

## Dendrons, Dendrimers New Materials for Environmental and Science Applications

Rachid Touzani<sup>1,2\*</sup>

<sup>1</sup> *Laboratoire de Chimie Appliquée et Environnement, LCAE-URAC18, COSTE, Faculté des Sciences, Université Mohamed Premier, Oujda-Morocco.*

<sup>2</sup> *Université Mohamed Premier, Faculté Pluridisciplinaire Nador. BP 300, Selouane 62702, Nador-Morocco.*

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Email: [touzani@yahoo.fr](mailto:touzani@yahoo.fr); Tel: (+212) 677 968 240; Fax: (+212) 536 609 147

### Abstract

The field of dendrimers has recently emerged as the most commercially viable technology of this century because of its wide-ranging potential applications in many fields such as: healthcare, electronics, photonics, biotechnology, engineering products, pharmaceuticals, drug delivery, catalysis, electronic devices, environmental issues and nanotechnologies. This is due to the easy of integration of these unique globular molecules with more mature areas of chemistry. This review summarizes the synthesis, the characterization of dendrimers and the selection of some examples from their applications.

**Keywords:** Dendrons; Dendrimers; Synthesis; Characterizations; Catalysis; Drug Delivery; Electronic devices; Environmental and Nanotechnologies.

## 1. Introduction

### 1.1. Historical notes

Dendrimers are globular macromolecules with a cauliflower shape prepared by iterative reactions. The Dendron term came from Greek which means tree, dendrimer term was proposed by Tomalia [1-5] (Figure 1). They are well interior and exterior defined materials. Newkome considered them also as monodisperse polymers by [6-10] with specific size, high degree of molecular uniformity, porosity, solubility and highly functional terminal groups on the surface. Their reactivity can also be rigorously controlled. The first reported dendrimer synthesis

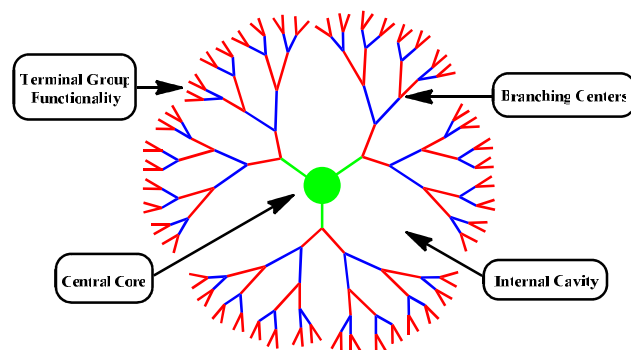
was in 1978, by Fritz Vögtle [11], now there are many groups around the world which have contributed to the dendrimer cause. They can be prepared by a divergent [12-13] or a convergent method [14-16]. The last one is characterized by multilevel branched architecture derived from successive iteration reactions [17-18].

## 2. Structure and Preparation of Dendrimers

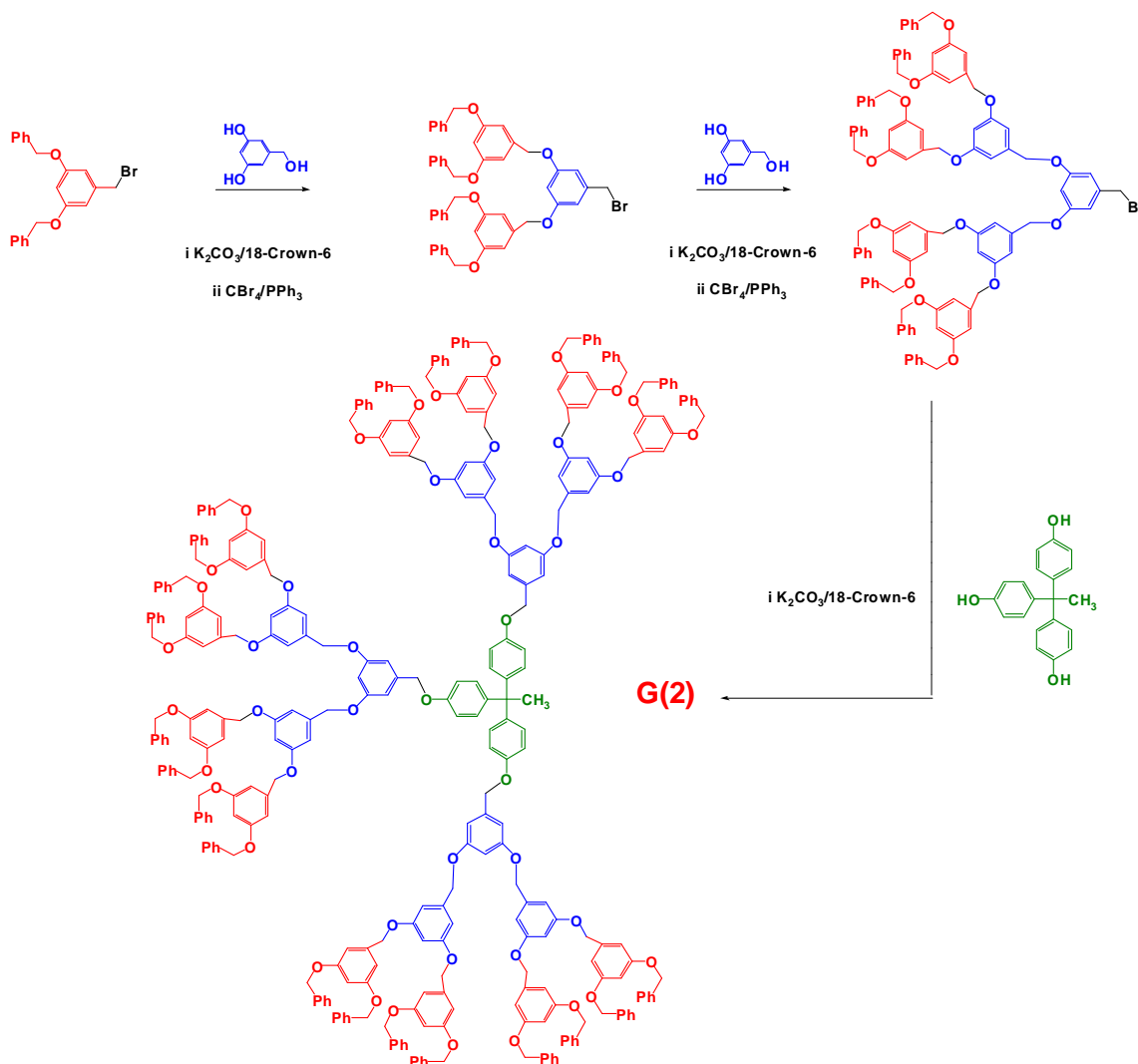
There are two main synthesis strategies for the construction of dendrimers, the convergent and the divergent syntheses. There are also few other methods, but they are really just variations or combinations of these two main strategies.

