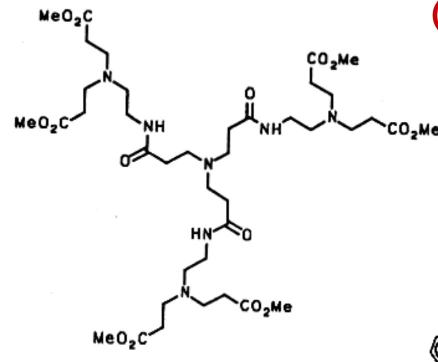
Πολυπροπυλενο ιμιδικό (G4)
PPI



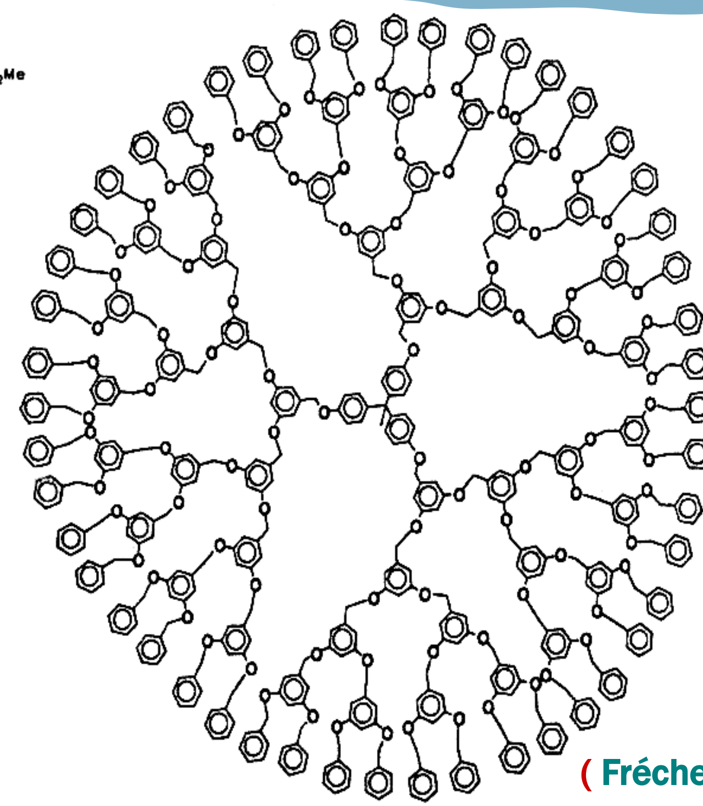
(Vögtle, De Brabander-van, Meijer)

Πολυαμινο-αμιδικό (G2)
PAMAM

(Tomalia)

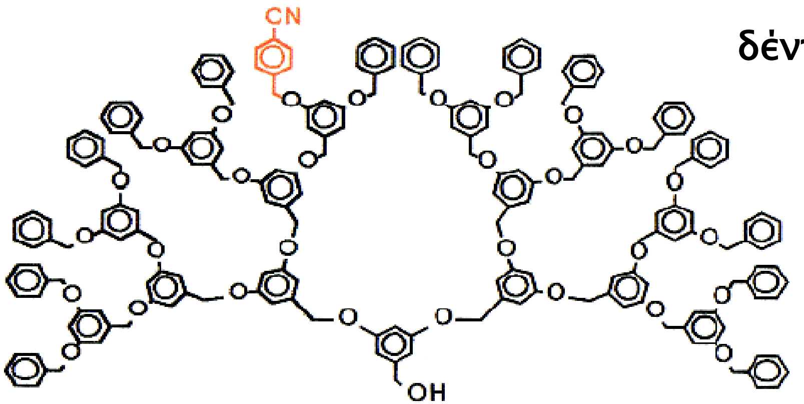


Πολυαιθερικό (G4)



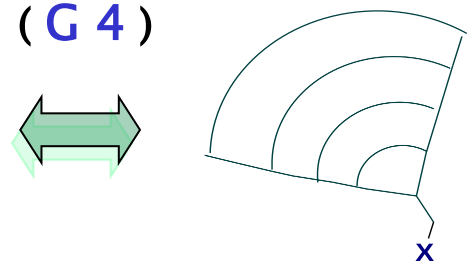
(Fréchet)

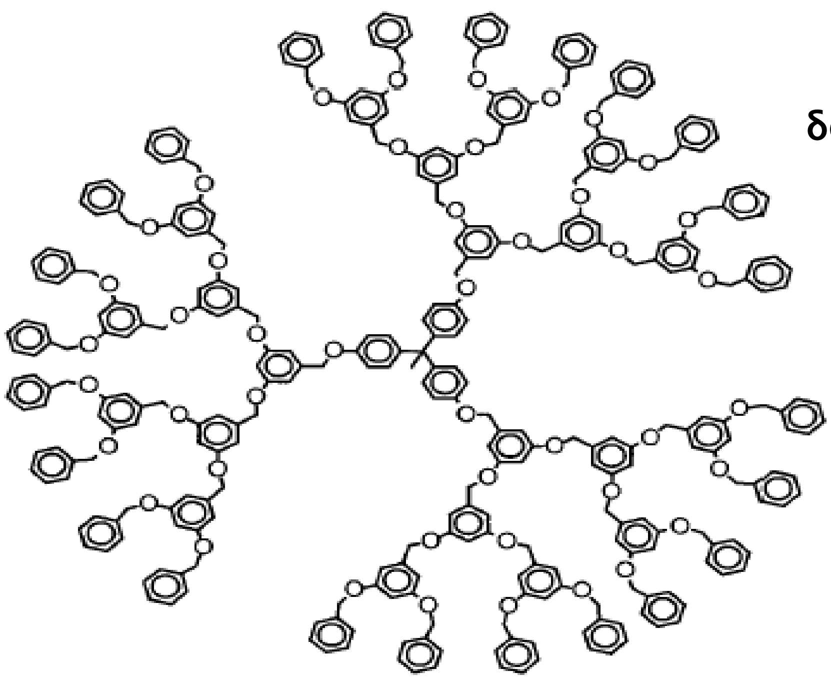
Generation of Dendrons / Dendrimers



δέντρο 4ης γενιάς

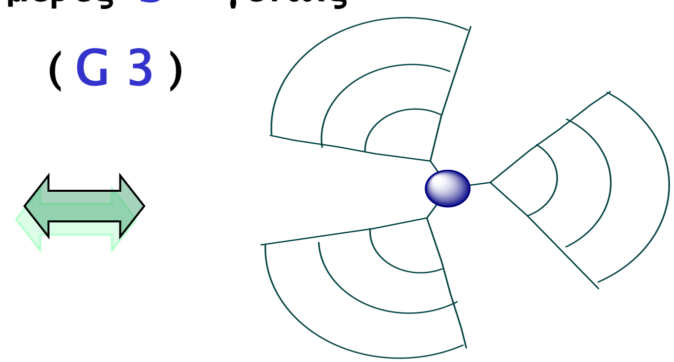
(G 4)



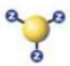
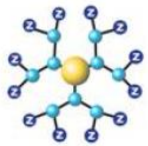
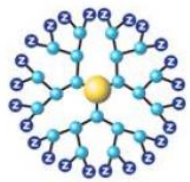
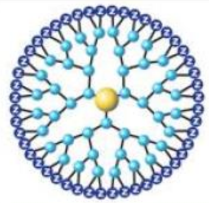
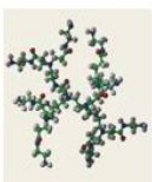
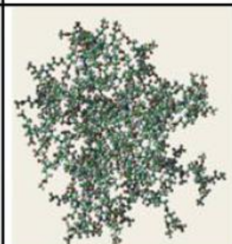
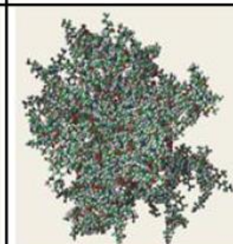


δενδρομερές 3ης γενιάς

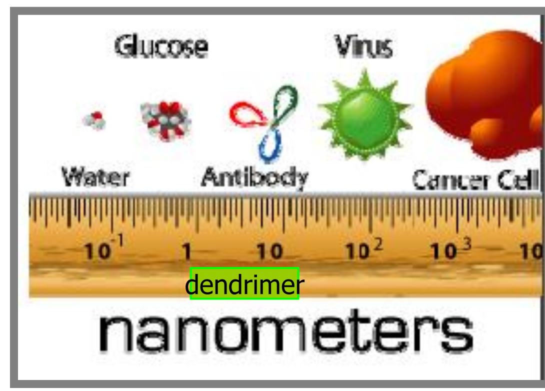
(G 3)



Dendrons & Dendrimers

Generation	G0	G1	G2	G3	G4
# of Surface Groups	3	6	12	24	48
Diameter (nm)	1.4	1.9	2.6	3.6	4.4
2D Graphical Representation					
3D Chemical Structure View					

- Η διάμετρος αυξάνει **γραμμικά** με τη γενιά
- Ο αριθμός περιφερειακών ομάδων **γεωμετρικά** με τη γενιά



- Τα δενδρομερή είναι από τα βασικά πλέον εμπορικά υλικά για **νανοδομημένες εφαρμογές**.
- Στη νανοτεχνολογία συχνά απαιτούνται υλικά **μεγαλύτερα των συνηθισμένων μορίων** αλλά και **μικρότερα των κλασσικών πολυμερών ή κυττάρων**
- **Τα δενδρομερή μπορούν να συντεθούν σε διάφορα μεγέθη ανάλογα με τις εκάστοτε απαιτήσεις**

Dendrons & Dendrimers

Because of their **well-defined**, unique **macromolecular structure**, dendrimers are attractive scaffolds for a variety of high-end applications. Their **highly branched**, **globular architecture** gives rise to a number of interesting properties that contrast those of linear polymers of analogous molecular weight.

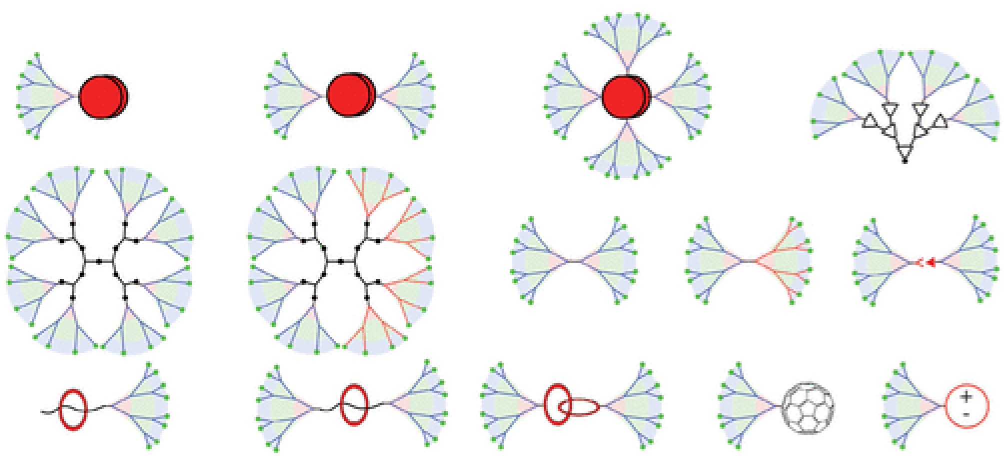
When compared to linear analogues, dendrimers demonstrate significantly **increased solubility** that can be readily tuned by derivatizing the periphery, and they also **exhibit very low intrinsic viscosities**.

Unlike linear polymers, properly designed high generation dendrimers **exhibit a distinct "interior" that is sterically encapsulated within the dendrimer**, for applications like

- **unimolecular container molecules**
- **in drug or gene delivery**
- **as transition state catalysts with high turnover.**
- **in light-harvesting or emission or amplification functions.**

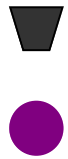
<u>Topologies generated by dendrons</u> having **<u>Covalent, non-covalent and ionic interactions</u>**

polycycles (red discs),
identical or different (Janus) dendrons,
pseudorotaxanes, rotaxanes, catenanes,
fullerenes,
ionic liquids (red circle with ± inside).

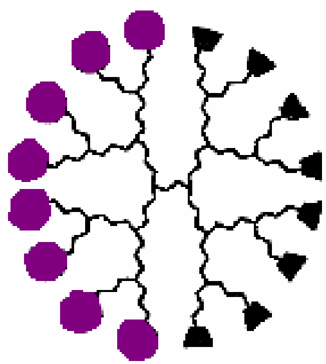


Functional Dendrimers

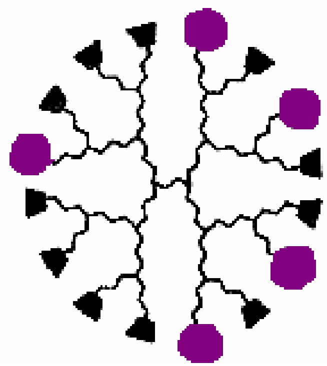
Functional Groups located at the :
(A) Periphery
(B) Center
(C) Inner Parts



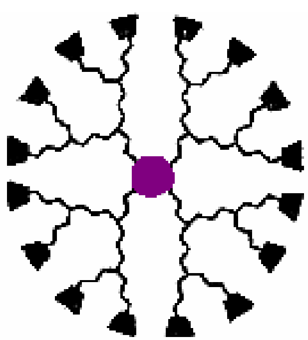
(A)



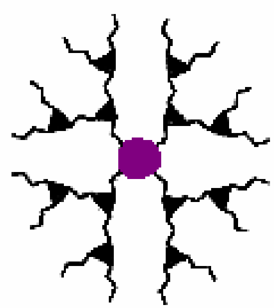
(A)

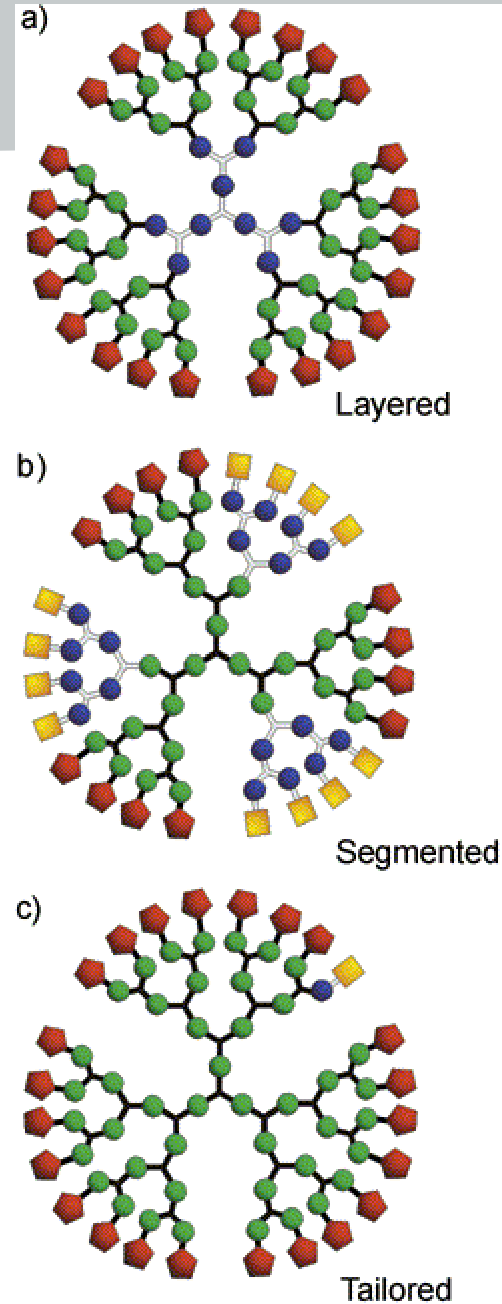


(A+B)

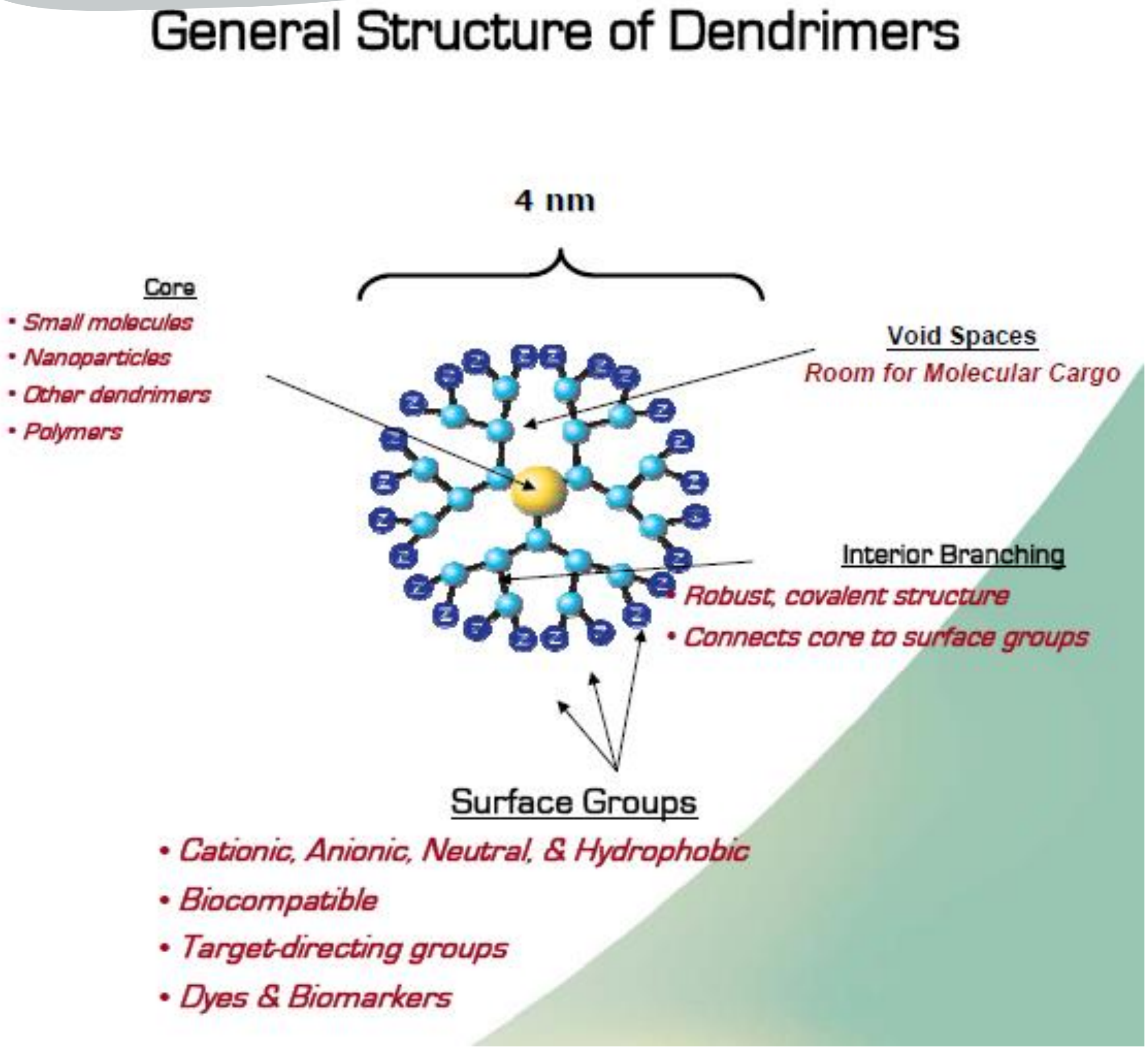


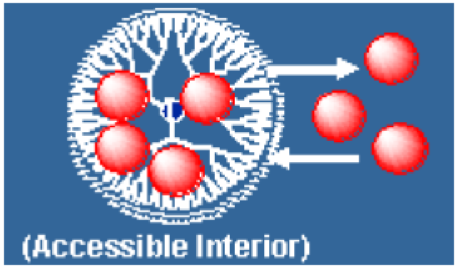
(A+C)



