

# Nanomaterials and Their Applications: A Critical Study on The Chemistry, Physics and Biology of Dendrimers

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## Abstract

Smaller than 100 nm nanomaterials are quite useful. Nanoparticles or single molecules are present. Nanoparticle-based functionality is not new. Older human societies utilised soot as a colourant, but more modern human populations employed colloidal gold particles, for example, in ruby-colored stained glass. Many nanotechnologies evolved in the recent several years, with several of which found on the market. While nanotechnology is often considered as cutting-edge, these substances are by no means novel from a chemical standpoint. Dendrimers are molecules with well-defined structures such as drug delivery vehicles and light-harvesting materials. Dendrimers can return to their centre of mass. resulting from this curvature, they are denser toward the centre shape-permanent polyphenylene dendrimers may be seen as individual nanosubstances using AFM. The density of the interior is smaller than that of the outside. because to the rigidity, excitation energy is unable to travel between them. Due to the limited mobility of the benzene rings, it means that the open space in the interior of the dendrimer remains constant and defined. Specificity in host-guest interactions allow the development of a nanoreactor, which resembles holes in inorganic materials like zeolites, which enable selective reactions to occur.

**Keywords:** Nanochemistry, Nanomaterials, Nanoparticles, Dendrimers, Applications

## **Introduction**

Nanomaterials are useful materials that have at least one dimension of less than 100 nanometers. These items might be nanoparticles (small clusters of molecules) or single molecules. Functional nanoparticles have a long and illustrious history. Soot, which contains nanosized (less than 1  $\mu\text{m}$ ) carbon particles, was employed as a colourant by the earliest people, whereas colloidal gold particles have been utilised as a pigment since the Middle Ages, for example, in ruby-colored stained glass. Nanoobjects such as polymer lattices or pigment particles, as well as technologies based on nanomaterials' distinctive characteristics, have grown in economic relevance in recent years. However, it's a bit of a contradiction because nanotechnology, which we describe as technology based on the special characteristics of nanomaterials, is seen as cutting-edge, despite the fact that these materials are far from novel from a chemical standpoint.

One of the most fascinating characteristics of nanoobjects is that their properties can differ dramatically from those of their bulk counterparts. For example, silver nanoparticles have biological (antimicrobial) activity whereas silver metal does not. Similarly, metal particle conductivity changes dramatically as their size decreases, and the optical and electrical characteristics of inorganic semiconductor nanoparticles are known to be dependent on particle size. As a result, it is reasonable to argue that studying the characteristics and manipulation of individual nanoobjects is a scientific field in and of itself (nanoscience). While a standard definition for a nanomaterial exists, there is still no agreement on the exact meaning of the terms nanoscience and nanotechnology, as evidenced by the varying definitions given in two recent overviews by leading figures in their development; the above descriptions are our personal attempts at defining them. More sophisticated functionalities of nanoobjects, such as the creation of devices with dimensions of less than 100 nm, must be included in nanotechnology and nanoscience, however they are defined. This feature has piqued the public's interest, prompting funding organisations throughout the world to start projects in both basic and applied research. As a result, one of the current buzzwords fueling research and development expenditure is "nano." (As an aside, physical scientists use the prefix "nano-," whereas biological scientists use the prefix "nanno-," as in nannoplankton.) The Royal Society in London and the Academies of Science and Technology in Paris have published substantial

papers examining the social and other impacts of these new technologies in response to popular enthusiasm and worry about the environmental and other elements of their growth. A variety of broad reviews and books on nanoscience and nanotechnology, as well as numerous topics and applications spanning from catalysis to food science, have also been published. The fascination with nanoscale devices, particularly those based on single molecules, stems in part from the fact that they represent the logical endpoint of ongoing miniaturisation of devices, such as integrated circuits in computers, which underpins the entire electronics revolution that has changed the face of our planet. As Richard Feynman famously pointed out, if 100 atoms were enough to store one bit (binary digit) of information, all of the books ever written might be stored in a cube with edges 6 mm long, thus nanotechnology's potential influence on information storage and processing is difficult to overestimate. Another intriguing aspect is that if nanoelectronics devices can be manufactured via chemical synthesis and processing, more devices might be produced in a single day than have ever been produced using lithographic methods!

Because the definition of nanoobjects by size is a little hazy—it includes materials with only one dimension in the nanometre range, such as functional self-assembled monolayers—much nanoscience focuses on the properties of single molecules or particles rather than ensembles, but it's important to remember that nanoobjects also include supramolecular materials. Single-molecule spectroscopy (SMS) and scanning tunnelling microscopy are two novel physical approaches for exploring their electrical and optical characteristics that have made it feasible to investigate single molecules (STM). These technological advancements have prompted chemists to look into ways to synthesise materials that perform well at the single-molecule level or can self-assemble into well-defined functional nanostructures; indeed, the design and synthesis of the latter is one of the most important aspects of nanoscience to chemists. Nanoscience and nanotechnology will hence require an integrated blend of synthetic and physical approaches to progress further.

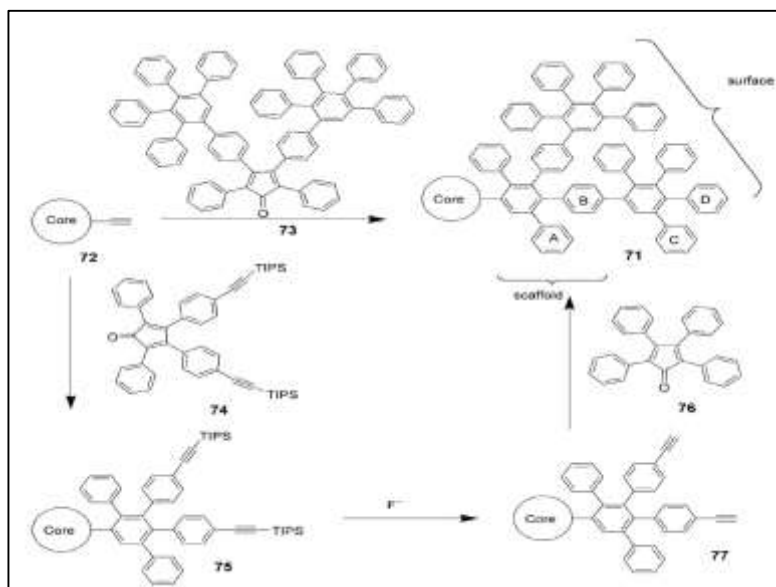
## Dendrimers

Unlike hyperbranched polymers, dendrimers [1–3] are normal macromolecules with well-defined structures that have been used as functional objects in nanotechnology and nanoscience, [4–6] such as drug delivery vehicles and light-harvesting materials. The flexible branches of most dendrimers are easily distorted by external stimuli and can even bend back towards the molecule's centre. They are generally denser in the centre than on the perimeter as a result of this back bending. Polyphenylene dendrimers, on the other hand, are hard, shape-permanent substances that may be seen as distinct nanoobjects using AFM. [13, 14] They are denser in the perimeter than at the centre, according to neutron diffraction measurements. Any two groups within the dendrimer or on its surface have well-defined spatial connections to each other as a result of this rigidity, which is critical for regulating their electronic interactions, notably the transmission of excitation energy between them. It also means that the shape of the empty space between groups in the interior of the dendrimer is well-defined and relatively invariant as a result of the limited mobility of the benzene rings within the structure, which allows for synthetic manipulation of this space to produce high selectivity for guest molecules. This specificity in host–guest interactions could then be used for sensing, such as selective molecule incorporation, or to create a nanoreactor in which reactions could occur selectively, similar to the use of pores in inorganic materials like zeolites to induce chemo- or regioselectivity in reactions.