2.1. Convergent method

The process of this approach begins ultimately at the surface and works inward, by gradually linking the surface units together with the interior units. This method allows us to synthesize perfect dendrimers since the biproducts and the incomplete reaction products can be removed by purification steps. However, this method is not practical for large scale synthesis because this approach involves purification at each step [19-29] (Figure 2).



**Figure 1:** Global scheme of dendrimer similar to the cauliflower shape



**Figure 2:** Poly-arylether dendrimer using convergent method (Fréchet)

## 2. 2. Divergent method

The dendrimers are assembled in a totally linear manner. Meanwhile, the exploitation of differential reactivity on the periphery of a dendrimer offers a synthetic route to divergent complexity unattainable through typical synthetic procedures. That is, the

dendrimer is induced to grow from the core outward [30-35].

The major disadvantage of this approach is that the incomplete growth and the side reactions lead to imperfect dendrimers. To minimize these side reactions and imperfections, it's recommended to use a large excess of reagents (Figure 3).

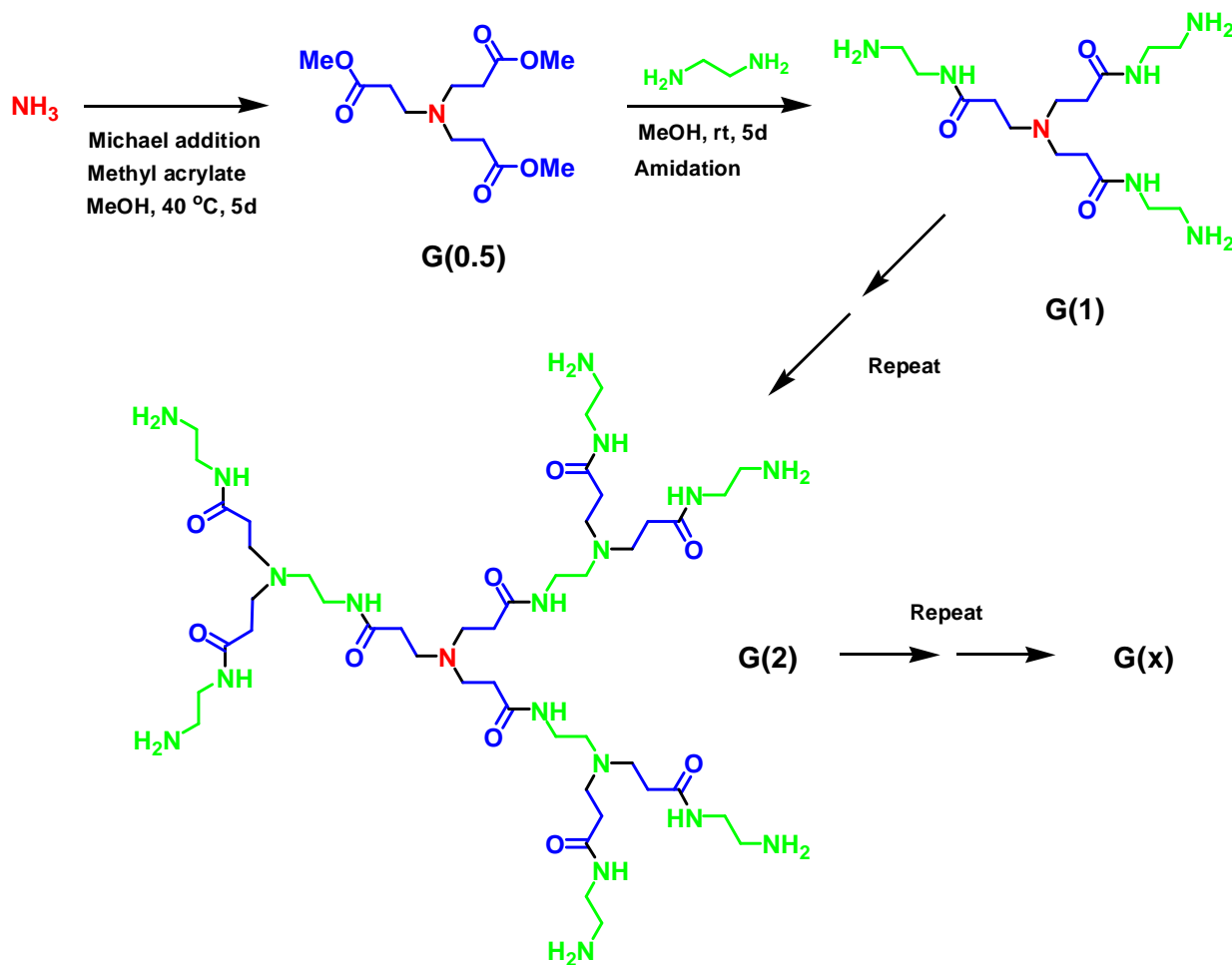


Figure 3: Divergent method for preparation of PAMAM dendrimers (Tomalia)

