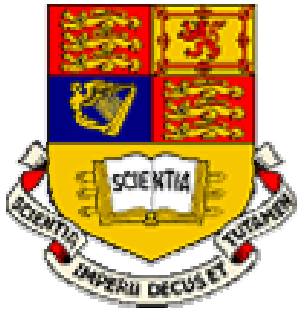
Supramolecular Chemistry of Nanomaterials

Joachim Steinke
Ramon Vilar

Lecture 7 –Increased Complexity and Size



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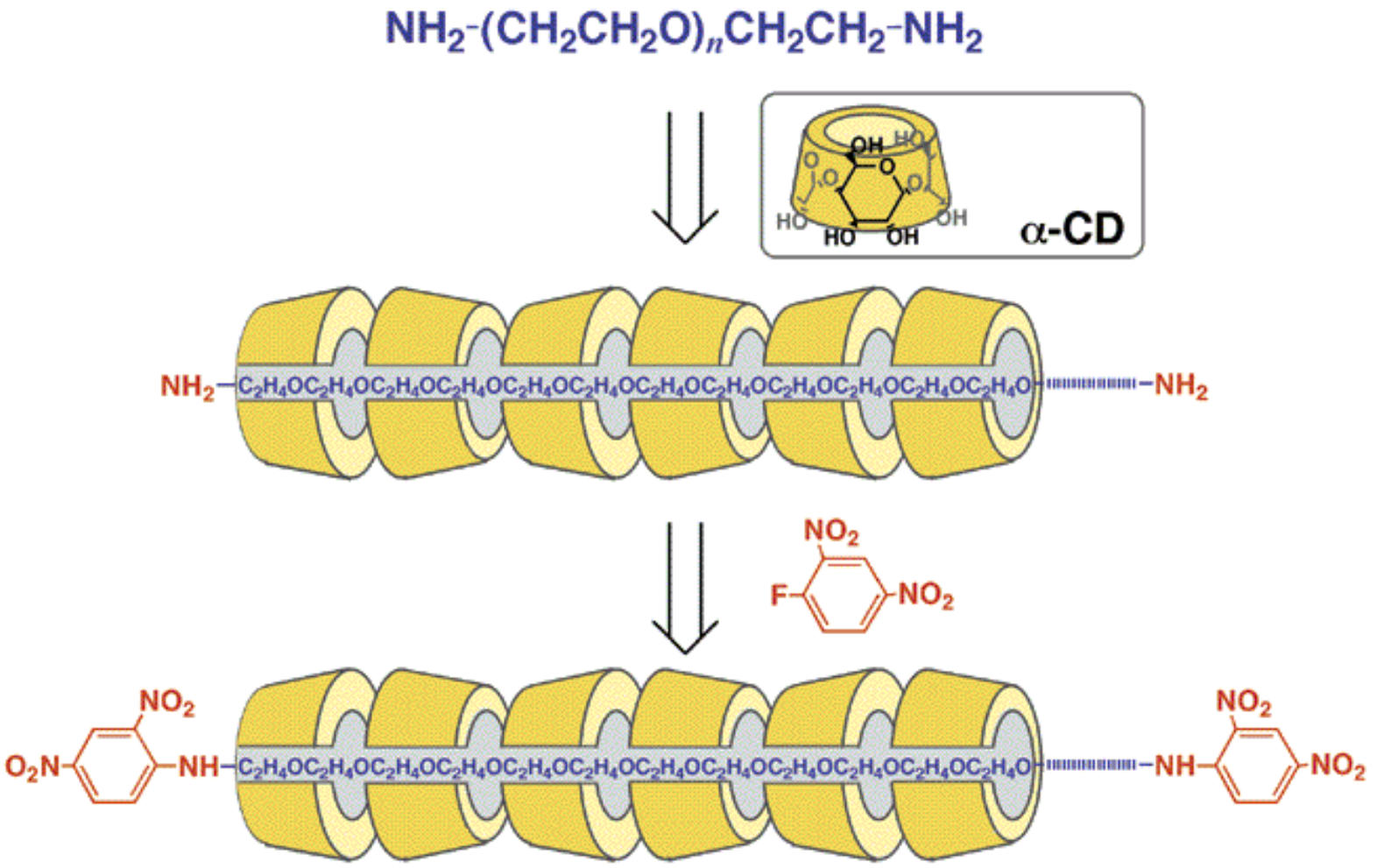
Lecture Content

- Polyrotaxanes
- Nanotubes
- Nanowires
- Supramolecular Dendrimers

Polyrotaxanes – Molecular Necklace

- Polyrotaxane containing alpha-cyclodextrins.

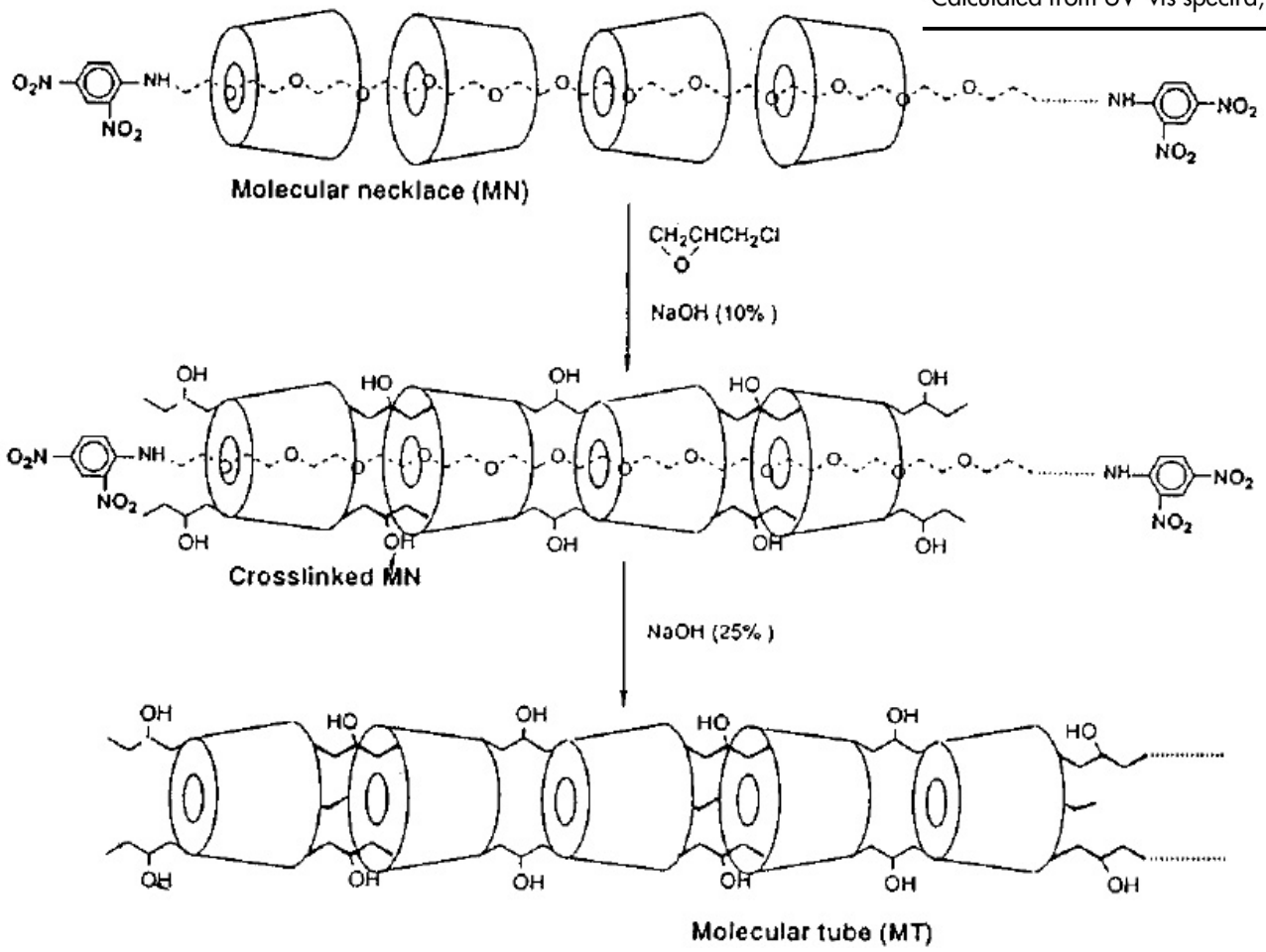


POLYMERS FOR ADVANCED TECHNOLOGIES, 8, 241 (1997)

Polyrotaxanes – Molecular Necklace

Polyrotaxane	*Molecular weight*[b]	*Number of ethylene glycol units (included + non-included)*	*Number of threaded α-CDs*[b]	*Molar ratio of ethylene glycol units to α-CD*
MN-1450	16,500	33 (33+0)	15	2.2
MN-2000	20,000	45 (36+9)	18	2.5
MN*-2001[a]	19,000	45 (34+11)	17	2.6
MN-3350	23,500	77 (40+37)	20	3.9
MN-8500	44,000	193 (72+121)	36	5.4
MN-20,000	89,000	454 (140+314)	70	6.5

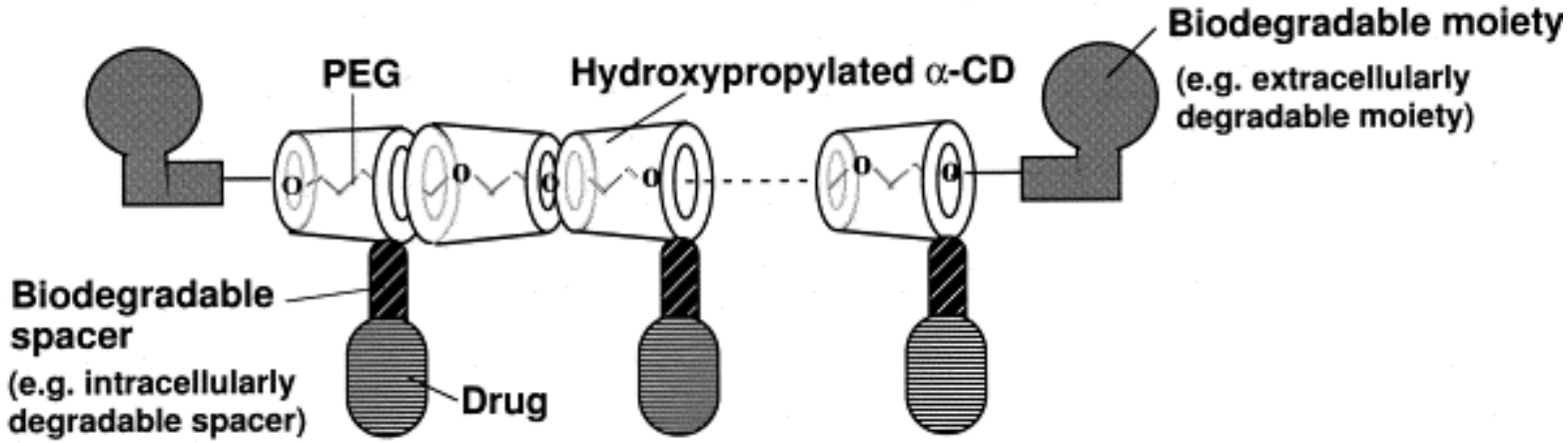
[a]Prepared from Jeffamine ED-2001.
[b]Calculated from UV–vis spectra, optical rotation and ^{1}H-NMR spectra.



POLYMERS FOR ADVANCED TECHNOLOGIES, 8, 241 (1997)

Polyrotaxane Drugs

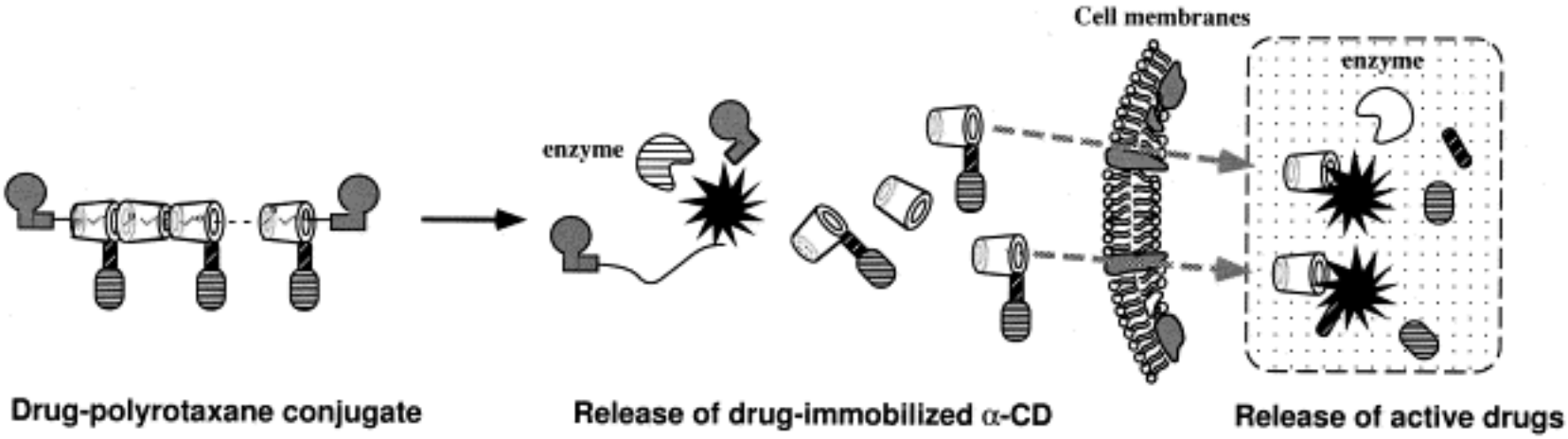
- Design of a drug–polyrotaxane conjugate.



J. Contr. Release 58, 1999, 251

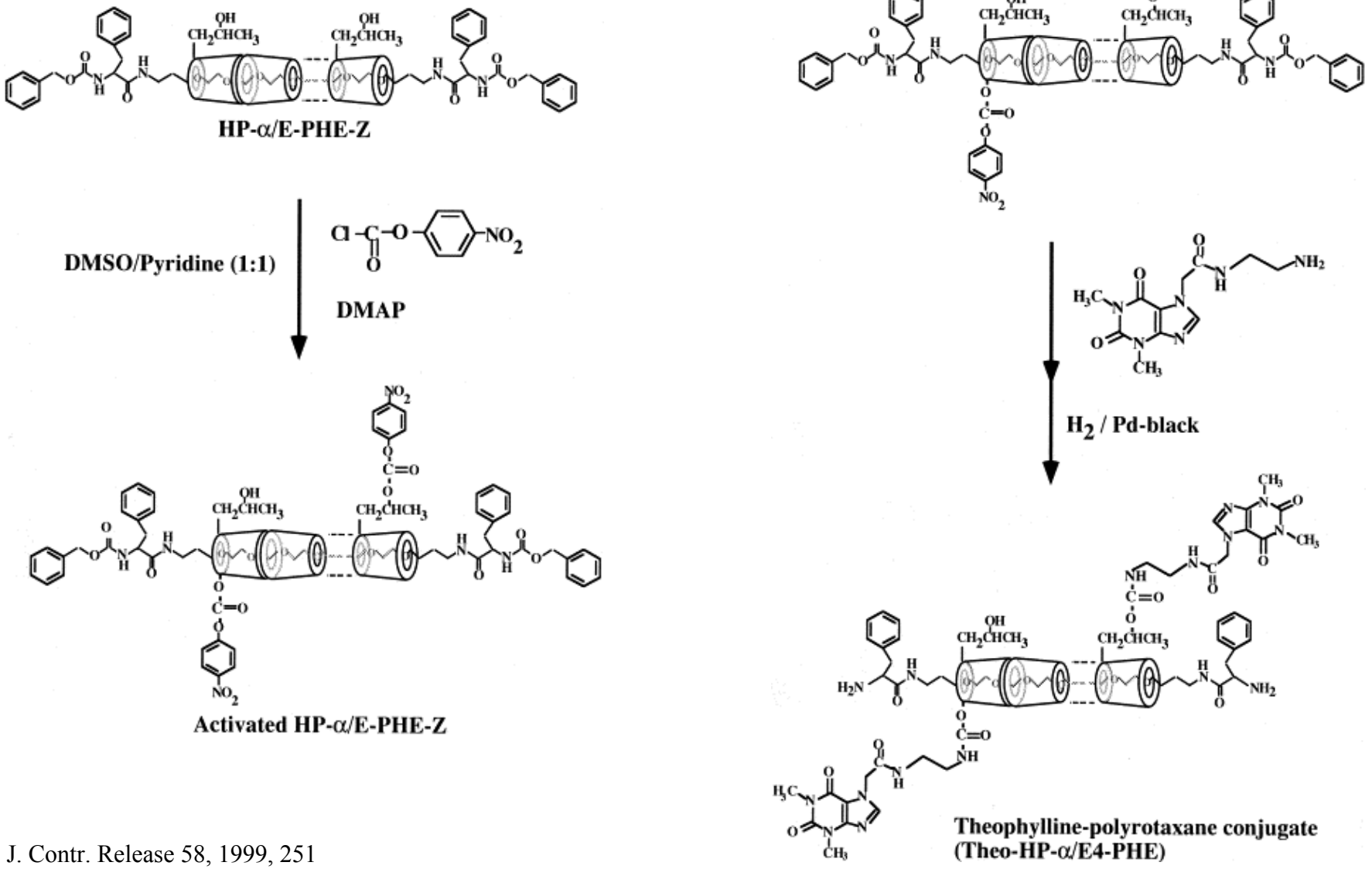
Polyrotaxane Drugs

- Final image of drug release from drug–polyrotaxane conjugates via enzymatic degradations.