## Synthesis of Polyphenylene Dendrimers

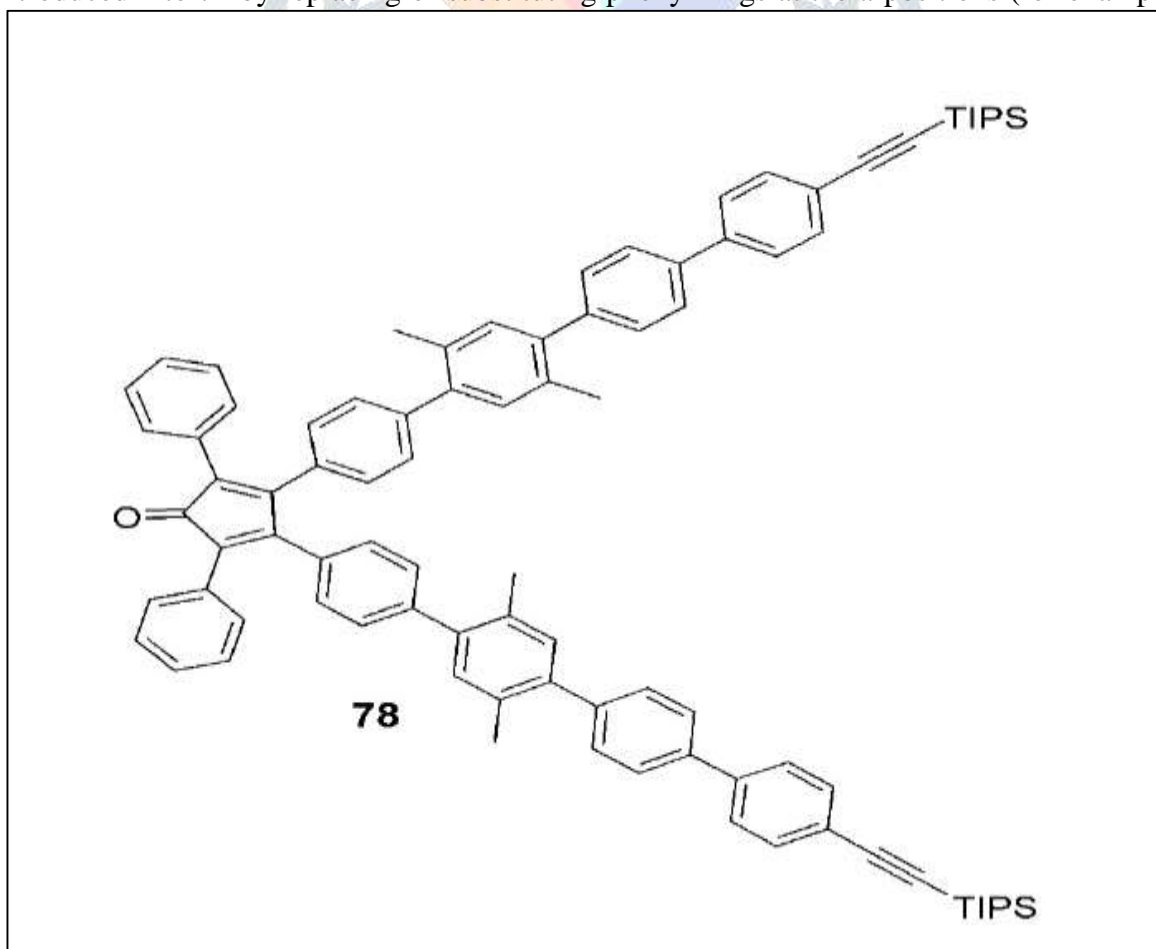
In Scheme 1 for a second-generation dendrimer 71, the two fundamental methods to the production of polyphenylene dendrimers [12] are shown. Diels–Alder cycloadditions of cyclopentadienones to alkynes are used in both methods. The ethynyl-substituted core 72 is treated with a cyclopentadienone 73 substituted with dendrons to produce 71 directly in the convergent technique. The dendrons in the divergent method are developed outwards from the core in an iterative manner by adding a cyclopentadienone 74 to 72, followed by deprotection and addition of a second cyclopentadienone 76 to the resultant ethynyl-substituted first-generation dendrimer 77. The intrinsic rigidity of the structure means that these macromolecules are well-defined shape-persistent nanoobjects, which must be stressed once more. The fourth-generation dendrimers are predicted to be 7 nm in size, which has been validated by light scattering, TEM, and AFM investigations. [13, 14] The use of the branching unit 78 (Scheme 2), in which a stiff spacer is placed between the cyclopentadienone and ethynyl groups on 74 to increase the distance between subsequent layers of the dendrimer, results in a dramatic increase in the size of these nanoobjects.

Using 78, full fifth-generation dendrimers may now be produced as spherical monodisperse particles with sizes up to 22 nm. [17]



**Scheme 1:** Convergent (top) and divergent approaches to second-generation polyphenylene dendrimers. Functionality may be incorporated into the dendrimer in three places, as shown in Scheme 1: at the core, in the scaffold (rings A and B in 62), and at the surface (rings C and D in 62). The synthesis of an ethynyl-substituted core molecule on which the dendrons can be built is required for functionalization of the core. Suitably functionalized cyclopentadienones are required for scaffold and surface functionalization.

**Scheme 2:** Expanded dendrimers can be synthesized by incorporating a cyclopentadienone. Multiple functional groups can be incorporated into the dendrimer in well-defined relationships to each other and to whatever groups exist at the core and surface thanks to the scaffold's functionalization. This method necessitates a change to the ethynyl cyclopentadienone 74 that is utilised to make higher-generation dendrimers. This may be accomplished in one of two ways (Scheme 3): 1) Functional groups can be introduced into 74 by replacing or substituting phenyl rings at the  $\alpha$ -positions (for example, in 79), or by