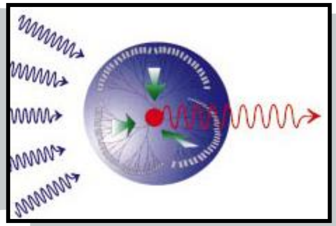


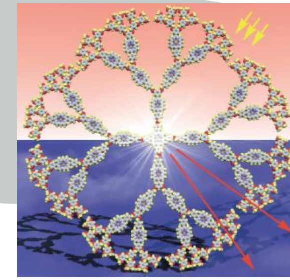
Dendrons & Dendrimers



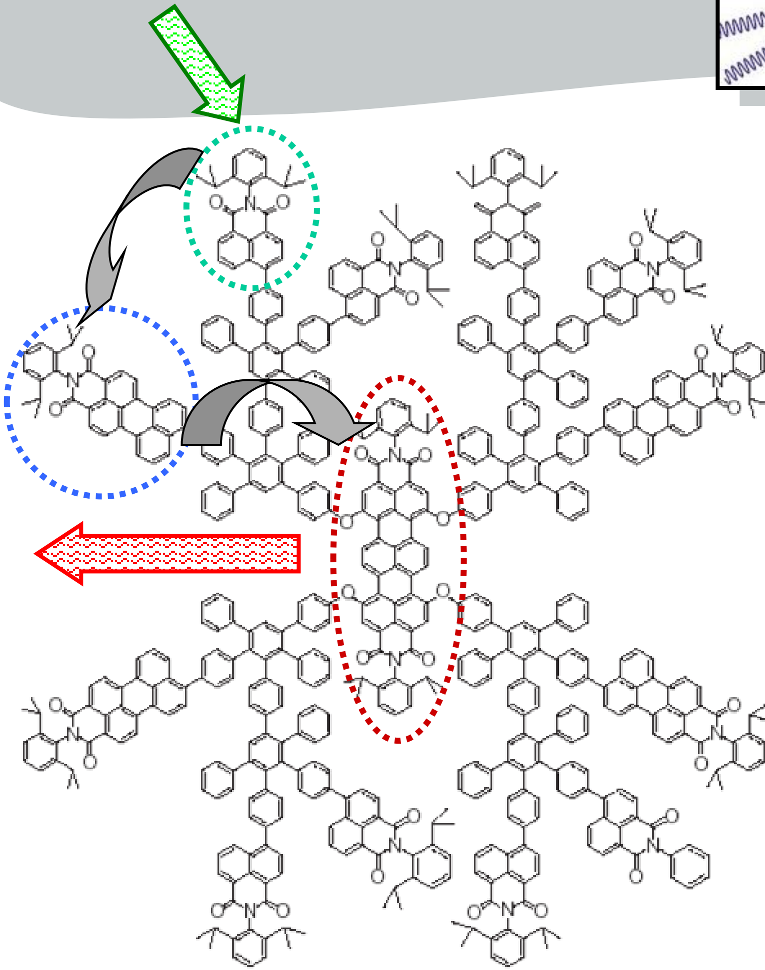


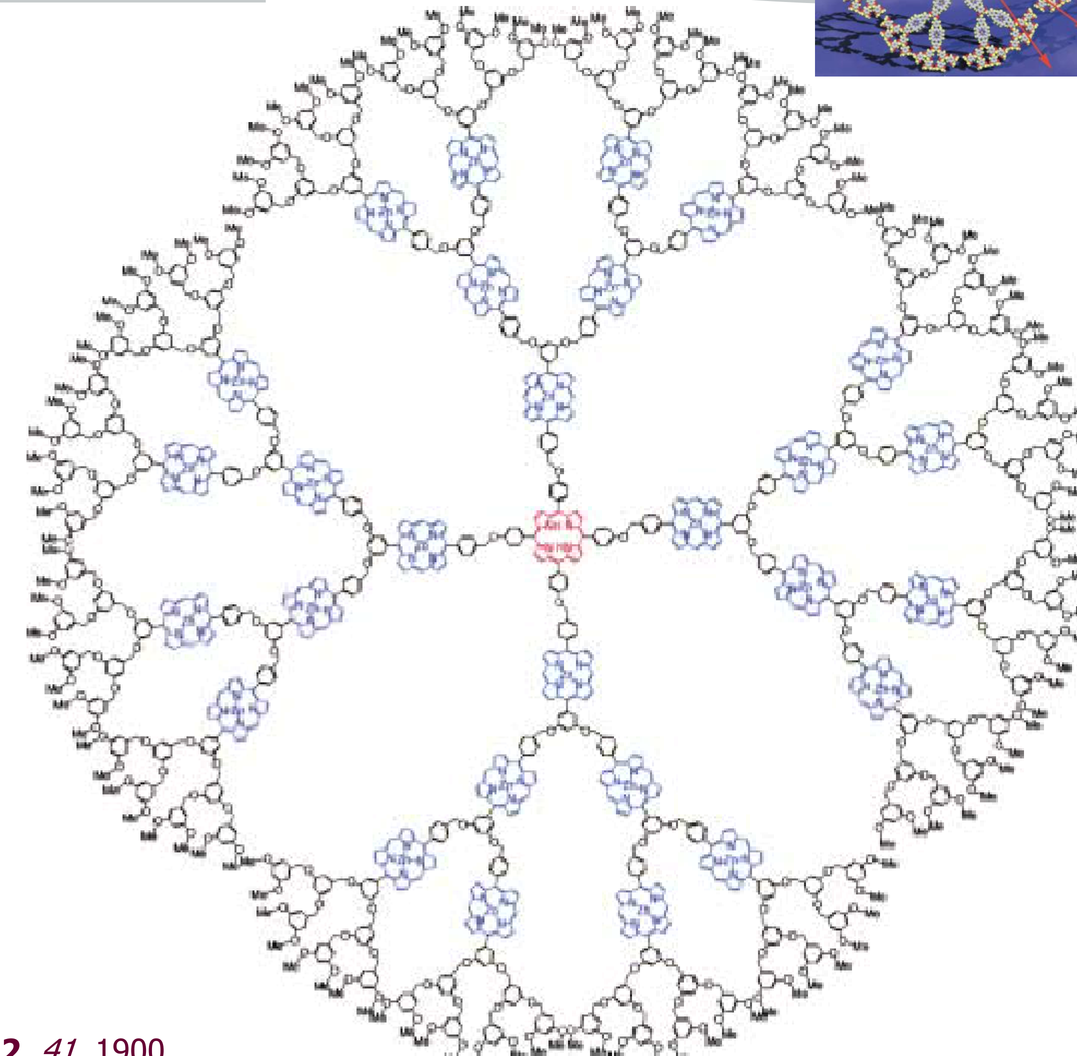
Light Harvesting





(7P-Zn)4 / P-FB



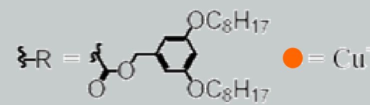


Excitation of the peripheral **NMI** &/or
in the scaffold **PMI** chromophores
increases by a factor of **3** the emission of **TDI**

T.Weil; E.Reuther; K.Müllen *Angew.Chem.Inter.Ed.* **2002**, *41*, 1900
A.Grimsdale; T.Vosch; M.Lor; M.Gotlet; S.Habuchi; J.Hofkens;
F.C.DeSchryver; K.Müllen *J. Lumin.* **2005**

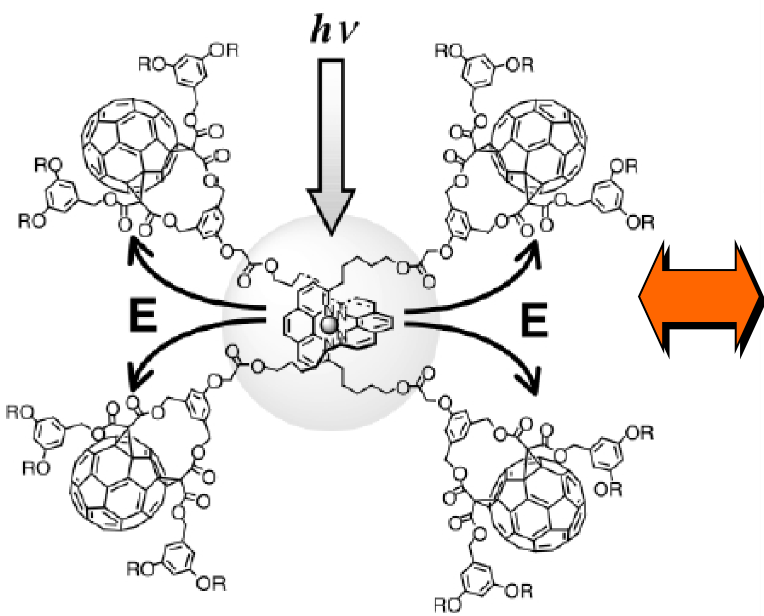
M-S.Choi; T.Aida; T.Yamazaki;
I.Yamazaki *Chem. Eur.J.* **2002**, *8*, 2667

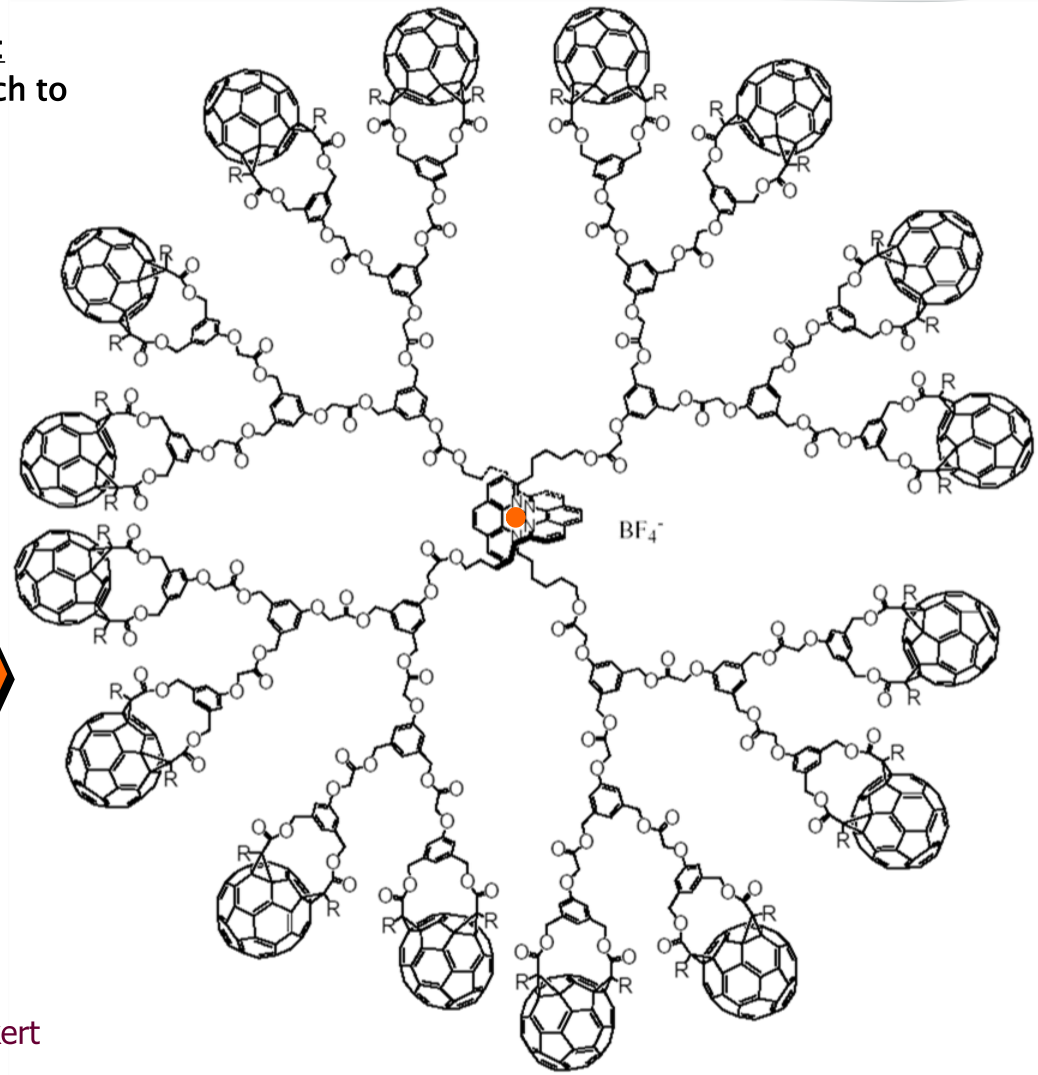
Dendritic Black Box



<u>Inaccessible dendritic phenanthroline–Cu^{2+} core:</u>
the peripheral fullerene units prevent its approach to the electrode thus no oxidation occurs.

<u>Strong Shielding Effect:</u>
only a small portion of light reaches the core & that returns back to the fullerene units via energy transfer





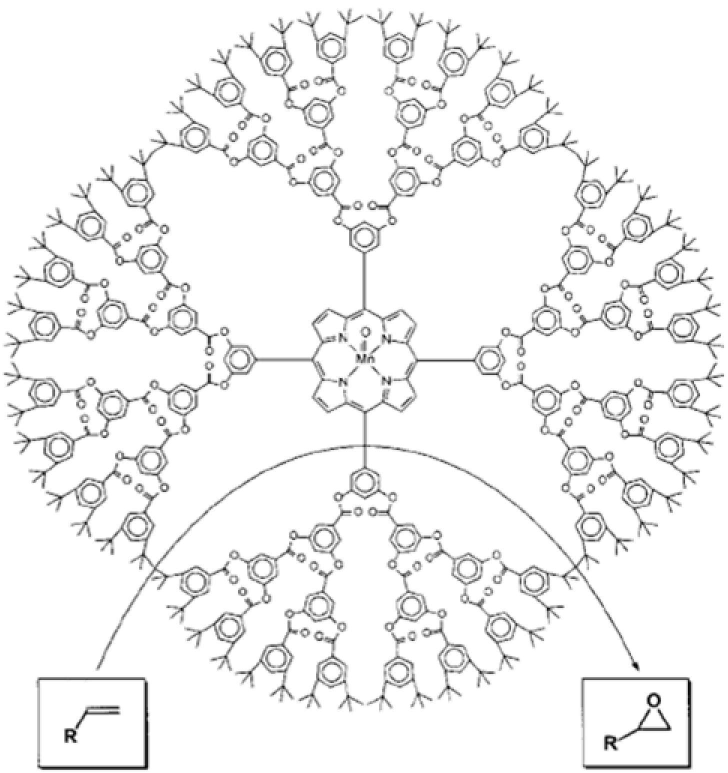
J-F. Nierengarten; N. Armanoli; G. Accorsi; Y. Rio; J-F. Eckert
Chem. Eur. J. **2003**, *9*, 36
N. Armanoli; C. Boudon; D. Felder; J-P. Gisselbrecht; M. Gross; G. Marconi; J-F. Nicoud; J-F. Nierengarten; V. Vicinelli
Angew. Chem. Inter. Ed. **1999**, *38*, 3730

CaTalysTs

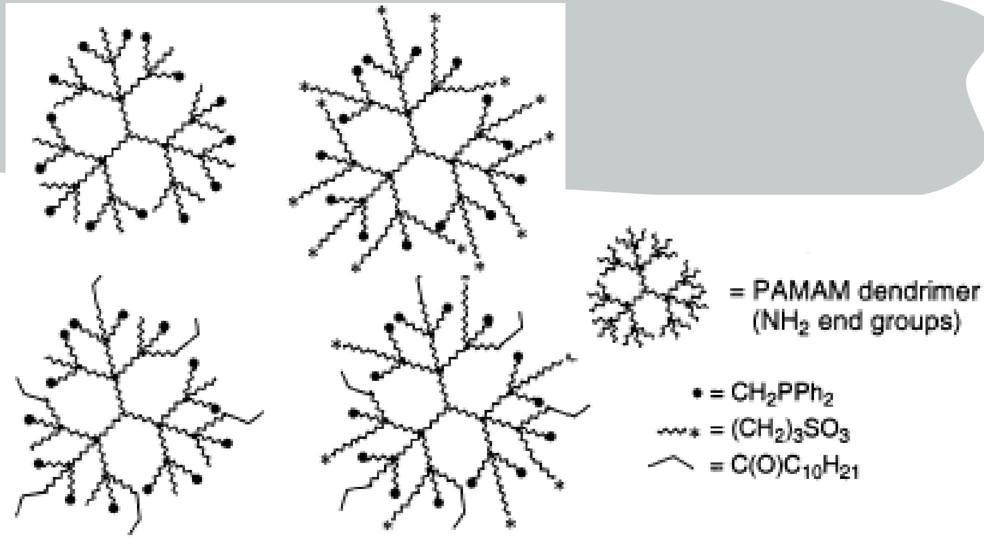
Shape Selective Olephine Epoxidation of Alkenes:

Manganese(III) porphyrine core = catalyst

Oxidetively inert polyphenylester dendrons

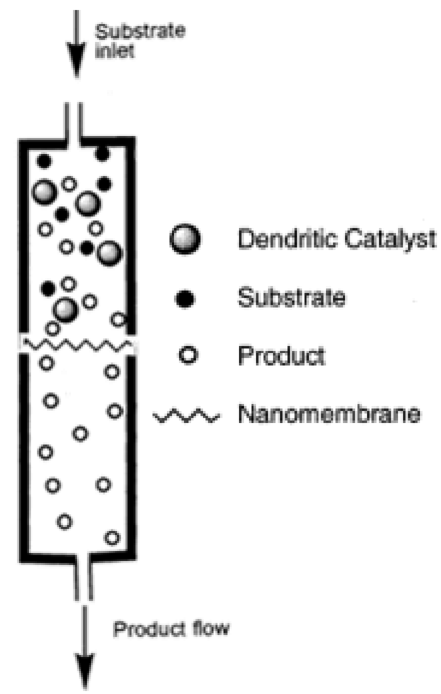


R.van Heerbeek; P.C.J. Kamer; P.W.N.M. van Leeuwen; J.N.H. Reek, *Chem. Rev.* **2002**, *102*, 3717



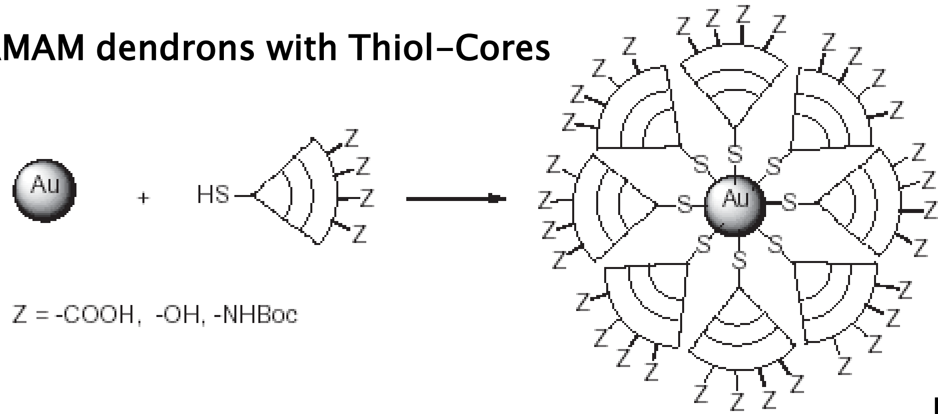
Water Soluble PAMAMs-phosphine ligands their Rh-Complexes are used for Hydroformylations

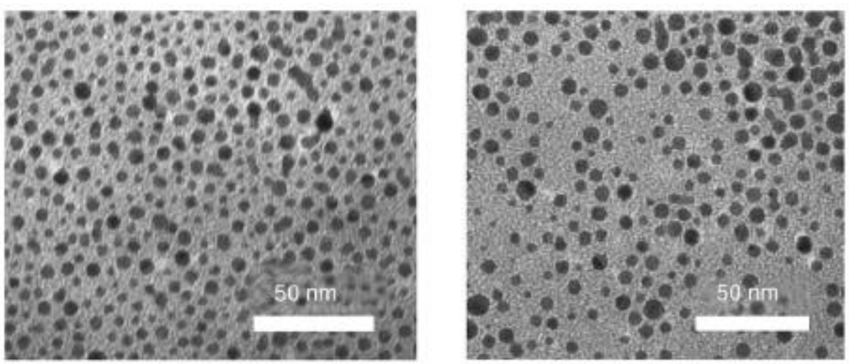
Membrane Reactor



NanoParticles

PAMAM dendrons with Thiol-Cores

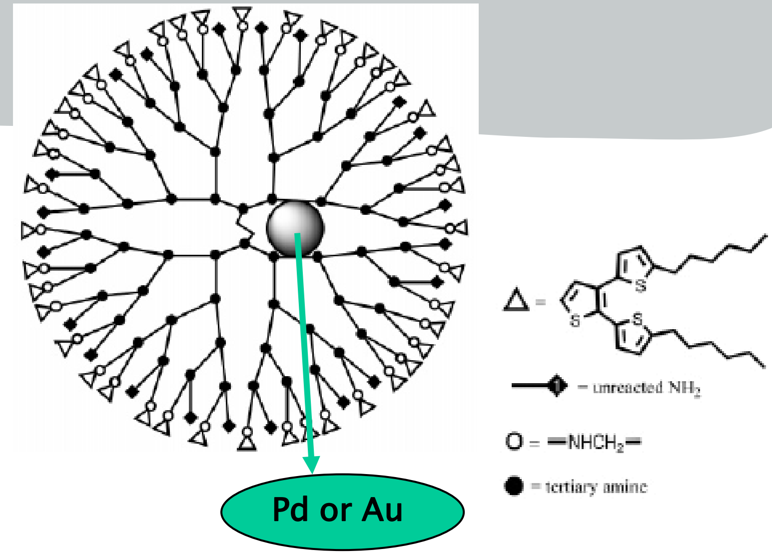




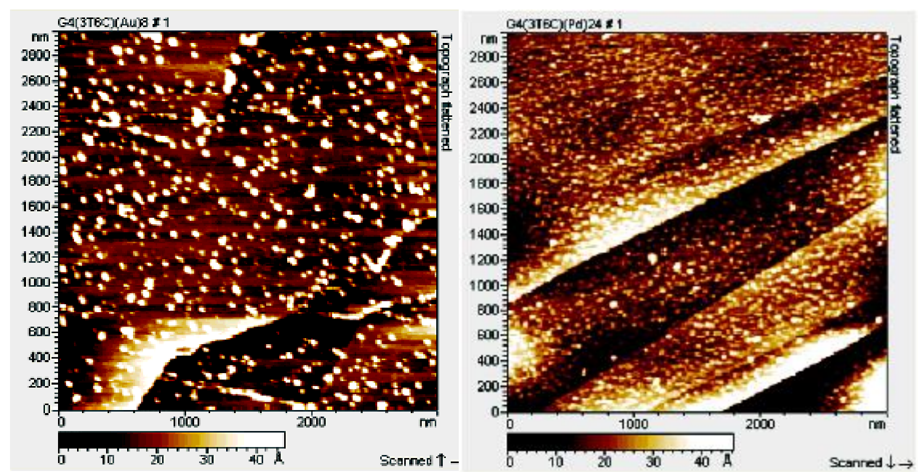
TEM images of gold-**G2**-COOH (left)
& gold-**G3**-COOH (right).