## 3. Dendrimers characterization

These two synthetic methods were applied to prepare many new dendrimers with different properties. However, these new materials need topologic, morphologic and topographic characterizations to fit their appropriate applications. We can cite some typical characterization methods, such as : molecular

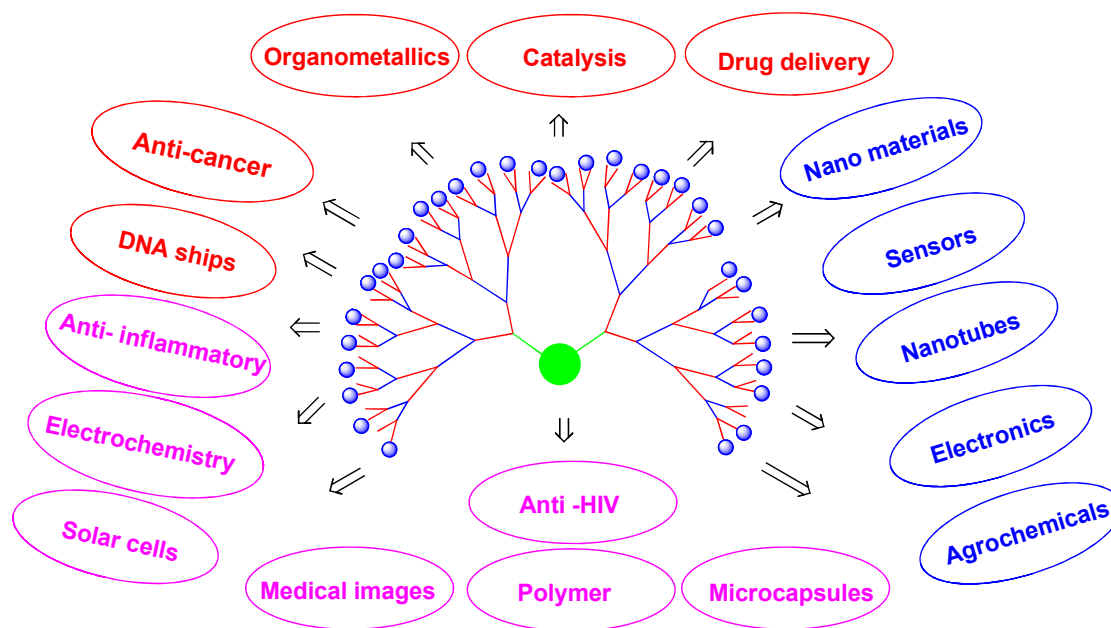
weight [36], viscosimetry [37], Thermogravimetry analysis [38], Infra-red spectroscopy [39], UV-visible spectroscopy [40], Fluorescence microscopy [41- 43], Electrochemical properties [44], MALDI-TOF Mass spectrometry [45-46],  $^{31}\text{P}$   $\{^1\text{H}\}$  Nuclear Magnetic Resonance spectroscopy in solution or in solid state [47-49], High resolution TEM [50], Energy Dispersive X-ray spectroscopy (EDX) [51], Surface modification detections by AFM

microscopy [52-53], Surface plasma resonance (SPR) [54] and layer-by-layer deposition [55].

#### 4. Dendrimers applications

After the discovery and the development of dendrimer materials, they began to attract interest for potential use in a variety of applications. These applications include adhesives [56-57], liquid crystals [58-59], molding components and MRI agents. Dendrimers can also act as either endo or exo host molecules by endo encapsulation [60-62], where dendrimers host cavity can accommodate small molecules in their interior. In this respect, dendrimers have been investigated for use as gene therapy vectors, vaccine and drug delivery agents [63-66]. Dendrimers can also act like protein, with its internal cavities and surface channels [67-72]. As an exo host molecule, the guest interacts with

the functional group located at the surface of the dendrimers like metal ion complexations. The dendrimers can be looked at as a complex and large ligand for a catalytic species [73-79]. Of course, one great advantage of using a dendrimer as a ligand is the relative easy recovery and thus potential to recycle the catalyst compared to its totally homogeneous counterpart [80-83]. Dendrimers, due to their large size, can be precipitated and removed by just ultra filtration from the product solution. In effect, dendrimers try to combine the advantages of homogenous catalysis such as faster kinetics to the recyclability of heterogeneous catalysts [84-85]. Dendritic catalysts also take advantage of the many functional sites which are easily accessible to the reactant. Indeed, there are many others applications related to the dendrimer topics.