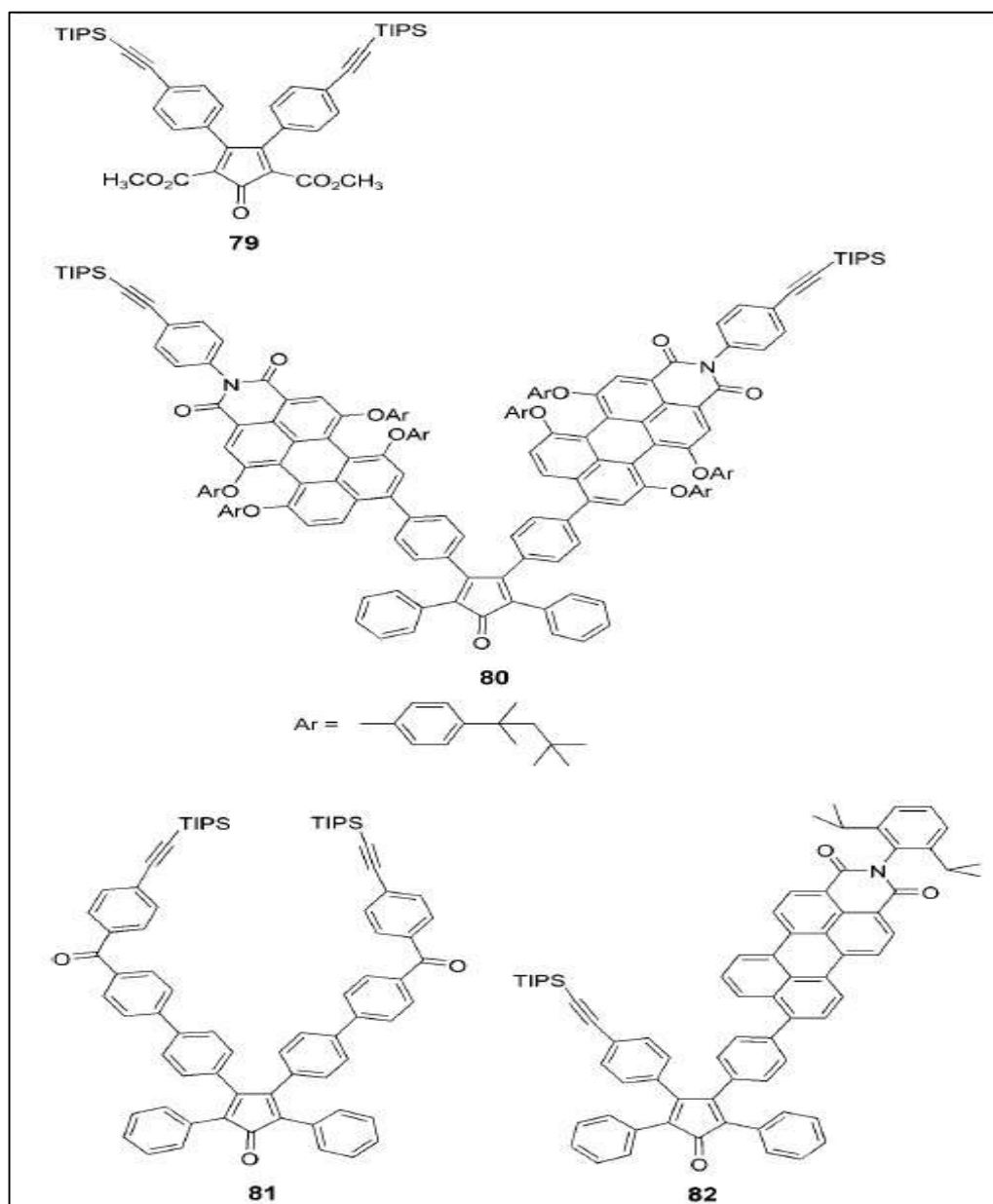


inserting them between the  $\beta$  phenyl rings and the ethyne bonds (for example, in 80 or 81) [29]; 2) 74 can be desymmetrized by replacing one of the ethynyl groups with a functional group, for example, 82 with

one perylene monomimide dye. [29] This is accomplished by combining diphenyl acetone with an asymmetrically functionalized benzil in a Knoevenagel condensation.

**Scheme 3:** Modified cyclopentadienones for introduction of functionality into scaffold.

The substituents in 79 and 80 bring functionality into the scaffold, which can influence the internal density of the dendrimer and the chemical characteristics of the cavities without impacting the number of possible branches or functional groups at the surface. Thus, using the reagent 79, ester groups may be introduced into a dendrimer, which can subsequently be hydrolyzed to carboxylates, resulting in charged cavities of specified sizes that can be utilised to form complexes with cationic species inside the dendrimers. [21] The perylenediimide groups in 80 not only provide functionality, but they also serve to increase the spacing between neighbouring layers, lowering the molecule's peripheral density. The total number of chromophores in the dendrimers can be considerably increased as a result, and the intensity of their overall absorption or emission can be significantly enhanced. Desymmetrized reagents like 82 have the effect of introducing bulky functional groups into a layer of the scaffold without increasing the space between the layers.



In bigger dendrimers, the inclusion of numerous functional groups also ensures efficient energy or charge transfer between the core and the surface. Furthermore, the ketone groups on 81 can be used for further chemistry, such as conversion to trityl radicals, allowing researchers to study radical interactions inside a nanosized dendrimer cage.

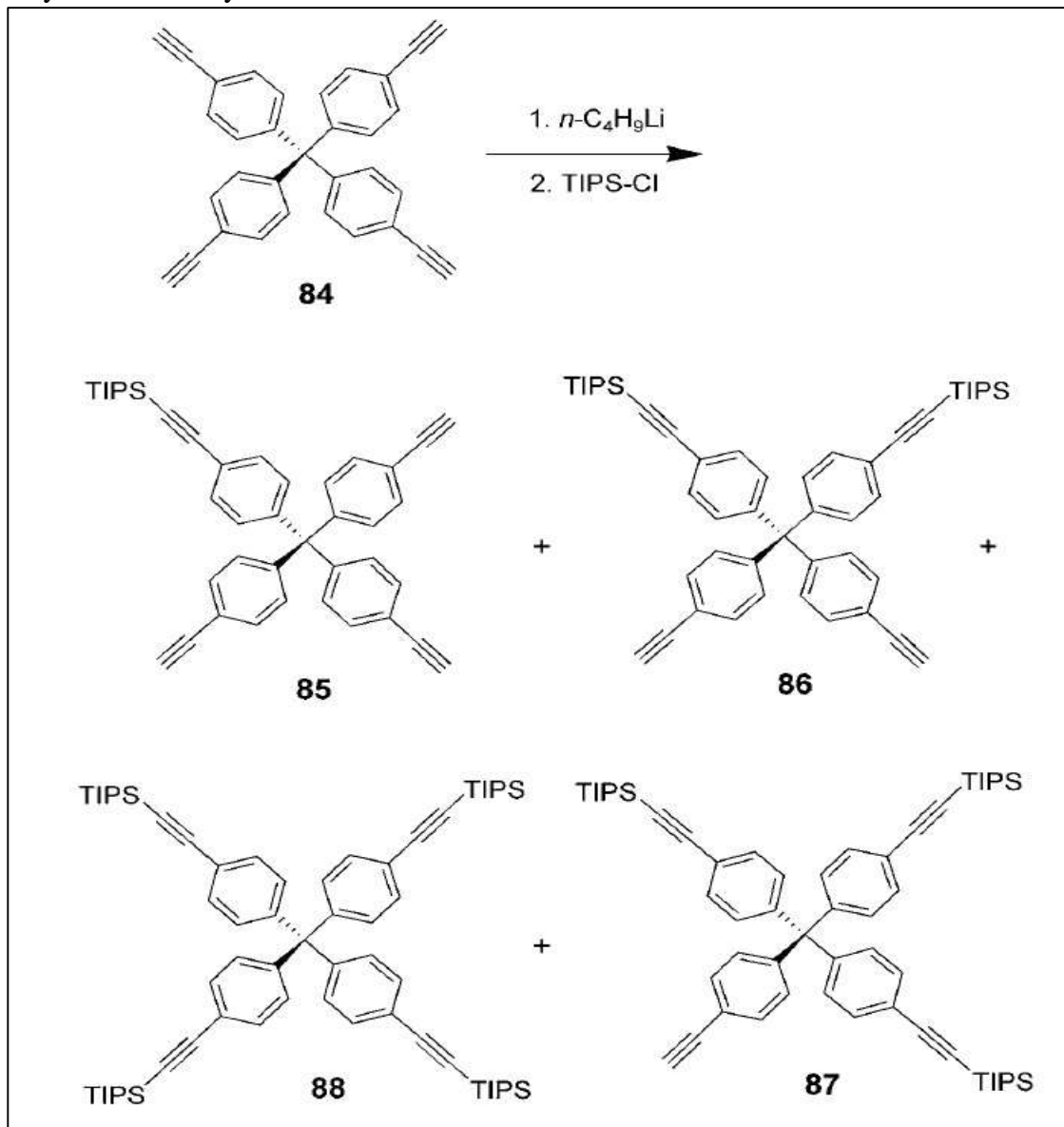
### Desymmetrized Dendrimers

Desymmetrization, or having distinct functional groups on various areas of the nanoparticle surface, is an interesting potential for customising the characteristics of functional dendrimers. [22] In bioassays, for