B. Huanga, D.A. Tomalia *J.Lumin.* **2005**

Thiophene-Jacked PAMAM dendrimers



Hybrid Nanoparticles by the "ship-in-a-bottle" approach

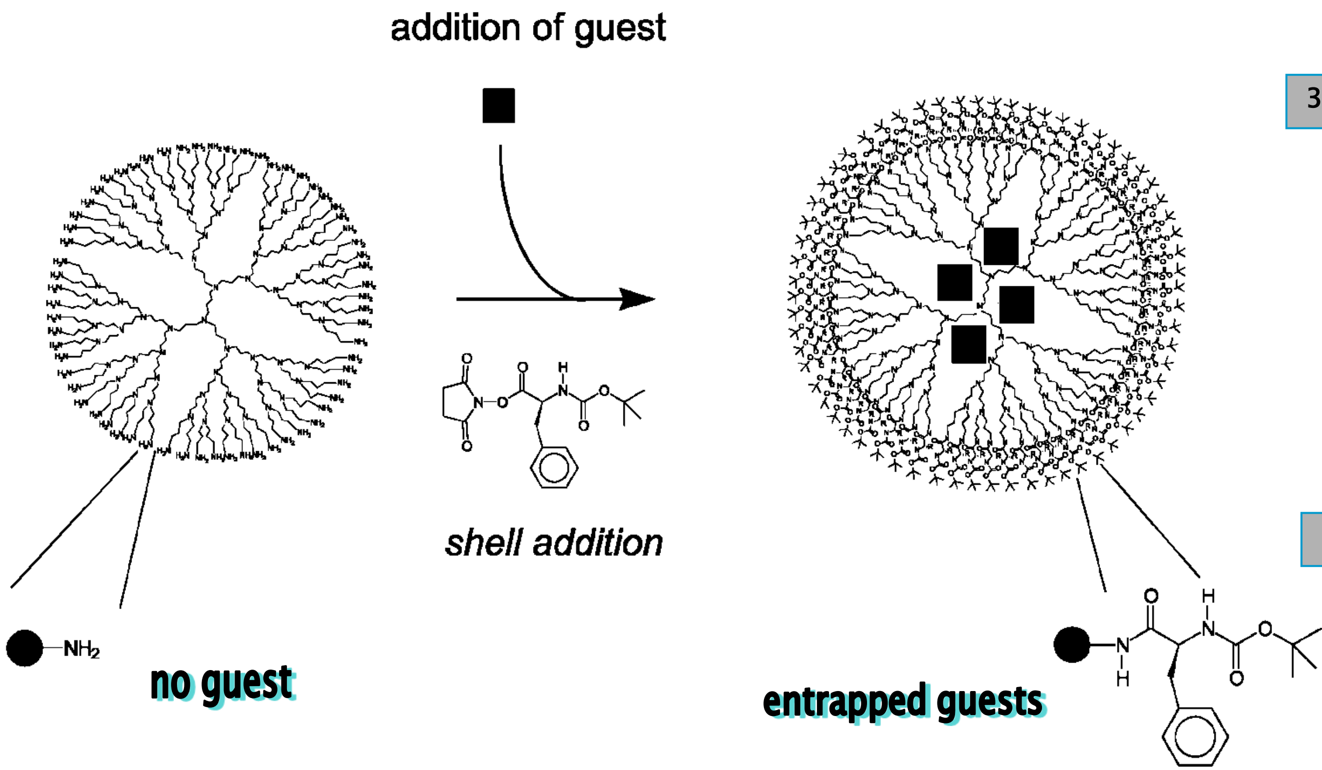


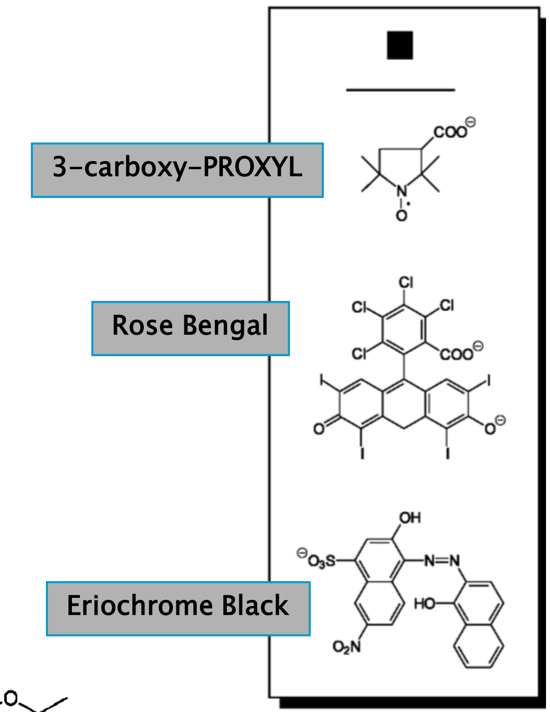
$G_4(3T6C)(Au)_8$ $G_4(3T6C)(Pd)_{24}$

S.Deng; J.Locklin; D.Patton; A.Baba; R.C.Advincula
J.Am.Chem.Soc. **2005**

Host Guest Systems - “Dendritic Box”

poly(propylene imine) / NH-R = DAB-dendr-(NH-R)n

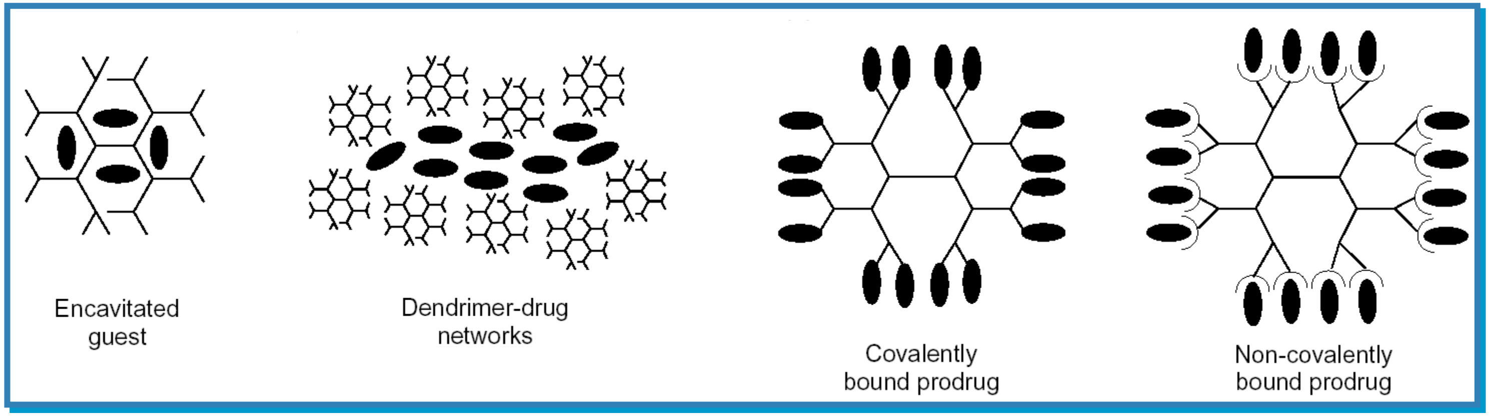




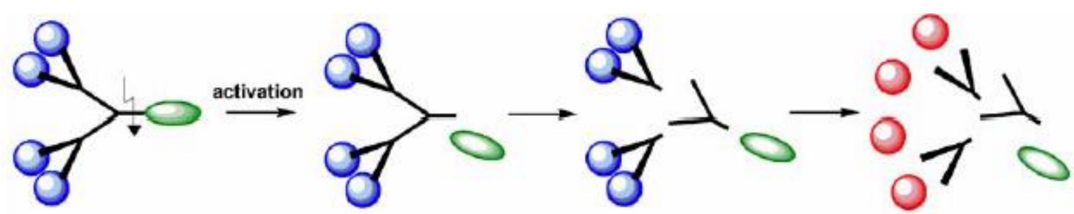
- Solid shell / flexible core model
- Number of guests proportional to the dendrimers generation
- Selective liberation e.g. after hydrolysis of the shell

M.W.P.L. Baars; E.W.Meijer Top. Curr. Chem. **2000**, *210*, 131

Bio-Applications / Drug Delivery

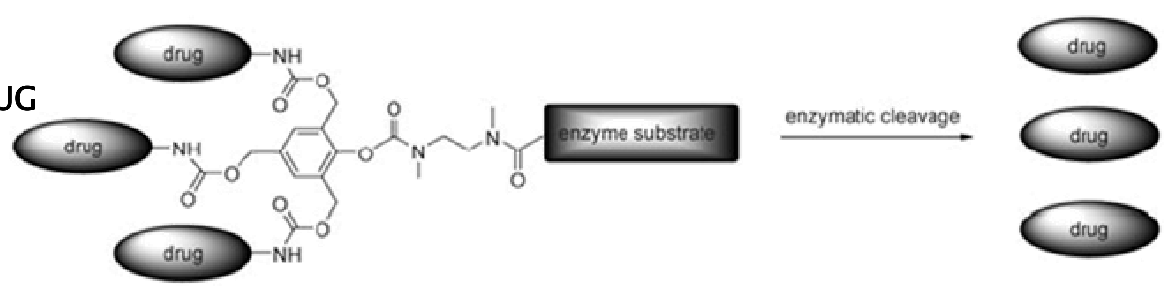


M.J. Cloninger *Curr. Opin. Chem. Biol.* **2002**, *6,* 742



Triggered Activation & Release of end-groups

Single-Triggered TRIMERIC PRODRUG

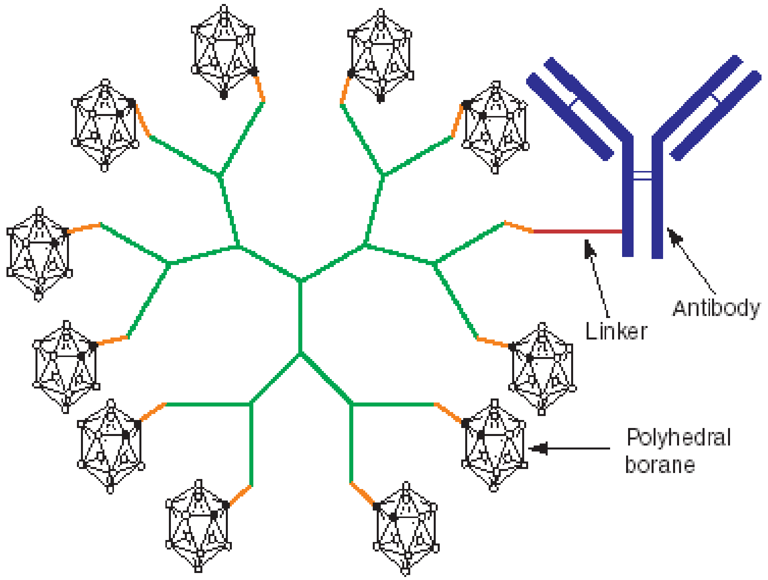


K. Haba; M. Porkov; M. Shamis;
R.A. Lerner; C.F. Barbas III; D. Shabat
Angew.Chem.Inter.Ed. **2005**, *44*, 716

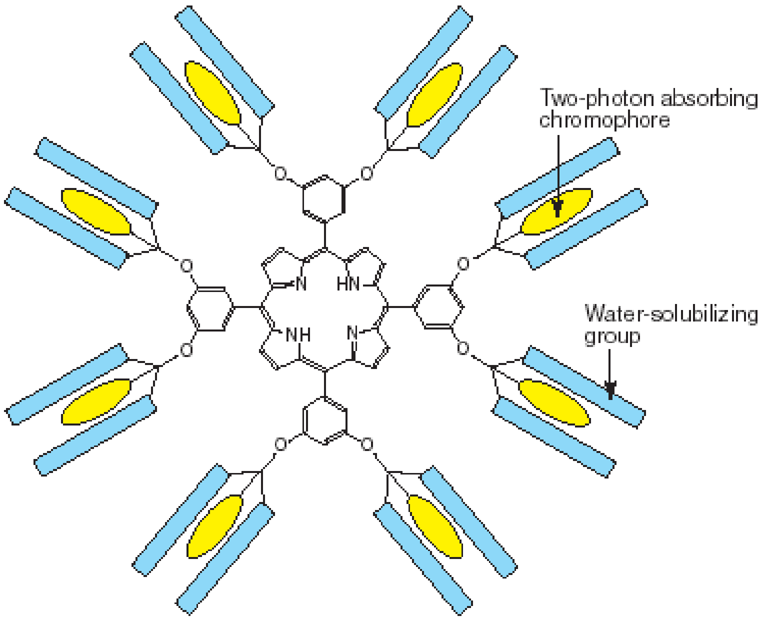
Bio-Applications / Drug Delivery

Biocompatible Dendrimers: PAMAM, Polylysine, Polyester(glycerol-succinic acid), Polyglycerol

BORON NEUTRON CAPTURE THERAPY
antibody targeted dendritic boron carrier



PHOTODYNAMIC THERAPY
two-photon excitation with near infrared lasers

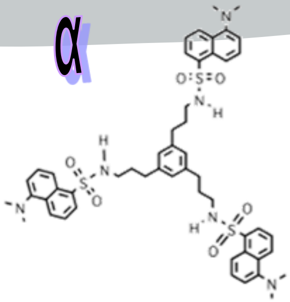


E.R. Gillies, J.M.J. Fréchet *DDT* **2005**, *10*, 35

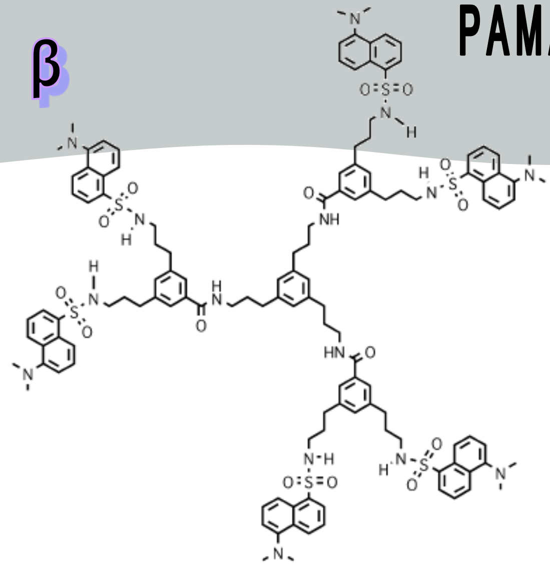
Bio-Applications

PAMAM cores

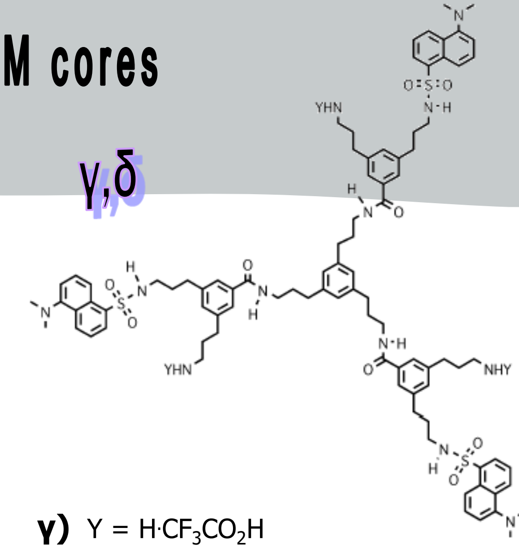
α



β

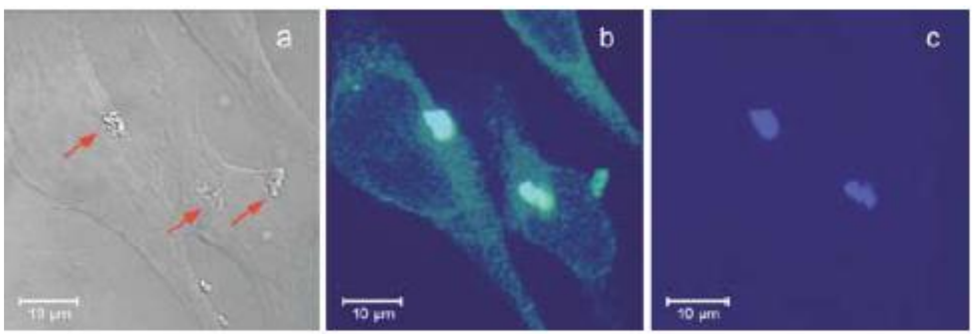


γ,δ

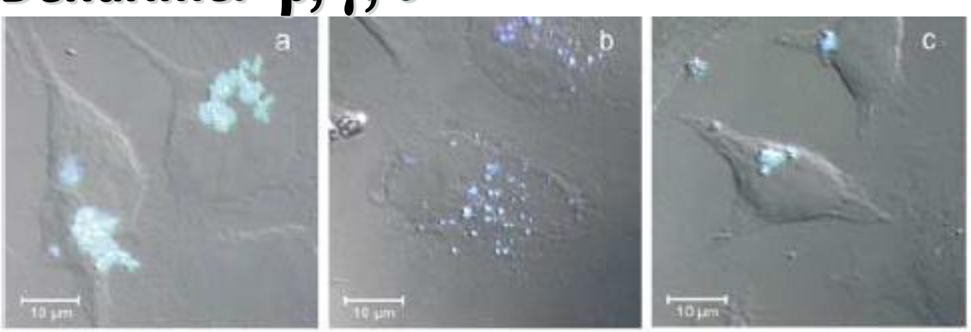


γ) Y = H·CF_3CO_2H
δ) Y = -CO-CH_2NH(H·CF_3CO_2H) -CH_2CH_2-NH(H·CF_3CO_2H)

Dendrimer α



Dendrimer β, γ, δ

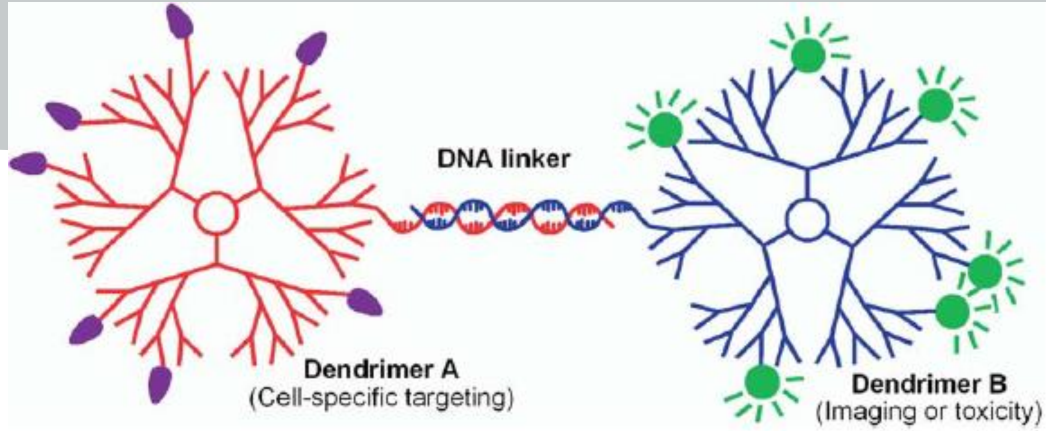


Confocal Fluorescence Microscopy (dansyl units excited at 364nm) & Differencial Interference Contrast Images for HeLa cells

- human breast cancer cell line MCF-7 used for cytotoxisity evaluations
- non-charged dendrons (protected or dansylated) = non-toxic but bioavailable (cellular up taken)
- diamine dendrimers = non-toxic

S. Fuchs; T. Kapp; H. Otto; T. Schöneberg; P. Franke; R. Gust; A.D. Schlüter *Chem. Eur. J.* **2004**, *10*, 1167

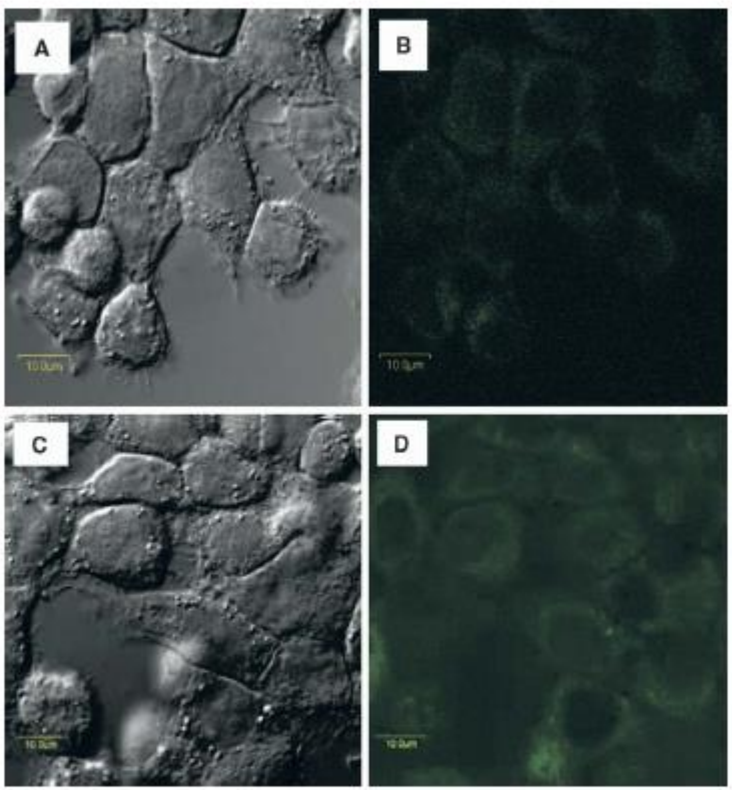
Bio-Applications



PAMAM cores

DNA linker =
5'-phosphate-modified
34-base-long oligonucleotide

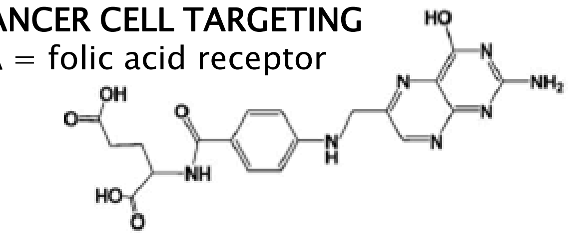
DIC – FLUORESCENT images for KB cells



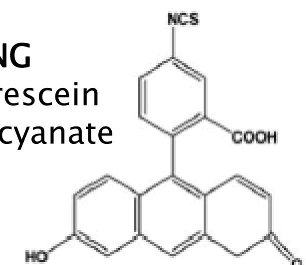
control cells

after 1hr treatment with the
DNA linked dendrimer clusters
FITC signals are seen inside the cells