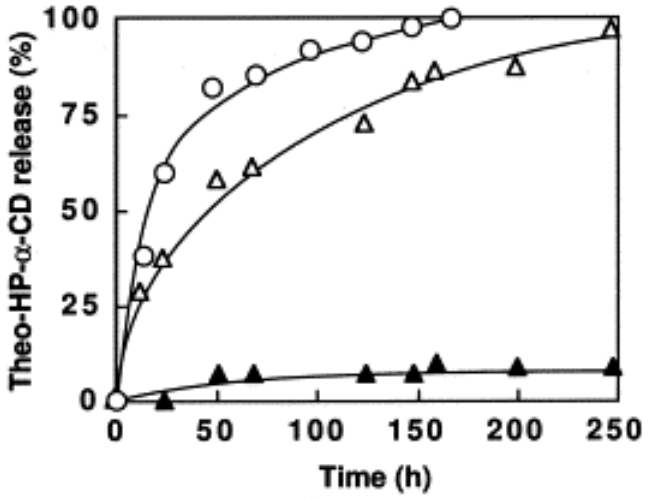
J. Contr. Release 58, 1999, 251

Polyrotaxane Drugs



J. Contr. Release 58, 1999, 251

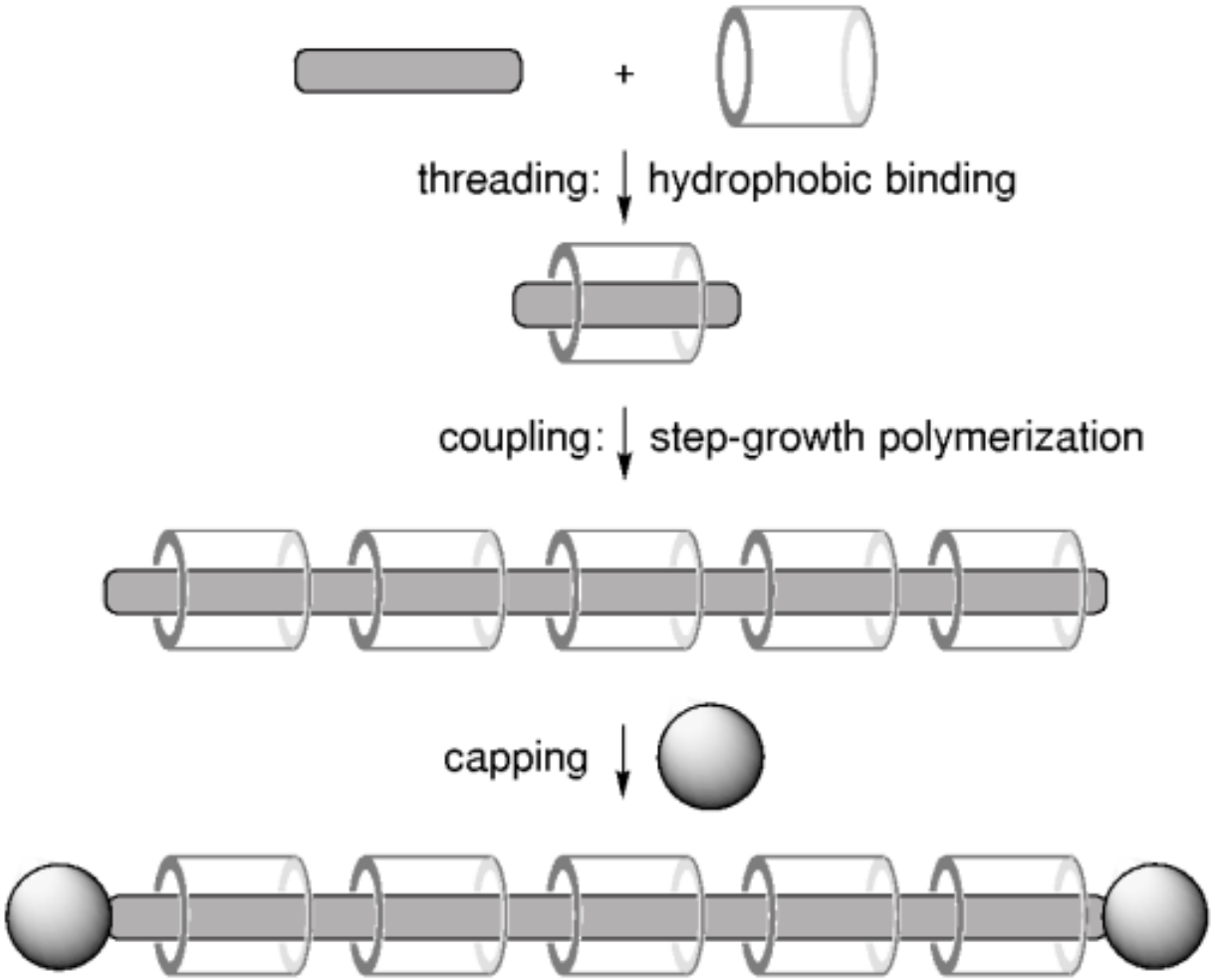
Polyrotaxane Drugs



Release profile of theophylline-immobilized HP-α-CDs (Theo-HP-α-CDs) from Theo-HP-/E4-PHE: (circle): Theo-HP- /E4-PHE 1 with 20 unit/ml of papain, (triangle): Theo-HP-/E4-PHE 2 with 20 unit/ml of papain, (filled triangles): Theo-HP- /E4-PHE 2 without papain.

J. Contr. Release 58, 1999, 251

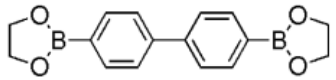
Insulated Molecular Wires



Hydrophobic binding directs the synthesis of an insulated molecular wire

Angew. Chem. Int. Ed. 39, 2000, 3456

Insulated Molecular Wires



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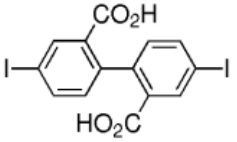

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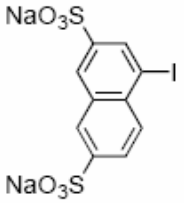
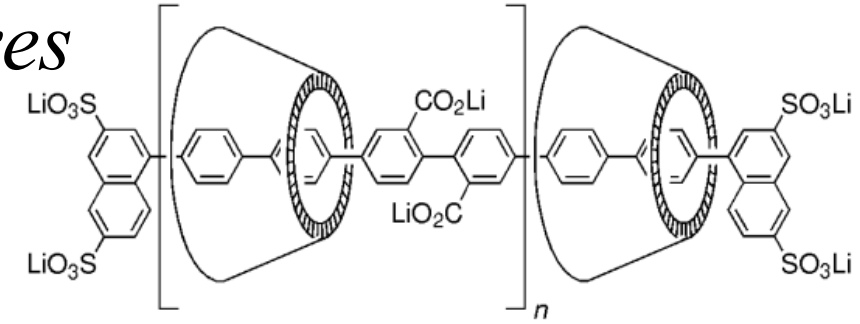
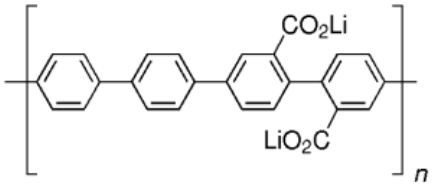
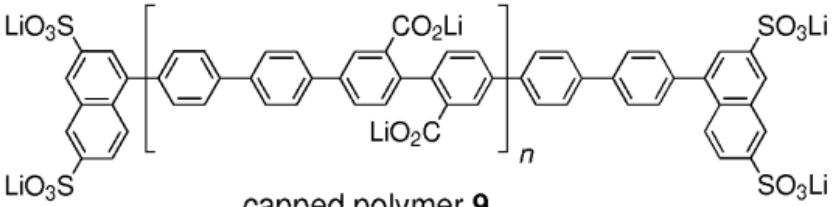