example, a dendrimer having groups capable of binding to a biologically active substance on part of its surface and chromophores on the other has uses. A desymmetrized core is required to make such dendrimers. Treatment of tetra(4-ethynylphenyl) methane (84) with less than four equivalents of *n*-butyllithium followed by an excess of triisopropyl chloride (TIPS-Cl) results in a statistical mixture of the easily separable mono- (85), di- (86), tri- (87), and tetrasilylated (88; this is unreactive and is converted back into 84) cores (Scheme 4) [23]. The protected ethynes may now be deprotected and utilised to construct new dendrons, resulting in a variety of novel molecular topologies.

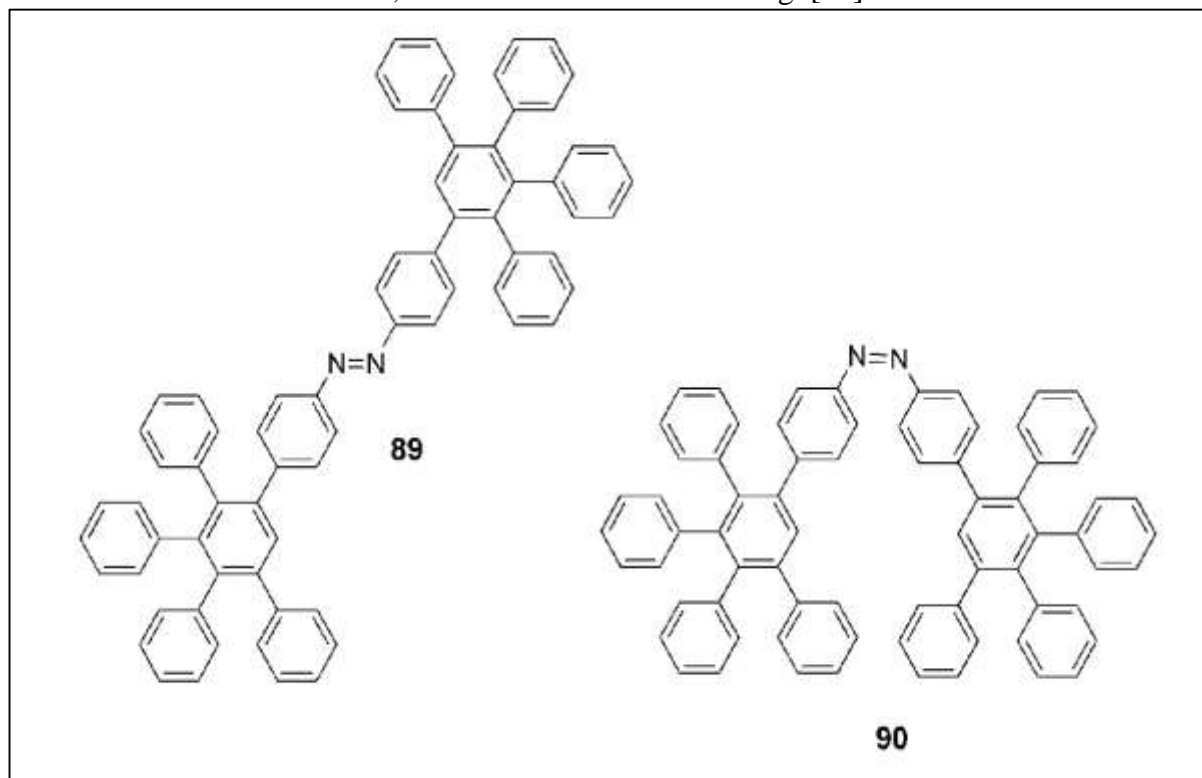
**Scheme 4:** Synthesis of desymmetrized dendrimer cores.



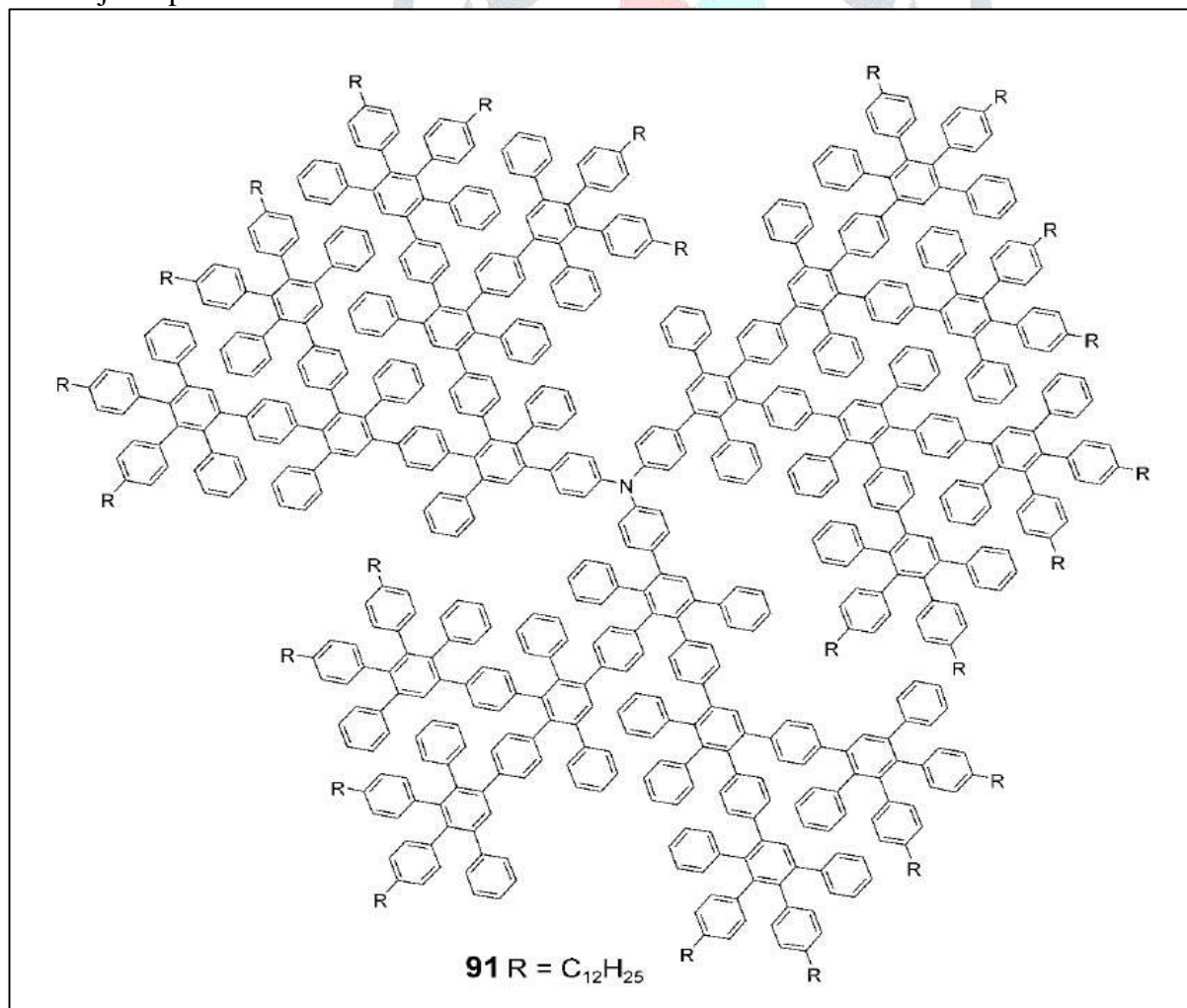
### Polyphenylene Dendrimers with Functional Cores