**Figure 4:** Some of numerous applications of dendrimers

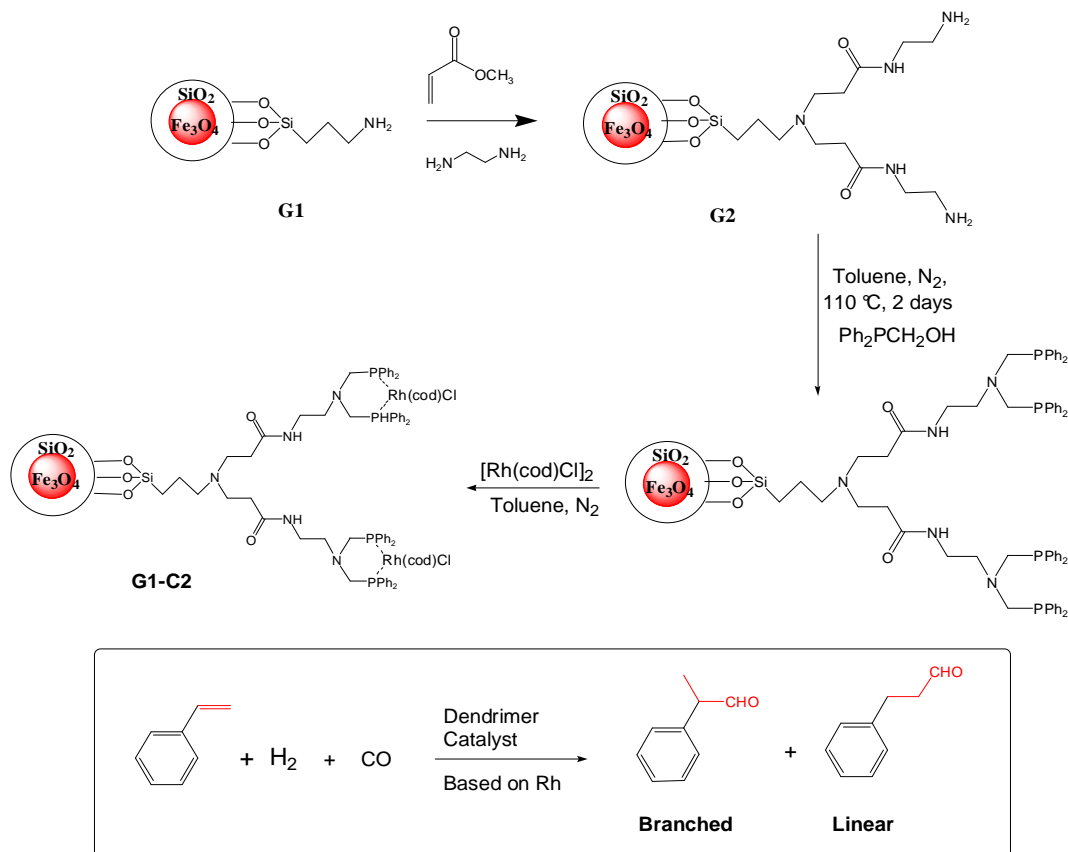
##### 4.1. Catalysis

There are many examples of using dendrimers in organometallics [86-87] such as ferric sandwich [88-89] with impressive redox catalysis properties. Since 1994 many works have been developed by pioneer research teams in the area of catalysis by fixing the catalyst in the periphery, the

scaffolding, or on the core of dendrimers, for examples: Brunner [90], Van Koten [91-92], DuBois [93-95], Astruc [96-99], Alper [100-104], Fréchet [105-106], Majoral [107], Newkome [108-109] and others [110-112]. All these excellent researchers want to find the ideal catalyst with High catalytic efficiency, selective for whatever reaction, versatile (substrate, metal, conditions), easily

recoverable or recyclable and longevity (durable and stable), we can present one example of using PAMAM dendrons based on silica-coated magnetic

nanoparticles for hydroformylation reaction with very high reactivity and selectivity [113] (Figure 5).