CANCER CELL TARGETING
FA = folic acid receptor



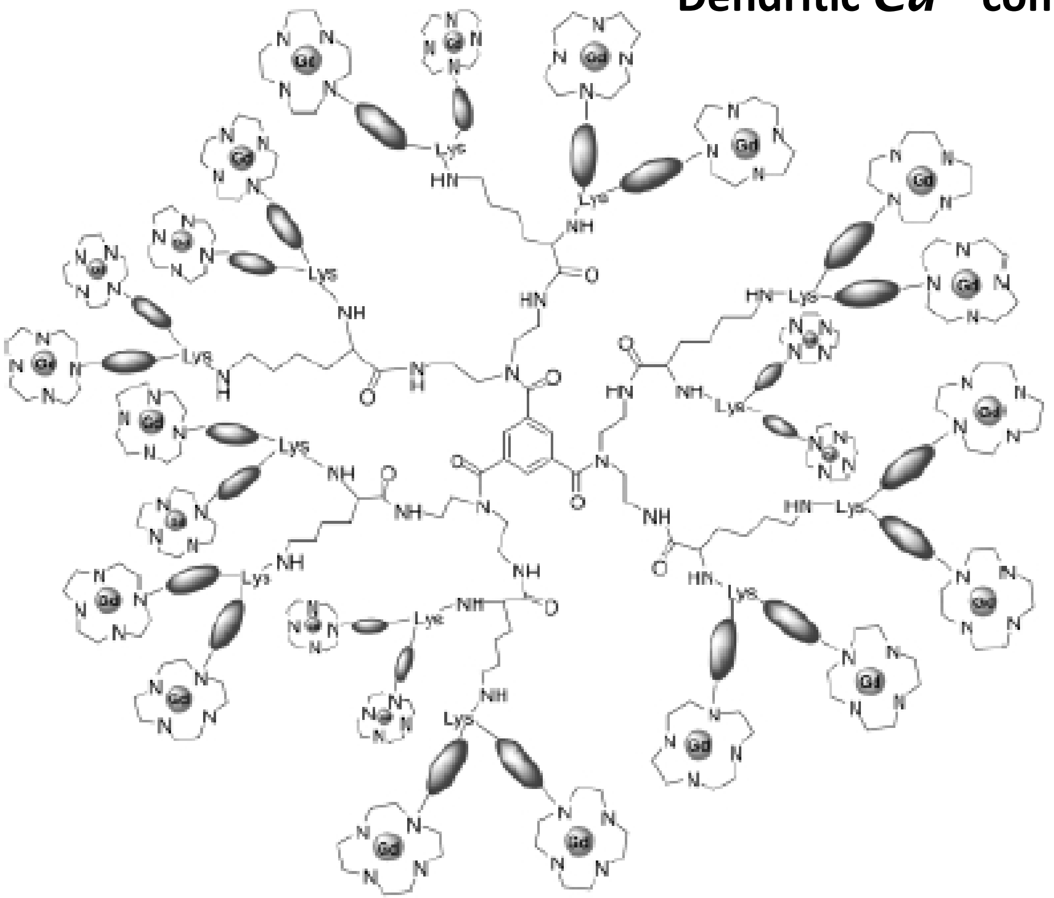
IMAGING
FITC = fluorescein
isothiocyanate

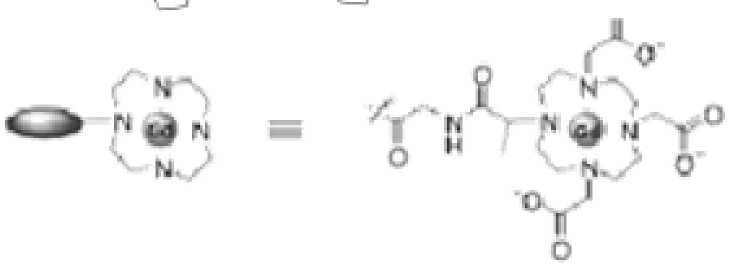


S.-G. Sampathkumar; K. J. Yarema *Chem. Biol.* **2005**, *12*, 5
Y. Choi; T. Thomas; A. Kotlyar; M. T. Islam; J. R. Baker, Jr. *Chem. Biol.* **2005**, *12*, 35

Medical Diagnostics - Magnetic Resonance Imaging (MRI)

Dendritic *Cd* – complex gadomer





Contrast-enhanced magnetic resonance image of the peripheral blood vessels of a dog after injection with gadomer
(dose: 50 mol per kg bodyweigh, ~ 3 min post injection).

S.-E. Stiriba; H. Frey; R. Haag,
Angew. Chem. Int. Ed. **2002**, *41*, 1329

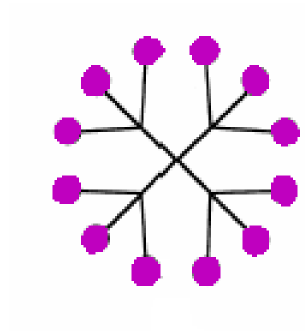
MetalloDendrimers

Metal – Ions =

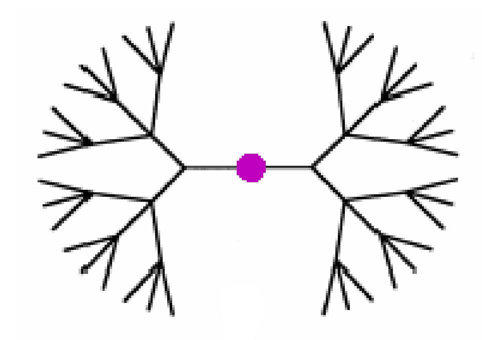
incorporated in the:

(A) Periphery
(B) Center
(C) Branching Points
(D) Repeating Units

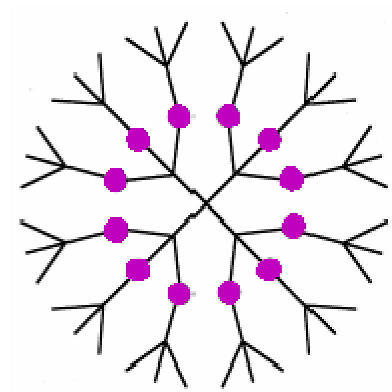
(A)



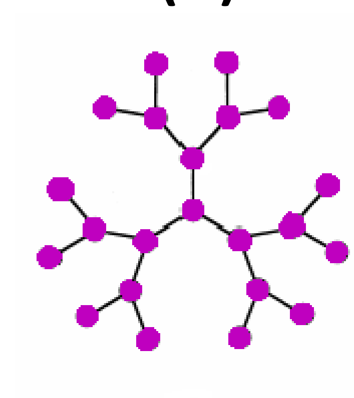
(B)



(C)

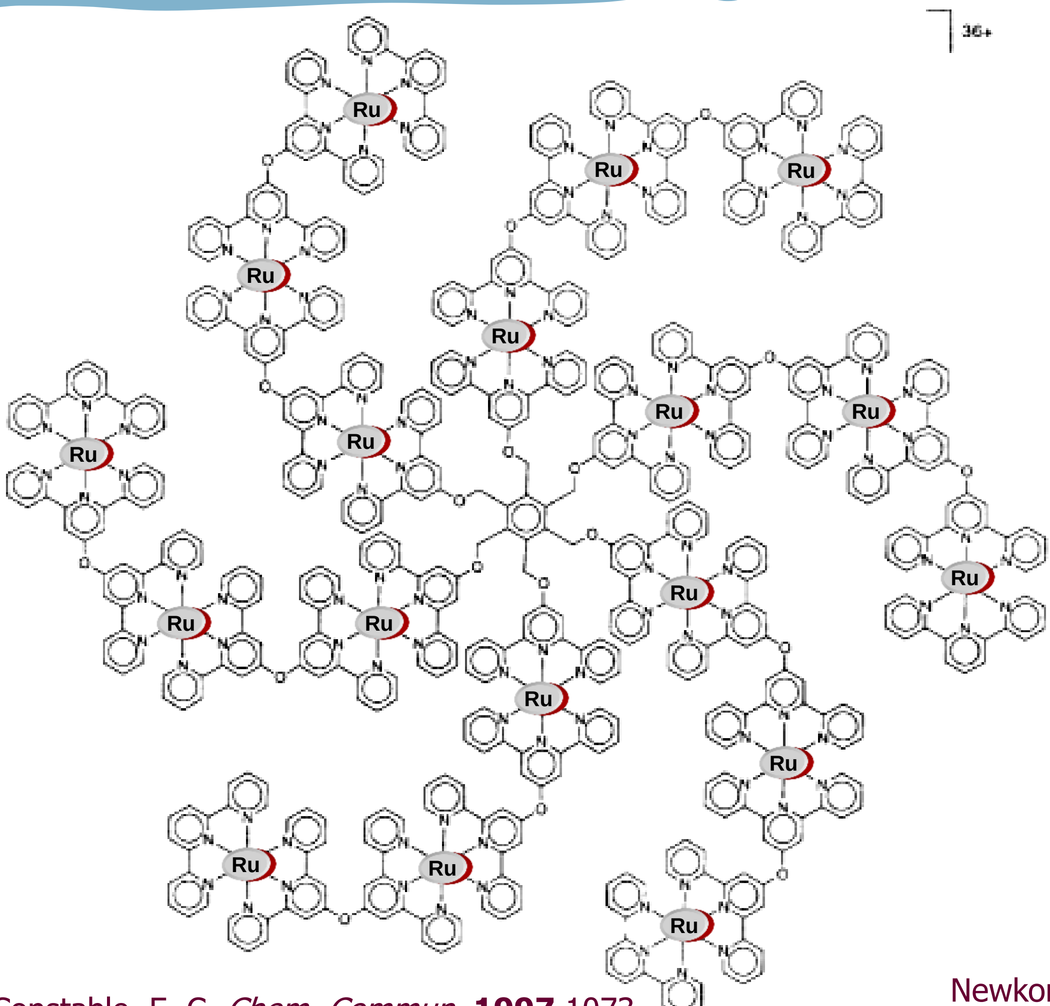


(D)



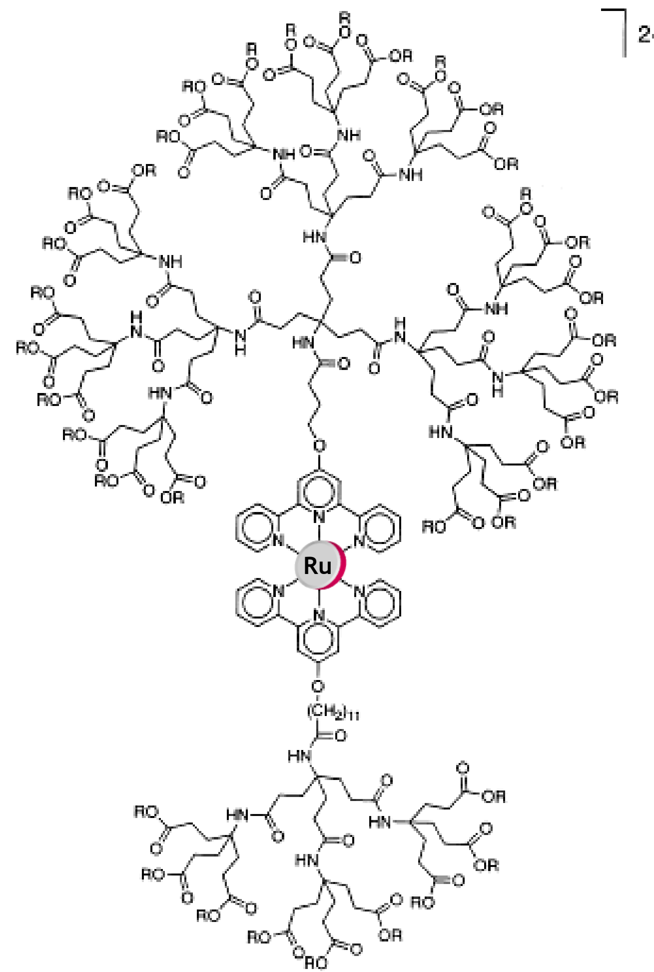
MetalloDendrimers

Metals as BRANCHING POINTS



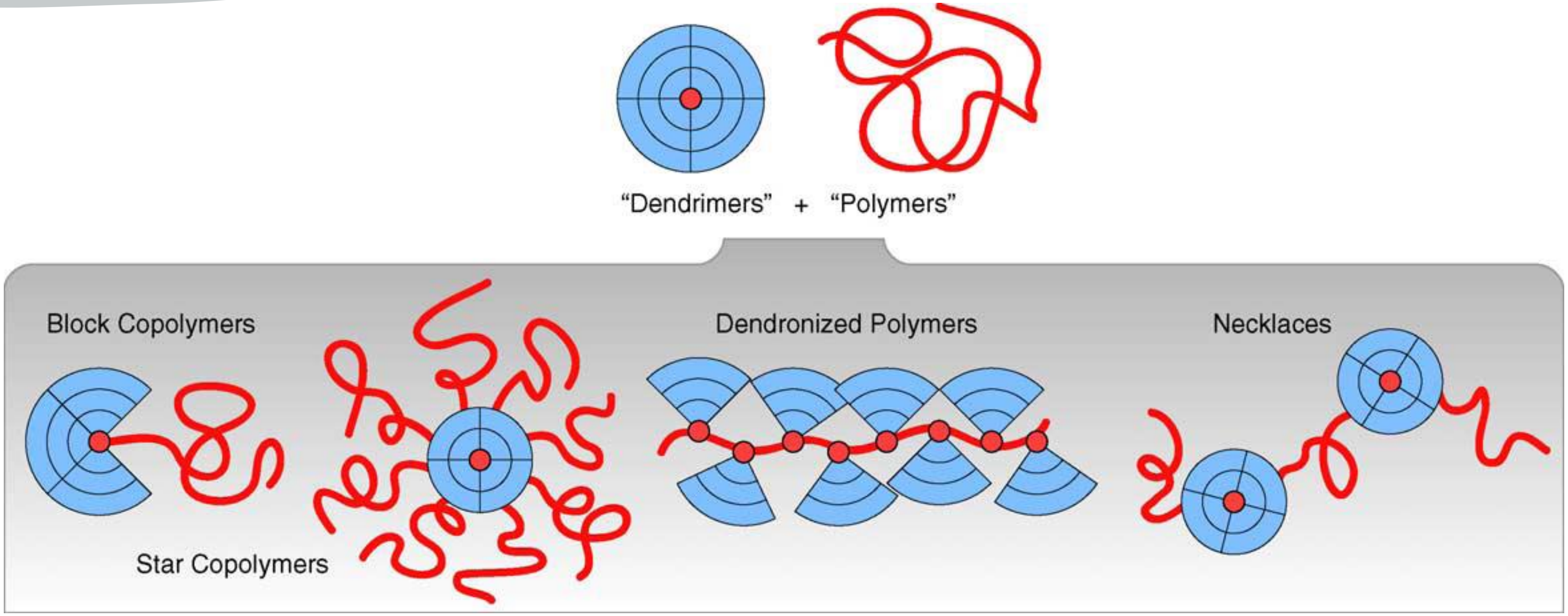
Constable, E. C. *Chem. Commun.* **1997**,1073

Metal in the CORE



Newkome, G. R. et. al. *Angew. Chem. Int. Ed.* **1995**, *34, 2023*

Dendrimers + Polymers

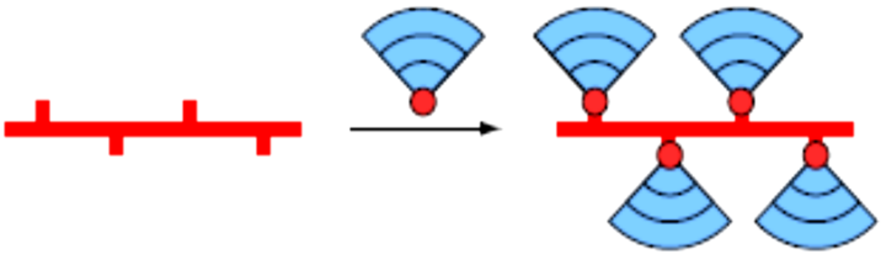


The first report on such a macromolecule which at that time was called "Rod-shaped Dendrimer" goes back to Tomalia in **1987**
followed by Percec's polymer with "tapered side chains" in **1992**
In **1994** the potential of these polymers as cylindrical nanoobjects was recognized.

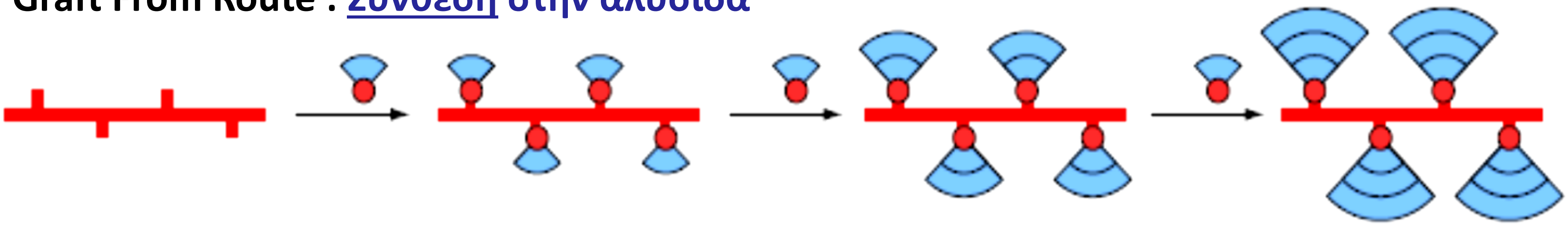
Finally named "**dendronized polymers**" by Schlüter in **1998**.

Dendronized Polymers or Side Chain Dendritic Polymers (SCDPs)

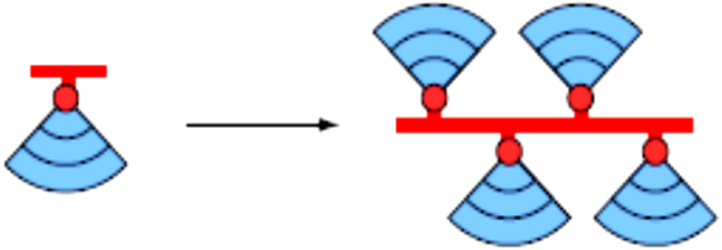
Attach to Approach / Graft To Route : Σύνδεση στην αλυσίδα



Graft From Route : Σύνθεση στην αλυσίδα

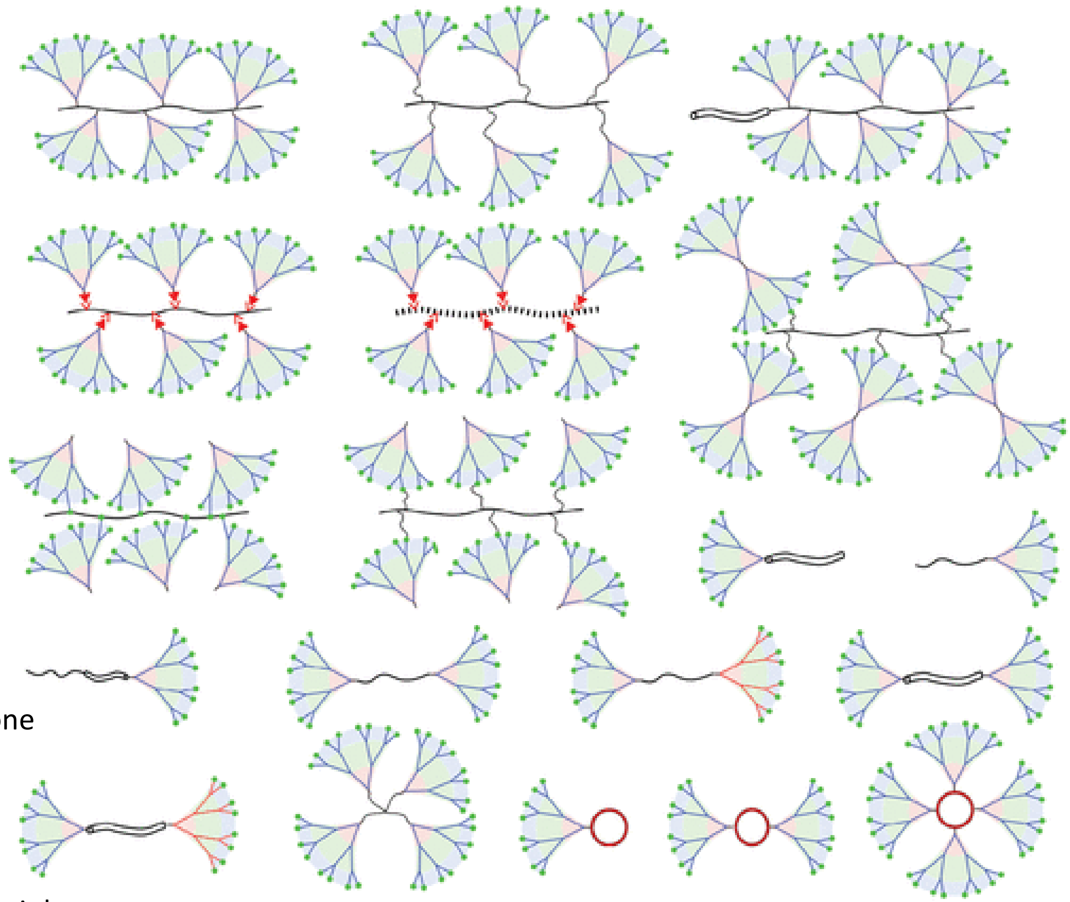


Macromonomer Route : Πολυμερισμός δενδρόμορφων(δενδριτικών) μακρο-μονομερών



Schlüter,D.A; Rabe,J.P. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 864
Frauenrath, H. Prog. Polym. Sci. **2005**, 30, 325–384

Topologies generated by dendronized linear, star, and macrocyclic polymers

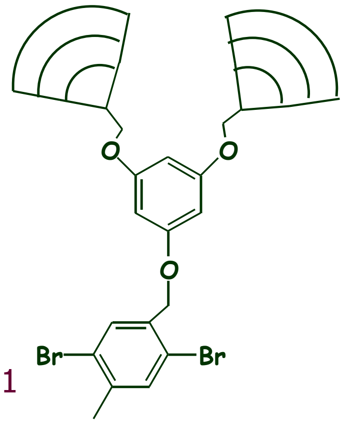


- dendron-jacketed polymers : dendron attached to the backbone
- dendron jacketed polymers connected by a flexible spacer
- dendron-jacketed block-copolymers
- noncovalently dendron-jacketed polymers
- dendronized supramolecular polymers
- polymers jacketed with dendrimers connected via dendron periphery
- polymers jacketed with dendrons connected via dendron periphery
- polymers jacketed with dendrons via dendron periphery through a flexible spacer
- rigid polymers fuctionalized at one chain end with a dendron
- flexible polymers functionalized at one chain end with a dendron
- block-copolymers of rigid and flexible segments dendronized at one chain end
- flexible polymers symmetrically functionalized with dendrons at both chain ends
- flexible polymers asymmetrically functionalized with dendrons at both chain ends
- rigid polymers symmetrically functionalized with dendrons at both chain ends
- rigid polymers asymmetrically functionalized with dendrons at both chain ends
- dendronized stars
- dendronized macrocycles

Dendrons (wedges), covalent polymers (long wavy lines), supramolecular polymers (dashed lines), rigid rods segments (wavy tubes), macrocycles (red rings), noncovalent interaction (red triangle and chevron), and their connectivities are pictured.