A first-generation dendrimer 89/90 (Scheme 5) with a photochromic azobenzene core that isomerises from the *trans* to the *cis* form when exposed to UV light is an example of a dendrimer with a functional core. The *trans* form 89 and the *cis* form 90 have significantly different volumes, as can be observed. Because of its significantly reduced (24–38 percent) hydrodynamic volume, the *cis* isomer 90 has a longer retention time on the column as measured by gel permeation chromatography (GPC). These dendrimers are thus an example of a nanosized so-called "smart material," in that they respond to an external stimuli in a consistent and repeatable manner (in this case light). With increased production or branching of the dendrimer, the rate of light-driven *trans*–*cis* isomerization and the fraction of the *cis* isomer in the photo stationary state decreases, whereas the rate of thermally induced reverse isomerization rises. Other research groups have made dendrimers with azobenzene cores, but due to the flexibility of their dendrons, photoisomerization does not cause a noticeable, well-defined change in the dendrimer form. Because of the twists between neighbouring benzene rings, the dendrons are unlikely to be excellent charge carriers. CV studies have verified this; for example, dendrimer 91 with a triphenylamine core (Scheme 6) exhibited a rise in the potential of the anodic peak in the oxidation cycle as it progressed from the first to the third

generation dendrimer, as well as a two-thirds drop in peak current. This finding indicates that the dendrons obstruct electron transport from the hole-accepting triphenylamine core. When enclosing an electrically active unit within a dendrimer, the shell should not be too big. [24]



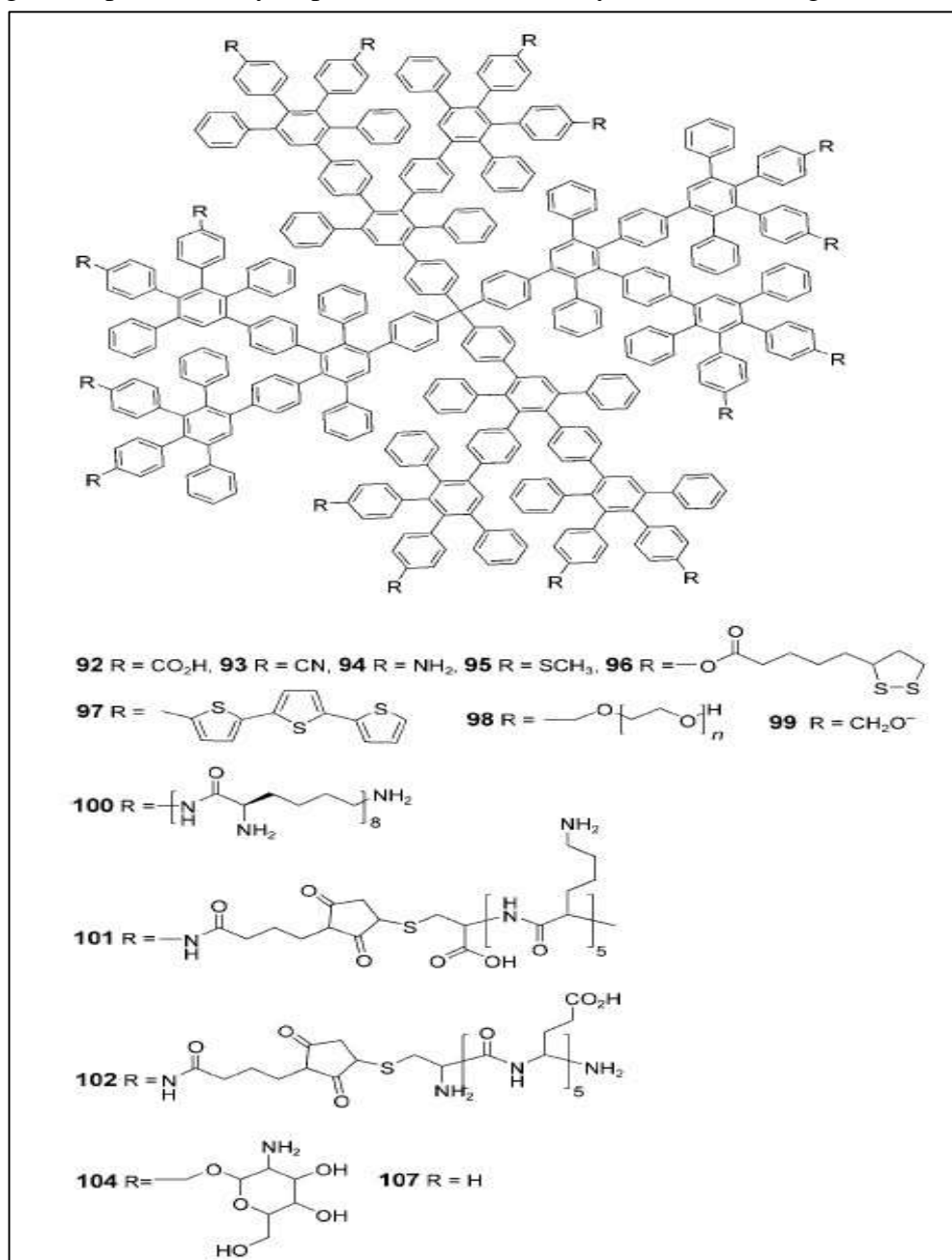
**Scheme 5:** First-generation azobenzene-cored dendrimers showing the marked change in volume of the nanoobject upon trans–cis isomerization.



**Scheme 6:** Third-generation dendrimer with a triphenylamine core.

## Dendrimers with Functionalized Surfaces and Scaffolds

Dendrimers with various polargroups, such as carboxylic acids (92), nitriles (93), amines (94), and thiols (95), have been produced (95, 96; Scheme 7). Such substituents can be utilised to increase water solubility (92) or aid in substrate binding, as the thiol-substituted dendrimers 95 and 96 do with gold. Dendrimers 92–94 preferentially incorporate volatile organic molecules inside their internal free space, resulting in chemical vapour sensors with sensitivity as high as 5 ppm for certain analytes on quartz microbalance layers. [27] A template for the production of gold nanoparticles is Dendrimer 95 with thiomethyl substituents. All of the particles are spherical, with typical sizes of around 4 nm, according to electron microscope investigations. The particles self-assemble into porous nanocomposites in which dendrimer "nanolinkers" separate the randomly distributed gold nanoparticles. [28] Layer-by-layer deposition of gold nanoparticles (ca. 4 nm in diameter) and the dithiane-substituted dendrimer 96 produced similar nanocomposites. When exposed to organic vapours, the electrical resistance of these porous nanocomposites films increased substantially and consistently. Because nonpolar solvents have a significantly higher sorption onto hydrophobic dendrimers, they have a much higher sensitivity. [29]