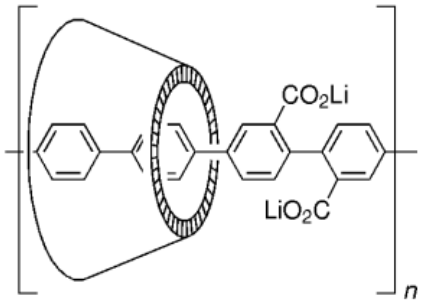
polyrotaxane **8**



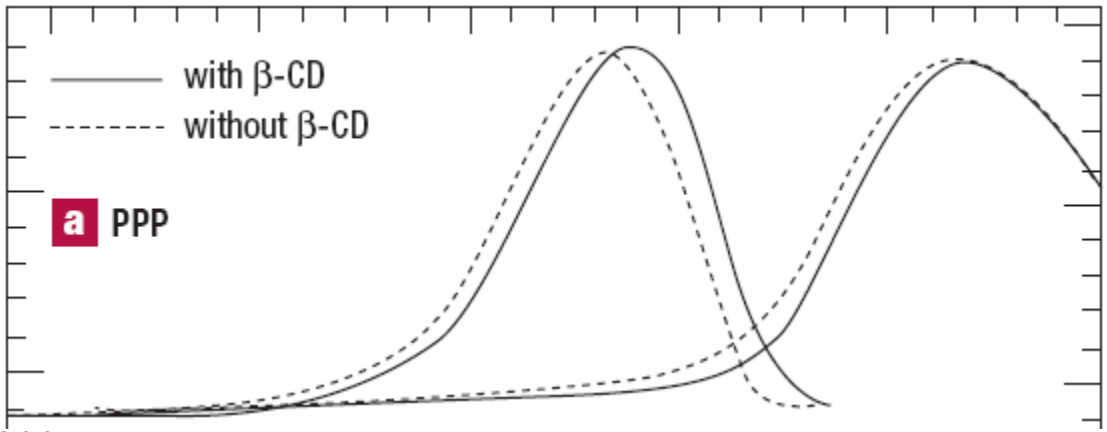
polymer **3**



capped polymer **9**

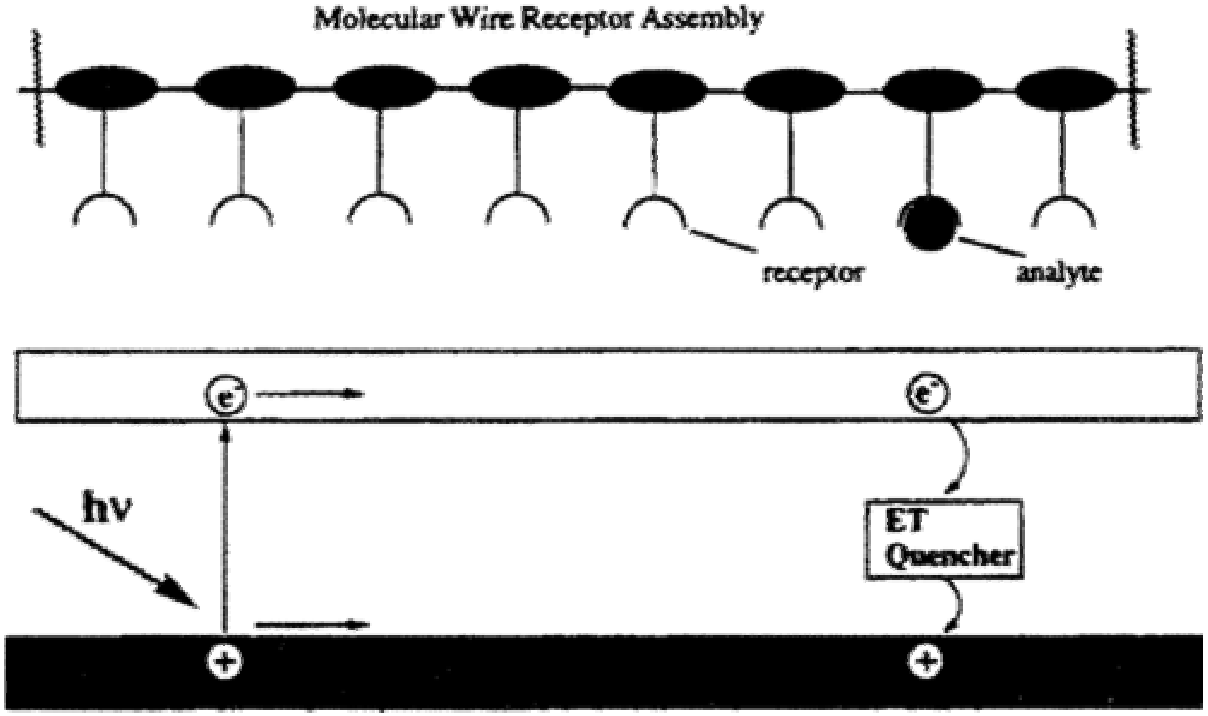


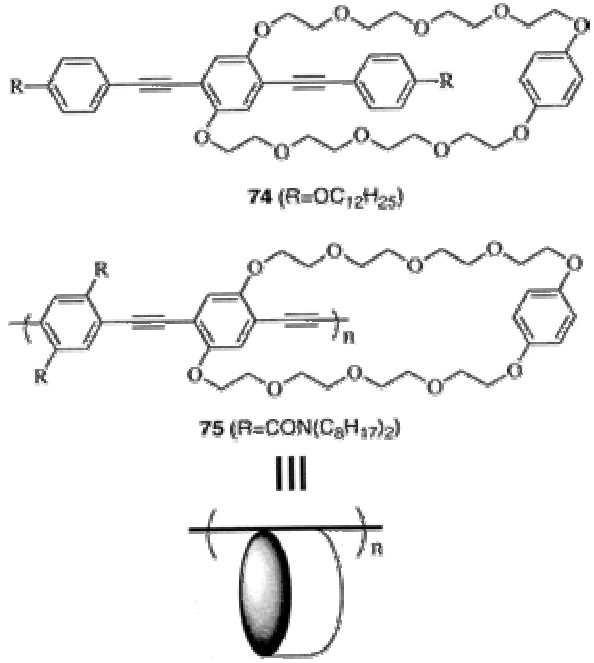
polypseudorotaxane **4**



Angew. Chem. Int. Ed. 39, 2000, 3456

Supramolecular Sensors



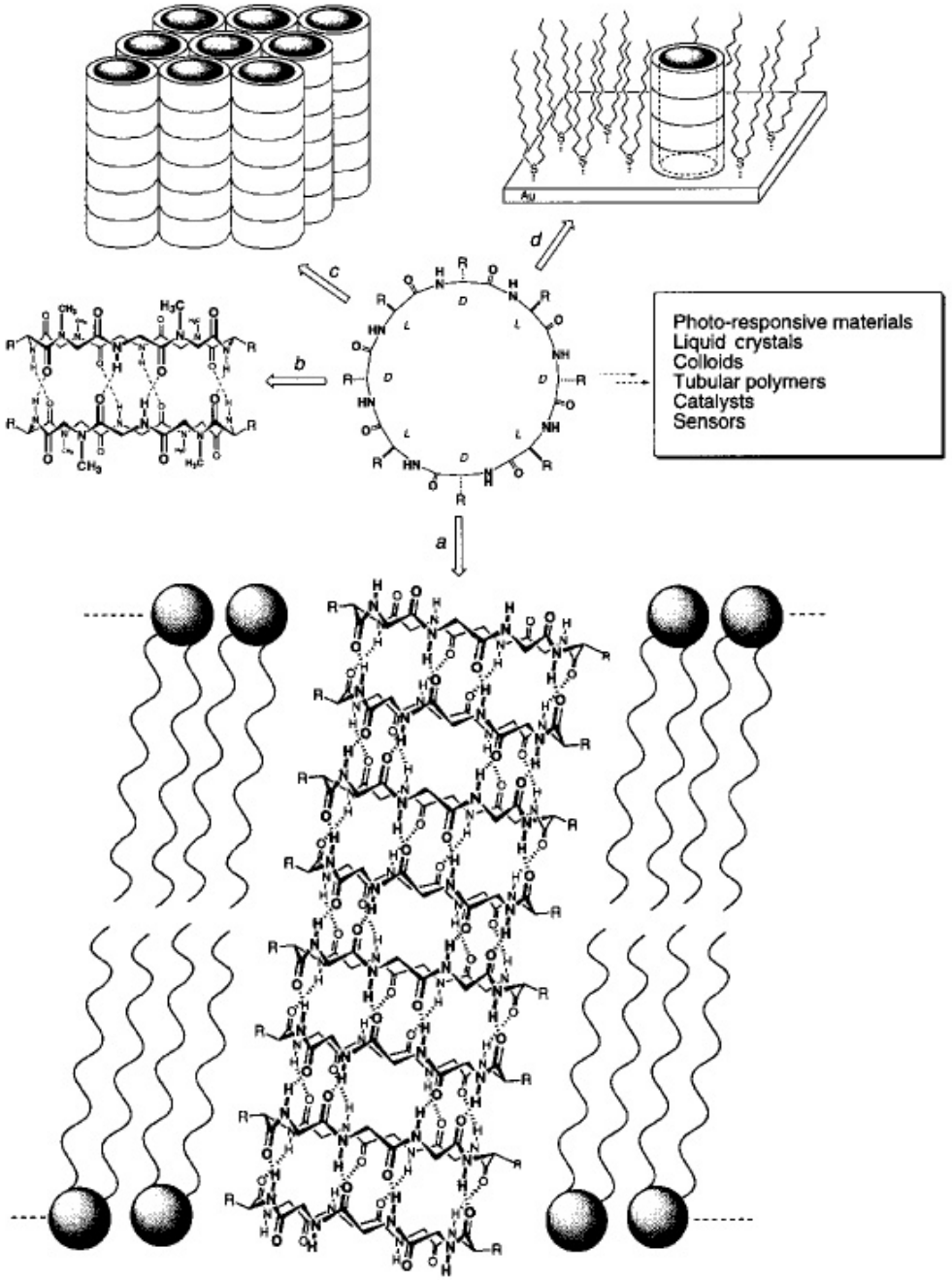


Band diagram illustrating the mechanism by which the molecular wire receptor assembly can produce an enhancement in a fluorescence chemosensory response. The horizontal dimension represents the position along the conjugated polymer shown schematically at the top. Excitons are created by absorption of a photon (*hν*) and then migrate along the polymer backbone. Analyte binding produces a trapping site whereby the excitation is effectively deactivated by electron-transfer quenching.

Nanotubes

(center) Appropriately designed cyclic d,l-α-peptides and β-peptides can adopt a low-energy flat ring-shaped conformation in which the amide backbone moieties lie nearly perpendicular to the plane of the ring structure with side chains radiating around a central pore, the size of which is determined by the number of amino acids employed (for illustrative purposes only an eight-residue cyclic d,l-α-peptide is depicted). Depending on the peptide sequence and conditions employed, peptide subunits can be assembled into:

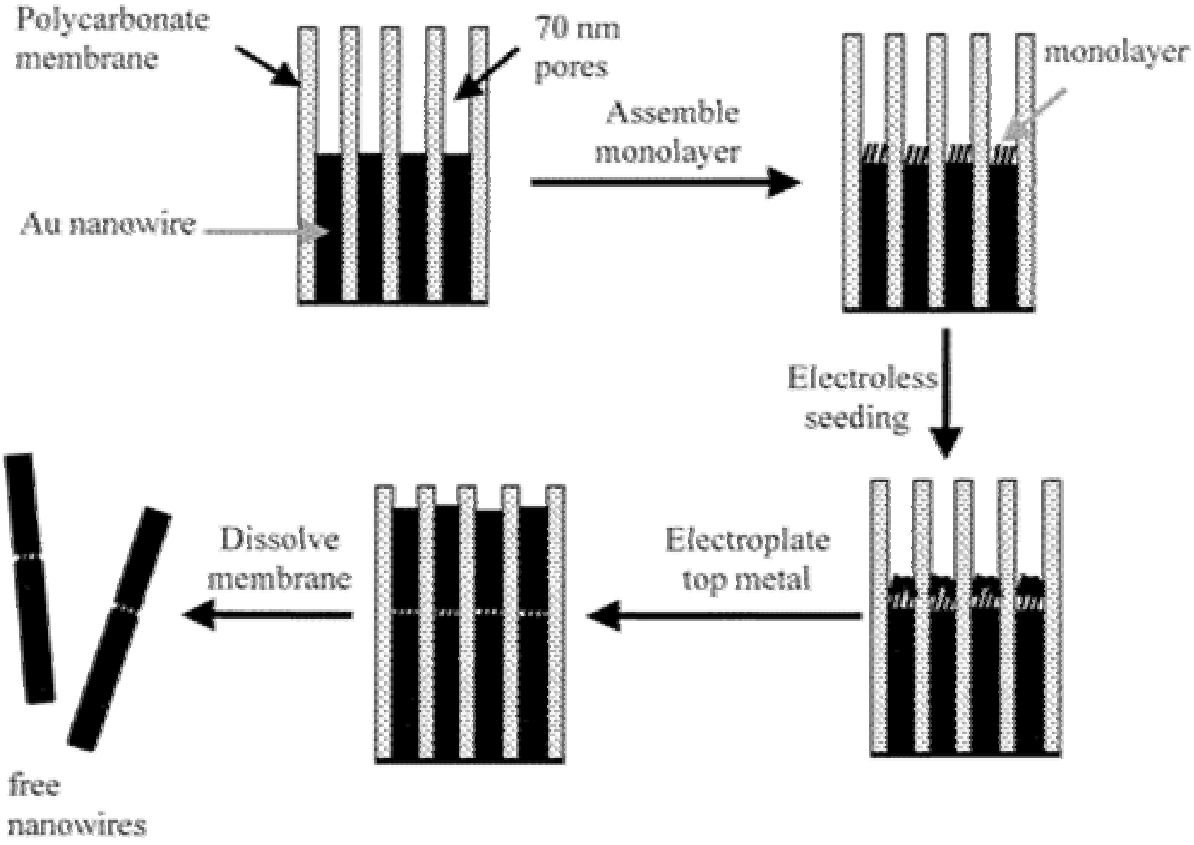
a) transmembrane ion channels and pore structures,
b) soluble cylindrical ensembles,
c) solid-state tubular arrays, and
d) surface-supported composites.



Chem. Eur. J. 1998, 4, 1368

Metal Nanowires - Junction

- Synthetic scheme for the fabrication of bimetallic nanowires with in-wire monolayer junctions.



J. Am. Chem. Soc., **124** (15), 4020 -4026, 2002

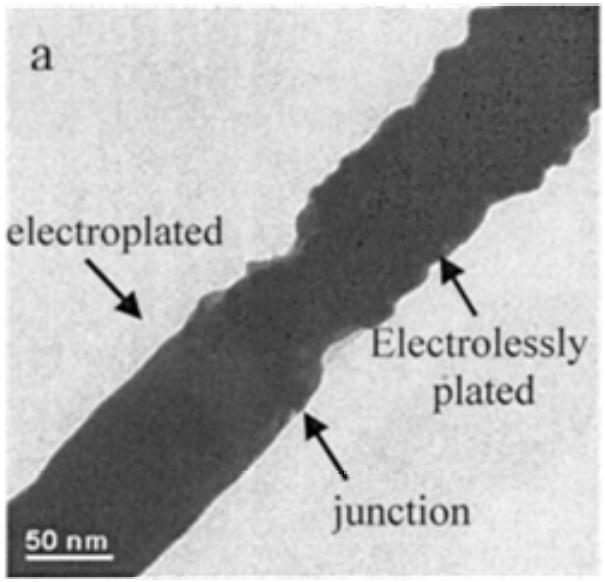
Metal Nanowires - Junction

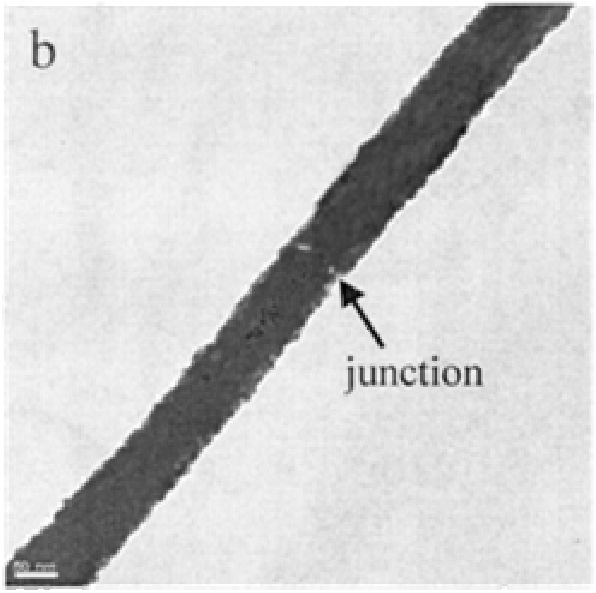
TEM images of

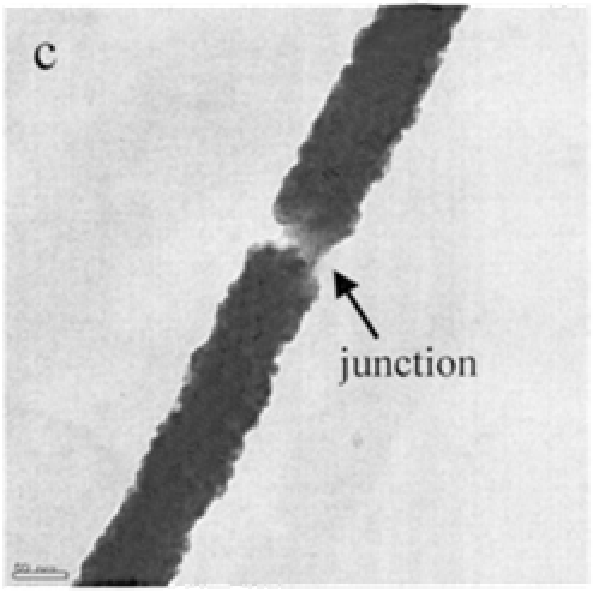
(a) a nanowire with a 16-mercaptohexadecanoic acid SAM between two Au segments (the bottom half of the wire was electroplated and the top half was grown electrolessly),

(b) a 16-mercaptohexadecanoic SAM junction between two electroplated segments of a nanowire; and

(c) a nanowire with a 16-mercaptohexadecanoic SAM junction after 5 min in the electron beam.



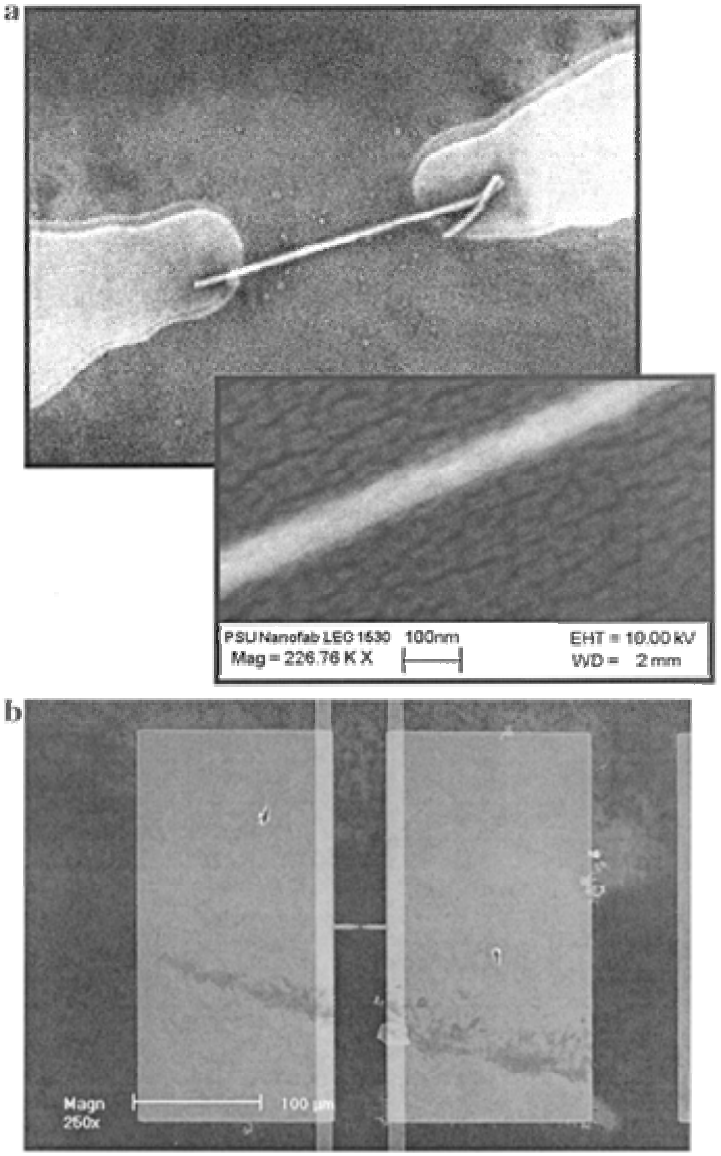




J. Am. Chem. Soc., **124** (15), 4020 -4026, 2002

Metal Nanowires - Junction

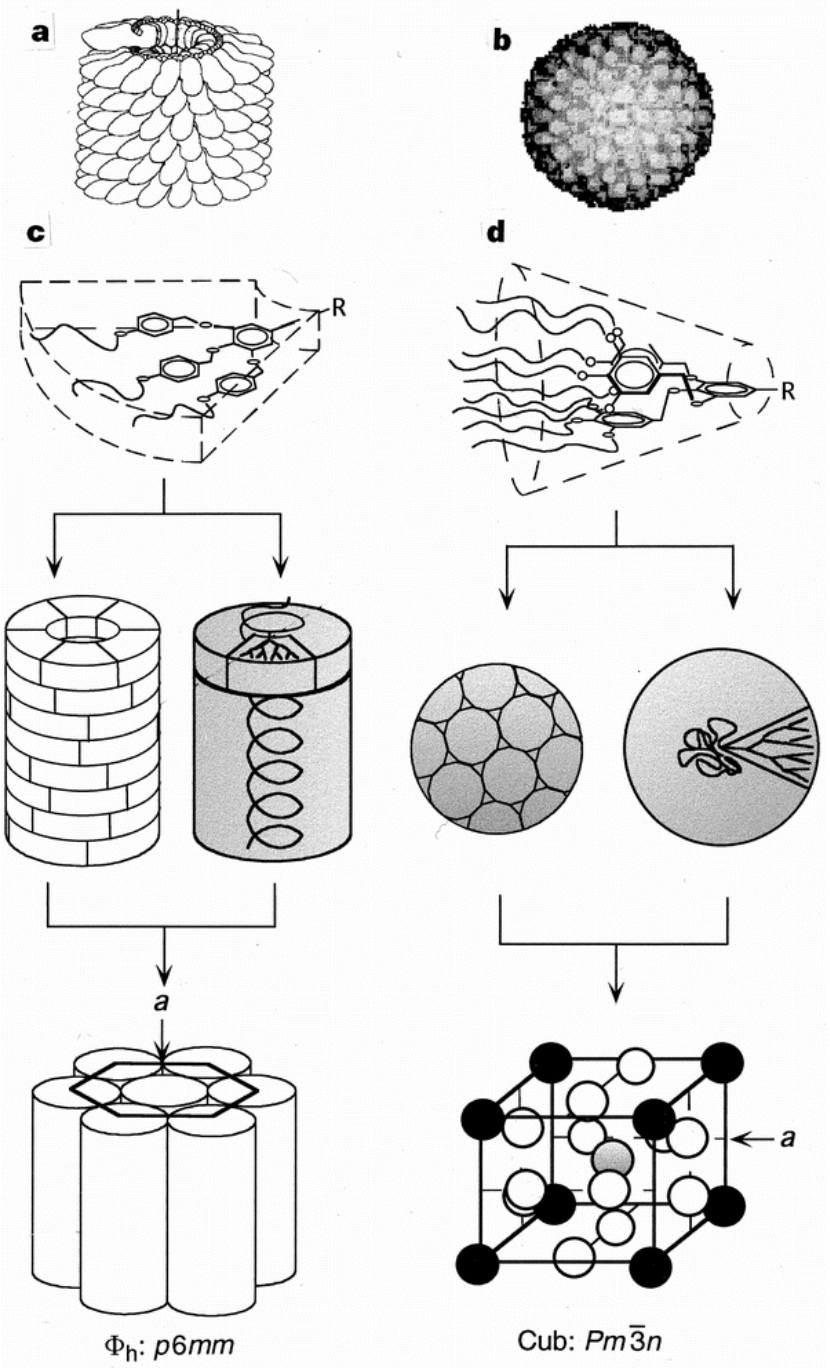
FESEM images of an Au-SAM-Au nanowire spanning the gap between Au contact electrodes (a) at high magnification and (b) at lower magnification showing the region making contact with the probe pads.