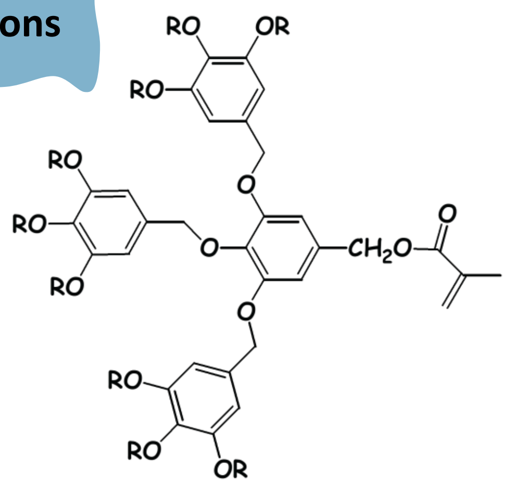
Dendronized Macromonomers

Macromonomers for Polycondensations



Bo,Z; Schlüter,A.D.
Macromol. Rapid Commun. **1999**, *20*, 21

Macromonomers for Radical Polymerizations

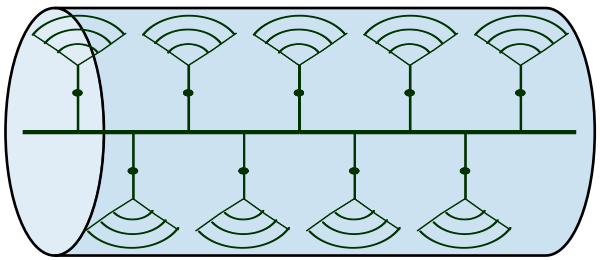


R = C_nH_{2n+1}

Percec,V; Ahn,C-H; Barboiu,B.
J. Am. Chem. Soc. **1997**, *119*, 12978

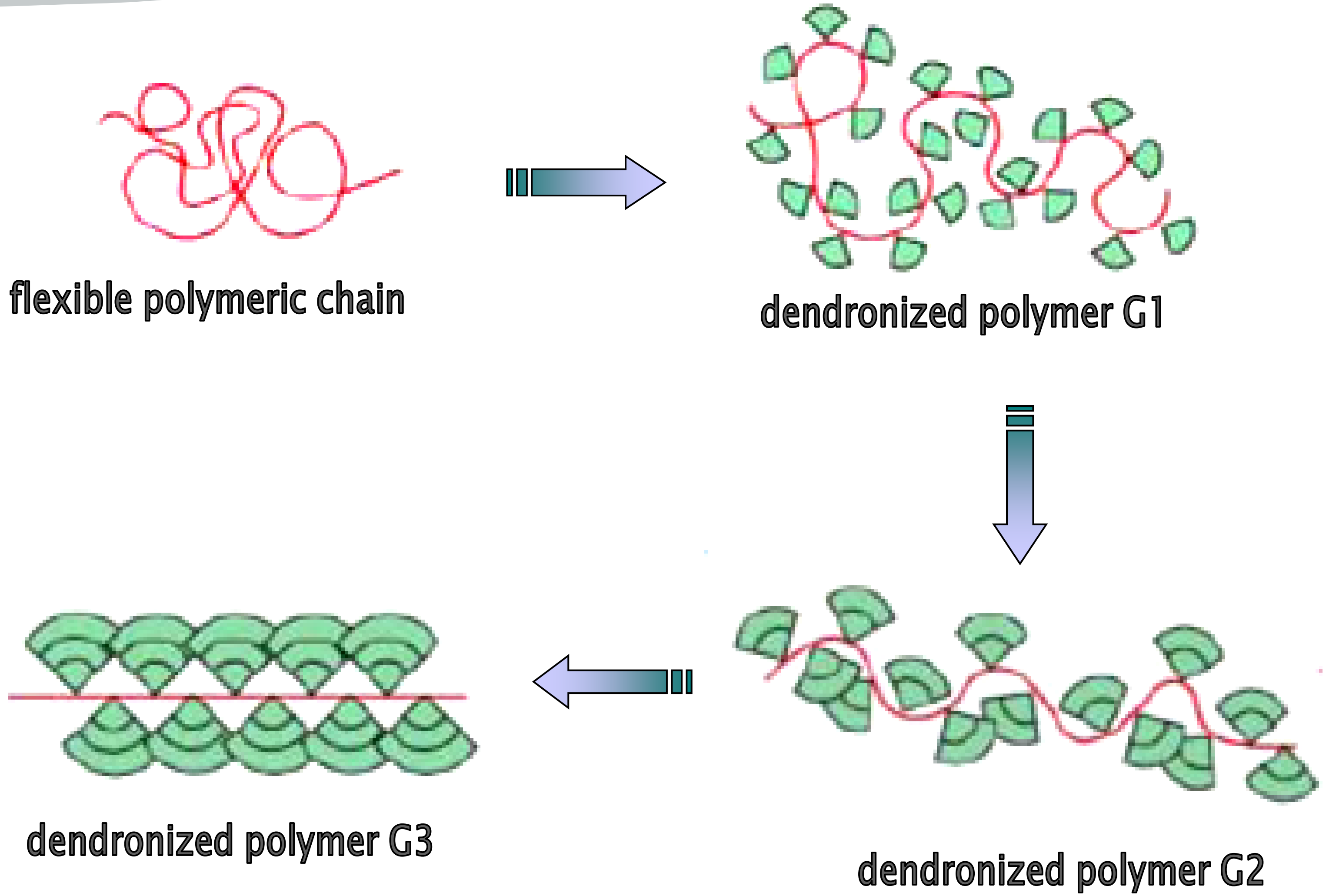
Side Dendrons Onto Every Repeating Unit

Macromonomer Route



Schlüter,D.A; Rabe,J.P.
Angew. Chem. Int. Ed. **2000**, *39*, 864

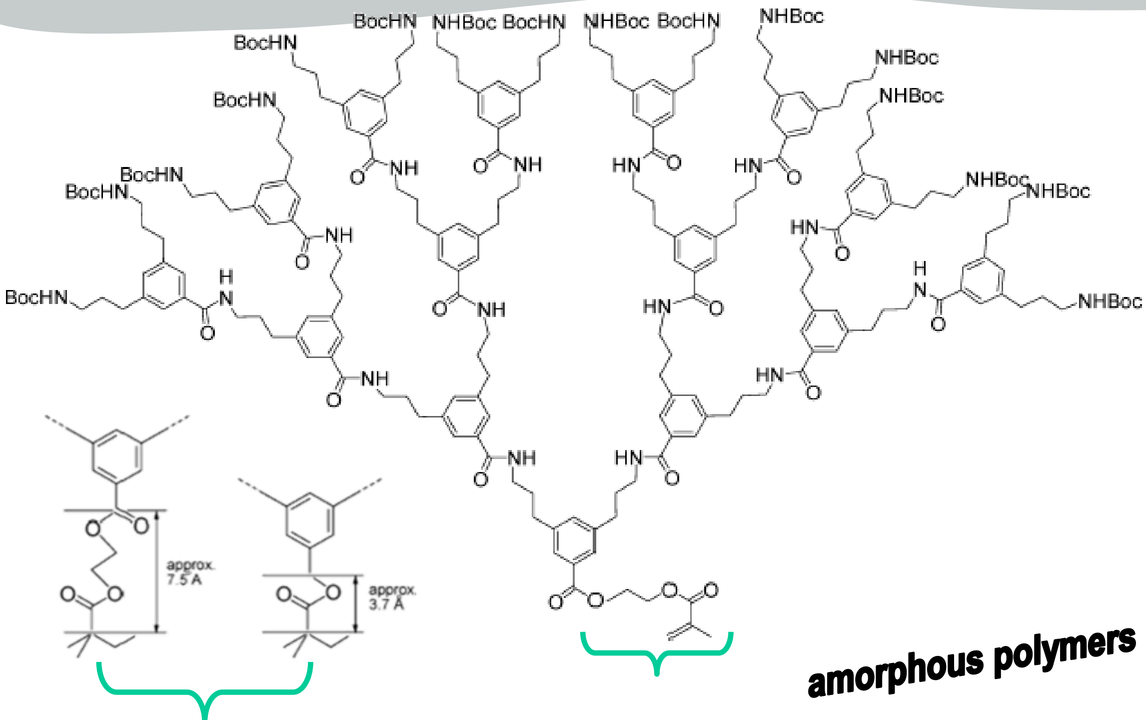
Dendronized Polymers



Zhang, A.; Shu, L.; Bo,Z; Schlüter, A.D. *Macromol. Chem. Phys.* **2003**, *204*, 328

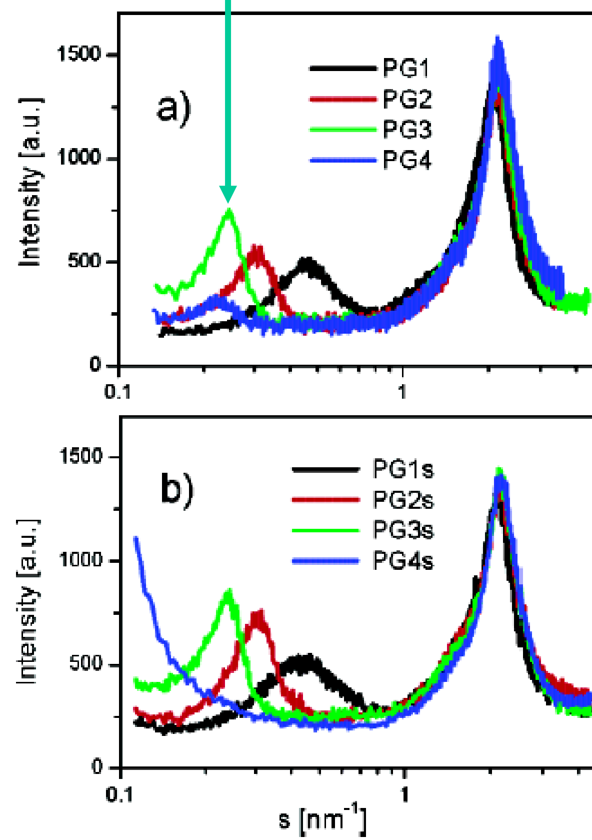
Dendronized PolyMethacrylates G1 – G4

Macromonomer Route



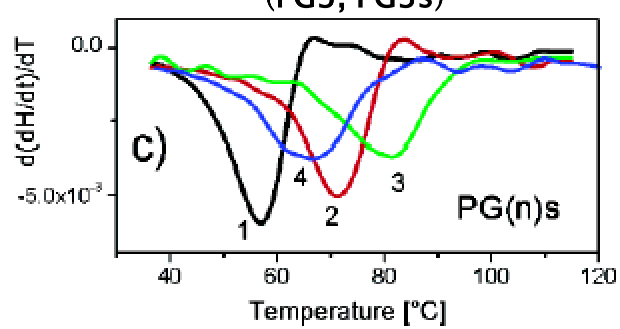
amorphous polymers

Low angle peaks =
thickness of densely branched polymers



Exclusion of neighbored chains

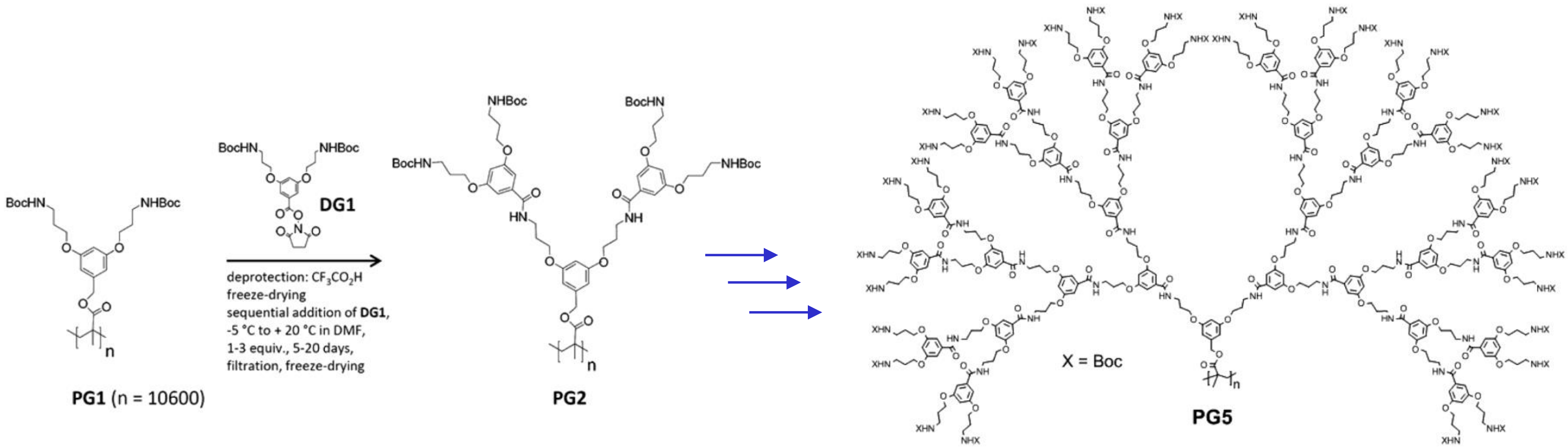
Increase of **Tg** up to **3rd** generation
(**PG3, PG3s**)

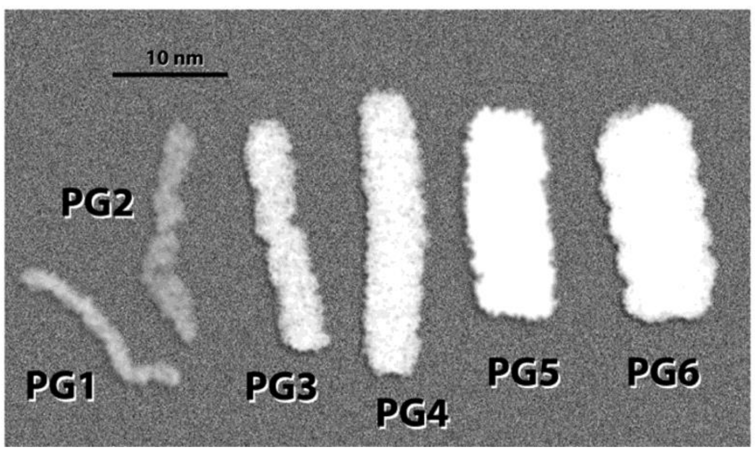


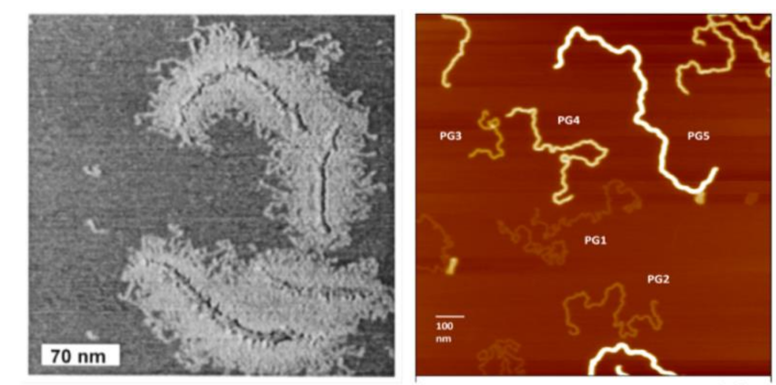
Zhang, A.; Okrasa, L.; Pakula, T.; Schlüter, A.D. *J. Am. Chem. Soc.* **2004**, *126*, 6658

Dendronized PolyMethacrylates G1 – G5

Graft from Route



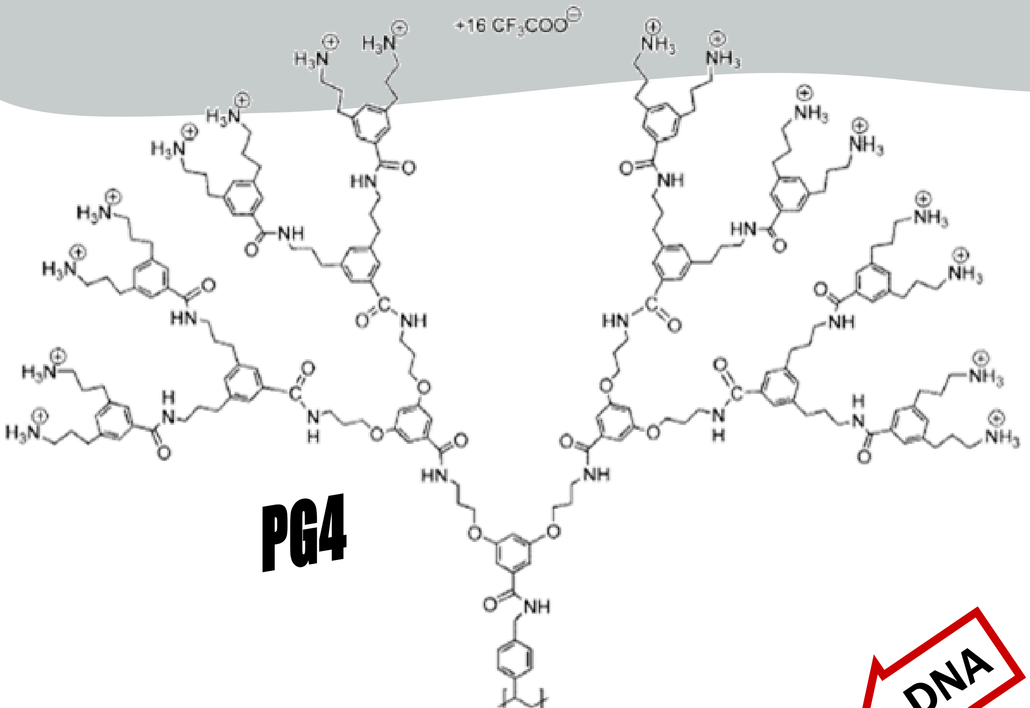


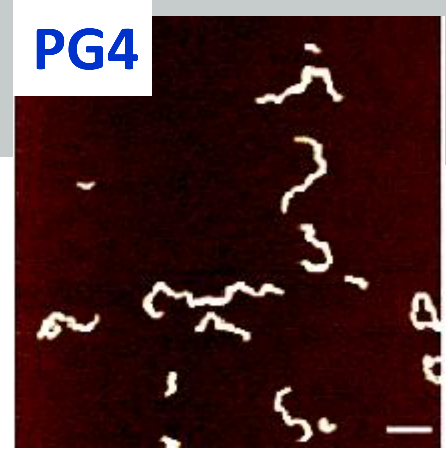


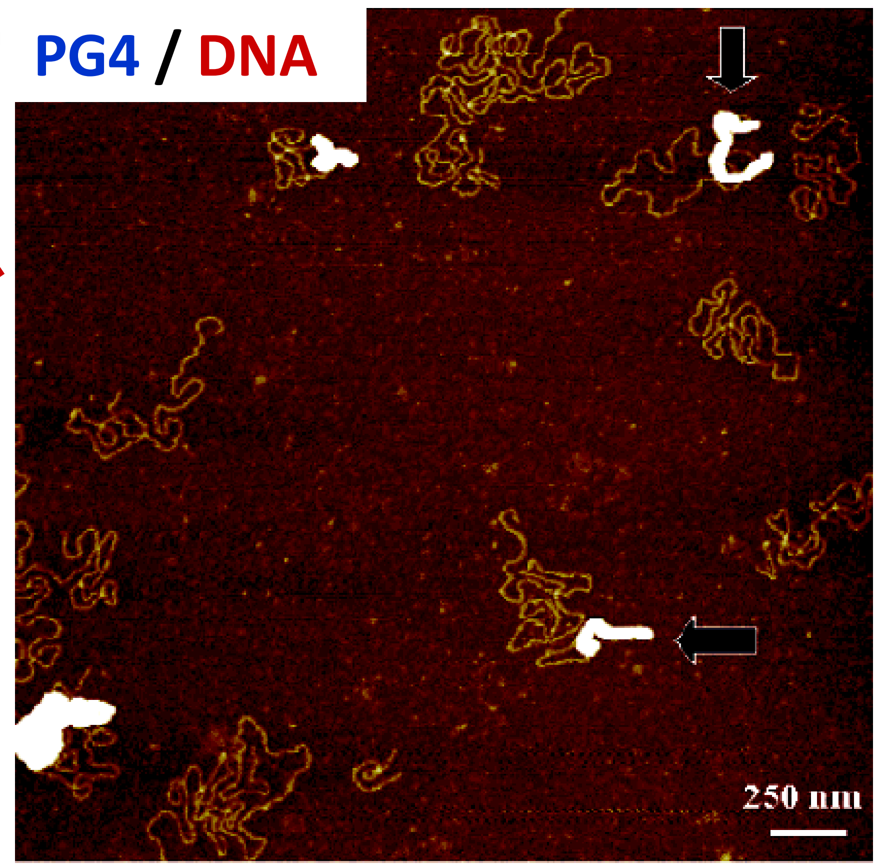
AFM images of bottlebrush polymers on mica and (d) coprepared **PG1**–**PG5** DPs on mica.