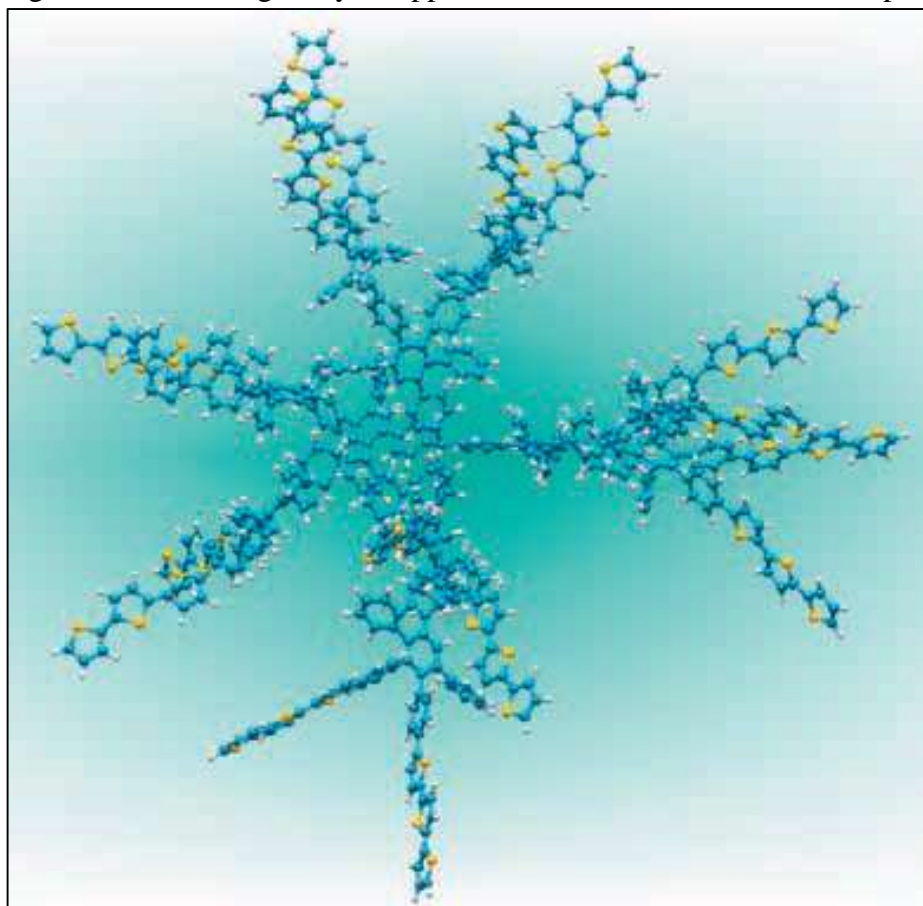


**Scheme 7:** Second-generation dendrimers with peripheral substituents.

Dendrimer surfaces can also be adorned with conjugated rods. These functionalized dendrimers may assemble into three-dimensional conjugated rod networks. Dendrimers containing terthiophene substituents, for example, have been produced (Figure 1). During the electrochemical oxidation of 97, two processes occur: coupling of the terthiophene chains to sexithiophene bridges, resulting in the formation of an oligothiophene–dendrimer 3D network, and partial cyclodehydrogenation of the dendrimers, resulting in a unique polythiophene–graphite hybrid. In situ conductivity studies of the resultant nanocomposites



revealed two distinct electrical conductivity processes that correlate to the network's various electroactive components. The right electrical charge may be applied to the material to handle both processes.



**Figure 1:** Molecular model of the terthienyl-substituted dendrimer 97.

Solid-supported metallocenes play a critical role in the polymerization of olefins in industry. [32] Immobilizing the metallocatalyst on the surface of a support using latex particles (usually 80–100 nm in diameter) with poly(ethylene oxide)(PEO) chains on their surface controls the product shape. As a result of interactions with methylalumoxane, which binds the catalyst, secondary particles develop. The solid support must fracture throughout the polymerization process to make catalyst sites available to the monomer, which is a major problem in the production of high-quality polyolefins. [33]

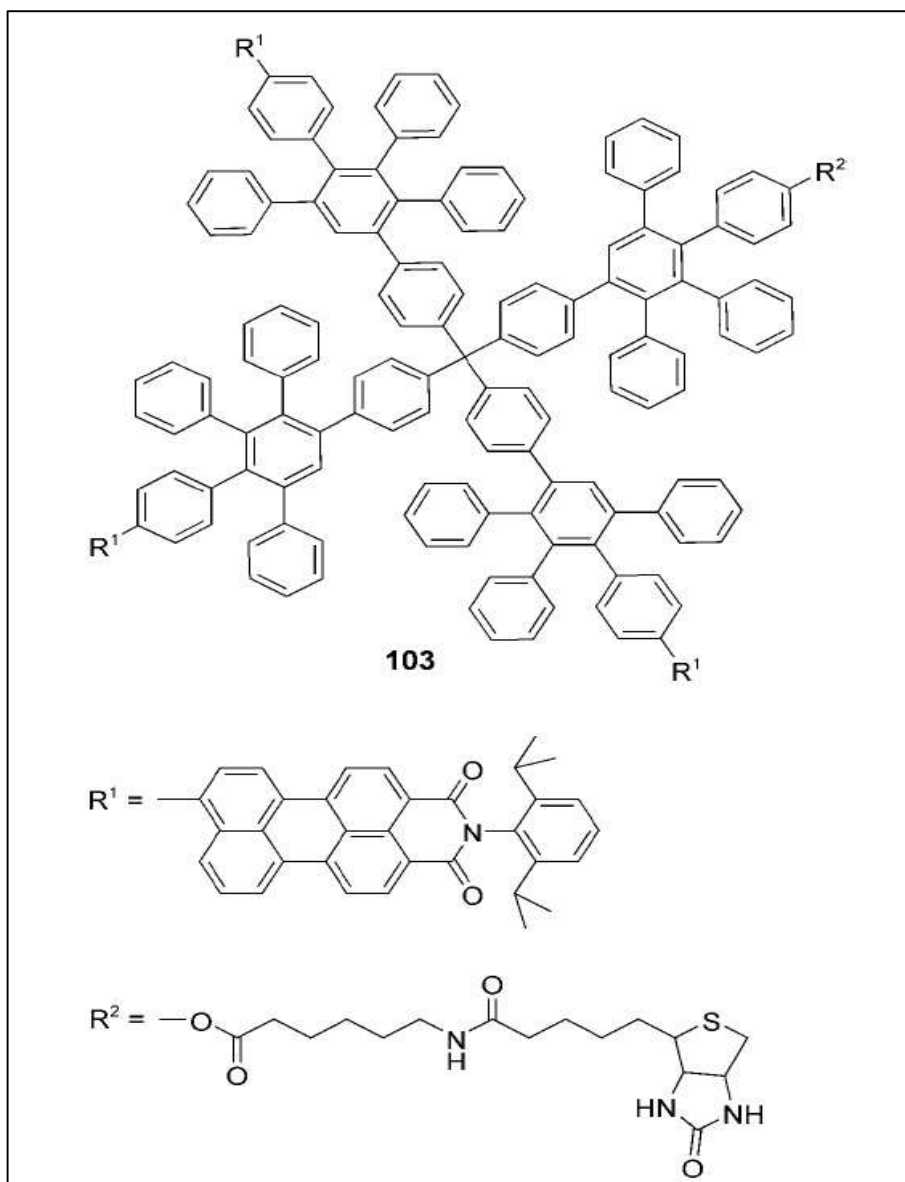
Polyphenylene dendrimers are attractive models for metallocene carriers because they are small discrete particles (less than 10 nm in diameter), and we have shown that zirconocene catalysts for olefin polymerization can be attached to the surface of a polyphenylene dendrimer. Both a "grafting-from" approach using 99 as a macroinitiator for anionic polymerization of ethylene oxide and a "grafting-onto" approach in which the ethylene oxide chains are attached to a substituted dendrimer have been used to prepare dendrimer-based core-shell systems, such as 98, with a rigid polyphenylene core surrounded by a PEO shell. The latex versions of these dendrimer models can then be compared. [34]