J. Am. Chem. Soc., **124** (15), 4020 -4026, 2002

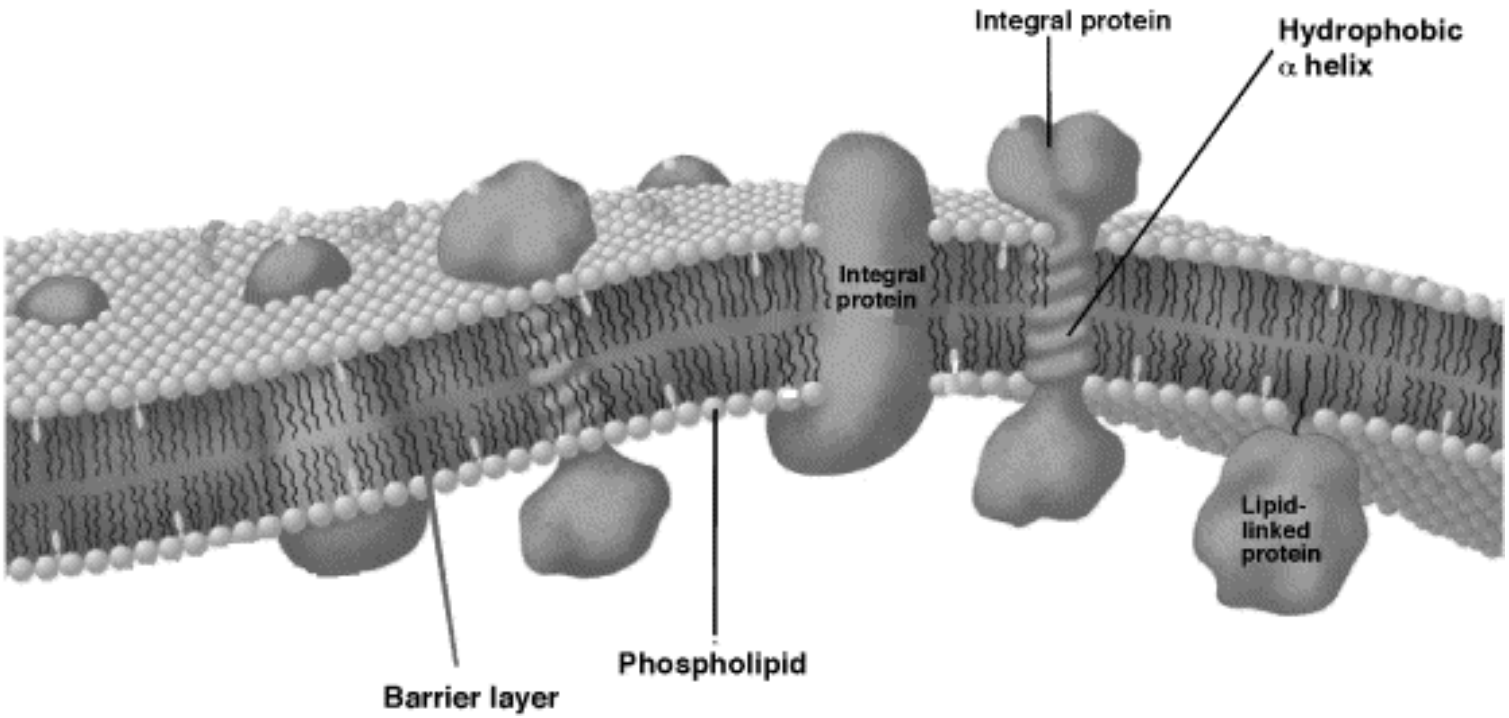
Supramolecular Wires

Natural and synthetic supramolecular systems with cylindrical and spherical shapes: **a**, tobacco mosaic virus; **b**, ico.



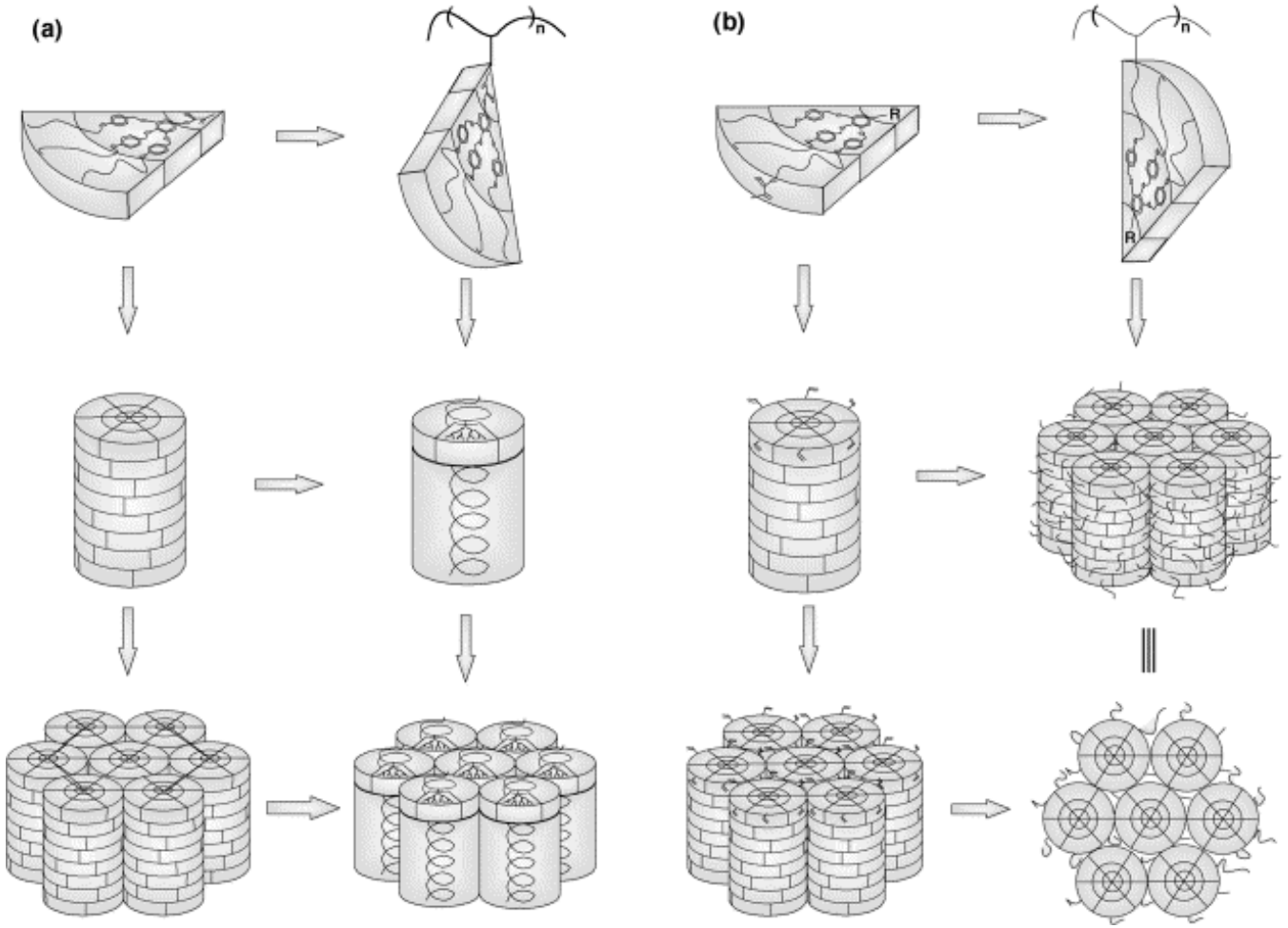
Membrane

Schematic representation of the bilayer fluid mosaic model of the cell membrane. Integral proteins are embedded in the bilayer composed of phospholipids.



Tetrahedron, 58, 4031, 2002.

Membrane

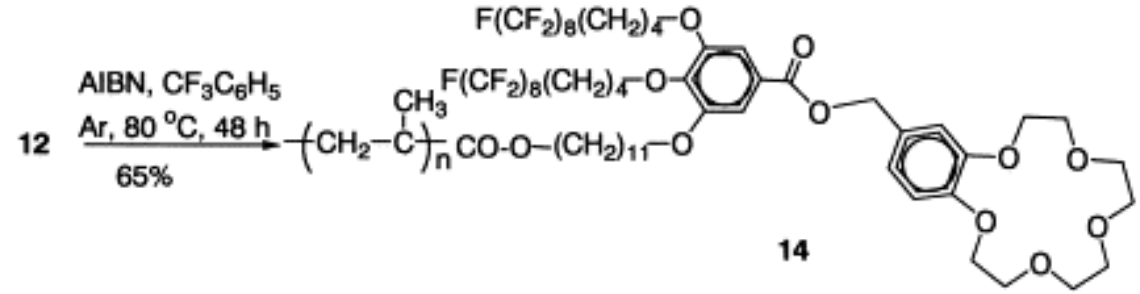


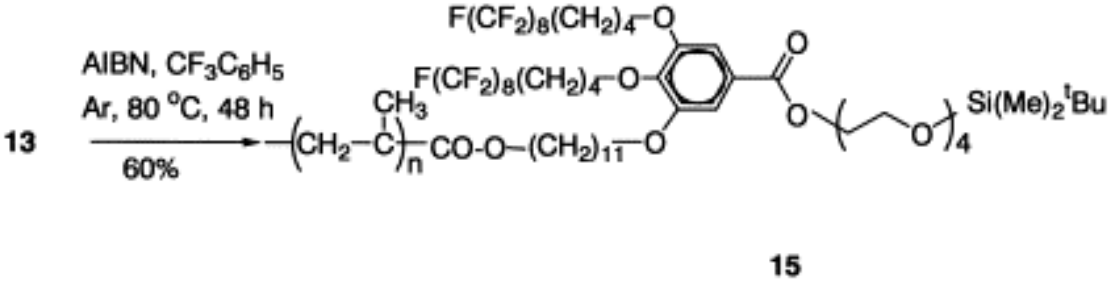
Self-assembly and self-organization followed by polymerization or polymerization followed by self-assembly and self-organization of tapered monodendrons containing a polymerizable group at the apex (a) or on the periphery of the taper (b). The R group in (b) represents the ionic, electronic or protonic active element.

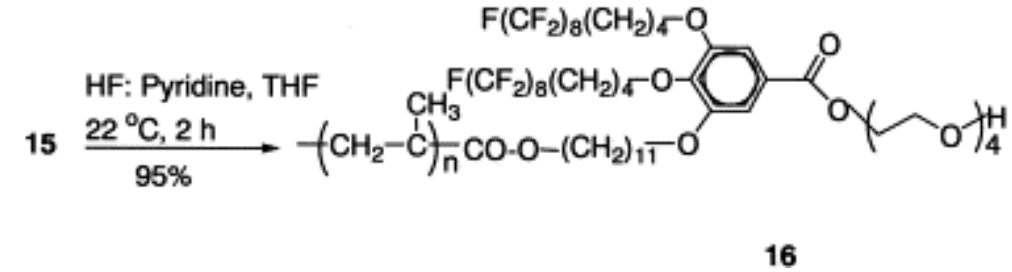
Tetrahedron, 58, 4031, 2002.

Membrane

The corresponding polymers (**14**–**16**) self-assemble and subsequently self-organize into supramolecular networks, which form a 2-D hexagonal columnar lattice via the fluorophobic effect. These networks consist of a continuous phase, which is based on the semifluorinated, paraffinic barrier layer and which is perforated in a hexagonal array by ion-selective or ion-active channels constructed from the benzo crown-ether and tetraethylene glycol respectively.

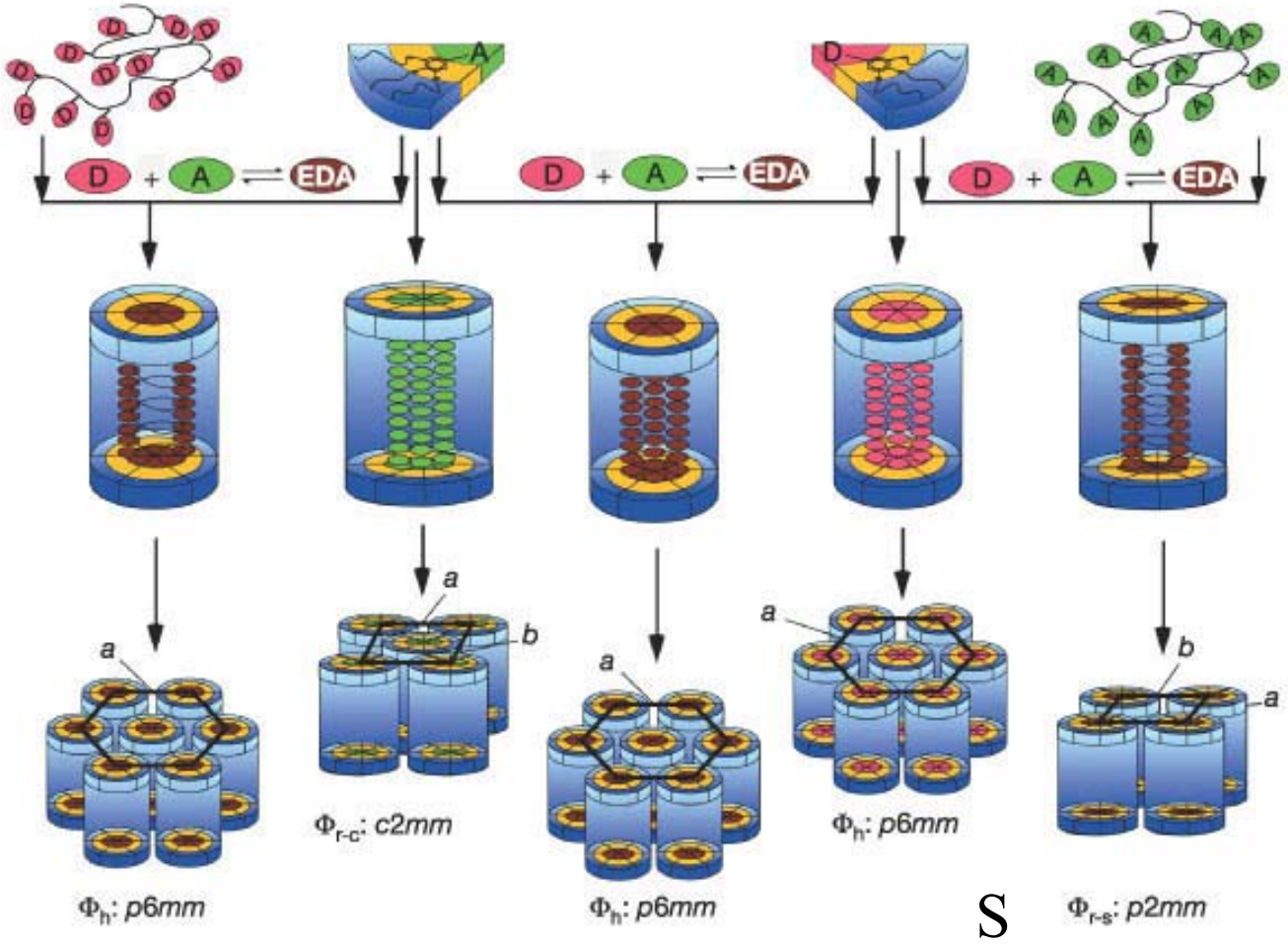






Tetrahedron, 58, 4031, 2002.