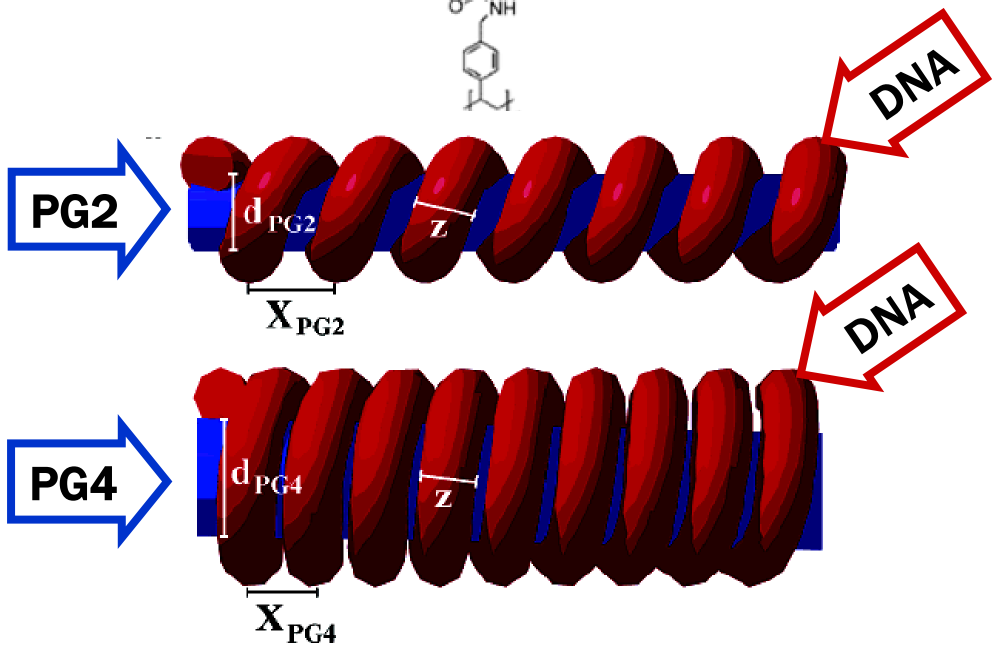
A. Dieter Schlüter et.al. ACS Macro Lett. 2014, 3, 10, 991–998

Complexes of DNA & Dendronized Polymers



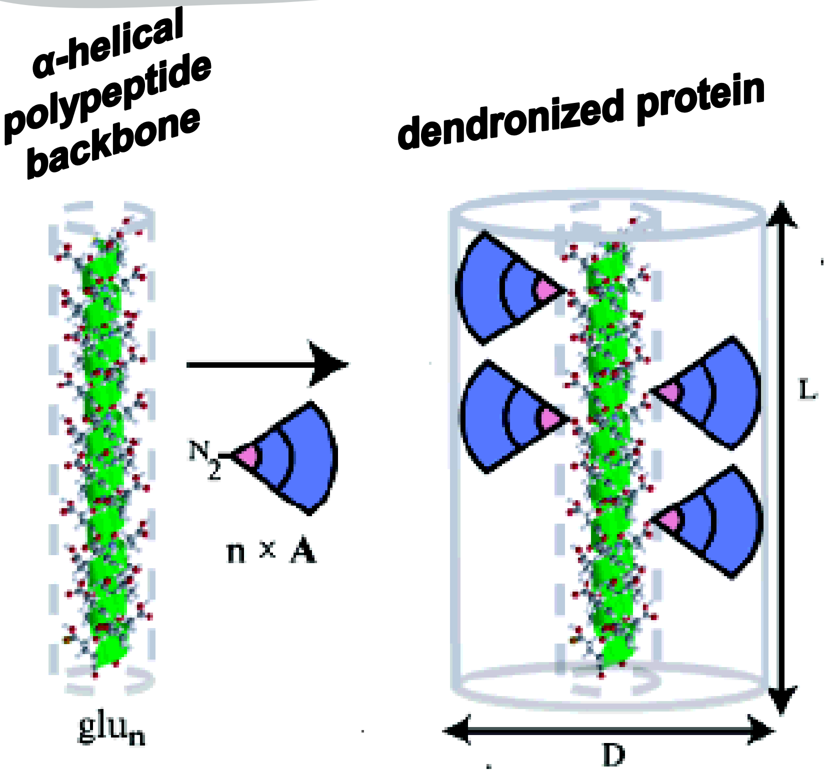


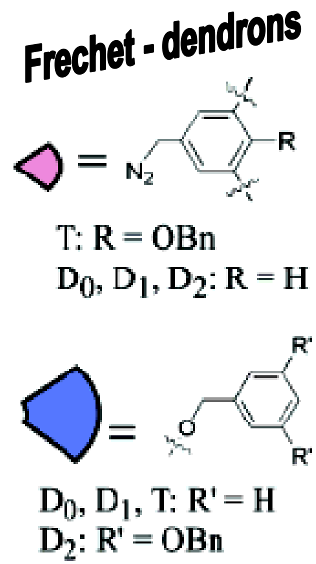


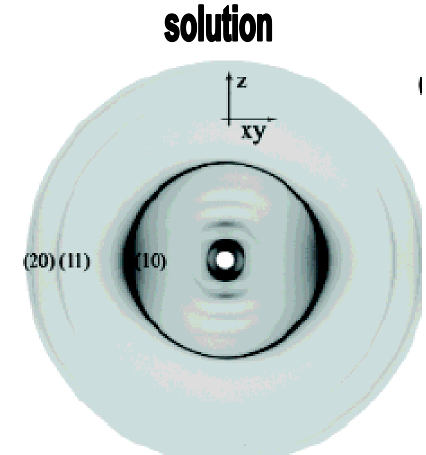


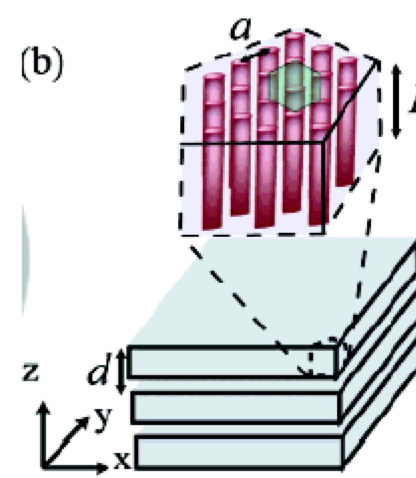
Gössl,I; Shu,L; Schlüter,A.D; Rabe,J. *J.Am.Chem.Soc.* **2002**, *124*, 6860

Dendronized Protein Monodisperse Polymers









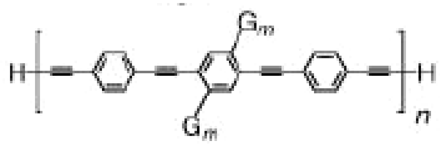
monodisperse chains expressed in *E.Coli* from a DNA template

stabile α-helicate
L defined by main chain &
D by side dendrons

40% wt in *m*-cresol : lamellar in *z* axis
hexagonal in *xy* plane

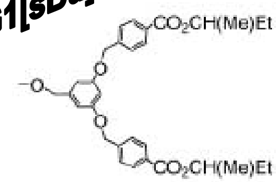
M.A. Zhuravel; N.E. Davis; S.B.T. Nguyen; I. Koltover *J. Am. Chem. Soc.* **2004**, *126*, 9882

Discrete Conjugated Wires Wrapped within Dendrimeric Envelopes: "Dendrimer Effects" on π-Electronic Conjugation

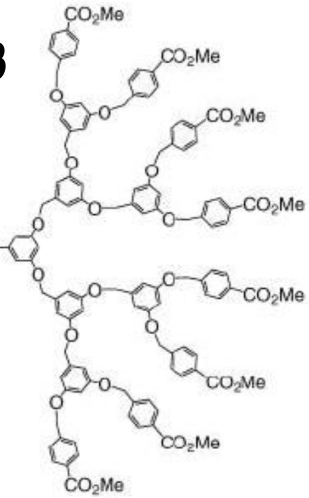


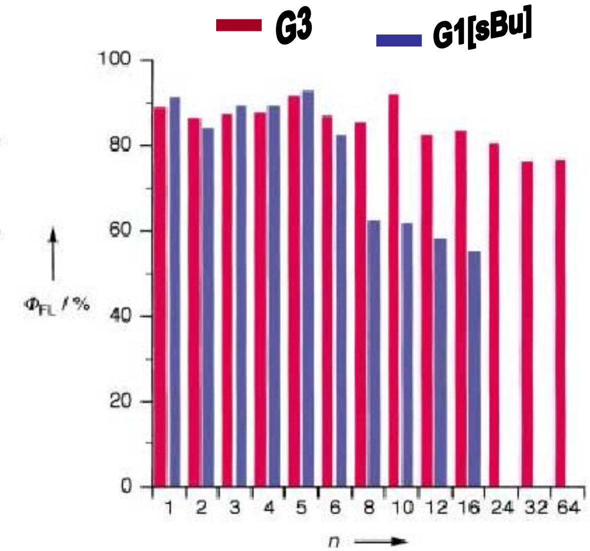
n = 1-6, 8, 10, 12, 16, 24, 32, 64

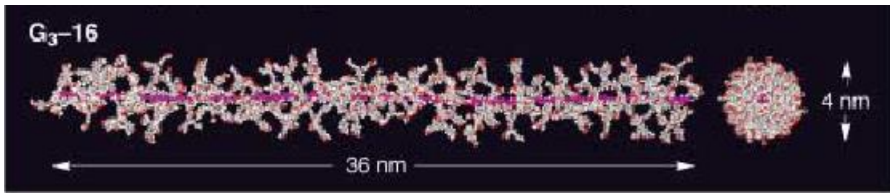
G1[sBu]



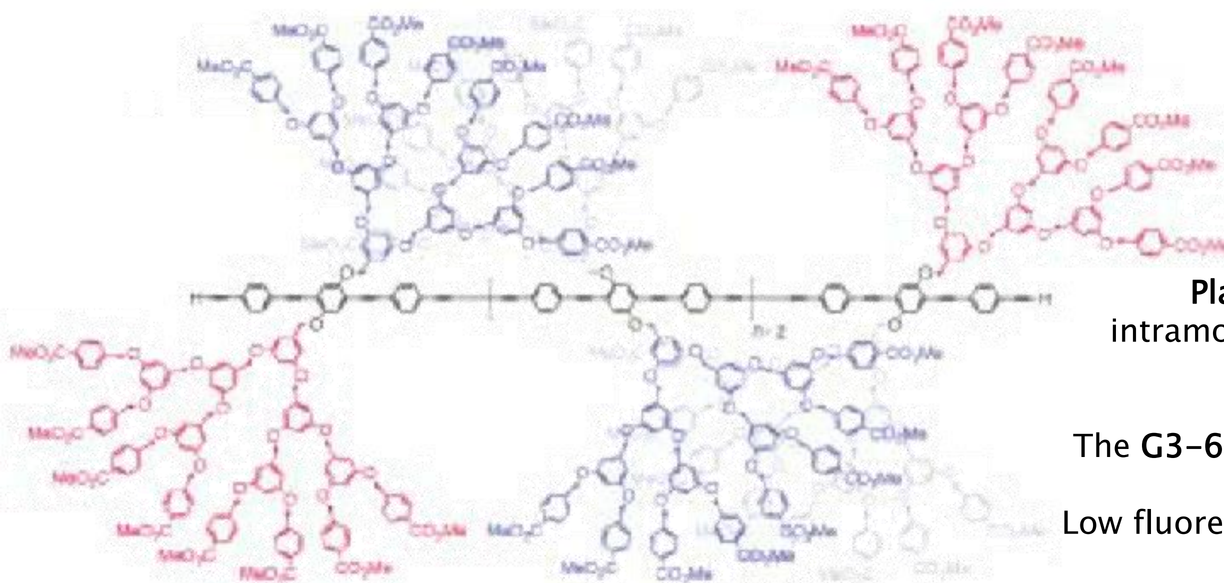
G3







G3 - Substituted polymers



Better **isolation** of the conjugated backbone

Planar conformation of the backbones due to intramolecular van der Waals interactions between the densely aligned side dendrons

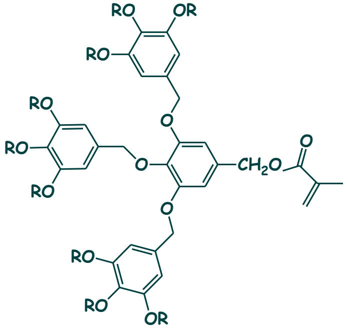
The **G3–64** polymer is a **147nm** long conjugated wire

Low fluorescence depolarization for exciton migration

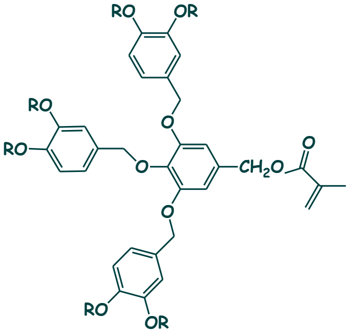
W.-S. Li; D.-L. Jiang; T. Aida *Angew. Chem. Int. Ed.* **2004**, *43*, 2943

Dendronized Systems with Alkoxy bearing dendrons

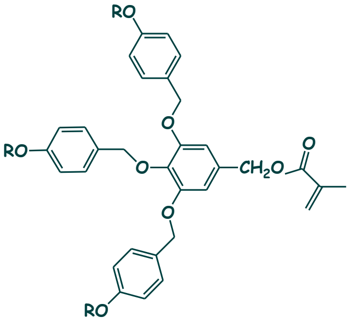
3,4,5-Substitution

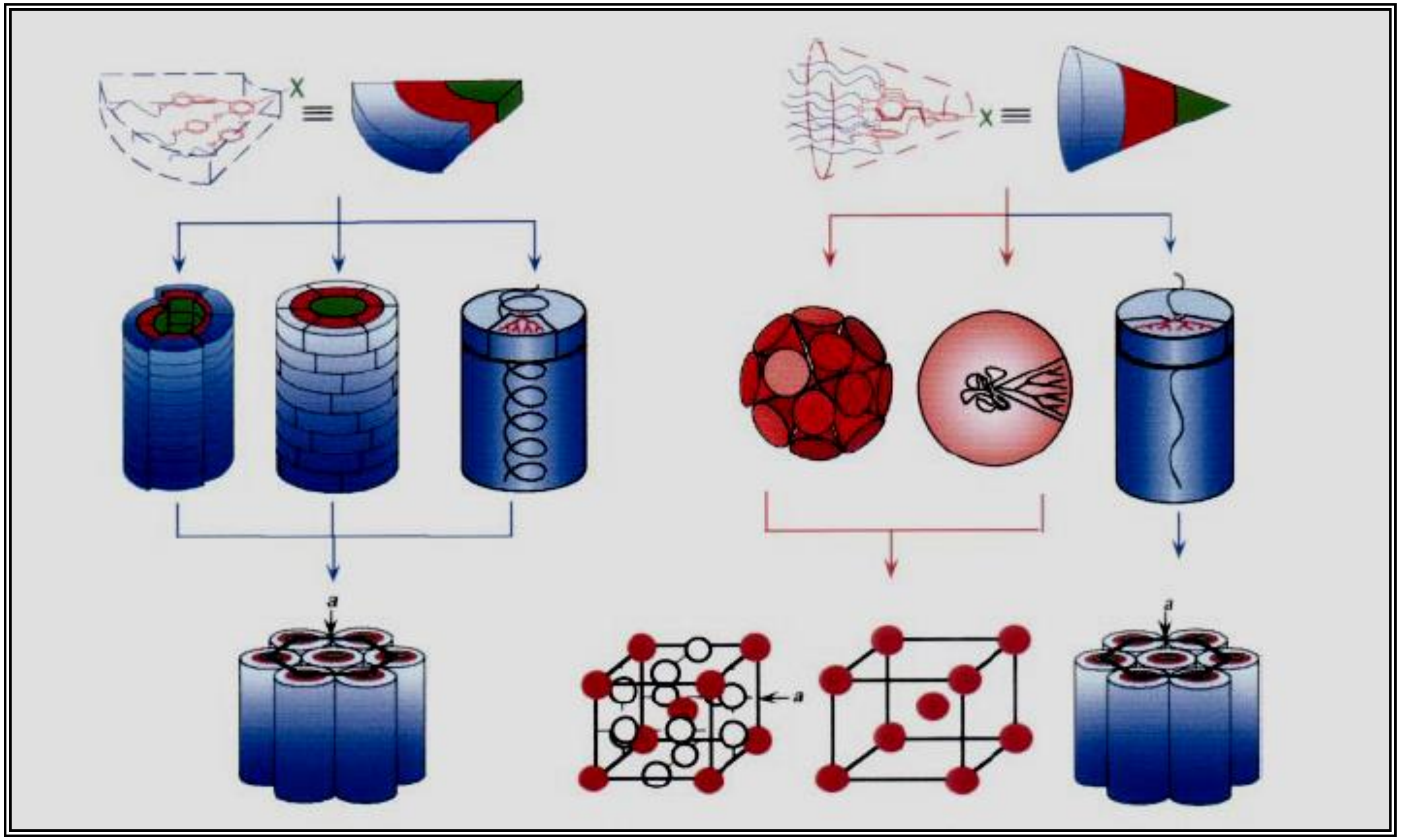


3,4- Substitution



4- Substituion

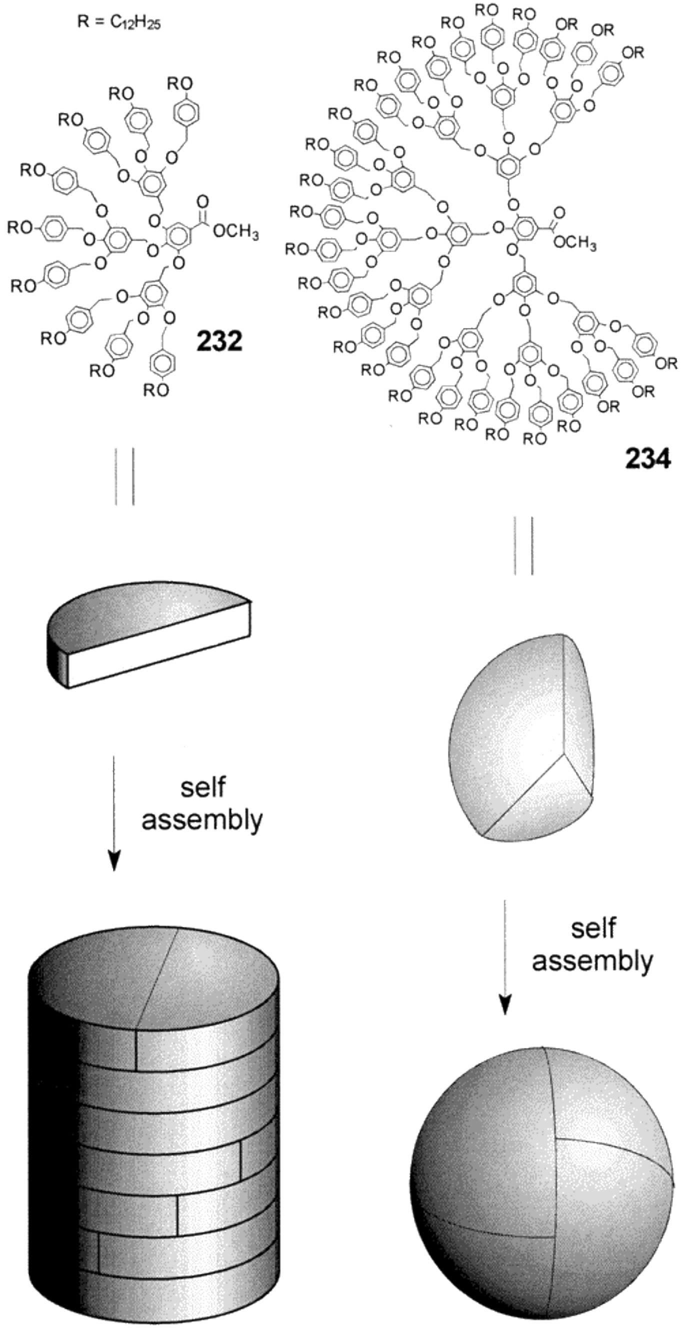




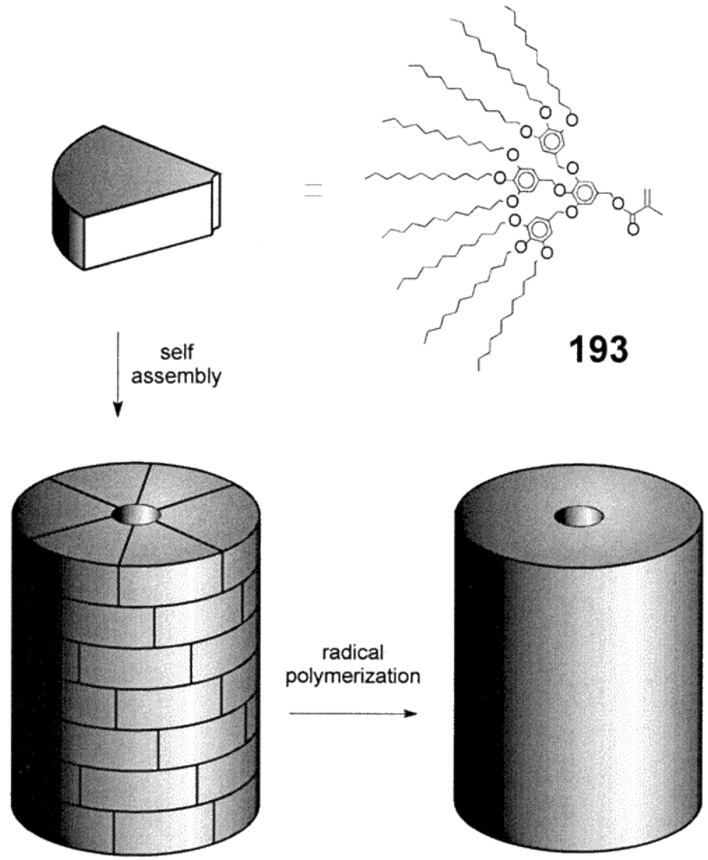
Percec, V.; C-H. Ahn.; Ungar, G.; Yeardley, D. J. P.; Moller, M.; Sheiko, S. S.; *Nature,* **1998**, *391*, 161
Duan., H.; Hudson, S. D.; Ungar, G.; Holerca, M. N.; Percec, V. C*hem. Eur. J.* **2001**, *7*, 4134