Dendrimers have attracted a lot of attention as potential medication or DNA delivery agents. Polyphenylene dendrimers are ideal substrates for biological applications because they are physiologically inert and hence harmless, but they can be functionalized quickly and precisely. Dendrimers with oligopeptide chains have been made either by functionalizing an amino-substituted dendrimer like 94 with a N-alkyl maleimide followed by a Michael reaction with a thiolendcapped peptide (dendrimer 100, for example) or by functionalizing an amino-substituted dendrimer like 94 with a N-alkyl maleimide followed by a Michael reaction with a thiol (for example, dendrimers 101 and 102). [35] Dendrimers like these are being utilised as model compounds for investigating DNA complexation and as RNA delivery agents in cells (transfection). [36]

Dendrimers with both physiologically active functionality and an optically or electrically active functional group in a nanosized array can be produced using the desymmetrization approach described in Section 6.2. The former group binds to a target biological moiety in the resultant bioassay, whereas the later group is employed for visualisation. The physiologically active moieties are kept in stable, well-defined relationships to each other and to the other active substituents by the stiffness and shape-persistence of the dendrimers. The asymmetrically functionalized dendrimer 103 (Scheme 8) has one biotin

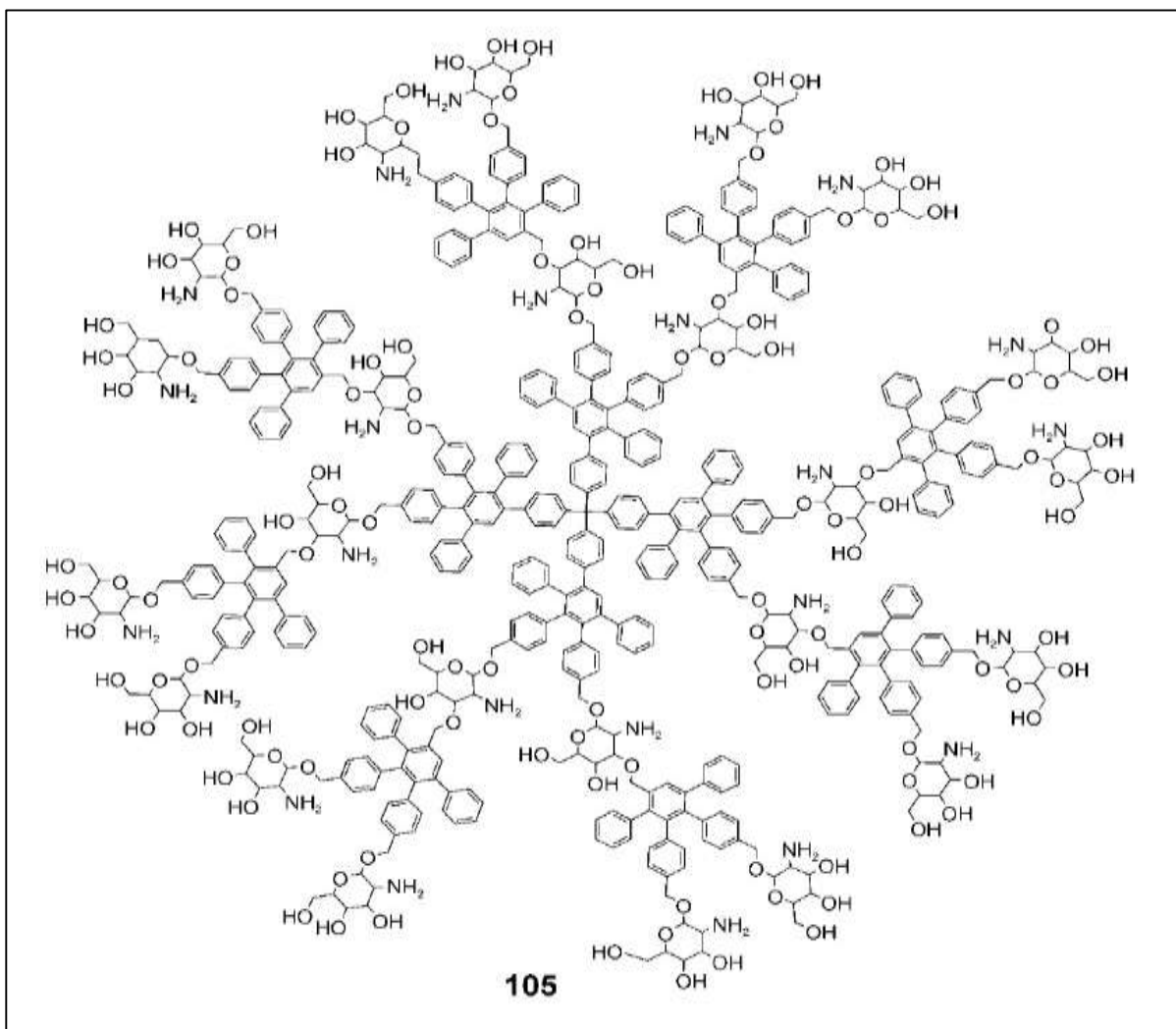


unit that binds tightly to the protein streptavidin, as well as three dye units that serve as fluorescent indicators. To achieve water solubility, the dendrimer must be combined with a non-ionic detergent. In aqueous conditions, the solubilized dendrimer binds strongly to streptavidin to form a highly fluorescent complex that remains intact in the presence of proteins, showing the approach's potential for bioassay applications. [37]



**Scheme 8:** Biotin-substituted dendrimer for applications in bioassays.

Sugar groups can be incorporated into a polyphenylene dendrimer not only on the perimeter (as in 104, Scheme 7) but also within the dendrimer scaffold (as in 105). (Scheme 9). [38] The peripheral sugar groups are responsible for the dendrimer's water solubility. The inner sugar groups in 105 are enclosed inside a hydrophobic environment of the nanosized molecule, similar to an active core located within a hydrophobic pocket as found in enzymes, according to fluorescence probe tests. These inner sugar groups are thought to be able to create stable hydrogen bonds with a guest, resulting in molecular recognition.