Supramolecular Electronics



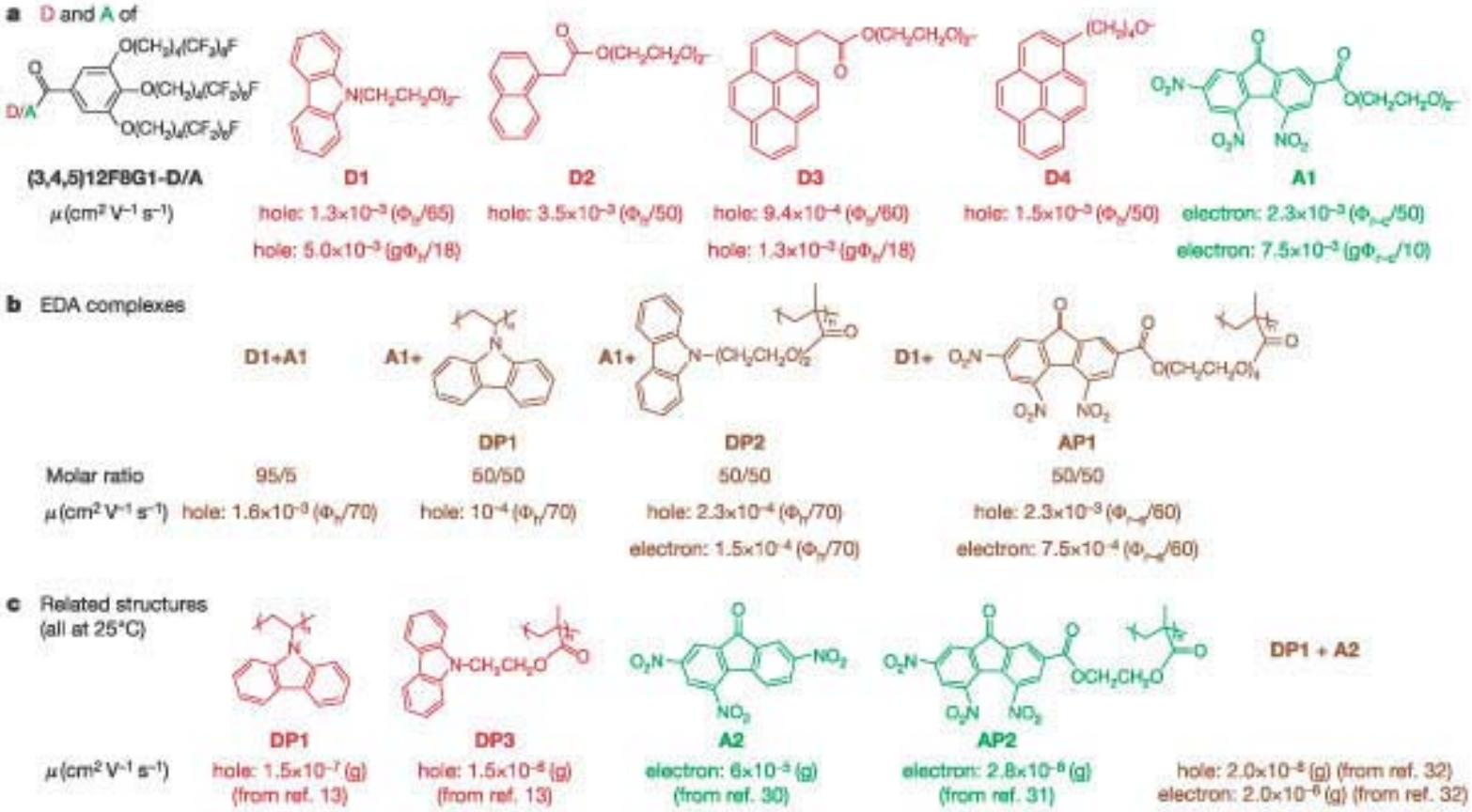
S

Shown are the self-assembly, co-assembly and self-organization of dendrons containing donor (D) and acceptor (A) groups with each other and with disordered amorphous polymers containing D and A side groups. The different systems form hexagonal columnar ($_{h}$), centred rectangular columnar ($_{r\text{-}c}$) and simple rectangular columnar ($_{r\text{-}s}$) liquid crystals. *a* and *b* are lattice dimensions; space groups are shown.

Nature **419**, 384 - 387 (2002)

Supramolecular Electronics

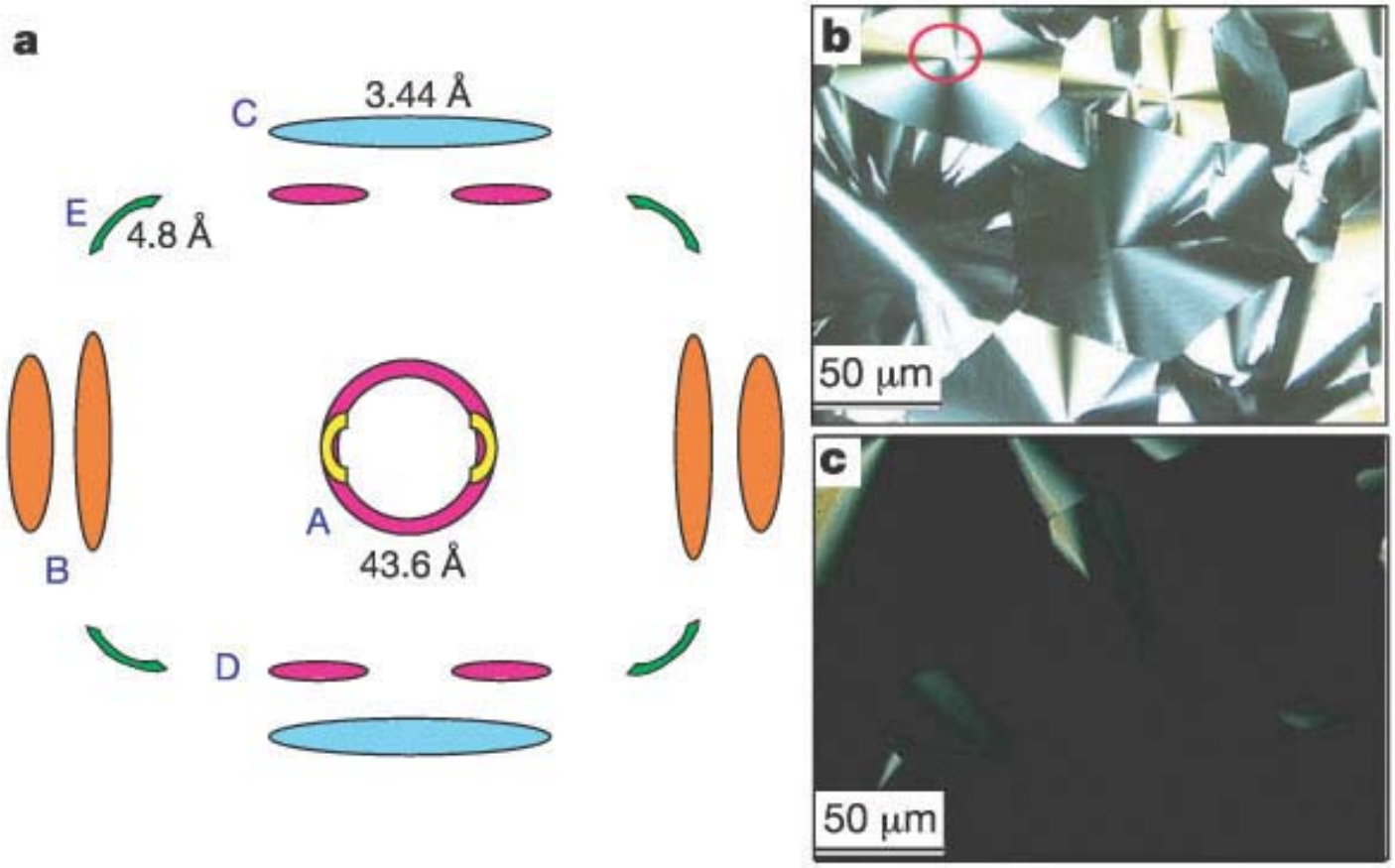
•Charge carrier mobility of supramolecular columns and related systems.



Nature **419**, 384 - 387 (2002)

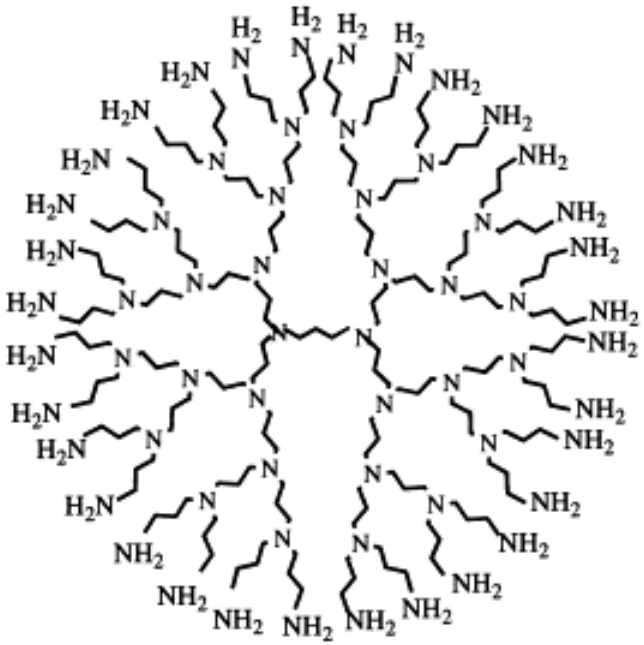
Supramolecular Polymers

- X-ray

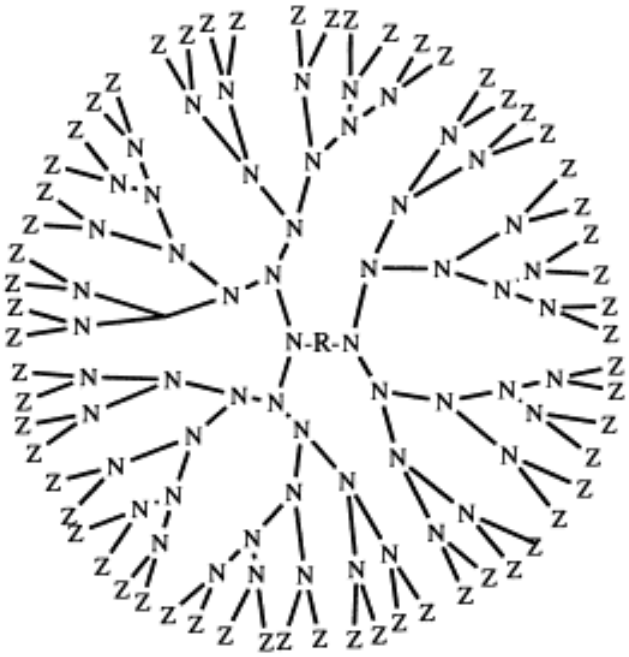


Nature **419**, 384 - 387 (2002)