Supramolecular Materials

dendrons-dendrimers



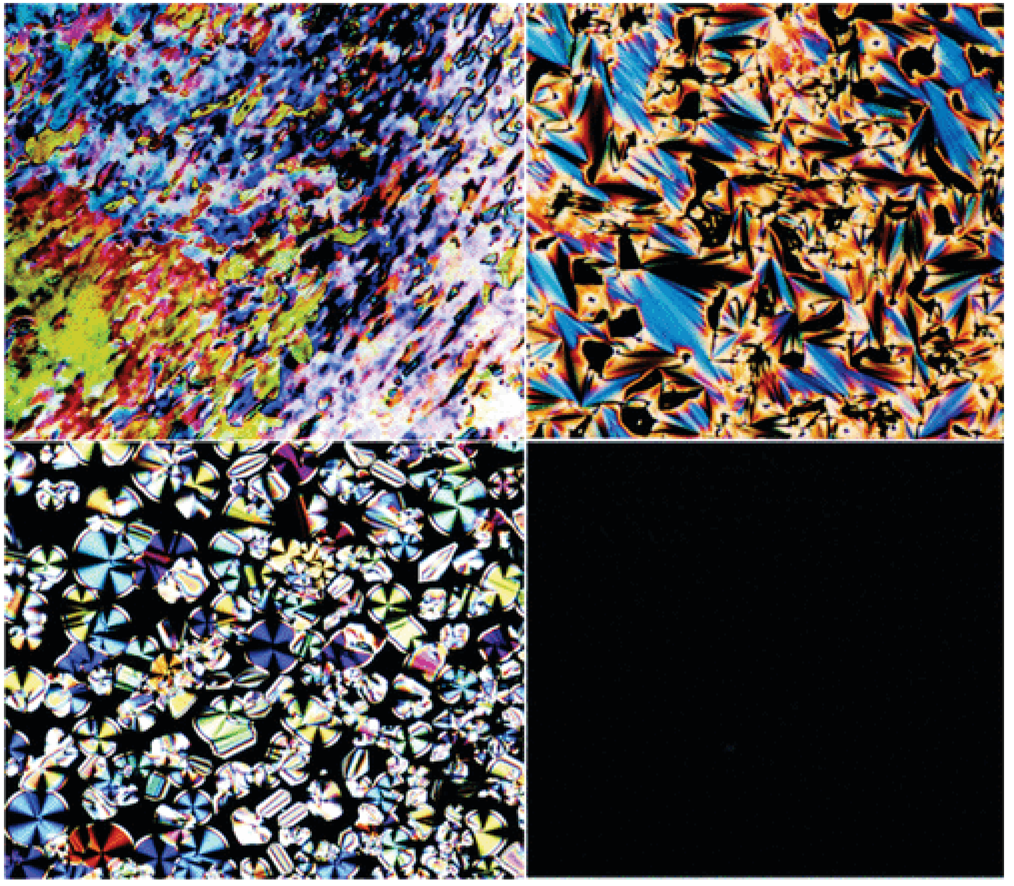
dendronized polymers



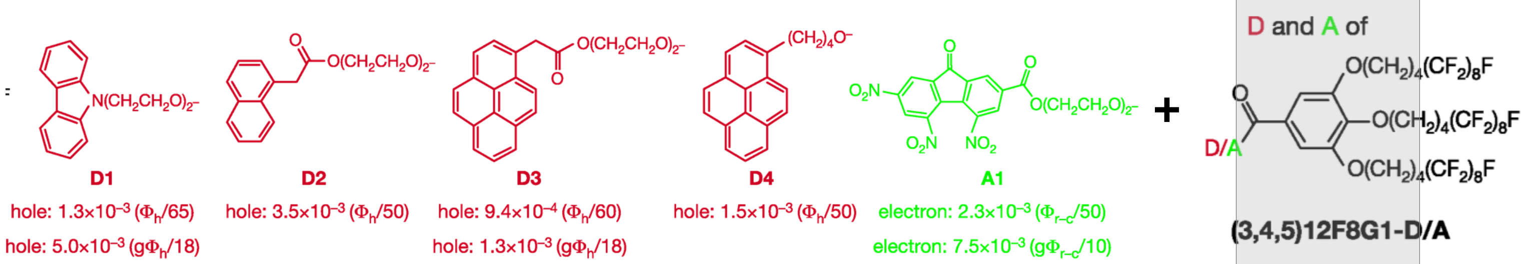
Supramolecular Materials

Phases exhibiting optical anisotropy through birefringent TOPM textures

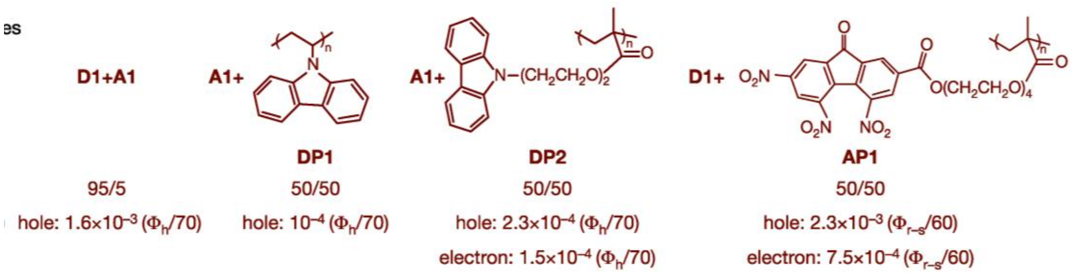
Nematic (top left), Smectic (top right), Φh (bottom left), and Cub (bottom right) phases



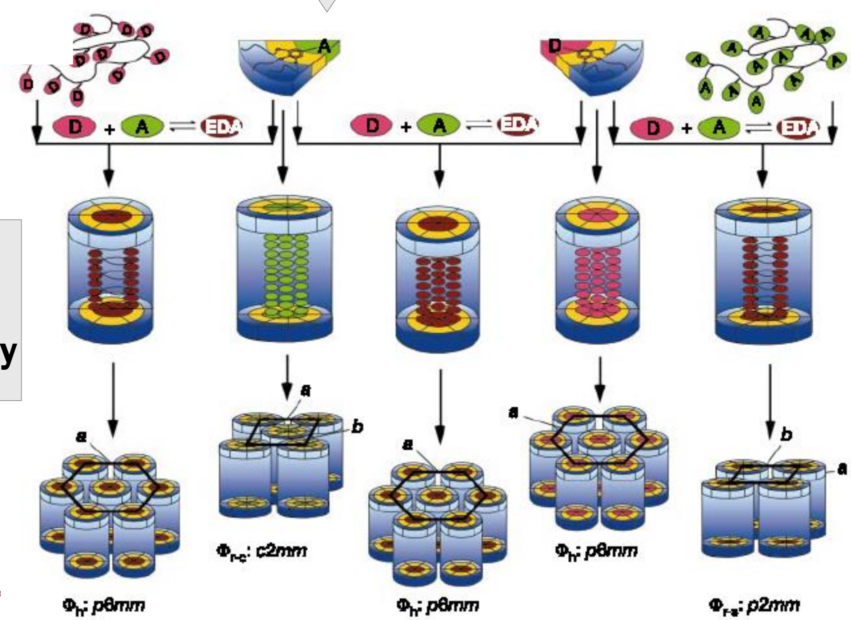
Supramolecular Electronic Materials

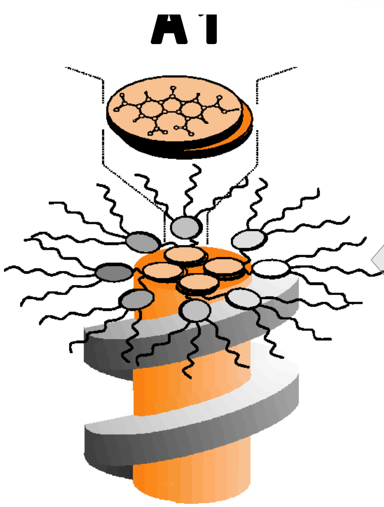


COMPLEXES with



= EDA complexes

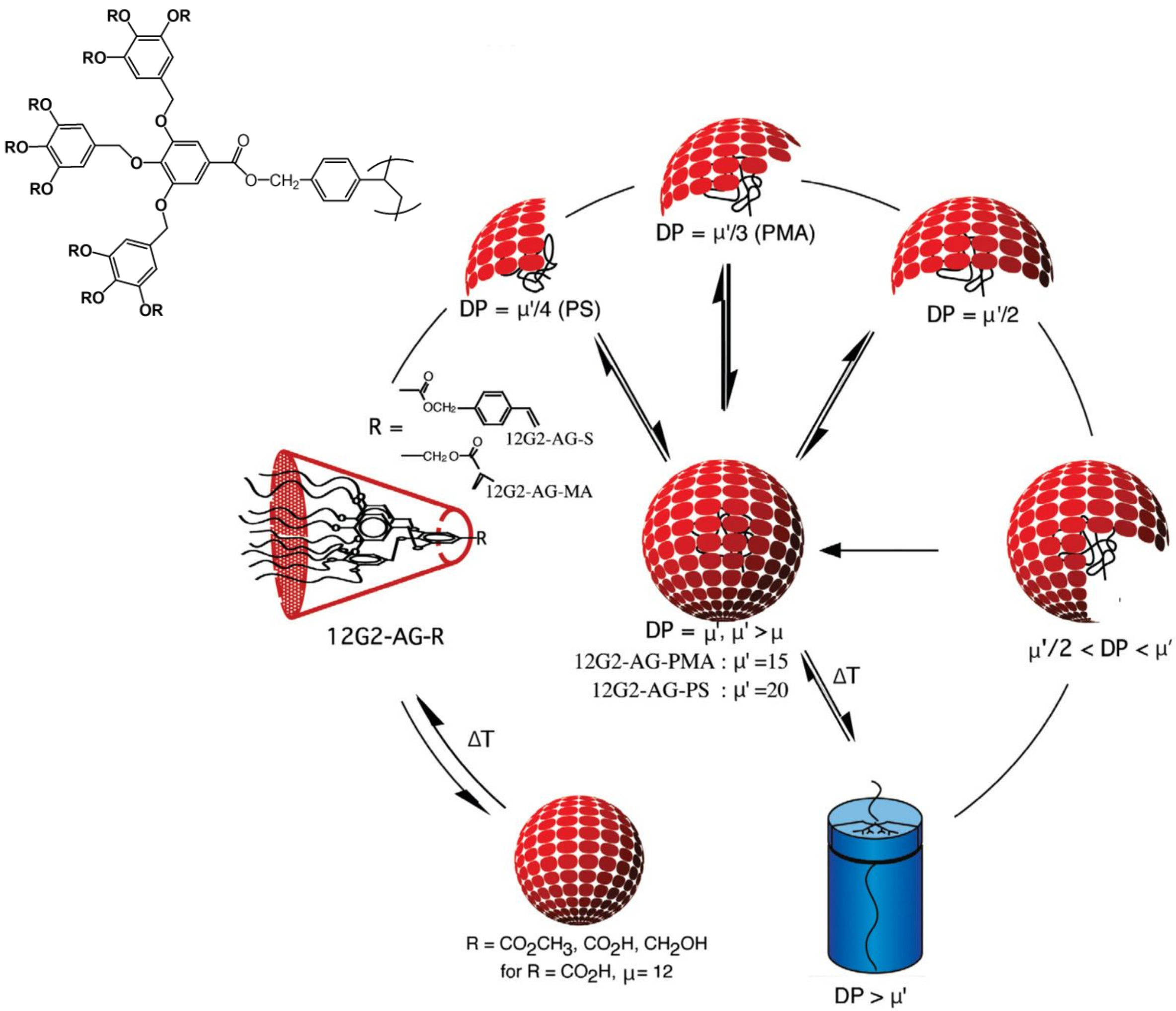




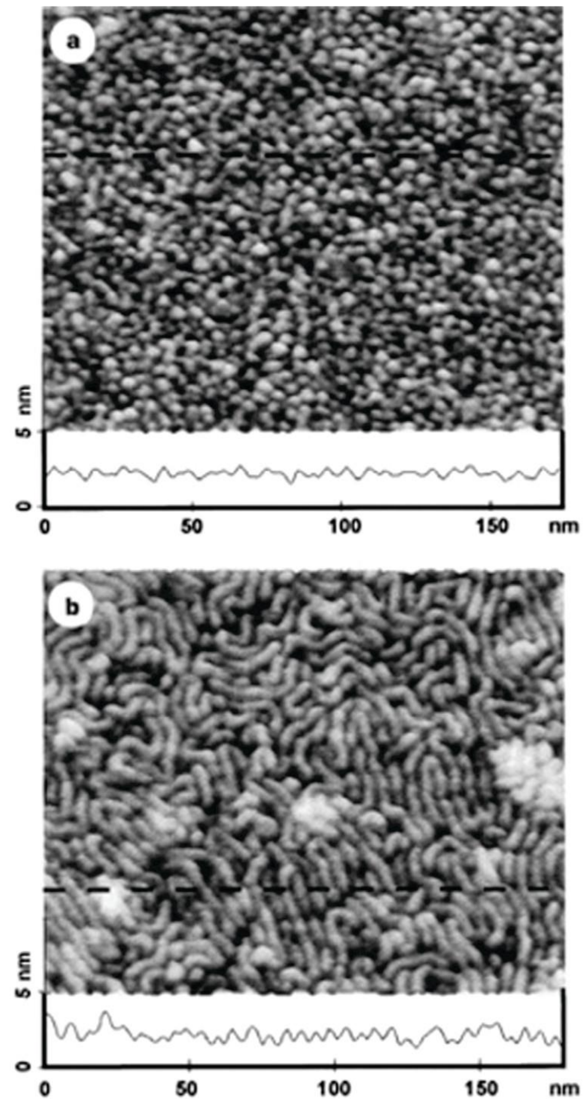
liquid crystalline columns
with "π – stacks"
of high electron & hole mobility

Percec, V. *USpatent*, 6,733,883 **2004 ;** Percec, et.al. *Nature*, **2002**,

Dendronized Polymers with Alkoxy bearing dendrons



AFM

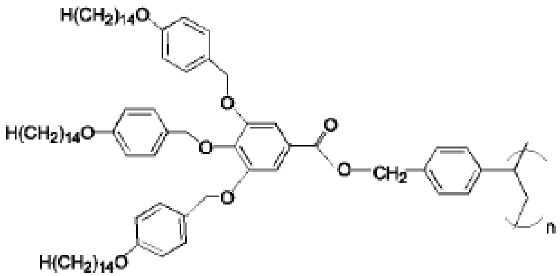


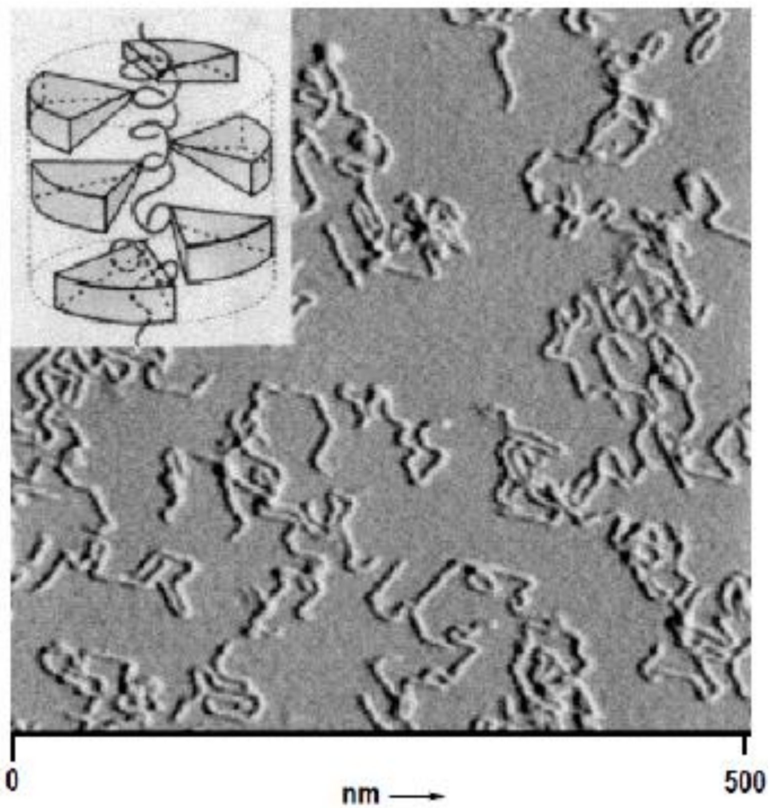
Percec, V.; C-H. Ahn.; Ungar, G.; Yeardley, D. J. P.; Moller, M.; Sheiko, S. S.; *Nature,* **1998**, *391*, 161

Dendronized Polymers with
Alkoxy bearing dendrons

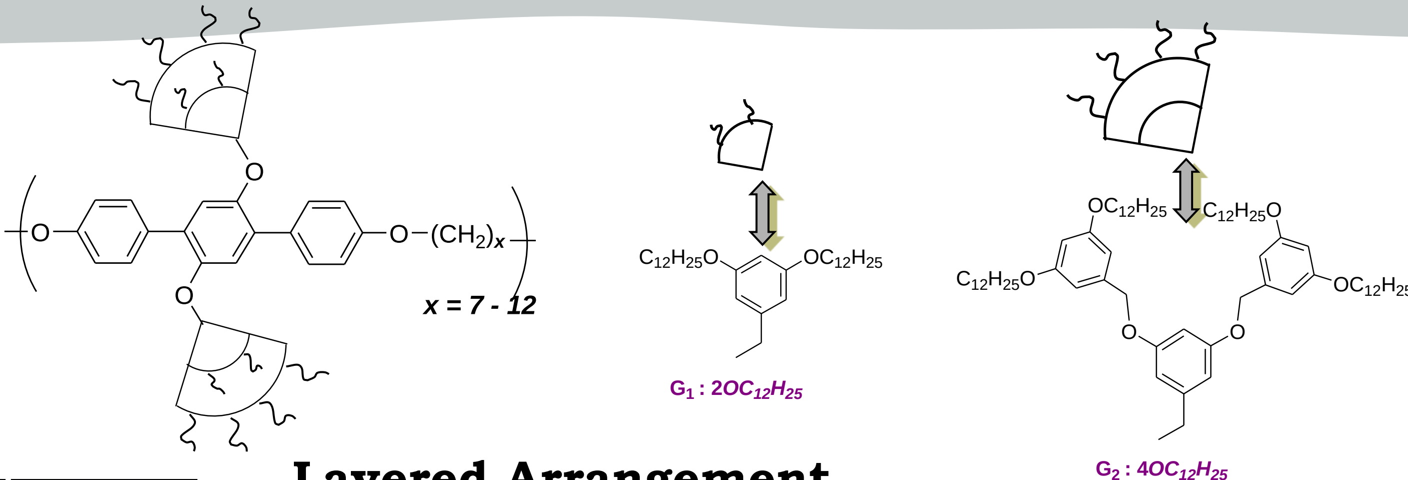
Individual molecules aligned parallel to the substrate