**Scheme 9:** Glycodendrimers with sugar groups at the periphery and in the scaffold.

### AFM Studies and Self-Assembly of Dendrimers

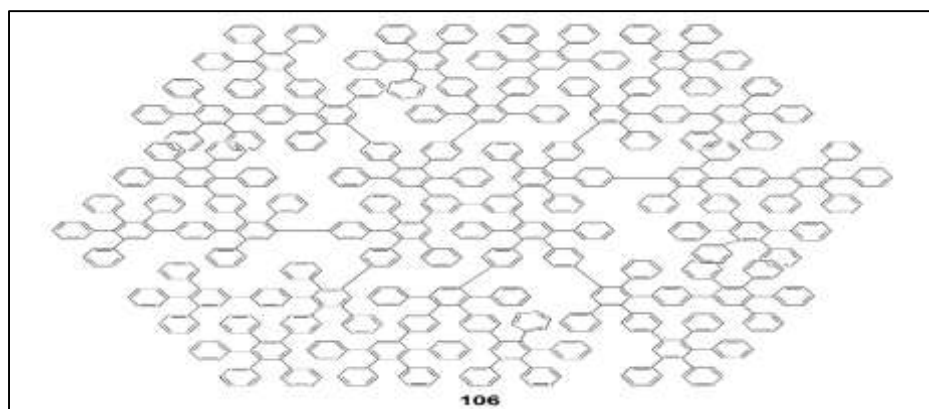
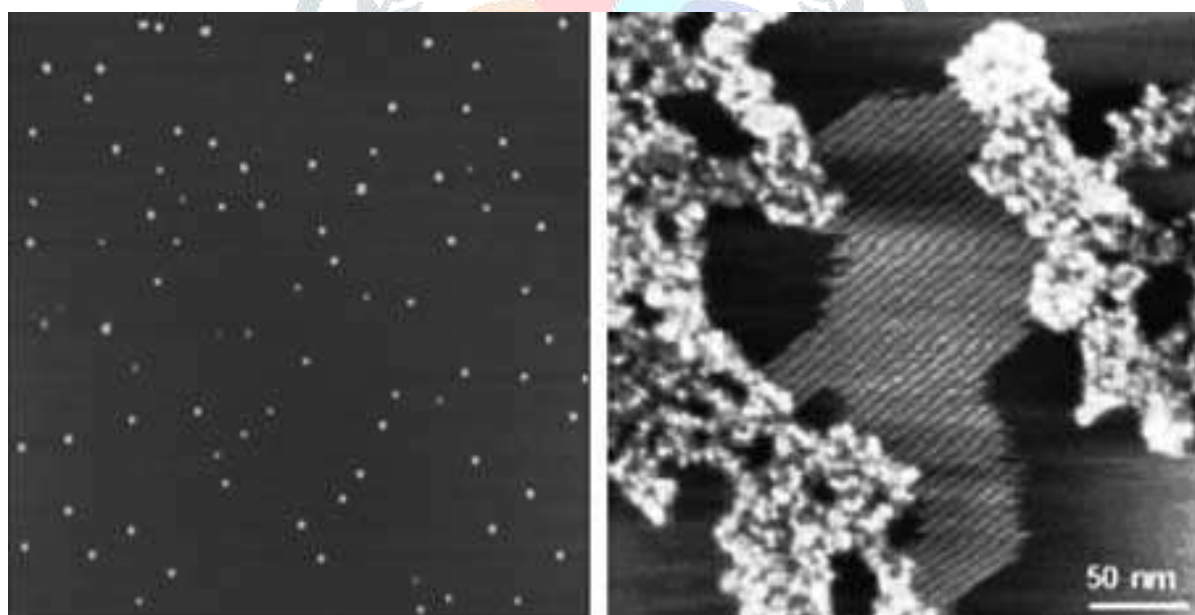
AFM can see polyphenylene dendrimers as distinct nanoobjects, as previously stated (Figure 2). Unlike other flexible dendrimers, the height of these structures corresponds to that calculated by molecular modelling studies, indicating their rigidity (the height of “soft” things is often overestimated by AFM due to deformation). Experiments with pulsed-force mode AFM proved their rigidity even more. Polyphenylene dendrimers can self-assemble to build more complicated architectures, much as flexible dendritic structures have been shown to generate self-assembled monolayers and a variety of complex structures. When spin-

cast on mica, the dumbbell-shaped third-generation dendrimer 106 with biphenyl core (Scheme 10) produces globular clusters with heights of about 6 nm and around 47 nm. [39] Drop casting generated nanofibers with widths of up to several hundred nanometres, heights of up to 100 nm, and lengths of up to 400 nm, whereas spin-casting produced monolayers on HOPG or silanized mica surfaces. Self-assembly of nonrigid dendrimers has also been observed to produce micrometre-sized fibres. Alkyl-substituted dendrimers on graphite surfaces also produce stable, pinhole-free monolayers. [40] Dendrimers with biphenyl (for example, 106) or trans-azobenzene (for example, 89) cores have also been demonstrated to produce such globular clusters or nanofibers up to the fourth generation. Lower dendrimer generations and more-separated dendrimer branches were shown to favour the production of nanofibers. P interactions between dendrimers as a result of branch interdigitation are the primary driving forces for aggregation. [41]

**Figure 2:** AFM images of: single third-generation unsubstituted dendrimers with a tetrahedral core (left) and nanorods of second-generation dendrimers with tetrahedral cores and alkyl substituents (right).

Light scattering studies revealed that the dendrimer 92 modified with carboxylic acid groups produces clumps as well. Thin deposits from extremely dilute solutions reveal objects with heights equivalent to three to eight dendrimer layers, according to AFM analyses. After adsorption onto a SAM ended with carboxylic acid groups by coupling with copper(ii) ions, [46] ionised molecules of 92 were observed using AFM. As a result of the strong interactions between the ions and the SAM, deformation of the SAM and a reduction in the measured height of the dendrimer ions compared to the estimated dimensions of the dendrimer were observed. [47] This dendrimer also self-assembles with poly(allylamine) in a Decher-style layer-by-layer manner, which can be seen via surface plasmon spectroscopy. [48] The lysine-substituted dendrimer 101 exhibits a similar self-assembly mechanism, whereas the glutamate-substituted dendrimer 102 forms compounds with cationic polyionenes. [49] Transmission electron microscopy may also be used to determine the size and form of bigger polyphenylene dendrimers. Single-molecule detection is achievable, but the size of the macromolecules relies on how they are laid out on the substrate surface.

**.Scheme 10:** Dendrimer with a biphenyl core that forms globular aggregates on mica and fibers on HOPG.  
**SMS Studies on Dendrimer–Dye Host–Guest Systems**



Polyphenylenedendrimers exhibit restricted conjugation due to the torsions between neighbouring phenylene units, and hence glow in the nearultraviolet with peaks about 365

nm. [50] With increasing generation number, there is a rise in the quantum efficiency of the emission, as well as increased crowding and stiffness of the structure, which reduces nonradiative decay pathways. The absorption band of the dyes is red-shifted following incorporation into the dendrimer as a result of the change in the polarizability of the environment, according to SMS research on host–guest systems in which cyanine dyes are integrated into dendrimer 92 modified with carboxylic acid groups. [51] The use of two distinct dyes allowed researchers to investigate the energy transfer between them. The energy-transfer efficiency was found to vary over time, which might be due to variations in the free volume inside the host or differences in the transfer modes available at the single-molecule level.

## Conclusion

Though the development of a technology based on nanometre-sized devices is still a long way off, significant progress has been made. Progress in the chemistry of nanomaterials— that is, the design, synthesis, processing, and characterization of materials capable of performing as functional elements in putative nanodevices— has gone hand in hand with the development of new methods for visualising and manipulating matter at the nanoscale. In this Review, we have discussed our work on the creation of such materials in the context of current nanoscience research.

All of the findings imply that functional devices based on individual molecules or tiny ensembles of molecules are no longer science fiction, but rather a genuinely feasible objective. More advancements in nanoscale manipulation techniques are required, as well as a solution to the problem of electronically addressing nanoparticles or single molecules. However, if present development and the productive interplay between chemists and physicists continue, we may soon be rewarded with sophisticated nanotechnology.

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