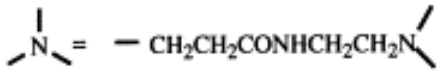
Dendrimer Synthesis



DAB-*dendr*-NH_2

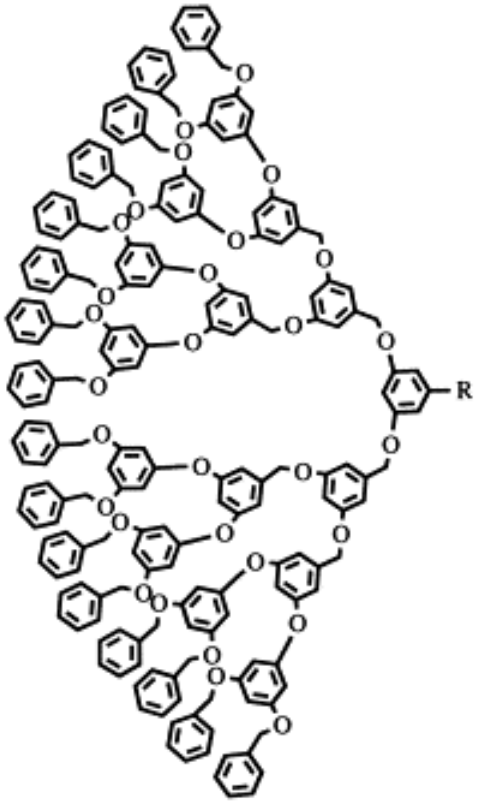


PAMAM Dendrimer



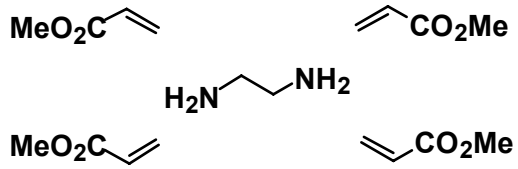
Z = $-NH_2$

R = $-(CH_2)_n-$

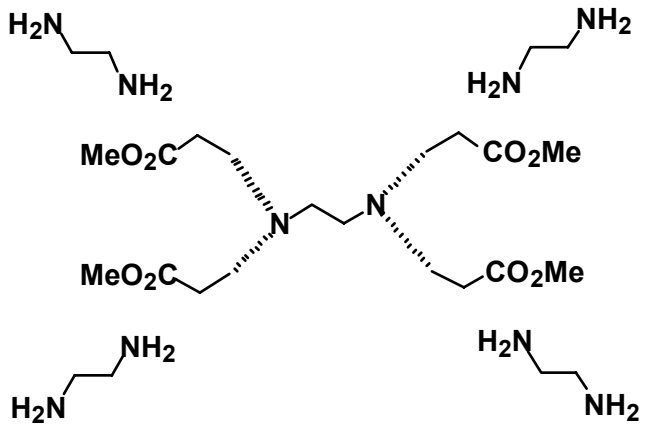


Fréchet's Dendron

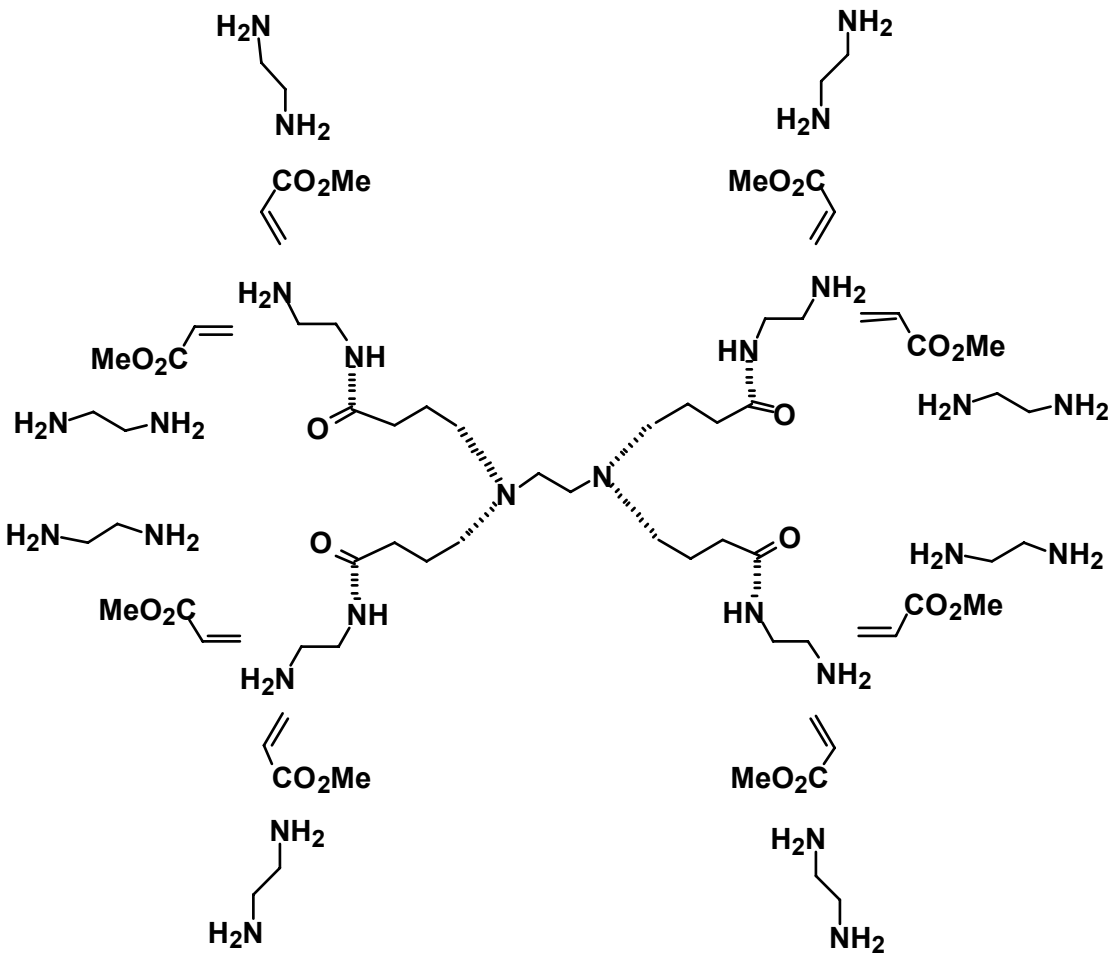
Divergent Synthesis



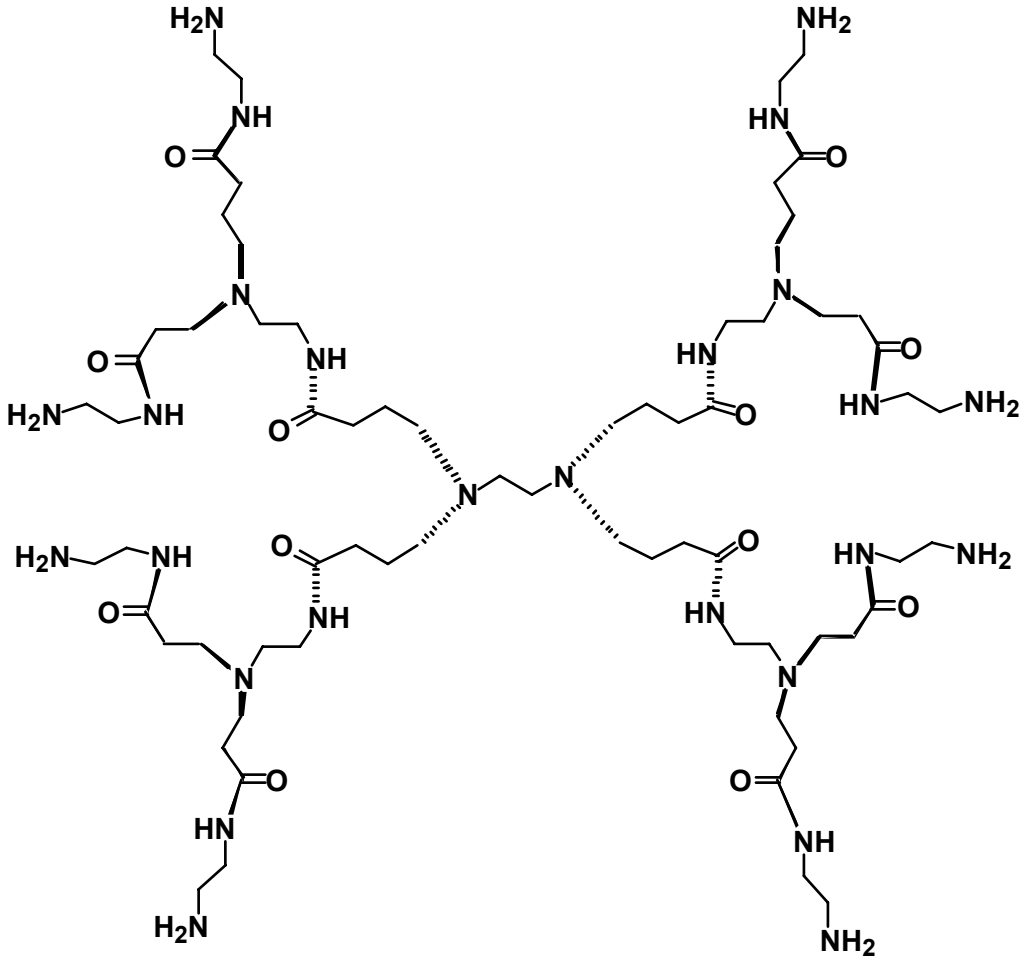
Divergent Synthesis



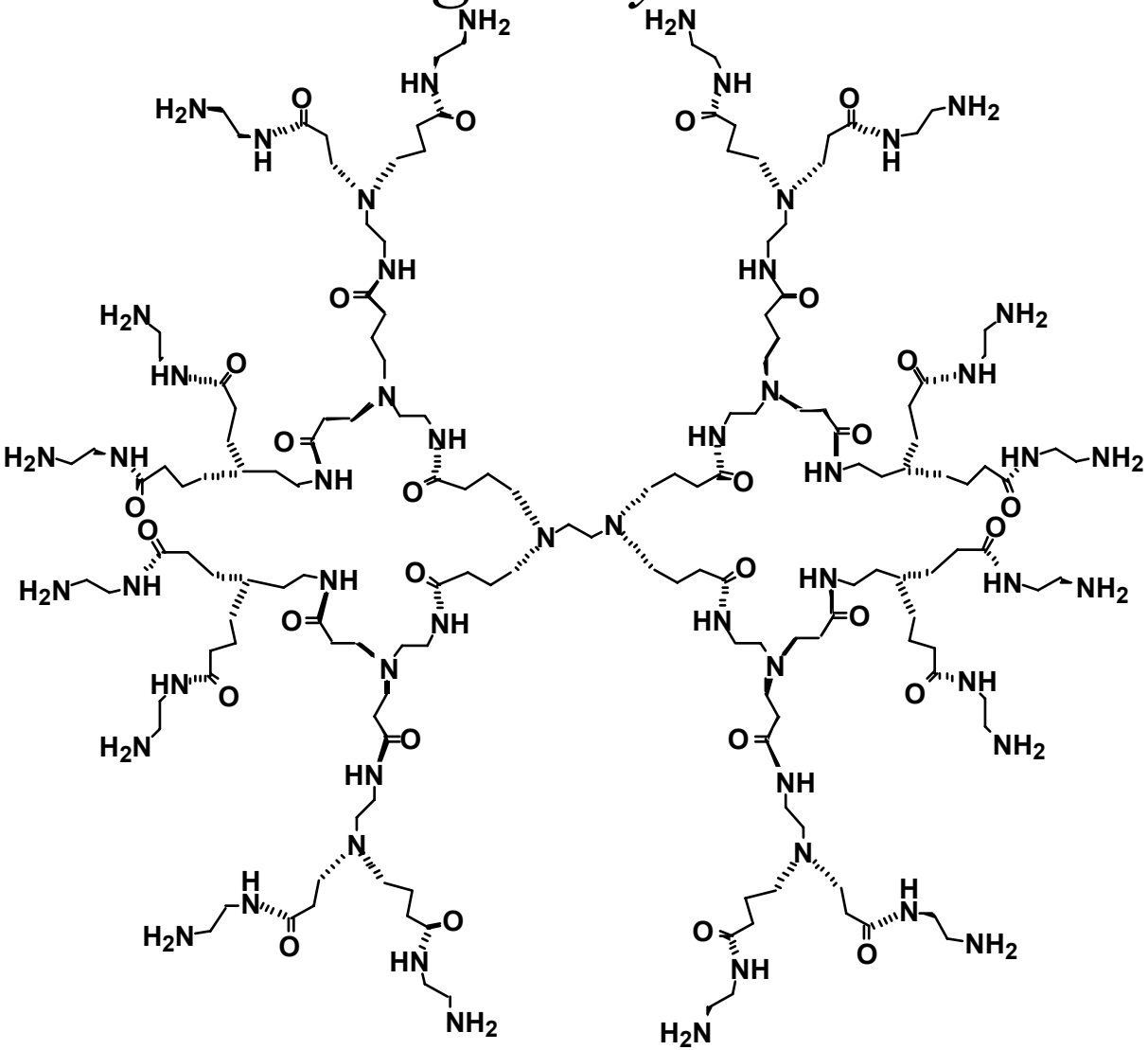