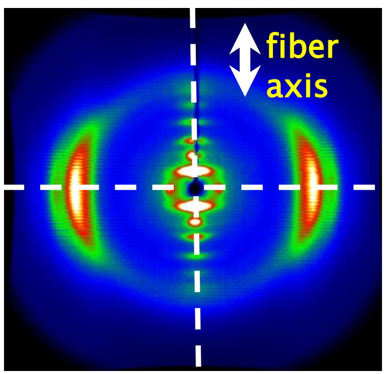
S F M
on HOPG



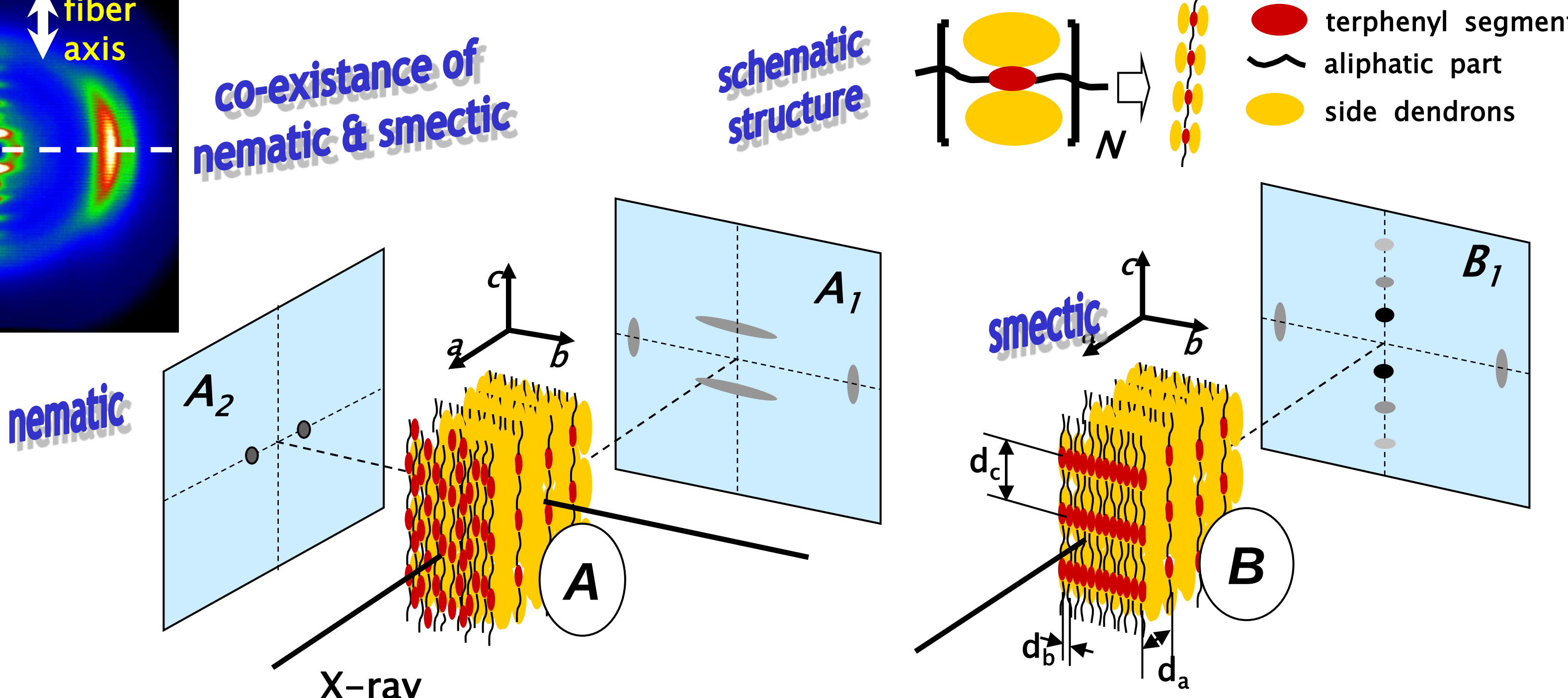


Dendronized Polymers with Alkoxy bearing dendrons





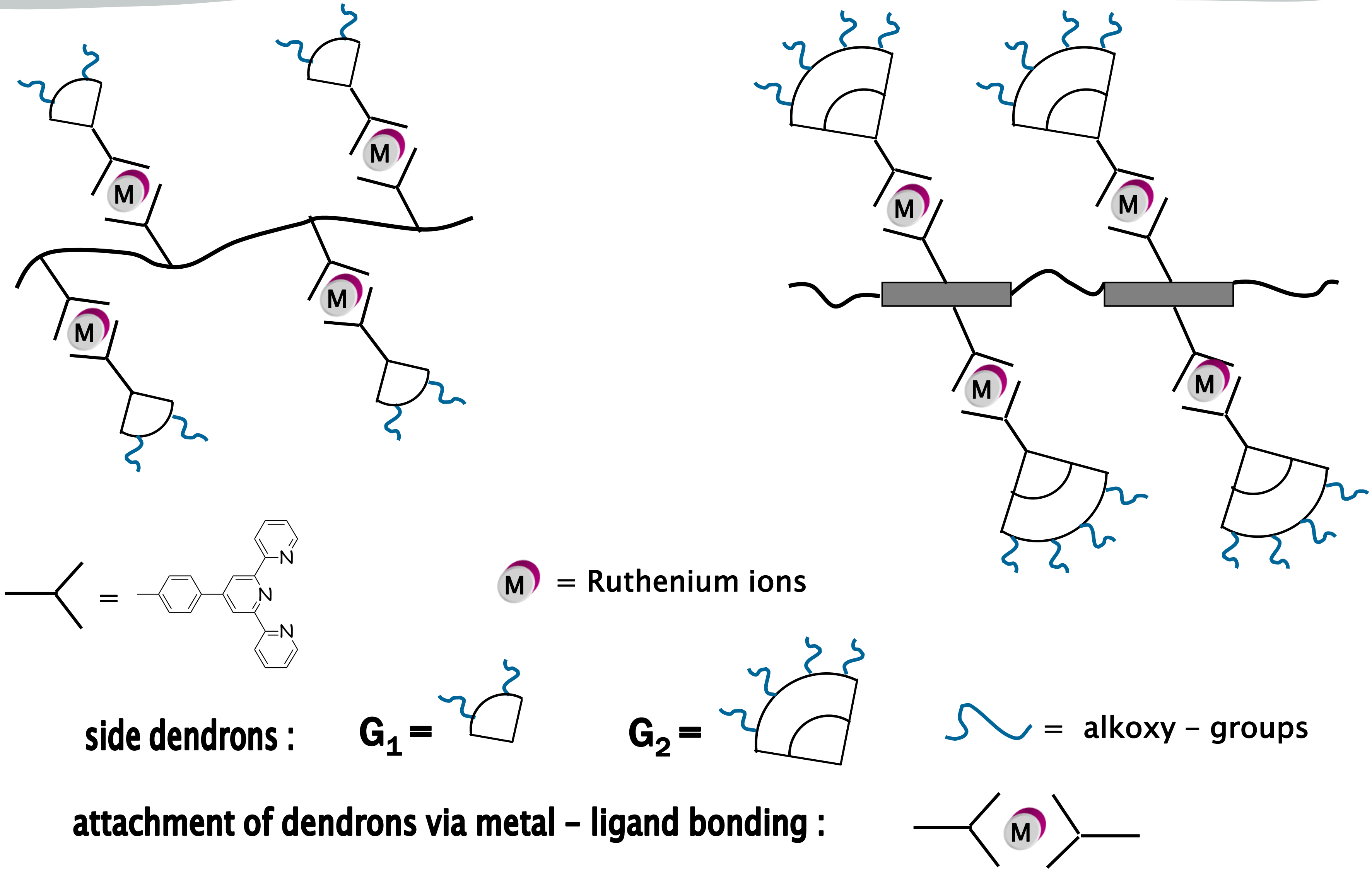
Layered Arrangement



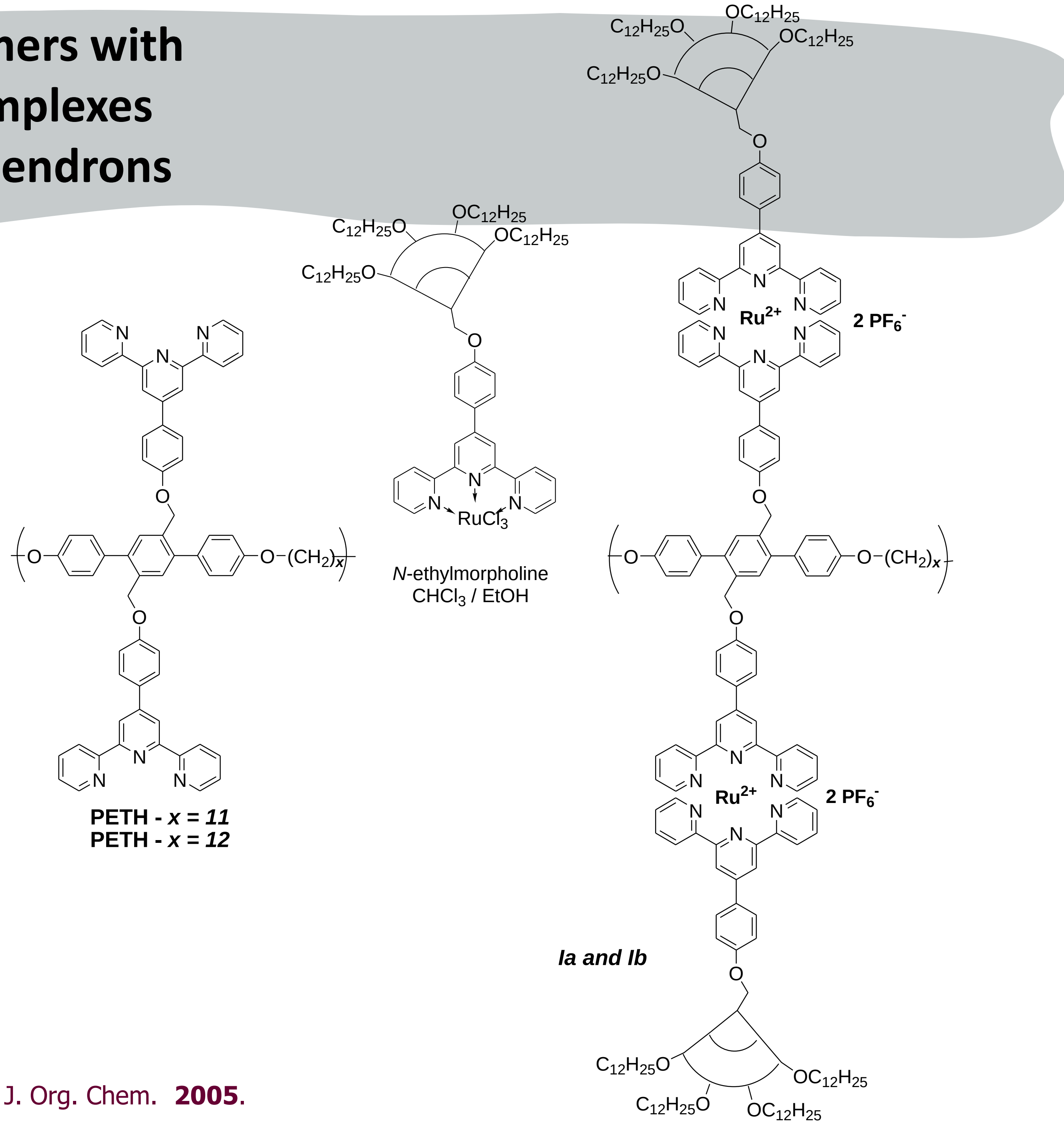
A.K. Andreopoulou, B. Carbonnier, J.K. Kallitsis, T. Pakula

Macromolecules **2004**, *37*, 3576 ; *Macromol. Chem. Phys.* **2005**, *206*, 66

Dendronized Polymers with Terpyridine-Ru Complexes & Alkoxy bearing dendrons

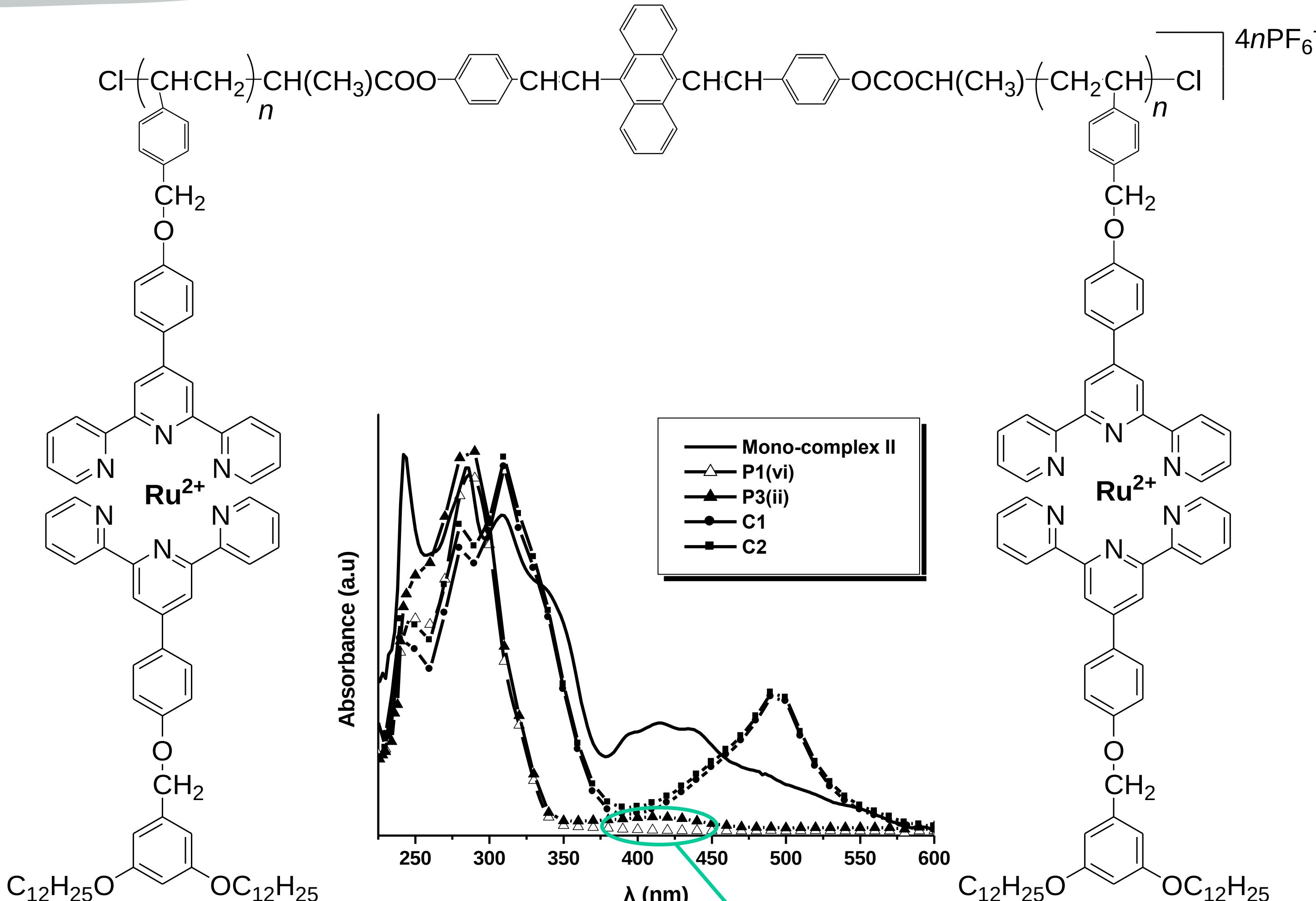


Dendronized Polymers with Terpyridine-Ru Complexes & Alkoxy bearing dendrons



A.K. Andreopoulou, J.K. Kallitsis, Eur. J. Org. Chem. **2005**.

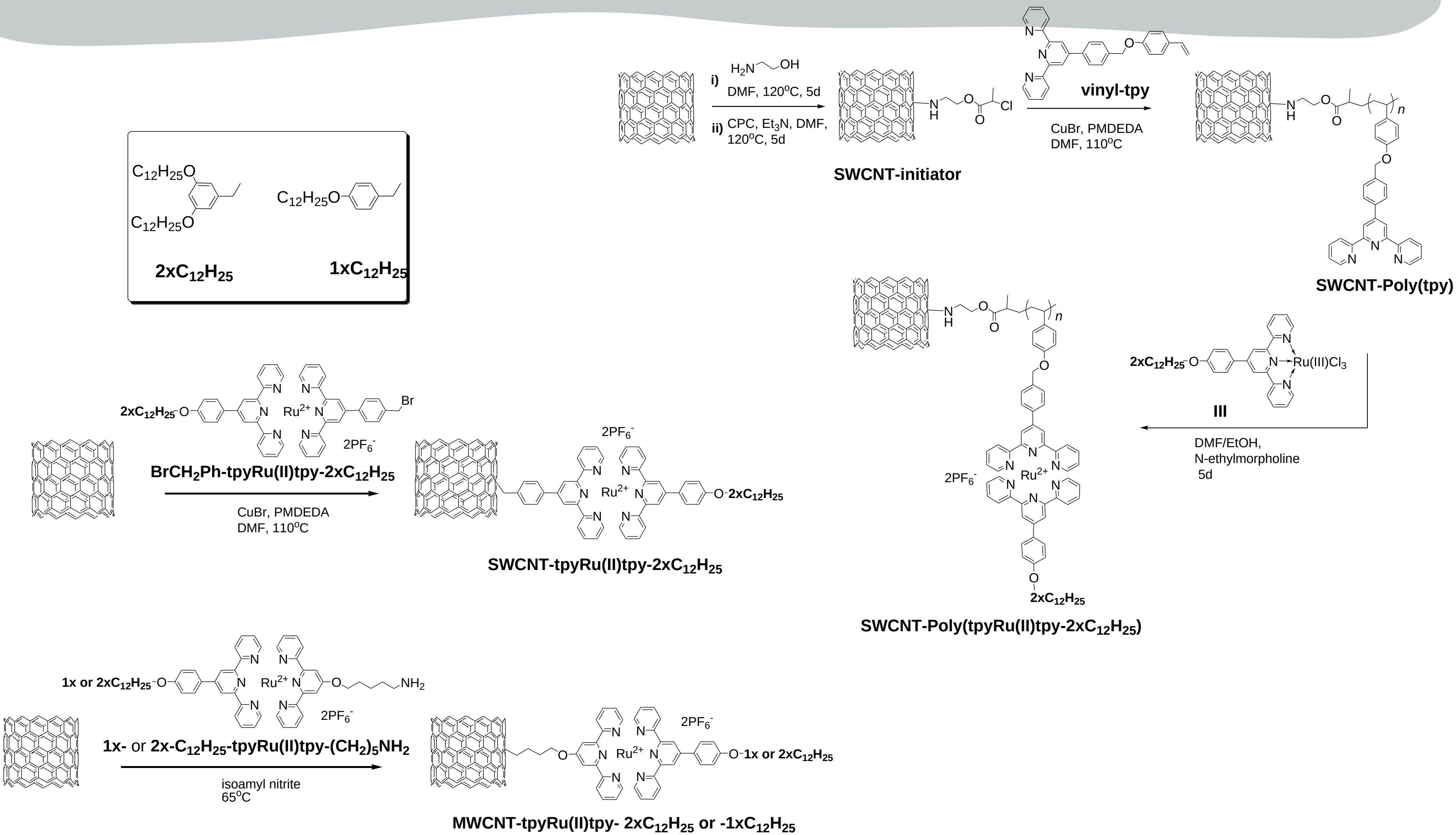
Dendronized Polymers with
Terpyridine-Ru Complexes & Alkoxy bearing dendrons



Polymer **P3** & Complex **C3**
414nm = di(styryl)anthracene block

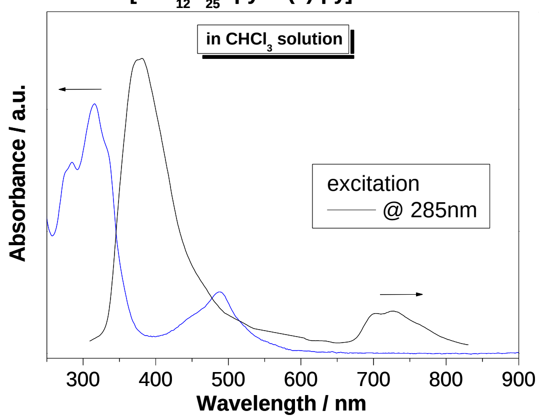
N.P. Tzanetos, A.K. Andreopoulou, J.K. Kallitsis
J. Polym. Sc. Part A, Polym. Chem. **2005**, *43*, 4838

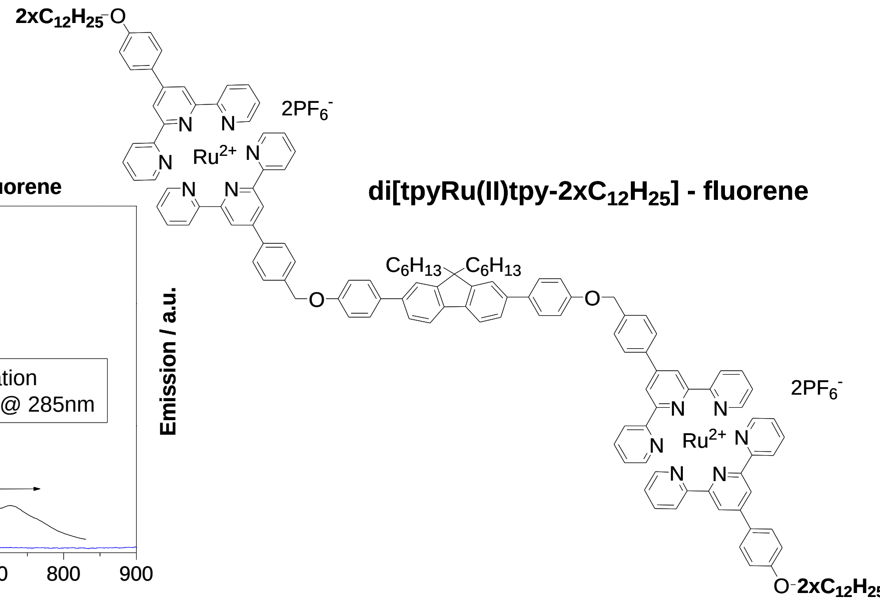
CNTs with Dendronized Terpyridine-Ru Complexes



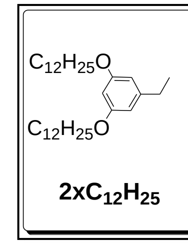
Dendronized Oligomers with Terpyridine-Ru Complexes

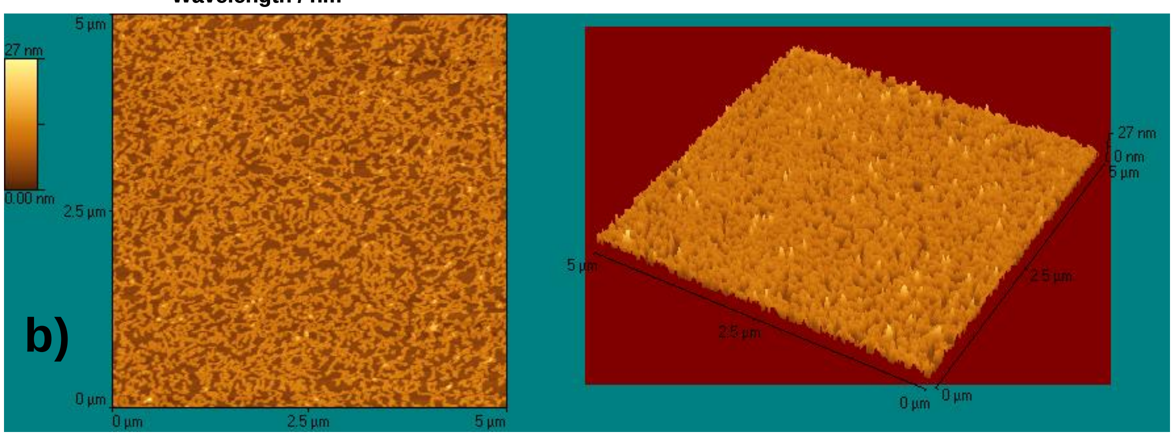
a) di[2xC$_{12}$H$_{25}$-tpyRu(II)tpy]-fluorene





di[tpyRu(II)tpy-2xC$_{12}$H$_{25}$] - fluorene





Dendrimer Chemistry
Impact on Material Science & Emerging Applications