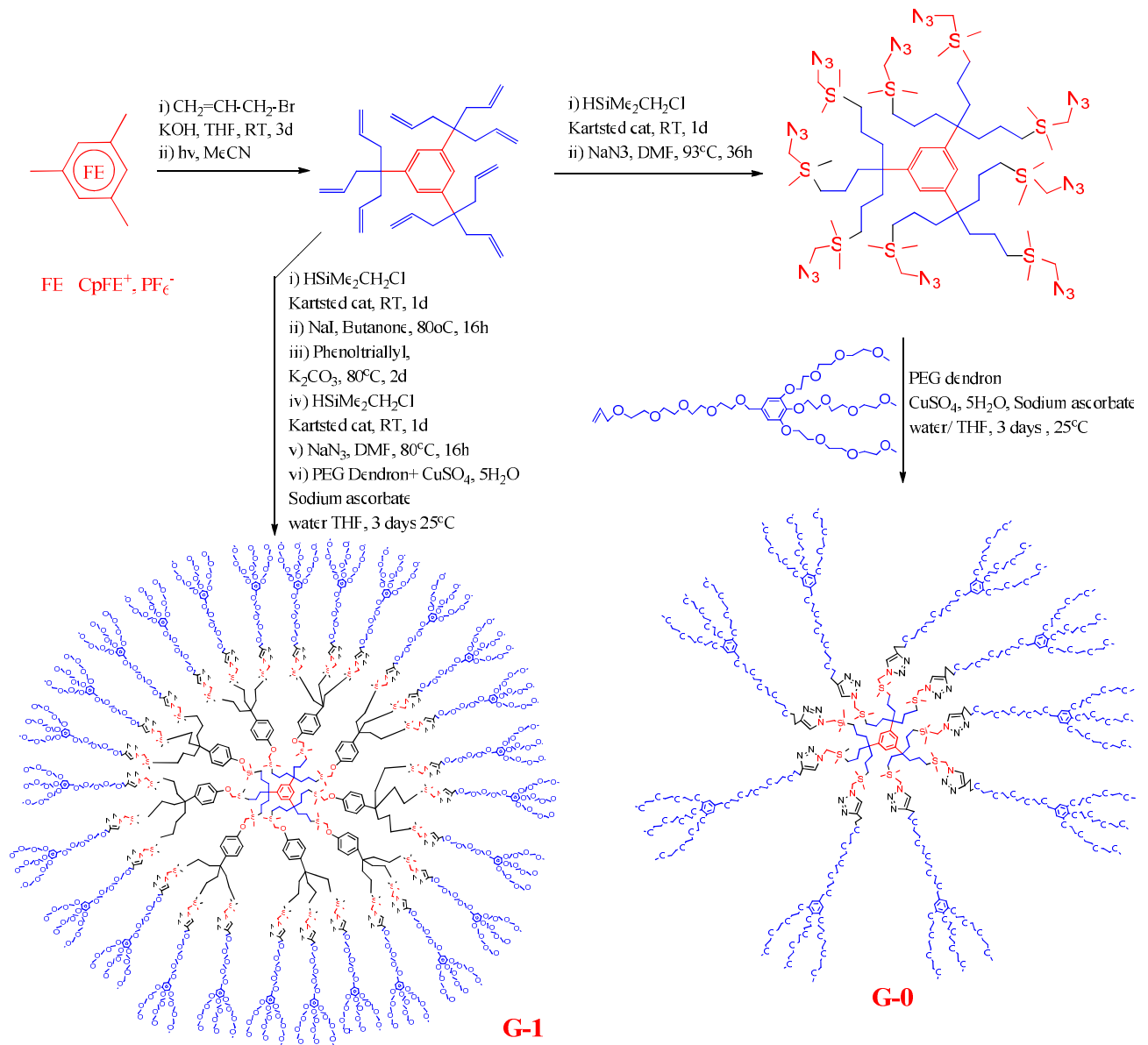


**Figure 5:** Example of dendritic catalyst for hydroformylation reaction easily recyclable magnetically with high reactivity and selectivity.

#### 4.2. Biomedicals

The formation of particulate systems with well-defined sizes and shapes is of eminent interest in certain medical applications such as drug delivery [114], gene transfection [115], and imaging [116-120]. The high level of possible control over the architectural design of dendrimers, their size, shape, branching length/density, and their surface functionality, clearly distinguishes these structures as unique and optimum carriers in those applications. The bioactive agents may be encapsulated into the interior of the dendrimers or chemically attached/physically adsorbed onto the dendrimer surface with the option of tailoring the carrier to the specific needs of the active material

and its therapeutic applications. In this regard, the high density of exo-presented surface groups allows attachment of targeting groups or functionality that may modify the solution behavior or toxicity of dendrimers. Quite remarkably, modified dendrimers have been shown to act as nano-drugs against tumors, bacteria, and viruses. Recent successes in simplifying and optimizing the synthesis of dendrimers such as the 'lego' and 'click' approaches, provide a large variety of structures while reducing the cost of their production. Astruc's group report the synthesis of dendritic nanoparticles system incorporating Gold (AuNPs) [96, 121] (Figure 6) by using very nice protocol "click" reaction to build super robust and stable Gold nanoparticles AuNPs.



**Figure 6:** The G-0 dendrimers were used to stabilize Gold Nanoparticles (AuNPs) and the G-1 dendrimers were used for the encapsulation of AuNPs.