Divergent Synthesis

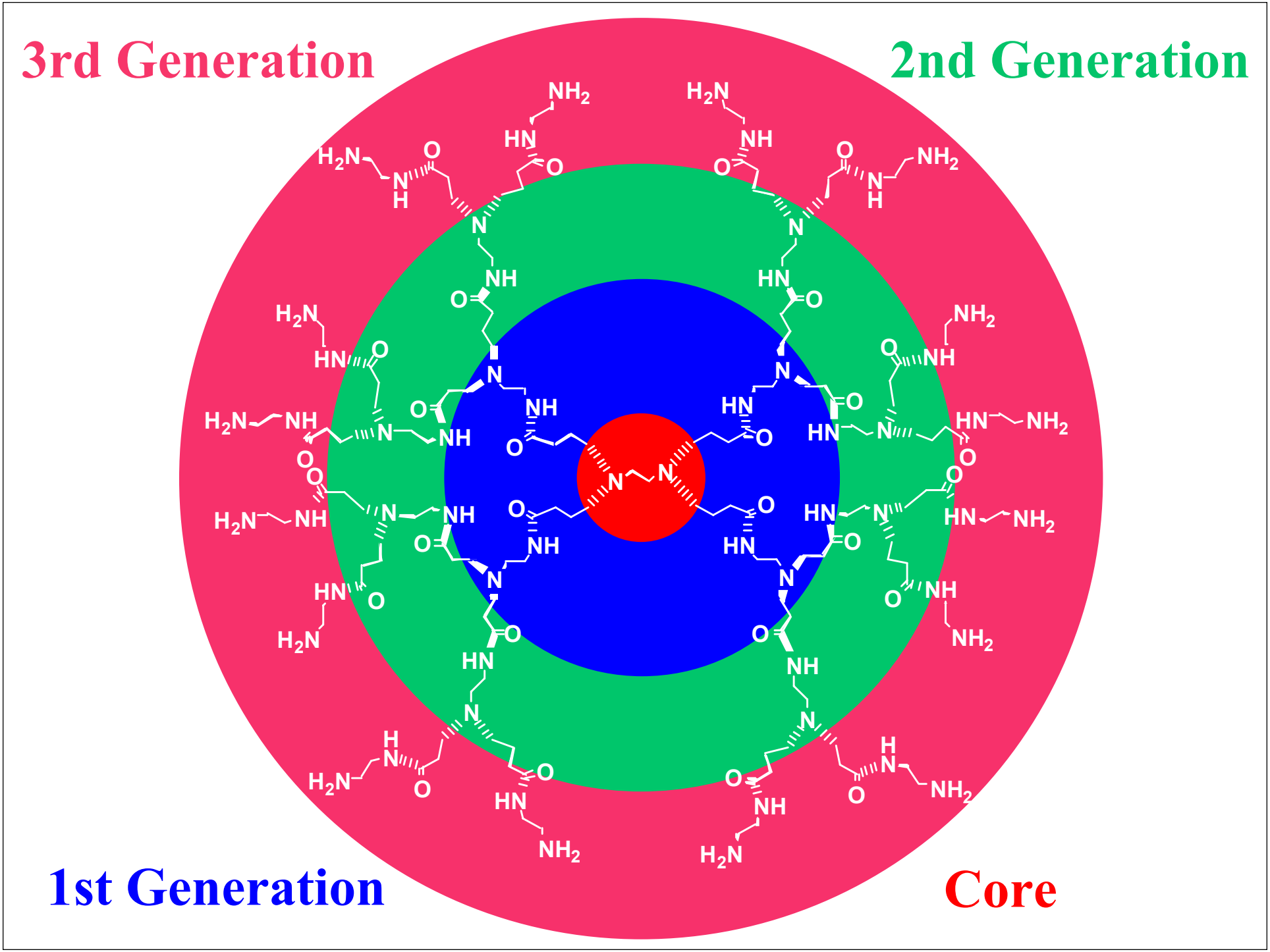


Divergent Synthesis

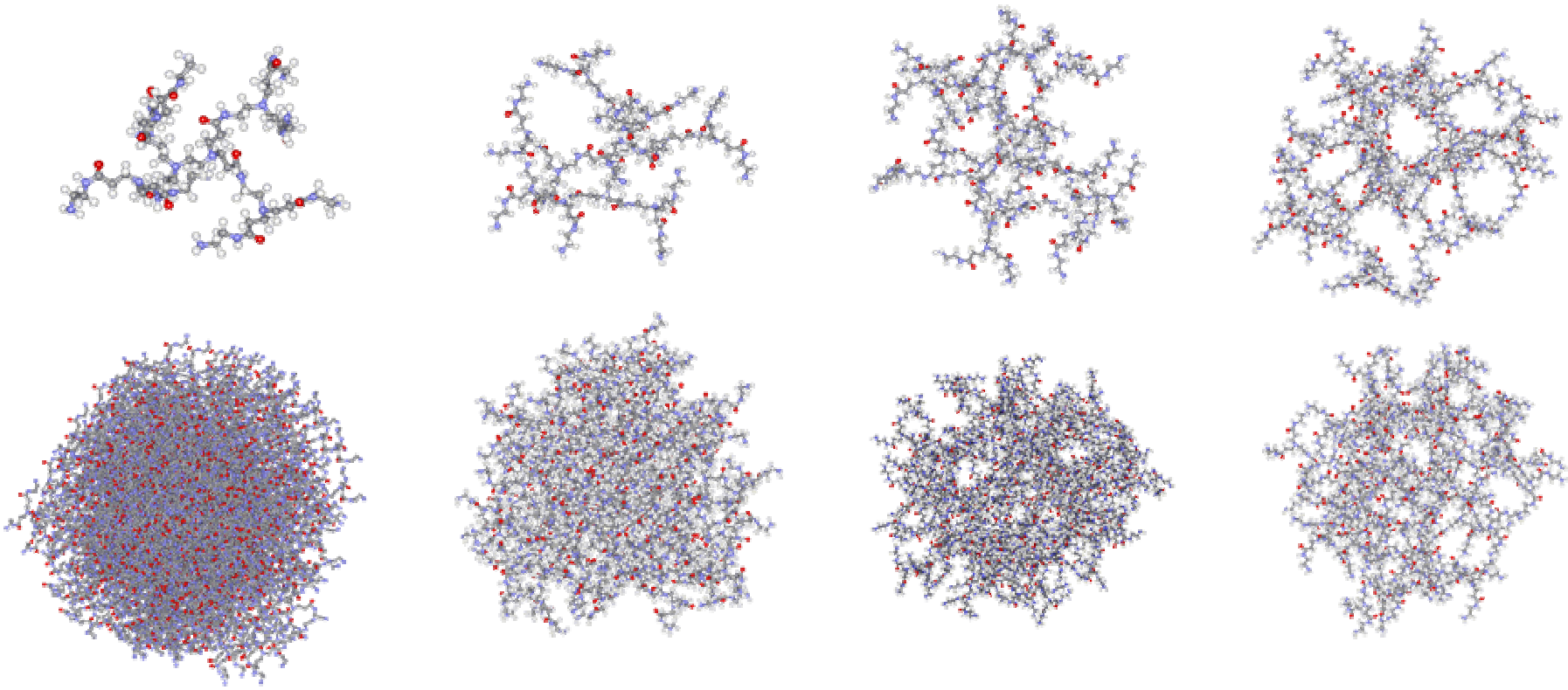


Divergent Synthesis

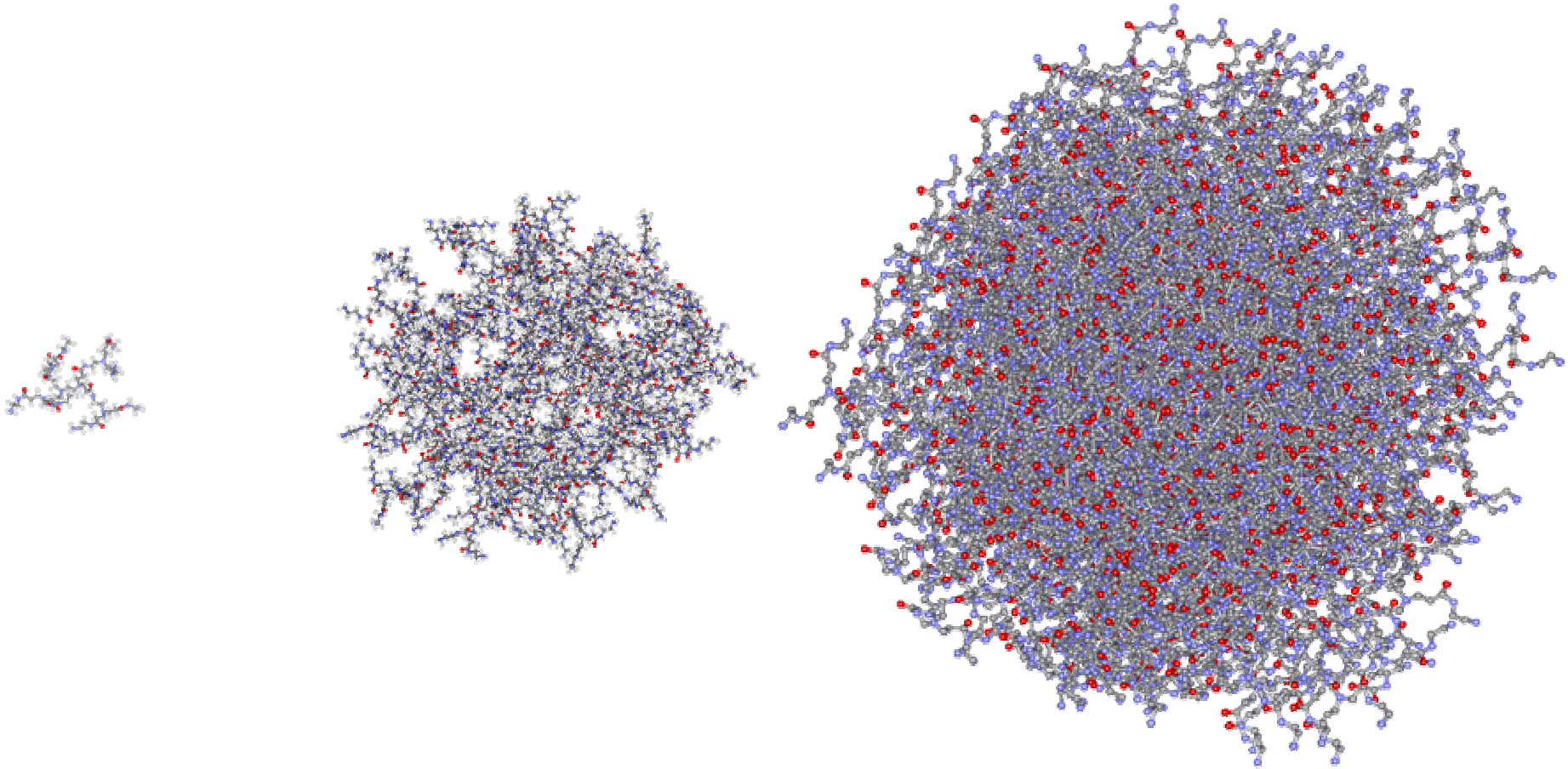



3rd Generation
2nd Generation
1st Generation
Core

Dendrimers - Architecture

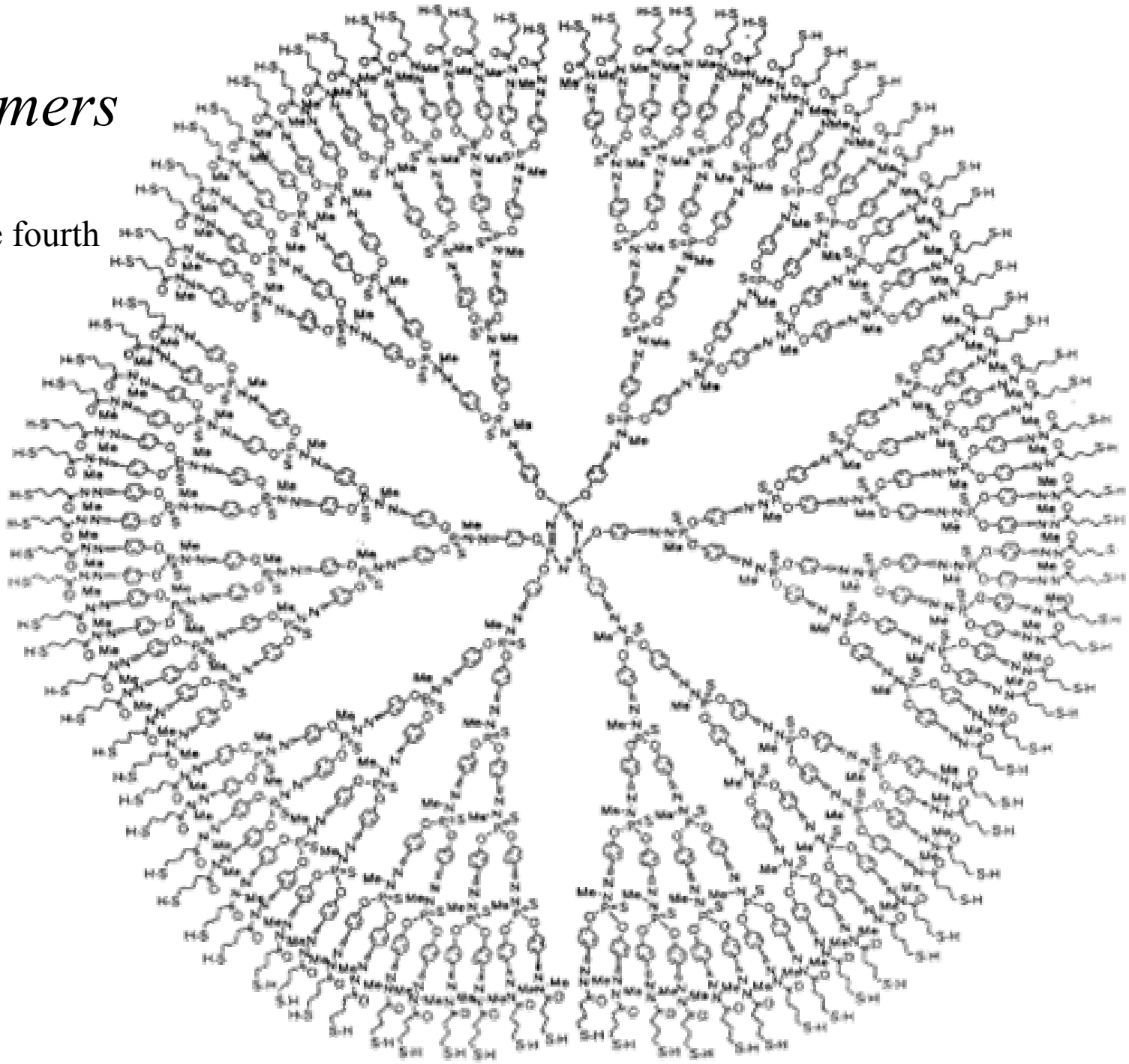


Dendrimers - Architecture



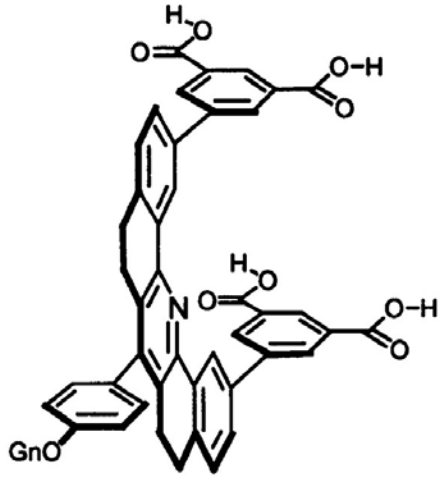
Dendrimers

Sketch of the fourth generation dendrimer G4-SH with 96 SH functions.

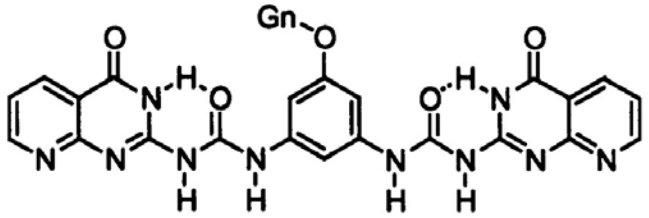


Nano Letters, **2** (11), 1239 -1242, 2002

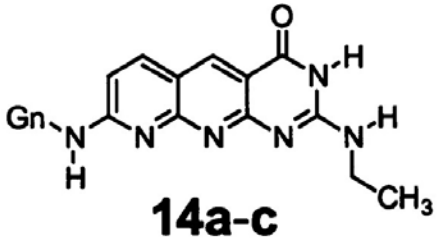
Dendrimers – Self-assembly



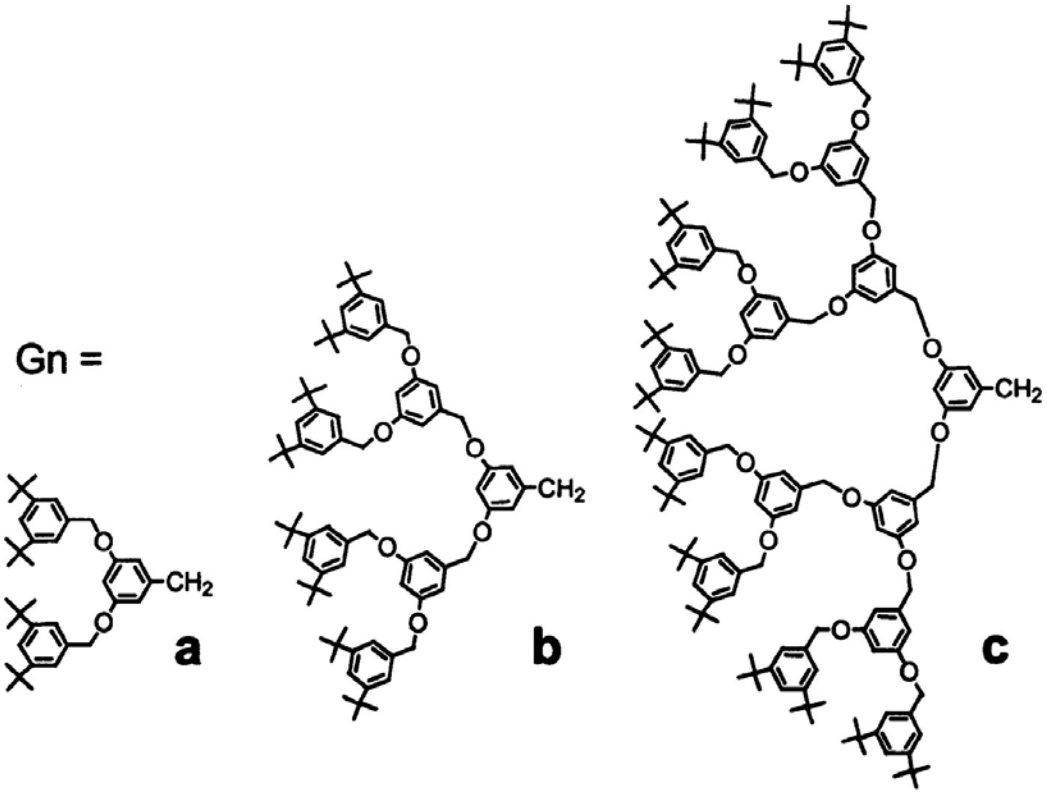
13a-c



7a-c



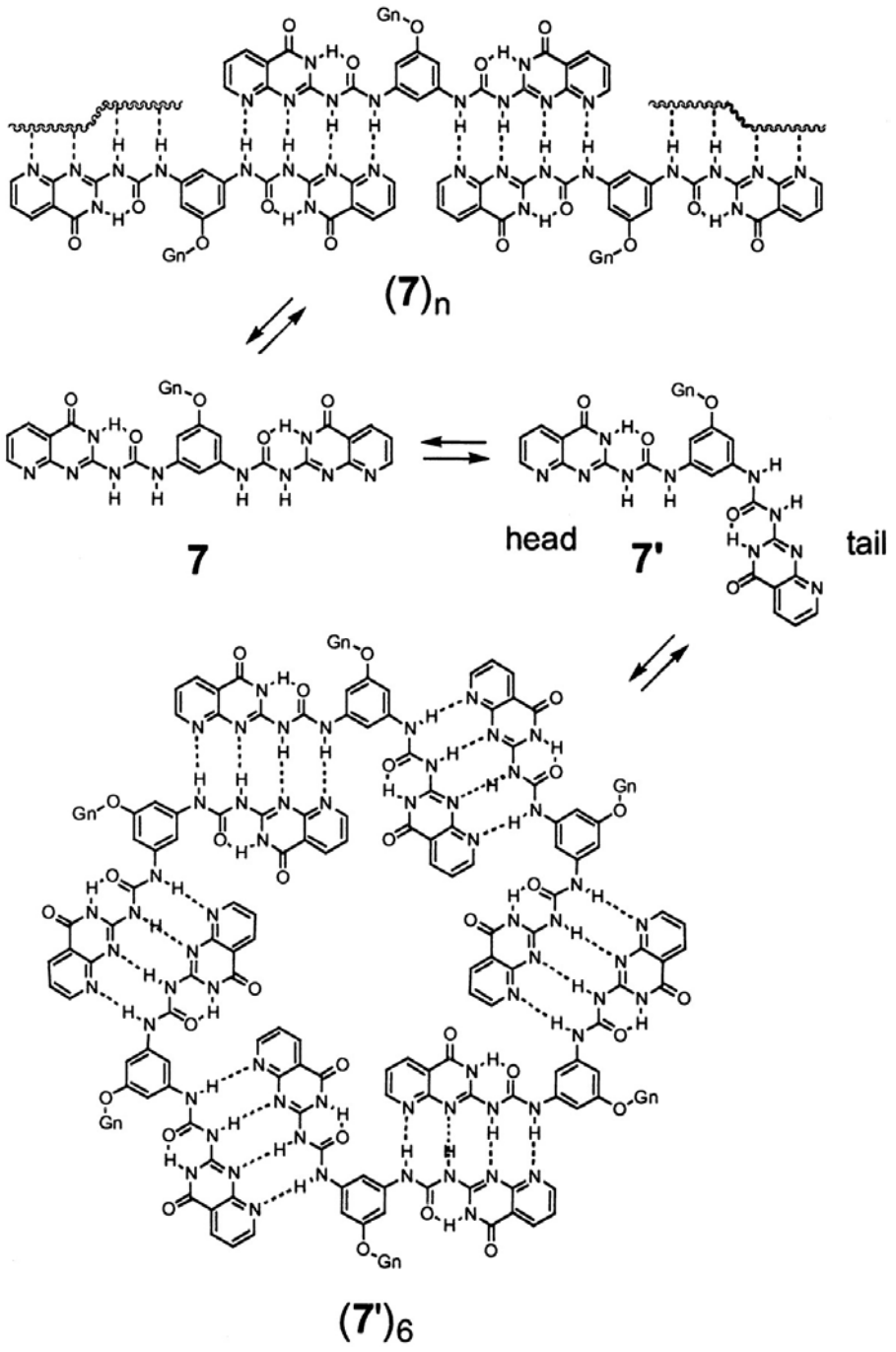
14a-c



Proc. Natl. Acad. Sci. U. S. A. 99: 5099-5104, 2002

Dendrimers – Self-assembly

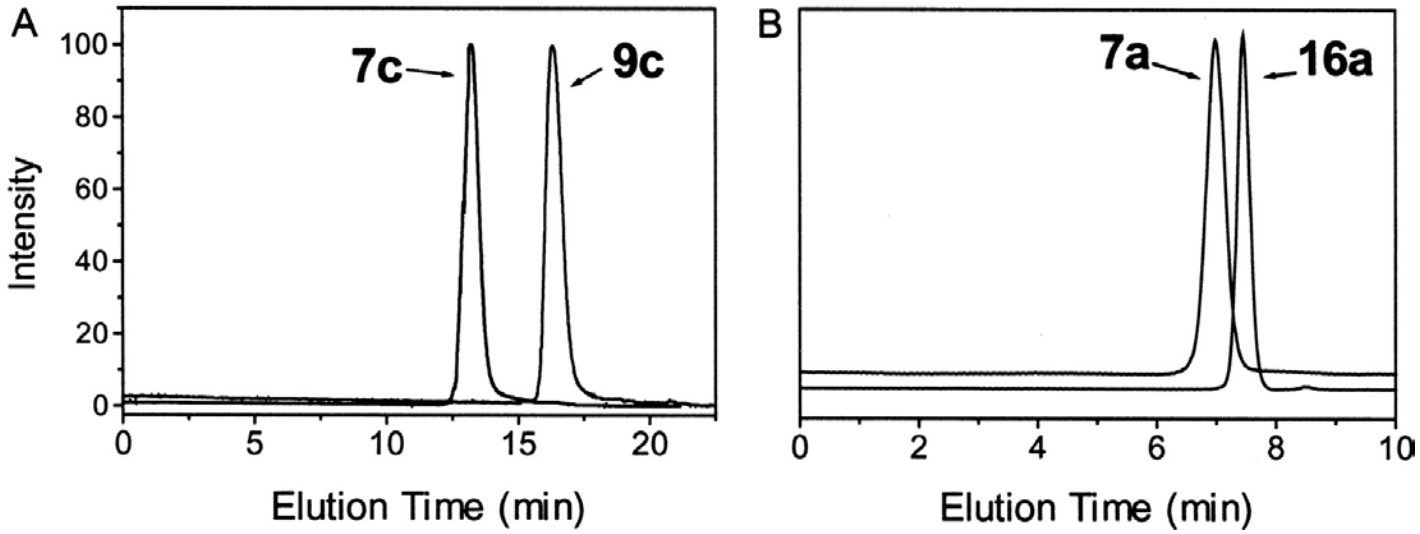
- Scheme showing different conformations of spacer unit of **7** and its affect on the assembly process.



Proc. Natl. Acad. Sci. U. S. A. 99: 5099-5104, 2002

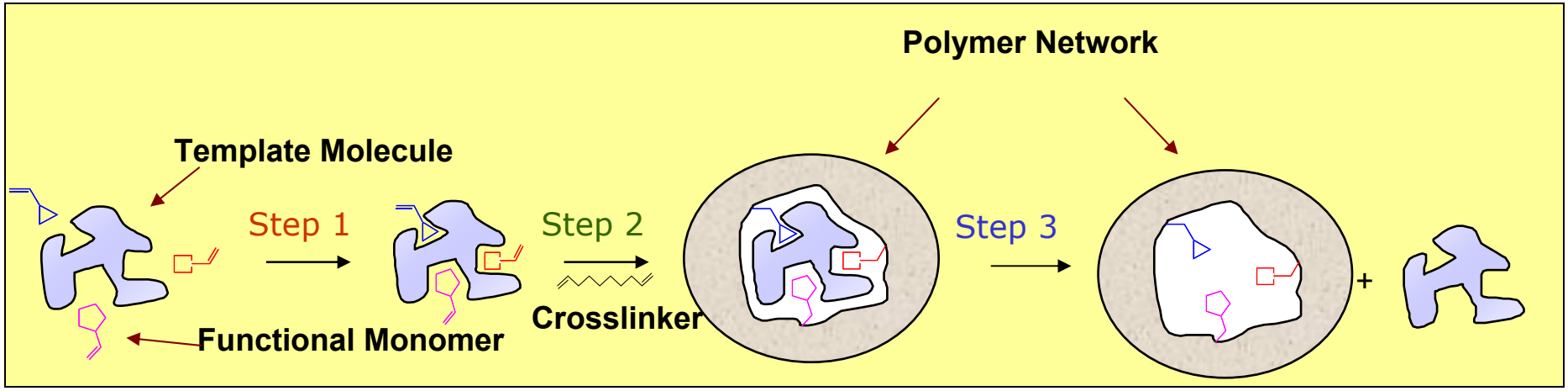
Dendrimers – Self-assembly

- Structural integrity - GPC

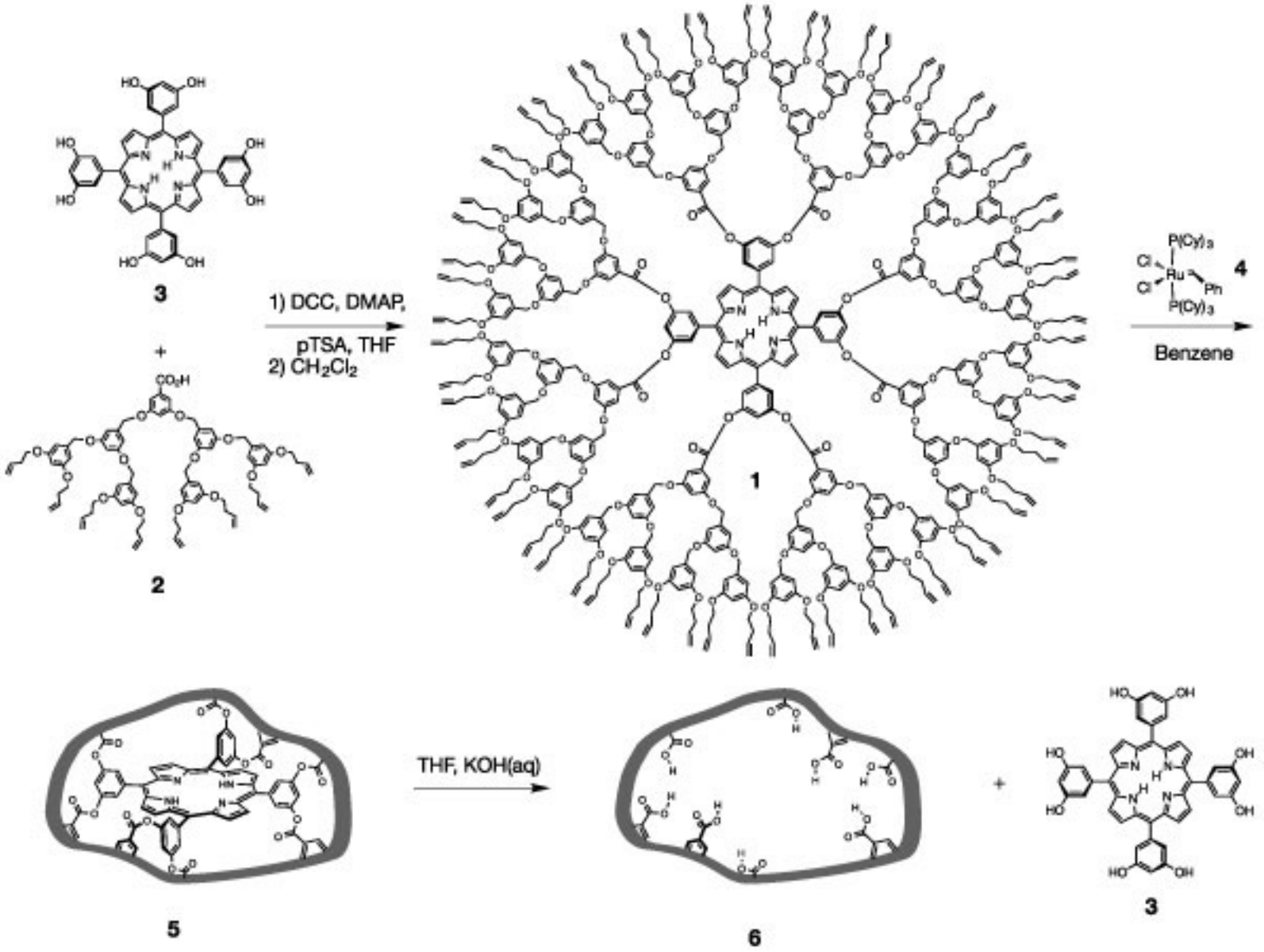


Proc. Natl. Acad. Sci. U. S. A. 99: 5099-5104, 2002

Dendrimers – Molecular Imprinting



Dendrimers – Molecular Imprinting



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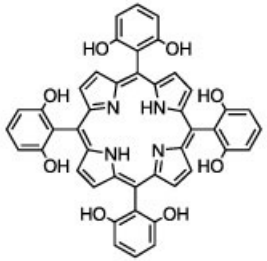
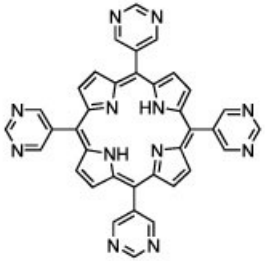
Dendrimers – Molecular Imprinting

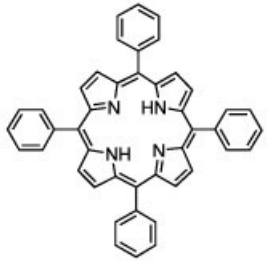
Porphyrins used to study binding properties of imprinted dendrimer **6**.



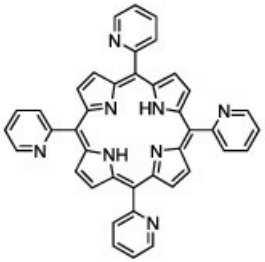
7
H_2T(2,6-OHPh)P
K_{app} = 10.0 (6.8)



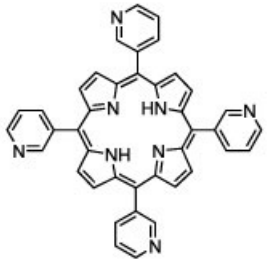
8
H_2T(3,5-pyrimidyl)P
K_{app} = 5 (0.8)



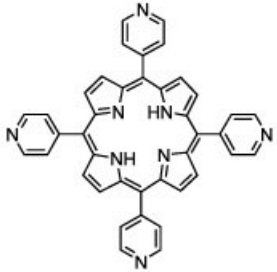
9
H_2TPP
K_{app} < 0.1 (0.0)



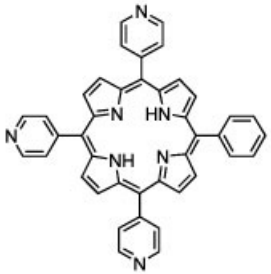
10
H_2T(2-pyridyl)P
K_{app} = 5 (3.0)



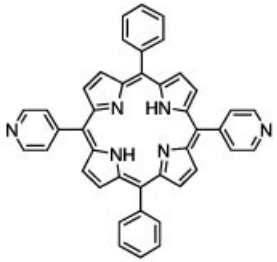
11
H_2T(3-pyridyl)P
K_{app} = 14 (5.8)



12
H_2T(4-pyridyl)P
K_{app} = 13 (5.4)

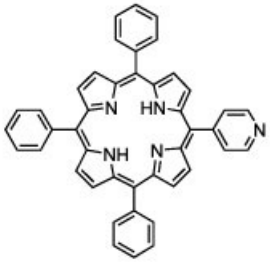


13
H_2tris(4-pyridyl)P
K_{app} < 0.1 (0.0)



14
H_2*trans*-bis(4-pyridyl)P

15
H_2*cis*-bis(4-pyridyl)P
K_{app} < 0.1 (0.0)



16
H_2mono(4-pyridyl)P
K_{app} < 0.1 (0.0)

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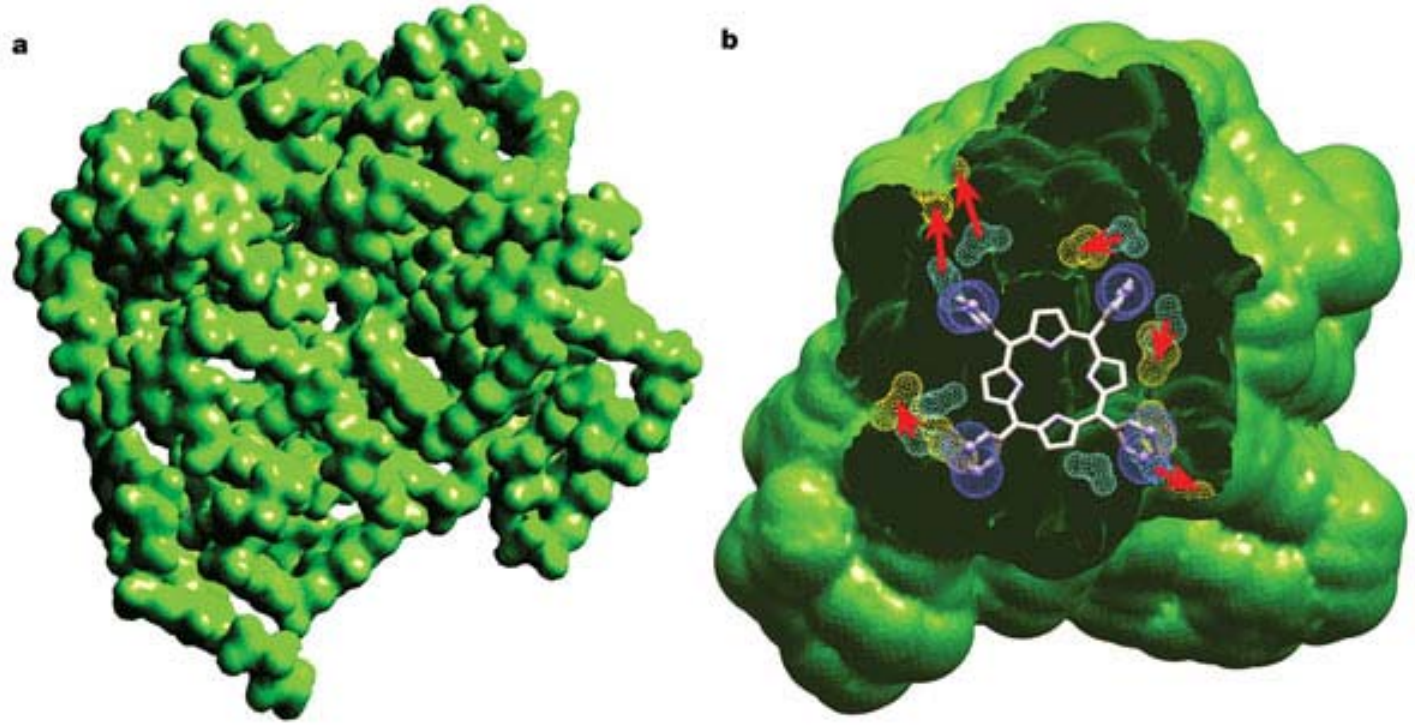
Dendrimers – Molecular Imprinting



Calculated structure of imprinted dendrimer **6** built by iterative attachment of dendrons to the core porphyrin, minimization and cross-linking of neighbouring double bonds. **a**, van der Waals surface of a representative dendrimer structure produced by a 60 ps annealed dynamics simulation. **b**, Calculated binding pocket inside **6**; yellow clouds represent positions of carboxyl groups when **6** is minimized without the host porphyrin **8**, cyan clouds represent positions of carboxyl groups when **6** is minimized in the presence of the host porphyrin **8**, red arrows show the movement of carboxylic groups.

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