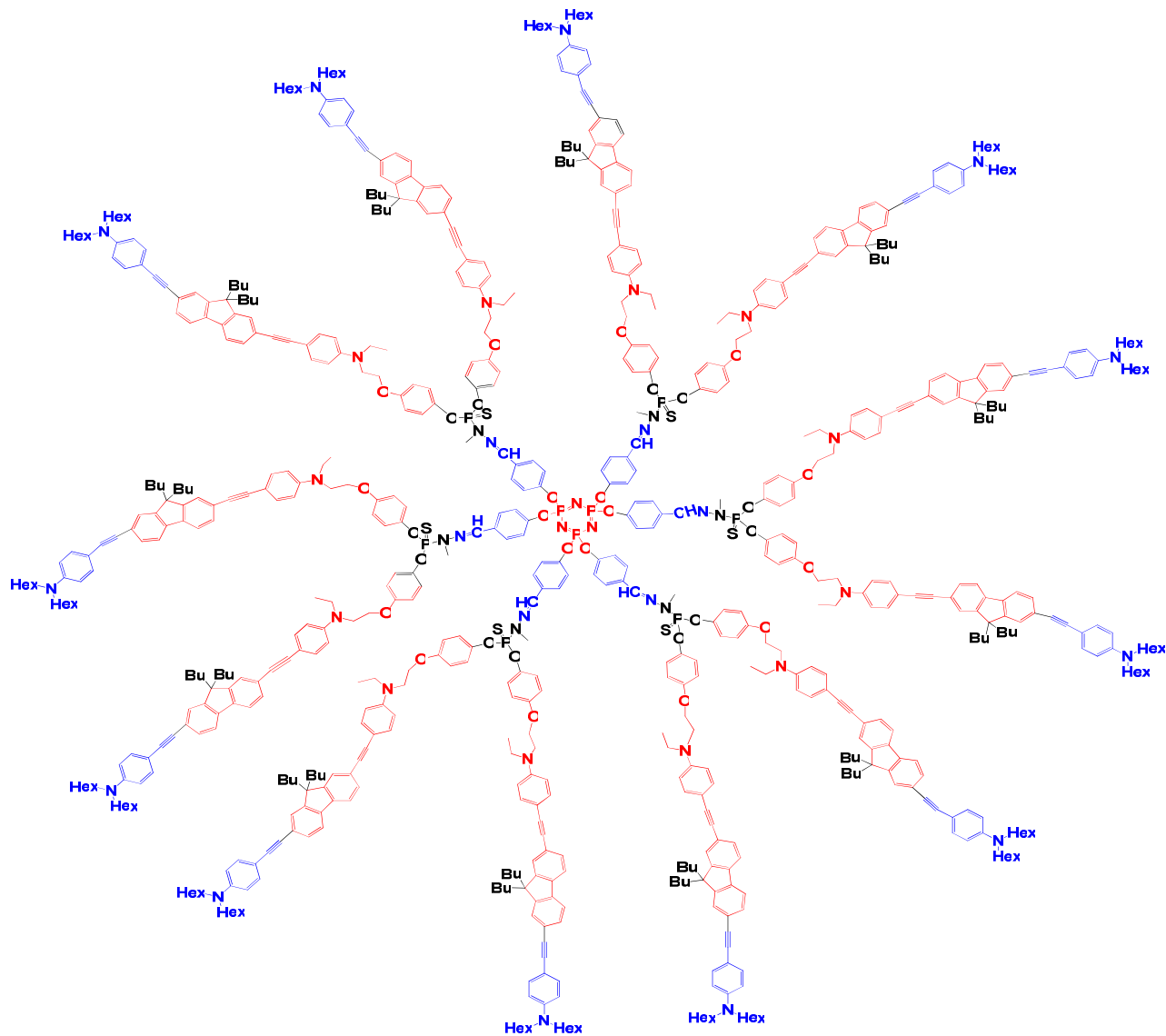
#### 4.3. Electronic devices

Organic electronic devices (e.g., organic integrated circuits, organic FETs, organic thin-film transistors, organic solar cells, organic field quenching devices, organic light-emitting transistors, light-emitting electrochemical cells, organic optical detectors,

organic photoreceptors, organic laser diodes, and organic electroluminescent devices) are described as linear or branched dendrimer compounds incorporating a specific component and serve as hole-injecting, hole-transporting, electron-transporting, or hole-blocking materials [122-123]. In Figure 7, Majoral's group has fixed fluorophores

on the periphery of different generations of dendrimers, which can absorb two photons [124]

and can be used as fluorescent markers for biomedical applications (Nanodots).



**Figure 7:** Chemical structure of the first generation of dendrimer with fluorophores on the periphery, which can absorb two photons (brilliant organic nanodots).

#### 4.4. Environment

Dendrimer molecules are considered as new class of polymers. These polymers are assembled around the center of a single molecule. As the layers build outwards from this core molecule, the fractal, or dendritic nature of the growing structure emerges. Large regions resemble the smaller Ys formed by

triplets of monomers. Because dendrimers have very regular and predictable patterns of growth, chemists can manipulate the characteristics of the interior and the outer surface. These polymers have many applications, such as environmental defence [125-128] labeled dendrimer acting as host molecules. In this example, novel NF membrane was developed from hyperbranched polyester

(HPE) in red color and (TMC) in bleu color by *in-situ* interfacial polymerization process using ultrafiltration polysulfone membrane as support. HPE molecule possesses a hydrophobic core, which could anchor to the support membrane through noncovalent supramolecular interactions. However,

the multiple arms ended with hydroxyl groups would improve the hydrophilicity of the membrane. The water permeability and the salts rejection of the membrane were measured under low trans-membrane pressures to assess their potential application in soft water [129].

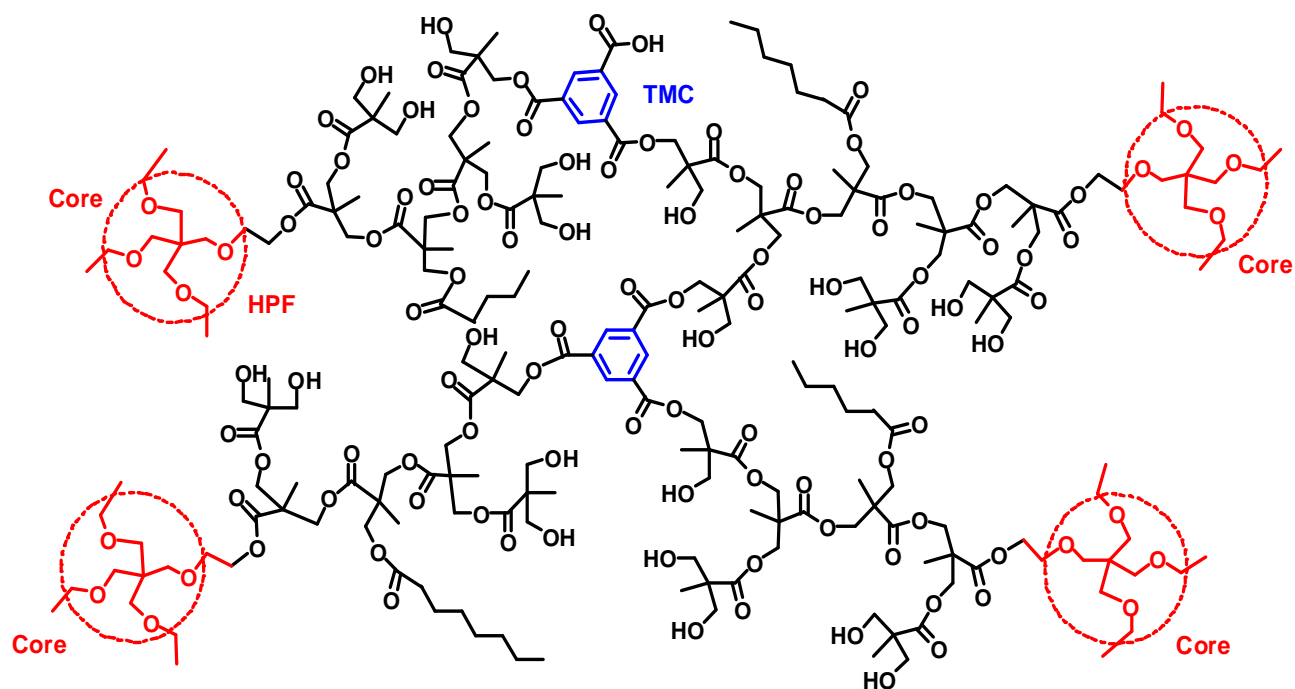


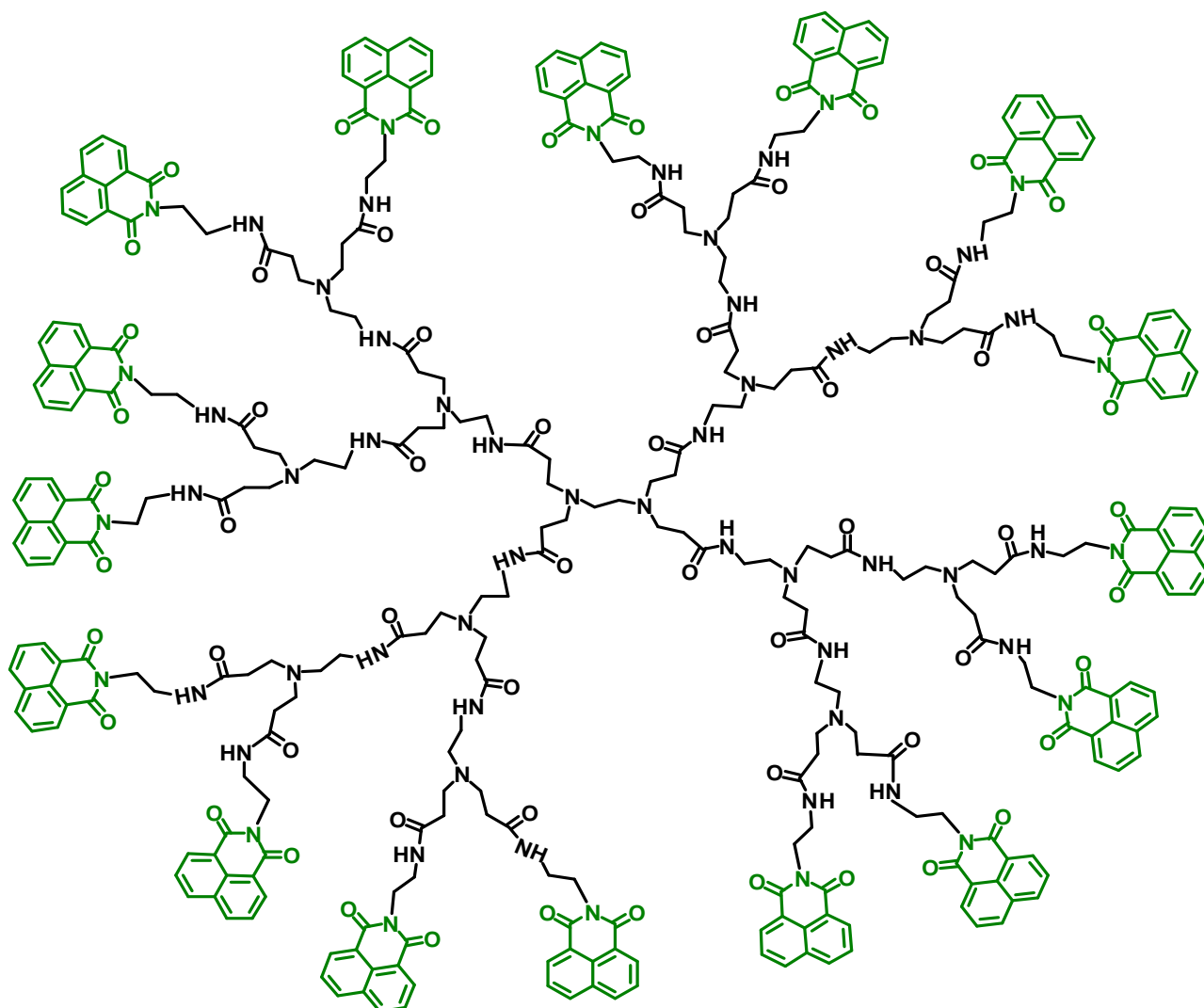
Figure 8: Scheme of membrane like based on dendrimers

#### 4. 5. Sensors

The structures and properties of dendimers evolved interest in interfacing the nanoscale dendrimers in the particular area of chemistry and biological sensing. Covalent bond formation is most important in dendrimer formation, followed by metal-ligand coordination bond formation and non-covalent bond formation. A compilation of dendrimers, constituted either by distinct monomers or the nature of linkage [130-132]. Rapid progress of the nanotechnological and advanced nanomaterials production offers significant opportunities for a wide range of applications for detection and remediation of a broad range of environmental contaminants. The convergence of analysis techniques and nanotechnology provides attractive possibilities for development of miniaturized, rapid,

ultrasensitive and inexpensive methods for *in-situ* and environmental monitoring devices. It has been reported that various nanoparticles and nanostructures used for this purpose, their integration into functional analytical devices, applications as electrode materials and gas sensing nanopores, in biosensors and as capture probes in immunomagnetic fields. Relevant, specific examples of nanomaterials-based chemical and biological sensors with applications in environmental monitoring have already been reported [133-138]. A polyamidoamine dendrimer with peripheral 1,8-naphthalimide groups capable for acting as a PET fluorescent sensor for rare earth and metal cations. The presence of metal ions was found to evoke a photoinduced electron transfer leading to an enhancement in the fluorescences [139-140] (Figure 9).





**Figure 9:** In the presence of metal ions the dendrimer changes his fluorescence at 478 nm

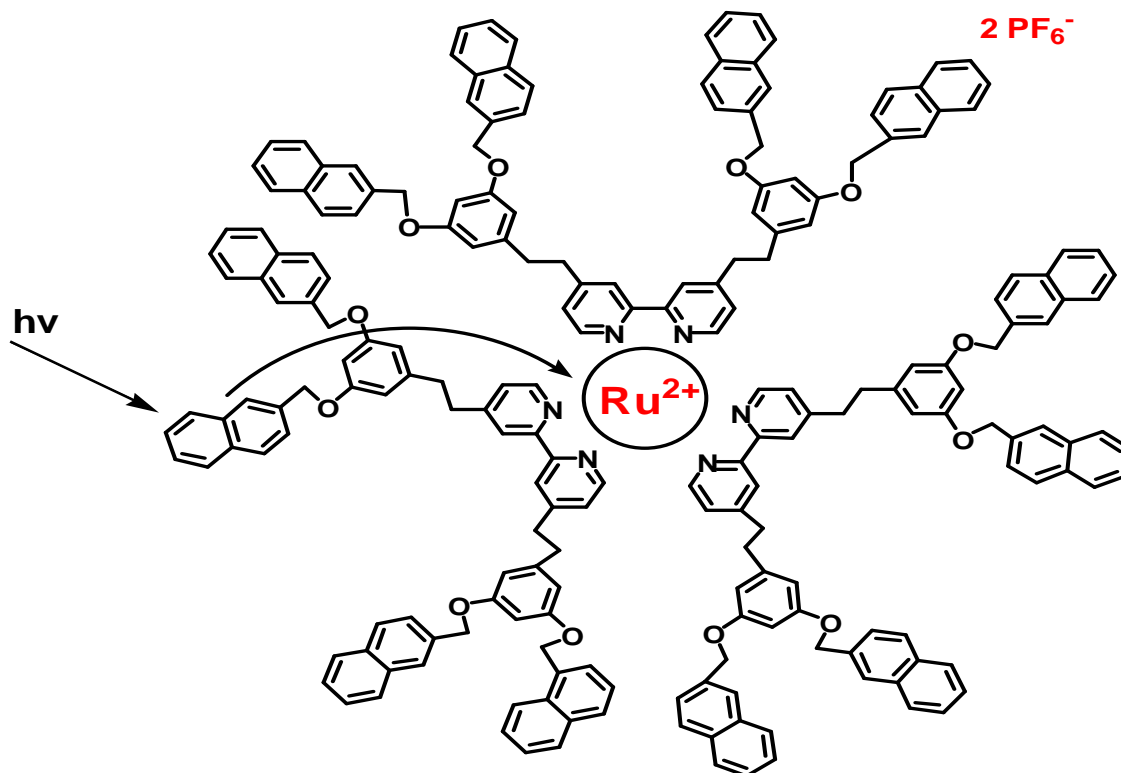
#### 4.6. Nanotechnologie

Dendritic polyglycerol represents hyperbranched polymer characterized by the combination of a stable, biocompatible polyether scaffold, high-end group functionality and a compact, well-defined architecture. These characteristics can be used to generate new materials properties and for biomedical applications to molecularly amplify or multiply effects or to create extremely high local concentrations of drugs, molecular labels, or probe moieties [141]. As supramolecular functional system, dendrimers show importante physical properties [142]. Nanostructures with uniform and

well-defined particle size and shape are of eminent interest in biomedical applications because of their ability to cross cell membranes and to reduce the risk of premature clearance from the body. The high level of control over the dendritic architecture (size, branching density, surface functionality) makes dendrimers ideal carriers in these applications. Many commercial small molecule drugs with anticancer, anti-inflammatory, and antimicrobial activity have been successfully associated with dendrimers such as poly(amidoamine) (PAMAM), poly(propylene imine) (PPI or DAB) and poly(etherhydroxylamine) (PEHAM) dendrimers, either via physical

interactions or through chemical bonding ('prodrug approach') [143]. Recent advances in the field of photoactive dendrimers containing metal complexes were reported. Dendrimers with  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a core exhibit the characteristic  $[\text{Ru}(\text{bpy})_3]^{2+}$ -type luminescence that can be (i) protected from external

quenchers by the dendrimère branches and (ii) sensitized by chromophoric groups contained in the periphery of the dendrimer (antenna effect) [144-145] (Figure 10).



**Figure 10:** Formula of dendrimère  $[\text{Ru}(\text{II})]^{2+}$  and schematic representation of the energy transfer processes taking place in the system

## Conclusion

In this review we highlighted some important aspect of dendrimers such as synthesis, characterization and examples from their applications.

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